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Organic geochemical characteristics, depositional environment and hydrocarbon potential of bituminous marls in Bozcahüyük (Seyitömer/Kütahya) Basin

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Research Article

Keywords:
Bituminous Marl, Organic Matter, Kerogen, GC, GC-MS, MFA, Synthetic Oil.

ABSTRACT

In this study, the geochemical properties, sedimentation conditions and hydrocarbon potential of the bituminous marls, having quite rich organic carbon content (average 9.27% TOC), composed of gray-green colored, dominant marl lithology with marl-claystone intercalation in the Bozcahüyük (Seyitömer/Kütahya) Basin has been evaluated. In this context, Rock-Eval pyrolysis, Gas Chromatography (GC), Gas Chromatography-Mass Spectrometry (GC-MS) and Modified Fischer Assay (MFA) analyses of the samples taken from the study area were performed and their organic facies have been evaluated. The marls have an excellent source rock characteristics, and include kerogen predominantly as Type I and rarely as Type II. The precipitation of organic matter took place under reducing anoxic redox conditions where oxygen was limited. Analysed samples contain terrestrial phytoclasts and palynomorphs as well as freshwater algae indicating Type-I kerogen such as *Botryococcus braunii*. Organic geochemical data show that the study area is deposited in the “AB” organic facies continental-marine transition zone. Carbon preference index (CPI), C_{27}, C_{28} and C_{29} steran abundance distribution of the samples as well as presence of Gamesaran as a salty environment indicator indicates that the lake enironment has been under marine environment influence from time to time and thereforethe study area have lagoon character. The average of the T_{max} values of analysed samples is 432 °C and it was determined that the bituminous marls in the region could not produce conventional petroleum due to their immaturity. However, it has been evaluated that these marls have the potential to produce synthetic petroleum as the kerogen types are dominantly Type-I, TOC and HI contents are high, as well as the analyzed samples have an average of 12.60% (133 L / ton) MFA oil content.

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1. Introduction

The study area is located 30 km from the center of Kütahya province in the Bozcahüyük locale linked to Seyitömer town and is found on İ23-c3 and c4 sheets of the 1/25,000 scale maps (Figure 1). In this study, the aim was to determine the organic geochemical features of grey-green colored bituminous marls outcropping in the Bozcahüyük (Seyitömer/Kütahya) Basin. Within this framework, samples had organic matter amounts, types and maturity, source rock depositional environment and petroleum yield identified in an attempt to estimate the hydrocarbon potential of the study area.

In this region, much research has been performed about general and economic geology topics to date due to outcrops of lignite along with bituminous marls

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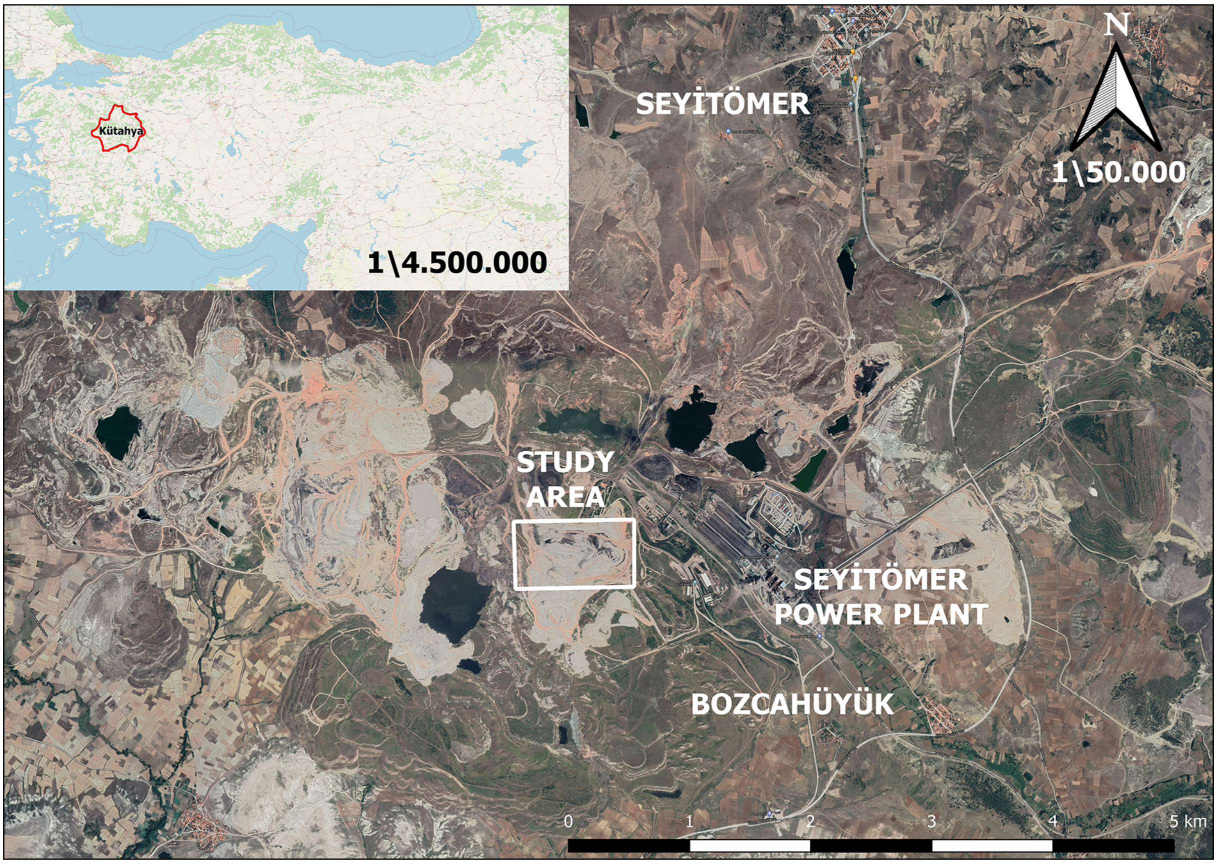

Figure 1- Satellite appearance of the study area on Google Earth and location map.

(Lebküchner, 1957, 1959; Nebert, 1960; Beseme, 1969; Ercan et al., 1978; Baş, 1986; Sarıyıldız, 1987; Şener et al., 1995; Şengüler et al., 1998; Şengüler, 1999; Kök et al., 2001; Çelik, 2003; Hepbaşlı, 2004; Kara Gülbay, 2004; Dikmen, 2005; Ekinci, 2006; Altun et al., 2006; Şengüler, 2007; Özburan, 2009; Murat, 2010; Kıratlı, 2019).

Organic matter-rich rocks which may be named bituminous shale, oil shale, bituminous schist, bituminous claystone and bituminous marl, generally have black, dark grey, grey, dark and light brown and dark green color and are mostly laminated, while some of the organic matter they contain comprises bitumen, which dissolves in organic solvents, and some comprises kerogen which cannot be dissolved with organic solvents (Dyni, 2003). These rocks are sedimentary units that may produce oil and gas with retorting and extraction processes and the residues provide ash which can be used in different sectors. Linked to technological developments, these rocks can be used for synthetic oil and gas production in addition to use as solid fuel with low-quality lignite in thermal power plants, while some major, trace and rare elements may be used for active carbon production and by paper, pharmaceutical, paint, plastic, ceramic, cement and fertilizer industries.

Studies by the Turkish Geological Survey (MTA) and other researchers have identified nearly 10 billion tons of bituminous rock resources in Turkey. However, it is very important to include this resource, calculated mainly in the possible and probable reserve category in past years, is made proven reserves with geophysical and drilling studies. This is because the bituminous rock potential is in second place among our country's energy resources after the 17.5 billion tons lignite resource (Büyük, 2019).

There is a need for synthetic petroleum to be produced from bituminous rocks due to increasing energy demands, external dependence on 88% of fossil fuels, excessive fluctuations in oil prices and rising energy bills. With the aim of searching for alternative energy sources globally and increasing local resources, it is important to complete technological innovations to meet these needs economically and to lower production costs.

2. Material and Method

Within the scope of organic geochemical investigations, analysis of a total of 23 samples taken from the study area were completed in Turkish Petroleum (TP) R and D Central Laboratories. All of these samples underwent Rock Eval pyrolysis analyses and Modified Fischer Assay (MFA) analysis was used for 6 samples chosen according to high TOC, S_2 and HI values on table 1. In order to make correlations with MFA analysis results, 3 samples chosen for MFA analysis according to variable TOC, S_2 and HI values in table 1 were assessed with gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Additionally, 5 samples chosen according to variable TOC, HI and OI values in table 1 and organic petrography (kerogen type identification) analyses were used for organic facies analysis.

Within this framework, with the aim of determining organic matter type, hydrocarbon potential and maturation status, pyrolysis analyses were performed using a Rock Eval VI device with IFP 160000 standard and samples had total organic carbon (%TOC), S_1, S_2, S_3, S_4, T_{max}, residual carbon (RC) and pyrolysable carbon (PC) values determined. Using this data, the following parameters were calculated: hydrogen index [$HI=(S_2/TOC)x100$], oxygen index [$OI=(S_3/TOC)x100$], production index [$PI=S_1/(S_1+S_2)$], hydrocarbon type index (S_2/S_3], genetic potential ($PY:S_1+S_2$) and bitumen/migration index (S_1/TOC).

In order to identify the oil, water and gas contents contained within the investigated bituminous marls with the retorting process in the laboratory environment, MFA analysis was performed according to the American Society for Testing and Materials (ASTM D) 3904 standard in order to determine the synthetic oil content as (%) and liter/ton that can be obtained from the bitumen (S_1) and kerogen within some samples (HB-8A, 10, 12, 14, 18 and 19A).

Dichloromethane was used as solvent to distil liquid hydrocarbon (bitumen) within the investigated samples (HB-7, 12 and 18) using an accelerated solvent extraction (ASE) 300 system for extraction analysis. The bitumen obtained from extraction of bituminous marls was used for GC and GC-MS analyses.

