ЕКОЛОГІЧНА БЕЗПЕКА, ОХОРОНА ПРАЦІ

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THE MACROKINETICS PARAMETERS OF THE HYDROCARBONS COMBUSTION IN THE NUMERICAL CALCULATION OF ACCIDENTAL EXPLOSIONS IN MINES

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ПАРАМЕТРИ МАКРОКІНЕТИКИ ГОРІННЯ ВУГЛЕВОДНІВ У ЧИСЕЛЬНОМУ РОЗРАХУНКУ АВАРІЙНИХ ВИБУХІВ У ГІРНИЧИХ ВИРОБКАХ

Purpose. Obtaining effective parameters of the macrokinetics of combustion of hydrocarbons in the deflagration and detonation regime for the numerical calculation of emergency explosions in mine workings.

Methodology. Mathematical modeling, numerical experiment, kinetics analysis of explosive combustion reaction, analysis and synthesis.

Findings. The paper analyzes the parameters of the kinetic equation against experimental data. Obtaining such data in a physical experiment for explosive chemical reactions meets serious difficulties. This is due to the size of the reaction zone not exceeding fractions of a millimeter, the lack of time resolution of experimental techniques and other factors leading to errors in direct measurements and the emergence of multiple solutions. This possibility contributes to obtaining a simultaneous numerical solution of the equations of gas dynamics and chemical kinetics. In the numerical experiment, a direct relationship between the macrokinetic characteristics of the chemical reaction and the parameters of the discontinuous flow of the reacting gas stream is established: velocity, pressure in the front and behind the front of the detonation and deflagration wave. Based on this, Arrhenius characteristics of the reaction – pre-exponential and effective activation energy for the hydrocarbons under consideration are obtained.

Originality. Macrokinetic parameters are established for simulating one-stage ignition and burning of the most probable hydrocarbons of the mine atmosphere in the deflagration and detonation regime. Modeling of explosive

combustion of premixed hydrocarbons in stoichiometric concentrations is performed. It is shown that the values of the effective activation energy in explosive combustion reactions are of less importance in contrast to steady-state combustion reactions because of the effect of the gas-dynamical effects of the shock wave on the reaction rate. The Arrhenius characteristics of the reaction – the pre-exponential and the effective activation energy – have been agreed upon, according to the gas dynamic and kinetic parameters of the course of the explosive combustion reaction.

Practical value. The obtained parameters of the macrokinetics of the explosive combustion reaction make it possible to apply simple kinetic mechanisms in practical calculations of the processes of deflagration and detonation combustion, and to predict the parameters of emergency explosions in conditions of mine workings with sufficient accuracy. This also makes it possible to solve the problem of accounting for the presence of heavy hydrocarbons in the mine atmosphere as products of coal pyrolysis in underground fires as factors of increasing the risk of emergency explosions.

Keywords: *gas-air mixture, emergency explosion, combustion kinetics, macrokinetic parameters, effective activation energy*

Introduction. Explosions of the mine atmosphere in mine workings are the most severe types of accidents in terms of destructive ability and impact on people. Especially dangerous is the possibility of repeated explosions in the event of underground fires. This is due to the pyrolysis of coal in the process of endogenous fire and release of heavy and unsaturated hydrocarbons into the atmosphere. Protection of personnel and mine rescuers conducting emergency work from shock air waves is ensured by safe distance and explosion-proof structures. Therefore, the problem of reliable calculation of shock wave parameters is relevant from the point of view of human security and the forecasting of dynamic loads on explosion-proof structures.

At present, to calculate the parameters of shock air waves, the method of computer simulation of the flow of gases is widely used – CFD Methods, which allows calculating the parameters of motion of supersonic discontinuous gas flows. The source of the energy of the initial pulse in such gas flows is most often a pressure jump in a certain region – the instantaneous explosion model. This model is a simplification of the deflagration and detonation processes of combustion of gas-air mixtures. The initial overpressure in the model is given on the basis of the experimental data. Such an approach is laid down in the current regulatory documents on the calculation of shock air waves. The significant number of affected mine rescuers in the last 10 years, namely, from repeated explosions, indicates incomplete consideration of factors of formation of shock air waves in emergency explosions. More approximate to reality is the use of combustion models of reactive gas flows in the calculation.

Analysis of the recent research and publications. The work in this direction was carried out in the Siberian Branch of the Russian Academy of Sciences [1] and the Institute of Mine Rescue "Respirator" [2] and National Mining University [3]. In the first paper, the combustion process is treated as an instantaneous temperature jump in a given volume, over which the gas pressure is then determined

$$T = T_0 + \frac{Q\rho_{CH4}}{C_v\rho}; \quad P = n \cdot k \cdot T,$$

where Q is the calorific value of methane; k is the Boltzmann's constant.

In fact, this is an instantaneous explosion model, which was also used in the work [4]. In [2], combustion is represented by the process of heat release in a layer propagating along a fixed methane-air mixture

$$Q_+ = Q \cdot \rho \cdot S \cdot U_{com} \cdot g(x),$$

where U_{com} is the flame propagation velocity; $g(x)$ is the U-shaped function, indication of presence of methane at a particular point in the design scheme.

A similar approach is implemented in the work [5]. In it, for modeling of combustion in the numerical scheme, the parameter "f" is a continuous Lagrangian marker that tracks the "source", "burned" and "burning" calculation cells. In the "burning" cell, heat generation by mass of methane is calculated. The rate of displacement of the combustion front is determined with respect to the change in temperature

$$U_B = U_{BNC}(T / T_{NC})^{\beta},$$

where U_{BNC} is the normal propagation velocity of a flame in a stationary mixture under normal conditions; T, T_{NC} are current and initial temperatures; β is the coefficient of power law.

In [6], the calculation of an emergency explosion was considered in the framework of the chemical kinetics of combustion of reacting gas streams. The burning rate and, accordingly, the rate of energy release were determined taking into account the law of the effective masses of the premixed mixtures.

