International Journal of Scientific Research and Engineering Development-– Volume 2 Issue 4, July – Aug 2019

Available at www.ijsred.com

RESEARCH ARTICLE OPEN ACCESS

Geochemical Analysis of Similarities in the Crude Oil Samples of the Coastal Swamp Depobelt of Niger Delta

Ezidiegwu P.C., *, Abrakasa S., *Ozumba B.M*Ikiesikiemama S.S

*(African Centre of Excellence, World Bank Centre for Oilfield Chemicals Research,
University of Port Harcourt
ezidiegwu.pamela@aceuniport.org)
* (Geological Sciences, University of Port Harcourt
sele.abrakasa@googlemail.com)
*Physics/Geology/Geophysics, Alex Ekwueme Federal University Nfufu Alike
Bertram.ozumba@sbcglobal.net
*(Petroleum Engineering, University of Port Harcourt
sunday.ikiensikimama@uniport.edu.ng)

----------**********----------

Abstract:

Geochemical analyses of six crude oil samples from six oil fields in the Coastal Swamp Depobelt of the Niger Delta Basin Nigeria, was performed to determine the similarities in the crude oil composition distribution intra-depobelt-wise by comparing GC fingerprints of the oils in the context of their organic matter source, thermal maturity, waxiness and environment of deposition. The samples arecoded KZ15, KZ18, KZ22, KZ24, KZ27 and KZ28.

Generic hydrocarbon ratios (such as Pr/Ph, Pr/nC_{17}, Ph/nC_{18}, Carbon Potential Index (CPI), Terrigenous/ Aquatic ratio (TAR) were used to infer the geochemical characteristics of these samples. Significantly, the ratios of *n*-alkanes and aliphatic isoprenoids revealed that Pr/nC_{17} ranged from 0.52 to 2.07 while Ph/nC_{18} ranged from 0.32 to 1.62 meaning that the oils were derived from organic matter of terrestrial origin and various degrees of marine inputs. Also, Pristane/Phytane ratios ranged from 2.23 to 3.17, suggesting that the organic matter was deposited in generally oxic (deltaic and shallow marine) environments. Several cross plots (such as waxiness versus (vs) Pr/Ph, CPI vs Pr/Ph and TAR vs Pr/Ph) were made. A plot of CPI and Pr/Ph revealed mixed organic matter input corroborating the results from some of the ratios especially n-alkanes/isoprenoid ratios. High TAR was observed and a crossplot of TAR against Pr/Ph showed more terrigenous input.

A star plot revealed that oils of the Coastal Swamp Depobelt of the Niger Delta have similar organic geochemical characteristics, thus are related, a slight deviation from this was attributed to degradation. Three distinct classes of Gas chromatogram fingerprints exist at various locations in the Coastal swamp depobelt and this observation is a quick and useful clue in spilled oil to suspected source correlation during spill investigation where a chromatogram profile of sample under investigation can be easily correlated to its source within this depobelt.

Keywords — **Geochemical analyses, Thermal maturity, oil to source correlation, depositional environment, Gas chromatogram**

----------**********----------

I. INTRODUCTION

The separation of the complex hydrocarbon mixtures into isolated units is effectively achieved through geochemical analysis. The fundamental of geochemical analysis is that each crude oil has its own unique profile that differentiates it from other oils. This unique profile is a replication of its source, environment of depositional environment and age. Accordingly, crude oils from the same source rock are composed of similar profiles that aid in their identification and correlation.

Oils differ in appearance and viscosity from field to field, thus characterization and source identification of oils from different fields is essential (Oforka et al 2012). One of such ways of doing this is by analyzing the hydrocarbon fractions.This is also a key way of identifying the similarities in crude oils from the same source within a field or a depobelt.

