Hydrocarbon Potential and Palaeodepositional Environment of Subsurface Sediments of the Anambra Basin, South Eastern Nigeria

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Abstract

Subsurface core samples obtained from Enugu 1325 and 1331 wells within the Anambra Basin were characterized by standard organic geochemical methods; Rock-eval and GC-Ms; to deduce the hydrocarbon potential, source input of the organic matter and palaeodepositional environment of the basin. The lithologies in both wells consist of coals, shales and siltstones and belong to the Mamu Formation. The Total Organic Carbon (TOC), Soluble Organic Matter (SOM) and Genetic Potential (GP) of the core samples ranged from 1.59 - 70.33wt%., 238.1 - 4095.2 ppm, 2.34 -177.36 respectively. These values indicate that the source rock is moderately to fairly rich in organic matter. A cross plot of hydrocarbon potential versus TOC, EOM versus TOC, indicated that the source rock is Type III and gas prone. Tmax values range from 426 – 435°C which indicate low maturation level for the source rock. The ratios of C_{29} hopane, / C_{30} hopane, and 22S/22S+22R C_{32} hopane ranged from 0.32 to 0.57; 0.20 to 0.59; and 0.49 to 0.56 respectively, suggesting immature organic matter. A cross plot of hydrogen index (HI) versus Tmax, production index (PI) versus Tmax, both suggest that the source rock is immature. Further maturity parameters such as MPI-1 (Methyl Phenanthrene Index), MDR (Methyl Dibenzothiophene Ratio), and Rm (calculated vitrinite reflectance), revealed ranges of 0.14-0.76, 0.99-4.21, and 0.62-0.82 respectively. These indicate that the samples are immature to marginally mature. High values were obtained from the C_{24} tetracyclic/ C_{24} tricyclic terpanes and the C_{19}/C_{20} tricyclic terpane ratios, (1.54-2.25) and (0.74-1.34) respectively, which are indicative of terrigenous organic matter. The dominance of C₂₉ over C₂₈ and C₂₇ indicate higher terrigenous input. The pristane/phytane ratio of 5.08 to 8.97 indicates oxic condition of deposition for the sediments. The results show that the sediments were deposited in oxic to suboxic environment with moderately to fairly rich organic matter of substantial terrigenous input. The source rock has the potential to generate gas rather than oil, given sufficient maturity.

Introduction

The Anambra Basin, with a total sediment thickness of about 9 km, presents an economically-viable hydrocarbon deposits. It is characterized by enormous lithologic heterogeneity in both lateral and vertical extensions derived from a range of paleoenvironmental settings ranging from Campanian to Recent [1].

The search for commercial crude oil in the Anambra Basin has remained a source of concern especially to oil companies and research groups. Initial efforts were unrewarding and this led to the neglect of this basin in favour of the Niger Delta, where hydrocarbon reserves have been reportedly put at 40 billion barrels of oil and about 170 trillion standard cubic feet of gas [2-4].

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¹Department of Geology, University of Ibadan, Nigeria ²Shell Petroleum Development Company, Port Harcourt, Nigeria Email: ntonme@yahoo.com Reports of various authors are valuable in the exploration activities in the Anambra Basin. Avbovbo and Ayoola [5] reviewed exploratory drilling results for the Anambra Basin and proposed that most parts of the basin probably contain gas-condensates due to abnormal geothermal gradient. Agagu and Ekweozor [6] concluded that the Senonian shales in the Anambra syncline have good organic matter richness with maturity increasing significantly with depth. Unomah [7] evaluated the quality of organic matter in the Upper Cretaceous shales of the Lower Benue Trough as the basis for the reconstruction of the factors influencing organic sedimentation. He deduced that the organic matter and shales were deposited under a low rate of deposition. Specific references to the organic richness, quality and thermal maturity in the Mamu Formation and Nkporo shales have been reported by Unomah and Ekweozor [8], Akaegbobi [1] and Ekweozor [9]. They reported that the sediments are organic rich but of immature

status. The present study, in line with current understanding, tries to examine the hydrocarbon potential of the Anambra Basin and ascertain its paleodepositional environ-ments.

