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RE-ESTERIFICATION OF MACAUBA ACID OIL USING GLYCEROL FOR ACIDITY REDUCTION AND BIODIESEL PRODUCTION

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Abstract - Biodiesel production using acid oils is an important alternative for biofuel cost reduction. However, it is a huge challenge for homogeneous transesterification, the main industrial route commonly used. This paper presents macauba oil with high acidity, 43.90 w/w%, as a potential raw material for biodiesel production. The acidity was reduced to 0.8 w/w% after re-esterification (80 min) with glycerol at high temperature (235 °C), without catalysts. Zinc (powder and coating) and NbOPO4 were also tested as catalysts in comparison with the reaction without a catalyst. Reactions catalyzed by metallic Zn produced a large amount of Zn carboxylate, an undesirable soap, due to the high Zn leaching. In contrast with the literature, Zinc did not show good catalytic activity, as confirmed by the kinetic parameters. $NbOPO_4$ was not a good catalyst, too. Reaction without catalysts was performed using nitrogen as a carrier gas and it was compared with reaction under vacuum to remove co-produced water. Nitrogen showed the best result for re-esterification, avoiding degradation reactions. Triglycerides (TG) were the prevalent products in reactions using nitrogen. After re-esterification, the oil was easily converted into biodiesel with high ester content (98.4%) of methyl ester by alkaline transesterification.

Keywords: Macauba; Glycerolysis; Re-esterification; Biodiesel; Free fatty acids.

INTRODUCTION

Biofuels have been used worldwide to reduce the consumption of fossil fuels and as an effort to minimize climate changes. Biodiesel has been used in large scale as a diesel substitute in many countries, especially Germany, United States, Brazil and Argentina. One of the most important challenges in this area is the production of biodiesel using non-edible oils with competitive price. One possible alternative is to use acid oils, cheaper than neutral vegetable oils, but the acidity makes the conversion process and biodiesel purification difficult.

Biodiesel, biofuel produced from vegetable oils and animal fats, is largely produced by the transesterification of triglycerides using mainly alkaline homogeneous catalysts. It can only be efficiently produced if the acidity of the raw material is lower than 2%, a value found only in noble and edible oils. The high acidity is a consequence of oil degradation producing free fatty acids (FFA) from triglycerides (TG). Due to the demand for high-quality oils, feedstock cost can contribute up to 80% of the total biodiesel cost (Tu et al., 2017). Soybean oil, canola oil, rapeseed oil, cotton oil, and palm oil are examples of noble and edible feedstock used to produce biodiesel. However, it is possible to use residual and/or non-edible oils for homogeneous transesterification as long as the acidity is reduced to at least 2% (Felizardo et al., 2011).

Another important way to reduce the raw material price is the use of feedstock with high availability and productivity, like palm trees. However, these trees need favorable climate conditions to grow, which are commonly found in tropical forest areas. These areas cannot be used for homogeneous plantation in order to save their biodiversity and minimize environmental

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impact. One good alternative is to use other palm trees such as macauba (*Acrocomia aculeata*), with large natural occurrence in other areas as Mexico, Central, and South America, which are rustic and do not demand special soil or climate.

Macauba is a naturally occurring palm tree in most areas of Brazil and can be found in many different environments, due to its robustness. Macauba has been pointed out as a suitable alternative to be used in areas of protection of water springs and to recover degraded areas. This makes macauba a very interesting tree for the production of vegetable oil for biodiesel production. Besides the robustness of the tree, its yield per hectare/year is also high, namely 4 up to 5 tons of oil, ten times higher than soybean (Nobre et al., 2014). Macauba fruit produces two kinds of oil: pulp oil, rich in unsaturated fatty acids, especially oleic acid; and almond oil, rich in saturated fatty acids with short chains such as lauric acid. The quality of the macauba pulp oil decreases rapidly after the fruit has fallen from the tree, as a consequence of enzymes (lipases) present in the fruit and the soil microorganisms. Some studies show that the quality of the fruit and oil rapidly deteriorates when the fruit is untreated or when the oil extraction does not occur within a few hours after fruit harvesting. This is a problem for the production of biodiesel via homogeneous catalysis, which requires oil with low acidity (Evaristo et al., 2016). It is possible to produce macauba oil with low acidity, but it would be necessary to control strictly all the process, from harvest to storage, which increases this oil price

Oil pre-treatment, such as free fatty acids (FFA) separation processes, solvent extraction, distillation, and neutralization can be used when the acidity is high enough to avoid the transesterification, but not so high as to make the process economically unfeasible (Bhosle and Subramanian, 2005). Another alternative for biodiesel production from acid oil is to use acid-catalyzed homogeneous esterification, producing alkyl esters from alcohol and free fatty acids in the presence of acid catalyst. However, acid-catalyzed esterification uses hazardous chemicals, such as H_2SO_4. In addition, acid-catalyzed esterification presents a lower reaction rate compared to alkaline catalysis (Tu et al., 2017).

