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Rock-Eval Pyrolysis Analysis of Agbada and Akata Shale from Niger Delta Basin, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Thirty (30) shale core samples from the Agbada and Akata formations in the Niger Delta, Nigeria were evaluated using a Rock-Eval pyrolysis to determine their richness, type, thermal maturity and hydrocarbon potential. Agbada and Akata formation samples show fair to Excellent content of total organic carbon (TOC > 0.5 wt.%) for oil generation. The S2 yield values for Agbada and Akata samples ranging between 0.1 and 10 mgHC/g rock and genetic potential (0.1 mgHC/grock<PG<20 mgHC/grock), indicating that organic matter generated fair to very good significant hydrocarbon. The results acquired from Rock-Eval analysis of Agbada and Akata Formation show low to medium hydrogen index (IH) values (32 to 216 mgHC/g TOC) which indicate gas prone kerogen Type III to minor mixed kerogen Type II/III. The Tmax values for the most of studied samples range from 410°C to 444°C. In Agbada formation, Tmax values varie between 414°C and 438°C, indicating an

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Immature to early mature organic matter. Tmax values for Akata formation range from 410°C to 444°C, suggesting immature to mature source rocks. This study concluded that Agbada formation has organic matter for world class oil generation but the limitation of the thickness of the formation gives Akata formation a better stand, with a fair generation capacity but an ocean of thick source rock, the thickness compensates for the fair generation capacity.

Keywords: Geochemistry; Niger Delta; Pyrolysis; Rock-Eval; source rock.

1. INTRODUCTION

Source rock characterization consists of determining sediment source richness, source quality, and thermal maturity and assessing the hydrocarbon generating potential of sediments by looking at the sediment's capacity for hydrocarbon generation The analytical methods most frequently used for this purpose are total organic carbon (TOC) content analysis and Rock-Eval pyrolysis analysis.

Various studies have been conducted on Niger Delta source rocks evaluation. Combining TOC, Rock-Eval pyrolysis, organic petrography, gas chromatography and mass spectrometry, ten years studies on samples from the Agbada-Akata transition, or uppermost Akata Formation, [1] suggested that the Niger Delta is mainly composed of a mixture of type II and III kerogen having little oil potential as defined by pyrolysis. In the Niger Delta province, [2] have highlighted one petroleum system and claimed that the main source rock is the Upper Akata Formation, the delta marine shale facies, possibly with the contribution of interbedded marine shales of the Lower Agbada Formation. This result is not in adequacy with the work of [3]; based on geochemical analysis of rock samples from three offshore fields and oil samples from offshore and onshore fields in the western Niger Delta revealing complex mixtures of organic matter and showing early mature to mature source rocks deposited in alternating oxic and anoxic environments. The results of this study highlighted that the Niger Delta has two petroleum systems, though the terrigenous system is more predominant.

According to [4], the principal sources for oil and gas in the Niger Delta are Type II, Type II/III and Type III kerogens and assumed that oil and gas in the Niger Delta originated mainly from terrigenous and nearshore marine source rock. [3] and [5], using total organic carbon (TOC), soluble organic matter concentration (SOM) and Rock-Eval pyrolysis for source rock characterization of one well from Agbada formation in offshore Niger Delta. The source rock assessment revealed that the soluble organic matter (SOM) ranges from 2430 ppm to 3900 ppm with an adequate mean value of 3282 ppm. The TOC ranges from 0.91 to 2.71 % by weight; HI ranges from 35 to 635 mgHC / g TOC; the Tmax value varies from 363 to 433 °C and the Production Index (PI) values range from 0.1 to 0.5 with an average transformation ratio (TR) of 0.15 wt%. These show that the amount of organic matter is medium to excellent and in high concentration with an excellent potential for generating hydrocarbons and consisting of type II and type III kerogen. Evaluation of hydrocarbon generating potential of 24 fine grained sediment samples from the Well located in the northern depositional belt of the Niger Delta Basin using Rock-Eval analysis techniques have been carried out in to elucidate the hydrocarbon generative potentials of the sediments from this part of the Niger Delta Basin [6]. Total organic matter (TOC), which range from 0.56 to 6.11, indicate fair to excellent potential. The hydrogen index (HI), production index (PI) and genetic potential (GP) ranges from 30 to 115, 0.08 to 0.32 and 0.25 to 7.39 respectively. Tmax ranged from 308 to 437ºC, indicating immature to marginally mature source sediments. HI based organic matter calibration constrained with S2/S3 indicates a dominance of types III and IV gas source and non-source kerogen types. Cross plots of HI vs OI further confirmed a dominant type III and IV kerogen.

The investigation made by [7] on hydrocarbon potential source rock for Agbada formation located in the Osioka south area in Western Niger Delta using total organic carbon (TOC), Rock-Eval analysis and vitrinite reflectance revealed good source rock potential (TOC values between 1.0 and 2.0%). Rock-Eval results indicated that 50% of samples from the southern Osioka area consist of Type II kerogen, capable of generating both oil and gas at an appropriate temperature at depth. The remaining half of the samples contain type III kerogen capable of generating gas [8] believe that the hydrocarbons from the Niger Delta originated mainly from the

Akata shales and subordinately from certain shale intervals of the Agbada Formation, containing terrestrial plant material that gave rise mainly to organic matter of the types III and II/III (mainly gas-prone) in an oil window that ranged from 9,000 to 14,000 feet in depth. It should be noted that the characteristics of the Akata and those of the Agbada shale in the transition zone do not differ significantly. However, it is suggested that the Agbada Shale was primarily a source of gas.

