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Assessment of Thermal Maturity of Crude Oils Using Biomarker Fingerprinting

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The study assesses the thermal maturity levels of crude oils from the Niger Delta Basin of Nigeria using biomarker fingerprinting technique. Thirteen (13) crude oil samples were deasphaltened by the addition of n-heptane. The maltene fractions were analysed using the Gas Chromatography-Mass Spectrometer (GCMS) in Selected Ion Mode (SIM) to obtain the biomarker chromatograms. The respective biomarker thermal maturation peaks were extracted and their ratios computed. The odd to even predominance (OEP) and carbon preference index (CPI) values vary from 0.94 to1.08, with an average value of 1.02 and 1.01 to 1.12, with a mean value of 1.07 respectively. The ratios of Pr/n-C17 and Ph/n-C18 for the samples vary from 0.44 to 1.04, with a mean value of 0.73 and 0.53 to 0.77 with a mean value of 0.63, respectively. The Ts/Tm ratio ranges between 0.56 to 1.25. The Ts/(Ts+Tm) ratio ranges from 0.36 to 0.56. The C_{32} 22S/(22S + 22R) hopane ratios for the samples range between 0.53 to 0.58. The C_{29} sterane maturity ratios 20S/(20S + 20R) and ββ/(ββ+αα), vary from 0.33 to 0.56 and 0.34 to 0.67, respectively. The estimated biomarker maturation parameters suggest the analysed samples reached and or exceeded the peak of the oil generation window, with high levels of thermal maturity.

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Keywords: Thermal maturity; crude oil; biomarker; Niger delta.

1. INTRODUCTION

The world energy demand is increasing continually and Africa has been a player in meeting this demand. African countries like Nigeria, Algeria, Angola, Libya, Ghana, and Egypt have steadily increased their average daily output yearly. However, the continent is currently ranked as the third largest exporter of oil after the Middle East and South America, with the Niger Delta as the most important petroliferous basin in Africa [1,2]. Investment in exploration and production of hydrocarbon in Africa has been massive especially in offshore basins and predictions show that investment in the West Africa sub region will exceed those of the Gulf of Mexico and the North Sea in the near future [3,2]. The Niger Delta Basin is located in the Southern part of Nigeria between latitudes 4°00''N to 6°00''N and longitudes 3°00''N to 9°00''N (Fig. 1), and occupies an area of about 300,000 km^2 with a sediment thickness of about 2 km at the flanks of the basin [4] and 12 km at the basin centre [5,6,2].

During any exploration activity, there is always an interest not only to know the source of the hydrocarbons in a reservoir but also to be informed on the thermal maturity of those oil samples, since this knowledge helps the petroleum geochemist with decisions on the production and development of a field [2]. The evaluation of the maturity level of petroleum has an important implication for hydrocarbon exploration because it allows for the determination of the possible maturation stage of oil expulsion. Also, prediction of the discovery of hydrocarbon accumulations and their phase types in the deeper parts of geological sections or undrilled zones of the basin[7]. Conventional geochemical methods used to assess source-rock maturity include Rock-Eval pyrolysis, compound class distributions, vitrinite reflectance (Ro), thermal alteration index (TAI) (spore coloration), and carbon preference index (CPI). However, few of these parameters can be applied to crude oils. Molecular parameters based on ratios and distributions of specific biomarkers have found increased use in studies of thermal maturity [8].

Biological markers (biomarkers) are present in soil extracts, sediment extracts, rock extracts, and oils. They are primarily hydrocarbon compounds, made of complex organic molecules. Diagenesis and oil generation processes do not significantly affect their chemical structures. This makes it possible for them to be retraced to the original molecules in once living organisms. Thus, this explains why they are usually referred to as molecular fossils. They are similar in structure and are products of diagenetic alteration of particular natural products [9]. Generally, biomarkers maintain all or majority of the natural product’s carbon skeleton, and this resemblance in structure called for the name "molecular fossils" [9]. Thermal stress can cause a chemical transformation from one chemical structure into another and as a result, these biomarkers’ ratios can be employed as a maturity marker [9]. Some terpane and sterane biomarker ratios are sensitive to changes in thermal maturity and likely record the maturity of the corresponding source rock at the time the oil was expelled (primary migration). These include C_{27} and C_{29} norhopanes, diahopanes, diasteranes, and triaromatic steranes as well as methyldibenzothiophenes. C_{29} sterane 20S and 20R isomer ratios are useful at lower maturities. Typically, biomarkers are measured using conventional GC-MS techniques (SIM mode) on saturate (or branched-cyclic) and aromatic hydrocarbon fractions derived from liquid chromatography [10]. This paper assesses the thermal maturity level of thirteen (13) Niger Delta crude oils using biomarker signatures.

