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GEOCHEMISTRY OF OIL SHALE IN AZERBAIJAN

Abstract: In the paper, the geochemical characteristics of more than 60 deposits and outcrops of oil shales in Azerbaijan, related to geological formations of the Cretaceous-Miocene age were considered. Samples of oil shale were taken from the surface outcrops and ejected materials of mud volcanoes. The main goal of the study is to determine the organic geochemical features of oil shales in order to know their role in the formation of hydrocarbons. A comparative analysis of the studied oil shale was performed with foreign countries in which the shale industry has a long history.

Key words: Azerbaijan, oil shale, geochemistry, organic matter, kerogen, hydrocarbon

Language: English

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Introduction and brief historical overview

Beside with well-known oil and gas deposits, there are numerous unconventional (alternative) sources of fuel and energy raw materials – natural bitumen, oil shale, gas hydrates, etc. in the territory of Eastern Azerbaijan.

In several countries of the world, oil shale is used as raw material for shale gas production (USA, Canada, China, etc.), at thermal power plants (Estonia, China, Germany, etc.), in cement production (Estonia, China, Germany), in agricultural for fertilizers production (Estonia, Switzerland), in medicine for the ichthyol ointment and ammonia production (France, Russia, China), in

obtaining chemical products (China, Estonia, Russia) and etc. [1, 13].

A more detailed study of oil shale in Azerbaijan was started in 2000 at the Institute of Geology and Geophysics of the National Academy of Sciences of Azerbaijan [2, 3-6, 9, 10].

Geological setting

In Azerbaijan, the outcrops of oil shale are located in the Shamakhi-Gobustan, Absheron and Pre-Caspian – Guba geological regions (Fig. 1) and are represented in the stratigraphic interval of the geological section from the Cretaceous to the Miocene deposits.



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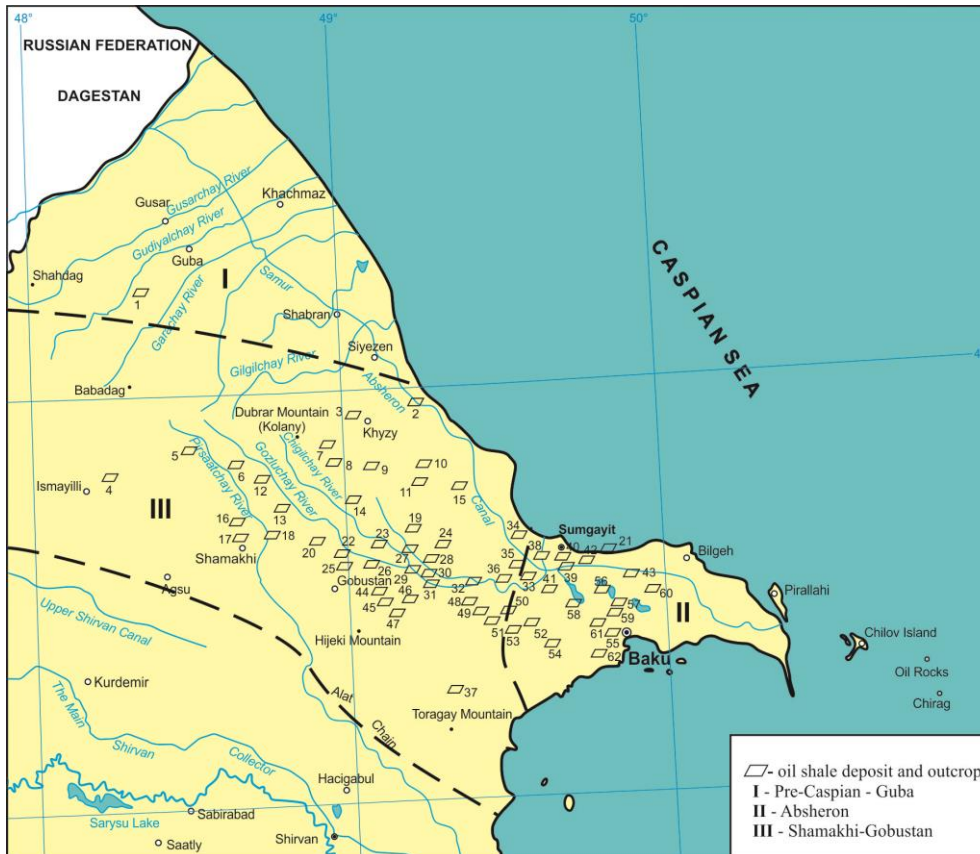


