Oil generative potential of shale from Asu river group in the Afikpo basin, Southeast Nigeria

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Shale from Asu River Group strata of the Afikpo Basin has been characterised by geochemical techniques. The aims of this study were to assess the quality of its organic matter, evaluate its thermal evolution and highlight its potential as a source rock. The determination of hydrocarbon potential of shale from the Asu River Group in Afikpo Basin, Southeastern Nigeria was carried out using some Rock-Eval pyrolysis parameters such as TOC, HI, OI, S₂/S₃ and S₁ + S₂. The shale samples were collected at Amenu and Amauro outcrop localities. The samples were examined and analyzed to determine their oil and gas potential. The HI values range from 3.95 to 47.98 mgHC/gTOC and average value of 23.17 mgHC/gTOC indicates a Type III kerogen. Tmax values ranging from 349 to 454 °C with an average of 405 °C shows that the shale samples are immature to marginally mature. The total organic carbon (TOC) (5.60 wt%) and S₁ + S₂ (3.05) of the shale constitutes that of excellent source rock with gas-prone kerogen indicated by Rock-Eval S₂/S₃ (1.71). The high oxygen index (OI) (20.84 mgCO₂g⁻¹TOC) suggest deposition in a shallow marine environment. Generated petroleum may not have reached the threshold for hydrocarbon expulsion but a review of petroleum system elements in the basin will stimu late high prospects in the Afikpo basin.

Key words: Shale, Hydrogen index, Total organic carbon, Hydrocarbon potential, Asu River Group, Afikpo Basin.

INTRODUCTION

The Afikpo basin is one of the complimentary basins that were formed after the deformation of the lower Benue trough during the Santonian episode. It is located between latitude 5°55' to 6°00' N and longitude 7°51' to 7°55' E Southeastern Nigeria. The area has an undulating landscape composed of mainly alternating shale and sandstone sequence with localized clay-siltstone-limestone intercalation.

The Sedimentary sequence of the basin comprises mainly the Albam marine sediments, the Turonian marine sediments and the Campanian-Recent marine sediments. The stratigraphy of the basin consists of the Asu River Group and the Eze-Aku Formation deposited in alternating transgressive and regressive phases. The Asu River Group which is the middle-upper Albian in age is the oldest formation in the basin (Whiteman, 1982; Simpson, 1955). White, 1982; Simpson, 1955 were of the opinion that the Asu River Group was deposited in a moderately, deep water environment during the Albian, with abundant ammonites, forams, radiolarians and pollens. The lithological units consist of shale, limestone, siltstone and sandstone.
Three petroleum systems are present in the Cretaceous Delta frame namely the Asu River Group, the Eze-Aku Formation and proto-Niger Delta sequences. Also, the Afikpo Basin has been correlated to three petroleum systems in the Lower Congo Basin, Niger Delta and the Anambra Basin (Odigi and Amajor, 2010). The high total organic contents, thermal maturity and terrigenous characteristics of the Asu River Group, Eze-Aku Formation and proto-Niger Delta sediments, suggest the presence of a large amount of natural gas with a small quantity of oil generation (Odigi and Amajor, 2010). The total organic carbon (TOC) content measures the quantity of organic matter present in a sedimentary rock in weight percentage (weight %). It is the most popular screening parameter for source rock appraisal and the basic parameter required to interpret any other geochemical information (Bordenave et al., 1993). The TOC is pre-requisite for sediments to generate oil or gas (Cornoef, 1998). Studies have shown that TOC content of 0.5 wt % as the threshold value for generating petroleum from clastic source rocks (Tissot and Welte, 1984). Other investigation on the organic carbon values for shale indicates that a threshold value of 1.5 wt % is necessary for the efficient hydrocarbon expulsion from source rocks (Bordenave et al., 1993). This study examines the hydrocarbon potential of the Asu River Group in Afikpo Basin using organic geochemical parameters in determining the organic matter type, maturity, quality and quantity, petroleum potential and depositional environment of the organic matter.

