

Geochemical Appraisal of Crude Oils from Umutu and Bomu Fields in the Niger Delta

Onojake, Mudiaga Chukunedum^{1*}, Osuji, Leo¹,
Chigbu and Abrakasa, Selegba^{2,3}

1. Petroleum Chemistry Research Group, Department of Pure and Industrial Chemistry,
University of Port Harcourt, PMB5323, Choba, Port Harcourt, Rivers State, Nigeria.

2. Centre for Petroleum Geosciences, Institute of Petroleum Studies, University of Port Harcourt
Port Harcourt, Nigeria.

3. Department of Petroleum Engineering, Niger Delta University, Amassoma, Bayelsa State, Nigeria.

*Corresponding author email: ononeed@yahoo.com, mudiaga.onojake@uniport.edu.ng

ABSTRACT

The geochemical appraisal of oils from the Umutu and Bomu fields in the Niger Delta reveals that the oils from the two fields bear an appreciable similarity considering their biomarker characteristics. The ternary plots for the % C₂₇, C₂₈ and C₂₉ steranes indicates that the samples consist of mixed terrigenous and minor marine inputs. The Pr/nC₁₇ vs the Ph/nC₁₈ plot indicate that the oils are derived from type III kerogen, inferring that the sourcing organic matter were deposited in an dysoxic–oxic environment. The plot also infers that the Umutu samples are slightly biodegraded while the Bomu oils are not degraded. All samples in this study show near similar maturity level.

Key words: Biomarkers, Environment, Biodegradation, Hopanes and oleanane

1. Introduction

The appraisal of oils provides detail information that could be used for comparative and correlation studies during frontier exploration bids. The gradual evolution of petroleum geochemistry from its conceptual mode to a more application based mode resulted to its extensive use in field development, i.e. location of injection and production wells for enhanced oil recovery projects, potential fluid communication studies in delineating compartmentalization, discerning and resolution of problems related to leaking casings and deconvolution and allocation of commingled production. In environmental oil geochemistry biomarker details could be applied to correlate leaked/spilled oils in the surrounding environment to the indigenous oils for evaluation of possible leakage after plugging

and abandonment of wells, suffice to include that though specific parameters are used, certain standards are maintained.

2. Geology of the study area

The study area (figure 1) lies within the Niger-Delta, which bears over 10 kilometers thickness of sediments. The area, which is typical of the Niger Delta Basin forms part of a geological sequence of the Quaternary and Tertiary formations of the Niger Delta sediments, consisting mainly of three main geologic formations, which are the Benin Formation, Agbada Formation, and Akata Formation (Sundararaman *et al.*, 2002).

Michele *et al.* (2010) identified the (Akata-Agbada) petroleum system as the active source of the Niger Delta oils. The primary source rock is the marine-shale facies of the Upper

Akata formation, with possible contributions from interbedded marine shale of the Lower Agbada Formation (Magoon *et al.*, 1994; Ekweozor and Daukoru, 1994).

3. Sampling and Sample preparation

Seven crude oils were collected at stratigraphic depths ranging from 9,800ft to 10,400ft for two producing oil fields namely: Umutu field and Bomu field onshore the Niger Delta. The crude oils collected were 4 samples from Umutu and 3 samples from Bomu fields. The crude oils were collected with glass vials with Teflon caps and stored in the refrigerator at a temperature below 4°C prior to laboratory analysis.

3.1 Fractionation of the oils

The crude oils were fractionated into saturates, aromatics and polar compounds by column chromatography on silica gel. The standard glass column was packed with silica gel (SiO₂) as the stationary phase, prior to which was rinsed with Dichloromethane and later with light petroleum spirit, the packed column rested on a pad comprised of activated cotton. The column was filled with petroleum ether. 2g of Alumina was added to keep the surface stable. The oil sample was introduced, then the eluents gently, about 70ml of petroleum ether was added to elute the aliphatic fraction, 70 ml of dichloromethane (DCM) was used to elute the aromatic fraction while 70ml of methanol was used to elute the polars (resins). The aliphatic fraction were reduced with nitrogen stream to about 1 ml and diluted with dichloromethane for GC and GC-MS analysis.

