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Source Rock Characterization for Hydrocarbon Generative Potential of Çilhoroz Coals, Eastern Anatolia Region, Turkey: Petrographic And Geochemical Approach

Nazan Yalçin Erik[1], Faruk Ay[2]*

[1] Sivas Cumhuriyet University, Depth. of Geological Engineering, Sivas-TÜRKİYE
[2] Sivas Cumhuriyet University, Depth. of Anthropology, Sivas-TÜRKİYE

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Abstract

This study reveals the hydrocarbon production potential and thermal maturity of Çilhoroz coals, which is the most important local coal field around Erzincan in the Eastern Anatolia Region. This area is one of the best examples of the continental collision zone in the world and is located in a north-south convergent collision zone between the Eurasian and Arabian Plates. The average thickness of the coal seam is about 4 m and these coals are currently mined by open pit mining methods. Coal is predominated by combined xylitic/attrital lithotypes and by huminite macerals with inertinite and minor liptinite macerals. The content of mineral matter is variable but generally low, it consists mostly of quartz, calcite, clay minerals, and pyrite. Although the Rock-Eval pyrolysis data show that the investigated coal bearing unit is represented by a significant hydrocarbon (oil and gas) potential, hydrocarbon species did not develop due to low maturation.

***Keywords**: Tertiary coal; Erzincan basin; Paleo-environment; Organic petrography; Hydrocarbon.*

1. Introduction

As the case all around the world, non-traditional energy sources are becoming more and more important for Turkey's increasing energy needs, and scientists, researchers and policy-makers focus on this issue. The vital importance of domestic energy supply for countries, especially in energy security issues, intensifies research for alternative and efficient use of resources with high reserves such as coal. Perhaps the most important one of these issues is the investigation of coal-based oil and gas generation potentials. After the discovery of coal-bearing sequences with source rock potential in China and the North Sea basin, many studies have focused on the gas and oil production potential of humic coals [1-7]. These studies indicate that humic coals generally have gas-producing potential and to a lesser extent oil and gas production potential [8]. In general, Paleozoic coals are considered the source rock for gas-prone hydrocarbon, while Cenozoic coals have the potential to produce liquid hydrocarbons [9]. Worldwide, oil-prone coals are mostly preserved in Eocene and Oligocene basins, such as those in China [10-12], Indonesia [13], Australia [14] and New Zealand [15-16].

A significant portion of Turkey's fossil fuel reserves are composed of Tertiary aged, low-calorie lignite and sub-bituminous coals (<2500 kcal/kg). These mentioned coals have a wide distribution area of about 230.000 km^2, especially in Western Anatolia (such as Soma, Tunçbilek, Yatağan, Seyitömer), and the thickness of the coal veins varies between 0.05-87 m [17]. As stated also by [18-20], Tertiary-aged basins in Turkey, influenced by Alpine orogeny, are Tethys remains, and they formed these coal formations, usually in intermountain lakes, when appropriate swamp conditions developed physically and chemically in the mountains [21]. As a result, during late Miocene and Pliocene, terrestrial conditions began to be dominant with an active regression process in late Miocene. These new paleoenvironment features had also created the beginning of many coal formation processes when combined with developing plant diversity and abundance thanks to a temperate-wet climate in the early Miocene [22].

Çilhoroz coal mine, which is examined in this study, is the only coalfield that meets the need for local coal in the Eastern Anatolian Region, and there are no detailed studies on the formation process and the economic properties of the coals It has been stated that the coals whose production activities continue in the Çilhoroz field are within the Miocene aged units [23], that coal thickness varies between 1.16 and 6.00 meters (av. 4 m), the coal seams seen in the outcrops can be monitored at a depth of 172 meters and that the visible + feasible + possible reserve total is 1.516.800 tons [23].

Identifying new areas of use, according to the developing technology and the requirements of the age, apart from the traditional usage areas of coal has been one of the most important research areas. In particular, the ability to produce hydrocarbons in the form of liquid and gas naturally or artificially from coals is at the forefront of these innovations. The transformation of conventional fuels into non-traditional sources requires a detailed study of coal properties. Therefore, it is of great importance to examine the hydrocarbon potential of Tertiary aged, low-quality coals similar to the coals examined in this study, with organic geochemical and organic petrographic evaluations. This study aimed to determine detailed organic geochemical, organic petrographic features and coal quality data of the coal-bearing unit samples, a geochemical characterization for source rock potential, as well as the paleo-depositional characteristics of Çilhoroz coal sequences in Neftlik Formation.

1.1. Regional geology and stratigraphic characteristics of the study area

The Erzincan Basin, in which the study area is located, is located in the suture zone of Pontids and Anatolites (Izmir-Ankara-Erzincan suture zone) [24], and it is a region whose tectonic activities have been active from past to present due to the influence of two important fault systems such as the North Anatolian fault zone (NAFZ) and the Eastern Anatolian fault zone (EAFZ) and therefore has geologically complex features (Figure 1a, b) [25].

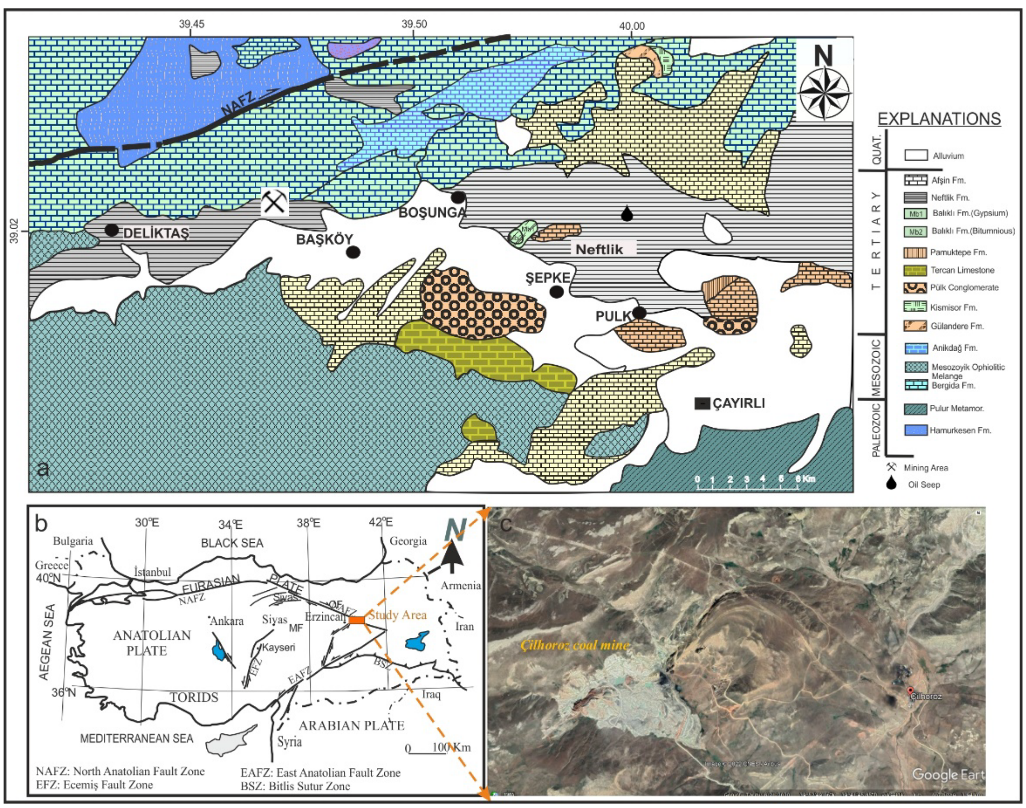

Figure 1. a) Geological map (modified from [41]), b) Outline tectonic sketch map of the main units in SE Turkey ([28]) and location map, c) Satellite view of the studied coal mine.

