

Article

Paleoenvironmental Reconstruction and Hydrocarbon Potential of the Westphalian-A Kozlu Formation Hard Coal in the Zonguldak Basin: Insights from Organic Geochemistry and Petrology

Neslihan Ünal-Kartal ¹ and Selin Karadirek ^{2,*}

¹ Department of Land Registry and Cadastre, Golhisar School of Applied Sciences, Burdur Mehmet Akif Ersoy University, 15400 Burdur, Türkiye; nunal@mehmetakif.edu.tr

² Department of Geological Engineering, Akdeniz University, 07070 Antalya, Türkiye

* Correspondence: selinhokerek@akdeniz.edu.tr

Abstract: The Zonguldak coal basin is the area with the most important hard coal reserves in Turkey. This study focuses on coal samples extracted from three seams of the Kozlu Formation, specifically from the Kozlu underground mine, to assess the coals' organic geochemical and petrographic properties. Analytical methods, including TOC-pyrolysis, biomarker analysis, and maceral distribution studies, were employed. Based on these analyses, the paleoenvironmental conditions and hydrocarbon generation potential of the coals were evaluated. The results reveal that the coals, characterized by high TOC, high HI, and low OI, contain type II–III kerogen. These findings, coupled with the high QI and low BI values, suggest the presence of oil–gas prone source rocks. Elevated Tmax (457–466 °C) and Rr (0.89%–1.17%) values indicate a maturity level ranging from mature to overmature stages. High GI and GWI values suggest a significant degree of gelification and wet conditions during formation. The high Pr/Ph (1–6.58), C₃₁R/C₃₀ hopane (<0.25), and low DBT/P (0.27–0.50) ratios show that the Acılık seam was formed in a lacustrine environment under anoxic–suboxic conditions, whereas the Büyük and Domuzcu seams were formed in a fluvial/deltaic environment under oxic conditions. The findings of this study suggest that the paleovegetation in coal-forming environments consisted of aquatic and herbaceous plants.

Keywords: biomarker; hydrocarbon potential; Kozlu coalfield; maceral components; paleoenvironment



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1. Introduction

Coal has an important role today and in the future in areas such as energy production, industrial fuel, the production of carbon-based materials, the conversion to alternative energy sources, and use as a raw material in various industrial processes. In this context, a detailed study of the petrographic, chemical, and physical properties of coal is critical to increase the efficiency of coal in these different fields and to determine the most appropriate utilization methods. The hydrocarbon generation potential of coal-bearing source rocks is well recognized today [1]. Moreover, when studying coal basins, it is crucial to assess both organic geochemical and organic petrographic properties together to determine the paleoenvironmental characteristics. On a global scale, coal-bearing source rocks of similar age and formation, such as those in the Tarim coal basin (Northwest China) [2], the Parana coal basin (Brazil) [3], the Tomago and Greta coals (Australia) [4], the South Karanpura coalfield (India) [5], and the Bohai Bay coal basin (Eastern China) [6], have been evaluated for their hydrocarbon (oil and gas) potential. Turkey's most significant bituminous coal deposits are located in the Zonguldak Basin, situated within the Istanbul Zone along the northwestern Black Sea coast between Ereğli (Zonguldak) and İnebolu (Kastamonu), spanning approximately 200 km along an east–west line. Coal mining in

this basin occurs in the Amasra, Kozlu, Karadon, Üzülmüş, and Armutçuk regions. The basin's total geological reserve of bituminous coal is estimated at 1.510 billion tons, with approximately 48% classified as visible reserves [7].

During the Late Devonian and Early Carboniferous periods, the Istanbul Zone was positioned on the southern edge of the Laurussian continent [8–10]. Carbonate sedimentation, which began in the Middle Devonian on the continental platform of the southern margin of Laurussia, was interrupted in the Middle Carboniferous due to the closure of the Paleotethys Ocean [11]. This led to a clastic succession as a result of basin uplift and associated sediment deposition [12]. The onset of terrestrial conditions during this period is represented by delta and pre-delta transitional environments. In the Westphalian, delta plains, floodplains, and braided and meandering river systems dominated the region, creating numerous coal seams under favorable environmental and climatic conditions. The presence of volcanic interlayers in the stratigraphy indicates the introduction of acidic volcanic material into the basin during this time. During the Late Westphalian-Stephanian period, the basin experienced uplift and erosion, a process that continued until the Jurassic (Early Malm) [13]. During this time, some areas underwent erosion, while others accumulated the eroded material [12]. In the Early Triassic, the Neotethys Ocean began to open [10], and a prolonged transgression occurred during the Early Malm [14–16]. This transgression fully covered the northern part of the Zonguldak Basin [14]. During the transgression, which lasted until the Early Cretaceous (Berriasian), shallow marine carbonates were deposited in the region [14–16]. However, this deposition was disrupted by block faulting, and sedimentation continued in a regressive manner [14]. After a brief erosion period from the Valanginian to the Hauterivian, a new transgressive phase began in the Late Barremian [16], submerging nearly all coal units in the basin below sea level [12]. The region experienced the formation of horst–graben systems due to increased extensional tectonics between the Aptian and Cenomanian, leading to the deposition of deep marine pelagic limestones during the Turonian [15]. A widespread igneous arc developed in the region during the Turonian-Campanian [16]. The Neotethys began to close in the Coniacian [17], and the region subsequently experienced compression-related tectonics. Transgression during the Maastrichtian continued until the Middle Eocene [16]. A new erosion phase began in the Middle Eocene and continues to this day.

In the Zonguldak Basin, coal-bearing levels are found in the Carboniferous-aged Alacağzı, Kozlu, and Karadon Formations. As seen from the geological evolution of the region, these coal-bearing layers have been affected by two major erosion and burial events, both critical for the coalification process in the basin. There are approximately 60 coal seams in the Zonguldak Basin [18]. Given its coal reserves and economic significance, the basin has been extensively studied by researchers across various fields, including sedimentology, stratigraphy, tectonics, palynology, petrography, and organic geochemistry. Notable studies have focused on regional geology, sedimentology, and stratigraphic evolution [9,12,14,19,20], coalbed methane potential [21–24], palynology [25–27], and petrography, mineralogy, and geochemistry [18,28–38]. In this study, the paleoenvironmental and paleoclimatic characteristics of three different Westphalian-A-aged coal seams (Acılık, Domuzcu, and Büyük seams) in the Zonguldak-Kozlu region were examined in detail by integrating organic geochemical and petrographic data to contribute to global studies.

2. Geological Setting

The basement of the study area consists of Silurian-Devonian-aged metasediments and Middle Devonian-Viséan-aged carbonates [16,18,24,39]. These units gradually transition into coal-bearing clastic sequences. The Carboniferous period in the Zonguldak Basin begins with the Alacağzı Formation (Figures 1 and 2). The Alacağzı Formation is composed of sandstone, siltstone, claystone, and thin coal seams deposited in a deltaic environment [19]. These coal seams, however, have limited lateral continuity and are not of significant economic importance. The Kozlu Formation, which is transitional between the lower Alacağzı Formation and the upper Karadon Formation [16], contains the most

economically significant coal seams in the region. This formation consists of conglomerate, sandstone, siltstone, claystone, and coal and has been dated to the Westphalian-A age [40]. According to Canca [41], the thickness of the Kozlu Formation reaches up to 925 m around Zonguldak. The Karadon Formation, composed of conglomerate, sandstone, siltstone, claystone, coal, and refractory clay layers [16], overlies the Kozlu Formation. Although the Westphalian-BC-aged Karadon Formation [40] presents a similar stratigraphy to the Kozlu Formation, it contains fewer coal seams. In the study area, the Karadon Formation is unconformably overlain by the Malm-Aptian-aged Zonguldak Formation [42]. The Zonguldak Formation is further overlain by thick sequences of marine, terrestrial, and volcanic interbedded sediments ranging from the Aptian to the Eocene [24,31,32,43]. Andesitic dykes have also been reported within both the cover unit and the Kozlu Formation [32].

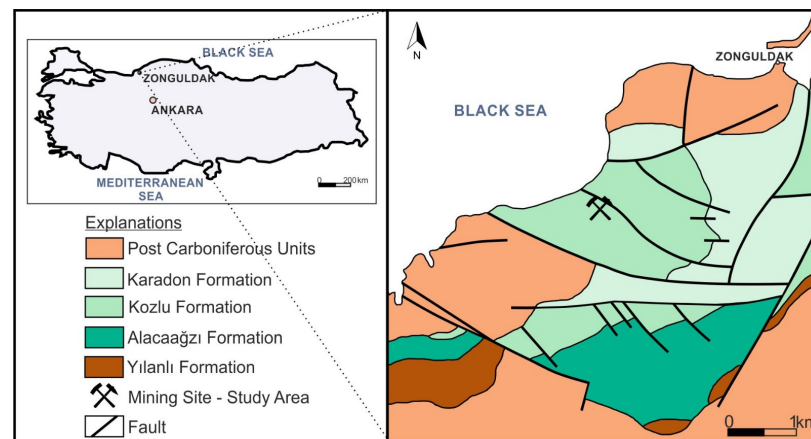


Figure 1. Geological and location maps of the investigated area (modified from [18,29,37,41]).