**STRATIGRAPHIC SETTING**

The Santonian deformational process resulted in the fragmentation of the lower Benue trough (Fig. 1) into the Abakiliki syncline (Kogbe, 1976). The predominantly Albian-Cenomanian marine depositional cycles which terminated by a phase of folding (Nwachukwu, 1972; Olade, 1975) affected the Asu River Group in the area.

A second transgressive – regressive of deposition in the Turonian to Santonian was again terminated by a phase of folding and faulting in the early Santonian times. This affected all the sediments deposited before the tectonism and this gave rise to the Afikpo (Abakiliki) syncline (Fig. 1). Imprint of tectonism on the sediments in the lower Benue trough were preserved by series of joints trending NW – SE. Typical depositional environments of a syncline are marine, continental and transitional environments which produced lithostratigraphic units of Asu River Group and Eze-Aku Group (Fig. 2) etc.

The first marine transgression in Nigeria occurred during the middle Albian. Albian sediments unnamed and undifferentiated constitute the Asu River Group and its equivalents (Ojoh, 1999).

Ukaegbu and Akpabio (2009) have differentiated the Asu River Group northeast of the Afikpo Basin as consisting of alternating shale, siltstone with occurrence of sandstone. The maximum thickness of the Asu River Group is 1000m, Albian in age and rich in ammonites as well as foraminifera, radiolarian and pollens. The shales are also characterized by species of monticeras and elobiceras ammonites (Offodile, 1976).

The regressive phase of the first marine transgression led to the deposition of the Cenomanian sediments. This is found in the southeastern part of the basin around Calabar. These beds have been assigned as Odukpani Formation (Reymont, 1965). It was deposited under shallow water conditions (Kogbe, 1976). The basal beds comprised of arkosic followed by quartzose –felspathic...
and siltstone facies while shales predominate in the upper part of the formation (Reyment, 1965). The type locality of the Eze-Aku Group is found at the Eze-Aku River valley in the southeast of Eze-Aku. The formation comprised of hard grey to black shale and siltstone. The thickness varies but may attain 100m locally. The Eze-Aku shale represents shallow marine deposits. The fossil contents indicate a basal Turonian age (Carter et al., 1963; Ukaegbu and Akpabio, 2009).

**MATERIALS AND METHODS**

A total of 12 outcrop shale samples were obtained from the Asu River Group at Amenu and Amauro localities in Albian age of the Afikpo Basin. Care was taking to avoid weathered portions of the outcrop and to obtain material sufficient for various geochemical analyses. The samples were hard, thickly laminated but not fissile, with texture indicative of low permeability. In the laboratory, the samples were reshaped using a rotating steel cutter to eliminate surface that could be affected by alteration. Chips were cut from the samples and dried in an oven at 105°C for 24 hours. The dried sample was pulverized in a rotating disc mill to yield about 50 g of sample for analytical geochemistry. The total organic carbon (TOC) and inorganic carbon (TIC) contents were determined using Leco CS 200 carbon analyzer by combustion of 100 mg of sample up to 1600°C, with a thermal gradient of 160°C min⁻¹; the resulting CO₂ was quantified by an Infrared detector. The sample with known TOC was analyzed using a Rock-Eval 6, yielding parameters commonly used in source rock characterization, flame ionization detection (FID) for hydrocarbons thermal conductivity detection (TCD) for CO₂.

**RESULTS AND DISCUSSION**

Table 1 shows the results of 12 bulk samples and molecular geochemical parameters used in source rock quality and maturity evaluation. The shale is low in carbonate and its organic matter content within the threshold for petroleum source rocks.
Organic matter quality

The TOC is a primary parameter in source rock appraisal, with a threshold of 0.5-1 wt% at the immature stage for potential source rocks (Tissot and Welte, 1984; Bordenave et al., 1993; Hunt, 1996). The average value of 5.60 wt% of the shale studied exceeds this threshold (Table 1). High TOC of 4.45 wt% was obtained in Mamfe basin and this value exceeds the threshold for oil generation (Eseme et al., 2006). However, high TOC is not a sufficient condition for oil generation. Coals usually have high TOCs that exceed 50 wt% but do not generate oil except when rich in liptinite, indicating the relevance of maceral composition. In contrast, deltaic sediments may have TOCs below 1 wt% but generate commercial accumulations of petroleum due to deposition of large volumes of sediments, as seen in the Niger Delta. High TOC content in shales indicates favorable conditions for preservation of organic matter produced during deposition.