Certain samples (HB-8A, 10, 12, 19A, 20) had organic facies analysis performed. Samples had terrestrial amorphous organic matter (AOM), terrestrial palynomorphs (spores and pollen), freshwater algae and herbaceous and woody phytoclast content identified. Using diagenesis and geochemical features of organic matter, based on pyrolysis data and dominant organic matter type, the depositional environment in the region was interpreted within the scope of identifying 7 separate organic facies types of A, AB, B, BC, C, CD and D.

Samples (HB-7, 12 and 18) firstly were diluted with dichloromethane solvent to determine organic matter type, general distribution of HC compositions, thermal maturity, biological degradation and depositional environment of bituminous marls. These samples were analyzed with GC according to the ASTM D 5307-97 method with an Agilent 6850 GC device. Data obtained from GC analyses were used to calculate the Pr (pristane)/Ph (phytane) ratio, isoprenoid/n-alkane ratio, and carbon preference index (CPI) and additionally interpretations related to the depositional environment were made based on n-alkane distributions. In this study, the formula of Bray and Evans (1961) was used [$CPI_{(16-24)}= (nC_{15} + nC_{17} + nC_{19} + nC_{21} + nC_{23}) /(nC_{16} + nC_{18} + nC_{20} + nC_{22} + nC_{24})$].

Samples (HB-7, 12 and 18) investigated with the aim of revealing biological fossils (biomarkers), separating molecules geochemically and obtaining information about storage environment of source rocks, maturity and degree of biological degradation had GC using Norwegian Oil Standards and GC-MS analyses performed in an Agilent 5975C-four tip mass spectrometer device with automatic liquid sample intake. Ion fragmentograms from the chromatograms assessed the m/z 191 peaks for triterpenes and m/z 217 peaks for steranes.

3. General Geology

The Bozcahüyük (Seyitömer/Kütahya) Neogene Basin investigated within the scope of the study is included in the "İzmir-Ankara Ocean Zone" as defined by Brinkmann (1971). Basins began to form with N-S strike under an extensional regime with E-Worientation in the early Miocene. The Seyitömer Basin formed during this process. The metamorphics, ophiolitic rocks and granitoids forming the basement of this basin before the Neogene are unconformably overlain by Miocene-Pliocene basin fill (Çelik, 2003). Sarıyıldız (1987) stated that the fill materials in the basin are generally ancient fluvial, lacustrine and modern fluvial sediments.

The Late Cretaceous Ayvalı formation (Ka) representing ophiolitic mélange containing radiolarites, serpentinite and crystallized limestone forming the basement in the region was described by Ercan et al. (1978). Above the Ayvalı formation (Ka) over an angular unconformity, there are fluvial sediments comprising conglomerates, sandstone and claystone belonging to the early Miocene Elmacık formation (Ne) (Nebert, 1960). The lacustrine Seyitömer formation (Ns) containing lower and upper lignite beds was deposited conformably overlying the Elmacık formation (Ne) in the basin in the middle-late Miocene (Lebküchner, 1957 and 1959). The lower lignite bed in the Seyitömer Basin was called the “main vein” by Lebküchner (1959), Nebert (1960) and Beseme (1969). The thickness of the lower coal bed reaches up to 36.75 m in some drill holes with mean 15 m thickness (Gökmen et al., 1993). Additionally, the thickness of the upper lignite bed in the region reaches up to 10 meters (Şengüler, 1999). The Seyitömer formation (Ns) was divided into five members by Şengüler (1999) of the lacustrine green clay member (Nsa), the lower lignite member (Nsb), the bituminous marl member (Nsc), the upper lignite member (Nsd) containing the burnt series (Nsy) with upper levels outcropping around Arslanlı village and the yellow clay member (Nse) from older to younger, respectively.

In the Western Anatolian region, the late Miocene was a period when the N-S effective extensional tectonic regime began in the region which had thickened and risen in elevation under a N-S oriented compressional regime. After the deposition of the Seyitömer formation (Ns), a break was experienced in sedimentation in the region for a short duration in the late Miocene. In the Pliocene the lacustrine İshakçılar formation (Ni) comprising silicified limestone and tuff interlayers was deposited unconformably above the Seyitömer formation (Ns). The region was a large freshwater lacustrine and fluvial basin in the late Miocene (Özburan, 2009). With the neotectonic period, grabens began to develop with west-east strike from the end of the Pliocene to the beginning of the Pleistocene with the effect of north-south oriented extension. Large clastics belonging to the Kocayataktepe formation (Nk) comprising reddish and cream colored, poorly consolidated conglomerate, sandstone and occasional tuffs and clays forming in a fluvial environment in the Pleistocene were unconformably deposited above the İshakçılar formation (Ni). The unit comprising large clastics reflecting the fluvial environment shows that lake waters regressed in the areas where it outcrops (Baş, 1986). In the present day, as the final stage in graben and deposition, alluvium (Qal) comprising unconsolidated pebbles, sand, clay and silt and alluvial fan deposits continue unconformably above all units (Figure 2).

There are uncommon local faults with N-S strike in the Seyitömer Basin (Figure 3). Tectonic deformation structures in Western Anatolia are not observed in the study area. The late Miocene bituminous marl member (Nsc) displays distribution east and west of ancient Seyitömer and partly to the north of Ayvalı village. According to Şener and Şengüler (1992), drilling by MTA in the region found the thickness

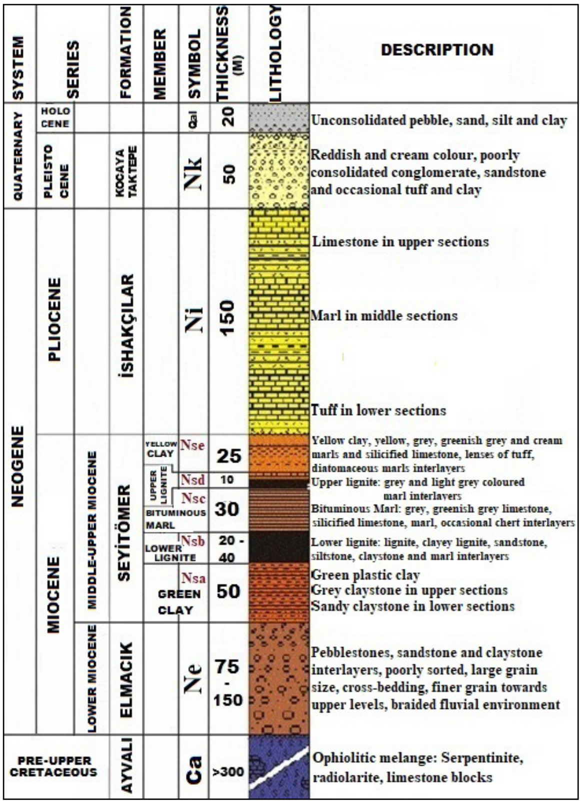

Figure 2- Generalized stratigraphic section for Seyitömer (Kütahya) (Şengüler, 1999; Dikmen, 2005; Büyük, 2019).

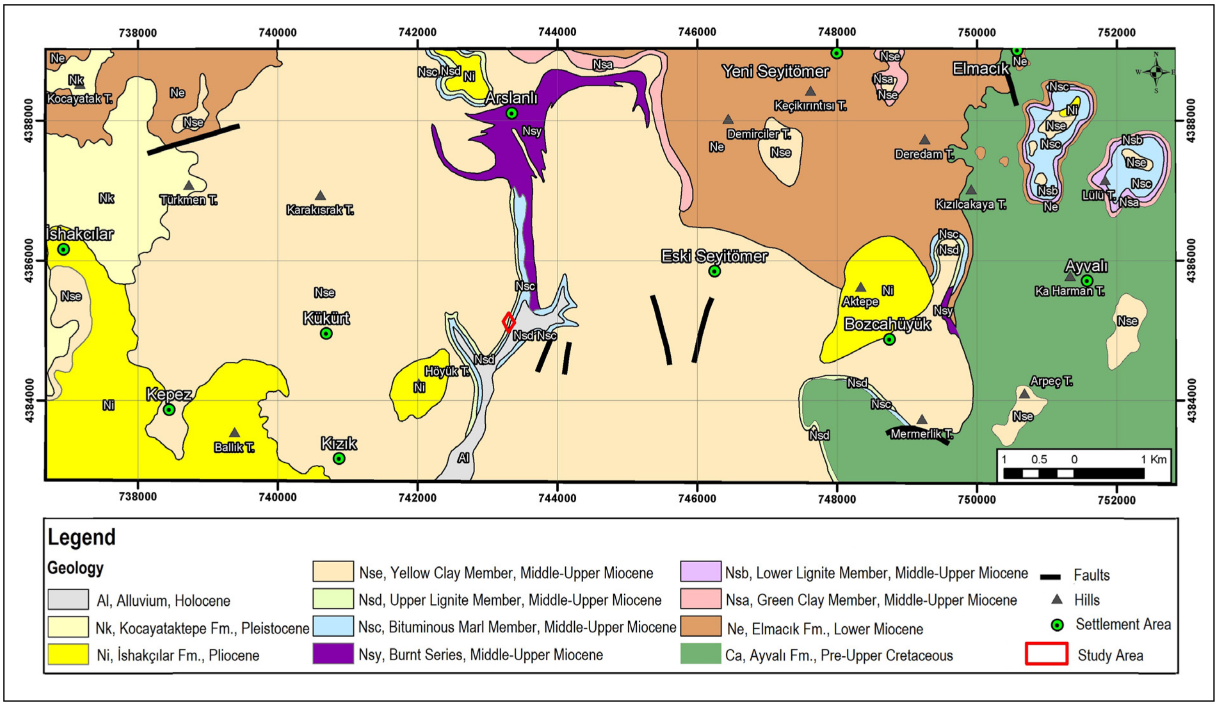

Figure 3- Geological map for Seyitömer (Kütahya) (Şengüler, 1999; Dikmen, 2005; Büyük, 2019).

of the bituminous marl member varied from 8.5-50.0 m and thickness increased from the edges of the basin toward the central sections. While coal and bituminous marl levels thicken toward the east of the basin, these units were not deposited in the west of the basin as the necessary depositional conditions did not exist. The Seyitömer Basin is stated to have nearly 110 million tons of economic bituminous rock resource. Mineralogical investigations revealed the bituminous marls, which should be dark colored normally due to high organic matter, have light colors due to high Mg/Ca ratio in the environment (montmorillonite in marls has Ca composition in dark-colored sections of the marls and Al, Fe and Mg composition in light-colored sections) and dense diatoms (Şengüler, 1999).