Figure 1 - Map of the location of oil shale deposits and outcrops in Azerbaijan (1:1000000)

1-Guba; 2-Zarat; 3-Bakhishli; 4-Diyalli; 5-Heybari; 6-Gizmeydan; 7-Altigaj; 8-Kemishdag; 9-Ambizlar; 10-Chargishlag; 11-Kurkechidag; 12-Talyshnuru; 13-Khilmilli; 14-Agdere; 15-Yashma; 16-Angikharan; 17-Shamakhi; 18-Arabshalbashi; 19-Shabandag; 20-Jairli; 21-Goradil; 22-Garaja; 23-Tuva; 24-Gibleldag; 25-Ahudag; 26-Shaiblar; 27-Kichik Siyeki; 28-Boyuk Siyeki; 29-Garayokhush; 30-Jangidag; 31-Jangichay; 32-Kechallar; 33-Pirekiaskyul; 34-Agburun; 35-Islamdag; 36-Mayash; 37-Goytepe; 38-Orjandag; 39-Saray; 40-Jorat; 41-Guzdek; 42-Kecheldag; 43-Fatmai; 44-Baygushgaya; 45-Alagishlag; 46-Garigishlag; 47-Baygushqaya; 48-Sungur; 49-Bayanata; 50-Saridag; 51-Girdag; 52-Shorbulag; 53-Cosmali; 54-Uchtepe; 55-Garaheybat; 56-Masazir; 57-Binagadi; 58-Khirdalan; 59-Zigilpiri; 60-Girmeki; 61-Shabandag; 62-Ateshgah.

In the Ismayilli region, oil shale is associated with the Diyalli village, located 7 km east of Ismayilli. In tectonic terms, the area belongs to the complex Vandam-Lahic zone, where favorable geological and geochemical conditions existed in the Upper Sarmatian period for the accumulation of pyrobituminous shales. The thickness of the oil shale layer is 300-370 m, in the north it is under the limestones of the Kemchi suite (Turon-Coniacian).

At the base of the upper Sarmatian section lays a bundle of basal conglomerates, up to 70 m thick, under which a bundle of layered clays with interlayers of sandstones and oil shales can be traced. The last ones are confined to the upper half of the section, they are black and light brown (weathered) colors, 1.5 km in length and contain 12 interlayers of oil shales [7, 8] (Fig. 2).

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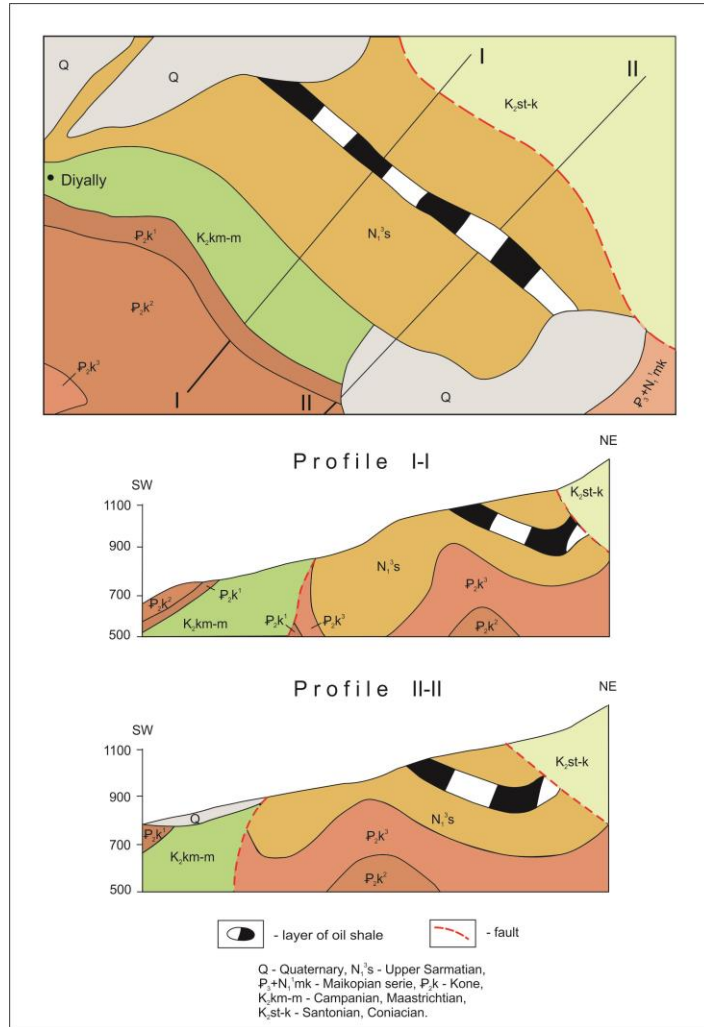


