Orbital: The Electronic Journal of Chemistry
journal homepage: www.orbital.ufms.br
e-ISSN 1984-6428

| Vol 10 | | No. 1 | | January-March 2018 |

SHORT COMMUNICATION

Evaluation of the Properties of *Calotropis procera* Oil Aiming the Production of Biodiesel

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Article history: Received: 01 November 2017; revised: 05 January 2018; accepted: 15 January 2018. Available online: 31 March 2018. DOI: http://dx.doi.org/10.17807/orbital.v10i2.1061

Abstract:

Heavy consumption of non-renewable raw materials and/or renewable energy production produces environmental imbalance. Thus, the search for a means of sustainable and environmentally appropriate life requires scientific research in new renewable biofuels. The *Calotropis procera*, exotic oilseed widely distributed is a hardy shrub well suited to the northeast that produces seeds with oil. So, in this work were made fruit collection, drying, extraction and analysis of physical, chemical and thermal properties of oil aiming its use in biodiesel synthesis. The oil was extracted with Soxhlet method and characterized through physical-chemical, thermal analysis, and FTIR and NMR spectroscopy analysis. The results indicate that it is possible to obtain 21% ± 2 by weight of an oil physicochemical quality within the standard recommended by the legislation, except for the acid value was high and indicates that the best way to transesterification it is to make the catalyzed by acid or heterogeneous. The thermal analysis showed that the oil has high purity and is constituted by two material strips of different mass or molecular structures and has high thermal stability and convenient for the synthesis reaction. FTIR and NMR spectroscopy confirmed that the major compounds present in the oil are saturated and unsaturated fatty acids.

Keywords: Calotropis procera oil; physicochemical characterization

1. Introduction

The exaggerated consumption of non-renewable and or renewable raw material for energy production produces environmental imbalance [1]. According to the energy balance released by Brazilian Institute of Geography and Statistics (IBGE), in the year 2013 the total energy demanded in the country reached 296.2 million tons of oil equivalent (Mtoe), registering a growth rate of 4.5% against an evolution of the national gross domestic product (GDP) of 2.3% [2]. Thus, the search for a more sustainable and environmentally correct way of life provokes constant scientific research in several areas, among which the development of renewable fuels stands out.

Produced from plants such as corn, soybeans, sugar cane, castor bean, canola, babassu, among others [3], biofuels favor a significant reduction of emissions of polluting gases, being renewable and ecologically correct energy sources [4-6]. For example, ecodiesel (a mixture of biodiesel and mineral diesel) started to be sold from November 1st, 2014 at Brazilian gas stations at the concentration of 7% biodiesel [7]. However, the use of edible oils for fuel production has been criticized for reducing the amount of food available in a world experiencing difficulties in providing food for all.

Thus, research on oils for the production of

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biodiesel from non-edible sources such as jatropha [8], faveleira [9], algae [10], residual oils [11] animal oils [12] etc., have been accepted and indicate these sources as potential producers of environmentally correct raw materials for biodiesel production.

Calotropis procera Ait R. Br (Asclepiadaceae), popularly known as Silk cotton, silk flower, beach cotton, milkmaid etc., a natural shrub from Africa and Asia [13,14], has an efficient capacity of dissemination in the arid regions and semi-arid regions, being also common throughout the Northeast of Brazil. The shrub fits well on poor soils with low levels of rainfall. The plant has a number of proven uses, among which the use of ruminant's food, control of parasites and phytotherapies [15-19] is an important ingredient and is widely used in India and Africa as a remedy for certain diseases and in popular medicine for various purposes in various places [20]. Research is being carried out to obtain, characterize and use its latex [21], as well as its seeds to obtain oil to be used in the synthesis of biodiesel. The versatility of *C. procera*, with its multiple uses and rapid growth, makes it an excellent raw material for research in depth, especially its potential to produce oil for biodiesel production. In this sense, preliminary studies by Barbosa and Oliveira (2010) indicate that the oil obtained from the seeds of this plant contains mainly palmitoleic (1.73% ± 0.24), oleic (33.26% ± 1.88) unsaturated fatty acids, (35.32% ± 1.78), elaidic (4.22% ± 0.19) and, to a lesser extent, saturated (palmitic) (15.77% ± 0.25) and stearic (9.49% 0.35) [22].

