

PYROLYSIS-GAS CHROMATOGRAPHY OF KEROGEN IN COALS AND SOURCE ROCKS FROM THE UPPER CRETACEOUS MAMU FORMATION, SOUTHEASTERN NIGERIA

Jude Etunimonuwa Ogala

Department of Geology, Delta State University, P.M.B. 1, Abraka, Nigeria

Received June 3, 2019; Accepted August 26, 2019

Abstract

Seven core samples comprising of coals and organic-rich shales recovered from five boreholes that penetrated the Upper Cretaceous succession in the Anambra Basin (SE Nigeria) were subjected to total organic carbon (TOC), Rock-Eval pyrolysis and pyrolysis-gas chromatography analytical methods in order to characterize their structural features, source rock kerogen type and liquid hydrocarbon-generative potential. The analyses indicated that the coal and shale intervals are rich in organic carbon content. The TOC and hydrogen index (HI) values range from 0.20 to 55.07 wt.% and 254 to 771 mg HC/g TOC respectively. Plots of HI versus oxygen index (OI) and HI versus Tmax classified the organic matter as Types III and mixed II/III. Pyrolysis-gas chromatographic fingerprint of the thermal extract revealed majorly a bimodal pattern dominated by the homologous series of n-alkene/n-alkane doublets, suggesting a mixed organic matter types (terrestrial and marine kerogen) and is typical of source rocks with liquid hydrocarbon generation potential given sufficient thermal maturity. Ternary plots of C₁-C₅, C₆-C₁₄ and C₁₅+ (n-alkenes + n-alkanes) pyrolysates suggests that the coal and shale extracts can generate paraffinic oil with high wax contents.

Keywords: *Coals; Kerogen; Mamu Formation; Nigeria; Paraffinic oil; Pyrolysis-gas chromatography.*

1. Introduction

Pyrolysis-gas chromatography (Py-GC) is the high temperature break-down of organic matter in the absence of oxygen into smaller molecular fragments. Pyrolysis-gas chromatography has been widely used as an analytical tool to elucidate the structural features of kerogens and to evaluate liquid hydrocarbon generation potential of source rocks [1-7]. Pyrolysis-gas chromatography is routinely utilized to characterize source rock kerogen type by examining the specific molecular distributions of pyrolysis products [8-16]. This analytical capability of making a positive identification of pyrolysis products is one of the important advantages of the Py-GC system because it can overcome problems associated with the interpretation of indirect production type indicators such as the hydrogen and oxygen indices used by the quick and inexpensive Rock-Eval pyrolysis technique [3]. Previous workers have attempted to classify the sedimentary organic matter in the Upper Cretaceous Anambra Basin by means of organic petrology and Rock-Eval pyrolysis [17-25]. However, results and interpretations obtained from Rock-Eval pyrolysis are usually affected adversely by drilling mud contamination, mineral matrix effects and low amount of kerogen [26-29]. According to Akinlua *et al.* [30], the difficulty of determining the actual nature of the organic matter in source rocks and correctly interpreting its petroleum-forming properties is also not always satisfactorily solved by Rock-Eval pyrolysis and petrological methods. Udo *et al.* [31] employed organic petrographic and programmed pyrolysis techniques to study sediments from northwestern Niger Delta and showed the effect of mineral matrix in classification based on Rock-Eval pyrolysis technique. Akinlua *et al.* [30] observed that microscopy approach suffers from the major drawback of using mainly qualitative information that may not be easily transformed into numerical data for assessing the quality of source rocks.

A classification of pre-isolated kerogens in sediments from the Niger Delta based on pyrolysis-gas chromatography was presented by [30]. They reported that quantitative pyrolysis-gas chromatography gives a better resolution of the intricate mixtures of kerogen in sediments from paralic sequences. According to Akande *et al.* [32], the coals in the Upper Cretaceous Mamu Formation have the capacity to generate hydrocarbons; however no study on the structural features and nature of the hydrocarbons have been carried out. This study was carried out using pyrolysis-gas chromatography technique in order to characterize the structure of kerogen, source rock kerogen type and to determine the tendency of Upper Cretaceous source rocks to generate liquid hydrocarbons.

2. Location of study area and geology

The study area lies within latitudes 6°20' to 7°55' N and longitudes 6°45' to 8°00' E in southeastern Nigeria and occupies an area of about 20,350 km² (Fig. 1). The geology, stratigraphy, paleogeography, palaeontology and tectonic evolution of the Anambra Basin have been discussed by different authors [33-41]. The evolution of the Anambra Basin is related to the opening of the South Atlantic Ocean following the breakup of African from South American Continents during the Early Cretaceous [34]. The Anambra Basin is bounded to the south by the Niger Delta Basin and extends into the Benue Rift Basins (BRB) on the northern side (Fig. 1). The Anambra Basin was formed during the Santonian folding episode of the Abakaliki Uplift in the southwestern part of the Benue Trough. The Anambra Basin hosts over 6km-thick sedimentary successions of Cretaceous and Cenozoic age [42-43] comprising siltstones, clays, sandstones, shales, sandy shales, limestones and coal seams. The oldest known stratigraphic unit in the Anambra Basin is the Campanian-Maastrichtian Nkporo Shale Group (that is Nkporo/Enugu Shales and their lateral/stratigraphic equivalents-Owelli Sandstone). This formation unconformably overlies the Awgu Formation (Coniacian-Santonian). The regional Santonian unconformity above the Awgu Formation resulted in the deposition of the Nkporo Group (Campanian-Maastrichtian). It was followed successively by the coal bearing deltaic Mamu Formation (Maastrichtian), fluvio-deltaic to tidal Ajali Sandstone (Middle Maastrichtian) and the fluvio-deltaic Nsukka Formation (Maastrichtian-Paleocene; Fig. 2)

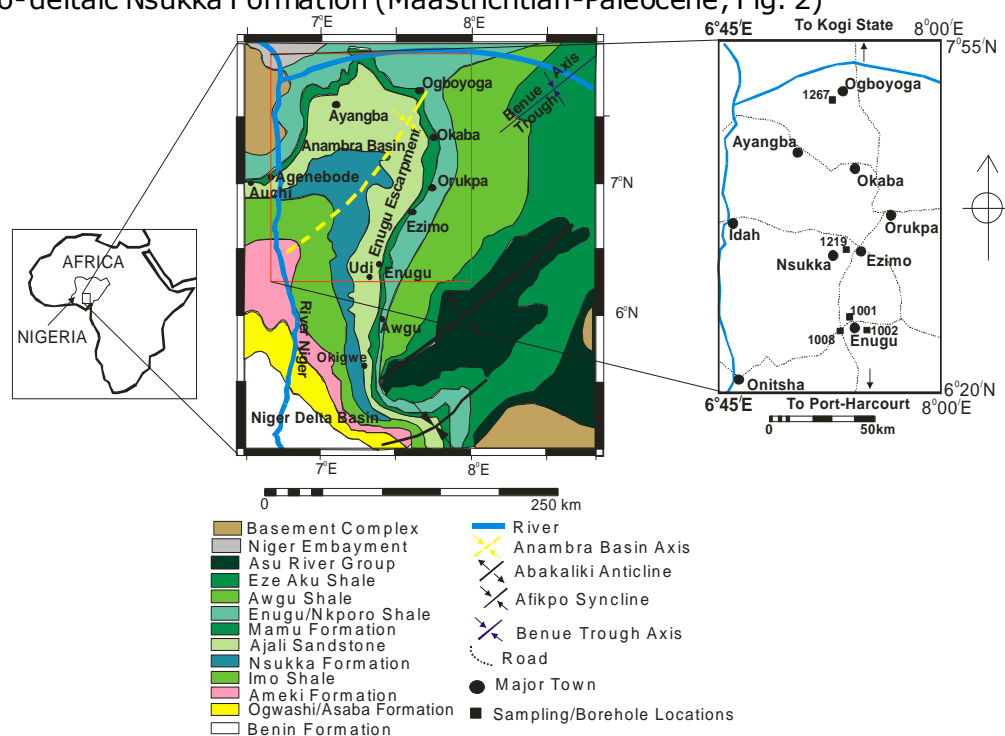


Fig. 1. Geological map of Anambra Basin showing borehole locations

ERA	PERIOD /AGE		FORMATION	LITHOLOGY	DEPOSITIONAL ENVIRONMENT	BASIN
Cenozoic	Quaternary		Benin Formation	Sandstones, clays, shales	Continental	Niger Delta Basin
	Neogene	Pliocene				
		Miocene				
	Paleogene	Oligocene	Ogwashi Asaba Formation	Clays, shales, sandstones, lignites	continental	
		Eocene	Amekei Formation/Nanka Sand	sandstones, clays, shales, limestones	estuarine, shallow marine	
		Paleocene	Imo Formation	Clays, shales, limestone, sandstones, marls	shallow marine, deltaic	
Mesozoic	Upper Cretaceous	Maastrichtian	Nsukka Formation	Sandstones, clays, shales, coals, limestones	fluvio-deltaic	Anambra Basin
			Ajali Sandstone	Sandstones, claystones	fluvio-deltaic	
			Mamu Formation	sandstones, shales, clays, coals	shallow marine, deltaic	
			Enugu/Nkporo/Owelli Formation	shales, sandstones, clays, ironstones, siltstones	shallow marine, deltaic	
		MAJOR UNCONFORMITY				
		Santonian	Awgu Formation	sandstones, limestones, clays, coals, siltstones	shallow marine, deltaic	Benue Trough
	Coniacian					
	Turonian	Eze-Aku Formation	shales, limestones, sandstones	shallow marine		
	Cenomanian	Odukpani Formation	sandstones, limestones, shales	shallow marine		
	Lower Cretaceous	Albian	Asu River Group	shales, limestones, sandstones	shallow marine	
Lower Paleozoic			MAJOR UNCONFORMITY			
			Basement complex	granites, gneisses, schists migmatites	igneous, metamorphic	

Fig. 2. Stratigraphic units in the Niger Delta, Anambra Basin and Lower Benue Trough of Nigeria [33]

3. Sampling and analytical methods

A total of seven core samples, comprising of three coals and four shales obtained at various depths from five boreholes (1001, 1002, 1008, 1219 and 1267) in the Anambra Basin, south-eastern Nigeria, were selected for this study (Fig. 1). The samples were subjected to total organic carbon (TOC), Rock-Eval pyrolysis and Py-GC analytical methods in order to determine their organic carbon richness, hydrocarbon generation potential, source rock kerogen type and to identify the possible production type (oil, condensate and gas).

The TOC content of the samples was determined using a LECO C-230 analyzer after pre-treatment of samples with concentrated hydrochloric acid to remove carbonates.

The Rock-Eval pyrolysis measurements were performed using a DELSI ROCK-EVAL II device according to the procedures described in detail by [44-45].

