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Evaluation of the thermal stability of biodiesel blends of castor oil and passion fruit

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Abstract The diversity of raw materials and technological routes employed in the biodiesel production has resulted in products with different chemical properties. This non-uniformity in the biodiesel composition may influence to the fuel quality. The aim of this study was to evaluate biodiesel blends of passion fruit and castor oil in different proportions and their thermal stability. Biodiesel blends of passion fruit and castor oil presented parameters in the standards of the Petroleum, Natural Gas and Biofuels National Agency. The TG curves indicated that castor oil biodiesel was more stable. Passion fruit biodiesel has a high content of oleic and linoleic acids, which are more susceptible to oxidation. Biodiesel blend of passion fruit and castor oil 1:1 increased the thermal stability in relation to passion fruit biodiesel. Biodiesel blend of passion fruit and castor oil 1:2 presented higher thermal stability, because castor oil has a high content of ricinoleic acid.

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Introduction

In Brazil, the soy, cotton, and palm oils are used more for the obtainment of biodiesel, besides the bovine suet. It is viewed to search for alternatives to guarantee the quantity of raw material necessary to the production of biodiesel and to the improvement of synthesis process [1–4].

Biodiesel blends have been tested; however, the diversity of raw materials and technological routes employed in the biodiesel production has resulted in products with different chemical properties. This non-uniformity in the biodiesel composition of different precedents may influence to the fuel quality [5].

The characterization of biodiesel blends will contribute to the detection of incompatibilities between the oleaginous. The castor oil (*Ricinus Communis* L.) as well as the passion fruit (*Passiflora edulis*) are oleaginous plants to be investigated regarding the characteristics as biofuel, presented oil content of 45–25%, respectively [6].

The aim of this study was to evaluate biodiesel blends of passion fruit and castor oil in different proportions, determining physical–chemical properties and its thermal stability.

Experimental

Pre-treatment of oils

Passion fruit and castor oil were neutralized with sodium hydroxide by Morais et al. [7].

Biodiesel synthesis

The passion fruit and castor oil biodiesels were prepared by transesterification reaction, in the molar ratio oil:ethanol of 1:9 and 1% of potassium hydroxide.

Purification

After the transesterification reaction, the ethyl esters were purified with HCl 0.1 N (15%, v/v) to neutralize the residual catalyst. The ethyl esters were washed with water and dried in stove during 1 h at 100 °C.

Preparation of blends

The biodiesel blends of castor oil and passion fruit were prepared in the proportions of 1:2, 1:1, and 2:1. Castor oil biodiesel content was 33.5, 50, and 66.5% (v/v), respectively, passion fruit biodiesel content was 66.5, 50, and 33.5% (v/v), at room temperature using a beaker. Each sample has a final volume of 300 mL.

The blends diesel and castor oil and passion fruit biodiesel were prepared with 5 and 20% of biodiesel (mixture of diesel and ethyl esters) at room temperature using a beaker. Each sample has a final volume of 300 mL.

Characterization of samples

The biodiesel samples were characterized according to the parameters established by the Technical Regulation no. 1/2008 of the Petroleum, Natural Gas and Biofuels National Agency [8–10]. The analyses were performed in duplicate.

The thermogravimetric curves (TG) were obtained in a Thermal Analyzer TA Instruments, atmosphere of synthetic air, heating rate of 10 °C min^{-1}, and temperature interval of 25–600 °C.

The FTIR spectra were obtained in a Spectrophotometer BOMEM MB-102, interval of 4000–400 cm^{-1} using pastilles KBr.

The chromatographic analyses were obtained in Chromatograph Shimadzu GCMS QP2010, helium atmosphere, Mass Detector, Library NIST02.

Results and discussion

Characterization of oils

The passion fruit oil (7.50 mg KOH g^{-1}) as well as the castor oil (1.95 mg KOH g^{-1}) presented high acid value, after neutralization they showed acid value of 0.30 and 0.70 mg KOH g^{-1}, respectively.

Biodiesel synthesis

After the purification, the biodiesels presented yield of 95.8% to passion fruit biodiesel and 91.0% to castor oil biodiesel.

The composition of fatty acids of oils is an important factor to evaluate the biodiesel performance. The ethyl esters contents were determined by gaseous chromatography (Tables 1 and 2). The passion fruit biodiesel indicated as major components the ethyl oleate and linoleate. In the castor oil biodiesel, the major component was ethyl ricinoleate.

