

INVESTIGATION OF FLASH PYROLYSIS OF KUKERSITE OIL SHALE

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Series of experiments on flash pyrolysis of fine-grained particles of kukersite oil shale were carried out on a laboratory-scale installation operated with gaseous heat carrier. It was shown that practically the whole of organic matter turns into volatile products at temperatures higher than 900 K. The pyrolysis gas consists of saturated and unsaturated hydrocarbons, CO₂, H₂, CO, and H₂S, and belongs to high-calorific fuels with lower calorific value of 33 MJ/Nm³. The yield of liquid products reaches its maximum (70%) in the temperature range 850–900 K. Kinetic parameters of formation of the volatile components were determined on the basis of obtained experimental data and available structural characteristics of kukersite kerogen. As the first approximation, the formation of shale oil components can be described by a single rate constant $6.3 \times 10^{13} \exp(-25600/T) \text{ s}^{-1}$. Their decomposition is governed by the rate constant $1.7 \times 10^{10} \exp(-20480/T) \text{ s}^{-1}$.

Introduction

Processing of solid fuels is a complex approach to their utilization, at which purely power processes (fuel combustion and heat release) are coupled with technological ones (gasification and pyrolysis) [1]. The main purpose of this approach is to increase the efficiency of fuel conversion to heat and electricity with simultaneous minimization of the environmental impact. As raw materials for processing, the fuels with high yield of volatiles (lignite and oil shale) are the most appropriate.

Oil shale is characterized by a high content of mineral components, which are closely connected with organic matter (kerogen). Therefore, direct combustion of oil shale in boilers of steam-generators is confronted with

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some technical difficulties. Nevertheless, oil shale is used in some countries (Estonia, Israel, China, and Germany) for electricity generation [2–7]. The oil shale kerogen is a homogeneous molecular compound insoluble in organic solvents and resistant to the action of the majority of chemicals. The kerogen is characterized by high content of hydrogen (the mass ratio C/H is approximately equal to eight and is close to the corresponding value for raw oil) [8]. In this connection, thermal processing of oil shale allows to transform up to 90% of its organic mass into vapour products and to produce not only high-quality boiler fuel, but also motor fuels [9] and valuable chemical raw materials [10].

Experimental data on the kinetics of oil shale pyrolysis concern, mainly, non-isothermal conditions, when oil shale particles are heated with comparatively low rates of the order of 0.1–1 K/s up to temperatures 600–800 K (so-called conventional pyrolysis or retorting) [11–13]. Pyrolysis products formed in the particles migrate outside. This process is accompanied by various secondary reactions such as condensation and polymerization to high-molecular compounds [14] with the deposition of a certain amount of solid carbon (coke) and release of the corresponding amount of gas [15].

Flash pyrolysis of fine-grained oil shale particles (less than 100 μm in size), of low internal thermal resistance, heated with rates of the order of 10^4 – 10^5 K/s, allows to minimize the influence of secondary processes and singling out the genuine kinetics of kerogen decomposition [14, 16]. The rate constant of the process becomes independent of particle diameter, heating rate, ambient conditions, etc. In this work a series of experiments on flash pyrolysis of kukersite oil shale were carried out. The kinetic model of component yield of the volatiles, which gives a wholly satisfactory description of the process in a wide range of its parameters, was constructed on the basis of obtained experimental data and structural characteristics of kukersite kerogen [17].

Experimental

Thermal decomposition of the kukersite oil shale was investigated on a laboratory-scale installation operated with gaseous heat carrier (carbon dioxide) in continuous and stationary conditions varying temperature and pyrolysis duration. The schematic diagram of the installation is given in Fig. 1. The mixing of fine-grained oil shale with hot heat carrier occurs in the outlet placed in the upper part of the reactor. The formed gas/solid mixture passes through the reaction volume, arrives at the exit and enters the system of gas cleaning (separator and cyclone). The process stops by means of an abrupt cooling of the refined pyrolysis products to temperature about 600 K at their mixing with cold carbon dioxide.

