

MODELING OF THE PROCESS OF PYROLYSIS OF SHALE PARTICLES

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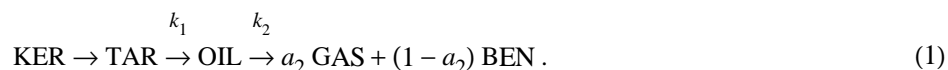
Based on an analysis of experimental data on the pyrolysis of Baltic shale, a kinetic model of the process with allowance for the polydispersity of fuel particles, secondary chemical reactions, and fragmentation of the particles has been constructed.

Oil shales are a solid fuel with a high content of mineral components which are closely related to the organic matter (kerogen). The mineral part is subdivided into carbonate and sandy components the relation between which is dissimilar for different shales and can vary over fairly wide limits. Kerogen is a homogeneous molecular compound insoluble in organic solvents and resistant to the action of the majority of chemical reagents. Although there are many technologies of processing of shales, comparatively little is known about the origin and composition of kerogen [1]. Kerogen is characterized by a high content of hydrogen (the mass ratio C/H is approximately equal to eight and is close to the value of this quantity for oil).

When shale particles are heated, kerogen (KER) transforms into a plastic state to release tar (TAR), subsequently disintegrating into the mixture of liquid hydrocarbons, gas (GAS), and coke (COKE). From the mixture of liquid hydrocarbons, one usually isolates a heavier component, i.e., shale oil, and a lighter component, i.e., natural gasoline (BEN). The available experimental data on the thermal destruction (pyrolysis) of kerogen and further behavior of pyrolysis products are used in the present work for construction of a kinetic model of the process and determination of the rate constants of its individual stages.

1. Experimental data on the kinetics of pyrolysis of shale are very limited and hold true mainly for the region of temperatures below 700 K (low-temperature pyrolysis, or retorting) [2]. The parameters of the process at higher temperatures (750–950 K) have been determined in [3]. Baltic shale kukersite, which has been much studied under laboratory and industrial conditions and is widely used in the shale-processing industry, was selected for the experiments. The pulverized shale was heated to the temperature of the process with a rate of the order of 10^5 K/sec in the cocurrent flow of an inert gas heat-transfer agent. The process was carried out in the isothermal regime with a characteristic time of 0.24 sec. The composition of the pyrolysis products is given in Table 1. It is seen that the release of shale oil increases with temperature, passes through its maximum in the temperature range 870–900 K, and decreases at 930 K. The maximum yield of the oil is a value of the order of 73% in calculation for the conventional combustible mass of the shale. The growth in the release of gas and natural gasoline with temperature is probably related to the subsequent decomposition of the heavy part of the oil, which is confirmed by the decrease in its total yield.

The analysis of the experimental data of [3] enables us to propose the following kinetic scheme of the process:



Under the assumption of the first order of the reaction in the concentrations of the components, the decomposition of the tar and the release of volatiles as a gas phase are described by kinetic equations of the form

$$\begin{aligned} dx_i/dt = w_i , \\ w_{\text{tar}} = -k_1 x_{\text{tar}} , \quad w_{\text{oil}} = k_1 x_{\text{tar}} - k_2 x_{\text{oil}} , \quad w_{\text{gas}} = a_2 k_2 x_{\text{oil}} , \quad w_{\text{ben}} = (1 - a_2) k_2 x_{\text{oil}} . \end{aligned} \quad (2)$$