The concept of depobelt is peculiar to Niger delta basin which depicts its structurally and depositionally most dynamic portion at each phase of its growth(Doust and Omotsola, 1990). This growth of the delta is controlled by pre- and synsedimentary tectonics as described by Evamy et al. (1978), Ejedawe (1981), Knox & Omatsola (1987) and Stacher (1995). The shape of the Cretaceous coast line (Reijers et al., 1997) gradually changed with the growth of the Niger Delta as it advanced basinward in southwest direction from the Eocene to the present, creating five depobelts .The Niger Delta basin has a reserve of about 23 billion barrels of oil and183 trillion cubic feet of natural gas and it is one of the major hydrocarbon provinces of the world located in Nigeria, (Sonibare et al., 2008).

The development of these five depobelts proceeded from north to south having the Northern (as the oldest) in the north, Greater Ughelli, Central swamp, Coastal swamp and Offshore (the youngest) in the South. Each depobelt is believed to form a more or less independent unit (Doust and Omatsola, 1990) and are about 30-60 km wide.

Earlier studies have shown that there may be a single petroleum system in the Niger Delta (Udo and Ekweozor, 1990; Eneogwe and Ekundayo, 2003; Akinlua et al., 2005.However, (Evamy et al, 1978) presumed that the bulk if not totality of source rocks of the Niger Delta are from the marine shale of the Akata Formation, the interbedded shale with sandstone in the lower Agbada Formation and the underlying Cretaceous shales.

It is therefore vital to investigate the petroleum system in the different fields within the Coastal Swamp depobelts in the Niger delta, to determine their similarities and differences in the crude oil composition within different fields in this depobelt.

Categorization of oils as well as source identification of oils from various fields is necessary (Onojake, et al., 2015) for an understanding of the compositional variation in the oils within a field and by extension, a depobelt since crude oil varies extensively in appearance and viscosity from one field to another.

This, however, requires a detailed geochemical analyses of the molecular evidences (biomarkers) present in crude oils to the identity of source rocks from which petroleum is derived, the biological source organisms which the organic matter was formed, the paleo environmental deposition, and the thermal maturity.

Geochemical analysis of the oils in this depobelt was employed in this study to identify subtle similarities and differences of these oils by determining organic matter type, their thermal maturity, and predominant environments of deposition of the precursor organic matter. This is very useful to reduce oil-type uncertainty exploration and development strategies for companies targeting particular oil types and in oil spill identification (Spill to source correlation).

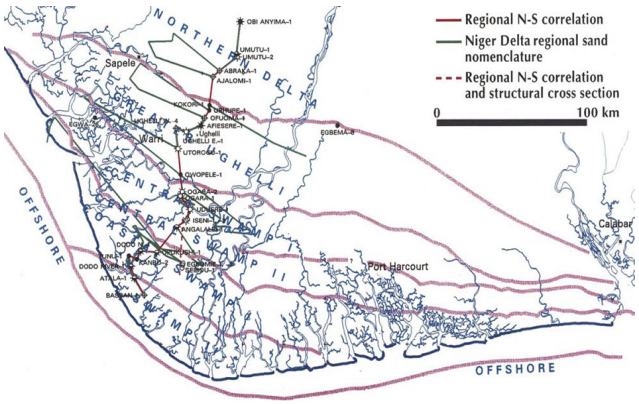


Fig. 1: Map of the Niger Delta showing the depobelts(Reijeirs, 2011)

II. MATERIALS AND METHODS

In this study, six (6) crude oil samples (KZ15, KZ18, KZ22, KZ25, KZ27 and KZ28) were collected from six (6) different fields in the Costal Swamp depobelt of the Niger Delta basin. These samples were collected from different fault blocks as revealed in (Fig. 2) within the Coastal Swamp depobelt toaid in the adequate vertical and lateral comparison of the oils within this depobelt .