Location of Study Area and Geological Setting

The study area is located between latitudes $6^{\circ}15'N - 6^{\circ}45'N$ and longitudes $7^{\circ}15'E - 6^{\circ}45'N$

 $7^{\circ}30$ 'E and falls within the Anambra Basin (Fig. 1). The Nigerian sedimentary basin was formed after the break up of the South American and African continents in the Early Cretaceous [10, 11]. Various lines of geomorphologic, structural, stratigraphic and paleontologic evidences have been presented to support a rift model [12-15].



Fig. 1: Geologic map of the southeastern Nigeria showing location of the study wells. Inset map of Nigeria with arrow pointing to study area (After Whiteman 1982).

The stratigraphic history of the region is characterised by three sedimentary phases during which the axis of the sedimentary basin shifted [16]. More than 3000m of rocks comprising those belonging to Asu River Group, Eze-Aku and Awgu Formations, were deposited during the first phase in the Abakaliki-Benue Trough and the Calabar Flank. The resulting succession from the second sedimentary phase comprises the Nkporo Group, Mamu Formation, Ajali Sandstone. Nsukka Formation, Imo Formation and Ameki Group. The third phase, which resulted in the formation of the petroliferous Niger Delta, commenced in the Late Eocene as a result of a major earth movement that structurally inverted the Abakaliki region, displacing the depositional axis further to the south of the Anambra Basin [17]. The stratigraphy of the Anambra Basin from oldest to youngest is explained below.

Nkporo-Enugu Shale Group

These units consist of dark grey fissile, soft shales and mudstone with occasional thin beds of sandy shale, sandstone and shelly limestone. A shallow marine shelf environment has been predicted due to the presence of foraminifera Milliamina, plant remains, poorly preserved molluscs and algal spores [2, 18 – 19]. Nyong [20] inferred the Nkporo Shale to have been deposited in a variety of environments ranging from shallow open marine to paralic and continental settings. North of Awgu, the Nkporo Shale shows a well-developed medium to coarse-grained sandstone facies referred to as Owelli Sandstone. The Owelli Sandstone member is about 600 metres thick [18]. Akaegbobi and Schmitt [21] evaluated the Nkporo Shales as having moderate to super-rich organic matter of types 111 and some types 11/111 of immature status, sourced mainly from terrestrial higher plants and deposited in cyclistic suboxic and anoxic conditions.

Mamu Formation

This formation was initially named the "Lower Coal Measures" [22], but later

renamed Mamu Formation [18]. It contains a distinctive assemblage of sandstone, sandy shale, shale, mudstone and coal seams [18]. Surface sections reveal that the Mamu Formation comprises mainly white, finegrained and well-sorted sands. There are frequent interbeds of carbonaceous shales with sparse arenaceous microfauna, and coal beds [19]. The exposed thickness of this Formation ranges from 5-15m. According to Reyment [18], the coals occurring in Enugu area are in five seams ranging from 30cm to nearly 2m with the middle seam, which is the thickest, outcropping along the Enugu Escarpment for a distance of about 11 km. The coals of Enugu area form only a part of the total coal resources of Nigeria [18]. On the basis of organic geochemical and biomarker parameters, Nton and Awarun [23] described the shale and coal units of the Mamu Formation as moderate to rich oil/gas proned, immature source rock of terrestrial precursor.

Ajali Sandstone

This is a Maastrichtian sandy unit overlying the Mamu Formation. It consists of white, thick friable, poorly sorted cross-bedded sands with thin beds of white mudstone near the base [24]. Studies have suggested that the Ajali Sandstone is a continental/fluviodeltaic sequence, characterized by a regressive phase of a short-lived Maastrichtian transgression with sediments derived from western areas of Abakaliki anticlinorium and the granitic basement units of Adamawa-Oban Massifs [25]. The Formation, where exposed, is often overlain by red earth, formed by weathering and ferruginization of the Formation [26]. According to Nwajide and Reijers [27], the coal-bearing Mamu Formation and Ajali Sandstone accumulated during the regressive phase of the Nkporo Group with associated progradation. The authors characterized the Ajali Sandstones as tidal sands. Tijani and Nton [24] reported that weathering induced geochemical processes with resultant formation of Fe-Mn-Al-oxyhydroxides and leaching/dissolution mobilization of metals including contaminant trace, constitute potential aquifer management problems in the Ajali Sandstone.