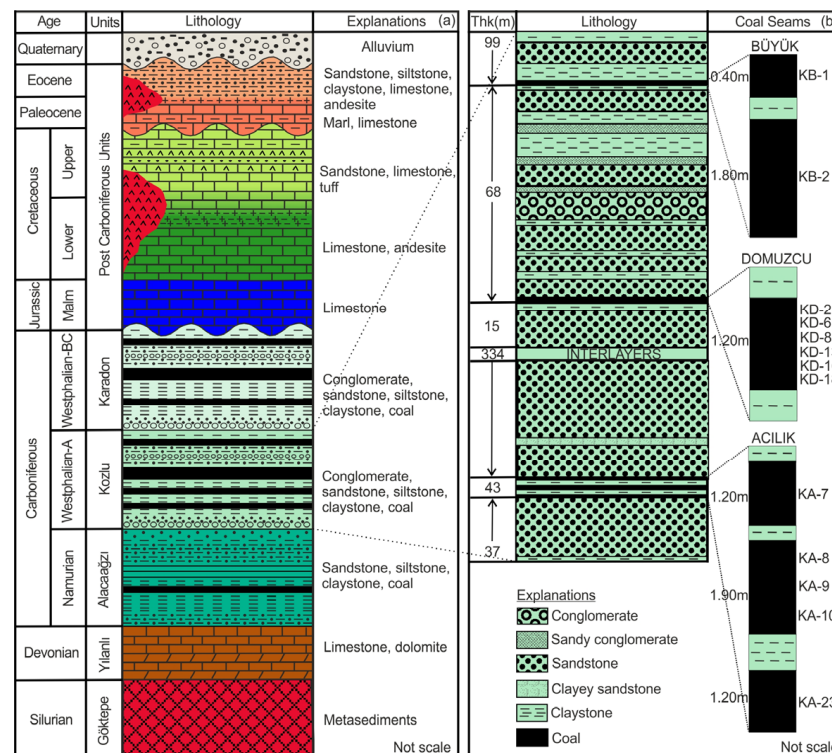


Figure 2. (a) Generalized stratigraphic section of the investigated area (modified from [18,22,41]). (b) The section of the Acılık, Domuzcu, and Büyük seams from the Kozlu Formation and location of samples (modified from [44]).

The coals of the Kozlu Formation exhibit an upper calorific value ranging from 34.5 to 35.4 MJ/kg on a dry ash-free basis. They have a volatile matter content of 28.6% to 32.4% (dry ash-free basis), total moisture content between 0.9% and 5.3% (as received), ash content ranging from 5.5% to 30% (dry basis), and total sulfur content of 0.3% to 0.6% (dry basis) [32]. The Kozlu Formation contains numerous coal seams, with thicknesses varying between 0.5 and 6 m [40]. In this study, samples from the Büyük, Domuzcu, and Acılık coal seams were analyzed (Figure 2).

3. Materials and Methods

Coal samples were collected from the Büyük, Domuzcu, and Acılık seams within the Westphalian-A-aged Kozlu Formation at the Kozlu active underground mine in the Zonguldak Basin using the channel sampling technique. The locations of the sampled seams are shown in Figure 2.

A total of 13 coal samples were subjected to TOC and pyrolysis analysis using a Rock-Eval VI device, following the IFP 160000 standard. During the analysis, various parameters were recorded, including the amount of free hydrocarbons (S_1), the hydrocarbons released from kerogen (S_2), the CO_2 produced via the thermal cracking of kerogen (S_3), and the temperature at which maximum hydrocarbon production occurs (T_{max}). Additionally, derived parameters such as the hydrogen index (HI), oxygen index (OI), production index (PI), potential yield (PY), bitumen index (BI), and quality index (QI) were calculated.

Biomarker distributions typically remain consistent within similar facies, provided that factors such as maturity, organic matter type, and depositional conditions do not vary significantly [45]. To further investigate this, gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) analyses were conducted on three coal samples from the Büyük, Domuzcu, and Acılık seams. These samples were selected based on TOC/pyrolysis analysis results and the thickness of the coal seams. The samples were extracted with dichloromethane (CH_2Cl_2) for 40 h using the ASE 300 system (Geochemistry Laboratories, Turkish Petroleum Corporation, Ankara, Türkiye). The entire extract was analyzed using an Agilent 6850 GC instrument, adhering to the Norwegian Petroleum Standard. Helium served as the carrier gas, while hydrogen and dry air were used for the flame ionization detector (FID). Asphaltene components were removed using column chromatography, while saturated hydrocarbons and aromatics were separated with an alumina–silica gel column. Elemental sulfur in the aromatics was eliminated with a copper column, and monoaromatics and triaromatics were isolated using an alumina column. GC-MS analyses of the saturated and aromatic fractions were conducted using an Agilent 5975C quadrupole mass spectrometer (Geochemistry Laboratories, Turkish Petroleum Corporation, Ankara, Türkiye) coupled with a 7890A gas chromatograph and a 7683B automatic liquid sampler (manufacturer, city, state abbreviation, country). Biomarker contents were identified through single-ion monitoring (SIM) at m/z 191 for terpanes, m/z 217 for steranes, m/z 253 for monoaromatics, m/z 231 for triaromatics, m/z 178–192 for phenanthrene and methyl phenanthrenes, and m/z 187–198 for dibenzothiophenes and methyl dibenzothiophenes.

Coal samples for petrographic analysis were prepared according to ISO 7404-2 [46]. Standard procedures from ISO 7404-3 [47] were followed for maceral analysis, and ISO 7404-5 [48] was used for vitrinite reflectance measurements. The maceral composition was determined using a Leitz MPV-SP microscope with a 50× oil-immersed reflected light objective. The identification and characterization of organic matter adhered to ICCP nomenclature, as updated by ICCP [49,50] and Pickel et al. [51]. Vitrinite reflectance measurements were conducted on a Leica DM 2500P using MSP200 software (Laboratory of the General Directorate of Mineral Research and Exploration, Ankara, Türkiye). For paleoenvironmental reconstruction, the diagrams proposed by Calder et al. [52] (GWI vs. VI) and Diessel [53] (TPI vs. GI) were applied.

Organic geochemical analyses, including TOC/pyrolysis, extraction, GC, and GC-MS, were conducted at the geochemistry laboratories of the Turkish Petroleum Corporation in

Ankara. Maceral determination and vitrinite reflectance were carried out laboratory of the General Directorate of Mineral Research and Exploration in Ankara.

4. Results

4.1. Rock-Eval Pyrolysis and TOC Analysis

The total organic carbon (TOC) results, Rock-Eval pyrolysis data, and various calculated parameters for the Westphalian-A-aged Kozlu Formation coal samples are presented in Table 1. The TOC content for samples from the Büyük and Domuzcu seams in the upper sections of the Kozlu Formation and the Acılık seam in its lower sections ranges from 44.92 to 52.95 wt% (avg: 49.40 wt%), 44.33 to 53.16 wt% (avg: 49.41 wt%), and 41.52 to 49.42 wt% (avg: 45.17 wt%), respectively. Across all coal samples, the mean TOC value was 48.07 wt%. Additionally, the average pyrolysis S_1 and S_2 values for the Büyük seam were 5.03 and 134.37 mg HC/g rock, for the Domuzcu seam were 4.48 and 134.21 mg HC/g rock, and for the Acılık seam were 3.93 and 122.36 mg HC/g rock, respectively (Table 1). The potential yield ($PY = S_1 + S_2$) values derived from the pyrolysis data were calculated as 139.41 mg HC/g rock for the Büyük seam, 138.69 mg HC/g rock for the Domuzcu seam, and 126.29 mg HC/g rock for the Acılık seam. Tmax values ranged between 458 and 460 °C for the Büyük seam, 457 and 460 °C for the Domuzcu seam, and 461 and 466 °C for the Acılık seam, indicating elevated levels for all three seams. The hydrogen index (HI) was relatively high, while the oxygen index (OI) was low across all coal samples (Table 1). The bitumen index (BI) for the coal samples from all three seams was low, whereas the quality index (QI) was high (Table 1). Production index (PI) values for the Westphalian-A-aged Büyük, Domuzcu, and Acılık seams were calculated as 0.04, 0.03, and 0.03, respectively (Table 1).

Table 1. TOC and Rock-Eval pyrolysis of coal samples from the Kozlu Formation in the Zonguldak-Kozlu basin.

Sample No	TOC (%)	S_1 (mg HC/g Rock)	S_2 (mg HC/g Rock)	S_3 (mg CO_2 /g Rock)	Tmax (°C)	HI	OI	PI	BI	QI	PY	S_2/S_3
KB-1	50.34	4.46	136.25	1.62	460	271	3	0.03	9	280	140.71	84.10
KB-1-1	52.95	5.83	137.19	0.71	459	259	1	0.04	11	270	143.02	193.23
KB-2	44.92	4.81	129.68	1.39	458	289	3	0.04	11	299	134.49	93.29
KD-2	53.15	7.7	143.05	1.05	460	269	2	0.05	14	284	150.75	136.24
KD-6	53.16	5.47	131.52	1.85	457	247	3	0.04	10	258	136.99	71.09
KD-8	51.33	5.42	138.67	0.52	458	270	1	0.04	11	281	144.09	266.67
KD-16	48.83	2.29	130.56	0.75	462	267	2	0.02	5	272	132.85	174.08
KD-18	44.33	4.75	136.09	1.13	457	307	3	0.03	11	318	140.84	120.43
KA-7	41.94	3.04	130.97	1.25	461	312	3	0.02	7	320	134.01	104.78
KA-8	46.79	3.51	124.85	1.19	465	267	3	0.03	8	274	128.36	104.92
KA-9	46.20	6.2	118.89	1.09	462	257	2	0.05	13	271	125.09	109.07
KA-10	49.42	3.55	114.05	1.26	466	231	3	0.03	7	238	117.6	90.52
KA-23	41.52	3.36	123.02	1.25	463	296	3	0.03	8	304	126.38	98.42
Mean	48.07	4.65	130.37	1.16	461	273	3	0.03	10	281	135.01	126.68
KB_mean	49.40	5.03	134.37	1.24	459	273	2	0.04	10	282	139.41	123.54
KD_mean	49.41	4.48	134.21	1.06	459	273	2	0.03	9	281	138.69	158.07
KA_mean	45.17	3.93	122.36	1.21	464	273	3	0.03	9	280	126.29	101.54

TOC = total organic carbon; S_1 = free hydrocarbons; S_2 = amount of hydrocarbons; S_3 = released carbon dioxide; Tmax = temperature maximum; HI = $(S_2/TOC) \times 100$; OI = $(S_3/TOC) \times 100$; PI = $S_1/(S_1 + S_2)$; BI = $S_1/TOC \times 100$; QI = $(S_1 + S_2)/TOC \times 100$; PY = $S_1 + S_2$; S_2/S_3 = hydrogen richness.

