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ORIGINAL ARTICLE

Dual-stage methodology for production, characterization, and storage stability of *Jatropha curcas* biodiesel

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Abstract The increasing demand for energy and environmental consciousness has encouraged a considerable amount of research effort to synthesize alternative fuels from renewable resources. Biodiesel as an alternative fuel for diesel engines has gained international attention. This study aimed to produce biodiesel using a dual-stage methodology from *Jatropha curcas* oil, a nonedible raw material, esterification followed by alkaline transesterification method. The physical and chemical determinations were carried out at such as acidity as high as 9.0 mg KOH g^{-1}. Therefore, esterification was first conducted with decreasing acidity to a suitable value of 1.75 mg KOH g^{-1} which is liable to subsequent transesterification stage. The chromatographic data shows that the oil fatty acids present in greatest quantity are 47.85 % oleic (C18:1) and 33.28 % linoleic (C18:2), with suitable lipids for biodiesel production. From the results obtained through the characterization of *J. curcas* biodiesel, it was noted that this had to be a promising oilseed for biodiesel production, with a yield of 97.5 % in the esterification reaction and 84.4 % in transesterification reaction, and obtained an ester content of 98.5 % (*w*/*w*). The oxidative stability was raised to 6.17 h with the addition of 2000 ppm of antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT). During the storage period, the sample of *J. curcas* biodiesel showed a decrease in oxidative stability and an increase in water content with time.

Keywords *Jatropha curcas* biodiesel · Production methodology · Storage stability · Shelf life · Antioxidant additives

1 Introduction

The concern about the growing population and increasing demand of fossil fuels encourages the search for renewable sources, in order to provide a steady increase in energy usage in a sustainable way. Fossil fuel combustion generates CO_2 into the atmosphere, which is believed to impact global climate [1, 2].

In this sense, biodiesel has been extensively studied and is an excellent choice, being defined as an alternative fuel, consisting of alkyl esters of long-chain carboxylic acids from renewable sources–such as vegetable oils, animal fats and/or residual–whose use is associated with the replacement of fossil fuels in ignition engines by compression [3, 4]. Brazil is the second largest consumer of biodiesel in the world and disputes with Argentina as the third in production (with 2.7 billion liters), while Argentina produces 2.2 billion liters. The first two positions are the USA and Germany, with about 5.1 billion and 3.6 billion liters, respectively [5].

However, the sources for biodiesel production are carriers of undesirable chemical characteristics, which are incorporated into the biodiesel during the production process. Examples include oilseeds such as soybeans, which have a significant amount of fatty acids with a high degree of unsaturation that

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facilitates the oxidation of biofuel, making its storage difficult for long periods [6]. Therefore, the profile of fatty acids in vegetable oil, used as a raw material, is an important factor in determining its stability [7]. The ester content parameters, kinematic viscosity, acidity, content of triglycerides, diglycerides, monoglycerides, free glycerol, and their total depend on the conversion process and the quality of the purification step. Other parameters such as oxidation stability, iodine value, and cold filter plugging point depend on the nature of the oil [8]. Thus, the oil properties are decisive for the quality of biodiesel, which is susceptible to oxidation when exposed to air, which results in increased acidity and viscosity, gum formation, and sediment irreversible polymerization [9]. It is noteworthy that biodiesel oxidation interferes not only in its own physical and physical-chemical characteristics but may also affect the integrity and stability of the materials in contact with this biofuel, such as metallic and polymeric materials present in car pieces and storage structures [10].

Hence, the supply of suitable raw materials for the biodiesel industry is currently a challenge and a major concern in many countries. The preferred option is the obtainment of exclusive oil for biodiesel production, especially those with potential use in family agriculture, i.e., requiring hand-intensive work and have sufficient productivity to pay them properly, contributing to regional economic development and social inclusion [11].

Most of the biodiesel produced in the world, including Brazil, uses soybean as raw material, but all vegetable oils classified as fixed or triglycerides can serve this purpose [12]. Brazil presents tropical and subtropical regions and is extremely heterogeneous in vegetable matrices for the extraction of vegetable oils such as castor bean, palm pulp, and babassu and other vegetables in the form of seeds, almonds, or pulps [13, 14]. In addition to a favorable climate, the country has about 90 million ha of land available for plantation of oilseed crops for biodiesel production [15].