Unsolved aspects of the problem. One of the difficulties in the joint solution of the gasdynamic problem of gas flow and the problem of the combustion kinetics of the reacting flows, which is solved in [6], is the selection and establishment of the parameters of the kinetic combustion mechanism. Existing detailed kinetic mechanisms that take into account many hundreds of reactions are mainly used for stationary combustion regimes. The accuracy of these models worsens in the transition to complex gas dynamic problems, when it is necessary to combine kinetics with fast flows of the medium (detonation, deflagration). In these cases, as a rule, a macrokinetic approach is used or parameters of "non-classical" kinetics characterizing the joint processes of the combustion kinetics and gas dynamics, for example, the generalized kinetic characteristic $\overline{P}$ [7]

$$\overline{P} = -\beta \cdot \partial c / \partial t; \qquad \beta = -\frac{(\gamma - 1)Q}{V},$$

where c is the concentration of fuel; t is the time; γ is the adiabatic index; Q is the thermal reaction effect; V is the specific volume.

In [6] the macrokinetic approach is used on the basis of the numerical solution of the problem by the large-particle method. However, the known parameters of the equation of the effective mass law for gross reactions cannot be used in this problem because of the discrepancy between the conditions for which they were obtained.

Objectives of the article. The paper aims at establishment of effective parameters for the macrokinetics of combustion of hydrocarbons in the deflagration and detonation regime for the numerical calculation of emergency explosions in mine workings.

Presentation of the main research and explanation of scientific results. The peculiarity of hydrocarbon burning reactions in the mode of detonation and deflagration during the motion of gas flows in extended channels is that the propagation velocity of the combustion front is caused not only by the chain-thermal and concentration effects of chemical reactions, but also by the gas dynamic effects of the flow: turbulence of the flow, shock compression, causing focal ignition, i.e. the occurrence of hot points of initiation of the reaction in a fresh mixture (leads to the appearance of a cellular front of detonation combustion) [8]. These effects cannot be taken into account in the detailed kinetic mechanisms of the reaction (DKM), so global mechanisms are used in such cases.

In the works by V. I. Babushok, A. N. Dakdancha systematization of macrokinetic parameters of high-temperature gas-phase reactions is given and it is shown that they are an approximation of the description of the kinetics of the course of a complex reaction. Its extrapolation to a different type of process can lead to incorrect results, because the gross stages are not independent as elementary ones are. The numerical values of the parameters depend on the type of process, the initial conditions and the gross scheme. The orders of reactions for individual components may not correspond to the stoichiometry of the reaction equation. To find the macrokinetic parameters of a particular process, three approaches are used. After defining the kinetic equation, its parameters are analyzed in relation to the experimental data in the first case [9], in the second case the data for numerical analysis with DKM can serve as a material for the comparative analysis, and in the third case, the DKM reduction to the global scheme occurs.

In this paper, the first approach is used. In this case, the inverse kinetic problem is solved, where the parameters of macrokinetics are usually obtained indirectly: experimental data, according to the law of acting masses, are processed by various methods (integral, differential ones, the method of half-transformation periods, graphical differentiation of the kinetic curve and etc.). However, obtaining experimental data for explosive chemical reactions encounters serious difficulties due to the size of the reaction zone not exceeding fractions of a millimeter, the lack of time resolution of experimental techniques (submicrosecond reaction time), and other factors that lead to errors in direct measurements and the emergence of non-unique solutions. As is known, a sufficient condition for the uniqueness of the solution is the ability to measure the concentrations of all components at any time with any accuracy. This possibility contributes to obtaining a simultaneous numerical solution of the equations of gas dynamics and chemical kinetics [6]. As a result, in a numerical experiment, it is possible to establish a direct connection between the macrokinetic characteristics of the chemical reaction and the parameters of the discontinuous flow of the reacting gas stream: velocity, pressure in the front and behind the front of the detonation or deflagration wave.

Let us consider the two-dimensional flow of gas in the mine, which in the mathematical formulation of the problem is represented in the form of a cylindrical channel in cylindrical coordinates z, r (z is the axis along the workpiece, r is the radius vector). Following the usual agreements on the insignificantness of viscosity, the dynamics of the flow of a reacting gas stream can be represented by Euler's equations, in a divergent form, in cylindrical symmetry (continuity and motion)

$$\frac{\partial \rho}{\partial t} + div(\rho \overrightarrow{W}) = 0; \tag{1}$$

$$\left.\begin{aligned} \frac{\partial \rho u}{\partial t} + div(\rho u \overrightarrow{W}) + \frac{\partial P}{\partial z} &= \tau_{fr} P_{er} dz \\ \frac{\partial \rho v}{\partial t} + div(\rho v \overrightarrow{W}) + \frac{\partial P}{\partial r} &= 0 \end{aligned}\right\}, \tag{2}$$

where ρ is the density; P is pressure; $\overrightarrow{W}$ is the velocity vector; τ_{fr} is the surface friction stress; S, P_{er} are the cross-section and perimeter of production; t is time; u, v are speed components $\overrightarrow{W}$ along the z-axis and r, respectively.

Dissipation of the energy of the gas flow due to friction losses on the channel wall is determined by the right-hand side of equation (2) and is found according to the theory of fluid and gas mechanics, as follows

$$\tau_{fr} = \frac{1}{8} c_f \rho u^2; \quad c_f = 0.0032 + \frac{0.221}{R_e^{0.237}};$$

$$R_e = \frac{\rho u D_{eq}}{\mu}; \quad D_{eq} = \frac{4S}{\Pi},$$

where c_f is the coefficient of resistance; μ is the coefficient of dynamic viscosity of gas; R_e is Reynolds number; D_{eq} is the equivalent diameter of the straight portion.

