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PHYSICOCHEMICAL PROPERTIES OF CHOBANDAG SHALE AND THE USE OF PRODUCTS OBTAINED FROM ITS THERMAL DESTRUCTION

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ABSTRACT
In this work, the physicochemical properties of Chobandag shale were studied and its thermal cracking was carried out. Fisher's analysis showed that the shale contained 23% organic matter, 21.94% kerogen, and 3.31% sulfur content. The density of shale is 2.31 g/cm^3. The IR spectrum of shale showed a significant number of aromatic rings, the presence of side chains, and carbonyl-carboxyl groups. The shale was subjected to thermal cracking, where the temperature varied from 500 to 650°C. The content of hydrogen sulfide gas (H_2S) was 11.9%.
We passed the gas over a catalyst prepared using German technology and obtained 76.2% of thiophene and 7.5% of its homologues. The yield of liquid products was 18.4%. We propose to use light resin (up to 200 °C) to isolate thiophene-aromatic concentrate, and heavy resin to obtain oxidized road bitumen.
Keywords: mining shale, kerogen, cracking, shale tar, thiophene, bitumen.

Introduction

Currently, the main pattern throughout the world is the use of fuel and energy resources in order to raise the living standards of the population. The shortage of oil and gas requires the inclusion of oil shale in the country's energy balance. About 60 oil shale deposits have been discovered in Azerbaijan (1), which are mainly concentrated in Gobustan, Shamakhi, and the Lower Kura Lowland. Kerogen is characterized by a high content of hydrogen (7-11%), volatiles (up to 90%), the heat of combustion of kerogen is from 29 to 37 mJ/kg (2). Shales differ from other solid fuels in their higher hydrogen content and greater yield of liquid products during the thermal process. Oil shale processing is developed in Estonia, China, Brazil, USA, Australia and Russia. The thermal decomposition of some shale begins already at a temperature of 300°C, but the maximum yield of decomposition products occurs at 480–520°C. With a further increase in temperature, the gas yield increases and the yield of resin decreases, in which the content of aromatic hydrocarbons increases (3).

Experimental technique.

We took the Chobandag shale for research. Laboratory studies have shown that in this shale organic matter is 23%, kerogen content is 21.94%; the yield of kerogen during pyrolysis is 18.61%, the amount of ash after combustion of oil shale is 70.16%; calorific value is 6.12 mJ/kg; sulfur content is 3.31%, resin yield is 3.21% and shale density is 2.13 g/cm^3.

In Fig. 1 shows the spectrum of the Chobandag shale.

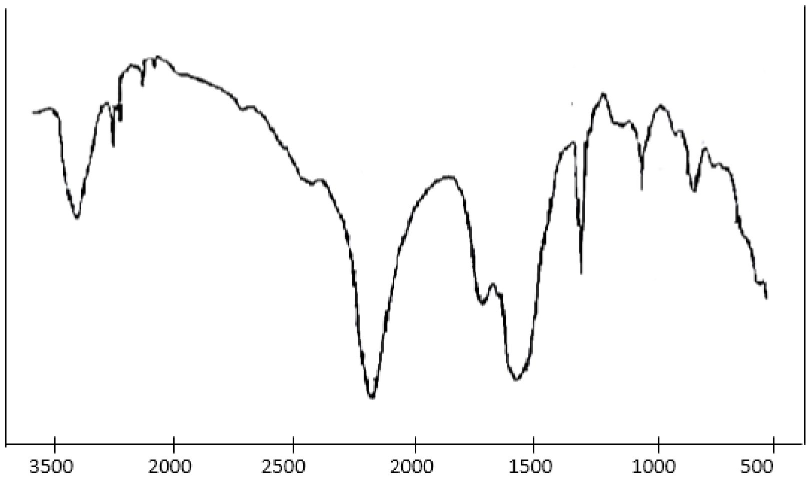

Fig.1. IR spectrum of Chobandag shale.

The absorption band at 3346 cm-1 corresponds to vibrations of OH bonds in phenol alcohols. Absorption bands at 2259.85 cm-1, 2341 cm-1 correspond to CO_2, and 3070 cm-1, 3035 cm-1 to CH_3 and CH_2 groups in alcohol molecules.

