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Study of Antioxidant Activity of a Phenyl Phosphorylated Compound Derived from Hydrogenated Cardol by Thermogravimetric Analysis

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Authors' contributions

This work was carried out in collaboration between all authors. Authors FJNM, VGPR and MOA designed the study, performed the spectrometric and thermo analysis. Author DL wrote the protocol, and wrote the first draft of the manuscript. Authors JM and SEM managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aims: Use a natural compound derived from cashew nut shell liquid to the production of an additive inhibitor of the oxidation of lubricants oils.
Study Design: This article describes the syntheses, characterization and evaluation of the antioxidant action of a phosphorylated compound derivate from hydrogenated cardol (diphenyl phosphorylated-cardol).
Place and Duration of Study: Department of organic and inorganic chemistry (Universidade Federal do Ceará), between June 2009 and July 2010.
Methodology: Cardol was isolated from hydrogenated cashew nut shell liquid through column chromatography eluted with a stepwise gradient of n-hexane/ethyl acetate. Diphenyl phosphorylated compound was synthesized through of reaction between cardol and diphenyl chloro-phosphate in basic medium. After purification and characterization the performance this compound was evaluated in minerals oils by thermal analyses, monitoring parameters as T(onset), T(endset), T(max) and IPDT, using samples doped in

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1 %.
Results: The cardol was isolated with 10 % of the yield and the diphenyl phosphorylated compound was synthesized with a yield of 61,4 %. The techniques of characterization (GC/MS, FT-IR and NMR) showed that the product was efficiently synthesized with a good degree of purity. The Thermo-gravimetric analysis showed that the addition of the new compound promoted a significant increase in thermal stability of mineral naphthenic oils, which confirms its action in inhibition of oxidative process.
Conclusion: According to the experimental data a new phosphorylated antioxidant derived from hydrogenated cardol was efficiently synthesized and characterized. This compound presented excellent performance as inhibitor of oxidation of mineral oils, become these oils more resistant to thermal degradation process.

Keywords: Cashew nut shell liquid; cardol; dipheyl phosphorylated compound; termo-gravimetric study; antioxidants.

1. INTRODUCTION

Phosphorous compounds are commonly used as pesticides [1], antifungal agents [2], flame retardants [3], antioxidants [4-6], lubricants [7], surfactants [8], enzyme inhibitors [9], lubricity additives [10] and others. Due to this large number of applications many works have attracted attention for the synthesis and characterization of new structures, especially phosphate esters. These compounds are extremely numerous and can be classified into mono, di and tri, according to the number of ester groups present, (Fig. 1a, b and c, respectively) [11].

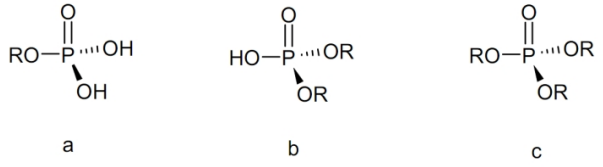

Fig. 1. Phosphate esters: a) mono, b) di, c) tri, replaced

In general, the phosphates are used as antioxidants in several chemical products, as lubricants, fuels, synthetic diesels, biodiesel, and others [12]. These compounds are classified as secondary antioxidants acting through the decomposition of hydro peroxides formed during process of oxidation of an organic material, preventing these species restarting the oxidative process [13]. They are generally used in small proportion in relation to oxidizable substrate reducing or preventing the oxidation of this material.

Recent papers have shown good results regarding the synthesis of phosphorylated antioxidants derived from constituents of cashew nut shell liquid (CNSL), a by-product of the cashew nut processing. In these works, antioxidants derived from hydrogenated cardanol are added to minerals naphthenic oils and its antioxidant action is evaluated based in increase of the thermoxidative stability of these oils [12,14].

Mineral oils are products derived from crude oil by various refining methods. An average oil molecule may contain several different structures, e.g., straight and branched-chain

saturated hydrocarbons, closed-ring saturated hydrocarbons (naphthenes), and unsaturated, aromatic hydrocarbons [4].

