FLAMMABILITY OF PARAFFIN HYDROCARBONS IN CONFINED AND UNCONFINED CONDITIONS.

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Flammability limits and combustion behaviour in near-limit mixtures have been investigated for four paraffins, methane to butane, in air.
Two experimental approaches have been used. Flammability limits and transient overpressures were measured in a spherical vessel to determine behaviour in confined conditions. An optical study was made of near-limit combustion in soap bubbles to provide information on flammability in essentially unconfined conditions. Similarities and differences in the behaviour of confined and unconfined gases are discussed. An attempt is made to present conclusions about flammability arising over a wide range of circumstances.

INTRODUCTION

The understanding of flammability characteristics of fuels is important for the practical assessment of hazards, and presents a considerable challenge for combustion science. The significance attached to flammability is evident from the vast body of literature on the subject, stretching back over many decades. Despite this, there are still considerable gaps in our knowledge and understanding. In this paper, we examine aspects of flammability behaviour from the standpoint of hazard assessment.

Flammability limits are commonly regarded as the boundaries between flammable and non-flammable mixtures. For example, the normally accepted limits for methane in air are 5 and 15% methane, implying that mixtures within these bounds will burn, while those outside will not. While this is not incorrect, we suggest and hope to demonstrate that the full picture is considerably more complex. Different degrees of combustion can occur in mixtures at and near limits, depending both on mixture composition and on the physical conditions encountered.

For a fuller appreciation of flammability characteristics, the following points should be considered :

- What are the limits of flammability and what hazard do they represent, i.e. what degree of combustion occurs? What overpressures can develop when near-limit mixtures are ignited, particularly in confined conditions?

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- The potentially flammable mixture may be confined, totally or partially, or unconfined. What effects does confinement have on flammability?

- Many different sizes of flammable clouds may be encountered. Can cloud dimensions have any influence on the burning of the cloud?

- Multi-component fuels are used in many processes. How well can flammability hazards arising from mixed fuels be predicted?

Undoubtedly, many other issues arise as well, but these are the questions for which we have tried in this paper to provide some answers. We have studied a range of simple paraffins - methane to butane.

Traditionally, flammability limits have been measured by observing flame propagation along a tube. It has long been acknowledged that wall quenching effects will interfere if the tube is not sufficiently wide. A tube diameter of 50 mm was thought sufficient by Coward and Jones (1) and this has been commonly used. More recent work (Andrews and Bradley (2) and Jarosinski and Strehlow (3)) has shown that this is incorrect and that wall effects are still significant. This must shed some doubt on the validity of tube experiments. Such experiments are useful for fundamental studies and provide a convenient means of grading the relative characteristics of different fuels. But there are circumstances where the information they provide is incomplete and may be misleading. They may mask certain types of combustion which are important, but only become apparent when studied in more open conditions. Furthermore, the mechanism of flame failure is almost certainly different when the flame is well removed from the influence of walls.

In recent years, there has been a growing trend towards studying flammability in spherical vessels to reduce wall effects. Particular attention is drawn to the work of Furno et al (4), Sapko et al (5), Margolin et al (6) and Crescitelli et al (7). This work has thrown new light on flammability characteristics. But such studies have their own problems. The vessel should be large enough to allow reasonable flame travel, so the flame is well removed from influence of the ignition source. The 3.65 m diameter spherical vessel used at the Bureau of Mines (4,5) is ideal. Some other work has involved vessels which are too small for the true picture to emerge. A second problem arises because the flammable mixture is totally confined. No venting occurs, so pressures build up during combustion. This may lead to wrong conclusions being drawn about flammability at constant pressure.

In this work, we have conducted two separate studies of flammability, using complementary experimental approaches. An enclosed spherical vessel of moderate size (0.6 m diameter) was used to establish the limits quantitatively, while combustion inside soap bubbles of smaller size (120 and 280 mm diameter) was used to study flammability at constant pressure.