One interesting acid oil pre-treatment to consider is glycerol esterification of FFA, sometimes referred to as glycolysis or re-esterification. It is a process in which glycerol reacts with FFA to form monoglycerides (MG), which can react with FFA to form diglycerides (DG), which can react with another FFA to form triglycerides (TG). Each of these reactions also produces water, in addition, glycerol may also react with MG, DG, and TG. Hence, there are five reversible reactions occurring simultaneously (Tu et al., 2017) as shown below:

$$\mathrm{Gly} + \mathrm{FFA} \rightleftharpoons \mathrm{MG} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{MG} + \mathrm{FFA} \rightleftharpoons \mathrm{DG} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{DG} + \mathrm{FFA} \rightleftharpoons \mathrm{TG} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{TG} + \mathrm{Gly} \rightleftharpoons \mathrm{DG} + \mathrm{MG} \tag{4}$$

$$\mathrm{DG} + \mathrm{Gly} \rightleftharpoons 2\mathrm{MG} \tag{5}$$

In order to shift the reaction equilibrium toward the product side, the water produced (eq. 1, 2 and 3) has to be purged from the reactor during the reaction (Felizardo et al., 2011). If purged efficiently, the free fatty acid concentration falls below 0.2% (Anderson et al., 2016). This process can be extremely beneficial for oils with high acidity, since free fatty acids are converted into raw material for biodiesel production instead of being removed from the oil. Furthermore, it is well known that there is over-production of glycerol from biodiesel manufacturing that is not completely absorbed by the market (Patil et al., 2017). Thus, this alternative route can be used to restore the oil quality in a cyclical process.

The drawbacks of the process are that it proceeds by a slow reaction, it demands high temperature, it is limited by equilibrium, and the solubility of glycerol in triglycerides is limited (Felizardo et al., 2011). In most studies, the reaction temperature was in the range of 160°C and 240°C, and a 1:1 stoichiometric molar ratio between glycerol and FFA has proved to be suitable for high conversions (Tu et al., 2017).

Taking into account that the reaction proceeds at high temperature, special attention is necessary regarding glycerol or oil decomposition and oxidation. Usually, the temperature limit is set at 250°C (Felizardo et al., 2011). Dark color and strong odor are indications of decomposition and oxidation (Anderson et al., 2016). The use of nitrogen flux is a common practice for two reasons: it helps water removal and maintains the reaction medium free from oxygen, preventing the oxidation of the product or reagents.

Inorganic catalysts have been reported in the literature as a way to increase the conversion rate, reducing temperature or time of reaction. Compounds containing zinc, for instance, zinc chloride, zinc acetate, Zn-Al_2O_3, and metallic zinc, have been reported as effective catalysts (Anderson et al., 2016; Felizardo et al., 2011).

Different mechanisms can be considered, depending on the zinc form in the catalyst. Zn^{2+} has an affinity for organic functional groups with lone pair electrons or pi bonds, and zinc salts are used as Lewis Acids to facilitate addition reactions. When the Zinc is metallic, the OH of the carboxylic groups, present in the FFA molecule, adsorbs in this metal surface. As a consequence, the carbon of the carboxyl group (C=O) becomes positive (carbocation), and the nucleophilic attack of glycerol is favored.

Jackam et al. (2014) investigated the reduction of FFA concentration from over 90% to below 0.3% in 3 hours, using refined glycerol in a batch reactor and reaction temperature between 221 °C and 238 °C, without catalyst.

Maquirrian et al. (2018) studied the esterification of FFA from soybean oil with glycerol using sulphuric acid, methanesulphonic acid, and p-toluenesulfonic acid as catalysts, in reaction temperatures between 80 °C up to140 °C. The worst performance among the three acids was achieved by sulphuric acid due to its lower solubility compared to the others. The authors managed to convert 90% of FFA in less than one hour. They observed that conversions are significant from 120 °C.

Still using soybean oil, Felizardo et al. (2011) studied the effects of temperature (180 °C, 220 °C and 230 °C), glycerol excess (4%, 11% and 52%), catalyst content (0.1 %, 0.2 %and 0.3% of Zn), stirring speed (300 and 500 rpm) and type of catalyst (metallic zinc, zinc chloride, zinc acetate) on FFA conversion. The conversion was considerably faster at 230 °C and 500 rpm. The equilibrium was achieved in 60 minutes with catalyst and it took more than 120 minutes without the catalyst. The glycerol excess did not present any effect on reaction kinetics.

Grease trap waste with 30% FFA was converted into glycerides using crude glycerol after methanol removal. The optimum reaction conditions were 1:1 molar ratio of glycerol and FFA, 230°C and 150 min, obtaining oil with FFA content below 1%. Triglycerides content decreased continuously until 60 min, after which the concentration started to increase. The concentrations of diglycerides increased by 30 min and then started to level out. Monoglycerides decreased rapidly to almost zero after 60 min (Tu et al., 2017).

Anderson et al. (2016) studied the esterification of FFA present in sewer grease (86 % FFA) with glycerol. The FFA reduction of 99.6% was achieved with 1.8 wt% Zn-Al_2O_3 (catalyst), 18.2 wt% of glycerol, 238°C and 1 hour. The authors concluded that the zinc-based catalyst increased the reaction rate considerably, from a rate constant of 2.57 (without catalyst) to 5.63 (with catalyst). The equilibrium conversion was achieved in 60 min for reactions with catalyst, half the time it took for the reaction without catalyst (120 min).

