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Ultrasound assisted interesterification of babassu oil with acetates using acid catalysts for biodiesel and triacetin production

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ABSTRACT

The ultrasound-assisted (US) interesterification of babassu oil with methyl, ethyl and butyl acetates was carried out via acid catalysis for biodiesel production with triacetin as an additive and therefore filling the gap in the field of US induced interesterification reactions. The scanning for the best catalyst was performed using sulfuric, methanesulfonic, p-toluenesulfonic, phosphoric and acetic acids. In order to achieve optimal conditions reactions varied in terms of reactant molar ratio, type and concentration of catalyst, temperature (20 to 50 °C) and ultrasonic energy (120 to 320 W). Using ethyl acetate, reactions were carried out at various molar ratios of oil to acetate (1:12 to 1:72) using sulfuric acid (0.5 % w/w_T). The 1:60 experiments were carried out with sulfuric acid concentrations ranging from 0.5 % to 3 % (w/w_T). The best catalytic activity was sought using the acids at a concentration of 2.5 %, with 200 W and 1:60. The best catalytic activities were achieved with H_2SO_4 followed by CH_3SO_3H and $CH_3C_6H_4SO_3H$ and the reactivity follows the ethyl→methyl→butyl trend. The best results were achieved using ethyl acetate with H_2SO_4 yielding 95.4 % biodiesel plus triacetin with a content of 17.6 % of triacetin in 180 min, which represents an intensification of 25.4 % compared to conventional heating.

1. Introduction

Recently, the climate impact caused by the use of fossil fuels has become increasingly severe, leading serious adversities for populations in the most different regions of the world. In fact, petroleum based products creates substantial pollution problems all around the world and many different ways are being explored currently to find new synthetic routes for environmentally friendly alternatives fuels such a biodiesel [1,2]. In this regard, the total or partial replacement of fossil fuels by biofuels is essential in order to meet climate goals, since the reduction in emissions of noxious gaseous and harmful particulate emissions with the addition of additives to biodiesel has already been proven, therefore minimizing the adverse health effects of fossil fuels as well as reducing environmental degradation and global warming [1-3]. Furthermore, biodiesel represents a renewable energy source that enables non-toxic, biodegradable production with a high cetane number and low flash point, without requiring engine modifications [3]. Transesterification

reactions for biodiesel production also yield glycerol in quantities up of to 10 % (based on the oil mass) of biodiesel obtained. Consequently, the biodiesel industry generates a huge amount of low-value products like glycerol [2].

Therefore, it is vital for sustainability to find a meaningful purpose for the large quantities of glycerol produced [4]. As an effort to find new and economical ways to utilize crude glycerol, recent works report glycerol on acetylation and ketalization reactions to obtain biodiesel additives [5-9].

Another more promising alternative approach for biodiesel production is interesterification, where the alcohol (typically methanol) in transesterification is replaced by an ester (e.g., methyl acetate). Indeed, interesterification process is an approach that avoids characteristic drawbacks associated with the transesterification process for biodiesel production, such as costs and the formation of low-value by-products like glycerol. In recent years the interesterification of edible oils or waste cooking oils (WCO) has been studied as a promising alternative to the

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transesterification in biodiesel production, primarily because it reduces costs and leads the formation of valuable by-products such as triacetin instead of glycerol [10-22].

More precisely, the interesterification reaction between acylglycerides and alkyl acetates can be undesirable as a reversible reaction in three-consecutive steps. First, triglycerides are converted to monoacetyldiglycerides, then to diacetylmonoglycerides in the second step, and finally to triacetin. The formation of an alkyl ester of fatty acid occurs in each step. As an initial approximation, Casas et al. [10] assumed that the interesterification reaction behaves like a irreversible second-order reaction, similar to the transesterification of triglycerides with methanol. The interesterification of vegetable oils with carboxylate esters have been reported using homogenous alkaline or acid catalysts [10-22], heterogeneous catalysts [23-29] as well as supercritical conditions [30-32].

High temperatures and pressures are generally required, along with long reaction times, resulting in higher costs of biodiesel production. Unconventional heating methods can be used to overcome these obstacles, such as microwave heating and the use of ultrasound. Regarding the intensification of interesterification reaction recently Priebe et al. [33] investigated microwave assisted interesterification of babassu oil with methyl, ethyl and butyl acetates employing homogeneous acid catalysts. Under such acid conditions they found that the reactivity of microwave or conventional heating follows the trend of ethyl→methyl→butyl, and microwave heating yields higher conversions in shorter times [33]. Regarding the use of ultrasound, the induction of homogeneous reactions is based on the collapse of cavitation bubbles, which in turn depends on acoustic factors such as frequency and intensity of ultrasonic waves, as well as solvent properties like viscosity, surface tension, density and vapor pressure. During collapse high local temperatures and pressures are achieved that increases the reaction rates thereby facilitating faster reaction times [34,35]."

Some works reporting, among others, on the interesterification of oils and residual oils employing ultrasound demonstrated the reliability and efficiency of this technique in such chemical reactions [36-48]. Indeed, very promising results have been reported using ultrasound to induce interesterification reactions of oils with methyl acetate catalyzed by potassium hydroxide or potassium methoxide [39-44] as well as in the heterogeneous catalysis using solid catalyst (Cu_2O) [48] or gamma-alumina [47].

In the present study a new pathway is proposed, specifically the interesterification reaction of babassu oil with alkyl acetates, via ultrasound-assisted homogeneous acid catalysis. Reactions were performed to investigate its efficiency as a method of intensifying these reactions compared to results obtained through microwave irradiation and conventional heating under the same reaction conditions. Employing ethyl acetate, a first set of reactions was carried out at various molar ratios of oil to acetate (from 1:12 to 1:72) using sulfuric acid (0.5 % w/w_T) as the catalyst. For the best molar ratio found (1:60), a new set of experiments was conducted varying the concentration of sulfuric acid from 0.5 % to 3 % (w/w_T). Measurements were performed for interesterification reaction with fixed ultrasound (US) power at various reaction temperature using the optimal molar ratio (1:60) and catalyst concentration (2.5 %). The influence of the applied US power on interesterification reactions was investigated by applying different US power at a mass ratio with a molar ratio of 1:60 oil to ethyl acetate, using 2.5 % sulfuric acid and a low reaction temperature (20 °C). The effects of different acid catalysts were studied using H_3PO_4, CH_3COOH, $CH_3C_6H_4SO_3H$ and CH_3SO_3H, employing the best molar ratio and 2.5 % of catalyst concentration. The best catalytic activity was achieved with H_2SO_4 and in order to study the influence of different acetates, another set of reactions were performed employing methyl and butyl acetates with a molar ratio of 1:60 oil to acetate and 2.5 % of sulfuric acid. Finally, these ultrasound results are compared with experiments under the same reaction conditions performed with microwave irradiation and conventional heating for acid catalyzed interesterification reactions in

biodiesel production.

The babassu palm (Orbignya Phalerata) is an endemic species of the Amazon rainforest, whose oil extracted from the seeds is mainly composed of saturated fatty acids, such as Caprylic (3.8 %), Capric (5.4 %), Lauric (47.8 %), Myristic (16.5 %), Palmitic (8.6 %) and Stearic (3.4 %) acids, in addition to the unsaturated Oleic (12.0 %) and Linoleic (2.5 %) acids, characterized by the provision of a biodiesel with a better cetane index and greater oxidative stability, compared to its unsaturated equivalents [49]. Furthermore, it demonstrates extraordinary potential as an alternative oil source for biodiesel production, since it is considered a second-generation raw material, escaping discussions related to food crops, in addition to promoting the variability of oil sources in biodiesel production, the possibility of reducing raw material costs and implementing its cultivation in areas that are not very suitable for agricultural and livestock practices [50].

2. Materials and methods

2.1. Materials

Butyl acetate (99,5 % LABSynth, Diadema, Brazil), ethyl acetate (99,5 % Neon, Suza no, 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), p-toluenesulfonic acid (95 %, Êxodo Científica, Hortolândia, SP-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).