The absorption bands 1936-1666 cm-1 belong to the overtones of aromatic nuclei, and 1478 cm-1, 1455 cm-1, 1377 cm-1 belong to the bending vibrations of the CH group.

The absorption bands at 1239 cm-1, 1129 cm-1, 1059 cm-1 show bending vibrations of OH in the COH and OH groups. 811 cm-1, 742 cm-1, 676 cm-1 show bending vibrations of CH bonds in aromatic rings, 1710 cm-1, 1610 and 1630 cm-1 show the presence of carbonyl-carboxyl groups and C=C vibrations of aromatic rings.

We determined the composition of the mineral part of the shale:

Table 1. Composition of the mineral part of shale % mass

Components	SiO_2	Fe_2O_3	CaO	MgO	K_2O	TiO_2	MnO	CuO	ZnO	SO_3	P_2O_5
Mineral part of the Chobandag shale	36,5	21,4	22,7	0,52	0,9	0,86	0,3	0,4	0,2	15,2	1,02

A sample of oil shale was crushed in a laboratory mill, a fraction of ≥0.1 mm was taken, dried at 105°C, and then we carried out thermal cracking at temperatures from 500°C to 650°C.

The diagram of the laboratory setup is shown in Fig. 2.

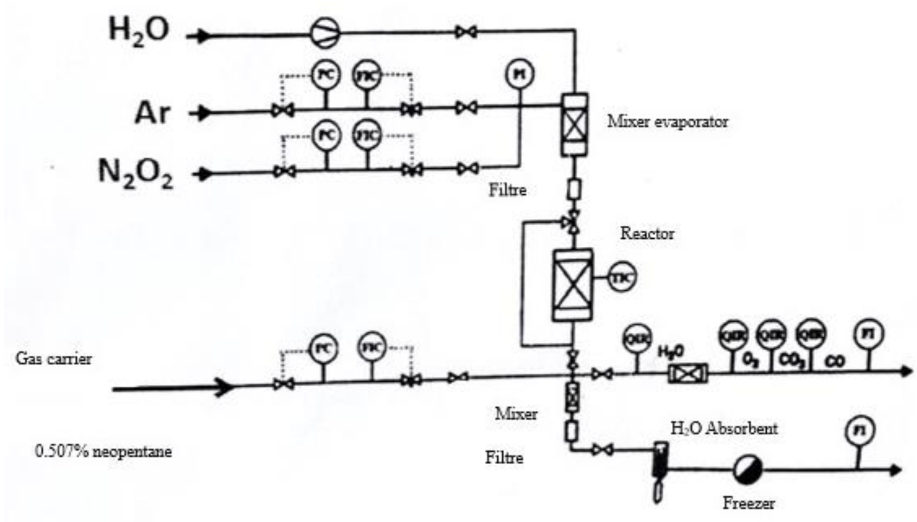

Fig.2. Laboratory setup diagram

The reactor has an internal diameter of 5 cm and is made of stainless steel. Temperature regulation was carried out using a thermostat. The solid residue was collected on a metal filter. The material balance is given in Table 2.

Table 2. Material balance of thermal cracking of Chobandag shale

Indicators	Yield, mass % at temperature			
	500°C	550°C	600°C	650°C
Taken: Slate Total	 100,0 100,0	 100,0 100,0	 100,0 100,0	 100,0 100,0
Received:				
Gas	6,3	6,7	6,95	7,3
Resin	12,68	14,6	16,7	18,4
Water	0,22	0,26	0,85	1,15
Bitumen	3,3	3,04	3,01	2,95
Remaining+ losses	77,5	75,4	72,49	70,2
Total:	100,0	100,0	100,0	100,0

As can be seen from the data in Table 2, the largest amount of liquid products and gas comes out at temperatures of 600°C and 650°C. The composition of the Chobandag shale cracking gas is presented in Table 3 at a temperature of 650°C.

