Available online at http://www.sjbas.com.ng
Savanna Journal of Basic and Applied Sciences (June, 2020), 2(1): 41-52

P:ISSN 2695-2335 | E:ISSN 2705-3164

Geochemical Characterization of Crude Oils from Tertiary Reservoir Units in Trinidad, Eastern Venezuela Basin

[1]Abubakar, A. S. and [2] Phillips, O. A.
[1] Geology Department, Federal University Birnin Kebbi, Kebbi State, Nigeria
[2] Geology Department, The Polytechnic, Ibadan, Oyo State, Nigeria

ABSTRACT

Twelve crude oil samples from eight Tertiary reservoir units in Trinidad were analysed by using gas chromatography combined with mass spectrometry (GC-MS)) to achieve their geochemical characterization. The specific objectives were to establish genetic relationships between the oils; determine their maturity and source lithology; and unveil the environment of deposition and extent of biodegradation. The biomarker characteristics established is an indication that the oils were generated from open marine source rocks deposited in a reducing environment. This is consequent upon, the moderate pristane/phytane ratio (1.0-2.0); carbon preference index (CPI) and odd over even preference (OEP) close to 1; low dibenzothiophene/phenanthrene ratios; absence of 18α(H)-oleanane and; abundance of tricyclic terpanes. The oils are also characterised by high relative abundances of regular steranes, diasteranae and hopanes compared to tricyclic terpanes and correlation between the set of analysed oils also made possible. Overall, a single genetic type was established for the oils based on aliphatic and aromatic hydrocarbon fractions contained. Biodegradation was clearly evident in the majority of samples analysed as demonstrated by the presence of unresolved complex mixture and high Pr/nC_{17} and Ph/nC_{18} values. Thermal maturity assessment based on saturated and aromatic hydrocarbon maturity parameters showed that the oils are at least marginally mature and corresponds to the early oil generation window.

Keywords: Trinidad, Biomarker, Geochemical classification, Thermal maturity, Genetic relationship, Biodegradation

INTRODUCTION

Trinidad is situated within the Serrania del Interior and the Maturin sub-basins of the Eastern Venezuelan Basin, and together they constitute one of the largest oil provinces in the world (Persad, 2009). It is located in the southeast corner of the Caribbean Plate (Persad, 2009), and within the northeastern South American geologic province. This region as a whole, comprises petroleum reserves comparable in size to those located in the Middle East with 38 giant oil fields and a daily production greater than 4 MMBO (Escalona and Mann, 2011). The accumulations vary from heavy oil in Orinoco, Heavy Oil Belt, and light oil in offshore Venezuela and, natural gas in the Columbus Basin, Trinidad. These reserves are divided into three distinct basins: The Maracaibo foreland basin of western Venezuela (Escalona, 2003); the Eastern Venezuela Basin i.e. Maturin sub-basin (Parra *et al.,* 1989) and the Columbus foreland basin offshore eastern Trinidad (Garciacaro *et al.,* 2011). Trinidad is considered part of the Eastern Venezuela Basin and consists of many giant fields, such as Quiriquire, Pedernales and Corocoro on the Venezuelan side and Oropouche, Penal-Barrackpore on the Trinidad side.

Three oil provinces have been discovered since petroleum exploration in Trinidad began in 1866. They are the Land-Southern province, the Gulf of Paria province and the East Coast- Atlantic province (Talukdar *et al.,* 1990). The discovery of each of the fields led to a new peak of oil production. Production in the country varied between 50-80 million bbl/year during the last two decades (Talukdar *et al.* 1990). The East Coast province alone currently produces around 70,000 b/d or roughly half of the country's production (Talukdar *et al.,* 1990). Trinidad's daily crude oil production has fallen considerably from 230,000 bbl in 1978 to 43 Mbbl in the present day, prompting new exploration interest. Within the last 18 years, a series of large gas fields were found in the East Coast province in deeper offshore areas where no major oil fields are located. In addition, extensive drilling off the north coast of Trinidad in the early to mid-1970s also made significant additional gas discoveries (Persad *et al.,* 1980). Exploration interest in Trinidad has increased greatly in recent years because of the discovery of giant oil fields in the Maturin sub-basin of Eastern Venezuela, as well as the growing recognition of the huge petroleum potential of the Eastern Venezuelan basin as a whole, of which Trinidad is a part (Talukdar *et al.,* 1990).

Previous geochemical studies of the Pliocene and younger shales in Trinidad have indicated a predominance of terrestrially-derived gas prone kerogens capable of only biogenic methane generation at the burial depths sampled. Therefore, the oils are not indigenous to the producing formations and must have been generated in the underlying Miocene, Paleogene and or Cretaceous sections. Trinidad has a proven Late Cretaceous source rock which is assumed to be the only viable source rock contributing to its hydrocarbon accumulations. Meanwhile, most of the earlier geochemical work suggested that the crude oils of Trinidad belong to a single genetic type (Leonard, 1983; Ames and Ross, 1985; Ross and Ames, 1988). Considering the scanty information that exist on the geochemical characterization and the genetic relationship of oils in this province, it is thus necessary to contribute to the existing data on the subject. Consequent upon this dearth of relevant literature as at the time of this research, geochemical investigation of twelve (12) oil samples from eight Tertiary reservoir Units in Trinidad was undertaken. In this study a.) the number and classes of oils in the Tertiary reservoir units were determined; b.) biomarker analysis of the oil samples was done to enable

*Corresponding author. E-mail: egbenzuaagaga@gmail.com;. Tel: +234 8124252876.

source to oil correlation; c.) organic geochemical parameters based on biomarker distribution were used to investigate the source and thermal maturity of the oils, and paleoenvironment and extent of biodegradation of the oils were also determined.

The fields from which the oils were obtained include; the Forest Reserve, Guapo, Point Liguoure, WD 5&6, Barrackpore, Palo Seco, Point Fortin central and Oropouche (Fig. 1). In this research, emphasis was laid on the geochemistry of the oils, oil to oil correlations and oil alteration processes. Geochemical techniques such as Basin modelling, Rock Eval pyrolysis analysis and Vitrinite reflectance were not used because the samples and data for those approaches were not available.

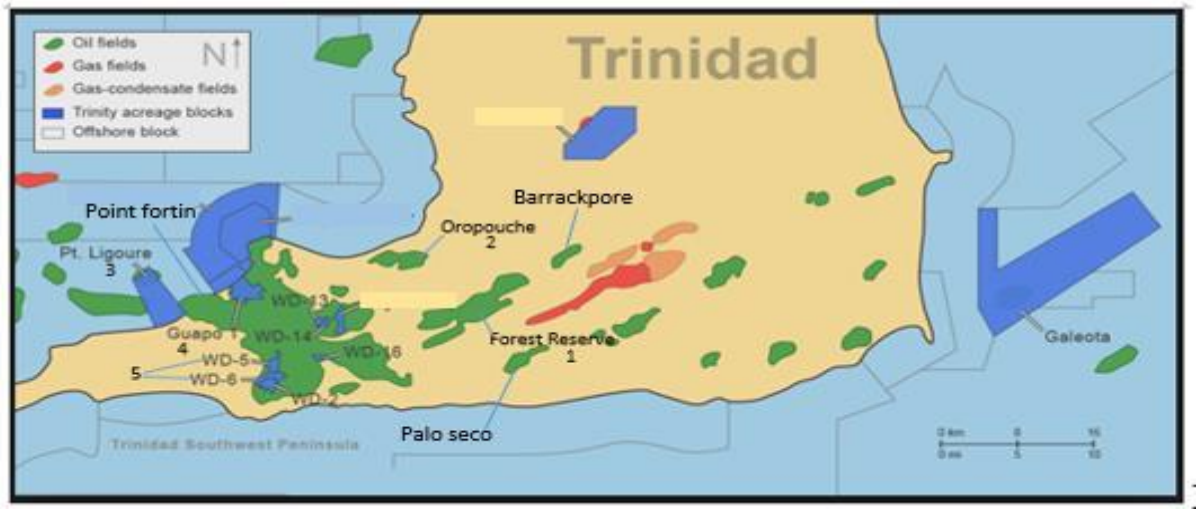

Figure 1. The location map of sampled oil fields in Trinidad Basin, Eastern Venezuela (Modified after Friedrich and Lavidas, 2015).

