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Rheology and MT-DSC studies of the flow properties of ethyl and methyl babassu biodiesel and blends

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Abstract Biodiesel is an increasingly attractive alternative to diesel fuel. The main component of Babassu biodiesel is lauric acid (C12:0), which is a saturated fatty acid with a high melting point. Controlling flow properties, such as viscosity and the cold filter plugging point, is critical because viscosity affects atomization, and crystal formation resulting from decreases in temperature can negatively affect engine starting and performance. To evaluate its flow characteristics more fully, the rheological properties of babassu biodiesel were analyzed, taking into account variations in temperature. The crystallization temperature was determined by modulated temperature differential scanning calorimetry (MT-DSC). The curve of biodiesel viscosity as a function of the biodiesel refrigeration temperature contained an inflection point (corresponding to a steep increase in viscosity) that was coincident with both the transition from a Newtonian-type flow to a pseudoplastic-type flow and the crystallization temperature obtained by MT-DSC, indicating that the appearance of crystals in the biodiesel increased its viscosity. The rheological properties of fatty acid methyl and ethyl mixtures (FAME and FAEE) with metropolitan diesel were also evaluated; a higher FAME percentage reduced viscosity in blends up to B100.

Keywords Biodiesel · Babassu · Viscosity · CFPP · MT-DSC

Introduction

The viscosity of biofuel limits its large-scale application, because viscosity affects fuel atomization in the injection chamber during the combustion process, damaging the system. Higher-viscosity fuels have an increased tendency to cause such problems [1].

Biodiesel viscosity depends on properties such as temperature and chemical structure. The dependence of viscosity on temperature has been analyzed for biodiesels obtained from rapeseed oil and waste oil [2]. Paraffin crystal nuclei that are visible to the naked eye form at low temperatures. As the temperature decreases, crystal growth and agglomeration continue until the crystals are large enough to restrict the free flow of fuel in the pipes and filters.

Rheology techniques have been used to investigate the correlation between the chemical structure and the physical properties of vegetable oil esters [3]. Fatty acid esters with different chain lengths and degrees of unsaturation were used to evaluate the influence of chemical structure on rheology and crystallization temperature. Although esters displayed Newtonian behavior at room temperature, pseudoplastic behavior was observed at temperatures

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below 5 °C. Similar results were obtained with methyl esters of soybean oil and mustard seed oil [4]. Microcrystal formation at low temperatures may be responsible for this high viscosity, which can cause serious problems in the engine fuel lines and filters.

The effect of the composition of three mixtures of fats was also investigated by Bell et al. [5], who studied rheological properties during cooling and observed that the crystallization temperature was dependent on composition. Differential scanning calorimetry (DSC) has also been used during sample cooling to evaluate the effect of low temperatures on biodiesel properties [6]. DSC is a more rigorous and efficient method to study crystallization temperature than that of traditional methods (cloud point, pour point, and cold filter plugging point) [6–8].

The babassu palm is a sustainable source of biomass in the Northeastern and Midwest Brazilian states [9] and has significant potential for biodiesel production, with oil production of about 900 kg/ha year. Babassu oil has excellent characteristics for biodiesel production because its composition is predominantly lauric (C12:0) acid. The medium-chain lauric acids interact efficiently with transesterification agents and catalysts to produce an outstanding biodiesel with excellent physical and chemical properties. However, data on babassu oil is limited, and a more detailed study of its rheological properties is needed because of its predominantly saturated fatty acid composition.

In this study, the rheological properties of biodiesel obtained from babassu oil were analyzed as a function of temperature. The results were correlated with the behavior observed using modulated temperature differential scanning calorimetry (MT-DSC).

Experimental

The biodiesel was obtained from crude babassu oil by the methyl (FAME) and ethyl (FAEE) routes and the alkaline transesterification method. An oil:alcohol molar ratio of 1:6 was adopted for both cases using 1.0% KOH catalyst by weight at room temperature (25 °C) for 40 min, as previously described [7, 10]. Ethyl and methyl biodiesels were blended with metropolitan diesel (500 ppm S) in proportions of 2, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, and 90% biodiesel. The kinematic viscosities were determined in a TVB 445, ISL viscometer at 40 °C using the ASTM D 445 test method [11]. The cold filter plugging point was analyzed with cold filter plugging point (CFPP) equipment, model AFP-102, Tanaka, following ASTM D 6371 [12]. The rheological properties of the samples were evaluated using a LV-DVII viscometer (Brookfield) with a small sample adapter, an isothermal bath at 20, 25, and 40 °C, and a temperature variation ranging from 5 to 90 °C. The MT-DSC curves were obtained under non-isothermal conditions in a TA Instruments DSC 2920 thermal analyzer in a nitrogen atmosphere between 40 to −60 °C and −60 to 100 °C, with a temperature modulation of ±1 °C/min and a sample mass of about 10 mg.