EXPERIMENTAL

Spherical Vessel Experiments

A diagram of the apparatus used for the experiments on confined gas mixtures is shown in Figure 1. The spherical steel vessel was 0.6 m in diameter with 12 mm thick walls, and 12 mm glass windows. An electric spark was used as an ignition source in all experiments; this was produced by discharging an 8 μF capacitor at about 850 V through a standard car ignition coil with the secondary windings connected to brass electrodes welded to heavy-duty sparking plugs. The spark gap, in the centre of the chamber, was about 10 mm.

For each experiment, the fuel and air were metered into the vessel by partial pressure measurements. Then the vessel was sealed and the contents were mixed thoroughly by a mechanical stirrer. A single spark was applied and, if ignition occurred, the flame propagation was observed visually, and the pressure changes were monitored using a Kistler 7031 piezoelectric pressure transducer connected through a Kistler 5001 charge amplifier to a Datalab DL 901 transient recorder. If no ignition occurred, repeated sparks were applied. If there was still no ignition, the gases were stirred again and more sparks were applied; if ignition still did not result, the mixture was taken to be non-flammable.

The gases used were CP grade (99%) alkanes supplied by Air Products Limited, and dried, compressed air from the atmosphere.

Soap Bubble Experiments

The aim of this work was to examine the burning of near-limit mixtures rather than to determine precise flammability limits. The investigation was restricted to lean methane-air mixtures.

A schematic diagram of the bubble apparatus is shown in Figure 2. Two types of bubble were used : 120 mm diameter spherical bubbles blown on top of a 45 mm diameter pedestal, and 280 mm diameter hemispherical bubbles blown on top of a horizontal flat plate.

Combustion mixtures were made from synthetic air and CP grade methane. The gases were metered separately, using capillary flow meters, and passed via a mixing chamber directly into the bubbles. The flow meters had been calibrated by taking gas samples from bubbles with a syringe, and analysing them by gas chromatography. The percentage of methane in a mixture was estimated to be accurate to ± 0.2%. It is possible that some diffusion occurred through the bubble skin.

Mixtures were ignited by passing an electric spark between electrodes positioned centrally. The electrodes were kept permanently in position, and bubbles formed around them. The ignition circuit used was essentially the same as that in the other apparatus, except that a 4 μF capacitor was used, charged to 1 KV, and the electrode gap was 8 mm.

Flame propagation was monitored by the shadowgraph method combined with high speed cinephotography. The shadow image was focused directly onto the film. Framing speeds up to 6000 per second could be used, but for most experiments 800 or 1000 frames per second were sufficient.

Films were analysed by projecting onto a screen and measuring flame positions with a ruler. Positions could be measured to an accuracy of 1 mm, except in the last stages of burning when flame wrinkling usually occurred.

Time was measured by simultaneously filming a singly notched wheel rotating at a constant speed of 200 revolutions per second. It was estimated that time was measured with an accuracy of 1 msec or better.

RESULTS AND DISCUSSION

Flammability Behaviour in Confined Conditions

General Observations. Fuel-air mixtures ignited in the closed vessel showed different types of flame propagation. These are described only briefly, since the observations have been reported previously (4,7). A fuller account of this closed vessel is also given in another report by Roberts (8).

Consider a lean mixture below the flammability limit and gradually increase the amount of fuel. The first observation is of very weak flames, burning around the ignition source but able to propagate only short distances before extinction. Mixtures in which this happened are considered to be non-flammable. In a mixture with slightly more fuel, a small cap of flame propagates upwards, expanding sideways slightly, until it strikes the roof of the vessel where it is extinguished. Such mixtures are deemed flammable. With further increase in fuel, this upward propagation is followed by downward movement from the roof of a thin, flat flame. This flame travels slowly, often appearing to be stationary before dying away. The extent of this downward propagation depends on fuel concentration : with enough fuel, the flame travels faster and continues to the bottom of the vessel, consuming all the fuel. In still richer mixtures, a stage is finally reached where the flame burns out in all directions from the ignition source. The same types of combustion are observed in rich mixtures near the limit, as the fuel concentration is reduced.