From the level of the "Höyük Pano" located in the study area, a measured stratigraphic section containing 37.25 meter sequence of only bituminous marls was taken and sampling was performed in this zone (Figures 4, 5).

4. Organic Geochemical Findings and Assessment

In this section, the organic geochemical analysis results from 23 bituminous rock samples taken from the study area are given and evaluated (Table 1). Additionally, as seen in table 1, only sample number HB-20* contained organic material (HI:16 mg HC/g TOC and OI: 231 mg CO_2/g TOC) that was oxidized and reworked according to the classifications by Peters and Cassa (1994) and Jones (1987) (HI<50 and OI>200), and was excluded from the assessment due to having inertinitic organic matter transported outside the depositional environment and kerogen type IV.

4.1. Source Rock Potential

TOC values vary from 1.06-29.87% with mean value of 9.27%. According to this data, the investigated samples were understood to have rich source rock potential according to Tissot and Welte (1984) (TOC>2), adequate according to Jarvie (1991) (TOC>1) and perfect according to Peters and Cassa (1994) (TOC>4).

Mean S_1 and S_2 hydrocarbon values were 2.11 mg HC/g rock and 66.40 mg HC/g rock and according to Peters and Cassa (1994) samples are source rocks with between generally good ($1<S_1<2$) and perfect ($4<S_1$) oil potential for S_1 and are source rocks with perfect ($20<S_2$) oil potential for S_2. Additionally, in all samples $S_2>S_1$ which indicates there is no organic contamination of the source rocks.

Figure 4- Distant and close-up general appearance of bituminous marl layer from the measured stratigraphic section preparation area.

4.2. Organic Matter Type

The investigated samples had HI values varying from 290 to 769 mg HC/g TOC with mean value of 654.59 mg HC/g TOC. As can be seen from the HI-OI and HI-T_{max} diagrams and also based on variable (S_2/S_3) hydrocarbon type index having values from 3.01 to 31.26 (Peters and Cassa, 1994), assessment of kerogen type identified dominant Type I kerogen ($15<S_2/S_3$) and rare Type II kerogen ($10<S_2/S_3<15$) types (Figures 6, 7). Again, samples examined with the HI associated with S_2-TOC diagram showed the samples had Type I-Type II kerogen types (Figure 8).

4.3.Thermal Maturity of Organic Matter

The investigated samples had T_{max} values varying from 426 °C to 441 °C with mean T_{max} of 432 °C. Accordingly the maturation parameters are in the immature-oil window ($430<T_{max}$(°C)<435) according to Espitalie et al. (1984) and in the immature stage (T_{max} (°C)<435) according to Peters and Cass (1984). According to the T_{max} standards of Espitalie et al. (1985), degree of maturity of bituminous marl samples determined to have kerogen Type I is immature-early mature (T_{max} (°C)<440); while samples HB-13 (Type II-III) and HB-18 (Type I) are in the oil window

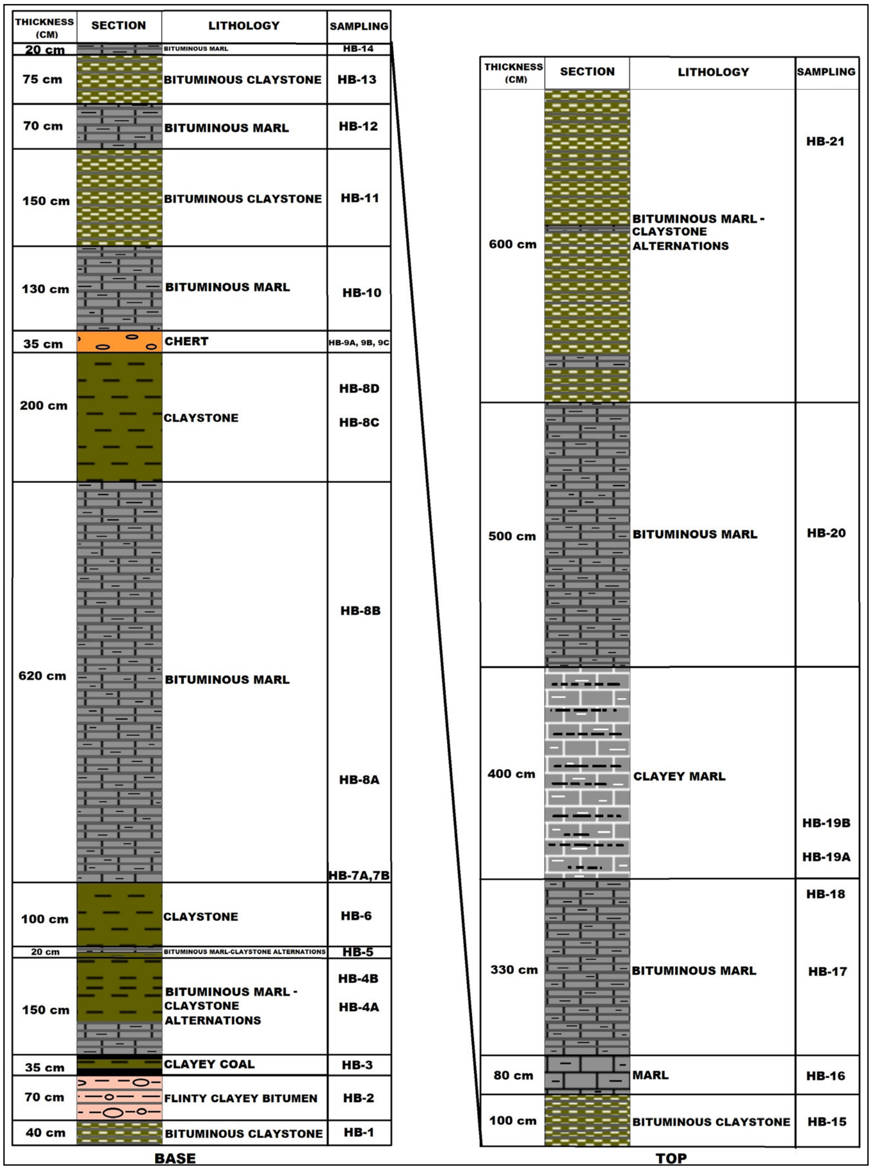

Figure 5- Measured stratigraphic section for bituminous marls in Höyük Pano in the Bozcahüyük (Seyitömer/Kütahya) Basin (Büyük, 2019).

(425<T_{max} (°C)<450); and sample HB-20 (Type IV-T_{max}:414°C) is in the immature stage. The HI-T_{max} diagram in figure 7 shows that five (HB-4, 8B, 12, 14, 18) of the samples have T_{max}>435 °C, and these are in the mature zone and have oil derivation potential. The other 18 samples have T_{max}<435 °Cso these samples are immature and are not in a position to produce hydrocarbons.

Due to the investigated samples having PI values lower than 0.1, they are in the immature zone on figure 9 and it appears oil derivation cannot occur from these samples.

Using the triterpene and sterane peak heights on the ion fragmentograms from GC-MS chromatograms in figures 24-29 according to the peak identifications in table 2, the biomarker parameters related to maturity of organic matter in the investigated samples were assessed on table 3. Though the 20S/(20S+20R) and ββ/(ββ+αα) sterane ratios on GC-MS m/z 217 chromatograms and 22S/(22S+22R) homohopane ratio and Ts/(Ts+Tm) ratio values on GC-MS m/z 191 chromatograms are very low, the moretane/hopane ratio is high which shows that bituminous marls in the region are in the immature stage complying with the pyrolysis results.

Table 1-Rock-Eval pyrolysis analysis results for bituminous rock samples from the Bozcahüyük (Seyitömer/Kütahya) Basin (Büyük, 2019).

#	Sample #	TOC (%)	S_1 (mg HC/ g rock)	S_2 (mg HC/ g rock)	S_3 (mg CO_2/ g rock)	T_{max} (°C)	HI (100xS_2)/ TOC	OI (100xS_3)/ TOC	PI S_1/ (S_1+S_2)	HC Type Index (S_2/S_3)	PY S_1+S_2 (ppm)	Bitumen Index S_1/TOC	RC (%)	PC (%)
1	HB-21	6.16	1.01	40.80	2.64	433	662.00	43.00	0.02	15.45	41.810	0.16	2.52	3.64
2	HB-20*	0.62	0.02	0.10	1.43	414	16.00	231.00	0.20	0.07	120	0.03	0.54	0.08
3	HB-19B	10.46	1.71	69.60	3.68	433	665.00	35.00	0.02	18.91	71.310	0.16	4.30	6.16
4	HB-19A	18.13	6.11	130.68	6.01	430	721.00	33.00	0.04	21.74	136.790	0.34	6.45	11.68
5	HB-18	29.87	3.52	229.56	10.05	441	769.00	34.00	0.02	22.84	233.080	0.12	9.99	19.88
6	HB-17	5.65	1.98	39.78	1.91	434	704.00	34.00	0.05	20.83	41.760	0.35	2.04	3.61
7	HB-16	8.21	1.94	57.38	3.15	432	699.00	38.00	0.03	18.22	59.320	0.24	3.09	5.12
8	HB-15	6.67	1.46	46.78	2.63	432	701.00	39.00	0.03	17.79	48.240	0.22	2.49	4.18
9	HB-14	11.35	5.34	86.40	3.61	438	761.00	32.00	0.06	23.93	91.740	0.47	3.53	7.82
10	HB-13	1.06	0.15	3.07	1.02	430	290.00	96.00	0.05	3.01	3.220	0.14	0.70	0.36
11	HB-12	27.56	5.05	203.60	9.81	436	739.00	36.00	0.02	20.75	208.650	0.18	9.70	17.86
12	HB-11	1.84	0.20	7.18	1.10	427	390.00	60.00	0.03	6.53	7.380	0.11	1.16	0.68
13	HB-10	11.53	3.62	78.04	4.19	430	677.00	36.00	0.04	18.63	81.660	0.31	4.52	7.01
14	HB-8D	6.80	1.14	50.96	2.17	435	749.00	32.00	0.02	23.48	52.100	0.17	2.32	4.48
15	HB-8C	9.71	2.02	71.46	2.61	432	736.00	27.00	0.03	27.38	73.480	0.21	3.43	6.28
16	HB-8B	8.00	2.70	60.88	2.69	436	761.00	34.00	0.04	22.63	63.580	0.34	2.54	5.46
17	HB-8A	19.92	4.23	151.46	6.08	434	760.00	31.00	0.03	24.91	155.690	0.21	6.64	13.28
18	HB-7	3.43	0.68	25.17	0.92	432	734.00	27.00	0.03	27.36	25.850	0.20	1.22	2.21
19	HB-6	4.81	0.69	29.23	1.60	429	608.00	33.00	0.02	18.27	29.920	0.14	2.20	2.61
20	HB-5	2.75	0.52	20.32	0.65	427	739.00	24.00	0.03	31.26	20.840	0.19	0.94	1.81
21	HB-4	5.89	2.06	40.49	1.98	436	687.00	34.00	0.05	20.45	42.550	0.35	2.23	3.66
22	HB-2	2.13	0.17	9.67	1.56	427	454.00	73.00	0.02	6.20	9.840	0.08	1.17	0.96
23	HB-1	2.08	0.15	8.22	1.32	426	395.00	63.00	0.02	6.23	8.370	0.07	1.24	0.84
Mean		**9.27**	**2.11**	**66.40**	**3.24**	**432.27**	**654.59**	**40.64**	**0.03**	**18.95**	**68.508**	**0.22**	**3.38**	**5.89**