1.1 Geological Setting

Three major stratigraphic units are present in the Niger Delta (Fig. 2); they are the Akata, Agbada and Benin Formations [4,11]. Although there is a strong indication of a Cretaceous shale that lies unconformably on the basement complex, however, the distribution is generally unknown[4]. However, recently Geoexpro was able to show that a regional Cretaceous shale exists on the basement complex with thicknesses of about 2 km in the offshore part of the Basin, based on 18 seconds two-way travel time (TWT) seismic measurements [12]. The Cretaceous shales have so far not been drilled in the Niger Delta region mostly because they are beneath the over pressured formation and the thick overburden pile above them [13]. The lateral equivalent of these Cretaceous shales and Akata Formation in the adjacent Anambra Basin (located at the northeast of the Niger Delta) were deposited in the Albian to Palaeocene when the shoreline was concave [14]. This resulted in tidal dominated and river dominated sedimentation during transgression and regression [13]. These Cretaceous shale equivalents in the Anambra Basin include; Asu River shales (Albian-Cenomanian); Eze-Uku/ Awgu shales (Cenomanian to Santonian); Nkporo shales (Campanian-Maastrichtian) [15].

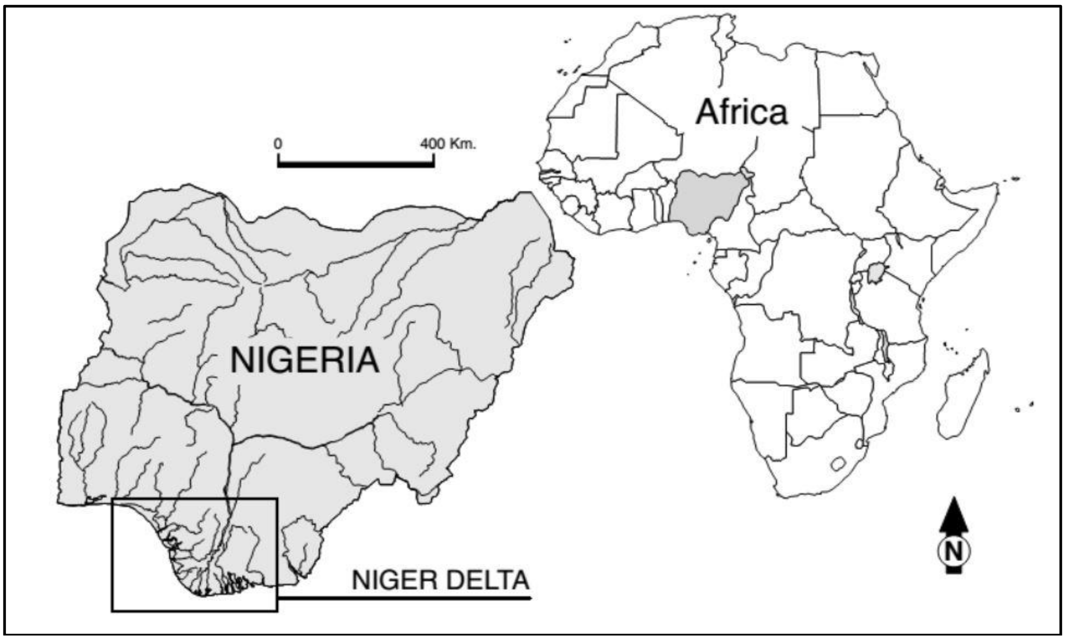

Fig. 1. Location of the Niger Delta Basin [11,2]

