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PYROLYTIC AND PROVENANCE EVALUATION OF ORGANIC MATTER FROM THE TERTIARY NIGER DELTA BASIN, NIGERIA: IMPLICATION ON HYDROCARBON GENERATION.

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ABSTRACT

The present work deals with evaluation of organic matter based on detailed Rock-Eval pyrolysis techniques studies to evaluate hydrocarbon generation potential of source rocks by collecting twenty- nine shale samples from well cuttings in the Tertiary Formations of the Niger Delta, Nigeria. The values of vitrinite reflectance (0.57–0.74%Ro) and maximum (Tmax: 420–445°C) confirmed that samples are at early maturity to matured stage enough to generate liquid and gaseous hydrocarbon. The cross-plot between hydrogen index (HI) and oxygen index (OI) atomic ratio indicates that samples were predominant in the bituminous rank and having kerogen Type III makes it suitable for hydrocarbon generation. Rock-Eval pyrolysis analysis (Types II-III and Type III kerogen) on shale samples from the Niger Delta reveals organic matter of predominantly terrestrial origin based on type III kerogen. The organic matter (OM) assemblages suggests a marine setting but dominated by terrestrial inputs likely related to fluvial processes which is function of most delta system. Based on high total organic carbon (TOC) value of 5.42wt% and Type III kerogen made the shale an excellent source rock, with gas-prone kerogen. The high OI, low total sulphur (TS) suggests terrestrially derived OM and deposition in an oxic and dysoxic shallow marine environment. In addition, HI and Tmax values describe the samples as a characteristic Type III dominant kerogen and potential to generate oil and gases while the Tmax, consistently indicate an immature to mature on the shale organic matter.

KEYWORDS: Shale, organic matter, kerogen type, maturity, source rock, oil generation, Niger Delta.

INTRODUCTION

The Niger Delta is situated in the Gulf of Guinea (Fig. 1) and extends throughout the Niger Delta Province as defined by Klett *et al*. (1997). From the Eocene to the present, the delta has prograded southwestward, forming depobelts that represent the most active portion of the delta at each stage of its development (Doust and Omatsola, 1990). The Niger Delta Province contains only one identified petroleum system (Kulke, 1995; Ekweozor and Daukoru, 1994). This system is referred to here as the Tertiary Niger Delta (Akata –Agbada) Petroleum System.

Petroleum source rocks are the primary component of the petroleum system concept (Tissot and Welte, 1984; Magoon and Dow, 1994). Source rocks constitute the precursors of petroleum which, under favorable conditions, may subsequently migrate to reservoirs and be sealed to form accumulation. Nexant (2003) estimated about 32 billion barrels of oil and about 170 trillion cubic feet of gas in Nigeria that derives solely from the onshore and offshore Niger Delta.

Organic geochemistry deals with the process governing the origin and fate of organic materials such as petroleum (crude oil and natural gas), coal,

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oil shale and tar sands.

The atomic ratios of HI and OI are also considered for assessment of hydrocarbon potential, maturity, kerogen types, and nature (Fisher *et al*. 1942; Tissot and Welte, 1984; Van Krevelen 1993). The high-volatile bituminous coals carrying vitrinite reflectance ranging from 0.49 to 1.02% and reactive macerals value >70% are most feasible for liquid hydrocarbon generation (Given et al. 1975, 1980; Singh *et al*. 2013). Panwar *et al.* (2019) in their report concluded that most of the bituminous coal samples are per-hydrous in nature; however, some samples also come in the bright band of Seyler's chart (Cornelius, 1978). Rock-Eval pyrolysis is prominently used for determination of hydrocarbon potential in source rocks as well as for maturity of organic material. Since Rock-Eval pyrolysis takes less time and is feasible in nature, a lesser quantity of the sample is needed for analysis (Carvajal-Ortiz and Gentzis, 2015; Hakimi *et al*. 2013). Maturity of source rocks can also be determined from the biomarker distribution in source rock extracts.

In the present investigation, twenty-nine shale samples were collected from well cuttings from the Tertiary Niger Delta region. The objective of this study is to evaluate the hydrocarbon generation potential of shale in the Agbada – Akata Formations of the Niger Delta, Nigeria.

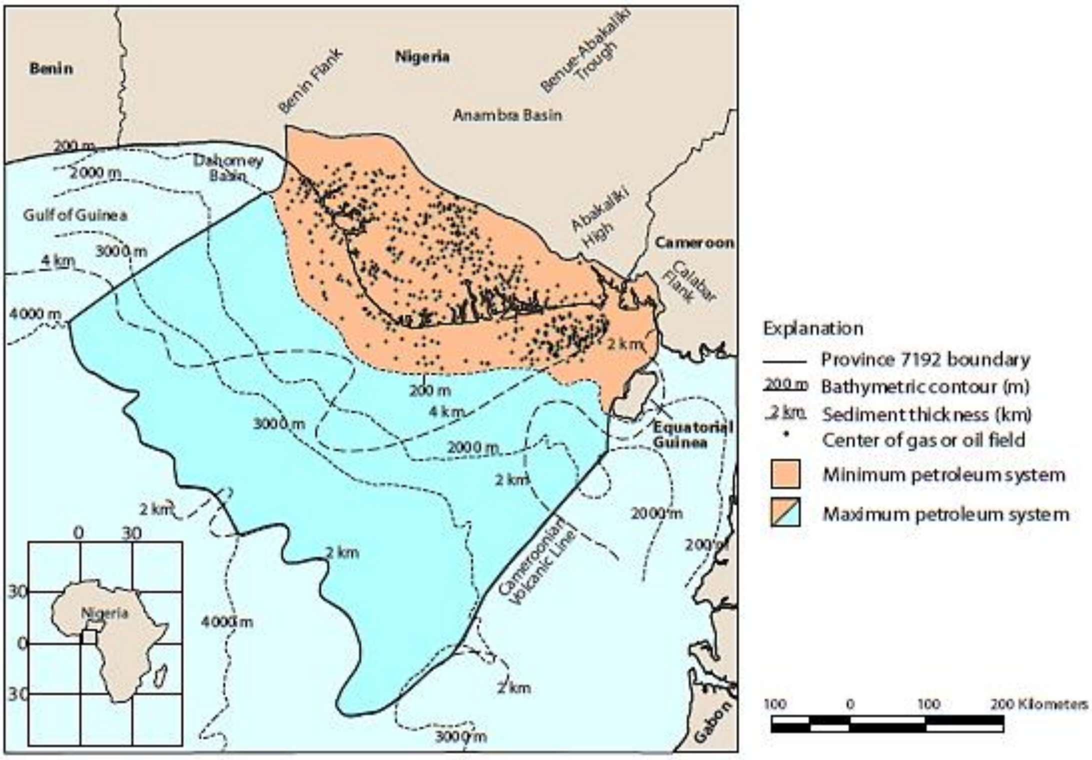

Figure 1: Map of the Niger Delta showing Province outline (maximum petroleum system); bounding structural features; minimum petroleum system as defined by oil and gas field center points (After Tuttle *et al*., 1999).

GEOLOGICAL SETTING: The studies of the Niger Delta have widely been done mostly by oil companies and academician because of its petroliferous province which is of economic importance. Many authors have investigated and summarized the basic geology, structural setting, depositional environments, production characteristics, and field development strategies among others. Short and Stauble (1967), outlined the regional geology of the Niger Delta. The origin of the Niger Delta were attempted and they established that the Tertiary deltaic fill is represented by a strong diachronous sequence (Eocene- recent), which is divided into three lithofacies units namely; the Akata, Agbada and Benin Formations.

