Characterization of Organic Matter and Hydrocarbon Potential of Shale from Uturu, Isigwuato, Se Nigeria

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Abstract- The Cretaceous sediments in the Anambra Basin (SE Nigeria) consist of a cyclic succession of coals, carbonaceous shales, silty shales and siltstones interpreted as deltaic deposits. The HI versus Tmax and HI versus OI diagrams were used in classifying the organic matter in the shale indicating the presence of Type III kerogen. Tmax values between 426 and 439ºC indicate that the shales are thermally immature to marginally mature with respect to petroleum generation. Hydrogen Index (HI) values range from 14.00 to 31.00mgHC/gTOC while S_1 + S_2 yields values ranging from 0.22 to 1.00mgHC/g rock, suggesting that the shale have gas generating potential. The TOC of shale samples of the studied Uturu locality ranges from 1.51 to 2.95%, an indication of a good to excellent source rock of terrestrially derived organic matter. The average oxygen index (OI) (8.00 $mgCO_2g^{-1}TOC$) suggest deposition in a shallow marine environment. Based on the kerogen type, shales from Uturu, Nkporo Formation have the capability of generating oil and gas if sufficient maturity attained since the studied area is part of active Cretaceous petroleum system in the Anambra Basin.

Index Terms- Kerogen type, Organic matter, Maturity, Shale, Source rock.

I. Introduction

The Anambra Basin became the site of major deposition following the Santonian folding in southeastern Nigeria. Compressional uplift of the Lower Benue Trough succession (Albian to Coniacian) along a NE-SW axis was accompanied by tectonic inversion and downwarping of the Anambra platform (Fig. 1). Estimates of total sediment thickness in the Anambra Basin from gravity measurements range from 1000-4500m [1], out of which between 3000 and 3500m were deposited during the late Cretaceous (Upper Campanian to Maastrichtian). At Uturu, there has not been detailed work on the shale deposit. Traditionally, organic petrographic studies are mainly used for determining coal and shale quality, composition, paleodepositional environment, or organic matter ranking [2]. Recently multi-analytical approach to organic petrography analysis uses SEM-EDS, microprobe, Rock-Eval 6 pyrolysis, solvent extract, and gas chromatography - Mass Spectrometry (GC – MS) (i.e biomarkers), hydrous pyrolysis (e.g [3], [2], [4], [5]).

Where shales are being assessed for their petroleum-generative potential (i.e hydrocarbon source rock perspective), Rock-Eval prolysis to source rock's approach is most informative, since organic matter (OM) are solely prone to diagenetic and catagenetic transformation into liquid petroleum (i.e bitumens, crude oils, e.g. [6]. This paper aims to determine the organic matter types and their corresponding depositional environment; the quality, maturity and characterization of organic matter.

