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Gas Chromatography Application as a Tool for Correlation of Crudes from Some Wells in Eastern Niger Delta Basin

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ABSTRACT: Six crude samples from wells in Eastern Niger Delta were correlated using gas chromatography. These samples were collected from X1, X2, X3, X4, X5 and X6 wells in the Eastern Niger Delta Port Harcourt and Eket areas. The main objective of this study was to identify the sources rocks, nature of organic matter (OM), environment of deposition and the redox potentials in the environment. The method of interpretation involves the use of Gas Chromatographic fingerprints to know the distribution of the chemical constituents, the invariance ratio in isoheptanes, mango C7 hydrocarbon parameters and ratios of pristane to phytane, isoprenoids to N- alkane were used as tools in the correlation. The Oils separated into two groups based on distinctions in invariance ratios of light hydrocarbon from Pristane/Phytane (Pr/Ph) ratios, the sources rocks responsible for Oils in wells X4,X5 and X6 received more terrigeneous organic matter than Oils from wells X1,X2,X3 with inputs of marine organic matter but their environment of deposition was the same (Oxic environment).The Pristane/C17 ratios show they were not deposited under marine conditions. Their Phytane/nC18 ratios indicate they are characteristic of petroleum from shale source rocks.

KEYWORDS: Crude, Chromatographic, Fingerprints, Isoprenoids, Invariance ratio**.**

I. INTRODUCTION

This study involves the use of gas chromatographic fingerprints of the six Crude samples from six Oil wells X1-X6 in different fields to know the distribution of the chemical constituents of the oils. The invariance ratio in Isoheptanes, Mango's C7 hydrocarbon parameters and ratio of Pristane/ Phytane, Isoprenoids to n-alkanes are used as tools in the correlation. Proper application of modern analytical of techniques has been critical to our ability to describe the chemical composition of fossil fuels and kerogen, to predict source potentials of sedimentary rocks, to correlate samples with each other and to predict transformation processes like bio- degradation.
Organic geochemical analyses are undertaken with one of two objectives in mind.
1) To evaluate the petroleum source potential of a rock or
2) To characterize a particular sample chemically, for the purpose of attempting a correlation with another sample.
Describing a sample chemically is simply amassing the largest possible amount of data about its bulk chemistry and determining the identities and Concentration of specific compounds in the sample. Evaluation of petroleum-sources potential in contrast has become more standardized in recent times. Any evaluation of source potential must provide three pieces of data: quantity, type and maturity of organic matter present in the rock.
The study area is the Niger Delta Oil Province which conventionally is divided into the eastern and western Niger Delta. This study location is the eastern Niger Delta section which covers many Oil fields. Six samples X1, X2,X3 – X6 were collected from Six different wells located in the Port Harcourt and Eket zones of the Niger Delta
basin (Fig 1).

