

Catalyst-free production of fatty acid ethyl esters (FAEE) from macauba pulp oil

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SUMMARY: In this study, the production of fatty acid ethyl esters (FAEE) from macauba pulp oil and pressurized ethanol was investigated. The experiments were conducted without the addition of catalyst, at 20 MPa, to determine the effect of temperature (200 to 300 °C) and the oil to ethanol mass ratio (1:1 and 1:2) on the FAEE content and different residence times (10 to 45 min). The effect of the addition of *n*-hexane to the oil (20 wt%) as a co-solvent was also evaluated. The use of high temperatures (275 and 300 °C) resulted in high FAEE content (~90%). Increasing the amount of ethanol in the reaction medium contributed to the formation of esters only at operating temperatures of 200 to 250 °C. It was also observed that with the addition of co-solvent (in the oil) it was possible to obtain high amounts of FAEE in a shorter reaction time. In addition, a low content of unreacted compounds (~8.0%) and the conversion of ~90 and 99% of the free fatty acids and triglycerides were observed, respectively.

KEYWORDS: *Acrocomia aculeate; Catalyst-free; Continuous; Ethanol*

RESUMEN: *Producción sin catalizador de ésteres etílicos de ácidos grasos (FAEE) a partir de aceite de pulpa de macauba.* En este estudio, se investigó la producción de ésteres etílicos de ácidos grasos (FAEE) a partir de aceite de pulpa de macauba y etanol presurizado. Los experimentos se realizaron, sin la adición de catalizador, a 20 MPa, para determinar el efecto de la temperatura (200 a 300 °C) y la relación de masa de aceite a etanol (1:1 y 1:2) en el contenido de FAEE, aplicando diferentes tiempos de residencia (10 a 45 min). También se evaluó el efecto de la adición de *n*-hexano al aceite (20% en peso) como co-disolvente. El uso de altas temperaturas (275 y 300 °C) dio como resultado un alto contenido de FAEE (~90%). El aumento de la cantidad de etanol en el medio de reacción contribuyó a la formación de ésteres solo a temperaturas de funcionamiento de 200 a 250 °C. También se observó que con la adición de co-disolvente (en el aceite) era posible obtener altas cantidades de FAEE en un tiempo de reacción más corto. Además, se observó un bajo contenido de compuestos sin reaccionar (~8,0%) y la conversión de ~90 y 99% de ácidos grasos libres y triglicéridos, respectivamente.

PALABRAS CLAVES: *Acrocomia aculeate; Continuo; Etanol; Libre de catalizador*

Conflict of interest: The authors declare that there is no conflict of interest.

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1. INTRODUCTION

Macauba (*Acrocomia aculeata*) is a promising oleaginous plant for the production of biodiesel, mainly due to its high oil content, with 23-46% in the pulp (Evaristo *et al.*, 2016; Lescano *et al.*, 2015) and 43-64% in the kernel (Evaristo *et al.*, 2016; Nunes *et al.*, 2018). Several reports indicate that the oil extracted from the pulp of macauba presents a high content in free fatty acids (FFA), as observed by Dona *et al.*, (2013) and Visioli *et al.*, (2018), who reported 79.24 and 65.20% of free fatty acids (FFA) in macauba pulp oil, respectively. The oil is often obtained by pressing and filtration without the need for refining steps (Colonelli *et al.*, 2017). Thus, the conventional method involving the use of homogeneous alkaline catalysts is not applicable for the transformation of this oil into biodiesel, since the presence of FFA neutralizes the catalyst and also produces soap emulsions, which hinders the separation of glycerol (Patil and Deng, 2009).