The sieve analysis of the oil shale shows that 50 wt.% of particles are smaller than 14 μm and 75 wt.% – less than 30 μm . As theoretical estima-

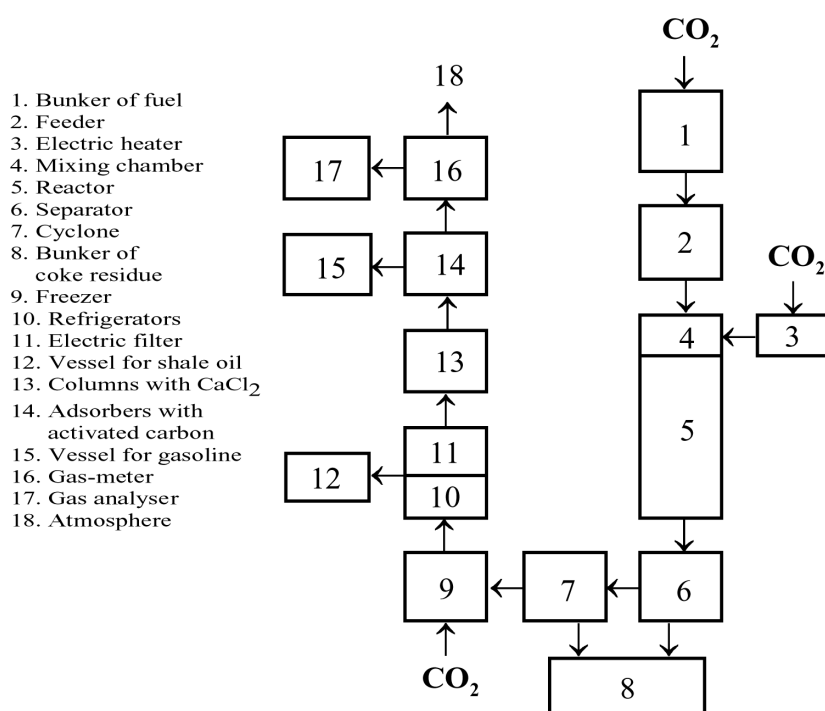


Fig. 1. Schematic diagram of the fast pyrolysis reactor.

tions show, at such high degree of oil shale milling the main fuel mass is heated with the rate of the order of 10^5 K/s, which allows to preserve the kerogen structure practically invariable up to reaction temperature. High dispersity of oil shale particles reduces to minimum the change of primary pyrolysis products under their passing through particles pores. The calculation of the process duration was carried out on the basis of average volume feeding rate of heat carrier/oil shale mixture and value of the reaction volume. This process parameter changes from 0.26 to 0.22 s depending on temperature ($T = 790\text{--}930$ K).

The system of condensation and catching of liquid pyrolysis products includes water and air refrigerators, electric filter, columns with calcium chloride, and adsorbers with activated carbon. The vapours of heavy fraction of shale oil and water were condensed in refrigerators. The rest of shale oil was caught by electric filter. The final step of gas drying was carried out on calcium chloride. The obtained shale oil underwent distillation in the rotor evaporator under vacuum for moisture removal. Gasoline was caught by activated carbon and then desorbed by distillation with overheated steam. Clean semicoking gas was passed through a gas-meter and thrown into the atmosphere. The average sample of 100 litres was collected for determination of gas composition. The discrepancy of 2% was accepted at formation of material balance.

The composition of pyrolysis gas was determined with the help of methods of gas and liquid chromatography (C_2 – C_4 hydrocarbons, CO_2 , and H_2S) and gas-adsorption chromatography (hydrogen, CO, and methane) [18]. The investigation of shale oil composition was carried out by a combined method. The phenol fraction of the shale oil was isolated firstly. Its individual composition was determined by means of gas and liquid chromatography. The rest was separated using preparative thin layer chromatography [19]. The composition of the gasoline was determined with the help of gas chromatography.

Kerogen structure

The modern kerogen models consider it to be a complicated three-dimensional polymer, which consists of aromatic, hydroaromatic, and heterocyclic structures (clusters) connected with each other by aliphatic chains and containing various functional groups (hydroxyl, methyl, carboxyl, etc.) as substitutes [20]. The investigation of the kerogen structure has been carried out using microscopic, spectroscopic, and pyrolytic methods, which allow identifying of its main units [21]. In accordance with the classification method [22], the type of kerogen was determined by the ratio of intensities of aliphatic (2860 and 2930 cm^{-1}), carboxyl/carbonyl (1710 cm^{-1}), and aromatic (1630 cm^{-1}) groups in infrared spectra.