The FFA conversion was compared between reactions performed without and with nitrogen flow. The reaction conditions were 220 °C with a glycerol excess of 4% and stirring speed of 500 rpm. The FFA content was reduced from 85 mg KOH/g to 2.6 mg KOH/g after 120 min without nitrogen flow, and to 1.5 mg KOH/g after 90 min with nitrogen flow (Islam et al., 2016), making clear the importance of this carrier gas in the process.

To the best of our knowledge, no paper about macauba re-esterification has been published, until now, in the literature. As a consequence, the present authors decided to investigate this subject, especially due to the increasing interest of many agents for macauba plantations in Brazil aiming at biofuel production. The objective of this research was to study the re-esterification process for macauba pulp oil with high acidity using different catalysts (zinc and niobium phosphate) and a carrier gas, aiming to perform the synthesis of biodiesel using homogeneous alkaline transesterification. Thus, the main objective is to show the technical feasibility of producing biodiesel by degraded pulp macauba oil as a promising alternative of low cost and high sustainability. It is important to point out that Brazil is the major producer of niobium products in the world, and these compounds have high acidity and availability. Due to its catalytic properties, $NbOPO_4$ can be tested as a potential catalyst for re-esterification, especially because it has already been used as a catalyst for transesterification with good results. Besides this, the reaction system with nitrogen flow, used to purge the co-produced water from the reaction medium and to keep the system oxygen-free was compared to a system with vacuum. The product obtained by the best re-esterification reaction, with low acidity, was chosen to produce biodiesel via alkaline transesterification, using methanol.

This study is important because macauba oil has not been used in large scale for biodiesel production yet, although some companies have begun to plant macauba in large extension in Brazil in the last years, but the control of its pulp oil acidity is difficult and indicates high costs This innovative route, using low cost and degraded oil is a new perspective and can stimulate more investments in macauba plantations for biodiesel production. This study certainly will reduce the pressure to produce macauba oils with low acidity, with cost minimization.

MATERIALS AND METHODS

Materials

The macauba pulp oil was extracted from fruit collected from native trees in the north of the State of Minas Gerais, Brazil (FFA content of 43.90 %). Other chemicals used were glycerol (ACS grade, 99.5%, purchased from Synth), metallic zinc (powder, 93%, purchased from Sigma-Aldrich), niobium phosphate $NbOPO_4$ (supplied by a local mining company), nitrogen (industrial grade, 99.99%, supplied by Linde). The mechanical stirrer was coated with a zinc film by a local factory.

Experimental set-up

The reactions were performed in a 250 mL glass reactor equipped with a thermocouple, nitrogen inlet with a flowmeter, gas outlet, magnetic stirrer, and heating mantle. The reaction temperature adopted was 235+5°C and the nitrogen flow was 1.0 L/min (smallest increment of the scale). The magnetic stirrer was replaced by a mechanical stirrer covered by a zinc film to test the zinc coating as a catalyst. This alternative was tested aiming to minimize zinc leaching during the reaction, in comparison with zinc powder. The nitrogen inlet was replaced by a vacuum pump inlet and the gas outlet was sealed to test the reaction with a vacuum system instead of nitrogen flow. Samples were taken with a glass syringe every 30 minutes to follow the reduction of the macauba oil acidity. The samples were centrifuged at 7000 rpm for 15 minutes before the analysis to remove solids, catalysts, water or residual glycerol. All reactions were performed using a glycerol excess of 100% considering that one mol of glycerol reacts with three moles of free fatty acids (i.e., the molar ratio of 2:3 glycerol/FFA) so that glycerol would not be the limiting reagent. The study was carried out using 10% w/w of catalysts (Zn and $NbOPO_4$).

Transesterification reaction

After FFA conversion into glycerides, the oil with low acidity (reduced from 43.90% w/w to 0.8% w/w) was transesterified to produce biodiesel. The oil was mixed with methanol at a molar ratio of 1:6 (macauba oil: methanol), and 0.5% w/w of NaOH, previously solubilized in the methanol. The mixture was kept under magnetic stirring and reflux (65 °C) for 1 hour, using a glass batch reactor and mantle heater. These conditions are widely used in scientific works and they are considered sufficient to achieve high biodiesel conversions. After the reaction and phase separation by decantation, the crude biodiesel phase was removed and washed with distilled water until the wastewater reached neutral pH. The excess water was removed in a rotary evaporator at reduced pressure (Maddikeri et al., 2012). The methyl ester production was confirmed by FTIR and the methyl ester content was determined by HPLC. The best result for biodiesel production was also quantified by gas chromatography, which is considered the standard methodology.

