



Full Length Article

Ethyl esters obtained from pequi and macaúba oils by transesterification with homogeneous acid catalysis



Raflem Christian Matos dos Santos^{a,*}, Paula Cristina Gurgel^a, Nizamara Simenremis Pereira^b, Rodolfo Andrade Breves^c, Paulo Roberto Rodrigues de Matos^d, Luciano Paulino Silva^e, Maria José Araújo Sales^c, Roseany de Vasconcelos Vieira Lopes^f

^a Departamento de Engenharia Mecânica, Universidade de Brasília, 70910-900, Campus Darcy Ribeiro, Brasília, DF, Brazil

^b Instituto Federal de Brasília, Campus Gama, 72405-025 Gama, DF, Brazil

^c Instituto de Química, Universidade de Brasília, Campus Darcy Ribeiro, 70904-970 Brasília, DF, Brazil

^d Centro de Pesquisas e Análises Tecnológicas (CPT), Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (ANP), 70830902 Brasília, DF, Brazil

^e Embrapa Recursos Genéticos e Biotecnologia, Laboratório de Nanobiotecnologia (LNANO), 70770-917 Brasília, DF, Brazil

^f Faculdade do Gama, Universidade de Brasília, 72405-610 Gama, DF, Brazil

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ABSTRACT

In this work, it was investigated the presence of ethyl esters in transesterified pequi (PO) and macaúba (MO) oils. To obtain the biodiesel, an acid-catalyzed homogeneous reaction was used. Yields of 95% for MO were obtained using an oil:ethanol ratio of 1:30 and sulfuric acid (H_2SO_4), reaction times of 4, 8, 12, and 24 h were used. The biodiesel samples obtained from the PO are denoted BP4, BP8, BP12, and BP24, and those from MO are denoted BM4, BM8, BM12, and BM24 according to the reaction time. The kinematic viscosity of the biodiesels was satisfactory and within the specifications stipulated by ANP. The density analysis showed that the biodiesels presented values that are within the limits stipulated by ANP and the European Union. With ^1H NMR measurements, the presence of ethyl esters and the conversion rates were verified. The results by oxidative stability showed that the biodiesel obtained for 24 h are close to the values required by the ANP. The analysis of the ester content showed that the biodiesels obtained with the longest reaction time are in accordance with ANP resolution specifications. Raman spectroscopy revealed the stretching band of the C-O-C group in the ethyl ester molecule at 870 cm^{-1} for all samples. Using thermogravimetry, the maximum degradation temperatures were 243 and $205\text{ }^\circ\text{C}$ for BP and BM, respectively. The characteristic absorption bands of the transesterified oils were identified by FT-IR at 1743 cm^{-1} (C=O group of the ethyl esters) and $1700\text{--}1700\text{ cm}^{-1}$ (C=O of esters).

1. Introduction

The large-scale use of fossil fuels is environmentally damaging. The burning of petroleum derivatives is responsible for most emissions of greenhouse gases (GHG), mainly CO_2 [1]. Thus, the use of fossil fuels should be reduced, and various alternative sources of energy should be used. Biodiesel is a suitable alternative energy source [2].

The National Agency for Petroleum Natural Gas and Biofuels (ANP) defines biodiesel as a fuel composed of alkyl esters of long carboxylic acids chains that is produced from the transesterification or esterification of fatty materials of vegetable or animal origin [3].

Biodiesel is considered the main substitute for petrochemical diesel because the physicochemical properties of biodiesel are similar to those of traditional fossil fuels; also, the raw materials for biodiesel are

renewable and abundant. Crucially, biofuel can be used in diesel engines without the need for modification and can be used pure or mixed with diesel oil [4,5].

Biodiesel is obtained via transesterification reactions, where the triglycerides present in a lipid are reacted with short chain alcohol, usually methanol or ethanol, in the presence of a catalyst, resulting in a mixture of alkyl esters of fatty acids (biodiesel) and glycerol [6,7].

Generally, the most commonly used alcohol in transesterification reactions is methanol, since it has some advantages over ethanol, such as easier separation of biodiesel and glycerol, and lower cost in most countries [8,9]. However, Brazil is the leading producer of ethanol from sugarcane, and therefore, ethanol is cheaper than methanol because of the large volume of production [10–12]. Allied to this, ethanol is obtained from a clean source, and so it is environmentally friendly to

* Corresponding author.

E-mail addresses: raflem.christian@gmail.com, 180058894@aluno.unb.br (R.C.M. dos Santos).

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reactions which ethanol is used [13,14]. Also, ethanol has better solubility for vegetable oils and is less toxic than methanol [15].

Some studies were considered in which ethanol was used to produce biodiesel, using different sources and heterogeneous catalysis: Turkkul et al. [13] produced ethyl esters from the lipid of two types of microalgae (*Nannochloropsis oculata* and *Spirulina* sp.) with 60 wt% CaO on Al₂O₃ catalyst. They obtained 90–99% biodiesel yield with 24:48 ethanol:lipid molar ratios. Belo Pasa et al. [14] produced ethyl esters from the macauba oil with heterogeneous acid catalyst, varying the reaction temperature and the molar ratio of ethanol:oil, and it obtained biodiesel in the best condition at 130 °C with ethanol:oil molar ratio of 9 and 16 wt% of catalyst. Silva et al. [2] produced ethyl and methyl esters from pequi oil using an alkaline homogeneous catalyst and obtained yields of 80 and 96% for ethyl and methyl biodiesel, respectively. Loures et al. [16] also produced ethyl esters, but instead of using vegetable oil, microalgae oil was used (*Chlorella minutissima*) via acid catalysis in a homogeneous and heterogeneous route, and yield of 96.5% and 98% for each of them were obtained, respectively.

For the homogeneous catalysts, the alkaline route is more used than the acid. However, its use has some limitations, such as the high sensitivity only when purity reagents are used, the quantity of water, and free fatty acids (FFA) of the oil. The FFA mainly, because this type of catalysis favors saponification reactions. Thus, for oils which have a high acid value, the most suitable homogeneous catalyst is the acid [17,18].

Another advantage of this route is that it is cheaper when the oil requires a reduction in the content of free fatty acids because when there is a large amount of FFA, it is necessary to perform pre-treatment. Therefore, with an acid route, the esterification step does not have to be done, and the costs are reduced [19].

Mathimani et al. [20] produced biodiesel from algae (*Chlorella* sp. BDUG 91771) using homogeneous and heterogeneous acid and alkaline catalysts. The highest concentration of biodiesel was obtained with a homogeneous acid catalyst, using 3.5% of sulfuric acid in 2.5 h of reaction at 60 °C in constant agitation, obtaining 60% conversion to methyl esters.