Naphthenic oils have a wide variety of applications where they are used as process oils. Differently from paraffinic oils, they are composed basically by closed-ring saturated hydrocarbons; possess lower viscosity, lower flash point, lower pour point and lower resistance to oxidation. Due these properties, naphthenic mineral oils are generally used in process with narrow temperature ranges and where a low pour point is required [4].

The CNSL consists of the alkyl-substituted phenolic compounds (Fig. 2) and can be obtained by extraction in hot oil process, technical CNSL; liquid extraction (solvents); mechanical expulsion from the shells or by vacuum distillation [15]. The variability of composition depends on the extraction method, but in general, the composition of natural CNSL is a mixture of anacardic acid, cardanol, cardol, and 2-methyl-cardol in smaller quantities.

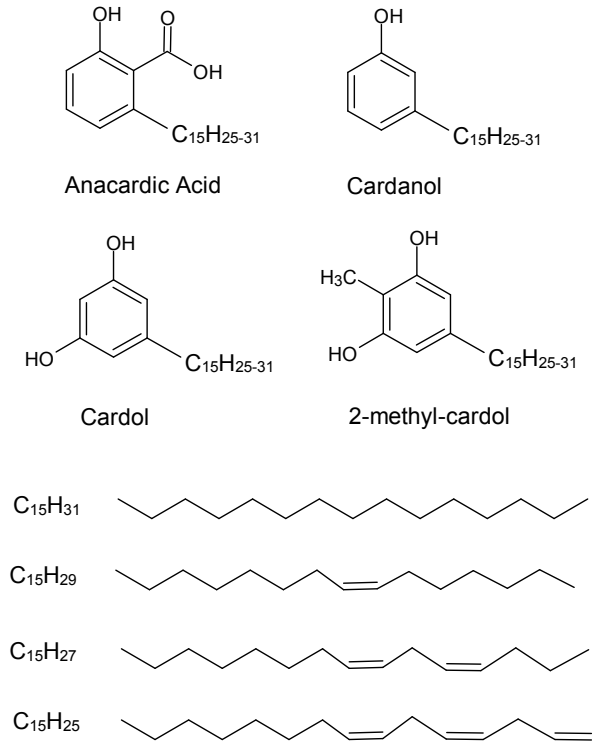

Fig. 2. Cashew nut shell liquid constituents

In relation to cardol, is possible to observe that its structure allows the formation of compounds with two phosphate groups, which may represent an advantage over cardanol derivatives that has a single group. In this context, this article has as main objective the synthesis of a new phosphorylated compound (CD-DPP) derivate from hydrogenated cardol and evaluation of its antioxidant action.

This evaluation will occur through thermo gravimetric analyses of minerals naphthenic oils doped with 1% of this compound. This study will investigate the degradation temperature

initial T(onset), finals T(endset), maximum T(max) and the integral procedure decomposition temperature (IPDT) of each oil sample [16]. Our goal is to continue the studies of the action of antioxidants derived from CNSL, developing ecofriendly products with improved action that can replace additives derived from petroleum.

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

Reagents and solvents were supplied by Aldrich and Vetec Química. Column chromatography was run using silica gel 60, while TLC was conducted on precoated silica gel polyester sheets (Kieselgel 60 F254, 0.20 mm, Merck). Cashew nut shell liquid (CNSL) was supplied by "Amêndoas do Brasil LTDA" and hydrogenated by catalytic hydrogenation method.

The samples obtained were analyzed by GC-MS on a Hewlett–PacModel 5971 using a (5 %-phenyl)-methylpolysiloxane (DB-5) capillary column (30 m x 0.25 mm) with film thickness 0.1 mm; carrier gas helium, flow rate 1 mL/min with split mode. The injector temperature and detector temperature were 250 and 200ºC, respectively.

