

Article

Differentiation of the Generation Potential of the Menilite and Istebna Beds of the Silesian Unit in the Carpathians Based on Compiled Pyrolytic Studies

Irena Matyasik¹, Małgorzata Labus^{2,*} , Maria Kierat¹ and Karol Spunda¹

¹ Oil and Gas Institute—National Research Institute, 25A Lubicz St., 31-503 Kraków, Poland; matyasik@inig.pl (I.M.); maria.kierat@inig.pl (M.K.); karol.spunda@inig.pl (K.S.)

² Institute for Applied Geology, Silesian University of Technology, 2 Akademicka St., 44-100 Gliwice, Poland

* Correspondence: malgorzata.labus@polsl.pl

Abstract: The study of the source rocks was carried out with the use of various analytical methods in order to assess their generation potential and to predict the decomposition products of organic matter. The selected samples from the Menilite Beds from the Silesian and Dukla units, as well as the Istebna layers from the Silesian unit, which are classified as weak and medium source rocks in the Carpathian oil system, were examined. The generation potential and type of the products obtained from the pyrolysis of the analyzed source rocks, despite the often comparable overall content of organic matter, are significantly different. Menilite shale generated a higher abundance of hydrocarbons (alkanes, alkenes, and isoalkanes) by stage pyrolysis, which suggested that the organic matter of Menilite shale is different from the Istebna source rocks. Moreover, the thermogravimetric analysis showed a two-stage weight loss in the case of Menilite shales, while the Istebna shales were characterized by a one-stage weight loss at higher temperature. For the Istebna layers, n-alkanes from the C₁–C₅ range were detected as the main pyrolysis products, which proves the gas-forming type of the organic matter dispersed in these sediments. Rock-Eval analyses showed that the organic matter reached a degree of maturity corresponding to the early thermocatalytic processes (the initial oil window stage) and therefore was able to generate liquid and gaseous hydrocarbons. The comparison of the decomposition temperatures of the organic matter from the Rock-Eval and TG analyses allowed us to conclude that both measurements correlate well and can be equally used to assess the level of thermal transformations of organic matter.



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1. Introduction

Pyrolysis studies with the use of various techniques of analysis, monitoring, and detection of the products allow for detailed information on the quality of the source rocks in petroleum systems. Compilation studies such as Rock-Eval, thermogravimetry (TG/DTG), and Pyrolysis Gas Chromatography (Py/GC) analysis have already been initiated by the authors of this paper in the analysis of the decomposition of organic matter contained in the source rocks of the Menilite Beds [1–4], which is considered to be the main source of hydrocarbon generation in the Outer Carpathians [5–10]. The results of this study helped to clarify the generation properties of these rocks and thus to improve the simulation of generation processes in the Carpathian Basin. In the Carpathians, the Menilite Beds of the Oligocene are considered to be good source rocks. They are among the best recognized flysch formations in terms of source rocks characteristic, as they were penetrated not only by boreholes reaching a depth of 3000 m but also in numerous surface outcrops.

Lots of work done so far on Menilite and Istebna Beds described their lithology, stratigraphy, and geochemical parameters from surface exposures and from boreholes [8,11,12], but there is no precise description of the generation processes. This study was based on

detailed geochemical investigations of representative samples (outcrops) of the Menilite Beds and core samples from the upper Istebna Beds from Silesian and Dukla Nappes of the Polish Outer Carpathians. Its objectives was to examine the quality of products obtained from the decomposition of organic matter and to demonstrate the relationship between three independent pyrolytic methods for generation processes interpretation.

The research presented here included selected samples from the Menilite Beds and has been extended to further regions of the Silesian and Dukla units. In addition to the Menilite Beds, the Istebna formations can also be included in the list of source rocks in the Carpathian petroleum system [13]. In the Silesian unit, they show characteristics of poor and fair source rocks, with the TOC reaching values of up to 4.37% in individual samples. However, this is mainly non-productive carbon, which is represented by the RC parameter (residual carbon) [14]. Despite the relatively high TOC and homogeneity of the samples over a wide sampling interval, the generating capacity of the Istebna Beds, especially the upper layers, is low due to the quality of organic matter dispersed in the rocks. They are markedly different from the Menilite Beds. To document the variation in their source nature, a multi-directional study of the distribution of organic matter contained in both types of potential source rock was performed. Each of the methods used contributes a specific element of information regarding generation capacity. The combination of the pyrolysis techniques used provides a complete picture of the generation features that characterize the Menilite Beds, resulting from the diverse genetic characteristics associated with the type of source material and their sedimentation environment, which have been discussed in previous studies [15–20]. The different interpretive approach to the data on organic matter and their direct impact on the quality assessment of the generated hydrocarbons was also due to the influence of biodegradation, which has also been highlighted in many studies [21]. A particularly important parameter in assessing the quality of source rock is the thermal maturity, which is determined in Rock-Eval review studies [22,23] by the T_{max} value. The T_{max} value may be slightly overestimated when analyzing samples containing organic matter that have been subjected to weathering and oxidation, which happens when redeposited material is present [24]. Interpreting and comparing the results obtained by different analytical methods of the source rock will allow a better assessment of the generation qualities of the source rock and may lead to a better prediction of its decomposition products [25,26]. The results of this work are important for modeling generation processes in petroleum systems and for genetic correlation work [15,27].

2. Research Material

2.1. Geological Background

The study area covered the area between the Nowy Targ and Krosno meridian, and the research material come from two structural units: Silesia and Dukla Nappe within the Polish part of the Outer Carpathians.

The Outer Carpathians are made of a series of overthrust nappes one on the other and thrust sheet build by Upper Jurassic to early Miocene sedimentary rocks. The oldest sediments from the Dukla Nappe region are Cenomanian–Turonian black shales, mudstones, and sandstones. Higher in profile, green and red shales with thin turbidites begin to appear. Upper Cretaceous and Paleocene deposits are represented by thin- to medium-bedded sandstone over which occurs thick-bedded sandstones. These rocks are covered by a complex of medium- to thin-bedded, fine, and medium-grained green shales known as Hieroglyphic Beds, over which are situated upper Eocene Globigerina marls, which are the chronostratigraphic boundary for Outer Carpathians, separating Eocene and Oligocene deposits. In the highest part of the Dukla Unit profile, the dark brown Menilite shales appear, covered by fine-grained sandstones and gray–green calcareous shales called Krosno beds.

The oldest member of the Silesia Unit are lower Tithonian Cieszyn shales, as represented by several dozen meters thickness dark gray calcareous mudstones deposited in euxinic environment interlaying by thin-bedded, fine-grained sandstones. Cieszyn beds pass upward in to Barremian–Aptian black shales called Verovice shales and Grodziszcz

sandstones. There are covered by black shales and thick-bedded or medium-bedded, coarse grained sandstones and conglomerates (Lgota beds, Albian). In Turonian to lower Senonian, the sedimentation of a very thick flysch series of Godula beds occurs. There are represented by thick- and thin-bedded sandstones intercalated by green shales. Higher in profile, a thick sandy complex of Istebna Beds appear (upper Senonian—Paleocene). It is interbedded by Istebna shales, which together with Menilite shales constitute potential source rock in the Polish part of Outer Carpathians. Above them, there is a sandstone series represented by Ciezkowice sandstones, and Hieroglyphic sandstones that pass upward into green shales and Globigerina marls. In the upper part of the Silesia Unit profile, there are present brown, bituminous shales (Menilite shales) locally replaced by Magdalenia sandstones. The age of these rocks is estimated to be early Oligocene. Menilite shales pass upward into Oligocene–Early Miocene Krosno beds developed as thick- and medium-bedded, calcareous sandstones.

2.2. Sample Material

Samples representing the Menilite Beds of the Silesian unit, collected from surface (outcrops) in the area of Gorlice, Folusz, and Wiśniowa—and one sample from the Dukla unit, which was characterized by a high level of thermal transformation—were used for the research. These samples are highly variable in terms of total organic carbon content (TOC ranging from 2.75% to 17.85%) and hydrocarbon index (HI ranging from 100 to 632 mg HC/g of TOC), with thermal maturity, represented as T_{max} , ranging from 407 to 456 °C, which directly affects the amount and type of hydrocarbons generated [16,17,28].

The second group of samples consisted of core samples from the upper Istebna Beds, which—based on previous studies [14,29]—were found to contain mainly type III kerogen with a preference for gas and condensate generation. This is evidenced by the low HI index, ranging from 73 to 102 mg HC/g of TOC, and the generation potential. Four of the samples came from the Równe-1 borehole from the 2421–2553 m interval, and one came from the Kryg-4 borehole from a depth of 1150 m. The location of the samples is shown in Figure 1. Such a selection of samples for pyrolytic analysis, especially the samples of the Menilite Beds taken from surface exposures, was dictated by the fact that the studies included samples representing the same lithostratigraphic section (Menilite Beds) from different locations and showing different geochemical parameters in terms of the level of thermal transformations and genetic features.

The full-scope study included analyses of seven rock samples from Carpathian outcrops, representing the Menilite Beds, and five rock samples from borehole core samples, representing the Istebna Beds. Additionally, tests were performed for four kerogen samples, separated from those representing the Menilite Beds, to demonstrate the influence of the rock matrix on the effects of the pyrolysis products and the rate of decomposition of concentrated organic matter. Weight loss during pyrolytic gas chromatography (Py/GC) was analyzed in only three kerogen samples.

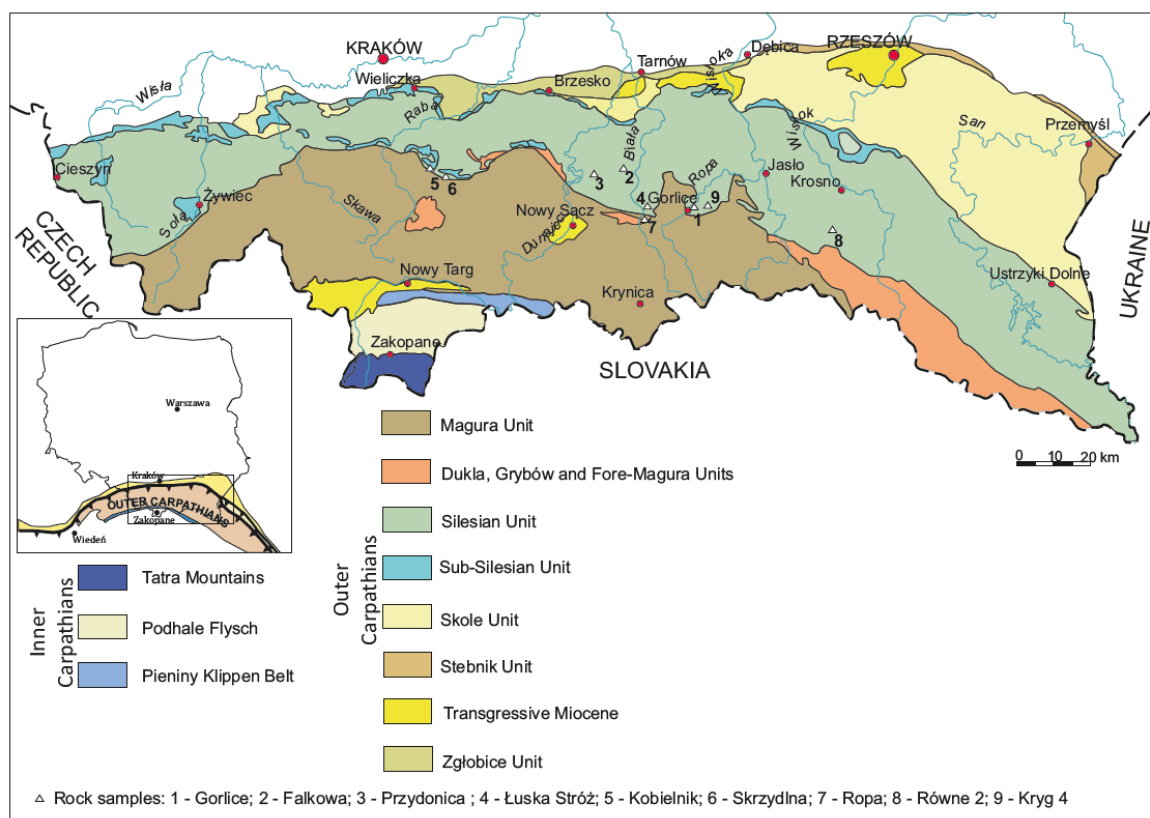


Figure 1. Geological sketch map (modified after Żytko et al. [30]).

