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An alternative method by pressurized DSC to evaluate biodiesel antioxidants efficiency

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Abstract The purpose of this article is to present an alternative method developed using pressurized differential scanning calorimetry (P-DSC) to evaluate the oxidative behavior of biodiesel obtained from soybean oil, produced by ethylic route (BSET), with and without the addition of synthetic antioxidants, as well as to compare the results with those obtained by Rancimat Method, which were carried out according to the European Official Standard Method EN 14112. BSET samples were analyzed using four different types of synthetic antioxidants at concentrations varying between 250, 500, and 1000 mg kg^{-1}. The measurements done by P-DSC were performed using static air at 80 psi and isothermal conditions at 110 °C, the same operating temperature than the Rancimat method. The experimental results of the oxidative stability measured from both methods have shown good correlations, which depend on the antioxidant, showing a gradual improvement in the oxidative stability of BSET with increasing added concentration of antioxidants. Opposite result behavior occurred for the measurements done in the presence of one of the antioxidants, which was composed by a significant content of components volatile below 110 °C, which accelerate the induction of the biodiesel oxidation in P-DSC method, but apparently do not interfere in the electrical conductivity measurement method (Rancimat). The advantages of the developed method using P-DSC technique with respect to Rancimat method is that it allows one to use a smaller sample, increases sensitivity to antioxidant action, reduces the analysis time for the evaluation of the antioxidant efficiency and detects any occurring oxidative process, independently of the volatility of the formed products, which may form oxidated products that remain in the liquid phase and that are non detectable by Rancimat method.

Keywords Biodiesel · Antioxidant efficiency · P-DSC · Rancimat · Oxidation stability

Introduction

For many reasons, ranging from reducing dependence on oil, concerns about climate change caused by the high carbon dioxide emissions and specially national energy security, many nations in the world have been concerned with the revision of their Energy Matrix structure, increasing the share of renewable energy sources [1–3].

With the purpose to comply the supply of the increased global energy demand in a sustainable way, clean technologies are being developed, fuel produced from vegetable oils or animal fats are highlighted, showing in the last decade a surprising development [4], exceeding all the expectations, as those predicted by Rudolf Diesel in 1912: "*The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time*" [5].

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In this context, biodiesel stands out among the products derived from modern biomass as an attractive alternative fuel to petroleum diesel. Among its advantages, we can list that it is obtained from renewable sources, it has a high calorific power, it is biodegradable, free of sulfur and generates lower CO_2 emissions [1, 6, 7]. However, unlike petroleum diesel, which is highly stable to oxygen exposure [5], vegetable oils and fats which are converted into biodiesel are susceptible to oxidation in contact with oxygen [2].

Biodiesel are fatty acids esters resulting from the condensation reaction of a carboxylic acid (with long alkyl chain) and an alcohol, usually methanol or ethanol [8, 9]. Fatty acids esters can also be produced by transesterification, the most frequently used process, by which an ester is transformed into another through the interchange of alkoxy structures [10]. The fatty acid methyl esters can be produced by a transesterification process, a reaction of triglycerides or triacylglycerols (TAGs) with methanol. Ethyl esters are obtained when ethanol is used instead of methanol. The TAGs, components of oils and fats, are long chains with single bonds (saturated) or double bonds (unsaturated), the most common being those who have about 12–22 carbon atoms [9].

The oils and fats are substances obtained from vegetable or animal sources, which are classified as lipids [2, 8, 9, 11]. Due to their high viscosity, TAGs cannot be used directly as fuel in compression ignition engines and for this reason, they have to be chemically processed to biodiesel, modifying their chemical structure [2, 5]. During transesterification reaction of a TAG, forming esters (biodiesel) and glycerol, the viscosity is decreased but the cetane number and the calorific value are maintained [12]. The cetane number measures the quality of the ignition of a fuel in the engines and the higher it is, the shorter is the time between the moment of fuel injection and its ignition [2].

Oxidative stability

The stability of a fuel is defined as its resistance to physical and chemical changes caused by the interaction with environmental factors. It concerns the oxidative stability (resistance under oxidizing conditions), thermal stability (resistance to heat stress), and storage stability (resistance to changes during storage) [13–15]. The oxidation stability of a fuel is considered an important evaluation parameter that insures its quality, allowing its commercialization and insuring higher storage times [16, 17].