Pyrolysis gas chromatography (Py-GC) was conducted in conjunction with thermal extract-gas chromatography (TE-GC). Samples to be analyzed were rinsed to remove drilling mud contaminants and handpicked to recover representative cuttings fragments for analyses. Seven samples were subjected to an initial TE-GC following the procedures described by Giraud [8]. Upon completion of the TE-GC analysis, the same 10-50 mg residual rock sample in the metal crucible was lowered back into the inlet that was pre-set to 600°C. It was then pyrolyzed for 2.45 minutes and raised back into the cool area. Gas chromatography was performed using a Hewlett Packard 6890 GC System. The GC was temperature programmed from 35°C (5 minutes hold) to 330 °C at 5 °C/minute with a final hold time of 30 minutes. This GC technique separates light hydrocarbons and allows identification of heavy molecular weight hydrocarbons up to C₄₂.

4. Results

4.1. TOC and Rock-Eval pyrolysis

The results of TOC and Rock-Eval analysis are presented in Table 1. The TOC values of the coal and shale samples ranges from 42.04 to 55.07 wt.% (averaging 50.24 wt.%) and 0.20 to 9.34 wt.% (averaging 5.09 wt.%) respectively (Table 1). The S₁ and S₂ yields for the coal vary from 5.3 to 8.23 mg HC/g rock and 147.4 to 323.99 mg HC/g rock respectively. The S₁ and S₂ yields in the shales ranges from 0.09 to 1.88 mg HC/g rock and 0.6 to 33.16 mg HC/g rock respectively (Table 1). Tmax values for the coals ranges from 432 to 434°C while those of the shales ranges from 418 to 434°C. The HI values in the coals and shales varies between 275 to 771 mg HC/g TOC and 254 to 444 mg HC/g TOC respectively (Table 1).

4.2. Pyrolysis-gas chromatography

The pyrolysis-gas chromatographic fingerprints and histograms of the studied coal and shale samples are presented in Figures 3a-g. The pyrograms are dominated by the homologous series of n-alkene/n-alkane doublets in the range of C₅-C₃₆. The homologous series of the n-alkene/n-alkane doublets has a bimodal distribution, maximizing at C₆ and C₂₉. The major n-alkane peaks are C₆, C₇, C₈, C₁₄, C₁₅, C₁₆, C₂₇, C₂₈, C₂₉, C₃₀ and C₃₁ with C₁₅ being dominant. Prominent peaks of pristane, phytane, C₁₃, C₁₄, C₁₅, C₁₆, and C₁₈, isoprenoids were observed (Figs. 3a-g). Aromatic compounds identified in the pyrograms include benzene and toluene (Figs. 3a-g).

5. Discussion

5.1. Hydrocarbon source potential

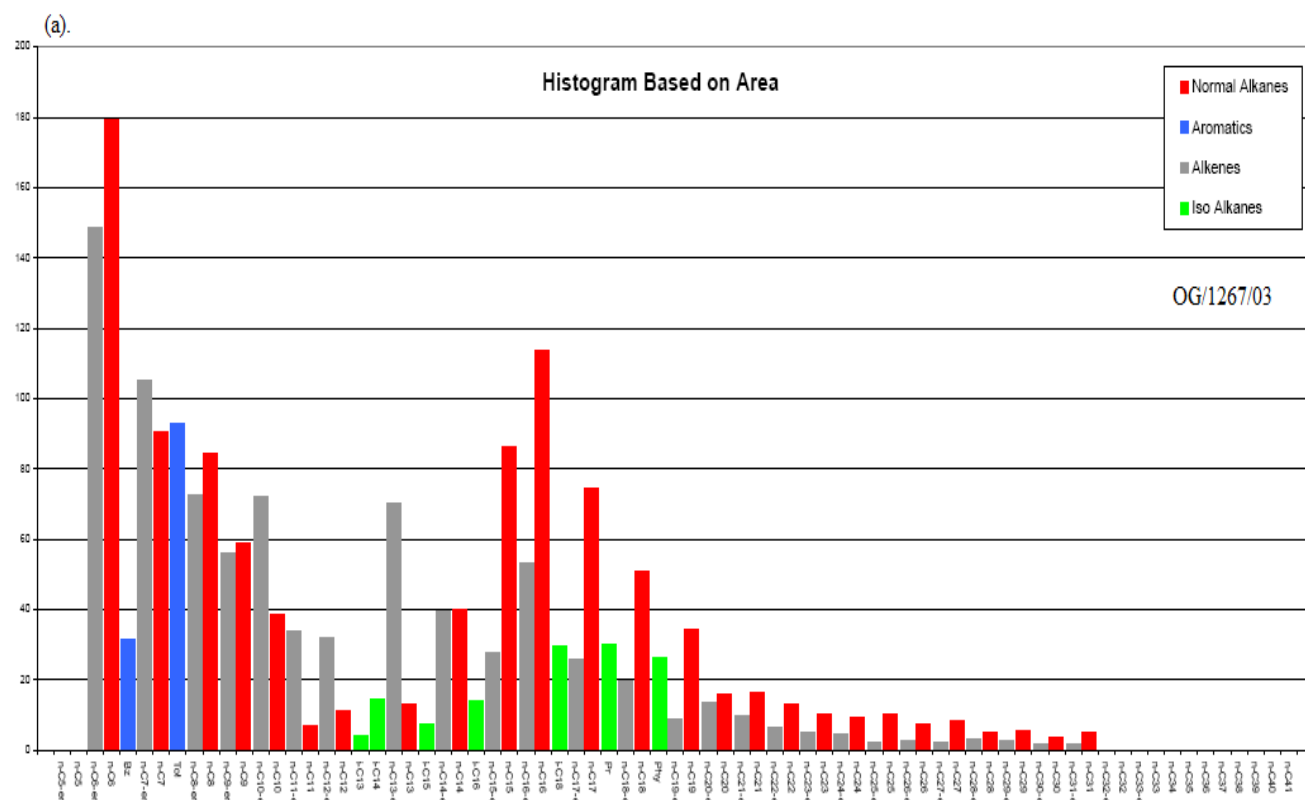
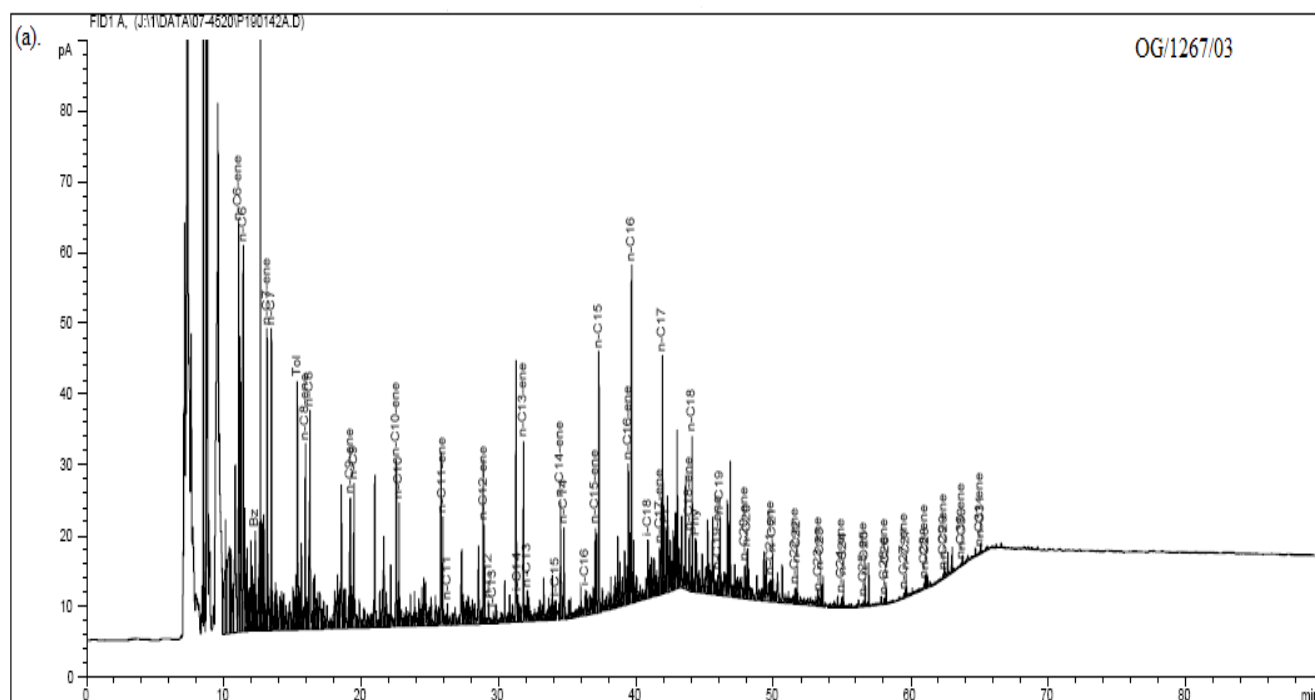
The results of total organic carbon (TOC) and Rock-Eval pyrolysis analyses of the studied coal and shale samples are summarized in Table 1. The TOC values of the coal samples analyzed range from 42.04 to 55.07wt.% while that of shales ranges from 3.35 to 9.34wt.%. These results indicate that the coal and shale samples possess good to very good organic carbon richness (TOC >0.5 wt.% [47]) required by a potential source rock to generate significant quantities of hydrocarbon. One sample (1267/03) had TOC value of 0.02wt.% (Table 1)