3. Methods

3.1. Rock-Eval

First, the Rock-Eval analysis was performed with an RE6 Turbo device with an FID detector (for hydrocarbon analysis) and two IR detectors (for CO and CO₂ analysis) using the BULK ROCK method on the BASIC cycle. For the rock sample analysis, 60 mg of powdered and averaged rock was dispensed, whilst for the separated kerogen analysis, the amount was 15 mg. The kerogen sample was isolated from the rock after extraction, and then, the mineral portion was removed [31].

3.2. TG/DTG

TG/DTG analysis was performed using a NETZSCH STA 449 F3 Jupiter analyzer. The measurements were carried out on a powdered samples heated in the temperature range of 40–1030 °C, with a heating rate of 10 °C/min. A dynamic flow of inert gas (nitrogen) was added at a rate of 50 mL/min in the temperature range 40–650 °C; above 650 °C, a flow of synthetic air was added. The heating of the samples was programmed so that the regime was similar to the course of the Rock-Eval pyrolytic analysis:

- I. Heating from 40 to 300 °C (10 °C/min, purge gas: N₂);
- II. Isothermal section at 300 °C (20 min, purge gas: N₂);
- III. Heating from 300 to 650 °C (10 °C/min, purge gas: N₂);
- IV. Isothermal stage at 650 °C (20 min, purge gas: N₂);
- V. Heating up to 1030 °C (10 °C/min, purge gas: O₂/N₂).

Tests were conducted for 12 rock samples and three samples of extracted kerogen. Ground and sieved rock samples of approximately 20 mg were placed in ceramic crucibles (Al₂O₃). A sample of kerogen weighing approximately 10 mg was similarly handled.

3.3. Py/GC

Pyrolysis gas chromatography investigations were carried out in the Laboratory of Oil and Gas Geochemistry of the Oil and Gas Institute—National Research Institute by means of an analytical system consisting of a Multi-Shot EGA/PY-3030D pyrolyzer, made by Frontier Laboratories, coupled with a GC-2010 Plus gas chromatograph from Shimadzu and equipped with a flame ionization detector (FID). A cryogenic trap, cooled by liquid nitrogen, was installed in the system before the chromatography column, by way of a MicroJet Cryo-Trap MJT-1030Ex freezer.

The sample, with a granularity analogous to that used for the Rock-Eval analysis (below 0.2 mm), was weighed directly in the analytical crucible; then, the crucible was installed in the sampler, and the entire assembly was placed in the pyrolyzer. In the case of rock material, approximately 10 mg of the sample was weighed out; in the case of kerogen, approximately 1 mg was used. The sample was inserted into a pyrolysis furnace, where it was pyrolyzed in a helium atmosphere at a programmed temperature and time. The products of thermal destruction of the analyzed sample were accumulated in a cryogenic trap connected to a gas chromatograph column, where they were directed after pyrolysis and analyzed using an FID detector.

The chromatographic analysis parameters were as follows:

- Ultra Alloy-5 capillary column with a length of 30.0 m, an inner diameter of 0.25 mm, and a film thickness of 0.25 μm ;
- FID detector;
- Helium as the carrier gas, with a constant flow rate of 1.98 mL/min;
- A dosing temperature of 250 $^{\circ}\text{C}$;
- An FID detector temperature of 360 $^{\circ}\text{C}$;
- Temperature program: 3 $^{\circ}\text{C}$ for 5 min with a temperature gradient of 1 $^{\circ}\text{C}/\text{min}$ to 360 $^{\circ}\text{C}$, then 360 $^{\circ}\text{C}$ for 2 min;
- A 10:1 split.

The pyrolysis was conducted in three stages, with the temperature range adjusted for Rock-Eval and similarly programmed thermogravimetric tests. In the multi-stage pyrolysis experiments, after pyrolysis was completed at a given temperature level, the sample was removed from the heating zone but left in the closed chamber of the pyrolyzer. The reaction products retained in the cryogenic trap were directed to the chromatograph, and after chromatographic analysis was completed and the system cooled, the same sample was pyrolyzed at a higher temperature. This cycle was repeated three times for each sample. The analysis was started by heating the sample at 300 $^{\circ}\text{C}$ for 1 min, which caused desorption of the free hydrocarbons. Then, the sample was inserted into a pyrolytic oven heated to 650 $^{\circ}\text{C}$, and pyrolysis was carried out for 0.4 min. The pyrolysis products in the temperature range of 300 to 650 $^{\circ}\text{C}$ are equivalent to the S_2 peak obtained from Rock-Eval analysis. In the third stage, the same sample was pyrolyzed at 1000 $^{\circ}\text{C}$ for 0.2 min, thus obtaining information on the potential for further transformation of the residual carbon. One of the objectives set in this study was to compare the sample weight loss after successive Py/GC stages with the results of TG/DSC analysis. The sample in the crucible was weighed before analysis along with the installation rod, then after pyrolysis at 650 $^{\circ}\text{C}$, and after finishing the analysis. The sample was not weighed after the desorption of free hydrocarbons at 300 $^{\circ}\text{C}$ because trace amounts of products were observed in this phase, representing at most tenths of one percent of the total pyrolysis products.

4. Results and Discussion

4.1. Rock-Eval

Rock-Eval (RE) pyrolytic analysis is the most common, preliminary, geochemical method of studying the hydrocarbon potential of source rocks, to determine, i.a. hydrocarbon potential, the type of kerogen contained in rocks and the thermal maturity of organic matter. Basing on the results of our investigation, the samples representing shale series of Menilite Beds can be divided into three groups with respect to the level of thermal

evolution, as confirmed by $T_{\max}$ values (Table 1). Samples from the Gorlice area showed the lowest thermal maturity, thus indicating the presence of a primary generation potential ranging from 17.39 to 87.73 mg HC/g of rock (Figure 2). The samples from the Wiśniowa area showed a slightly higher level of thermal transformation equivalent to an oil window (a $T_{\max}$ in the range of 437–441 °C), and thus, the hydrocarbon potential was partially realized through the generation processes initiated (S_2 in the range of 5.8–22.7 mg HC/g of rock). The highest thermal maturity was observed in case of Sample 7, collected from the Dukla unit (tectonic window), which had an S_2 generation potential of 15.7 mg HC/g of rock and an HI of 226 mg HC/g of TOC. All samples from the Menilite Beds can be classified as excellent-quality source rock (Figure 2), for which TOC contents are very high, in the range of 5.8% to 17.85%. The Mienilite samples contain different types of kerogen (Type II, mixed II/III, and III).

The Istebna Beds demonstrated significantly lower parameters for hydrocarbon generation quality, for which the S_2 generation potential did not exceed 5 mg HC/g of rock; the TOC for all samples was less than 4%, and the HI remained in the range of 73 to 102 mg HC/g of TOC. These values of parameters mean that these sediments can be classified as medium-quality source rock (Table 1, Figure 2). The level of thermal transformation at the oil window indicates a low degree of realization of the original generation potential. The level of thermal transformation at the beginning of the oil window level indicates a low degree of depletion of the original generation potential. It means that low hydrogen index is not a result of generation processes, but it is characterized by a type of organic matter classified as type III kerogene.

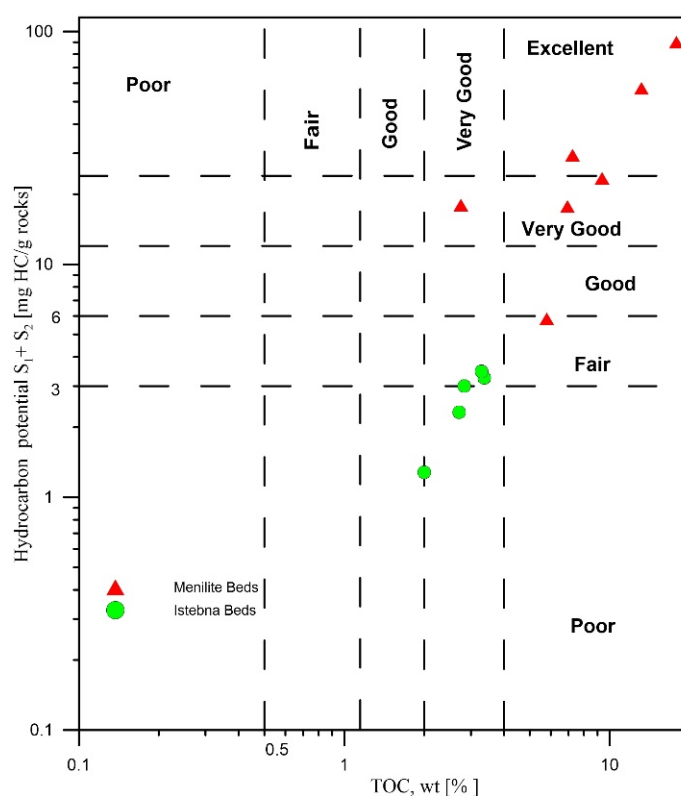


Figure 2. Variation in generation potential of Menilite and Istebna Beds. Boundaries according to Peters and Cassa [32].

Table 1. Rock-Eval pyrolysis results [17].

Location	No.	T _{max}	S ₁	S ₂	PC	RC	TOC	HI	OI	MINC
Menilite Beds										
Gorlice	1	407	1.65	55.45	4.86	8.31	13.17	421	16	0.25
Falkowa	2	413	2.14	87.73	7.57	10.28	17.85	491	8	0.25
Przydonica	3	424	0.59	17.39	1.53	1.22	2.75	632	18	4.33
Łuska Stróż	4	426	0.49	28.95	2.65	4.59	7.24	400	52	0.33
Wiśniowa area	6	441	0.04	5.80	0.62	5.18	5.80	100	44	0.2
	5	437	0.67	22.77	2.08	7.27	9.35	244	24	0.37
Ropa (Dukla Unit)	7	456	2.06	15.68	1.5	5.44	6.94	226	12	4.06
Istebna Beds										
Równe-2	8a	437	0.19	3.44	0.34	3.03	3.37	102	10	0.34
Równe-2	8b	439	0.18	3.29	0.32	2.97	3.29	100	10	0.31
Równe-2	8c	439	0.13	2.45	0.25	2.46	2.71	90	17	0.29
Równe-2	8d	437	0.15	2.85	0.29	2.54	2.83	101	17	0.32
Kryg-4	9	438	0.17	1.45	0.15	1.85	2.00	73	11	0.27

Explanations: T_{max}—the temperature at which the maximum amount of organic hydrocarbons is generated (°C); S₁—the quantity of free hydrocarbons at moderate temperature (300 °C) (mg HC/g of rock); S₂—hydrocarbons generated by the pyrolytic degradation of the heavy products and kerogen (300–650 °C) (mg HC/g of rock); PC—pyrolytic carbon content (wt %); RC—residual carbon content (wt %); TOC—Total Organic Carbon (wt %); HI—Hydrogen Index (mg HC/g of TOC); OI—Oxygen Index (mg CO₂/g of TOC); MINC—Mineral Inorganic Carbon (wt %).

4.2. TG/DTG

Another thermal method, which was used for the analysis and differentiation of the studied source rocks, was the widely used and valued TG/DTG method. The results of thermogravimetric analysis are presented in Figure 3, which shows a loss of mass in subsequent non-isothermal stages of the experiment (in sections 30–300 °C, 300–650 °C, and 650–1050 °C). At each of these stages, the weight loss—which is a result of gas evolution from the sample during heating—can be determined from the TG curve. The results, taking into account the weight losses in individual temperature ranges, are compared in Tables 2–4. An example thermogram for a rock sample from Menilite layers (Sample 1), depicting the entire measurement cycle, is presented in Figure 3. In the range 30 to 300 °C, a DTG curve (a TG derivative) is generated, which makes it possible to interpret the temperature at which the fastest weight loss of the sample takes place and thus the highest reaction rate. For the TG/DTG analysis, these temperatures were marked with the symbols T_{TG} to distinguish them from the T_{max} obtained in the Rock-Eval analysis.

