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Research Paper

Biodegradation ranking show Offshore and Coastal Swamp oils more degraded in Niger Delta Basin

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ABSTRACT.;*The biodegradation of oils is a vital in–reservoir alteration process, the rank of oil accumulations ought to be certain,since it is one of the criteria that is considered in derisking a prospect. The biodegradation rank of oils fosters a better field development and helps in appropriate production planning. A suite of oils was analyzed to evaluate the biodegradation levels and modelled a biodegradation ranking.The biodegradation parametric ratios suchas(Pr+Ph)/(nC_{17}+nC_{18}),C_{29}αβ25norhopane/C_{30}αβhopane,C_{30}αβhopane/(Pr+Ph)and1,3,6/1,2,4trimethylnaphthalene were used in ranking the oils. The rankingtrend for (Pr+Ph)/(nC_{17}+nC_{18}), C_{29}αβ–25–norhopane/C_{30}αβhopane, C_{30}αβhopane/(Pr+Ph) parameters were fairly similar and different for that of 1,3,6/1,2,4–trimethylnaphthalene ratio. The biodegradation ranking for C_{30}αβhopane/(Pr+Ph) ratio show that the oils from Offshore and Coastal Swamp depobelts are more degraded relative to oils from the Northern, Greater Ughelli and Central Swamp depobelts.*

Keywords:*Biodegradation, meteoric water, ranking reservoir, water flushing.*

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I. INTRODUCTION

In contemporary times, it is believed that modern advanced and industrial societies which consist the fabulous metropolitan cities, urban and suburban cities are developed by the income accruing from the dynamics of petroleum marketing. Globally petroleum production is estimated at about 12 metric tons annually (Uche & Dadrasnia, 2017). However, one of the demerits of the petroleum economy is the fact that imperfect petroleum technologies and the inefficient ways of handling petroleum and its byproducts derived from petroleum processing has resulted to changing ecosystems that has resulted into a retrogression effect on the capacity of the ecosystems to sustain the increasing human populations (Uche & Dadrasnia, 2017). Petroleum in reservoirs can be subjected to biodegradation by the fact that the reservoirs are low temperature reservoirs and sustains the existence of microbes with the availability of nutrients such is minerals and oxygen.

Meteoric waters from the surface may influx reservoirs through faults and fractures which could have been sustained during tectonic events, these waters carry along the necessary minerals and oxygen which foster the action of microbes on petroleum as substrates for production of energy.

However, for high temperature reservoirs the sustenance of microbes is limited to mostly the thermophilic bacteria which are mostly sulphate reducing bacteria (SRB). Though the most thermophilic microbe has maximum surviving temperature of 121ºC and can survive for 2hours at 130ºC (Magot, 2005). They can exist in starved conditions which later become favorable,thereby resuscitating them from dormancy to strive again. On a wider horizon, thermophiles belong to a class known as extremophiles which are microbes that are sustained and grow under extreme conditions such as high temperature, salinity, pH, and pressure. They are respectively termed thermophiles for high temperature, psycrophiles for low temperature, halophiles for high salinity, acidophiles for acidic condition, alkaliphiles for alkaline conditions and barophiles for high pressure environments, (Arulazhagan et al., 2017).

The microbes in the reservoir has been proposed to be indigenous, thus representing communities that were trapped in the matrix during the deposition of the sediments. Series of studies have shown differences between the microbial communities in the reservoir and those in the drilling fluid, inferring that the communities in the reservoirs are indigenous and were never introduced by meteoric water or water flooding. (Azadpour & Vadie, 1996), (Belyaev, et al., 1983), (Spark, et al., 2000).

The lighter hydrocarbon fractions are the most vulnerable, excluding of the gases (C_1–C_4), the C_6–C_{15} n–alkane are rapidly biodegraded and susceptible to water washing. The aromatic hydrocarbon components of petroleum are more recalcitrant to biodegradation relative to the aliphatic hydrocarbons. The demerits of bacteria apart from depleting the lighter fraction of hydrocarbons, also contributes to reservoir souring by using the sulphate to generate H_2S as metabolite. Their activity increases wax content in the reservoir which couldreduce the efficiency of the reservoir performance in the context of fluid flow. On the positive side, bacteria have been applied in cleaning up oil spill contaminated land/soil.