Doust and Omatsola (1990), observed that sands of the Niger Delta are poorly consolidated with porosity as high as 40% in oil bearing reservoir, reservoir sands of more than 15m thick in most places consists of two or more stacked channel. They also observed gradual reduction of porosity with depth and permeability in hydrocarbon bearing reservoirs are commonly in the range of 1-2 Darcy and sands shallower than 3000m have porosity of more than 15%, but below 3000m only a few sands have more than 15% porosity. Bustin (1988) established that the Niger Delta basin is divided into continental, marginal marine and marine facies. He also observed that sediments of the onshore are separately mapped as alluvium in contrast with the offshore sediments, in which the youngest sediments were not investigated because cutting samples could not be collected from the upper hundred feet below sea level.

Akaegbobi and Schmitt (1998), established that heterogeneity of reservoir, and formation evaluation problems can make it difficult to characterize fluid distribution, determine permeability and estimate hydrocarbon in place. They suggested that the approach used in characterizing a reservoir involves a combination of analysis of geological framework of the reservoir, hydrocarbon trapping components (stratigraphic and structural), formation evaluation and calculation of volumetric hydrocarbon in place. Haack *et al*. (2000) discussed the tertiary petroleum systems of the Niger Delta. He observed the lower Cretaceous petroleum system is characterized by lacustrine source rocks which occurs in the north-western part of the delta and might be present in the Benin trough and the upper cretaceous lower Paleocene petroleum system, which is characterized by marine source rocks, is defined for the north-western part of the delta.

Various depositional processes gave rise to the Niger Delta Cenozoic stratigraphy. The studies of Short and Stauble (1967), Frankyl and Cordey (1967) and Avbovbo and Ogbe (1978) provided the initial information on the stratigraphic units distribution of the Niger Delta subsurface. Also, the works of Evamy *et al*. (1978), Ejedawe *et al*. (1984), Nwachukwu and Chukwura (1986), Haack *et al*. (2000), Doust and Omatsola (1990) among others provided useful information on the stratigraphic units of the region. Doust and Omatsola (1990) divided the Niger Delta subsurface was into three major lithostratigraphic units such as the Akata, Agbada and Benin Formations (Fig. 2). Basin-ward, there is a decrease in age, which reflects the overall regression of the Niger Delta clastic wedge depositional environments. In the south southern Niger Delta, stratigraphic units equivalent to these three formations are exposed, and it reflect a gross coarsening upward progradational clastic wedge (Short and Stauble, 1967), deposited in marine, deltaic and fluvial environments (Weber and Daukoru, 1975; Weber, 1987).

METHODOLOGY

The oil-source rock correlation is essential to define the petroleum system present in the Niger Delta Region. Sample preparation and analyses were performed at Trican Geological Solutions, Alberta, Canada. Details on analytical methods and compound identifications are described in Peters and Moldowan (1993). A total of twenty-nine bulk shale samples (about 30-50 g) were used for the analyses. The samples were washed using water/organic solvent to remove the dirty and sands on them. The washed samples were kept in the oven for 24hours to dry at temperature of 40°C. The dried samples were crushed by mortar and pestle. After that, each of these crushed samples were divided into two equal parts. Half of the crushed samples in each case was packaged in a plastic bag and the remaining half was pulverized by vibratory disc mill Model RS 100 to <50μm size. A mass of 20 – 30mg of the pulverized samples weighed in crucibles were placed in a Rock-Eval 6 pyrolysis for S_1, S_2, S_3 and Tmax and Leco C-S for TOC.

After initial screening by Rock-Eval Pyrolysis and total organic carbon determination, all the samples were selected for further detailed studies. The rock samples were selected from organic-rich shale intervals within the Agbada and Akata Formations (Fig. 2).

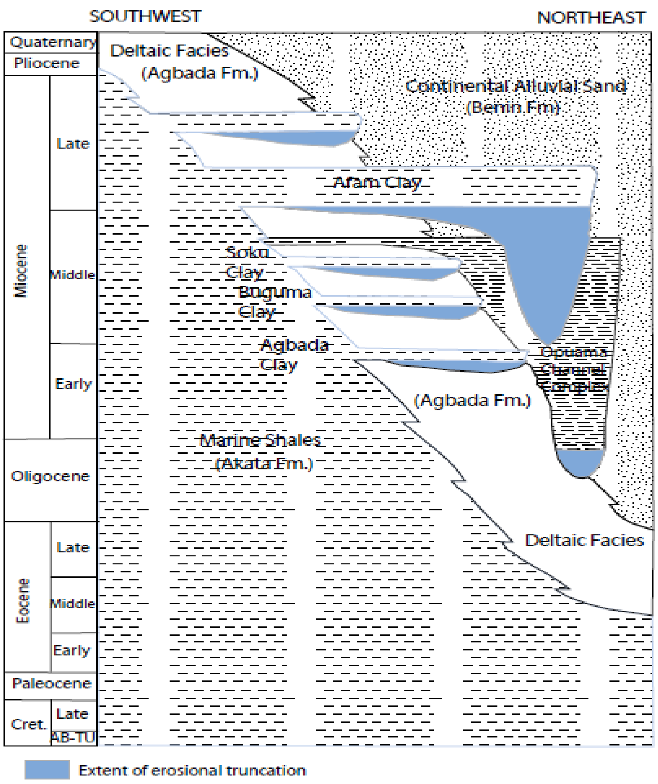

Fig. 2: Stratigraphic column showing the three formations of the Niger Delta. Modified from Shannon and Naylor (1989) and Doust and Omatsola (1990).

RESULT AND DISCUSSIONS

In shale samples, average total organic carbon (TOC) of 2.0 wt% is considered an excellent source rock as hydrogen index (HI) greater than 350mg HC/g TOC is proposed to generate high commercial quantity of petroleum (Tissot and Welte, 1984). Highest TOC content of 5.42 wt% was obtained from the shale samples from Niger Delta. Its values range from 0.51 to 5.42 wt% with a mean of 1.80 wt% (Table 1). Carbon is an essential element of any organic compound, and one way to assess the organic richness of a rock is to measure its carbon content. The amount of organic carbon is usually measured as TOC (Jarvie, 1991; Ratnayake and Sampei, 2015a). The highest TOC value of 5.42 wt% was obtained from the top of Akata sample number KAT 21. The organic matter content of the first sample number (GBA 02) from the top of the outcrop locality is quite low (0.51 wt%) compared with that of the GBA 11 sample which has a moderate organic matter content of 2.42 wt%. TOC of 4.35 wt% was obtained from the Akata sample number KAT 01. This made the second location (KAT) best in organic richness as compared to location GBA.

The overall tendency towards lower total sulphur (TS) with increasing TOC, as well as the TOC/TS ratios for Niger Delta (av. TOC/TS = 0.37) shale samples, argues for a marine environment during deposition as observed from the sulphur content (Berner, 1984; Ratnayake and Sampei, 2015a; Uzoegbu and Ikwuagwu, 2016; Uzoegbu *et al*., 2013). High TOC contents of >>5.42 wt% and HI between 35.00 and 221.00 mg HC/g TOC characterize the shale beds of the Niger Delta region. The shale have TOC contents of 0.51 to 5.42 wt.% and HI values between 35.00 and 221.00 mg HC/g TOC. Variation in HI between 35.00 and 221.00 mg HC/g TOC on the shale samples, suggests Type III OM (Peters, 1986). Samples from the Niger Delta region are having their S_2 values within the range of 0.23-8.12 mg/g with an average of 2.17. The S_2 vs. TOC diagrams gave an average HI values of 147 and 132mg HC/g TOC for shale samples in the Agbada and Akata Formations (Figs 3 and 4) respectively. Therefore, most of the Niger Delta Basin shale samples were dominated type III with associated type II. The gas-prone nature of these shales (S_2/S_3; 0.25-3.64) from Niger Delta rules out type II kerogen, which usually shows S_2/S_3 greater than 5 (Eseme *et al*., 2006; Uzoegbu *et al*., 2016) (Table 1).

