

Dielectric Properties During Microwave-Induced Interesterification Reactions for Biodiesel and Triacetin Production

Jonas Miguel Priebe,^{a,b} Evandro L. Dall'Oglio,[✉]*:a Leonardo G. de Vasconcelos,^a Paulo T. de Sousa Jr.,^a Andressa A. Ramos,^a Emanuel D. Rodrigues^a and Carlos Alberto Kuhnen^c

^aDepartamento de Química, Universidade Federal do Mato Grosso, Av. Fernando Corrêa da Costa s/n, Coxipó, 78090-600 Cuiabá-MT, Brazil

^bDepartamento de Ensino, Instituto Federal Mato Grosso (IFMT), Campus Cuiabá-Bela Vista, Av. Vereador Juliano da Costa Marques, s/n, Bela Vista, 78050-560 Cuiabá-MT, Brazil

^cDepartamento de Física, Universidade Federal de Santa Catarina, Campus Universitário Trindade, 88040-970 Florianópolis-SC, Brazil

The microwave-assisted interesterification of babassu oil with methyl, ethyl and butyl acetates was carried out via acid catalysis, using sulfuric, phosphoric, methanesulfonic and acetic acids for the production of biodiesel with triacetin as an additive. Dielectric measurements in the range of 0.3 to 13 GHz of pure reactants and reactions media lead to a clear understanding of the interaction between the medium and microwave irradiation, allowing achieving optimal conditions in terms of microwave power, kind and catalyst concentration, reactant molar ratios, and temperatures. Using ethyl acetate, reactions were carried out at various oil to acetate molar ratio (1:12 to 1:72) using sulfuric acid (0.5% m/m_T) as a catalyst. For 1:60 molar ratio, the experiments were carried out with 0.5 to 2% m/m_T sulfuric acid. The kind of catalyst and the applied microwave power to mass ratio were investigated using H₃PO₄, CH₃COOH and CH₃SO₃H. The best catalytic activities were achieved with H₂SO₄ and CH₃SO₃H. It was found that under microwave or conventional heating the reactivity follows the ethyl→methyl→butyl trend. The best results were achieved using ethyl acetate with H₂SO₄ which yields 91.1% biodiesel and 18.3% triacetin in 120 min under microwave heating while using CH₃SO₃H yields 80.1% biodiesel and 11.2% triacetin.

Keywords: interesterification, microwave heating, dielectric properties, triacetin, biodiesel

Introduction

Nowadays, there is an urgent need to develop green technologies due to the growing climate impact caused by using fossil fuels; this way, renewable resources and their biorefinery concept are promising alternatives to achieve more environmentally friendly methodologies.

Many experimental studies that have been reported aimed at the increase and yield of biodiesel production together with the reduction of reaction time and the use of cheaper raw materials.¹⁻⁶ The interesterification process is one of the options to overcome characteristic drawbacks associated with the transesterification process for biodiesel production, such as high costs and generation of low-value products like glycerol.^{7,8}

In recent years, some works involving the interesterification of vegetable oils with carboxylate esters have been reported to mainly employ alkaline or acid homogenous catalysis,⁹⁻²² heterogeneous catalysis,²³⁻²⁹ and supercritical conditions.³⁰⁻³² Several heterogeneous catalysts have been used in the interesterification of edible and waste cooking oils such as tin oxide,²⁵ mesoporous silica (SBA-15-phenyl-SO₃H and SBA-15-propyl-SO₃H),²³ ferric sulfate,²⁴ ion-exchange resin,²⁶ hydrotalcite²⁷ and γ -alumina²⁸ that showed good activity but required longer reaction times and higher temperatures. Alternatively, enzymes (lipases) have also been shown to be efficient and refractory to reaction contaminants, but the relatively expensive costs combined with slower kinetics make the use of enzymes less promising.³³

The works above mentioned were carried out using conventional heating and therefore present the flaws inherent to such a procedure, for example, high temperatures

*e-mail: dalloglio.evandro@gmail.com

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and pressures and long reaction times, which entails higher costs for the production of biodiesel. One way to resolve these obstacles is to look for non-conventional heating methods such as the use of ultrasound and microwave heating; indeed, the use of ultrasonic method in biodiesel production has been most widely adopted in the transesterification process.³⁴⁻³⁶ However, some works reporting the intensification of the interesterification process of oils and residual oils using ultrasound demonstrated that this route is a reliable and efficient technique in chemical reactions by focusing acoustic energy that results in enhanced interesterification rate at mild conditions with low excess amounts of methanol and increasing the yield. Very promising results were found with ultrasound both in the homogeneous catalysis in reactions of oils with methyl acetate catalyzed by potassium hydroxide or potassium methoxide³⁷⁻⁴² and in the heterogeneous catalysis with the use of gamma-alumina⁴³ or solid catalyst (Cu₂O).⁴⁴ Another approach was reported in a work by Subhedar *et al.*,³⁴ with ultrasound-assisted interesterification of waste cooking oil (WCO) employing the enzymatic route.

As it is well known, microwave irradiation has been widely used as an alternative heating system to overcome the characteristic reaction drawbacks associated with conventional heating. A complete review regarding the use of microwave heating in biodiesel production revealed the complete lack of studies related to microwave-assisted interesterification reactions and that the studies with this approach are all regarding transesterification.^{1-3,35,36} The clear advantage of microwave heating comes from the possibility of its enhancement by controlling variables such as the power level, the frequency of the applied field and the initial temperature of the sample. Electromagnetic interactions with the reaction medium are at the heart of microwave heating technology applied to chemical reactions and therefore to achieve optimum conditions its development depends on the knowledge of the dielectric properties of the materials being processed. To achieve optimum conditions, dielectric heating must be clearly understood as a macroscopic effect of the interaction of electromagnetic fields in the microwave region with continuous media characterized by their intrinsic dielectric properties. The dielectric properties of materials are defined by their complex relative permittivity $\hat{\epsilon} = \epsilon' - j\epsilon''$ where the real part ϵ' is the relative dielectric constant and $\epsilon'' = (\epsilon'' + \sigma / \omega\epsilon_0)$ 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.⁴⁵ Ionic conduction and dipolar rotation are the major mechanisms of electromagnetic energy dissipation in continuous media.

The loss tangent, defined by $\tan\delta = \epsilon'' / \epsilon'$, is an important parameter in describing the dielectric response of materials; for example, 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 is the penetration depth (dp), that is related to the loss tangent and therefore is frequency and temperature-dependent. Due to their temperature and frequency-dependence, knowledge of both the dielectric constant and the loss factor is important in the design of a process involving microwave technology as well as from the theoretical point of view.⁴⁵

In this work, interesterification reactions of babassu oil with ethyl, methyl and butyl acetates were performed by microwave irradiation and conventional heating. Employing ethyl acetate, a first set of reactions was carried out at various oil to acetate molar ratios (from 1:12 to 1:72) using sulfuric acid (0.5% m/m_T) as the catalyst. For the best molar ratio found (1:60), a new set of experiments was done by varying the sulfuric acid concentration from 0.5 to 2% (m/m_T). The effect of different acid catalysts and the influence of the applied microwave power on the mass ratio in the interesterification reactions were investigated with a 1:60 oil to ethyl acetate molar ratio using 2% (m/m_T) of H₃PO₄, CH₃COOH and CH₃SO₃H. The best catalytic activities were achieved with H₂SO₄ and CH₃SO₃H and another set of microwave-assisted interesterification reactions was performed employing methyl and butyl acetates with 1:60 oil to acetate molar ratio and 2% (m/m_T) of catalyst. Dielectric properties in the microwave range of pure reactants methyl, ethyl, butyl acetates and babassu oil were measured as a function of frequency in the range of 0.3 to 13 GHz at various temperatures. For the acetates, such measurements allow us to obtain the activation energies for the relaxation process in these pure liquids. For the interesterification reactions performed with conventional heating, measurements of the dielectric properties of the reaction mixtures during the reactions were performed too; they were measured in the same frequency range and at the specific temperature of each reaction.

Experimental

Materials

Butyl acetate (99.5% LABSynth, Diadema, Brazil), ethyl acetate (99.5% Neon, Suzano, Brazil), methyl acetate (99% Dinâmica Química, Indaiatuba, Brazil), acetic acid (99.7% LABSynth, Diadema, Brazil), phosphoric acid (85% Cinética Química, Itapevi, Brazil), methanesulfonic acid (99.5% Vetec Química Fina, Rio de Janeiro, Brazil), sulfuric acid (95-99% Dinâmica Química, Indaiatuba,

Brazil), sodium bicarbonate (99%, Química Geral do Nordeste Ltda., Camaçari, Brazil), cyclohexane (99.7%, Sigma-Aldrich, St. Louis, USA), methyl heptadecanoate (98% Tokyo Chemical Industry, Tokyo, Japan), babassu oil (COPPALJ-Cooperative of small Agroextractive producers of Lago do Junco Ltda., Lago do Junco, Brazil), anhydrous sodium sulfate (99% Neon, Suzano, Brazil), and *n*-heptane (99%, Sigma-Aldrich, St. Louis, USA) were used.

Equipment

The dielectric properties of the pure liquids at various temperatures and reaction mixtures at reaction temperature were measured 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 specific procedures applied to measure the dielectric parameters of pure liquids and reaction mixtures were based on the methodology developed in previous studies.^{46,47} The accuracy in the measured values of the relative dielectric constant and dielectric loss factor employing the network analyzer are $\Delta\epsilon'/|\epsilon^*| = \pm 0.05$ and $\Delta\epsilon''/|\epsilon^*| = \pm 0.05$ respectively, where $|\epsilon^*|$ is the modulus of complex permittivity.⁴⁸ The experiments of the interesterification reactions induced by microwave heating were performed in a monomode reactor as described elsewhere.⁴⁹ The reactions were carried out under continuous microwave emission and mechanical stirring at 600 rpm, and the temperature of the medium was determined using a digital thermometer (Minipa, APPA ET-2609, true rms multimeter, São Paulo, Brazil). The reactions were monitored with biodiesel and triacetin quantification by gas chromatograph coupled with a flame ionization detector (Shimadzu GC-2010, Tokyo, Japan) and with an automatic injector, model AOC-5000, according to the Brazilian standard ANP No. 920/2023.⁵⁰

Interesterification reactions

The interesterification reactions were carried out with babassu oil under mechanical agitation (600 rpm) in the presence of acid catalysts (acetic acid, phosphoric acid, methanesulfonic acid and sulfuric acid) in different mass percentages, ranging from 0.5 to 2.0% m/m_T, in the presence of ethyl acetate in different stoichiometric ratios (1:12, 1:24, 1:36, 1:48, 1:60 and 1:72) as shown in Table S7 in Supplementary Information (SI) section. The reactions in the presence of methyl or butyl acetate were carried out under the best reaction condition defined for sulfuric acid, according to the data described in Table S8 (SI section).