The energy equation has the form

$$\frac{\partial \rho E}{\partial t} + div(\rho E \overrightarrow{W}) + div(PW) = q\Pi + q_x \rho \frac{\partial a}{\partial t}, \tag{3}$$

where E is the specific total energy; q is the density of heat flow into the channel wall; q_x is the thermal effect of chemical reaction of combustion of hydrocarbons; α is the mole fraction of hydrocarbon in the mine atmosphere.

The balance of thermal energy in the heat exchange with the wall of the channel, represented in the right part of equation (3) by a member of the qP, is taken into account by boundary conditions of the third kind of the heat

$$q = \alpha_s(T_s - T),$$

where α_s is the heat transfer coefficient; T_s is the wall temperature; T is the average gas temperature.

$$\alpha_s = \frac{N_u \cdot \lambda_B}{D_{eq}}; \quad N_u = 0.22\, R_e^{0.5} P_r^{0.47} B; \quad P_r = \frac{\rho l}{\lambda_g},$$

where N_u is the Nusselt number; P_r is the Prandtl number; λ_g is the coefficient of thermal conductivity of the channel wall gas; B is a correction factor for the influence of the roughness of the walls of heat exchange process.

To close the system, let us use the equation of state for gas

$$P = (\gamma - 1)\rho \cdot J, \tag{4}$$

which in the form coincides with the equation of state of an ideal gas; however, in equation (4), the adiabatic exponent γ and, accordingly, the heat capacity c_p and c_ν are given as functions of temperature for both air and a hydrocarbon-air mixture

$$c_v(T), \quad c_p(T), \quad \gamma = \gamma(T) = c_p(T) / c_v(T).$$

The right side of the energy balance equation (3) includes a member of the influx speed of heat in the process of explosive combustion $q_x \cdot \rho \cdot \partial\alpha / \partial t$, which is a function of the kinetics of chemical reactions. Kinetics is calculated by the global mechanism. For this purpose the following gross equation of the most probable combustion of hydrocarbons (methane, ethane, propane, acetylene) in the air are adopted:

$CH_4 + 2(O_2 + 3.76N_2) = CO_2 + 2H_2O + 7.52N_2$;

$C_2H_6 + 3.5(O_2 + 3.76\,N_2) = 2CO_2 + 3H_2O + 13.16\,N_2$;

$C_3H_8 + 5(O_2 + 3.76\,N_2) = 4H_2O + 3CO_2 + 18.8\,N_2$;

$C_2H_2 + 2.5(O_2 + 3.76\,N_2) = 2CO_2 + H_2O + 9.4\,N_2$.

The reaction rate of the i^{th} component $i = 1, 2$ is set according to the law of mass action, in the form of Arrhenius

$$-\frac{dc_i}{dt} = Z \cdot \exp\left(-\frac{E_a}{RT}\right) \Pi c_i^{\nu_i}, \tag{5}$$

where Z, E_a, ν_i is the effective macrokinetic parameters: pre-exponential factor, activation energy and order of reaction in the i^{th} component.

$$Z = AT^{\beta},$$

where A, β are coefficients of the temperature dependence of the pre-exponential factor.

In this particular case of the reaction for the hydrocarbons taken, equation (5) for the fuel component has the form

$$-\frac{dc_f}{dt} = Z \cdot \exp\left(-\frac{E_a}{RT}\right) c_f^{\nu_f} \cdot c_o^{\nu_o}, \tag{6}$$

where ν_f, ν_o are effective values of the indicator of the degree of concentration of fuel and oxidizer.

Thus, the system of equations (1–3) is closed and completely describes the medium when solving gas dynamic problems. Solutions of the system of equations were carried out using a homogeneous circuit of the through account. As such a scheme, a modified method of large particles [6] was applied.

Initial conditions for the kinetics of the chemical reaction. From the methane oxidation equation it follows that the rate of oxygen consumption is 2 times the rate of methane consumption

$$-\frac{dc_1}{dt} = -\frac{1}{2} \cdot \frac{dc_2}{dt}. \tag{7}$$

Integrating the equation (7) in time, we obtain $c_2 = 2c_1 + A$, where A is the integration constant, which can be determined from the initial conditions: $A = c_{2H} - 2c_{1H}$.

Index "H" indicates the initial concentration values. As a result, we get

$$c_2 = 2(c_1 - c_{1H}) + c_{2H} \Rightarrow c_2 = c_{2H} + 2(c_1 - c_{1H}). \tag{8}$$

Thus, knowing the dependence of the change in concentration on time $c_1(t)$, we can use the formula (8) to determine the function $c_2(t)$.

Suppose at the initial instant of time $c_1 = c_{1H}$, thence $c_2 = c_{2H}$. With complete burnout of methane $c_1 = 0$, the oxygen concentration will be: $c_2 = c_{2H} - 2c_{1H}$.

With the stoichiometric composition $c_{2H} = 2c_{1H}$. Therefore, methane and oxygen completely burn out at the same time $c_1 = 0$, $c_2 = 0$. If $c_{2H} > c_{1H}$, then $c_2 > 0$, so there is a balance O_2. When $2c_{2H} < c_{1H}$ oxygen burns out earlier, and the rest of methane is equal to

$$c_1 = c_{1H} - \frac{c_{2H}}{2}.$$

Similarly, we determine the initial conditions for the remaining hydrocarbons.

A numerical scheme for realizing the initial conditions. The equations of chemical kinetics were solved numerically together with the equations of gas dynamics and equations of state. The difference analogue of equation (6) was represented in the following form

$$-\frac{\left[c_1\right]_{i,j}^{n+1} - \left[c_1\right]_{i,j}^{n}}{\Delta t} = k \cdot \left(\left[c_1\right]_{i,j}^{n}\right)^{\nu_1} \cdot \left(\left[c_2\right]_{i,j}^{n}\right)^{\nu_2},$$

where $k = Z \cdot \exp\left(-E_a / RT\right)$ is the rate constant of the chemical reaction of combustion; i, j are integer coordinates of the calculated cell (coarse particle); n is the time slot number.

