



Phosphorus cardanol: chemical characterization and thermal stability

Fósforo cardanol: caracterização química e estabilidade térmica

M. A. S. Rios^{1*}, F. S. C. L. Batista², F. A. M. Sales³, S. E. Mazzetto⁴

^aGrupo de Inovações Tecnológicas e Especialidades Químicas, Universidade Federal do Ceará,

¹Departamento de Engenharia Mecânica/Grupo de Inovações Tecnológicas e Especialidades Químicas/Centro de Tecnologia, Universidade Federal do Ceará, 60.440-554, Fortaleza-Ceará, Brasil

²Departamento de Química/ Grupo de Inovações Tecnológicas e Especialidades Químicas/Centro de Ciências, Universidade Federal do Piauí, 64.049-550, Teresina-Piauí, Brasil

³Instituto Federal do Ceará, 63.503-790, Iguatu – Ceará, Brasil

⁴Departamento de Química Orgânica e Inorgânica/ Laboratório de Produtos e Tecnologia em Processos LPT/Centro de Ciências, Universidade Federal do Piauí, 60.455-760, Fortaleza-Ceará, Brasil

*alexandrarios@ufc.br

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Devido à grande utilização do cardanol para o desenvolvimento de novos aditivos, o presente trabalho tem como objetivos apresentar a caracterização química do fósforo cardanol, a qual foi verificada utilizando-se FTIR e técnicas termoanalíticas (TG/DSC/DTA) e, a avaliação antioxidante do composto em um óleo lubrificante de base naftênica. Neste trabalho, os autores incluíram também o estudo térmico do fósforo cardanol por aquecimento em estufa, com monitoramento das alterações em FTIR. De acordo com os resultados, o fósforo cardanol apresentou boa estabilidade térmica quando comparado a outros ésteres de fosfato de mesma classe e, não apresentou alterações antes e após aquecimento a 120 ° C, sob atmosfera de ar. Desta forma, o composto de fósforo obtido a partir do cardanol apresenta potencial de aplicação, como aditivo, em óleos lubrificantes e produtos petroquímicos do mesmo segmento.

Palavras-chave: LCC, oxidação, estabilidade térmica

Due to the wide use of the cardanol to develop new additives, this study presents the chemical characterization of phosphorus cardanol using FTIR and Thermoanalytical techniques (TG / DSC / DTA), and the evaluation of the antioxidant potentiality of compound when added to a lubricating oil. In this paper, the authors also included the thermal study of phosphorus cardanol by heating in an oven, monitoring changes in FTIR. According to results, the phosphorus cardanol showed good thermal stability when compared with other compounds of the same class "phosphate esters" and showed no changes before and after heating at 120 ° C, under air atmosphere. Thus, the phosphorus compound derived from cardanol has potential application as additive for lubricating oils and petrochemicals of the same segment.

Keywords: CNSL, oxidation, thermal stability

1. INTRODUCTION

Cashew Nut Shell Liquid (CNSL) and its derivatives are an important group of molecules, which play a fundamental role in organic chemistry [1-4]. They have potent antioxidant activity in several industrial areas such as: fuels and biofuels; tribology; polymers [5,6]; rubbers [7-10] and can be used in the biological industry too as antibacterial, anti-fungal and anti-tumor [11,12].

Due to chemical versatility of these compounds and increasing concern with the environmental legislation on the maintenance of greenness in industrial processes led us to develop a method using a reagent that is less hazardous and non-toxic to the environment [13,14]. In this context, in the last years, the CNSL has gained importance in the development of sustainable chemistry [15] as a raw material for new primary and secondary antioxidants, flame-retardants, porphyrins, composites and biopolymers [16-19].

CNSL is constituted of anacardic acid, cardanol and cardols, which are *alkyl*-substituted phenolic compounds, Figure 1 [13,20]. In accordance with the literature, the quantity and quality

of constituents vary with the method of extraction. The CNSL extracted from the shells by mechanical expulsion contain a mixture of anacardic acid, cardanol and cardols in smaller quantities and the CNSL obtained by the hot oil process is entitled "technical CNSL", due to the decarboxylation of the anacardic acid and subsequent formation of cardanol [21-23].

