FULL PAPER

In situ Transesterification of Babassu for Production of Biodiesel as Sustainable Energy Option for Aratuba Community in State of Ceará, Brazil

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Abstract:

This work reports the obtaining biodiesel of babassu (Atallea speciosa) collected in Aratuba-CE-Brazil using transesterification in-situ methodology, and chromatographic, spectroscopic and thermogravimetric characterization as way of improving its utilization as energetic resource by local producers. Lauric acid was found as majority compound of the oil (46.65%) by chromatographic analysis (CG-MS). Spectroscopy analysis of nuclear magnetic resonance of hydrogen and carbon (1H and 13C NMR) confirmed the obtaining of the biodiesel and reaction conversion was 99.8 ± 0.6 %. Physicochemical analyzes as specific mass at and kinematic viscosity at 20 and 40°C, acid number, iodine number and free glycerin were performed, and the parameters were in accordance with Brazilian legislation for biodiesel. Thermogravimetric analysis (TG) in oxidative and inert atmosphere and three different heating rates were made in order to evaluate the thermal stability of babassu biodiesel and the average value of the activation energy (Ea) determined by isoconversional method proposed by Flynn-Wall-Ozawa and modified by Doyle was Ea = 96.87 ± 3.59 kJ.mol⁻¹ for inert atmosphere and Ea = 108.04 ± 15.19 kJ.mol⁻¹ for oxidative atmosphere. Rancimat curve showed induction time higher than specified by the Brazilian legislation for biodiesel (11.57h). Thus, the results corroborated the production of biodiesel as cleaner and sustainable option for the peasants of Aratuba.

Keywords: babassu; biodiesel; in-situ transesterification; spectroscopy; thermogravimetric analysis

1. Introduction

The recent advances in the study of the biodiesel as source energy demonstrate the crescent worldly worry about the use of the fossil resources, once fuels as petroleum, coal, natural gas and others are non-renewable and pollutants. Thus, the biodiesel topic is largely discussed in terms of economy world and environment question [1-3]. In Brazil, one of the larger world producer and consumer of biodiesel, the scenario of the production is peculiar and not favorable: the most important natural resource used in the biodiesel production is edible oil, the soybean, and this fact constitutes an embarrassment to the sustainability of the process of production and consumption [4-5].

Other interesting point in the discussion about biodiesel in Brazil is related to consuming and production by familiar producers and in theory must be fomented by Brazilian government through the Nacional Program for Biodiesel. Use of biodiesel as fuel for family farmers and the possible gains in Brazilian communities is discussed in the literature [6-7]. One of the most important factors in this case is the use of...
alternative raw materials as non-edible oils and palm trees in the biodiesel production instead edible oils [8-9].

Native of the North and Northeast of Brazil, babassu (*Attalea speciosa*) (Figure 1) is an example of palm tree with potential for biodiesel production [4, 10-11]. The specie belongs to the Arecaceae family. Known as “tree of life”, babassu extraction is important to income of peasant households [12] and in Brazil is notorious the extraction of babassu for use as material for house constructions, energetic finality and food applications.

![Figure 1. Babassu tree located in Aratuba, state of Ceará, Brazil.](image1.png)

Babassu coconut used in this research was collected in Aratuba region, located in Ceará state, Brazil. It is important to emphasize the using of babassu as energetic resource by Aratuba community by a cooperative: in this local, the residents use the babassu coconut as solid fuel for steam boiler and the straw for handicrafts (Figure 2). Unfortunately, it was observed that the potential of the babassu as source for the production of biodiesel is completely ignored by the local producers. In order to offer to the rural producers of region of Aratuba a practical and clean way to produce babassu biodiesel and to improve the using of babassu coconut as energetic resource *in-situ* transesterification was evaluated in this research. *In-situ* transesterification process consists in the transesterification of the botanical material without the extraction of the oil. Once the steps as extraction and purification of the oil are eliminated, production costs of the biodiesel are reduced [13-14] and the *in-situ* process becomes a simple and feasible alternative for the future of the obtaining of the biodiesel [15]. Thus, the aim of this work is to investigate the potential of the babassu coconut from Aratuba – CE – Brazil as raw material for the production of biodiesel through *in-situ* transesterification methodology, to characterize the bioproduct using spectroscopy and thermogravimetric techniques and evaluating the quality of the biofuel through physicochemical analysis. Once the quality of biofuel can be proved, babassu biodiesel could be presented to Aratuba community cooperative as option of fuel.