Physical–chemical analysis of biodiesel and biodiesel blends

The acid value (Table 3) is a direct measure of the free fatty acids in the biodiesel. It is an indicator of the stability of the biodiesel and may increase with time as the fuel degrades. High acid value is associated with corrosion and engine deposits, particularly, in the fuel injectors. The acid value of edible oils or their corresponding esters indicates the quantity of free fatty acids and mineral acids present in the sample. Acids can also be formed when traces of water causes hydrolysis of the esters into alcohol and acids. According to ASTM D 664 and EN 14104, the acid value is expressed in milligrams potassium hydroxide required to neutralize 1 g of sample.

Pour and cloud points (Table 3) of castor oil biodiesel and biodiesel blends 1:1 and 1:2 presented a lower temperature to the formation of crystals, favoring the storage and transport, besides diminishing the risks of engines obstruction.

Biodiesel blends 2:1 presented a high cloud point—temperature which determines a suspension caused by particle formation. As a consequence, its point pour also increased in comparison to other samples, a factor that might allow us clogging oil filters and injection system, in environments of low temperatures, causing an increase in viscosity of biodiesel.

Table 1 Composition of passion fruit biodiesel

Ethyl ester	Retention time/min	Content/%
Palmitic	9.704	11.432
Linoleic	14.944	64.357
Oleic	15.197	19.653
Stearic	16.416	2.920
Total		98.362

Table 2 Composition of castor oil biodiesel

Ethyl ester	Retention time/min	Content/%
Ricinoleic	13.808	85.981
Linoleic	7.933	5.602
Oleic	7.696	4.700
Stearic	6.027	1.530
Total		97.813

Table 3 Analyses of biodiesel blends

Samples	Acid value/mg KOH g^{-1}	Pour point/°C	Cloud point/°C
Passion fruit biodiesel	0.27	−5.0	−4.0
Castor oil biodiesel	0.46	−20.0	−12.0
BPFCO 1:1[a]	0.42	−8.0	−7.0
BPFCO 1:2[a]	0.49	−9.0	−8.0
BPFCO 2:1[a]	0.41	−8.0	−6.0

[a] Biodiesel blends of passion fruit and castor oil in the proportions 1:1, 1:2, and 2:1

Table 4 Analyses of biodiesel blends

Samples	Viscosity/ $mm^2 s^{-1}$	Density 20 °C/g cm^{-3}	Carbon residue/%
Passion fruit biodiesel	3.7	0.860	0.013
Castor oil biodiesel	11.6	0.898	0.035
BPFCO 1:1	4.3	0.881	0.026
BPFCO 1:2	5.7	0.883	0.027
BPFCO 2:1	3.8	0.851	0.019

Higher viscosity will lead to poor fuel atomization, incomplete combustion, and higher carbon residue values. According to ASTM D4530, all samples were in the limit for carbon residue (Table 4). The biodiesel blends of passion fruit and castor oil 2:1 presented the best result.

The viscosity of biodiesel is higher than diesel, indicated by the specifications. The structures of the components of biodiesel, mainly esters of fatty acids, influence the kinematic viscosity. The viscosity is lower for short-length strings. An OH group in the chain increases the viscosity, as in ethyl ricinoleate. Esters with short-chain acids, but long-chain alcohol, show lower viscosities than esters of long- and short-chain alcohol. Saturated esters with high melting point have little influence in the kinematic viscosity at low temperatures. Analyses of kinematic viscosity at 40 °C were performed in TVB445 ISL viscometer (Table 4).

Analyses of biodiesel blends with diesel

Parameters were in accordance with the ANP. The biodiesel blend (passion fruit biodiesel with diesel—B5) was the least tended to form carbon deposits (Table 5). It is believed that blending biodiesel with diesel up to 20% will improve the viscosity properties of the biodiesel. The density is directly proportional to biodiesel content.

Fourier transform Infrared spectroscopy (FTIR) spectra

In the FTIR spectra of biodiesels and blends (Figs. 1 and 2) were identified as strong band due to axial deformation of the carbonyl group (C=O) of ester from 1735 to 1743 cm^{-1} and two medium bands at 1172 and 1196 cm^{-1} related to axial deformation of CO bond characteristic of esters. The presence of the group $(CH_2)_n$ at 725 cm^{-1} as well as low moisture, evidenced by the lack of width band from 2500 to 3300 cm^{-1}.

The absorption band at 3300 cm^{-1} attributed an axial deformation of O–H bond, characteristic of ricinoleic acid, presented lower intensity in the biodiesel blends.