Plots of $S_2$ vs. TOC and determining the regression equation 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. 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 (Espitalie et al., 1985) and that using the regression equation derived from the $S_2$ vs. TOC graph (Fig. 3) automatically correct HI for this effect. The average HI of the shale samples, from the $S_2$ vs. TOC plots is very reliable (correlation coefficient is 0.89 and has indicated a value of 23.17 which is still 0-50mgHC/gTOC and below (Peters, 1986), hence supporting the predominant of the type IV with associated type III organic matter in the Asu River Group of the Afikpo Basin. This may be related to the redox condition, with high oxygen favoring organic matter oxidation, also amount of organic matter type III produced. The high oxygen index of 20.84 mgCO$_2$ g$^{-1}$TOC suggests high contribution from terrestrial organic matter poor in hydroxyl groups (Tissot and Welte, 1984) and that the depositional environment was oxic.

The kerogen content of 1.10 mgHC g$^{-1}$rock was described as good, with an $S_2$/S$_3$ of 1.71 indicative of gas-prone organic matter is consistent with its $T_{max}$ of 349 to 454°C, indicative of immaturity to early maturity while the S$_1$/TOC of 0.29 indicates early generation of petroleum. The hydrogen index (HI) is low compared with values slightly below 50 mg g$^{-1}$TOC for Type III - IV kerogens at the immature stage. Type IV which is mostly inert was obtained in this area of Afikpo Basin (Fig. 4). The oxygen index (OI) is high, suggesting deposition in a high oxygen environment and high terrestrial higher plant contribution (Uzoegbu and Ikwuagwu, 2016a,b).

Rock-Eval pyrolysis yields parameters that are used to describe the generation potential of a source rock by providing information on organic matter quality, type and maturity, with the TOC, $S_2$ and HI as relevant parameters (Peters, 1986). The HI of 41.20 mgHC g$^{-1}$TOC of this shale is low and results to a Type III - IV kerogen at immaturity to early maturity stage. The gas-prone nature of this rock rules out Type II kerogen, which usually shows $S_2$/S$_3$ greater than 5, while the maturity from $T_{max}$ suggest that the current HI results from thermal evolution of a Type III - IV kerogen, with initial HI between 600 mgHC g$^{-1}$TOC and 850 mgHC g$^{-1}$TOC (Lafrague et al., 1998).
Figure 3. A diagram of S2 versus TOC of shale samples from Asu River Group with calculated average hydrogen indices (Av. HI).

Figure 4. Showing kerogen type from modified van Krevalen diagram (After Peters, 1986).

**Maturity indicators**

HI vs. Tmax diagram (Fig. 5) classifies the organic matter in the shales of the Asu River Group as type IV (inert) kerogen (Akande et al., 2007) with some samples slightly above the threshold (430°C) stage.