The most commonly used raw materials to produce biodiesel in Brazil are soybean oil and bovine tallow. In 2015, these sources represented about 95% of the total biodiesel production, and, although they are already consolidated in the market, biodiesel production can be diversified by using other crops, which, as well as helping supply-demand, may increase the value of poorly utilized, high-potential species such as macaúba and pequi, oleaginous crops of the Cerrado ecoregion [1,5].

The Cerrado occupies about 22% of the Brazilian territory and has a high degree of biodiversity, possessing more than 7000 species of plants. It is considered the most diverse tropical savannah in the world [21].

Pequi (*Caryocar brasiliense* Camb.) fruit is produced between September and February, and it consists of a seed surrounded by an oily pulp. One of the advantages of using pequi oil for biodiesel production is the number of antioxidant substances that it possesses, which means that the fuel has greater oxidative and thermal stability [22]. Macaúba (*Acrocomia aculeata* (Jacq.) Lood. ex. Mart) is a coconut tree that produces fruits with oil contents of 50–60%, having an oil productivity that can reach 4220 L ha⁻¹. From its fruit, it is possible to extract two types of oils, one from its seed and one from its pulp, which is the most used [1,23,24]. It is an oil that has a high value of free fatty acids, and this makes it not commonly used as food [25,26]. Table 1 shows some properties of the pequi (PO) and macaúba (MO) oils.

The composition of FFAs of the two oils (Table 1) shows similarities to the acids that are found in greater quantity (oleic acid); regarding the MO the composition is mostly of this acid (oleic acid), reaching values close to 60%. In the PO the composition varies with two predominant FFAs (oleic acid and palmitic acid) with an average of 45% and 39% respectively.

The viscosity of the two oils also showed similarity, with mean values close to 35 mm² s⁻¹. The viscosity of the oils is a determining factor so that they are not used directly in engines or machines, because the high viscosity affects the operation of the entire machinery structure. Thus, when there is a reduction of the viscosity after the transesterification reactions, it may indicate that there has been the conversion into ethyl or methyl esters [22].

Regarding the saponification number, Coimbra and Jorge [32] stated that this parameter is inversely proportional to the average molecular weight of the FFA present in the oil. Therefore, this parameter correlates the size of the fatty acid chains according to the type of the oil analyzed, which can be inferred from Table 1 that the FFA present in MO are heavier because they have more unsaturations, indicated by the high amount of acid, oleic acid (18:1), which is unsaturated. This same comparison can be made with the values of Iodine, which has a direct relation with the number of unsaturations that the oils have [22].

Finally, Table 1 shows the oxidative stability of each oil. PO has a higher stability than MO, and according to Silva et al. [2] oxidative stability is a parameter that indicates the presence of natural antioxidants, such as carotenoids, and this characteristic is desirable and interesting for raw materials that will be used to produce biodiesel as it will result in samples with greater chemical stability.

Therefore, the objective of this work was to subject PO and MO to homogeneous acid-catalyzed transesterification in the presence of ethanol and investigate the formation of esters by means of proton nuclear magnetic resonance (¹H NMR), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TG), and derivative thermogravimetry (DTG) measurements. Also, the crude and catalyzed oils were characterized using the acidity and viscosity indexes, kinematic viscosity, esters content, density and oxidative stability.

2. Materials and methods

2.1. Materials and reagents

The PO and MO were purchased from Mundo dos Óleos company. The sulfuric acid (95.0–98.0% purity), ethyl alcohol (99.7% purity), and isopropyl alcohol (99.8% purity) were purchased from Isifar.

2.2. Acidity index (AI) of the oils and biodiesels

Before the transesterification reaction, the oils were characterized by their acidity index, which shows the amount of FFA in the sample. The AI was calculated according to the AOCS Ca 5a-40 method, and measurements were carried out in triplicate. This method was also used to calculate the AI of the biodiesels.

2.3. Sample preparation and transesterification reaction

The samples were prepared by adding oil and ethanol in the ratio of 1:30. The proportion of the original transesterification equation is 1:3 but, to achieve higher conversions, it is necessary to increase the amount of alcohol. This also helps to prevent the reverse reaction [35]. Sulfuric acid was further added as a catalyst in a 10% w/w ratio.

The transesterification reactions were performed with magnetic stirring at 80 °C reflux in a mineral oil bath. To verify the influence of the reaction time on the final conversion of the esters, the reactions were carried out for 4, 8, 12, and 24 h.

After the reaction, the samples were transferred to a separating funnel to separate the biodiesel from the glycerin and other components. After this step, the produced biodiesel was washed three times with 15% w/v aqueous NaCl solution so that all impurities and other heavy components were removed.

The biodiesels samples are denoted BP4, BP8, BP12, and BP24 for

Table 1
Physical and chemical properties of pequi and macaúba crude oils.

Properties		MO	PO	Refs.
Free fatty acids content (%)	Oleic Acid (C18:1)	52–58	34.2–55.87	[22,27–32]
	Palmitic Acid (C16:0)	22.1–25	31.4–46.6	[22,27–32]
	Linoleic Acid (C18:2)	9.7–15.7	13.3–15.6	[22,27–32]
	Steriacid (C18:0)	1.08–5	2.2–3.9	[22,27–32]
Viscosity ($\text{mm}^2 \text{s}^{-1}$) 40 °C		33–41.9	34.61–35	[2,14,22,28]
Saponification value (mg KOH g^{-1})		178.5–206	198.48–205.42	[27,32–34]
Iodine value ($\text{g I}_2 100 \text{g}^{-1}$)		76,94–80	55.05–71.97	[22,27,31,32]
Oxidative stability (h)		4.87–10.7	14.4	[2,28,32]

those obtained from PO and BM4, BM8, BM12, and BM24 for those obtained from MO according to the reaction times.

2.4. Viscosity analysis

2.4.1. Kinematic viscosity (ν)

The kinematic viscosity of the biodiesel was calculated using the NBR 10441 standard [36], and a Herzog HVU 490 automatic viscometer was used. The run-off times were calculated at 40 and 100 °C, with a maximum temperature variation of 0.02 °C, and 20 mL of the sample was used for each measurement.

2.4.2. Viscosity index (VI)

The VI of the biodiesels was calculated according to the NBR 14358 standard [37]. Raw oils from Pennsylvania and the Gulf of Mexico were used as standards, having IR values of 100 and 0, respectively.

2.5. Density

Density analysis was performed using approximately 2 mL of the sample that was introduced into an oscillating tube. The change in oscillation frequency caused by the mass change in the tube was used, in combination with calibration data, and it determined the specific mass, density or °API of the sample.