Thermal study

The TG/DTG curves of castor oil biodiesel (Fig. 3) presented two steps of mass loss (92 and 7.2%) in the temperature range of 147–306 °C and 306–423 °C, attributed to the volatilization followed by combustion of ethyl esters, mainly ethyl ricinoleate, which have a boiling point of 425–426 °C.

The TG/DTG curves of passion fruit biodiesel (Fig. 4) presented two steps of mass loss (95 and 4.4%) in the temperature range of 116–277 °C and 277–412 °C, attributed to the volatilization followed by combustion of ethyl esters, mainly oleate and ethyl linoleate, which have a boiling point of 216–217 °C and 270–275 °C, respectively.

The biodiesel blends of passion fruit and castor oil 1:1 (Fig. 5) increased the thermal stability (initial decomposition temperature of 120 °C) in relation to passion fruit biodiesel, because the major component of castor oil is ricinoleic acid. This was confirmed by the profile of the biodiesel blends with higher (Fig. 6) and lower content of castor oil (Fig. 7), with initial decomposition temperatures of 129 and 116 °C, respectively.

Passion fruit biodiesel is less stable than castor oil biodiesel, due to the content of oleic and linoleic acids, which are more susceptible to oxidation.

The difference in the fatty acid composition for the two vegetable oils used to produce the biodiesels, the passion fruit oil having higher content of (C18:1) oleic and (C18:2) linoleic acids (19 and 64%, respectively) and the castor oil

Table 5 Analyses of biodiesel blends with diesel

Analysis	B-5 BPF[a]	B-20 BPF[a]	B-5 BCO[b]	B-20 BCO[b]	B-5 BPFCO 1:1[c]	B-20 BPFCO 1:1[c]	Diesel
Viscosity/mm^2 s^{-1}	3.0	3.3	3.9	4.3	3.1	3.5	2.9
Density 20 C/g cm^{-3}	0.843	0.849	0.858	0.866	0.844	0.853	0.835
Carbon residue/%	0.10	0.12	0.11	0.16	0.13	0.14	0.19

[a] Diesel with 5 and 20% passion fruit biodiese

[b] Diesel with 5 and 20% castor oil biodiesel

[c] Diesel with 5 and 20% of biodiesel blend of passion fruit and castor oil 1:1

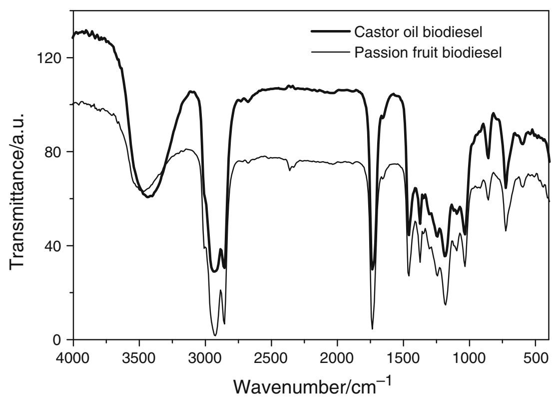

Fig. 1 FTIR spectrum of castor oil and passion fruit biodiesels

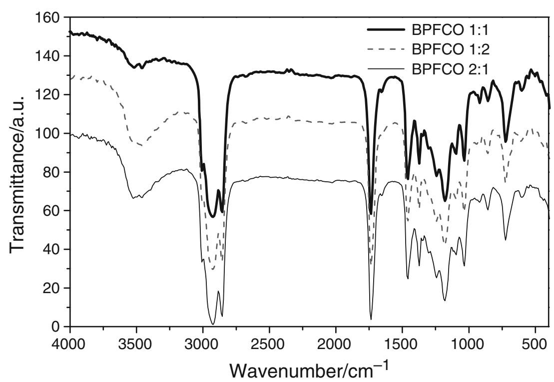

Fig. 2 FTIR spectrum of biodiesel blends of passion fruit and castor oil 1:1, 2:1, and 1:2