Most previous studies have given mixed and conflicting results. This study aims to re-evaluate the hydrocarbon potential of the Agbada and Akata formations of the Niger Delta basin using the analysis of Rock-Eval pyrolysis data. This will make it possible to better understand the origin, richness and thermal maturity of the samples studied and also to increase the existing knowledge in organic geochemistry in the basin.

1.1 Geological Setting of Niger Delta Basin

The Niger Delta is one of the most prolific petroleum provinces in the world, it is located in the Southern Nigeria margin of the Gulf of Guinea, with latitude 4°49' N and longitude 6°0' E [9]. The Niger Delta sedimentary basin covers an area of about 256,000 km^2 [8]. It is bounded to the south by the Gulf of Guinea and the north by older tectonic elements (Cretaceous) including the Anambra Basin, the Abakaliki uprising and the Afikpo syncline, and to the east and west by the Cameroon volcanic line and the Dahomey basin respectively (Fig. 1b). The Niger Delta basin began to form in the Cretaceous when the African plate separated from the South American plate; the basin is delimited by rift faults on its northwest and northeast edges [10]. After the rifting, gravity tectonics became the main deformation process [2]. Pre- and syn-sedimentary tectonics described by [11] characterized the evolution of the Niger Delta basin. The regressive clastic sequence in the Niger Delta began to form in the Paleocene and has since formed sediments which now reaches a thickness of 12,000 m [5]. The Niger Delta Basin consists of three main lithostratigraphic units of Cretaceous to Holocene origin (Fig. 1a). These units represent the prograding depositional environments which are distinguished mainly based on shale-sand ratios and are continental, transitional, and marine environment [12]. This Tertiary sequence in the Niger Delta consists of the three formations that are locally designated in ascending order (from the bottom) the Akata Formation, Agbada Formation, and Benin Formation [2,13]. At the base of the system is the Akata Formation, a sequence of planktonic foraminifera-rich non-compacted transgressive Paleocene-to-Holocene marine shale, clays, and silt. This interstratified unit of sandstone and shale is called the Agbada Formation (Recent Eocene). The Agbada Formation represents the delta system (delta front, fluvio-deltaic facies) of the sedimentary sequence [2]. The Agbada Formation is overlain by the third formation, the Benin Formation, a last continental deposit from the Eocene to Recent alluvial and upper coastal plains [14].

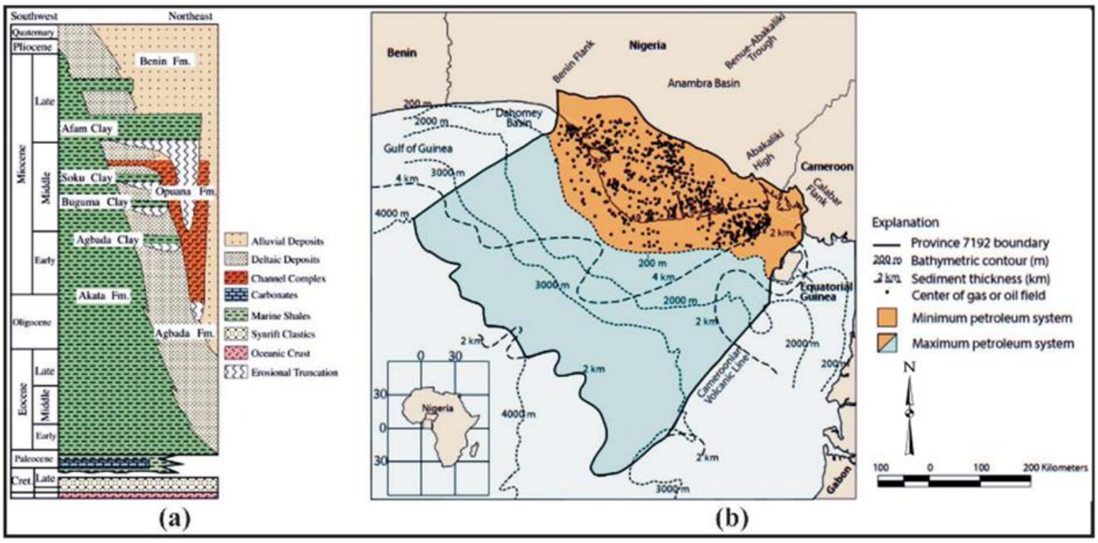

Fig. 1. (a) Stratigraphic column showing the three formations of the Niger Delta [13]; (b) Niger Delta Map showing Province outline (petroleum system) and bounding structural features [2]

2. MATERIAL AND METHODS

Thirty (30) core samples were recovered from twenty-four (24) exploration wells located in the onshore part of the Niger Delta Basin. The samples were analysed at the PETROCI Analysis and Research Center in Abidjan (Côte d'Ivoire). Approximately 70 gram of the core sample was collected. Then, the samples were ground into a fine powder for Rock-Eval analysis [15]. The analyses were performed on the 30 samples by using Rock-Eval 6 instrument. The experimental procedure followed for Rock-Eval pyrolysis was that described by [16] and [17]. The method consisted in estimating petroleum potential of rock samples by pyrolysis according to a programmed temperature pattern (300°C<T<650°C). Released hydrocarbons are monitored by FID (Flame ionization Detector), forming the peaks S1 (represents the free hydrocarbons already present in the rocks and can be obtained at 300°C) and S2 (hydrocarbons generated due to pyrolysis of kerogen). In addition, CO and CO_2 released during pyrolysis is monitored in real time by mean of an IR cell, giving information on the oxidation state of organic matter (peak S3). The method is completed by oxidation of the rock sample according to a programmed temperature pattern (300°C<T< 850°C). Recovered parameters include volatile hydrocarbon content (S1), remaining HC generative potential (S2) and temperature of maximum hydrocarbon release (Tmax). Tmax is the oven temperature that corresponds to the maximum rate of S2 hydrocarbon generation. The hydrogen index (HI), oxygen index (OI), production index (PI), the ratio S2/S3 and genetic potential (GP=S1+S2) were calculated.

