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Comparative Maturity Profile and Biodegradation Levels of Imo and Soku Crude Oils from Niger Delta, Nigeria

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ABSTRACT

This study carried out comparative maturity profile and biodegradation levels of selected crude oil samples from two producing field from the Niger Delta notably Imo and Soku fields. Representative crude oil samples of from the fields Imo (IM_A and IM_B) and Soku (SK_A and SK_B) were quantitatively analysed using Gas Chromatography Mass Spectrometry (GC-MS). Diagnostic ratios such as Ts/(Ts+Tm) and C29 norhopane/C30 hopane were used for thermal maturity and biodegradation of the crude oil samples. The results revealed that the Thermal maturity indicators placed all samples within the low to moderate maturity window, with Ts/(Ts+Tm) ratios of 0.53 (IM_A), 0.50 (IM_B), 0.42 (SK_A) and 0.40 (SK_B). These values are consistent with oils that have not yet reached peak thermal maturity, while biodegradation assessments using C29 norhopane/C30 hopane levels revealed different microbial alteration, with ratios of ratios of 0.52 (IM_A), 0.54 (IM_B), 0.55 (SK_A) and 0.59 (SK_B). The biodegradation parameters revealed that SKA and SKB crude oil were more biodegraded compared to the IMA and IMB crude oil samples. The study demonstrates the efficiency of aliphatic biomarker in distinguishing crude oil samples within a petroleum province.

Keywords: Biomarkers; Biodegradation; hopanes; Thermal maturity, Niger Delta

Introduction

The global demand for energy has been steadily rising due to industrialization and population growth. In order to meet societal energy demands, they have resulted in an increase in oil exploration activities to produce crude oil, the primary energy source. Crude oil biodegradation and the ensuing decline in its value are primarily found in reservoirs that are colder than approximately 80°C[1,2].

Saturated hydrocarbons are eliminated first when crude degrade gradually in the reservoir, concentrating the significant polar and asphaltene fractions in the residual crude. Over time, physical, chemical and biological weathering brought on by crude oil degradation modifies the oil's characteristics. Evaporation, emulsification, natural dispersion, water-soluble compound dissolution, photooxidation, sedimentation and biodegradation are some of these processes. These activities decrease the API gravity and raising the viscosity, sulphur and metal content, this tends to lower the crude oil's commercial value. Due to a drop in the volume of refinery distillates and an extraordinary increase in vacuum residue yields, biodegradation significantly reduces the commercial significance of crude oil[3,4].

Biodegradation process in the oil reservoir has a significant impact on the fluid characteristics of hydrocarbons. The initial stage of biodegradation is defined by the loss of regular alkanes and acyclic isoprenoids (pristane and phytane). Terpanes and steranes have a strong resilience to biodegradation, however studies have shown that these biomarkers can deteriorate to some extent (extensive microbial degradation) during a harsh weathering process[5].

According to Vergeynst, et al.[6], the microbial communities will undergo dynamic changes throughout oil degradation in response to modifications in the characteristics and composition of the oil. A more varied group of genera that break down polycyclic aromatic hydrocarbons (PAHs) and progressively more complex structures will follow a few hydrocarbonoclastic species that usually predominate in the first phase, breaking down readily accessible n-alkanes and volatile compounds[7,8]. The majority of bacteria that break down oil are members of the Alpha- and Gammaproteobacteria groups.

The thermal maturity of crude oils is determined by the hopanes and steranes biomarkers, which indicate the oil's thermal history[9,10]. Over the whole oil-generative window, biomarker measures are a useful way to rank the relative maturity of petroleum.

Petroleum rank can be correlated with oil window regions (e.g., early, peak or late generation). This information can provide a clue to the quantity and quality of the oil that may have been generated and when combined with quantitative petroleum conversion measures (e.g., thermal modelling programs), can help estimate the timing of petroleum expulsion[11,12].

This study undertakes a comparative evaluation of the biodegradation and maturity levels of some crude oils from two producing fields in the Niger Delta, Nigeria.

Study area

The study was conducted within the Niger Delta region of Southern Nigeria, a geologically significant and hydrocarbon-rich basin situated between latitudes 4°N and 6°N and longitudes 5°E and 8°E. Covering approximately 70,000 square kilometers, this region hosts several prolific oil and gas fields, making it the epicenter of Nigeria's petroleum industry[13,14]. The area is ecologically sensitive, consisting of mangrove swamps, rivers, estuaries and floodplains. These geographical features, combined with intensive oil exploration, have rendered the region susceptible to environmental degradation and complex hydrocarbon dispersion patterns[15].