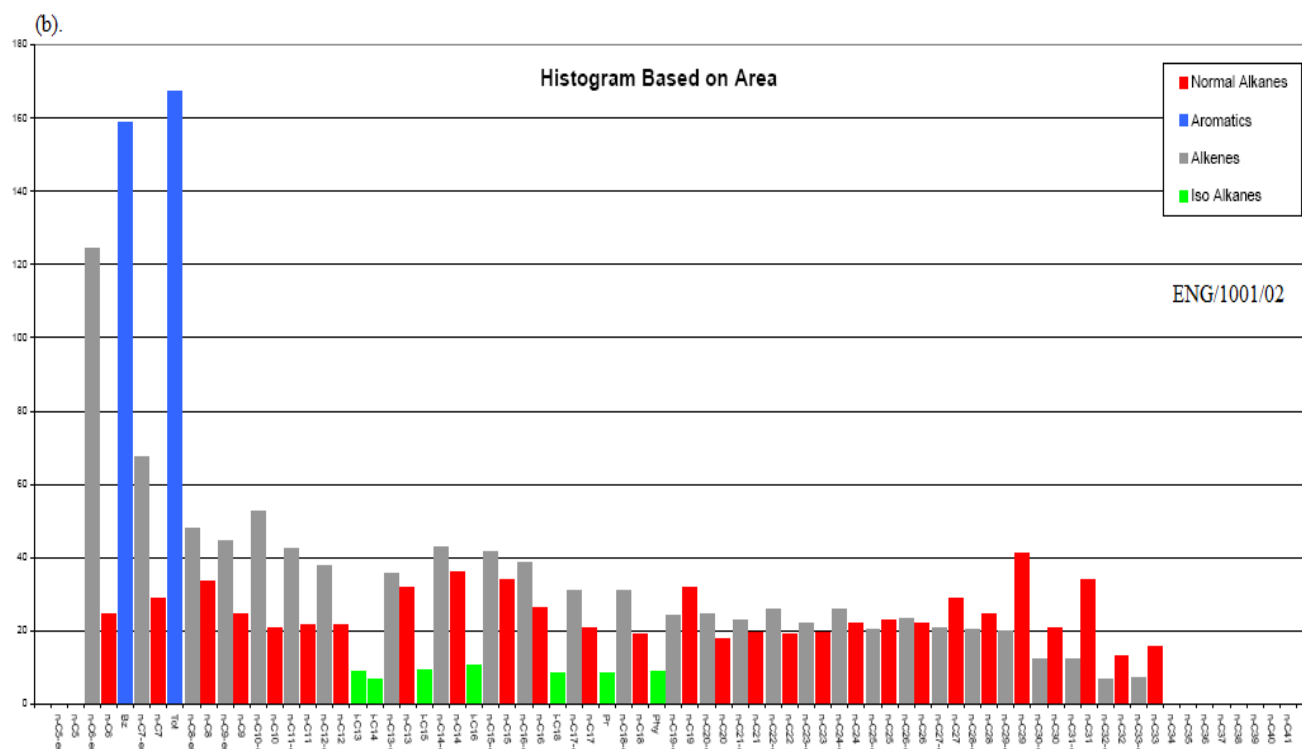
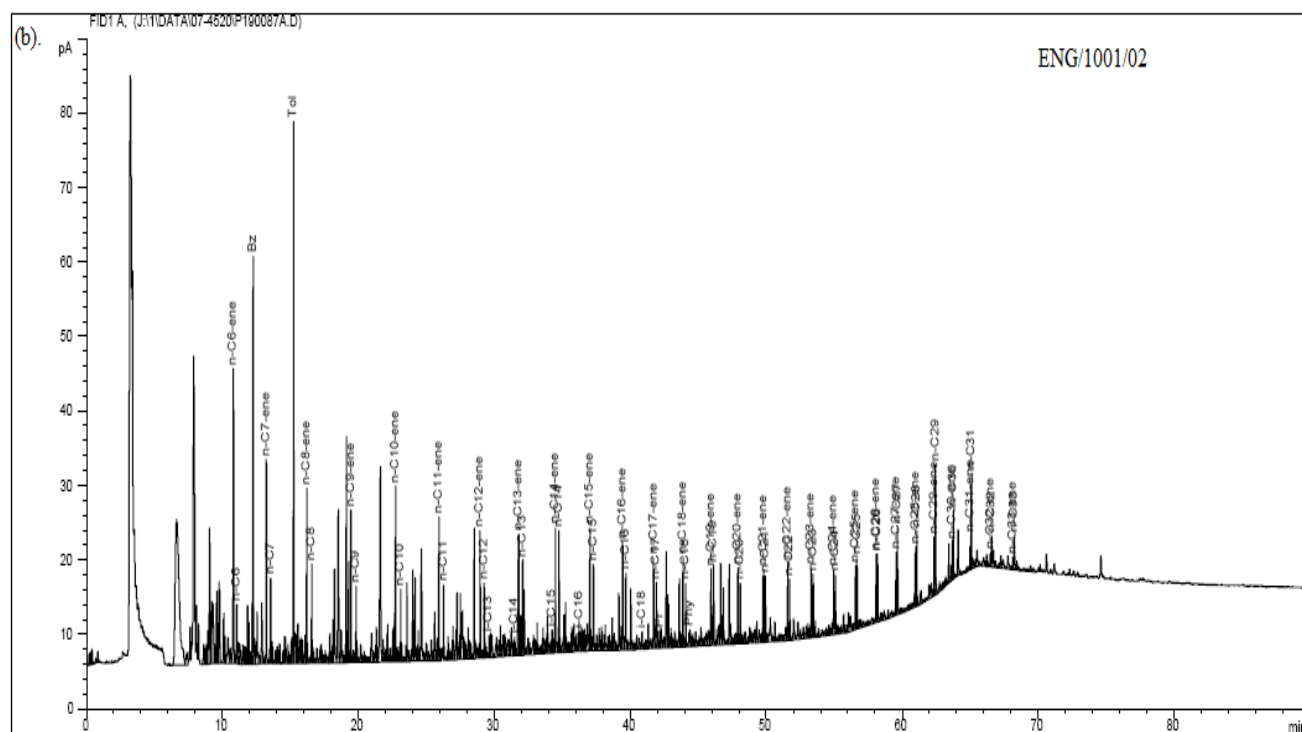
The Rock-Eval pyrolysis results (Table 1) show that the coals and shales have the ability to generate hydrocarbons. HI values vary from 275 to 771 mg HC/g TOC in the coals and 254 to 444 mg HC/g TOC in the shales. The high HI values (>200 mg HC/g TOC) suggest that the coals and shales contain type II-III organic matter (mixed origin) which are capable of generating both oil and gas (Fig. 4). The calculated vitrinite reflectance (Cal. Ro%) and T_{max} values range from 0.36 to 0.65 % and 418 to 434°C respectively (Table 1), signifying their thermally immature status. The S₁ and S₂ yields for the studied samples are 0.09 – 8.23 mg HC/g rock and 0.06 – 323.99 mg HC/g rock (Table 1), suggesting their potential to generate gas and oil. These results are in agreement with those reported by [6, 32, 48-54]. The hydrocarbon generative potential (based on Rock-Eval S₁ + S₂) of the studied samples ranges from 0.69 - 332.22 mg HC/g rock, indicating moderate-good source rock [55].

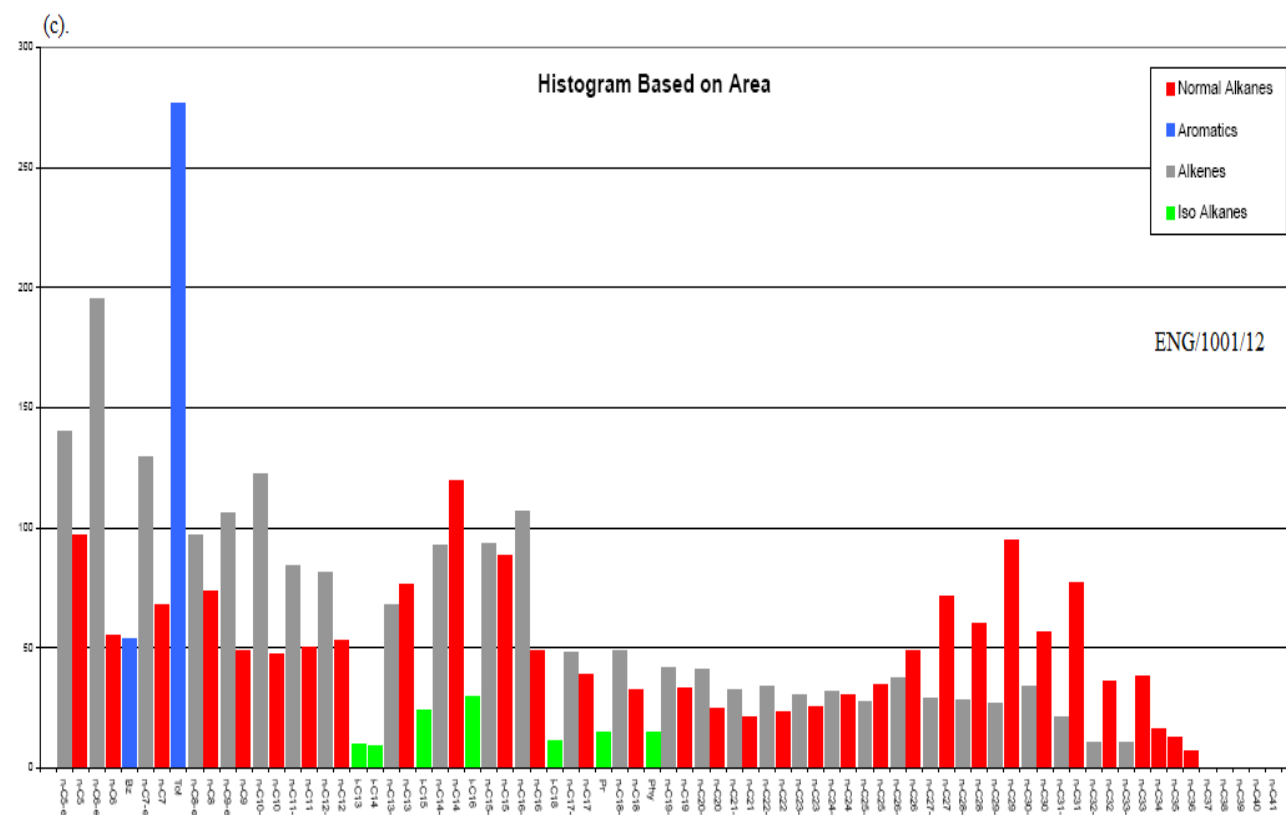
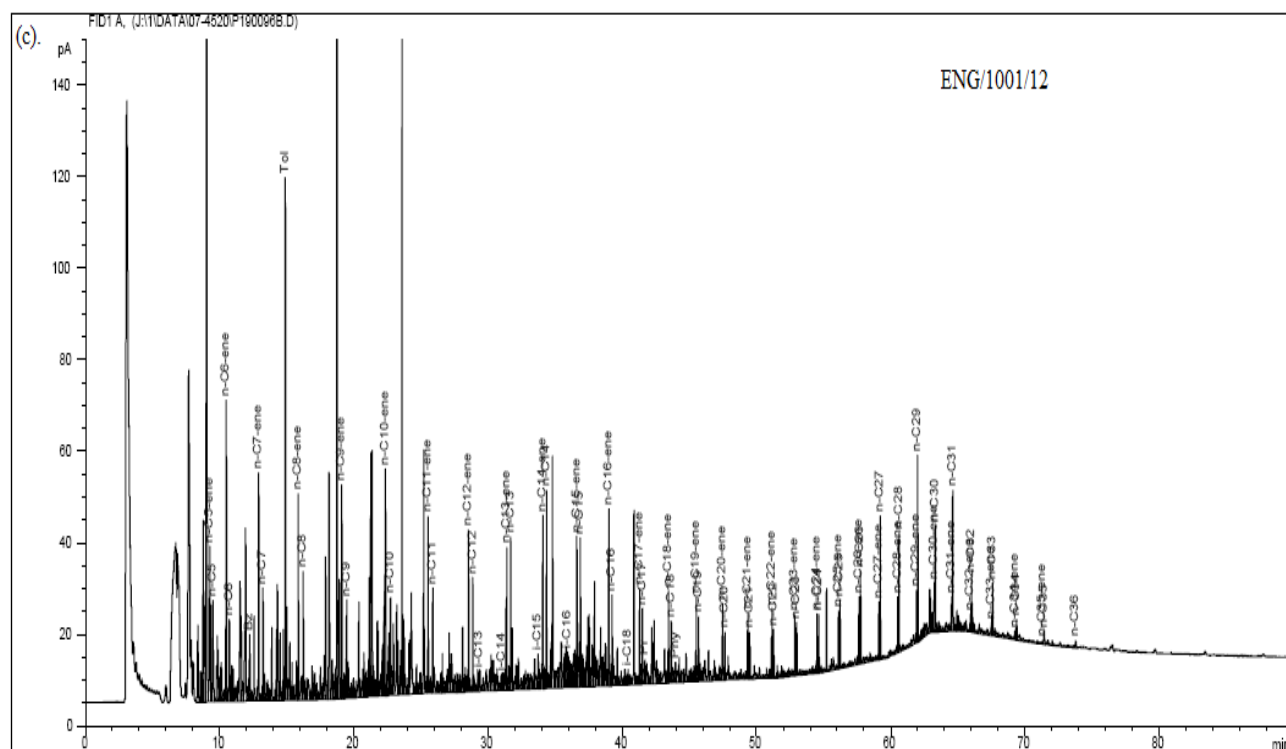
Table 1. Total organic carbon and Rock-Eval data