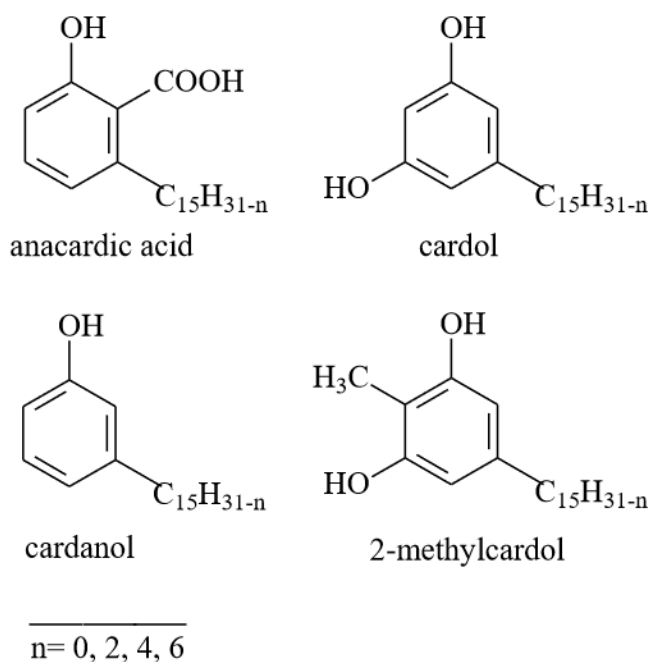


Figure 1: Chemical structures of CNSL constituents.

Therefore, considering the great importance of this group of molecules and their potentiality for the development of new eco-friendly compounds, the present study shows the investigation of the thermal and oxidative stability, and antioxidant effectiveness of a phosphorus compound derived from the main constituent of technical CNSL: the cardanol. This constituent after catalytic hydrogenation (3-*n*-pentadecylphenol or hydrogenated cardanol) was used as raw material of this investigation. For evaluation of the thermal properties, the authors used thermal analysis (TG-DTG, DSC and DTA) in different atmospheres [14]. Lubricant oil (naphthenic lube base oil) was used as organic substrate to study the antioxidant activity of the obtained phosphorus [24-26]. To study the antioxidant activity of the phosphorus compounds, the researchers used a lubricant oil as organic substrate (naphthenic lube base oil).

2. MATERIAL AND METHODS

Material

The hydrogenated cardanol (HC) was obtained by catalytic hydrogenation method [27,28] and was purified by column chromatography (silica gel) employing hexane as eluent [27, 29]. After purified, the HC was alkylated by Friedel Crafts mechanism using tert-butyl chloride in the presence of zinc chloride (Lewis acid), obtaining hydrogenated alkylated cardanol.

The hydrogenated alkylated cardanol was phosphorated by nucleophilic substitution (S_N2), using sodium hydroxide and diethyl chlorophosphate, generating an alkyl phosphate. The syntheses and chemical characterizations of the hydrogenated alkylated cardanol and their derivatives were described in the previous work of our group [13, 27, 28]. Petrobras (Brazilian Oil Company, Brazil) supplied the lubricant oil with no further distillation procedure and without additive and the Aldrich Chemical Company supplied the reagents and solvents (analytical grade).

Physical measurements

NMR (^1H , ^{13}C and ^{31}P) spectra were recorded by AVANCE DRX 500 BRUKER spectrometer, at a frequency of 500 MHz under the following conditions: solvent, CDCl_3 ; tetramethylsilane (TMS) as an internal standard for ^1H and ^{13}C , and phosphoric acid (H_3PO_4) for ^{31}P .

FTIR spectra were obtained by use of a FTIR spectrophotometer Shimadzu, model 8300.

