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Fuel Droplet Burning Rates in a Combustion Gas Environment

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Measurements were made of droplet burning rates in the combustion products of a flat flame burner at atmospheric pressure. Various alcohols and paraffins were tested at ambient temperatures from 1660°K to 2530°K and ambient oxygen concentrations in the range 0-37%. Existing theories of droplet combustion (when corrected for flame zone dissociation) gave an adequate prediction of the variation in burning rate with changes in the ambient temperature and oxygen concentration. However, the theories progressively overestimated the burning rate as the fuel molecular weight increased, with errors as high as 50% for the heavier hydrocarbons.

Nomenclature

- a, b = constants in the expression $C_p = a + bT$
 C_p = specific heat at constant pressure
 d = droplet diameter
 H_c = heat of reaction of liquid fuel and gaseous oxidizer
 K = burning rate constant
 \dot{m} = mass evaporation rate
 Pr = Prandtl number
 Re = Reynolds number
 Sc = Schmidt number
 t = time
 T = temperature
 V = gas velocity
 Y_x = effective ambient oxygen mass fraction
 γ_o = ratio of the stoichiometric mass flow rate of oxygen to fuel
 Δh = fuel heat of vaporization
 λ = thermal conductivity
 ρ = liquid density

Subscripts

- l = droplet surface
 o = pertains to no-flow conditions
 ∞ = ambient conditions

Introduction

BECAUSE of its importance as an elemental process in the combustion of sprays, many investigators have studied the burning of single fuel droplets. Most of these studies were

conducted by burning droplets at low-ambient temperatures with oxygen concentrations ranging from air to pure oxygen. Studies of droplet combustion in an environment more representative of combustion chamber conditions, however, have been much more limited.

Wood et al.¹ considered the droplet combustion of hexadecane, kerosene and a number of heating oils within a gaseous premixed flame. Droplet burning was observed for oxygen mass fractions in the range 0-0.81. The gas temperature was kept constant at 1775°K. Average burning rate constants were inferred from measurements of the initial droplet diameter and the total time of combustion luminosity. This technique is of limited accuracy, however, due to uncertainties in the relationship between the start and end of combustion luminosity and the start and end of the steady burning period.

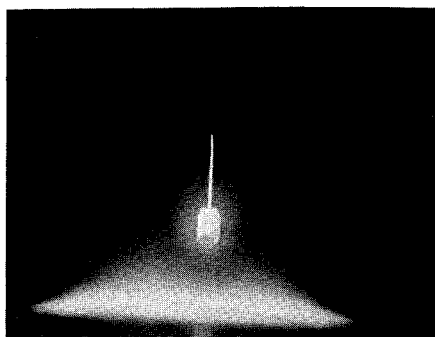
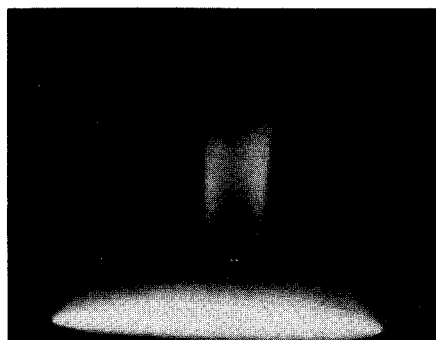
Ingebo² has made measurements of ethanol evaporation rates in a rocket engine combustion chamber and Bolt et al.³ considered the combustion of a number of hydrocarbons in a burning spray. However, the state of the gas surrounding the droplets in these experiments was not sufficiently well-defined to allow comparison of the results with theoretical predictions of droplet burning rates.

The present study provides more extensive measurements of droplet burning rates at high-ambient temperatures. The droplets were subjected to the combustion products of a flat flame burner at atmospheric pressure. The burner was operated with various gas compositions to yield temperatures in the range 1660-2530°K and oxygen mass fractions in the range 0-0.37, at the droplet location. The fuels considered in the study included methyl, 1-butyl and 1-decyl alcohol as well as the paraffin hydrocarbons n-pentane, n-heptane, iso-octane, n-decane, n-tridecane, and n-hexadecane.

