BIODIESEL FROM OITICICA OIL (*Licania rigida*, Benth): PRODUCTION, THERMOGRAVIMETRIC, AND OXIDATIVE STABILITY STUDIES

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ABSTRACT

Oiticica is a feedstock with energetic potential for biofuel due to the presence of high oil content in its almond (54-60%). In this work, biodiesel from oiticica was produced by methyl transesterification using alkaline catalysts. Fatty acid methyl ester (FAME) obtained at 32 °C, with 1.5% of KOH and 2h of reaction time was higher (92%) than that with NaOH (85%). At the temperature of 50 °C, no difference between the catalysts was found, both resulting in a conversion of 91%. The best acid index was obtained with 1% of NaOH (0.40 mg KOH g⁻¹ oil at 50 °C) and the best value of viscosity (9.61 mm² s⁻¹) with 1.5% of KOH at 50 °C. Oiticica oil and biodiesels exhibited high viscosities due the predominance of unsaturated compounds. Thermogravimetric analysis demonstrated to be a feasible technique, when compared to chromatography, in terms of time of analysis, conversion of the esters, and reagent consumption. All the biodiesels presented an oxidation temperature of 90 °C via Pressure Differential Scanning Calorimetry (PDSC).

KEYWORDS

oiticica oil; biodiesel; transesterification; thermogravimetry; oxidative stability

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1. INTRODUCTION

The worldwide increase in the consumption of liquid fuels generated a growing demand for clean energy and economic feasibility. With the possible intensification of global warming and the goal of replacing fossil diesel by biofuels gradually, the need for energy security policies, including those in development in the field of agriculture, has grown substantially (La Salles et al., 2010; Tiosso et al., 2014). Among various renewable energy resources are sunlight, wind, and geothermal energy. In this context, bio-based fuels, such as biodiesel, bioethanol, and biogas represent great alternatives (Huber et al., 2006; Hasheminejad et al., 2011; Shirazi et al., 2013), especially in Brazil.

Currently, more than 95% of the biodiesel produced in the world comes from edible oils, which are easily available on a large scale from the agricultural industry. However, a growing and large-scale production of biodiesel from edible oils may cause a negative impact on the world, such as the depletion of food supply leading to economic imbalance (Dwivedi and Sharma, 2016a).

Biodiesel is a mixture of fatty acid methyl esters (FAMES) usually derived from crude vegetable oils (triacylglycerol or triglycerides), which may also contain several non-edible compounds. These compounds need to be removed by a chemical or physical refining process before human consumption (Piloto-Rodríguez et al., 2014).

Due to its extensive geographic area, Brazil has an ideal environment for agriculture. This, associated to its weather and soil conditions, allow for the cultivation of a variety of raw materials favorable for biodiesel production. Among these materials, edible and non-edible oleaginous crops are included.

According to the Brazilian Statistical Yearbook of Petroleum, Natural Gas, and Biofuels (ANP, 2016), most of the biodiesel produced in Brazil comes from soybean oil (77%), followed by animal fats (19%), and cotton oil (2%). This high dependence on the cultivation of soy, along with the fact that soy is also destined for human nourishment, leads to an increase in the number of researches and incentives aiming at the biodiesel production from other oilseed crops (Rosa et al., 2014).

There are study records with fourteen different species of oilseeds, and more than twenty different types of oilseeds in Brazil. Silva (2011) reported that there are thirty oleaginous plants, which are not used widely for food that can be grown in different regions of Brazil with the purpose of oil extraction for biodiesel production.

The main raw materials (oilseeds) used for biodiesel production are: peanuts (*Arachis hypogaea*), canola (*Brassica napus*), sunflower (*Helianthus annuus* L.), babaçu (*Attalea speciosa*), buriti (*Mauritia flexuosa*), macaúba (*Acrocomia aculeata*) (BRASIL, 2010; Galvão et al., 2011), andá-açu (*Joannesia Princeps*), andiroba (*Carapa guianensis*), bacaba (*Oenocarpus bacaba*), baru (*Dipteryx alata*), canudo-de-pito (*Senna bicapsularis*), safflower (*Carthamus tinctorius*), castanet (*Terminalia catappa* Linn), catolé (*Syagrus oleracea*), chichá (*Sterculia striata*), cumaru (*Dipteryx odorata*), faveleira (*Cnidioscolus quercifolius*), inajá (*Attalea maripa*), licuri or ouricuri (*Syagrus coronata*), moringa (*Moringa oleifera*), neem (*Azadirachta indica*), oiticica (*Licania rigida*, Benth), paupola-do-méxico (*Argemone mexicana* L.), copaíba or pau d'óleo (*Copaifera langsdorffii*), pequi (*Caryocar brasiliense*), pereiro (*Aspidosperma pyrifolium*), pinhão-bravo (*Jatropha mollissima*), sapoti (*Manilkara zapota*), sapucaia (*Lecythis pisonis*), tucumã (*Astrocaryum aculeatum*), and tung (*Vernicia fordii*) (Silva, 2011; Pinto et al., 2005; Bergmann et al., 2013). Eighteen of these species are found in the Northeast Region of the Country.

Oiticica is originated from the *Chrysobalanaceae* family. It is a riparian species found in temporary watercourses of the Brazilian semi-arid Northeast. Oiticica is of great importance, both due to its environmental role of preserving the river banks and temporary streams in the Caatinga region, as well as to its suitability as an oil-producing species. This oilseed is promising for the semi-arid Northeast scenario and for other regions. It can be found in the watersheds of Piauí, Ceará, Paraíba, and beyond the state of Rio Grande do Norte (Queiroga et al., 2014; Beltrão and Oliveira, 2007). Freshly harvested oiticica almonds contain about 60-63% of oil, as elucidated by Pinto (1963). In mature fruits, the oil content is reduced to about 54-60% (Queiroga et al., 2014; Macedo et al., 2011). The main applications of oiticica oil are in the automotive paint industry, in printers (inkjet),

varnishes, enamels, tarpaulins, and soap in Brazilian factories with a history of exportation to North America (Queiroga et al., 2014; Macedo et al., 2011). Oiticica oil is applied also as bio-lubricant due to its chemical composition.

Few researches investigate the application of oiticica oil to biodiesel synthesis, motivating this study. Furthermore, oiticica presents a series of advantages. The almond contains high amounts of oil and is not an edible feedstock. Specific agronomic care is not demanded, and, thus, it can be cultivated in unproductive lands, together with other species or in between other crops. The sustainability of oiticica biodiesel production in the Brazilian semi-arid region can be achieved by stimulating small producers in the months of December to February, a period of shortage in the total income of farming families.

The evaluation of biofuels properties is necessary since different raw materials have different physicochemical values depending upon their fatty acid composition (Pelegri et al., 2017). Commonly, the physicochemical properties most investigated are acid index, iodine value, saponification index, density, kinematic viscosity, and water content.

Among the methodologies available to identify chemical compounds present in vegetable oils, gas chromatography coupled with a mass spectrometer detector has been applied. The identification of the products is carried out using NIST (National Institute of Standards and Technology) Mass Spectral Library. For raw materials conventionally applied to biodiesel production, there is a wide database consolidated in the literature. For less-studied oilseeds, the NIST Mass Spectral Library becomes an advantageous tool to determine their compounds and validate them along with another technique, if necessary.