Jatropha (*Jatropha curcas*) is considered a potential raw material for biodiesel production in Brazil, since this species has desirable properties such as high oil grain and good oil quality for biodiesel production. This species demands a great amount of sunlight and small amount of water to grow. Thus, *J. curcas* is found in almost all tropical areas, occurring predominantly in tropical and temperate regions and only on a small proportion in cold regions. This species shows a quite varied geographical and climatic distribution once it adapts to dry conditions and can survive during long periods of drought; it adapts to arid environments and rocky terrain [16, 17]. The *J. curcas* crop represents a valuable chance for small farmer's cooperatives, increasing job opportunities and net profits related to its potential for biodiesel production. Furthermore, after the oil extraction, the obtained residue can be used to recuperate damaged soils. The jatropha is not intended for food use, but *J. curcas*' cultivation has the advantage of low production cost and the capability to grow in poor soil matrices that would be inappropriate for subsistence agriculture. *J. curcas* also presents high-yield index, and it is grown and harvested simply; likewise, its seeds present long-term storage potential without oil quality prejudice [16–18].

Thus, the aims of this study were (a) to produce biodiesel by conventional esterification route, followed by transesterification using jatropha oil; (b) to characterize physical-chemical properties; and (c) to evaluate the effectiveness of a synthetic antioxidant (2,6-di-*tert*-butyl-4-methylphenol (BHT)) on the extension of shelf life and maintaining the quality of biodiesel for 90 days, by means of physical appearance, density at 20 °C, kinematic viscosity at 40 °C, water content (Karl Fischer coulometry), acid value, and oxidation stability.

2 Materials and methods

2.1 Raw material

2.1.1 Crude jatropha oil

The crude jatropha oil used as raw material was supplied by the Brasil Ecoenergia de Piracuruca enterprise (Piauí). According to the supplier, the oil extraction process began with seeds cooked for half an hour, followed by pressing step. In this step, the oil is separated of residual presscake, which is used as fertilizer in the plant itself. The extracted oil is filtered and transferred to a receptor tank.

2.2 Methods

2.2.1 Physical-chemical characterization of jatropha oil

The physical-chemical characteristics of a vegetable oil, which will be used as raw material for biodiesel production, are very important when choosing the technology to be used in the processing of the oil [19].

Crude jatropha oil has been featured in the Corrosion and Protection Laboratory–LACOR, in the National Institute of Technology, through physical and chemical analyses: water content (the Karl Fischer coulometric method was used, following the ASTM D 6304 [20]. The equipment used was the Karl Fischer titrator Metrohm model 756 KF with support of the analytical balance Mettler XP-205); saponification index (AOCS Cd 3-25) [21]; density at 20 °C (using the digital densitometer Anton-Paar, DMA 5000 model, in accordance with ASTM D 4052) [22]; iodine value (AOCS Cd 1-25) [23]; kinematic viscosity at 40 °C (ASTM D 445) [24]; acid value (EN 14104) [25]; peroxide value (AOCS Cd 8-53) [26]; oxidation stability at 110 °C (Rancimat method according to EN 14112) [27]. At the same time, the determination of fatty acid

composition was made (%) by gas chromatography in Green Technologies Laboratory–GREENTEC (EQ/UFRJ). This determination used a gas chromatograph, Shimadzu, GC-2014 model, coupled to a flame ionization detector (FID), injector split/splitless type (injection with or without flow division), and a capillary column 20 M (polyethylene glycol polymer), 30 m length, 0.32 mm inner diameter and film thickness of 0.25 μm. The operating parameters included injected volume, 1 μl; carrier gas, hydrogen; column flow, 1 ml min^{-1}; oven temperature, 200 °C; injector and FID temperature, 250 °C. The injections were performed in duplicate.

Based on the results of the gas chromatography of jatropha oil, the average molar mass of oil was calculated using the following equation:

$$MM_{\text{jatropha oil}} = \frac{\sum \left(\%_{\text{fatty acid}} \times MM_{\text{fatty acid}}\right)}{\sum \%_{\text{fatty acid}}} \times 3 + 38.04 \quad (1)$$

where $MM_{\text{jatropha oil}}$ represents the average molar mass of vegetable oil (g mol^{-1}); $MM_{\text{fatty acid}}$ is the molar mass of each fatty acid present; $\%_{\text{fatty acid}}$ is the molar percentage of the fatty acid; and 38.04 is the difference between the glycerin molecular mass and the molecular mass of three water molecules that replace glycerol [28].