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a) $Y_z = 0.227$, $T_\infty = 2530^\circ\text{K}$, $V_\infty = 62.5 \text{ cm/sec}$ b) $Y_z = 0$, $T_\infty = 2350^\circ\text{K}$, $V_\infty = 46.7 \text{ cm/sec}$ **Fig. 1 Dark field photographs of n-hexadecane combustion.**

The experimental results were compared with existing droplet burning rate theories. Although some comparisons were made with constant property theories,⁴ present emphasis was placed on the variable property solution of Goldsmith and Penner.⁵ This theoretical model postulates property variations that are particularly suitable for the hydrocarbon types considered in the present study. Furthermore, the use of a variable property model provides a more fundamental test of the over-all concepts employed in droplet combustion theories, due to restrictions in the latitude available in the selection of properties to fit the experimental data.

Apparatus

Only a brief description of the apparatus is given here; further details may be found in Ref. 6. The test droplets were supported on quartz filaments having a diameter of approximately 100μ . The bottom end of the filament was slightly enlarged to assist in supporting the droplet.

The high-temperature gaseous environment was produced by a 5-cm-diam flat flame burner, similar to the one employed

by Friedman and Macek.⁷ The burner was mounted on a carriage so that it could be rapidly moved under the test droplet and brought to a stop when the droplet was positioned 1 cm above the center of the burner.

The burner was operated with various mixtures of carbon monoxide, hydrogen, oxygen and nitrogen (commercial grade) in order to achieve the desired test conditions. The gas flows were measured with rotameters, which were previously calibrated with a wet test meter. The heat loss from the flame to the burner was determined by measuring the flow rate and temperature rise of the burner cooling water. The composition and temperature of the gas at the droplet location was computed from thermochemical calculations allowing for dissociation and heat loss to the burner.

The flow of gases was adjusted to give two different test series. In the first, the ambient gas temperature and velocity were kept relatively constant at 2530°K and 62.5 cm/sec respectively, while the oxygen mass fraction was varied in the range 0.046–0.371. In the second series, the flame was operated fuel-rich to provide a negligible oxygen concentration, with gas temperatures in the range 1660 – 2530°K at a relatively constant velocity of 46.7 cm/sec . Table 1 summarizes the computed properties of the gas at the droplet location for all the test conditions. The oxygen mass fraction quoted in this table is an effective mass fraction based on the concentrations of possible oxidizing species (O_2 , O , NO).

Figure 1 shows dark field photographs of n-hexadecane droplets in the burner gases, that are typical of the appearance of most of the fuels tested. For a finite ambient oxygen concentration (Fig. 1a) a well-defined luminous flame zone was present around the droplet. With decreasing ambient oxygen concentration, this flame zone would move away from the droplet and the intensity of the luminosity would decrease. For negligible ambient oxygen concentration (Fig. 1b), while there is no flame zone resulting from exothermic reaction, a diffuse luminous wake was present. This wake was probably due to radiation from hot carbon particles formed by decomposition of the fuel in the burner gases.

Unlike the remainder of the fuels, methanol did not exhibit a luminous wake at negligible ambient oxygen concentrations. This behavior probably results from the high resistance of methanol to the formation of carbon particles upon decomposition. The behavior of methanol was similar to the other fuels under oxidation conditions, however, although the flame luminosity was less intense.

Droplet diameters were measured as a function of time from shadowgraphs recorded by a 16 mm cine camera. The camera was operated at speeds on the order of 100 pictures per second. The elliptical shape of the droplet was corrected to a sphere of equal volume as discussed by Kobayasi.⁸

Some typical plots of droplet diameter squared as a function of time are shown in Fig. 2 for representative alcohols and paraffins. In this figures, time is plotted from the instant that the droplet enters the burner gases. During the early stages of the process, the droplet diameter remained relatively con-