3.2 GC, GC-MS Analysis

The GC-MS analyses for the aliphatic hydrocarbon was performed using a Hewlett-Packard 5890II GC with a split/splitless injector (280°C) linked to a Hewlett-Packard 5890II GC with a split/splitless injector (280°C) linked to a Hewlett-Packard 5972 MSD with an electron voltage of 70ev,

filament current of 220μA, source temperature of 160°C, a multiplier voltage 1600V and interface temperature of 300°C. The acquisition was controlled by an HP Vectra PC chemstation computer in both full scan mode and selected ion mode. The sample (1μl) in DCM was injected by an HP7673 auto-sampler and the split opened after 1 min. Separation was performed on a fused silica capillary column (30m × 0.25mm i.d.) coated with 0-25μm, 5% phenylmethylsilicone (HP-5). The GC was temperature programmed for 40°C – 300°C at 4°C per minute and held at a final temperature for 20mins. The carrier gas was helium (flow 1ml/min., pressure of 50KPa, slit at 30ml/min.). The acquired data was on DAT tape for later processing. The data was processed using Chem Station G1701BA (version B.01.001989 - 1998) software and integration of peaks was done with the RTE integrator.

4. Results and Discussion

4.1 Type and quality of organic matter

Organic matter typing has proved that the source and type of organic matter determines the quality of organic matter, if it is oil prone or gas prone. The Pr/nC₁₇ vs Ph/nC₁₈ plot (figure 2) show that all the oils plot below the diagonal. This indicates that the sourcing organic matter of all the oils in this study was deposited amidst sufficient oxygen; this invariably means the oils were sourced from a type III kerogen, which comprises degraded planktonic organic matter or high phytoclast inputs (unoxidised woody materials). Type III kerogen is mostly sourced from vascular higher plant materials, which is highly gas prone with little oil (Hanson *et al.*, 2000). Oils with CPI ≥ 1 are also inferred to be sourced from epicuticular waxes of vascular land plants (Waples and Machihara, 1991; Peters and Moldowan, 1993). The mass chromatogram for the m/z 191 (figure 6) indicates the presence of oleanane, which is a diagnostic marker for sourcing organic materials that comprises vascular higher land plant materials

(Ekweozor, 1981). The plot of Pr/Ph vs. Oleanane/C₃₀ hopane (figure 3) indicates that the Bomu samples are very identical with less higher plants inputs, while the Umutu samples

show slightly dissimilarity which may suggest slight changes in deposited organic matter over time.

