Organic Petrographical and Organic Geochemical Evaluations of Enugu Coals, Anambra Basin, SE Nigeria

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ABSTRACT

In this investigation, petrographic and organic geochemical characteristics of the Cretaceous Enugu coals (Anambra basin) were performed. Determination of coal quality was based on chemical (moisture, volatile matter, fixed carbon, ash) and elemental analyses (C, H, O, S, and N). The values of the huminite reflectance in organic matter-rich coal levels change between 0.368 and 0.573 %, which correspond to low maturity levels. These parameters are in good agreement with their fluorescence colors, calorific value (average original-2266, dry-3177 Kcal/kg, upper calorific value) and average Tmax (428ºC) values. The organic material in studied coals show low grade transformation due to low lithostatic pressure. Therefore, the petrographic characteristics and quality values of Enugu coals suggest classification as sub-bituminous coal – Lignite.

RockEval analysis results point to an immature to early mature hydrocarbon generation for hydrocarbon derivatives formed by type II/III and III kerogen with average Tmax values of 428ºC. The coals mainly constitute huminites, with few accounts of inertinite and liptinite type macerals. The Enugu coals have high contents of ash and sulfur, clay and calcites as minerals, and gelinites, alginites, cutinites, and sporinites as individual macerals.

(Keywords: Enugu, Anambra basin, organic geochemistry, organic petrography, Cretaceous coal)

INTRODUCTION

Coal, as one of the most important energy sources, takes an important place in human life. Coal is mostly used in thermic power plants to produce electricity, thermal energy, coke for steel production, natural gas, and used in various branches of industry such as production of chemical materials.

Besides use as an energy source, substantial amounts of coal are used in petrochemical products. Because of these, finding new sources near the present reserves and hydrocarbon generation potential of coal have attracted the researchers' interests. Particularly some studies showing that the organic material included in terrestrial sediments have potential in producing oil and natural gas due to increasing heat by deep burial (Hubbard, 1950). After pyrolysis analysis showed that some coals gas generation potential the studies have been concentrated in these fields (Durand and Paratte, 1983; Espitale, *et al.*, 1985; Kalkreuth, *et al.*, 1998; Kavak and Toprak, 2012).

The studies show that the coals of Jurassic-Tertiary age interval tend to have high petroleum generation index (Wilkins and George, 2002). Increasing oil prices and demands, even in our country, has brought up the efficient utilization of coal and research as on hydrocarbon generation potential of coals recently. The study area is located within the Enugu State, Anambra basin (Figure 1).

Besides the known coal area, there are other localities near Onyeama, 3 km to the South of Millikin Hills in Enugu such as Iva Valley, Okpara, Akwuke, containing sub-bituminous seams of Cretaceous flysch. The seam is very thin, 0.30 m thick at most, and carries no economic value at all, therefore, only the coals in Enugu area were found to be valuable to study. The coal region is 3 km away from Enugu-Onitsha road, 5 km away from Enugu Town and comprised of folds from North to South. The Millikin Hills and Ekulu River limit the coal extension. Enugu coals have many industrial utilizations.

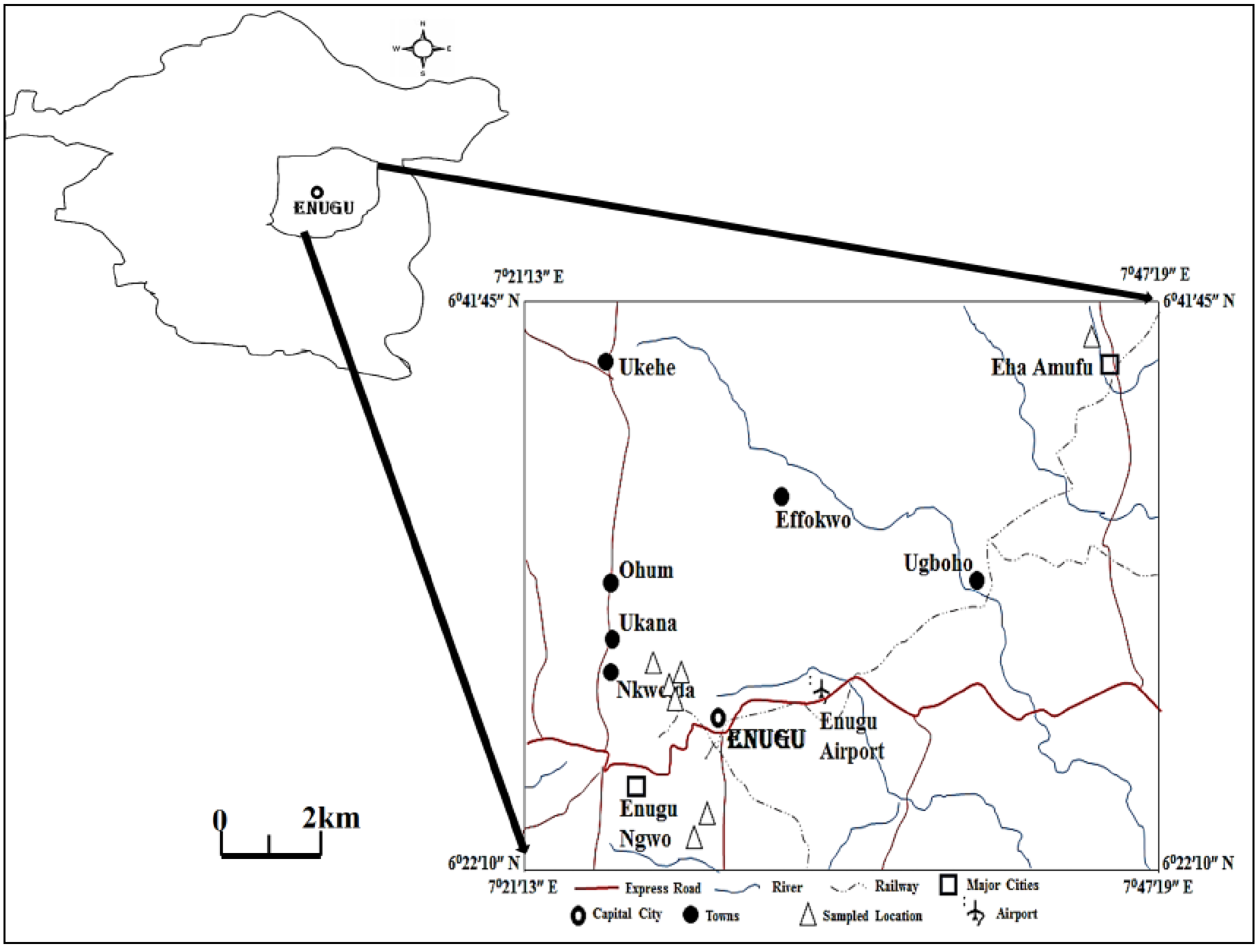

Figure 1: Location Map of the Study Area.

The coal reserve of the region was calculated as 13,909,105 tons for open pit, 74,935,652 ton for underground mining, with considering the density as 1.5 ton/m^3. 10 % of operation loss for open pit, and 25 % for underground operation, were encountered and the coal reserves were calculated respectively as 9,989,149 tons for open pit 46,555,995 tons for underground mining. The analysis results of the main characteristics of the coal were figured out (Table 1).

According to a study performed by Nigerian Mining Corporation (NMC), it was reported that 26,124,200 tons of coal could be produced with conducting 276,107,939 m^{3}of overburden removal and taking a calorific value of 1,458 Kcal/kg as the lower calorific value into consideration, it was suggested that the reserve meets over 20 years fuel demand of a 100 MW power plant. The objective of this study is to exhibit geochemical, petrographical and quality properties of the coals and their relations with each other. Hydrocarbon generation potential of source rocks was also investigated in the study.

REGIONAL GEOLOGICAL SETTING

The tectonism in Southern Nigeria probably started in Early Cretaceous, with the separation of Africa from South America due to the opening of the Atlantic. This resulted in the development of the Benue Trough which stretched in a NE-SW direction (Figure 1), resting unconformably upon the Pre-Cambrian basement complex. It extends from the Gulf of Guinea to the Chad Basin and is thought to have been formed by the Y-shaped (RRR) triple junction ridge system that initiated the breaking up and dispersion of the Afro-Brazilian plates in Early Cretaceous (Kogbe, 1989).

Table 1: Analyzed Results of the Enugu Coals.

Analysis	Available site suitable for open pit operation	Underground operation sites
Moisture %	6.80	5.40
Ash %	12.30	18.40
Volatile Matter %	53.30	45.40
Fixed Carbon %	27.80	42.70
Total Sulphur %	0.56	0.80
Low Calorific Value (Kcal/kg)	6434.10	7025.00

After the evolution of the Benue Trough, sediments started depositing in the Trough. Stages of sedimentations in the trough were in three cycles; the Pre-Cenomanian deposit of Asu River Group followed by the Cenomanian-Santonian sedimentation. According to Hogue (1977) the inversion tectonics of the Abakaliki anticlinoria which led to the evolution of both Afikpo Syncline and Anambra basin, represented the third cycle of sedimentation which produced the incipient Nkporo shale, Enugu shale and Owelli sandstone. The Nkporo group is overlain conformably by the Coal Group consisting of the Mamu, Ajali and Nsukka Formations that form the terminal units of the Cretaceous series.

The Cretaceous series overlying unconformably to the Santonian deformational episode, starts with shales and clays. It continues upward with a succession of silt, sand, gravel, tuff, and tuffite levels. The coal deposited right straight on these units. The coal thickness varies between 4 - 13 m and has an average thickness of 8.5 m. Two coal containing levels are present in the area. Two poor quality coal levels composing of 0.30-0.75 m thick coaly clay and 0.90 m thick clayey coal take place in the alternation of clay and sand 30-35 m above the lower coal seam.

The dip angle of the coaly Cretaceous layers is about 2-5 ^{0}C, and almost horizontal (Dagyaran, 1976). The angles eastwardly tend to increase. Enugu Fault, extending along Ekulu River and Milikin Hills, divides the coaly area into two sectors (Figure 2 and Figure 3).

STRATIGRAPHIC SETTING

The sandstones which are about 330 m thick are an extensive stratigraphic unit conformably overlying the Lower Coal Measure (Mamu Formation) and Nkporo Formations that are 400 and 200 m thick, respectively and underlying the Upper Coal Measure (Nsukka Formation) in the Maastrichtian (Reyment, 1965; Nwajide, 1990) (Figure 2).

