

# ANTIWEAR AND ANTIOXIDANT STUDIES OF CARDANOL PHOSPHATE ESTER ADDITIVES

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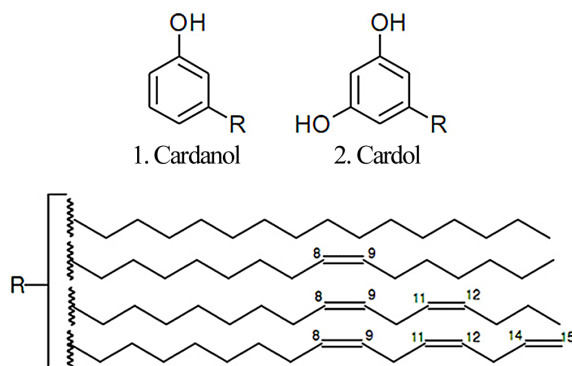
**Abstract** - In the search for new applications and products derived from Cashew Nut Shell Liquid (CNSL), we report herein the synthesis and characterization (GC/MS and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR) of four phosphate esters derived from hydrogenated cardanol, including their applications as antiwear additives for diesel (S500) and as antioxidant additives for mineral oils, evaluated through the HFRR test and oxidative stability analyses, respectively. The results obtained showed very good to excellent performances promoted by the bio-additives evaluated, especially for the thiophosphorylated derivative, which notably reduced the sludge residue and the acidity index of the oxidized oil (0.52 mg NaOH/g sample) and also improved the diesel lubricity, reducing the wear of metal parts by more than 50% (330 μm).

**Keywords:** Cardanol; Antiwear; Antioxidant; Diesel; Mineral oil.

## INTRODUCTION

Cashew Nut Shell Liquid (CNSL), a by-product obtained from the industrial processing of cashew (*Anacardium occidentale* L.), is a dark viscous oil, with a characteristic odor, very rich in non-isoprenoid phenolic lipids. Commercially available CNSL, also called "technical CNSL", is composed basically by a mixture of two compounds: cardanol and cardol, as shown in Figure 1 (Mazzetto *et al.*, 2009).

According to FAO (2011) (Food and Agriculture Organization of the United Nations), the worldwide production of cashew nuts in 2009 was around 3.3 Mt and the main producers were Vietnam, India, Nigeria, Cote d'Ivoire and Brazil, in this order. Knowing that CNSL comprises around 25% of the total weight of the cashew nut, it can be estimated that, in 2009, the global production of this oil was near 800,000 tons.



**Figure 1:** Main constituents of technical CNSL.

Cardanol is the predominant component of technical CNSL, representing more than 70% (w/w) of its composition and is also the most studied in the scientific literature (Vasapollo *et al.*, 2011). Among the many articles published, we highlight some

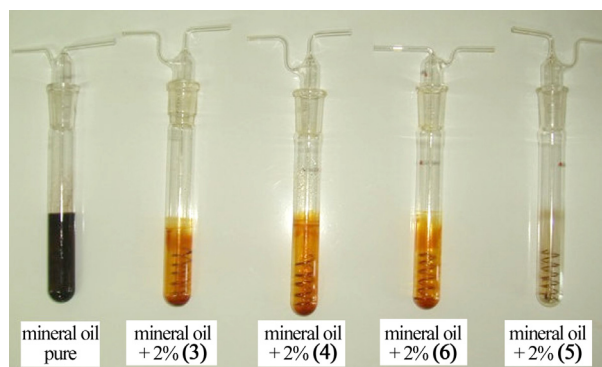
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important fields of applications of this interesting molecule, such as: phenolic resins (Cardona *et al.*, 2012), porphyrins (Vasapollo *et al.*, 2011), benzoxazines (Li *et al.*, 2011), antioxidants (Amorati *et al.*, 2011), larvicides (Lomonaco *et al.*, 2009), and composites (Barreto *et al.*, 2011).

In the last few years, our group has dedicated special attention to the antioxidant properties exhibited by cardanol and its phosphorylated derivatives in different materials (Lomonaco *et al.*, 2011; De Souza Rios *et al.*, 2009; Lopes *et al.*, 2008; Rios Façanha *et al.*, 2007). The results obtained were very satisfying, keeping us focused on improving the performance and expanding the areas of utilization of these fascinating compounds.

