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SOYBEAN AND SUNFLOWER BIODIESELS: EVALUATION OF OXIDATIVE STABILITY BY RANCIMAT AND DSC

Igor de Mesquita Figueredo
Universidade Federal do Ceará, Campus do Pici, s/n, Fortaleza – CE.
igor.figueredo@gpsa.ufc.br

Maria Alexsandra de Sousa Rios
Universidade Federal do Ceará, Campus do Pici, s/n, Fortaleza – CE.
alexsandrarios@ufc.br

Rubém Samuel Freitas de Paula
Universidade Federal do Ceará, Campus do Pici, s/n, Fortaleza – CE.
rubem_sam@hotmail.com

Rodrigo Silveira Vieira
Universidade Federal do Ceará, Campus do Pici, s/n, Fortaleza – CE.
rodrigo@gpsa.ufc.br

Célio Loureiro Cavalcante Júnior
Universidade Federal do Ceará, Campus do Pici, s/n, Fortaleza – CE.
celio@gpsa.ufc.br

Abstract. *The biodiesel has a low oxidative stability compared to mineral diesel. Focusing on this problem, the goal of this work was evaluated the oxidative stability of soybean (BSy) and sunflower (BSf) biodiesels comparing two methods used for this purpose: Rancimat and Differential Scanning Calorimetry (DSC). In addition, this work aimed to evaluate the kinetic parameters involved in the oxidative degradation of biodiesel. In the methodology, both biodiesels were produced by a methyl route and characterized according to the National Agency of Petroleum, Natural Gas and Biofuels (ANP) rules. The results showed that most of the measured properties were in accordance to the Resolution N°45/2014. Regarding oxidative stability by the Rancimat test, the induction period (IP) was 4.80 hours for BSy and 1.73 hours for BSf. By DSC, the beginning of the oxidation process was at 458.85 K for BSy and 453.14 K for BSf. The kinetic results showed the activation energy (Ea) was higher for BSy compared to BSf and the opposite for the oxidized biodiesels (RBSy and RBSf). Based on oxidation resistance results, the BSy was more stable than BSf. The DSC showed advantages, because it does not require a large quantity of sample, takes 1 hour to complete the whole analysis, depending on the heating rate, and it is already used to determine the thermal behavior of biodiesel.*

Keywords: *biodiesel, oxidative stability, Rancimat, Differential Scanning Calorimetry, kinetic.*

1. INTRODUCTION

The economic and social development of any country is closely linked with the production and consumption of energy. According to the International Energy Agency (IEA) about 80% of the world's energy consumption comes from based-fossil fuels: oil, coal and natural gas. These fuel sources accounting for 98% of the carbon dioxide emitted into the atmosphere. The replacement of these fuels by others less aggressive to the environment is a challenge to preserve the health of the Earth.

Biodiesel, a mixture of linear esters of fatty acids from vegetable oil or animal fat (Parente, 2003), can contribute to reduce the emission of most of the polluting gases in the atmosphere by replacing mineral diesel (Knothe et al., 2006). In addition, when biodiesel is from a vegetable source, there is a great social contribution, stimulating the formation of cooperatives and the practice of family agriculture for the cultivation of oilseeds, mainly soybean (CONAB, 2016).

However, although biodiesel having several properties similar to mineral diesel, its low oxidative stability is an inconvenience to use it as a substitute for diesel. The low oxidative stability of biodiesel can be related to the number of unsaturations present in its chemical structure. The oxidation of biodiesel can affect its physicochemical properties, causing problems in the handling and storage of it, generating deposits and, consequently, damaging the full functioning of the diesel engine (Kumar, 2017).

Therefore, the investigation of the biodiesel oxidative stability is relevant and two techniques have been used to study the biofuel oxidative stability: Rancimat and DSC. Rancimat corresponds to an accelerated oxidation method by indirect measurement (Sharma, 2011). The DSC is a thermal analysis that identifies and determines the enthalpy of physicochemical phenomena, which occurs when a substance is subjected to a programmed temperature variation (Bernal et al., 2006).

Besides that, the determination of kinetic parameters, by DSC apparatus, can be useful to complete the oxidative stability evaluation. For instance, substances that has high values for activation energy of the oxidation reaction imply greater stability than substances that has small values for Ea (Borsato et al., 2012).