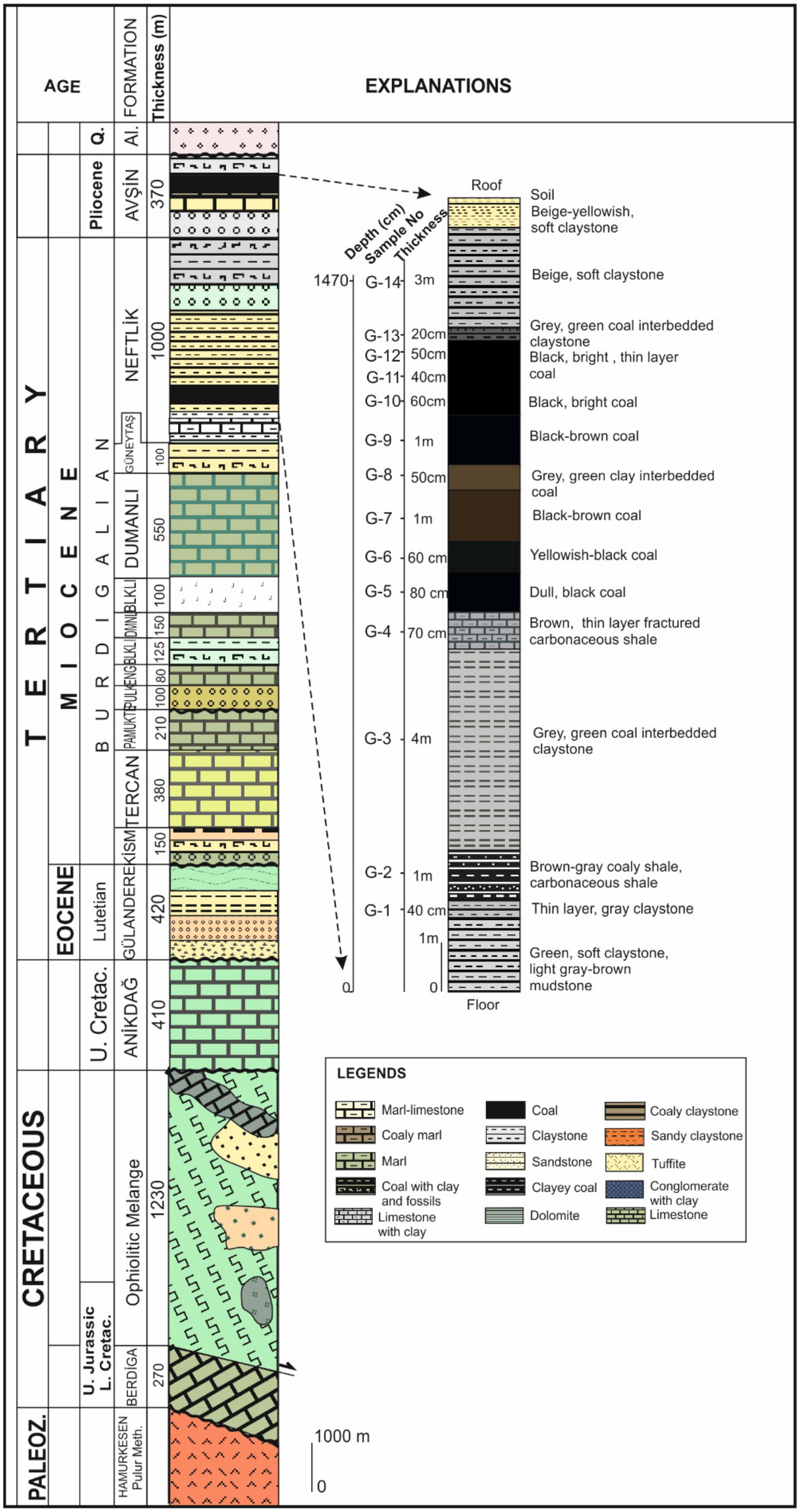

Figure 2. Generalized stratigraphic section of the study area (after [41]), detailed section of the coal seam of the coal-bearing unit and sampling/sample details

As it is now at the intersecting point of important fractures such as the North Anatolian Fault and the Ovacık Fault, these structural elements that have historically caused major earthquakes to continue to have tectonic activity and this area is a check-allocating basin that is approximately 50 km long and 10 km wide. The North Anatolian Fault zone passes through the Erzincan region, which also includes the study area, in the SE-NW direction. Because of the active tectonic features of the region, many comprehensive studies have been carried out, mainly on general geology and tectonism [25-43]. Palaeozoic aged metamorphic rocks (Pulur metamorphites and Hamurkesen Formation) form the basis of the study area. There is a complex and Upper Cretaceous-aged Anikdag Formation with Berdiga limestone, a tectonically settled and fairly thick mass of Cretaceous-aged ophiolite on the metamorphics in the Çayırlı district and its vicinity, where the coal formation is located. Tertiary clastic and carbonate sediments were deposited on these units unconformably [41] (Figure 1c and Figure 2a).

The Tertiary sequence begins with the Lower-Middle Eocene (Lutetian) Gülandere Formation with turbiditic flysch character [41]. Andesitic and basaltic lavas and olistostromal levels are also observed in the unit, which consists of alternations of sandstone, conglomerate, shale, tuff and agglomerate [36,41]. The Miocene aged Kismisor Formation, consisting of red and purple coloured clay, marl, sandstone and conglomerates, unconformably is present on this unit [31,41]. Burdigalian-Early Miocene aged Tercan limestone, consisting of light yellow, greyish white coloured, fossiliferous limestones, overlies the metamorphites and ophiolites with an angular unconformity in the south of Çayırlı [38,41,44]. It is overlapped by the Early Miocene (Burdigalian) Pamuktepe Formation limestones and the Pülk conglomerate of the same age [31]. The Pamuktepe limestone is composed of light grey, hard, well-coated, sandy limestone, sandy, and fossiliferous limestone at the bottom, and the Engice formation shows similar lithological properties to limestone. The Balıklı formation of the same age consists of clay, bitumen, classical component limestone levels and gypsum [31,41]. The lithology of the Dumanlı limestone, which is about 500 m thick, is limestones containing conglomerate and void fragments at the lower level. Clay, sandstone and marl layers overlie the relatively thin (100 m) Güneytaş Formation [41]. This unit is overlapped by the Pliocene aged Avşin Formation, which consists of an alternation of conglomerate, sandstone, claystone and sandy marl alternating with broad outcrops and Miocene aged Neftlik Formation with coal seams at the base levels, with well cemented conglomerate and coarse and medium-grained sandstone in the lower levels [31,38,45]; on the upper part, there are marl, coaly clay, coal and tuffs [30]. All these units are incompatible covered by the alluvium of Quaternary age (Figure 2a).

2. Material and analytical procedures

In the Cilhoroz coalfield, 1.5 meters of measured stratigraphic sections were made in the coal layer at the lower levels of Neftlik formation and 14 systematic samples were compiled (Fig.2b). Portions of the collected coals and organic-rich samples were ground and homogenized before further application. Chemical and elemental analysis of 7 coal and 3 carbonate shale samples were carried out in accordance with [47-48] (D 7582, D 3175, D 4239, D 5865) in the laboratories of the M.T.A. Department of Mine Analysis and Technology (MAT-Ankara). Coal quality data (total moisture, ash, volatile matter, fixed carbon, upper calorific value) were determined by IKA 4000 adiabatic calorimeter and elemental composition (C, H, O, N, S) was determined with LECO analyzer.

Coal samples for petrographic analysis were prepared and interpreted according to the [49-52]. The Petrographic evaluations are done with the Leitz MPV-SP reflective light microscope and 50X lens. The Leica DM2500 P and MSP200 windows-based programs were used for random huminite/vitrinite reflection measurements, and they were evaluated according to [52-53]. Special oils (refractive index (n) 1.518) and sapphire (R= 0.589%) and glass (R= 1.23%) standards were used in reflection measurements. In addition, fluorescence examination was performed in liptinite macerals with the Leica standard 621059. TIDAS CCD UV-NIR device was used in these measurements. The GI, TPI, WI, GWI, WI, TI parameters required for the depositional environment interpretation have been determined according to the formulas prepared by [54-55] and organized by [56] for Tertiary aged lignite.

In order to figure out the variation in the amount of organic matter content and practically examine general characteristics of organic matter within the coal and other organic matter rich sediments with Rock Eval pyrolysis analysis [57] a total of 5 samples were analyzed (Turkish Petroleum Corp., (TPAO) Research Center in Ankara). This analysis was obtained using a Rock Eval-6 (RE-6) instrument with IFP 160,000 (Institut Francais du Petrole) standards. Additional parameters calculated from the pyrolysis data are the hydrogen index (HI), oxygen index (OI), and production index (PI). Equivalent vitrinite reflectance (%Reqv) was calculated with formulas suggested by different researchers [2,58-59].