Crude Oil Analysis

A wide diversity of sophisticated techniques is presently applied in the analysis of crude oil for excellent hydrocarbon profiling and characterization, this comprises of gas chromatography (GC), gas chromatography–mass spectrometry (GC– MS), high performance liquid chromatography (HPLC), thin layer chromatography (TLC), and ultraviolet (UV) spectroscopy etc. (Wang and Fingas, 2003)

The six crude oil samples for this study were analyzed employing whole oil- GC–FID analysis, using Gas Chromatogram instrument which has the ability to separate crude oil samples into estimated one thousand (1000) components, these separated components are potential tracers for oil to oil correlation.

Firstly, the samples collected were fractionated into saturated hydrocarbons, aromatic hydrocarbons and resins by using hexane, toluene and methanol, respectively, by means of column chromatography (Eneogwe et al. 2002). The solvents were allowed to evaporate in a stream of nitrogen. GC analysis of whole oil samples was carried out using a Hewlett Packard 5890 series II Plus chromatograph equipped with a 50 m x 0.2 mm x 0.5µm film thickness (DB-1) column with a flame ionization detector (FID). The carrier gas was hydrogen (H_2) at a flow rate of 300 ml/sec and the oven was programmed from 30°C to 305°C at 5°C/min. The initial and final temperatures were held for 5 min and 20 min, respectively.

The peak areas were electronically integrated and identification based on retention times and comparison with standards. The integration of peak areas was achieved using HIRES interpretation software (HIRES is an SPDC in-house software for peak identification. Peaks are compared with a known standard) and Chemstation. The integrated peaks were later compared and it was discovered that HIRES software gave a better peak resolution.

Geochemical analyses were carried out at the Production Chemistry Laboratory of Shell Petroleum Development Company (SPDC) Port-Harcourt, Nigeria.

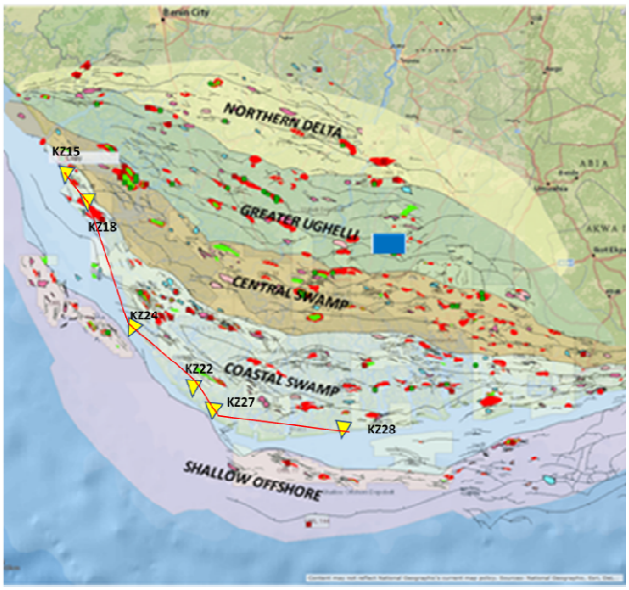


Fig 2: Map showing the sampled locations within the Coastal Swamp depobelt (Modified from Reijers, 2011)

III. RESULTS AND DISCUSSION

The chromatogram profiles (Fig. 3) of all the analyzed crude oil samples were used to generate parametric ratios for oil correlation, depositional

environment and thermal maturity. Three distinct patterns of chromatogram are prominent within this depobelt. They are classified in this study as Class A, Class B and Class C.

	Pr/Ph	Pr/nC17	Ph/nC18	TAR	CPI	WAX-INESS	API
KZ1	2.23	2.04	1.01	2.6	0.79	0.77	28.6
KZ18	2.9	2.07	1	2.7	0.79	0.78	30.1
KZ22	2.5	1.6	1.62	1.97	1.58	1.39	24.5
KZ24	3.17	1.1	0.44	4.62	0.88	0.61	22.3
KZ27	2.31	0.52	0.32	4.1	0.76	0.7	28.2
KZ28	2.4	0.73	0.63	2.3	1.45	0.78	39.8

Class A comprises KZ15 and KZ18, Class B is made up of KZ27 and KZ28 while KZ 22 and KZ24 belong to Class C. Each of the Classes possess similar chromatogram which could imply that they are from the same source, environment of deposition as well as age (having undergone similar degree of alteration).

