



Thermal Stability of 3-pentadecylphenol Derivatives

Pereira¹, F. M. M., Gomes¹, A. M. M., Ricardo¹, N. M. P. S.

¹Department of Organic and Inorganic Chemistry, UFC,
PO. Box 11200, Fortaleza, Brasil

Abstract: Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were used to evaluate the thermal stability of 3-pentadecylphenol (hydrogenated cardanol (3-PDP)) and its derivatives (alkylated 3-PDP; alkylated and nitro 3-PDP) under O₂ and N₂ atmosphere. The results were compared to the ones obtained with the antioxidant BHT, largely used in fuels. The alkylated and nitro derivatives (3-PDP-NIT) showed higher thermal stability, which can be useful in high temperatures applications, as lubricating and combustible oils.

Keywords: antioxidant, cardanol, 3-pentadecylphenol, gasoline.

Introduction

Cardanol is a mixture of 3-alkylphenols, which has an aliphatic chain of 15 carbon atoms in the meta position to the OH group on the aromatic ring (1). It is obtained by the distillation of cashew nut shell liquid (CNSL) *in vacuo*. It is mainly produced after decarboxylation of anacardic acid, during heat treatment of cashew nut at higher temperatures (2). Because its phenolic character and long chain alkyl linked to the nucleus benzene, whose degree of unsaturation varies, cardanol possesses many applications mainly in the plastic, synthetic fiber, fuel, lubricant and food industries (1). It could be a natural alternative of phenolic antioxidant used in the petrochemical industry (3). The phenols and aromatic sterically hindered amines are the largest and main class of well-known antioxidants. The steric hindrance is produced by substitution in 2 and 6 positions for tertiary alkyl groups (the most common substituent is the tert-butyl group) (4). Kajiyama and Ohkatsu (5), stated that phenolic antioxidants are one of the most important additive to scavenges peroxy radicals and to impede or to delay the auto-oxidation of fuels, mainly if it has a substituent para position. Another advantage of the polynuclear phenols or types with high molecular weight substituents in para position, is the reduction of the volatility due to the high molecular weight, which turns these products suitable for high temperatures applications (6). Dawson and Wasserman (7) and Wasserman et al. (8) stated that para nitro and amino cardanol or 3-PDP derivatives are very efficient antioxidant or gum inhibitors for gasoline, mineral hydrocarbons, petroleum products, and mainly lubricating oil. The aim of this study was to evaluate the thermal stability of two cardanol derivatives and to compare them to a standard antioxidant (BHT) used in fuels.

Experimental

Materials

Hydrogenated cardanol or 3-pentadecylphenol (3-PDP) was used after hydrogenation of cardanol (9); alkylated 3-PDP (3-PDP-ALQ), synthesized after alkylation of the 3-PDP by Friedel-Crafts reaction; alkylated and nitro 3-PDP (3-PDP-NIT), synthesized after nitration of the 3-PDP-ALQ, according to Dawson and Wasserman (7).

Thermal Analysis

Thermogravimetric analysis (TG) was performed on a Shimadzu DTA-50H thermobalance. Approximately 10 mg of sample was placed into an aluminium pan sample vessel and subject to thermogravimetric analysis in O₂ and N₂ atmosphere (50 mL/min) at a temperature range from 30 to 800 °C. The mass loss and structural changes were analysed. Differential scanning calorimetry measurements were performed on a Shimadzu DSC-50. For this purpose, 5 mg of sample was weighed in aluminium pan and submitted to heating from 20 to 400 °C in N₂ atmosphere (20 mL/min), at constant heating rate $\beta = 10$ °C/min

