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Thermal characterization of oil and biodiesel from oiticica (*Licania rigida* Benth)

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Abstract Searching for other alternative sources, which are not part of the food chain, and which are able to supply the biofuel market is a promising option. In this context, it has been searched to investigate the oiticica oil, approaching its availability to the biodiesel synthesis, as well as its thermal stability. Few works retreat parameters such as: the optimization of the biodiesel synthesis, its physical–chemical properties, and thermal parameters etc. The characterization results revealed that the oil showed very high kinematic viscosity, and acidity value around 13 mg KOH/g, requiring a pre-treatment. To reduce the acid in the oil, it has been done the esterification of oil, which was studied in different molar ratios oiticica oil/ethanol (1:9) and 2.0% catalyst, in order to get the best reduction the index of acidity. The lowest level of acidity of the oil obtained after the esterification was 4.4 mg KOH/g. The reaction rate for the synthesis of biodiesel, compared to the initial mass of oiticica oil ester was 85%. This income can be overcome by pursuing an even smaller reduction of acid value of biodiesel oiticica. The acid value of biodiesel was 1.8 mg KOH/g. The results have revealed that the oiticica oil and biodiesel are stable at 224 and 179 °C, respectively.

Keywords Oiticica oil · Synthesis · Thermal stability

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Introduction

Brazil is the country with the greatest biodiversity, which explains its richness in oleaginous plants. Currently, there are various types of oleaginous plants which have an oil content higher than that of soybean [1, 2], such as *Jatropha curcas* L. [3], castor oil, oiticica, and others. However, such oleaginous plants still need evaluations (search). Therefore, given these facts, the oiticica oil was chosen to be investigated in this work, as raw material for biodiesel production. Considering three motivating factors for this choice: (a) oil content in seed oiticica around 60%; (b) not being part of the food chain; and (c) being an oilseed crop typical in the caatinga region.

The oiticica (*Licania rigida* Benth), of the family Chrysobalanaceae, is a sort of riparian temporary water courses of the Semi-Arid Northeast, and has great importance, either by the environmental aspect, or to oil-producing species. The seed of a ripe fruit contains a kernel rich in a drying oil (seed oil content: about 54–60%), currently employed in the industry of automotive paints and inks for inkjet printers, as well as varnishes and other purposes [4].

According to EMBRAPA [5], oiticica oil has a high drying effect. As for chemical composition, it is noted among the fatty acids the licanic (C18:3, 70–80%) and linolenic (C18:2, 10–12%) with small amounts of oleic acid (C18:1), palmitic (C16), and stearic (C18). This species may be important for the sustainability of biodiesel in

the semiarid, and the fact of the harvest season to be held between the months from December to February, a period of complete lack of income for family farms [5].

This study has aimed to investigate oilseed oiticica checking its availability for the synthesis of ethyl biodiesel, as well as evaluating the thermal stability of the oilseed before and after synthesis.

Methods and materials

The crude oiticica oil was obtained commercially from the Industry Resibras S/A. It was necessary to opt for a pretreatment to reduce the free fatty acids, in this case, the esterification of oil for transesterification and then produce biodiesel.

The esterification proceeded to add the link oiticica oil/ethanol. After 5min, the catalyst was added concentrated H_2SO_4 to the reaction mixture, under constant stirring at 60 °C for 90 min. Then, the reaction mixture was transferred to the decantation funnel in order to separate the aqueous phase of the esters. The sedimentation lasted 2 h.

Biodiesel was obtained in the reaction conditions: molar ratio of 6:1 ethanol/oiticica oil ester, the presence of 0.5% catalyst (KOH) under constant agitation, and temperature of 32 °C in a closed system for 60 min. [6, 7].

Characterizations of oil and biodiesel

The physicochemical properties of oiticica oil were analyzed according to the technical standards established by competent bodies. The vegetable oil was followed by the specification of the AOCS [8], while the biodiesel was followed by the specification for biodiesel (B100) ASTM 6751 or EN 14214 [9]. The Chromatography (CG-MS)—The fatty acid content was determined by gas chromatography using the AOCS official method Ce 1–62 and Ce 2–26.

TG curves were obtained in a thermal analyzer, TA Instruments brand, model SDT 2960, through the dynamic method of analysis, with ratios of heating at 10 °C min^{-1}, in atmospheres of synthetic air and nitrogen with a flow of 110 mL min^{-1}, range 28–600 °C using an alumina crucible and sample weight 10 mg [10]

Results

Physical and chemical parameters of oiticica oil

According to the characterization results shown in Table 1, note that the oil showed very high kinematic viscosity, and acidity value around 13 mg KOH/g, requiring a pre-treatment [2]. To reduce the acid in the oil (free fatty acid content), it has been done the esterification of oil, which was studied in different molar ratios oiticica oil/ethanol (Table 2) in order to get the best reduction the index of acidity. According to Table 2, the lowest level of acidity of the oil obtained after the esterification was 4.4 mg KOH/g. Importantly, this will require a little acidity on the yield of production of biodiesel. However, there was a considerable reduction from the value of the acidity prior to esterification. All these measurements were performed in triplicate.

