The Composition Dependence of the Burning Velocity of Lean Hydrocarbon Flames

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ABSTRACT

The laminar burning velocities of lean fuel-oxygen-nitrogen bunsen flames were measured for methane, propane, and ethylene. At constant theoretical adiabatic flame temperature, each fuel exhibits a limiting value of the burning velocity as the oxygen/fuel ratio is increased. The ratio of burning velocity to this limiting value shows the same functional dependence on equivalence ratio for the three fuels studied. With the assumption that this dependence is valid for other volatile hydrocarbons, a method is proposed for the prediction of the burning velocity of hydrocarbon-oxygen-nitrogen mixtures over the complete fuel-lean region. Application of the proposed procedure to published data is shown.

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INTRODUCTION

The search for methods of predicting burning velocities is based on the need of a characteristic of a flame, a property that will be useful in the determination of the general behavior of the flame. The laminar burning velocity fills this requirement through the empirical and theoretical relationships between it and quenching distance,[2] critical boundary velocity gradients,[9] and ignition energies.[2] Its position as an important means of characterizing flames is also shown by the use of burning velocities as a test of combustion theories.[6]

Methods for prediction of burning velocity are most readily applicable to practical problems if they do not require the complex calculations of the rigorous theories of combustion. Thus, although more rigorous theories are available, many attempts have been made to describe laminar burning velocities in terms of approximate theories.[6] The resulting analytical functions are based on admittedly incorrect assumptions concerning the reaction and energy transfer rates within the flame. The ultimate justification of these assumptions is in the success of the result in adequately describing the observed burning velocity.

Examination of the reported attempts to describe laminar burning velocities readily shows that success is achieved only when the range of variables is suitably limited. Thus most applications of the approximate theories have pertained to hydrocarbon-oxygen-nitrogen mixtures, fuel/oxygen ratios near the stoichiometric value and atmospheric pressure. Of the analytical functions proposed, those based on the Semenov treatment have been applied over the greatest range of variables. Two such functions are:[2,5]

$$v_b \propto \frac{T_o T_f}{T_o - T_f} X_f^{0.5} \left[\frac{1 - \varphi}{(\pm\varphi)} + \frac{RT_f^2}{E(T_o - T_f)} \right]^{0.5} e^{-E/2RT_f} \qquad (1)$$

$$v_b \propto \frac{T_o T_f}{(T_o - T_f)^{0.5}} \frac{X_f^{0.4}}{\varphi^{0.4 \pm 0.9}} e^{-E/2RT_f} \qquad (2)$$

where

E is the energy of activation of the over-all reaction,
T_o is the temperature of the primary or feed mixture,
T_f is the adiabatic flame temperature,
X_f is the primary fuel fraction and
φ is the equivalence ratio, the fuel/oxygen ratio relative to the stoichiometric fuel/oxygen ratio.

The positive sign is used for fuel-lean primary mixtures and the negative sign for fuel-rich primary mixtures.

An assumption of these functions is that the same chemical kinetics and temperature dependence applies to most hydrocarbons and equivalence ratios. That the success of this assumption is limited is indicated by measurements of the over-all order of combustion reactions.[12] In such studies, the evidence is that the over-all order of the reaction is a function of the fuel, the diluent, and the equivalence ratio. These conclusions are further supported by the observation that with increasing oxygen fraction or decreasing equivalence ratio, the burning velocity tends to become independent of the equivalence ratio for hydrocarbon-oxygen-nitrogen mixtures.[8,10]

In spite of the theoretical and experimental limitations of the above functions, their partial success indicates that a relatively simple empirical method may be more successful in fulfilling the practical purposes of prediction of burning velocities. The presumed existence of a simple method is based on:

a) the apparent similarity, among hydrocarbons, of the dependence of burning velocity on temperature and composition,
b) the apparent separability of the dependence of burning velocity on flame temperature and on equivalence ratio, and
c) the similar heat capacity and transport properties of oxygen and the most common diluent, nitrogen, thereby simplifying the relation between flame temperature and primary gas composition and minimizing the variation of transport properties with composition.