The mineral naphthenic oil samples (NH10 and NH20) were supplied by PETROBRAS. The samples were evaluated according to ASTM methods (Table 1). The specific gravity analysis was done at 20ºC using DMA 4500 (Anton Paar). The pour point was measured by the automatic apparatus (ISL – CPP 5Gs). Flash point by the Cleveland open cup measurements were carried out using a Koehler apparatus. The kinematic viscosity was measured at 40ºC and 100ºC using an Ostwald viscosimeter (Koehler).

Table 1. Properties of mineral naphthenic oils

Property	Unit	NH 10	NH 20	Method
Specific gravity at 20ºC	kg/m3	0.885	0.894	ASTM D1298
Pour point	ºC	−39	−33	ASTM D97
Flash point	ºC	148	162	ASTM D 93
Kinematic visc. at 40ºC	cSt	10.5	19.9	ASTM D445
Kinematic visc. at 100ºC	cSt	2.9	4.8	
Viscosity index		131	174	ASTM D2270
Total acid number	mgKOH/g	0.010	0.015	ASTM D664

The NMR spectra were recorded on a Bruker Avance DRX-500 (500 MH ^{1}H, 125 MHz for ^{13}C and 202.5 MHz for ^{31}P NMR) using $CDCl_3$ as solvent phosphorylated cardol derivatives and $(CD_3)_2CO$ for cardol.

The infrared measurements were performed using a Perkin Elmer 2000 spectrophotometer in the 400 to 4000 cm^{-1} range. The samples were previously dried and grounded to powder and pressed (10 µg of sample to 100 mg of KBr) in disk format for measurements.

2.1 Isolation of Cardol

Cardol (2.1g) was isolated from Hydrogenated CNSL (20.0g) through column chromatography eluted with a stepwise gradient of n-hexane/ethyl acetate (from 9:1 to 7:3 by volume). The fractions obtained in the column chromatography were analyzed through thin layer chromatography, reunited according their retention factors and submitted to

evaporation under reduced pressure. The product obtained was characterized by FT-IR, GC/MS, 1H and 13C NMR. The data obtained in this analysis are summarized below:

Hydrogenated cardol: ^{1}H NMR (δ): 0,88 (t, 3H); 1,28 (m); 1,56 (m, 2H); 2,43 (t, 2H); 6,16 (s, 2H), 6,17 (s, 1H). ^{13}C NMR (δ): 14,46; 23,42; 29,78; 29,94; 30,09; 30,16; 30,25; 30,36; 30,46; 30,50; 32,16; 32,72; 36,70; 101,01; 107,74; 145,86; 159,35. GC/MS: m/z = 320 (M+). IR = 698; 995; 1157; 1465; 1506 e 1595; 2910; 2848; 3421.

2.2 Synthesis of Diphenyl Phosphorylated Compound

Hydrogenated cardol (1 mmol), diphenyl chloro-phosphate (2 mmol) and potassium carbonate (2 mmol) was magnetically mixed in a reaction flask containing 100 mL of acetone. The reaction was kept under reflux (56ºC) for a period of 10 hours (monitored by thin-layer chromatography). After the reaction time, the removal of the solvent left an oily residue, which was then purified by column chromatography on silica gel (hexane/ethyl acetate 7:3) The fractions obtained were analyzed through thin layer chromatography, reunited according their retention factors and submitted to evaporation under reduced pressure. The product obtained (Fig. 3) a viscous yellow with a yield of 61, 4 % was characterized by FT-IR, GC/MS, 1H and 13C NMR.