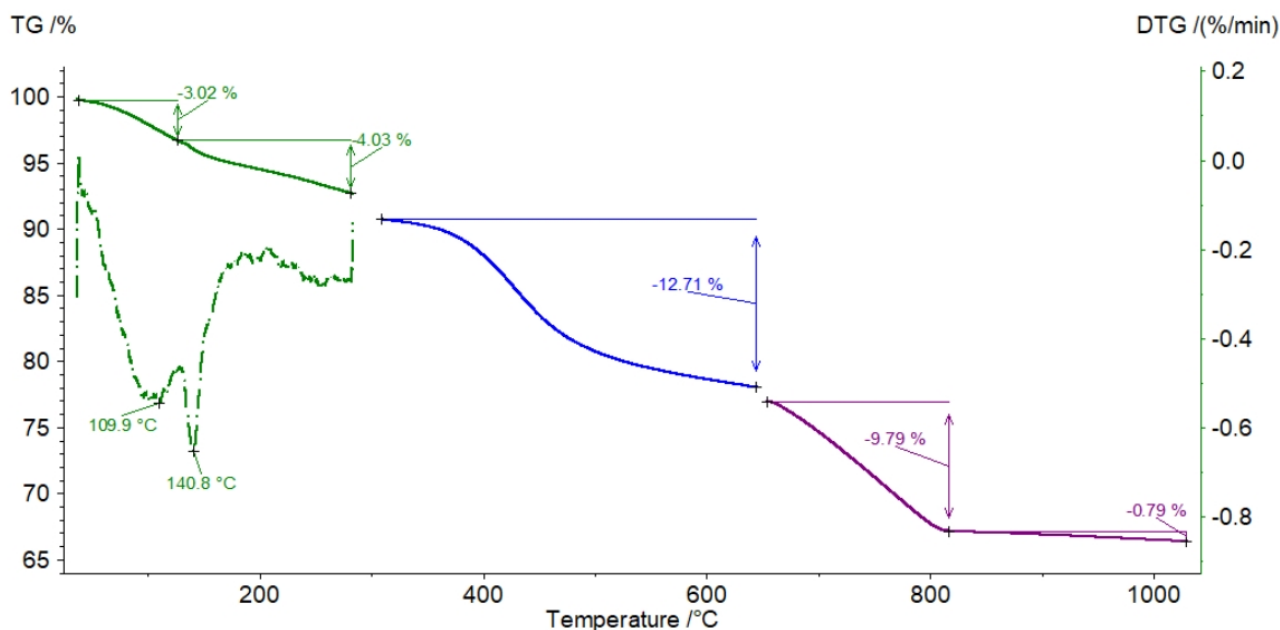


Figure 3. An example of the thermogravimetric analysis for Sample 1. Weight loss in subsequent non-isothermal stages is determined from the TG curve (solid line). The DTG curve (dashed line) enables the T_{TG} temperature to be determined.

Table 2. Comparison of weight loss in samples representing Menilite Beds in the three-part Py/GC and TG analyses in relation to generation potential values.

Menilite Beds—Outcrop Samples		Py/GC				TG		RE
Location	Sample No.	3	4	5	6	7	8	9
Gorlice	1	27.48	22.96	4.51	23.29	12.71	10.58	55.45
Falkowa	2	28.74	n.a.	n.a.	30.03	18.37	11.66	87.73
Przydonica	3	23.05	6.64	16.41	16.30	4.47	11.83	17.39
Łuska Stróż	4	18.67	16.04	2.63	14.72	8.41	6.31	28.95
Wiśniowa area	6	7.94	5.18	2.76	6.51	3.10	3.41	5.80
Wiśniowa area	5	26.98	5.79	21.18	19.22	5.34	13.88	22.77
Ropa	7	24.01	5.90	18.11	19.22	5.34	13.88	15.68

3—total weight loss during Py/GC at 300–1000 °C (%); 4—weight loss during Py/GC from 300 to 650 °C (%); 5—weight loss during Py/GC from 650 to 1000 °C (%); 6—total weight loss during TG analysis from 300 to 1050 °C (%); 7—weight loss during TG analysis from 300 to 650 °C (%); 8—weight loss during TG analysis from 650 to 1000 °C (%); 9— S_2 parameter from Rock-Eval pyrolysis, representing the amount of HC obtained during pyrolysis from 300 to 650 °C; n.a.—not tested between stages.

Table 3. Comparison of the weight loss of kerogen samples separated from Menilite Beds in the three-stage Py/GC and TG analyses.

Sample		Py/GC				TG		RE
1	2	3	4	5	6	7	8	
7 K	52.16	29.96	22.20	75.12	17.70	57.42	92.10	
1 K	63.83	55.65	8.18	76.52	38.17	38.35	261.76	
3 K	41.91	36.13	5.78	81.86	42.97	38.68	335.00	
2 K	na	na	na	82.30	41.50	40.80	307.25	

1—kerogen sample number according to the location from Tables 1 and 2; 2—total weight loss during Py/GC from 300 to 1000 °C (%); 3—weight loss during Py/GC from 300 to 650 °C (%); 4—weight loss during Py/GC from 650 to 1000 °C (%); 5—total weight loss during TG analysis from 300 to 1050 °C (%); 6—weight loss during TG analysis from 300 to 650 °C (%); 7—weight loss during TG analysis from 650 to 1000 °C (%); 8— S_2 parameter from Rock-Eval pyrolysis, representing the amount of HC obtained during pyrolysis from 300 to 650 °C; n.a.—not analyzed.

Table 4. Comparison of the weight loss of samples representing Istebna Beds in the three-stage Py/GC and TG analyses.

Istebna Beds				Py/GC			TG		RE
1	2	3	4	5	6	7	8	9	10
Równe-2	2421.5	8a	12.92	7.18	5.74	11.44	7.03	4.41	3.44
Równe-2	2491.4	8b	10.74	6.98	3.77	11.29	7.03	4.26	3.29
Równe-2	2551.6	8c	9.27	5.60	3.67	8.01	5.41	2.60	2.45
Równe-2	2553.8	8d	9.26	7.07	2.19	10.86	7.22	3.64	2.85
Kryg-4	1150.7	9	10.64	7.22	3.42	9.75	7.21	2.54	1.45

1—Borehole name; 2—depth (m); 3—sample no.; 4—total weight loss during Py/GC from 300 to 1000 °C (%); 5—weight loss during Py/GC from 300 to 650 °C (%); 6—weight loss during Py/GC from 650 to 1000 °C (%); 7—total weight loss during TG analysis from 300 to 1050 °C (%); 8—weight loss during TG analysis from 300 to 650 °C (%); 9—weight loss during TG analysis from 650 to 1000 °C (%); 10— S_2 parameter from Rock-Eval pyrolysis, representing the amount of HC obtained during pyrolysis from 300 to 650 °C.

In the first range (30–300 °C), the weight loss visible from the TG curve (Figure 3) is not only a result of water being released from the sample (free and bound water in clay minerals), but it also indicates the possibility of CO₂ emission and free hydrocarbon release, which corresponds to the S_1 peak in the Rock-Eval analysis [33,34]. The presence of free hydrocarbons provides information on the maturity level of the sample (unless they are migration hydrocarbons). In the case of the Istebna Bed samples, the weight loss was single-staged, with the peak at about 90 to 100 °C, which is associated with the evaporation of free water. However, in the case of rock samples from the Menilite Beds, the weight loss in the first stage of the experiment (30–300 °C) usually occurs in two stages (Figure 3), which indicates the presence of free hydrocarbons. Free hydrocarbons in sample 1 are also confirmed to have a relatively high S_1 parameter (RE).

During thermogravimetric experiments in the temperature range of 300–650 °C, organic matter is pyrolyzed from rock samples heated in an inert atmosphere, and the residual organic matter is then burnt in an oxidizing atmosphere (in the interval 650–1050 °C) [2]. A thermogram for a rock sample representing the Istebna Beds depicting the whole measurement cycle is shown in Figure 4. From 300 to 650 °C, the DTG curve (dashed line) is generated as a derivative of the TG curve.

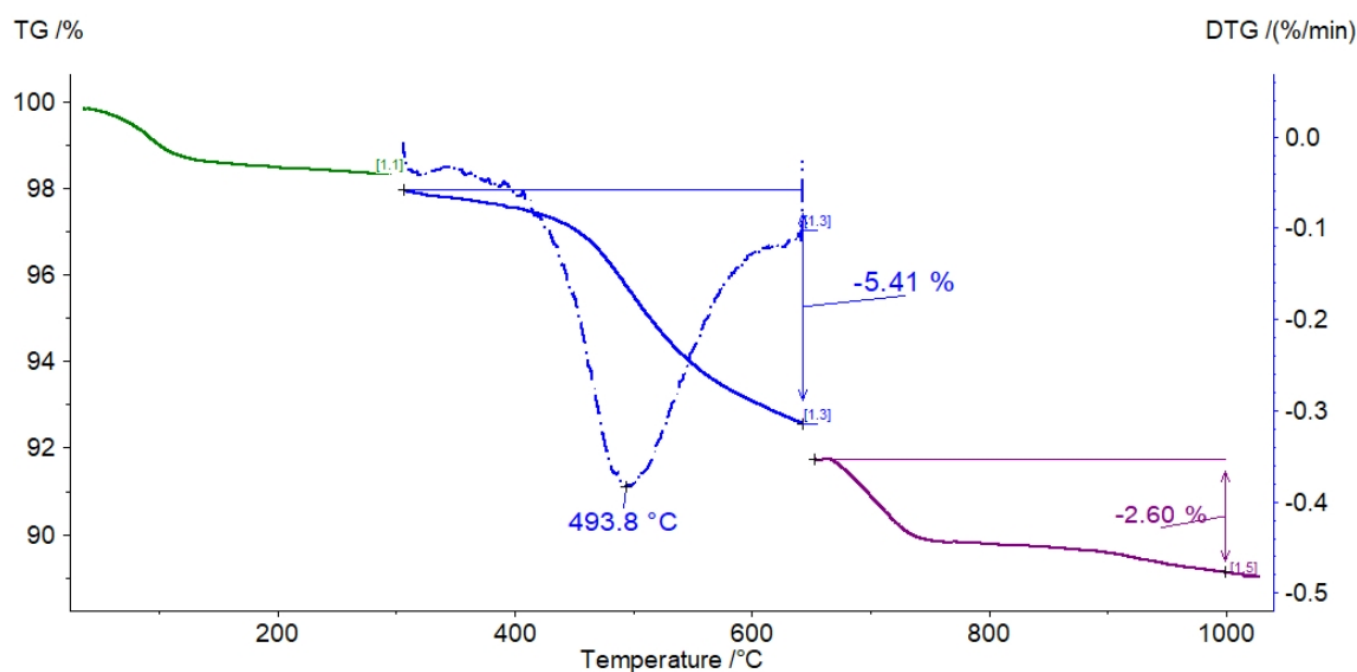


Figure 4. An example of the thermogravimetric analysis in non-isothermal intervals (Sample 8c from the Istebna Beds). The solid line shows the mass loss (TG). The dashed line shows the DTG in the range of 300–650 °C.

All samples representing the Istebna layers show a single-staged decomposition process from 300 to 650 °C. The temperature at which the mass is lost at the fastest rate (T_{TG}) for rock samples belonging to the Istebna Beds was from 493.8 to 529.7 °C. In the case of menilite rock samples, the maximum mass loss temperature (T_{TG}) was from 428.4 to 538.9 °C. This is a very wide range, indicating the varied thermal maturity of menilite shales. In addition, in the case of this group of rocks, the decomposition of the sample is not always single-staged, as in the case of rocks from the Istebna layers. An example comparison of the course of two-staged pyrolysis (for sample 5) and single-staged (for sample 7) is shown in Figure 5.

