On One Model of the Combustion of Nonvolatile Explosives

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On One Model of the Combustion of Nonvolatile Explosives

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In papers ([1–3]) it was shown that the regularities of combustion of nonvolatile explosives (e.s.) in a number of cases are associated with dispersion of the initial condensed substance. However, the question of the mechanism of this phenomenon has not yet been clarified. In the present work, developing the ideas of Parr and Crawford ([4]) on the formation of foam in the condensed reaction zone, one of the possible mechanisms of dispersion in liquid and melting nonvolatile systems during combustion is considered, and an attempt is made at a quantitative description of the phenomenon.

The consideration is based on the following physical assumptions.

1. A one-stage combustion model is investigated, taking into account the reaction in the liquid phase under conditions of a strong increase in volume caused by the formation in the reaction zone of foam, which upon its destruction turns into an aerosol. The influence of the reaction in the gas phase is not taken into account; the conditions of applicability of this will be given below.

2. Conditions are considered under which the pressure in the foam bubbles is close to the external pressure, and the ideal-gas equation of state is applied to the foam and aerosol,

$$\frac{\rho}{\rho_0} = \frac{1}{1 + \eta z \left(\rho_0 \frac{RT}{p\mu} - 1\right)}, \tag{1}$$

where ρ/ρ_0 is the change in density; ρ_0 is the initial density; η is the depth of decomposition; z is the fraction of gaseous product upon decomposition; T is temperature; p is pressure; μ is the mean molecular weight of the gaseous reaction products; R is the gas constant. This equation is invalid both at very high pressures, because of the deviation of the gas properties from ideality, and at very low (vacuum) pressures, because the Laplace pressure cannot be neglected.

3. Dissolution of the gaseous reaction products in the liquid phase and the

associated possibility of an autocatalytic reaction proceeding are, for simplicity, not taken into account.

4. The heat capacity is assumed constant, and the thermal conductivity in the foam and aerosol is described by the formula, obtained from additivity considerations,

$$\lambda = \lambda_{\text{g}} V_{\text{g}} + \lambda_{\text{k}} V_{\text{k}} = \lambda_{\text{k}} \frac{1 + \eta z \left(\frac{\lambda_{\text{g}}}{\lambda_{\text{k}}} \rho_0 \frac{RT}{p\mu} - 1 \right)}{1 + \eta z \left(\rho_0 \frac{RT}{p\mu} - 1 \right)}, \tag{2}$$

where λ_{g} and λ_{k} are the coefficients of thermal conductivity of the gas and condensed substance, respectively; V_{g} and V_{k} are their volume fractions, respectively. As follows from the theory of heat transfer in disperse media ([5]), such a representation corresponds to reality with satisfactory accuracy (it gives an overestimate by 10-15%).

5. The influence of melting on the regularities of combustion is taken into account by introducing an effective initial temperature ($T_{\text{eff}} = T_0 - Q_{\text{melt}}/c$), which is apparently valid if melting occurs in the preheating zone.

6. Heat losses from the reaction zone are not taken into account. Thus, in accordance with what was said above, the original system of equations describing combustion under conditions of a strong increase in volume has the form

$$\lambda_{\kappa} \frac{d}{dx} \left[\frac{1 + \eta z \left(\frac{\lambda}{\lambda_{\kappa}} \rho_0 \frac{RT}{p\mu} - 1 \right)}{1 + \eta z \left(\rho_0 \frac{RT}{p\mu} - 1 \right)} \frac{dT}{dx} \right] + u\, c \frac{dT}{dx} + Q \frac{k_0 \rho_0 (1 - \eta)}{1 + \eta z \left(\rho_0 \frac{RT}{p\mu} - 1 \right)} e^{-E/RT} = 0,$$

$$u \frac{d\eta}{dx} + \frac{k_0 \rho_0 (1 - \eta)}{1 + \eta z \left(\rho_0 RT/p\mu - 1 \right)} e^{-E/RT} = 0; \tag{3}$$

boundary conditions: at $x = \infty$, $T = T_0$ and $\eta = 0$; at $x = -\infty$, $dT/dx = 0$, $\eta = 1$, where x is the coordinate; u is the mass burning rate; c is the heat capacity; Q is the heat effect of the reaction; k_0 is the preexponential factor; E is the activation energy; T_0 is the initial temperature.

