MULTIZONE COMBUSTION OF CONDENSED SYSTEMS

A. G. Merzhanov, É. N. Rumanov, and B. I. Khaikin

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In the general case the combustion of condensed systems is of a stage-wise character and the combustion front is multizone [1, 2]. Following the investigation of two-zone models [3-5] it became clear that, during multizone combustion, one of the zones of heat evolution is the controlling zone. The velocity of the front is equal to the velocity of the controlling zone; however, with a change in the parameters of the system, there is the possibility of a transition of the controlling role from one zone to another, as well as of the coalescence and splitting of zones. This paper discusses a generalization of the two-zone problem which makes it possible to go over to the analysis of a complex, multizone front and shows that, for a front with two reactions (in the condensed phase and in the gas) and with dispersion, there are in all three possible arrangements of the zones of heat evolution (two three-zone variants and one two-zone variant). All possible types of dependence of the combustion rate on the depth of the dispersion are found.

Combustion Model. We shall consider a model of a multizone front which, obviously, describes the principal special characteristics of the combustion of many condensed systems. Let a reaction take place in the c-phase (the condensed phase) with a heat effect Q_1 and an activation energy E_1 (pre-exponent k_1). The gaseous products enter the second reaction with the parameters Q_2, E_2, k_2. As a result of dispersion, a part η_d of the condensed substance breaks away from the hot surface. Since the density of the heat evolution for the first reaction falls sharply with dispersion, it terminates in the c-phase (in the fumes) at a certain distance from the surface at a higher temperature. Therefore, the second reaction also may take place in two stages. At the same time, different variants of the coalescence of these zones are possible.

The investigation of the above-described complex front was based essentially on results which refer to two-zone models, which have been previously calculated numerically and analyzed [3-5]. We shall evaluate here the problem of two-zone combustion from the point of view of the mechanism of the restructuring of the front.

Control, Coalescence, and Breakaway Conditions. The exponential dependence of the rate of the chemical processes on the temperature makes it possible to divide a front with a single reaction into two zones, i.e., heat-evolution and heating zones. However, for the same reason, in a front with several reactions, several heat-evolution zones are possible. Each zone occupies a narrow temperature interval ($\sim RT_i^2/E_i$, where T_i is the temperature in the i-th zone, and E_i is the activation energy of the i-th reaction), in comparison with the total change over the front. At a higher temperature, the reaction does not proceed, since the starting substances (for this reaction) have been expended, while at a lower temperature the rate of the reaction is negligibly slow.

In the intervals between the heat-evolution zones, the heat flux is connected with the temperature linearly (Michelson's law), while in the zones themselves it varies sharply. The jump in the heat flux in the i-th reaction zone is equal to $Q_i U$, where Q_i is the heat of the reaction, and U is the mass flux (the mass combustion rate). The large curvature of the temperature profile permits an approximate integration of the heat-conductivity equation in the reaction zone, with the convective term dropped [6]. We write the integral in the form

$$(Q_i U + q_i)^2 - q_i^2 = (Q_i \rho_i)^2 a_i k_i e^{-E_i/RT_i} F_i$$
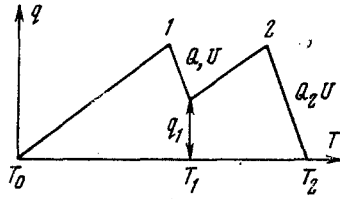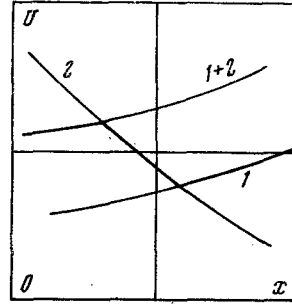
(1)

Fig. 1   Fig. 2

Here q_i is the heat flux flowing into the reaction zone; T_i is the temperature in the zone; ρ_i is the density; a_i is the thermal diffusivity. The dimensionless quantity F_i, which takes on small values, was introduced by D. A. Frank-Kamenetskii [7] in a description of single-zone combustion. The smallness of F_i is connected with the smallness of the parameter $\gamma_i = (RT_i^2/E_i) (c/Q_i)$. Accurate determination of all values of F_i is possible only with the solution (for the whole front) of a system made up of the thermal-conductivity equations and equations describing the (multicomponent) diffusion of the starting substances, the products, and the intermediate products. For a single-zone front in a gas with a reaction of the n-th order

$$F = 2n!\gamma^{n+1}$$

Since the temperature dependence of F_i is of an exponential character and, consequently, weak compared with the Arrhenius factor $\exp(-E_i/RT_i)$, a qualitative investigation of the front can be made without taking changes in these quantities into account.

