Egyptian Journal of Petroleum xxx (2017) xxx–xxx

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Contents lists available at ScienceDirect

Egyptian Journal of Petroleum

journal homepage: www.sciencedirect.com

Full Length Article

# Assessment of n-alkanes and acyclic isoprenoids (geochemical markers) in crudes: A case study of Iraq and Niger delta, Nigeria

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ARTICLE INFO

*Article history:*
Received 20 October 2016
Revised 20 December 2016
Accepted 24 January 2017
Available online xxxx

*Keywords:*
Assessment
n-Alkanes
Acyclic isoprenoids
Pristane
Phytane
Maturity

ABSTRACT

This study was designed to determine the ratios of the isoprenoids and n-alkanes in an imported crude oil sample (Bassrah from Iraq) and four crude oil samples (Bodo, Bonny-Export, Escravos and Penningston) from the Niger Delta region of Nigeria to ascertain the levels of maturity and as an indicator of the depositional environment of the crudes. The physical properties of the crudes: viscosity, density and °API gravity were also determined. Fractionation of the crudes was done using a new approach coded NAASAR, (n-alkanes, asphaltenes, aromatics and resins) comprising urea adduction followed by gas chromatographic analyses (for n-alkanes), n-heptane precipitation (for asphaltenes) and column chromatography (for resins). Results showed °API gravities Bassrah 28.03°, Bodo 31.89°, Bonny-Export 33.8°, Escravos 33.8°, and Penningston 33.8° indicating that Escravos, Penningston and Bonny-Export crudes are light crudes while Bodo and Bassrah crudes are medium crudes. The n-alkanes profiles of the five crudes were determined by gas chromatography ranged from n-$C_8H_{18}$ to n-$C_{40}H_{82}$ with total weight percent n-alkane yield Bassrah 11.2, Bodo 47.41, Bonny-Export 32.47, Escravos 5.58, Penningston 30.75 were obtained by urea adduction. The pristane to phytane ratios were computed, Bassrah 1.51, Bodo 1.48, Bonny-Export 1.08, Escravos 1.01 and Penningston 2.41. Isoprenoids to n-alkane ratios Pr/n-$C_{17}$ in the same order of the crudes were 0.85, 0.83, 0.67, 0.65, 0.95 while phytane to n-$C_{18}$ ratios were 0.61, 0.55, 0.62, 0.61 and 0.43. The results established the increasing level of maturity as obtained from Pr/n-$C_{17}$ ratio in the order: Penningston < Bassrah < Bodo < Bonny-Export < Escravos. The result of Pr/Ph ratios show the same trend in the level of maturity. Penningston crude with Pr/Ph ratio 2.41 shows that the crude is deposited in fluviomarine and coastal swamp environment while Bassrah, Bodo, Bonny-Export and Escravos crudes indicate aquatic depositional environment (anoxia) condition.



## 1. Introduction

Petroleum biomarkers are "molecular fossils". They are complex hydrocarbon molecules that retain a remarkable structural similarity to the original natural product formed from dead organisms in the source rock [1]. Therefore, each crude oil has a unique fingerprint that can potentially be determined using biomarkers. Biomarkers are the most important hydrocarbon groups in petroleum because they can be used for chemical fingerprinting which provides unique clues to the identity of source rocks from which petroleum samples are derived. Also, biological sources of organisms which generated the organic matter, the environmental conditions that prevailed in the water column and sediment at that time, the thermal history (maturity) of the crude oil, and the degree of microbial biodegradation [2] are ascertained. Thermal maturity of crude oil is when the heavy components in crude oil (nitrogen, sulphur and oxygen, NSO compounds and heavy saturates and aromatic compounds) have undergone cracking to form light hydrocarbons during thermal changes in the generation of the oil.