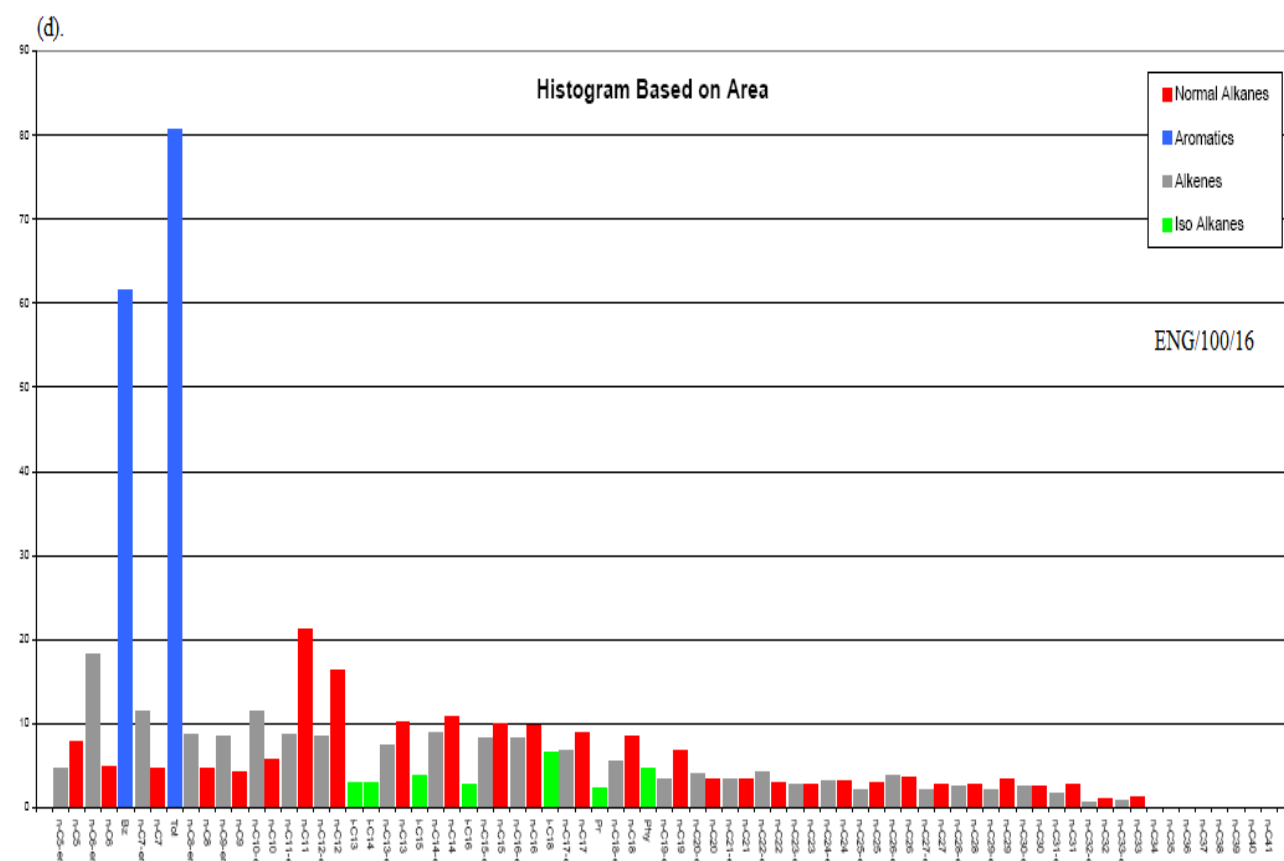
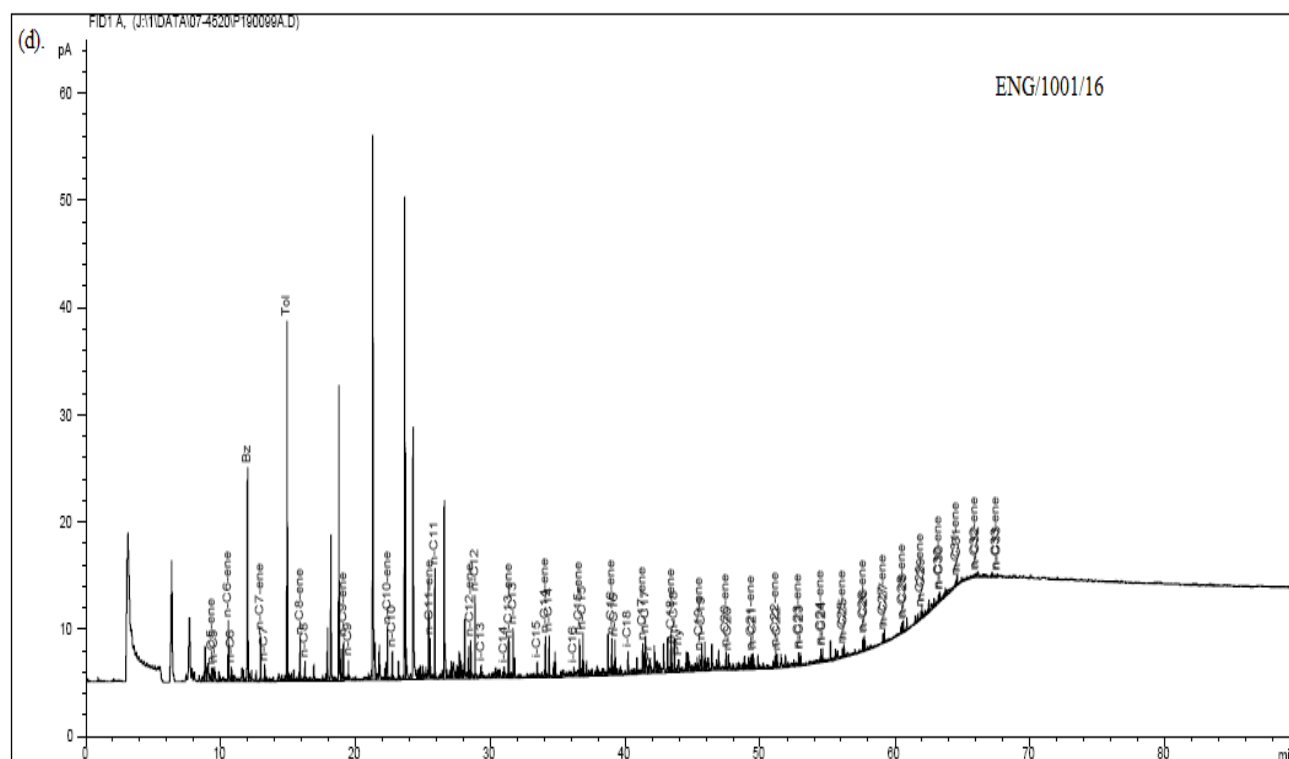
Sample No.	Depth (m)	Lithology	TOC (%)	S ₁	S ₂	S ₃	Tmax (°C)	Calc. %Ro	HI	OI	GP	S ₂ /S ₃	S ₁ /TOC	PI
1001/02	157	Shale	9.34	1.88	30.53	1.79	434	0.65	327	19	32.41	17	20	0.06
1001/12	186-187	Coal	42.04	8.23	323.99	10.15	434	0.65	771	24	332.22	32	20	0.02
1001/16	205	Shale	3.35	0.46	8.52	0.94	434	0.65	254	28	8.98	9	14	0.05
1002/06	167-178	Shale	7.47	1.68	33.16	2.92	432	0.62	444	39	34.84	11	22	0.05
1008/13	220-221	Coal	55.07	5.30	289.98	6.48	432	0.62	527	12	295.28	45	10	0.02
1219/08	80-82	Coal	53.61	7.58	147.40	12.31	432	0.62	275	23	154.98	12	14	0.05
1267/03	75-76	Shale	0.20	0.09	0.60	1.37	418	0.36	300	685	0.69	0	45	0.13