Table 1 Properties of the ambient gas for the test conditions

Y_z	T_∞ , $^\circ\text{K}$	V_∞ , cm/sec	Product mole fraction							
			CO	CO ₂	H ₂	H ₂ O	NO	N ₂	O	O ₂
0.046	2530	62.5	0.099	0.415	0	0	0.009	0.430	0.004	0.043
0.138	2530	62.5	0.058	0.439	0	0	0.014	0.339	0.007	0.143
0.227	2530	62.5	0.041	0.423	0	0	0.017	0.270	0.009	0.240
0.308	2530	62.5	0.033	0.402	0	0	0.016	0.208	0.011	0.330
0.371	2530	62.5	0.022	0.381	0	0	0.015	0.172	0.009	0.401
0	2350	46.7	0.288	0.427	0	0	0	0.285	0	0
0	2220	46.7	0.251	0.374	0	0	0	0.375	0	0
0	2060	46.7	0.371	0.429	0.029	0.171	0	0	0	0
0	1830	46.7	0.294	0.353	0.029	0.134	0	0.190	0	0
0	1660	46.7	0.245	0.296	0.026	0.109	0	0.324	0	0

stant as the droplet liquid temperature rose toward the steady burning condition. In this period, the diameter often increased slightly for the heavier paraffins due to reduced liquid density at higher liquid temperatures. For comparable conditions, the heat-up period became longer as the molecular weight of the fuel was increased. Since the steady burning liquid temperature is near the boiling temperature, this increase in heat-up time can be directly related to the higher boiling temperatures (requiring a larger liquid temperature rise during heat-up) of the higher molecular weight materials.⁴

Figure 2 also illustrates, in agreement with earlier investigations of fuel droplet combustion^{5,8,9} that the diameter squared plots were reasonably linear during the steady burning period of the droplet. Therefore, the combustion data were summarized by measuring the slope of this curve to yield the burning rate constant (or evaporation rate constant for conditions with negligible ambient oxygen concentration), defined as follows^{1,5}:

$$(d/dt)(d^2) = -K \quad (1)$$

It is known that for fixed ambient conditions, convection causes an increase in droplet burning rates with increasing droplet diameter.^{9,10} In order to reduce burning rate variations due to convection, the slope was measured about a fixed average diameter $1100 \mu \pm 25 \mu$. As apparent from Fig. 2, this diameter was sufficiently removed from the droplet size during the heat-up period to provide a good estimation of the steady burning (or evaporation) rate of the droplet.

The burning (or evaporation) rate constants were taken as the slope of the least squares curve fitted through the data balanced about the average diameter. The constants reported here are average values obtained from four separate tests. The normalized standard deviation of all the tests from the individual averages quoted here was 3.05%. The standard errors of the slopes of the individual least squares curves, used to represent the data, were all less than 4.6%.

Theory

The variable property droplet burning rate model of Goldsmith and Penner⁵ was chosen for comparison with the experimental measurements. This analysis considers the quasi-steady combustion of a fuel droplet during its steady burning period (the state where all the energy reaching the droplet is utilized for the heat of vaporization of the evaporating fuel). Convection is neglected, and reaction is confined to an infinitely thin, spherically symmetric flame surface where fuel and oxidizer combine in stoichiometric proportions. Only concentration diffusion is considered, the pressure is taken to be uniform and radiation is neglected.

In the region between the droplet surface and the flame surface, the fuel specific heat is assumed to be a linear function of temperature. This characteristic helps to provide for the strong temperature dependence of the specific heat of the heavier hydrocarbons. In the same zone, the analysis assumes that the thermal conductivity increases linearly with temperature and is independent of composition. This assumption is not overly restrictive since the thermal conductivities of the fuels under study are similar to those of the combustion products and nitrogen.⁴

In the region outside the flame surface, the thermal conductivity is also assumed to be a linear function of temperature and independent of composition. In this region, the binary diffusivities of all species are taken to be equal. The specific heats of all diffusing species are assumed to be independent of temperature, however, they do not have to be equal. Finally, the Lewis number based on the binary diffusivity and the specific heat of oxygen is assumed to be a constant (although not necessarily unity).