Class A are positioned towards the NW flank of the depobelt and are in the proximal to the Central swamp depobelt, Class B is located at SW section of the depobelt while Class C areat the bulgy part of this depobelt in the south part and closest to the Offshore depobelt. The significance of this is could be that at different locations in the depobelt, there exist different charge systems and thus compositional variation in oil type or merely a depiction of the degree of alteration each of the classes of oil has undergone.

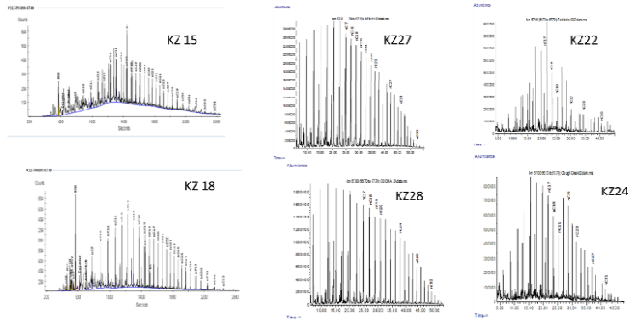


Fig.3 : Profiles of analyzed crude oil samples showing the Normal Alkanes (n-Alkanes) and Isoprenoids distribution.

Table 1 outlined the geochemical data of all the oil samples used in this study. Values for the Pristane/nC_{17}, Phytane/nC_{18}, Pristane/Phytane (Pr/Ph) ratio, Carbon Preference Index (CPI), Terrestrial Algae Ratio (TAR) and Waxiness were generated from the GC data.

The API gravity was also calculated using the formula **API =** (141.5 / SG) - 131.5,where API = Degrees API Gravity and SG = Specific Gravity (at 60^{o} F or 15.5^{o}) (Saliu et al, 2013).

Table 1: Geochemical parameters extracted from Gas chromatogram (GC)

Abbreviations: Pr – Pristane, Ph – Phytane, TAR – Terrestrial/algae ratio = [nC_{17}+nC_{18}+nC_{19}/ nC_{27}+nC_{28}+nC_{29}]; Carbon Preference Index (CPI)= ½ [(nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33})/ (nC_{24} + nC_{26} + nC_{28} + nC_{30} + nC_{32}) + (nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33})/ (nC_{26} + nC_{28} + nC_{30} + nC_{32} + nC_{34})]; Waxiness = [nC_{21}+nC_{22}+nC_{23}/ nC_{24}+nC_{27}+nC_{26}+ nC_{27}+ $nC_{28}$$nC_{29}$+ nC_{29} +nC_{30}/ nC_{15}+nC_{16}+nC_{17}+nC_{18}+nC_{19}+nC_{20}]

A. Determination of Organic matter type and Reconstruction of Paleoenvironment of deposition

One of the most widely used geochemical parameters for determining organic matter type and depositional environment is the Pr/Ph ratio. It is an indicator of the prevalent redox condition in the depositional environment and also the source of organic matter (Salisu et al., 2017). Source rocks from terrestrial plants usually produce oils that have high Pr/Ph ratio (>3.0) due to the presence of oxygen during the early diagenesis of chlorophyll while low Pr/Ph ratio is related to oils of marine origin. Also, Pr/Ph ratio >1.0 specifies oxic condition while less <1.0 suggests anoxic condition. Pr/Ph values for all the six samples ranged from 2.3 to 3.20 signifying mixed organic input and an oxic depositional environment are dominant in this depobelt.