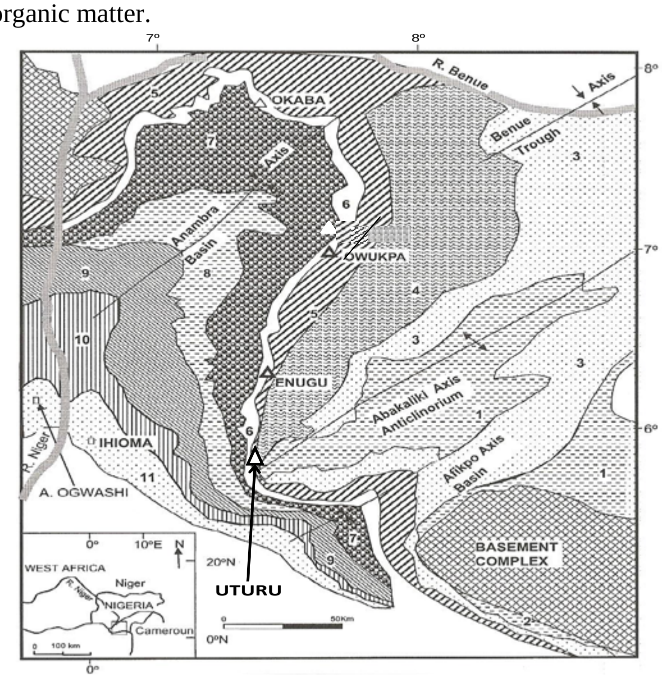
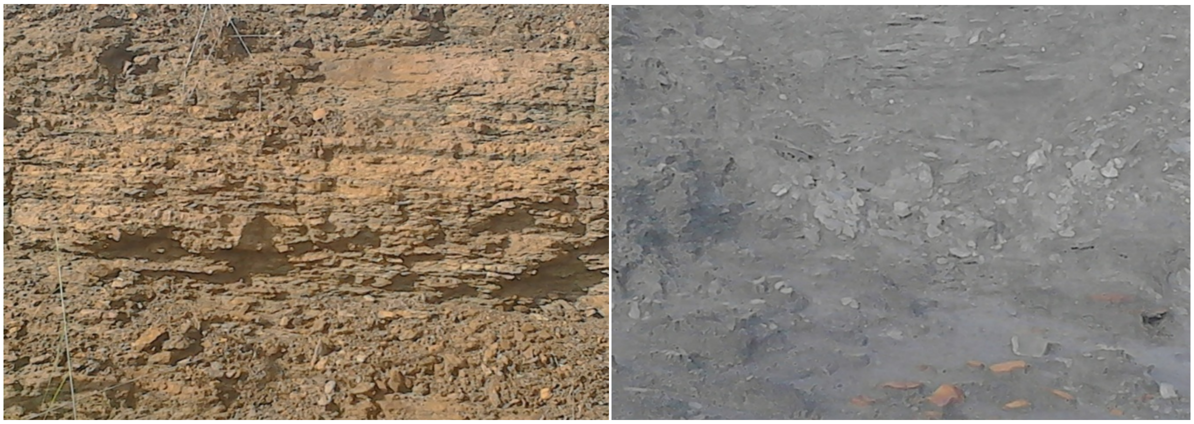


Fig. 1: Generalised geological map of the SE Nigeria (boxed areas of inset) showing the location of the coal deposits. Numbers indicate Cretaceous and Tertiary formations shown in Fig. 7 as **f**ollows: **1.** Asu River Group; **2.** Odikpani Formation; **3.** Eze-Aku Shale; **4.** Awgu Shale; **5.** Enugu/Nkporo Shale; **6.** Mamu Formation; **7.** Ajali Sandstone; **8.** Nsukka Formation; **9.** Imo Shale; **10.** Ameki Formation and **11.** Ogwashi-Asaba Formation (modified from [7]).

Materials and Methods

A total of 6 samples were collected from Uturu. The number of samples from any of this locality was based on the accessibility of the sample area and the extent to which the shale is development at the outcrop (Plates A and B).



(a) (b)

Plates a, b: Field photograph of shale outcrop at Uturu along the Okigwe- Arochukwu road.

Samples Preparation

For each of these samples, 30 to 50g was used for the analyses. The samples were washed to remove the dirts and sands on them. The washed samples were kept in the oven for 24 hours to dry at temperature of 40°C. The dried samples were crushed by mortar and pestle. After crushing the samples, 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.

Rock-Eval 6 Pyrolysis

A mass of 11 – 36mg of the pulverized samples were weighed in crucibles with a balance weighing instrument model Sartorius ISO 9001. The weighed samples together with the crucibles were placed in a Rock-Eval 6 machine where the samples were subjected to initial temperature of 100°C before it was increased to 300°C and finally to the temperature of 850°C. In between these temperatures, the Tmax, the temperature at maximum rate of pyrolysable (S2) hydrocarbon generation, was determined. Also free oil content (S1), pyrolysable hydrocarbon content (S2), and amount of CO_2 (S3) were determined (Fig. 2).