2.2.2 Esterification reaction of jatropha oil

For the esterification reaction of jatropha oil, methyl alcohol PA was used (V VETEC Fine Chemicals Ltd.) and sulfuric acid PA as a catalyst (V VETEC Fine Chemicals Ltd.). The reaction time was established for 90 min, H_2SO_4 concentration of 1.45 %, the reaction system temperature of 70 °C, and a molar ratio of oil/methanol (1:3.4) [29]. After completion of the reaction, the mixture was transferred to a decantation funnel to carry out the washes. The oil was subjected to washing using distilled water heated to 60 °C. Then, moisture and alcohol traces were removed by drying at 100 °C.

2.2.3 Alkaline transesterification reaction

For the transesterification reaction of jatropha oil into biodiesel, we used methyl alcohol PA (V VETEC Fine Chemicals Ltd.) and sodium hydroxide PA as a catalyst (ISOFAR–Industry and Trade of Chemicals), which was first dissolved in alcohol, and after complete dissolution, added to the oil. The reaction time of 60 min was established, KOH concentration of 2 %, the reaction system temperature of 42 °C, and a molar ratio of oil/methanol (1:6) [30]. After the reaction was completed, the mixture was transferred to a decantation funnel in order to separate the phases. The biodiesel was then subjected to washing using distilled water heated to 60 °C. Then, traces of moisture and alcohol were removed by drying at 100 °C.

2.3 Calculation of esterification and transesterification reactions yield

The mass yield of esterification reaction was defined as the value that expresses jatropha oil mass obtained after esterification, washing, and drying in relation to the mass of crude jatropha oil. Equation 2 was used to calculate the esterification reaction yield [31]:

$$R_1 = \left(\frac{M_{\text{oe}}}{M_{\text{o}}}\right) \times 100 \quad (2)$$

where R_1 is the yield of the esterification reaction; M_{oe} is the mass of jatropha oil obtained after the esterification, washing, and drying; and M_{o} is the mass of crude jatropha oil.

The mass yield of the transesterification reaction was defined as the value expressing the weight of biodiesel obtained after washing and drying, in relation to the mass oil obtained after the esterification. Equation 3 was adopted for calculating the yield of the transesterification reaction [31]:

$$R_2 = \left(\frac{M_{\text{bio}}}{M_{\text{oe}}}\right) \times 100 \quad (3)$$

where R_2 is the yield of the transesterification reaction; M_{bio} is the biodiesel mass obtained after washing and drying; and M_{oe} is the mass of oil obtained after the esterification. Esterification and transesterification reaction experiments were conducted in triplicate.

2.4 Characterization of methylic biodiesel of jatropha oil

The biodiesel produced was characterized by the following standards established by the Brazilian National Agency for Petroleum, Natural Gas and Biofuels (ANP) resolution 45/2014 [32].

2.4.1 Ester content

The content of methyl esters of fatty acids was determined according to the ABNT NBR 15764 [33], using gas chromatograph, Agilent Technologies, model 7890A, coupled with a FID, injector-type cool on-column and a capillary column DB-5HT (composition 5 % phenyl-polydimethylsiloxane), 25 m in length, 0.32 mm inner diameter, and film thickness of 0.10 μm. The operating parameters included the following: injected volume 0.5 μl; column flow 3 ml min^{-1}; carrier gas, helium with average linear velocity of about 0.54 m s^{-1} and hydrogen with average linear velocity of about 0.70 m s^{-1}; oven temperature program 50 °C for 1 min; from 50 to 180 °C (gradient of 15 °C per min); from 180 to 230 °C (gradient of 7 °C per min); from 230 to 380 °C (30 °C gradient min) isotherm for 10 min; temperature detector 380 °C, auxiliary

gas was N_2 at 30 ml min^{-1}, H_2 at 35 ml min^{-1}, and synthetic air at 350 ml min^{-1}.

2.4.2 Free and total glycerin content, mono-, di-, and triglycerides

The free, connected (mono-, di-, and triglycerides), and total glycerin analyses (sum of bound and free glycerin) by gas chromatography were performed according to the ABNT NBR 15908 [34], using a gas chromatograph, Agilent Technologies, model 7890A coupled to a FID, the injector-type cool on-column (the entire sample was introduced directly into the column), and HT-DB5 capillary column (composition 5 % phenyl-polydimethylsiloxane) 25 m in length, 0.32 mm inner diameter, and film thickness of 0.10 μm. The operating parameters included injected volume, 1 μl; carrier gas, hydrogen or helium; column flow, 3 ml min^{-1}; oven temperature program, 50 °C for 1 min; from 50 to 180 °C (gradient of 15 °C per min); from 180 to 230 °C (gradient of 7 °C per min); from 230 to 380 °C (30 °C per min gradient) and isotherm for 10 min; temperature detector, 380 °C; type, ionization flame of H_2.

