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GC-MS characterization of Nigerian gulf heavy crude oil fractions

Odebunmi, E.O* and R.O Ismaeel.

Department of Chemistry, University of Ilorin, P.M.B 1515, Ilorin, Kwara State, Nigeria.

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ABSTRACT

Gulf heavy crude oil samples were separated into four fractions of saturates, mono-, di- and polyaromatics by elution open column chromatography. Alumina and a mixture of equal amount of silica and alumina stationary phases were separately used to study the effect of these stationary phases on the separation. The Gas Chromatography – Mass Spectrometry (GC – MS) results of the fractions show that the nature of the stationary phase may affect the elution of both aromatic and the saturate components of the oil. The pristane/phytane ratio ranging from 0.63-2.00 obtained for the crude oil fractions using the two stationary phases indicates an oxygen depositional environment for the source rocks.

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Introduction

Crude oil or petroleum is a complex mixture of hydrocarbons that represents several classes of organic compounds such as alkanes, naphthenes and aromatics [1] with carbon and hydrogen in proximate ratio of 1:6 by weight and other related inorganic elements. These elements are nitrogen, sulphur, oxygen, phosphorus and trace amounts of metals usually nickel, vanadium, titanium, iron etc [3,4] which may cause adverse effects during refining processes by causing corrosion or poisoning of the cracking catalysts [3]. Classifications of crude oils into families helps to locate hydrocarbons in explored areas and different stratigraphic units of the basin [5,6]. Gas Chromatography-Mass Spectrometry (GC-MS) is a useful technique for the analysis of compounds present in minute quantities (usually ppm) in oil [7].

The GC-MS analysis of eleven (11) crude oil types obtained from different productive oil fields across the world indicates that only Nigerian crude oils show the presence of oleanane among others [8]. Similarly, the GC and GC-MS analysis of crude oil from an onshore field in the Niger Delta, Nigeria had been studied [9]. The results indicate abundances of C₂₇, C₂₈ and C₂₉ stearanes. In another report, GC-MS analysis of n-hexane fraction of crude oil sample showed the presence of a homologous series of long-side-chain n-alkylaromatics, namely mono-, di- and tri-n-alkylbenzenes in the C₇ – C₂₇ range and di- and tri-n-alkylbenzothiophenes in the C₃ – C₂₃ range [10]. Gas Chromatographic (GC) analysis of Nigerian crude oil samples obtained from an oil spillage site in the Niger Delta was carried out by Inimfon and Leo [11]. The results show abundance of n-alkanes within the C₈-C₂₃ region as well as polycyclic aromatic hydrocarbons (PAH) whose presence showed that the hydrocarbon fractions might have undergone combustion and/or there was bush burning at the site prior to the oil spill incidence.

In our earlier reports, we have characterized crude oil and petroleum fractions obtained by elution liquid chromatography using Gas Chromatography (GC) [12] and Infrared and Ultraviolet Visible Spectroscopy (IR-UV) [13]. Thus, this study aims at separating Gulf heavy crude oil sample into four

fractions by elution liquid chromatography using different stationary phases (alumina and mixed silica-alumina) to study their effects on the separation. Gas Chromatography- Mass Spectrometry (GC-MS) technique was used to characterize the fractions. The crude oil sample analyzed was obtained at the NNPC Kaduna, Nigeria.

Experimental

Chemicals: All chemicals used for this study were of analytical grade and were used without further purification.

Elution liquid chromatography: A 50cm³ standard laboratory burette initially cleaned with chromic acid and sulphuric acid was used as the column for the elution chromatography. The column was then rinsed with distilled water and allowed to dry in air. Thereafter, the column was then carefully packed with alumina stationary phase and prewetted with 25cm³ of n-hexane [12-15]. Elution liquid chromatography for the fractionation of crude oils into saturates, monoaromatics diaromatics and polyaromatics was carried out in the column. The procedure involved the introduction of 10cm³ of the crude oil sample in about 15cm³ of n-hexane to the top of the column. The column was then eluted at an appropriate flow-rate of 2-3cm³ min⁻¹ with 100% n-hexane for saturates, 5% benzene and 95% n-hexane for monoaromatics, 15% benzene and 85% n-hexane for diaromatics and 60% methanol, 20% diethylether, and 20% benzene for polyaromatics. The concentrates of the four fractions were collected by consecutive elution. The separation scheme that was used for the elution process was given in figure 1 [16] and it is a modification of other scheme reported in the literature [2,16,17]. The procedure is repeated with mixed silica-alumina stationary phase and the fractions obtained were characterized using GC-MS technique.