Kukersite is an Ordovician oil shale formed in marine environment. Its principal biological component is probably an extinct microorganism *Gloeocapsomorpha prisca* that determines the structural characteristics of oil shale organic mass [23]. Kukersite kerogen belongs to intermediate II/I type in classification scheme [22] with high value of ratio H/C (kerogen of aliphatic type) [24]. Spectroscopic investigation of this kerogen by FTIR and solid ^{13}C NMR methods shows the presence of a considerable quantity of aromatic constituents, mainly oxygenated ones corresponding to phenols. Oxygenated aromatic structures are also presented in the kerogen decomposition products obtained under fast pyrolysis. This group of compounds consists of three main subgroups that correspond to the following basic structures: 3-*n*-alkylphenols, 5-*n*-alkyl-1,3-benzenediols (alkyl-resorcinols), and *n*-alkylhydroxybenzofurans [23, 25].

Cyclic structures in the kukersite kerogen are connected with each other with the help of long (up to C_{19}), linear alkyl chains, which disintegrate under pyrolysis yielding aliphatic hydrocarbons, mainly *n*-alkanes and *n*-alkenes-1. Relatively low intensity of methyl groups ($-CH_3$) on the FTIR-spectrograms as compared with corresponding values for other aliphatic groups ($-CH_2-$) indicates a low branching level of alkyl chains. Remainder of chain yields to the gas phase under heating phenols considered above as well as *n*-alkyl-cyclohexanes, *n*-alkylbenzenes, and 1-*n*-alkyl-2-methylbenzenes. Additionally, the pyrolysis products of kukersite kerogen contain polycyclic

aromatic compounds (naphthalene, C₁–C₃ alkyl naphthalenes, indene, etc.), which represent the remainders of condensed aromatic clusters [23].

Alkylated phenolic structures, mainly alkylresorcinols and condensed alicyclic rings connected by aliphatic chains, underlie the molecular model of kukersite kerogen elaborated in [17] on the basis of spectroscopic investigations. The analysis of the distribution of chemical elements over the functional groups in this model shows that carbon concentrates mainly in the chain structure of kerogen (up to 65%). The greater part of oxygen belongs to hydroxyl groups connected with aromatic and hydroaromatic structures, which are the precursors of phenols' formation under pyrolysis.

Kinetics of kerogen thermal destruction

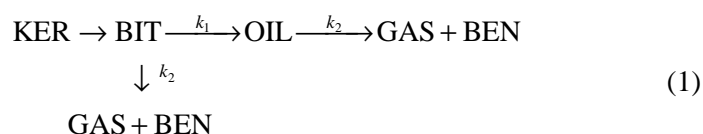
Heating of oil shale particles leads to conversion of kerogen (KER) into plastic state – bitumen (BIT) followed by its decomposition into a mixture of liquid hydrocarbons, semicoking gas (GAS), and coke residue (COKE) [26]. The mixture of liquid hydrocarbons is usually divided into a heavy constituent – shale oil (OIL) and a light one – gasoline (BEN). Bitumen is a non-volatile matter soluble in benzene in contrast to kerogen, which is not soluble in organic solvents. During conventional pyrolysis, which is characterized by comparatively low heating rates, a considerable part of bitumen is coked. Flash pyrolysis allows practically complete decomposing of bitumen into volatile components [27].

In spite of considerable progress in understanding of kerogen structure and mechanisms of its depolymerization at high temperatures, the modeling of the process is, as a rule, limited by simple kinetic models, which describe conversion of an initial macromolecule as a whole without specifying of formed products. These are first of all one-stage models with one [28, 29] or more [30, 31] first-order chemical reactions. Two-stage and multi-stage models consider the conversion of kerogen into bitumen followed by separation of gas and shale oil and coke residue formation [27, 32–34]. Kinetic parameters of kerogen pyrolysis for various kinds of oil shales are determined basing on experimental data using manifold analysis techniques including: the Direct Arrhenius Method [29], Integral and Differential Methods [29, 35], Friedman Procedure, Maximum Rate Method, etc. [13, 31].