2.4.3 Physical-chemical analysis

The samples were submitted to the following physical-chemical analysis: appearance (ABNT NBR 16048) [35]; water content (Karl Fischer method according to ASTM D 6304) [20]; iodine value (standard EN 14111, with the titration performed in Titrando equipment model 905 following configuration of tiamo 2.2 software) [36]; oxidation stability (Rancimat method according to EN 14112) [27]; kinematic viscosity at 40 °C (ASTM D-445) [24]; specific mass at 20 °C (ASTM 4052) [22]; acid value (ASTM D664-11a B method, with the titration performed in Titrando equipment model 905 following configuration of tiamo 2.2 software) [37]; carbon residue (ASTM D 4530) [38]; ash content (ABNT NBR 6294) [39]; flash point (ABNT NBR 14598) [40]; cold filter plugging point (ABNT NBR 14747) [41]; potassium, phosphorus, calcium+magnesium (ABNT NBR 15553) [42]; total sulfur (ASTM D 5453) [43].

2.5 Storage procedure of jatropha biodiesel

The jatropha biodiesel volumes were stored for a period of 90 days (3 months), during which the monthly monitoring was performed of the storage stability loss process. The containers were made of steel 1L AISI 1020, equipped with a polymer screw cap and venting. Figure 1 illustrates the appearance of the containers, which were kept near the window of the external runner in the laboratory; the temperature and humidity were monitored locally, which fluctuated in the range from 21.6 to 33.4 °C and between 41 and 75 g cm^{-3} of relative humidity over the 90-day trial.

Fig. 1 Storage containers for jatropha biodiesel shelf life analysis during 90 days trial

3 Results and discussion

3.1 Physical-chemical characterization and molar mass calculation of jatropha oil

Table 1 shows the physical-chemical parameters of jatropha oil used as raw material.

Since jatropha oil showed acidity of 9 mg KOH g^{-1}, it was necessary to submit this oil to previous esterification reaction before the esterification stage [29]. In this process, the free fatty acids are esterified to ensure that the raw material, to be processed by alkaline transesterification technology, has low content of free fatty acids.

The peroxide index value was 8.0 mEq kg^{-1}; this parameter indicates the stage of deterioration in terms of oxidative rancidity. The process of oxidative rancidity in lipids is accelerated by several factors, such as the presence of high oil composition to the proportion of unsaturated fatty acids [44]. According Brazilian legislation, a maximum peroxide value of

Table 1 Physical-chemical parameters of jatropha oil

Parameter	Results
Acid value	9.0 mg KOH g^{-1}
Saponification value	212.7 mg KOH g^{-1}
Iodine value	99.0 g I_2 100 g^{-1}
Peroxide value	8.0 mEq kg^{-1} *óleo*
Viscosity at 40 °C	35.4 mm^2 s^{-1}
Oxidation stability	1.6 h
Density	915.5 g cm^{-3}
Water content	922.0 ppm

10 mEq kg^{-1} of oil is accepted for vegetable oils, since higher values mean early oxidative rancidity [45]. In studies based on jatropha, Tapanes [11] and Souza [46] found peroxide index values of 10.0 and 4.83, respectively, for biodiesel produced from jatropha oil.

The iodine value of 99.0 g I_2 100 g^{-1} indicates a high degree of unsaturation of oil. This test represents the amount of iodine required for reaction with the unsaturation of constituent fatty acids in the oil. Tapanes [11] and Souza [46] also found the iodine values of 95.0 and 96.0, respectively, for biodiesel produced from jatropha oil.

It is worth noting that for the evaluation of oxidative stability, the peroxide value should be analyzed along with the iodine value, since the presence of unsaturation favors the oil degradation process; therefore, the greater the value of this index, the less the oxidative stability of the oil [47].