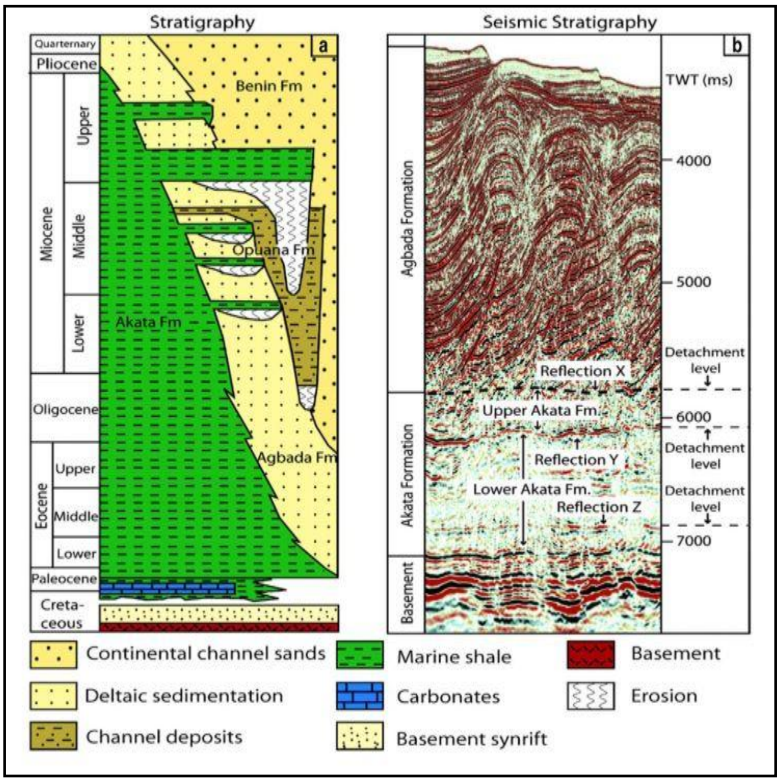

Fig. 2. Stratigraphy of the Niger Delta [16,17]

2. METHODOLOGY

Thirteen (13) crude oil samples from the Niger Delta Basin were used for this study. The samples were deasphaltened by the addition of n-heptane, and the maltene fraction fractionated into aromatics, saturates, and polar fractions. The saturates were further subjected to GCMS analysis. The biomarker chromatogram accession was controlled by the chemstation software in selected ion mode (SIM). The n-alkanes and isoprenoids for the analysed samples were distinguished using m/z 85, the sterane biomarkers were detected on m/z 218 and that of triterpane and hopane were identified on m/z 191. The biomarker chromatograms were compared to that of [8] for the identification of their peaks.

3. RESULTS AND DISCUSSION

To obtain an initial estimate of the thermal maturity of crude oil, the relative abundance of odd and even carbon numerated n-alkanes was used. The carbon preference index (CPI) [18] and the Odd-to-Even Predominance (OEP) [19] are included in these measurements. These parameters together with some biomarker thermal maturity parameters were used to evaluate the thermal maturity of the crude oils from the Niger Delta.

Low thermal maturity is suggested by CPI or OEP values significantly below 1.0. Values of 1.0 or higher indicate that an oil or rock extract is thermally mature [8]. The studied crude oil samples have OEP and CPI values varying from 0.94 to 1.08, with an average value of 1.02 and 1.01 to 1.12, with a mean value of 1.07 respectively. These values suggest that the studied samples are of high maturity levels [20]. The cross-plot of Pr/Ph against CPI in Fig. 3 corroborates the above conclusion. Only two (2) samples recorded OEP values less than 1.0 (0.94 and 0.97 respectively).

The ratios of Pr/n-C_{17} and Ph/n-C_{18} for the studied samples vary from 0.44 to 1.04, with a mean value of 0.73 and 0.53 to 0.77 with a mean value of 0.63, respectively. The low values for Pr/n-C_{17} and Ph/n-C_{18} ratios suggest high maturation levels for the studied crude oils as well as no biodegradation effects [21].

The Ts and Tm biomarkers ratio is often used as a maturity indicator in the terms Ts/(Ts + Tm) and Ts/Tm ratios [22,8,23,24], where Ts is more stable than Tm for thermal maturation. The Ts/(Ts + Tm) ratios, however, increases with increasing maturity [8,23,24]. The Ts/Tm ratio (0.56 to 1.25) for the studied samples reflects the same interpretation (high maturity) as do the ratios of Ts/(Ts+Tm) of 0.36 to 0.56.

