### ORGANIC RICHNESS AND ORGANIC MATTER QUALITY STUDIES OF SOURCE ROCKS IN IMIEGBA AND ENVIRONS, BENIN FLANK, SOUTH-WESTERN ANAMBRA BASIN, NIGERIA.

#### \* O. I. Imasuen, C. Mordi and O. J. Imarhiagbe

Department of Geology, University of Benin, P.M.B 1154, Benin City, Nigeria. \*Email: okpeseyi.imasuen@uniben.edu

*Received:* 06-04-16 *Accepted:*25-05-16

#### ABSTRACT

The hydrocarbon potential of the Upper Cretaceous units (Maastrichtian Mamu Formation) exposed at Imiegba and environs of the Benin Flank, Western Anambra Basin was assessed by Total Organic Carbon (TOC) and Rock-Eval Pyrolysis Analyses. The investigated sections of the Mamu Formation consist of dark grey to black carbonaceous and coaly shales, brownish to grey siltstone, whitish claystones and milky white to reddish brown sandstones. The organic richness assessment based on free hydrocarbons generated before pyrolysis (S1), hydrocarbons resulting from kerogen conversion (S2) and Total Organic Carbon content (TOC) indicates poor to excellent source rocks in the sections studied and can therefore be considered as potential source rocks. Quality and Type of Organic Matter was evaluated using hydrogen and oxygen indices and plot of HI against Tmax which show that they are predominantly Type III kerogen (gas prone). This means that the organic matter is immature and predominantly terrestrial. Part of the study area, Imiegba is therefore considered to be of good petroleum potential particularly gaseous hydrocarbon.

Key words: Organic Richness, Kerogen, Organic Matter, Source Rock

#### **INTRODUCTION**

The Anambra Basin is а structural depression located at the western synclinal arm of the Abakaliki Anticlinorium in the Lower Benue Trough. It was formed after the Santonian tectonic pulse as a sub-basin from the differential subsidence of fault block of the Benue Trough formed as a failed arm of the triple junction when the North and South Atlantic were created during the Jurassic (Burke et. al., 1972). The basin is estimated to contain over 5000m of Upper Cretaceous to Recent sediments (Ojo et al., 2009). A number of researchers have conducted a wide range of organic geochemical studies of source rocks in parts of the Anambra Basin to assess their source rock potential or characteristics and their results are well documented in literature. Olubayo, (2010) reported that The Mamu Shale and Mamu Coal Formations, have average TOC values of 1.98 and 56.05 wt. %, respectively. This indicates that both shale and coal have adequate organic matter to generate hydrocarbon. The plot of T max against Hydrogen index (HI) suggests that the coal samples are of type III/IV kerogen while that of the shale sample suggest type II/III kerogen (mixed environment).

Ogala, (2011) studied the hydrocarbon potential of the Upper Cretaceous units

(Maastrichtian Mamu Formation) of the Anambra Basin and suggested that the coal and shale samples are thermally immature to marginally mature with respect to petroleum generation. According to Akande et al. (1992), the lower Maastrichtian Coals of the Mamu Formation are characterized by moderate to high concentrations of huminite and some minor amounts of inertinites and liptinites. It is obvious that most of the previous investigations on the Anambra Basin focused mainly East of the River Niger or the Central and Eastern Flank. This work is to contribute to geosciences documenting hydrocarbon research by generation potentials of the source rocks of the Maastrichtian Mamu Shales at Imiegba and environs in the Benin Flank of the South-Western Anambra Basin by accessing the organic richness, types and quality of organic matter.

#### **Geology and Location of Study Area**

Tectonism in Southern Nigeria probably started in Late Jurassic to Early Cretaceous times with the formation of the Benue-Abakaliki Trough (Murat, 1972). This structure is one arm of a rift-rift-rift (rrr) triple junction associated with the separation of the Africa and South America Continents and subsequent opening of the South Atlantic (Murat, 1972). The Cretaceous compressional folding that affected the Lower Benue Trough took place during the Santonian (Benkhelil, 1989.) and the main fold structure produce was the NE-SW trending Abakaliki Anticlinorium which resulted from inversion of the Abakaliki Trough. The second tectonic episode (renewed rifting) occurred during Post-Santonian time and produced the main PostSantonian depocentre, the Anambra Basin (Burke et. al., 1972).