Analytical procedures

The fatty acid profile of macauba pulp oil was determined using gas chromatography with a flame ionization detector (GC-FID), according to EN14103:2011. For that, triglycerides were converted into fatty acid methyl esters with one hydrolysis step and one methylation step (Christie, 1989). For hydrolysis, approximately 10 mg of sample was dissolved in 100 µL of 95% ethanol solution (95%)/ potassium hydroxide 1 mol/L (5%), which was then microwaved at 80 W for 5 min. After cooling, 400 µL of 20% hydrochloric acid and 600 µL of ethyl acetate were added. The mixture was stirred and left to rest for 5 min. An aliquot of 300 µL of the organic layer was then removed and dried by evaporation, yielding free fatty acids. These were methylated with 100 µL BF_3/methanol (14%) and heated for 10 min. in a water bath at 80 °C. They were then diluted with 400 µL of methanol and analyzed on a GC-2010 Shimadzu GC-FID using a 15 m × 0.25 mm column, temperature gradient: 100 °C, 1 min, 7 °C/min until 240 °C, detector at 250 °C and injection volume of 1 µL. Identification of peaks was made by comparison with SUPELCO37 fatty acid methyl ester standards.

The acidity of macauba oil was measured via acid-base volumetric titration using a 0.1 mol/L aqueous NaOH solution. Approximately 2 g of sample was weighed and solubilized in a 2:1 ethyl ether: ethanol mixture (v/v), according to the AOCS Cd3d-63.10 method. The acidity was calculated and expressed in mass percentage of oleic acid.

The products and the raw material were characterized by thermogravimetry to estimate the FFA conversion and, eventually, the presence of any side reaction, generating products with a mass loss in a different temperature range in comparison with the initial oil. Tri-, di-, and monoglycerides evaporated at a much higher temperature due to the elevated average molar mass of triglyceride compounds, as compared with the free fatty acid. The mass loss region centered on 240 °C, approximately, mostly corresponds to free fatty acids, and the mass loss centered on 380 °C includes the triglycerides. This methodology showed good results for the quantification of samples with high ester contents and for binary mixtures at all concentration levels (Sousa et al., 2013). The thermogravimetric curves were obtained using a Shimadzu model TGA50H thermobalance at a heating rate of 10 °C/min, from 15 to 900 °C, with a nitrogen flow of 60 mL/ min.

Some of the samples were analyzed by High-Performance Liquid Chromatography - HLPC, aiming to evaluate the concentration of tri-, di-, monoglycerides, and free fatty acids. An HPLC system of Shimadzu was used, pre-column: Shim-pack GVP-ODS 10 x 4.6 mm, column: Shim-pack CLC-ODS(M) 25cm x 4.6 mm, mobile phase A: methanol and mobile phase B: isopropanol:hexane (5:4 v/v), injection volume 6 µL, flow 1.0 ml/min, column heating 40 °C and DAD- Diode Array Detector.

Fourier transform medium-range infrared spectroscopy (FTIR) was used to identify, qualitatively, the composition of the reaction product. The equipment used was Nicolet iS5 FTIR ThermoFisher. The presence of leached zinc in the oil was evaluated by Energy-dispersive X-ray Spectroscopy (EDX) using a Shimadzu EDX-800.

The ester content in the biodiesel produced from oil samples previously treated for acidity reduction was determined according to EN 14103-2011 standard (Determination of ester and linolenic acid methyl ester contents), using a Shimadzu GC-2010 Gas Chromatograph.

RESULTS AND DISCUSSION

Glycerol Esterification

In order to evaluate the catalyst effect on glycerol esterification of FFA present in macauba pulp oil, tests were performed under the same conditions (235+5°C and the nitrogen flow was 1.0 L/min), using different catalysts and without catalyst (Blank). The acidities of samples collected every 30 minutes, expressed in percentage of oleic acid, are presented in Figure 1.

Results in Figure 1 showed that the kinetics of acidity reduction is faster for the reactions without catalyst and with the zinc coated stirrer. Hence, the zinc coating did not exhibit considerable catalytic activity. It took slightly more than 80 minutes to reach the equilibrium for both reactions. The final acidities were 0.8% w/w and 1.1% w/w for reactions without catalyst and with the zinc coating, respectively. For reactions with niobium phosphate, the kinetics were slower, the equilibrium was achieved after 140 minutes, and the final acidity was 3.5% w/w of FFA. Hence, niobium phosphate not only did not have catalytic activity, but also made the reaction slower.

The acidity result for reaction with metallic zinc presented contradictory results when compared with those found in the consulted literature. It decreased until 15% w/w following the same behavior observed for reaction with niobium phosphate, then the acidity increased until 25% w/w, differently from the reaction catalyzed with $NbOPO_4$. Thermogravimetric analyses (TGA/DTG) were performed in order to investigate this behavior. Thermogravimetric curves of products obtained from reactions without catalyst and with metallic zinc after 180 minutes of reaction are shown in Figures 2 and 3. The curve of crude macauba oil is also presented for comparative purpose.

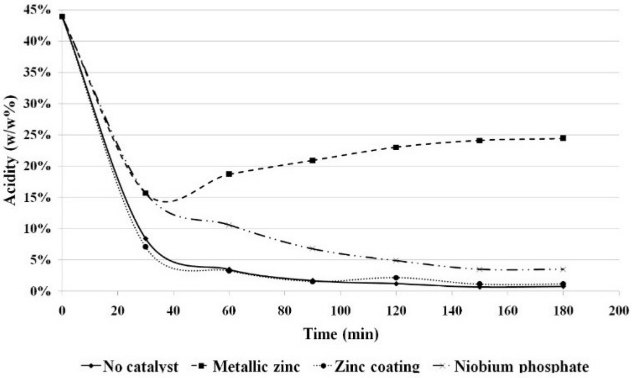

Figure 1. Acidity content by titration of macauba oil for different catalysts and time of re-esterification at 235+5 °C, N_2 flux 1.0 L/min, molar ratio glycerol: FFA 2:3.