Table 3. Gas composition

Components	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	H_2S
Gas composition, % mass	0,55	1,4	14,8	13,0	11,0	7,2	8,0	4,1	11,6	16,45	11,9

As can be seen from Table 3, thermal cracking gas contains significant amounts of hydrogen sulfide, which can be used to produce thiophene and its homologues (4.5). The practical application and use of a number of products that are synthesized on the basis of thiophene are known - these are pharmacological preparations, pesticides, fungicides, polyorganosiloxanes, which require ~1000 thiophene per year for large-scale production. Livestock consumes approximately 250,000 tons per year of methyl thiophene. In Europe, thiophene is produced by the reaction of hydrogen sulfide and furan at a temperature of 400 °C on oxide catalysts (6).

To obtain thiophene from gas, we prepared a catalyst with the following mass% composition: SiO_2-84%, Al_2O_3-10%, Fe_2O_3-5.4%, K_2O-0.4%; Na_2O-0.2%.

The temperature of the process for producing thiophene and its derivatives on the above catalyst was changed from 550°C to 650°C.

The gas obtained from thermal cracking of oil shale was passed through the prepared catalyst. The results are presented in Table 4.

Table 4. Dependence of product yield on temperature

Temperature °C	H_2S, % mass.		Catalyst composition , % mass				
	From reactor		Thiophene	2-methyl thiophene	3-methyl thiophene	Benzene	Toluene
	before	after					
550	11,9	3,5	48,5	16,1	6,9	16,2	12,3
600	11,9	2,1	55,1	15,4	6,1	16,0	7,4
650	11,9	0,15	76,2	2,2	5,3	10,6	5,7

As can be seen from the data in Table 4, the highest yield of thiophene, 76.2%, was obtained at a temperature of 650°C and the amount of H_2S was reduced to 0.15%. The amount of thiophene homologues obtained was 7.5 mass%. Benzene 10.6% and toluene 5.7% mass were also obtained.

For light thermal cracking resin boiling up to 200°C, the chemical composition presented in Table 5 was determined.

Table 5. Composition of lightweight thermal cracking resin

Components	% yield on resin fraction
Benzene	31,7
Thiophene	16,1
Toluene	6,3
Methyl thiophene	25,5
Ethylbenzene and xylenes	5,8
Other components	14,6

As can be seen, the light cracking resin from Chobandag shale contains 41.6% thiophene and methyl thiophene, which allows the resin to be used to extract thiophene-aromatic concentrate from it.

We propose to use heavy pyrolysis resin as a raw material for the production of bitumen

The resin was placed in a 2.0 liter flask. A glass tube is lowered into the flask, through which air is supplied and stirred all the time. The temperature was maintained at 180-185°C.

The main factors influencing the process are: air flow, raw material oxidation time and process temperature. If the temperature is reduced below 170°C, then the oxidation process has to be carried out for a long time (more than 12 hours). If you increase the air flow, the softening temperature of bitumen increases and the viscosity decreases.

Table 6 shows the results of resin oxidation at a temperature of 180°C depending on the oxidation time and air flow.

Table 7 shows the characteristics of the resulting bitumen.

Results and its discussion

The kerogen content of the Chobandag shale is 21.94%. The results of Fisher's analysis and elemental analysis showed that the shale consists of 70.16% mineral content, the amount of sulfur in it is 3.31%, and the density of the shale is 2130 kg/m^3. The shale was subjected to thermal cracking at temperatures from 500 to 650°C.

The thermal cracking gas of shale contains significant amounts of hydrogen sulfide, which we used to obtain thiophene and its homologues (7).

Based on thiophene, significant amounts of valuable substances needed in medicine, agriculture and other industries are obtained.

Table 6. Oxidation of pyrolysis resin with changes in air flow and oxidation time

№	Oxidation time	Air quantity l/min.	Amount of bitumen obtained	
			Softening temperature according	Conditional viscosity at 60°C
1	8	1	42	73
2	8	3	53	39
3	8	4	57	35
4	6	1	40	74
5	6	3	52	57
6	6	4	56	40
7	4	1	39	74
8	4	3	49	58
9	4	4	54	36