In this paper, these three characteristics are made the basis of an empirical method of predicting the laminar burning velocities of hydrocarbon-oxygen-nitrogen mixtures at atmospheric pressure and room temperature.

APPARATUS AND PROCEDURE

Burning velocities were determined by the total area method from shadowgraphs of bunsen flames. For the range of burning velocities encountered, four burners were used. For the flames of 1800°K flame temperature, the burner diameter was 5/8 in.; 2000°K, 3/8 in.; 2250°K, 1/4 in.; and for 2500°K, 3/16 in. Wall thicknesses were 0.06 in. or less and a cooling jacket came within 1/8 in. of the burner rim. In all cases the initial gas temperature was 300°K.

The gas metering system, based on that of Andersen and Friedman,[1] and the 'Z' optical system[7] have been described elsewhere.[14]

The primary mixtures of hydrocarbon, oxygen, and nitrogen were chosen to have a preassigned adiabatic flame temperature. The burning velocity was determined for mixtures covering the complete fuel-lean region for particular adiabatic flame temperature levels. The choice of temperature levels was in part determined by the ability to achieve stable flames at laminar flow conditions.

All flame temperatures were calculated with the usual assumptions of chemical equilibrium and adiabatic combustion.

RESULTS

The hydrocarbons studied were methane, propane, and ethylene. The results of these studies are summarized in Figures 1-3. Those for methane were presented previously,[14] but are included to permit comparison with the other fuels. The abscissa used is the reciprocal of the more commonly used equivalence ratio because of its greater convenience for the composition range covered in these studies.

For the several fuels and temperature levels, the burning velocity variations with equivalence ratio are qualitatively similar. The strong dependence on the equivalence ratio near the stoichiometric point is in qualitative agreement with the functions (1) and (2). However, with large excesses of oxygen, the burning velocity is only weakly dependent on the amount of oxygen. While in disagreement with the above expressions, this behavior can be seen in the results of other investigators.[8,10]

In the cases of propane and ethylene, the data show no indications other than that the burning velocity approaches a limiting value with increasing primary oxygen fraction along a constant temperature level. (In these studies, a constant temperature level very nearly corresponds to a constant primary fuel fraction.) In the case of methane, however, there is a real decrease in burning velocity at the extreme lean end of the curves. This decrease amounts to about 10% and places only a minor limitation on the concept, to be used below, that there exists a limiting burning velocity as the oxygen fraction increases along a constant adiabatic flame temperature level.

CORRELATION OF BURNING VELOCITY DATA

The restriction of these data to ternary mixtures at one atmosphere and 300°K initial temperature implies that any adiabatic process parameter such as flame temperature or burning velocity is a function of only two variables for a given ternary system. The most convenient factors are the fuel fraction and the equivalence ratio.

As reported above, there exists a limiting value of the burning velocity at high oxygen to fuel ratios which is characteristic of the flame temperature. If it is assumed that the dependence of burning velocity on the equivalence ratio and on the flame temperature can be expressed as independent functions, then the ratio of the observed burning velocity (v_b) to the limiting value (v_{b-m}) at the same flame

