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

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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,
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 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 is 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 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 important, 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].

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 Pensiky 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).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Fatty acids composition of <em>J. curcas</em> (% p/p of methyl ester).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat acid</td>
<td>Caboverde</td>
</tr>
<tr>
<td>C10:0</td>
<td>0.1</td>
</tr>
<tr>
<td>C14:0</td>
<td>0.1</td>
</tr>
<tr>
<td>C16:0</td>
<td>15.1</td>
</tr>
<tr>
<td>C16:1</td>
<td>0.9</td>
</tr>
<tr>
<td>C18:0</td>
<td>7.1</td>
</tr>
<tr>
<td>C18:1</td>
<td>44.7</td>
</tr>
<tr>
<td>C18:2</td>
<td>31.4</td>
</tr>
<tr>
<td>C18:3</td>
<td>0.2</td>
</tr>
<tr>
<td>C20:0</td>
<td>0.2</td>
</tr>
<tr>
<td>C22:0</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Individual components were identified by computer search (Wiley 229 library).

2.4. Extraction of the oil for biodiesel synthesis

The samples of *J. curcas* kernels provided by EMBRAPA from Teresina-Piauí, Crateús-Ceará and Janaúba-Minas Gerais, were crushed in a blender and submitted to extraction with hexane for 18 h in Soxhlet. At the end of extraction, the solvent was removed in rotary evaporator at 50 °C. This procedure was performed several times until we obtained approximately 2 L of oil. The *J. curcas* oil was degummed with water or H3PO4 [32] in order to evaluate the process's influence on the conversion of triacylglycerol into methyl or ethyl esters.

2.4.1. Degumming of oil with water

In a beaker of 250 mL, 100 g of oil and 3 mL of heated water (70 °C) were added. The mixture was stirred for 30 min, and after, was left to decant. The precipitate was removed and the oil was filtered off in anhydrous sodium sulfate [32].

2.4.2. Degumming of oil with H3PO4

The crude oil (1000 mL) was pre-heated at 60 °C, 0.1% of phosphoric acid (based on the mass of oil used), some NaOH (8%) sufficient to neutralized 70–90% of added acid, and 2% of water. The mixture was heated and stirred until the formation of the gum. Subsequently, the mixture was cooled and the gum was separated from the solution by simple filtration. This procedure was repeated using 3% water, to remove the remaining gums. The oil was filtered off with anhydrous sodium sulfate [32].

2.5. Biodiesel synthesis

The ethyl and methyl biodiesel were synthesized using *J. curcas* oil from Teresina-Piauí, Crateús-Ceará and Janaúba-Minas Gerais. The transesterification reaction was performed using rates of 100:20:1 (oil: methanol: NaOH) and 100:40:1 (oil: ethanol: NaOH) [33] under constant stirring for a period of 60 or 120 min for methyl and ethyl esters, respectively, at room temperature [34,35]. At the end of the reaction, the mixture was transferred to a decanting funnel and the esters were separated from the glycerin, washed with water and heated to 100 °C. The biodiesel was analyzed by TLC with silica gel using as eluent hexane-EtOAc (95:5). The spots on the TLC plates were revealed with iodine steam. The reaction yield was calculated by the formula:

\[
\text{Yield(%) = (mass of biodiesel/oil mass) } \times 100.
\]

The rate of conversion of triglyceride oil into biodiesel was determined by 1H NMR analysis in CDCl3 and using the following expression [36]:

\[
C = \frac{2\text{ACH}_3}{3\text{ACH}_2} \times 100
\]

where:

C = % conversion

ACH3 = integration area of the signal at δ 3.7 from hydrogen methoxylic

ACH2 = integration area of the signal at δ 2.3 from methylene hydrogen α-carbonyl esters and triacylglycerol.

The conversion of triacylglycerol into ethyl esters was effected from the equation [37]

\[
C = \frac{2\text{ACH}_2}{3\text{ACH}_3} \times 100
\]

where:

C = % conversion

ACH2 = integration area of the signal at δ 3.7 from ethoxylates

A′CH2 = integration area of the signal at δ 2.3 from methylene hydrogen α-carbonyl esters and triacylglycerol.