Results and discussion

The decrease in viscosity during the transesterification reaction can be used to monitor biodiesel production [1]. The babassu biodiesel exhibited viscosity values one order of magnitude lower than that of the crude babassu oil (Fig. 1).

Viscosity increases with chain length and the degree of saturation [3]. FAEE had a slightly higher viscosity than did FAME (Fig. 1). The increased chain size in FAEE leads to an increased number of electrons in the molecule, enhancing London-type interaction forces. The physical properties of biodiesel obtained from different raw materials have been correlated with their chemical structures [3]. The viscosity of the babassu biodiesel was lower, than that of biodiesel from other materials, due to its composition rich in saturated fatty acid esters.

As expected, the biodiesel viscosity decreased as the temperature increased (Fig. 1). Methyl biodiesel had a lower viscosity than diesel at all temperatures, indicating that this biodiesel could be used in diesel engines without causing problems during atomization in the injection chamber. Ethyl biodiesel had the highest viscosity, but the viscosity was still within the acceptable range defined by ASTM D 6751 or by the Brazilian market.

The correlation between stress and the shear rate at 25 °C was used to evaluate the flow behavior of the FAEE and FAME (Fig. 2a). Both exhibited Newtonian fluid behavior. The behavior of FAEE was also evaluated at the

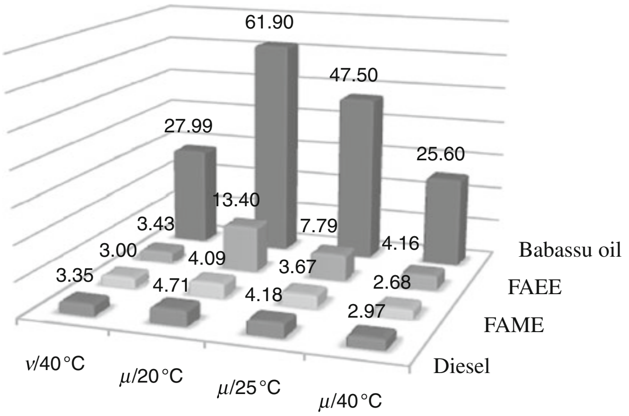
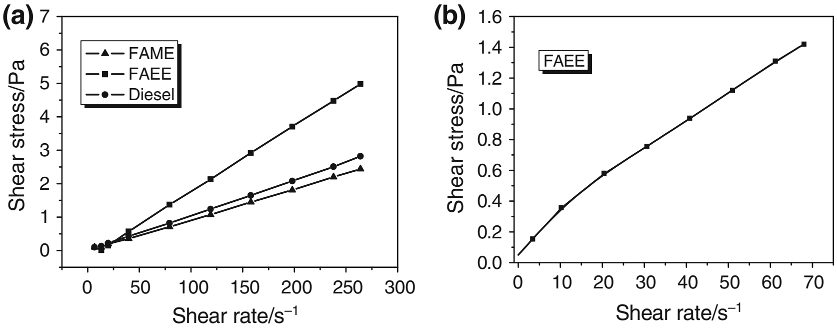


Fig. 1 Dynamic (μ/mPa s) and kinematic viscosities (ν/mm^2 s^{-1}) of babassu oil, diesel, FAME, and FAEE

Fig. 2 **a** Diesel, FAME, and FAEE flow curves at 25 °C. **b** Flow curve of FAEE at 14 °C



CFPP temperature (14 °C) (Fig. 2b). To evaluate this behavior, the Ostwald de Waal Model [13] was used, which is defined by the equation $\tau = K\gamma^n$, where K is the consistency index, γ is the shear rate, τ is the shear stress, and n is the flow rate index. The n value was 0.734, characteristic of pseudoplastic flow ($n < 1$).

Most fluids, including mineral diesel and biodiesel, increase in viscosity with decreasing temperature [14]. A meaningful increase in viscosity may be accompanied by a transition to non-Newtonian behavior. These changes in the rheological properties can restrict the passage of fluid through the injection system.