The analysis of crude oil for °API gravity, the biomarkers such as pristane (2,6,10,14-tetramethylpentadecane) to phytane (2,6,10,14-tetramethylhexadecane) ratio and isoprenoids/n-alkanes (Pr/n-$C_{17}$ and Ph/n–$C_{18}$ ratio are necessary and are used to ascertain the levels of maturity and as an indicator of the deposition environment of the crudes.

Crudes with °API of 40–45° gravity are generally classified as very light crudes, 34–39° as light crudes, 22–23° as medium crudes while less than 22° are classified as heavy crudes [3]. Fractionation method was employed using a new approach coded NAASAR, (n-alkanes, asphaltenes, aromatics and resins) followed by gas chromatographic analyses of the n-alkanes.

Peer review under responsibility of Egyptian Petroleum Research Institute.

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http://dx.doi.org/10.1016/j.ejpe.2017.01.005
1110-0621/

Please cite this article in press as: C.A. Nwadinigwe, T.N. Alumona, Assessment of n-alkanes and acyclic isoprenoids (geochemical markers) in crudes: A case study of Iraq and Niger delta, Nigeria, Egypt. J. Petrol. (2017), http://dx.doi.org/10.1016/j.ejpe.2017.01.005

Geochemical studies on oils from south western Niger Delta had been carried out by many workers. L.C. Osuji [4] worked on multivariate analysis of source rock and maturity biomarker indices of crude oils. C. Enogwe et al. [5] worked in Geochemical correlation of crude oils in the North Western Niger Delta, M.C. Onojake et al. [6] concluded that the crude oil from South Western Niger Delta originated from terrestrial organic sources deposited in an oxic paleoenvironment.

Although, biomakers correlation studies had been done on Nigeria crudes [4–6] but this present study aims to determine the n-alkane profiles of five different crudes, the diagnostic ratios of their acyclic isoprenoids and hence ascertain the degree of maturity and depositional environments of the crudes.

## 2. Materials

The five crude oil samples used for this study viz: Escravos (sourced from Western Niger Delta) Bodo, Bonny-Export, Penningston (sourced from Eastern Niger Delta) and Bassrah (imported crude from Iraq) were obtained from the Research and Development Division of the Nigerian National Petroleum Corporation (NNPC), Port-Harcourt and Kaduna, Nigeria.

## 3. Methodology

Physical properties of the crude oils.

The physical properties of the crude oils were determined using ASTM methods, i.e. density, specific gravity (ASTM D1298-95), API gravity (ASTM D287-92) and viscosity (ASTM D 445-01).

### 3.1. Extraction of n-alkanes by Urea-adduction method

In the urea-n-alkane adduction procedure, the weighed crude (Mettler H315) was poured into a reaction vessel and diluted with a calculated volume of dichloromethane ($CH_2Cl_2$) to obtain a viscosity of 1.5 $mm^2/s$. The diluted samples were mixed at room temperature (30 °C) with an equal weight of urea activated with 4% aqueous methanol ($CH_3OH$). The mixture was stirred for 60 min at 1400 r.p.m using a mechanical laboratory stirrer (Heldolph RZ-RI n-280-2200/35-250). The content was filtered with the suction pump. The residue, solid urea-n-alkane adduct was washed with benzene (100 ml) and then decomposed with warm water at 60 °C in a separatory funnel to give semi-solid/solid n-alkanes (upper layer) and an aqueous (lower) layer which was carefully drained off. The n-alkanes were melted, kept at 75 °C and mixed with 1 g of anhydrous granular calcium chloride ($CaCl_2$) to remove traces of water. The hot mixture was then centrifuged at 2000 r.p.m for 3 min to separate the n-alkanes from the $CaCl_2{\cdot}XH_2O$ precipitate. The decanted n-alkanes were cooled and weighed [7].

### 3.2. Analysis of the extracted n-alkanes by gas chromatography

Gas chromatography (GC) was performed using GC Model Agilent 6980 and HP-5 columns. The method of analysis was United States Environmental Protection Agency (USEPA) 8270. Injection volume was 3 µl with helium as the mobile phase and flame ionization detector (FID), injection and detection temperatures were 250 °C and 340 °C respectively.

