Oxidative Stability of Soybean Biodiesel in Mixture with Antioxidants by Thermogravimetry and Rancimat Method

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The effects of three antioxidants on the oxidative stability of soybean biodiesel were studied using two techniques: Thermogravimetry (TG-DTG curves) and the Rancimat method. The onset (T_{onset}) and endset (T_{endset}) temperatures were determined from TG curves, the peak temperatures (T_{peak}) were determined from DTG curves, and induction times were determined by the Rancimat method. The compounds butylated hydroxyl anisole (AO1), 2,6–di-*tert*-butyl-4–methylphenol (AO2) and the mixture 2,6–di-*tert*-butylphenol + 2,4,6–tri-*tert*-butylphenol (AO3) were studied and among the hindered phenols evaluated the AO1, AO2 and AO3 proved to protect the soybean biodiesel against thermo-oxidation process, and in the Rancimat method AO2 proved to be more effective than AO1 and AO3 for protection of the biodiesel against oxidation process in the conditions of the method.

Key words:
IPDT, TG, Rancimat, 2,6–di-*tert*-butyl-4–methylphenol, butylated hydroxyl anisole

Introduction

Thermogravimetry and Rancimat are the techniques that have been applied to the evaluation of the oxidative stability of biodiesel as well as to the study of the antioxidant potentiality of new molecules.[1,2] The thermal analysis technique of thermogravimetry (TG) provides information concerning the thermo-oxidative stability of the samples,[3] and the Rancimat method, based on the conductometric determination of volatile degradation products,[4,5] provides the oxidative stability of the oils, fats and biodiesels.

Due to the chemical structure, the biodiesel is susceptible to oxidation processes.[6–8] Its raw material (vegetable oils, animal fats and used frying oils) contains a significant amount of fatty acids with double bonds, so, its oxidative stability is a reason for concern, especially when storing it over an extended period of time.[9] According to the literature,[10,11] biodiesel oxidation follows a free radical mechanism that starts with the abstraction of a hydrogen atom. The group between two double bonds ($\text{-CH}=\text{CH-CH}_2\text{–CH}=\text{CH-}$) is particularly prone to losing a hydrogen atom, and the radical form (R·) rapidly reacts with oxygen to form a peroxy radical via a free radical chain reaction and the peroxy radical (ROO·) can gain a hydrogen atom to form a hydroperoxide (ROOH).[12]

Therefore, in order to control the oxidation problem, the chemical industries have been adding antioxidants in their formulations, seeking to improve the oxidative stability of the biodiesel. Antioxidants are substances that retard and/or minimize oxidation by atmospheric oxygen.[13] These additives (AH) are widely used in organic materials acting as radical trapping (the molecule competes with the substrate as a source of hydrogen for peroxy radicals, $\text{ROO·} + \text{AH} \rightarrow \text{ROOH} + \text{A·}$) or peroxide decomposing (the antioxidant reduces the hydroperoxidic and peroxidic products of oxidation to more innocuous compounds), markedly reducing the oxidation rate.[14]

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In this context, the present work involved the investigation of the effect of three antioxidants on the oxidative stability of soybean biodiesel, determined by Thermogravimetry analysis and the Rancimat method. The parameters: onset temperature (T_{onset}); peak temperature (T_{peak}); endset temperature (T_{endset}); loss of mass (Δm (%)) and the integral procedure decomposition temperature – IPDT [15] were determined in this study.

Material and methods

Materials

Refined soybean oil was obtained in the local trade and the soybean biodiesel was synthesized by catalytic transesterification.[16] The reagents, solvents and antioxidants AO1 (butylated hydroxyl anisole), AO2 (2,6–di-*tert*-butyl-4–methylphenol), 2,6–di-*tert*-butylphenol and 2,4,6–tri-*tert*-butylphenol were acquired from Sigma-Aldrich. The AO3 was obtained from the mixture of 2,6–di-*tert*-butylphenol and 2,4,6–tri-*tert*-butylphenol.

Physical measurements

The soybean biodiesel analysis was carried out with a GC-MS system. The configuration used here was the Shimadzu QP5050 equipped with a DB-1 column (30 m × 0.25 mm id × 0.25 µm film) and an oven temperature program that initiated data collection at a temperature of 100 °C and ramped at 10 °C min^{-1} to 300 °C, holding this temperature for the remaining duration of the data collection. Electron impact (EI, 70 eV) mode was used and sample of 1 mL was injected into the column.

