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Gaseous products of organic matter thermal decomposition depending on the type of kerogen

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Abstract:
The aim of the research was to ascertain the possibility of determining the type of kerogen based on gaseous products of pyrolysis of rocks containing organic matter. The relationship between the type of kerogen and the obtained gas products is important in assigning an appropriate role to the source rocks in the process of modeling petroleum systems. 13 rock samples were analyzed, representing type I, II and III kerogen, classified by the Rock Eval analysis. Thermogravimetry coupled with Fourier Transform Infrared Spectroscopy was used for evaluation of thermal decomposition and pyrolysis gaseous products determination. It was stated that the most appropriate temperature for which gas detection should be recorded and compared is 450 and 510 °C. Determining the composition of gas released in the process of pyrolysis of rocks containing organic matter, as well as the temperatures at which the maximum emission occurs allows the characterization of the type of kerogen and its maturity. Fourier transform infrared spectroscopy spectra for rocks containing type I kerogen are characterized by the presence of a CH_4 peak, significant intensities of C-H stretching vibrations and the presence of C=O vibrations. During the pyrolysis of rocks containing type II kerogen, methane peaks are low, but CO_2 is intensively released, and the structures of aromatic hydrocarbons disintegrate, as indicated by C=C vibrations. In the FTIR spectra of rocks representing type III kerogen, the CH_4 peak and C=C vibrations at temperatures of 450 and 510 °C are most often absent, and the CO_2 peaks are characterized by low intensity.

1. Introduction

In studying the decomposition process of fossil fuels, a frequently used research method is TG-DTG-DSC thermal analysis. In recent years, this analysis has been combined with simultaneous gas detection using Fourier transform infrared spectroscopy (FTIR) (Kaljuvee et al., 2004). However, studies on the composition and distribution of products formed during kerogen pyrolysis in real time are still scarce.

The FTIR method for solid rock samples is used to determine the mineral composition of rocks, the type of organic matter, its maturity, the type of kerogen and the generation potential of source rocks (Labus and Lempart, 2018; Tanykova et al., 2021). FTIR spectroscopy assigns specific absorption bands to individual chemical components in complex kerogen molecules (Ganz and Kalkreuth, 1987; Dang et al., 2015), however, when examining the entire sample, only one spectrum is obtained, while combined Thermogravimetry coupled with Fourier Transform Infrared Spectroscopy (TG-FTIR) analysis allows for simultaneous analysis of the released gases as the sample temperature increases. Here, in turn, there is a difficulty in determining the temperature at which gas detection should be recorded and compared.

Knowledge of the nature of kerogen is of great importance for the geochemistry of crude oil, natural gas and oil shale.

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Kerogen, defined as sedimentary organic matter, insoluble in organic solvents, comes from biological particles forming polymerized networks (so-called geopolymers), or is organic fragments coming directly from living organisms after minor transformation, or may also be a product of the erosion of old sediments. The basic biological molecules leading to the construction of geopolymers are usually lipids, carbohydrates, proteins and, less often, lignin. Lignin is present when organic matter comes from land plants, in which it is the main component, forming wood cells together with cellulose. Under conditions of high pressure and temperature, under the influence of diagenesis and metamorphism processes, crude oil and natural gas are formed from kerogen (Durand, 1980; Bordenave et al., 1993).

Depending on the type of source organic matter and the environment of its deposition, four types of kerogen are distinguished. A commonly used method to distinguish the types of kerogen in rocks is the analysis of the elemental composition and atomic ratios of hydrogen, carbon and oxygen (H/C and O/C), determined by chemical analysis or interpretation of the results of the Rock Eval (RE) pyrolysis. Then the equivalents of atomic ratios are the indices: Hydrogen (HI) and oxygen (OI). The degree of transformation is determined by the temperature at which the maximum amount of hydrocarbons is generated (T_{max}). The latter indicator is the basic determinant of kerogen maturity and can also be successfully obtained with use of thermal analysis (Matyasik et al., 2021).

Chemically, kerogen is a heterogeneous mixture of aromatic and aliphatic hydrocarbons and organic compounds containing certain amounts of oxygen, nitrogen and sulfur (Gathogo, 2011). The chemical composition of kerogen depends on the degree of its metamorphosis. The chemical composition of type II kerogen is dominated by hydrogen atoms over oxygen atoms.

When the hydrogen index HI reaches values below 150 mg HC/g TOC, kerogen has the potential to generate gas (mainly type III kerogen) (Waples, 1985). If the HI is in the range of 150-300 mg HC/g TOC, the source rock contains more type III kerogen compared to type II kerogen, therefore it has a mixed gas-oil generation potential, with gas predominating. A hydrogen index HI exceeding 300 mg HC/g TOC indicates the predominance of type II kerogen and is considered an indicator of high productivity of the source rocks and the possibility of generating oil with a lower share of gas. Kerogen with an HI index above 600 mg HC/g TOC is usually type I or II, which is associated with a high generation potential for crude oil (Waples, 1985).

Type I kerogen is rather rare because the genetic material for this type is lake (freshwater) algae. The best-known example of the rock containing type I kerogen is the Green River Shale (Wyoming, Utah and Colorado). The formation of this type of kerogen is believed to be limited to anoxic lake conditions, although specific marine environments are also known to occur, such as the kukersite studied here.

Type II kerogen is formed from various types of source material, including: Marine algae, resins and waxes filling cells, spores and pollen, leaf epithelium of land plants, as well as plant detritus. The sedimentation environment is usually a reducing marine environment. Type II kerogen has significant generation potential for liquid hydrocarbons.

Type III kerogen is formed from the woody material of land plants, therefore the basic ingredients are cellulose and lignin, and, as previously mentioned, it is rather gas-forming.

Type IV kerogen mainly contains inert organic matter of various origins and is considered unproductive. Tyson (1995) defined this type of kerogen as characterized by anomalously low hydrogen content and high oxidation level. Chemically, it is dominated by polycyclic aromatic compounds with molecules of phenolic components.