Figure 2 - Geological map (1:20000) and profiles of the Diyalli oil shale deposit

In the Pre-Caspian – Guba region, is separated the Guba oil shale deposit (Khanagah) is located 25 km south of the city of Guba. The shale containing interval of the section was confined to the lower part of the upper Sarmatian, with a thickness of 27 m to 255 m, alternating with strata of strongly

bituminous clays, almost not differing from oil shales. The practical interest is present the segment of the strip of development of the Upper Sarmatian deposits, 29 km long, stretched in the NW-SE direction from the River Qudiyalchay to the River Velvelechay (Fig. 3).

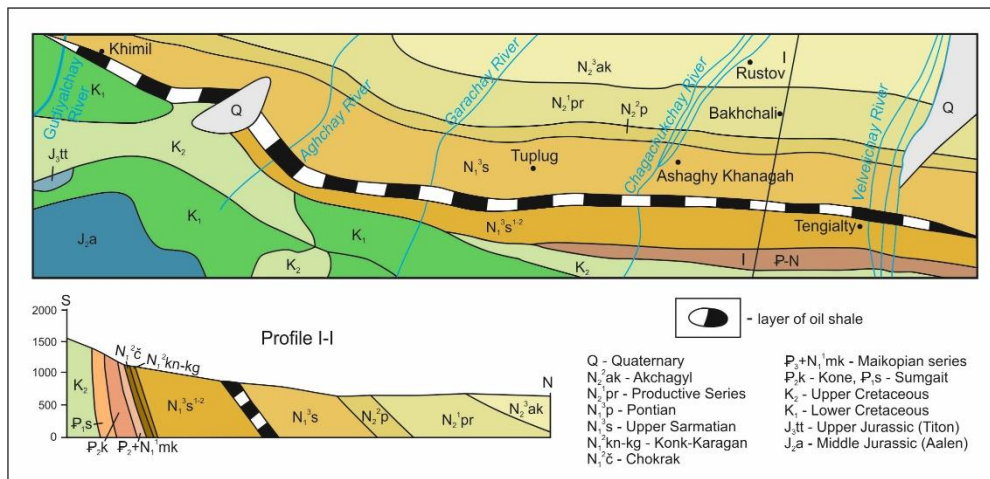


Figure 3 - Geological map (1:100000) and profile of the Guba oil shale deposits

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The **Shamakhi-Gobustan region** covers the southeastern end of the Greater Caucasus. The studied deposits and outcrops of oil shales are located mainly in Central Gobustan and in the Shamakhi zone, in the geological structure of which sediments of Mezo-Cenozoic age participate. Oil shales in the territory of Central Gobustan are associated with interruptions in the accumulation of organic residues during lithogenesis, which began in the time interval from the middle Eocene and lasted until the end of the Miocene [11, 12]. In the southeastern direction, the number of outcrops increases. The outcrops related to the category of deposits (K. Siyeki, B. Siyeki, Jangidag, Jangichay, etc.) are closer to the center of the district.

The geological structure of the **Absheron Peninsula**, its western part, involves the clastic-carbonate rocks of the Miocene. More than 15 surface outcrops of oil shale have been identified here. They are associated mainly with sediments of the lower and upper Miocene. Here, in a depth of 120 m thick of the Karagan-Konc sediments can be

traced a stack of gray, brown-gray leafy shales, 18.7 m thick.

Oil shale in sections Meotian spread across the area characterized by different thickness.

Geochemical properties of oil shale

Geochemical analysis of oil shale samples taken from the deposits and outcrops of various above-mentioned regions of Azerbaijan were performed, and the studies have shown that, despite the relatively high amount of shale ash (up to 70%), they do not lose the ability to burn.

Based on geochemical analyzes of the oil shales from the Diyalli deposit, the bitumen content is 0.52-4.72%, gases is 3.04-6.0% and sulfur is 0.36-0.92% for low-temperature pyrolysis. A small amount of sulfur in the shale is an important factor from an environmental point of view.

Comparison of geochemical features of oil shale in different regions of the country was carried out. Particular attention was drawn to the amount of oil fraction in the bitumen of the Diyalli deposit (48.49%) and Jangichay (67.45%) (Table 1).