3. Results and discussions

3.1. Macroscopic features of coal

The coals in the study area are mainly located at the base level of the Miocene Neftlik Formation consisting of marl, sandstone, sandy marl, medium-thick vein thickness (1.5-4 m), clay, coaly clay, carbonate shale banded and laterally transitional to carbonates (Fig. 2b). In the coal layer, matte black coloured coal bands, grey-dark grey and brown coal levels and thinner shiny black coal bands are seen consecutively (Fig. 2b). The coals are characterized by prismatic fracture surfaces and some of their places show dispersive and matte properties due to mineralogical and petrographic properties. The dominant lithotype in coal is vitrene, claro-durene and durene, respectively. As mentioned by [60], one of the characteristic features of Tertiary aged coals in Turkey is the levels of gastropod cavae. Although plant parts and some gastropod cavities are observed at matte and dispersed levels in these coals, this feature is seen as scattered at the levels of coal-bearing claystones or grey claystones that do not form a uniform guide level as in the Kalburçayırı-Kangal (Sivas) and Hafik coals [61-62].

3.2. Microscopic constituents

The data obtained from organic petrographic studies are very important for the evaluation of the sedimentation and diagenesis processes of coal formation in sedimentary basins. The stages of change experienced since the deposition of organic matter can be interpreted together with paleo-geothermal history and paleo-chemical conditions can be explained [63-68]. Information about the coalification process, as well as the palaeo-depositional characteristics, and the maceral types, maceral associations, depositional rates, change processes, mineral ratios, physical and chemical properties of the peat formation environment can be obtained [69-70].

To evaluate the coalification process of the coals examined, the proportional distribution of maceral compositions was determined first as seen in Table 1 [71]. The dominant maceral group in these coals is vitrinite (hüminite) macerals and ranges from 36-47% (40.33% on average). In this group, the main telohuminite (tekstinite, ulminite), detrohuminites (artinite, densinite) and gelohuminite (gelinite, corpuminite and phlobaphinite) maserals were determined (Figure 3a, b, c). Ulminite and densinites are the most abundant components in vitrinite group (Table 1) (Figure 3b,c). The gelohuminite subgroup is relatively low in total huminite composition (6-16%), consisting of bridal, corpuminite and phlobaphinite maserals. The corpohuminites, which are found between 1-6% in the composition, are formed by the bacterial activity of woody parts and the change processes in environments with high water levels. The phlobaphinite ratio in the examined coals is quite low (1-6%).

There are 13-20% liptinite (av. 15.83%) and 33-42% inertinite group macerals (av.39.16%) in the coal composition. Sporinites are the dominant component (8-14%) in liptinites and can be observed more clearly in fluorescent light (Figure 3f, g). Suberinites are seen as a cell wall structure associated with corpohuminites and are dark in reflected light and light yellow in fluorescence light (Figure 3d, e). The resinite and cutinite maceral ratios are quite low (Fig.3f) in the examined samples and alginite maceral has not been determined (Table 1). Sporinite macerals range from 8-14% in the composition. Macrinites, which range from 14-21%, are defined as " gelatinous" components which formed as a result of oxidation and are the most abundant maceral in the inertinite group (Figure 3g) [69,72]. The second most abundant maceral, inertodetrinites, can also be expressed as "re-precipitated organic accumulation" (Figure 3). In addition, fusinite, semifuscinite and funginites are other macerals in the composition (Figure 3d,e,h). The maceral groups determined in the Çilhoroz lignite samples are plotted in triple diagrams (Fig. 4a, b, c). In the samples examined, the ratio of inorganic matter (clay, etc.) is not high (2-7%), and the components with the highest ratio are pyrites and clays, then carbonate (calcite), sulfated (gypsum) minerals (Table 1).

Table 1. Coal-petrography results of studied coal samples from the Çilhoroz coal mine (Çayırlı-Erzincan)

Maceral/ sample No	G-5	G-7	G-8	G-9	G-11	G-10
Whole Coal Composition (vol.%, on mineral – matter free basis)						
Textinite	2	1	4	3	2	2
Ulminite	15	14	12	10	16	11
Telohuminite	17	15	16	13	18	12
Attrinite	2	3	4	1	0	1
Densinite	14	16	11	12	14	10
Detrohuminite	16	19	15	13	14	11
Gelinite	4	3	4	7	7	5
Corpohuminite	2	1	2	3	4	6
Phlobaphinite	1	2	2	6	4	2
Gelohuminite	7	6	8	16	15	13
Total Huminite	38	40	39	42	47	36
Sporinite	10	11	12	8	13	14
Alginite	0	0	0	0	0	0
Resinite	1	1	3	2	1	2
Cutinite	1	1	3	2	1	2
Suberinite	2	1	2	3	2	1
Total Liptinite	14	13	20	14	15	19
Fusinite	2	0	2	2	0	1
Semi-fusinite	1	1	3	4	4	2
Inertodetrinite	14	15	12	12	8	19
Funginite	4	5	5	6	3	4
Micrinite	0	0	0	0	0	0
Macrinite	20	21	17	16	18	14
Total InertinitE	41	42	39	40	33	40
Mineral substance ratios in the whole coal composition (vol.%)						
Clay	3	1	-	1	1	1
Carbonaceous	2	1	-	1	1	0
Quartz	1	1	1	-	1	1
Pyrite	1	2	1	2	2	3
Total	7	5	2	4	5	5
Average Ro (%)	0.59	0.58	0.56	0.55	0.53	0.57
Paleo-Depositional Environment Parameters						
TPI	0.62	0.43	0.65	0.56	0.76	0.54
GI	0.78	0.74	0.62	0.73	1.17	0.74
GWI	1.56	1.49	1.40	2.36	1.58	2.48
VI	0.56	0.39	0.62	0.74	0.69	0.39
WI	0.59	0.63	0.57	0.9	0.72	0.71
TI	1.38	1.13	1.53	1.62	1.79	1.91
A, B, C	35,21,44	31,23,43	39,19,41	32,21,34	39,21,34	38,20,42
T, D, F	17,28,3	15,32,1	16,33,5	13,25,6	18,2,4	12,29,3