The somewhat inconsistent treatment of specific heat variations in the Goldsmith and Penner analysis (namely,

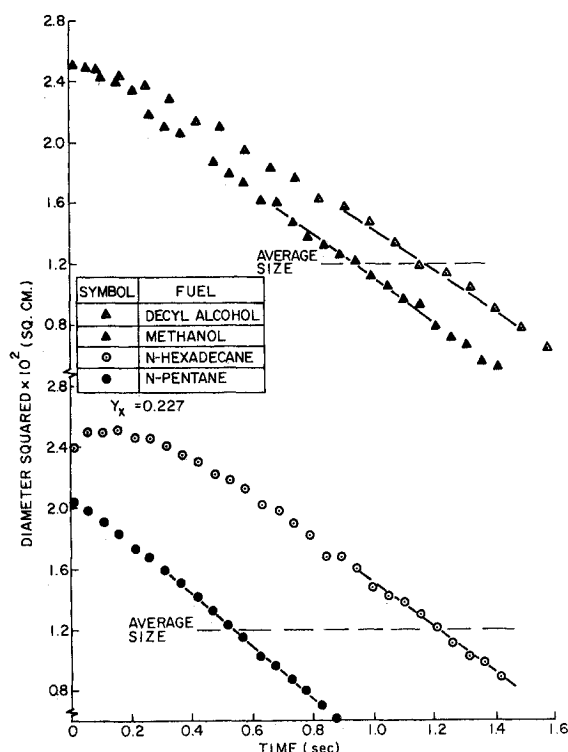


Fig. 2 Typical plots of droplet diameter squared as a function of time, $V_\infty = 62.5$ cm/sec, $T_\infty = 2530^\circ\text{K}$.

allowing for a linear temperature variation of fuel specific heat in the inner region while neglecting any temperature dependence for specific heats in the outer region) has been pointed out by Kassoy and Williams.¹¹ This approach, however, is quite adequate for comparison with the present experiments due to the high-ambient temperatures of these tests (2530°K for the oxidation tests where the outer region must be considered). Under these conditions, the specific heat variation of the light molecules in the outer region is small enough to be neglected in comparison to the other property uncertainties. Lazar¹² has recently extended the Goldsmith and Penner analysis to consider variable specific heats in both regions, for use in situations where the original solution is not adequate.

The test conditions were far removed from the critical point of the fuels under study. For this situation, Williams¹³ has shown that the steady burning temperature of the droplet is only a few degrees below the boiling point of the fuel. Therefore, the heat of vaporization and the liquid density were evaluated at the boiling point. The use of liquid properties at the actual steady burning temperature (computed following Ref. 4), resulted in a slight reduction of the calculated burning rate from the values presented here. However, the difference between the two methods never exceeded 3% over the present experimental conditions.

Table 2 lists properties used in the calculations for a representative sample of the fuels considered in this investigation. The linear thermal conductivity correlations inside and outside the flame were evaluated at the average composition of fuel, oxygen and combustion products in these regions. The values shown in the table pertain to the individual components. For the fuels, the specific heat constants a and b were used directly in the Goldsmith and Penner formulation. However, for oxygen and the combustion products, these parameters were only employed to obtain constant specific heat values at the average temperature outside the flame. This same average temperature condition was also employed to compute the Lewis number pertaining to the outer region. The remaining property correlations required to compute the

Table 2 Selected properties used in the calculations

Material	T_i , °K	ρ_i , g/ml	Δh_i , cal/g	γ_o	H_o , cal/g	a , cal/g°K	b , cal/g°K ²	$\lambda \times 10^4$ ^b , cal/sec cm°K
n-pentane	309	0.611	85.2	3.55	10,750	0.440	0.400	1.97
n-decane	447	0.608	65.3	3.48	10,570	0.440	0.400	1.76
n-hexadecane	560	0.570	53.5	3.46	10,510	0.440	0.400	1.76
Methanol	338	0.745	264.0	1.50	4,760	0.450	0.290	2.95
Butanol	391	0.742	141.5	2.59	7,890	0.450	0.290	3.35
1-decyl-alcohol	506	0.687	88.5	3.03	9,220	0.450	0.290	2.80
Oxygen ^a	0.226	0.034	1.54
Products ^a	0.278	0.083	1.96

^a For these materials a and b were only used to compute constant average specific heats for the region outside the flame.

^b At 1000°K, $\lambda = \lambda_i (T/T_i)$ at any other condition.

Lewis number as well as a complete listing of all liquid and gas phase property values and correlations may be found in Refs. 4 and 12. These references also indicate the sources of all property data.

