Shale gas prospect of different source rock types from Early Maastrichtian Mamu Formation, Anambra Basin, Nigeria

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Abstract. The gas prospect of three identified source rock types from the Early Maastrichtian Mamu Formation of the Anambra Basin, Nigeria was evaluated by thermal simulation, followed by gas composition analyses of the generated hydrocarbons. The amounts of C₁ and ∑C₁⁻⁵ generated at the highest examined pyrolysis temperature of 480°C (Easy Ro of 3.27%) range from 3.52 to 32.00 ml/g rock and 4.08 to 43.44 ml/g rock, respectively. The sub-bituminous coal has the highest gaseous hydrocarbon generative potential up to late gas generation stage, followed by carbonaceous shale while shale has the least productive capacity. The recovery of gaseous hydrocarbons may be influenced by the ratio of TOC to clay content in all the source rocks. The gas dryness index indicates that the shale is the driest among the source rock types.

1. Introduction
Many countries searching for unconventional hydrocarbon pools have focused on organic-rich shales as potential targets for shale gas production [1, 2]. Contrary to the conventional hydrocarbon system, the shale gas is typically a continuous self-contained source-reservoir of unconventional natural gas [3], serving as both the gas generating source rock as well as gas storing reservoir rock. Constrained by various depositional environments, shale characteristics are diverse, likewise its gas generative potential [4-6]. For the evaluation of the total gas in place (GIP) and for successful production of shale gas, assessment of parameters such as the thermogenic gas generative potential, gas storage capacity and brittleness of the overall mineralogical composition of an organic-rich source rock are very critical [2]. High maturity of source rock is necessary for the generation of thermogenic shale gas. Vitrinite reflectance (Ro) between 1.3% and 3.5% is important for the formation of shale gas [5]. Petroleum close contact with source rock mineralogy and kerogen could also be a decisive factor in shale gas generation [7]. In addition, expanding three-layer clays are most active in retaining pyrolysate and could as well catalyse the conversion of compounds to lower molecular weight [8], leading to the generation of gaseous hydrocarbons enriched in methane. The ratio of the TOC to clay content could likewise influence the adsorption of pyrolytic organic compounds [9]. Shale gas could be stored in a free state within fractures and pores or as adsorbed dry gas on the surface of kerogen and clay particles,
as well as in a dissolved form within the kerogen and asphaltene structures, where the majority of the space is filled with free and adsorbed gas [4, 10-12].

The Anambra basin in Nigeria is one of the sedimentary basins where hydrocarbon exploration is currently underway. The geologic and stratigraphic settings of the Anambra basin have been well reported by many authors [13-16]. The Mamu Formation within the basin has been associated with enormous potential for shale gas generation [15-18]. The stratigraphy of the lower part of the Formation has been reported to have shale interbedding with coal at several intervals [19]. Presently, there is paucity of information on the state of gas occurrence and the potential yields of gaseous hydrocarbon from the different types of source rocks within the Formation. Therefore, this present study was conducted to evaluate the gas occurrence and shale gas productive potential of the distinct lithology of source rocks identified in Mamu Formation by thermal simulation of the immature rocks up to the thermogenic gas generative windows. The possible mineralogical influence on the recovery of shale gas was also assessed by comparing the gaseous hydrocarbon yields from the bulk rocks and kerogens.

2. Materials and methods

2.1. Samples
Shale (ONP1-41), carbonaceous shale (ONP1-38) and sub-bituminous coal (ONP1-39) samples representing the different lithofacies of source rocks in the Mamu Formation from Anambra Basin were selected for this study. The basic geochemical parameters of the samples are listed in Table 1.

| Sample No. | Lithology              | TOC °C | Kerogen Type | Tmax °C | Quartz | Clay | Feldspar |
|------------|------------------------|--------|--------------|---------|--------|------|----------|
| ONP1-41    | Shale                  | 7.37   | II/III       | 419     | 35.6   | 55.1 | 9.3      |
| ONP1-38    | Carbonaceous shale     | 24.61  | III          | 420     | 23.2   | 74.7 | 2.2      |
| ONP1-39    | Sub-bituminous coal    | 58.28  | III          | 420     | 51.8   | 48.2 | 0        |

2.2. Thermal simulation and gas composition analysis
Kerogens were isolated from the rocks by treatment with HCl and HF. The bulk rocks and the extracted kerogens were thermally simulated by closed system pyrolysis using glass tube experiment at selected temperatures for 72 h (Table 2).