The reactions took place with a fixed duration of 180 min, in a reaction cavity made of 304 stainless steel, with dielectric heating induced by electromagnetic waves in the microwave range (2450 MHz) by a power supply with variable power from 0.3 to 3.0 kW, which made it possible to adjust the power applied to promote variation in the power/mass ratio by 1.5, 1.75, 2.0, 2.25 and 2.5 (W g⁻¹), as described in Table S9. Tables S10 and S11 (SI section) present the quantities used in the reactions carried out with conventional heating in the dielectric measurement cell. During all reactions, at time intervals of 30 min, samples of the liquid phase (1 mL) were collected for subsequent analysis and the temperature of the medium was determined using a digital thermometer. The collected samples were neutralized with the addition of pure sodium bicarbonate until pH 7, then anhydrous sodium sulfate was added as a drying agent, which was filtered, and, after evaporation of the solvent, they were sent for chromatographic analysis. To determine the content of ethyl and methyl esters derived from fatty acids, the sample analysis procedure was adapted (SI section) from the international British standardization, using the standard described in the European Standard BS EN 14103.⁵¹

Results and Discussion

Dielectric properties of reactants

The efficiency of microwave heating that can accelerate chemical reactions is directly related to the knowledge of the dielectric properties of the reactants and appropriate polar solvents and/or catalysts to be used. Moreover, the measurements of dielectric spectra of complex liquids such as the reaction media become a basic and important challenge for microwave energy applications. In this sense, the dielectric properties of alcohols and their mixtures have been studied early⁵²⁻⁵⁶ and the dielectric properties of the pure solvents have become available in the literature.⁵⁷ Data on the behavior of dielectric properties of reaction mixtures during the reaction process are scarcer. A few dielectric measurements of reaction media during transesterification reactions of vegetable oils for biodiesel production have been reported.^{5,46-49} More recently, glycerol ketalization and acetylation reactions had their dielectric properties determined as a function of reactant molar ratios and of the different catalysts used at various concentrations.^{58,59} Therefore, it is expected that based on the knowledge of dielectric properties, polar solvents and/or appropriate catalysts can be selected in order to enhance to a greater or lesser extent microwave-assisted chemical reactions.

In the present study, to understand the contribution of each reactant to the dielectric properties of the reaction mixtures during the interesterification of vegetable oils with alkyl acetates, dielectric parameters measurements were carried out firstly on the reactants as pure liquids. The dielectric properties of some vegetable oils (soybean, babassu, chestnut) have been previously published^{46,48} and, in the present work, the dielectric measurements of babassu, soybean, chestnut and palm oils are detailed in the SI section (Figures S1 to S4). For these oils, in the frequency range studied, the measured dielectric constants vary little with temperature (between 20 and 80 °C), with average values around 3.2 at low frequencies (300 MHz), decreasing to values around 2.4 at high frequencies (> 10 GHz), as can be seen in Figures S1 to S4 in the SI section. The loss factor of these oils is notoriously low⁴⁶ and varies very little with temperature, exhibiting values between 0.30 at low frequencies and 0.15 at high frequencies. Therefore, in the microwave range, vegetable oils exhibit low values for the loss tangent and high values for the penetration depth and consequently present very low absorption of the energy of the electromagnetic field.

Figures 1a and 1b show the dielectric constant and the loss factor of the ethyl acetate in the range of 0.3 to 13 GHz at various temperatures. In the range of measured frequencies, the dielectric constant of ethyl acetate decreases as temperature increases. Figures S5 and S10 demonstrate that the same behavior is also observed in the constant dielectric of methyl and butyl acetates. Furthermore, the values of the dielectric constant at each temperature decrease as the carbonic chain increases, denoting the fact that molecular alignment with the field is more and more hindered as the carbon chain grows.

The observed decrease of dielectric constant in the acetates that contain a single carbonyl group, with increasing the temperature, was also observed in acetone, with its single C=O bond,⁵⁸ and acetic anhydride which exhibits two carbonyl group (two C=O double bonds).⁵⁹

This behavior is the opposite that occurs in glycerol (3 OH bonds), ethanol and acetic acid (one OH bond), where the dielectric constant increases with the temperature.^{46,58,59} In such liquids, the interaction of the media with the electromagnetic field is affected due to the existence of hydrogen bonds and as temperature increases, molecular kinetic energy also increases causing them to stay further apart from each other, breaking H bonds. In such conditions, the molecular response to variations in the electric field becomes easier, which means an increase in the process of molecular realignment, resulting in an increase of the dielectric constant at higher temperatures at high frequencies. Figure 1b shows that the loss factor of ethyl acetate decreases as temperature increases, having small values in the entire frequency range being less than 0.5 at 2.45 GHz at all temperatures. Moreover, Figure 1b makes it clear that the loss factor shows relaxation frequencies shifted to increasingly higher frequencies as the temperature increases. The relaxation frequencies vary from 15.5 GHz (10 °C) to 23.1 GHz (70 °C), obtained by fitting the data to a Cole-Davidson model (see Table S3 of SI section). The loss factors of methyl and butyl acetates as a function of frequency and temperature have similar behavior and an overall decrease in their values, with an increasing carbonic chain also being observed. Dielectric measurements show that, for acetates, both the dielectric constant and the loss factor decrease with increasing carbonic chain, however, the loss tangent and therefore the penetration depth does not necessarily follow the same trend.

This fact is demonstrated in Figure 2, where the penetration depth and loss tangent for methyl, ethyl and butyl acetates are shown as a function of temperature at 2.45 GHz. Microwave heating is commonly applied at a microwave frequency of 2.45 GHz and hence the knowledge of the behavior of loss tangent and penetration depth of the samples in such frequency at different temperatures is crucial in determining the efficiency of microwave heating for these samples. The acetates have very small values

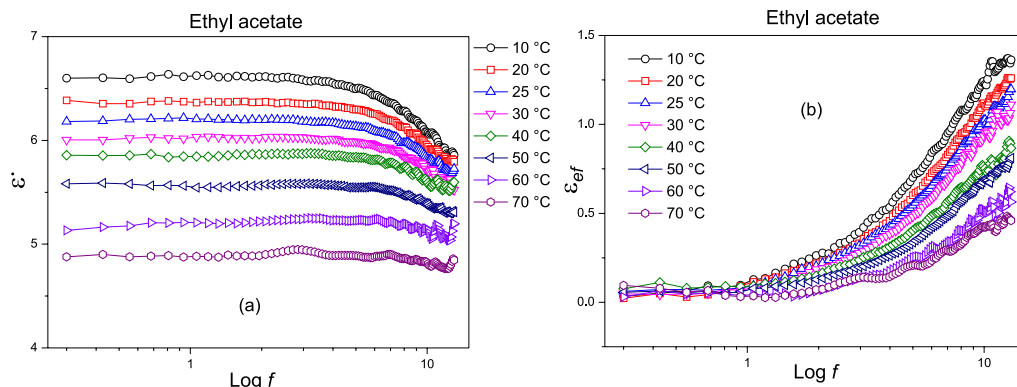


Figure 1. (a) Dielectric constant (ϵ') and (b) loss factor (ϵ'') for ethyl acetate as a function of frequency at various temperatures. Frequency in Gigahertz.

for the loss tangent which is a decreasing function of the temperature whereas the penetration depth exhibits high values that increase with temperature (Figure 2).

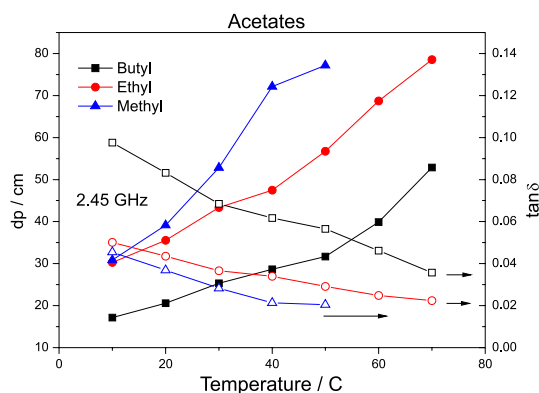


Figure 2. Penetration depth (dp) and loss tangent ($\tan\delta$) at 2.45 GHz for the methyl, ethyl and butyl acetates as a function of temperature.

The high values reached by penetration depth in the acetates (Figure 2) mean an almost transparency to microwave field mainly at high temperatures reflecting the poor absorption of electromagnetic energy by these liquids. Contrary to the dielectric constant and loss factor, the loss tangent, at each temperature, decreases with carbonic chain length, and hence penetration depth increases with chain length. This behavior of the loss tangent occurs because, at all temperatures, the dielectric constant decreases faster with the increase in the carbon chain than the rate at which the loss factor decreases, as demonstrated by comparing the dielectric measurements for these three acetates (Figures 1 and S5 and S10 of SI section). Therefore, among these acetates, during microwave heating butyl acetate heats up much more rapidly than ethyl and methyl acetates since the heating rate is highly dependent on the loss tangent values.

The obtained dielectric spectra of the acetates may be fitted with some current dielectric relaxation models which have been also applied for glycerol/water and glycerol/ethanol mixtures,^{52,54} alcohols mixtures^{53,55} or solketal/water and solketal/water/acetone mixtures.⁵⁸ The complex permittivity of acetates was fitted using these models for the relaxation process (Debye, Cole-Cole, and Cole-Davidson models). The main parameters, such as relaxation frequencies

and relaxation times at different temperatures, were obtained using the different models and are presented in the SI section. Treating the dielectric relaxation as a rate process the free activation energy for the dielectric relaxation process in pure liquids and some mixtures can be evaluated using Eyring's rate equation. Table 1 shows the free activation energies of the studied acetates and the respective applied models for the dielectric relaxation phenomenon that best fits the measurements of the complex permittivity.