3. RESULTS AND DISCUSSION

3.1 Organic Matter Richness and Generative Potential

The organic matter richness and hydrocarbon generative potential of the source rocks in the Niger Delta basin can be evaluated by bulk geochemical data such as TOC content and pyrolysis S1 and S2 yields (Table 1 and Table 2). Total Organic Carbon (TOC) expressed as a percentage by weight of the total rock (% by weight), it allows the petroleum potential of the source rock to be determined. [18] defined the minimum quantity of TOC that carbonates and shales must contain to be qualified as source rock. The S2 is hydrocarbon produced during the cracking of non-extractable organic matter (kerogen). This parameter is therefore an evaluation of the quantity of gas and oil likely to be produced during the evolution of this rock. It is expressed in mgHC/g rock. The TOC is expressed as the relative dry weight percentage of organic carbon in the sediments [19], but not a direct measure of the total amount of organic matter. It is generally accepted that for a rock to be a source of hydrocarbons, it must contain sufficient organic matter for significant generation and expulsion for many years; this was taken as 0.5 wt.% TOC for shales and somewhat less 0.3 wt.% TOC for carbonates [19]. The minimum TOC content of a source rock needs to be within the range of 1–2 wt.% [17].

Based on the criteria developed by [17], the TOC (wt.%) of the samples collected in the twenty-four (24) wells of the Niger delta basin varies between 0.47 and 5.23 wt.% (Table 1 and Table 2). All the samples have a TOC greater than 0.5 wt.%, except one well (Kokori, 7000ft) from Agbada formation which has a TOC of 0.47 wt.%.

The TOC contents of Agbada shales range from 0.47 to 3.06 wt.%, suggesting that these samples correspond to potential source rocks with a richness in organic matter varying from fair to very good (Fig. 2). The TOC contents of Akata shales range from 0.6 to 5.23 wt.%. All the studied samples have a TOC greater than 0.5 wt.%, covering a potential interval from fair to excellent. The TOC values obtained for Agbada formation shales are consistent to the finds of [5,6,21]. However, the TOC obtained for Akata formation samples are greater than those founded by [1].

The S2 values of Agbada formation samples analysed range from 0.15 to 4.36 mgHC/g rock (Fig. 3). Thus, pyrolysis yields indicate that Agbada shale samples are poor to good generative potential. One (1) out of ten (10) samples showed medium to good hydrocarbon generation potential. The S2 values of Akata formation samples range from 0.3 to 7.96 mgHC/g rock. About fifty percent have a generative potential ranging from 2.82 to 7.96 mgHC/g rock, indicating fair to good generative potential.

The volatile hydrocarbon content (S1) and the hydrocarbon yields (S2) are in agreement with TOC content, indicating that the shales of Akata and Agbada formation of onshore Niger Delta are poor to good source rock generative potential based on the classification by [17]. Thus, Agbada and Akata formations can be considered as potential source rocks for the hydrocarbon generation in the Niger Delta Basin.

3.2 Type of Organic Matter

Determination of the type of organic matter is necessary. It allows to have a general idea on the petroleum potential of the source rock on the one hand and its origin on the other hand.For this, we mainly use the IH-IO diagram established from the indexes of hydrogen (IH) and oxygen (IO) [16]. IH (Hydrogen Index) corresponds to the degree of aliphaticity of organic matter, expressed in mgHC/g TOC (S_3 x 100 / TOC). It allows to determine the type of organic matter present. Oxygen Index (IO) corresponds to the degree of oxidation of organic matter and is expressed in mg CO_2 / g TOC (S3 x 100 / TOC).

The hydrogen index (IH) values of the samples studied are between 32 and 216 mgHC/g TOC (Table 1 and Table 2). Most of the samples analysed have HI values of 50 – 200 mgHC/g TOC, which indicate gas prone kerogen Type III. Some studied samples show the mixed kerogen Type II/III which has the potential to yield oil and/or gas. The modified Van Krevelen diagram (HI versus OI) (Fig. 4) shows that almost all the samples from the twenty-four (24) exploratory wells consist predominantly of Types III and minor Types II/III kerogens, which are capable of generating gas and gas-oil respectively at a suitable temperature at depth. The Type II/III describes a transitional composition between types II and III that represents a mixture of marine and terrigenous organic matter deposited in a paralic marine setting and Type III Kerogen originates from terrigenous plants. About fifteen percent (15%) of studied samples from Akata and Agbada formations indicate Type IV kerogen which generates neither oil nor gas, with HI less than 50 mgHC/g TOC. The similar results have been obtained by several authors such as [5,6,21-24]. The S2/S3 ratio (hydrocarbon type index) was also used for determination of kerogen type [25]. Like HI/OI, the S2/S3 ratio is the indicator of the ratio of hydrogen to oxygen. In the Agbada formation wells, hydrocarbon type index are between 0.18 and 3.28 (Table 1).These values may indicateType III kerogen with gas and oil (condensate) potential (Fig. 5). Hydrocarbon type index of Akata formation samples are between 0.23 and 3.09 (Table 2).These values yield Type III kerogen with gas and oil (condensate) potential (Fig. 5).