The oxidation stability of a biodiesel is influenced by the composition and chemical structure of the fatty acids from which it was originated, as well as by the number and positions of their double bonds [2]. The oxidation of a fatty oil is a spontaneous phenomenon caused by several factors such as the presence of oxygen, exposition to light, high temperature, and metals present in the storage tank, which can directly influence the fuel quality [2, 18]. Fatty acids with high levels of unsaturated bonds are much more prone to oxidative degradation in contact with pro-oxidant agents. Because of the different sources of biomass used as raw materials for biodiesel production, and the various existent production processes, biodiesel may have different compositions and different levels of oxidation stability [2].

The use of degraded fuel oil cause engine problems such as clogging fuel filters, which can cause poor performance of the engine [12, 13]. Therefore, it is essential to standardize the parameters of fuel quality to insure the smooth running of the operation of spark ignition engines [2, 5, 18]. Since oxidative stability affects fuel quality, specifications for the marketed product have been established to insure proper performance, besides preserving the integrity of the engine from possible degradation of the fuel during storage [18, 19]. Many procedures have been developed for the analysis, characterization and quality control of biodiesel, mainly because the methods used in the analysis of fossil fuels are not appropriate to fuels manufactured from vegetable oils [2].

Methods for the determination of oxidative stability

With the purpose to predict the shelf life and to insure their quality, assessment methods are used to determine the oxidative stability of biodiesel. As the natural phenomena of oxidation are slow processes, which can happen over months, the stability tests in real time become unavailable for industrial quality control [20]. In this context, methods for accelerated oxidative stability of oils and biodiesel have been developed to predict the maximum storage time for which they may be kept without compromising product quality. In general accelerated oxidation tests under standard conditions are used (to promote forced aging) and a typical transformation onset point is chosen, when there is evidence of oxidative deterioration. These tests use extreme conditions, when high temperatures are applied and in the presence of an oxidizing gas (oxygen or synthetic air) to accelerate the rate of oxidation reaction, to quickly estimate the oxidative stability of the product [2, 17, 21].

Several methods have been developed to evaluate the resistance to oxidation of fuels using accelerated procedures. The greenhouse method, known as Schaal and active oxygen method (AOM), also known as Swift Test is the oldest one, and it is still used nowadays. Currently, automated methods based on measurements of electrical conductivity are the most used, among which is the Rancimat Method. In these newer methods stability of biodiesel is related to the secondary oxidation products, while in the older methods, the primary products (peroxide) are measured [17, 21]. This methodology is now standard in Brazil in accordance with European standard EN 14112 method and is part of the Brazilian Government Technical Regulation (ANP 07/2008) proposed by the “National Agency of Petroleum, Natural Gas and Biofuels”/ANP, which is the Brazilian Government Institution that controls the quality of fuels commercialized in Brazil. This Resolution establishes a minimum of 6 h for the oxidation induction time (OIT) determined by this method.

Thermal analysis of oils, fats, and biodiesel

Thermal analysis has been one of the analytical techniques used in recent years to monitor the stability of vegetable oils and animal fats [17, 22–29]. Samples can be characterized by thermal analysis techniques measuring several properties such as thermo-oxidative behavior, specific heat, thermal decomposition activation energy, temperature and enthalpy of crystallization, action of antioxidants in oil thermal stability, unsaturation degree from melting and crystallization oil profile curves, and high-pressure OIT measurements [23].

Fatty acids thermal transitions are induced by temperature changes (heating/cooling). As the reaction of an oxygen molecule with an unsaturated fatty acid is exothermic and corresponding measures of changes in enthalpy can be used to monitor oxidative stability of vegetable oils, differential scanning calorimetry (DSC) technique is presented as the most indicated to identify and quantify these transformations [11, 30]. With the advances in recent decades in analytical instrumentation, the number of scientific papers suggesting new methodologies using the DSC technique and mainly pressure DSC (P-DSC) for the determination of kinetic parameters to assess the stability oils, fats and biodiesel has substantially increased. Since the 70s [24, 30], this technique was first used as a method of accelerated oxidation of oils and fats. Cross in 1970 conducted a study comparing the DSC method and AOM obtains a reasonable correlation of results. Hassel in 1976 was the first to use the technique P-DSC in isothermal mode with pure oxygen gas action, obtaining a linear correlation and better results than those of the AOM.

