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THERMO-OXIDATIVE STABILITY AND COLD FLOW PROPERTIES OF BABASSU BIODIESEL BY PDSC AND TMDSC TECHNIQUES

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The babassu (*Orbignya Phalerata* Mart.) biodiesel has lauric esters as main constituents, resulting in high oxidative stability and low cloud and freezing points. In order to reduce these side effects, the saturated ethyl esters content was reduced by means of winterization process. The TMDSC and PDSC techniques were used to verify the thermal and oxidative stabilities of the ethyl babassu biodiesel. During the heating stage, the winterized solid phase of ethyl esters presented an endothermic transition associated to the solidification process. This behavior was not observed for the liquid winterized FAEE, confirming the efficiency of the winterization process.

Keywords: *Biodiesel, PDSC, TMDSC*

Introduction

There are several reasons to increase the biodiesel market, among them the greenhouse effect appears one of the main issues. Although biodiesel is an alternative fuel for diesel engines, its performance at low temperature conditions has a negative impact over its commercialization, particularly in moderate climate regions, due to its flow properties. At low temperatures paraffinic crystals are produced causing restriction to the fuel flow in pumps and plumbing [1].

The crystal formation tendency is extremely associated to the fatty acid composition of the biodiesel. In general, high amount of saturated components increases the cloud and freezing points of the biofuel. A method to enhance these points is the reduction of the saturated esters content by winterization process, which consists in the crystallizing of the saturated esters [2–4]. The properties of biodiesel at low temperatures can be evaluated by differential scanning calorimetry (DSC) techniques at cooling regime. The onset and the initial oxidation temperatures obtained from DSC curves can be used to determine the oxidative induction time (OIT) of the sample. Onset temperature can also be used for studying the cold filter plugging point (CFPP) [1, 5].

On the other hand, unsaturated fatty acids become biodiesel susceptible to oxidation. The oxidative process can be affected or catalyzed mainly by the presence of light, heat and metal traces, usual parameters in long-term storage [6]. The oxidative stability is expressed by the induction period, which corresponds to the time between the initial and the abrupt increase of oxidation products formation, obtained from thermal analytical curves. The oxidation products affect the biodiesel quality and its qualitative and quantitative determinations are considered relevant for the commercialization of such biofuel [7].

In order to evaluate the susceptibility to oxidation, the biodiesel is submitted to accelerated oxidation under controlled conditions. The Rancimat method, established by the European standards EN14112, uses 110°C as oxidative test temperature and six hours for induction period. However, such technique requires long time runs for the measurements and a complex evaluation of the oxidation products. To overcome these disadvantages, thermal analytical techniques like DSC and pressure differential scanning calorimetry (PDSC) have been used for oils and lubricants evaluation [8–14]. Recent studies [15, 16] outlined the importance of non-isothermal PDSC analyses for biodiesel oxidative stability determination by means of the high-pressure oxidative induction time (HPOIT). Park and co-workers examined the effects of the fatty acid compositions in biodiesel blends on the oxidative stability and the CFPP [17].

Therefore, this work aimed to investigate the flow properties at low temperature and the thermal and oxidative stabilities of methyl, ethyl and winterized ethyl babassu biodiesel by means of TMDSC and PDSC.

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Experimental

Fatty acid methyl (FAME) and ethyl (FAEE) esters were obtained by base-catalyzed transesterification of babassu oil [18]. Both biodiesel types were physico-chemically characterized according to the Brazilian commercialization standards. FAEE were winterized at 14°C for the separation of saturated (solid phase) and unsaturated (liquid phase) fatty acids. The solid and liquid phases of winterized FAEE were separated by centrifugation in Sorvall RC 5C Plus centrifuge at 8000 rpm during 30 min.

The temperature modulated differential scanning calorimetry (TMDSC) curves were recorded at non-isothermal conditions using a Thermal Analyzer TA Instruments DSC 2920, in dynamic nitrogen atmosphere (100 mL min^{-1}), in the temperature ranges of 40–60 and –60–100°C, applying a modulation temperature of ±1°C min^{-1} and 10.0 mg of sample. The pressure differential scanning calorimetry (PDSC) curves were obtained in a TA Instruments DSC 2920 coupled to a pressure cell. In the dynamic mode 10 mg of the sample was recorded using platinum pan, oxygen atmosphere of 1400 kPa, heating ratio of 5°C min^{-1} between 25–600°C. Such heating rate was selected since this gives a reasonable combination of resolution characteristics and timeliness. The isothermal analyses were carried out at the same conditions of atmosphere, pressure and sample quantity, but with 140°C of isotherm temperature. The high-pressure oxidative induction times (HPOIT) were determined by the difference between the onset and the initial oxidation temperatures [19]. Prior to the experiments, the PDSC and TMDSC equipments were calibrated by means of the baseline slope, cell constant and temperature calibration using indium as standard metal (156.6°C).