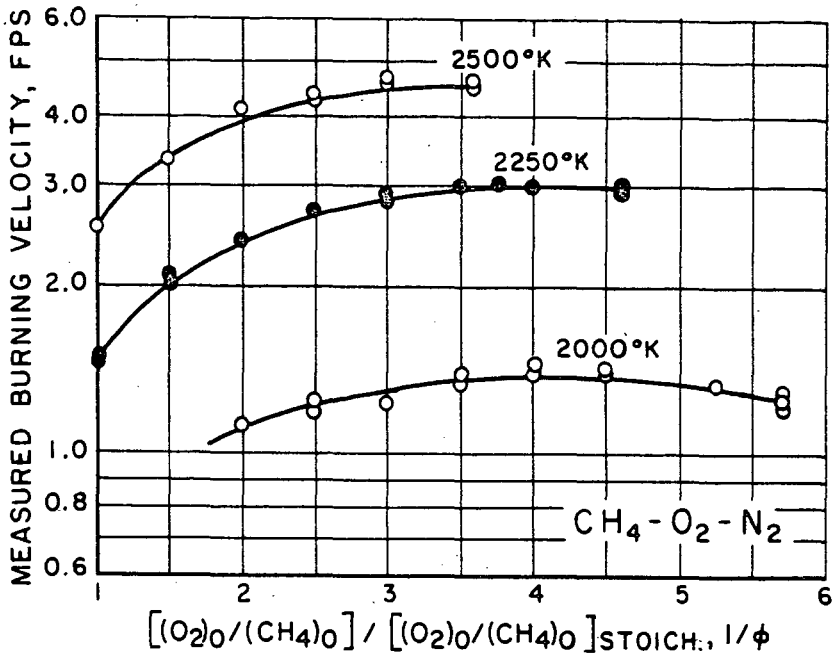

Fig. 1.-BURNING VELOCITIES OF CH_4-O_2-N_2 SYSTEM

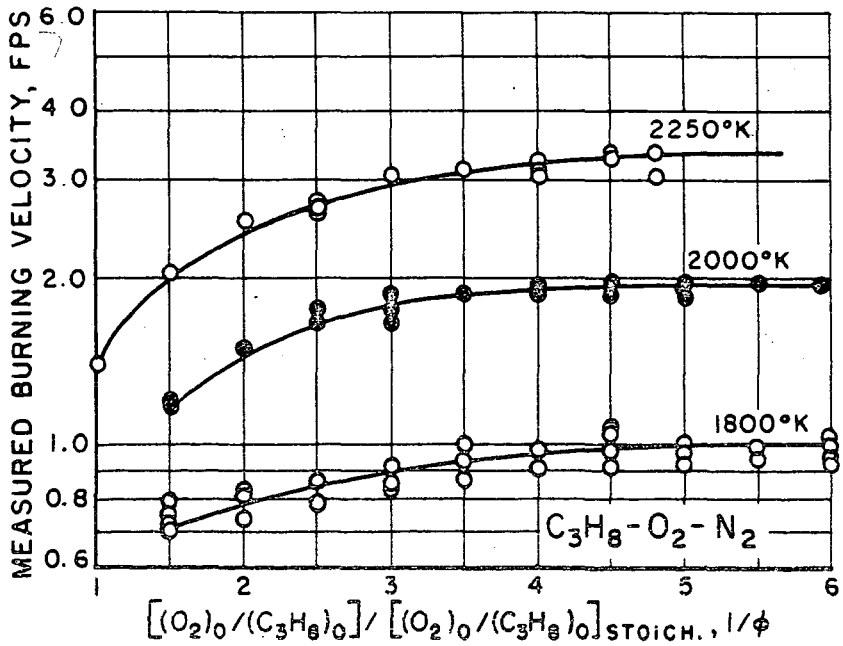

Fig. 2.-BURNING VELOCITIES OF C_3H_8-O_2-N_2 SYSTEM

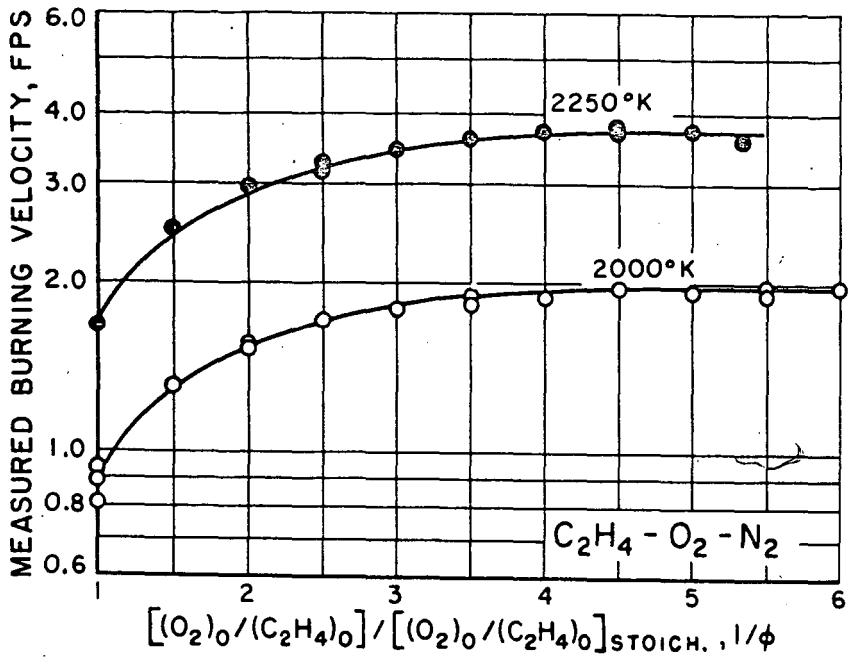

Fig. 3.-BURNING VELOCITIES OF C_2H_4-O_2-N_2 SYSTEM

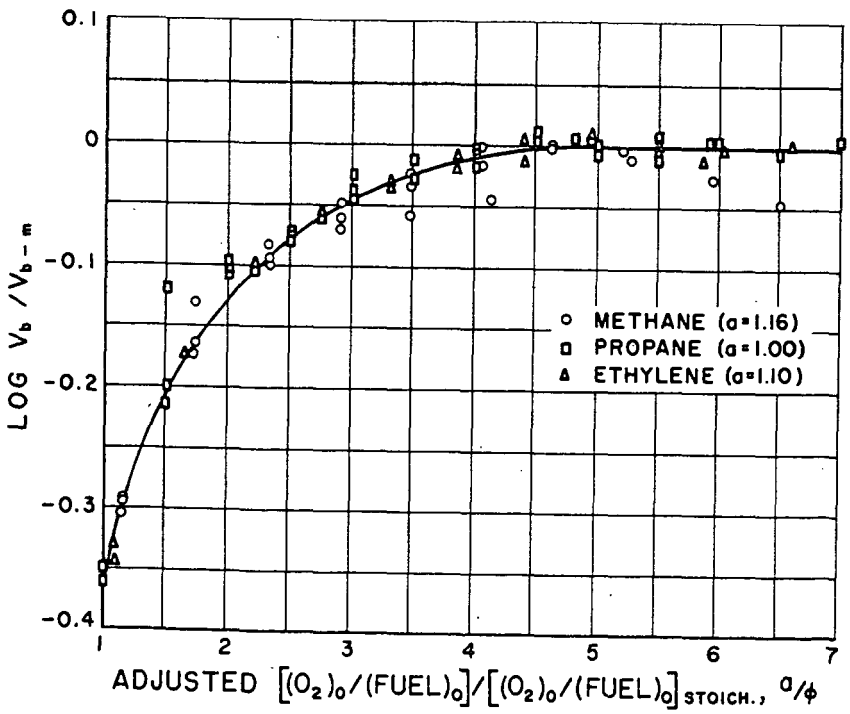

Fig. 4.-CORRELATION OF BURNING VELOCITIES OF HYDROCARBON-O_2-N_2 SYSTEMS

temperature would be a function of equivalence ratio (φ) only. Furthermore, the dependence of v_b/v_{b-m} on the equivalence ratio, according to previous correlations,[2,5] may possibly be generalized among the hydrocarbons through the use of a proportionality factor. Such a correlation is shown in Figure 4 where the ratio v_b/v_{b-m} is plotted against a/φ where the experimental parameter a is 1.00 for propane, 1.10 for ethylene, and 1.16 for methane. Each point was obtained from the average of observed burning velocities and corresponds to a particular mixture of hydrocarbon, oxygen, and nitrogen. The data include all of the eight hydrocarbon-flame temperature combinations measured. The curve represents the function:

$$v_b/v_{b-m} = \left[-0.05640\ (a/\varphi)^2 + 0.5389\ (a/\varphi) - 0.3026\right]^{1/2} \qquad (3)$$

up to $a/\varphi = 4$. The choice of function is arbitrary and serves only as a means of testing the correlation. Of the 52 points for which v_b/v_{b-m} is significantly less than unity, ($a/\varphi \leqslant 4.2$), 47 are within 5% of the curve and 51 are within 9% of the curve. The average deviation for this portion of the data is 2.5% of the burning velocity. For values of $a/\varphi \geqslant 4.2$, it is assumed that the burning velocity is at the limiting value. In this range, 26 of the 28 mixtures have values of v_b/v_{b-m} within 5% of unity and the average deviation is 1.7%. It is possible, therefore, to express the burning velocity of these mixtures well within experimental precision in the form:

$$v_b = v_{b-m}\ f(a/\varphi) \qquad (4)$$

where v_{b-m} includes all dependence on flame temperature.