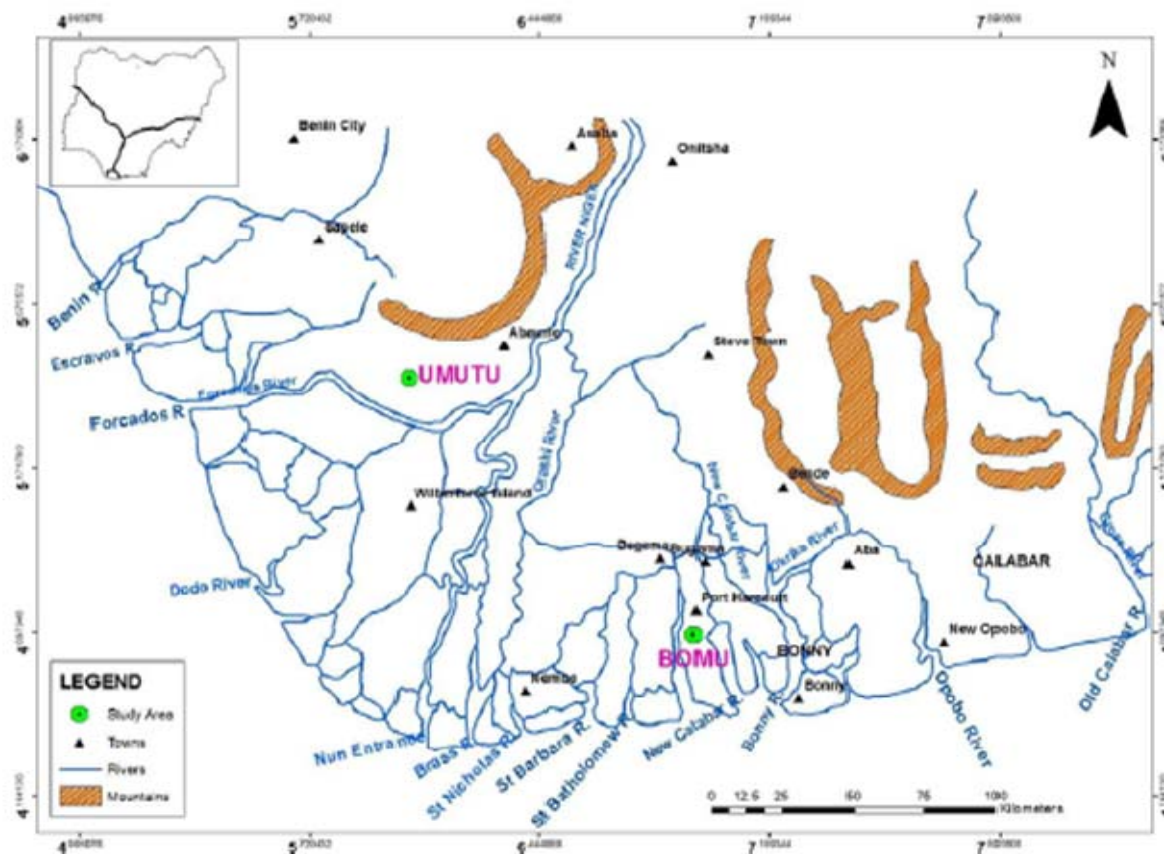


Figure 1. Map of Niger Delta showing the study locations.

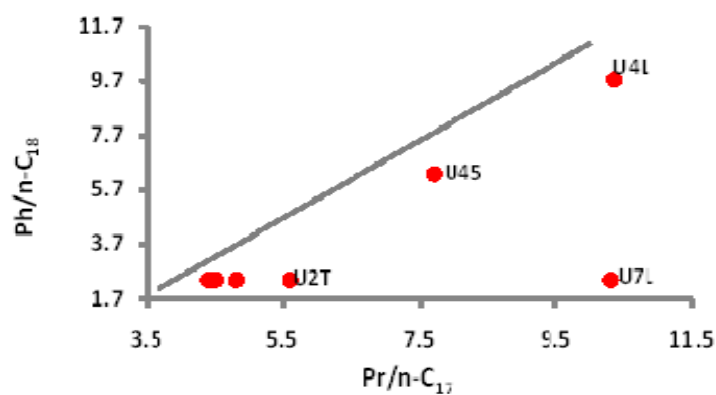


Figure 2. Plot of Pr/nC₁₇ vs Ph/nC₁₈.

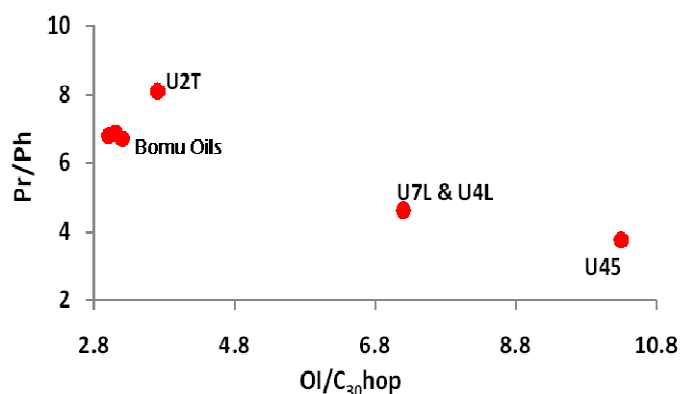


Figure 3. Plot of Pr/Ph vs Ol/C₃₀ hopane.