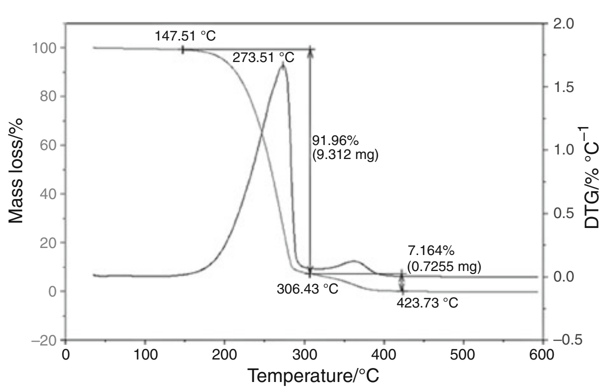

Fig. 3 Curves TG/DTG of castor oil biodiesel

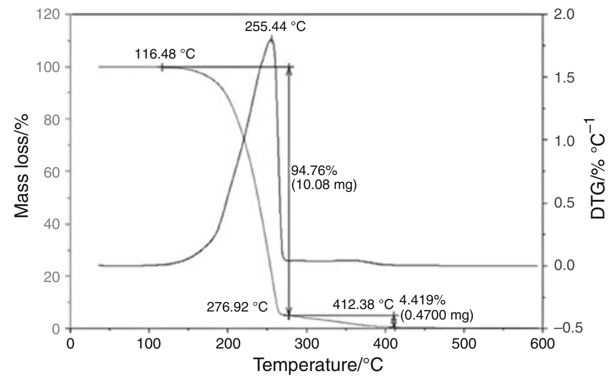

Fig. 4 Curves TG/DTG of passion fruit biodiesel

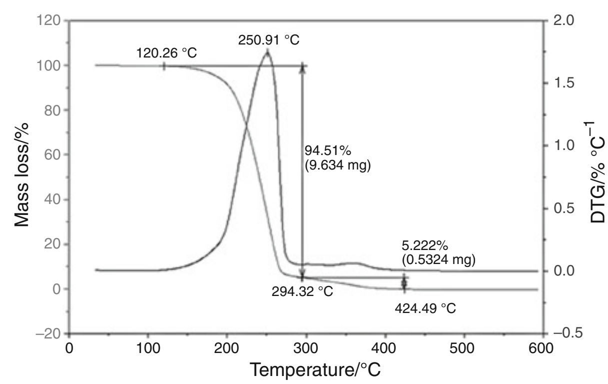

Fig. 5 Curves TG/DTG of biodiesel blend of passion fruit and castor oil 1:1

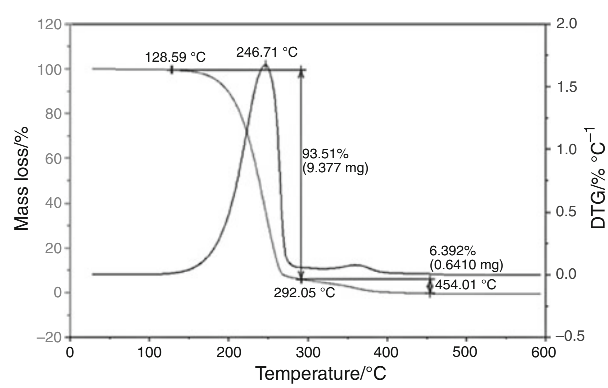

Fig. 6 Curves TG/DTG of biodiesel blend of passion fruit and castor oil 1:2

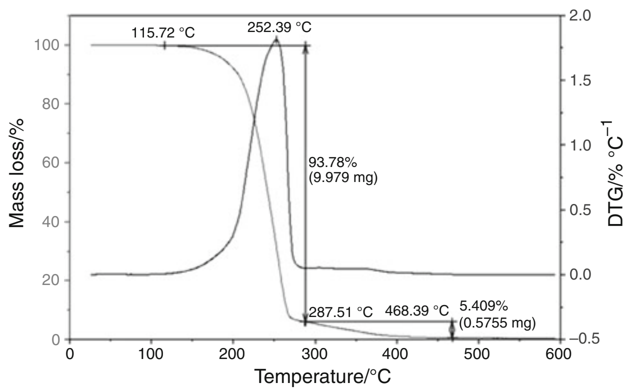

Fig. 7 Curves TG/DTG of biodiesel blend of passion fruit and castor oil 2:1

having higher content of (C18:1) ricinoleic acid (85%), may play some role in the oxidation mechanism.

The biodiesel blends with diesel (B5 and B20) presented low thermal stability, similar to diesel.

Conclusions

The stability of biodiesel depends on the fatty acid compositions, high contents of the unsaturated fatty acids, which are sensitive to oxidative degradation.

The TG curves indicated that castor oil biodiesel was more stable. Passion fruit biodiesel has a high content of oleic and linoleic acids, which are more susceptible to oxidation.

Biodiesel blend of passion fruit and castor oil 1:1 increased the thermal stability in relation to passion fruit biodiesel. Biodiesel blend of passion fruit and castor oil 1:2 presented higher thermal stability, because castor oil has a high content of ricinoleic acid.

Biodiesel blends of passion fruit and castor oil with diesel (B5 and B20) showed low stability, with volatility similar to diesel.

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