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UV-Visible Spectroscopy Study of Oxidative Degradation of Sunflower Biodiesel

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Abstracts

In this study, three antioxidants (blend (hydrogenated cardanol + 5-*n*-pentadecyl-2-*tert*-butylphenol), 5-*n*-pentadecyl-2-*tert*-butylphenol and ionol BF200) were evaluated for their potential to reduce the degree of oxidation of sunflower biodiesel under thermal stress condition. Each antioxidant was added at a concentration of 1000 ppm. The oxidative degradation was investigated by UV-visible spectroscopy and iodometry were used to monitor the changes using peroxide values. The results showed that, blend and 5-*n*-pentadecyl-2-*tert*-butylphenol possess significant potentiality when compared with ionol BF200. The blend and 5-*n*-pentadecyl-2-*tert*-butylphenol reduced the absorbance around 31%. The peroxide value showed that, the formulations: sunflower biodiesel/A2, sunflower biodiesel/A3 and sunflower biodiesel/AC showed better results when compared with sunflower biodiesel without antioxidant.

Key words: Antioxidants; Peroxide value; Accelerated oxidation test

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INTRODUCTION

Ultraviolet – visible spectroscopy analysis methods are fast becoming workhorse techniques for providing analytical data on degradation of biodiesel[1-3]. This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (visible, 400-800 nm) regions. The technique studies the changes in electronic energy levels within the molecule arising due to the transfer of electrons from π- or non-bonding orbitals. It commonly provides the knowledge about π-electron systems, conjugated unsaturations, aromatic compounds and conjugated non-bonding electron systems etc[4]. Therefore, the conjugated dienes presents in the oxidized biodiesel can be monitored by UV-visible spectroscopy[5, 6].

Biodiesel is an alternative fuel derived from vegetable oils, animal fats, or used frying oils[7-9]. This biofuel is generally produced by the catalytic transesterification of triglycerides with methanol or ethanol and can be used as a neat fuel, or it can be blended with petroleum or Fischer tropsch diesel. The oxidation stability of biodiesel is a function of the fatty acid composition, and decreases with higher contents of linoleic and linolenic acids[10]. In linoleic acids, polyunsaturated fatty acid chains contain two (C18:2) double bonds, while linolenic acids contain three (C18:3) double bonds. As a result, undesirable products like gums, organic acids, and aldehydes, formed as a result of degradation, may cause injector and filter blockages resulting in engine problems[11].

Due to the fact that many vegetable oils contain a significant amount of fatty acids with double bonds, oxidative stability is of concern, especially when storing biodiesel over an extended period of time[10]. Biodiesel oxidation follows a free radical mechanism that starts with

the abstraction of a hydrogen atom. The group between two double bonds (-CH = **CH-CH** = CH-) is particularly prone to losing a hydrogen. 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**). Almost immediately after peroxides are formed, the non-conjugated double bonds that are present in biodiesel are converted to conjugated double bonds[1,2]. These double bonds absorb strongly at 232 nm, therefore, the authors used UV spectroscopy and peroxide value (PV) to evaluate the oxidative degradation of sunflower biodiesel[12].

In this study, three antioxidants (blend (hydrogenated cardanol + 5-*n*-pentadecyl-2-*tert*-butylphenol), 5-*n*-pentadecyl-2-*tert*-butylphenol and ionol BF200) were evaluated for their potential to reduce the degree of oxidation of sunflower biodiesel under thermal stress condition[2]. Each antioxidant was added at a concentration of 1000 ppm. The oxidative degradation of sunflower biodiesel with or without antioxidants was investigated by UV-visible spectroscopy and iodometry were used to monitor the changes using peroxide values[13].