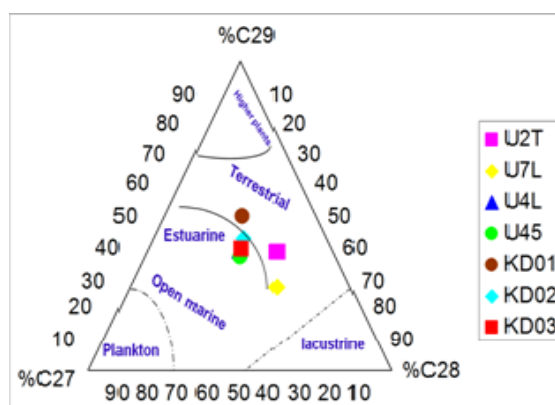


Figure 4. Sterane ternary diagram.

4.2 Source rock depositional environment

The depositional environment is a major control on the type and invariably the quality of organic matter. The ternary plot using the % C₂₇, %C₂₈, %C₂₉ is normally employed to discriminate oils according to their depositional environment or different source facies. The sterane ternary plot (figure 4) indicates that all the oils except U2T and U7L is sourced from dysoxic–oxic environments with minor marine influences i.e. low marine.

The Pr/nC₁₇ vs Ph/nC₁₈ plot (figure 2) showing all samples lower than the diagonal indicates source rock in dysoxic–oxic environment (Hanson *et al.*, 2000). The m/z 191 mass chromatogram show limiting occurrence of the extended homohopanes to C₃₃, which is normally observed for source rocks deposited in deltaic environment where there is sufficient oxygen. The environment may be distal i.e. oceans, low marine or proximal i.e. estuarine, coastal; the sediments are normally fed by runoffs (Evamy *et al.*, 1978; Eneogwe and Ekundayo, 2003; Mackenzie, 1984; Roushdy *et al.*, 2010).

Table 1. Peak identification for m/z 191 mass chromatogram.

Peak	Compound	Formula	MW	Ion Monitored
<i>Pentacyclic triterpanes</i>				
Ts	Ts: 18 α (H),2 β (H)-22,29,30-Trisnorhopane	C ₂₇ H ₄₆	370	191
Tm	Tm: 17 α (H),21 β (H)-22,29,30-Trisnorhopane	C ₂₇ H ₄₆	370	191
C ₂₉	17 α (H),21 β (H)-30-Norhopane	C ₂₉ H ₅₀	398	191
C ₂₉ Ts	18 α (H),21 β (H)-30-Norneohopane	C ₂₉ H ₅₀	398	191
Ole	α - Oleanane			
C ₃₀	17 α (H),21 β (H)-Hopane	C ₃₀ H ₅₂	412	191
Mo	17 β (H),21 α (H)-Hopane (Moretane)	C ₃₀ H ₅₂	412	191
C ₃₁ S	22S-17 α (H),21 β (H)-30-Homohopane	C ₃₁ H ₅₄	426	191
C ₃₁ R	22R-17 α (H),21 β (H)-30-Homohopane	C ₃₁ H ₅₄	426	191
C ₃₂ S	22S-17 α (H),21 β (H)-30,31 -Bishomohopane	C ₃₂ H ₅₆	440	191
C ₃₂ R	22R-17 α (H),21 β (H)-30,31 -Bishomohopane	C ₃₂ H ₅₆	440	191
C ₃₃ S	22S-17 α (H),21 β (H)-30,31,32-Trishomohopane	C ₃₃ H ₅₈	454	191
C ₃₃ R	22R-17 α (H),21 β (H)-30,31,32-Trishomohopane	C ₃₃ H ₅₈	454	191
C ₃₄ S	22S-17 α (H),21 β (H)-30,31,32,33-Tetrakishomohopane	C ₃₄ H ₆₀	468	191
C ₃₄ R	22R-17 α (H),21 β (H)-30,31,32,33-Tetrakishomohopane	C ₃₄ H ₆₀	468	191
C ₃₅ S	22S-17 α (H),21 β (H)-30,31,32,33,34-Pentakishomohopane	C ₃₅ H ₆₂	482	191
C ₃₅ R	22R-17 α (H),21 β (H)-30,31,32,33,34-Pentakishomohopane	C ₃₅ H ₆₂	482	191