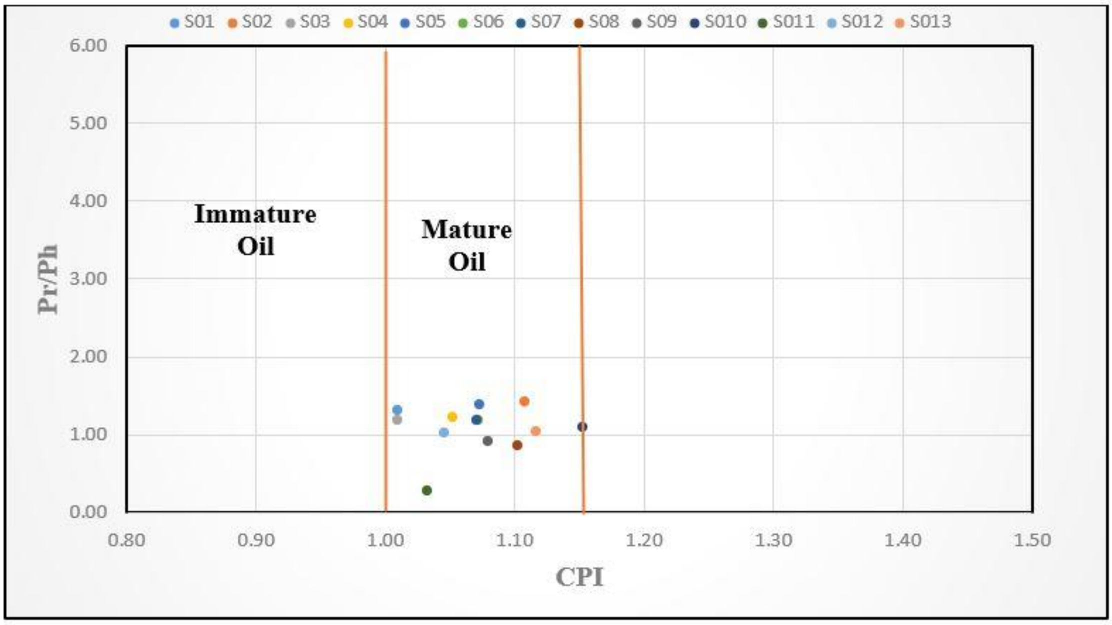

Fig. 3. Pristane/Phytane versus CPI showing the Maturity of studied Crude Oils

The hopane ratio, computed using the relation; C_{32} 22S/(22S + 22R) is a frequently used biomarker maturity parameter [8]. The ratio of C_{32} 22S/(22S + 22R) increases during maturation from 0 to 0.6 (0.57 to 0.62 = equilibrium) [25,8].Crude oil samples that show C_{32} 22S/(22S + 22R) ratios in the 0.50 to 0.54 range have just entered oil generation, whereas ratios in the interval 0.57 to 0.62 denote the principal stage of oil generation has been reached or exceeded [25,8]. The samples analysed indicate values in the range of 0.53 to 0.58, denoting high maturity levels for the studied oils [25,26]. This oil maturity level is also examined from the C_{29} sterane ratios of 20S/(20S + 20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$ as these ratios step-up with increasing maturity [27]. The C_{29} sterane maturity ratios 20S/(20S + 20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$, varying from 0.33 to 0.56 and 0.34 to 0.67, respectively, denote thermal maturation levels of low to high for the studied samples, consistent with their generation from early-oil window to peak oil window [8,22] as shown in Fig. 4.

The above assertion is corroborated by the C_{29} steranes cross-plot of $\beta\beta/(\alpha\alpha + \beta\beta)$ versus 20S/(20S + 20R) (Fig. 5). The cross-plot is particularly effectual in explaining the thermal maturity of source rocks or oils and could be applied in comparing one maturity parameter with another [27].

The majority of the studied samples fell within the zone of equilibrium (peak oil window), with some above the zone of equilibrium, denoting high maturity. However, a few samples fell below the equilibrium zone (early maturity/ early oil window).

The cross-plots in Figs. 6 and 7 are consistent with the above conclusions. The moretane/C_{30} hopane has eminent specificity for immature to early oil generation and it is evaluated by using *m/z* 191 chromatograms [8]. The 17β,21α(H)-moretanes ratio to their corresponding 17α,21β(H)-hopanes diminishes with thermal maturation, approximately 0.8 in bitumen to <0.15 in mature source rocks and oils to a minimal of 0.05 [28,25]. The hopane ratios moretane/C_{30}, for the studied samples have low concentrations with values ranging from 0.21 to 0.43. The low values in concentration for the studied samples indicate the studied samples were generated at the initial stage of thermal maturation [28,25].