In this perspective, the plant stands out as a potential economic source for the Northeast and may have its leaves used to feed ruminants [23], use of latex for the production of glue and manufacture of medicines [24, 25], seeds for oil extraction for biodiesel synthesis [26].

The objective of this work was to determine the physicochemical properties (viscosity, acidity index, free fatty acids, iodine, saponification index, peroxide index and refraction), thermal and spectroscopic properties ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR), and infrared spectroscopy with Fourier Transformed (FTIR) of the oil of this plant widely distributed in the vegetation of the Brazilian semi-arid, making possible its rational use in the production of biodiesel.

2. Results and Discussion

Physical characteristics of seed and oil content

Seeds in different maturation stages, called green and mature, were found in the same collection, as shown in Figure 1S (supplementary material). It is noteworthy that metabolic changes involved in the protection of seed tissues against desiccation damage occur during maturation, such as increased ABA (acid abscisic) content, LEA (late embryogenesis abundant) protein translation, increased sugar abundance such as sucrose, raffinose and stachyose [30]. As the constitution compounds present in green and mature seeds may be different [31] it was decided to make a drying to eliminate water and volatile compounds, allowing the standardization of the samples, as we can see from Figure 2S, which shows that green and mature seeds Presented losses of different masses when submitted to drying, both in greenhouse and at room temperature. As expected, oven drying provides mass loss in less time and with greater efficiency. In 4 hours the loss of water mass and volatiles are completed in the two types of seeds studied. Similar results, with seeds of *Sesbania virgata*, were reported by Silva et al. [30].

Physicochemical characterization

The data obtained for the physicochemical properties are presented in Table 1. In this, it is possible to verify that the acidity index is above the values for the transesterification to be done using traditional alkaline synthesis. This result is confirmed by the fatty acid index, and a large amount of free fatty acids, such as the one obtained, indicates that the product could be suffering from oxidative deterioration. It is known that high acidity is indicative of the first stage of oil decomposition. In this case, the raw material must undergo a prior treatment, in order to be used in a basic transesterification, or preferably, to use acid or heterogeneous synthesis to make the transesterification.

For the refractive index the obtained value (1.463 g/100g) is very close to that found in the literature that is between 1.473-1.477 g/100g [32]. Despite the high acidity, the peroxide index, parameter used to evaluate the degree of oxidation, is still within accepted standards [33],

since the value should not exceed 10 meq/1000g of sample. The sample had no presence of water and sediments showing that the extraction and purification processes are well done. For the saponification index the value obtained is close to that of other vegetable oils [34], for example for peanut oil it varies from 187 to 196 mg KOH/g, for canola oil it goes from 182 to 193 mg KOH/g for soybean oil from 189 to 195 mg KOH/g.

Table 1. Results obtained for the purposes of unproven calculation of *C. procera*.

Properties	Results
Acidity index (mg KOH / g)	5.540
Free fatty acid content (mg KOH / g)	108.570
Saponification index (mg KOH / g)	196.804
Index of Refraction	1.463
Peroxide content (mEv / kg)	9.370
Density (g/dm^3)	0.912
Water and sediment (%)	0.000
Viscosity (cSt)	36.583
Iodine (gI_2/100g)	43.010

The value found for the iodine index was low when compared to that of other oils, for example, Brazil nut (100.2 g I_2/100g) [35]. The importance of determining the iodine content is that through it one can have an idea of the content of unsaturated fatty acids and the propensity to oxidative rancidity.

The density was close to that of the oils commonly used for biodiesel synthesis and is within the accepted values in the legislation [36].

The kinematic viscosity obtained is within acceptable values and close to the reference values of other vegetable oils [37]. It should be noted that high oil values make the synthesis reaction slower and require changes in its conditions.

