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Title of Thesis: Flame Propagation at Elevated Temperatures Summary:

A study of flame propagation at elevated temperatures, using the burning velocity as the characteristic of the phenomenon, has been made. Extensive measurements of burning velocity of propane air mixtures over the range of initial temperatures of 0 to 640°C have been made with burners of several lengths and diameters.

Prediction of relative burning velocity values on the basis of the simplified thermal and diffusion theories was made. The agreement with the measured values is good with either scheme in the low temperature region (0 to 550° C), whilst at higher temperatures the thermal theory appears to be the better of the two.

Fairly extensive data on blow-off limits was compiled over the same range of variables as was covered for the burning velocity studies.

Some recommendations about future work that could be carried out on the apparatus used by the author have been made and it is felt that additional useful information can be obtained by such studies.

FLAME PROPAGATION AT ELEVATED

TEMPERATURES

by

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Thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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SUMMARY

A study of flame propagation at elevated temperatures, using the burning velocity as the characteristic of the phenomenon, has been made. Extensive measurements of burning velocity of propane air mixtures over the range of initial temperatures of 0 to 640 °C have been made with burners of several lengths and diameters.

Prediction of relative burning velocity values on the basis of the simplified thermal and diffusion theories was made. The agreement with the measured values is good with either scheme in the low temperature region (0 to 550°C), whilst at higher temperatures the thermal theory appears to be the better of the two.

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Some recommendations about future work that could be carried out on the apparatus used by the author have been made and it is felt that additional useful information can be obtained by such studies.

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NOTATIONS

A [*]	Cross sectional area of the burner tube.		
Af	Surface area of the flame cone.		
a	Concentration of fuel molecules.		
Bi	Free radical recombination factor.		
Cp	Specific heat at constant pressure.		
C'	Concentration of the combustible.		
C n	Concentration of combustion products.		
D	Diffusion coefficient.		
E	Activation energy.		
H	Enthalpy.		
Ħ	Heat of reaction.		
K	Equilibrium constant.		
k	Constant in the reaction rate equation.		
L	Burner length.		
	Number of molecules before and after combustion.		
n_1 and n_2	Number of molecules before and after combustion.		
n _l and n ₂ P	Number of molecules before and after combustion. Pressure.		
n _l and n ₂ P P*	Number of molecules before and after combustion. Pressure. Steric factor.		
n ₁ and n ₂ P P* p	Number of molecules before and after combustion. Pressure. Steric factor. Partial pressure.		
n ₁ and n ₂ P P* P Q	Number of molecules before and after combustion. Pressure. Steric factor. Partial pressure. Heat liberated by combustion of one molecule of fuel.		
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n ₁ and n ₂ P P* Q Q	Number of molecules before and after combustion. Pressure. Steric factor. Partial pressure. Heat liberated by combustion of one molecule of fuel. Reaction rate (usually expressed as the number of molecules reacting per unit volume per second.)		
<pre>n1 and n2 P P* P* Q Q Q R</pre>	Number of molecules before and after combustion. Pressure. Steric factor. Partial pressure. Heat liberated by combustion of one molecule of fuel. Reaction rate (usually expressed as the number of molecules reacting per unit volume per second.) Gas constant.		
n ₁ and n ₂ P P* Q Q R	Number of molecules before and after combustion. Pressure. Steric factor. Partial pressure. Heat liberated by combustion of one molecule of fuel. Reaction rate (usually expressed as the number of molecules reacting per unit volume per second.) Gas constant. Sometimes used for tube radius also, as specified in the text.		
<pre>n1 and n2 P P* P* Q Q R R</pre>	Number of molecules before and after combustion. Pressure. Steric factor. Partial pressure. Heat liberated by combustion of one molecule of fuel. Reaction rate (usually expressed as the number of molecules reacting per unit volume per second.) Gas constant. Sometimes used for tube radius also, as specified in the text. Reynolds number.		
<pre>n1 and n2 P add the second secon</pre>	Number of molecules before and after combustion. Pressure. Steric factor. Partial pressure. Heat liberated by combustion of one molecule of fuel. Reaction rate (usually expressed as the number of molecules reacting per unit volume per second.) Gas constant. Sometimes used for tube radius also, as specified in the text. Reynolds number. An arbitrary radius.		

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Vh	Burning	velocity.
*h	1701 IL III E	ACTOCT ON .

Vg Mean gas velocity.

v An arbitrary velocity.

W Mass rate of combustion per unit area of flame front.

Z Collision frequency.

S Density

λ Thermal conductivity.

μ Viscosity.

V Kinematic viscosity.

 \mathcal{T} Time (used with appropriate subscripts)

 ΔH_c Heat of combustion.

Subscripts

- 1 Initial condition.
- e Equilibrium state.
- f Condition at the flame front.
- i Condition corresponding to ignition.

Sometimes used to denote an arbitrary atomic or molecular species as mentioned in the text.

- m Refers to a mixing process.
- p Product species.
- r Reactant species.

Note: Any departure of the notations from the above is adequately explained in the text.



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INTRODUCTION

The advent of the aircraft gas turbine engine has necessitated the development of high output combustion chambers that have to operate over wide ranges of pressure, temperature and The most exacting requirements are demanded as far as flow rate. stability of operation is concerned. Whilst it is true that present designs are quite successful, they have been accomplished only at the expense of accumulating a vast amount of empirical experience through model and proto-type testing. Confined, too often, to the effects of what may be called 'engineering parameters' on the overall performance, it is conceivable that the importance of the controlling physical, chemical and aerodynamic factors is not appreciated fully. Fundamental research into the nature and effect of these factors may facilitate future development, guite apart from enabling a fuller understanding of these combustion processes to be obtained.

Spontaneous ignition, flame propagation, flame stabilization, spark ignition, mixing of hot and cold air streams, fuel atomization and droplet combustion are some of the basic processes that enter into the overall problem of combustion in a gas turbine engine. Some or all of these problems have been met with even in combustion processes of the Otto and Diesel engines. Nevertheless, systematic investigation into some of the phenomena like spontaneous ignition, flame stabilization and mixing of hot and cold air streams dates back only to one or perhaps two decades. On the other hand, the phenomenon of flame propagation has been investigated for much longer, although the emphasis on aerodynamic factors is of recent origin.

Flame propagation in explosive media is dependent on heat transfer, chemical kinetic and fluid flow phenomena. A vast field is covered in the literature on the influence of such chemical factors as addition of catalysts and inhibitors, variation of reactant compositions and presence of inert gases on flame propa-Influence of turbulence and allied fluid mechanical gation. problems has been investigated in recent years. Effect of initial temperature of the reacting gases on flame propagation has been studied only at relatively low temperatures. Entering, as it does, into both the heat transfer and chemical kinetic aspects, the effect of high temperature on flame propagation is considerable and a study of the latter would be of great value in helping to formulate the theoretical concepts of the problem.

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GENERAL CONSIDERATIONS

The significance of the terms flame and combustion has been rather arbitrary due to their wide usage even before clear scientific concepts were formed. Due, however, to the inherent complications of even a simple combustion process, some of the terminologies like flame front, flame speed and flame temperature do not have very precise meanings. Exothermic chemical reaction between two gases or even in one gas when it reaches explosive proportions gives rise to what is generally connoted as flame. Most flames are associated with emission of light, although examples of non-luminous flames are not infrequent. In fact the emission of light has been used as a criterion for locating flame fronts in moving and stationary gases. It would appear to be more logical to refer to the surface at which the energy release rate is a maximum as the flame front rather than the surface at which the emission of visible light is a maximum. The former surface would also correspond to the surface of steepest temperature rise. The difficulties encountered in locating such a surface are two fold. Firstly, it has not been possible yet to determine satisfactorily the temperature distribution through the flame experimentally and secondly in the reaction zone where equipartition of energy between the various states may not be established, the meaning of temperature is not very precise.

It would be appropriate to discuss at some length the theoretical aspects and experimental considerations of measuring flame temperature as the latter enters into the theories of

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Temperature defines a state of statistical flame propagation. Molecules of a gas possess energies of translation, equilibrium. rotation, vibration and electronic excitation. The energy of translation is practically unquantized whilst the other forms are. In a state of equilibrium, there will be a definite distribution of energy among the different degrees of freedom and in principle the parameters of any one of the energy states may be used for temperature determination. In the absence of such a thermodynamic equilibrium, the temperature determined on the basis of the parameters of one of the energy states should not be regarded as the true temperature. Further, in the case of a mixture of gases, the experimental technique may allow the determination of the temperature derived from one of the energy states (assuming that equilibrium does exist) of a particular molecular species which may bear no relationship to the true gas temperature. Thus one frequently comes across terms like rotational temperature of OH.

Lewis and von Elbe (Ref. 1) and Gaydon and Wolfhard (Ref. 2) feel that departures from equilibrium are slight for small, steadily burning flames of the Bunsen type. Nevertheless considerable anomalies are reported on the temperature determinations based on different energy states of different and sometimes even the same molecular species of complex combustion systems such as hydrocarbonair mixtures.

Conventional methods of temperature measurement are not applicable for flame temperature determination. For instance, use of thermocouples, apart from the practical limitation of finding suitable materials that can withstand temperatures in excess of

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2000 °K, upsets the field of flow and introduces extraneous stabilizing effects. The effects of surface catalysis or inhibition are also likely to appear. Optical methods i.e. spectroscopic and methods based on the change of refractive index have the limitation that they do not give point measurements. Further, interpretation of spectroscopic and interferometric data is often complicated as such interpretation should allow for departures of the system from equilibrium conditions. Establishing a sound calibration is also not easy. In some spectroscopic methods using line reversal techniques, substances like sodium chloride or iron carbonyl are injected into the gas stream and the effects of these on the reaction mechanisms must be investigated and allowed for.

Owing to these fundamental and practical limitations it would appear that the adiabatic flame temperature calculated on the basis of thermodynamic equilibrium from thermo-chemical data is a good enough approximation and will be used hence forth. Whilst it must be admitted that this temperature may not have much of a practical significance, it is certainly a unique function of the variables controlling the flame propagation such as nature of the fuel, fuel oxygen ratio and initial temperature and is therefore a parameter controlling the phenomenon of flame propagation.

When ignition is initiated in a quiescent mixture of explosive gases or in a stream of the latter, the flow of heat and probably chain carriers from the ignition source initiates chemical reaction in the adjacent layer of the explosive medium, which becoming itself a source of heat and chain carriers, initiates chemical reaction in the next layer. Thus a zone burning or reaction propagates through the explosive medium.

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In the case of the one dimensional problem of the explosive medium flowing to and supporting a stationary flame, with the flame front normal to the flow of the gases, the gas velocity must be equal to the velocity of propagation of the combustion wave. The latter, also referred to as the velocity of flame propagation corresponds to the burning velocity, which is defined as the velocity of the flame front with respect to the unburnt gases. The burning velocity is a fundamental variable in the phenomenon of flame propagation and is of practical significance in the problems of flame stability.

In spite of the fundamental significance of the burning velocity, it is very difficult to define it in a way applicable to all systems. If for instance a case of spherical flame is considered where the gas mixture is supplied at the centre of the sphere, the velocity dependence on radius is as shown in Fig. 1.



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The gas velocity at first decreases due to the increase of flow area till the rise in temperature due to combustion and the consequent increase of flow volume makes up for this area increase. Then the gas velocity starts to increase and keeps rising till combustion is completed (strictly speaking till the increase of flow volume can outpace the increase of flow area) and then starts to fall off again. Fig. 2 shows the velocity variation for the case of the plane flame front where the explosive gas mixture is assumed to be flowing from $x = -\infty$ to $x = +\infty$. By definition, the burning velocity $v_b = v_x$ as x approaches $-\infty$, for $x = -\infty$ corresponds to the unburnt gas. For the case of the spherical flame, the choice of a surface separating the burnt and unburnt parts becomes rather difficult. The best choice would appear to be v_b , the velocity corresponding to the minimum on the v_r against r variation. v_b is greater than v_b and would approach the latter asymptotically if the gases started flowing from $r = -\infty$ rather than r = 0; i.e. if the flame front had an infinite radius of curvature.

The choice of a suitable flame surface becomes even harder in the case of the more complex Bunsen burner flame, as will be seen later. Though some amount of arbitrariness enters into the definition of the burning velocity, the determinations of the latter using a given set of experimental conditions would be quite compatible amongst themselves. Care will have to be exercised in comparing burning velocity measurements obtained from using different experimental techniques. This point will be discussed in greater detail later on. In the study of the dependence of

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burning velocity on factors like initial temperature, fuel air ratio, turbulence and others, the arbitrariness of definition does not matter as long as the same experimental technique is used.

Apart from burning velocity, its measurement and dependence on the various parameters, the other problem of flame Flames of the Bunser propagation is that of flame stability. burner type or flames from the port of a tube or nozzle are stable only within certain ranges of gas flow. Considering a Bunsen burner flame, the gas velocity as well as the burning velocity varies over the tube cross section. In the equilibrium position, at some point on the combustion wave profile, the burning velocity is equal to the gas velocity. At all other points, the gas velocity exceeds the burning velocity. If at any point on the flame profile the gas velocity becomes less than the burning velocity. then the flame strikes into the tube against the gas flow. This phenomenon is called 'Flash back'. On the other hand, if the gas velocity at every point on the combustion wave is in excess of the burning velocity, the flame lifts off the rim of the burner and eventually 'blows off'. The limits of flame stability namely blow off and flash back are again intimately connected with the parameters such as initial temperature, chemical composition of the mixture and flow conditions at the burner port.

The work done in connection with this thesis is confined to studies on the dependence of burning velocity of premixed propane air flames on initial temperature. Quite extensive determinations of the effects of burner diameter and mixing length

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on the burning velocity have been made. Flame stability limits have been determined over a similar range of variables.

The subject matter is divided into three main parts, the first one deals with the methods of measuring the burning velocity, its theoretical predictions, qualitative and quantitative discussion of the factors affecting it and the scope and results of the author's experiments. Correlation of these experimental results with the several theories of flame propagation is also carried out. The second part is devoted to theory and experiments on flame stability. The third part covers a general discussion of the work done, conclusions drawn therefrom and recommendations for future work.

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PART I

METHODS OF MEASURING BURNING VELOCITY

The several methods of measuring burning velocity fall into two broad categories depending on whether the flame front is moving or stationary. The methods could also be classified on the basis of the flame shape.

1. Moving flames.

The simplest method, for the case of a moving flame front, consists in using a tube (open at both ends) which is evacuated to start with and then filled with a combustible mixture of the



Fig. 3

desired composition. A spark initiates the combustion and as the flame travels down the tube, the photocells arranged along the tube length (Fig. 3) pick up the light signals. The flame speed

can be calculated on the basis of the time interval between the signals on two photocells. The flame front can be photographed and its area measured from the photograph and the burning velocity = the observed flame speed / flame surface area.