Some works attempt to elaborate general principles for construction of pyrolysis models, in which multitude chemical characteristics of kerogen are used to reproduce its structure [36–38]. Chemical changes occurring in kerogen during its heating are described by a set of chemical reactions established by experiments with model chemical agents. Nevertheless, in spite of the fact that these models are based on a more detailed conception of kerogen structure and processes occurring at its thermal decomposition, they are not suitable enough for practical use.

In the present work, behaviour of kukersite kerogen at high temperatures is described using the model of functional groups, which has been successful in description of pyrolysis of coals [39] and synthetic resins [40]. In accordance with the process mechanism described above, fast heating of oil shale particles leads to the abstraction of substituted groups from ring clusters and decomposition of hydroaromatic and aliphatic chain structures. The process results in the formation of methane from methyl ($-\text{CH}_3$) groups, CO from ether ($-\text{O}-$) and carbonyl ($>\text{C}=\text{O}$) groups, CO_2 from carboxyl and ester ($-\text{COO}-$) groups, H_2O from hydroxyl ($-\text{OH}$) groups, hydrocarbons from aliphatic ($-\text{CH}_2-$) groups, and H_2S from sulphides. The abstraction of large molecular fragments from organic matrix leads to the separation of high-molecular aliphatic and aromatic hydrocarbons and asphaltenes into the gaseous phase. Hydroaromatic and aliphatic structures are the source of donatable hydrogen, which is consumed for stabilization of free radicals and formation of H_2 .

The model of functional groups describes the release of components into the gaseous phase as a first-order chemical process [39]. The analysis of experimental data as applied to flash pyrolysis of kukersite [27] allows proposing the following global kinetic scheme of the process:



In accordance with this scheme, the yields G_i (kg/kg of dry oil shale) for components of shale oil are determined from the system of kinetic equations:

$$\begin{aligned} dG_i / dt &= k_1 Y_i - k_2 G_i, \\ dY_i / dt &= -k_1 Y_i - k_2 Y_i, \end{aligned} \quad (2)$$

where Y_i is the content of i th functional group in oil shale (kg/kg of dry oil shale), k_i are the rate constants (s^{-1}). The initial conditions are the following: $Y_i|_{t=0} = Y_{i0}$, $G_i|_{t=0} = 0$. It is assumed that the release of every component into the gaseous phase and its decomposition into light constituents is described by individual rate constants. The integration of system (2) as applied to isothermal conditions when rate constants do not depend on time allows to derive the following analytical expression for the dependence $G_i = G_i(t)$:

$$G_i = Y_{i0} \exp(-k_2 t) [1 - \exp(-k_1 t)]. \quad (3)$$

The analytical expression for the yields G_i of gas and gasoline components assuming that their formation occurs at both abstraction of corresponding functional groups from bitumen macromolecule and decomposition of shale oil components can be written as:

$$G_i = Y_{i0} [1 - \exp(-k_2 t)]. \quad (4)$$

The kinetic parameters of the model as applied to flash pyrolysis of kukersite were obtained in the present work by the fit of calculated curves that describe process dynamics in isothermal conditions to the experimental data. Determination of the initial content of functional groups in organic mass of oil shale was carried out basing on distribution of carbon and oxygen over the structural units presented in [17].

Results and discussion

The main purposes of the experimental investigation were determination of product composition at various temperatures of the process and revealing conditions with the maximum yield of shale oil. The experiments were carried out with the kukersite oil shale, which was thoroughly studied under laboratory and industrial conditions. The average composition of kerogen in considered oil shale specimens is as follows: C = 67.6; H = 8.2; O = 19.0; S = 4.8; N = 0.4 wt.%. The average content of kerogen is equal 0.426 kg/(kg of dry oil shale).

Pyrolysis gas formed in experiments consists of saturated and unsaturated hydrocarbons, carbon dioxide, hydrogen, CO, and H₂S, and belongs to high-calorific fuels with lower calorific value of the order of 33 MJ/Nm³ and average density 1.3 kg/Nm³. Figure 2 shows the gas composition at various temperatures. Its characteristic feature is high content of unsaturated hydrocarbons, which reaches 26.5 vol.% at $T = 930$ K.