Although we have already tested cardanol and its derivatives as oil additives in previous works, in this paper the antioxidant activity of these compounds is evaluated by oxidative stability analyses for the first time, with special attention to the sludge residues and the acidity index of the oil samples.

Another interesting application for which CNSL derivatives have not yet been studied is as diesel lubricant additives. Considering the molecular structure of cardanol derivatives, especially the long C15 side chain, one might expect that a phosphate polar head (hydrophilic phosphate group) could increase the interaction with metal parts of the engine, creating a lubricated layer, reducing the friction and, consequently, the wear of motor parts. This property was evaluated by the HFRR (High Frequency Reciprocating Rig) method, which measures the ability of a fluid to modify friction between and wear of surfaces in motion under load (Figure 2) (Sukjit and Dearn, 2011).



**Figure 2:** Oxidized mineral oil samples.

In this sense, this work has, as its main objectives, the syntheses of phosphate esters derived from hydrogenated cardanol and the study of their application as new lubricating additives for biodiesel, as well as

evaluate its antioxidant performance upon mineral oil through oxidative stability analysis.

## EXPERIMENTAL

### Materials

The technical cashew nutshell liquid was supplied by Amêndoas do Brasil LTDA, a Brazilian cashew company. Petrobras S/A graciously supplied mineral oils. All reagents were supplied by SigmaAldrich and solvents by Vetec Química. Column chromatography was performed using silica gel 60 (70–230 mesh, Vetec Química), while TLC was conducted on precoated silica gel polyester sheets (Kieselgel 60 F254, 0.20 mm, Merck).

### Measurements

The samples obtained were analyzed by gas chromatography/mass spectrometry on a Shimadzu GCMS QP5010 Ultra using a (5%-phenyl)-methylpolysiloxane (Restek Rxi-5ms) capillary column; the carrier gas was helium (He) with a flow rate of 1 mL/min in splitless mode. The injector and detector temperatures were 250 and 200 °C, respectively.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance DRX-300 (300 MHz for  $^1\text{H}$ , 75 MHz for  $^{13}\text{C}$ , and 121.5 MHz for  $^{31}\text{P}$ ) using  $\text{CDCl}_3$  as solvent.

High Frequency Reciprocating Rig (HFRR) tests were performed on a PCS Instruments Ltd. model HFR2. All tests were conducted according to ASTM D6079-99 (Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig) and ISO 12156-1:1997 (Diesel fuel - Assessment of lubricity using the high-frequency reciprocating rig) specifications. The HFRR reported the wear ( $\mu\text{m}$ ) related to lubricant film concentration.

Oxidative Stability Analyses were performed on a Koehler K12200 Oxidation Stability Apparatus. The 1% and 2% additivated oil samples (25 g) were oxidized under an oxygen flow (1000 mL/h) at 100 °C for 164 hours in contact with a spiral copper coil (30 cm). At the end of the tests, the oil samples were titrated with a sodium hydroxide solution to measure their acidity index.

### Synthesis of Cardanol Phosphate Esters

Cardanol was isolated from technical CNSL and then hydrogenated, as described in a previous

published method (Lomonaco *et al.*, 2009).

Products 3, 4 and 5 were synthesized (Scheme 1), as follow: to a solution of 10 mmol of cardanol 1 (3004 mg) and 10 mmol of the respective organophosphate chloride (diethyl chlorophosphate for product 3; diphenyl chlorophosphate for product 4; and diethyl chlorothiophosphate for product 5) in 50 mL of chloroform under magnetic stirring, 10 mmol of potassium hydroxide (561 mg) were added. The reaction mixture was heated under reflux (60 °C) for 4 hours. After this period, 30 mL of distilled water was added, and the pH was neutralized with a solution of HCl (5%). The organic material was extracted with ethyl acetate (2 x 30 mL), dried with sodium sulfate (NaSO<sub>4</sub>) and concentrated under reduced pressure.