It is proposed that the observed correlation of the data of this study can be applied to hydrocarbons in general. The test of the correlation with data of other investigators must be indirect since the required information is not available. The information required for a particular fuel is the value of the equivalence ratio adjustment factor, a, and the function v_{b-m} in terms of known quantities. To test the equation (4) for a particular fuel and initial temperature and pressure, the following assumptions are made:

a) $f(a/\varphi)$ is given by Figure 4 or equation (3).
b) The value of a for propane may be applied to all paraffinic hydrocarbons other than methane.
c) The flame temperature is a single-valued function of the fuel fraction in lean hydrocarbon-oxygen-nitrogen mixtures.

The third assumption avoids the need of calculating the flame temperature; it is reasonably accurate for flame temperatures below 2500°K and, as will be seen below, proves adequate for the purpose at higher temperatures.

APPLICATION OF THE CORRELATION

The most extensive data with respect to the composition range are those on methane of Jahn[10] and of Singer and Heimel.[11] The data from the two sources are not consistent. Therefore, the burning

velocities reported by Singer and Heimel were multiplied by a factor, 0.742, to bring them in line with those of Jahn. The ratio v_b/v_{b-m} was obtained from Figure 4 with $\underline{a}$ = 1.16. The values of v_{b-m} were then calculated from the reported values of Jahn and the adjusted values of Singer and Heimel. The resulting dependence of v_{b-m} on the fuel fraction is shown in Figure 5. The data include 18 fuel-rich mixtures for which a/φ is greater than unity, that is mixtures for which v_b/v_{b-m} can be found from Figure 4. Of the 81 mixtures represented in Figure 5, the deviations of v_{b-m} from the least squares line are such that 64 are within 5% and 75 are within 10%.

It is felt to be significant that all the mixtures that have deviations greater than 10% are binary mixtures of methane and oxygen or contain at most 1.5% of nitrogen. These deviations correspond to low values of the burning velocity and support the observations concerning a maximum in the v_b vs. $1/\varphi$ curves for methane (Figure 1). This effect does not appear until less than 10% of the primary mixture is nitrogen, and roughly corresponds to the region where equilibrium amounts of nitrogen oxides fall off sharply. It may be taken as evidence of an effect of nitrogen oxides on the combustion rate. For the purpose of the correlation and its practical application, it is noted that if at least 1.5% nitrogen is present, the error is no greater than 15%. Furthermore, the large deviations occur predominantly for flames of lower temperatures. The limitation on the overall correlation due to this effect, therefore, occurs in a relatively small range.

The correlation of the burning velocities of methane-oxygen-nitrogen mixtures at one atmosphere and initial temperatures near room conditions, as presented in Figures 4 and 5, cover the following range of experimental conditions:

Fuel fraction: 8-36%
Equivalence Ratio: 0.25 - 1.16
Flame Temperature: 2000-3000°K
Burning Velocity: 24 - 330 cm/sec

As an example of the coalescence of the reported values, the group of seven points near 15% methane correspond to equivalence ratios of 0.98 - 0.35 and burning velocities of 99 - 169 cm/sec.

Another set of data of sufficient range to test the proposed correlation is that of Golovina and Fyodorov[8] on the burning velocity of hexane. The factor $\underline{a}$ was assigned the value of 1.00 and the results are presented in Figure 6. The precision of the calculated values of v_{b-m} with respect to the straight line is not as good as observed in the case of methane. Of the forty points, 22 are within 5% and 28 are within 10% of the line. Of the four points that deviate by more than 15%, three are those of nitrogen-free mixtures, at low temperatures and may be considered further evidence of anomalous behavior of binary fuel-oxygen mixtures.