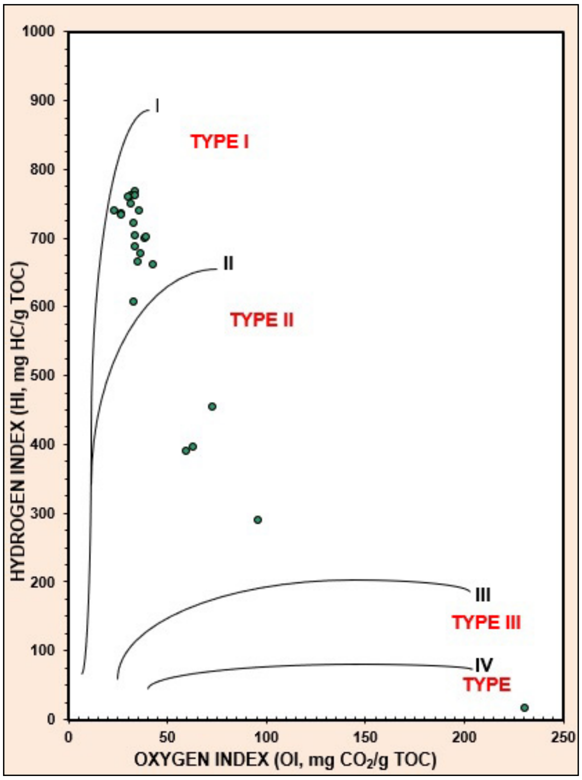

Figure 6- HI-OI diagram (Van Krevelen, 1993).

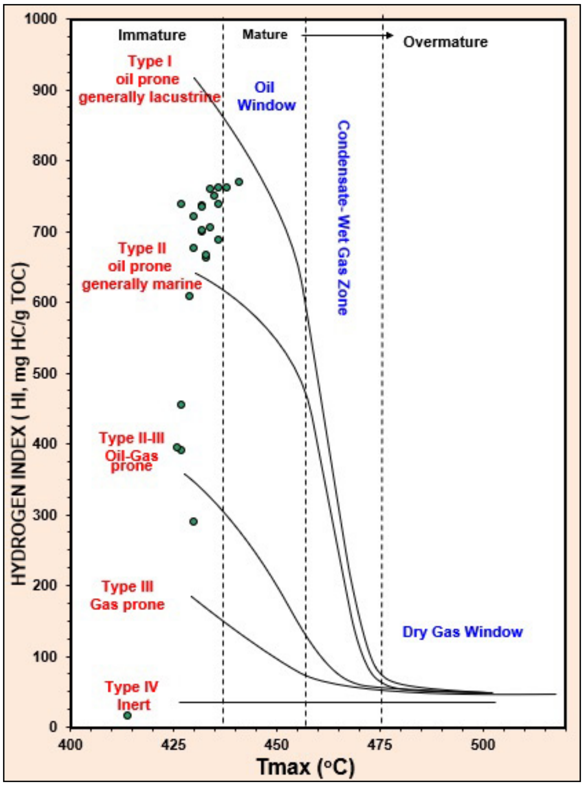

Figure 7- HI-T_{max} diagram (Hunt, 1995; Mukhopadhyay et al., 1995).

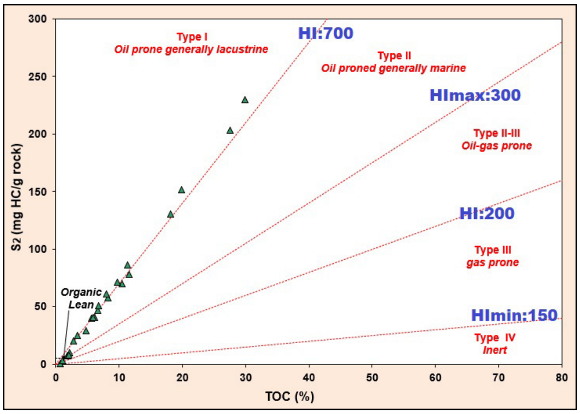

Figure 8- S_2-TOC, HI diagram (Langford and Blanc-Valleron, 1990).

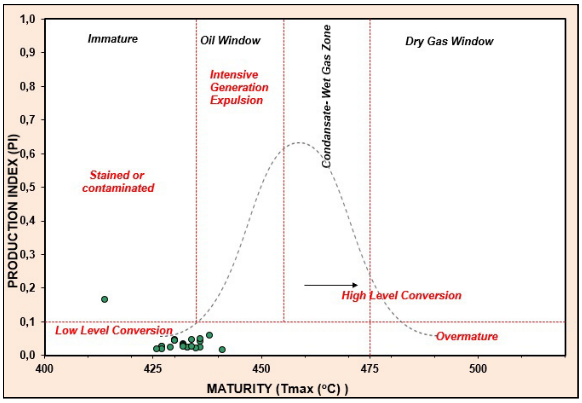

Figure 9- PI-Tmax maturation with kerogen maturation diagram (Peters, 1986).

Table 2- Identification of triterpene and sterane peaks on ion fragmentograms in a) m/z 191 and b) m/z 217 GC-MS chromatograms.

COMPONENT #	COMPONENT NAME
1	C_{19} Tricyclic Terpene
2	C_{20} Tricyclic Terpene
3	C_{21} Tricyclic Terpene
4	C_{22} Tricyclic Terpene
5	C_{23} Tricyclic Terpene
6	C_{24} Tricyclic Terpene
7	C_{25} (22S+22R) Tricyclic Terpene
8	C_{24} Tetracyclic Hopane (SECO)
9	C_{26} 22 (S) Tricyclic Terpene
10	C_{26} 22 (R) Tricyclic Terpene
11R	C_{28} Tricyclic Terpene (R)
11S	C_{28} Tricyclic Terpene (S)
12R	C_{29} Tricyclic Terpene (R)
12S	C_{29} Tricyclic Terpene (S)
13	C_{27} 18α (H)-22, 29, 30-Trisnorhopane (Ts)
14	C_{27} 17α (H)-22, 29, 30-Trisnorhopane (Tm)
15	17α (H)-28, 30-Bisnorhopane
16	C_{30} Tricyclic Terpene
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	C_{32} 17α (H)-21β (H)-30, 31-Bishomohopane (22S)
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-Trishomohopane (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)
(a)	

COMPONENT #	COMPONENT NAME
1	C_{27} 13β (H)-17α (H)-Diasterane (20S)
2	C_{27} 13β (H)-17α (H)-Diasterane (20R)
3	C_{27} 13α (H)-17β (H)-Diasterane (20S)
4	C_{27} 13α (H)-17β (H)-Diasterane (20R)
5	C_{28} 13β (H)-17α (H)-Diasterane (20S)
6	C_{28} 13β (H)-17α (H)-Diasterane (20R)
7	C_{28} 13α (H)-17β (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_{28} 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), 14α (H), 17α (H)-Sterane (20S)
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_{30} 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_{30} 5α (H), 14α (H), 17α (H)-Sterane (20R)
(b)	

4.4. Hydrocarbon Generation Potential

Assessment of the “migration index” or “bitumen index” (S_1/TOC) used to identify the depth at which a source rock will begin to generate hydrocarbon, in other words expel oil, found that 10 of the samples were in the initial generation-migrationstep ($0.1<S_1/TOC<0.2$), while another 10 had too much generation-migration ($0.2<S_1/TOC$) and the remaining 3 had no generation-migration($S_1/TOC<0.1$) (Smith, 1994; Hunt, 1995).

The S_2-TOC diagram in figure 10 shows the samples dominantly had perfect hydrocarbon potential. The mean hydrocarbon type index (S_2/S_3) value was 18.95 with samples identified to have oil derivative potential ($5.0<S_2/S_3$) according to Clementz (1979) and Peters (1986). Additionally, the HI-TOC diagram in figure 11 to determine the hydrocarbon generation potential of samples shows they are good-perfect oil sources origin. The mean potential product/genetic potential PY (ppm /mg HC/g rock): (S_1+S_2) value of these samples is 68,508 ppm which indicates good

Table 3- Biomarker parameters calculated for maturity of organic matter in samples according to m/z 191 and m/z 217 GC-MS chromatograms.