The kinematic viscosity (υ) measurements were determined by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer at 40 °C, per the test method ASTM D 445, utilizing the TANAKA AKV-202 automated viscometer. The density measurements were done at 20 °C and 101.325 kPa by using Anton Paar (DMA 4500M) density meter, per the test method ASTM D 1298. The flash point (Pensky-Martens Closed Cup Tester) measurements were obtained in a TANAKA APM-7 mark apparatus, per the test method ASTM D 93.

Thermoanalytical measurements were obtained in a Mettler Toledo TGA/SDTA85, using alumina pans and a heating rate of 10 ºC min^{-1}, in the temperature range of 25–800 °C, and mass of approximately 5 mg. The samples were carried out in synthetic air atmosphere (50 mL min^{-1}).

The oxidative stability was determined using a Metrohm 743 Rancimat per the EN14112 method. In this test, a 10 L h^{-1} stream of dry air is bubbled into 3 g samples maintained at 110 °C, volatile oxidation products are carried through the detector chamber containing demineralized water. The change in conductivity is measured and recorded every 36 s. The end of the Induction Period (IP) is indicated when the conductivity begins to increase rapidly, occasioned by the dissociation of volatile products generated during the oxidation process.[17]

Methods

Synthesis of soybean biodiesel

Biodiesel from soybean oil was synthesized by the catalytic transesterification of the soybean oil using methanol as aliphatic alcohol and KOH as base.[16] The mixture was heated under reflux for one hour and monitored by thin-layer chromatography. After this time, the mixture was poured into a separation funnel, and for difference of absolute density, the biodiesel was separated from the glycerin (major by-product). The light phase (rich in biodiesel) was separated, washed with hydrochloric acid solution (5 %) and water, dried with anhydrous sodium sulfate and concentrated using rotary vacuum evaporator at 70 °C (±1 °C). The biodiesel was characterized by GC-MS, TG-DTG, Kinematic viscosity, Density, Flash point and Rancimat per the EN 14112 method.

Sample preparation

The soybean biodiesel was additivated with AO1, AO2 and AO3 at concentrations of 500 and 1000 ppm by simple mixtures. The effects of the antioxidants were investigated.

Results and discussion

Analysis of synthesized soybean biodiesel

GC-MS

GC-MS analysis showed the preponderance of methyl linoleate [62 %; *m/z* 294]; methyl cis-9–octadecenoate [16 %; *m/z* 296]; methyl palmitate [13 %; *m/z* 270] and methyl octadecanoate [6 %; *m/z* 298] in the mixture of the methyl esters, compatible with the molecular ions of fatty acids methyl esters (FAME).

Density, kinematic viscosity and flash point

In general, the density of the biodiesel varies between 850 and 950 kg m^3 (20 °C). In this study, the density of the produced biodiesel is between these values, showing a value of 882 kg m^{-3}. As in the density measurement, the kinematic viscosity of biodiesel varies in the range of 3.000–6.000 mm^2 s^{-1} (40 °C). In our study, the kinematic viscosity of the soybean biodiesel is between these values, showing a value of 4.146 mm^2 s^{-1}. The flash point values are a function of the apparatus design, the condition of the apparatus used, and the operational procedure carried out.[18] So, according to the standard test method ASTM D 93, the flash point of the produced soybean biodiesel showed a value of 230 °C.

Thermogravimetry analyses

Figs. 1–7 show the TG and DTG curves of the samples: soybean biodiesel; soybean biodiesel + AO1 (500 ppm); soybean biodiesel + AO2 (500 ppm); soybean biodiesel + AO3 (500 ppm); soybean biodiesel + AO1 (1000 ppm); soybean biodiesel + AO2 (1000 ppm); and soybean biodiesel + AO3 (1000 ppm). Table 1 gives details of their thermo-oxidative stabilities based on the onset (T_{onset}), peak (T_{peak}) and endset (T_{endset}) temperatures, loss of mass (Δm (%)) and the integral procedure decomposition temperature –IPDT.

