*Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 649–652*

# THERMOGRAVIMETRIC AND CALORIMETRIC EVALUATION OF BABASSU BIODIESEL OBTAINED BY THE METHANOL ROUTE

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The growing petroleum deficit requires the development of alternative fuel sources. Biodiesel is a good alternative, as it is a biodegradable and renewable product, which obeys the carbon cycle. In this work, the biodiesel from babassu was synthesized using the methanol route, and characterized by physico-chemical analyses in order to make able the investigated biodiesel to fulfill with its properties the requirements of Brazilian National Agency for Petroleum, Natural Gas and Biofuel (ANP). Besides gas chromatography, IR spectroscopy experiments and thermoanalytical measurements in air and in nitrogen were done to determine the main thermal decomposition processes and calorimetric events. The evaporation temperature of babassu biodiesel was similar in both atmospheres, started around 52 in air and around 60°C in nitrogen.

**Keywords:** *babassu, biodiesel, thermogravimetry*

## Introduction

Most of the energy consumed in the world originates from petroleum, coal and natural gas. The depletion of the energy sources, especially fossil fuels, knowing that they are non-renewable sources, has been motivated the development and make able technologies to use alternative fuel sources [1].

According to the definition of the National Biodiesel Board of the USA, biodiesel is a mono alkyl ester derived from long chain fatty acids originating from renewable sources such as vegetable oils or animal fat. The use of biodiesel is associated to the substitution of fossil fuels in Otto cycle engines. Biodiesel is a biodegradable and renewable product which obeys the carbon cycle [2].

The coconut of babassu (*Orbinya martiana*) contains in average 7% of almonds with 62% of oil. Among them lauric acid ($C_{12}H_{24}O_2$) is the most important fatty acid. On the pragmatic point of view, babassu can not be considered as an oleaginous species, once it contains only 4% of oil. However, considering the millions of hectares of tropical forests with a great amount of babassu palm trees and the possibilities of the integral usage of the coconut, babassu constitutes, potentially an extraordinary raw material source for biodiesel oil production, meanwhile the other parts of the tree can be used for other purposes [3]. The endocarp of babassu, one of these components, produces a high quality charcoal, which was successfully tested by Brazilian steel industry [4].

Thus, this work aims to study the thermal behavior of the methanol biodiesel from babassu. Besides thermal analysis, gas chromatography and infrared spectroscopy were used for supplementary characterization.

## Experimental

### *Methyl ester production*

Babassu biodiesel was obtained by transesterification in order to modify some important technological parameters of the vegetable oil to make them closer to the parameters of mineral diesel oil.

The reaction was carried out keeping 6:1 molar ratio of methyl alcohol and babassu vegetable oil, using KOH as catalyst (1%), under constant agitation at room temperature. After breakage of triglyceride molecules, a mixture of methyl esters of the corresponding fatty acids was obtained, resulting also glycerin as co-product [5].

The mixture was transferred to a separation funnel, for phase separation. After 20 min two different phases were observed: the methyl ester one (less dense and clearer) and the glycerin one (denser and darker).

After resting for 24 h, the glycerin was removed. The remaining material was submitted to a washing process in order to purify the esters. The process

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*1388–6150/$20.00*

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started with a neutralization step, using 0.1 M HCl solution, followed by water rinsing. The neutralization of the catalyst was confirmed using a 1% phenolphthalein solution in rinsing water. The washing was followed by the evaporation step at 100°C. After purification the biodiesel was characterized.

### *Methods*

#### Physico-chemical analyses

The physico-chemical tests were performed according to standardized methods. Tests for sulfur content, specific density at 20°C, flash point and acid number determinations were done according to the standards adopted by ANP (Brazilian National Agency for Petroleum, Natural Gas and Biofuels) [6], based on ASTM standards. The tests to determine the free and total glycerin, moisture content, saponification number and free fatty acids were carried out in agreement with the standards of the American Oil Chemists Society.

#### Infrared spectroscopy

Infrared spectroscopy was used to investigate the compounds formed by the transesterification reaction of the babassu oil. The IR spectra were recorded using a Bomem model MB-102 spectrometer, using KBr pellets, in the range of 4000–400 $cm^{-1}$.

#### Gas chromatography

The obtained biodiesel was qualitatively analyzed by gas chromatography (GC) in order to evaluate the conversion of fatty acids esters during the transesterification reaction. A GC-FID Varian 3800 chromatograph was used with split/splitless injector operating with or without flow division coupled to a FID detector. The stationer phase was the blend of 5% phenyl siloxane and 95% polydimethylsiloxane. The temperature of the injector was 290°C and the detector was kept at 300°C with flow rate of 1:50.

#### Thermal analyses

Thermogravimetric and calorimetric curves were obtained in a simultaneous TG/DTA thermal analyzer (model SDT 2960, TA Instruments). The applied heating rates were 10, 15 and 20°C $min^{-1}$, under air and nitrogen atmospheres, with a flow rate of 100 mL $min^{-1}$ in the temperature range of 25–600°C.