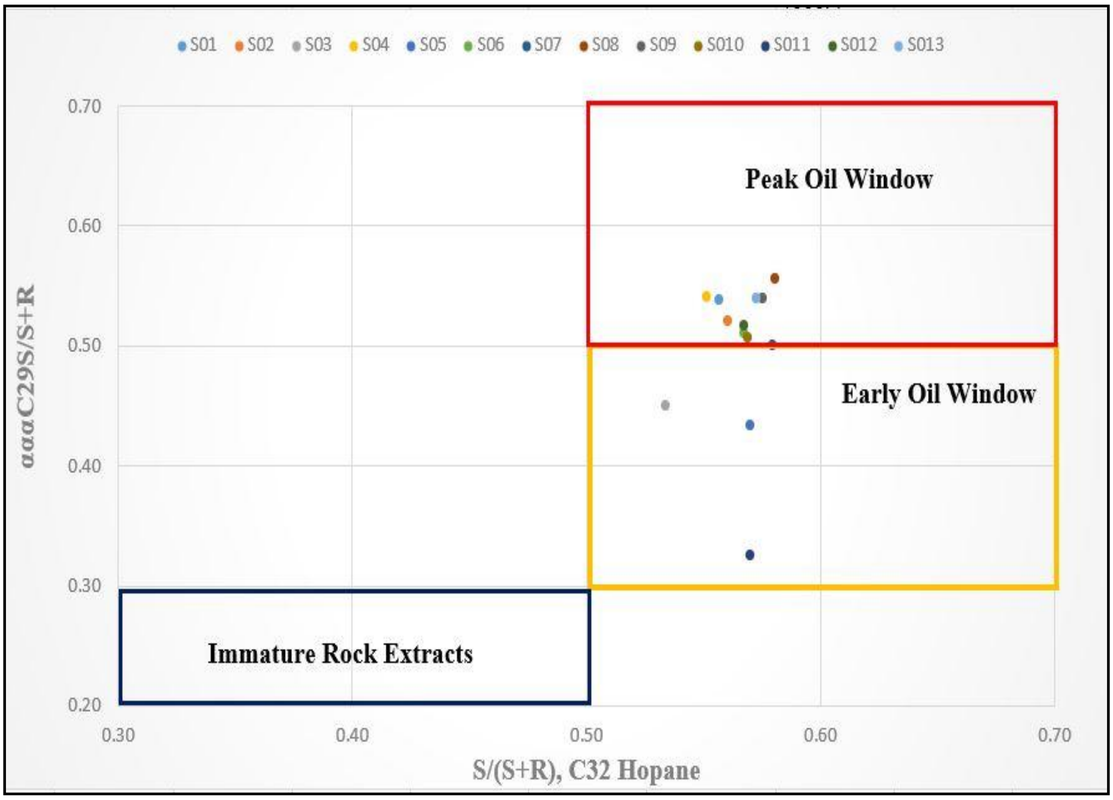

Fig. 4. C_{29} Sterane S/(S + R) versus C_{32} Hopane S/(S+R)