The Benin Flank is a South-Western Extension of the Anambra Basin and becomes part of the Okitipupa structure westward (Figure 1). The study area lies within Latitudes  $07^{0} 10' 11.9''$  N to  $07^{0} 11'$ 27.2" N of the Equator and Longitudes  $06^{\circ}$ 25' 54.4'' E to  $06^{0}$  26' 51.4'' E of the Meridian. Greenwich The areas of investigation include the Imiegba village and Okpekpe-Imiegba Road, all in Etsako East Local Government Council Area of Edo State, Nigeria (Figure 2). Its evolution is associated with the tectonic events which accompanied the initial separation of the South America and Africa plates (Fairhead and Okereke, 1987). The sediments of the Benin Flank include the Nkporo Group which indicates a major transgression and the Coal Measure represents a major regression of the Late Cretaceous Sea (Nwajide, 2005). In the South eastern end, the Nkporo Shales which constitute prodelta shales and subordinate sands and limestone, its lateral equivalent, Enugu Shales and Owelli Sandstones constitute the basal beds of the Campanian. The Nkporo Shale is replaced by the Lokoja Basange Sandstone Formation in parts of the Benin Flank (Figure 3). The shallow marine paralic sequence of the Mamu Formation was then deposited which has been described as the Lower Coal Measures and was later overlain by the Continental sequence of the Ajali Formation followed by the paralic deposition of the Nsukka Formation, the Upper Coal Measures (Kogbe 1989). Table 1 shows the Stratigraphic Sequences in Anambra Basin Nwajide, (after 2005.).









Imasuen O. I., Mordi C. and Imarhiagbe O. J.: Organic Richness and Organic Matter Quality Studies of Source Rocks in...

Figure 3: Geologic Map of the Study Area

 Table 1: The Stratigraphic Sequences in Anambra Basin (after Nwajide, 2005).

Age	Basin	Stratigraphic Units								
Thanctian	Niger		Imo	Imo Formation						
Danian	Delta									
Daman				Nsukka Formation						
Maastrichtian	Anambra Basin	Coal Measur	es	Ajali Formation						
-				Mamu Formation						
Campanian		Nkporo Fm	Nkpord	Enugu Fm	Owelli Ss	Afikpo Ss	Otobi Ss	Lafia Ss		
Santonian	Southern Benue Trough	Awgu Formation								

## MATERIALS AND METHODS

The methods of investigation involved both field study and laboratory analyses. In this study, 10 samples of potential source rock facie consisting of 10 shales were collected from mapped and logged outcrop sections. The geologic mapping exercise involved the physical identification of rocks in hand specimen. Bedding characteristics in terms of structure, texture, bed thickness. elevation and lithology were studied and described in the study area. Laboratory studies of the samples were based on organic geochemical analysis such as Rock-Eval Pyrolysis and Total Organic Carbon content (TOC) analyses. The analysis of the were samples done at Getamme Laboratories Limited, Port Harcourt. Nigeria

# TotalOrganicCarbon(TOC)Determination

Ten shale samples were selected for preliminary total organic carbon content determination using Walkley Black wet oxidation method. 0.5g of each of the pulverized sample was subjected to chromic oxidation following the procedure of (Walkley and Black 1965). This assessment served as preliminary screening for further detailed Rock-Eval analysis. Three representative samples of black carbonaceous shales were further subjected to LECO-CS Analyser Instrument. 200 mg of the pre-cleaned shale was crushed and accurately weighed into clean LECO crucibles. The rocks were de-mineralised by hot 10 % HCl and afterwards washed repeatedly with distilled water. After drying at  $60^{\circ}$ C the crucibles were automatically introduced into the furnace for combustion and measurement of the organic carbon content.