Geological Settings

Trinidad and its offshore areas occupy the eastern extension of the Eastern Venezuelan basin and can be considered as parts of larger north-eastern South American geologic province (Figueira, 2012). Its geologic history during Jurassic to Lower Cretaceous times, involves deposition of thick sediments in response to crustal attenuation and cooling during rifting of the North American and South American continents (Ames and Ross, 1985). The Upper Cretaceous to Eocene period followed with uninterrupted sedimentation on the passive continental margin of northern South America. During the Upper Cretaceous time upwelling conditions prevailed and prolific oil source rocks were deposited in outer shelf-upper slope environments along the entire passive margin of northern and north-western South America in what are now Trinidad, Venezuela, Colombia, Ecuador, and Peru (Talukdar *et al.,* 1990). Paleocene-Eocene sediments of Trinidad and Eastern Venezuela were deposited in marine environments along the passive margin and show progressive northward regression of the sea.

The tectonic setting changed dramatically in the region since Late Eocene/Oligocene times. An oblique collision of the Caribbean Plate with the South American Plate proceeded diachronously eastward along the northern margin of South America, becoming progressively younger eastward (Persad *et al.,* 1993). As a result, foreland basin conditions became prevalent (Persad *et al.,* 1993). The sediments deposited in this setting during the Oligocene-Middle Miocene period were tectonically emplaced as an east- northeast trending fold-thrust belt by the end of Middle Miocene time. The interior mountain belt of Eastern Venezuela and the Central Range and its subsurface extension to the north (up to El Pilar fault zone) in Trinidad are the eroded remnants of this deformed belt (Persad *et al.,* 1980). The foreland basin axis and the deformation migrated southward during the late Miocene. During Pliocene-Pleistocene times, as a result of the diachronous nature of the oblique collision, the depocenters and deformation moved eastward (Leonard, 1983). The infilling of the Maturin subbasin of Eastern Venezuela and the Caroni and Southern sub-basins of Trinidad all became increasingly continental (Talukdar *et al.,* 1990). In this post-sutural stage, construction of a continental embankment off the east coast of Trinidad took place. It is characterized with the deposition of very thick suites of deltaic and associated sediments that progrades over the continental shelf edge onto the oceanic crust (Talukdar *et al.,* 1990). With the building of the continental embankment, syndepositional detached listric and related growth faults and associated rollovers were developed. Oblique collision in Plio-Pleistocene times resulted in wrenching and associated structures in these sediments (Leonard, 1983).

Two Petroleum systems are recognised to exist in Trinidad, both of which share a common Cretaceous source, but geographically located in separate areas with different reservoir rocks and reaching maturity at different times (Persad *et al.,* 1993). The petroleum systems recognised includes the Naparima Hill-Cruse/Forest/M L'Enfer system known to exist in the Southern Basin onshore and in its extension offshore in the Gulf of Paria. The system has as its principal sources the Cretaceous Naparima Hill and Gautier formations (Persad, 1988) with its reservoir rocks being the much younger Cruse, Forest, and Mome L'Enfer marginal marine sands of Pliocene age. The second petroleum system is the Naparima Hill-Gros Mome system that is found mainly offshore the south and east coasts of Trinidad. This system shares the Naparima Hill and to a lesser extent the Gautier Formation with the Southern Basin as the principal source of the oil.

The principal reservoir rocks of this system are the Gros Mome and Mayaro formations of the Maruga group (Persad *et al.*, 1993).

MATERIALS AND METHODS

Sample Treatment and Experimental techniques

A total of 12 oil samples collected from Tertiary reservoir units in the Trinidad province were made available for this study by the Department of Geoscience in the Faculty of Civil Engineering and Geoscience, University of Newcastle, United Kingdom. The hydrocarbon fractions of all the samples were analyzed by Gas Chromatography with flame ionisation detection (GC-FID) to screen the main geochemical properties of the crude oils and for further detailed analyses by chromatography-mass spectrometry (GC-MS). The various analytical procedures considered include thin layer chromatography (TLC), gas chromatography (GC) and gas chromatography-mass spectrometer (GC-MS).

Thin Layer Chromatography

A glass plate coated with activated silica gel (0.5mm thick) was prepared by adding 80 ml of distilled water to 40g of silica gel (60F laser-coded) to form a slurry which was spread on the glass plates using a spreader. The plates were dried up in an oven to a temperature of about 110°C and then reactivated at least 2 hours before being used. Approximately 15 to 20 mg of the crude oil was diluted with 3-5 drops of dichloromethane (DCM), and then, carefully spotted onto the plate in a horizontal line using a pipette. Standards anthracene, phenyldodecane and docosane (n-C_{22}), were also spotted using a pippete in a single spot by dropping a single drop of each standard onto the plate across a vertical line drawn to avoid mixing of the standards with oil sample. A development tank was then filled with nearly 2 cm depth of light petroleum ether and the prepared plate then placed into the tank, covered and left undisturbed to allow the solvent rise up by capillary action. This was done without allowing the solvent cover the spots on the plate. The plate was then allowed to develop until the solvent reaches about half a centimeter below the top of the plate. At this point, the plate is fully developed and was removed from the glass tank and left to dry for a few minutes. Once dry, the plate was sprayed with Rhodamine 6G dye and visualized under ultraviolet light; to aid identification of aliphatic and aromatic hydrocarbon fraction bands. Subsequently, these bands were scraped off separately. Short glass columns were then clamped to a retort stand and prepared using a small piece of pre-extracted cotton wool with 1 cm of activated alumina on top, and washed through with some light petroleum ether. The fractions were collected in clean round bottom flasks using 25 ml n-hexane for the aliphatic fractions and a 25 ml mixture of DCM and n-hexane in the ratio 1:1 for the aromatic fractions. The solvent was removed using rotary evaporator, and the fractions transferred to GC vials and blown under a stream of nitrogen gas to 1 ml and 0.5 ml for aliphatic and aromatic fractions respectively. The fractions were then taken for further analysis by gas chromatography (GC-FID), and gas chromatography- mass spectrometry (GS-MS).

Gas Chromatography (GC-FID)

GC-FID analysis of aliphatic and aromatic hydrocarbon was performed on an Agilent 5890 GC in split less mode with the injector at 280°C and the FID at 300°C. The sample (1ul) in hexane was injected by an HP7673 auto sampler and the split opened after 1 minute. After the initial injection the GC temperature programme and data acquisition commenced. Separation was performed on a fused silica capillary column (30m x 0.25mm i.d) coated with 0.25um phenylmethyl polysiloxane (HP-5 phase). The GC temperature was programmed from 50°C-310°C at 5°C min and held at final temperature for 20 minutes with hydrogen as the carrier gas (flow 1ml/min, pressure of 50kPa, split at 30 mls/min). The GC data was acquired and stored for further data processing on a Thermo-Atlas laboratory data system.

