

GC-MS characterization of the aromatic fractions of Gulf heavy crude oil sample

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Abstract

This research work was carried out to separate crude oil (Gulf heavy) sample into four fractions by elution open column chromatography. A mixture of equal amount of silica and alumina was used as stationary phase. The aromatic fractions were characterized using Gas chromatography – Mass spectrometry (GC – MS). The total composition of aromatic constituents in the fraction was 10.6% and the most significant compound was naphthalene (4.1%). The mass spectra of the fraction also show the presence of aliphatic oxygenated compounds in the fraction. The predominant compound in this class was octadecanoic acid, 2-hydroxy-1-(hydroxyl methyl) ethyl ester (15.4%) which indicates an oxygen depositional environment for the source rock.

Key words: Crude Oil fraction, silica, alumina, aromatic

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1. Introduction

Crude oil is naturally occurring oil, bituminous liquid composed predominantly of various organic chemicals. It is found in large quantities below the surface of the earth and the products are used as fuels and as raw materials in the chemical industries [1,2]. It is also known to contain mixture of hydrocarbons including alkanes, naphthenes and aromatics and heteroatom compounds of sulphur, nitrogen and oxygen as well as trace metals [3-5].

The term aromatics refer to benzene and its structural derivatives. They are common to all petroleum and are often classify as mono-, di-, and polyaromatics depending, on the number of aromatic rings present in the molecule. Polar and higher molecular weight aromatics may fall in the resin or asphaltene fraction [6-9]. The average weight of aromatics in petroleum is 15% [10].

Despite the overall non-polar nature of crude oil, some heteroatom containing classes nevertheless exhibit water solubility. Therefore, it is reasonable that heterocyclic aromatic NSO-containing crude oil species should display similar water-solubility [11, 12]. Compared to all crude oil oxygen containing compounds (i.e. diols, aldehydes, esters e.t.c), carboxylic acids are most toxic because of their low volatility. Therefore, most oxygen containing compounds in crude oils are soluble in water [13]. Up to 3% w/w of crude oil may be acids, of which naphthenic acids are most abundant [14].

Odebunmi and Adeniyi [15] characterized crude oil, and petroleum product, fractions using infrared and ultraviolet visible spectroscopy. The infrared data confirmed the C=C stretching vibrations and C-H out of plane bending vibrations of aromatic in the mono-, di- and polyaromatic fractions. The characteristic UV spectra of alkyl benzenes and naphthalene were observed in the monoaromatic and diaromatic fractions as well as anthracene and phenanthrene in the polyaromatic fractions. Inimfon and Leo [16] employed gas chromatographic technique to analyse crude oil from an oil spillage site in Niger Delta, Nigeria. Polycyclic aromatic hydrocarbon (PAH) fractions were obtained in the oil sample. This shows that the aromatic fractions might have undergone combustion and/or that there was bush burning at the site prior to the oil spill incidence.

Gas Chromatography – Mass Spectrometry (GC-MS) technique was used to characterized n-hexane fraction of crude oil. The results 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 [17]. The same technique was also used to analyzed polynuclear aromatic hydrocarbons in sediment samples from the Niger Delta region of Nigeria [18]. Sixteen polyaromatic hydrocarbons among which were naphthalene, acenaphthalene, phenanthrene, anthracene and pyrene were found in most of the samples with concentrations ranging from 0.1µg/kg to 28µg/kg. The

results also indicate high concentrations of 5 and 6- ring PAHs among all the other compounds, indicating their high resistance to microbial degradation. In another report, the 16 polynuclear aromatic hydrocarbons were also found to be present in significant amount in the GC-MS analysis of fish, sediment and water samples of a fishing settlement in the Niger Delta region of Nigeria which is supposed to be extensively polluted by sea pages from oil discharge terminals [19].

In our earlier reports, crude oils and petroleum products had been fractionated using elution liquid chromatography. The fractions obtained were then characterized using gas chromatography [20] and infrared and ultraviolet spectroscopic techniques [15]. The need for the molecular analysis of crude oil help to give detailed knowledge of the chemical composition of the acidic components responsible for corrosion problems during refining. The present study therefore aims at separating a crude oil sample (Gulf heavy) and characterizing the aromatic fractions by GC-MS technique.

2. Materials and methods

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

2.2. 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, it was then carefully packed with mixed silical – aluminal stationary phase and prewetted with 25cm³ of n-hexane [15,21,22]. 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. It 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 [23] and it is a modification of other schemes reported in the literature [24-26]. The aromatic fractions were analyzed using Gas chromatography – Mass Spectrometry (GC-MS).

2.3. 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 x 0.32mm internal diameter; 1.0µm film thickness. About 1µL of each sample was injected by an auto sampler; the oven 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.