Nsukka Formation

The Nsukka Formation is a Late Maastrichtian unit, lying conformably on the Ajali Sandstone. The unit consists of alternating succession of sandstone, dark shales and sandy shales with thin coal seams at various horizons. Reyment [18] assigned the name 'Upper Coal Measures' to this formation. The Formation begins with coarse medium-grained sandstones passing to upward into well-bedded blue clays, finegrained sandstones, and carbonaceous shales with thin bands of limestone [17, 18]. Agagu [19] reported that the Formation has a thickness range of 200-300m and consists of alternating succession of fine-grained sandstone/siltstones, grey-dark shale with coal seams at various horizons. A strand plain/marsh environment with occassional fluvial incursions similar to that of the Mamu Formation was inferred for this Formation.

Imo Shale

The Imo Shale overlies the Nsukka Formation in the Anambra Basin and consists of blue-grey clays and black shales with bands of calcareous sandstone, marl and limestone [18]. Whiteman [2] described the formation as fine textured, dark grey and bluish grey shale with occasional admixture of ironstone and thin sandstone bands, which occur especially towards the top of the unit. Ostracod and foraminifera recovered from the basal limestone unit indicate a Paleocene age for the Formation [28]. Lithology and trace fossils of the basal sandstone unit reflect foreshore and shoreface or delta front sedimentation [29]. The Imo Formation is the up-dip lateral equivalent of part of the Akata Formation in the subsurface Niger Delta [16]. The Formation becomes sandier towards the top where it consists of alternations of sandstone and shale [28]. The sedimentary succession indicate a paralic environment.

Materials and Methods

Samples |

Borehole samples from Enugu 1325 and 1331 wells, located in the Anambra basin were obtained from the Nigerian Geological Survey Agency (NGSA) Kaduna, for this study. The samples were logged based on lithological characteristics and taken into well-labelled sample bags which were eventually taken to the Sedimentological Department Geology, Laboratory, of University of Ibadan, for detailed description and selection for subsequent laboratory analyses. The borehole samples of the Enugu 1325 range in depths from 163 to 178 meters while the well 1331 samples range in depth from 218 to 234 meters (Figs. 2 & 3). A total of thirteen (13) samples were systematically selected to cover the entire depth of the core samples obtained.



Fig. 2: Litholog of Enugu well 1325.



Fig. 3: Litholog of Enugu well 1331.

Enugu Well 1325 has a sequence beginning from shale overlain by siltstone, coal, shale and siltstone sequence successively. The shales are dark grey and fissile and the siltstone are brown to light grey in colour while the coal is blackish. In the Enugu Well 1331, the sequence comprises from bottom to top coal, shale and siltstone successively. In the middle, there is another shale, siltstone, shale and coal sequences. These sequences are successively overlain by shale, siltstone, shale-siltstone sequence in the uppermost part. The shale is fissile, dark to grey while the coal is dark. The siltstone ranges from brown to light grey. In both wells, the lithological sequences are cyclical.

Total Organic Carbon (TOC)

Approximately 0.10 g of each pulverized sample was weighed and then treated with concentrated hydrochloric acid (HCl) to remove carbonates. The samples were left in hydrochloric acid for a minimum of two (2) hours. The acid was separated from the sample with a filtration apparatus fitted with a glass microfiber filter. The filter was placed in a LECO crucible and dried at 110°C for a minimum of one hour. After drying, the sample was analysed with a LECO 600 Carbon Analyzer. The analysis was carried out at the Weatherford Geochemical Laboratory, Texas, USA.

Rock Eval Pyrolysis

Based on adequate TOC, thirteen samples were further characterized by Rock Eval pyrolysis using LECO 600 Analyzer. About 100mg of each pulverized samples was heated in an inert environment to measure the yield of three groups of compounds (S1, S2 and S3), measured at three peaks on a programme. Sample heating at 300°C for 3 minutes produced the S1 peak by vapourising the free hydrocarbons. The oven temperature was increased by 25°C per minute to 600°C. The S2 and S3 peaks were measured from the pyrolytic degradation of the kerogen in the sample. The S2 peak represents the amount of hydrogen-rich kerogen in the rock, and the S3 peak measures the amount of carbon dioxide released providing an assessment of the oxygen content of the rock. The temperature at which maximum amount of S2 hydrogen is generated is known as Tmax, which is a measure of the source rock maturity.