Gas Chromatography-Mass Spectrometry (GC-MS)

In order to identify peaks in the gas chromatogram, the sample was also analysed by a GC-MS in SIM and scan mode to give a mass spectra or ion chromatograms. GC-MS analysis of the aliphatic and aromatic compounds was performed on an Agilent 7890A GC with a split/split less injector (280°C) linked to an Agilent 5975C MSD (electron voltage 70eV, source temperature 230°C, quad temperature 150°C multiplier voltage 1800V, interface temperature 310°C). The acquisition was controlled using Chemstation software, initially in full scan mode (50-600 amu/sec) and in selected ion mode (30ions 0.7cps 35ms dwell) for greater sensitivity.

The sample (1ul) in hexane was injected by an Agilent 7683B auto sampler and the split opened after 1 minute. After the solvent peak had passed the GC temperature programme and data acquisition commenced. The Separation was performed on an Agilent fused silica capillary column (30m x 0.25mm i.d) coated with 0.25um phenylmethyl polysiloxane (HP-5) phase. The GC was temperature programmed from 50-310°C at 5°C min and held at final temperature for 10 minutes with Helium as the carrier gas (flow rate of 1ml/min, initial pressure of 50kPa, split at 30 mls/min). The acquired data was later stored on DVD for later data processing, integration and printing. Peaks were identified and labelled after comparison of their mass spectra with those of the NIST05 library if > 90% fit or from their elution order from geochemistry literature.

The biomarkers of interest to this research are the n-alkanes, isoprenoids, steranes, tricyclic terpanes, hopanes phenanthrenes, dibenzothiophenes and their isomers. The individual biomarkers were identified by comparing the mass chromatograms with standard mass chromatograms. Non-biomarker parameters such as carbon preference index (CPI) and odd over even preference (OEP) were also assessed and reported.

RESULTS AND DISCUSSION

The resulting chromatograms showed the distribution of n-alkane, isoprenoids, sterane and hopane. Their individual peaks were identified, areas measured, and the data generated are displayed in Tables 1, 2, 3 and 4.

Table 1. Distribution of n- alkanes and isoprenoids ratios, and related parameters

Sample Name	Depth (m)		Reservoir Unit	Age	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	CPI	DBT/P	OEP
	Top	Bottom								
A	2390	1964	Forest Reserve	E. Pliocene	0.3	0.4	0.2	-	0.29	-
B	2170	2070	Guapo	E. Pliocene	0.2	0.2	0.6	-	0.35	-
C	7858	7790	Point Ligoure	E. Pliocene	1.1	0.3	0.2	-	1.11	-
D	6286	6173	WD 5 & 6	E. Pliocene	1.2	0.3	0.8	-	0.29	-
E	6390	6040	Forest Reserve	E. Pliocene	1.3	2.6	1.2	-	0.31	-
F	9858	7020	Guapo	E. Pliocene	0.4	0.1	0.5	-	0.29	-
G	3286	9770	Point Ligoure	E. Pliocene	0.9	0.3	1.4	-	0.74	-
H	3286	3176	WD 5 & 6	E. Pliocene	1.4	0.3	0.5	-	0.29	-
M	-	-	Oropouche	Pliocene	1.2	0.8	0.5	-	0.23	-
PFC	-	-	Point Fortin		1.2	0.6	0.4	0.93	0.02	1.1
PS	-	-	Palo Seco		1.2	1.2	1.1	0.89	0.02	1.0
BRK	-	-	Barrackpore		2	0.5	0.3	1.1	0.13	0.95

Data Reproducibility

To determine the reproducibility of the entire measurement and indeed the machine, sample G from Point Ligoure was analysed in triplicate (G-1, G-2, and G-3) and the peak areas obtained showed a very close reproducibility between sample G-1 and G-3 in Ts and Tm for example. Worthy of note is the considerable difference when compared to G-2 (Figs. 2, 3 & 4). This is said to have occurred probably due to manual integration employed to obtain the peak area values. Standard error was determined by first, calculating the average of the three samples to establish the mean and then evaluating the standard deviation to estimate the variation of the sample under investigation. The error bar established represents 95% confidence interval for the percentage sample (Figs. 2, 3 and 4).

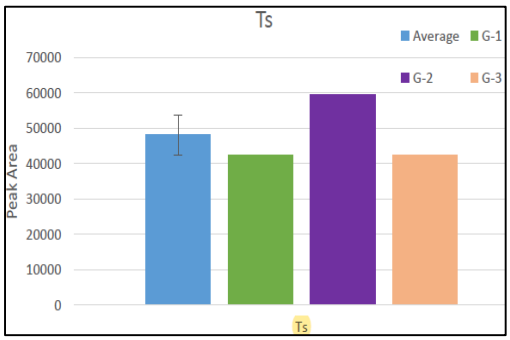

Figure 2. The comparison between the triplicate samples of Point Ligoure (G-1, G-2 and G-3) of maturity parameter Ts. The blue bar represents the mean percentage of samples, green bar represents sample G-1, purple sample G-2 and orange G-3. The error bar represents the 95% confidence interval for the percentage Peak areas.

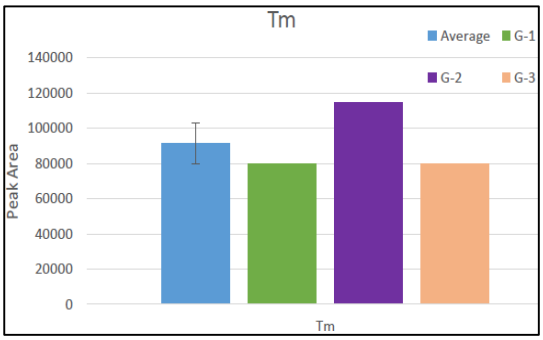

Figure 3. The comparison between the triplicate samples of Point Ligoure (G-1, G-2and G-3) of maturity parameter Tm. The blue bar represents the mean percentage of samples, green bar represents sample G-1, purple sample G-2 and orange G-3. The error bar represents the 95% confidence interval for the percentage Peak areas.

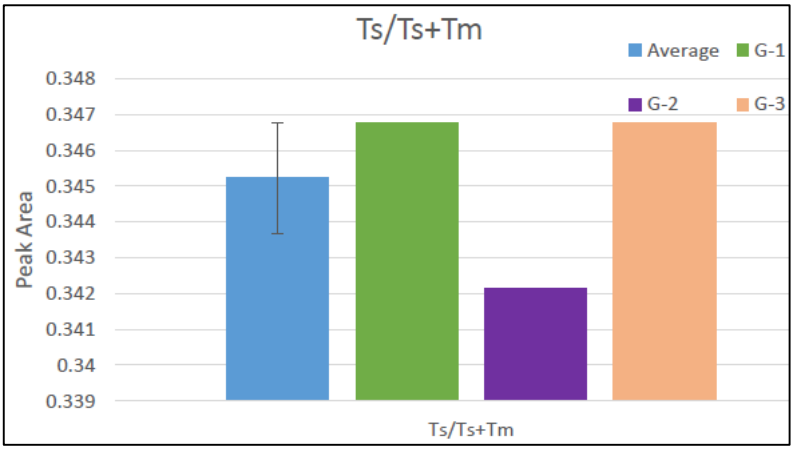

Figure 4. The comparison between the triplicate sample of Point Ligoure (G-1, G-2 and G-3) of maturity parameter Ts/Ts+Tm. The blue bar represents the mean percentage of samples, green bar represents sample G-1, purple sample G-2 and orange G-3. The error bar represents the 95% confidence interval for the percentage Peak areas.

Generally, Ts and Tm are resistant to biodegradation (Figs. 2 and 3). Even in the heavily biodegraded oils, Ts and Tm are barely affected. If both compounds are biodegraded, the biodegradation rates are nearly equal (Ma et al., 2017). The Ts/(Ts + Tm) ratios contained in Table 4, depends on both source and maturity (Peter *et al*., 2005). For common-sourced oils of consistent organic facies, the Ts/(Ts + Tm) ratio is the most reliable maturity indicator.