3. Results and Discussion

3.1. 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 sample using mixed silica-alumina stationary phase. The colours of the four fractions obtained were yellow, dark brown, dark brown and black for the saturates, mono -, di - and polyaromatics respectively. It was observed that the colour was deepens on proceeding from saturates to polyaromatics. This compared favourably well with the earlier reports in the literatures [15, 20, 21]. The results also revealed that fractions of elution open column chromatography can be characterized using colours.

3.2. Gas chromatography – Mass Spectrometry: The Kovats retention indices, relative percentages and identities of the constituents of the aromatic fractions (fraction II^b) obtained from the heavy crude oil sample separated using mixed silica-alumina stationary phase is presented in Table 2. The Table presents a total of 26 compounds representing 84.8% identified from their mass spectra. Four compounds (naphthalene, 1-methylnaphthalene, 2,4-bis (1,1-dimethyl) ethyl phenol, and 1,2-benzene dicarboxylic acid, diisooctyl ester) were identified as aromatics with a total composition of 10.6%. The most significant compound was naphthalene (4.1%). The results agreed with the earlier reports by Odebunmi and Adeniyi [15] when crude oil fractions were characterized by IR and UV spectroscopic techniques. The presence of 1-methyl naphthalene in the fraction also compared well with the literature [20].

Table 2 also presents the composition of the aliphatic oxygenated compounds obtained in the fraction of the oil. A total of six compounds that constitute 23.7% were identified from their mass spectra. The predominant compound was octadecanoic acid, 2-hydroxy-1-(hydroxyl methyl) ethyl ester (15.4%). It has been reported that most Nigerian crude oils are obtained at the oxygenated depositional environments [27-30]. The higher percentage of octadecanoic acid, 2-hydroxy-1-(hydroxyl methyl) ethyl ester in the crude oil analyzed therefore indicates oxidizing depositional environment for the source rocks.

4. Conclusions

The knowledge of the distribution of major structural classes of hydrocarbons in crude oil is needed in various fields in the petroleum industry such as studies related to reservoir evaluation, migration and maturity, degradation process, processing and environmental affects [31]. Oxygen containing compounds in crude oils have been reported to contribute to the total number of oil acids and are toxic to aquatic lives [32]. Among all the oxygen compounds in crude oils, carboxylic acids are the most toxic because they are less volatile and very soluble in water [13].

We therefore concluded based on the detailed characterization of the sample studied (Gulf heavy crude) using GC-MS technique, that aromatic and other oxygenated compounds in crude oils must be determined for industrial processing of petroleum.

Table 1: Colours of fractions of elution open column chromatography of crude oil (Gulf heavy) using mixed silica-alumina stationary phase

S/No	Sample	Fraction I saturates	Fraction II monoaromatics	Fraction III Diaromatics	Fraction IV polyaromatics
1.	Gulf (Heavy Crude)	Yellow	Dark Brown	Dark brown	Black

Table 2: Chemical composition (%) of constituents of fraction II^b (aromatic fraction) of heavy crude oil sample separated using mixed silica-alumina stationary phase

S/No	Compounds	% Comp.	Kovats RI ^b	MS Data
1.	Undecane	1.7	1146	127,98,85,71, <u>57</u>
2.	Naphthalene	4.1	1179	128,102,75,63, <u>51</u>
3.	Dodecane	3.1	1200	146,112,85,71, <u>57</u>
4.	1-methylnaphthalene	2.0	1298	<u>142</u> , 137,126,102,96
5.	Tridecane	5.2	1300	184,160,127,112, <u>57</u>
6.	Tetradecane	3.8	1400	155,141,113,85, <u>57</u>
7.	2-tetradecene (E)	1.7	1406	97,83,69, <u>57</u> ,55
8.	Pentadecane	4.4	1500	188,173,141,99, <u>57</u>
9.	Hexadecane	4.1	1600	226,169,113,99, <u>57</u>
10.	Heptadecane	6.2	1700	182,141,99,85, <u>57</u>
11.	Octadecane	3.6	1800	155,127,113,85, <u>57</u>
12.	2,6,10,14-tetramethyl pentadecane	2.4	1755	183,155,127,99, <u>57</u>
13.	2-pentadecanol	2.2	1690	125,111,69,55, <u>45</u>
14.	2,6,10,14-tetramethyl hexadecane	1.8	1804	282,144,99,71, <u>57</u>
15.	Pentadecanoic acid, 14-methyl methyl ester	3.2	1884	268,127,85,71, <u>57</u>
16.	Nonadecane	3.8	1900	167,127,99,85, <u>57</u>
17.	2,4-bis (1,1-dimethyl ethyl) phenol	2.3	1927	<u>191</u> , 175, 147, 128, 115
18.	Eicosane	2.4	2000	282,141,99,85, <u>57</u>
19.	I-Docosene	2.8	2194	252,179,83,69, <u>57</u>
20.	Octacosane	1.8	2800	155,127,113,85, <u>57</u>
21.	Tetratriacontane	1.7	3400	290,225,169,97, <u>57</u>
22.	Octadecanoic acid, methyl ester	5.6	2128	298,157,97,83, <u>74</u>
23.	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester	9.5		299,257, <u>239</u> ,213,196
24.	1,2-benzene dicarboxylic acid, diisooctyl ester	2.2		390,279,167, <u>149</u> , 113
25.	Octadecanoic acid, 2-hydroxy-1- (hydroxyl methyl) ethyl ester	15.4		365, 298, 267,210, <u>98</u>
26.	I-Eicosanol	1.8	2296	181,125,97, <u>57</u> ,43
	Total		84.4%	