## Results and discussion

The quality of the oil influences the transesterification reaction. Therefore, the acid number of the oil must have below 1.0 mg KOH $g^{-1}$, and should have also low moisture content to allow a good reaction yield in the biodiesel production, and besides to avoid corrosion problems in the diesel engines.

The results of acid number, free fatty acids, saponification number and moisture content of babassu oil were 1.23 mg KOH $g^{-1}$, 2.82, 126.89 and 0.05%, respectively, indicating that the quality of babassu oil is adequate for the biodiesel production (Table 1).

**Table 1** Physico-chemical data of babassu biodiesel

| Property | Biodiesel | Limit |
|---|---|---|
| Nature | limpid and free from impurities | – |
| Color | yellow | – |
| Acid number (max)/ mg KOH $g^{-1}$ | 0.03 | 0.80 |
| Specific density at 20°C/kg $m^{-3}$ | 879.5 | note |
| Flash point (min)/°C | 112.0 | 100.0 |
| Copper corrosion (max) | 1 | 1 |
| Total sulfur (max)/mass% | 0.005 | note |
| Free glycerin (max)/mass% | 0.0075 | 0.02 |
| Total glycerin (max)/mass% | 0.12 | 0.38 |
| Moisture (max)/mass% | 0.05 | 0.05 |
| Saponification number/mass% | 121.8 | – |
| Free fatty acids/mass% | 0.06 | – |

Surveying the data in Table 1, it can be noticed that babassu biodiesel obtained by the methanol route is in agreement with parameters established by the Resolution 42 of ANP [6].

The infrared spectrum (Fig. 1) of the methanol babassu biodiesel presents bands, which are characteristic for esters: a strong band attributed to the axial deformation of the C=O bond (1742 $cm^{-1}$) and two medium bands are attributed to the axial deformation of the C–O bond (1100 and 1170 $cm^{-1}$).

The gas chromatography data (Table 2) indicated 97.38% of conversion of the triglycerides to methyl esters. The composition of the babassu biodiesel presented methyl laureate as the major constituent (25.81%).

The babassu biodiesel, whose major component is methyl laureate is composed of a blend of fatty acid esters. More than 70% of these esters are saturated. Thus, it has a higher stability against oxidation than a blend of unsaturated fatty acid esters, since unsaturation of the vegetable oils and their corresponding esters (biodiesel) increases their susceptibility to oxidation [7].

**Table 2** Composition of the fatty acids present in the methanol babassu biodiesel

| Numerical symbol | Systematic name | Common name | Fatty acid ester composition/mass% |
|---|---|---|---|
| C 6:0 | hexanoic acid | caproic acid | 0.37 |
| C 8:0 | octanoic acid | caprylic acid | 3.81 |
| C 10:0 | decanoic acid | capric acid | 5.63 |
| C 12:0 | dodecanoic acid | lauric acid | 25.81 |
| C 14:0 | tetradecanoic acid | myristic acid | 17.27 |
| C 16:0 | hexadecanoic acid | palmitic acid | 12.69 |
| C 18:0 | octadecanoic acid | stearic acid | 19.36 |
| C 18:1(9) | 9-octadecanoic | oleic acid | |
| C 18:2(9,12) | 9,12-octadecadienoic acid | linoleic acid | 6.70 |
| C 18:3(9,12,15) | 9,12,15-octadecatrienoic acid | linolenic acid | 0.15 |

**Table 3** Temperatures and mass losses, taken from the TG curves

| Heating rate/°C min$^{-1}$ | Steps | Air atmosphere | | Nitrogen atmosphere | |
|---|---|---|---|---|---|
| | | temperature range/°C | mass loss/% | temperature range/°C | mass loss/% |
| 10 | 1st | 52–294 | 92.9 | 60–262 | 85.1 |
| | 2nd | 294–414 | 5.5 | 262–380 | 14.2 |
| | 3rd | 414–535 | 1.9 | | |
| 15 | 1st | 60–283 | 85.0 | 65–276 | 85.2 |
| | 2nd | 283–353 | 9.1 | 276–404 | 13.9 |
| | 3rd | 409–492 | 3.5 | | |
| 20 | 1st | 68–286 | 85.2 | 76–291 | 85.3 |
| | 2nd | 286–382 | 12.5 | 291–414 | 13.8 |
| | 3rd | 497–559 | 1.1 | | |

All thermogravimetric profiles (Fig. 2, Table 3) of the babassu biodiesel in air atmosphere presented three mass loss steps. In nitrogen two steps were noticed. These steps were related to the evaporation of biodiesel followed by the decomposition of the residue in nitrogen or by combustion in air.

The temperatures and the corresponding mass losses are presented in Table 3.

Increasing of the heating rate, the mass loss steps shifted towards higher temperatures. This occurs since at higher heating rates the heat distribution is less uniform, which increases the temperature gradient and provokes temperature displacement [8]. It should be emphasized that the first mass loss may be associated to the evaporation of esters, since the boiling point of methyl laureate is of 262°C [9].