Thus, other strategies need to be adopted for the synthesis of biodiesel using low quality raw materials, particularly when high concentrations of free fatty acids are present (Mardhiah *et al.*, 2017). Reactions using alcohol under pressurized conditions have been widely investigated for biodiesel production (Visioli *et al.*, 2016; Santos *et al.*, 2017; Trentini *et al.*, 2018). These are associated with the same energy cost as reactions conducted at low pressures using a basic homogeneous catalyst and generate a product with higher purity (Demirbas, 2002), eliminating the need for separation from the catalyst. In this method, high yields of esters are obtained without the use of catalysts in a relatively short time (Nan *et al.*, 2015) since, under conditions of high temperature and pressure, the miscibility of the triglycerides with the alcohol increases due to the decreasing polarity of the alcohol (Farobie and Matsumura, 2017; Kusdiana and Saka, 2004; Liu *et al.*, 2018; Osmieri *et al.*, 2017), which also behaves as an acid catalyst in the reaction besides being a solvent (Kusdiana and Saka, 2004). Another advantage to this method is the efficiency and good results which have been reported for reactions where the oil had a high content in free fatty acids (Postaue *et al.*, 2019; Trentini *et al.*, 2018; Visioli *et al.*, 2018). Thus, this appears to be a viable alternative for studies on macauba pulp oil.

The efficiency of the reaction under pressurized conditions is dependent on the adjustment of the operating variables (pressure, temperature and time), the nature of the raw material (oil and alcohol), the oil-to-alcohol ratio used and the additives added to the reaction medium. The reaction is commonly conducted at pressures in the order of 20 MPa at temperatures between 275 and 350 °C (Silva and Oliveira, 2014).

The amount of alcohol used in the process is higher than that of the stoichiometric oil-to-alcohol molar ratio of 1:3, since an excess of alcohol will favor the formation of the esters, shifting the reaction toward the formation of products (Colonelli *et al.*, 2017). This is because there is an increase in the miscibility and the area of contact between the substrates, which benefits the production of esters (Musa, 2016). Some authors have reported that the use of an oil-to-alcohol molar ratio of 1:40 (which equates to a mass ratio of ~1:2) gives the highest ester yield (Silva *et al.*, 2007; Trentini *et al.*, 2018). However, other authors have found that the formation of esters was favored up to an oil-to-alcohol molar ratio of 1:20 (mass ratio of ~1:1) (Colonelli *et al.*, 2017; Silva *et al.*, 2010; Trentini *et al.*, 2011).

Another aspect to be considered is the addition of a co-solvent to the reaction medium, which can act to improve the operating conditions of the technology using alcohol under sub- and supercritical conditions. This generally involves the reduction of some adjustable parameters of the reaction, such as temperature, pressure, residence time and/or oil-to-alcohol ratio (Akkarawatkhoosith *et al.*, 2019c, 2019a; Osmieri *et al.*, 2017; Tobar and Núñez, 2018). In addition, the miscibility and solubility of the reaction mixture are also improved (Akkarawatkhoosith *et al.*, 2019a, 2019b; Đokić-Stojanović *et al.*, 2019; Muppaneni *et al.*, 2013), ensuring a high production of esters in a short period of time and without the use of a catalyst (Lim and Lee, 2013). Several co-solvents are cited in the literature. Notably, the use of *n*-hexane has proved to be efficient for reactions under supercritical conditions without the use of a catalyst (Abdala *et al.*, 2014a; Colonelli *et al.*, 2017; Lim and Lee, 2013; Muppaneni *et al.*, 2013; Silva and Oliveira, 2014), besides reducing the viscosity of the reaction mixture and allowing the production in a continuous process (Sawangkeaw *et al.*, 2011).

Recently, obtaining oil esters from macauba pulp in a catalyst-free medium using pressurized ethanol was reported by *Colonelli et al.*, (2017). These authors found that the addition of a co-solvent (*n*-hexane) and the use of higher amounts of alcohol in the reaction medium were the variables that had the greatest influence on the formation of esters. However, the effects of these variables were observed in a fixed residence time.

In this context, the objective of this study was to evaluate the kinetics of ester production from macauba pulp oil (MPO) using ethanol under pressurized conditions and without the use of a catalyst. Experiments were carried out at different temperatures (200 °C to 300 °C) and the influence of adding a greater amount of ethanol to the reaction medium was evaluated. The effect of the addition of a co-solvent (*n*-hexane) and the ester yield at different residence times were also investigated.

