Flame Spread over Liquid Fuel Films on Metallic Substrates

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New experimental studies of parametric dependences of the flame spread velocity and limits for liquid fuel films on metallic substrates confirmed the main features of the physical model proposed previously. For thermally thin layered systems "fuel–substrate," a steady-state regime of flame spread is possible. It is shown that the flame velocity depends on the effective thermal diffusivity of the layer system, and its value is determined mainly by the volumetric heat capacities of the components of the system and, to a lesser degree, by their thermal conductivities. The mechanism of flame spread includes a series of interrelated elementary processes: heat conduction over the substrate from the combustion zone to the preflame zone, heating and evaporation of the fuel by the substrate, formation of a combustible mixture, and heating of the metallic substrate by the combustion products. The flame edge is located at the liquid surface, where the temperature corresponds to the formation of a stoichiometric mixture under equilibrium conditions. The liquid fuel is completely evaporated from the substrate at temperatures below the boiling point.

Flame spread over the surface of a combustible material in an oxidizing atmosphere is one of the most often encountered combustion processes. A flame is capable of spreading over the surface of wood metallic articles, combustible fluids, fabrics, plastics, and other materials. The main applications of studies of this phenomenon are related to modeling of flame spread over various structural members [1, 2].

Flame spread over the surface of materials has been extensively studied both theoretically and experimentally [1, 3–5]. Data on the determining parameters, flame velocity and structure, and spread limits have been obtained, and mathematical models have been developed [5–10]. Although the mechanism of the process is generally clear, many problems still remain to be solved. Among them is the role of elementary processes in the flame spread mechanism, and in particular, the effects of the thermophysical parameters of fuels and substrates. Studies of this problem involve difficulties for several reasons: the multi-parameter nature of the problem, the small ranges of the parameters varied due to the specificity

of the objects under investigation, and the complex types of physicochemical transformations in flames, such as pyrolysis, gasification, melting, and evaporation of fuel.

Korzhavin et al. [11] develops a new approach that allows one to eliminate some of the indicated limitations. This approach uses a thermally thin, binary, layered system "a liquid fuel on a metallic substrate." In the present paper, the range of objects of investigation and determining parameters are extended for further development of the physical model.

EXPERIMENTAL TECHNIQUE

The system "a liquid fuel on a metallic substrate" practically has not been studied, although it is of interest in many respects. Below, it will be shown that the flame velocities in such systems are an order of magnitude higher than the velocities of flames spreading over paper, polymer, and wood materials. The system allows one to separately study the effects of the properties of the fuel and substrate on the flame velocity, structure, and other characteristics. This system is easy to analyze because of

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the well-determined physicochemical and thermodynamic properties of the gas phase, liquid fuel, and substrate.

In the present paper, as the fuel we used films of ethanol, isopropanol (thickness $h_f = 8$ μm), n-butanol ($h_f = 8$ μm), and n-undecane ($h_f = 7$ μm), and the substrates were steel, brass, niobium, molybdenum, aluminum, and copper foils with thickness $h_s = 7$–120 μm.

In a thermally thin system, the effective thermophysical parameters and the parameters of the components of the system play a leading role because of the fast heat exchange between the layers. Thus, the thermal diffusivity of the system is defined [6] by

$$\varkappa_* = \frac{\lambda_f h_f + \lambda_s h_s}{c_f \rho_f h_f + c_s \rho_s h_s}, \qquad (1)$$

where λ is the thermal conductivity, c is the specific heat, and ρ is the density: the subscripts "f" and "s" refer to the liquid fuel and the solid substrate, respectively.

In a thermally thin system, the heat-transfer rate across the fuel-layer thickness and the thickness of the substrate should be higher than the heat-transfer rate along the substrate. In the examined system, the characteristic times for heat transfer along the substrate and thermal relaxation in the fuel layer and in the solid substrate are in the ratio $(10^{-1}$–$10^{-2}) : 10^{-3} : (10^{-4}$–$10^{-6})$ sec [11]. Hence, the chosen system is truly thermally thin.