Gas Chromatography-Mass Spectrometry (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 chromatograph, with a splitless injector (at 250°C), fitted with a flexible silica capillary column of 30m x0.32mm internal diameter; 1.0µm film thickness. About 1µL of each sample was injected by an auto sampler; the oven

Tele:

E-mail addresses: yibaf01@yahoo.com

temperature was programmed from 40 to 350°C at a rate of 4°C/min and held at 300°C for 20min, using helium, carrier gas at a flow rate of 1ml/min. the samples were run using full scan, single ion monitoring (SIM) and recorded using HP chemstation system.

Results and Discussion

Elution liquid chromatography: Table 1 shows the colours of the four fractions (saturates, monoaromatics, diaromatics and polyaromatics) obtained from elution liquid chromatography of Gulf heavy crude oil samples separated using alumina and mixed silica-alumina stationary phases. The Table clearly showed that the colour of each fraction deepens on proceeding from saturates to polyaromatics. For instance, the colours were yellow, brown, dark brown and black for fractions I, II, III and IV respectively using alumina stationary phase. The results also showed that the nature of the stationary phase may affect the colours of the fractions obtained. For instance, in fraction II, the colours was brown using alumina and dark brown in mixed silica-alumina stationary phases. The colours of fractions I, III and IV remained yellow, dark brown and black respectively in the two stationary phases. Thus, fractions obtained from elution liquid chromatography of crude oil samples can be characterized using colours. The results also compared favorably well with the earlier reports [12, 13].

Gas chromatography – Mass Spectrometry: Table 2 presents the Kovats retention indices, relative percentages and identities of the constituents of the saturates fraction obtained from the heavy crude oil sample separated using alumina stationary phase. A total of 21 compounds that constitutes 96.3% were identified from their mass spectra. Only saturates were collectively separated from the sample as shown in the Table. The predominant compound in the fraction of the oil was 2,6,10,14-tetramethyl pentadecane (18.0%).

The relative percentage composition, Kovats retention indices and identities of the constituents of the saturates fraction of heavy crude oil sample separated using mixed silica-alumina stationary phase is presented in Table 3. The Table also gave a total of 21 compounds representing 98.4% out of which 20 were saturates of 97.2% total composition identified from their mass spectra. The compound that was present in significant amount was tricosane (16.5%). The results show that the nature of stationary phase may affect the percentage composition of saturates in the oil since the predominant compounds obtained were different in the results presented in Tables 2 and 3 using the two stationary phases. The results compared favorably well with the literature [11]. A higher total percentage composition of saturates obtained in the saturates fraction of the oil presented in Tables 2 and 3 suggested that the separations were successful.

Table 4 presents the percentage composition, Kovats retention indices and identities of the aromatics fraction of heavy crude oil sample separated using alumina stationary phase. A total of 19 compounds that constitute 97.3% were identified from their mass spectra. Twelve (12) saturate compounds that represent 45.9%, Two (2) aromatic compounds with a total composition of 6.2% and 5 other compounds representing 45.2% were identified in the Table. The compound that exist in significant quantity among the aromatics was 2,4-bis (1,1-dimethyl ethyl) phenol (4.3%). Meanwhile, octadecanoic acid, 2-hydroxy-1-(hydroxyl methyl) ethyl ester was the predominant oxygenated and non-aromatic compound with a relative percentage of 21.2% in the fraction of the oil. A higher percentages of oxygenated compounds in the oil compared favorably well with the earlier reports [8,9,17].