The unknowns in (1) are U, q_i, and T_i. For N reaction zones we have N equalities of the type of (1) and N relationships of the type

$$(Q_i U + q_i) - q_{i-1} = Uc(T_i - T_{i-1}) \tag{2}$$

which determine the changes in the heat flux in the intervals between the heat-evolution zones. Together with the condition $q_N = 0$, they completely determine the structure of the front, i.e., U and all the values of q_i and T_i. It can be shown that, to calculate the reaction rate U, relationships (1) for the last zone are sufficient, since $q_N = 0$, while T_N is obviously the combustion temperature. Under these circumstances, the other (low-temperature) zones have no effect on the combustion rate, a fact already noted by Ya. B. Zel'dovich in 1942 [8]. Nevertheless, a detailed examination has not yet made it possible to determine either the actual structure of the front or the combustion rate.

The dependence of the heat flux q on the temperature T for a two-zone front is shown on Fig. 1. The temperature of the first zone T_1, in distinction from T_2 (the combustion temperature), cannot be found by a thermodynamic calculation. With a given value of U, the value of T_1, which determines the rate of the first reaction, must be such that the rates of both reactions will be equal, which is required under steady-state conditions. The fully developed distance l between the zones is thus given by a determined value of the temperature T_1 and of the uniquely related value of the flux q_1. These values are determined using equations of the type (1), (2). With an increase in the inter-zone distance l, the temperature, and of course also the rate of the first zone, decrease, and the zones again approach one another. With a decrease in l, a rise in the value of T_1 accelerates the first zone and re-establishes the previous value of the distance, so that the described structure of the front is stable. The combustion rate is the "normal rate" of the second (controlling) zone

$$U_2(T_2) = \rho_2 (a_2 k_2 e^{-E_2/RT_2} F_2)^{1/2}, \qquad T_2 = T_0 + \frac{Q_1 + Q_2}{c} \tag{3}$$

The first zone also must move at the same rate. Its "normal rate" due to the "inherent" heat effect is

$$U_1(T_{10}) = \rho_1 (a_1 k_1 e^{-E_1/RT_{10}} F_1)^{1/2}, \qquad T_{10} = T_0 + Q_1/c \tag{4}$$

If $U_1(T_{10}) < U_2(T_2)$, the second zone heats the first up to a temperature $T_1 > T_{10}$, by the same token increasing its own rate up to $U_2(T_2)$. However, at $U_1(T_{10}) > U_2(T_2)$, control of the first zone is no longer
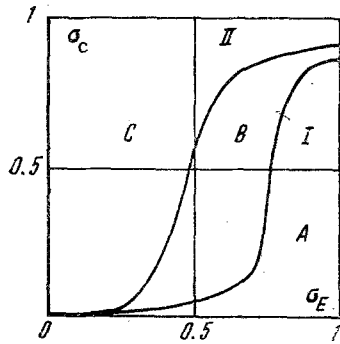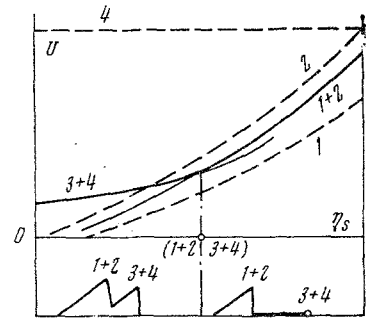
Fig. 3

Fig. 4

possible; it "breaks away" from the second zone and becomes the controlling zone. The combustion rate $U = U_1(T_{10})$. Since this value is greater than $U_2(T_2)$, the second reaction proceeds under autoignition conditions [9, 10].

On the other hand, the temperature T_1 cannot be greater than T_2 and, if the quantity

$$U_1(T_2) = \rho_2 \left(a_2 k_1 e^{-E_1/RT_2} F_{12} \right)^{1/2} \tag{5}$$

is found to be less than $U_2(T_2)$, both zones come together, and the velocity of a single-zone front is equal to $U_1(T_2)$ [4].

Thus, along with "control" conditions (shown on Fig. 1), in which the second zone is actually the controlling zone (high-temperature), there is also the possiblity of "breakaway " conditions (with a controlling first zone) and "coalescence," when the two-zone front degenerates into a single-zone front. Which of these sets of conditions must exist with given values of the parameters of the system can be determined by comparing the normal rates (3)-(5) [4]. Here it must be borne in mind that it is always true that $U_1(T_2) > U_1(T_{10})$, since $T_2 > T_{10}$. Therefore, on the curve illustrating the dependence of the normal rates on some parameter x (for example, such a curve is shown on Fig. 2) the lines for $U_1(T_{10})$ and $U_1(T_2)$ (lines 1 and 1 + 2 on Fig. 2, correspondingly) do not intersect and, at all values of x, 1 + 2 lies above 1.