Thermogravimetric Analysis (TGA) has been used widely in the evaluation of the thermal properties of several systems, including the characterization of thermal stability and thermo-oxidative phenomena of different types of vegetable oils used for biodiesel production. Furthermore, studies of kinetic and biodiesel conversion, indicating its degree of purity, are also determined by TGA (Zhou et al., 2017b; Yuan et al., 2016; Vega-Lizama et al., 2015; Arruda et al., 2016; Silva et al., 2012; Silva et al., 2014; Souza et al., 2004).

The most frequently methods employed in the evaluation of the oxidative stability of vegetable oils and biodiesels are Racimat (EN 14112), PetroOxy (ASTM D7545), and PDSC (ASTM D6186 and E2009) (Zhou et al., 2017a). The issue of oxidative stability affects the quality of biodiesel, especially concerning long periods of storage (Knothe et al., 2005b). Factors such as the presence of air, light, metals, and high temperatures facilitate the oxidation process. Dwivedi and Sharma (2016a) reported that one of the main problems related to biodiesel is stability, both oxidative and thermal. Storage time is also a concern.

The present work focused on four primary goals. The first one was the characterization of oiticica oil by gas chromatography coupled with a mass spectrometer detector. This was carried out to determine fatty acid compounds with confidence, since literature is scarce, incomplete, and doubtful. The next goal is the report of a new set of experimental data for the synthesis of biodiesel from oiticica oil by methyl transesterification using homogeneous catalysts within a range of conditions. The studied variables were temperature, reaction time, and the action of two different catalysts. Then, the thermal decomposition of the oil, the conversion to esters (biodiesel) and thermal stability were evaluated by thermogravimetric analysis (TG/DTG) for the oiticica oil and biodiesels. Finally, the oxidative stability of the biodiesels was determined by PDSC (Pressure Differential Scanning Calorimetry).

2. 2. MATERIALS AND METHODS

2.1 Source of oiticica seeds

Freshly harvested, mature and previously sun-dried seeds of *Licania rigida Benth* were collected in the city of Água Nova, in the state of Rio Grande do Norte, located in the Potiguar West, Northeast of Brazil. This region has a hot and dry climate throughout most of the year (Queiroga et al., 2014) and is characterized by scarcity of rain and harsh climate (Silva et al., 2012).

2.2 Oil extraction and characterization

Oiticica seeds were sundried during a period of 4 days, 8h each. Afterwards, they were placed in an

air circulating oven (Marconi MA 035/5) for 8 h at 50 °C. The seeds were then submitted to a mini electric press (Ecirtec MPE 40) for the oil extraction. After the mechanical extraction, the oil was kept in a closed container for 24 - 48h in a light-free environment. This was done to prevent photooxidation and to ensure sedimentation of the oiticica fine solid particles, which resulted from the pressing process. The extracted oil was then filtered and stored in amber glass bottles. The yield was evaluated based on the ratio between the mass of oil extracted and the mass of the seeds.

Derivatization of the oiticica oil was performed according to the methodology described by **AOAC (1997)**. It was employed to determine the fatty acids content in the oil and fats. Conversion of the fatty acids present in the oiticica oil into methyl esters was carried out with the aid of the derivatizing agent, i.e., boron trifluoro methanol (BF_3/MeOH , analytical grade from Sigma Aldrich). An amount of 250 mg of oiticica oil was mixed with 6 mL of 0.5 M NaOH/MeOH solution and submitted to agitation under reflux conditions for 10 min. The fatty acids were converted into methyl esters by the addition of 7 mL of BF_3/MeOH under reflux of 2 min. Fatty acid methyl esters (FAMES) were recovered by adding 5 mL of n-hexane under reflux of 1 min. All solvents used were of chromatographic grade ($\geq 99\%$). Subsequently, 10 mL of saturated NaCl solution were added and the organic phase was separated. Humidity in the rich hexane phase was removed by the addition of c.a. 100 mg of Na_2SO_4 anhydride. This was mixed, quickly, in a vortex shaker. The samples were then filtered (PTFE-45/25 0.45 μm), transferred to vials and stored in a freezer for two hours for chromatographic analysis.

2.3 Chromatographic analysis of the oil and biodiesel

The composition of the fatty acids present in the *Licania rigida* oil was obtained using a Shimadzu gas chromatograph (model GC-2010) coupled with a mass spectrometer detector (GCMS-QP2010 plus), equipped with a Rxi-5HT fused-silica capillary column (diphenyl dimethyl polysiloxane, 30m x 0.25mm x 0.10 μm).

Samples of 1 μL were injected in a 1:50 ratio and in splitless mode. The interface and ion source temperatures were 280 °C and 200 °C, respectively.

The temperature of the injector was 250 °C. Helium at 3 mL min^{-1} was the carrier gas. The column starting temperature was 110 °C, remaining for 5 min in this condition. Later, the temperature was increased at a constant heating rate of 5 °C min^{-1} up to 230 °C, remaining at this temperature for 8 min. Then, the temperature was raised to 270 °C in a heating rate of 20 °C min^{-1} , remaining at this temperature for 10 min. The total analysis time was 49 minutes.

Identification of the compounds present in the oil and oiticica biodiesel was accomplished by comparing the resulting spectrums with a mixture of chemical standards (FAME mix C8 - C24, 100 mg, neat). This standard was provided from Supelco by Sigma Aldrich. It included the FAME derived from the many components of the oiticica oil, containing carbon chains ranging from C16:0 to C18:3, as well as the mass spectra of standards in the software library (Mass Spectral Database, NIST/EPA/NIH).

FAMES were prepared following the methodology described by EN 14103 (**CEN, 2003**). Basically, 100 mg of oiticica biodiesel were accurately weighed (± 0.01 mg) into a volumetric flask (10 mL) and completed with n-hexane (chromatographic grade, $\geq 99\%$). Then, 200 μL of this solution were transferred to a second volumetric flask (1 mL), where 50 μL of the methyl heptadecanoate internal standard solution (99% neat, of Sigma Aldrich) were added. The remaining volume was completed with n-hexane. Finally, samples were transferred to vials using a suitable syringe filter (PTFE-45/25; 0.45 μm) and taken to chromatographic analysis.