From equations (6, 7) it follows that

$$\left[c_1\right]_{i,j}^{n+1} = \left[c_1\right]_{i,j}^{n} - \Delta t \cdot k \cdot \left(\left[c_1\right]_{i,j}^{n}\right)^{v_1} \cdot \left(\left[c_1\right]_{i,j}^{n}\right)^{v_2};$$

$$\left[c_2\right]_{i,j}^{n+1} = \left[c_2\right]_{i,j}^{n} + 2\left(\left[c_1\right]_{i,j}^{n+1} - \left[c_1\right]_{i,j}^{n}\right).$$

When calculating the energy conservation equation, a term is added to the right-hand side

$$\Delta t \cdot Q \cdot A \cdot \exp\left(-E_a / RT\right) \cdot \left(\left[c_1\right]_{i,j}^{n}\right)^{v_1} \cdot \left(\left[c_2\right]_{i,j}^{n}\right)^{v_2},$$

where Q is the heat of combustion of methane in air at stoichiometric composition of methane-oxygen, J/kg.

Differential equations (1–3, 6) obtained on the basis of general laws of gas dynamics and physical chemistry, describe a whole class of fast chemical combustion reactions in a stream of reactive gases. The establishment of macrokinetics parameters for specific combustible gases requires the definition of uniqueness conditions. As such conditions, we will accept the implementation of the coordination of the macrokinetic parameters of the numerical calculation with the thermodynamic and gas dynamic parameters of the explosive combustion process. For agreement, we use the marker experimental data on the combustion of hydrocarbons in the deflagration and detonation regime in stoichiometry (Table 1), i.e. the required parameters of macrokinetics should ensure the flow of gas-phase reactions in test calculations with marker gas dynamic parameters. These parameters are published in well-known works, for example [10].

As the initial kinetic parameters of the combustible gases for which the constants of the Arrhenius equation are established in the processes of explosive combustion, the data on the combustion of these gases in a laminar flame, in flare combustion (Table 2).

Thermodynamic analysis of the ignition and combustion process, according to the law of acting masses (Fig. 1) shows that in the general case, a decrease in the activation energy or an increase in the number of active collisions (the value of the pre-exponential) leads to a decrease in the ignition temperature, while the acceleration of the reaction due to the chain mechanism of the thermal explosion remains constant, as can be judged from the slope angle α of the asymptotic lines (within the combustion temperature) of the graphs W_1, W_2. The latter value is very important because it determines one of the main dynamic characteristics of the explosion – the rate of increase in pressure (Korolchenko A. Y. Fire and explosion hazard of substances and materials and their fire extinguishing tools). The change in the acceleration of the reaction is determined by the exponent at the reagent concentrations (graphs W_1 and W_3). The same effect is caused by a simultaneous change Z and E_a (graphics W_2 and W_4). In the first case, this is due to the concentration mechanism, in the second – to the chain-thermal one.

The presented dependences (Fig. 1) are approximate, since calculated by the quasistatic process in stoichiometric values of reagent concentrations. However, this analysis allows us to evaluate the nature of the relationship between the parameters of macrokinetics and gas dynamics of the explosion. Each kinetic parameter of equation (6) characterizes one of the mechanisms of the combus-

Table 1

Experimental characteristics of explosive combustion of hydrocarbons

	CH_4	C_2H_6	C_3H_8	C_2H_2
Autoignition temperature, K	650	515	470	305
Detonation velocity, m/s	2390	2369	2357	2350
Detonation pressure, MPa	2.9*	3.4	3.6	4.5**
Deflagration wave velocity, m/s	54.3	–	–	49.7
Deflagration wave pressure, MPa	0.3–1.4	–	1.8	–
Ignition temperature by a thermal spherical source, K	1473	–	1223	1096

* – in the CJ plane; ** – at the point ZND

Table 2

Effective kinetic parameters of the global combustion mechanism of gases*

Gas	Type and characteristics of the process	Pre-exponential Z, s^{-1}	Activation energy E_a, kJ/mol	Response order fuel, ν_f/ oxidant, ν_o	Stoichiometry, %
CH_4	flame	$1.1 \cdot 10^6$	125.4	-0.3/1.3	9.5
C_2H_6	flame	$9.2 \cdot 10^{11}$	125.4	0.1/1.65	5.5
C_3H_8	torch nozzle	$8.6 \cdot 10^{11}$	125.4	0.1/1.65	4.03
C_2H_2	torch burner	$6.5 \cdot 10^{12}$	125.4	0.5/1.25	7.75

* – Westbrook C. K., Dryer F. L. Simplified reaction mechanisms for the oxidation of hydrocarbon fuel in flames

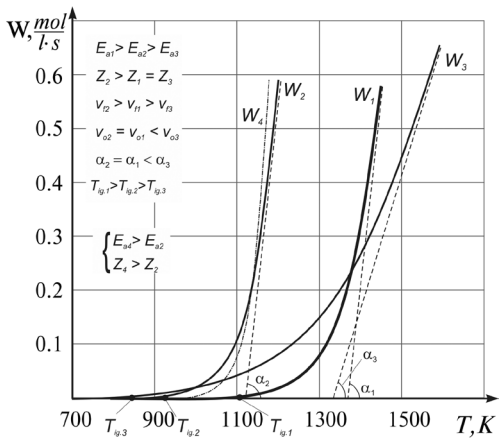

Fig. 1. Kinetic curves of the dependence of the reaction rate W on the temperature

tion theory: the activation energy determines the thermal mechanism of reaction development, the pre-exponent is a chain mechanism, the exponents are the concentration mechanism. In detail, the role of each mechanism in the effect on the velocity of explosive gas-phase combustion reactions was studied in the works by V. V. Azatyan [11, 12]. They show a difference in the development of explosive combustion reactions: with increasing temperature, the role of the chain avalanche does not decrease, but rather increases. As a result, it was clarified that the dependence of the rate of explosive combustion reactions on temperature is "exponential in exponent"

$$\frac{W}{[B]_0} = k_p n_0 \{\exp \int_{t_0}^{t} [f_o \exp(-E_p / RT) - g]\} dt ,$$

where $[B]_0$ is the initial concentration of initial reagent; f_0, E_p is the pre-exponent and the activation energy of chain branching; n_0 is the concentration of radicals at time t_0, after which the reaction of the original molecular components with each other can be neglected; k_p is the effective rate constant of the limiting branching stage.

