Mineral Res. Expl. Bull., 144, 23-50, 2012

ORGANIC GEOCHEMICAL AND PETROGRAPHİCAL CHARACTERISTICS OF KARLIOVA HALIFAN (BINGOL) COALS

Orhan KAVAK* and Selami TOPRAK**

ABSTRACT.- In this study, petrographic and organic geochemical characteristics of the Tertiary Karlıova-Halifan coals (Bingöl) were investigated. Determination of coal quality was based on chemical (moisture, volatile matter, fixed carbon, ash) and elemental analyses (C, H, O, S, N). The values of the huminite reflectances in organic matter-rich coal levels change between 0.368 and 0.573 %, which correspond to low maturity levels. These parameters are in good aggrement with their fluorescence colors, calorific value (average original-2266, dry-3177 Kcal/kg, upper calorific value) and average T_{max} (417 °C) values. The organic material in studied coals show low grade transformation due to low lithostatic pressure. Therefore, the petrographic characteristics and quality values of Karlıova Halifan coals suggest classification as sub-bituminous coal – Lignite. Rock Eval analysis results point to an immature to early mature hydrocarbon generation for hydrocarbon derivatives formed by type II/III and III kerogen with average T_{max} values of 417 °C. The coals mainly constitute huminites, with small amounts of inertinite and liptinite type macerals. The Karlıova Halifan coals have high contents of ash and sulphur , clay and calcites as minerals, and gelinites as individual macerals.

Key words: Halifan, Bingöl Karlıova, Organic Geochemistry, Organic Petrography, Tertiary, 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 also used in various branches of industry such as production of chemical materials.

Besides to be an energy source, substantial amount of coal is used in petrochemical products. Because of these, finding new sources near the present reserves and hydrocarbon generation potential of coal have atracted the resarchers' 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, formed basement for detailed studies (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). The studies show that the coals of Jurassic-Tertiary age interval tent 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 coals and research as on hydrocarbon generation potential of coals recently.

The study area is located in around Halifan (Derinçay) Village of Karlıova Town of Bingöl City (Figure 1). Besides the known coal area, there is another locality near Hacatur, 30 km to the South of Kiği Town in Bingöl, containing three lignite seams within Eocene flysch. These seams are very thin, 0.30 m thick at most, and carry no economic value at all, therefore, only the coals in Halifan (Derinçay) regions were found to be valuable to study. The coal region is 5 km away from Bingöl Karlıova road, 45 km away from Bingöl City and

* Dicle Üniversitesi Mühendislik Fakültesi, Maden Mühendisliği Bölümü 21280 Diyarbakır
** Maden Tetkik ve Arama Genel Müdürlüğü, Maden Analizleri ve Teknoloji Dairesi 06800 Ankara

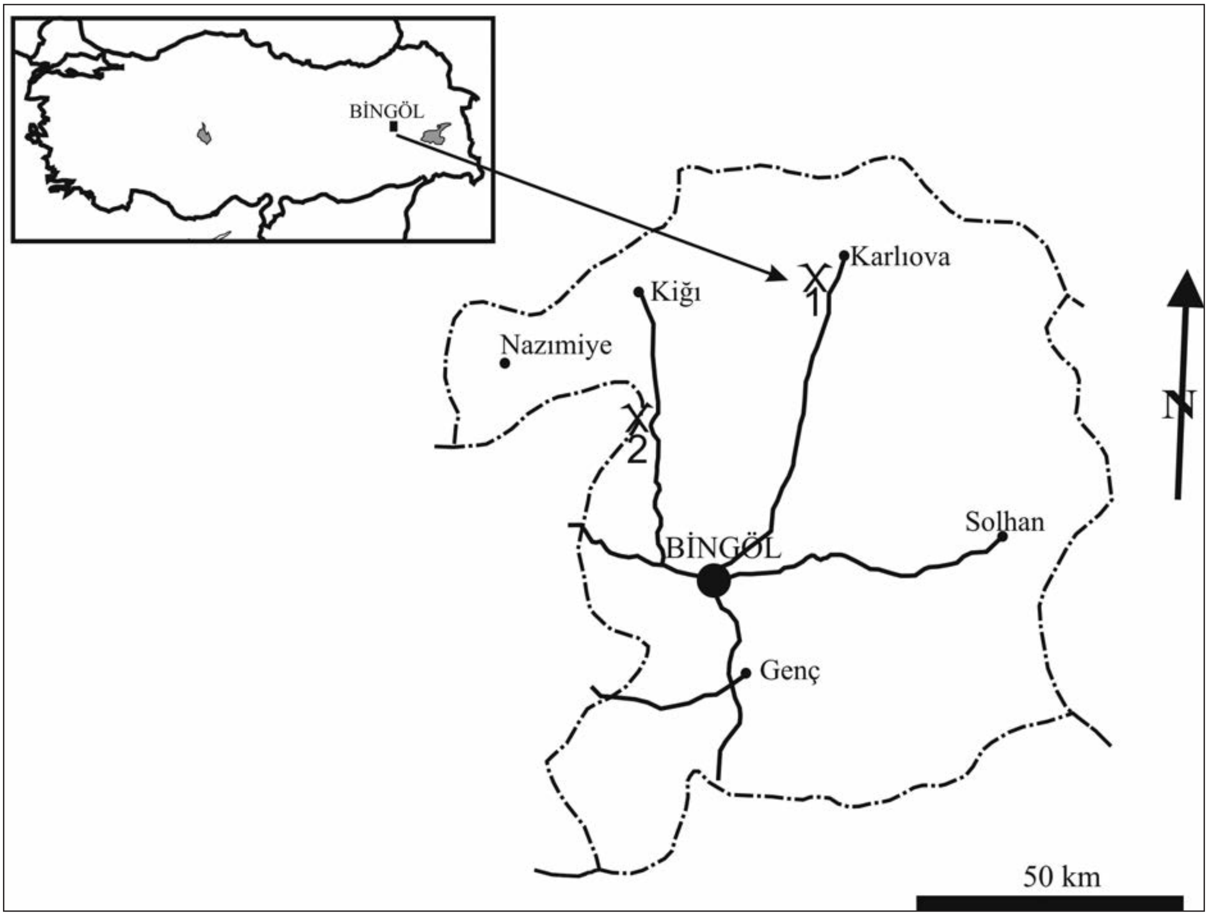


Figure 1- Location map of the studied area.

comprise of folds from North to South. Göynük Creek limits the coal extention. Karliova Halifan (Derinçay) coals have many industrial utilisations.

The first study in the region started in 1965 by MTA with geologic mapings. 5722 m of driling and nine outcropping work were conducted between 1968 - 1974 years. Geologic studies continued in the years between 1978 - 1981 . After these works, investments were conducted by TKI, later 2 - 3 thousand tons of coal was produced with open pit operation. In order to determine the utilisation of the reserve in a power plant, an operation Project was requested from the METU Mining Engineering Research Center by TKI (ODTÜ, 1984). The coal reserve of the region was calculated as 13.909.105 ton for open pit, 74.935.652 ton for under ground mining, with considering the density as 1.5 ton/m^3. 10 % of operation loss for open pit, and 25 % for under ground operation, were encountered and the coal reserves were calculated respectively as 9.989.149 ton for open pit 46.555.995 ton for under ground mining. The analysis results of the main characteristics of the coal were figured out on table 1.

According to a study performed by METU Mining Engineering Research Center in 1984, 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 1458 Kcal/kg as the lower calorific value into consideration, it was suggested that the reserve meets 24 years fuel demand of a 100 mw power plant. The purpose of this study is to exhibit geochmical, 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.

GENERAL GEOLOGY OF THE STUDIED AREA

Geologic history of the East Anatolia is subdived into four main sections. Palaeozoic Early Mesozoic aged metamorphics of these comprise the oldest units (granite, gneiss, mica, schist, calcschist, marble and so on). Early Mesozoic-Late Cretaceous aged ophiolithic melanges are the products of the Northern Branch of Neotethys (Şengör, 1980). While Late Cretaceous, Middle Miocene marine sediments are represented by flysch, reefal, limestone and limestones. Middle Miocene recent formations are the products of the Neotectonic era and contain the structures of this period (Şaroğlu et al., 1987). Coal formation has developed in Neotectonic period in the studied area. As a result of continent-continent collision at the end of Middle Miocene time, the topography of the region started to be undulated by the effect of N-S directed compressive tectonies which caused to form individual basins separated by uplifted ridges. The coalification has predominantly developed in shallow lake facies within an intermontane basin, as a result of the locality changes of the coastal facies. Very fast erosion took place, soon after Pliocene period, related to the thickening of the continental crust which caused the erosion of the big amount of the Neogene series. This erosional period has been accompanied by a volcanic activity in the region which is continued in the Middle Pleistocene time and volcanic material spreaded out almost over the whole region and covered the Neogene units (Gümüşsu, 1984). In Pliocene period, the swampy area was submerged under water and cyclic depositions took places with epeirogenic events. A thickness of 40 m of basalt flow was encountered over the Pliocene aged coal deposits. Volcanism continued also towards to the end of Pliocene period. Andesite, basalt and tuffs cover the Pliocene units unconformably.

Pliocene age series in the area are mostly NE-SW directed. The region has been experienced by effective faultings at the end of Pliocene, NE extending Göynük Fault brought juxtapose the Mesozoic age crystallized limestone and the Pliocene series. The fault forms a boundary of two different reliefs. While the metamorphic series form the higher places of the region, the Pliocene series cover the low lands. Along with Göynük Creek at North, the basement basalts exhibit contacts with the coaly series by faulting. The fault with 100 m dip-slip displacement caused the coal horizon to be at much deeper places at the east of the line between Kurik and

Table 1- Analysis results of the coals.

Analysis	Available site, suitable for open pit operation	Underground operation sites
Moisture %	48,5	43
Ash %	24,2	24,6
Volatile Matter %	16	18,3
Fixed Carbon %	12,3	15,2
Total Sulphur %	0,4	0,6
Low Calorific Value (Kcal/kg)	1318	1663

Azizan Villages (Gümüşsu, 1984).