Fig. 1(a) shows that highly and medium volatile matters are represented by mass losses measured between 107 and 276 °C, the DTG curve for soybean biodiesel presents clear evidence for the three degradation steps, and in this type of curve this information is in a form that is more visually accessible. The DTG curves allow the ready determination of the temperature at which the rate of loss of mass is a maximum, T_{peak}, and this provides additional information to the extrapolated onset temperature T_{onset} and the extrapolated endset temperature T_{endset}.[3] In our study, a reactive gas environment – synthetic air – was used to evaluate the stability of the samples so the volatilization, degradation and oxidation of the methyl esters that compound the soybean biodiesel could be analyzed. In the synthesized biodiesel, the important changes in mass probably occurred because of evaporation and/or oxidation of the methyl linoleate, the most abundant unsaturated methyl ester (62 %) in this biofuel.[19, 20]

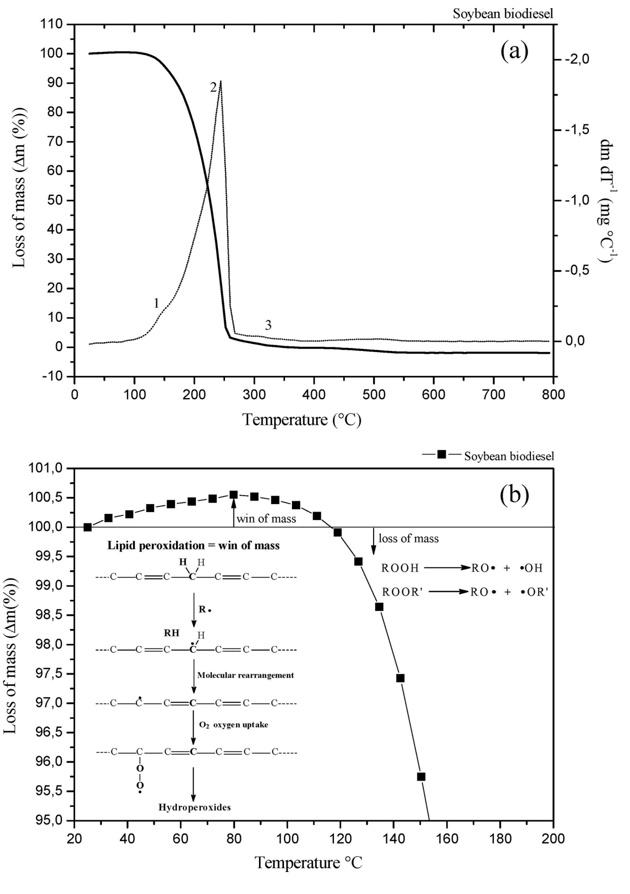

Fig. 1 – *(a) TG-DTG curves of soybean biodiesel in synthetic air atmosphere, (b) TG curve of soybean biodiesel – a careful evaluation*

Since GC-MS result shows that soybean biodiesel was mainly composed of methyl linoleate and methyl cis-9–octadecenoate, unsaturated fatty acids methyl esters, this biofuel has the propensity to oxidize, resulting in the formation of peroxide and hydroperoxides among other products. The initiation of a peroxidation in a polyunsaturated fatty acid methyl ester is due to the attack of any species that has sufficient reactivity to abstract a hydrogen atom (H·, allylic or bis-allylic) from a methylene (-CH_2–) group. In the thermal oxidation, the increase in temperature weakens the C-H bonds on the carbon atom adjacent to the double bond and thus makes H· removal easier. Hence, the polyunsaturated FAME side chains of the soybean biodiesel are particularly sensitive to peroxidation, and biodiesel thermogram presented the win of mass of 0.06 % before the first step, indicating the lipid peroxidation (see Fig. 1(b)).

The lipid peroxyl radical (–C–O–O·) is the main species of the lipid peroxidation chain reaction. This radical can abstract a bis-allylic hydrogen from an adjacent FAME to form a lipid hydroperoxide and a second lipid radical, propagating the autoxidation.[21] The –O–O– bond is the weakest in both peroxides and hydroperoxides and their scission gives rise to the powerfully oxidizing alkoxy or hydroxyl radicals, which play a vital role as initiators in the autoxidation chain mechanism. Medium temperatures (50 to 160 ºC) can break this bond (–O–O–) so, from the results shown in the thermogram of the soybean biodiesel (Fig. 1(b)), after 116 °C, the sample initiated its process of loss of mass (degradation process), probably due to the break of the bond –O–O–.[22, 23]

The TG-DTG curves for soybean biodiesel + antioxidant 500 ppm (AO1, AO2 or AO3) showed three stages of weight loss (Figs. 2(a), 2(b) and 2(c)). The first stages varied among initial temperature of 115 and final temperature of 196 °C, with loss of mass of 8.09 % for soybean biodiesel + AO1 500 ppm, 28.00 % for soybean biodiesel + AO2 500 ppm and 14.26 % for soybean bio-