Table 1

Comparative analysis of bitumen of the oil shale samples taken from the Diyalli and Jangichay deposits

Composition	Oil shale (Diyalli), %	Oil shale (Jangichay), %
Asphaltenes	0.32	4.87
Oils	48.49	67.45
Resin (benzene)	1.77	12.41
Resins (alcohol-benzene)	0.77	4.31

More than 10 microelements have been determined in the mineral part of the studied oil shales (Table 2).

Table 2

Microelement composition of oil shale samples [1]

Deposit	Microelement, g/t										
	Sr	Ba	Cu	Zn	V	Cr	Mo	Mn	Fe	Co	Ni
Jangichay (South)	220	170	26	160	116	20	4	240	3.36	11	9
Jangichay (North)	168.5	145	77	245.5	103	23	5	185	3.87	17.9	13
Jangidag	350	400	16	236	140	36	<1	960	3.40	17	10
Bayanata	305	188	68	319	129	20	8	243	3.75	9	14.7

The comparative analysis of the oil shale of Azerbaijan and 16 foreign countries (China, Romania, Germany, Brazil, Russia, France, the USA, etc.), according to the main indicators of their quality, showed that oil shale deposits and outcrops of Azerbaijan (Diyalli, Guba, Boyuk and Kichik

Siyeki, Jangichay, Jangidag and Kechallar) outperform in many respects the oil shale of most countries with a developed shale industry, with the exception of the high-calorie oil shales of Estonia and the Sydney field in Australia (Table 3).

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Table 3

Comparative analysis of geochemical features oil shale of Azerbaijan and foreign countries [1]

Deposits	Organic matter, %	Sulfur, %	Ash, %	Calorific value, mJ/kg
Azerbaijan	15.0-31.0	0.4-1.2	65.0-85.0	6.0-12.0
Foreign countries	12.0-28.0	0.7-6.0	51.0-79.0	4.0-10.5

Mud volcanic breccias also contain oil shales of the Paleogene-Miocene age rich in organic matter (OM). The laboratory analysis of these rocks gives a positive result for the search for deep-seated (Eocene-Miocene) oil and gas deposits in the study areas [15], and also as an indicator of hydrocarbon generation.

Geochemical analysis of the oil shales of the Eocene and Maikopian series ejected on the earth's surface by the mud volcanoes of Central and Southern Gobustan was performed. The amount of OM of these oil shales is within 7.56-42.55% (Fig. 4).

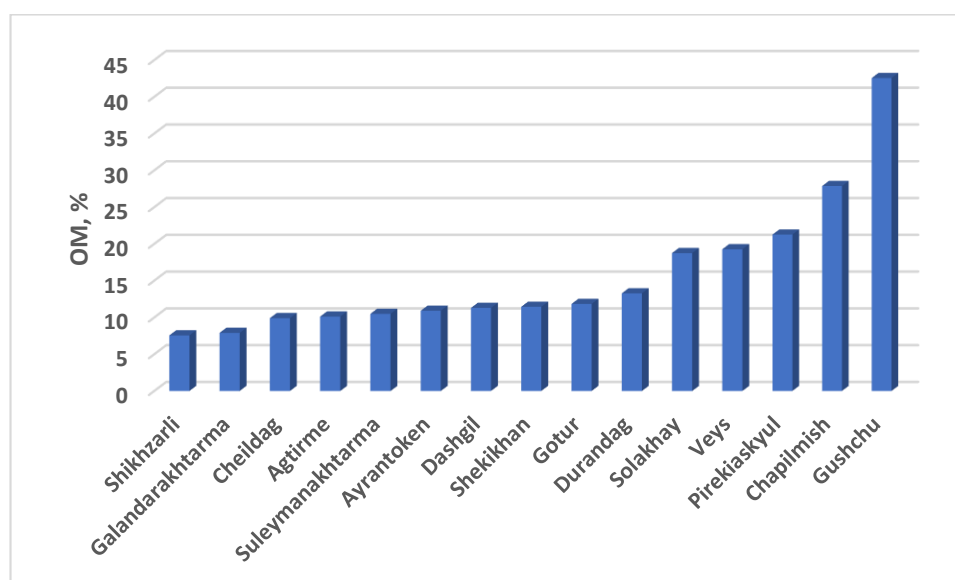


Figure 4 - Amount of OM in oil shale samples taken from the mud volcanoes of Gobustan

The highest amount of soluble organic substances was found in the sample of the oil shale from the Gushchu mud volcano (Shamakhi district) - 8.34% (kerogen - 34.02%). A comparatively less amount (0.56%) is characterized by oil shales from mud volcanoes Chapilmish and Cheildag in Southern Gobustan (Table 4).