The geologic units in the Bingol Karliova coal region are illustrated in figure 2, the basement of the coal containing Pliocene series is composed of a dense volcanic activity which has 50 - 100

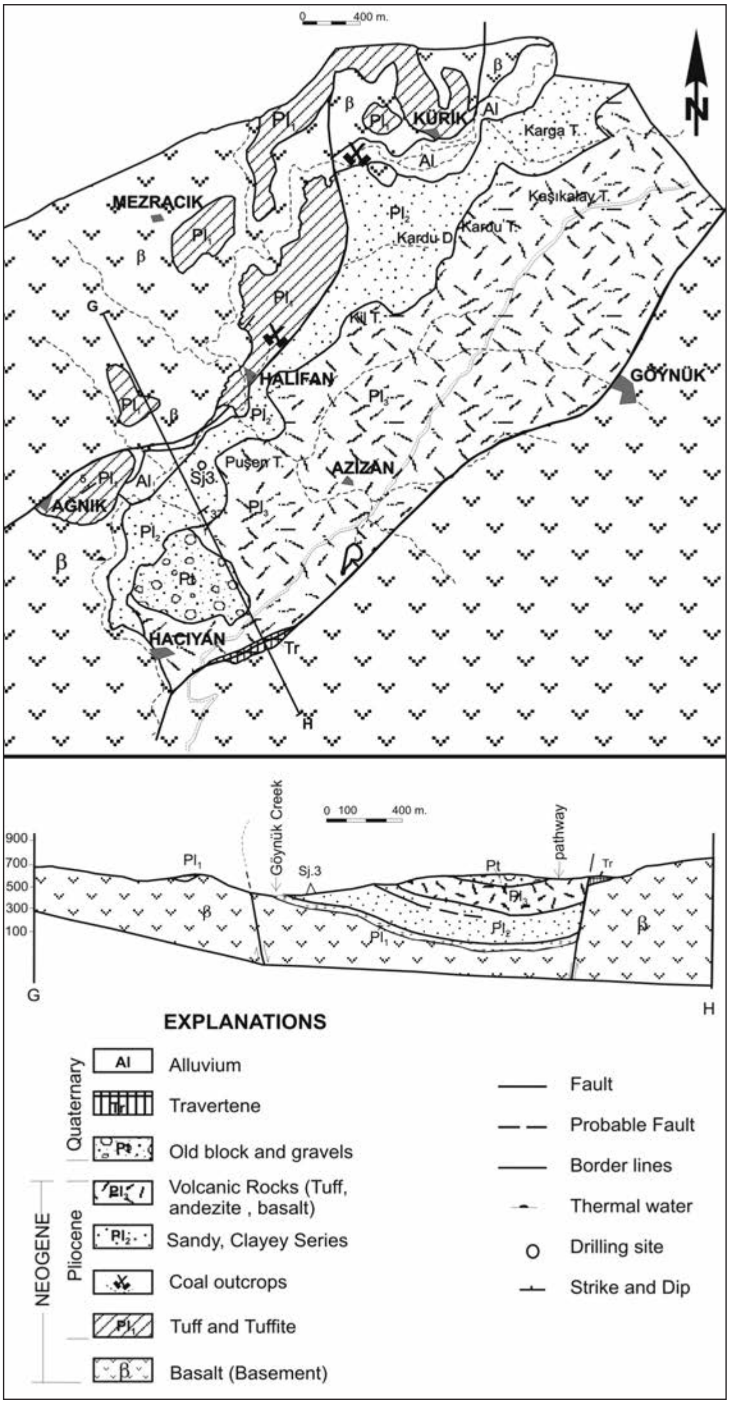


Figure 2- Geological map and geologic section, the coal seams and drilling sections of the studied coals (Gökmen et al., 1993).

m thick basalt, andesite and trachyte flows occurred at the end of Miocene period. Pliocene series overlying unconformably the basement rock, starts with agglomerates and braccias. 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 basin. 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, tuffite, sand and gravel 30-35 m above the lower coal seam. Young volcanic products such as aglomerate, tuff, andesite and basalts cover the coal containing series. The dip angle of the coaly Pliocene layers are about 2-5 ^{0}C, and almost horizontal (Dagyaran, 1976). The angles eastwardly tend to increase . Halifan Fault, extending along Berce Creek, divides the coaly area into two sectors (Figure 2 and 3).

Figure 3- Field views (a,c,d) and drilling sites (b) of the studied coals.

MATERIAL AND METHODS

20 channel coal samples with 5 - 10 cm intervals have been collected. Inorganic composition of the samples was analyzed at Ankara TPAO Research Laboratory with XRD instrument. For chemical and elementary analysis, the coal samples were ground along ASTM standarts.(Figure 4) Firstly, they were ground to < 100 mesh size, then, homogenized and analyzed in MTA General Directorate's MAT Department Laboratories. Chemical analysis (total moisture, ash, volatiles , fixed carbon and calorific value) were conducted with IKA

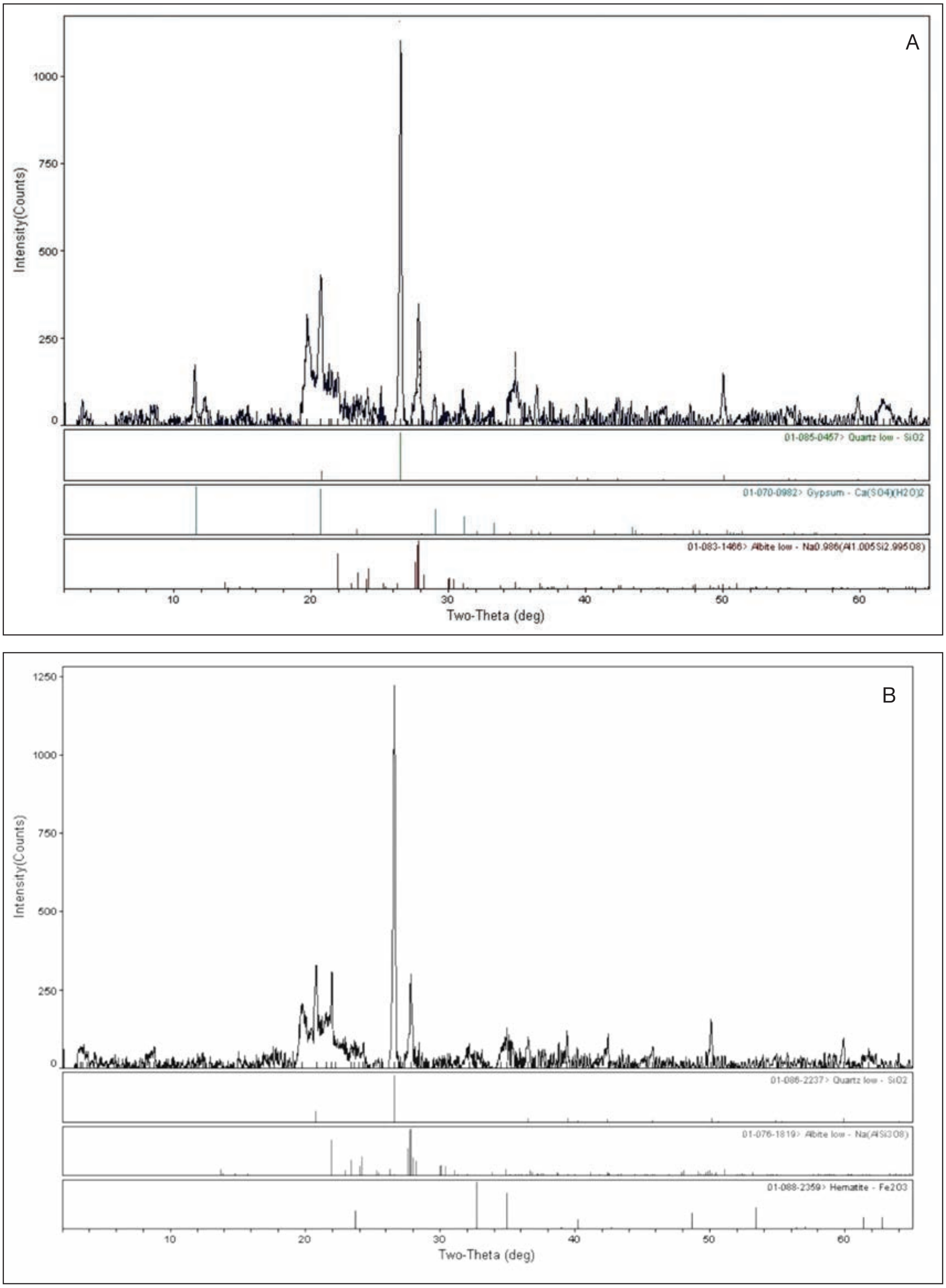


Figure 4- X-ray graphics of the samples . A(the sample contains of quartz, gypsum, albite and the rel evant peak signs are shown at below) B(the sample contains of quartz, albite and very low amount of hematite, and the relevant peak signs are shown at below)

4000 adiabatic calorimeter and in TUBİTAK MAM Laboratories. Elementary analysis, as total sulphur, carbon, hydrogen and nitrogen, were carried out in the same laboratory with LECO analyser. Evaluations were performed on each 7 samples, for the analysis. For coal petrographic analysis, 14 samples were prepared according to ICCP standart (1998 and 2001) 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 with using 32x and 50x oil objectives, at 546 m wavelengths. For each modal analysis, 500 point and 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 standart, saphire, is 0.548 %. MPV Geor software programme was used for the reflectance measurements.

Standart palynologic methods (Durand and Nicaise, 1980; Tissot and Welte, 1984) were used to prepare kerogen slides of 5 samples, taken from the studied area. Kerogen spore alteration color indexes as well as organic content of the samples were determined with polarized microscope in the TPAO Research Center Laboratories (in Ankara). Hydrocarbon source rock properties of 14 samples were determined with TOC-Rock Eval pyrolysis analysis (Espitalié 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 in TUBİTAK MAM Laboratories with agilent 7890A/5975C GC-MS instrument.