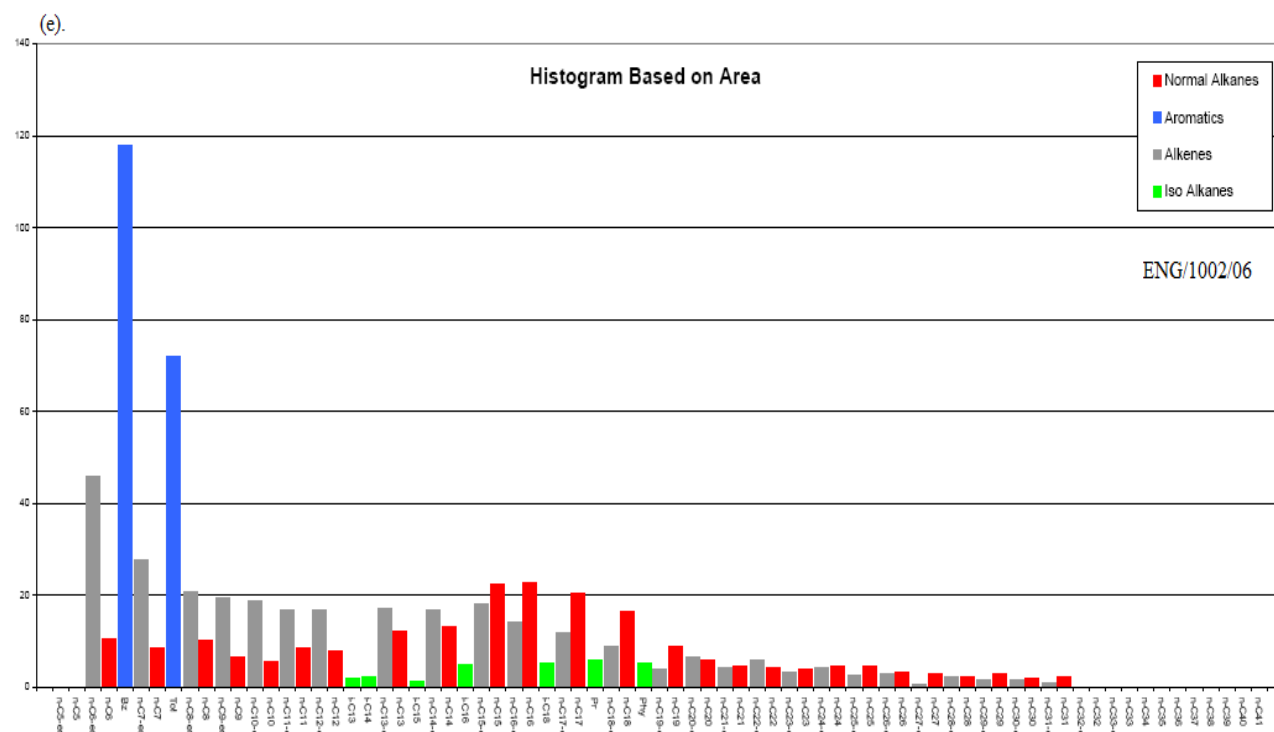
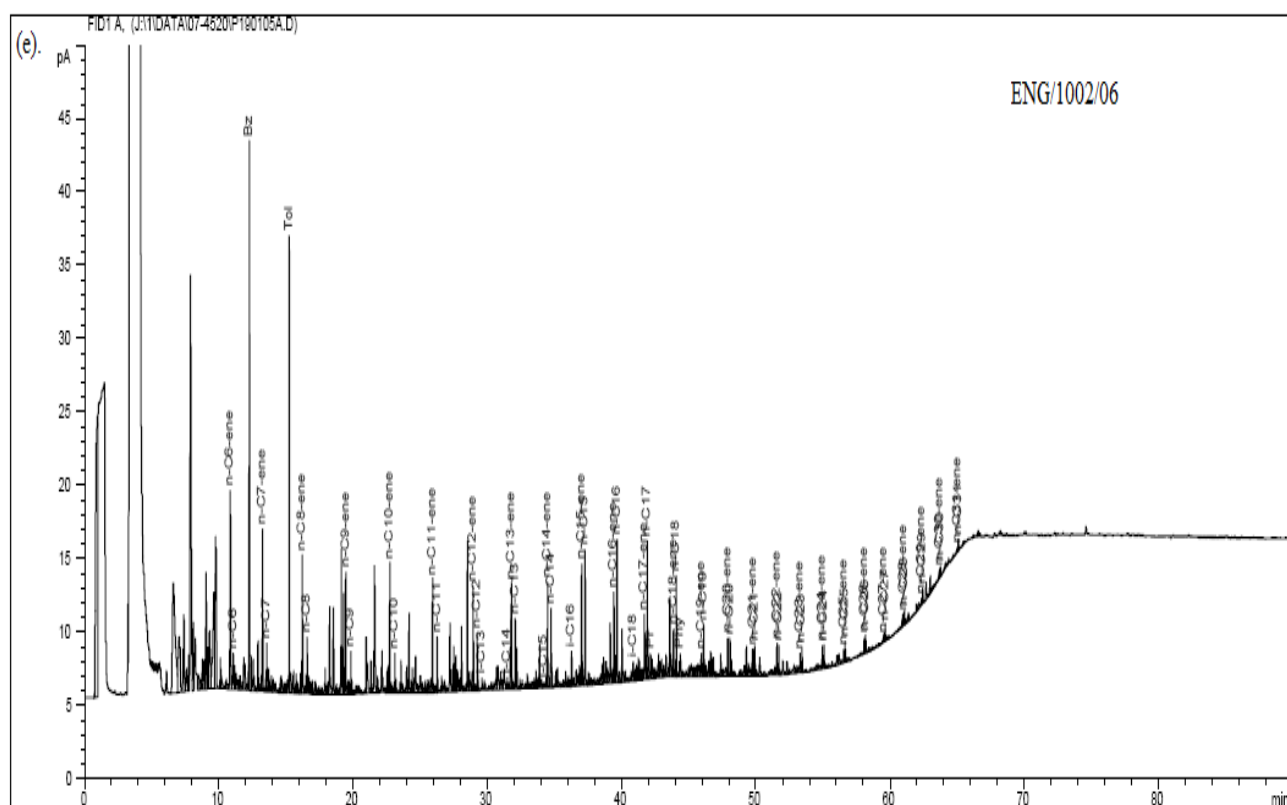
HI = hydrogen index = $S_2 \times 100 / \text{TOC}$ (mg HC/g TOC); OI = oxygen index = $S_3 \times 100 / \text{TOC}$ (mg CO₂/g TOC); GP = Generation Potential = $S_1 + S_2$ (mg HC/g rock); S_1/TOC = normalized oil content = $S_1 \times 100 / \text{TOC}$; PI = production index = $S_1 / (S_1 + S_2)$; Calc. %Ro = Calculated vitrinite reflectance = $0.0180 \times \text{Tmax} - 7.16^{[46]}$; TOC = total organic carbon in rock (weight percent); S_1 = milligrams of hydrocarbons that can be thermally distilled from 1 gram of rock; S_2 = milligrams of hydrocarbons generated by pyrolytic degradation of the kerogen in 1gram of rock; S_3 = milligrams of carbon dioxide per gram of rock; T_{max} = the temperature at which the maximum amount of S_2 hydrocarbons are generated (in °C)

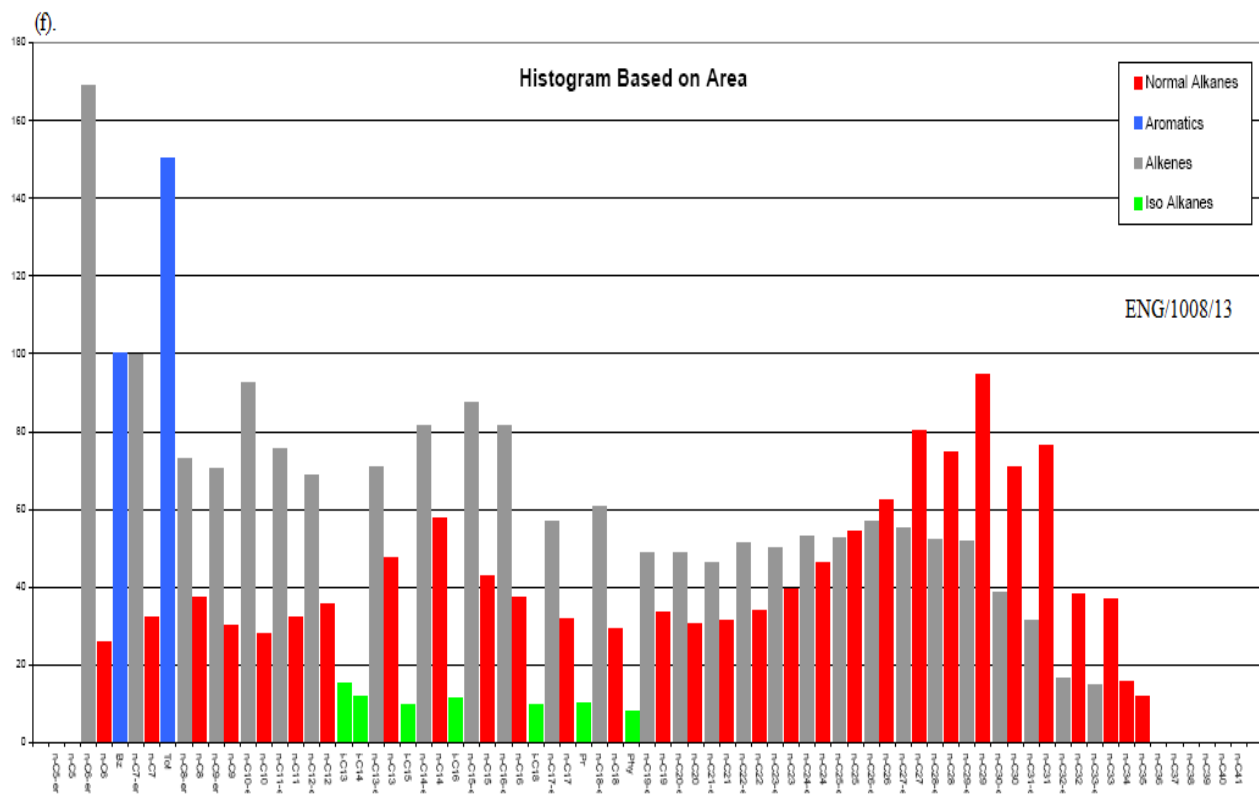
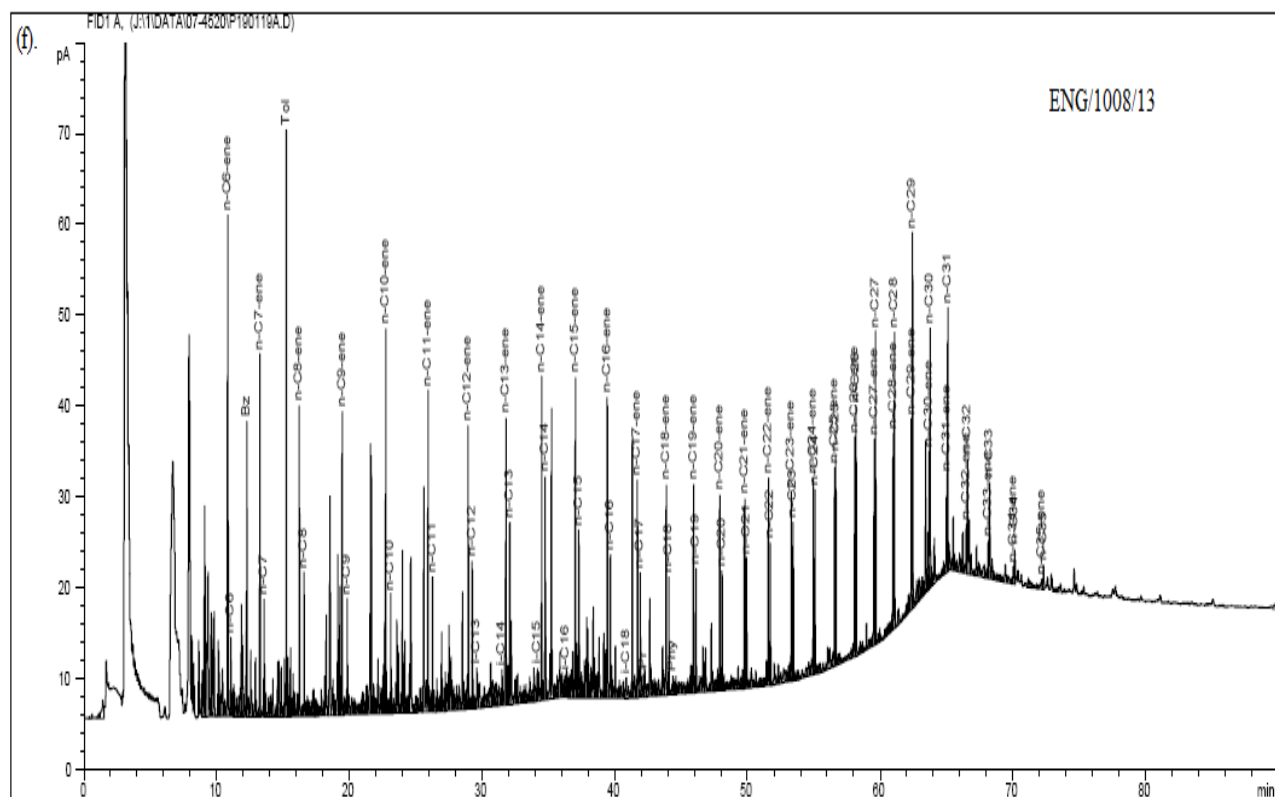