2.6. ^1H NMR analysis

The ^1H NMR spectra of the biodiesel were obtained using a Bruker Avance III HD 14 T spectrometer with a frequency of 600 MHz, and deuterated chloroform (CDCl_3) was used as solvent and reference. The spectrometer was equipped with an automated triple broadband (ATB) probe with a diameter of 5 mm. A 1.0 s pulse interval was used with 16 transients.

The ^1H NMR spectra were used to calculate the reaction conversion following the method of Ghesti et al. [10]. In this method, two peaks are selected for the calculations. Eq. (1) shows the calculation.

$$\%C_{EE} = \frac{4(I_{TAG+EE} - I_{TAG})}{4(I_{TAG+EE} - I_{TAG}) + 12I_{TAG}} \quad (1)$$

Here, C_{EE} represents the conversion into ethyl esters (biodiesel). I_{TAG+EE} is the integrated peak area between 4.10 and 4.20 ppm where the glycerol methyl hydrogen atoms and the CH_2 groups belonging to the formed ethoxy group can be found; the presence of these peaks indicates the production of biodiesel. I_{TAG} is the integrated peak area between 4.25 and 4.35 ppm, where only non-transesterified glycerol methyl hydrogen atoms are found. The constants 4 and 12 appear in Eq.1 because of the four hydrogen atoms of glycerol in triglyceride molecules and the six hydrogen atoms in the ethyl ester, respectively.

2.7. Ester content

Quantitation of C18 carbon chain predominant in biodiesel samples was performed according to ABNT NBR 15764 standard [38], using an

analytical curve prepared with methyl octadecenoate. The samples were analyzed by gas chromatography, using the external standardization method to quantify the esters present in biodiesel, regardless of the type of raw material used in its production. The equipment used was an Agilent 6890 GC with an automatic on-column injector, and flame ionization detector, with injection volume of 0.5 microliters, 30 m \times 0.32 mm \times 0.1 μm DB5-HT column. The running occurred at a constant flow rate of 3.0 mL min^{-1} . The temperature ramp started at 50 °C min^{-1} , heated to 180 °C at 15 °C min^{-1} and then a new heating up to 230 °C at 7 °C min^{-1} , with the last step up to 380 °C at 20 °C min^{-1} , remaining at this temperature for 10 min. The flows of hydrogen, air, and nitrogen (makeup) were 35, 350 and 35 mL min^{-1} .

2.8. Oxidative stability

Oxidative stability tests were performed according to EN 15751 [39]. The test was performed at ANP, in a Metrohm Rancimat 743 equipment, at 110 °C, 10 L h^{-1} airflow and electrodes for readings of 0 $\mu\text{S cm}^{-1}$ to 300 $\mu\text{S cm}^{-1}$. 50 mL of demineralized water and 3 g of the sample were used for the analysis.

2.9. Dispersive Raman analysis

The Raman spectra were acquired using a WITec Confocal Raman Microscope (WITec alpha300 RA, Ulm, Germany) with an XTRA II single-frequency diode laser at wavelength and laser power of 785 nm and 400 mW, respectively. The signal was detected by a thermoelectrically-cooled charge-coupled device. For the biodiesel analysis, samples were deposited on the surface of aluminum foils. All spectra were acquired in spectroscopy mode using a Zeiss EC Epiplan-Neofluar 20 \times air objective. The integration time was set to 0.05 s with 100 acquisitions for each evaluated sample following by spectra processing.

2.10. TG and DTG analyses

The TG curves of the biodiesels were obtained using Shimadzu DTG-60H TGA. In each measurement, approximately 10 mg of each sample was used in a platinum cell. The analysis was performed in a synthetic air atmosphere (30 mL min^{-1}) at 10 °C min^{-1} from 25 to 300 °C. The thermal decomposition temperatures (T_d) were obtained from the DTG curves.

2.11. FT-IR analysis

The FT-IR spectra were obtained using a Spectrum Two spectrophotometer from PerkinElmer operating in transmission mode in the range of 4000–400 cm^{-1} , at room temperature. The resolution was 4 cm^{-1} averaged over 4 scans.

3. Results and discussion

3.1. Acidity index (AI)

Free fatty acids (FFA) in the sample are detrimental to the reaction because they can react with the catalyst and be transformed into undesirable compounds. Thus, the FFA concentration must be controlled to obtain high-quality biodiesels. Based on the AI, the catalytic route can be chosen [40–42].

For AI values up to 6 mg KOH g⁻¹ oil, a homogeneous base-catalyzed reaction is appropriate. For higher AI values, homogeneous acid catalysis is more suitable because the high acidity value can result in side reactions during transesterification, such as saponification [43]. The PO and MO had AI values of 0.842 and 18.23 mg KOH g⁻¹ oil, respectively. Thus, homogeneous acid catalysis was chosen because of the high AI of MO. Santos et al. [44] and Barbosa et al. [45] found similar values for PO, i.e., lower than 6 mg KOH g⁻¹ oil. For MO, Coimbra and Jorge [32] found values higher than 6 mg KOH g⁻¹ oil: 9 to 11 mg KOH g⁻¹ oil; these values are consistent with those found in this work.

The AI values (mg KOH g⁻¹) of the biodiesels formed by the transesterification reaction are listed in Table 2.

According to the ANP, the maximum acceptable AI for biodiesel is 0.5 mg KOH g⁻¹ [46]. Thus, only BP24 was within this limit, i.e., 0.28 mg KOH g⁻¹ biodiesel. Similar AI values for BP have been reported: 0.57 ± 0.05 mg KOH g⁻¹ biodiesel [2] and 0.78 mg KOH g⁻¹ biodiesel [47]. For BM4 and BM24, the values obtained were high, probably because of the presence of large amounts of FFAs, as indicated by the high AI value of the crude oil.

Also, the transesterification reactions with acid route showed that although the oils have high AI values, the acid catalyst helps to reduce the volume of FFAs, and thus the AI value reduces after biodiesel production. For the PO, the reduction of the AI of the oil to the biodiesel was 66.7% and 13% for OM. Souza et al. [27] used an acid catalysis in a reactor under pressure and obtained a reduction of 88.07% in the AI of macaúba oil, this value differs from that obtained in this work due to the use of different reaction parameters, mainly the pressure, where the authors used 70 psi in the reaction.

3.2. Kinematic viscosity and viscosity index

As reported by Mahmudul et al. [4], the kinematic viscosity is a parameter that analyzes the resistance of a liquid to flow. The VI indicates viscosity variation with temperature. Also, the kinematic viscosity is one of the most important parameters when it comes to analyzes the use of biodiesel in engines. Viscosity is directly related to fuel-burning efficiency, as is the lubrication and automation of engines. Biodiesel with high viscosity value tends to resist more when it combusted and therefore require more energy, leading to the emission of more pollutant gases and smoke [48]. The kinematic viscosity and viscosity index values obtained for biodiesel are shown in Table 3.

