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Study of ethylic Babassu biodiesel properties at low temperatures

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Abstract Nowadays the growing fuel deficit requires the development of alternative fuel sources. Biodiesel is a good substitute to the conventional diesel because it is quite similar to the fossil fuel in its main characteristics. However, there are some obstacles, as the properties of cold-flow, to the development of a more useful alternative fuel. In this work we use the X-ray diffraction and differential calorimetry scanning to study low temperature properties of ethylic Babassu biodiesel. Our results show that the nucleation of crystals starts below −8 °C and the crystallization temperature does not change significantly when the sample was submitted to a winterization process. The higher concentrations of ethyl esters from saturated fat acid are probably responsible for this characteristic. The X-ray diffraction, combined with DSC measurements, was efficiently employed in the characterization of cold-flow biodiesel properties, showing to be very helpful techniques.

Keywords Babassu biodiesel · Cold-flow properties · X-ray diffraction · DSC

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Introduction

Compared with the other biomass source, vegetable oils represent an alternative for the generation of energy through its utilization to produce biodiesel to substitute the fossil fuel. Among the accepted sources of biodiesel, there are various types of vegetable oils [1–5], which are generally transesterified to a mixture of fatty acid into methyl or ethyl esters to reduce viscosity and improve combustion behavior. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics [6].

In Brazil, biodiesel has been priority considered appropriated and available for consolidation of renewable energy programs. The cultivation of the vegetable oils can be act as a strong support to family farms, creating better living conditions. Among the variety palm found in Brazil available to production oil, the Babassu (*Orbinya Martiana*) is one of the most important. The Babassu nut contains ~62% of oil. Among them lauric acid ($C_{12}H_{24}O_2$) is the predominant fatty acid (~44%)[7]. This characteristic facilitates the production of Babassu biodiesel with excellent physical and chemical properties [8].

Although the biodiesel properties are quite similar to conventional diesel fuel there are obstacles to the development of an alternative fuel [9–11]. One of the mainly problems is the cold-flow properties [12–14], that is, at low temperature the esters from saturated fat acid present in the biodiesel suffer crystallization, resulting in the solidification of biodiesel [15, 16]. In this way, the study of biodiesel crystallization at low temperatures is the great importance to improve the biodiesel cold-flow properties.

In this work, the ethylic Babassu biodiesel properties at low temperature are evaluate using differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Besides, the influence of winterization process in these properties is studied. We also use the gas chromatography technique for supplementary characterization of winterized fractions.

Experimental procedure

The Babassu biodiesel was obtained by transesterification reaction through the ethanol route. The physical chemistry parameters of the biodiesel were in accordance to the limits established by Brazilian National Agency for Petroleum, Natural Gas and Biofuels (ANP).

The cold filter plugging point (ASTM D6371 method) and cloud point (ASTM D6371 method) analysis were performed according to standards adopted by ANP based on ASTM standards [17]. The ethylic Babassu biodiesel rheological properties were evaluated using a Brookfield model LV-DVII viscometer adapted to small samples with thermal bath. The viscosity properties were evaluated at cloud point (15 °C), room temperature (25 °C), and in the temperature range of 5 to 105 °C.

Measurements of differential scanning calorimetry (DSC) were obtained in a thermal analyzer (model SDT 2920, TA Instruments) under air atmosphere cooling in the temperature range of 40 to −40 °C and subsequently heating in the temperature range of −40 to 40 °C. The applied heating or cooling rates were 10 °C min^{-1}. In order to study biodiesel crystallization, in situ X-ray measurements were performed in a Philips powder diffractometer (CuKα radiation) operating at 40 kV/30 mA with an Anton-Par TTK450 temperature chamber attached. The samples were cooled down at −50 °C. Subsequently, it was heated and monitored by X-ray diffractions measurements at several temperatures until the sample become complete liquid. The patterns were collected at 0.03° (2θ) step size and 2 s/step in the 18°–27° (2θ) range.

The Babassu biodiesel sample was also submitted to a winterization process [18, 19]. A sample of ~50 mL was placed in a refrigerated centrifuge and cooled with a temperature rate of 1 °C min^{-1} down to −5 °C, the temperature where the crystallization process begins. When appropriate amounts of crystals accumulated within the sample (24 h after the temperature was lowered), the liquid and solid fractions was separated by centrifugation process. Subsequently both liquid and solid fractions were re-winterized. Thereafter, we observe separation of the solid fraction in two different phases, one solid fraction (denominated EBBS#1) and another like-gel fraction (denominated EBBS#2).