For determination of rate constants k_{2i} of gaseous components formed from bitumen and shale oil, Eq. (4) was rewritten as:

$$k_{2i} = -\ln(1 - G_i/Y_{i0})/t. \quad (5)$$

The values of G_i entered in Eq. (5) were measured in experiments. The process time t in each experimental series was fixed and changed from 0.26 to 0.22 s depending on process temperature ($T = 790$ – 930 K). Eq. (5) allows to construct the experimental dependence $k_{2i} = k_{2i}(T)$ at known values of Y_{i0} .

As mentioned above, the formation of molecular hydrogen under thermal destruction of kerogen and decomposition of shale oil is mainly the result of recombination of H atoms released from hydroaromatic structures during the process of their aromatisation. One hydroaromatic structural unit (cyclic $>CH_2$ group) evolves one H atom. Methane is formed under abstraction of methyl ($-CH_3$) groups from kerogen macromolecule. Carbon oxide is generated owing to evolving of ether ($-O-$) and carbonyl ($>C=O$) groups. The initial content of functional groups Y_{i0} in kukersite kerogen can be estimated on the basis of its elemental composition and the distribution of carbon and oxygen over the structural units in the molecular model of kerogen [17]. For the given gas components, the values of Y_{i0} are equal: H₂ = 0.0024; CH₄ = 0.0161; CO = 0.0463 kg/(kg of dry oil shale).

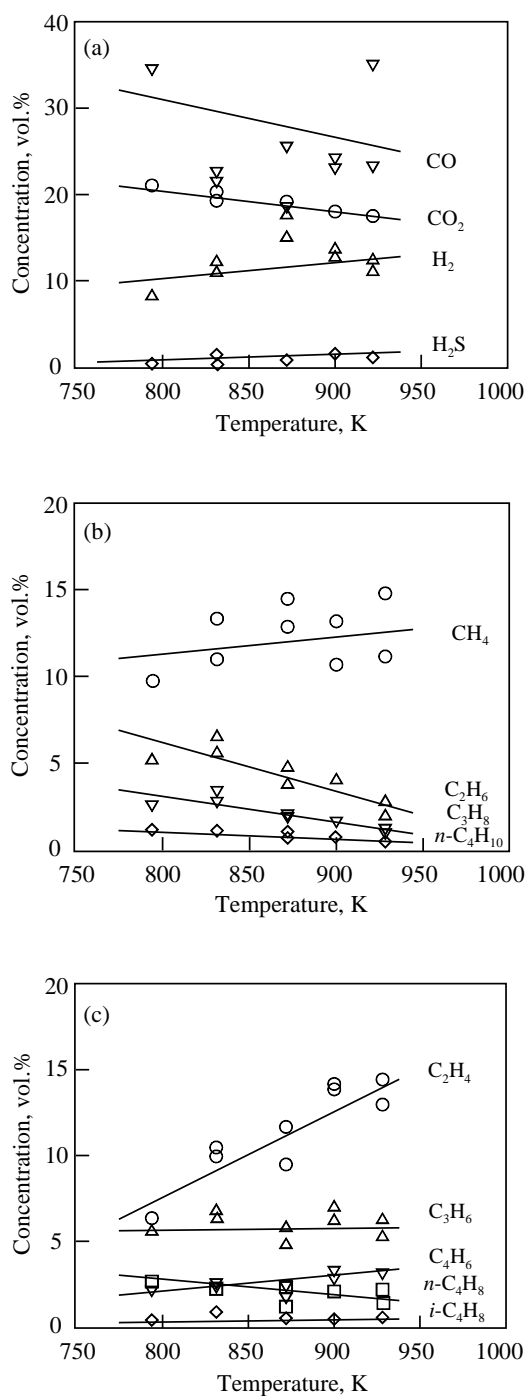


Fig. 2. Semicoking gas composition: (a) non-hydrocarbon components; (b) paraffins; (c) olefins.