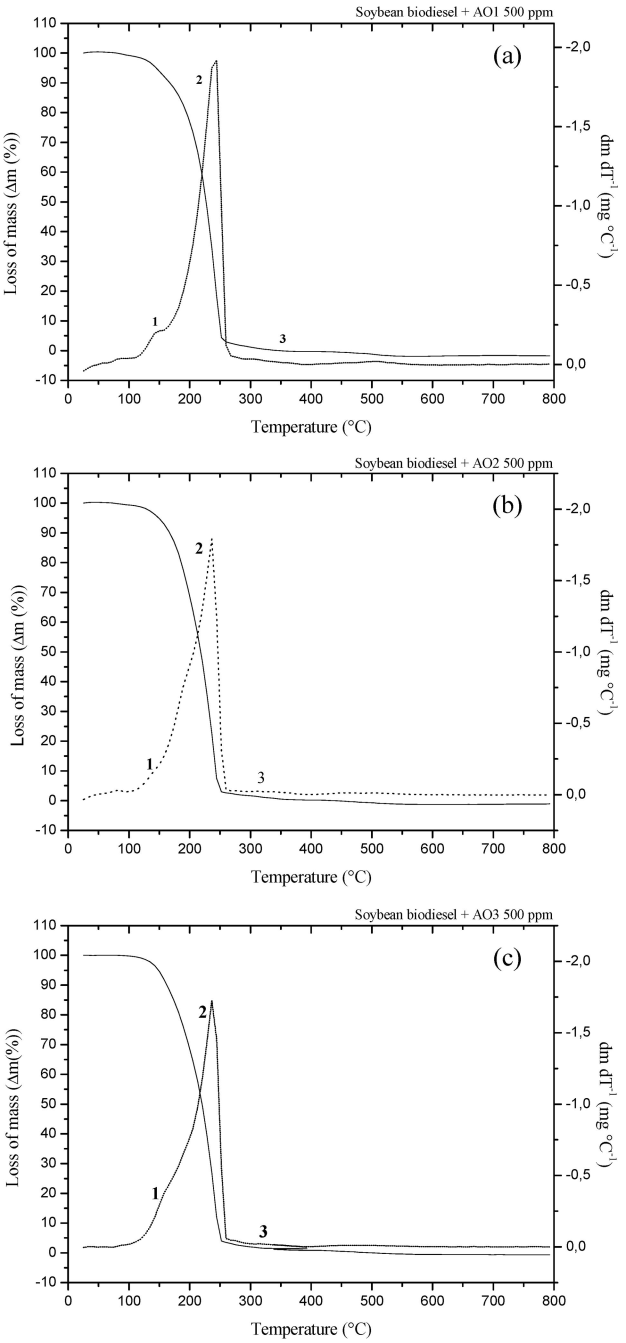

Fig. 2 – *(a) TG-DTG curves of soybean biodiesel + AO1 (500 ppm), (b) TG-DTG curves of soybean biodiesel + AO2 (500 ppm), and (c) TG-DTG curves of soybean biodiesel + AO3 (500 ppm), in synthetic air atmosphere*

diesel + AO3 500 ppm (Table1), which may be due to the volatilization and/or thermo-oxidative degradation of the samples. The second stages (rapid weight change) and the third stages (slow weight change) were attributed to the thermo-oxidative degradation and/or combustion of the formulations, biodiesel + antioxidant.[20] Fig. 3 shows TG curves of the soybean biodiesel formulations. According to the results, the additives used in this study were able to reduce the lipid peroxidation and hence reduced the win of mass before the first step. The samples showed the win of mass of : 0.04 % soybean biodiesel + AO1 500 ppm, 0.03 % soybean biodiesel + AO2 500 ppm and 0.00 % soybean biodiesel + AO3 500 ppm. As demonstrated in Fig. 1(b), the lipid peroxidation in an unsaturated fatty acid methyl ester is propagated by peroxyl radical (-C-O-O·). This species abstracts a hydrogen atom from another FAME to continue the process. So, any molecule that can donate a hydrogen atom to the peroxyl radical should be able to break the chain reaction, or at least interfere. The compounds that donate a hydrogen atom to leave a relatively inert radical are referred to as chain-breaking antioxidants,[21] and inside this class of additives, the phenolic compounds are the most well-known chain-breaking molecules. In our study, the AO3 obtained the better result (see Fig. 3) since it showed no win of