The *n*-alkanes and isoprenoids

The distribution of the n-alkanes and isoprenoids; and hopane and tricyclic terpanes are represented by the total ion- and mass chromatograms in Figures 5, 6, 7 and 8. The qualitative and quantitative results unveiled compositional similarities between the oils in which all of the straight chain alkanes ranging from *n*-C_{10} to *n*-C_{35} have been removed as evident in samples A-M of the Forest Reserve, Oroupouche, Guapo and WD 5&6 reservoir units (Table 2). Also, there is no predominance of odd over even numbered n-alkanes, and carbon preference index is highly insignificant (Table 1). This may have resulted from biodegradation (Peters and Moldowan, 1993). With increasing thermal maturation, more and more n-alkanes are expected to be generated compared to isoprenoid compounds like pristane and phytane (Shanmugam, 1985). Therefore, with increasing maturity, Pr / n-C_{17} and Ph / n-C_{18} decrease. This is only noticeable in oils from Palo Seco, Point Fortin Central and Barrackpore, in increasing order of thermal maturation (Table 2). In evidence, samples from Barrackpore, Palo Seco, and Point Fortin central showed unimodal and smooth n- alkane distribution pattern ranging from n-C_{11} to n-C_{35} with maximum peaks occurring at n-C_{15} and n-C_{17} respectively (Fig. 7).

Carbon Preference index (CPI) and odd over even preference (OEP) of straight chain n-alkanes are generally considered to be good indicators of organic matter type in oils where high abundance of n-$C_{17\text{-}18}$ and odd abundance of $C_{27\text{-}33}$ n-alkanes indicates aquatic source and terrigenous organic matter respectively (Hunt, 1995 and Asif *et al.*, 2011). The calculated CPI and OEP for oils from Barrackpore, Palo Seco and Point Fortin central, all tends towards unity (Tables 1 and 2), indicating mid-oil window thermal maturities of the source at the time of expulsion for these oils. Organic matter maturity alters the abundance of n-alkanes significantly (Asif *et al*., 2011) and this explains the fate of the rest of the samples described. Interestingly, immature to marginally mature oils usually have n-alkane distributions with a single mode maximizing in the nC17-nC20 range, and a regular decrease towards the higher homologues are consistent with a marine source of organic matter (Affouri *et al.*, 2013).

Table 2. Distribution of isoprenoids and normal alkane values

Sample	Pr	Ph	nC_{17}	nC_{18}	nC_{21}	nC_{22}	nC_{23}	nC_{24}	nC_{25}	nC_{26}	nC_{27}	nC_{28}	nC_{30}
A	0.30	0.90	0.80	0.50	-	-	-	-	-	-	-	-	-
B	0.40	1.80	5.10	2.40	-	-	-	-	-	-	-	-	-
C	4.40	4.30	1.10	0.60	-	-	-	-	-	-	-	-	-
D	0.60	0.60	2.40	0.60	-	-	-	-	-	-	-	-	-
E	5.50	4.10	2.10	0.50	-	-	-	-	-	-	-	-	-
F	0.60	0.60	0.50	1.30	-	-	-	-	-	-	-	-	-
G	5.10	5.50	1.10	0.60	-	-	-	-	-	-	-	-	-
H	1.30	0.90	3.90	0.70	-	-	-	-	-	-	-	-	-
M	0.90	0.70	0.50	1.40	-	-	-	-	-	-	-	-	-
PFC	2.30	1.90	4.40	4.20	2.20	1.90	1.90	1.60	3.90	3.30	2.0	2.0	1.10
PS	3.60	3.10	3.60	3.10	7.10	5.80	5.30	4.80	3.90	1.00	0.70	0.60	0.20
BRK	3.0	1.50	5.50	5.30	11.60	12.0	11.4	12.1	11.5	8.90	9.00	8.00	4.80

Note: a. Carbon Preference Index (CPI) is calculated as $2(C_{23} + C_{25} + C_{27} + C_{29}) / \{(C_{22} + 2(C_{24} + C_{26} + C_{28}) + C_{30}\}$

b. Odd over even Preference (OEP) $(C_{21} + 6 \times C_{23} + C_{25}) / (4 \times C_{22} + 4 \times C_{24})$

Peak areas from the total ion chromatograms were used to calculate n-alkane and isoprenoid ratios and related parameters such as the CPI, DBT/P and OEP (Table 1). The samples showed Pr/Ph ratios (1.0–2.0) which infer marine oxic depositional environment of the organic matter (Didyk *et al.,* 1978). Exemptions are A, B and F oils with values of 0.2, 0.3 and 0.35 respectively (Table 1), implying hypersaline depositional conditions (Peters *et al.,* 2005). The isoprenoids to n-alkane ratios were observed to be inconsistent as there is marked difference in the range of values for the different samples (0.2-2.6) as illustrated in table 1. This could be consequent upon the predominance of isoprenoids over n-alkanes in samples A-M. Based on the distribution of saturated hydrocarbon biomarkers, the oil samples can be broadly classified into two groups. Group I consists of oils from Barrackpore, Point Fortin Central and Palo Seco, which are typically mature and non- biodegraded, generated under oxic depositional environment, while Group II are oils mainly deposited under sub-oxic to saline conditions with low maturity which may have resulted from biodegradation. These oils are from Forest Reserve, Oropouche, Point Liguore and Guapo oils (Figs. 5, 6 and 8).