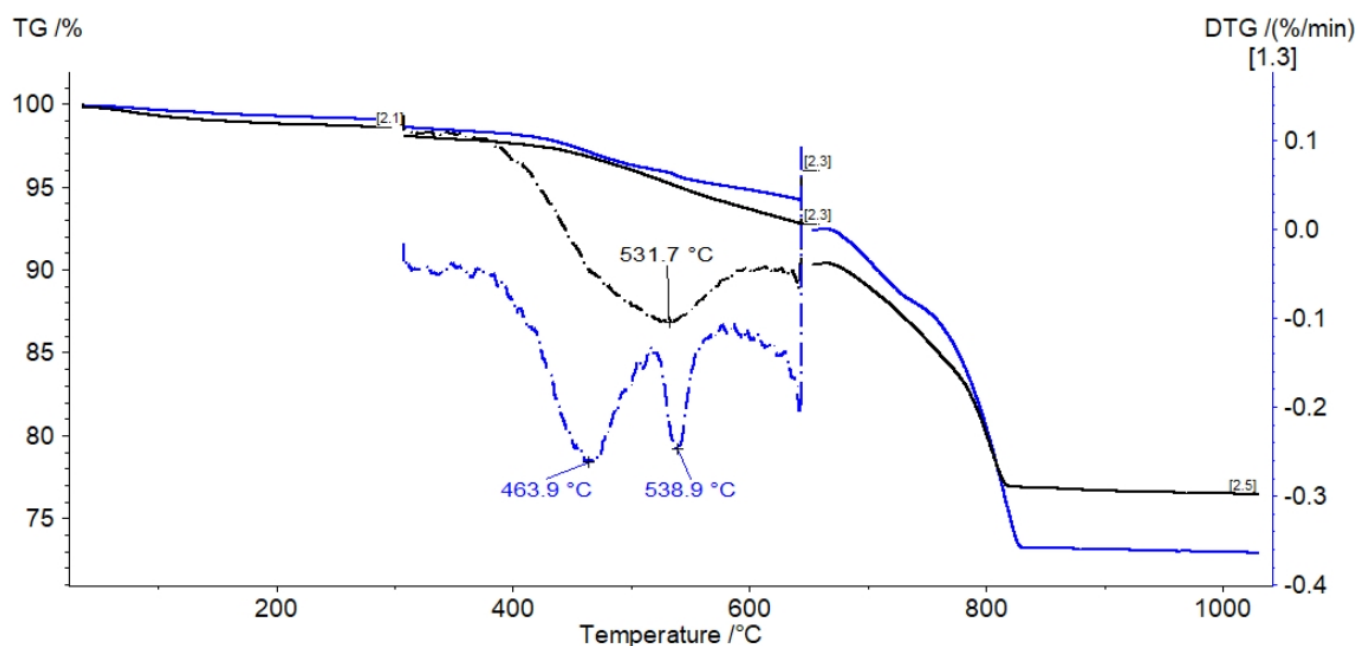


Figure 5. Comparison of TG curves (solid line) and DTG curves (dashed lines) for menilite layer samples (sample 5 in blue and sample 7 in black).

The temperature range of 300–650 °C is the main stage of decomposition (pyrolysis) of organic matter. In the case of Sample 5, this process was two-staged (T_{TG} : 463.9 and 538.9 °C), whilst for sample 7, it was single-staged (T_{TG} : 531.7 °C). The peaks determined on the DTG curves indicate episodes of gas evolution from the sample during pyrolysis. According to Durand [31], the hydrocarbons from the sample are released below 500 °C, whilst above this threshold, there is a thermal remodeling of the internal structure of the organic matter without any significant loss of mass. Our research indicated the higher maximum temperatures of the pyrolysis process. In the case of some samples belonging to the Menilite layers (e.g., samples 6 and 7), the pyrolysis process is single-staged, with the maximum temperature (T_{TG}) above 530 °C. This discrepancy with the results reported by Durand [31] is due to the fact that the data described here refer to rock samples (and not to isolated kerogen, as discussed below), but it also indicates the high maturity of the organic matter present in these samples, which were derived from the Menilite layers. The presence of a double peak in the DTG curves (as in the case of sample 5, see Figure 5) indicates a two-staged course of the pyrolysis process.

In the temperature range of 650–1000 °C, there is a significant weight loss (on the TG curves) for both samples shown in Figure 5. This is due to the presence of carbonates in the samples, which decomposes at 700 to 800 °C [35,36].

In the case of the rock samples from the Menilite layers, four samples of separated kerogen were additionally analyzed. The temperature at which the pyrolysis reaction proceeded the fastest (T_{TG}) in the tested kerogen samples was in a narrow range: from about 414 to 440 °C. The mass loss as a result of the pyrolysis process in the range of

300–650 °C spanned from 17.70% to 42.97% of the sample's mass. In the next stage of the experiment, the combustion of the remaining organic matter took place at above 650 °C. The weight loss at this stage ranged from 38.71% to 57.42% (Table 3); sample 7K demonstrated the highest loss as well as the lowest weight loss in the pyrolysis process (in the range of 300–650 °C). The reason for this is the high maturity of the organic matter in the sample, which is confirmed by the high T_{TG} (531.7 °C) observed for the rock from which the kerogen originated (sample 7). Therefore, in the kerogen sample, the pyrolysis process did not end at 650 °C, when the experiment conditions were changed; the non-pyrolyzed organic matter was only burnt in the last stage of the experiment, which caused a substantial loss of mass (close to 60%).

Figure 6 shows a comparison between the results obtained for a whole rock sample and the kerogen separated from it, using Sample 7 as discussed above. In the rock sample, the pyrolysis process began at a temperature of about 420 °C and remained fairly uniform up to a temperature of almost 600 °C, reaching T_{TG} at 533.1 °C. The combustion of residual organic matter ended at 815 °C. The process of pyrolysis in a kerogen sample begins earlier than in rock, owing to the presence of inorganic matter in the rock that inhibits pyrolysis [26]. The T_{TG} for the kerogen sample was 424.5 °C. The residual organic matter and a large part of the organic matter that had not undergone pyrolysis burnt up to a temperature of almost 956 °C. Thus, it can be seen that under the conditions of this experiment, it was not possible to fully pyrolyze it in the range of 300–650 °C. The presence of inorganic matter not only inhibits the pyrolysis of organic matter but also can disturb the thermogram of pyrolysis process. Some minerals, including sulfides (pyrite, marcasite) or some clay minerals (e.g., kaolinite), decompose in the temperature range between 300 and 650 °C [26,37–39].

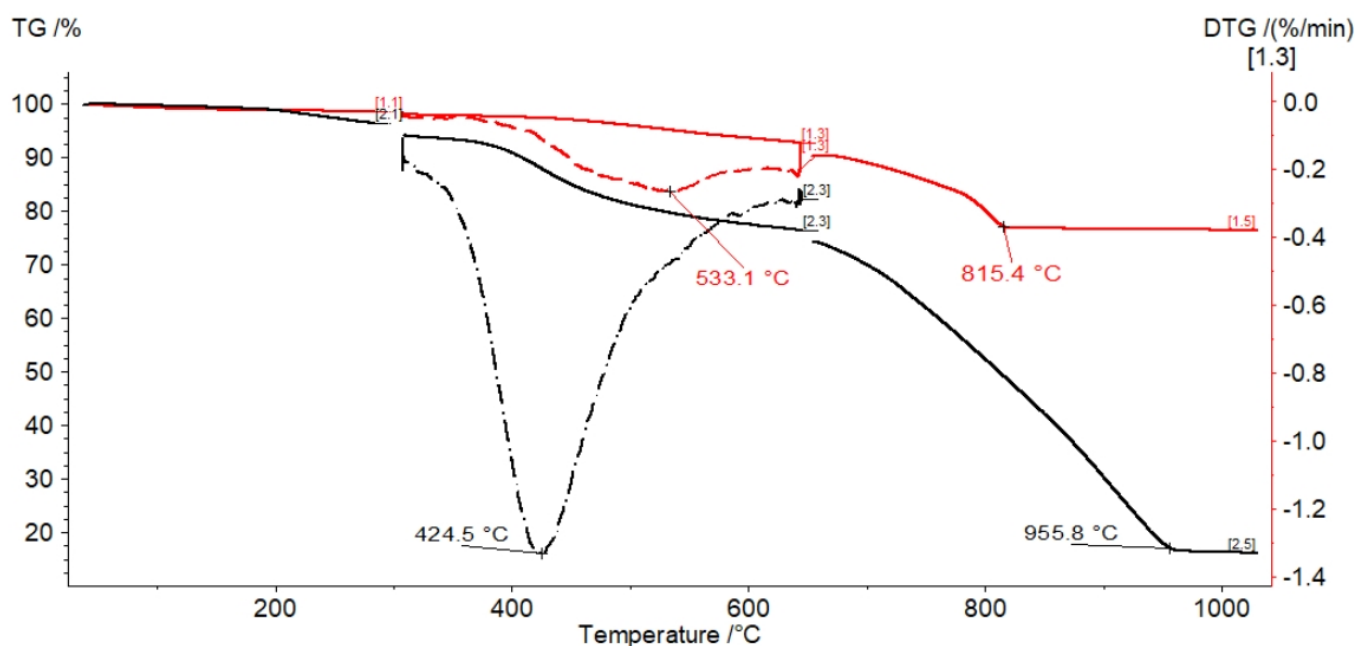


Figure 6. Results of thermogravimetric analysis obtained for the rock sample no. 7 (red curves) and the kerogen separated from it (7K; black curves). TG—solid lines; DTG—dashed lines.

4.3. Py/GC

The Py/GC analysis was used to determine the distribution of hydrocarbon fractions generated by both types of source rocks, in the C_1 – C_9 , C_9 – C_{15} and C_{15+} ranges, in three pyrolytic stages. Applying pyrolysis combined with gas chromatography on the same samples allowed determination of the decomposition products, in addition to the degree of weight loss in the same temperature ranges [3]. All results of the three types of pyrolysis, including weight loss and the yield of the hydrocarbons produced, are summarized in

Table 2 for the Menilite Beds, in Table 3 for selected samples of the kerogen isolated from them, and in Table 4 for the Istebna Beds. The weight loss during the Py/GC experiments was very similar to the monitored steady-state weight loss during TG analysis, especially in the 300–650 °C temperature range, which corresponds to the main phase of hydrocarbon production in the Rock-Eval analysis, which is an indicator for assessing the generation potential of source rocks. The sample with the highest generation potential had the highest overall weight loss in Py/GC pyrolysis: 28.74% over the entire temperature range of 300–1000 °C, with higher product yields in the 300–650 °C range. This sample had a low level of thermal transformation below the threshold of the oil window. For samples of higher maturity, both from the Silesian unit (samples 6 and 5) and the Dukla unit (sample 7), the maximum weight loss was shifted toward higher temperatures: 650–1000 °C (Table 2, Figure 7).

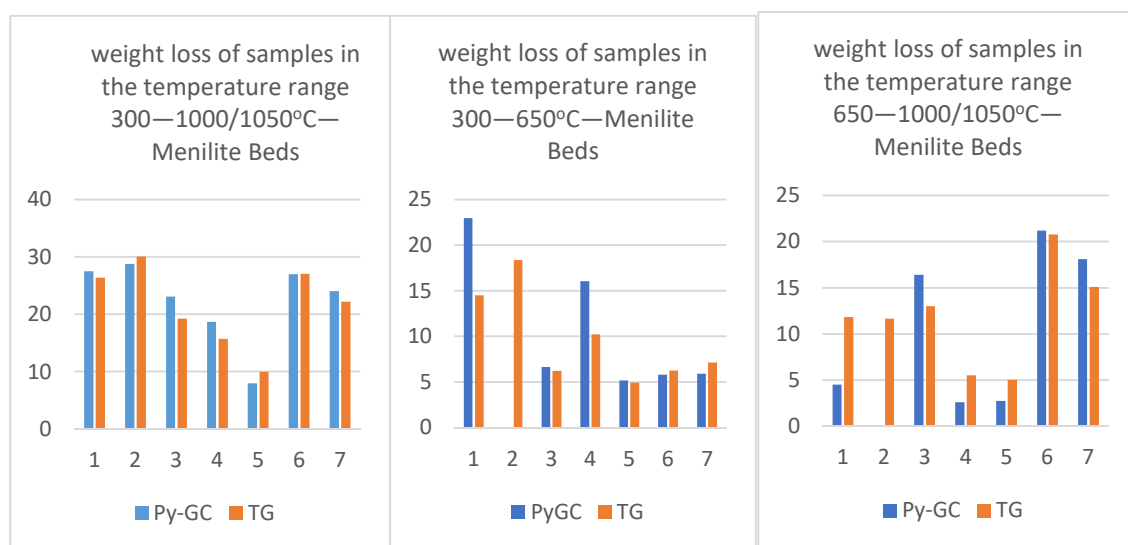


Figure 7. Comparison of weight loss (%) during Py/GC and TG/DSC pyrolysis of Menilite Bed samples in total and in two temperature ranges.