Figure 3 represents the experimental values of the rate constants k_{2i} expressed in Arrhenius coordinates. As can be seen from the figure, the data scattering at fixed temperatures is slight, which gives grounds for their approximation with a single rate constant: $k_2 = 1.7 \times 10^{10} \exp(-20480/T) \text{ s}^{-1}$. This statement is confirmed by the results of comparison of experimental and calculated values of the components yields G_i , which are shown in Fig. 4. Identification of Y_{i0} values for the other gas components is difficult because of complexity of the kerogen structure and the mechanisms of its decomposition. Nevertheless, the relative constancy of the semicoking gas composition at various temperatures, as one can conclude from Fig. 2, allows using the obtained value of k_2 for all gaseous components.

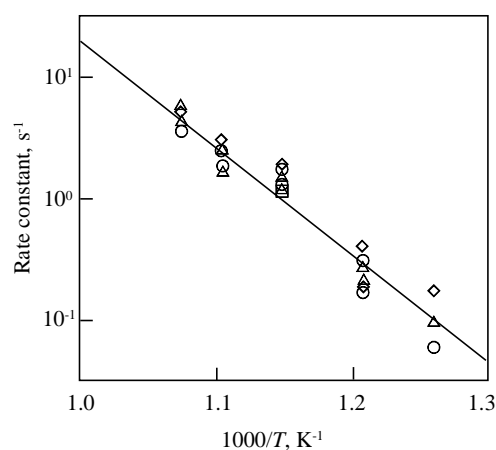


Fig. 3. Arrhenius plot for various gaseous components: (O) – H_2 ; (◇) – CO ; (Δ) – CH_4 . Points are the experimental data; line is the approximation result.

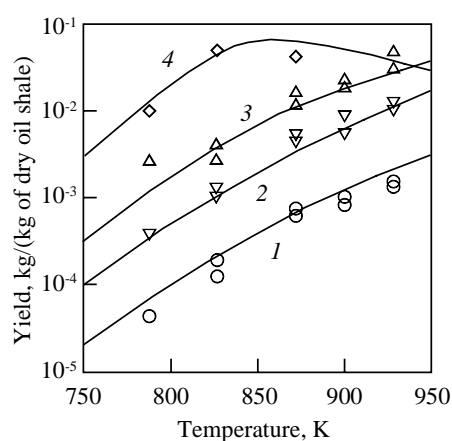


Fig. 4. Comparison of calculated (lines) and experimental (points) yields of various components: (1, O) – H_2 ; (2, ∇) – CH_4 ; (3, Δ) – CO ; (4, ◇) – phenols.

The shale oil obtained in conditions of fast pyrolysis represents a viscous, deep-brown and foxy liquid. Its yield grows with the increase in process temperature, reaches the maximum in the temperature range 850–900 K, and thereafter decreases, which is the consequence of OIL decomposition into GAS and BEN as shown on the scheme (1). The composition of the shale oil determined with the help of chromatographic methods is given in Table 1. One can see that concentration of phenols has a maximum at $T = 830$ K. The content of aliphatic and aromatic hydrocarbons decreases at the temperature rise, whereas the part of asphaltenes and other heavy constituents increases.

Thus, the shale oil composition changes within wider limits than that of gas. Nevertheless, the yields of oil components as a first approximation can be described by a single rate constant: $k_1 = 6.3 \times 10^{13} \exp(-25600/T) \text{ s}^{-1}$. It should be noted that the obtained shale oil is of high activity and forms a considerable amount of insoluble sediments in contact with alkalis and acids, which distorts the ratio between its components.

The composition of phenols was studied by means of gas and liquid chromatography. The main representatives of the fraction are simple phenols, cresols, xylenols, naphthols, and alkylresorcinols with the length of side chain from C_4 to C_9 (see Fig. 5). At process temperature $T = 790$ K, the fraction consists mainly of alkylresorcinols, whereas the relative concentration of the simple phenols is insignificant. The picture somewhat changes with the increase in temperature, and at $T = 870$ K the prevalence of resorcinols is not observed.

The formation of phenols occurs at abstraction of aromatic fragments containing hydroxyl group (cyclic $-OH$ group) from the kerogen macromolecule. The initial concentration Y_{i0} for phenols can be estimated on the basis of structural characteristics of kukersite kerogen [17] and its elemental composition. Its value is equal 0.102 kg/(kg of dry oil shale), if heptylresorcinol $C_6H_4(OH)_2(CH_2)_6CH_3$ is chosen as a typical representative of phenols. In Fig. 4, the experimental values of G_i for this fraction are compared with the curve calculated using Eq. (4). A wholly satisfactory agreement of represented data was observed.