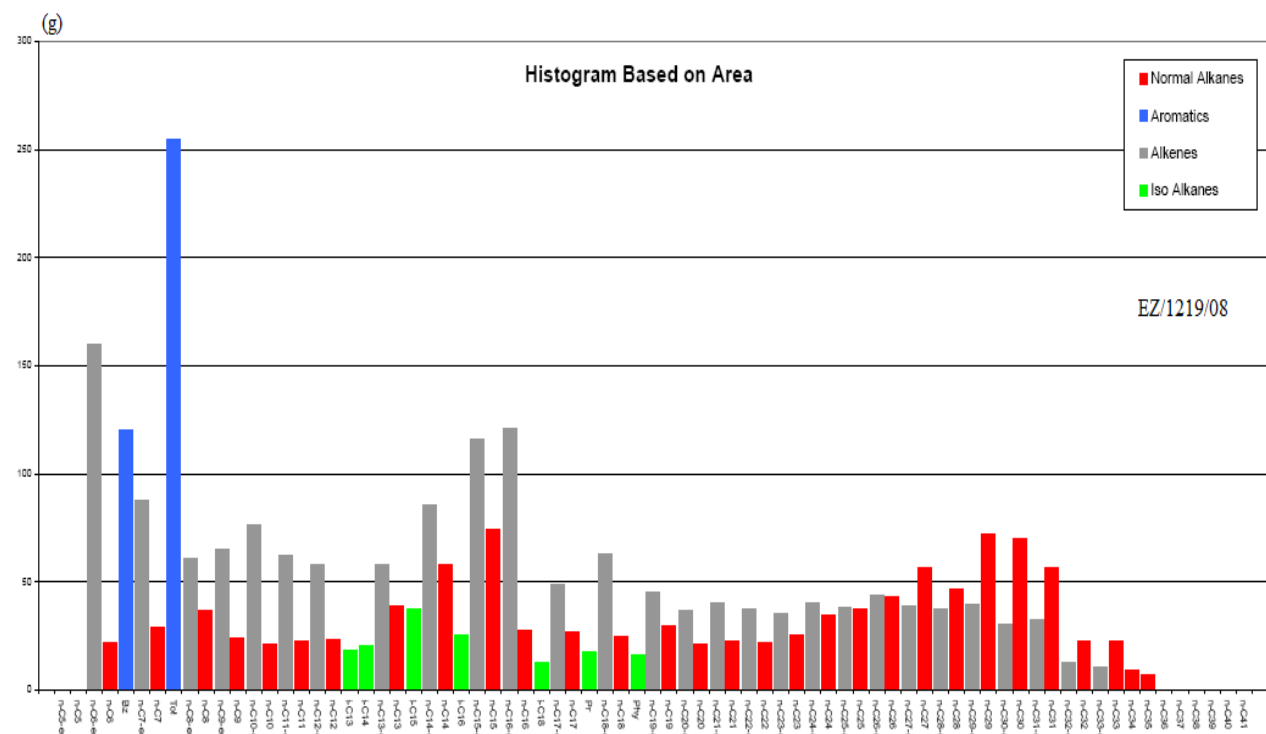
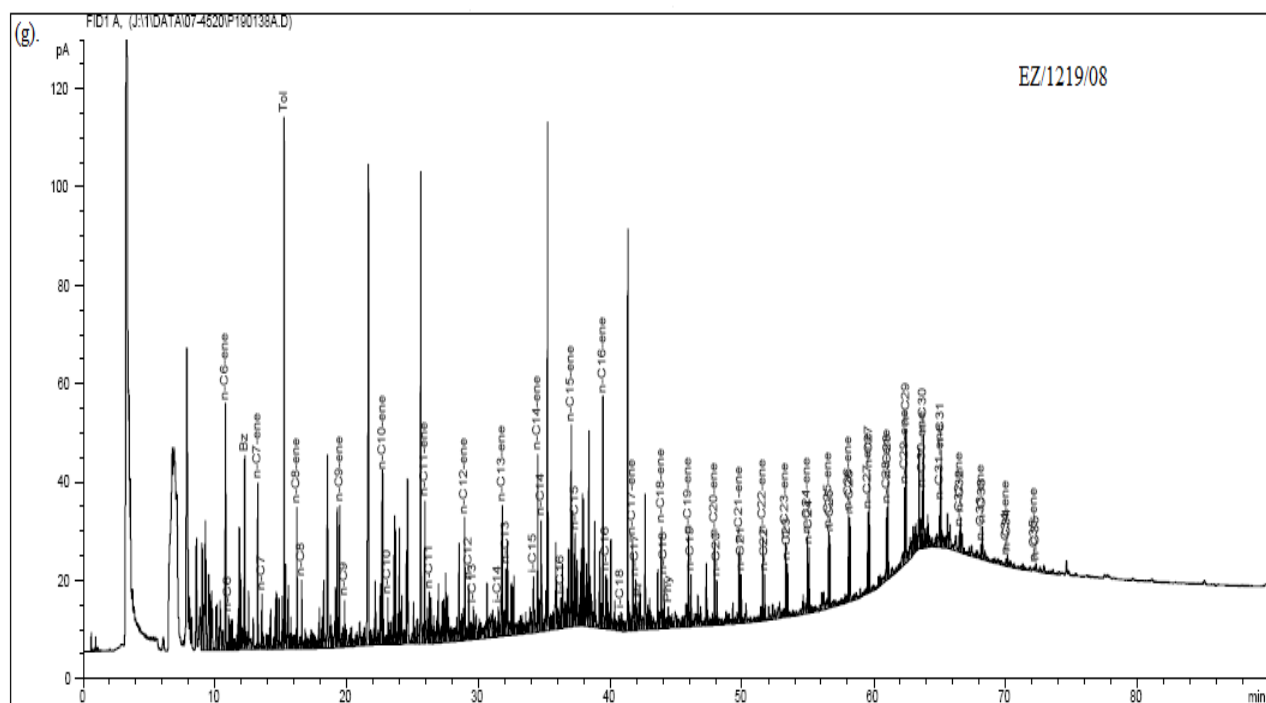












Figures 3a-g. Pyrolysis gas chromatographic fingerprints and histograms obtained on samples

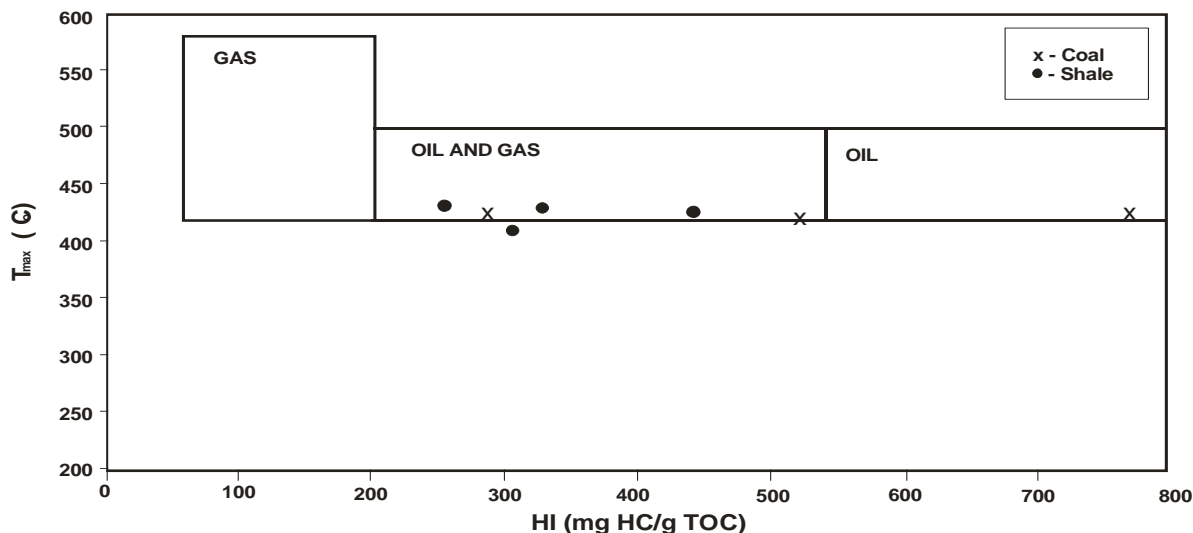


Figure 4. Rock-Eval pyrolysis T_{\max} versus HI for core samples from the Mamu Formation [32]

The prominence of *n*-alkene/*n*-alkane doublets with substantial low-molecular-weight aromatic compounds in the studied samples (Figs. 3a-g), suggests mixed organic matter types [6, 16]. Also, the abundance of *n*-alkene/*n*-alkane doublets indicates that the studied coal and shale samples from the Upper Cretaceous Mamu Formation are capable of liquid hydrocarbon generation given sufficient thermal maturity. This is consistent with the findings of [3-4, 6, 13, 16, 56-58].