Two simplified theoretical methods were employed for the determination of the energy release in the reaction zone. In the first approach, dissociation was neglected and the standard heat of reaction for liquid fuel at 298°K was used in the calculations. The correction to the heat of reaction required by the theory,⁵ due to the enthalpy change of the liquid fuel between 298°K and the boiling temperature, is very small and was neglected. In this first method, the assumption of constant specific heats for the oxidizer and products in the outer region also formally requires a correction to the heat of reaction. While the use of average specific heats between the flame and ambient temperatures provides the best values for approximating the transport characteristics of the outer reaction; the chemical energy release in the flame is better represented through the use of average specific heats between the flame and datum temperatures. Due to the high-ambient temperatures of the present experiments, the average specific heats used in the calculation are greater than the values appropriate to the energy release. However, since this correction to the heat of reaction was relatively small (on the order of 5% of the heat of reaction) compared to dissociation effects, it was also neglected.

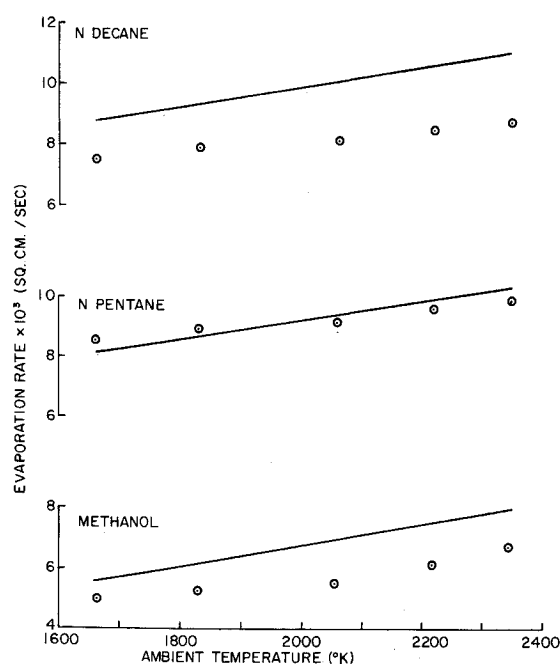


Fig. 3 Theoretical and experimental high temperature droplet evaporation rates, $V_\infty = 46.7$ cm/sec, $Y_z = 0$, $d = 1100 \mu$.

In the second method for determining the energy release in the reaction zone, the heat of reaction was corrected to compensate for dissociation. The corrected heat of reaction was taken to be the actual chemical energy release, in the presence of dissociation, for a stoichiometric mixture at the flame temperature. The correct flame temperature was then determined by iteration.

It was necessary to correct the theoretical burning rate constant for the influence of the flow of burner gas past the test droplet. For steady droplet evaporation or burning, numerous investigators have suggested a convection correlation of the following form

$$\dot{m}/\dot{m}_o = 1 + f(Re, Pr, Sc) \quad (2)$$

where \dot{m}_o is the evaporation rate at no-flow.^{9,10,14-16} At a fixed droplet diameter, the ratio of the flow and no-flow burning rate constants takes the same form as Eq. (2) (Ref. 4). The specific correlation employed for the present calculations follows a form suggested by Rosner¹⁶

$$K/K_o = 1 + 0.278 Re^{1/2} Pr^{1/3} (1 + 1.237/Re Pr^{4/3})^{-1/2} \quad (3)$$

This expression has the advantage of asymptotically approaching the mathematically rigorous results of Fendell et al.¹⁰ for small Peclet numbers as well as agreeing with the data of Frössling,¹⁵ Yuge,¹⁷ and Allender¹⁸ for $10 < Re < 800$.

The properties in Eq. (3) were taken to be those of the ambient gas, as suggested by Combs.¹⁹ Since the Reynolds numbers of the present tests were in the range 1.3–2.2, the flow correction was relatively small, never exceeding 23%.

Results

The first series of tests considered the influence of ambient temperature on high-temperature droplet evaporation. For these tests, the ambient oxygen concentration was negligible and the velocity was maintained constant at 46.7 cm/sec.

