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The role of dielectric properties in the microwave glycerol acetylation and gaseous emissions of blended biodiesel

Jonas Miguel Priebe^{1,2} · Eduardo G. R. Taques Filho¹ · Evandro L. Dall'Oglio¹ · Leonardo Gomes de Vasconcelos¹ · Letícia Barbosa Ceron¹ · Paulo T. de Sousa Jr.¹ · Flávio Telles³ · Carlos Alberto Kuhnen⁴

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Abstract

Microwave assisted glycerol acetylation reactions in a monomode pilot reactor were performed in order to obtain glycerol derivatives as potential biodiesel additives. The reactions were carried out with acetic acid and acetic anhydride using sulfuric acid, pyridine and triethylamine as catalysts. The acetylation reactions yielded a mixture of mono, di and triacetin respectively with short irradiation time and high selectivity to triacetin. Pyridine exhibits 100% of selectivity to triacetin in 30 min of microwave heating with 0.88% (w/w_T) of catalyst concentration. Microwave-heating technology has been demonstrated as an alternative to reach a green chemistry and to this end becomes essential the knowledge of the dielectric properties of the materials involved in microwave heating in order to operate under optimal conditions. Dielectric properties of the pure reagents and during the glycerol acetylation under conventional heating were measured. High loss tangent were obtained for reactions mixtures employing H₂SO₄ and triethylamine and dielectric heating is dominated by ionic conductivity whereas with pyridine the dielectric heating of the reaction mixture is governed by dielectric relaxation process. Physical–chemical analysis of blended biodiesel with triacetin show values for viscosity, flash point, water content, density and acid number in accordance with current international standards. Gaseous emissions analyses of blended biodiesel showed significant reduction of CO emission (50%), CO₂ (25%) and 30% reduction in unburned hydrocarbon (UBHC) and 50% of NOx emissions. The best values were observed in the samples containing 5 and 10% of triacetin.

Evandro L. Dall'Oglio dalloglio.evandro@gmail.com

- ¹ Departamento de Química, Universidade Federal do Mato Grosso, Av. Fernando Corrêa da Costa s/n, Coxipó, Cuiabá, MT CEP 78090-600, Brazil
- ² Departamento de Ensino, IFMT/Campus Cuiabá-Bela Vista, Av, Vereador Juliano da Costa Marques, s/n, Bela Vista Cuiabá, MT CEP 78050-560, Brazil
- ³ Laboratório de Motores–UNEMAT, Barra do Bugres, Brazil
- ⁴ Departamento de Física, Universidade Federal do Santa Catarina, Campus Universitário Trindade, Florianópolis, SC CEP 88040-970, Brazil



Graphical abstract



Keywords Acetylation · Glycerin · Microwave heating · Dielectric properties · Triacetin · Blended biodiesel

Introduction

- Microwave assisted acid and alkaline glycerol acetylation were investigate.
- Pyridine exhibits 100% of selectivity to triacetin in 30 min of microwave heating
- Pyridine exhibits 100% of selectivity to triacetin in microwave heating
- Reactions mixtures with H₂SO₄, triethylamine and pyridine exhibits high loss tangent
- With H₂SO₄ and triethylamine dielectric heating is dominated by ionic conductivity
- With pyridine dielectric heating is dominated by relaxation process
- Triacetin blended biodiesel showed significant reduction of CO, CO₂, UBHC and NOx emissions
- Triacetin blended biodiesel showed reduction of CO, CO₂, UBHC and NOx emissions

Nowadays large scale biodiesel production is followed by glycerol accumulation as a byproduct and therefore is vital for the sustainability of industry to give a useful to avoid harmful environmental effects. Glycerol have innumerous applications in pharmaceutical, medical, and food industries (Fan et al. 2010) and has been used as a plasticizer, lubricant, and cryoprotectant in the automotive and chemical industries (Aroua et al. 2013). Nowadays it is very clear that alternatives for glycerol destination, as the transformation into value-added products, are recognized as a promising contribution for the biodiesel industry economic viability (Johnson and Taconi 2007). Glycerol can undergo many chemical transformations such as oxidation, dehydration, acetalization and etherification. Ketals or acetals can be formed by the reaction of glycerol with aldehydes or ketones producing five or six members' cyclic compounds (Garcia et al. 2008; Nanda et al. 2016; Zahid et al. 2020; Li et al. 2022; Vivian et al. 2021; Alptekin and Canakci 2017; Esposito et al. 2019; da Silva et al. 2020). In an earlier work Garcia et al. (2008) reported oxygen compounds obtained from glycerol that can serve as additive in mixture of diesel and biodiesel. Their results showed that the acetal 2,2-dimetil-1,3-dioxolan-4-metanol (solketal) improves the viscosity of the biodiesel as well as satisfy the European and American standards, EN 14214 and ASTM D6751 respectively.

purpose for this large amount of produced glycerol in order

In the recent years many works reported the solketal properties as a fuel additive, showing an expressive reduction in harmful emissions and the gum formation, improving the oxidation stability and enhancing the octane number when added to gasoline (Garcia et al. 2008; Alptekin and Canakci 2017). In general glycerol oxygenate products are reported to be excellent fuel additives on the basis of their improved anti-knocking, anti-freezing and viscosity. In particular the effect of oxygenated fuels on engine performance and exhaust emission has been studied (Alptekin and Canakci 2017; Lapuerta et al. 2008; Giakoumis et al. 2012; Xue et al. 2013; Zare et al. 2016). Adding triacetin to diesel fuel oil and biodiesel afforded significant reduction in CO, and small changes in the emissions of CO₂ and NOx. In fact, most results reported in the literature (Lapuerta et al. 2008) show that using oxygenated fuels leads to higher NOx formation due to cetane number, density, viscosity and higher bulk modulus of the biofuels. In this sense employing acetic acid or acetic anhydride for glycerol acetalization produces mono (MAG), di (DAG) and tri (TAG) acetylated esters of glycerol (Nda-Umar et al. 2020; Keogh et al. 2019; Mufrodi et al. 2018; Bagheri et al. 2017; Mallesham et al. 2016; Okove et al. 2017). Such acetylated esters have several applications in cryogenics being raw materials for biodegradable polyester production and cosmetics (Kaur et al. 2020). Moreover, the DAG and TAG products are well established as oxygenated fuels additives enhancing the cold flow properties of conventional diesel fuel, increasing its cetane number and reducing noxious gas emission (Garcia et al. 2008; Lapuerta et al. 2008). On experimental and theoretical grounds (Liao et al. 2010) glycerol acetylation with acetic acid is thermodynamically unfavorable. The consecutive three-step reaction that produces mono, di and triacetin exhibits a positive Gibbs free energy. Further, glycerol acetylation with acetic anhydride and sulfuric acid is highly exothermic having negative Gibbs free energy (Liao et al. 2010). Such exothermic reaction must be carried out with a cooling system to absorb the generated heat. Consequently acetic acid is usually adopted as acylation agent (Keogh et al. 2019; Mallesham et al. 2016 and Okoye et al. 2017).

In order to overcome the limitations imposed by some technical and environmental drawbacks as catalyst separation, toxic reagents, reactor corrosion, waste production, and so on, several heterogeneous catalysts have been employed (Nda-Umar et al. 2020) in glycerol acetylation. For example, K-montmorillonite (Venkatesha et al. 2016), silica functionalized acids (Ghoreishi et al. 2013), heteropoly acids (Ferreira et al. 2011; Zhu et al. 2013 and Magar et al. 2020), Sulphated ZrO₂-modified mesoporous KIL-2 silica (Popova et al. 2014), WO₃ functionalized polypyrrole (Ghoreishi et al. 2013), CeO₂-ZrO₂ metal oxide (Kulkarni et al. 2020) were reported as catalysts in acetylation reactions where is afforded and triacetin selectivity.