2. METHODOLOGY

2.1 Biodiesel production

Samples of soybean and sunflower biodiesel were produced by similar methodology. Both were produced from a transesterification reaction between the vegetable oil (soybean and sunflower), with 100% excess of methanol and basic homogeneous catalyst (potassium hydroxide), with 85% purity. The catalyst was initially prepared by the mixture of potassium hydroxide with methanol. The solution was added to a round bottom flask, which contained the respective vegetable oil. The transesterification reaction was performed under intense stirring at room temperature (25 °C) during a period of 2 hours. After that the glycerin was separated from the methyl esters by decantation. The methyl esters were washed with 10 % distilled water per mass of vegetable oil initially used and heated at 60 ° C for 35 min under vacuum to remove the excess alcohol. In the final step, the esters were filtered with anhydrous sodium sulfate to remove residual water and submitted to physicochemical characterization.

2.2 Biodiesel's physicochemical characterization

The verification of conformity of the biodiesel produced and commercialized in Brazil is subject to parameters described in the ANP Resolution N° 45/2014. In this work, the following parameters were determined: acidity index (ABNT 14448); kinematic viscosity at 40 °C (ASTM D445); density at 20 °C (ASTM D4052) and ester content by gas chromatography (GC-FID, Varian, model GC 450 and column CP-Wax 52 CB) and water content (EN 12937).

2.3 Oxidative stability tests

The oxidative stability tests were performed using the Metrohm's 893 Professional Rancimat Biodiesel, following the EN 14112 standard. The operation conditions were: air injection rate of 10 L/min, temperature of 110 ± 0.9 °C and sample mass of 3.0 ± 0.1 g. The analyses were executed in quadruplicate. The accuracy adopted for calculating induction time was ± 1 %.

The oxidative stability tests were also carried out using the DSC 1 500 2624 cell from Mettler Toledo. Aluminum crucibles were used with five holes in the lid, synthetic air atmosphere, air flow rate of 50 mL/min, sample mass of 6 ± 1 mg, heating rate of 10 K/min and temperature range from 30 to 500 °C. These specifications were chosen following ASTM E537-12 standard, denominated "Standard Test Method for The Thermal Stability of Chemicals by Differential Scanning Calorimetry". The curves were plotted using the software STAR SW 12.10, provided by Mettler Toledo. The equipment was previously calibrated with indium and zinc standards. The analyses were performed for the soybean and sunflower biodiesel samples.

As mentioned, both of these techniques can be used to evaluate the biodiesel oxidative stability (using different principles and criteria). Rancimat consists of injecting ambient air directly into the sample and maintaining it at a constant temperature (isotherm), while the DSC, in this case, consists of injecting synthetic air into the chamber (not directly into the sample) and heating progressively from 25 to 500 °C. The time and amount of the sample are also very different. Rancimat uses at least 3 g of sample per test, but it is advisable to do it, at least in duplicate, and it takes a long time of preparation and running the test. In another hand, DSC uses 5 – 10 mg and takes 1 hour to complete the whole analysis, depending on the heating rate. However, the accelerated oxidation test accepted in EN14112 standard is the Rancimat method.

2.4 Kinectics parameters

All of kinetic parameters were obtained from DSC curves, following Method A of the ASTM E2041-13 standard, namely "Standard Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimetry Using the Borchardt and Daniels Method". The parameters calculated were Arrhenius pre-exponential factor (Z), reaction order (n), activation energy (Ea) and reaction rate (k), see Equation (1).

$$\ln\big(k(T)\big) = \ln(Z) - \frac{E_a}{R_g T} \quad (1)$$

$R_g = gas\ constant$

In addition, the statistical treatment of thermoanalytical data was realized following the ASTM E1970-16 standard (Standard Practice for Statistical Treatment of Thermoanalytical Data).

3. RESULTS

The physicochemical analyses of soybean and sunflower biodiesel showed that practically all parameters complied with the limits established in ANP Resolution N° 45/2014. Regarding the study of oxidative stability, the results in Rancimat showed that soybean biodiesel is more stable to oxidation than sunflower biodiesel, but both biodiesels did not reach the minimum limit of 8 hours required by ANP for biodiesel commercialization in Brazil.

