[Contribution from the Lewis Flight Propulsion Laboratory of the National Advisory Committee for Aeronautics]

Flame Propagation. I. The Effect of Initial Temperature on Flame Velocities of Propane–Air Mixtures[1]

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A knowledge of the effect of initial temperature on the flame velocity of fuel–air mixtures is necessary to the understanding of the combustion process. Theories of flame propagation predict that flame velocity will increase with temperature. Passauer[2] found flame velocity to be approximately proportional to the square of the absolute temperature. The data of Johnston[3] on natural gas–air flames show a slight increase in the rate of change of flame velocity with temperature up to 480°. Sachsse[4] reported an increasing rate of change for methane–oxygen flames from 20 to 1000°, although he found a linear relationship between flame velocity and temperature for propane–oxygen flames from 20 to 500°. Broeze[5] reported a linear relationship for propane–air and butane–air flames from 20 to 200°.

The investigation reported here was undertaken as a part of the fundamental combustion research program of the Lewis Flight Propulsion Laboratory. Flame velocity has been determined as a function of composition at various temperatures for propane and air by the Bunsen burner method. An attempt has been made to correlate these data with a thermal and a diffusion theory.

Experimental

The apparatus for this investigation is diagrammatically illustrated in Fig. 1. The fuel was commercial propane with a minimum purity of 95%, the major impurities being ethane and isobutane. Laboratory service air containing approximately 0.3% water by weight was used. Propane and air were metered separately, mixed, preheated, and burned above a vertical tube.

Burner Tubes.—The burner tubes were 108-cm. lengths of brass or stainless steel tubing having inside diameters of 10.2, 15.7 and 22.2 mm. The preheating section was a 108-cm. length of 9.5 mm. i. d. stainless steel tubing connected to the base of the burner tube. Both the preheater and the burner tube were wrapped with resistance wire, the burner being wrapped to prevent heat loss from the heated gases to the burner tube wall. The preheater-burner assembly was insulated with 85% magnesia pipe covering. A 76-mm. diameter collar was soldered to the lip of each burner tube to give a flat horizontal lip above the insulation. A Lucite draft shield was placed around the burner port.

Metering System.—The propane and air flows were metered by two sets of critical flow orifices.[6] Each set consisted of six orifices in parallel in a manifold, giving approximately a 64:1 flow range. A flexible hose was used to connect the downstream end of the orifice in use to the mixing section, the other orifices in the manifold being capped. Ruby bearing-jewels of appropriate sizes were used as the orifice plates. The orifices were calibrated in place with wet test meters. Upstream and downstream pressures were read on mercury manometers. The flow rate through a given orifice was directly proportional to upstream pressure as long as upstream-to-downstream ratio was greater than 2:1.

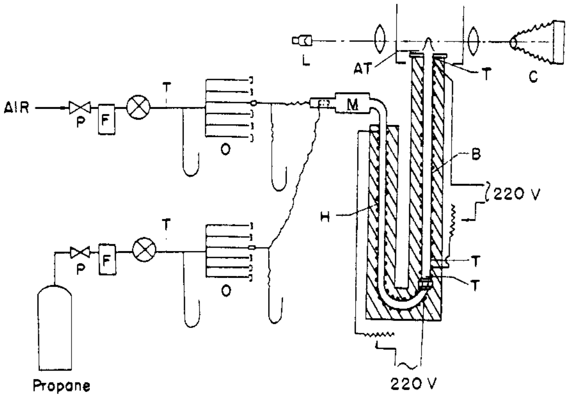

Fig. 1.—Apparatus: AT, aspirating thermocouple; B, burner tube; C, camera; F, filter; H, heater tube; L, concentrated arc lamp; M, mixer; O, critical flow orifice manifold; P, pressure regulator; T, thermocouple.

Temperature Measurement and Control.—Temperatures were measured by iron-constantan thermocouples installed at the inlet to each orifice manifold, at the burner tube inlet for both wall and gas temperature, and at the burner tube port for both wall and gas temperature. The thermocouple for measuring the gas temperature at the port was an aspirating couple in a bolt-action sliding probe, which could be positioned or withdrawn rapidly, allowing the temperature to be checked just before ignition and after extinction of the flame. The tube wall was maintained at this port temperature ± 10° by means of the Variac-controlled heating elements.