The TG-DTG curves were obtained using a SHIMADZU TGA-50H, in synthetic air and nitrogen atmospheres, with a flow of $50 \text{ mL}\cdot\text{min}^{-1}$, sample mass of approximately 10 mg, heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and temperature range of 25 – 800 $^\circ\text{C}$. The DSC curves were carried out using a DIFERENTIAL SCANNING CALORIMETER 2920 TA instruments, in nitrogen atmosphere, with a flow of $50 \text{ mL}\cdot\text{min}^{-1}$, sample mass of approximately 10 mg, heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, and temperature range of 25 – 500 $^\circ\text{C}$. DTA curves were obtained using a SHIMADZU DTA-50H, in synthetic air atmosphere, with a flow of $50 \text{ mL}\cdot\text{min}^{-1}$, sample mass of approximately 10 mg, heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and temperature range of 25 – 800 $^\circ\text{C}$. Extrapolated scale (1 g) decomposition was carried out in a stove at a fixed temperature of 120 $^\circ\text{C}$ ($\pm 2 \text{ }^\circ\text{C}$) under air atmosphere; after five hours, a sample was removed for analysis by infrared spectroscopy.

Methods

Synthesis of hydrogenated alkylated cardanol

Hydrogenated alkylated cardanol was synthesized by the alkylation of hydrogenated cardanol (HC) (3.3 mmol) with *tert*-butyl chloride (3.3 mmol) in the presence of Lewis acid (zinc chloride), according to the methodology presented in previous work [13, 29, 30].

Synthesis of phosphorus cardanol

The phosphorus cardanol was synthesized by nucleophilic substitution ($\text{S}_\text{N}2$). The stoichiometry ratio of the reaction system was of 1.0 mol of HC: 1.0 mol of sodium hydroxide: 1.0 mol of diethyl chlorophosphate, respectively. The reagents were dissolved in chloroform (30 mL), and the mixture was heated under the reflux system with constant agitation at 60 $^\circ\text{C}$ ($\pm 1 \text{ }^\circ\text{C}$) for two hours and thirty minutes. After the reaction time, was obtained a viscous yellow oil [27]. After synthesis and purification, the alkyl phosphate was characterized using NMR ^{13}C and ^{31}P , TG-DTG and DSC [4, 13, 27, 30].

Characterization of phosphorus cardanol - NMR (^1H , ^{13}C and ^{31}P)

Physical state: viscous yellow oil. The analysis by ^1H NMR, showed the following, (500 MHz, CDCl_3): 0.87 (t, 3H, $-\text{CH}_2-(\text{CH}_2)_{12}-\text{CH}_3$); 1.29 (t, 6H, $(-\text{O}-\text{CH}_2\text{CH}_3)_2$); 1.32 (m, 24H, $-(\text{CH}_2)_n-$); 1.42 (s, 9H, $-(\text{CH}_3)_3$); 2.55 (t, 2H, $-\text{CH}_2-\text{Ar}$); 4.23 (q, 4H, $(-\text{O}-\text{CH}_2\text{CH}_3)_2$); 6.87 (d, 1H, Ar-H); 7.22 (d, 1H, Ar-H); 7.29 (s, 1H, Ar-H).

$^{13}\text{C}\{^1\text{H}\}$ NMR, showed the following, (500 MHz, CDCl_3): 14.16 (1C, $-\text{CH}_2-(\text{CH}_2)_{12}-\text{CH}_3$); 16.1 (2C, $(-\text{O}-\text{CH}_2\text{CH}_3)_2$); 34.4 (3C, $-(\text{CH}_3)_3$); 52.9 (1C, $-\text{C}(\text{CH}_3)_3$); 64.3 (2C, $(-\text{O}-\text{CH}_2\text{CH}_3)_2$); 119.2 (1C, Ar-C3), 124.1 (1C, Ar-C4), 127.1 (1C, Ar-C6), 136.5 (1C, Ar-C5), 142.3 (1C, Ar-C2), 150.0 (1C, Ar-C1), in accordance with the literature data (Rios (2008), Silverstein et al. (2005)). $^{31}\text{P}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3): -5.570 (s, 1P, $\text{O}=\text{P}(\text{OR})_3$), Figure 2, in accordance with the literature data [27,28,30,31].