2. MATERIALS AND METHODS

2.1. Materials

Macauba pulp oil (Cocal - Brasil), ethanol (JT Baker 99.8%) and *n*-hexane (Vetec 98.5%) were used for the reaction. The fatty acid composition of macauba pulp oil used in this study was previously reported (*Colonelli et al.*, 2017), with the oil presenting predominance of oleic (70%) and palmitic acids (13%). The oil has FFA content of 70.26 ± 0.05 wt% and water content of 0.76 ± 0.001 wt%. For analysis of the reaction products, standard analytical methyl heptadecanoate (Sigma Aldrich, 99.9%) and heptane (F Maia, 95%) were used.

2.2. Reaction procedure

In order to carry out the reaction between macauba pulp oil and ethanol, the mixture of these substrates was fed by a high-pressure liquid pump in a reactor operated in continuous mode. For reactions with *n*-hexane, the co-solvent was added directly into the reaction mixture before pumping. The reactor was at the test temperature and after filling the system, it was pressurized. The residence time was calculated by the ratio between the reactor volume and the feed rate of the reaction mixture. Before collection, the reaction mixture was cooled to 15 °C by a thermostatic bath. The apparatus and experimental

procedure is described in greater detail by *Mello et al.*, (2017) and *Visioli et al.*, (2016) and the experiment for each experimental condition was performed at least in duplicate.

Samples were collected after the residence time for each reaction had been reached, and the excess ethanol was removed at 80 °C. To remove the glycerol formed the procedure described by *Trentini et al.*, (2018) was used.

2.3. Analytical methods

To determine ester content, the samples were diluted in heptane and the internal standard (methyl heptadecanoate) was added and then the samples were injected, in triplicate, in the gas chromatograph (Agilent GC 7890), equipped with flame ionization detector and capillary column (ZB-WAX, 30 m x 0.25 mm x 0.1 μm), using the chromatographic conditions reported by *Colonelli et al.*, (2017). The quantification of the ester content in the samples followed the standard UNE-EN 14103 method (2003), using Equation 1 to calculate the ethyl ester content:

$$\text{Esters content (\%)} = \left(\frac{\sum A_{CP}}{AP \cdot CA} \right) \times 100 \quad (1)$$

where $\sum A$ is the sum of the peak areas corresponding to the esters, AP is the area for the methyl heptadecanoate, CP and CA are the concentrations of the methyl heptadecanoate and injected sample, respectively.

In order to determine the contents in mono-, di- and triglycerides, 100 mg of sample were derivatized with MSTFA (15 min at room temperature) (*Standard UNE-EN 14105, 2003*) and then to a concentration of 3 mg·mL⁻¹. The diluted sample (2 μL) was analyzed with a gas chromatograph (Shimadzu, GC-2010 Plus) equipped with a capillary column (Zebron ZB-5HT, 10 m × 0.32 mm × 0.10 μm), flame ionization detector and on-column injector. The information concerning oven temperature gradient, detector temperature and the heating program for the injector were presented by *Trentini et al.*, (2019). Calibration curves were constructed using chromatographic standards of triolein, diolein and monolein for the quantification of the compounds. FFA content was determined from the acid-base titration method as recommended by AOCs Ca 5a-40 (*American Oil Chemists' Society, 1990*).

3. RESULTS AND DISCUSSION

3.1. Ethyl ester content

Figure 1 shows the results from the experiments conducted with a mass ratio of MPO-to-ethanol of 1:1, as well as the effect of increasing the ratio to 1:2 and adding 20 wt% of co-solvent (*n*-hexane) at a ratio of 1:1, at temperatures of 200 to 300 °C. The mass ratios of MPO-to-ethanol of 1:1 and 1:2 are equivalent to molar ratios of triglycerides-to-ethanol of ~40 and 122 and of free fatty acids-to-ethanol of 9 and 18, respectively.