Plots of S_2 vs. TOC and determining the regression equation of average HI of 147 and 132mg HC/g TOC has been used by Langford and Blanc-Valleron (1990) as the best method for determining the true average HI and measuring the adsorption of hydrocarbons by the rock matrix. HI obtained from Rock-Eval pyrolysis of shaly source rocks, in most cases, may be less than the true average HI of the sample due to the hydrocarbons adsorptive capacity of the source rock matrix (Espitalie *et al*., 1985). Therefore, the regression equation derived from the S_2 vs. TOC graph can be used to automatically correct HI for this effect. The average HI of the Niger Delta shale samples from the S_2 vs. TOC plots is very reliable (correlation coefficient is 0.70 and 75) which indicated a value of 147 and 132mg HC/g TOC (Figs 3 and 4) which is below 300 mg HC/g TOC (Peters, 1986) supporting the predominant of the type III with associated type II organic matter of the Niger Delta Basin. The cross plots of HI versus OI and HI versus Tmax on the Niger Delta samples suggests OM within Type III. Generally all the samples indicate a high contribution of OM from high marine organism (Figs 5 and 6) (Bechtel *et al*., 2006). The S_2 values correspond to the hydrocarbons that evolve from the sample during the second programmed heating stage of pyrolysis. These hydrocarbons result from the cracking of heavy hydrocarbons and from the thermal breakdown of kerogen. It represents the milligrams of residual hydrocarbons in one gram of rock, thus indicating the potential amount of hydrocarbons that the source rock might still produce if thermal maturation continues.

HI vs. Tmax (Fig. 6) diagram classifies the OM in the shale as type III kerogen (Akande *et al*., 2007, 2012; Ayinla *et al*., 2017; Ayoola *et al*., 2019). HI values for the Niger Delta samples range from 35.00 to 221.00 mgHC/g TOC and $S_1 + S_2$ yields range from 0.73 to 8.75 mg HC/g rock, suggesting that the shales have gas and oil-generating potential (Akande *et al*., 2007). Peters (1986) has suggested that at thermal maturity equivalent to vitrinite reflectance of 0.6% (Tmax 435^{o}C), rocks with HI above 300 mg HC/g TOC produce oil; those with HI between 300 and 150 produce oil and gas; those with HI between 150 and 50 produce gas, and those with less than 50 are inert (Figs 5 and 6).

The van Krevelen diagrams for the shale samples show a dominance of type III (Fig. 5 and 6). The highest HI samples may be assigned to a high-potential type II kerogen at the diagenesis/ catagenesis boundary (Obaje *et al*., 2004).

The corresponding HI-Tmax diagram based on the values given by Peters (1986) indicates some potential between oil and gas with gas dominating (Figure 5 and 6). Majority of the samples fell into fields that have hydrocarbon generative potential of Type III. The Niger Delta samples are mixed with recycled terrestrial organic worked OM pointing to type III (Fig. 5). These recycled OM might have been transported by fluvial processes (Bird *et al*., 1995; Obaje *et al*., 2004; Uzoegbu *et al*., 2016) as found in prodelta shales of the Niger Delta region.

Several authors have attempted to relate the thermostability (Tmax) of OM to carbon structures (Oberlin *et al*., 1980; Monthious *et al*., 1982; Landis *et al*., 1984), their terrestrial or marine origin (Walker et al., 1983; Leckie *et al*., 1988) and the initial hydrogen content as a function of reaction kinetics (Fang and Jianyu, 1992). This has led to the proposal that the thermostability of carbon structure increases with the increase in oxygen content due to cross linkages such that the oxygenated functions can form between stacks of adjacent molecules (Rouxhet *et al*., 1979; Furimsky *et al*., 1983).

Table 1: The results of Rock-Eval pyrolysis.

Sample ID	Depth (m)	Lithology	Formation	TOC (wt%)	S_1 (mg/g)	S_2 (mg/g)	S_3 (mg/g)	Tmax (°C)	HI (mgHC/ gTOC)	OI (mgCO$_2$/ gTOC)
GBA 02	2134	Shale	Agbada	0.51	0.05	0.23	0.68	433.00	35.00	155.00
GBA 03	2225	"	"	2.01	0.33	1.56	2.09	432.00	86.00	102.00
GBA 05	2256	"	"	0.75	0.08	0.32	1.61	437.00	39.00	191.00
GBA 06	2323	"	"	0.65	0.09	0.72	1.64	439.00	77.00	172.00
GBA 07	2324	"	"	1.03	0.25	0.61	1.44	431.00	63.00	123.00
GBA 09	2362	"	"	1.17	0.14	1.43	2.46	430.00	96.00	132.00
GBA 11	2390	"	"	2.42	2.58	3.78	1.34	437.00	192.00	54.00
GBA 12	2487	"	"	1.72	0.62	1.36	1.18	438.00	75.00	75.00
GBA 15	2694	"	"	1.16	2.37	2.24	1.03	431.00	190.00	74.00
GBA 17	2877	"	"	1.76	1.46	2.46	2.58	429.00	134.00	139.00
KAT 01	2912	Shale	Akata	4.35	0.31	2.98	3.65	432.00	91.00	104.00
KAT 02	2956	"	"	1.03	0.06	0.57	1.24	436.00	63.00	112.00
KAT 04	2975	"	"	1.49	2.59	1.42	1.35	434.00	88.00	89.00
KAT 06	2987	"	"	2.23	2.75	3.35	1.64	438.00	148.00	78.00
KAT 07	3048	"	"	1.21	0.14	0.73	1.71	434.00	79.00	181.00
KAT 08	3243	"	"	1.37	2.06	0.81	1.64	420.00	52.00	106.00
KAT 09	3233	"	"	1.34	0.74	2.24	2.34	445.00	64.00	173.00
KAT 13	3389	"	"	5.12	0.69	8.12	3.42	427.00	174.00	61.00
KAT 15	3574	"	"	0.65	0.13	0.34	1.36	431.00	161.00	182.00
KAT 18	3597	"	"	1.65	5.38	2.81	1.41	433.00	152.00	95.00
KAT 19	3700	"	"	2.32	2.59	3.96	1.09	439.00	189.00	72.00
KAT 21	3719	"	"	5.42	4.75	6.30	2.83	438.00	147.00	101.00
KAT 22	3737	"	"	2.36	6.24	3.43	1.54	436.00	132.00	68.00
KAT 25	3761	"	"	2.42	7.03	5.21	1.72	433.00	141.00	124.00
KAT 28	3876	"	"	1.47	0.34	1.03	0.83	436.00	221.00	56.00
KAT 32	4042	"	"	0.82	1.32	0.76	1.03	433.00	72.00	69.00
KAT 33	3594	"	"	1.57	0.48	0.87	1.62	438.00	104.00	74.00
KAT 35	3658	"	"	1.24	0.68	1.80	1.64	432.00	98.00	53.00
KAT 37	3719	"	"	1.04	2.16	1.41	1.35	431.00	174.00	123.00

Table 1: Continued.