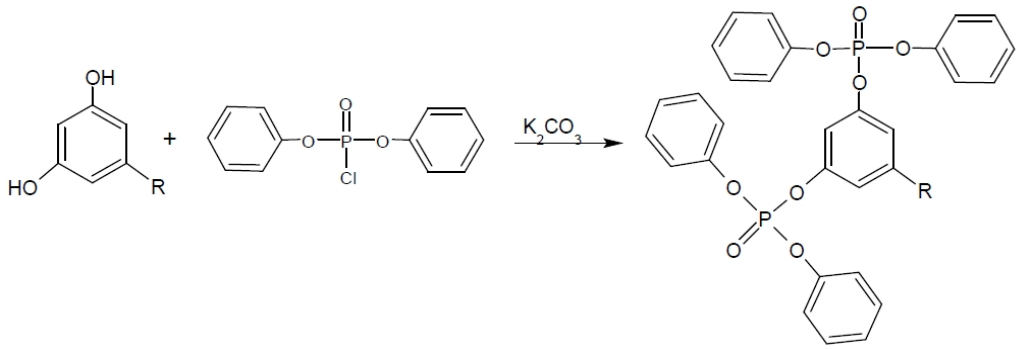

Fig. 3. Syntheses of diphenylphorylated cardol (CD/DPP)

The dada obtained on the characterization of diphenyl-phosphorylated compound (CD-DPP) are summarized below:

Compound (CD-DPP) - IR v_{max} (KBr) cm^{-1}: 2929, 2837, 1600, 1486, 1307, 1183, 863, 766; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.353-7.164 (20H, m), 7.113 (1H, sl, H-2), 7.007 (2H, sl, H-4 and H-6), 2.579 (2H, t, *J*=12 Hz, H-1'), 1.574 (2H, m, H-2'), 1.320 (24H, sl, H-4' to H-14'), 0.931 (3H, t, *J*=10 Hz, H-15'); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 150.75-150.20 (C-1, C-3 and C-1"), 146.61 (C-5), 129.77-129.64 (C-3" and C-5"), 125.60 (C-4"), 120.00-119.93 (C-2" and C-6"), 117.37 (C-6 and C-4), 109.83 (C-2), 35.54 (C-1'), 31.83 (C-2'), 30.69 (C-13'), 29.609-29.01 (C-3' to C-12'), 22.65 (C-14'), 14.03 (C-15'); ^{31}P NMR ($CDCl_3$, 202.5 MHz) δ: 18.0 ($O=P(OR)_3$); EM-MS *m/z* (rel. int.): 784(23), 602(26), 588(100), 534(10), 379(14), 251(18), 181(12), 77(20), 43(35).

2.3 Thermal Analyses

Thermo gravimetric (TG) measurements were carried out using a Mettler-Toledo TGA/SDTA 851e analyzer, at a scanning rate of 10ºC/min. Samples of approximately 5 mg were heated from 25 to 500ºC. The measurements were carried out at oxidative (synthetic air) atmosphere (50 mL/min).

3. RESULTS AND DISCUSSION

3.1 Characterization of the Diphenyl Phosphorylated Cardol (CD-DPP)

The diphenyl phosphorylated cardol (CD-DPP) was obtained using diphenyl chloro-phosphate as esterified agent. The IR spectrum of CD-DPP (Fig. 4) exhibited no characteristic absorption band of hydroxyl group, indicating the incorporation of two groups of diphenyl phosphate in the product reaction. This spectrum also showed the absorption band to the diphenyl phosphate group at 1307 cm^{-1} (P=O), 1163 and 860 cm^{-1} (C-O-P).