2.4 Synthesis of biodiesel

The methodology of biodiesel synthesis from oiticica was partially developed by the authors. The reaction conditions used were based on the preliminary experiments. Biodiesels were synthesized by methyl transesterification using homogeneous base catalysts (NaOH and KOH) under previously evaluated reaction conditions. Reactions occurred at 50 °C, with 1.0 and 1.5 wt.% catalysts in relation to the mass of oil, oil/alcohol molar ratio of 1:9 and reaction times of 1 h and 2 h. At 32 °C, a reaction with 1.5 wt.% catalyst was also performed. In this study, the temperature of 32° C was used based on the work of **Macedo et al. (2011)**. The catalyst was dissolved in methanol and mixed with the preheated oil at the defined

reaction temperatures (32 and 50 °C). At the end of the reaction, the remaining mixture of esters (biodiesel), glycerine, catalyst and alcohol was taken to a separation funnel, remaining there for 12h to complete phase separation between the FAME and the glycerol. After that time, successive washing steps were performed with warm distilled water (50 - 65 °C) until reaching a neutral pH (7). While the wash water was white in color, an indication of catalyst presence, the pH of the ester phase was still alkaline. This check was monitored with the aid of a pH indicator paper. At pH 7, the system presented no color. This was followed by oven drying at 105 °C for a period of 3 - 5 h, and cooling in a desiccator for 2 h. Finally, the purified biodiesel was weighed in an analytical balance (Shimadzu AUW220).

The reaction yield was calculated from the transesterification stoichiometry, considering the initial mass of the oil and the mass of the biodiesel obtained in the synthesis reaction. The average molar mass of the oil and biodiesel were determined from the composition of methyl esters obtained in the gas chromatography with mass spectrometry, considering the proportion of 1 mol of oil to 3 mols of esters.

2.5 Physicochemical properties

The physicochemical properties of the oil and biodiesel samples were evaluated in accordance with the normative methods of the Brazilian Association of Technical Standards (ABNT), the standards of the American Society of Testing and Materials (ASTM) and the European Committee for Standardization (CEN), as established by Resolution 45/2014 (ANP, 2014) of the Brazilian National Agency of Petroleum, Natural Gas, and Biofuels (ANP).

The specific masses at 20 °C of the oil and biodiesels were analyzed using digital densimeters (Anton Paar DMA 4500M and Rudolph Research Analytical DDM 2911), following the method described in ABNT NBR 14065 (ABNT, 2013).

The rheological behavior of the oil was evaluated by a R/S Brookfield Rheometer in the temperature range of 20 to 75 °C. The biodiesels were analyzed by an Anton Paar SVM 3000 Stabinger Viscometer at 40 °C. Kinematic viscosity values at 40 °C were determined according to the method ABNT NBR 15983 (ABNT, 2012).

The acid index values of the oil and the biodiesel and the saponification and iodine indexes of the oil were determined in accordance with the methodologies described by Moretto and Alves (1986).

The water content in the oil and biodiesel was determined by a Mettler-Toledo Karl-Fischer Coulometer (model DL39) using the standard ASTM D 6304 (ASTM, 2007).

2.6 Thermogravimetric analysis of oil and biodiesel (TG/DTG)

Thermogravimetric analyses were carried out using a thermobalance (Shimadzu DTG-60), in the temperature range of 50 - 600 °C, under a nitrogen atmosphere flowing at a rate of 50 mL min⁻¹, using an alumina crucible (50 µL) and in a heating rate of 10 °C min⁻¹. The masses of the samples were 7.5 - 9.5 mg.

Conversion of biodiesel was determined by thermogravimetric analysis and expressed in terms of the mass percentage of fatty acid methyl esters formed.

2.7 Pressurized differential scanning calorimetry (PDSC)

The PDSC curves were obtained through a differential scanning calorimeter coupled to a pressure cell - DSC 204 Phoenix (NETZSCH) - under dynamic conditions, using an aluminum crucible, in an atmosphere of oxygen, at a pressure of 7000 kPa, temperature from 50 to 250 °C, and heating rate of 10 °C min⁻¹.

3. RESULTS AND DISCUSSION

3.1 Oil extraction

The maximum oil yield (44.2%) was achieved from seeds which were harvested four months prior to the experiment, and were properly stored. The lowest oil yield (6.5%) was obtained from 12-month old seeds, as shown in Table 1. It is noteworthy that oil content in these oleaginous almonds decreases gradually over time after falling of the fruits. For 3-month old oilseeds, the oil yield was lower than those obtained from the 4-month old ones, due to the presence of larvae (*Peonea*

Table 1. Oil content mechanically extracted from the oiticica and extraction efficiency in function of the time from harvest and of storage of the fruits.

Age of oiticica (in months)	Oil content extracted from the oiticica (%)*	$\eta_{\text{extraction}}$ ** (%)
3	36.3	63.7
4	44.2	77.5
6	21.0	36.8
9	11.7	20.5
12	6.5	11.4

*Oil content is obtained according to Equation 1, as function of the oil and seed masses;

**Extraction efficiency is defined according to Equation 2, as function of the corresponding oil content and the average value reported by the literature (57%) for mature fruits.

sp.) and weevils (*Conotrachelus sp.*). It was observed that the presence of these organisms provokes the decomposition of the almonds, reducing the amount of oil yield extracted. Commonly, in the first crop, between November and December, many oilseeds may be vulnerable to pests, although the oiticica is highly resistant to adverse conditions.

$$\text{Oil content (\%)} = \frac{\text{Oil mass}}{\text{Seed mass}} \cdot 100 \quad (1)$$

$$\eta (\%) = \frac{\text{Oil content obtained}}{\text{Average oil content for mature fruits}} \cdot 100 \quad (2)$$

The observed oil contents are in accordance with the values obtained by [Queiroga et al. \(2014\)](#). The results presented were: 61.10% for fruits harvested and stored for 7 days, 56.83% for those stored for 30 days, and 17.75% for 365 days. Therefore, the variability in oil content depends on the degree of maturation of the oiticica fruits during the period from December to March.

The extraction efficiency was evaluated in relation to the average value of the oil content present in the oiticica seed of mature fruits, and it was determined to be 57% according to [Queiroga et al. \(2014\)](#), as explained in Equation 2. Table 1 shows that satisfactory efficiency was obtained for seeds stored for 4 months (77.5%), demonstrating a loss of more than 20% in the mechanical extraction. However, for storage times higher than 4 months, the loss was significantly higher, indicating that to have a better yield for the oiticica, processing should be performed as soon as possible after harvesting and drying the seeds.

In comparison to the oil yields of other oilseeds used to produce biodiesel, the values referring to oiticica oil extraction are higher than those reported in the literature ([Arruda et al., 2016](#)). Cotton presents an average oil extraction of 30%, soybean of 15%, and sesame of 35 to 63%, which is close to the yield range of oiticica oil. It is important to emphasize that the oil yield for oiticica tends to be higher because its almond is much bigger and richer in oil content than the sesame seed. Nevertheless, mechanical compression produces a more significant loss in the oiticica bagasse due to its larger size.

3.2 Characterization of oiticica oil

Chromatographic analysis of the oil by derivatization technique evidenced the conversion of the fatty acids present in the oiticica oil into methyl esters. Table 2 lists the composition of the fatty acids found in the oiticica oil, where a conversion of 97.3% was observed.

[Pinto \(1963\)](#) referenced the composition of oiticica oil reported by other researchers, emphasizing among its fatty acids the licanic (70-80%), the linolenic (10-12%), and small amounts of palmitic, oleic, and stearic. The presence of eleostearic acid was assumed by several investigators, but without quantitative evidence. However, [Kaufmann and Sud \(1960\)](#) reported a study of the fatty acid composition of several conjugated oils, including oiticica, by FTIR (Fourier Transform Infrared Spectroscopy) and paper chromatographic analysis, where they identified α -eleostearic (14%), α -licanic (58%), and oleic (18.1%) unsaturated fatty acids, as well as unspecified

Table 2. Chemical composition of oiticica oil by gas chromatography with mass spectrometry (GC-MS).

