Research Paper

Preliminary geochemical investigation of some crude oils from the Niger Delta Basin Nigeria

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ABSTRACT

Geochemical studies on twenty-eight crude-oil samples from nine oilfields, onshore-offshore parts of Niger Delta Basin, were performed to classify the oils into various classes, determine the bulk compositions of oils, organic matter inputs, source depositional environment, thermal maturation, and in-reservoir processes, for petroleum system prediction. The oils were fractionated into individual bulk compositions of saturates, aromatics, resins, and asphaltenes (SARA), using the Iatroscan thin-layer chromatography-flame ionization detector (FID) technique. Column chromatography was utilized to separate the saturates, and were further analyzed with gas chromatography-FID for n-alkane and acyclic isoprenoid distributions. SARA results, classified the oils into: paraffinic (>72%Hc, sat/arom: 2.61-3.68); paraffinic-naphthenic (63-70%Hc, sat/arom:1.77-2.31) and aromatic-naphthenic/aromatic-intermediate (<60%Hc, sat/arom: <1.44) oils, generated from source rocks of terrigenous-deltaic origin. Pristane/phytane and n-alkane/isoprenoid ratios delineated the oils into terrigenous (Type III kerogen) and mixed (terrigenous-marine) Type II/III kerogen organic matter source, deposited in oxidizing to transitional environment conditions. Thermal maturity parameters suggest the oil originated from source rocks of early to peak oil window maturity. Additionally, n-alkane/isoprenoid and saturate/aromatic ratios established evidence of biodegradation in a few samples across the depobelts. However, SARA compositions, n-alkane, and isoprenoid distributions of the oils critically permit preliminary assessment study, consequently allows a first-hand geochemical interpretation of the Niger Delta petroleum systems.

Keywords*: Geochemical assessment, oil class, saturate/aromatic ratio,SARA composition*

I. INTRODUCTION

The Niger Delta is strikingly the most prolific hydrocarbon province in the sub-Sahara Africa. It is strategically located in the southern part of Nigeria on the continental margin of West African [1] (Figure 1). The basin represents a geologically active region, with rapid sedimentation and subsidence rates. Consequently, creating complex structural settings, which indicate an extensional area in the northern part and compressional-thrust region in the shallow-offshore area, as a result of the over-pressured Akata shale [1]. The basin includes an area of about 75,000 km^2 [2], with petroleum production dating back to the late1950s. Since then, a great number of studies on various aspects of the reservoired petroleum have been scientifically documented in scholarly literature [1-16].

The principal organic composition of the source rocks are mainly Type III kerogens with some mixed Type II/III [8, 10], although Akinlua et al. [14] revealed mixed Type II/III as the main kerogen, EkweozorandDaukoru [15] work indicated that the source rocks consist mainly of vitrinite, and plants' liptinitemacerals, including some amorphous materials, probably derived from bacterial reworking. Interestingly, they all agree that the oils are mainly sourced from terrigenous and marine source rocks, with respect to organic matter source [3-10]. Additionally, the source rocks possess geochemical characteristics indicative of oxic to anoxic bottom water conditions [5, 7, 8, 10, 11, 13-15].

Furthermore, 'several compound class geochemical techniques have been used in grouping hydrocarbons into genetic family, for example saturated, aromatics, resins, and asphaltenes (SARA) contents'[17], source fingerprinting, thermal maturation of oils, paleo-environment depositional condition and post expulsion alterations. Nevertheless, preliminary geochemical studies on the composition of crude oils