2.2. Equipment

The experiments of the interesterification reactions induced by ultrasound were performed in a Ultrasonic Processor Hielscher UP400 S, immersion probe H40, 24 KHz, maximum power of 400 W (Serial No 350,111,603, produced in Germany). The temperature of the reaction medium was stabilized using a Chiller-type recirculator (Buchi brand, model F-108, Serial No 613,511), an ultra-thermostatic bath (SOLAB brand, model SL 152/10, Serial No 21,050,029) and monitored with a digital thermometer (Minipa, APPA ET-2609, true rms multimeter, São Paulo, Brazil). The reactions were monitored with biodiesel and triacetin quantification using a gas chromatograph coupled with a flame ionization detector (Shimadzu GC-2010, Tokyo, Japan) equipped with an automatic injector, model AOC-5000, according to the Brazilian standard ANP N°920/2023 [51]. The viscosity measurements were performed using a microprocessor rotary viscometer with concentric cylinders (Quimis Aparelhos Cientificos brand, model Q86M26; serial number 15,030,838). Density values were obtained using a digital density meter (KEM brand – Kyoto Electronics MFG, Model DA/500, serial number RKK53A19).

2.3. Interesterification reactions

The interesterification reactions were carried out in batches by adding the vegetable oil to a beaker and adding the acid catalyst (sulfuric, phosphoric, methanesulfonic and p-toluenesulfonic acids and acetic acid) in different mass percentages, varying from 0.5 at 3.0 % w/w_{total}, under magnetic stirring for one minute. Subsequently, while still stirring, alkyl acetate (methyl, ethyl or butyl acetate) was added, in different stoichiometric ratios (1:12, 1:24, 1:36, 1:48, 1:60 and 1: 72) as shown in Tables S1, S2 and S3 in Supplementary Information. This

mixture was then transferred to a borosilicate cell inserted in an SB1 acoustic protection box lined with polyurethane foam (30 mm thick). The jacketed cell was connected to a Chiller-type recirculator (Buchi brand, model F-108, Serial No 613,511), pre-stabilized at working temperatures (20, 30, 40 and 50 °C). The H40 ultrasonic immersion probe was inserted into the cell and the reactions occurred with a fixed duration of 180 min, under ultrasonic irradiation from a portable ultrasonic processor (Brand Hielscher Ultrasound Technology, Model UP 400S, 24 kHz, 400 W, Serial No 350,111,603, produced in Germany), with ultrasonic power varying from 120 to 400 Watts.

During all reactions, at 30 min intervals (30, 60, 90, 120, 150 e 180 min), samples of the liquid phase (1mL) 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. After filtration and solvent evaporation, the samples were prepared for chromatographic analysis. The reactions were monitored with ethyl, methyl and buthyl esters derived from fatty acids 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 N°920/2023 [51]. The sample analysis procedure was adapted (Supplementary Information, section III) from the international British standardization, using the standard described in the European Standard BS EN 14,103, published in the BSI Electronic Catalog or British Standards [52].

The results for the conversions were obtained taking into account the production of biodiesel with triacetin as additive, where the overall theoretical yield was calculated from the percentage composition of fatty acids present in the oil, the molar mass and the stoichiometry of the reaction for the different alkyl acetates used. Thus, the conversion of 100 % of biodiesel with additives corresponds to 77.2 % of biodiesel and 22.8 % of triacetin for the reactions with methyl acetate, 78.1 % of biodiesel and 21.9 % of triacetin for ethyl acetate and 80.5 % of biodiesel and 19.5 % of triacetin for butyl acetate.

2.4. Viscosity measurements

The viscosity measurements were performed using a microprocessor rotary viscometer with concentric cylinders (Quimis Aparelhos Cientificos brand, model Q86M26; serial number 15,030,838). A 35 mL aliquot of the homogenized solution was used, carefully transferred to the rotor to avoid the formation of bubbles and with the working temperature (20 °C to 50 °C) stabilized using an ultra-thermostatic bath (SOLAB brand, model SL 152/10, Serial No 21,050,029) and monitored using an attached digital thermometer. During the reaction development, viscosity was measured three times: the first before the start of acoustic cavitation, and the others after 90 min and 180 min of incidence of ultrasonic waves.

3. Results and discussion

3.1. Effect of varying the molar ratio

In this work, the interesterification of babassu oil was initially carried out with ethyl acetate using sulfuric acid as the catalyst. The best reaction conditions for ultrasound-assisted interesterification process using acid catalysts are determined by variables such as molar ratio of reactants, concentration and type of acid, reaction temperature, intensity of the sound source. Although in interesterification reaction the stoichiometry is one mole of oil to three moles of acetate, it is always recommended to use excess of acetate [46] so that the equilibrium is shifted towards higher yields of products. A first series of experiments were carried out varying the molar ratio of reactants and with a low concentration of acid. Babassu oil interesterification reactions with ethyl acetate were carried out, varying from 1:12 to 1:72 the oil/acetate molar

ratio and using 0.5 % (w/w$_T$) of sulfuric acid as a catalyst. It is known that acid catalysis using conventional heating requires high reaction temperatures and longer reaction times to achieve conversions higher than 80 % in the interesterification of oils with acetates [11]. Aiming to highlight the effectiveness of ultrasound as an inducer of acid-catalyzed reactions, this first set of reactions were carried out under moderate conditions. This initial choice is based on the fact that it is known that at high temperatures ultrasonic waves do not promote reactions induction as effectively. This is because the simultaneous increase in vapor pressure leads to a greater amount of vapor inside the bubbles and consequently the collapse of the cavitation bubbles is less violent, as are the shock waves generated by their collapse resulting in lower conversion of reactants into products [36-48]. Therefore, the search for the best molar ratio were carried out at a reaction temperature of 20 °C and with 80 % of the maximum sound intensity provided by the source (400 W). On the other hand, as we shall see below, increased ultrasound power input does not necessarily lead to an increased in the products.

The conversions of biodiesel and triacetin obtained from the interesterification reactions of babassu oil and ethyl acetate at the various molar ratios are shown in Fig. 1. The first point to be emphatically highlighted is that under conventional heating and acid catalysis and with reaction temperature of 20 °C the interesterification reaction does not occur because the energies involved are not sufficient to reach the activation energy of the reaction. Therefore, the conversions achieved in Fig. 1 are due to the efficiency of ultrasonic energy in promoting such reactions at low reaction temperature. The conversions obtained (Fig. 1) can be attributed to cavitational events produced by propagation of ultrasonic waves in a liquid medium, which can intensify the inherent physicochemical processes related to the chemical reaction. During the first 30 min of the reaction, the molar ratios 1:12, 1:24 and 1:72 present equivalent and higher conversion values (between 20 and 25 % of conversion) compared to other molar ratios and 1:36 showed the lowest conversion. After 120 min, there is a fast increase in conversion for the reaction mixture at the 1:60 molar ratio, demonstrating its superior efficiency with a conversion reaching 55 % at 180 min, while other molar ratios achieve conversions below 40 %. From the obtained data it can be seen that subsequent rise in molar ratio to 1:72 results in a reduction in conversion, reaching only 40 %. As shown in Fig. 1, under mild conditions conversions to triacetin are very low achieving a maximum of 3 % of triacetin for all molar ratios used. The results from Fig. 1 along with recently published results [33] on acid-catalyzed interesterification using conventional heating and microwave methods, demonstrate that under acid catalysis, the interesterification of vegetable oils with ethyl acetate yields superior results for the 1:60 molar ratio, which occurs regardless of the type of inducing procedure for these reactions, that is, conventional or microwave heating or ultrasonic energy. This experimental observation demonstrated that the best molar ratio for acid-catalyzed interesterification comes from the molecular properties of the reactants and their intermolecular interactions, as well as the macroscopic properties of the reaction medium such as surface tension, viscosity and vapor pressure. To verify a potential relationship between conversions, molar ratio, and viscosity of the reaction medium, viscosity measurements were carried out during reaction for all molar ratios used.