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TABLE 1. Yield of the Pyrolysis Products of Baltic Shale

| T, K | Pyrolysis products of the shale, wt.% ^{*)} | | | | |
|------|---|----------|-------|-------------|------|
| | oil | gasoline | water | coke breeze | gas |
| 790 | 8.9 | 0.7 | 1.2 | 86.4 | 0.8 |
| 830 | 18.0 | 1.4 | 1.1 | 76.1 | 1.4 |
| 830 | 22.3 | 1.6 | 1.6 | 70.5 | 2.0 |
| 870 | 26.6 | 3.0 | 1.8 | 60.4 | 6.2 |
| 870 | 27.3 | 2.6 | 3.6 | 58.3 | 6.2 |
| 900 | 26.8 | 2.7 | 3.3 | 56.7 | 8.5 |
| 900 | 27.2 | 2.8 | 2.5 | 55.6 | 9.9 |
| 930 | 21.8 | 4.1 | 2.5 | 55.4 | 14.2 |
| 930 | 19.8 | 3.4 | 4.9 | 54.4 | 15.5 |

^{*)}The loss is taken to be 2%.

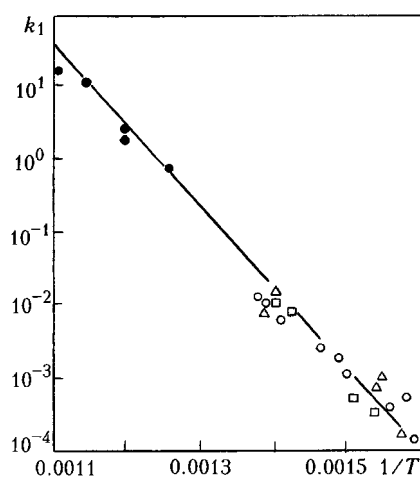


Fig. 1. Rate constant of decomposition of kerogen vs. temperature. Points, experimental data for three different shales (light points) in the low-temperature region [2] and for Baltic shale (dark points) in the high-temperature region [3]. k_1 , sec^{-1} ; T , K.

In such a simplified scheme, the steam is part of the gas.

Figure 1 shows as points the k_1 values restored in [3] on the basis of the experimental data on the isolation of the products of pyrolysis of Baltic shale. In the region of temperatures under study, we can approximate them by the dependence $k_1 = 6.31 \cdot 10^{13} \exp(-25,600/T) \text{ sec}^{-1}$, which describes these data at low temperatures well [2].

The analysis of Table 1 shows that the ratio $x_{\text{gas}}/x_{\text{ben}}$ is approximately the same in all the experiments and is equal to four (with allowance for the fact that water is part of the gas). Therefore, we can take a value of 0.8 for the coefficient a_2 . Figure 2a gives experimental values of the concentrations of the products of pyrolysis of the shale x_i and the calculated dependences $x_i = x_i(T)$ obtained with the use of the kinetic equations (2) for a characteristic time of the process of 0.24 sec. The best approximation of the experimental data in the temperature region in question, which has been obtained with the least-squares method, is attained for $k_2 = 9.0 \cdot 10^3 \exp(-7400/T) \text{ sec}^{-1}$.

2. The system of kinetic equations (2) and the values of the rate constants k_1 and k_2 obtained hold true for small shale particles (less than 100 μm in size) having a low internal thermal resistance and heated with rates of the order of 10^4 – 10^5 K/sec. The kinetics of the process is independent of the particle diameter. Larger particles are heated not instantaneously, and considerable temperature gradients appear in them. Pyrolysis products formed in the particles migrate through the pores outward. As this takes place, different secondary reactions occur — mainly cracking, condensation, and polymerization of the tar with the deposition of a certain amount of carbon (coke) and release of the