The large amount of double bonds (unsaturations) present in the molecule of biodiesel increases the number of susceptible sites to oxidation. The fact that sunflower biodiesel has a lower IP than soybean biodiesel (see Tab.1) refers to the large content of linoleate ester (18:2), derivative from linoleic acid. This fatty acid has double bonds at carbons 9 and 12, generating a bis-allylic position at C-11 and, consequently, facilitating the occurrence of biodiesel autoxidation.

In addition, the linolenic acid (18:3), which is more present in soybean oil than in sunflower oil, is even more affected by autoxidation because it has double bonds at carbons 9, 12 and 15, generating two bis-allylic positions at C-11 and C-14 (Knothe et al., 2006). The presence of fatty acids with double bonds at different proportions contributes to the difference between the biodiesel induction periods. In this case, aiming to fulfill the minimum threshold of oxidative stability established for the biodiesel commercialized in Brazil, antioxidants could be used. The use of antioxidants to retard the biodiesel oxidation process has been shown effective in several recent works (Buosi et al., 2016; Fattah et al., 2014; Varathajan & Pushparani, 2018). Table 1 shows the soybean (BSy) and sunflower (BSf) biodiesel physicochemical properties.

Table 1. Experimental results for the soybean (BSy) and sunflower (BSf) biodiesel physicochemical properties

Properties	**ANP range**	**BSy**	**BSf**
Acidity index [mg KOH/g]	0.5, max.	0.3 ± 0.04	0.2 ± 0.06
Kinematic viscosity at 40 °C [mm^2/s]	3.0 – 6.0	4.2 ± 0.8	4.4 ±0.5
Density at 20 °C [kg/m^3]	850 – 900	882.8 ± 3.6	880.6 ± 4.3
Ester content [%]	96.50, min.	> 96.5	> 98.2
Water content [mg/kg]	200, max.	144.2	161.8
Induction period [h]	8, min.	4.80 ± 0.16	1.73 ± 0.18

Based on thermal characterization performed by DSC analyses is possible to point out the temperature which the biodiesel begins to oxidize. Figure 1 presents DSC curves of soybean (BSy) and sunflower (BSf) biodiesel.

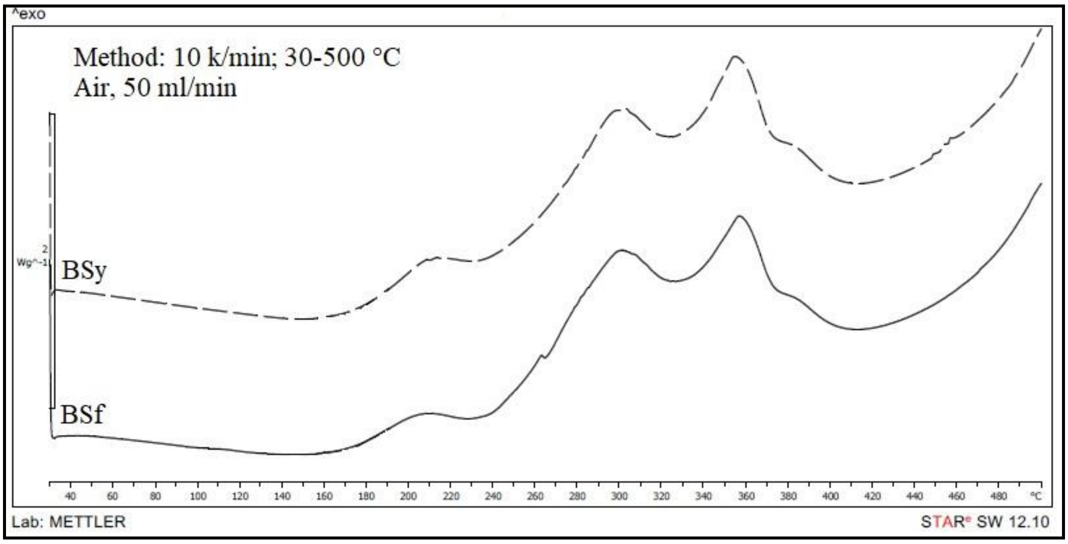

Figure 1: DSC curves of soybean (BSy) and sunflower (BSf) biodiesel expressed in heat flux *versus* temperature