**Table 1**
Some physical properties (viscosities, densities, °API gravities and kinematic viscosities) of the crudes.

| Crude Sample | Viscosity (centistokes) | Density g/$cm^3$ | °API gravity (Degrees) | Kinematic viscosity $mm^2$/sec. |
|---|---|---|---|---|
| Escravos | 4.48 | 0.856 | 33.8 | 5.23 |
| Penningston | 6.54 | 0.856 | 33.8 | 5.36 |
| Bonny Export | 8.40 | 0.866 | 33.8 | 6.97 |
| Bodo | 9.11 | 0.856 | 31.9 | 8.82 |
| Bassrah | 19.52 | 0.887 | 28.0 | 18.52 |

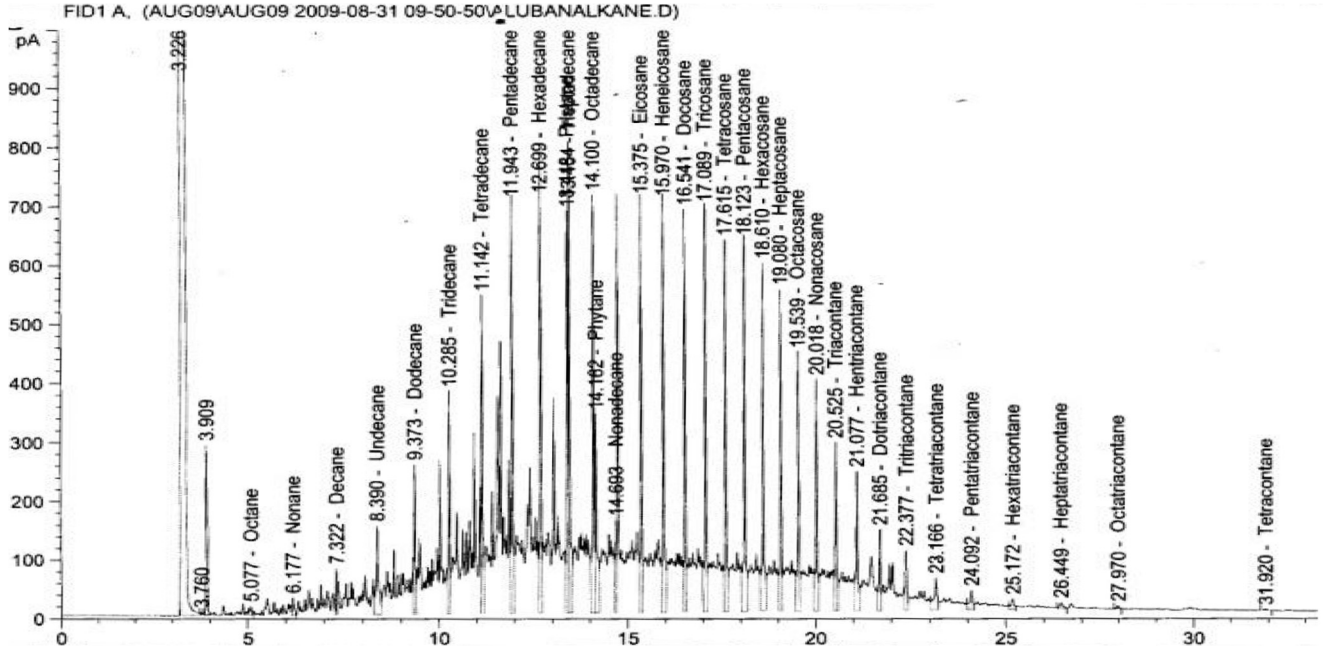


**Fig. 1.** Chromatographic peaks showing different n-alkanes in Bassrah Crude.

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