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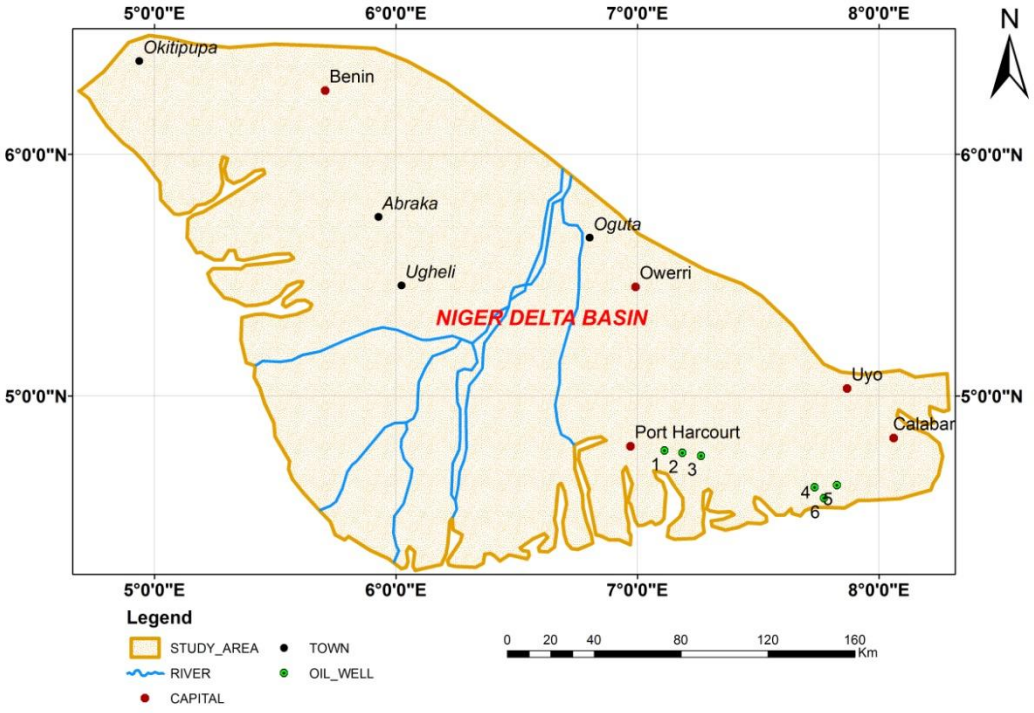

Fig. 1: Map of the Niger Delta showing location of oil samples X1 – X6

II. STRATIGRAPHY

The Niger Delta is situated on the continental margin of the Gulf of Guinea West Africa between Latituds 3^0 and 6^{0N} and longitudes $5^{0\ and}\ 8^0$E. It extends from the Calabar Flank and the Abakaliki Trough in the east to Benin flank in the west and opens to the Atlantic Ocean in the South.

This basin is an offshoot of the Benue Trough – Anambra basin Complex which together with the basin are Closely linked with the triple Junction type (RRR) rift – ridge, a system that initiated the separation of south America from Africa in the Late Cretaceous times (Lehner and De Ruiter, 1977) the Niger Delta complex consists of Cenozoic formations deposited in a high energy constructive deltaic environment and differentiated into continental upper Delta top facies (Benin) paralic delta front (Agbada) and prodelta marine shales (Akata) (Table 1). The Akata Formation is basal, time transgresive lithologic unit of the Niger Delta complex composed mainly of marine shales deposited as the high energy delta advanced into deep water. It also contains sandy and silty sediments laid down as turbidtes and continental slope channel fills. The Akata shales are very rich in planktonic foraminifera (Weber, 1971) which make up more than 50% of the micro fauna.

The Agbada Formation overlies the Akata. It consists of alternating sands, sandstone and shales. The sandstones forming the main reservoirs of the Niger Delta. The Benin Formation is the upper most unit of the Niger delta basin. The formation consists of gravels, sandstones , siltstone and Shale. The shale content increases towards the base (Short and Stauble,1967). The formation can be recognized because of high sand content (70 - 100%), minor shale intercalations and the absence of brackish water and marine Faunas.

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Table 1: Stratigraphic Column of Niger Delta Formations (after short and Stauble, 1967)

AGE	SURFACE	SUBSURFACE	MEGA DEPOSITIONAL ENVIRON.
Pliocene Recent	Benin Formation	Benin Formation	Continental
Miocene Recent	Ogwashi-Asaba Formation	Agbada Formation	Paralic
Eocene Recent	Ameki/Nanka Formation	Agbada Formation	Paralic
Paleocene	Imo State	Akata Formation	Marine

Oil and gas reservoirs in the Niger Delta basin occur in sand–sandstones throughout Agbada Formation, usually trapped in rollover anticlines associated with growth faults. Other forms of trap occur in the Niger Delta basin because of stacked sand/shale alternation. Most Oil fields in the Niger Delta have multiple reservoir levels with Oil Column heights averaging between 15-50m (Reijer, 1996).

Niger Delta crudes Consists of the following:
1) Light crude which is paraffinic and waxy and pour point from -7 to 45^0C
2) Medium crude which is predominantly naphthenic, non waxy and has pour point less than – 25^0C.

