

## **THERMAL DECOMPOSITION OF THE KENDERLYK OIL SHALE UNDER CONDITIONS OF HIGH-SPEED HEATING\***

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The Kenderlyk oil shale and coal deposit with its prospected reserves estimated at 4 milliard tons plays an important role in industrial development of East Kazakhstan. Lanin and Yershov [1], Semyonova, Fomina and Vainshtein [2] have investigated oil shales and some coals of this deposit from the chemical and technological point of view.

All researchers who have investigated those shales have agreed that by the composition of organic matter those shales are of humus-sapropelitic origin. The Kenderlyk oil shale differs from shales of other deposits by low sulfur content. In the composition of its mineral matter silica and sesquioxides dominate. The content of alkali and alkaline-earth metal oxides is low.

The maximum economical effect may be achieved processing Kenderlyk shales and brown coals by a complex of power-technological methods separating gaseous and liquid products of thermal decomposition for further utilization in chemical industry and burning the coke residue in boiler furnaces of thermal power plants.

Development of the methods suitable for power-chemical utilization of a solid fuel is intensively carried out both in Soviet Union and abroad. Theoretical basis for that advanced method for fuel utilization has been developed by Chukhanov et al. [4-6].

According to theoretical forecasts of Chukhanov [5], confirmed by experimental data, the heating up of fuel particles with velocity of several hundred degrees per second excludes almost completely non-isothermal decomposition of organic matter and enables to carry out the process of its pyrolysis at designed final temperature. This procedure also alters the yield and composition of decomposition products: the yields of gas and low-boiling liquid products increase and the amount of heavy oil decreases significantly.

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High-speed heating may be realized most easily in units for thermal processing of pulverized fuel. Kashirskii et al. [7] have established that high-calorific gas is the main product of thermal decomposition of pulverized shale from Volga Basin and Obschii Syrt.

We have studied the yield and composition of pyrolysis of Kenderlyk shale in pulverized state with heating velocity up to 1700 °C per second considering the prospects of its utilization for producing gas and chemicals.

We studied the shale from a wavy band mined in an adit exploited during World War II. This shale has a laminated structure and is hardly breakable in ball mills. The composition of an averaged sample is presented in Table 1.

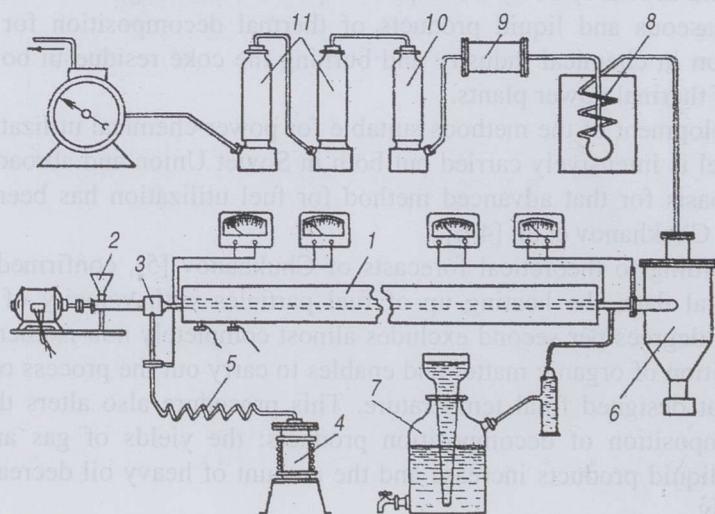
Table 1. Shale Composition (% , on dry matter basis)

A	C	H	S <sub>total</sub>	N	O	CO <sub>2</sub> carb.	The yield of volatiles	Q <sub>bomb</sub> <sup>d</sup> , kcal/kg
45.9	41.48	4.88	0.89*	1.14	5.93	–	42.25	4166

\* Including sulfatic sulfur 0.22 and organic sulfur 0.67 %. Pyritic sulfur was not detected.

Kenderlyk shale kerogen is characterized by resistance to the action of organic solvents. Bitumen A is extracted, by the mixture of alcohol and benzene, in yields up to 3 %, the yield of bitumen C is 1.36 %, on dry shale basis. The content of humic acids, determined by the Kucharenko method [3], made up only 0.64 %, on dry shale basis.

A laboratory-scale unit supplied with a tube reactor from heat-resistant steel is presented in the Figure.