The dielectric spectra data were fitted with good values for the standard deviation only with the Debye and Cole-Davidson models. In the case of butyl acetate, only the Debye model provided a good fitting with the standard deviation closest to the unit. Therefore, Table 1 gives the trends in the free activation energies as the carbonic chain increases in those acetates. The relatively lower value of activation energy for the acetates compared with the values found for acetone, 8.58 kcal mol⁻¹, and acetic anhydride, 2.50 kcal mol⁻¹, can be approached as follows.^{58,59} Firstly, despite the acetone exhibiting more simple structural features than the acetic anhydride and the acetates, it must be reminded that in liquid acetone a keto-enol equilibrium occurs with the coexistence of two kind molecules (CH₃-(C=O)-CH₃ and CH₂=(C-OH)-CH₃). Such coexistence undoubtedly contributes to enhancing the free activation energy due to the presence of the enol through the formation of hydrogen bonds that must be broken to allow an appreciable reorientation of the molecular dipole moments due to the applied electric field. This reduction in the reorientational mobility reflects large relaxation times and high free activation energy of the relaxation process in liquid acetone. The great influence of hydrogen bonds in the free activation energy can be easily seen by taking water as an example. Despite its simple structure, the existence of H bonds makes alignment with the field difficult, and, consequently, water has free activation energy of 3.6 kcal mol⁻¹, a value higher than that found for acetic anhydride. Likewise, glycerol, with its three OH bonds, has free activation energy of 8.52 kcal mol⁻¹. Three OH groups may be involved in 6 H-bonds in glycerol, however, it is supposed to be 3 H bonds *per* glycerol molecule.⁵⁴ For the liquids acetates as well as for acetic anhydride, there is no

Table 1. Experimental dipole moment (μ) and calculated free activation energy (ΔF) of the dielectric relaxation process for the acetates involved in the interesterification of babassu oil

Acetate	μ / Debye	ΔF / (kcal mol ⁻¹)	R ² (SD)	Model
Methyl	1.71	1.52 (1.39)	0.999 (0.987)	Debye (Cole-Davidson)
Ethyl	1.78	1.38 (1.06)	0.955 (0.961)	Debye (Cole-Davidson)
Butyl	1.87	0.798	0.962	Debye

R²(SD): standard deviation.

formation of H bonds, and Table 1 makes it clear that the van der Waals interactions are sufficiently weak to allow a fast reorientation of the molecular dipole moments due to the applied field which results in lower free activation energies. In fact, from the results of Table 1 together with results found for other pure liquids, it becomes clear that, in addition to the concentration of H bonds, the structural features of the constituent molecules have an important contribution to the process of dielectric relaxation in liquids. Table 1 shows the molecular dipole moments whose values demonstrate that the dipole moments of the constituent molecules of the medium do not strongly correlate with the free activation energy. Indeed, there can be a very weak correlation or no correlation at all. These results quite agree with those found for many liquids and their mixtures,^{58,59} demonstrating that dielectric relaxation occurs because the molecules that make up the liquid medium are polar but the free activation energy does not depend explicitly on the molecular dipole moments. An additional comment should be made at this point: the measurements show that both vegetable oils and acetates exhibit very low-loss tangents and thus mixtures of these liquids must, obviously, also exhibit low-loss tangent values. This means very little absorption of microwave energy by the mixture. Any significant change in the loss tangent of the reaction mixture will depend on the kind and amount of catalyst used, which may or may not improve the absorption of electromagnetic energy by the reaction mixture. In the next section, we will elucidate this issue by verifying how the efficiency of dielectric heating is influenced by the values of the loss tangent of the reaction media.

Interesterification reactions

Interesterification reactions with acid catalysis and microwave irradiation

Interesterification reactions of babassu oil were carried out with ethyl acetate, varying from 1:12 to 1:72 the

oil/acetate molar ratio and using 0.5% (m/m_T) of sulfuric acid as a catalyst. These reactions were carried out through conventional and microwave heating. For reactions with conventional heating, dielectric measurements of the reaction medium were taken during the reactions. Figures 3a and 3b show the dielectric constant and loss factor at various times of the interesterification reaction using the molar ratio 1:12. It can be observed that the dielectric properties of the mixture change during the reaction but not significantly since the products formed, biodiesel and triacetin, also present values for the dielectric constant and loss factor compared to those of the reactant esters. By comparing Figure 3 with the dielectric measurements of babassu oil (Figure S4, SI section) and ethyl acetate (Figure 1), it becomes evident that the behavior of the mixture is dictated by the acetate with little contribution from the oil, which occurs in order to reduce both the values of the dielectric constant and the loss factor of the reaction mixture. Despite acids such as H₂SO₄, H₃PO₄ and CH₃SO₃H exhibiting very high loss tangent⁴⁷ increasing fast for frequencies below 1.5 GHz, it can be seen in Figure 3 that sulfuric acid at the concentration used (0.5% m/m_T) does not contribute to either the dielectric constant or the loss factor of the reaction mixture. This fact arises from the size and high molecular weight of reactant molecules which act as molecules of the first solvation shell, completely inhibiting the mobility of the ions in the mixture hence the loss factor has no ionic contribution, only due to the dielectric relaxation process.

In Figures S14 to S18 (SI section), there are the dielectric measurements of the reaction media for the 1:24, 1:36, 1:48, 1:60 and 1:72 oil/acetate molar ratios. It can be seen that the dielectric constant remains in the same range of values reflecting the high concentration of ethyl acetate molecules. However, for the loss factor, for molar ratios greater than 1:24, an increase in its values is observed for frequencies below 1.5 GHz. This behavior is due to the fact that increasing the acetate concentration raises the

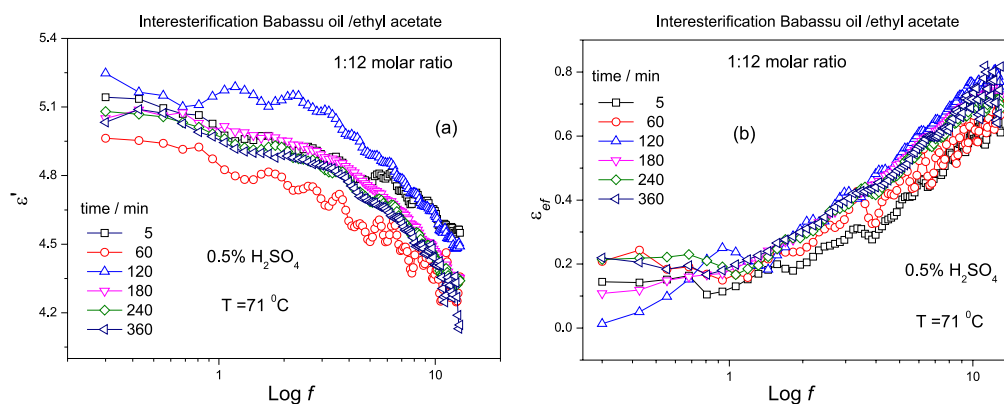


Figure 3. (a) Dielectric constant and (b) loss factor, as a function of frequency, during interesterification of babassu oil with ethyl acetate using 1:12 oil to acetate molar ratio and 0.5% (m/m_T) of H₂SO₄. Reaction temperature: 71 °C. Frequency in Gigahertz.

probability that the first solvation shell is made up of acetate molecules, which are much smaller in size and mass than oil molecules. In this way, a small mobility of the ions arises under the action of the electric field at low frequencies and the loss factor in this range is mostly due to the ionic contribution. The same behavior was observed both in the acid-catalyzed (H_2SO_4 , H_3PO_4 , $\text{CH}_3\text{SO}_3\text{H}$, ClHSO_3) methanolysis and ethanolysis of vegetable oils and in the acid-catalyzed reactions of ketalization and acetalization of glycerol, where for frequencies below 1 GHz there is a fast increase in the loss factor which occurs due to the increasing mobility of ions at low frequencies.^{46,48,58,59}

The behaviors of the loss tangent and penetration depth at 2.45 GHz during the interesterification reaction for different oil/acetate molar ratios are shown in Figure 4.

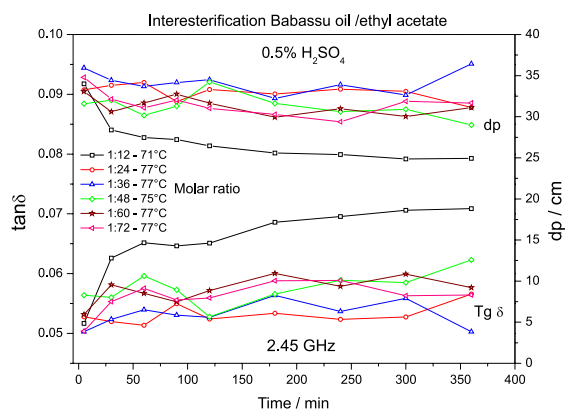


Figure 4. Loss tangent ($\tan\delta$) and penetration depth (dp) at 2.45 GHz during interesterification of babassu oil with ethyl acetate using various oil to acetate molar ratios and 0.5% (m/m_T) of H_2SO_4 .

The loss tangent is the ratio between the loss factor and the dielectric constant and thus carries information about changes in the reaction medium as the reaction proceeds. Firstly, it can be seen in Figure 4 that the loss tangents of the reaction media present very low values and are contained within a narrow range of values during the reaction. This behavior reflects the fact that the products (triacetin and biodiesel) have dielectric properties whose values are in the range that do not differ appreciably from the reactant esters. These very small values for the loss tangent (and consequently high values of the penetration depth) in these interesterification reactions contrast strongly with the high values found in the methanolysis and ethanolysis reactions of vegetable oils catalyzed by acids such as H_2SO_4 , H_3PO_4 , $\text{CH}_3\text{SO}_3\text{H}$ and ClHSO_3 , where the loss tangents of these reaction media present values between 0.15 and 0.44 in methanolysis and between 0.13 and 0.33 in ethanolysis. In these transesterification reactions, in addition to biodiesel as a product, glycerol formation occurs which contributes to an appreciable change in the loss tangent during the reaction.