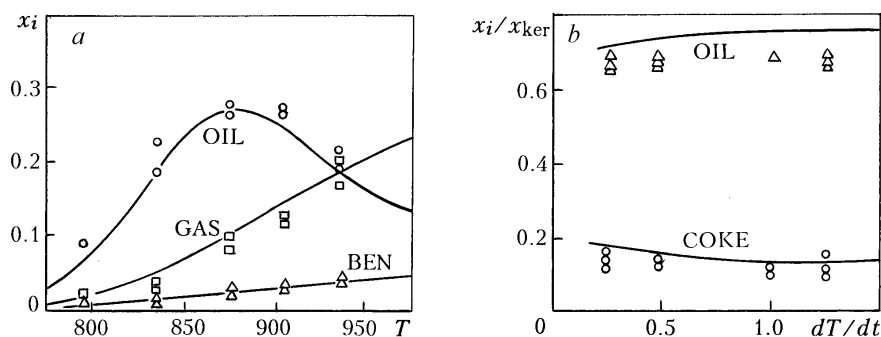


Fig. 2. Comparison of the calculated and experimental data on the yield of the pyrolysis of Baltic shale (a) and carbonization of tar within shale particles (b). x_i , kg/kg of shale; T , K; dT/dt , K/sec.

corresponding amount of gas. In this connection, the kinetic scheme of the process (1) must be supplemented with the competitive mechanism



For determination of k_3 we used experimental data [4] on the pyrolysis of large particles (average particle size of the order of 10 mm). In the experiments, shale particles were heated with a prescribed heating rate to a certain temperature and were rapidly cooled after a 15-min period of holding. The system of evacuation of volatiles and the arrangement of shale particles in a single layer ensured a short duration of contact of the pyrolysis products with the hard material, which eliminated the distorting action of secondary contact-pyrolytic processes. The values of the rate constant k_3 were found by fitting the calculated data on the pyrolysis of shale particles to the experimental data. The calculations were carried out for particles 10 mm in diameter with allowance for the nonuniform heating of the particles (the heat-conduction equation was solved). The kinetic scheme of the process included two competitive mechanisms described by Eqs. (1) and (3). A value of 0.6 has been taken for the coefficient a_3 involved in the kinetic scheme (3). Results of a comparison of the calculated and experimental data are given in Fig. 2b, the calculated curves are obtained for $k_3 = 5.5 \cdot 10^{11} \exp(-23,000/T) \text{ sec}^{-1}$.

The volatiles released as a result of the pyrolysis are filtered through the layer of solid particles of the fuel and the heat-transfer agent (ash) in the upper part of the reactor before they arrive at the zone of free space. Since the mass flow rate of the heat-transfer agent is much higher, as a rule, than the flow rate of the fuel, a considerable contribution to the kinetics of secondary chemical reactions can be made by the carbonization of shale oil on the ash particles. The carbonization kinetics has been considered in [5], where, to describe a change in the coke concentration x_{coke} (kg/kg of dry shale), the following kinetic equation has been proposed:

$$dx_{\text{coke}}/dt = (G_a/G_f) k_{\text{coke}} y_{\text{oil}} (1 + B_{\text{coke}} k_{\text{coke}} y_{\text{oil}} t_{\text{coke}})^{-1}. \quad (4)$$

The quantity y_{oil} in this case can be represented in the form $y_{\text{oil}} = \rho_{\text{gas}} G_{\text{oil}}/G_{\text{gas}}$. On the basis of an analysis of the experimental data [3], we can propose the following approximation expression for ρ_{gas} : $\rho_{\text{gas}} = 1.10 (300/T) \text{ kg/m}^3$. The quantities G_{oil} and G_{gas} are determined as a result of the numerical modeling of the process of pyrolysis of shale. The kinetic carbonization constants, in accordance with the data of [5], are $B_{\text{coke}} = 215$ and $k_{\text{coke}} = 0.0104 \text{ m}^3/(\text{kg} \cdot \text{sec})$.

3. The experience gained in operation of power-technological units for processing of shales by the method of low-temperature carbonization of the initial fuel by a solid heat-transfer agent (ash) [6] shows that the most simple and efficient structure of a pyrolysis reactor is a rotary horizontal drum. Not only does continuous movement of a material in such a reactor eliminate the phenomena of consolidation and caking of particles, which are observed in bunker-type reactors, but it also ensures self-cleaning of coke deposits from the walls [7].