The above mentioned heterogeneous or homogeneous acetylation reaction of glycerol were performed under conventional heating and a crucial issue pertaining such reactions, together with the high temperatures needed, are long reaction times to achieve high conversions and desired selectivity (Mallesham et al. 2016; Magar et al. 2020). Over the past few years it became well known the high synthetic potential of microwave irradiation as an alternative heating system and some works can be found in the literature concerning microwave-assisted ketalization and acetylation of glycerol (Xie et al. 2018; Khan et al. 2022; Taques Filho et al. 2022; Troncea et al. 2011; Zhang et al. 2017; Marwan et al. 2019; Dill et al. 2019). The interactions between electromagnetic fields in the microwave range with continuous media, which are characterized by their dielectric properties lead to the macroscopic effect known as microwave heating (Metaxas and Meredith 1993). Therefore, empirical measurements of dielectric properties for both simple and complex materials are required to a complete knowledge of the dielectric heating phenomenon. The frequency and temperature-dependent relative complex permittivity of materials is defined by the relative dielectric constant, ϵ' , and the dielectric loss factor of the material, $\varepsilon_{ef} = (\varepsilon'' + \sigma / \omega \varepsilon_0)$. Here σ is the conductivity and ε'' is the imaginary part of the complex permittivity that accounts for the dielectric relaxation process (Metaxas and Meredith 1993). An important parameter concerning the dielectric response of materials to an applied electromagnetic field is the loss tangent defined by $\tan \delta = \epsilon_{ef}/\epsilon'$. 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 (d_p) , that is related to the loss tangent (Metaxas and Meredith 1993). Therefore $d_{\rm p}$ is frequency and temperature-dependent. In fact the non-uniformity of temperature distribution inside a dielectric material is mainly determined by its penetration depth. It denotes the effective region of the sample where the electrical field penetrates and consequently defining the volume of the sample where the dielectric heating effectively occurs. It follows that the knowledge of dielectric properties of complex liquids is clearly a basic and important challenging for microwave energy applications. In other words based on the knowledge of dielectric properties appropriate polar solvents and/or catalysts can be selected,

in order to inhibit or accelerate microwave-assisted chemical reactions. In the last fifteen years the dielectric properties of pure liquids and their mixtures have been widely studied (Gregory and Clarke 2009; Behrends et al. 2006; Yang et al. 2010; Kaatze 2012 and Jie and Guo-Zhu 2013) and some works reported data on the dielectric behavior of reaction mixtures during chemical reaction (Taques Filho et al. 2022, 2016; Campos et al. 2014; Dall'Oglio et al. 2015). In reaction mixtures formed by polar and non-polar molecules their intrinsic different interactions with the electromagnetic field lead to the well-known phenomenon of selective heating of polar components in detriment of non-polar ones (Xie et al. 2018; Khan et al. 2022; Taques Filho et al. 2022; Troncea et al. 2011; Zhang et al. 2017; Marwan et al. 2019; Dill et al. 2019; Behrends et al. 2006; Yang et al. 2010; Kaatze 2012; Campos et al. 2014; Dall'Oglio et al. 2015; Taques Filho et al. 2016 and Priebe et al. 2016).

In this work, acetylation reactions of glycerol with acetic acid, acetic anhydride, pyridine and triethylamine were performed by microwave irradiation in a monomode guide reactor, adapted in a WR 340 guide. These reactions were carried out in both alkaline and acid environment with and without solvent employing continuous microwave emission. With the aim of understanding the efficiency of microwave heating in the esterification reactions, in the second part of this study dielectric measurement of these reactions were carried out during the esterification process. Such measurements provide a clear understanding of the greater or lesser degree of absorption of electromagnetic energy by these reaction media resulting from the use of different catalysts and different molar ratios of the reactants. More importantly, the dielectric properties measured during the reaction allow us to understand how the interaction of the reaction medium with the electromagnetic field changes as the reaction proceeds. Dielectric properties in the microwave range of acetic acid, acetic anhydride, pyridine, triethylamine and triacetin were measured as a function of frequency and temperature. These measurements allows to obtaining the activation energies for the relaxation process in these liquids. Measurements of the dielectric properties of reaction mixture during the glycerol acetylation with acetic acid, acetic anhydride, pyridine and triethylamine were performed too. The dielectric properties of the pure liquids and mixtures were studied in the range of 0.3-13 GHz at various temperatures, whilst for the reaction mixture the measurements were done in the same frequency range at reaction temperature (80 °C). In the present study, in addition to the microwave-assisted glycerol acetylation reactions for the production of triacetin and the respective dielectric measurements of the reaction media, an analysis of the physico-chemical properties and combustion gas emission of biodiesel mixed with triacetin was also carried out. Such measures determine what reductions occur in harmful gases expelled during combustion, allowing the classification of biodiesel mixed with triacetin as environmentally friendly. In this sense, the markedly performance of blended fuel in combustion engine was reported earlier (Garcia et al. 2008; Lapuerta et al. 2008; Giakoumis et al. 2012; Xue et al. 2013; Zare et al. 2016), with very promising results. Therefore "Physico-chemical and emission analyses" includes a physico-chemical analysis of blended biodiesel where the values of kinematic viscosity, flash point, water content, specific mass and acidity were quantify with triacetin concentration. The performance of blended biodiesel with triacetin in gaseous emission such as CO, CO₂, NOx and unburned hydrocarbons (UBHC) were also investigated.

Materials and methods

Materials

Sulfuric acid (95–99% Spectrum, Gardena, USA), Acetic acid (99.7% Synth), acetic anhydride (PA Proquimios, Rio de Janeiro, Brazil), glycerin (99.5% Vetec, Rio de Janeiro, Brazil), pyridine (99.5% Sigma-Aldrich, São Paulo, Brazil), triethylamine (99% Tedia, São Paulo, Brazil), triacetin (99% B&L, Joinvile, Brazil), sodium bicarbonate (PA Controltec, Rio de Janeiro, Brazil), dichloromethane (99.5% Tedia, São Paulo, Brazil), anhydrous sodium sulfate (PA Synth, São Paulo, Brazil), n-heptane HPLC spectroscopic grade (Tedia, São Paulo, Brazil), CDCl₃ (99.9% Sigma Aldrich, St Louis, USA).

Equipment

The dielectric properties of the pure liquids at various temperatures as well as 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 (Campos et al. 2014; Dall'Oglio et al. 2015). The accuracy in the measured values of the relative dielectric constant and dielectric loss factor employing the network analyzer are $\Delta \varepsilon' / |\varepsilon^*| = \pm 0.05$ and $\Delta \varepsilon'' / |\varepsilon^*| = \pm 0.05$ respectively where $|\epsilon^*|$ is the modulus of complex permittivity. (Taques Filho et al. 2016). The experiments of the acetylation of glycerin reactions induced by microwave heating were performed in a monomode reactor inserted in the waveguide WR340 as described elsewhere (Dall'Oglio et al. 2015). The reactions were carried out under continuous microwave emission and mechanical stirring at 280 rpm.

¹H and ¹³C NMR analyses for triacetin structure were performed in a 500 MHz NMR apparatus (Bruker, Rheinstetten, Germany) at the Department of Chemistry at the Federal University of Mato Grosso (UFMT), Brazil. The measurements were performed with 50 μ L of sample and 550 μ L of CDCl₃ at 25 °C. The reactions and dielectric measurements were monitored with structural determination of the products and triacetin quantification by a gas chromatograph coupled to mass spectrometer (Shimadzu GCMS-QP5050A, Tokyo, Japan) and gas chromatograph coupled to flame ionization detector (Shimadzu GC-2010, Tokyo, Japan).

For the biodiesel physico-chemical and emissions analyses it was used the B5 fuel (5% biodiesel in diesel), B100 (100% biodiesel) and blended B100 with 5-20% with triacetin, according to the Brazilian standard ANP N° 920/2023. The quantification of gaseous emissions, CO, CO₂, NO_x and unburned hydrocarbons (UBHC) were performed using the MODAL 2010- AO system (Napro Electronic São Bernardo do Campo, Brazil). These analyses were performed at the Motor Laboratory-State University of Mato Grosso (Brazil). The analyses were performed according to NBR14489 standard using a steady engine (Yanmar, NSB95 Indaiatuba, Brazil) with 6.5 kW in 1800 RPM and 9 kW in 2400 RPM, with one energy generator Bambozzi model 46535/04 (Matão, Brazil) out 6 kW, using charge 1-2 kW (on in 220 V) and charge 2-4 kW (on in 220 V).