The ANP limits the kinematic viscosity variation at 40 °C of biodiesel to 3 to 6 mm² s⁻¹. Of the samples analyzed, only BP4 did not fit within this limit because the conversion of this sample was only 50% (Section 3.3), i.e., much crude oil remained in the sample, resulting in a high viscosity variation. According to Mahmudul et al. [4], the kinematic viscosity of crude oils tends to be higher than those of biodiesel. A similar value was obtained for the biodiesel of MO: 3.1 mm² s⁻¹ at

Table 2

AI of PO and MO biodiesels (BP and BM, respectively).

Reaction time (h)	BP (mg KOH g ⁻¹)	BM (mg KOH g ⁻¹)
4	0.83 ± 0.01	16.6 ± 0.04
24	0.28 ± 0.02	15.8 ± 0.04

Table 3

Kinematic viscosity and viscosity index values for 4 and 24 h biodiesel samples.

Samples	$\nu_{40\text{ }^\circ\text{C}}$ (mm ² s ⁻¹)	$\nu_{100\text{ }^\circ\text{C}}$ (mm ² s ⁻¹)	VI
BP4	11.9	3.4	178.2
BP24	4.1	1.8	226.9
BM4	3.8	1.4	111.3
BM24	3.5	1.3	73.1

40 °C [27].

As reported by Folayan et al. [48], biodiesels tend to suffer a decrease in their kinematic viscosity values when the triglycerides are transesterified, and the ethyl esters obtained, since its saturated chains are transferred to the biodiesel molecule, as happened with the viscosity values obtained in this work.

Concerning the VI, BP24 showed the most stable viscosity of all the biodiesels analyzed. In this sample, there was only 56.1% viscosity reduction with increase in temperature, compared to 63.1% of the MO biodiesel; of these samples, BM4 presented greater stability.

3.3. Density

Fuel density directly affects engine performance by changing the amount of injected mass, fuel combustion characteristics, and other characteristics such as cetane number and heating value [49]. The density limit for biodiesel ranges from 850–900 kg m⁻³ [46] to 860–900 kg m⁻³ [50]. Table 4 shows the values obtained for the 4 samples analyzed, where all meet the required limit. Comparing the samples to each other, BM obtained lower values than those of BP. This indicates that BM esters have lower carbon chains than BP esters since density is directly related to the molecular structure of biodiesel [27,51]. Also, density serves as a quality parameter for biodiesel as it indicates the presence of impurities such as alcohol and adulterating substances [2,27]. Thus, both samples are of good quality as they are within the standard according to two norms.

Similar results were found by Souza et al. [27] in the production of ethyl esters from macaúba oil, at a density of 875 kg m⁻³ and by Cardoso et al. [52], which obtained for pequi biodiesel a value of 890 kg m⁻³.

3.4. ¹H NMR analysis

The ¹H NMR spectra obtained for the PO and MO are shown in Fig. 1. Only the spectra for the 4 and 24 h reactions are shown because of the similarity of the spectra of other reactions with that of the 24 h reaction.

In the analysis of biodiesel produced from the two oils in this study, the main peaks were identified between 4.10 and 4.35 ppm. The signal identifying the presence of ethyl esters is a quadruplet between 4.10 and 4.20 ppm, which arises from methylene hydrogen atoms of glycerol and the hydrogen atoms of the ethoxy group (CH₃CH₂O –). Between 4.25 and 4.35 ppm, there is a pair of doublets indicating the methylene hydrogen atoms of glycerol, indicating the presence of non-transesterified oil in the reaction. In the spectrum of BM4, these two peaks are not present, indicating that the oil was completely transesterified, as shown in Fig. 1b. In the spectrum of the PO sample obtained after 4 h reaction

Table 4

Quantitative and qualitative parameters of the biodiesel obtained after the transesterification step.

Sample	BP4	BP24	BM4	BM24	ANP 45/14 limits
Density (kg m ⁻³)	898.6	882.9	874.2	867.1	850–900
Ester content (%)	60.7	97.9	91.1	96.7	96.5
Induction period (h)	0.20	10.95	10.28	10.55	12

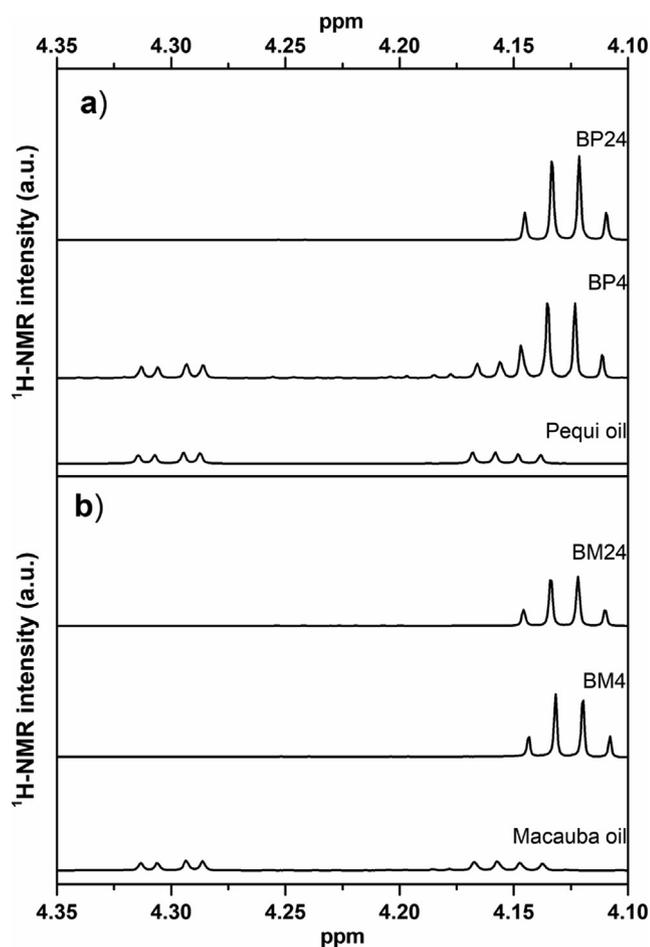


Fig. 1. ^1H -NMR spectra: a) PO and its biodiesel and b) MO and its biodiesel.

(Fig. 1a), an overlap of peaks between 4.10 and 4.20 ppm can be observed, indicating the presence of a mixture of oil and the ethyl esters formed. Similar ^1H NMR peaks for biodiesel obtained from PO have been reported [2,10].