Comparative analysis was also performed for the kerogen separated from the Menilite Beds (four samples), the results of which indicate much higher total weight loss values in TG pyrolysis than in Py/GC pyrolysis; additionally, these values were very similar in all samples, ranging from 75.12% to 82.30%, whilst in Py/GC pyrolysis, the total weight loss values (analyzed in only three kerogen samples) were more varied: from 41.91% to 63.83%. This fact can be explained by the higher temperature range (up to 1050 °C) in TG. This means that a larger range of organic matter decomposition in all Menilite samples occurs at much higher temperatures, close to 1000 °C (Table 3). This is particularly evident for the sample exhibiting the highest involvement of thermal evolution of organic matter in the Dukla unit (Sample 7). In that case, hydrocarbon production is already lower due to the partially realized generation potential, as illustrated by the Rock-Eval results. An additional reason is that the sample size was too small in the case of kerogen, and thus, there was a greater possibility of error during Py/GC analysis, where weight loss monitoring is not conducted online. Thus, for the analysis of isolated kerogen, the TG technique yields more reliable results regarding the weight loss and measures the total hydrocarbon yield in this temperature range. The amount of hydrocarbons measured during Rock-Eval pyrolysis is directly proportional to the total weight loss during TG analysis as well as to the weight loss in the temperature range of 300–650 °C. The stages observed in the thermal decomposition, the varying yields in the respective temperature ranges with TG, and the S_2 values for kerogen clearly indicate that the kinetic features of the Menilite Beds vary.

The Istebna Beds are characterized by the dominance of type III kerogen with a low HI and low hydrocarbon production, as represented by the S_2 parameter from Rock-Eval,

ranging from 1.45 to 3.44 mg HC/g of rock. They also had low weight loss values, which is appropriate for the quality of the source rocks (Table 4, Figure 8). It is worth noting that in all the analyzed samples, the highest weight loss values were recorded between 300 and 650 °C, both in Py/GC and TG, which may indicate that lower temperature values are necessary for the complete decomposition of organic matter of the Istebna Beds. Furthermore, the analyzed samples from the Istebna Beds showed little variation between the weight loss values in Py/GC and TG analyses. In all the samples, the total weight loss was approximately 9–11%. It can be concluded that the organic matter is highly homogeneous, serving as the substrate for hydrocarbon generation.

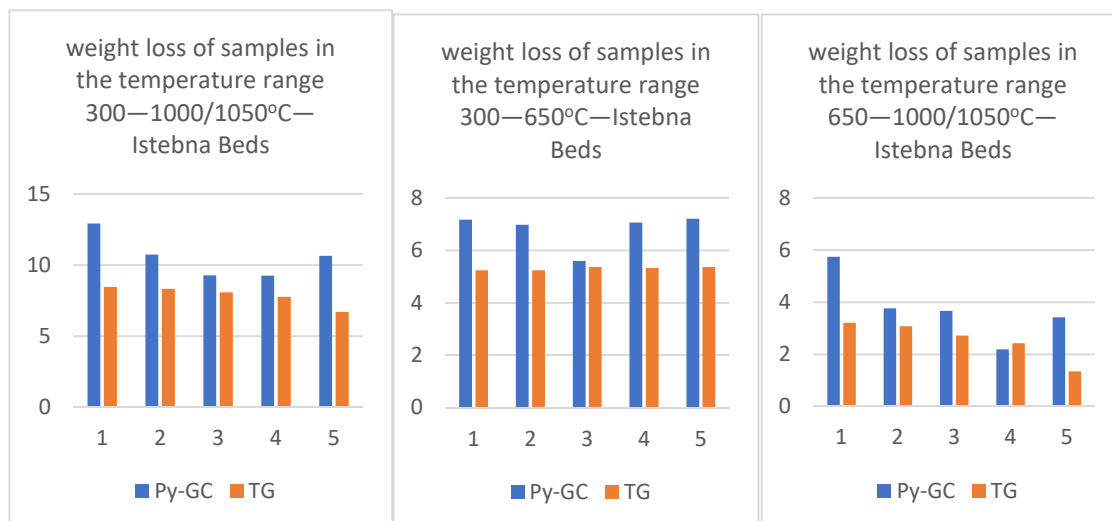


Figure 8. Comparison of the weight loss of samples (%) from the Istebna Beds during Py/GC and TG/DSC pyrolysis in total and over two temperature ranges.

Comparing the weight loss values exhibited by the two pyrolysis methods for the two sets of samples differing in their generation potential values, a very good correlation between the Py/GC and TG methods is clearly evident for both Menilite and Istebna Beds, especially in the temperature range of 300–650 °C. The values of the weight loss correlation coefficient R^2 over this range are 0.96 and 0.98, respectively (Figure 9).

For the Menilite Beds, the weakest correlation between the methods was observed at temperatures from 650 to 1050 °C. However, this can be explained by the different course of analysis at this stage of the experiments. During Py/GC, each stage of the analysis is carried out under inert gas environment without oxygen/air. Under these conditions, only pyrolysis processes are possible. The TG analysis in temperatures between 650 and 1050 °C was carried out in an oxidizing atmosphere, as with the oxidation stage in Rock-Eval pyrolysis, leading to the combustion of residual organic matter rather than just decomposition, and possibly to the oxidation of some rock minerals. Moreover, the third Py/GC stage covered the temperature range of 650–1000 °C, while the last TG stage reached a slightly higher temperature, 1050 °C [40].

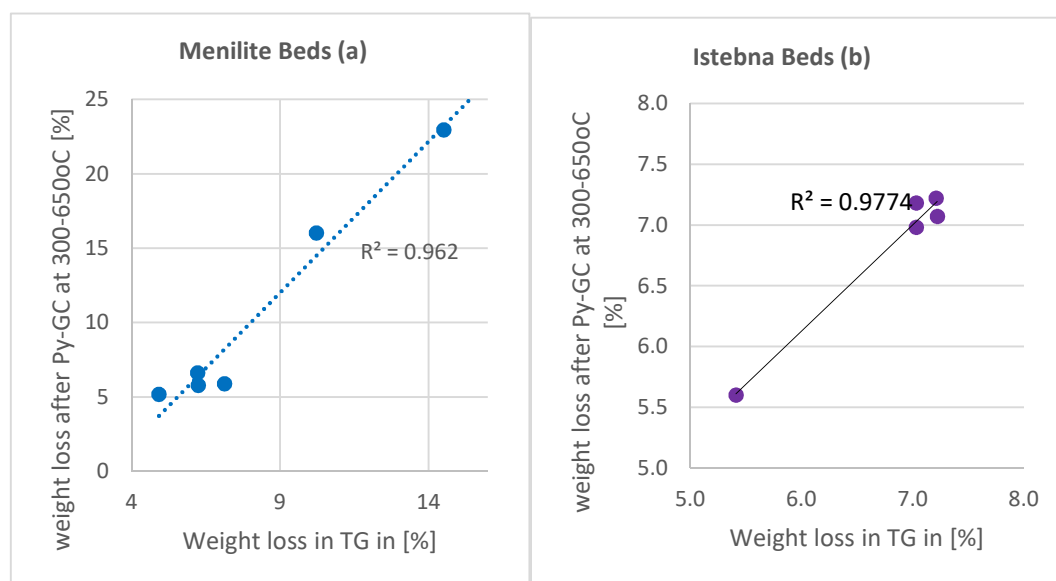


Figure 9. Correlation of Py/GC and TG results in the temperature range of 300–650 °C for samples from the Menilite (a) and Istebna Beds (b).

The reference point for the comparative studies was the S_2 generation potential, which is expressed in milligrams of hydrocarbons generated from one gram of rock under Rock-Eval pyrolysis conditions [41]. The dependence of weight loss on the S_2 generation potential between 300 and 650 °C is illustrated in the graphs, which show a good correlation of the results for Menilite shale, including a slightly better correlation in the TG method than Py/GC. A trend of higher weight loss values in the range of 300–650 °C in Py/GC analysis was observed for higher generation potential values together with low thermal maturity level. In general, a high coefficient of correlation with S_2 was observed (Figure 10). For core samples from the Istebna Beds, no correlation of S_2 with weight loss was observed in either the TG or Py/GC method (Figure 11). This can be explained by the very low generation rates and low hydrocarbon productivity implied by the type of kerogen [42].

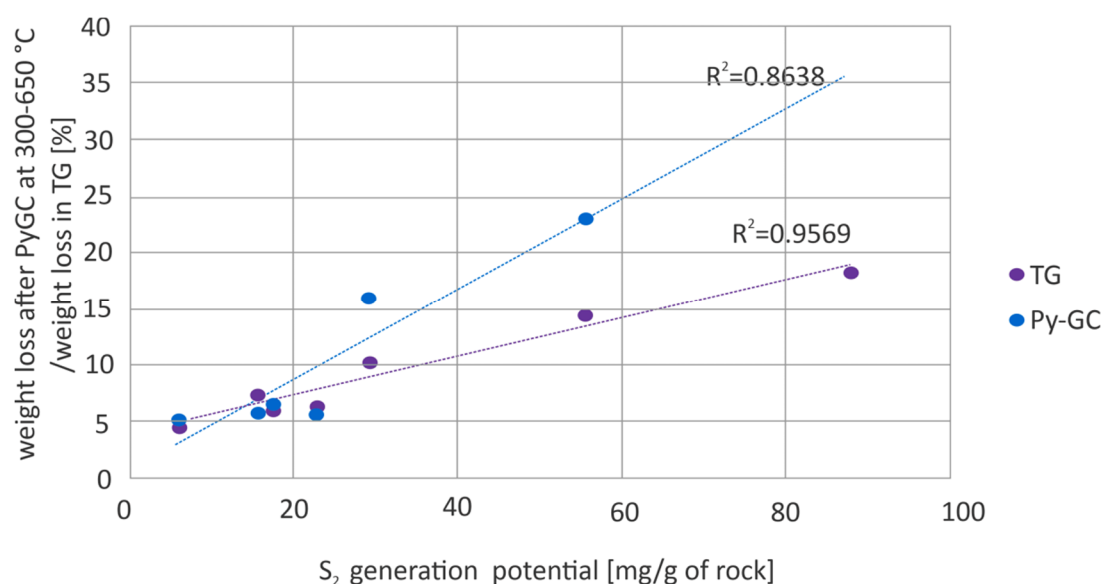


Figure 10. Dependence of weight loss on S_2 generation potential for Menilite samples during Py/GC and TG/DTG pyrolysis at temperatures of 300 to 650 °C.

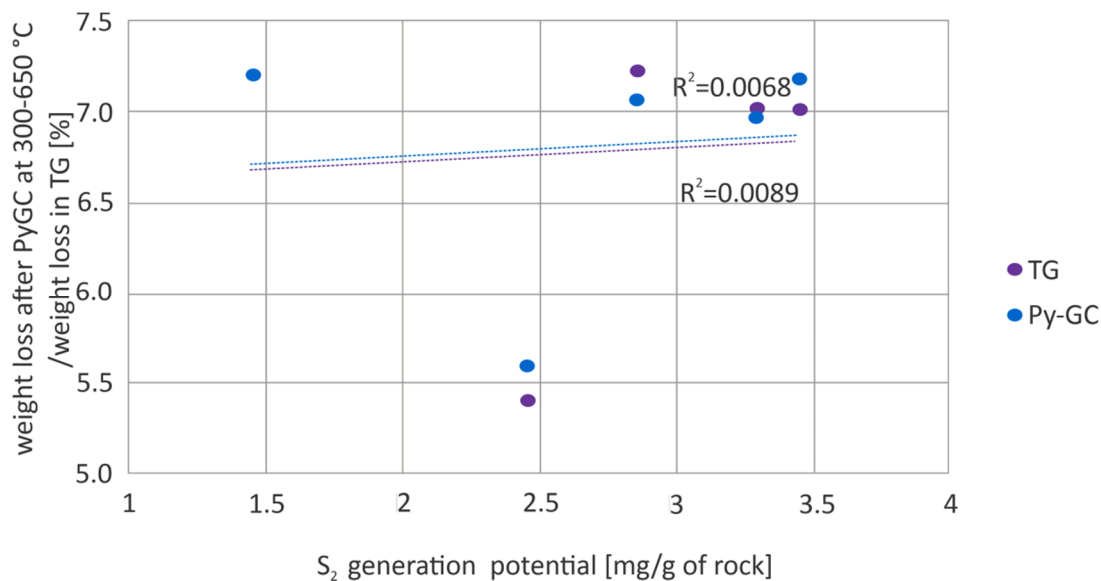


Figure 11. Dependence of weight loss on S_2 generation potential for rock samples from the Istebna Beds during Py/GC and TG/DTG pyrolysis at temperatures of 300 to 650 °C.

Taking into account that during the pyrolysis of source rocks with good quality and low thermal maturity, mainly hydrocarbons are produced, an attempt was made to trace the relationship of the S_2 values for generation potential with the yield indices of Py/GC pyrolysis products in the range 300–650 °C. A very high correlation index was obtained, even for samples from Istebna Beds, for which weight loss does not correlate with the value of generation potential (Figures 12 and 13). The sample weight loss also consisted of mineral degradation products that were not monitored in Py/GC [43].