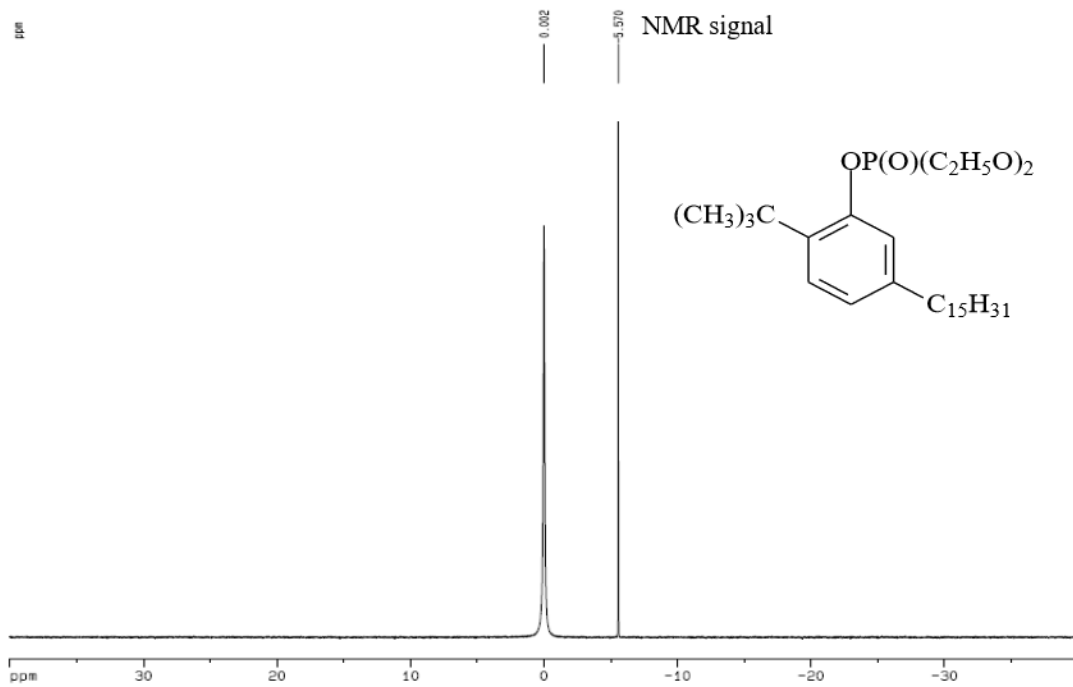
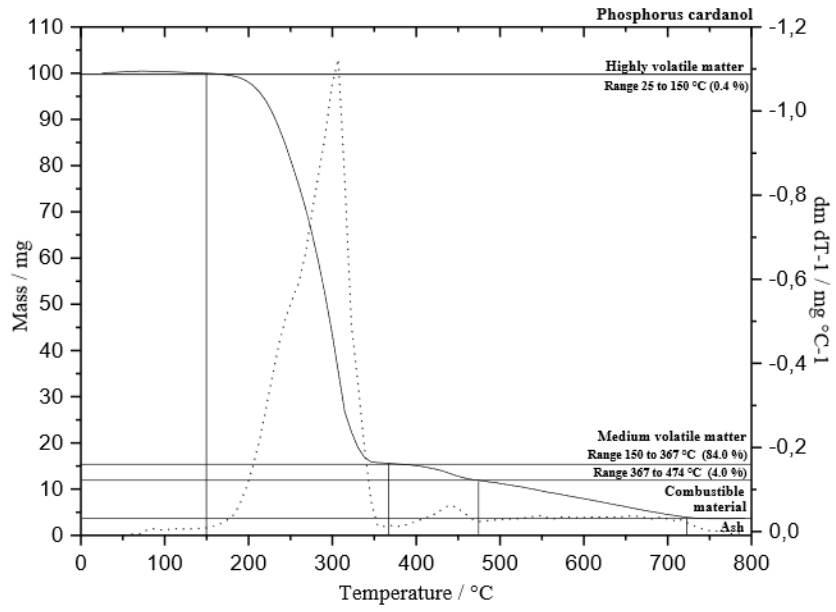


Figure 2: ^{31}P $\{^1\text{H}\}$ NMR (500 MHz, CDCl_3), phosphorus cardanol.