Glycerol acetalization reaction

The reactions were induced by microwave dielectric heating using sulfuric acid, acetic acid, acetic anhydride, pyridine and triethylamine, with various catalysts concentration, and varying glycerol/anhydride or acetic acid molar ratios. To

Table 1Conversion (%) of glycerol to product (1)

perform the acetylation reactions, the reactor was loaded with the glycerol and acetylation agent, the acid or alkaline catalyst was added to the mixture under mechanical stirring (280 rpm), followed by 800 W microwave continuous emissions. The reaction mixture was neutralized with sodium bicarbonate, diluted in dichloromethane, with subsequent addition of anhydrous sodium sulfate, before filtration and solvent removal in a rotary evaporator. Aliquots of the products thus obtained were dissolved in heptane and CDCl₃ and analyzed by GC-MS, GC-FID and ¹H and ¹³C NMR. Data on the mass and molar ratios of the components for each reaction are given in Table 1. The conversion percentages were obtained through the peak areas, calculated by the integral of all products in the respective chromatograms. This is accomplished by the quantification routine available in the GC solution software. Details are given at supplementary information (section IV). The ¹H and ¹³C NMR spectra for triacetin, chromatograph methods, chromatograms and mass spectra, for all reactions performed in this work are available in the Supplementary Information at Figures S20-S26. Molar ratios and sulfuric acid concentrations for the reactions are available at table S13.

Results and discussion

Microwave assisted reactions

A mixture of triacetin $(\underline{1})$, diacetin $(\underline{2})$, and monoacetin $(\underline{3})$ was obtained as products of the acetylation of glycerol as shown in scheme 1.

The acetylation of glycerol under microwave heating was studied through the following reactions: (i) with acetic acid in sulfuric acid and with the addition of acetic

Entry	Glycerin m (g); n (mmol)	Acetic acid glacial m (g); n (mmol)	Acetic anhydride m (g); n (mmol)	Sulfuric acid m (g); n (mmol)	Irradiation time (min)	Reaction temperature range (°C)	Conversion (1) (%)
1	15.7; 171	61.7; 1026		2.5; 26	90	104.5–107.7	41
2	15.7; 171	31.5; 524		0.77; 7.9	30	104.5-107.7	50
3	15.7; 171	67.9; 1130		0.07; 0.75	90	104.5-107.7	41
4	15.7; 171	67.9; 1130		1.28; 14.5	90	104.5-107.7	63
5	15.7; 171	92.8; 1546		3.62; 37.1	90	104.5-107.7	58
6	15.7; 171	31.5; 524	54.0; 529	0.77; 7.9	30	108.2-110.2	68
7	15.7; 171		69.8; 684	0.07; 0.75	-	-	100
8	15.7; 171 ^a		69.8; 684		30	117.3–121.6	100
9	6.3; 68 ^b		28.1; 275		60	125.5-125.9	41

^aPyridine 0.76 g (9.62 mmol)

^bTriethylamine 21.76 g (215.4 mmol); Mechanical stirring of 280 rpm

Scheme 1 Acetylation of glycerol with acetic acid or acetic anhydride using acid or alkaline catalysts



anhydride, (ii) with acetic anhydride and sulfuric acid, (iii) with acetic anhydride in pyridine and in triethylamine as alkaline catalysis. The reactions were performed varying the molar ratio of reactants, the acid (H_2SO_4) concentration and the alkaline catalysts (pyridine and triethylamine). The acetylation of glycerol with microwave heating produces a mixture of triacetin (1), diacetin (2), and monoacetin (3) (scheme 1). Table 1 shows the conversion of glycerol into triacetin (1) for the ten different performed acetylation reactions under microwave heating.

The acetylation with acetic acid catalyzed by sulfuric acid affords 100% of conversion of glycerol to a mixture of (1), (2) and (3) with conversion to (1) varying from 41 to 63% (entries 1–5 in Table 1). As it can be seen from Table 1 in reactions 1 and 3 the molar ratios used were nearly equal but markedly different acid concentrations were employed. These reactions were irradiated for a long time (90 min) giving the same conversion into triacetin (41%). Such results demonstrate that long reaction times and high sulfuric acid concentrations (entry 1) do not favor conversion. On the other hand, between reactions 3 and 4 with the same molar ratio and equal irradiation times, greater conversion was obtained for the entry 4 (1.53% w/wt of H_2SO_4). Moreover the comparison between entries 2 and 6 clearly shows that the addition of acetic anhydride greatly favors conversion into triacetin in the same reaction time (30 min) and employing a less sulfuric acid concentration as shown in Table 1. Comparing entries 1-5 in Table 1 it can be seen that increasing acid concentration increases triacetin conversion as it was found in heterogeneous acid catalyzed reactions (Bartoli et al. 2020) as well as in homogeneous acid catalyzed reactions (Dall'Oglio et al. 2016; Priebe et al. 2016). But those results in Table 1 merits further detailed analysis. Indeed entry 2 with low glycerol/acetic acid molar ratio (1:3) and 1.63% of H_2SO_4 gives better conversion in 30 min of irradiation time than entries 1 and 3 with higher and lower acid concentrations and higher irradiation times (90 min). A same behavior was observed comparing entries 4 and 5 where increasing the glycerol/acetic acid molar ratio from 1:6.6 to 1:9 and more than doubling the acid concentration reduces de conversion to triacetin from 63 to 58% in the same irradiation time.

Such observed different conversions to triacetin can be related to an increasing H₂SO₄ concentration and high irradiation times as follows. Firstly for longer irradiation times the observed decreased conversion is an indication of an optimum irradiation time. After this point the degradation of and glycerol begins. This can be attributed to the chemical transformation of glycerol in the presence of sulfuric acid submitted to a high electromagnetic energy density inside the reactor, leading to acrolein, aliphatic ethers, and other byproducts. This was already reported on microwave induced homogeneous acid catalyzed transesterification reactions to biodiesel production (Dall'Oglio et al. 2016; Priebe et al. 2016) and also in alkaline-catalyzed transesterification reactions a considerable decrease in the biodiesel conversion was observed for longer reactions times (Refaat and Sheltawy 2008). Another fact that contributes to the decrease to triacetin conversion is water formation during the acetylation of glycerol. The reverse reaction can be increased since high acid concentration and irradiation times contribute in the hydrolysis of the acetins. The water formation and the reverse reactions together with the appearance of side reactions under microwave heating, as acrolein formation where the catalyst acts in the dehydration of glycerin, can contribute for the reduction of the amount of triacetin produced. The same behavior under microwave heating was observed recently in the conversion of glycerol into solketal for different acid concentration and irradiation times. In such reactions of glycerol ketalization with acetone, water formation during the reaction can contribute also for the drop in the conversion since in acid media and under microwave irradiation water interacts with solketal leading to the opening of dioxolane ring releasing glycerol and acetone back to the reaction (Taques et al. 2022).

As shown in Table 1 the reactions performed in the microwave reactor under continuous emission occur in a temperature range, since as the reaction proceeds, the dielectric properties of the reaction medium change, modifying the degree of absorption of electromagnetic energy by the media. Therefore the reaction temperature changes as reported previously in acid catalyzed transesterification reactions where the increasing in the temperature of the reaction media with continuous microwave emission was explicitly measured (Priebe et al. 2016). In general temperature control during microwave induced chemical reactions is carried out through the intermittent application of microwaves and in this case the reactions are induced partially by microwaves and partially by heat transfer. An equilibrium configuration that originates mainly from heat transfer and not electromagnetic energy absorption is achieved by applying an intermittent emission of microwave irradiation to control the temperature. With this approach, no appreciable differences will be observed between microwave and conventional heating, as previously reported (Mazubert et al. 2014). In the present work the reaction temperature varies as the reaction proceeds since the reaction media interacts continuously with the microwave irradiation.

Therefore employing acetic acid as acetylating agent and H₂SO₄ as catalyst demands a careful balance among molar ratio, sulfuric acid concentration and irradiation time as shown in Table 1 where the best configuration is given by entry 2. Employing acetic acid with the addition of acetic anhydride using H_2SO_4 (0.76% w/w_T) as catalyst yields 100% conversion of glycerol with 68% of triacetin and 32% of diacetin and reduced irradiation time (30 min). As it can be seen in Table 1 in the reaction of glycerol with acetic anhydride using H₂SO₄ as catalyst 100% of conversion to triacetin occurred without microwave emission and it was necessary an ice bath to temperature control since the reaction is highly exothermic. This reaction therefore does not require heating (conventional or microwave) for it to occur, since it occurs naturally and clearly has no relationship with the catalyst used. The other reactions of Table 1 exhibits energy barrier with their respective activation energy and so energy must be employed to overcome such barriers. Pyridine affords 100% of conversion to triacetin with only 0.88% (w/w_T) of catalyst in 30 min of microwave heating whereas triethylamine with an irradiation time of 60 min and high catalyst concentration $(38.7\% w/w_T)$ affords only 41% of conversion to (**1**) and this can be easily explained by the greater ability to transfer positive hydrogen by the intermediate cation formed by the pyridine catalyst than that formed by triethylamine.