Soluble Organic Matter (SOM)

The Soluble Organic Matter content was done using the Soxhlet System HT2 Extraction Unit and Methylene Chloride/Methanol mixture (9:1) as reagents. Each weighed pulverized sample, was taken into cellulose thimbles and extracted by standard methods. After the evaporation of the solvent, soluble organic matter was transferred into preweighed, labelled 20 ml glass vials and dried under nitrogen gas at 40°C. The dried extracts were measured at room temperature in parts per million (ppm). The asphaltene in the extracts were precipitated by the addition of 10ml pentane and centrifuged. The solvent left was separated into saturates, aromatics and NSO fractions using liquid chromatography. The saturate and aromatic hydrocarbons and polar were eluted using 20ml hexane, n-alkanes/dichloromethane (90:10,25 ml) and dichloromethane/methanol (50:50, 30ml) respectively.

Gas Chromatography and Gas Chromatography-Mass Spectrometry

The analyses were carried out in a Hewlett Packard 6890A gas chromatograph, equipped with dual flame ionization detectors. The chromatograph was fitted with HP-1 capillary column ($30 \text{ m} \times 0.32 \text{ mm I.D} \times 0.52 \text{ microns}$) using helium as the carrier gas. The column temperature was programmed at 35° C to 300° C/min with a flow rate of 1.1 ml/min. Chromatographic data were acquired using an Hp Vectra XM series 3 computer. Peak integration and associated data processing were accomplished using Hp Chemstation software. Peak identification was accomplished by matching chromatographic peaks and profiles using Hp Naptha standard.

The saturates and aromatic fractions recovered were analysed for their biomarker composition by gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring mode (SIM). The samples were mixed with a vortex mixer to agitate and were then transferred to an auto-sampler vial and capped. Vials were then placed on the autosampler to be run in an HP 6890 gas chromatograph silica capillary column $(30m \times 0.25mm \text{ ID}, 0.25 \ \mu\text{m} \text{ film thickness})$ coupled with HP 5973 MSD and equipped with a flame ionization detector. The extract was rapidly injected into the gas chromatograph using a 10 µl syringe. Helium was used as the carrier gas with oven temperature programmed from 80°C to 290°C. The mass spectrometer was operated at electron energy of 70 Ev, an ion source temperature of 250°C and separation temperature of 250°C. The chromatographic data were acquired using Ms Chemstation software, version G1701BA for Microsoft NT®.

Results and Discussions *Organic Richness*

The Total Organic Content of the samples ranged from 1.59 to 70.33wt% (Table 1). The TOC of the coal samples – V2, V3 (Enugu well 1331) and P2 (Enugu well 1325) are higher than what was recorded for the shale samples. Nevertheless, all the samples have values above 0.5 wt% TOC considered as minimum for clastic source rocks to generate petroleum (Tissot and Welte 1984). The Soluble/extractable Organic Matter (SOM) of the samples generally exceeds 500 ppm except for samples EN 1325(P3) and EN 1331(V5) with SOM values of 238.1 and 436.9 ppm respectively. These show that the samples can be classified as fair to excellent source rocks. Based on the quality definition of Baker [30], the organic matter is adequate and it indicates good hydrocarbon potential for the studied wells. Petroleum generating potential (GP) ranges from 2.34 to 177.36.