Flame Velocity Measurement.—Flame velocities were determined from shadowgraphs by the total area method, wherein the average normal flame velocity is equal to the volume rate of flow of the unburned mixture divided by the surface area of the cone formed by the combustion zone. This flame surface area A_f was determined by the approximate relation for cone-like surfaces of revolution

$$A_f = \pi A_p l/h \qquad (1)$$

where A_p is the projected area of the cone-like flame as outlined by the demarcation between black and white in the shadowgraph; l, the length of the generating curve, excluding the base, of the cone-like surface; and h, the height. A 25-watt Western Union concentrated-arc lamp was used as the light source for the shadowgraph system, which is schematically shown above the burner port in Fig. 1.

Results and Discussion

The flame velocity data obtained with a 15.7-mm. stainless steel tube at two stream flow

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[1] Presented before the Physical and Inorganic Division of the American Chemical Society, Detroit, Michigan, April, 1950.

[2] Passauer, *Gas- und Wasserfach*, **73**, 317, 392 (1930).

[3] Johnston, paper presented at Society of Automotive Engineers Summer Meeting, French Lick, Indiana, June, 1947.

[4] Sachsse, *Z. physik. Chem.*, **180**, sec. A, 305 (1937).

[5] Broeze, "Third Symposium on Combustion, Flame and Explosion Phenomena," The Williams and Wilkins Company, Baltimore, Md., 1949, pp. 152–153.

[6] See Andersen and Friedman, *Rev. Sci. Instruments*, **20**, 61 (1949).

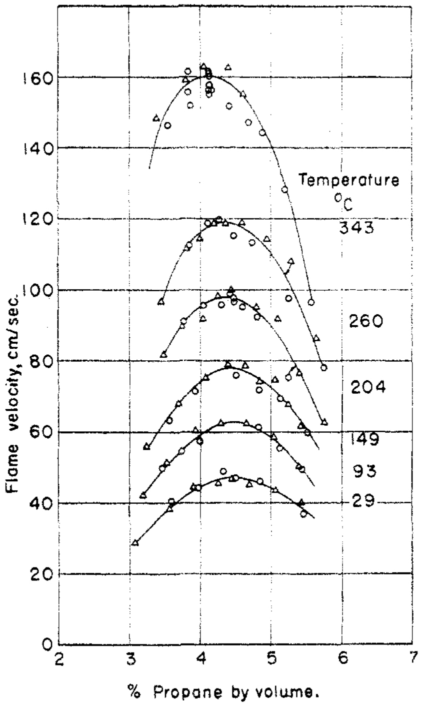

Fig. 2.—Flame velocity as a function of per cent. propane at various temperatures: O, N_{Re} = 2100; △, N_{Re} = 1500.

Reynolds numbers, 1500 and 2100, are plotted in Fig. 2 as flame velocity against volume per cent. propane at each of six temperatures: 29, 93, 149, 204, 260 and 343°. Each of the curves shows the maximum flame velocity for a given temperature to occur at a mixture composition slightly richer than stoichiometric. The data of Fig. 2 show that a change in stream flow Reynolds number from 1500 to 2100 produced no measurable effect on flame speed. Preliminary data obtained with 10.2, 15.7 and 22.2 mm. brass tubes by photographing the luminous bunsen cone showed tube size to have no effect on laminar flame velocity. A few comparative values are given in Table I.

TABLE I

COMPARISON OF FLAME VELOCITIES OBTAINED WITH DIFFERENT TUBE DIAMETERS

Init. temp., °C.	Tube diam., mm.	Max. flame velocity (luminous cone), cm./sec.
29	10.2	38
	15.7	39
	22.2	39
204	10.2	83
	15.7	82
	22.2	83

The flame velocity maxima from the curves of Fig. 2 are plotted against initial temperature to give curve AB in Fig. 3. The flame velocity increases with increase in temperature from 47 cm./sec. at 29° to 160 cm./sec. at 343°. The rate of increase of flame velocity increases with temperature.