This is confirmed by the fact that explosive combustion reactions proceed with a higher rate of growth (acceleration) than burning in laminar flames. In this case, with respect to the classical Arrhenius equation in the global mechanism, the activation energy should be less, which simulates more intensive chains initiation processes. Therefore, when developing a global mechanism, it is necessary to make changes to this parameter and to reconcile it with the pre-exponent and exponents of gas dynamics and the kinetics of the reaction. The determination of the rational parameters of macrokinetics is based on the results of a numerical experiment of deflagration and detonation combustion under the following conditions. The model of the mining section is presented in the form of a cylindrical channel 0.2 m in diameter, 1.5 m long, the canal edges freely open.

In the initial conditions, the central part of the channel is filled with a gas-air mixture in the stoichiometric concentration of the corresponding hydrocarbon (Table 2). To reduce the effect of shock wave reflection effects during the experiment and create a flat shock front, ignition of the mixture was carried out by a transverse layer of hot gas 0.01 m thick. The temperature of the layer was chosen in such a way as to obtain a stationary regime of deflagration and detonation. The layer was located on the contact surface of the air–gas-air mixture.

The following approximations were adopted in the problem: the concentration of the explosive gas-air mixture is uniformly distributed over the volume of the gas-filled section, the boundary conditions for the thermal conductivity into the channel wall are conditions of the third kind with a constant heat exchange coefficient of the gas flow with a wall of 50 W/(m^2·K) and wall thermal conductivity (argillite) 2 W/(m·K), the roughness of the channel wall corresponds to the installed support of SVP-19 type with a setting step of 1.0 m. In a numerical experiment, rational macrokinetic parameters were determined by the method of successive approximations.

Calculation results. Fig. 2 shows the dynamics of the pressure profile and the gas concentration (for methane as an example) during the ignition and combustion of the gas-air mixture in the deflagration and detonation regime obtained in a numerical experiment.

The first mode occurs at the ignition source temperature of 1200 K and the ignition source energy is 460 J, the second mode at 1900 K and the source energy 730 J. The set values of E_a, Z, ν_1, ν_2 (Table 3) give the following combustion indices: in the deflagration mode, the pressure at the CJ point is 0.8 MPa (Fig. 3, *a*), in the detonation mode the wave amplitude (ZND point) was 3.2 MPa, which satisfactorily coincides with the experimental values of the parameters and is good with the calculated [13].

In the graphs of Fig. 2, the dashed line shows the pressure profile for the parameters of macrokinetics of

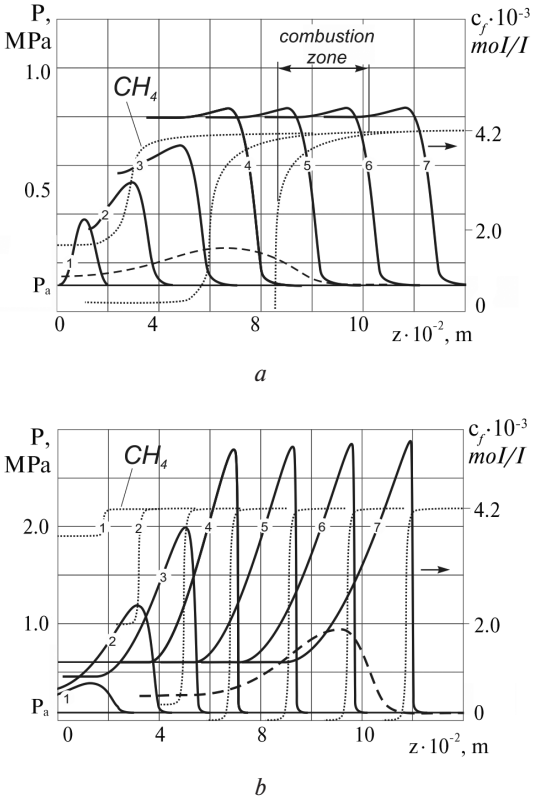

Fig. 2. Dynamics of the pressure profile P and methane concentration cf during the ignition and combustion of the gas-air mixture in the deflagration (a) and detonation (b) mode, along the z axis, for the macrokinetics parameters of the explosive (solid line) and laminar combustion (dotted line)

Table 3

Effective parameters of the macrokinetics of combustion reactions in the regime of deflagration and detonation in an extended channel

Gas	Z, s^{-1}	E_a, kJ/mol	ν_f	ν_o
CH_4	$1.3 \cdot 10^6$	115.0	-0.3	1.3
C_2H_6	$9.7 \cdot 10^{11}$	110.7	0.1	1.65
C_3H_8	$9.1 \cdot 10^{11}$	104.5	0.1	1.65
C_2H_2	$5.2 \cdot 10^{12}$	98.3	0.5	1.25

