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Abstract

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ON THE THERMAL SELF-IGNITION OF A HOMOGENEOUS GAS MIXTURE IN A FLOW

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In our work ([1]), by means of special experiments, it was found that for certain explosive systems (pyroxylin, nitroglycerine powder) processes in the flame have practically no effect on the burning rate. This means that in the gas phase there is no normal flame propagation and that the reaction proceeds in the regime of self-ignition (afterburning). The occurrence of a flame by self-ignition of the gas phase during the combustion of powder was experimentally observed by P. F. Pokhil ([2]).

(Figure: Fig. 1. Temperature profiles)

Fig. 1. Temperature profiles for $\beta = 0.05$; $\gamma = 0.01$ and $n = 2$. Profiles: 1–$\delta = 0.1$; 2–$\delta = 0.1 \cdot 10^{-1}$; 3–$\delta = 0.1 \cdot 10^{-2}$; 4–$\delta = 0.35 \cdot 10^{-3}$; 5–$\delta = 0.3 \cdot 10^{-3}$; 6–$\delta = 0.1 \cdot 10^{-3}$; 7–$\delta = 0.1 \cdot 10^{-4}$; 8–$\delta = 0.1 \cdot 10^{-5}$.

In the present work, within the framework of the physical assumptions of the classical theory of combustion ([3]), the problem of thermal self-ignition of a combustible gas mixture in a flow and its application to the conditions of combustion of condensed explosive systems is considered.

The initial stationary system of equations has the form:

$$\lambda d^2T/dx^2 - cu_{\text{m}}\, dT/dx + Q\rho k_0 e^{-E/RT}(1-\eta)^n = 0, \qquad (1)$$

$$D\rho d^2\eta/dx^2 - u_{\text{m}}\, d\eta/dx + \rho k_0 e^{-E/RT}(1-\eta)^n = 0.$$

Boundary conditions: $x = 0,\ T = T_0,\ \eta = 0; \quad x = \infty;\ dT/dx = 0;\ d\eta/dx = 0.$ Notation: T–temperature (°K); x–coordinate (cm); η–concentration of reacted products; $(1-\eta)$–concentration of the reacting substance; n–reaction order; T_0 –temperature at the beginning of the flow (°K); u_{m}–mass velocity of the flow (g/cm^2 · sec); ρ–density (g/cm^3); λ–thermal-conductivity coefficient (cal/cm · sec · deg); c–specific heat (cal/g · deg); Q–thermal effect of the reaction (cal/g); D–diffusion coefficient (cm^2/sec); K_0–pre-exponential factor (1/sec); E–activation energy (cal/mol).

The system of equations (1) describes the behavior of a combustible gas mixture in a flow with initial temperature T_0 and constant mass velocity u_{m}. The flow is assumed laminar; thermal and diffusion losses are neglected. In contrast to the problem of normal flame propagation, the reaction at T_0 is substantial, and the quantity u_{m} is a determining parameter rather than an unknown quantity.

The system of equations (1), taking into account the similarity of the temperature and concentration distributions ([3]), $\frac{c}{Q}(T - T_0) = \eta$, and also the temperature dependence of the gas density $\rho = \rho_0 T_0/T$ (where ρ_0 is the density at temperature T_0), can be represented in the following dimensionless form:

$$\frac{d^2\theta}{d\xi^2} - \frac{d\theta}{d\xi} + \delta \exp\left(\theta/(1+\beta\theta)\right) \frac{(1-\gamma\theta)^n}{1+\beta\theta} = 0. \tag{2}$$

Boundary conditions: $\xi = 0,\ \theta = 0,\ \xi = \infty,\ d\theta/d\xi = 0.$

Here

$$\theta = \frac{E}{RT_0^2}(T - T_0); \quad \xi = \frac{cu_{\text{m}}}{\lambda}x; \quad \delta = \frac{Q\lambda\rho_0}{c^2 u_{\text{m}}^2}\frac{E}{RT_0^2}k_0 \exp(-E/RT_0);$$

$$\beta = \frac{RT_0}{E}; \qquad \gamma = \frac{c}{Q}\frac{RT_0^2}{E}.$$

Equation (2) was integrated numerically on an electronic computer. The dependence $\theta = \theta(\xi, \delta, \beta, \gamma, n)$ was studied, as well as certain quantities connected with it: ξ_m—the coordinate of the point corresponding to the maximum rate of heat release, $a = (d\theta/d\xi)_{\xi=0}$—the heat flux into the fresh mixture,

$$b = \delta \int_0^\infty \exp(\theta/(1+\beta\theta)) \frac{(1-\gamma\theta)^n}{1+\beta\theta}\, d\xi$$

—the integral rate of heat release. The range of variation of the parameters was: $10^{-6} \le \delta \le 10$; $0.004 \le \beta \le 0.15$; $0.008 \le \gamma \le 0.15$; $n = 1$ and $n = 2$.