The saponification value of 212.7 mg KOH g^{-1} identifies the presence of oil and fats containing a lift content of low molecular fatty acids. Thus, the lower the molar mass of the fatty acid, the higher the saponification value. Tapanes [11] and Souza [46] found saponification values of 166.0 and 189, respectively, for jatropha oil. Concerning rheological behavior, the kinematic viscosity of vegetable oils generally varies in the range of 30–40 mm^2 s^{-1} at 40 °C; the value of jatropha oil viscosity is within the expected range.

The alkaline transesterification is undoubtedly the dominant route for the ethyl or methyl biofuel production in national and international commercial production. However, alkaline transesterification requires high-quality raw materials, particularly low acid contents (<0.5 mg KOH g^{-1}), and water in the reaction medium (<1 %). As a result, there is a high cost associated with raw materials, reaching up to 80 % of the total production costs and making the biodiesel cost now up to twice than diesel, which turns its economic viability questionable. In oils that have high acidity, there is the need to develop alternative and specific technologies that enable the use of this raw material for biodiesel production. The esterification process is used in this case. In this process, the free fatty acids are esterified or transformed into biodiesel, using sulfuric acid as a catalyst until the reaction mixture has a low content of free fatty acids. The free fatty acids in the transesterification reaction with the presence of a basic catalyst generate soaps. Thus, the esterification reaction is necessary to avoid saponification.

It can be observed in Table 2 that the acid value of jatropha oil was suitably reduced, allowing the achievement of transesterification reaction while avoiding the formation of soap.

Table 3 shows the profile and fatty acids chromatogram encountered in the jatropha esterified oil, respectively.

The difference in the properties of the various vegetable oils is primarily a consequence of the fatty acid composition thereof, and this chemical profile is incorporated and impacts the final product obtained, in this case, biodiesel.

Table 2 Esterification reaction yield and physical-chemical parameters of jatropha oil after esterification reaction and drying

Assay	Results
Esterification reaction	97.50 %±1.36
Acid value	1.75 mg KOH g^{-1}
Water content	406.70 ppm

In this sense, the oxidation stability is a parameter of great importance for the quality control of biodiesel. The oxidative degradation process of biodiesel depends on the nature of the fatty acids used in its production, in particular, the degree and position of unsaturation of the carbon chain alkyl esters of which it is composed, in addition to humidity, temperature, and light absorption [48]. Therefore, the fatty acids profile in vegetable oil, used as raw material, is a key factor in determining the stability of the biodiesel produced. Generally, the more unsaturated fatty acids, such as linoleic and linolenic acids, respectively, with two and three unsaturations that are more susceptible to oxidation [7, 49].

The acid profile of jatropha oil was obtained by gas chromatographic analysis, with flame ionization detector, and 82.48 % of unsaturated fatty acids were found, predominantly oleic acid (47.85 %) followed by linoleic acid (33.28 %) and 17.5 % saturated fatty acids, with palmitic acid in the highest percentage (13.59 %).

According to Cunha [50], soybean oil by gas chromatography showed 17.92 % of saturated fatty acids, 82.08 % of unsaturated fatty acids, mainly linoleic acid (46.48 %), followed by oleic acid (34.77 %). The beef tallow oil by gas chromatography showed 65.62 % of saturated fatty acids, 34.48 % of unsaturated fatty acids, mainly of stearic acid (33.69 %),

Table 3 Fatty acid profile of jatropha esterified oil

Compound	Formula	Fatty acids %	Fatty acids molar mass	∑ (fatty acids % × fatty acids molar mass)
Myristic	C14:0	0.0518	228.37	11.82
Palmitic	C16:0	13.5941	256.42	3485.79
Palmitoleic	C16:1	1.2248	254.00	311.09
Estearic	C18:0	3.6643	284.47	1042.38
Oleic	C18:1	47.8493	282.46	13515.51
Linoleic	C18:2	33.2830	280.00	9319.24
Linolenic	C18:3	0.1441	278.43	40.12
Arachidic	C20:0	0.1295	304.46	39.42
Gadolinic	C20:1	0.0254	310.00	7.87
Behenic	C22:0	0.0040	340.58	1.36
Erucic	C22:2	0.0083	338.57	2.81
Lignoceric	C24:0	0.0195	368.63	7.18
Nervonic	C24:1	0.0018	366.62	0.66
Total		99.99		27785.31

followed by oleic acid (30.09 %) and palmitic acid (26.18 %). Thus, it is possible to say that the jatropha oil has a lipid profile close to that of soybean oil.