prepare the stage for more comprehensive studies. In addition to several advantages, it offers first-hand information on the source of oils, thermal maturity, paleo-environment depositional conditions, post-generation alteration processes, as well as low cost of analysis and simple analytical procedures. Its application complements the more sophisticated geochemical approaches. Consequently, providing background geochemical information for a possible interpretation of the Niger Delta petroleum systems. The current work defines the source of the various organic matter associated with the oils, the maturity of the oils, depositional environment conditions of the source rock(s), post-generation alteration processes that may have influenced the compositions of oils, hence classifying them into various groups.
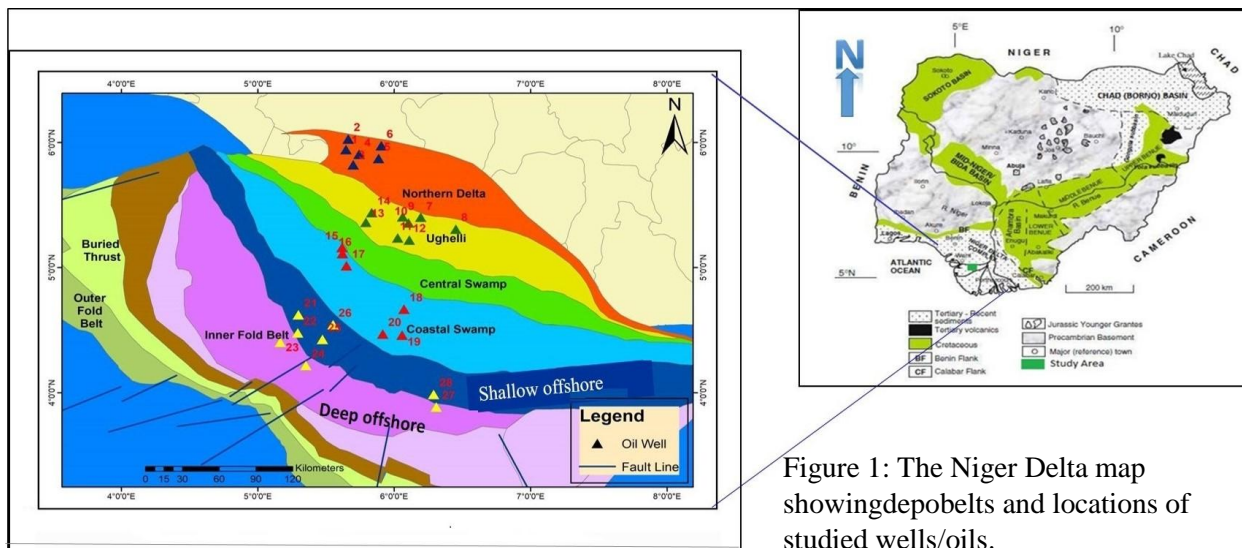

Figure 1: The Niger Delta map showingdepobelts and locations of studied wells/oils.

II. GEOLOGICAL SETTING

The Niger Delta (Figure 1) is located in the southern part of Nigeria covering an area of 75,000 km square [9]. The sediment pile is about 9–12 km thick, with 3 main formations: The Benin Formation, this formation is of Oligocene age and also the last main deposition in the delta. It is mainly composed of sands and sandstone, and generally average about 2 km thick [9]. Sedimentological studies indicates that deposition was mainly in fluvio-deltaic environment. The second formation in the delta is the Agbada Formation, and deposition started during the Eocene times. This formation serves as the reservoir to the delta hydrocarbons and it is composed mainly of inter-bedded sandstones and shales (with the ratio of sands to shale decreasing with depth), deposited in a deltaic environment with several transgression and regression periods. The thickness of the formation is about 3.7 km at the basin center and is less to the flank of the basin [9]. The earliest deposit in the delta is the Akata Formation, with onset of deposition during the Paleocene times, and is mainly a thick shale deposit and some turbidites to the offshore part of the basin, with thickness of about 7 km thickness [9]. Meanwhile, Merki [18] explained that the progradational features of the actual Niger Delta sequences have been critically constrained by syn-sedimentary faults, folding, and the interactions between the rates of basement subsidence, and sediments supply The hydrocarbon in the basin is believed to be sourced from source rocks of the Agbada and Akata formations, and possibly from a yet unknown Cretaceous sediments underlying the delta, or a combination of the 3 [3, 5, 7, 13, 15, 16].

III. MATERIALS AND METHODS

Twenty-eight dead oil samples retrieved from 9 producing oilfields from four depobelts (i.e., onshore and offshore depobelts) across the Niger Delta were collected for the present study.

3.1. Iatroscan thin- layer chromatography-flame ionization detector (TLC-FID) analysis.

The relative composition of saturates, aromatics, resins, and asphaltenes (SARA) of the oil samples were determined using the Iatroscan TLC-FID analyzer. 3µl aliquot of each diluted oil sample was used. Each sample was analyzed in duplicate to estimate the repeatability of the process. Blanks were additionally analyzed on all the racks to assess any contamination. The bottom of the rack of each rods was immersed in a tank comprising 150 ml of n-hexane as a mobile phase until the applied solvent moved a conspicuous mark of ~95%. The rods were then left to dry for 3 minutes, later the rods were immersed in a tank containing 150 ml of toluene, which was allowed to pass up the rods until it reached the 60% mark. All the rods were later removed from the tank and left to dry normally for 6 minutes, before being immersed in the last container containing 150

ml of a mixture of Dichloromethane/Methanol (93:7, v/v), and the solvent front was allowed to get to the 30% mark before removing the rods and then analyzed on the TLC-FID analyzer.

3.2. Gas chromatography-flame ionization (GC-FID) analysis

Gas chromatographic (GC) method was carefully applied to analyze the saturated hydrocarbon fraction, to obtain n-alkanes and acyclic isoprenoid distributions of the considered crude oils. The GC-Flame ionization detector (FID) analysis of each oil sample was performed on the Buck Scientific Gas Chromatograph (BSGC) model 910, fitted to FID, and a Restek 30m MXT-1 columns. 1 µl of each oil sample was injected by an HP6890 auto-sampler in splitless mode. The injector and detection temperature was programmed to 250°C and 280°C, respectively, with helium used as the carrier gas.