The data presented herein (Table 1) for the microwave assisted acetylation of glycerol with irradiation time of 30 min show better results as compared with earlier results employing conventional heating. For example, recently Brønsted-Acidic Ionic Liquids were used as catalyst in acetylation reaction of glycerol and N-methyl-2-pyrrolidinium hydrogen sulfate [H-NMP][HSO₄] was found as the best catalyst, where under optimized reaction conditions > 99% glycerol conversion was achieved with 42.3% selectivity to triacetin whereas di and triacetin selectivity > 95% was achieved within 1 h of reaction (Keogh et al. 2019). In an earlier work, Mufrodi et al. (2012) performed acetylation reactions using 0.51-1.0% (w/w_T) of H_2SO_4 as catalyst, 1:3 glycerol to acetic acid molar ratio and temperature range 100-120 °C and their best results afforded a selectivity of triacetin 77.84% with reaction time of 90 min. In another work (Mufrodi et al. 2014) employing sulfuric acid as catalyst acetylation of glycerol using batch reactor afforded 96.30% of glycerol conversion and continuous reactive distillation column resulted in glycerol conversion of 98.51%. Their results (Mufrodi et al. 2014) showed a low selectivity of triacetin for both batch reactor (13.69%) and reactive distillation (8.98%). Therefore Table 1 indicates clearly the efficiency of microwave heating in terms of selectivity to triacetin and shorter reaction times as compared with the above-mentioned studies on glycerol acetylation employing conventional heating.

On the other hand concerning microwave heating in glycerol acetylation, more recently Khan et al. (2022) reported selective esterification of glycerol using various supported ionic liquid as heterogeneous catalysts. They found that, among them, the silica-based imidazolium hydrogen sulphate supported on cellulose (IMDSi/HSO₄@ Cellulose) showed best selectivity and product yield. Under microwave heating the reaction of glycerol with acetic acid (at 100 °C) catalyzed by IMDSi/HSO₄@Cellulose afforded mono, di and triacetin showing very high selectivity for triacetin up to 99% in short reaction time (8 min). In an earlier work of acetylation of glycerol employing hydroxylated magnesium fluorides as catalysts and nonconventional heating (microwave, ultrasound) reported by Troncea et al. (2011) optimal glycerol conversions (>90%) and selectivities to the desired compounds (over 85%) were obtained. Under microwave heating they found a great rate enhancement to glycerol conversion; therefore, the reaction time of 22 h using conventional heating was reduced to 4 h with microwave heating. This rate enhancement appears explicitly in the increasing of the turnover frequency (TOF) from 50.5 to 381 h^{-1} . The reactions were performed using 1:3 glycerol/acetic acid molar ratio and reaction temperature of 100 °C (Troncea et al. 2011). Venkatesha et al. (2016) using American montmorillonite (GK-129) activated by methanesulfonic acid as catalyst for glycerol acetylation after dealumination under microwave heating, reaction temperature 120 °C and molar ratio glycerol/ acetic 1:3, reported 96% glycerol conversion in 1 h while employing conventional heating glycerol conversion reached a maximum of 82% in 48 h. Microwave assisted acetylation of glycerol using activated natural zeolite was studied by Marwan et al. (2019) where it was obtained more than 95%of glycerol conversion with reaction time of 1 h and catalyst loading of 3% employing 1:9 molar ratio glycerol/acetic acid. Their findings showed that the selectivity towards mono, di and triacetin was 80.1%, 15.4%, and 4.5% in 1 h and 43.0%, 48.6%, and 8.3% in 1.5 h respectively (Marwan et al. 2019). By means of clay minerals activated with H_3PO_4 as catalysts Dill et al. (2019) performed glycerol acetylation under microwave heating using glycerol/acetic molar ratio of 1:3 and 10% (w/w_T) catalyst (relative to glycerol mass), reaction temperature of 90 °C and reaction time of 1 h. They reported (Dill et al. 2019) selectivity towards monoacetin around 23-73% under microwave heating and by comparison conventional heating produce more diacetin instead (Liu et al. 2011; Dill et al. 2019), which indicates different selectivities depending on kind of the heating system used. This can be viewed as consequence of the strong interaction of the microwave with polar molecules including here the water molecules formed in each step of esterification which are able to hydrolyze the produced diacetin releasing monoacetin. That is, microwave heating can enhance the reverse reaction too. Moreover Dill et al. (2019) found that triacetin was more scarcely produced under conventional than under microwave heating. Therefore from Table 1 and all these reported results becomes clear that acetylation of glycerol under microwave irradiation is a better alternative synthetic route to obtain triacetin. In the present study the better performance is obtained with entry 8 of Table 1. The acetylation with anhydride employing pyridine under microwave heating and reaction time of 30 min exhibits high selectivity to triacetin (100% of conversion).

Dielectric properties

In order to understand the contribution of each reactant for the dielectric properties of these reaction mixtures during the acetalization of glycerol, dielectric parameters measurements were carried out in reactants as pure liquids. Concerning glycerol, its dielectric properties in microwave range and at various temperatures were reported in the literature (Taques Filho et al. 2022; Yang et al. 2010), but the same is not true for the other reactants, and therefore dielectric measurements at various temperatures were done in pure liquids acetic anhydride, acetic acid, and in the alkaline catalysts pyridine, and triethylamine. Measurements also were done for liquid triacetin since it appears in the reaction medium as product of the reaction. Complex permittivity measurements in sulfuric acid were done previously (Dall'Oglio et al. 2015). Figure 1a, b show the dielectric constant and the loss factor of the acetic anhydride in the range 0.3 to 13 GHz at various temperatures. More detailed results for the pure liquids glycerol, acetic acid and acetic anhydride are presented in the supplementary material. (Figures S1 to S6 and Tables S1 to S6). For frequencies below 3 GHz figure 1a shows that the



dielectric constant of acetic anhydride, which exhibits two C=O double bonds, decreases with temperature, behavior also observed in acetone with its single C=O double bond (Taques Filho et al. 2022).

This behavior is opposite that occurs in glycerol (3 OH bonds) and acetic acid (one OH bond) where the dielectric constant increases (Figures S1a, S5a) with temperature. In such liquids hydrogen bond occurs affecting the interaction of the media with the electromagnetic field but as temperature increase the kinetic energy of the molecules increases causing them to stay further apart from each other breaking H bonds. In this condition, the molecules respond quickly to variations in the electric field, which means an increase in the process of molecular realignment, increasing the dielectric constant at higher temperatures at high frequencies, as shown in Figures S1a and S5a of supplementary material. Figure 1b show that the values of the dielectric loss of acetic anhydride are in the same range (slightly below) as glycerin (Fig. S1b) but with relaxation frequencies (frequencies for which ε_{ef} has a maximum) shifted to increasingly higher frequencies as the temperature increases, a behavior which is more close related to acetone loss factor (Taques Filho et al. 2022). Indeed, glycerin (Fig. S1b) has much lower relaxation frequencies, that is, much longer relaxation times that come from a greater number of hydrogen bonds that are possible to be formed in liquid glycerin which means a greater number of intermolecular interactions increasing the time to return to equilibrium after removing the applied electrical field. On the other hand acetic acid with its single OH bond exhibits a loss factor (Fig. S5b) with relaxation frequencies at relative higher frequencies and small values for ε_{ef} (0.5 < ε_{ef} < 2.0) in the entire range of mesaured frequencies. When employing microwave heating it is commonly applied a microwave

frequency of 2.45 GHz and therefore it is important to know the behavior of loss tangent and penetration depth of the samples in such frequency at different temperatures. Figure 2 shows the loss tangent ($tg\delta$) and penetration depth (dp) as function of temperature at 2.45 GHz for the pure liquids glycerin, acetic anhydride and acetic acid. Glycerin has higher values of loss tangent (Fig. 2a) that increases with temperature whereas acetic acid loss factor varies slightly and acetic anhydride loss tangent decreases with temperature. Therefore in microwave field glycerol heats up much more rapidly than acetic acid and anhydride since the heating rate is highly dependent on the loss tangent values.

The penetration depth in acetic anhydride varies markedly with temperature (Fig. 2b) which is mostly due to the strong decrease of loss factor in this temperature range, from $\varepsilon_{ef} = 6.2$ at 10 °C to $\varepsilon_{ef} = 1.6$ at 70 °C (Fig. 1b), whereas dielectric constant varies little, from $\varepsilon t = 21.2$ at 10 °C to $\varepsilon t = 19.9$ at 70 °C (Fig. 1a). The high values reached by penetration depth in acetic anhydride (> 10 cm) reflects the poor absorption of electromagnetic energy by this liquid at higher temperatures.