A direct consequence of the small values of the loss tangent (Figure 4) for the reaction media is the low absorption of electromagnetic energy by the medium and therefore one cannot expect the same efficiency in inducing these reactions by microwaves, compared to conventional heating, such as the efficiency achieved in microwave-induced acid-catalyzed transesterification reactions where a significant reduction in reaction time is observed. According to reports in the literature, transesterification reaction times range from 12 to 60 h, when sulfuric, hydrochloric or phosphoric acids are employed as catalysts under conventional heating whereas for microwave (MW) heating reaction times were reduced to values between 20 to 120 min.^{47,48,60-63} Dielectric measurements were performed during interesterification reactions of babassu oil/ethyl acetate employing 0.5% (m/m_T) of phosphoric and acetic acids for molar ratios varying from 1:12 to 1:72. The dielectric parameters as a function of frequency for these reactions at each specific reaction temperature are shown in Figures S19 to S30 (SI section). For both acids for molar ratios below 1:24, no noticeable contribution of ionic conductivity appears in the loss factors of the reaction media (Figures S19b, S20b, S25b and S26b). In the case of H_3PO_4 and acetic acid, ionic contribution becomes appreciable at frequencies below 1.5 GHz for molar ratios around and above 1:36, although such contributions are lesser as compared with the observed in the case of sulfuric acid as a catalyst. The low absorption of electromagnetic energy in the microwave range by these reaction media comes from the behavior of the loss tangent (and penetration depth) during the reaction. Figure S31 shows these properties of the reaction media in the interesterification reactions with 0.5% of phosphoric and acetic acid. The loss tangent values do not vary significantly during the reactions and their values are very small, in the range between 0.025 and 0.060, while the penetration depth varies between 30 and 60 cm. Based on such values for $\tan\delta$ and dp , it can be anticipated a low efficiency of microwave heating to induce interesterification reactions using the adopted reaction conditions. Before investigating the effect of increasing the concentration of the catalyst used or even the use of another catalyst such as methanesulfonic acid, it must be analyzed the results achieved for the conversions to biodiesel and triacetin of the reactions carried out with conventional and microwave heating with the adopted reaction conditions in this section.

The biodiesel conversions obtained by the interesterification reactions of babassu oil and ethyl acetate at the various molar ratios are shown in Figure 5 together with the temperature profile of each reaction. As can be seen, the applied microwave power for each molar ratio varies in order to maintain the power to mass ratio constant and equal

to 1.5 W g^{-1} . The temperature profiles show a fast increase in temperature in the first 30 min (heating ramp), followed by an almost stabilization in the temperature of the reaction medium. Except for the reaction with a molar ratio of 1:12, whose temperature stabilizes around $100 \text{ }^\circ\text{C}$ until 120 min, reaching around $110 \text{ }^\circ\text{C}$ at 180 min, for the other molar ratios the temperature of the reaction medium stabilizes around $110 \text{ }^\circ\text{C}$ after the heating ramp. The heating of these reactions by microwaves was carried out with continuous emission of radiation and the stabilization of the temperature was mainly due to the low values of the loss tangent of these reaction media. The absorption of electromagnetic energy is minimal and the heating of the medium occurs by transferring heat from hot points to colder points in the medium. The temperature profiles of Figure 5 differ greatly from that presented by reaction media with a high loss tangent, such as in acid-catalyzed ethanolysis of crude and residual oil employing 3% of H_2SO_4 .⁴⁸ In these cases, after the heating ramp, the temperature tends to increase during the reaction.⁴⁹ It was observed that the temperature in the liquid phase is dependent on the molar ratio and applied power/mass ratio, and this dependence is more prominent at lower ethanol content (1:6 oil to ethanol molar ratio), where a temperature increase of $60 \text{ }^\circ\text{C}$ during the reaction was observed. In fact, for a molar ratio of 1:6, the liquid is superheated by microwave absorption after 10 min, with temperatures well above the ethanol boiling point, reaching values around $147 \text{ }^\circ\text{C}$ at the end of the process when applying 2.25 W g^{-1} . The temperature increase, during ethanolysis for a molar ratio of 1:12, is around $16 \text{ }^\circ\text{C}$, and the liquid maintains temperatures above $84 \text{ }^\circ\text{C}$, reaching almost $100 \text{ }^\circ\text{C}$ at the end of the reaction.

For a molar ratio of 1:30, the temperature increased by around $5 \text{ }^\circ\text{C}$, ranging from 80 to $85 \text{ }^\circ\text{C}$. A large amount of ethanol in the mixture brings the liquid temperature close

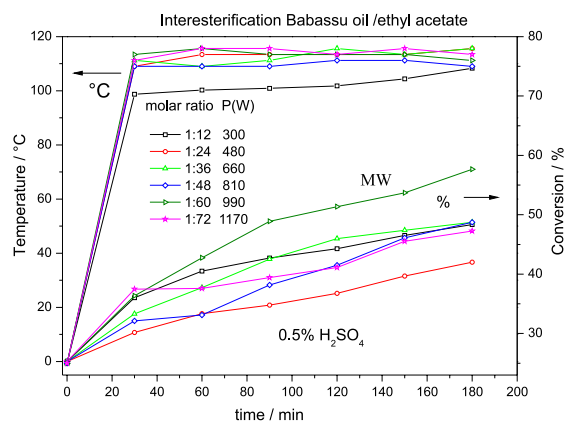


Figure 5. Measured reaction temperature and biodiesel conversion in the interesterification (MW heating) of babassu oil with ethyl acetate using various oil to acetate molar ratios and 0.5% (m/m_T) of H_2SO_4 . Applied microwave power, P (W), in watts.

to the boiling point of ethanol.⁴⁹ Therefore, the reaction temperature during continuous emission of radiation may or may not stabilize depending greatly on the loss tangent of the mixture as well as the molar ratio of reactants that are employed. Figure 5 makes it clear that the conversion into biodiesel is dependent on the molar ratio employed since the temperature of the reactions does not differ so much (around $110 \text{ }^\circ\text{C}$), and all reactions were performed with the same catalyst concentration. However, it can be observed that there is no linear relationship between conversion and molar ratio during the reactions. During the heating ramp, the molar ratios 1:12, 1:60 and 1:72 present equivalent and higher conversion values than the conversions of the other molar ratios. After 60 min, it becomes evident that the 1:60 molar ratio has the best efficiency in terms of conversion, reaching 70% conversion in 180 min while the other molar ratios achieve conversions of less than 50% . The dielectric measurements carried out above in the reaction media show low values for the loss tangent of these media, which means, compared to other reaction media, little absorption of electromagnetic energy. Even in such a condition, MW heating is expected to be more efficient, achieving greater conversions in less time than conventional heating. Table 2 shows the conversions into biodiesel and triacetin achieved with the two approaches to the interesterification reactions using different molar ratios and 0.5% (m/m_T) of H_2SO_4 . While for microwave heating the samples were collected at 180 min, for conventional heating they were collected at 240 min. The physical-chemical analysis of blended biodiesel with triacetin was studied in a previous work⁵⁹ and the values found for viscosity, flash point, water content, density and acid number are in accordance with current international standards. Furthermore, gaseous emissions analyses of blended biodiesel showed a significant reduction of CO emission (50%), CO_2 (25%) and 30% reduction in unburned hydrocarbon (UBHC) and 50% of NO_x emissions.⁵⁹

Table 2. Conversions (biodiesel and triacetin) in the interesterification of babassu oil with ethyl acetate employing various oil to acetate molar ratios and 0.5% (m/m_T) of H_2SO_4 , using microwave (MW) and conventional heating (CnvH). Samples were collected at 180 min (MW) and 240 min (CnvH)

Molar ratio	MW (180 min)		CnvH (240 min)	
	Biodiesel / %	Triacetin / %	Biodiesel / %	Triacetin / %
1:12	50.6	8.5	31.1	5.4
1:24	36.7	6.8	14.8	2.0
1:36	51.4	8.9	19.5	2.6
1:48	51.4	7.6	26.4	3.2
1:60	71.0	9.0	40.1	5.2
1:72	48.2	8.2	36.6	4.0

Table 2 clearly indicates that, as observed for heating with MW, there is no linear correlation between conversion to biodiesel and the increase in the oil/acetate molar ratio for conventional heating. All conversions achieved for biodiesel and triacetin with MW in a much shorter reaction time are significantly greater than those obtained by conventional heating in a substantially longer reaction time. For biodiesel, conversions with MW are increased by 20% to 31% relative to those obtained by conventional heating, except for the 1:72 molar ratio where the conversion is only 11% greater than that obtained by the conventional process. It should be noted that the best molar ratio is the same for the two different heating processes (1:60), providing the highest conversions into biodiesel and triacetin but with much superior results for MW heating. The higher conversions obtained by MW heating are directly related to higher reaction temperatures. The temperatures of the reactions with conventional heating are shown in Figure 4 with values of 71 °C for the molar ratio 1:12, 75 °C for the molar ratio 1:48 and 77 °C for the other molar ratios. On the other hand, reactions induced by MW have temperatures around 110 °C. Therefore, a rapid heating ramp combined with a higher reaction temperature due to continuous microwave absorption is reflected in greater conversions in shorter reaction times as shown in Table 2. Nevertheless, the data in Table 2 makes it clear that the advantages of MW heating in interesterification reactions are not prominent as they occur in acid-catalyzed transesterification reactions, where the reduction of hours to minutes in reaction times was observed and such difference is related to small loss tangent for the reaction media in the interesterification and the high loss tangent for reaction media in the transesterification reactions.

In order to verify the efficiency of microwave heating, the conversions achieved in Figure 5 can be compared with those reported early employing acid catalysis and conventional heating. For example, in previous work, Battistel *et al.*¹¹ carried out a screening of homogeneous and heterogeneous catalysts (acid and base) in the interesterification of tributyrin with methyl acetate. With a reaction temperature of 130 °C and using an oil/methyl molar ratio of 1:20 and with 0.27% (m/m_T) of H₂SO₄, it was obtained the conversion of 50% of tributyrin into biodiesel, 10% of monoacetin, 39% of diacetin and 1% of triacetin in a reaction time of 20 h. The best result was obtained by trifluoromethanesulfonic acid with acetic anhydride where, at the same temperature and reaction time, the conversion of 99% to biodiesel, 4% to monoacetin, 19% of diacetin and 78% of triacetin was obtained. On the other hand, when applying heterogeneous acid catalysis, the best result was obtained by Nafion SAC13, where at a reaction temperature

of 130 °C for 20 h, 98% conversion into biodiesel and 60% into triacetin was reported. Similarly in the homogeneous acid-catalyzed interesterification of rapeseed oil employing tin octoate, Galia *et al.*¹⁸ report conversions of 90% (70%) into biodiesel and 50% (20%) into triacetin using methyl (ethyl) acetate at a 1:40 molar ratio (oil/acetate), high temperature (210 °C) and long reaction time (20 h). Therefore, these two examples compared with the results of Figure 5 and Table 2 highlight the efficiency of microwave heating concerning conventional heating in acid-catalyzed interesterification reactions despite the small values of the loss tangent of these reaction media as shown in Figure 4.

