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Abstract

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ON THE RELATION BETWEEN SELF-IGNITION AND THE RATES OF LAMINAR AND TURBULENT COMBUSTION OF PARAFFIN HYDROCARBONS

(Presented by Academician V. N. Kondrat̕ ev, January 23, 1961)

In the new model of a turbulent flame, the rate of turbulent combustion is determined directly by the ignition delay upon mixing of fresh and burned gases (^{1}). In this connection, comparison of the rates of turbulent combustion with the known kinetic characteristics of self-ignition is of considerable interest, for example for methane and for propane–butane, for which a different dependence of the self-ignition delay at a given temperature on the composition of the hydrocarbon-air mixture was noted (^{2}). At temperatures of 700–750°, the self-ignition delay for methane decreases as the mixture becomes leaner, whereas for propane and butane it decreases as the mixture is enriched with fuel (for more detail see (^{3}), p. 73). Unfortunately, this fundamentally important difference, discovered 30 years ago, in the high-temperature self-ignition of methane and of the higher hydrocarbons of the paraffin series has not been investigated in greater detail.

In the present work an attempt is made to compare the change in the laminar and turbulent burning velocities of air mixtures of methane, propane, and butane with the change in self-ignition delay as a function of mixture composition, using the constant-volume bomb method. Let us recall that the procedure for determining the turbulent burning velocity under closed-volume conditions includes photographic recording of the propagation of a laminar flame in order to measure the volume of laminar flame that gives an equivalent pressure rise from combustion (for a description of the method, see (^{4})). The laminar burning velocity is determined from the recorded visible flame velocity $u_v = dr/dt$ from the equality $u_r = u_v/\varepsilon$. Here the expansion ratio ε may be determined as $\varepsilon \simeq T_{\text{ad}}/T_0$, replacing the actual flame temperature T_ϕ by the calculated adiabatic one and neglecting the change in the number of moles during combustion, n/n_0.

Since in hydrocarbon flames $n/n_0 > 1$, while $T_\phi < T_{\text{ad}}$, the error allowed in

Figure 1

Figure 1: Figure 1

replacing $\varepsilon = \frac{T_\phi}{T_0}\frac{n}{n_0}$ by $\varepsilon \simeq \frac{T_{\text{ad}}}{T_0}$ is smoothed out and does not exceed the limits of measurement error. Comparison of the course of the normal burning velocities u_n with mixture composition for methane and for the hydrocarbons C_3 and C_4 reveals a sharp difference in the region of rich mixtures: for methane there are substantially lower velocities and a lower upper limit of flame propagation than for propane and butane (Fig. 1). Since, for all three flames considered, the combustion temperatures T_g are very close, while the transport coefficients (thermal conductivity and diffusion) for rich methane mixtures are higher than for propane and butane, this difference in normal flame velocities can be attributed only to the difference in reaction rates in the flame—to a considerably higher reaction rate for propane and butane as compared with methane.

An even sharper difference for the same two types of fuels is found when the mixture composition is changed for the turbulent burning velocity u_t. As is seen from Fig. 2, at constant absolute intensity of turbulent-

···velocity $u'_\Sigma = 4.2$ m/sec*, in the region of rich mixtures the values of u_t and the propagation limit for propane and butane are considerably higher than for methane. Conversely, in the region of lean mixtures, although to a lesser degree, there is a noticeable increase in u_t for methane as compared with propane and butane. Correspondingly, the maximum turbulent velocity for propane and butane is shifted appreciably into the region of rich mixtures (about 120% excess fuel) as compared with methane, for which the maximum lies near the stoichiometric composition. An analogous difference in the position of the maximum turbulent velocities for methane-air and butane-air mixtures was also noted in ([5]).

Fig. 1. a —methane, b —propane, v —butane

The observed parallelism in the relationship between the velocities of laminar and turbulent flames for two types of hydrocarbons in different ranges of mixture compositions cannot, however, be regarded as evidence that turbulent combustion itself takes place in laminar flames, i.e., as indirect proof of the surface-laminar model. The groundlessness of such a conclusion is easy to see by comparing the turbulent combustion velocities when the normal flame velocity is varied in Fig. 3. In the range of lean mixtures, each value of the normal velocity corresponds to different turbulent combustion velocities: a higher one for methane and a lower one for propane and butane. We note that, in accordance with Fig. 1, for this range of compositions, close values of the combustion temperatures correspond to a given value of the normal velocity. Thus, for lean mixtures the turbulent combustion velocities for methane are higher than the velocities for propane and butane at identical values of u_n and T_g.

Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

Fig. 2. For point designations see Fig. 1.
$u'_\Sigma = 4.2$ m/sec

In the range of rich mixtures, each value of the normal flame velocity corresponds to still more different values of u_t: lower for methane and higher for propane and butane. In this case, a given value of the normal velocity corresponds to a higher (by approximately 100–150°) combustion temperature for methane than for propane (see Fig. 1). Thus, in the range of rich mixtures, for a given value of the normal velocity, the turbulent combustion velocity of methane proves to be substantially lower than that of propane and butane, despite the higher temperature for methane.

It remains, therefore, to assume that there exist certain kinetic differences for methane and for the higher alkanes, which manifest themselves also in facil—

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[*] For the definition of u'_Σ, see (4).

of high-temperature self-ignition, and in the acceleration of the propagation of laminar and turbulent flames—for methane with depletion, and for C_3 and C_4 with enrichment of the mixture.

These kinetic differences, in any case, cannot be connected with the stage of chain initiation, since there is no basis for assuming any significant difference in the rate of the reaction of formation of active centers for methane and the higher alkanes. Moreover, this stage, which limits the high-temperature self-ignition of hydrocarbons (see [3], p. 64 and following), is eliminated in the reactions of laminar and turbulent flames: in the former, owing to diffusion of active centers from the zone of their maximum concentration; in the latter, as a result of turbulent mixing of the burning and fresh gases.

Fig. 3. For the notation of the points see Fig. 1. 1 $-u'_\Sigma \sim 5.6$ m/sec; 2 $-$ $u'_\Sigma \sim 4.2$ m/sec.

Nor can the observed influence of mixture composition on self-ignition and on flame velocities be attributed to the chain-branching stage. The mechanism of chain branching in high-temperature self-ignition of hydrocarbons proceeds through degenerate branching with aldehydes as an intermediate active product. At the same time, from general considerations and from experimental data it follows that degenerate branching does not participate in the development of reactions in a flame. Both in laminar and in turbulent flames, of hydrogen as well as of hydrocarbons, branching apparently occurs through one and the same reaction:

$$H + O_2 \to HO + O,$$

as noted in [3] (p. 188 and following) and in [1].

It remains to assume that the difference in the self-ignition characteristics for methane and the C_3 and C_4 alkanes, and in the velocities of laminar and turbulent flames as a function of mixture composition, is determined by the difference, for these two types of hydrocarbons, in the chain-propagation stage; i.e., that it is precisely the rate of reaction in this stage that increases with depletion of the mixture for methane and with enrichment of the mixture for the higher alkanes. It therefore becomes of special interest to study the mechanism of this stage both in the process of high-temperature self-ignition and in the development of the reaction in flames. It also follows from the results presented that in laminar and turbulent flames the reaction develops under analogous conditions of mixing of the burning and fresh gases and therefore by a similar mechanism, but with a fundamentally different mechanism of reaction propagation—in laminar flames through continuous molecular transfer of heat and matter, and in turbulent flames through turbulent mixing.

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