

# Evaluation of Crude Oil Thermal Maturity from Some Oil fields in Niger Delta, Nigeria \*Oraegbunam Charles, Osuji Leo, Onojake Mudiaga

Petroleum Chemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria. \*Corresponding author: oray2k7@yahoo.com

# ABSTRACT

Niger Delta region of Nigeriais is a hub for huge deposits of hydrocarbons. Five crude oil samples collected from Azuzuama, Clough creek and Tebidaba oil fields were analyzed to ascertain their degrees of thermal maturity. The studied oils were fractionated by column chromatography into saturated hydrocarbon and aromatic compounds. Gas chromatographymass spectrometery (GC-MS) was used to analyze the saturated/aliphatic hydrocarbons. Hopane and sterane ratio results indicated that  $\alpha\alpha\alpha$  C<sub>29</sub> isomerization ratios ranged from 0.33 – 0.40 which was evidence of thermal maturity. There is also a similar maturity trend for Ts/Ts+Tm ratios ranging from 0.40- 0.55 and C<sub>31</sub> Hopane Isomerization ratio range of 0.50 – 0.60, which also was evidence of oil generation from an early-mature to mature source rock. The C<sub>29</sub> $\alpha\alpha\alpha$  Steranes and Ts/Ts+Tm ratio supports a moderate maturity levels for the five sampled oils. **Keywords:** Biomarker, crude oil, hopanes, Niger Delta, steranes, thermal maturity.

# **INTRODUCTION**

Biomarker parameters are useful in assessing the thermal maturity of crude oils and this thermal maturity points to the thermal history of oils [1,2]. Hopanes and steranes are used as maturity assessment parameters [2, 3].

Terpanes, hopanes and steranes are characteristic organic matter fingerprints [4, 5]. This further shows the practical application and usage of biomarkers in interpreting the thermal maturity for organic source matter [3, 6].

Farrimond *et al* [7] stated that before an oil window onset, the maturity parameters approach their equilibrium level and often substantiate a high maturity level inversions and this disqualifies them as maturity indicators. According to Radke [8], maturity parameters of aromatic hydrocarbons are sensitive to changes in maturity especially in the mid- to- late parts of the generation window.

Living organisms were counted as the biological origin of biomarkers. They are resident in rocks whose carbon structure is connected to a formerly living organism. Biomarkers are termed "biological markers". Petroleum geochemists have been utilizing biomarker fingerprinting in the crude oil characterization for correlation of oils with their environment of deposition, organic source input, crude oil thermal maturity and biodegradation levels [3].

This paper examines the geochemical parameters of three oil fields (five crude oil samples) within Bayelsa State, Nigeria to characterize and deduce their maturity levels.

Given below are the structures of some biomarkers found in crude oil.





Figure 1: Molecular structures of some biomarkers found in crude oil

# MATERIAL AND METHODS

## **Sample Collection**

The studied samples were collected from well heads at Azuzuama, Tebidaba and Clough Creek fields in Bayelsa State, Nigeria (Figure 2) and are representatives of the oil bulk.





http://www.unn.edu.ng/nigerian-research-journal-of-chemical-sciences/

The samples were collected from Azuzuama, Clough Creek and Tebidaba fields and were labeled: AZU ST, WELL 2, TEB 12, TEB 08 and CCST. These samples were retained in a glass vials and stored in a refrigerator for preservation till when needed for analysis.

## **Samples Preparation**

30 mg of the oil sample was transferred to a 2 ml bottle with Teflon lined plastic cork, and diluted with 1 ml dichloromethane. The oil samples were fractionated and subjected to Gas Chromatography-Mass Spectrometry analysis. Abrakasa [9] outlined the procedures used for the fractionation of oil samples and these were followed in the study.

The saturated fractions were subjected to Gas Chromatography analysis using HP389OGC serial II, separation performed in a silica capillary column (30 m x 0.25 mm id.) coated with 0.25  $\mu$ m, 5 % phenyl methyl silicone (HP—5) by HP (Agilent HP389OGC, United Kingdom). Hydrogen gas was used as carrier gas at 2 ml/min with a spilt/splitless injector, the temperature at 50 °C for 2 mins then progressed at 4 °C/min to 300°C at which it was held for 20 mins.

Procedures and conditions for the GC-MS analysis were carried out as outlined by [10] at Giolee Global resources Limited.

# **RESULTS AND DISCUSSION**

Table 1: Thermal maturity parameters in the studied oils using Gas chromatography- aass spectrometry

WELLS	C <sub>29</sub> /Tot.Sterane	$\alpha\alpha\alpha C_{29}S/S+R$	$S/S+R\alpha\beta C_{31}Hopane$	$Pr/nC_{17}$	Ph/nC <sub>18</sub>	Ts/Ts+Tm
AZU ST	0.45	0.33	0.56	1.52	0.69	0.40
CCST	0.54	0.40	0.56	1.09	0.44	0.53
TEB 12	0.59	0.39	0.60	1.64	0.68	0.49
<b>TEB 08</b>	0.49	0.33	0.49	1.04	1.01	0.47
WELL 2	0.51	0.36	0.56	0.73	0.52	0.43



Figure 3: Cross plot of Ts/Ts+Tmvs S/S+RαβC<sub>31</sub>Hopane indicating Maturity of the crude oils



Figure 4: Cross plot of aaaC<sub>29</sub>S/S+R Vs S/S+RaβC<sub>31</sub>Hopane



Figure 5: Chart showing Ts/ Ts+Tm distribution in the studied oils

Several biomarker parameters have been examined to estimate the thermal maturity of the studied samples (Tables 1), and to assess the effect of oil-oil correlations to thermal maturation.