Effect of varying molar ratio and microwave power

The same molar ratios were used in the interesterification of babassu oil with ethyl acetate using 0.5% (m/m_T) of H₃PO₄ and CH₃COOH as acid catalysts. Figure 6 shows the conversions obtained in these experiments with conventional and microwave heating. The reaction temperatures and microwave powers used in each reaction are detailed in Figures 6a and 6b. The microwave power that was applied varied with the molar ratio so that the power/mass ratio was kept constant (1.5 W g⁻¹) as the molar ratio increased. The results draw attention due to the low conversions achieved in these experiments relative to those obtained having H₂SO₄ as a catalyst (Figure 5). In this set of experiments, the lowest conversions were obtained employing CH₃COOH (Figure 6b) with conversions below 10%. For H₃PO₄, the highest conversions were obtained employing high molar ratios (1:60 and 1:72) whereas for acetic acid the highest conversions occur for small values of the molar ratio (1:12 to 1:36). Further, CH₃COOH gives higher conversions for conventional than by microwave heating for long reaction times (>180 min). It is also observed that for both catalysts the conversions obtained show no marked differences in applying microwave or conventional heating. The different results shown in Figures 5, 6a and 6b can certainly be attributed to the different catalytic activities of H₂SO₄, H₃PO₄ and CH₃COOH. The lower values obtained for the conversion in the interesterification reactions employing H₃PO₄ with microwave irradiation or conventional heating were also reported for the transesterification reactions under MW⁴⁷ and conventional heating.⁴⁷ These results suggest that phosphoric acid exhibits a low carbonyl protonation capacity in such reactions, which may be related to its higher pK_a value relative to other catalysts such as H₂SO₄ or CH₃SO₃H. However, the absorption of electromagnetic energy that heats the medium to enable the reacting molecules to overcome the energy barrier imposed by the activation energy directly depends on the dielectric properties of the reaction medium as a whole. As can be

seen in Figure 4, using 0.5% of H_2SO_4 and molar ratios between 1:12 and 1:72 produces reaction media that present loss tangents between 0.05 and 0.07 during the reaction. Figure S31 (SI section) shows that, when employing H_3PO_4 and CH_3COOH at the same molar ratios and acid concentration, the loss tangents for the reaction media are in the range between 0.025 and 0.05. Therefore, higher loss tangent values of the reaction mixture with H_2SO_4 translate into greater conversions to products. This fact has already been reported in transesterification reactions with strong acids (H_2SO_4 , ClSO_3H , $\text{CH}_3\text{SO}_3\text{H}$) where the loss tangents of the reaction media present high values, between 0.15 and 0.40,⁴⁸ in acid-catalyzed glycerol ketalization reactions⁵⁸ and acid and base-catalyzed acetylation of glycerol.⁵⁹

For the reactions catalyzed by H_2SO_4 , the highest conversions were obtained by a 1:60 oil/acetate molar ratio (Figure 5) and this value was taken to investigate the influence of increasing concentration of the catalyst on the efficiency of the interesterification reaction induced by microwaves both in conversion to biodiesel and triacetin, as well as its effect on reaction time. Figure 7 shows the behavior of the penetration depth and loss tangent at the frequency of 2.45 GHz during the interesterification reaction for different catalyst concentrations. The reaction temperatures for each acid concentration are shown in Figure 7. Due to the high concentration of acetate, the linear increase in the concentration of ions in the solution does not necessarily lead to a linear increase in the loss tangent. The increase in the number of ions does not increase their individual mobility and the ionic conductivity depends both on the number of ions and (more strongly) on their mobility. Figure 7 shows that the loss tangent during the reaction has a non-linear dependence on the catalyst concentration, as it is dictated by the ionic conductivity and the dielectric relaxation process involving the polar molecules that make up the medium. A decrease in the loss tangent can be observed

for 1% of catalyst throughout the reaction time, while for 1.5 and 2% of catalyst it is observed that the $\tan\delta$ values fluctuate around 0.06, as it occurs for 0.5% of catalyst. Based only on this behavior, it could be expected that in microwave-induced reactions there will be obtained a lower conversion for 1% of catalyst and equivalent conversions for three other catalyst concentrations. However, the loss tangent is not the determining factor, but it combines with the catalytic activity to favor the reaction towards the products. Moreover, it is known that increasing catalyst concentration leads to an increase in product formation that is contrary to the above expectation.

These issues are clarified through Figures 8a and 8b which show the conversions into biodiesel and triacetin for reactions induced by microwaves and conventional heating at different catalyst concentrations. The conversions obtained make it clear that microwave heating is more efficient than conventional heating at all catalyst concentrations. But the differences in Figure 8 between MW and conventional heating are not as striking as those observed when comparing the results by MW with those obtained by Battistel *et al.*,¹¹ and Galia *et al.*,¹⁸ where reaction times of the order of 20 h are required to achieve similar conversions. In this sense, the results shown in Figures 8a and 8b can be classified as not big differences between MW and conventional heating. For example, in 180 min of reaction with 2% of catalyst, biodiesel conversions are 85 and 67% for MW and conventional heating, respectively. This slight difference is directly related to the reduced values of the loss tangent of the reaction mixtures as shown in Figure 7. Figure 8 shows, as expected, that increasing catalyst concentration reflects an increase in conversion. However, it is interesting to note that the increase from 0.5 to 1% of the catalyst leads to a decrease in conversion and at the same time it is observed in Figure 7 that there is also an appreciable decrease in the loss tangent of the reaction mixture at 1% of catalyst.

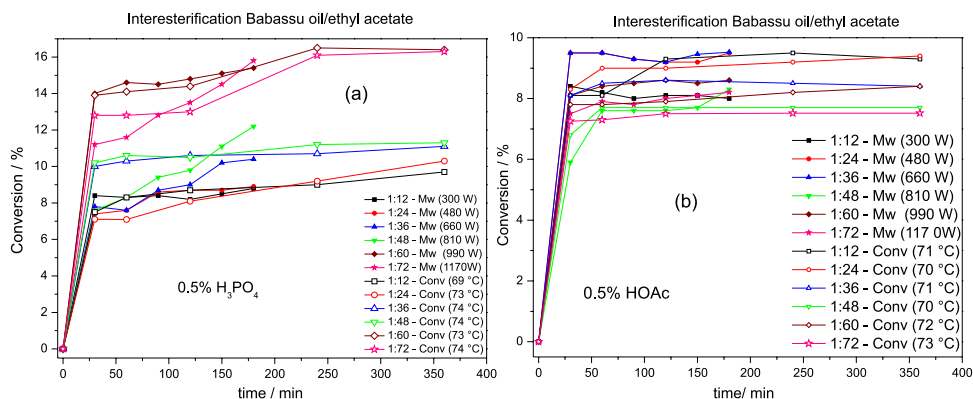


Figure 6. Conversion to biodiesel in the interesterification of babassu oil with ethyl acetate (MW and conventional heating) using various oil to acetate molar ratios and employing 0.5% (m/m_T) of (a) H_3PO_4 and (b) CH_3COOH .

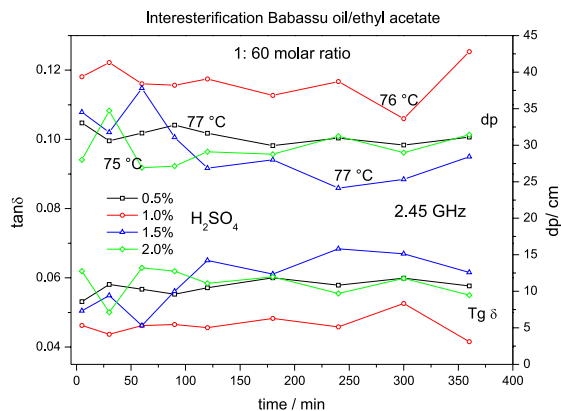


Figure 7. Loss tangent ($\tan\delta$) and penetration depth (dp) at 2.45 GHz during interesterification of babassu oil with ethyl acetate at 1:60 oil to acetate molar ratio and various H_2SO_4 concentrations.

This observed decrease in conversion only occurs with MW heating since, as shown in Figure 8, for conventional heating there is a continuous increase in conversions as the catalyst concentration increases from 0.5 to 2%. Therefore, these results make it clear that the response of the reaction medium to dielectric heating can only be interpreted correctly if it is known its dielectric properties.

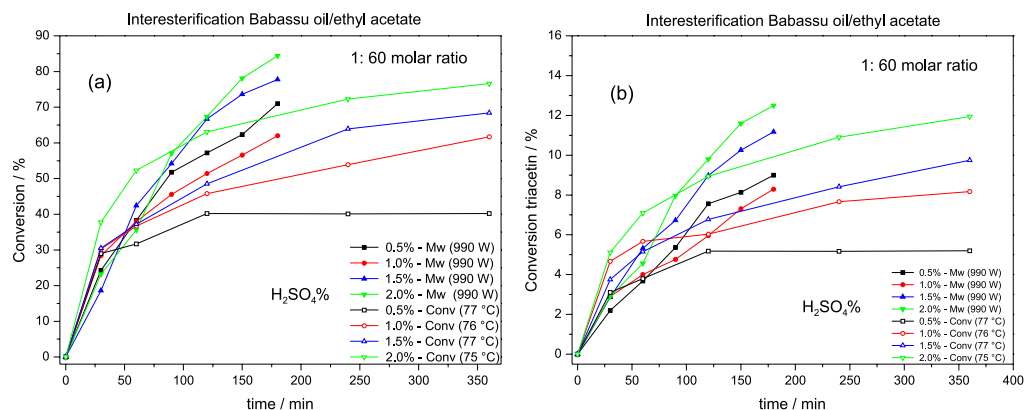


Figure 8. Conversion to: (a) biodiesel and (b) triacetin in the interesterification of babassu oil with ethyl acetate (MW and conventional heating) using various sulfuric acid concentrations and a 1:60 oil to acetate molar ratio.

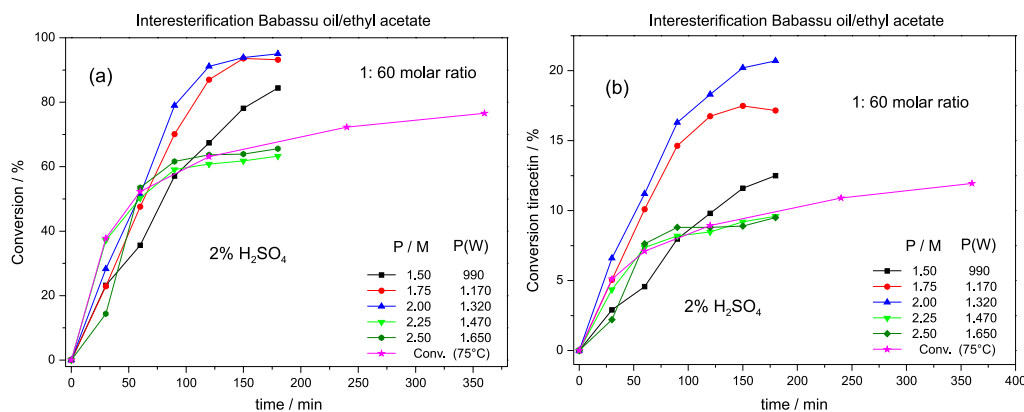


Figure 9. Conversion to: (a) biodiesel and (b) triacetin in the interesterification of babassu oil with ethyl acetate employing various microwave power to mass ratios (P/M in $W g^{-1}$). Conversion with conventional heating at 75 °C is shown for comparison. Reaction conditions: 1:60 oil to acetate molar ratio and 2% (m/m_T) of H_2SO_4 .