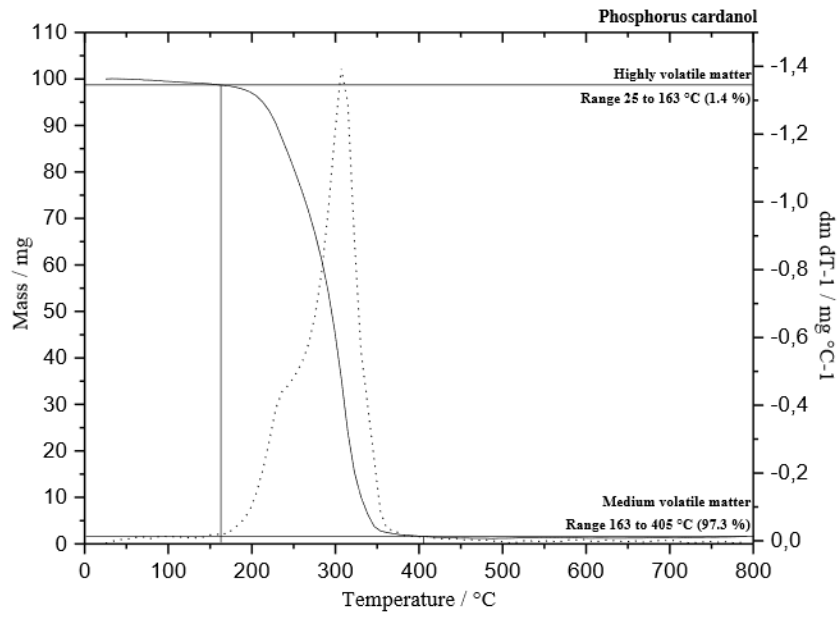
3. RESULTS AND DISCUSSION

Thermal and oxidative analyses of phosphorus cardanol

The thermo-oxidative analyses of the phosphorus cardanol were verified with basis of the results of thermogravimetry and differential scanning calorimetry, which gave details concerning thermal behavior of the sample in the presence of different atmospheres. Figures 3 (a) and (b) show the TG-DTG curves, these curves showed the amount of highly volatile matter, medium volatile matter, combustible material and the residual mass remaining after the heating [32]. In this procedure was used a constant rate of $10.0\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Table 1 gives details of the thermal and oxidative behavior based on the start temperature, final temperature, loss of mass and residual mass remaining after the heating (ash or nonvolatile matter) [33-36].



(a)



(b)

Figure 3: (a) TG-DTG curves of phosphorus cardanol, air atmosphere and (b) TG-DTG curves of phosphorus cardanol, nitrogen atmosphere.

Table 1: Thermal and oxidative data of phosphorus cardanol.

Sample	Atmosphere	Component	Start Temperature/°C	Final Temperature/°C	Mass/%
Phosphorus cardanol	Air	Highly volatile	25	150	0.4
		Medium volatile	150	367	84.0
			367	474	4.0
		Combustible	474	723	8.2
	Ash	723	800	3.4	
	Nitrogen	Highly volatile	25	163	1.4
		Medium volatile	163	405	97.3
Nonvolatile		405	800	1.3	

According to results, the phosphorus cardanol showed a thermal behavior compatible with commercial phosphorus compounds, for example triaryl phosphate and diphenyl phosphate, which present mass losses starting at 150 °C [37]. The stable behavior that phosphorus compounds show can be attributed to the high stability of the P-O-C bond [9, 38]. Therefore, the obtained results suggest the possibility of application of these compounds as antioxidants for lubricant oils, once the degradation of these petrochemical products, in general, starts at 91 °C [4]. As the phosphate esters find use in a variety of commercial applications (lubricants, hydraulic fluids, polymers and others), and some of these systems may be contaminated by solids and/or metals, water, engine oils, solvents and oxygen; it is very important know their thermal behaviors, once that degradation can be a limiting factor of the application of these phosphorus compounds [39-42].