Sample ID	Depth (m)	Lithology	Formation	S_2/S_3	PG S_1+S_2	PI S_1/S_1+S_2	HI/OI	S1/TOC	TS (%)	TOC/ TS	%Ro
GBA 02	2134	Shale	Agbada	0.34	0.73	0.15	0.23	0.10	3.56	0.14	0.61
GBA 03	2225	"	"	0.75	2.42	0.44	0.84	0.16	4.17	0.48	0.65
GBA 05	2256	"	"	0.20	1.69	0.40	0.20	0.11	4.02	0.19	0.67
GBA 06	2323	"	"	0.44	1.73	0.21	0.45	0.14	4.84	0.13	0.67
GBA 07	2324	"	"	0.42	1.69	0.59	0.51	0.24	4.86	0.21	0.57
GBA 09	2362	"	"	0.58	2.60	0.24	0.73	0.12	4.95	0.24	0.67
GBA 11	2390	"	"	2.82	3.92	0.91	3.56	1.07	4.69	0.52	0.66
GBA 12	2487	"	"	1.15	1.80	0.54	1.00	0.36	5.04	0.34	0.58
GBA 15	2694	"	"	2.17	3.40	0.09	2.57	2.04	4.74	0.24	0.74
GBA 17	2877	"	"	0.95	4.04	0.53	0.96	0.83	4.58	0.38	0.64
KAT 01	2912	Shale	Akata	0.82	3.96	0.38	0.88	0.07	5.90	0.74	0.72
KAT 02	2956	"	"	0.46	1.30	0.13	0.56	0.06	5.94	0.17	0.73
KAT 04	2975	"	"	1.05	3.94	0.46	0.99	1.74	4.60	0.32	0.72
KAT 06	2987	"	"	2.04	4.39	0.35	1.90	1.23	4.90	0.46	0.64
KAT 07	3048	"	"	0.43	1.85	0.33	0.44	0.12	3.98	0.30	0.74
KAT 08	3243	"	"	0.49	3.70	0.17	0.49	1.50	3.93	0.35	0.73
KAT 09	3233	"	"	0.96	3.08	0.77	0.37	0.55	4.88	0.27	0.72
KAT 13	3389	"	"	2.37	4.11	0.29	2.85	0.13	4.91	1.04	0.60
KAT 15	3574	"	"	0.25	1.49	0.52	0.88	0.20	4.88	0.13	0.71
KAT 18	3597	"	"	1.99	6.79	0.70	1.60	3.26	4.80	0.34	0.60
KAT 19	3700	"	"	3.63	3.68	0.71	2.63	1.12	4.78	0.49	0.71
KAT 21	3719	"	"	2.23	7.58	0.13	1.46	0.88	5.27	1.03	0.65
KAT 22	3737	"	"	2.23	7.78	0.80	1.94	2.64	4.66	0.51	0.64
KAT 25	3761	"	"	3.03	8.75	0.32	1.14	2.90	4.97	0.49	0.64
KAT 28	3876	"	"	1.24	1.17	0.27	3.95	0.23	5.20	0.28	0.71
KAT 32	4042	"	"	0.74	2.35	0.79	1.04	1.61	4.56	0.18	0.69
KAT 33	3594	"	"	0.54	2.10	0.89	1.41	0.31	4.60	0.34	0.72
KAT 35	3658	"	"	1.10	2.32	0.62	1.85	0.55	4.86	0.26	0.71
KAT 37	3719	"	"	1.04	3.51	0.07	1.41	2.08	4.62	0.23	0.67

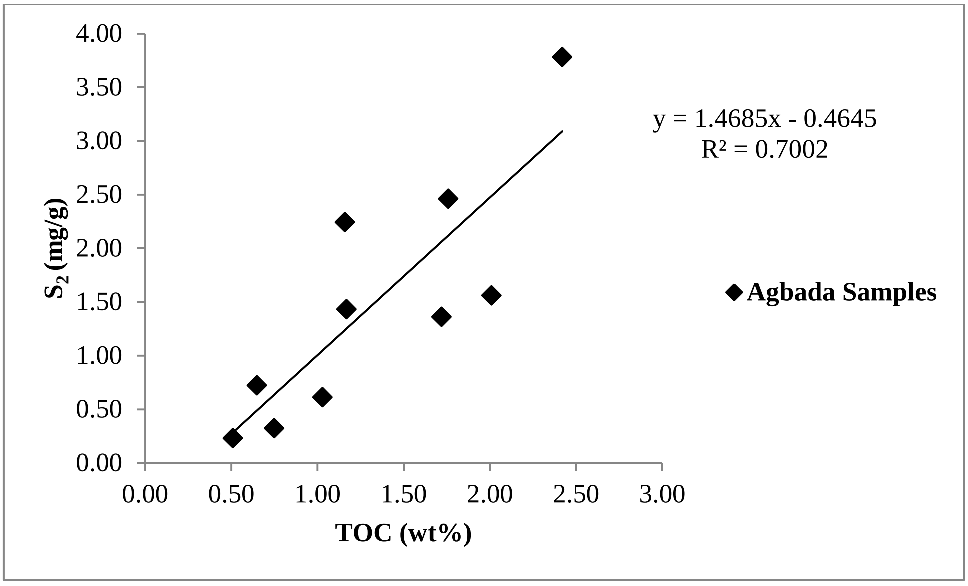

Fig. 3: A diagram of S_2 versus TOC of shale samples from the Agbada Formation.

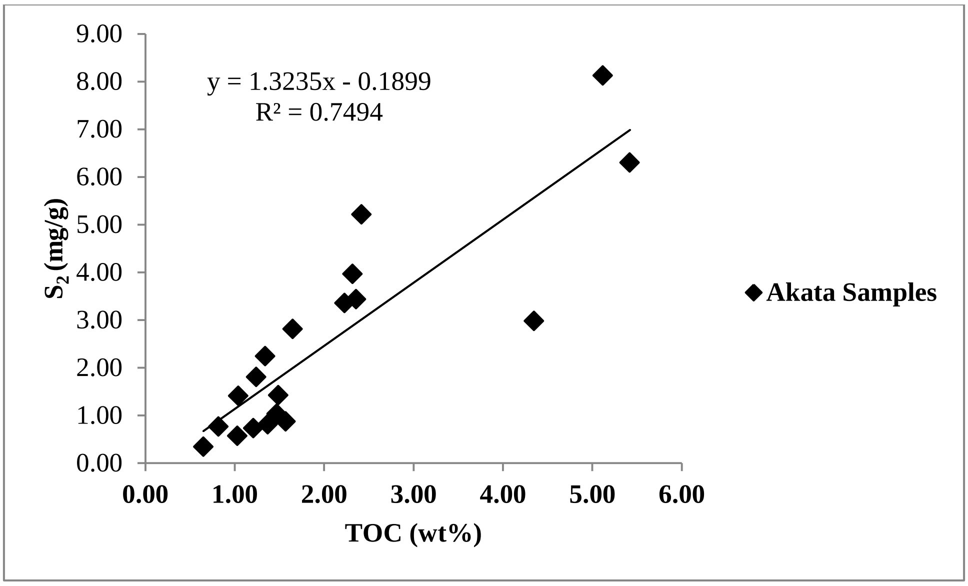

Fig. 4: A diagram of S_2 versus TOC of shale samples from the Akata Formation.