	HB-7	HB-12	HB-18
20S/(20S+20R) Sterane Ratio (C_{29}) = [18/(18+21)] height of peaks (m/z 217 GC-MS) If this ratio is <0.5 it is immature (Hunt, 1995).	0.04 Immature	0.12 Immature	0.06 Immature
ββ/(ββ+αα) Sterane Ratio (C_{29}) = [(19+20)/(18+19+20+21)] height of peaks (m/z 217 GC-MS) This ratio is 0.72 in the oil formation zone of thermal maturation equilibrium (Peters et al., 2005).	0.23 Immature	Could not be identified	0.26 Immature
22S/(22S+22R) Homohopane Index (C_{31}) = [25/(25+26)] height of peaks (m/z 191GC-MS) This ratio reaches 0.5 thermal equilibrium value in the oil formation zone (Peters et al., 2005).	0.02 Immature	0.10 Immature	0.05 Immature
Ts/(Ts+Tm) = [13/(13+14)] height of peaks (m/z 191 GC-MS) This ratio reaches 1.0 in the late mature oil formation field (Peters et al., 2005).	Could not be identified	0.11 Immature	Could not be identified
Moretane/Hopane Ratio (C_{30}) = (24/23) height of peaks (m/z 191 GC-MS) This ratio may fall from 0.8 to 0.15-0.05 with the increase in thermal maturation (Seifert and Moldowan, 1986).	0.95 Immature	5.52 Immature	0.87 Immature

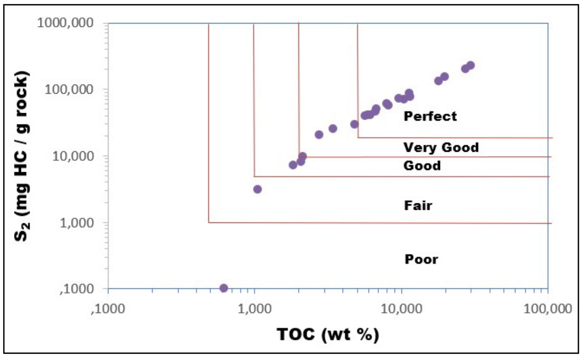

Figure 10- Hydrocarbon potential according to S_2 and TOC values (Ghori, 2000).

source rock potential (6,000 ppm<S_1+S_2) according to Tissot and Welte (1978). The samples are observed to dominantly plot in the perfect source rock potential area on the PY-TOC diagram (Figure 12). The S_1-TOC diagram used with the aim of differentiating migrated hydrocarbons from indigenous hydrocarbons shows the hydrocarbon in the samples is locally produced, with no mechanical or anthropogenic contamination from outside (Figure 13).

The investigated samples have %RC values from 0.70% to 9.99% which are not on the residue carbon line (TOC=RC) so they are observed to still have oil generation potential (Figure 14). The reason for samples being more distant from the TOC=RC line on figure 14 is that samples still have excess amounts of S_1 and S_2 hydrocarbons that can be generated. The %PC values vary from 0.36% to 19.88% which is close to the pyrolysable carbon line (TOC=PC) on figure 15 showing that the kerogen type in samples is suitable

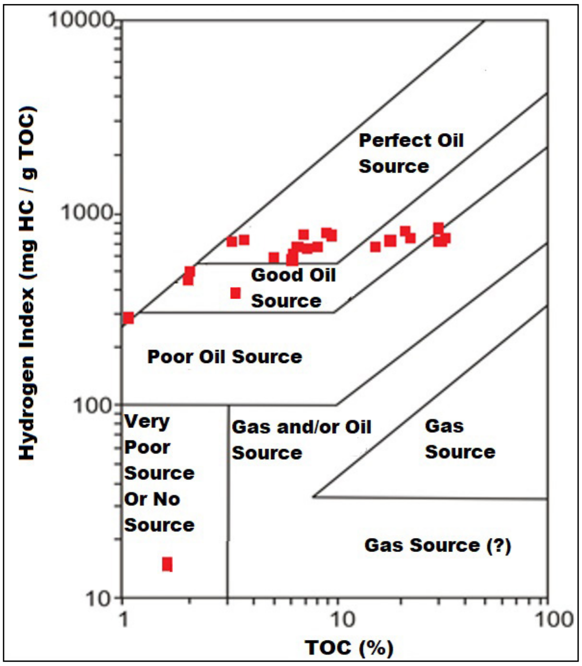

Figure 11- HI-TOC diagram (Jackson et al., 1985).

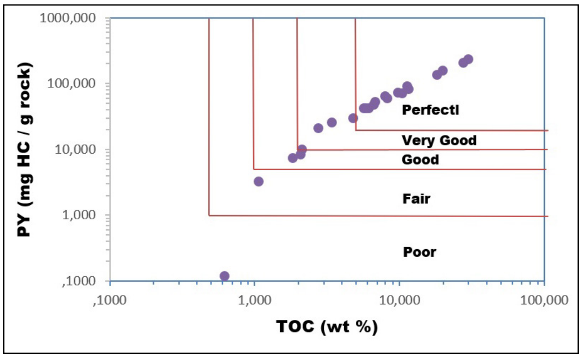

Figure 12- PY - TOC diagram (Ghori, 2002).

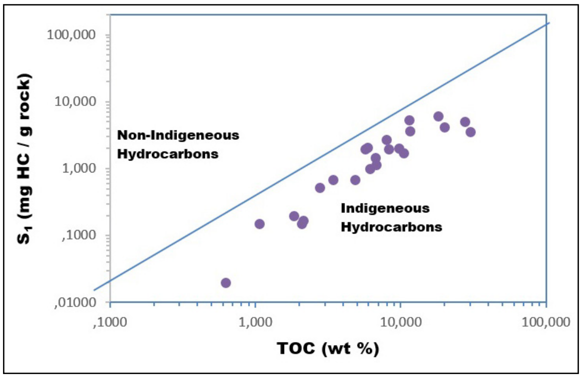

Figure 13- S_1 (mg HC/ g rock) - TOC (%) HC characterisation diagram (Hunt, 1995).

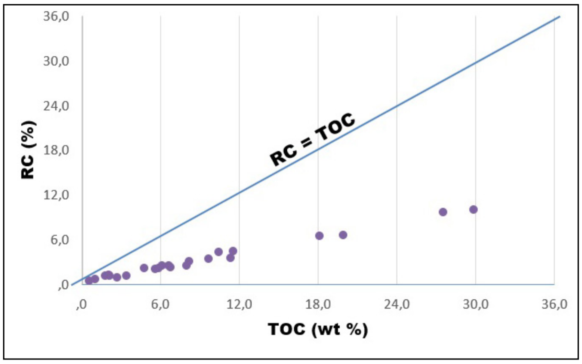

Figure 14- RC (%) - TOC (%) diagram (English et al., 2004).

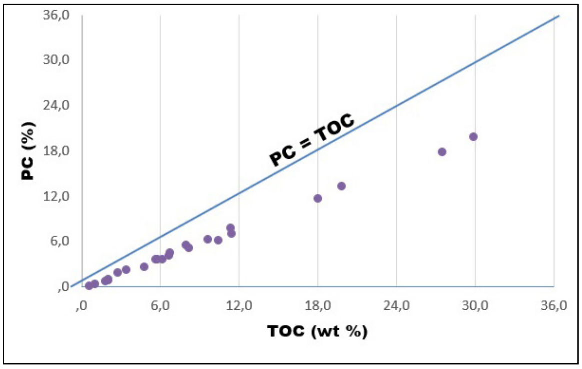

Figure 15- PC (%) - TOC (%) diagram (English et al., 2004).

for oil generation. During pyrolysis, as the amount of organic matter increases, the generation from S_1 and S_2 hydrocarbons increases; however, all samples are not on the TOC=PC line which indicates the presence of pyrolysable S_1 and S_2 hydrocarbons.

4.4.1.Modified Fischer Assay (MFA) Analysis and Synthetic Petroleum Production

Bituminous marl samples (HB-8A: 21.57%; HB-10: 3.22%; HB-12: 14.66%; HB-14: 5.38%; HB-18: 21.28%; HB-19A: 9.48%) analyzed with the MFA method had mean oil content of 12.6% (3.22%-21.57%). Economic assessment of synthetic petroleum that can be produced by these samples found potential was dominantly very highly economic according to Hou (1984), dominantly very economic according to Snape (1995) and has dominantly very good economic potential according to Committee Office of Mineral Resources in China (1987), Liu et al. (2006) and Tao et al. (2010) (Table 4).

When the correlations of the MFA yield of samples with TOC, S_1 and S_2 are assessed, these samples of perfect source rock were determined to be able to produce oil with very good economic potential (Tables 1 and 4, figures 16-18). Figures 16 and 18 show a strong positive correlation between MFA petrol content with %TOC (r= 0.848, p= 0.033) and with S_2 (r= 0.875, p= 0.022) and these are statistically significant. This indicates that with the increase in %TOC and S_2 values, the MFA yield increases. In other words, it appears the Type I kerogen features may produce oil at very good economic levels from these samples. However, statistical assessment did not find a correlation between MFA oil content with S_1 (r = -0.285, P=0.584) and there did not appear to be a strong correlation with HI (r =0.735, P=0.096) (Tables 1 and 4, figures 17 and 19).

Generally, about 5-10% of the TOC value of a rock comprises S_1 hydrocarbons, while 90-95% comprises S_2 hydrocarbons derived from kerogen. As a result, while the S_1 values obtained from pyrolysis analyses are low, S_2 values are high. All conventionally produced oils comprise S_1 and S_2 hydrocarbons. Due to this, the relationships between MFA analysis results with S_1 and S_2 data should be assessed. While the samples show positive correlation for S_2-MFA values on figure 18, the reason for the perception of

Table 4- Economic assessment criteria related to Fischer Assay yield (oil content) according to some researchers.