The used of bacteria in microbial enhanced oil recovery as yielded unexpected positive results. Enhanced bacterial growth produces gas such methane, CO_2, and hydrogen, these could be captured and reinjected to enhance production (Van Hamme et al., 2003) (Bass & Lappin-Scott, 1997)

The Niger delta reservoirs have been influxed by marine waters as well as meteoric waters through faults and extensive sand stringers(Dickey, George, & Barker, 1987). This has render the Niger Delta reservoir susceptible to in–reservoir biodegradation, in this wise, the relative biodegradation status is worth understanding, this will foster a better field developmentin the context of appropriate well placement and production planning.

Various standardshave been devised to delineate biodegradation and estimate biodegradation level, excluding the decreasing concentration of individual compound with increasing biodegradation, parametric ratios such as Pr/nC_{17}, Ph/nC_{18},C_{30}αβhopane/(Pr+Ph), (Pr+Ph)/(nC_{17}+nC_{18}) and C_{29}αβ–25–norhopane/C_{30}αβhopane have been used to estimate biodegradation level and establish biodegradation profiles in reservoirs (Huang et al., 2004).

Petroleum do inherit compositional differences from their genetic source organic matter, due to these inherent compositional differences, the oils have different degree of resistance to biodegradation. This differential in biodegradation resistance can be used to rank biodegradation, various compound class have particular profile that corresponds to the level/extent of biodegradation. (Alexander et al., 1983)

Different compound both aliphatics and aromatics do have different biodegradation profiles, thus ranking profiles.Moldowan et al., (1992) modified the proposed ranking of biodegraded oils, assigning rank levels of 1 to 10. This was based on biomarker degradation sequence which were mostly empirical observations in the field and laboratory. In most cases, the descriptions of the degree of biodegradation scale is based on the bioresistance of petroleum compounds.

The most reliable method of biodegradation assessment is quantitative, which is parametric based, though some parametric ratio does not cover the broadest extent of biodegradation, since they are compound dependent expressionof biodegradation, particularly due to the difference in resistance to biodegradation exhibited by the compounds. This is captured inthe biodegradation scale of (Wenger, Davis, & Isaksen, 2002) who proposed that the level of biodegradation should be expressed based on changes that occur in the oils as reflected by biomarkers. Head et al., (2003) presented a combined modified version of Moldowan, et al., (1992), the derived model based on the biomarkerconcept is presented in figure 2.

In this study, biodegradation rankings of some Niger Delta oils is performed, using various biodegradation parametric ratios such as C_{30}αβhopane/(Pr+Ph), (Pr+Ph)/(nC_{17}+nC_{18}) and C_{29}αβ–25–norhopane/C_{30}αβhopane to rank the oils to unravel the most degraded and least degraded(undegraded) for each parameter. The objectives of the study include i) calculating various parametric ratios, ii) ranking the oils base on the ratios and iii) relating the rank profiles to geological concept within the Niger Delta Basin.

This assessment may on a wider horizon provide the bases for derisking the exploration of a prospectin terms of oil quality. The difference in biodegradation ranking may provide insight into compartmentalization of reservoir, this will further foster informed decision on development of the field and improved planning for productionstrategies of biodegraded oils.