2.6. Physicochemical analysis and thermogravimetric oil and biodiesel

The physicochemical properties of biodiesel were done according to the rules of the American Society of Testing and Materials (ASTM) and Comité Européen de Normalisation (CEN) listed in ANP Resolution 14/2012 [38] of the National Agency of Petroleum, Natural Gas and Biofuels from Brazil. The acidity index of oil and biodiesel, and the saponification index of the oil were carried out in accordance with the standards of the Adolfo Lutz Institute. TG curves of the oils of *J. curcas* crude, degummed with water and degummed with acid, as well as biodiesel were obtained in a temperature range 30–600 °C with a heating rate of 10 °C/min in nitrogen atmosphere with a flow rate of 50 mL/min using an aluminum pot with a hole in the lid of about 0.5 mm in diameter. The weight loss of the sample was determined as the difference between the initial and final weight loss. The boiling point was taken as the point of intersection of the tangent of the slope of mass loss with the initial baseline (temperature "onset"). The software of the equipment was used to draw the tangent lines and compute the boiling temperature [39–41].

2.7. Tests for oxidation stability

The oxidation stability was measured according to EN 14112, where 3 g of samples were analyzed under heating at 110 °C and constant air flow (10 L/h). In the Rancimat, the flow of air passes through the sample, and then bubbles into a flask containing deionized or distilled water, dragging the volatile carboxylic acids (breakdown products), which solubilize and increase the conductivity of the water. The response is a curve of conductivity versus time in which two tangents intersect at a point, corresponding in time scale, the induction period or oxidation stability [42].

3. Results and discussion

3.1. Characterization of oil of *J. curcas*

3.1.1. Chemical composition and yield of oil

The seeds from Janaúba-Minas Gerais had higher yield in oil, 64.16 ± 2.88%, while the sample from Teresina-Piauí exhibited an intermediate value, 60.69 ± 0.84%, and the seeds coming from Crateús-Ceará were those that obtained a lower yield, 54.71 ± 0.47%. The sample results were compared by analysis of variance (ANOVA) and showed that the values are significantly different at a significance level of 5%. These results indicate that the quantity of the oil yield from *J. curcas* seeds can vary depending on the region of cultivation, and may be influenced by the conditions, culture or even age [18]. Table 2 lists the compositions of the *J. curcas* oils from the Janaúba-Minas Gerais, Teresina-Piauí, Crateús-Ceará, and Caboverde-Africa variety, for comparative purposes, in addition to the compositions for soybean oil [14,21].
All the samples from *J. curcas* oil showed a percentage of oleic acid (18:1) greater than linoleic acid (18:2), thus resembling the range of *Caboverde* variety. With regards to the content of unsaturated acids, we observed lower values compared with the percentage found in the literature for soybean oil. The increase in unsaturated acids provides a decrease in oxidation stability of oil and consequently of biodiesel [43].

### 3.1.2. Physicochemical characterization of oil

The crude oil extracted from the seeds supplied by Teresina-Piauí, and the oils subjected to degumming with water and *H*3PO4 showed the physicochemical properties listed in Table 3.

The ANOVA test was applied in the values found to acidity index and results were significantly different, with a significance level of 5%. When the crude oil was degummed with water, a decrease in content of free fatty acids present was verified. A reduction of approximately 50% in the acidity index was observed when the degumming was done with phosphoric acid. All samples showed an acidity index above the limit established for refined oils, whose value is less than 0.6 mg KOH/g oil [30].

The rate of the saponification index varies with the nature of fatty acids that comprise the triacylglycerol. The lower the average molecular weight of these compounds, the higher the value of this parameter [32]. There was no significant difference between the values of the saponification index between the three samples [14,20,21].

The density values obtained for all samples found in the range observed in the literature [21,34,44] from 0.8950 to 0.9186 kg/m³. The induction periods obtained for the oils of *J. curcas* crude, degummed with both water and with *H*3PO4 were 7.92, 7.83 and 7:09 h, respectively (Table 3). A small decrease in the induction period of the crude oil was observed with application of the process of degumming. However, the analysis of variance indicated no significant difference between these values, showing that the degumming does not affect the oxidative stability of oil.

### 3.1.3. Thermogravimetric analysis

TG/DTG curves of *J. curcas* crude oil from Teresina-Piauí subjected to water and *H*3PO4 degumming showed the thermal events listed in Table 4. Two thermal events were observed in the oils and can be attributed to the volatilization of triacylglycerols, the second event can be attributed to the volatilization of higher molecular weight triacylglycerols [41].

It was found that as crude oil goes through water degummed and acid-degummed processes, there is a slight decrease in the percentage of the total mass loss, suggesting that part of the phospholipids is actually withdrawn. Moreover, an increase in the *t*<sub>onset</sub> of the first event in the degummed oil was observed, especially in the latter case, suggesting that the removal of phospholipids may contribute to the increase of thermal stability of the oil.