A good knowledge of the petroleum systems in mature basins is important for petroleum exploration efforts. Ekweozor and Daukoru, 1994; kulke,1995, Michael L.W Turtle et al 1999, identified one petroleum system the Tertiary Niger Delta (Akata – Agbada) petroleum system. Haack et al (2000) defined three petroleum systems for the Niger Delta, a Lower Cretaceous petroleum system Characterized by lacustrine source rocks in the North-western part of the delta; an Upper Cretaceous to Lower Paleocene petroleum system characterized by marine source rock also in the north-western part of the delta and a Tertiary deltaic petroleum system, comprising source rocks containing type II,II-III and type III kerogens that extends across the entire delta including the deep–water areas.

Based in organic matter content and type, Evamy et al (1978) proposed that both the marine shale (Akata Formation) and the shale interbedded with paralic sandstone lower Agbada Foration) were the source rocks for the Niger Delta of crudes. Ekweozor et al (1979) used ab-hopanes and Oleananes to finger print crudes with respect to their source on the western side of the delta.

Ekweozor and Okoye (1980) used geochemical maturity indicator including vitrinite reflectance data indicated rocks younger than the deeply buried lower part of the paralic sequence to be immature.

Ejedawe et al (1984) used maturity models to conclude that the central part of the Agbada shale sources the Oil while the Akata shale sources the gas. In other parts of the delta they believed that both shales source the Oil.

Stacher (1995), proposed that the Akata Formation is the only source rock volumetrically significant and whose depth of burial is consistent with the depth of the oil kitchen/ window.

Eneogwe et al (2002) analysed oils from onshore and offshore oil fields in the Niger delta, they found that the many of oils contain three Oleananes isomers. Oils generated at the early stage of hydrocarbon generation contain Oleananes. Those generated at peak of hydrocarbon generation do not contain Oleananes identifiable quantities.

Eneogwe and Ekundayo (2003) geochemically analysed some oils from eleven offshore and onshore field in the Northwest Niger Delta for their biomarker and isotopic compositions. In their finding, the oils grouped into three generic families. Family1 located in the onshore swamp to transition area, received sediments from predominantly Late Cretaceous or younger marine source rock laid down in a suboxic to oxic environment. Family 2, near offshore area, oils derived from Tertiary source facies with mix terrigenous and marine organic matter and family 3, located in the offshore area, sediments derived from Tertiary source rocks typical of those in oxic, near shore or deltaic setting receiving significant organic matter.

Eneogwe (2003) analysed fifty one oils from eleven fields in the Niger Delta for their C7 hydrocarbon contents using Hierarchical cluster Analysis and Principal Component analysis to discriminated the Oils into four sets which were distinct in all the seven variables used in the cluster analysis. The distribution of C7 hydrocarbons in the oils indicated two of the eleven fields are homogeneous in terms of oil type, whereas the rest are not.

Using the invariance ratios K_1 and two-ring preference ratios, Eneogwe (2003) analysed thirty- five Oils from two fields in the offshore eastern Niger Delta. These Oils separated into two. Also Eneogwe and Ekundayo(2004) used mango's light hydrocarbon parameters to correlate some oil samples from the Western Niger delta which showed two groups. Based on their findings, two petroleum systems are present, the first being a terrigneous system deposited under oxic and non – stratified conditions. The second petroleum system shows evidence of generation from a source rock of marine organo–facies deposited under sub-oxic and stratified conditions.