A thermal analysis of the oil shale was carried out, which showed the T_{max} of the shale samples. So, samples of the Pirekiashkyul mud volcano with a less content of OM, burned in stages at a temperature of 400 and 500°C. Shales from the Chapilmish mud volcanoes (400°C) and Veys (200 and 400°C), which also contain a comparatively large amount of OM, likewise lose weight in the mass (Fig. 5).

Table 4

Extraction results of oil shales ejected from mud volcanoes in Gobustan

Mud volcano	Amount of dissolved organic matter, %		Amount of kerogen, %
	Chloroform	Alcohol-benzene (1:1)	
Shikhzarli	0.44	0.97	6.15
Pirekiashkyul	1.00	0.61	19.97
Veys	0.51	0.42	16.85
Gushchu	2.54	5.80	34.02

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Chapilmish	0.34	0.22	27.31
Suleymanakhtarma	1.12	0.62	8.75
Cheildag	0.18	0.38	9.35
Galendarakhtarma	1.04	0.74	6.12
Shekikhan	0.59	0.50	10.36
Agtirme	1.16	0.48	8.47
Solakhay	0.82	1.05	9.88
Dashgil	0.72	0.56	10.02
Ayrantoken	0.93	1.02	8.96
Durandag	1.01	0.52	12.35
Gotur	1.22	0.55	10.06

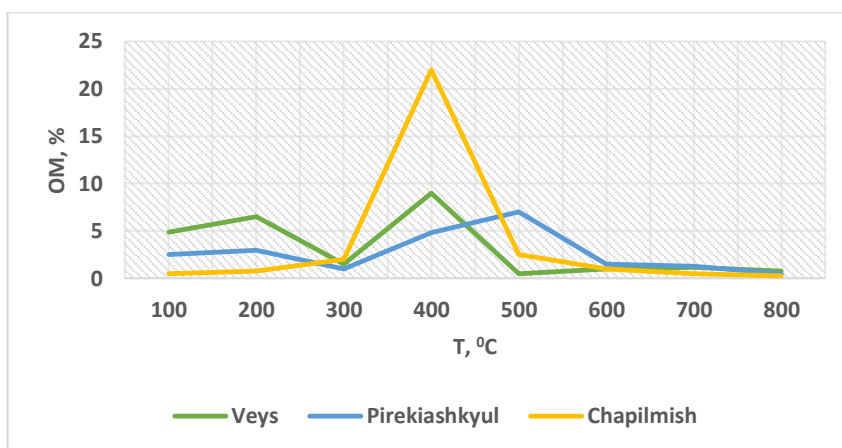


Fig. 5 Results of thermal analysis of oil shale samples taken from mud volcanoes Veys, Pirekiashkyul and Chapilmish

OM, usually, undergoes minor changes. With an increase in temperature, a heteroatomic bond breaks between the nuclei [14]. As a result of the release of high molecular weight heteroatomic derivatives soluble in the solvent, products similar to those of resin and asphaltenes are formed. Kerogen loses the light part (CH_4 , H_2O , CO_2 and C_2H_6) and a high degree of aromatization is observed. Later, the kerogen is changed and the formation of a high molecular heteroatomic compound and relatively small molecules from it. In a sufficiently mature structure of the kerogen, the aromatic plastic layers, forming subparallel rows, increase the ordering between the layers. During the change of organic matter contained in combustible shales under the influence of temperature, the parent rocks undergo catalytic action and this process is accelerated. In this case, a condensed organic substance of an aromatic or aliphatic structure is formed in carbonate rocks. In connection with the lack of polyaromatic groups and heteroatomic bonds in the organic matter of the aliphatic structure, its characteristic feature is an excess of H_2 and a deficiency of O_2 .

Since in OM of the aromatic structure a large number of polyaromatic and O_2 -containing functional groups, long alkane chains and naphthenic acids are of secondary importance, and heteroatomic ketone and carboxyl groups constitute the majority [16, 17]. The content of heteroatomic organic

substances in such compounds, under the influence of temperature, accelerates their decay. Due to the low content of heteroatomic compounds, an additional temperature is required in the organic substances of the aliphatic structure. Thus, organic substances that lose mass at high temperatures correspond to aliphatic structures, and at low temperatures (200°C) to aromatic type structures.

