Thermal studies of new biodiesel antioxidants synthesized from a natural occurring phenolic lipid

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This article reported the synthesis of phosphorylated compounds derived from cardanol, a phenolic by-product of the cashew (Anacardium occidentale L.) industry, and its application as antioxidants for biodiesel. These compounds were added in biodiesel samples in three different concentrations (500, 1000 and 2000 ppm) and their antioxidants activities were tested by thermogravimetric analysis (TG), analyzing the onset ($T_o$) and endset ($T_e$) temperatures values as reference parameters, as also by evaluating their integral procedure degradation temperatures (IPDTs). The results showed that the addition of new antioxidants increased the thermal stability of biodiesel, making this biofuel more resistant to thermo-oxidative process.

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1. Introduction

Biodiesel is an alternative diesel fuel derived from transesterification of vegetables or animals oils, is composed of saturated and unsaturated long-chain esters, is also extender proposed for applications ranging from on- and off-road compression-ignition (diesel) engine powered vehicles to locomotives, stationary power, heat generation and aviation fuels [1]. Compatibility with the existing fuel infrastructure, renewability, domestic origin, biodegradability, inherent lubricity in the neat form, and competitiveness with petrodiesel in terms of many fuel properties are significant attributes of biodiesel [2]. Biodiesel provides enhanced lubricity property and produces low exhaust emissions, such as particulate matter, polycyclic aromatic hydrocarbons, carbon dioxide, sulfur dioxide and smoke [3].

However, the rates of oxidation of unsaturated fatty acids or esters can vary considerably, modifying the properties of this material. The understanding of oxidation is complicated by the fact that fatty acids usually occur in complex mixtures, with minor components in these mixtures catalyzing or inhibiting oxidation. This observation affects biodiesel because, usually, significant amounts of esters of oleic, linoleic and linolenic acids, as well as minor components, which may affect oxidation, are present. Oxidation of fatty materials is promoted by factors such as elevated temperature, presence of light or extraneous materials such as metals or initiators. The nature of the radicals also influences the products observed and double bond geometry can also play a role [3].

In order to slow the oxidation process, several additives are added to these fuels with the aim of inhibiting or retarding such undesirable reactions. Among them, the phenolic antioxidants are especially considered because they are able to directly seize peroxyl radicals formed during oxidative degradation, thus breaking the auto-oxidation chain reaction [4]. Synthetic antioxidants like, tert-butyl hydroxyquinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and propyl gallate (PG) has been reported in many studies as important examples of phenolic antioxidants [5,6].

Another class of compounds that have been reported for its antioxidant potential is the phosphorylated compounds; in general, these compounds are used in several chemical products, such as lubricants, fuels, synthetic diesels, biodiesel, and others. The oxidation stability and performance of these products are dependent upon the chemical structure of the molecule and formation of stable compounds of decomposition during usage [7]. The phosphorus stabilizers are considered as hydroperoxide decomposers, also named secondary antioxidants, which also react with peroxo and oxyl radicals by non-radical reaction [8,9].

Recent studies have reported the antioxidant capacity of the constituents of cashew nut shell liquid (CNSL) (Fig. 1), a by-product...
of the cashew (Anacardium occidentale L.) nuts industrial processing, and its derivatives and proved their antioxidant properties upon mineral oils and polymers [7,10,11].

A typically solvent-extracted CNSL is composed mainly by: anacardic acid (60–70%), cardol (15–20%), cardanol (10%), and traces of 2-methylcardol. When obtained as a residue from the industrial roasting shell process, which employs elevated temperatures, anacardic acid suffers a decarboxylation reaction and CNSL is then considered as technical CNSL, which contains mainly cardanol (60–70%), cardol (15–20%), polymeric material (10%), and traces of 2-methylcardol (Fig. 2) [12].

According to Food and Agriculture Organization of the United Nations (FAO), the worldwide production of cashew nuts in 2009 was around 3,300,000 tonnes, and the main producers were Vietnam, India, Nigeria, Cote d’Ivore and Brazil, in this order [13]. Knowing that CNSL comprises around 25% the total weight of the cashew nut was estimated that in 2009 the global production of this oil was near 800,000 tonnes.

