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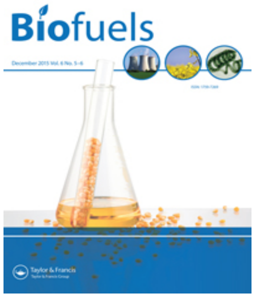

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Cashew nutshell liquid extract as antioxidant for gasoline stabilization

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Investigations have been carried out converting hydrogenated cardanol, a compound extracted from cashew nutshell liquid, into compounds with structural characteristics of antioxidants similar to the ones used in product derived from petroleum. Thin-layer chromatography (TLC) analysis of the raw oil indicated that the major components were cardanol (66.7%), cardol (23.8%) and 2-methyl cardol (9.5%). The intended changes were carried out through exhaustive alkylation with *n*-butyl chloride. FTIR analysis confirms the formation of phenolic acid 2-*n*-butyl properties of the antioxidant produced. The performance of the product was estimated in terms of oxidative stabilization during storage of cracked naphtha. The compound 2-*n*-butyl pentadecylphenol (new antioxidant) has presented good efficiency in the storage assays when compared to the commercial additives used in the refinery.

Keywords: cashew nutshell liquid; antioxidant; gasoline; stabilization

Introduction

The petroleum industry is composed of various upstream and downstream segments, from prospecting oil to production of petrochemicals. Products derived from petroleum, such as gasoline and lubricants, and petrochemicals, such as plastics, fibres and rubbers, are susceptible to oxidation and can be further decomposed by auto-oxidation.[1] One of the important areas of the petroleum industries is the stabilization of gasoline using additives. Several additives are added to these mineral compounds 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 oxidation degradation, thus breaking the auto-oxidative chain reaction.[2]

The shell of the cashew nut (*Anacardium occidentale* L.) contains alkyl-substituted phenolic compounds called cashew nutshell liquid (CNSL). The oil is obtained as a by-product from mechanical processing of the edible cashew kernel and its composition is a mixture of anacardic acid, cardanol and smaller amounts of cardol and 2-methylcardol.[3] One of its highest-yield derivatives, cardanol, is currently being used as an antioxidant in the petrochemical industry,[4] and such studies have evolved research activities based on renewable and sustainable energy. Since cardanol is an important natural source of phenolic compounds and thus possesses antioxidant properties, many synthetic mechanisms involving this type of additive have been developed based on CNSL derivatives.[5]

CNSL is a unique natural source of meta-alkyl phenols with a variable degree of unsaturation attached to the benzene ring. Based on the mode of extraction from the cashew nutshell, CNSL is classified into two types: solvent-extracted CNSL and technical CNSL. A typical solvent-extracted material contains anacardic acid (60–65%), cardol (15–20%), cardanol (10%) and traces of 2-methyl cardol. Depending on the conditions of the roasting process, the composition of the technical CNSL can change and have higher cardanol content (83–84%), less cardol (8–11%) and maintain polymeric material at 10% and 2-methyl cardol content at 2%.[5] Its constituents have been widely used as 'synthesizer' for the preparation of many compounds with potential biological activities.[5] Other applications are the synthesis of polymers and agricultural products.[5,6]

Chemical identity of gasoline

Gasoline is a refined product of petroleum consisting of a mixture of hydrocarbons, additives and blending agents. The composition of gasoline varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand and the product specifications. The typical composition of gasoline hydrocarbons (% volume) is as follows: 4–8% alkanes, 2–5% alkenes, 25–40% isoalkanes, 3–7% cycloalkanes, 1–4% cycloalkenes and 25–50% total aromatics (0.5–2.5% benzene). Additives and blending agents are added to the hydrocarbon mixture to improve the performance and stability of gasoline. These compounds include anti-knock agents, antioxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents and dyes. At the end of the

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production process, finished gasoline typically contains more than 150 separate compounds.[7]

Methodology

The extraction of CNSL was carried out using a Soxhlet extractor (Scientific Equipment Development Institute, Minna), and *n*-hexane as solvent. A total of 350 ml of hexane was charged into a round bottom flask of Soxhlet apparatus. Subsequently, 20 g of crushed cashew nutshell was charged into the thimble and fitted into the Soxhlet extractor. The apparatus was assembled. The solvent in the set-up was heated to 68°C and the vapour produced was condensed by water flowing in and out of the extraction set-up. This process of heating and cooling continued until a sufficient quantity of CNSL was obtained. At the end of the extraction, the thimble was removed while the remaining solvent in the extractor was recharged into the round bottom flask for a repeat of the process. The set-up was then re-assembled and heated to recover the solvent from the oil. The methods used are reported by other researchers.[3–5,7]

Results and discussions

The cardanol and its derivatives were characterized according to the physical and chemical analyses shown in Tables 1 to 4 and Figures 1 and 2. The physical parameters determined are the physical state and colour. The physical state for both samples is liquid. The colour of cardanol, which was determined by close observation, is pale brown in colour, which darkened on alkylation.