The Kovats retention indices, relative percentages and identities of the aromatics fraction of heavy crude oil sample separated using mixed silica-alumina stationary phase is presented in Table 5. The Table presents a total of 26 compounds that constitute 98.8% as identified from their mass spectra. The percentage composition of the saturates, aromatics and other compounds obtained in the fraction and shown in the Table were 46.0%, 10.6% and 42.2% respectively. In the Table, fourteen (14) saturate compounds and four (4) aromatic compounds were identified. The most significant aromatic compound was naphthalene (4.1%) which again indicates that the nature of the stationary phase used for the separation may affect the quantity of aromatics in the sample. Similarly, eight (8) other compounds were identified and the predominant compound was octadecanoic acid, 2-hydroxy-1-(hydroxyl methyl) ethyl ester (15.4%) which agreed with the results presented in Table 4 when alumina was used for the separation. This also compared favorably well with the earlier reports [8,9,17]. The low total percentage composition of saturates obtained in the aromatic fractions of the oil as presented in Tables 4 and 5 indicate that the separations were very successful.

Table 6 shows the percentage pristane/C₁₇, phytane/C₁₈ and the pristane/phytane ratio of the fractions obtained from the separation of the heavy crude oil samples using the two stationary phases. The percentage Pr/C₁₇ ranges from 1.9%-7.6% averaging 5.05% while the percentage Ph/C₁₈ ranges from 3.0%- 3.7% with an average of 3.33% for the two stationary phases. The Pr/Ph ratio ranges from 0.63-2.20 averaging 1.51 using the two stationary phases indicates an oxygen depositional environment for the source rocks since the Pr/Ph ratio was greater than one [8,9,18,19].

We therefore concluded based on the characterization of the fractions of the crude oil sample studied using GC-MS Technique, that Gulf heavy crude oil has a higher amounts of aromatics and oxygenated compounds compared to the saturates. The results also show that the chemical nature of the stationary phase may affect the quantity of the constituents of crude oil samples since the predominant compounds varied with the nature of the stationary phase. Finally, the higher percentages of pristane and phytane obtained for the sample using alumina indicates a better separation compared to the mixture [20-22].

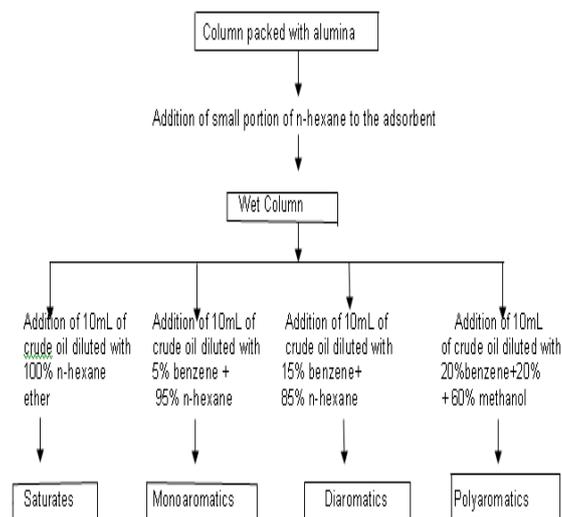


Fig 1: Flow chart for chromatographic separation scheme [16]

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Table 1: Comparison of the colours of fractions of elution liquid chromatography of Gulf heavy crude oil samples separated using alumina and mixed silica-alumina stationary phase

Stationary phase	Fraction I <i>Saturates</i>	Fraction II <i>monoaromatics</i>	Fraction III <i>diaromatics</i>	Fraction IV <i>polyaromatics</i>
Alumina	Yellow	Dark Brown	Dark brown	Black
Silica-Alumina	Yellow	Deep Brown	Deep brown	Black

Table 2: Chemical composition (%) of constituents of the saturates fraction of the crude oil sample separated using Alumina stationary phase