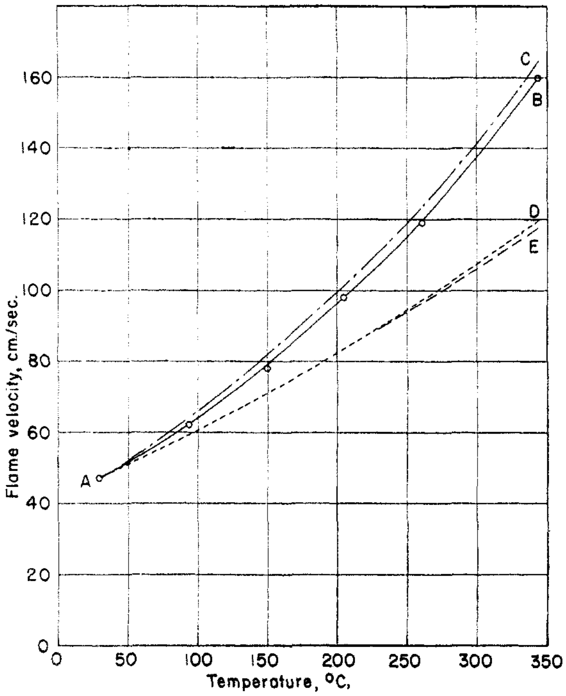

Fig. 3.—Effect of temperature on flame velocity of propane–air mixtures: AB, experimental; AC, thermal theory; AD, square root law, $\Sigma_{pi} = 6.5\, p_{\mathrm{H}} + p_{\mathrm{OH}} + p_{\mathrm{O}}$; AE, square root law, $\Sigma_{pi} = p_{\mathrm{H}}$.

The values of flame velocity shown in Figs. 2 and 3 are based on the areas of the shadowgraphs of the bunsen cones, as described earlier. Andersen and Fein[7] pointed out that measurements based on the area from a shadowgraph of the flame cone are more nearly the absolute values than measurements based on the area from a photograph of the luminous cone, since the former give good agreement with values they obtained by the stroboscopically illuminated particle method. The value of 47 cm./sec. at 29° for propane and air reported here is in agreement with their values of 45.5 and 45.0 cm./sec. by the shadowgraph and illuminated particle methods, respectively. It might be noted that the values in Table I based on the area of the luminous cone are roughly 20% lower than the values in Fig. 2 based on the area of the shadow cone.

Two proposed mechanisms for the propagation of flame are considered—one based primarily on

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(7) Andersen and Fein, University of Wisconsin CM-552, NOrd 9938, Task WIS-1G, July 20, 1949. For further discussion of the total area method and the use of the shadowgraph technique in flame velocity measurements, see also Broeze (footnote 5) and Linnett and Hoare, "Third Symposium on Combustion, Flame and Explosion Phenomena," The Williams and Wilkins Company, Baltimore, Md., pp. 195–204, Culshaw and Garside, *ibid.*, pp. 204–209, and Sherratt and Linnett, *Trans. Faraday Soc.*, **44**, 596 (1948).

the conduction of heat from the combustion zone into the unburned gases and the other based on the diffusion of active radicals from the combustion zone into the unburned gases. Both of these theories were used to predict the relative effect of temperature on flame velocity.

In considering a thermal theory, Zeldovich and Frank-Kamenetsky,[8] Jost[9] and others have pointed out that early heat theories which assumed that (1) reaction begins at the self-ignition temperature, and (2) that the reaction rate is constant between the self-ignition temperature and the flame temperature, are inadequate. Semenov[10] has derived an approximate equation which involves only the initial mixture temperature, combustion temperature and gas properties at these temperatures. If the controlling step is a bimolecular reaction, the appropriate final equation is

$$u_f = \sqrt{\frac{2\lambda_f K a_0\, c_{p(f)}{}^2}{\bar{c}_p{}^3}\left(\frac{T_0}{T_f}\right)^2\left(\frac{\lambda}{c_p \rho D_f}\right)^2\left(\frac{n_1}{n_2}\right)^2\left(\frac{RT_f{}^2}{E}\right)^3 \frac{e^{\frac{-E}{RT_f}}}{(T_f - T_0)^3}} \qquad (2)$$

where

T_0 = initial mixture temperature, °K.
T_f = flame temperature, °K.
ρ_0, ρ_f = density of gas mixture at T_0 and T_f, g./cm.^{3}
λ_f = thermal conductivity at T_f, cal./cm.^{2} – sec.-cm.
$c_{p(f)}, \bar{c}_p$ = specific heat at T_f, and mean specific heat, T_0 to T_f, respectively, cal./g.-°K.
n_1/n_2 = mols reactants/mols products by stoichiometric equation
D_f = diffusion coefficient at T_f cm.^{2}/sec.
R = gas constant, cal./g.-mole-°K.
E = activation energy, cal./mole
K = constant from reaction rate equation
a_0 = no. of molecules per unit volume of combustible in initial mixture