Crude oil samples for this study were sourced from four strategic locations within the Niger Delta Imo field, Nembe field, Soku field and the FPSO Rio Spirit field each with distinct geochemical characteristics and operational histories **(Figure 1)**.

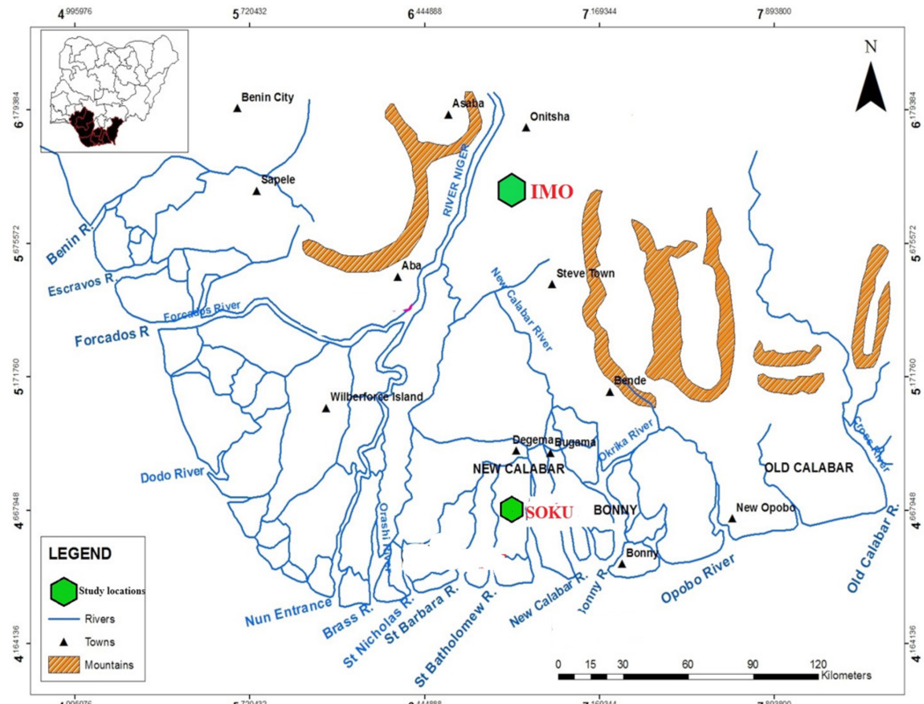

Figure 1: Map of study area showing sample locations in Southern Nigeria.

Reijers[16] opines that the geology of the study area in southern Nigeria dictates the onshore limits of the Niger Delta basin and hence the eastern edge of the Dahomey basin and eastern offshore limits of the Niger Delta basin. Its three geologic formations-Benin, Agbada and Akata-are located in the Gulf of Guinea **(Figure 1)**, according to Haack, et al.[17]. The petroleum system of Niger Delta has been built as the Tertiary Petroleum System (also kownn as the Akata-Agbada Petroleum System, **Figure 2**). The basin in the area has been divided into three lithostratigraphic units namely the Benin, Agbada and Akata formations[18]. In the coastal environment the youngest formation is Benin (Oligocene), under which, in a transitional to marine environment, is the Agbada (Eocene) formation, which consists of interbedded sandstone and shale. The Akata is a massive marine shale reservoir that is interbedded with a sandstone reservoir, with a paralic sequence; it is of paleocene age. According to Ekweozor and Daukoru[19] and Onojake and Abrakasa[20], crude oil might be found in the Agbada and Akata formations in the Niger Delta area. There are six or seven east-west bound units in the basin, which map to depobelts.