Compound ^a	Kovats RI ^b	Percentage composition	Mass spectra data
Dodecane	1200	1.9	146, 112, 85, 71, 57
7-methyl tridecane		1.9	183, 169, 112, 71, 57
Tridecane	1300	1.7	141, 112, 99, 85, 57
Tetradecane	1400	2.0	155, 141, 113, 85, 57
Pentadecane	1500	3.5	188, 173, 141, 99, 57
Hexadecane	1600	4.7	226, 169, 113, 99, 57
Heptadecane	1700	4.5	182, 141, 99, 85, 57
2,6,10,14-tetramethyl pentadecane	1755	18.0	183, 155, 127, 99, 57
Decahydro-4,4,8,9,10-pentamethyl Naphthalene		7.6	193, 165, 151, 137, 123
1,3-dimethylbutyl cyclohexane		1.8	250, 169, 97, 83, 69
Octadecane	1800	4.2	155, 127, 113, 85, 57
2,6,10,14-tetramethyl hexadecane	1804	7.3	282, 144, 99, 71, 57
2,6,10-trimethyl dodecane	1570	7.9	212, 127, 85, 71, 57
Nonadecane	1900	3.7	167, 127, 99, 85, 57
Eicosane	2000	4.4	282, 141, 99, 85, 57
Heineicosane	2100	3.7	296, 127, 99, 85, 57
Docosane	2200	3.4	310, 197, 113, 85, 57
Tricosane	2300	3.5	324, 225, 113, 99, 57
Tetracosane	2400	3.0	338, 169, 99, 85, 57
Hexacosane	2600	5.2	252, 183, 113, 99, 57
Octacosane	2800	2.4	294, 225, 113, 71, 57
Total		96.3%	

^aCompounds are listed in order of elution from silica capillary column coated in CP-Sil 5; ^bretention indices on fused capillary column coated with CP-Sil 5.

Table 3: Chemical composition (%) of constituents of the saturates fraction of Gulf heavy crude oil sample separated using mixed silica-alumina stationary phase

Compound ^a	Kovats RI ^b	Percentage composition	Mass spectra data
2,6-dimethyl octane	936	1.2	113, 85, 71, 57, 43
Dodecane	1200	1.3	146, 112, 85, 71, 57
Tridecane	1300	2.3	114, 112, 99, 85, 57
3-methyl tridecane	1472	1.9	154, 127, 99, 71, 57
Pentadecane	1500	2.8	188, 173, 141, 99, 57
Hexadecane	1600	1.7	226, 169, 113, 99, 57
Heptadecane	1700	1.9	182, 141, 99, 85, 57
2,6,10,14-tetramethyl pentadecane	1755	1.9	183, 155, 127, 99, 57
Octadecane	1800	3.0	155, 127, 113, 85, 57
2,6,10,14-tetramethyl hexadecane	1804	2.7	282, 144, 99, 71, 57
Cyclohexadecane	1881	1.0	
Eicosane	2000	3.3	282, 141, 99, 85, 57
Heineicosane	2100	3.7	296, 127, 99, 85, 57
Tricosane	2300	16.5	324, 225, 113, 99, 57
Tetracosane	2400	9.7	338, 169, 99, 85, 57
Hexacosane	2600	10.9	252, 183, 113, 99, 57
Nonacosane	2900	14.3	310, 127, 85, 71, 57
Batilo		1.2	320, 133, 97, 71, 57
Tetradecyl oxirane		1.4	303, 191, 85, 71, 57
Tetratriacontane	3400	9.9	290, 225, 169, 97, 57
Tetratetra contane	4400	6.7	240, 141, 85, 71, 57
Total		99.3%	

^aCompounds are listed in order of elution from silica capillary column coated in CP-Sil 5; ^bretention indices on fused capillary column coated with CP-Sil 5

Table 4: Chemical composition (%) of constituents of the aromatics fraction of Gulf heavy crude oil sample separated using Alumina stationary phase