The mass chromatogram for the m/z 191 (figure 6) indicates the presence of oleanane, which is a diagnostic marker for sediments deposited in deltaic environments (Ekweozor, 1981). Pr/Ph > 3 indicates strong oxic conditions (Ten Haven,

1996), while Oleanane/C₃₀ hopane \geq 3 is synonymous with deltaic environments, i.e. Gippsland, Mahakam, Mackenzie and Sumatra deltas.

Table 2. Biomarker ratios.

	Sample						
	U2T	U7L	U4L	U45	KD01	KD02	KD03
Pr/Ph	4.05	2.31	2.31	1.88	3.36	3.44	3.40
Pr/n-C ₁₇	0.56	1.30	1.35	0.77	0.48	0.45	0.44
Ph/n-C ₁₈	0.16	0.16	0.65	0.42	0.16	0.16	0.16
nC ₂₅ /nC ₁₈	0.53	0.49	0.67	0.64	0.40	0.38	0.37
CPI	1.01	0.72	1.08	1.02	1.09	1.02	1.04
(Pr +C ₁₇)/(Ph +C ₁₈)	1.52	1.52	1.58	1.26	1.40	1.53	1.50
Ts/Tm	1.19	0.82	0.79	0.86	1.25	1.15	1.47
Ts/(Ts + Tm)	0.54	0.45	0.44	0.46	0.56	0.53	0.59
C ₂₉ /C ₃₀ hop	0.62	0.65	0.69	0.67	0.64	0.65	0.60
OI/C ₃₀ hop	0.37	0.72	0.72	1.03	0.32	0.31	0.03
Ole Index	0.37	0.72	0.72	1.03	0.32	0.31	0.03
Homo Index	0.03	0.04	0.01	0.01	0.04	0.04	0.05
C ₃₀ M/C ₃₀ hop	0.15	0.14	0.17	0.17	0.17	0.14	0.15
Sterane/hopane	0.08	0.14	0.13	0.20	0.09	0.06	0.02
22S/(22S+22R)	0.56	0.52	0.56	0.55	0.55	0.58	0.55
C ₃₀ */C ₂₉ Ts	6.57	8.35	6.86	7.39	7.03	7.20	6.36
20S/(20S+20R)	0.60	0.50	0.51	0.50	0.63	0.55	0.46
C ₂₇ Steranes(%)	18.32	24.27	30.64	31.36	23.92	27.24	29.72
C ₂₈ Steranes(%)	43.16	48.39	30.01	31.57	25.92	29.96	30.68
C ₂₉ Steranes(%)	38.52	27.34	39.35	37.07	50.16	42.80	39.60
αβ/αβ+βα	0.87	0.87	0.86	0.85	0.88	0.88	0.87
αββ/αββ+ααα	0.40	0.50	0.49	0.50	0.37	0.45	0.54

4.3 Maturity of the oils

The CPI of the oils are all about 1.0 which implies slightly or marginally mature oils, however the sterane isomerization ratios ranges from 43% to 63%, this indicates that the organic matter sourcing the oils was at the oil window during generation of oils (Muhammad *et al.*, 2010; Peters *et al.*, 2005; Tissot and Welte, 1984).

The plot of Ts/(Ts+Tm) vs 20S/(20S+20R) (figure 5) showed some correlation, indicating that Ts/(Ts+Tm) increases linearly with 20S/(20S+20R) (Hanson *et al.*, 2000; Seifert and Moldowan, 1986; Peters and Moldowan, 1993).

