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Study of degumming process and evaluation of oxidative stability of methyl and ethyl biodiesel of *Jatropha curcas* L. oil from three different Brazilian states

Francisca Diana da Silva Araújo [a], Iranildo C. Araújo [a], Isabella Cristhina G. Costa [a], Carla Verônica Rodarte de Moura [a], Mariana H. Chaves [a, *], Eugênio Celso E. Araújo [b]

[a] Departamento de Química – CCN, Universidade Federal do Piauí, 64049-550 Teresina, PI, Brazil
[b] Empresa Brasileira de Pesquisas Agropecuária – Embrapa Meio-Norte, 64049-550 Teresina, PI, Brazil

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ABSTRACT

This work describes the production of biodiesel from *Jatropha curcas* oil. The kernel samples provided by Embrapa-PI, were first crushed in a blender and then subjected to extraction with hexane. The oil yield was between 54.71 ± 0.47 and 64.16 ± 2.88%. The *J. curcas* oil was then submitted to two different kinds of degumming, first with water and second with H_3PO_4 to evaluate the influence of these processes in the yield of the transesterification reaction. Methyl and ethyl biodiesel prepared from the degummed oil with H_3PO_4 had higher conversions than those prepared with the degummed with water. Therefore, among the processes of degumming studied, H_3PO_4 was more suitable for the treatment of *J. curcas* oil. The study shows the results about oxidation stability were good, because the biodiesels methyl and ethyl biodiesel have induction period at 13.51 h and 13.03 h without antioxidant addition when submitted a Rancimat text. Such biodiesels had their physicochemical parameters defined under the specifications of ANP Resolutions n° 14/2012 (ANP- National Agency of Petroleum, Natural Gas and Biofuels from Brazil). The results showed that *J. curcas* cultivation in Brazil is an adequate source for biodiesel production, considering the technical standards available.

1. Introduction

Global warming, a spurt in population growth and an increase in demand for transport fuels in developing economies, all coupled together with limited reserves of fossil fuels, are realities that have convinced many countries of the need to develop alternative and renewable energy sources such as biofuels [1]. Currently, most biofuels are obtained from either carbohydrate-based feedstock (sugar, starch, cellulose) or oil-based feedstock [2]. Oil-based feedstock or biodiesel can be produced from vegetable oils of agricultural plants such as rapeseed, sunflower, soybean, oil palm and groundnut [2]. As a feedstock, more than 80% of Brazilian biodiesel production is derived from soybean oil [2]. However, in accordance to Johnson et al., the use of edible oils in developing countries for biofuel purposes could lead to shortages of edible oils or an escalation of their prices [2]. Besides, the cost of biodiesel is not competitive to petroleum diesel without subsidies or tax incentives as the cost of raw materials is high. The cost of crop oil accounts for a large percent of direct biodiesel production cost which includes capital cost and returns [3]. Therefore, it is necessary to find new feedstock suitable for biodiesel production, which would not drain the edible vegetable oil supply and that would be capable of growing in marginal lands with minimum agricultural inputs. Besides, from the industrial point of view, using unrefined oils is very important since the refining of oil is a costly process [4]. However, the use of crude oil, without at least going through the process of degumming and neutralization, can cause problems such as emulsification in the transesterification process. By degumming, the impurities like protein, phosphatides, colorants, etc, are removed [5].

Non-edibles oils such as jatropha oil, castor oil and others are considered to be renewable and sustainable solutions [6].

Jatropha curcas L. or physic nut, belonging to the Euphorbiaceae family, is seen as one of the most appropriate renewable alternative sources of biodiesel in terms of availability and cost [7,8]. It is a perennial plant that is easily cultivated, requires much sunshine, is

* Corresponding author. Tel.: +55 86 3215 5841; fax: +55 86 3237 1812.
E-mail address: mariana@ufpi.edu.br (M.H. Chaves).

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strongly resistance to drought and grows under a wide range of regional rainfall from 200 to 1500 mm per year [8], and it is a hardy plant amenable to cultivation on marginal land [9]. This condition provides an alternative oil source without directly competing with food production [10]. This type of condition is found in north-eastern Brazil, where there is a large arid area that is in need of development. Due of the potential to transform *J. curcas* oil in biodiesel, their cultivation area, mainly in India, China, Mexico and Brazil are growing [11]. The new demand for development to improve of cultivars, in recent years, leading the cultivation and domestication of *J. curcas* [11].

The productivity of this species varies by planting region, cultivation method and soil fertility [12]. The production of *J. curcas* reached levels around 8000 kg of seed per hectare per year [13]. The maximum productivity of the plant occurs in five years and it can survive for more than 50 years. The fruit's ripening occurs in 30–45 days, observing the changes in color from green to yellow, to brown and finally, to black [14,15]. Jatropha is considered unsuitable for ingestion in certain cases because the oral intake of its leaves and seeds can cause hypercatharsis or diarrhea; moreover, it contains the toxin curcin (a protein with a molecular weight of 28.2 kDa and 251 amino acids) as well as phorbol esters which are known for being tumor-promoters in cell proliferation, activation of blood platelets, lymphocyte mitogenesis, inflammation (erythema of the skin), prostaglandin production and stimulation of degranulation in neutrophils [16,17]. Curcin becomes nontoxic on denaturation by heating; however, phorbol esters persist in oil fractions [18].

Jatropha curcas can still be considered as a semi-wild, undomesticated plant, showing considerable performance variability, and the profit margin realized from this crop is still very small compared in its cultivation [11]. Then a study about variety of oil in different species is very important.