The Ajali Formation is typically characterized by white colored sandstone (Reyment, 1965) while the Mamu Formation is essentially composed of sandy shale and some coal seams; the Nkporo Formation consists mainly of grey-blue mudstone and shale with lenses of sandstone (Obaje, 2009). According to Reyment (1965), the prevailing unit of Ajali Formation consists of thick, friable, poorly sorted sandstone.

MATERIAL AND METHODS

Fifteen (15) coal samples with 5 - 10 cm intervals were collected. The inorganic composition of the samples was analyzed with XRD instrument. For chemical and basic analysis, the coal samples were ground according to ASTM standards (Figure 4).

Firstly, they were ground to < 100 mesh size, then, homogenized and analyzed. Chemical analyses (total moisture, ash, volatiles, fixed carbon and calorific value) were conducted with IKA4000 adiabatic calorimeter. Elementary analysis of total sulfur, carbon, hydrogen, and nitrogen, were carried out in the same laboratory with LECO analyzer.

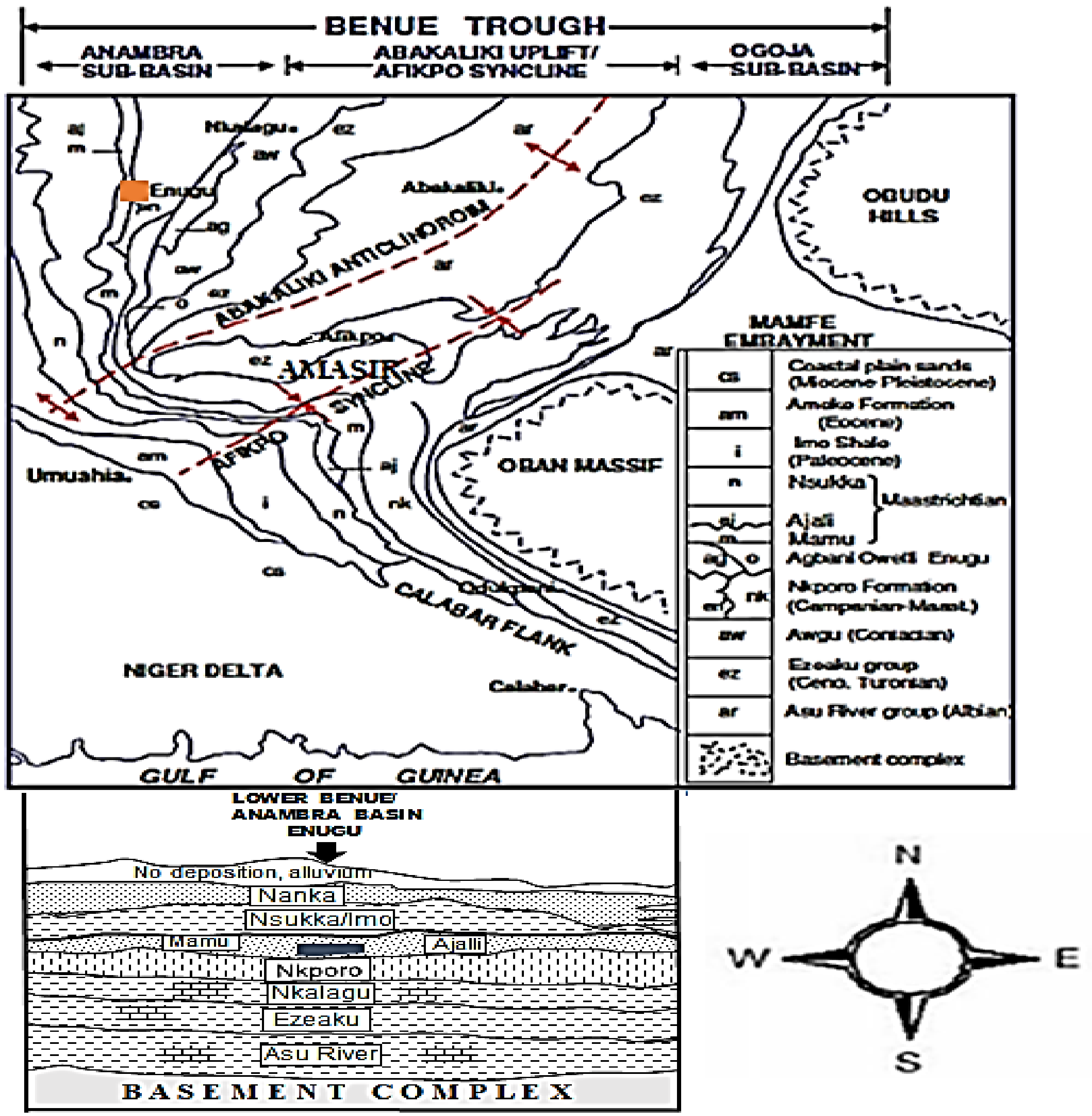

Figure 2: Geologic Map and the Geologic Section of the Enugu Coals under Study (Modified after Akande et al., 2011).

Evaluations were performed on each 7 samples, for the analysis. For coal petrographic analysis, 14 samples were prepared according to ICCP standard (1998 and2001) technics. In order to determine maceral and mineral contents, white, reflected and fluorescence lights were used. A Leitz MPV-SP microscope was used to determine petrographic and mineralogic properties as well as reflectance measurements of the samples. Reflectance values of the samples were performed using 32x and 50x oil objectives at 546 m wavelengths.

Figure 3: Field Views and Mining Sites of the Studied Coals.

For each modal analysis, 500 point measurements were taken; while for reflectance measurements, 100 point measurements were taken as basis. The refractive index (n) of the oil, used for reflectance measurement is 1.518 and the reflectance value of the used standard, saphire, is 0.548 %. MPV Geor software program was used for the reflectance measurements.

Standard palynologic methods (Durand and Nicaise, 1980; Tissot and Welte, 1984) were used to prepare kerogen slides of 5 samples taken from the study area. Kerogen spore alteration color indexes as well as organic content of the samples were determined with polarized microscope. Hydrocarbon source rock properties of 14 samples were determined with TOC-Rock Eval pyrolysis analysis (Espitalie, *et al*., 1985; Peters, 1986).

For biomarker analysis, 5 samples differentiated with aid of Rock Eval, TOC results, were taken to dissolve in 40 hours within Dicloromethane in ASE 300 (Accelerated solvent Extraction). After dissolving, the leached materials were separated from asphalts with column chromatography and the dense material were analyzed with Agilent 6850 whole leachate GC, but gas chromatography mass spectrometer analysis were carried out with Agilent 7890A/5975C GC-MS instrument.

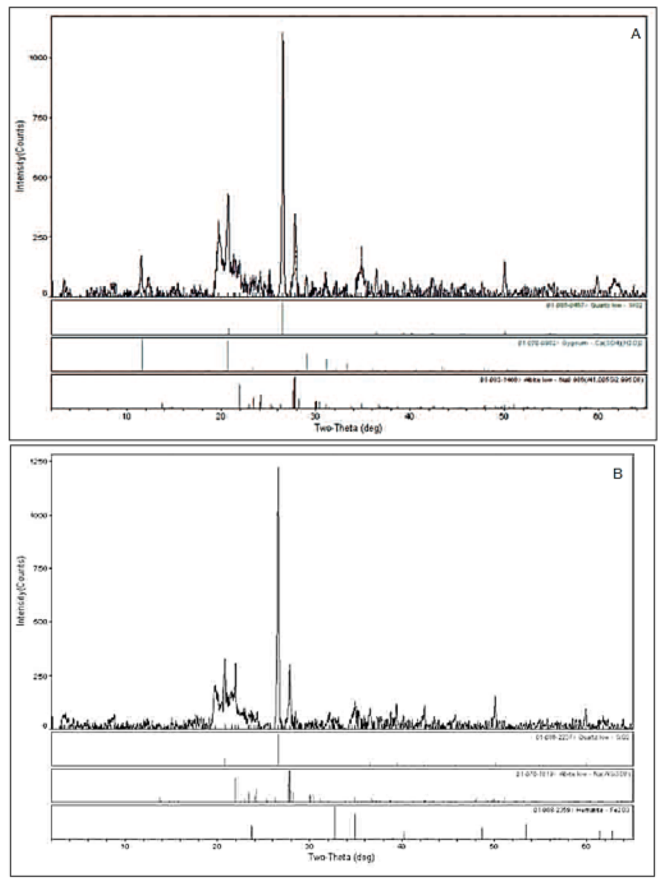

Figure 4: X-ray Graphics of the Samples; A (the sample contains of quartz, gypsum, albite and the relevant peak signs are as shown) B (the sample contains of quartz, albite and very low amount of hematite, and the relevant peak signs are as shown).

Table 2: Basic Analysis of the Enugu Coals.

Sample N0.	Original Sample C (%)	H (%)	(N+O) (%)	S (%)	Dry Sample C (%)	H (%)	(N+O) (%)	S (%)
ENU-1	23.10	2.16	12.80	0.65	36.30	3.31	15.40	1.09
ENU-2	24.40	2.12	10.85	0.64	36.42	3.15	15.63	1.11
ENU-3	23.50	2.15	11.26	0.64	35.55	3.17	16.11	1.11
ENU-4	24.70	2.35	12.30	0.61	35.72	3.14	15.56	1.07
ENU-5	25.10	2.17	12.20	0.60	35.69	3.12	15.27	1.09
ENU-6	24.10	2.20	12.97	0.65	36.01	3.32	15.12	1.12
ENU-7	25.10	2.15	12.04	0.63	35.16	3.18	15.45	1.08

Table 3: Ash Components of the Enugu Coal Samples.

Sample N0.	SiO_2 (%)	$Al_2O_3 + TiO_2$ (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O+K_2O (%)
ENU-1	44.50	17.10	8.77	12.69	4.85	10.66	1.40
ENU-2	32.40	17.10	8.20	20.05	4.50	16.33	1.42
ENU-3	42.40	15.70	7.84	14.30	5.80	12.50	1.51
ENU-4	33.50	18.10	8.10	18.09	4.50	16.36	1.35
ENU-5	43.50	16.10	8.70	14.79	4.87	10.60	1.48
ENU-6	35.40	15.00	8.22	20.10	4.60	16.24	1.40
ENU-7	41.30	15.10	8.20	13.62	4.80	15.44	1.50

Chemical Evaluations

The basic analysis of coals includes C, H, N+O, and S. Basic analysis of the samples showed the C ratio to be (23 - 25 %), H to be 2.1 - 2.3 %, N+O 10.9 – 13 %, S 0.6 - 0.7 %. Air dried samples tend to have C ratio as 35.2 - 36.4 %; H content to be as 3.1 - 3.3 %; N+O, as 15.1 - 16.1 %; S, as 1.09 - 1.12 % (Table 2).