Figure 1. Approximate Locations of the oilfields studied

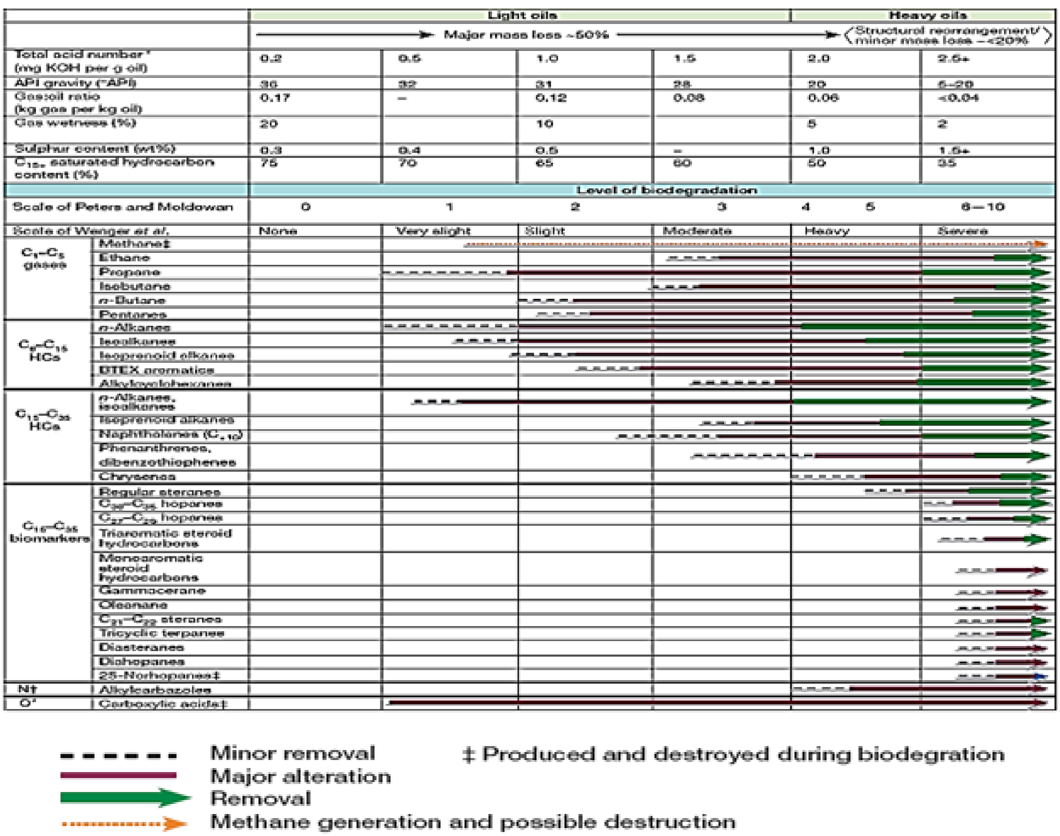

Figure 2. Biodegradation ranking model proposed by Head et al, 2003.

II. MATERIALS AND METHOD.

Samples and Sampling.

Samples for this study is a suite of oil samples obtained from oils fields (figure 1) in the Niger Delta basin. The samples were obtained randomly of different levels of degradation. Samples were obtained from well heads in a sample vial with Teflon caps, samples were further stored in a chest of ice to preserve sample compositional integrity(Giles & Mills, 2010)

Sample preparation and Analysis.

Sampleswere prepared by appropriately measuring 0.2mg into 0.2mL of hexane to achieve 1μg/μL which is the recommended concentration that was injected into GC–MS for full scan analysis. The GC-MS analysis was done using a HP5890 II GC with a split/spiltless injector linked to a HP 5972 MSD (Mass Selective Detector). The GC was temperature programmed for 40ºC–300ºC at 4ºC per minute and held at final temperature for 20 min. The carrier gas was Helium (flow rate 1ml/min., pressure of 50kPa, slit at 30ml/min). The ionization and identification was carried out in the HP 5972 MSD, which was equipped with electron voltage of 70 eV, filament current of 220μA, source temperature of 160ºC, a multiplier voltage of 1600V and interface temperature of 300ºC. The acquisition was monitored by HP Vectra 48 PC chemstation computer in both full scan mode (30ions 0.7 cps 35m dwell). HP is currently known as Agilent, UK. Peak integration was done using the RTE integrator. Data was obtained from the percentage report from the Enhanced MSD ChemStation 2011 software by Agilent Technologies(Peters et al., 2005).

III. RESULT AND DISCUSSION.

Mass chromatograms of m/z 85, 191, 177 were extracted from the various data file generated from the analysis using Enhanced MSD Chemstation 2011 software by Agilent Technologies. The abundances used for the calculation of the parametric ratios were extracted from the corresponding percent report.