The results obtained show that the viscosity decreases significantly with increasing acetate quantity, and remains constant during the reaction, with the exception of the molar ratio of 1:12, which can be attributed to the reduced amount of acetate used, which is transformed with the oil into biodiesel and triacetin leading the viscosity to show a small linear increase during the reaction (see supplementary material, Table S4). Table 1 shows the viscosity values of the reaction medium and the conversions obtained for the different molar ratios. For the 1:12 molar ratio, we used the mean value of the viscosity obtained from measurements at *t* = 0, 90 and 180 min. Table 1 shows also the conversions obtained employing microwave (MW) and conventional heating (C$_{nv}$H). Data for MW and C$_{nv}$H are from reference [33]. The reaction temperature in the case of US was 20 °C whereas it was 77 °C for MW
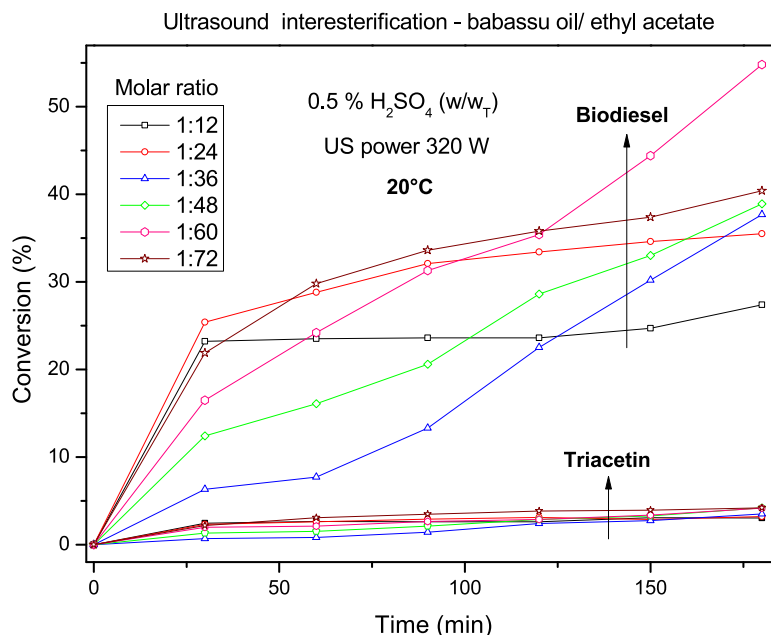
Fig. 1. Conversion to biodiesel and triacetin during interesterification of babassu oil with ethyl acetate induced by ultrasound for various molar ratios.

Table 1
Measured viscosity (centipoise, cP) of the reaction mixtures and conversions (%) for the different used molar ratios. See text for reaction conditions. MW and $C_{nv}H$ data from reference [33].

	Oil to acetate molar ratio					
	1:12	1:24	1:36	1:48	1:60	1:72
η (cP)	1.77	1.29	1.21	1.13	1.04	1.03
C (%) US	27.4	35.5	37.7	38.9	54.8	40.4
C (%) MW	50.6	36.7	51.4	51.4	71.0	48.2
C (%) $C_{nv}H$	31.1	14.8	19.5	26.4	40.1	36.6

and $C_{nv}H$ [33]. Conversions in Table 1 were obtained at 180 min for US and MW and 240 min for $C_{nv}H$ and all reactions were performed using 0.5 % H_2SO_4 (w/w$_T$) as catalyst.

The viscosity data of the reaction media shown in Table 1 make it clear that this physical property is determined, even at the lowest molar ratio adopted, by the amount of ethyl acetate in the mixture since at 20 °C the viscosity of babassu oil is 62.3 cP falling to 48.5 cP at 25 °C. Similarly it can be inferred that properties such as surface tension and vapour pressure of the medium, are dictated by the amount of ethyl acetate in the reaction medium. Since cavitational effects occurs by overcoming natural cohesive forces acting within a liquid the formation of voids or vapour filled microbubbles should be more difficult to produces in viscous liquids, where such cohesive forces are high. Cavitational effects are stronger for liquids with lower viscosity, increasing the chemical activity of ultrasound energy. This relationship becomes evident in the Table 1, where an increase in conversion is observed as the viscosity of the reaction medium decreases with increasing molar ratio. Conversion increases until molar ratio reaches 1:60 and for higher molar ratios, there is a decrease in conversion. This result can be explained by the fact that a higher molar ratios lead to diluted products (biodiesel and triacetin) that might initiate reverse reactions reducing conversion. In this sense, it can be observed in Table 1 that the best molar ratio is 1:60, also for MW and $C_{nv}H$ heating. Hence, 1:60 is considered the best molar ratio for these reaction mixtures under those specified conditions. On the other hand for ultrasound-induced reactions, the increase in reaction rate is related to cavitational effects releasing energy through the collapse of microbubbles, allowing kinetics to occurs at low temperatures as 20 °C, but such effects can be reduced

wih a large amount of solvent since bubbles filled with an increasing amount of solvent molecules lead to cushioning effect during the compression cycle, decreasing the chemical activity of the ultrasonic energy.

The results from Fig. 1 and Table 1 show that in acid-catalyzed interesterification reactions, significant reaction rates are only achieved at high molar ratios, which is the opposite of that occurs in alkaline catalysis where best yields are achieved [10,12,45,46] using oil/acetate molar ratios in the range of 1:6 to 1:20. Furthermore, with conventional heating, besides high molar ratios, interesterification via the acid route requires high temperatures and long reaction times. For example, in the work of Battistel et al. [11] interesterification of tributyrin with methyl acetate was performed using an oil/acetate molar ratio of 1:20, reaction temperature of 130 °C and with 0.27 % (w/w$_T$) of H_2SO_4. They achieved 50 % conversion of tributyrin into biodiesel, 10 % monoacetin, 39 % diacetin and 1 % triacetin over a reaction time of 20 h. Table 1 demonstrates that better results can be reached via US or MW heating in much shorter reaction times under milder conditions.