Ash content of 7 coal samples were determined, the dominant ingredient was found to be SiO_2 with 32.4 - 44,5 % Al_2O_3+TiO_2 content is between 15.0 - 18.1 %, Fe_2O_3 between 7.8 - 8.8 %, CaO between 13 - 20 %, MgO between 4.5 - 5.8 %, SO_3 between 10.6 - 16.4 % and Na_2O+K_2O between 1.4 -1.5 % (Table 3). High calcium rate stands for plant remnant's bacterial decay, high collinite and pyrite content of coals are thought to be derived from bacterial reduction of sulfates.

Pyrite content of the Enugu coals and the associated clays are considerably high and observed as framboidal at most (Figures 5a and 5b). Minerals within macerals are observed with various shapes, thicknesses and as filling voids as well as veins (Figures 5c and 5d).

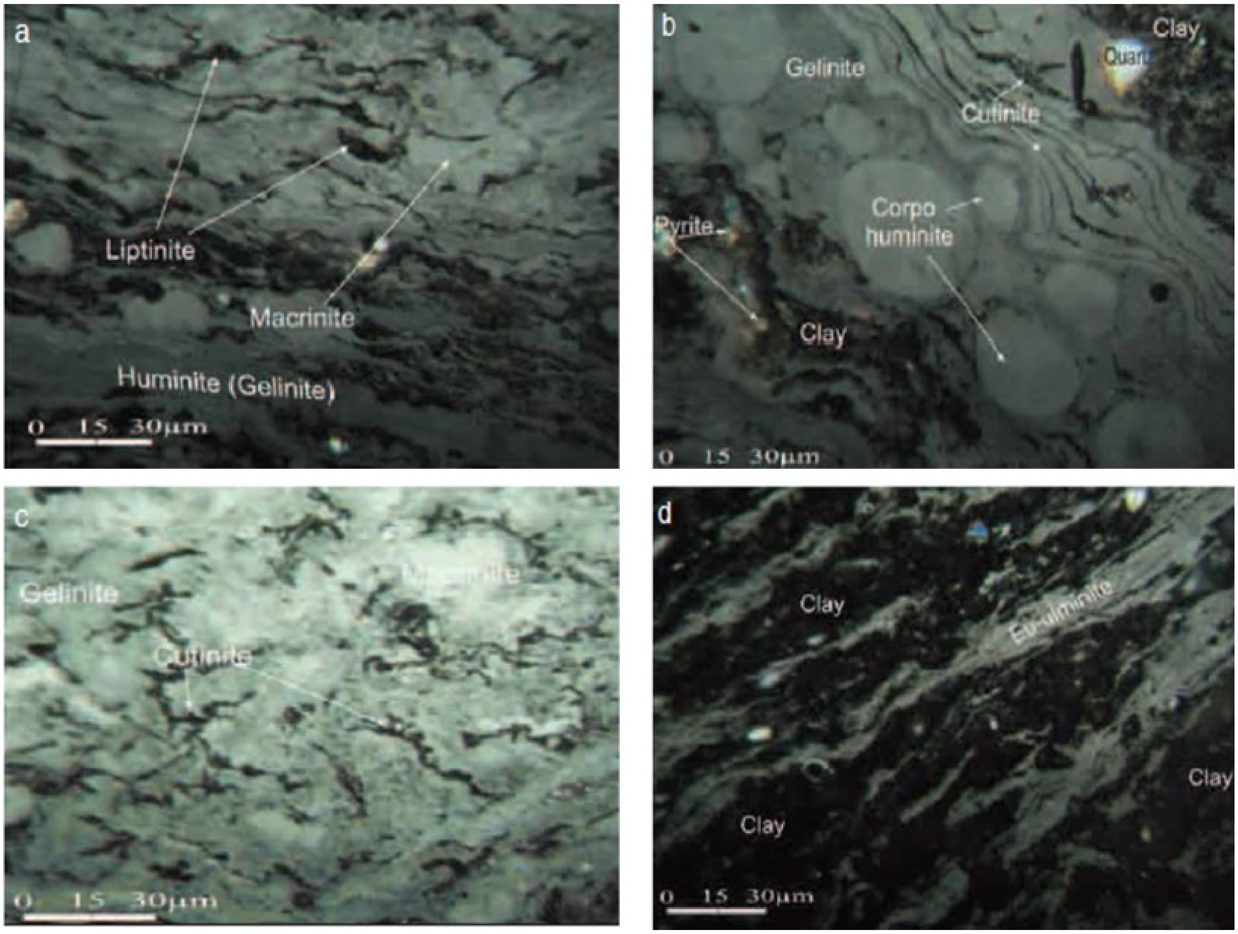

Figure 5: Petrographic Images of the Enugu Coals; a). Common maceral appearances of the coals, gelinite, liptinites and white shapeless macrinites; b). Rounded corpohuminites, dark colored clay, quartz, cutinites, and pyrites observed in the coals; c). Inertinite (macrinite) macerals, cutinites showing lineations, and predominant texture-less gelinites, observed in the area; and d). A succession of common dark colored clays with eu-ulminites which possess textures of the coals.

Table 4 and Table 5 exhibit the coal's moisture, ash, volatile matter, petrographic composition, and calorific value as well as huminite reflection (Rmax) values. Carbon values of the coals, in original sample, vary between 23 – 25 %, 35– 36 % as air dried basis; the hydrogen content of the original samples between 2.1 - 2.3 %, 3.1 - 3.3 % as air dried basis; sulfur content of the original samples between 0.15-0.77 %, 0.30-1.07 %, as air dried basis; in addition, nitrogen + oxygen values of the original samples vary between 10.9 – 13 % and 16.7 % as air dried basis.

The ash content of the coals are high and show variations between 16 - 56 % for original samples, 26 - 76 % for air dried samples, which comply with petrographic composition as well. This data reveals the coal formation, mostly in brackish water conditions, high organic material decaying and abundant inorganic material composition as a result of these (Teichmüller, *et al*., 1998; Kavakand Toprak, 2012).

Table 4: Proximate Analysis of the Enugu Coal Samples.

In Original Samples						
Sample N0.	Moisture (%)	Volatile Matter (%)	Ash (%)	Total Sulphur (%)	High Calorific value (Kcal/kg)	Low Calorific Value (Kcal/kg)
ENU-1	28.30	31.20	18.40	0.77	3237	2938
ENU-2	20.00	34.00	25.00	0.67	2968	2717
ENU-3	14.80	31.90	32.00	0.76	3265	3037
ENU-4	26.20	10.40	56.00	0.36	828	645
ENU-5	49.20	12.80	33.50	0.15	774	457
ENU-6	34.70	20.10	32.90	0.34	1954	1679
ENU-7	38.10	26.30	16.10	0.59	2834	2614

In Dry Samples					
Sample N0.	Volatile Matter (%)	Ash (%)	Total Sulphur (%)	High Calorific value (Kcal/kg)	Low Calorific Value (Kcal/kg)
ENU-1	45.50	25.70	1.07	4510	4318
ENU-2	42.50	31.30	0.83	3703	3533
ENU-3	37.40	37.50	0.90	3825	3659
ENU-4	14.10	75.90	0.48	1121	1069
ENU-5	25.20	65.90	0.30	1520	1432
ENU-6	30.80	50.50	0.53	2989	2856
ENU-7	42.50	26.00	0.96	4571	4380

The Enugu coals indicate 0.2 - 0.8 % original and 0.3 - 1.07 % air dried sulfur content and high amount of ash content, the coals imply to be deposited in a highly elevated continental area. The inorganic content of the coals were also analyzed and clay-mica minerals, quartz as well as plagioclase minerals were found abundantly (Figure 4a, b). The volatile matter content of the coals with 10 – 34% as original and 14 - 46 % as air dried, and the elementary analysis of the coals seem to comply with the coal rank (Figure 4).

Higher calorific values of the coals exhibit 774-3265 (averagely 2266) Kcal/kg of the original samples, as in air dried basis 1121 - 4571 (averagely 3177) Kcal-kg. The chemical analysis and reflectance (Rmax) measurements indicate the coals as sub-bituminous-lignite coalification ranks (ASTM, 1983 and 1992) (Table 5). As ash content of the coals increases, calorific value decreases, while fixed carbon and volatile matter content increases, in some way and rate.

Fixed carbon values are in dried basis and match with organic carbon determined with Rock Eval method. As hydrogen content increases, carbon ratio increases as well, but oxygen decreases. There is a negative relation between volatile matter and ash contents which are the parameters to determine coal quality.

High sulfur content of the coals may be resulted from lake water or brackish water conditions or high pH as well as low Eh conditions and sulphate ion abundances within the lake waters or be derived from primary organic material as well as associated rocks (Stach, *et al.*, 1982).