Hou (1984)		Snape (1995)		Hou (1984); Committee Office of Mineral Resources in China (1987); Liu et al. (2006); Tao et al. (2010)		
FISCHER ASSAY YIELD (%)	**ECONOMIC ASSESSMENT**	**FISCHER ASSAY YIELD (%)**	**ECONOMIC ASSESSMENT**	**FISCHER ASSAY YIELD**		**ECONOMIC ASSESSMENT**
				(%)	**(L/ton)**	
< 4.0%	Not economic	**< 4.0%**	Not economic	**< 3.5%**	**< 35**	Weak
4.0%-10.4%	Moderately economic	**4.0%-13.8%**	Moderately economic	**3.5%-5.0%**	**35-50**	Moderate
10.4%-13.8%	Highly economic	**13.8%-23.6%**	Highly economic	**5.0%-10.0%**	**50-100**	Good
> 13.8%	Very highly economic	**> 23.6%**	Very highly economic	**> 10.0%**	**> 100**	Very Good

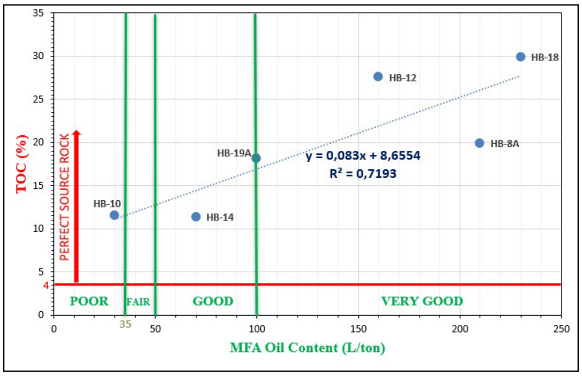

Figure 16- MFA oil content (L/ton)-TOC (%) diagram (Büyük, 2019).

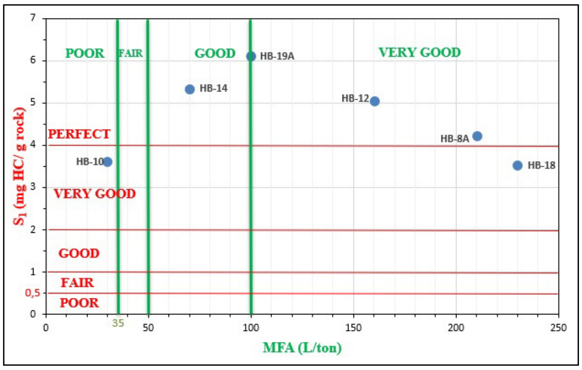

Figure 17- MFA oil content (L/ton)-S_1 (mg HC/ g rock) diagram (Büyük, 2019).

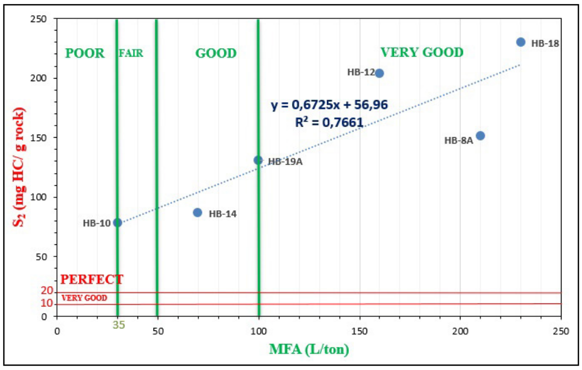

Figure 18- MFA oil content (L/ton)-S_2 (mg HC/ g rock) diagram (Büyük, 2019).

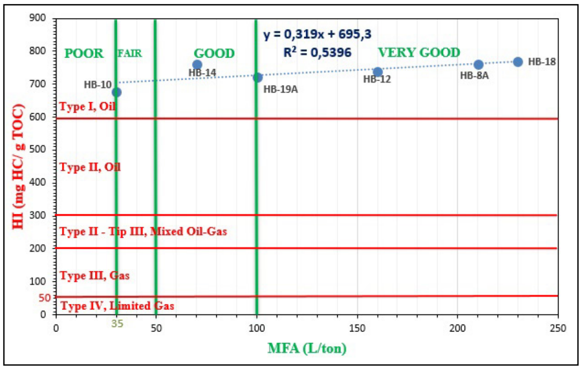

Figure 19- MFA oil content (L/ton)-HI (mg HC/ g TOC) diagram (Büyük, 2019).

a negative correlation between S_1 and MFA values on figure 17 is the oil and gas derived from a very small portion of 5-10% of organic matter comprising S_1 in the rock. In spite of this, according to MFA assessment of the S_1 hydrocarbon values on figure 17, most appear to be within very good economic boundaries.

In previous years, bituminous marls in the Seyitömer Basin were revealed to have oil content of 30-38 liters/ton according to Ünalan (1978), 5% oil content (54.3 L/ton) according to Şener et al. (1995), have 22 API gravity heavy oil equivalent of synthetic oil produced with density 0.92 g/mL according to Şengüler (1999), oil content of 4-5.9% (56 kg/ton) according to Hepbaşlı (2004), and be able to produce 4.46 L/ton synthetic petroleum with the in-place pyrolysis method according to Kök et al. (2008). Additionally, Ekinci (2006) reviewed many studies related to the Seyitömer Basin and stated 2.41% oil, 1.51% gas and 88.67% residue could be obtained from bituminous shale according to Fischer assay (FA) analysis results. Though there was low oil content and high ash, after representative distillation from bituminous shale with Type I kerogen 14% naphtha, 21.5% kerosene, 14.5% mild gas-oil, 29% atmospheric gas-oil, 18% vacuum distillation and 2% residue could be obtained and pyrolysis of the bituminous shale had FA percentage 7 gpt (26.5 L/ton). In other words, the region had uneconomic potential in terms of synthetic oil production. Şengüler (1999) stated that the 5meter economic bituminous marl zone had thermal values of 800-1,000 kcal/kg and that there were levels suitable to obtain synthetic oil occasionally among levels with highest TOC values. However, as the lateral continuity of these levels was variable and there was general inadequacy of thickness in the region, synthetic oil production from bituminous marls was revealed not to be economic. Due to this, the recommendation was made to evaluate these units as solid fuel in thermal power plants using fluid-bed incineration systems with 20% bituminous marl and 80% lignite.

4.5. Biomarker Investigations

4.5.1. Gas Chromatography Analysis (GC)

n-Alkane Distributions: GC analyses were performed to make interpretations about the depositional environment, organic matter type, biological degradation and thermal maturity. Gas chromatograms belonging to samples investigated in figures 20-22 have a skewed n-alkane distribution toward the nC_{23}-nC_{30}array; in other words, as the long-chain C_{23}, C_{25}, C_{27} and C_{29}peaks are higher compared to others, the depositional environment reflects a terrestrial lacustrine environment containing high plants and non-marine phytoplankton algae (Tissot and Welte, 1984; Peters and Moldowan, 1993). This situation, along with the dominant Type I kerogen type on figures 6-8 and the observation of green freshwater algae, *Botryococcus branuii* on organic facies analyses, is compatible with indications of a freshwater lacustrine environment.

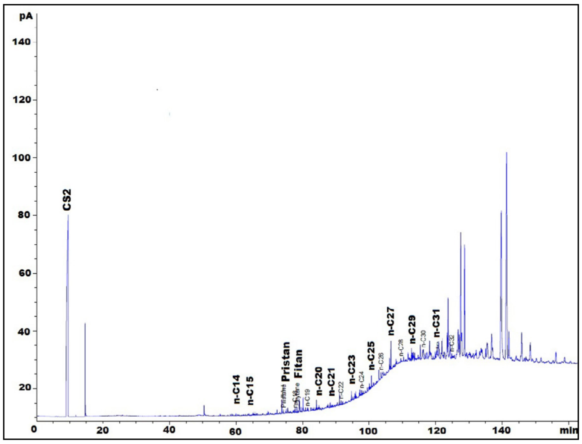

Figure 20- Gas chromatogram for sample no. HB-7.

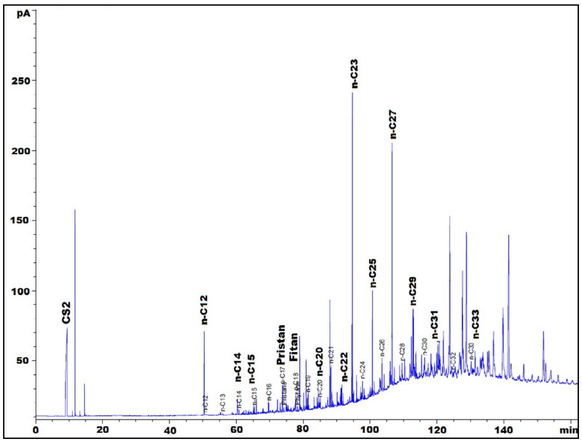

Figure 21- Gas chromatogram for sample no HB-12.

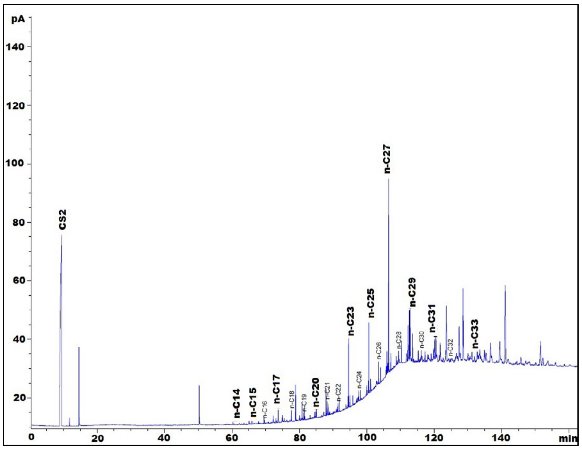

Figure 22- Gas chromatogram for sample no HB-18.

It was observed that the investigated samples were deposited in the terrestrial-marine transition zone in the distribution of C_{27}, C_{28} and C_{29} sterane abundances in the triangular diagram in figure 23 (Huang and Meinschein, 1979).