Symbol (Double bond position)	Oiticica oil	
	Fatty acid	wt.%
C16:0	Palmitic	5.0
C18:0	Stearic	8.3
C18:1 (9c)	Oleic	10.6
C18:2 (9c.12c)	Linoleic	3.0
C18:3 (9c.11t.13t)	α -Eleostearic	16.9
C18:3 (4-keto;9c.11t.13t)	Licanic	43.2
Others		10.3
Total		97.3
Total saturated		14.2
Total unsaturated		83.1

saturated fatty acids (9.9%). Decades later, these compositions were confirmed by **Bergter and Seidl (1984)** through nuclear magnetic resonance (NMR) and gas-liquid chromatography (GLC). **Güner et al. (2006)** emphasized also the presence of the following fatty acids in the oiticica oil: palmitic (6%), stearic (4%), oleic (8%), linoleic (8%), and licanic (74%). However, these researchers did not mention the presence of α -eleostearic acid.

In the study carried out by **Bergter and Seidl (1984)**, they claimed that oiticica oil is composed by the fatty acids: licanic (4-oxo-cis, trans, trans-9,11,13-octadecatrienoic), α -eleostearic (cis, trans, trans-9,11,13-octadecatrienoic), palmitic, stearic, oleic, and linoleic. The analysis was conducted by gas liquid chromatography (GLC) and proved through a complete assignment of the carbon-13 spectrum of oiticica oil by nuclear magnetic resonance (NMR). They interpreted the chemical shifts in conjugated systems, emphasizing that the Carbon-13 NMR spectrum of the licanic acid had not been interpreted before and that the keto group in the 4-position allowed for a comparison with the spectra from α -eleostearic, β -licanic (4-oxo-trans, trans, trans-9,11,13-octadecatrienoic) and β -eleostearic (trans, trans, trans-9,11,13-octadecatrienoic) acids. These researchers further emphasized that the complete assignment of olefinic carbons was possible. Thus indicating that considerations based on steric effects must be treated with appropriate care. The oil composition obtained by them was: C16:0 - 6.8%; C18:0, C18:1, C18:2 - 22.6%; C18:3 (conj) - 15.1%; C18:3 (oxo, conj) - 55.4%.

In this work, the composition of the oiticica oil

was determined by GC-MS and the results were consistent with those obtained by **Bergter and Seidl (1984)**. Even though the spectrum of licanic acid methyl ester is not available in the MS database (NIST/EPA/NIH), it was the major component in all the samples analyzed. Therefore, in accordance with the values found by the literature, licanic presence can be affirmed. The α -eleostearic spectrum, on the other hand, is part of the mass spectrometer library, which allows the peaks to be identified based on molecular weight and spectrum similarity. The molecular weight of the α -eleostearic acid is slightly lower than that of the licanic. This difference is seen only in the keto group, as it may be observed in Table 2. Therefore, the α -eleostearic acid peak must precede the peak of the major component (licanic acid), as it was evidenced in all chromatograms analyzed, eliminating the identification problem of these two main acid components in the oiticica oil samples.

Based on the results shown in Table 2, 83.1% of the oil is composed of unsaturated fatty acids and 14.2% by saturated. The predominance of unsaturated acids, especially of licanic acid, is highlighted. Therefore, the high content of polyunsaturates makes the oiticica oil more susceptible to oxidation, due to the number and position of its double bonds. In addition to oxidation, polymerization occurs due to the presence of double bonds to form higher molecular weight products, resulting in a more viscous biodiesel, as pointed out by **Issariyakul and Dalai (2013)**. **Knothe et al. (2005b)** reported that the *bis*-allylic positions are even more susceptible to oxidation than the allylic ones.

Table 3. Physicochemical properties of the oiticica oil.

Properties (unit)	Oiticica oil (this work)	Other authors			
		Pinto (1963)	Melo et al. (2009)	Melo et al. (2014)	Macedo et al. (2011)
Acid index (mg KOH g ⁻¹)	1.52	-	1.19	10.8	13.0
Saponification index (mg KOH g ⁻¹)	194.0	194.0	-	-	188.3
Iodine index (g I ₂ 100 g ⁻¹)	95.4	142.0	-	100.2	-
Specific mass at 20 °C (kg m ⁻³)	966.7	960.0	962.6	-	-
Kinematic viscosity at 40 °C (mm ² s ⁻¹)	138.6	-	133.9	130.9	-

The physicochemical properties of the oiticica oil were determined in triplicate and the average values are reported in Table 3. The results are also compared with the data available in the literature. It can be observed that the values obtained are, in general, similar to those reported by the other researchers. Specific mass and kinematic viscosity measurements are slightly higher than the values found in the literature, 1 and 5 %, respectively. Furthermore, the difference in viscosity between the source oil and its alkyl ester derivative can be used to monitor biodiesel production, according to the literature (Silva et al., 2012; Knothe et al., 2005b).

On the other hand, the iodine content observed in this study was lower than in other researches. The iodine content indicates the level of oil unsaturation. Other indicatives are the susceptibility of the oil to oxidation, the polymerization and the formation of deposits in the engine. Pelegrini et al. (2017) highlighted the iodine values (g I₂/100 g) of various vegetable oils: soapberry (83.40), soapnut (84.86), babassu (100.50), buriti (87.99), castor (87.50), corn (122.60), cottonseed (105.70), soybean (112.50), sunflower (125.50), soursop (111.07), and karanja (86.50). These were compared with the iodine value of oiticica oil obtained in this work (95.4) and the values found by other researchers, see Table 3. The iodine index of the oiticica oil was lower than 115, which is the value recommended by the literature (Pelegrini et al., 2017). Knothe et al. (2005b) emphasized that the European standards EN 14214 and EN 14213 report values of 120 and 130, respectively. Thus, the iodine value found for oiticica oil evidences its potential for biodiesel production.

Melo et al. (2014) and Macedo et al. (2011) reported higher acid index values for oiticica oil (Table 3). They used refined oil from Resibras S/A Company (Ceará, Northeast Brazil) in 2009. Because of the time of storage, a pre-treatment (esterification) before alkaline methanolic synthesis (transesterification) was necessary to obtain lower acid level. In this work, crude oiticica oil was used without any prior treatment since acid index was satisfactorily low.

The saponification index varies with the nature of the fatty acids that comprise the triacylglycerols. The lower average molecular weight of these compounds, the higher the saponification index (Moretto and Alves, 1986; Araújo et al., 2014). Table 3 shows that there was no significant difference between the saponification indices observed in this study and those pointed out by other researchers.

The best reaction yields were obtained with the KOH catalyst, both at 1 and 1.5%, in mass basis. Biodiesels with 1% of catalyst presented 77.1% (NaOH) and 81.7% (KOH). Those with 1.5% of NaOH resulted in yields of 55.1% (at 32 °C) and 58.6% (at 50 °C), while 1.5% of KOH resulted in 73.8% (at 32 °C) and 68.8% (at 50 °C).

