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# ANTIOXIDATIVE PROPERTIES OF HYDROGENATED CARDANOL FOR COTTON BIODIESEL BY PDSC AND UV/VIS

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Biodiesel is a non-toxic biodegradable fuel that consists of alkyl esters produced from renewable sources, vegetal oils and animal fats, and low molecular mass alcohols, and it is a potential substitute for petroleum-derived diesel. Depending on the raw materials used, the amount of unsaturated fatty acids can vary in the biodiesel composition. Those substances are widely susceptible to oxidation processes, yielding polymeric compounds, which are harmful to the engines. Based on such difficulty, this work aims to evaluate the antioxidant activity of cashew nut shell liquid (cardanol), as additive for cotton biodiesel. The oxidative stability was investigated by the pressure differential scanning calorimetry (PDSC) and UV/Vis spectrophotometer techniques. The evaluated samples were: as-synthesized biodiesel – Bio $T_0$, additivated and heated biodiesel – Bio A (800 ppm $L^{-1}$ of hydrogenated cardanol, 150°C for 1 h), and a heated biodiesel – Bio B (150°C, 1 h). The oxidative induction time (OIT) analyses were carried out employing the constant volume operation mode (203 psi oxygen) at isothermal temperatures of 80, 85, 90, 100°C. The high pressure OIT (HPOIT) were: 7.6, 15.7, 22.7, 64.6, 124.0 min for Bio $T_0$; 41.5, 77.0, 98.6, 106.6, 171.9 min for Bio A and 1.7, 8.2, 14.8, 28.3, 56.3 min for Bio B. The activation energy ($E$) values for oxidative processes were 150.0±1.6 (Bio $T_0$), 583.8±1.5 (Bio A) and 140.6±0.1 kJ $mol^{-1}$(Bio B). For all samples, the intensities of the band around 230 nm were proportional to the inverse of $E$, indicating small formation of hyper conjugated compounds. As observed, cardanol has improved approximately four times the cotton biodiesel oxidative stability, even after the heating process.

***Keywords:** biodiesel, PDSC, UV/Vis*

## Introduction

In order to replace the petroleum-based fuels, biodiesel became a significant alternative between the biomass products as consequence of its economic, social and environmental positive impacts [1–5]. Although the renewable origin and biodegradability of the biodiesel are widely presented as advantage, its decomposition property confers to itself lower oxidative stability in comparison to mineral diesel [2, 6]. In the course of storage, biodiesels are oxidized by metal traces, oxygen and temperature, and their stability is also influenced by the unsaturated fatty acid composition [7–10]. Such process yields substances that corrode the engine chamber or obstruct the injection filters of vehicles [11, 12]. In order to control the oxidation, many oxidant agents can be used, typically to improve or preserve existing estates, suppressing those undesirable and introducing new ones. Recently, several research groups are speculating about using low cost antioxidants derived from renewed sources [13]. Cardanol and its derivates are examples of such compounds and present significant antioxidant characteristics, being applied as additive for food, lubricants, polymers and rubber industries [14–20], as well as like antibacterial [21], antifungal [22] and antitumor products [21]. In magnitude, its antioxidant activity is comparable to that of 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 2-*t*-butyl-4-methoxyphenol (BHA), synthetic antioxidants [23].

By definition, cardanol is a complex mixture of 3-*n*-pentadecylphenol, 3-(*n*-pentadeca-8-enyl) phenol, 3-(*n*-pentadeca-8,11-dienyl) phenol, 3-(*n*-pentadeca-8,11,14-trienyl) phenol, extracted from the cashew nut shell liquid (from Brazilian Portuguese – LCC). Brazil and India use hydrogenated cardanol in fine chemical processes in order to confer higher thermo-oxidative stability to a series of substances [24, 25]. Adding to biodiesel LCC reduces the biofuel decomposition ratio due to deactivation of the single oxygen (radical oxidation reaction) by means of the hydroxyl group presents in its aromatic ring.

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The oxidative induction time (OIT) is used to estimate the relative stability of several specimens exposed to an oxidizing gas under elevated isothermal test temperatures. This index is widely used for quality control management and evaluation of oxidation inhibitors [26]. The OIT values for vegetal oils, animal fatty, greases or lubricants are often determined by means of differential scanning calorimetry (DSC). Even at low temperatures these measurements can be accelerated by using increased partial pressure purge oxygen or higher-pressure system. When pressure differential scanning calorimetry (PDSC) is applied, the high pressure oxidative induction time (HPOIT) is determined as a function of the elapsed time from the beginning of the heating ($t_0$) to the onset of the oxidative endotherm ($t_{\text{onset}}$). In that case, the sample is immediately exposed to oxygen pressure at the starting temperature up to the isothermal experimental temperature ($T_0$), at a constant heating rate. By definition, $t_0$ refers to the moment when the isothermal experimental temperature is reached [27].