1. MATERIALS AND METHODS

1.1 Materials

The antioxidants blend (A2) and 5-*n*-pentadecyl-2-*tert*-butylphenol (A3) were supplied by Grupo de Inovações Tecnológicas e Especialidades Químicas – GRINTEQUI and ionol BF200 (AC) was supplied by Abiove. Refined sunflower oil was obtained in the local trade and the sunflower biodiesel was synthesized by catalytic transesterification[1,2]. The reagents and solvents were supplied by Aldrich (analytical grade).

1.2 Methods

1.2.1 Experimental

1.2.1.1 Synthesis of Sunflower Biodiesel

Biodiesel from sunflower oil was synthesized by the catalytic transesterification of sunflower oil using methanol as aliphatic alcohol and KOH as base[2]. The mixture was heated under reflux for one hour and was monitored by thin-layer chromatography. After this time, the mixture was poured into a separatory funnel and for difference of absolute density, the biodiesel was separated of the glycerin (major by-product). The light phase (rich in biodiesel) was separated, washed with hydrocloridric acid solution (5 %) and water, dried with anhydrous sodium sulfate and concentrated using rotary vacuum evaporator at 70 °C (± 1 °C).

1.2.1.2 Formulations Antioxidant/Biodiesel

The sunflower biodiesel, obtained by the methyl route, was additivated with A2, A3 and AC antioxidants at the concentration of 1000 ppm by simple mixtures.

1.2.2 Peroxide Value - PV

Peroxide value (PV) was determined by iodometric addition and tritation against sodium thiosulphate as describe by Morreto and Fett (1989)[13].

1.2.3 Physical Measurements

GC-MS analyses were performed by the use of Hewlett-Packard 5890 gas-chromatograph and by a Hewlett-Packard 5971A spectrometer equipped with a DB-5 column (0.25 mm, 30 m, 0.25 μm film) used 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. Sample of 1 μL was injected into the column.

UV-vis absorption spectra were recorded using a HITACHI U-3000 spectrophotometer, using 1:1000 (v/v) dilution ratio in hexane. All data were collected in the range of 200–400 nm.

1.2.4 Accelerated Oxidation Test - AOT

Accelerated oxidation test (AOT) was carried out in an oxidation apparatus with base in the Rancimat method[14,15]. The biodiesel samples were placed in a 100 mL vessel of glass, kept at a constant temperature (120 °C), in the presence of air atmosphere (21% oxygen)[2]. The oxidation process was monitored by UV-vis spectroscopy and by peroxide value determination, where the samples were collected at intervals of 1 hour and analyzed[2].

2. RESULTS AND DISCUSSION

2.1 Characterization of Antioxidants – GC

The Figures 1-3 present the chromatograms of the antioxidants blend (A2), 5-*n*-pentadecyl-2-*tert*-butylphenol (A3) and ionol BF200 (AC).

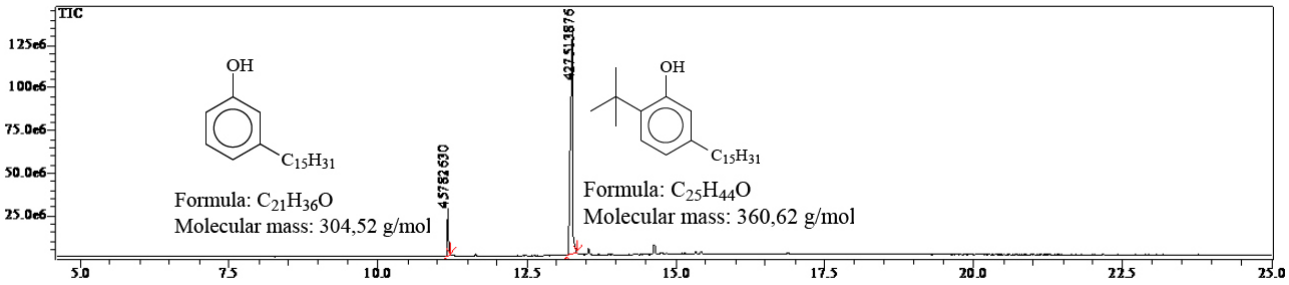

Figure 1
Chromatogram of Blend (A2)