Product 6 was synthesized (Scheme 1) as described: to a solution of 3040 mg of cardanol 1 (10 mmol) and 460 mg of phosphorus oxychloride (POCl<sub>3</sub>, 3.3 mmol) in 50 mL of chloroform, 10 mmol of potassium hydroxide (561 mg) were added. The reaction mixture was heated under reflux (60 °C) for 4 hours. After this period, 30 mL of distilled water was added, and the pH was neutralized with a solution of HCl (5%). The organic product was extracted with ethyl acetate (2 x 30 mL), dried with sodium sulfate (NaSO<sub>4</sub>) and concentrated under reduced pressure.

The residual oils were purified through column chromatography (silica gel 60) using as eluent mixtures of hexane/ethyl acetate, giving the desired products (3, 4, 5 and 6), which were characterized by GC/MS and <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR.

### *O,O*-diethyl *O*-(3-pentadecylphenyl) phosphate (3)

<sup>1</sup>H NMR: 0.88 (t); 1.26 (m); 1.33 (m, 6H, -P-O-CH<sub>2</sub>-

CH<sub>3</sub>); 1.60 (m, 2H); 2.58 (t, 2H); 4.19 (m, 4H, -P-O-CH<sub>2</sub>-CH<sub>3</sub>); 7.05 (m, 3H); 7.22 (t, 1H) ppm. <sup>13</sup>C NMR: 14.07; 16.01; 22.64; 27.17; 27.20; 28.96; 29.19; 29.36; 29.72; 31.20; 31.77; 35.71; 64.46; 117.04; 119.82; 125.04; 129.75; 144.93; 150.65 ppm. <sup>31</sup>P NMR: -5.1 ppm. GC/MS: *m/z* 440 (M<sup>+</sup>).

### *O,O*-diphenyl *O*-(3-pentadecylphenyl) phosphate (4)

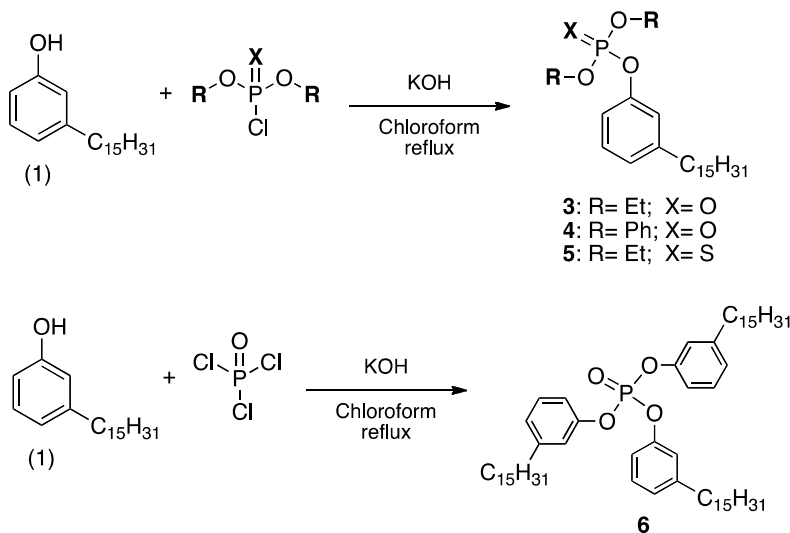
<sup>1</sup>H NMR: 0.90 (t, 3H); 1.58 (m, 2H); 2.61 (t, 2H); 6.88 (m, 2H); 7.03 (s, 1H) 7.20 (m, 11H) ppm. <sup>13</sup>C NMR: 14.02; 22.89; 29.59; 31.31; 33.49; 35.71; 117.09; 120.57; 120.59; 120.77; 126.03; 129.22; 129.93; 130.09; 130.16; 143.39; 150.08; 150.17 ppm. <sup>31</sup>P NMR: -17.6 ppm. GC/MS: *m/z* 536 (M<sup>+</sup>).