Laboratory-scale unit for thermal decomposition of oil shale

Superheated steam from evaporator 4 directed through superheater 5 into mixer of dust shale feeder 3 is used to transport pulverized shale through the channel in reactor 1. Leaving the reactor 1 mixture of dust, vapour and gas enters the cyclone dust separator 6 where the most part of dust-like coke precipitates. Thereafter vapours and gas are directed via spiral condenser 8 into column 10 filled with calcium chloride and then into adsorbers 11 filled with activated coal for catching gas naphtha. The gas flow is passed through a gas meter and released into the atmosphere.

Thermal decomposition of pulverized shale was investigated at reactor temperatures 900 and 1000 °C. Some series of experiments were carried out at shale consumption 12 g/min and vapour-to-shale ratio 1 : 3. The steam entering the shale feeder 3 was overheated to 450 °C. The temperature of the flow at the reactor outlet, measured by a thermocouple located in the centre of the dust and gas flow, was 750 and 850 °C, depending on the reactor temperature, respectively.

Supposing that the velocity of the particle movement in the reactor channel corresponds to the average velocity of the gas and dust flow, one can calculate the time of heating, equal to the time of particle stay in the reactor high-temperature zone. It does not exceed 0.4–0.5 seconds. Consequently, in the conditions used for the experiments carrying out, the heating velocity of particles suspended in the flow achieved 1400–1700 °C per second.

After each experiment the yield and composition of pyrolysis gas, oil, gas naphtha, condensate of unreacted vapour and coke were determined. Investigation of these products enabled to establish some specific features of the high-temperature decomposition of Kenderlyk shale in conditions of intensive heat exchange.

Table 2. Composition of Nitrogen-Free Pyrolysis Gas

Indices	Reactor temperature, °C	
	900	1000
The yield of gas, dry matter basis, ml/kg	270	498
Gas composition, vol. %:		
H <sub>2</sub> S	0.7	0.3
CO <sub>2</sub>	9.5	7.5
iC <sub>4</sub> H <sub>8</sub>	0.6	–
C <sub>3</sub> H <sub>6</sub> , C <sub>4</sub> H <sub>8</sub>	6.4	1.0
C <sub>2</sub> H <sub>4</sub>	24.0	10.9
CO	17.0	16.3
H <sub>2</sub>	29.1	52.4
C <sub>n</sub> H <sub>2n+2</sub>	12.7	11.6
Q <sub>n</sub> <sup>l</sup> , kcal/nm <sup>3</sup>	7192	4626

The yield and composition of gas obtained on the pyrolysis of pulverized shale in conditions of high-intensive heat exchange in the turbulent flow at close contact of solid particles with vapour-gaseous products is presented in Table 2.

Pyrolysis gas is characterized by low content of ballast constituents and high calorific value. Especially noteworthy is that the gas has an elevated content of unsaturated hydrocarbons, which represent a valuable raw material for organic synthesis industry. In some pyrolysis conditions used by us the gas obtained from pulverized Kenderlyk shale contained up to 35 wt.% unsaturated hydrocarbons (mainly ethylene).

High-temperature thermal processing of Kenderlyk shale in pulverized state enables to create resources of raw material for production of synthetic alcohols, high-molecular compounds and other valuable products in one of the most important industrial regions of Kazakhstan. Pyrolysis gas after removal of unsaturated hydrocarbons (so-called "dry" gas) may be used as a high-quality fuel for industrial and domestic gas supply.

As a result of deep decomposition of shale organic matter, in addition to gaseous components also some oil condensed in spiral condenser 8, and gas naphtha, recovered on activated coal in columns 11 are obtained.

Characteristics of gas naphtha are presented in Table 3.

Table 3. Characteristics of Gas Naphtha

Indices	Reactor temperature, °C	
	900	1000
The yield, on dry shale basis, %	2.20	3.14
$d_4^{20}$	0.8706	0.8810
$n_D^{20}$	1.4982	1.5011
$S_{total}$ , %	0.75	1.13
Iodine number	33.1	6.2

It is necessary to note that on steam distillation of gas naphtha adsorbed on the activated coal, the light fractions get lost; in Table 3 the under-estimated yields of gas naphtha are given.

As one can see in Table 3, the gas naphtha obtained is a strongly aromatized product and, in fact, proves to be crude benzene including also benzene derivatives and polynuclear aromatic compounds. With increasing the reactor temperature up to 1000 °C the yield of gas naphtha increases considerably and its composition also changes. A steep decrease in iodine number points at the decrease in the content of compounds with double-bond containing side chains (Table 4).

A more complete understanding of the composition and properties of liquid products recovered by activated carbon may be achieved basing on the results of distillation of gas naphtha samples in the rectification column.