The quantities of esters of ethylic Babassu biodiesel and winterized fractions were analyzed isothermally at 230 °C by using a SHIMADZU gas chromatography model GCMS-QP2010 coupled with a mass spectrometer (CG-MS) and equipped with split injector with autosampler. The capillary column utilized was a Durabond-DB-23 (Agilent Technologies) and a He flow of 3 mL min^{-1} was used as entrainment gas. The fat acids characterization was performed by comparison with the software Mass Spectral Database NIST/EPA/NIH standard.

Results

The analysis of physical–chemical properties of Babassu ethylic biodiesel confirms the biodiesel characteristic was in agreement with the values accepted by ANP Brazilian agency. The DSC results for ethylic Babassu biodiesel (EBB) sample shows large exothermic peak overlapped with a narrow one below −10 °C (see Fig. 1, cooling curve). This broad peak indicates more than one type of phase transition occurring during the solidification process. Temperature dependence of DSC curves for the respective fractions of the winterized samples is also shown in Fig. 1. The EBBL sample represents the liquid fraction and the EBBS#1 represent the solid fraction obtained with the winterization process, whereas the EBBS#2 represents a faction like-gel also obtained from the winterization process as discussed in the experimental part of this article. The DSC results for the winterized fractions EBBL and EBBS#1 do not show significant changes in the ethylic Babassu low temperature properties. On the other hand, for the EBBS#2 sample a small exothermic broad peak around 20 °C can be associated to the amorphous phase transition from liquid to like-gel.

The DSC heating curves for EBB, EBBL, EBBS#1, and EBBS#2 are shown in Fig. 2. A single peak associated with the melting process is visible in EBB, EBBL and EBBS#1.

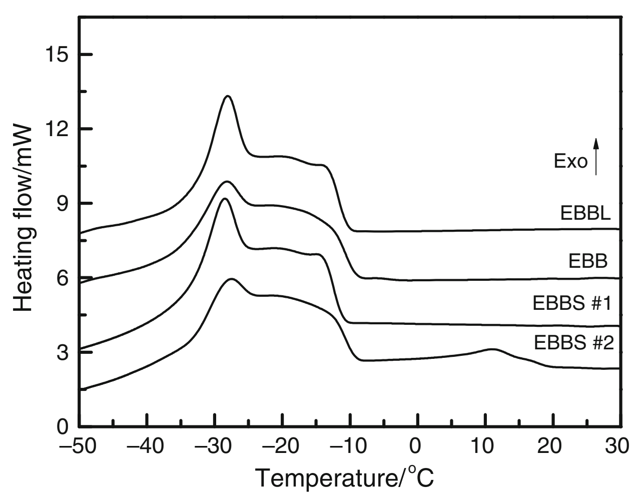

Fig. 1 DSC cooling curves obtained for the ethylic Babassu biodiesel and for the respective fractions obtained with the winterization process. *Curve* offsets on the *y*-axis: 5.2, 3.3, and 1.58/mW for EBBL, EBB, and EBBS#1, respectively

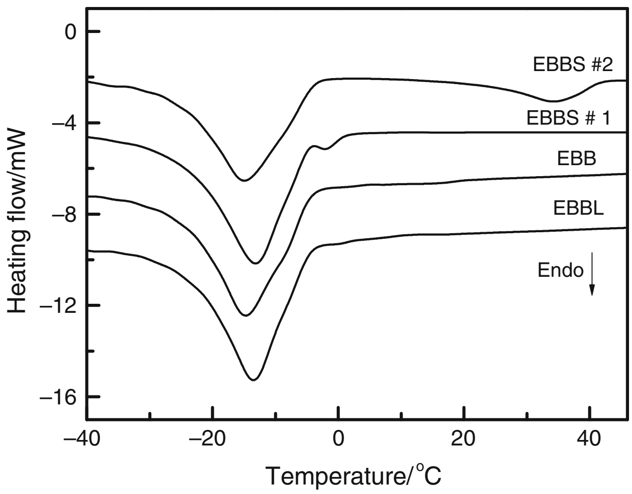

Fig. 2 DSC heating curves obtained for the ethylic Babassu biodiesel and for the respective fractions of the winterized sample. Curve offsets on the y-axis: −7.8, −5.8, and −2.58/mW for EBBL, EBB, and EBBS#1, respectively

Table 1 Temperatures observed in the DSC curves (cooling and heating)

Sample	T_c/°C	P_c/°C	T_f/°C
EBB	−8.6	−28.8	−13.5
EBBL	−10.1	−28.7	−12.6
EBBS#1	−9.8	−28.5	−13.2
EBBS#2	−7.7	−28.4	−14.0

However for the EBBS#2, the main peak can be associated with a transition from solid to like-gel phase and a second peak correspond to transition from like-gel to liquid phase.