Table 1. Bulk compositions, n-alkane and acyclic isoprenoid distributions of the studied Niger Delta oils.

Well	Field	Depobelts	A* (%)	B* (%)	C* (%)	D* (%)	Sat. (%Hc)	Arom (%Hc)	S/A	Pr/Ph	Pr/nC$_{17}$	Ph/n C$_{18}$	nC$_{17}$/ nC$_{27}$	CPI -1
1	A	Northern Delta	52.25	36.40	10.36	0.99	58.94	41.06	1.44	3.06	1.40	0.47	1.73	1.00
2	A	Northern Delta	51.05	34.07	12.78	2.10	59.97	40.03	1.50	3.32	1.37	0.44	1.97	1.03
3	B	Northern Delta	69.53	21.66	6.99	1.82	76.25	23.75	3.21	2.39	0.70	0.33	2.20	0.99
4	B	Northern Delta	57.25	33.20	8.61	0.94	63.29	36.71	1.72	3.72	0.87	0.27	2.60	0.99
5	C	Northern Delta	75.52	20.51	3.50	0.47	78.64	21.36	3.68	3.88	0.82	0.25	3.99	1.03
6	C	Northern Delta	36.66	48.88	12.34	2.12	42.86	57.14	0.75	2.96	0.76	0.29	1.88	1.02
7	D	Greater Ughelli	41.96	51.20	6.81	0.02	45.04	54.96	0.82	3.35	1.09	0.37	2.30	1.16
8	D	Greater Ughelli	55.20	31.05	12.45	1.30	64.00	36.00	1.78	1.88	1.35	0.83	2.58	0.97
9	D	Greater Ughelli	36.18	53.92	9.09	0.81	40.16	59.84	0.67	3.13	1.03	0.29	0.86	1.00
10	D	Greater Ughelli	29.32	62.56	5.75	2.37	31.91	68.09	0.47	3.30	33.58	2.57	0.15	1.03
11	D	Greater Ughelli	33.58	55.38	9.97	1.07	37.75	62.25	0.61	3.50	6.47	1.17	0.65	1.05
12	D	Greater Ughelli	64.18	31.91	3.72	0.19	66.79	33.21	2.01	2.65	0.92	0.36	1.82	1.10
13	E	Greater Ughelli	71.82	26.48	1.53	0.17	73.06	26.94	2.71	4.03	0.83	0.23	2.93	1.09
14	E	Greater Ughelli	76.23	21.57	1.90	0.30	77.94	22.06	3.53	2.80	0.71	0.31	3.26	1.09
15	F	Coastal Swamp	41.23	54.81	3.45	0.51	42.93	57.07	0.75	2.49	1.48	0.70	2.43	1.11
16	F	Coastal Swamp	39.38	57.50	2.33	0.79	40.65	59.35	0.68	3.75	1.33	0.41	3.50	1.21
17	F	Coastal Swamp	27.47	53.92	17.75	0.86	33.75	66.25	0.51	3.91	0.59	0.19	5.25	1.17
18	G	Coastal Swamp	58.63	39.31	1.92	0.14	59.86	40.14	1.49	3.78	0.59	0.19	5.18	1.16
19	G	Coastal Swamp	65.89	32.02	1.99	0.10	67.30	32.70	2.06	2.85	0.87	0.36	2.96	1.07
20	G	Coastal Swamp	68.13	29.49	2.33	0.05	69.80	30.20	2.31	3.85	0.65	0.20	3.42	1.07
21	H	Offshore Delta	71.64	22.39	4.25	1.72	76.19	23.81	3.20	2.56	0.73	0.24	3.91	1.00
22	H	Offshore Delta	53.32	35.60	8.52	2.56	59.96	40.04	1.50	2.83	0.83	0.43	2.40	0.98
23	H	Offshore Delta	70.39	26.98	2.51	0.12	72.29	27.71	2.61	2.29	0.47	0.29	1.01	1.11
24	H	Offshore Delta	63.04	30.33	6.10	0.53	67.52	32.48	2.08	2.33	0.77	0.39	0.82	1.08
25	H	Offshore Delta	47.94	48.78	2.95	0.33	49.57	50.43	0.98	2.91	0.90	0.48	2.67	1.09
26	H	Offshore Delta	63.37	28.51	7.79	0.33	68.97	31.03	2.22	2.51	0.49	0.33	3.14	1.06
27	I	Offshore Delta	70.20	26.43	3.26	0.11	72.65	27.35	2.66	2.45	0.54	0.33	4.03	1.14
28	I	Offshore Delta	42.98	53.63	2.98	0.41	44.49	55.51	0.80	2.69	0.65	0.21	3.49	1.07