In petroleum geochemistry, one of the widely applied maturity parameters is  $C_{29}$  aaasteranes. The aaa  $C_{29}$  isomerization ratio range from 0.33 - 0.40 (figure 4) of the studied samples show evidence of thermal maturity (evidence of peak oil generation onset). The studied oils are generated from an early-mature to mature source rock [3]. In contrast, low steranes and sterane/hopane ratios are more indicative of terrigenoussource organic input[11] showing the same level of maturation for the organic matter in the samples, a crude oil early-mature to mature window.These relationship and values of  $C_{29}$  sterane isomer support a moderate maturity levels for studied samples.

Though Ts/Tm is not appropriate for determining crude oil thermal maturity [12] but during maturation, it starts todecrease very late [13]. The studied samples (CCST & TEB 12) have a predominance of Trisnorneohopane (Ts) over Trisnorhopane (Tm). The predominance of Ts over

Tm is less pronounced in the AZU ST (Figure 5). Obviously, Ts/Ts+Tm ratios display maturity trends similar to  $S/(S + R\alpha\beta C_{31})$  hopane ratios. The studied samples have Ts/Ts+Tm ratios range from 0.40- 0.55 and C<sub>31</sub> Hopane Isomerization ratio range from 0.50 – 0.60 (figure 3) showing that the studied samples are moderately mature.

 $Pr/n-C_{17}$  and  $Ph/n-C_{18}$  are widely used source maturation indicators [3]. Due to increased prevalence of normal alkanes, the ratios of  $Pr/n-C_{17}$  and  $Ph/n-C_{18}$  decrease with maturation. Thermal cracking causes a decrease in the isoprenoid/n-alkane value with maturation. This results in the elimination of pristane and phytane and production of n-alkanes [14].  $Pr/n-C_{17}$  and  $Ph/n-C_{18}$  ratios in the studied samples are displayed in Table 1. These values show the moderate maturity levels for the studied samples.

# CONCLUSIONS

The geochemical appraisal of crude oil samples from different producing fields based on their component biomarkers were investigated and characterized. The thermal maturity of these oil samples were assessed using fingerprints generated from steranes and isoprenoids of aliphatic biomarkers. Thermal maturity parameters such as Ts/Ts+Tm,  $C_{29}\alpha\alpha\alpha$  Steranes and  $C_{31}$ hopanes in the studied samples showed an evidence of thermal maturity. Maturity estimates based on biomarker trends (Sterane /Hopane Isomerisation ratio) indicate that the studied samples are moderately mature.

## ACKNOWLEDGMENT

Authors sincerely appreciate Mr. Cashmoney Anyamalem of the Nigerian Agip Oil Company for supplying the samples used for this research. We are also grateful to Dr. Selegha Abrakasa of the Center for Petroleum Geosciences, University of Port Harcourt for his qualitative assistance in the course of this work.

## REFERENCES

- 1. Peters, K., Fraser, H., Amris, W., Rustanto, B. & Hermanto, E. (1999). Geochemistry of crude oil from eastern Indonesia, *AAPG Bulletin*, 83, 1927-1942.
- Seifert, W.K. & Moldowan, J.M. (1978). Application of steranes, terpanes and monoarornatics to the maturation, migration and source of crude oil, *Geochimica et CosmochirnicaActa*, 42, 77-95.

- 3. Peters, K. & Moldowan, J. (1993). The Biomarker Guide: Interpreting Molecular Fossils, inPetroleum and Ancient Sediments, Prentice Hall, New Jersey, p. 363.
- El-Sabagh, S. M., El-Naggar, A. Y., El Nady, M. M., Badr, I. A., Ebiad, M. A. & Abdullah, E. S. (2018). Fingerprinting of biomarker characteristics of some Egyptian crude oils in Northern Western Desert as evidence for organic matter input and maturity level assessment. *Egyptian Journal of Petroleum*, 27(2),201-208.
- 5. Volkman, J. K. (2006). Lipid markers for marine organic matter. In *Marine organic matter: Biomarkers, isotopes and DNA*. Springer, Berlin, Heidelberg. pp. 27-70.
- 6. Peters K., Walters C. & Moldowan, J.M. (2005). The Biomarker Guide. Cambridge University Press, UK, p 1155.
- 7. Farrimond, P., Taylor, A. & Telnaes, N. (1998). Biomarker maturity parameters: the role of generation and thermal degradation. *Organic Geochemistry*, 29(5-7), 1181-1197.
- 8. Radke, M. (1988). Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Marine and Petroleum Geology*, 5(3), 224-236.
- Abrakasa, S. (2006). Newly identified Molecular Marker Compound in Some Nigerian oils. Nigeria Journal of chemical Research11,15 – 21.
- Onojake, M. C., Abrakasa, S. &Osuji, L. C. (2015). Chemometric representation of molecular marker data of some Niger Delta crude oils. *Egyptian Journal of Petroleum*, 24(2), 139-143.
- Noriyuki, S., Masaru, S. &Kuniaki, T.(1996). Biomarker distributions in oils from the Akita and Niigata Basins, Japan, Alexander Chekhmakhchey. *Chemical Geology*. 133, 1– 14.
- Waples, D. W. & Machihara, T. (1991).Biomarkers for geologists-a practical guide to the application of steranes and triterpanes in petroleum geology (AAPG Methods in Exploration, 9). *Tulsa: American Association of Petroleum Geologists*. 129(6), 793.
- Van Graas, G. W. (1990). Biomarker maturity parameters for high maturities: calibration of the working range up to the oil/condensate threshold. *Organic Geochemistry*, 16(4-6), 1025-1032.
- Tissot, B., Califet-Debyser, Y., Deroo, G. & Oudin, J. L. (1971). Origin and evolution of hydrocarbons in early Toarcianshales, Paris Basin, France. AAPG Bulletin, 55 (12), 2177-2193.