FINDINGS AND DISCUSSIONS

Chemical and elementary analysis evaluations

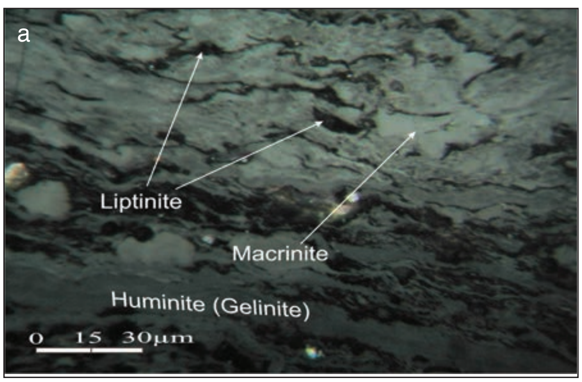
Elementary analysis of coals include C, H, N+O and S. Elemantary analysis of the samples showed the C ratio to be (23 - 25 %), H to be 2.1 - 2.3 %, N+O 10.9 – 13 %, S 0.6 - 0.7 %. Air dried samples tend to have C ratio as 35.2 - 36.4 %; H content to be as 3.1 - 3.3 %; N+O, as 15.1 - 16.1 %; S, as 1.09 - 1.12 % (Table 2). Ash content of 7 coal samples were determined, the

Table 2- Elementary analysis of Karlıova Halifan coals.

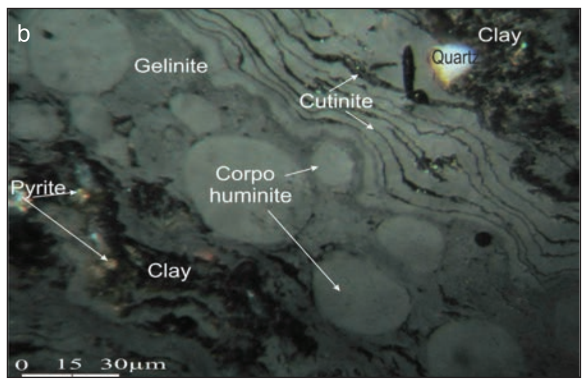
Sample	Original Sample				Dry Sample			
	C (%)	H (%)	(N+O) (%)	S (%)	C (%)	H (%)	(N+O) (%)	S (%)
BNOK-1	23,1	2,16	12,80	0,62	36,30	3,31	15,40	1,09
BNOK-2	24,4	2,12	10,85	0,64	36,42	3,15	15,63	1,11
BNOK-3	23,5	2,15	11,26	0,64	35,55	3,17	16,11	1,11
BNOK-4	24,7	2,32	12,30	0,61	35,72	3,14	15,56	1,07
BNOK-5	25,1	2,17	12,20	0,60	35,69	3,12	15,27	1,09
BNOK-6	24,1	2,20	12,97	0,65	36,01	3,32	15,12	1,12
BNOK-7	25,1	2,15	12,04	0,63	35,16	3,18	15,45	1,08

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

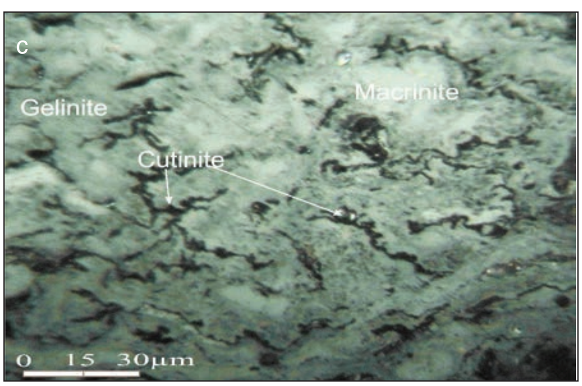
Table 4 and 5 exhibit the coal's moisture, ash, volatile matter, petrographic composition and calorific value as well as huminite reflection (R_{max}) values. Carbon values of the coals, in original sample, vary between 23 – 25 %, 35 – 36 % as air dried basis; the hydrogen content of the original samples between 2.1 - 2.3 %, 3.1 - 3.3 % as air dried basis; sulphur content of the original samples between 0.6-0.65 %, 1.07-1.12 as air dried basis; in addition, nitrogene + oxygene values of the original samples vary between 10.9 – 13 and 16.7 % as air dried basis. The ash content of the coals are ratherly high and show variations between 16 - 56 for original samples, 26 - 76 % for air dried sam-



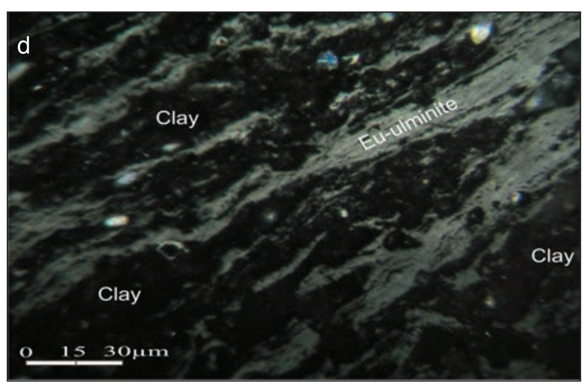
5a. Common maceral appearances of the coals, gelinite, liptinites and white shapeless macrinites.s



5b.Rounded corpohuminites, dark colored clay, quartz, cutinites and pyrites observed in the coals.



5c. Inertinite (macrinite) macerals, cutinites showing lineations and predominant textureless gelinites, observed in th



5d. A succession of common dark colored clays with eu-ulminites which possess textures.e coals.

Figure 5- Petrographic images of the Bingol Halifan Coals.

Table 3- Ash components of Karlıova Halifan coal samples.

Sample	SiO_2 (%)	Al_2O_3 + TiO_2 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O+K_2O (%)
BNOK-1	44,5	17,1	8,77	12,69	4,85	10,66	1,40
BNOK-2	32,4	17,1	8,20	20,05	4,50	16,33	1,42
BNOK-3	42,4	15,7	7,84	14,30	5,80	12,50	1,51
BNOK-4	33,5	18,1	8,10	18,09	4,50	16,36	1,35
BNOK-5	43,5	16,1	8,70	14,79	4,87	10,60	1,48
BNOK-6	35,4	15,0	8,22	20,10	4,60	16,24	1,40
BNOK-7	41,3	15,1	8,20	13,62	4,80	15,44	1,50

Table 4- Proximate analysis of Karlıova Halifan coal samples.

In Original Samples						
Sample	**Moisture %**	**Volatile Matter %**	**Ash %**	**Total Sulphur %**	**High Calorific Value (Kcal/kg)**	**Low Calorific Value (Kcal/kg)**
BNOK-1	28,3	31,2	18,4	0,77	3237	2938
BNOK-2	20	34	25	0,67	2968	2717
BNOK-3	14,8	31,9	32	0,76	3265	3037
BNOK-4	26,2	10,4	56	0,36	828	645
BNOK-5	49,2	12,8	33,5	0,15	774	457
BNOK-6	34,7	20,1	32,9	0,34	1954	1673
BNOK-7	38,1	26,3	16,1	0,59	2834	2614

In Dry Samples					
Sample	**Volatile Matter %**	**Ash %**	**Total Sulphur %**	**High Calorific Value (Kcal/kg)**	**Low Calorific Value (Kcal/kg)**
BNOK-1	45,5	25,7	1,07	4510	4318
BNOK-2	42,5	31,3	0,83	3703	3533
BNOK-3	37,4	37,5	0,9	3825	3659
BNOK-4	14,1	75,9	0,48	1121	1069
BNOK-5	25,2	65,9	0,3	1520	1432
BNOK-6	30,8	50,5	0,53	2989	2856
BNOK-7	42,5	26	0,96	4571	4380

ples, 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 (Teichmuller et al., 1998). The coals showing 0.2 - 0.8 % original and 0.3 - 1.07 % air dried sulphur content and high amount of ash con-

Table 5- Maceral analysis and Rmax (as %) values of Karlıova Halifan coal samples.

No	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																	
1	BNOK-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
2	BNOK-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
3	BNOK-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
4	BNOK-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
5	BNOK-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
6	BNOK-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
7	BNOK-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
8	BNOK-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
9	BNOK-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
10	BNOK-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
11	BNOK-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
12	BNOK-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
13	BNOK-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
14	BNOK-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.

tent, the coals imply to be deposited in a highly elevated continental area. 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 (R_{max}) measurements indicate the coals as subbituminous-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 the 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 oxygene 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)

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 diagrammes (Figure 6a). Petrographic composition of the samples re-

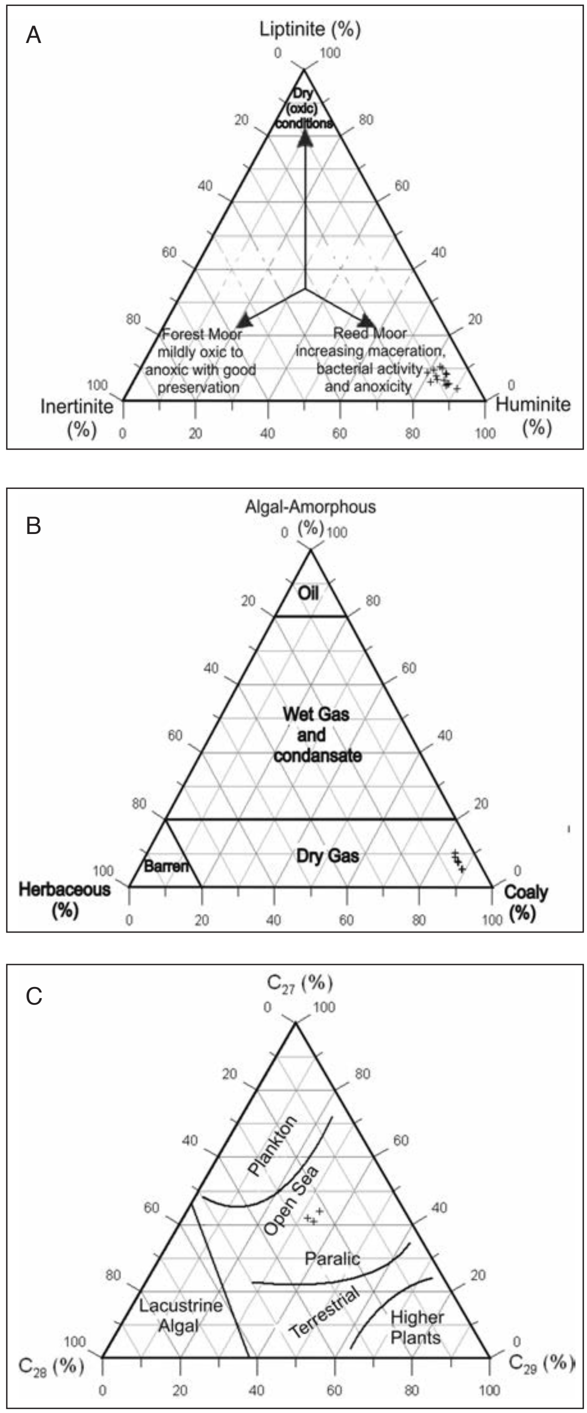


Figure 6- A, B, C. Triangular diagrammes of organic material types, of Karlıova Halifan coal samples.