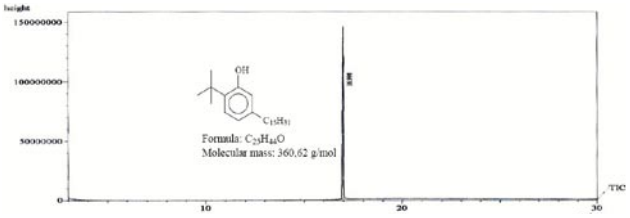

Figure 2
Chromatogram of 5-*n*-pentadecyl-2-*tert*-butylphenol (A3)

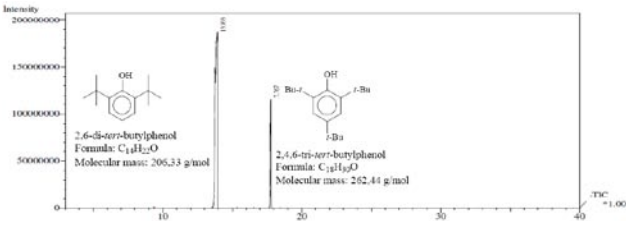

Figure 3
Chromatogram of Ionol BF200 (AC)

According to the results, the chromatogram of 5-*n*-pentadecyl-2-*tert*-butylphenol (A2) showed only one peak, proved its purity. This factor is very important because the potentiality of the phenolic antioxidants and the effect of their tert-butyl substituents were evaluated on the oxidative degradation of sunflower biodiesel[16-18]. On the other hand, the chromatograms of the blend (A3) and ionol BF200 (AC) showed mixtures of the phenolic antioxidants, where A3 present 10% of the hydrogenated cardanol and 90% of the 5-*n*-pentadecyl-2-*tert*-butylphenol and AC present 86% of the 2,6-di-*tert*-butytlphenol and 14% of the 2,4,6-tri-*tert*-butylphenol. In this case, the probable synergism action existent between phenols and hindered phenols, in the stabilization of sunflower biodiesel (AOT, 120 °C), was verified.

2.2 Accelerated Oxidation Test - AOT

The Figures 4-8 show UV-vis of sunflower biodiesel in the presence and absence of the phenolic antioxidants (A2, A3 and AC), at different times of oxidation: 0, 1, 2, 3, 4, 5 and 6 hours.

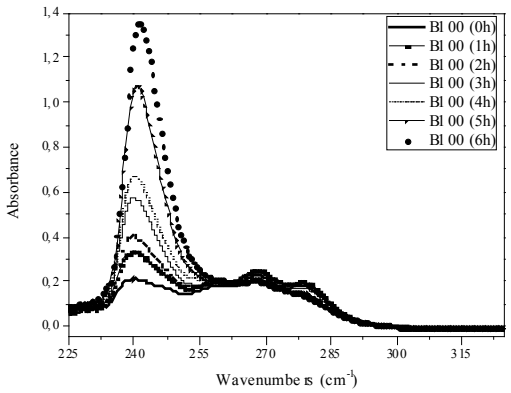

Figure 4
UV-vis of Sunflower Biodiesel (B100) at Different Times of Oxidation

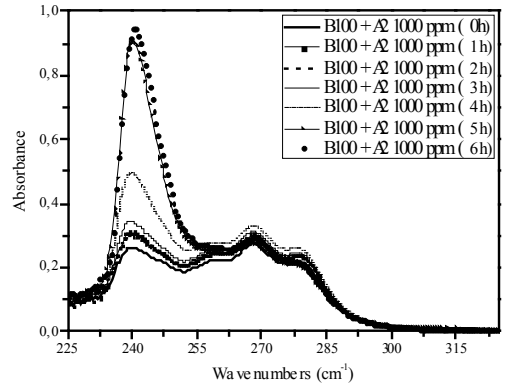

Figure 5
UV-vis of Sunflower Biodiesel/A2 (1000 ppm) at Different Times of Oxidation