The average molar mass (g mol^{-1}) of jatropha oil was calculated according to Eq. 1, the value obtained was 871.68 g mol^{-1-1}. The average molar mass value (g mol^{-1}) obtained was used for the molar ratio calculations of 1:3.4 and 1:6 of oil/methanol used in the esterification and transesterification reactions, respectively.

3.2 Calculation of esterification and transesterification reaction yields

The transesterification reaction yield obtained in this study was 84.4 %±1.07 using 2 % KOH (*w*/*v*) for 1 h at 45 °C. In other works, under conditions of KOH 0.5 %, reactional time of 3 h, molar ratio at 70 °C of 9:1, and mixture proportion of fry/jatropha biodiesel of 70/30, a mass yield of 80.42 % was obtained [51]. Silva and Mendes [52] carried out a transesterification in triplicate of fry oil with 6:1 methanol/oil proportion and KOH 1 % *w*/*w* at 80 °C for 1 h, and an average mass yield of 82.4+ 2.5 % was obtained.

Ferreira [53] carried out transesterification of castor oil, cotton oil, and the 1:1 mixture of castor oil and cotton. The transesterification of castor oil was under the conditions of 0.5 % NaOH and 6:1 ratio methanol/oil. For transesterification of cotton oil 1.0 % NaOH was used and a 6:1 methanol/oil. The 1:1 mixture of castor oil and cotton was performed under conditions of 1.0 % NaOH and a 6:1 methanol/oil. All reactions were performed at 50 °C for 1 h. The mass yields obtained were 74.5, 74.5, and 72.4 %, respectively [53].

Araújo et al. [54] obtained a mass yield of 88.13 % for ungumed oil of *Dipteryx lacunifera* (belonging to the Leguminoseae-Papilionoideae family and is a plant native to South America, popularly known as garampara, burro nuts, and gurguéia nuts), with phosphoric acid with oil/methanol molar ratio of 1:6 and 1 % NaOH at room temperature for 1 h [54].

3.3 Physical-chemical characterization of jatropha biodiesel

The methylic biodiesel, produced from the previously characterized jatropha oil using the esterification route followed by transesterification, was characterized according to the quality standards established by the ANP resolution [32] (Table 4).

All physical-chemical properties evaluated are within the established limits, but the oxidation stability parameter, demonstrating the potential of jatropha as an alternative source of raw material for biodiesel. Oxidation stability of biodiesel is directly related to the degree of alkyl esters unsaturation, as well as the position of the double bonds in the carbon chain from the raw material. For biodiesel obtained in this study, it was not possible to reach the minimum limit of 8 h of oxidation stability as specified by EN 14112. Thus, the antioxidant 2.6-di-*tert*-butyl-4-methylphenol (BHT) incorporation was assayed in order to increase oxidative stabilization in storage stability study (Table 5).

Table 4 Physical-chemical characterization of jatropha biodiesel

Features	Results	Standard
Aspect	LII	NBR 16048
Flash point	184.00 °C	NBR 14598
Ester content	98.50 % weight	NBR 15764
Specific mass at 20 °C	877.20 kg m^{-3}	ASTM D 4052
Kinematic viscosity at 40 °C	4.20 mm^2 s^{-1}	ASTM D 445
Free glycerol	0.01 % weight	NBR 15908
Total glycerol	0.08 % weight	NBR 15908
Monoacylglycerol	0.24 % weight	NBR 15908
Diacylglycerol	0.06 % weight	NBR 15908
Triacylglycerol	0.01 % weight	NBR 15908
Oxidation stability at 110 °C	2.34 h	EN 14112
Total sulfur	4.30 mg kg^{-1}	ASTM D 5453
Potassium	<5.00 mg kg^{-1}	NBR 15553
Phosphorus	<1.00 mg kg^{-1}	NBR 15553
Calcium+magnesium	<2.00 mg kg^{-1}	NBR 15553
Sulfated ash	0.01 % weight	NBR 6294
Carbon waste	0.02 % weight	ASTM D 4530
Cold filter plugging point	1.00 °C	NBR 14747
Iodine value	97.84 g I_2 100 g^{-1}	EN 14111

The derived sulfur products are quite harmful to the environment, the engine, and its components. Sulfur forms compounds that promote the wear of engines, either through corrosion or through deposits. The sulfur oxides resulting from the combustion form sulfuric acid in the presence of water, attacking cylinders and piston rings, particularly in the cold starting phase and heating of the motor [55]. It is important to notice that pure biodiesel is free of sulfur, which is derived from vegetable and/or animal fats or waste oils, but when added to conventional diesel or when the esterification reaction is done before the transesterification reaction using sulfuric acid as a catalyst, sulfur is incorporated [56]. The Jatropha biodiesel was in accordance with the sulfur compounds limit specified by the ANP resolution [32].