Analyzing the TG and DTG curves for macauba acid oil, two major regions of mass loss, centered on approximately 240 °C and 380 °C are observed. The first region corresponds mostly to free fatty acids (about 40% weight loss) and the second region includes the triglycerides mass loss (about 60% weight loss).

The mass loss region related to FFA was not observed in the TG and DTG curves for reaction products without catalyst or with metallic zinc. According to Figure 1, this result was expected for the product from reaction without catalyst which reached low final

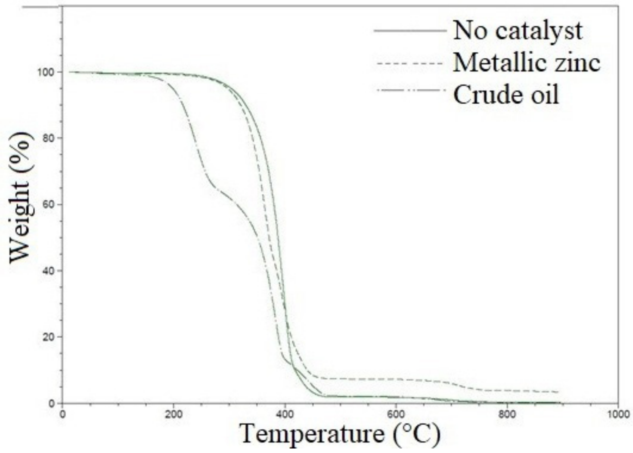

Figure 2. TG curves for samples of macauba acid oil and for products of reactions without catalyst and with metallic zinc as the catalyst, after 180 minutes of reaction.

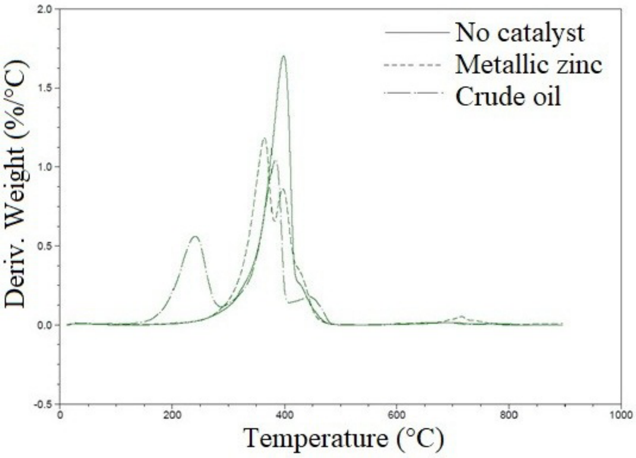

Figure 3. DTG curves for samples of e macauba acid oil and for products of reactions without catalyst and with metallic zinc as the catalyst, after 180 minutes of reaction.

acidity. However, it is contradictory regarding reaction with metallic zinc which reached 25% of acidity after 180 minutes of reaction. Comparing the DTG curves for the product without catalyst and the product with metallic zinc, another event centered close to 360 °C is observed in the latter case, indicating the occurrence of a side reaction. This secondary product can explain why the acidity reduced up to 15% and then increased again up to 25%. More investigation was performed to elucidate this behavior.

Another way to estimate the acidity is by thermogravimetry. According to previous studies, oleic acid presents almost 100% of mass loss up to 265 °C at the same heating rate (10 °C/min) and nitrogen flow (60 mL/ min; thus, the first event (Figure 2) was related to the oil acidity for all samples. The mass losses until 265 °C, for each product, generated at different times of reaction, are presented in Figure 4. They can be related to product acidity. These values are lower than those shown in Figure 1, probably because the free fatty acids were not completely volatilized in this temperature range. Although the values are different, the same trend was observed for the reactions, except for that performed using metallic Zn as the catalyst.

The acidity values measured by titration and estimated by thermogravimetry are divergent for reaction with metallic zinc as a catalyst, as mentioned before. This behavior was investigated by infrared spectroscopy. Products obtained from all reactions were analyzed by FTIR and compared with crude macauba pulp oil. The FTIR spectra are shown in Figure 5.

Analysis of the crude oil spectrum reveals typical bands at 1742 cm^{-1} (C = O of esters), present in triglycerides and the band at 1712 cm^{-1} (C = O carboxylic acid), due to the presence of FFA (Sousa et al., 2018). The disappearance of the band at 1712 cm^{-1} was observed in the products of all reactions, which means that the FFA was consumed to produce glycerides, except in the reaction catalyzed with $NbOPO_4$.

