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Sunflower biodiesel

Use of P-DSC in the evaluation of antioxidant efficiency

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Abstract The higher is the degree of unsaturation in ester chain of a biodiesel, the smaller is its oxidation stability. Sunflower biodiesel obtained by the ethyl route possesses a high amount of unsaturated fatty acids, mainly oleic acid (C18:1) and linoleic acid (C18:2), thus being more prone to the oxidation process. In Brazil, with the purpose of meeting the specifications of the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP), antioxidant additives, from synthetic and natural origins, have been added to the biofuel. Antioxidants are an alternative to prevent the oxidative deterioration of the fatty acid derivatives, as they are substances able to reduce the oxidation rate. In this study, the oxidative stability of sunflower biodiesel, obtained by the ethyl route and additivated with different concentrations of the antioxidants butylated hydroxytoluene (BHT) and t-butylhydroquinone (TBHQ), was evaluated by means of Pressure differential scanning calorimetry (P-DSC) and the Accelerated oxidative stability test (Rancimat, Method EN 14112). The results obtained by the two techniques showed the same oxidation tendency. Thus, P-DSC can be used as an alternative to determine the oxidative stability of biodiesel. The antioxidant TBHQ, added to biodiesel at the concentrations of 2000 and 2500 mg kg^{-1}, raised the oxidation induction time to a value higher than 6 h, the limit established by the Resolution ANP number 7/2008, thus being the best alternative among the studied antioxidants.

Keywords Biodiesel · Sunflower oil · Thermo-oxidative stability · Antioxidants

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Introduction

The utilization of petroleum in large scale during the second half of the XX century gave rise to a huge increase of the emission of gases responsible for the retention of solar heat and consequently by the increase of global temperature. Biofuels have been pointed out as one of the ecological alternatives to petroleum, in order to reduce, at the short period, the CO_2 emissions in the atmosphere, thus contributing to reduce the greenhouse effect. Biodiesel possesses all the characteristics needed to replace diesel oil, with the advantage of being practically free of sulfur and organic compounds harmful to mankind. Besides, it is a source of renewable energy, it is biodegradable and it is not toxic [1, 2].

In Brazil, the vegetable oils more commonly used for obtaining biodiesel are oils from soybean, castor bean fruit, sunflower, cotton, palm, and others [3, 4].

The oxidation resistance is an important issue for the life cycle of biodiesel, once the triacylglycerides of unsaturated fatty acids, such as linoleic and linolenic, present oxidation-sensitive reactive sites. These esters under specific conditions of heat, UV radiation, moisture, atmospheric air,

and metals, even during small periods, are sequentially induced to reactions of free radical formation, combination of such radicals with oxygen, formation and cleavage of peroxides and subsequent liberation of aldehydes, carboxylic acids, and polymers. These products cause corrosion in engine parts and formation of deposits, leading to the plugging of filters and injection systems. Therefore, the more resistant to corrosion, the better is the biodiesel quality along its life cycle [5, 6].

The biodiesel obtained from sunflower oil is constituted of 98 to 99% triacylglycerides, displaying an elevated content of unsaturated fatty acids (around 83%), being 72% of linoleic acid and a small amount of linolenic acid (≤0.4%).The presence of these fatty acids favors the development of oxidative rancidity. It is possible to block the free radical formation by means of additives (antioxidants), which, in small amounts, act interfering in the lipid oxidation processes [7].

The Resolution number 7 from the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) [8] requires that the biodiesel oxidative stability has to be determined as per the standard EN 14112. Such standard states, for this purpose, the usage of an isothermal at 110 °C, under a pure oxygen atmosphere at a flow rate of 10 L h^{-1}, employment a Rancimat apparatus [9]. On the other hand, Pressure differential scanning calorimetry (P-DSC) has been applied to oxidation analysis of petroleum derivatives, synthetic lubricants and oils [10–13].

Studies showed that P-DSC has the advantage of increasing the overall number of oxygen mols present in the cell, thus allowing increasing the reaction rate at low temperatures [14]. Induction period results also showed a direct correlation with the Rancimat test results, with 6–12% variation. Stavinoha and Kline [15] demonstrated that P-DSC is a proper technique to assess the effects of antioxidant type and concentration on relative biodiesel oxidation resistance.

Therefore, this study has the objective of evaluating the thermal and oxidative stabilities of sunflower biodiesel, obtained by the ethyl route, with and without antioxidant additives BHT and TBHQ.

Experimental

The transesterification reaction of sunflower oil was carried out using basic catalysis, ethyl route, 6:1 ethyl alcohol/oil molar rate. The sunflower oil and the sunflower biodiesel ester compositions were ascertained by a Shimadzu, CGMS-QP2010 model GC–MS chromatograph, equipped with split injector and automatic controller.