Table 1. Parametric ratios used for ranking biodegradation. Pr= Pristane, Ph= Phytane, TMN= Trimethylnaphthalene

OILS	C_{29} Norhopane/C_{30} Hopane	C_{30} Hopane/(Pr+Ph)	(Pr+Ph)/(nC_{17}+nC_{18})	136/124 TMN
ATHBASCA	NA	NA	NA	2.59
BOSCAN	0.32	0.13	1.19	5.09
CALFORNIA	0.30	NA	NA	11.50
NORTH SEA 1	0.21	1.05	0.28	10.55
NORTH SEA 2	0.21	NA	NA	4.46
ABO	0.26	0.32	0.42	11.46
AFAM	0.37	0.07	1.92	NA
AZUZUMA	0.35	0.50	0.82	5.69
CLOUGH	0.29	0.49	0.64	3.49
ENANG	0.52	1.16	1.48	5.13
NEMBE	0.43	0.29	0.33	11.59
RUMUEKPE	0.28	0.30	1.83	7.64
TEBIDABA	0.35	0.54	0.83	2.28
UMUTU	0.37	0.06	0.27	11.68
USAN	0.17	0.58	1.25	11.95
UTOROGU	0.16	0.10	8.42	13.50
AHIA	0.19	0.07	0.54	19.34
BONGA	0.28	0.53	1.35	12.11
OBAGI	0.27	0.24	1.35	11.60
CAWTHRONE	0.16	0.35	1.12	7.81

The biodegradation ranking as portrayed by the different parameters show different ranking positions for the suite of oils studied, this is due to different stages of biodegradation of the oils, for example the Athabasca oil sample have been stripped of almost all aliphatics except the aromatics. Thus none of the aliphatic parametric ratio is calculated. However, most of the Niger Delta oils are vary from non–degraded oils to moderately degraded oils.

The (Pr+Ph)/(nC_{17}+nC_{18}) biodegradation parametric ratio is very sensitive, it increases with increasing trend of biodegradation, this is because the isoprenoids (Pr+Ph) are more resistance to biodegradation relative to the alkanes (nC_{17}+nC_{18}), this parametric ratio could be reliably use for monitoring oils that are light to moderately biodegraded. Ranking profile of the oils using (Pr+Ph)/(nC_{17}+nC_{18}) is presented in figure 3, the figure shows that Umutu oils is lest degraded while Utorogu oil is the most degraded in terms of the alkanes, the figure (3) shows a subtle change in biodegradation, this parameter best express the degradation of alkanes. There was no observed relationship between the ranking profile and the depobelts of the oils.

The C_{30} Hopane/(Pr+Ph) ratio is also another parameter for expressing biodegradation, mostly when the alkanes have been depleted and the isoprenoids are intact. The hopanes are more resistant to biodegradation relative to the isoprenoids, this ratio increases with biodegradation. This ratio is efficient on the assumption that isoprenoids are depleted remaining the hopanes that are more stable and resistance to biodegradation. Figure 4, which represents the biodegradation ranking using C_{30} Hopane/(Pr+Ph) shows that oils from Offshore and Coastal Swamp depo belts are more degraded than oils from Central Swamp, Greater Ugehelli and Northern depo belt, thus Umutu oil (Northern depo belt) is the least degraded and Enang (Offshore depobelt) is the most degraded.

Figure 5, shows the biodegradation ranking using C_{29} Norhopane/C_{30} Hopane ratio, the ratio represents the generation and increase of 25–norhopanes via microbial removal of a methyl group or the accumulation of the preexisting 25–norhopanes in the source rock generating the oils during biodegradation. 25–norhopanesare generally observed to be significantly present in severely biodegraded oil (Huang et al., 2004).

C_{29} Norhopane/C_{30} Hopane ratio increases with biodegradation, figure 5 which expresses the ranking of the oils infers that Utorogu and Cawthorne oils ranks least degraded and Enang oil ranks most degraded in terms of the presence of 25–Norhopanes, which reflects the degree of biodegradation and did not show any relationship relative to the depobelts of the oils. The 25–Norhopanes are reliably used in assessment of severely degraded oils.

The aromatic hydrocarbons are more resistant to biodegradation relative to the aliphatics by virtue of the of their chemical structure which is basically characterized by aromatic rings, alkyl substituent groups and the positions of the alkyl substituents groups. Generally, the rate of biodegradation decreases with increasing aromatic rings and alkyl groups. In a compound class, an isomer may be more recalcitrant to biodegradation than the other.