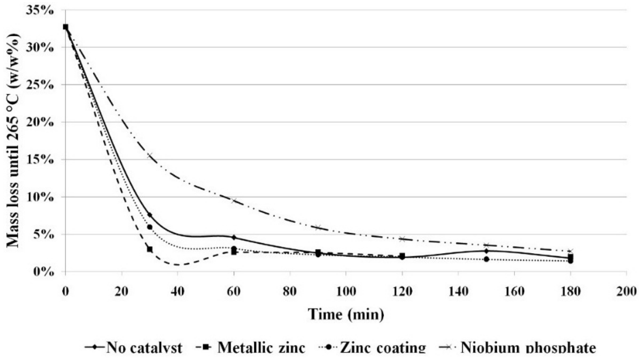

Figure 4. FFA content estimated by thermogravimetry for macauba oil with time for esterification at 235+5 °C, N_2 flux 1.0 L/min, molar ratio glycerol: FFA 2:3.

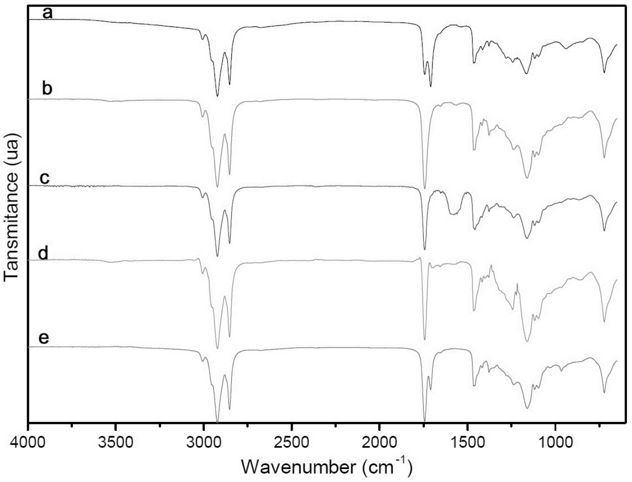

Figure 5. FTIR spectra of (a) crude macauba pulp oil and products from reactions (b) without a catalyst, (c) with metallic zinc, (d) with zinc coating, (e) with niobium phosphate after 180 minutes.

There is a new band at 1536 cm^{-1} significantly present only in the product from reaction with metallic zinc. This band was assigned to the carboxylate group in the zinc soap (COO^-) (Hermans et al. 2015). This means that metallic zinc reacted with the FFA producing zinc soap. This soap presents the mass loss in the same region as neutral oil (mono-, di- or triglycerides) in TG curves. It can explain the presence of two peaks in the range of 300-400 °C (Figure 3), one for the soap and the other for the oil glycerides. Overlapping bands were also observed around 1465 cm^{-1} (Figure 5) for products from reaction with metallic Zn due to COO^- symmetric deformation, reinforcing the evidence for zinc carboxylate formation.

Taking into account all the results, especially those presented in Figure 1, the production of this salt can be explained as follows. During the first 30 minutes of esterification, the reaction between glycerol, monoglycerides, and diglycerides with the free fatty acids (reactions 1, 2 and 3) occurred intensely, generating a large amount of water, which will sum with the humidity present in the oil. This water oxidizes the metallic zinc to Zn^{2+} which reacts strongly with FFA, yielding zinc carboxylate. After 30 minutes, the zinc carboxylate reacts with water, yielding acid due to the excess of water, which was not immediately purged from the medium. This explains the enhancement of acidity during the reaction catalyzed by metallic zinc (Figure 1). This was not observed for niobium phosphate due to its low solubility in water.

Another important band observed in all spectra (Figure 5), almost unchanged, is the one around 3008 cm^{-1} indicating the presence of carbon unsaturation. This means that the oil did not degrade under the reaction conditions.

Energy-dispersive X-ray Spectroscopy (EDX) was used to confirm the presence of zinc in the final products from reactions with metallic zinc and zinc coating. It is important to explain that all solids in the oil were previously separated by centrifugation before its characterization. The inorganic residue obtained by thermogravimetry after 900°C was used in conjunction with EDX to give us a reasonable view of the order of magnitude of the results, presented in Table 1. The presence of zinc in the product was evident from reaction with metallic zinc, confirming the band at 1536 cm^{-1} in the spectrum. However, the zinc is present, to a lesser extent, in the product from reaction with the zinc coating, indicating the leaching of zinc, although not enough to be detected by FTIR and thermogravimetric analyses. Potassium and calcium are naturally occurring elements in the oil. These results are innovative and relevant because other papers, which investigated the use of zinc as a catalyst, did not present the zinc leaching and soap formation effects. As the presence of soap is undesirable because the phase separation becomes more difficult during biodiesel production, we concluded that zinc was not a good catalyst to be used for macauba oil re-esterification.

It is important to point out that the sample of macauba oil used in the present study has high initial water content which probably contributed to enhancing zinc solubility and soap formation. This parameter can explain the divergence of the bad performance of zinc as a catalyst in comparison with the literature that has stated that zinc is an excellent catalyst for re-esterification.

The effects of nitrogen flow and vacuum on water removal were also investigated in the reactions. The analysis regarding the acidity was measured by titration and estimated by thermogravimetry for the products obtained in the reactions carried out with vacuum, both without a catalyst. The vacuum pump was set to keep the system under a pressure of 350 mmHg, enough to remove the water without distilling the oil. The results are presented in Figure 6 and Figure 7.