Table 4 reports experimental values for the characterization of the oiticica biodiesels in terms of physicochemical properties. The acid indices of biodiesel were slightly above the limit specified by the ANP (2014). The transesterification reaction employing 1% NaOH catalyst, and conducted at 50 °C, presented an acid index below this limit.

All values of specific mass and viscosity were higher than the intervals established by the current resolutions. Nevertheless, all viscosity results for

Table 4. Physicochemical properties of the oiticica biodiesel.

Properties (Unit)	Biodiesel						ANP Specification	
	1% cat.; 50 °C		1.5% cat.; 50 °C		1.5% cat.; 32 °C		B100*	Diesel**
	NaOH	KOH	NaOH	KOH	NaOH	KOH		
Acid index (mg KOH g ⁻¹)	0.41	0.54	0.52	0.55	0.55	0.54	0.50	-
$\rho_{20^{\circ}\text{C}}$ (kg m ⁻³)	927.5	927.2	926.0	927.0	926.0	927.0	850 - 900	815 - 850 (S10) 815 - 865 (S500)
$\nu_{40^{\circ}\text{C}}$ (mm ² s ⁻¹)	10.4	10.3	9.91	9.61	9.70	9.94	3 - 6	2 - 4.5 (S10) 2 - 5 (S500)
H ₂ O (mg kg ⁻¹)	n.a.	n.a.	1305.52 (0.13%)	2207.76 (0.22%)	1291.31 (0.13%)	2589.89 (0.26%)	200 (0.02%)	200 (S10) 500 (S500)

*Resolution ANP 45 (ANP, 2014); ** Resolution ANP 50 (ANP, 2013); S10/S500: diesel with sulfur (10 and 500 ppm); n.a.: not analyzed.

the catalyst at 1.5% were equivalent among them and somewhat lower than the values with 1% of catalyst. The viscosity of biodiesel increases with an increase in the carbon chain length, the degree of saturation of the fatty acid and its ester, and, finally, with the presence of free fatty acids (Melo et al., 2014; Knothe et al., 2005a; Damasceno et al., 2013; Yaakob et al., 2014). Samples with *cis* double bond configurations have lower viscosity, whereas samples with *trans* double bonds have higher viscosity. The position of the double bond, however, has a minor effect on the viscosity (Knothe et al., 2005a; Damasceno et al., 2013). Likewise, the presence of branching in the chain attached to the ester has little to no influence on

the viscosity values. Some researches (Zhou et al., 2017a; Knothe et al., 2005a; Yaakob et al., 2014) claim that highly viscous samples have a high tendency for oxidation and the main reason for that is the isomerisation of the double bond, usually *cis* to *trans*, along with the formation of high molecular weight products. Furthermore, Yaakob et al. (2014) emphasized that the viscosity is useful for the measurement of the oxidation progression of biodiesel. The products of polymeric secondary oxidation cause the formation of soluble gums and insoluble sediments, which will result in an increase in viscosity. This is a possible explanation for the results obtained for the oiticica biodiesel in this work. Another factor contributing

Figure 1. Rheological behavior: (a) oiticica oil between 20 °C and 75 °C; (b) oiticica biodiesels at various conditions.

to oxidation is the presence of water, according to **Knothe et al. (2005b)**, since biodiesel is also potentially susceptible to hydrolytic degradation. Table 4 shows that all samples presented relatively high water contents. However, it is noted that the biodiesel produced with NaOH as the catalyst had 50% less water content. Nevertheless, both oil and biodiesel presented a Newtonian behavior. A linear relationship between shear stress and shear rate was observed, leading to a viscosity independent from the shear stress, see Fig. 1. In a study carried out by **Conceição et al. (2005)**, it is affirmed that the same behavior was observed in mineral diesel oil, resembling that of the oiticica oil and biodiesel.

Thermal analysis has the advantage of being

faster and less expensive when compared to chromatography, provided that it is used to verify the conversion and not specifically the composition of the esters. However, it is possible to determine the decomposition temperatures of many vegetable oils and biodiesels by combining it with other techniques, such as chromatographic analysis.

Fig. 2 shows the thermogravimetric curves (TG/DTG) for four different conditions of biodiesel synthesis and oiticica oil. This technique may serve as a tool for the analysis of the conversion of the fatty acid methyl esters, as evidenced also by **Galvão et al. (2011)**, **Pelegri et al. (2017)**, **Souza et al. (2004)**, **Dwivedi and Sharma (2016b)**, and

Figure 2. TG/DTG curves of the oiticica oil and biodiesel under an inert atmosphere (N_2): (a) 32 °C using NaOH; (b) 32 °C using KOH; (c) 50 °C using KOH; (d) 50 °C using NaOH; and (e) Curve TG/DTG oiticica oil.

Silva et al. (2016). The best result observed was for condition b, which achieved 92% of conversion, using KOH as catalyst at 32 °C and a reaction time of 2 h. The other reactions also resulted in relatively high conversions: 90.8% (NaOH) and 90.9% (KOH) at 50 °C. The lower conversion (85%) was observed in condition a: 1.5% of NaOH at 32°C.

Based on Fig. 2, one can observe that every reaction of the oiticica biodiesel occurred in more than one step. The TG/DTG curves of the oiticica biodiesels, under an inert nitrogen atmosphere in the four different synthesis conditions studied showed degradation in three steps. For all curves, the first event occurred at a temperature higher than 100 °C. It is possible to conclude that this step does not refer to an eventual loss of the water present in the samples, but can be associated with the volatilization of methyl esters, which are lighter in terms of molecular weight. The second and third events are assigned to the volatilization of the other esters, which have higher molecular weights. These two last steps are a result of the not fully transesterified unsaturated fatty acids, possibly the licanic acid, since it is the major constituent of oiticica oil. Several authors emphasize that the formation of high molecular weight compounds may change the TG/DTG profiles of the biodiesel, which could present different steps of mass loss

relative to the decomposition and/or volatilization of methyl esters and of oxidation products (**Zhou et al., 2017b**). The thermal behavior of oiticica oil (Fig. 2e) showed that the degradation of the sample occurred in a single step, marking the decomposition and/or volatilization of the fatty compounds, starting at 240 °C and ending at 495 °C. The observed degradation behavior is similar to the one observed for castor oil in the temperature range of 230 - 573 °C, as presented by **Pelegri et al. (2017)**. The observed events are also in agreement with the profiles shown in the thermal decomposition and/or volatilization of the vegetable oils and biodiesels reported in the literature (**Macedo et al., 2011; Silva et al., 2015; Borugadda and Goud, 2014; Santos et al., 2010; 2014**). In this work, the residual mass was associated with the amount of unsaturated fatty acids of the oiticica oil. **Vega-Lizama et al. (2015)** also brought up this connection. Table 5 shows the thermal behavior in three steps and the mass losses for each reaction system to biodiesel and one step to oiticica oil sample.