4.2. Biomarker Composition of the Coal Extracts

In this study, the distribution of biomarkers—including n-alkanes, isoprenoids, terpenes, and steranes in the aliphatic hydrocarbon fractions, as well as phenanthrenes, dibenzothiophenes, and triaromatic and monoaromatic steroids in the aromatic hydrocar-

bon fractions—was analyzed in Zonguldak-Kozlu coal samples using GC chromatography and GC-MS mass fragmentograms.

4.2.1. Extract Composition

Table 2 presents the extractable organic matter (EOM) yields from samples taken from the Kozlu underground mine, along with the contents of saturated and aromatic hydrocarbons, hetero-compounds (NSO), and asphaltenes. The EOM yields were notably high in samples from the Büyük (19,662 ppm, 23.78%), Domuzcu (21,770 ppm, 26.33%), and Acılık (41,263 ppm, 49.90%) seams. The relative contents of saturated hydrocarbons and hetero-compounds were low (3.36%–7.08% and 5.69%–7.48%, respectively; Table 2), whereas the contents of asphaltenes (57.44%–71.58%) and aromatics (19.37%–28.00%) were elevated. The extracts contained a higher abundance of aromatic hydrocarbons compared to saturated hydrocarbons. The variation in saturated hydrocarbon content reflects the origin of the plant material and the extent of biodegradation [54,55]. The relative proportions of hydrocarbons (35.08%, 28.31%, and 22.73%) were relatively high, while the ratio of saturated to aromatic hydrocarbons (Sat/Aro < 0.25) was low. NSO compounds were present in low quantities in the EOM, with asphaltenes constituting the majority of the EOM.

Table 2. Extractable organic matter (EOM) and relative proportion of saturated and aromatic hydrocarbons, hetero-compounds, and asphaltenes of EOM.

Seam/Samples	Büyük Seam KB-2	Domuzcu Seam KD-6	Acılık Seam KA-8
EOM (ppm)	19,662	21,770	41,263
Saturated hydrocarbons (%)	7.08	5.50	3.36
Aromatic hydrocarbons (%)	28.00	22.81	19.37
Hetero-compounds (NSO) (%)	7.48	7.39	5.69
Asphaltenes (%)	57.44	64.30	71.58
Saturated/Aromatic Hydrocarbons (%)	0.25	0.24	0.17
	35.08	28.31	22.73

EOM = extractable organic matter; NSO = nitrogen, sulfur, oxygen components; Hydrocarbons = (saturated + aromatic).

4.2.2. Normal Alkanes and Acyclic Isoprenoids

The n-alkane distribution in the analyzed coal samples predominantly ranges between n-C₉ and n-C₃₄ (Figure 3). Generally, two distinct patterns of n-alkane distribution were observed. In the Büyük and Domuzcu seam samples, the distribution is unimodal with a peak at n-C₁₄, whereas in the Acılık seam sample, the distribution is bimodal with peaks at both n-C₁₄ and n-C₂₀. In the Büyük and Domuzcu seam coal samples, short-chain n-alkanes (<n-C₂₀) are more prevalent than medium and long-chain alkanes (n-C₂₃–n-C₃₅). In the Acılık seam coal sample, the proportions of short- and medium-chain n-alkanes were relatively similar, while long-chain n-alkanes were less abundant (Table 3).

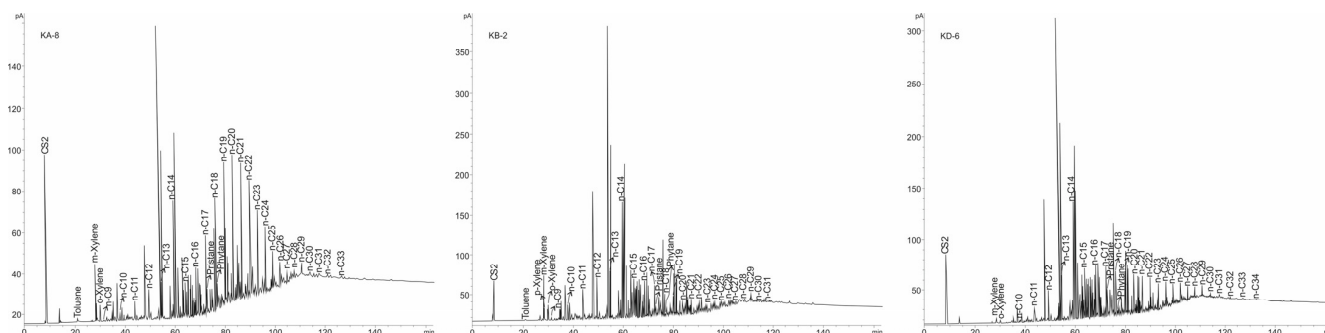


Figure 3. n-Alkane and isoprenoid distribution of selected coal samples.

Table 3. Biomarker ratios based on n-alkanes and isoprenoids for selected coal samples.

n-Alkanes and Isoprenoids	KA-8	KB-2	KD-6
Short-chain n-alkanes (<n-C ₂₀)	47.42	76.10	60.32
Middle-chain n-alkanes (n-C _{20–25})	41.15	14.28	23.10
Long-chain n-alkanes (n-C _{25–35})	11.43	9.62	16.57
Pr/Ph	1.00	6.58	4.77
Pr/nC ₁₇	0.39	0.42	0.71
Ph/nC ₁₈	0.35	0.09	0.17
CPI (24–34) [56]	1.16	1.44	1.00
OEP [57]	2.20	4.21	1.52
TAR [58]	0.20	0.30	0.30
Waxiness index	0.99	0.62	0.85
Paq [59]	0.80	0.47	0.67
Pwax [59]	0.27	0.59	0.45
ACL [60]	33.78	19.63	33.29

Pr = pristane; Ph = phytane; CPI = carbon preference index = $\frac{1}{2} [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34})]$; OEP = odd-to-even predominance = $(n-C_{21} + 6n-C_{23} + n-C_{25}) / (4n-C_{22} + 4n-C_{24})$; TAR = $(n-C_{27} + n-C_{29} + n-C_{31}) / (n-C_{15} + n-C_{17} + n-C_{19})$; Waxiness index = $[\Sigma (n-C_{21} - n-C_{31})] / [\Sigma (n-C_{15} - n-C_{20})]$; Paq = $(C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31})$; Pwax = $(C_{27} + C_{29} + C_{31}) / (C_{23} + C_{25} + C_{27} + C_{29} + C_{31})$; ACL = $(27 \times C_{27} + 29 \times C_{29} + 31 \times C_{31} + 33 \times C_{33}) / (C_{27} + C_{29} + C_{31} + C_{33})$.

The odd-to-even carbon number n-alkane ratio (OEP), indicating the preference for odd-numbered carbon chains along with the carbon preference index (CPI), were determined to be 4.21 and 1.44 for the Büyük seam, 1.52 and 1.00 for the Domuzcu seam, and 2.20 and 1.16 for the Acılık seam, respectively (Table 3). The waxiness index exhibited low values across all three seams. The terrigenous/aquatic ratio (TAR) values were 0.20 for the Acılık seam and 0.30 for both the Büyük and Domuzcu seams.

The pristane to phytane ratio (Pr/Ph) is greater than 1.00 in the Büyük and Domuzcu coal samples, while in the Acılık coal sample, the Pr/Ph ratio was determined to be exactly 1.00 (Table 3). The Pr/n-C₁₇ and Ph/n-C₁₈ ratios were also calculated (Table 3). All analyzed coal samples exhibit a relatively high concentration of n-C₁₇ compared to pristane, resulting in Pr/n-C₁₇ ratios of 0.42, 0.71, and 0.39 for the Büyük, Domuzcu, and Acılık coal samples, respectively. Similarly, the coal samples show a higher concentration of n-C₁₈ compared to phytane, with Ph/n-C₁₈ ratios ranging from 0.09 to 0.35.

4.2.3. Steroids and Terpenoids

Tricyclic terpanes are more abundant than hopanes in the analyzed coal extracts (Figure 4). The presence of C₁₉ and C₂₀ tricyclic terpanes in the Büyük seam suggests a contribution from vascular plants, while the dominance of C₂₃ tricyclic terpanes indicates a significant input from algae and bacteria in the organic matter [55,61]. In the Acılık seam coal extract, C₃₀-diahopane (C₃₀*) and C₃₀ hopane are the most abundant hopanes. In the Domuzcu seam, C₃₀ hopane is the predominant component, followed by C₂₉ norhopane, 17 α (H)-trisnorhopane (Tm), and C₃₀*. In the Büyük seam, the most abundant components are C₃₀ hopane, C₃₀*, C₂₄ tetracyclic terpanes, and C₂₃ tricyclic terpanes (Figure 4).

The coal samples exhibit a lower abundance of C₂₉ norhopane compared to C₃₀ hopane. The low C₂₉/C₃₀ hopane ratio, which is less than 1, indicates clay-rich clastic facies. Hopanes (C₃₁–C₃₅) display a regularly decreasing distribution pattern in the order C₃₁ > C₃₂ > C₃₃ > C₃₄ > C₃₅. The C₃₀ hopane is also more abundant than the C₃₁R homohopane (Figure 4), resulting in a relatively low C₃₁R/C₃₀ ratio (Table 4). The C₃₀*/C₂₉ Ts ratios were high in samples from the Acılık (3.46), Domuzcu (2.75), and Büyük (3.17) seams. Additionally, gammacerane, which is typically indicative of salinity in the depositional environment [62], was extremely low (<0.04) in all coal extracts (Table 4). The Ts/(Ts + Tm) ratio exhibited high values (0.36–0.55) in the analyzed coals. Furthermore, various biomarker maturity ratios of hopanes in the *m/z* 191 mass fragmentogram were calculated, including the 22 S/(22 S + 22 R) (C₃₂) homohopane ratio, moretane/hopane ratio, and C₂₉Ts/C₂₉Ts + C₂₉H ratio, as shown in Table 4.