The gas composition analyses of the generated gases were performed on an Agilent 7890A gas chromatograph (GC) fitted with column HP-AL/S (25 m × 0.32 mm × 80 µm film thickness). The GC oven temperature was held at a constant temperature of 60 °C for 3 min, ramped from 60 °C to 190 °C at 25 °C/3 min and held for 3-8 min. Helium was employed as the gas carrier. The evolved gases were detected by FID and TCD and measured based on external standard calibration.

| Temperature (°C) | Easy R_o (%) |
|------------------|--------------|
| 350              | 1.08         |
| 380              | 1.45         |
| 420              | 2.09         |
| 450              | 2.66         |
| 480              | 3.27         |
3. Results and discussion

3.1. Yield of gas generated from different source rocks types
A maturity indicator equivalent of the vitrinite reflectance (i.e. Easy R%,) derived from the formula by Sweeney and Burnham [20] was employed in determining the thermal maturities of the source rock samples (Table 2). The result indicates that the equivalent thermal maturity during the pyrolysis is in the range of Easy R% 1.08 to 3.27. These values cover the oil, wet gas and dry gas generative windows [21].

The hydrocarbon yields obtained from the closed-system pyrolysis of the bulk rocks and kerogens are shown in Table 3. The gas generated from both the bulk rocks and kerogens generally show an increasing trend with increasing pyrolysis temperature (thermal maturity) (Fig. 1a-d). The kerogen generated higher amounts of gaseous hydrocarbons than the bulk rock except for sub-bituminous coal.

The maximum C1,5 hydrocarbon gases produced by the bulk shale, carbonaceous shale and sub-bituminous coal rocks at the highest studied temperature of 480°C (Easy Rv of 3.27%) are 4.08, 20.42 and 43.44 ml/g rock, respectively, whereas that of the kerogen concentrates are 30.15, 39.15 and 33.18 ml/g TOC, respectively. These values indicate that the mineralogical compositions, especially the clay contents in the rocks under study may have influenced the gaseous hydrocarbon yields. The gas contents (ΣC1,5) generated from the bulk rocks at Easy Rv of 3.27% for the carbonaceous shale and sub-bituminous coal far exceed the 3m³/t rock required for economic shale gas production [22].

Table 3. Amounts of gas components (ml/g) produced with wetness during rock/kerogen cracking experiments

| Sample  | T (°C) | Wt. (mg) | ΣC1 (ml/g) | ΣC2-5 (ml/g) | ΣC1,5 (ml/g) | Dryness index | Wt. (mg) | ΣC1 (ml/g) | ΣC2-5 (ml/g) | ΣC1,5 (ml/g) | Dryness index |
|---------|--------|----------|------------|--------------|--------------|---------------|----------|------------|--------------|--------------|---------------|
| ONP1-41 | 350    | 1012.3   | 0.23       | 0.13         | 0.35         | 64.40         | 158.8    | 1.42       | 0.86         | 2.28         | 62.40         |
|         | 380    | 1072.5   | 0.12       | 0.04         | 0.16         | 72.51         | 158.0    | 2.95       | 2.15         | 5.11         | 57.82         |
|         | 420    | 1059.9   | 1.13       | 0.59         | 1.72         | 65.52         | 154.5    | 2.88       | 2.19         | 5.07         | 56.85         |
|         | 450    | 1053.6   | 2.15       | 0.70         | 2.86         | 75.31         | 154.2    | 15.99      | 7.14         | 23.13        | 69.13         |
|         | 480    | 1097.1   | 3.52       | 0.56         | 4.08         | 86.18         | 157.6    | 24.11      | 6.04         | 30.15        | 79.97         |
| ONP1-38 | 350    | 409.6    | 0.66       | 0.45         | 1.12         | 59.37         | 157.6    | 1.75       | 0.98         | 2.72         | 64.08         |
|         | 380    | 406.4    | 0.46       | 0.34         | 0.81         | 57.52         | 154.8    | 3.41       | 2.32         | 5.73         | 59.56         |
|         | 420    | 408.2    | ND         | ND           | ND           | ND            | 152.9    | 9.60       | 7.09         | 16.69        | 57.53         |
|         | 450    | 402.6    | 8.79       | 5.15         | 13.94        | 63.03         | 152.3    | 20.18      | 9.33         | 29.52        | 68.37         |
|         | 480    | 376.3    | 15.62      | 4.81         | 20.42        | 76.46         | 154.4    | 31.86      | 7.29         | 39.15        | 81.38         |
| ONP1-39 | 350    | 205.6    | 1.44       | 0.87         | 2.30         | 62.41         | 154.3    | 2.17       | 1.25         | 3.41         | 63.52         |
|         | 380    | 207.8    | 4.93       | 3.84         | 8.77         | 56.22         | 154.7    | 3.05       | 2.04         | 5.09         | 59.91         |
|         | 420    | 208.8    | 11.45      | 10.41        | 21.86        | 52.36         | 155.9    | 8.19       | 6.21         | 14.40        | 56.86         |
|         | 450    | 207.8    | 20.05      | 12.12        | 32.17        | 62.32         | 154.3    | 18.29      | 8.22         | 26.51        | 69.00         |
|         | 480    | 204.0    | 32.00      | 11.44        | 43.44        | 73.66         | 152.8    | 26.21      | 6.97         | 33.18        | 78.99         |