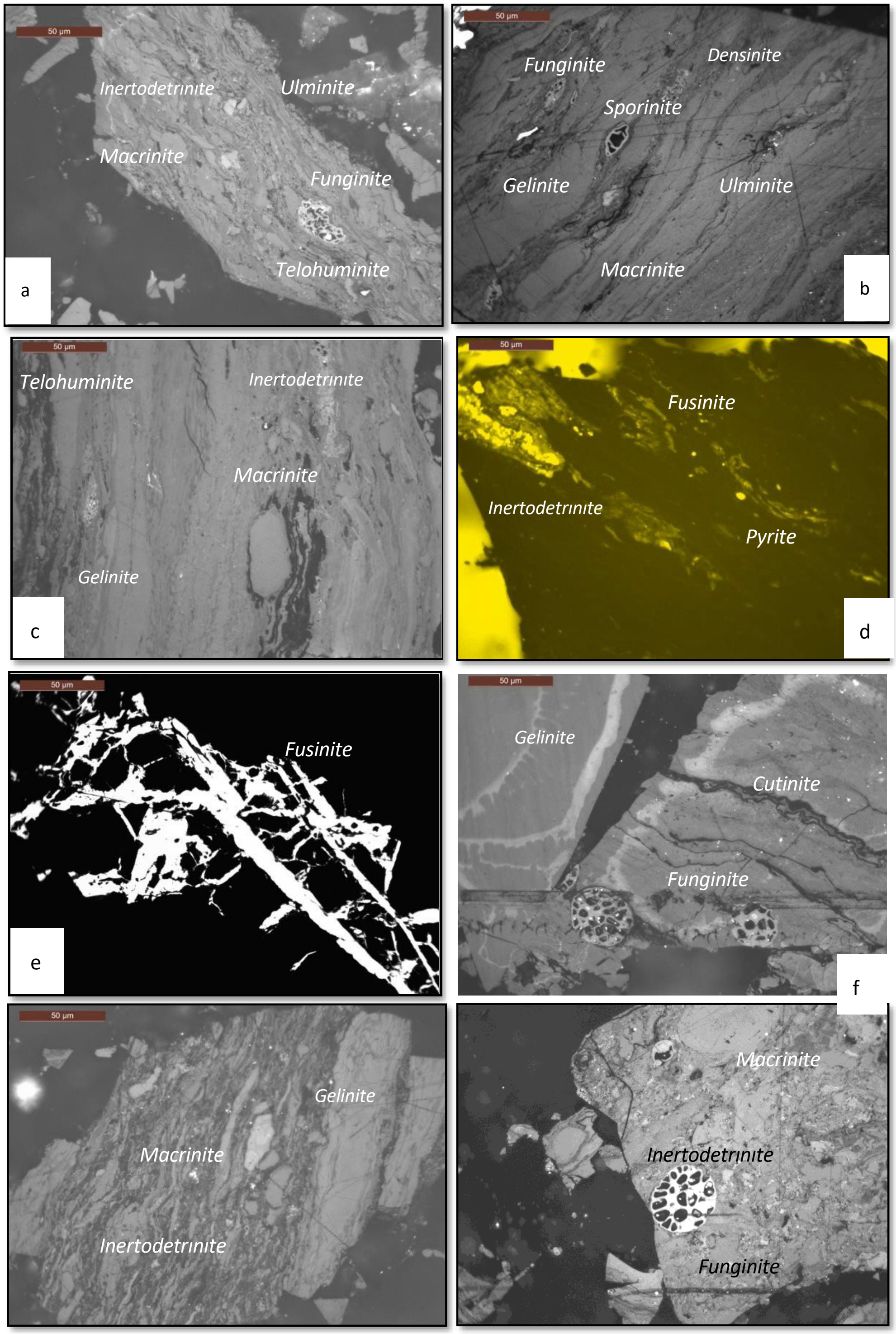

Figure 3. Photomicrograph of a) Ulminite, macrinite and funginite macerals observed in a sample rich in inertodetrinite maceral, b) the presence of gelinite, sporinite, densinite macerals, c) ulminite, gelinite, macrinite and telohuminite macerals, d) The appearance of fusinite, inertodetrinite and pyrite minerals, e) The view of photo 3d in UV light, f) Gelinite and cutinite macerals observed in a sample rich in funginite macerals, g) An example where inertodetrinite is the dominant maceral, h) Similar to figure 3a, the appearance of funginite and coarse macrinite macerals in a sample in which inertodetrinite is the dominant maceral.All photos were taken under oil immersion

3.3. Chemical characteristics

The results of chemical (proximate) and elemental (ultimate) analysis and gross calorific values of coal and carbonate shale samples of Çilhoroz coalfield are given in Table 2. The moisture values of the coal samples belonging to the study area vary between 8.35-12.67% (av. 10.38%, on dry-basis). In carbonate shale samples, the moisture value is lower than that of coals (on av. 8.4%, db). The ash content is between 6.9-22.38% (av. 17.01%, daf) in coals and quite high (>50%) in carbonated shale samples. Volatile matter (VM) ratio in coals varies between 36.45-46.77% (av. 40.40%, daf), fixed carbon (FC) values between 36.07-52.05% (av. 42.59%) and gross calorific values (GCVs) between 5649-9630 Kcal/kg (Table 2).

The carbon values of coal samples on a dry ash-free basis vary between 69.26-82.11% (av. 78.28%), hydrogen% values range between 2.98-4.23 (av. 3.95%), nitrogen% range between 1.16-1.44 (av. 1.47%), and oxygen% between 10.19-23.98 (av. 17.03%). The sulphur content of the examined coals is low. While the total sulphur values are between 1.17-2.08 % in coals (1.5 % on av.), it varies between 0.92 - 2.01 % (1.39% on av.) in shales with carbon (Table 2). The coal samples are characterized by low sulphur contents (average value for coal samples; 1.54%) and moderately low ash values (av. 17.01%) consisting of the highly surfaced coastal area [73].

Table 2. Proximate and ultimate analysis results of Çilhoroz (Çayırlı) coal and carbonaceous shale samples

Sample No	Total moisture (%)	Ash (%)	Volatile Matter (%)	Fixed carbon (%)	S (%)	C (%)	H (%)	N (%)	O (%)	H/C	O/C	N/C	Gross Calorific Value kcal/kg	MJ/kg
G-2	0.92	56.05	27.54	16.41	0.92	41.23	0.63	2.66	54.56	0.18	0.99	0.06	882	3.69
G-4	6.82	53.53	32.4	14.07	2.01	49.99	1.5	2.58	43.92	0.36	0.66	0.04	1128	4.72
G-5	10.16	19.32	38.5	42.18	1.42	69.26	3.98	1.36	23.98	0.69	0.26	0.02	6232	26.09
G-6	11.46	54.26	28.27	17.47	1.24	46.81	0.87	2.69	48.39	0.22	0.78	0.05	974	4.08
G-7	9.77	13.7	46.77	39.53	1.28	78.52	3.93	1.44	14.83	0.60	0.14	0.02	5701	23.87
G-8	11.26	22.1	36.45	41.45	1.38	80.37	2.98	1.46	13.81	0.44	0.13	0.02	5649	23.65
G-9	8.69	22.14	39.53	38.33	1.17	79.93	3.69	1.58	13.63	0.55	0.13	0.02	9630	40.32
G-10	8.35	22.38	41.55	36.07	1.47	76.41	3.42	1.53	17.17	0.54	0.17	0.02	9477	39.68
G-11	12.67	6.9	41.05	52.05	2.08	82.11	4.23	1.39	10.19	0.62	0.09	0.01	6664	27.90
G-12	11.16	12.53	38.97	48.5	1.98	81.37	4.01	1.16	11.48	0.59	0.11	0.01	6487	27.16

3.4. Coalification degree and coal type

The mean random huminite (vitrinite) reflection values measured in the coal samples examined are in the range of 0.53-0.59% (mean 0.56%) (Table 1). These values indicate that the samples examined are not yet mature and are in the diagenesis stage. H/C ratios calculated from elementel analysis results are 0.44-0.69 and O/C ratios are 0.11-0.26 (Table 3). According to UN-ECE and German DIN classifications based on the chemical properties and gross calorific values of coal, it is at the level of "Bituminous coal-lower bituminous coal", "Brown Coal" according to ISO (2005) classification, A.S.T.M. According to the (1991) classification, it is at the level of "A high volatile bituminous coal". The distribution of the samples examined in the Van Krevelen diagram [74], which is widely used in the classification of coals and in determining the kerogen types of rocks rich in organic matter, is seen in Figure 5, indicating the type of bituminous coal.

According to the petrographic composition characteristics, the predominance of huminite maceral group in the studied coals and the great amount of detrohuminite and telohuminites from these coals enable it to be defined as detrital lignites. Coals containing mainly textinite and ulminite (telohuminite subgroup) are generally defined as xylitic coals [75]. The textinite ratios in Çilhoroz coals are lower than in ulminites (Table 1). This property is associated with an increase in the degree of gelification in the swamp, as well as an increase in ulminites or herbaceous properties of primary organic matter [76]. However, since the gelification Index (GI) is not very high during the formation of these coals (0.62-1.17), it can be said that vegetable materials are mainly herbaceous or woody components with a low cellulose ratio. It would be more accurate to call Çilhoroz coals "xylitic coal containing detrital component" since their mineral substance ratios are lower than detrital coals (2-7%).