Table 4. Cont.

Steranes	KA-8	KB-2	KD-6
Diasterane/sterane	77.45	144.51	65.33
C ₂₇ sterane (%)	26.91	24.10	11.11
C ₂₈ sterane (%)	30.04	27.56	38.11
C ₂₉ sterane (%)	43.05	48.34	50.78
Iso-sterane (%)	53.2	48.03	56.34
n-Sterane (%)	40.21	30.35	31.30
Dia-sterane (%)	26.48	26.9	18.78
20 S/(20 S + 20 R) (C ₂₉)	0.51	0.52	0.51
$\beta\beta/(\beta\beta + \alpha\alpha)$	0.52	0.55	0.54
Sterane/hopane	2.34	2.33	2.71

The m/z 217 mass fragmentograms of saturated hydrocarbons in the coal samples reveal significant amounts of steranes (Figure 4). Among the C₂₇–C₂₉ regular sterane distributions, C₂₉ sterane was the most abundant, with the overall order being C₂₉ > C₂₈ > C₂₇ in all samples (Table 4). The 20 S/(20 S + 20 R) sterane ratio for C₂₉ was calculated as 0.51, 0.52, and 0.51, while the $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratio was calculated as 0.52, 0.55, and 0.54 in the Acılık, Domuzcu, and Büyük seam coals, respectively (Table 4).

4.2.4. Aromatics and Polar Compounds

The distribution of C₂₉, C₂₈, and C₂₇ monoaromatic (MA) steroids in the analyzed coal samples varies in dominance across the Acılık, Büyük, and Domuzcu seams, although their overall abundance is relatively similar (Table 5). The high concentration of different MA steroids in the coals suggests the contribution of mixed organic material (Figure 5). The MA(I)/MA(I + II) ratio was calculated as 0.48 for the Acılık seam, 0.62 for the Domuzcu seam, and 0.76 for the Büyük seam.

Table 5. Parameters derived from aromatic biomarker distributions (m/z 231, 253, 178, 192, 187, and 198 mass chromatograms) for the selected coal samples.

Steroids	KA-8	KB-2	KD-6
TA(I)/TA(I + II)	1	1	1
C ₂₈ -TA/(C ₂₉ MA + C ₂₈ -TA)	0	0	0.01
MA(I)/MA(I + II)	0.48	0.76	0.62
C ₂₇ MA steroid (%)	33.94	41.56	26.85
C ₂₈ MA steroid (%)	34.81	31.69	35.13
C ₂₉ MA steroid (%)	31.25	26.76	38.03
Dia/(Dia + R) MA	0.69	0.85	0.50
C ₂₉ /(C ₂₈ + C ₂₉) MA	0.5	0.5	0.5
Phenanthrene	KA-8	KB-2	KD-6
MPR	1.83	1.55	1.40
MPR1	0.84	0.90	1.38
MPR2	1.53	1.39	1.92
MPR3	0.55	0.82	1.09
MPR9	0.60	1.03	1.59
1-MP/9-MP	1.18	0.87	0.91
MPI-1	1.28	1.14	1.14
MPI-2	1.89	1.43	1.45
MPI-1*	1.45	1.15	1.02
Dibenzothiophene	KA-8	KB-2	KD-6
MDR	18.77	9.90	5.04
MDR'	0.95	0.91	0.83
DBT/P	0.50	0.30	0.27

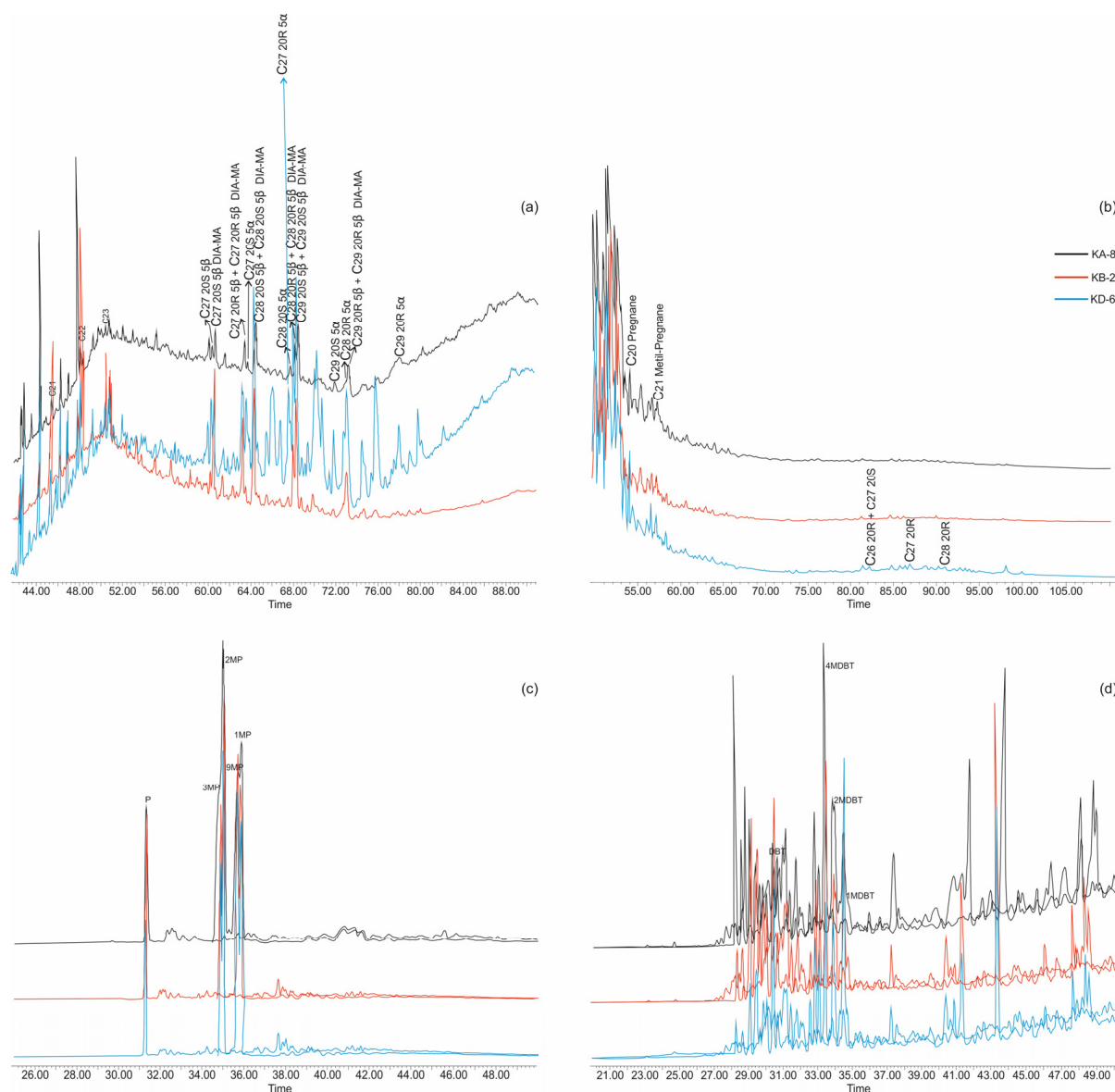


Figure 5. (a) m/z 231 mass fragmentograms, (b) m/z 253 mass fragmentograms, (c) m/z 178 + 192 mass fragmentograms, and (d) m/z 184 + 198 mass fragmentograms of aromatic hydrocarbons for selected coal samples.

Various maturity parameters derived from the phenanthrene (P) and methylphenanthrene (MP) distributions in the coal samples are presented in Table 5. The MPI-1, MPI-2, and MPI-1* ratios across all three seams were similar and exceeded a value of 1. The Dibenzothiophene (DBT)/phenanthrene (P) ratios in the samples ranged from 0.27 to 0.50 (Table 5). The methyldibenzothiophene ratio (MDR) and MDR' values exhibited similar levels across the Acılık, Domuzcu, and Büyük seams (Table 5). The MPR1, MPR2, MPR3, and MPR9 values were higher in the Domuzcu seam sample compared to those from the Acılık and Büyük seams.

4.3. Organic Petrography

Table 6 presents the results of the maceral analysis and vitrinite reflectance measurements conducted on the coal seam samples. The vitrinite random reflectance of the coal samples exhibits a range of 0.89% to 1.17%. In accordance with the ASTM D-388 [63] standard for coal classification, the rank of the coal in question falls within the medium to high volatile-A bituminous range.

Table 6. Maceral composition, vitrinite reflectance, and calculated paleoenvironmental indices of the coal samples from the Kozlu Formation.