The sunflower biodiesel, obtained by the ethyl route, non-additivated and additivated with BHT and TBHQ antioxidants at the concentrations of 200, 500, 1000, 2000, and 2500 mg kg^{-1} were analyzed according to the European Standard EN 14112, using the METROHM Models 743 and 847 Rancimat equipment.

The P-DSC curves were obtained by a differential scanning calorimeter coupled to a pressure cell, model DSC 2920, from TA Instruments, utilizing dynamic analysis conditions. Samples of about 10 mg, in platinum pans, were analyzed under pure oxygen atmosphere at a pressure of 1400 kPa, with flow rate of 10 °C min^{-1}, at the 25–600 °C temperature range.

Results and discussion

Chromatographic analyses of the sunflower biodiesel obtained by the ethyl route

Figure 1 illustrates the chromatogram of ethyl esters present in the sunflower biodiesel. The peaks of the chromatogram denote the preponderance of ethyl linoleate and ethyl oleate, as the triacylglycerides from linoleic and oleic acids prevails in the sunflower oil chromatogram.

The contents of the fatty acids ethyl esters show that the overall amount of ethyl esters was 99.6%, what confirms the efficiency of the purification process carried out after the biodiesel synthesis, Table 1. According to the European Standard EN 1403, the overall ester content must be higher than 96.5%.

Chromatography is considered a very efficient technique to evaluate the composition and purity of esters. The prevalence of unsaturated fatty acids (86.7%) showed that the sunflower biodiesel, obtained by the ethyl route, is unstable toward the oxidative rancidity degradation process, as compared with other biodiesel types, which mainly

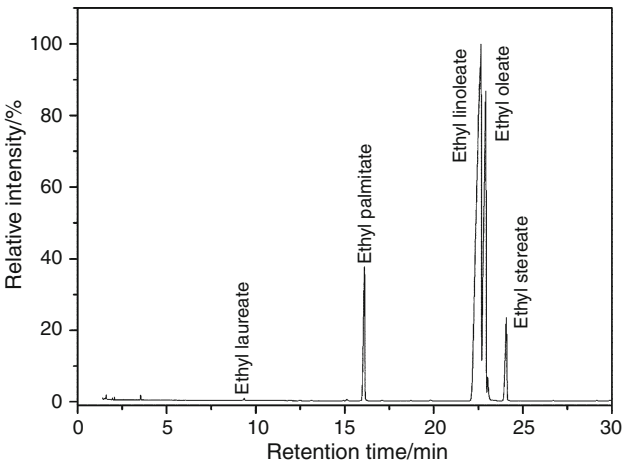

Fig. 1 GC/MS chromatogram of the sunflower biodiesel obtained by the ethyl route

Table 1 Chemical composition of the sunflower biodiesel obtained from the ethyl route

Fatty acid ethyl esters	Retention time/min	Concentration/%
Ethyl laureate	9.3	0.1
Ethyl palmitate	16.1	7.3
Ethyl linoleate	22.7	57.2
Ethyl oleate	22.9	29.5
Ethyl stearate	24.1	5.1
Others	–	0.4
	Overall ester content:	99.6

shows esters from saturated fatty acids. The absence of double bonds in the acyl group chains (R–CO–) reduces the possibility of oxygen attack in these sites and thus, these saturated fatty acids contribute to increase the biodiesel stability toward the oxidative process.

Oxidative stability tests

By means of the dynamic P-DSC curve, it was possible to obtain the onset temperature and the peak temperature related to the biodiesel oxidation. Figure 2 depicts the P-DSC curve of the sunflower biodiesel, obtained by the ethyl route, including its oxidation temperature (T_{onset} = 141 °C), peak temperature of the dimerization process (T_p = 163 °C) and also the remaining peak temperatures related to the combustion of low and high thermal stability polymers.

The oxidative induction period (IP) of the sunflower biodiesel, obtained by the ethyl route, determined by the Rancimat analysis was 0.75 h, a value that does not meet the ANP specifications established in the ANP Resolution number 7/2008, which requires a minimum time of 6 h. According to the aforementioned Resolution, this biodiesel can not be commercialized without an antioxidant.

P-DSC curves of the sunflower biodiesel, obtained by the ethyl route, without and with the addition of the antioxidant BHT at the concentrations of 200, 500, 1000, 2000, and 2500 mg kg^{-1} are depicted in Fig. 3. These curves are overlapped aiming at noticing the highest oxidation temperature, in other words, the highest oxidative stability.