# **Rock-Eval Pyrolysis**

Three (3) representative samples of black carbonaceous shales were further analysed by Rock-Eval Pyrolysis to determine the hydrocarbon generation potential and source rock quality and hydrogen richness (HI) using a Rock-Eval VI Pyrolyser machine at Getamme Laboratories Limited, Port Harcourt. The samples were heated in an inert atmosphere to 550 C using a special temperature programme. The analysis process involved the transfer of each sample into the furnace where it was heated initially at 300<sup>°</sup>C for three minutes in an atmosphere of helium to release the free hydrocarbons (S1). Pyrolysis of the bound hydrocarbons to give the S2 peak followed immediately as the oven temperature was ramped up rapidly to  $550^{\circ}$ C at the rate of  $25^{\circ}$ C/min. Both the S1 and S2 Hydrocarbon peaks were measured using a Flame Ionization Detector (FID). A splitting arrangement permitted the measurement of the  $S_3$  peak (Carbon Dioxide) by means of Thermal a Detector Conductivity (TCD). The instrument automatically recorded the temperature corresponding to the maximum of the S2 peak, i.e. Tmax. An in-built computer processed the raw data to afford the values corresponding to the respective Rock-Eval indices.

# **RESULTS AND DISCUSSION**

# Lithologic Description of Outcrops Sampled

Two outcrops locations of the Mamu Formation were logged and sampled for this study. These are Okpekpe Road Section, along the Okpekpe – Imiegba Road (Plates a, b and c); the Imiegba Road Section, near the Imiegba Village in Estako East Local Government Area, Edo State (Plate d). The 29m thick outcrop at Imiegba and environs consist of dark grey to black carbonaceous and coaly shales, brownish to grey siltstone, whitish claystones and milky white to reddish brown sandstones. The sandstone are planar and based on grain size can be categorised into very fine, fine, medium and coarse grained Sandstones microfacies with the fine and medium grained sandstones dominating. The grey shale consist of hard and fairly soft beds and well-laminated, the black carbonaceous shale is very hard.



**Plates a - d:** Outcrops of the Mamu Formation showing well developed dark grey to black shale beds (a, b and c) at Okpekpe, located along the Okpekpe Road. Coaly black shale bed at the base and reddish brown/pink to whitish sandstone beds (d) at Imiegba, located along Imiegba-Okpekpe Road, Imiegba Village, Edo State.

### **Organic Richness**

Petroleum is a generative product of organic matter disseminated in the source rock, the quantity of the petroleum should be co relatable with the organic richness of the potential source rock (Tissot & Welte, 1984). Quantity is determined by amount of organic inputs, the degree to which it is preserved and by its dilution with inorganic mineral matter (Walters, 2007). Adequate amount of organic matter, measured as weight percentage total organic carbon (TOC), is a necessary pre-requisite for sediment to generate oil or gas (Conford, 1986) and a measure of the organic richness of sedimentary rocks (Jarvie, 1991). Parameters used in this work to determine organic matter (OM) richness are: total organic carbon content (TOC), free hydrocarbons generated before pyrolysis (S1) and hydrocarbons resulting from kerogen conversion (S2).

Table 2: TOC and Rock-Eva	l Pyrolysis Result of Blac	k Shale Sample from	Imiegba and environs
---------------------------	----------------------------	---------------------	----------------------

SAMPLE ID	TOC (wt.%)	S1 (mgHC/g rock)	S2 (mgHC/g rock)	S3 (mgCO <sub>2</sub> /g	GP (mgHC/g rock)	Tmax ( <sup>0</sup> C)	HI (mgHC/g TOC)	OI (mgCO <sub>2</sub> /g TOC)	S2/S3	S1/TOC *100	PI
OKP A1	0.80	-	-	-	-	-	-	-	-	-	_
OKP A3	0.21	-	-	-	-	-	-	-	-	-	_
OKP A5	0.52	_	_	_	_	-	-	_	-	-	_
OKP A6	0.48	-	-	-	-	-	-	-	-	-	_
OKP A9	0.31	-	-	-	-	-	-	-	-	-	_
IMG B1	2.61	0.30	4.31	0.35	4.61	426	165	13	12.3	11	0.07
IMG B6	4.98	0.32	8.05	0.83	8.37	424	162	17	<b>9.7</b>	6	0.04
IMG B7	8.55	0.61	13.63	0.56	14.24	423	160	7	24.3	7	0.04
IMG B8	0.06	-	_	-	-	-	-	-	-	-	_
IMG B9	0.91	_	_	_	_	_	-	_	_	-	_