Since the reaction media in Figure 8 shows small values for $\tan\delta$, one way to increase the achieved conversions can be done by increasing the MW power applied to these media. Using 2% of H_2SO_4 , the efficiency of MW heating in the interesterification reaction at 1:60 molar ratio was investigated by varying the MW power to mass ratio, P/M (in $W g^{-1}$). Figures 9a and 9b show the results for conversion to biodiesel and triacetin respectively by varying the microwave power applied to the reaction. For comparison, the conversions obtained by conventional heating at a reaction temperature of 75 °C at the same 1:60 molar ratio and acid concentration. It is observed a clear increase in the conversions as the P/M ratio increases from 1.50 to 2.0 $W g^{-1}$ mainly for triacetin at 180 min of the reaction.

However, continuous increases in P/M are not allowed, causing a decrease in conversions as seen in Figure 9 in such a manner that for P/M above 2.0 the conversions become lesser than those obtained by conventional heating. Such a result is expected since the power absorbed by the reaction medium is proportional to the square of the electric field of the applied microwave. The polar molecules of the catalysts

interact strongly with the electric field of the microwave and high absorption of electromagnetic energy implies that high local temperatures easily appear with microwave heating, that is, instantaneous localized superheating,⁴⁵ and as a consequence increasing microwave power can lead to the appearance of side-reactions and the thermal decomposition of the catalyst that leads to SO_2 and other undesirable by-products, reducing markedly the catalytic activity and lowering the conversions as reported early.⁴⁷ Therefore, as seen in Figure 9 these measurements indicate that optimal condition is achieved by applying a P/M ratio equal to 2.0 W g^{-1} , giving 95% of biodiesel and 22% of triacetin in 180 min of reaction, a considerable increase concerning the values obtained by a P/M ratio of 1.5 W g^{-1} . Despite small conversions were obtained employing phosphoric and acetic acids (Figures 6a and 6b), interesterification reactions were performed to investigate the catalytic activity of H_3PO_4 and CH_3COOH by varying the P/M ratio employing 2% of catalyst and 1:60 oil to acetate molar ratio. For H_3PO_4 as the catalyst, the conversions to biodiesel and triacetin are shown in Figure 10 for the various applied P/M ratios. Results obtained by conventional heating at 77°C and the same molar ratio are shown for comparison. Must be noticed that the conversions to triacetin were negligible, being less than 1.5% for $\text{P/M} = 1.50 \text{ W g}^{-1}$, whereas biodiesel conversion achieved small values, around 14% in 180 min. Figure 10 for H_3PO_4 shows that increasing the P/M ratio tends to decrease conversions noticeably, in such a way that conventional heating becomes much more efficient than using MW heating for a P/M ratio greater than 1.50 W g^{-1} . Such a behavior can be attributed partially to the poor dielectric properties of this reaction medium (see Figure S31 in SI section) as well as side reactions and thermal decomposition of the phosphoric acid that can appear as a consequence of high input of microwave power. For acetic acid as the catalyst, the conversions to biodiesel

and triacetin for various applied P/M ratios are shown in Figure S33 (SI section). As can be seen in Figure S33, the highest conversions were obtained by $\text{P/M} = 1.5$ and increasing this ratio a continuous decrease in conversions occurs. Furthermore, the conversions achieved with MW heating present values very much below those obtained by conventional heating. The low efficiency of MW heating using acetic acid is due to the small values of the loss tangent exhibited by the reaction medium. In fact, in Figure S32, the reaction medium with acetic acid presents the lowest $\tan\delta$ values during the reaction compared to the reactions catalyzed by H_2SO_4 , $\text{CH}_3\text{SO}_3\text{H}$ and H_3PO_4 .

To achieve better performance using homogeneous acid catalysis in microwave-irradiated interesterification reactions, methanesulfonic acid was adopted as a catalyst. Experiments were carried out by varying the power/mass ratio for the reaction at the oil/ethyl acetate molar ratio of 1:60 and with 2% (m/m_T) of $\text{CH}_3\text{SO}_3\text{H}$.

The conversions obtained for biodiesel and triacetin are shown in Figures 11a and 11b. Results obtained by conventional heating at 75°C and with the same molar ratio are also shown. It is evident that the efficiency of MW heating is not much higher than conventional heating, which is due to the small values of the loss tangent of the reaction mixture (see Figure 12), as also observed above by using the other acids as catalysts in these interesterification reactions. In a reaction time of 180 min, only reactions induced with P/M ratios of 1.50 and 1.75 exhibit conversions to biodiesel that are greater than those obtained by conventional heating. For triacetin, conversions are higher than conventional heating for P/M ratios of 1.50, 1.75 and 2.0. Furthermore, using methanesulfonic acid, the conversions (Figures 11a and 11b) show an opposite behavior as the P/M ratio increases relative to the one that occurs by using sulfuric acid. While for H_2SO_4 the conversions increase as P/M increases from 1.50 to 2.0 and

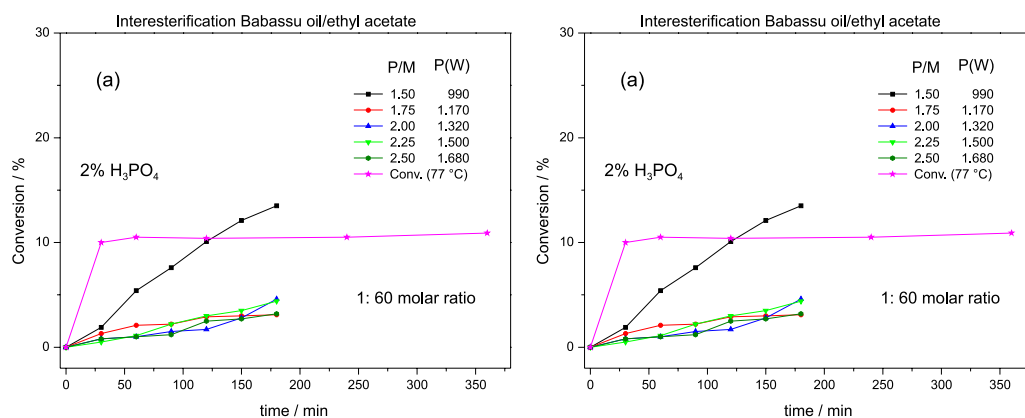


Figure 10. Conversion to: (a) biodiesel and (b) triacetin in the interesterification of babassu oil with ethyl acetate employing abundant microwave power to mass ratio (P/M in W g^{-1}). Conversion with conventional heating at 77°C is shown for comparison. Reaction conditions: 1:60 oil to acetate molar ratio and 2% (m/m_T) of H_3PO_4 .

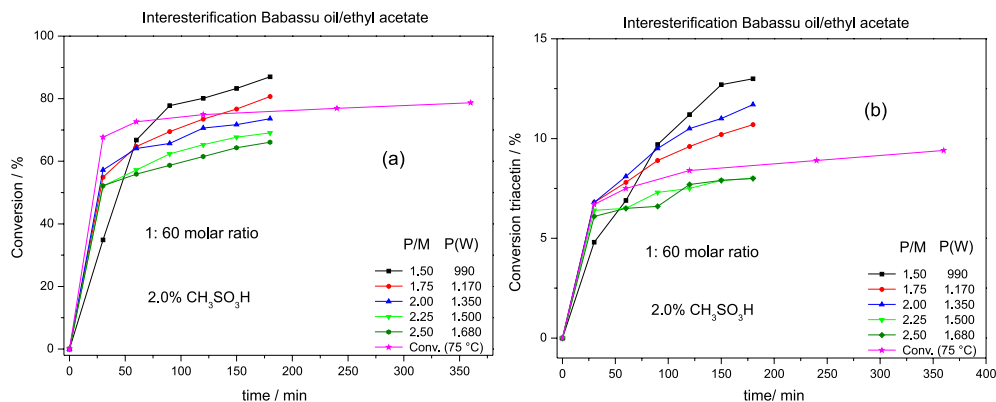


Figure 11. Conversion to: (a) biodiesel and (b) triacetin in the interesterification of babassu oil with ethyl acetate employing abundant microwave power to mass ratio (P/M in W g^{-1}). Conversion with conventional heating at $77\text{ }^\circ\text{C}$ is shown for comparison. Reaction conditions: 1:60 oil to acetate molar ratio and 2% (m/m_T) of $\text{CH}_3\text{SO}_3\text{H}$.

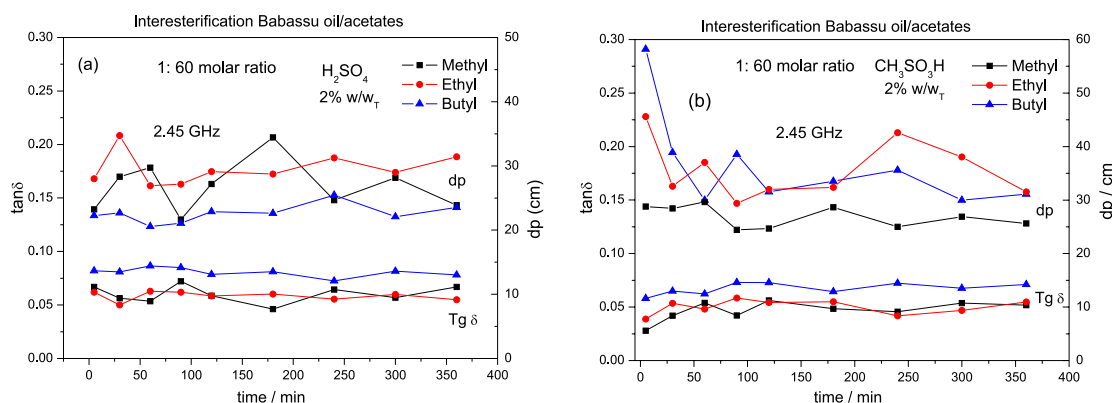


Figure 12. Loss tangent ($\tan\delta$) and penetration depth (dp) at 2.45 GHz during interesterification of babassu oil with alkyl acetates at a 1:60 oil to acetate molar ratio and 2% (m/m_T) of catalysts. (a) H_2SO_4 and (b) $\text{CH}_3\text{SO}_3\text{H}$.

decrease for higher values of P/M, for $\text{CH}_3\text{SO}_3\text{H}$ there is a continuous decrease as the P/M ratio increases as observed in Figure 11. In this case, the high loss factor of the catalyst favors its thermal decomposition by localized superheating allowing the emergence of side reactions as the microwave power increases lowering the efficiency of the process.

