Petroleum and Coal

EVALUATION OF THE LEVEL OF BIODEGRADATION OF BONNY LIGHT, UGHELLI BLEND AND OKORDIA-IKARAMA CRUDE OILS FROM NIGER DELTA NIGERIA

M. C. Onojake*, and S. O. Adesi

Petroleum Chemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B 5323, Choba, Port Harcourt, Nigeria

Abstract

Representative samples of Bonny light, Ughelli Blend and Okordia-Ikarama Crude oils collected from some oil fields in the Niger Delta were quantitatively analysed using oil Gas chromatography flame ionization detector to determine the extent at which biodegradation has impacted on the crude oil quality. The chromatograms of crude oil samples show loss of lower hydrocarbon range from nC_1 to nC_9 either due to evaporative loss during fractionation or biodegradation. The paraffinicity and aromaticity of the crude oil sample were determined using various ratios. The percentage loss of the paraffin showed Bonny light 75.40%, Ughelli Blend 78.36%, and Okordia-Ikarama 46.24%; while the percentage loss of aromatics showed Bonny light 66.02%, Ughelli Blend 78.62%, and Okordia-Ikarama 55.38%. Pristane/$nC17$ and Phytane/$nC18$ ratios were used to complement the results of the percentage loss of paraffinic and aromatic content. The results showed that Ughelli Blend crude oil was heavily biodegraded with extensive loss of the parrafins and the aromatics. While the Bonny light and Okordia-Ikarama crude oils were slightly biodegraded. Biodegradation of hydrocarbons is undesirable because it can lead to lowering of the API gravity, impact crude oil quality and consequently affect the commercial value.

Keywords: *Biodegradation; crude oils; Gas chromatography; Paraffinicity; aromaticity.*

1. Introduction

The general growth in the world's population and industrialization has constantly made the demand for energy on the increase worldwide. These have led to increasing oil exploration activities to obtain crude oil, which is the principal source of energy, to meet societal energy demand. Crude oil is an intricate combination of thousands of C_1 to C_{60+} aliphatic, alicyclic and aromatic hydrocarbons. One of the problems facing the hydrocarbon production is biodegradation. Biodegradation of crude oil and the subsequent deterioration in the value of crude oil is mostly encountered in reservoirs cooler than nearly 80°C [1-2]. When crude degrade progressively in the reservoir saturated hydrocarbons are removed first, making the substantial polar and asphaltene fractions to be concentrated in the remaining oil. This tends to reduce the commercial value of the crude oil by lowering the value of API gravity and increasing viscosity, sulphur, and metals content. The commercial significance of the crude oil largely decreases with biodegradation due to a reduction in the volume of the refinery distillates and an unprecedented rise in vacuum residue yields. Additionally, biodegradation increases the amount of naphthenic acid formed, leading to an upsurge of the acidity of the crude oil, which is customarily computed as Total Acid Number (TAN). TAN can cause a reduction in the value of the crude oil and perhaps add to production and handling problems encountered in the downstream sector, which includes emulsion formation and corrosion [3]. Other compounds present in crude oils are the asphaltic (nitrogen, sulphur, and oxygen compounds), some organometallic compounds of sulphur and vanadium, and dissolved gases, such as hydrogen sulphide [4].

Hydrocarbons from the productive basin in the Niger Delta occurs at different prospects are from separate depth [5]. Whole oil gas chromatography permit for the appraisal of an array of hydrocarbons in crude oil or source rock extract which enables a geochemist to infer the level of biodegradation, thermal maturity by applying some peak ratios to establish the extent of thermal cracking for oil generation, and source characteristics such as a marine, lacustrine, fluvial, or terrestrial depositional environment. Furthermore, comparing peaks and some peak ratios from the chromatograms obtained from the whole gas chromatographic analysis, reservoir continuity can be ascertained.

The aim of this research is to establish the level of biodegradation of crude oils from some fields in the Niger Delta and ascertain its influence on crude oil quality and the commercial value.