Litwinienko studied by DSC the oxidation of unsaturated fatty acids (oleic, linoleic, linolenic, erucic) [27], saturated fatty acids (lauric, myristic, palmitic and stearic) [28] and of their ethyl esters by determining the kinetic parameters by Ozawa–Flynn–Wall method. The results of thermal analysis for the unsaturated fatty acids showed that their oxidative stability is lower than that of the ethyl esters, confirming that the oxidative stability depends on the number of double bonds and carbon chain length. For saturated fatty acids (C12–C18), oxidation data are not correlated with the length of the chain.

Kowalski [24, 25, 29] used the P-DSC technique to study the oxidative stability and determination of kinetic parameters of vegetable oils commonly used in industry, in some cases with addition of synthetic antioxidants. His results show that the technique can be successfully applied for samples with or without antioxidants. According to his conclusions, P-DSC isothermal mode is more suitable in studies of lipid oxidation than non-isothermal DSC. As the analysis is performed at lower temperatures, the heat of transitions can be better defined. During the analysis by P-DSC, with the pressure cell sealed during the oxidation process the heat released is continuously recorded. From the resulting P-DSC curve, the oxidation onset temperature or time may be determined. In isothermal evaluations, the higher is this oxidation onset time, the higher is the oxidative stability [25].

To attend biodiesel quality control, the development of techniques for fast and reliable analysis is necessary. Thus, many studies have been developed using thermal analysis, comparing the results of oxidative stability obtained either by DSC [31–33] or P-DSC [34–38] with those of the Rancimat method (EN 14112), which is the official method used at industrial level. In all studies, the authors report the consistency between the results obtained by both techniques. The advantages of using the P-DSC is that with the high pressure cell sealed, the loss of volatile compounds of the antioxidants decreases but the pressure of the oxidant gas (oxygen or air) adjusted to exceed the ambient pressure accelerates the oxidation reaction rate, promoting a faster analysis [39].

This can be confirmed by the work of Kowalski and co-workers [33, 34]. When comparing the result of oxidation of oils by DSC and P-DSC, they concluded that although there was consistency and good correlation with the results of the Rancimat method, the results obtained by DSC were not as good as those obtained using P-DSC.

In the present study, the oxidative stability of a Brazilian soybean biodiesel was analyzed by an alternative P-DSC isothermal method performed at 110 °C and 80 psi, which was developed to evaluate the efficiency of four commercial anti-oxidants. Results are compared and discussed with corresponding data obtained by Rancimat method.

Experimental

Materials and methods

The soybean biodiesel (BSET B-100) used in this study, was produced by a Brazilian manufacturer (SP/Brazil) using ethylic route. In Table 1 are presented the physical and chemical analysis data. Except for oxidation stability, all results were in accordance with the specifications of the

Table 1 Ethylic soybean biodiesel (BSET B-100) characterization data

Characteristics		Units	Method	Specification/ANP limits[a]	Analysis result
Volatility	Specific mass at 20 °C	kg/m^{-3}	ASTM D4052	Note	876.4
	Flash point	°C	ASTM D93	100 min	129
Fluidity	Kinematic Viscosity at 40 °C	cSt/mm^{2} s^{-1}	ASTM D445	Note	4.389
	Low-temperature filterability tests	°C	ASTM D6371	Note	−9
Composition	Ester content	Mass%	EN 14103	Note	96.8
	Sulfur content	mg kg^{-1}	ASTM D5453	Note	1.3
Combustion	Carbon residue of 100%	Mass%	ASTM D524	0.1 max.	0
	Sulphated ash content	mass%	EN ISO 3987	0.02 max.	0.000
Corrosion	Corrosiveness to copper, 3 h, 50 °C	–	ASTM D 130	1 max.	1 b
Contaminants	Group I metals: Na	mg kg^{-1}	EN 14108/	10 max.	1.9
	Group I metals: K	mg kg^{-1}	EN 14109	10 max.	<1.0
	Group II metals: (Ca + Mg)	mg kg^{-1}	EN 14538	Note	<1.0/<1.0
	Phosphorus content	mg kg^{-1}	EN 14107	Note	1.8
	Free glycerol	Mass%	ASTM D6594	0.02 max.	<0.01
	Total glycerol	Mass%	NBR 15344	0.38 max.	0.239
	Total glycerol	Mass%	ASTM D6584	0.38 max.	0.22
	Monoglyceride content	Mass%	ASTM D6594	Note	0.64
	Diglyceride content	Mass%	ASTM D6594	Note	0.24
	Triglyceride content	Mass%	ASTM D6594	Note	0.16
	Methanol or ethanol content	Mass%	EN 14110	0.5 max.	<0.01
Acid value		mg KOH g^{-1}	ASTM D664	0.8 max.	0.22
Iodine index		g (100 g)$^{-1}$	EN 14111	Note	120
Oxidation stability a 110 °C		H	EN 14112	6 h	5.76 h
Water content/Karl Fischer		mg kg^{-1}	ASTM D6304	Note	168