The iodine value indicating the unsaturation content of the fuel, thereby evaluates the oxidation tendency of the fuel, thus, favors the occurrence of the polymerization and formation of gum deposits in diesel cycle engines [57]. Therefore, the result obtained for the iodine value to jatropha biodiesel indicated the high degree of

Table 5 Stability of pure jatropha biodiesel during storage for 90 days

Analysis	Unit	Time (days)				ANP specification[b]	Standard
		0	30	60	90		
Physical appearance[a]	–	LII	LII	LII	LII	LII	NBR 16048
Specific mass at 20 °C	kg m^{-3}	877.2	878.2	878.0	879.3	850.0–900.0	ASTM D 4052
Kinematic viscosity at 40 °C	mm^2 s^{-1}	4.2	4.8	4.8	4.9	3.0–6.0	ASTM D 445
Water content	mg kg^{-1}	343.4	871.5	1104.8	1208.3	Max of 350.0	ASTM D 6304
Acid value	mg KOH g^{-1}	0.29	0.48	0.49	0.50	Max of 0.5	EN 14104
Oxidation stability at 110 °C	h	6.17	<5.00	<3.00	<3.00	Min of 6.0	EN 14112

Max maximum, *Min* minimum

[a] LII: clear and without impurities

[b] ANP resolution 14/2012

unsaturation of fatty acids present, indicating a higher oxidative instability, a disadvantage for the industrial applications of the biodiesel as a lubricant [57] and as fuel.

Density is a property that does not suffer large variations due to the fact that oil has similar density to their methyl esters, but the control thereof is very important because high density can cause problems in the fuel injection of the chamber compression, which may cause clogging of nozzles, thereby low fuel injection; likewise, low density causes an exaggerated injection, enabling incomplete burning or excessive consumption of fuel [58]. The result obtained for the jatropha biodiesel shows that the transesterification reaction provided a slight reduction in the biodiesel density, compared to jatropha oil. The kinematic viscosity is also responsible for the proper fuel injection in appropriate amounts, and high viscosity cannot provide enough fuel to the engine [58]. The jatropha biodiesel showed adequate viscosity value, reflecting the efficient conversion to esters, which is also responsible for reducing oil viscosity.

The flash point is the property that is of importance in regards to safety in transportation, storage, and handlings [58]. The jatropha biodiesel had a higher flash point value than the one it was specified by the ANP resolution for soy biodiesel [32], which increases its safety in transportation, avoiding risk of explosion or fire.

The cold filter plugging point determines the temperature that the fuel loses filterability when cooled. The value of the cold filter plugging point for Jatropha biodiesel was 1 °C and conforms to the maximum limit of 5 to 14 °C, which depends on the season and region of country and is established by ANP resolution [32], suggesting that it may be used in any region of the country and in different weather conditions [59].

Fuels with excess free glycerin cause clogging of fuel filters, glycerol deposition in storage tanks, and thereby problems in the engine combustion. Moreover, the burning of glycerin generates, among other toxic compounds, acrolein–which is a carcinogenic aldehyde and may cause respiratory problems in the case of long periods of inhalation–such as traffic jams inside tunnels, something common in big cities [60]. According to the results obtained for methylic biodiesel of jatropha, the washing process was effective to remove free glycerin.

3.4 Analysis of the shelf life of jatropha biodiesel

The assays of mensal samples were planned aside for physical-chemical analysis to monitor shelf life of pure jatropha biodiesel through the following analysis: physical appearance, density at 20 °C, kinematic viscosity at 40 °C, water content (Karl Fischer coulometric), acid value, and oxidation stability (Table 5).

Figure 2 shows the variability of temperature and humidity, which fluctuated from 21.6 to 33.4 °C and from 41 to 75 g cm^{-3}, respectively.

The methodology used to evaluate the biodiesel's physical appearance aimed to observe the degree of turbidity and the presence of impurities, compared to a standard letter of turbidity ranging from 1 (limpid) to 6 (high level of turbidity). The classification identified for jatropha biodiesel was degree 1, proving to be clear and free of impurities as specified in the ANP resolution [32]. Figure 3 shows the appearance of jatropha biodiesel during a study of 90 days in storage.