Coward and Hartwell (Ref. 3) were the first to use this method, though in their set up the tube was closed at one end. Gernstein, Levine and Wong (Ref. 3) introduced the idea of using photocells to study the flame movement. Gernstein et al could use shorter lengths of the tube as they chose tubes open at both ends. The flame shape was found to be approximately hemi-

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spherical. Jermain et al (Ref. 3) using a similar method reported difficulties encountered with sonic waves, which were subsequently overcome by lengthening the tube and using sound absorbing devices at the tube ends.

The tube method, as this is referred to, has the advantage that relatively small quantities of the gas mixtures are needed. Linnett (Ref. 4) points out that the cooling effect of the tube walls would be considerable and that the measured values would be low. The extent of the cooling effect may be determined by using tubes of different diameter. A further limitation of the method is that it is suitable for fast flames only.

Another instance of a moving flame front used for burning velocity determination is the soap bubble method. In this method, originally developed by Stevens (Ref. 4), the gas mixture is admitted into a soap bubble and is ignited at the centre by a spark so that a spherical flame spreads through the gas at constant pressure. The course of the flame is followed photographically and the flame speed deduced therefrom. The burning velocity V_b is given by

$$V_{b} = \frac{observed flame speed}{Expansion ratio}$$
where the expansion ratio
ratio = $\left(\frac{Final \ radius \ of \ the \ soap \ bubble}{Initial \ radius \ of \ the \ soap \ bubble}\right)^{3}$ which is also
equal to $\left(\frac{radius \ of \ the \ sphere \ of \ burnt \ gas}{radius \ of \ the \ sphere \ of \ unburnt \ gas}\right)^{3}$. It will be seen
that small discrepancies in the measurement of the soap bubble
radii can throw the value of the expansion ratio and hence the
burning velocity considerably. Whilst the initial diameter of
the soap bubble can be determined quite accurately, the final

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diameter is liable to be in greater error as the flame edge is likely to be diffuse. Distortion of the flame shape is also possible under certain conditions. Gas diffusion from the bubble is also a serious defect of this method as the composition of the mixture may be changing continuously and at any particular time it may be indeterminable. Further the presence of water rules out the possibility of using the method for tests on dry mixtures. However, this objection seems to be overcome, as pointed out by Strehlow and Stuart (Ref. 6) who used a nonaqueous bubble mixture of very low vapour pressure made from a glycerine base.

The constant volume method developed by Fiock (Ref. 5) and used by Lewis and von Elbe (Ref. 1) also employs a spherical flame front. Instead of using a soap bubble, a rigid spherical vessel is employed and the charge of explosive gas is ignited by a spark at the centre. To deduce the burning velocity from the observed flame speed, it is necessary to allow for the rise of pressure. This method as well as the soap bubble method has the advantage that only small quantities of the explosive mixture are needed. The constant volume method does not suffer from gas diffusion as was pointed out for the soap bubble method, although the interpretation of results from the former is more complicated.

The three methods described so far, all have the feature that the aerodynamic aspect of mixing has been completely done away with. In flames of premixed gases the nature of the flame is materially changed by flow factors like turbulence and the degree of mixing. Further these methods are not suitable for study of burning velocity at elevated mixture temperatures.

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For instance in the case of the soap bubble methods, the gas mixture may start reacting with the material of the bubble at these temperatures. In addition, the flames met with in gas turbine combustion systems and other industrial applications correspond to the case of stationary flames in flow streams. The methods of determining burning velocity in flow systems will now be discussed in some detail.

2. Stationary flames.

The most common example of a stationary flame is the Bunsen burner flame. Most of the burning velocity data obtained so far is on flames of this type. The crux of the method lies in determining the area of the flame surface. There has been considerable variation in the choice of the latter.



Considering the case of a symmetrical flame front conical in shape with the cone angle equal to $2 \prec$, the burning velocity at any point on the cone is given by

 $v_b = v_g \sin \mathcal{O}$ where v_g is the gas velocity at the point.

If A is the cross sectional area of the burner and V_g the mean gas velocity and A_f the area of the flame surface corresponding to the separation between the unburnt and burnt parts, then by definition

$$A_{f} \circ V_{b} = A \circ V_{g}$$

where $V_{\mathbf{b}}$ is the normal burning velocity.

In the case of the cylindrical burner, due to the parabolic distribution of flow, the cone assumes the shape shown in Fig. 5.



Fig. 5.

Theoretically, a combustion wave over which the burning velocity is constant can be shown to take the shape of the dotted profile in Fig. 5 (Mache, Ref. 2). Damköhler (Ref. 2) points out that the distortion of the cone shape (i.e. rounding at the tip and overhang at the base) is due to flame thrust.

He also obtains an expression for the pressure difference across a flame front due to expansion and acceleration of the gases. The pressure difference AP across the flame front is given by

 $\Delta P = P_{1} V_{b}^{2} \left(\frac{P_{1}}{P_{f}} - 1 \right)$

where \mathcal{C}_1 is the initial gas density, \mathcal{C}_f the final gas density and V_b is the burning velocity.

In reality the burning velocity is not constant over the entire cone, it being much lower at the burner rim due to cool wall effects. Linnett (Ref. 5) also mentions that the burning velocity at the centre (i.e. tip of the cone) would be much higher than over the rest of it due to heat flow to the tip from all the sides. One arrives at the same conclusion by observing that the heat losses at the centre of burner are a minimum and increase towards the rim. Hence there is further distortion of the flame cone.

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Considerable divergence of opinion exists on two aspects of determining the burning velocity for the burner flame (Ref. 1, 2 and 4). The first one is whether to use the luminous cone or the schlieren cone or the shadow-graph cone and the second one whether to use the angle method or the total area method for obtaining the burning velocity from the desired flame cone.

Unlike the case of the plane flame front where no matter what technique of photography is used the same flame surface area results, in the case of conical shaped flames, the flame surface area differs from the schlieren to the luminous and shadowgraph Broeze (Ref. 8) points out that the schlieren cone is cones. inside the luminous cone and favours using that as the basis. Gaydon and Wolfhard (Ref. 2) suggest that as the schlieren cone gives the surface of the maximum refractive index and as the refractive index is proportional to the inverse of the temperature (neglecting changes of chemical composition) that it corresponds to the surface of the first temperature rise. They refute the suggestion of Van der Poll and Westerdyk (Ref. 2) that most of the reaction takes place in the schlieren cone. Due to the exponential effect of temperature on chemical reaction, the bulk of the reaction takes place at a high temperature say around 1000 °C or over and the schlieren effect (varying as I/T) would be quite small at this It is likely therefore that the reaction zone may temperature. be much nearer the luminous cone than the schlieren cone. The significance of the shadow cone in relation to the temperature variation or the growth of reaction is not too well understood. However, Wohl (Ref. 9) mentions that the outer edge of the shadow

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cone is inside of the visible cone and separated from it by a few tenths of a millimeter, and further that the separation between the visible and schlieren cones is of the order of 0.2 mms.

From the foregoing it can be seen that for a burner of 1 cm diameter the deviation in the flame surface area would be of the order of 4% whether the luminous or the shadowgraph or the schlieren cone is considered and this deviation becomes smaller as the burner size increases. Further if one is content with the relative variation of the burning velocity, the choice of the cone surface is immaterial as long as there is consistency in the choice.

There are three methods generally used for deducing the burning velocity from the flame cone, the total area method, the partial area method and the angle method.



Fig. 6.

Fig. 7.

Fig. 8.

In the total area method the flame surface is divided into a series of strips normal to the burner axis, as shown in Fig. 6 and by approximating each strip with a frustum of a cone or any other solid of revolution, the surface area of the flame is established. Thus the surface area of the strip at the base of

,t

the flame is given by $\pi s_1 (r_1 + r_2)$ and total area, on the basis of a series of such conical strips is equal to $\leq \pi (r_n + r_{n+1}) s_n$. It may be necessary to replace the tip portion by a spherical segment whose area will be 2 π rh where h is the height of the segment and r the sphere radius (Fig. 7).

Gaydon and Wolfhard (Ref. 2) suggest another method for estimating the surface area. Their method is illustrated in Fig. 8. The surface area of element AF is $* s_1 (r_1 + r_2)$ and the area of figure AFGC is given by $1/2 h_1 (r_1 + r_2)$. From Fig. 8, $h_1 = s_1 \cos \alpha$. If at each section say GF, the radius i.e. GF is increased in the ratio of $1/\cos \alpha$, points like H are obtained and the curve DE is established. Planimetering figure DEBC, one obtaines the value of $\sum_n 1/2 s_n (r_n + r_{n+1})$ and the flame surface area which is equal to $\sum_n * s_n (r_n + r_{n+1})$ is given by 2 * x area of figure DEBC.

Once the area of the flame surface is obtained, the burning velocity may be determined from the relationship

$$V_{b} = V_{g} \cdot \frac{A}{A_{f}}$$

The main objection levelled against this method is that no account is taken of the cold wall effects at the rim and the tip effects which are such that the burning velocity is too low at the rim and too high at the tip. However if the diameter of the burner is large (say of the order of one inch) these effects are quite small:

The partial area method used by Dery (Ref. 1) eliminates the tip and base effects and should be favoured for burners of small diameter. Here the areas at the tip and base are neglected and the burning velocity is calculated by dividing the flow through the annular area between two radii over which the tip and base effects are absent, by the corresponding frustum area. The angle method also uses the same principle except that the burning velocity is calculated by multiplying the mean gas velocity by the sine of the mean cone angle of the frustum.

It may be observed again, as was remarked when discussing the choice of the flame surface, that what really matters is consistency in the method used as any of them can only give relative variations of the burning velocity. Consequently, one has to be very cautious when comparing values determined on the basis of the different methods.

An improvement in the burner method which facilitates the burning velocity calculation is the use of a nozzle at the burner top. Mache and Hebra (Ref. 2) demonstrated that the use of a nozzle gave a uniform velocity profile and hence a flame surface approximating a perfect geometrical cone. The use of such a nozzle would save the labour of determination of the area or the mean cone angle of the relatively irregular flame surface of an ordinary burner. On the other hand, the evaluation of parameters like mixing time of the gas mixture before combustion becomes quite difficult.

Lewis and von Elbe (Ref. 1) have used another method for determining the burning velocity for burner flames. This consists in injecting into the flow stream fine particles which can follow the accelerations in the flow stream. By illuminating them strongly, the flow lines can be observed. Further by using a stroboscopic photography technique, the particle velocity can be

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determined. From such measurements, the burning velocity can be deduced. Magnesium oxide particles were used for such studies. Effect of particle inertia is hard to allow for. Also surface effects of the particles may introduce additional complications. However, this method has the advantage that variation of the burning velocity over the burner cross section can be studied.

A discussion of the methods of burning velocity measurement is incomplete without a mention of the Flat flame method developed by Egerton and Powling (Ref. 10).



By an ingenious design of the burner, a condition when the burning velocity is just equal to the gas velocity is obtained with the result that a flat flame is maintained. The burner is illustrated in Fig. 9. The flame could be photographed either directly or for a schlieren image and the same area is obtained. This method, unfortunately, has the limitation that

it can be used only for slow flames where the burning velocity does not exceed 15 cms/sec.

The continuous flow burner method is the mostly widely used of all methods of burning velocity determination, due to the fact that the apparatus needed and technique used are very simple. However, considerably larger quantities of gas mixtures are needed than for the other methods. But this is a secondary consideration for flames of such common gases as methane, propane or hydrogen.

THEORIES OF FLAME PROPAGATION

The first attempt at formulating a theory of flame propagation was made by Mallard and Le Chatelier (Ref. 11).



They assumed that below a certain T_{f} temperature T_{i} - the ignition temperature, no reaction took place and that once this temperature was reached, reaction proceeded at a constant rate till the maximum temperature T_{f} was

attained. The temperature distribution is shown in Fig. 10. The gas mixture, flowing from $x = -\infty$ at temperature T_1 gets heated to temperature T_1 purely by conduction and reaction takes place in the region x = 0 to $x = \langle ,$ and its temperature rises to T_f and remains at T_f , if there are no heat losses. Assuming constant specific heat and coefficient of thermal conductivity for the gas in the temperature range of T_1 to T_f , the temperature distribution may be expressed by the equation

$$\frac{d^2T}{dx^2} - \frac{WCP}{\lambda} \frac{dT}{dx} + \frac{9Q}{\lambda} = 0 \dots (1)$$

where W is the mass rate of combustion per unit area of the flame front (and is equal to $\langle_1 V_b\rangle$, q the reaction rate (expressed as number of molecules reacting per unit volume per sec) and Q the heat liberated by combustion of one molecule of the fuel. The term $\frac{W Cp}{\lambda} \frac{d T}{d x}$ corresponds to the heat conducted away by the flowing gas and the term $\frac{q}{\lambda}$ corresponds to the heat produced by chemical reaction.

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For $-\infty < x < 0$, q = 0 and equation (1) simplifies to

$$\frac{d^2T}{dx^2} - \frac{W C p}{\lambda} \frac{dT}{dx} = 0 \qquad \dots \dots (2)$$

For $0 < x < \varepsilon$, q is constant and

$$\frac{d^2T}{dx^2} - \frac{w c_P}{\lambda} \frac{dT}{dx} + \frac{q_Q}{\lambda} = 0 \qquad \dots \dots (3)$$

With the boundary conditions x = 0, $T = T_1$

 $x = \varepsilon$, $T = T_f$

and the continuity conditions i.e. $(\frac{d T}{d x})$ shall be the same for solutions from both (2) and (3), the equation

$$\frac{T_i - T_i}{T_f - T_i} = \frac{1 - e^{-\varphi}}{\varphi} \text{ is obtained where } \varphi = \frac{W C_P E}{\lambda}$$

If a_1 is the initial concentration of the fuel molecules (expressed as number of molecules / unit vol of initial mixture), then $\varepsilon = \frac{V_b \cdot a_1}{q}$ (valid as q, the reaction rate is constant). Substituting for $W = \varsigma_1 V_b$ and for ε ,

$$\mathcal{G} = \frac{C_{P} \, \mathcal{G}_{I} \, V_{b}^{2} \, \alpha_{I}}{\lambda \, \mathcal{G}_{I}}$$

Further as \mathcal{C} is proportional to ε , the flame thickness, which is small, $e^{-\mathcal{C}}$ can be expanded as a series up to the first two terms, whence

$$\frac{T_{i}-T_{i}}{T_{i}-T_{i}} = \frac{1-(1-\frac{4}{3}+\frac{6^{2}}{3}-\frac{1-6}{2})}{\frac{6}{3}} = 1-\frac{6}{2}$$

or

$$V_{b} = \left[\frac{2\lambda q_{b}}{c_{p} q_{1} \alpha_{1}} \left(\frac{T_{f} - T_{i}}{T_{f} - T_{i}}\right)\right]^{\frac{1}{2}} \qquad \dots \dots (4)$$

 $\varphi = 2 \frac{T_f - T_i}{T_f - T_i}$ which gives

The obvious short-comings of this simplified theory are (1) the assumption of an ignition temperature below which no reaction occurs, and

(2) the assumption of a constant reaction rate in the reaction zone.