(Figure: Fig. 2)

Fig. 2. Dependence $\xi_m(\delta)$ for
$\beta = 0.05;\ \gamma = 0.01;\ n = 1$ and 2

In Fig. 1, as an illustration, temperature profiles are shown for various δ at $\beta = 0.05$, $\gamma = 0.01$, and $n = 2$, and in Figs. 2, 3, 4—the dependences $\xi_m(\delta)$, $a(\delta)$, and $b(\delta)$ for $\beta = 0.05$, $\gamma = 0.01$, $n = 1$ and $n = 2$.

As is seen from these figures, there exist two regimes of the course of the process, separated by clearly expressed critical conditions ($\delta = \delta_{\text{cr}}$). For $\delta < \delta_{\text{cr}}$ there is a self-ignition regime, characterized by large dimensions of the preflame zone ξ_m

(the induction zone), very small values of the heat flux throughout the induction zone, and constancy of the integral rate of heat release. In this regime the determining reaction is that occurring at the temperature T_0 ($\theta = 0$). For $\delta > \delta_{cr}$ a "combustion" regime occurs. It is characterized by small values of ξ_m, large values of a, and a dependence of b on δ.

In the "combustion" regime the determining reaction is that occurring at the temperature

$$T_r = T_0 + Q/C; \qquad (\theta_r = 1/\gamma).$$

The existence of two regimes of the process is easy to understand physically by comparing the flow velocity u_m with the velocity of normal flame propagation $(u_m)_r$ in the given mixture. If $u_m > (u_m)_r$, then the flame cannot move against the flow. The stationary existence of the flame in this case is due to the continuous self-ignition of new portions of the mixture. If, on the contrary, $u_m < (u_m)_r$, then the flame, having arisen during self-ignition, will move in the direction opposite to the motion of the mixture until the stabilizing effect of the boundary conditions at $\xi = 0$ comes into play. Hence it is easy to understand the difference in the values of ξ_m, a, and b. The equality $u_m = (u_m)_r$ corresponds to the critical conditions separating these two regimes. Thus, the critical value of the parameter δ in the given problem determines the velocity of normal flame propagation*.

(Figure: Fig. 3)

Fig. 3. Dependence $a(\delta)$ for
$\beta = 0.05$; $\gamma = 0.01$; $n = 1$ and 2

* It should be noted that the larger the values of the parameters β and γ, i.e., the more noticeable the reaction at T_0, the less sharply the critical conditions are expressed. Thus the difficulty in the theory of normal flame propagation associated with the "cutting off" of the exponential appears in the present formulation as a "smearing" of the critical conditions.

The dependence of δ_{cr} on the parameters β and γ (for $\beta < 0.1$, $\gamma < 0.1$ and $\beta/\gamma < 6$) for a monomolecular ($n = 1$) and bimolecular ($n = 2$) reaction, obtained as a result of processing the calculated data, can be represented with an accuracy of up to $\pm 20\%$ by the following formula:

$$\delta_{cr} = \left[1 + (0.34n + 0.16)\left(\frac{\beta}{\gamma}\right)^{3/2}\right] \frac{\gamma^n \exp\left(-\frac{1}{\gamma+\beta}\right)}{2n!(\gamma+\beta)^2(n+1)}. \qquad (3)$$

The well-known approximate formula of Ya. B. Zeldovich for the normal combustion velocity (3), written in the dimensionless quantities used in the present work, has the form

$$(\delta_{\text{cr}})_r = \frac{\gamma^n \exp\left(-\frac{1}{\gamma+\beta}\right)}{2n!(\gamma+\beta)^2(n+1)}. \tag{4}$$

The coefficient of discrepancy $[1+(0.34n+0.16)(\beta/\gamma)^{3/2}]$ in the first approximation has been expressed in the form of a function of the ratio of the parameters β and γ. The discrepancy between (3) and (4) is due to the fact that formula (4) does not take into account the dependence of the gas density on temperature and was obtained using the approximate transformation of the exponential according to D. A. Frank-Kamenetskii (4), and, finally, it was obtained by neglecting the middle term in equation (2). The discrepancy associated with the latter circumstance, as shown by Ya. B. Zeldovich and G. I. Barenblatt (5), is small.