2. Materials and methods

2.1. Regional geology of study area

The province geology is that of the Niger Delta Basin where crude oil samples were collected. It is located in the Gulf of Guinea and lengthens through the Niger Delta Region [6]. The geologic formations in the area are The Benin Agbada and Akata Formations [7]. The region ranks one of the largest hydrocarbon provinces in the world with approximately 34.5 billion barrels of recoverable oil and 93.8 trillion cubic feet of recoverable gas. The depobelts of the area is one of the principal regressive deltas in the world with an expanse of 300,000 km^2, a sediment capacity of 500,000 km^3 and a sediment thickness of more than 10 km in the basin depocenter [8]. The petroleum system of the study area is known as the Tertiary Niger Delta or Akata –Agbada Petroleum System (Figure 1).
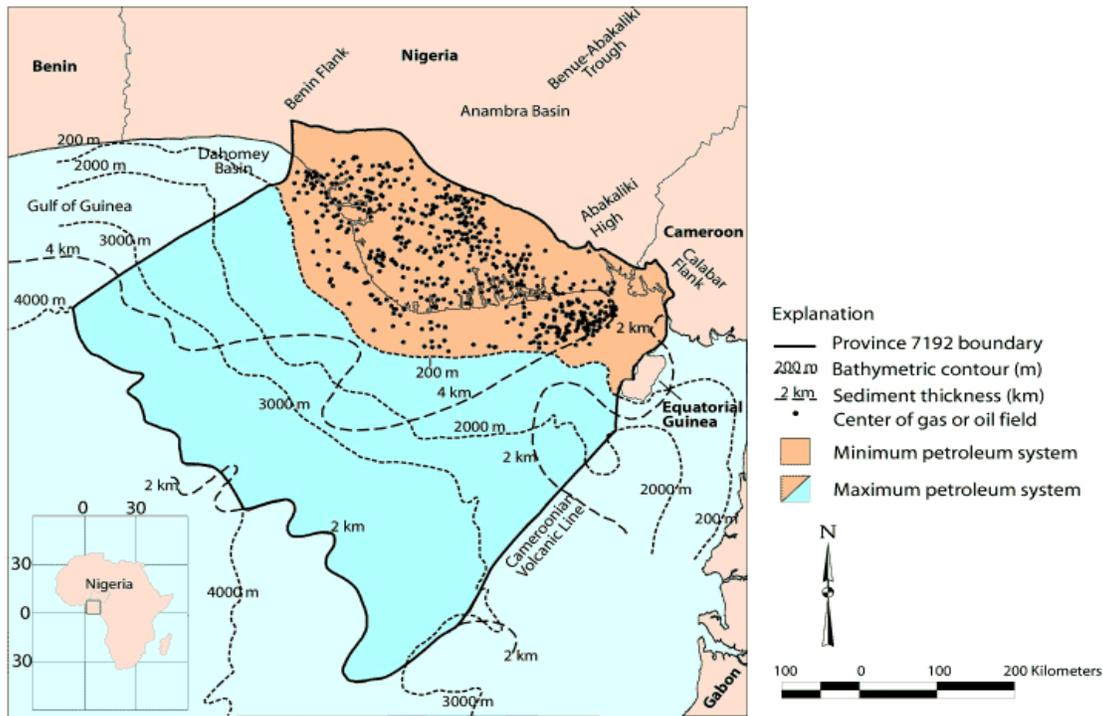

Figure 1. Map of the Niger Delta showing Province outline. *(Source: U. S. Geological Survey Open File Report)*

The onshore part of the study area (Niger Delta Region) is synonymous with the geology of southern Nigeria and south-western Cameroon (Figure 1). The northern margin is the Benin border, an east-northeast trending hinge line south of the West Africa basement massif. The north-eastern margin is demarcated by outcrops of the Cretaceous on the Abakaliki high and

further east-south-east by the Calabar margin; a hinge line is bordering the adjacent Precambrian. The offshore margin of the region is demarcated by the Cameroon volcanic line to the east, the eastern border of the Dahomey basin to the west, and the two kilometer sediment thickness contour or the 4000-meter bathymetric contour in zones where sediment depth is more than two kilometres to the south [9-10].

2.2. Sample collection

Representative samples of crude oils were obtained from producing fields in the Niger Delta region. Glass vials used for sampling were rinsed with trioxonitrate (v) acid, distilled water and properly dried. The crude oil samples were then placed in a cooler containing ice block at a temperature of about 4°C preceding laboratory analyses.