3.2. Varying the catalyst concentration

The acid catalyst load plays a crucial role in enhancing the reaction rate, as less quantity will hamper the reaction rate and much higher quantity of catalyst can lead difficulties in separation and corrosion issues. To study the influence of the catalyst, the same previous reaction conditions were used, that is, reaction temperature at 20 °C, ultrasonic energy at 320 W, and with the molar ratio that provided the best conversions under these conditions (1:60). The results obtained for the influence of acid catalyst load on biodiesel and triacetin yield are presented in Fig. 2 where it can be seen, as expected, that higher catalyst concentrations ead to increased product yields. At the initial catalyst concentration (0.5 %) yields are low because triglyceride conversion is not perfect under these reaction conditions. It is clear that conversions steadily increase with acid concentration up to 2.5 %. However, further increasing the catalyst concentration from 2.5 to 3.0 % does not show a significant increase in the biodiesel yield. Furthermore, high concentrations of catalyst (acid or base) can cause mass transfer resistance, slowing down the reaction rate, therefore decreasing the yelds of biodiesel and triacetin. Hence, from now on, interesterification experiments were carried out using 2.5 % acid concentration. Regarding cavitational
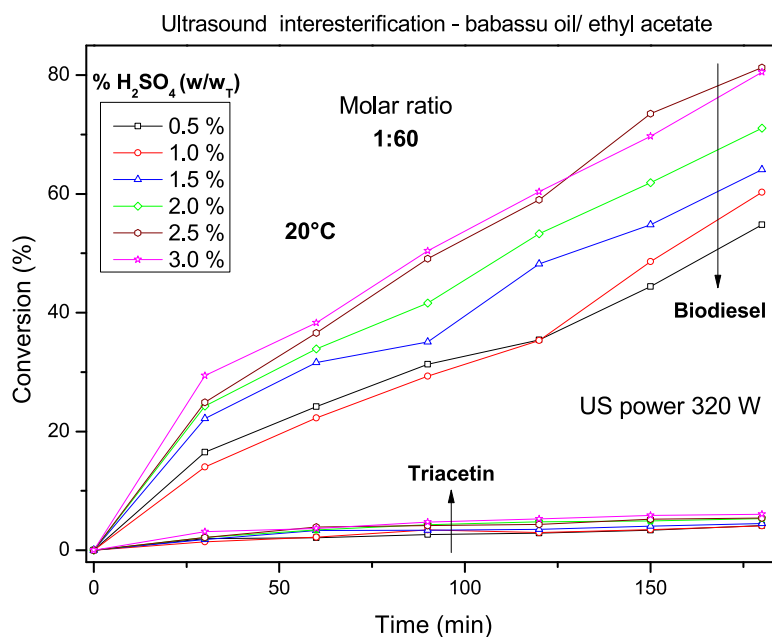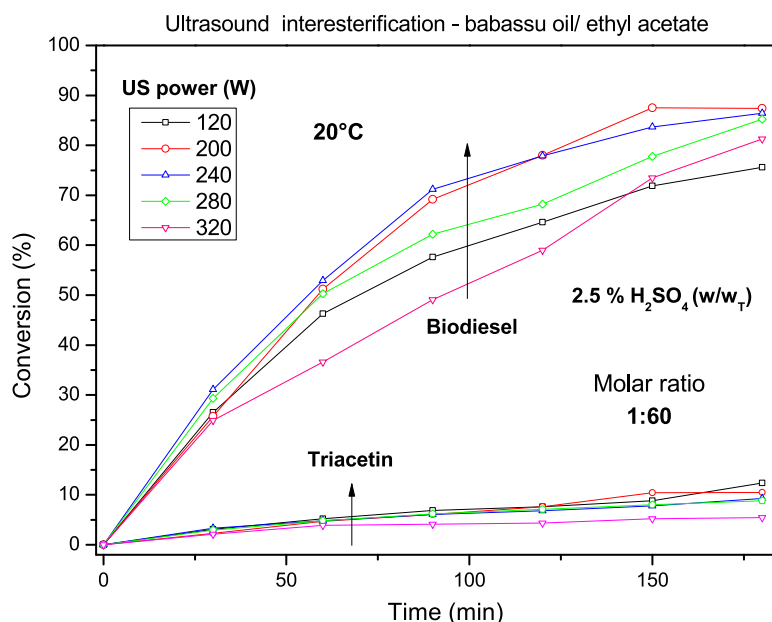
Fig. 2. Conversion to biodiesel and triacetin during interesterification of babassu oil with ethyl acetate induced by ultrasound for various sulfuric acid concentrations.

effects, viscosity measurements (Table S5) of the reaction media for different catalyst concentrations show small variations, increasing from 1.04 to 1.21 cP with the increase in acid concentration (0.5 to 3 %). Any decrease in cavitational effects due to this marginal increase in the viscosity of the reaction medium is strongly outweighed by the concomitant increase in catalyst concentration. Similarly, this variation in catalyst percentage will necessarily result in minor variations in vapor pressure and surface tension of the reacting samples, since these physical properties depends on intermolecular interactions in the liquid, mainly ditatect by the large number of solvent molecules. Therefore, the formation and collapse of cavitation bubbles should occur equivalently for different catalyst concentrations, ensuring that cavitation effects remain consistent across different concentrations.

3.3. Varying ultrasonic power

As is the case for MW heating [33] ultrasonic power is an important factor in the enhancement of chemical reactions. Cavitational effects increase with the increase in applied ultrasonic energy and this more intense energy transfer promotes the formation of a greater number of cavitation bubbles in the medium, providing higher cavitational effects and hence benefiting process intensification, consequently increasing biodiesel yield in equivalent reaction times. Similarly, to the excessive increase in applied power in MW induced reactions, ultrasound re-actions also exhibit deleterious effects that reduce process efficiency. Pressure waves with very high amplitudes tend to collapse the cavitation bubbles formed during the rarefaction period very quickly, drastically reducing the effects produced by the shock waves arising from the

Fig. 3. Conversion to biodiesel and triacetin during interesterification of babassu oil with ethyl acetate induced by ultrasound varying ultrasonic power.

collapse of these bubbles. In this work, the effect of ultrasonic power on the intensification of acid-catalyzed interesterification reactions was investigated over the range 120–320 W, meaning that the percentage of the amplitude of the ultrasonic probe ranging from 30 to 80 % respectively. For these different US power, conversions into biodiesel and triacetin in reactions employing a 1:60 molar ratio of oil to acetate with 2.5 % catalyst and a reaction temperature of 20 °C are shown in Fig. 3. It is very clear that conversions increase as US power increases from 120 W to 240 W denoting the favourable increasing of the cavitational effects. At 200 W the conversion into biodiesel and triacetin is 87.5 % and 10.5 % respectively, within 150 min of reaction. For additional high power levels Fig. 3 shows an appreciable decrease in conversions indicating significant cavitation events resulting in decoupling losses as well as cushioned collapse of cavities reducing energy transfer into the reaction media and hence lower biodiesel and triacetin yelds. Hence, 200 W is considered best level of US power to be applied in the next set of experiments performed in the present study. Fig. 3 leaves clear the tremendous difference between ultrasound assisted reactions and the conventional approach employing conventional heating in acid-catalyzed interesterification. Firstly, at a lower temperature as 20 °C this reaction do not proceed conventionally; instead, is necessary high temperature (130 °C) and longer reactions times (20 h) as reported in the literature [11]. Even in another alternative method, as in MW heating reaction temperatures are high (77 °C).

3.4. Effect varying reaction temperature

An important parameter that plays a crucial role in interesterification is the reaction temperature, which determines the reaction rate, resulting in higher or lower conversions into biodiesel. The effect of reaction temperature was investigated by varying temperature from 20 to 50 °C. The operational parameters kept constant were oil to acetate molar ratio (1:60), catalyst loading (2.5 %) and ultrasonic power (200 W). Conversions into biodiesel and triacetin are shown in Fig. 4 for five different temperatures. The results make clear the marked influence of temperature in the first 30 min. While the conversion for biodiesel reachs 25.7 % at 20 °C, it increases to about 40 % at 25 °C and 30 °C, with a more appreciable increase occurs at 40 °C where the conversion reaches 67 %. This result is related to the fact that higher temperatures contribute to overcoming the energy barrier with supply of necessary

amount of energy. Classicaly, the obtained results can be understood on the basis of an enhanced solubility of acetate and oil due to increase in the reaction temperature resulting into better contact of the reactants increasing the number of effective collisions that favor the reaction to proceed at faster rate. However, an increase of another 10° in temperature (50 °C) results in only a very moderate increase in conversion, reaching a value of 73 %, leaving clear the non linearity between conversion and temperature. Since for longer reaction times, conversions at temperatures between 20 °C and 30 °C grow slightly more pronounced than for temperatures of 40 °C and 50 °C, the final conversions tend not to be as disparate. As shown in Fig. 4, at 180 min the conversion for 20 °C and 25 °C reach 87 % (82 % for 30 °C) while at 40 °C and 50 °C they achieve 87.6 % and 95.4 %. These results clearly show the efficiency of ultrasonic energy in promoting interesterification reactions via the acid route in all studied temperature.