Comparisons between the theoretical and experimental results for these test conditions are shown in Fig. 3, for methanol, n-pentane, and n-decane. The theory appears to give a reasonable prediction of the variation of the evaporation rate with temperature. The discrepancy between theory and

Table 3 Comparison of flame temperatures (°K) for standard and corrected heats of reaction

Fuel	Heat of reaction	Ambient oxygen mass fraction		
		0.046	0.227	0.371
Methanol	Std.	2921	4100	4705
	Corr.	2761	2953	3043
n-pentane	Std.	2984	4558	5527
	Corr.	2816	3161	3213
n-decane	Std.	2983	4553	5521
	Corr.	2817	3169	3223

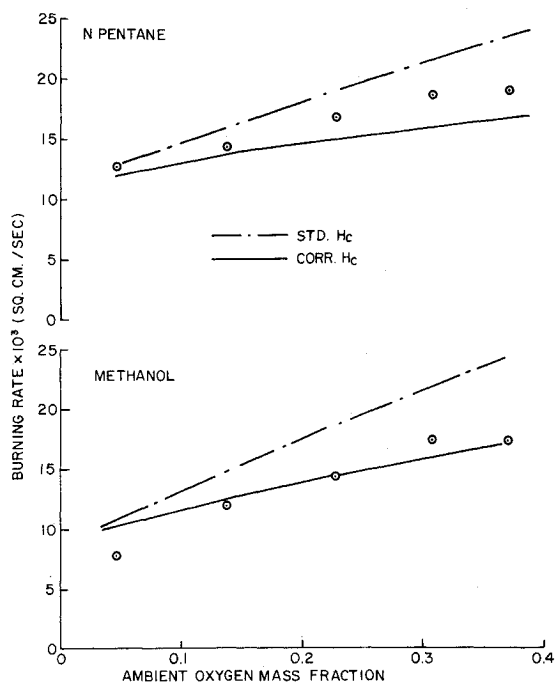


Fig. 4 Theoretical and experimental burning rates at various oxygen concentrations, $V_{\infty} = 62.5$ cm/sec, $T_{\infty} = 2530^{\circ}\text{K}$, $d = 1100$ μ .

experiment is greatest for n-decane, reaching 26% at the highest temperature tested.

Figure 4 shows some of the results of the second series of tests. For these tests, the ambient gas temperature and velocity were maintained essentially constant at 2530°K and 62.5 cm/sec, respectively. The plot shows burning rate measurements for methanol and n-pentane at various ambient oxygen concentrations. The two theoretical curves for each fuel illustrate the effect of using the standard heat of reaction and the heat of reaction corrected for dissociation in the flame. The curves constructed with the corrected heat of reaction show better agreement with the data at high oxygen concentrations. This was true for all the fuels tested. The corrected heat of reaction is also conceptually more satisfying, since the use of the standard heat of reaction yields absurdly high values of flame temperature.⁵ Table 3 compares the flame temperatures given by the two models in the present calculations for a variety of fuels and oxygen concentrations.

The results of the experiments at various ambient oxygen concentrations are examined for a broader range of fuels in Figs. 5 and 6. Figure 5 compares theory and experiment for normal paraffins ranging from n-pentane to n-hexadecane. Figure 6 is a similar comparison for the 1-alcohols ranging from methyl to decyl alcohol.

The theoretical curves shown on these figures were based on the corrected heat of reaction since this approach gave the best representation of the effect of varying oxygen concentration. For the paraffin hydrocarbons, the theoretical results are extended below n-pentane in order to indicate the general trends of the data with fuel type. It should be recognized, however, that the theory may not be applicable to the lighter paraffins due to condensation of water vapor, produced in the reaction zone, on the relatively cool droplet surface.²⁰

For both the alcohols and the paraffins, the trend of the theory with respect to fuel molecular weight is not in good agreement with the experimental results. The theory increasingly overestimates the burning rate of the heavier hydrocarbons with a maximum error of nearly 50% for n-hexadecane at low-ambient oxygen concentrations.

Burning rate calculations were also performed for a constant property analysis. For this model, properties were

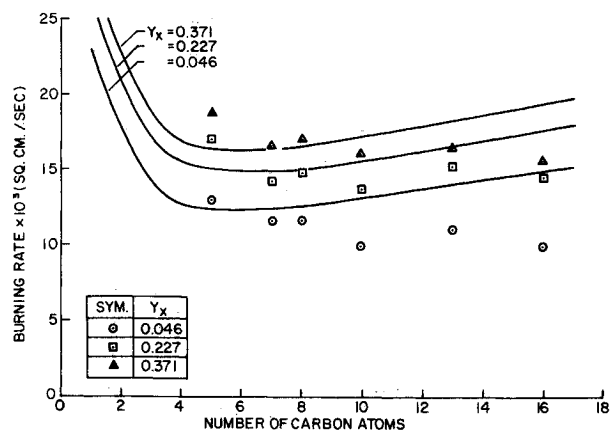


Fig. 5 Theoretical and experimental burning rates for various paraffins, $V_{\infty} = 62.5$ cm/sec, $T_{\infty} = 2530^{\circ}\text{K}$, $d = 1100$ μ .