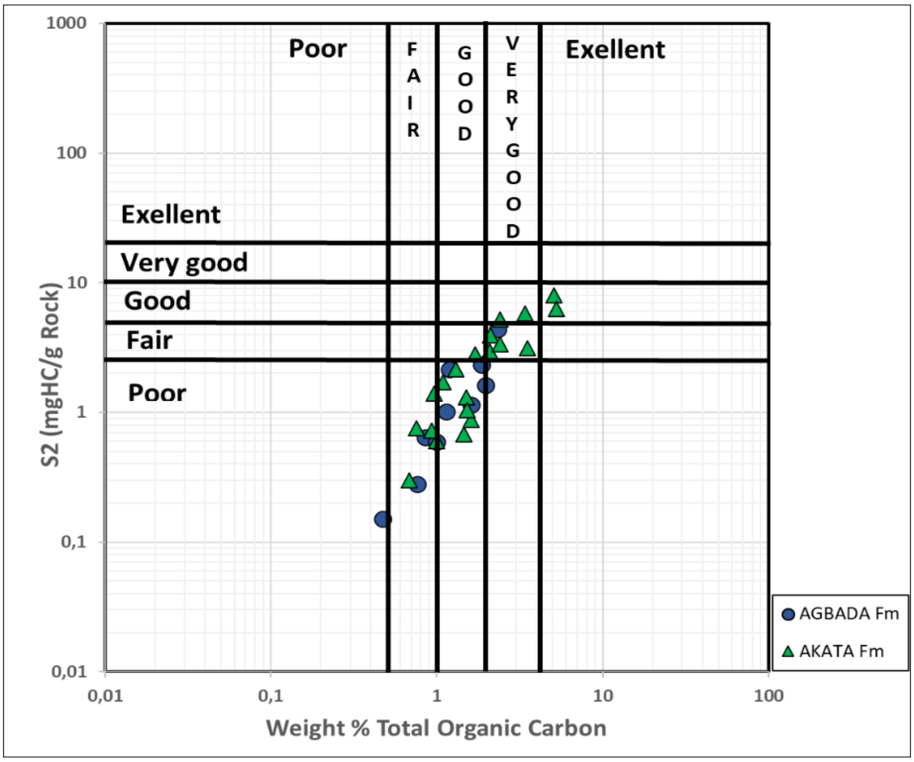

Fig. 2. Crossplot showing the organic matter quantity with S2 values for the Agbada and Akata Formations (Modified from [20])

Table 1. Result of rock-eval analysis of Agbada formation samples

Formation	Wells	Depth (ft)	S1	S2	S3	Tmax	HI	OI	TOC	S2/S3	PG	PI
AGBADA	Kokori	7000	0,03	0,15	0,79	423	32	167	0,47	0,19	0,18	0,17
	Eriemu	7300	0,31	1,63	2,05	427	83	104	1,97	0,80	1,94	0,16
	Warri river	7400	0,06	0,28	1,53	419	36	200	0,76	0,18	0,34	0,18
	Rumuekpe	7620	0,07	0,64	1,56	431	75	184	0,85	0,41	0,71	0,1
	Bodo west	7625	0,23	0,59	1,29	420	59	128	1	0,46	0,82	0,28
	Okan	7750	0,12	1,02	1,69	427	90	148	1,14	0,60	1,14	0,11
	Benin west	7840	2,56	4,36	1,33	438	187	57	2,33	3,28	6,92	0,37
	Egbema	8160	0,74	1,15	1,16	421	72	73	1,61	0,99	1,89	0,39
	Opobo south	8840	2,45	2,16	0,93	421	181	78	1,19	2,32	4,61	0,53
	Meji	9440	1,23	2,34	2,78	420	125	149	1,87	0,84	3,57	0,34

S1 : Volatile hydrocarbon (HC) content, mg HC/g rock; S2 : remaining HC generative potential, mg HC/g rock; S3 : Carbon dioxide yield, mg CO_2/g rock; HI : hydrogen index = S2 × 100/TOC, mg HC/g TOC; OI : oxygen index = S3 × 100/TOC, mg CO_2/g TOC; TOC : Total Organic Carbon, wt.%; Tmax : temperature at maximum of S2 peak; PI : production index = S1/(S1+S2); PG : Potential yield = S1+S2, mg HC/g rock

Table 2. Result of rock-eval analysis of Akata formation samples

Formation	Wells	Depth (ft)	S1	S2	S3	Tmax	HI	OI	TOC	S2/S3	PG	PI
AKATA	Iyede 1	9555	0,27	3,13	3,77	422	89	107	3,53	0,83	3,4	0,08
	Abiteye	9700	0,1	0,6	1,15	426	60	116	0,99	0,52	0,7	0,14
	Assa	9760	2,63	1,3	1,38	424	86	91	1,51	0,94	3,93	0,67
	Ubefan	9800	2,82	2,95	1,55	428	142	75	2,07	1,90	5,77	0,49
	Kolo creek	10000	0,13	0,72	1,67	434	77	179	0,93	0,43	0,85	0,15
	Isoko	10640	2,07	0,68	1,55	410	47	107	1,45	0,44	2,75	0,75
	Delta north	10610	0,72	2,16	2,2	444	166	170	1,3	0,98	2,88	0,25
	Ughelli	11120	0,67	7,96	3,01	424	157	59	5,07	2,64	8,63	0,08
	Osiomo	11725	0,1	0,3	1,29	421	44	189	0,68	0,23	0,4	0,25
	Iyede 1	11790	0,45	0,88	1,54	423	55	96	1,6	0,57	1,33	0,34
	Apara	11800	5,36	2,82	1,2	429	166	70	1,7	2,35	8,18	0,66
	Ughelli	12000	0,87	1,7	1,08	428	155	99	1,09	1,57	2,57	0,34
	Kokori	12140	2,65	3,95	1,34	426	188	64	2,1	2,95	6,6	0,40
	Kolo creek	12200	2,18	1,4	1,18	423	145	122	0,96	1,19	3,58	0,61
	Eriemu	12200	4,64	6,27	2,81	426	120	54	5,23	2,23	10,91	0,43
	Warri river	12260	6,17	3,33	1,53	423	138	64	2,4	2,18	9,5	0,65
	Udeduma creek	12340	6,91	5,19	1,68	428	216	70	2,4	3,09	12,1	0,57
	Ogbogene	12715	0,29	1,04	0,79	431	69	52	1,52	1,32	1,33	0,22
	Opukushi	13260	0,93	0,75	0,95	424	100	128	0,75	0,79	1,68	0,55
	Isoko	13400	8,99	5,76	1,87	425	169	55	3,4	3,08	14,75	0,61