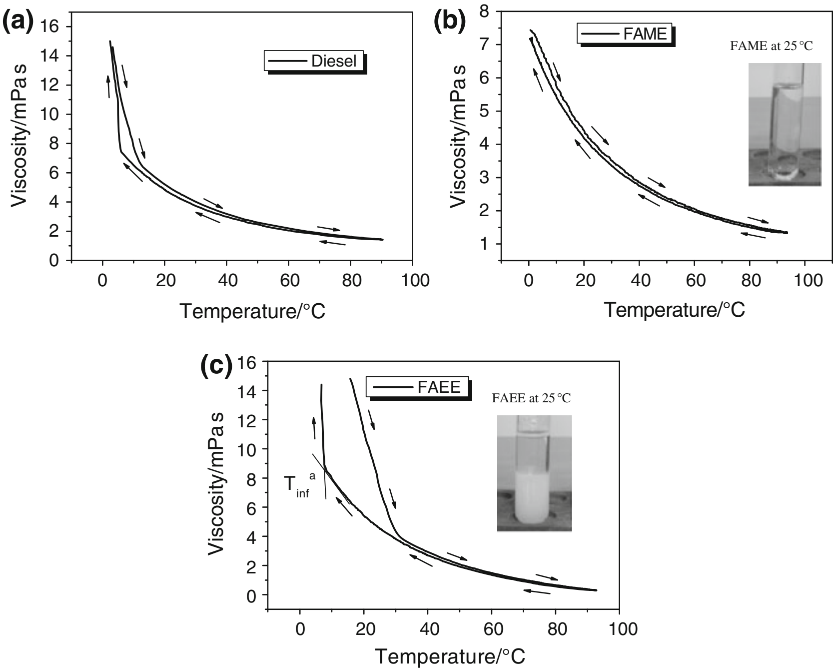
The viscosities of the methyl and ethyl babassu biodiesels were measured between 5 and 90 °C and compared with that of diesel (Fig. 3). In this temperature range, diesel had viscosity values between 15 and 1.4 mPa, and the heating curve showed an inflection point at 12 °C. Above this temperature, the fuel was fully liquid. In the cooling curve, the inflection point shifted slightly to a lower temperature (6 °C), at which paraffinic nuclei formation initiated.

The viscosity of FAME was similar during the heating and cooling stages and varied from 7.4 to 1.35 mPa. The cooling curve of FAEE followed a pattern similar to that of diesel (Fig. 3c), with an inflection point at 7.7 ± 0.1 °C. The inflection point (30.5 ± 0.1 °C) during heating was shifted slightly higher than that of diesel. For this sample, acceptable results were only obtained above 15 °C because the biodiesel was solid below this temperature during heating.

MT-DSC curves were obtained to understand the mechanism of the change in biodiesel rheological behavior (Figs. 4, 5). Crystallization of the saturated esters in FAEE promoted solidification of the unsaturated esters, resulting in a single broad peak of freezing with a shoulder (Fig. 4). FAEE exhibited a saturated ester crystallization transition followed by an unsaturated ester crystallization transition in two successive peaks. Only baseline changes were observed for diesel (Fig. 5).

The viscosity, MT-DSC, and CFPP measurements are presented in Table 1. The crystallization and melting

Fig. 3 Viscosity curves of the fuels between 5 and 90 °C. **a** Diesel, **b** FAME, and **c** FAEE



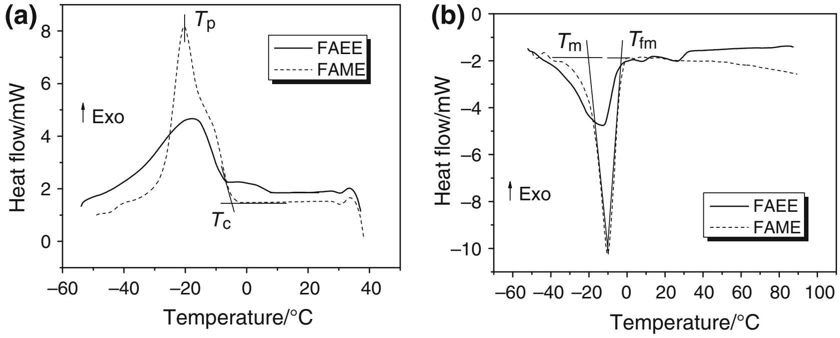


Fig. 4 MT-DSC curves of babassu methyl and ethyl biodiesel: **a** cooling and **b** heating. T_p peak temperature, T_c onset temperature of the crystallization peak, T_m onset temperature of the melting peak, T_{fm} final temperature of the melting transition

