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Evaluation of the oxidative induction time of the ethilic castor biodiesel

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Abstract Oxidative stability is very important in the quality control of oils and biodiesel. Chemical characteristics, as acid, iodine and peroxide values, show the differences among samples and can be used by industries to evaluate the oxidation degree. In relation to advanced techniques, the use of PDSC to measure the oxidative induction time is very important. These measurements were used to evaluate the properties of castor oil after refining process and consequently the biodiesel characteristics. Oxidative induction time indicated that biodiesel samples were more stable than the refined oils. The biodiesel obtained from neutralized oil had a higher stability being probably related to the acid value.

Keywords Oxidative induction time · PDSC · Castor biodiesel

Introduction

Castor oil (known as green petrol) can be used as a renewable energy source in substitution to diesel oil. This plant is rightly adapted to the Brazilian conditions, being cultivated in the whole country. Its latest application is in biodiesel production [1, 2].

Ribeiro and Servalli [3] stated that oil conservation is directly related to the nature and raw material quality as well as to the purity of the oil. Moreover, processing and storage conditions must be considered as glyceride decomposition is accelerated by heating and light exposure, while rancidity is almost always related to the formation of free fatty acids.

Biodiesel consists of long-chain fatty acid esters produced by transesterification reaction of vegetable oils with short chain alcohols. It is compatible with fossil diesel and already comprises a commercial fuel in Europe. However, some chemical and physical properties of biodiesel are affected by oxidation of the fuel during storage. One drawback of biodiesel is that it is more prone to oxidation than fossil fuel and, in its advanced stages, this can cause acidity in the fuel and form insoluble gums and sediments that can block fuel filters [4].

According to Angelucci et al. [5], the high oil acidity increases the loss during neutralization process and indicates the use of low quality seeds, improper handle or storage and also an unsatisfactory processing. These parameters are important in the oxidation stability and may be evaluated by thermal analysis techniques by using Pressure Differential Scanning Calorimetry (PDSC) [6].

Pressure Differential Scanning Calorimetry has been used in several studies to measure the oxidation stability of oils and esters with and without added antioxidants. When the actual run is an isothermal procedure, the time required to detect an exothermic reaction is considered as induction time (OIT). When a non-isothermal procedure is applied, the temperature where an exothermic peak is detected is called the oxidation temperature (OT) [7, 8].

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This work aims at determining the oxidation temperature as well as the oxidative induction time of castor oils refined used different procedures and their biodiesel, using Pressure Differential Scanning Calorimetry.

Experimental

Castor oil extraction

The castor oil was directly extracted from the previously owen-dried seeds (in an air circulation at 60 °C until constant mass). Mechanical extraction was done in a hydraulic press with a pressure of 30 ton and then the oil was filtered.

The oil was degummed with H_3PO_4, degummed with water (washed) and neutralized. In degumming process, the oil was heated at 80 °C and treated with 1% (m/m) of H_3PO_4 (85%) and 2% (m/m) of distilled water. The mixture was vigorously stirred for 30 min and centrifuged for gum separation (proteins, phospholipids and impurities). The liquid was transferred for separation for 30 min, three phases were formed and only the intermediate one was collected.

In the neutralization process, the acidity of oil was determined by titration with sodium hydroxide solution. Values below 1.0 mg KOH g^{-1} indicate that no neutralization process is necessary. Acidity between 1.0 and 1.3 was found and neutralization was done by addition of NaOH solution at room temperature. The mixture was vigorously stirred for 30 min and heated at 70 °C to break the emulsion. Emulsion was transferred for separation, the heaviest part was discarded and the oil was washed with boiling water and dried.

Four oil samples were analyzed: as extracted, degummed, neutralized and washed. Characterization was done according to AOCS standards (American Oil Chemists Society) and acidity, iodine and peroxide values were determined [9].

Biodiesel synthesis

The biodiesel from castor oil (B100) was obtained by ethylic transesterification reaction at room temperature. Reaction was done with an oil:ethanol molar ratio of 1:9, adding 1% of KOH as catalyst. After reaction, the system was transferred to separate biodiesel from glycerin. Then the biodiesel was washed with a 0.1 N HCl solution for neutralization and with water. Residues of humidity and alcohol were removed by drying at 100 °C and pure biodiesel was obtained.

Physico-chemical analyses were done according to the ANP standards (National Agency of Petroleum, Natural Gas and Biofuels) [10–15].

Oxidation temperature and oxidative induction time

Pressure Differential Scanning Calorimetry analyses were done by using TA Instruments model 2920 DSC, coupled to a pressure cell under dynamic and isothermal conditions. Dynamic analyses were done at a heating rate of 5 °C min^{-1} up to 600 °C in oxygen atmosphere and 14 bar of pressure. Isothermal analyses were done in the same conditions of pressure and atmosphere and 105 °C to determine the oxidative induction time (OIT).