vealed that a heterogeneous input of materials were common during peatification period. To the analyses of 14 coal samples, the coals tend to contain of huminite macerals dominantly (33 - 55 %) and the predominant maceral is gelinite. Gelinite is a submaceral 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 (as on Figure 5a, b, c). In Halifan coals, eu-ulminite (Figure 5d) which shows cellular sructure traces and corpohuminite macerals (Figure 5b) may clearly be observed. Corpohuminites exhibit distinctive large surrounded shapes. Inertinite and liptinites are comperatively lesser in the coals (Table 5). Some of the liptinites show lineations of cutinites as if they are wood tissue lines (Figure 5b) some own various lineations and shapes which they are sporinites and cutinites (Figure 5a, c). Liptinite contents vary between 2 - 6 %, liptinite and huminite macerals sow much more resistance, there fore they are rather more abundant and indicate woddy moor type depositranal environments (Flores, 2002). Macrinite and fusinites are the most common (3 – 8 %) inertinite maceral group (Figure 5 a and b) .The result shows that high inertinite containing coals carry ratherly higher gas generation potentials. Maceral group raties and huminite reflection values of the coals, which vary between 0.368 - 0.573 %, are shown on table 5.

High gelinite content imply 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 (Figure 5a, c) (Flores, 2002; Stach et al., 1982). The coals contain high amount of spores and clay minerals also which indicate abundant bacterial activities as well as decayings, in reed moor environment and underwater conditions. 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 (Figure 5b, c). 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, bacterias the imply formations of humic gells, nitrogene and hydrogen rich coal products (Teichmuller 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 the 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 preservation conditions (Kolcon and Sachsenhofer, 1999; Bechtel et al., 2005). TPI values for Karlıova Halifan coals vary between 0.15 – 0.35 %. The GI value indicates under ground water level and/or pH level. For gelification, regular water flow, bacterial activity and low asidic conditions are essentials (Kolcon and Sachsenhofer, 1999). For Karliova Halifan samples, GI values change between 2.3 - 6.2; GWI value between 2.9 – 11 %; VI value between 0.57 - 1.6 % TPI's value being lower than 0.5 % GI value higher than 1, GWI value heigher 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 lake environment. Coal formation took place within high under ground water table, average subsidence rate and autochotonous to hypoautochotonous way of depositon. Here, high alkaline conditions and fresh water effects are mainly observed. Low TPI value indicates high bacterial activity and high pH value, in addition, common presence of gastropods are good supporting evidences for alkaline environmental conditions such as seen in

Amyneto Basin (Greece) (Iordanidis and Georgakopoulos, 2003). 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 (NAF and EAF). According to the XRD analysis results, plagioclase ratio change between 5 - 15 %, quartz between 7 - 15 %, gypsum 3 - 8 % and clay+ mica 70 - 85 % (Table 6 and figure 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 mineral distribution of Karlıova Halifan coals.

Sample	Plagioclase (%)	Calcite (%)	Quartz (%)	Gypsum (%)	Hematite (%)	Clay+Mica (%)
BNOK-1	10	-	7	3	-	80
BNOK-2	10	-	15	-	trace	75
BNOK-3	5	-	15	-	trace	80
BNOK-4	7	-	15	8	-	70
BNOK-5	5	-	10	-	-	85
BNOK-6	15	-	10	-	trace	75
BNOK-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 Rock–Eval pyrolysis data. This tecnique 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 (Teichmuller 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).

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 Karliova Halifan 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 be 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 which is called as biologic productivity. As grain size decreases in sediments, organic material contents get 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). Determined low content of organic materials of the studied samples

Table 7- Total organic carbon (TOC %) and Rock-Eval pyroliysis results of Karliova Halifan coal samples.

Sample	TOC	S1	S2	S3	S2/S3	Tmax	HI	OI	PI	PY
BNOK-1	38,6	0,7	44,0	35,1	1,25	409	114	91	0,015	44,72
BNOK-2	41,1	1,5	42,2	64,2	0,65	410	103	156	0,034	43,66
BNOK-3	38,6	4,4	58,7	32,1	1,82	405	152	83	0,07	63,08
BNOK-4	4,1	0,03	0,8	3,1	0,25	431	19	74	0,03	0,8
BNOK-5	12,8	0,5	19,4	23	0,84	432	152	180	0,026	19,91
BNOK-6	23,5	0,96	41,2	20,1	2,05	418	175	85	0,022	42,17
BNOK-7	32,4	0,8	42	41,5	1,01	419	130	128	0,017	42,7
BNOK-8	38,8	0,7	44,1	35,1	1,25	405	112	93	0,015	44,77
BNOK-9	41,2	1,4	42,1	64,2	0,65	415	107	152	0,032	43,52
BNOK-10	38,3	4,3	58,6	32,1	1,82	401	150	87	0,068	62,95
BNOK-11	4,01	0,1	0,8	3,1	0,25	435	16	71	0,02	0,93
BNOK-12	12,9	0,6	19,3	22,9	0,85	425	151	179	0,029	19,92
BNOK-13	23,4	0,9	41,2	20,1	2,05	422	178	82	0,021	42,12
BNOK-14	32,5	0,8	42	41,6	1,01	415	133	130	0,018	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), T_{max}: Maximum thermal value as S_2 gets 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).

may also be originated from the mentioned reasons (Burwood et al., 1992)

ORGANIC MATERIAL TYPE

In order 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 diagrammes of the samples. According to HI and OI data, organic material points out three types of kerogones which may carry petroleum generation potentials; TYPE I: This group has the highest liquid hydrocarbon generation potential. Its oxygen ratio is low, hydrogen ratio is high. TYPE II: Hydrogen quantity of them are less than those of the type 1 but oxyen amount is much higher. It represents algae, spore, pollen, cuticule and woody organic material content. TYPE III: Hydrogen content is very low and oxygen content is ratherly very high. They may generate very little amount of gasses (Tissot and Welte, 1984; Hanson et al., 2000).

Hydrogen index values of Karlıova Halifan coals vary between 16 - 178 mg HC/g TOC and oxygen index values between 71 - 180 mg CO_2/g TOC. Production İndex (PI): Sı / (S_1+S_2) value especially should be higher than 0.05 %, then, interpretation becomes important. Karlıova Halifan samples exhibit an average of 0.034 % value (Figure 8).Some high oxygene index values (>150 mg CO_2/g TOC) have probably developed due to mineral matrice and mineral decomposition during pyrolysis. If mineral matter content of the studied 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 developes 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. Besides this, there is a negative relation between mineral matter content and hydrogen index, TOC, Pc, Rc, values, the correlation coefficient (Pearson Coefficient) is very low, therefore, was not shown on the graphics.

According to the samples' values, put on Van Krevelen (Hydrogen Index-Oxygen Index) and HI-Tmax diagrammes, most of the samples tend

Table 8- Biomarker parameters derived from the m/z 217 and m/z 191 mass chromatograms.

			191			217			
Samples	^{13}C	Standart Deviation	H/(H+M)	Ts/Tm	C_{31} $\frac{22S}{22S+22R}$	C_{29} $\frac{20S}{20S+20R}$	C_{27} %	C_{28} %	C_{29} %
BNOK-1	-27,31	0,19	0,82	0,15	0,53	0,55	42	26	32
BNOK-6	-22,95	0,09	0,83	0,13	0,55	0,56	41	25	34
BNOK-7	-22,45	0,07	0,85	0,14	0,57	0,57	44	22	34

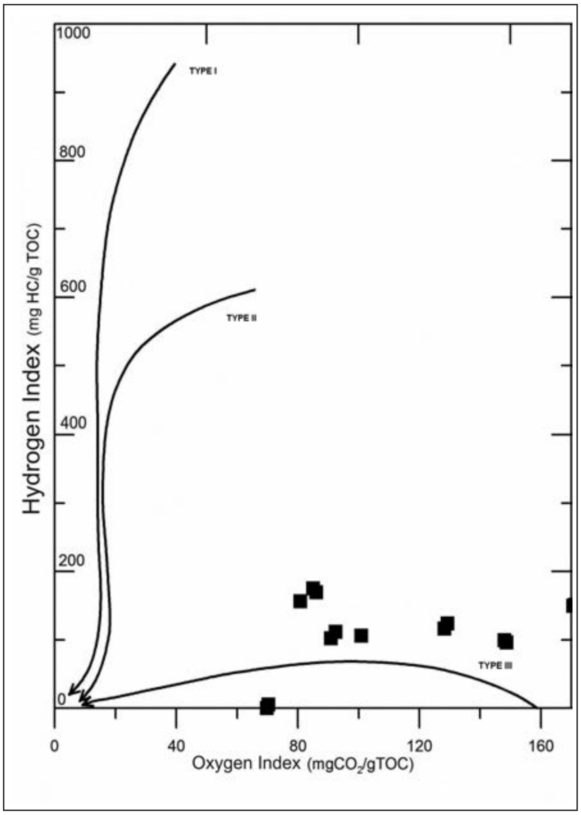


Figure 7- Hydrogen Index-Oxygen Index diagramme of the studied samples (Tissot and Welte, 1984).