![Figure 2. Benefit of babassu coconut by local peasant from Aratuba.](image2.png)

2. Results and Discussion

Physicochemical properties as acid value, kinematic viscosity and specific gravity at 20 and 40 °C, iodine value and free glycerin were determined. Acid value found was lower than the value stablished by the Brazilian legislation for biodiesel samples. Specific gravity and kinematic viscosity at 20 and 40 °C were also in accordance with the Brazilian legislation [19]. Iodine value demonstrates the low content of unsaturation of the fatty acid chain and consequent desirable chemical stability of the biodiesel. The free glycerin value is also in accordance with legislation for biodiesel. The values of the physicochemical parameters were compiled in Table 1. It is important to emphasize that the Brazilian legislation for biodiesel is in according with international parameters.
Fatty acid composition of babassu oil was determined through chromatographic analysis of methyl esters. Lauric acid was found as majority compound (46.65%) followed by miristic acid (17.59%) and oleic acid (16.37%). Around 85% of the oil composition do not present unsaturation that reflects the low value of the iodine number and suggest a good chemical stability of the biodiesel. The composition of the oil was described in Table 2.

Table 1. Physicochemical properties of babassu biodiesel.

| Property                                      | Babassu biodiesel | ANP 45/2014 |
|-----------------------------------------------|-------------------|-------------|
| Specific gravity at 20 °C (Kg m⁻³)            | 854 ± 9.2         | 850-900     |
| Specific gravity at 40 °C (Kg m⁻³)            | 832 ± 8.0         | Not specified |
| Kinematic viscosity at 20 °C (mm² s⁻¹)        | 6.75 ± 0.22       | Not specified |
| Kinematic viscosity at 40 °C (mm² s⁻¹)        | 3.04 ± 0.12       | 3.0-6.0     |
| Acid number (mgKOH/g)                         | 0.013 ± 0.002     | 0.50        |
| Iodine number (gI₂/100g)                      | 48.6 ± 1.1        | Registered  |
| Free glycerin (%)                             | 0.024 ± 0.002     | 0.25        |

Table 2. Fatty acid composition of the babassu oil.

| Compound                | Composition (%) |
|-------------------------|-----------------|
| Caprilic acid (8:0)     | 2.19            |
| Capric acid (10:0)      | 3.60            |
| Lauric acid (12:0)      | 46.65           |
| Miristic acid (14:0)    | 17.59           |
| Palmitic acid (16:0)    | 8.17            |
| Estearic acid (18:0)    | 3.13            |
| Oleic acid (18:1)       | 16.37           |
| Linoleic acid (18:2)    | 2.15            |
| Total                   | 99.85           |

³H NMR spectrum (Figure 3) showed signal at 3.65 ppm correlated to methoxide protons of the ester function and confirming the obtaining of the methyl ester of babassu while the triplet at 2.28 ppm is correlated to the α-methylene protons to ester. The absence of the peaks at the region between 4.0 and 4.5 ppm in the ³H NMR excludes the possibility of the presence of glycerol in the biodiesel sample. The signal between 5.2 and 5.5 ppm is related to the hydrogens of -C=O- and its low intensity reflects the low content of unsaturation of the oil that is also observed in the low value of the iodine number in physicochemical analysis. The conversion can be calculated from the ³H NMR through equation (Eq. 1) that is largely discussed in the literature [20-21]. Equation 1 is based in the area of the peaks of methoxide protons, signal around 3.60 ppm, and α-methylene protons, signal around 2.30 ppm. The average value found was 99.8 ± 0.6%.

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\text{Conversion(\%)} = 100 \times \frac{\text{2A\text{Methoxide}}}{\text{3A\text{α-carboxyl methylene}}} \quad \text{Eq. 1}
\]

Figure 3. ³H NMR spectrum of the babassu biodiesel.
$^{13}$C NMR (Figure 4) corroborates the results found with the analysis of the $^1$H NMR. Peak at 51.4 ppm confirms the presence of methoxide carbon of ester function. Signal at 174.29 ppm is correlated to the carbonyl of ester. The low intensity of the signals near 130 ppm confirms the low content of unsaturation of the fatty acid chains observed in the others analysis.

**Figure 4.** $^{13}$C NMR spectrum of the babassu biodiesel.

Result of conversion obtained by in-situ transesterification from babassu was interesting in comparison with other techniques: Enzymatic route with microwave irradiation as heating was utilized in order to obtaining babassu biodiesel and Da Rós and contributors obtained a product in accordance with international parameters for biodiesel [10]. Conversion observed using NMR analysis was 100% [10]. But enzymatic process is expensive in comparison with in-situ process and it is necessary to be careful in the handling of the enzymes and reaction time of enzymatic route was higher than applied in this research, around 10 hours. Babassu biodiesel was also obtained by ultrasound [27] and the time of reaction was lower than in-situ process even when other factors as reactants, temperature or turbulence were not optimized. The conversion was similar between the methods (97%). Heterogeneous catalysis by catalyst of Cu(II) and Co(II) ions adsorbed in chitosan showed yield between 71.89% and 94.01% and this conversion depended on metal complexed with chitosan. Reaction time was similar to applied in in-situ transesterification [28]. Several advantages for in-situ transesterification were observed in comparison with these techniques: reaction time was similar or lowest, conversion was highest, and the process was less expensive. This way in-situ transesterification will can be applied by Aratuba community in biodiesel production easier than these methods.