During the pyrolysis process, kerogen decomposes with the release of pyrolysis gases. Analysis of the composition of these gases, as well as the temperature at which the maximum of their emission occurs, allows the characterization of the type of kerogen (You et al., 2019). Typical gases released during pyrolysis are: CH_4, H_2, CO_2, CO and H_2O.

Depending on the oxygen content in kerogen, corresponding amounts of oxygen are released during the decomposition reaction. Under the influence of increasing temperature and pressure over geological time, kerogen, as a high-molecular organic compound, decomposes into short-chain aliphatic and aromatic hydrocarbons. The higher the maturity of the kerogen, the more aromatic structures in relation to aliphatic hydrocarbons. In the FTIR spectrum, this manifests itself as an increase in the intensity of the CH_3 absorption spectrum with respect to CH_2. Hence, the CH_2/CH_3 ratio is used to determine the maturity of kerogen (Marshall et al., 2005; Dang et al., 2015).

During the pyrolysis of a rock containing an organic matter, kerogen is decomposed simultaneously with the inorganic components of the rock. This process is complex and is therefore the subject of many studies. Many researchers confirm that the decomposition process of oil shales is multi-stage, which makes interpretation difficult (Janković, 2013; Yan et al., 2013; Bai et al., 2017; Liu et al., 2019; Bai et al., 2020).

For many years, research has been conducted on the kinetics of the kerogen pyrolysis reaction and the impact of individual mineral components in the source rocks on this process. Opinions on the impact of these components are strongly divided, which results from, among others, the diversity of research material. Patterson et al. (1991), as well as Patterson (1994) indicate the catalytic effect of carbonates in the source rocks. Dembicki (1992), examining Kimmeridge black shales, found that quartz, calcite and dolomite increase the activation energy, while clay minerals, such as kaolinite and montmorillonite, lower the activation energy of the pyrolysis process (Gu et al., 2024). On the other hand, many researchers believe that mineral components in the rock have a negligible impact on the pyrolysis process (Pelet, 1994; Reynolds and Burnham, 1995; Pan et al., 2016).

Baruah and Tiwari (2022) used TG analysis with FTIR gas analysis for real-time detection of pyrolysis products. Using the example of type II kerogen, they found the influence of mineral components of oil shale on the occurrence of secondary cracking reactions and delaying the pyrolysis reaction, and thus shifting the release of gas products to higher temperatures. The authors of this work, based on previous ex-

Table 1. Characteristic infrared absorption bands of selected gases and functional groups.

Gas/functional group/vibration type	Wavenumber (cm^{-1})
CO_2	2,400-2,240 780-560
CO	2,240-2,060
H_2O	4,000-3,500 1,900-1,300
CH_4	3,016
SO_2	1,374
O-H stretching	4,000-3,500
C-H stretching (aliphatic compounds)	3,200-2,850
C-H bending	
Saturated aliphatic hydrocarbons	1,500-1,300
Unsaturated aliphatic hydrocarbons	1,300-900
Aromatic rings	750-400
C=O stretching (carbonyl/carboxyl groups)	1,850-1,600
C=C stretching (aromatic compounds)	1,600-1,420
S=O stretching (sulfur-oxygen compounds)	1,420-1,300
N-H stretching (amine)	3,600-3,200

perience and research results of sedimentary rocks containing organic matter (including source rocks for oil and gas) (Labus and Lempart, 2018; Labus and Matyasik, 2019; Matyasik et al., 2021; Labus et al., 2023), selected several representative samples containing different types of kerogen in order to characterize the gas products of pyrolytic decomposition in real time and assign them to particular types of kerogen.

2. Methods

The type of kerogen in the samples was determined based on Rock-Eval pyrolysis analysis, interpreting the HI and OI indicators, along with T_{max}. The analysis was performed on the standard Rock-Eval-6 model. Samples of the tested rocks were ground in an agate mortar to a grain fraction of <0.02 mm. In the first stage, the sample was placed in a pyrolysis furnace in an atmosphere of inert gas (nitrogen), at a programmed temperature from 300 to 650 °C, with temperature increase of 25 °C/min. At this stage, hydrocarbons associated with kerogen are released, as well as oxygen-containing compounds. In the next stage, the sample is combusted in an oxidizing atmosphere, in the temperature range from 300 to 850 °C (temperature increase 20 °C/min).

Thermal analysis was performed using a NETZSCH STA 449 F3 Jupiter® analyzer. Powdered samples were placed in a ceramic crucible (Al_2O_3) in an amount of approximately 20 mg. The measurement was carried out while heating the sample in the temperature range of 40-1,030 °C, at a rate of 10 °C/min. A dynamic flow of inert gas (nitrogen) was used at a rate of 250 ml/min over the entire temperature range.

TG-FTIR was used to examine the gases released during the experiments. The measuring device-an "alpha" type FTIR spectrometer from Bruker was directly coupled to the STA F3 set (STA-Simultaneous Thermal Analysis). In this solution, the FTIR spectrometer is placed directly on the STA furnace, so there is no need for any transmission line. Spectra were recorded every 16 s from 400 to 4,000 cm^{-1}, with a resolution of 4 cm^{-1}. The gas cell is maintained at a constant temperature of 200 °C to prevent gas condensation. The results were analyzed using dedicated OPUS software. FTIR absorption bands have been identified as characteristic of certain gases and functional groups in gas products (Table 1) (Yan et al., 2013; Fan et al., 2015; Gu et al., 2024).

3. Samples

Based on the results of the RE analysis, rock samples containing various types of kerogen (from I to III) were selected (Table 2). Type I kerogen (Sample 1) is represented by only one sample (so-called kukersite). Kukersite is the name of combustible shale originating from the Baltic Sea Oil Shale Basin (Estonia), stratigraphically belonging to the Ordovician. The kerogen contained in kukersite rock represents type I and is mainly composed of alginite (Mastalerz et al., 2003; Petersen et al., 2010).

Type II kerogen (Sample 2-6) is represented here by samples from various units of the Carpathian Flysch, which are the subject of numerous studies due to their generation potential (samples 2-4). Stratigraphically, they belong to the Upper Cretaceous to the Oligocene strata. Samples of copper-bearing shales from the Fore-Sudetic Monocline (samples 5, 6) are exploited by company KGHM Polska Miedz S.A., as a rock containing metal ores, mainly copper; however, their potential as a source rock for hydrocarbons is currently under investigation.