In addition to the identification of the formed ethyl esters, ^1H NMR analysis can also provide the rate of conversion of the transesterification reaction. The rate is calculated from the integrated peak areas using Eq. (1). For PO, the reaction time influenced the conversion rate. After 4 h, the conversion was 50%, whereas, after 24 h, the conversion was 95%. For MO, the reaction time did not influence the conversion, so both the 4 and 24 h reactions showed a conversion rate of 98%. Although the AI of MO indicates the presence of a large amount of FFA, the conversion rate is high, which means that the fatty acids were converted to ethyl esters. Similar results were obtained by Rosset et al. [53] with basic catalysis of soybean oil in the presence of ethanol. The spectra presented the same characteristics of quadruplets and doublets in the same signals, with the presence of two doublets in 4.10–4.20 ppm (with 50% biodiesel).

3.5. Esters content

Ester content analysis in biodiesel samples is a characterization that quantifies the percentage of mass concerning to the total mass of the sample which contains methyl or ethyl esters. It is one of the most important analyzes in the biofuels industry because it presents the number of intermediate compounds such as monoglycerides, diglycerides, and triglycerides that have not been converted into esters. Also, this analysis shows the amount of glycerol present in the sample, and since the more glycerol molecules present in the sample, the lower the

percentage of ethyl or methyl esters, this analysis become important to the biofuels [54].

The ANP states that the minimum acceptable ester content for a sample to be considered a biodiesel is 96.5% w/w. Table 4 shows the results obtained for BP4, BP24, BM4 and BM24.

Table 4 results indicate that the highest yields were obtained with 24 h reaction and agree with the results of ^1H NMR analysis. BP4 presented the lowest value among the samples and its low level of esters can be explained by its low conversion (50%) compared to the other samples (98%). In addition, the results indicate that the biodiesels obtained with the longest reaction time (24 h) were in accordance with ANP 45/14 [46] resolution specifications and can be considered a biodiesel.

Ferreira et al. [22] obtained biodiesel from pequi using basic homogeneous transesterification, and at the end they observed values similar to those of this study for the esters content in the sample. They obtained biodiesel with 98% content of methyl esters with higher concentration of linoleic acid (18:2). Souza et al. [27] obtained biodiesel with 93.9% ester content from esterification of macaúba pulp oil in the presence of ethanol, and these results are also in agreement with those obtained in this work. Also, they showed that the biodiesel obtained from macaúba presented higher oleic acid content (18:1).

Despite the satisfactory results, the fatty acid profile of the MO reaction showed significant amounts of light esters with odd chains, which indicates many volatile esters. Therefore, these biodiesels have a higher storage sensitivity, which can lead to a loss of its components. This problem can be remedied with the addition of stabilizing additives and antioxidants in the biodiesel produced from macaúba.

3.6. Oxidation stability

The oxidation stability of biodiesel is directly related to double carbon chain connections and the degree of unsaturation of alkyl esters present, where the more unsaturated, the more likely a molecule to thermally and oxidatively degrade, thus forming insoluble products that can cause clogging in injection system of engine fuel [51,55]. Until August 2019 the minimum time set by the ANP at 110 °C was 8 h, but in September this parameter changed to 12 h [46]. The standard adopted by the European Union (EN 14214) is 6 h [50].

Table 4 shows the results obtained for BP and BM. Among the samples studied, the ones that most closely match the new ANP standard are the biodiesel of 24 h for both feedstocks, which is coherent since this reaction time got higher ester conversion. In addition, they meet the standards required by the European Union. Silva et al. [2] also failed to obtain values within the ANP limit for pequi oil biodiesel; however they clarified the possibility of using antioxidant to make the fuel more stable.

3.7. Dispersive Raman spectroscopy

To identify the presence of ethyl esters after transesterification in the Raman spectra, the identification of stretches of specific bands of the ester molecule is required. Ghesti et al. [10] quantified the presence of biodiesel using Raman spectroscopy and validated their method and its reliability.

Figs. 2 and 3 show the spectra acquired from the oil samples and their respective biodiesels. The spectra have a high peak density and bands between 800 and 1500 cm^{-1} , but previous studies using this technique to quantify biodiesel did not report the specific bands corresponding to ethyl esters in this area [10,56]. In the spectra of the esters obtained from the transesterification of PO and MO (Figs. 2 and 3), the band at 870 cm^{-1} increased with increasing reaction time. This band was reported by Sahoo et al. [57] to be near 873 cm^{-1} and was identified as the C-O-C stretch band present in the ethyl ester molecule.

Another relevant band was identified between 300 and 400 cm^{-1} , and it is possible to observe an increase in the intensity of the peak at

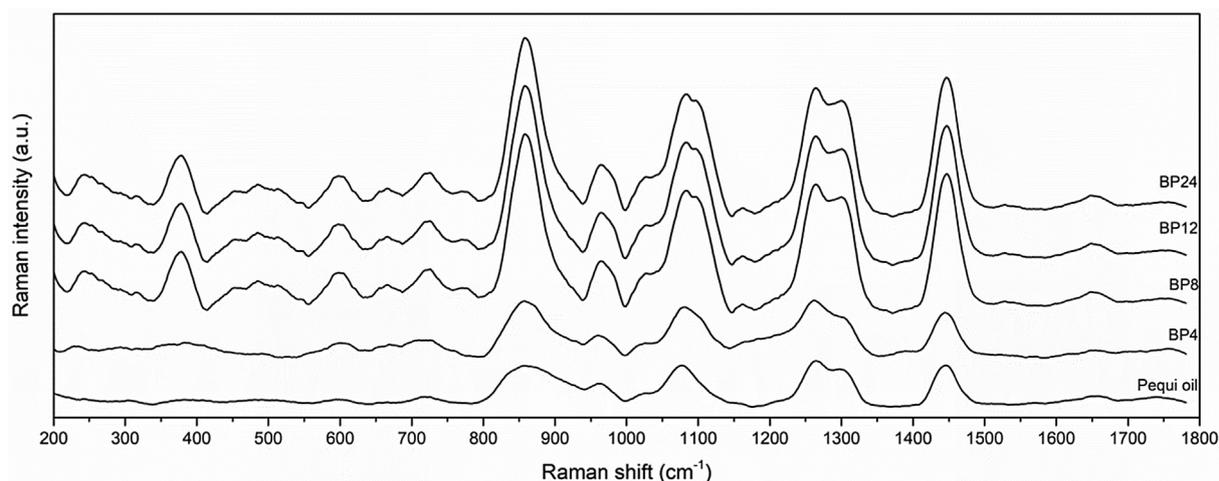


Fig. 2. Raman spectra of PO and its respective biodiesels.

370 cm^{-1} in both spectra. In Fig. 2, this peak is only visible in the BP8 spectrum because this sample showed more than 90% biodiesel conversion efficiency, unlike BP4, which showed only 50% conversion (Section 3.3). This band is related to the CO-O-C groups present in ethyl esters, indicating their formation [10].