In the preparation of the samples, the thickness of the fuel film on the substrate was checked by the gravimetric method, which ensured an accuracy of 2%. The change in the film thickness with time due to gravity was evaluated by weighing the upper and lower parts of the foil (after cutting it into two parts) at a time interval equal to the characteristic time of the experiment (180 sec). In the case of n-undecane, film flow leads to a change of 20% in the film thickness. Measurements of the loss of mass due to evaporation show that evaporation has a significant effect on the alcohol film thickness even at room temperature. Therefore, studies with these substances were performed over a period of time during which the film thickness changed only slightly, or at lower initial temperatures.

A diagram of the experiment is shown in Fig. 1. A metal foil strip more than 5 mm wide and 0.2–2 m long was fixed vertically. In this case, the velocity does not depend on the width, and a 40-mm foil was mainly used. A thermocouple junction (copper–Constantan) was located against the horizontal slot of the photomultiplier. The copper element of the thermocouple was the foil strip itself. The reliability
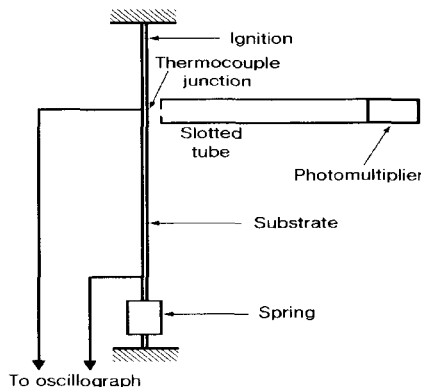

Fig. 1. Diagram of experiment.

of the junction was provided for by spring contraction. This setup allowed one to refer the edge of the flame front to the temperature profile of the foil with an accuracy of 0.8 mm.

Besides the flame luminosity and the substrate temperature, we measured the velocity of flame spread over the film surface by direct photorecording and schlieren visualization. Optical observations were performed in a direction perpendicular to the plane and along the surface of the sample. In some experiments, a fuel film was placed on both sides of the foil and a two-sided flame was studied.

EXPERIMENTAL RESULTS

Flame Structure. The experiments showed that for all examined samples with flame spreading downward, a certain unsteady period is followed by a steady-state regime. The flame velocity is constant (with an accuracy of up 2%) on samples as long as 2 m. This means that the combustion-wave structure is a time-invariable aggregation of phase, temperature, concentration, and other profiles. It is possible to distinguish the following characteristic elements of the flame (Fig. 2): a flame front with an edge, a roller of the liquid fuel ahead of the flame edge, a wedge-shaped liquid area, and fuel "fingers" ahead of the liquid roller. The flame edge is an even straight line perpendicular to the lateral edges of the substrate. Ahead of the edge there is a certain thickening of the liquid film — the roller 10–15 mm long. Ahead of the roller, the flow zone is located with an uneven leading edge in the form of fingers ≈ 50 mm long and ≈ 5–7 mm wide. Under the glow zone behind the flame edge there is the wedge-shaped liquid area 1–10 mm long.
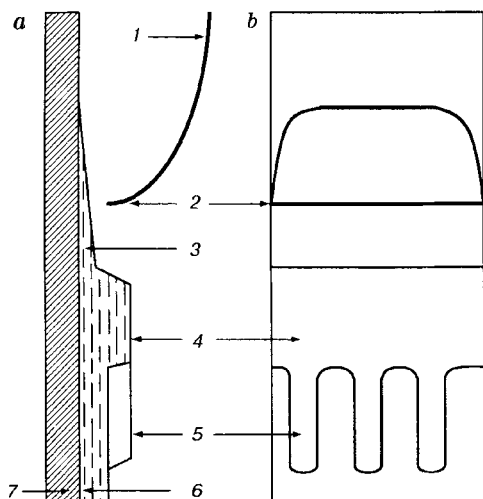
Fig. 2. Qualitative structure of the combustion wave: side view (a) and frontal view (b); 1) flame front; 2) front edge; 3) fuel wedge; 4) roller; 5) fuel "fingers;" 6) fuel film; 7) metallic substrate.
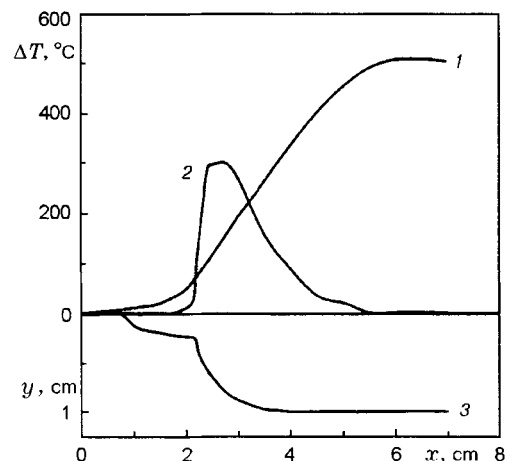

