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Comparison of aromatics released via hydropyrolysis with their solvent extractable counterpart for biodegraded Nigeria crude oil

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The molecular profiles of aromatics generated through hydropyrolysis with the free (maltene) counterpart were compared, with a view to assessing the effectiveness of using molecular information for the aromatics bound in asphaltene matrix for polycyclic aromatic hydrocarbon source apportionment studies. The results obtained from gas chromatograph-mass spectrometry (GC-MS) total and selected ion molecular profiles of free and bound aromatics for Nigeria crude oil shows that the solvent extractable aromatics has either been heavily biodegraded or covered by humic materials arising from microbial activity and will therefore need further purification to resolve the aromatic hydrocarbons present. However, the aromatics released via hydropyrolysis (trapped in asphaltene matrix) are still preserved. The molecular profile of asphaltene derived aromatics is highly dominated by both alkylated parent and parent polycyclic aromatic hydrocarbons such as methyl fluoranthene and pyrene, Benzo (b/k) fluoranthene.

Key words: Crude oil, aromatics, hydropyrolysis.

INTRODUCTION

The Niger Delta oil is a medium crude with American petroleum institute (API) gravity greater than 20.6° and is naphthenic, non-waxy with pour point less than -25°C (-13°F) (Evamy et al., 1978). Studies have revealed that oils from throughout the Delta are from one source type such that one super family of oils occurs in the Niger Delta (Haack et al., 1997; Rooney et al., 1998). The processing of crude oil into different components and the combustion of these components as fuel liberates hazardous chemical substances into the atmosphere such as polycyclic aromatic hydrocarbons.

When polycyclic aromatic hydrocarbons come in contact with biological entities in particular and the environment in general, it carries negative consequences, given that they are genotoxic (have harmful effect on genes) and they could find their way into the atmosphere as aerosols or other forms in soil, water, or come directly in contact with man, other animals and

plants. Jones et al. (1989) reported a steady increase in the polycyclic aromatic hydrocarbon content of an agricultural soil over the last century.

Hydrocarbons are the principal constituents of petroleum, usually exceeding 75%. The proportions of minor constituents such as sulphur, oxygen, nitrogen compounds, the organometallic complexes; and the organic salts vary considerably according to the type of petroleum. The non-hydrocarbon heteroatom compounds form the greater part of certain heavy crude oils (Tissot and Welte, 1984).

Saeed and Al-Mutairi (2000) in a comparative study on the composition of polycyclic aromatic hydrocarbons (PAHs) in the sea water-soluble fractions of different Kuwaiti crude oils reported that the total polycyclic aromatic hydrocarbons in the water-soluble fractions ranged from 171 to 2176 µg/L. Naphthalene and its homologs formed the bulk of the polycyclic aromatic hydrocarbons (ranging from 88.4 to 97.5% of the total polycyclic aromatic hydrocarbons). Significant levels of fluorene, phenanthrene and their homologs were also present in all of the water-soluble fractions. Polycyclic aromatic hydrocarbons with molecular weight higher than

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than phenanthrene were also detected at very low concentrations.

However, where biodegradation of polycyclic aromatic hydrocarbons and biomarkers have occurred in analytical samples, a number of pyrolytic techniques can be used to generate molecular profiles for both correlation purpose and environmental studies, usually involving hydrous or anhydrous pyrolysis carried out in a closed system (Rubinstein et al., 1979; Larter, 1984; Cassini and Eglinton, 1986) as well as open system flash pyrolysis coupled with on-line identification of products.

A major drawback associated with these techniques is that they are notoriously poor at routinely providing quantitatively significant and /or generating biomarker/hydrocarbon data, which accurately reflects actual, compositions of biomarkers and hydrocarbons bound in asphaltene matrix (Murray, 2001). Asphaltene hydro-pyrolysis has been found formidable in providing reliable data for correlation studies (Murray, 2001).

Pyrolysis, at high hydrogen pressures (>10 mPa) has been developed as an analytical pyrolysis technique that possesses the exclusive ability to release high yields of bound biomarkers from petroleum source rocks (Love et al., 1995, 1997).

This paper therefore compares the molecular profiles of solvent extractible crude oil aromatics with that generated via hydro-pyrolysis to ascertain whether the later can be effectively used for oil, oil correlation and environmental studies, where it is impossible to obtain credible data from the former.