Therefore, this work has as main objectives the syntheses of phosphorylated compounds from cardanol and the study of their application as new antioxidants for biodiesel, evaluating its performance through thermogravimetric analyses (TG), its derivative (DTG) and their integral procedure degradation temperatures (IPDTs).

2. Experimental procedure

2.1. Materials

Reagents and solvents were supplied by SigmaAldrich. Column chromatography was run using Silica Gel 60, while TLC was conducted on precoated silica gel polyester sheets (Kieselgel 60 F254, Merck). Technical CNSL was supplied by Amêndoas do Brasil LTDA. Biodiesel was gently supplied by Petrobras S/A. Physicochemical properties of the biodiesel are in accordance with the ASTM requirements as shown in Table 1 [16].

2.2. Measurements

The samples obtained were analyzed by GC/MS on a Hewlett-Packard Model 5971 using a DB-5 capillary column (30 m × 0.25 mm); carrier gas was helium (He), flow rate 50 mL/min with split mode. The injector temperature and detector temperature were 250 and 200 °C, respectively.

NMR spectra were recorded on a Bruker Avance DRX-300 (300 MHz for 1H, 75 MHz for 13C, 121.5 MHz for 31P) using CDCl3 as solvent.

Table 1

<table>
<thead>
<tr>
<th>Physicochemical analyses</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity value (mg KOH g⁻¹)</td>
<td>0.26</td>
</tr>
<tr>
<td>Peroxide value (m Eq kg⁻¹)</td>
<td>37.10</td>
</tr>
<tr>
<td>Iodine value (mg I₂ 100 g⁻¹)</td>
<td>139.60</td>
</tr>
<tr>
<td>Kinematic viscosity (mm² s⁻¹)</td>
<td>4.20</td>
</tr>
<tr>
<td>Density (kg m⁻³)</td>
<td>877.5</td>
</tr>
</tbody>
</table>
Scheme 1. Synthetic route to cardanol derivatives.

Fig. 4. Mass and $^1$H NMR spectra of CDN-P (6a).
Thermoanalytical measurements were carried out using a Mettler-Toledo TGA/SDTA851e analyzer. The measurements were performed at scanning rate of 10 °C/min. Samples of 10 mg were heated from 25 to 500 °C. The measurements were carried out at synthetic air atmosphere (50 mL/min). All data obtained were analyzed using Mettler-Toledo STARé Software version 10. The definition of the initial degradation temperature is the extrapolated onset temperature ($T_e$), which is basically the intersection of the tangents of the curve at the upper horizontal baseline and the steepest part of the curve, as showed in Fig. 3 [14].

2.3. Methods

2.3.1. Isolation of cardanol from CNSL
Cardanol was isolated from CNSL by a methodology previously published [15], with few modifications. To a solution of technical CNSL (1000 g) dissolved in methanol (30 mL), ammonium hydroxide (25%, 20 mL) was added and stirred for 10 min. This solution was then extracted with hexane (4 × 40 mL). The organic layer was washed with 5% HCl (20 mL), followed by distilled water (50 mL), then dried over anhydrous sodium sulfate and concentrated to get pure cardanol (5.30 g, 53%).

Cardanol–(Z)-3-(pentadec-8-enyl)phenol (3): NMR 1H: 0.86 (t); 1.36; 1.45; 1.50; 1.71; 2.19 (t, 2H); 2.65; 2.94; 2.95; 5.11; 5.13; 5.18; 5.21; 5.53; 5.92; 6.79 (m, 1H); 6.82 (m, 1H); 6.86 (d, 2H); 7.22 (t, 1H) ppm. NMR 13C: 13.87; 14.14; 14.18; 14.18; 22.79; 25.74; 25.83; 27.37; 29.12; 29.38; 29.45; 29.55; 29.81; 29.89; 31.35; 31.65; 31.94; 35.98; 112.84; 115.53; 120.94; 126.97; 127.77; 128.18; 128.35; 129.44; 129.97; 130.06; 130.22; 130.48; 144.89; 155.66 ppm. GC/MS (m/z): 302 (M+, rel. int. 6%).