Self sustaining combustion is possible only if the rate of heat production by the chemical reaction is in excess of the rate at which heat is lost to the surroundings. Thus the minimum temperature at which a gas mixture may ignite and burn to an explosion, which is defined as the ignition temperature, is dependent on the rate of heat loss from the system. It can be seen, therefore, that the ignition temperature is not an absolute quantity and cannot have a physical significance without reference to a particular system. This fact has been confirmed by experiments. Thus for hydrogen air mixtures, containing about 28% of hydrogen, ignition temperatures from 467 to 700 °C are reported (Ref. 12).

Further, chemical kinetic studies have established the exponential variation of reaction rate with temperature and on the basis of the simple collision theory

$$q = P Z e^{-E/RT}$$

where E is the activation energy for the reaction, Z the collision frequency and P*a probability factor called the steric factor. The exponential term $e^{-E/RT}$, on the basis of the kinetic theory of gases, just corresponds to the fraction of total particle collisions involving a joint energy greater than E.

Zeldovich, Frank-Kamenetsky and Semenov (Ref. 13), while retaining the approach of Mallard and Le Chatelier, compromised the latters' theory to conform with the chemical kinetic evidence

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of a temperature dependent reaction rate. They retained the notion of the ignition temperature, but demonstrated that the final expression for V_{b} is independent of the value chosen for T_{i} . Thus in equation (4) for V_b the term

$$\frac{q_{i}}{a_{i}} (\mathbf{T}_{f} - \mathbf{T}_{i}), \text{ which is really } \frac{1}{a_{i}} \int_{T_{i}}^{T_{f}} d\tau \text{ if q is}$$

not a constant, can be written as $\frac{1}{a_{i}} \int_{T_{i}}^{T_{f}} dT$ where **T'** is an arbitrary temperature.

On the premise that most of the reaction takes place very near the maximum temperature, Semenov showed that for a monomolecular reaction where

$$\begin{aligned} \mathcal{Q} &= k \alpha e^{-\frac{E}{RT}} \\ \mathbf{I} &= \frac{1}{\alpha_1} \int_{T^1}^{T_f} \mathcal{Q} dT &= \frac{k e^{-\frac{E}{R}T_f}}{T_f - T_1} \frac{T_1}{T_f} \left(\frac{R T_f^2}{E}\right)^2 \end{aligned}$$

The equation for V_b becomes

ar

$$\mathbf{v}_{\mathbf{b}} = \begin{bmatrix} \frac{2}{\sqrt{p}} \frac{\lambda}{S_{1}} & \frac{k e^{-E/k} T_{f}}{(T_{f} - T_{1})^{2}} & \frac{T_{1}}{T_{f}} & \left(\frac{R T_{f}^{2}}{E}\right)^{2} \end{bmatrix}^{1/2}$$

Allowing for the variation of Cp and λ and the change in the number of molecules after the combustion, this equation becomes

$$\mathbf{V}_{\mathbf{b}} = \left[\frac{2\lambda_{\mathbf{f}} C_{\mathbf{p},\mathbf{f}} \mathbf{k}}{S_{\mathbf{i}} (\Delta H_{\mathbf{c}})^{2}} \frac{T_{\mathbf{i}}}{T_{\mathbf{f}}} \left(\frac{\lambda}{\mathbf{p}_{\mathbf{f}} c_{\mathbf{p}}} \right)_{\mathbf{f}} \left(\frac{\eta_{\mathbf{i}}}{r_{\mathbf{f}}} \right) \left(\frac{\mathbf{R} \mathbf{f}_{\mathbf{f}}^{2}}{\mathbf{E}} \right)^{2} C_{\mathbf{p},\mathbf{f}}^{2} \mathbf{f}_{\mathbf{f}}^{2} \right]^{\frac{1}{2}} \dots (5)$$

where the property values with subscripts f refer to conditions at the flame.

In this equation, D is the diffusion coefficient, $\frac{n_1}{n_2}$ the ratio of the number of molecules before and after combustion and ΔH_c the heat of combustion of unit mass of the initial gas mixture which is also equal to \overline{Cp} ($T_f - T_1$), if \overline{Cp} is the average specific heat between temperatures T_1 and T_f . For a bimolecular reaction, the expression for V_b takes the form

$$\mathbf{V}_{\mathbf{b}} = \left[\frac{2\lambda_{f} \, \mathrm{k} \, \alpha_{1} \, \mathrm{C}_{\mathrm{F}, \mathrm{f}}}{P_{1} \, (\Delta^{1+1})^{3}} \left(\frac{T_{1}}{T_{f}}\right)^{2} \left(\frac{\lambda}{\mathrm{D}\mathcal{C}\mathcal{F}}\right)_{\mathrm{f}}^{2} \left(\frac{\gamma_{1}}{n_{2}}\right)^{2} \left(\frac{\mathrm{R} \, \mathrm{r}_{\mathrm{f}}^{2}}{\mathrm{E}}\right)^{3} \, \mathrm{e}^{\frac{\mathrm{R}}{\mathrm{R}}\mathrm{r}_{\mathrm{f}}}\right]^{\gamma_{2}} \dots (6)$$

The accuracy of equations (5) and (6) is good if the fictitious ignition temperature T' approaches T_f , i.e. if the activation energy is large so that the extent of reaction taking place very near T_f is far in excess of that occurring earlier. Semenov (Ref. 13) emphasizes that these equations are satisfactory for $T_f - T' \leq 0.25 T_f$. For a bimolecular reaction, for values of $RT_{f/E} > 0.1$, $T_f - T'$ becomes greater than 0.25 T_f and the accuracy of equation (6) deteriorates. The validity of equation (5) is tolerably good over a wider range.

The foregoing analyses considered the phenomenon of flame propagation as purely thermal in character and that the reaction rate was proportional to the number of successful collisions of the reactant molecules. However, there is sufficient evidence to indicate that chain reactions with atoms and free radicals initiating and accelerating the growth of the reaction may be the controlling processes, at least in some gas-phase reactions.

Tanford (Ref. 15) observed a very good correlation between the equilibrium hydrogen atom concentration and burning velocity for several mixtures of moist carbon monoxide flames in air and oxygen. Tanford and Pease proposed that the concentration of the hydrogen atom at any point determined the rate of reaction. They demonstrated that diffusion of hydrogen atoms and other active centres upstream into the unburnt gas was greatly in excess of the local equilibrium concentrations. Their equation for $V_{\rm b}$, generalized to include all the atoms and free radicals, is:

$$V_{b} = \left[\sum_{i} \frac{k_{i} P_{i} D_{i} \bar{L} c'}{B_{i} c''}\right]^{2} \dots (7)$$

where i refers to each of the species considered and k_i is the rate constant for interaction with the combustible, p_i the partial pressure of the i th species in the burnt gases, D_i the diffusion coefficient into the unburnt gas, C' the concentration of the combustible, C" the concentration of the combustion products, B_i a factor which allows for the loss of the radicals through recombination, and \overline{L} the number of molecules per unit volume of the gas at some appropriate temperature.

Attention is drawn to the fact that while this theory usually referred to as the Diffusion theory - accounts for the importance of free atoms and radicals on the reaction, the formation of these is considered as being thermal. The possibility of the active particles being formed due to chain reactions is discounted and the concentration at any point in the reaction zone is attributed entirely to diffusion from the flame front. Another limitation of this theory is the assumption that the reaction zone is isothermal, which is used to facilitate the solution of the diffusion equations.

Both the theories described so far, i.e. the thermal and the diffusion theories, suffer from the fact that the picture of flame propagation is grossly simplified. However, both have been found to explain certain sets of experimental data quite satisfactorily. Nevertheless, these theories and their many derivatives

cannot be regarded as general solutions to the problem. Hirschfelder and his co-workers (Ref. 17) have made the most systematic investigation of the problem by starting off with equations of conservation of mass, energy and momentum and the transport equations for the various chemical species. By making suitable assumptions, they have reduced the equations in such a way that differential analyzers can be used for getting the solution. Starting off with the same set of basic equations, von Karman and Penner (Ref. 18) have formulated the eigen value problem and solved the equations for the cases of hydrazine decomposition and ozone decomposition. The solution of the equations for such relatively simple reactions has necessitated the use of very involved mathematical techniques. One wonders if such a procedure would be fruitful at all for a complicated reaction like hydro-carbon oxidation, where the available chemical kinetic data is very limited. If in fact a knowledge of every reaction step is required to predict the normal velocity of flame propagation or other flame properties, one may conclude that the problem is solved in principle but much too complicated to be of any practical value. The multiplicity of the kinetic possibilities and the dependence of the latter on such indeterminate factors as wall effects may indeed make the search for solutions of this type almost hopeless.

Hence, theories that can connect the properties of flame propagation without special reference to or at least with a minimum of such reference to chemical kinetic aspects would be very desirable. Thus, if the simplified theories can at least serve as

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good first approximations, their usefulness is considerable. The agreement of the predictions made on the basis of the thermal and diffusion theories with experimental results will be investigated later on.

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PRESENT EXPERIMENTAL INVESTIGATIONS

1. Description of the Apparatus

Fig. 11 shows a schematic diagram of the experimental apparatus used. It consisted of a gas to air counterflow heat exchanger which served to heat the air going to the burner. A propane fired combustion chamber supplied hot gases to the gas side of Fig. 12 shows the constructional features of the heat exchanger. the heat exchanger and combustion chamber. The heat exchanger consisted of a 1" O.D. outer tube arranged in the form of a U and the inner tubes (air side) were two 3/8" 0.D. tubes also bent into U form. A construction like this eliminated troubles with differential expansion. Stainless steel was used for all parts of the heat exchanger and combustion chamber. The latter had a cast alumina refractory liner and provision was made for air cooling of its outer walls.

Air leaving the heat exchanger passed through a straightener section and four chromel alumel thermocouples located in the latter measured the air temperature. The flow disturbance caused by these thermocouples and the 90° bend in the exit from the heat exchanger was removed by a series of stainless steel meshes followed by a contracting nozzle. Fig. 13 shows a half sectional view of the straightener section. The double wall construction was adopted to reduce heat conduction from the thermocouple wells. The contracting nozzle was designed to ensure a uniform velocity distribution at the throat section.

Four circular pieces of stainless steel meshes (mesh size 28 x 30) held apart by snug fitting spacers, were used and the

FIG. 11 - SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS



thermocouples were located between the first two. A 16 gauge hypodermic needle passing axially through the straightener section served as the propane jet. (This can be seen in Fig. 12). The burner tubes made of vycor or quartz fitted into the socket at the end of the straightener section and asbestos rope was used to pack the joint. For burner sizes less than 1" in diameter, the tubes were enlarged at the end to fit into the socket.

The heat exchanger, combustion chamber and the straightener section were located in a transite box filled with fibre frax (blown aluminum oxide, used as insulator) to reduce the heat losses. The large mass of insulation acted both as a sink and source of heat and helped in damping down any temperature fluctuations. The burner tube was also insulated with fibre frax held in place by a 3" diameter pyrex tube located concentrically with the burner.

The temperature of the air passing up the burner tube was controlled by the propane flow into the combustion chamber. For fine control, the secondary air flow to the combustion chamber was varied, which changed the maximum gas temperature at the heat exchanger entry. The temperature of the air, as measured by the thermocouples in the straightener section, could be held to within \pm 5°C in the range of 0 - 700°C; although control up to \pm 3°C was achieved in some cases when more time was allowed for the rig to reach a steady state.

Air was supplied to the burner from the laboratory air lines and a swirl separator was included in the line to separate any oil or water from the air. The flow was measured with a differential manometer connected across either of two orifices,

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one suitable for high and the other for low flow rates. These orifices were calibrated against a standard orifice and check calibrations were made from time to time.

The propane supply was taken from the laboratory propane lines. Liquified Gas Utilities Ltd., Lachine, supplied this gas, and the composition by volume was:

> Propane 94 - 97 % (usually 95%) Propylene 3 - 5 % Butane Ethane Traces less than 1 % Isobutane

and traces of sulphur.

The propane flow was measured with a differential manometer connected to a suitable orifice in the line, which was calibrated against a precision wet gas meter. As with the other orifices, the calibration was checked frequently.

The thermocouples used in the straightener section and their circuits were all calibrated and extensive calibrations were conducted to determine the extent of lag due to conduction effects. Temperature traverses were also made along the length of the burner tube using a platinum and platinum + 13% rhodium thermocouple (wires were 0.005" in diameter). For the case of the longest burner used (about 20"), the temperature drop along the length was of the order of 3°C in 550°C, which indicated that the insulation around the burner was quite effective.

A general view of the instrument panel is shown in Fig. 14.



2. Details of the experimental technique

The burning velocity determination was made using the total area of the visible inner cone of the flame. A 35 mm. Robot camera with a 1.9 f lens was used in combination with a Robot no. 2 close up lens for photographing the flame. Ilford high speed HP3 film was used for all the flame photography work.

After a series of preliminary tests, it was found that an exposure of 1/500 second gave the best definition for the inner cone and it was decided to standardize on this. The films were developed in Kodak D-11 or Ilford ID-2 developer and fixed in Kodak rapid hardening fixer. Care was taken to ensure reproducible conditions during processing of the films.

The films were projected on to a screen with a still projector and the outline of the inner cone traced therefrom. A magnification of about 8 to 1 was used which aided in reducing the extent of error in tracing and area measurement of the flame cone. The area was measured by approximating the profile with regular geometric figures and calculating the area of surface of revolution of the several elements and then summing these together.

The procedure used in carrying out the experiments was as follows. At a given value of the preheat temperature and air flow rate, the propane flow was varied over a range of values and at each one of these, the flame was photographed. (Actually at any point, two pictures of the flame were taken so that a reliable mean area could be obtained). The range of propane flow was, of course, limited by flash back or blow off, depending on the magnitude of the gas velocity in the burner, at the fuel

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weak end and by the merging of the inner and outer cones, as in a diffusion flame, at the fuel rich end.

The gas velocity in the burner tube, for a set of experiments of this nature, remained perceptibly constant, neglecting the change in velocity due to changes in the propane flow, which was of the order of 3%. Thus the mixing time between the propane and air and the Reynolds number remained constant and by changing the air flow rate, the effect of the change of mixing time was studied. Further as the range of stability differed from one air flow setting to another, a wide range of air fuel ratios could be covered by choosing four or five values of the air flow.