Niger Delta stratigraphic column

The three primary formations of the Niger Delta are the Akata, Agbada and the Benin formations, which is located in the south of Nigeria and is rich in petroleum. The first formation, Akata, is a structure formed from the sea at the bottom of the delta. In addition, it starts in the Paleocene and continues into the Recent, is very pressured and is under the delta. The composition of this formation is displayed in **(Figure 2)**, which is composed of thick shale structures, marine sedimentary sand, potential source rocks, reservoirs in deep water and only a small amount of clay and silt. Stacher[21] reports that low energy, low oxygen conditions are responsible for the formation of the akata, which occurs in low-lying areas where organic debris and clays from land were transported deeper in water. Doust and Omotsola[18] estimate that the formation's thickness is around 7,000 m. The Agbada is the dominant shale and sand block containing petroleum and believed to have been formed during the Eocene to Recent Period. The deltaic formation is the upper part of a sequence that is more than 3,700 m thick and consists of paralic siliciclastic. The lower Agbada formation consists of nearly equal amounts of both sandstone and shale. In the upper part, however, there are occasional shale interbeds; most of the upper part consists of sand. Continental sediments and high coastal plain sands up to 2000 mitres thick make up the Benin formation, which is located after the Agbada formation and dates back to the late Eocene to the recent past[22]. The higher Benin formations contain continental rocks that contain freshwater. Continental sand and gravel stone make up the upper Benin formations, which include freshwater. Between the late Eocene and the recent past, a continental deposit of the sediments of the upper littoral plain, possibly as thick as 2000 meters, was formed **(Figure 2)**.

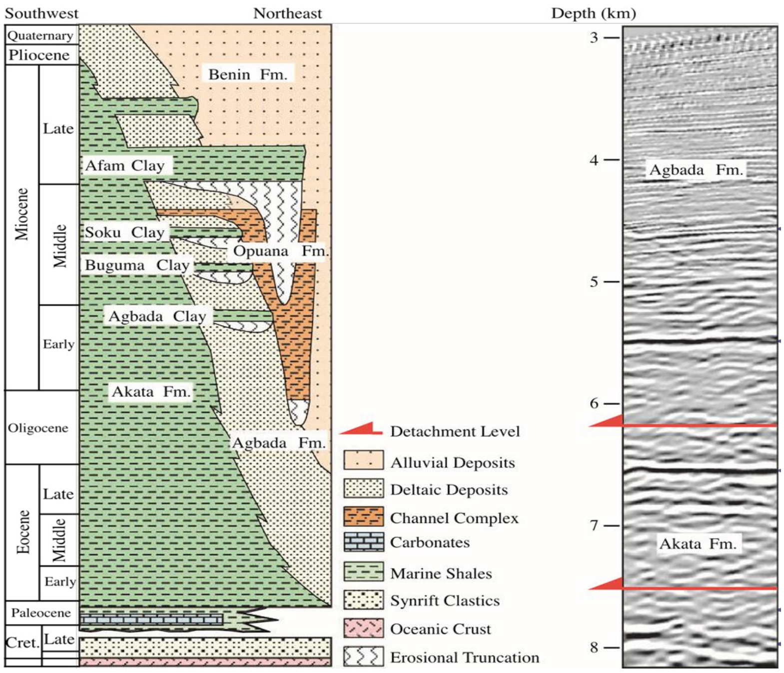

Figure 2: Regional stratigraphy of the Niger Delta basin and the variable density-seismic display of the major stratigraphic sections

Materials and Methods

Sample collection

Crude oil samples were collected from the Imo and Soku producing field using glass sample vials with Teflon caps. The caps of the vails were tightly sealed immediately after collection to prevent contamination and minimize volatilization of light hydrocarbons. All sample containers were clearly labelled with relevant metadata, including field name, date and time of collection. Following collection, the sealed vails were stored in ice coolers and transported under controlled conditions to the laboratory for analysis.

Fractionation of crude oil samples by column chromatography

The column chromatography oil sample fractionation was carried out with dichloromethane (DCM) (70mL) for the aromatic fraction and petroleum ether (70mL) for the aliphatic fraction. The excess solvent was removed by careful evaporation in a sand bath followed by removal of the N2 gas, which resulted in the recovery of the aliphatic portion[20].

Gas chromatography-mass spectroscopy analysis of the aliphatic fraction

Gas chromatography-mass spectrometry (GC-MS) was used for the analysis of aliphatic hydrocarbon fraction. A split/

split less inlet/injector of 280 ° C was connected to a standard Hewlett Packard 5890II GC and an HP 5972 MSD (mass spectrometry detector). The above apparatus was used under operating conditions of 70eV electron voltage, 220A filament current and 160°C source temperature. It was monitored for the data collection with the HP Vectra PC chem station computer in full scan mode (FSM) and selected ions mode (SIM). The sample was diluted and 1μL injected into the intake using the auto-sampler HP 7376 (290 oC); it was then split open after 1 minute. A capillary column (30 m x 0.25 mm ID DB-5) coated with 0.25 m (film thickness) 5% phenylmethyl silicone (HP-5) and sintered with silica was used to accomplish components separation. The gas chromatograph (GC) was heated from 40 to 300^{0}C at 4^{0}C/minute for an additional 16.7 to 20 minutes. Helium was the carrier gas with a slit size of 30 mL/min and 1.0 mL/min at 500 Kpa. A digital audio cassette (DAT) was used to capture the data and the RTE integrator was used to integrate the peak **(Figures 3A, 3B)**.