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III. METHOD OF STUDY

The study is based on the analysis of six crude samples randomly pooled from the eastern Niger Delta using Gas Chromatography. Gas chromatographic analyses are usually carried out on the saturated hydrocarbon fraction of crudes and bitumen. A gas chromatograph is an oven containing a long, thin coiled column of metal or glass. One end of if is attached to a heated injection port, through which the samples to be analysed can be introduced onto the column.
The other end is attached to a detector that can monitor the passage of the compounds out of the column after they have been separated. Sample to be analysed is injected with a syringe into the hot injection port. The molecules in the sample are vaporized rapidly and swept onto the column by an inert gas flowing continuously through the column. The components of the injected mixture separate as a result of differences in vapour pressure above the liquid phase and in solubility phase in the liquid phase. The rate of movement of a particular molecule through the column depends on how much time it spends in the vapour (in a state which it can be swept along) and how much time it spends immobilised in the liquid phase. Heavy molecules generally move more slowly than light ones. As the analysis is in progress, the oven can be gradually heated to increase the volatility and mobility of the heavier molecules. The gradual increase in column temperature permits both light and heavy components to pass through the column in a reasonable length of time.
As the compounds emerge from the column they are detected and a signal proportional to their concentration is recorded. The trace representing all the emerging compounds is known as gas chromatogram. Each peak ideally represents a single compound but sometimes two or more compounds emerge almost at the same time, and the peaks overlap. Two fundamentally different types of characteristics can be measured by geochemical techniques: they include bulk and specific parameters. Bulk parameter refer to properties of the whole sample which include, API gravity, sulphur content, saturated – hydrocarbon content, pour points etc. The specific parameters in contrast, measure in detail one characteristic of a small fraction of the sample: they include for example, the many types of biomarker ratios.

IV. RESULTS AND INTERPRETATION

A.) GAS CHROMATOGRAPHIC FINGERPRINTS

Some gas chromatographic finger prints are indicative of certain types of organic matter input. Least mature oils show a ummodal n- paraffin (< C_{15}) can be related to low thermal maturity, migrational effects (phase separation) evaporative loss (weathering or water washing). Almost all the oils analysed contained hydrocarbons of the range C_3-C_{33}which made them Suitable for this study.
The X1- X3 crudes showed reduced light ends (Unimodal), while X4- X6 indicated bimodal n-paraffin distribution and contain more heavy ends (Figures 3-8).

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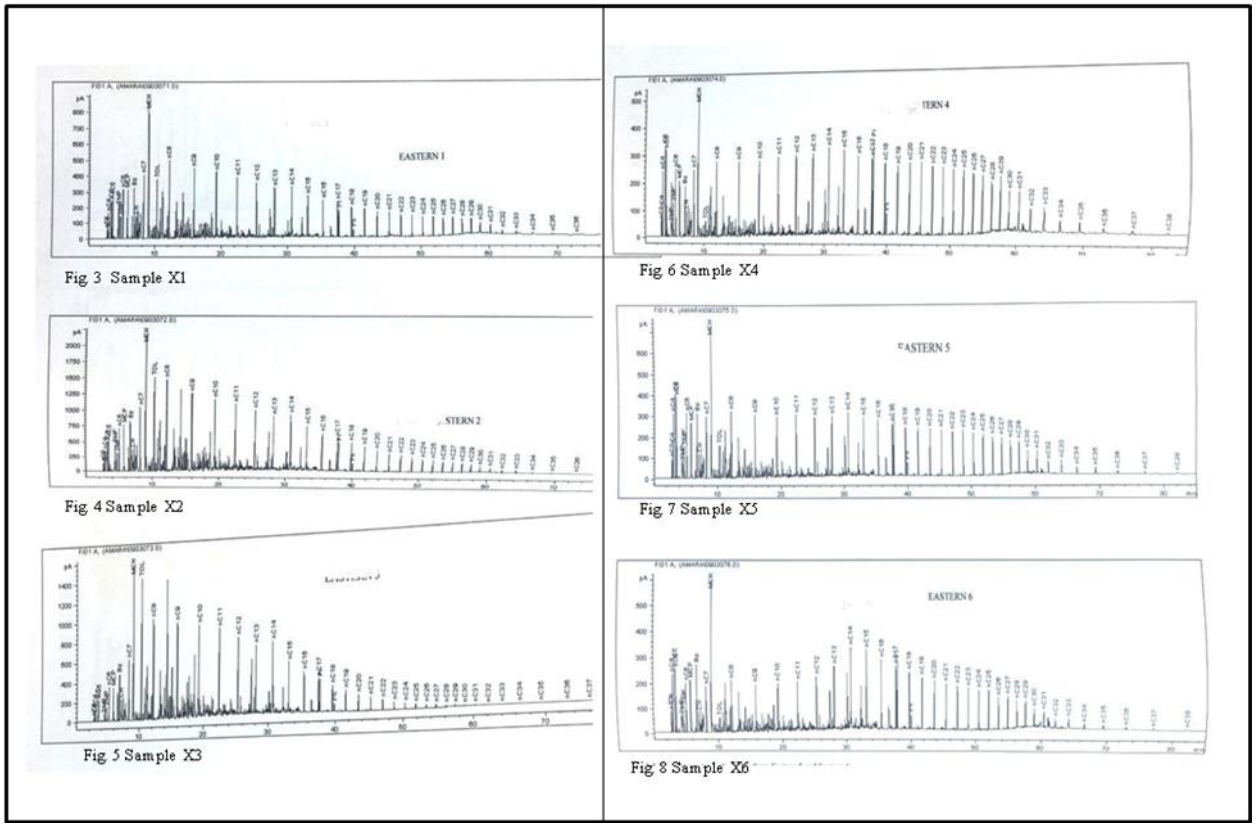