Result of conversion was also interesting in comparison with others biomass when in-situ transesterification is applied: linseed was submitted to in-situ transesterification using tetrahydrofuran as co-solvent and the conversion was slight lower than obtained in this research [29]. It is important to emphasize there is no co-solvent in the process with babassu. Comparable results for castor seeds were also reported [30]. In-situ process is also interesting when applied to algae [31-33] but reaction parameters must be evaluated careful to provide conversions levels similar to observed for others raw materials.

Thermogravimetric analyses were performed in three different heating rates and two atmospheres: oxidative (synthetic air) and inert (N$_2$). Both TG curves (Figures 5 and 6) showed one thermal event. This event can be correlated to the volatilization and/or pyrolysis of the methyl esters in the inert atmosphere and/or combustion in the oxidant atmosphere. Onset temperature in inert atmosphere was higher than observed in oxidative atmosphere in all heating rates considered in this work, proving the action of the oxygen to accelerate the thermal decomposition. Others representative data (burn-out temperature, peak temperature and mass degradation) were compiled in Table 3.
Table 3. Representative TG curve data of the thermal degradation of the babassu methyl biodiesel.

|          | T\textsubscript{onset} (°C) | T\textsubscript{peak} (°C) | T\textsubscript{burn-out} (°C) | α (%) |
|----------|-----------------------------|-----------------------------|-------------------------------|-------|
|          | Air                         | N\textsubscript{2}          | Air                           | N\textsubscript{2}          | Air   | N\textsubscript{2}          |
| 10 °C min\textsuperscript{-1} | 224.17                      | 245.73                      | 365.12                        | 368.16                      | 299.61 | 342.23                      | 90.01 | 99.45 |
| 20 °C min\textsuperscript{-1} | 254.38                      | 257.30                      | 383.92                        | 387.99                      | 317.34 | 364.09                      | 91.29 | 99.47 |
| 30 °C min\textsuperscript{-1} | 255.02                      | 267.22                      | 387.08                        | 402.86                      | 318.01 | 382.37                      | 91.81 | 99.45 |

Thermogravimetric data allowed the determination of the activation energy – $E_a$ for the babassu methyl biodiesel. The method proposed by Flynn-Wall-Ozawa and modified by Doyle [16-18] do not require the knowing of the kinetic mechanism and the value of activation energy is obtained by the linear regression between the $\ln(\beta)$, where $\beta$ is the heating rate, and the reciprocal temperature of the conversion considered. The isoconversional interval studied was 10-90% (Figures 7 and 8) and the values were compiled in the Table 4. The average values found were $E_a = 96.87 \pm 3.59$ kJ mol\textsuperscript{-1} for inert atmosphere and $E_a = 108.04 \pm 15.19$ kJ mol\textsuperscript{-1} for oxidative atmosphere. These values are higher than reported for mineral fuels [22-24] and demonstrate the good thermal stability of the babassu biodiesel [22-26].
Oxidative stability of babassu biodiesel can be considered excellent for a biodiesel sample. Figure 9 shows Rancimat curve obtained during biodiesel analysis where green line is correlated to electric conductivity due to oxidized compounds and blue line is obtained by second derivative of green line and its maximum indicates the induction time. Induction time (Pointed by red line) established by Brazilian legislation for biodiesel (ANP, 2014) is 6 hours. The time determined by Rancimat curve for babassu biodiesel was around 11 hours. This behavior can be explained by the low content of unsaturation. The result is complementary to the chromatographic, spectroscopy, physicochemical and thermogravimetric analysis that suggest the low content of unsaturation and corroborates with the thermal stability observed for babassu biodiesel.

Table 4. Correlation coefficient ($R$) and activation energy ($E_a$) obtained from Flynn-Wall-Ozawa method for babassu methyl biodiesel.

| Conversion (%) | Oxidative atmosphere | | Inert atmosphere | |
| | $R$ | $E_a$ (kJ mol$^{-1}$) | $R$ | $E_a$ (kJ mol$^{-1}$) |
| 10 | 0.9689 | 130.64 | 0.9981 | 97.05 |
| 20 | 0.9696 | 119.01 | 0.9974 | 99.26 |
| 30 | 0.9717 | 120.38 | 0.9973 | 97.05 |
| 40 | 0.9552 | 121.78 | 0.9977 | 104.01 |
| 50 | 0.9529 | 108.79 | 0.9991 | 95.86 |
| 60 | 0.9548 | 99.25 | 0.9989 | 93.80 |
| 70 | 0.9495 | 89.62 | 0.9981 | 97.04 |
| 80 | 0.9679 | 91.99 | 0.9994 | 96.89 |
| 90 | 0.9712 | 93.90 | 0.9991 | 90.89 |

As cited in the introduction, botanical fresh material was obtained in Aratuba – CE – Brazil through local producers.