Fig. 3. Combustion-wave structure: 1) substrate temperature; 2) luminous intensity of the flame front (relative units); 3) external boundary of optical nonuniformity; n-undecane–copper system, $h_s = 45\ \mu\mathrm{m}$, and $u = 1.8$ cm/sec; one-sided flame.

Figure 3 gives the distributions of the temperature and luminous intensity of the flame front along the substrate, and the external boundary of the region of optical nonuniformity. Flame glow occurs at the moment when the temperature of the substrate reaches 65°C, which is close to the lower temperature limit for n-undecane (62°C). Side by side, at a distance of 2 mm, the temperature of the substrate reaches the value at which the fuel-vapor pressure corresponds to the stoichiometric concentration. The temperature dependence and the position of the external boundary of optical nonuniformity indicates the presence of a rather extended ($\approx$2 cm) heating zone ahead of the flame edge.

Parametric Dependences. Figure 4 shows dependences of the flame velocity on the thickness of the substrate for one-sided and two-sided flames. It is evident that in both cases, the flame velocity decreases with increase in the thickness of the substrate. This result is in agreement with the data of [5]. At $h_s > 120\ \mu\mathrm{m}$, combustion becomes impossible. It was assumed that if the heat losses from the rear side of the substrate to the ambient medium do not affect the flame velocity, the flame velocity for one-sided combustion (u_1) should be the same as the that for two-sided combustion (u_2) with doubled thickness of the substrate: $u_2(2h_s) = u_1(h_s)$. Figure 4 supports this assumption.

Figure 5 gives dependences of the flame velocity on the initial temperature. It is evident that in the range $T_0 = (-35)$–$(+30)°\mathrm{C}$, the dependences are ap-

proximated by straight lines. With increase in T_0, the flame velocity increases. With decrease in T_0 for n-undecane, conditions are attained under which combustion is impossible, and a limit on T_0 is observed.

The dependence of the flame velocity on the thermophysical properties of the substrate and the system as a whole is of great interest. Figure 6 gives dependences of the flame velocity on the thermal diffusivity of the substrate $\varkappa_s = \lambda_s/c_s\rho_s$ for various values of h_s and $c_s\rho_s h_s + c_f\rho_f h_f = \mathrm{const}$. For thin sub-
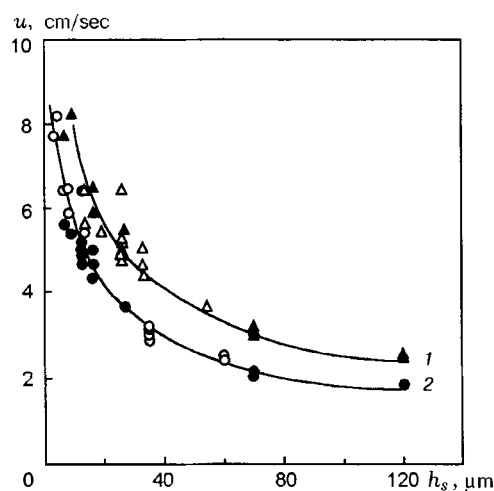