The oil yield and the physicochemical analysis obtained (See Figure 1 and Table 1) indicate that the seeds oil of *C. procera* can be extracted in good quantity and has favorable properties and that are within the specifications of the Brazilian legislation to undergo reaction Transesterification. Acidity index and kinematic viscosity (5.540 mg KOH g^{-1} and 36.583 cSt, respectively) indicate that transesterification must be carried out with acid or heterogeneous catalysis with high alcohol/oil ratio in order to avoid saponification reaction and low incomes.

Thermal characterization (TG / DTG / DSC)

Differential scanning calorimetry (DSC), thermogravimetry (TG) and derivative thermogravimetry (DTG) provide the study of the thermal behavior of the sample. The TG/DTG curves (Figure 1) show two thermal events that correspond to the presence of the compound of materials with two characteristic bands of volatilization; One between the temperature ranges of 133-301 °C with a maximum at 252 °C and one that occurs between the temperature ranges of 301-479 °C with a maximum at 411 °C.

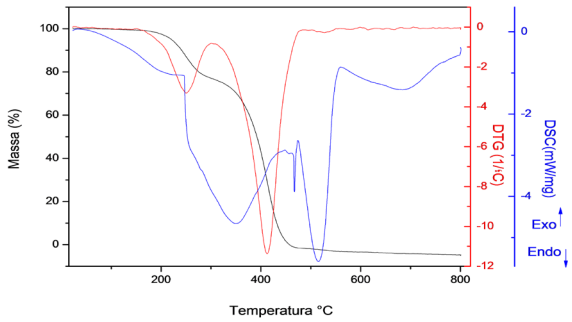

Figure 1. Thermal curves showing the typical *C. procera* oil behavior.

The TG/DTG curves (Figure 1) indicate that most of the material is volatilized, with no indication of organic impurities (solvent residues) or water in it. At the end of the experiment there is a small amount of residue, which may be due to inorganic impurities or compounds of high molecular mass arising from reactions that occurred during the experiment and which increase or cause chain cross-linking and thus prevent their volatilization.

Table 2 specifies the percentage loss, the initial and final temperature of each event, the maximum loss temperature and the final residual weight.

Table 2. Thermogravimetric data obtained for *C. procera* oil.

Event	T (ºC)	T ºC) Max.	Mass loss (%)	Residual weight (%)
1	133-301	252	20.97	1.6
2	301-479	411	77.43	

These results indicate that the oil exhibits good thermal stability to be used in the transesterification reactions which are generally carried out at low or medium temperatures (below 100 °C) depending on the characteristics of the oil and the conditions chosen to carry it out.

The DSC curves of Figure 1 shows that the peaks with maxima at 252 °C and 411 °C are endothermic and as they occur with mass losses, are interpreted as being the volatilization of compounds of different molecular weight or with different structures. In addition, two exothermic peaks are seen with maximum points in ± 470 °C and 580 °C, which would correspond to the thermal degradation of the present compounds. Note that these peaks occur without mass loss in TG indicating that these reactions occur in the gaseous state. Lastly, we have a long endothermic peak in the range of 580 °C to 800 °C with peak maximum at approximately 700 °C, indicating that the degradation products are volatilized or can react again and form the carbonized residues obtained at the end.

FTIR

The structural characterization via infrared spectroscopy (FTIR) obtained for *C. procera* oil in the 500 to 4000 cm^{-1} range is shown in Figure 3S (Supplementary Material). For the natural oil, the intense carbonyl stretching band at 1745 cm^{-1} and the C-O bond vibrations at 1240, 1168 and 1096 cm^{-1} are diagnostic for the ester linkage at triacylglycerol. The low intensity band at 3000 cm^{-1} can be attributed to the C-H stretch of unconjugated double bonds, symmetrically disubstituted in *cis* position. This assignment is supported on the out-of-plane CH strain at 719 cm^{-1}. At approximately 1455 and 1376 cm^{-1}, the axial deformation band of the aliphatic C-H groups is observed.

The asymmetric and symmetric axial deformations of the C-H bond of alkanes appear at 2854 and 2925 cm^{-1}.

^{1}H and ^{13}C Nuclear Magnetic Resonance

Figures 4S and 5S (Supplementary Material) shows the ^{1}H and ^{13}C NMR spectra of *Calotropis procera* oil.