If the generality of Figure 4 is accepted, the data required for the establishment of the v_{b-m} dependence on fuel fraction can be obtained from the fairly common fuel-air and similar binary mixture studies.

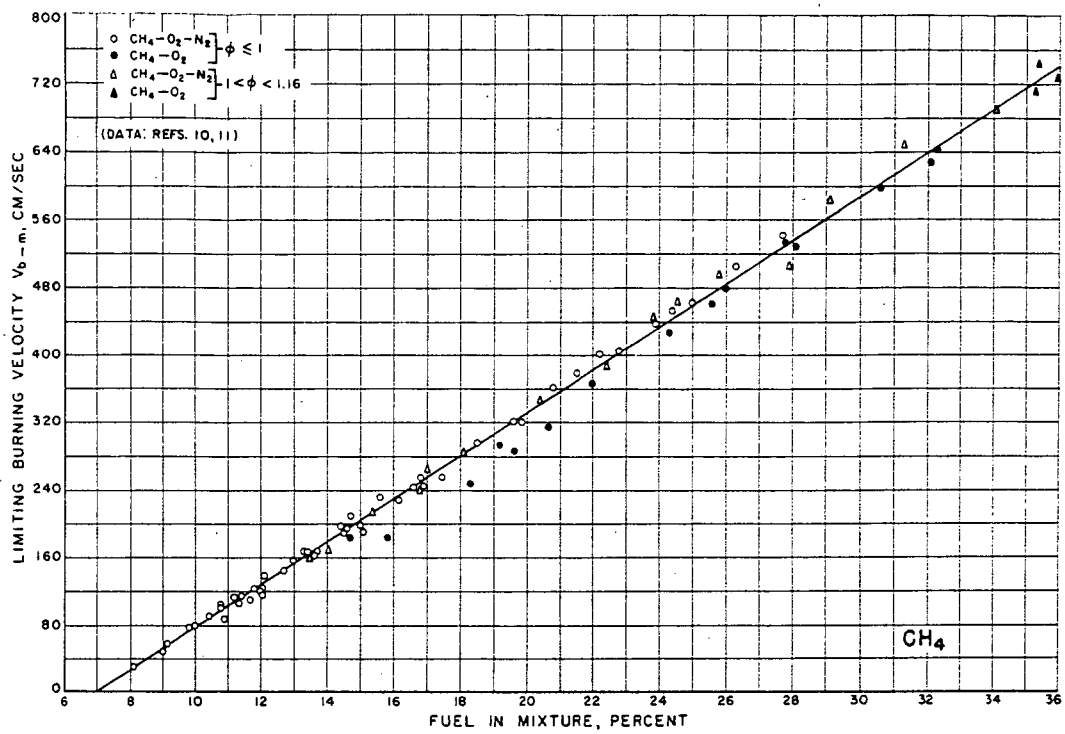

Fig. 5.-LIMITING BURNING VELOCITIES OF CH_4-O_2-N_2 SYSTEM

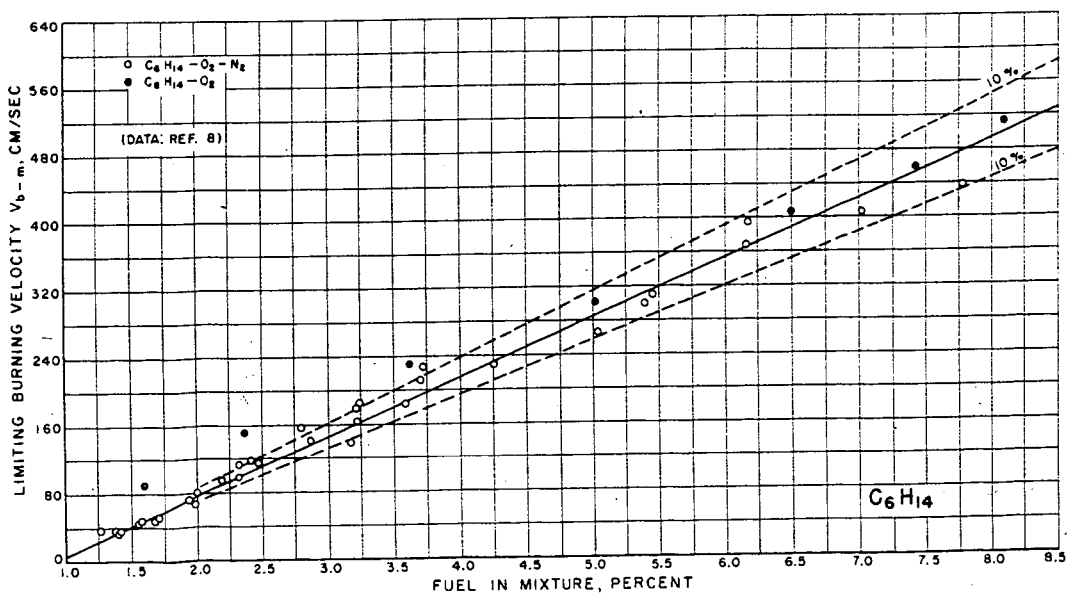

Fig. 6.-LIMITING BURNING VELOCITIES OF C_6H_{14}-O_2-N_2 SYSTEM

Examples based on the data for binary mixtures are shown in Figure 7 for ethylene and propyne based on the results of Simon and Wong[13] and for iso-octane and propane based on the results of Dugger and Graab.[3,4] If, as in the case of the data of Simon and Wong, only fuel-air mixtures were studied, the flame temperature range is small. While the proposed method is based on the empirical determination of the v_{b-m} -fuel fraction curve, the occurrence of straight lines in the extensively covered cases of methane and hexane indicate the strong possibility that linear relationships in general may be valid. If so, the line obtained for fuel-air mixtures would be sufficient for use over the whole range of lean fuel-oxygen-nitrogen mixtures. The use of linear functions appears satisfactory for the limited data of ethylene, propyne, and iso-octane. In the latter case, a trend at higher fuel fractions is apparent, but the straight line fit is still within 5% in this region. The propane results are nearly linear over most of the range, but show a definite tail at the low fuel fractions.