MATERIALS AND METHODS

The asphaltenes prepared from Nigeria crude oil by precipitation with 40-fold excess of n-heptane (Jones et al., 1988) were mixed with sand or silica in the proportion of 50 mg of asphaltene to 1 g of silica. The mixture is then impregnated with an aqueous methanol solution (20% v/v) of ammonium dioxodithiomolybdate catalyst to give a nominal solution of 3-wt %. The catalyst was prepared by slow addition of ammonium heptamolybdate to ammonium sulphide solution. The heptamolybdate salt was then dissolved using a magnetic stirrer and solution stirred until a precipitate of ammonium dioxodithiomolybdate is formed. The precipitate was collected with the aid of a Buchner funnel and dried in a vacuum oven. The purpose of the ammonium dioxodithiomolybdate catalyst is to aid the release of aromatics trapped in asphaltene matrix, precipitated from the Nigeria crude oil. The sample is then dried in a vacuum oven at 60 to 70°C after which it is placed in a reactor tube. When attached to the hydro-pyrolysis set-up, it is resistively heated from ambient temperature (50 to 250°C) at 300°C min⁻¹, then to 500°C at 8°C min⁻¹ maintaining a hydrogen pressure of 15 mPa and a flow rate of 10 dm³min⁻¹. The liquid hydro-pyrolysate is then collected in a trap cooled with dry ice and recovered with dichloromethane (2 to 5 ml) for subsequent separation into aliphatic, aromatic and polar hydrocarbon components (Love et al., 1995; Murray, 2001; Meredith et al., 2004; Ivwurie et al., 2011).

The dichloromethane-soluble Nigeria crude oil and the hydro-pyrolysis product were dried, weighed and separated by silica gel adsorption chromatography into aliphatic, aromatic and polar fractions by successive elution with hexane to eliminate the aliphatics, dichloromethane-Hexane mixture (20% v/v) for the

removal of the aromatic components and dichloromethane/methanol mixture (50% v/v) to obtain the polar hydrocarbon components.

Characterization of polycyclic aromatic hydrocarbons was carried out by comparing the sample gas chromatograph-mass spectrometry trace with standard containing 16 polycyclic aromatic hydrocarbons listed by United States environmental protection agency.

Gas chromatography-mass spectrometry analysis was performed on a Fisons instruments 8000 gas chromatograph interfaced to a MD 800 mass spectrometer with a quadrupole mass analyzer (ionizing energy 70 eV, source temperature 280°C). The gas chromatograph capillary column is 50 m long; internal diameter is 0.32 mm and a film thickness of 0.25 µm, stationary phase is polyphenylmethylsiloxane. Laboratory base software written by VG was used for data acquisition and mass lynx for interpretation.

RESULTS

The total ion chromatogram for both solvent extractible and asphaltene derived polycyclic aromatic hydrocarbons from the Nigeria crude oil has been presented in Figure 1. Aromatics detected represent polycyclic aromatic hydrocarbons present in sample or co-eluting at similar retention time.

Selective ion resolution profile, m/z 202, 228 and 252 corresponding to fluoranthene/pyrene, Benzo(a)anthracene/ chrysene, and Benzo(b/k)fluoranthene/Benzo(e)pyrene, respectively are also presented in Figure 2. Whereas, a neat resolution was obtained for the asphaltene derived aromatics, the solvent extractible aromatics were not resolved, being dominated by unresolved complex mixtures (UCM).

Diagnostic ratios for alkylated parent and parent polycyclic aromatic hydrocarbons are computed in Table 1. These ratios correspond to the ratios of peak areas obtained from the gas chromatogram of the aromatics shown in Figure 1. Diagnostic ratios are used to detect the sources of polycyclic aromatic hydrocarbons (Sun, 2001).

DISCUSSION

The efficacy of using hydro-pyrolysis for hydrocarbon source apportionment was tested using biodegraded Nigerian crude oil. The gas chromatogram for the free aromatic fraction of the Nigerian crude oil was dominated by unresolved complex mixture arising from severe biodegradation, which had taken place in the solvent extractible aromatics. Both aromatics were obtained from the Nigeria crude oil. This unresolved complex mixture usually arises from the accumulation of humic materials formed from the biodegradation process (Tissot and Welte, 1984) (Figure 1). However, the gas chromatograph profile obtained from asphaltene hydro-pyrolysis aromatics shows complex distribution of aromatics dominated by both alkylated and parent polycyclic aromatic hydrocarbons, consistent with gas

