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Comparison of Nigeria Crude Oil Solvent Extractible and Bound Biomarker Distribution for Correlation Studies

Ivwurie W.[1], Snape C.E.[2] and Sun C.[2]

Department of Chemistry, Federal University of Petroleum Resources,
Effurun, Delta State
Nottingham Fuel and Energy Centre, the University of Nottingham,
University Park, Nottingham, United Kingdom.
**Corresponding Author E-mail: wivwurie@yahoo.co.uk*

Abstract

Solvent extractible and bound biomarker profile for Nigeria crude oil were compared using GC-MS with a view to ascertaining whether data for asphaltene-derived biomarker can be used for effective correlation studies, where serious alterations arising from biodegradation and other environmental factors affect the use of the solvent extractible ones The results obtained shows that the free Nigeria crude oil aliphatics has been heavily biodegraded with the loss of n-alkanes and isoprenoids, but the asphaltene derived is well preserved. For both the free and asphaltene-derived aliphatics, the R isomers have higher abundance than their corresponding S isomer for the steranes at C_{27} and C_{28}, indicating that the steranes have not been biodegraded. The major difference between the free and bound hopanes is that the former is more matured than the latter, this is a general trend found for most hydropyrolysis products.

Keywords: Biomarker, crude oil, asphaltene

Introduction

Biological markers are organic compounds that have an established biological origin, and exhibit little or no change in chemical structure from their parent precursor compound found in living organisms.

They can be used as signatures of organic matter sources (Azevedo *et al.*, 1999; Kavouras *et al.*, 1999).

There are diverse biomarkers; the most studied classes are the aliphatic hydrocarbons. These molecular markers have been employed either in isolation or joined with other molecular distributions or information as confirmatory indicators for petroleum residues, higher plant wax, resin residues and for petrogenic components (1, 2, 3, 4). For instance, the 17α(H), 21β(H)-hopanes, the extended triterpanes, the steranes and the isoprenoids (pristane and phytane) have been used for this purpose.

The distribution signatures of hopanes, which are normally present in low concentrations, can be determined by GC-MS using the m/z 191 ion intensity, the base peak of most of the triterpanes and the extended tricyclic terpanes. The identification of hopanes suggests an input from fossil fuel utilization (i.e. vehicular emission)(1, 2, 3, 5). Other biomarkers commonly found in petroleum often in lower concentrations than hopanes, are steranes and diasteranes. They are not found in contemporary biogenic materials. They can be identified by GC-MS spectra using m/z 217 and 218. Steranes get into the atmosphere through vehicular emissions, and are thus used as signatures for petroleum-derived input. The chemical distribution of alkanes can provide useful information for source apportionment. When the odd-to-even carbon number predominates, it is indicative of biogenic alkanes. Organic matter of recent biological origin typically has CPI values of 6-9 or even higher. In general, CPI values higher than 3 indicates that the n-alkanes are predominantly from biological materials. However, CPI values for petroleum, vehicular emissions and coal utilizations are much closer to unity (1, 6).

However a major constraint to obtaining reliable information during source apportionment is when aliphatic hydrocarbons have been heavily biodegraded. This makes it difficult to obtain compositional information to carry out reliable source apportionment studies.

Love *et al* (1997) (7) reported that the molecular integrity of biomarkers is well preserved in asphaltene when they are released through hydropyrolysis. If biodegradation of solvent extractible biomarkers constitute a constraint to reliable source apportionment studies, information obtained from the asphaltene derived counterpart, which is well preserved, can significantly aid source apportionment.

This research papers compares the solvent extractible with bound biomarker profile for Nigeria crude oil with a view to ascertaining whether data for asphaltene-derived biomarker can be used for effective correlation studies, where serious alterations arising from biodegradation and other environmental factors affect the use of the solvent extractible ones.

Methods

Biodegraded Nigeria crude oil sample was fractionated using open column chromatography to obtain aliphatic fraction from which different biomarkers were investigated. Asphaltenes were obtained from low temperature coal tar by precipitation with 40-fold excess of n-heptane (8). The asphaltenes were mixed with silica in the range of 10-50 mg of asphaltene to 1 g of silica. The mixture is then impregnated with an aqueous methanol solution (20 %v/v) of ammonium dioxydithiomolybdate 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 dioxydithiomolybdate is formed. The precipitate was collected with the aid of a Buchner funnel and dried in a vacuum oven. The sample is then dried in a vacuum oven at 60-70°C after which it is placed in a reactor tube. When attached to the hydropyrolysis set-up, it is resistively heated from 50 °C to 250°C at 300°C min^{-1}, then to 500°C at 8° min^{-1} maintaining a hydrogen pressure of 15 mPa and a flow rate of 10 dm^3min^{-1}. The liquid product is then collected in a trap cooled with dry ice and recovered with dichloromethane (2-5 ml) for subsequent separation (9, 10).

The biomarker distribution for the solvent extractible (free) and hydropyrolysis products (bound) were compared using GC-MS on a Fisons instruments 8000 gas chromatograph interfaced to a MD 800 mass spectrometer with a quadrupole mass analyzer (ionizing energy 70eV, source temperature 280° C). The gas chromatograph capillary column is 50 m long; i.d. is 0.32 mm and a film thickness of 0.25µm, stationary phase is polyphenylmethylsiloxane.

Results and Discussion

Biodegraded Nigeria crude oil was investigated in this comparative study.

The Gas Chromatographic profiles for Nigeria crude oil aliphatics (free and asphaltene-derived products) is presented in Figures 1.