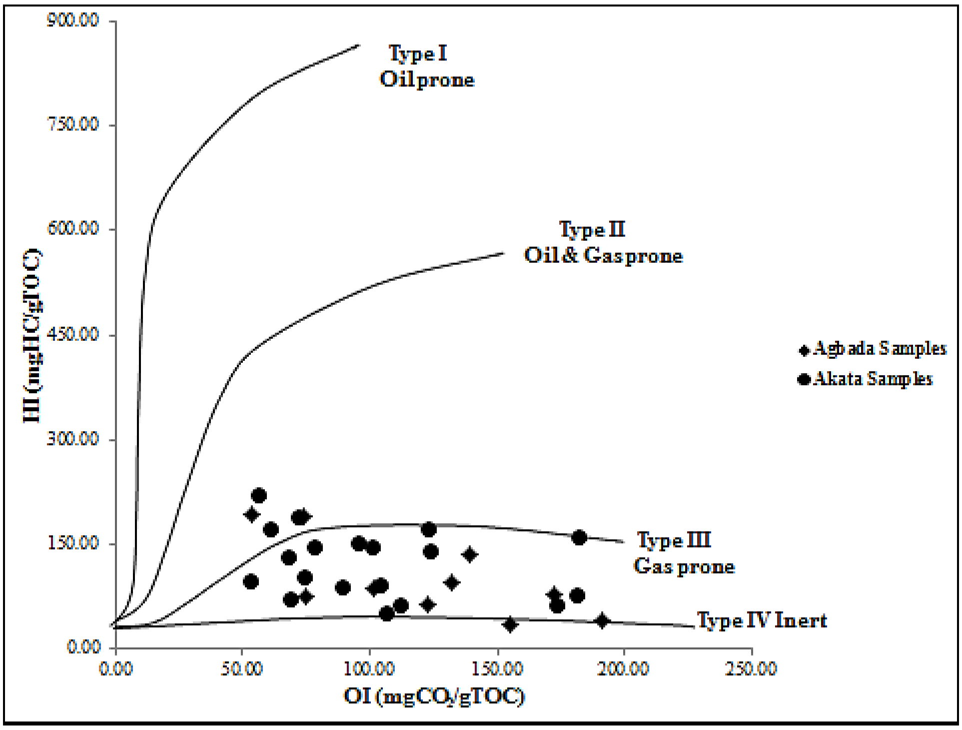

Fig. 5: Showing kerogen type from modified van Krevalen diagram (After Peters, 1986).

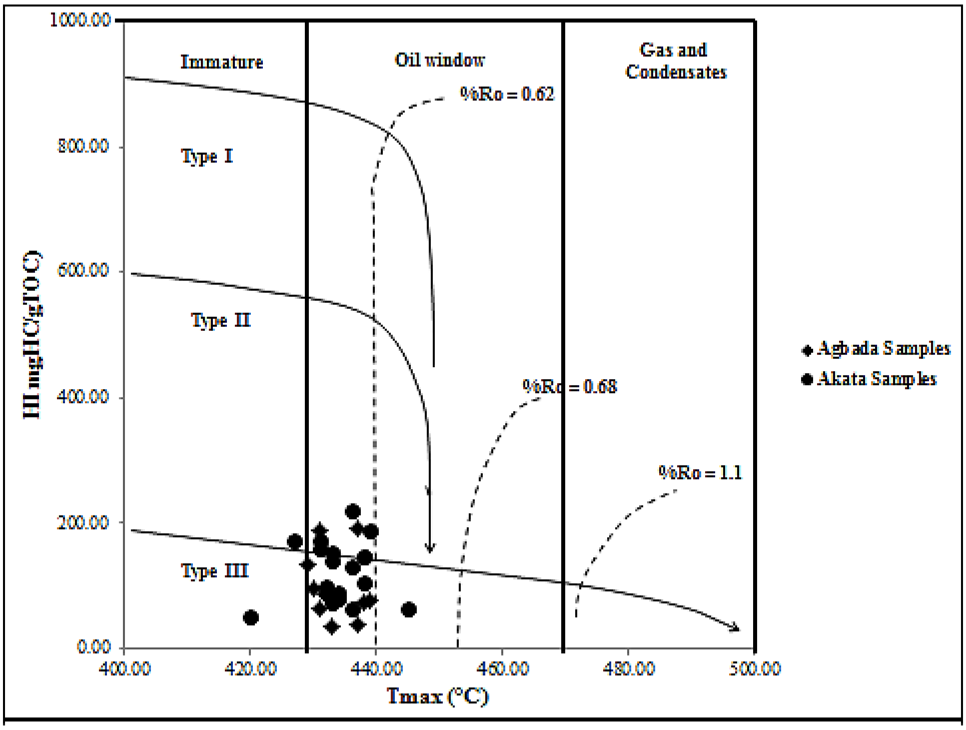

Fig. 6: A plot of HI versus Tmax indicating type of organic matter and maturity level.

Walker et al. (1983) suggested marine derived amorphous-rich kerogens mature at lower temperatures than land plant (Type III) OM. Other investigators have demonstrated that terrestrial vitrinitic OM matures more rapidly than liptinic dominated organic matter (Tissot and Welte, 1984; Price and Barker, 1985; Wenger and Barker, 1987) or that Tmax values for marine sediments increase more slowly with increasing maturation than for non-marine sediments (Leckie *et al*., 1988). OI vs. Tmax are plotted (Fig. 7) as proposed by Landis *et al*. (1984) who concluded that the initial hydrogen contents of vitrinite macerals under different redox conditions are different and hence have different reaction kinetics, because there is a strong deviation from the normal trend expected of Type III OM on their OI vs. Tmax diagram. This led to their conclusion that the anomalies recorded are not a result of the thermal conditions. Applying these principles to the area of study, samples from Niger Delta area were plotted on the OI vs. Tmax diagram of Landis *et al*. (1984) to test if samples followed the typical trend for Type III OM, and hence to determine if the Tmax anomalies have any relationship to thermal conditions. The trends in Niger Delta shale samples showed essentially a decrease in OI as Tmax increases indicating the maturity level (Fig. 7). This reflects the samples under study contain essentially Type III kerogen since they follow Landis *et al*. (1984) typical trend for Type III OM.

Also in agreement with the report of Fang and Jianyu (1992), thermal conditions are partially responsible for the suppression of Tmax and vitrinite reflectance (%Ro) in the samples. According to Fang and Jianyu (1992), if Ro variations are caused by thermal conditions, Tmax and Ro values would have to increase with decreasing OI values as obtained in this study. In the diagram Tmax vs. HI (Fig. 8) indicates that most of the OM falls into gas portion and some in oil and gas portion which implies that the OM contains some oil and most gas potential. A Plot of the SOM (extract yield) against TOC as proposed by Landis and Connan (1980) in Jovancicevic *et al*. (2002) for the shale samples indicates that no migration of oil has taken place (Fig. 9). This diagram does not recognize the oil source rock potential of coals and coaly samples and can therefore not be used to evaluate such samples.

This is supported by the diagram of S_1 + S_2 vs TOC (Fig. 10) characterizing the shale samples from Niger Delta as fair to excellent source rocks with TOC and S_1 + S_2 above 0.50 wt% and 20.0 mg/g respectively. Over 80% of shale samples from the Niger Delta show good to excellent source rocks generative potential (Fig. 10). This is also supported by Beka *et al*. (2007) from their investigations on shaly facies of gas prone sequences in the Anambra Basin based on the values of TOC (1.31-2.94 wt%). Their soluble organic matter (SOM) (137-450 ppm) also indicates fair to good and adequate source potential.