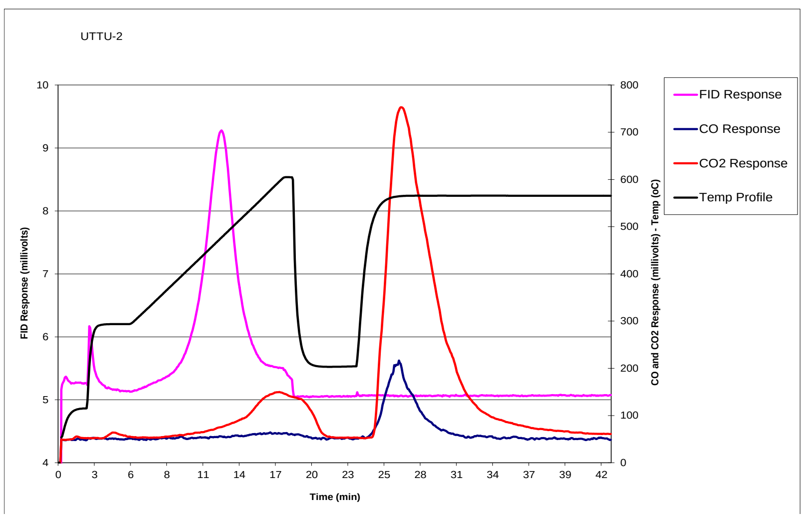


Fig. 2: Programmed pyrolysis result profile.

Result and Discussions

In shale samples, average TOC of 2.0wt% is considered an excellent source rock as HI greater than 350mgHC/gTOC is proposed to generate high commercial quantity of petroleum [8]. Highest TOC content of 2.95wt% was obtained from the shale samples from Uturu. Its values range from 1.34 to 2.95wt% with a mean of 1.85wt% (Table 1). The TOC of the shale samples range from 1.34-2.95 wt% with an average of 1.85 wt% from the Uturu shale samples. The highest TOC value of 2.95 wt% was obtained from the sample number UTTU-2. The organic matter content of the UTTU-3 from the outcrop locality is quite low (1.34 wt%) compared with that of the UTTU-2 sample which has a high organic matter content.

High TOC contents of >>2.95wt.% and HI between 14.00 and 31.00mgHC/gTOC characterise

Table 1: Rock-Eval data of shale samples from Uturu ,Campanian Formation.

Sample Name	Locality	Lithology	Tmax (°C)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	PI	S2/S3	S1/TOC	TOC (%)	HI (mgS2/ gTOC)	OI (mgS3/ gTOC)
UTTU-1	Uturu	Shale	435	0.04	0.25	0.19	0.14	1.32	0.03	1.51	16	12
UTTU-2	Uturu	Shale	438	0.07	0.93	0.21	0.07	4.43	0.02	2.95	31	7
UTTU-3	Uturu	Shale	432	0.04	0.18	0.13	0.18	1.38	0.03	1.34	14	9
UTTU-4	Uturu	Shale	426	0.04	0.25	0.09	0.14	2.78	0.03	1.38	18	6
UTTU-5	Uturu	Shale	435	0.05	0.45	0.11	0.10	4.09	0.03	1.54	29	7
UTTU-6	Uturu	Shale	439	0.06	0.72	0.18	0.08	4.00	0.03	2.4	30	7

the shale beds of the Uturu locality. The shale have TOC contents of 1.34 to 2.95wt.% and HI values between 14.00 and 31.00mgHC/gTOC. Variation in HI between 14.00 and 31.00mgHC/gTOC on the shale samples, suggests Type III OM [9]. The Uturu samples are within Type III OM. Generally all the samples indicate a high contribution of OM from higher terrestrial organism (Figs 4 and 5) [10].

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. Samples from the Uturu locality are having their S_2 values within the range of 0.18-0.93mg/g with an average of 0.46.