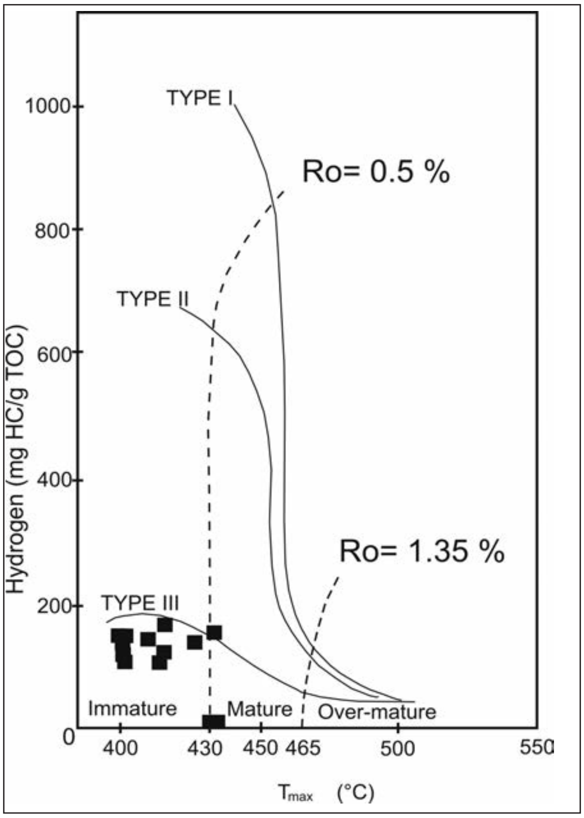


Figure 8- Classificiation of kerogene types by Hydrogen Index- T_{max} diagramme (Mukhopadyay et al., 1995).

to stay at the TYPE II-III (terrestrial and marine) and TYPE III areas (Figure 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 seem to be of 84 - 89 %, woody 11 – 16 %, herbaceous 5 % and 10 % of algae amorphous organic matter (Figure 6). It is thought that amorphous organic materials probably formed during transportation of the terrestrial materials by alteration and disintegrations.

As a result of comparison, different analysis 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 increases, as well, but ash content decreases. Pyrolyzed carbon amount and fixed carbon, oxygene index-oxygene content have positive relation but S_3 ash and oxygene 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 of organic compounds above C_{32} in g as chromatogrammes, point out terrestrial as well as marine originated organic materials.İn biomarker analysis of the Halifan samples, high molecular abundat (C_{20}+) compounds on n-alkanes are predominant and predeminancy 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.

T_{max} (°C) value represents thermal maturity and it expresses maturation with the depth increase. T_{max} values of Karlıova Halifan coals vary between 401-435 °C and show 417 °C as average (Table 7). These values indicate organic matter rich parts of the coals to be immature and at premature zone. In kerogen preparantions light yellow and light brown organic material altertion colors, light yellow, colorless spores, low R_{max} values all support T_{max} data about maturation. Most of the samples scattered in the pre-mature and immature zones, on HI-T_{max} diagramme (Figure 8). PI values of these samples are < 0.1 and indicate low maturations. Huminite reflection (R_{max}) 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 considerations. Although both data individually indicates immature levels, there is a meaningful linear relation between huminite reflectance (R_{max}) and T_{max} values due to different petrographic compositions. 20 (S)/(20 s+20R), the ßß/(ßß+αα) sterane ratio and T_{max}, as well as reflection values inerease proportionally. Sterane ratios of the studied 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 maretials. 18 α (H) - 22, 29, 30- trisnorneonhopane (Ts)/(Tm) of Karlıova Halifan coals is between 0.13 - 0.15 (Table 7). Generally, C_{31} or C_{32} homohopanes are used to determine 25S / (22 S+22 R) ratios. This ratio increase, is between 0.53 - 0.57 for the studied samples. Diasterane /sterane ratios are ratherly 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 decreasses with maturation increase (Kvenvolden and Simoneit, 1990).

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

Hydrocarbon generation potential

For this, analysis of the studied samples are used in source abundance diagramme (HI-TOC) (Jackson et al, 1985) (Figure 9). S1 values of the samples are considerably low, between 1.7 - 4 mg HC/g rock; S2 values between 38 - 63 mg HC/g rock (Table 6). Since S2 value of 4 mg HC/g rock is low, it indicates weak rock potential; but when higher than 4.0, a source rock is considered, in addition that S2 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 hydrogene index value and HI-T_{max} diagramme scatter indicate the samples to contain of partial marine organic material influx and limited gas generation potential.

As in the studied samples, humic coals form from TYPE III kerogens and may generate gasses. Besides there is a capability of gas generation potential of Karlıova Halifan coals, their incomplete maturation has prevented it. Hydrocarbon generation index is also named as genetic potential or production index and show

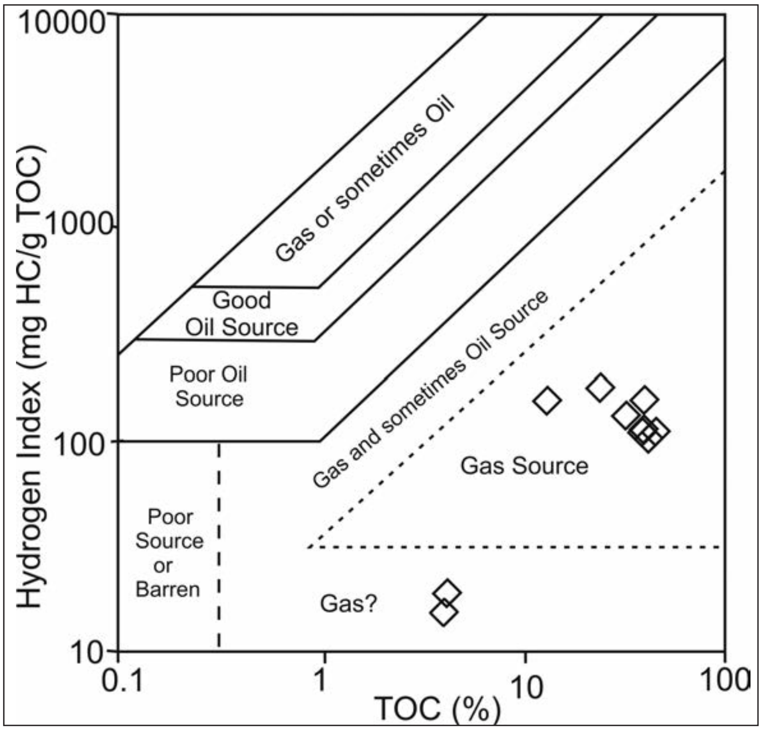


Figure 9- Hydrogen Index- T_{max} diagramme of Karlıova Halifan coal samples (developed from Jackson et al.,1985).

similar results in the same way of using (S1+S2), 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 2 mg HC/g of the studied samples shows that they carry rare gas generation potentials (Welte, 1965; Tissot and Welte, 1984). Low values of S2/S3 from 2, PI value lower than 0.1 and T_{max} values indicate immature stages. Some samples scatter in the weak generation potential area of the HI-TOC diagramme 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 ßß/ (ßß/αα) ratio of T_{max} value, there is also a negative relation between R_{max} and C_{32}(22S / (22S + 22R)) ratios, in adition 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 contain 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 (Table 8, 9, 10, 11 and 12). 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 CS_2 and benzene were determined. Typical saturated hydrocarbon GC-Mg data of the samples are shown on figure 11. Comperative 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 Karlıova Halifan 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/z 217 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. Karlıova Halifan coal samples contain of 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 Karlıova Halifan coal samples, C_{29} norhopane 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 differantiate 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 standarts, are thought to have formed in suitable terrestrial and limnic conditions which the plant parts get decayed at mostly high but oscillating

Table 9- Sterane peak determinations on m/z 217 mass chromatograms.

Component	Component Name
1	C27 13β(H),17α(H)-DIASTERANE (20S)
2	C27 13β(H),17α(H)-DIASTERANE (20R)
3	C27 13β(H),17α(H)-DIASTERANE (20S)
4	C27 13β(H),17α(H)-DIASTERANE (20R)
5	C28 13β(H),17α(H)-DIASTERANE (20S)
6	C28 13β(H),17α(H)-DIASTERANE (20R)
7	C28 13β(H),17β(H)-DIASTERANE (20S)
8	C27 5α(H),14α(H),17α(H)-STERANE (20S)+C28 13α(H),17β(H)-DIASTERANE (20S)
9	C27 5α(H),14β(H),17β(H)-STERANE (20R)+C29 13β(H),17α(H)-DIASTERANE (20S)
10	C27 5α(H),14β(H),17β(H)-STERANE (20S)+C28 13α(H),17β(H)-DIASTERANE (20R)
11	C27 5α(H),14α(H),17α(H)-STERANE (20R)
12	C29 13β(H),17α(H)-DIASTERANE (20R)
13	C29 13α(H),17β(H)-DIASTERANE (20S)
14	C28 5α(H),14α(H)-17α(H)-STERANE (20S)
15	C28 5α(H),14β(H)-17β(H)-STERANE (20R)+ C29 13α(H),17β(H)-DIASTERANE (20R)
16	C28 5α(H),14β(H)-17β(H)-STERANE (20S)
17	C28 5α(H),14α(H),17α(H)-STERANE (20R)
18	C29 5α(H),14β(H),17α(H)-STERANE (20R)
19	C29 5α(H),14β(H),17β(H)-STERANE (20R)
20	C29 5α(H),14β(H),17β(H)-STERANE (20S)
21	C29 5α(H),14α(H),17α(H)-STERANE (20R)
22	C29 5α(H),14α(H),17α(H)-STERANE (20S)
23	C30 5α(H),14β(H)-17β(H)-STERANE (20R)
24	C30 5α(H),14β(H)-17β(H)-STERANE (20S)
25	C30 5α(H),14α(H),17α(H)-STERANE (20R)

water levels. This event may be explained predominantly with abundance of huminite (gelinite) macerals. Abundance of gelinite macerals reveals terrestrial moor conditions, but fusinites moor oxidations or fires taken places (Toprak, 1996; Altunsoy and Özçelik, 1993). According to the reflection values (R_{max} %) and paleo-thermal values (Boggs, 1987), the environment was probably undergone, was of <100 °C or 100-125 °C thermal history.

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). As the ratio decrease, from C_{31} to C_{35} reflects clastic facies, high C_{31} hopane ratio indicates peat and coal presences. As evaluated in this manner, in the three samples, homohopanes are recorded and a gradual decrease of homohopane peak intensitive between C_{31}, and C_{35}, are typically observed for clastic lithol-

Table 10- Triterpane peak determinations on m/z 191 mass chromatograms.