3.3 Pressurized differential scanning calorimetry (PDSC)

The analysis of the oxidative stability of the biodiesels by PDSC indicated that the onset

Table 5. TG data of the oiticica oil and biodiesel samples in inert atmosphere (N₂).

Sample	Step	Temperature range (°C)	T _{max} (°C)	Mass loss (%)	Residual mass (%)
Biodiesel - 1.5% NaOH 32 °C	1	129 - 310	268	85.0	-
	2	310 - 398	347	10.2	-
	3	398 - 490	439	4.4	0.65
Biodiesel - 1.5% KOH 32 °C	1	130 - 290	258	92.0	-
	2	290 - 390	306	6.3	-
	3	390 - 490	439	1.9	0.10
Biodiesel - 1.5% KOH 50 °C	1	129 - 290	260	90.8	-
	2	290 - 390	316	7.6	-
	3	390 - 492	444	1.3	0.24
Biodiesel - 1.5% NaOH 50 °C	1	130 - 295	261	90.9	-
	2	295 - 400	331	7.6	-
	3	400 - 495	440	1.3	0.21
Oiticica oil	1	240 - 495	405	99.5	0.50

Figure 3. Dynamic PDSC curves of oiticica biodiesels.

oxidation temperatures for all reactions were around 90 °C, regardless of the catalyst used, see Fig. 3. There was almost no difference between the curves since the same oil was used for all reactions.

However, these values of dynamic PDSC curves for the oiticica biodiesels presented onset temperatures lower than the biodiesels of: jatropha (120 °C) reported by [Freire et al., \(2012\)](#), and cotton (158.2 °C) and sunflower (154.2 °C) presented by [Galvão et al., \(2011\)](#). Several factors can explain the low values observed for the oiticica biodiesels, i.e., the number of double bonds, the existence of allylic and bis-allylic hydrogens and esters with large amounts of unsaturated fatty acids, once these are much more susceptible to oxidation ([Freire et al., 2012](#)).

4. CONCLUSIONS

From this work with oiticica oil and biodiesel, one can be notice that even the oil formed mainly of unsaturated fatty acids presented results that can be considered satisfactory. Even though the biodiesel had high density and viscosity, a Newtonian fluid behavior was observed. This is a positive aspect, but it does not mean that biodiesel from oiticica is promising to be used in engines in the form of B100. The synthesis using NaOH and

KOH as basic catalysts demonstrated to be satisfactory in terms of reaction yield and conversion to esters. NaOH catalyst (1 %, at 50 °C) was more favorable in terms of acid index of the resulting biodiesel. Thermogravimetric analysis showed that it is a feasible technique to obtain a faster response. It has advantages over the chromatography in relation to the cost, the time of analysis, and the amount of sample used. The PDSC analysis for biodiesel showed that there was no influence of the catalysts employed, indicating that the initial oxidation temperature for all the studied conditions was the same (90 °C).

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5. REFERENCES

- ABNT - **Associação Brasileira de Normas Técnicas**. ABNT NBR 14065: Destilados de petróleo e óleos viscosos – determinação da massa específica e da densidade relativa pelo densímetro digital. Rio de Janeiro, 2013. (In Portuguese)
- ABNT - **Associação Brasileira de Normas Técnicas**. ABNT NBR 15983: Produtos de petróleo – Determinação da viscosidade dinâmica e massa específica de líquidos através de viscosímetro Stabinger (e o cálculo de viscosidade cinemática). Rio de Janeiro, 2012. (in Portuguese)
- ANP - **Agência Nacional do Petróleo, Gás Natural e Biocombustíveis**. Resolução ANP 50/2013. Available at: <https://www.legisweb.com.br/legislacao/?id=263587>. Accessed on: 07 June 2017. (in Portuguese)
- ANP - **Agência Nacional do Petróleo, Gás Natural e Biocombustíveis**. Resolução ANP 45/2014. Available at: <https://www.legisweb.com.br/legislacao/?id=274064>. Accessed on: 14 November 2016. (in Portuguese)
- ANP - **Agência Nacional do Petróleo, Gás Natural e Biocombustíveis**. Anuário estatístico brasileiro do petróleo, gás natural e biocombustíveis: 2016. Available at: http://www.anp.gov.br/wwwanp/images/publicacoes/Anuario_Estatistico_ANP_2016.pdf. Accessed on: 25 April 2017. (in Portuguese).
- AOAC. **American Oil Chemists' Society**. Arlington: AOAC Official Method 969.33 - Fatty acids in oils and fats - Preparatio, 16th ed., Method 969.33 (vol. 2), 1997.
- Araújo, F. D. S.; Araújo, I. C.; Costa, I. C. G.; Moura, C. V. R.; Chaves, M. H.; Araújo, E. C. E. Study of degumming process and evaluation of oxidative stability of methyl and ethyl biodiesel of *Jatropha curcas* L. oil from three different Brazilian states. **Renewable Energy**, v.71, p. 495–501, 2014. <https://doi.org/10.1016/j.renene.2014.06.001>
- Arruda, T. M. G.; Rodrigues, F. E. A.; Arruda, D. T. D.; Ricardo, N. M. P. S.; Dantas, M. B.; Araújo, K. C. de. Chromatography, spectroscopy and thermal analysis of oil and biodiesel of sesame (*Sesamum indicum*) - An alternative for the Brazilian Northeast. **Industrial Crops and Products**, v. 91, p. 264–271, 2016. <https://doi.org/10.1016/j.indcrop.2016.07.029>
- ASTM - **American Society for Testing and Materials**. ASTM D 6304: standard test method for determination of water in petroleum products, lubricating oils and additives by coulometric Karl Fischer titration. West Conshohocken, 2007.
- Beltrão, N. E. M.; Oliveira, M. I. P. **Oleaginosas potenciais do Nordeste para a produção de biodiesel**. Campina Grande, Embrapa Algodão. 2007, 54p. (Documentos 177) Available at: <http://ainfo.cnptia.embrapa.br/digital/bitstream/CNPA/21063/1/DOC177.pdf>. Accessed on: 04 March 2014. (in Portuguese)
- Bergmann, J. C.; Tupinambá, D. D.; Costa, O. Y. A.; Almeida, J. R. M.; Barreto, C. C.; Quirino, B. F. Biodiesel production in Brazil and alternative biomass feedstocks. **Renewable and Sustainable Energy Reviews**, v. 21, p. 411–420, 2013. <https://doi.org/10.1016/j.rser.2012.12.058>
- Bergter, L.; Seidl, P. R. Complete assignment of the carbon-13 NMR spectrum of oiticica oil: Interpretation of chemical shifts in conjugated systems. **Lipids**, v. 19, p. 44–47, 1984. <https://doi.org/10.1007/BF02534607>
- Borugadda, V. B.; Goud, V. V. Thermal, oxidative and low temperature properties of methyl esters prepared from oils of different fatty acids composition: A comparative study. **Thermochimica Acta**, v. 577, p. 33–40, 2014. <https://doi.org/10.1016/j.tca.2013.12.008>
- BRASIL. Ministério da Ciência e Tecnologia. Centro de Gestão e Estudos Estratégicos. **Química verde no Brasil 2010-2030**. Brasília. MCT/CGEE. 2010. 433 p. Available at: http://www.cgee.org.br/publicacoes/quimica_verde.php. Accessed on: 16 June 2018. (in Portuguese)
- CEN - **European committee for Standardization** - EN 14103: Fat and oil derivatives – Fatty acid methyl esters (FAME) - Determination of Ester and linolenic acid methyl Ester contents; Brussels, Belgium, 2003.
- Conceição, M. M.; Candeia, R. A.; Dantas, H. J.; Soledade, L. E. B.; Fernandes, V. J.; Souza, A. G. Rheological Behavior of Castor Oil Biodiesel. **Energy and Fuels**, v. 19, p. 2185–2188, 2005. <https://doi.org/10.1021/ef050016g>