5.2. Organic matter type

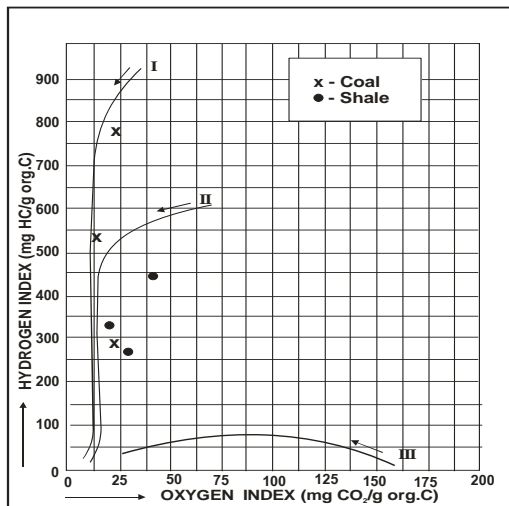


Figure 5. Plot of Rock-Eval pyrolysis HI versus OI showing various kerogen types for the studied coal and shale samples from Mamu Formation [44]

The type of organic matter in the studied coal and shale samples was assessed using hydrogen index (HI) and oxygen index (OI) data obtained by Rock-Eval pyrolysis method (Table 1). The HI (mg HC/g TOC) versus OI (mg CO₂/g TOC) diagram (Fig. 5; [44]) obtained from Rock-Eval pyrolysis suggest a dominance of hydrogen-poor type III organic matter. However, two samples plot between the type I and type II kerogen reference curves (Fig. 5). According to [16], samples plotting in the region between type II and type III reference curves (Fig. 5) would comprise of variable mixtures of hydrogen-rich and hydrogen-poor organic matter. Plot of HI versus T_{\max} (Fig. 6), also classifies the organic matter in the studied coals and shales as containing mainly type II/III with subordinate type II and I kerogen.

The pyrolysis-gas chromatograms give a more detailed picture of the kerogen type than the HI versus T_{\max} plot. The chromatograms for the studied samples are characterized by prominent peaks of *n*-alkene/*n*-alkane in all the samples (Fig. 3a-g). The bimodal distribution (Fig. 3a-g) of the *n*-alkene/*n*-alkane doublets in the studied samples reflects as already mentioned contribution of organic materials from both terrestrial and marine sources [6, 16]. These bimodality have peak maxima at the *n*-C₆ and *n*-C₂₉. The pyrolysis-gas chromatography interpretative ratio for the studied samples are listed in Table 2. The Pr/Ph ratios (>1), Pr/*n*-C₁₇ (0.22-0.67), Ph/*n*-C₁₈ (0.28-0.64) and CPI (1.30-1.76) of the samples are indicative of organic

matter supply from terrestrial source [59]. However, sample 1001/16 with Pr/Ph ratio of 0.4 may be attributed to marine shale source [59].

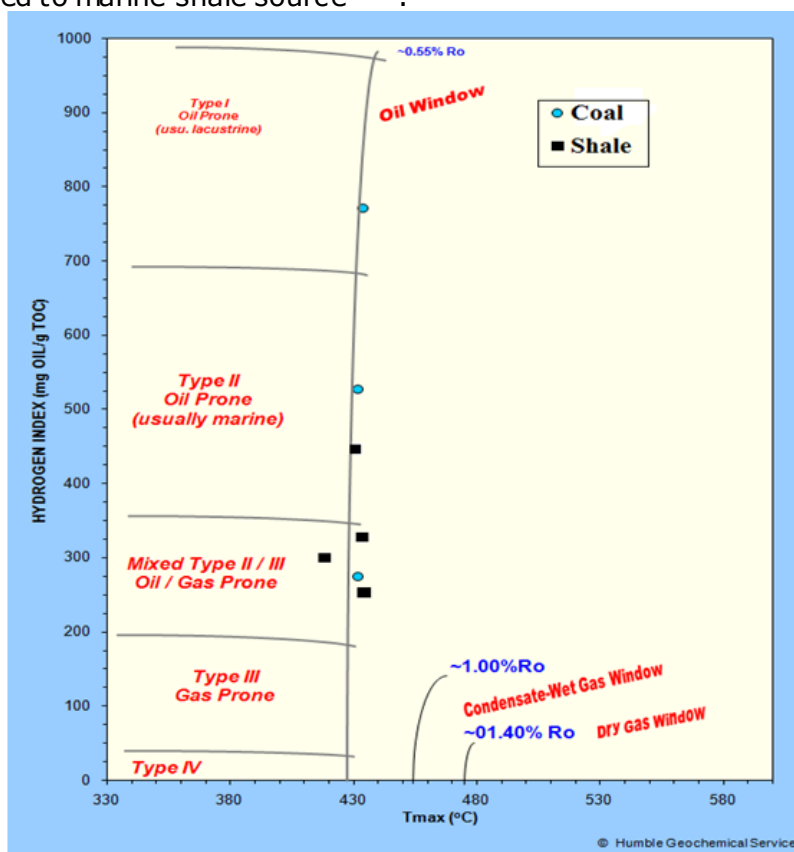


Figure 6. Plot of Rock-Eval pyrolysis HI (mg HC/g TOC) versus T_{max} (°C) showing various kerogen types [44]

Table 2. Pyrolysis-gas chromatography interpretative ratios

Sample number	Depth (m)	Lithology	Pristane	Phytane	Pristane/Phytane	Pristane/nC17	Phytane/nC18	CPI
1001/02	157	Shale	9	9	1	0.43	0.47	1.76
1001/12	186-187	Coal	15	15	1	0.39	0.46	1.54
1001/16	205	Shale	2	5	0.4	0.22	0.63	1.37
1002/06	167-178	Shale	6	5	1.2	0.29	0.29	1.65
1008/13	220-221	Coal	10	8	1.25	0.31	0.28	1.33
1219/08	80-82	Coal	18	16	1.13	0.67	0.64	1.30
1267/03	75-76	Shale	30	26	1.15	0.41	0.51	1.68

5.3. Hydrocarbon products

Pyrolysis-gas chromatography have been used by different authors to evaluate the nature of hydrocarbon products (oil, condensate and gas) generated from sedimentary rocks upon thermal maturation [2-3,16]. According to Dembicki *et al.* [3], the identification of hydrocarbon products from kerogen pyrolysates can avoid the deficiency of organic petrographic techniques such as distinguishing between hydrogen-rich and hydrogen-poor organic matter [60], and the shortcoming of Rock-Eval oxygen index mentioned by [28]. Hydrocarbon products are recognized either qualitatively by gas chromatography fingerprint or quantitatively by hydrocarbon composition (C_1 - C_4 , C_5 - C_{14} and C_{15+}) from kerogen pyrolysate [3]. The pyrograms of the coals and shales are similar qualitatively and quantitatively (Fig. 3a-g) and are dominated by a series of n-alkane/n-alkene doublets from C_5 - C_{33} with maximum peak height obtained in the

nC_{16} – nC_{29} (Figs. 3a–g). The samples also yields hydrocarbon compositions (Figs. 3a–g) dominated by aromatic compounds in the less than $n-C_{15}$ fraction. The decrease in peak heights with increasing carbon number and the bimodal nature of the pyrograms (Figs. 3a–g) are typical of mixed organic sources [16]. Ternary diagram (Fig. 7) of the C_1 – C_5 , C_6 – C_{14} and C_{15+} pyrolysates, show that the studied coal and shale samples generated paraffinic oil high wax. This result is consistent with the findings of [10,61].

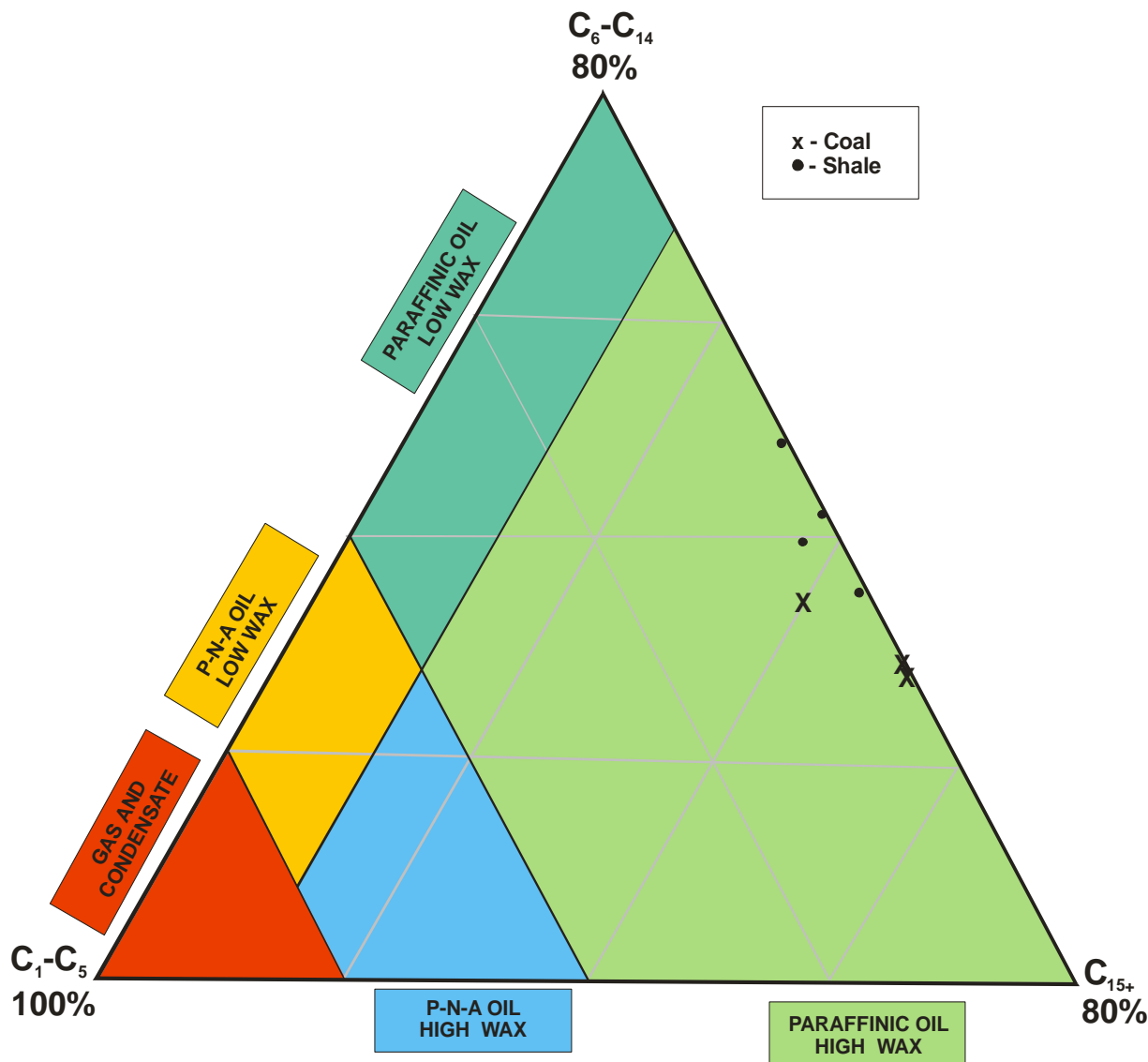


Figure 7. Ternary diagram showing the position of relative concentration of C_1 – C_5 , C_6 – C_{14} and C_{15+} pyrolysates of coal and shale samples from the Mamu Formation [62]

6. Conclusion

The organic matter contained in coals and source rocks from the Maastrichtian Mamu Formation, Anambra Basin, were investigated using pyrolysis–gas chromatography in order to characterize their source rock kerogen type and liquid hydrocarbon generation potential. The pyrolysis–gas chromatographic finger print revealed two types of kerogen (Type III and mixed Type II/III) corresponding to terrigenous and terrigenous/marine derived organic matter respectively. These kerogen types are typical of source rocks with liquid hydrocarbon generation potential and were adjudged to be the precursor of paraffinic oil high wax content of the Anambra Basin.