The increase in reaction medium temperature in ultrasonic-assisted reactions results in changes in cavitational effects. In this sense, the viscosity measurements of the reaction medium in Fig. 4 were carried out at the reaction temperatures. The viscosity of the medium decreases as temperature increases within the range of 20–50 °C (see Table S6). Mean values during the reactions vary from 1.20 cP at 20 °C to 0.98 cP at 50 °C (Table S6). Naturally, this decrease favors cavitation, leading to better sonochemical activity. It should also be noted that an additional increase in temperature from 40 to 50 °C did not reflected in a greater increase in reaction yield due to negative effects on cavitational intensity as the temperature reaches higher values. As observed, higher temperature reduces viscosity and similarly reduce surface tension, which controls the reduction of cohesive forces within the reaction medium and regulates the energy required to break the liquid molecules, facilitating cavitation, as occurs for temperature between 20 °C and 40 °C. However, a further increase in temperature and the consequent increase in vapor pressure lead to vaporous cavities formation resulting in cushioning effect and thus the collapse of bubbles will occur with less intensity. Therefore, a lesser degree of intensification is observed when the temperature rises from 40 to 50 °C. Such influence on cavitational effects as temperature increases has recently been reported recently in alkaline catalyzed interesterification reactions, where similar temperature effect trends were have also been observed [43-47]. From the data in Fig. 4, it can be inferred that the negative effects of temperature on cavitation tend to increase more noticeably at higher temperatures so
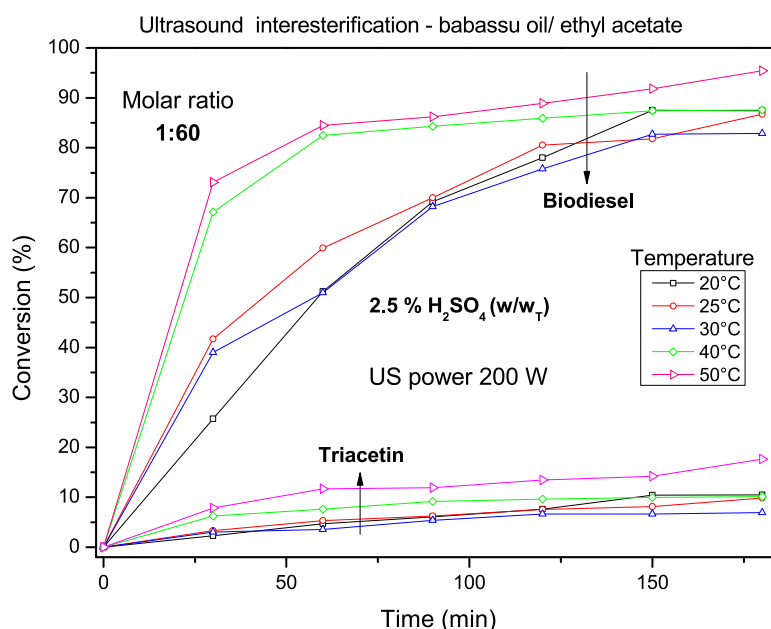

Fig. 4. Conversion to biodiesel and triacetin during interesterification of babassu oil with ethyl acetate induced by ultrasound for various reaction temperatures.

measurements were not carried out for temperatures above 50 °C, since the general trends is a reduction in reaction yield due to negative cavitation effects. Therefore, based on the conversions observed in Fig. 4, the temperature of 50 °C in the scope of this study, is considered the best for subsequent interesterification reactions via acid catalysis to investigate the influence of different acids and acetates.

As a final step of this section, the data obtained at different temperatures were used to evaluate the kinetic parameters (rate constant and activation energy) assuming that interesterification reactions follow a second-order irreversible reaction pathway. This approach aligns with methodologies used in the literature [10,12,41,43]. The concentrations (mmol/L) of biodiesel and oil over time are presented in the supplementary material (Fig. S1) and were analyzed to determine the kinetic rate constant. The irreversibility of this reaction is favored by the excess of ethyl acetate, which drives low concentrations of triglycerides towards equilibrium, resembling an irreversible reaction [41]. Data regarding the behavior of a second order reaction at different reaction temperatures (20, 25, 30, 40 and 50 °C) are presented in Fig. S2. The angular coefficient of each fitted straight line in Fig. S2 is the reaction rate constant at each temperature. The constants and their respective correlation coefficients are also shown in Fig. S2. The correlation coefficient values indicate that the experiments at higher temperatures resulted in a better model fit. However, the rate constants obtained from the experiments at 30 and 40 °C are identified as outliers, since its values do not exhibit the expected linear relationship between the logarithm of the rate constant and the inverse of temperature. Measurements issues compounded by a small number of samples collected during the reactions may explains these outliers. In order to determine activation energy (E_a) of the reaction, the Arrhenius equation was used, with the three reaction rate constants from Fig. S2 (without the outliers) and their respective temperatures. The neperian logarithm of the reaction rate as a function of the inverse of temperature is shown in Fig. S3. The angular coefficient of the fitted line in Fig. S3 provides the ratio between the activation energy and the universal gas constant, while the linear coefficient is the neperian logarithm of the pre-exponential factor in Arrhenius equation. As shown in Fig. S3 the activation energy obtained was 71.577 kJ mol^{-1}, and the pre-exponential factor was 1.75×10^8 L mol^{-1} min^{-1} (correlation coefficient, 0.966). This activation energy for acid-catalyzed interesterification reaction with the ultrasound is higher than the value reported by Maddikeri et al. [41] (58.170 kJ mol^{-1}) and

the value obtained by Medeiros et al. [43] (65.541 kJmol^{-1}) where the authors performed a kinetic study of the interesterification employing US-induced alkaline catalysis with methyl acetate. As expected, acid catalyzed interesterification reactions have higher activation energies that explain why acid catalysis requires higher temperatures and longer reaction times.

3.5. Effect varying acid catalyst

The highly satisfactory results obtained using sulfuric acid as a catalyst in ultrasound-assisted interesterification suggest the feasibility of the promising catalytic action of other acids in such processes. Based on the results obtained in this study, interesterification reactions with ultrasound-enhanced were carried out using phosphoric acid, methanesulfonic acid, toluene sulfonic acid and acetic acid using the optimal reaction conditions obtained above.

Conversions obtained for biodiesel and triacetin for the optimized reaction conditions (2.5 % catalyst, 50 °C, 200 W, US power and 1:60 molar ratio) are shown in Figs. 5 and 6. The initial observation is that phosphoric and acetic acids have their catalytic activity inhibited in reactions assisted by ultrasonic energy with null results for the conversion to biodiesel and triacetin. On the other hand, it is noted that methanesulfonic and para-toluene sulfonic acids have appreciable catalytic activities with conversions for both biodiesel and triacetin, reaching practically equal values for reaction times after 60 min and conversions to biodiesel in 180 min of 82.4 and 82.2 % respectively and almost equal conversions for triacetin (around 5 %).

Figs. 5 and 6 show that the yields of reactions catalyzed by sulfuric acid are significantly higher at all reaction times for biodiesel and triacetin conversions. Therefore, the scanning done for the best acid catalysts in ultrasound-assisted reactions shows that among those studied, is sulfuric acid the most promising, achieving 95 % conversion for biodiesel in 180 min, followed by methanesulfonic and para-toluene sulfonic with 82 % conversion. This excellent catalytic activity exhibiths by sulfuric acid also applies to microwave-assisted reactions as displayed in Table 2 where it is shown the conversions for biodiesel for different acids using US, MW and $C_{nv}H$ heating (data for MW and $C_{nv}H$ from reference 33).