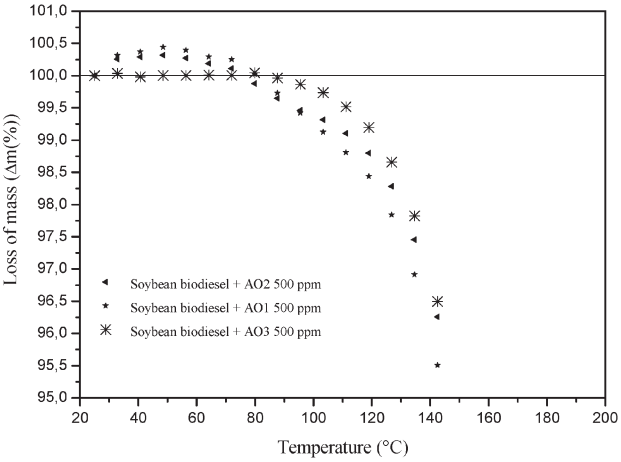

Fig. 3 – *TG curves of soybean biodiesel and soybean biodiesel + antioxidants 500 ppm (AO1, AO2 and AO3)*

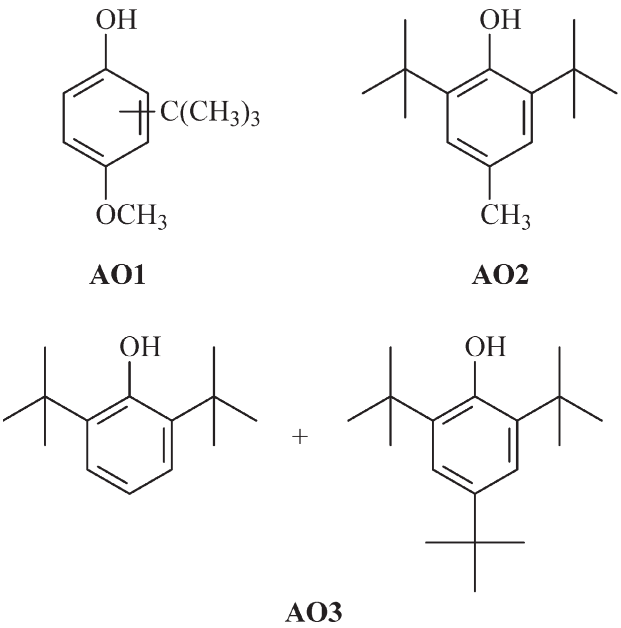

Fig. 4 – *Chemical structures of AO1, AO2 and AO3*

Table 1 – *Thermo-oxidative stability data of the soybean biodiesel with and without antioxidants*

Sample	Antioxidant (ppm)	Degradation steps (n°)	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	Mass (%)	IPDT (°C)
Soybean biodiesel	0	3	107	139	169	8.62	186
			169	245	276	89.14	
			282	329	376	1.86	
Soybean biodiesel + AO1	500	3	115	144	170	8.09	215
			170	243	270	87.77	
			284	317	351	1.86	
	1000	3	118	152	171	15.63	211
			171	229	280	81.10	
			297	326	373	1.71	
Soybean biodiesel + AO2	500	3	117	178	196	28.00	211
			196	237	276	69.00	
			314	346	392	1.98	
	1000	3	113	147	177	13.00	281
			177	234	288	81.00	
			303	322	350	0.76	
Soybean biodiesel + AO3	500	3	118	152	176	14.26	223
			176	237	288	82.46	
			308	336	375	0.93	
	1000	3	118	156	176	16.56	244
			176	229	294	79.47	
			294	320	358	0.79	

mass before the first stage. This performance occurred probably due to the synergistic effect of the mixture of the phenolic compounds that compose the AO3 (see Fig. 4).