The plot also indicate that the Bomu oils show a fair cluster implying apparently very close maturity ranking, however, the Umutu oils show a slight variability in maturity of the Umutu oils, this on the concept of lateral maturity gradient represents successive charging fronts with varying maturity ranks.

4.4 Biodegradation

The ratio of the isoprenoids to the normal alkanes serves as a screening indicator of biodegradation, the Pr/nC₁₇ ratio in table 2 indicates that the Umutu oils are more degraded than the Bomu oils. However, based on the Ph/nC₁₈ ratio, except samples U4L and U45 others did not show any significant level of biodegradation. The Pr/nC₁₇

vs Ph/nC₁₈ plot (figure 2) indicates that the Umutu oils are generally biodegraded, the level

of biodegradation may be suggested as moderate.

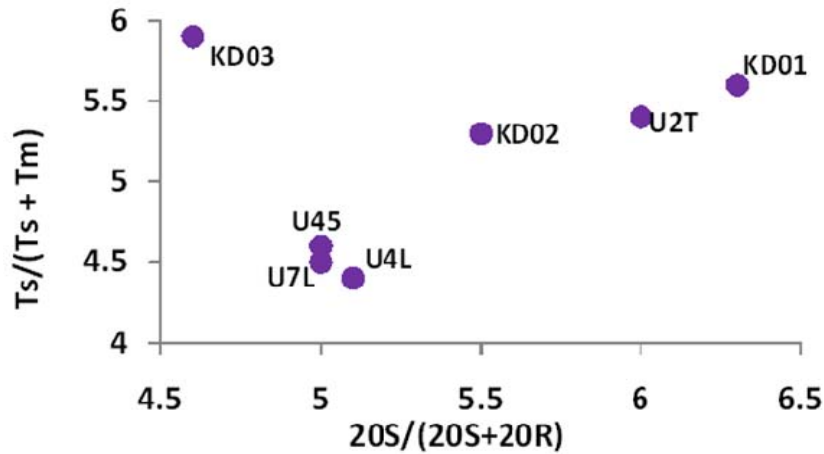


Figure 5. Plot of Ts/(Ts+Tm) vs 20S/(20S+20R).