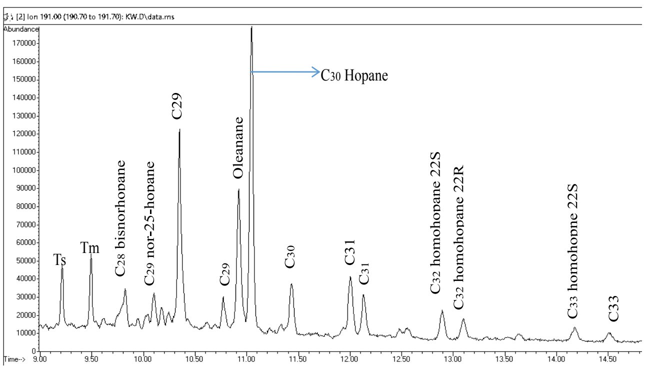

Figure 3(A): Representative GC–MS chromatogram of m/z 191 of hopanes for Imo crude oil samples.

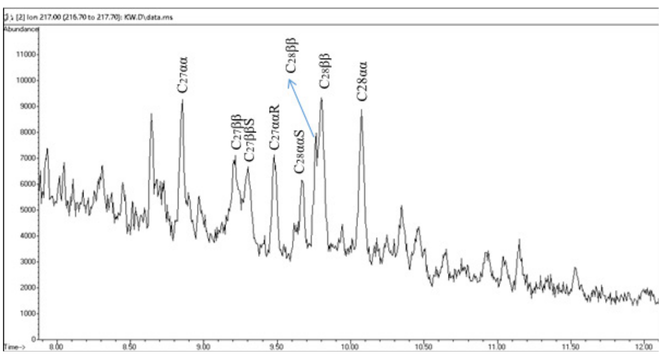

Figure 3(B): Representative GC–MS chromatogram of m/z 217 of the steranes for Soku crude oil sample.

Results and Discussion

Results

Results discussion

Crude oil thermal maturity: The thermal maturity experienced by source rock or crude oil (catagenesis) and the degree of biodegradation can be evaluated using biomarkers. The thermal maturity of the crude oil samples was evaluated using the calculated Ts/(Ts+Tm) ratio, a widely accepted geochemical parameter for assessing the maturity of petroleum systems. This biomarker ratio reflects the degree of isomerization of hopanes under increasing thermal stress and is particularly useful in distinguishing immature from mature oils. In this study, all four crude oil samples exhibit Ts/(Ts+Tm) values ranged between 0.40 to 0.53 and the values were less than 1.0, which suggests that the oils are within the early to mid-stages of maturity, but have not yet reached full thermal maturity **(Figure 4)**.

Table 1: Concentration of different Hopane components in crude oil samples.

	WELLS			
HOPANE COMPONENTS	**IM_A CRUDE**	**IM_B CRUDE**	**SK_A CRUDE**	**SK_B CRUDE**
Ts	46128	46130	15438	15440
Tm	40851	40852	21436	21436
αβC_{28}BisnorHopane	-	-	-	-
αβC_{29}Hopane	134279	134282	65263	65268
C_{29}Ts	35538	35540	12403	12412
Oleanane	218709	218712	92974	92981
αβC_{30}Hopane	260390	260393	126120	126126
βαC_{30}Moretane	46192	46197	29063	29065
αβC_{31}SHopane	80943	80950	29090	29097
αβC_{31}RHopane	58526	58530	20732	20738
αβC٣٠Gammacerane	-	-	-	-
αβC_{32}SHopane	70757	70760	27354	27360
C_{32}abRHopane	43873	43878	13497	13499
C_{33}abSHopane	34181	34190	9364	9367
C_{33}abRHopane	35105	35110	9479	9482
C_{34}abSHopane	23840	23845	6444	6455
C_{34}abRHopane	12323	12329	4049	4059
C_{35}abSHopane	13797	13799	-	-
C_{35}abRHopane	5995	5999	-	-

Table 2: Calculated biomarker indicators from different Hopane components in crude oil samples.