Udofia and Akaegbobi (2007) also investigated the Maastrichtian sediments around Enugu escarpment of the Anambra Basin which revealed the exceeding minimum threshold TOC value (0.65-1.82 wt %) for shale samples. The Anambra Basin being part of the lower Benue Trough, the TOC content indicates that the quality and quality of the OM found in the Niger Delta is enhanced by the supply of OM from the lower Benue Trough. Thermal maturity was confirmed by plotting the profiles of Tmax vs TOC (Fig. 11) which shows that all the shale samples from Niger Delta attained the “oil window” (430ºC) except shale samples of GBA 17, KAT 08 and KAT 13 that did not attained to threshold value but indicated immaturity status. These are also supported by plotting the diagrams of OI vs Tmax and HI vs Tmax (Figs. 6 and 7) that determined the maturity status of the entire samples from Niger Delta. The values of %Ro which ranges from 0.57 – 0.74 (Table 1) also supported the immature to maturity of the organic matter from the Niger Delta. The hydrocarbon generative capacity (S_1 + S_2) shows that the Niger Delta shale sample (8.75) of KAT 25 of the Akata Formation have the highest residual potential to expel hydrocarbons as compared to the shale sample (0.73) of GBA 02 from the Agbada Formation. The thermal maturation for Niger Delta shale is, however, still low. Although the S_1 + S_2 of the locality involve are below but their thermal gas generation based on Tmax vs. HI and HI vs. OI indicates oil and gas potential (Uzoegbu *et al*., 2016; Kouadio *et al*., 2021). The observed increase in PI and S_1/TOC supports the hydrocarbon generative potential of these shale samples.

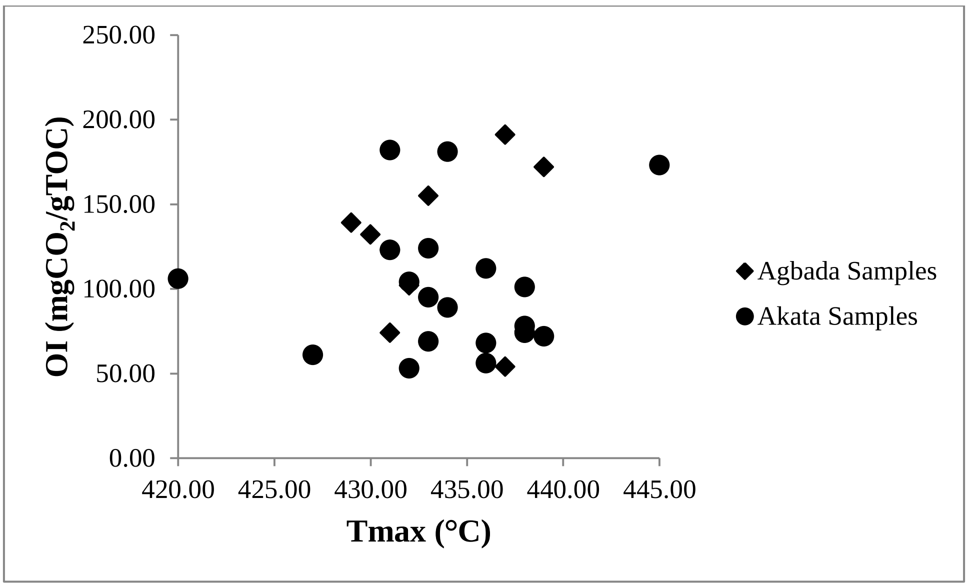

Fig. 7: A diagram of OI versus Tmax describes the anoxic and thermal maturity of the organic matter in the shale samples within the diagenesis to catagenesis stages (Landis *et al*., 1984).

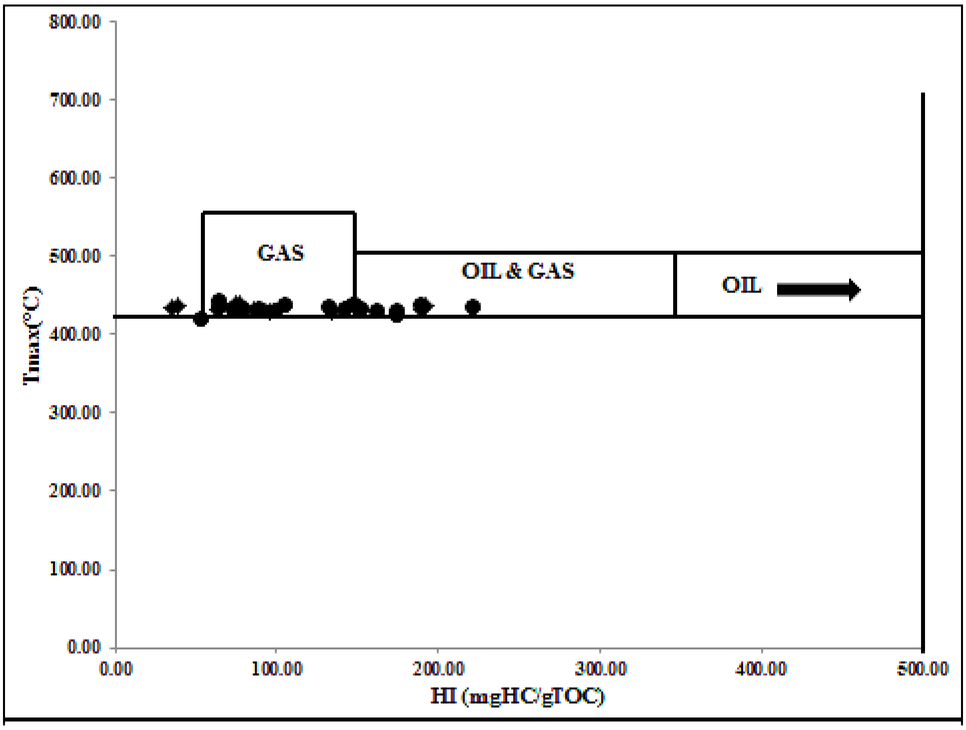

Fig. 8: A diagram of Tmax versus HI of shale samples from Niger Delta describes the quality of organic matter.

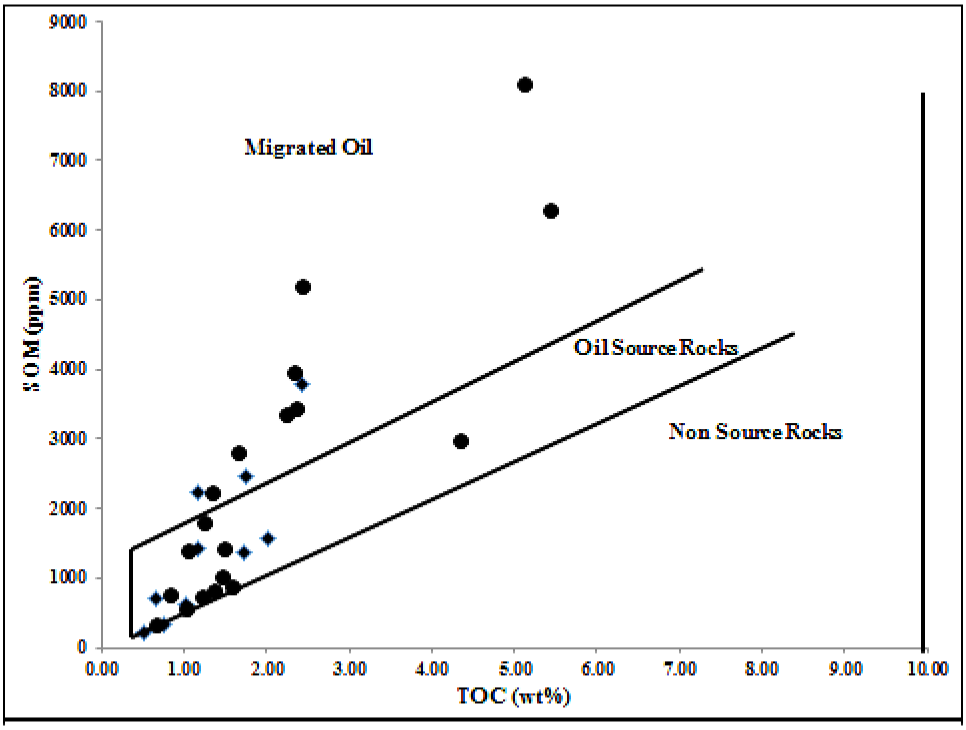

Fig. 9: A diagram showing the characterization of organic matter: SOM. vs TOC (based on Landais and Connan in Jovancicevic *et al*., 2002) of samples from Niger Delta Basin indicating no migrated oil in the area.