#### **Total Organic Matter Content (TOC)**

Table 3 shows the TOC values and interpretation of organic matter concentrated for the samples. The studied Okpekpe shale have TOC values between 0.21 and 0.80 (Av. 0.46), which indicates poor to fair organic matter (Peters and Cassa, 1994). While the studied Imiegba shales have TOC values between 0.06 and 8.55 (Av. 3.42), which indicates poor to excellent organic matter (Peters and Cassa, 1994). On the average, the shale at Okpekpe indicates that,

it is not rich in organic matter and has poor petroleum potential while the shale in Imiegba is rich in organic matter and has very good petroleum potential, thus have a capacity to yield petroleum. Figure 4 shows a pictorial frequency distribution presentation of TOC values for Okpekpe and Imiegba areas. Four (4) of the shale from Imiegba and two (2) from Okpekpe satisfied the required threshold value of 0.5wt% TOC for clastic rocks to generate petroleum (Tissot and Welte 1984).

SAMPLE CODE	THICKNESS (M)	TOC (WT %)	ORGANIC RICHNESS
OKP A1	2	0.80	FAIR
ОКР АЗ	2	0.21	POOR
OKP A5	1.2	0.52	FAIR
OKP A6	2	0.48	POOR
OKP A9	2	0.31	POOR
IMG B1	2	2.61	VERY GOOD
IMG B6	1.8	4.98	EXCELLENT
IMG B7	2.3	8.55	EXCELLENT
IMG B8	3.4	0.06	POOR
IMG B9	3.6	0.91	FAIR

TABLE 3: Total Organic Carbon (Toc) Content Interpretation for Imiegba and Environs



Figure 4: Bar Chart showing frequency of total organic carbon content for Shale source rocks from Imiegba and environs.

# Free Hydrocarbons Generated Before Pyrolysis (S1)

The S1 values for the shales range from 0.30mgHC/g rock to 0.61mgHC/g rock, with an average 0.41mgHC/g rock. This can be interpreted as POOR TO MODERATE, but with a mean of 0.41 mgHC/g rock which can be interpreted as POOR (Peters 1986). Generally, if S1 is greater than 1mg/g in any organic rock, it is indicative of hydrocarbon shows (Dembicki *et al*, 1983).

## Hydrocarbons Resulting From Kerogen Conversion (S2)

It is the magnitude of the pyrolysate yield obtained from cracking of kerogen that provides a measure of the source rock organic matter to generate further hydrocarbons. The values of S2 for the shales show a range of 4.31mgHC/g rock to 13.63mgHC/g rock (Table 2), with an average of 8.66mgHC/g rock. This can be interpreted as moderate to very good, but with an average of 8.66mgHC/g rock, it can be interpreted as good (Peters and Cassa 1994).

# Organic Matter Quality (Organic Matter Type)

The organic matter type in a sedimentary rock, among other conditions influences to a large extent the type and quality of hydrocarbon generated due to different organic matter type convertibility (Tissot and Welte, 1984). Kerogen quality is mainly a function of hydrogen content. The parameters used here for the evaluation of the type of OM are: hydrocarbon potential S2 versus TOC, hydrogen and oxygen indices (HI & OI) and plot of HI against Tmax.