Results and discussion

Figure 1 shows the dynamic PDSC curves of FAME and FAEE. For both samples, the initial oxidation temperatures were equivalent (≈146°C) being attributed to the initiation of the oxidative reactions (first step). The propagation and termination steps were assigned at about 180 and 170°C, respectively. Such results can indicate that FAME sample is stabler than FAEE biofuel. The peak maximum temperatures were 201 and 203°C, for FAME and FAEE, respectively.

After the oxidation, polymerization reactions of the fatty acid ester chains take place resulting in gum formation for all biodiesel samples. In conclusion, it was observed the combustion of the yielded polymers with peak temperatures of 316 and 420°C, for FAME and FAEE. The HPOIT of these samples indicated an oxidative stability higher than 20 h (1200 min) (Fig. 1).

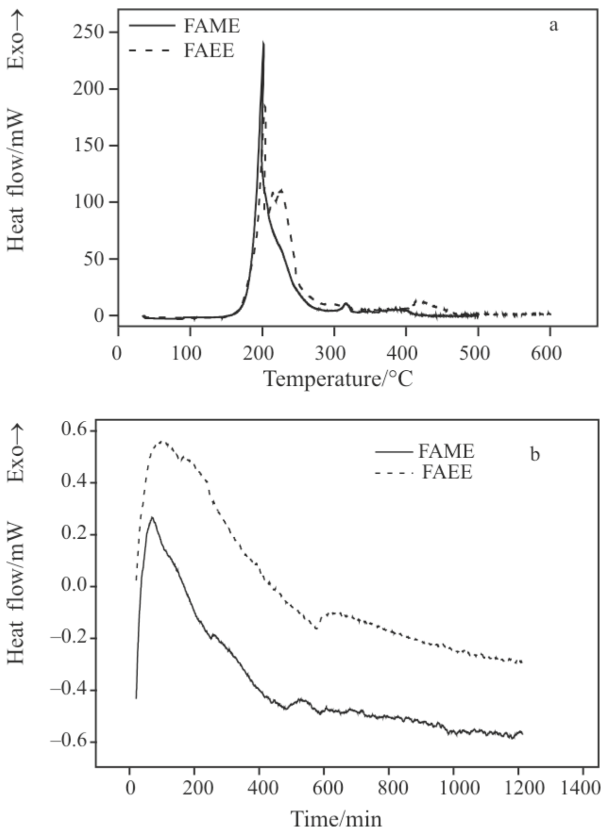

Fig. 1 a – Dynamic and b – isothermal (140°C) PDSC curves of methyl and ethyl babassu biodiesel

As expected, methyl and ethyl babassu biodiesel showed high oxidative stability since they are mainly constituted by saturated fatty acids weakly susceptible to oxidative degradation. Nevertheless, such chemical arrangement disfavors the flow properties of the biodiesel.

During cooling only a single exothermic peak was observed being ascribed as the freezing point of the samples (Fig. 2a). Comparatively the exothermic peak of FAEE was larger and less intense than that of FAME. The melting peak of FAME was narrower than that of FAEE suggesting that the former system may be more homogeneous and organized.

Three endothermic transitions were observed in the FAME heating curves (Fig. 2b). In addition, for both cases a secondary transition peak at about 27°C was observed. For the cooling runs, the absence of such transitions results of the initial heating used during the data collection that eliminates the thermal memory of the samples.

Since molecular mass and the chain size affect the melting point a minor increase in these factors cause the solidification of the ethyl esters at higher crystallization temperatures (T_c=8°C) than that of methyl esters (Table 1). The crystallization temperature is defined as the beginning of the solidification process (onset temperature) during the cooling ramp [5].