TLC analysis of cardanol

Thin-layer chromatography (TLC) is the technique used in identifying the composition of compounds in a sample. From the study carried out, the component of the hydrogenated cardanol sample determined before alkylation is presented in Tables 1 and 2. From Table 1, three spots separated out, the upper spot, with an $Rf = 0.59$, corresponds to cardanol, a middle spot appearing at $Rf = 0.38$ corresponds to 2-methylcardol and a lower spot with an $Rf = 0.10$ corresponds to cardol.

The percentage compositions were determined to be cardanol (66.7%), cardol (23.8%) and 2-methyl cardol (9.5%). This shows that cardanol is a predominant component of the CNSL extracted.[8]

Table 1. Analytical TLC results of cardanol.

Sample	Distance travelled (cm) Spot (A)	Distance travelled (cm) Solvent (B)	Retention factor (Rf) = A/B
Cardanol	3.01	5.20	0.59
	1.98	5.20	0.38
	0.52	5.20	0.10

Table 2. Infrared transmittance assignment for cardanol.

Vibration mode	Functional group	Wave no. (cm^{-1})
C-H stretch	Methyl	2928
C = C ring stretch	Aromatic	1452, 1647
In plane C-O-H deformation	Aromatic C-O-H	1227
Out of plane C-H bend	Methylene	721

Table 3. Infrared transmittance assignment for 2-*n*-butyl pentadecylphenol.

Vibration mode	Functional group	Wave no. (cm^{-1})
O-H stretch	Methyl	3405
C-H stretch	Methyl	2936; 2874
C = C ring stretch	Aromatic	1451, 1641
In plane C-O-H deformation	Aromatic C-O-H	1232
Out of plane C-H bend	Methylene	728

FTIR analysis of samples

The Fourier transform infrared spectrometry (FTIR) technique is a useful analytical method for identification of constituents in a sample. From the study, the constituents of the hydrogenated cardanol sample determined before and after alkylation are presented in Figures 1 and 2. Figures 1 and 2 are the FTIR spectrum showing peak values corresponding to different constituents. The increases and decreases in the spectrum shows how the experimental conditions affect the structure of the sample. The spectra of the samples could be analysed in terms of fixed mix

Table 4. Ambient storage data for gasoline samples in phases I through III.

Phases	Sample description	Potential gum, mg/100 ml ambient storage: 0 week	2 weeks	4 weeks
I	99% SRN, 1% AO	0.4	0.07	0.05
	97% SRN, 3% AO	0.2	0.06	0.03
	95% SRN, 5% AO	0.1	0.02	0.0
II	100% SRN	0.6	1.20	1.9
III	100% Commercial gasoline	0.0	0.0	0.01

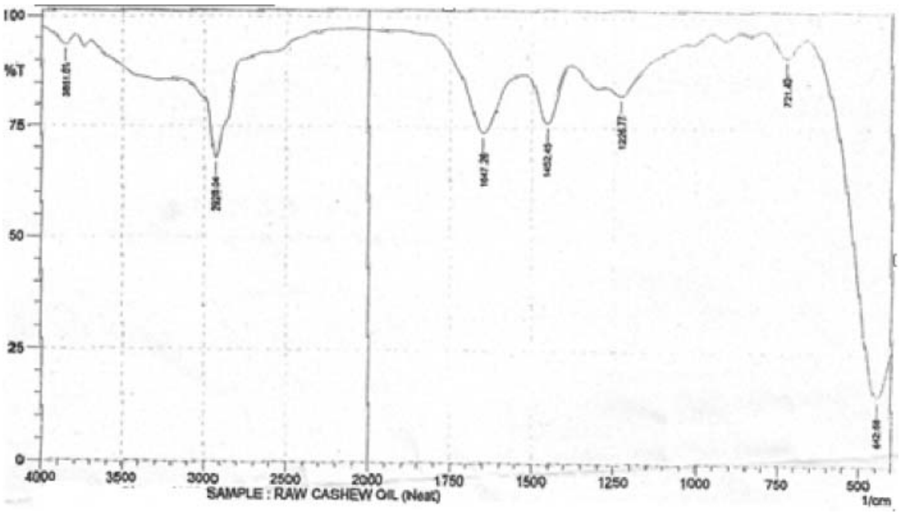

Figure 1. FTIR of cardanol produced from CNSL.