### *O,O*-diethyl *O*-(3-pentadecylphenyl) phosphorothioate (5)

<sup>1</sup>H NMR: 0.88 (t, 3H); 1.42 (m, 6H, -P-O-CH<sub>2</sub>-CH<sub>3</sub>); 1.56 (m, 2H); 2.01 (m); 2.60 (t, 2H); 4.24 (m, 4H, -P-O-CH<sub>2</sub>-CH<sub>3</sub>); 7.01 (m, 3H); 7.22 (t, 1H) ppm. <sup>13</sup>C NMR: 14.18; 15.95 (d); 22.74; 25.66; 27.35; 29.10; 29.35; 29.51; 29.71; 29.89; 31.20; 31.89; 35.91; 65.03; 118.09; 120.98; 127.71; 129.40; 144.83; 150.81 ppm. <sup>31</sup>P NMR: 64.7 ppm. GC/MS: *m/z* 456 (M<sup>+</sup>).

### tris(3-pentadecylphenyl) phosphate (6)

<sup>1</sup>H NMR: 0.91 (t, 9H); 1.28; 1.32 (m); 2.57 (t, 6H); 6.68 (m, 6H); 6.83 (d, 3H); 7.15 (t, 3H) ppm. <sup>13</sup>C NMR: 14.28; 22.89; 29.55; 29.72; 29.80; 29.89; 31.46; 32.14; 36.05; 112.71; 111.55; 121.19; 129.57; 145.18; 155.69 ppm. <sup>31</sup>P NMR: -17,5 ppm.



**Scheme 1:** Synthetic scheme for the cardanol derivatives.

## RESULTS AND DISCUSSION

### Oxidative Stability Analyses

In the oxidative stability analysis, the oil samples were heated at 100 °C for 164 hours in an oxygen (O<sub>2</sub>) flow of 1000 mL/h. At the end of this process, the differences between the samples were very evident. Non-additivated oil was completely oxidized, appearing like an opaque black sludge, whereas all the additivated samples maintained some of their initial transparency, the immersed copper coils still visible, as a result of the antioxidant effect promoted by the cardanol derivatives. It can be seen that compound 5 had the best antioxidant activity among the derivatives studied for mineral oil degradation. The sample additivated with this substance maintained its transparency and showed almost no change in its color. Although samples additivated with compounds 3, 4 and 6 presented some change in their color, this effect was greatly minimized by the cardanol antioxidants compared to the pure mineral oil sample. In Figure 3 are shown the mineral oil samples additivated with 2% of the cardanol phosphate esters after the oxidation analysis.

The oxidized samples had their acidity measured in order to evaluate the degree of oxidation by their acidity index, as expressed in Table 1.

The results confirmed what was observed in Figure 3. Compound 5 exhibited the best antioxidant activity among the phosphorylated derivatives; the oil sample additivated with this derivative showed almost no sludge production (Figure 3) and an acidity index of 0.52 mg NaOH/g sample when added at a concentration of 2%. The results obtained for the samples additivated with the other compounds were very similar to each other, varying from 5.46 to 6.20 mg NaOH/g sample of compounds 4 and 3, respectively.

The results obtained for compound 5 showed that the presence of a sulfur atom in the phosphate group has a positive influence on the antioxidant action. According to Günther *et al.* (1997), organic sulphur compounds can act as secondary antioxidants, decomposing peroxides radicals formed during the oxidation process. Recently, Mangolini *et al.* (2009) proposed that, under elevated temperatures, a scission of the P=S bond occurs to give triphenyl phosphite, followed by a thermo-oxidative reaction that leads to oxidation to triphenyl phosphate (Scheme 2).