2.3. Whole - Oil Gas chromatographic analysis

The Gas chromatographic analysis of crude oil samples was done using Gas Chromatograph, fitted with Flame Ionization Detector model Shimadzu 14B series with a film thickness of 30m × 0.25 mm and 0.25 μm fused silica capillary columns, coated with methyl silicone. One micro litre (1 μL) of crude oil sample was introduced in splitless mode with a syringe through a rubber septum into the column. The flame ionization detector (FID) and injector temperatures were kept at 250 and 280°C, respectively. The oven temperature was automated from 60 to 280°C at 4°C /min with an original hold time of 1 min and final hold time of 15 mins. The carrier gas used was Helium at a linear velocity of 2 mL/min. The data were collected from retention time: 0-71 minutes [11].

3. Results and discussion

Representatives crude oil samples of Bonny light (BL), Ughelli blend (UB) and Okordia Ikarama (OI) crude oils were analysed using Gas Chromatographic Flame ionization detection (GC-FID) to ascertain the different degrees of degradation.

Detailed examination of the chromatograms of the samples shows a complete depletion of the n-alkanes from C_1 to C_9 (Figure 2) which are an indication of severe degradation of the samples. The n-alkanes, cycloalkanes, 2-methylhexanes through 1, 1- dimethylcyclopentanes are somewhat reduced as shown in Table 1. The ratio of parafinicity for all crude oils was also calculated as shown in Table 2. The ratio of n- Heptane/(Cyclohexane + Mcyclohexanes ranges from 0.0004, 0.0092 and 0.729 for BL, UB, and IO crude samples, n-heptane/Mcyclohexane ranges from 0.0008, 0.0664 and 1.2011, (n-hexane+n-heptane)/(cyclohexane+Mcyclohexane) are also low for all crude oil samples (Table 2) is an indication that the amount of paraffin in the crude oil samples has been significantly affected.
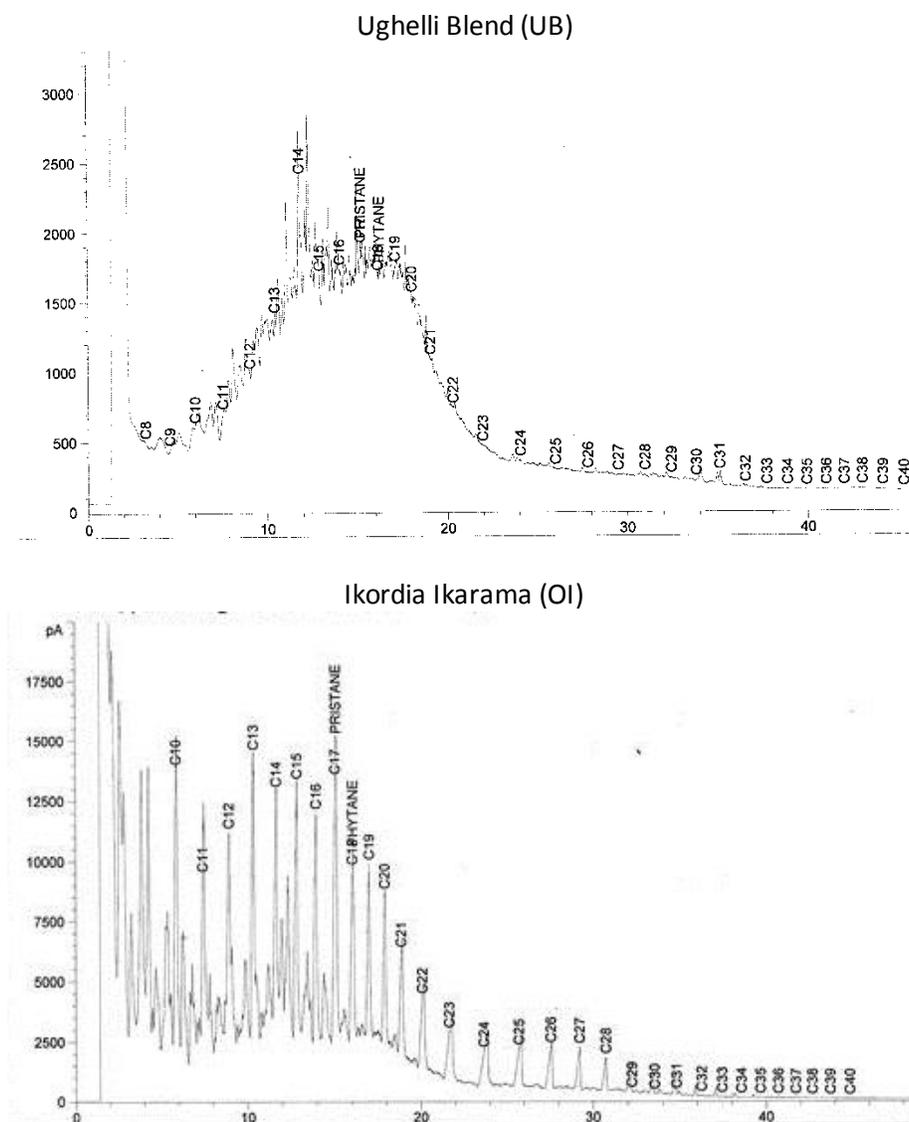
Bonny light (BL)