The seed cake has been used as a natural fertilizer since it is rich in NPK. The cake contains about 6% nitrogen, 3% phosphorus, 1% potassium, and traces of calcium and magnesium. After detoxification, this product can be used as animal feed [13].

J. curcas nuts contain 40.0–60.0% of oil, 4.0–4.7% of ash, 3.7–10.1% of fiber, 17.8–28.9% of protein and 4.4–5.5% of moisture. The composition of seed oil includes capric acids (0.0–0.1%), myristic (0.0–1.4%), palmitic (13.0–19.5%), palmitoleic (0.8–1.4%), stearic (6.8–9.7%), oleic (34.3–53.0%), linoleic (20.0–43.2%), linolenic (0.0–3.0%), arachidic (0.0–0.4%) and behenic (0.0–0.2%) [14,19–22]. Table 1 shows the composition of the oil varieties from different regions of the world. It is observed that in some areas the major constituent of oil is oleic acid, while in others it is linoleic acid.

J. curcas as a substitute for diesel fuel will be very import, since the oil has calorific contents, which were 4980.3 cal g^{-1} for the seed, 9036.1 cal g^{-1} for the fraction of oil, and 9704.4 cal g^{-1} for the fraction of hydrocarbons [23]. Many researchers have studied the potential of oil *J. curcas* for use in biodiesel production [24–26].

Table 1
Fatty acids composition of *J. curcas* (% p/p of methyl ester).

Fat acid	Caboverde [14]	Nicaragua [14]	Benin [21]	Mexico [21]	Togo [21]	Brazil [21]
C10:0	0.1	0.1	–	–	–	–
C14:0	0.1	0.1	–	–	–	–
C16:0	15.1	13.6	14.6	15.2	15.0	13.1
C16:1	0.9	0.8	0.8	–	–	–
C18:0	7.1	7.4	7.4	9.1	6.0	6.6
C18:1	44.7	34.3	47.5	37.5	44.0	32.8
C18:2	31.4	43.2	28.7	38.0	35.7	46.9
C18:3	0.2	0.2	1.0	–	–	–
C20:0	0.2	0.3	–	–	–	–
C22:0	0.2	–	–	–	–	–

The literature shows the non-refined *J. curcas* oils revealed a high content in free fatty acids (about 15–20%), hence this can leads to soap formation and lower yield of biodiesel if the catalyst is basic [27]. Crude oil also contains many gums, such as phospholipids, which can deactivate the catalyst during biodiesel production and reduce drastically the conversion of methyl esters [28].

The aim of this study was to extract, characterize the oil from the fruit seeds of *J. curcas*, grown in northeastern Brazil, as well as do two texts degumming of oil procedures, and subsequent application to obtain biodiesel, and study the oxidative stability of jatropha biodiesel, using Rancimat technique.

2. Materials and methods

2.1. Instruments

The physicochemical characterizations were performed using automatic densimeter Anton Paar DMA 4500, viscometer Quimis®, Metrohm Rancimat 743. Benchmark unit 2000, Koehler Instrument Company, Inc. (determination of water and sediment); apparatus Pensky Martens Closed Cup APM-7 (measured flash point); equipment Petrotest® (copper corrosivity); Tanaka Scientific Limited-AFP 102 (filter plugging point of the cold). The percentages of total and free glycerin, mono-, di- and Triacylglycerol were obtained in a gas chromatograph with a flame ionization detector (GC-FID), Varian 3800 and the methanol content by GC-FID coupled with static headspace, Varian 3900. To determine the composition of oil, a Shimadzu gas chromatograph model GC17A with mass detector (GC–MS) QP5000 was used. NMR spectrometer Varian Inova 500 (500 MHz) and TGA-2050 balance TA Instruments were used to obtain the NMR and TGA spectra, respectively. Some of the parameters were performed in triplicate, and presented both the mean and standard deviation measures.

2.2. Collection of seeds

Mature and sun-dried seeds of *Jatropha curcas* L. were collected from trees in different regions of Brazil and donated by EMBRAPA – Brazilian Company of Agriculture and Livestock. The samples came from of three different cities (Teresina, Crateús and Janaúba). Teresina is located at Piauí State (northeast of Brazil), Crateús is located at Ceará State (northeast of Brazil) and Janaúba is located at Minas Gerais State (southeast of Brazil). All of these cities are located in very dry and hot climates.

2.3. Determination of oil composition fatty acid

Fatty acid methyl esters (FAME) were prepared following the methodology described by IUPAC with some modifications [29–31]. 100 mg of jatropha oil was accurately weighed into a 20 mL centrifuge tube and a methanolic KOH solution (2 mol L^{-1}) was added (0.2 mL). The tube was sealed and mixed vigorously for 20 min in a vortex shaker. Saturated NaCl solution (2.0 mL) was added and the organic phase was separated. An aliquot (1.0–2.0 μL) of the hexane solution was submitted to GC–MS analysis, under the following conditions: Capillary column: 5% phenyl-methylpolysiloxane DB-5 (30 m × 0.25 mm, 0.25 μm film thickness); carrier gas: helium; flow 0.6 mL/min; acquisition time from 42.5 min and solvent cut in 4 min; mass range from 40 to 400, electron energy of 70 eV; multiplier voltage of 1.3 kV; analyzer quadrupole; injector temperature: 230 °C; interface temperature: 250 °C; column temperature: 150 °C (2 min); 150–230 °C at 5 °C/min; 230 °C (7 min); 230–260 °C at 4 °C/min; 260 °C (10 min).