Fig 3 - 8: Chromatographs of Eastern Niger Delta Oil Samples X1 –X6

B.) INVARIANCE RATIO IN ISOHEPTANE

Invariance ratio in Isoheptane seen in all primary oils proved a useful tool for Oil correlation in Tertiary Niger Delta. Mango (1987) has shown that a ratio of Isoheptane (Invariance ratios) remains remarkably constant in all primary Oils. Mango (1994) divided C7 ratios into two categories – invariant ratios, which remain relatively constant in all oils and ring preference ratios which show substantial variance.

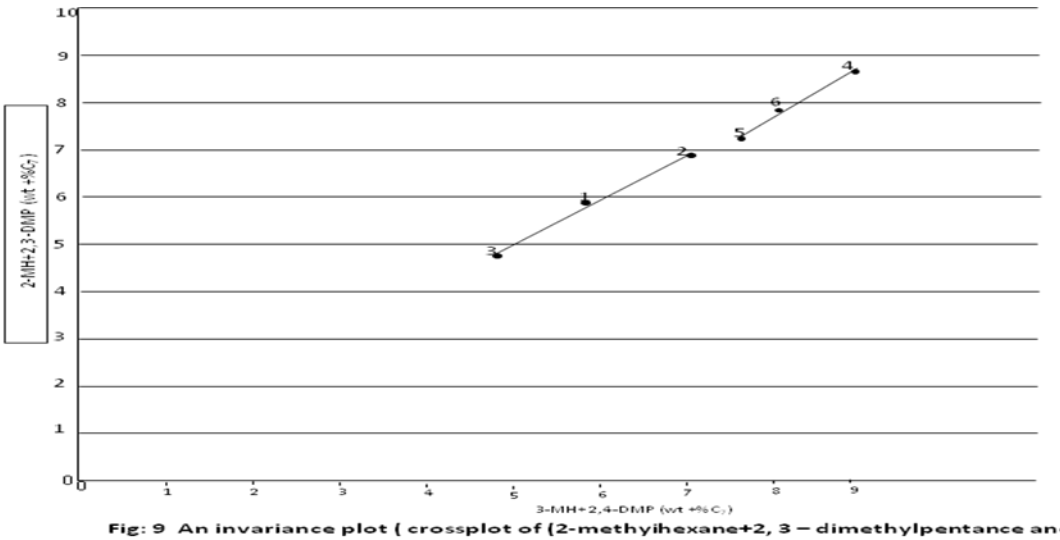

Fig: 9 An invariance plot (crossplot of (2-methyihexane+2, 3 – dimethylpentance and 3-methylheane+2, 4-dimethylpentane)