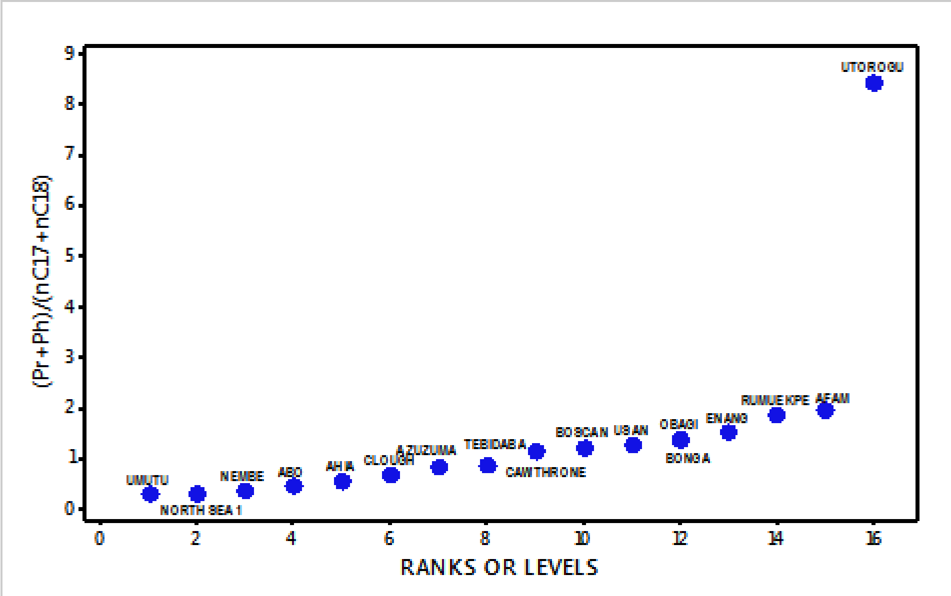

Figure 3. Biodegradation ranking for the oils using(Pr+Ph)/(nC_{17}+nC_{18})

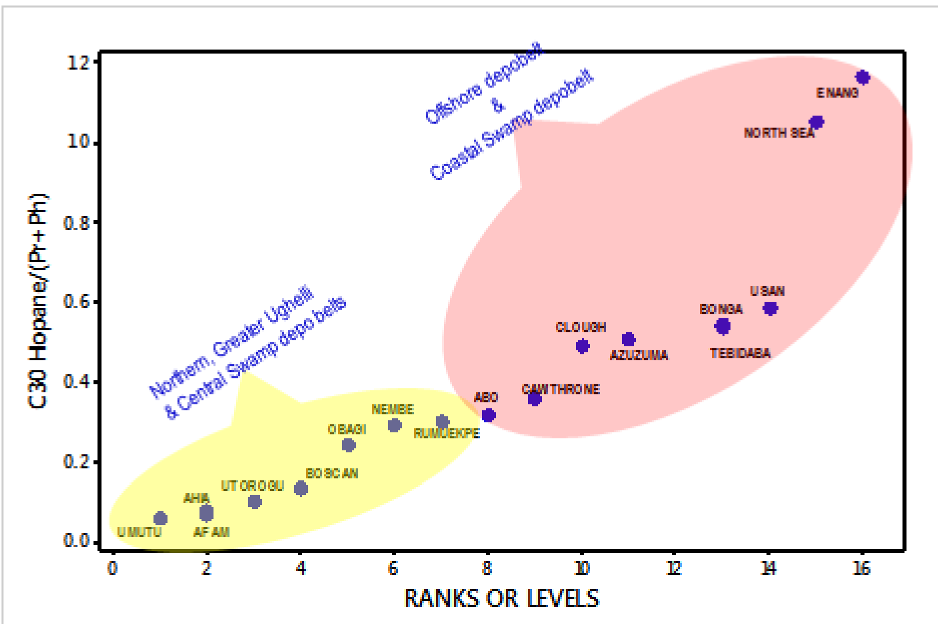

Figure 4. Biodegradation ranking for oils usingC30 Hopane/(Pr+Ph). Exception of North Sea and Boscan oils, Niger Delta oils show that the Offshore and Coastal swamp oils are more degraded.