Note: **A*** =%saturates, **B*** =%aromatic, **C*** = %NSO, **D*** = %asphaltenes, **Sat%Hc**= %saturate in hydrocarbon, **Arom.%Hc** =%aromatic in hydrocarbon, **S/A** = saturate/aromatic hydrocarbon ratio; **Pr/ph**= pristane/phytane, **Pr/nC$_{17}$** = pristane/nC$_{17}$, phytane/nC$_{18}$, **CPI-1**=Carbon preference index

IV. RESULTS AND DISCUSSION

4.1 Bulk compositions

The relative content of saturates, aromatics, resins and asphaltenes is presented in (Table 1). The result indicates that the percentage saturates ranges from 27.47 to 76.23%, the percentage aromatic ranges from 20.51 to 62.56%, while the percentage resin compounds ranges from 1.53 to 17.75%, and the percentage asphaltenes range from 0.02 to 2.56% (Table1). This broadly indicates that the oils were sourced from terrigenous organic matter origins [19]. Also, the saturated hydrocarbon fraction range from 31.91 to 78.64%, while the aromatics typically range from 21.36 to 68.69% hydrocarbon (Table 1), which reasonably suggests the oil class span from paraffinic to paraffinic-naphthenic oil classes [20]. The ratio of saturates to aromatics (Sat/Arom) hydrocarbons, is considered to provide useful information on the composition of the oil presumed to be generated by the source rock [20]. Though, the ratio is significantly affected by thermal evolution and post-generation alteration processes, hence not dependable. Take, for instance, water-washing can severely deplete aromatics, whereas biodegradation preferentially removes the saturate fraction [21]. However, the results of saturated and aromatic hydrocarbons, and the calculated sat/arom ratios for the studied samples, are typically shown in Table 1 and plotted in Figure 2.

Besides, the investigated crude oils are distinguished by a low to moderate sat/arom ratios, which range from 0.47–3.68 (Table 1). Generally, the saturate/aromatic ratio increases with a reasonable increase in API gravity, reflecting the maturity level of the considered oils, conversely biodegradation often reverses this trend.