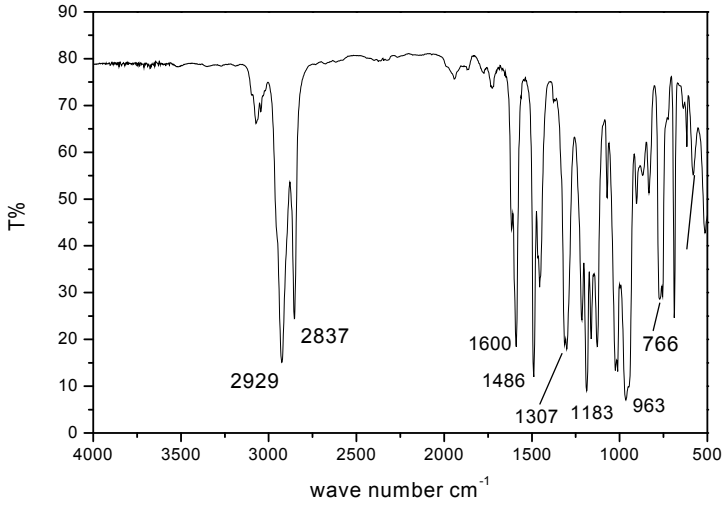

Fig. 4. Infrared spectrum obtained for diphenyl phosphorylated cardol

In the ^{1}H NMR spectrum (Fig. 5) was observed the characteristic signals of the alkyl chain and the increase of signals of aromatic protons. It was observed the signals of cardol aromatic protons at δ 6.947 (2H) and δ7.054 (1H), and the signals of diphenyl group of phosphate moiety 7.127 (8H) and δ 7.219 (12H).

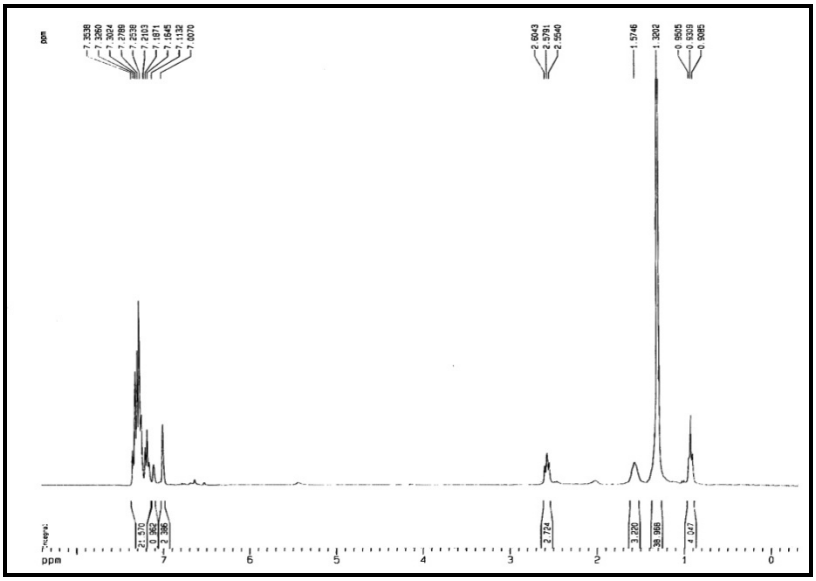

Fig. 5. 1H NMR obtained for for diphenyl phosphorylated cardol

These data were corroborated by the 13C NMR (Fig. 6), which showed additional signals at δ 150.30 (C); δ 129.76 (CH) and δ 120.00 (CH). The incorporation of phosphate group on CD-DPP was confirmed through the signal at δ 18 in the ^{31}P NMR spectrum. The total diphenyl phosphate ester of cardol was confirmed by the mass spectrum of CD/DPP, which showed the molecular ion peak at m/z 784 daltons. This value was in agreement with the molecular formula $C_{45}H_{54}O_8P_2$.

