



Comparative study on GC-MS Characterisation of atmospheric and vacuum oil residue from KRPC, Kaduna, Nigeria

Habib B^{1*}, Dabai MU², Faruk UZ³

¹⁻³ Department of Pure and Applied Chemistry, Faculty of Science, Usmanu Danfodiyo University Sokoto, Sokoto, Nigeria

DOI: <https://doi.org/10.33545/26646765.2019.v1.i1a.12>

Abstract

This Study focused on identification and quantification of Atmospheric and vacuum oil residue using GCMS technique. A total of ten Oil residues samples were used in this study, five each from atmospheric and vacuum distillation. The samples were obtained from Kaduna Refining and Petrochemical Company (KRPC), a subsidiary of Nigeria National Petroleum Corporation (NNPC). The samples were prepared and analysed using GC-MS. The results inferred that the crude oils studied have similar hydrocarbon group type's I.E paraffinic, olefinic and Aromatic group types but differ in individual hydrocarbon. Atmospheric oil residue has higher amounts of Paraffinic and Aromatics than Vacuum residue and lower amounts of Oxygenates and Olefins compare to Vacuum residue.

Keywords: GC-MS, Characterisation, Vacuum, quantification, NNPC

1. Introduction

Petroleum/crude oils are naturally occurring, complex mixtures of hydrocarbons with varying amounts of sulfur, oxygen and nitrogen, as well as trace amounts of metals such as nickel and vanadium. Chemical and physical compositions vary with the origin and age of the crude oil ^[9]. Crude oil can be thought of as a distribution of paraffinic, naphthenic and aromatic species of increasing molecular weight and complexity with the largest and most complex being the Asphaltenes. The proportions of the constituents in different crude oils vary and the physical properties also vary accordingly ^[3].

The identification of hydrocarbon constituents, especially those in the higher boiling fractions, is an important aspect of petroleum science. Determination of the skeletal structures of the hydrocarbons gives indications of the types of locations in which the heteroatoms might be found ^[9].

However, because of the complexity of the structures in heavy oils and residue, it is difficult on the basis of the data obtained from synthesized hydrocarbons to determine the identity or even the similarity of the synthetic hydrocarbons to those that constitute many of the higher boiling fractions of petroleum ^[8].

Nevertheless, it has been well established that the hydrocarbon components of petroleum are composed of paraffinic, naphthenic, and aromatic groups. Olefinic groups are not usually found in crude oils, and acetylenic hydrocarbons are very rare indeed.

Thus, methane is the main hydrocarbon component of petroleum gases with lesser amounts of ethane, propane, butane, *iso*-butane and some C₅ _ light hydrocarbons. Other gases, such as hydrogen, carbon dioxide, hydrogen sulfide and carbonyl sulfide, are also present ^[7].

The naphtha fraction is dominated by the saturates with lesser amounts of mono- and di-aromatics. Within the saturate fraction, every possible paraffin from the simplest C₁ hydrocarbon (methane) to n-C₁₀ (normal decane) is present. Depending upon the source, one of these low boiling paraffins may be the most

abundant compound in a crude oil reaching several percent. The iso-paraffins begin at C₄ with iso-butane and the number of isomers grows rapidly with carbon number ^[4]. The saturate fractions also contain cycloalkanes (Naphthenes) with mainly five or six carbons in the ring. Fused ring dicycloalkanes such as Cis- and trans-decahydronaphthalene (decalin) are also common. The numerous aromatics in naphtha begin with benzene, but the C₁ to C₃ alkylated derivatives generally are present in larger amounts. Benzene with fused cycloparaffin rings (naphthoaromatics) such as indan and tetralin have been isolated along with a number of their respective methyl derivatives. Naphthalene is included in this fraction while the 1- and 2-methyl naphthalenes and higher homologues of fused two ring aromatics appear in the mid-distillate fraction ^[5].

In our previous report we have characterized crude oil residue from atmospheric and vacuum distillation using Atomic Absorption Spectroscopy ^[2]. This study aims at identification and quantification of oil residue from atmospheric and vacuum residue using Gas Chromatography- Mass Spectrometry (GC-MS). The Crude oil residue analysed was obtained from Kaduna Refining and Petrochemical Company (KRPC), a subsidiary of NNPC, Kaduna, Nigeria.