Table 7. Characteristics of the resulting bitumen

№	Indicators	The resulting bitumen	PRB 60/90 CFS 050-2000
1	Density, kg/m^3	1144	Not normal.
2	Viscosity at 135 °C, mPa*sec	233	no less than 230
3	Softening temperature, ºC	54	49-54
4	Penetration at 25 °C 0.1 mm	59	50-70
5	Fragility, ºC	-9	No more than -8
6	Extension, cm	8,5	no less than 8

Using a catalyst prepared using German technology, we obtained 76.2% of thiophene and 7.5% of its homologues. Light cracking resin, boiling up to 200°C, contains 41.6% thiophene and methyl thiophene, as well as 43.8% benzene, toluene and xylenes, which makes it possible to extract a thiophene-aromatic concentrate from the resin. We propose to use heavy pyrolysis resin as a raw material for the production of oxidized bitumen according to CFS 050-2000 at PRB 60/90.

Conclusion

We investigated the Chobandag shale for the first time. It has been shown that shale contains 23% organic matter, 21.94% kerogen, and 70.16% mineral content. The IR spectrum showed the presence of aromatic nuclei and carbonyl-carboxyl groups. The mineral part contains minerals Mg, K, Mn, Zn, P, S, Si, etc.

During thermal cracking of oil shale, the gas contains 11.9% H_2S, which is used to produce thiophene and its homologues. As a result, 76.2% of thiophene and 7.5% of its homologues were obtained. In addition, light pyrolysis resin (up to 200°C) contains 41.6% thiophene and homologues and 43.8% benzene, toluene and xylenes, which can be isolated and used in the chemical industry. Oxidized road bitumen BND 60/90 was obtained from heavy resin.

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TERMİKİ DESTRUKSİYA ZAMANI ALINAN ÇOBANDAĞ ŞİSTİNİN FİZİKİ-KİMYƏVİ XASSƏLƏRİ VƏ ONUN İSTİFADƏSİ

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XÜLASƏ Fişerin analizi göstərmişdir ki, şistin tərkibində 23% üzvi maddələr, 21,94 % keroqen və 3,31% kükürd vardır. Şistin sıxlığı 2,31 q/sm3 təşkil edir. Şistin İQ spektri onda əhəmiyyətli dərəcədə aromatik halqaların, yan zəncirlərin və karbonil-karboksil qruplarının olduğunu göstərmişdir. Şist temperaturun 500° C-dən 650 ° C dərəcəyə qədər dəyişməsi ilə termiki krekingə uğradılmışdır. Hidrogen sulfid (H2S) miqdarı 11,9% təşkil etmişdir.

Qazı alman texnologiyası ilə hazırlanmış katalizatordan keçirərək 76,2% tiofen və 7,5% onun homoloqu əldə edilmişdir. Maye məhsulların məhsuldarlığı 18,4% təşkil edib. Biz tiofen-aromatik konsentratı təcrid etmək üçün yüngül qatranlardan (200 °C-ə qədər), oksidləşmiş yol bitumunun istehsalı üçün isə ağır qatranlardan istifadə etməyi təklif edirik.
Açar sözlər: mədən şisti, kerogen, krekinq, şist, tiofen, bitum

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ЧОБАНДАГСКОГО СЛАНЦА И ИСПОЛЬЗОВАНИЕ ПРОДУКТОВ ЕГО ТЕРМИЧЕСКОГО КРЕКИНГА.

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Резюме. Анализ Фишера показал, что сланец содержит 23% органического вещества, 21,94% керогена и 3,31% серы. Плотность сланца составляет 2,31 г/см^3. ИК-спектр сланца показал значительное количество ароматических колец, наличие боковых цепей и карбонильно-карбоксильных групп. Сланец подвергался термическому крекингу, при котором температура изменялась от 500 до 650°C. Содержание сероводорода (H_2S) составило 11,9%.

Пропуская газ через катализатор, приготовленный по немецкой технологии, мы получили 76,2% тиофена и 7,5% его гомологов. Выход жидких продуктов составил 18,4%. Мы предлагаем использовать легкие смолы (до 200 °C) для выделения тиофен-ароматического концентрата, а тяжелые смолы для получения окисленных дорожных битумов.
Ключевые слова: горночий сланец, кероген, крекинг, сланцевая смола, тиофен, битум.