3.1.1. Effect of temperature

In the overall analysis of the data shown in Figure 1 it can be seen that an increase in temperature led to higher ester yields. When the temperature was increased from 200 to 250 °C and from 250 to 300 °C, with a residence time of 10 min, it was possible to obtain an increase in the ester content in the ratios of ~2.35 and ~1.15, respectively, for the three reaction media evaluated. The temperature effect is significant ($p < 0.05$) up to the residence time of 45 min (analysis not shown in Figure 1).

In reactions at high temperatures, changes in the solubility, density, dielectric constant and solvation of the mixture in the reaction medium occur (Farobie and Matsumura, 2017). This favors a reduction in the mass transfer limitations and increases the reaction rate (Abbaszaadeh *et al.*, 2012; Pinnarat and Savage, 2010). In addition, near the critical temperature, the polarity of the alcohol decreases, and the alcohol starts to solvate the non-polar triglycerides, forming a practically homogeneous mixture (Srivastava, Paul, and Goud, 2018), which allows higher ester yields to be obtained.

Tobar and Núñez (2018) showed that the reaction kinetics are affected by increasing temperature due to an increase in the kinetic energy of the particles and the relative probability of collisions between them.

In a study conducted by Silva *et al.*, (2014), increased ester yields were observed on increasing the temperature from 250 to 300 °C, with a difference of ~42% in only 10 min of reaction. A similar result was reported by Santos *et al.*, (2018) with a 30% increase in the ester yield for the same temperature range. In addition, Zhou *et al.*, (2017) and Akkarawatkhoosith *et al.*, (2019a) obtained

an increased ester content of ~60% on increasing the operating temperature from 250 to 300 °C.

Under the conditions where ethanol was below its critical temperature (243.2 °C), the results demonstrated an FAEE content of 30 to 60%. This is due to the high concentration of FFA in the macauba oil used (70.26%), resulting in the esterification reaction predominating, since FFAs are more reactive than triglycerides (Go *et al.*, 2014; Vieitez *et al.*, 2012).

Pinnarat and Savage (2010) studied non-catalytic esterification and reported that an ester content of 70% was obtained at 230 °C with a residence time of 80 min and pressure of 5.2 MPa. Go *et al.*, (2014) reported an ester yield of ~60% with the reaction conducted at 200 °C for 30 min at a pressure of 2.8 MPa. At the same temperature but with a pressure of 20 MPa, Abdala *et al.*, (2014b) achieved ~70% conversion of oleic acids to esters in only 10 min of reaction. Santos *et al.*, (2017) obtained an esters content of ~75% at 220 °C and 10 MPa with 80 min of reaction. Jesus *et al.*, (2018) observed that the reaction between oleic acid and ethanol yielded ~66% esters at 200 °C with a reaction time of 30 min and pressure of 15 MPa.

3.1.2. Effect of oil to ethanol mass ratio

Increasing the MPO-to-ethanol mass ratio from 1:1 to 1:2 had a more pronounced effect on the formation of esters for the reactions conducted at temperatures of 200 to 250 °C, particularly at the shortest times evaluated (10 and 15 min). At the highest temperatures considered, that is 275 °C (Figure 1d) and 300 °C (Figure 1e), the increase in the amount of alcohol in the reaction medium did not influence the FAEE content.

A greater amount of alcohol in the reaction boosts the formation of the products, since increasing the volume of ethanol available in the medium results in a decrease in the critical temperature of the reaction mixture (Osmieri *et al.*, 2017), promoting the occurrence of the reaction occurring in a homogeneous phase region and increasing the reaction kinetics. MPO is mainly composed of FFA and esterification predominates in the reaction medium. As reported by Santos *et al.*, (2017), this reaction occurs in a single homogeneous phase at 10 MPa with an FFA-to-ethanol molar ratio of 1:1 to 30:1 from 220 to 280 °C.