Component	Component Name
1	C19 TRICYCLICTERPANE
2	C20 TRICYCLICTERPANE
3	C21 TRICYCLICTERPANE
4	C22 TRICYCLICTERPANE
5	C23 TRICYCLICTERPANE
6	C24 TRICYCLICTERPANE
7	C25 TRICYCLICTERPANE (22S+22R)
8	C24 TETRACYCLICHOPANE (SECO)
9	C26 TRICYCLICTERPANE 22 (S)
10	C26 TRICYCLICTERPANE 22 (R)
11	C28 TRICYCLICTERPANE
12	C29 TRICYCLICTERPANE
13	C27 18α(H)-22,29,30-TRISNORHOPANE (Ts)
14	C27 17α(H)-22,29,30-TRISNORHOPANE (Tm)
15	17α(H)-29,30-BISNORHOPANE
16	C30 TRICYCLICTERPANE
17	17α(H)-28,30-BISNORHOPANE
18	C29 17α(H),21β(H)-30-NORHOPANE
19	C29 Ts (18α(H)-30-NORHOPANE
20	C30 17α(H) DIAHOPANE
21	C29 17β(H),21α(H)-30 NORMORATENE
22	OLEANANE
23	C30 17α(H),21β(H)-HOPANE
24	C30 17β(H),21α(H)-MORETANE
25	C31 17α(H),21β(H)-30-HOMOHOPANE (22S)
26	C31 17α(H),21β(H)-30-HOMOHOPANE (22R)
27	GAMMACERANE
28	HOMOMORETANE
29	HOMOHOPANE
30	C32 17α(H),21β(H)-30,31-BISHOMOHOPANE (22R)
31	C33 17α(H),21β(H)-30,31,32-TRISHOMOHOPANE (22S)
32	C33 17α(H),21β(H)-30,31,32-TRISHOMOHOPANE (22R)
33	C34 17α(H),21β(H)-30,31,32,33-TETRAKISHOMOHOPANE (22S)
34	C34 17α(H),21β(H)-30,31,32,33-TETRAKISHOMOHOPANE (22R)
35	C35 17α(H),21β(H)-30,31,32,33,34-PENTAKISHOMOHOPANE (22S)
36	C35 17α(H),21β(H)-30,31,32,33,34-PENTAKISHOMOHOPANE (22R)

Table 11- Gas chromatography results of Karliova Halifan coal samples

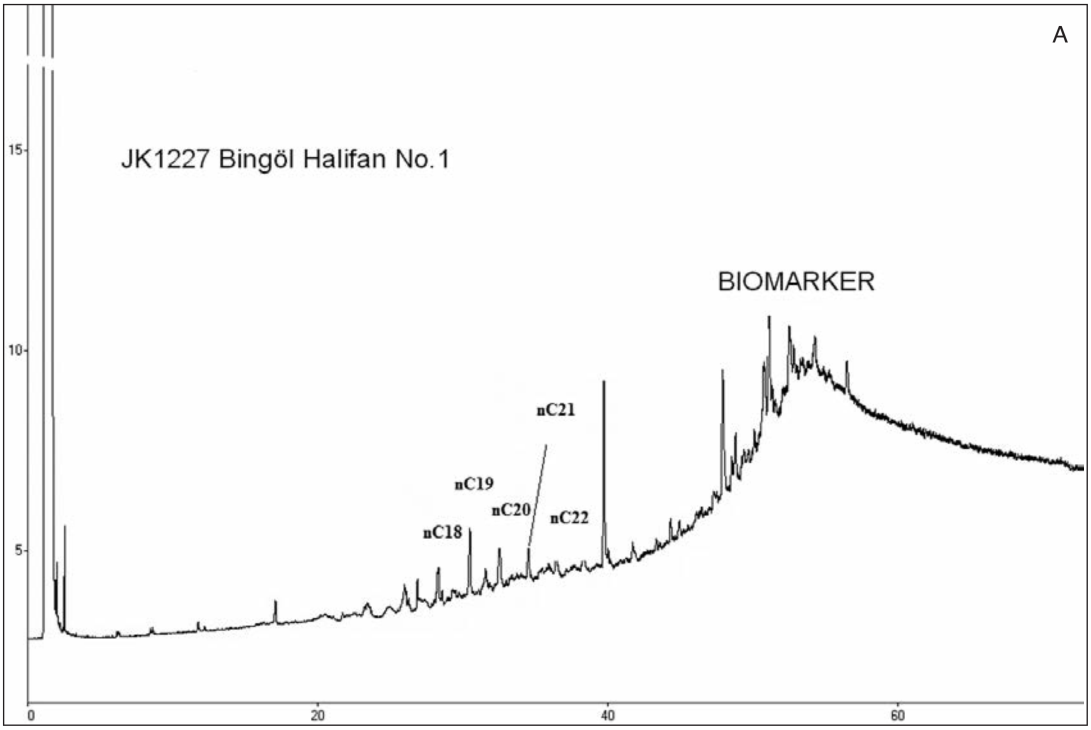
Sample	Pr/Ph	n-Alkan Distribution	Explanation
BNOK-1	Not certain	n-C_{15}-n-C_{22} interval is distinctive	Biyomarkers are distinctive
BNOK-2	<1	n-C_{15}-n-C_{22} interval is distinctive	Biyomarkers are distinctive
BNOK-3	>1	n-C_{16}-n-C_{19} interval is distinctive	further Bio-degradation level second organic material
BNOK-6	Not certain	n-C_{15}-n-C_{32} interval is distinctive	Biyomarkers are distinctive
BNOK-7	>1	n-C_{15}-n-C_{22} interval is distinctive	Biyomarkers are distinctive

Table 12- Leach amount of the samples of Karliova Halifan Coals and their organic properties.

Sample	Asph %	Saturated %	Aromatic %	Polar %	Aromatic (g)	Saturated (g)	Total Leachate (ppm)	Total Leachate Amount (g)
BNOK-1	50	0.97	1.8	47.2	0.013	0.002	82.1	0.117
BNOK-2	51.7	0.44	1.9	45.9	0.003	0.001	92.4	0.110
BNOK-3	57.8	1.04	0.2	40.9	0.003	0.001	82.4	0.073
BNOK-4	-	-	-	-	0.0006	0.0001	14.7	0.010
BNOK-5	36.6	1.24	0.7	41.4	0.011	0.001	58.2	0.033
BNOK-6	48	0.59	0.3	51.1	0.013	0.002	71.5	0.117
BNOK-7	55.8	0.76	0.67	42.8	0.014	0.002	92.1	0.169

ogy (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).

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. Comperative ratio of C_{24} tetracylic terpanes indicates terrestrial organic materrial content (Peters et. al., 2004). αß – moretane/ αß - hopane (moretane / hopane) ratio is between 0.5 - 0.6 and points out immature stage as well as salty depositional environment for organic material. 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/Pn (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), common gastropod shells and petrographic findings, all claim that the 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 occurences are very common in Turkey and



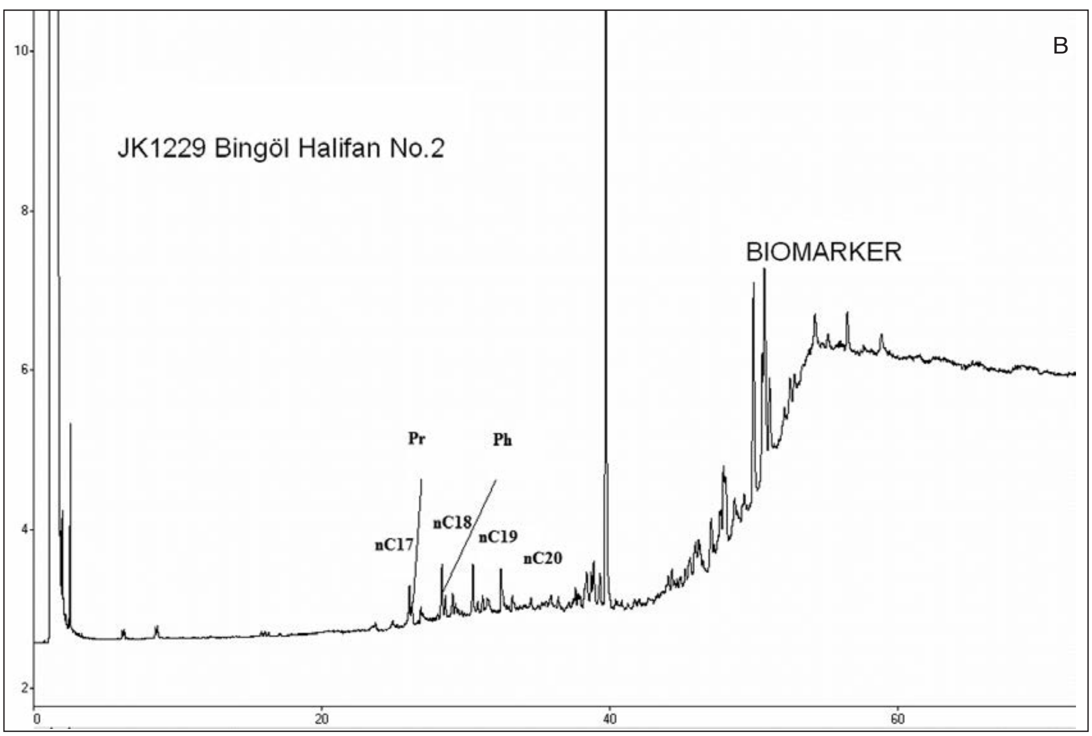


Figure 10- a,b. GC diagrammes (the mos important n-alkane series are shown on their peaks).