Figure 3a demonstrates that, as in the case of acetic anhydride, the dielectric constant of pyridine decreases with temperature but due to the weakness of the intermolecular interactions in liquid pyridine the decreasing is observed in the entire range of measured frequencies. As temperature increases the loss factor decreases at all frequencies (Fig. 3b) and concomitantly the relaxation frequencies (obtained with Cole-Davidson model) are shifted towards higher frequencies with $f_r = 14.3$ GHz at 10 °C and $f_r = 20.2$ GHz at 60 °C (see table S7) and consequently for pyridine the dielectric loss is very low at 2.45 GHz at all temperatures ($\varepsilon_{ef} < 1.0$).



Fig. 2 a Loss tangent ($tg\delta$) and b penetration depth (dp) at 2.45 GHz for glycerol, acetic anhydride and acetic acid as a function of temperature



Fig. 3 Dielectric constant and loss factor for pyridine as a function of frequency at various temperatures



Fig. 4 Penetration depth (dp) and loss tangent ($tg\delta$) at 2.45 GHz for pyridine and triacetin as a function of temperature

The loss tangent and penetration depth in liquid pyridine as function of temperature at 2.45 GHz is shown in Fig. 3 together with the behavior of these quantities for triacetin. The dielectric behavior of triacetin and triethylamine are detailed in supplementary material. Pyridine exhibits (Fig. 4) very low loss tangent decreasing with temperature and since the dielectric constant decreases too, a marked increase in penetration depth is observed reaching high values (> 36 cm) at 70 °C, that is, pyridine becomes almost transparent to microwave field at high temperatures and consenquently its contribution to dielectric properties of the reaction mixture in the glycerol acetylation reaction will be prominent only at very high catlyst concentration as we shall see below (reducing the absorption of microwave energy of the reaction mixture as a whole).

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On the other hand, triacetin that appears in the reaction mixture as product during the acetylation reaction has loss tangent values greater than pyridine (Fig. 4) and that are more close to the values of loss tangent of acetic acid and acetic anhydride (Fig. 2a). Dielectric properties of triacetin are given in Figures S13-S15 of supplementary material. Therefore during the reaction the appearance of triacetin contributes to the absorption of the electromagnetic energy by the reaction mixture as whole whereas pyridine contributes very little to the dielectric properties of the reaction mixture. Moreover, triethylamine shows no contribution for the dielectric properties of the reaction mixture due to its poor dielectric properties (Figures S10–S12 and table S9) which are reflected in very low loss tangent and large penetration depth for this liquid mainly at high temperatures (dp increases from 68 cm at 10 °C to 155 cm at 70 °C) and therefore it can be taken as transparent to microwave energy (see Fig. S11).

The obtained dielectric spectra of the reactants involved in glycerol acetylation (Figs. 1 and 3 and Figs. S1, S5, S7 and S10) may be fitted with some current dielectric relaxation models which has been also applied for glycerol/ water and glycerol/ethanol mixtures (Behrends et al. 2006; Kaatze 2012), alcohols mixtures (Yang et al. 2010; Jie and Guo-Zhu 2013) or solketal/water and solketal/water/ acetone mixtures (Taques Filho et al. 2022). The complex permittivity of pure liquids glycerin, acetic anhydride, acetic acid, pyridine, triethylamine and triacetin were fitted using these models for the relaxation process (Debye, Cole-Cole, Cole-Davidson models). The relevant parameters, like relaxation frequencies and relaxation times at different temperatures, were obtained using these different models and presented and discussed in detail in the Supplementary Material. Treating the dielectric relaxation as rate process the free activation energy for the dielectric relaxation process in pure liquids and some mixtures can be evaluated using Erying's rate equation. In this model the relaxation time τ_r is given by Eq. (1):

$$\tau_r = \frac{A}{T} e^{\frac{\Delta F}{RT}},\tag{1}$$

where ΔF is the free activation energy, R is the gas constant and T the temperature (in kelvin). The results obtained fitting the dielectric spectra with different models allow an estimate of the free activation energy of the dielectric relaxation process for the samples using Eq. 1.

Table 2 shows the free activation energies of the studied liquids and the respective applied models for the dielectric relaxation phenomenon that best fits the measurements of the complex permittivity. The standard deviation closest to the unit was obtained with the Debye fitting for the triethylamine, while for glycerin the best fitting was obtained via the Cole-Cole model but with a low standard deviation (0.962). For glycerin, the free activation energy obtained is close to the value reported by Kaatze (2012) $(9.21 \text{ kcal mol}^{-1})$ using the experimental data for the relaxation times in glycerin. With the exception of glycerin no data were found in the literature concerning the activation energies for the remaining pure liquids of Table 2. The relatively lower value of activation energy for acetic acid compared with the value for glycerin can be explained as follows. For alcohols, mixtures of alcohols or alcohols/water mixtures a general dependence of relaxation time with the number (or concentration) of hydrogen bonding groups is expected (Kaatze 2012). Despite holding four H bond sites, it is commonly assumed that water contributes with one H-bond. In liquid glycerin glycerol-glycerol molecular interactions are the dominant mechanism and three OH groups may be involved in 6 H-bonds however it is supposed 3 H-bonds per glycerol molecule. Hence in glycerol molecule more than a single H bond has to be broken to

Table 2 Experimental dipole moment (μ) and calculated free activation energy (ΔF) of the dielectric relaxation process for the liquids involved in the glycerol acetalization. R^2 is the standard deviation

Sample	μ (Debye)	ΔF (kcal mol-1)	$\overline{R^2(\mathrm{SD})}$	Model
Glycerol	2.56	8.52	0.962	Cole – Cole
Acetic acid	1.70	3.62	0.982	Cole – Davidson
Acetic anhydride	2.80	2.50	0.988	Cole – Davidson
Pyridine	2.21	1.68	0.970	Debye
Triethylamine	0.66	0.93	0.994	Debye
Triacetin	2.73	7.91	0.985	Cole – Davidson

allow for an appreciable reorientation of dipole moment due to the applied electric field meaning a reduction in the reorientational mobility reflecting in large relaxation times and high free activation energy of the relaxation process.

The value of the free activation energy for acetic acid (Table 2) is close to that of water $(3.6 \text{ kcal mol}^{-1})$ as well as the values found for the liquids ethanol, 4.55 kcal mol⁻¹ and methanol, 3.09 kcal mol⁻¹ (Campos et al. 2014) whose molecules contributes with one H-bond. Clearly specific structural features of these molecules explain the observed differences in activation energies in these liquids.

Indeed the findings of Table 2 for the others pure liquids indicates that beyond the concentration of H bonds it is clear that structural features of the constituting molecules has an important contribution on dielectric relaxation in liquids. Triacetin is as an example where the spatial arrangement of the atoms dictates the inter molecular interactions in its liquid phase and these structural features implies in a delay in the reorientation of dipole moment due to the applied electric field leading a reduction in the reorientational mobility and high free activation energy of the relaxation process as shown in Table 2. For the liquids acetic anhydride, pyridine and triethylamine there is no formation of H-bonds too and Table 2 leaves 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. Triethylamine has the smallest free activation energy and the lower dipole moment among these molecules being almost transparent to microwaves in the frequency range studied as detailed in the supplementary material. Concerning dipole moments it is important to keep in mind the values of the dipole moments of the molecules to verify it correlation or not with the free activation energy of the relaxation process. The experimental values of dipole moments (in Debye) for the molecules involved in glycerol acetalization are shown in Table 2. For comparison the measured dipole moments (in Debye) of water, ethanol and methanol are 1.85, 1.69 and 1.70 respectively. Therefore, analyzing the activation energy values for the relaxation process in Table 2 together with the values for water, ethanol and methanol it can be seen that molecular dipole moment and the free activation energy are not strongly correlated. In fact, they are very weakly correlated or have no correlation. Therefore dielectric relaxation occurs because the molecules that make up the liquid medium are polar but the activation energy do not depends explicitly on the molecular dipole moments.