Type III kerogen (Sample 7-14) is represented by three source rocks of the Carpathian flysch (samples 7-9). The most typical rocks representing type III kerogen are Miocene formations (samples 10-13), which are composed of humus material originating from terrestrial vegetation, containing large amounts of oxygen compounds. They are treated as source rocks for gas generation, which is mainly classified as low-temperature biogenic gas.

4. Results

The results of TG-FTIR experiments are presented below, divided into the groups distinguished above, according to the type of kerogen determined on the basis of RE analysis. As indicated by & Wood and Hazra (2018), the Rock-Eval technique provides quick and readily interpreted analysis, but in detail the petroleum transformation of shales varies greatly due to their kerogen type, level of thermal maturity already reached, burial history and other non-organic minerals present.

The examined samples were placed on van Krevelen diagrams (Fig. 1). The position of sample 1, as having a high HI index, raises no doubts as to its affiliation to kerogen type I. In the case of the remaining samples, the designation of the

Table 2. Performance of back-judgment models.

No.	Geological unit/stratigraphy	T_{max}	S1	S2	S3	PI	PC	RC	TOC	HI	OI	MINC
1	Estonia, Baltic Oil Shale Basin/Ordovician	433	2.28	303.70	6.87	0.01	25.78	10.68	36.46	833	19	2.48
2	Carpathians/Menilite, Dukla Unit/Oligocene	430	0.30	45.07	1.73	0.01	3.91	3.25	7.16	629	24	0.27
3	Carpathians/Menilite, Dukla Unit/Oligocene	437	0.52	37.87	0.58	0.01	3.26	3.74	7	541	8	0.09
4	Carpathians/Menilite, Silesian Unit/Oligocene	411	0.82	36.66	1.01	0.02	3.20	5.35	8.55	429	12	0.17
5	Fore-Sudetic Monocline/Permian	442	1.79	36.30	0.29	0.05	3.19	5.27	8.46	429	3	4.00
6	Fore-Sudetic Monocline/Permian	439	2.48	63.65	0.33	0.04	5.51	10.38	15.89	401	2	1.16
7	Carpathians/Spaskie Unit	431	0.02	2.11	0.25	0.01	0.21	2.43	2.64	80	9	0.84
8	Carpathians/Lgota Beds	430	0.03	0.77	0.25	0.04	0.08	0.81	0.89	87	28	0.60
9	Carpathians/Istebna Beds.	427	0.02	0.29	0.23	0.06	0.05	0.49	0.54	54	43	0.07
10	Carpathian Foredeep/Miocene	410	0.04	0.8	0.34	0.04	0.08	0.39	0.47	170	72	1.76
11	Carpathian Foredeep/Miocene	430	0.18	1.99	1.21	0.08	0.23	0.55	0.78	255	155	1.72
12	Carpathian Foredeep/Miocene	430	0.06	1.08	0.83	0.06	0.12	0.57	0.69	157	120	1.86
13	Carpathian Foredeep/Miocene	428	0.05	1.25	0.72	0.04	0.14	0.66	0.80	156	90	1.82

Kerogen type I: Sample 1, Kerogen type II: Sample 2-6, Kerogen type III: Sample 7-13, T_{max} (°C): temperature of maximum of S2 peak, S1 (mg/g): volatile hydrocarbons, S2 (mg/g): Residual hydrocarbon generating potential, S3 (mg/g): Organic carbon dioxide, PI: Production index S1/(S1+S2), PC (wt %): pyrolytic carbon content, RC (wt %): residual carbon content; TOC (%): Total organic carbon, HI ((mg/g)/(mg/g TOC)): Hydrogen index, OI ((mg/g)/(mg/g TOC)): Oxygen index, MINC (wt %): Mineral Inorganic Carbon.

kerogen type is not as clear, which indicates the comparison of the HI\OI and HI\T_{max} diagrams. However, it should be noted that the continuous lines shown in Fig. 1(b) indicate three different evolutionary paths rather than the boundaries between kerogen types. Based on the above diagrams, it was concluded that samples 2-6 should be classified as kerogen II, while samples 7-13 as type III kerogen; considering that, however, the sample 11 may contain mixed type II/III kerogen.

In case of some samples (especially sample 1 and 5) the parameter MINC (Mineral Inorganic Carbon) is high, indicating the presence of carbonates in the samples. Taking into account the catalytic properties of carbonates, mentioned in the Introduction, the lower decomposition temperatures of organic matter should be expected in these samples. The maturity of the samples, determined by T_{max} values is at a similar degree, although samples 3, 5 and 6 should be considered as containing high maturity kerogen ($T_{max} > 435$ °C).

4.1 Kerogen type I

Kukersite is a sedimentary rock with a relatively high content of organic matter (10%-65%), composed of kerogen and bitumens. The organic substance in combustible shales from older formations (such as kukersite - Ordovician) contains more volatile components and has a higher percentage of tar yield, compared to younger combustible shales, especially Tertiary ones. The remaining components typical of kukersite are carbonate minerals (20%-70%) and components of terrigenous origin (quartz, feldspars and clay minerals) (Motlep et al., 2007).

The tested sample (1) comes from the Kohtla-Järve deposit in Estonia, belonging to the Baltic Shale Basin. The composition of the inorganic matter of the tested shale, using XRD analysis, revealed the presence of calcite, quartz and feldspar (microcline).