Tests, as described above, were conducted at several preheat temperatures in the range of 0 to 640°C and over a range of burner tube lengths and diameters.

3. Experimental Results

Most of the burning velocity measurements were made on a 1" diameter Vycor tube (96% silica) with an effective mixing length between the propane jet and air of 16.38". In addition, tests were conducted with mixing lengths in the range of 10.5" to 20.5" for the 1" diameter burner and some on a 0.652" diameter and 17.75" mixing length burner.

Fig. 15 shows the results obtained from all these experiments. The burning velocity V_b is shown as a function of air fuel ratio (by weight) with the initial temperature as a parameter. At a constant value of the latter, the burning velocity measurements show a scatter of about \pm 5%, which is due to change of factors



Air Fuel Ratio (by weight).



like mixing time, mixing length and burner diameter. This is particularly noticeable for $T_1 = 414$ °C and 515 °C where V_b was determined over a wide range of burner lengths and diameters.

It can be seen from Fig. 15 that all the measurements correspond to values of air fuel ratio less than 15.5, i.e. to the fuel rich side of stoichiometric. The reason is that at larger values of the air fuel ratio, the flame would lift off the burner rim, at some point, and the two dimensional flame photograph would give a spurious indication of the flame surface area. On reducing the air flow, the flame would flash into the tube. The only way to have the flame burning at air fuel ratios in excess of the stoichiometric would have been to use an external stabilizing influence i.e. by having a wire mesh across the burner tube end or by heating the burner rim. Using a wire mesh, the flow pattern would be changed and the flame would assume a multiconical structure which is unsuitable for burning velocity measure-Heating of rim with a pilot flame or electrically, whilst, ments. no doubt, widening the limits of stability, would affect the preheat temperature and complicate the problem. So it was decided to investigate the region within the normal limits of stability of the burner.

From Fig. 15, it can be seen that the burning velocity, at any given temperature T_1 , increases at first, reaches a maximum and then starts to fall off with air fuel ratio. The maximum can be clearly seen for the curves at some of the preheat temperatures while for others, the lack of data at high values of air fuel ratio prevents a well defined maximum being shown.

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Fig. 16 shows the variation of the maximum burning velocity with the inverse of the preheat temperature (in degrees Kelvin) on a logarithmic basis. On the same figure is shown the results of Dugger's work at the N.A.C.A. Laboratories (Ref. 19). These measurements were made using the total area of the outer edge of the shadow cone of a Bunsen burner flame. It is seen that the agreement between Dugger's results and those of the author is good. This is very encouraging, as quite often, in the literature, doubt is expressed over the extent of reproducibility of burning velocity data.

On the same figure (16) is also shown the burning velocity results plotted on a constant air fuel ratio basis. As mentioned earlier the range of air fuel ratios refers to mixtures richer than stoichiometric.

Fig. 17 is typical of the extent of scatter that was found in the burning velocity determination. This set of experiments was done with a single burner (constant length and diameter) and at a preheat temperature of 591 °C (864°K). The temperature was held close to \pm 4°C. The only parameters that were changed were the air fuel ratio and the air flow rate (the equivalent of mixing time). Four settings of air flow were used. The points corresponding to a constant value of mixing time do not follow a common trend and the scatter appears to be random. However, this scatter is nowhere in excess of \pm 5% from the mean curve.

The effect of change of tube diameter can be seen from Fig. 18 where the burning velocity data for two burner sizes is plotted against the air fuel ratio for $T_1 = 515$ °C (788°K). An

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attempt has been made to separate the points referring to different mixing times, with more success than in the case of Fig. 17.

Two interesting features may be observed from Fig. 18. Firstly, the scatter of the points for the 0.652" diameter burner for both $\mathcal{T}_{m}(\text{mixing time}) = 0.0343$ and 0.0375 seconds is very much less than for the 1" diameter burner under similar conditions. The Reynolds number for the smaller diameter burner is 2380 for one set of points and 2640 for the other, whilst for the larger burner the Reynolds number is in the range of 3440 to 3970. Thus the flow, with the smaller burner, remains laminar and more nearly developed. For, the minimum length of tube required for the flow to be fully developed may be expressed as

 $L_m = constant \cdot Re \cdot d$.

The constant is about 0.03 (Ref. 2). With the 0.652" diameter burner, the product Re . d is smaller than with the 1" burner, both due to reduced Reynolds number and diameter.

Hence the flame propagation in the case of the 0.652" diameter burner is more laminar and the burning velocity results are less affected by turbulence. But with the 1" diameter burner, the Reynolds number corresponds to the critical range and the nature of flow may be changing from laminar to turbulent (probably small scale turbulence) which could give rise to the scatter of the points.

The other interesting feature is that the burning velocity with the smaller burner is lower than with the larger one over the full range of air fuel ratios. The reason for this lies in the fact that the flame on the small size burner is more affected by cooling at the rim. The burning velocity measured by the total

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area method would be lower for small diameter burners, where the flame area at the rim forms a larger proportion of the total area than with burners of larger diameter.

It may be observed, in passing, that the rounding at the tip of the cone, which means that the burning velocity at the tip is higher than it should be, does not compensate for the rim effect, as the area contributed by the tip portion of the cone is small in relation to that contributed by the base.

Attention may also be drawn to the fact that the dependence of burning velocity on Reynolds number is not systematic, as can be seen from Fig. 18. This is substantiated by the data presented in Fig. 19, which refers to $T_1 = 556$ °C (829°K).

The effect of change of mixing length on burning velocity is shown in Fig. 20 at two values of the preheat temperature, namely 515°C and 414 °C. The range of mixing lengths covered was from 10.5" to 20.5" at 515°C and from 16" to 20.5" at 414°C. In the latter case, the burning velocity data shows a random scatter although the points lie within \pm 5% from the mean line. The same is true of the results at 515°C except that with $L_m = 10.5$ ", the points lie everywhere above the mean line. This may be explained as follows.

Due to the shortness of the tube (for $L_m = 10.5$ "), the flow has had no chance to develop into the normal parabolic profile and the flame has a tendency to become turbulent. (Refer to Gaydon and Wolfhard (2), who point out that insufficient length rather than high Reynolds number can give a turbulent flame). This is

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Air Fuel Ratio (by weight)



not the case for $L_m = 16.38$ ", 18.34" etc. For, although the difference in burner length is not sufficient to ensure a fully developed flow pattern - the latter condition being attained only asymptotically with $L_m = 0.03$ Re . d, which is of the order of 10 ft. - it is still sufficient to make laminar flame propagation more probable. Imperfect mixing and flow which is not developed, with $L_m = 10.50$ ", is responsible for giving a turbulent flame and hence an apparently high value of V_b .



One may appreciate this by referring to Fig. 21, as the flame surface area measured on the assumption of bulent eatly aggerated) a laminar flame is smaller than that possessed by the multi-cellular turbulent flame front.

Fig. 21

In spite of this systematic scatter, the V_b values at 515°C are within \pm 6% from the mean curve, when the mixing time has changed from 0.0238 secs to 0.0476 secs., a variation of \pm 33.4% over the mean value. This indicates that the effect of change of mixing time \mathcal{T}_m (or the mixing length L_m) on V_b is not significant when the magnitude of \mathcal{T}_m is about a few hundredths of a second.

One may have expected that the preflame reactions, the extent of which is dependent on \mathcal{T}_m , would have affected the problem of flame propagation more significantly. For instance, in the phenomenon of spontaneous ignition, these preflame reactions are responsible for maintaining a stable flame front.

Although cool flames in continuous flow systems have been observed for propane air mixtures around 450 - 500 °C (Ref. 47), the residence time (usually referred to as induction time in cool flame and slow oxidation studies) is of the order of a few minutes or more. Extensive data on high temperature spontaneous ignition, connecting the ignition delay (i.e. the time required for a flame front to appear after fuel is admitted into the hot air stream) with the air temperature is available for a number of hydrocarbons.

Fig. 22 shows the spontaneous ignition data for two hydrocarbons of the paraffin series,n-hexane $(C_{6}H_{14})$ and ethane $(C_{2}H_{6})$. This data, taken from the work of Mullins (Ref. 20) was obtained from spontaneous combustion studies in a vitiated air stream (i.e. air stream containing combustion products arising from burning some fuel in order to preheat it). Unfortunately, no data for propane air mixtures was available. However, for the purposes of the present discussion only the order of magnitude of the ignition delay is of interest and it will suffice to use the data from Fig. 22.

The results of Mullins' investigations are confined to preheat temperatures in the range of 750 °C to 1000 °C. From theoretical considerations, it can be shown that the temperature and ignition delay for the spontaneous ignition process are connected by the equation.

$$Log(\mathcal{T}_{i} T_{i}^{V_{2}}) = Constant + \frac{E}{RT_{i}} \dots \dots (8)$$

(Refer to the appendix III for the derivation of this relationship).

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Thus one would obtain a straight line by plotting log $(\mathcal{T}_i \cdot \mathbf{T}_1^{1/2})$ against $1/\mathbf{T}_1$ and it is possible to extrapolate the ignition delay results to lower temperatures.

The ignition delay for propane air mixtures, assuming that it is of the same order of magnitude as for ethane air and n-Hexane air, is about 57 seconds at 515°C (788 °K). In actual fact, as the activation energy for propane oxidation based on low temperature studies, is less than that for ethane oxidation, this value may be high. In any case, \mathcal{T}_i could not be much smaller than about 40 seconds. Hence the residence time \mathcal{T}_m , allowed in the flame propagation studies described above, is only about 0.06% (for $\mathcal{T}_m =$ 0.0238 secs.) and 0.12% (for $\mathcal{T}_m = 0.0476$ secs) of \mathcal{T}_i . It is therefore understandable that changes in burner length did not affect the measured values of V_h significantly.

Even at $T_1 = 700$ °C, which was about the maximum value of the preheat temperature that could be attained with the apparatus used by the author, the magnitude of \mathcal{T}_i would be about 0.24 seconds in comparison with a mean value for \mathcal{T}_m of about 0.03 seconds, which is only 12.5% of \mathcal{T}_i . Over a similar range of burner lengths i.e. 10.50" to 20.50" that was covered for $T_1 = 515$ °C, the residence time would vary from about 8 to 16% of \mathcal{T}_i . Bearing in mind that the measurement of burning velocity was not reproducible to closer than $\pm 5\%$ due to uncertainties of area measurement, turbulence (both flame created and otherwise) and the inherent limitations of the technique, the effect of changes in \mathcal{T}_m would be just beginning to be discernible at about the maximum temperature of the present series of experiments. It is justifiable therefore to conclude that in the range of preheat temperatures studied presently i.e. 0 to 640 °C and the range of burner lengths and diameters covered, the burning velocity is independent of the latter factors. It is emphasized, however, that the dependence of ignition delay on initial temperature is exponential and that the conditions may change considerably for $T_1 =$ 750 °C. Since the present experiments could not be extended to this region, due to the limitations of the equipment, it is difficult to say whether a stable flame can be had at the rim without it stabilizing inside the tube and if it could be had, whether the burning velocity would still be independent of mixing time.

Fig. 23 shows the results obtained by Bula (Ref.52), with the same apparatus, on the effect of varying the oxygen content of 'air' on burning velocity. In one case nitrogen and the other oxygen were introduced into the air stream in order to change the proportion of oxygen in the oxygen-nitrogen mixture. The curves of $V_{b max}$ against T_1 have been extrapolated and they seem to converge at $T_1 =$ O°K. Although in practice, the propane will have liquified much before then and flame propagation will not extend to that temperature, the fact that the curves start at $T_1 = 0$ °K, fit in with the Arrhenius picture of reaction rates.

Fig. 24 shows the data from Fig. 23 replotted to show the combined effect of initial temperature and composition of the oxygen nitrogen mixture on the maximum burning velocity. The latter has been expressed as a percent of the value corresponding to natural air. It is seen that with an enrichment of the oxygen content by 18.5%, the $V_{\rm b\ max}$ increases by about 30 to 50%.

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Maximum Burning Velocity Cms/sec.



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(Weight fraction)

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Similarly when the oxygen content is reduced by 12.5%, the decrease in $V_{b max}$ is between 25 and 45%.

4. Correlation of experimental results

An attempt has been made to predict the relative variation of the maximum burning velocity with initial temperature on the basis of the simplified thermal theory and the diffusion theory. The relative variations seem to be predicted fairly well according to both these theories.

As can be seen from equations (5) and (6), the flame temperature T_f enters explicity into the equations for the burning velocity V_b . In equation (7) the term T_f does not appear directly, although the active particle concentrations p_i in the reaction zone depend on the flame temperature. In the earlier discussion on flame temperature (page 5), the difficulties in measuring this quantity were mentioned and it was proposed to use the adiabatic flame temperature calculated on the basis of thermochemical data instead of the actual value.

In the case of constant pressure combustion (neglecting the small pressure drop across the flame front),

$$\overline{H}_{f} = \overline{H}_{I} + \int_{T}^{T_{f}} (C_{Pf} - C_{PI}) dT \qquad \dots \dots (9)$$

where $\overline{H_1}$ and $\overline{H_f}$ are the heats of reaction at the initial temperature T_1 and final temperature T_f and Cp_1 and Cp_f the initial and final specific heats of the gases respectively. Equation (9) is just another way of expressing the conservation of energy

$$\sum_{p} m_{ep}(H_{fp}) = \Delta H_{c} + \sum_{r} m_{ir} H_{ir} \dots (10)$$

where $m_{e p}$ = the equilibrium concentration of product p at T_{f} (in moles)

 $m_1 r =$ the concentration of reactant r at T_1 (in moles) $H_f p =$ enthalpy per mole of product p at T_f $H_1 p =$ enthalpy per mole of product p at T_1 $H_1 r =$ enthalpy per mole of reactant r at T_1 $\Delta H_c =$ heat liberated by combustion.

and the summation is carried over all the product molecules p (allowing for dissociation) and reactant molecules r.

The calculation of the adiabatic flame temperature for a given initial temperature and air fuel ratio has to be done by a process of trial and error, as the composition of the mixture at the flame front is required for the flame temperature evaluation whilst the composition itself depends on the latter. Various systematic methods of simplifying the calculation are available and Appendix I (a) indicates, in detail, the method used by the author.