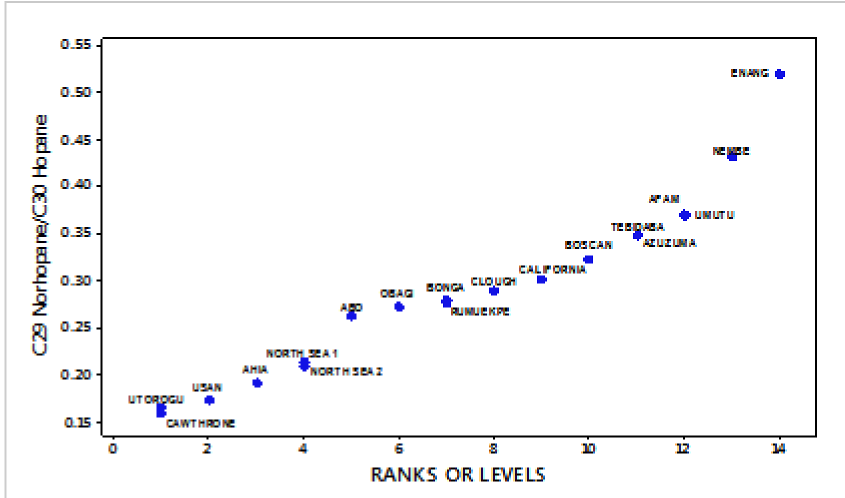

Figure 5. Biodegradation ranking for the oils using C29 Norhopane/C30 Hopane

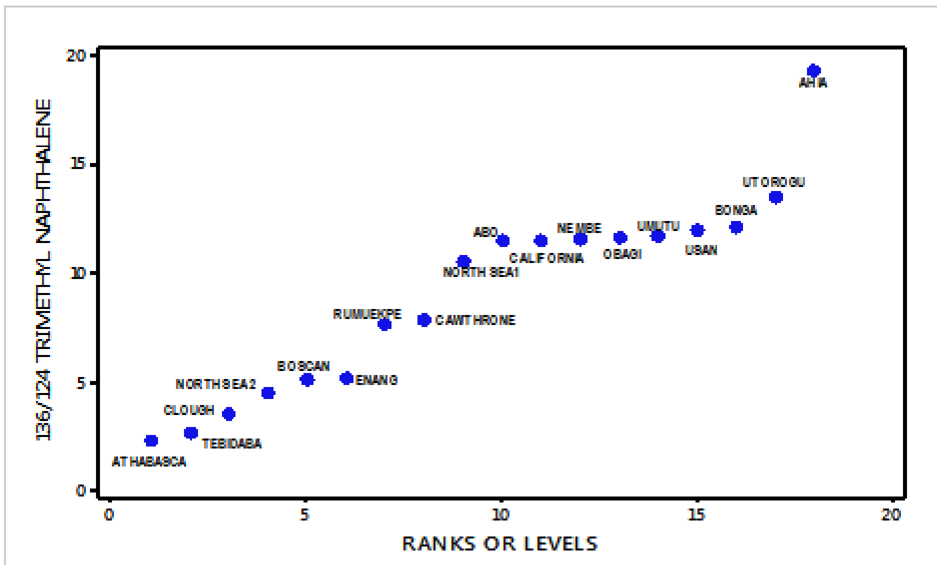

Figure 6. Biodegradation rankings for the oils using 136/124 TMN (Trimethylnaphthalene)