P-DSC and Rancimat results are summarized in Table 2. The sample containing no antioxidant BHT presented the smallest value of oxidation temperature (T_{onset}). Growing values of both oxidation temperature (T_{onset}) and induction period (IP) were noticed upon the increase of the antioxidant concentration. Although the biodiesel samples containing the antioxidant BHT displayed higher oxidative stability than the sample of BHT-free biodiesel, such increase in the oxidative stability was not sufficient to raise the induction period to a value no smaller than 6 h at 110 °C (Table 2), as required by the ANP Resolution number 7/2008.

The procedure for adding the antioxidant TBHQ at several concentrations to the sunflower biodiesel, obtained by the ethyl route, aiming at ascertaining the best concentration, was similar to the one employed for the antioxidant BHT. Figure 4 shows the P-DSC curves of the sunflower biodiesel to which the antioxidant TBHQ was added at the concentrations of 0, 200, 500, 1000, 2000, and 2500 mg kg^{-1}.

P-DSC and Rancimat results for the antioxidant TBHQ are summarized in Table 3. The values of oxidation temperature determined by the dynamic P-DSC (T_{onset}) for the biodiesel samples additivated with TBHQ at the concentrations of 200 mg kg^{-1} and 500 mg kg^{-1} were very

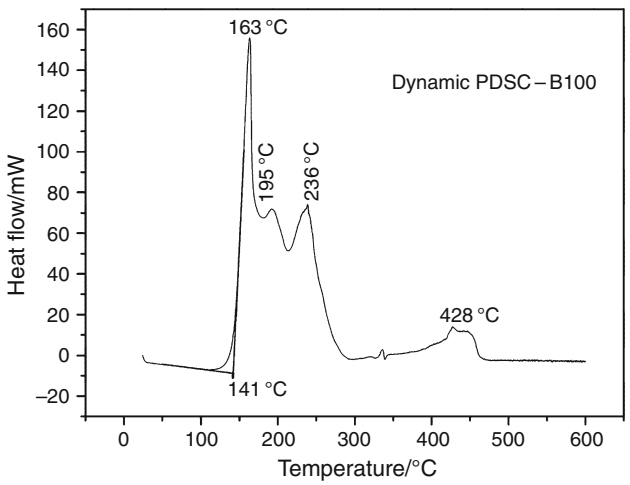

Fig. 2 P-DSC curve of the sunflower biodiesel obtained from the ethyl route

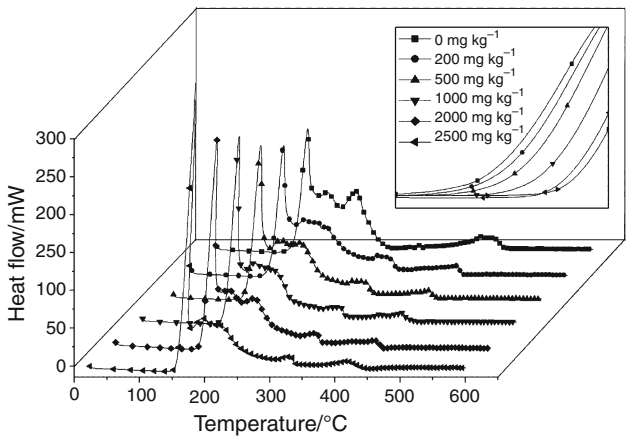

Fig. 3 Overlapping of the dynamic P-DSC curves of sunflower biodiesel obtained by the ethyl route with and without the addition of antioxidant BHT. The *inset* shows the oxidation temperature (T_{onset}) of the biodiesel samples

Table 2 Results of onset temperature and peak temperature, by P-DSC, and induction period (IP) by Rancimat from the sunflower biodiesel obtained by the ethyl route (B100) with and without BHT

Samples	P-DSC		Rancimat
	*T_{onset}/°C	*T_p/°C	IP/h
B100	141	163	0.75
B100 + 200 mg kg^{-1} BHT	145	165	1.28
B100 + 500 mg kg^{-1} BHT	148	169	2.01
B100 + 1000 mg kg^{-1} BHT	153	175	2.98
B100 + 2000 mg kg^{-1} BHT	157	179	4.44
B100 + 2500 mg kg^{-1} BHT	160	187	5.09

* Onset temperature (T_{onset}) and peak temperature (T_p)