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The variation in ratio (K_1) that exist in all oils can be explained by the variations in homologous oil sets, that is sets of oils from a common source as observed by Eneogwe, 2003. Thus various source rocks generate oils with constant and distinct K_1s. Light hydrocarbons have proved very effective in oil–oil and oil- source rock correlation (koons et al, 1974, Erdman and Morris, 1974, Williams, 1984, Cardwell, 1977; Deroo et al, 1977 Phillipi, 1984, Kornack, 1993; Harpen, 1995) Ratios of light hydrocarbons (LHs) defined by Mango, 1987, may provide another means of evaluating the Niger Delta Petroleum systems independent of higher hydrocarbons.
Cyclopentane-rich oils are distinct from all other oils in essentially all light hydrocarbon ratios but similar distinctions between oil types exhibiting high concentrations of cyclothexanes are less clear. Methyclohexanes and Toluene were the most important discriminating variables. Plot of the oil samples on Methyclonexane versus Toluene is shown in Fig.10

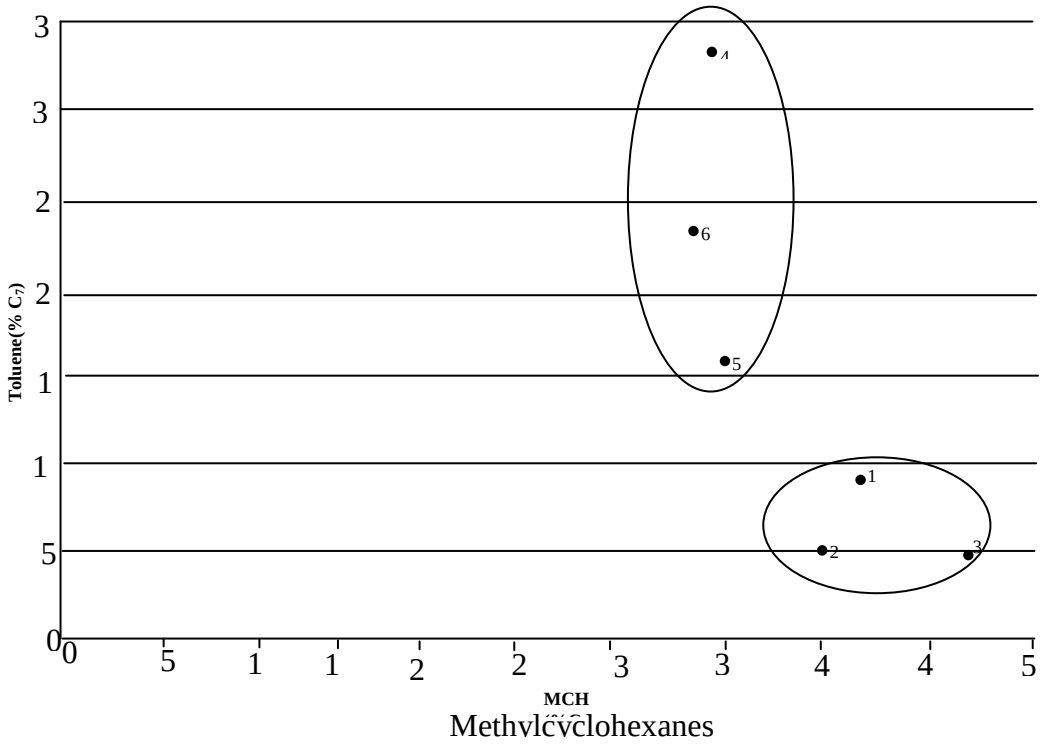

Fig 10 Cross Plot of Methylcyclohexane Versus Toluene (%C_7)

This plot shows that oil samples 4,5 and 6 indicates higher six ring preference (6RP) than oils from samples 1, 2 and 3 wells in Niger Delta. The light hydrocarbons (LHs) from the six wells in eastern Nigeria Delta from the plot shows strong six-ring preference, consistent with oil from terrestrial deltaic source rocks.
A ternary plot of Cyclopentane (CP), Methycyclohexane (MCH) and Toluene (TL) Fig. 11 showed that the two homogous oil sets identified remained tight constrained and distinct.