Compound ^a	Kovats RI ^b	Percentage composition	Mass spectra data
Naphthalene	1179	1.9	122,102,75,63,51
Tridecane	1300	2.0	141, 112, 99, 85, 57
Tetradecane	1400	4.4	155,141, 113, 85, 57
Pentadecane	1500	4.3	188, 173, 141, 99, 57
Hexadecane	1600	6.7	226, 169, 113, 99, 57
Heptadecane	1700	7.6	182, 141, 99, 85, 57
Octadecane	1800	4.4	155, 127, 113, 85, 57
Nonadecane	1900	1.7	167, 127, 99, 85, 57
Hexadecanoic acid, methyl ester	1926	4.3	227,185,143,97,74
2,4-bis (1,1-dimethyl ethyl) phenol	1927	4.3	191,175,147,128,115
1-Eicosene	1993	1.6	280,125,111,97,83
Eicosane	2000	3.7	282, 141, 99, 85, 57
Heineicosane	2100	3.5	296, 127, 99, 85, 57
Octadecanoic acid, emthyl ester	2128	7.5	298,157,97,83,74
Docosane	2200	3.3	310, 197, 113, 85, 57
Tricosane	2300	2.2	324, 225, 113, 99, 57
Tetracosane	2400	2.1	338, 169, 99, 85, 57
Hexadecanoic, 2-hydroxy-1-(hydroxymethyl) ethyl ester		10.6	299,257,239,213,196
Octadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester		21.2	365,298,267,210,98
Total		97.3%	

^aCompounds are listed in order of elution from silica capillary column coated in CP-Sil 5; ^bretention indices on fused capillary column coated with CP-Sil 5

Table 5: Chemical composition (%) of constituents of the aromatics fraction of Gulf heavy crude oil sample separated using mixed silica-alumina stationary phase

Compound ^a	Kovats RI ^b	Percentage composition	Mass spectra data
Undecane	1100	1.7	127,98,85,71,57
Naphthalene	1179	4.1	122,102,75,63,51
Dodecane	1200	3.1	146,112,85,71,57
1-methyl naphthalene	1298	2.0	142, 137,126,102,96
Tridecane	1300	5.2	141, 112, 99, 85, 57
Tetradecane	1400	3.8	155,141, 113, 85, 57
2-Tetyradecene (E)	1406	1.7	97,83,69,57,55
Pentadecane	1500	4.4	188, 173, 141, 99, 57
Hexadecane	1600	4.1	226, 169, 113, 99, 57
2-Pentadecanol	1690	2.2	125,111,69,55,45
Heptadecane	1700	6.2	182, 141, 99, 85, 57
2,6,10,14-tetramethyl pentadecane	1755	2.4	183,155,127,99,57
Octadecane	1800	3.6	155, 127, 113, 85, 57
2,6,10,14-tetramethyl hexadecane	1804	1.8	282,144,99,71,57
Pentadecanoic acid, 14-methyl methyl ester	1884	3.2	268,127,85,71,57
Nonadecane	1900	3.8	167, 127, 99, 85, 57
2,4-bis (1,1-dimethyl ethyl) phenol	1927	2.3	191,175,147,128,115
Eicosane	2000	2.4	282, 141, 99, 85, 57
Octadecanoic acid, methyl ester	2128	5.6	298,157,97,83,74
1-Docosene	2194	2.8	252,179,83,69,57
1-Eicosanol	2296	1.8	181,125,97,57,43
Octacosane	2800	1.8	155,127,113,85,57
Tetratriacontane	3400	1.7	290,225,169,97,57
Hexadecanoic acid,2-hydroxy-1-(hydroxymethyl) ethyl ester		9.5	299,257,239,213,196
Octadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester		15.4	365,298,267,210,98
1,2-Benzene dicarboxylic acid, diisooctyl ester		2.2	390,279,167,149,113
Total		98.8%	

^aCompounds are listed in order of elution from silica capillary column coated in CP-Sil 5; ^bretention indices on fused capillary column coated with CP-Sil 5.

Table 6: Percentage Pristane(Pr/C₁₇), Phytane(Ph/C₁₈) and Pristane/Phytane (C₁₇/C₁₈) ratio of Gulf Heavy crude oil samples separated using alumina and mixed silica-alumina stationary phase

Gulf Heavy crude	Stationary phase	%Pr/C ₁₇	%Ph/C ₁₈	Pr/Ph ratio
Saturates	Alumina	4.5	4.2	1.07
Aromatics	Alumina	7.6	4.4	1.73
Saturates	Silica-Alumina	1.9	3.0	0.63
Aromatics	Silica-Alumina	6.2	3.6	2.00