The alcohol concentration has little effect at higher operating temperatures, as observed at 275

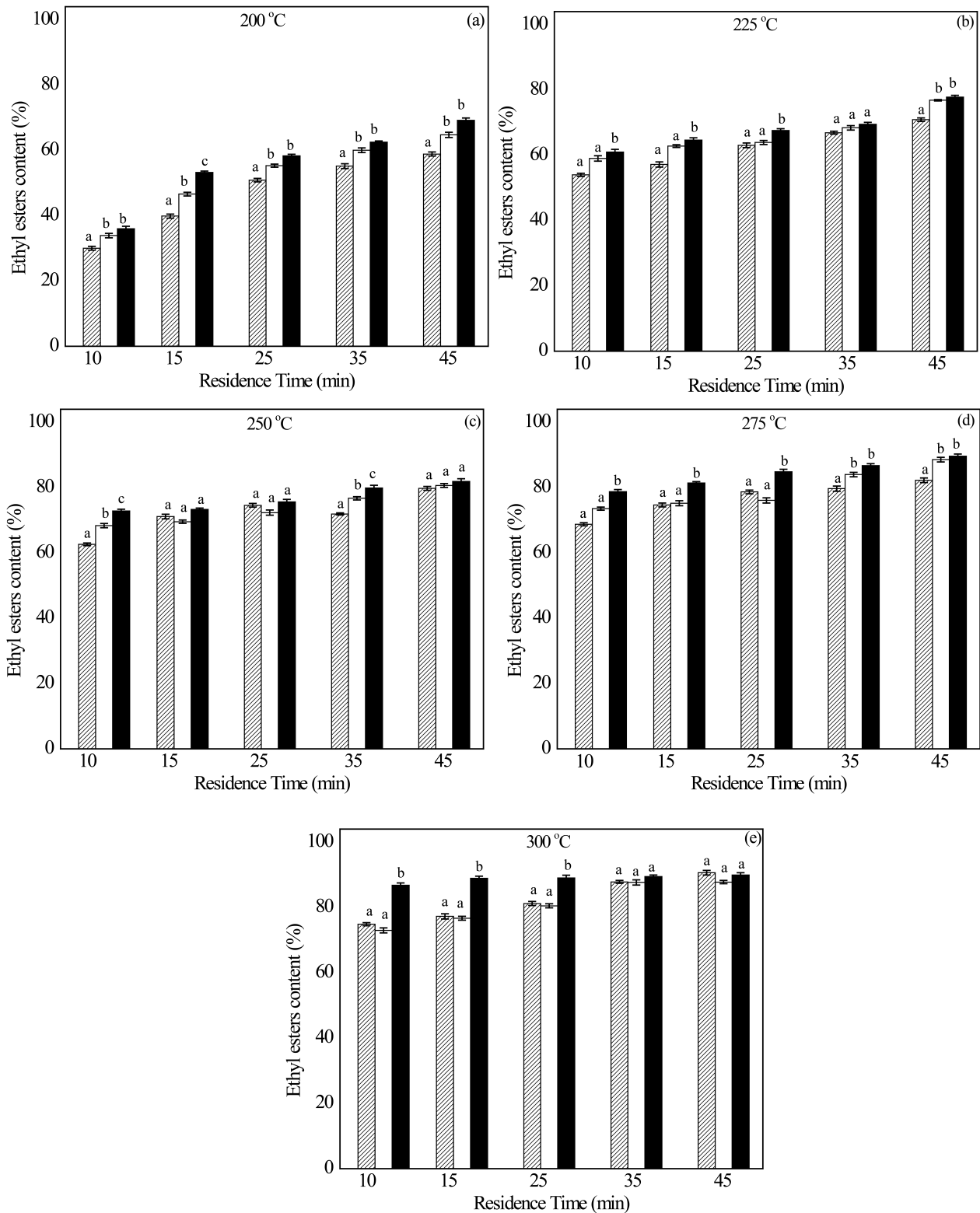


FIGURE 1. Ethyl ester contents of macauba pulp oil obtained at different temperatures: (a) 200 °C, (b) 225 °C, (c) 250 °C, (c) 275 °C and (e) 300 °C at 20 MPa, MPO-to-ethanol mass ratio of 1:1 (▨) and 1:2 (□), and MPO-to-ethanol mass ratio of 1:1 with 20 wt% of co-solvent (in oil) (■). The values in the graphs represent the means of two determinations, with SD < 2.0%. Means followed by the same lowercase letters (with the same residence time) did not differ statistically ($p > 0.05$) using ANOVA (Tukey's test).