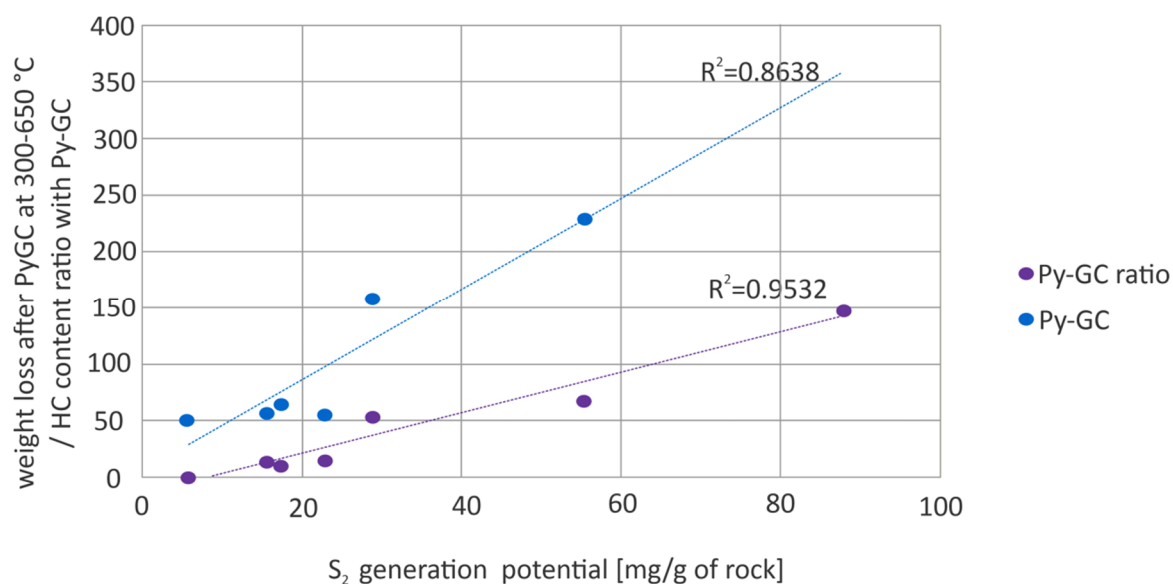


Figure 12. Correlation between the S_2 generation potential and Py/GC pyrolysis parameters in the temperature range of 300–650 °C for Menilite samples.

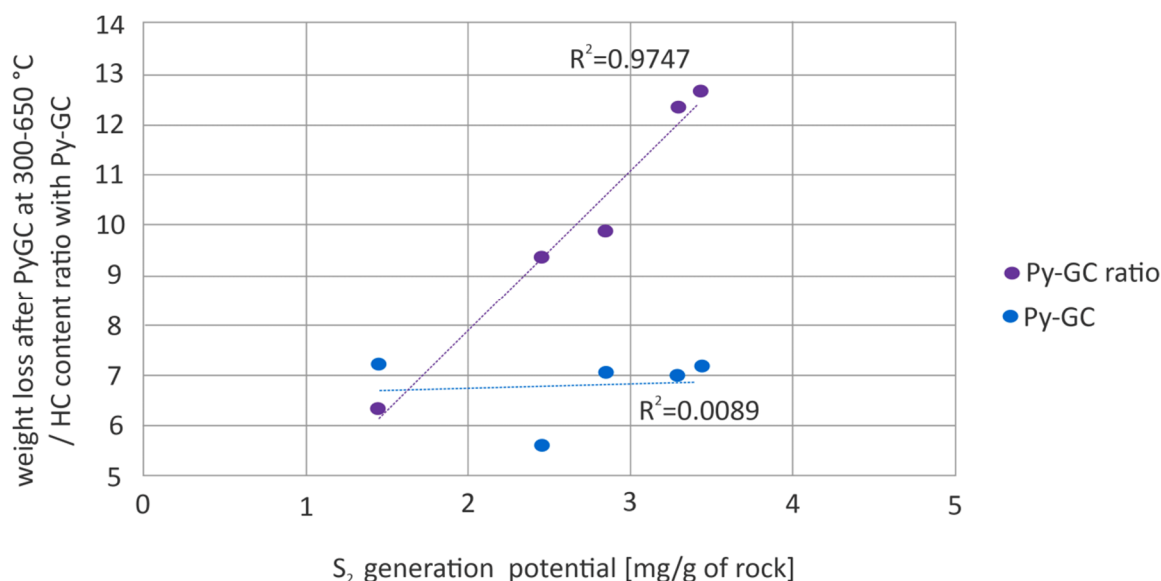


Figure 13. Correlation between the S₂ generation potential and Py/GC pyrolysis parameters in the temperature range of 300–650 °C for core samples from the Istebna Beds.

In addition to analyzing weight loss values in TG and Py/GC experiments, hydrocarbon generation rates were also compared with the maximum temperatures recorded during thermal decomposition in TG and Rock-Eval, which provide indirect information about the rate at which generation processes are occurring and the degree of thermal transformation of the rock under study. In this case, the actual maximum temperature of the S₂ peak (T_{pmax}) was considered, rather than the parameter T_{max} , scaled according to R_o , reflecting the level of thermal maturity. In Figure 14, which presents the temperature correlations from the two methods for both the Menilite and Istebna Beds, a good correlation ($R^2 = 0.82$) can be observed. Thus, both techniques for the thermal decomposition of organic matter can provide equivalent information about the maximum efficiency of hydrocarbon generation.

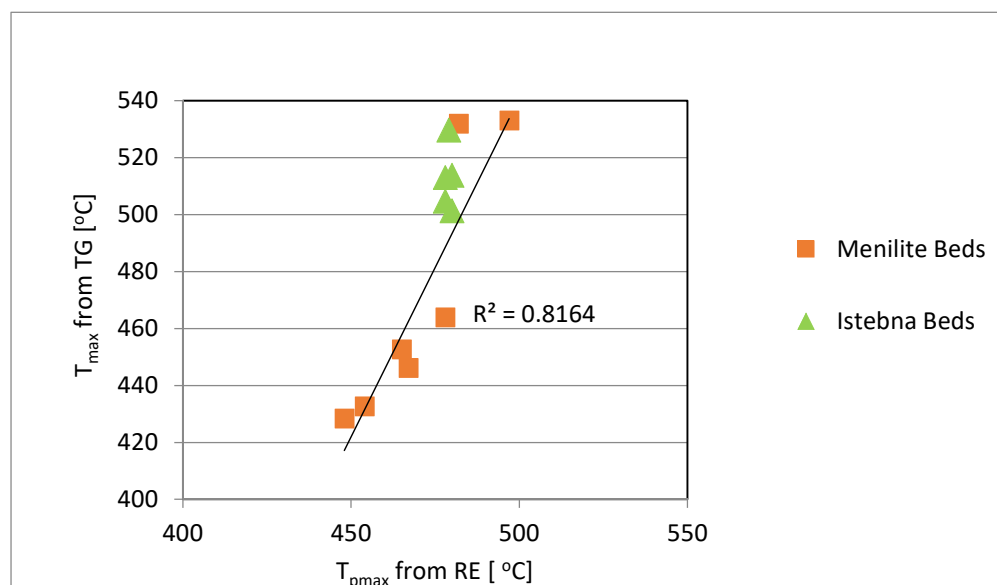


Figure 14. Correlation diagram of the maximum temperature at which the maximum decomposition of organic matter occurs in TG and Rock-Eval pyrolysis.

Py/GC experiments, in comparison to other thermal methods, primarily provide information about the fractional composition of hydrocarbons that are produced by subsequent stages of pyrolysis, of which the most interesting are those obtained between 300 and 650 °C, as they represent hydrocarbons generated from source rocks and are related to the generation potential. As shown in previous studies [4], a proper distribution of the hydrocarbons that can be generated by source rocks is obtained by Py/GC pyrolysis in a narrower temperature range of 300–500 °C, due to the fact that the partial cracking of higher hydrocarbons and enrichment of the C₁–C₉ fraction occur at temperatures over 500 °C. As a result of the reference to the S₂ peak, the experiments were conducted in three stages. The Py/GC results are summarized in the following tables (Tables 5–7) and figures, after desorption at temperatures up to 300 °C was omitted, by taking the average of the results for a given group of samples. In the case of the Menilite formations, the sample from Wiśniowa area (Sample 6)—which differs from the others in character, possibly due to its low hydrocarbon potential and higher maturity—was not included in the mean.

The results of this study clearly indicate the qualitative distinctness of the products being generated, with a predominance of light hydrocarbons generated by the Istebna Beds (97–100%) Figures 15 and 16, in contrast to the much higher proportion of C₁–C₉ and C₉–C₁₅ fractions obtained from the Menilite Beds. These fractions together account for an average of 85% of all products obtained from the Menilite Beds (Figures 15 and 17).

Table 5. Results of Py/GC analysis of the Menilite Bed samples from surface exposures.

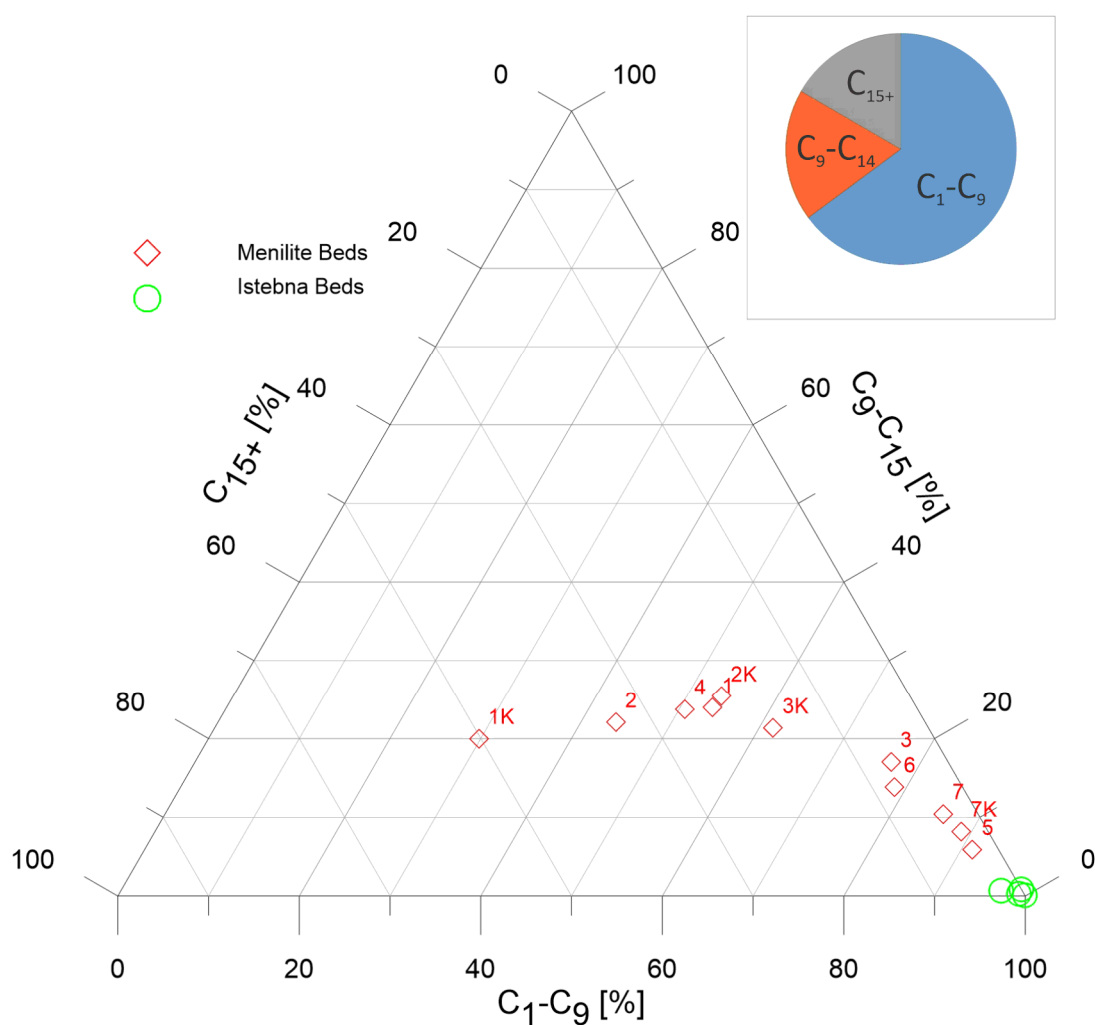
Py/GC Pyrolysis Stage		II 300–650 °C			III 650–1000 °C		
Hydrocarbon Fractions		C ₁ –C ₉	C ₉ –C ₁₅	C ₁₅ +	C ₁ –C ₉	C ₉ –C ₁₅	C ₁₅ +
Location	Sample No.	Fraction Share [%]			Fraction Share [%]		
Gorlice	1	53.54	24.00	22.46	100.00	0.00	0.00
Falkowa	2	43.85	22.09	34.06	99.85	0.07	0.08
Przydonica	3	76.69	17.01	6.30	100.00	0.00	0.00
Łuska Stróż	4	50.63	23.76	25.61	99.88	0.12	0.00
Wiśniowa area	6	91.24	5.87	2.89	100.00	0.00	0.00
	5	78.68	13.81	7.52	100.00	0.00	0.00
Ropa (Dukla Unit)	7	85.73	10.42	3.85	100.00	0.00	0.00

Table 6. Results of Py/GC analysis of kerogen isolated from selected Menilite Bed samples from surface exposures.