Based on the evidences reported in the literature, four mechanisms can contribute to the degradation of alkyl and aryl phosphate esters, depending of the environmental conditions to which the compound is exposed [37, 40]. In the case of phosphate esters, all decomposition pathways produce 'strong' acids (phosphoric acid derivatives) as the main degradation product, normally as result of hydrolysis and oxidation (see Figure 5). In lubrication systems, this step is followed by reaction of the acid with the metals components to form metal soaps that cause an increase of oxidation of the lubricant, more acid and higher levels of metal soaps [40, 41, 42]. Therefore, the information on thermal behavior of phosphate esters has significant practical importance. Data of this type can be used for assessment of product life, stability, and quality control, and for design and synthesis of phosphate esters to meet new or existing requirements [41].

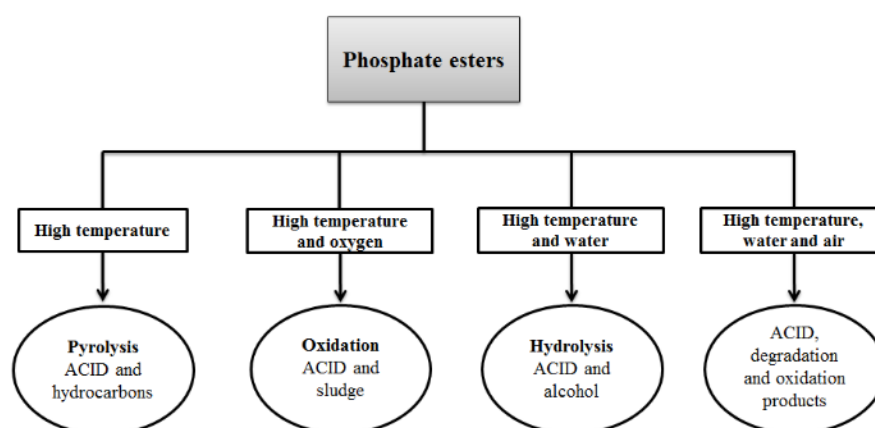


Figure 5: Some possible decomposition pathways for phosphate esters (Adapted from Exxon Technical Bulletin).

Differential scanning calorimetry (DSC) was used to study the thermal properties of the phosphorus cardanol, see Figure 6. In this procedure was used a constant rate of $10.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. DSC curve showed two endothermic peaks probably due to the volatility/thermal degradation of phosphorus compound. The curve exhibited the first onset temperature at $311\text{ }^{\circ}\text{C}$, reflecting the good thermal stability of the sample. The other step, probably, is involved with thermal degradation process of the phosphorus cardanol [29, 41].

In this work, the authors included the thermal study of the phosphorus cardanol using the heating on a stove. The changes were monitored by FTIR. The infrared spectra of the organophosphate before and after heating in stove are displayed in Figure 7. The spectra contain C-O absorption at $1273/\text{cm}^{-1}$, P-O-CH₂-CH₃ absorption at $1158/\text{cm}^{-1}$, (RO)₃P=O absorption at $1027/\text{cm}^{-1}$, P-O-C₆H₅ absorption at $982/\text{cm}^{-1}$ and P-O-CH₂-CH₃ absorption at $823/\text{cm}^{-1}$. According to results, it is clear from the infrared spectra that, no changes were observed before and after heating in stove at $120\text{ }^{\circ}\text{C}$ ($\pm 2\text{ }^{\circ}\text{C}$), under air atmosphere. Therefore, degradation products, if any, are present in small amounts under this condition. This result is in accordance with literature, once that some authors related that, the thermal degradation of phosphate esters only becomes significant at very high temperatures (above $150\text{ }^{\circ}\text{C}$) [29,38,40-42].