The differences in the dielectric properties among pure substances and reaction mixtures reside in different dynamics of the hydrogen-bond networks which determine intermolecular interactions based on instantaneous dipole moments whose responses to applied microwave fields are responsible for the phenomenon of dielectric relaxation. The measurements of the dielectric properties of the reaction mixtures for the acetylation of glycerol (conventional heating) were performed for all the entries of Table 1 with the exception of entry 7. The reactions for the dielectric measurements were all carried out with the same reaction conditions as the entries of Table 1 with the exception of temperature, that is, with conventional heating the reactions were carried out at lower temperatures. In the present work, dielectric measurements with the impedance analyzer use water as the reference liquid and therefore measurements must be carried out at temperatures below 100 °C. It is clear that the dielectric properties of a reaction mixture under basic or acid conditions are not additive properties (by summing up the properties of the pure substances) since in such mixtures strong electrical fields are generated due to the presence of ions affecting the molecular interactions between the solute and the solvent and their interactions with external applied microwave fields. More precisely the dielectric response depends on the specific environment which is defined by the kind of molecules and ions that constitutes the liquid medium. This fact becomes evident in Fig. 5 that shows the complex permittivity of the reaction mixture during the acid catalyzed acetylation of glycerol with acetic acid at the initial stage of the reaction and at 100% conversion of glycerol (with 58% conversion to triacetin—entry 5 in Table 1). For comparison the dielectric spectra of glycerin, acetic acid and triacetin pure liquids are also shown in Fig. 5. It was employed a 1:9 glycerol/ acetic acid molar ratio which increases the hydrogen-bond networks in the liquid mixture relative to pure glycerin and the high amount of acetic acid in the mixture reduces appreciably the values of dielectric constant (Fig. 5a) at low frequencies relative to pure liquid glycerin.

Moreover the dielectric constant increases as reaction proceeds, meaning less number of allowed H-bond networks due to the conversion of glycerol and acetic acid into triacetin. A markedly change is observed in the loss factor of the mixture (Fig. 5b) relative to the pure liquids due to the presence of 3.34% (w/w_T) of H₂SO₄. The high loss factor mainly at low frequencies, where it increases asymptotically behaving like as a branch of hyperbole, originates from the high mobility of the ions and counterions presents in the solution. For this high concentration of sulfuric acid the absorption of electromagnetic energy by the reaction mixture (Fig. 5b) occurs by ionic conductivity and the dielectric relaxation process has a negligible or any effect. The same behavior was reported early in acidcatalyzed transesterification reactions (Campos et al. 2014; Dall'Oglio et al. 2015; Taques Filho et al. 2016) and glycerol ketalization with acetone (Taques Filho et al. 2022). Taques et al. (2022) reported that for mixtures of solketal/water/ acetone (1:1:0.5 molar ratio) at sulfuric acid concentrations greater than 2.5% (w/w_T) the ionic contribution must surpass the contribution due to dielectric relaxation and it is no longer possible to attribute a relaxation frequency for the mixture.

Dielectric measurements were also performed for the reactions specified by the entries 1–4 in Table 1 and their complex permittivity are depicted in Figures S16 and S17 of supplementary material where becomes explicit the ionic contribution of sulfuric acid at different glycerol/acetic acid molar ratios. As shown in Figs. S16 and S17 for the reactions corresponding to the entries 1, 2 and 4 of Table 1, where sulfuric acid concentration are greater than 1.5% (w/w_T) , the loss factor is dominated by ionic conductivity, whereas for the entry 3 of Table 1, the loss factor (Fig. S16b)



Fig. 5 a Dielectric constant and b loss factor, as a function of frequency, during glycerol acetylation with acetic acid. Measurements in the reaction made at the beginning (ini) and with 58% conversion to triacetin (fini)

comes from the dielectric relaxation process due to the small amount of sulfuric acid (0.09% w/w_T). In the same manner the reaction mixture specified by entry 6 of Table 1, where it was used a 1:3:3 glycerol/acetic/anhydride molar ratio and 0.76% (w/w_T) of sulfuric acid, exhibit a dielectric spectra dominated (Fig S18) by relaxation process with a very small ionic conductivity contribution at low frequencies.

Measurements of the dielectric behavior of the reaction mixture in the alkaline catalyzed acetylation of glycerol with acetic anhydride were done for the entries 8 and 9 of Table 1. Despite the high values of dielectric constant of glycerin and anhydride, the dielectric constant of the reaction mixture (Fig. 6a) has values mostly determined by the anhydride concentration. The differences in the dielectric properties among pure substances and reaction mixtures reside in different dynamics of the hydrogen-bond networks which determine intermolecular interactions based on instantaneous dipole moments whose responses to applied microwave fields are responsible for the phenomenon of dielectric relaxation. Figure 6b exemplifies this kind of behavior where it can be seen that the loss factor of the reaction mixture reflects the contribution of glycerol and anhydride but with lowered values due to presence of pyridine. Both dielectric constant and loss factor in Fig. 6 decreases at the end of reaction due to the conversion of glycerol into triacetin and the presence of the remaining anhydride. Figure 6b reveals that the reaction mixture at the beginning and at the end of the reaction exhibits relaxation frequencies (f_r) intermediates to the values of glycerin $(f_r = 1.4 \text{ GHz at } 70 \text{ }^{\circ}\text{C})$ and anhydride $(f_r = 12.8 \text{ GHz at } 70 \text{ }^{\circ}\text{C})$ °C).

Indeed fitting the ε_{ef} versus frequency curves for the initial (ini) and final (fini) stages of the reaction (Fig. 6b)

employing the Cole-Cole model it is obtained nearly equal relaxation frequencies that is, $f_r = 6.39$ GHz at the beginning and $f_r = 6.52$ GHz at the end of the reaction. In order to investigate the influence of the catalyst pyridine in the dielectric properties of the reaction mixture measurements were performed using the same 1:4 glycerol/ anhydride molar ratio and very high concentration of pyridine (39% $w/w_{\rm T}$). The dielectric spectrum is shown in Fig. S19 where it can be seen that both dielectric constant and loss factor exhibits lowered values due to presence of high concentration of pyridine and as reaction proceeds the dielectric loss decreases more due to the conversion of glycerol into triacetin and the presence of high concentration of the catalyst. As shown in Fig. S19b even at high catalyst concentration the absorption of electromagnetic energy is dominated by the relaxation process. In this case, the best fitting of the dielectric loss curves for the initial (ini) and final (fini) stages, (Fig. S19b), was obtained employing the Havriliak-Negami model and nearly equal relaxation frequencies are obtained, that is, $f_r = 4.14$ GHz at the beginning and $f_r = 4.34$ GHz at the end of the reaction.

Despite that triethylamine has poor dielectric properties a quite different behavior was obtained in the complex permittivity of the reaction mixture in the acetylation of glycerol with acetic anhydride with triethylamine as catalyst as shown in Fig. 7.

The dielectric constant (Fig. 7a) at initial and final stages is mainly due to the glycerol and anhydride contributions since 41% of conversion was achieved during the reaction. In Fig. 7 it is also shown the dielectric constant and loss factor for the reaction mixture at initial stage with 1% (w/w_T) of triethylamine. The fact that triethylamine contributes little to dielectric constant of the mixture can be viewed by



Fig.6 a Dielectric constant and **b** loss factor, as a function of frequency, during glycerol acetylation with acetic anhydride in pyridine. Measurements in the reaction made at the beginning (ini) and with 100% conversion to triacetin (fini)



Fig.7 a Dielectric constant and **b** loss factor, as a function of frequency, during glycerol acetylation with acetic anhydride in triethylamine. Measurements in the reaction made at the beginning

reducing its concentration from 38.7 to $1\% (w/w_T)$ which causes a reduction in the dielectric constant instead of an increase, showing definitively that the dielectric constant of a mixture is one of its non-additive properties. For high catalyst concentration a remarkable change is observed for loss factor (Fig. 7b) which increases as a branch of hyperbole and reaching high values at low frequencies in a similar manner as occurs for the reaction mixture using sulfuric acid as catalyst (Fig. 5b). This behavior can be explained only by the appearance and consequent high concentrations of ions triethylammonium and respective acetate counterions in the reaction mixture and loss factor become only due to ionic conductivity. This high concentration of triethylammonium ions comes from the higher pKa value (10.75). Figure 7b leaves clear that even a reduced amount of this catalyst (1% $w/w_{\rm T}$) creates a considerably amount of ions and despite the observed reduction in its values the loss factor of the mixture is dictated by ionic conductivity. The difference relative to pyridine catalyst where ionic conductivity is not observed (Figs. 6b and Fig. S19b) is due to lower pKa value (5.21) which leads to a low concentration of pyridinium ion and therefore the reaction mixture exhibits low loss factor. For all studied reactions of Table 1 the loss tangent and penetration depth at 2.45 GHz at the beginning and at the end of the reaction are shown in table S12. An inspection of table S12 leaves clear that among the reaction mixtures that one with triethylamine as catalyst has highest loss tangent (0.969 at the beginning and 0.869 at the end of the reaction). Although an efficient absorption of microwave energy occurs employing this catalyst the reaction reveals a poor conversion to triacetin (41% in a reaction time of 90 min) as compared with the reaction employing pyridine where it was achieved 100% of conversion to triacetin in a reaction time



(ini) and with 41% conversion to triacetin (fini). ^a Reaction mixture with 1% (w/w_T) of triethylamine

of 30 min (Table 1). This marked difference is explained on chemical grounds by observing that the intermediated triethylammonium cation is less stable as compared with the higher stability of the pyridinium cation, intermediated formed during the reaction using pyridine.