By eliminating from equation (1) the terms not dependent on temperature, substituting as approximate relations for the temperature-dependent terms those determined for air ($\lambda \propto T^{0.84}$, $c_p \propto T^{0.09}$, $D \propto \eta/\rho \propto T^{1.67}$,[11] $\rho \propto T^{-1}$, $a_0 \propto T^{-1}$), and combining terms, the equation reduces to the form

$$u_f \propto \sqrt{T_0{}^2\, T_f{}^{4.9}\, e^{-ERT_f}/(T_f - T_0)^3} \qquad (3)$$

This reduced form of the equation may be used to estimate the relative effect of temperature on flame velocity for hydrocarbons burning with air, when the relationships between the physical properties and temperature for the mixtures are near those for air.

A diffusion mechanism of flame propagation may also be considered for the prediction of the effect of temperature on flame speed. Tanford and Pease[12,13] have proposed that the rate of diffusion of active radicals ahead of the flame front determines the rate of flame propagation. This concept is expressed by what has been called the square root law of burning velocity

$$u_f = \left(\Sigma_i\, p_i\, D_i\, k_i\, L\, \frac{Q'}{QB_i}\right)^{1/2} \qquad (4)$$

where

p_i = mole fraction or partial pressure of a given radical in the burnt gas
D_i = the coefficient of diffusion of the radical into the unburnt gas
k_i = a rate constant for its interaction with the combustible material
L = number of molecules per cm.^{3} of gas at some mean temperature
Q' = mole fraction of combustible in the unburnt gas
Q = mole fraction of potential combustion product in the burnt gas
B_i = term, near unity, arising from radical recombination.

If a correlation exists between the flame velocity of a hydrocarbon–air mixture and its equilibrium active radical concentrations, the relative effect of temperature on flame velocity could be estimated by the square root law. Assuming that only p_i, D_i and L are appreciably temperature dependent ($D_i \propto D_{i,r}T_0{}^{1.67}$, where $D_{i,r}$ is the relative diffusion coefficient of the given radical with respect to the other radicals; $L \propto T_{av}{}^{-1}$, where $T_{av} = (T_0 + T_f)/2$), the square root law would reduce to

$$u_f \propto \sqrt{(\Sigma p_i\, D_{i,r})\, T_0{}^{1.67}\, T_{av}{}^{-1}} \qquad (5)$$

A comparison of the relative effect of initial temperature on flame velocity predicted by the above reduced expressions 3 and 5 is presented in Fig. 3. The experimental value of 47 cm./sec. at 29° was used as the basis for computation of relative values at higher temperatures by these expressions. For computation of values for the thermal theory curve AC and diffusion theory curves AD and AE the following values and approximations were used

E ≅ 38,000 cal./mole[8]
ΔT_f ≅ 0.45 ΔT_0 (from theoretical flame temperature calculations, where ΔT_f is the change in T_f resulting from ΔT_0, the change in T_0)
T_f ≅ 2200°K. at room temperature,[14] Na D line measurement

Equilibrium partial pressures of hydrogen atoms, hydroxyl radicals and oxygen atoms for a 4.2% propane mixture were calculated by the graphical method of Huff and Calvert[15] and are presented in Table II. The desired partial pressures for curves AD and AE were obtained by logarithmic interpolation from Table II. Curve AD is based upon $\Sigma p_i D_{i,r} = 6.5\ p_H + p_{OH} + p_O$,

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[8] Zeldovich and Frank-Kamenetsky, *Acta physicochim.* (*USSR*), **9**, 341 (1938).

[9] Jost (Croft), "Explosion and Combustion Processes in Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1946.