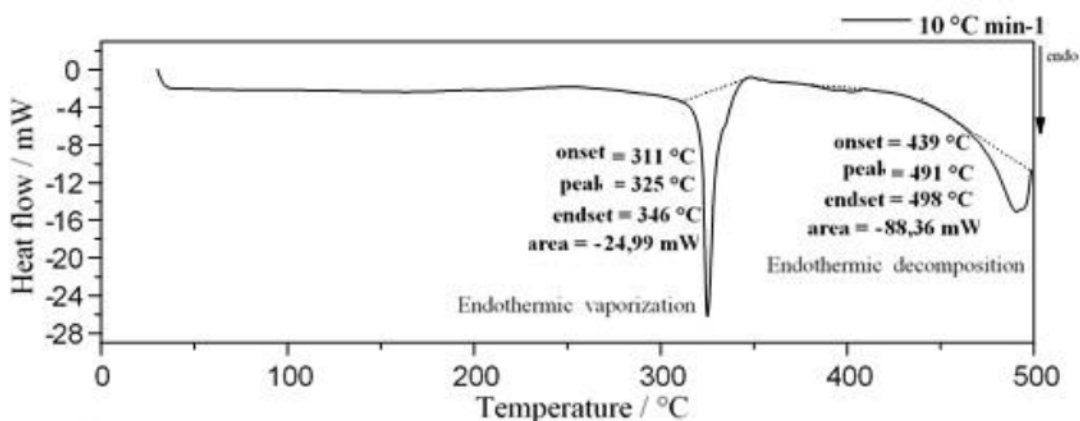


Figure 6: DSC curves of phosphorus cardanol, nitrogen atmosphere.

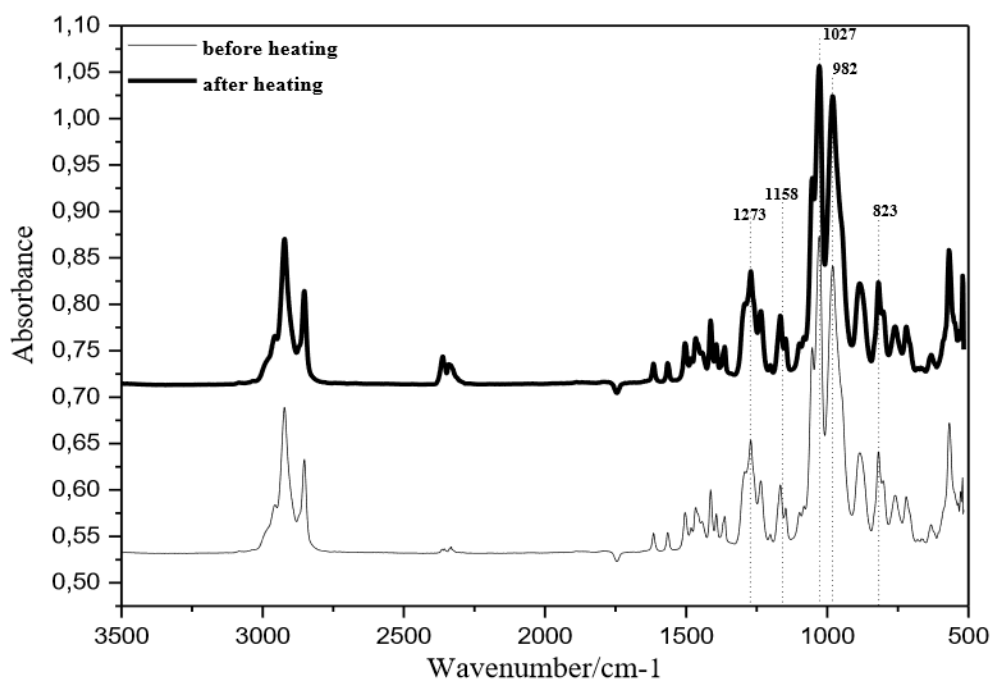


Figure 7 - FTIR of phosphorus cardanol after and before heating.

Antioxidant effectiveness of phosphorus cardanol

For evaluation of antioxidant, potential of the phosphorus cardanol the Differential Thermal Analysis (DTA) was used (see Figure 8). This technique permits the prediction of the Initial Decomposition Temperature – IDT (It is reported as the temperature of a sudden increase in the rate of oxidation), which precedes the main oxidation process. The existence of the reactions occurring during the IDT is not detected by the experimental technique used so that seemingly no reaction takes place. In fact, IDT is a preparatory stage in which the entities needed for the full development of auto-oxidation are formed. The high IDT is considered a relative measure of the stability of materials [39].