This work aims to evaluate the anti-oxidative properties of the hydrogenated cardanol for cotton oil derived biodiesel by means of the pressure differential scanning calorimeter (PDSC) and UV/Vis spectrophotometer techniques.

## Experimental

### *Extraction of cardanol*

The cardanol sample was supplied by the Laboratório de Desenvolvimento de Produtos e Processos (LDPP) from Brazilian Federal University of Ceará. In order to increase the yield of extraction reaction, the LCC was heated at 197°C during 15 min. Following, the cardanol was extracted from the cashew nut shell liquid [13].

### *Synthesis and characterization of the cotton biodiesel*

The ethyl cotton biodiesel was synthesized by transesterification reaction using oil:alcohol molar ratio and KOH (1 mass/mass%), according to [3]. The yielded biodiesel was partitioned in three samples, being classified as: Bio $T_0$ – as-synthesized biodiesel; Bio A – doped (800 ppm $L^{-1}$ of hydrogenated cardanol) and heated biodiesel (150°C, 1 h); and Bio B – heated biodiesel (150°C, 1 h). All samples were characterized by iodine index, hydrogen peroxide content and acidity [27]. UV/Vis absorption spectra were recorded using a Shimadzu 2520 spectrophotometer, using 1:1000 (*v*/*v*) dilution ratio in dichloromethane (Merck). All data were collected in the range of 200–400 nm.

The PDSC curves were recorded using a DSC 2920 (TA Instrument) with pressure cell, under isothermal conditions, using alumina pans, heating rate of 5°C $\text{min}^{-1}$, 14 bar oxygen gas (99.5% purity and constant volume) at the temperature range of 25–600°C and at isothermal experimental temperature of 80, 85, 90, 95 and 100°C.

### *Kinetic parameters*

The kinetic studies for the thermal oxidation of ethyl cotton biodiesel were based on the Arrhenius rate law, which gives the dependence of kinetic rate constant $k$ of chemical reactions on the absolute temperature $T$ ($K$) and activation energy $E$ (J $\text{mol}^{-1}$), as shown by Eq. (1) [27–29]:

$$k(T)=A\exp^{(-E/RT)} \tag{1}$$

where $A$ is the pre-exponential factor and $R$ is the gas constant (8.314472 J $K^{-1}$ $\text{mol}^{-1}$).

The kinetic parameters $E$ and $A$ were determined from the plot of the natural logarithm (ln) of the HPOIT *vs.* the reciprocal of the absolute isothermal experiment temperature, whose slope is equal to ($E/R$) (Eq. (2)) [26].

$$\ln \text{HPOIT}=\left[\left(-\frac{E}{R}\right)\frac{1}{T}\right]+\text{const.} \tag{2}$$

## Results and discussion

### *Pressure differential scanning calorimetry (PDSC)*

The curves for each sample are displayed in Fig. 1.

The as-synthesized biodiesel (Bio $T_0$) presented higher HPOIT compared to the Bio B, as result of its natural antioxidants compounds (*D*-α-tocopherols), since those substances were released from the Bio B during the thermal stress. Conversely, additivated biodiesel showed increased HPOIT, confirming the antioxidative capability of hydrogenated cardanol, even after heating.

Table 1 lists the HPOIT values for all cotton biodiesel samples at different isothermal temperatures.

### *Determination of the kinetic parameters*

Figure 2 presents the ln HPOIT *vs.* $T^{-1}$ curves and their respective linearization, showing a linear correlation between them. Thus, the activation energies and pre-exponential factor of the thermal oxidative decomposition were determined by means of Eq. (1).

Table 2 summarizes the kinetic parameters for all the ethyl cotton biodiesel. The Bio A is approximately four times higher in magnitude if compared to the Bio $T_0$ and Bio B. This significant thermo-oxidative