# Hydrogen and Oxygen Indices

Hydrogen index (HI) represents the hydrogen richness and oxygen index (OI) depicts the oxygen content of the kerogen, both relative to the total organic carbon content (Snowdon, 1989). HI values for the samples range from 160 to 165 mg HC/g TOC (Av. 162). Oxygen index values ranges from 7 - 17mg CO<sub>2</sub>/g TOC, with an average of 12.3 mg CO<sub>2</sub>/g TOC. The OI values are less than 200 mg  $CO_2/g$  rock and indicate that there is no intensive weathering or mineral decomposition in analyzed rock samples (Jarvie and Tobey, 1999). McCarthy et al., (2011) classified source rocks with HI between 50 and 200 as gasprone. According to (McCarthy et al., 2011), the values of (HI) for the shale samples of Mamu Formation at Imiegba shows that the types of OM present (Type III) can generate gaseous hydrocarbon. Figures 5, 6 and 7 show that they contain type III kerogen which indicates an oxic depositional milieu.



Imasuen O. I., Mordi C. and Imarhiagbe O. J.: Organic Richness and Organic Matter Quality Studies of Source Rocks in...

The Hydrogen index gives the origin of organic matter and kerogen type which could be identified from the HI values (Tissot and Welte, 1984). The HI for the shales ranges from 160 - 165 mg HC/g TOC with an average of 162.3 mg HC/g TOC (Table 2). This can be interpreted as Type III kerogen as reported by (Peters 1986 and Peters and Cassa, 1994).

#### Hydrocarbon Potential (S2) Versus TOC

Cross plot of hydrocarbon potential versus TOC (Figure 6) indicates Type III kerogen for the shale samples. This Type III points to an organic matter having prospects to generate gas at appropriate maturation (Peters, 1986). This indicates that the sediments are gas prone and reflects terrestrial precursor for the kerogen.



Figure 6: Kerogen Quality Plot for Imiegba and Environs

#### **Plot of HI against Tmax**

The plot of HI versus T max (Figure 7), confirms the predominance of Type III organic matter, indicating that the rock would generate gas.



Figure 7: Kerogen Type and Maturity Plot for Imiegba and Environs

According to (Baskin's 1997) classification, Gas prone source rocks are typical of type III kerogen. With the substantial volume of the source rocks in the study area, coupled with the obtained average HI value of 160-165mgHC/gTOC, the shales of the Mamu Formation will be an effective source of gaseous hydrocarbon in the Anambra Basin.

From the available organic geochemical data documented in this work, it can be concluded that; the organic matter richness of the source rock is good and adequate, the sediments are immature, and the contained organic matter of the shale is Type III kerogen with prospect to generate gaseous hydrocarbon at appropriate maturity. The prevalence of Type III kerogen suggests a terrestrial source of sediments. The study area is therefore considered to be of good petroleum potential particularly gaseous hydrocarbon.

# REFERENCES

- Akande, S.O., Hoffknecht, A., Erdtmann,
  B.D. (1992a): Rank and Petrographic
  Composition of Selected Upper
  Cretaceous and Tertiary Coals of
  Southern Nigeria. *Int. J. Coal Geol.*20, pp. 209–224.
- Baskin, D. K. (1997): "Atomic H/C Ratio of Kerogen as an Estimate of Thermal Maturity and Organic Matter Conversion". American Association of Petroleum Geologists Bulletin, 81: pp. 1437-1450.
- Benkhelil, J. (1989): "The Origin and Evolution of the Cretaceous Benue Trough, Nigeria". Journal of African Earth Science, 8: pp. 251-282.
- Burke, K. C., Dessauvagie, T. F. J. and Whiteman, A. J. (1972): Geological

History of the Benue Valley and Adjacent Areas. In: Dessauvagie, T. F. J., Whiteman, A. J. (Eds.), African Geology. *Ibadan University Press, Ibadan*, pp. 187–205.

