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Fig. 1

Figure 1: Fig. 1

Abstract**Full Text****PHYSICAL CHEMISTRY****N. N. BAKHMAN and Yu. A. KONDRASHKOV****ON ONE MODEL OF THE COMBUSTION FRONT OF CONDENSED MIXTURES***(Presented by Academician V. N. Kondrat'ev on 1 VIII 1961)*

In work ⁽¹⁾ it was shown experimentally that, for condensed mixtures whose components gasify before mixing, the dependence of the combustion velocity u on the determining particle size of the components d has an S-shaped form: for $d \leq d_{\min}$, u does not depend on d at all; then u begins to decrease noticeably with increasing d , but at large d the dependence $u(d)$ again weakens.

The available theoretical works ⁽²⁾ and others) in no way describe the experimental curve $u(d)$. This discrepancy, in our opinion, cannot be eliminated within the framework of a one-dimensional problem.

In the present work a simple model of the combustion front is considered which makes it possible to take into account the nonuniformity of the problem and to construct an approximate expression for the dependence $u(d)$, suitable for comparison with experiment and not contradicting it.

Fig. 1. $a-d = d_{\min}$; $b-d > d_{\min}$ ($d/d_{\min} \sim 1$); $v-d \gg d_{\min}$

For $d \leq d_{\min}$, when mixing of the components has time to be completely completed before the onset of the reaction, the combustion front is plane (Fig. 1a), and the combustion is kinetic in character ⁽³⁾. When d passes through d_{\min} , the cones of mixing* cease to fit within the limits of the preparatory zone (Fig. 1b). On the surface of the front there appear cone-shaped protrusions, where the combustion already has a diffusion character. The sizes of the protrusions increase with increasing d , and the surface of the front becomes more and more curved (Fig. 1v). It is important to note, however, that for any arbitrarily large d the points of the flame that penetrate most deeply into the solid phase ("flame tips") are located in a homogeneous mixture, since mixing of the components begins earlier than the reaction between them. Accordingly, combustion at the tips (at points A in Fig. 1b and v) proceeds in the kinetic regime.

Meanwhile, experiments have shown ^(4, 5) that the combustion velocity of the

system as a whole depends only on those processes that occur in a fairly narrow zone near the flame tip. Thus, for any d , the combustion velocity is determined to a considerable extent by kinetic factors**. We shall use this circumstance to construct a model of the combustion front.

* The real form of the mixing surface (the surface of stoichiometric composition) for the system considered is very complicated and, moreover, nonstationary. Schematically, we shall regard the mixing surface as a system of straight circular cones, identical for both components.

** In other words, combustion of condensed mixtures with gasifying components can never proceed in a purely diffusion regime.

Let the burning rate be determined by such a narrow zone at the flame tip that

$$u \sim p^n \exp\left(-\frac{E}{2RT_A}\right), \quad (1)$$

where T_A is the temperature at the center of the tip. This temperature, generally speaking, is lower than the temperature on a plane combustion front (for $d \leq d_{\min}$) because of heat losses to the sides; this is what causes the burning rate to decrease as d increases.

Let us write the heat balance at point A :

$$\rho u Q + q_{\text{diff}} = \rho u c(T_A - T_0) + q_y. \quad (2)$$

Here Q (in cal/g) is the thermal effect of the reaction occurring at point A ; q_{diff} is the heat flux to the tip from the diffusion flame above; $\rho u c(T_A - T_0) = \lambda(dT/dx)_A$ is the heat flux for heating the mixture (which then reacts at point A)*; q_y is the lateral flux (spent on heating the mixture reacting away from the tip).

The lateral heat losses are greater the smaller the size of the portions of the plane front in Fig. 1 (we shall characterize this size by the quantity \emptyset) or the greater the curvature of the front at point A in the case of Fig. 1. For simplicity, we shall characterize the curvature of the front by the same quantity \emptyset (\emptyset is related by a simple relation to the radius of curvature and does not differ too greatly from it). Note that for a plane front q_y must vanish. Taking these considerations into account, we write q_y in the form

$$q_y = \lambda \frac{T_A - T_*}{k_1} \frac{1}{k_2 \emptyset} \left(1 - \frac{\emptyset}{d}\right), \quad (3)$$

where k_1, k_2 are proportionality coefficients. In view of the qualitative nature of the derivation, we shall everywhere take $T_* = T_0$. Let us express \emptyset through d and u . From Fig. 1 it follows:

$$\emptyset = d \frac{h_1}{h}. \quad (4)$$

From dimensional considerations,

$$h_1 = h_0 \frac{u_0 \lambda_1}{u \lambda_0}, \quad (5)$$

where h_0, u_0, λ_0 are, respectively, the width of the mixing zone, the burning rate, and the thermal conductivity at $d = d_{\min}$. Further, also from dimensional considerations, for $\rho = \text{const}$ we obtain:

$$\frac{h}{h_0} = \frac{u}{u_0} \frac{d^2}{d_{\min}^2} \frac{D}{D} \left| \frac{d_{\min}}{d} \right|, \quad (6)$$

where D is the diffusion coefficient. For small d , mixing is effected by molecular diffusion, and therefore

$$\frac{h}{h_0} = \frac{u}{u_0} \left(\frac{d}{d_{\min}} \right)^2. \quad (7)$$

The thermal conductivity is likewise purely molecular: $\lambda_1 = \lambda_0 = \lambda$. Conversely, at sufficiently large d , convective mixing plays a significant role⁽⁶⁾, and in the limit $D \sim ud\rho_t/\rho$, where ρ_t is the density of the solid phase, which gives

$$\frac{h}{h_0} = \frac{k_3 d}{u_0 d_{\min}^2}. \quad (8)$$

Accordingly, in (3) one should substitute the coefficient of convective thermal conductivity $\lambda = \lambda_1 \sim ud\rho c$.

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* It is assumed that the total thermal effect of the gasification reactions is equal to zero. For the heat capacity c , an average value is adopted.

From (2)–(5), (7) or (2)–(5), (8) we obtain:

$$T = T_0 + \frac{\rho u Q + q_{\text{diff}}}{\rho u c + \frac{\lambda_0}{k_1 k_2} \frac{u^2 d}{(u_0 d_{\min})^2} \left[1 - \left(\frac{u_0 d_{\min}}{ud} \right)^2 \right]} \quad \text{for small } d; \quad (9)$$

$$T = T_0 + \frac{\rho u Q + q_{\text{diff}}}{\rho u c + \frac{\lambda_0}{k} \frac{u}{(u_0 d_{\min})^2} [1 - k'(u_0 d_{\min})^2]} \quad \text{for large } d. \quad (10)$$

Fig. 2

Figure 2: Fig. 2

Let us note that $u_0 d_{\min} = (u_0 d_{\min})_{p_*} = \text{const}$, where p_* is any fixed pressure, since $d_{\min} \sim \frac{1}{u_0}$ (see (1)).

Substituting (9) or (10) into (1), we obtain a transcendental equation for determining $u(d)$, but in its general form it is too cumbersome and unsuitable for comparison with experiment. However, if $q_{\text{diff}} \ll \rho u Q$ and if $T_0 \ll T$, this equation is sharply simplified, and after taking logarithms we obtain:

$$\lg u = a - bud \left[1 - \left(\frac{u_0 d_{\min}}{ud} \right)^2 \right] \quad \text{for small } d; \quad (11)$$

$$\lg u = a - b' \frac{1}{(u_0 d_{\min})^2} [1 - k'(u_0 d_{\min})^2] \quad \text{for large } d. \quad (12)$$

It is seen from (12) that for sufficiently large d the burning rate does not depend on d , which agrees with experiment¹. In Fig. 2, in the coordinates $\lg u$,

$$ud \left[1 - \left(\frac{u_0 d_{\min}}{ud} \right)^2 \right],$$

experimental data are plotted for a mixture based on bitumen at various external pressures. For not too large d , the experimental points satisfactorily fall on the straight line (11); then, as the argument increases (due to an increase in d), the straight line (11) goes below the experimental points, and the latter approach the straight line $\lg u = \text{const}$, as follows from (12). The coefficient b , determined from the experimental points, decreases with increasing pressure (see Table 1), especially at low pressures, which can be explained by an increase in the completeness of combustion with increasing pressure.

Fig. 2. 1–5 atm, 2–10 atm, 3–20 atm, 4–60 atm, 5–80 atm

Table 1

p , atm	5	10	20	40	60	80	100
b , sec/cm ²	39.7	20.6	18.8	14.4	12.8	11.05	10.7

Formula (11) also shows the effect known from experiment—the weakening of the dependence $u(p)$ as d increases (as long as d is not too large).

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

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