evaluated at the average composition and log mean average temperature in each region. The trends of these calculations were similar to the present variable property results, with maximum absolute differences of 15% between the two theories.⁴

Discussion

The use of the Goldsmith and Penner⁵ model removes most possibilities for arbitrary property adjustment to achieve agreement between theory and experiment. An apparent exception involves the use of the corrected heat of reaction, however, since this yields a more realistic flame temperature, it is not just a matching procedure.

Naturally, uncertainties in original property values as well as errors introduced by correlating properties to fit the Goldsmith and Penner variable property model influence the computed results. Parametric study indicated, for example, that one of the greatest sources of error was the uncertainty in λ_i , a factor proportional to the thermal conductivity in the inner region. The uncertainty of the computed burning rate is directly proportional to the uncertainty of λ_i . This parameter alone is not known very accurately for the complex gas mixture present in the inner region. In view of this and other property uncertainties, the present discrepancies between theory and experiment are perhaps quite reasonable.

However, the failure of the theory to give the correct trend of the burning rate with increasing fuel molecular weight is somewhat disturbing. This is particularly the case when dealing with fuels in a homologous series (as in the present experiments) which exhibit a fairly systematic variation in thermal

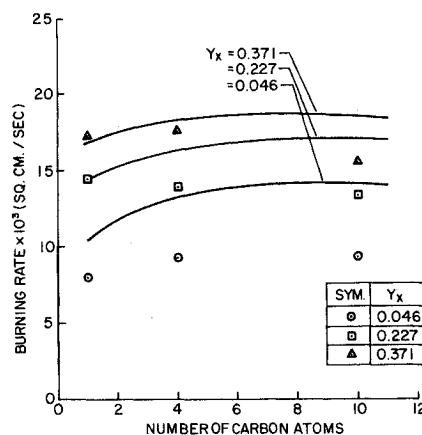


Fig. 6 Theoretical and experimental burning rates for various alcohols, $V_{\infty} = 62.5$ cm/sec, $T_{\infty} = 2530^{\circ}\text{K}$, $d = 1100$ μ .

and transport properties. This failure raises questions that are worthy of further consideration.

The trend of the present experimental data with increasing fuel molecular weight appears to be in general agreement with the findings of other investigators. Aldred and Williams²¹ studied the combustion of normal paraffins ranging from n-pentane to n-hexadecane in motionless air and oxygen at room temperature. Although the experimental conditions are not comparable with the present test conditions, they also observed a reduction of burning rate with increasing fuel molecular weight. The same behavior was observed by Hottel et al.²² during an investigation of the burning rate of heavier paraffins (n hexadecane-eicosane) in a furnace operating at temperatures on the order of 1000°C. Thus the experimental trend of decreasing burning rate with increasing molecular weight, for paraffins heavier than n-pentane, appears to be quite firmly established.

There is less agreement concerning the theoretical influence of molecular weight on the burning rate constant. Using constant property theories, Aldred and Williams,²¹ and Sioui and Roblee²⁴ show predicted burning rates that decrease with increasing molecular weight for the paraffins. Sioui and Roblee seek only to determine empirical methods of selecting properties in order to match the theory with the data, thus agreement in this case is only a measure of the success of the empirical fit and has little fundamental significance.

The methods employed by Aldred and Williams for determining properties are not sufficiently specified to allow evaluation of their procedures. However, a decreasing burning rate with increasing molecular weight can be obtained by a seemingly reasonable selection of properties. For example, the burning rate increase with molecular weight in the present theory is primarily due to reduced liquid density and heat of vaporization at the higher boiling temperatures of the heavier hydrocarbons. This increasing trend can be eliminated by employing room temperature values for these properties (e.g., using room temperature liquid properties, the computed burning rate at $Y_\infty = 0.046$ is 0.0122 and 0.0105 cm²/sec for n-pentane and n-hexadecane as opposed to the present values of 0.0123 and 0.0148 cm²/sec). This is hardly more than empirical fitting, however, since the droplet is close to its boiling point for steady burning at low pressures,¹³ making properties at this condition more appropriate for the analysis.