[10] Semenov, *Progress of Phys. Sci.* (*USSR*), **24**, No. 4 (1940). Translation appears as Natl. Adv. Comm. Aeron. Technical Memorandum, No. 1026, 1942.

[11] These relations for λ, c_p and η (viscosity) were estimated from McAdams, "Heat Transmission," Second Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1942, pp. 379–411.

[12] Tanford and Pease, *J. Chem. Phys.*, **15**, 431 (1947).

[13] Tanford, "Third Symposium on Combustion, Flame and Explosion Phenomena," The Williams and Wilkins Company, Baltimore, Md., 1949, pp. 140–146.

[14] Perry, "Chemical Engineers Handbook," Second Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 2410.

[15] Huff and Calvert, Natl. Adv. Comm. Aeron. Technical Memorandum No. 1653, 1948.

TABLE II

EQUILIBRIUM PARTIAL PRESSURES OF RADICALS

T_f, °K.	p_H, atm. × 10^3	p_{OH}, atm. × 10^3	p_O, atm. × 10^3
2200	0.43	1.62	0.087
2300	0.77	2.9	.25
2400	1.35	5.2	.70

since the diffusion rate for hydrogen is roughly 6.5 times that for the other radicals. Curve AE is based on the hydrogen atom concentration alone and falls upon curve AD within the accuracy of the calculations.

The curves in Fig. 3 show that the relative increases in flame velocity with initial temperature predicted by the thermal theory are in satisfactory agreement with experimental results, while those predicted by the square root law are as much as 35% lower at the higher temperatures.[16] Approximately the same increases were predicted by the square root law when only the hydrogen atom concentration was considered as when hydroxyl radical and oxygen atom concentrations were also considered.

Other calculations, not shown here, indicate that the data of Broeze[5] for propane–air flames at concentrations near stoichiometric would give similar relations between observed values and values predicted by the theories on the relative basis. Johnston's data[3] on natural gas–air flames and acetylene–air flames also appear to be in fair agreement with relative increases predicted by the thermal theory, while the increases predicted by the square root law are again low.

Although the square root law does not appear to predict the experimental results as well as the thermal theory does for these hydrocarbon–air flames, this does not necessarily mean that the diffusion of active radicals is unimportant, nor does it mean that some other relation based on diffusion might not predict the experimental results. The calculated equilibrium radical concentrations would not correspond to the true radical concentrations if (1) equilibrium is not attained, (2) any appreciable reaction took place at the initial temperature, or (3) there is, as Lewis has suggested,[13] a large chain branching term affecting the radical distribution in and ahead of the flame zone.

Summary

1. The maximum flame velocity of propane–air mixtures increases from 47 cm./sec. at 29° to 160 cm./sec. at 343°. The rate of increase of flame velocity increases with temperature. The results are independent of tube diameter in the range 10.2 to 22.2 mm. and of stream flow Reynolds number in the range 1500 to 2100.

2. Approximate calculations indicate that both the thermal theory as presented by Semenov (for bimolecular reactions) and the diffusion theory of Tanford and Pease predict that flame velocity will increase with temperature at an increasing rate. Relative increases in flame velocity predicted by the thermal theory are in satisfactory agreement with experimental results, while those predicted by the square root law are as much as 35% lower at the higher temperatures. The square root law yields approximately the same results whether based on the hydrogen atom concentration alone or on the summation of the effective relative concentrations of hydrogen atom, hydroxyl radical and oxygen atom.

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(16) The effects of using different values of T_f, ΔT_f and E were checked and found to be as follows: (1) Increasing T_f from the measured 2200°K. to the theoretical 2390°K.[13] at t_0 = 32° resulted in predictions of the relative increases in flame speed at 343° that were 5% low for the thermal theory and 35% low for the diffusion theory. (2) Using $\Delta T_f = 0.50T_0$ rather than $0.45T_0$ gave increases at 343° that were 12% high for the thermal theory and 32% low for the diffusion theory. (3) Using E = 25,000 instead of 38,000 cal./g.-mole gave an increase at 343° that was 5% low for the thermal theory. (4) Combining (1) and (3) gave an increase that was 17% low for the thermal theory. It might also be noted that if the term B_l in equation (4) were greater than unit (references 2 and 3), the values for the diffusion theory curve would be even lower.