The start of crystallization temperature (T_c), freezing point (P_c), and the melt temperature (T_f) were obtained using the DSC data. T_c was taken as the onset point of the transition, which is the point at which the extrapolated baseline intersects the extrapolated slop in the higher peak of DSC cooling curve. The P_c were assigned to each cooling curve, based on the temperature at which the greatest value for the heat flow occurred, while T_f were assigned to each heating curve, based on the temperature at which the lowest value for the heat flow occurred. Table 1 shows the respective values of T_c, P_c, and T_f. The winterization process do not changes the freezing point and the melting temperature of the different fractions of winterized. Also the start of the crystallization does not decrease significantly with the winterization process, both the solid (EBBS#1) and the liquid (EBBL) fractions present similar values of T_c and the difference of 2.4 °C observed between EBBL and EBBS#2 possible can the be attributed to the differences in the physics properties of this two fractions, this is to EBBL the crystallization occurs between the liquid to solid state, whereas for EBBS#2 it occurs between like-gel to solid state.

Using gas chromatography CG-MS, we determine the fat acid ethyl esters amounts of the winterized EBBL, EBBS#1, and EBBS#2 samples compared with the non-winterized ethylic Babassu biodiesel (showed in Table 2). The analysis for EBB shows saturated compositions (97.2%), unsaturated (2.6%), and non identified fat acid trace (∼0.2%). The concentration of saturation and unsaturation not change significantly to the EBBL, EBBS#1, and EBBS#2 samples. This result shows a very large predominance of esters from saturated fat acid in the ethylic Babassu biodiesel and because of this, the winterization process does not provoke significantly changes in the respective fractions of winterized sample.

Figure 3 shows the X-ray diffraction pattern as a function of temperature for ethylic Babassu biodiesel. We see through the diffraction peak widths (full width at half maximum) that the sample becomes more crystalline as the temperature decreases and the crystallization process beginning around −8 °C, where the small diffraction peak can be observed.

Table 2 Gas chromatography results for winterized fractions and nonwinterized ethylic Babassu biodiesel

Samples	C8:0/% caprilic	C10:0/% capric	C12:0/% lauric	C14:0/% miristic	C16:0/% palmitic	C18:0/% stearic	C18:1n-9/% oleic	C18:2n-6/% linoleic
EBB	6.40	6.85	37.57	18.63	14.39	8.12	18.46	2.34
EBBL	2.76	3.74	29.13	17.00	10.92	5.14	20.22	1.92
EBBS#1	4.70	5.40	33.13	17.61	12.01	6.18	16.08	1.47
EBBS#2	4.86	5.75	35.27	18.24	12.41	6.97	14.61	1.33

Samples	Saturated/%	Unsaturated/%
EBB	97.2	2.6
EBBL	98.6	1.3
EBBS#1	98.4	1.5
EBBS#2	97.8	2.1

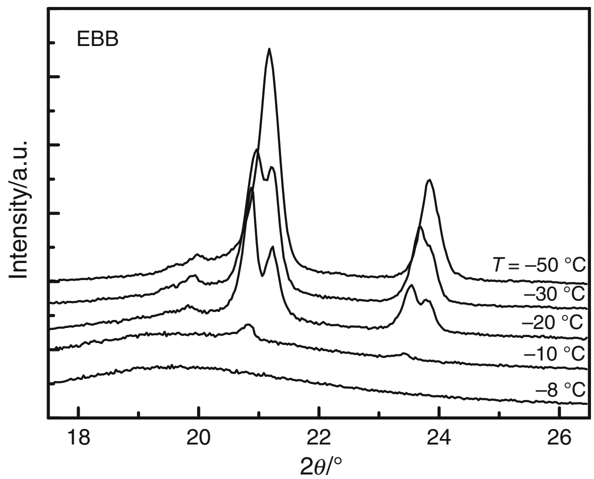

Fig. 3 X ray diffraction (XRD) for ethylic Babassu biodiesel (EBB). The X-ray pattern was obtained at −50, −30, −20, −10, and −8 °C. The measurements were performed in a sequence of heating the sample

