THE BASIS OF THE DEPENDENCE OF BURNING RATE ON PRESSURE IN THE RELAXATION THEORY OF PROPAGATION OF COMBUSTION

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It is shown that the physical basis of the dependence of burning rate on pressure, lacking in the relaxation theory of propagation of combustion, actually forms part of the relaxation mechanism itself. The corresponding formulas of the relaxation theory are refined.

It is noted in [2] that the cause of the influence exerted by pressure on burning rate should be sought chiefly in the pressure dependence of the temperature T_g at the interface between the condensed and gas phases, but this dependence was not given a physical basis.

In [1] (Fig. 3) the thermal conditions that must prevail in the condensed phase during the combustion process were examined. We may supplement the remarks in [1] by noting that to realize the relaxation mechanism of propagation of combustion, it is not necessary to have ignition; it is sufficient to have rapid exothermic expansion of the component, designated by circles the figure, when a certain temperature is reached. This temperature will be equivalent to the ignition point. Exothermic reduction of this component is also a possibility.

Since ignition of the next elementary layer occurs within the condensed phase, high-temperature gases are formed in the surface layer of the substance and create a rapidly rising pressure. On reaching a certain pressure, they force open the surface layer, suddenly expand to the pressure of the external medium, whereupon their temperature drops to T_g. The higher the external pressure, the less the degree of expansion of the gases, and the higher the temperature T_g, i. e., T_g must depend on the pressure. Thus, the physical basis for the pressure dependence of the burning rate forms part of the relaxation mechanism itself and does not require additional assumptions.

Obviously, when the gases force open the surface layer, they must reduce the latter to fine particles and eject them into the gas phase, forming a gas-smoke mixture. Therefore, a necessary feature of the relaxation mechanism of combustion propagation must be a smoke-gas mixture in the gaseous phase. All the components of the initial materials may occur as solid particles in the smoke-gas mixture, including partially unburnt particles of fuel and some products of the primary reactions. On the surface of the condensed phase there must form a region of primary reaction products with a relatively low temperature T_g, in which there is still little or no heat release ("dark zone"), while beyond the limits of this zone secondary, essentially exothermic reactions must take place in the smoke-gas mixture — further combustion of fuel particles and products of incomplete oxidation. The thermal effect of the secondary reactions may be much greater than that of the primary reactions, since only a small part of the fuel should be consumed before the disruption of the surface layer. The lower the pressure, the longer the "dark zone," not only because of the influence of pressure on the rate of the chemical reactions, but also because the smoke-gas mixture must be ejected to a greater distance [3-5].

Disruption of the surface layer must occur when the difference between the pressure within the material and the external pressure reaches a certain level. This pressure difference will depend on the strength of the disrupted layer, but not on the external pressure, since there is no reason why it should. Therefore,

$$p_q - p_g = p_p = \text{const.} \tag{1}$$

The temperature T_q of the primary reaction products up to disruption of the material is determined by the thermal effect of these reactions and by the specific heat of their products (if we neglect heat transfer during their formation, which is valid, as a first approximation, because ignition time is so short) and should not depend on the pressure p_q, i. e., we may assume that $T_q = \text{const.}$

Assuming that the primary reaction products are a perfect gas and that their expansions are adiabatic, we may consider that the temperatures T_g and T_q are related by the Poisson equation. In that case

$$T_g = T_q \, (p_g/p_q)^\nu = T_q \, [p_g/(p_g + p_p)]^\nu , \tag{2}$$

where $\nu = (C_p - C_v)/C_p$. For monatomic gases $\nu = 0.38$, for diatomic $\nu = 0.29$, and for triatomic gases and beyond $\nu = 0.25$. All values of ν between 0.25 and 0.38 are possible, since the primary reaction products may contain gases of different atomic weights in various proportions.

Assuming two different pressures p_g and corresponding temperatures with subscripts 0 and 1, we obtain

$$T_{g1} = T_{g0} (p_{g1}/p_{g0})^\nu \left[\frac{(p_{g0} + p_p)}{(p_{g1} + p_p)} \right]^\nu,$$

(3)

if temperature is measured in °K.