Sample	KB-1	KD-2	KD-6	KD-8	KD-13	KD-16	KD-18	KA-8	KA-10	KA-23
Maceral										
	vol% (on mineral matter free basis)									
Collotellinite	6.1	5.3	2.1	4.1	3.1	4.0	3.0	4.1	4.1	4.2
Vitrodetrinite	5.1	5.3	4.2	4.1	4.1	5.1	5.1	4.1	4.1	5.2
Corpogelinite	1.0	1.1	1.0	-	-	-	-	2.1	1.0	1.0
Gelinite	51.0	76.8	76.0	74.2	73.2	67.7	63.6	72.2	74.5	64.6
Total Vitrinite	63.3	88.4	83.3	82.5	80.4	76.8	71.7	82.5	83.7	75.0
Sporinite	5.1	3.2	4.2	3.1	2.1	3.0	3.0	3.1	2.0	3.1
Cutinite	2.0	1.1	1.0	1.0	-	3.0	3.0	1.0	1.0	2.1
Resinite	6.1	1.1	2.1	2.1	2.1	1.0	4.0	2.1	1.0	2.1
Total Liptinite	13.3	5.3	7.3	6.2	4.1	7.1	10.1	6.2	4.1	7.3
Fusinite	5.1	2.1	3.1	4.1	4.1	4.0	4.0	3.1	3.1	5.2
Semifusinite	3.1	-	-	2.1	2.1	2.0	4.0	2.1	2.0	2.1
Macrinite	9.2	1.1	2.1	2.1	4.1	5.1	5.1	3.1	3.1	4.2
Micrinite	-	1.1	1.0	-	-	-	-	-	-	-
Inertodetrinite	6.1	2.1	3.1	3.1	5.2	5.1	5.1	3.1	4.1	6.3
Total Inertinite	23.5	6.3	9.4	11.3	15.5	16.2	18.2	11.3	12.2	17.7
	vol% (on whole sample)									
Mineral Matter	2.0	5.0	4.0	3.0	3.0	1.0	1.0	3.0	2.0	4.0
Vitrinite Rr%	1.11	1.00	0.91	0.89	0.97	1.12	1.04	1.08	1.06	1.17
Standard Deviation (±)	0.01	0.01	0.01	0.02	0.02	0.05	0.01	0.04	0.02	0.02
	Indices (dimensionless)									
TPI	0.20	0.08	0.06	0.12	0.11	0.12	0.14	0.11	0.11	0.14
GI	5.07	17.00	11.71	9.11	7.45	7.36	5.85	10.38	9.44	5.85
GWI	4.82	7.90	13.00	9.38	10.57	7.56	8.00	9.38	9.50	7.44
VI	1.54	1.33	0.88	1.71	1.57	1.00	1.36	1.57	1.43	1.18

TPI = (Telovitrinite + Fusinite + Semifusinite)/(Detrovitrinite + Geolovitrinite + Inertodetrinite + Micrinite + Macrinite) [53]; GI = (Vitrinite + Macrinite)/(Fusinite + Semifusinite + Inertodetrinite + Micrinite) [53]; GWI = (Gelovitrinite + Mineral Matter)/(Telovitrinite + Detrovitrinite) [52]; VI = (Telovitrinite + Fusinite + Semifusinite + Suberinite + Resinite)/(Collodetrinite + Inertodetrinite + Alginite + Liptodetrinite + Sporinite + Cutinite) [52].

The vitrinite content of Zonguldak-Kozlu coals ranges from 63.3% to 88.4%, while the inertinite content varies between 6.3% and 23.5%. The liptinite content is between 4.1% and 13.3%, and the mineral matter content is between 1.0% and 5.0%. Representative microphotographs of the various macerals are presented in Figure 6. The vitrinite group is represented by gelovitrinite and minor amounts of telovitrinite and detrovitrinite. A detailed maceral analysis revealed that the coal samples were predominantly composed of gelinite, which constituted over 50% of the macerals in all seams. In addition to fusinite, macrinite, and inertodetrinite, the inertinite group is represented by minor amounts of semifusinite. Micrinite was also observed in some particles. The liptinite group comprises sporinite, cutinite, and resinite, with average values typically below 3.0% mmf. The GI values range from 5.07 to 17.0, the TPI from 0.06 to 0.20, the GWI from 4.82 to 13.0, and the VI from 0.88 to 1.71.

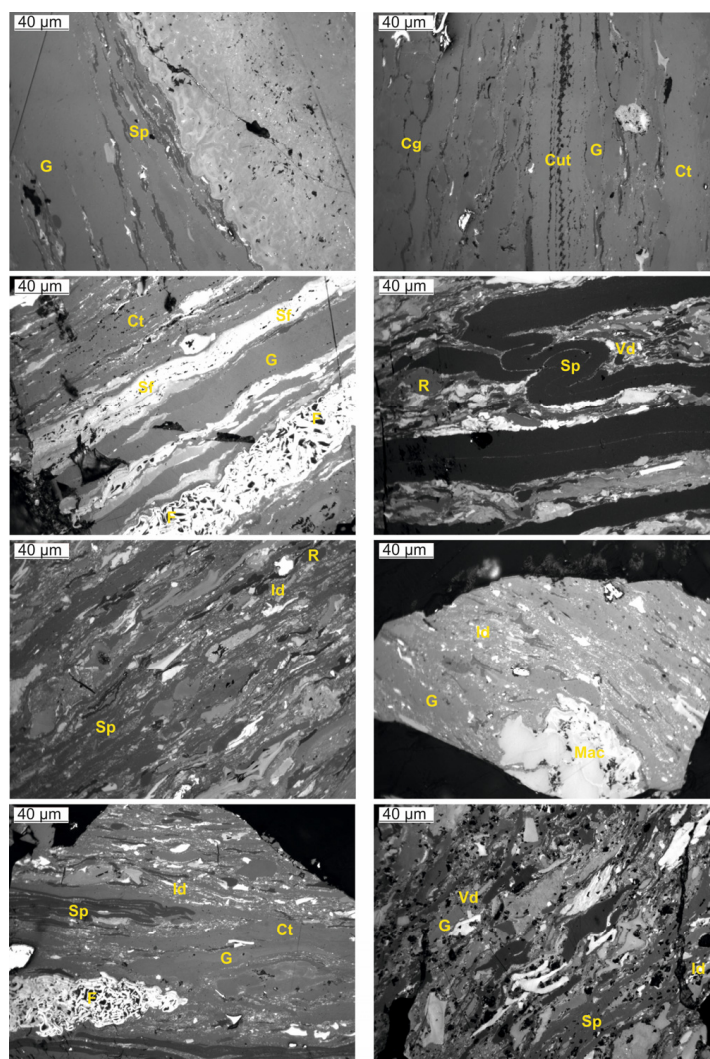


Figure 6. Representative microphotographs of the various macerals of coal samples from Kozlu Formation. Gelinite (G), Sporinite (Sp), Cutinite (Cut), Corpogelinite (Cg), Fusinite (F), Semifusinite (Sf), Vitrodetrinite (Vd), Resinite (R), Inertodetrinite (Id), and Macrinite (Mac).

5. Discussion

5.1. Type and Source of Organic Matter

As aromatics and asphaltenes are generally abundant in higher plants, while saturated and heteroatomic compounds are typically associated with phytoplankton [64], the Sat/Aro hydrocarbon ratio can be used to infer the source of organic matter. The Sat/Aro ratios for the Büyük, Domuzcu, and Acılık seams are 0.25, 0.24, and 0.17, respectively (Table 2), indicating a predominance of terrestrial organic matter input in these coal samples. The variation in n-alkane distribution suggests different origins of the organic matter [62]. It is generally understood that n-alkanes with carbon numbers below C_{21} are usually derived from aquatic microorganisms and algae, those between C_{21} and C_{25} from aquatic macrophytes, and those above C_{25} from terrestrial higher plants [64–68]. In the Acılık seam coal sample, the n-alkane distribution is dominated by short- and medium-chain n-alkanes, while in the Büyük and Domuzcu coal seam samples, short-chain n-alkanes are more prevalent. This suggests that the Acılık seam coal sample is derived from a mixture of aquatic organisms and terrestrial plants, whereas the Büyük and Domuzcu seam samples indicate a greater contribution from aquatic material. Moreover, the waxiness index values were calculated as 0.99 for the Acılık seam, 0.62 for the Büyük seam, and 0.85 for the Domuzcu seam. These values suggest that the Acılık seam is primarily formed from a mix

of aquatic and terrestrial plants and microorganisms, while the Büyük and Domuzcu seam coals are predominantly derived from aquatic plants and organisms. The Pr/n-C₁₇ and Ph/n-C₁₈ ratios further support the interpretation of the organic matter source in these coals (Figure 7). The TAR ratios for the samples ranged from 0.20 to 0.30 (Table 3), with values below 1 indicating a dominant input of aquatic organic matter [55,69]. A CPI value greater than 1 typically reflects a high contribution from terrestrial plants, while values below 1 are indicative of marine organic matter [70]. The relatively high CPI values (ranging from 1.00 to 1.44) in the studied coals confirm the terrestrial origin of the organic matter.

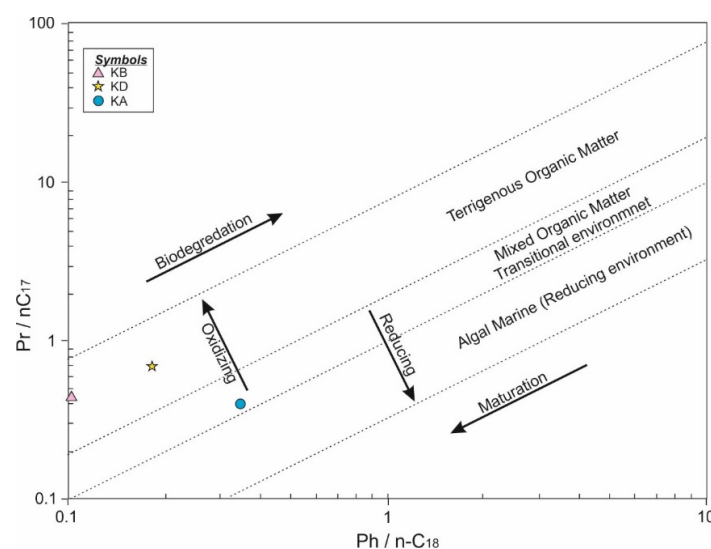


Figure 7. Pr/n-C₁₇ vs. Ph/n-C₁₈ diagram illustrating the organic matter source input for analyzed coal samples from the Kozlu Formation.

The C₂₇–C₂₈–C₂₉ regular steranes are widely used as biomarker parameters to indicate the source of organic matter [71,72]. Typically, C₂₇ steranes are associated with algae, C₂₈ steranes with lacustrine algae and diatoms, and C₂₉ steranes with terrestrial vascular plants [55,62,73]. It is important to note that microalgae can contain high levels of 24-ethyl cholesterol, which can elevate the C₂₉ sterane content in C₂₇–C₂₉ regular sterane distributions [74,75]. The average percentages of C₂₇, C₂₈, and C₂₉ regular steranes in the analyzed coal samples were 26.91%, 30.04%, and 43.05% in the Acılık seam; 24.10%, 27.56%, and 48.34% in the Büyük seam; and 11.11%, 38.11%, and 50.78% in the Domuzcu seam, respectively.