From the results presented in Figure 6 it is possible to conclude that the kinetics is similar for the reactions with nitrogen flow and under vacuum. In other words, the atmosphere does not interfere considerably with the reaction rate or the reaction equilibrium. It took slightly more than 80 minutes to reach the equilibrium for both reactions (acidity of 0.8% w/w and 1.3% w/w for reactions with nitrogen and vacuum, respectively).

Table 1. The inorganic residue obtained by thermogravimetry and percent content of metals of reaction products (% w/w) obtained by EDX analysis.

Properties (%)	No catalyst	Metallic zinc	Zinc coating
Inorganic residue	0.132	3.542	0.366
K	61.163	3.596	43.809
Ca	38.837	0.191	37.695
Zn	-	96.213	18.496

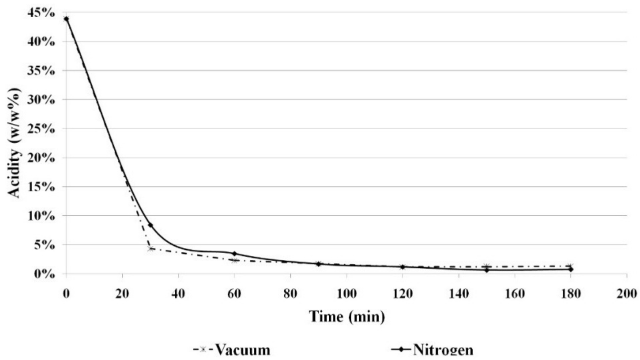

Figure 6. Acidity reduction by titration of macauba oil with time for esterification without catalyst at 235+5 °C, for reactions with a N_2 flux of 1.0 L/min and with the vacuum system.

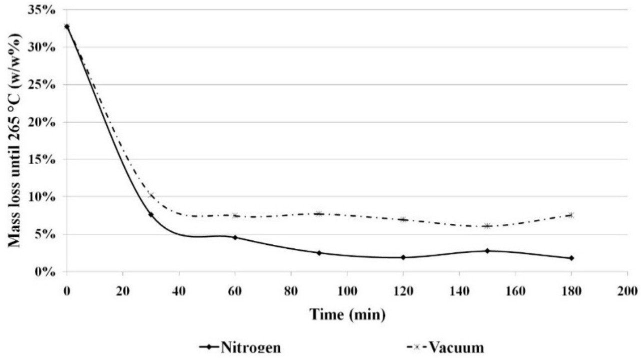

Figure 7. The acidity of macauba oil, estimated by thermogravimetry, with time for esterification without catalyst at 235+5 °C, for reactions with a N_2 flux of 1.0 L/min and with the vacuum system.

Although the values are different between Figures 6 and 7, the same trend was observed for these two reactions.

The product from reaction with nitrogen presented a yellowish color while the product from the reaction with vacuum presented a dark brownish color, suggesting a lower thermal degradation for the reaction with N_2. The infrared spectrum for the reaction using vacuum (Figure 8) presented a small band centered at about 3500 cm^{-1} due to water presence (O-H) in the oil. This band is especially small for the product obtained in the nitrogen atmosphere. Another very small peak was observed at 3008 cm^{-1}. This peak seems to be more prominent for the oil reacted in vacuum due to its oxidation, which explained its brown color.

The excess of glycerol had no effect on the reaction rate (Felizardo et al., 2011), which is dependent only on the concentration of FFA (Felizardo et al., 2011; Anderson et al., 2016). Except for the reaction with metallic zinc, which produced zinc soap as co-product, all reactions best fitted according to a second-order reaction model.

The rate constants (k) were calculated and assumed the values 0.839, 0.501, 0.444, and 0.159 min/FFA%

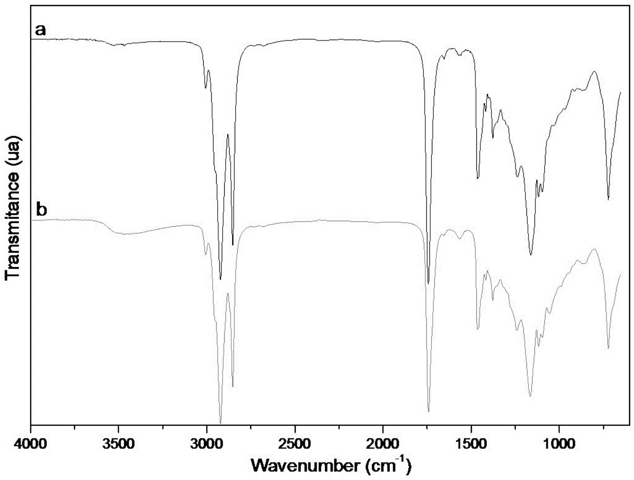

Figure 8. FTIR spectra of products from reactions (a) with nitrogen and (b) under vacuum.

for reactions without a catalyst, zinc coating, vacuum and niobium phosphate, respectively. These results confirmed that the best experimental condition is to perform the reaction without catalyst using nitrogen as carrier gas.