Despite the wide use of rotary drums in various industries (cement, silicate, chemical, metallurgical, and others), their investigations are not universal in character and are far from being adequate. Most of the works deal with investigation of the motion of material in open-end tilted drums with a relatively large length and low coefficients of filling of the working volume. The special property of a drum-type pyrolysis reactor is that it belongs to short (the relation between the length L and the diameter D is equal to 2–3) horizontal drums rotating with a low velocity (1 to 2 rpm) and operating with a high degree of filling of the volume with material ($\phi = 0.3$ – 0.6) at a relatively short time of stay of the solid phase here ($\tau_r = 600$ – 1000 sec) and a comparatively high temperature ($T = 700$ – 900 K) [8].

The simplest way of filling the reactor volume with the solid phase is by installing supporting rings at the ends of the drum. To them one welds connections on which end seals of special structure are installed. The solid phase is charged and discharged through these connections. Loose material moves in the axial direction due to the difference in the heights of the layer at the inlet to the drum and at the outlet from it. The design of the outlet end of the reactor according to such a scheme is determined by the supporting device in the form of a ring with a hole diameter d (relatively small as compared to D) and a cylindrical connection of length l . The slot between the exterior surface of the rotary connection and the stationary system is blown with vapor to keep the vapor-gas mixture from the reactor from arriving there.

The quantities u_r and ϕ depend on the flow rate of the fuel G_f and the flow rate of the heat-transfer agent (ash) G_a , the angular rotational velocity of the reactor ω , and its diameter D and length L (in the reactor with an end orifice, they also depend on the dimensions of the supporting device). In [8], based on an analysis of experimental data it has been established that

$$\phi = AR_s^p \text{Fr}^{0.05} (d/D)^q (1 + l/D), \quad \tau_r = \rho_s \phi V / (G_f + G_a), \quad (5)$$

where $R_s = 2\pi(G_f + G_a)/\rho_s\omega V$, $\text{Fr} = (\omega/2\pi)^2 D/g$, and $V = \pi D^2 L/4$. For $R_s = 0.01$ – 0.20 , $\text{Fr} = (3$ – $110) \cdot 10^{-5}$, $L/D = 1.8$ – 5.0 , $d/D = 0.24$ – 0.64 , and $l/D = 0.005$ – 0.5 , the parameters A , p , and q in (5) are equal to $A = 0.066 \exp(0.95L/D)$, $p = 0.18(L - D)d/D^2$, and $q = 0.5(L - 3.1D)/D$. For $G_f = 200$ tons/day = 2.32 kg/sec, $G_a/G_f = 3$, $\omega = 0.15$ sec⁻¹ (1.43 rpm), $D = 2$ m, $L = 4$ m, $d = 1$ m, and $l = 0.5$ m, we have $\phi = 0.369$, $\tau_r = 600$ sec, and $u_r = 6.667 \cdot 10^{-3}$ m/sec.

4. One fundamental stage in creation of a mathematical model of pyrolysis of a solid fuel is the development of the model of behavior of an individual fuel particle placed in the high-temperature region. To elucidate the basic regularities of heat exchange between the particles of the solid fuel and those of the heat-transfer agent in the pyrolysis reactor we use the model of an ideal-displacement reactor, in which each volume element of a moving medium is considered as an open chemical system moving along the reactor axis with a velocity u_r and exchanging the substance and energy only with the ambient medium.

Let us assume that the size of heat-transfer-agent particles is sufficiently small for the particles to be considered isothermal and that their mixing with fuel particles occurs instantaneously and uniformly at the inlet to the reactor. To take account of the polydispersity of the fuel we break the fuel particles into fractions in each of which the particle size is the same. We can write the equation of energy balance between the particles of the heat-transfer agent and the fuel for constant heat capacities of the particles and in the absence of heat loss as

$$c_a G_a [T_{a,0} - T_a(t)] = c_f G_f \sum_k f_k \left(\frac{4}{3} \pi R_k^3 \right)^{-1} \int_0^{R_k} [T(r, t) - T_{f,0}] 4\pi r^2 dr. \quad (6)$$

It is assumed that the thermal effect of the reactions of thermal decomposition of the organic mass of the fuel is small [9].