The C₂₇–C₂₉ ternary diagram (Figure 8) further illustrates that the coal samples from the Acılık seam fall within the mixed source range of plankton and terrestrial plants, while those from the Büyük and Domuzcu seams are predominantly of terrestrial origin. A low sterane/hopane ratio suggests terrestrial or microbiologically reprocessed organic matter, whereas a high sterane/hopane ratio indicates a significant contribution from algae [55]. The elevated sterane/hopane ratios (ranging from 2.33 to 2.71) in the studied samples support the contribution of algae to the organic matter (Table 4).

The HI values from pyrolysis data were used to determine the kerogen types in the coal samples. The HI values for the studied samples were consistently above 200 mg HC/g TOC. Specifically, the HI ranged from 231 to 312 mg HC/g TOC for the Acılık seam, 259 to 289 mg HC/g TOC for the Büyük seam, and 247 to 307 mg HC/g TOC for the Domuzcu seam, with an average of 273 mg HC/g TOC across all three seams. These values indicate a Type II–III kerogen, suggesting a significant input from bacterial sources and plankton relative to terrestrial input. In contrast, the OI values were very low (<3 mg CO₂/g TOC) across the Acılık, Büyük, and Domuzcu seam coals. This classification of kerogen types is further supported by the HI-Tmax diagram, which places the samples within the Type II–III area (Figure 9a).

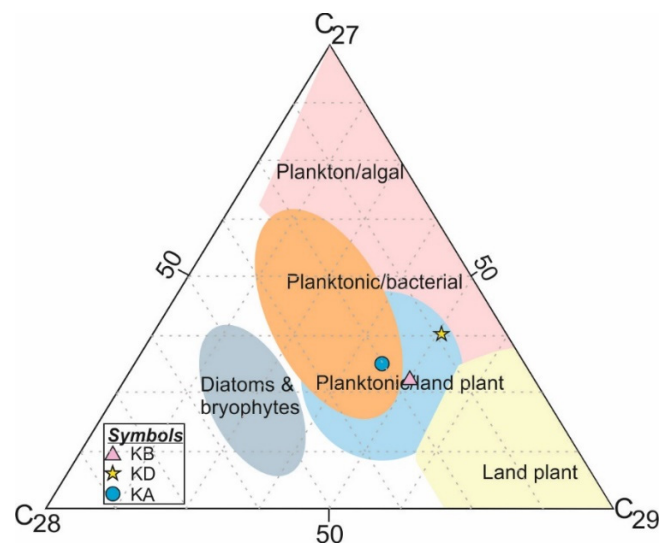


Figure 8. C₂₇-C₂₈-C₂₉ sterane ternary diagram for coal samples from the Kozlu Formation.

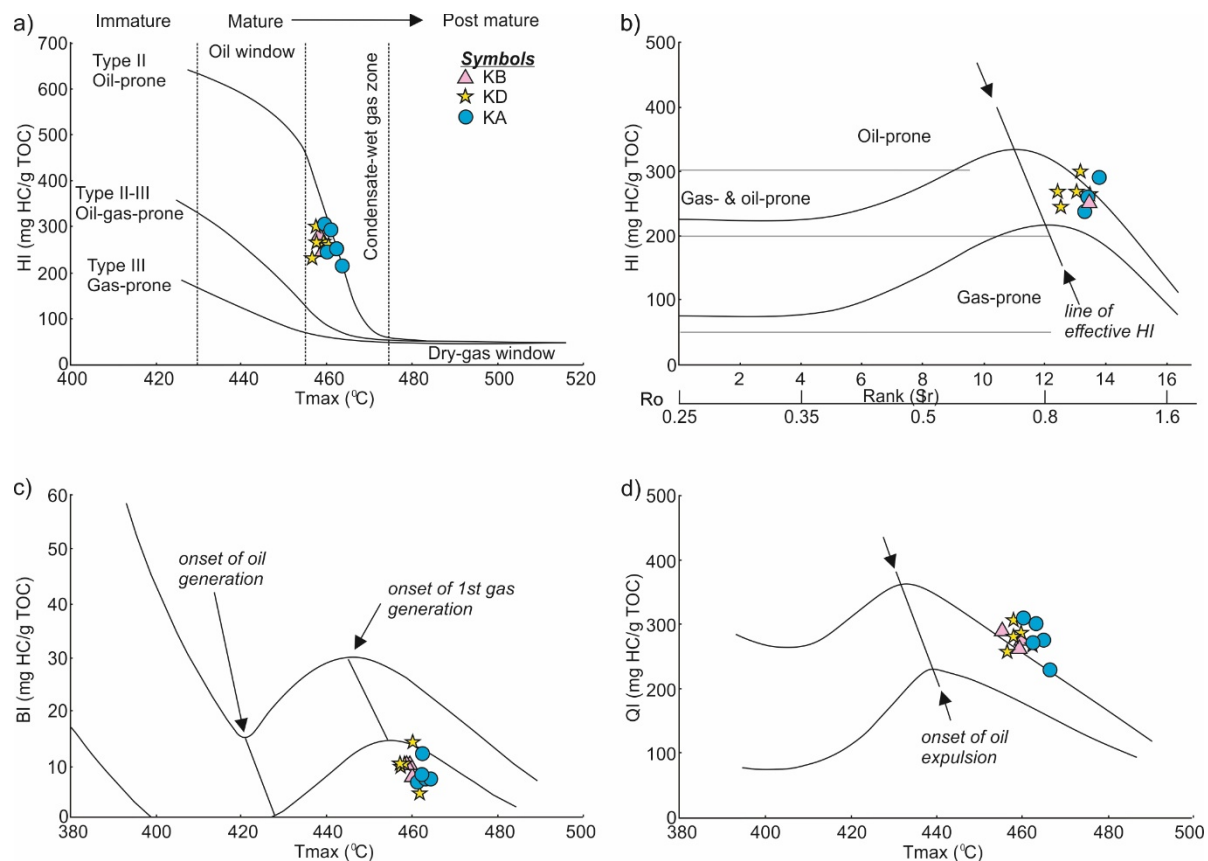


Figure 9. Cross plot of (a) HI versus Tmax, (b) HI-Ro, (c) BI-Tmax, and (d) QI-Tmax for analyzed coal samples.

The petrographic composition of the coal samples shows significant similarities between the Acılık and Domuzcu seams, but the Büyük seam displays more distinct characteristics. The Büyük seam has the lowest vitrinite content (63.3% mmf) and the highest levels of inertinite (23.5% mmf) and liptinite (13.3% mmf). This difference may be due to variations in peat facies or vegetation type. The tissue preservation index (TPI) indicates the extent of humification and the type of vegetation in the peat [53,76]. The TPI for fern-influenced

habitats is typically low [77]. In the study area, the TPI values are low (<0.2), indicating a high degree of maceral humification and low tree density. Comparing macerals from trees with those from herbaceous and aquatic species, a high vegetation index (VI) value suggests a predominantly forested peatland [52]. The VI values of the coal samples are generally around 1.0. Values below 1.0 indicate herbaceous rather than forested vegetation, while values below 3.0 suggest a transitional environment, characterized by marginal aquatic or herbaceous vegetation [52,78]. The data suggest that aquatic and herbaceous plants were the dominant vegetation in the paleomire. The relatively stable VI values across the seams indicate that the proportion of plants with different preservation potentials has remained consistent. The relatively high VI values in some samples may reflect short-term increases in woody plants.

5.2. Paleoclimate and Paleodepositional Environment

The aliphatic chain length (ACL) index values are commonly used to infer paleoclimatic conditions during peat formation [79]. Typically, vascular land plants in hot and dry climates produce longer-chain n-alkanes compared to those in colder climates. The ACL values for the studied samples from the Acılık, Büyük, and Domuzcu coal seams were 33.78, 19.63, and 33.29, respectively.

Low proxy aqueous (Paq) values (<0.1) suggest a terrestrial plant input, while medium (0.1–0.4) and high (0.4–1.0) Paq values indicate the presence of emergent and submerged/floating plants, a high-water table, and a relatively wet and humid climate [80]. In the studied coal samples, the Paq values ranged from 0.47 to 0.80. The proxy wax (Pwax) values varied between 0.27 and 0.59. High Pwax values (>0.7) usually indicate a significant input from vascular plants in dry climatic conditions, whereas lower values (<0.7) reflect relatively humid conditions [81].

The presence of gelinite exceeding 50% in all samples suggests deposition in a non-acidic limnic environment. However, there is a relative increase in the liptinite and inertinite components in the lower parts of the Domuzcu and Acılık seams and in the Büyük seam. The rise in inertinite content may be attributed to the lowering and/or fluctuation of the water table or to forest fires. The increased liptinite content, coupled with a decrease in vitrinite, could result from accelerated peat degradation. Additionally, the higher levels of liptinite associated with increased inertinite content are likely due to their resistance to degradation, as previtrinitic plant materials are lost through burning and/or decomposition [82].

The high macrinite content in the Büyük seam suggests microbial degradation of botanical material. The presence of fusinite and semifusinite indicates woody vegetation and associated forest fire activity. In contrast, the occurrence of liptinite macerals, such as sporinite, cutinite, and resinite, points to moisture-rich conditions [83]. This suggests that fluctuations in the water table likely occurred during peat accumulation. The elevated vitrinite content in the upper levels of the Domuzcu and Acılık seams indicates wet periods, while the increased fusinite and semifusinite in the lower levels of these seams and in the Büyük seam suggest relatively dry and oxidizing conditions.