Fig. 25 shows the adiabatic flame temperature, calculated with heat losses not taken into account, as a function of air fuel ratio and preheat temperature for propane air mixtures. The maximum value of the adiabatic flame temperature with an initial mixture temperature of 25°C is 2285°K as against a measured value by sodium line reversal method of 2198 °K quoted by Lewis and von Elbe (Ref. 1). This difference of 3.8% between the theoretical and measured values could be easily accounted for by heat losses. Assuming that the heat losses would be of the same order of magnitude over the full range of initial temperatures, no



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discrepancy would be introduced in calculating the relative burning velocity by using the adiabatic flame temperature in place of the actual one .

Correlation with the thermal theory:-

Propane oxidation stoichiometrically is represented by

$$C_3H_8 + 5 O_2 = 3 CO_2 + 4 H_2O \dots(11)$$

but kinetically the rate controlling step may be only a monomolecular or bimolecular reaction. Hence a correlation of the maximum burning velocity data with both the monomolecular and bimolecular expressions has been carried out. Referring to pages 23 and 24,

$$V_{\rm b} = \left[\frac{2\lambda_f C_{\rm Pf} k}{\varrho_{\rm i} (\Delta H_c)^2} \frac{T_{\rm i}}{T_f} \left(\frac{\lambda}{D\varrho_{\rm CP}}\right)_f \frac{\eta_{\rm i}}{\eta_{\rm c}} \left(\frac{RT_f^2}{E}\right)^2 e^{-E/RT_f}\right]^{1/2}$$

for a monomolecular reaction and

$$V_{b} = \left[\frac{2\lambda_{f}c_{pf}^{2}ka_{1}}{S_{1}(\Lambda H_{c})^{3}}\left(\frac{\Gamma_{1}}{\Gamma_{f}}\right)^{2}\left(\frac{\lambda}{DSCp}\right)_{f}^{2}\left(\frac{n_{1}}{N_{2}}\right)^{2}\left(\frac{RT_{f}^{2}}{E}\right)^{3}e^{\frac{E}{R}T_{f}}\right]^{1/2}$$

for a bimolecular reaction.

 n_1/n_2 , the ratio of the number of molecules before and after combustion does not change very much with temperature. For instance, as can be seen from Appendix I (c), for an air fuel ratio of about 14.5 (which corresponds to the region of maximum V_b), n_1/n_2 is 0.941 for $T_f = 2250$ °K and is 0.930 for $T_f = 2600$ °K. Since V_b is proportional to $\sqrt{n_1/n_2}$ for the monomolecular and to n_1/n_2 for the bimolecular cases, the variation of V_b due to this change of n_1/n_2 is only 0.58% and 1.17% respectively. Hence, as far as the temperature dependent parts of the above expressions are concerned, the term n_1/n_2 may be safely omitted. Further $\Delta H_c = \overline{C}p (T_f - T_1)$ where $\overline{C}p$ is an average specific heat for the gas mixture in the range of T_1 to T_f . Cp is approximately proportional to $T^{0.09}$ in the region T = 0 to 2600 °K and $\overline{C}p$ may be taken as proportional to Cp_f and hence to $T_f^{0.09}$. Over the same range, λ may be taken to vary with $T^{0.84}$. Assuming that the diffusion coefficient D is proportional to μ/ς or \mathcal{V} (Ref. 21) which varies with temperature as $T^{1.67}$, D is proportional to $T^{1.67}$ (Ref. to Appendix II for a discussion on the variation of property values with temperature). Since ς_1 is proportional to T_1^{-1} , the expression for V_b on the monomolecular basis becomes

$$V_{\rm b} \propto \left[T_{\rm i}^2 T_{\rm f}^{3\cdot83} \left(\frac{R}{E}\right)^2 \frac{e^{-E/RT_{\rm f}}}{(T_{\rm f}-T_{\rm i})^2} \right]^{1/2} \dots (12)$$

and since a_1 is the number of fuel molecules per unit volume of the initial mixture, a_1 is proportioned to T_1^{-1} , the equation for V_b for the bimolecular case takes the form

$$\mathbf{V}_{\mathrm{b}} \propto \left[\mathbf{T}_{\mathrm{i}}^{2} \mathbf{T}_{\mathrm{f}}^{4\cdot9} \left(\frac{\mathbf{R}}{\mathbf{E}}\right)^{3} \frac{e^{-\mathbf{E}/\mathbf{R} \mathbf{T}_{\mathrm{f}}}}{(\mathbf{T}_{\mathrm{f}}-\mathbf{T}_{\mathrm{i}})^{3}} \right]^{1/2} \dots (13)$$

R is the gas constant and is independent of temperature while E, the activation energy is probably temperature dependent. But no data is available on its variation. In fact the only activation energy data available for propane oxidation is from low temperature slow oxidation studies and the validity of using such results in the present calculations is questionable. However, in the absence of any other information, the values of E from slow oxidation kinetic studies are used. Jost (Ref. 12) quotes values of activation energy for propane oxidation in the range of 29 to 38 kcals per gm mole. The relative values of $V_{b\ max}$ on the monomolecular basis were calculated using an activation energy of 40 kcals and these values were normalized so that the calculated and experimental values were coincident at $T_1 = 305^{\circ}C$ (578°K). This value of E was chosen to get the best agreement between the predicted and actual values of $V_{b\ max}$.

The value of T_{f} used in equation (12) and (13) to determine $V_{b \max}$ was taken from Fig. (25) at the air fuel ratio giving the maximum value for V_{b} in Fig. 15.

A value of 36 kcals for E was found to give the best prediction for $V_{b max}$ on the basis of the bimolecular equation (13). Values of $V_{b max}$ determined according to equation (12) and (13) are shown as functions of T_1 in Figs. (26) and (27). The experimental results are also shown for purposes of comparison.

Fig. (28) shows the deviation of the calculated values of $V_{\rm b\ max}$ from the experimental mean values expressed as percentages of the latter, as a function of T_1 . Over the range of initial temperatures covered, the relative maximum burning velocity values are predicted to within -6.7% and +5.7% by the monomolecular thermal theory (with E = 40 kcal/gm mole) and to within -6.8% and +8.7% by the bimolecular thermal theory (with E = 36 kcal/gm mole).

This agreement is very good indeed when it is borne in mind that the experimental values of V_b are reproducible to only <u>+</u> 5%. It would be possible to fit in the curve predicted on the basis of the thermal theory more closely with the experimental data, if one assumes a variable activation energy.

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Fig. 26.

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Initial Temperature °K

Fig. 27.

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It is surprising that some authors like Zeldovich and Frank-Kamenetsky (Ref. 2) have expressed doubts as to the applicability of equations (5) and (6) for hydrocarbon flames. The reason is perhaps due to the possibility that in such a reaction the kinetics may be of a high order and the controlling step, even if it were a simple monomolecular or bimolecular reaction, might change with temperature. In other words, the reaction rate may not vary with temperature according to any simple exponential law with a fixed value for E, due to the large number of alternative chain reactions, whose importance on the overall reaction may be affected by temperature differently.

It will also be recalled that the accuracy of equations (5) and (6) is not very good at low values of activation energy (Ref. to page 24). This is particularly true for the bimolecular case and Semenov (Ref. 13) goes as far as recommending that the latter equation be restricted to cases with $E \ge 40$ kcals/mole. He demonstrates that for values of E smaller than 40 kcals, the thickness of the reaction zone becomes large enough to contradict the fundamental assumption of the thermal theory that most of the reaction takes place very near the flame temperature.

In spite of these limitations, the agreement between the calculated and observed values is quite good, it being slightly better with the monomolecular equation. However, it is not possible to draw any conclusion as to whether the actual reaction is controlled by a monomolecular or bimolecular step.

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Correlation with Diffusion theory:-

On the basis of the diffusion theory of Tanford and Pease, the burning velocity is given by (Ref. to page 25)

$$\mathbf{v}_{\mathbf{b}} = \left[\sum_{i} \frac{k_{i} \not\models_{i} \ \mathbf{D}_{i} \ \mathbf{L} \ c'}{\mathbf{B}_{i} \ c''} \right]^{2}$$

The ratio of the concentration of the combustible to the combustion products at the flame front, c'/c'' must be some function of n_1/n_2 and is therefore almost independent of temperature (Refer to page 56).

The radical recombination factor B_i may also be taken as independent of temperature. Therefore

$$V_{b} \propto \left[\sum_{i} p_{i} D_{i} \overline{L} \right]^{1/2} \qquad \dots \dots (14)$$

where \overline{L} , the number of molecules per unit volume is proportional to T_m^{-1} , T_m being the mean reaction zone temperature.

Tanford (Ref. 16) suggests that the value of the diffusion coefficient D_i , which changes throughout the reaction zone, be replaced by a mean value reckoned at a temperature $T_m = k T_f$, k being about 0.7. Following this suggestion, Dugger (Ref. 19) shows that

$$\sum_{i} P_{i} D_{i} \propto \sum_{i} P_{i} D_{i,r} \frac{T_{i}^{2}}{T_{f}^{\circ \cdot 33}}$$

where $D_{i r}$ is the relative diffusion coefficient of the ith radical with respect to the others. Thus the expression for V_b becomes

$$V_{\rm b} \subset \left[\left(\sum_{i} P_i P_i P_{i,r} \right) \frac{T_i^2}{T_i^4} \right]^{\frac{1}{2}} \qquad \dots (15)$$

Tanford suggests (Ref. 16) that for hydrocarbon oxidation, the diffusion of hydrogen, hydroxyl and oxygen atoms be considered. There may be other free radicals and atoms which may also play an important part in the reaction but it is likely that being heavier than H atoms, their diffusion coefficients relative to the latter would in all probability be small. In fact the relative diffusion

coefficients for H, OH and O atoms are roughly in the ratio of

6.5:1:1 and $\leq p_1 D_1 r$ may be taken as $(6.5 p_H + p_{0H} + p_0)$.

The equilibrium concentrations of H, OH and O were calculated from thermochemical data. The dissociation of these atoms and radicals may be represented by

	$H_20 \Rightarrow 1/2 H_2 + 0H$]
	$1/2 H_2 = H$,(16)
	$1/2 0_2 \rightleftharpoons 0$	i A
and	$K_{4} = \frac{P_{OH} \sqrt{P_{H_{2}}}}{P_{H_{2}O}}$]
	$\mathbf{K}_5 = \frac{\mathbf{P}_H}{\sqrt{\mathbf{P}_{H_2}}}$	(17)
	$\mathbf{K}_6 = \frac{\mathbf{p}_o}{\sqrt{\mathbf{p}_o}}$	

where K refers to the equilibrium constant and p the concentration expressed as a partial pressure. The actual method of computing $p_{\rm H}$, $p_{\rm OH}$ and $p_{\rm O}$ is outlined in Appendix I (b).

Figures (26), (27) and (28) show the values of the maximum burning velocity predicted according to the diffusion theory both on the basis of the hydrogen atoms alone and on the basis of


Initial Temperature °K

Fig. 28.

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H, OH and O concentrations. These values are normalized so that the predicted $V_{b\max}$ value at 305°C (er 578°K) corresponds to the experimental one. It is seen that for T_1 less than 305°C (or T_f less than 2412°K), the values predicted on the basis of H atoms only and on the basis of H, OH and O atoms, are almost identical whilst for higher values of T_1 (or of T_f) the predictions on the latter basis are lower than on the former.

A resume of the predicted values of $V_{b max}$ and the experimental values is given in Table I. The deviation of the predicted values from the experimental values is given as percent of the latter.

An interesting correlation between log V_{b}/T_{f} and log $1/T_{f}$ has been observed and as can be seen from Fig. 29, for a constant value of AFR, a straight line relationship exists between these two quantities. This stresses the importance of the flame temperature on burning velocity, for a given set of initial conditions.

A unique relationship between V_b and T_f given by

fitted with the experimental data to within 7%. In equation (23-a), V_b is expressed in cms/sec and T_f in degrees Kelvin. R_{eq} is the equivalence ratio i.e. the ratio of the actual AFR to the stoichiometric AFR. The above relationship is valid for $0.63 < R_{eq} < 0.93$.

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Initial temperature of propane air mixture.		Experi- mental max. burn- ing velocity	Semenev's mono- molecular equation. E = 40 kcals/mole		Semenov's bi- molecular equation. E = 36 kcals/mole		Tanford and Pease 6.5 p _H + p _{OH} + p _O		Tanford and Pease p _H only.	
T1°C	T ₁ °K	cms/sec	cms/sec	Deviation from ex- perimental value %	cms/sec	Deviation from ex- perimental value %	cms/sec	Deviation from ex- perimental value %	cms/sec	Deviation from ex- perimental value %
25	298	48.0	46.5	-3.12	44.3	-7.70	50.4	+5.00	50.5	-4.95
160	433	87.3	82.8	-5.15	80.9	-7.25	86.4	-1.03	86.1	-1.38
255	528	118.2	116.0	-1.86	115.0	-2.71	117.8	-0.34	117.8	-0.34
305	578	136.4	136.4	0.00	136.4	0.00	136.4	0.00	136.4	0.00
355	628	153.1	158.8	+3.72	160.1	+4.56	156.3	+2.09	156.9	+2.48
414	687	177.0	188.8	+6.66	192.5	+8.76	180.9	+2.20	181.3	+2.43
515	788	238.0	248.6	+4.45	258.3	+8.57	232.6	-2.27	235.3	-1.13
556	829	282.0	276.5	-1.95	289.4	+2.62	255.7	-9.33	259.3	-8.05
591	864	317.0	302.0	-4.73	318.4	+0.44	276.2	-12.86	280.9	-11.40
640	913	365.0	340.0	-6.85	361.8	-0.88	305.5	-17.70	311.3	-14.70

.

Note. The experimental maximum burning velocities were taken from Figure 15.

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$$v_{\rm b} = \frac{T_{\rm f}}{10} \left(\frac{T_{\rm f}}{2512}\right)^{2\,9\cdot72} R_{\rm eq} - 11\cdot10 \dots(23-{\rm b})$$

Thus for $T_1 = 829$ °K and AFR = 13.4 ($R_{eq} = 0.868$), $T_f = 2512$ °K (Fig. 25) and V_b obtained from (23-b) becomes 251.2 cms/sec as against a measured value of 274 cms/sec (Fig. 19), which gives a deviation of 8.4% from the latter. The agreement is worse at low values of R_{eq} and T_f . For instance, for $R_{eq} = 0.74$ and $T_f = 2075$ °K, the value for V_b calculated from (23-b) is 30% lower than the experimental value.

DISCUSSION

Thermal versus diffusion theories

A correlation of the burning velocity data over an initial temperature range of $0 - 640^{\circ}$ C was obtained with both the thermal theory of Semenov and the diffusion theory of Tanford and Pease. In the range of preheat temperatures of $0 - 550 \,^{\circ}$ C, the prediction by either of the two theories is equally good. However, for higher temperatures, the thermal theory appears to be superior to the diffusion theory, as the latter gives low values for burning velocity.