Table 1

λ	χ	$\sigma \cdot 10^2$	π	Ω, numerical calculation	Ω by formula (4)	Discrepancy, %
1	0.13	7.72	$0.70 \cdot 10^{-5}$	$0.45 \cdot 10^{-5}$	$0.41 \cdot 10^{-5}$	11
1	0.337	7.72	$0.7 \cdot 10^{-9}$	$0.12 \cdot 10^{-5}$	$0.11 \cdot 10^{-5}$	12
1	2.02	1.285	$7 \cdot 10^{-9}$	$0.63 \cdot 10^{-9}$	$0.53 \cdot 10^{-9}$	19
1	0.337	3.85	$17 \cdot 10^{-5}$	$0.885 \cdot 10^{-6}$	$0.825 \cdot 10^{-6}$	7
1	0.937	3.85	$7 \cdot 10^{-4}$	$0.275 \cdot 10^{-5}$	$0.260 \cdot 10^{-5}$	6.5
16	0.337	3.85	$7 \cdot 10^{-4}$	$0.31 \cdot 10^{-5}$	$0.28 \cdot 10^{-5}$	10

For $z \to 0$, this system describes the ordinary combustion regime without allowance for a change in volume. We note that in the present problem the mechanism of volume dispersion is considered. The notion of dispersion as a surface process ([3]) is valid for nonmelting substances. Consideration of volume dispersion makes it possible, from a unified point of view, to describe processes occurring in the condensed and smoke-gas zones (in the presence of foaming, there is no sharp boundary between these zones). Therefore, in this work the usual concepts of a burning surface and its temperature are not used.

We also note that the volume dispersion of the liquid phase considered in this work is the limiting regime of maximum dispersion, in which the motion of the initial substance and of the expanding gaseous products occurs with the same velocity.

An approximate analytical solution of system (3) is found using the assumption of Ya. B. Zel' dovich and D. A. Frank-Kamenetskii, which consists in neglecting convective heat transfer in the reaction zone ([6]):

$$u^2 = \frac{\lambda_\kappa k_0 \rho_0}{Q} \frac{RT_m^2}{E} \frac{1}{\dfrac{(b-a)^2}{b^3} \ln(1+b) + \dfrac{a}{b}\left(2 - \dfrac{a}{b} + \dfrac{a}{2}\right)} e^{-E/RT_m}, \qquad (4)$$

where

$$a = \left(\rho_0 \frac{RT_m}{p\mu} - 1\right) z, \qquad b = \left(\frac{\lambda}{\lambda_\kappa} \rho_0 \frac{RT_m}{p\mu} - 1\right) z, \qquad T_m = T_0 + \frac{Q}{c}.$$

Fig. 1

Figure 1: Fig. 1

In order to check the validity of this approximation under conditions of a strong change in volume, and also to analyze the structure of the combustion zone, system (3) was solved numerically on an electronic computer. The following dimensionless variables and parameters were used:

$$\vartheta = \frac{T - T_0}{T_m - T_0}, \qquad \xi = \frac{cu}{\lambda_\kappa} x, \qquad \Omega^2 = \frac{u^2 c}{\lambda_\kappa \rho_0 k_0}, \qquad \sigma = \frac{RQ/c}{E},$$

$$\chi = \frac{cT_0}{Q}, \qquad \pi = \frac{p\mu}{\rho_0 E}, \qquad \Lambda = \frac{\lambda_\kappa}{\lambda}.$$

The calculation was carried out while varying the parameters in the following intervals:
$\sigma = (1.285 \div 7.72) \cdot 10^{-2}$; $\varkappa = 0.13 \div 2.02$; $\pi = 10^{-8} \div 10^{-2}$; $\Lambda = 1 \div 80$. The results of the numerical solution, some of which are given in Table 1, showed that the approximate formula (4) describes combustion with good accuracy. In connection with this, the analysis of combustion regularities can be carried out by formula (4).