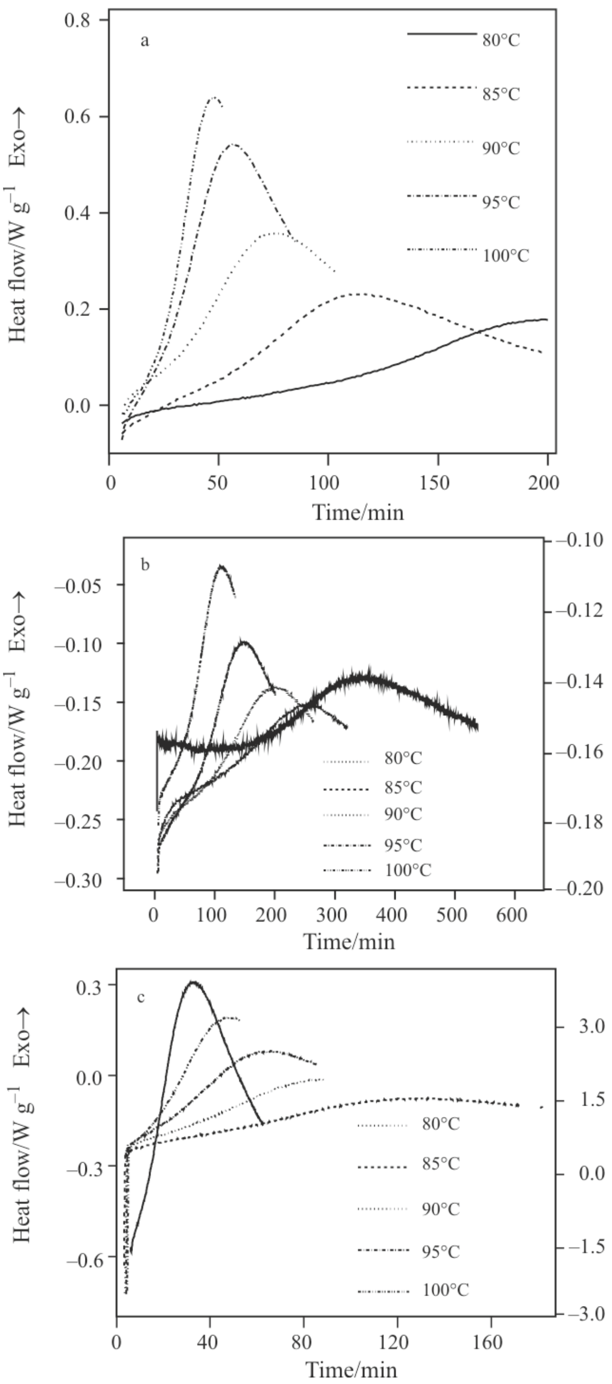

**Fig. 1** HPOIT for a – Bio $T_0$, b – Bio A and c – Bio B samples, at isothermal temperatures

stability results from the hydrogenated cardanol activity, which reduces the formation of secondary and tertiary products (aldehydes, ketones and polymers). The cardanol acts as a primary antioxidant (phenyl compound), either removing or deactivating the free radical formation during initial and propagation oxidation steps, once its hydrogen atoms are donned to the reactive species, as follow:

$$\mathrm{ROO^{\bullet}+AH\rightarrow ROOH+A^{\bullet}}$$

or

$$\mathrm{R^{\bullet}+AH\rightarrow RH+A^{\bullet}}$$

where $\mathrm{ROO^{\bullet}}$ and $\mathrm{R^{\bullet}}$ – free radicals, AH – active hydrogenated antioxidant and $\mathrm{A^{\bullet}}$ – low reactive radical [7].

**Table 1** HPOIT for samples Bio $T_0$, Bio A and Bio B at several experimental isothermal temperatures

| Sample | Isothermal temperature/°C | HPOIT/min |
|---|---|---|
| Bio $T_0$ | 80 | 124.03 |
| | 85 | 64.60 |
| | 90 | 22.68 |
| | 95 | 15.67 |
| | 100 | 7.58 |
| Bio A | 80 | 171.96 |
| | 85 | 106.63 |
| | 90 | 98.64 |
| | 95 | 76.96 |
| | 100 | 41.50 |
| Bio B | 80 | 53.30 |
| | 85 | 28.30 |
| | 90 | 14.83 |
| | 95 | 8.17 |
| | 100 | 1.68 |

**Table 2** Kinetic parameters for the thermal oxidation of ethyl cotton oil biodiesel

| Sample | $E$/kJ mol$^{-1}$ | $A$/s$^{-1}$ |
|---|---|---|
| Bio $T_0$ | 150.6±1.6 | $6.8\cdot10^{-21}$ |
| Bio A | 583.8±1.5 | $3.9\cdot10^{-7}$ |
| Bio B | 140.6±1.0 | $8.8\cdot10^{-20}$ |

### *UV/Vis absorption study*

According to Fig. 3, the molar absorptive coefficients at 230 (C=C) and 270 (C=O) nm indicate diversity in the chemical composition of the several biodiesel samples. Furthermore, such spectroscopic profile results from secondary compounds (keto-aldehyde) due to transitions $\pi\rightarrow\pi^*$ of conjugated unsaturated groups. The spectroscopy data agree with the thermal profile and the kinetic parameters, in which the intensity of the Bio A absorption indicates a lower oxidative degree in comparison with the Bio $T_0$ and Bio B, proving the efficiency of the hydrogenated cardanol as antioxidant for biofuel. Comparatively, Bio $T_0$ shows higher stability than Bio B due to its natural antioxidants.