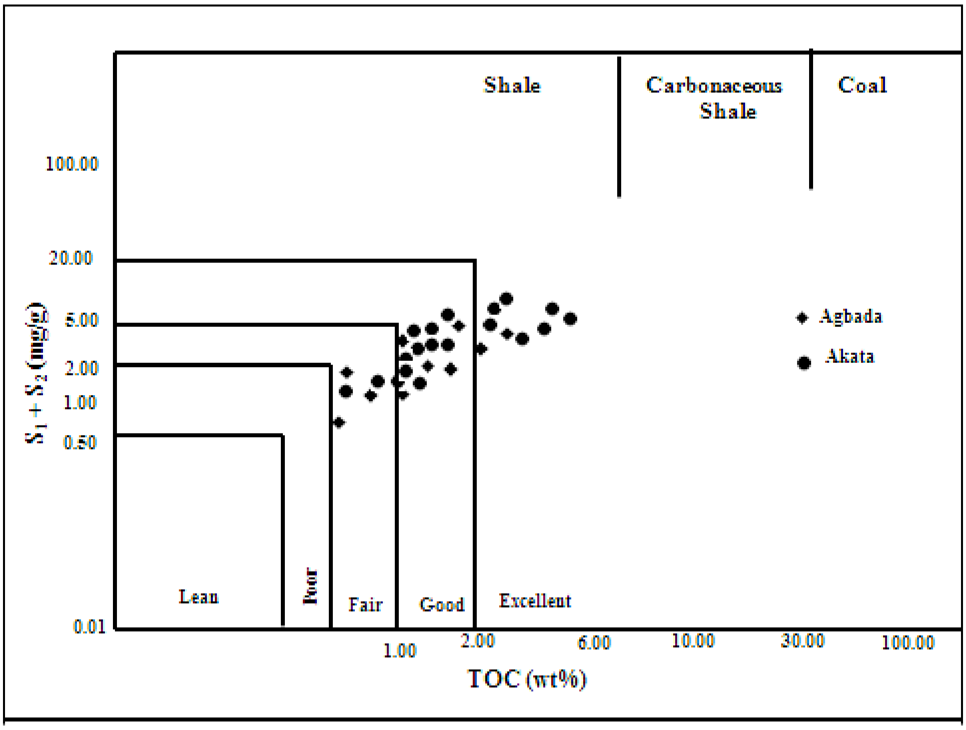

Fig. 10: A diagram indicating the quality of kerogen type in the shale samples from Niger Delta: $S_1 + S_2$ versus TOC.

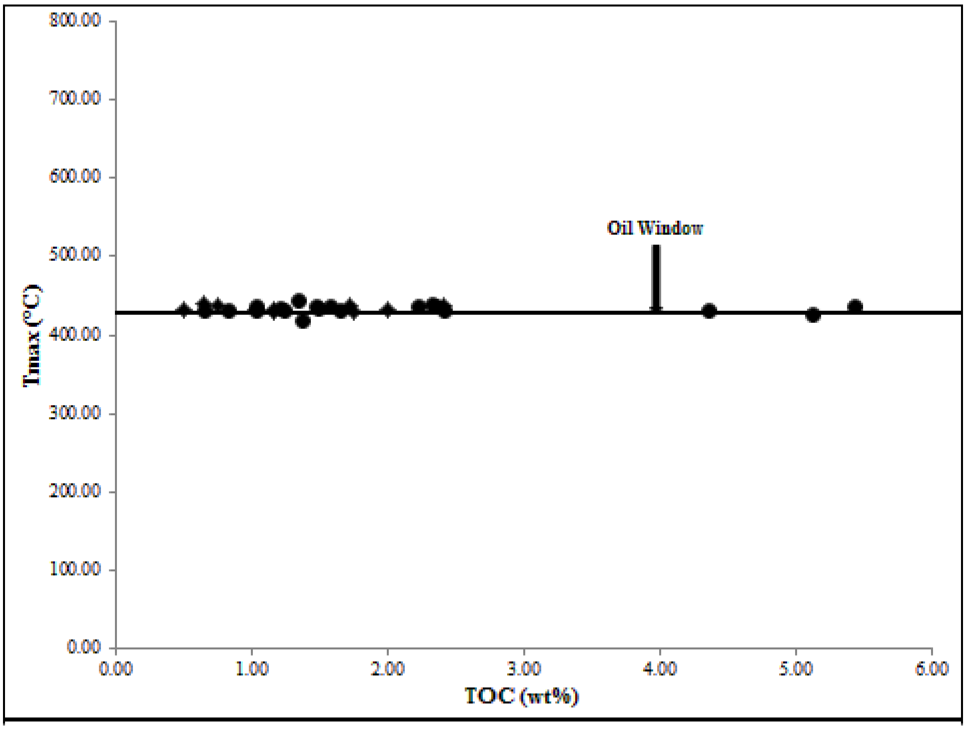

Fig. 11: To determine the maturity of the organic matter from Niger Delta shales: Tmax versus TOC.

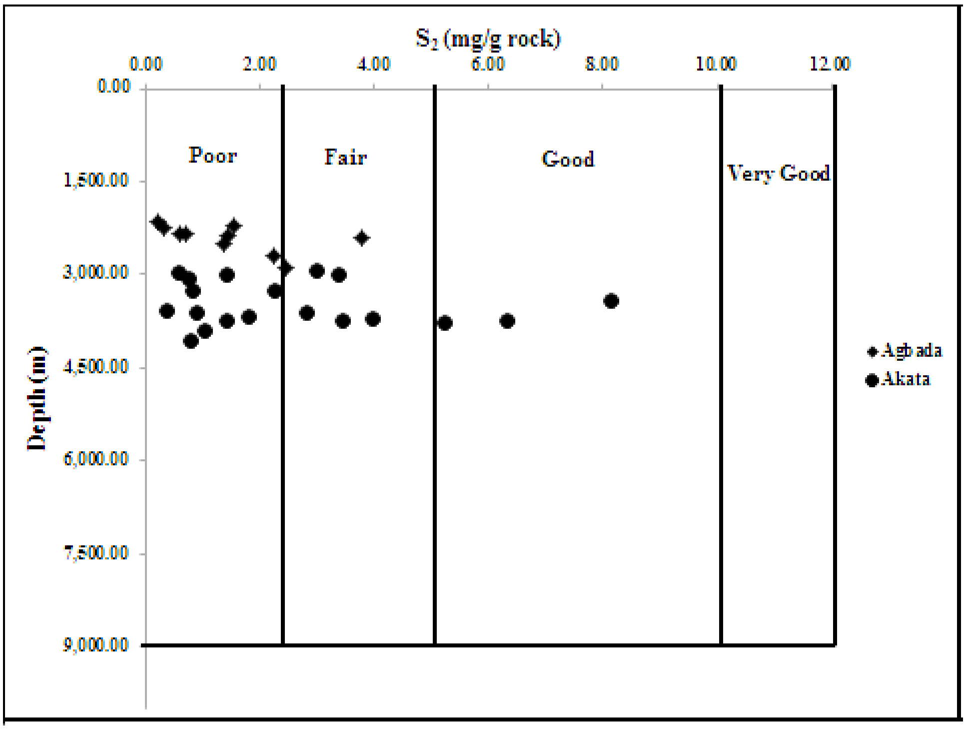

Fig. 12: Plot of S_2 vs. Depth determining the hydrocarbon potential of the studied samples.