Table 3. Comparison of Tmax and vitrinite reflectance measurements determined and calculated in the samples

				Calculated vitrinite reflection values, (%)			
Sample No	Measured Ro (%)	Rock-Eval Tmax (°C)	Calculated Tmax, (°C) [2]	[58]	[100	[59]	[101]
G-2	-	432	-	0.62	0.7	0.58	0.61
G–4	0.54	426	426.45	0.51	0.9	0.49	0.52
G–7	0.58	426	426.45	0.51	0.9	0.49	0.52
G–9	0.55	430	427	0.58	0.83	0.55	0.58
G-11	0.53	426	426	0.51	0.9	0.49	0.52

Reference	**[2]**	**[58]**	**[100]**	**[59]**	**[101]**
Calculated Tmax, oC	51.96	-7,16	-13,5	-2,7914	-6,5143
Calculated Ro, %	398.39	0,0180	1/30	0,0085	0,0165

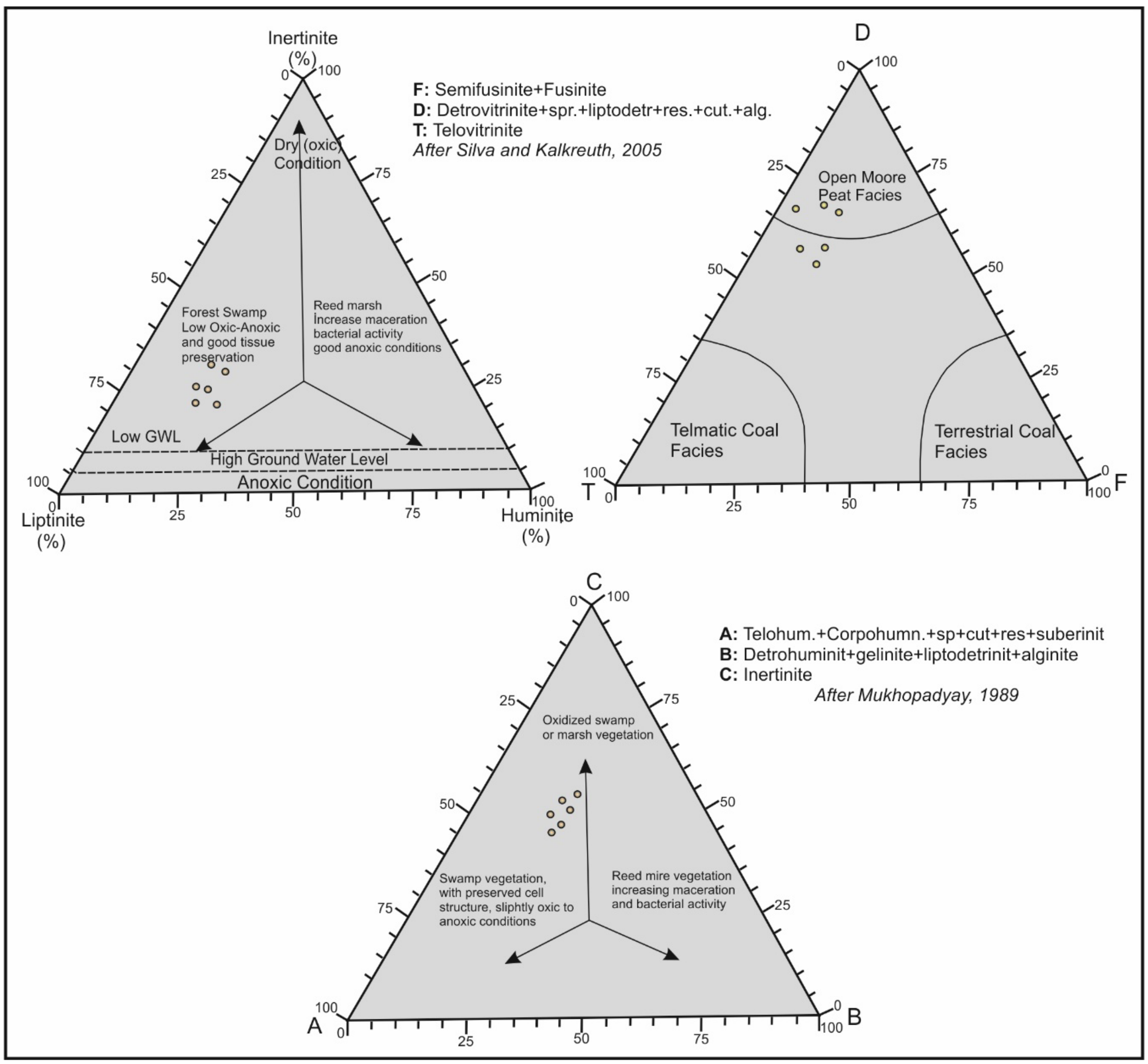

Figure 4. Organic matter type ternary diagrams of Çilhoroz lignite samples

3.5. Source rock characterization

Initial geochemical screening of potential hydrocarbon source rocks and potential unconventional petroleum reservoirs, in terms of the quantity, quality, and maturity of the organic matter is an important step in their characterization [7,77]. The Rock-Eval pyrolysis and TOC analysis technique is easy to use and widely applied for this purpose [57,78-79]. According to detailed studies carried out in many parts of the world, traditional oil window parameters are not valid for humic coals. In fact, the heterogeneous and unique characteristics of the coals required the consideration of different factors for each coalfield. Although it has the potential of producing hydrocarbon humic coals, in vitrinite/huminite (Type III Kerogen) of dominance, vitrinite/huminite heterogeneous chemical composition and the mineralogical composition of macerals, data analysis and pyrolysis, especially the rock-eval method have required careful interpretation [1,4]. For example, in pyrolysis analysis, it may cause some misinterpretations due to the matrix effect and the compositional properties of coal macerals. Therefore, care should be taken when applying traditional source rock evaluation parameters to coals [2,3,15,72,81-82]. In addition to organic geochemical evaluations, organic petrographic methods are also widely used, especially for the investigation of hydrocarbon generation potentials of sediments rich in terrestrial organic matter such as coal [83-84]. The liquefaction potential is highly influenced by nature and the amount of maceral present in coal [85]. For example, it is known that the liptinite and vitrinite maceral group has a higher hydrocarbon production potential than the inertinite group [74]. When evaluated in terms of oil and gas potential, vitrinites are prone to gas generation due to their compositional properties, exinites tend to oil and inertinites do not have oil and gas potential [69,74]. The high-volatile bituminous coals carrying vitrinite reflectance ranging from 0.49 to 1.02% and reactive macerals value >70% are most feasible for liquid hydrocarbon generation [86-87].

3.6 Organic matter amount

The abundance of organic matter in that source rocks is mainly represented by total organic carbon (TOC) content as weight percent, which is used to assess the amount of organic matter in the source rocks and their ability to generate petroleum upon thermal maturity [88-90]. In the coal seam sections in Çilhoroz lignites, all samples are rich in organic matter which reached 72.45 wt% (Table 4). The average TOC content of coal samples is 54.18wt% and 9.84wt.% carbonaceous shales.

Table 4. Rock-Eval analysis result of investigated samples

Sample No	TOC	S1	S2	S2/ S3	Tmax	HI	OI	PI	RC	PC	S1+S2	BI	QI	Lithology
G-2	6.35	0.38	38.27	31.12	432	603	19	0.01	3.05	3.3	38.66	5.98	3.87	Carbonaceous shale
G–4	13.32	0.59	58.08	23.7	426	436	18	0.01	8.24	5.08	58.67	4.43	5.87	Carbonaceous shale
G–7	47.86	0.52	71.6	6.2	426	150	24	0.01	40.78	7.08	72.12	1.09	7.21	Coal
G–9	58.17	0.94	67.87	5.6	430	117	21	0.01	51.27	6.9	68.81	1.62	6.88	Coal
G-11	56.52	1.06	69.63	5.1	426	123	24	0.01	49.25	7.27	76.69	1.88	7.67	Coal

*TOC: total organic carbon (wt.%); S1, mg HC/grock; S2, mg HC/g rock; T_{max}, °C);HI: hydrogen index = S2 × 100 / TOC; oxygen index = S3 CO_2 × 100 / TOC PI: production index = S1 / (S1 + S2) RC: residual carbon; PC: pyrolysable carbon Kerogen: percent portion of kerogen in the sample; S1+S2; Hydrocarbon generation potential Index, BI - Bitumen Index; BI=(S1/TOC)*100, QI – Quality Index; QI=(S1+S2)*100.*

Hydrogen index (HI) can be used as a reliable parameter for the determination of kerogen type present in the source rock [74] Limit values to be source rock potential were interpreted according to HI values defined by [89]. Accordingly, samples containing Type III vitrinitic kerogen with a hydrogen index of <200 mg HC/g TOC are expected to produce gas, while for values higher than 200 mg HC/g TOC with a hydrogen index, there may be oil generation potential, along with mainly gas and condensate [91]. Additionally, suggested that >300 mg HC/g TOC values are suitable for oil, 200-300 mg HC/g TOC values are suitable for gas and oil, and 50-200 mg HC/g TOC values are suitable for gaseous generation [92].