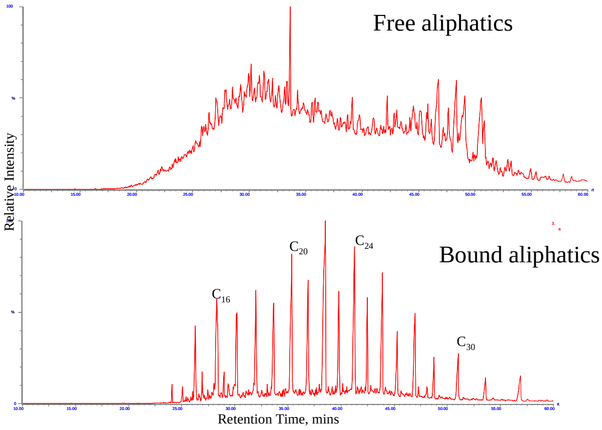

Figure 1 : Total ion chromatogram of aliphatic hydrocarbons from the Nigerian crude oil

The Nigerian crude oil free (solvent extractible or maltene fraction) aliphatic hydrocarbons have been biodegraded as can be seen from the chromatogram in Figure 1. The molecular profile is dominated by unresolved complex mixtures (UCM). The alkanes and isoprenoids have been biodegraded in the free aliphatics, but this is either in low concentration or not present in the bound (see figure 1).

The level of biodegradation was ascertained as 5.0 using the Peter and Moldowan biodegradation scale. This implies loss of n-alkanes and isoprenoids (11).

The distribution of the aliphatics generated from asphaltene hydropyrolysis of the oil was found to be preserved (not biodegraded) and provided clear information about the molecular profile. The Nigeria crude oil asphaltene-derived aliphatics contains n-alkanes up to n-C_{32} with a carbon preference index (CPI) value of 0.9. (1, 6) The alkanes present in the Nigeria crude oil show a bimodal distribution.

The large unresolved complex mixtures (UCM) present in the free (maltene or solvent extractible) aliphatic hydrocarbons in the Nigerian crude oil is thought to be due to biodegradation (12).

The ratios for steranes and hopanes have been compared in Table 1 and Figures 2 and 3. The 29ααα S/S+R sterane maturity ratios for the asphaltene-derived and free are 0.27 and 0.19, respectively.

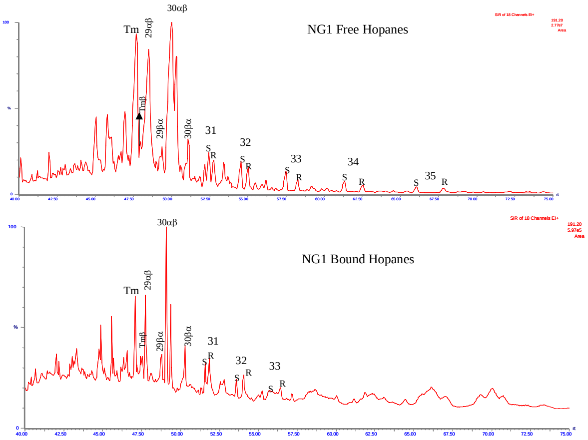

Figure 2 m/z 191 (hopane) fragmentograms for Nigeria crude oil aliphatics (free and bound)

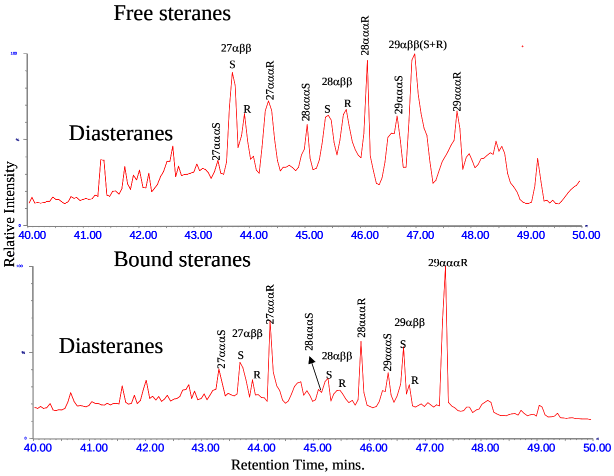

Figure 3 m/z 217 fragmentograms for Nigeria crude oil free and bound aliphatics

Table 1 : Sterane and hopanes ratios for free and asphaltene-derived constituents from Nigerian crude oil

Biomarker	NG free biomarker ratio	NG asphaltene-derived biomarker ratio
29βα/αβ Hopane	0.17	0.32
30βα/αβ Hopane	0.20	0.44
31αβ S/S+R Hopanes	0.50	0.34
29αααS/S+R Sterane	0.27	0.19

NG means Nigeria crude oil; values represent ratios of peak areas of biomarkers

For both the free and asphaltene-derived aliphatics, the R isomers have higher abundance than their corresponding S isomer for the steranes at C_{27} and C_{28}, indicating that the steranes have not been biodegraded (11). However, the major difference between the free and bound hopanes is that the former is more matured than the latter. Whereas in the free oil, the S configuration dominates, in the asphaltene-derived C_{31}, C_{32}, and C_{33} hopanes the R isomer has higher abundance relative to the S, suggesting immaturity. This has been further supported by the 31αβ S/S+R hopanes in which the free had value of 0.50, while the asphaltene-derived had a value of 0.34. The C_{34} and C_{35} are still immature (11).

Conclusion

The free (maltene derived) and asphaltene derived aliphatics were compared in terms of mol to build a molecular/biomarker database for source apportionment and geochemical studies. The free Nigeria oil has been heavily biodegraded with the loss of n-alkanes and isoprenoids, but the asphaltene- derived is well preserved. For both the free and asphaltene-derived aliphatics, the R isomers have higher abundance than their corresponding S isomer for the steranes at C_{27} and C_{28}, indicating that the steranes have not been biodegraded. However, the major difference between the free and bound hopanes is that the former is more matured than the latter.

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