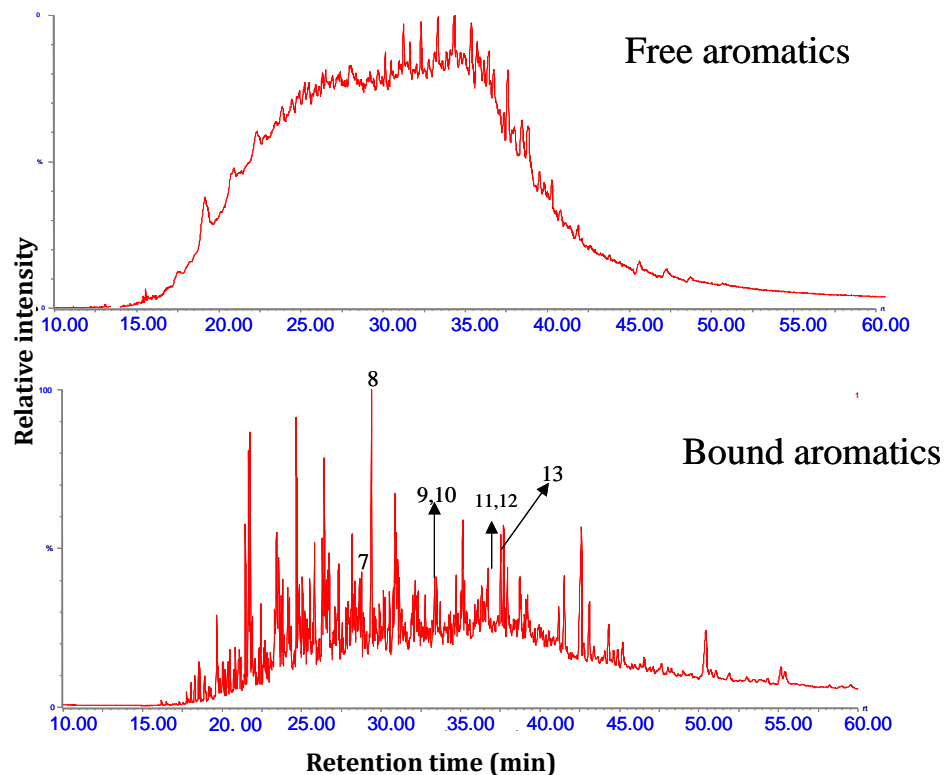


Figure 1. Total ion chromatogram for free and bound neutral aromatics from Nigeria crude oil. Key: 7 - Fluoranthene; 8 - Pyrene; 9 - Benzo(a)anthracene; 10 - Chrysene; 11 - Benzo(b)fluoranthene; 12 - Benzo(k) fluoranthene.

chromatographic profiles for crude oil generally (Tissot and Welte, 1984; Ivwurie et al., 2011). Alkylated parent polycyclic aromatic hydrocarbons such as methyl phenanthrene and fluoranthene, fluoranthene, pyrene and higher molecular weight polycyclic aromatic hydrocarbons were detected in the gas chromatographic profile of the asphaltene derived aromatics. This could not be found in the solvent extractible aromatic gas chromatographic profile of the Nigeria crude oil (Love et al., 1995).

Table 1 gives the diagnostic ratios for a few alkylated and parent polycyclic aromatic hydrocarbons from the bound aromatics for the Nigerian oil. No ratios could be calculated for the solvent extractible aromatics since polycyclic aromatic hydrocarbons could not be detected by the gas chromatograph due to severe biodegradation. Diagnostic ratios of 0.15, 0.09, 0.77 and 0.48 were obtained for fluoranthene (fluoranthene + pyrene), methylphenanthrene/phenanthrene, methylfluoranthene/fluoranthene, and Benzo(e)pyrene/ (Benzo(e)pyrene + Benzo(a)pyrene, respectively. The diagnostic ratios for the free sample could not be computed due to unresolved complex mixture (UCM). The ratios obtained in Table 1 are within the range reported by Tissot and Welte (1984) and Masclat et al. (1987) for crude oil.