In the thermal theory, apart from the initial state of the reacting mixture, only three quantities enter the expression for the burning velocity; the flame temperature, the activation energy and the steric factor. The value of activation energy for a large number of hydrocarbons is close to 40 kcals/gm mole. It can be shown that the value of burning velocity predicted on the basis of the thermal theory does not vary too greatly for small changes in E.

	$T_1 = 298 {}^{\circ}K$	T ₁ = 578 °K	T ₁ = 864 °K
E = 34 kcals/mole	44.8	136.4	315.0
= 36 "	44.3	136.4	318.4
= 38 "	43.8	136.4	321.4

TABLE II

(a) Burning velocity in cms/sec predicted by Semenov's bimolecular equation.

	T ₁ = 298 °K	T ₁ = 578 °K	T ₁ = 864 °K
E = 38 kcals/mole	46.9	136.4	299.0
= 40 ¤	46.4	136.4	302.0
= 42 *	45.9	136.4	305.1

TABLE II (cont'd)

(b) burning velocity in cms/sec predicted by Semenov's monomolecular equation.

Thus in Table II, values of V_b are predicted according to Semenov's equations using different values of the activation energy. The steric factor (which corresponds to the normalizing constant) is chosen to give a constant value of V_b at $T_1 = 578$ °K. It is seen from Table II that a change of about $\pm 5.6\%$ in E gives a maximum change in V_b of about $\pm 1.1\%$.

The steric factor is the probability that molecular collisions are successful i.e. it depends on whether a definite orientation of the molecules is required before a collision is successful. In fact it is extremely difficult to define this factor for the case of the kinetically complex hydrocarbon oxidation and as may be expected, no numerical values are available. It is therefore taken as the proportionality constant and obtained by comparing the predicted relative value with the experimental value.

From the foregoing, it will be seen that for a given set of initial conditions the thermal theory merely expresses the burning velocity as a function of the flame temperature. The same is true of the diffusion theory as well, when it is borne in mind that the equilibrium concentration is a function of the flame temperature and the relative diffusion coefficient of the particular active particle is a constant as long as the density of the rest of the gas medium does not change too greatly.

Thus in reality both the thermal theory and the diffusion theory express the burning velocity as functions of the flame temperature. This similarity extends even further due to the fact that the equations of heat conduction and diffusion are almost identical. Whether one or the other of the theories explains the actual phenomenon may be determined by comparing the predictions made by them with experimental data covering all the parameters.

The effect of initial temperature on the relative burning velocity over the range of 0-550 °C is predicted quite well by both the theories. Similar conclusions have been reached at by other workers but at lower temperatures; for instance by Dugger for temperatures between -73°C and 343°C (Ref. 19).

The influence of inert gases on burning velocity has been studied to throw light on the relative importance of heat conduction and diffusion on the flame propagation phenomenon. The thermal theories predict that

$$V_{\rm h} \propto \sqrt{\lambda}$$
(24)

whilst the diffusion theories predict that

$$V_{\rm b} \propto \sqrt{\mathcal{D}}_{\rm i}$$
(25)

If it is possible to measure V_b for gas mixtures having all properties except λ and D_1 the same, then it would be possible to establish which of the two theories represents the actual process better.

Thus by replacing helium with argon in a hydrocarbonoxygen and inert gas mixture the flame temperature and heat capacity per unit volume (i.e. Q Cp) and equilibrium concentrations remain fairly constant, while the thermal conductivity and the diffusion coefficient differ. Where as a test of this nature may be expected to give valuable information, the ambiguity of the problem persists as reliable values of the thermal conductivity of the gas mixture at the flame temperature and the diffusion coefficient of the active particles are not available.

Studies on inert gas addition covering a series of hydrocarbons like methane, acetylene, ethylene are reported by Mellish and Linnett (Ref. 23), Freidman (Ref. 24) Simon (Ref. 25) and others. But no such experiments on propane flames have been reported. Results given by Mellish and Linnett show that $\frac{V_{b}}{V_{b}}$ as determined experimentally lies between the values determined by the thermal theory and the diffusion theory.

The diffusion coefficients were obtained from considerations of the kinetic theory of gases and the diffusion coefficient of the ith component into the gas mixture was estimated from

where N_k is the mole fraction of the kth component and D_{ik} the diffusion coefficient of the ith into the kth substance.

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The thermal conductivity of the mixture was calculated from

$$\lambda = \sum_{k} N_{k}^{1.5} \lambda_{k} \qquad \dots (27)$$

The index 1.5 given as an average value by Freidman (Ref. 24) on the basis of empirical correlations of some experimental values is hard to justify.

Taking
$$\lambda = \sum_{k} N_{k} \lambda_{k}$$
,

the value of $(\frac{V_b \text{ helium}}{V_b \text{ argon}})$ based on the thermal theory for a gas mixture containing 10% methane, 71% inert gas (by volume) and the rest oxygen becomes 2.00 instead of 2.65 obtained by using equation (27). In fact, Bartholome (Ref. 27) using theoretical thermal conductivities at the flame temperature obtained a value of 1.32 for this ratio. By way of comparison $\frac{V_b \text{ helium}}{V_b \text{ argon}}$ was equal to 1.39 experimentally and 1.32 on the basis of the diffusion theory (taking into account H, OH and O atoms).

In the absence of reliable data of the property values at the temperature of and applicable to conditions similar to those existing in the reaction zone, it is not possible to use the results of the studies made with inert gases to determine the relative importance of the two theories of flame propagation.

The pressure dependence of burning velocity is considered by some as the cruicial test between the two schemes of flame propagation. Unfortunately, the experimental results on the effect of pressure on burning velocity are not too reliable. The burner methods of measurement suffer from the fact that the thickness of the flame increases at low pressures and hence the location of the flame surface becomes more arbitrary that at atmospheric or higher pressures. For the same reason and also due to increased heat losses, other methods like the soap bubble method also suffer.

The dependence of burning velocity on pressure may be expressed as

In the Semenov equations (Eq. 5 and 6), the only pressure dependent terms are $\mathbf{a_1}$ and $\boldsymbol{\beta_1}$ both of which are directly proportional to P. Thus for the monomolecular case,

$$v_b \ll \sqrt{1/s}, \quad or \ll P_i^{-1/2}$$

and for the bimolecular case

$$v_b \propto \sqrt{a_{1/S_1}}$$
 or independent of pressure.

The terms p_i , D_i and L of the Tanford and Pease equation (Eq.7) are dependent on pressure. D_i is inversely and L is directly proportional to pressure and hence D_i . L is independent of pressure. Therefore, the only pressure dependent term is p_i , the equilibrium partial pressure of the ith component. This would be approximately inversely proportional to \sqrt{P} , assuming that the free radicals and atoms are formed from binary dissociations. Thus V_b is proportional to $P^{-0.25}$ according to the diffusion theory of Tanford and Pease.

The experimental evidence on the variation of burning velocity with pressure is very confusing. Values of n (Eq. 28) in the range of 0 to 0.49 have been quoted in the literature (Refs. 1, 2 and 25) for several hydrocarbon flames. Egerton and Sen (Ref. 28) using the flat flame method for burning velocity measurement found n to be 0.49 for methane air and 0.30 for propane air flames.

From the foregoing, it is seen that the importance of the thermal theory over the diffusion theory or vice versa cannot be established conclusively. It is seen that the effect of some of the parameters is predicted fairly well with either scheme, while both fail to explain other experimental facts. The fact that both the theories have been obtained by making some very bold approximations makes them liable to considerable deviations from results of experiments.

As to the importance of diffusion itself, very useful information may be obtained by studies on hydrocarbons containing deuterium in place of hydrogen where by all the properties except the diffusion coefficient would be the same. However, some complications may be introduced due to the influence of deuterium on the chemical reaction. The dissociation equilibrium is also liable to be affected.

Effect of Turbulence



When the flow in the burner tube is turbulent, the flame surface assumes a wrinkled appearence and the random fluctuation of the flame is responsible for giving the so called brush in the flame picture. In fact the inner

Fig. 30

and outer boundaries of the brush (Fig. 30) correspond to the limits of fluctuation of the flame. The extent to which the smooth surface of a laminar flame breaks up depends on the degree of turbulence.

Laminar flow in pipes is not usually maintained above Re = 2000. Between Re = 2000 and 5000, the transition region extends and beyond Re = about 5000, the flow is usually turbulent. However, if the pipe is smooth and the flow at entry uniform and there are no obstructions in the flow, laminar flow may be had for Re > 2000 and turbulence may not set in till much later than Re = 5000.

For the investigations presently reported, the Reynolds number was in the range of 2000 to 8000. However, as the flow at entry into the tube was quite uniform - due to a contracting cone which was preceeded by meshes to smoothen the flow, turbulence might have set in only towards the top end of the range. But owing to the fact that the flow was in the transition region over a good portion of the test range the results may have suffered from effects of sudden changes in the flow pattern. Referring to Fig. 19, one Whilst it has been possible to may see that this is the case. separate the curves for the different Reynolds numbers, the dependence on the latter appears to be unsystematic. This can be attributed to turbulence which is unpredictable for flow in the transition region.

It may be felt that the measurements of burning velocity may be in doubt due to the ambiguity of the flow nature. The chances of this appear to be small due to two reasons. Firstly,

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as can be seen from the instantaneous schlieren pictures of turbulent flames (Ref. 1), the base of the flame cone is not wrinkled or broken up even for Re = 10,000. As the major contribution to the flame surface area is from the base, it is safe to assume that turbulence effects may not throw the area into error very much. Secondly, the area used for determining V_b was that corresponding to the outer edge of the inner cone and Damköhler (Ref. 1) has shown that the burning velocity determined thus (for a turbulent flame) could be identified as the laminar burning velocity.

Bollinger and Williams (Ref. 29) point out that this conclusion of Damköhler may only be fortuitous. Nevertheless, the maximum burning velocity, at room temperature, obtained during the present investigations, is 48.5 cms/sec which compares favourably with 45 cms/sec for laminar flames, given by Bollinger and Williams. For the tests at the room temperature, the Reynolds number is higher than for the tests at higher temperatures. Thus, apart from flame created turbulence, which may be expected to be more serious at the elevated temperatures, turbulence is likely to be felt more at the low temperature end. Even here the agreement of the values of $V_{\rm b}$ obtained by the author with those obtained from laminar flame studies is quite good.

The turbulence generated by the flame can be explained as follows. The thermal expansion of the combustion products introduces a velocity component normal to the flame front at every point on it. This expansion is responsible for the conical flame and the flow pattern is as shown in Fig. 31. Whilst for the case of laminar flow, the flow pattern remains orderly even after



combustion, in the case of turbulent flow, due to the fluctuation of the elements of the flame, the orientation of the increase of velocity (due to combustion) changes in a random fashion. Thus on the original stream turbulence is superposed the flame created turbulence.

Fig. 31.

The intensity of the flame created turbulence would in some way be connected to the pressure drop across the flame which in turn is approximately proportional to the square of the burning velocity. (Actually $\Delta P = \Im_1 V_b^2 (\Im_1 / \Im_f - 1)$. Thus at high values of the initial temperature, where V_b is high, the flame generated turbulence is more intense. This was indeed the case, for in some of the tests at high values of T_1 , there was a slight roaring noise associated with the flame. However, due to the fact that the stream flow turbulence decreased as T_1 increased, the tendency for excessive turbulence was partly compensated.

From the foregoing, it would appear that the results of burning velocity studies over the whole range of initial temperatures may be affected by turbulence to more or less the same extent. Thus the unsystematic scatter which is attributable to turbulence remains the same at about $\pm 5\%$.

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PART II

GENERAL CONSIDERATIONS OF STABILITY OF BURNER FLAMES

The stability of the flame in a moving stream of combustible gases is dependent on the transport of heat and of active centres of reaction to the zone of burning. This transport could be by heat conduction and diffusion taking place in the direction of or against that of the flow, being determined by the temperature gradient and the concentration gradient respectively. When quenching of the flame with a 'cold wall' takes place, the temperature field is affected by the cooling occurring at the wall. In addition, there are aerodynamic effects of the wall on the flow field. Further adsorption of active free radicals and atoms may take place at the wall which will also affect the flame characteristics. In general, the solid boundaries in flames acting as sinks of heat and possibly of atoms and free radicals determine the stability of flame propagation.

The burning velocity over the surface of the Bunsen burner flame is not uniform and due to the cooling effect of the rim there is a dead space at the burner tube wall.

This fact has been established experimentally by Lewis and von Elbe (Ref. 1) who used a particle trace method with a rectangular burner to study the burning velocity variations. Fig. 32 shows qualitatively a variation of this nature.

In addition to the dead space at the wall, there is a dead space above the rim of the burner tube also. Wohl, Kapp and Gazley (Ref. 32) have measured this quantity and report its magnitude to be between 0.0075" and 0.025" for some butane air flames. The



Fig. 32.

Fig. 33.

actual value depends on the relative magnitudes of the gas velocity and the burning velocity.

Lewis and von Elbe explain the existence of this dead space as follows. When the flame surface is close to the rim, (position A in Fig. 33), the cooling effect of the rim is so serious that the burning velocity decreases and a condition is reached where by the gas velocity exceeds the former everywhere. Thus the gas flow drives the flame back to some position represented by B where the gas velocity and burning velocity are equal at least at one point P. (Actually this is true over the circumference of the circle of radius OP). When the position of the flame corresponds to C, the gas velocity is less than the burning velocity and the flame moves upstream into some new position of equilibrium B. The actual location of the flame surface B depends on the magnitude of the gas velocity. The ability of the flame to find a new position of equilibrium is by no means unlimited for if $|V_b - V_g|$ exceeds a certain value, the flame will flash back for $V_b > V_g$ and will blow off for $V_g > V_b$. Since for a given set of initial conditions, the burning velocity is a function of air fuel ratio, the flash back and blow off limits are dependent on the air fuel ratio in addition to the gas velocity.



Assuming Poiseuille flow, the gas velocity at the boundary will have a linear variation. This condition is quite closely approximated for laminar flow. Even for turbulent flow, the existence of a laminar sublayer justifies such

an assumption.