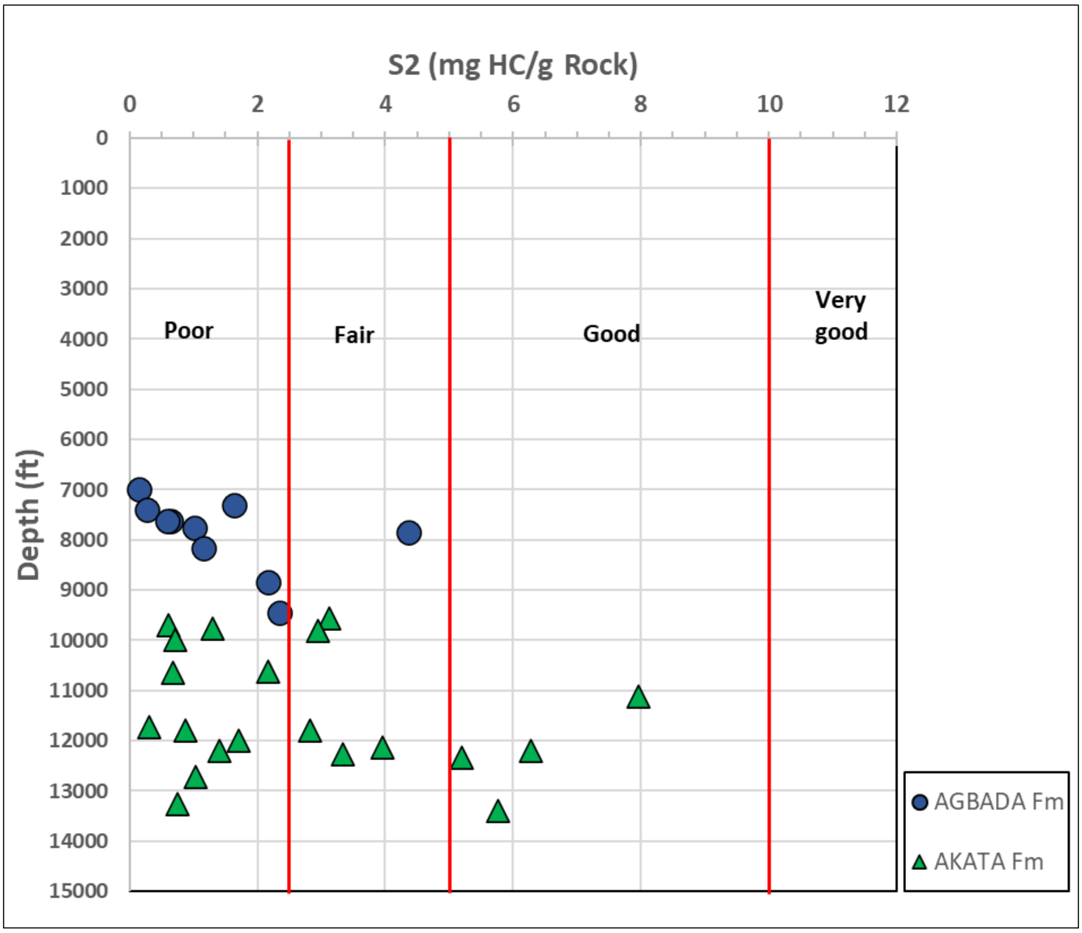

Fig. 3. Plot of remaining hydrocarbon potential S2 (mg HC/g rock) versus Depth

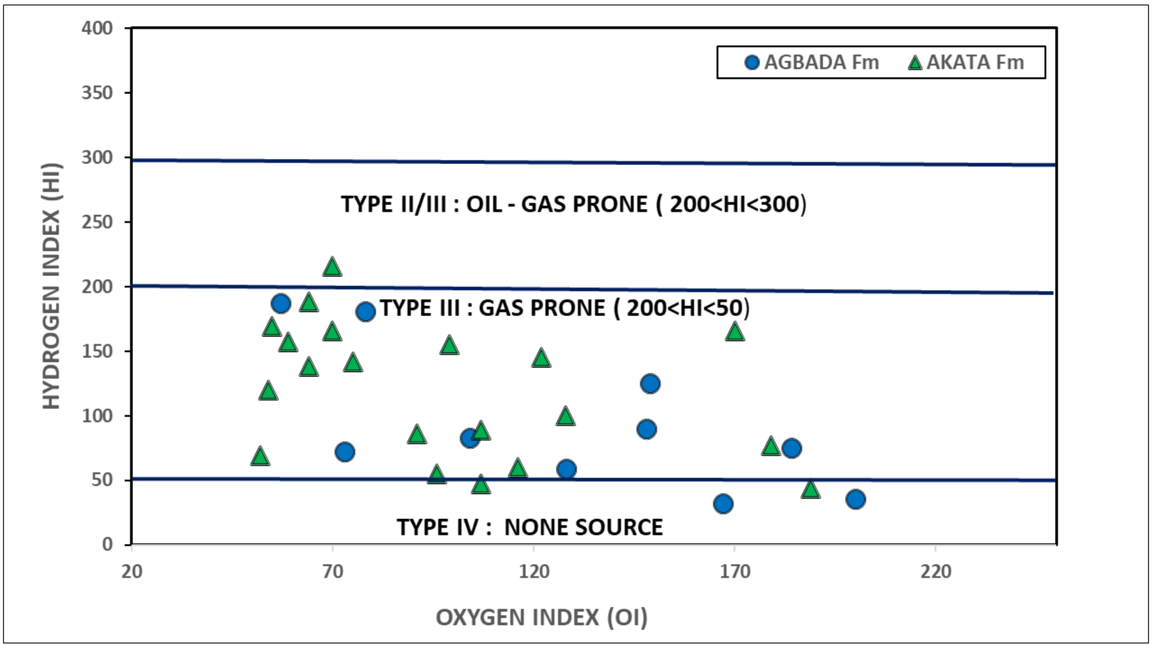

Fig. 4. Modified Van Krevelen diagram showing kerogen quality of Agbada and Akata Formations

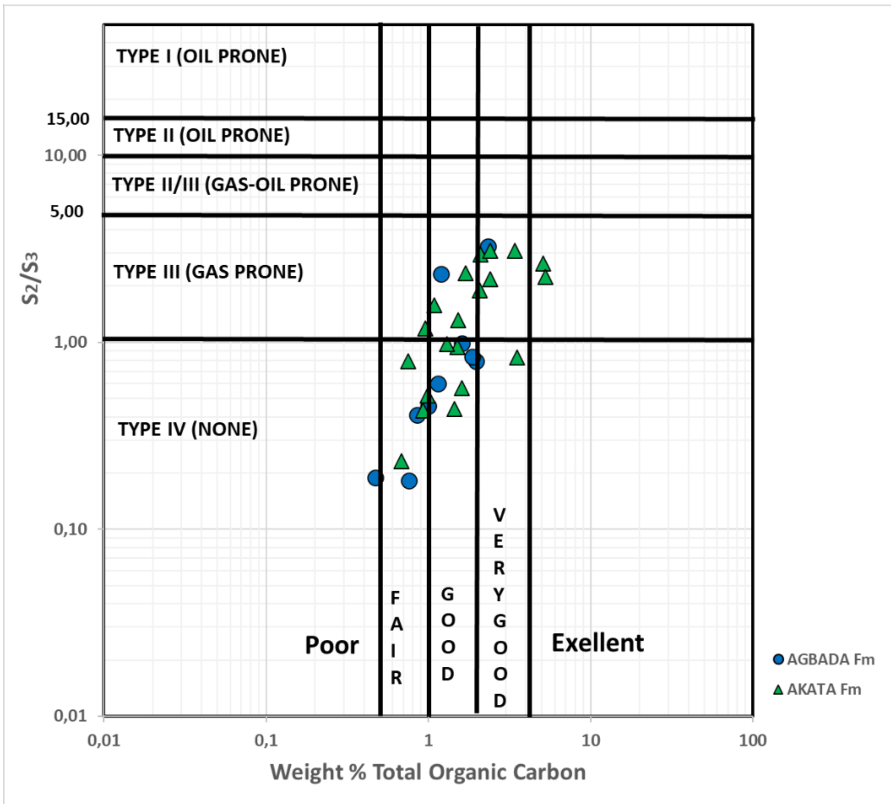

Fig. 5. Plot of S2/S3 versus TOC indicating kerogen types and generation potential

3.3 Thermal Maturity of Organic Matter

Rock-eval Tmax (°C) is used to evaluate source rock maturity stage. The pyrolysis Tmax is the maximum temperature of hydrocarbon production (top of peak S2). It characterizes the thermal maturity of the rock. It depends on the nature of the kerogen (and therefore on the type of Organic Matter) and on its degree of diagenetic evolution. This parameter is only credible if S2 is greater than 0.2 mgHC/g rock [17].

The maturity of Thirty (30) core samples of Niger Delta Formations has been investigated by plotting the results in Tmax versus Depth diagram (Fig. 6). The Tmax values for the most of studied samples range from 410°C to 444°C, indicating an Immature to mature organic matter. Tmax values may be influenced by kerogen type [26] and mineral matrix [27], the presence of free hydrocarbon, burial depth and age [18]. Thus, the defined maturity windows are only approximate. Fig. 6 shows that most of studied samples are immature, however