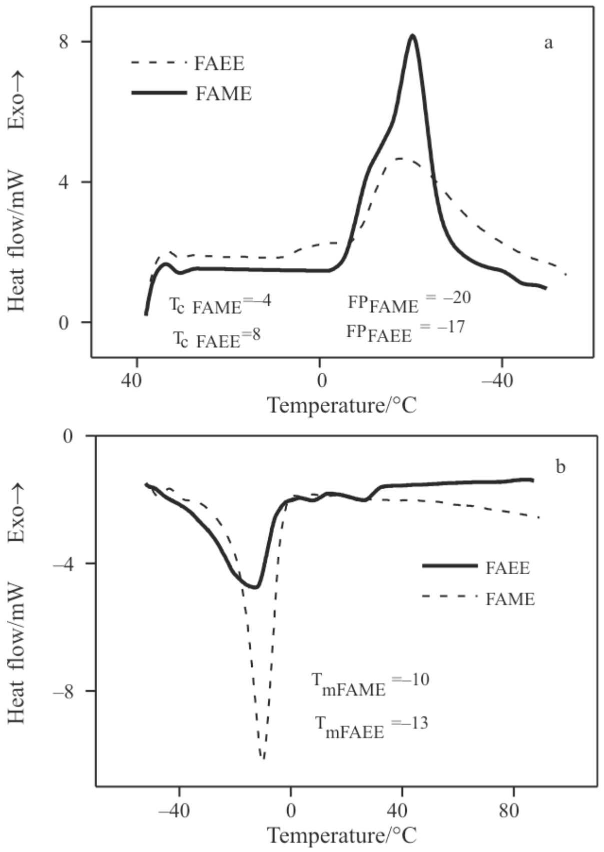

Fig. 2 a – cooling and b – heating TMDSC curves of methyl and ethyl babassu biodiesel

Table 1 Results from TMDSC analysis of FAME and FAEE

Sample	T_c/°C	FP/°C	T_m/°C
FAME	–4	–20	–10
FAEE	8	–17	–13

FAME and FAEE showed CFPP of –4 and 14°C, respectively, close to the crystallization temperatures obtained by TMDSC suggesting that the crystal formation can restrict the fuel flow resulting in the raising of this parameter. At this point the applicability of the TMDSC as a tool for determination of such parameter established in the quality standards can be emphasized.

During winterization at 25°C, large amount of paraffinic crystals is formed in FAEE. After this process, the solid (crystals) and liquid (unsaturated biodiesel) phases were separated by centrifugation and each phase was separately analyzed by TMDSC. The crystals (solid phase) showed crystallization temperatures of 30°C, while for the liquid this temperature was 0°C (Fig. 3). The freezing and melting points were identical for both samples (–19°C and –18°C, respectively). The crystals displayed an endothermic transition during heating with peak temperature of 40°C ascribed as solidification. The absence of transition in this region for the liquid phase confirmed the effectiveness of the winterization process.