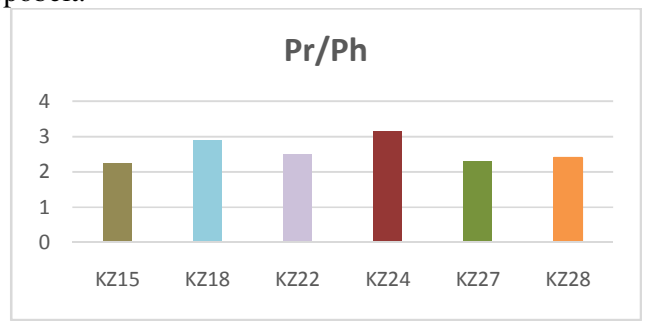


Fig. 4 A plot of Pr/Ph ratios

Additional parameters used to decipher the environment deposition are the Pr/nC_{17} and

Ph/nC$_{18}$ values. These values range from 0.52 to 2.04 and 0.32 to 1.62 respectively (Table 1). These range of values signifies both terrestrial and marine contributions implying that all the oil samples were derived from mixed organic matter. A scatter plot of Pr/nC$_{17}$ and Ph/nC$_{18}$ showed that KZ15 and KZ18 high terrigenous input, KZ22 source input is marine while kZ27 and KZ28 are of mixed organic matter contribution. Samples KZ15, KZ18 and KZ22 are biodegraded.

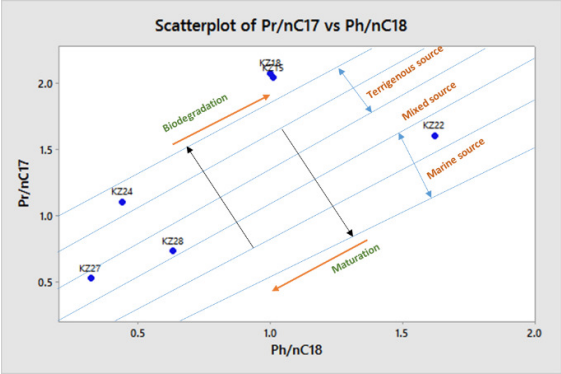


Fig. 5. A Scatterplot of Pr/nC$_{17}$ and Ph/nC$_{18}$ of Costal Swamp depobelt of Niger Delta oils

B.Assessment of Thermal Maturation of Crude oil

A numeral means of representing the odd-over-even predominance in *n*-alkanes is the Carbon Potential Index (CPI). This is regularly used as a maturity parameter. The CPI values for all the samples are approximately 1.0. A cross-plot of CPI versus Pr/Ph (Fig.6) indicates that all the classes of oil samples were derived from mixed organic matter deposited in transitional environmentwith various degrees of marine inputs.

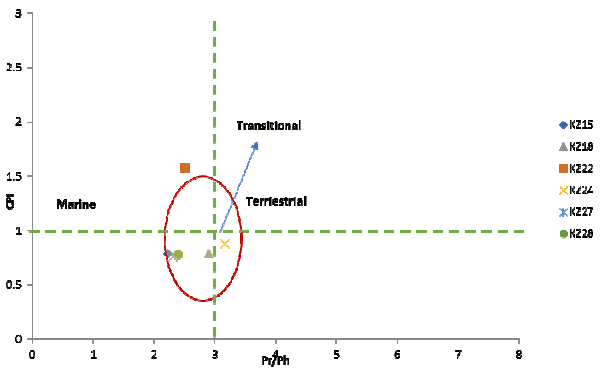
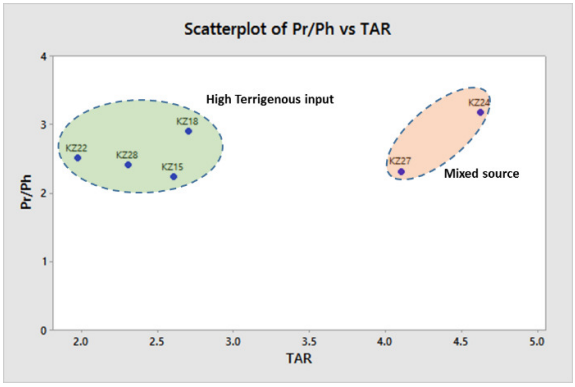