some of Agbada formation from wells Rumuekpe (7620 ft) and Benin west (7840 ft) have maturity successively 431 and 438°C, indicating early mature source rocks. The Akata formation samples from wells Kolo Creek (10000 ft), Delta North (10610 ft), Apara (11800 ft) and Ogbogene (12715 ft) have Tmax values between 430°C to 444°C. These values indicate early mature to mid-mature kerogen (Fig. 6).

According to these values, the Agbada and Akata formations source rocks are immature/early mature and there are locally within the oil window. The recent studies of [6] and [21] confirm these results.

For [28] and [29], The Agbada and Akata formations, however, rarely reach thickness sufficient to produce a world-class oil province and are immature in various parts of the delta.

3.4 Hydrocarbon Generation Potential and Production Index

[18] proposed a genetic potential (PG=S1+S2) for the classification of source rocks. The hydrocarbon yield (S1+S2) generated during pyrolysis is a useful parameter to evaluate the hydrocarbon generation potential of source rocks [17,30]. According to the classification scheme proposed by [18], rocks having PG of less than 2

mg HC/g rock correspond to gas-prone rocks or non-generative ones, rocks with PG between 2 and 6 mgHC/g rock are moderate source rocks, and those with PG greater than 6 mgHC/g rock are good source rocks.