[a] Parameters for B-100 are specified by the ANP Technical Regulation # 07/2008

Technical Regulation (ANP 07/2008). As mentioned in several papers, biodiesel derived from saturated fatty acids are more stable than the unsaturated ones, with respect to oxidation. The soybean oil, which has high levels of unsaturated fatty acids—linoleic acid (53 mass%) and oleic acid (23 mass%), is prone to oxidation [9], justifying its low oxidative stability.

Because soybean oil is highly susceptible to oxidation, antioxidants are utilized as a way to increase its shelf life, insuring its acceptance in the market. In order to evaluate the effectiveness of antioxidants in improving the oxidative stability, four different types of synthetic antioxidants were used in this study: phenol + amine mixture, phenolic, biphenolic, and organic acid + hydroquinone mixture. Samples were analyzed with concentrations varying between 250, 500, and 1000 mg kg^{-1} for each of the four tested antioxidants.

The P-DSC developed method

Pressure accelerated thermal oxidation runs were performed in a TA Instruments, P-DSC, model P-DSC Q20. Approximately 3 ± 0.2 mg of sample was used in each analysis, in open 110 μL platinum pans and the reference pan was an empty platinum pan of same capacity. Calibration runs were performed with same kind of pans and indium as standard metal. After inserting the sample and reference pans, the DSC cell was sealed and pressurized using synthetic air atmosphere up to 80 psi (551.6 kPa). Then, by using pressurized static air mode conditions, the sample was heated from 30 to 110 °C at a heating rate of 10 °C min^{-1} and maintained at this temperature until oxidation of the sample has occurred, which was evidenced by respective exothermic peak. This temperature is the same than that which the sample is exposed to oxidation conditions in Rancimat method as detailed in next item. Experimental data were analyzed using TA Instruments Universal Analysis software, through which the oxidation on set time of each case was determined. This time, named OIT, was determined from the intersection of the tangent to the initial baseline and the tangent to the increasing heat flux side of the respective exothermic DSC peak [40], as shown in Fig. 1a.

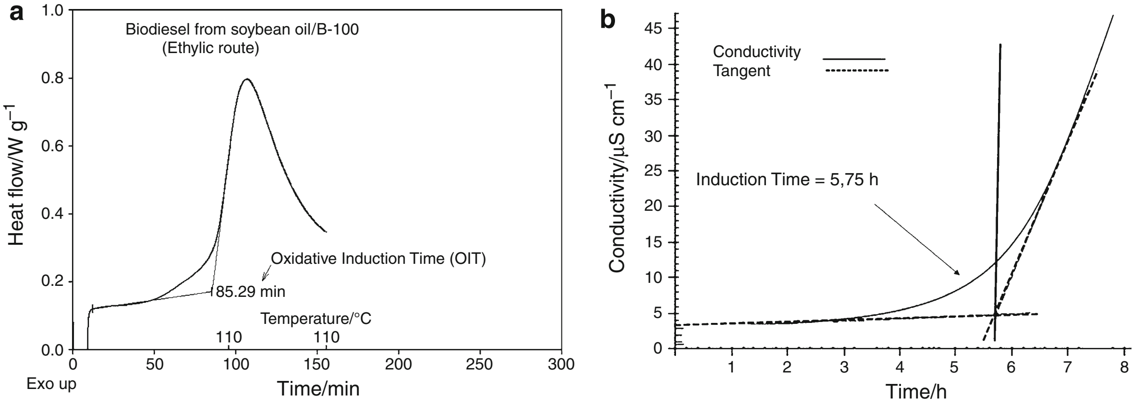

Fig. 1 Typical curves of developed P-DSC (**a**) and Rancimat method (**b**), used in respective determinations of OIT