Table 1 Physicochemical properties of Oiticica oil

Characterizations	Method	Unit	Value
Acidity of index	Cd 3a-63 da AOCS	mg KOH/g	13
Saponification of index	TI 1a-64 da AOCS	mg KOH/g	188.3
Density at 20 °C	ASTM D 4052	kg/m^3	962.6
Kinematic viscosity at 40 °C	ASTM D 445	mm^2/s	133.9

Table 2 Acidity before and after esterification oil

Test	Molar ratio (oiticica oil/ethanol)	% Catalyst H_2SO_4	Acidity of index (mg KOH/g)	
			Before	After
1	1:12	4.0	13	12.0
2	1:12	2.0	13	7.2
3	1:12	0.5	13	7.0
4	1:9	2.5	13	10.5
5	1:9	2.0	13	4.4
6	1:9	1.5	13	11.9
7	1:9	0.5	13	8.1

In TG/DTG, Fig. 1a under synthetic air atmosphere it can be observed three stages of mass loss within the range 224–560 °C. In nitrogen atmosphere (Fig. 1b) only two events occurred, which started between intervals of 249–343 °C with 8.2% mass loss and 343–489 °C with 91.8% mass loss. The final reaction in oxidizing atmosphere occurred in higher temperature, which can be attributed to polymerization of oiticica oil.

The oiticica oil is constituted by 75% of licanic acid ($C_{18}H_{28}O_3$, correspondent to 4-Oxo-9,11,13-octadecatrienoic acid [11]), formed by system of double conjugated connections of reactive character, and presence of ketona groupings, the same is susceptible to reactions of oxidations, and in turn, polymerization, confirming the result obtained in the thermogravimetry under oxidant atmosphere. It is believed that the polymerization is due to the increase of temperature, providing energy to rupture of connections C–H and/or C=O and, with this, the favoring of new molecular rearranges.

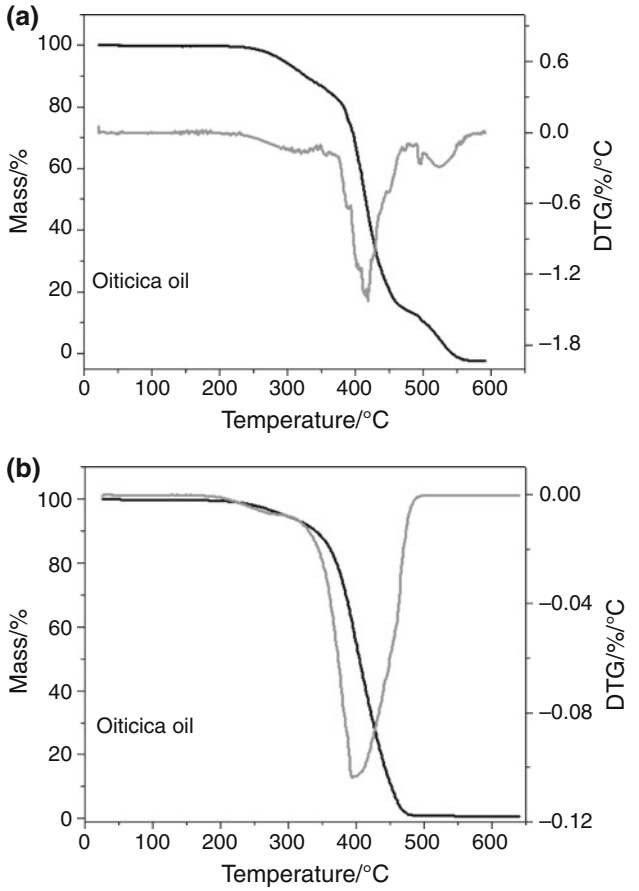

Fig. 1 Curves TG/DTG oil Oiticica in synthetic air atmosphere (**a**) and Nitrogen (**b**) with a heating rate of 10 °C min^{-1}

Oiticica oil biodiesel physical chemical parameters

The reaction rate for the synthesis of biodiesel, compared to the initial mass of oiticica oil ester was 85%. This income can be overcome by pursuing an even smaller reduction of acid value of biodiesel oiticica. The acid value of biodiesel was 1.8 mg KOH/g.

The compositions of ethylic oil and biodiesel from oiticica are presented in Table 3. The chromatogram of biodiesel indicates greater predominance for oleate, linoleate, and stearate of ethyl. Concluding, levels in esters of saturated and unsaturated fatty acids of 69.76 and 28.15%, respectively. An interesting fact was the greater retention of unsaturated fatty acids in the chromatographic column, indicating that the increase of the number of double connections from 1 to 3 of the oleic acid to the linolenic one generates an increase of electronegativity in the compound and according to the theory of hybridization, by adding to a better distribution of the pairs over the carbonic chain, it improves the interaction of the compounds with the chromatographic column, producing a better income in the process of separation by the equipment. It explains the greater values of time of retention by the chromatographic column, which possesses composition with 2% of phenol, for more unsaturated compounds.