The results from Table 2 indicate that sulfuric and methanesulfonic acids under conventional heating lead to better results than phosphoric
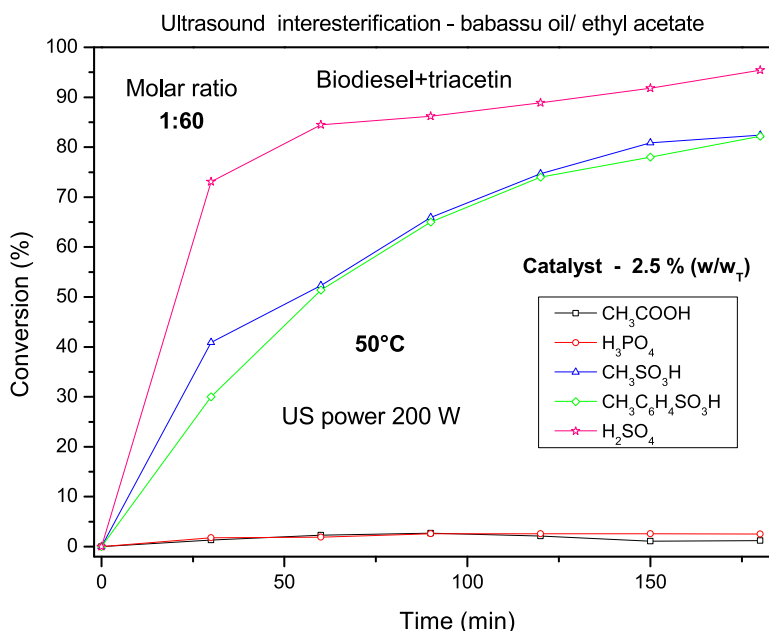

Fig. 5. Conversion to biodiesel plus triacetin during interesterification of babassu oil with ethyl acetate induced by ultrasound employing different acid catalysts.
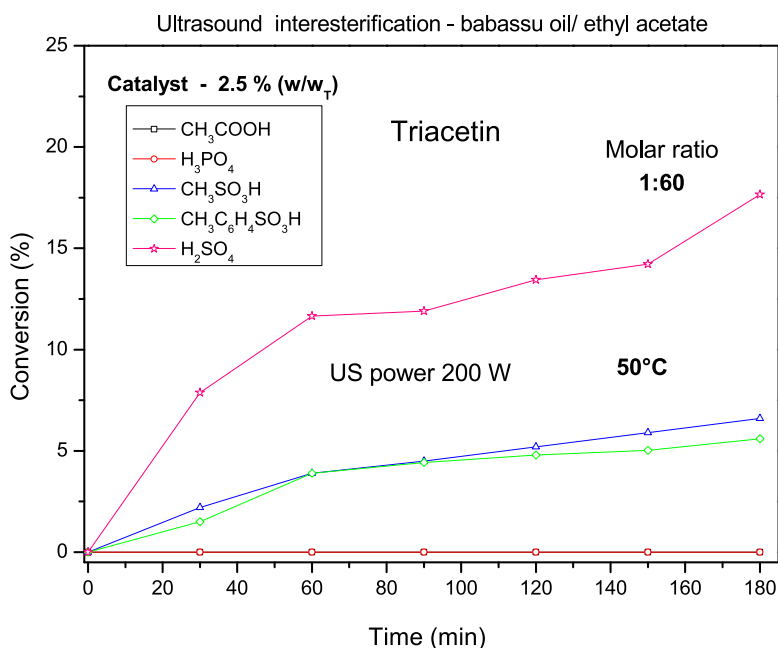
Fig. 6. Conversion to triacetin during interesterification of babassu oil with ethyl acetate induced by ultrasound employing different acid catalysts.

Table 2
Conversions to biodiesel (%) with acid catalysts using different methods. Reaction conditions. US: 50 °C, 2.5 % acid; MW and $C_{nv}H$: 77 °C and 2.0 % acid. US and MW reaction time: 180 min. $C_{nv}H$ reaction time: 240 min. MW and $C_{nv}H$ data from ref. [33].

	H_2SO_4	CH_3SO_3H	H_3PO_4	OHAc
US	95.4	82.4	2.5	1.2
MW	95.0	90.0	14.0	5.0
$C_{nv}H$	70.0	75.0	10.5	9.0

and acetic acids employing MW heating by or ultrasound, with the latter two having their catalytic activities much more inhibited in reactions assisted by ultrasound. In the case of MW heating, the reaction media with H_3PO_4 and OHAc exhibiths a reduced loss factor and loss tangent, resulting in lower microwave energy absorption [33]. Regarding reactions with ultrasound, viscosity measurements for reaction mediums with different acids show a very small variation in their values across the different acids and the variation in viscosity during the reactions is negligible occurring a slightly increase due to the conversion of reactants into products (see Table S7). At the beginning of the reaction, viscosity values range from the lowest value for para-toluene sulfonic acid (0.82 cP) to the highest value for sulfuric acid (0.94 cP). Similarly, from a physicochemical perspective, the presence of different acids in the reaction medium should not substantially alter the values of properties such as surface tension and vapor pressure. Therefore, cavitational effects in these media are equivalent and for acids H_3PO_4 and OHAc the low efficiency observed in reactions via conventional heating are not increased by the effects of cavitation, on the contrary, the specific catalytic activities of these acids are reduced in a medium subjected to shock waves arising from the of cavitation bubbles collapse. It is worthy to note that in the study employing conventional heating of Battistel et al. [11] methanesulfonic acid was used in the interesterification of tributyrin with methyl acetate achieving negligible conversions after 20 h of reaction at 130 °C, that is, 9 % conversion to biodiesel and absence of triacetin. They also found 94 and 99 % conversions to biodiesel using pure trifluoro methanesulfonic acid with the addition of acetic acid or acetic anhydride respectively, under similarly high temperature and longer reaction time (20 h). Therefore, in relation to such experiments there is no doubt concerning the greater advantage of using US to induce

acid-catalyzed interesterification reactions.

Indeed, the conversions shown in Figs. 5 and 6 with H_2SO_4, CH_3SO_3H and $CH_3C_6H_4SO_3H$ as catalysts can be compared with others methods such as homogeneous and heterogeneous alkaline catalysis using conventional heating as well as ultrasound to promote the intensification of the interesterification reaction. For example, these results compare favorably with those reported in the study of Chuepeng et al. [16] where using NaOH and CH_3COOH as homogeneous catalysts in the interesterification of waste cooking oil and ethyl acetate they obtained 77.5 % of biofuel using 0.010:1 NaOH /oil and 1:30 oil/acetate molar ratios and reaction temperature of 80 °C during 3 h, while with acetic acid under the same conditions resulted in only 52.4 % conversion. Regarding reactions employing CH_3COOH, it is clear that the results achieved by Chuepeng et al. [16] are much better than those obtained in this study where conversions are insignificant using ultrasound energy (the same occurs employing MW, Table 2). Another example is the work on of palm oil and ethyl acetate interesterification developed by Akkarawatkhoosith et al. [25] where ion-exchange resinwas used as a catalyst with molar ratio of oil to ethyl acetate of 1:16.7, achieving 99 % of biodiesel at a reaction temperature of 113 °C and total mass flow rate of $5.4 \times 10{-}4$ kg h^{-1}. In the study reported by Usai et al. [23] it was performed the interesterification of extra virgin olive oil with ethyl acetate to obtain biodiesel using sulfonic acid-functionalized mesoporous silica-based materials. A scan on these heterogeneous catalysts indicated SBA-15-phenyl-SO3 as the most promising catalyst reaching 39 % of biodiesel and 48 % of triacetin with a 1:20 oil/ethyl molar ratio and 30 % (w/woil) of catalyst at a reaction temperature of 130 °C during 6 h Utilizing a sodium methoxide solution in methanol Sustere et al. [14] studied the reactivity of the methyl, ethyl, propyl and isopropyl acetates in the interesterification of rapeseed oil. Their findings showed that reactivity decreases from methyl to isopropyl acetate. As we shall see below, under acid catalysis the reactivity of acetates may exhibit different trends in the interesterification reactions employing ultrasonic waves. In the work of Sustere et al. [14] the interesterification with ethyl acetate using a 1:18 oil/ ethyl molar ratio and 1:6.25 catalyst/oil molar ratio, they found 60.3 % of biodiesel and 5.7 % of triacetin at a temperature of 55 °C after 1 h of reaction. By increasing the oil/ethyl molar ratio to 1:36 and reaction temperature to 75 °C, they reached 72 % of biofuel after 30 min. Clearly, the alkaline route is favored due to the strong catalytic activity of sodium methoxide dissolved in liquid

methanol. Nonetheless, the best results reached with base catalysis have been associated with inherent drawbacks, such as the effect of methanol and water on the catalyst and reactants, with reduce the yield of triacetin, forming instead diacetin, monoacetin and glycerol [12]. Moreover, base catalysis requires pre-treatment steps if low-quality feedstocks are used as is the case of waste cooking oil. Furthermore, saponification of acetins and methyl or ethyl esters can occur, leading to emulsification and causing difficult separation of the product. From the examples above, it can be observed that ultrasound-induced interesterification reactions employing acid catalysts exhibths promising results regarding conventional heating. Therefore, the next step is to expand the results achieved with US by including interesterification with other alkyl acetates. Two additional sets of experiments were carried out with methyl and butyl acetate using sulfuric acid as catalyst at a concentration of 2.5 % (w/w$_T$) and same reaction conditions of Figs. 5 and 6 which provided very good results in reactions with ethyl acetate.