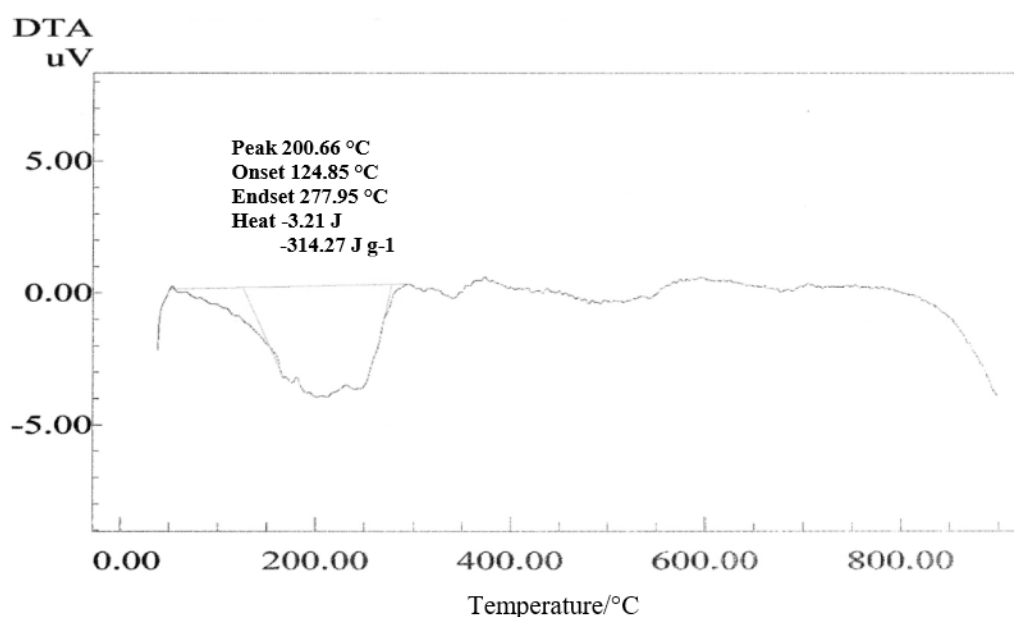


Figure 8: DTA curve of naphthenic lube base oil + 1% phosphorus cardanol, air atmosphere.

The parameters obtained by DTA measurements are given in Table 2. According to results, antioxidant effectiveness of phosphorus cardanol was verified by the difference between initial decomposition temperature (IDT) for lubricant oil (91.28 °C) and the sample: lubricant oil + 1.0% phosphorus cardanol (124.85 °C). Table 2 also shows the decrease of energy involved in the oxidation process of the lubricant oil ($\Delta H / J.g^{-1}$), in the presence of the phosphorus cardanol [29, 36]. DTA has been used to study of oxidation processes because, endothermic and exothermic peaks observed in this technique, in inert and oxidative atmosphere, gives additional information about the degradation process.

Table 2: DTA measurements describing antioxidant effectiveness of phosphorus cardanol.

Sample	IDT ^a /°C	T _{max} ^b /°C	$\Delta H / J g^{-1}$ ^c
	Air	Air	
Lubricant oil	91.28	225.75	-952.80
Lubricant oil + 1,0 % phosphorus cardanol	124.85	220.66	-314.27

^a Initial Decomposition Temperature

^b Temperature of maximum degradation rate

^c Energy involved in oxidation process

4. CONCLUSION

The phosphorus compound derived from hydrogenated cardanol was characterized using spectroscopy and thermal analyses. The phosphorus cardanol displayed a good thermal stability, mainly when compared with to the commercial products of the same class. Hence, according to the results, the organophosphate derived from biomass (CNSL) comes as a promising eco-friendly antioxidant, for the petrochemical industry, being in consonance with green chemistry.

5. ACKNOWLEDGEMENTS

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