### 3.2. Characterization of *J. curcas* biodiesel

#### 3.2.1. TLC and 1H NMR analysis

Thin-layer chromatography (TLC) analysis of biodiesels suggested the occurrence of the transesterification reaction to the oils, especially for ethyl biodiesel where the oil was degummed with water (EB-DW) and ethyl biodiesel where the oil was degummed with *H*3PO4 (EB-DPA). In methyl biodiesels (MB-DW and MB-DPA), it has been verified that there is a presence of spots with retention factor (*R*<sub>f</sub>) similar to that of triacylglycerol oil, showing that it even left part of the starting material.

The 1H NMR spectrum of *J. curcas* oil presented nine major signals consistent with the structure of triacylglycerols, a triplet in δ 0.85 (J = 6.4 Hz), attributed to terminal methyl hydrogens of the

### Table 3

<table>
<thead>
<tr>
<th>Property</th>
<th>CO</th>
<th>DW</th>
<th>DPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity index (mg KOH/g oil)</td>
<td>6.20 ± 0.01</td>
<td>5.00 ± 0.00</td>
<td>3.60 ± 0.01</td>
</tr>
<tr>
<td>Saponification index (mg KOH/g oil)</td>
<td>185.75 ± 0.69</td>
<td>186.99 ± 0.45</td>
<td>186.77 ± 0.86</td>
</tr>
<tr>
<td>Density, 20°C (g/cm³)</td>
<td>0.911 ± 0.000</td>
<td>0.914 ± 0.000</td>
<td>0.915 ± 0.000</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>7.92</td>
<td>7.83</td>
<td>7.09</td>
</tr>
</tbody>
</table>

#### No water was detected in the oil after degumming with water or *H*3PO4 as can be seen in the TG curve shown in Fig. 1.

### Table 4

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature range (°C)</th>
<th>Weight loss [%]</th>
<th>Onset temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>307.95–446.44</td>
<td>89.45</td>
<td>330.93</td>
</tr>
<tr>
<td></td>
<td>446.44–495.63</td>
<td></td>
<td>496.23</td>
</tr>
<tr>
<td>Water degumming oil</td>
<td>288.27–447.95</td>
<td>87.02</td>
<td>355.19</td>
</tr>
<tr>
<td></td>
<td>447.95–494.12</td>
<td></td>
<td>470.85</td>
</tr>
<tr>
<td><em>H</em>3PO4 degumming oil</td>
<td>304.16–447.20</td>
<td>87.75</td>
<td>408.15</td>
</tr>
<tr>
<td></td>
<td>447.20–505.47</td>
<td>10.23</td>
<td>469.81</td>
</tr>
</tbody>
</table>

#### Table 2

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Teresina</th>
<th>Crateús</th>
<th>Janaúba</th>
<th>Caboverde variety [14]</th>
<th>Soybean oil [21]</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:0</td>
<td>14.69 ± 1.33</td>
<td>11.53 ± 0.77</td>
<td>11.35 ± 0.32</td>
<td>15.10 ± 0.00</td>
<td>11.00 ± 0.00</td>
</tr>
<tr>
<td>16:1</td>
<td>0.39 ± 0.09</td>
<td>0.34 ± 0.19</td>
<td>0.90 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:0</td>
<td>7.04 ± 1.94</td>
<td>7.00 ± 0.83</td>
<td>4.58 ± 3.24</td>
<td>7.10 ± 0.00</td>
<td>4.00 ± 0.00</td>
</tr>
<tr>
<td>18:1</td>
<td>42.30 ± 2.42</td>
<td>41.77 ± 4.65</td>
<td>42.64 ± 8.49</td>
<td>44.70 ± 0.00</td>
<td>22.00 ± 0.00</td>
</tr>
<tr>
<td>18:2</td>
<td>35.48 ± 2.90</td>
<td>39.60 ± 4.97</td>
<td>39.34 ± 8.59</td>
<td>31.40 ± 0.00</td>
<td>54.30 ± 0.00</td>
</tr>
<tr>
<td>18:3</td>
<td></td>
<td></td>
<td></td>
<td>0.20 ± 0.00</td>
<td>7.50 ± 0.00</td>
</tr>
<tr>
<td>20:0</td>
<td>0.09 ± 0.04</td>
<td></td>
<td></td>
<td>0.08 ± 0.03</td>
<td>0.20 ± 0.00</td>
</tr>
<tr>
<td>∑UFA (%)</td>
<td>78.17</td>
<td>81.15</td>
<td>82.21</td>
<td>77.00</td>
<td>83.80</td>
</tr>
<tr>
<td>∑SFA (%)</td>
<td>21.82</td>
<td>18.62</td>
<td>16.01</td>
<td>22.40</td>
<td>15.00</td>
</tr>
</tbody>
</table>