Fig. 5 and Table 1 show the details of loss of mass, T_{onset}, T_{peak} and T_{endset} for the formulations : biodiesel + antioxidant 1000 ppm. Based on the results, the T_{onset} of soybean biodiesel without antioxidants is found as 107 °C. When the biodiesels are additivated with AO1, AO2 or AO3 antioxidants, T_{onset} will increase to 118, 113 and 118 °C. Hence, it can be concluded that AO1 and AO3 obtained the best thermo-oxidative inhibition performances. The other thermal parameter determined was IPDT. The IPDT (decomposition temperature near the temperature of 50 % of total mass loss) of soybean biodiesel containing antioxidants is shifted to higher temperatures as compared with that without antioxidant. This proves that the presence of antioxidants improves the thermo-oxidative stability of soybean biodiesel,[10,13,16] which is confirmed based on the thermal parameters by TG (see Table 1). The antioxidative activity of AO1, AO2 and AO3 is associated with the ability of hindered phenolic compounds to scavenge reactive free radicals.[24,25] Another important factor of these molecules is the presence of bulkier substituents on the *ortho* and/or *para* positions.[26] According to the literature,[24–26] the presence of bulky substituents was important for antioxidant activity of these molecules, because the substituents influence the specificity of the phenols by blocking phenoxyl radicals from abstracting hydrogen atoms from organic substrates,[24] and AO1, AO2 and AO3 possess substituents in their rings (*methoxy*, *methyl* and *tert*-butyl), on the *ortho* and *para* positions (see Fig. 4).

The hindered phenols are known to exhibit various stabilization activities, depending on the kind and number of substituents on the *ortho* and/or *para* positions. The electron-donating nature of a substituent can enhance the activity of a phenol, resulting in the increase in the rate of trapping a peroxy radical.[24] From the literature,[23,24] the substituents influence the number of peroxy radicals trapped, and hindered phenol having bulky substituents on the *ortho* and/or *para* positions can scavenge about 2 moles of peroxy radicals of the organic substrate.[24,26] Considering the chemical structures of the substituents, the bulkier such as *tert*-butyl on *ortho* and/or *para* positions have been recommended to inhibit coupling reaction of phenoxy radicals, resulting in an increased number of trapped peroxy radicals.[25]

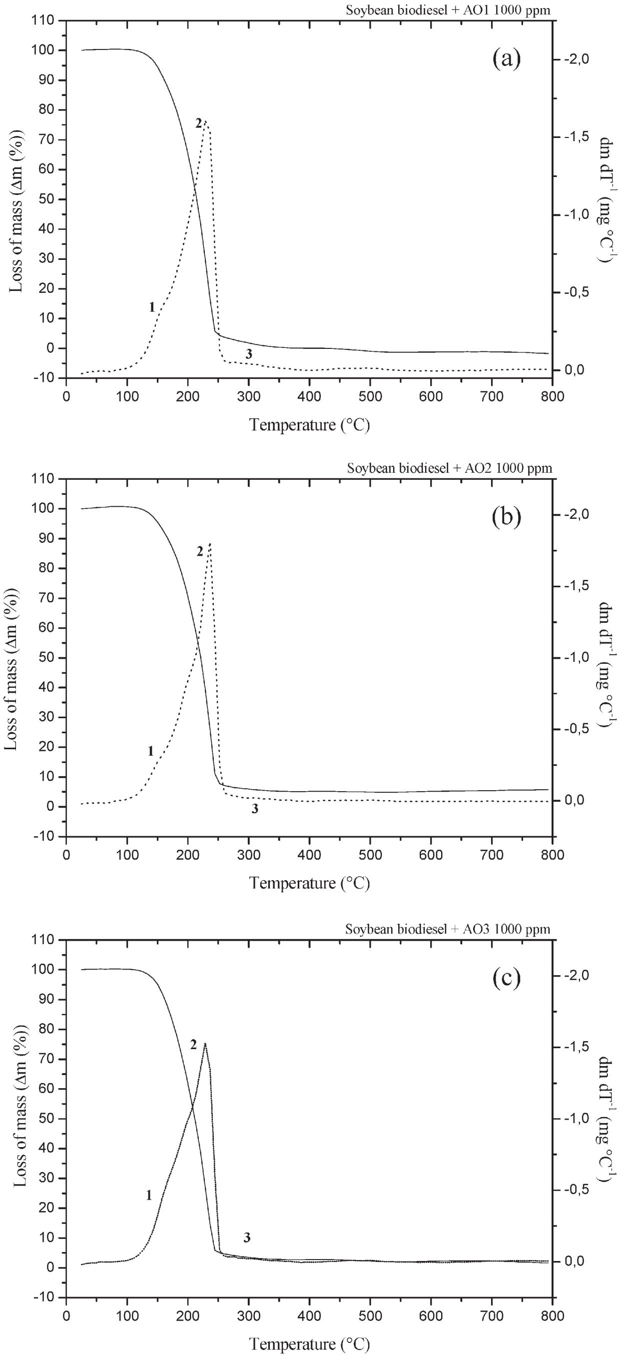

Fig. 5 – *(a) TG-DTG curves of soybean biodiesel + AO1 (1000 ppm), (b) TG-DTG curves of soybean biodiesel + AO2 (1000 ppm), and (c) TG-DTG curves of soybean biodiesel + AO3 (1000 ppm), in synthetic air atmosphere*