4.2Alkane and acyclic isoprenoid distributions

The n-alkane chromatograms (Figure 3) are generally of unimodal distributions between n-C_9 and n-C_{35} peaks. Besides, a few samples from Coastal swamp depobelts, show slight bimodal distribution (Figure 3), with maximum peaks between n-C_{15} and n-C_{20}. Samples from Coastal swamp and Offshore delta depobelts show decline in n-alkane peaks from n-C_{25} and get to a minimum at around n-C_{35}, while the Northern delta gradually decrease from n-C_{15}, samples from Greater Ughellidepobelts decrease from n-C_{25}. These features suggest limited contributions of higher-plant to thesource rocks that generated the Niger Delta oil. Interpretation based on the shapes of the chromatograms alone reveals that the Niger Delta oils are derived from mature organic matter of mainly marine algal/microbial origin, conversely oil of high thermal maturity will show similar shape of chromatogram [22].
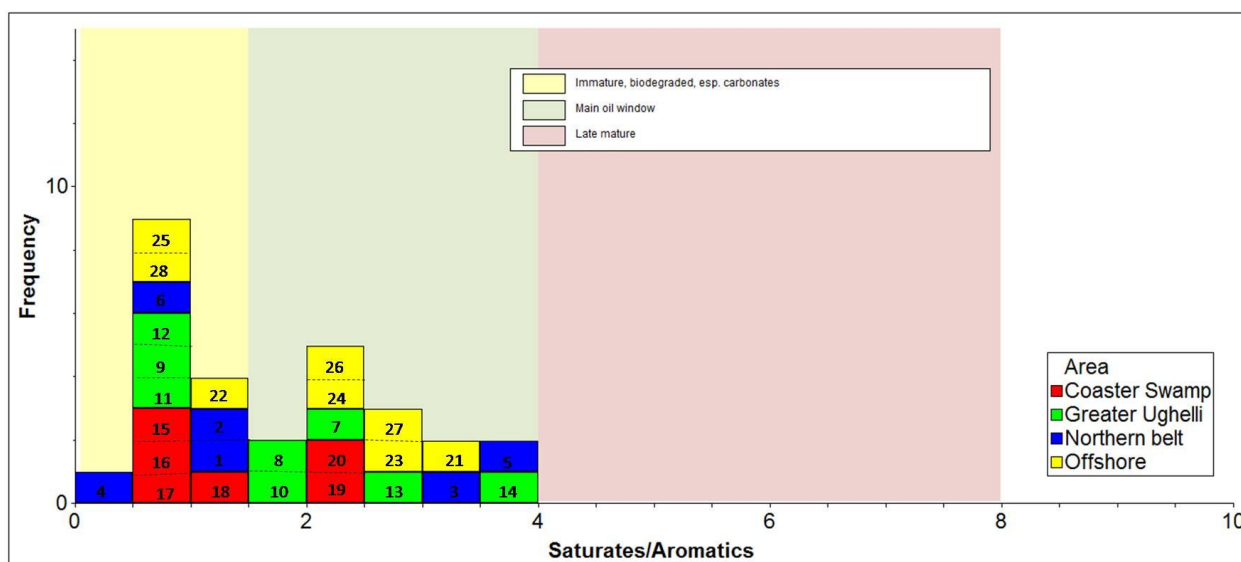
Figure 2: Graphical plot of saturate/aromatic ratio of studied oils as a maturity parameter, (number represent oil sample from each well).
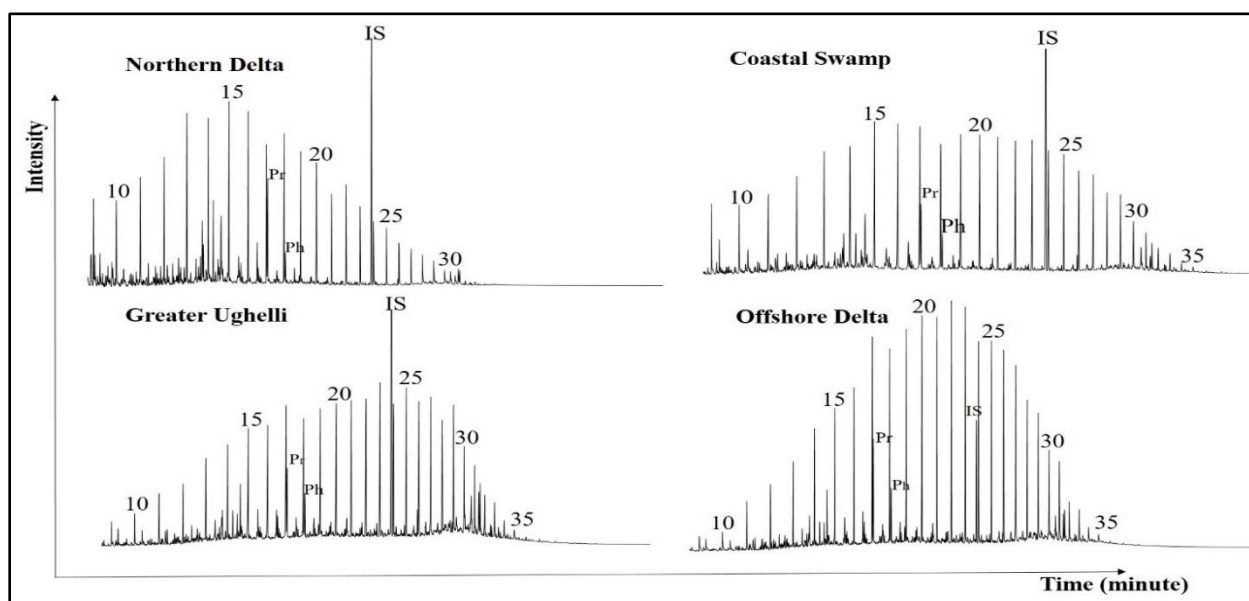

Figure 3: Representatives GC of n-alkane profiles of non-biodegraded oils from the various study depobelts of the Niger Delta, 10= nC_{10}, Pr =Pristane, Ph=Phytane and IS=internal standard (n-heptadecylcyclohexane).

The investigated crude-oil samples chromatograms are mainly composed of abundant normal alkanes and isoprenoids distributions, with moderately odd/even carbon preference (n-C_{23} to n-C_{25}). Representative samples from each of the depobelts (Figure 3), shows that in the Northern delta and Offshore samples, n-C_{17}>n-C_{27}, but the Greater Ughelli samples show n-C_{17}=n-C_{27}. Whereas in the Coastal swamp samples, n-C_{17} slightly

predominates over n-C_{27}. These profiles suggest the proportionate contributions of terrigenous to marine sourced organic matter of the possible source rocks [24], though thermal evolution plays a critical role.