UFA: unsaturated fatty acids. SFA: saturated fatty acids.
hydrocarbon chain, a singlet at δ 1.23 from chain methylene, a multiplet at δ 1.58 from β-methylene carbonyl groups, a multiplet at δ 2.00 from the allylic methylene hydrogens, two triplets at δ 2.28 (J = 7.4 Hz) and 2.75 (J = 7.0 Hz) α-methylene groups of carbonyl and bis-allylic, respectively, two signals at δ 4.11 (dd, J = 6.0 and 11.8 Hz) and δ 4.27 (dd, J = 4.2 and 11.6 Hz) from the hydrogens CH2O from glycerol portion, a multiplet between δ 5.90 and 5.42 referent to the chain olefinic hydrogens and CHO of glycerol portion [45–47].

The NMR 1H spectra of biodiesels from oils subjected to different processes of degumming were similar. The occurrence of the transesterification was confirmed by signals at δ 3.61 (s) concerning the methoxyl and δ 4.06 (q, J = 7.0 Hz), assigned to the oxy-methylene hydrogens to methyl and ethyl biodiesels, respectively [45,46].

Through the 1H NMR analysis, it was observed that the conversions in esters were relatively high for all J. curcas biodiesels, because there were no obvious signs placed between δ 4.10 and 4.40 characteristic of triacylglycerols.

3.2.2. Effect of degumming on the yield and conversion

Degumming was done to decrease the acidity of the oils tested in this study, and to removal gums and other interferences that might reduce the yield of biodiesel. The methyl and ethyl biodiesels had higher yields and conversions in esters, when prepared from oil degummed with H3PO4 (Fig. 2).

Phospholipids as well as some by-products formed during the process of obtaining biodiesel by transesterification alkaline, such as soaps, mono- and diacylglycerol, can act as surfactants [48], hindering the phase separation from the stabilization of emulsions, and helping to decrease yield and conversion rate. Whereas the degumming process with water does not produce the complete removal of phospholipids, since only a few of these have solubility in water [35], and probably a significant amount of these substances remained present in the reaction medium, contributing to the reduction in income from transesterification of J. curcas oil.

In turn, in the degumming process with H3PO4, non-hydratable phospholipids are decomposed and transformed into insoluble lipids, which are separated by decantation after the addition of water [49]. This process provided greater efficiency in the reaction.

Yields and conversion rates into esters, obtained by methylic route, had the best results, which were expected, considering that methanol has a higher nucleophility than ethanol. As the degumming with phosphoric acid presented the best performance, the analysis thermogravimetric and determination of physicochemical parameters were carried out only for biodiesels prepared from J. curcas oil which had undergone such a process.

3.2.3. Thermogravimetry

The biodiesel is a mixture of alkyl esters, so its physical properties are very similar to pure esters. Therefore, it tends to show volatility and a boiling point that depend on the fatty acid composition, especially chain length and number of double bonds. Thus, for a specific biodiesel, the boiling point will be the average of fatty acid esters mixture [39–42].

Thermogravimetric analysis has been recommended as a rapid technique to measure the boiling point and vapor pressure of many organic compounds, including vegetable oils or alkyl esters. This method does not indicate visible evidence that the samples of esters decompose before or during the volatilization [39].

TG/DTG curves of MBJC and EBJC, which were prepared with H3PO4 degummed oil, showed similar results; in both, two thermal events were observed as shown in Table 5.

The first interval of mass loss observed for both biodiesels was in the range of 79.40–246.65 °C (79.47%; MBJC) and 77.88–263.30 °C (80.10%; EBJC); this is attributed to volatilization of unsaturated esters and lower molecular weight. The second thermal event was in the range of 246.65–301.14 °C (18.32%; MBJC) and 263.30–338.22 °C (18.75%; EBJC), and may be due to the higher molecular weight esters. The presence of esters in the samples is evidenced by the displacement of the main event, observed on the oil curve by lower temperatures, since these substances have boiling points lower than those of triacylglycerols, volatilizing therefore, in different temperatures [7]. TG/DTG curve did not show any events in the range of 304–505 °C, suggesting that the transesterification reaction was complete [7]. The ethyl esters showed higher boiling points (Tonset) than the methyl esters in the two thermal events and indeed were consistent with a view that the former has higher molecular weights (Table 5). The mass loss of the two thermal events showed positive correlation between the percentages of fatty acids unsaturated (78.2%) and saturated (21.8%) as determined by gas chromatography [50].