Damasceno, S. S.; Rosenhaim, R.; Gondim, A. D.; Tavares, M. L. A.; Queiroz, N.; Santos, I. M. G.; Souza, A. G.; Santos, N.A. Flow properties of biodiesel: Correlation between TMDSC and dynamic viscosity. **Journal of Thermal Analysis and Calorimetry**, v. 114, p. 1239–1243, 2013.

<https://doi.org/10.1007/s10973-013-3146-8>

Dwivedi, G.; Sharma, M. P. Experimental investigation on thermal stability of Pongamia Biodiesel by thermogravimetric analysis. **Egyptian Journal of Petroleum**, v. 25, p. 33–38, 2016b.

<https://doi.org/10.1016/j.ejpe.2015.06.008>

Dwivedi, G.; Sharma, M. P. Investigation of Oxidation stability of Pongamia Biodiesel and its blends with diesel. **Egyptian Journal of Petroleum**, v. 25, p. 15–20, 2016a.

<https://doi.org/10.1016/j.ejpe.2015.06.005>

Freire, L. M. D. S.; Santos, I. M. G.; Carvalho Filho, J. R.; Cordeiro, A. M. T. D. M.; Soledade, L. E. B.; Fernandes Jr, V. J.; Araujo, A. S.; Souza, A. G. Influence of the synthesis process on the properties of flow and oxidative stability of biodiesel from Jatropha curcas biodiesel. **Fuel**, v. 94, p. 313–316, 2012.

<https://doi.org/10.1016/j.fuel.2011.10.054>

Galvão, L. P. F. C.; Santos, A. G. D.; Gondim, A. D.; Barbosa, M. N.; Araujo, A. S.; Souza, L. D.; Fernandes Jr, V. J. Comparative study of oxidative stability of sunflower and cotton biodiesel through P-DSC. **Journal of Thermal Analysis and Calorimetry**, v. 106, p. 625–629, 2011.

<https://doi.org/10.1007/s10973-011-1411-2>

Güner, F. S.; Yagci, Y.; Erciyes, A. T. Polymers from triglyceride oils. **Progress in Polymer Science**, v. 31, p. 633–670, 2006.

<https://doi.org/10.1016/j.progpolymsci.2006.07.001>

Hasheminejad, M.; Tabatabaei, M.; Mansourpanah, Y.; Khatam far, M.; Javani, A. Upstream and downstream strategies to economize biodiesel production. **Bioresource Technology**, v. 102, p. 461–468, 2011.

<https://doi.org/10.1016/j.biortech.2010.09.094>

Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. **Chemical Reviews**, v. 106, p. 4044–4098, 2006.

<https://doi.org/10.1021/cr068360d>

Issariyakul, T.; Dalai, A. K. Biodiesel Biodiesel from Vegetable Oils Biodiesel. **Renewable and Sustainable Energy Reviews**, v. 31, p. 446–471, 2014. <https://doi.org/10.1016/j.rser.2013.11.001>

Kaufmann, H. P. and Sud, R. K. Die Papier-Chromatographie auf dem Fettgebiet. XLI: Über die Fettsäure-Zusammensetzung einiger Konjungenöle, Fette Seifen. **Anstrichm**, v. 3, p. 160–164, 1960.

<https://doi.org/10.1002/lipi.19600620302>

Knothe, G.; Gerpen, J. V.; Krah, J. **The Biodiesel Handbook**. In: Knothe, G., AOCS Press, editor. Oxidative stability of biodiesel, Champaign: 1st ed., p. 130–134, 2005b.

Knothe, G.; Gerpen, J. V.; Krah, J. **The Biodiesel Handbook**. In: Knothe G, AOCS Press, editor. Viscosity of biodiesel. Champaign: 1st ed., p. 89–90, 2005a. <https://doi.org/10.1201/9781439822357>

La Salles, K. T. S.; Meneghetti, S. M. P.; La Salles, W. F.; Meneghetti, M. R.; Santos, I. C. F. dos; Silva, J. P. V.; Carvalho, S. H. V. de. Soletti, J. I. Characterization of Syagrus coronata (Mart.) Becc. oil and properties of methyl esters for use as biodiesel. **Industrial Crops and Products**, v. 32, p. 518–521, 2010.

<https://doi.org/10.1016/j.indcrop.2010.06.026>

Macedo, F.L.; Candeia, R.A.; Sales, L. L. M.; Dantas, M. B.; Souza, A. G.; Conceição, M. M. Thermal characterization of oil and biodiesel from oiticica (Licania rigida Benth). **Journal of Thermal Analysis and Calorimetry**, v. 106, p. 531–534, 2011. <https://doi.org/10.1007/s10973-011-1580-z>

Melo, J. C. de; Juca, J. F. T.; Neves, A. M.; Barbosa, F. L. P.; Pacheco, J. G. A.; Stragevitch, L. Otimização da produção de biodiesel de óleo de algodão por transesterificação. **Revista Biodiesel**, p. 4–6, 2009. Accessed on: 14 November 2016. (in Portuguese)

Melo, M. A. M. F.; Melo, M. A. R. de; Pontes, A. S. G. C.; Farias, A. F. F.; Dantas, M. B.; Calixto, C. D.; Souza, A. G. de; Carvalho Filho, J. R. de. Non-conventional oils for biodiesel production: A study of thermal and oxidative stability. **Journal of Thermal Analysis and Calorimetry**, v. 117, p. 845–9, 2014. <https://doi.org/10.1007/s10973-014-3825-0>

Moretto, E.; Alves, R. F. **Óleos e gorduras vegetais: processamento e análises**. 1st ed., Florianópolis: Editor of the Federal University of Santa Catarina, 1986. (in Portuguese)

Pelegrini, B.L.; Sudati, E.A.; Ré, F.; Moreira, A. L.; Ferreira, I. C. P.; Sampaio, A. R.; Kimura, N. M.; Lima, M. M. de Souza. Thermal and rheological properties of soapberry *Sapindus saponaria* L. (Sapindaceae) oil biodiesel and its blends with petrodiesel. **Fuel**, v. 199, p. 627–640, 2017. <https://doi.org/10.1016/j.fuel.2017.02.059>

Piloto-Rodríguez, R.; Melo, E. A.; Goyos-Pérez, L.; Verhelst, S. Conversion of by-products from the vegetable oil industry into biodiesel and its use in internal combustion engines: A review. **Brazilian Journal of Chemical Engineering**, v. 31, p. 287–301, 2014. <https://doi.org/10.1590/0104-6632.20140312s00002763>

Pinto, A. C.; Guarieiro, L. L. N.; Rezende, M. J. C.; Ribeiro, N. M.; Torres, E. A.; Lopes, W. A.; Pereira, P. A. de P.; Andrade, J. B. de. Biodiesel: An overview. **Journal of the Brazilian Chemical Society**, v.16, p.1313–1330, 2005. <https://doi.org/10.1590/S0103-50532005000800003>

Pinto, G. **Características físico-químicas e outras informações sobre as principais oleaginosas do Brasil**. Recife: Instituto de Pesquisa e Experimentação Agropecuárias do Nordeste (IPEANE), Boletim Técnico, 18, 1963. p. 47–49.