The S_2 vs. TOC diagrams gave an average HI value of 44mgHC/gTOC for shale samples (Fig. 3). Therefore, most of the Anambra Basin shale samples were type III dominated with associated type II. The gas-prone nature of these shales (S2/S3; 1.33-4.43) from Uturu rules out type II kerogen, which usually shows S2/S3 greater than 5 [11] (Table 1).

Plots of S_2 vs. TOC and determining the regression equation of average HI of 44mgHC/gTOC has been used by [12] as the best method for determining the true average HI and measuring the adsorption of hydrocarbons by the rock matrix. They noted that 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 [13] and that using the regression equation derived from the S_2 vs. TOC graph automatically correct HI for this effect. The average HI of the Uturu shale samples from the S_2 vs. TOC plots is very reliable (correlation coefficient is 0.95) which indicated a value of 44mgHC/gTOC (Fig. 3) which is below 300 mgHC/gTOC [9], hence supporting the predominant of the type III with associated type II organic matter of the Anambra Basin.
HI vs. Tmax diagram classifies the OM in the shale as type III kerogen [10]. HI values for the shale samples range from 14 to 31 mgHC/gTOC and S1 + S2 yields range from 0.22 to 1.00 mgHC/g rock, suggesting that the shale also have gas and oil-generating potential as seen in Ihube [7]. [9] has suggested that at thermal maturity equivalent to vitrinite reflectance of 0.6% (Tmax 435 ^{o}C), rocks with HI above 300mgHC/gTOC 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 (Fig. 4).

The van Krevelen diagrams for the shale samples show a dominance of type III (Fig. 4). The highest HI samples may be assigned to a high-potential type II kerogen at the diagenesis/ catagenesis boundary [13]. The corresponding HI-Tmax diagram based on the values given by [9] indicates some potential between oil and gas with gas dominating (Fig. 4).

Majority of the samples fall into fields that have hydrocarbon generative potential as seen in shales from Uturu samples (Figs. 5 and 6). The Uturu samples are mixed with recycled terrestrial organic worked OM pointing to type III (Fig. 5). These recycled OM might have been

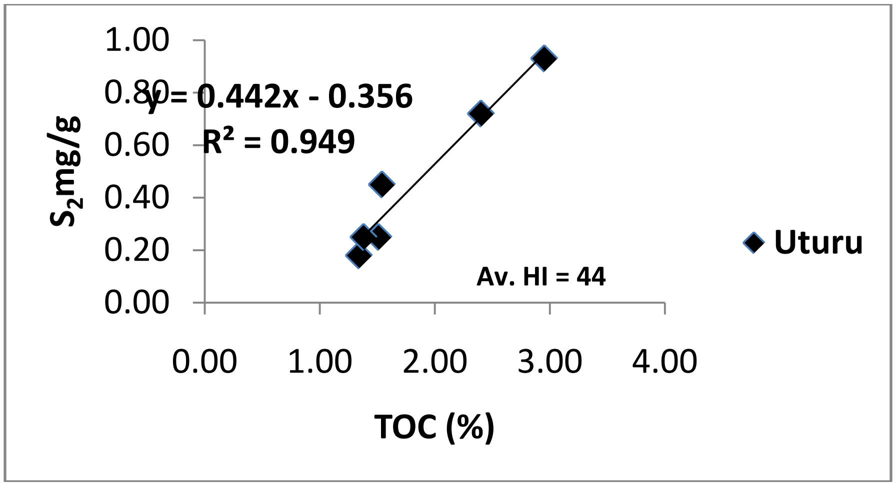


Fig. 3: A diagram of S2 versus TOC of shale samples from Uturu with calculated average hydrogen indices (Av. HI).

transported by fluvial processes [13], [14] as found in prodelta shales of a delta system.