Table 5: Maceral Analysis and Rmax as Percentage Values (%) of the Enugu Coal Samples
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Sample	Rmax (%)	Huminite								Liptinite						Inertinite					Pyrite				INOR (Cl+Qz +Ca)
		HTEL			DHUM		HCOL		TOT HUM	Sp	Alg	Rs	Cut	Ldt	TOT LIP	Fus	Ma	Fg	Idet	TOT INER	Fr	Eu	Fil	TOT PYR	
		Tex	Tul	Eul	Att	Dn	Gel	Cor																	
ENU-1	0,378	6	5	4	2	6	28	1	52	3	1	0	1	0	5	1	3	0	0	4	3	1	1	5	34
ENU-2	0,462	2	3	4	2	4	32	1	48	2	0	0	1	0	3	1	3	0	0	4	3	1	0	4	41
ENU-3	0,456	3	4	5	2	7	28	1	50	2	2	0	1	0	5	1	3	0	0	4	2	1	1	4	37
ENU-4	0,532	3	4	4	0	5	26	1	43	2	2	0	0	0	4	2	3	0	0	5	2	0	0	2	46
ENU-5	0,517	1	2	3	0	3	24	0	33	2	0	0	0	0	2	0	3	0	0	3	2	0	0	2	60
ENU-6	0,468	3	5	6	3	7	23	2	49	3	2	0	1	0	6	1	3	0	0	4	3	1	1	5	36
ENU-7	0,573	2	4	7	3	8	29	2	55	3	2	0	1	0	6	2	6	0	0	8	2	1	0	3	28
ENU-8	0,368	7	4	4	3	7	23	2	50	2	1	0	1	0	4	2	4	0	0	6	4	1	1	6	40
ENU-9	0,478	3	2	2	5	4	29	1	46	3	2	0	1	0	6	1	3	0	0	4	4	1	0	5	44
ENU-10	0,446	4	3	4	2	6	30	2	51	2	1	0	0	0	3	1	4	0	0	5	3	0	1	5	41
ENU-11	0,541	3	2	2	4	5	26	1	43	4	1	0	0	0	5	2	3	0	0	5	3	0	0	4	47
ENU-12	0,509	4	2	2	3	4	29	2	46	1	1	0	0	0	2	2	1	0	0	3	3	0	0	2	49
ENU-13	0,491	5	3	3	4	4	33	1	53	1	3	0	0	0	4	1	4	0	0	5	4	1	1	2	38
ENU-14	0,548	4	2	3	2	5	24	1	41	1	2	0	0	0	3	1	5	0	0	6	3	1	0	4	50

HTEL- Telohuminite; DHUM- Detrohuminite; HCOL- Gelohuminite; TOT- total; HUM- huminite; LIP- Liptinite; INER- Inertinite; PYR- Pyrite; Cl- Clay; Qz- Quartz; Ca- Calcite; INOR- Inorganic Material; Tex- Textinite; Tul- Texto-ulminite; Eul- Eu-ulminite; Att- Attrinite; Dn- Densinite; Gel- Gelinite; Cor- Corpohuminite; Sp- sporinite; Alg- Alginite; Rs- Resinite; Cut- Cutinite; Ldt- Liptodetrinite; Fus- Fusinite; Ma- Macrinite; Fg- Funginite; Idet.- Inertodetrinite; Fr.- Framboidal; Eu- Euhedral crystalline; Fil.- Crack or void filling pyrite.

Petrographic Evaluations

The studied coal succession is dominantly dull, in addition, they are observed as with dull banded succession of lithotypes. The bands were not defined in detail because of high inorganic material contents of the coals. The coal petrographical determinations were carried out according to Stach, *et. al*., (1982) and ICCP methods (1998 and 2001), the maceral groups' lignite, huminite and inertinite were determined and exhibited on ternary diagrams (Figure 6a).

The petrographic composition of the samples revealed that a heterogeneous input of materials was common during peatification period. To the analysis of 14 coal samples, the coals tend to contain huminite macerals dominantly (33 -55 %) and the predominant maceral is gelinite.

Gelinite is a sub-maceral of huminite-maceral group, showing gelification but no cellular structures at all. Gelinite content of coals varies between 23-33 % and their characteristic features are exhibited on microphotos (Figures 5 a, b, c). In Enugu coals, eu-ulminite (Figure 5d) which shows cellular structure traces and corpohuminite macerals (Figure 5b) may clearly be observed.

Corpohuminites exhibit distinctive large surrounded shapes. Inertinite and liptinites are comparatively lesser in the coals (Table 5). Some of the liptinites show lineation of cutinites as if they are wood tissue lines (Figure 5b), some own various lineation and shapes which they are sporinites and cutinites (Figures 5a and 5c).

Liptinite contents vary between 2-6 %, liptinite and huminite macerals show much more resistance, therefore they are rather more abundant and indicate woody moor type depositional environments (Flores, 2002).

Macrinite and fusinites are the most common (3-8 %) inertinite maceral group (Figures 5a and 5b). The results show that high inertinite containing coals carry more high gas generation potentials. Maceral group raties and huminite reflection values of the coals, which vary between 0.368 - 0.573 %, (Table 5).

High gelinite content implies tissue deterioration of the organic materials, pH value increases up to neutral levels during formation. Fusinite and inertinite macerals indicate increase of oxidation and decrease of water levels within swamps (Figures 5a and 5c) (Flores, 2002; Stach, *et al*., 1982).

The coal contains high amounts of spores and clay minerals also which indicate abundant bacterial activities as well as decaying, in reed moor environment and underwater conditions.

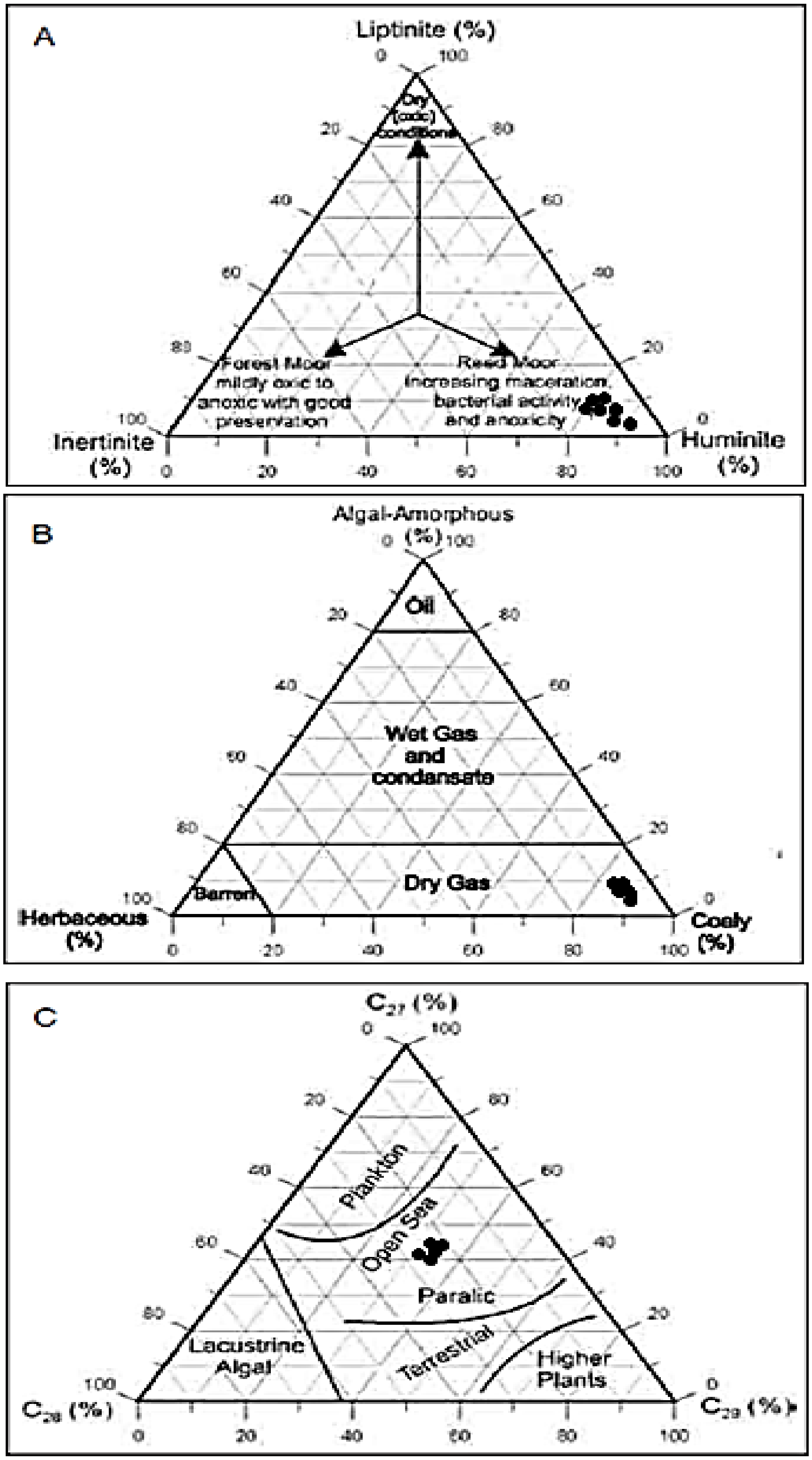

Figure 6: Triangular Diagrams of Organic Material Types of the Enugu Coal Samples.

The mineral matter ratio changes between 31 - 62 % and mostly formed with carbonates, clays and silicate minerals which probably formed as a result of biologic activities in the region (Figures 5b and 5c).

Petrographic compositions of Turkish coals, as pointed out by Toprak (2009), show similarities, and give impressions to have limnic formations.

This claim was supported also with other clues. As seen in the studied coals, high calcium rate indicates alkaline depositional environment, bacteria imply formations of humic gels, nitrogen, and hydrogen rich coal products (Teichmüller, *et al.*, 1998). These properties were also observed in the Amyneto Basin Pliocene aged lignites as in the same way (Iordanidis and Georgakopoulos, 2003).

TPI (Tissue Preservation Index) and VI (Vegetation Index) values were used to determine the paleodepositional environments, in this study. GWI (Ground water Index), GI (Gelification Index) values are used by Georgakopoulos and Valceva (2000) and TPI-VI by Diessel (1986) to determine paleoenviroments for coal depositions. Low TPI values developed either depending on the vegetation type (high angiosperm / gymnosperm ratio), or on low tissue reservation conditions (Kolcon and Sachsenhofer, 1999; Bechtel, *et al.*, 2005). TPI values for Enugu coals vary between 0.15 – 0.35 %. The GI value indicates underground water level and/or pH level. For gelification, regular water flow, bacterial activity, and low acidic conditions are essential (Kolcon and Sachsenhofer, 1999).

For Enugu samples, GI values change between 2.3 and 6.2; GWI values between 2.9 – 11 %; VI values between 0.57 - 1.6 %. TPI's value being lower than 0.5 %. GI value higher than 1, GWI value higher 1 and VI value less than 2, in addition to higher pyrite content, as well as common gastropod shells, indicate the coals to be deposited in a lacustrine environment.