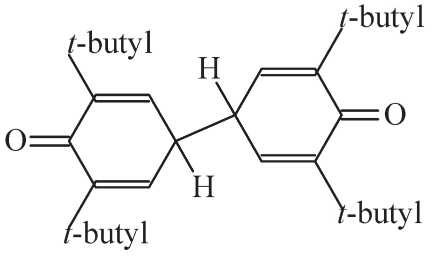

Fig. 6 – *Coupling of phenoxy radicals*

However, the presence of small *alkyl* substituents on *para*-position can enable the coupling of phenoxy radicals (see Fig. 6). In this study, the AO2 has two bulkier *tert*-butyls on *ortho* positions, but a *methyl* group on *para*-position.[26] From Table 1, it was observed that the increase in the AO2 content (500 ppm → 1000 ppm) does not increase onset temperatures (T_{onset}). This result could be explained by the idea that the presence of *methyl* group on *para*-position is favorable for the coupling of phenoxy radicals, decreasing the antioxidant activity of the AO2. On the other hand, the AO3, a mixture consisting of 2,6–di-*tert*-butylphenol (86 %) + 2,4,6–tri-*tert*-butylphenol (14 %), shows an increase in the onset temperatures with the increase of its content. This behavior may be based on the interaction between the two phenols: 2,6–di-*tert*-butylphenol and 2,4,6–tri-*tert*-butylphenol. This phenomenon called "synergism" occurs through a combination of two phenols with comparatively lower oxidation potentials.[28] Within this context, the AO1 proves more effective as antioxidant than AO2 and AO3 since the onset temperatures increased with the increase of its content in the formulation of soybean biodiesel + antioxidant. These results show that the antioxidant activity of AO1 was probably correlated with its low oxidation potential. From the literature,[27] the phenols with a methoxy group on the 4–position presents low oxidation potential, and the AO1 has a methoxy group in its ring on the 4–position.

Fig. 7 shows TG curves of soybean biodiesel and its formulations. From the results, AO1 and AO3 reduced the win of mass before the first step. The samples showed the win of mass of : 0.046 % soybean biodiesel + AO1 1000 ppm and 0.03 % soybean biodiesel + AO3 1000 ppm. On the other

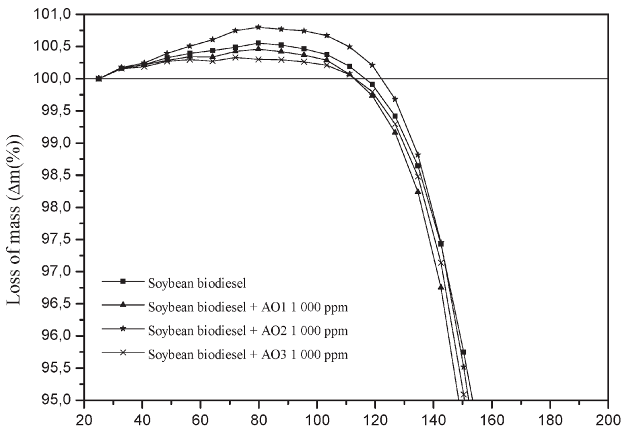

Fig. 7 – *TG curves of soybean biodiesel and soybean biodiesel + antioxidants 1 000 ppm (AO1, AO2 and AO3)*

hand, the sample soybean biodiesel + AO2 1000 ppm (0.08 %) did not obtain the same performance. This result could probably be explained by the idea that the presence of *methyl* group on *para*-position is favorable to the coupling of phenoxy radicals, decreasing the antioxidant activity of the AO2, as mentioned previously.