Py/GC Pyrolysis Stage		II 300–650 °C			III 650–1000 °C		
Hydrocarbon Fractions		C ₁ –C ₉	C ₉ –C ₁₅	C ₁₅ +	C ₁ –C ₉	C ₉ –C ₁₅	C ₁₅ +
Sample No.		Fraction Share [%]			Fraction Share [%]		
7 K		88.86	8.20	2.94	100.00	0.00	0.00
1 K		29.79	19.99	50.22	100.00	0.00	0.00
2 K		53.80	25.44	20.76	100.00	0.00	0.00
3 K		61.54	21.34	17.12	100.00	0.00	0.00

Table 7. Results of Py/GC analysis of core samples from Istebna Beds.

Py/GC Pyrolysis Stage		II 300–650 °C			III 650–1000 °C		
Hydrocarbon Fractions		C ₁ –C ₉	C ₉ –C ₁₅	C ₁₅ +	C ₁ –C ₉	C ₉ –C ₁₅	C ₁₅ +
Sample No.	Borehole/Depth	Fraction Share [%]			Fraction Share [%]		
9	Kryg-4 (1150.7 m)	100.00	0.00	0.00	100.00	0.00	0.00
8a	Równe-2 (2421.5 m)	97.00	0.68	2.32	100.00	0.00	0.00
8b	Równe-2 (2491.4 m)	99.90	0.10	0.00	100.00	0.00	0.00
8c	Równe-2 (2551.6 m)	99.15	0.29	0.56	100.00	0.00	0.00
8d	Równe-2 (2553.8 m)	99.15	0.85	0.00	100.00	0.00	0.00

**Figure 15.** Fractional composition of pyrolysis products of the Menilite Beds, Istebna Beds, and kerogen samples from the Menilite Beds in the range of 300–650 °C and the average fractional composition for the Menilite Beds.

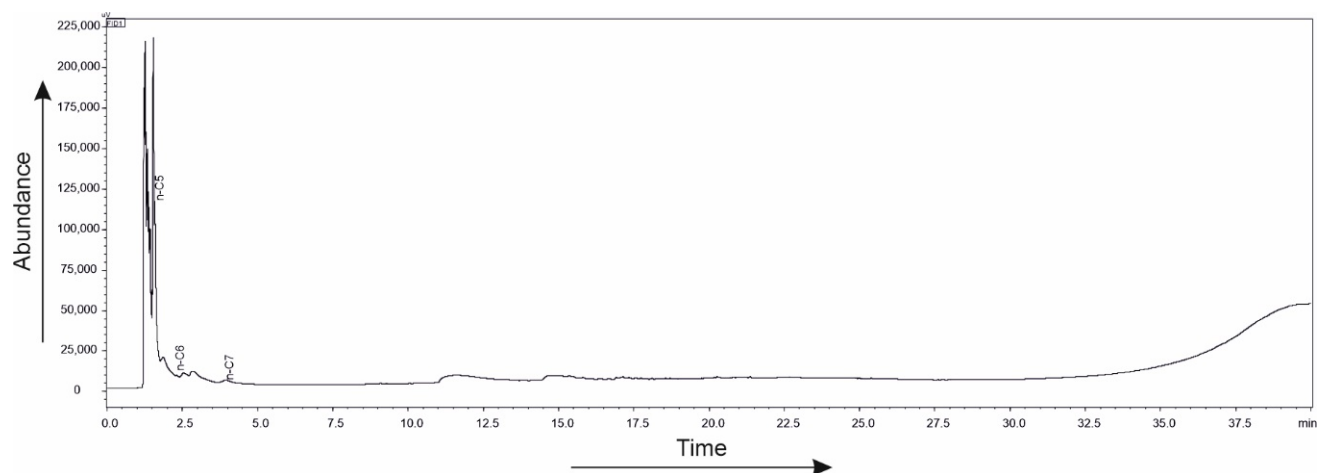


Figure 16. Distribution of hydrocarbon fractions generated through Py/GC at 300–650 °C, using the example of Sample 9 from the Istebna Beds.

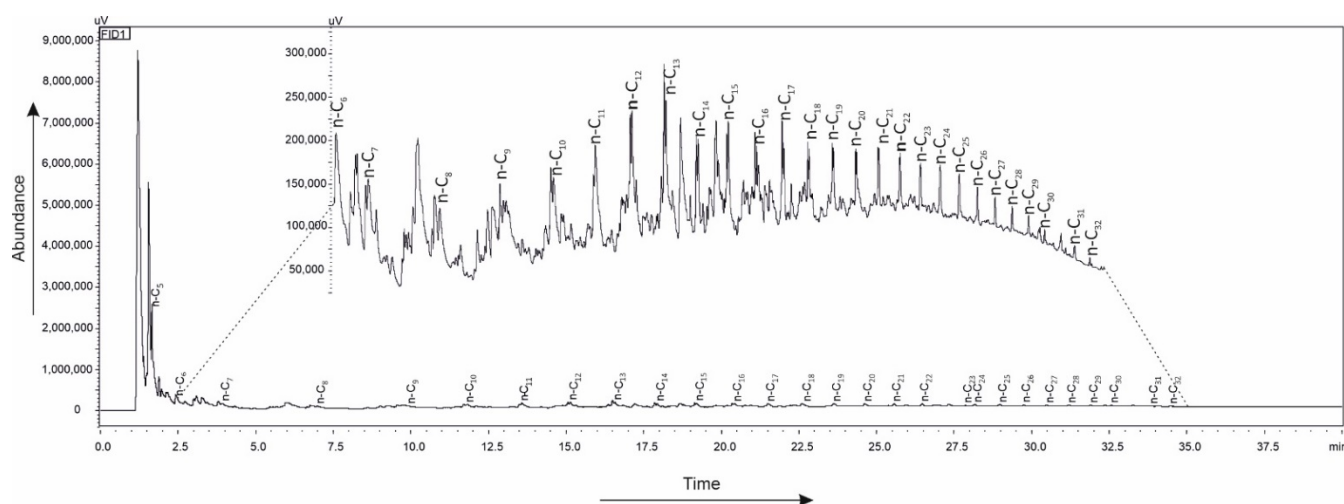


Figure 17. Distribution of hydrocarbon fractions generated through Py/GC at 300–650 °C, using the example of Sample 5 from the Menilite Beds.

The small loss of mass in the first stage of the pyrolysis process can be attributed to the release of free hydrocarbons and volatile compounds at temperatures of 100–350 °C [32]. The main weight loss occurring around 367–521 °C (average temperature) is due to the pyrolysis of bitumen, which is an intermediate material in the generation of hydrocarbons and the kerogen present in the source rocks [44]. The composition of the products generated in this temperature range is shown in Figures 16 and 17. The hydrocarbon pyrolysis products showed a homology distribution of n-alkane/n-alkene doublets from C₇ extending beyond C₃₂, for the pyrolysis of samples representing the Menilite Beds. In the pyrolysis of samples from the Istebna Beds, only the lightest hydrocarbons are visible on the chromatogram.

The gas evolution-related weight loss of all heat-treated samples can be divided into three stages: (1) below 300 °C (minor weight loss stage), (2) the main stage of organic matter degradation (weight loss of 4.92–18.37% at 300–650 °C), and (3) the stable stage (weight loss of 5.03–15.08% at 650–1050 °C). The first stage can be compared to the thermogravimetric analysis of oil shales [43], which was associated with water loss (dehydration and evaporation); in the case of the Menilite Beds under study, the products produced in the first stage included adsorbed hydrocarbons. The main stage of organic degradation occurred at temperatures between 450 and 550 °C, as indicated by the rapid weight loss peak. This is associated with the cracking of macromolecules of kerogen compounds, such as lipids and aromatic groups. Similarly, this stage is mainly the oil and gas production stage during

the pyrolysis process [45]. Above 550 °C, the rate of weight loss slows down and remains constant as the compounds bound to the kerogen were almost completely cracked in the previous stages, and the occluded compounds were released after the destruction of the macromolecular kerogen network.

5. Conclusions

Conducting the experiments, including three types of pyrolysis, one of which has been combined with gas chromatography (Py/GC), allowed the following conclusions to be drawn:

1. The generation potential and type of the products obtained from the pyrolysis of the Menilite and Istebna Beds in the Silesian Unit of the Outer Carpathians, despite the often comparable overall content of organic matter, are significantly different.
2. The application of three pyrolytic methods such as Rock-Eval, TG/DTG, and Py/GC can provide more information about the hydrocarbons produced and can reveal the characteristics of the rate of thermal decomposition of different source rocks.
3. Menilite Beds contain different types of kerogen (Type II, mixed II/III, and III), while Istebna Beds contain mainly Type III kerogen.
4. Thanks to the Py/GC analysis, the distribution of hydrocarbon fractions generated by both types of source rocks was obtained. This made it possible to distinguish between the generation capabilities for light hydrocarbons by Istebna Beds and oil by Menilite Beds. The variation between these groups is a direct result of their source nature.
5. The hydrocarbon pyrolysis products showed a homology distribution of n-alkane/n-alkene doublets from C7 extending beyond C32, for the pyrolysis of samples representing the Menilite Beds. In the pyrolysis of samples from the Istebna Beds, only the lightest hydrocarbons are visible on the chromatogram. For the Istebna Beds, n-alkanes from the C1–C5 range were detected as the main pyrolysis products, which proves that the organic matter dispersed in these sediments are of the gas-prone type. Rock-Eval analysis showed that the organic matter reached a degree of maturity corresponding to the early thermocatalytic processes (the initial oil window stage) and show a high correlation with the generation potential S2.
6. TG/DTG analysis results indicate a greater variation in the thermal maturity of the Menilite source rocks, where the most active decomposition of organic matter occurred in the wide range of 428–540 °C. In the case of rock samples from the Istebna Beds, the peaks of this decomposition fell between 494 and 530 °C.
7. The most significant difference between the two groups of rocks revealed by TG/DTG analysis was a two-stage weight loss in the case of Menilite shales, while the Istebna shales were characterized by a single-stage weight loss at the main decomposition temperature range. The two-stage decomposition of Menilite samples demonstrates the complexity of the organic matter in these rocks and the two distinct episodes of pyrolysis gas release.
8. TG/DTG thermal analysis provided additional information about the initial stage of sample decomposition at temperatures below 300 °C, enabling the weight loss effects resulting from sample dehydration to be distinguished from those associated with the release of free hydrocarbons.
9. By comparing the actual temperature of organic matter decomposition from the Rock-Eval analysis (Tpmax) with the temperature of maximum weight loss TTG during the thermogravimetric analysis, it was concluded that the two measurements correlate closely and can be used to assess the level of thermal transformation of organic matter with equal success.
10. The TG analysis of kerogen from the Menilite Beds showed regardless of the generation potential, weight loss values over the entire temperature range of TG analysis amounting to approximately 80%.
11. The application of the three methods mentioned above seems to have brought about a better understanding of the mechanism of hydrocarbon generation, resulting from

the different nature of organic matter in the two groups of source rock. This is a progression toward the reliable application of organic matter decomposition parameters to simulating the generation and expulsion processes in petroleum basin modeling.