Coal formation took place within high underground water table, average subsidence rate and autochthonous to hypo-autochthonous way of deposition. Here, high alkaline conditions and freshwater effects are mainly observed. Low TPI value indicates high bacterial activity and high pH value, in addition, common presence of gastropods is good supporting evidence for alkaline environmental conditions such as seen in Amyneto Basin (Iordanidis and Georgakopoulos, 2003; Kavakand Toprak,2012). Relatively higher reflectance values of the coals than the other Turkish coals which possess the same quality are probably due to the little distance of the coals to very important tectonic lines (Iordanidis and Georgakopoulos, 2003). The results of the XRD analysis indicate that plagioclase ratio change between 5 - 15 %, quartz between 7 -15 %, gypsum 3 – 8 % and clay + mica 70 – 85 % (Table 6, Fig. 4). Most of the inorganics are clay-mica minerals, quartz and plagioclase and are thought to be of continental origin (Stach, *et al.*, 1986; Toprak, 1996).

Table 6: XRD Analysis Results and the Mineral Distribution of the Enugu Coals.

Sample N0.	Plagioclase (%)	Calcite (%)	Quartz (%)	Gypsum (%)	Hematite (%)	Caly+Mica (%)
ENU-1	10	–	7	3	–	80
ENU-2	10	–	15	–	trace	75
ENU-3	5	–	15	–	trace	80
ENU-4	7	–	15	8	–	70
ENU-5	5	–	10	–	–	85
ENU-6	15	–	10	–	trace	75
ENU-7	5	–	10	–	–	85

Geochemical Evaluations

As geochemical evaluations, Total Organic Carbon (TOC), organic material type and for maturation, Rock-Eval Pyrolysis analysis was carried out. GC, GC-MS and GC-IRMS analysis were conducted to determine biomarker data of the samples. Organic material abundance, organic type, diagenetic development, and source rock potential of the organics were produced with RockEval pyrolysis data. This technique is mainly performed on carbonate shale like rocks, which are thought to have source rock potentials, since Rock- Eval device works well on coaly samples and has well additions to petrographical investigations, the usage of it became very common for coal researches, as well (Teichmüller and Durand, 1983; Durand and Parette, 1983; Fowler, *et al.*, 1991; Korkmaz and Gulbay, 2007; Erik, *et al.*, 2008; Kavak, *et al.*,2010; Kavak and Toprak, 2011; 2012).

Organic Material Quantity (Total Organic Carbon)

Total Organic Carbon (TOC %) analysis was applied on 14 samples and the values vary between 4 - 41.2 % (Table 7). These results show that Enugu coals are rich in organic material contents (TOC > 0.1) and indicate that the coals may be thought as source rocks. Irregular TOC values of the coals may have resulted from biologic productivity, physico-chemical conditions, grain size, sedimentation velocity and the rock type which all have effects on organic material productions in an environment.

As water column over the sediments is rich in organics, the organic material content, as well, gets enriched known as biologic productivity.

As grain size decreases in sediments, organic material contents increased (Hunt, 1967) in addition with sedimentation velocity increase, organic material quantity gets increased as well (Heath, *et al.*, 1977). Organic material quantity is also dependent on rock types; clay and mudstones are rich in organics, but sandstones are poor and carbonates stand between these two (Kavak, 2011). The determined low content of organic materials of the studied samples may also be originated from the mentioned reasons (Burwood, *et al.*, 1992).

Organic Material Type

For a rock to carry the properties of a source rock, it should absolutely contain enough organic material. Besides organic petrographic analysis, Hydrogen Index (HI), Oxygen Index (OI) and Tmax analysis' results are used to determine organic types of the materials with evaluating HI-OI and HI-Tmax diagrams of the samples. According to HI and OI data, organic material points out three types of kerogens which may carry petroleum generation potential.

Type I is a group that has the highest liquid hydrocarbon generation potential. Its oxygen ratio is low, hydrogen ratio is high. For Type II, hydrogen quantity is less than those of the type 1 but amount oxygen is much higher. It represents algae, spore, pollen, cuticle, and woody organic material content. Type III hydrogen content is very low and oxygen content is higher than Type II. Type IV may generate very little amounts of gasses (Tissot and Welte, 1984; Hanson et al., 2000).

The hydrogen index values of the Enugu coals vary between 16 - 178 mg HC/g TOC and oxygen index values between 71 - 180 mg CO_2/g TOC. Production İndex (PI): S_1 / (S_1+S_2) value especially should be higher than 0.05 %, then, interpretation becomes important. The Enugu samples exhibit an average of 0.034 % value (Figure 8).

The low PI may have been caused by the immaturity status of the organic matter. Some high oxygen index values (>150 mg CO_2/g TOC) have probably developed due to mineral matrices and mineral decomposition during pyrolysis. If mineral matter content of the samples is especially rich in clay and carbonates, the results of pyrolysis process may then be affected (Peters, 1986; Langford and Blanc-Valleron, 1990).

While there is a negative relation between HI and liptinite content, a positive relation develops with HI, when huminite ratio is added to liptinite content (Figure 7). Carbon values with addition of total organic carbon and elementary analysis tend to exhibit a strong positive relation.

Table 7: Total Organic Carbon (TOC %) and Rock-Eval Pyrolysis Results of the Enugu Coal Samples.

Sample N0.	TOC (wt.%)	S_1 (mg HC/ g rock)	S_2 (mg HC/ g rock)	S_3 (mg HC/ g rock)	S_2/S_3	Tmax (^{0}C)	HI (mg HC/ g TOC)	OI (mg CO_2/ g TOC)	PI $S_1/(S_1+S_2)$	PY (S_1+S_2)
ENU-1	38.60	0.70	44.00	35.10	1.25	427.00	114.00	91.00	0.02	44.72
ENU-2	41.10	1.50	42.20	64.20	0.65	428.00	103.00	156.00	0.03	43.66
ENU-3	38.60	4.40	58.70	32.10	1.82	428.00	152.00	83.00	0.07	63.08
ENU-4	4.10	0.03	0.80	3.10	0.25	426.00	19.00	74.00	0.03	0.80
ENU-5	12.80	0.50	19.40	23.00	0.84	429.00	152.00	180.00	0.03	19.91
ENU-6	23.50	0.96	41.20	20.10	2.05	428.00	175.00	85.00	0.02	42.17
ENU-7	32.40	0.80	42.00	41.50	1.01	431.00	130.00	128.00	0.02	42.70
ENU-8	38.80	0.70	44.10	35.10	1.25	429.00	112.00	93.00	0.02	44.77
ENU-9	41.20	1.40	42.10	64.20	0.65	429.00	107.00	152.00	0.03	43.52
ENU-10	38.30	4.30	58.60	32.10	1.82	428.00	150.00	87.00	0.07	62.95
ENU-11	4.01	0.10	0.80	3.10	0.25	429.00	16.00	71.00	0.02	0.93
ENU-12	12.90	0.60	19.30	22.90	0.85	428.00	151.00	179.00	0.03	19.92
ENU-13	23.40	0.90	41.20	20.10	2.05	428.00	178.00	82.00	0.02	42.12
ENU-14	32.50	0.80	42.00	41.60	1.01	429.00	133.00	130.00	0.02	42.73

TOC: Total organic carbon (%), S_1: mg HC\g rock, S_2: Hydrocarbons formed as a result of disintegrations Kerogens (mg HC/ g TOC); S_3: CO_2 value (mg CO_2\g TOC), Tmax: Maximum thermal value as S_2gets to maximum level along Pyrolysis analysis; HI: Hydrogen Index (mg HC/ g TOC), OI: Oxygen Index (mg CO_2\g TOC), PI: Production İndex (mg HC\g TOC), S_2\S_3: Hydrocarbon type index, PY: Potential efficiency (mg HC\g TOC).

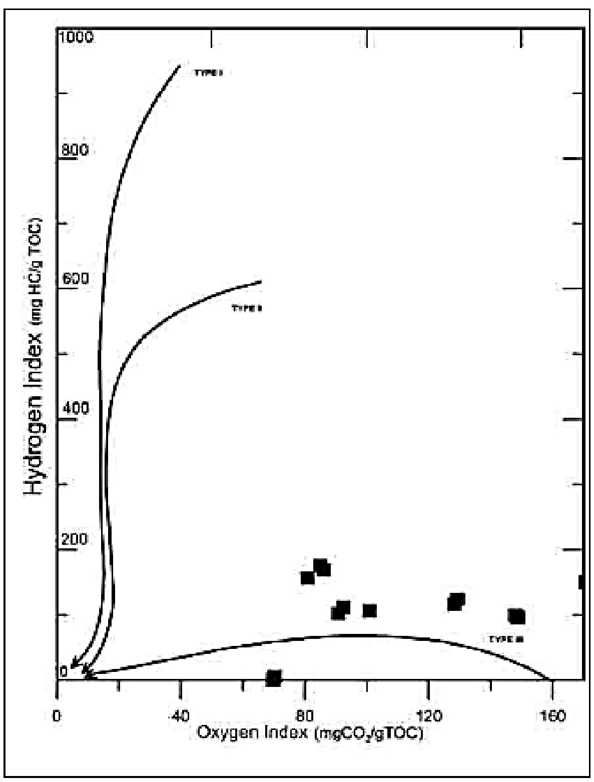

Figure 7: Hydrogen Index-Oxygen Index Diagram of the Studied Samples (Tissot and Welte, 1984).

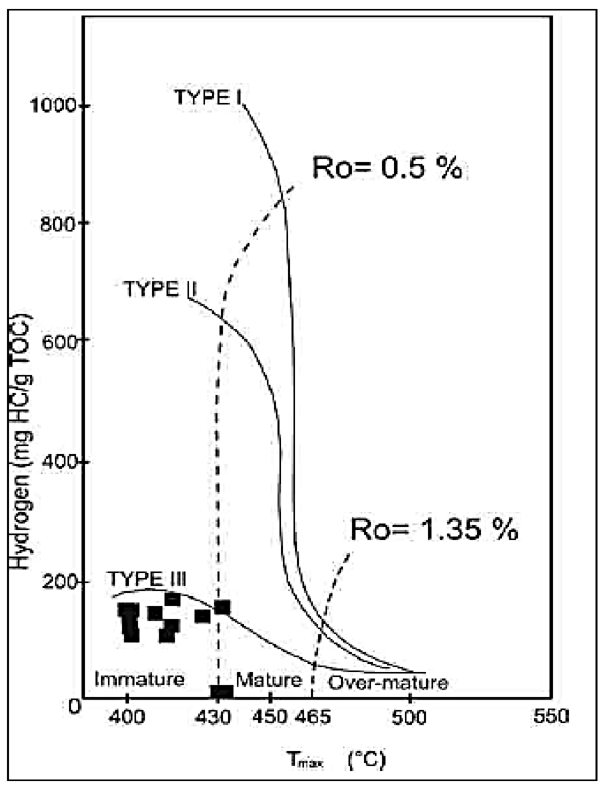

Figure 8: Classification of Kerogen Types by Hydrogen Index-Tmax Diagram (Mukhopadyay, *et al.*, 1995)

According to the values of the samples plotted on Van Krevelen (Hydrogen Index-Oxygen Index) and HI-Tmax diagrams, most of the samples tend to fall at the Type II-III (terrestrial and marine) and Type III areas (Figures 7 and 8). This definition is also supported with palynologic determinations from the Kerogen preparations, which indicates coaly-woody material dominance.