Thus in Fig. 34, the lines 1 to 5 represent the gas velocity and A, B and C the burning velocity. The horizontal scale is greatly exaggerated. Gas velocity variations corresponding to 1 and 3 determine the limits of stability of the flame. A velocity variation given by 4 indicates flash back as the burning velocity exceeds the gas velocity over a portion of the flame front. Similarly, case 5 refers to blow off as the gas velocity is larger than the burning velocity at all points of the flame front. The stability limits are therefore intimately connected with the velocity variation in the boundary layer. v, the velocity in the boundary layer may be expressed as

where g is the velocity gradient and y the distance of the element from the wall. Now

$$g = \frac{4 V_g}{R} \qquad \dots \dots (30)$$

for fully developed laminar flow, where V_g is the mean gas velocity and R the tube radius. For cases where the flow is not fully developed (i.e. the effective mixing length is less than about 0.03 Re. d) Wilson and Hawkins give the value of g as

$$g = \frac{2 v_g}{R} \phi(\gamma) \qquad \dots (31)$$

where $\gamma = \frac{\overline{v}_g - v_g}{v_g}$ (\overline{v}_g is the maximum gas velocity) and

$$\phi(\eta) = \frac{1+\eta}{2-\left[4-\frac{6\eta}{1+\eta}\right]^{1/2}}$$

The quantity γ is given as a function of $\xi = \frac{L}{R \cdot Re}$. The quantity ϕ approaches a value of 2 as L approaches 0.03 Re \circ d. Appendix IV shows the relationships between ξ , γ and ϕ .

For fully developed turbulent flow g becomes

$$g = \frac{f \cdot Re \cdot V_{g}}{4 R} \qquad \dots (32)$$

where f is the friction factor.

For partially developed turbulent flow and for flow in the transition region, the estimation of the wall velocity gradient becomes very difficult. In fact, in the transition region (2000 < Re < 8000), f can change by as much as a factor of 4 and hence can vary the value of g in the same proportion.

Although in the literature, extensive correlations of flame stability data with wall velocity gradient have been presented, experiments by Lewis and von Elbe on inverted flames stabilized by a coaxial wire in the burner seem to indicate that parameters other than the velocity gradient are affecting the problem. Longwell (Ref. 34) reports having found a reasonably good correlation between the air fuel ratio at blow off and the ratio of the stabilizer radius to the gas velocity, for experiments covering a wide range of stabilizer shapes and sizes. On this premise, one may expect a reasonably good correlation between the air fuel ratio and gas velocity at blow off for flames stabilized on the burner rim.

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EXPERIMENTAL TECHNIQUE AND RESULTS

The technique used to determine the blow off limits was quite simple. At a chosen value of the initial temperature of the propane air mixture, the flame was initiated. The propane flow was then progressively reduced till the flame just blew off. The flow rate of propane corresponding to the point of blow off was then recorded. Several gas flow rates in the burner tube were selected at a given temperature and the air fuel ratio at blow off was determined at each of these rates of flow.

When the propane flow was changed with a fixed air flow, the preheat temperature of the gas mixture was liable to change. But as the propane flow formed a small fraction of the total gas flow, a small change in the former would cause an insignificant change in the temperature. In fact, the galvanometer indicator used with the thermocouples in the gas stream, showed no noticeable change.

The determination of the blow off data extended over a series of burner lengths varying from $L_m = 12.44$ to 20.31" for a 1" diameter burner. Some data was obtained for a burner 0.652" in diameter.

A typical set of blow off data is shown in Fig. 35 where the air fuel ratio at blow off is plotted against the mean gas velocity, with the initial temperature as a parameter. These data refer to an effective burner length of 18.34". Data similar to that in Fig. 35 for different burner lengths have been interpolated and replotted in Fig. 36. The latter is substantially similar to Fig. 35 except that the results of tests at several

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Air Fuel Ratio (by weight)

-86-

values of L_m have been plotted on the same basis for purposes of comparison.

It may be observed that the data corresponding to the different tube lengths at any given temperature can be approximated by a single line and the maximum deviation is about \pm 5.7%.

On Fig. 36 is also shown the results of blow off experiments on the 0.652" diameter burner. The mean gas velocity at blow off for the same temperatures is higher with the smaller burner than with the larger. This is in general agreement with the results of von Elbe and Mentser on hydrogen flames (Ref. 1) who report that for a given value of the initial concentration of hydrogen in the mixture, the critical boundary velocity gradient at blow off is higher for a smaller burner than for a larger one. As can be seen from equations 30, 31 and 32, the boundary velocity gradient is directly proportional the mean gas velocity V_g and hence the agreement between the two sets of results.

The determination of the flash back data has been very limited. At low values of T_1 , the flash back occurred at very small values of the total gas flow and hence only a few points of flash back could be established. At the higher temperatures, however, flash back set in much earlier but the determinations were not very reproducible. The reason for this was that the rate of decrease of propane flow seemed to have an influence on when flash back set in. Since the propane flow regulation was manual, the rate of decrease of flow rate was rather arbitrary.

Fig. 37 shows the gas velocity plotted against air fuel ratio for $T_1 = 515$ °C. All the data obtained from burning velocity

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Air Fuel Ratio (by weight)

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and stability tests for this temperature have been included in this figure. The flash back line has been established as the extreme limit of the points on the low gas velocity side. The points on the blow off line are all experimental ones. The two lines give the extreme limits and correspond to the most favourable conditions. The region of partly lifted but stable flame is also shown in the figure.

Fig. 38 is identical to Fig. 37 except that the former refers to an initial temperature 25°C. The flash back curve was recalculated from the data of Harris, Grummer, von Elbe and Lewis (Ref. 35) and the points obtained during the present investigations agree quite well with this curve.

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Air Fuel Ratio (by weight)

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DISCUSSION

A correlation using the boundary velocity gradient as a variable was not attempted. Since the Reynolds number was in the transition region and the burner length insufficient for the establishment of a fully developed flow, the estimation of the velocity gradient would have been very uncertain. Further, the physical significance of this quantity in relation to the problem of flame propagation is not very clear. In so far as it is a parameter describing the flow pattern, a connection with stability limits of the burner may exist. Due to the special flow conditions met with in the present investigations, it was thought wiser to use the mean gas velocity as the parameter to correlate the stability data rather than the velocity gradient obtained on doubtful premises.

The mixing of the propane and air stream was investigated in a qualitative way by observing the smoke pattern of the flow. Hydrochloric acid vapour was injected into the air stream and ammonia vapour through the propane jet and the mixing pattern was observed by photographing the smoke at the burner rim. Fig. 39 shows some of the patterns obtained. The mixing process seems to be quite uniform. Hence the scatter in the blow off data cannot be attributed to differences in the degree of mixing.

The same observation as was made on the influence of the mixing length on the burning velocity is arrived at even for the problem of burner stability. Over the range of tube lengths studied, (I_m between 12.44" and 20.31"), the random variation of the mean gas velocity at blow off, for a given value of air fuel ratio, is about $\pm 6\%$. It would appear that a good part of this

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Re = 7760



Re = 5030 Fig. 39

variation is inherent in the very technique used. A few percent of the error can easily be accounted for by the non-reproducibility of the actual point of blow off which was obtained by trial. Some inertia effects were noticed in the valves, even when great caution was exercised over the rate of reduction of the propane flow. Thus the propane flow would become smaller than that which corresponded to the actual point of blow off.

Only data on two sizes of burners (d = 1.00" and 0.652") is reported and although some tests were done on a burner of 0.40" diameter, the results were not useful for purposes of comparison. The air fuel ratio values obtained were much lower (i.e. mixtures were very fuel rich) than for the 1" and 0.652" diameter burners. Higher values of AFR could have been obtained by using smaller gas flows but this was inconvenient due to two reasons. Firstly, the air flow range was too small to be measured accurately even with the low range orifice and secondly, the heat transfer in the heat exchanger was poor due to low velocities. However, the trend of the change in the gas velocity at blow off when the diameter was changed from 1" to 0.652" is similar to that observed by other workers.

PART III

CONCLUSIONS

An extensive investigation into the problem of flame propagation at high temperatures has been made, using the burning velocity as the characteristic of the phenomenon. A satisfactory technique of measurement ensuring a fair amount of reproducibility was developed. The results of the measurements at the low temperatures (0 to 300 °C) were in reasonably good agreement with similar work done by other workers using a slightly different technique. This would substantiate the validity of the results obtained by the author in the temperature region of 300 - 640 °C, data on which was not available in the literature.

The burning velocity for propane air mixtures shows about a sevenfold increase when the initial temperature is increased from room temperature to 640 °C. A similar increase in burning velocity with temperature may be expected for flame propagation in other hydrocarbon mixtures also. The gain in the burning velocity is greatest for mixtures slightly richer in fuel than stoichiometric.

Experiments on the effect of changes in the burner length and diameter showed, that within the limits of the technique used, the burning velocity is independent of these variables. An apparent contradiction on the effect of residence time on the twin phenomena of flame propagation and spontaneous ignition has been satisfactorily explained and it is shown that the reason for this is the exponential dependence of reaction rate on temperature. On this premise it has been demonstrated that for propane air mixtures and perhaps for many other hydrocarbon air

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mixtures too, there will be a zone of initial temperatures around 750 °C where flame propagation as encountered in burner flames may exist, but where the preflame reactions will have a bearing on the problem. In fact if the burner lengths are increased sufficiently, without incurring serious heat losses, the residence time will be long enough for the flame to stabilize inside the tube. Unfortunately, the limitations imposed by the experimental apparatus prevented close study of this very interesting transition region.

A critical analysis of the theories of flame propagation was made and relative values of the maximum burning velocity for propane air mixtures, over a range of initial temperatures, were calculated on the basis of the simplified thermal and diffusion theories. The effect of initial temperature was predicted by both these schemes quite well, the agreement being slightly better with the thermal one. With a view to judging which was the more probable controlling process - heat conduction or diffusion -, a review of the literature on the effects of such factors as inert gas addition and pressure on the burning velocity was made. Lack of reliable property values in one case and reliable experimental data in the other made it impossible to assess the relative importance of the two processes.

It has been emphasized that both theories connect the burning velocity with flame temperature in somewhat different ways and that as long as accurate kinetic and thermochemical data are not available, a clear decision as to which of the two theories corresponds to the actual case cannot be made. Under the circumstances it appears advisable to accept both the theories and

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use the more converient one in any given problem. In the author's opinion the thermal theory is the easier of the two to use as it uses fewer and perhaps better established kinetic and thermochemical data. This (the thermal theory) may be used for many instances of flame propagation including hydrocarbon air systems and in cases like carbon monoxide combustion where it breaks down, a diffusion scheme may be applied.

The influence of turbulence on the measurements of burning velocity has been analyzed in a general and qualitative fashion and it is felt that the values of burning velocity obtained are quite close to those that would be obtained for laminar flame propagation.

Significant changes in burning velocity have been observed by Bula for relatively small changes in the oxygen content of air. The percentage variation, relative to the value for standard air, for a given enrichment or depletion of oxygen is more at the lower temperatures than at the higher ones. The reason for this may be the increased dissociation taking place in flames of gas mixtures at high initial temperatures. In other words, a given amount of oxygen enrichment would give a larger increase in the flame temperature for lower values of initial temperature than for higher values of the latter. A similar argument may be applied for the case of oxygen depletion.

Fairly extensive information on blow off limits was obtained for initial mixture temperatures in the range of 0 - 640°C. Effects of tube length and diameter were also investigated but the reproducibility of the technique used was such as to be insensitive to these secondary parameters. However, for all tube lengths and diameters, it was seen that the mean gas velocity at blow off, with a given value of the air fuel ratio, increased with temperature. Rather limited data on flash back limits also indicated the same behaviour i.e. the flash back limit moved into the region of higher gas velocity. Further the stability range, measured by the difference in gas velocities at blow off and flash back, increased with the initial temperature. The extent of this increase depended on the air fuel ratio.

RECOMMENDATIONS FOR FUTURE WORK

The phenomenon of flame propagation is composed of so many different fundamental processes, knowledge on each of which is far from complete, that the scope of further research work is indeed unlimited. In fact, considerable work on some or all of these processes is being carried out by several workers in the field, which should help in the formulation of a clear picture of the whole Recommendations for future work may be split into two problem. The first will cover those experiments that can be sections. conducted using the experimental apparatus and technique used by the author, with suitable improvements and alterations, results from which would throw more light on certain aspects of the mechanism of flame propagation. The second section will deal with the problem in a general way and work which, in the author's opinion, would help in formulating the fundamental concepts of the problem will be described.

Section 1

In order to complete the picture of flame propagation at elevated temperatures, an investigation of the transition region between rim stabilized burner flames and flames maintained by spontaneous ignition is very desirable. To accomplish this, it is necessary to attain preheat temperatures in the range of 700 -800 °C. It may be possible to push the upper limit of about 700 °C of the apparatus to some extent. However, indirect heating to temperatures much higher than this is awkward.

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It may be possible to use direct electrical heating to reach Another possibility is internal heating through higher temperatures. combustion of some fuel (say propane) and then making up the oxygen content to that of standard air. This is feasible as the amount of air used and hence the oxygen that needs to be injected is quite small. For instance the maximum air flow used in the experiments described in this thesis was about 0.007 lbs/sec. To obtain a temperature of 900 °C by burning fuel in the air, the oxygen content gets depleted to about 13% by volume. In order to make this up to the normal value of 21%, about 2.2 lbs/hour of oxygen is required. Thus a standard oxygen cylinder containing about 220 cft of free oxygen would last for about eight hours.

However, if a scheme of internal heating through combustion were adopted, it will be necessary to determine the effect of the presence of combustion products notably carbon dioxide and water vapour on the phenomenon of flame propagation. The experimental set up used by the author is well suited for such work on additives.

Additional data on the effect of enriching the oxygen and nitrogen content of the air stream on burning velocity at high temperature is also desirable. This would mean an extension of the measurements over a wider range of $\frac{O_2}{O_2 + N_2}$ values.

The effect of atmospheric oxygen on burner flames is worthy of some investigation. Although the entrainment of air and the consequent increase of oxygen may not be serious at low temperatures, such effects are liable to get accentuated at higher temperatures. A study of this nature may be accomplished by having a blanket of nitrogen or any other inert gas around the flame. It will be

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necessary to heat the gas (nitrogen or the inert gas) to the temperature of the premixed gases in the test section to eliminate heat losses from the latter.

Flame propagation at elevated temperatures taking turbulence as a systematic variable can be studied quite conveniently using the existing set up and by making provision for inserting turbulence grids at the burner tube inlet. Although estimation of the original turbulence (without any grid) is difficult, the results obtained by introducing a series of grids would facilitate extrapolation and hence the determination of the laminar burning velocity. Measurement of the flame created turbulence would be difficult but it may be possible to establish an arbitrary scale by measuring the intensity of the roaring sound associated with turbulent flames.

Another very important phase of work that can be carried out using the present technique is the extension of burning velocity measurements at high temperatures to other hydrocarbon flames. It may be possible to observe similarities in behaviour of members belonging to a particular series (i.e. the paraffins, the aromatics etc). Alternatively a correlation of the flame characteristics of the hydrocarbons on the basis of the molecular weight and the number of carbon atoms may be found.