The heat-conduction equation describing the heating of the fuel particles will be represented in the spherical coordinate system in the form

$$\rho_f c_f \partial T(r, t) / \partial t = \lambda_f r^{-2} \partial / \partial r [r^2 \partial T(r, t) / \partial r]. \quad (7)$$

The boundary conditions on the surface of a particle of the k th fraction and at its center have the form

$$-\lambda_f \partial T(r, t) / \partial r \Big|_{r=R_k} = \alpha [T(R_k, t) - T_a(t)], \quad \partial T(r, t) / \partial r \Big|_{r=0} = 0. \quad (8)$$

In [10], it has been shown that heat from the charge is transferred to the heated fuel particle mainly by conduction through the gas interlayer. We can represent this process as the heat exchange between two surfaces separated by δ with a Nusselt number of $\text{Nu} = \alpha\delta/\lambda_{\text{gas}} = 1.0$. We can take $\delta \cong 0.13R$ for the effective gas-interlayer thickness when $R_k = 5\text{--}10$ mm [10].

Numerical solution of the system of heat-exchange equations (6)–(7) simultaneously with the system of kinetic equations enables us to calculate the dynamics of the process of thermal decomposition of the solid fuel in its motion along the reactor axis. For the rate of release G_i of the i th component from the shale particles into the free volume of the reactor throughout its length we have

$$G_i = G_f \int_0^{\tau_f} \left[\sum_k 3f_k R_k^{-3} \int_0^{R_k} r^2 w_i(r, t) dr + w_{\text{coke},i}(t) \right] dt. \quad (9)$$

Here it is assumed that the volatiles released rapidly seep into the free reactor volume, where OIL begins to decompose into GAS and BEN. Integration in (9) with respect to time to the value $t = \tau_f$ yields the release rate of the i th component on the segment from the beginning of feeding of the fuel and the heat-transfer agent to the coordinate $z = u_f t$.

Shale represents a finely granular porous structure consisting of an inorganic skeleton and organic patches whose size attains 100 μm . The initial porosity of shale particles ε_0 is fairly high and is equal to 0.19 for kukersite shale [11]. In the process of thermal destruction of the organic mass of the shale, the porosity of the particles increases, attaining its maximum value ε_{max} with total conversion of the organic mass to volatiles. The inorganic skeleton is destroyed as a result of the mechanical action of the ash heat-transfer agent.

In the process of heating of large fuel particles, thermal destruction of the organic mass begins from the periphery, gradually moving into the particle. The value of the porosity is maximum near the particle surface. Let us assume that the process of destruction of the inorganic skeleton of the particle begins when the local porosity $\varepsilon(r, t)$ near the particle surface attains a certain critical value ε_{cr} . The particle radius decreases, while the outer shell spalled collapses and mixes with the ash mass, acquiring its temperature and rapidly losing the remains of the organic mass. Mathematically this manifests itself in the fact that solution of the heat-conduction equation (7) in the radial direction is carried out to the quantity R_{cr} for which the porosity ε attains its critical value ε_{cr} and no longer to the particle radius R_k . Boundary condition (8) is also shifted into the initial particle, which leads to an increase in the heating rate of the particle and correspondingly to a decrease in the characteristic time of the basic process. On the other hand, integration with respect to r in Eq. (9) is continued to the quantity R_k , which enables us to take account of the release of volatiles from the remains of the organic mass in the fragments of the particle shell spalled.