Table 1. Composition of shale oil

Compounds	Temperature, K		
	790	830	870
Phenols	11.02	21.53	14.14
Aliphatic hydrocarbons	9.01	4.80	3.85
Monocyclic aromatic compounds	6.34	3.83	1.41
Polycyclic aromatic compounds	8.23	6.14	6.06
Heterocyclic compounds	20.12	19.54	20.12
Asphaltenes and resinous compounds	12.49	18.86	18.52
Inclined to resinification and losses	32.79	25.30	35.90
Shale oil yield, kg/(kg of dry oil shale)	0.089	0.233	0.266

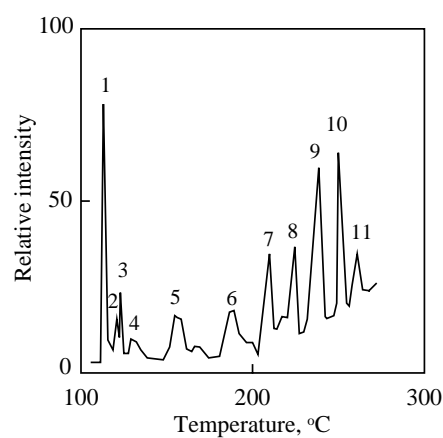


Fig. 5. Chromatogram of phenol fraction: 1 – simple phenols; 2 – *o*-cresol; 3 – (*m+p*)-cresols; 4 – xylenols; 5 – naphthols; 6 – 5-butyl-resorcinol; 7 – 5-pentyl-resorcinol; 8 – 5-hexyl-resorcinol; 9 – 5-heptyl-resorcinol; 10 – 5-octyl-resorcinol; 11 – 5-nonyl-resorcinol.

Identification of initial concentrations Y_{i0} for other shale oil components is difficult. In the present study, the attempt was made to restore these values on the basis of experimental data given in Table 1. In Fig. 6, the experimental yields G_i of shale oil components are compared with their calculated values. The calculations were carried out using Eq. (3) with Y_{i0} , which were

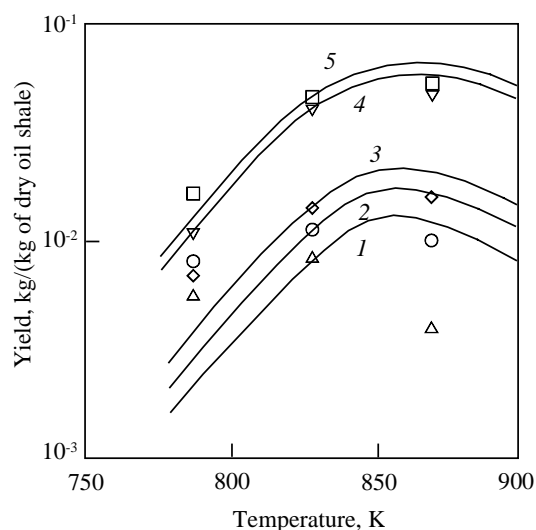


Fig. 6. Yields of shale oil components: (1, Δ) – monocyclic aromatic compounds; (2, O) – aliphatic hydrocarbons; (3, \diamond) – polycyclic aromatic compounds; (4, ∇) – asphaltenes; (5, \square) – heterocyclic compounds. Points are the experimental data; lines are the calculation results.

obtained under the condition that measured and calculated values of G_i coincide at $T = 830$ K. The analysis of Fig. 6 shows that a satisfactory agreement is observed only for heteroatomic compounds and asphaltenes.

Gasoline (BEN) consists of paraffins (from n -pentane to n -nonane and 2,7-dimethyloctane), olefins (from butene-1 to nonene-1), and aromatic hydrocarbons (from benzene to 1-methyl-4-ethylbenzene). The average concentrations of these constituents of gasoline fraction are equal to 15, 35 and 50 wt.%, respectively. At the temperature increase, the mass content of paraffins and aromatics decreases, whereas the corresponding value for olefins grows. The decrease of aromatics mass content is mainly the result of lowering the concentration of heavy alkyl derivatives of benzene. The yield of gasoline increases about three times more when process temperature grows from 830 to 930 K. The kinetics of gasoline components' formation yield is characterized by rate constant k_2 . As the results of measurements show, the ratio G_{gas}/G_{ben} is equal to 4. Therefore, one ought to use the rate constant $0.2 k_2$ when dealing with the kinetics of gasoline fraction formation.