3.6. Varying the acetates

Most of the works found in the literature on the interesterification of oils with acetates for the production of biodiesel and triacetin via conventional heating or using ultrasound use methyl acetate [36,37,39] in alkaline route. Some authors have reported studies investigating the efficiency of other alkyl acetates in interesterification reactions [39]. In the present study US assisted-interesterification reactions were also performed using methyl and butyl acetates under the best conditions established for acid catalysis using ethyl acetate. The conversions obtained for biodiesel and triacetin are shown in Fig. 7. As can be seen, while the conversions for biodiesel with methyl and butyl acetate in 30 min of reaction are equivalent (26.6 % and 27.9 % respectively), the conversion for ethyl acetate is much higher, reaching 73.1 % in this reaction time. Additionally, in the first 30 min the conversions to triacetin are negligible compared to methyl and butyl, while in the case of ethyl there is already 7.87 % conversion.

For times after 30 min, methyl and butyl acetates lead to equivalent conversions and always much lower than those shown by ethyl acetate and with 180 min of reaction the conversions for biodiesel reach 71.2 %, 95.4 % and 66.9 % for methyl, ethyl and butyl acetates respectively. Conversion to triacetin has appreciable values only for methyl (7.3 %) and ethyl (17.6 %) while for butyl acetate the conversion to triacetin is

insignificant (1.3 %). Therefore under acid catalysis the reactivity of the methyl, ethyl and butyl acetate shows a quite different behavior compared to alkaline catalysis. As shown in Fig. 7 the reactivity of the esters decreases as ethyl → methyl → butyl, whereas Sustere et al., [14] reported the sequence methyl → ethyl → propyl → isopropyl using sodium methoxide solution in methanol as the catalyst. This trend observed in the reactivity of esters in ultrasound-assisted interesterification reactions was also obtained in reactions carried out with microwave and conventional heating [33]. The reactivity exhibited by the esters in the previous [33] and in the present study clearly originates from the different reaction mechanisms occurring in acid catalysis. For example, reverse reactions can be enhanced in acid catalysis leading to a reduction in triacetin and promoting the formation of diacetin and monoacetin during the reaction which clearly is more pronounced with methyl acetate.

Steric effects can play an important role in the case of butyl acetate since the large volume of such molecules generates an appreciable repulsive effect on neighboring molecules, contributing to reducing their reactivity. Regarding the cavitational effects in different reaction media, viscosity measurements during the reactions show that only a slight increase occurs as products are formed (see Table S8). At the beginning of the reaction, the viscosity values are 0.90 cP, 0.94 cP and 1.12 cP for the media with methyl, ethyl and butyl acetate respectively. These values show that this property is dictated by acetates in this high oil/acetate molar ratio (1:60) since the viscosities of methyl, ethyl and butyl acetates as pure liquids at 50 °C are 0.284 cP, 0.325 cP and 0.500 cP respectively. The reaction with butyl acetate has the highest viscosity value, which leads to a reduction in cavitation effects compared to reactions with methyl and ethyl, which have the same viscosity and certainly similar cavitation effects should occur for these reaction media, but reactions with methyl has a lower yield and is analogous to reactions with butyl, demonstrating that intermolecular interactions that depend on specific molecular characteristics are predominant in determining the greater or lesser rate at which the reaction proceeds under the same reaction conditions and equivalent cavitational effects.

At this point, it is important to compare the results obtained using the three methods adopted to investigate interesterification reactions in acid environment, that is, conventional heating (C$_{nv}$H) and by MW and US. Fig. 8 shows the conversions for reactions with ethyl acetate using these three methods. The US results are for two temperatures (20 °C and 50
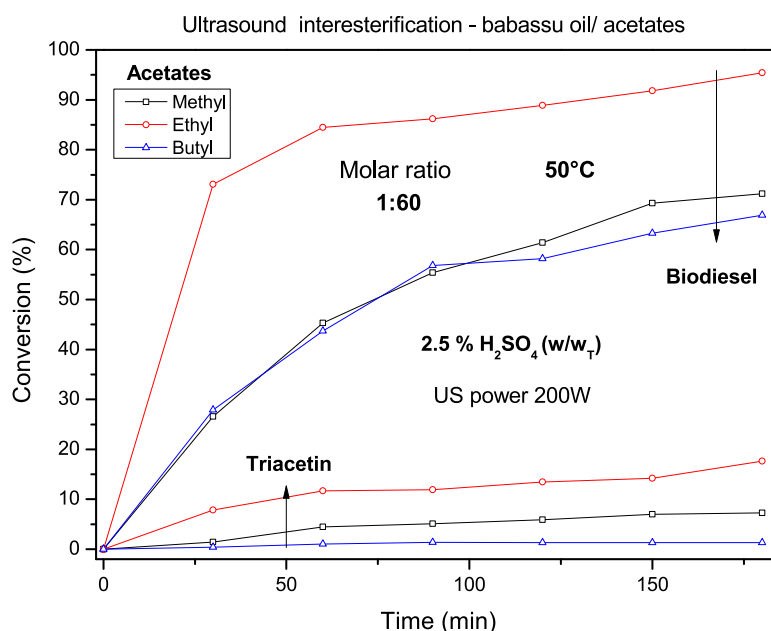

Fig. 7. Conversion to biodiesel and triacetin during interesterification of babassu oil with methyl, ethyl and butyl acetates induced by ultrasound.
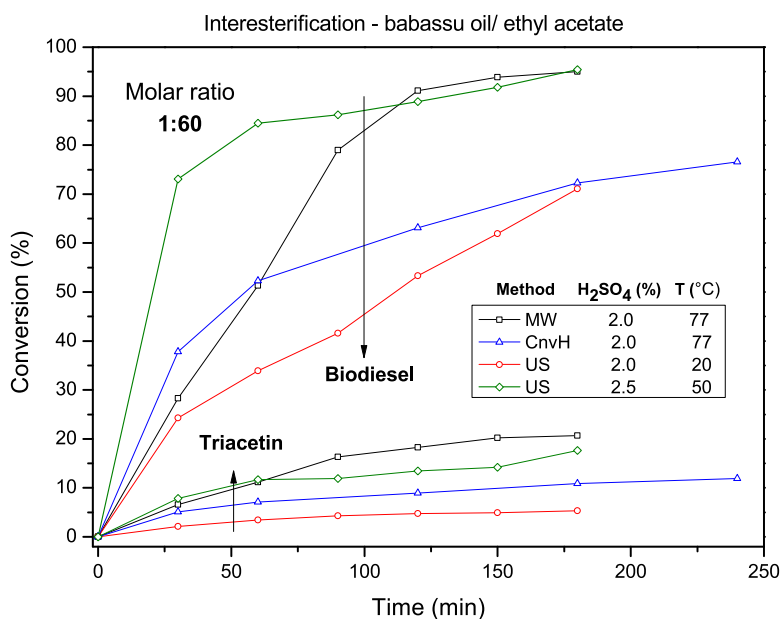
Fig. 8. Conversion to biodiesel and triacetin during interesterification of babassu oil with ethyl acetate employing US, MW and conventional heating.

°C) and acid concentrations of 2 % and 2.5 %. In 30 min of reaction it is observed that the use of US at 50 °C leads to much higher conversions than in other cases, while in 180 min the reaction with US at 20 °C shows the same efficiency as that carried out with conventional heating at 77 °C, showing the great advantage of using US to induce these reactions. However, at this temperature the production of triacetin with US is much lower than that obtained with $C_{nv}H$. The best conversions are obtained with US (with 2.5 % acid at 50 °C) and MW (with 2.0 % acid at 77 °C), both methods achieving 95 % conversion in 180 min. The lower temperature in reactions with US denotes that the energy efficiency in this procedure is greater than that achieved using MW.