As the $\sum(nC_{21}-nC_{31})$ / $\sum(nC_{15}-nC_{20})$ ratio is >1 (HB-7 7.38; HB-12 12.29; HB-18 14.99), it indicates the degree of waxiness increases; in other words, there was input of terrestrial organic material into the depositional environment (Bakr, 2009). Additionally, the n-alkane ratio (TAR) of the terrestrial environment source/aquatic environment source, or the ratio of the total of long-chain n-alkanes with odd carbon number ($C_{27}+C_{29}+C_{31}$) to the total of short-chain n-alkanes with odd carbon number ($C_{15}+C_{17}+C_{19}$) is larger than 1 (HB-7 6.7; HB-12 7.7; HB-18 13.5), the depositional environment reflects terrestrial environment source with high plant content (Rieley et al., 1991). Again, as the ($n\text{-}C_{17}/n\text{-}C_{31}$) ratio is smaller than 1 (HB-7 0.34; HB-12 0.62; HB-18 0.43), the depositional environment indicates terrestrial organic matter input (Koralay, 2018).

Pristane/PhytaneRatio (Pr/Ph): According to GC graph data in figures 20-22, the Pr/Ph ratios are smaller than 1 (HB-7 0.87 and HB-12 0.68) so the depositional environment was identified to have reducing/anoxic redox conditions (Tissot and Welte, 1984).

Carbon Preference Index (CPI): The CPI values of bituminous marl samples in the region were calculated according to the formula of Bray and Evans (1961) using the GC graph data in figures 20-22 and values of 1.18 for HB-7, 5.88 for HB-12 and 3.06 for HB-18 were found. This indicates a terrestrial/lacustrine environment with marine connection fed by marine plankton in sample HB-7 and fed by high terrestrial plants in samples HB-12 and HB-18. Additionally, CPI>1 indicating dominant odd-number carbons and the high CPI values for samples HB-12 and HB-18 emphasize that the samples are in the immature field (Tran and Philippe, 1993).

Isoprenoid/n-Alkane Ratios: According to the GC graph data in figures 20-22, sample HB-12 had Pr/nC_{17}: 0.15 and Ph/nC_{18}: 1.00 and sample HB-7 had Pr/nC_{17}: 0.70 and Ph/nC_{18}: 1.82. According to Petersen et al. (2001), these samples were deposited in an anoxic reducing environment, while according to Chaula et al. (1987) this indicates an algal source for kerogen.

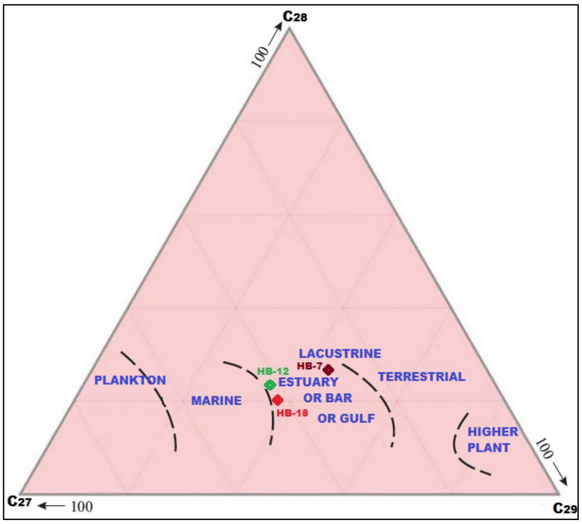

Figure 23- C_{27}, C_{28} and C_{29} sterane abundance and precipitation environment diagram for bituminous marls in the region (Huang and Meinschein, 1979).

4.5.2. Gas Chromatography-Mass Spectrometry Analysis (GC-MS)

Using the triterpene and sterane distributions on m/z 191 and m/z 217 mass chromatograms belonging to samples HB-7, 12 and 18, biomarker parameters were calculated and attempts were made to interpret the depositional environments for bituminous marls in the region (Figures 24-29 and table 2).

On the m/z 191 mass chromatograms, the presence of Gammacerane (0.25 and 0.13, respectively) in samples HB-12 and HB-18 indicates a saline and reducing environment under marine effect in the region (Peters and Moldowan, 1993). All three samples did not have Oleanane observed, indicating terrestrial environments; however, this situation does not mean that the depositional environment did not have terrestrial organic matter input (Peters and Moldowan, 1991; Hunt, 1995). The (C_{29}/C_{30}) hopane ratio was larger than 1 for sample HB-7 (1.16) due to marl source rock according to Peters and Moldowan (1993) and is smaller than 1 in samples HB-12 and HB-18 (0.55 and 0.96, respectively) reflecting source rock with high clay content according to Waples and Machihara (1991).

Again, on m/z 191 chromatograms, the C_{31} 22R/C_{30} hopane ratios in samples (HB-7: 3.89; HB-12: 2.07; HB-18: 1.82) were larger than 0.25 reflecting marl source rock (Koralay, 2009). Additionally, a lacustrine depositional environment with high clay content was indicated due to the [C_{29} Ts/(C_{29}Ts+C_{29} Norhopane)] ratio being smaller than 1 (HB-7: 0.06 and HB-12: 0.69) (Philip and Gilbert, 1986). The [Ts/(Ts+Tm)] ratio was calculated as 0.11 for HB-12 assessed as reflecting an environment suitable for carbonate

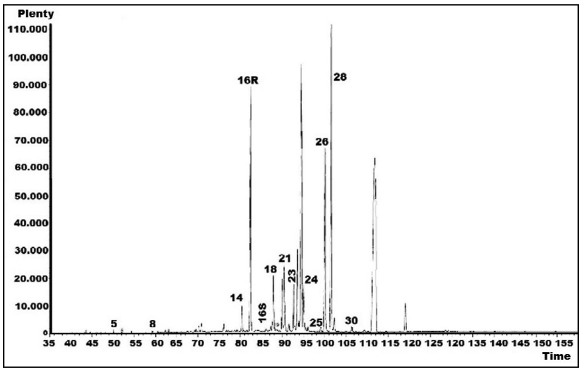

Figure 24- GC-MS m/z 191 chromatogram for HB-7 bituminous marl sample.

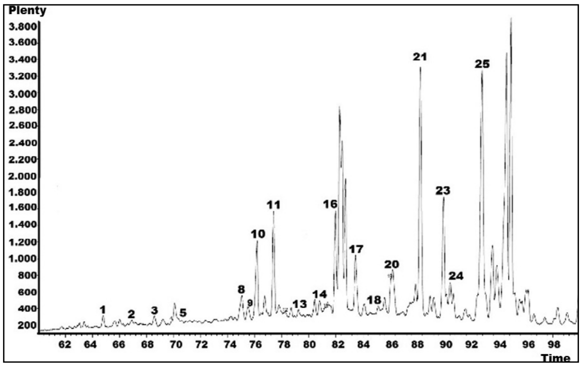

Figure 25- GC-MS m/z 217 chromatogram for HB-7 bituminous marl sample.

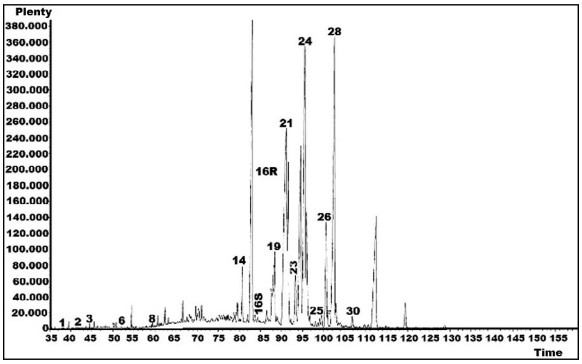

Figure 26- GC-MS m/z 191 chromatogram for HB-12 bituminous marl sample.

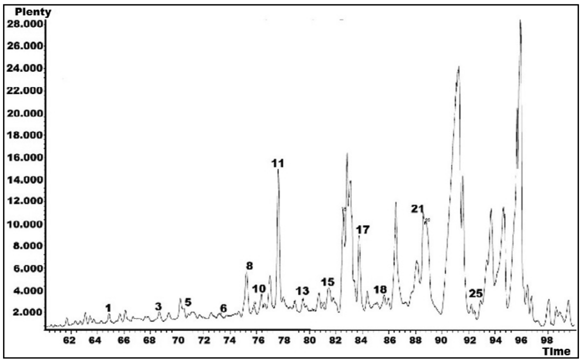

Figure 27- GC-MS m/z 217 chromatogram for HB-12 bituminous marl sample.

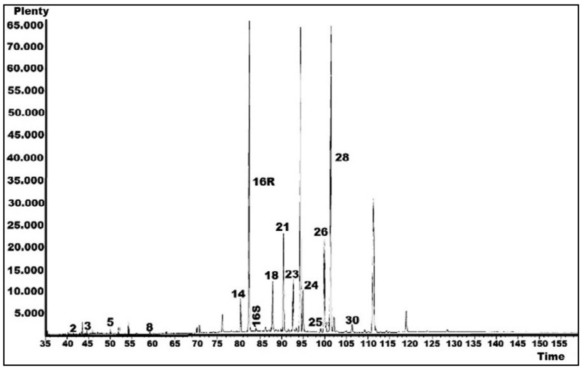

Figure 28- GC-MS m/z 191 chromatogram for HB-18 bituminous marl sample.

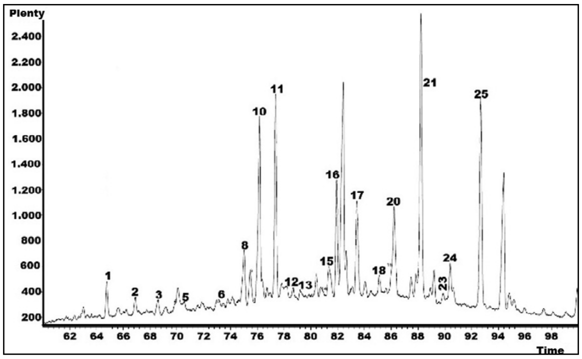

Figure 29- GC-MS m/z 217 chromatogram for HB-18 bituminous marl sample.

deposition in the region, while the environment was identified as anoxic as the (Ts/Tm) ratio was <1 for sample HB-12 (0.12) (Peters and Moldowan, 1993).

The abundance of C_{30} formethyl sterane on m/z 217 mass chromatogram for samples indicates lacustrine environment according to Koralay (2009). The high diasterane/sterane ratios (HB-7: 13.4; HB-12: 4.7; HB-18: 21.2) indicate the depositional environment included clastic sediments with high clay ratio containing organic matter with algal source (Mello et al., 1988; Peters and Moldowan, 1993). However, it can be seen that the samples fall in the terrestrial-marine transition zone on the pyramid diagram in Figure 23 showing C_{27}, C_{28} and C_{29} sterane abundances and depositional environment.