Preliminary interpretation from the n-alkane and isoprenoiddistributions of oils can provide pertinent information on source, depositional environment, thermal maturity and secondary alteration processes [22]. The isoprenoids/n-alkanes ratios (pr/n-C_{17} and ph/n-C_{18}) for the studied oils range from (0.47 to 33.58 and 0.19 to 2.57), respectively (Table 1), showing wide range of values. The upper-limit values observed in some samples, reflected severely biodegraded samples, while the low-limit values were generally seen as samples of high thermal maturity or samples sourced from rocks deposited in sub-oxic depositional environment (Figure 4), particularly samples 10 and 11 (Table 1).
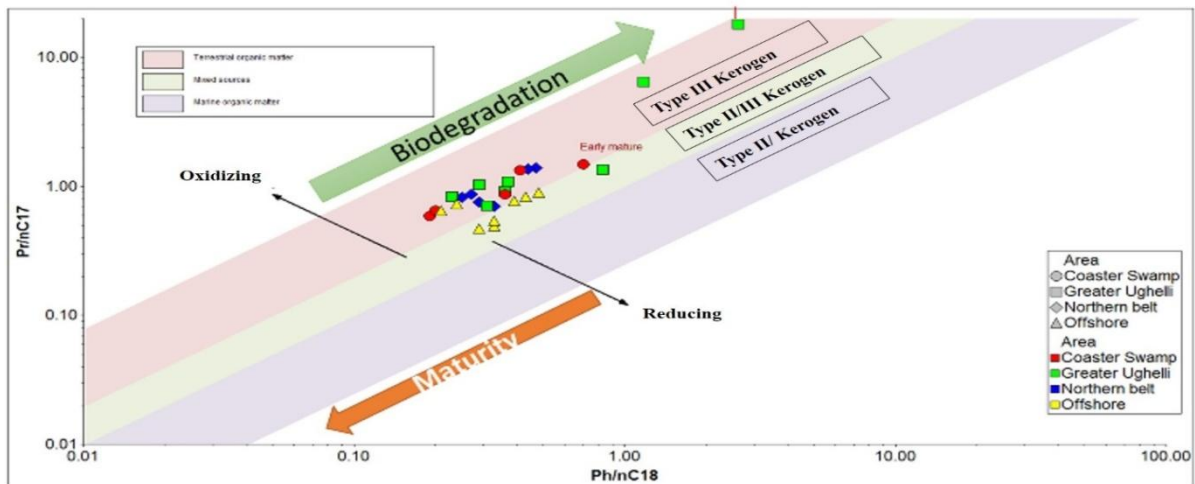

Figure 4: Isoprenoids/n-alkanes (pr/n-C_{17} vsph/n-C_{18}) ratios of oil samples[22], showing mainly Type III organic matter with some mixed Type II/III organic matter from the offshore samples, with samples generally deposited in oxidizing environment and the offshore samples deposited in a more reducing/transitional environment. Biodegradation is indicated in two samples from Greater Ughellidepobelt, with elevated isoprenoids/n-alkane ratio.

The plot of ph/n-C_{18} against pr/n-C_{17} helps separate oil set into different source organic matter, environment of deposition, thermal maturity as well as the degree of biodegradation [25, 22]. This ratios delineated the investigated oils into mainly terrigenous (Type III kerogen) and some mixed marine-terrigenous (Type II/III kerogen, mainly from offshore Niger Delta samples), organic matter inputs deposited in mainly oxidizing to transitional depositional conditions (Figures 4 & 5).
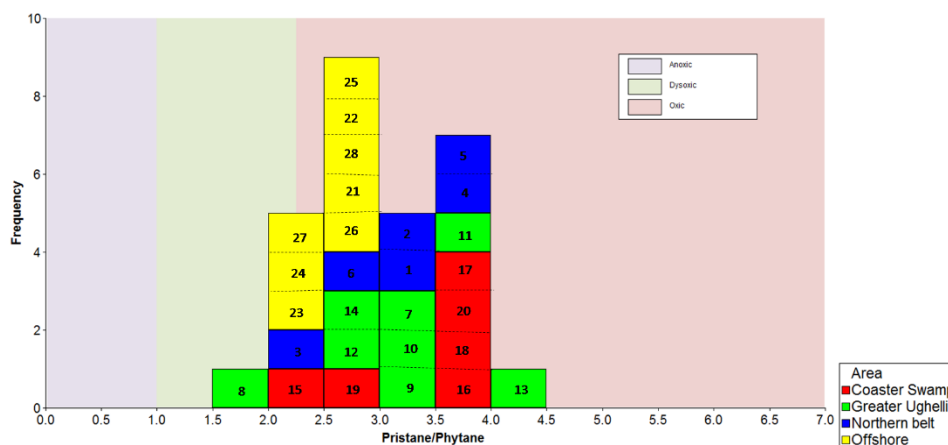

Figure 5: Pristane/phytane ratio of samples inferred that the oils were sourced from source rock deposited in mainly oxic environment with the possibility of some oil samples sourced from rocks deposited in sub-oxicenvironment(note that numbers in the histograms represent sample numbers).

The depositional environment of source rocks can be inferred from the pr/ph ratio, which in turn helps to reconstruct source depositional environment conditions [26]. Ratio lower than 1.0 is associated with anoxic conditions during deposition, and those higher 1 are typically oxic whereas pr/ph greater than 3 are usually

associated with coals [27]. The pristane/phytane ratios of the oils range from 1.88 to 4.03 (Table 1), which indicate that the samples were derived mainly from source rocks of terrigenous origin with possible very low contribution of marine organic matter. These samples were deposited in mainly oxic to sub-oxic redox conditions (Figure 5).