For reactions with methyl and butyl acetates, comparisons of yields obtained using $C_{nv}H$, MW and US are shown in Figs. S4 and S5. For methyl reactions, temperatures were set at 55 °C for $C_{nv}H$ and MW (with 2 % acid) and 50 °C for US (using 2.5 % acid). Fig. S4 shows that the conversions are equivalent during the reaction with US showing lower conversion values, and at 180 min of reaction MW and US show 72.9 % and 71.2 % conversion into biodiesel while $C_{nv}H$ shows conversion of 70.9 % only at 240 min. On the other hand, with MW the conversion to triacetin is negligible (1.52 %), lower than that obtained with $C_{nv}H$ (3.5 %) and the highest conversion occurs for US (7.3 %). These data show that the use of US is more advantageous, despite using a slightly higher percentage of acid it presents a much higher yield (at lower temperature than MW) for triacetin and conversions to biodiesel equivalent to those obtained with MW.

Fig. S5 shows very different results for the conversions obtained with butyl acetate compared to the use of methyl or ethyl acetates. In these US-assisted reactions the same acid percentage (2.5 %) and reaction temperature (50 °C) were maintained, while for MW and $C_{nv}H$ reactions the temperatures were 115 °C and 80 °C respectively, with the same acid concentration (2 %). With butyl acetate the use of US shows a clearer advantage compared to MW. In 180 min the conversion to biodiesel reaches 66.9 % while with MW it reaches 58.8 % (Fig. S5). The use of $C_{nv}H$ for butyl shows the lowest result among the acetates, with a conversion of only 48.3 % in 240 min. Furthermore, among the acetates, butyl acetate presents the lowest yield for conversion into triacetin, with insignificant conversions of only around 1.5 % for all three methods (Fig. S5). Therefore, the present study demonstrates that under acid catalysis it is inappropriate to use butyl acetate and that it is more advantageous to use ethyl acetate instead of methyl acetate as is usually adopted in alkaline catalysis.

The results obtained in this study through interesterification using US-induced acid catalysis clearly demonstrate it advantage over conventional heating in homogeneous and heterogeneous acid catalysis after the selection of the best catalyst. Indeed, US approach show better performance than MW-induced reactions since it can operate under mild conditions that are not possible to achieve under MW heating. On the other hand, US-induced acid catalysis, in certain aspects, is not as competitive as base catalysis, which also has its inherent disadvantages. Studies with ultrasound found in the literature are mostly restricted to the use of methyl acetate in interesterification reactions catalyzed by sodium methoxide (or potassium methoxide) in methanol solution. Hence, some disadvantages of alkaline catalysis are present in this kind of approach. To get a more precise understanding of the results achieved with the present US approach, it is possible to compare the conversions obtained in this work with methyl acetate using with previous works using US and alkaline route. Maddikeri et al. [41,42] reported a higher conversion in US-induced interesterification reaction of waste cooking oil with methyl acetate using potassium methoxide. In a reaction time of 30 min and reaction temperature of 40 °C, they found a maximum biodiesel yield (90 %) using a 1:12 molar ratio and catalyst concentration of 1.0 % (w/w$_{oil}$). Additionally, an increase in the oil/acetate molar ratio did not significantly raise the conversion of oil to biodiesel and these authors explain such results as done in the present study. That is, independently of acid or alkaline catalysis this behavior is related to the fact that for higher molar ratios a dilution of the products (biodiesel and triacetin) which increases the possibility of reverse reaction, thereby reducing conversion.

Comparatively, using a conventional approach in sunflower oil interesterification, Casas et al. [10] reported a maximum biodiesel yield of 76.7 % using a 1:50 molar ratio and 1.04 % of catalyst (w/w$_{oil}$) at 50 °C. However, selectivity for conversion to triacetin was not analyzed. Applying ultrasound in the interesterification of karanja oil with methyl acetate in the presence of γ-alumina as the heterogeneous catalyst Kashyap et al. [47] report a 69 % conversion of biodiesel employing a 1:9 oil/ methyl molar ratio and 1 % (w$_T$) of a catalyst loading at a reaction temperature of 50 °C for 50 min. Another approach is the use of ultrasound in enzyme-catalyzed reactions, as reported in the work of Subhedar et al. [38]. They performed ultrasound-assisted synthesis of biodiesel from waste cooking oil using methyl acetate and immobilized lipase. The biodiesel yield was 96.1 % using 1:9 oil to methyl acetate molar ratio, enzyme loading of 3 % (w/v), and reaction time of 3 h For

comparison using conventional heating, 24 h are needed to achieve 90 % of biodiesel employing a molar ratio of 1:12 and an enzyme loading of 6 % (w/v) at a reaction temperature of 40 °C [38]. Unfortunatley, their work does not present an analysis of selectivity to 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 [5,9]. In the present work, the US-induced acid catalysis led clear that conversions achieved for methyl and butyl acetate, although significant, were lower than those obtained with 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 acid catalyzed US-induced approach compare very well with the yield of MW-induced acid catalysis in chemical interesterification of babassu oil. Such US and MW approaches, besides reducing energy costs, are of practical interest for the production of renewable fuel without producing glycerol.

4. Conclusion

In this work, the intensification of interesterification reactions was investigated through the application of ultrasonic energy in acid-catalyzed reactions. The experiments carried out revealed the best reaction conditions using sulfuric acid and ethyl acetate at a mild temperature (50 °C), a high oil/ethyl molar ratio (1:60) and 2.5 % catalyst loading. The reactivity of methyl and butyl acetates in the acid-catalyzed interesterification of babassu oil induced by ultrasound was investigated using the best conditions determined in the present study. It was found that the reactivity of these esters decreases in the order ethyl → methyl → butyl, which is opposite to what occurs in alakline catalysis where a decrease in reactivity is observed with increasing carbon chain length. Interesterification with ethyl acetate provides 95.4 % conversion into biodiesel in 180 min of reaction time, while for methyl and butyl acetates the conversions are reduced to 71.2 % and 66.9 % respectively.

The results obtained in the present work with ultrasound-assisted acid-catalyzed interesterification reactions show the feasibility of such approach as highly promising for producing biodiesel enriched with triacetin. Regarding acid catalysis the present methodology is much superior to conventional heating and is also equivalent to other methodologies such as microwave-intensified reactions. Additionally, the advantages reached by employing this methodology are equivalent to those obtained in the production of biodiesel via microwave-induced acid-catalyzed transesterification reactions. Moreover, instead of glycerol, it simultaneously produces triacetin, which as an additive improves the quality of biodiesel promoting a reduction in harmful gases emitted during combustion process. This contributes to minimizing the environmental impact generated by the use of fossil fuels. Furthermore the results achieved with this methodology were equivalent to those obtained in recent studies found in the literature using ultrasound but using only the alkaline route. This methodology is quite promising in terms of its economic viability, considering the reduction in its energy cost, since it achieves excellent conversions at relatively low reaction temperatures. Furthermore, it can be expected that future studies will be able to overcome some obstacles that allow a scale-up of this methodology, providing a key to industrial-scale production.

CRediT authorship contribution statement

Jonas Miguel Priebe: Methodology, Investigation. **Evandro L. Dall'Oglio:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis. **Leonardo Gomes de Vasconcelos:** Methodology, Investigation. **Paulo T. de Sousa:** Writing – original draft, Project administration, Funding acquisition. **Andressa Alves Ramos:** Methodology, Investigation. **Emily Cristina O. da Silva:** Methodology, Investigation. **Carlos Alberto Kuhnen:** Writing – review & editing, Writing – original draft, Project administration, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cep.2024.110028.

Data availability

No data was used for the research described in the article.

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