We consider the region in which the equation of state of an ideal gas is valid, and therefore
$\rho_0 \dfrac{RT_m}{p\mu} \gg 1$. For the case $\lambda_k/\lambda_g = 1,\ z = 1$, from (4) we obtain

$$u_m^2 = \frac{\lambda k_0 \rho \mu T_m}{QE} e^{-E/RT_m}, \tag{5}$$

i.e., the mass burning rate does not depend on the density* and is proportional to the square root of the pressure (i.e., $\nu = \dfrac{p}{u}\dfrac{du}{dp} = 0.5$). For $\lambda_k/\lambda_g > 1$ and $z < 1$, two pressure regions must be considered (Fig. 1). At smaller values of p the regularities are the same; at larger p, u_m increases with increasing density ρ_0, while the exponent ν increases with increasing λ_k/λ_g and decreases with decreasing z.

Fig. 1. Dependence of the burning rate on pressure.
1 $-\Lambda = 1,\ z = 0.04$; 2 $-\Lambda = 1,\ z = 1$;
3 $-\Lambda = 30,\ z = 1$; 4 $-\Lambda = 80,\ z = 1$

A strong change in volume, as expected, had a noticeable influence on the structure of the combustion zone (Fig. 2). The most characteristic features are:

1. The presence of a broad heat-release zone, comprising approximately half of the entire temperature-change zone.

Fig. 2

Figure 2: Fig. 2

2. A mismatch between the positions of the maxima of the heat-release and reaction rates (the heat-release maximum corresponds to $\eta_q \simeq 0.4$ and $T_q \simeq T_m - 4RT_m^2/E$, the magnitude of which for $z = 1$ depends only weakly on the parameters).

3. A very low value of the substance density corresponding to the maximum heat-release rate (indeed, from (1), for $z = 1$ we obtain $\rho_q \simeq 2.5\rho_g$, where $\rho_g = p\mu/RT_m$ is the gas density at the temperature maximum). It should be emphasized that the presence of a density-change zone is a specific feature of the problem under consideration. The calculation showed that this zone constitutes approximately one third of the width of the temperature-change zone.

Fig. 2. Structure of the combustion-front profile for the following parameter values:
$\varkappa = 0.337,\ \sigma = 3.85 \cdot 10^{-2},\ \pi_1 = 0.7 \cdot 10^{-3};\ \pi_2 = 0.7 \cdot 10^{-4};\ \eta'$ and q are the dimensionless reaction rate and heat release per unit volume

If the gaseous reaction products in the condensed phase are capable of further exothermic transformation, then, in accordance with the results of works ([7],[8]), one can indicate a criterion according to which the reaction in the gas phase proceeds in the self-ignition regime and does not affect the burning rate

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* As we see, the independence of the mass rate from density cannot serve as an unambiguous criterion that the limiting stage of combustion is located in the gas phase.

affects. For this it is necessary that

$$u_m > \frac{\lambda_r k_{0r} \rho_r}{c_r} \frac{2n! \left(c_{rRT} m^2 / Q_{rE} r\right)^{n+1} \left(1 + Q_r / c_{rT} m\right)^{2(n+1)}}{1 + (0.34n + 0.16) \left(Q_r / c_{rT} m\right)^{3/2}} \exp \times \left[- \frac{E_r}{RT_m} \frac{1}{1 + Q_r / c_{rT} m} \right], \tag{6}$$

where u_m is the mass burning rate calculated from (4) for the condensed zone, T_m is the temperature at the hot end of the condensed zone ($T_m = T_{0\text{eff}} + Q/c$), n is the order of the reaction in the gas, and the remaining thermokinetic constants refer to gaseous intermediate products.

Thus, the model considered makes it possible to analyze regularities and to calculate absolute values of the burning rates of liquid or melting nonvolatile substances.

The regularities obtained correspond to some extent to the experimental material available in the literature (values for pyroxylin ([7,9,10]) and for mercury fulminate ([11]), the structure of the burning zone in pyroxylin ([12]), the dependence of the burning rate of pyroxylin on density ([9]), etc.); however, in order to establish a more rigorous correspondence, special detailed experimental investigations are necessary.

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