The viscosity of biodiesel derived from the oiticica was 38.32 mm^2 s^{-1}. As seen in Table 1, the viscosity of biodiesel is significantly lower than the viscosity of vegetable oil. However, even then the biodiesel produced showed high levels of kinematic viscosity and is recommended mixing it with biodiesel from other oil and/or blend with petroleum diesel.

The thermal profile shown in the TG/DTG ethyl biodiesel in synthetic air atmosphere (Fig. 2a), presents three stages of mass loss: 12, 72, and 16% in the temperature range 179–285, 285–454, and 454–560 °C. While in nitrogen atmosphere (Fig. 2b) ethyl biodiesel consists of two stages of mass loss: 13.5 and 86.5% whose temperature ranges were 180–298 and 298–488 °C, respectively. Therefore, it is believed that the first and second steps in a synthetic air atmosphere and the 1st step in nitrogen atmosphere are associated with volatilization of ethyl esters (mainly of its major components among its fatty acids according to EMBRAPA, Licania (70–80%), and linolenic (10–12%) with small amounts of oleic acid, palmitic, and stearic acid ethyl ester) [5]. The third stage of mass loss shown in Fig. 2a suggests that before the heating, the polymerization of the biodiesel occurred, followed by its combustion process. According to the curve TG illustrated in Fig. 1a, the oiticica oil above 450 °C shows this same

Table 3 Chemical composition of oiticica oil and biodiesel

Oiticica Oil			Biodiesel		
Fatty acids	Retention time/min	Level in fatty acids/%	Esters of fatty acids	Retention time/min	Level in ester/%
Palmetic	11.605	12.346	Palmitate	7.139	11.94
Stearic	13.516	11.610	Stearate	8.984	16.21
Oleic	13.740	34.603	Oleate	9.253	30.37
Linoleic	14.202	30.376	Linoleate	9.772	14.62
Linolenic	17.415	9.406	Linolenate	14.174	24.77
Others		32.035	Others		2.09

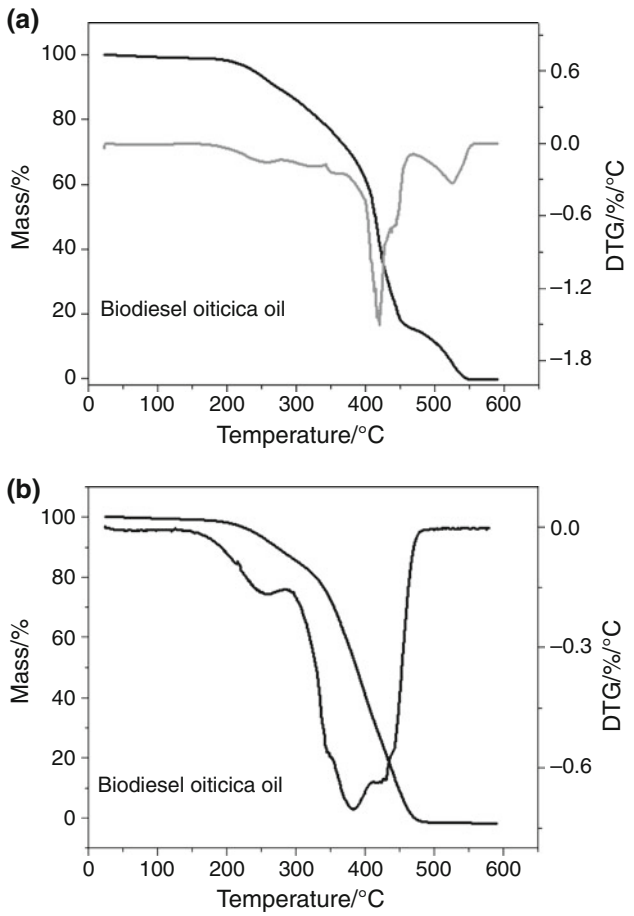

Fig. 2 Curves TG/DTG Ethyl Biodiesel Oiticica Oil in synthetic air atmosphere (**a**) and Nitrogen (**b**) with a heating rate of 10 °C min^{-1}

behavior, being completed at a temperature of 560 °C (to air oxidation) and 489 °C (for inert atmosphere).

The oil and ethyl oiticica biodiesel proved to be quite stable in oxidizing atmosphere until the temperature of 224 and 179 °C, respectively. Comparing these thermal values of oiticica already studied with the values of the oilseed soybean, it is possible that the oiticica has greater stability. For, according to the literature [2, 12, 13], oil and ethyl soybean biodiesel have thermal stability at around 184 and 97 °C, respectively.

Conclusions

Considering the results presented in this study, oiticica oil despite being a drying oil, carrier of viscosity high acidity index, it is a promising oilseed to be applied as the basis for biodiesel. It has very significant thermal stability for use as biofuel, around 224 °C (for oil) and 179 °C (for biodiesel). Such temperatures are significant in the storage process.

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