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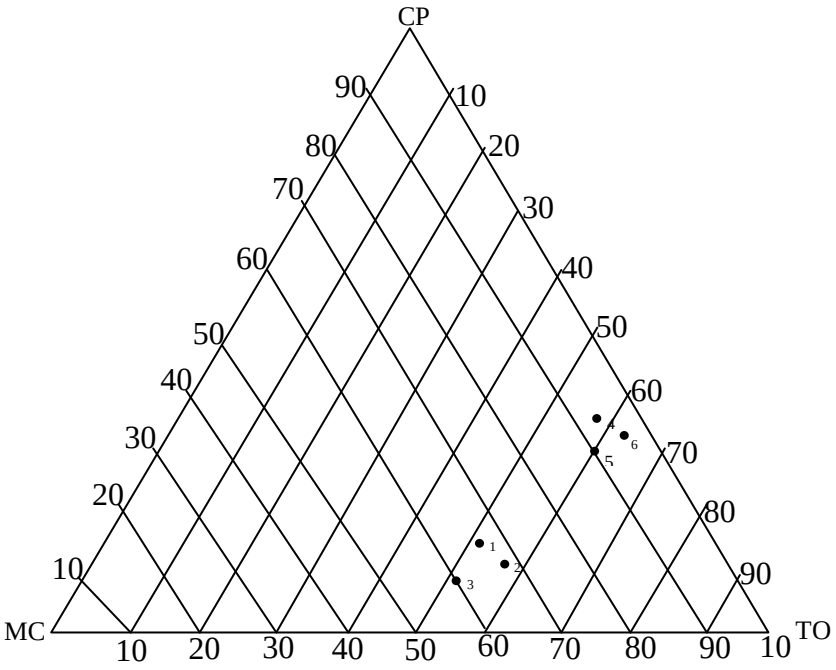

Fig: 11 Ternery plot of Cyclopentane, Methylcyclohexane and Toluene.

C.) BIOMARKERS

Pristane/Phytane ratios are commonly used in correlations. High wax non-marine source rocks have Pr/ph ratio between 4 to 11 while low wax oils from marine source rocks have ratios of Pr/Ph from 1 to 3. Pr/Ph ratios of petroleum ordinary reflect the nature of the contributing organic matter; it also increases with thermal maturation.
The Pr/Ph ratio is a good indicator of the redox potential of the source sediments (Didyk et, al, 1978). Their finding shows Pr/Ph ratios less than unity (<1), indicate anoxic depositional environment while oxic environments are indicated by Pr/Ph greater than unity (>1).

Application of this ratio to this study showed the following:

Oil sample		Pr/Ph	
X_1		1.05/0.32 1	= 3.23
X_2	"	1.88/0.65	= 2.88
X_3	"	1.56/0.38	= 4.14
X_4	"	3.42/0.76	= 4.52
X_5	"	2.76/056	= 4.98
X_6	"	2.78/0.62	= 4.49

From the result, all the oil samples are greater than unity indicating organic matter deposited in an oxic environment. Pr/Ph value greater than one (>1) are believed also to be characteristic of petroleum from shale source rocks, Connan, (1981) Hughes, (1984), Palacas, (1984), Moldowan et al (1985); ten Haven et al (1988). Marine Organic matter usually has Pr/Ph ratios < 2.5, while organic matter from the terrestrial environment indicates ratios from 3.0 upwards. The result of this as shown above indicated that the six oil samples from the eastern Niger Delta were all derived from terrestrial in origin and from shale as a source rock.
Isoprenoid / n-paraffin ratio
Pristane/nC_{17} and Phytane/n-C_{18} are used also in the correlation of the crude samples. Lijimbach (1975) observed that oils from rocks deposited under marine conditions indicated Pr/nC_{17} ratios < 0.5. Phytane/nC_{18} ratio > 0.3 are

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characteristic of petroleum from shale source rock while Ph/n C_{18} < 0.3 is from carbonate source rocks,(Palacas, 1984; Connan,1981).