Ughelli Blend (UB)

Ikordia Ikarama (OI)
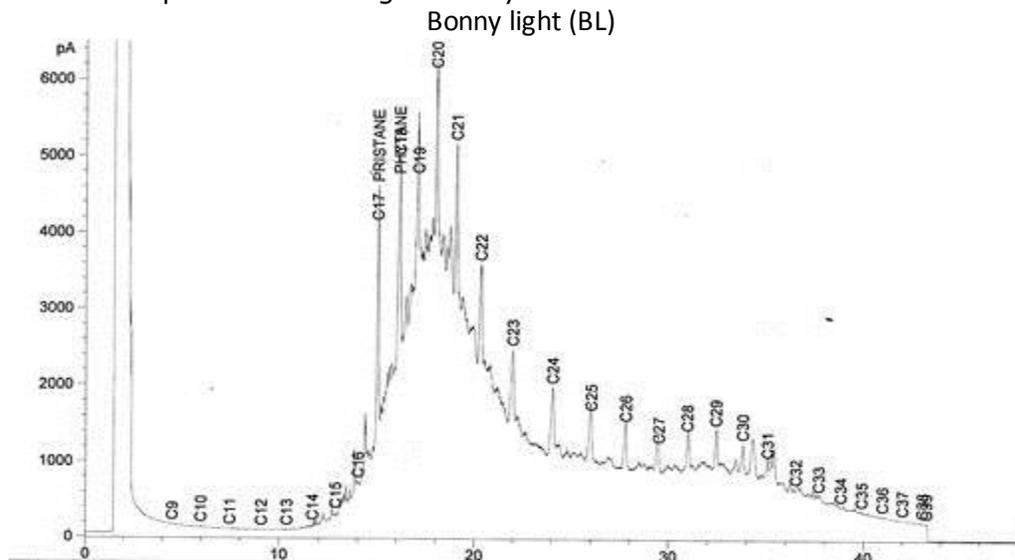
Figure 2. Gas chromatogram of crude samples

Table 1. Results of the percentage area (PA) of crude oil samples

Name	Hydrocarbon	Oil sample	Bonny light	
		BL	UB	OI
n- Hexane	nC_{10}	19809.80	84.57	52420.20
2,4-DMP	nC_{11}	158.55	49877.90	349.98
Benzene	nC_{12}	76.42	41.04	16.41
Cyclohexane	nC_{13}	4671.68	964.64	3991.76
2-Mhexane	nC_{14}	99.83	650.64	178.77
2,3-DMP	nC_{15}	208.33	114.08	2990.48
1,1-Dimethycyclopentane	nC_{16}	2606.10	172.46	20861.70
Pristane	Pr	48.96	42.89	39.70
3-Mhexane	nC_{17}	20.32	136.62	15.60
1-c-3-DMCP	nC_{18}	37.24	138.81	19.85
Phytane	Ph	989.73	33.03	780.05
1-t-2-DMCP	nC_{19}	37.62	101.76	254.71
2,2,4-TMP	nC_{20}	31.80	31.62	37.44
n- Heptane	nC_{21}	3.31	10.33	7407.11