In all the DTA curves of the biodiesel (Fig. 3 and Table 4), in air one endothermic and two exothermic transitions were observed, while only one endothermic transition was noticed in nitrogen. These transitions are detailed in Table 4.

Comparing the thermal analyses carried out in different atmospheres, it was observed that the temperature of evaporation of the biodiesel has no meaningful

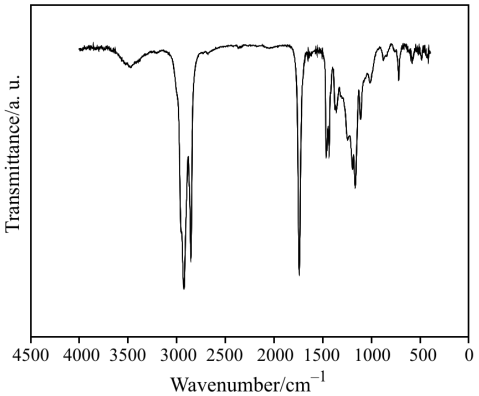

**Fig. 1** Infrared spectrum of the methanol biodiesel from babassu

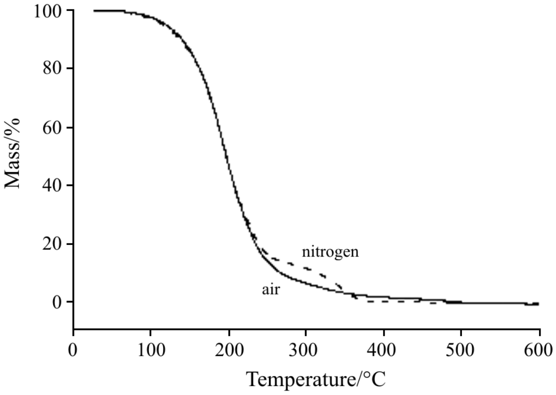

**Fig. 2** TG curves of biodiesel in air and nitrogen (heating rate: 10°C min$^{-1}$)

**Table 4** DTA results of babassu biodiesel in air and nitrogen atmospheres

| Heating rate/°C min$^{-1}$ | Air atmosphere | | Nitrogen atmosphere | |
|---|---|---|---|---|
| | transitions | peak temperature/°C | transitions | peak temperature/°C |
| 10 | 1st (endo) | 194 | 1st (endo) | 199 |
| | 2nd (exo) | 255 | | |
| | 3rd (exo) | 380 | | |
| | 4th (exo) | 511 | | |
| 15 | 1st (endo) | broad band | 1st (endo) | 208 |
| | 2nd (exo) | 253 | | |
| | 3rd (exo) | 341 | | |
| | 4th (exo) | 473 | | |
| 20 | 1st (endo) | 220 | 1st (endo) | 220 |
| | 2nd (exo) | 327 | | |
| | 3rd (exo) | 488 | | |
| | 4th (exo) | 541 | | |

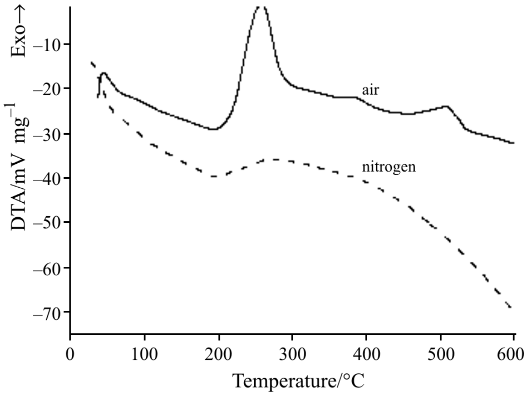

**Fig. 3** DTA curves of biodiesel in air and nitrogen (heating rate: 10°C min$^{-1}$)

change. Babassu biodiesel was thermally stable up to 52°C in air and up to 60°C in nitrogen. On the other hand, higher temperatures of decomposition are observed in an oxidizing atmosphere comparing to an inert one, indicating that oxidation occurs, leading to the formation of more stable compounds. In air, all the transitions observed in the DTA curves are exothermic and a higher number of decomposition steps are present.

## Conclusions

According to the physico-chemical of babassu biodiesel its parameters fit the expectations established by 42 resolution of ANP.

The infrared spectrum of the methanol biodiesel presents characteristic bands of esters, confirming that a biodiesel was obtained. Gas chromatography data indicated a 97.38% of conversion of the triglycerides to methyl esters.

The thermal behavior of the biodiesel using TG and DTA simultaneous method was investigated. The evaporation of the biodiesel did not change remarkably in different atmospheres. On the other hand, in air, biodiesel presents more decomposition steps with higher decomposition temperatures indicating the formation of more stable compounds, which is due to oxidation processes. The combustion of these more stable compounds takes place at higher temperatures. In nitrogen the methyl esters of biodiesel decompose.

## Acknowledgements

The authors acknowledge CNPq and CAPES for the financial support.

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DOI: 10.1007/s10973-006-7765-1