The Rancimat method

The analysis of the oxidative stability of the samples was also performed using the Rancimat method, by using model 743 Metrohm equipment, according to EN 14112 standard method. This method, proposed by Hadorn and Zurcher in 1974, consists on exposing a sample of approximately 3.0000 g (±0.0010 mg) in a closed vessel heated isothermally at 110 °C to a flow of 10 L h^{-1} of air, which is being sprayed through the sample, to induce its oxidation. At these conditions, the formation of oxidized compounds is accelerated, initially forming peroxides as primary oxidation products. Then, formation of secondary oxidation compounds occurs, such as low molecular weight organic acids and other volatile oxidized organic compounds. The air current drags the evolved gases into a distilled water phase maintained in an adjacent electrical conductivity measurement cell. As the conductivity of the distilled water is continuously monitored, the time from the beginning of the test to the time that these secondary dragged oxidation products begin to promote a significant conductivity change behavior in the water phase, is known as Oxidation Stability Index or induction time (IT) [21, 41, 42]. This onset time measurement is illustrated in Fig. 1b.

Results and discussion

The results obtained by applying the developed P-DSC method are shown in Fig. 2. It can be seen that as the antioxidant content is increased from 0 (pure BSET) to 1,000 mg kg^{-1}, the OIT is increased and the way that this happens depends on the nature of the antioxidant.

Although BSET biodiesel presents a low oxidative stability according to the official ANP specification, it is observed that with the addition of antioxidants it greatly improves its oxidative stability. For all the tested antioxidants, with the addition of 250 mg kg^{-1}, the measured OIT values are above the minimum required. This can be observed by the overlay of the respective P-DSC plots in Fig. 2, whose results show a gradual increase of the OIT with increasing concentration of antioxidant. The Rancimat method applied to the same mixtures shows the same trend, as seen by respective results in Table 2.

In a critical analysis of the results of P-DSC curves, to evaluate the tested additives, phenol + amine antioxidant (Fig. 2a) shows a good efficiency, quickly reaching, at a concentration of 250 mg kg^{-1}, very good OIT and IT (OIT/IT) values. However, with increasing concentration this value is not significantly changed, showing a tendency of saturation of its effect.

Biphenolic antioxidant (Fig. 2b) also presents a good efficiency. Although not so quickly, it gets the same values of OIT/IT when compared to the phenol + amine antioxidant cases and we can see that this antioxidant does not show signs of saturation at the different used concentrations.

Among the three first antioxidants listed in Table 2, the phenolic antioxidant (Fig. 2c) presents the worst results of all antioxidants, because even at the highest concentration, it does not allow to obtain the same order of values of OIT and IT than the others do with a lower concentration.

In terms of OIT/IT values, the sample with organic acid + hydroquinone antioxidant has the best performance of all antioxidants, when analyzed by the Rancimat method. However, when using P-DSC method, the opposite occurs. In an attempt to explain this different behavior of this antioxidant, thermogravimetric analysis of all antioxidants was performed from 30 to 280 °C, at a heating rate of 10 °C min^{-1} in platinum pans and 100 mL min^{-1} of air flow, to observe their thermal stability at the operating temperatures and conditions of the used methods. As shown in Fig. 3, which compares the TG/DTG curves of all antioxidants, the antioxidant in question presents a first DTG peak ending before 100 °C, which can be attributed