Coaly organic matter of the samples seems to be 84 - 89 % woody, 11 – 16 %, herbaceous, 5% and 10 % of algae amorphous organic matter (Figure 6). It is thought that amorphous organic materials were probably formed during transportation of the terrestrial materials by alteration and disintegration.

As a result of comparison, different analytical data exhibit important interrelations (Figure 8). Total organic carbon and high heat value show a strong positive bond. Total organic carbon and high calorific value exhibit a strong positive relation. As remnant carbon, which is a parameter of Rock Eval increases, fixed carbon and carbon values increase, as well, but ash content decreases.

Pyrolyzed carbon amount and fixed carbon, oxygen index-oxygen content has positive relation but S_3 ash and oxygen index high calorific value as well as C and fixed carbon values. Very low detection value of low carbon numbered n-alkanes, especially of n-C_6 and n-C_{17}, additionally not having organic compounds of above C_{32} in gas chromatograms, point to terrestrial as well as marine originated organic materials. İn biomarker analysis of the Enugu samples, high molecular abundant (C_{20}+) compounds on n-alkanes are predominant and predominant of odd numbered n-alkanes between C_{25}-C_{31} as well as C_{29} steranes against to C_{27} - C_{28}, and abundance of C_{29}αααR isomers indicate organic matters derived from terrestrial materials.

Organic Maturation

For hydrocarbon formation and the realization of the maturity of the organic matter, it is required that the thermal conditions should be raised to the thermal disintegration levels of the kerogens. Tmax (˚C) value represents thermal maturity, and it expresses maturation with the depth increase.

Tmax values of Enugu coals vary between 426-431 ˚C and show 428 ˚C as average (Table 7).

These values indicate organic matter rich parts of the coals to be immature and at premature zone. In kerogen preparations light yellow and light brown organic material alteration colors, light yellow, colorless spores, low Rmax values all support Tmax data about maturation.

Most of the samples scattered in the pre-mature and immature zones, on HI-Tmax diagram (Figure 8). PI values of these samples are < 0.1 and indicate low maturations. Huminite reflection (Rmax) values of the samples vary between 0.368 - 0.573 %. Since high ash content effect, the comparison of the samples, huminite reflection values of calorific values of the samples containing less than 15% of ash were taken into consideration.

Although both data individually indicate immature levels, there is a meaningful linear relation between huminite reflectance (Rmax) and Tmax values due to different petrographic compositions. 20 (S)/(20S+20R), the ββ/(ββ+αα) sterane ratio and Tmax, as well as reflection values increase proportionally. Steraneratios of the samples are less than 1 and correspond with immature phase. Ts / (Ts+Tm) ratio of the samples are between 0.11 - 1.15. Ts/Tm=1 value indicates the border between immature (Ts/Tm<1) and mature (Ts/Tm>1) organic materials. 18 α (H) - 22, 29, 30-trisnorneonhopane (Ts)/(Tm) of Enugu coals is between 0.13 - 0.15 (Table 7).

Generally, C_{31} or C_{32} homohopanes are used to determine 25S / (22S+22 R) ratios. This ratio increase is between 0.53 - 0.57 for the studied samples. Diasterane/sterane ratios are low for immature sediments and are 2.9 - 4.2 for the samples (Arfaouni et. al., 2007). Moretane / Hopane ratio is between 0.55 - 0.57 and generally decreases with maturation increase (Kvenvolden and Simoneit, 1990; Kavak and Toprak, 2012).

Besides low bitumen/TOC ratio and dense peak scattering of sterane and triterpanes at chromatograms indicate the immature zone (Tissot and Welte, 1984). Another maturity parameter derived from C_{29} regular stranes is 5 α(H), 14β (H), 17β (H) C_{29}sterane and 5 α (H), 14α (H), 17α (H) C_{29}sterane (αββ) / (αββ+ ααα) ratio.This ratio is always larger than 1. Ts/Tm ratio for the samples is 0.13 - 0.15.

Hydrocarbon Generation Potential

Analysis of the samples is used in source abundance diagram (HI-TOC) (Jackson *et al.*, 1985) (Figure 9). S_1 values of the samples are considerably low, between 1.7 and 4mg HC/g rock; S_2 values between 38 and 63 mgHC/g rock (Table 6). Since S_2 value of 4 mgHC/g rock is low, it indicates weak rock potential; but when higher than 4.0, a source rock is considered, in addition that S_2 values define whether or not it is a good or better source rock (Table 8).

To this data, the coals may be the source rocks and the other organic rich carbonate levels have no source rock potential at all.

The most critical value is the presence of hydrogen-rich organic material. To Hunt (1995), in order to generate hydrocarbons from coals and terrestrial materials, larger hydrogen index value from 200 mg HC/g TOC is essential. High hydrogen index value and HI-Tmax diagram scatter indicate the samples to contain partial marine organic material influx and limited gas generation potential.

As in the studied samples, humic coals form from Type III kerogens may generate gasses. Besides there is a capability of gas generation potential of Enugu coals, their incomplete maturation has prevented it. Hydrocarbon generation index is also named as genetic potential or production index and show similar results in the same way of using (S_1+S_2), TOC values.

Genetic potential values vary between 0.1 - 9.5 mg HC/g rock, but 6.18 mg HC/g as average. Due to finding lower values than 2mg HC/g of the studied samples shows that they carry rare gas generation potentials (Welte, 1965; Tissot and Welte, 1984). Low values of S_2/S_3 from 2, PI value lower than 0.1 and Tmax values indicate immature stages. Some samples scatter in the weak generation potential area of the HI-TOC diagram and some samples indicate gas and little petroleum generation potential.

According to organic maturation data of the coals as well as organically rich levels, despite containing enough amounts, their maturation level is considerably low for generation. It was determined that there was a negative relation between diasterane / sterane ratio and positive relation between ββ / (ββ/αα) ratio of Tmax value, there is also a negative relation between Rmax and C_{32}(22S / (22S + 22R)) ratios, in addition to these, their correlation coefficients are considerably low and were not given on the graphics.

Molecular Composition of the Coals

The leaching amount of the studied coals are low (between 14.7 and 92.4), the composition contains mostly resins and asphalthenes which are of low organic maturity. The distributions of steranes and triterpanes and their peak definitions were carried out on m/z 191 and m/z 217 chromatogrammes (Tables 8, 9, 10, 11, and 12).

Table 8: Biomarker Parameters Derived from the m/z 217 and m/z 191 Mass Chromatograms.

Sample	^{13}C	Standard Deviation	191			217			
			H/H+M)	Ts/Tm	C_{31} 22S / (22S + 22R)	C_{29} 20S / (20S + 20R)	C_{27} %	C_{28} %	C_{29} %
ENU-1	-27.31	0.19	0.82	0.15	0.53	0.55	42	26	32
ENU-6	-22.95	0.09	0.83	0.13	0.55	0.56	41	25	34
ENU-7	-22.45	0.07	0.85	0.14	0.57	0.57	44	22	34

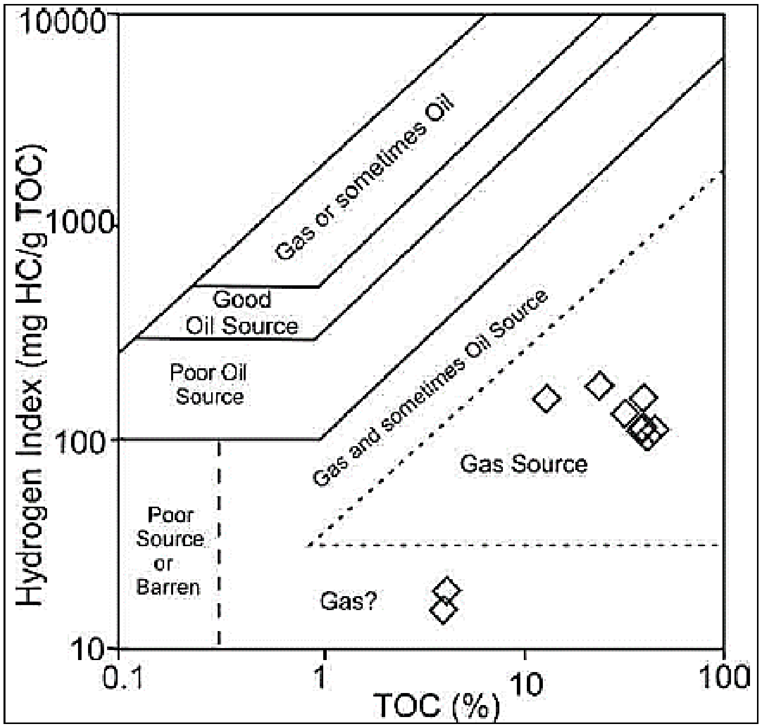

Figure 9: Hydrogen Index- Tmax Diagram of Enugu Coal Samples (developed from Jackson, *et al.*, 1985).

Table 9: Sterane Peak Determinations on m/z 217 Mass Chromatograms.