The S1+S2 yields range from 0.18 to 14.75 mg HC/g rock in the samples of Akata and Agbada formations (Table 1 and Table 2) and vary with TOC content (Fig. 7). These TOC contents and (S1+S2) yields meet the accepted standards of a source as having “poor to very good” source rock potential (Fig. 7) as classified by [17].

Based on the above criteria, 70% of Agbada samples with PG less than 2 mgHC/g are either gas-prone rocks or non-generative rocks. Two (2) samples, Opobo South (8840 ft) and Meji (9440ft) with PG values between 2 and 6 mgHC/g are moderate source rocks. One (1) sample, Benin west (7840 ft) with PG value greater than 6 mgHC/g exhibit good source rock potential at sufficient depths. In the Akata formation, 40 % of samples with PG less than 2 mgHC/g shows poor Petroleum Potential, while 60% shows fair to very good source rocks generative potential. Seven (7) samples out of forteen (14) have good to very good source rocks potential (Fig. 7).

Fig. 8 shows the cross plot of the Production index (PI) versus Tmax. Most of Agbada formation well samples are PI values ranging from 0.1 to 0.4, thereby making them thermally mature (oil windows) and indigenous. Fifty pourcent of the samples in Akata wells with PI values between 0.4 and 0.75 are within oil window-dry gas zone and non-indigenous. In the others samples from Akata wells, PI values indicate that the formation (0.1–0.4) is within oil window. The results of this study supports the findings of [10].