Results and discussion

Physico-chemical characterization

Physico-chemical properties of the oil samples are presented in Table 1. A meaningful difference was observed among the samples, indicating the improvement of the oil quality after each treatment step. The ideal acidity for transesterification is below 2 mg KOH g^{-1}.

After synthesis of the biodiesel, samples properties were in accordance to the Standard established by the 42 Resolution from ANP (Table 2).

Table 1 Physico-chemical properties of oils

Analyses	As extracted	Degummed	Neutralized	Washed
Acidity value (mg KOH g^{-1})	1.30	1.10	0.40	0.36
Iodine value (mg I_2 100 g^{-1})	75.95	79.73	86.62	98.25
Peroxide value (meq Kg^{-1})	3.87	3.87	5.88	7.84

Table 2 Physico-chemical properties of the castor biodiesel samples

Analyses	Neutralized	Washed	ANP limit (Res. 42)
Acidity value (mg KOH g^{-1})	0.54	0.59	Below 0.80
Iodine value (mg I_2 100 g^{-1})	77.45	79.39	Take note
Peroxide value (meq Kg^{-1})	2.65	3.87	Take note

Table 3 Oxidation, initial and peak temperatures obtained from Pressure Differential Scanning Calorimetry curves (dynamic procedure) of oil and biodiesel samples

Sample	Conditions	Oxidation temperature (°C)	Initial temperature (°C)	Peak temperature (°C)
Oil	As extracted	189	185	208
	Degummed	165	160	188
	Neutralized	178	174	192
	Washed	180	175	195
Biodiesel	B100 from neutralized oil	171	162	190
	B100 from washed oil	170	157	178

Oxidative stability

Data (in dynamic procedure, indicated oxidation temperature (OT), initial temperature and peak temperature of oils) taken from the Pressure Differential Scanning Calorimetry curves are summarized in Table 3. Initial temperatures varied between 160 and 185 °C attributed to first step of oxidation (initiation), while the oxidation temperatures changed in the 165–189 °C temperature range attributed to propagation process and peak temperatures varied of 188–208 °C are due to termination process. Transitions observed in the 200–300 °C temperature interval were attributed to polymerization process, polymeric of higher molecular masses were decomposed at higher temperatures. The combustion of gum took place between 350 and 400 °C (Fig. 1a).

Comparing the different oil samples, it can be observed that refining decreases the oil stability. This may be due to some compounds remained during refinement process as natural anti-oxidants and vitamins. Degumming led to oils with a less stability than neutralized and washed ones (Fig. 1a).

In relation to biodiesel samples, small differences were observed between the two samples (Fig. 1b). Pressure Differential Scanning Calorimetry curves (Table 3), non-isothermal procedure indicated the oxidation temperature (OT), initial temperature and peak temperature of biodiesel samples. Initial temperatures varied from 157 to 162 °C attributed to first step of oxidation (initiation), oxidation temperatures varied between 170 and 171 °C attributed to propagation process and peak temperatures varied in the 178–190 °C temperature range attributed to termination process. Transitions observed in the 200–470 °C temperature interval were attributed to polymerization process, polymeric with higher molecular masses were decomposed at higher temperatures (Fig. 1b).

Oxidation enthalpy of first transition from neutralized oil to biodiesel was 1,051 J/g (exothermic) and 1,804 J/g (exothermic) from washed oil to biodiesel (Fig. 1b).

Oxidative induction time (OIT) indicated that the as-extracted oil has a higher stability than refined ones (Fig. 2a). In relation to refined oils, the highest stability was obtained for the neutralized one (Table 4). Increased