	WELLS			
CALCULATED BIOMAKRER INDICATORS	**IM_A CRUDE**	**IM_B CRUDE**	**SK_A CRUDE**	**SK_B CRUDE**
Ts/Ts+Tm	0.53	0.50	0.42	0.40
S/S+RαβC_{31}Hopane	0.58	0.58	0.58	0.58
Oleanane/C_{30}Hopane	0.84	0.85	0.73	0.78
C_{29}/C_{30} Hopane	0.52	0.54	0.55	0.59
Moretane/C30 hopane	0.18	0.19	0.23	0.25
Ts/Tm	1.13	1.18	0.72	0.77
C_{29}/C_{29}Ts	3.78	3.79	5.26	5.30
C_{31}S/C_{31}R	1.38	1.40	1.40	1.47
C_{32}S/C_{32}R	1.61	1.66	2.03	2.08
Gammacerane/C_{30} Hopane	-	-	-	0.42

The calculated maturity ratios are as follows: IMA crude (0.53), IMB crude (0.50), SKA crude (0.42) and SKB crude (0.40) **(Table 2)**. These values indicate that all samples are in a moderately mature state The ratio between Ts/(Ts+Tm) diastereoisomers, indicates incomplete isomerisation of the biomarker compound[23]. Anyanwu, et al.[24] previously reported similar findings in a geochemical study of Niger Delta oils, where the Ts/(Ts+Tm) ratio was used as a maturity indicator and found to be effective in classifying oils in the early to mid-oil window. Likewise, Omotoye, et al.[25] confirmed that values below 0.6 generally reflect a low to moderate level of maturity.

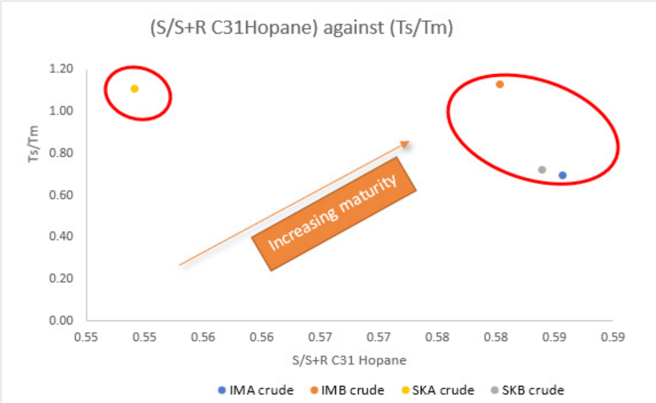

Figure 4: Plot of (Ts/Tm against S/S+R C31 Hopane).

Gas chromatography-mass spectrometry (GC-MS) analysis supports this conclusion, as the distribution of aliphatic and aromatic hydrocarbons especially tricyclic terpanes and hopanes remains consistent with oils generated from source rocks that have not yet reached peak maturity. Previous studies by Xu[26] emphasized that while hopane-based ratios such as Ts/(Ts+Tm) are useful, other parameters like methylphenanthrene indices and triaromatic steroids offer complementary insights into oil maturity, especially in oils that have undergone alteration or biodegradation. Some authors further noted that maturity trends in crude oils can be cross-verified using aromatic biomarkers, which tend to respond more sensitively to thermal stress than hopanes or steranes[26,27].

In addition to individual ratios, the maturity trend can be visualized through biomarker cross-plots, such as Ts/Tm versus the S/(S+R) αβC31 hopane ratio **(Figure 4)**, which offers a comparative maturity profile. In the current dataset, the four crude oil samples IMA crude, IMB crude, SKA crude and SKB crude, cluster closely in their Ts/Tm values (1.13, 1.18, 0.72 and 0.72 respectively), indicating a consistent maturity range across these samples **(Table 2)**.

While the overall results suggest moderate maturity, it is important to consider that observed maturity can be influenced by additional geological factors such as source rock facies, burial depth and post-depositional alterations including biodegradation. These factors may affect biomarker integrity and should be accounted for in comprehensive maturity assessments[24,25].

Biodegradation status of the crude oils

The process of Biodegradation of petroleum hydrocarbons is a complex process and depends on the nature and the amount of the hydrocarbons present. These Petroleum Hydrocarbons varies in their vulnerability to microbial attack. High molecular weight compounds, such aromatics and most biomarkers are resistant to microbial degradation[28].

The biodegradation status of the crude oil samples (IMA crude, IMB crude, SKA crude and SKB) were evaluated using the C29 norhopane to C30 hopane ratio, a recognized biomarker indicator for microbial alteration in petroleum systems **(Table 2)**. This ratio reflects the generation or accumulation of 25-norhopanes, which typically increase in concentration as a result of microbial demethylation of hopanes during biodegradation. According to Shi, et al.[29], this biomarker serves as a reliable proxy for identifying severely biodegraded oils, especially when combined with other geochemical data.