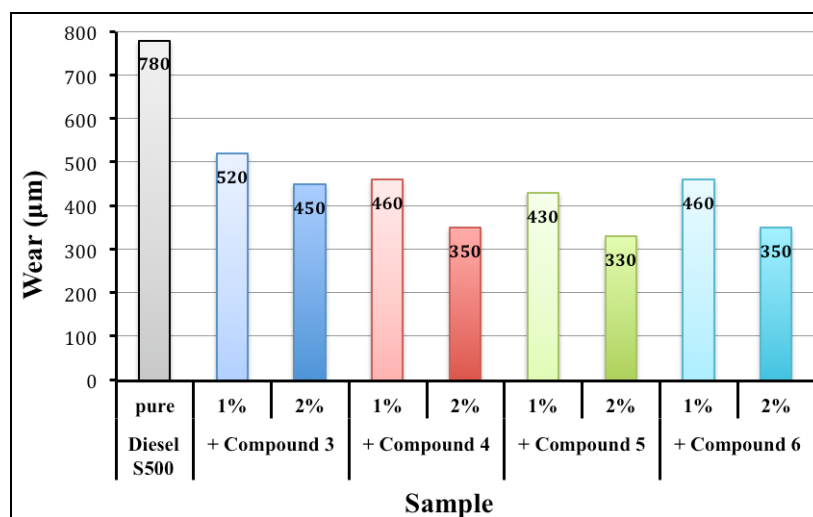
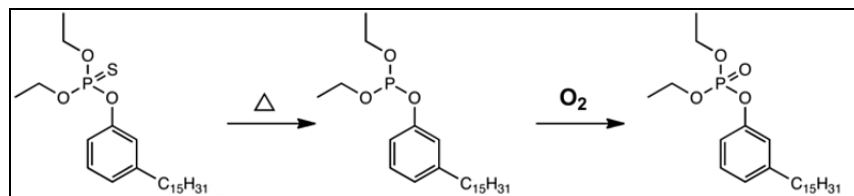


Figure 3: Wear scar values from the HFRR lubricity test.

Table 1: Acidity Index obtained for the samples analyzed.

Oil sample	Acidity Index (mg NaOH/g oil)
Non additivated	8.55
Oil + Compound 3 (1%)	6.20
Oil + Compound 3 (2%)	6.05
Oil + Compound 4 (1%)	5.81
Oil + Compound 4 (2%)	5.46
Oil + Compound 5 (1%)	0.57
Oil + Compound 5 (2%)	0.52
Oil + Compound 6 (1%)	6.14
Oil + Compound 6 (2%)	6.02

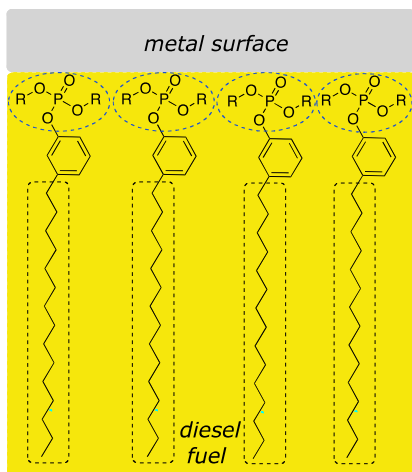


**Scheme 2:** Proposed reactions of compound **5** under elevated temperatures.

### High Frequency Reciprocating Rig (HFRR) Tests

Figure 3 shows the HFRR lubricity test results for Diesel S500. It can be seen that all the additives promoted a great reduction in the wear rates of the metal parts, i.e., increasing the protection between the sliding surfaces of the diesel by diminishing the friction. Compound **5** presented the best lubricating ability, reducing the wear scar from 780 to 330  $\mu\text{m}$  when added at a concentration of 2%. Similar results were obtained for compounds **4** and **6**, which reduced the wear to 350 and 460  $\mu\text{m}$  when added at concentrations of 2% and 1%, respectively.

This is due to the surfactant-like structure of the cardanol derivatives, which permits the interaction with the metal parts through the hydrophilic groups (phosphate ester) and with the diesel fuel through its hydrophobic groups (C15 side chain), thus creating a lubrication film adsorbed onto the rubbing surface of the metal, as shown in Figure 4.



**Figure 4:** Interaction between cardanol derivatives and the metal parts.

### CONCLUSIONS

We report the synthesis and characterization of four phosphorylated esters derived from hydrogenated cardanol, the main component of CNSL. The studies

of their antioxidant activity in mineral lubricant oil through oxidative stability analyses showed good to excellent results, as seen by the lower acidity index values obtained and sludge residues of the additivated samples. Furthermore, the lubricity capacity of these compounds evaluated through High Frequency Reciprocating Rig (HFRR) tests presented a great reduction of the wear scars, confirming their good ability to diminish the friction between the metal parts of diesel motors. Special attention should be given to the thiophosphorylated derivative (**5**), which presented the best results in all analyses. Our results demonstrate that cardanol, a valuable, renewable and low-cost natural material, widely available as a by-product of the Brazilian cashew industry, is a promising building block for the development of antioxidants and wear reduction additives.

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