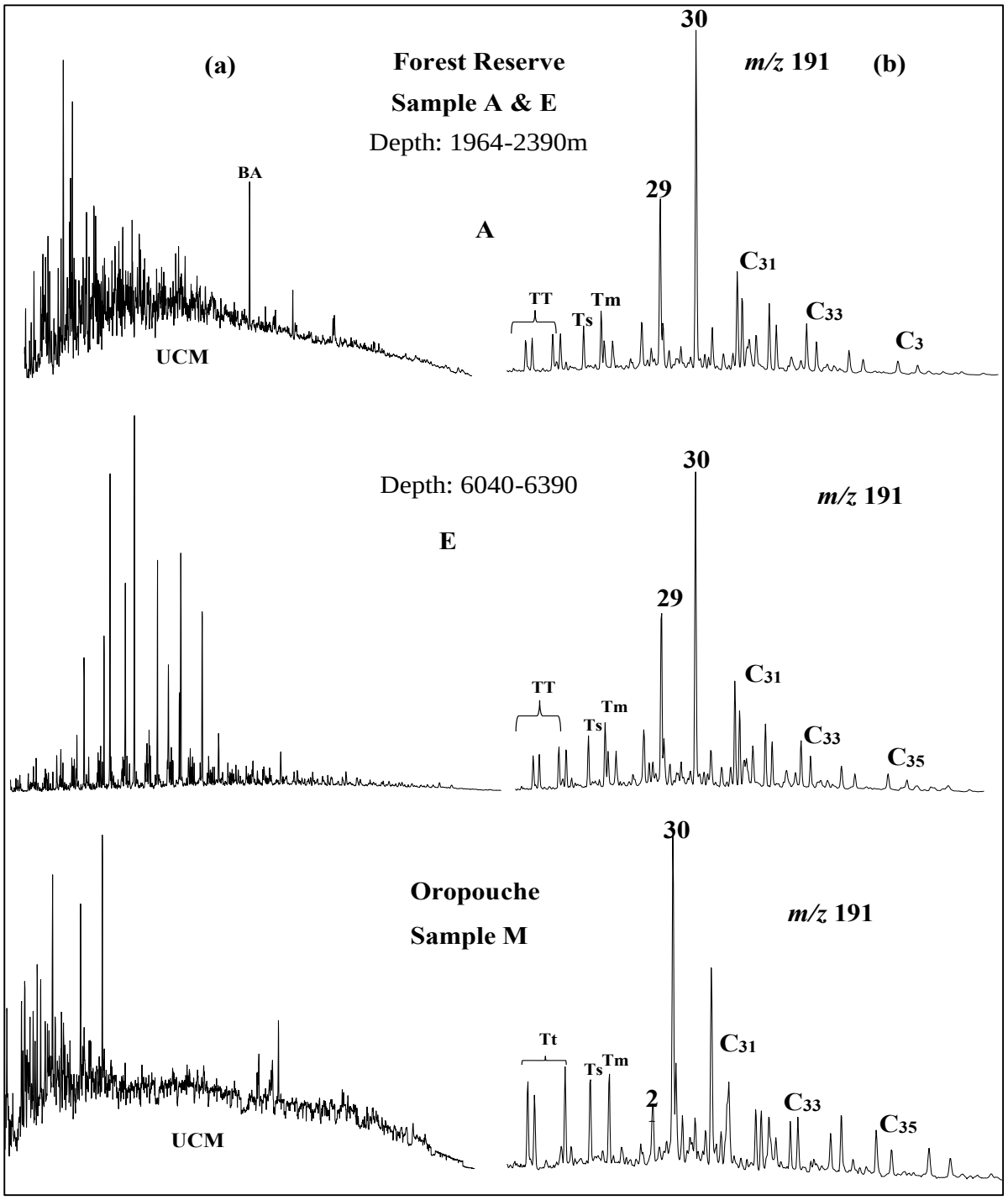

Figure 5. **(**a) Total ion Chromatograms of saturated hydrocarbon fractions showing *n*-alkanes and isoprenoids distribution, (b)

m/z 191 mass Chromatograms showing hopane and tricyclic terpane distribution for Forest Reserve and Oropouche oils Peak.

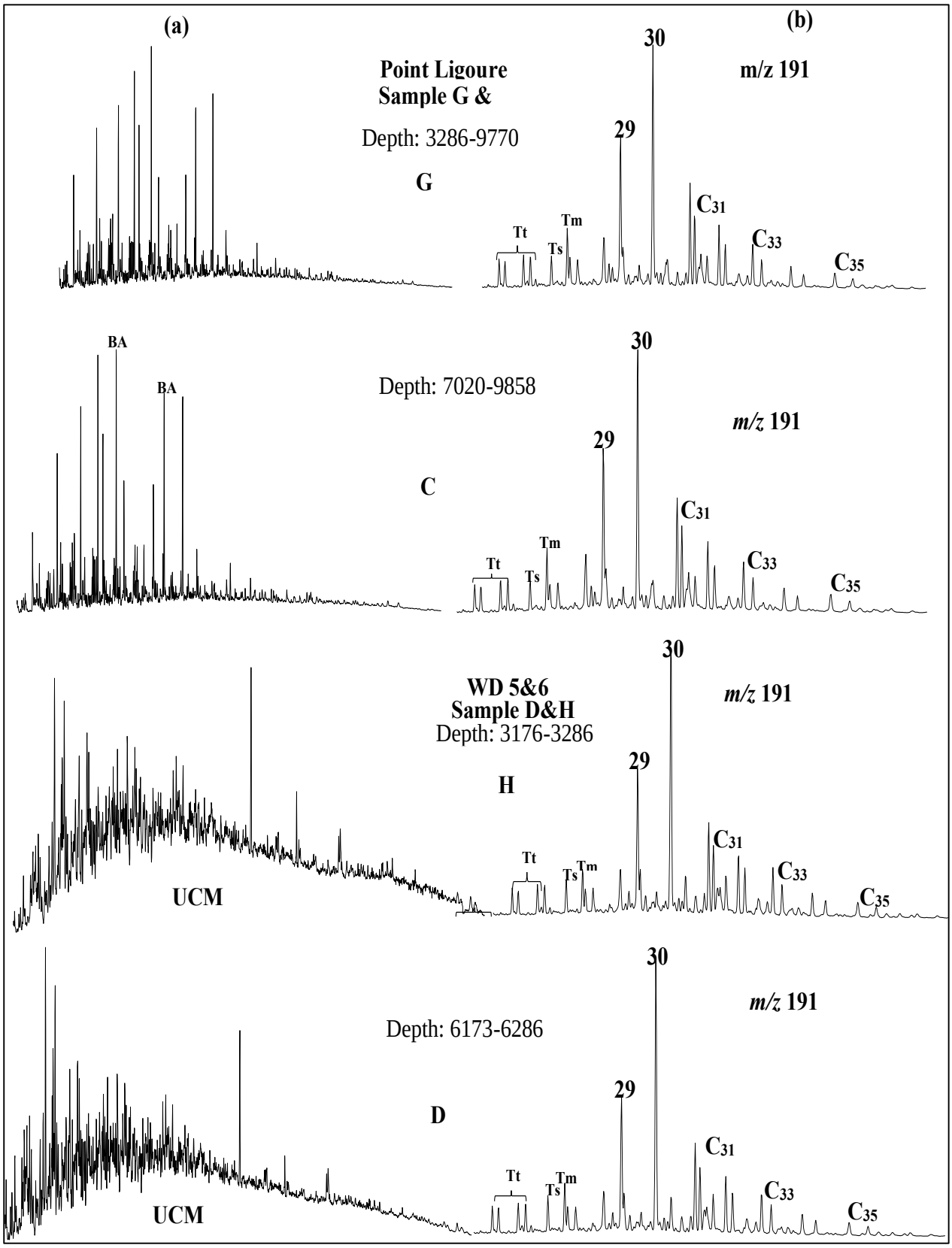

Figure 6. (a) Total ion Chromatograms of saturated hydrocarbon fractions showing *n*-alkanes and isoprenoids distribution, (b) *m/z* 191 mass Chromatograms showing hopane and tricyclic terpane distribution for Point Ligoure and WD 5 & 6 oils Peak.