2. Materials and Methods

The petroleum products used in this research work were residues from atmospheric and vacuum distillation obtained from Kaduna Refining and Petrochemical Company (KRPC), a subsidiary of NNPC, Nigeria

3. Reagents

All the reagents used in this work are of Analytical grade.

4. Sample Collection

Ten Crude oil Residue samples were collected from oil movement unit of Kaduna Refining and Petrochemical Company

(KRPC), a subsidiary of NNPC, two ^[2] litres each were obtained, the samples were put in a clean sample bottles and kept away from sunlight. Atmospheric residue samples were collected first from the same pool and Vacuum Residue Samples were then collected a week later.

5. GC-MS

The GC-MS analysis was performed on the Hewlett Packard

5972 mass spectrometer operated at ionization energy of 70eV linked to an HP-5890 gas chromatogram, with a splitless injector (at 250°C) fitted with a flexible silica capillary column of 30m *0.32mm internal diameter, 1.0µm film thickness. 1µl of each sample was injected by an auto sampler; the oven temperature was programmed from 40 to 300°C at a rate of 4°C/min and held at 300°C for 20min, using helium as the carrier gas at flow rate of 1ml/min. The samples were run using full scan and recorded.

6. Results

Table 1: Compounds of atmospheric residue (A) by GCMS

Compound	Area %
Non Aromatics	
9-12 –octadecadienal	1.75

Table 2: Compounds of atmospheric residue (A) by GCMS

Compounds	Area %
Aromatics	
Naphthalene-1-methyl	1.54
Naphthalene 2,7-dimethyl	1.05
Naphthalene 2,6-dimethyl	1.92
Naphthalene 1,4-dimethyl	0.64
1,4-dimethyl Azulene	0.68
4,6,8-trimethyl Azulene	0.55
Non-Aromatics	
1-bromo eicosane	1.22
tetradecane-1-chloro	1.59
Nonadecane	0.67
Tridecane	0.6
Dodecane,3-methyl	0.55

Table 3: Compounds of Atmospheric Residue (A) by GCMS

Compounds	Area %
Aromatics	
Naphthalene-2-methyl	1.56
Naphthalene 2,6-dimethyl	0.85
Naphthalene 2,7-dimethyl	0.92
Naphthalene 2,3,6-trimethyl	1.97
Non-Aromatics	
Pentadecane	0.80
Undecane	0.85
Hexadecane	1.16
Heptadecane	1.46
Octadecane	1.00
Eicosane	0.99
Octadecane-2-methyl	1.33

Table 4: Compounds of atmospheric residue (A) by GCMS

Compounds	Area %
Aromatics	
Naphthalene, 2-methyl	0.98
Non-Aromatics	
Hexatriacontane	0.94
1,15-pentadecanediol	1.31
Pent-1-yn-3-ene,4 methyl-3-phenyl	1.21
Sulfurous acid, butylheptadecyl ester	1.32

Table 5: Compounds of atmospheric residue (A) by GCMS

Compounds	Area %
Aromatics	
Naphthalene,2-methyl	1.25
Naphthalene,1,6-dimethyl	0.87
Non-Aromatics	
tetracontane,3,5,24-trimethyl	1.08
Octadecane-1-chloro	0.85
Carbonic acid, undecyl vinyl ester	0.82
Hexadecane-1-bromo	0.80

Table 6: Compounds of Vacuum residue, (V) by GCMS

Compounds	Area %
Aromatic	
Naphthalene,1-methyl	1.15
Naphthalene,2,7-dimethyl	0.76
Non-Aromatics	
Pentadecane,1-bromo	0.94
Hexadecane-1-chloro	1.18
Oxalic acid, allyl dodecyl ester	0.94

Table 7: Compounds of Vacuum residue, (V) by GCMS

Compounds	Area %
Aromatics	
Naphthalene,2,6-dimethyl	2.68
Non-Aromatics	
Hexadecanoic acid, methyl ester	4.7
Trans-13-octadecenoic acid, methyl ester	6.66
Z-13-Octadecen-1-yl-acetate	3.19
Oxalic acid, cyclobutylheptadecyl ester	2.52