Fig. 4. Curves of $u(h_s)$ for two-sided flame (curve 1) and one-sided flame (curve 2); filled points are test data and open points are data calculated under the assumption of $u_2(2h_s) = u_1(h_s)$; n-butanol–aluminum system.
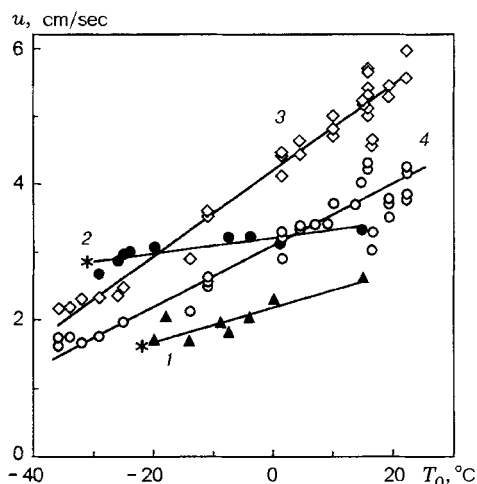
Fig. 5. Curves of $u(T_0)$: 1) n-undecane–copper, h_s = 45 μm, and two-sided flame; 2) n-undecane–aluminum, h_s = 25 μm, and two-sided flame; 3) ethanol–copper, h_s = 45 μm, and two-sided flame, 4) ethanol–copper, h_s = 45 μm, and one-sided flame; points * denote flame-spread limit.

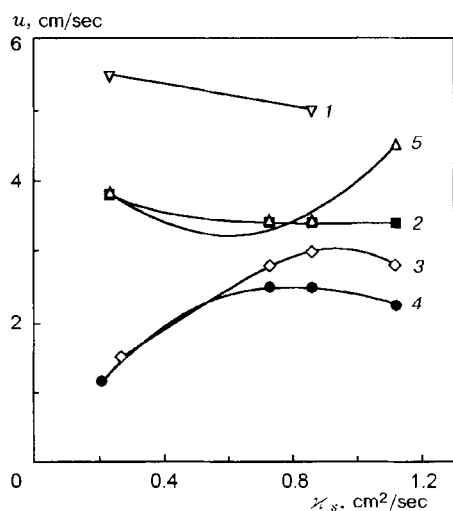**Fig. 6.** Curves of $u(\varkappa_s)$ for h_s = 25 (1), 50 (2), 64 (3), and 100 μm (4); curve 5 refers to $c_s\rho_s h_s + c_f\rho_f h_f$ = const; system: n-butanol on various materials.

strates (25 and 50 μm), the velocity decreases somewhat with increase in $\varkappa_s$. For thick substrates (64 and 100 μm), the velocity increases with increase in $\varkappa_s$ and then begins to decrease. This effect was observed for ethanol, n-butanol, and isopropanol. The ambiguous and nonmonotonic nature of the dependence $u(\varkappa_s)$ is apparently due to the fact that in the thermally thin system studied, the flame characteristics are determined not only by the parameters of the components of the system but also by some integral parameters.
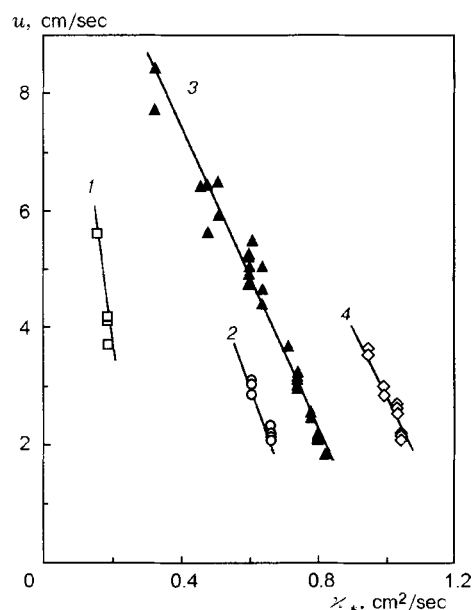