The samples from Uturu were plotted on the OI vs. Tmax diagram of [15] to test if samples followed the typical trend for Type III OM, and hence to determine if the Tmax anomalies have

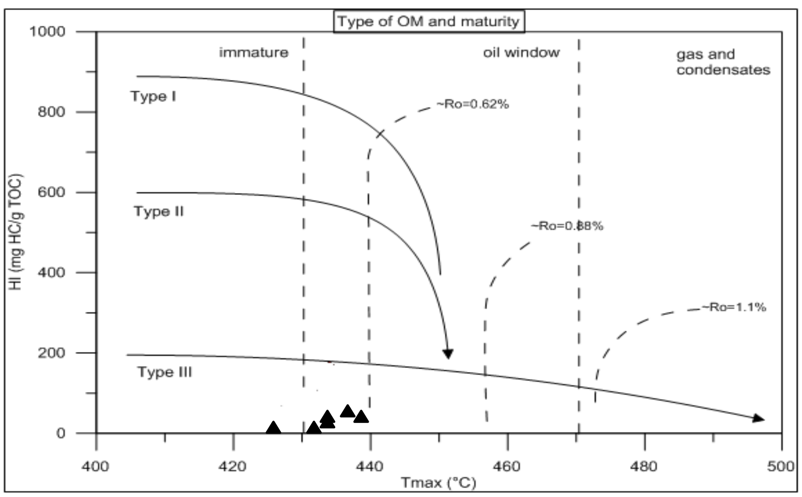


Fig. 4: A plot of HI versus Tmax indicating type of organic matter and maturity level.

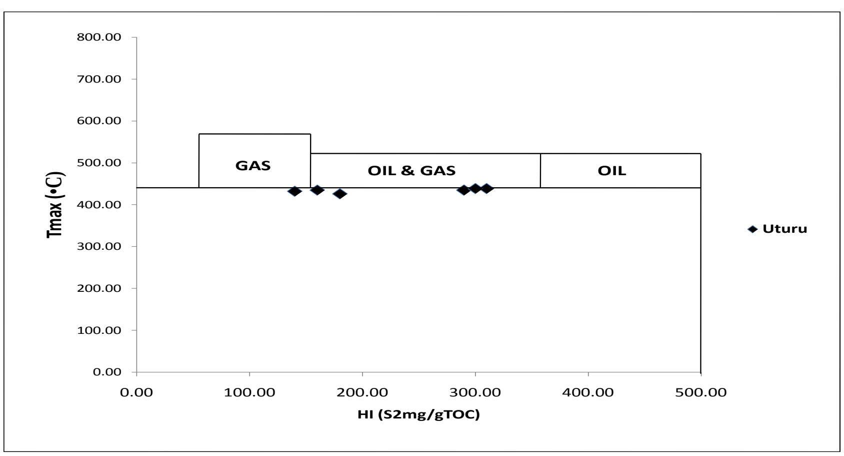


Fig. 5: A diagram of Tmax versus HI of shale samples from Uturu describing the quality of organic matter.

any relationship to thermal conditions. The trends in Uturu shale samples show essentially a decrease in OI as Tmax increases indicating the maturity level (Table 1). This reflects the samples under study contain essentially Type III kerogen since they follow [15] typical trend for Type III OM.

In the diagram Tmax vs. HI (Fig. 6) indicates that most of the OM falls into oil and gas portion which implies that the OM contains oil and gas potential. A Plot of the SOM (extract yield) against TOC as proposed by Landis and Connan (1980) in [16] for the shale samples indicates that migration of oil has taken place (Fig. 6). 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 S1 + S2 vs TOC (Fig. 7) characterizing the shale samples from Uturu as good to excellent source rocks with TOC and S1 + S2 of 1.85wt% and 51.0mg/g respectively. This is also supported by the report of [17] from their investigations on shaly facies of gas prone sequences in the Anambra Basin based on the values of TOC (13.1-29.4wt%) and soluble organic matter (SOM) (137-450ppm) which are indicative of fair to good and adequate source potential. [18] also investigated the Maastrichtian sediments around Enugu escarpment of the Anambra Basin which revealed the exceeding minimum threshold TOC value (0.65-1.82wt %) for shale samples. Thermal maturity was confirmed by plotting the profiles of Tmax vs TOC (Table 1) showing that only UTTU-4 shale sample from Uturu that did not attain to “oil window”