According to the DSC curves presented in Figure 1, it is possible to see three exothermic peaks. These peaks indicate the oxidation process for both biodiesels and are related to the alkyl esters mixtures in the biodiesel, with different chemical structures and properties, including oxidative stability. Analyzing each curve separately, the first peak represents the beginning of the oxidation process. For BSy the oxidation starts at 458.85 K (185.70 °C) and for

BSf at 453.14 K (179.99 °C). The DSC results are in accordance with Rancimat results, showing that soybean biodiesel is more stable than sunflower biodiesel.

Focusing on the comparison between Rancimat and DSC techniques, both biodiesels (BSy and BSf) were submitted to the DSC analysis again, immediately after the Rancimat test. The oxidized samples were entitled RBSy and RBSf. These samples were analyzed by DSC again, to identify possible changes in their thermal profiles. Figure 2 shows the thermal profiles of BSy and RBSy while Figure 3 presents the thermal profiles of BSf and RBSf.

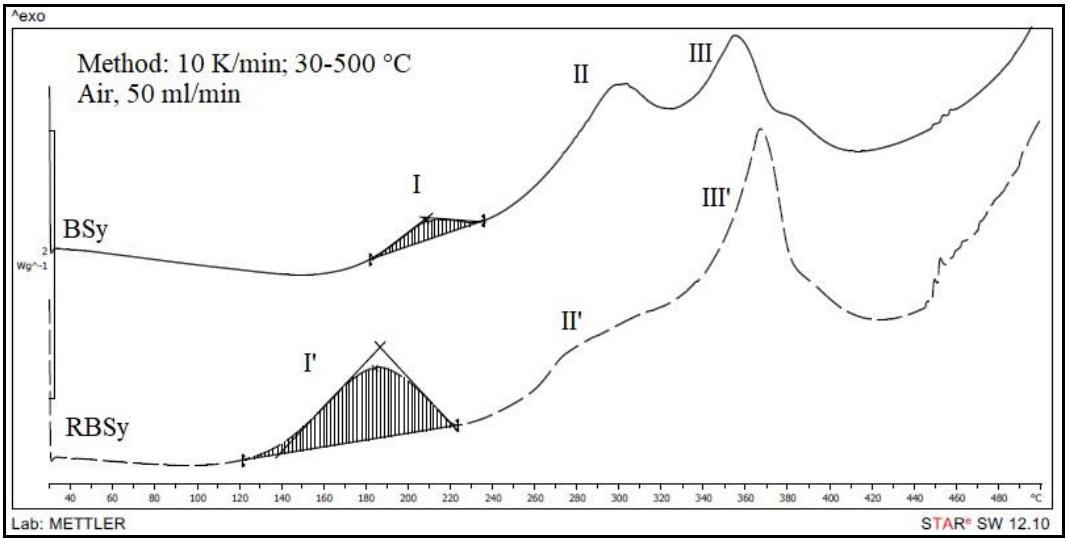

Figure 2: DSC curves of BSy and RBSy expressed in heat flux (W/g) *versus* temperature (°C)