The Raman spectra of the oils show differences in the peak positions and intensities because of the different fatty acid compositions; however, there are similarities between 800 and 1500 cm^{-1} , where the spectra contain four main bands. The most common band is that between 1400 and 1500 cm^{-1} , which corresponds to the CH_3 group of the ethyl ester [58]. All such bands and stretches demonstrate the suitability of dispersive Raman spectroscopy to identify and quantify the presence of ethyl esters in samples.

3.8. TG and DTG analysis

Figs. 4 and 5 show the TG and DTG analyses of the transesterified oils (BP and BM, respectively) prepared at different reaction times.

As shown by the TG curves, there was only one thermal degradation step, which is also shown by the DTG peak. The same observation was made by Bezerra et al. [59] and Raslavičius et al. [60] who observed that biodiesel thermally decomposes in one step. Also, the maximum degradation temperatures were obtained: 243 and $205\text{ }^\circ\text{C}$ for BP and BM, respectively. Similar values for BP and BM were found by Tutunea [61] and Vega-Lizama et al. [62]: 240 and $213\text{ }^\circ\text{C}$, respectively.

For BP4, the degradation temperature was different because only

50% conversion to biodiesel was achieved. For this reaction, the mass loss was only 52.6% , whereas, for the biodiesel samples, the mass losses were 95% with only 5% residual mass. BP4 also showed a difference in the initial degradation temperature (T_{onset}), which started at $237\text{ }^\circ\text{C}$, whereas, for the other reaction, the average was $222.7\text{ }^\circ\text{C}$, indicating higher thermal stability and suggesting that some FFAs were not transesterified. For BM, all reaction times yielded similar results: an average mass loss of 98% with T_{onset} around $178.07\text{ }^\circ\text{C}$ and a maximum degradation temperature around $205\text{ }^\circ\text{C}$, as determined by DTG.

Similar values for BM were found by Mothé et al. [63] for ethyl biodiesel obtained from residual oil: degradation occurred in only one step starting at $180\text{ }^\circ\text{C}$, and it had a loss of mass of 98% . Bezerra et al. [59] obtained a 97% mass loss for sesame oil biodiesel in one degradation step beginning at $121\text{ }^\circ\text{C}$. Comparatively, BP was more thermally stable than BM, as indicated by the higher mass loss temperature onset. This interpretation is supported by the work of Vega-Lizama et al. [62], who related the T_{onset} values for ester degradation with the type of fatty acid. They reported that when oleic acid makes up more than 50% of the PO, the T_{onset} average was $218\text{ }^\circ\text{C}$. In general, the initial biodiesel degradation temperature occurs between 155 and $392\text{ }^\circ\text{C}$ [60].

3.9. FT-IR analysis

It was also investigated the presence of ethyl esters in the samples using FT-IR spectroscopy. This technique is advantageous because both solids and liquids can be analyzed without the need for pretreatment

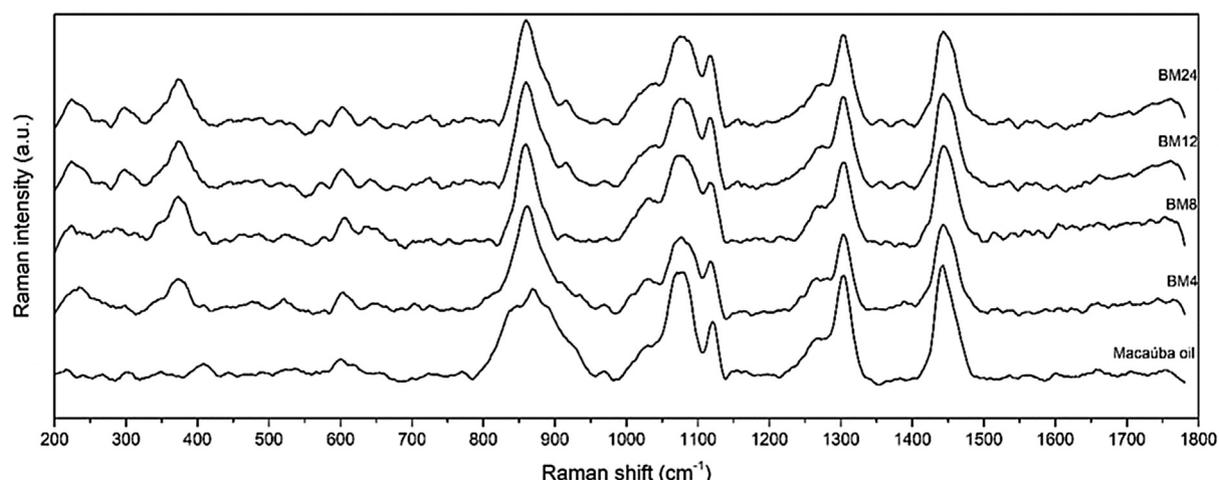


Fig. 3. Raman spectra of MO and its respective biodiesels.

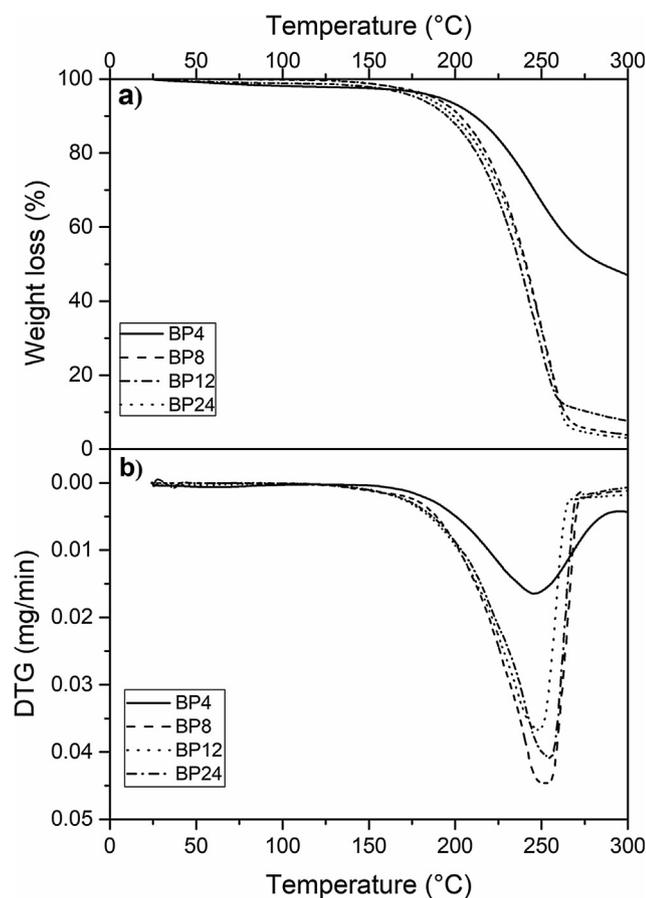


Fig. 4. (a) TG and (b) DTG curves of the PO biodiesel.