The gelification index (GI) measures the degree of wetness and the continuity of peat-forming conditions [53,76]. For the selected coal samples, the GI shows high values (>5.0), indicating significant gelification and wet conditions. The seams exhibit a trend from low GI and high TPI values at the base to high GI and low TPI values towards the top. These findings suggest that, although the water level fluctuated, the peat surface remained consistently submerged.

The high vitrinite content suggests that the coal deposits were formed in a planar, topogenous marsh with an anoxic water environment. Isoprenoid ratios can provide insights into paleodepositional environments [55,84]. A high Pr/Ph ratio (>3.0) indicates the input of terrestrial organic matter deposited under oxic conditions, while a Pr/Ph ratio between 1 and 3 suggests mixed organic matter in a suboxic environment. A low Pr/Ph ratio (<1) reflects organic matter deposition in anoxic conditions [45,85]. A very low Pr/Ph ratio (<0.6) is indicative of anoxic and often highly saline environments [45]. The

Acılık seam coal sample has a Pr/Ph ratio of 1.00, reflecting anoxic–suboxic depositional conditions, while the Büyük and Domuzcu seam samples exhibit Pr/Ph ratios of 6.58 and 5.44, respectively, indicating oxic depositional environments.

Gammacerane serves as an indicator of water salinity during sedimentation in aquatic environments [45,62]. A gammacerane index ($G/C_{30}H$) greater than 0.3 suggests reducing and hypersaline conditions [62]. In the Kozlu Formation coals, the $G/C_{30}H$ index ranges from 0.01 to 0.04 (Table 4). The low $G/C_{30}H$ index and relatively high Pr/Ph values suggest freshwater deposition under oxidizing conditions. High $C_{30}^*/C_{29}Ts$ ratios further support oxic–suboxic depositional conditions, while low values suggest anoxic environments [55]. The samples from the Acılık (3.46), Domuzcu (2.75), and Büyük (3.17) seams exhibited high $C_{30}^*/C_{29}Ts$ ratios. The $C_{31}R/C_{30}$ hopane ratio is a valuable biomarker for distinguishing marine environments with shales and mudstones from lacustrine settings. A lacustrine environment is characterized by a $C_{31}R/C_{30}$ hopane ratio below 0.25, while marine environments typically have values above 0.25 [55,86]. The $C_{31}R/C_{30}$ hopane ratios were 0.20 for the Acılık seam, 0.26 for the Büyük seam, and 0.22 for the Domuzcu seam. The Pr/Ph versus $C_{31}R/C_{30}$ hopane suggests that these coal samples were deposited in lacustrine and fluvial to fluvial-deltaic environments (Figure 10).

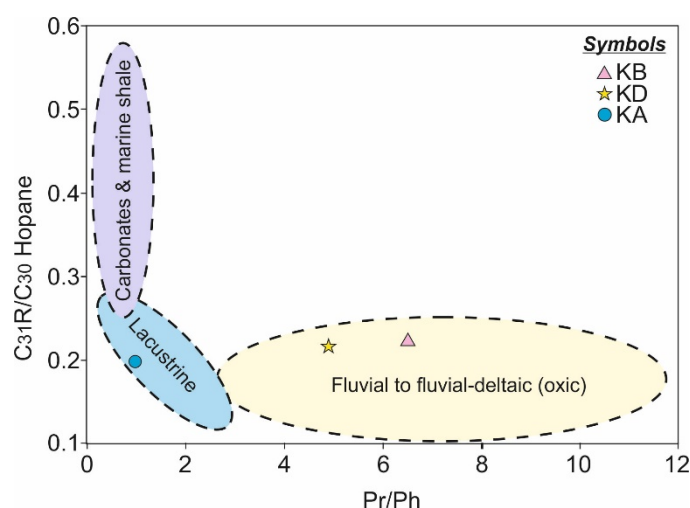


Figure 10. Relation between $C_{31}R/C_{30}$ hopane and Pr/Ph ratios for the analyzed samples.

The ground water index (GWI) reflects the relative water table level during peat formation, with higher GWI values indicating higher water levels [52]. A GWI value between 3.0 and 5.0 suggests a limno-telmatic environment, while a value exceeding 5.0 indicates peat drowning [52,78]. The elevated GWI values (>4.0) observed in all examined coal samples align with the characteristics of environments with standing water levels, such as floodplains and topogenous mires. Sedimentological evidence further supports that these coals were deposited in a floodplain environment [19]. The position of the samples on the GI-TPI diagram suggests that the coals were formed in a limnic environment (Figure 11a). The position of the samples on the GWI-VI diagram suggests that the coals originated in inundated marshes under rheotrophic conditions (Figure 11b).

The coal samples showed a lower abundance of C_{29} norhopane compared to C_{30} hopane. The C_{29}/C_{30} hopane ratios were 0.73, 0.55, and 0.56 for the Acılık, Büyük, and Domuzcu seams, respectively (Table 4), indicating a clastic source rock. A regular decrease in homohopane distribution (C_{31} – C_{35}) from low-carbon to high-carbon homohopanes suggests clastic facies [87], which is associated with oxic–suboxic depositional conditions [55,56,88]. The homohopane distribution in the samples is dominated by C_{31} homohopane, with a gradual decrease from C_{31} to C_{35} . The homohopane index (C_{35}/C_{31} – C_{35} hopane ratio) yielded low values (between 0.03 and 0.07) (Table 4).

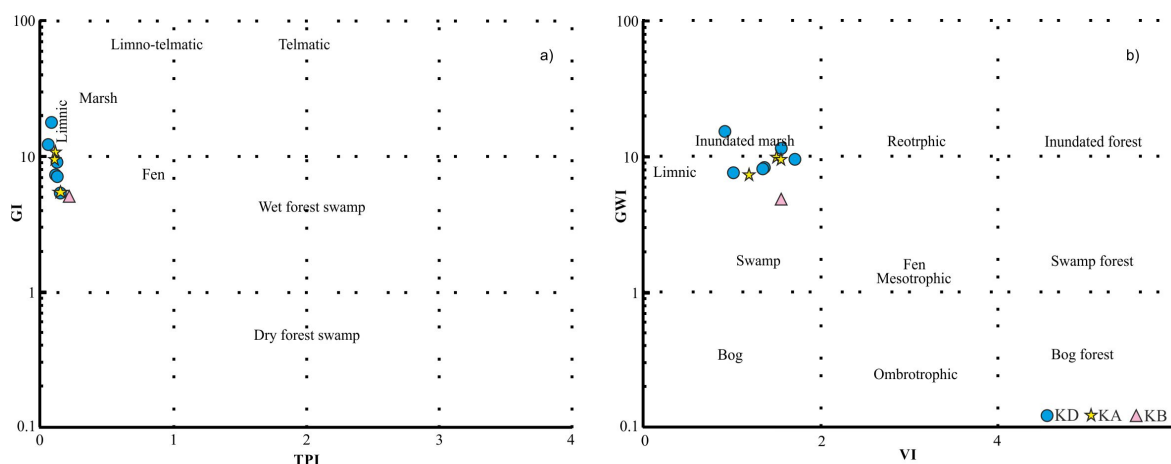


Figure 11. Coal facies diagrams for the analyzed coal samples. (a) TPI-GI (modified from [53]) (b) VI-GWI (modified from [52]).

The C_{22}/C_{21} tricyclic terpane (TT) and C_{23} TT/(C_{23} TT + C_{30} hopane) ratios are low, while the C_{24}/C_{23} TT ratio is relatively high in the coal samples. These values suggest a clastic depositional environment, likely lacustrine-fluvial/deltaic, with a slight marine influence [55].

The diasterane/sterane ratio is a useful indicator for distinguishing between carbonate and clastic depositional environments [62]. A low diasterane/sterane ratio suggests a carbonate environment with deposition under anoxic marine conditions, whereas a high ratio indicates a clastic depositional setting [62,89]. The coal samples analyzed exhibited very high diasterane/sterane ratios (Table 4), supporting the presence of a clastic environment. Additionally, the Dia/(Dia + R) monoaromatic ratios, which ranged from 0.50 to 0.85 (Table 5), further confirm the clastic facies and suggest that these coals are rich in clastic material with a dominant terrestrial organic contribution [55].

The dibenzothiophene (DBT)/phenanthrene (P) ratios in the samples ranged from 0.27 to 0.50 (Table 5). Low DBT/P ratios indicate that organic matter primarily accumulated in a terrestrial environment, reflecting significant terrestrial input [90,91]. In the Kozlu coals, Karayiğit et al. [32] reported the sulfur content as <1% on a dry ash-free basis. The low sulfur content (<1%) in these coals, consistent with the low DBT/P ratio, aligns with a freshwater depositional environment [91,92]. On the DBT/P vs. Pr/Ph diagram, the Acılık seam sample plots in the lacustrine, sulfate-poor region, while the Büyük and Domuzcu seam samples fall within the fluvial/deltaic region (Figure 12). The paleoenvironmental difference between the Acılık seam and other seams may have resulted from vertical tectonic movements in the basin during the Carboniferous period [19].

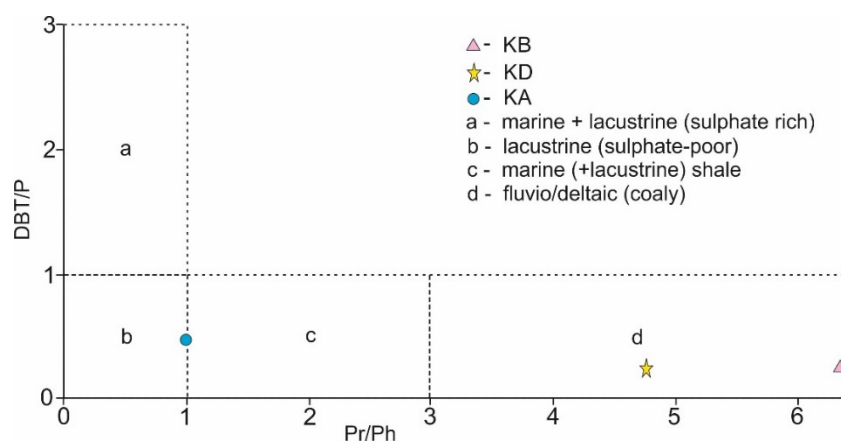


Figure 12. DBT versus Pr/Ph for the analyzed coal samples.