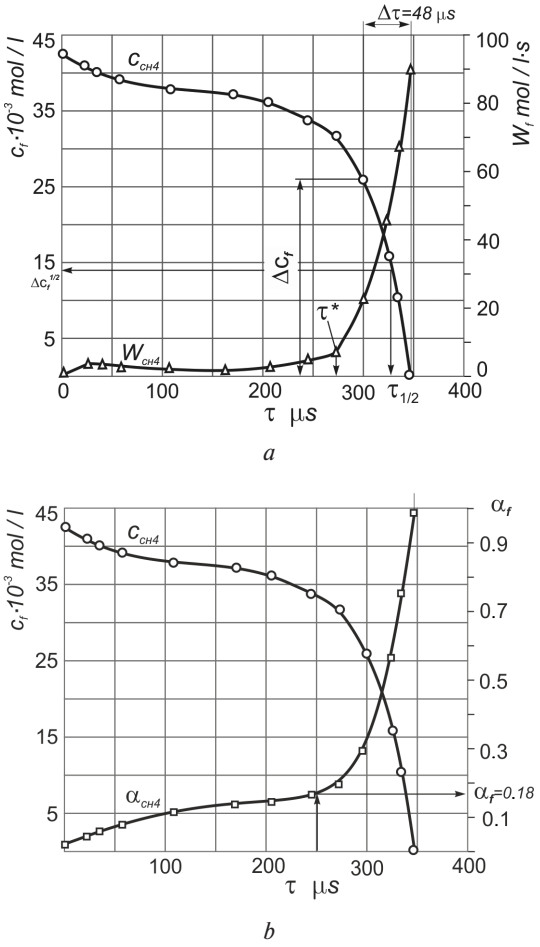

Fig. 3. Kinetic curves for the change in the methane concentration with c_f (○), the burning rate W_f (Δ) and the fraction of methane of the reactioned α_f (□) as a function of the reaction time τ

combustion of methane in a flame (Table 2). As you can see, the profile shape of the graph is closer to the acoustic wave, the amplitude of the wave is understated by 2.5–3 times, which gives errors in determining the explosion parameters. The autoignition temperature was determined in a numerical experiment by establishing the preset initial temperature in the entire volume of the gas-air mixture. Thus, uniform heating of the reaction gases. The obtained temperature of the beginning of the oxidation reaction corresponded to 620 °C, the error with the experimental data 4.8 %. Data on the temperature of the ignition of a mixture by a thermal source were obtained from a numerical experiment where a spherical heat source was modeled as a cylinder with dimensions of height and diameter close in value. A numerical experiment showed stable ignition of 9 % methane-air mixture at source temperature 1590 °C. Thus, the discrepancies in the numerical calculation with the experimental values do not exceed 8 %.

At the next stage of justifying the effective parameters of the macrokinetics of combustion of hydrocarbons in the regime of deflagration and detonation, a kinetic analysis of the reaction [14]. To do this, the inverse problem was solved by the method for determining the reaction rate constant and the activation energy from the experimental data obtained in a numerical experiment. The paper considers the global reaction mechanism which is formal kinetics, therefore it can be considered as an elementary reaction and accordingly it is possible to apply this method. The kinetic parameters of the reaction were estimated from experimental data that were registered in the steady state in the combustion zone. In the detonation mode, this zone coincides with the detonation zone, and in the deflagration mode it was behind the front of the shock wave (Fig. 2). Let us consider the analysis using the example of the combustion reaction of methane.

The kinetic curves constructed from the data of the deflagration combustion experiment of methane have a form close to the exponential (Fig. 3), which reflects the chain-thermal reaction mechanism and corresponds to the combustion theory.

According to the experimental data (Table 2), the total order of the methane reaction is unity. In this case, the differential equation of the reaction rate for the first order $W = W(C, T)$ has the form

$$-\frac{dC}{d\tau} = kC\,, \qquad (9)$$

where $k = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right)$ is the rate constant of chemical reaction.

Starting from the theory of the kinetics of chemical reactions, from equation (9) it is possible to obtain an integral expression for the reaction rate constant

$$k = \frac{1}{\tau}\ln\left(\frac{C_0}{C}\right),$$

where C_0, C are the initial and current concentration of reagent.

Determination of the rate constant is done graphically. For this, we represent the reaction constant in the following form

$$k\tau = \ln C_0 - \ln C \;\Rightarrow\; \ln C = \ln C_0 - k\tau\,.$$

It is necessary to plot the graph in coordinates $ln(C) - \tau$, and in the case of its linearization with respect to the slope of the straight line one can find the rate constant $tg\alpha = -k$. By plotting this graph for several values $T = const$, we also graphically determine the activation energy from the following considerations. We shall logarithm the equation of the constant of the chemical reaction

$$k = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \;\Rightarrow\; \ln k = \ln k_0 - \frac{E_a}{R}\frac{1}{T}\,.$$

Graph in coordinates $ln(k) - 1/T$ allows obtaining activation energy $tg\alpha = E_a/R$.

However, finding the function $ln(C) - \tau$ at $T = const$, is impossible, because the burning reaction proceeds with an intensive release of heat, which determines its self-acceleration. But if we turn to the reaction rate graph (Fig. 4, *a*), it can be seen that two sections with a low and high

speed can be distinguished on the kinetics curve. Since the reaction rate is determined by the temperature, accordingly, in the general process, two combustion phases can be distinguished, the low- and high-temperature phases with quasistationary temperature. The latter can be taken as the weighted average of its value in each phase. This approach was used in [9], where in the kinetics of the description of the multi-stage oxidation of hydrocarbons, low- and high-temperature reaction regions were singled out for which the kinetic parameters were independently determined. The point of the region section was a certain switching temperature. In our case, such a point is the temperature of 1007 K, which is fixed at $\tau^* =$ 273 μs of the reaction, at the average temperatures in two phases of 983 and 1316 K (Fig. 3). Constructed function graphs $ln(C) - \tau$ for these phases for times 0–273 μs and 273–348 μs (Fig. 4) are very close to a linear function, so they can be approximated by a straight line. The approximation in this case is satisfactory and has a coefficient of determination of 0.94 and 0.95, which is entirely acceptable from the variance of the random calculation error. This error arises because of the relatively coarse grid of graphs on which the parameters are counted in a numerical experiment.