In spite of the fact that the model of functional groups is unable to predict the yield of all products of oil shale flash pyrolysis, the obtained data allow to describe quite well the process kinetics as a whole. In Fig. 7, the experimental values of the concentrations of the main products are compared with the data calculated using the global kinetic model (1). The figure shows that the organic mass of coke residue quickly decreases with temperature growth, and at $T \geq 900$ K becomes insignificant. This allows to draw the conclusion that in conditions of flash pyrolysis practically the whole of organic matter of oil shale turns into volatile products. The growth of gasoline yield at high temperatures is obviously related to decomposition of heavy fraction of shale oil, which is confirmed by the decrease of oil total yield at $T \geq 870$ K. The

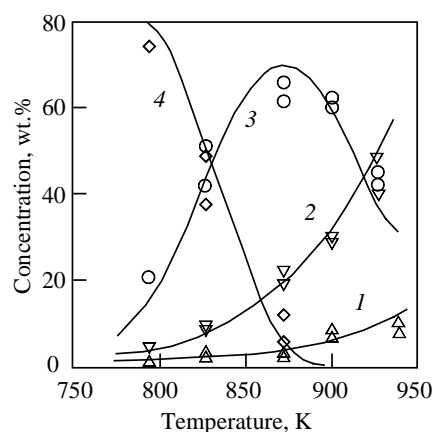


Fig. 7. Mass concentrations of various fractions in products of fast pyrolysis of kukersite: (1, Δ) – semicoking gas; (2, ∇) – gasoline; (3, \circ) – shale oil; (4, \diamond) – coke residue. Points are the experimental data; lines are the calculation results.

maximum yield of liquid pyrolysis products reaches the maximum in the range 850–900 K and is about 70 wt.%.

It should be noted that the understated values of concentrations calculated for temperatures exceeding 900 K (see Fig. 7) can be explained, on the one hand, by self-inhibition action of pyrolytic reactions [41], which reduces the decomposition rate at the increase in organic mass conversion. On the other hand, the same functional groups usually contain various structural units with different bond energies whose thermal decomposition occurs at different rates [42].

The error analysis of experimental data shows that the discrepancy of the material balances in measurements reaches 10 wt.%. This can be explained by large dilution of pyrolysis products with carbon dioxide. The difference between experimental and theoretical data observed for some components (monocyclic and polycyclic aromatic compounds, aliphatic hydrocarbons, etc.) is due to imperfection of the used global kinetic model. In particular, every component of shale oil is a set of compounds with different rate constants of their decomposition. Their determination requires additional experimental data.

Conclusions

The process of flash pyrolysis of kukersite oil shale was investigated on a laboratory-scale installation operated with gaseous heat carrier (carbon dioxide) in continuous and stationary conditions. The composition of the main pyrolysis products (semicoking gas, shale oil, and gasoline) was determined by means of gas and liquid chromatography. It was found that the yield of liquid products reached maximum in the temperature range 850–900 K amounting to the value of the order of 70%. The pyrolysis gas consists of saturated and unsaturated hydrocarbons, CO₂, H₂, CO, and H₂S, and belongs to high-calorific fuels with lower calorific value of 33 MJ/Nm³.

The kinetic parameters of formation of volatile components, which give a quite satisfactory description of the process, were determined on the basis of experimental data and available structural characteristics of kukersite kerogen. As the first approximation, formation of shale oil components can be characterized by a single rate constant $6.3 \times 10^{13} \exp(-25600/T) \text{ s}^{-1}$. Their decomposition is governed by the rate constant $1.7 \times 10^{10} \exp(-20480/T) \text{ s}^{-1}$. These parameters will be used in a subsequent work for construction of a mathematical model for pyrolysis of large oil shale particles including migration of volatile products in the interior of the particle and various secondary reactions (cracking, condensation, and polymerization of the shale oil with coke deposition).

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