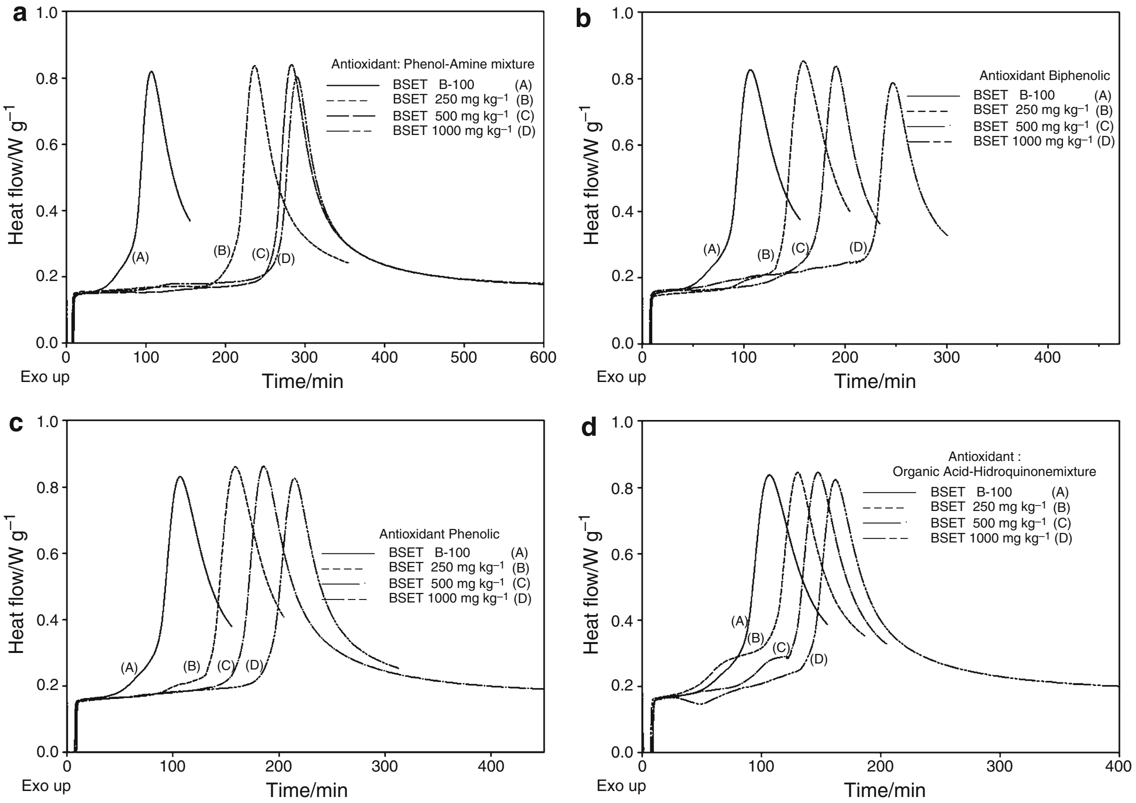

Fig. 2 Overlay of the P-DSC plots obtained from BSET with an antioxidant additive: phenol + amine mixture (**a**), biphenolic (**b**), phenolic (**c**), organic acid + hydroquinone mixture (**d**)

Table 2 OITs obtained by the developed P-DSC and Rancimat methods

Oil stability index (OSI)	Antioxidant	Concentration/mg kg^{-1}			
		0	250	500	1000
P-DSC (static mode)	Phenol + amine mixture	1.42	3.56	4.34	4.47
Oxidation onset/h	Phenolic	1.42	2.28	2.73	3.21
	Biphenolic	1.42	2.28	2.84	3.78
	Organic acid + hydroquinone mixture	1.42	1.84	2.12	2.35
Rancimat instrument	Phenol + amine mixture	5.76	8.66	9.66	10.24
IT/h	Phenolic	5.76	6.16	6.77	7.45
	Biphenolic	5.76	7.61	9.60	12.00
	Organic acid + hydroquinone mixture	5.76	9.62	13.00	21.00

to a high volatile component loss, a fact that is not observed in the analysis of the other three antioxidants. This release of volatile component(s), which certainly occurs during the analysis by P-DSC when the cell temperature is increased to 110 °C and maintained afterward at this temperature, increases the experimental pressure of the gaseous phase containing air above the sample in the P-DSC heating cell. Consequently, this fact increases the oxygen partial pressure acting on the sample, accelerating its oxidation process. Thus, the higher is the content of this organic acid + hydroquinone antioxidant mixture added to the biodiesel, the higher is this oxidative accelerating effect and the lower is the respective measured relative OIT, as noticed.

As can be seen from Fig. 3, at 80 °C, this antioxidant already presents a loss of 20.1% of its mass, the phenolic antioxidant has already lost 1.0% of its mass, the phenol + amine antioxidant 1.5 mass% and the biphenolic antioxidant shows a very little increase in mass (0.1%), due to a resulting little oxidation. However, at 110 °C, while the biphenolic antioxidant maintains its mass, the phenolic has already lost 5.8% of its mass, the phenol + amine

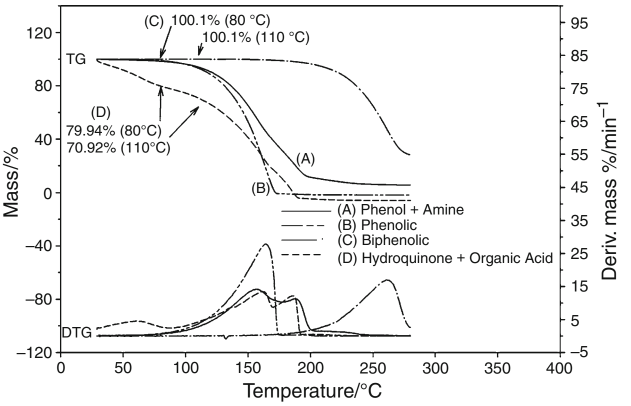

Fig. 3 TG and DTG curves of each antioxidant in air flow at 10 °C min^{-1}

antioxidant 6.6%, and the organic acid + hydroquinone antioxidant sample has already lost a total of 29.1% of its mass. This much higher release of volatile matter at experimental conditions explains why the organic acid + hydroquinone antioxidant presents the worse performance in P-DSC experiments as discussed.