A change in conditions corresponds to the intersection of these lines by the line 2, illustrating the dependence $U_2(T_2, x)$. Its intersection with the upper line 1 + 2 corresponds to a transition from control conditions to coalescence conditions and the reverse ($2 \longleftrightarrow 1 + 2$), when the combustion rate U coincides with the lesser of the two normal rates, $U_2(T_2)$ and $U_1(T_2)$. With the intersection of line 2 and the lower line 1, U coincides with the greater of the two values $U_2(T_2)$ and $U_1(T_{10})$ (a transition between the sets of conditions $2 \longleftrightarrow 1$, i.e., control—breakaway). Therefore, the controlling zone is always the zone which has an average normal rate. This rule was established in [4] in an analysis of the results of a numerical integration of the two-stage process.

Variants of the Zone Structure. Passing on to an investigation of the model of the multizone combustion of condensed systems described at the start of the article, we note that, in distinction from the other parameters, the depth of the dispersion η_d is not a given quantity, but must itself be determined by a solution of the complete problem including an analysis of the physicochemical processes in the c-phase,which bring about the dispersion. Such a solution for a solid porous substance is briefly described in [3]. With an increase in the pressure, η_d decreases. An analogous behavior of η_d can be postulated also in other cases, although at the present time no overall investigation of the dispersion exists. Eliminating the dispersion mechanism from the problem by the introduction of η_d, we can isolate the effects connected with the multizone character of the front. In what follows we shall use the quantity $\eta_s = 1 - \eta_d$, which rises with a rise in the pressure.

As has been said above, four heat-evolution zones formally arise in the model under consideration.

1) Reaction in a fixed bed of the c-phase (at the surface of a hot sample); the heat effect is $Q_1 \eta_s$; the kinetic parameters are k_1, E_1. The temperature of the surface is T_1.

2. Reaction in the gas — product zone 1. The parameters are $Q_2 \eta_s$, k_2, E_2. The temperature in the zone is T_2.
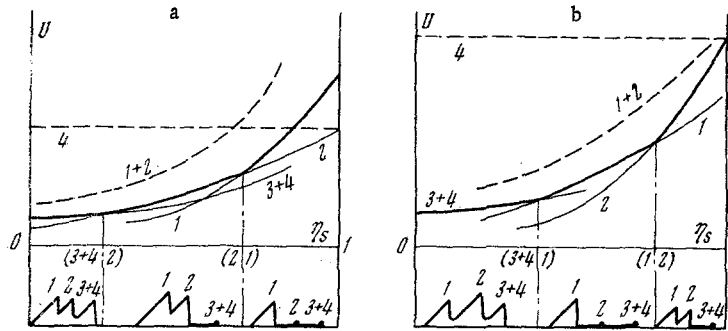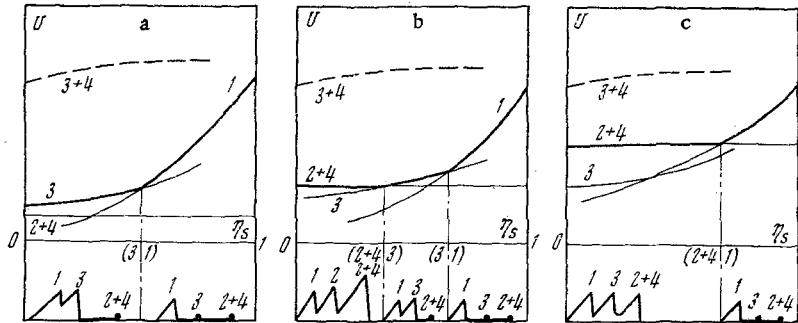
Fig. 5

Fig. 6

3. Reaction in the zone consisting of the fumes and particles of the c-phase torn away from the surface (dispersion). The parameters are $Q_1(1-\eta_s)$, k_1, E_1, T_3. Zones 1 and 2 are necessarily separated in space. The density of the heat evolution in zone 3 (the disperse phase) is approximately ρ/ρ_s times less than in zone 1 (ρ and ρ_s are the densities of the gas and of the condensed substance). In order that both zones can move at an identical rate, T_3 must exceed T_1 by a determined finite value.