Physico-chemical and emission analyses

This section intends to emphasize the fact that the production of triacetin with the experiments carried out in the first part of this work has an important application as an additive to biodiesel with the aim of producing a fuel that presents a very significant reduction in polluting gases during combustion. The physicochemical properties and exhaust gas analysis were carried out for different concentrations of triacetin in biodiesel. Analyses were performed in pure and blended biodiesel with triacetin varying concentration from 5 to 20% ($v/v_{\rm T}$), and are in agreement with Brazilian ANP 920/2023 and NBR14489 standards. Table 3 shows the standard values for the physico-chemical properties of pure biodiesel and the B5 fuel (5% biodiesel in diesel, standard values) together with the measured values for the B100 fuel (100% biodiesel) and blended B100 fuel with 5 to 20% with triacetin. For comparison purposes are shown the measured values for triacetin.

As shown in Table 3, in the concentration range studied, increasing the triacetin concentration in pure biodiesel (B100) increases linearly its specific mass ($R^2 = 0.998$) and acidity number ($R^2 = 0.980$) increasing faster its kinematic viscosity (cubic growth, $R^2 = 0.994$). It was also observed a decrease in the brightness and a small variation in moisture content.

	Density at 20 °C (kg/m ³)	Viscosity at 40 °C (mm ² /s)	Water content (mg/kg)	Flash point (°C)	Acidity number (mgKOH/g)
Standard	ASTM D 4052	ASTM D 445	ASTM D 6304	ASTM D 93-A	ASTM D 664
Biodiesel	850–900	3–6	Max. 500	Min. 100	Max. 0.50
B5	820-880	2.5-5.5	500	40-360	_
Sample					
B100	881.2	4.212	367	172.5	0.20
^(a) 5%	894.1	4.231	387	160.5	0.32
^(a) 10%	908.4	4.258	446	157.5	0.41
^(a) 15%	919.6	4.300	439	156.5	0.59
^(a) 20%	933.2	4.416	446	148.5	0.66
Triacetin	1153.4	6.951	346	140.5	2.25

Table 3 Standard values for pure biodiesel and B5 fuel (5% biodiesel in diesel)

Measured values for B100 (100% biodiesel), blended B100 fuel with triacetin and pure triacetin. ^(a)Percent of triacetin in blended B100 fuel

The flash point is characterized as the lowest temperature at which a mass of sample vapors in contact with a heat source causes an explosion. Pure soybean biodiesel has a characteristic flash point around 180 °C and pure triacetin in a closed vessel has a flash point around 140 °C. As a more oxygenated compound, triacetin leads to an almost linear ($R^2 = 0.855$) decrease in the flash point with increasing concentration. Regarding the water content, it was observed that the addition of triacetin up to 20% (v/v) in the mixture caused small variations in the moisture concentrations in relation to pure biodiesel, with an average value of 443 mg/ kg for 10–20% of triacetin. The increase in the acidity number is related to impurities contained in triacetin, such as free acetic acid. Up to 10%, doped biodiesel has a profile within current legislation, with the kinematic viscosity and flash point values remaining in compliance with the B5 specification and biodiesel certification with the exception of the specific mass parameter.

A limited number of studies have used triacetin as a fuel additive in combustion engines. Earlier studies (Lapuerta et al. 2008; Giakoumis et al. 2012; Xue et al. 2013; Zare et al. 2016) reported that adding triacetin to biofuel increases the viscosity and oxygen content and decreases the heating value and cetane number. A comparative study using diesel oil, coconut oil biodiesel and blended coconut oil biodiesel with triacetin mixtures in a direct injection diesel engine were carried out by Rao et al. (2012) indicating that the blend with 10% triacetin showed better engine performance, with reduced gas emissions. The triacetin was added to diesel fuel oil and biodiesel in proportions from 5 to 10% v/v, and the mixtures were tested in an electrical generator by Lacerda et al. (2015) and they found small reductions in CO, O2 and opacity, but no changes were observed in the emissions of NOx and CO_2 . In the present study from emission analyses with varying the load (free, load 1, load 2) it was performed the quantification of CO, CO₂, UBHC and NO_x, in samples of B5, pure biodiesel, and biodiesel with 5%, 10%, 15% and 20% of triacetin. Figure 8 shows the emissions of CO in percent. In the unloaded condition there is a markedly reduction in the emission of CO reaching 50% in the case of B100 with 5% of additive relative to B5 fuel. The emission of CO relative to B100 remains unaltered with increasing content of triacetin (10–20%).

In the loaded condition with load 1 the emission of CO remains constant for all the fuels, whereas for load 2 it can be observed a reduction of 50% in the emission of CO of additive biodiesel (5% to 20% of triacetin) relative to B100 and B5 fuels. These results indicate a best burning of blended biodiesel which, despite its high viscosity, avoids difficulties in its pulverization in the combustion chamber. Hence blended biodiesel with triacetin decreased the amount of CO released in the atmosphere and such result can be expected from the high oxygen content inherent to biodiesel and triacetin which favors complete combustion. The present observed CO reduction compares well with a maximum of



Fig.8 Percent of emission of carbon monoxyde. B100 (100% biodiesel); B5 (5% biodiesel in diesel); B100_5% to B100_20% (B100 with triacetin)

30% CO reduction compared to the reference diesel fuel reported by Nabi et al. (2016) whereas Zare et al. (2016) studying the effect of blended waste cooking biodiesel with triacetin on exhaust emissions reported CO reduction up to 82% at higher loads compared to the diesel fuel. The CO₂ concentration decreases when the fuel is oxygenated as shown in Fig. 9. The reason is due to the lower fuel burning rate of the oxygenated fuels at different loading conditions. In general it was obtained a reduction in CO₂ emission in the unloaded and load conditions. In the unloaded condition the best reduction (28%) in the emission relative to B5 fuel was achieved for 10% of triacetin.

In the loaded condition (load 1) there is a 26% reduction in CO₂ emission relative to B5 for 5, 15 and 20% of triacetin content, reaching a 33% of reduction for 10% of triacetin concentration. For the load 2 condition the reduction in CO₂ emission relative to B5 fuel increases for all additive biodiesel achieving 34% of reduction for 10% of triacetin. For the waste cooking biodiesel blended with triacetin Zare et al. (2016) reported CO₂ reduction up to 2.5% relative to diesel fuel.

Another incomplete combustion product which is related to the air fuel mixture is unburned hydrocarbon (UBHC) emissions. From the literature, using biofuels can decrease UBHC formation due to the oxygen content of fuel and absence of aromatics, since both conditions promotes more complete combustion (Lapuerta et al. 2008; Giakoumis et al. 2012; Xue et al. 2013). Figure 10 shows UBHC (ppm) emissions for the fuels in the unloaded and loaded conditions. In the unloaded condition there is a markedly reduction mainly for 15% of concentration of triacetin (48% reduction).

For loaded condition (load 1 and 2) it was obtained an anomalous behavior in the emission of UBHC with greater emission, relative to B5 fuel, for B100 and B100 additive with the exception of the B100 with 5% of triacetin where 20% of reduction in emission occurred with load 1 and



Fig.9 Percent of emission of carbon dioxyde. B100 (100% biodiesel); B5 (5% biodiesel in diesel); B100_5% to B100_20% (B100 with triacetin)





Fig. 10 Percent of emission of unburned hydrocarbons (UBHC). B100 (100% biodiesel); B5 (5% biodiesel in diesel); B100_5% to B100_20% (B100 with triacetin)

43% of reduction with load 2. For both load conditions the mixture with 5% of triacetin shows the best behavior relative to B100 fuel with 72% UBHC emissions reduction. The observed reductions in UBHC (Fig. 10) are in good agreement with the findings of Zare et al. (2016) and Nabi et al. (2016) where they report reductions up to 64% and 55% of UBHC relative to diesel fuel respectively.