2.3.2. Synthesis of phosphorylated compounds (5), (6) and (7)
General procedure. To a suspension of cardanol (3) (1000 mg, 3.31 mmol) and potassium carbonate (456.7 mg, 3.31 mmol) in acetone (60 mL), under magnetic stirring, the reactant (571.1 mg of diethyl chlorophosphate (5a); or 624.2 mg of diethyl chlorothiophosphate (5b); or 889.1 mg of diphenyl chlorophosphate (5c), 3.31 mmol) was added slowly at room temperature. The resulting mixture was warmed to reflux temperature (60 °C) and stirred for 4 h. After this period, brine (40 mL) was added and the resultant solution was extracted with ethyl acetate (3 × 40 mL). The combined organic extracts were washed with distilled water (50 mL), dried over anhydrous Na2SO4 and concentrated in vacuum. The crude product was then purified by column chromatography using hexane/ethyl acetate (ratio 1:1) as eluent, to afford the desired products (6a) or (6b) or (6c) as clear yellow oils (Scheme 1). The isolated products were characterized by gas chromatography/mass spectrometry (GC/MS) and 1H, 13C and 31P nuclear magnetic resonance (NMR). Fig. 4 shows the mass and 1H NMR spectra of compound CDN-P (6a).

CDN-P (1246 g, 86%) – (Z)-diethyl [3-(pentadec-8-enyl)phenyl]phosphate (6a): NMR 1H: 0.86 (t); 1.26 (m); 1.32 (m, 6H, –P–O–CH2–CH3); 1.58 (m, 2H); 2.00 (m); 2.56 (t, 2H); 4.19 (m, 4H, –P–O–CH2–CH3); 5.33 (m, 2H); 6.96 (m, 2H); 7.01 (s, 1H) 7.19 (t, 1H) ppm. NMR 13C: 14.07; 16.01 (d); 22.64; 27.17; 27.20; 28.96; 29.19; 29.36; 29.72; 31.20; 31.77; 35.71; 64.46 (d); 117.04 (d); 119.82; 119.89; 125.64; 129.31; 129.75; 129.90; 130.00; 144.93; 150.65 (d) ppm. NMR 31P: –5.3 ppm. GC/MS (m/z): 438 (M+, rel. int. 33%).

CDN-S (1352 g, 90%) – (Z)-diethyl [3-(pentadec-8-enyl)phenyl] phosphorothioate (6b):
NMR \(^1\)H: 0.89 (t); 1.31 (m); 1.41 (m, 6H, –P–O–CH\(_2\)–CH\(_3\)); 1.58 (m, 2H); 2.01 (m); 2.59 (t, 2H); 4.24 (m, 4H, –P–O–CH\(_2\)–CH\(_3\)); 5.37 (m, 2H); 7.01 (m, 3H); 7.22 (t, 1H) ppm. NMR \(^1\)C: 14.18; 15.95 (d); 22.75; 25.68; 27.32; 29.08; 29.31; 29.47; 29.74; 29.84; 31.26; 31.88; 35.81; 65.01 (d); 118.09 (d); 120.98; 121.04; 125.37; 127.71; 129.23; 129.40; 130.46; 144.83; 150.81 (d) ppm. NMR \(^31\)P: 64.2 ppm. GC/MS (m/z): 454 (M+, rel. int. 35%).