Due to samples investigated on m/z 191 and m/z 217 GC-MS chromatograms having sterane/hopane ratios ≥1 (HB-7: 1.0; HB-12: 2.69; HB-18: 2.23), samples were identified to have algal organic matter content (Peters and Moldowan, 1993). On the m/z 191 mass chromatogram, the reason for the high peak value for C_{23} tricyclic terpene is the lacustrine source of the depositional environment and it is understood that it came from a source rock in the carbonate lithology containing diagenetic products of cell membranes from single-celled organisms (Hunt, 1995).

4.6. Organic Facies Investigations

Organic facies analysis was completed to determine the organic matter content of bituminous marls and in order to be able to evaluate the depositional environment (Figures 30-32). However, as sample HB-20 contained oxidized and inertinitic organic matter, this sample was excluded from the assessment. Organic palynofacies analysis linked to organic matter type (Figure 30) shows;

- Terrestrial amorphous organic matter (AOM) was observed at similar values (40%) in all samples. Palynomorph groups generally reflected terrestrial bisaccate pollens and flowering plant pollens (angiosperm) assemblages.

- *Botryococcus braunii* freshwater algae (25%) was observed to be present in all samples, but highest in sample HB-19A.

- Semi-quantitative analysis generally did not identify marine palynomorph findings, with the presence of terrestrial organic matter and terrestrial palynomorphs along with freshwater algae reflecting a freshwater lacustrine environment.

When the maceral group composition and HC generation potential of these samples are assessed on pyramid diagrams, 80% of samples appear to fall in the oil-generating algal and amorphous kerogen field (Figure 32). The HI values for samples from the region were 290-769 mg HC/g TOC (mean 654.59 mg HC/g TOC), OI values were 24-96 mg HC/g TOC (mean 40.64 mg HC/g TOC) and TOC values varied from 1.06%-29.87% (mean 9.27%) (Tables 1-5).

All samples were dominantly observed to have terrestrial amorphous organic matter input. According to Ebukanson and Kinghorn (1985), large particles like vitrinite and inertinite deposit close to the coast, while fine-grained particles like spores, pollen and waxy organic matters deposit in deeper water environments. When samples are investigated from this aspect, terrestrial organic matter content comprising spores and pollen appears to comprise 25% of the total organic content (Figure 30). Linked to this, in addition to the HI, OI and TOC values, dominantly Type I with lower rates of Type II kerogen is observed in this facies and hence it was assessed that mostly oil with lower rates of gas may be observed according to maturity stage. However, as the source rock in the region is in the immature field, according to current depositional conditions of bituminous marls, conventional oil and gas generation was identified not to have occurred. Along with all this data, when figures 30-32 and table 5 are investigated, bituminous marls in the region were assessed to have deposited in the AB organic facies region. As this facies is included in the terrestrial-marine environment transition zone, it may be considered that the study area reflects a lacustrine environment with marine effects observed like occasional estuary-bay-tidal plane-lagoon settings.

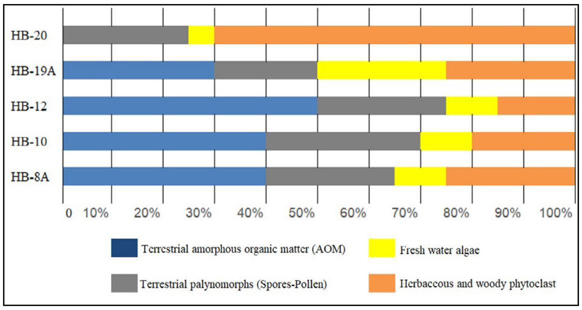

Figure 30- Organic facies analysis for 5 samples from bituminous marl in the region.

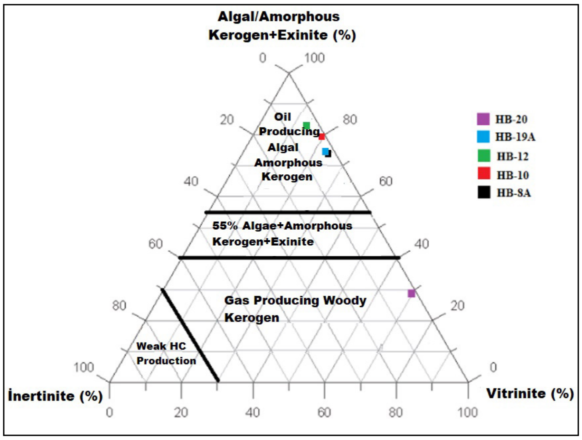

Figure 31- Schematic illustration of relationship between organic facies and precipitation environments (Altunsoy and Özçelik, 1993).

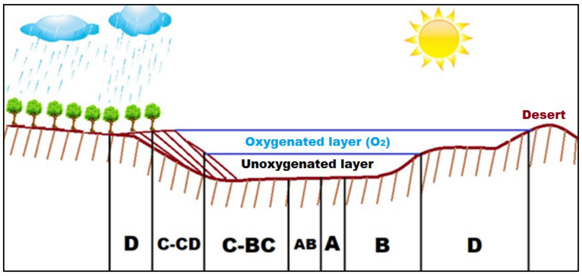

Figure 32- Pyramid diagram for maceral group composition and HC type potential (Stach, 1982).

Çelik (2003) stated that the lower lignite bed in the Seyitömer formation contained clay bands and that these clay bands formed in a freshwater lacustrine environment with relatively high water table during formation of fine clasts and peat. Şengüler (1999) interpreted the marls in Seyitömer Basin as having deposited in shallow and stagnant lacustrine environment due to the presence of abundant gastropods, lamellibranch, and ostracod fossils and fauna like coalified leaves and branches in the bituminous marls. Later studies by Şengüler (2007) proposed that the Seyitömer bituminous marls deposited in lake and lagoon environments connected with swamp environments. Again, Dikmen (2005) revealed the increase in Mg amount in the water mass in the lake environment reflected an alkali and saline environment and that the water mass in this region varied from freshwater to bitter-saline water and back to freshwater again in a study performed to determine the organic facies properties of the coal-bituminous marl transition around Aslanlı (Seyitömer/Kütahya).

5. Discussion and Conclusion

In this study, bituminous marls with mean 9.27% TOC in the Bozcahüyük (Seyitömer/Kütahya) Basin had perfect source rock properties, with dominant Type I and rare Type II kerogen type deposited in reducing anoxic redox conditions, and were understood to have lacustrine depositional environment due to containing terrestrial phytoclasts and palynomorphs along with freshwater algae like *Botryococcus braunii*. However, according to data from the investigated samples, the inclusion of the depositional environment in the "AB" terrestrial-marine organic facies transition zone, CPI data along with C_{27}, C_{28} and C_{29} sterane abundance distributions and presence of Gammacerane as saline environment indicator, the study area had lagoonal features and occasionally the lacustrine environment came under marine effect. Mean T_{max} value was 432°C and based on assessment of other pyrolysis, GC and GC-MS data, it was determined the bituminous marls in the region had not produced conventional oil due to still being immature. According to the results of hydrocarbon generation potential assessment, bituminous marls in the region appear to have perfect petroleumgeneration potential.

Contrary to oil content (2.4-5.9%) of bituminous marls in the Seyitömer Basin in previous years and studies about synthetic oil production from these marls, MFA analysis of samples taken from bituminous marls from near Bozcahüyük locale within the scope of this study had mean oil content of 12.6% (3.22-21.57%) in addition to mean value of 133 L/ton (30 L/ton-230 L/ton). In addition to these values, considering

Table 5- Organic facies distribution in the region (Jones and Demaison 1982; Jones 1984,1987).

ORGANIC FACIES	PYROLYSIS DATA			DOMINANT ORGANIC MATTER	KEROGEN TYPE	SEDIMENTARY STRUCTURE
	HI, mg HC/ g rock	OI, mg CO₂/ g rock	TOC, wt %			
A	> 850	10 - 30	5(3) - 20+	Algal; amorphous	Tip I	Laminated
AB	650 - 850	20 - 50	3-10+	Amorphous; very little terrestrial	Tip I / Tip II	
B	400 - 650	30 - 80		Amorphous, widespread terrestrial	Tip II / Tip I	Good bedding - Laminated
BC	250 - 400	40 - 80	3(1) - 3+	Mixed; sometimes oxidised	Tip II / Tip III	Weak bedding
C	125 - 250	50 - 150	≤ 3	Terrestrial; sometimes oxidised	Tip III / Tip II	Very weak bedding - bioturbated
CD	50 - 125	40 - 150+	< 0.5	Oxidised; transported	Tip III / Tip IV	Massive; bioturbated
D	< 50	20 - 200+		Highly oxidised; transported	Tip IV	

the presence of dominant Type I kerogen and high TOC, S_2 and HI pyrolysis data, the bituminous marls in the study area have synthetic petroleum production potential as they abide by the required criteria accepted internationally for economic and technological use of bituminous rocks according to Hufnagel (1989) of minimum petrol content limit 4% and thermal value of 750 kcal/kg.

For production of Seyitömer lignites, the bituminous marls overlying the lignite are removed during mining activities as stripping material and piled in tallow/spoil heaps. As a result, acquiring these marls for the economy by use in a retorting facility for synthetic oil production from these bituminous marls; use with low-quality lignite as solid fuel; production of some major, trace and rare earth elements and use in cement, fertilizer and other industrial areas from residual ash after processing or pyrolysis of bituminous marls will make the region more advantageous without additional mining costs.

To date, only 20% of the bituminous rocks distributed in lignite fields in our country have had source potential determined. For the rapid, effective and continuous assessment of this hydrocarbon potential as alternative energy resource, exploration activities like in the Göynük (Bolu) region should be popularized through the country in general and it is necessary to create pilot retorting facilities in regions suitable for synthetic oil production. Within this scope, it is important to implement incentives for the sector like tax exemptions, and guaranteeing use of synthetic oil produced from bituminous rocks in energy production.

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