[64]. FT-IR is widely used in the monitoring of transesterification reactions for the quantification and identification of the substances present in the samples [65,66].

Figs. 6 and 7 show the FT-IR spectra of PO and MO and their respective biodiesels.

According to Zhou et al. [65], who studied the oxidative degradation of biodiesel blends using FT-IR, the absorption band around 1743 cm^{-1} can be attributed to the C=O group of the ethyl esters. This result was also obtained by Li et al. [66], and the band at 1742 cm^{-1} was attributed to the C=O bonds in their study of the thermal degradation of biodiesel obtained from peanut oil. This main absorption band can be used as an indicator of biodiesel production because the bands between 1800 and 1700 cm^{-1} are attributed to the carbonyl groups of the formed esters [67]. This band was also observed in the BP and BM samples, as shown in Figs. 6 and 7, respectively, and the most intense peak was at 1737 cm^{-1} . This peak at 1737 cm^{-1} was also observed by Niu et al. [68], who used FT-IR to characterize the ethyl esters formed from oleic acid, the major fatty acid in PO that is also present in MO.

Other absorption bands that can be used to identify the presence of ethyl esters include the band at 1034 cm^{-1} present in the two spectra (Figs. 6 and 7); this band is only present in the spectra of transesterified oils, and its area increases with an increasing amount of ethyl ester in the sample. As shown in the spectrum of BP4 (Fig. 6), the band at 1034 cm^{-1} is less intense than those in the spectra of the other biodiesels (50% conversion), which have the same conversion efficiency (98% conversion) (Section 3.3). In contrast, the band in the spectrum of BM4 is the same as those in the spectra of the other BM samples because all BM samples underwent the same conversion. The band at 1034 cm^{-1} is associated with the symmetrical vibration of the C–O–C group and is present only in transesterified oils that contain oleic acid;

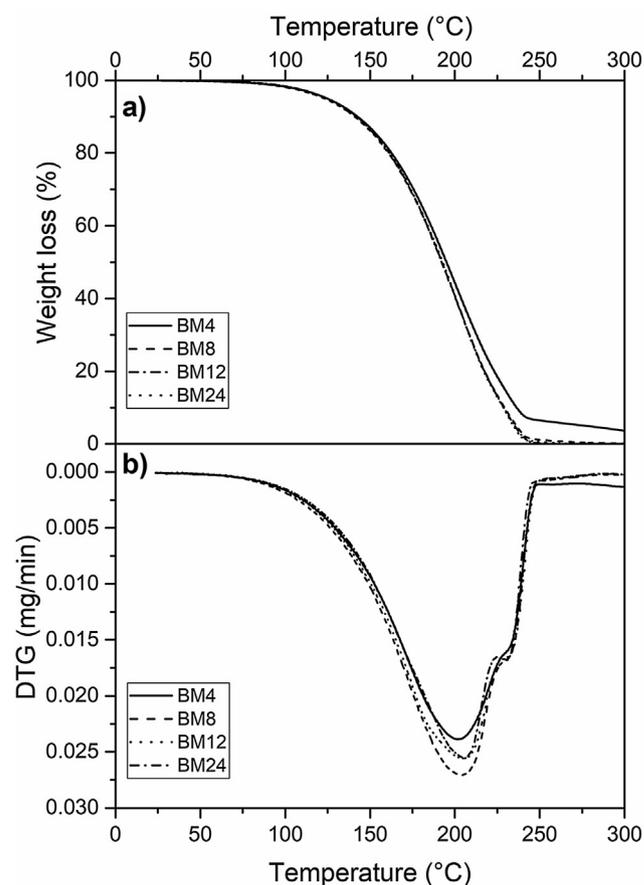


Fig. 5. (a) TG and (b) DTG curves of the MO biodiesel.

this band indicates the presence of ethyl esters [68].

Other bands that may indicate the presence of ethyl esters identified in Figs. 6 and 7 are listed in Table 5.

4. Conclusions

In this work, it was investigated the ethyl esters formed from pequi and macaúba oils by homogeneous acid catalysis in the transesterification reaction. For the AI of the crude oils, it was found that PO stayed in the limit ($0.842\text{ mg KOH g}^{-1}$), but MO had high value ($18.23\text{ mg KOH g}^{-1}$), indicating that the most suitable route is a homogeneous acid-catalyzed reaction, which was the route chosen for this work. Due to the large quantities of FFAs in the oil, the only biodiesel that had the limit stipulated by the ANP (0.5 mg KOH g^{-1}) was the BP24 ($0.28\text{ mg KOH g}^{-1}$). Regarding the kinematic viscosity, of all samples analyzed, BP4 was the only one that did not fit within limits indicated by the ANP because the conversion rate for this sample was about 50%. The viscosity index showed that although both biodiesels have greater stability, the BP is more stable than the BM. By the density analysis it was verified that the macaúba and pequi biodiesel presented values within the ranges specified by the ANP and the European Union. With the transesterified oils, it was calculated the yield of the biodiesel conversion by means of $^1\text{H NMR}$, and it was found for PO that the reaction time was a factor that influenced the conversion rate. In the 4 h reaction, there was a conversion of 50%, whereas for 24 h the conversion was 95%. For MO, the reaction time did not influence the conversion, so both the 4 h and the 24 h reactions showed a conversion rate of 98%. The evaluation of biodiesel by oxidative stability showed that the biodiesel samples obtained in 24 h were the closest to the limit established by the ANP. However, the results obtained are within the standards required by the European Union. The results obtained from