4.3 Maturity assessment

The carbon preference index (CPI), 'is regarded as the ratio of the long-chain odd carbon numbers n-alkanes to those of the long-chain even carbon numbers' [22]. 'The ratio is frequently utilized in interpreting the thermal maturity level of oil source rocks, particularly where nC_{25}-nC_{33} n-alkanes are present' [23].There are several modification to this ratio and the most popular one is that presented by [23].

The CPI values normally reduce with elevated thermal maturation, with values of about 0.95-1.10 interpreted as thermally mature[21]. Elevated CPI value is usually associated with oil sourced from rocks deposited in terrigenous/deltaic environments [28]. On the other hand, the high even-numbered n-alkanes dominance is generally observed in oils sourced from either evaporate or carbonate rocks [22]. Conversely, CPI can be overprinted by thermal maturity and organic matter input.
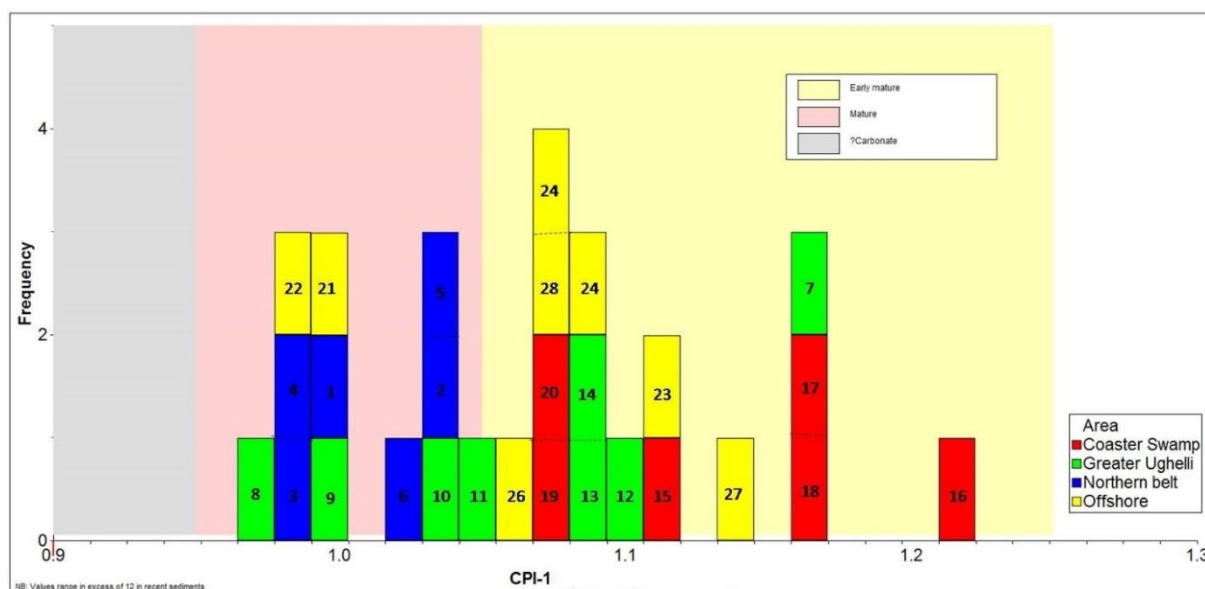

Figure 6: Graphical plot of CPI-1 as maturity parameter overlaid on maturity scale, (numbers symbolize well/sample).

However, the calculated CPI values of the samples are approximately 1.0, mainly ranging from 0.9 to 1.2 (Table 1and Figure 6). This clearly indicates that the studied oils were within early to peak oil window thermal maturity [22]. In addition, the cross plot of isoprenoids/n-alkanes ratios (pr/n-C_{17} and ph/n-C_{18}) Figure 4, and the saturate/aromatic ratio, apparently corroborate these interpretations, with relatively high values suggesting elevated thermal maturity in the studied oils [20, 29].

The ternary plot (Figure 7) shows that the most abundant chemical class are the saturates, whilethe NSO's are the least abundant, this also possibly an indication of elevated maturity level in thestudied samples.