Acknowledgements

I am indebted to Dan Jarvie for providing the laboratory facilities for this study. I am also grateful to the staff of Humble Geochemical Laboratory, Humble, Texas, for performing the Rock-Eval TOC and pyrolysis-gas chromatography analysis.

References

- [1] Barker C. Pyrolysis techniques for source-rock evaluation. *American Association of Petroleum Geologist Bulletin*, 1974; 58: 2349-2361.
- [2] Larter SR, and Douglas AG. A pyrolysis gas chromatographic method for kerogen typing. In: Douglas, A.G., and Maxwell, J.R., (editors), *Advances in Organic Geochemistry*, Pergamon Press, Oxford 1980, pp. 579-585.
- [3] Dembicki H, Horsfield B, and Thomas TYH. Source rock evaluation by pyrolysis-gas chromatography. *American Association of Petroleum Geologists Bulletin*, 1983; 67: 1094-1103.
- [4] Gormly JR, and Mukhopadhyay PK. Hydrocarbon potential of kerogen types by pyrolysis-gas chromatography. *Organic Geochemistry*, 1983; 10: 597-606.
- [5] Horsfield B. Pyrolysis study and petroleum exploration. In: Brooks, J., and Welte, D., (editors), *Advances in Petroleum Geochemistry*, Volume 1, Academic Press, London 1984, pp. 247-290.
- [6] Hendrix MS, Brassell SC, Carroll AR, and Graham SA. Sedimentology, organic geochemistry and petroleum potential of Jurassic coal measures: Tarim, Junggar, and Turpan Basins, North-west China. *American Association of Petroleum Geologist Bulletin*, 1985; 79: 929-959.
- [7] Sachsenhofer RF, Bechtel A, Gratzer R, and Rainer TM. Source-rock maturity, hydrocarbon potential and oil - source-rock correlation in Well Shorish-1, Erbil Province, Kurdistan Region, Iraq. *Journal of Petroleum Geology*, 2015; 38(4): 357-382.
- [8] Giraud A. Application of pyrolysis and gas chromatography to geochemical characterization of kerogen in sedimentary rock. *American Association of Petroleum Geologists Bulletin*, 1970; 54(3): 439-455.
- [9] Leventhal JS. Step-wise pyrolysis-gas chromatography of kerogen in sedimentary rocks. *Chemical Geology*, 1976; 18: 5-20.
- [10] Garg AK, and Philp RP. Pyrolysis-gas chromatography of asphaltenes/kerogens from source rocks of the Gandhar Field, Cambay Basin, India. *Organic Geochemistry*, 1994; 21(3/4): 383-392.
- [11] Behar F, and Pelet R. Pyrolysis-gas chromatography applied to organic geochemistry: structural similarities between kerogens and asphaltenes from related rock extracts and oils. *Journal of Analytical and Applied Pyrolysis*, 1985; 8: 173-187.
- [12] Larter SR, and Senftle T. Improved kerogen typing for petroleum source rock analysis. *Nature*, 1985; 318: 277-280.
- [13] Solli H, and Leplat P. Pyrolysis-gas chromatography of asphaltenes and kerogens from source rocks and coals - A comparative structural study. *Organic Geochemistry*, 1986; 10: 313-329.
- [14] Philp RP, and Gilbert TD. A review of biomarkers in kerogens as determined by pyrolysis-gas chromatography and pyrolysis-gas chromatography-mass spectrometry. *Journal of Analytical and Applied Pyrolysis*, 1987; 11: 93-108.
- [15] Mukhopadhyay PK. Characterization of amorphous and other organic matter types by microscopy and pyrolysis-gas chromatography. *Organic Geochemistry*, 1989; 14(3): 269-284.
- [16] Katz BJ, Kelly PA, Royle RA, and Jorjorian T. Hydrocarbon products of coals as revealed by pyrolysis-gas chromatography. *Organic Geochemistry*, 1991; 17(6): 711-722.
- [17] Agagu OK, and Ekweozor CM. Source rock characteristics of Senonian shales in the Anambra Syncline, Southern Nigeria. *Journal of Mining and Geology*, 1982; 19: 52-61.
- [18] Ekweozor CM, and Gormly JR. Petroleum geochemistry of Late Cretaceous and Early Tertiary Shales penetrated by Akukwa-2 well in the Anambra Basin, Southern Nigeria. *Journal of Petroleum Geology*, 1983; 6: 207 - 216.
- [19] Hagemann HW, and Pickel W. Characteristics of Upper Cretaceous coals from Enugu (Nigeria) related to bitumen generation and mobilization. *Organic Geochemistry*, 1991; 17: 839-847.
- [20] Unomah GI. Organic geochemical characteristics of the pre-uplift Awgu Shale at Okpa River: Implication for petroleum potential of the Anambra Basin, Nigeria. *Journal of African Earth Sciences*, 1991; 13: 377-385.
- [21] Unomah GI, and Ekweozor CM. Petroleum source-rock assessment of the Campanian Nkporo shale lower Benue Trough, Nigeria. *Nigerian Association of Petroleum Explorationists Bulletin*, 1993; 8(2): 172-186.

- [22] Akaegbobi IM. The petroleum province of southern Nigeria-Niger Delta and Anambra Basin: Organic geochemical and organic petrographic approach. Unpublished Ph.D Dissertation. Technischen Universität 1995, Berlin, 182p.
- [23] Akaegbobi IM, and Schmitt, M. Organic facies, hydrocarbon source potential and the reconstruction of depositional paleoenvironment of Campano-Maastrichtian Nkporo shale in the Cretaceous Anambra Basin, Nigeria. Nigerian Association of Petroleum Explorationists Bulletin, 1998; 13(1): 1-19.
- [24] Akande SO, Hoffknecht A, and Erdtmann BD. Rank and petrographic composition of selected Upper Cretaceous and Tertiary coals of southern Nigeria. International Journal Coal Geology, 1992; 71: 209-224.
- [25] Ogala JE. Hydrocarbon potential of the Upper Cretaceous coal and shale units in the Anambra Basin, southeastern Nigeria. Petroleum and Coal, 2011; 53(1): 35-44.
- [26] Clementz DM. Effect of oil and bitumen saturation on source-rock pyrolysis. American Association of Petroleum Geologists Bulletin, 1979; 63: 2227-2232.
- [27] Espitalie J, Madec M, and Tissot B. Role of mineral matrix in kerogen pyrolysis: Influence on petroleum generation and migration. American Association of Petroleum Geologists Bulletin, 1980; 64: 59-66.
- [28] Katz BJ. Limitation of "Rock-Eval" pyrolysis for typing organic matter. Organic Geochemistry, 1983; 4: 195-199.
- [29] Peters KE. Guidelines for evaluating petroleum source rock using programmed pyrolysis. American Association of Petroleum Geologists Bulletin, 1986; 70(3): 318-329.
- [30] Akinlua A, Ekweozor CM, and Ubwa ST. New classification scheme for Niger Delta kerogen based on pyrolysis gas chromatography. In: Garg, A.K., Banerjee, V., Swamy, S.N., Dwivedi, P., (editors), Proceedings of the 5th International Petroleum Conference and Exhibition on Petroleum Geochemistry and Exploration in the Afro-Asian Region. B.R. Publishing Corporation, New Delhi 2000, India, pp. 81-86.
- [31] Udo OT, Ekweozor CM, and Okogun JI. Organic petrographic and programmed pyrolysis studies of sediments from Northwestern Niger Delta, Nigeria. Journal of Mining and Geology, 1986; 24: 85-96.
- [32] Akande SO, Ogunmoyero IB, Petersen HI, and Nytoft HP. Source rock evaluation of coals from the lower Maastrichtian Mamu Formation, SE Nigeria. Journal of Petroleum Geology, 2007; 30(4): 303-324.
- [33] Reyment RA. Aspects of geology of Nigeria. University of Ibadan Press 1965, 145p.
- [34] Murat RC. Stratigraphy and paleogeography of the Cretaceous and Lower Tertiary in Southern Nigeria. In: Dessauvage, T.F.J. and Whiteman, A.J (editors), African Geology, University of Ibadan Press 1972, pp. 251-266.
- [35] Adeleye DR. Late Cretaceous stratigraphy and paleogeography. American Association Petroleum Geologists Bulletin, 1975; 59: 2302-2313.
- [36] Agagu OK, and Adighije C. Tectonic and Sedimentation framework of the Lower Benue Trough, Southeast Nigeria. Journal of African Earth Sciences, 1983 1: 267-274.
- [37] Agagu OK, Fayose EA, and Petters SW. Stratigraphy and sedimentation in the Senonian Anambra Basin of eastern Nigeria. Journal of Mining and Geology, 1985; 22: 25-36.
- [38] Nwajide CS. Eocene tidal sedimentation in the Anambra Basin, Southern Nigeria. Sedimentary Geology, 25: 1980; 187-207.
- [39] Nwajide CS. Cretaceous sedimentation and paleogeography of the central Benue Trough. In: Ofoegbu, C.O., (editor), The Benue Trough structure and evolution. Braunschweig and Wiesbaden, Germany, Vieweg and Sohne Verlag 1990, pp.19-38.

To whom correspondence should be addressed: Dr. Jude Etunimonuwa Ogala, Department of Geology, Delta State University, P.M.B. 1, Abraka, Nigeria, E-mail: etunimogala@yahoo.com