Name	Hydrocarbon	Oil sample	Bonny light	
		BL	**UB**	**OI**
McycloHexane	nC_{22}	3960.24	155.66	6166.73
2,5-DMhexane	nC_{23}	5.39	11.36	7.03
2,3,4-TMP	nC_{24}	4.55	20.64	7.34
Toluene	nC_{25}	11.78	7.64	5.27
3-Mheptane	nC_{26}	6.74	56.27	1177.06
2,2,5-TMP	nC_{27}	16.25	83.84	3.68
Cycloheptane	nC_{28}	2.50	20.76	2.77
n-Octane	nC_{29}	1.87	7.82	9.30
Ethylbenzene	nC_{30}	1.89	58.91	93.21
m-Xylene/p-Xylene	nC_{31}	1.58	12.11	53.77
o-Xylene	nC_{32}	5.92	26.08	36.43
n-Nonane	nC_{33}	1.14	2.19	29.32
Cyclooctane	nC_{34}	8.85	1.38	16.06
	nC_{35}	12.95	1.70	9.07
	nC_{36}	2.41	1.27	0.00
	nC_{37}	3.40	6.05	5.89

BL= Bonny light, UB = Ughelli Blend, IO = Okordia-Ikarama

Table 2. The calculated paraffinicity of crude oil samples

Parameters	Crude oil samples		
	BL	UB	IO
n- Heptane/(Cyclohexane + Mcyclohexanes)	0.0004	0.0092	0.7292
n- Heptane/ McycloHexane	0.0008	0.0664	1.2011
(n-hexane+n-heptane)/(cyclohexane+Mcyclohexane)	2.2953	0.0847	5.8894
2, & 3 Mcylohexanes/DMcyclopentanes)	1.6049	3.2724	0.7079
Total	3.9015	3.4327	8.5276
%Remained	24.59666	21.64111	53.76223
%lost	**75.40334**	**78.35889**	**46.23777**

Table 3. The calculated aromacity of crude oil samples

Parameters	crude oil samples		
	BL	UB	IO
Benzene/nhexane (C_{12}/C_{10})	0.0039	0.4853	0.0003
Toulene/n heptane (C_{25}/C_{21})	3.5540	0.7394	0.0007
Xylene/nOctane (C_{31}/C_{29})	0.8471	1.5483	5.7827
Total	4.4049	2.7729	5.7837
%Remained	33.9843	21.39354	44.62216
%lost	**66.0157**	**78.60646**	**55.37784**

Table 4. The calculated ratios used in crude oil biodegradation studies

Ratios	Crude oil samples		
	BL	UB	IO
Pr/Ph	0.05	0.03	0.05
Pr/nC_{17}	2.41	0.31	2.54
Ph/nC_{18}	26.57	0.24	39.30

The percentage of the paraffin lost were also calculated, and this indicates the BL 75.40%, UB 78.36% and is 46.24% for the IO crude oils (Table 3, Fig. 3). The low values of the paraffinicty of the oils show the light-end of the hydrocarbons have been severely depleted, and the paraffinic content of the crude samples have been greatly reduced. Some researchers have shown that those anaerobic sulphate-reducing bacteria are in charge of the slight biodegradation [12]. More also the light ends ranging from (C_1 – C_9) fraction have been totally removed from the gas chromatograms of the crude oil samples (Fig.2). This may be due to anaerobic bacteria attack deep in the reservoir or loss of the volatile light ends through evaporative fractionation or phase separation [13]. The aromatic content of oil crude oils samples under study are shown in Table 3. The ratios Benzene/nhexane (C_{12}/C_{10}), Toulene/n heptane (C_{25}/C_{21}) and Xylene/nOctane (C_{31}/C_{29}) is low for the crude oil samples. The aromatics have

shown to be more resistant to biodegradation, but the low values indicate that they have remained seriously degraded, therefore may be under sulphate reducing conditions [14].
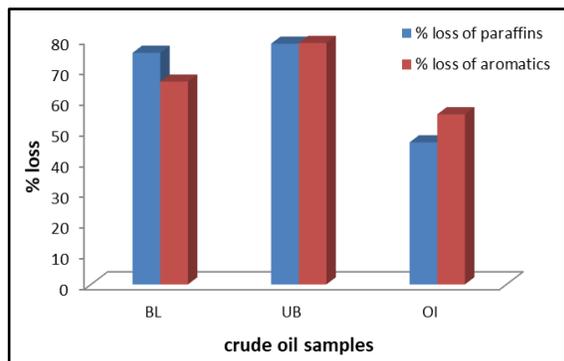