In-situ transesterification was conducted in system formed with round bottom flask and condenser. The babassu coconut was cracked and pulverized (Figure 10). Oil content of babassu coconut was determined through Soxhlet system and extraction yield found was 41.92% ± 4.66. This way solution formed by methanol P.A (1/90 oil/alcohol molar ratio) and potassium hydroxide (5% w oil) as catalyst was added to pulverized babassu coconut. An amount of alcohol higher than observed in homogeneous transesterification process is needed since the alcohol acts as transesterification agent and oil extractor and the covering of the material by alcohol is important for the reaction success. Reactional medium was kept under stirring and reflux temperature for 3 hours. At the end of the reaction time, the liquid phase was filtered, and the biodiesel formed was extracted with hexane P.A. Biodiesel was extracted with hexane due reaction be conducted in laboratory scale. For reactions in pilot and/or industrial scale, after separation between glycerol and liquid phase, unreacted alcohol can be removed by evaporation under reduced pressure. Hexane was removed through evaporation with reduced pressure and biodiesel was washed until the neutralization of wash water and dried with anhydrous sulfate. After, biodiesel was kept on oven at 105 °C for removal water traces.

Physicochemical properties were determined under international parameters. Acid value was conducted using ASTM D-298 method, EN 14111 method for iodine value, ASTM D-1298 method
for specific mass at 20 °C, ASTM D-445 method for kinematic viscosity at 40 °C and EN 14106 method for free glycerol content. The analyses were made in triplicate and the value reported represents the average value. Additional analysis of specific mass at 40 °C and kinematic viscosity at 20 °C were performed.

Chromatographic analysis (CG-MS) was performed in gas analyzer using column DB-1 controlled by 27-split rate, inlet pressure of 100 KPa, injector and detector temperatures of 280 °C, total flow of 50 mL per minute, automatic sample port, oven ramp of 80 to 180 at 5 °C min⁻¹ and 180 to 280 at 10 °C min⁻¹ and helium as carrier gas. The high-resolution mass spectra of the constituents were obtained by electrospray ionization in mass spectrometer model LCMS-IT-TOF (225-07100-34) SHIMADZU®.

Nuclear magnetic resonance (NMR ¹H and ¹³C) data were recorded using a Bruker® spectrometer model DRX-500 operating in 500 MHz of frequency for the hydrogen spectra and 125 MHz of frequency for the carbon spectra. Deuterium chloroform was utilized as solvent.

Thermogravimetric curves were obtained using TA Instruments® equipment model Q50 V20. It was used synthetic air and nitrogen, gas flow of 40 mL min⁻¹, three constant heating rates (10, 20 and 30 °C min⁻¹), analysis temperature interval of 25 to 600 °C and platinum plate as sample port. Analysis was performed under three different rates Ozawa-Flynn-Wall method [16-18] with approximation proposed by Doyle, which the plot of the neperian logarithm of the heating rate versus the reciprocal temperature allows the determination of the activation energy in different degrees of conversion, was used to determine the thermodynamic parameter of the biodiesel sample.

Stability oxidative was evaluated through Rancimat analysis using 3 g of sample, analysis temperature of 110 °C and oxygen flow of 10 L h⁻¹. Metrohm® equipment was used and analysis was conducted under international parameter EN 14112.

4. Conclusions

The babassu showed itself as a good option for the production of biofuel and represents an alternative for energetic use by the peasants of Aratuba-CE-Brazil. The in-situ transesterification provided a simple method to obtaining the biodiesel and steps as oil extraction and using of solvents which demand time and resource were not necessary. In addition to production biodiesel, at the end of the process the rejects of the babassu coconut could be utilized as solid fuel for the steam boiler by the peasants of Aratuba as well. The spectroscopy, thermogravimetric and oxidative analysis were important in the characterization of the biofuel and their results were complementary. The ¹H NMR and ¹³C NMR proved the obtaining of the methyl ester and demonstrated the low content of unsaturated chains in the fatty acids of the babassu oil. The thermogravimetric analyses corroborate the quality of the biofuel once the onset temperature in oxidative atmosphere was relatively high and the values of activation energy found were higher than values reported to mineral fuels. Allied to these results, the induction time determined by Rancimat analysis was higher than stablished in legislation for biodiesel and proved the excellent oxidative stability, beyond the thermal stability. Once the quality of the babassu biodiesel was proved and the in-situ transesterification do not required specific equipment or reactants, this work shows its social and economic importance and reinforces the necessity of better employment of the babassu as energetic resource.

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