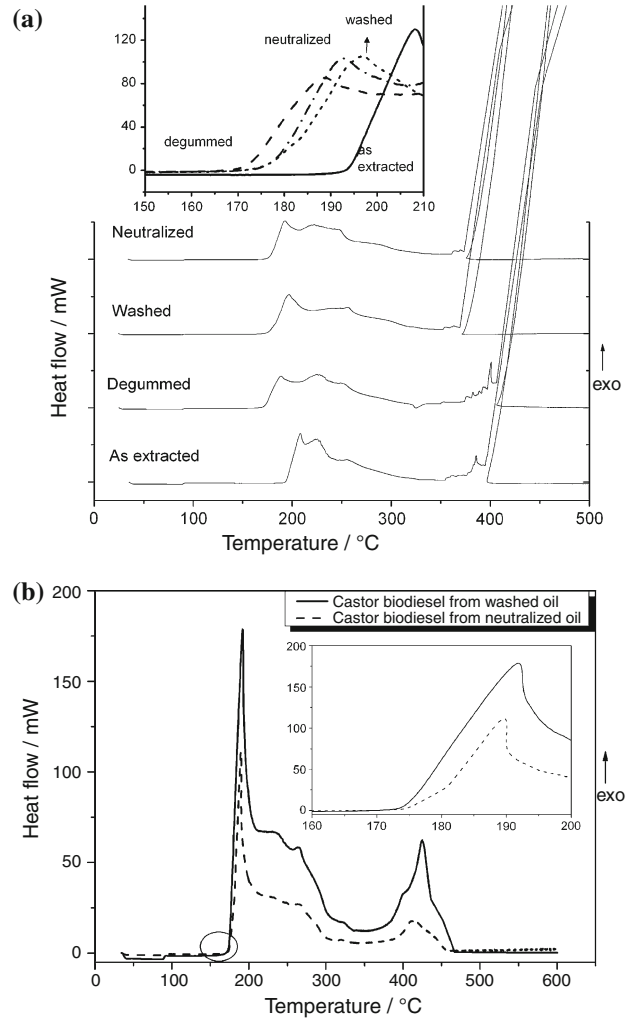

Fig. 1 Pressure Differential Scanning Calorimetry curves of the oils (**a**) and biodiesels (**b**)

acidity is always a result of oxidation of fatty oils and biodiesel, due to the formation of shorter chain fatty acids.

According to oxidative induction time, biodiesel samples were more stable than the refined oils. Biodiesel obtained from washed oil (Fig. 2b) presented the lowest oxidative induction time. This was probably due the acidity and other parameters as peroxide and iodine, as indicated in physico-chemical results (Table 2).

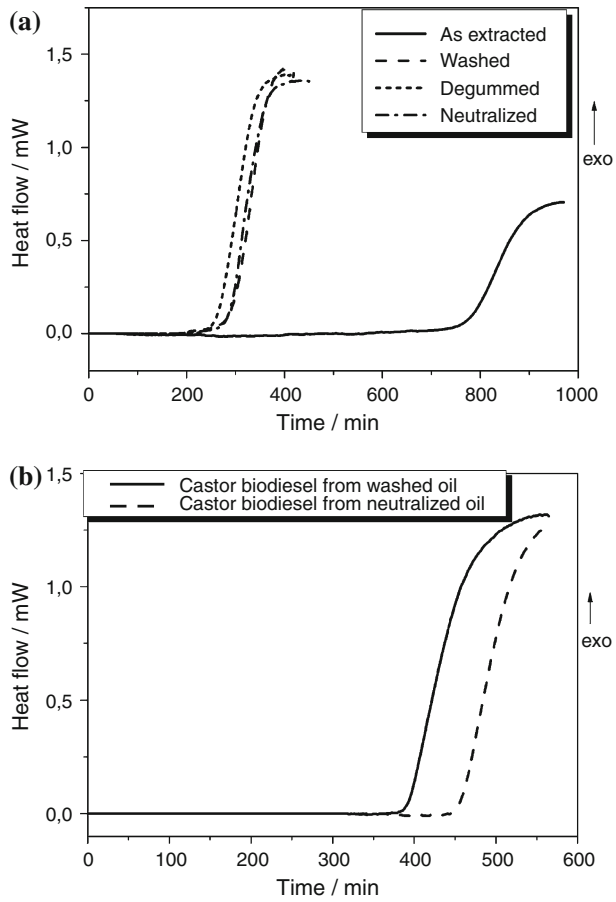

Fig. 2 Pressure Differential Scanning Calorimetry curves of the oils (**a**) and biodiesels (**b**)

Table 4 Oxidative induction time obtained from Pressure Differential Scanning Calorimetry curves (isothermal procedure) of oil and biodiesel samples

Sample	Conditions	Oxidative induction time/min.
Oil	As extracted	723
	Degummed	237
	Neutralized	281
	Washed	268
Biodiesel	B100 from neutralized oil	431
	B100 from washed oil	388

Conclusions

Castor oil has a high oxidative stability due to its fatty acid composition. A decrease in the stability is observed after refining process due to the remaining of natural antioxidants. In relation to the biodiesel samples, a good stability was observed with small difference in the oxidation temperatures. The oxidative induction time indicated that biodiesel obtained from neutralized oil had a higher stability being probably related to the acidity value.

Pressure Differential Scanning Calorimetry technique was useful in the determination of the oxidative stability of the oil and biodiesel samples, being sensitive to the changes in the raw material. This technique can be used for quality control to avoid the use of a degraded raw material in the biodiesel synthesis.

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