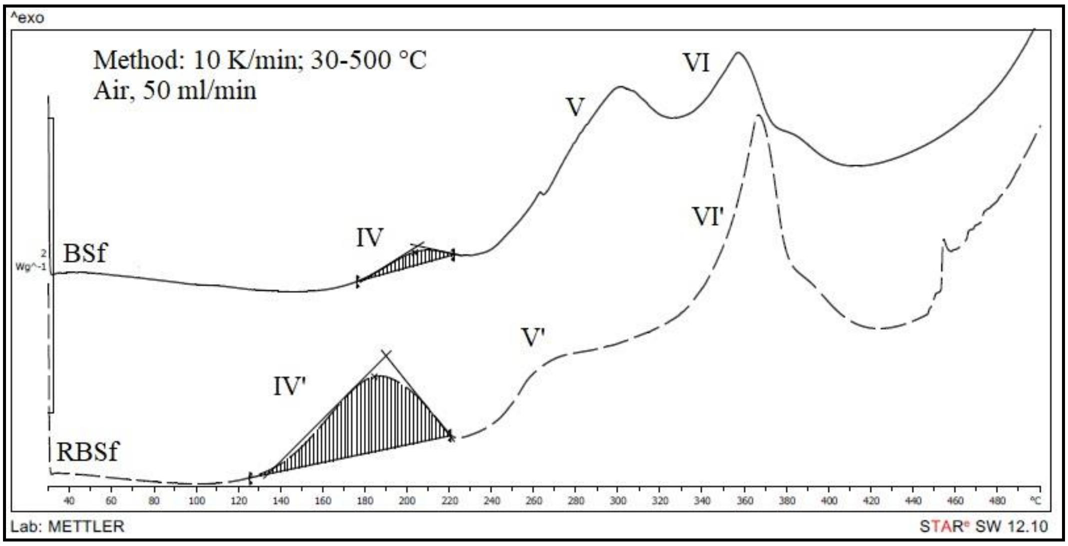

Figure 3: DSC curves of BSf and RBSf expressed in heat flux (W/g) *versus* temperature (°C)

In the Figures 2 and 3, the Roman numerals identify the main exothermic events of the samples. The peaks I, I’, IV and IV’ represent the oxidation reaction and they were used to calculate the kinetic parameters. The hatched area under each initial peak refers to enthalpy (ΔH) involved in the oxidation phenomenon.

Analyzing the Figures 2 and 3, it is possible realizes that the oxidation process at the Rancimat test caused important changes in the samples. The curves of the residual biodiesels (RBSy and RBSf), the oxidation peaks (I’ and IV’) begins at lower temperatures than their correspondent non-oxidized biodiesels (BSy and BSf): 412.74 K for RBSy and 411.70 K for RBSf. Another interesting point is about the area under the initial peaks, the area under peaks I’ and IV’ are larger than peaks I and IV. This fact means more energy involved at residuals initial peaks, indicating more unstable substances compared to initial peaks of biodiesel non-oxidized by Rancimat test (I and IV).

Also, residuals final peaks III’ and VI’ have more energy involved than final peaks III and VI. This increase of energy can be related to the rearrangement products formed during oxidation reaction at the Rancimat test. These products probably are more stable than those presents in the biodiesel before Rancimat test.

Indeed, Table 2 presents the summary of these DSC parameters, considering T onset the temperature that starts the oxidation reaction and ΔH the area under the first oxidation peak (I, I', IV and IV').

Table 2. DSC parameters of samples studied (BSy, BSf, RBSy, and RBSf)

Sample	**Peak**	**ΔH [mJ]**	**T_{onset} [K]**
BSy	I	146.86	458.85
BSf	IV	99.13	453.14
RBSy	I'	1083.5	412.74
RBSf	IV'	949.0	411.7

Despite the differences between Rancimat and DSC, in this work, both showed qualitatively the same result: soybean biodiesel is more stable to oxidation than sunflower biodiesel and Rancimat residuals are more unstable than biodiesels previously Rancimat test. However, a quantitative correlation between DSC (T_{onset} and ΔH) and Rancimat (Induction period) parameters has not been observed. By this work, it is impossible to determine if the difference of 4 hours between the induction period for BSy and BSf corresponds to results encountered by DSC analysis (T_{onset} and ΔH).

The other results are referent to kinetic of the biodiesel's reaction of oxidation. The main parameters kinetic were calculated and presented in Table 3.

Table 3. Kinetic parameters of samples studied (BSy, BSf, RBSy, and RBSf)

Kinetic parameters	**BSy**	**BSf**	**RBSy**	**RBSf**
Activation energy **(E_a)**, [kJ/mol]	263.85 ± 0.52	234.29 ± 0.30	123.96 ± 0.12	124.16 ± 0.16
Reaction order **(n)**	1.3	1.0	1.1	1.1
Arrhenius pre-exponential factor **(Z)**, [min^{-1}]	$1.81x10^{33}$	$3.42x10^{29}$	$8.66x10^{14}$	$8.57x10^{14}$
Reaction rate at 110 °C **(k)**, [min^{-1}]	$1.93x10^{-3}$	$3.92x10^{-3}$	$1.09x10^{-2}$	$1.01x10^{-1}$
R^2, data adjustment	0.9978	0.9982	0.9988	0.9983