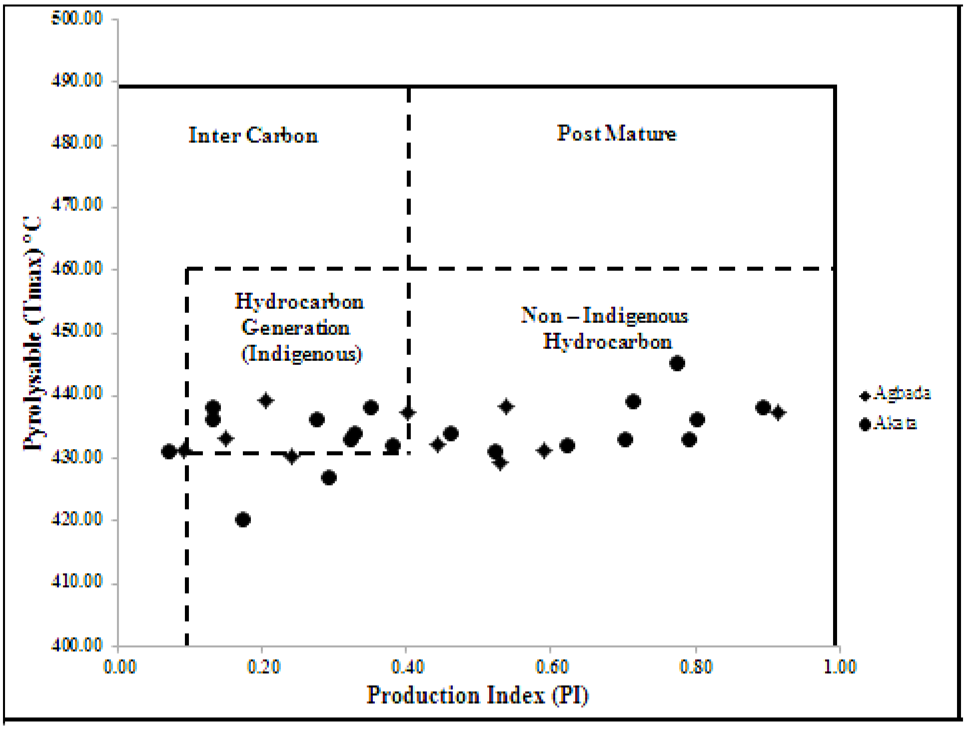

Fig. 13: Plots of PI vs. Tmax showing the level of thermal maturity of the studied samples

The generative capacities of these shales are high and with prospect for hydrocarbons, despite the moderate PI (0.09 to 0.91) and S_1/TOC (0.06 to 3.26) for some of the samples that is closer to the "oil window" of 1.0 (Tissot and Welte, 1984).

The Hydrogen Index (HI) is proportional to the amount of hydrogen contained within the kerogen, and high HI indicates a greater potential to generate oil. Kerogen types can be inferred from these indices as well. The HI is derived from the ratio of hydrogen to TOC; i.e, S_2/TOC x 100. Samples within the Niger Delta area are having HI values within the range of 35.00-221.00 mg HC/g TOC with an average value of 115.10 mg HC/g TOC. The van Krevelen diagram is generated by plotting the Hydrogen Index (HI) against maximum temperature (Tmax) as shown in Figs. 6 and 8 above.

According to Baskin (1997) classification, source rock with (HI) between 100-200 mg HC/g TOC are product of the organic matter type III. Peters and Cassa (1994) classified samples with (HI) less than 50 mg HC/g TOC as organic matter type IV. The relatively low hydrogen index (HI) values of the studied samples which range from 35.00 mg HC/g TOC to 221.00 mg HC/g TOC (Table 1) suggest that the source rocks have potential for gas. The low (HI) values reported in this study is comparable with low trend of HI reported in the Cretaceous source rock facies (except Coal samples) in the Nigerian sedimentary basins (Obaje *et al*., 2004; Ehinola *et al*., 2005; Akande *et al*., 2012; Ayinla *et al*., 2017; Ayoola *et al*., 2019; Kouadio *et al*. (2021). The values of S_2 from the Agbada Formation range from 0.23 to 3.78mgHC/g rock (Fig. 12) The S_2 values of the Akata Formation samples range from 0.34 to 8.12mgHC/g rock). These values of S_2 from these formations samples indicate fair to excellent generative potential.

The cross plot of the PI vs. Tmax shows that the Agbada Formation samples have PI values ranging from 0.09 to 0.91, thereby making the organic matter thermally mature (oil windows) and indigenous (Fig. 13). In Akata samples PI values is between 0.07 and 0.89 and are within oil window-dry gas zone and non-indigenous (Kouadio *et al*. (2021). All the samples from the Akata Formation with PI values of 0.1–0.4 indicate maturation within oil window. This is supported by observations of Whiteman (1982).

CONCLUSION

The samples were analyzed using a source rock screening technique (Rock Eval Pyrolysis) which is a basic source rock screening tool. The S_1, S_2, HI and Tmax were determined. It was reported that temperature increases with increase in depth and this has a direct effect on organic matter from from shale samples from the Niger Delta region. This effect can be observed among the samples from the Agbada Formation with Tmax values ranging 429 to 439°C and the Akata with Tmax values of 420 to 445°C described organic matter in the area as immature to matured stage by attaining the threshold of 430°C. The $S_1 + S_2$ versus TOC plot describe the shale samples as good source rock and capable of generating hydrocarbon in commercial quantity. According to Peters and Cassa (1994), TOC values >4.0wt% with S_1 and S_2 values > 4.0 and 20.0mg/g respectively will generate bitumen and hydrocarbons >4000 and 2400ppm. In this study, highest values of TOC and $S_1 + S_2$ obtained were 5.42wt% and 8.75mg/g respectively. The Tmax vs. OI, S_2 vs. OI, $S_1 + S_2$ vs. TOC and Tmax vs. TOC enhanced generation of van Krevelen diagrams. These plots provided information on the organic matter types III, source rock quality, maturity level and their corresponding depositional environments.

Based on Type III kerogen obtained from this studied shale samples, OM from the Niger Delta region are predominantly of terrestrial origin. Evidence for marine productivity is limited in these samples since the OM is greatly influenced by terrestrially derived sources. These OM assemblages suggests a marine setting (depositional environment) but dominated by terrestrial inputs which may likely controlled by the fluvial processes which is a function of most delta system. The delivery of high amounts of terrestrial organic matter likely stimulated sedimentary microbial activity, including sulphate reduction. The shale is an excellent source rock, with gas-prone kerogen. The high OI, low TS suggests terrestrially derived OM and deposition in an oxic and dysoxic shallow marine environment. In addition, HI and Tmax values described the samples as a characteristic of Type III dominant kerogen (gas - prone) and potential to generate oil and gases while the Tmax, consistently indicates an immature to matured organic matter on the shale samples.

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