Data on the fractional composition of its neutral part are presented in Table 4.

Table 4. Characterization of the Fractions of Gas Naphtha

Fraction	Yield (% on neutral petrol basis)	$d_4^{20}$	$n_D^{20}$	$S_{total}, \%$	Iodine number	Average molecular weight
Reactor temperature 900 °C						
Up to 60 °C	1.8	—	1.4738	—	—	—
60–95 °C	69.2	0.8790	1.4989	0.48	12.8	77.9
95–122 °C	5.0	0.8807	1.4960	2.0	22.0	81.7
Residue	17.6	0.8860	1.5030	2.3	21.0	91.6
Reactor temperature 1000 °C						
60–95 °C	88.8	0.8821	1.5011	0.76	2.5	80.3
Residue	8.4	0.8983	1.5039	3.0	14.7	97.1

Product losses on distillation of the first sample made up 6.4 % and those of the second one – 2.8 %.

In both samples of distilled gas naphtha the fraction boiling at 78.8–78.9 °C dominates. Sulfur compounds accumulate in high-boiling fractions and in the residue. Sulfur in gas naphtha seems to be represented by thiophene derivatives. Still bottom represents a dark oil-like mass containing crystals of polynuclear aromatic compounds.

The oil precipitated in the spiral condenser 8 together with the condensate of unreacted steam is characterized by particularly high content of polynuclear aromatic compounds. That product was obtained in an amount of 2.6 %, on dry shale basis, at 900 °C and 1.4 % at 1000 °C, respectively. The first oil sample contained 46.8 % fractions boiling at 200 °C, the second one – 40.6 %.

After the fractions <200 °C were distilled off and the residue was cooled down, a dark-yellow crystalline substance smelling like naphthalene was obtained in both cases. In order to identify aromatic compounds present in the residue, we used the picrate method applied by Lanin, Pronina and Karnayeva [9] for studying the aromatic part of Baltic shale oil. Picrates, separated on treating the alcoholic solution of high-boiling aromatized part of oil with picric acid, were purified by manifold re-crystallization and then their melting points were determined. As judged by colour and melting points of separated picrates it was established that the high-boiling residue of oil contains naphthalene in admixture with small quantities of  $\alpha$ -methyl naphthalene,  $\beta$ -methyl naphthalene and 1,6-dimethylnaphthalene.

Formation of aromatic compounds on high-temperature decomposition of Kenderlyk shale in pulverized state broadens the possibilities to utilize the products of its processing in chemical industry even more.

Dust-like coke of Kenderlyk shale precipitated in cyclon dust separator contains 22–26 % carbon, 1–1.2 % hydrogen and has calorific value of 2000–2400 kcal/kg enabling to use it as a fuel in thermal power plants.

As in our experiments separation of dust-like coke from dust and gas flow takes place in cyclone at temperatures less than 100 °C, it is quite possible that on fast cooling shale coke holds some quantity of liquid high-boiling hydrocarbons that in some degree elevates its calorificity. When average coke samples separated in cyclone were processed in standard conditions, separation of a small quantity of oil with specific weight more than one takes place. For example, on secondary semicoking of a sample of dust-like coke obtained at higher temperatures of decomposition 2.18 % of heavy oil was obtained.

Condensate of unreacted steam separated in coil cooler has a pale-yellowish colour and contains dissolved organic substances in the following ranges, g/l: ammonia 2.7–1.6, pyridine 0.36–0.16, fatty acids 3.7–2.7, volatile phenols – 0.36–0.23, non-volatile phenols – 0.43–0.18. With increasing the temperature of shale processing the content of water-soluble compounds in the condensate decreases.

Laboratory data on the yield and composition of the products of high-speed thermal decomposition of pulverized Kenderlyk shale presented above point at the necessity to work out industrial methods for utilization of that fuel in power and chemical industry. Thermal decomposition of pulverized shale in the flow-reactors with external or combined heating to obtain gas and aromatic hydrocarbons and using dust-like coke as an energetic fuel may be recommended as one of the possible methods of utilizing Kenderlyk shale.

## Conclusions

1. High-temperature thermal decomposition of pulverized Kenderlyk shale in a tube-reactor in the steam flow and at particle heating velocities over 1400 °C per second has been investigated.
2. It has been established that high-calorific gas and aromatic hydrocarbons are the main decomposition products at the final temperatures in the range 750–860 °C. The possibility to produce pyrolysis gas rich in unsaturated hydrocarbons has been elucidated.
3. The ideas about complex utilization of Kenderlyk deposit oil shale to produce gas and chemicals are presented.

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