4.4 Class of crude oils

The calculated saturate/aromatic ratio for the considered crude-oil samples are presented in Table 1. Interpretation are derived based on the chemical class content and the relative composition of several compounds in the studied samples [30], and by the classification schemes of [20, 21].Paraffinic oils, paraffinic-naphthenic oils, and aromatic-naphthenic/aromatic-intermediate oils, were identified, viz: *Paraffinic oils:*This class consists of light crude-oil, with amount of resins + asphaltenes<10% [20, 21]. Some of the studied crude oils belong to this class (Figure 7). The proportion of alkanes in hydrocarbon in this class range from (72-79) %, aromatics is <30% hydrocarbons, and polar fraction range from (1.7-8.8) % (Table 1).
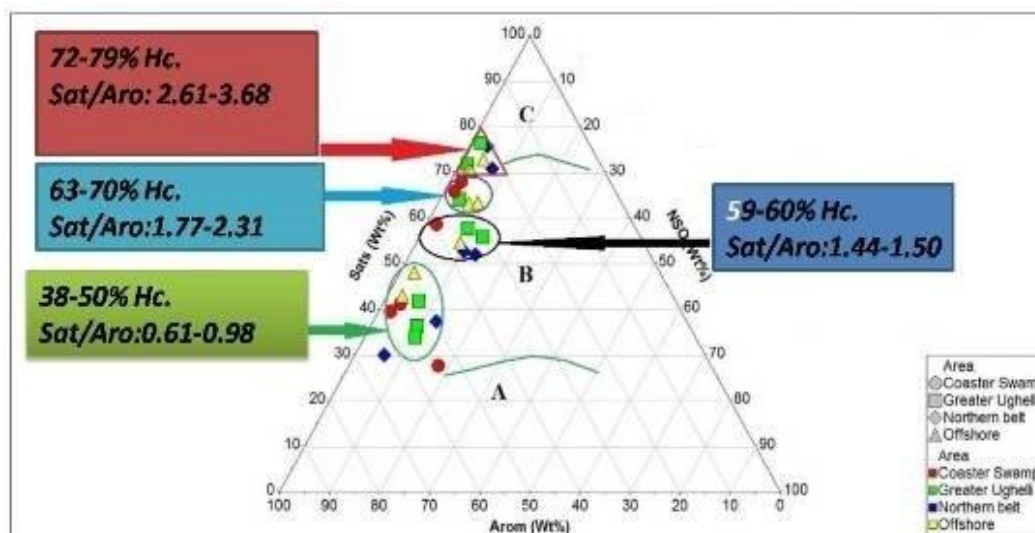
Figure 7: Ternary plot of gross composition of saturated Hcs, Aromatics Hcs, and Resins+Asphaltenes of studied oils showing maturity/class of oils [**A:** field of immature oils and source rock extract (Ro< 0.6 %) **B**: Field of mature oils and source rock extract (Ro 0.7-0.9%)**C**: Field of very mature oils and source rock extract (Ro>0.9%)] modified after [21].

Paraffinic-naphthenic oils: This class of crude-oil has a moderate resins + asphaltenes content (5-15) % [20] and aromatics range from 25-40% hydrocarbons [21]. Some of the studied oils may be group into this class, since their values fit into this class. From Table 1 and Figure 7, the oils with alkanes in the range 59-70% hydrocarbons, and resins + asphaltenes range (2.37-11.35) %, typically belong to this class [21].*Aromatic-naphthenic/aromatic-intermediate oils:*Aromatic-naphthenic/aromatic-intermediate oils. In the studied oils, this class contains aromatic hydrocarbons amounting to >50%, with resins + asphaltenes<20% (Figure 7).

The paraffinic and paraffinic-naphthenic classed oils, which seldom contain < 1% sulfur, are usually sourced from rocks deposited in deltaic/coastal/continental margins [20, 21]. Also, source with more than 1% sulfur (aromatic-intermediate oils), mostly originates from marine sediments, deposited during reducing condition/bottom water anoxia [20, 21]. However, Tissot and Wette[20] emphased that thermal evolution and biodegradation processes often change the composition of crude oils. Consequently, this application is limited. For example, thermal evolution of paraffinic-naphthenic oils ultimately gives rise to paraffinic oil. Whereas secondary alterations (i.e., biodegradation) generally leads to viscous oils of aromatic-naphthenic or aromatic-aphaltenic oils. Moreover, 'paraffinic and paraffinic-naphthenic oils are often altered to aromatic-naphthenic oils, which also increase thesulfur content as a result of biodegradation' [20].All these sum together might have influenced the current content of the oil samples.

V. CONCLUSIONS

Based on bulk compositions of SARA compounds, the studied crude-oils are carefully classified into three distinct classes: the paraffinic, paraffinic-naphthenic, and the aromatic-naphthenic oils. The third class comprises of thick oils that are likely biodegraded equivalent of paraffinic and paraffinic-naphthenic oils. Proportions of saturated and aromatic hydrocarbons typically infer the crude oils' original classes, range from paraffinic to paraffinic-naphthenic oils. SARA result suggests that the oils originated from terrestrial/deltaic (non-marine organic matter) sources. Similarly, n-alkane and isoprenoid (e.g., pristane, phytane) distributions affirmed this consideration and further suggest the oils originated from terrigenous and mixed organic matter (majorly terrestrial plus valuable contribution from marine algal/planktons) sources, deposited in oxidizing to transitional environment conditions. Thermal maturity parameters applied in this study suggest that oils originated from source rocks that have attained early to peak oil window maturity. Saturate/aromatic and isoprenoids/n-alkanes ratios of the studied oils established evidence of biodegradation in a few samples.

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