Component	Component Name
1	C_{27} 13β(H), 17α(H)-Diasterane (20S)
2	C_{27} 13β(H), 17α(H)-Diasterane (20R)
3	C_{27} 13β(H), 17α(H)-Diasterane (20S)
4	C_{27} 13β(H), 17α(H)-Diasterane (20R)
5	C_{26} 13β(H), 17α(H)-Diasterane (20S)
6	C_{28} 13β(H), 17α(H)-Diasterane (20R)
7	C_{28} 13β(H), 17α(H)-Diasterane (20S)
8	C_{27} 5α(H), 14α(H), 17α(H)-Sterane (20S)+ C_{28} 13α(H), 17β(H)-Diasterane (20S)
9	C_{27} 5α(H), 14β(H), 17β(H)-Sterane (20R)+ C_{29}13β(H), 17α(H)-Diasterane (20S)
10	C_{27} 5α(H), 14β(H), 17β(H)-Sterane (20S) + C_{28} 13α(H), 17β(H)-Diasterane (20R)
11	C_{27} 5α(H), 14α(H), 17α(H)-Sterane (20R)
12	C_{29}13β(H), 17α(H)-Diasterane (20R)
13	C_{29}13α(H), 17β(H)-Diasterane (20S)
14	C_{28}5α(H), 14α(H), 17α(H)-Sterane (20S)
15	C_{28}5α(H), 14β(H), 17β(H)-Sterane (20R) + C_{29}13α(H), 17β(H)-Diasterane (20R)
16	C_{28}5α(H), 14β(H), 17β(H)-Sterane (20S)
17	C_{28}5α(H), 14α(H), 17α(H)-Sterane (20R)
18	C_{29}5α(H), 14βH), 17α(H)-Sterane (20R)
19	C_{29}5α(H), 14β(H), 17β(H)-Sterane (20R)
20	C_{29}5α(H), 14β(H), 17β(H)-Sterane (20S)
21	C_{29}5α(H), 14α(H), 17α(H)-Sterane (20R)
22	C_{29}5α(H), 14α(H), 17α(H)-Sterane (20S)
23	C_{30}5α(H), 14β(H), 17β(H)-Sterane (20R)
24	C_{30}5α(H), 14β(H), 17β(H)-Sterane (20S)
25	C_{29}5α(H), 14α(H), 17α(H)-Sterane (20R)

Table 10: Triterpane Peak Determinations on m/z 191 Mass Chromatograms.

Component	Component Name
1	C_{19}Tricyclicterpane
2	C_{20}Tricyclicterpane
3	C_{21}Tricyclicterpane
4	C_{22}Tricyclicterpane
5	C_{23}Tricyclicterpane
6	C_{24}Tricyclicterpane
7	C_{25}Tricyclicterpane (22S+22R)
8	C_{24}tetracyclichopane
9	C_{26}Tricyclicterpane 22 (S)
10	C_{26}Tricyclicterpane 22 (R)
11	C_{28}Tricyclicterpane
12	C_{29}Tricyclicterpane
13	C_{27} 18α(H)-22,29,30-Trisnanorhopane (Ts)
14	C_{27} 17α(H)-22,29,30-Trisnorhopane (Tm)
15	17α(H)-29,30-Bisnorhopane
16	C_{30}Tricyclicterpane
17	17α(H)-28,30-Bisnorhopane
18	C_{29} 17α(H), 21β(H)-30-Norhopane
19	C_{29}Ts[(18α(H)]-30-Norhopane
20	C_{30} 17α(H) Diahopane
21	C_{29} 17β(H), 21α(H)-30- Normoretane
22	Oleanane
23	C_{30} 17α(H), 21β(H)- Hopane
24	C_{30} 17β(H), 21α(H)- Moretane
25	C_{31} 17α(H), 21β(H)-30-Homohopane (22S)
26	C_{31}17α(H), 21β(H)-30-Homohopane (22R)
27	Gammacerane
28	Homomoretane
29	Homohopane
30	C_{32} 17α(H), 21β(H)-30,31-Bishomohopane (22R)
31	C_{33} 17α(H), 21β(H)-30,31,32-Trishomohopane (22S)
32	C_{33} 17α(H), 21β(H)-30,31,32-Tishomohopane (22R)
33	C_{34} 17α(H), 21β(H)-30,31,32,33-Tetrakishomohopane (22S)
34	C_{34} 17α(H), 21β(H)-30,31,32,33-Tetrakishomohopane (22R)
35	C_{35} 17α(H), 21β(H)-30,31,32,33,34-Pentakishomohopane (22S)
36	C_{35} 17α(H), 21β(H)-30,31,32,33,34-Pentakishomohopane (22R)

Table 11: Gas Chromatography Results of the Enugu Coal Samples.

Sample N0.	Pr/Ph	n-Alkane Distribution	Explanation
ENU-1	Not certain	n-C_{15}-n-C_{22} interval is distinctive	Biomarkers are distinctive
ENU-2	< 1	n-C_{15}-n-C_{22} interval is distinctive	Biomarkers are distinctive
ENU-3	> 1	n-C_{16}-n-C_{19} interval is distinctive	Further Bio-degradation level Second organic material
ENU-6	Not certain	n-C_{15}-n-C_{32} interval is distinctive	Biomarkers are distinctive
ENU-7	> 1	n-C_{15}-n-C_{22} interval is distinctive	Biomarkers are distinctive

Table 12: Leach Amount of the Samples of the Enugu Coals and their Organic Properties.

Sample No.	Asp (%)	Saturated (%)	Aromatic (%)	Polar (%)	Aromatic (g)	Saturated (g)	Total Leachate (ppm)	Total Leachate Quantity (g)
ENU-1	50	0.97	1.8	47.2	0.013	0.002	82.1	0.117
ENU-2	51.7	0.44	1.9	45.9	0.003	0.001	92.4	0.11
ENU-3	57.8	1.04	0.2	40.9	0.003	0.001	82.4	0.073
ENU-4	—	—	—	—	0.0006	0.0001	14.7	0.01
ENU-5	36.6	1.24	0.7	41.4	0.011	0.001	58.2	0.033
ENU-6	48	0.59	0.3	51.1	0.013	0.002	71.5	0.117
ENU-7	55.8	0.76	0.67	42.8	0.014	0.002	92.1	0.169

n-alkane are distributed in C_{20}/C_{32} (Table 11) interval (Figure 10). In GC analysis low carbon numbered n-alkanes as n-C_{17}, n-C_{27}, n-C_{30} and n-C_3, as well as n-alkanes with CS2 and benzene were determined. Typical saturated hydrocarbon GC-Mg data of the samples are shown in Figure 11. Comparative abundance of long chained C_{27}-C_{31} alkanes to total n-alkanes indicate terrestrial plants (Moldowan, *et al.*, 1985), the short-chained n-alkanes (<C_{20}) with their low ratio within the Enugu samples mostly present abundantly in algaes and microorganisms.

Predominantly medium and high molecular weighted n-alkanes (C_{21}-C_{25}) are common in the samples, indicating the presence of terrestrial and limnic organic material together. In m/z217 mass chromatogrammes of the samples, C_{27}, C_{28}, C_{29} steranes and their 20S as well as 20R epimers (Table 8 and Figure 11) were defined. Enugu coal samples contain C_{27} and C_{29} steranes with low amount of non-aromatic hydrocarbon compounds. C_{28} steranes and C_{28} diasteranes ratio of the samples are considerably low (C_{29}>C_{27}>C_{28}) (Figure 6). As it is indicated that algaes are the primary source of C_{27} steranes, C_{29} steranes are mostly derived from terrestrial plants. In addition, C_{20}, C_{21}, C_{23},C_{24}, C_{26}, C_{28}, C_{29} tricyclic terpanes were also determined in the samples. The abundance of C_{24} tetracyclic terpane within the leachate is a 0.84 - 1.52; C_{28}/C_{29} sterane ratio between 1.30 - 1.45 in the coal samples.

Especially, as in the coal samples, marine water influx to peat formation in terrestrial environments may be traced with C_{27} regular sterane abundance within C_{29} and C_{28} steranes. To Bray and Evans (1961), CPI (C_{24}-C_{34}) =1, CPI (C_{16}-C_{26}) = 2. At the m/z 191 mass fregmantogrammes, very low tricyclicterpane were traced in two samples. In Enugu coal samples, C_{29}n orhopane is much more abundant than C_{30} hopanes. Higher carbon numbered components from C_{32} homohopanes were recorded from three samples.

Sterane/hopane ratio is between 0.82 - 0.85 and steranes are much more common. C_{29}/C_{30} hopane is used to differentiate carbonates from clastic lithologies (Waples and Machihara, 1991), and this ratio is between 0.53 - 0.57 for the samples (Table 8).

Depositional Environment Properties

The studied coals, complying with ASTM standards, are thought to have formed in suitable terrestrial and limnic conditions which the plant parts get decayed at mostly high but oscillating water levels. This event may be explained predominantly with abundance of huminite (gelinite) macerals.

Abundance of gelinite-macerals reveals more terrestrial conditions, but fusinites, more oxidations or fires taken place (Toprak, 1996; Altunsoy and Ozcelik, 1993). According to the reflection values (Rmax %) and paleo-thermal values (Boggs, 1987), the environment has probably undergone thermal history of <100 °C or 100-125°C.

Biomarker analysis of the coals is essential to reveal paleo-environmental properties. For instance, 17 α (H)-Homohopane ratio is an indicator of paleo climates (Waples and Machihara, 1991).