Thus, two values of the rate constants of the chemical reactions 819.9 and 28135 at temperatures of 983 and 1316 K were obtained from the approximation equations

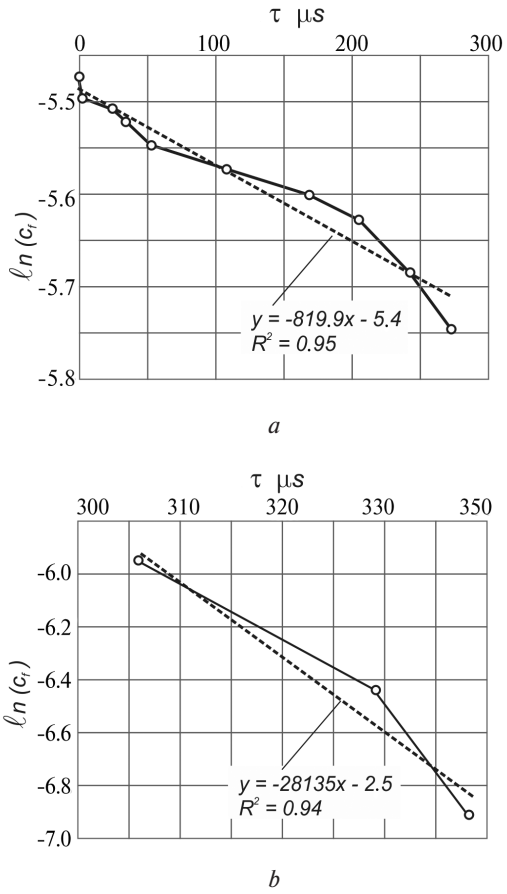

Fig. 4. Functions of the logarithm of the methane concentration ln (c_f) at time τ in the low (a) and high-temperature (b) phase of the explosive combustion reaction

for the $\ln(C) - \tau$ dependence, which makes it possible to plot the function $\ln(k) - 1/T$ (Fig. 5).

The equations of the direct experimental dependence $\ln(k) - 1/T$ make it possible to determine the activation energy of the explosive burning process for methane, кJ/mol.

$$E_a = - tg\alpha \cdot R = 13734 \cdot 8.31 = 114.1.$$

Therefore, the graph of $ln(k) - 1/T$ is the value of the pre-exponential factor of the Arrhenius equation. This value is cut off on the y-axis by the line of the graph (Fig. 5)

$$ln(k_0) = 11.7 => k_0 = 1.21 \cdot 10^5\ s^{-1}.$$

The values of E_a and k_0 obtained with acceptable accuracy coincide with the values established in the course of the experiment (Table 3). The relative error for E_a was 2.5 %, for k_0 – 7.4%.

Next, we estimate the correspondence of the half-transformation time $\tau_{1/2}$ and the degree of conversion of the reagent α to the kinetics of the first-order reaction. In this case

$$\tau_{1/2} = ln2/k; \quad \alpha = 1 - e^{-k\tau}.$$

The methane half-conversion time can be estimated from the high-temperature phase of the reaction, and the degree of conversion of the reagent through a low-temperature one at the time of 250 μs

$$\tau_{1/2} = 0.693 / 28135 = 24;$$
$$\alpha = 1 - exp(-820 \cdot 250 \cdot 10^{-6}) = 0.18.$$

The results obtained for the half-transformation period coincide with the center of the kinetic curve of the second phase of the reaction (Fig. 3, *a*), and the degree of methane conversion in the first phase corresponds to the calculated α = 0.18 (Fig. 3, *b*).

Thus, the kinetic characteristics of the explosive combustion reaction correspond to the accepted reaction order and the established effective values of E_a and Z.

Fig. 6 shows the kinetic curves of the dependence of the reaction rate on temperature constructed from the established effective parameters of the explosive combustion macrokinetics.

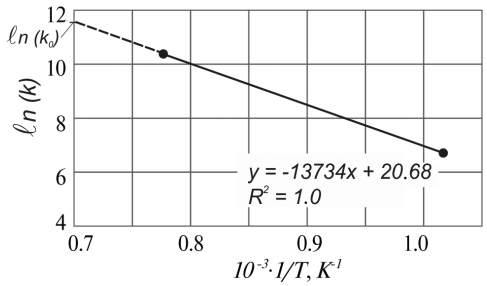

Fig. 5. The experimental dependence of the logarithm of the reaction rate constant ln(k) on the reciprocal temperature of 1/T reaction

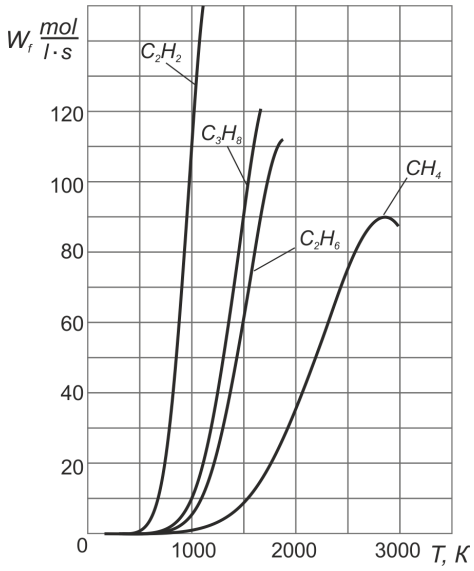

Fig. 6. Kinetic curves of the dependence of the reaction rate W on the temperature T, in a numerical experiment using the established parameters of macrokinetics

The graph clearly shows the differentiation of hydrocarbon characteristics from the ignition temperature and the rate of reaction build-up, which corresponds to the gradation of explosive properties of the gases under consideration: the minimum detonation initiation energy for acetylene, the maximum in methane [15]. Kinetic data obtained for stationary combustion processes (Table 1) have identical values of activation energy and do not give similar effects, since the dynamics of the ordinary combustion for which these values were established are practically the same. The established values of E_a, in contrast to the steady-state combustion process, are obtained lower due to the effect on the speed of the combustion processes of gas-dynamic effects from the action of shock waves.