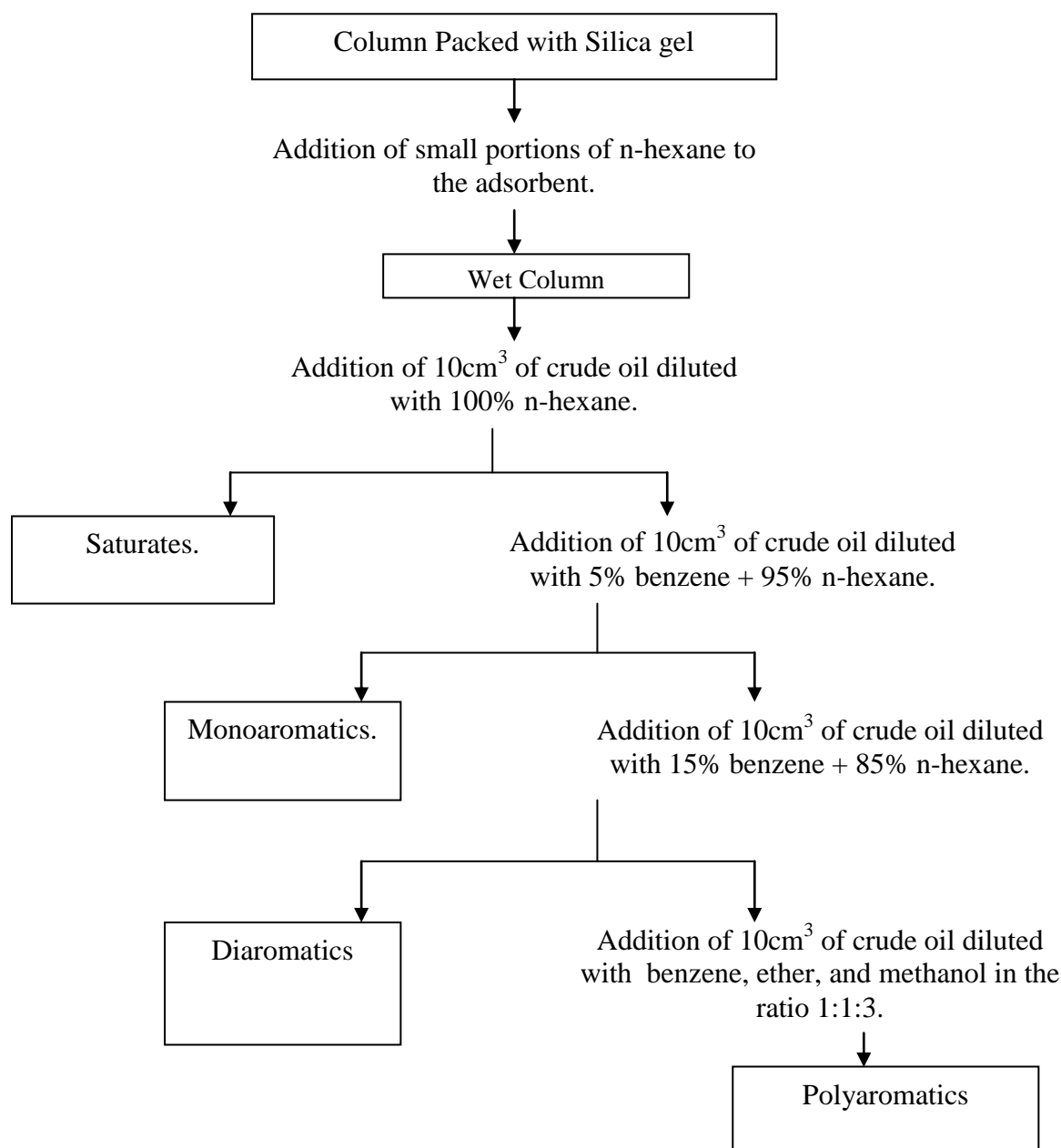


Fig. 1. Flow chart for chromatographic separation scheme [15].

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