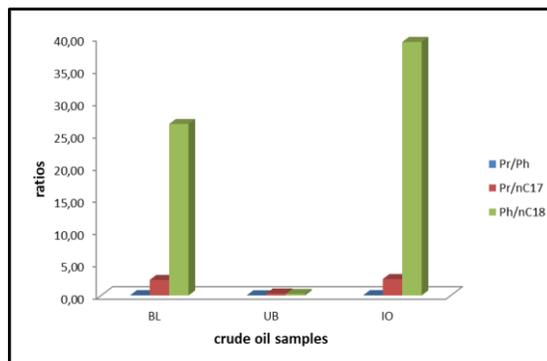Figure 3. Comparison of the % loss of the par-affins and aromatics in crude oil samples

Figure 4. Plot of biodegradation ratios for crude oil samples

These low ratios show that the aromatics have been degraded. The percentage of aromatics lost to biodegradation are 66.02% for BL, 78.60 for UB and 55.38% for IO oil showing that the UB is more affected by the degradation followed by the BL oils (Table 3). The UB crude oils are obtained from the onshore fields in the coastal swamp depobelt of the Niger Delta. The superficial onshore reservoirs may have an influx of meteoric water which is originator high degree of biodegradation [15]. Most researchers have shown that fresh, oxygenated waters which usually come in contact with crude oil in reservoirs can cause extensive aerobic biodegradation. Also, it is acknowledged that fermenting and anaerobic sulphate reducing bacteria can also degrade petroleum [15].

The level of biodegradation in the crude oil samples from the calculated percentages can be ranked (BL>UB>IO), these will affect the fluid properties and hence the value and producibility of the oil accumulations in the basin [16]. The calculated Pr/Ph ratios for the BL are 0.05, UB is 0.03 and OI are 0.05 (Table 4). The ratios are low for the all crude oil samples which is a strong indication of degradation of the oils and a reducing source of organic matter [17].

The near loss to low ratios of Pr/Ph, Pr/nC$_{17}$, and Ph/nC$_{18}$ (Table 4) portray heavy biodegradation for UB crude oil samples and slight biodegradation for BL and OI crude oil [15]. The Ph/nC$_{18}$ ratio is 26.57 for BL, and 39.30 for IO crude oil samples (Table 4, Figure 4). These values are high for the two crude oil samples which show that the oil samples are moderately biodegraded [12]. All components of petroleum such as the gases, alkanes (paraffins), cycloalkanes (naphthenes) and aromatics are vulnerable to microbial degradation. The preferential attack of low molecular weight hydrocarbon components increases the high density (low API 23 gravity) of the unconsumed hydrocarbons. Meteoric water penetrates into a basin and alters any petroleum accumulation in that basin. Water moving past an oil field preferentially dissolves the most soluble hydrocarbons such as methane, ethane, benzene, and toluene. Microbes in the water can also consume the small hydrocarbon molecules producing heavy oils with low API gravity. Meteoric waters have been shown to be responsible for degraded hydrocarbons especially in the Niger Delta [18].

4. Conclusion

The whole oil gas chromatographic analyses of the three crude oil samples under investigation elucidate a progression of biodegradation. This was confirmed by the high percentage loss of the paraffinic and aromatic content of the crude oil samples. The ratios of Pr/Ph, Pr/nC$_{17,}$ and Ph/nC$_{18}$ were used to complement the results of the percentage loss of paraffinic and aromatic content. The results revealed that crude oils were biodegraded with extensive loss of the parrafins and the aromatics. The intensities of biodegradation could be caused by fresh, oxygenated waters which usually come in contact with crude oil in reservoirs. Also, it is

acknowledged that fermenting and anaerobic sulphate reducing bacteria can also degrade petroleum hydrocarbons which can lead to lowering of the API gravity, impact crude oil quality and consequently affect the commercial value. In addition to low-quality crude produced as a result of biodegradation, completely new compounds such as naphthenic acids can be formed during biodegradation which could be also undesirable for crude oil quality.