It is interesting to note that in the work of Battistel *et al.*,¹¹ it was employed methanesulfonic acid as a catalyst in the interesterification of tributyrin and methyl acetate reaching negligible conversions after 20 h of reaction at $130\text{ }^\circ\text{C}$, that is, 9% conversion to biodiesel and absence of triacetin. On the other hand, they found 94 and 99% of conversions to biodiesel employing pure trifluoro methanesulfonic acid and with the addition of acetic acid or acetic anhydride, respectively, but requiring also the same high temperature and longer reaction time (20 h). Hence, relative to such experiments it is very clear the greater advantage in the use of MW heating to induce acid-catalyzed interesterification reactions. Furthermore, the conversions shown in Figures 9 and 11 employing H_2SO_4 and $\text{CH}_3\text{SO}_3\text{H}$ as catalysts can be compared with alternative approaches such as homogeneous and heterogeneous base catalysis as well as the application

of ultrasound to promote the interesterification to biodiesel and triacetin production. As shown in Figures 9 and 11, in the reaction time of 3 h the better results employing H_2SO_4 are 95 and 22%, and using $\text{CH}_3\text{SO}_3\text{H}$ are 90 and 13% of biodiesel and triacetin conversions, respectively. These results compare well with those reported in the work of Chuepeng *et al.*,¹⁵ where the interesterification of waste cooking oil and ethyl acetate was performed using NaOH and CH_3COOH as homogeneous catalysts. They found that 77.5% of biofuel was reached at 0.010:1 NaOH /oil and 1:30 oil/acetate molar ratios with a reaction temperature of $80\text{ }^\circ\text{C}$ for 3 h, whereas for CH_3COOH at the same reaction conditions the conversion found was reduced to 52.4%. Regarding the reactions catalyzed by CH_3COOH , it is clear that the results achieved by Chuepeng *et al.*,¹⁵ are much better than those obtained in this study where conversions are of the order of 10% as shown in Figure 6b. In the work reported by Akkarawatkhosith *et al.*,²⁶ using ion-exchange resin as a catalyst in the interesterification of palm oil and ethyl acetate (molar ratio of 1:16.7) performed in a packed-bed reactor, it was obtained 99% of biodiesel at a reaction temperature of $113\text{ }^\circ\text{C}$ and total mass flow rate of

$5.4 \times 10^{-4} \text{ kg h}^{-1}$. Heterogeneous acid catalysis was reported by Usai *et al.*,²³ in the interesterification of extra virgin olive oil with ethyl acetate to produce biodiesel employing sulfonic acid-functionalized mesoporous silica-based materials. Their findings indicate SBA-15-phenyl-SO₃ as the most promisor catalyst reaching 39% of biodiesel and 48% of triacetin employing a 1:20 oil/ethyl molar ratio and 30% (m/m_{oil}) of catalyst at a reaction temperature of 130 °C for 6 h. In another work, Sustere *et al.*¹² investigated the reactivity of the methyl, ethyl, propyl and isopropyl in the interesterification of rapeseed oil employing sodium methoxide solution in methanol. They found that reactivity decreases from methyl to isopropyl acetate. As we shall see below, the reactivity of the acetates can show different trends in the interesterification reactions under microwave and conventional heating in acid catalysis. In the interesterification with ethyl acetate using a 1:18 oil/ ethyl molar ratio and 1:6.25 catalyst/oil molar ratio, it was obtained 60.3% of biodiesel and 5.7% of triacetin at a reaction temperature of 55 °C after 1 h of reaction.¹² Increasing to 1:36 the oil/ethyl molar ratio and reaction temperature to 75 °C, they achieved 72% of biofuel after 30 minutes. Clearly, the basic route is favored due to the strong catalytic activity of sodium methoxide dissolved in liquid methanol. Nonetheless, the very good results achieved with base catalysis have been associated with some drawbacks such as the effect of methanol and water on the catalyst and reagents reducing the yield of triacetin, forming instead diacetin, monoacetin and glycerol.¹⁰ Furthermore, base catalysis for biodiesel production has drawbacks such as the requirement of pre-treatment steps if low-quality feedstock is used, as waste cooking oil. Saponification of acetins and methyl or ethyl esters can occur leading to emulsification, causing difficult product separation.

Through the examples mentioned above, it is observed that interesterification reactions induced by microwaves using acid catalysis present very promising results

concerning conventional heating. In this sense, it is important to expand the results achieved with microwaves by including reactions with other alkyl acetates. Two other sets of experiments were carried out with methyl and butyl acetate using sulfuric and methanesulfonic acids as catalysts at a concentration of 2% (m/m_T) which provided very good results in reactions with ethyl acetate (Figures 9 and 11).

Results for methyl, ethyl and butyl acetates

For these acetates, the same oil/acetate molar ratio that provided the best results for ethyl acetate was used, that is, 1:60. Reactions using methyl and butyl acetate were also carried out with conventional heating during which dielectric measurements of the reaction medium were carried out. Figure 12 shows the behaviors of the penetration depth and loss tangent of these media as the reaction proceeds. The results of the reaction with ethyl acetate are included for comparison purposes. It can be observed that the loss tangents of the reaction medium for the three acetates are slightly higher with H₂SO₄ as the catalyst.

Furthermore, for the two catalysts, the reaction media with methyl and ethyl acetate present very close tanδ values during the reaction and with butyl acetate the loss tangent has the highest values during the reaction. In this way, reactions with methyl and ethyl acetate will absorb equivalent amounts of microwave energy, and reaction media with butyl acetate tend to absorb greater electromagnetic energy. However, due to the very small values of tanδ, the greater or lesser energy absorption is not a determining factor for the reaction yield as we shall see below.

Figures 13 a and 13b show the conversions achieved for biodiesel and triacetin for the reactions using different acetates with conventional and microwave heating using

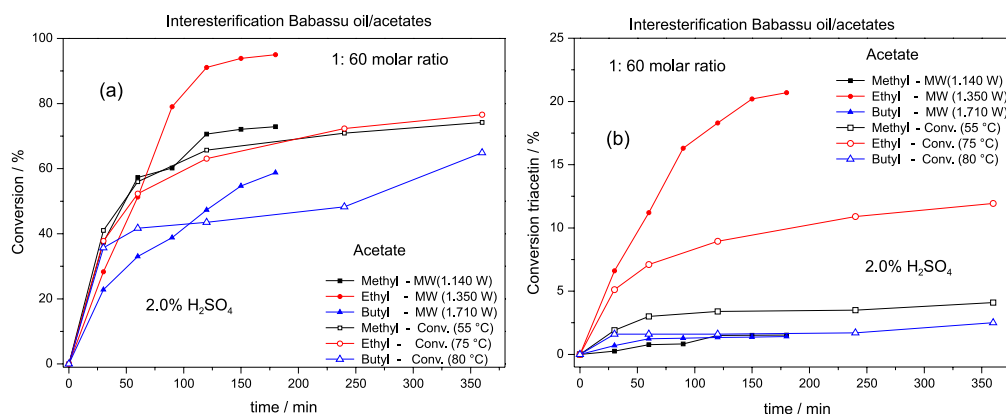


Figure 13. Conversion to: (a) biodiesel and (b) triacetin in the interesterification of babassu oil with methyl, ethyl and butyl acetates employing 1:60 oil to acetate molar ratio and 2% (m/m_T) of H₂SO₄. Conversions with conventional heating at respective reaction temperatures are shown too. Power/mass ratio equal to 2.0 W g⁻¹.

H_2SO_4 as a catalyst. For the MW-induced reactions, the power/mass ratio is taken as $P/M = 2.0 \text{ W g}^{-1}$. The first observation is that the conversions follow the order of ethyl \rightarrow methyl \rightarrow butyl. Therefore, the high-loss tangent of the reaction medium with butyl acetate (see Figure 12) has no determining influence on the efficiency of the reaction. However, in all reactions, MW heating has an advantage over conventional heating, and greater selectivity for triacetin was obtained by employing ethyl acetate as shown in Figure 13b. The selectivity for triacetin is very low using methyl and butyl acetates. Moreover, for methyl and butyl, the results in Figure 13b show that the selectivity for triacetin is greater when employing conventional heating. It must be observed that the microwave power in Figure 13 increases as it goes from methyl to butyl to keep constant the power/mass ratio for all reactions (2.0 W g^{-1}).

Using $\text{CH}_3\text{SO}_3\text{H}$ under the same reaction conditions, the conversions to biodiesel and triacetin shown in Figures 14a and 14b were obtained. Again, a decreasing trend of reactivity in ethyl \rightarrow methyl \rightarrow butyl acetates is observed. However, comparing with the results for H_2SO_4 (Figure 13a), it can be seen in Figure 14 that while the conversions with butyl acetate remain equivalent, reaching nearly 60% conversion in 180 min, for methyl acetate there is a decrease in the conversion into biodiesel, reaching a level around 60% conversion between 90 and 180 min. The selectivity for triacetin presents lower values when using $\text{CH}_3\text{SO}_3\text{H}$, with negligible values in the case of butyl acetate. But unlike what happens with the H_2SO_4 catalyst, in Figure 14b the selectivity for triacetin employing methyl and butyl acetates is slightly greater using MW heating.

Table 3 quantifies the conversions achieved with the three acetates at two different times obtained by microwave and conventional heating. The reduced selectivity for triacetin with methyl and butyl acetate for both catalysts and types of heating demonstrates that in acid catalysis the

use of ethyl acetate under the given reaction conditions is the most promising to produce biodiesel and triacetin as an additive. Table 3 makes it clear that despite the low selectivity, conversions into triacetin are greater for conventional heating using methyl and butyl acetates in reactions catalyzed by H_2SO_4 . But for the reactions catalyzed by $\text{CH}_3\text{SO}_3\text{H}$ with MW heating, there is an increase in the selectivity to triacetin with methyl acetate and the conversions into triacetin become greater than using conventional heating. The conversions employing butyl acetate are very small, less than 1%, and again with better conversions for conventional heating as shown in Table 3.