Results and Discussion

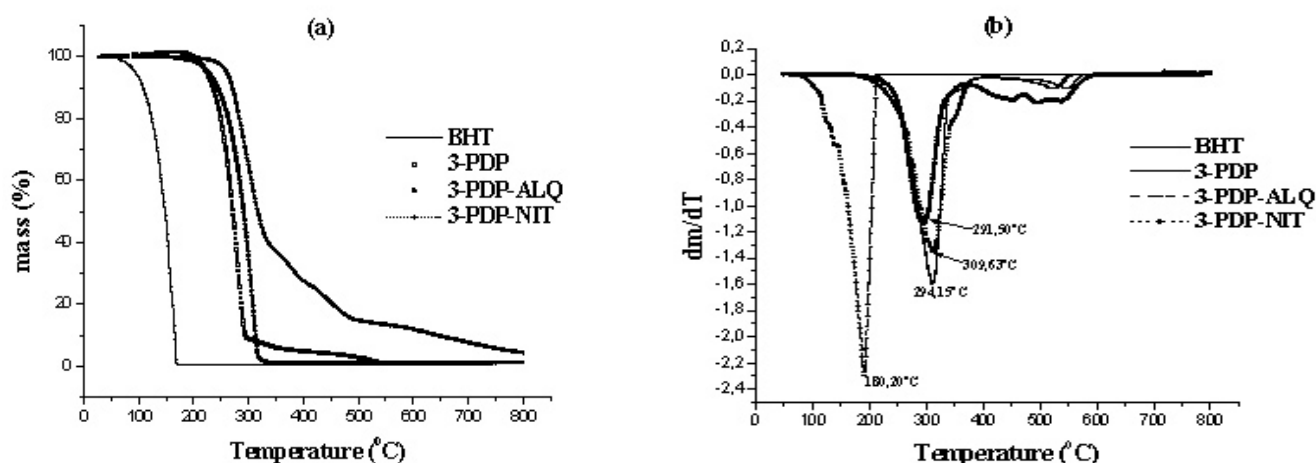
Thermogravimetric Analysis (TGA)

The TGA data of BHT, 3-PDP, 3-PDP-ALQ and 3-PDP-NIT are shown in Table 1.

Table 1. Thermogravimetric data of BHT, 3-PDP, 3-PDP-ALQ, 3-PDP-NIT in O₂ and N₂

Compounds	Mass loss (mg) in O ₂			Residue (%)	Mass loss (mg) in N ₂			Residue (%)
	1 ^a	2 ^a	3 ^a		1 ^a	2 ^a	3 ^a	
BHT	9.9 (180.2°C)	-	-	0.7	9.7 (180.7°C)	-	-	0.8
3-PDP	9.0 (294.2°C)	0.7 (536.7°C)	-	7.1	9.2 (292.7°C)	0.3 (546.3°C)	-	3.1
3-PDP-ALQ	9.2 (309.6°C)	0.69 (520.8°C)	-	7.0	9.6 (307.7°C)	-	-	0.9
3-PDP-NIT	6.6 (291.5°C)	1.4 (456.2°C)	1.8	2.0	6.1 (297.4°C)	0.9 (380.2°C)	1.5 (449.9°C)	5.2

Table 1 and Figure 1 show the TG and DTG curves of 3-PDP and 3-PDP-ALQ in oxidant atmosphere (O₂). It was observed the presence of two decomposition peaks, where the first mass loss was in 294.2 °C and 309.6 °C the second in 536.7 °C and 520.9 °C, with a residue of 7.1% and 7.0%, respectively. The 3-PDP-NIT presented three decomposition peaks, where the first mass loss was at 291.5 °C, the second at 456.0 °C and the third at 496.0 °C, with a residue of 18.4%; while BHT presented only one decomposition peak at 180.2 °C and a final residue of just 0.7%. 3-PDP-NIT was more stable compared to 3-PDP-ALQ, 3-PDP, and BHT, where the temperatures of initial decomposition were 188 °C, 174.5 °C, 163 °C and 80 °C, respectively. Hence the stability order in O, was: 3-PDP-NIT>3-PDP-ALQ>3-PDP>BHT.