Table 2 Results of ratios of Pr/nC_{17} and Ph/nC_{18} of the Eastern Niger Delta oil samples

Samples	Pr/n C17)	Ph/nC18
X1	1.05/1.1.15 = 0.91	0.32/0.99 = 0.32
X2	1.88/2.01 = 0.94	6.65/1.80 = 0.36
X3	1.56/1.41 = 1.11	0.38/1.14 = 0.33
X4	3.42/2.34 =1.46	0.76/2.16 = 0.35
X5	2.78/1.95 = 1.43	0.56/1.79 = 0.31
X6	2.78/2.24 = 1.24	0.62/1.95=0.32

V. DISCUSSION

The chromatogram indicated that the analysed oil samples contain hydrocarbons of the range C_3-C_{33}. X1 X2 and X3 oil samples showed reduce light ends (Unimoda). X4, X5 and X6 are bimodal n–paraffins and contain more heavy n-paraffins.

From Mango (1987) invariance ratio in isoheptane, the six oil samples indicated they are terrestrial origin with little or no marine organic matter but samples X4, X5 and X6 being terrestrials contains organic matter derived from marine environment. On the ratios of the Pristine/Phytane (Pr./Ph), high wax non marine source rocks has ratios from 1-3. From this study, it showed that two of the six samples X1 and X 2 are close to marine source rocks while X3, X4, X5 and X6 are indicating non marine source rocks (Pr/ph = 4.14 – 4.98). Pr/Ph ratios > 1 also indicate petroleum from shale source rocks. Based on the result from Mango, 1987, all the samples in this study may have been derived from shale source rock. The result of Pr/Ph ratios in this study also falls in line with the finding of Didyk et al, (1978) that showed Pr/Ph ratios less than unity (<1) indicating anoxic environment of deposition. In this study all the Pr/Ph ratios are greater than >1, hence oxic environment of deposition. Again Pr/Ph ratios less than < 2.5 indicate marine organic matter. While terrestrial organic matter is greater than > 2.5.

From sample analysis of the oils in this study, the Pr/Ph ratios are greater than 2.5 this clearly indicated that the oils are terrestrial. On the account of the isoprenoid/n-paraffin ratio results show that all the Pr/n C17 ratios are greater than 0.5. The ratios range from 0.91-1.46 supporting the terrestrial environment of the organic matter. The phytane/n C18 ratios are greater than 0.3, the highest ratio for carbonate source rocks. Ph/n-C18 results (0.31,-O.35) based on this study confirms that the source rock of the studied Eastern oils is Shale.

VI. CONCLUSION

The results presented in this study, suggest that the six crude samples from the eastern Niger Delta basin can be grouped into 2 families consisting of oils with more terrigeneous matter and the ones with less terrigeneous organic matter.

The bimodal distribution of X4, X5 and X6 oils from the Chromatograms is associated with more mature oils as opposed to the unimodal distribution of the eastern X1, X2 and X3 oils that is less mature. Eastern X4,X5 and X6 oils have the greater land plant input, which is seen by the average value of the Pristane/phytane ratio (4.66) and higher six ring-paraffins (6RP). These attributes simply support belief that the oils were generated from sources rocks with abundant terrestrial organic matter deposited under oxic (Pr/Ph72.5) condition.

Eastern X1, X2 and X3 oils have Pristane/Phytane ratio of 3.42 suggesting terrigeneous source with input of marine organic matters. Pr/Ph ratios also indicated that the organic matter that formed the crudes was deposited under oxic conditions. The Plot of Methylcyclohexane and Toluene shows that though all oils exhibited high 6Rp, the oils from eastern X4, X5 and X6 wells showed higher 6RP than the oils from eastern X1, X2 and X3 which is consistent with oils from terrestrial deltaic source rocks.

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