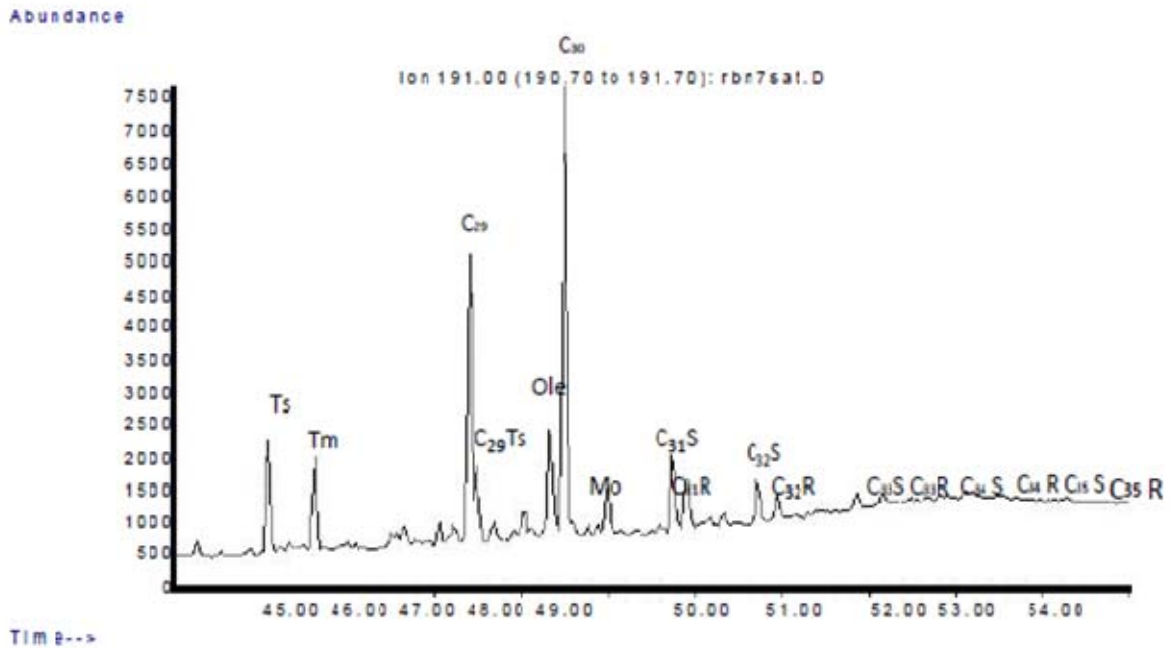


Figure 6. Mass chromatogram of *m/z* 191.

5. Conclusion

The suite of oils used in this study was obtained from the Niger Delta Basin; they comprise oils from Umutu and Bomu fields. GC, GC-MS is the analytical method employed.

The Pr/nC₁₇ vs Ph/nC₁₈ plot indicated that oils were derived from organic matter deposited in dysoxic – oxic environment, which corresponds to near shore or coastal environment (proximal) and low marine, ocean (distal). The organic matter comprises mainly degraded planktonic organic matter, or high phytoclast/vascular high plant inputs (unoxidised woody materials).

The CPI data and the Ts/(Ts+Tm) vs 20S/(20S+20R) plots indicate that the oils are marginally mature. The Pr/nC₁₇ ratio indicates that the Umutu field oils are more degraded compared to the Bomu field oils.

6. Acknowledgements

The researchers are sincerely grateful to the Nigerian Department of Petroleum Resource (DPR) and Platform Petroleum Nigeria Limited for granting us access to the crude oils samples used for this research work. We also appreciate the efforts of Mrs. Yvonne Hall of Newcastle University, United Kingdom, Mr. Oteiva, Frank of Chromatography Laboratory, INDORAMA-Elleme petrochemical Company Ltd for his assistance during some the laboratory analyses of the crude oil samples.

7. References

- Ekweozor, C. M., Daukoru, E. M. 1994. Northern delta depobelt portion of Akata-Agbada Petroleum system, Niger Delta, Nigeria. *AAPG memoir Tulsa, American Association of petroleum Geologists*. 60, 599- 614.
- Ekweozor, C. M., Okogun, J. I., Ekong D. E. U, Maxwell, J. R. 1981. C24 – C27 degraded triterpanes in Nigerian petroleum: Novel molecular markers of source/input or organic maturation. *J. Geochem. Explor.* 15, 653 – 662.
- El-gayer, M. S. H., Mostafa, A. R., Abdelfattah, A. E., Barakat, A. O. 2002. Application of geochemical parameters for classification of crude oils from Egypt into source-related types. *Fuel processing technology*. 79, 13-28.
- Eneogwe, C. and Ekundayo, O. 2003. Geochemical correlation of crude oils in the NW Niger Delta, Nigeria. *Journal of Petroleum Geology*. 26 (1), 95-103.
- Evamy, B.D., Haremboure, J., Kamerling, P., Knaap, W.A., Molloy, F. A, Rowland, P.H. 1978. Hydrocarbon habitat of Tertiary Niger Delta. *AAPG Bulletin*, 62, 1-39.
- Hanson, A. D., Zhang, S. C., Moldowan, J. M., Liang, D. G., Zhang, B. M. 2000. Molecular Organic Geochemistry of the Tarim Basin, North West China. *AAPG Bulletin*, 84, 6, 1109–1128.
- Hwan, R. J., Heidrick, T., Mertani, B., Qivayanti, L. M. 2002. Correlation and migration studies of North Central Sumatra oils. *Org. Geochem.* 33, 1361–13792,
- Hunt, J. M., 1996. *Petroleum Geochemistry and Geology*. New York, W. H. Freeman and Company. Second Edition, p. 486.
- Huc, A.Y., 2003. Petroleum Geochemistry at the Dawn of the 21st century. *Oil and Gas Science and Technology – Rev. IFP*, 58, (2), 233-241,
- Killops, S. D., Killops, V. J. 1993. *An introduction to organic geochemistry*. John Willey, New York. p.138-141.
- Klett, T. R., Ahlbrandt, T. S., Schmoker, J. W., and Dolton, J. L. 1997. Ranking of the
- Onojake *et al.*, 2014. Geochemical appraisal of crude oils in Niger Delta. Vol. 6, No. 1, 31-39