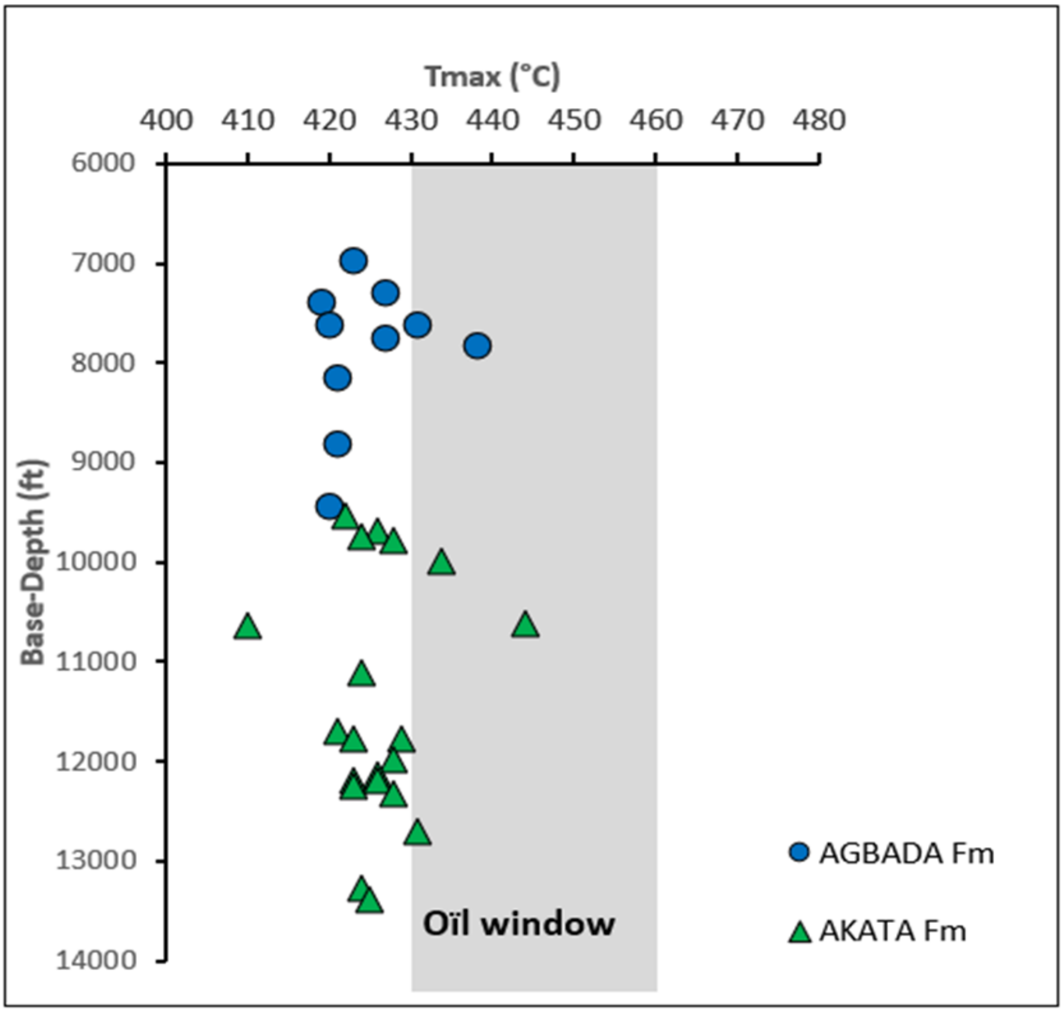

Fig. 6. Plot of Tmax variation versus depth for Agbada and Akata Formations

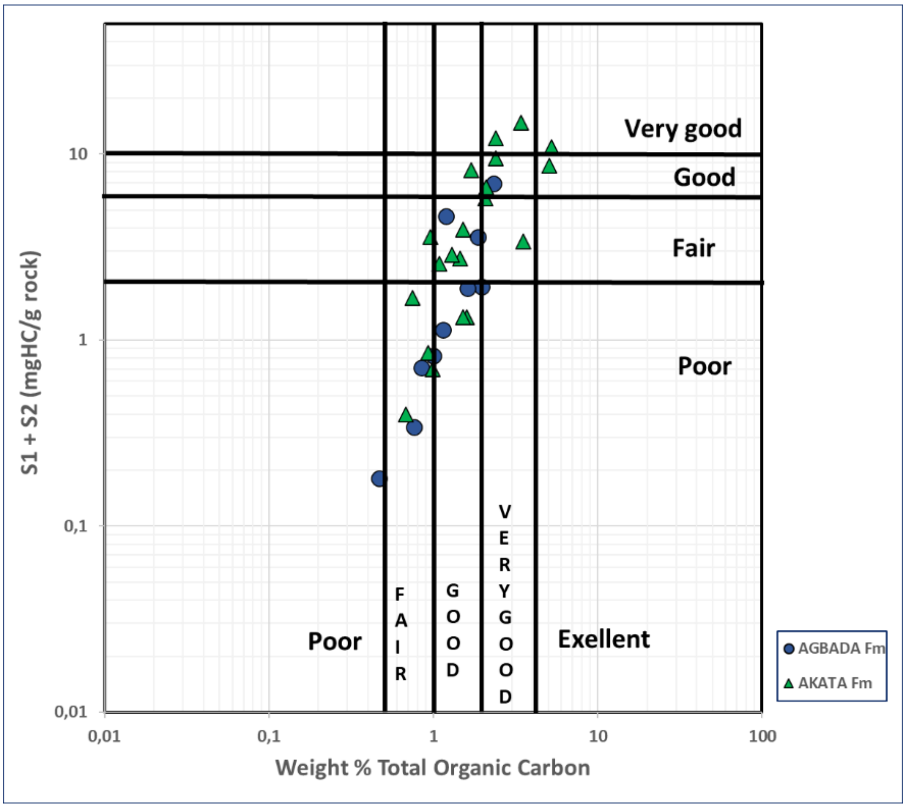

Fig. 7. Plot of S1+S2 versus TOC showing the genetic potential for the studied samples

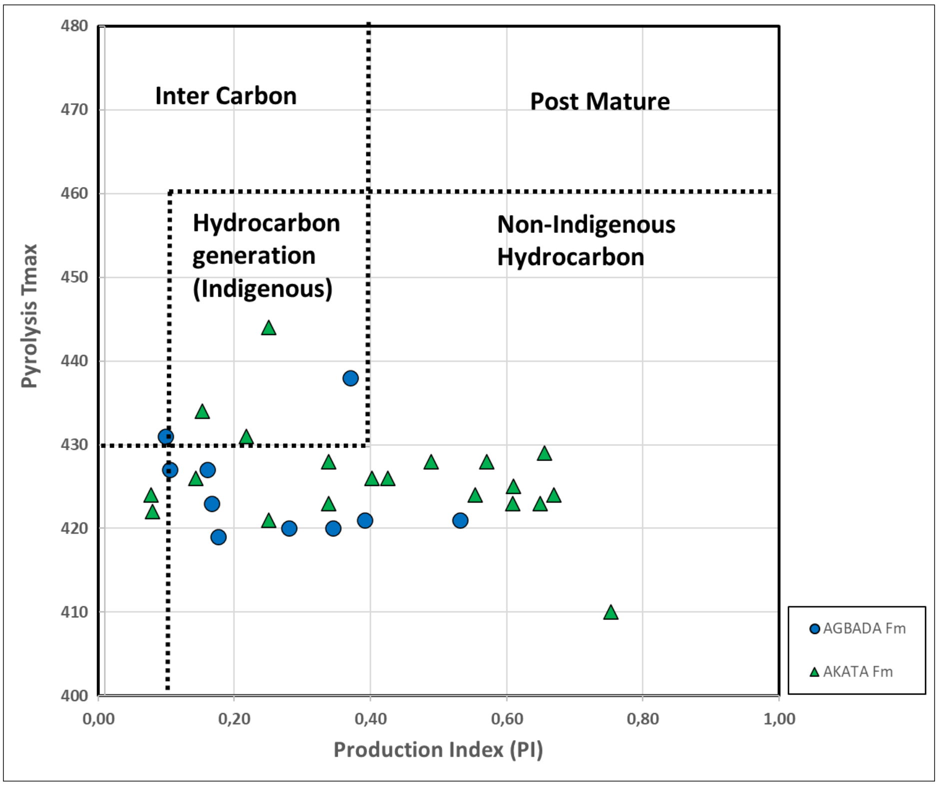

Fig. 8. Plots of Production Index (PI) versus Tmax showing the level of thermal maturity of the studied samples

4. CONCLUSION

The analysed samples from Agbada formation show fair to very good content of total organic carbon (TOC) for the samples in respect to hydrocarbon potential. The organic matter generated fair to very good significant hydrocarbon. This is supported by the presence of mainly Type III kerogen, few Type II/III kerogen, generating oil and gas and thus few Type IV kerogen. Almost all (90%) analysed samples from Akata formation show good to excellent content of total organic carbon (TOC) for the samples in respect to hydrocarbon potential. The organic matter for Akata formation shales generated fair to very good hydrocarbon, supported by the presence of mainly Type III kerogen (terrestrial origin), few Type II/III kerogen (marine and terrestrial), which are capable of generating oil and gas. As thermal maturity, Agbada and Akata formation samples show immature to early mature source rocks in their entirety. Agbada formation has organic matter for world class oil generation but the limitation of the thickness of the formation gives Akata formation a better stand, with a fair generation capacity but an ocean of thick source rock, the thickness compensates for the fair generation capacity.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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