According to the Table 3, the activation energy of sunflower biodiesel is smaller than soybean biodiesel, and the reaction rate (k) at 110 °C is greatest on the BSf, which means that BSf is more prone to suffer oxidation than BSy. According to the Thurgood et al. (2007), k is the most important kinetic parameter to determinate which sample is more prone to oxidation. In this way, higher k values represent a greater susceptibility to oxidation. Thus, comparing BSy and BSf one more time is observed that BSy is more stable than BSf. In addition, by both criteria, the oxidized samples (RBSy and RBSf) had smaller values of Ea and greater of k, when compared to the biodiesels pre-Rancimat. These results were expected because both residuals were oxidized by the Rancimat test.

Figures 4 presents the plot of ln [k (T)] versus 1/T. This relation shows that for any value of 1/T, ln [k (T)] (and consequently, k (T)) is greater for BSf than BSy. However, about both oxidized samples, there is an apparent overlap between the curves, which likely means similar samples composition.

In addition, the relation between 1/T and ln [k (T)] is considered linear, with a data adjustment of $R^2 > 0.9978$.

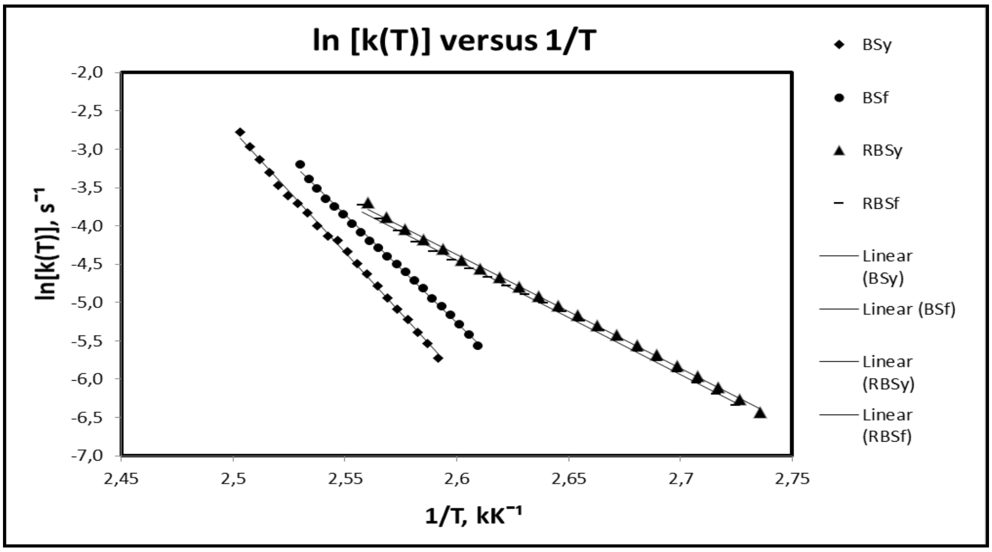

Figure 4. Plot of ln [k (T)] *versus* 1/T

4. CONCLUSIONS

The influencing factors the oxidative stability of biodiesel include the number of unsaturations present in the chemical structure, the presence of antioxidants, the storage conditions, and the exposure to light, air, humidity, and temperature. Regarding oxidative stability, soybean and sunflower biodiesels did not meet the compliance requirement set established by the ANP resolution, at least 8 hours measured by the Rancimat method. However, antioxidants can be used to retard the biodiesel's oxidation process, and consequently increase the induction period in Rancimat oxidative stability test (h).

According to the results, Rancimat test, DSC analysis, and the kinetic study showed that soybean biodiesel is more stable than sunflower biodiesel. A quantitative correlation between DSC (Tonset and ΔH) and Rancimat (Induction period) results has not been observed, once that each method is based on the measurement of different parameters.

The two evaluated methodologies (DSC and Rancimat) can be used to determine the oxidative stability of biodiesels, and if the results are expressed in percentage change, maybe a better correlation between Rancimat and DSC data can be obtained.

5. ACKNOWLEDGEMENTS

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