The information of the Figures 5-7 are summarized as follows:

Hydrocarbon	Source of Data	a	v_{b-m} cm/sec
Methane	Refs. 10, 11	1.16	$2555x_f - 179.3$
Ethylene	Ref. 13	1.10	$3932x_f - 124.1$
Propane	Ref. 3	1.00	non-linear
Propyne	Ref. 13	1.00	$5770x_f - 140$
Hexane	Ref. 8	1.00	$6615x_f - 63.0$
Iso-octane	Ref. 4	1.00	$12350x_f - 120.2$

where x_f is the fraction of fuel in the primary mixture. As in the comparison of the data of Jahn and of Singer and Heimel which differed by a proportionality factor, it must be recognized that the above formulation can be expected to describe the results of any particular investigation only within a proportionality factor.

The proposed method of empirical prediction of burning velocity applies to lean mixtures at atmospheric pressure and initial temperatures near room conditions. The limitation to lean mixtures may possibly be lifted, according to the methane data, to include mixtures of $a/\varphi \geqslant 1$ even if $1/\varphi \leqslant 1$. Further extension into the rich region must involve modifications since the fuel fraction is no longer a single-valued function of the flame temperature nor is the curve of v_b/v_{b-m} vs. a/φ available. However, the correlations that are based on the Semenov theory imply the same flame temperature dependence in both rich and lean mixtures and similar equivalence ratio dependence. It is quite possible, therefore, that the proposed correlation can be extended to rich flames if the inconvenience of flame temperature calculation is accepted as part of the procedure.