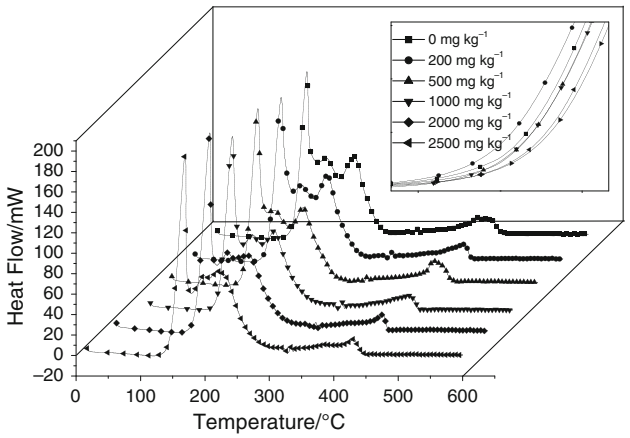

Fig. 4 Overlapping of the dynamic P-DSC curves of sunflower biodiesel obtained by the ethyl route with and without the addition of antioxidant TBHQ. The *inset* shows the oxidation temperature (T_{onset}) of the biodiesel samples

Table 3 Results of the peak temperature and onset temperature, by P-DSC, and induction period (IP) by Rancimat of the sunflower biodiesel obtained from the ethyl route (B100) with and without TBHQ

Samples	P-DSC		Rancimat
	*T_{onset}/°C	*T_p/°C	IP/h
B100	141	163	0.75
B100 + 200 mg kg^{-1} TBHQ	141	162	1.08
B100 + 500 mg kg^{-1} TBHQ	142	165	1.63
B100 + 1000 m kg^{-1} TBHQ	143	164	3.11
B100 + 2000 m kg^{-1} TBHQ	146	168	11.43
B100 + 2500 m kg^{-1} TBHQ	147	169	24.57

* Onset temperature (T_{onset}) and peak temperature (T_p)

similar to the antioxidant-free sunflower biodiesel, ethyl route. As expected, higher induction periods were found for the sunflower biodiesel, obtained by the ethyl route, to which higher amounts of antioxidant TBHQ were added.

Induction periods higher than 6 h, at 110 °C were only achieved for TBHQ concentrations over 2000 mg kg^{-1}. Thus, TBHQ addition, at the concentrations of 2000 and 2500 mg kg^{-1} was efficient to rise the induction period to a value higher than 6 h, the limit established by ANP. In relation to the cost/benefit relation, the antioxidant TBHQ at the concentration of 2000 mg kg^{-1} is the best alternative.

It should be pointed out that correlation between Rancimat and P-DSC results could not be done. This fact should be evaluated considering the oxidation mechanism. The first exothermic reaction occurs at the beginning of the propagation step, being detected in the P-DSC analysis. On the other hand, volatile conducting products are only formed in the termination step, being detected by Rancimat. This way the authors believe that the different techniques do not reflect the same step of the oxidation mechanism and can not be correlated. On the other hand they are complementary and the use of both techniques can make the understanding of the oxidation process clearer.

Regarding the use of antioxidants, BHT increased the oxidation and dimerization temperatures but was not effective in raising the induction period. On the other hand, TBHQ did not modify the oxidation temperature significantly but effectively corrected the induction period of the biodiesel. This effect was attributed to the antioxidation mechanisms. The TBHQ forms quinone and hydroquinone molecules by disproportionation of semiquinoid radicals initially formed during the reaction [16]. These molecules act as an antioxidant in the propagation step preventing the formation of autoxidation products that are detected by Rancimat. It did not actively influence the oxidation temperature, not being detected in P-DSC curves. BHT only changed the initial oxidation step of biodiesel but did not avoid the product formation.

In general, these results agree with the report of Ferrari and Souza [14] for distilled sunflower biodiesel, also obtained by the ethyl route. The authors studied the antioxidants TBHQ, BHT, and BHA. Their results were similar to the ones of this study, as TBHQ met the ANP specifications, whereas BHT and BHA, although improving the oxidative stability, did not reach the ANP standards.

Thus, TBHQ can be considered as a good option to retard the oxidative processes of sunflower biodiesel, obtained by the ethyl route.

Conclusions

The presence of ethyl esters from the unsaturated oleic, linoleic, and linolenic fatty acids in the sunflower biodiesel, obtained by the ethyl route, confirms its smaller oxidative stability. The addition of the BHT antioxidant to the

sunflower biodiesel, at concentrations not higher than 2500 mg kg^{-1}, was not enough to meet the ANP requirements. However, the addition of the antioxidant TBHQ at the concentrations of 2000 and 2500 mg kg^{-1} succeeded in rising the induction period in order to achieve a value of at least 6 h at 110 °C, lower limit established by ANP. In relation the cost/benefit analysis, the usage of the antioxidant TBHQ at the concentration of 2000 mg kg^{-1} is the best alternative. Results obtained by the Rancimat method and by the P-DSC technique were consistent in terms of the best performance of TBHQ. P-DSC was shown to be an alternative technique to determine the biodiesel oxidative stability.

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