The production index (PI) is used to assess the generation status of source rocks but is often useful when homogeneous source rocks of different rank are compared, in which case it is characterized as the transformation ratio (Bordenave et al., 1993). Hunt (1996) suggested that a PI from 0.06 to 0.96 is characteristic of source rocks in the oil window. The value of 0.41 of this shale is consistent with its Tmax of 405°C. This maturity is also consistent with the fairly well fluorescing organic matter as well as Rock Eval Tmax of 430°C, reaching the 430-435°C for low sulphur immature source rocks containing Type III (Bordenave et al., 1993; Hunt, 1996). The PI is not affected by expulsion (Rullkötter et al., 1988) and this will not limit its use as an indicator of the organic matter transformation because
generation may start for rocks with Type II at 0.55%R₀ (Leythaeuser et al., 1980). Rullkötter et al. (1988) used a mass balance scheme to show that, at 0.68% R₀, the transformation ratio in the Posidonia shale from northern Germany had reached 30%. Various maturity indicators suggest that this shale is at the immature to onset of oil generation and its current HI of 23.17 mgHC/g TOC is thought to reflect thermal evolution due to labile kerogen from an initial HI between 600 mgHC g⁻¹TOC and 850 mgHg⁻¹TOC, characteristics of Type III kerogens (Lafargue et al., 1998).

A Plot of the SOM (extract yield) against TOC (Fig. 6) 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. 6). This is supported by the diagram of S₁ + S₂ vs TOC (Fig. 7) characterizing the shale samples from the Afikpo Basin as good to excellent source rocks with TOC and S₁ + S₂ above 1.0wt% and 5.0mg/g respectively. Four samples with TOC greater than 0.6wt% were derived from shaly carbonaceous samples. This is also supported by the report of Beka et al. (2007) from their investigations on shaly facies of gas prone sequences in the Afikpo Basin based on the values of TOC (1.09-18.24wt%) and soluble organic matter (SOM) (190-2900ppm) which are indicative of good to excellent and adequate source potential. Udofia and Akaegbobi (2007) also investigated the Maastrichtian sediments around Enugu escarpment.

**Figure 5.** A diagram of Tmax versus HI of shale samples from Asu River Group describing the quality of organic matter.

**Figure 6.** A diagram showing the characterization of organic matter SOM vs TOC (based on Landais and Connan in Jovancicevic et al., 2002) of samples from Afikpo Basin indicating no migrated oil in the area.
of the Anambra Basin which revealed the exceeding minimum threshold TOC value (0.65-1.82wt %) for sediment samples and (18.35-19.12wt %) for coal samples. Thermal maturity was confirmed by plotting the profiles of Tmax vs TOC showing that almost all the samples did not attain to “oil window” (430°C) except few samples. This is also supported by plotting the diagram of HI vs Tmax (Fig. 5) which determine the immaturity status of the entire sample except few samples.

HYDROCARBON POTENTIAL

In the Marginal Basins of Brazil and West Africa (Gabon, Angola and Congo), the Cretaceous Shale’s are important source of hydrocarbons (Mello et al., 1988a,b, 1989,1991). Similar potential source rocks exist in the Calabar Flank, Anambra Basin and Afikpo Basin. Recent discoveries on the hydrocarbon generation potential of the inland basins have generated a renewed interest for further studies. The buildup of any prospect or of a petroleum system requires the availability of good-quality source rocks. Additionally, the stratigraphic position of the source rocks, the availability of good-quality reservoir and seal lithologies, timing of hydrocarbon generation, favourable regional migration pathways, and trapping mechanisms must also be considered. Shale from the Asu River Group in the Afikpo basin has been characterized for its source potential using bulk and molecular geochemistry. The HI values range from 3.95 to 47.98 mgHC/gTOC with a mean value of 23.17 mgHC/gTOC with an immature to early mature source. The shale is a good quality source rock, with gas-prone kerogen. Generated petroleum may not have reached the threshold for hydrocarbon expulsion but a review of petroleum system elements in the basin will stimulate high prospects in the Afikpo basin.

ACKNOWLEDGEMENTS

Gratitude is expressed to all the Staff in the Department of Geology, Michael Okpara University of Agriculture, Umudike on their advice towards the success of this work. Trican Geological Solutions, Alberta, Canada is gratefully acknowledged for the analyses of these samples.
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Accepted 12 March, 2017.

Citation: Uzoegbu MU, Amoke AI (2017). Oil generative potential of shale from Asu river group in the Afikpo basin, Southeast Nigeria. International Journal Geology and Mining 3(1): 081-089.

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