**Figure 1.** (a) TG and (b) DTG curves of BHT, 3-PDP, 3-PDP-ALQ, 3-PDP-NIT in O₂.

Under inert atmosphere (N₂) (Figure 2), BHT and 3-PDP-ALQ compounds presented only one decomposition peak in 180.7 °C and 307.7 °C, with final residues of 0.8%, 0.9% and 5.2% respectively, while 3-PDP-NIT presented three decompositions peaks at 297.7 °C, 380.2 °C and 449.9 °C and final residue of 5.2%. When 3-PDP-NIT is compared to BHT (standard antioxidant), 3-PDP and 3-PDP-ALQ in N₂, it was observed that the former was thermally more stable, because its initial decomposition temperature (~205 °C) was higher than 3-PDP (~194 °C), 3-PDP-ALQ (~156.5 °C) and BHT (~85 °C). Hence the stability order was: 3-PDP-NIT>3-PDP>3-PDP-ALQ>BHT. This characteristic make it suitable to high temperature applications, as in lubricating and combustible oils.

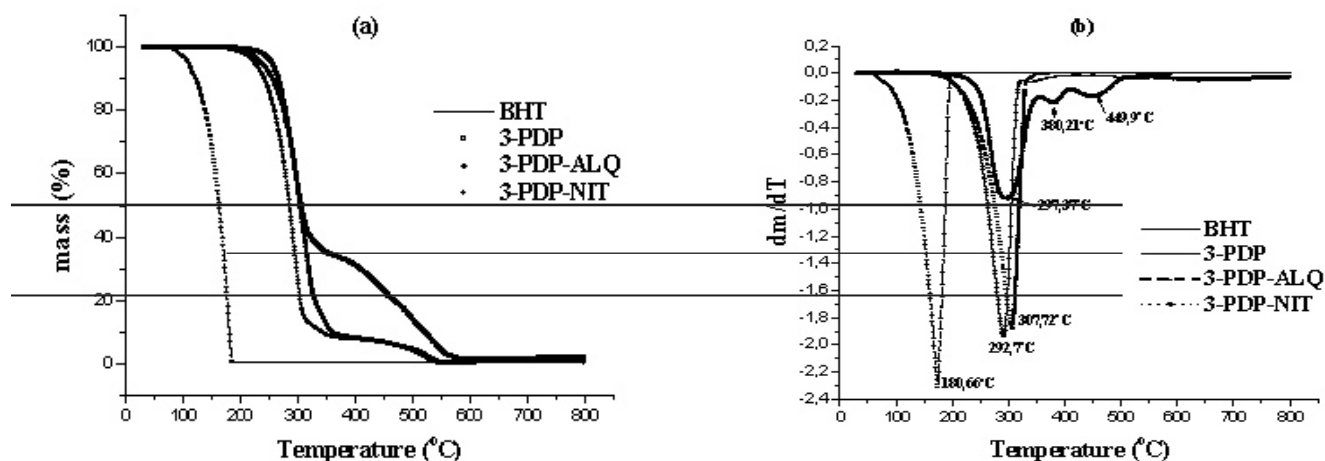


Figure 2. TG (a) and DTG (b) curves of BHT, 3-PDP, 3-PDP-ALQ, 3-PDP-NIT in N₂

Differential Scanning Calorimetry (DSC)

DSC analyses data of BHT, 3-PDP, 3-PDP-ALQ and 3-PDP-NIT are shown in Table 2.

Table 2. Results of DSC of BHT, 3-PDP, 3-PDP-ALQ e 3-PDP-NIT

Compounds	T _o * (°C)		T _p * (°C)		T _c * (°C)		ΔH* (J/g)	
	To ₁	To ₂	Tp ₁	Tp ₂	Tc ₁	Tc ₂	ΔH ₁	ΔH ₂
BHT	69.4	168.4	69.4	185.2	81.3	198.6	-82.4	-65.3
3-PDP	40.6	358.6	53.3	383.4	65.4	388.5	-147.2	-94.7
3-PDP-ALQ	45.4	286.9	45.6	309.4	56.1	319.1	-103.5	-85.8
3-PDP-NIT**	57.7	251.9	67.7	274.1	83.7	289.8	-89.9	75.1

*T_o=initial temperature T_p=maximum temperature, T_c=conclusion temperature, ΔH=enthalpy variation