- world's oil and gas provinces by known petroleum volumes. *U.S. Geological survey open-file report*. 97- 463.
- Knox, G. J. and Omatsola, E. M. 1978. Development of the Cenozoic Niger Delta in terms of the "Escalator Regression" Model and impact on hydrocarbon distribution. *Proceedings KNGMA symposium coastal Lowlands, Geology and Geotechnology*. Eds. W.J. M. Van der Linden et al. (Eds) Dordrecht, Kluwer Academic publishers, pp 181-202.
- Mackenzie, A. S. 1984. Application of biological markers in petroleum geochemistry. In: Brooks, J., Welte, D.H. (Eds.), *Advances in Petroleum Geochemistry*, Vol.1. Academic Press, London, pp. 115 – 214.
- Magoon, L.B. and Dow, W.G., 1994. The petroleum system, in Magoon, L.B., and Dow, W.G. eds. *The petroleum system from source to trap, AAPG memoir 60: Tulsa, American Association of Petroleum Geologists*, pp 2-24.
- Michele, L. W. T., Michael, E. B. and Charpentier, R. R., 2010. The Niger Delta petroleum system: Niger Delta province, Nigeria, Cameroon and Equatorial Guinea, Africa. *Open-file report 99-50-H. U.S Department of the interior U.S geological survey*, pp 1-15.
- Muhammad, I. J., Fazeelat, T., and Hina, S., 2010. Study on the geochemical correlation of crude oils of Palaeocene and Jurassic ages from the Potowar Indus Basin in northern Pakistan. *Chin. J. Geochem.* 29, 082–093.
- Peters, K. E and Moldowan, J. N. 1993. *The Biomarker Guide: Interpreting Molecular fossils in Petroleum and Ancient sediments*. Prentice Hall, Englewood cliffs, New Jersey.
- Peters, K. E., Watters, C. C. and Moldowan, J. W. 2005. *The Biomarker Guide*, 2nd ed, Cambridge University press, Cambridge UK.
- Roushdy, M. I., El Nady, M. M., Mostafa, Y. M., El Gendy, N.S., and Ali, H. R. 2010. Biomarkers Characteristics of Crude Oils from some Oilfields in the Gulf of Suez, Egypt. *Journal of American Science*, 6 (11), 911 - 925
- Seifert, W.K and Moldowan, J.M. 1986. The effect of biodegradation on steranes and terpenes in crude oils. *Geochim-cosmochim-Acta*, 43, 111 – 126.
- Sundararaman, C., Nicholas, J., Diedjomahor, J. O. 2002. Niger Delta Petroleum System: Regional Geology, organic facies and Thermal Maturity. *AAPG annual meeting March 10-13, Houston Texas*.
- Ten Haven, H. L. 1996. Applications and limitations of Mango's light hydrocarbon parameters in petroleum correlation studies. *Organic Geochemistry*. 24, 957–976.
- Tissot, P. B. and Welte, D. H. 1984. *Petroleum formation and occurrence*. 2nd edition, Springer verlag, Berlin, Heidelberg
- Waples, D. W. and Machihara, T. 1991. Biomarkers for geologist. *American Association of Petroleum Geologists AAPG Methods in Exploration Series*. 9, 91- 99.