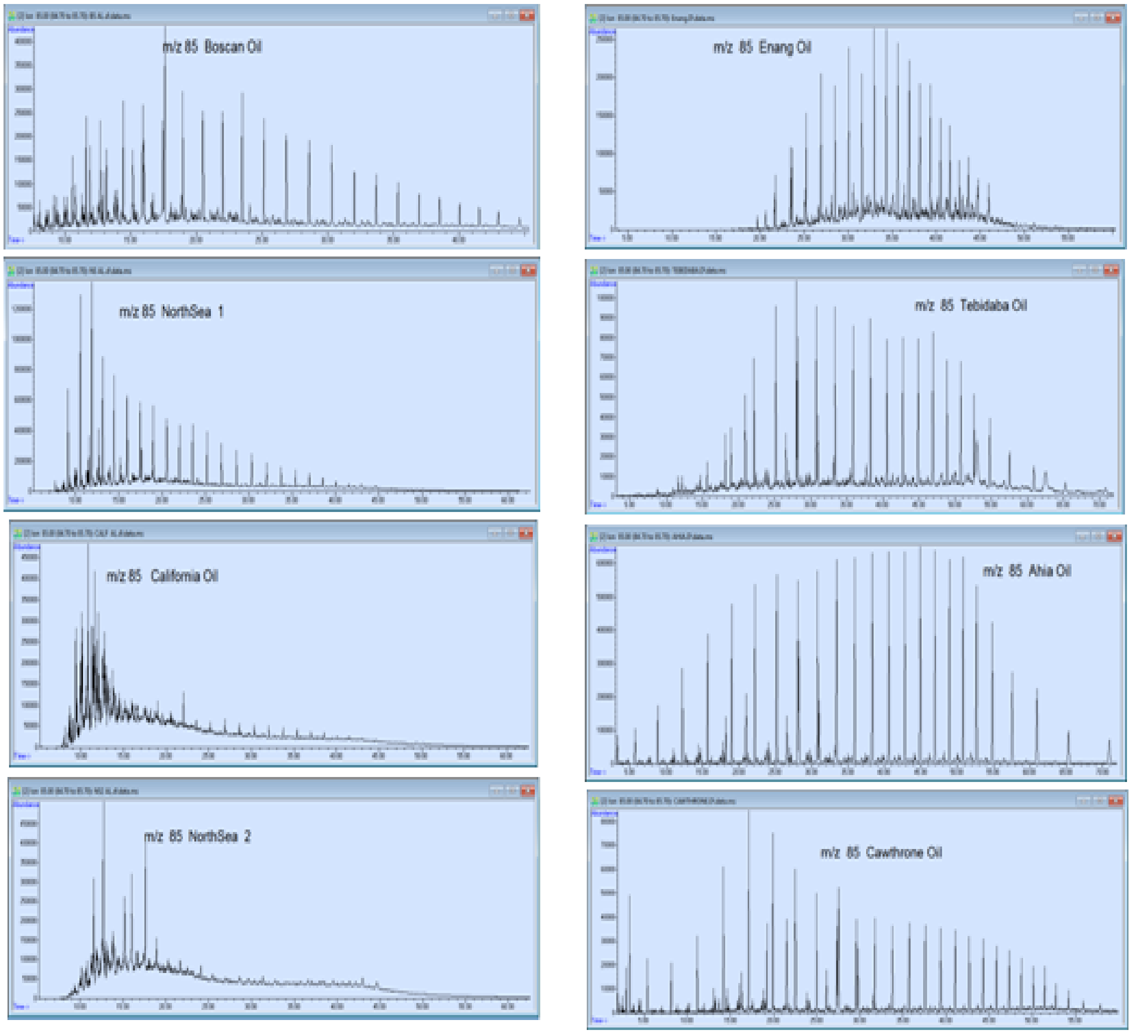

Figure 7. Chromatograms of various oils showing different degree of biodegradation

The more resistant isomers tend to have adjacent alkyl (methyl) groups that inhibit bacterial attack due to steric hindrances(Sykes , 1985). In this study the alkyl naphthalene has been used as one of the biodegradation ranking parameters, specifically 1,3,6/1,2,4– trimethylnaphthalene ratio has been used. The trend is that the 1,3,6–trimethylnaphthalene is more susceptible to biodegradation, while the 1,2,4–trimethylnaphthalene is more resistant to biodegradation (Huang et al., 2004), this invariably means that the ratio will decrease with increasing biodegradation. The trimethylnaphthalene are stable during the removal of alkane in biodegradation process and are only affected during the removal of isoprenoids. This observation means that 1,3,6/1,2,4– trimethylnaphthalene ratio can be used for moderately to severely degraded oils. Figure 6 shows the use of 1,3,6/1,2,4– trimethylnaphthalene ratio for ranking biodegradation in respect of the suite of oils studied. The figure show that Athabasca oil is the most degraded oil while Ahia oil is the least degraded oil. Figure 7 presents some m/z 85 mass chromatograms (reconstructed chromatograms) reflecting different degree of biodegradation of the oils.

IV. CONCLUSION.

The study generated ranking profiles for some oils including the Niger Delta oils based on the biodegradation parametric ratios, each biodegradation parameter represents a certain degree of biodegradation, though not restricted, but may present potential trend or profile of the oils at different biodegradation stages. The C_{30} Hopane/(Pr+Ph) parametric ratio show that among the Niger Delta oils, the Offshore and Coastal Swamp depobelt oils are more degraded relative to the oils of the Northern, Greater Ughelli and Central Swamp depobelts.

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