Geochemical characterisation of Lower Maastrichtian Mamu Formation kerogens, Anambra Basin, Nigeria

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Abstract. The source rock potential of kerogen isolated from shales, carbonaceous shales and sub-bituminous coals from the Lower Maastrichtian Mamu Formation in the Anambra Basin were determined using the total organic carbon (TOC) contents and Rock-Eval. analysis data. The TOC contents exhibit wide variations, ranging from 1.30 to 58.28 wt%. The hydrogen index (HI) and the genetic potential (GP) values ranged from 160 to 235 mg HC/g TOC and 32 to 133.11 mg HC/g rock, respectively. Plots from the Rock-Eval pyrolysis and elemental compositions classified the organic matter as mixture of Type II and III kerogens. The carbon isotopic values ranged from −28.12 to −26.49‰, supporting the mixed origin (Type II/III kerogen) although, the carbonaceous shale and coal samples are typically dominated by Type III kerogen. The Tmax values for the samples ranged from 417 to 422 °C. This study shows that the samples contain high quantity and good quality organic matter capable of generating oil and gas but are thermally immature within the intervals studied.

1. Introduction

The Mamu Formation is an important sedimentary unit within the Anambra Basin. The Formation consists of shales interbedded with coal seams, sandstones and mudstones [1]. The co-existence of shales with coal seams at several intervals in the Formation creates a considerable potential for both conventional oil and unconventional natural gas generation as both shale gas and coalbed methane could also be produced in commercial quantity. The Formation has considerable thickness especially at the central part where it reaches over 300 m [1]. Studies on the hydrocarbon potential and thermal maturity of the Mamu Formation have been fairly reported [2-4]. Some authors argued that the shales and sub-bituminous coals from the Formation could only generate gas while others opined that both oil and gas could be sufficiently generated [2-4]. Due to possible variation in the lithologic composition and other factors across the Formation, and from the outcrop to the subsurface, we believed that the analyses of the kerogen which contains the bulk of the organic matter could be accurately used to quantify the oil generation potential and thermal maturity of the organic matter within the Formation.
Therefore, the present study was conducted to assess the hydrocarbon potentials of kerogen extracted from shale, carbonaceous shales and sub-bituminous coal from Mamu Formation.

2. Geological background

The Anambra basin is virtually a triangular basin in the south-central Nigeria that covers about 40,000 km$^2$ (Fig. 1). The basin represents one of the sub-basins of the Benue rift structure. It is flanked at the western side by basement complex rocks and Bida basin. The eastern part is bounded by Abakaliki/Benue Basin while the northern and southern sides are delimited by middle Benue Trough and Niger Delta basin, respectively. The separation of the South American and African plates led to the geological evolution of the southern sedimentary basins. This occurred during the Lower Cretaceous age with the formation of the Benue Trough as a failed arm of the rift triple junction. The Anambra basin holds up to 6,000 m thickness of Cretaceous and Tertiary sediments. The descriptions of the geological settings of Anambra basin with the Formations have been well reported [3].

3. Materials and methods

3.1. Samples

Twelve core samples were collected from two shallow wells; ONP1 (7°27’39.0″N, 7.45’27.0″E) and ONP4 (7°27’13.9″N, 7°45’53.5″E) located at Onupi, Ankpa Local Government Area of Kogi State, Nigeria (Fig. 1). Three lithofacies of rock samples were identified including, shales (S), carbonaceous shales (CS) and inter-bedded sub-bituminous coals (SBC) at depth interval of 7.65 to 50.5 m from the Lower Maastrichtian Mamu Formation in the Anambra Basin. The geological map of Anambra basin and the location of the studied wells are shown in Fig. 1.

3.2. Geochemical Analysis

Core samples were crushed to 200 mesh and then oven dried for at least 4 hr at 80°C under vacuum prior to geochemical analyses. For the total organic carbon (TOC) analyses, 80 - 100 mg powdered samples in porous crucibles were treated with 5% hydrochloric acid (HCl) at 80°C for 2 hr. The
samples were cleansed from the residual HCl with deionised water. TOC content was determined using an ELTRA CS800 carbon/sulfur analyser. Kerogen was isolated from the rock samples by treatment with HCl and HF. Rock-Eval pyrolysis parameters were acquired by Rock-Eval 6 (Vinci Technologies, France). Approximately 3 - 6 mg of the kerogen extracted from the rock samples were progressively heated to 850 °C using a special temperature program. The computerised system output the pyrograms as well as the calculated parameters. The elemental (C, H, and N) compositions of the kerogen samples were determined on Elementar Vario EL CUBE while oxygen (O) content was measured with Elementar Vario EL III instrumental analysers. The carbon isotope analyses of the kerogens were carried out using a Thermo Scientific Delta V mass spectrometer. The δ¹³C values are reported relative to the V-PDB Belemnite standard.