**CDN-Ph** (1467 g, 83%) – (Z)-3-(pentadec-8-enyl)phenyl diphenyl phosphate (6c):

NMR \(^1\)H: 0.90 (t); 1.29 (m); 1.59 (m, 2H); 2.18 (m); 2.61 (t, 2H); 5.45 (m, 2H); 6.88 (m, 2H); 7.03 (s, 1H) 7.20 (m, 11H) ppm. NMR \(^1\)C: 14.01; 22.82; 29.54; 31.19; 33.50; 35.71; 117.04; 120.56; 120.69; 120.71; 125.04; 129.12; 129.64; 129.90; 130.10; 130.19; 143.42; 150.03; 150.20 ppm. NMR \(^31\)P: –17.3 ppm. GC/MS (m/z): 534 (M*, rel. int. 27%).

3. Results

3.1. Thermogravimetric analyses

The TG curve obtained from samples with and without addition of antioxidants showed that the degradation of this fuel occurs in a prolonged mass loss event (Fig. 3). It was possible to observe that the degradation of the pure biodiesel starts at 219.1 °C and presents a mass loss of 98%. According to Dantas et al. [16] the onset temperature (\(T_o\)) values is related to the level of oxidation of the biodiesel. The authors state that the more the sample is oxidized before the thermogravimetric analysis, the lower is the onset temperature (\(T_o\)) of the first mass loss step. This occurs due to the volatilization of the aldehydes and ketones previously formed during the oxidative process [16].

In Fig. 5 are shown the curves obtained from the analyses of biodiesel samples containing different concentrations of compound 6a, CDN-P. It’s observed that all antioxidant additives promoted a delay in the initiation of the thermo-oxidative degradation process of biodiesel, as the mass losses observed in the curves of the thermogram are dislocated to the right side in comparison to the curve presented by the pure biodiesel sample, which indicate that these processes are occurring at higher temperatures. In Table 1 are summarized the values of the initial degradation temperature (\(T_o\)) obtained from the TG and DTG analyses of the biodiesel samples, that confirm the antioxidant effect promoted by compound 6a.

TG experiments for samples additivated with compound 6b, CDN-S, showed that this compound promoted a significant increase in the onset temperature (\(T_o\)) values at all evaluated concentrations (500, 1000 and 2000 ppm), which also confirmed its efficient performance inhibiting the thermo-oxidative process of biodiesel (Fig. 6). The values of \(T_o\) obtained from the thermogravimetric analyses are shown in Table 1.

TG curves for samples additivated with the phenyl phosphorylated compound (6c), CDN-Ph, at same concentration range as applied to the others antioxidants, showed the same pattern observed for compound 6b (Fig. 7), in which a concentration of 2000 ppm was less effective than 500 ppm, and at 1000 ppm the best activity was achieved. The values observed in the TG analyses are summarized in Table 2.
The antioxidant activities promoted by the cardanol derivatives were increased when the concentrations applied raised from 500 to 1000 ppm (Table 2), except when additivated with 2000 ppm, in this concentration the biodiesel samples exhibited a lower effect in thermo-oxidative stabilization, in contrast with the continuous raising values of $T_e$ observed.

Considering the values of the initial degradation temperature ($T_e$) was observed that the three compounds reached their maximum activity at a concentration of 1000 ppm, where all the biodiesel samples exhibited their highest values of $T_e$. This result shows that there is a limit on the use of antioxidants, where an increase in concentration does not imply an increase in the performance of these substances.

In order to evaluate more precisely the capacity for retarding the starting of thermo-oxidative processes demonstrated by the phosphorylated CNSL derivatives, we confronted these thermogravimetric data (obtained from the samples additivated with 1000 ppm) and compared them with the utilization of the commercial antioxidant BHT (butylated hydroxytoluene) in the same concentration. The combined curves are plotted in Fig. 8.

The results obtained suggested that compound 6b, CDN-S, was the best antioxidant among the CNSL based additives tested (Table 3). The onset ($T_e$) and the offset ($T_o$) temperatures determined were 235.6 and 285.1 °C, respectively, slight higher than those for compounds 6a and 6c. Also the values of temperature of maximum degradation ($T_{max}$), obtained from the derivative (DTG) of the thermogravimetric curve, showed a better efficiency for antioxidant 6b, 272.3 °C. Confronting these values with those obtained using BHT as antioxidant (also at 1000 ppm), was possible to observe that biodiesel samples additivated with CDN-S, 6b, exhibited slightly better values for both $T_e$ and $T_o$, while the temperature of maximum degradation ($T_{max}$) was higher, 273.6 °C, for samples with BHT, than with CDN-S, 272.3 °C.