The result of the TG/DSC analysis (Fig. 2) indicates a significant share of carbonates (calcite). The mass loss of 13.37% detectable on the TG curve is the amount of CO_2 released during the thermal decomposition of calcite (Galan et al., 2013). After multiplying by the appropriate factor (2.274), the calcite content in the sample can be determined to be approximately 30%. The weight loss resulting from the pyrolysis of organic matter is over 48%. The mass loss in the temperature range of 40-200 °C, caused by the dehydration of

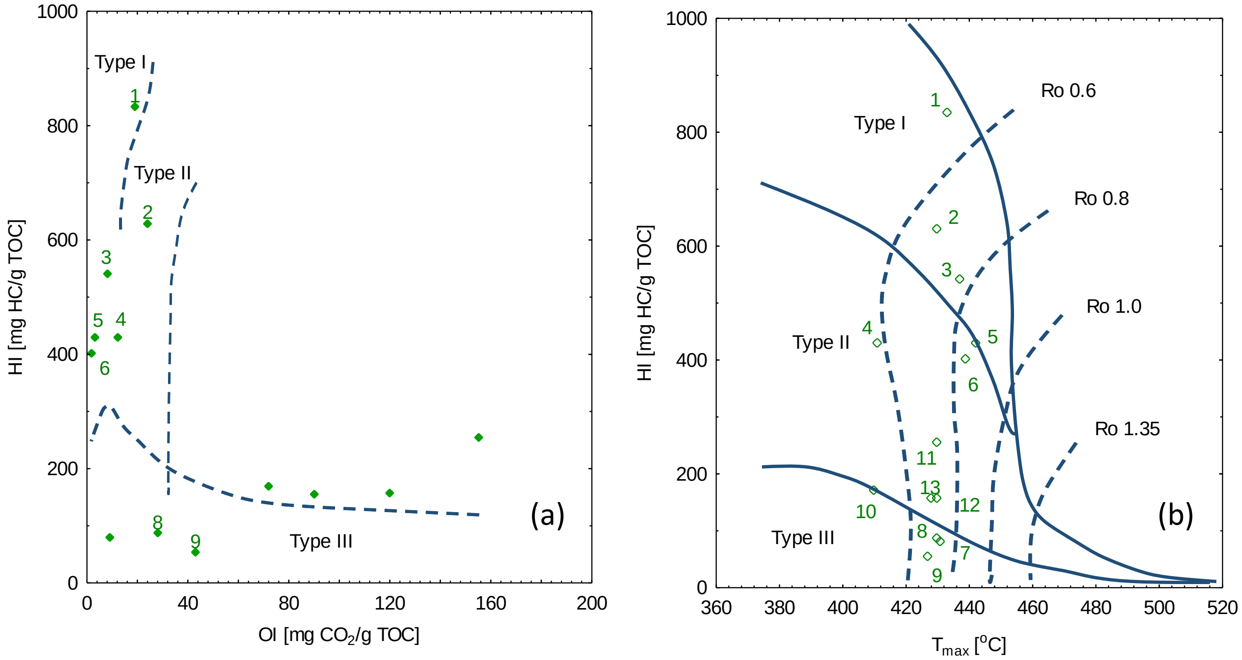

Fig. 1. Modified van Krevelen diagrams indicating the kerogen types of the studied samples: (a) HI versus OI, (b) HI versus T_{max}.

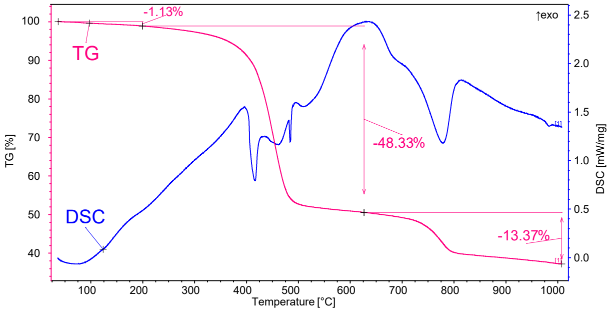

Fig. 2. Result of TG-DSC analysis of sample 1 (kukersite) representing type I kerogen.

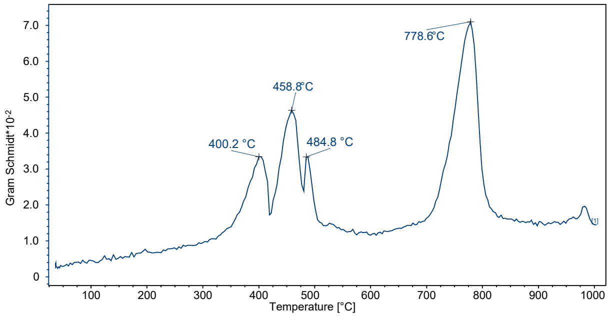

Fig. 3. Gram-Schmidt curve of gas emission episodes during thermal decomposition of sample 1.

hydrated minerals is very insignificant (1.13%), which confirms the results of the XRD analysis, which did not indicate the presence of clay minerals.

The shape of the DSC curve indicates the complex course of pyrolysis of organic matter. Two sharp endothermic peaks are visible here, and one with a milder course between them. Maaten et al. (2016) report that the pyrolysis of combustible shale takes place in two stages. In the case of the examined kukersite sample, the pyrolysis process is also two-stage, but three episodes of gas evolution are important, recorded in the range of 300-600 °C on the Gram-Schmidt curve (Fig. 3). The first of the observed stages of oil shale decomposition could be attributed to kerogen conversion into plastic stage-bitumen. This is further converted to complicated mixture of liquid hydrocarbons with varying chain length. The last two peaks on DSC and GS curves are related to the release of heavy constituent (shale oil) and lighter ones (Maaten et al., 2016).

The GS curve shows the total amount of gases released during the experiment. The maximum gas emissions in the temperature range of the pyrolysis process are at: 400.2, 458.8 and 484.8 °C. The last high peak, with a maximum at 778.6 °C, corresponds to CO_2 emission from the decomposition of carbonate minerals (Kemp et al., 2022).

FTIR spectra are shown for three temperature values from the GS curve (approx. 400, 458 and 485 °C) (Fig. 4). All spectra show peaks from CO_2 emissions (bands in the range of 2,400-2,240 and 780-560 cm^{-1}), as well as vibrations in the range of 3,000-2,850 cm^{-1}, characteristic of C-H bonds, indicating the presence of aliphatic hydrocarbons. At higher temperatures (458 and 595 °C) they are accompanied by a small, sharp peak in the absorption band around 3,014 cm^{-1}, characteristic of the released CH_4.