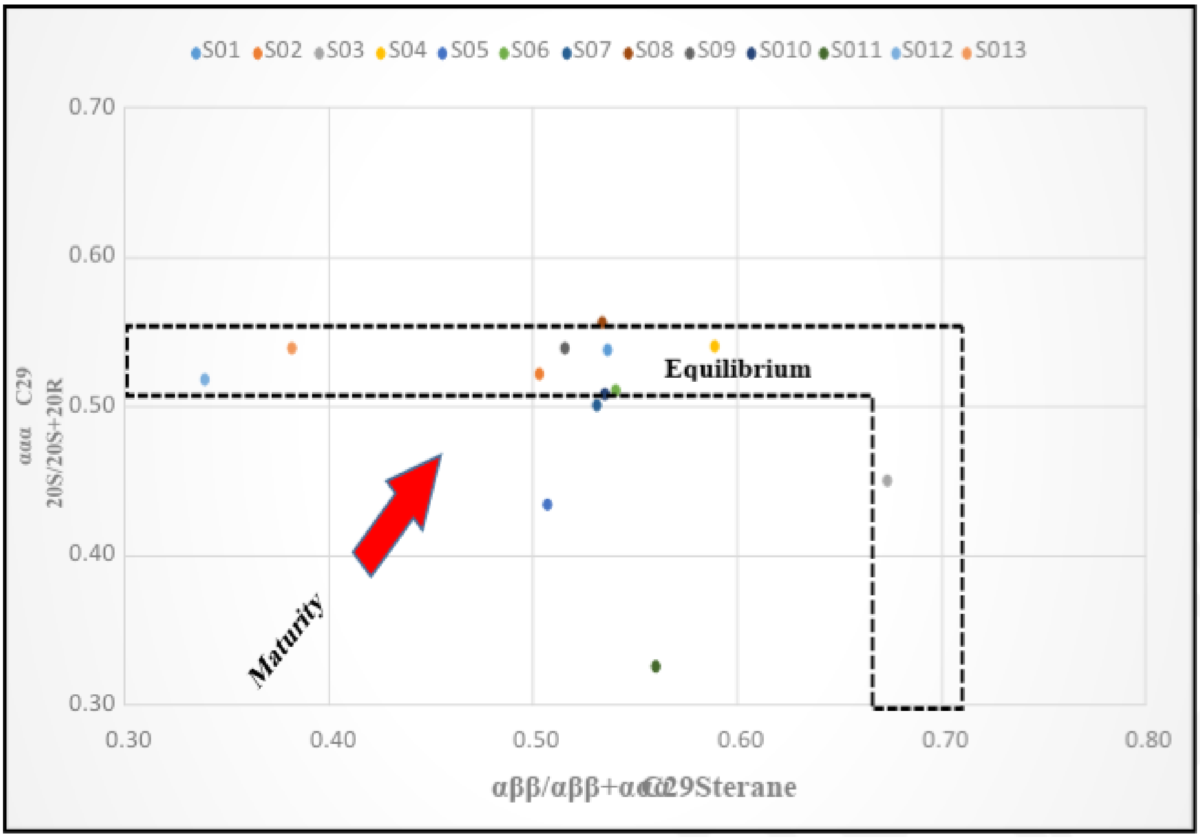

Fig. 5. Relationship between C_{29}ααα20S/(20S+20R) and C_{29} αββ/(αββ+ααα)