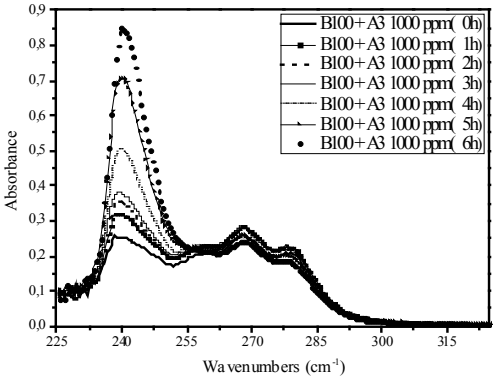

Figure 6
UV-vis of Sunflower Biodiesel/A3 (1000 ppm) at Different Times of Oxidation

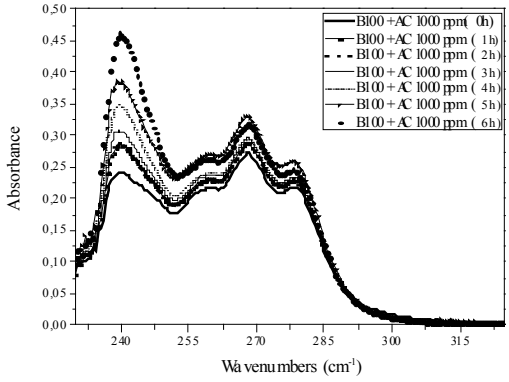

Figure 7
UV-vis of Sunflower Biodiesel/AC (1000 ppm) at Different Times of Oxidation

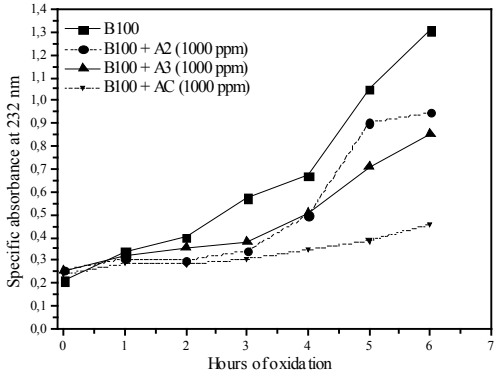

Figure 8
Specific Absorbance at 232 nm of Sunflower Biodiesel at Different Times of Oxidation

According to the UV-vis spectroscopy data, it is noteworthy that this technique can supply indications about quality of sunflower biodiesel and its oxidation products derived from accelerated oxidation test (AOT) [2]. This UV-vis spectroscopy determination constitutes a different approach from the measure of primary and secondary oxidation products, for example, peroxides, ketones, acid, aldehydes and others, and actually, it has been adopted more and more[5]. In this direction, the authors used a specific absorbance at 232 nm to monitor the appearance of conjugated dienes in consequence of peroxidation products of sunflower biodiesel[3,15].

The Figures 4-8 showed that the samples presented absorption maxima at 232 nm. This behavior occurs because the oxidation of polyunsaturated fatty acids, is accompanied of the displacement of isolated double bonds for conjugated double bonds[1,2,4]. Figure 4 showed UV-vis spectrum of sunflower biodiesel with absorbance at 232 nm from 0,207 (0 h of oxidation) to 1,359 (6 h of oxidation). On the other hand, after antioxidants addition in a concentration of 1000 ppm, the formulations (sunflower biodiesel/antioxidant) became more stable than sunflower biodiesel without antioxidant (Figures 5-7). The UV-vis spectra showed that, formulations absorbance (232 nm) varied among 0,947 (sunflower biodiesel/A2 1000 ppm) and 0,461 (sunflower biodiesel/AC 1000 ppm) for 6 h of oxidation, providing reductions of the order of 31 % and 66 %, when compared with sunflower biodiesel without antioxidant (Figure 8).