Hydrogen Index values in the coal samples evaluated in this study were determined in the range of 117-150mg HC/g TOC. S1 values for coal samples are extremely low ranging from 0.38 to 1.06 mg HC/g rock; with an average value is 0.49 mg HC/g rock; S2 values for coal samples varies between 38.27 to 71.6 mg HC/g rock, with an average value of 48.18 mg HC/g rock (Table 4). The S1 and S2 values of the carbonate shale samples are higher than the coals (0.84 and 69.70, respectively). While S2 values less than 4.0 mg HC\g rock are generally considered to be source rocks with poor generative potential; yields greater than 4.0 are common in known hydrocarbon source rocks [93]. Thus, S2 yields indicate that all samples are good and have very good source rock potential.

3.7. Organic matter type

The type of organic matter and the content of hydrocarbons were evaluated based on organic geochemical and optical data in the samples belonging to the investigated coal-bearing succession [89,94]. To determine the organic matter type of Çilhoroz coals HI vs. T_{max} kerogen classification diagram was used [95]. In this diagram, samples of Çilhoroz coals are plotted in Type II and Type III kerogen fields (Fig.6). Type III (terrigenous organic matter) and Type II kerogen also result from spores, pollen, and leaf and steam cuticles of land plants in the peat area. In the study area, the high abundance of vitrinite maceral and a significant amount of liptinite maceral indicate that they are gas prone with mixed hydrocarbon (oil/gas prone) signature.

It can be concluded that the petroleum inclination of the examined samples is mainly related to suberinite and related macerals such as resinite, cutinite, bituminite, sporinite and exudatinite. It has also been stated that suberinite and cutinite are associated with the formation of abundant waxy oils [96], while resinite and other liptinite macerals are also related to the formation of naphthenic oils [4]. The inertinite content shows that coal can only produce gas.

Some marine influences were determined in investigated samples and this characterized relatively high hydrogen index value. This organic compound known as Type II was developed from deterioration of terrestrial or humic organic material. The humic material formed from deterioration of wax, spore, pollen, cuticle, resin particulates, during peat formation.

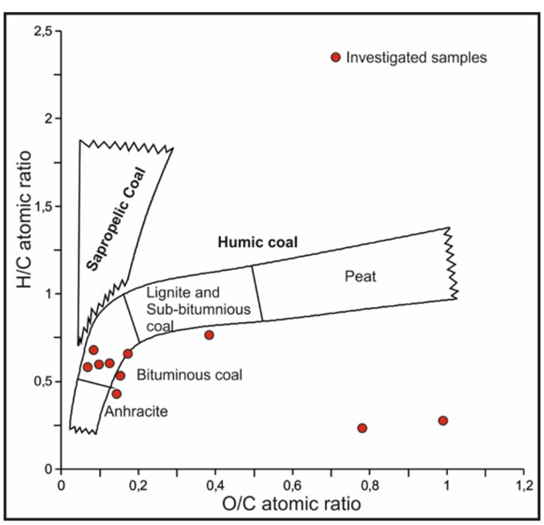

Figure 5. The appearance of the examined coals in the H/C vs O/C diagram and the type of coal

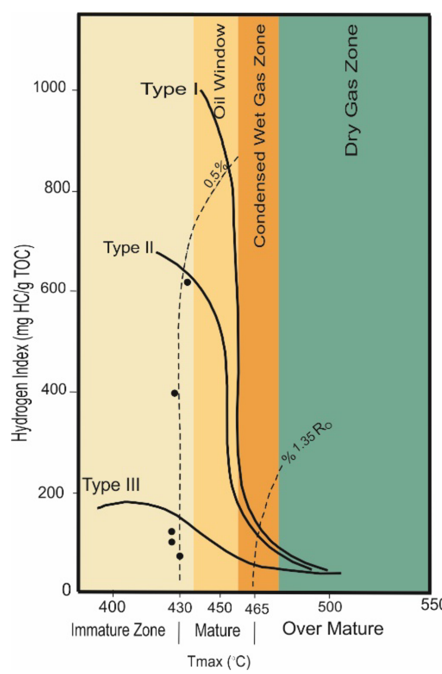

Figure 6. Cross plot of HI-Tmax for Çilhoroz samples (after [78])

3.8. Organic matter maturation

For the assessment of the generative potential of dispersed organic matter (coal), it is required to know their maturity [97]. Vitrinite reflectance is a good indicator of coal rank [71,98]. Based on reflectance value, the maturity has four stages starting from immature (less than 0.8 %Ro), early gas (0.8-1.2 %Ro), peak gas (1.2-2.0 %Ro), and late gas (more than 2.0 %Ro) [99]. The values of mean vitrinite reflectance vary from 0.53 to 0.59 %Ro, indicating an immature to early mature stage. In order to obtain data supporting the measured vitrinite reflections, vitrinite reflectance values were also calculated from the T_{max} value with the formulas suggested by various researchers [58-59, 100-101]; (Table 3). Among these formulas, especially [101] formulas were found to give the closest reflection value to the measured values. Also, T_{max} values very close to the Rock Eval pyrolysis analysis results were determined in the formula proposed by [2] to determine the T_{max} value from the vitrinite reflection value (Table 3). The T_{max} and PI are another reliable parameter for maturity [88] though unreliable when the hydrocarbon yield (S2) is below 0.2 mg HC/g rock. The values of T_{max} and PI varies from 426 to 432 °C with a mean of 428 °C and 0.0 to 0.1 with a mean of 0.1 (Table 3) indicating that the organic matter is immature to early mature in nature [88-89]. In addition, the plot of HI with T_{max} [95] and % Ro, also supports that these coals are thermally immature to early mature in nature (Fig. 6).

3.9. Hydrocarbon generation potential

Hydrocarbon generating potential is estimated by the measurement of total pyrolitic hydrocarbon yield (S1+S2). S1+S2 values are generally similar to TOC values. Genetic Potential values are range between 38.66 to 72.16 mg HC/g rock; with an average; 62.59 mg HC/g rock. Values of 5 samples among the studied samples have higher S2/S3 values than 2 mg HC/g rock, which implies such samples to indicate gas generation potentials [102]. Bitumen index (BI) and Quality index (QI) values were calculated for coal samples and vary from 1.09 to 5.98 mg HC/g TOC and from 3.87 to 7.87 mg HC/g TOC, respectively. The obtained BI and QI values show that the examined coal samples have very low gas production potential.

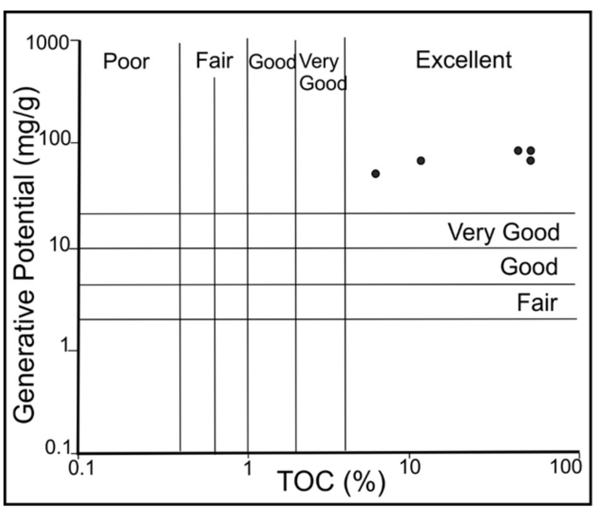

Figure 7. Petroleum generation potential (S1+S2) vs TOC (wt.%) classification after [89]

Overall petrographic and Rock-Eval analyses of the studied samples suggest a predominance of type III and III/II OM mainly derived from (bio) degraded marine organic matter. Some samples are scattered in poor petroleum zone in generative potential (S1+S2) vs TOC diagram. All examined samples are scattered in the area of excellent source rock potential (Fig. 7). According to organic maturation data (T_{max} and vitrinite reflectance), investigated coaly and organic-rich samples have sufficient organic matter and type but show early mature and diagenesis stages (Table 3).