Vibration bands with wave numbers in the range of 4,000-3,500 cm^{-1} and 1,900-1,300 cm^{-1} are characteristic for O-H functional groups. In the case of spectra obtained at temperatures of 458 and 485 °C, the bands resulting from the presence of water in the rock are minimized, thanks to the correction taking into account atmospheric moisture; only a sharp peak

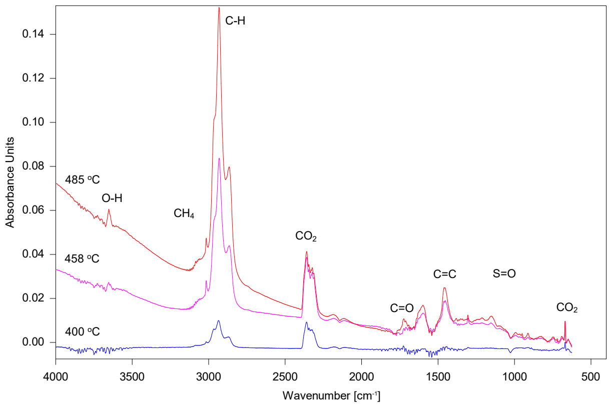

Fig. 4. FTIR spectra of kukersite decomposition (sample 1).

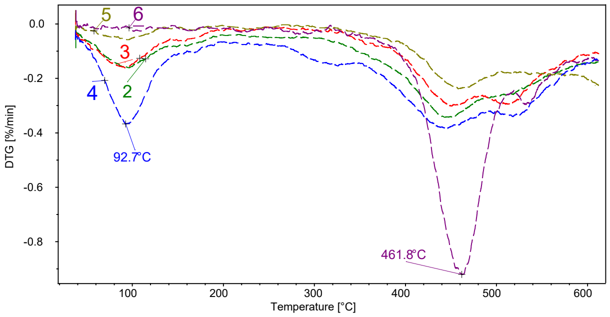

Fig. 5. DTG curves of the samples representing type II kerogen.

with a wave number of 3,654 cm^{-1} is visible, indicating a high degree of order in the structure of hydrated minerals.

The most interesting spectrum range is between 1,800 and 1,300 cm^{-1}. The broad peak in the 1,722 cm^{-1} band indicates stretching vibrations of C=O double bonds, while the peaks in the 1,600-1,460 cm^{-1} range come from C=C stretching vibrations, indicating the decomposition of aromatic hydrocarbons. The small peak in the absorption band of 1,304 cm^{-1} comes from the stretching vibrations of S=O bonds, which can be attributed to the presence of organosulfur compounds such as sulfones, sulfoxides, etc. (Yan et al., 2013).

4.2 Kerogen type II

Thermal decomposition of samples representing type II kerogen takes place in three temperature ranges. At temperatures in the range of 40-160 °C, dehydration of clay minerals proceeds. As can be seen in Fig. 5, which shows the DTG curves of these samples in the range of 40-620 °C, the strongest effect is shown by the DTG curve for sample 4. This effect is associated with a mass loss of 2.32% of the total mass of the sample. From the point of view of the decomposition of organic matter, the most interesting range is the temperature range of 400-600 °C, where the kerogen macromolecules are broken. The unstable intermediates produced at lower temperatures are further polymerized into more stable intermediates, which is accompanied by the release of volatiles (Yan et al., 2013). In this interval (400-600 °C), one or two maxima appear on the DTG curve, which are marked as T_{maxTG}. This is the temperature at which mass loss occurs at the maximum rate and is compared with the T_{max} parameter from the RE measurement, indicating the maturity of organic matter. The most intense effect on the DTG curve is visible in the case of sample 6, with a maximum at 462 °C. This is due to the significant content of organic matter, which is manifested by a mass loss of 8.75%, and correlates well with the S2 parameter from the RE analysis (Wood and Hazra, 2018) (Table 2). In the case of the remaining samples from this group, the DTG curve usually reveals two maxima, as shown in Table 3. The maturity of organic matter should rather be taken from the peak with a lower value, located in the temperature range of 440-470 °C, due to the fact that it is stronger than the second peak at temperatures above 500 °C.

Table 3. Temperatures of maximum mass loss (T_{maxTG}) and maximum methane emission (T_{met}) in the tested samples.

No.	T_{maxTG} (°C)	T_{met} (°C)
1	454	458
2	450; 518	455
3	451; 505	448
4	447; 518	447
5	456	518
6	462; 533	510
7	509	/
8	510	/
9	510	/
10	526	/
11	425	/
12	445; 517	/
13	427; 500	/

The last range, not shown in the thermogram in Fig. 5, covers temperatures above 620 °C, where in some samples the decomposition of carbonate minerals (dolomite and calcite) occurs, similarly to the kukersite sample (Fig. 2).

In the Table 3 is given also a third temperature value, the so-called T_{met} (methane peak), which corresponds to the temperature at which methane is most intensively released from the sample. This temperature can be read from FTIR spectra, based on the absorbance value at the wavelength corresponding to methane emission (3,016 cm^{-1}). As it is visible, in the example of sample 2, the T_{met} value does not coincide with the T_{maxTG} temperature read from the DTG curve.

As can be seen from Table 3, the main T_{maxTG} peak for samples representing type II kerogen, determined on the basis of thermogravimetric curves, corresponds to a temperature of approximately 450 °C, while the second, weaker one, is located around 510 °C. Therefore, in order to enable comparison of the obtained gas spectrometry results, these two temperature values were considered as the base ones and are shown in the following graphs containing FTIR spectra (Figs. 6 and 8).

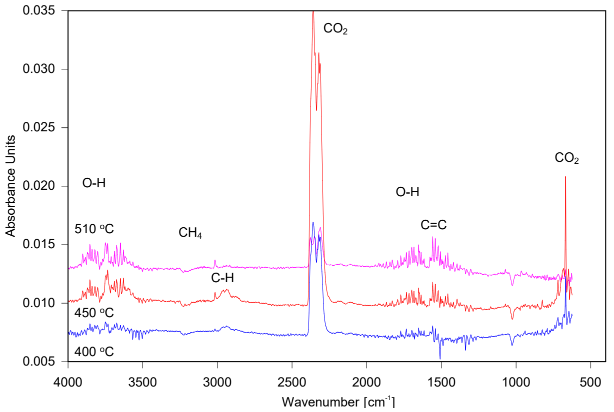

Fig. 6. FTIR spectra of sample 2 decomposition (kerogen type II).