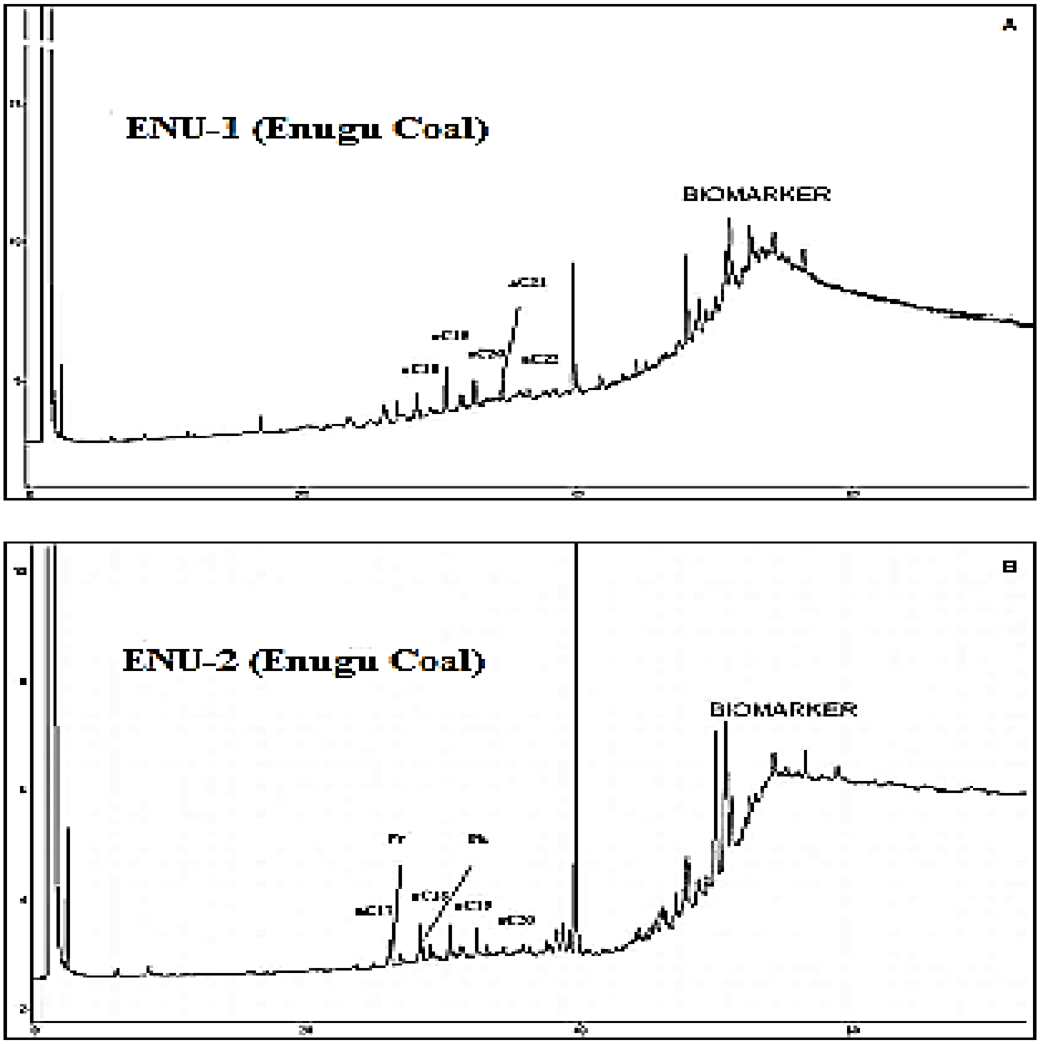

Figure 10 A & B: GC Diagrams (the most important n-alkane series are shown on their peaks).

The decrease in the ratio of 17 α (H)-Homohopanefrom C_{31} to C_{35} reflectsclasticfacies. High C_{31} hopane ratio indicates peat and coal presences. Evaluation in this case on the three samples, homohopanes are recorded and a gradual decrease of homohopane peak intensities between $C_{31}$and C_{35} are typically observed for clastic lithology (Waples and Machihara, 1991).

In order to define carbonate and clastic lithology, C_{29}/C_{30} is used to characterize clastic deposition, C_{29} norhopane carbonate/ evaporite lithology (Connan et. al., 1986). Gammacerane ratio, which is an indicator of salinity, indicates layering in water column of deposition of the coals and the samples to be of Late Proterozoic age (Waples and Machihara, 1991; Connan et al., 1993; Peters and Moldowan, 1993; Hunt 1995; Kavak and Toprak,2012).

According to the C_{28}/C_{29} ratio, the obtained age data complies with geologic age (Figure 11). Tricyclic terpanes are present in the whole samples. Comparative ratio of C_{24} tetracylic terpanes indicates terrestrial organic material content (Peters et al., 2004). αβ– moretane / αβ -hopane (moretane / hopane) ratio is between 0.5 - 0.6 and points out immature stage as well as salty depositional environment for organic material.

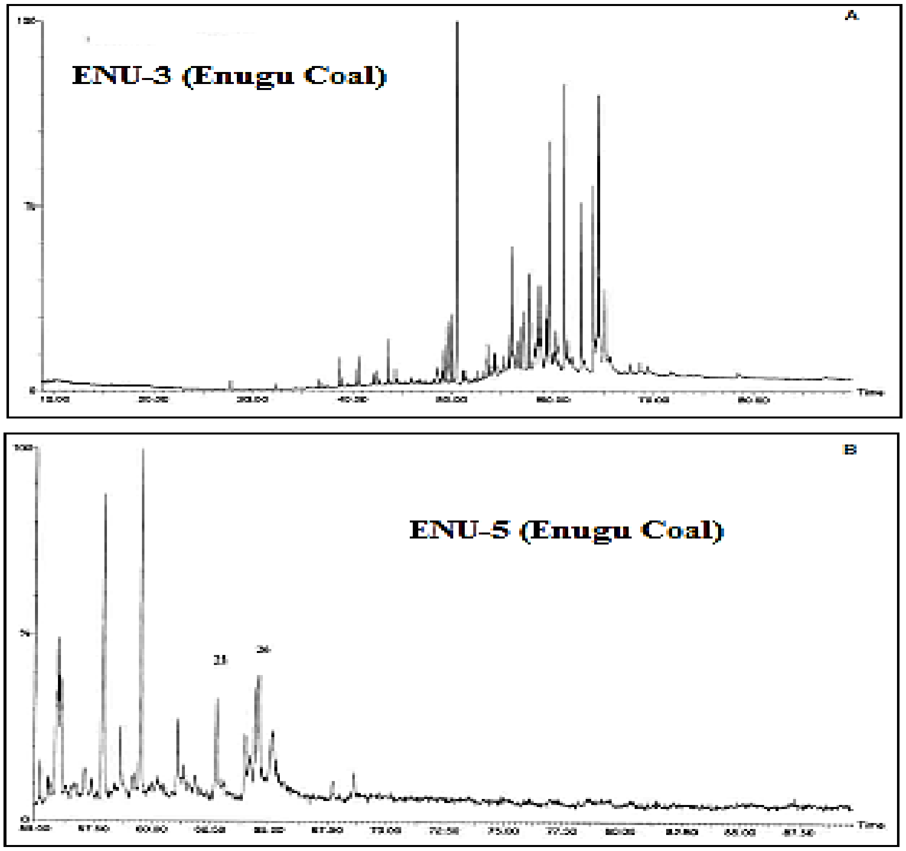

Figure 11 A & B: a). GC-MS Total Ion Current (TIC) Diagram, b). GC-MS Diagram for 191.

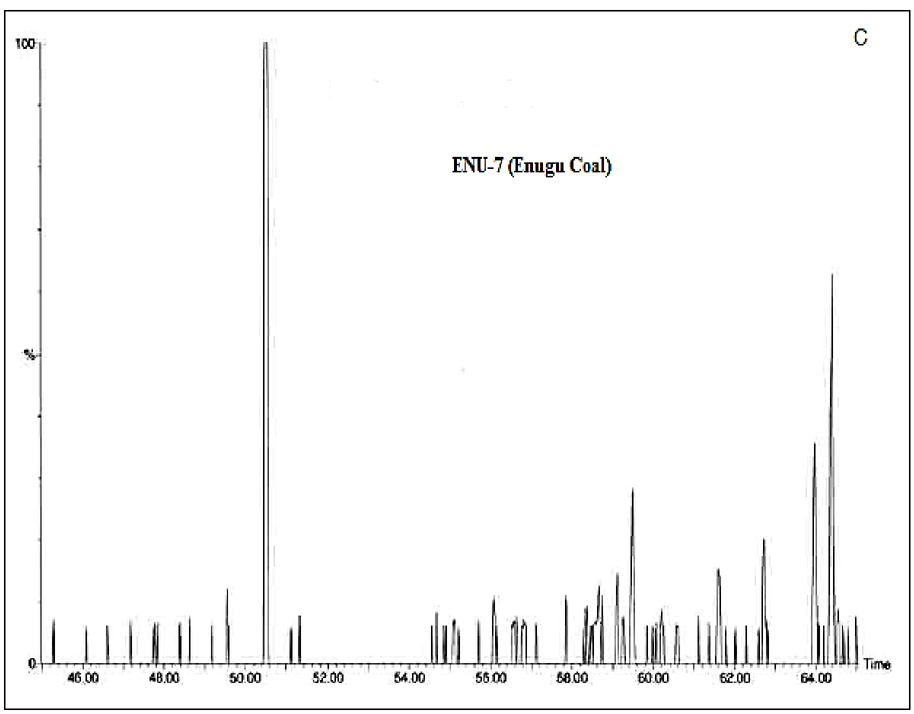

Figure 11C: GC-MS Diagram for 217.

Framboidal pyrites were recorded from the whole coal veins vastly and reflects anaerobic environmental conditions. Pr/Ph and diasterane/sterane ratios remark the variations in redox and depositional conditions (Peters and Moldowan, 1993; Bechtel, *et al.*, 2005). Low Pr/Ph (Ten Haven, *et al.*, 1987) value as between <0.5 and ≤ 2 as well as Pr/n C_{17} ratios to be <0.5 indicate anoxic and hypersaline environment.

Low value or absence of C_{30} steranes point out limnic environment deposition, low values of C_{28} besides diasterane/sterane ratios also indicate limnic depositional environments (Peters and Moldowan, 1993). These data, previous geologic studies (Gumussu, 1984) use common gastropod shells and petrographic findings to claim that coals have deposited in a limnic moor environment which was partially hypersaline, fault controlled and consisting of vast amount of volcanic as well as clastic materials (Table 11). Toprak (2009) also points out that similar coal occurrences are very common in Turkey and most of Tertiary coals were deposited in limnic environments.

CONCLUSIONS

In Enugu Cretaceous (Maastrichtian) coal region, organic geochemical, petrographic analysis and coal quality evaluation studies were carried out on the organically rich and the coaly series. The petrographic evaluation result indicates that Enugu coals are rich in huminite group macerals but poor in liptinite and inertinites. Gelinite is the most abundant huminite-maceral of the coals. Pyrite content of the coals is considerably high, mostly in the form of framboids.

Huminite reflection values changes correspond to a diagenetic stage of maturity. The reflection values of the coals imply that the coals have little lignitic and more sub-bituminous in ranking. Associated minerals of the coals are mostly clay, mica, quartz and plagioclase minerals.

Tmax values indicate immature-mature organic stage. Alkane ratios, due to resin and asphalthene content, are considerably low and the maturity is low as well. On HI-Tmax and hydrogen index-oxygen index diagrams, Type II-III and Type III organic material seem to be much more abundant. The parameters obtained from organic geochemical analysis and coal petrography as well as coal quality values are supportive. Moretane/hopane and C32 homohopane isomerisation ratios comply with the other maturity parameters which correspond to an immature to mature stage.

For petrographic data, coal quality parameters also are compatible with Enugu coalification rank and indicate terrestrial, marine dysoxic environments. In general, there is a good correlation between optical and geochemical data. The whole parameters indicate low lithostatic pressure effect and low maturity level. High low content and low coalification rank of Enugu coals enhance the utilization potential of coals.

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