3.10. Evaluation of coal facies and paleo-depositional environment

Organic facies analysis is an evaluation method in which paleoenvironmental characteristics are determined for marshes, and it is based on quantitative evaluation of the maceral association data that make up the composition of the coals with various diagrams [54-55, 103-106]. The pros and cons of existing indices and models are also widely discussed, especially in recent years, thanks to more detailed coal petrography studies and recent developments in organic petrology [56,108]. The main reasons for the failure of petrographic models are oversimplification and uniformity of the effects of humification on tissue preservation versus destruction, use of post-diagenetic processes (e.g., gelification) to determine depositional environments, changes in petrographic composition associated with the evolution of plants, ignoring geological age, degree of coalification and compaction effect can be classified as being ignored [54-56,69,71,75,103,108].

Coal facies analysis (maceral ratios and coal-facies diagrams) is applied to assess the palaeo-environmental conditions (hydrological and tectonic regimes, climate conditions, plant types, etc.) during accumulation [54-55,66]. The detailed maseral compositional properties of the Çilhoroz coal samples, when interpreted according to the triangular diagram created by [109] and [103], indicate that they were deposited in a limnic and partially limno-telmatic environment, under low anoxic and generally suboxic-oxic conditions (Fig. 4a,b,c). While the abundance of macrinite and inertinite macerals in the samples confirms this result, the movements for the basin during peatification and the disintegration of the organic agglomeration may have participated in the coalification process again. The fact that ulminite macerals are more abundant in composition than textinites (on av. 13%) can be explained by the increase in gelling under anoxic conditions; it may also reflect the primary characteristics of plants deposited in a marshy environment [110]. This is also supported by the low tide rates. In particular, gymnosperms are better preserved in coals formed from conifer forests than angiosperms, so more abundant telohuminite macerals are observed [111]. The reed peats and the brown coals formed from them contain weaker lignin texture and cellulose [70,110], which is observed in the petrographic composition as structureless macerals (Detrohuminite). As in the samples examined, the fact that densinites are more abundant than atrinites in the detrohuminite maceral subgroup can be explained by the biochemical changes of root parts or leaves of woody components under aerobic conditions during the peatification process, as well as by the transformation of atrinites into densinite during charring. In addition, atrinite and densinite macerals are defined as the main components reflecting the treeless swamp environment of peat and brown coal [51,70,112-113].

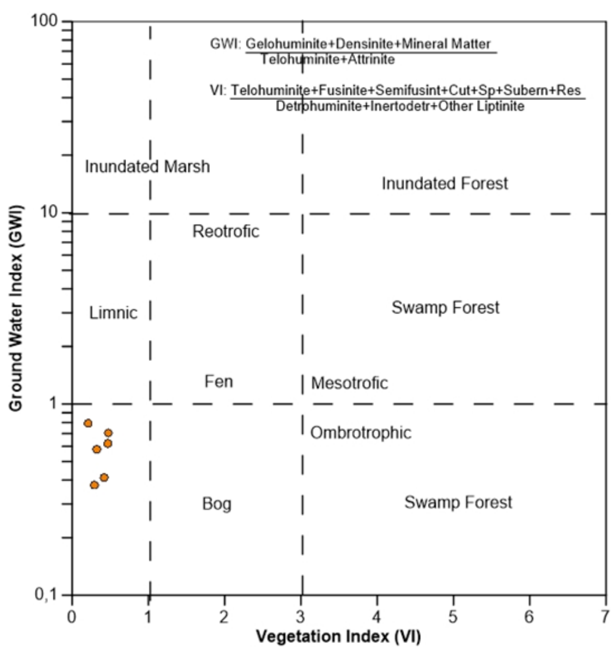

Figure 8. a) VI vs. GWI plot (After [54]; as modified [56])

As stated by [75] and [114], the presence of corpohuminite macerals, even at low rates, indicates that woody materials have participated in peatification [69,115]. For example, cutinite, suberinite, liptodetrinite, resinite, sporinite and flourinite are observed in the liptinites determined in the coals deposited in the forest swamp, and the same is true for Çilhoroz coals (Table 1 and Fig.8a,b) [108].
The examined coals were filled by herbaceous plants dominated by marsh in a paleo-depositional environment is a swamp mostly covered with freshwater (Figure 8, 9a, b). According to petrographic and mineralogical data, this environment is an open water forest swamp-reed swamp, and due to seasonal changes, the occasional change in water level, structural movements or mass movements that develop simultaneously with the collapse of the swamp, formed the dominant macerals in composition, especially humid, macrinite and densinite [62, 108,116].

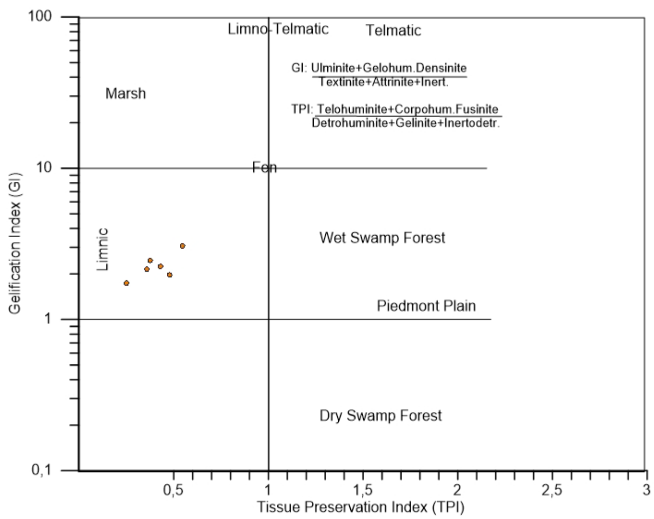

Figure 8. b) GI and TPI plot of the of the investigated samples of Çayırlı coal area (after [55]; as modified [56]).

The environmental characteristics here are transitive due to water intrusion/conservation and seasonal effects. According to the TDF triangle diagram prepared by [117], the examined coals seem closer to the "Limnic environment" characteristics (Figure 4a, b). In addition, the precipitation environment is an environment dominated by temperate climatic conditions with ombrogenic conditions that show a change in the water level due to atmospheric precipitation [117]. This indicates that the resulting maceral composition is also affected by degradation conditions in the marshes as indicated by the percentage of funginite maceral [118-119].

Coal formation usually occurred in conditions ranging from autochthon to hypo-autochthonous, where the suboxic-anoxic, alkaline environment, superficial flow effect is high compared to groundwater and with a slow burial rate [51,62,84]. Low oxygen index values, nitrogen content (av. 1.47%) and sulphur content in the composition of coal are low, indicating that the seawater effect is quite a few [120]. Tissue preservation index values and low ash content indicate grassy-reed environments and cellulosic organic composition, which is characteristic of the central parts of swamped (uplifted) peat and marshes fed by low-velocity precipitation atmospheric precipitation. Peatification and humification develop at a slow rate in such environments [69, 121-123].

In petrographic facies assessments, the petrographic composition of coal seams and petrographic facies indicators were used to observe the evolution of the peat formation environment. Tissue Preservation Index (TPI), Gelification Index (GI), Groundwater Influence Index (GWI), and Vegetation Index (VI) which were proposed by [54-55] and later modified by [56,103] and for low-rank coals are used as useful indicators for lignites. Calculated GI and GWI values of coals are mostly low (with ranges of 0.54–0.64 and 0.87–1.84, respectively), TPI and VI indexes are very low (with ranges of 0.43–0.58 and 0.7–0.85, respectively) (Table 1).

The Tissue Preservation Index (TPI) values of the Çilhoroz coalfield samples ranges from 0.43 to 0.76. In the samples examined, the gelification index (GI) values ranged from 0.62 to 1.17, the groundwater impact index (GWI) values range from 1.40 dec 2.48%, and the vegetation index (VI) values ranged from 0.39 dec 0.74% (Table 1, Figure 8).