Fig 6. A plot of CPI against Pr/Ph of Costal Swamp depobelt of Niger Delta oils



Terrigenous/ Aquatic Ratio (TAR) versus Pr/Ph

A plot of TAR against Pr/Ph shows more terrigenous organic matter input as characterize by low terrigenous aquatic ratio (TAR) ranging between (Fig.7), suggesting high contribution of terrigenous organic matter.This is also supported by the scatter plot of waxiness versus Pr/Ph.

Fig 8. A plot of Waxiness against Pr/Ph

C. Crude oil correlation

In crude oil correlation, the ratios of isoprenoids to n-paraffin are often used for oil- source correlation, maturation and biodegradation studies (Oforka et al 2012). A star plot of the geochemical analyses involving the CPI, Pr/Ph, Pr/nC17, Ph/nC18, waxiness and TAR of all the six oil samples shows are near perfect match indicating that these oils are related and are from more or less similar environment of deposition. The slight mis-match in the star plot could be as a result of alteration processes each of these oils has undergone (degradation). A further plot of

these oil in pairs based on their location in the Coastal swamp depobelt revealed a subtle lateral variation in composition as you prograde along this depobelt.

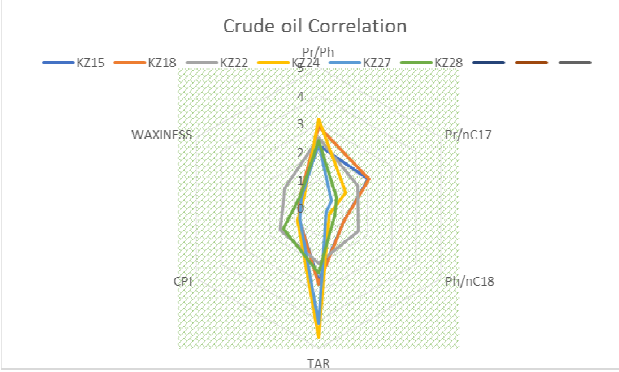


Fig. 9. Star plot of all the geochemical ratios of the analyzed samples

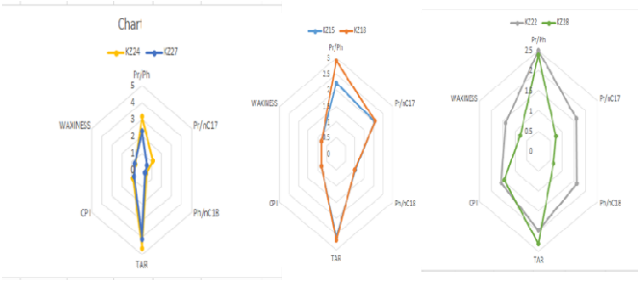


Fig. 10. Star plot of all the geochemical ratios of the analyzed samples in pairs based on their position in the Coastal Swamp depobelt

1V.CONCLUSIONS

The Geochemical analyses of oil samples from different fields in the Coastal Swamp Depobelt in the Niger Delta Basin indicated that the oils are from organic matter of mixed origin with high input of terrigenous organic matter and are thermally mature. The environment of deposition is transitional. An attempt on correlating the oils showed a near perfect match showing that all the oils are related. This is of great importance in uncertainty assessment in oil exploration and exploitation within this depobelt.

However, three distinct classes of chromatogram exist at various locations in the Coastal swamp depobelt. This is a quick and useful clue in oil to source correlation during spill investigationwhere a chromatogram profile of sample under investigation can be easily correlated to its source within this depobelt.

ACKNOWLEDGMENT

My appreciation goes to World Bank for providing the research grant for this study via World Bank African Centre of Excellence for Oilfield Chemicals Research.