Fig. 7. Curves of $u(\varkappa_*)$ for substrates: Nb with $\varkappa_s$ = 0.235 cm²/sec (1), Mo with $\varkappa_s$ = 0.73 cm²/sec (2), Al with $\varkappa_s$ = 0.86 cm²/sec (3), and Cu with $\varkappa_s$ = 1.12 cm²/sec (4); the fuel is n-butanol; two-sided flame.

Figure 7 shows dependences of the flame velocity on the thermal diffusivity of the system $\varkappa_*$, which is determined by Eq. (1) with variation in the thickness of the substrate h_s. For one fuel and different substrates, the straight lines are shifted with respect to each other depending on the value of $\varkappa_s$. The larger the value of $\varkappa_s$ (for $\varkappa_*$ = const), the higher the straight line is located. For substrates of a particular metal, the flame velocity decreases with increase in $\varkappa_*$.

DISCUSSION OF RESULTS

In systems "a liquid fuel on a metallic substrate," the properties of both the fuel (latent heat of evaporation, boiling point, and reactivity) and the substrate can vary widely. For example, for steel and copper substrates, $\varkappa_s \simeq 0.2$ and $\simeq 1$ cm²/sec, respectively, while for paper and polymer samples, $\varkappa_s \simeq 10^{-3}$ cm²/sec. Therefore, systems with metallic substrates can have broad heating zones. Indeed, for the examined samples, numerical calculations give values $\varkappa_*/u \simeq 0.1$–0.5 cm, which is in agreement with the experiment. For heat conduction over the gas and liquid phases at u = 2–8 cm/sec, similar calculations of the possible heating zones give values $\varkappa_*/u \simeq 10^{-1}$–$10^{-2}$ and 10^{-4} cm, respectively.

These and other data on the thermal-wave structure suggest that the main channel of heat transfer and, hence, the reaction propagation mechanism is heat conduction through the condensed phase. Therefore, one might expect that under steady-state wave conditions, the temperature distribution in the heating zone obeys the equation

$$T - T_0 = (T_* - T_0)\exp(ux/\varkappa_*), \qquad (2)$$

where T_* is the temperature at the point $x = 0$. Indeed, for various fuels, the dependence in the coordinates $\log(T - T_0)$, x is linear up to the point T_*, above which the linearity is violated because of the change in the nature of thermal conditions. Data processing gives the following values of T_*: 72°C (71.4 and 195.8°C) for n-undecane, 43°C (45 and 117°C) for n-butanol, and 42°C (22.1 and 78.5°C) for ethanol. The temperature at which a stoichiometric mixture of fuel vapors with air (T_{st}) forms under equilibrium conditions at atmospheric pressure and the boiling point are given in brackets. These data (except for ethanol) also indicate that the edge of the flame front is above the coordinate of the substrate where the temperature is close to T_{st}.

Considering the longitudinal heat transfer in the direction of flame propagation, it is necessary to note that the thermal conductivity of the foil is much higher than the thermal conductivity of the fuel, and the heat transfer is generally determined by the metal foil. The fuel film makes an additional contribution to the integral heat capacity of the system. Calculations show that $\lambda_f h_f \ll \lambda_s h_s$ but $c_f\rho_f h_f$ and $c_s\rho_s h_s$ are of the same order.