Low tissue preservation index is either due to the type of vegetable material (more abundant angiosperm ratio than gymnosperms, high herbaceous material), low tissue protection conditions in the swamp (high bacterial activity, high pH, slow depositional rate) or slow-moving humification [84,112]. On the other hand, it is stated that tissue preservation depends on the water level and climatic conditions during peat deposition rather than the properties of the accumulated vegetative material [107]. However, some high TPI values (>0.60), especially in the studied samples, indicate that coals are affected by changes in the amount of water or flow regime during peat deposition, or transitional environmental conditions [12].

The GI index is related to the water level and the wet or dry state of the swamp, as well as its durability. A high gelification index usually indicates high water level, non-acidic environment, bacterial activities, and gelation, while a low GI value (<1) is related to low water content or woody property of plant material. The GI values of the samples examined indicate a short-term change in the water column during precipitation. In general, coals with low TPI (<1) and high GI are composed of forest marsh or marshes in reeds with dense treeless-herbaceous plants [12,84,123]. In addition, high detrohuminite ratios and low VI values also indicate plants in reedy areas of material deposited mainly in swamps [84,124]. Resinite, suberinite and cutinites determined at low rates also show that plants in the swamp have lower cellulose content [84].

The distribution of the examined samples in the TPI and GI diagram is shown in Figure 8a. According to this diagram, it can be said that paleomire was a marshy environment dominated by herbaceous plants. However, it is stated that coals formed in swamp and woodland swamps, which are considered a type of mineralotrophic swamp, generally have relatively high ash yields [121-123].This situation is not confirmed for the examined coals, it can be said that it is suitable for carbonate and coaly shale-clay levels. Coal facies indices (GI and GWI), as well as the framboidal pyrites (Table 1), indicate wet to dry, slightly anoxic conditions and relatively stable water levels during peat accumulation. This wet to dry environment could explain the relatively high detrohuminite content and low gelinite and gelohuminite (Table 1). Hence, changes on high intertinite content (33 to 42 vol.%) might be related to generally water-level changes. On the other hand, inertodetrinite is dominant and generally associated with detrohuminite macerals pointing to an allochthonous origin and water-borne transport of inertodetrinite [125].

It can be said that herbaceous plants (in reed areas) dominate especially in peatlands. The data that can support these ambient features is the Wetness Index (WI) and tissue index (TI), two new fascination rates recommended by [126]. According to these researchers, the preservation of the structural properties of their cellular tissues not only indicates woody plants but also covers the groundwater table, physics-chemical properties of the environment, oxidation-reduction conditions and the properties of the plant component. The TI values of the examined samples are in the range of 1.13-1.91 and the WI values are in the range of 0.57-0.90. High TI and low-medium WI values indicate an irregular water regime in paleomire. However, the characteristics of plant materials (herbaceous, reedy type plants) that came to the swamp and accumulated influenced this data more. Moreover, the low ratio of mineral substances with low WI and its homogeneity in the coal vein also indicate relatively stationary swamp conditions during deposition [54], therefore, the pH levels of the Çilhoroz coals show a homogeneous sequence characteristic with relatively few decoupages. The proportion of clayey, carbonated bands in the coal vein is quite low, which indicates that the water-energy does not change much during the formation of coals, conditions under which inorganic material can come from outside do not occur, and there is a uniform vegetative accumulation.

The VI-GWI diagram is also widely used for coal facies assessment (Figure 8b). The vegetation index (VI) and groundwater index (GWI) parameters developed by [54] for Westafalian coals of Nova Scotia express the characteristics in the coal formation environment [54]. In this diagram, the samples of Çilhoroz coal fall into the limnic environment area. Low VI values indicate the presence of herbaceous organic matter according to high telohuminites, high detrohuminites rates and low TPI values; low levels of textinite, semifusinite and fusinite components also indicate that a smaller proportion of woody components contribute to peatification. Non-acidic conditions during peat formation are also monitored by the discovery of well-preserved fossil assemblages with a calcium carbonate composition at the levels of coals and coal-bearing claystones, as well as carbonate clay coal [70,123]. Coaly clays with gastropod crumb observed at the lower levels of the coal vein in the study area are also another data that supports alkaline environmental conditions.

Low TPI and low ash content have been described similarly, especially in Tanjung Enim coals (Sumatran Baseni, Indonesia) and Maryville coals (New Zealand) [103,121]. Also, the Çilhoroz coals are similar in petrographic and chemical composition to the coals of the Mur-Mürz fault system (Eastern Alps, Austria), which has a pull-apart basin feature and contains Miocene-aged coals [127]. Though Çilhoroz coals are mineralogically and petrographically similar to Tertiary aged coals in Turkey in general [17,40,45-46,128-132], they offer a limnic coal feature that is formed from surface water sources in residual intermountain lakes in decimated basins without volcanic activity and unaffected by the sea.

4. Conclusion

The coals examined in this study are in the northeast of the Çayırlı district of Erzincan Province, near the village of Çilhoroz, and are the only coalfields within this region that meet the local fuel needs. The coals in the study area are mainly located at the base level of the Miocene Neftlik Formation consisting of marls, sandstone, sandy marls, medium-thick vein thickness (1.5-4 m), fine clay, coal clay, carbonate shale banded and laterally transitional to carbonates. In the coal vein, matte black coloured coal bands, gray-dark grey and brown coal levels and thinner shiny black coal bands are seen consecutively. Prismatic fracture surfaces are observed in the coals, and due to their mineralogical and petrographic properties, they show diffuse and matt properties at some levels. The dominant lithotype in coal is alternating vitrene, klaro-durene and durene. Although the dominant maceral group is huminite (av. 40.33%), there are also liptinite and inertinite macerals. The most important component of coals is 'macrinite' which is the most dominant type of inertinite maceral group. Sporinites in the liptinite group, ulminites and densinites in the huminite group, macrinite and inertodetrinites are the most abundant macerals in the inertinite group. In the HI - Tmax diagram, OM is predominantly determined as Type III kerogen and Type II-III mixture. This data is also supported by the low to moderate amount of liptinite maceral and dominant huminite composition determined as a result of petrographic examinations of the samples.

The coals examined are considered "low-medium quality coals" due to their medium-high calorie value (gross calorific value on a dry basis av. 6920.1 Kcal/kg), low-to-medium ash content (av. 14.43%), low mineral substance content (av. 3.33%) and low moisture (av. 10.4%) and low maturation rating (av. R_{max} 0.61%). They are at the level "Bitumen coal" according to elementary data, "Bitumen coal-sub-bitumen coal" according to UN-ECE and German DIN classifications, "Brown Coal" according to ISO classification, and "High-volatile A bitumen coal" according to the [48] classification. It has been defined as "xylitic coal containing detrital component" according to its petrographic composition properties. The ratio of inorganic matter in the samples examined is quite low, the highest ratio is pyrite and clays, followed by carbonate (calcite) and sulphated (gypsum) minerals. Herbaceous plants predominate in the paleo-depositional environment, and this environment is mostly a limnic marshland. According to petrographic and mineralogical data, it has been concluded that this environment is an open water forest swamp-reed swamp. The fact that coals are alternated with carbonaceous shale and clayey coals and contain limestone and claystone interlayers might indicate that the environment was deepened from time to time and changed to the lake and during the formation of the deposition of the sequence, lake and swamp conditions were repeated several times.

In the coal seam sections in Çilhoroz lignites, all samples are rich in organic matter which reached 72.45 wt%. The average TOC content of coal samples is 54.18wt% and 9.84wt.% carbonaceous shales. Coal, carbonaceous shale, and clayey coal samples are represented by moderate-high HI and very low OI values. Very high HI values imply that the samples contain a significant amount of pyrolysable organic matter. Potential yield (S1 + S2) values of the samples are very high which indicate noteworthy hydrocarbon generation potential. High HI and Potential Yield (PY) values and Type II kerogen character show that samples from the Çilhoroz coal-bearing units are represented by a significant hydrocarbon (oil and gas) potential. The immature-early mature character of the samples propounds that hydrocarbon generation of economic significance has not been taken place.

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To whom correspondence should be addressed: Nazan Yalçin Erik, Sivas Cumhuriyet University, Depth. of Geological Engineering, Sivas-TÜRKİYE; e-mail: nyalcin@cumhuriyet.edu.tr