Analytical studies have shown that in the process of thermolysis, the interval of maximum loss of mass depends on the structural structure of the organic matter, primary substances, geological conditions, and also the thermal catalytic effects, etc.

In the process of two-stage pyrolysis at low temperatures, an increase in the amount of bitumen and pyrolysis water is observed, and with increasing temperature and an increase in the amount of gas. Under stable conditions at a constant temperature, large macromolecules of the kerogen structure do not change. At high and low temperatures, the gassing process is clearly observed.

Thus, with the increase in temperature at the final stage during the carbonization process, complete decomposition of the OM takes place. Bitumen obtained in laboratory conditions as a result of pyrolysis of sample samples confirms the possible HC content in these rocks.

Samples from various volcanoes (Veys, Gushchu, Pirekiashkyul, Galandrakhtarma, etc.) at a

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temperature of 500°C form a substance similar to oil (Table 5). In some samples, along with OM,

inorganic compounds are also found.

Table 5

Two-stage pyrolysis of oil shale samples taken from mud volcanoes in Gobustan

Mud volcano	500-550°C			800-850°C		
	Pyrolysis water, %	Bitumen, %	Gas, %	Pyrolysis water, %	Bitumen, %	Gas, %
Shikhzarli	0.24	3.21	3.13	0.84	–	2.64
Pirekiashkyul	0.42	4.12	4.53	0.32	0.42	2.81
Veys	4.25	5.60	6.31	–	–	1.19
Gushchu	1.35	6.18	17.69	0.32	–	11.77
Chapilmish	0.12	1.20	24.0	1.27	–	2.81
Suleymanakhtarma	0.81	3.87	2.34	0.43	–	2.27
Galandaraktarma	0.25	4.15	2.12	0.33	–	2.11
Dashgil	1.80	3.12	7.01	–	–	0.80
Durandag	2.78	3.38	4.17	–	–	1.30
Gotur	0.56	0.45	10.67	–	–	5.53

In the process of heat treatment of kerogen, its decomposition proceeds stepwise, and the process proceeds as follows (Fig. 6).

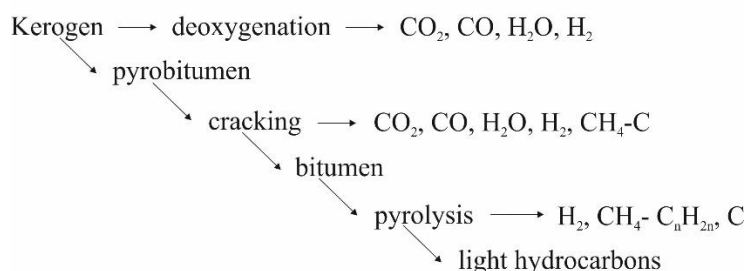


Figure 6 - Stages of decomposition of kerogen in the process of heat treatment

The performed analyzes showed that resinous components are present in the composition of oil shales of some mud volcanoes, which indicates the aliphatic structure of OM, others - gas and light hydrocarbons, which indicates their aromatic structure, which was confirmed by pyrolysis data.

Conclusions

The greatest deposits and outcrops of oil shale in Azerbaijan was registered in Gobustan and on the Absheron Peninsula in Middle Eocene and Upper Miocene (Meotian) sediments. The oil shales of the Diyalli deposit in the Sarmatian age.

It is established that the kerogen of oil shale samples taken from the mud volcanoes Chapilmish, Gotur, etc., takes an active part in the process of oil and gas formation, in others (Gushchu, Veys, Pirekiashkyul, Galandrakhtarma, etc.) is more passive.

The results of geochemical analyzes of oil shales indicate a change in organic matter at the stage of catagenesis. Long aliphatic bonds of C-C are violated, organic matter in the composition of kerogen and minerals are separated from each other and the whole process ends with the formation of hydrocarbons.

The maturity of the kerogen of the oil shales of the Eocene and Maikopian series in southern Gobustan (mud volcanoes Dashmardan, Suleymanakhtarma, etc.), their potential for the generation of hydrocarbons is considered more promising. In addition, a comparative analysis of bitumens obtained from kerogen of oil shales in Eocene-Maikopian age sediments and heavy bitumen fractions (asphaltenes) from Miocene oil saturated rocks indicates their genetic relationship. It is assumed that hydrocarbons can form in the Eocene-

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Maikopian sediments and migrate to the Miocene reservoirs.

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