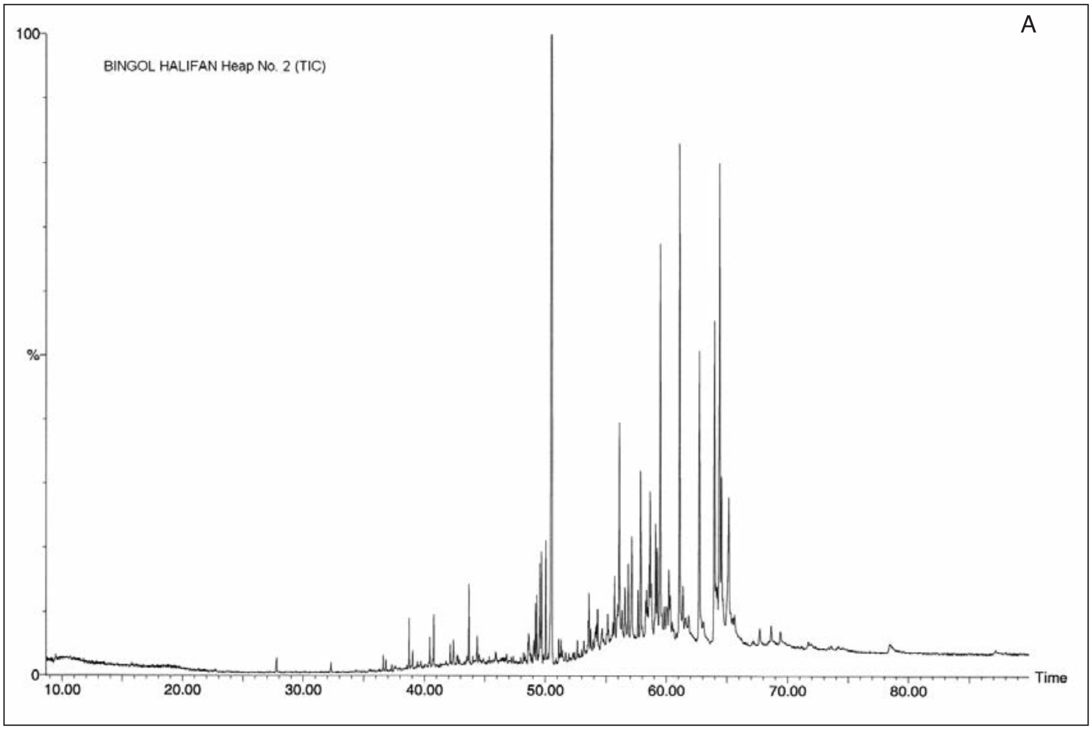


Figure 11a- GC-MS Total Ion Current (TIC) diagramme.

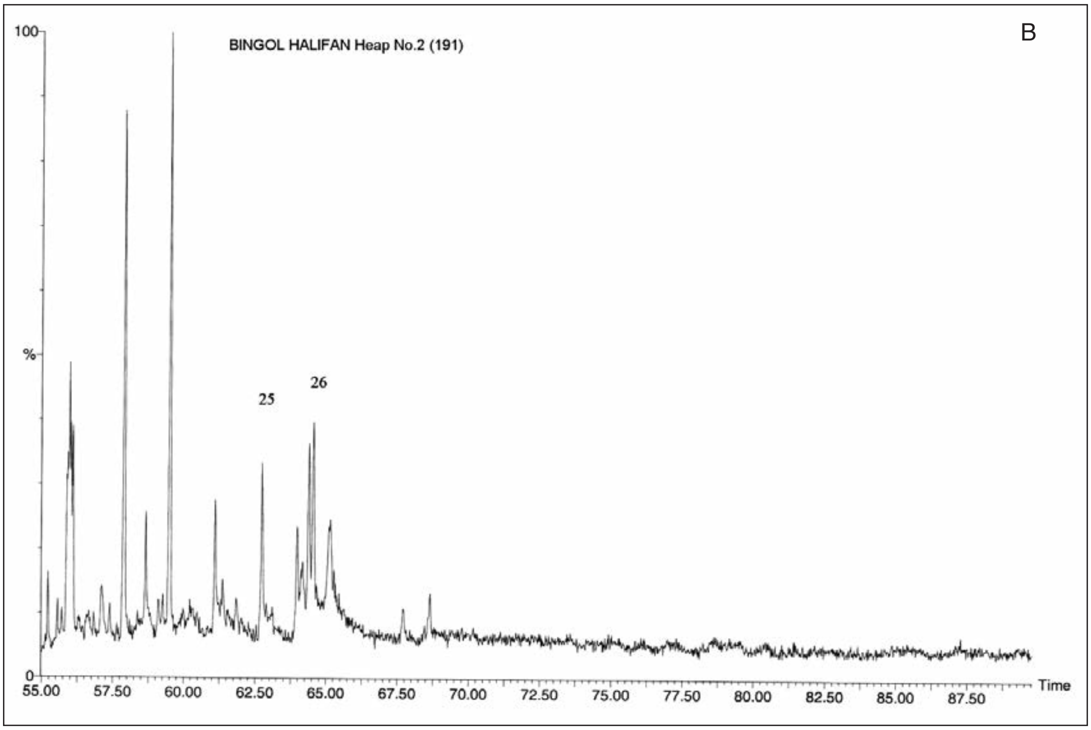


Figure 11b- GC-MS diagramme for 191

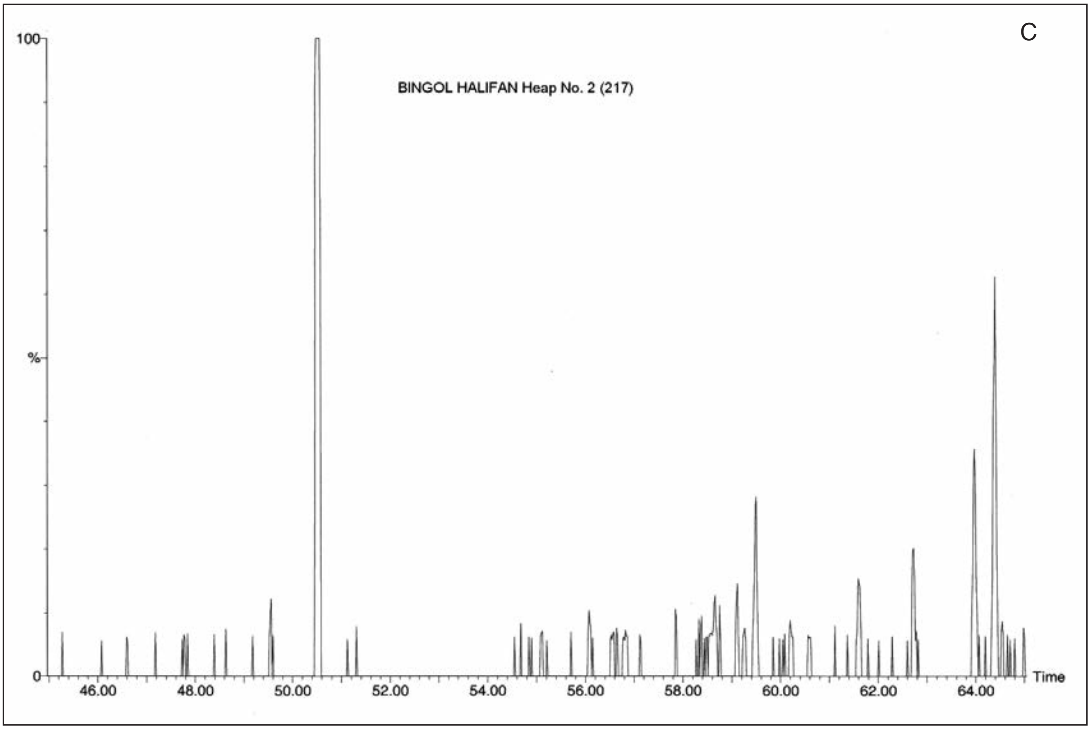


Figure 11c- GC-MS diagramme for 217

most of Tertiary coals were deposited in limnic environments.

CONSCLUSIONS AND RESULTS

In Karlıova Halifan Tertiary (Pliocene) coal basin, organic geochemical, petrographic analysis and coal quality evaluation studies were carried out on the organically rich and the coaly series. To petrographic evaluation results, Karlıova Halifan coals are rich in huminite group macerals but ratherly poor in liptinite and inertinites. Gelinite is the most abundant huminite maceral of the coals. Pyrite content of the coals is considerably high, mosty in the form of framboids.

Huminite reflection values change between 0.368 and 0.573 % and correpond to a diagenesis stage of maturity which is ratherly low. The reflection values of the coals imply that the coals have lignite and sub-bituminous coal ranks. Associated minerals of the coals are mostly clay-mica minerals, quartz and plagioclase minerals. T_{max} values vary between 401 and 435 °C (average T_{max} value is 417 °C).

These values indicate immature- premature organic stage. Alkane ratios, due to resin and asphalthene content, are considerably low and the maturity is low as well. On HI-T_{max} and hydrogen index-oxygen index diagrammes, 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 match with each other. Moretane/hopane and C_{32} homohopane isomerisation ratios comply with the other maturity parameters which correspond to an immature stage. As petrographic data, coal quality parameters also are compatible with Karlıova Halifan coalification rank and indicate alkaline as well as reduction 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 ash content and low coalification rank of Karlıova- Halifan coals limit the utilization potential of them. According to the coal quality data, organic geochemistry and petrographical analysis results, the coals carry low maturity properties. Although they seem to exhibit some gas generation potentials, the low maturity level limits this potential.

Manuscript received september 9, 2011

ACKNOWLEDGEMENTS

This study was made possible along with DÜAPK-03-MF-85 and DÜBAP 10-MF-105 projects. The authors are thankful to Kıvılcım Önen, Veysel Yalçındağ, Muhyettin Sever, Ali Ekber Ulufer, Hüseyin Karakaş, Merve Fakıllı, Selçuk Gördük and Emine Cicioğlu Sütçü for their efforts and helps.

REFERENCES

Altunsoy, M. and Özçelik, O., 1993. Organik Fasiyesler, Jeoloji Mühendisliği Dergisi, 43, 34 - 39.

Arfaouni, A., Montacer, M., Kamoun, F. and Rig ane, A., 2007. Comperative study be tween Rock-Eval pyrolysis and biomarkers parameters: a case study of Ypresian source rocks in central-northern Tunisia: Marine and Petroleum Geology, 24, 566-578.

ASTM, 1983 and 1992. Annual book of ASTM Standarts. Gaseous Fuels; Coal and Coke (D-388-82, D-2798-79, D-3172-73, D-2799-72, D-3174-82, D-3175-82): 1916 Race Street, Philadelphia, PA 19103, 05.05, 520p.

Bechtel, A., Saschsenhofer, R. F., Zdravkov, A., Kostova, I. and Gratzer, R. 2005. Influence of floral assemblage, facies and diagenesis on petrography and organic geochemistry of the Eocene Bourgas coal and the Miocene Maritza East lignite (Bulgaria): Organic Geochemistry, 36, 1498–1522.

Boggs, S. 1987. Principles of Sedimentology and Stratigraphy. Merill Publishing Company: A Bell and Howell Company, 784p., Columbus Toronto London Melbourne.

Bray, E. E. and Evans, E. D. 1961. Distribution of n-paraffins as a clue for recognition of source beds: Geochimica et Cosmochimica Acta 22, pp. 2-15.