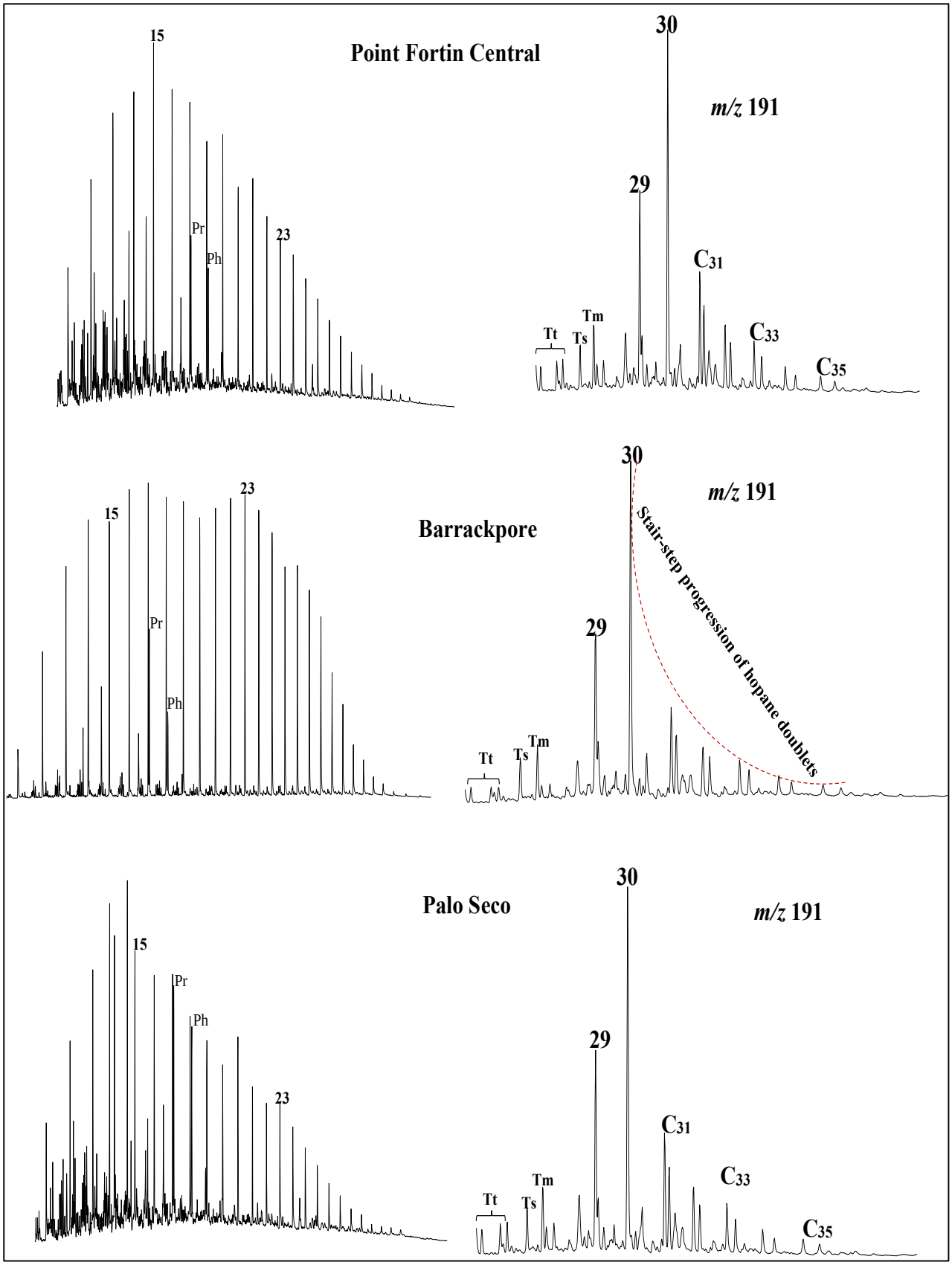

Figure 7. (a) Total ion Chromatograms of saturated hydrocarbon fractions showing *n*-alkanes and isoprenoids distribution, (b) *m/z* 191 mass Chromatograms showing hopane and tricyclic terpane distribution for Point Fortin Central, Barrackpore and Palo Seco oils Peak.

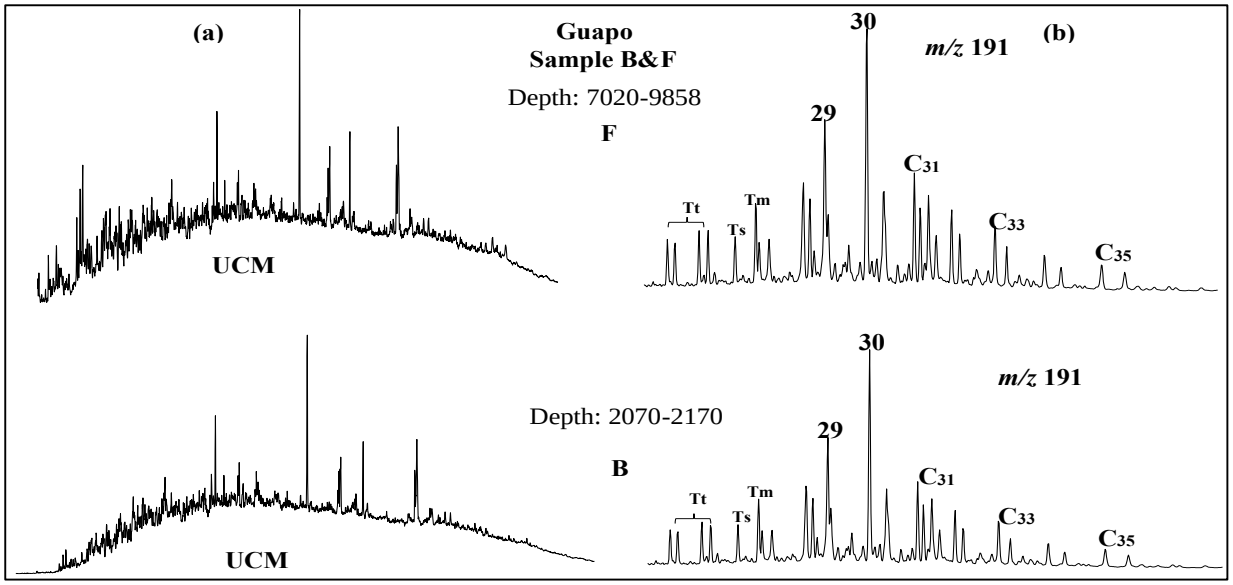

Figure 8. (a) Total ion Chromatograms of saturated hydrocarbon fractions showing *n*-alkanes and isoprenoids distribution, (b) *m/z* 191 mass Chromatograms showing hopane and tricyclic terpane distribution for Guapo oils Peak.

Tt	**Tricyclic Terpane**	**Pr**	**Pristane**
Ts	**18α(H), 22,29,30-Trisnorhopane**	**Ph**	**Phytane**
Tm	**17α(H), 22,29,30-Trisnorhopane**	**15**	**C_{15} *n*-alkane**
29	**17α(H), 21β(H)-30-norhopane**	**23**	**C_{23} *n*-alkane**
30	**17α(H), 21β(H)-hopane**	**UCM**	**Unresolved Complex Mixture**
31	**17α(H), 21β(H)-C_{31} hopane**	**A-M**	**Samples from oil fields**
33	**17α(H), 21β(H)-C_{33} hopane**		

This range of pristane/phytane ratios, typically around 2.0 (table 2), which inferred marine origin of the organic matter in these oils was also complemented by Peters and Moldowan (1993). The absence or lack of odd over even numbered n-alkanes in the range C_{24}- C_{34} and carbon preference index, associated with reasonably high concentration of tricyclic terpanes (Tt) and the absence of 18α(H) oleanane (e.g. Fig. 8) also supports a marine origin for the crude oils in the Tertiary reservoir units of Trinidad. "Well documented cases have demonstrated that the presence of 18α(H)-oleanane in crude oils is a straightforward indicator of terrestrial organic matter in source rocks" (Alberdi and Lopez, 2000). Consequentially, the lack of 18α(H)-oleanane, and the presence of molecular marker compounds such as tricyclic terpanes, hopanes, dibenzothiophenes and their isomers may suggest a Tertiary source for these oils (e.g. Fig. 8).

Generally, only one genetic oil type is recognised from the analysis of the crude oils in the Miocene and Pliocene reservoir units as shown in (Figs. 5, 6, 7 & 8) using GC and GC-MS. A non- biodegraded oil from marine organic matter in a reducing environment (Rodriquez, 1988) is indicated by the gas chromatograms for Barrackpore, Palo Seco and Point Fortin Central oils (Fig. 7). Here, the distribution of both isoprenoids and n-alkanes are not nebulous. The average value of the carbon preference index (CPI) is close to 1 in the range C_{24}-C_{34}. The general abundance of tricyclic terpanes (Figs. 5-8) and the predominant C_{30} hopane amongst the pentacyclic triterpanes also corroborate the earlier suggested marine origin for these oils (Simoneit, 1977).

Considering the aromatic related parameters (Table 3), the quantitative data illustrated that concentrations of thermally stable isomers (3-MP, 2-MP, and 4-MDBT) are highest in samples A (Forest Reserve) and F (Guapo), relatively low at Oropouche, Point Fortin, Palo Seco and Barrackpore and least at Point Ligoure (G) indicating decreasing maturity in relative order. Exemption to this, is the 4-MDBT having its highest concentrations at Barrackpore and Point Liguore while Oropouche, Point Fortin and Palo Seco retains the least contents of this variable. Conversely, the highest contents of thermally unstable isomers (9-MP, 1-MP, and 1-MDBT) are almost invariable in the oils except for the disparity in the distribution of 1-MDBT marked by high concentrations at Oropouche, Point Fortin and Palo Seco. The distribution of the isomers of methyldibenzothiophene ratio (MDR) in the oils, ranged from 0.62 to 0.83, implying that the oils have attained early maturation.