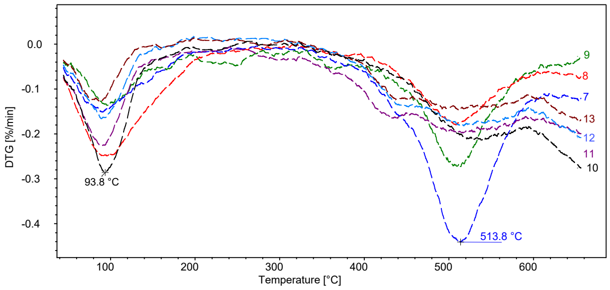

Fig. 7. DTG curves of the samples representing type III kerogen.

All spectra show relatively high peaks resulting from CO_2 emissions (bands in the range of 2,400-2,240 and 780-560 cm^{-1}). As TG/DTG analysis did not reveal the presence of carbonates in these samples, CO_2 generation should be associated with the breakdown of carbonyl and carboxyl compounds (Baruah and Tiwari, 2022; Li et al., 2016). At the same time as the intensity of the CO_2 peaks increases the absorption bands by 1,700 cm^{-1} appear which is also subsequently referred to as C=O stretch vibration in carbonyl/carboxyl groups. FTIR spectra also reveal vibrations in the range of 3,000-2,850 cm^{-1}, characteristic for C-H vibrations, indicating the presence of aliphatic hydrocarbons. At a temperature of approximately 450 °C, they are accompanied by a small, sharp peak in the absorption band of approximately 3,016 cm^{-1}, characteristic of the released CH_4.

In the range of wave numbers 4,000-3,500 cm^{-1} and 1,900-1,300 cm^{-1}, vibrations characteristic of O-H functional groups are visible. If their intensity is low, C=C stretching vibrations can be observed in the range of 1,600-1,460 cm^{-1}. However, in the case of samples belonging to type II kerogen, such vibrations are visible only in sample 2 (Fig. 6).

4.3 Kerogen type III

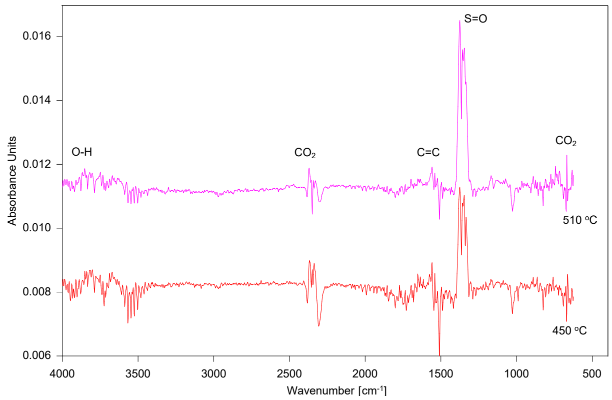

Fig. 8. FTIR spectra of sample 7 decomposition (kerogen type III).

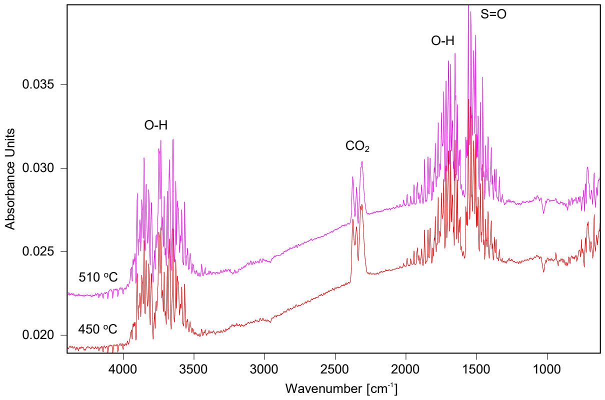

Fig. 9. FTIR spectra of sample 11 decomposition (kerogen type III).

The samples of rocks containing type III kerogen examined here can be divided into two groups. The first one includes source rocks from the Flysch Carpathians (Matyasik et al., 2021; Labus et al., 2023), the second one contains Miocene clay rocks. All samples show a characteristic deflection of the DTG curves in the range from 420 to 600 °C, with a maximum at approximately 510 °C (Table 3, Fig. 7).

Thermograms of samples belonging to the second group (samples 10-13) indicate a significant share of clay minerals, which is manifested by a sharp loss of mass in the range of 40-150 °C, while the decomposition of organic matter is less marked than in the case of samples 7-9 (Fig. 7). Samples of Miocene clay rocks of the Carpathian Foredeep also contain a significant amount of carbonates, which decompose in the range of approximately 700-800 °C. Moreover, in sample 13, in the temperature range of 940-965 °C, can be observed an endogenous reaction combined with a mass loss, indicating the presence of sulfates in the sample (most likely anhydrite). This effect in the FTIR spectrum is combined with the release of sulfur compounds.

Despite the fact that in the case of samples containing type III kerogen we do not observe the first stage of decomposition, as in the case of type II kerogen, in the range from 400 to 470 °C, in order to compare gas emissions from all samples, FTIR spectra for a temperature of 450 °C were also taken into account. As observed, there are some differences between the group representing the source rocks of the Flysch Carpathians (samples 7-9) and the Miocene rocks (samples 10-13). Hence, the examples of spectroscopic spectra for samples with type III kerogen for both groups are shown separately (Figs. 8 and 9).

In all cases, unlike in case of samples containing type II kerogen, CO_2 emission (vibrations in the range of 2,400-2,240 and 780-560 cm^{-1}) is poorly marked. There are no visible vibrations coming from C-H bonds (vibrations in the range of 3,000-2,850 cm^{-1}), nor "methane" peaks. The lack of a CH_4 peak in the absorption band of approximately 3,016 cm^{-1} means that the Tmethane temperature cannot be determined for these samples (Table 3), which makes it difficult to interpret the maturity of organic matter.