In the ^{1}H NMR spectrum the signals of the olefinic hydrogens were observed in the region between 5.20 and 5.38 ppm. The signals at 1.99 ppm and 2.73 ppm correspond to the allylic protons ($-CH_2-CH=CH-$) and internal allylic protons ($-CH=CH-CH_2-CH=CH-$), respectively. The latter indicates the presence of polyunsaturated acids, such as linoleic (C18: 2).

The sign of the α-carbonylic hydrogens appears as a triplet at 2.27 ppm. The double doublets at 4.10 and 4.26 ppm are assigned to the hydrogens of the methylene groups of that portion of the glycerol. The signal at 0.84 ppm was assigned to the methyl methyl group.

The ^{13}C RMN spectrum shows two signals, at 172 and 173 ppm, relating to the carbonyl groups of esters. The corresponding olefinic carbons of the unsaturated fatty acids were identified as the signals between 127 and 130 ppm. The signals at 62 and 68 ppm refer to the carbons attached to the oxygen atoms of the glycerol moiety, CH_2 and CH, respectively. Signals between 22 and 34 ppm refer to the other ($-CH_2-$) carbons present in the triglyceride structure of *C. procera* oil. The signal at 14 ppm is assigned to the methyl group.

By analyzing the ^{1}H NMR spectrum of the *C. procera* oil (Figure 4S, supplementary M.), integrating the glycerolic hydrogens (4H, δ 4.10 and δ 4.26) and the allylic hydrogens (9H, δ), the fatty acid composition of unsaturated fatty acids was estimated to be 75.3% and 24.7%, respectively. Among the unsaturated fatty acids, 34.0% were from polyunsaturated fatty acids and 41.3% of monounsaturated fatty acids. These results are very close to those reported by Barbosa and Oliveira [21].

Therefore, from the obtained results it can be concluded that:

• From the seeds of *C. procera* can be extracted, in good quantity (21 ± 2%), oil with the most physicochemical properties good or chemically contoured for the synthesis of biodiesel.

• The high acidity index indicates that the transesterification must be by acid or heterogeneous route to avoid reactional problems.

• ^{1}H and ^{13}C NMR spectroscopic analyzes confirmed that the constituents of the raw material

are saturated (24.7%) and unsaturated (75.3%) fatty acids.

• Thermal analysis indicated that the oil is thermally convenient to be transesterified and that the sample has high purity and no moisture.

3. Material and Methods

The seeds of *C. procera* were collected in the municipality of Mossoró, dried in greenhouse and in the environment. Subsequently, the oil of the seeds was extracted in an apparatus soxhlet with *n*-hexane as solvent for 4 hours, obtaining about 21% (± 2) of average yield. Figure 2 shows the % of oil extracted as a function of extraction time, indicating that the time of 4 hours is sufficient to extract all the oil from the seeds. This percentage is very close to that obtained by Barbosa et al. [27] and larger than that extracted from soybean seeds, which today is the most commonly used oilseed for the production of biodiesel oil.

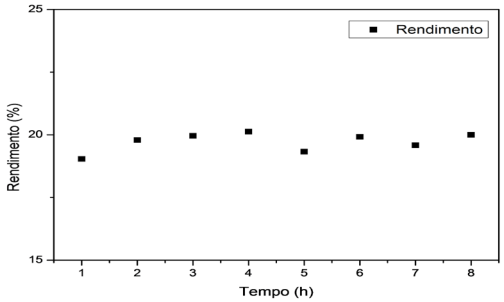

Figure 2. % of oil extracted as a function of extraction time.

The physicochemical properties of the oil were determined according to standard procedures [28, 29].

4. Conclusions

The results indicate that the *C. procera* oil presents a good potential to be used in the synthesis of biodiesel, indicating that it is necessary to deepen the research on the uses of *C. procera*, since these, along with oil exploration for the synthesis of biodiesel is a promising economic, social and environmental activity, which can generate jobs and income for a region without these resources.

Supporting Information

Figures 1S, 3S, 4S, 5S, and the material and methods used in this work are described in supplementary material, available online at: http://www.orbital.ufms.br/index.php/Chemistry/article/downloadSuppFile/1061/310

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