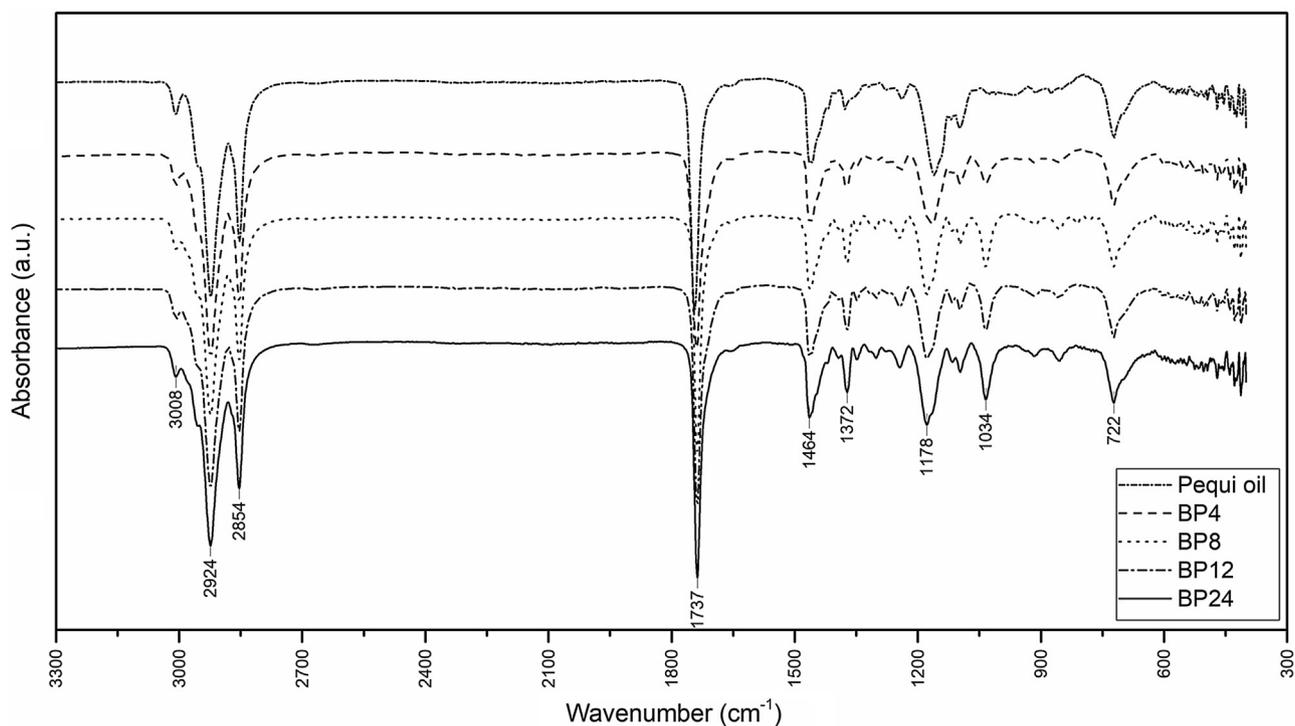


Fig. 6. FT-IR spectra of PO and its respective biodiesels.

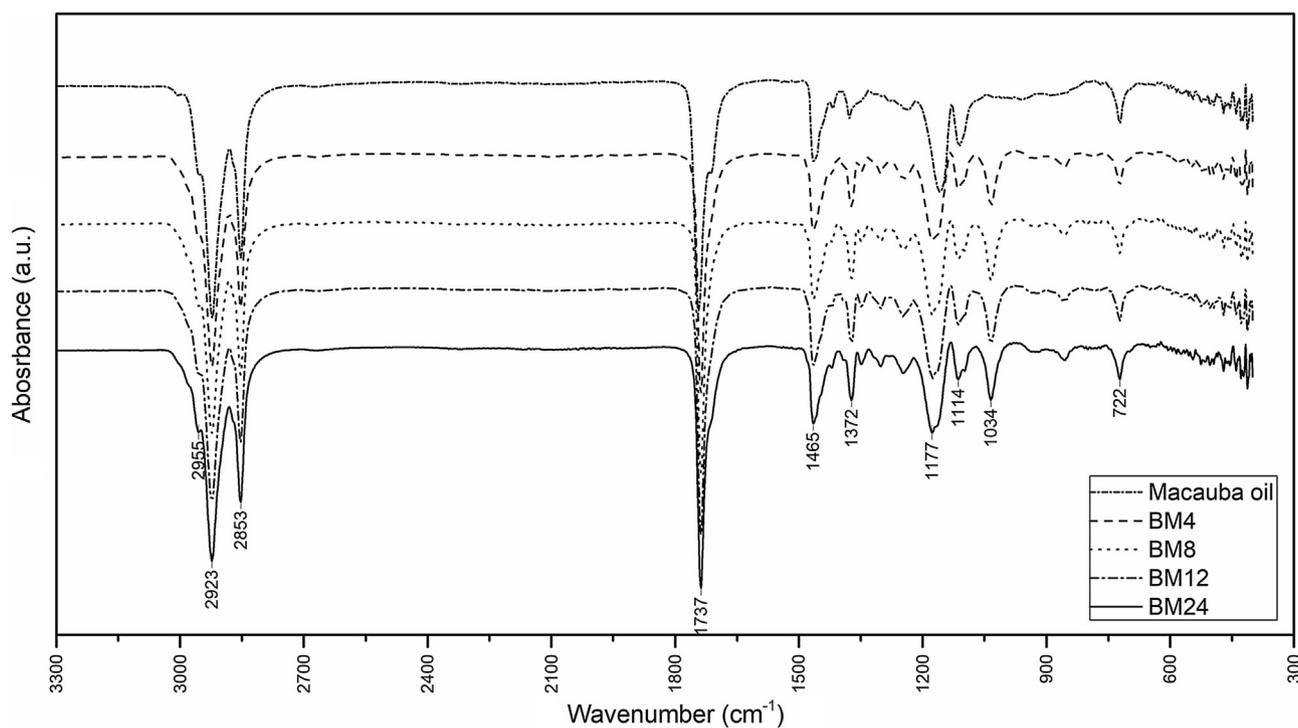


Fig. 7. FT-IR spectra of MO and its respective biodiesels.

the ester content showed that the highest yields in ethyl esters were obtained with 24 h reaction and are in agreement with the results of the ^1H NMR analysis, besides meeting the ANP 45/14 resolution specifications. From the Raman, FT-IR, and ^1H NMR analyzes, it was possible to verify the presence of ethyl esters. From TG and DTG, it was possible to see that for both biodiesels; thermal degradation occurred in a single step. The only biodiesel in which the reaction time interfered with the beginning of thermal degradation was BP4, indicating higher thermal stability and suggesting the presence of untransesterified fatty acids.

Although macaúba has advantages in the quantity of oil production, pequi is a better source for biodiesel production, because it presents a fuel of lower acidity and greater stability, besides the oil has less FFAs, allowing other catalytic routes. According to the results obtained, these biofuels can be classified as biodiesel.

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Table 5
Characteristic absorption bands of the ethyl esters formed during the reaction.

Group	BP (cm ⁻¹)	BM (cm ⁻¹)	Reference (cm ⁻¹)	References
Out-of-plane vibration of C–H of the CH ₂ group	722	722	722 723	[66,68]
Asymmetric axial vibration of C–O–C	1178	1177	1175 1183	[67,69]
Symmetric vibration of H–C–H	1372	1372	1377	[68]
Vibration of the CH ₂ group	1464	1465	1463	[68]
Axial vibration of C–H in the CH ₂ group	2854	2853	2853 2853	[66,68]
Axial vibration of C–H in the CH ₃ group	2924	2923	2923 2923	[66,68]
Axial vibration of C–H in olefin unsaturation	3008	–	3009	[68]

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