I also wish to acknowledge the supports of the Department of Petroleum Resources of the Ministry of Petroleum Resources, Nigeria, the production chemistry department of Shell Petroleum Development Company as well as the University Liaison Office of Shell Petroleum Development Company, Port Harcourt Nigeria towards the success of this research work.

REFERENCES

[1] Akinlua, A., Ajayi, T. R. and Adeleke, B. B., 2005. A re-appraisal of the application of Rock-Eval pyrolysis to source rock studies in the Niger Delta. *Journal. Petrol. Geol.* **28** (1), 39–48.

[2] Doust, H. and Omatsola, E., 1990. Niger Delta. In: Divergent/Passive margin basins. In: J.D. Edwards and P.A. Santogrossi (Eds), *AAPG Memoir* **48,** 201–238.

[3] Ejedawe, J.E., 1981. Patterns of incidence of oil reserves in Niger Delta Basin. American Association of Petroleum Geologists Bulletin **65**, 1574–1585.

[4] Eneogwe, C. and Ekundayo, O., 2003. Geochemical correlation of the crude oils in the NW Niger Delta, Nigeria. *Journal. Petrol. Geol.,* **26**, 95–103.

[5] Evamy, B. P., Haremboure, J., Kamerling, P., Knoop, W.A., Molly, F. A. and Rowlands, P. H., 1978. Hydrocarbon habitat of tertiary Niger Delta. *AAPG Bulletin,* **62,** 1–39.

[6] Knox, G.J. & Omatsola, M.E., 1987. Development of the Cenozoic Niger Delta in terms of the escalator regression model. [In:] Proceedings of the KNGMG Symposium 'Coastal Lowlands – Geology and Geotechnology'. Kluwer Academic Publishers, 181–202

[7] Onojake, M.C. Abrakasa, S., Osuji L.C. 2015. Chemometric representation of molecular marker data of some Niger Delta crude oils, Egyptian Journal Petroleum **24**, 139–143.

[8] Reijers, T.J.A. 2011. Stratigraphy and sedimentology of the Niger Delta. Geologos, 17 (3): 133–162

[9] Reijers, T.J.A., Petters, S.W., Nwajide, C.S., 1997. The Niger Delta Basin. [In:] R.C. Selley (Ed.): African basins. Sedimentary Basins of the World (Elsevier, Amsterdam) 3, 145–168.

[10] Sonibare, O., Alimi, H., Jarvie, D., and Ehinola, O. A. (2008). Origin and occurrence of crude oil in the Niger Delta, Nigeria. *J. Pet. Sci. Eng.* 61:99–107.

[11] Stacher, P., 1995. Present understanding of the Niger Delta hydrocarbon habitat, In: M. N. Oti and G. Postma (Eds), Geology of Deltas. A. A. Balkema / Rotterdam / Brookfield, p 257–267.

[12] Salih M.A , and HebaSadoon A. (2013). Statistical Analysis of the Relations between API, Specific Gravity and Sulfur Content in the Universal Crude Oil International Journal of Science and Research (IJSR) ISSN (Online): Vol. 4.

[13] Salisu N., Nasir M. A., Ali A.S. and Geoff A. 2015. Geochemical Applications and Limitations of Pristane to Phytane ratio in determining the Redox Condition of North Sea Oil and Kimmeridge Source Rocks' Paleoenvironment of Deposition. Dutse Journal of Pure and Applied Sciences96 – 103.

[14] Udo, O. T. and Ekweozor, C. M., 1990. Significance of Oleanane occurrence in shales of Opuama Channel Complex. Niger Delta. *Energy and Fuels*, **4,** 248 – 254.

[15] Wang, Z., & Fingas, M. F. (2003). Development of oil Hydrocarbon Fingerprinting and Identification Techniques. Marine Pollution Bulletin, 47, 423–452.