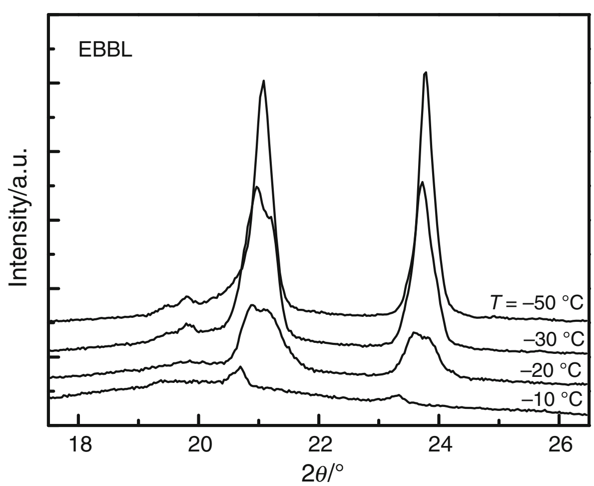

Fig. 4 X-ray diffraction (XRD) for the liquid fraction of winterized ethylic Babassu biodiesel (EBBL), obtained at −50, −30, −20 and −10 °C. The measurements were performed in a sequence of heating the sample

Figures 4 and 5 show the X-ray diffraction pattern as a function of temperature for EBBL, EBBS#1, and EBBS#2, respectively. Both solid fractions and the liquid fraction of the winterized biodiesel present the same begins of crystal nucleation temperature observed in the EBB.

These results are in agreement with the DSC experiments in which the star of crystallization temperature was estimated around to −8 °C. For EBBS#2 we performed X-ray diffraction measurements up to 25 °C and indeed the crystallization peaks appears only below −8 °C, indicating that the phase transition observed around 20 °C in DSC curve is characteristic of a glass transition.

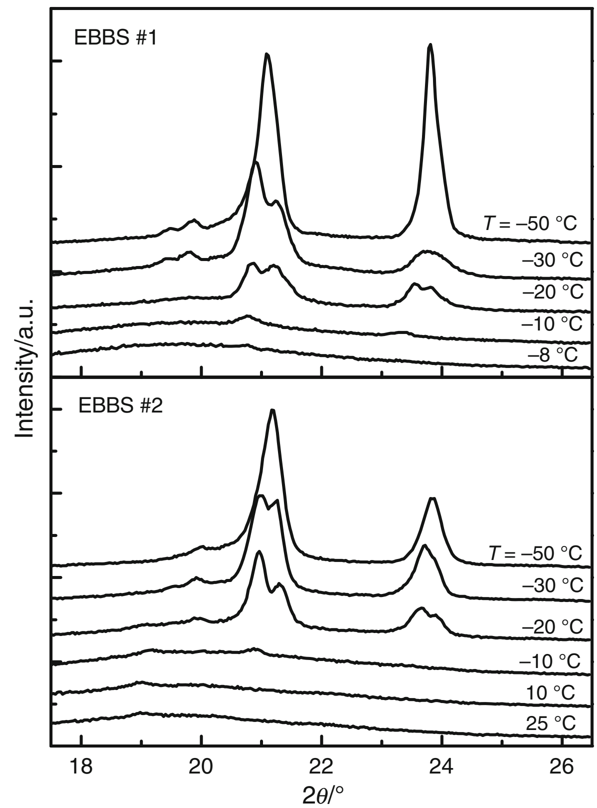

Fig. 5 X-ray diffraction (XRD) for the solid and like-gel fraction of winterized ethylic Babassu biodiesel, EBBS#1 (*top*) and EBBS#2 (*bottom*). The measurements were performed in a sequence of heating the sample

Conclusions

The physical–chemical properties of ethylic Babassu biodiesel obtained in this work attend the specifications required by national (ANP) and international (ASTM and EN) standards.

Measurements of DSC and X-ray diffraction were used to evaluate the low temperature properties of Babassu biodiesel. Both techniques agree with the crystallization of Babassu biodiesel occurs around −8 °C, i.e., the ethyl esters from saturated fat acid suffer nucleation and form crystals resulting in the solidification of biodiesel.

The Babassu biodiesel was submitted to a winterization process at low temperature and three distinct fractions (liquid phase, solid phase, and like-gel phase) were obtained. The characterization of low temperatures properties shows that the start of crystallization temperature remains unaltered for all winterized fractions. On the other hand, to EBBS#2 the transition from like-gel phase to liquid phase occurs only around 20 °C. Our results indicate not change in Babassu biodiesel crystallization temperature with winterization process. The higher concentrations of ethyl esters from saturated fat acid are probably responsible for this characteristic of ethylic Babassu biodiesel.

The X-ray diffraction, combined with DSC measurements, was efficiently employed to the monitoring of Babassu biodiesel crystallization process and for the elucidation of the like-gel fraction nature as an amorphous phase. These techniques are very helpful technique in the characterization of cold-flow biodiesel properties.

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