4. Results and discussion

4.1. Organic matter quantity

The TOC contents and pyrolysis parameters obtained for the Lower Maastrichtian Mamu Formation are listed in Table 1. The TOC contents of the samples vary widely from 1.3 to 58.28 wt% with a mean value of 18.24 wt% (Table 1), indicating good to excellent hydrocarbon generation potential [6] and this is clearly depicted in Fig. 2. The values obtained for the volatile hydrocarbon (S1), pyrolysable hydrocarbon (S2), and the genetic potential (GP) for the samples vary from 1.83 and 6.36 mg HC/g rock (mean value of 3.79 mg HC/g rock), 30.17 to 128.91 mg HC/g rock (mean value of 95.82 mg HC/g rock) and 32 to 133.11 mg HC/g rock (mean value of 99.61 mg HC/g rock), respectively. These values indicate that all the samples have high hydrocarbon generative potential [6]. The hydrogen index (HI) ranges from 174 to 235 mg HC/g TOC (mean value of 196.58 mg HC/g TOC). These values are greater than 150 mg HC/g TOC, corroborating the high capacity of the samples to generate both oil and gas [6].

Table 1. TOC content and Rock-Eval pyrolysis data of kerogen from the Lower Maastrichtian Mamu Formation shale and sub-bituminous coal.

| Sample No. | Depth (m) | Lithology | TOC  | Pyrolysis data |
|------------|-----------|-----------|------|----------------|
|            |           |           | S1   | S2  | GP | Tmax (°C) | HI | PI |
| ONP1-37   | 11.5 - 19.0 | S         | 4.23 | 6.36 | 97.23 | 103.59 | 421 | 235 | 0.06 |
| ONP1-38   | 22.75 - 23.08 | CS        | 24.61 | 4.5 | 121.32 | 125.82 | 420 | 193 | 0.04 |
| ONP1-39   | 23.08 - 25.41 | SBC      | 58.28 | 4.2 | 128.91 | 133.11 | 417 | 201 | 0.03 |
| ONP1-40   | 25.41 - 31.0 | CS        | 23.99 | 2.19 | 118.31 | 120.5 | 420 | 176 | 0.02 |
| ONP1-41   | 31.0 - 37.0 | S         | 7.37 | 2.98 | 103.03 | 106.01 | 419 | 227 | 0.03 |
| ONP1-42   | 37.0 - 41.5 | CS        | 14.87 | 3.39 | 109.91 | 113.3 | 417 | 206 | 0.03 |
| ONP1-43   | 41.5 - 41.62 | SBC      | 57.71 | 3.05 | 119.42 | 122.47 | 417 | 187 | 0.02 |
| ONP1-44   | 41.62 - 42.44 | CS   | 17.07 | 3.61 | 109.27 | 112.88 | 418 | 174 | 0.03 |
| ONP1-45   | 42.44 - 50.5 | S         | 5.85 | 5.98 | 116.43 | 122.41 | 421 | 185 | 0.05 |
| ONP2-46   | 7.65 - 8.5  | S         | 1.69 | 5.45 | 46.62 | 52.07 | 417 | 194 | 0.10 |
| ONP2-47   | 9.94 - 14.5 | S         | 1.3  | 1.83 | 30.17 | 32 | 421 | 160 | 0.06 |
| ONP2-48   | 42.5 - 45.0 | S         | 1.91 | 1.95 | 49.19 | 51.14 | 422 | 221 | 0.04 |
| Mean      | 18.24      | 3.79   | 95.82 | 99.61 | 419 | 196.58 | 0.04 |
4.2. Organic matter type and thermal maturity

The cross plot of HI against Tmax (Fig 3a) shows that the organic matter contains mixed Type II/III kerogen. Although some of the samples plotted closer to Type III evolution path, suggesting major contribution from Type III kerogen. The results of the elemental and carbon isotope composition of the kerogen are shown in Table 2. It had been argued that kerogen typing of samples with fragments of coal could be best determined by atomic H/C vs. O/C diagrams and organic petrography [6]. The plot of H/C against O/C confirms the mixed origin (Type II/III) of the organic matter contained in the samples (Fig. 3b).