The method of property selection in the convection correction also affects the predicted influence of molecular weight on the burning rate. The present use of approach conditions tends to minimize the discrepancy between theory and experiment. The use of average properties, as suggested by some authors,⁹ would cause the predicted burning rate to increase even more rapidly with increasing fuel molecular weight (thus further aggravating the error).

Another possible source of error involves the relaxation of temperature gradients within the droplet during the steady burning period. While these gradients are more important during heat-up, both calculations²³ and experiments^{6,25} indicate that temperatures near the center of the droplet are still increasing throughout most of the so-called steady burning period. The sensible energy flowing into the droplet while this relaxation process continues has the effect of reducing the experimentally observed burning rate from the value predicted by the steady burning theory (which assumes a uniform droplet temperature). This effect becomes more significant for materials with high boiling points, since the sensible energy increase is greater in these cases.

Numerical calculations of droplet life histories in Ref. 6 compared results allowing for temperature gradients within the drop with those obtained under the assumption of a uniform droplet temperature at each instant of time. While the study was made for monopropellants, the energy and mass fluxes at the droplet surface were similar to those encountered in the present study. Aside from differences in the heat-up period, the results show that the apparent steady burning

rate is reduced when allowance is made for the continued relaxation of internal temperatures. Differences in the apparent steady burning rates for the two cases were on the order of 5% for materials with volatilities comparable to those of the heavier hydrocarbons employed in the present study. Thus, while this effect probably has influenced the present results, it does not appear to be large enough to entirely explain the discrepancies.

The possibility of liquid phase fuel decomposition was also examined. Since the present tests were conducted at atmospheric pressure, droplet liquid temperatures were limited to values below the normal boiling point of the fuel. At these temperatures, significant liquid phase decomposition is most unlikely during the present experiments. Even for the most adverse case of n-hexadecane, characteristic decomposition times in the liquid phase are several orders of magnitude larger than the droplet lifetimes observed during the present tests.²⁶

In contrast to liquid phase effects, gas phase fuel decomposition in the region between the droplet surface and the oxidation zone could be a contributing factor that is not modeled by the theory. While the details of hydrocarbon decomposition and carbon formation are still debated, it is generally agreed that unsaturated hydrocarbons and radicals are initially formed by thermal cracking and dehydrogenation. Recent studies of sampled diffusion flames have confirmed the presence of significant amounts of unsaturated hydrocarbons on the fuel side of some diffusion flames.²⁷⁻²⁹

The initial formation of unsaturated hydrocarbons involves endothermic steps which would alter the temperature distribution in the gas phase, tending to reduce the evaporation rate of the droplet (structure analysis of a methane-air diffusion flame by Tsuji and Yamaoka has disclosed an endothermic zone on the fuel side of the flame²⁹; similarly, Nakagawa et al. found an inflection in the temperature profile on the fuel side of an ethanol-air flame which they attribute to gas phase cracking).³⁰ Since the heavier hydrocarbons decompose more readily,²⁶ it is feasible that this effect has a greater influence on the evaporation rate than is the case for the lighter hydrocarbons. Whether such processes have contributed to the discrepancies observed in the present investigation can only be conjectured in the absence of more detailed mechanisms and information on the influence of droplet size and convection on this type of decomposition.

In summary, the Goldsmith and Penner theory agreed with the experimental results with a maximum error of 50% over the test range. In view of the approximations of the variable property model, the uncertainties in property values and the crude methods currently available for making convection corrections, these results are perhaps satisfactory. However, the failure of the theory to predict the correct trend with increasing molecular weight raises the possibility of even greater errors for heavier hydrocarbons. This indicates a need for re-examining existing droplet burning rate models if confident predictions of droplet combustion characteristics are to be obtained. In this regard, it is suggested that the role of fuel decomposition between the droplet surface and the oxidation zone should be examined.

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