** T_{o3}=294.05 °C; T_{p3}=310.80 °C e T_{c3}=335.82 °C, ΔH₃=25.05 J/g

The data presented in Table 2 and the DSC curves (Figure 3) of BHT, 3-PDP and 3-PDP-ALQ showed two endothermic peaks, the former is characteristic to sample fusion (69.4 °C, 45.4 °C and 40.6 °C, respectively) while the latter is characteristic of degradation products (168.4 °C, 286.9 °C and 358.6 °C, respectively). The 3-PDP-NIT curve presented three peaks, which indicate that three phenomena are happening; the first (endothermic) probably characterizes the crystalline lattice melting of the compound (57.7 °C), while the second and the third (exothermic) can be attributed to degradation and decomposition of the compound (251.67 °C and 294.05 °C), as revealed by TG analysis.

These results indicate that 3-PDP-NIT bonds are probably more organized (crystalline network more packed, stronger bonds), shifting T_o to higher temperature than 3-PDP, 3-PDP-ALQ and closer to BHT. This suggests a larger stability in relation to 3-PDP and 3-PDP-ALQ in high temperatures. The DSC results are in good agreement with those obtained by TGA.

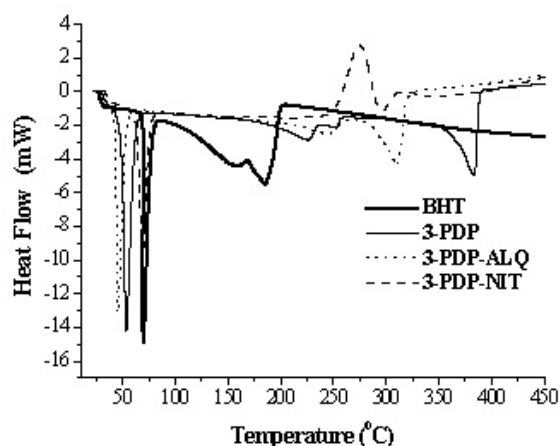


Figure 3. DSC curves of BHT, 3-PDP, 3-PDP-ALQ and 3-PDP-NIT

Conclusions

The entrance of alkyl and nitro groups in 3-PDP gave a higher thermal stability, confirmed by DSC and TGA analyses. The 3-PDP-NIT possibly can be used as antioxidant in fuels, lubricants or as gum inhibitor for gasoline, in accordance with the results obtained by thermal stability study.

References

- (1) Gedam, P. H. and Sampathkumaran, P. S. Cashew Nut Shell liquid – extraction, chemistry and applications. *Prog. Org. Coatings*, v. 14, p. 115-157, 1986.
- (2) Avellar, I. G. J.; Godoy, K.; Magalhães, G. C. de. New Quaternary Ammonium Salts Derived from Cardanol and their Use Phase Transfer Catalyst. *J. Braz. Chem. Soc.*, v. 11, n. 1, p. 22-26, 2000.
- (3) Blazdell, P. The Mighty Cashew. *Int. Sci. Ver.*, v. 25, p. 220-226, 2000.
- (4) Kajiyama, T., Ohkatsu, Y. Effect of Meta-substituents of Phenolic Antioxidants–Proposal of Secondary Substituent Effect. *Polym. Degrad. Stab.*, v. 75, p. 535-542, 2002.
- (5) Kajiyama, T., Ohkatsu, Y. Effect of Para-substituents of Phenolic Antioxidants. *Polym. Degrad. and Stab.*, v. 71, p. 445-452, 2001.
- (6) Braun, J. and Omeis, J. *Additives*. In: *Lubricants e Lubrications*. Cap 6. Mang, T. e Dressel, W (eds), Nova York: Wiley-VCH, p. 85-113, 2001.
- (7) Dawson, C. R. and Wasserman, D. *Nitro-hydrogenated cardanol and process for preparing same*. US Pat. 2 508 708, abr. 4, 1950.
- (8) Wasserman, D. and Caplan, S. *4-amino cardanol*. US Pat. 2 571 091, 16 Out. 1951.
- (9) Madhusudhan V. et al. Catalytic Hydrogenation of Cardanol. Part 1: Laboratory Scale Studies. *Indian J. Tech.*, v. 11, p. 347-350, 1973.