Table 8: Compounds of Vacuum Residue (V) by GCMS

Compounds	Area %
Non-Aromatics	
Hexadecane	4.40
Heptadecane	4.64
6-octen-1-ol,3,7-dimethyl-, (R)	2.64

Table 9: Compounds of vacuum residue, (V) by GCMS

Compounds	Area%
Aromatic	
Naphthalene,1,6-dimethyl	3.68
Non-Aromatics	
Tridecane-1-bromo	3.50
1,13-tetradecadiene	3.76
Trans-Traumatic Acid	8.15

Table 10: Compound of Vacuum residue, (V) by GCMS

Compound	Area%
Aromatic	
Naphthalene,1,6-dimethyl	3.65
Non Aromatics	
Oleic acid	7.12
3-octyne,6-methyl	7.32
Trichloro acetic acid Undec-10-enyl ester	4.49

7. Discussion

Tables 1 to 10 present a total of fifty five compounds as identified from the NIST14 GCMS Library, In Atmospheric residue sample; a total of Sixteen Paraffins compounds were identified with heptadecane (1.46%) as the most significant, thirteen Compounds were identified for Aromatics with Naphthalene 2,3,6-trimethyl (1.97%) having the most significant, Four Compounds were identified for Oxygenates with 9-12-octadecadienal (1.75%) as the most significant and One Compound was identified for Olefins with Pent-1-yn-3-ene,4 methyl-3-phenyl (1.21%) as the most significant While for Vacuum residue Sample, a total of five compounds were identified for Paraffins with heptadecane (4.64%) being the most significant, similarly, five compounds were also confirmed for Aromatics with Naphthalene,1,6-dimethyl (3.68%) as the most

significant, a total of nine Oxygenated compounds were identified with Trans –Traumatic Acid(8.15%) as the most significant and two compounds for Olefins with 3-Octyne,6-Methyl (7.32%) as the most Significant. The result agrees with the earlier works reported [1, 6].

8. Conclusion

This study concludes that the atmospheric and vacuum residues analysed have similar hydrocarbon group type's i.e paraffinic, olefinic and aromatic group types but differ in individual hydrocarbons. Atmospheric oil residue has higher amounts of Paraffins and Aromatics than Vacuum residue and lower amounts of Oxygenates and Olefins compare to Vacuum residue.

9. Acknowledgement

This work was carried out with the supports of Department of Pure and Applied Chemistry, Usmanu Danfodiyo University Sokoto, Sokoto, Nigeria.

10. Reference

- Ahmad I, Sohali SM, Khan H, Khan R, Ahmad W. Characterisation of Petroleum Crude oils by Fourier Transform Infrared (FT-IR) and Gas Chromatography-Mass Spectrometers. *Petroleum and Petrochemical Engineering Journal*. 2018; 2(2):000148
- Dabai MU, Habib B, Faruk UZ, Rabah AB. Comparative Analysis on Trace Metals in Atmospheric and Vacuum Residue. *International Journal of Research and Innovation in Applied Sciences*. 2018; 3(11):50-52.
- Favenec JP. *Petroleum Refining, Refinery operation and Management*, 2001, 5. Editions TECHNIPS
- Igor NE, Aleksandr PL. On the Nature of UV/Vis Absorption Spectra of Asphaltenes, 2011. <http://eee.gubkin.ru>
- Ma X, Sakanishi K, Isoda T, Mochida I. *Fuel*, 1997, 76:329.
- Odeunmi EO, Ismaeel RO. GCMS Characterisation of Nigerian gulf heavy crude oil fractions. *Elixir International Journal of Organic Chemistry*, 2012; 42:6472-6477.
- Peng I, Xiaogi W, Yongan G. Characterization of asphaltenes precipitated with three light alkanes under different experimental conditions: fluid phase equilibria, *journal*, 2010; 291:103-110.
- Speight JG. *Handbook of Petroleum Analysis. Chemical Analysis: A Series of Monographs on Analytical Chemistry and its Applications*, ed. J.D. Wineforder. Vol. 158. New York: Wiley Inter-science, 2001.
- Speight JG. *The Chemistry and Technology of Petroleum*, 4th Edition, CRC Press Taylor & Francis Group, Boca Raton, Florida, 2007, 98-105.