and 300 °C (Figure 1), this effect occurs due to the increase in the critical pressure in the mixture, which makes it necessary to use high pressure to obtain a homogeneous phase, as noted by Nan *et al.*, (2015) who obtained similar ester yields at 310 °C, after 30 min at 14 MPa, using microalgae oil-to-ethanol molar ratios of 1:26 and 1:42. The experiments conducted by Bezerra *et al.*, (2018) also provided similar conversion to ethyl esters for oil:ethanol molar ratios of 1:20 and 1:40 at 350 °C, after 40 min at 20 MPa. A similar result was obtained by Costa *et al.*, (2019) on raising the oil:methanol molar ratio from 1:21 to 1:41, at 300 °C, for 10 min of reaction at 20 MPa.

At lower temperatures (200 to 250 °C) the effect of the ratio between the lipids (triglycerides or FFA) and the alcohol in the matrix can be noted (Figure 1). Mello *et al.*, (2017) reported a 12% increase in the ethyl ester yield on increasing the ratio of alcohol to crambe oil hydrolyzate from 12:1 to 15:1 (molar basis) in a reaction conducted at 275 °C, for 10 min at 15 MPa. Jesus *et al.*, (2018) conducted the reaction at 250 °C and 15 MPa and found that on increasing the ethanol:oleic acid molar ratio from 1:1 to 6:1 the conversion of FFA to esters increased by 22%.

3.1.3. Effect of co-solvent

The addition of 20 wt% of co-solvent to the reaction mixture (with an oil-to- ethanol mass ratio of 1:1) promoted an improvement in ester production. Thus, for a residence time of 10 min it was possible to obtain increases of 30 to 36% and 75 to 87% in the ester content at 200 and 300 °C, respectively. The use of a co-solvent improves the mutual solubility between the alcohol and the oil (Tobar and Núñez, 2018), allowing for the presence of a homogeneous phase (Osmieri *et al.*, 2017), increasing the reaction rate and making it possible to obtain high ester yields at moderate temperatures (Maçaira *et al.*, 2014).

Zhou *et al.*, (2017) performed a coupled extraction and reaction process. When the reaction was conducted at 340 °C, for 120 min, with an *n*-hexane flow of 0.2 mL·min⁻¹, there was an increase of 63% in ester yield compared to the reaction without the addition of the co-solvent. In research conducted by Tobar and Núñez (2018), the highest yield of ethyl esters (68%) was obtained with the addition of CO₂ (0.001 g CO₂ per g of ethanol) as a co-solvent at 300 °C and

20 MPa. Akkarawatkhoosith *et al.*, (2019c) reported that an iso-propanol:oil weight ratio of 0.1:1 for only 3 min at 350 °C gave a 37% increase in the ester yield. The same research group (Akkarawatkhoosith *et al.*, 2019b) also found that in the reaction conducted at 300 °C for 4 min the addition of a co-solvent (55 wt% ethyl acetate) promoted an increase in the ethyl ester production of ~68% compared to the reaction with no co-solvent added.

It should be noted that adding more alcohol to the process would significantly increase the production costs, as the ethanol (99.5%) used for this purpose is ~21% more expensive than *n*-hexane (95%), according to the company Tedia Brazil®. Thus, the costs related to increasing the oil-to-ethanol mass ratio to 1:2 would be ~85% higher than using the mass ratio of 1:1 with 20 wt% of *n*-hexane (basis of calculation: 1 L of reaction mixture). However, it needs to be considered that high ester content (~89%) can be obtained in a relatively short time (15 min) at 300 °C, further enhancing the benefits of using the co-solvent. In addition, as noted by Sawangkeaw *et al.*, (2011), *n*-hexane, the solvent most commonly used in the extraction of vegetable oils, can be removed after the oil extraction and employed in the production of biodiesel.