Figure 11 shows the emissions (ppm) of NO_x for the samples for both unloaded and loaded conditions. It is well known that NOx formation highly depends on temperature, residence time, oxygen content, fuel properties and injection-related factors. Three mechanisms contribute to NOx formation (Lapuerta et al. 2008; Giakoumis et al. 2012; Xue et al. 2013; Zare et al. 2016). In the first place, due to a high temperature thermal NOx is produced by combining air nitrogen with oxygen in the combustion chamber and such mechanism is the highest provider of NOx emissions from the combustion of diesel fuel. The second way is prompt NOx that is formed in the combustion chamber after the reaction of hydrocarbon species with nitrogen to form HCN. The nitrogen-born fragments are then reacted with airborne nitrogen. Fuel NOx is the third way where NOx



Fig. 11 Percent NO_x emission. B100 (100% biodiesel); B5 (5% biodiesel in diesel); B100_5% to B100_20% (B100 with triacetin)

is produced during combustion process when fuel borne nitrogen combines with excess oxygen. In this case NOx formation depends on the formation of intermediate species of nitrogen (HCN, NH, NH₃, and CN) that are then oxidized to form NOx. In the present study, the blended biodiesel samples inherently do not contain nitrogen and therefore it is expected that fuel NOx with biodiesel blends be minimal.

Concerning NOx emissions it has been reported in the literature higher NOx formation using oxygenated fuels due to reasons such as higher bulk modulus, cetane number, density and viscosity of the biofuels (Lapuerta et al. 2008; Giakoumis et al. 2012; Xue et al. 2013; Zare et al. 2016; Rao et al. 2012; Lacerda et al. 2015; Nabi et al. 2016; Tesfa et al. 2014; Subramanian and Lahane 2013; Rahman et al. 2014; Szybist et al. 2005; Jeyaseelan et al. 2014). For example in the work of Nabi et al. (2016) they found that the NO emissions are higher for five oxygenated blends having 6.02–14.23% oxygen compared to those of the reference diesel (0% oxygen) whilst in the work of Zare et al. (2016) it was observed an increase NOx emissions up to 31%. On the other hand some authors observed no changes in the NOx emissions or even showed better engine performance with reduced gas emissions (HC, CO, CO₂, NO_x) employing blended biodiesel (Lapuerta et al. 2008; Giakoumis et al. 2012; Xue et al. 2013; Rao et al. 2012; Szybist et al. 2005 and Jeyaseelan et al. 2014).

Contrary to the expected increasing in the NO_x emissions for biodiesel and its mixtures, Fig. 11 reveals a sensible reduction in NOx emissions for B100 and its additives relative to B5 fuel. For unloaded condition the greatest reduction in the NO_x emission occurs for 20% of triacetin content. In general, for unloaded and loaded conditions, relative to B5 fuel the B100 and its additives (5-20% of triacetin) shows around 40% in NO_x emission reduction. Considering the present results and that some authors find an appreciable increase up to 30% (Zare et al. 2016; Tesfa et al. 2014) and others no appreciable changes or even a small increase in NOx emissions (Lacerda et al. 2015; Subramanian and Lahane 2013; Rahman et al. 2014; Szybist et al. 2005) and based in the fact that has been argued that the oxygen content of biodiesel or blended biodiesel does not directly influence the NOx emissions it can be suggested that more research may be needed regarding the other properties of biodiesel and its mixtures and their effects on combustion and the fuel system to explain in what circumstances the increased/decreased NOx emissions can occur (Xue et al. 2013). It is important to note as previously reported in the reviews of Lapuerta et al. (2008) and Xue et al. (2013) that different results regarding NOx emissions were achieved. Despite the majority of the published works found increase in NOx emissions, in some cases emissions are reduced and in others no significant differences in NOx emissions were found. For example in the experimental analysis of Rao et al. (2012) of blended biodiesel with 10% of triacetin they found a 28% reduction in NOx emissions at highest load relative to reference diesel. In another work Jeyaseelan et al. (2014) found that NOx emissions are higher for biodiesel at all loads with a maximum increase of 7.5% compared with those for diesel in an engine having a mechanical-type injection system. However these authors stress that for an engine with a modern common-rail direct-injection system, the injection timings remain unchanged and hence NOx emissions with biodiesel or diesel blends remain the same to that of diesel emissions. Despite some opposite results found in the literature concerning NOx emissions it's clear that such results do not preclude the reasonability in employing additives in biodiesel fuel from glycerol derivative in order to obtain an overall decreases of the gaseous and particulate emissions contributing to a reduction of global warming and of environmental degradation and minimizing the adverse health effects of fossil fuels.

Conclusions

Microwave-assisted acetylation of glycerol performed in this work showed that acetic acid catalyzed by sulfuric acid gives 100% of conversion with a mixture of mono, di and triacetin and selectivity to triacetin varying from 41 to 63%. In such reactions 100% of selectivity to triacetin was not achieved since high H₂SO₄ concentration and high irradiation times favor the reverse reaction, that is, the hydrolysis of the acetins due to water formation during reaction. Also it was observed that increasing the glycerol/acetic acid molar ratio from 1:6.6 to 1:9 and more than doubling the acid sulfuric concentration reduces the conversion to triacetin from 63 to 58% in the same irradiation time, leaving clear that the use of acetic acid as acetylating agent and H_2SO_4 as catalyst demands a careful balance among molar ratio, sulfuric acid concentration and irradiation time to achieve higher selectivity to triacetin. The best results employing microwave heating was reached with pyridine which gave 100% of conversion to triacetin with 0.88% (w/w_{T}) of catalyst in 30 min of irradiation time whereas triethylamine under 60 min of irradiation time and high catalyst content gave only 41% of conversion. Such difference in selectivity can be easily explained by the greater ability to transfer positive hydrogen by the intermediate cation formed by the pyridine catalyst than that formed by triethylamine.

The measured dielectric properties of the various reactions mixtures demonstrated that in acid catalyzed reactions with sulfuric acid dielectric heating is dictated by ionic conductivity with loss tangent reaching high values (at reaction temperature) at commonly used frequency (2.45 GHz). The reaction mixture with glycerol/ acetic acid/acetic anhydride with low sulfuric acid concentration exhibits low loss tangent and the microwave heating of this mixture is governed by the relaxation process. Due to the poor dielectric properties of pyridine the reaction mixture using this catalyst has small loss tangent values and the dielectric heating of this reaction mixture is dominated by relaxation process. The behavior of loss factor with frequency of the reaction mixture with triethylamine is analogous to that of mixtures with sulfuric acid. Such behavior can be explained only by the appearance and consequent high ions triethylammonium and counterions acetate concentration in the reaction mixture which implies that the loss factor of the mixtures is due only to ionic conductivity. This high concentration of triethylammonium ions comes from its higher pKa value whereas in reaction mixtures with pyridine ionic conductivity is not observed which is due to the lower pKa value for pyridine leading to a low concentration of pyridinium ion and hence the reaction mixture exhibits low loss factor that is governed by relaxation process.

Physico-chemical analyses of pure biodiesel (B100) with increasing content of triacetin showed an increasing in the specific mass, kinematic viscosity and acidic number and lower flash point of the mixtures relative to B5 Fuel. Contents of 15% and 20% of triacetin gave mixtures with specific mass and acidic number out of the range the current standards. Analyses of gaseous emissions for samples of B5 fuel, pure biodiesel (B100) and biodiesel additive with 5% to 20% of concentration of triacetin showed the triacetin as an alternative choice as additives for fuel, compared to diesel leading to a reduction in CO, CO₂, HC, O_2 and NO_x emissions relative fossil fuel. These results showed a significant reduction of 50% in CO emission, 25% in CO2 and 30% in UBHC (ppm). Despite the present results agree with earlier studies that showed a reduction in NOx emissions up to 28% the appreciable reduction found in the present work contradict previously reported results that found an increase in NOx emissions up to 30%. Indeed the results presented here indicate the need for future measurements to solve the current controversy. The best values were observed in the samples containing 5 and 10% of additive. On the basis of 10% content of triacetin in biodiesel there will be the absorption of 100% of the glycerol produced in the biodiesel production process.

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Declarations

Conflict of interest The authors declare no competing interests.



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