If the exhaust gases meet appreciable resistance in the exhaust channel, then the pressure p_g will be greater than the external pressure p by the amount of the pressure drop in the exhaust channel Δp, i.e.,

$$p_g = p + \Delta p.$$

(4)

From (3), taking account of (4) and the equation for the rate of propagation of combustion [1], we obtain

$$\frac{u_1}{u_0} = C \left\{ A \left[\left(\frac{p_1 + \Delta p_1}{p_0 + \Delta p_0} \right)^\nu \left(\frac{p_0 + \Delta p_0 + p_p}{p_1 + \Delta p_1 + p_p} \right)^\nu - 1 \right] + B \right\},$$

(5)

$$C = \frac{T_{e0} - T_i + \eta/c + 4\omega/c\gamma d}{T_{e1} - T_i + \eta/c + 4\omega/c\gamma d}, \quad A = \frac{T_{g0} + 273}{T_{g0} - 0.4 T_{e0} - 0.6 T_i},$$

$$B = \frac{T_{g0} - 0.4 T_{e1} - 0.6 T_i}{T_{g0} - 0.4 T_{e0} - 0.6 T_i}.$$

If the ignition temperature depends only slightly on pressure, which should be true in most cases, or $(\eta/c) + (4\omega/c\gamma d) \gg (T_e - T_i)$, then the values of B and C must be close to unity. Moreover, in many cases it may be assumed that Δp_0 and Δp_1 are negligibly small compared with p_0 and p_1. Under these conditions

Pressure dependence of burning rate at $\nu = 0.3$, A = 3, $p_0 = 9.8 \cdot 10^4$ N/m²: 1) $p_p = 9.8 \cdot 10^6$ N/m²; 2) $49 \cdot 10^6$ N/m²; 3) ∞. The upper curves are for $p_1/p_0 \leq 200$.

$$\frac{u_1}{u_0} = A \left[\left(\frac{p_1}{p_0} \right)^\nu \left(\frac{p_0 + p_p}{p_1 + p_p} \right)^\nu - 1 \right] + 1.$$

(6)

When $p_p = 0$, Eq. (5) gives $u_1/u_0 = BC$, while Eq. (6) gives $U_1/U_0 = 1$, i.e., in the latter case the burning rate does not depend on pressure, while in the former case it does, but only very slightly.

When $p_p = \infty$, Eqs. (5) and (6) coincide with Eqs. (1) and (2) of [2]. For practical calculations Eq. (6) is quite satisfactory.

All possible values of the function $u_1/u_0 = f(p_1/p_0)$ with p_p varying from zero to infinity are included with the limits defined by the above formulas. The upper limit cannot be reached, since at $p_p = \infty$ disruption of the surface layer is impossible, which means that combustion is also impossible. The lower limit at $p_p = 0$ can be reached in theory, and evidently in practice.

The value of p_p can be roughly estimated from the formula

$$p_p \approx \sigma_p \frac{S_1}{S_2}.$$

(7)

Apparently, for the materials in question the ultimate strength may not lie outside the range $5 \leq \sigma_p \leq 49 \cdot 10^5$ N/m² . Usually the volume of fuel particles in 4-12% of that of the material. For 4%, $S_1/S_2 \approx 9$, and for 12%, $S_1/S_2 \approx 4$. Therefore the pressure p_p may lie in the range $19.6 \cdot 10^5$ to $44 \cdot 10^6$ N/m², but in practice it must lie within much narrower limits. The figure shows curves computed from Eq. (6). It is clear that if p_p is varied by a factor of five, then at $p_1/p_0 = 4000$, u_1/u_0 varies from 10 to 17, i.e., by a factor of only 1.7. At smaller values of p_1/p_0, and also when $\nu < 0.3$ and A < 3, the variation of u_1/u_0 will be less. Thus, an accurate determination of p_p is not necessary; an approximate value will give only a small error.

The actual combustion process differs from that assumed in deriving the equations, and one should know to what extent this difference affects the formulas obtained.

In the first place, the process of expansion of the gases is not adiabatic, since, during the ignition time, part of the energy liberated must go toward heating the condensed phase and disruption of the surface layer. It is to be expected,
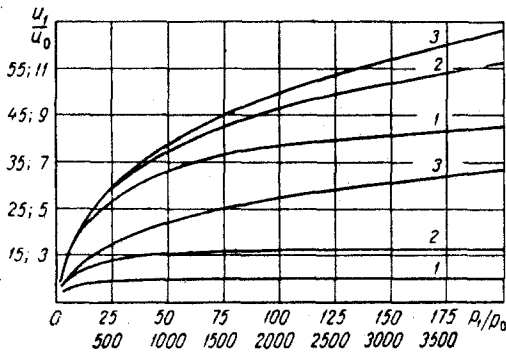
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however, that the influence of these losses on the temperature T_g will be only slight and will be felt only at low values, i.e., at low pressure.