In this study, the reactivity of the methyl, ethyl and butyl acetate under acid catalysis, shows a quite different behavior from what occurs in base catalysis. In Table 3, under microwave or conventional heating the reactivity of the esters decreases as ethyl \rightarrow methyl \rightarrow butyl, whereas Sustere *et al.*,¹² reported the sequence methyl \rightarrow ethyl \rightarrow propyl \rightarrow isopropyl using as the catalyst sodium methoxide solution in methanol. And, as was explained above, the reactivity of the esters is not related to the dielectric properties of the reaction mixtures since according to the dielectric measurements, the reaction mixture employing butyl acetate has high loss tangent but conversions with this ester are lower. The reactivity exhibited by the esters is the same for both acid catalysts employed (H_2SO_4 , $\text{CH}_3\text{SO}_3\text{H}$) and clearly its origin is related to the different reaction mechanisms occurring in acid catalysis. Reverse reactions that can be enhanced in acid catalysis can lead to a reduction in triacetin by reversing the reaction that increases di and monoacetin in the reaction medium. In the case of butyl acetate, steric effects can play an important role since the large volume of such molecules generates an appreciable repulsive effect on neighbor molecules contributing to reducing its reactivity.

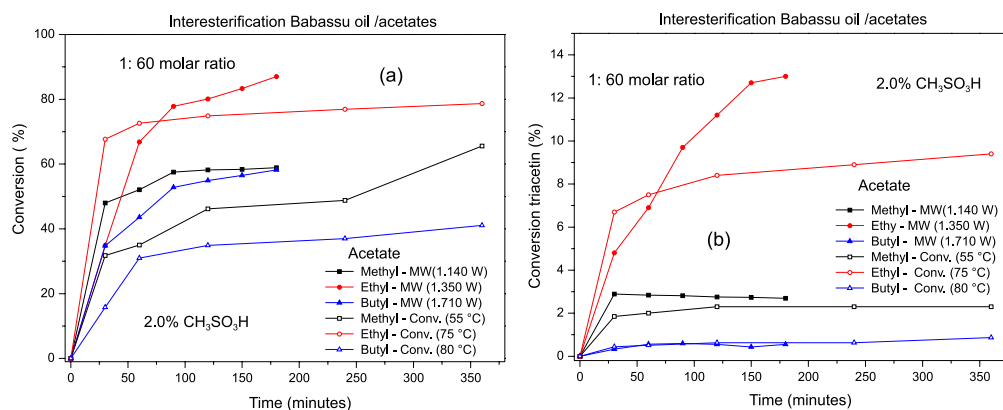


Figure 14. Conversion to: (a) biodiesel and (b) triacetin in the interesterification of babassu oil with methyl, ethyl and butyl acetates employing 1:60 oil to acetate molar ratio and 2% (m/m_T) of $\text{CH}_3\text{SO}_3\text{H}$. Conversions with conventional heating at respective reaction temperatures are shown too. Power/mass ratio equal to 2.0 W g^{-1} .

Table 3. Conversions (biodiesel and triacetin) in the interesterification of babassu oil with different acetates (methyl, ethyl and butyl) employing 1:60 oil to acetate molar ratio and 2% (m/m_T) of catalyst using microwave (MW) and conventional heating (CnvH)

	H ₂ SO ₄							
	Biodiesel / %				Triacetin / %			
	MW		CnvH		MW		CnvH	
time / min	120	180	120	240	120	180	120	240
Methyl	70.6	72.9	65.7	70.9	1.49	1.52	3.4	3.5
Ethyl	91.1	95.0	63.1	72.3	18.3	20.7	8.9	10.9
Butyl	47.3	58.8	43.5	48.3	1.34	1.4	1.6	1.7
	CH ₃ SO ₃ H							
	Biodiesel / %				Triacetin / %			
	MW		CnvH		MW		CnvH	
time / min	120	180	120	240	120	180	120	240
Methyl	58.2	58.9	46.2	48.8	2.75	2.69	2.3	2.3
Ethyl	80.1	87.0	74.9	76.9	11.2	13.0	8.4	8.9
Butyl	54.9	58.2	34.9	37.0	0.5	0.5	0.6	0.6

The results obtained by interesterification via MW-induced acid catalysis clearly demonstrate the advantages of this approach over conventional procedures in homogeneous and heterogeneous acid catalysis as long as the best catalysts are selected. However, this approach, in certain aspects, is not as competitive as base catalysis, which also has its inherent disadvantages as already mentioned. Another alternative approach is the induction of interesterification reactions via the use of ultrasound (US) as reported in some previous works.^{34,37,38} However, studies with ultrasound were found in the literature, mostly restricted to the use of methyl acetate in interesterification reactions catalyzed by sodium methoxide (or potassium methoxide) in methanol solution. Therefore, some disadvantages of basic catalysis are present in this kind of approach. To obtain a more precise idea of the results achieved by these two approaches (US and MW), it is possible to compare the conversions obtained in this work with methyl acetate using MW with previous works using US. In a previous study by Maddikeri *et al.*,^{37,38} a higher conversion was observed in the interesterification reaction of waste cooking oil with methyl acetate using potassium methoxide in the presence of ultrasound compared to the conventional method in a reaction time of 30 min. A maximum yield (90%) of biodiesel was obtained at a molar ratio of 1:12, catalyst concentration of 1.0% (m/m_{oil}) and temperature of 40 °C. They found that for reactions enhanced by the US, an increase in the oil/acetate molar ratio did not significantly raise the conversion of oil to biodiesel and these authors attribute such results to the fact that for higher molar ratios a dilution of the products (biodiesel and triacetin) occurs, making it possible to increase the reverse reaction, leading to a reduction in conversion. This fact does not occur

in the conventional procedure and, as demonstrated in this work, it also does not occur with MW heating and must be a behavior entirely due to the application of ultrasound in the reaction medium. Comparatively, Casas *et al.*^{9,10} performed an interesterification of sunflower oil using a conventional approach and reported a maximum biodiesel yield of 76.7% under conditions of a 1:50 molar ratio and 1.04% of catalyst (m/m_{oil}) at 50 °C. In these studies, the selectivity for conversion to triacetin was not analyzed. An alternative procedure is the use of ultrasound in reactions performed with enzymes as catalysts. However, relatively long reaction times needed for high conversions are the major drawback of such an approach, as reported in the work of Subhedar *et al.*³⁴ They performed ultrasound-assisted synthesis of biodiesel from waste cooking oil using methyl acetate and immobilized lipase. The biodiesel yield was 96.1% using the optimum conditions: 1:9 oil to methyl acetate molar ratio, enzyme loading of 3% (m/v), and reaction time of 3 h. For the conventional approach (without the US), 24 h are needed to achieve 90% of biodiesel employing a molar ratio of 1:12 and an enzyme loading of 6% (m/v) at a reaction temperature of 40 °C.³⁴ But, their work does not present an analysis of selectivity to triacetin. Better results were reported by Kashyap *et al.*,⁴⁰ applying ultrasound in the interesterification of karanja oil with methyl acetate in the presence of γ -alumina as the heterogeneous catalyst. They report a 69% conversion of biodiesel employing a 1:9 oil/methyl molar ratio and 1% (m_T) of a catalyst loading at a reaction temperature of 50 °C for 50 min. The experiments mentioned above present very promising results, yet, as stated before, they carry with them the disadvantages inherent to base catalysis. Furthermore, in the experiments above the

authors did not detail the selectivity for triacetin, which is an important product since as an additive to biodiesel it improves its physico-chemical features enhancing the combustion process and reducing the percentage of harmful gases released into the environment.^{59,64,65} The comparisons made above between different approaches to obtain biodiesel and triacetin as an additive through interesterification reactions clearly show the possibility of using microwave-assisted homogeneous acid catalysis with very promising results using ethyl acetate and acids such as sulfuric and methanesulfonic acid as catalysts. On the other hand, the results for methyl and butyl acetate, although significant, were lower than those obtained by ethyl acetate, where 95% conversion into biodiesel and 20% conversion into triacetin were obtained. Moreover, an important aspect of the present approach is that the yield of biodiesel and triacetin found with MW-induced acid catalysis in chemical interesterification of babassu oil with the acetates compare very well with the yield of MW-induced acid-catalyzed transesterification reactions of vegetable oils to biodiesel production.^{47,60} In addition, this chemical interesterification is of practical interest for the production of renewable fuel without producing glycerol.

Conclusions

The measured dielectric properties demonstrated that, in the acid-catalyzed interesterification reactions of vegetable oils and acetates, the dielectric heating is dictated by the relaxation process with very little or no ionic contribution. This behavior arises from the low loss tangent of the reaction mixtures due to the small values achieved by the loss factor of vegetable oils and acetates, which exceeds the high values of the loss factor of catalysts such as sulfuric, phosphoric and methanesulfonic acids.

Under microwave heating, it was found that conversions rise with increasing power until reaching an optimum value from which conversions decrease, due to the thermal decomposition of the catalyst leading to a reduction in catalytic activity and, consequently, low conversions. It was found that the reactivity of methyl and butyl acetates in the acid-catalyzed interesterification of babassu oil under MW and conventional heating decreases according to ethyl → methyl → butyl, which is opposite to what occurs in basic catalysis where a decrease in reactivity was observed with the increase in the carbon chain.

The results found in this work with acid-catalyzed and microwave-induced interesterification reactions show that this approach is very promising in obtaining biodiesel added with triacetin and is much superior to those obtained by conventional heating and is also equivalent to those

obtained by other methodologies such as ultrasonic-intensified reactions. The advantages achieved with this methodology are equivalent to those obtained in the production of biodiesel via microwave-induced acid-catalyzed transesterification reactions. Furthermore, instead of glycerol, it simultaneously produces triacetin, which as an additive improves the quality of biodiesel in terms of its physical-chemical properties, as well as reducing harmful gases emitted in the combustion process, minimizing the environmental impact generated using fossil fuels.

Supplementary Information

Supplementary data are available free of charge at <http://jbcbs.sbgq.org.br> as a PDF file.

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Author Contributions

Evandro L. Dall'Oglio, Paulo T. de Sousa Jr. and Carlos Alberto Kuhnen were responsible for obtaining resources, supervision, writing, revision, and project administration; Jonas Miguel Priebe, Leonardo G. de Vasconcelos, Andressa A. Ramos and Emanuel D. Rodrigues for investigation and designing methodology.

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