5. The released products of thermal destruction of the shale do not leave the reactor immediately — they move for a certain time in the pyrolysis-reactor volume free of the fuel and the heat-transfer agent. The reaction of decomposition of OIL into GAS and BEN occurs. To take account of this process we use the model of an ideal-mixing reactor in which a homogeneous composition of the reacting gas mixture is attained due to intense mixing. The initial mixture with constant mass velocities of the components $G_{i,0}$ (these velocities are a result of the solution of the problem considered above (see expression (9) in which the G_i are replaced by $G_{i,0}$)) is fed to the reactor volume. The temperature in the volume is assumed to be equal to the steady-state temperature of the charge consisting of the fuel and the heat-transfer agent.

In the case in question, the system of kinetic equations that describes the time change in the concentration x_i has the form [12]

$$dx_i/dt = -(x_i - x_{i,0})/\tau + w_i, \quad (10)$$

where $\tau = \rho_{\text{gas}}(1 - \phi)V/G_{\text{gas}}$. The rates of chemical reaction for individual components w_i include just the decomposition of the shale oil OIL into the gas and the natural gasoline.

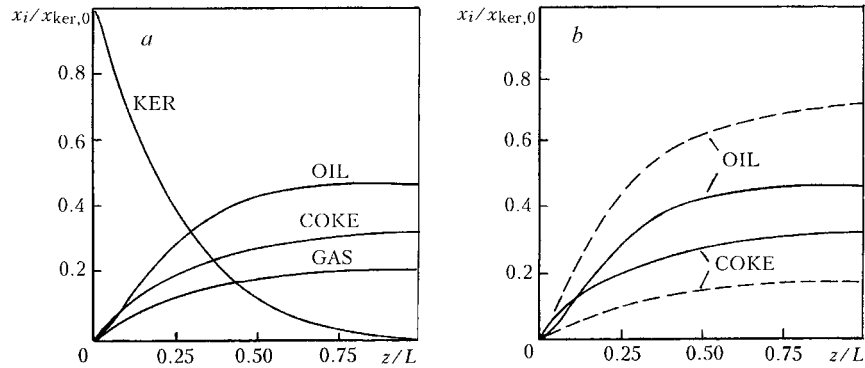


Fig. 3. Dynamics of transformation of kerogen into the products of its thermal destruction (a) and the dynamics of carbonization of shale oil (b) in motion of the fuel-heat-transfer-agent mixture along the axis of the pyrolysis reactor: $G_a/G_f = 3$, $T_{a,0} = 850$ K, and $T_{f,0} = 293$ K; dashed curves, calculation without allowance for the deposition of OIL on ash particles.

The most important feature of the processes in the ideal-mixing reactor for a constant rate of mass transfer is the establishment of the steady-state regime, when $dx_i/dt = 0$. In the steady state, from (10) we have $x_i = x_{i,0} + \tau w_i$. Since the chemical-reaction rates w_i are linear relative to the concentrations, the concentrations x_i in this expression can be replaced by the corresponding mass flow rates. With account for expressions (2) for the quantities w_i we obtain the following system of algebraic equations relative to unknown quantities G_i :

$$G_{\text{gas}} = G_{\text{gas},0} + \tau a_2 k_2 G_{\text{oil}}, \quad G_{\text{oil}} = G_{\text{oil},0} - \tau k_2 G_{\text{oil}}, \quad G_{\text{ben}} = G_{\text{ben},0} + \tau (1 - a_2) k_2 G_{\text{oil}}.$$

Using simple transformations we reduce the system to a quadratic equation for the velocity G_{gas} . Thus, somewhat changed values of the mass flow rates G_i as compared to $G_{i,0}$ are obtained at the outlet from the pyrolysis reactor.

6. Calculation of the physicochemical processes in a drum-type pyrolysis reactor begins with determination of the characteristic time of stay of a solid material in the reactor τ_r . For this purpose we prescribe the flow rates of the fuel and the heat-transfer agent and the angular rotational velocity of the reactor and its geometric dimensions. The subsequent computational procedure involves the solution of the heat-conduction equation (7) and the heat-balance equation (6), which enables us to describe the process of heating of fuel particles and that of cooling of heat-transfer-agent particles.