(Figure: Fig. 4. Dependence $b(\delta)$ for $\beta = 0.05;\ \gamma = 0.01;\ n = 1$ and 2)

Fig. 4. Dependence $b(\delta)$ for $\beta = 0.05;\ \gamma = 0.01;\ n = 1$ and 2

Table 1

	Solution of the full equation	Solution of the full equation	Convective approximation			
	"combustion" regime $\delta = 0.1 \cdot 10^{-2}$	"combustion" regime $\delta = 0.35 \cdot 10^{-3}$	self-ignition regime $\delta = 0.3 \cdot 10^{-3}$	self-ignition regime $\delta = 0.1 \cdot 10^{-3}$	self-ignition regime $\delta = 0.1 \cdot 10^{-4}$	Convective approximation Convective approximation
$\xi_m\delta$	$0.98 \cdot 10^{-3}$	$1.35 \cdot 10^{-3}$	1.12	1.216	1.217	1.22
a/δ	$41.9 \cdot 10^3$	$5.1 \cdot 10^3$	1.003	1	1	1
b	142	102	100	100	100	100

In the self-ignition regime, as follows from general considerations, convective heat transfer from the hot layers of gas to the more "cold" ones should have a weak influence on the characteristics of the process, i.e., the course of the process should be described by equation (2), in which the second derivative, expressing conduction, is set identically equal to zero (convective approximation):

$$-\frac{d\theta}{d\xi} + \delta \exp(\theta/(1+\beta\theta))\frac{(1-\gamma\theta)^n}{1+\beta\theta} = 0. \tag{5}$$

The boundary condition is $\xi = 0,\ \theta = 0$. As follows from equation (5), the characteristics of the process must have the form:

$$\xi_m \delta = \varphi(\beta, \gamma, n); \quad a = \delta; \quad b = 1/\gamma.$$

Table 1 gives the values of these characteristics, calculated from the full (2) and reduced (5) equations for the parameter values ($\beta = 0.05$, $\gamma = 0.01$ and $n = 2$).

As is seen from Table 1, the convective approximation in the self-ignition regime is realized with high accuracy.

For $\beta < 0.1$, $\gamma < 0.1$, $n = 1$ and $n = 2$, the function $\varphi(\beta, \gamma, n)$ can, with an accuracy no worse than $\pm 20\%$, be represented by the formula $\varphi(\beta, \gamma) = 1 + 80\beta^2 + 0.6\gamma^{1/2*}$, obtained as a result of processing numerical solutions of equation (5).

* The dependence of φ on n is very weak.

Thus, the width of the preflame zone in the self-ignition regime has the form

$$\xi_m = \frac{1 + 80\beta^2 + 0.6\gamma^{1/2}}{\delta}. \tag{6}$$

The results of the solution of this problem can be used in analyzing the combustion mechanism of condensed explosive systems. Under combustion conditions the gas flow is produced either as a result of decomposition of the initial substance (nonvolatile systems), or by its evaporation (volatile systems) ([6]). In the first case, T_0 is taken to be the temperature at the end of the decomposition zone of the dispersed particles ([7–9]), and in the second, the boiling temperature.

Let us compare the results of the solution of the problem with the experimental data available in the literature. Knowing from experiment the burning velocity u_m and the width of the preflame zone x_m, one can calculate $(\xi_m)_{\text{expt}} = \dfrac{cu_m}{\lambda} x_m$. From formula (6), at $\delta = \delta_{\text{cr}}$, one can find the smallest value $(\xi_m)_{\min}$ in the self-ignition regime. If $(\xi_m)_{\text{expt}} > (\xi_m)_{\min}$, then the process in the gas phase proceeds in the self-ignition regime. If, on the contrary, $(\xi_m)_{\text{expt}} < (\xi_m)_{\min}$, then the "combustion" regime takes place. The results of calculations for pyroxylin, nitroglycerine powder, and hexogen at pressures from 10 kg/cm^2 to 50 kg/cm^2 are given in Table 2*.

Thus, comparison of the calculation results with experiment shows that the reaction in the gas phase during combustion of pyroxylin and nitroglycerine powder proceeds in the self-ignition regime, whereas for hexogen it proceeds in the "combustion" regime, which is in full agreement with existing ideas concerning the combustion mechanism of condensed explosive systems ([2,6]).

Table 2

	Pyroxylin, nitroglycerine powder	Hexogen
$(\xi_m)_{\text{expt}}$	$10^3 \div 10^4$	$30 \div 50$

	Pyroxylin, nitroglycerine powder	Hexogen
$(\xi_m)_{\min}$	$5 \div 30$	$10^2 \div 10^8$

It should be noted that the self-ignition regime is very widespread in combustion processes. Thus, for example, R. M. Zaidel' and Ya. B. Zel' dovich ([11]) have recently shown that it can be realized in a number of such modern technical devices as jet engines.

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* In the calculations the following values were used: $c = 0.4$ cal/g·deg.; $\lambda = 10^{-4}$ cal/cm · sec · deg.; $E = 20\,000 \div 50\,000$ cal/mole; u_m from ([1,10]). Data of V. M. Mal' tsev ([8]): $T_0 \simeq 700^\circ$ K, $Q \simeq 1100$ cal/g (hexogen); $T_0 \simeq 1200 \div 1400^\circ$ K, $Q \simeq 500$ cal/g (pyroxylin, nitroglycerine powder).

Note: Figure translations are in progress. See original paper for figures.