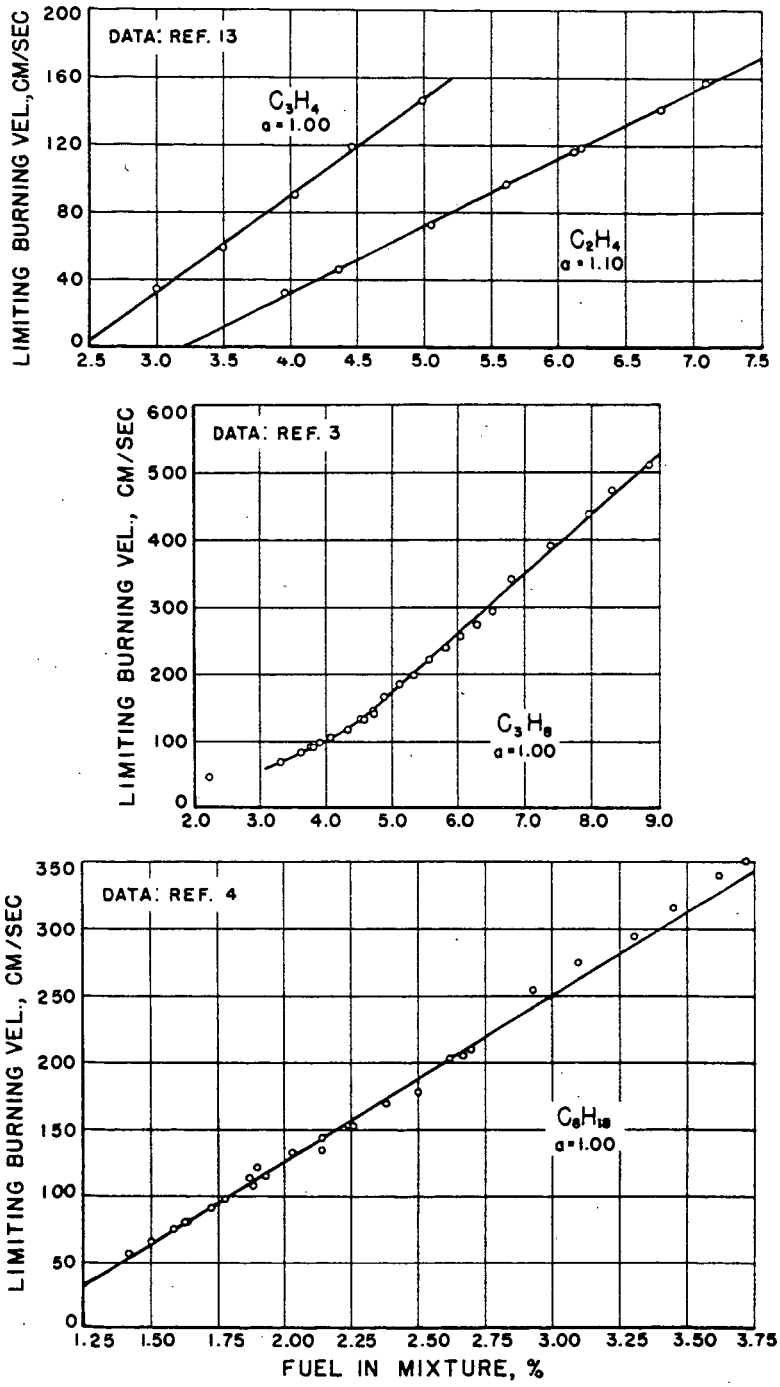

Fig. 7.-LIMITING BURNING VELOCITIES OF HYDROCARBON-O_2-N_2 SYSTEMS

SUMMARY

It is shown that the burning velocity of lean hydrocarbon-oxygen-nitrogen mixtures can be expressed as the product of a function of the equivalence ratio and a function of the fuel function. With data of this study, the required function of equivalence ratio has been established empirically. The function of fuel fraction has been determined for several hydrocarbon fuels from data of other investigators. For most of these fuels, the function of fuel fraction appears to be linear. If this dependence can be generalized, it would be possible to predict the burning velocities of lean hydrocarbon-oxygen-nitrogen mixtures from data based on fuel-air studies only.

Although applied to lean mixtures only, there is evidence that the proposed method of prediction of burning velocities is applicable to some fuel-rich mixtures, and potential means of covering the significant fuel-rich region are offered. Although empirical, the method should prove suitable for practical application and covers regions for which the assumptions of the approximate theories are invalid.

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