Another aspect of the role of the liquid is its convective motion. There is a motion due to the combustion process itself: an increase in the flame-zone temperature leads to a decrease in the surface tension and viscosity of the liquid fuel. These factors give rise to a liquid flow ahead of the flame front in the direction of temperature gradient (Marangoni effect). As a result, a liquid roller (see Fig. 2) parallel to the flame edge is formed. For the flame moving downward, the directions of the gravitational and thermocapillary flows coincide, and for a flame moving upward, they are opposite. The flow in the roller is apparently vortex and unsteady. The unsteadiness is manifested in the "finger-shaped" stream flow (see Fig. 2). The liquid flow contributes to longitudinal heat transfer over the system. However, this contribution can obviously be neglected since the values of $\varkappa_*$ evaluated from experimental data by Eq. (2) are close to those calculated by Eq. (1).

As regards the dependences $u(\varkappa_s)$ and $u(\varkappa_*)$, attention is drawn to two circumstances. First, the parameter $\varkappa_s$ is not representative for the two-layer thermally thin system considered. Second, both $\varkappa_s$,
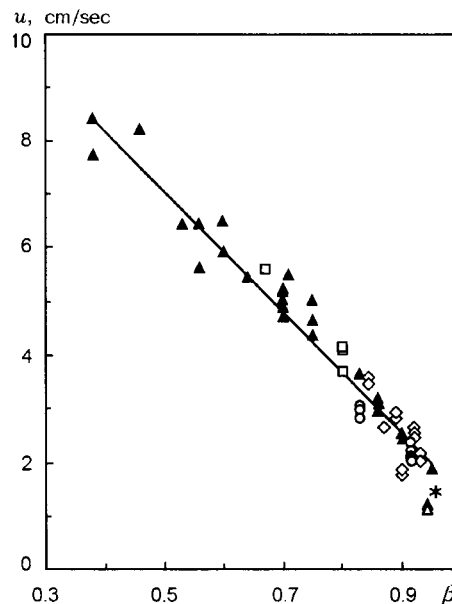

Fig. 8. Curves of $u(\beta)$ for steel (points △), Nb (points □), Mo (points ○), Al (▲), and Cu (◇); point ∗ refers to flame spread limit; the fuel is n-butanol.

and $\varkappa_*$ allow for two processes: heating or cooling of the condensed phase and its capacity to transfer heat from point to point. It is difficult to vary the parameters of these processes separately. Figure 7 illustrates one of such attempts: the dependences $u(\varkappa_*)$ are obtained by changing only h_s for various values of $\varkappa_s$. An increase in h_s increases the contribution of the thermal capacity of the substrate to the thermal capacity of the layered system: $\beta = c_s\rho_s h_s/(c_s\rho_s h_s + c_f\rho_f h_f)$. Naturally, the flame velocity decreases in this case. Since $\lambda_s h_s \gg \lambda_f h_f$, we can write

$$\varkappa_* \simeq \frac{\lambda_s h_s}{c_s\rho_s h_s + c_f\rho_f h_f} = \beta\varkappa_s. \qquad (3)$$

Figure 8 gives dependences of $u(\beta)$ for n-butanol and various substrates. It is evident that all data are well generalized by the dependence $u = 12.75 - 11.34\beta$ with a regression factor of 0.95. The dependence is valid in the region $\beta = 0.4$–0.92. The flame-spread limit corresponds to $\beta = 0.95$. Taking into account Eq. (3), we conclude that for $\beta = \mathrm{const}$, the flame velocity remains constant with change in $\varkappa_*$ due to change in $\varkappa_s$. In other words, without denying the significance of the thermal conductivity of the substrate λ_s in the reaction propagation mechanism in the combustion wave, it must be recognized that its role is concealed behind a stronger factor — the heat capacity of the system. This situation is possible if in the two successive processes — heat transfer from combustion products to the substrate and heat transfer along the substrate to the heating zone and evaporation of the liquid — the limiting process is interphase heat exchange.

CONCLUSIONS

Thus, new experimental data support the physical model of [11] for flame spreading over a liquid fuel film on a substrate.

The complicating factors (Marangoni effect, viscosity variation in the combustion zone, instability of the liquid flow ahead of the flame front, and flameout) require additional investigation.

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