4. Reaction in the gas — product zone 3. The parameters are $Q_2(1-\eta_s)$, k_2, E_2, $T_4 = T_0 + (Q_1 + Q_2)/c$.

So long as the temperature T_2 is lower than T_4, zones 2 and 4 cannot move at an identical rate. Therefore, these zones are either merged into the zone 2+4, or zone 4 merges with zone 3 (3+4). As a result, in all, three variants of the arrangement of the heat-evolution zones over the front are possible:

$$A - 1 + 2,\ 3 + 4$$
$$B - 1,\ 2,\ 3 + 4$$
$$C - 1,\ 3,\ 2 + 4$$

Analogously to [4], we introduce the quantities

$$\sigma_E = E_1/(E_1 + E_2), \qquad \sigma_c = k_1 F_1/(k_1 F_1 + k_2 F_2) \tag{6}$$

As is shown on Fig. 3, each of the three variants of the arrangement of the reaction zones corresponds to a determined region of values of $\sigma_c \sigma_E$. Line I, separating regions A and B, is given by the equation

$$(1/\sigma_c) - 1 = (\rho_s \lambda_s/\rho\lambda) \exp\{(E_1/RT_2)[(1/\sigma_E) - 2]\} \tag{7}$$

(λ_s and λ are the thermal conductivity of the c-phase and the gas), while line II, separating B and C, is given by the equation

$$(1/\sigma_c) - 1 = \exp\{(E_1/RT_4)[(1/\sigma_E) - 2]\} \tag{8}$$

Equations (7) and (8) express the conditions for the coalescence of zones 1, 2 and 3, 4, respectively (compare the condition for coalescence in a two-zone front). Below its limit the lines of the zone are merged, while above it they are separated spatially.

The position of line I depends not only on the kinetic parameters, but also on η_s. However, with a change in η_s, the topology of Fig. 3 does not change; lines I and II do not intersect (anywhere except at the
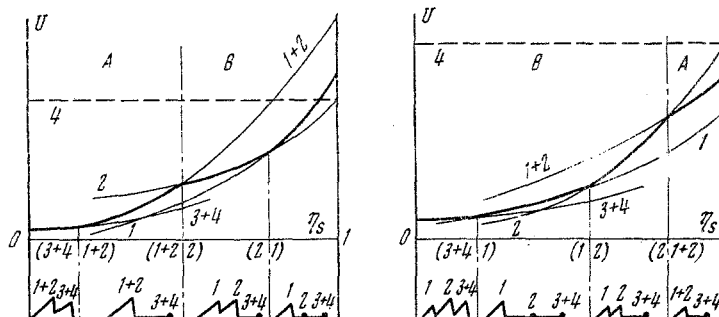
Fig. 7

origin of coordinates). With their intersection, there would arise a region with the arrangement of the zones 1+2, 3, 4. Such an arrangement is impossible; the rate of zone 1+2 is less than the rate of zone 2 which, in turn, is less than the rate of zone 4.

Dependence of the Combustion Rate on η_S. After the arrangement of the heat-evolution zones in the front has been clarified, we can determine $U(\eta_S)$ for given values of the kinetic parameters and of the heats of reaction, i.e., we can find the critical values of $\eta_S = (m/n)$ corresponding to different transitions (between sets of conditions under which the controlling zones are the m-th and the n-th zones, respectively) of the control—breakaway type. For the three variants of the front which are possible in the model under consideration, all the types of dependence of the combustion rate U on η_S are shown on Figs. 4-6.

The method used to plot these dependences is clear from the figures themselves. Line $U(\eta_S)$ is made up of segments of the lines of the normal rates. (On Figs. 4-7 these rates are illustrated by the thin solid lines. Sometimes, for purposes of orientation, the dotted lines show also the normal rates for the zones existing in the given variant of the front.) The expressions for the normal rates of the various zones are obtained by the obvious use of formulas (3)-(5). For each set of conditions, there is shown on the lower part of the figure the distribution of the heat flux q(T) over the front, in accordance with type of Fig. 1; the points indicate the presence of heat-evolution zones under conditions of auto-ignition.

The plot on Fig. 4 was constructed for variant A of the structure of the front (region A of values of $\sigma_C \sigma_E$ on Fig. 3); line 1 is $U_1(\eta_S)$; line 1+2 is $U_{1+2}(\eta_S)$, etc. The rate of the gas reaction is great and it takes place immediately after the formation of the gaseous products during the reaction in the c-phase, so that zone 2 is merged with zone 1, and zone 4 with zone 3 [see the diagrams of q(T) in the lower part of the figure]. With $\eta_S < (1+2 \mid 3+4)$, the controlling zone is zone 3+4, while, at large values of η_S, the controlling zone is zone 1+2. Line 2 must everywhere lie above line 1+2; with $U_2 < U_{1+2}$, zone 2 would appear in the front (variant B). With $\eta_S = 1$, $U_2 = U_4$.