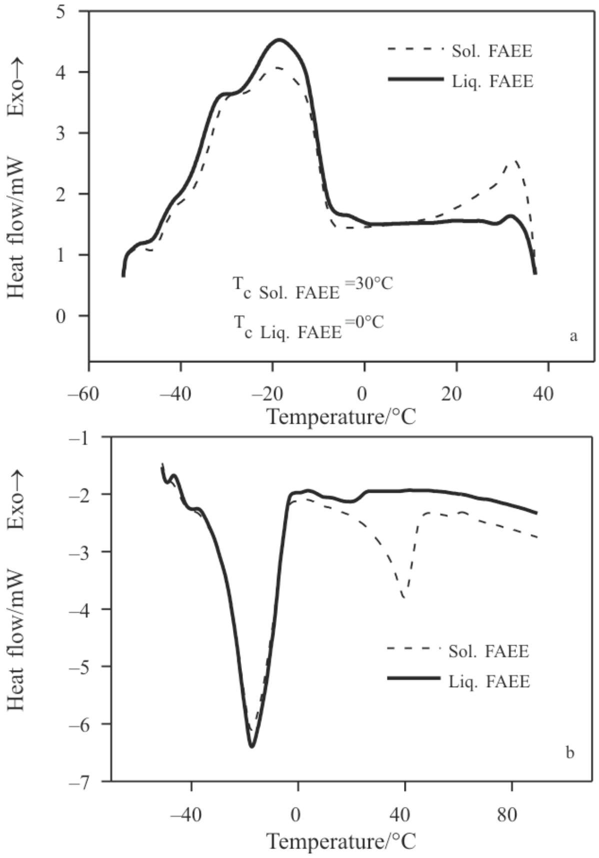

Fig. 3 a – cooling and b – heating TMDSC curves of winterized FAEE

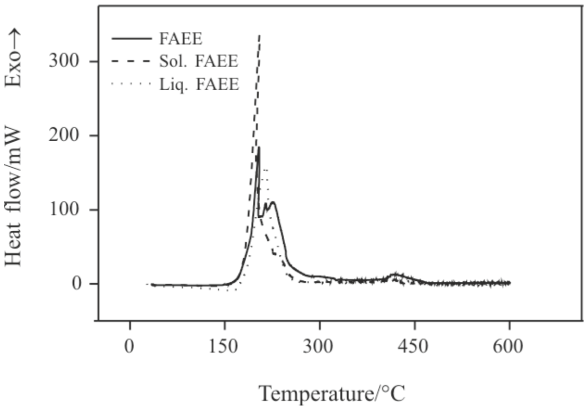

Fig. 4 PDSC curves of solid and liquid phases of winterized ethyl babassu biodiesel

PDSC curves of winterized samples (Fig. 4) indicate that the crystals (saturated fatty acids) and the unsaturated biodiesel have close oxidation initial temperatures, 152 and 155°C, respectively. The peak temperature of the solid phase occurs at 204°C, coincident to the first peak temperature of FAEE. On the other hand, the peak temperature of the liquid phase (214°C) was coincident with the peak temperature of the second ramp of that biodiesel. This fact highlights the separation of the saturated and unsaturated ethyl esters by winterization.

It is important to mention that both winterized biodiesel phases showed higher oxidation temperatures in comparison to the FAEE. Another important aspect of the winterization is the decrease of the CFPP for the FAEE sample (6°C), improving the quality of this biofuel since its flow property at low temperature was improved.

Conclusions

The physicochemical parameters of babassu biodiesel were inside the established limits and this biofuel showed an oxidative stability higher than 20 h, as determined by PDSC.

TMDSC and CFPP results were equivalent in magnitude, suggesting that TMDSC can be an alternative technique to pattern determinations established by the standards. During the heating ramp, the winterized solid phase of FAEE presented an endothermic transition (approximately 40°C) associated to the solidification process. This behavior was not observed for the liquid winterized FAEE, confirming the effectiveness of the winterization process.

References

1 R. O. Dunn, JAOCS, 76 (1999) 109.
2 G. Knothe, Fuel Process. Technol., 86 (2005) 1059.
3 R. O. Dunn, M. W. Shoickley and M. O. Bagby, JAOCS, 73 (1996) 1719.
4 M. E. G. Gómez, R. Howard-Hildige, J. J. Leary and B. Rice, Fuel, 81 (2002) 33.
5 P. Claudy, J. Létoffé, B. Neff and B. Domin, Fuel, 65 (1986) 861.
6 W. W. Nawar, Food Chem., 2 (1985) 176.
7 R. O. Dunn, ASABE, 49 (2006) 1633.
8 B. K. Sharma and A. J. Stipanovic, Thermochim. Acta, 402 (2003) 1.
9 C. D. Gamelin, N. K. Dutta, D. K. Choudhury and J. Matisons, Thermochim. Acta, 357 (2002).
10 A. T. Riga, R. Collins and G. Mlachak, Thermochim. Acta, 324 (1998) 135.
11 A. Zeman, V. Becker and K. Peper, Thermochim. Acta, 219 (1993) 305.
12 M. V. Kök, G. Pokol, C. Keskin, J. Madarász and S. Bagci, J. Therm. Anal. Cal., 75 (2004) 781.
13 M. V. Kök, J. Therm. Anal. Cal., 84 (2006) 361.
14 M. V. Kök and C. Acar, J. Therm. Anal. Cal., 83 (2006) 445.
15 R. O. Dunn, Trans. ASAE, 43 (2000) 1203.
16 R. O. Dunn, Fuel Process. Technol., 86 (2005) 1071.
17 J. Ji-Yeon Park, D. Kim, J. Lee, S. Park and J. Kim, Bioresour. Technol., 99 (2008) 1196.
18 N. A. Santos, M. L. A Tavares, R. Rosenhaim, F. C. Silva, V. J. Fernandes Jr., I. M. G. Santos and A. G. Souza, J. Therm. Anal. Cal., 87 (2007) 649.
19 D. R. J. Kodali, Agric. Food Chem., 53 (2005) 7653.

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