3.2. Triglyceride, diglyceride and monoglyceride contents

In the samples obtained at 300 °C, the triglyceride (TG), diglyceride (DG), monoglyceride (MG) and free fatty acid (FFA) contents were determined, as shown in Figure 2, considering that the highest levels of FAEE were obtained at this temperature. The contents in these compounds in the MPO were also determined at: 18.42 ± 0.15 wt%, 15.2 ± 0.62 wt%, 3.85 ± 0.12 wt% and 70.26 ± 0.05 wt% of TG, DG, MG and FFA, respectively. In general, the increase in mass ratio and addition of co-solvent did not influence the conversion of TG or the formation of DG. The reaction conducted with a mass ratio of MPO-to-ethanol of 1:1, showed a higher concentration of MG when compared to the others. It can also be seen that there was a higher consumption of FFA for the reaction with a mass ratio MPO-to-ethanol of 1:2.

For all conditions evaluated, high TG conversions were achieved, with contents in these

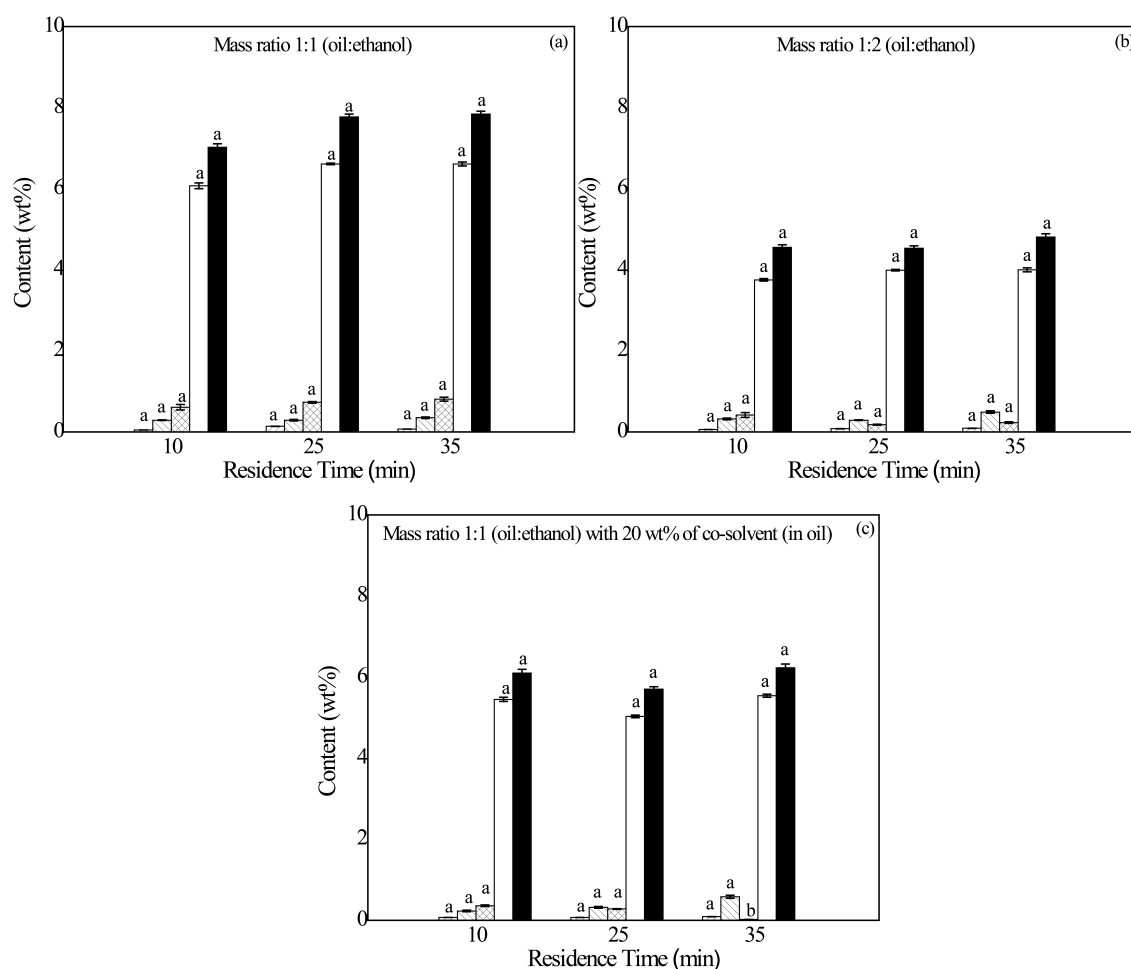


FIGURE 2. Triglyceride (▨), diglyceride (▩), monoglyceride (▤), free fatty acids (□) and total contents obtained (■) at 300 °C: MPO-to-ethanol mass ratio of (a) 1:1 and (b) 1:2, and (c) MPO-to-ethanol mass ratio of 1:1 with 20 wt% of co-solvent (in oil). The values in the graphs represent the means of two determinations, with SD < 1.0 wt%. Means followed by the same lowercase letters (for the same compound) did not differ statistically ($p > 0.05$) using ANOVA (Tukey's test).

compounds in the samples obtained being below 0.14 wt%. In other studies on the transesterification reaction under pressurized conditions conducted at the same temperature, the TG contents of 0.2 to 22 wt% (Santos *et al.*, 2018; Trentin *et al.*, 2011; Trentini *et al.*, 2019; Vieitez *et al.*, 2010) were detected under the conditions that provided maximum ester yields.