An increase was observed in the water content during the storage period, exceeding the maximum water content limit of 200 ppm, established by the ANP resolution [32], after 30 days of storage. This is due to the hygroscopic behavior of the biodiesel. Moisture is an essential parameter in biodiesel quality, since water can cause a reaction of unwanted hydrolysis, producing free fatty acids, which may cause engine problems [60]. Water is also associated with the proliferation of microorganisms,

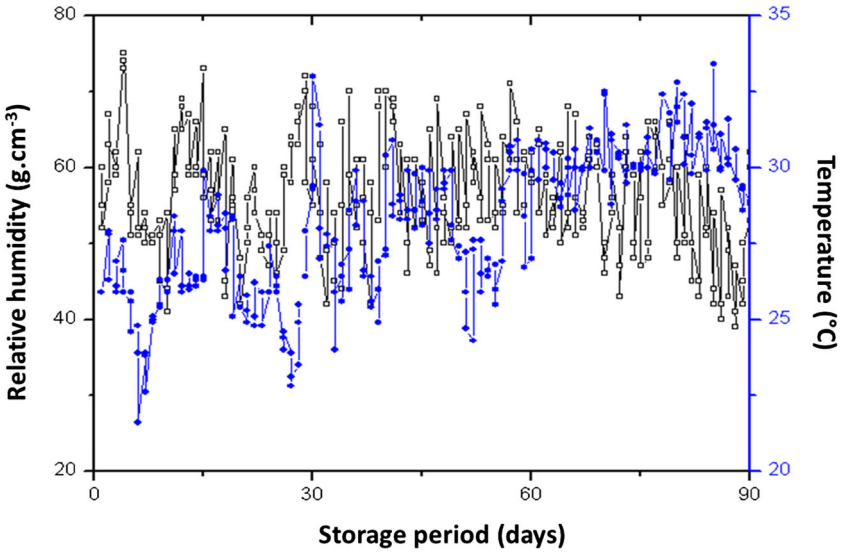

Fig. 2 Variability of temperature and humidity during 90 days of storage

causing corrosion in storage tanks with sediment deposition [61]. Studies to evaluate strategies for reducing hygroscopic behavior of jatropha biodiesel are ongoing.

A decrease in the oxidative stability was also observed for jatropha biodiesel during storage time. The oxidative stability of the produced biodiesel did not achieve the minimum limit of 6 h, as established by the ANP specification [32]. Studies to evaluate strategies for reducing hygroscopic behavior of jatropha biodiesel are ongoing. The oxidation stability of biodiesel is directly related to the degree of unsaturation of alkyl esters but also with the position of double bonds in the carbon chain. The greater the amount of unsaturation, the more susceptible the molecule is to oxidative and thermal degradation, which form insoluble products causing problems of fouling and deposit formation in the engine fuel injection system [10]. In the chemical composition of jatropha biodiesel, there is a prevalence of unsaturated fatty acids estimated at 82.48 %, which are more susceptible to oxidation, and this is related with the decrease in oxidation stability during the storage period.

During 90 days of storage, there was an increase in the acid value, but jatropha biodiesel was within the limit allowed by the ANP specifications [32] that is 0.50 mg KOH g^{-1}. The acidity of a fuel is also an essential factor control, since the presence of free fatty acids can trigger an oxidative process of fuel and is also responsible for oxidation of internal engine parts, causing corrosion, sediment, and incrustation formation [52]. The values obtained for specific mass at 20 °C and for kinematic viscosity at 40 °C were in accordance with ANP specifications [32] during 90 days of storage.

4 Conclusions

The jatropha oil showed a suitable lipid profile for biodiesel production. A great part of fatty acids identified were oleic and linoleic acid, ideal for biodiesel production. The results of physical-chemical characterization of jatropha oil highlighted the need for an esterification step prior to transesterification. The physical-chemical parameters of methylic biodiesel samples of jatropha were in accordance with Brazilian legislation, except for water content limit and oxidation stability. The shelf life of jatropha biodiesel was established for 90 days in the storage conditions studied; significant loss of oxidative stability and water content were found to be the limiting factors. Studies to evaluate strategies for reducing hygroscopic behavior and to increase oxidation stability of Jatropha biodiesel are ongoing.

Fig. 3 Physical appearance of jatropha biodiesel after 30, 60, and 90 days, respectively

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