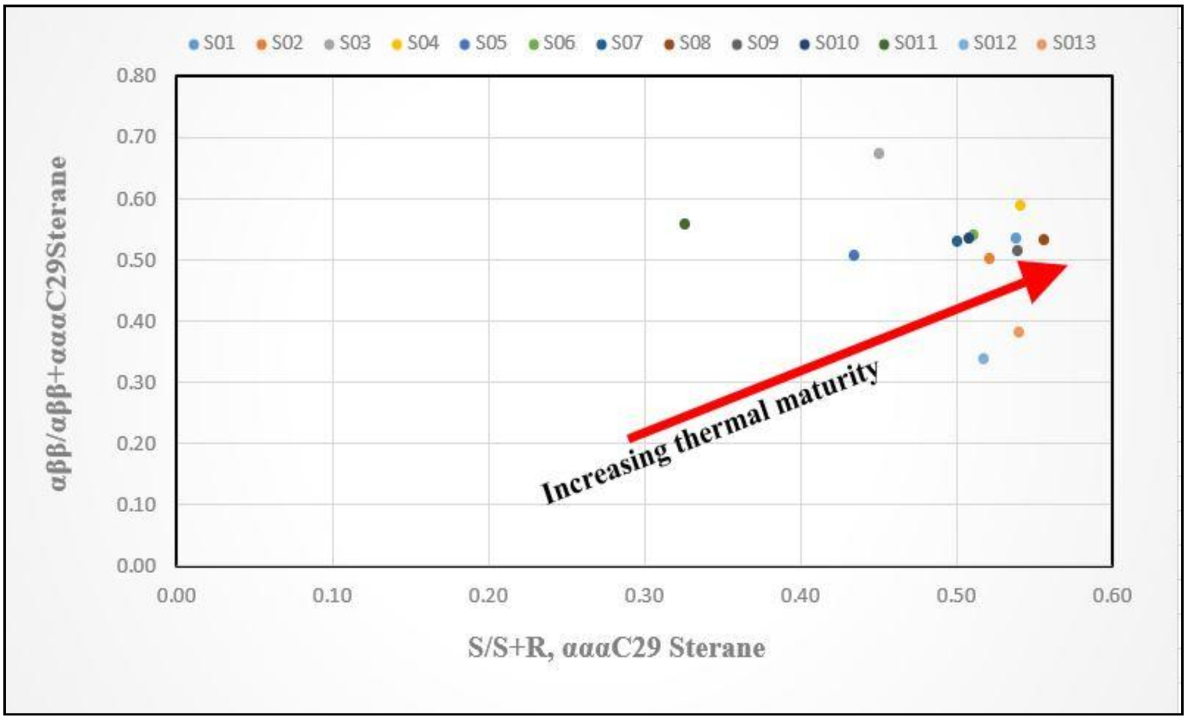

Fig. 6. Plot of the Sterane Index C_{29}αββ/(αββ+ααα) versus the Sterane Index C_{29}ααα 20S/(20S+ 20R)

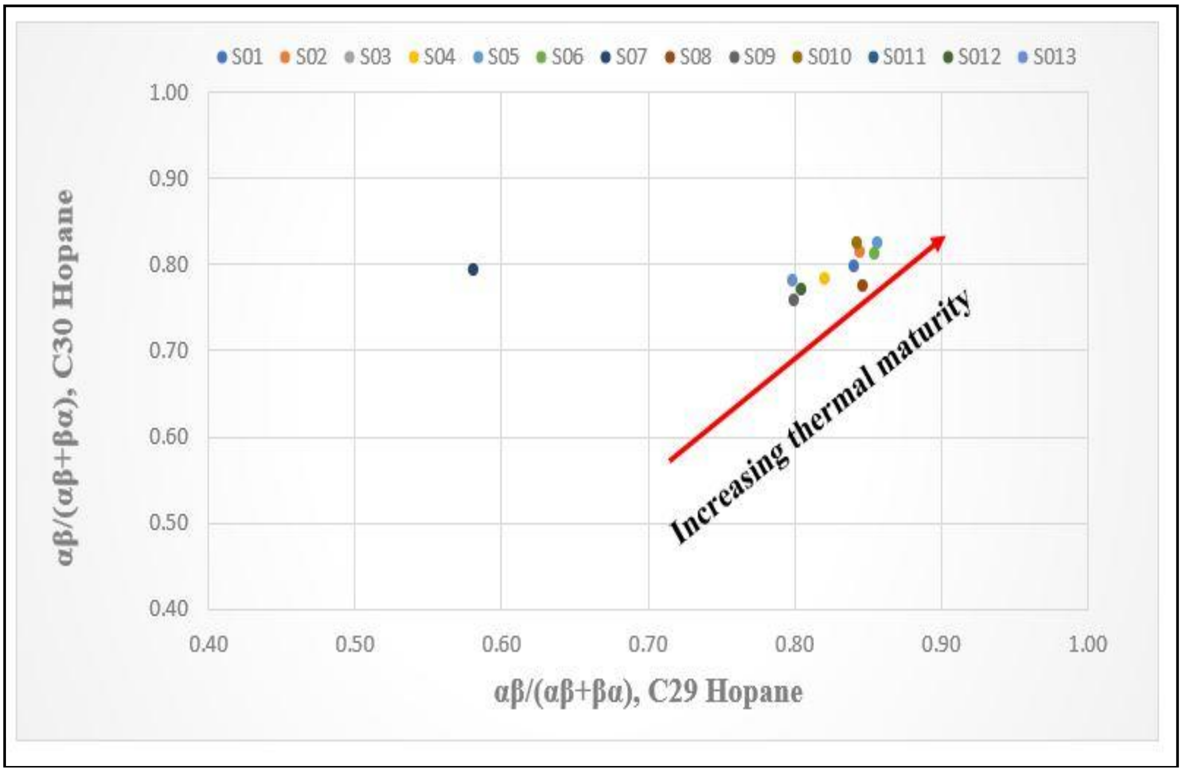

Fig. 7. Cross-plot of αβ/(αβ+βα) C_{30} hopane versus αβ/(αβ+βα) C_{29} hopane

4. CONCLUSION

The estimated biomarker maturation parameters derived from the saturate fraction of the analysed oils indicate that the oils have reached and or exceeded the peak of the oil generation window, with high levels of thermal maturity. The study demonstrates the effectiveness of the use of biomarker techniques in the assessment of crude oil thermal maturity levels and can be used to complement other thermal maturity assessment techniques.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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