Even tough the parameters evaluated in the TG experiments are very substantial, additionally we calculated the integral procedure degradation temperatures (IPDTs) of biodiesel samples containing 1000 ppm of the CNSL antioxidants and BHT. This element, which sums up the shape of thermogravimetric curves [7], also recognized the biodiesel samples additivated with CDN-S (6b) to be more thermally stable than with the others antioxidants studied (Table 3).

The good performance of similar compounds was also evidenced in others works [17,18]. Result showed that the presence of a sulfur atom has a positive influence on the antioxidant action.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Antioxidant concentration (ppm)</th>
<th>$T_e$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodiesel</td>
<td>0</td>
<td>219.1</td>
</tr>
<tr>
<td>+CDN-P (6a)</td>
<td>500</td>
<td>230.2</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>235.6</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>233.1</td>
</tr>
<tr>
<td>+CDN-S (6b)</td>
<td>500</td>
<td>235.5</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>237.6</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>232.1</td>
</tr>
<tr>
<td>+CDN-Ph (6c)</td>
<td>500</td>
<td>232.5</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>236.1</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>230.7</td>
</tr>
</tbody>
</table>

![Fig. 7. TG curves obtained from samples additivated with CDN-Ph (6c).](image)
According to Giinther [17] organic sulfur compounds can act as secondary antioxidants decomposing peroxides radicals formed during the oxidation process. Recently, Mangolini et al. [18] proposed that under elevated temperatures occurs a scission of the P=S bond to give triphenyl phosphite, succeeded by a thermo-oxidative reaction which leads to the oxidation to triphenyl phosphate (Scheme 2).

4. Conclusions

Herein, we synthesized and characterized new biodiesel antioxidants from cardanol, the main component of the agroindustrial residue cashew nutshell liquid (CSNL).

Thermogravimetric analyses confirmed their antioxidant capacity upon biodiesel, increasing the initial temperature of degradation ($T_e$). However, the best results were obtained in concentrations of 1000 ppm, indicating that an increase in concentration does not imply in better a performance.

The CNSL derivatives synthesized showed very good antioxidant activity, which can also be comparable with BHT values.

CDN-S (6b) showed the best results, explained by the presence of the sulfur atom, which enhances the antioxidant effect.

Integral procedure degradation temperatures (IPDTs) values for these samples also verified the great capacity to inhibit the degradation processes improving the thermo-oxidative stability of the biofuel.

![Fig. 8. TG curves obtained from samples additivated with 1000 ppm cardanol derivatives.](image)

**Table 3**

Thermogravimetric values obtained from analyses of the biodiesel samples additivated with 1000 ppm of cardanol derivatives.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_e$ (°C)</th>
<th>$T_o$ (°C)</th>
<th>$T_{max}$ (°C)</th>
<th>IPDT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodiesel</td>
<td>219.1</td>
<td>282.0</td>
<td>267.3</td>
<td>251.2</td>
</tr>
<tr>
<td>+CDN-P</td>
<td>235.6</td>
<td>285.1</td>
<td>270.8</td>
<td>265.9</td>
</tr>
<tr>
<td>+CDN-S</td>
<td>237.5</td>
<td>286.3</td>
<td>272.3</td>
<td>266.5</td>
</tr>
<tr>
<td>+CDN-Ph</td>
<td>236.1</td>
<td>286.0</td>
<td>271.5</td>
<td>261.5</td>
</tr>
<tr>
<td>+BHT</td>
<td>234.2</td>
<td>286.1</td>
<td>273.6</td>
<td>254.3</td>
</tr>
</tbody>
</table>

**Scheme 2.** Proposed reaction mechanism of CDN-S under elevated temperatures.
Acknowledgments

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References