Although the compositions of the antioxidants are proprietary, it must be noted that the initial significant amount of volatile matter lost from the organic acid + hydroquinone antioxidant mixture does not affect on the same way the Rancimat analysis results, because in this method, the volatiles, which are entrained by the air flow to the Rancimat conductivity cell that is maintained at 110 °C, keep being entrained by the air flow in this cell, and actually, they do not experimentally change the conductivity of the absorbing aqueous phase in a significant way. As in case of the use of Rancimat method, this antioxidant presents the best performance, this suggests that these volatile components, even if they could be apparently absorbed in the aqueous phase, they did not dissociate in water, changing the resulting conductivity. Thus, this phenomenon does not affect the recorded onset time by the Rancimat method measuring system, what explains the much higher recorded OITs measured for this antioxidant addition by this method than when measuring the oxidation process by P-DSC method.

In Fig. 4 are shown, for each antioxidant, the percentual increase of the OIT with respect to that of the biodiesel for each antioxidant, as a function of their concentrations, for both methods. It can be noted that the resulting curves in both techniques show the same trend, but the results obtained by P-DSC method show a higher resolution,

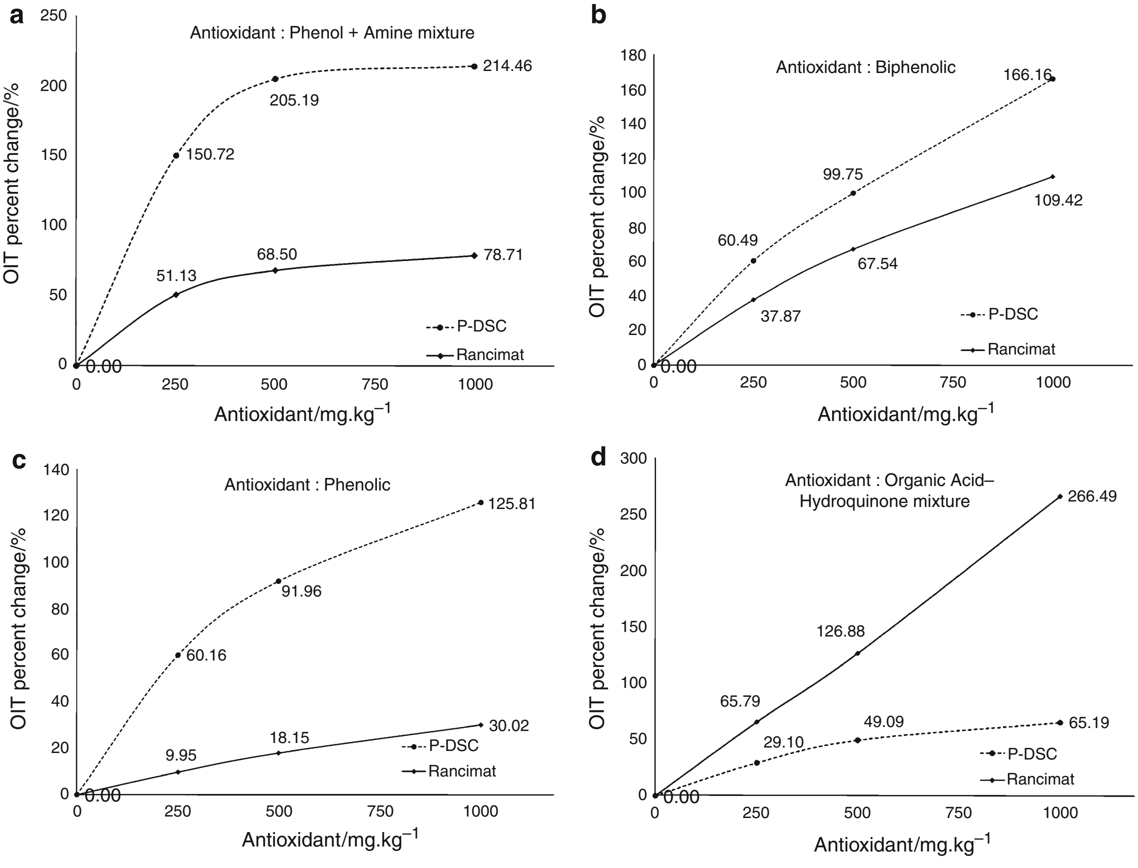

Fig. 4 Percentual change of the OIT versus the concentration of antioxidant when using P-DSC and Rancimat methods

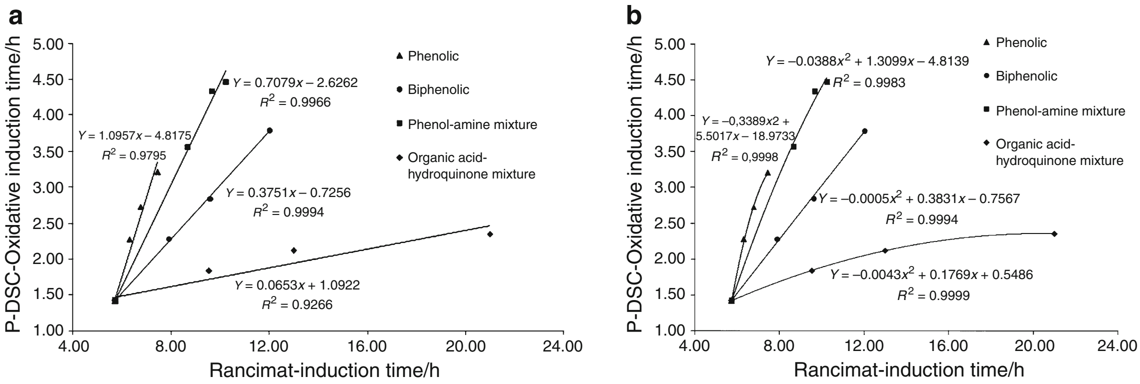

Fig. 5 Correlations between results of the developed P-DSC method and Rancimat method

because, when we compare the percentual change of the OIT of the samples of biodiesel with antioxidant with that of the biodiesel without any antioxidant, a higher percentual change occurs for a same change in antioxidant concentration, which is true for all antioxidants, except for the organic acid + hydroquinone antioxidant used in this study, for the already discussed reasons. In this case (Fig. 4d) there is a different behavior, when an inversion of efficiency occurs.