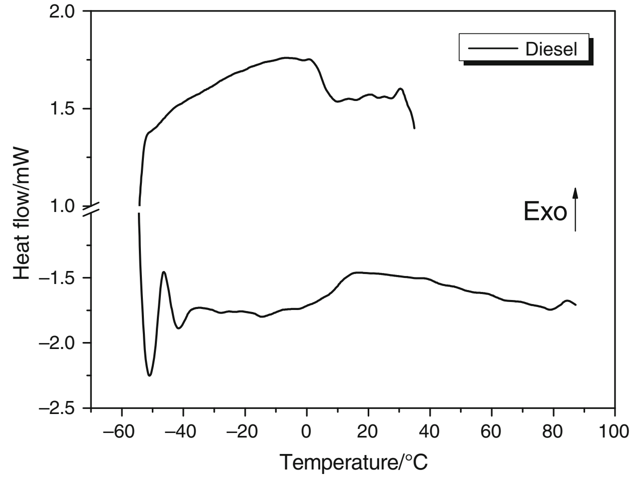


Fig. 5 Cooling and heating diesel MT-DSC curves

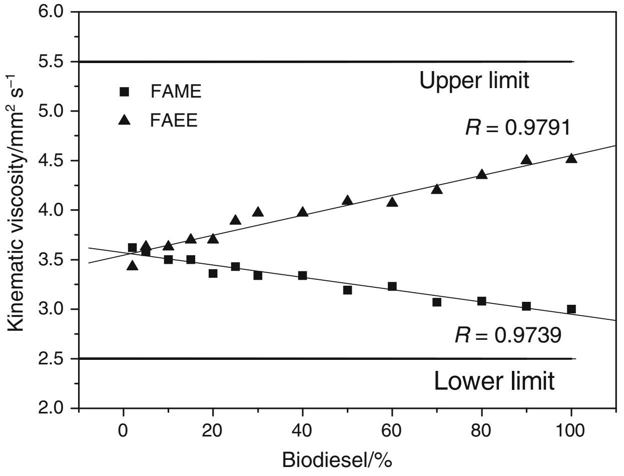


Fig. 6 Kinematic viscosities of methyl and ethyl biodiesel and their corresponding blends

points of FAEE corresponded to the inflection points observed in the viscosity curves. Dynamic rheological analysis can therefore give an indication of the initial crystallization temperature based on the inflection point of the viscosity curve. The CFPP values were also similar to the crystallization temperatures calculated by MT-DSC, suggesting that the appearance of crystals restricted the biodiesel flow, resulting in high CFPP values.

MT-DSC analysis can lead to a better understanding of the parameters established by the ASTM D 6371 standard. In this case, the results indicated that ethyl babassu biodiesel use in cold regions would require preheating.

Binary mixtures

The kinematic and dynamic viscosities of ethylic and methylic biodiesel mixed with diesel (B2, B5, B10, B15, B20, B25, B30, B40, B50, B60, B70, B80, and B90) were also analyzed.

The kinematic viscosities (Fig. 6) reflect different behaviors for FAME and FAEE. For FAME, viscosity decreased with an increasing percentage of diesel, whereas viscosity increased for FAEE mixtures. This phenomenon may be related to the higher molecular weight of ethylic esters relative to methylic esters. All of the results were within the limits established for diesel (ASTM D975) [15].

Table 1 MT-DSC, Viscosity, and CFPP values of FAME, FAEE, and diesel (°C)

Samples	MT-DSC					Viscosity curves		CFPP
	Cooling curves		Heating curves			Cooling curves	Heating curves	
	T_p	T_c	T_p	T_m	T_{fm}	T_{inf}	T_{inf}	
Diesel	0.7 ± 0.1	8.4 ± 0.1	–	–	13.8 ± 0.1	5.8 ± 0.1	12.2 ± 0.2	10 ± 1
FAME	−20.5 ± 0.2	−4.9 ± 0.1	−10.1 ± 0.1	−20.3 ± 0.1	0.8 ± 0.1	–	–	−4 ± 1
FAEE	−17.7 ± 0.1	7.9 ± 0.1	−13.0 ± 0.1	−39.4 ± 0.1	31.8 ± 0.1	7.7 ± 0.1	30.5 ± 0.1	14 ± 1