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References

- Labus, M.; Matyasik, I. Application of different thermal analysis techniques for the evaluation of petroleum source rocks. *J. Therm. Anal. Calorim.* **2019**, *136*, 1185–1194. [\[CrossRef\]](#)
- Labus, M.; Kierat, M.; Matyasik, I.; Spunda, K.; Kania, M.; Janiga, M.; Bieliń, W. *Charakterystyka Generacyjna Warstw Menilitowych w Oparciu o Zintegrowane Wyniki Analiz Termicznych*; Conference Paper, Geopetrol Zakopane-Kościelisko; Instytut Nafty i Gazu—Państwowy Instytut Badawczy: Kraków, Poland, 2018.
- Matyasik, I.; Spunda, K.; Kania, M.; Janiga, M.; Bieliń, W.; Kierat, M. Comparison of generation products of potential source rocks in the Outer Carpathians in Poland. In Proceedings of the 29th International Meeting on Organic Geochemistry, Gothenburg, Sweden, 1–6 September 2019.
- Matyasik, I.; Kierat, M.; Kania, M.; Brzuszek, P. Ocena jakościowa węglowodorów generowanych z różnego typu skał macierzystych oparta na wynikach badań PY-GC, Rock-Eval i Leco. *Nafta-Gaz* **2017**, *10*, 719–729. [\[CrossRef\]](#)
- Matyasik, I.; Dziadzio, P.S. Reconstruction of petroleum system based on integrated geochemical and geological investigation: Selected examples from middle Outer Carpathians in Poland. In *The Carpathians and Their Foreland: Geology and Hydrocarbon Resources*; AAPG Mem 84 (CD Edition); Golonka, J., Picha, F.J., Eds.; AAPG: Tulsa, OK, USA, 2006; pp. 497–518.
- Matyasik, I. Oil system of the Silesian and Dukla unit in the Jasło-Krosno-Sanok area. *Nafta-Gaz* **2009**, *3*, 201–206.
- Matyasik, I.; Leśniak, G.; Such, P. *Elementy Systemu Naftowego Karpat*; INiG-PIB: Kraków, Poland, 2015.
- Koster, J.; Kotarba, M.J.; Lafargue, E.; Kosakowski, P. Source rock habitat and hydrocarbon potential of Oligocene Menilite Formation (Flysch Carpathians, Southeast Poland): An organic geochemical and isotope approach. *Org. Geochem.* **1998**, *29*, 543–558. [\[CrossRef\]](#)
- Koster, J.; Rospondek, M.; Schouten, S.; Kotarba, M.J.; Zubrzycki, A.; Sinninghe Damste, J.S. Biomarker geochemistry of a foreland basin: The Oligocene Menilite Formation in the Flysch Carpathians of Southeast Poland. *Org. Geochem.* **1998**, *29*, 649–669. [\[CrossRef\]](#)
- Kotarba, M.J.; Koltun, Y.V. The origin and habitat of hydrocarbons of the Polish and Ukrainian parts of the Carpathian Province. In *The Carpathians and Their Foreland: Geology and Hydrocarbon Resources*; Golonka, J., Picha, F.J., Eds.; AAPG: Tulsa, OK, USA, 2006; Volume 84, pp. 395–442.
- Matyasik, I.; Steczko, A. Existence and variability of specific biomarkers in source rocks of the Carpathians flysch formations. *Nafta-Gaz* **2004**, *9*, 451–456.
- Matyasik, I.; Kupisz, L. Geological-geochemical generation conditions of menilite beds of the Strzyżów depression. *Nafta-Gaz* **1996**, *11*, 469–479.
- Matyasik, I.; Steczko, A.; Philp, R.P. Biodegradation and migrational fractionation of oils from the Eastern Carpathians, Poland. *Org. Geochem.* **2000**, *31*, 1509–1523. [\[CrossRef\]](#)
- Spunda, K.; Matyasik, I. Geochemiczna charakterystyka próbek z warstw istebniańskich jako skał potencjalnie macierzystych. *Nafta-Gaz* **2019**, *3*, 13–149. [\[CrossRef\]](#)
- Kotarba, M.J.; Więclaw, D.; Dziadzio, P.; Kowalski, A.; Bilkiewicz, E.; Kosakowski, P. Organic geochemical study of source rocks and natural gas and their genetic correlation in the central part of the Polish Outer Carpathians. *Marine Petrol. Geol.* **2013**, *45*, 106–120. [\[CrossRef\]](#)
- Jankowski, L. Nowe spojrzenie na budowę geologiczną Karpat—ujęcie dyskusyjne. In *Prace Instytutu Nafty i Gazu—Państwowego Instytutu Badawczego*; INiG-PIB: Kraków, Poland, 2015; Volume 202, p. 154.

17. Dziadzio, P.S.; Matyasik, I. Sedimentary environment and geochemical correlation of the Oligocene deposits from the Dukla and Grybow units. *Nafta-Gaz* **2018**, *6*, 423–434. (In Polish, with English summary) [[CrossRef](#)]
18. Dziadzio, P.S. The Lower Oligocene—Still deep-water turbidites or rather shallow-marine deposits? Field-trip topic 3. In *Some Current Sedimentological Controversies in the Polish Carpathian Flysch. Guidebook for Field Trip Accompanying 31st IAS Meeting of Sedimentology*; Leszczyński, S., Dziadzio, P.S., Nemec, W., Eds.; Polish Geological Society: Kraków, Poland, 2015; pp. 270–279.
19. Dziadzio, P.S.; Matyasik, I.; Garecka, M.; Szydło, A. Lower Oligocene Menilite Beds, Polish Outer Carpathians: Supposed Deep-Sea Flysch Locally Reinterpreted as Shelfal, Based on New Sedimentological, Micropalaeontological and Organic-Geochemical Data. In *Prace Naukowe INiG—PIB, 213; INiG—PIB*: Kraków, Poland, 2016. [[CrossRef](#)]
20. Ziemianin, K. Petrographic-geochemical characterization of the dispersed organic matter in Menilite shales from the Silesian Unit in the Carpathian Mountains of SE Poland. *Nafta-Gaz* **2017**, *11*, 835–842. [[CrossRef](#)]
21. Zielińska, M.; Fabiańska, M.; Więclaw, D.; Misz-Kennan, M. Comparative petrography and Org. Geochem. of different types of organic matter occur ring in the Outer Carpathians rocks. *Geol. Q.* **2020**, *4*, 165–184.
22. Peters, K.E. Guidelines for evaluating petroleum source rock using programmed pyrolysis. *AAPG Bull.* **1986**, *70*, 318–329.
23. Lafargue, E.; Marquis, F.; Pillot, D. Rock-Eval 6 applications in hydrocarbon exploration, production and in soil contamination studies. *Oil Gas Sci. Technol.* **1998**, *53*, 421–443. [[CrossRef](#)]
24. Copard, Y.; Di-Giovanni, C.; Martaud, T.; Albéric, P.; Olivier, J.E. Using Rock-Eval 6 pyrolysis for tracking fossil organic carbon in modern environments: Implications for the roles of erosion and weathering. *Earth Surf. Process. Landf.* **2006**, *31*, 135–153. [[CrossRef](#)]
25. Coats, A.; Redfern, J.P. Kinetic Parameters from Thermogravimetric Data. *Nature* **1964**, *201*, 68–69. [[CrossRef](#)]
26. Yan, J.W.; Jiang, X.M.; Han, X.X.; Liu, J. A TG-FTIR investigation to the catalytic effect of mineral matrix in oil shale on the pyrolysis and combustion of kerogen. *Fuel* **2013**, *104*, 307–317. [[CrossRef](#)]
27. Lewan, M.D.; Kotarba, M.J.; Curtis, J.B.; Więclaw, D.; Kosakowski, P. Oil-generation kinetics for organic facies with Type-II and II-S kerogen in the Menilite Shales of the Polish Carpathians. *Geochim. Cosmochim. Acta* **2006**, *70*, 3351–3368. [[CrossRef](#)]
28. Dziadzio, P.S. Sedimentary environment of the Menilite Beds in the Stróże Thrust Sheet, Silesian Unit, Carpathians. *Nafta-Gaz* **2018**, *11*, 813–820. (In Polish, with English summary) [[CrossRef](#)]
29. Spunda, K. Modelowanie 1D procesów generowania węglowodorów z warstw istebniańskich w profilu odwiertu nawiercającego utwory jednostki śląskiej. *Nafta-Gaz* **2020**, *2*, 57–75. [[CrossRef](#)]
30. Żytko, K.; Zając, R.; Gucik, S.; Ryłko, W.; Oszczytko, N.; Garlicka, I.; Nemcok, J.; Elias, M.; Mencik, E.; Stranik, Z. Map of the tectonic elements of the Western Outer Carpathians and their foreland. In *Geological Atlas of the Western Outer Carpathians and their Foreland*; Poprawa, D., Nemczok, J., Eds.; Państwowy Instytut Geologiczny Warszawa/GUDS Bratysława/Uug: Praha, Czech Republic, 1989.
31. Durand, B. (Ed.) *Kerogen. Insoluble Organic Matter from Sedimentary Rocks*; Éditions Technip: Paris, France, 1980.
32. Peters, K.E.; Cassa, M.R. Applied source-rock geochemistry. *AAPG Mem.* **1994**, *60*, 93–120.
33. Marshall, C.P.; Kannangara, G.S.K.; Wilson, M.A.; Guerbois, J.P.; Hartung-Kagi, B.; Hart, G. Potential of thermogravimetric analysis coupled with mass spectrometry for the evaluation of kerogen in source rocks. *Chem. Geol.* **2002**, *184*, 185–194. [[CrossRef](#)]
34. Schmidt, C.M.; Heide, K. Thermal analysis of hydrocarbons in Paleozoic black shales. *J. Therm. Anal. Calorim.* **2001**, *64*, 1297–1302. [[CrossRef](#)]
35. Földvári, M. *Handbook of Thermogravimetric System of Minerals and Its Use in Geological Practice*; Geological Institute of Hungary: Budapest, Hungary, 2011.
36. Karunadasa, K.S.P.; Manoratne, C.H.; Pitawala, H.M.T.G.A.; Rajapakse, R.M.G. Thermal decomposition of calcium carbonate (calcite polymorph) as examined by in-situ high-temperature X-ray powder diffraction. *J. Phys. Chem. Solids* **2019**, *134*, 21–28. [[CrossRef](#)]
37. Fan, C.; Yan, J.; Huang, Y. XRD and TG-FTIR study of the effect of mineral matrix on the pyrolysis and combustion of organic matter in shale char. *Fuel* **2015**, *139*, 502–510. [[CrossRef](#)]
38. Horsfield, B.; Douglas, A.G. The influence of minerals on the pyrolysis of kerogens. *Geochim. Cosmochim. Acta* **1980**, *44*, 1119–1131. [[CrossRef](#)]
39. Labus, M. Pyrite thermal decomposition in source rocks. *Fuel* **2021**, *287*, 119529. [[CrossRef](#)]
40. Pan, L.W.; Dai, F.Q.; Li, G.Q. A TGA/DTA-MS investigation to the influence of process conditions on the pyrolysis of Jimsar oil shale. *Energy* **2015**, *86*, 749–757. [[CrossRef](#)]
41. Skala, D.; Kopsch, H.; Sokic, M.; Neumann, H.J.; Jovanovic, J. Thermogravimetrically and differential scanning calorimetrically derived kinetics of oil shale pyrolysis. *Fuel* **1987**, *66*, 1185–1191. [[CrossRef](#)]
42. Zhou, G.Q.; Luo, R.L. Thermal analysis techniques and applications of kerogen. *Exp. Pet. Geol.* **1983**, *15*, 132–138.
43. Zhang, T.; Wang, Z.; Wang, Y.; Weia, Z.; Lia, X.; Houa, X.; Suna, Z.; Wang, G.; Qiane, Y. The characteristics of free/bound biomarkers released from source rock shown by stepwise Py/GC-MS and thermogravimetric analysis (TGA/DTG). *J. Petrol. Sci. Eng.* **2019**, *179*, 526–538. [[CrossRef](#)]
44. Yu, M.; Shixin, Z.; Jing, L.; Yuanju, L.; Kefei, C.; Yuhong, Z.; Deliang, F. Pyrolysis characteristics analysis of Chang-7 oil shale using thermal analysis and pyrolysis-gas chromatograph-mass spectrometry. *Energy Explor. Exploit.* **2018**, *36*, 1006–1021.
45. Lin, Y.; Liao, Y.; Yu, Z.; Fang, S.; Lin, Y.; Fan, Y.; Peng, X.; Ma, X. Co-pyrolysis kinetics of sewage sludge and oil shale thermal decomposition using TGA-FTIR analysis. *Energy Convers. Manag.* **2016**, *118*, 345–352. [[CrossRef](#)]