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Thermal stability evaluation of methylic biodiesel obtained for different oilseeds

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Abstract Biodiesel is defined as a mixture of mono- or di-alquil esters of vegetable oil or animal fats. During long-term storage, oxidation caused by contact with air (autoxidation) presents a legitimate concern in relation to monitoring and maintaining fuel quality. Extensive oxidative degradation may compromise the quality by adversely affecting kinematic viscosity, acid value, or peroxide value. The oxidation susceptibility of biodiesel, due to the presence of triacilglycerides of poly-unsaturated fatty acids, was evaluated in this study. Samples of sunflower, castor, and soybean biodiesels were obtained through the transesterification reaction, with the intention of achieving the thermal stability study through thermogravimetrical analyses and differential scanning calorimetry high pressure. It was furthermore observed through thermogravimetry and pressure differential scanning calorimetry curves that castor biodiesel exhibited the highest thermal and oxidative stability.

Keywords Biodiesel · Thermal stability · Pressure differential scanning calorimetry · Thermogravimetry

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Introduction

Brazil is a country that due to its tropical and subtropical territorial extension and climate propitiates ample raw material diversity for the biodiesel production [1]. The country holds a position as a bulwark in the technology and production of ethanol and presents a natural trend for agribusiness [2].

These factors associated to the localization of petroleum in geographic areas of conflicts, prospection in places of raised cost for the extraction, related climatic changes due to the emissions of noxious gases, heat liberated due to the intense fossil fuels use, redirect the search to new power plants, which make possible the renewal and assure the sustained development [2].

Although sufficiently promising, the obtained biodiesel through transesterification is susceptible to the degradation process, when displayed to air, light, and heat, due to the chemical composition of each feedstock [3]. According to USDA, production of sunflower, castor, and soybeans from 2007 to 2008 has grown considerably, though two of these are directed to the food sector. In recent years, the cultivation of castor beans was encouraged, especially by displaying socio-economic benefits and the tendency of having a high oil content compared to other oilseed crops [4, 5], although its use as biodiesel is limited due to some physicochemical properties that do not meet the required specifications. One of the relevant criteria for the quality of biodiesel is its stability, during storage, some studies focus on accelerated oxidative techniques, to obtain the induction period and temperature of oxidation induction [6, 7]. Literature shows that thermogravimetry can be important to verify this trend [8]. Rudnik et al. [9] presented thermogravimetrical results, which correlates with the oxidative thermal stability. This study aims to compare the thermal stability of biodiesel from different oils obtained through TG and P-DSC dynamic mode.

Experimental

The samples were obtained through the transesterification reaction, using a homogeneous catalyst KOH, with a molar concentration of 1% m/m vegetable oil/methanol 1:6 (sunflower and soybean) and 1:9 (castor) [10]. Initially, methanol and potassium hydroxide were placed to react under stirring until achieving a complete homogenization of the base catalyst, resulting in potassium methoxide. Afterward, this was added to each oilseed in a reactor.

The mixture remained under constant stirring for 1 h at room temperature for the transesterification reaction to be performed. At the end of the reaction, two phases were clearly observed; the mixture was transferred to a decanting funnel, with the aim of improving the phase separation through gravity. After 24 h, glycerin was collected, leaving only the biodiesel, they underwent a process of washing with warm distilled water. At the end of the washing process, traces of moisture content of methanol in the biodiesel were eliminated through the process of heating, in a furnace at 100 °C for 3 h.

After the process was implemented, physicochemical characterization of the biodiesel samples were performed according to the rules of the American Society of Testing and Materials (ASTM), British Standard (BSEN), and Brazilian Association of Technical Standards (ABNT) in accordance with Resolution no. 7/2008 of the National Agency of Petroleum and Biofuels (ANP) [11].

In order to obtain the initial oxidation temperature of the material a pressure differential scanning calorimeter; model DSC 204 HP from NETZSCH, under pressure of 1100 kPa, in synthetic atmosphere air, in a dynamic mode was used. Initially 10 mg of each sample were weighed and packed in a crucible of open aluminum; the analysis was initiated and submitted to a heating rate of 10 °C min^{-1} to 600 °C.

TG curves were obtained in a thermobalance TGA/SDTA 851-Mettler Toledo. The samples were initially placed in an alumina crucible of 900 μL, using a mass of about 60 mg in a temperature range of 30–600 °C under synthetic air flow (60 mL/min) and a heating rate of 10 °C min^{-1}.

Results and discussion

Table 1 presents the data on physicochemical characterization of the biodiesel samples. It could furthermore be noted that sunflower and soybean biodiesel met the specifications, while castor biodiesel had a high density, kinematic viscosity, and acidity.

The initial oxidation temperatures obtained by the dynamic mode PDSC and temperature ranges that occurred in the mass losses of samples are shown in Table 2.

TG curves made it possible to check the temperatures of decomposition of methyl biodiesel, as shown in Fig. 1. Through the same, it was observed that the decomposition occurred in a single step, which could be attributed to the decomposition of methyl esters [12]. Curves for PDSC in dynamic mode in Fig. 3 show a higher oxidative stability for castor biodiesel, compared to sunflower and soybean. This behavior could be attributed to the high content of ricinoleic acid found in the composition of that oil [13].