In region C of values of $\sigma_C \sigma_E$, the rate of the reaction in the c-phase is great in comparison with the gas phase. Zones 1 and 3 are located in the front ahead of zone 2+4. Depending on the rate of this latter, as shown on Fig. 6 it either (6a) goes over to autoignition conditions or (6b, c), in some region of η_S, becomes controlling. When the value of U_4 is greater than the maximal value of U_1 (with $\eta_S = 1$), zone 2+4 is controlling at all values of η_S, which corresponds to the model of A. F. Belyaev and Ya. B. Zel'dovich [8].

While variants of the front A and C are at least evident as limiting cases, and the method used in the present work permits determining only the region of their existence and indicating the abrupt character of the transitions between sets of conditions, the intermediate variant of the front, B, is detected only as the result of analysis. In this variant, a gas flame (zone 2) precedes combustion of the fumes (zone 3+4). The corresponding combustion conditions are shown on Fig. 5. Line 4 lies above line 3+4; with $U_4 < U_{3+4}$, zone 4 would appear (variant of the front C). While (5a) the temperature dependence of the reaction in the c-phase is stronger than in the gas-phase reaction, $\sigma_E > 0.5$, conditions 2 exist in the "average" region of values of η_S between conditions 3+4 and 1. With $\sigma_E < 0.5$, with an increase in the value of η_S, there follow conditions 3+4, 1 and 2 (5b).

As has been pointed out above, the position of line 1 on Fig. 3 depends on η_S. Therefore, with some values of η_S, certain points of $\sigma_C \sigma_E$ may lie in the region A, and, with other values, in region B. In this case, at a certain value $\eta_S = \eta_*$, there is a restructuring of the heat-evolution zones in the front, as shown on Fig. 7. With such a restructuring (a transition of the type control—coalescence), zone 2 (or 1+2), having

a lower rate, becomes controlling. With $\sigma_E > 0.5$ (Fig. 7a), zone 2 appears in the region $\eta_* < \eta_s < 1$, while with $\sigma_E < 0.5$ (Fig. 7b), it appears in the region $0 < \eta_s < \eta_*$ [η_* is $(2|1+2)$ or $(1+2|2)$].

It has been assumed throughout that both reactions are exothermic and that they have comparable heats of reaction. If the reaction in the c-phase has a small heat effect or is endothermic, out of the combustion conditions described, there remain only conditions of the control type (from the side of the gas reaction) and coalescence conditions. If the gas reaction is endothermic, the only possible conditions are variant A (coalescence) and the conditions of variant B, under which zone 3 +4 is controlled by zone 2 (see Fig. 5).

LITERATURE CITED

1. K. K. Andreev, Thermal Decomposition and Combustion of Explosives [in Russian], Izd. Nauka, Moscow (1966).
2. N. N. Bakhman and A. F. Belyaev, Combustion of Heterogeneous Condensed Systems [in Russian], Izd. Nauka, Moscow (1967).
3. B. I. Khaikin and A. G. Merzhanov, "The combustion of substances with a solid reaction layer," Dokl. Akad. Nauk SSSR, 173, No. 6 (1967).
4. B. I. Khaikin A. K. Filonenko, and S. I. Khudyaev, "Propagation of a flame during the course of two consecutive reactions in a gas," Fiz. Goreniya i Vzryva, 4, No. 4 (1968).
5. A. K. Filonenko, B. I. Khaikin, and S. I. Khudyaev, "The stage-wise combustion of nonvolatile condensed substances," Second All-Union Symposium on Combustion and Explosion, Erevan, 1969. Authors' summaries of papers, Chernogolovka (1969), p. 47.
6. Ya. B. Zel'dovich and D. A. Frank-Kamenetskii, "The theory of the thermal propagation of a flame," Zh. Fiz. Khim., 12, No. 1 (1938).
7. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics [in Russian], Izd. Nauka, Moscow (1967).
8. Ya. B. Zel'dovich, "The theory of the combustion of powders and explosives," Zh. Éksp. i Teor Fiz., 12, Nos. 11, 12 (1942).
9. R. M. Zaidel' and Ya. B. Zel'dovich, "Possible conditions of steady-state combustion," Zh. Prikl. Mat. i Tekh. Fiz., No. 4 (1962).
10. A. G. Merzhanov and A. K. Filonenko, "The thermal auto-ignition of a homogeneous gas mixture in a flow," Dokl. Akad. Nauk SSSR, 152, No. 1 (1963).