- Cornford, C. (1986): Source Rocks and Hydrocarbons of the North Sea. In: Glennie, K.W., (ed.), Introduction to the Petroleum Geology of the North Sea, *Oxford, U.K.*, pp. 197-236.
- Dembicki H. Horsfield B., and Ho TTY. (1983): Source Rock Evaluation by Pyrolysis-Gas Chromotogrophy. *American Association of Petroleum Geologist (AAPG), Bulletin*, 67: pp. 1094- 1103.
- Fairhead, J. D. and Okereke, C. S. (1987):
  "A Regional Gravity Study of the West African Rift System in Nigeria and Cameroon and its Tectonic Interpretation". *Tectonophysics*. 143: pp. 141-159.
- Jarvie, D. M. (1991a): Total Organic Carbon (TOC) Analysis. In: Merril, R.K., (ed.), Treatise of Petroleum Geology: Handbook of Petroleum Geology, Source and Migration Processes and Evaluation Techniques. *AAPG*, pp. 113-118.
- Jarvie, D. M., and Tobey, M. H. (1999): TOC, Rock-Eval, or SR Analyzer Interpretive Guidelines. *Humble, TX: Humble Geochemical Services.* Application Note 99-4.
- Kogbe, C.A. (1989): Geology of Nigeria. *Rockview (Nigeria) Limited.* pp. 325-333.
- McCarthy, K., Rojas, K., Niemann, M., Palmowsky, D., Peters, K. and Stankiewicz, A. (2011): Basic Petroleum Geochemistry for Source

- Murat, R. C. (1972): Stratigraphy and Paleogeography of the Cretaceous and Lower Tertiary in the Southern Nigeria. In Dessauvagie, T.F.J. and Whitman, A.J., (Eds), African Geology, *University of Ibadan Press*, pp. 251 - 226.
- Nwajide C. S. (2005): Anambra Basin of Nigeria: Synoptic Basin Analysis as a Basis for Evaluating its Prospectivity. Hydrocarbon In Okogbue, C. O (ed.) Hydrocarbon Potentials of the Anambra Basin: Geology, Geochemistry and Geohistory Perspectives. Great AP Express Publ., Ltd., Nsukka. pp. 1 -46.
- Obaje, N. G., (2009): Geology and Mineral Resources of Nigeria. London: Springer Dordrecht Heidelberg, pp. 5-14.
- Ogala, J. E. (2011): Source Rock Potential and Thermal Maturity of the Tertiary Lignite Series in the Ogwashi-Asaba Formation, Southern Nigeria. *Asian Journal of Earth Sciences.* 4 (3): pp. 157-170.
- Ojo. O. J., Ajibola, U. K. and Akande, S. O. (2009): "Depositional Environments, Organic Richness and Petroleum Generating Potential of the Campanian-Maastrichtian Enugu Formation, Anambra Basin, Nigeria". *Pacific Journal of Science and Technology*. 10 (1): pp. 614-627.

- <u>ISSN 1118 1931</u>
- Olubayo L. B. (2010): "The Main Oil Source Formations of the Anambra Basin, Southeastern Nigeria". AAPG Search and Discovery Article #90108. pp. 1-9.
- Peters, K. E. (1986): Guidelines for Evaluating Petroleum Source Rock using Programmed Pyrolysis, *AAPG Bull.*, 70 (3): pp. 318-329.
- Peters, K. E., and Cassa, M. R. (1994): Applied Source Rock Geochemistry. In: The Petroleum System - From Source to Trap (L. B. Magoon and W. G. Dow, Eds.), *AAPG Memoir*, 60, Tulsa, OK, pp. 93-117.
- Snowdon L. R. (1989): Organic Matter Properties and Thermal Evolution. In: Short Course in Burial Diagenesis.
  Edited by: Hutcheon, I. E. Mineralogical Association of Canada, Short Course Handbook 15, pp. 39-40.
- Tissot, B. P. and Welte, D. H. (1984): Petroleum Formation and Occurrence, 2nd ed. *Springer Verlag, Berlin.* 699 p.
- Walkley, A. and Black, T. A. (1965): "An Examination of the Titration Method for Determining Soil Organic
  Matter and Proposed Modification of the Chromic Acid Titration Methods". *Soil Science*. 37: pp. 29-38.
- Walters, C. C. (2007): The Origin of Petroleum. In: Practical Advances in Petroleum Processing (Eds. Chang S. H. and Paul R. R.), Springer Science and Business Media, New York. 1: pp. 79-101.