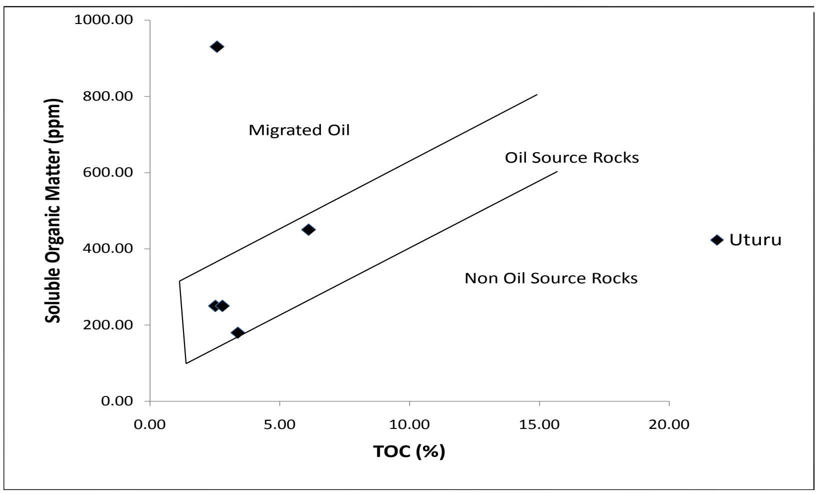
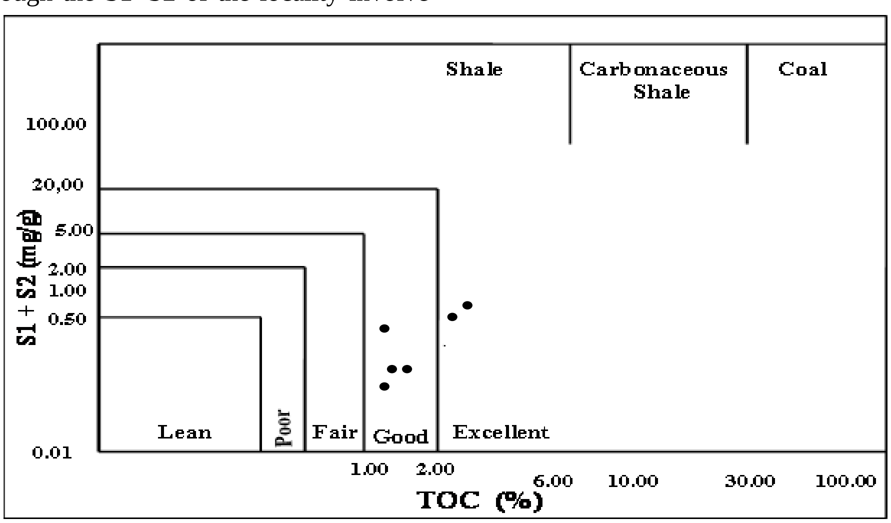


Fig. 6: A diagram showing the characterization of organic matter: SOM. vs TOC [30] of samples from Anambra Basin indicating no migirated oil in the area.

(430ºC) while the rest of samples attained to threshold value and are mature. The hydrocarbon generative capacity (S1 + S2) shows that the Uturu shale (0.22 to 1.00) UTTU-2 has the highest residual potential to expel hydrocarbons as compared to the UTTU-3 sample. The thermal maturation for Uturu shale is, however, moderate. Although the S1+S2 of the locality involve are low but their thermal gas generation based on Tmax vs. HI indicates oil and gas potential. The observed increase in PI and S1/TOC supports the hydrocarbon generative potential of these shale samples.



Fig, 7: A diagram indicating the quality of kerogen type in the shale samples from Uturu: S1 + S2 versus TOC.

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