Selective ion m/z 202, 228 and 252 resolution corresponding to fluoranthene/ pyrene,

Benzo(a)anthracene/ chrysene and Benzo(b/k) fluoranthene/Benzo(e)pyrene profiles of the free and bound aromatics obtained from gas chromatograph-mass spectrometer has been further compared in Figure 2. Selective ion resolution in gas chromatography-mass spectrometry is usually employed for both qualitative and quantitative treatment of chemical species of analytical interest (Love et al., 1997; Meredith, 2004). In this report, it was used to detect the presence of parent polycyclic aromatic hydrocarbons with m/z of 202, 228 and 252. Whereas, in the free aromatics, large hump corresponding to unresolved complex mixtures are seen, parent polycyclic aromatic hydrocarbons are well resolved in the asphaltene derived aromatics. This is consistent with the report of Love et al. (1998) and Murray (2001), that hydrolysis of asphaltene can provide credible data for correlation studies where signatures of the free (solvent extractible product) profile has been altered.

Conclusion

This paper compared the molecular distribution of free and bound aromatics from the Nigeria crude, as a primary source. Both the free and asphaltene derived aromatics were compared for the purpose of building

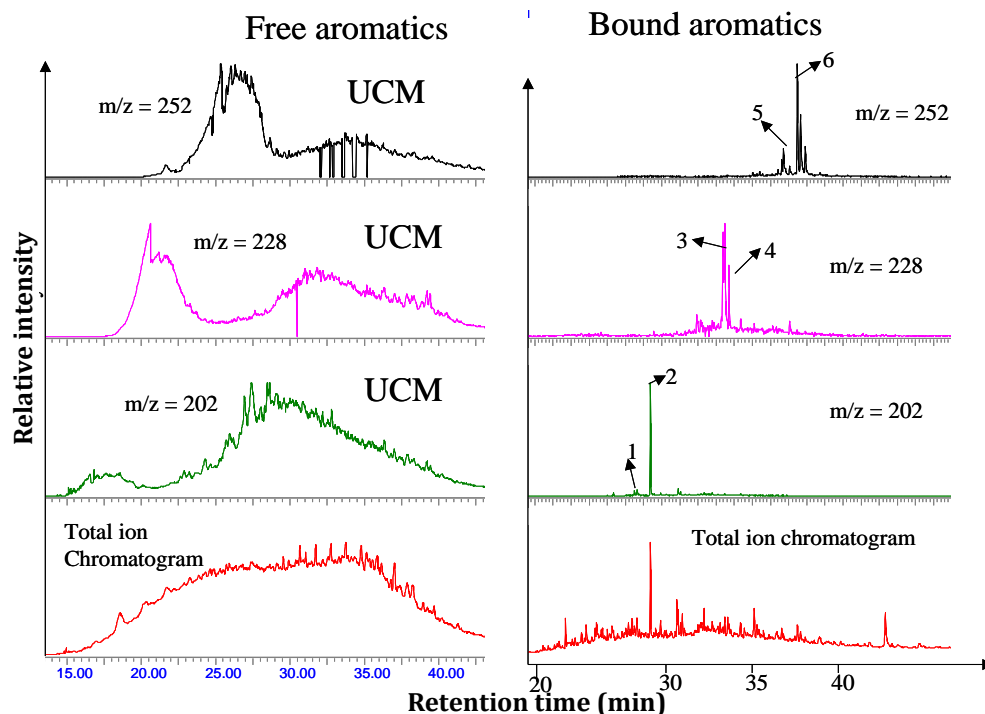


Figure 2. Comparison of GC-MS fragmentograms for m/z , 202, 228, 252 Nigeria crude oil PAHs (free and bound). Key: 1 - Fluoranthene; 2 - Pyrene; 3 - Benzo(a)anthracene; 4 - Chrysene; 5 - Benzo(b/k)fluoranthene; 6. Benzo(e)pyrene.

Table 1. Polycyclic aromatic hydrocarbon diagnostic ratios for Bound Nigeria crude oil aromatics.

Diagnostic ratio	Bound PAHs
Fl/(fl+py)	0.15
MePh/Ph	0.09
MeFl/fl	0.77
BeP/(BeP+BaP)	0.48

Values in the table represent ratios of peak areas of PAHs/alkyl derivatives.

credible molecular database for source apportionment.

The Nigeria crude oil aromatics were dominated by unresolved complex mixtures arising from biodegradation, but those obtained from asphaltene hydrolysis were well resolved, showing the presence of both alkylated and parent polycyclic aromatic hydrocarbons from their gas chromatographic profile and the diagnostic ratios computed. The free Nigeria oil has been heavily biodegraded, but the asphaltene derived, well preserved.

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