Product Characterization

The fatty acid profiles for all esterification products are shown in Table 2, including the composition for macauba pulp oil before the reactions. They exhibited similar profiles among them and crude acid oil. This means that both the vacuum system and nitrogen flow performed their role of keeping the reaction medium free from oxygen, avoiding the oil degradation on a large scale.

The products from the esterification reactions were characterized by HPLC (Table 3) to determine the final composition in terms of mono-, di-, triglycerides, glycerol and free fatty acids. For reaction with metallic zinc, which generated zinc oleate instead of glycerides, this analysis was not performed, since this conversion route is not efficient. The results (Table 3) showed that, except for reactions with vacuum and catalyzed by $NbOPO_4$, the glycerol was completely reacted. The triglycerides were the main reaction product for reactions with nitrogen flow. The diglycerides content was higher for reaction with vacuum system than reactions with nitrogen flow. Probably the presence of residual water (Figure 8) can explain the difficulty to convert DG into TG in vacuum.

It is important to point out, comparing the free fatty acid contents (Table 3 with Figure 1 and 6), that the results obtained by titration and by HPLC are similar. However, there was an underestimation of FFA content (2.22%) by HPLC (Table 3) for the NbOPO4 catalyzed product in comparison with the result obtained by titration (about 4.4%) (Figure 1). This acidity seems to be higher because a signal was observed in its FTIR spectrum assigned to FFA (Figure 5 e), which confirmed that titration is the best methodology for FFA quantification, followed by HPLC. TGA analysis is less accurate for this purpose.

Table 2. Fatty acid profile of macauba crude oil and esterification products after 180 min. of reaction.

Fatty acid	Common name	Composition (% w/w)					
		Macauba oil	No catalyst	Metallic zinc	Zinc coating	$NbOPO_4$	Vacuum
C8:0	Caprylic acid	0.163	0.147	0.151	0.136	0.123	0.223
C10:0	Capric acid	0.142	0.140	0.146	0.130	0.113	0.158
C12:0	Lauric acid	1.343	1.289	1.280	1.230	1.089	1.386
C14:0	Myristic acid	0.483	0.475	0.462	0.463	0.432	0.499
C16:0	Palmitic acid	15.346	14.819	13.961	14.746	14.573	15.460
C16:1	Palmitoleic acid	2.913	2.962	3.092	2.951	2.887	3.040
C18:0	Stearic acid	1.701	1.779	1.611	1.775	1.849	2.061
C18:1	Oleic acid	56.681	57.851	58.332	57.693	58.813	57.853
C18:2	Linoleic acid	17.381	17.346	17.855	17.481	16.149	16.454
C18:3	Linolenic acid	1.504	1.250	1.272	1.446	1.015	1.266
C20:0	Arachidic acid	0.143	0.155	0.473	0.450	0.597	0.474
C20:1	Eicosenoic acid	0.254	0.392	0.097	0.096	0.125	0.088
Others		1.947	1.395	1.266	1.403	2.237	1.039
Saturated		19.320	18.804	18.084	18.930	18.775	20.261
Unsaturated		78.732	79.801	80.649	79.667	78.988	78.700

Table 3. Mono-, di-, triglycerides and glycerol contents obtained by HPLC of macauba oil and esterification products after 180 min of reaction.

Compound	Composition (% w/w)				
	Macauba oil	No catalyst (N_2)	Zinc coating (N_2)	$NbOPO_4$ (N_2)	No catalyst Vacuum
Monoglycerides	0.00	1.15	1.00	1.10	10.55
Diglycerides	12.93	17.20	15.30	11.71	41.37
Triglycerides	42.07	81.42	83.48	84.97	45.55
Free Fatty Acids	45.00	0.23	0.22	2.22	2.28
Glycerol	0.00	0.00	0.00	0.00	0.25

However, if the objective is biodiesel production, it is important that the free fatty acids content decreases, which was observed in all reactions.

Biodiesel Production

The product from reaction without catalyst was used to produce biodiesel via homogeneous alkaline transesterification following well-known operational conditions. The ester content of sample after transesterification was determined by HPLC and by gas chromatography according to the EN 14103-2011 standard, obtaining 96.5% and 98.4%. Both results are in accordance with ASTM D6751-15a (Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels). As the conversion of glycerides into esters in a homogeneous alkaline transesterification is extremely affected by the presence of FFA, the high ester content means that the deacidification was efficient for this purpose.

CONCLUSIONS

The acidity of macauba oil was reduced (from 43.9 to 0.8 % w/w) by glycerolysis at 235+5°C, without a catalyst, 80 minutes and nitrogen flux to remove the water generated as a by-product. NbOPO4 and Zinc catalysts were tested without good performance. Zn metal leached, yielding Zn soaps besides glycerides, in contradiction with the literature, probably due to higher initial humidity of the degraded macauba oil used as feedstock. Nitrogen flux and vacuum were investigated. The acidity was reduced for both systems, with the predominance of triglycerides for N_2 atmosphere, while for vacuum the same content of triglycerides and diglycerides and a brownish oil was obtained. After re-esterification, biodiesel with high ester content (98.4 %) was obtained using alkaline homogeneous catalysis. This route is promising for industrial conversion of acid macauba oil into biodiesel, dispensing care in collecting and storing the fruit.

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