These studies could also cover such technical fuels as aviation kerosene and other lighter motor fuels. On the experimental side suitable vapourizers would be needed. It may be necessary to study the effect of heat only on such complex fuels to ascertain the degree of cracking of the heavy molecules. No thought was given to this aspect in the present set of experiments

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on propane air flames. The problem would, of course, be more serious for the heavier hydrocarbons.

Such studies on the technical fuels may enable linking in a qualitative and quantitative way the data obtained from flame propagation experiments with the actual combustion process in an internal combustion engine or in a gas turbine engine.

Section 2

As far as the question of measuring the burning velocity is concerned, a more direct and reliable method than the area methods would be very valuable. Some preliminary work done by the author showed that a spectroscopic tracer may be used for this purpose. If a gas which emits or absorbs radiation strongly can be introduced into the air-fuel stream, then the time interval between the spectroscopic excitations at two chosen normal sections of the flow would give a direct measure of the velocity. In this way the velocity of the unburnt gases passing through the flame front may be measured.

The gas tracer must have two properties. Firstly it must have a density approximately equal to the mean density of the fuel air mixture and secondly it must not affect the reaction mechanism in any way. Nitric oxide has a density very near that of air and emits and absorbs radiations in the ultraviolet region. However, it is known to inhibit several organic reactions. In those cases where it does not, nitric oxide would be a very good tracer.

For this method to be used, a suitable electronic timing device, operating in conjunction with photo-multipliers, needs to be developed. A satisfactory triggering device to inject the

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tracer into the air stream would also be required. The electronic timer should be such that when the tracer passes through a particular section in the gas stream (where a slit and a photo tube would be mounted), the timing would start and when the tracer passes through another chosen section (with another slit and photo tube) the timing would stop.

A rectangular burner may have to be used, in this method, to overcome the two dimensional flow profile of a conical flame. This method of measuring the burning velocity would also enable the effect of stationary cold walls or other obstacles to be determined quantitatively.

Studies on the kinetics of hydrocarbon oxidation at high temperatures is another phase of work which is very necessary, as the growth of reaction forms the very basis of flame propagation. In recent years, considerable work on high temperature spontaneous ignition of various hydrocarbons has been done. This work usually covers two aspects, the ignition delay measurements and spectroscopic studies of preflame kinetics. Whilst the former has helped in establishing the overall activation energy of oxidation mechanisms, the latter has not yet yielded much information. Intelligent use of simple sampling methods may give useful information. On the other hand, spectroscopic studies may help in establishing reliable thermochemical data applicable for conditions existing in flames. Better thermochemical data and undisputed property values will be invaluable in predicting quantities like burning velocity from theoretical considerations.

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Use of radioactive isotopes has prospects of enabling a definite decision in the controversy of the relative importance of heat conduction and diffusion on the phenomenon of flame propagation. Substitution of deuterium for hydrogen would change the diffusion coefficients of active particles like hydrogen atom and hydroxyl radical, without altering other properties too much. Besides radioactive tracers may also enable a direct measurement of the burning velocity. The focussing of the radiations may not be very simple. Further the radioactive species may influence the progress of reaction for which allowance will have to be made.

APPENDIX I

a) Calculation of the adiabatic flame temperature

The equilibrium concentrations and the adiabatic flame temperature were calculated by a systematic iterative process. The method was suggested by Lin (Ref. 37) and is outlined here briefly.

The reaction between propane and air can be represented by

$$x (C_{3}H_{8}) + 5 O_{2} + 18.8 N_{2} \rightarrow A(CO_{2}) + B(CO) + C(H_{2}O) + D(H_{2})$$

+ $E(O_{2}) + F(NO) + G(N_{2}) \dots (33)$

where A, B, C....G and x refer to the number of moles of the various substances. When x = 1, i.e. the amount of propane in the initial mixture is one mole, the L.H.S. of the equation corresponds to stoichiometric conditions.

In order to simplify the calculations, formation of hydrogen atoms, oxygen atoms and OH radicals was neglected. For flame temperatures less than 2600 °K, the formation of these atoms and radicals is small. Whilst their concentrations may be sufficient to affect the reaction, their effect on the flame temperature (in the form of energy lost through their formation) is of a secondary nature.

Considering the dissociation of CO_2 and H_2O and the formation of NO, we have

 $2 CO_{2} = 2 CO + O_{2} \cdots K_{1}$ $H_{2} + CO_{2} = H_{2}O + CO \cdots K_{2}$ $N_{2} + O_{2} = 2 NO \cdots K_{3}$ (34)

where the K's are the equilibrium constants.

If the equilibrium concentrations refer to some constant P, the following results are obtained from (34)

$$K_{1} = \frac{B^{2} E}{A^{2}} \left(\frac{P}{M}\right)$$

$$K_{2} = \frac{B \cdot C}{A \cdot D}$$

$$K_{3} = \frac{F^{2}}{E \cdot G}$$
(35)

where M = A + B + C + D + E + F + G.

Equating the number of carbon, hydrogen, oxygen and nitrogen atoms on both sides of equation (33)

$$3 X = A + B$$

$$8 X = 2(C + D)$$

$$10 = 2A + B + C + 2E + F$$

$$18.8 = F/2 + G$$
(36)

Lin (Ref. 37) proposes using $\mathbf{r}_{\mathbf{E}} = \frac{\mathbf{E}}{\mathbf{M}}$ i.e. the mole fraction of free oxygen at the flame temperature, as an independent variable and solves the sets of equations (35) and (36) simultaneously to get

$$A = \frac{3/4 \, \alpha \, (1+\alpha) \left[10 - (2E+F) \right]}{\alpha \, (K_2 + \alpha) + 3/4 \, (1+\alpha) (K_2 + 2\alpha)}$$
$$B = \frac{3/4 \, K_2 \, (1+\alpha) \left[10 - (2E+F) \right]}{\alpha \, (K_2 + \alpha) + 3/4 \, (1+\alpha) (K_2 + 2\alpha)} = \frac{K_2 \, A}{\alpha}$$

$$C = \frac{(K_2 + d) d [10 - (2E + F)]}{d (K_2 + d) + \frac{3}{4} (1 + d) (K_1 + 2d)}$$

$$D = \frac{(K_2 + d) [10 - (2E + F)]}{d (K_2 + d) + \frac{3}{4} (1 + d) (K_2 + 2d)} = \frac{c}{d}$$

$$F = \frac{\sqrt{(K_3 E)^2 + 300 K_3 E} - K_3 E}{4}$$

$$G = \frac{18 \cdot 8 - \frac{F}{2}}{4}$$
(37)

and E is obtained from

$$\frac{1}{Y_{E}} = \frac{(1+\alpha/2)(7K_{2}+4\alpha)-3/2K_{2}}{(5\alpha+3)(2\alpha+K_{2})+2K_{2}\alpha} \left[(\frac{K_{3}}{4}-2) + \frac{10}{E} - \frac{K_{3}}{4} \sqrt{1+\frac{300}{K_{3}E}} \right] + \frac{23\cdot8}{E}$$

where $\alpha = K_{2} \sqrt{\frac{\rho}{K_{1}}} \sqrt{\frac{r}{E}}$.

P, the pressure at the flame front (expressed in atmospheres) was taken as unity for the present calculations.

From considerations of heat balance, we have heat available by combustion + heat content in the gas mixture before combustion above some datum $T_0 = \leq A_1 (H_{\ddagger i} - H_0 i)$ where $A_1 = A$, B, C...G. The heat available by combustion may be obtained as the difference between the heat of complete combustion of propane to CO_2 and H_2O and the heat lost through formation of CO, H_2 and NO.

Complete combustion of propane (at 25°C) liberates 877,500 Btu/lb mole and heat losses associated with the formation of CO, H_2 and NO are 122,000 Btu/lb mole, 104,000 Btu/lb mole and 38,746 Btu/lb mole respectively. Thus we have

(877,500 x - 122,000 B - 104,000 D - 38,746 F)

+ 5
$$(H_{1 0_2} - H_{0 0_2})$$
 + 18.8 $(H_{1 N_2} - H_{0 N_2})$
= $\sum_i A_i (H_{f i} - H_{0 i})$

This equation is approximate to the extent that the heat of propane between T_1 and T_0 (taken as 25 °C) has been neglected. This was done to simplify the calculations. Further, no allowance was made for the heat losses occurring during combustion, (i.e. conduction to the walls, radiation from the flame etc).

The steps involved in establishing T_{f} as a function of T_{1} and AFR were as follows:

(1) Assume a value for T_{f} and obtain the appropriate equilibrium constants.

(2) Assign a value for r_E , obtain \ll and calculate the A_i 's bearing in mind the checks that $M = \sum_{i}^{\infty} A_i = \frac{E}{r_E}$ and that x = 1/3 (A + B) = 1/4 (C + D).

(3) Calculate $\sum_{i} A_{i} (H_{f i} - H_{o i})$ (4) Calculate $\Delta H_{c} = 877,500 \times -122,000 B - 104,000 D - 38,746 F.$ (5) Determine $(\sum_{i} A_{i} (H_{f i} - H_{o i}) - \Delta H_{c})$ which is equal to 5 $(H_{1 0_{2}} - H_{0 0_{2}}) + 18.8 (H_{1 N_{2}} - H_{o N_{2}})$. By referring to temperature enthalpy tables or to a diagram relating the latter function with T₁, obtain T₁.

(6) Repeat the calculations for a range of r_{E} values at the particular temperature T_{f} .

(7) Repeat such calculations for a series of T_{f} values.

Results of such calculations are shown in Fig. 40 where T_1 is plotted against AFR with T_f as a parameter. Data from this figure has been replotted in Figs. 41 and 42 and from the latter, Fig. 25 was derived.



A.F.R. (by weight)

Fig. 40

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Jo stuterequet LaitinI

Adiabatic Flame Temperature oK

(b) Calculation of equilibrium active particle concentrations

When obtaining a correlation of the burning velocity data with the diffusion theory of Tanford and Pease, the concentrations of hydrogen and oxygen atoms and OH radical at the flame front were required.

No allowance for the formation of these atoms and radicals was made when estimating the flame temperature. However, the concentrations were obtained from the latter. This is justifiable as the dissociation energy involved in the formation of small concentrations of the atoms and radicals is not large enough to affect the energy balance seriously.

The formation of OH radical and H and O atoms may be

and

$$p_{H} = \kappa_{5} \sqrt{p_{H_{2}}}$$

$$p_{0} = \kappa_{6} \sqrt{p_{0_{2}}}$$

$$p_{0H} = \kappa_{4} \frac{p_{H_{2}0}}{\sqrt{p_{H_{2}}}}$$

$$(39)$$

where the p's represent the partial pressures of the different constituents.

The values of p_{H_2} , p_{O_2} and p_{H_2O} at the flame front were obtained from the calculations indicated in section (a). Figs. 43, 44 and 45 show the equilibrium partial pressures of H_2 , O_2 and H_2O as functions of T_f . The equilibrium constants K_4 , K_5 and K_6 were taken from Gaydon and Wolfhard (Ref. 2). Figs. 46 and 47 show the K's as functions of temperature.

(c) Change in the number of moles due to combustion

While using Semenov's equations for predicting the burning velocity, the variation of $\frac{n_1}{n_2}$ (i.e. the ratio of the number of molecules before and after combustion) was discussed.

Following the notations of section (a)

$$\frac{n_1}{n_2} = \frac{23.8 + x}{M} \text{ where } M = \begin{cases} x \\ 1 \end{cases} A_1^{2}.$$

Values of this ratio were calculated for several values of T_f over the full range of AFR values. They are shown in Fig. 48.





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Fig. 44.

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Fig. 45.

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Fig. 46.

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APPENDIX II

Temperature dependence of the property values.

When predicting the variation of burning velocity with initial temperature on the basis of the thermal and diffusion theories, the temperature dependence of the property values like thermal conductivity, viscosity and specific heat were considered. To simplify matters, it was assumed that the properties of the gas mixture did not differ very much from those for pure air.

Fig. 49 shows the thermal conductivity λ , kinematic viscosity \mathcal{V} and the specific heat Cp plotted against temperature, on a logarithmic basis. The data was taken from the "Gas Tables" by Keenan and Kaye (Ref. 38). It has been possible to obtain good approximations for the property values as follows

$$C_{P} \propto T^{0.09}$$

$$\lambda \propto T^{0.84}$$

$$\nu \propto T^{1.67}$$

The units used for these properties and the temperature in Fig. 49 are different from those used in other parts of the thesis, but this difference affects the constants of proportionality only.

By the application of the principle of similarity for the processes of mass transfer and heat transfer, Schmidt and Nusselt (Ref. 21) postulated that the diffusion coefficient is proportional to the kinematic viscosity. Sherwood (Ref. 21) and others have confirmed experimentally that $\frac{v}{D}$, the Schmidt number, is in fact nondimensional.

Hence the diffusion coefficient was taken as being proportional to $T^{1.67}$.





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APPENDIX III

<u>Relationship</u> between temperature and delay period for spontaneous <u>ignition</u>.

At a given temperature T_1 , the ignition delay varies inversely with the reaction rate. Thus

$$\mathcal{T}_{i} \propto \frac{1}{q}$$
 where $q = P \times Z e^{-\frac{E}{RT_{1}}}$

P* is the steric factor. Z, the collision frequency is proportional to the root mean square velocity of the molecules and hence to $\sqrt{T_1}$. Therefore,

$$\mathcal{T}_{i} \propto (\sqrt{T_{1}} e^{-\frac{E}{RT_{1}}})^{-1}$$

or $(\mathcal{T}_{1} \mathbf{T}_{1}^{1/2}) \propto e^{E/RT_{1}}$.

Hence log $(\tau_1 T_1^{1/2}) = \text{constant} + \frac{E}{RT_1}$ (40)

Thus a linear relationship exists between log ($T_i T_1^{1/2}$) and $1/T_1$.

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APPENDIX IV

Calculation of wall velocity gradient for partially developed laminar flow.

For fully developed laminar flow, the velocity gradient at the boundary is given by

$$g = \frac{4 V_g}{R}$$

and for the partially developed case

$$g = \frac{2 V_g}{R} \phi(\gamma)$$

Wilson and Hawkins (Ref. 1) give $\phi(\gamma)$ as

$$\frac{1+q}{2-(4-\frac{6q}{1+q})^{1/2}}$$

The problem of calculating γ as a function of tube length L was treated by Schiller (Ref. 1).

Fig. 50 shows γ as a function of $\xi = \frac{L}{R \cdot Re}$ and Fig. 51 connects γ with ϕ . It is seen that when $\xi = 0.0575$, $\gamma = 1$ and $\phi = 2$, which corresponds to the case of fully developed flow. Thus L = 0.02875 Re . d for fully developed laminar flow. The constant has been rounded off to 0.03 in the earlier discussions.





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