Table 2. Elemental and carbon isotope composition of kerogen from the Lower Maastrichtian Mamu Formation shale and sub-bituminous coal.

| Sample No. | Depth (m) | Lithology | Elements (%) | Atomic Ratio | δ¹³C |
|------------|-----------|-----------|--------------|--------------|------|
|            |           |           | C  H  O  N   | H/C  O/C     |      |
| ONP1-37    | 11.5 - 19.0 | S        | 48.95 4.13 13.81 1.12 | 1.01 0.21 | -27.12 |
| ONP1-38    | 22.75 - 23.08 | CS       | 69.04 4.76 21.23 1.54 | 0.82 0.23 | -26.49 |
| ONP1-39    | 23.08 - 25.41 | SBC      | 72.68 4.95 18.46 1.35 | 0.81 0.19 | -27.09 |
| ONP1-40    | 25.41 - 31.0 | CS       | 68.46 5.09 22.43 1.34 | 0.89 0.25 | -26.73 |
| ONP1-41    | 31.0 - 37.0 | S        | 50.96 5.18 16.44 1.05 | 1.21 0.24 | -27.22 |
| ONP1-42    | 37.0 - 41.5 | CS       | 58.96 4.08 17.86 1.07 | 0.82 0.23 | -27.15 |
| ONP1-43    | 41.5 - 41.62 | SBC      | 69.92 5.19 22.5 1.27 | 0.88 0.24 | -26.87 |
| ONP1-44    | 41.62 - 42.44 | CS       | 68.15 5.14 23.7 1.38 | 0.9 0.26 | -26.85 |
| ONP1-45    | 42.44 - 50.5 | S        | 67.68 4.88 22.53 1.41 | 0.86 0.25 | -27.48 |
| ONP2-46    | 7.65 - 8.5 | S        | 27.63 2.85 9.41 0.61 | 1.23 0.26 | -28.12 |
| ONP2-47    | 9.94 - 14.5 | S        | 22.51 2.14 7.47 0.58 | 1.13 0.25 | -27.62 |
| ONP2-48    | 42.5 - 45.0 | S        | 27.89 2.46 8.55 0.76 | 1.05 0.23 | -27.48 |
| **Mean**   |           |           | 54.4 4.24 17.03 1.12 | 0.97 0.24 | -27.185 |
Stable carbon isotope composition can provide useful and consistent information to distinguish OM type as it excludes the influence of thermal evolution [8]. It was suggested that kerogens originating from plankton, algae, and other hydrobionts have δ^{13}C values in the range of −32.0 to −29.0‰, while kerogens from high terrestrial plants have δ^{13}C values ranging from −26.0 to −20.0‰ [8]. The carbon isotopic values obtained for the samples range from −28.12 to −26.49‰ (Table 2), supporting the mixed origin (Type II/III kerogen) of the source rocks [8]. Most of the shale samples have δ^{13}C less than −26.0‰, indicating mixed Type II/III kerogen. However, the carbonaceous shale and coal samples typically display dominant of Type III kerogen as also noted from elemental analysis results (Fig 3b). The range of carbon isotope values obtained for these deltaic samples is quite different from the values recorded for most marine-continental transitional shales in some basins from China, which are considered to be mainly gas-prone Type III kerogen [9, 10].

The Tmax values for the samples fall within a narrow range of 417 to 422 °C, with a mean value of 419 °C (Table 1) indicating that all the samples are thermally immature [6]. The thermal immaturity status of the samples is also clearly shown on the plot of HI against Tmax in Fig. 3a. The production index (PI) values range from 0.02 to 0.10, with a mean value of 0.04. With the exception of sample ONP2-46, all the samples have PI values less than 0.1, supporting the immature stage of the samples [6].

5. Conclusions

The genetic potential and thermal maturity of rock samples from the Lower Maastrichtian Mamu Formation in the Anambra Basin were evaluated using the total organic carbon (TOC) contents and geochemical data obtained from their kerogens analysis. The mean TOC and HI values obtained for the samples are 18.24 wt% and 196.68 mg HC/ g TOC, respectively, implying high quantity and considerable quality of organic matter capable of generating oil and gas. The results from the elemental and carbon isotopic compositions indicate organic matter of mixed Type II/III and III kerogens. The organic matters are thermally immature within the interval studied with a mean Tmax value of 419 °C. This study shows that the organic matter contained in shales, carbonaceous shales and sub-bituminous coals in the Lower Maastrichtian Mamu Formation could sufficiently generate oil and gas at appropriate thermal maturity.
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