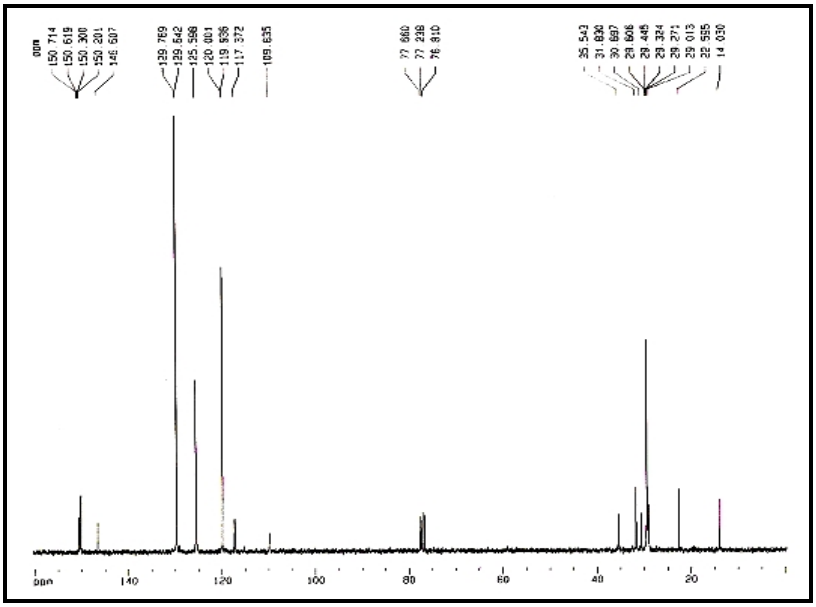

Fig. 6. 13C NMR obtained for for diphenyl phosphorylated cardol

3.2 Thermogravimetric Analysis

Fig. 7 (a) and (b) shows the thermal degradation profile of the samples of mineral oils (NH10 and NH20) absent of additive (solid line) and doped in 1% with the CD-DPP (dashed line). The comparison between the curves showed a shift for higher values of temperature, due to the presence of antioxidant. In other words, samples doped with CD-DPP showed a higher thermal stability than the non-doped samples. These results can be confirmed by data presented in Table 2. It can be seen that all the thermo gravimetric parameters relative to doped samples are superior the not doped samples showing that there was an significant increases in thermal stability these oils due the presence of phosphorylated compound.

The results also showed that the NH 20 oil presented highest resistance to thermo-oxidative process than the NH 10 oil. According to Santos et al. this difference can be attributed to different chemical composition of each oil [17]. In this sense, we can say that the oil NH 20 is composed of hydrocarbons more thermally resistant. The results observed in Table 1 also collaborate with this statement, in this table we can verify that all the rheological properties of the NH 20 oil exhibit higher values than oil NH10, revealing the presence of hydrocarbons with higher molecular weight and consequently thermally more stable.

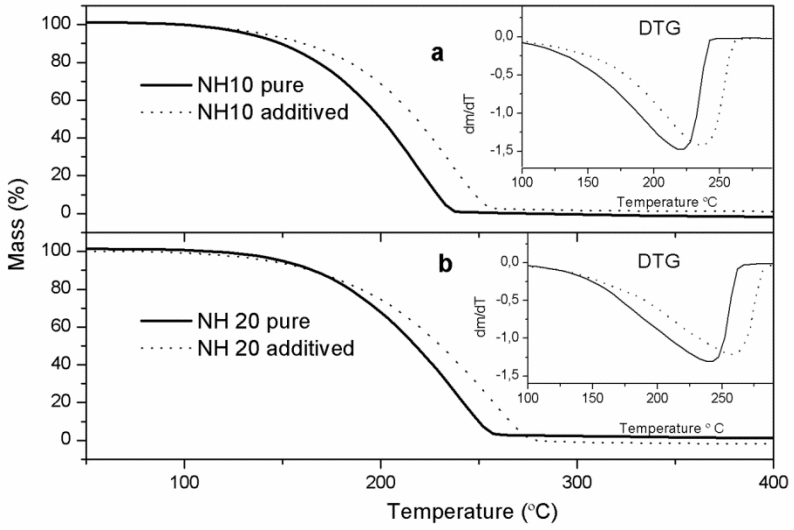

Fig. 7. Thermal gravimetric profile of minerals naphthenic oils pure (—) and doped with CD-DPP (----)

The Table 2 summarizes the values of T(onset), T(endset) and T(max) observed in the thermo gravimetric analysis of the two oils with and without additive. The results confirm the action of the new compound showing that the CD-DPP was effective in inhibition of the oxidation process of these oils. For the oil NH10 the addition of CD-DPP promoted an increase of 16ºC in the T(onset) value and an increase of 18ºC in the T(endset) and T(max) values. For the oil NH20 was observed an increase of 11, 17 and 16º C in the T(onset), T(endset) and T(max) values, respectively.