Queiroga, V. P.; Barbosa, C. R. C.; Firmino, P. T.; Almeida, F. A. C. **Oiticica: Exploração agrônômica e aproveitamento energético**. 1^a ed. Campina Grande: Editora Ronaldo Gonçalves de Campina Grande, 2014, 212p. (in Portuguese).

Rosa, H. A.; Wazilewski, W. T.; Secco, D.; Chaves, L. I.; Veloso, G.; Souza, S. N. M. de; Silva, M. J. da; Santos, R. F. Biodiesel produced from crambe oil in Brazil - A study of performance and emissions in a diesel cycle engine generator. **Renewable and Sustainable Energy Reviews**, v. 38, p. 651–655, 2014.

Santos, A. G. D.; Araujo, A. S.; Caldeira, V. P. S.; Fernandes, V. J.; Souza, L. D.; Barros, A. K. Model-free kinetics applied to volatilization of Brazilian sunflower oil, and its respective biodiesel. **Thermochimica Acta**, v. 506, p. 57–61, 2010. <https://doi.org/10.1016/j.tca.2010.04.015>

Santos, A. G. D.; Souza, L. D.; Caldeira, V. P. S.; Farias, M. F.; Fernandes, V. J.; Araujo, A. S. Kinetic study and thermoxidative degradation of palm oil and biodiesel. **Thermochimica Acta**, v. 592, p. 18–22, 2014. <https://doi.org/10.1016/j.tca.2014.08.006>

Shirazi, M. M. A.; Kargari, A.; Tabatabaei, M.; Mostafaeid, B.; Akia, M.; Barkhi, M.; Shirazi, M. J. A. Acceleration of biodiesel-glycerol decantation through NaCl-assisted gravitational settling: A strategy to economize biodiesel production. **Bioresource Technology**, v. 134, p. 401–406, 2013. <https://doi.org/10.1016/j.biortech.2013.02.026>

Silva, G. A. M.; Rós, P. C. M. Da; Souza, L. T. A.; Costa, A. P. O.; De Castro, H. F. Physico-chemical, spectroscopical and thermal characterization of biodiesel obtained by enzymatic route as a tool to select the most efficient immobilized lipase. **Brazilian Journal of Chemical Engineering**, v. 29, p. 39–47, 2012. <https://doi.org/10.1590/S0104-66322012000100005>

Silva, J. C. T. da; Gondim, A. D.; Galvão, L. P. F. C.; Evangelista, J. P. da C.; Araujo, A. S.; Fernandes, V. J. Thermal stability evaluation of biodiesel derived from sunflower oil obtained through heterogeneous catalysis (KNO₃/Al₂O₃) by thermogravimetry. **Journal of Thermal Analysis and Calorimetry**, v. 119, p. 715–720, 2015. <https://doi.org/10.1007/s10973-014-4145-0>

Silva, T. A.; Assunção, R. M. N. de; Vieira, A. T.; Oliveira, M. F. de; Batista, A. C. F. Methylic and ethylic biodiesels from pequi oil (*Caryocar brasiliense* Camb.): Production and thermogravimetric studies. **Fuel**, v. 136, p.10–18, 2014. <https://doi.org/10.1016/j.fuel.2014.07.035>

Silva, V. P. **Gestão Ambiental: reflexões e estratégias de aplicação**. Natal: IFRN. 2011. Available at: <http://portal.ifrn.edu.br/pesquisa/editora/livros-para-download/gestao-ambiental>. Accessed on: 05 November 2013.

Silva, W. C.; Castro, M. P. P.; Perez, V. H.; Machado, F. A.; Mota, L.; Sthel, M. S. Thermal degradation of ethanolic biodiesel: Physicochemical and thermal properties evaluation. **Energy**, v. 114, p. 1093–1099, 2016. <https://doi.org/10.1016/j.energy.2016.08.052>

Souza, A. G. de; Santos, J. C. O.; Conceição, M. M.; Silva, M. C. D.; Prasad, S. A thermoanalytic and kinetic study of sunflower oil. **Brazilian Journal of Chemical Engineering**, v. 21, p. 265–273, 2004. <https://doi.org/10.1590/S0104-66322004000200017>

Tiosso, P. C.; Carvalho, A. K. F.; Castro, H. F. de; Moraes, F. F. de; Zanin, G. M. Utilization of immobilized lipases as catalysts in the transesterification of non-edible vegetable oils with ethanol. **Brazilian Journal of Chemical Engineering**, v. 31, p. 839–847, 2014. <https://doi.org/10.1590/0104-6632.20140314s00003006>

Vega-Lizama, T.; Díaz-Ballote, L.; Hernández-Mézquita, E.; May-Crespo, F.; Castro-Borges, P.; Castillo-Atoche, A.; González-García, L. M. Thermogravimetric analysis as a rapid and simple method to determine the degradation degree of soy biodiesel. **Fuel**, v. 156, p.158–162, 2015. <https://doi.org/10.1016/j.fuel.2015.04.047>

Yaakob, Z.; Narayanan, B. N.; Padikkaparambil, S.; Unni, K. S.; Akbar, P. M. A review on the oxidation stability of biodiesel. **Renewable and Sustainable Energy Reviews**, v. 35, p. 136–153, 2014. <https://doi.org/10.1016/j.rser.2014.03.055>

Yuan, X.; Leng, L.; Xiao, Z.; Lai, C.; Jiang, L.; Wang, H.; Hui, L.; Chen, X.; Zeng, G. Pyrolysis and combustion kinetics of glycerol-in-diesel hybrid fuel using thermogravimetric analysis. **Fuel**, v. 182, p. 502–508, 2016. <https://doi.org/10.1016/j.fuel.2016.06.008>

Zhou, J.; Xiong, Y.; Gong, Y.; Liu, X. Analysis of the oxidative degradation of biodiesel blends using FTIR, UV-Vis, TGA and TD-DES methods. **Fuel**, v. 202, p. 23–28, 2017b. <https://doi.org/10.1016/j.fuel.2017.04.032>

Zhou, J.; Xiong, Y.; Liu, X. Evaluation of the oxidation stability of biodiesel stabilized with antioxidants using the Rancimat and PDSC methods. **Fuel**, v. 188, p. 61–68, 2017a. <https://doi.org/10.1016/j.fuel.2016.10.026>