 Table 1: TOC and Rock Eval Pyrolysis Data for the Sediments of Anambra basin

Sample ID No.	Depth (meter)	SOM (ppm)	TOC (wt%)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	Tmax (°C)	ні	OI	S2/S3	PI (S1/S1+S2)	GP (S1+S2)
V1	-224.5	ND	3.30	0.55	4.57	1.11	428	138	34	4.12	0.11	5.12
V2	-223	3381	66.24	4.28	153.7	12.07	431	232	18	12.73	0.03	158.51
V3	-222	3160	63.51	3.87	155.8	15.79	434	245	25	9.87	0.02	159.67
V4	-220.5	ND	1.91	0.12	3.54	1.11	432	185	58	3.19	0.03	3.66
V5	-227.5	436.9	7.49	0.54	17.71	1.67	433	237	22	10.6	0.03	18.25
V6	-231.5	1904.8	8.52	0.71	14.25	2.33	426	167	27	6.12	0.05	14.95
V 7	-232.5	ND	3.20	0.28	2.66	1.31	428	83	41	2.03	0.10	2.94
V8	-232	4095.2	70.33	7.75	169.61	14.33	429	241	20	11.84	0.04	177.36
P1	-168.5	546.7	7.98	0.77	12.55	2.53	435	157	32	4.96	0.06	13.32
P 2	-169	ND	67.77	6.22	153.35	12.68	427	226	19	12.09	0.04	159.57
P 3	-172.5	238.1	2.24	0.37	3.70	1.30	431	165	58	2.85	0.09	4.07
P4	-174.5	ND	1.59	0.31	2.25	1.43	431	142	90	1.57	0.12	2.56
P5	-175.5	ND	1.96	0.25	2.09	0.49	427	107	25	4.27	0.11	2.34

TOC=Weight percentage organic carbon in rock S1,S2= mg hydrocarbons per gram of rock S3=mg carbon dioxide per gram of rock GP= Petroleum generic potential= S1 + S2 ND=Not Done

Organic Matter Type

The organic matter type in a sedimentary rock, among other conditions, influences to a large extent the type and quality of HI= Hydrogen Index= $S2 \times 100/TOC$ OI=Oxygen Index= $S3 \times 100/TOC$ Tmax=°C PI= Production Index= S1/(S1+S2)

hydrocarbon generated due to different organic matter type convertibilities [31]. The plot of hydrocarbon potential versus TOC (Fig. 4) indicates that the organic matter contained in the samples belong to type II/III. Cross plot of hydrogen index (HI) versus oxygen index (OI) (Fig. 5) corroborates that the kerogen is type II/III with majority belonging to type III. The HI in the sample ranged from 83 to 245. These values suggest that the samples have potential to generate both oil and gas [31-32] which indicate a good source rock [33]. The plot of EOM (Extractable Organic Matter) against TOC (Total Organic Matter) shows that the organic matter is gas prone (Fig. 6). Sonibare [34] reported that the abundance of 1,2,5 TMN (Trimethyl naphthalene) suggests a significant land plant contribution for the coals of Benue Trough. The occurrence of such biomarker in this study may also be attributed to such contribution.





Fig. 5: A plot of hydrogen index against oxygen index for the studied wells (Modified after Van Krevelen 1961).





Thermal Maturity

The degree of thermal evolution of the sedimentary organic matter was derived from Tmax and biomarker parameters. The Tmax values range from $426 - 435^{\circ}C$ (av. $430^{\circ}C$) (Table 1). This indicates that the maturity status of the shales and coal range from

immature to early peak mature (oil window). Cross plot of hydrogen index (HI) versus Tmax (Fig. 7) strongly support immature status for majority of the samples. Further plot of Production Index (PI) against Tmax (Fig. 8) also indicate immature sediments [35].



Fig. 7: Cross plot of Hydrogen Index Vs Tmax (°C).



Fig. 8: A plot of Production Index vs. Tmax.

The m/z 191 (hopanes) and 217 steranes mass chromatograms of all the samples are shown in Figures 9 and 10 respectively. All the samples have similar distributions of hopanes and steranes mass chromatograms. C_{30} hopanes are the most abundant in the m/z 191 chromatogram. The maturity and source parameters derived from the hopane distributions in the shales and coals are shown in Table 2. Calculated aromatic

biomaker parameters such as MPI-1 (Methyl Phenanthrene Index). DNR-1 (Dimethyl Naphthalene Ratio), TMNR (Trimethyl Naphthalene ratio) and MDR (Methvl Dibenzothiophene Ratio) derived from the samples range from 0.14 to 0.76; 0.75 to 2.51; 0.17 to 0.50 and 0.99 to 4.21 respectively. According to Radke [36] the samples are immature to marginally mature.