In general, aromatic hydrocarbons are not diagnostic compounds for the evaluation of source organic matter characteristics of mature crude oils and sediments (Asif, 2010). However, the general similarity in their distributions indicates a profound similarity in the source and depositional environment of the organic matter. Also, the distribution and relative abundance of each class of the aromatic compounds displayed in Figure 9 (phenanthrene, dibenzothiophene, and their isomers) combined with commonly used aliphatic biomarkers in the Trinidad oils, have been used for the evaluation of thermal maturity and source of organic matter, depositional environment and

the extent of biodegradation. Most of the oils gave C_{32}S / (S + R) Hopane (Table 4) between 0.49-0.61, implying that the oils were derived from source rocks that already attained the oil window (*Cf.* Peter *et al*., 2005). Meanwhile, the calculated ratios of Ts / (Ts + Tm) found within the range of 0.31-0.48 is indicative of relatively low maturation.

Table 3. Distribution of aromatic related parameters

Sample	1-MP	2-MP	3-MP	9-MP	DBT	P	4-MDBT	1-MDBT
A	5.1E+04	6.0E+05	5.5E+05	7.8E+05	3.4E+05	1.2E+06	3.7E+05	1.6E+05
B	2.5E+06	3.4E+06	4.1E+06	4.5E+06	2.3E+06	6.7E+06	2.9E+05	1.3E+05
C	3.2E+04	4.5E+04	5.4E+04	1.0E+05	5.8E+05	5.2E+05	6.2E+05	3.0E+05
D	3.7E+05	4.5E+05	4.2E+05	6.3E+05	3.1E+05	1.0E+06	3.1E+05	1.4E+05
E	3.4E+05	3.7E+05	3.3E+05	5.0E+05	2.1E+05	6.7E+05	2.7E+05	1.0E+05
F	4.6E+05	5.5E+05	5.2E+05	6.6E+05	3.0E+05	1.0E+06	3.9E+05	1.9E+05
G	1.8E+06	1.8E+06	1.9E+06	3.1E+06	4.2E+06	5.6E+06	4.3E+06	1.9E+06
H	3.4E+05	3.5E+05	4.0E+05	5.8E+05	2.6E+05	8.9E+05	2.8E+05	1.2E+05
M	2.2E+06	3.1E+06	3.3E+06	3.7E+06	1.2E+06	5.0E+06	1.4E+06	4.6E+05
PFS	3.0E+05	3.3E+05	2.3E+05	3.5E+05	1.4E+04	4.9E+05	1.5E+05	7.0E+04
PS	2.9E+05	3.2E+05	2.2E+05	3.4E+05	1.3E+04	5.4E+05	1.3E+05	6.5E+04
BRK	3.4E+05	3.5E+05	2.2E+05	3.5E+05	7.1E+04	5.6E+05	7.0E+04	2.3E+04

Note: a. Methylphenanthrene Index (MPI-1), according to Radke et al., 1982, is calculated as 1.5 x (3-MP + 2MP) / (P + 1-MP +9-MP)
b. Vitrinite reflectance (RC) is calculated as (0.6 x MP-1 + 0.4) (After Radke & Walte, 1983)
c. Methyldibenzothiophene ratio (MDR): 4-MDBT / 1-MDBT (After Radke et al., 1986)

Table 4. Distribution of saturated hydrocarbon parameters

Sample	Ts	Tm	C32-22S	C32-22R	C29-20S	C29-20R	C27ααα-20R	C28ααα-20R	C29ααα-20R
A	8.1E+05	1.0E+06	1.2E+06	8.8E+05	1.1E+05	1.4E+05	1.3E+05	1.4E+05	1.4E+05
B	1.4E+06	2.4E+06	2.3E+06	1.6E+06	7.5E+04	8.2E+04	6.2E+04	3.0E+04	8.2E+04
C	5.8E+05	1.0E+06	1.0E+05	7.2E+04	5.0E+04	7.7E+04	4.8E+04	5.5E+04	3.4E+04
D	1.5E+06	2.0E+06	2.6E+06	1.8E+06	2.8E+06	3.5E+06	3.2E+06	1.1E+06	3.5E+06
E	3.9E+05	5.1E+05	5.7E+05	4.1E+05	6.0E+05	6.0E+05	5.7E+05	5.4E+05	6.0E+05
F	2.3E+06	3.9E+06	3.8E+06	2.0E+05	3.9E+04	9.7E+05	1.6E+06	3.9E+04	9.7E+06
G	4.2E+04	8.0E+04	1.3E+06	9.3E+05	1.0E+06	1.1E+06	8.1E+05	9.0E+05	1.1E+06
H	1.9E+05	2.9E+05	3.9E+05	2.8E+05	3.4E+05	5.4E+05	4.2E+05	4.7E+05	5.4E+05
M	9.8E+04	9.4E+04	7.1E+04	7.2E+04	1.3E+05	1.1E+05	5.0E+04	7.3E+04	1.1E+05
PFS	3.7E+04	5.1E+04	5.4E+04	4.0E+04	4.4E+04	6.5E+04	3.9E+04	4.1E+04	5.0E+04
PS	1.8E+04	2.0E+04	2.1E+04	1.7E+04	1.4E+04	2.2E+04	5.7E+04	5.7E+04	6.5E+04
BRK	3.8E+04	5.0E+04	4.7E+04	3.4E+04	3.5E+04	5.0E+04	5.7E+04	1.7E+04	2.2E+04

C_{32} S/(S + R) Hopane: 22/(20S + 22R). 17α(H)-bishomopane
C_{29} 20S/(S + R) Sterane: 20S/(20S + 20R) 14 α(H).21 α(H)-sterane

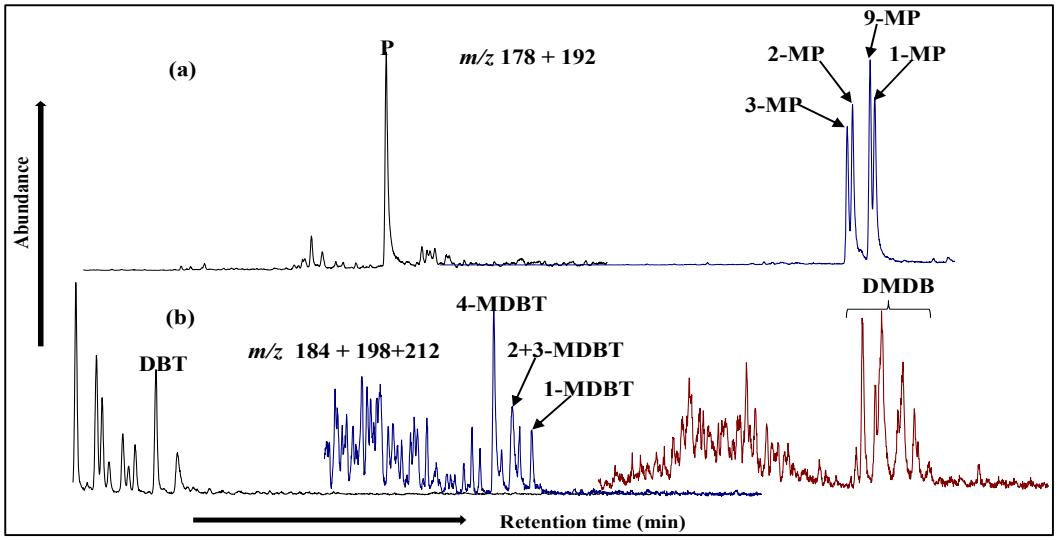

Figure 9. Representative mass chromatograms of aromatic hydrocarbon fractions for oil sample from Barrackpore showing the distribution of a.) Phenanthrene, b.) Dibenzothiophene, and their isomers.
Note: P Phenanthrene; MP MethylPhenanthrene; DBT Dibenzothiophene;
MDBT Methyldibenzothiophene; DMDBT Dimethyldibenzothiophene.