The remaining FFA contents in the samples ranged from 4.0 to 6.6 wt%, which correspond to an FFA conversion of above 90%. A similar result was obtained by Visioli *et al.*, (2016) for conversion under the thermodynamic equilibrium in the esterification reaction of soybean oil deodorizer distillate with pressurized ethanol. Vieitez *et al.*, (2012) performed the supercritical alcoholysis of raw materials with 0 to 100 wt% of

FFA and achieved a maximum conversion of FFA to ethyl esters of ~ 90%.

The total amount of unreacted compounds detected was less than 8.0 wt%. Soto *et al.*, (2014) found DG, MG and FFA contents of 11, 3 and 2%, respectively, in the reaction between sunflower oil and methanol with 40 min of reaction at 18 MPa. Ortiz-Martínez *et al.*, (2016) reported a higher value of unreacted compounds, with ~18 and 27% of MG and DG, respectively, for the reaction between *Pongamia pinnata* oil and methanol, with a reaction time of 20 min at 18 MPa. Low contents in MG (2%), DG (4%) and TG (0.2%) were reported by Trentini *et al.*, (2019) for the reaction between grease trap waste lipids and ethanol, with the addition of 2.5 wt% water, with a residence time of 30 min at 20 MPa.

4. CONCLUSIONS

Increasing the operating temperature up to 300 °C for the reaction between macauba pulp oil (MPO) and ethanol led to high ester contents. Moreover, it was found that the reactions conducted at high temperatures (275 and 300 °C) required less alcohol in the reaction medium in shorter residence times, demonstrating that temperature is a key factor to be considered in studies on the production of esters. The addition of *n*-hexane to the reaction, which increased the diglyceride and monoglyceride contents by only 0.6 wt%, allowed for a reduction in the reaction time of ~44% and increased the ester production by up to ~25%. The reaction in a pressurized medium without catalyst was effective, and produced low contents in unreacted compounds (~ 8.0%) and high consumption of triglycerides (~ 99%) and free fatty acids (~90%). The highest FAEE content (~90%) was obtained with an MPO-to-ethanol mass ratio of 1:1 with 20 wt% of co-solvent (in the oil) at 300 °C after 15 min of reaction.

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