This profile is corroborated with other data from physicochemical characterizations, whereas the low iodine value indicates that the castor oil biodiesel presents few

Table 2 Initial oxidation temperatures (T_{OI}) obtained by dynamic mode pressure differential scanning calorimetry method and mass loss temperatures (T_{ML}) obtained through Thermogravimetry

Samples	*T_{OI}/°C	**T_{ML}/°C
Sunflower biodiesel	155	150–350
Castor biodiesel	198	200–350
Soybean biodiesel	164	155–350

Table 1 Physicochemical characterization of sunflower, castor and soybean biodiesel

Parameter	Sunflower biodiesel	Castor biodiesel	Soybean biodiesel	Limits
Total sulfur/mg kg^{-1}	0.4	0.3	0.5	50
Acid value/mg KOH g^{-1}	0.3	0.9	0.2	≤0.5
Iodine value/g. 100 gI_2^{-1}	125.2	87.7	126.4	–
Specific mass 20 °C/kg m^{-3}	883.3	920.4	881.9	850–900
Flash point/°C	182	236	184	100
Kinematic viscosity 40 °C/mm^2 s^{-1}	4.38	13.03	4.58	3.0–6.0

ANP resolution no. 7, 19.03.2008–DOU 20.03.2008

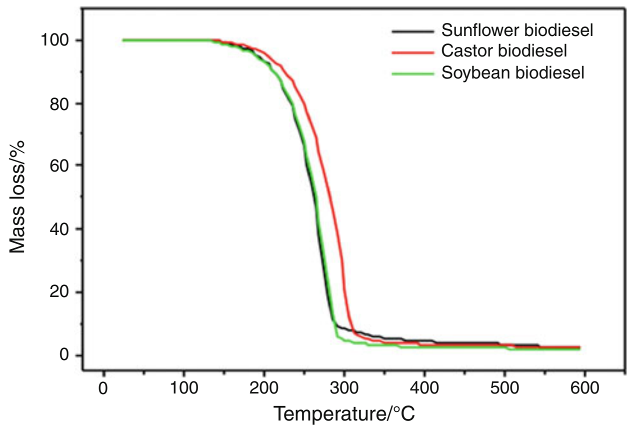

Fig. 1 TG curves of the sunflower, castor, and soybean methylic biodiesel

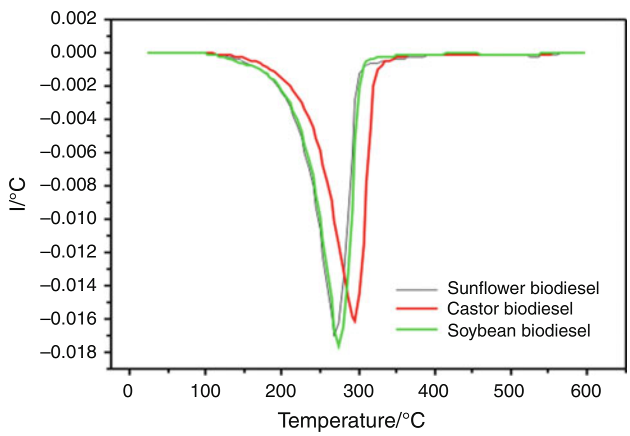

Fig. 2 DTG curves of the sunflower, castor, and soybean methylic biodiesel

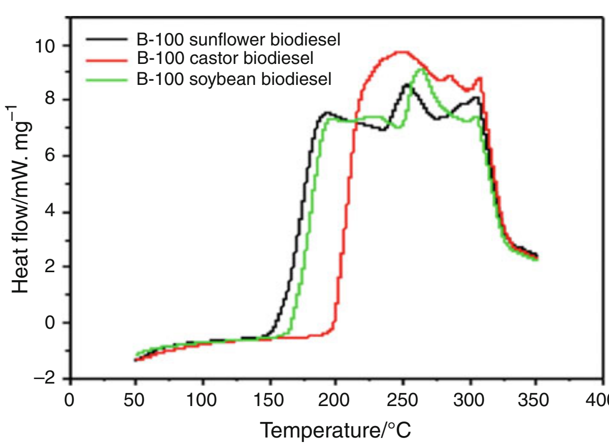

Fig. 3 Profile PDSC curves for sunflower, castor, and soybean biodiesel obtained by dynamic method

instaurations, which implies greater oxidative stability and a high flash point, which furthermore indicates a higher thermal stability.

Conclusions

The sunflower and soybean samples met the specifications of Resolution no. 7/2008 ANP, whereas the castor biodiesel had values of density and kinematic viscosities beyond the required specifications, such properties limit its use as fuel. Furthermore from the TG curves it was observed that castor biodiesel has a higher thermal stability then the others, this could be attributed to the high content of ricinoleic acid in their composition, showing the importance of this technique for this type of evaluation. These results suggest that castor biodiesel could be used as an antioxidant additive for other fuels of thermal stability and lower oxidative tendency.

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