To take account of the polydispersivity of the fuel we break the shale particles into a certain number of fractions and find the calculated fraction size as the average size within the limits of each fraction. We prescribe as an example the following fractional composition of the fuel:

| | | | | | |
|------------|------|------|------|------|------|
| f_k | 0.07 | 0.23 | 0.40 | 0.25 | 0.05 |
| R_k , mm | 1.25 | 2.50 | 5.00 | 7.50 | 10.0 |

We will assume that the initial temperature of dry fuel particles is $T_0 = 293$ K and the initial temperature of the heat-transfer agent is $T_{a,0} = 850$ K. We take the following values for the thermophysical characteristics of solid particles [13]: $c_f = 1.0$ kJ/(kg·K), $\rho_f = 1200$ kg/m³, and $\lambda_f = 0.3$ W/(m·K). The initial mass content of kerogen in the dry mass of the shell is $x_{\text{ker},0} = 0.376$ and the initial porosity is $\epsilon_0 = 0.19$.

The results of calculation of the dynamics of heating of particles in motion of the fuel-heat-transfer-agent mixture along the pyrolysis axis show that the heating of particles with a radius of 5 mm is completed on a reactor length z/L of the order of 0.6. Smaller particles are heated more rapidly and the chemical processes in them are completed at a shorter distance from the site of feeding of the fuel and the heat-transfer agent.

We carried out a series of calculations with different values of the critical porosity ϵ_{cr} to evaluate the influence of fragmentation of particles on their heating and the rate of release of volatiles. For Baltic shale the particle porosity changes from the initial porosity $\epsilon_0 = 0.19$ to the maximum porosity $\epsilon_{\text{max}} = 0.50$ when the entire organic mass

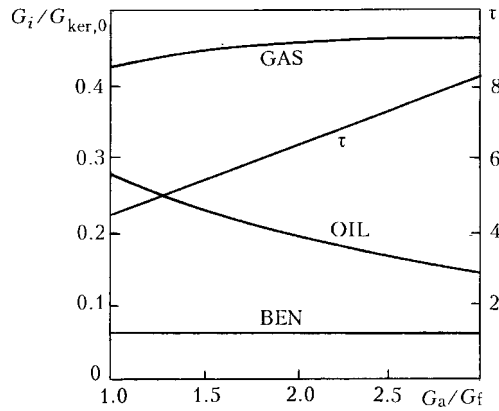


Fig. 4. Composition of the gaseous pyrolysis products at the outlet from the ideal-mixing reactor and time of stay of the mixture τ in the reactor vs. G_a/G_f at $T_a = 710$ K and $G_a + G_f = 9.27$ kg/sec. τ , sec.

is released as a gas phase in the form of volatiles. As the calculation results have shown, a change of 0.25 to 0.50 in ϵ_{cr} influences the behavior of x_{ker} only slightly. For subsequent calculations we took the most real value of ϵ_{cr} equal to 0.4, which corresponds to a residual concentration of kerogen of 0.1 kg/kg of shale.

The dynamics of conversion of kerogen into the products of its thermal destruction in the ideal-displacement regime (without allowance for the decomposition of shale oil in the solid-phase-free volume of the pyrolysis reactor) is presented in Fig. 3a. An analysis of the figure shows that, as the kerogen is destroyed, the concentration of both the shale oil OIL and the condensed carbon COKE in the particles of the fuel and the ash heat-transfer agent increases due to the occurrence of secondary chemical processes. The role of the kinetics of deposition of OIL on the ash particles in the general process of carbonization of the pyrolysis products is shown in Fig. 3b. As is clear from the figure, carbonization on the ash particles yields nearly half the total amount of coke removed with the solid phase from the pyrolysis reactor.