Table 2. Thermo gravimetric parameters

Sample	Degradation temperature (ºC)			
	T(onset)	T(endset)	T(max)	IPDT
NH 10 (pure)	168	236	218	191,3
NH 10 (additive)	184	254	236	213,9
NH 20 (pure)	181	256	241	210,2
NH 20 (additive)	192	273	257	226,5

According to Kriston et al. [13] phosphorylated compounds act as secondary antioxidants, eliminating hydroperoxides formed in the propagation stages of oxidation and thus making the oils more resistant to the thermo-oxidative process [13]. The good performance of other phosphorylated compounds derived from hydrogenated cardanol was already evaluated by our group in other works [18-19]. Analyzing these results it was observed that the CD-DPP showed antioxidant activity superior to phosphorylated compounds derivate of the hydrogenated cardanol, revealing that compounds with a double phosphate groups are more efficient antioxidants.

Table 1 also shows the values of the integral procedure decomposition temperature (IPDT) of the pure oils and additive with the CD/DPP. According to Chiang et al. the IPDT can be calculated from the following equations [20]:

$$\text{IPDT (ºC)} = A^*K^*(Tf - Ti) + Ti$$
$$A^* = (S1 + S2)/(S1 + S2 + S3)$$
$$K^* = (S1 + S2)/S1$$

Where A^* is the area ratio of total experimental curve defined by the total TGA thermogram, Ti the initial experimental temperature, Tf the final the initial experimental temperature. Fig. 8 shows a representation of $S1$, $S2$ and $S3$ for calculating A^* and K^*.

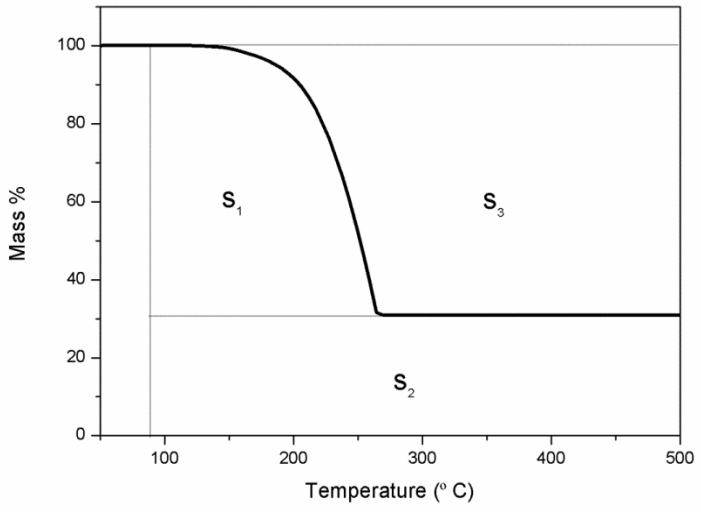

Fig. 8. Schematic representation of S1, S2 and S3 for A* and K*

According to the data presented in Table 2 is possible to claim that the highest values of IPDT are related to oil samples of higher thermal stability. Thus this parameter can be efficiently used to evaluate the performance of CD/DPP. The Table 2 shows that the oils NH10 and NH20 present an increase in the IPDT values of 22,6 and 16,3ºC, respectively. These results certify the performance of CD-DPP and confirm the data obtained in the analysis of the other thermo gravimetric parameters: T(onset), T(endset) and T(max).

4. CONCLUSION

According to the experimental data a new phosphorylated antioxidant derived from hydrogenated cardol was efficiently synthesized and characterized. A critical analysis of thermo gravimetric parameters revealed an increase in thermal stability of the oils due to inhibition of the oxidative process, which in turn is caused by the presence of the phosphorylated compound. Therefore our results showed that the CD-DPP can be efficiently applied as retardant of the oxidative process this particular type of substrate. In this sense we can say that this new compound derived from natural and renewable raw can be applied directly in the productive sectors by improving the performance of lubricants and helping to reduce excessive consumption of petroleum derivatives.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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