Figure 5a and b show the correlations between the measurements obtained by the two methods for each kind of antioxidant addition as its content was increased. The results indicate that for three of the studied antioxidants, for which the linear correlation coefficient was higher than 0.979 there is a linear correlation between the measurements done by the compared methods. However, the correlation coefficient is practically one when a second-degree polynomial regression is considered, indicating that there is effectively a good correlation between the results of the developed P-DSC method and Rancimat method, but this correlation depends on the used antioxidant.

Conclusions

- In the oxidative stability determination of biodiesel, the use of the alternative developed P-DSC method to evaluate antioxidant efficiency, at lower manometric pressures than those usually used so far, presents as advantages the use of a smaller sample, lower analysis time and a higher sensitivity than the Rancimat method.
- When the antioxidant releases volatile components in a significant amount at temperatures lower than 110 °C, they may affect the Rancimat Method results, only when they act on the electrical conductivity measurements. But the released components affect the results obtained by the developed P-DSC method, because they increase the actual P-DSC cell operating pressure, which in turn accelerates the oxidation process, resulting in much lower relative IT measurements than those obtained in corresponding Rancimat measurements.
- For the tested antioxidants at different used concentrations, the results obtained by the developed P-DSC method and those obtained by Rancimat method present good correlations between each other, which depend on the antioxidant composition.
- The fact that different correlations between the applied methods were obtained for each antioxidant, indicates that in each case, different oxidation mechanisms may have occurred, which in turn may or not form volatile oxidated products detectable by Rancimat method.
- It must be noted that the developed P-DSC method detects any occurring oxidative process, independently of the volatility of the formed products, because it actually measures the exothermic effects of the oxidative transformations in a global way, as they occur in the biodiesel sample, which may form oxidated products that remain in the liquid phase and that are non detectable by Rancimat method.

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