Rancimat

All the three antioxidants were mixed in soybean biodiesel and the Rancimat method was conducted for the evaluation of the effectiveness of these additives, and the results are given in Figs. 8–10 and Table 2. The results show that all antioxidants, in the two dosages (500 and 1000 ppm), increased the oxidative stability of the biodiesel. Finally, it is found that the dosage of 500 ppm of AO1 or 500 ppm of AO3, or 1000 ppm of AO3 are concentrations that satisfy EN 14112 specification for biodiesel oxidative stability.

Conclusion

According to the results, it was observed that the increase of biodiesel oxidative stability occurred with the increase in the dosage of antioxidant. It was found that the three antioxidants evaluated (AO1, AO2 and AO3) improved the thermo-oxidative stability of soybean biodiesel, since the onset temperatures showed increase from 5.31 % to 9.73 %. The results also showed that the antioxidants reduced lipid peroxidation at the beginning of the chain reaction. In general, AO1 and AO3 presented the better results in the thermal analysis – onset temperature – when mixed into the biodiesel. These behaviors probably occur due to their thermal resistance, and could be used in accelerated oxidation tests with appreciable performance. However, in the Rancimat method, the formulation with AO2 showed the highest oxidative stability.

Both TG-DTG and Rancimat techniques showed that the AO1, AO2 and AO3 improved the thermal and oxidative stabilities of the samples. These species acted as sources of hydrogen atom, breaking the chain reactions, and hence, increasing the stability of the soybean biodiesel.

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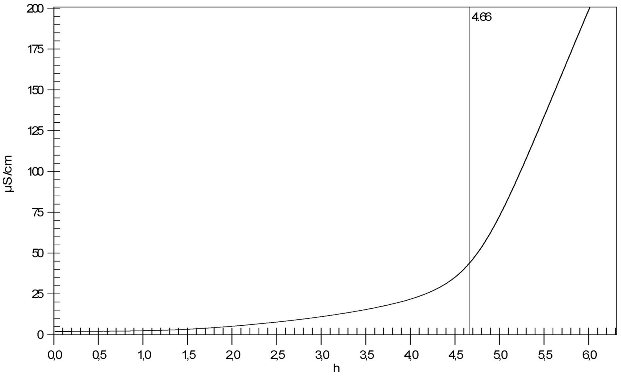

Fig. 8 – *Rancimat curve of soybean biodiesel*

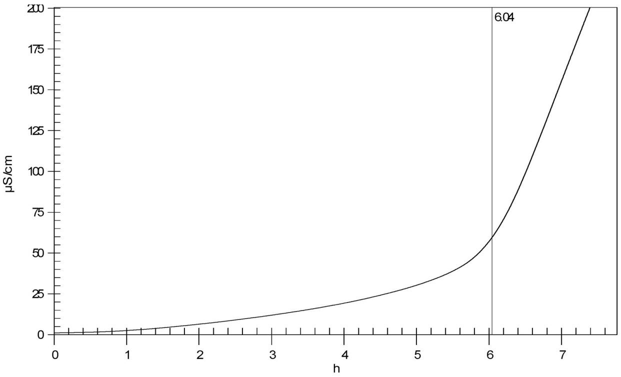

Fig. 9 – *Rancimat curve of soybean biodiesel + AO1 (500 ppm)*

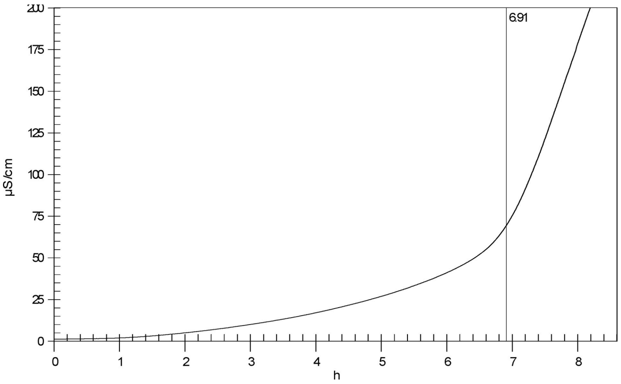

Fig. 10 – *Rancimat curve of soybean biodiesel + AO1 (1000 ppm)*

Table 2 – *Oxidative stability data – Rancimat method.*

Sample	Antioxidant (ppm)	Induction time (h)
Soybean biodiesel	0	4.66
Soybean biodiesel+AO1	500	6.04
	1000	6.91
Soybean biodiesel+AO2	500	7.43
	1000	7.51
Soybean biodiesel+AO3	500	5.55
	1000	6.28

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