Burwood, R., Leplat, P., Mycke, B. and Paulet, J. 1992. Rifted margin source rock deposition: a carbon isotope and biomarker study of a West African Lower Cretaceous “Lacustrine” Section”: Organic Geochemistry 19, 41-52.

Connan, J. 1993. Molecular geochemistry in oil exploration (in: M. L. Bordenave, Editor): Applied Petroleum Geochemistry, Editions Technip, Paris, 175-204.

———, Bouroullec J. and Dessort, Albrecht, P. 1986. The microbial input in carbonate - anhydrite facies of a sabkha paleoenvironment from Guatemala: a molecular approach: Organic Geochemistry 10, 29-50.

Dağyaran. Y. 1976. Bingöl – Karlıova - Selekan Linyit Sahasına Ait Jeoloji Raporu Maden Tetkik ve Arama Genel Müdürlüğü Rapor No. 6134, Ankara (unpublished)

Diessel, K. 1986. The correlation between coal facies and depositional environments. Advances in the Study of the Sydney Basin: Proceedings of 20^{th} Symposium, University of Newcastle, 19-22.

Durand, B. and Nicaise, G. 1980. Procedures for kerogen isolation. In: B. Durand, (Ed.), Kerogen- insoluble organic matter from sedimentary rocks): Paris, Editions Techniq, 35-53.

——— and Paratte, M. 1983. Oil potential of coals: a geochemical approach (in: Brooks, J. (Ed.), Petroleum Geochemistry and Exploration of Europe): Blackwell, Ox ford, 255-265. 51.

Erik. Y.N., Sancar, S. and Toprak, S. 2008. Hafik Kömürlerinin (Sivas) organik jeokimyasal ve organik petrografik özellikleri, TPJD Bülteni, Cilt 20, sayı 2, sayfa 9-33

Espitalié, J., Deroo, G., and Marquis, F. 1985. La pyrolyse Rock-Eval et ses applications (deuxiémepartie): Revue Institut Francais du Pétrole, v. 40, 755-784.

Flores, D. 2002. Organic facies and deposi-tional palaeoenvironment of lignites from Rio Maior Basin (Portugal): International Journal of Coal Geology, 48, 181-195.

Fowler, M. G., Gentzis, T., Goodarzi, F. and Foscolos, A. E., 1991. The petroleum potential of some Tertiary lignites from northern Greece as determined using pyrolysis and organic petrological tech-niques: Organic Geochemistry. 17, 805-826.

Georgakopoulos, A. and Valceva, S. 2000. Petrographic characteristics of Neogene Lignites from the Ptolemais and Servia basins, Northern Greece: Energy Sources, 22, 587-602.

Gökmen, V. Memikoğlu, O., Dağlı, M., Öz, D. and Tuncalı, E., 1993. Türkiye Linyit Envanteri, Maden Tetkik ve Arama Genel Müdürlüğü, Ankara.

Gümüşsu M. 1984. Bingöl İli Karlıova İlçesi Çilliköy Kömür Sahası Jeolojisi Maden Tetkik Arama Genel Müdürlüğü Rapor No. 7686, Ankara (unpublished)

Hanson, A. D., Zhang, C., Moldowan, J. M., Liang, D. G. and Zhang, B. M., 2000. Molecular organic geochemistry of the Tarim Basin, Northwest China: American Association Petroleum Geology Bulletin 84, 1109-1128.

Heath, G.R. Moore, T.C. and Dauphin, J.P., 1977. Organic Carbon In Deep-Sea Sediments In: R.N.Andersen (Ed.), The Fate Of Fossil Fuel CO2 In The Oceans: Plenuem Press, New York.

Hubbard, B., 1950. Coal as a possible petroleum source rock: American Association Petroleum Geology Bulletin 34 (12), 2347-2359.

Hunt, J.M. 1967. The Origin Of Petroleum In Carbonate Rocks, In G.V. Chilingar, H.J.Bissel And R.W. Farbridges eds, Car bonate Rocks, New York, Elsevier, 225-251.

———, 1995. Petroleum Geochemistry and Geology: W. H. Freeman and Company, New York, 743p.

International Committee for Coal and Organic Petrology (ICCP), 1998. The new vitrinite classification: Fuel 77, 349-358.

———, 2001. The new inertinite classification: Fuel 80, 459-471.

Iordanidis, A. and Georgakopoulos, A. 2003. Pliocene lignites from Apofysis mine, Amynteo basin, Northwestern Greece: Petrographical characteristics and depositional environment: International Journal of Coal Geology., 54, 57-68.

Jackson, K. S., Hawkins, P. J. and Bennett, A. J. R., 1985. Regional facies and geochemical evolution of Southern Denison Trough: APEA Journ., 20, 143-158.

Kalkreuth, W., Keuser, C., Fowler, M., Li, M., Mcintyre, D., Püttmann, W and Richardson, R., 1998. The petrology, organic geochemistry and palynology of Tertiary age Eureka Sound Group coals, Arctic Canada: Organic Geochemistry 29, 799-809.

Kavak, O., 2011. Organic Geochemical Comparison of Asphaltites of Şırnak Area with the Oils of the Raman and Dinçer Fields in Southeastern Turkey, Fuel, 90 (4), 1575-1583.

———, Connan, J., Erik, N.Y. and Yalçın, M.N., 2010. Organic Geochemical Characteristics of Şirnak Asphaltites in Southeast Anatolia, Turkey, Oil Shale, 27 (1), 58–83.

Kavak, O. and Toprak, S. 2011. "Gölbaşı Harmanlı (Adıyaman) Kömürlerinin Organik Jeokimyasal ve Petrografik Özellikleri", Jeoloji Muhendisliği Dergisi, Cilt 35, Sayı 1, Sayfa 43-78, Haziran, JMO, Ankara.

Kolcon, I. and Sachsenhofer, R. F. 1999. Petrography, palynology and depositional environments of the early Miocene Oberdof lignite seam, (Styrian Basin, Austria): International Journal of Coal Geology., 4, 275-308.

Korkmaz, S. and Kara G. R., 2007. Organic geochemical characteristics and depositional environments of the Jurassic coals in the Western Taurus of Southern Turkey: International Journal of Coal Geology., 70, 4, 292-304.

Kvenvolden, K. A. and Simoneit, B. R. T. 1990. Hydrothermal derived petroleum examples from Guaymas Basin, Gulf of California, and Escabana Trough, north-east Pacific Ocean: AAPG, 74, 223-237.

Langford, F. F. and Blanc-Valleron, M. M. 1990. Interpreting Rock-Eval pyrolysis data using graphs of pyrolizable hydro-carbons vs. total organic carbon:. American Association Petroleum Geology Bulletin 74, 799-804.

Moldowan, M., Seifert, W. K., and E. J., 1985. Gallegos, Relationship between petroleum composition and depositional environment of petroleum source rocks: American Association Petroleum Geology Bulletin. 69, 1255-1268.

Mukhopadhyay, P. K., Wade, J. A. and Kruge, M. A., 1995. Organic facies and maturation of Jurassic/Cretaceous rocks, and possible oil-source rock correlation based on pyrolysis of asphaltenes: Scotian Basin, Canada, Org. Geoch., 22 (1), 85-104.

Peters, K. E. 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis: American Association Petroleum Geology Bulletin., 70, 318-329

——— and Moldowan, J. M. 1993. The Biomarker Guide: Interpreting molecular fossils in petroleum and ancient sedi-ments: Prenctile-Hall, Englewood Cliffs, NJ.

————, Walters, C.C. and Moldowan, J.M., 2004. The Biomarker Guide Volume 2: Biomarkers and Isotopes in Petroleum Exploration and Earth History (second ed.): Cambridge, 475-1155.

ODTU,1984. Bingöl Karlıova Linyit Yatağı 100 MW Termik Santral İçin 1.115.000 Ton Yıl Üretim Kapasiteli Açık İşletme Projesi, Maden Mühendisliği Araştırma Merkezi.

Stach, E., Mackowsky, M.-Th., Teichmüller, M., Taylor, G. H., Chandra, D. and Teichmüller, R., 1982. Stach's textbook of coal petrology: Gebrüder Borntraeger, Berlin, 535p.

Şaroğlu. F. and Yılmaz. Y., 1987. Doğu Anadolu daki Neotektonik Dönemdeki Jeolojik Evrim ve Havza Modelleri Maden Tetkik Arama Dergisi Sayı 107. Ankara

Şengör. A. M. C., 1980. Türkiyenin Tektonik Esasları TJK Konferans Serisi 2-40 Ankara

Teichmuller, M. and Durand, B., 1983. Fluorescence microscopical rank studies on liptinites and vitrinites in peat and coals, and comparison with results of the Rock-Eval pyrolysis: International Journal of Coal Geology., 2,197- 230.

Teichmuller, M. and Littke, R. and Taylor, G. H., 1998. The origin of organic matter in sedimentary rocks (In Taylor, G. H., Teicmüller, M., Davis, A., Diessel, C. F. K., Littke, R., Robert, P., (eds)): Organic petrology, Gebrüder Borntraeger, Berlin, 704p

Ten Haven, H. L., de Leeuw, J. W., Rullkotter, J. and Sinninghe Damste, J. S. 1987. Restricted utility of the pristane/phytane ratio as a paleoenvironmental indicator: Nature 330, 641- 643.

Tissot, B. P. and Welte, D. H. 1984. Petroleum Formation and Occurrence: Springer-Verlag, Berlin, 699p.

Toprak, S. 1996. Alpagut-Dodurga (Osmancık Çorum) bölgesi çevresindeki kömürlerin oluşum ortamları ve özelliklerinin belirlenmesi, Hacettepe Üniversitesi Fen Bilimleri Enstitüsü, Doktora tezi çalışması, Ankara. (un published)

———, 2009. Petrographic properties of major coal seams in Turkey and their formation, International Journal of Coal Geology, V78, pp 263-275

Waples, D. W. and Machihara, T., 1991. Biomarkers for geologists-a practical guide to the application of steranes and triterpanes in petroleum geology: AAPG 9, p. 91.

Welte, D.H. 1965. Relation between Petroleum and Source Rock, American Association Petroleum Geology, Vol: 49, 2246-2267.

Wilkins, R. W. T. and George, S. C. 2002. Coal as a source rock for oil: a review: International Journal of Coal Geology., 50, 317–361.