Moreover, the properties of the primary reaction products may differ more or less markedly from those of a perfect gas. The most important difference is that in the primary reaction products heat is transported by solid particles as well as gases. Calculations taking account of the heat content of the condensed particles showed that the formulas derived above remain valid, the only difference being that A must be replaced by a quantity A_1 given by the formula:

$$A_1 = \frac{C_g}{C_m} \frac{T_{g0} + 273}{T_{g0}^* - 0.4T_e - 0.6T_i} . \tag{8}$$

When $C_g = 0$, i.e., in the absence of gases in the primary reaction products, the burning rate will not depend on pressure; there are thus two quite different reasons for the burning rate not depending on pressure.

Finally, the primary reaction products give up heat to the condensed phase and receive it from the secondary reaction zone, and, depending on the ratio of heat gain to heat loss, the temperature T_g may be less than, equal to, or greater than the calculated value. It may be less than the calculated value at low pressure, when the secondary reaction zone moves away from the surface of the condensed phase. At increased pressures, this zone draws nearer to the condensed phase, and at sufficiently high pressures, the temperature T_g may exceed the calculated value. With further increase of pressure the temperature T_g may increase more rapidly than the theoretical value. However, the change of sign at the point of inflection may be due not only to the cause mentioned, but also to a change in the mechanism of propagation of combustion [1].

From the foregoing considerations, it follows that in the relaxation mechanism of propagation of combustion, the main reason for pressure dependence of the burning rate is not an increase in the heat influx from the gas reaction zone with increase of pressure, as is usually assumed, but an increase in the temperature T_g resulting from reduced expansion of the gases from the primary reactions. An increase in this heat influx may have some influence on the dependence in question, but it cannot be its cause. The exothermic process in the condensed phase is independent and controlling, while the combustion process in the gas phase can exist only to the extent that the former exists, in spite of the greater heat release. Thus, for example, at low pressure, there may be no heat release in the secondary reaction zone at all, but a process of propagation of combustion will exist if the temperature difference $T_g - T_i$ is sufficient to bring the next elementary layer to the ignition point, which can always be achieved by increasing T_g, as was done in [3]. This easily explains the well-known, but little understood fact that there is no definite relation between the caloricity of a substance, its maximum combustion temperature and the burning rate.

It may be seen from the figure that at pressures of the order of a hundred or a thousand atmospheres, the burning rate does not depend, or depends only slightly on the pressure (curves 1 and 2), and these pressures are lower, the lower the mechanical strength of the material. This form of dependence of burning rate on pressure was observed experimentally in [6]. The authors of [6] consider that as the pressure increases, there is a change in the law of dependence of burning rate on pressure, and they have constructed a curve for this dependence in three sections with different laws. This assertion is erroneous; the law remains the same throughout the whole range of pressures and is expressed by the formulas obtained in the present paper. Exceptions are possible, however, and their causes have been indicated above.

From our present point of view, reference [2] contains an incorrect statement. It is said that ν may lie in the range $0 \leq \nu \leq 0.38$, whereas, in fact, it may only lie in the range $0.25 \leq \nu \leq 0.38$. Moreover, it is said that the burning rate can not depend on the pressure when the heat-transfer agents in the primary reaction products are condensed particles. This is true, but is linked with the condition $\nu = 0$, which is false (in reality, one must have $C_g = 0$). Moreover, it was not known that the burning rate may not depend on pressure owing to the low mechanical strength of the material.

The results obtained here remove the one valid objection to the relaxation theory advanced in [7]. The remaining objections are incorrect and do not give cause for further refinement of the theory.

NOTATION

p_q, p_g, and p_p — pressure inside the material, at the interface between the condensed and gas phases, and pressure difference; T_{e0} and T_{e1} — temperatures at external pressures p_0 and p_1, respectively. σ_p — ultimate strength of the material when tested to destruction; S_1 and S_2 — cross-sectional area of specimen and total cross-sectional area of fuel particles in section S_1; C_g — heat capacity of gases after expansion; C_m and T_{g0}^* — average heat capacity and average temperature of all primary reaction products; T_{g0} — temperature of gases after expansion.

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