Figure 4 gives results of a calculation of the kinetics of decomposition of shale oil in the volume of the pyrolysis reactor (ideal-mixing reactor), free of the fuel and the heat-transfer agent. The calculation has been carried out for different ratios G_a/G_f for constant total flow rate of the mixture of the fuel and the heat-transfer agent and final temperature of the mixture. As is clear from the figure, the mass concentration of the gas and the natural gasoline weakly depends on the G_a/G_f ratio. The decrease in the mass concentration of OIL with increase in G_a/G_f is attributed to the growth of carbonization of OIL on the ash particles with increase in the flow rate G_a . The effect of the kinetics of decomposition of the shale oil in the superlayer space is pronounced when we compare the mass concentrations of the components in Fig. 3a (where the data of calculation for $G_a/G_f = 3$ are given) and the mass concentrations of the components in Fig. 4. The GAS concentration is doubled due to the decomposition of OIL, and the OIL concentration decreases nearly three times.

Thus, the results of the numerical modeling of the process of pyrolysis of shale show that the fragmentation of particles exerts no substantial influence on the dynamics of the process. Secondary chemical reactions lead to a considerable removal of carbon on the ash particle from the reactor. The reactions of decomposition of pyrolysis products in the superlayer reactor space lead to a decrease in the fraction of the shale oil in the total mass of the gas-phase pyrolysis products and an increase in the fraction of the gas and the natural gasoline.

NOTATION

a_2 , mass fraction of the gas in decomposition of the shale oil into the gas and the natural gasoline; a_3 , mass fraction of the coke in decomposition of the tar into the coke and the gas; B_{coke} , deactivation constant in the process of carbonization of the shale-oil vapor; c , heat capacity, J/(kg·K); D , diameter of the reactor, m; d , diameter of the connection of the supporting device, m; Fr , Froude number; f_k , mass fraction of the particles of the k th fraction in the total mass of the fuel; g , free-fall acceleration, m/sec²; G , mass flow rate, kg/sec; G_i , rate of release of the i th component from the shale particles throughout the reactor volume, kg/sec; k_{coke} , rate constant of carbonization of the

shale-oil vapor on ash particles, $\text{m}^3/(\text{kg}\cdot\text{sec})$; k_1 and k_2 , rate constants of decomposition of the tar and the shale oil, sec^{-1} ; k_3 , rate constant of condensation of the tar within shale particles, sec^{-1} ; L , length of the reactor, m; l , length of the connection of the supporting device, m; R_k , radius of the particle of the k th fraction, m; R_s , specific solid-phase stress of the reactor; r , radial coordinate within a particle, m; T , temperature, K; t , time, sec; t_{coke} , time of contact of the ash particles with the shale-oil vapor, sec; u_r , velocity of motion of the loose material in the horizontal direction, m/sec; V , volume of the reactor, m^3 ; w_i , rate of formation of the i th component in the process of pyrolysis, kg/sec (kg of dry shale); x_i , concentration of the i th component, kg/kg of dry shale; y_{oil} , concentration of the shale oil in the gas, kg/m^3 ; z , axial coordinate of the reactor, m; α , coefficient of heat exchange between the fuel particle and the heat-transfer agent, $\text{W}/(\text{m}^2\cdot\text{K})$; δ , effective thickness of the gas interlayer between the fuel particle and the heat-transfer agent, m; ϵ , porosity of the fuel particles; ϕ , degree of filling of the reactor with the solid phase; λ , thermal conductivity, $\text{W}/(\text{m}\cdot\text{K})$; ρ , density, kg/m^3 ; τ , time of stay of the gas mixture in the free volume of the reactor, sec; τ_r , average time of stay of solid particles in the reactor, sec; ω , angular rotational velocity of the reactor, sec^{-1} . Subscripts: 0, initial value; a, heat-transfer agent; ben, natural gasoline; coke, coke, carbonization; cr, critical value; f, fuel; gas, gas; i , No. of the component; k , No. of the fraction; ker, kerogen; max, maximum value; oil, shale oil; r, reactor; s, solid phase; tar, tar.

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