ND: not determined.

The gaseous hydrocarbons yields produced by the kerogen from the different litho-types of source rocks do not show much variation with increasing thermal stress (Fig. 1b and d), whereas significant disparity is observed in the gaseous hydrocarbon yield of the bulk rocks samples among different rocks lithology (Fig. 1a and c). In the present study, the TOC to clay ratios in the shale, carbonaceous shale and sub-bituminous coal are 0.13, 0.33 and 1.21, respectively. Therefore, the lack of considerable differences in the hydrocarbon generative potential of the extracted kerogens where the
bulk of the organic matter lies, also suggest that the ratio of TOC to clay content may also play a significant role in the gaseous hydrocarbon recovery from the different source rock types in the Formation. This observation also indicates that the gas is mostly in the adsorbed state with the clay mineral.

In the bulk rock samples, the maximum methane (C$_1$) generated at the highest studied temperature of 480°C (Easy Ro of 3.27%) by shale, carbonaceous shale and sub-bituminous coal are 3.52, 15.62 and 32.00 ml/g rock, respectively. This implies that the sub-bituminous coal could produce higher amounts of methane than shale and carbonaceous shale, at the same level of thermal maturity (Fig. 1a and c). This underlines the huge gas generative potential of the sub-bituminous coal in the Formation. The maximum amounts of gaseous hydrocarbons (C$_{1-5}$) generated from the cracking of sub-bituminous coal is 43.44 ml/g rock. This is over ten times higher than the gas production from shale (4.08 ml/g rock), and twice higher than the production capacity of carbonaceous shale (20.42 ml/g rock). The maximum generation of wet gases (C$_{2-5}$) occurs at 450°C (Easy Ro of 2.66%) and marks the end of wet gases generation for all the different rock types (Figs. 1e and f). The sub-bituminous coal has the highest wet gases generation potential with maximum yield value of 12.12 ml/g rock, followed by

![Graphs showing changes in hydrocarbon yields with increasing thermal stress.](image-url)
carbonaceous shale, having the maximum C_{2-5} yield of 5.15 ml/g rock while shale has the least yield of C_{2-5} with a value of 0.7ml/g rock.

3.2. Gas dryness
The gas dryness index (C_{1}/\sum C_{1-5} \times 100) of the bulk rocks and kerogens are depicted in Fig. 2a and b, respectively. The gas dryness index generally shows two-stages of evolutionary pattern. There is initial decrease in the gas dryness up to the maximum temperature of 420°C (Easy R_o 2.09%), and then a sudden increase with increasing thermal stress (Fig. 2). The first stage could be attributed to the thermal cracking of C_6+ aliphatic compounds and the depolymerisation reactions of non-hydrocarbon compounds leading to the enrichment of C_{2-5} gases while the second stage could as well be ascribed to the cracking of C_{2-5} hydrocarbons and demethylation reactions of aromatics [23]. However, there is possibility of the overlap of these reactions to form a methane predominated gas [23]. Shale indicates a relatively higher gas dryness index in the bulk rocks as compared to both carbonaceous shale and sub-bituminous coal. However, the kerogen of the three litho-types of rocks does not display any variation in dryness index, suggesting the combining effects of TOC to clay ratio and clay contents influencing the adsorption/catalyses of the gaseous hydrocarbons in the bulk rocks [8, 9].

![Fig. 2 Changes in dryness index with increasing thermal stress](image)

4. Conclusions
The gas prospect of different source rock types found in the Mamu Formation in the Anambra Basin were evaluated by thermal simulation, followed by gas composition analyses of the generated hydrocarbons. The results indicate that significant amount of gaseous hydrocarbon could be generated from the carbonaceous shale and sub-bituminous coal, even at late gas generative windows. This study also reveals that the gas is mostly in the adsorbed state with the clay mineral while shale gas production may be greatly influenced by the TOC to clay ratio.

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