Conclusions. The obtained parameters of macrokinetics of the global reaction mechanism of explosive combustion, for the hydrocarbons under consideration, are consistent according to gas-dynamic and kinetic characteristics. They allow us to apply simple kinetic mechanisms in practical calculations of the processes of deflagration and detonation combustion, and to predict the parameters of emergency explosions in conditions of mine workings with sufficient accuracy. This also makes it possible to solve the problem of accounting for the presence of heavy hydrocarbons in the mine atmosphere as products of coal pyrolysis in underground fires as factors of increasing the risk of emergency explosions.

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Мета. Встановлення ефективних параметрів макрокінетики горіння вуглеводнів у режимі дефлаграції й детонації для схеми чисельного рахунку аварійних вибухів у гірських виробках.

Методика. Математичне моделювання, чисельний експеримент, аналіз кінетики реакції вибухового горіння, аналіз і узагальнення результатів.

Результати. У роботі аналізуються параметри кінетичного рівняння по відношенню до експериментальних даних. Отримання таких даних у фізичному експерименті для вибухових хімічних реакцій зустрічає серйозні труднощі. Це обумовлено розмірами зони реакції, які не перевищують часток міліметра, недостатньою можливістю за часом експериментальних методик та іншими факторами, що призводять до похибок у прямих вимірах і виникненню неєдиного рішення. Можливість отримання даних забезпечує спільне чисельне рішення рівнянь газодинаміки й хімічної кінетики. У проведеному чисельному експерименті встановлено прямий зв'язок макрокінетичних характеристик хімічної реакції з параметрами розривної течії газового потоку, у якій протікає хімічна реакція горіння: швидкістю, тиском у фронті й за фронтом детонаційної й дефлаграційної хвилі. На підставі цього отримані арреніусовські характеристики реакції – предекспонента та ефективна енергія активації для розглянутих вуглеводнів.

Наукова новизна. Встановлені макрокінетичні параметри для моделювання одностадійного запалювання та горіння найбільш імовірних вуглеводнів рудникової атмосфери в режимі дефлаграції й детонації. Проведено моделювання вибухового горіння попередньо перемішаних вуглеводнів у стехіометричних концентраціях. Показано, що значення ефективної енергії активації в реакціях вибухового горіння мають менше значення на відміну від реакцій стаціонарного горіння через вплив газодинамічних ефектів ударної хвилі на швидкість реакції. Виконано узгодження арреніусовських характеристик реакції – предекспоненти та ефективної енергії активації – за газодинамічними й кінетичним показниками протікання реакції вибухового горіння.

Практична значимість. Отримані параметри макрокінетики реакції вибухового горіння дозволяють застосовувати прості кінетичні механізми у практичних розрахунках процесів дефлаграційного й детонаційного горіння і прогнозувати з достатнім ступенем точності параметри аварійних вибухів в умовах гірничих виробок. Це також дозволяє вирішити задачу обліку наявності важких вуглеводнів у рудничній атмосфері як продуктів піролізу вугілля при підземних пожежах як факторів збільшення ризику аварійних вибухів.

Ключові слова: *газоповітряна суміш, аварійний вибух, кінетика горіння, параметри макрокінетики, ефективна енергія активації*

Цель. Установление эффективных параметров макрокинетики горения углеводородов в режиме дефлаграции и детонации для схемы численного счета аварийных взрывов в горных выработках.

Методика. Математическое моделирование, численный эксперимент, анализ кинетики реакции взрывного горения, анализ и обобщение результатов.

Результаты. В работе анализируются параметры кинетического уравнения по отношению к экспериментальным данным. Получение таких данных в физическом эксперименте для взрывных химических реакций встречает серьезные трудности. Это обусловлено размерами зоны реакции, не превышающими долей миллиметра, недостаточностью разрешения по времени экспериментальных методик и другими факторами, приводящими к погрешностям в прямых измерениях и возникновению неединственности решений. Возможность получения данных обеспечивает совместное численное решение уравнений газодинамики и химической кинетики. В проведенном численном эксперименте установлены прямая связь макрокинетических характеристик химической реакции с параметрами разрывного течения реагирующего газового потока: скоростью, давлением во фронте и за фронтом детонационной и дефлаграционной волны. На основании этого получены аррениусовские характеристики реакции – предэкспонент и эффективная энергия активации для рассматриваемых углеводородов.

Научная новизна. Установлены макрокинетические параметры для моделирования одностадийного зажигания и горения наиболее вероятных углеводородов рудничной атмосферы в режиме дефлаграции и детонации. Проведено моделирование взрывного горения предварительно перемешанных углеводородов в стехиометрических концентрациях. Показано, что значения эффективной энергии активации в реакциях взрывного горения имеют меньшее значение в отличие от реакций стационарного горения из-за влияния газодинамических эффектов ударной волны на скорость реакции. Выполнено согласование аррениусовских характеристик реакции – предэкспонент и эффективной энергии активации – по газодинамическим и кинетическим показателям протекания реакции взрывного горения.

Практическая значимость. Полученные параметры макрокинетики реакции взрывного горения позволяют применять простые кинетические механизмы в практических расчетах процессов дефлаграционного и детонационного горения и прогнозировать с достаточной степенью точности параметры аварийных взрывов в условиях горных выработок. Это также позволяет решить задачу учета наличия тяжелых углеводородов в рудничной атмосфере как продуктов пиролиза угля при подземных пожарах как факторов увеличения риска аварийных взрывов.

Ключевые слова: *газовоздушная смесь, аварийный взрыв, кинетика горения, параметры макрокинетики, эффективная энергия активации*

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