The C=C stretching vibration spectra appear in the range of 1,600-1,460 cm^{-1}. They are clearly visible in the spectra of samples belonging to the first group (Fig. 7), while in the second group (Fig. 9) they are masked by O-H vibrations originating from the water contained in the samples. A characteristic feature of the spectra of type III kerogen decomposition is the presence of asymmetric stretching vibrations of S=O bonds with maxima in the range of 1,374 and 1,345 cm^{-1} wave numbers (Fig. 8). These peaks show greater intensity at the temperature of 510 °C. In the case of samples 10-13, similarly to the C=C vibrations, the S=O vibrations are probably masked by the O-H vibration spectrum.

5. Discussion

The TG/DTG analytical method used in this article was pyrolysis with simultaneous gas detection. Some authors (e.g. Oudghiri et al., 2016) also used comparative combustion experiments in thermal analysis and noticed that the emission of some gases is better readable in FTIR spectra in the case of combustion, because during pyrolysis the band in the 1400 wavelength range -1800 cm^{-1} are masked by the released water. In the case of the pyrolysis experiments carried out in this study, these bands are, in most cases, clearly visible, as shown, for example, in Figs 6 and 8. However, in the case of clay rock samples originating from the Miocene formations of the Carpathian Foredeep (Fig. 9), the above-mentioned masking by vibrations originating from O-H bonds is present.

As mentioned in the introduction to this work, simultaneous TG-FTIR analysis has the advantage of enabling the detection of gaseous decomposition products in real time as the temperature increases. On the other hand, it provides much larger amount of information, which may make it difficult to compare test results because the temperature, or temperature ranges at which gas detection should be recorded and compared, must be determined. The comparison of the temperature values at which the fastest mass loss occurs (so-called T_{max}) shows that in the case of a sample containing type I kerogen the temperature is close to 450 °C, while in the case of type II kerogen there are two peaks (approx. at 450 and 510 °C). In turn, the maximum decomposition of organic matter containing type III kerogen occurs at a temperature of approximately 510 °C for samples from Carpathian flysch formations (Table 3). However, in the case of Miocenie samples, this temperature is in a lower range - approximately about 425 °C. This phenomenon can be explained, among other things, by the presence of clay minerals in these rocks, which catalyze the decomposition process of organic matter (Dembicki, 1992; Gu et al., 2024). Moreover, this fact may prove that Miocene rocks have a higher mass loss in the first stage of pyrolysis, indicating that this kerogen is rich in oxygen and within the gaseous products are small amounts of H_2O, CO_2, SO_2 and H_2S (Skala et al., 1997). However, when we look at the GS curves in the thermograms and the FTIR spectra, it turns out that the gas emission from the latter group of samples is very similar throughout the entire range of 425-450 °C. Therefore, in order to standardize the reading procedure, it was decided that a temperature of 450 °C would be representative for this lower temperature range. Hence, in conclusion, the two values: 450 and 510 °C were considered the most appropriate for comparison purposes. Previous research on PyGC pyrolysis also led the authors to similar conclusions, where it was found that a temperature of approximately 500 °C is sufficient to analyze the composition of gas products (Labus et al., 2023).

It should be noted here that the results we obtained concern whole rock samples, not isolated kerogen. As numerous studies show, the temperature range at which kerogen decomposition occurs is influenced not only by its type, but also by other, including inorganic, components of the rock. Baruah and Tiwari (2022) observed that the decomposition of organic matter and the evolution of gases (mainly the presence of C-H vibrations of aliphatic compounds) take place at lower temperatures for the separated kerogen than for the whole rock. On the other hand, Yan et al. (2013) believe that the presence of carbonates in the rock has a catalytic effect, which produces the opposite effect (accelerates the decomposition of organic matter) to that described above.

An important issue in hydrocarbon exploration is determination of the degree of thermal maturity of organic matter. This maturity is established using various indicators, including vitrinite reflectance (R_o), biomarkers and the most commonly used T_{max} indicator from the Rock Eval analysis (Bieleń and Matyasik, 2018). The T_{max} temperature is defined as the temperature at which the greatest amount of hydrocarbons is generated, and its measurement refers to the maximum of the S2 peak (Espitalié et al., 1977). Some researchers also point to the adequacy of the T_{max} parameter determined on the basis of TG/DTG experiments (Schmidt and Heide, 2001).

TG-FTIR analysis allows the determination of the methane peak (T_{met}) listed in Table 3, which corresponds to the temperature at which methane is most intensively released from a given sample (Dang et al., 2015; Labus et al., 2023). In the case of the results of thermal experiments presented here, this parameter cannot be determined for samples representing type III kerogen, hence it is difficult to take it into account in further considerations. The lack of a methane peak in the case of samples containing type III kerogen may reflect the diversification of the evolution path of this kerogen in relation to type I and II kerogen. In the case of type III kerogen, containing a lot of oxygen compounds, the second stage of its decomposition, i.e., secondary cracking, is less noticeable (Durand, 1980). This type of kerogen therefore shows the greatest diversity during thermal evolution and thus the simulation of thermal decomposition.

FTIR spectrum analysis allows conclusions about the maturity of organic matter based on the presence of specific particle vibrations. It is based, among others, on: the detection of absorption of stretching bonds of aliphatic C-H (3,000-2,850 cm^{-1}) and aromatic C=C (1,600-1,420 cm^{-1}) components (Labus and Lempart, 2018; Tanykova et al., 2021). As thermal maturity alters, the group composition of organic matter changes. With increasing degree of maturity the increase in the absorption of aromatic bands and decrease in the absorption of aliphatic bands is observed (Lis et al., 2005). In the case of the tested here samples, this is confirmed by the intense vibrations of the C=C groups in the samples of copper-bearing shales (samples 5 and 6) with a high degree of maturity (T_{max} values 442 and 439 °C respectively).