In the present study, **(Figure 5)** ranks the samples according to their biodegradation levels. The results indicate that SKA and SKB are more degraded than the IMA and IMB crudes as inferred from elevated 25-norhopane concentrations. This observation aligns with the findings of Wang, et al.[30], who emphasized that the relative abundance of 25-norhopanes increases significantly in oils subjected to microbial activity, especially under reservoir conditions conducive to biodegradation. In the addition **(Figure 6)** is the comparison of the biodegradation levels of the crude showing that SKA and SKB were more degraded than the IMA and IMB crude oil samples.

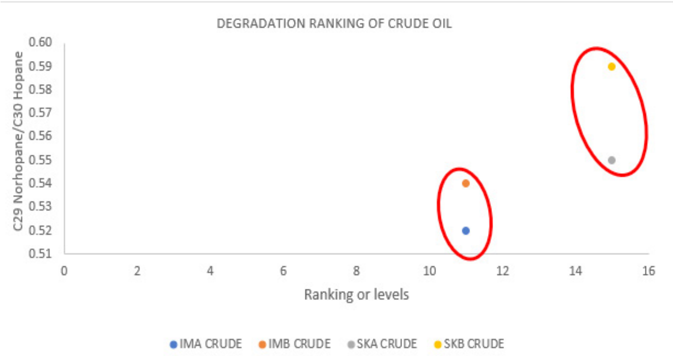

Figure 5: Plot of Degradation Ranking of Crude Oil.

The formation of 25-norhopanes has been linked to the microbial removal of methyl groups at the C-10 position of regular hopanes a process commonly referred to as demethylation. Xiao, et al.[31] explained that this transformation occurs under anaerobic conditions and is facilitated by specific microbial consortia that thrive in shallow reservoirs or near the oil-water contact, where biodegradation is most active. Therefore, the observed differences among the crude oils can be attributed to variations in reservoir conditions, microbial exposure and oil residence time[31].

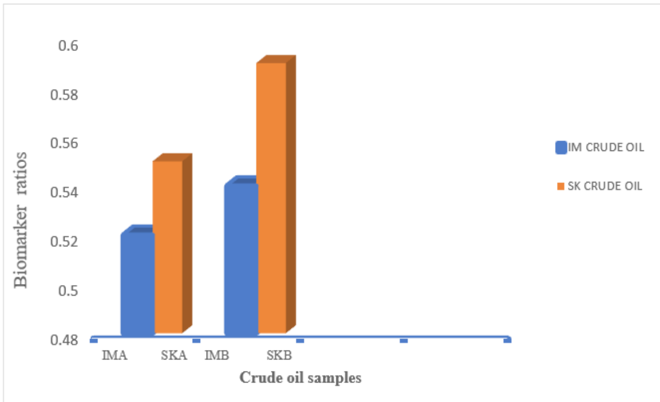

Figure 6: Comparison of the level of biodegradation using biomarker ratios

In addition to biomarker changes, the chemical structure of hydrocarbons influences their resistance to biodegradation. Aromatic compounds, for instance, are generally more resistant than aliphatic ones due to their stabilizing ring structures and alkyl substituents. Xiao, et al.,[31] noted that within a homologous series, isomeric forms may also exhibit different biodegradation resistance, making it crucial to consider molecular configurations in assessing oil alteration. The implication is that while hopanes and their norhopane derivatives are excellent indicators of microbial alteration, the overall hydrocarbon composition can modulate the visible effects of biodegradation[31].

Furthermore, environmental conditions such as temperature, pH, water saturation and nutrient availability can significantly impact biodegradation intensity. Shi, et al.[29,32-35]. emphasized that oils exposed to more favorable microbial environments may undergo extensive alteration, even if they originate from the same geological formation.

Conclusions

This research evaluated the maturity profile and biodegradation levels of crude oil samples from two producing fields: Imo and Soku fields in the Niger Delta. The biodegradation of the crude oils in terms of C29 norhopane/C30 hopane proportion revealed that SKA and SKB crude oil were more biodegraded compared to the IMA and IMB crude oil samples. The thermal maturity of the crude oils was evaluated through the plot of the ratio of Ts/Ts+Tm indicating that all samples are of moderate maturity and that they belong to the early to mid-oil generation range.

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Competing Interests

Authors have declared that there is no competing interests.

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