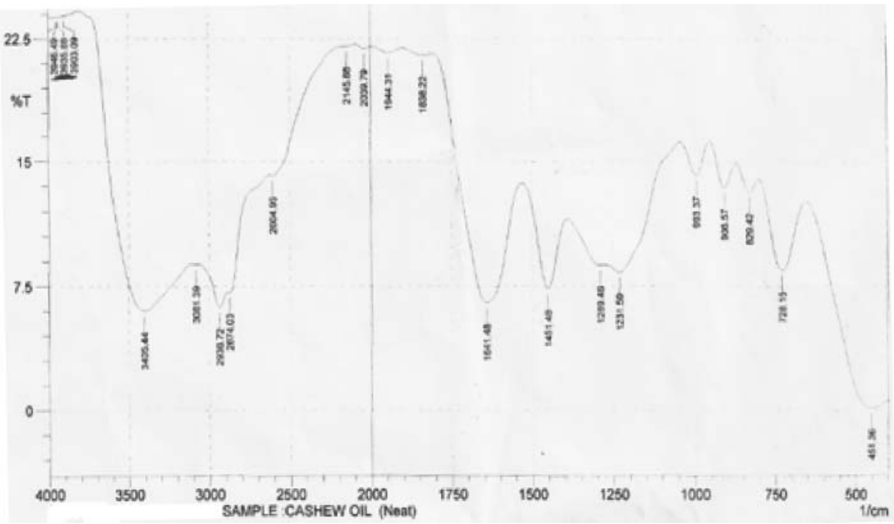

Figure 2. FTIR analysis results of 2-*n*-butyl pentadecylphenol produced from CNSL.

of functional groups; alcohol OH band stretching in between 3200 and 3600 cm^{-1}; C-H aromatic stretching in between 3000 and 3100 cm^{-1}; and C-H aliphatic in between 2850 and 3000 cm^{-1}. The strong CH stretch bands close to 3000 cm^{-1} comes from carbon-hydrogen bonds in the CH_2 and CH_3 groups; C = C and C-O stretching between 1450 and 1650 cm^{-1} attributed to phenolic ester, carboxylic acid and conjugated ketone structures. C-O absorption stretching between 1000 and 1300 cm^{-1} with no O-H band. The region in between 650 and 1000 cm^{-1} contains various blends related to aromatics, out of plane C-H blending with different degree of substitution. In the spectrum of Figure 1, peaks at 721 cm^{-1} are due to vinyl unsaturation in the side chain. The absorption band at 1647cm^{-1} indicates the presence of the phenolic group. [3,9]

From Figure 2 it was observed that the highest band of the sample lies on 3405 cm^{-1}, which shows that the sample is attributed to the hydrogen-bonded OH group of phenol; 2936 and 2874 (CH_2, CH_3); 1232cm^{-1} (Ar-O aromatic ring vibrations); 1451 cm^{-1} and 1641cm^{-1} (C = C aromatic ring vibrations); 728 cm^{-1} (angular C-H deformation of the aromatic ring) (see Tables 2 and 3).

From this comparison, it shows the evidence that 2-*n*-butyl pentadecylphenol when compared with the cardanol have more surface functional groups.

Ambient aging test

Ambient aging test is a useful technique for the determination of gum formation in gasoline. From the study carried out, the groups ambient storage data for test samples, which were essentially finished gasoline, are presented in Table 4 using straight run naphtha (SRN) and antioxidant (AO).

Table 4 indicates the storage stability of gasoline that has low initial gum values. It was observed that the addition of the phenolic compound to the reference gasoline produced a clear break point with increasing number of days. Ambient storage varied from 0−4 weeks with the gum formation being a function of phenolic concentration. At equal storage period, the highest phenolic concentration produces the lowest potential gum. Similarly, from phase II, the potential gum formation increases with increasing number of days, which was mainly due to the effect of oxidation. While from phase III, it was observed that the formation of gum is significantly lower with negligible increment during the fourth week of storage, which might be due to unforeseen circumstances.

Conclusion

The antioxidant 2-*n*-butyl pentadecylphenol was developed by alkylation with *n*-butyl chloride. The aging test results obtained during this study show some promising storage stability test results, providing a tentative method for oxidation stability of motor gasoline, with some slight modification to give potential gum values, in predicting motor gasoline stability. This method has also been shown to correlate gasoline stability at ambient conditions by observing gum formed in gasoline stored up to four weeks in ambient conditions. Based on the data generated under the three phases of this storage stability program, the developed pentadecylphenol (cashew nutshell liquid derivative) could be an alternative antioxidant for gasoline stabilization which is environmentally benign.

Disclosure statement

No potential conflict of interest was reported by the author.

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