Moreover, the immature organic substance is characterized by a predominance of polar compounds (containing heteroatoms such as: O, N, S). As thermal maturity increases, the share of "pure" hydrocarbons, both aliphatic and aromatic, increases. The results described above, however, do not completely correspond to these assumptions. The presence of stretching vibrations originating from N-H bonds was revealed in the case of sample 9. Based on the T_{max} value from the RE analysis (427 °C), the kerogen present in it can be classified as immature, which would confirm that the presence of nitrogen in the sample means the low maturity of organic matter (Bennet and Love, 2000). As is commonly known, rocks containing organic matter of low maturity are relatively rich in sulfur and nitrogen compounds, which undergo gradual degradation during thermal transformations. Nitrogen in shale rocks usually occurs in the form of pyrrole, pyridine, and quaternary nitrogen groups. As a result of simulated pyrolysis, N-H functional groups of stretching bands: 3,600-3,200 cm^{-1} (Table 3), in the form of amine or acylamide compounds, are generated (Bennet and Love, 2000). It is worth mentioning that N-H vibrations in sample 9 are visible during the decomposition of this sample in a wide temperature range, from 300 to 495 °C.

When comparing the gas products of the pyrolysis process obtained for rocks containing particular types of kerogen, the following regularities can be observed:

Type I kerogen is quite rare, therefore in this study it is represented by only one sample of oil shale-kukersite; therefore, it should be taken into account that the results presented here are not universal. Nevertheless, FTIR spectra for kukersite are characterized by significant intensities of C-H stretching vibrations, indicating the presence of aliphatic components, which is consistent with the alginite nature of organic matter. Above a temperature of 480 °C, C=O vibrations appear in the FTIR spectrum, indicating the oxidation of organic compounds, which may result from the specific sedimentation environment of this rock (Motlep et al., 2007). A characteristic feature of the spectroscopic spectra obtained during the pyrolysis experiment is the presence of distinct methane peaks.

In turn, FTIR spectra of pyrolysis of rocks containing type II kerogen are characterized by a relatively weak methane peak. High absorbance values, however, show peaks indicating intensive evolution of carbon dioxide, starting from about 360 °C until the end of the experiment. The products of pyrolysis are both aliphatic and aromatic hydrocarbons, manifested by the presence of C-H and C=C vibrations.

In FTIR spectra of rocks representing type III kerogen, the CH_4 peak is most often absent, which is confirmed by research conducted by Wright et al. (2015). In contrast to rocks representing type II kerogen, the intensities of CO_2 peaks are significantly lower. Of course, we do not take into account the decomposition of carbonate minerals, which begins at temperatures above 650 °C. C=C vibrations are absent in most of the tested samples, which may be due to the insufficient maturity of the organic matter. However, intense asymmetric S=O stretching vibrations are observed, indicating the presence of sulfur compounds, which may occur here both in the form of inorganic and organic sulfur. The high share of sulfur compounds in type III kerogen is related to the presence of sulfates in the original sediment (mostly marine), which are then reduced by anaerobic bacteria(Waples, 1985). Sulfur content however should not be treated as a distinguishing feature of the type of kerogen - in this case-type III kerogen. The thermal decomposition of type III kerogen is definitely different than that of type I or II, and methane generation is the result of the primary cracking of kerogen (Zhang et al., 2021).

At this point it is also worth noting the case of sample 11, whose affiliation to the kerogen type was doubtful based on the position on the van Krevelen diagrams (Fig. 1). We assumed then that it represented a mixed type II/III kerogen. However, it turns out that the analysis of the emitted gases allowed for unambiguous assignment of this sample to type III kerogen.

As can be seen in the examples presented above, the use of the TG-FTIR method is a very effective way to complement the classical methods used in petroleum geology. Since the 1970s, the RE pyrolysis analysis has been the most widespread, preliminary, geochemical method for examining potential source rocks for hydrocarbons, in order to determine, among others, the hydrocarbon potential, the type of kerogen contained in the rocks and the thermal maturity of organic matter (Espitalié et al., 1977). In some cases, as shown in the example of the samples examined in this study, the affiliation to individual kerogen types, and consequently, the generation potential of individual potential source rocks, is not unambiguous. As shown by the authors' previous studies (Labus and Matyasik, 2019; Matyasik et al., 2021; Labus et al., 2023), the TG analysis is a powerful complementary method to the classical RE pyrolysis method. In addition, the enrichment of this method by the analysis of gases released during pyrolysis gives new perspectives in the geochemical studies of parent rocks.

The studies conducted here constitute an initial stage of work that should be expanded in the future to include broader examination of more diverse sedimentary rocks with generation potential. Particular attention should be paid to relatively rare rock samples containing type I kerogen. Another important direction for further research should be to identify how to use the gas components released during the thermal decomposition of kerogen to predict the potential for oil and natural gas generation.

6. Conclusion

1) Analysis of the composition of gas released in the process of pyrolysis of rocks containing organic matter, as well as the temperature at which the maximum emission occurs, allows the characterization of the type of kerogen and its maturity.
2) Based on the conducted research, it was found that the most appropriate temperature values for interpreting and comparing FTIR spectra, obtained during the pyrolysis of rocks containing organic matter, are 450 and 510 °C. These higher temperature range is particularly important for samples representing type I hydrogen-rich kerogen, where the gaseous products are mainly hydrocarbons.
3) FTIR spectra for samples containing type I kerogen are characterized by the presence of a CH_4 peak, significant intensities of C-H stretching vibrations resulting from the presence of aliphatic components, and the appearance of C=O vibrations, indicating the oxidation of organic compounds. In addition to hydrocarbon indicators, the vibrations of CO_2, SO_2 and H_2S also occur at lower intensities.
4) FTIR spectra of rocks containing type II kerogen are characterized by a relatively weak methane peak, intense CO_2 emission, and the presence of C=C vibrations.
5) In FTIR spectra of rocks representing type III kerogen, the CH_4 peak is most often absent. In most cases, C=C vibrations are also invisible. Additionally, low CO_2 peak intensities are usually characteristic. The lack of a methane peak makes it impossible to determine the maturity of organic matter using the thermogravimetric method.

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Conflict of interest

The authors declare no competing interest.

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