5.3. Thermal Maturity of Organic Matter

Thermal maturation parameters, such as vitrinite reflectance, Tmax, and biomarker ratios, are commonly used to assess the maturity level of organic matter [55]. The Tmax values for coal samples from the Acılık, Büyük, and Domuzcu seams ranged between 457 °C and 466 °C, indicating a high level of thermal maturity (Table 1). These results suggest that the samples are in the mature to overmature stage. Vitrinite reflectance measurements are considered the most reliable indicator of organic maturity and the oil production potential [93]. The vitrinite reflectance values for the studied samples, ranging from 0.89% to 1.17% Rr, indicate that they are in the late oil to early gas window stage, consistent with thermal maturity [89]. Cross plots of HI versus Tmax and HI versus Ro further support the maturity levels of these samples (Figure 9a,b).

Saturated and aromatic hydrocarbon maturity parameters are widely used in the assessment of crude oil and coal maturity [94,95]. As thermal maturity increases, the 22 S/(22 S + 22 R) homohopane (C₃₂) ratio also increases, reaching equilibrium at around 0.6, which is indicative of a mature level [96,97]. A ratio below 0.50 suggests an immature source rock. The 22 S/(22 S + 22 R) homohopane ratios for the analyzed coal samples range from 0.58 to 0.59, suggesting they are in the mature to overmature stage. Additionally, if the 20 S/(20 S + 20 R) sterane (C₂₉) and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratios exceed 0.30 and 0.40, respectively, the oil window is reached, with equilibrium values at 0.55 and 0.7 [45,87,96,98]. The 20 S/(20 S + 20 R) sterane ratios for the Acılık, Domuzcu, and Büyük seam coals are 0.51, 0.52, and 0.51, respectively, while the $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratios are 0.52, 0.55, and 0.54, respectively, indicating that these source rocks are in the mature to overmature range.

The moretane/hopane ratios also support this interpretation of maturation. As maturity increases, the moretane/hopane ratio decreases from around 0.8 in immature source rocks to less than 0.15 in mature ones [99–101]. The low moretane/hopane ratios of 0.13 to 0.14 in the analyzed coal samples indicate they are mature source rocks. Additionally, while the abundance of Ts is higher than Tm in the Acılık and Büyük seams, the reverse is observed in the Domuzcu seam. The Ts/(Ts + Tm) ratio increases with maturation, and the high values (0.36–0.55) observed in these coals further indicate their maturity.

The C₂₉Ts/C₂₉Ts+C₂₉H ratio also tends to increase with maturation. In the analyzed coals, this ratio is 0.32 for the Acılık seam, 0.22 for the Domuzcu seam, and 0.36 for the Büyük seam, confirming their mature status. Monoaromatic and triaromatic steroid distributions, which increase from 0% to 100% during thermal maturation, are also used to assess maturity [55]. The MA(I)/MA(I + II) ratio was calculated as 0.48 for the Acılık seam, 0.62 for the Domuzcu seam, and 0.76 for the Büyük seam, while the TA(I)/TA(I + II) steroid ratio was consistently 1 in all samples, indicating that the coal samples are in the mature to overmature stage.

The methyl phenanthrene index (MPI) is a widely used biomarker maturity parameter that typically increases with thermal maturation and then decreases as the thermal maturation level reaches its peak [102,103]. However, MPI ratios can be influenced by variations in the type of organic matter and lithology in the source rock [104]. In the analyzed samples, the MPI-1, MPI-2, and MPI-1* ratios were all similar and exceeded 1, indicating that the samples are within the mature range. Additionally, the methyldibenzothiophene ratio (MDR), another key maturity parameter, generally increases with thermal maturity. The MDR values in the studied samples ranged from 5.08 to 18.77, further confirming that these are mature source rocks (Table 4).

5.4. Hydrocarbon Generative Potential

Rock-Eval pyrolysis provides essential data for assessing the hydrocarbon production potential of organic-matter-rich sediments. The high TOC values observed in the coals of the Acılık, Büyük, and Domuzcu seams within the Westphalian-A-aged Kozlu Formation (Table 1) indicate that these coals are excellent source rocks. The potential yield (PY = S₁ + S₂) values derived from pyrolysis, which average 139.41, 138.69, and 126.29 mg HC/g rock for the Büyük, Domuzcu, and Acılık seams, respectively, further

support their classification as excellent source rocks. Moreover, all the coal samples exhibit a high bitumen content (>4000 ppm; [89]), indicating a strong hydrocarbon potential (Table 2). The investigated samples showing excellent hydrocarbon generation potential based on the association between the TOCs and S_2 values obtained by Rock-Eval pyrolysis are shown in Figure 13. HI values between 200 and 300 mg HC/g TOC suggest that the kerogens are of Type II and III, composed of mixed organic material [89]. The HI values for the Acılık, Büyük, and Domuzcu seam coals range between 231 and 312 mg HC/g TOC, 259 and 289 mg HC/g TOC, and 247 and 307 mg HC/g TOC, respectively, indicating potential for oil and gas production.

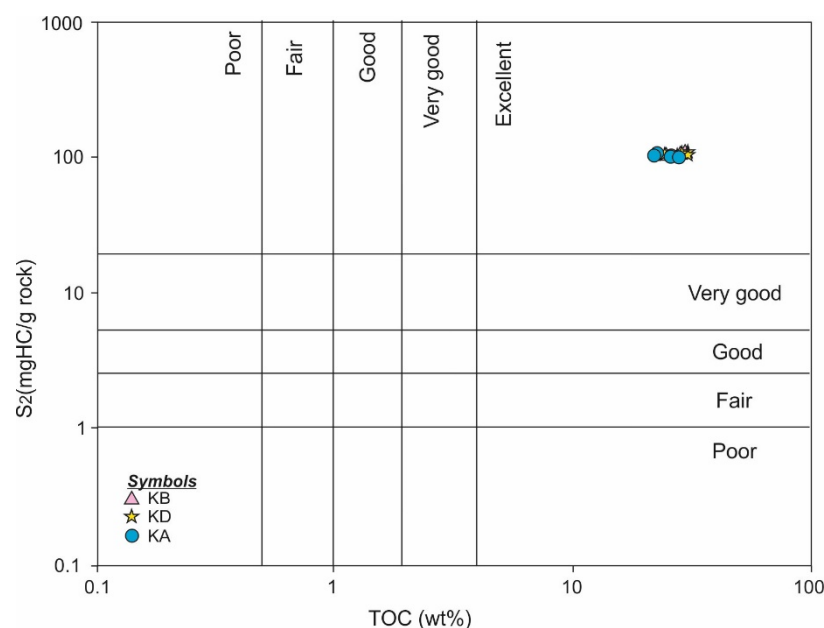


Figure 13. Cross-plot of TOC versus Rock-Eval S_2 for the analyzed samples.

Despite the relatively high HI values and very low OI values (<3 mg CO_2 /g TOC) associated with high liptinite content, these coals are humic coals with low liptinite content (Table 6). This discrepancy arises because there is not a straightforward relationship between HI and maceral composition [105,106]. Factors such as the volatile matter content of the coal and the chemical variability of vitrinite also influence the HI value [107]. The low OI values are probably associated with the reduced unstable oxygen content, which can be attributed to the depositional environment of the coal and the decarboxylation and dehydration processes that take place during coalification [108]. The HI and OI values, along with the HI-Tmax and HI-Ro cross plots, indicate the presence of Type II and III kerogen with high Tmax and TOC content that are mixed and exhibit good hydrocarbon production potential. The BI and QI values were within ranges of 7–13 and 238–320 for the Acılık seam, 9–11 and 270–318 for the Büyük seam, and 5–14 and 258–318 for the Domuzcu seam, respectively. The low BI values, relatively high QI values, and the BI-Tmax and QI-Tmax diagrams suggest that these coals are prone to generating both gas and oil and have passed the rank threshold for oil formation and exploitation (Figure 9c,d).

6. Conclusions

Coal samples from the Westphalian-A-aged Kozlu Formation were collected from three different seams in the Kozlu (Zonguldak) underground mine and subjected to geochemical and petrographic analysis. TOC-pyrolysis, biomarker, and petrographic data were utilized to assess the paleomire conditions during coal formation and the hydrocarbon production potential.

The concluding remarks of the study are as follows:

- Based on the TOC and EOM parameters, the Kozlu Formation coals have excellent source rock potential. Pyrolysis data and vitrinite reflectance values suggest that the hydrocarbon production potential spans from the late oil window to the condensate-wet gas window.
- The Rock-Eval pyrolysis, biomarker analysis, and organic petrography data indicate that the organic matter is predominantly Type II-III kerogen derived from mixture of organic matter and with a significant input from aquatic sources.
- The Pr/Ph and C_{30}^*/C_{29} Ts ratios suggest that the organic matter was deposited under oxic to anoxic conditions. Maceral analysis further indicates a high degree of gelification and the presence of wet conditions. Based on the Paq and Pwax values, the paleoclimate during the peat accumulation was relatively wet and humid.
- The thermal maturity of the organic matter was determined to be in the mature to over-mature stage, based on Tmax, Rr, MPI* values, and the hopane, sterane, monoaromatic, and triaromatic ratios.
- The quantity, type, and maturity level of the organic matter suggest that the coals have the potential to generate both gas and oil, exceeding the maturity level required for oil formation and extraction.
- n-Alkane distributions, along with saturated–aromatic hydrocarbon data, maceral distributions, and facies indices, collectively indicate that the paleomire accumulation occurred in fluvial/deltaic environments under limnic–limnotelmatic conditions.

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