UV-vis results indicated too, the antioxidants A2 and A3 showed a good efficiency antioxidant when compared to AC, an important commercial hindered phenolic antioxidant. However, the AC was the antioxidant that propitiated the best stability to the biodiesel. This result is compatible with the literature of the hindered phenolic antioxidants, which say that, their bulky substituents influence the specificity of the phenols by blocking phenoxyl radicals from abstracting hydrogen atoms from organic substrates[17,18], and AC is a mixture of 2,6-di-*tert*-butylphenol and 2,4,6-tri-*tert*-butilphenol, two hindered phenolic antioxidants. According to literature, in solution each hindered phenolic moiety consumed two peroxy radicals, as illustrates the equation 1.

$$\begin{aligned} &ROO\bullet + AH \rightarrow ROOH + A\bullet \\ &ROO\bullet + A\bullet \rightarrow ROOA \end{aligned} \quad (1)$$

Once that, the peroxides are initiators of oxidation, their removal from sunflower biodiesel are very important in the inhibition of oxidation[19]. So, the authors used the determination of peroxide value (PV) to monitor oxidation. Figure 9 shows the results of peroxide values, carried out during 6 h of oxidation, to the sunflower biodiesel and its formulations.

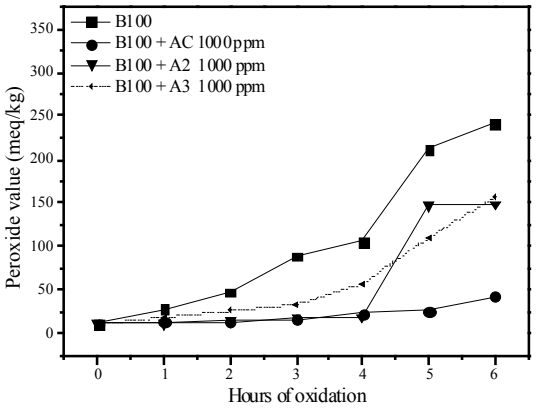

Figure 9
Peroxide Value *Versus* Hours of Oxidation for Sunflower Biodiesel and Its Formulations

According to the data, it is verified that the sunflower biodiesel without antioxidant oxidizes more quickly than its formulations, presenting a peroxide value (PV) of 330 meq/kg for 6 h of oxidation (120 °C). This PV is considered extremely high, which demonstrates the susceptibility of biodiesel to the oxidation, under extreme conditions. It is also observed that the formulations: sunflower biodiesel/A2 and sunflower biodiesel/AC showed the better results for 4 h of oxidation (120 °C) when compared with sunflower biodiesel/A3. This behavior is probably in consequence of the synergist effect of the mixture of phenolic antioxidants presents in A2 and AC antioxidants. The literature suggests that, the mixture of antioxidants is more efficient than any one used separately[20], once that, when determined antioxidant (mixture component) in an organic substrate reacting with peroxyl or alkylperoxyl radicals, a phenoxy radical is formed. This phenoxy radical can be regenerated when interacting with another mixture component, in its original state, generating a second phenoxy radial[20]. The second phenoxy radical can still react with a peroxyl radical of the organic substrate and this way, potentiate the antioxidant action of the mixture.

CONCLUSIONS

The phenolic antioxidants A2 and A3 showed significant potentiality after addition in sunflower biodiesel, when compared with ionol BF200 (AC). The A2 (1000 ppm) and A3 (1000 ppm) reduced the absorbance around 31%. The peroxide value showed that, sunflower biodiesel possesses susceptibility of the oxidation, under extreme conditions. On the other hand, the formulations: sunflower biodiesel/A2, sunflower biodiesel/A3 and sunflower biodiesel/AC showed better results when compared with sunflower biodiesel without antioxidant. So, according to the results, the compounds derived from biomass (A2 and A3) come as promising eco-friendly antioxidants, for biofuels industry being in consonance with sustainable development.

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