T_{inf} inflection temperature of viscosity curve. T_p, T_c and T_{fm} are defined in Fig. 4

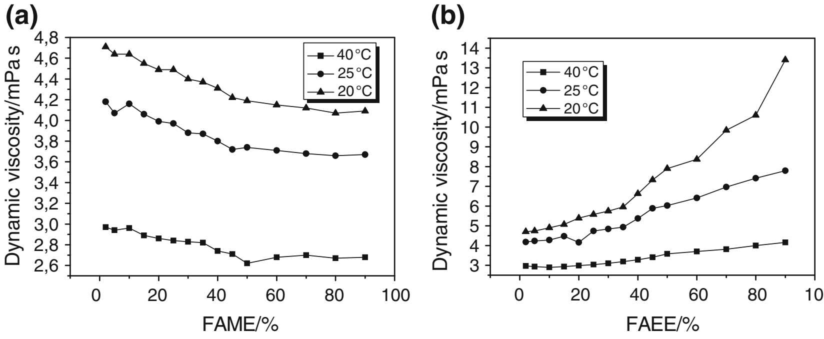


Fig. 7 Dynamic viscosities at 20, 25, and 40 °C of **a** FAME blends and **b** FAEE blends

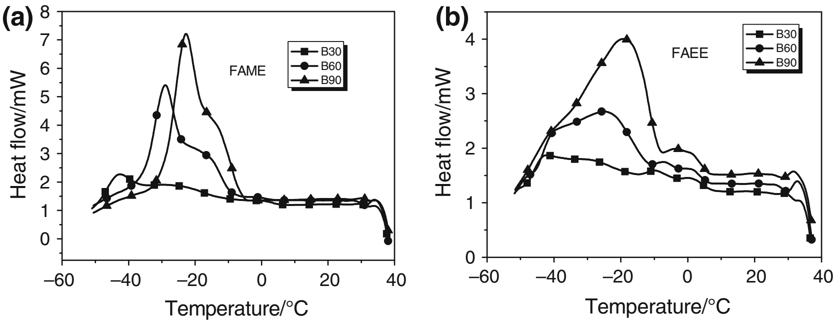


Fig. 8 MT-DSC cooling curves of mixtures **a** FAME and **b** FAEE

Table 2 Comparison of CFPP values and MT-DSC results for FAME/FAEE:diesel mixtures

Sample	FAME			FAEE		
	T_p/°C	T_c/°C	CFPP/°C	T_p/°C	T_c/°C	CFPP/°C
B30	−42.9 ± 0.1	5.6 ± 0.1	6 ± 1	−41.7 ± 0.1	7.0 ± 0.1	23 ± 1
B60	−29.0 ± 0.2	3.6 ± 0.1	7 ± 1	−24.6 ± 0.3	5.8 ± 0.1	23 ± 1
B90	−22.8 ± 0.1	−6.4 ± 0.1	4 ± 1	−18.9 ± 0.2	6.3 ± 0.1	21 ± 1

T_p and T_c values were defined in Fig. 4

The dynamic viscosities of the biodiesel samples and their mixtures with diesel at different temperatures are illustrated in Fig. 7. The FAME and FAEE mixtures exhibited the same behavior observed in the kinematic viscosity curves at all temperatures.

The MT-DSC curves of the mixtures (Fig. 8) were similar to those of the original biofuels, with exothermic transitions assigned to the crystallization process. The peak temperatures were displaced to lower values when higher amounts of diesel were used, indicating that diesel inhibits interactions among the ester chains.

The CFPP and T_c values were similar for the FAME blends (Table 2). For FAEE, the CFPP correlated with the baseline change observed in the MT-DSC curves, which is related to carbon chain mobility. Thus, the cause of a decrease in biodiesel flow may differ for different biodiesels.

Conclusions

Decreases in temperature resulted in a crystal formation-related shift from Newtonian to pseudoplastic flow. The viscosity of methyl biodiesel was lower than that of diesel at all temperatures, indicating that this biodiesel could be used in diesel engines. The viscosity curves during cooling of both biodiesels exhibited a sharp increase from 8 °C that coincided with the crystallization temperature obtained by MT-DSC, indicating that the appearance of crystals increased the viscosity and restricted normal biodiesel flow. For biodiesel:diesel mixtures, different phenomena were responsible for the decrease in flow. The CFPP was assigned to crystallization for FAME and to reduced mobility among chains for FAEE.

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