Sample ID	Ts/(Ts+Tm)	Oleanane/ hopane	Hopane C30/C29	Hopane C32	Hopane C29	Hopane C30	Sterane C29	Tetracyclic/ Tricyclic C24	Dia/Reg C27	Tri C19/ C20 ratio	DNR	TMNR	MPI-1	MDR
P1	0.02	0.62	1.98	0.49	0.49	0.52	0.15	1.50	0.93	1.29	2.15	0.19	0.47	0.99
P 3	0.19	0.18	0.17	0.50	0.32	0.20	0.26	2.25	0.55	1.41	2.12	0.17	0.76	4.21
V8	0.01	0.02	1.01	0.53	0.55	0.57	0.13	1.84	0.38	1.37	1.64	0.48	0.34	2.68
V6	0.05	0.12	1.32	0.49	0.37	0.42	0.24	1.74	1.28	0.75	2.25	0.50	0.26	1.04
V5	0.02	0.03	1.12	0.49	0.51	0.56	0.14	2.22	0.27	1.09	0.75	0.21	0.24	2.00
V2	0.05	0.08	0.72	0.56	0.50	0.51	0.27	1.86	0.44	1.10	2.51	0.44	0.17	2.02
V3	0.01	0.01	1.09	0.54	0.57	0.59	0.16	2.16	0.55	1.34	1.54	0.48	0.14	1.20

 Table 2: Biomarker Parameters
 Computed for the Sediments of Anambra Basin

Some n-paraffin ratios can be used to estimate the thermal maturity of sediments [37]. Pristane/ nC_{17} and phytane/ nC_{18} can be used to calculate thermal maturity. For the studied wells, the Pr/ nC_{17} values ranged

between 0.80 and 3.91 (Table 3); this falls in the immature zone. Ph/nC₁₈ values ranged from 0.20 to 0.57, which is below the threshold value, indicating immature organic matter.

Sample ID	Pr/Ph	Pr/nC17	Ph/nC18	СРІ	OEP-1	OEP-2
EN 1331 (V2)	5.88	0.8	0.57	1.57	0.4	0.57
EN 1331 (V5)	7.26	1.98	0.33	1.83	0.43	0.56
EN 1331 (V6)	8.97	3.91	0.46	1.53	0.4	0.57
EN 1325 (P1)	5.5	1.62	0.4	1.69	0.56	0.57
EN 1325 (P3)	5.08	1.1	0.2	1.75	0.43	0.61

Table 3: Biomarker Parameters derived from Gas Chromatograms of the Sediments

Carbon Preference Index (CPI) is the relative abundance of odd versus even carbonnumbered n-paraffins and can also be used to estimate thermal maturity of organic matter [38]. In this study, the CPI values obtained range from 1.53 to 1.83 (Table 3). Hunt [39] has pointed out that CPI, considerably greater than 1.0, shows contribution from terrestrial plants of immature status. From this study, it is indicative that the organic matter is of terrestial setting with low maturity status. Maxwell [40] have shown that strong odd/even bias of heavy n-alkanes is indicative of sediment immaturity. In this study, the odd numbered n-alkanes are more abundant than the even numbered n-alkanes, indicating that the sediments are immature. The Odd Even Predominance (OEP) values are less than 1.0, this is indicative of low maturity [41].

Palaeodepositional Environment

Moldowan [42] indicated that the presence of bisnorhopane and diasterane are indicative of sub-oxic conditions. The presence of such biomarkers in this study supports suboxic conditions of deposition. As reported by Peters [43], the Pristane/Phytane (Pr/Ph) ratio of sediments can be used to infer depositional environment. Pr/Ph ratios < 1 indicate anoxic depositional environment, while values > 1indicate oxic conditions. The values obtained from the studied wells ranged from 5.08 to 8.97, thus indicating a terrigenous-sourced organic matter deposited in an oxidizing environment. This is further supported by the crossplots of Pr/nC_{17} versus Ph/nC_{18} (Fig. 11).



Fig. 11: Plot of pristane/ nC_{17} versus phytane/ nC_{18} (After Moldowan et al. 1994).

Conclusions

Subsurface sediments of the Manu Formation within the Anambra Basin, southeastern Nigeria have been investigated for hydrocarbon potential and palaeodepositional environment. The study reveals that the sediments are organic rich and mainly of gasproned type III kerogen. The organic matter contained in the sediments are thermally immature, derived from terrestrial source and deposited in an oxic environment.

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