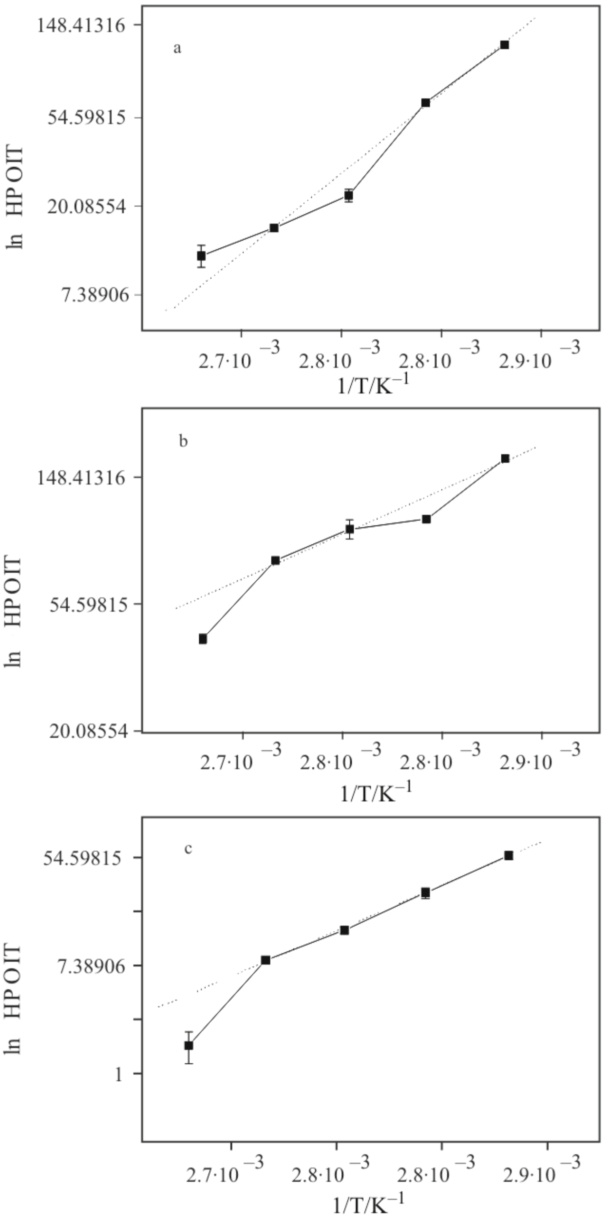

**Fig. 2** ln HPOIT *vs.* $T^{-1}$ curves for a – Bio $T_0$, b – Bio A and c – Bio B samples

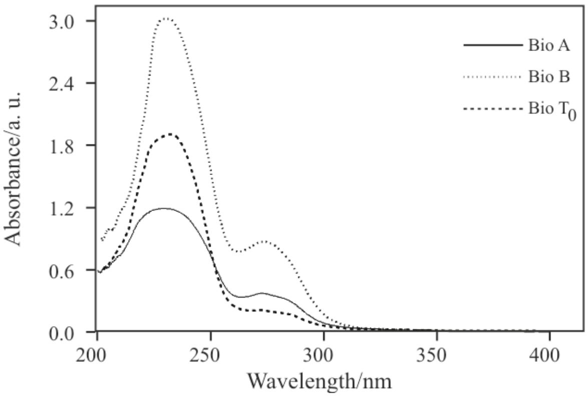

**Fig. 3** UV/Vis spectra for a – Bio $T_0$, b – Bio A and c – Bio B samples

## Conclusions

The thermal and spectroscopic data indicate that the hydrogenated cardanol acts as natural antioxidant additive against the oxidative degradation for ethyl cotton biodiesel. As observed, the overall activation energy for the oxidative process increases from 150 (as-synthesized biodiesel) to 583 kJ mol$^{-1}$ for the additivated sample. This work also shows the high applicability of pressure differential scanning calorimetry to monitor the oxidative reactions during the long-term storage and thermal condition of biofuel, as supported by means of UV/Vis data.

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