Acknowledgements

References

[1]   Connan J, Biodegradation of crude oils in reservoirs. In:Brooks J, Welte DH (eds) Advances in petroleum geochemistry, vol 1. Academic Press, London 1984, pp 299 –335.

[2]   Barnard PC and Bastow MA. Hydrocarbon generation, migration, alteration, entrapment and mixing in the Central and Northern North Sea. In: England WA, Fleet AJ (eds) Petroleum migration, geological society. Special Publication, London, 1991 pp 167–190

[3]   Laredo GC, Lopez CR, Alvarez RE., Cano JL. Naphthenic acid, total acid number and sulphur content profile characterization in Isthmus and Maya crude oils. Fuel, 2004; 83: 1689 - 1695.

[4]   Onojake MC, Abrakasa S, and Osuji LC. Chemometric representation of molecular marker data of some Niger Delta crude oils. Egyptian J. Petrol., 2015; 24(2): 139-143.

[5]   Sonibare O, Alimi H, Jarvie D and Ehinola OA. Origin and occurrence of crude oil in the Niger Delta, Nigeria. J. Petrol Sci. Eng., 2008; 61: 97–107.

[6]   Klett TR, Ahlbrandt TS, Schmoker JW and Dolton JL. Ranking of the world's oil and gas provinces by known petroleum volumes. U.S. Geol. Surv. Open-File Report 97- 463.

[7]   Sundararaman C, Nicholas J and Diedjomahor JO. Niger Delta Petroleum System: Reg. Geol., org. facies and Thermal Maturity. AAPG annual meeting March 10-13, 2002, Houston Texas.

[8]   Kaplan A, Lusser CU and Norton IO. Tectonic map of the world, panel 10. American Assoc. of Petrol. Geolo. 1994, Tulsa.

[9]   Kulke H. Nigeria. In: Kulke H (ed) Regional Petroleum Geology of the World. Part II: Africa, America, Australia and Antarctica. Gebru¨der Borntraeger, Berlin 1995, pp 143–172.

[10]   Michele LWT, Ronald RC, and Michael EB. The Niger Delta Petroleum System: Niger Delta Province, Nigeria, Cameroon, and Equatorial Guinea, Africa. U. S. Department of the Interior U.S. Geol. Surv. Open-File Report 99-50-H.

[11]   Peters KE, and Moldowan JN. The Biomarker Guide: Interpreting Molecular fossils in Petroleum and Ancient sediments prentice Hall. Englewood Cliffs 1993, New Jersey

[12]   Mode AW, Anyiam OA, Amobi JO and Nweke SU. Gas chromatographic analysis of whole oil samples: implications for biodegradation in the Niger Delta J. Petrol. Explor. Prod Technol., 2017; 7: 389–398.

[13]   Oforka NC, Osuji LC, and Onojake MC. Petroleum hydrocarbon fingerprinting of crude oils from umutu/bomu oil fields in Niger Delta, Nigeria. Arch. Appl. Sci. Res, 2012; 4(1), 246-253.

[14]   Margesin R and Schinner F. 2001. Biodegradation and bioremediation of hydrocarbons in extreme environments. J Appl Micro Biotechnol., 2001; 56: 650–663.

[15]   Wenger LM., Davis CL and Isaksen GH. 2002. Multiple controls on petroleum biodegradation and impact on oil quality. SPE Reserv Evaluat & Engr, 2002; 5(05): 375-383.

[16]   Miiller DE, Holba AG and Huges WB. Effects of biodegradation on crude oils. In: Meyer RF (ed) Exploration for heavy crude oil and natural bitumen. AAPG studies in geology. AAPG 1987, Tulsa, pp 233–241.

[17]   Hunt JM. Petroleum geochemistry and geology, 2nd ed. WH Freeman and Co. 1995, USA, p 743.

[18]   Ahsan A, Karlsen DA and Patience RL. 1997. Petroleum biodegradation in the Tertiary reservoirs of the North Sea. Mar and Petrol Geol, 1997; 14(1): 55-64.

To whom correspondence should be addressed: Dr. M. C. Onojake, Petroleum Chemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B 5323, Choba, Port Harcourt, Nigeria, mudiaga.onojake@uniport.edu.ng