3.2.4. Physicochemical parameters of MBJC and EBJC

The physicochemical parameters of MBJC and EBJC stood within the limits established by ANP Resolution 14/2012 (Table 6). The flash point of both samples, although within specifications, was less

Table 5

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature range (°C)</th>
<th>Weight loss (%)</th>
<th>Onset temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBJC</td>
<td>79.40–246.65</td>
<td>79.47</td>
<td>175.81</td>
</tr>
<tr>
<td></td>
<td>246.65–301.14</td>
<td>18.32</td>
<td>287.52</td>
</tr>
<tr>
<td>EBJC</td>
<td>77.88–263.30</td>
<td>80.10</td>
<td>186.17</td>
</tr>
<tr>
<td></td>
<td>263.30–338.22</td>
<td>18.75</td>
<td>319.19</td>
</tr>
</tbody>
</table>

Fig. 2. Yield of biodiesel and percentage conversion of triacylglycerols to corresponding methyl and ethyl esters. MB: methyl biodiesel; EB: ethyl biodiesel; DW: degumming with water; DPA: degumming with H3PO4.
than that reported in the literature for biodiesel methyl (163–191 °C) and ethyl (190 °C) [11,19]. The residues of free and total glycerin were quite satisfactory and lower than those obtained by titrimetric analysis, which were 0.0192 ± 0.0035% and 0.1779 ± 0.0109% (MBJC), and 0.0203 ± 0.0095% and 0.2268 ± 0.0559% (EBJC) respectively.

Gas chromatography analyses showed quantities of mono, di- and triacylglycerols in MBJC; however, the EBJC did not present triacylglycerols. Methanol is more reactive than ethanol, so we used 1 h to make the methyl route and 2 h for the ethyl route. However, the results showed the presence of triacylglycerol in biodiesel methyl only it is believed that the time of 1 h was not enough for total transesterification.

3.2.5. Oxidation stability

The oxidation stability of the biodiesels was relatively high (MBJC = 13.51 h, EBJC = 13.03 h). Values over 6 h were obtained without the addition of antioxidants. This corroborates the results of the lipid composition of the oil, which was mainly oleic acid, because it has only one double bond in the chain and the ester corresponding undergoes oxidation at a slower speed than the polyunsaturated esters. However, the conditions of storage, handling of raw materials and processing of biodiesel may compromise the oxidation stability [49]. Furthermore, depending on the treatment of the raw material, natural antioxidants such as tocopherols, carotenes, vitamin C and other phytochemicals, may be removed decreasing the stability. In research conducted by Sarin et al. [22] for example, biodiesel produced from J. curcas oil showed an induction period of 2.33 h, although the main constituent of the oil is also oleic acid. The results suggest that the oil J. curcas grown in Brazil is rich in natural antioxidants and these substances have not been fully removed in the degumming process used; industrially, this point is very important because it is not necessary to add antioxidants to this particular biodiesel.

4. Conclusions

The samples of Jatropha curcas L. (Physic nut) from Teresina-Piauí, Crateús-Ceará and Janaúba-Minas Gerais showed high levels of oil with 60.69, 54.71 and 64.16%, respectively. Oleic acid was a major constituent, with a percentage of 42.30, 41.77 and 42.64%. Degummed oils only, without any further processing or refining, showed conversion into esters very high; these results point to H3PO4 degumming as a more effective process than water degumming. The routes obtaining methyl and ethyl biodiesels showed physicochemical characteristics compatible with the limits established by ANP Resolution 05/2012. The TG/DTG curves showed the occurrence of transesterification reactions by the displacement of the main event as observed on the curve of oil and in the lowering of temperatures in view of the boiling points of the esters being lower than those of triacylglycerol. Analysis by 1H NMR also confirmed the occurrence of the transesterification reaction of triacylglycerols in the oil and allowed determination of the rate of conversion into esters. The results about oxidation stability were good, because the biodiesels MBJC and EBJC have induction period of 13.51 h and 13.03 h without antioxidant addition when submitted a Rancimat text.

The results showed that J. curcas cultivation in Brazil represents an adequate source for biodiesel production, considering the technical standards available.

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