CONCLUSION

Based on the geochemical characteristics and biomarker distributions (Pr/Ph, CPI, OEP, Ts/Ts+Tm, MPI-1 and MDR) of the analysed oils from the Tertiary reservoir units of Trinidad, it can be concluded that the composition of higher molecular weight hydrocarbons in the Trinidad oils is an indication of related genetic family which can be correlated to upper Cretaceous organic facies, sourced predominantly from marine organic matter. The molecular characteristics and gross geochemical properties of the analysed oils also correlate strongly with crude oils from Naprima Hill and Gautier formations indicating a possible genetic association. Arising from the distributions of isomers of methyldibenzothiophene ratio (MDR), early maturation stage was inferred for the oils. Saturated hydrocarbon biomarkers have indicated at least marginal thermal maturity. The various aromatic hydrocarbon parameters also revealed early/marginal maturity for these oils. Similar distribution and abundance of both saturated and aromatic hydrocarbon biomarkers were observed in all the oil samples analysed, and have suggested identical genetic characteristics.

REFERENCES

Affouri, H., Montacer, M. and Disnar, J. (2013). Organic geochemistry of the Cenomanian-Turonian Bahloul Formation Petroleum source rock, Central and Northern Tunisia. *Resource Geology* 63(3): 262-287.

Alberdi, M. and López, L. (2000). Biomarker 18α (H)-oleanane: a geochemical tool to assess Venezuelan petroleum systems. *Journal of South American Earth Sciences*, 13(8): 751- 759

Ames, R. L. and Ross, L. M. (1985). Petroleum geochemistry applied to oilfield development, offshore Trinidad. In Transactions of the First Geological Conference of the Geological Society of Trinidad and Tobago, Port-of-Spain, Trinidad. 227-236.

Asif, M. (2010). Geochemical Applications of Polycyclic Aromatic Hydrocarbons in Crude Oils and Sdiments from Pakistan (Doctoral dissertation, University of Engineering & Technology, Lahore).

Asif, M., Fazeelat, T. and Grice, K. (2011). Petroleum geochemistry of the Potwar Basin, Pakistan: 1. Oil–oil correlation using biomarkers, δ 13 C and δD. *Organic Geochemistry*, 42(10): 1226-1240.

Barman, B. N., Cebolla, V. L. and Membrado, L. (2000). Chromatographic techniques for petroleum and related products. *Critical Reviews in Analytical Chemistry*, 30(2-3): 75-120.

Didyk, B., Simoneit, B., Brassel, S. and Eglinton. G. (1978). Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature* 272: 216-222.

Escalona, A. (2003). Regional Tectonics, Sequence Stratigraphy and Reservoir properties of Eocene clastic sedimentation, Maracaibo Basin, Venezuela. Graduate School. Austin, University of Texas at Austin. Ph. D thesis: 241.

Escalona, A. and Mann, P. (2011). Tectonics, basin subsidence mechanisms and paleogeography of the Caribbean-South American plate boundary zone. *Marine and Petroleum Geology* 28: 8-39.

Figueira, B. (2012). An examination of the spatial and temporal evolution of a complex transition zone in the Gulf of Paria, Trinidad-Venezuela (Eastern Venezuela Basin/EVB). Universitet I Stavanger, M. Sc. Thesis, 506.

Friedrich, D. and Lavidas, G. (2015). Combining offshore and onshore renewables with energy storage anddiesel generators in a stand-alone Hybrid Energy System. in Offshore Energy & Storage 2015. Edinburgh. *Offshore Energy*, 7p.

Garciacaro, E., Escalona, A., Mann, P., Wood, L., Moscardelli, L. and Sullivan, S. (2011). Structural controls on Quaternary deepwater sedimentation, mud diapirism, and hydrocarbon distribution within the actively evolving Columbus foreland basin, eastern offshore Trinidad. *Marine and Petroleum Geology*, 28(1): 149-176.

Leonard, R. (1983). Geology and hydrocarbon accumulations, Columbus Basin, offshore Trinidad. *AAPG Bulletin*, *67*(7), 1081-1093.

Ma, A., Jin, Z., Zhu, C. and Bai, Z. (2017). Cracking and thermal maturity of Ordovician oils from Tahe Oilfield, TarimBasin, NW China. *Journal of Natural Gas Geoscience*, 2: 239-252.

Parra, J. L., Guinea, J., Manresa, M. A., Robert, M., Mercade, M. E., Comelles, F., et al. (1989). Chemical characterization and physicochemical behaviour of biosurfactants. *Journal of American Oil Chemical Society.* 66 141–145 10.1007/BF02661805.

Persad, K.M. (1988). *Petroleum Potential Trinidad*, second licensing round 1988 in Petroconsultant's Report.

Persad, K. M. (2009). The petroleum geology and prospects of Trinidad and Tobago. Trinidad and Tobago: Celebrating a Century of Commercial Oil Production. Official centenary publication of the Ministry of energy and energy studies, First Publishing, London, 178- 186.

Persad, K.M., Talukdar, S.C. and Dow, W.G. (1980), Review of the hydrocarbon prospects of the Trinmar area. GPE Report 323: 34.

Persad, K. M., Talukdar, S. C., and Dow, W. G. (1993). Tectonic control in source rock maturation and oil migration in Trinidad and implications for petroleum exploration. Mesozoic and early Cenozoic development of the Gulf of Mexico and the Caribbean region: A context for hydrocarbons exploration, 237-49.

Peters, K.E. and Moldowan, J.M. (1993) The Biomarker Guide. Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, New Jersey. 363.

Peters, K. E., Walters, C. C. and Moldowan, J. M. (2005). The biomarker guide, volume 2 biomarkers and isotopes in petroleum exploration and earth history. *Cambridge: Cambridge University Press*, 475: 634.

Radke, M. and Welte, D.H. (1983). *The MP Index (MPI): a maturity parameter based on aromatic hydrocarbons.* In: Bjøroy, M. (Ed.), Advances in Organic Geochemistry 1981. John Wiley and Sons Limited, 504–512.

Radke, M., Welte, D.H. and Willsch, H. (1982). Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta* 46: 1–10.

Radke, M., Welte, D.H.and Willsch, H. (1986). Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. In: Leythaeuser, D., Rullkötter, J. (Eds.), Advances in Organic Geochemistry 1985, *Organic Geochemistry* 10: 51–63.

Rodrigues, K. (1988). Oil source bed recognition and crude oil correlation, Trinidad, West Indies. *Organic Geochemistry*, 13(1): 365-371.

Ross, L. M. and Ames, R. L. (1988). Stratification of oil in Columbus Basin of Trinidad: *Oil & Gas Journal*, 86 (39): 7

Shanmugam, G. 1985. Significance of coniferous rain frost and related organic matter in generating commercial quantities of oil, Gippsland basin, Australia. *AAPG Bulletin*, 69:1241-1254.

Simoneit, B. R. T. (1977). Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochimica et Cosmochimica Acta* 41: 463–476.

Talukdar, S. C., Dow, W. G. and Persad, K. M. (1990). Geochemistry of oils provides optimism for deeper exploration in Atlantic off Trinidad. *Oil & Gas Journal*, 88(46): 118-122.