We have designated these different types of combustion by symbols as shown in Table 1.

TABLE 1 - Types of Flame Propagation observed in the Closed Spherical Vessel.

Symbol	Brief Description of Flame Behaviour
↑	Cap of flame went up to roof and died out.
↑↓	Cap of flame went up to roof; then started to burn back down, dying out in the top half of the vessel.
↕	Flame went up to roof; then burned back down to the bottom, consuming all the mixture.
✥	Flame burned outwards in all directions from the spark.

Having given this very general description, it is important to note that not all types of flame are observed for all fuels at both the lean and rich limits. For example, methane displays all four categories near the lean limit, but only two types (↕ and ✥) near the rich. With the other fuels, this pattern is reversed. This is shown in Table 2.

As a final comment, we note that traditional tube experiments cannot provide this amount of detail about flammability behaviour.

Flammability Limits of Pure Fuels. Flammability limits in air for the four fuels, methane, ethane, propane and butane, as measured in the spherical vessel, are shown in Table 2 and Figures 3 and 4.

TABLE 2 - Limits for the Various Types of Flame Propagation in the Closed Vessel for Pure Fuels. (Volume % Fuel in Air).

	Fuel Lean				Fuel Rich			
	↑	↿⇂	↕	✥	✥	↕	↿⇂	↑
Methane	4.9	5.3	5.6	6.4	13.4	15.0	-	-
Ethane	-	-	2.85	3.4	9.4	11.15	12.55	12.6
Propane	-	-	2.15	2.4	6.4	7.5	9.0	9.8
Butane	-	-	1.7	1.9	5.25	6.0	6.9	8.5

The widest limits obtained should be taken as the absolute limits of flammability. They depend on an initial upward flame propagation which is free from wall effects. Thus they should represent the widest possible limits in any circumstances. These are the values which should be used to ensure complete safety.

The limits for all four fuels agree fairly well with accepted values from standard tube experiments, given by Zabetakis (9). Where differences arise, our measurements generally give wider limits. Heat losses and wall quenching in the tube experiments are probably the major causes of the discrepancies. For this reason, we consider our values to be more reliable. It may be argued that our experiments did not allow sufficient flame travel and that in a larger vessel flames in mixtures at the extreme limits might extinguish before reaching the wall. But we find excellent agreement with the results for butane obtained in a 3.65 m diameter vessel (4), suggesting that the use of a larger vessel would make very little difference.

Transient Overpressures. It was seen in the last section that some types of limit flames are less vigorous than others. Upward propagation alone (designated ↑) is a marginal occurrence : flame propagation is slow and little of the fuel is consumed. Similarly, flames which propagate upwards and only partially downwards (↿⇂) generally lack intensity. Thus although this behaviour is taken to lie inside the region of flammability, the consequences of such flames may be slight.

This point emerges more clearly from a consideration of the transient overpressures produced in the closed vessel. These are shown in Table 3 for the limit mixtures and in Figures 3 and 4 for a range of compositions. The actual values obtained are only applicable in similar spherical vessels. Combustion in other enclosures will produce different overpressures. But the values here give a relative guide to the overpressures that could occur in other circumstances.

TABLE 3 - Overpressures (Bar) Observed at the Limits for Pure Fuels in the Closed Vessel.

	Fuel Lean				Fuel Rich			
	↑	↥	↕	✥	✥	↕	↥	↑
Methane	0.05	0.3	1.5	2.0	2.1	1.4	-	-
Ethane	-	-	1.7	2.7	2.9	1.3	0.1	0.1
Propane	-	-	1.9	2.6	3.6	1.7	0.2	0.05
Butane	-	-	1.8	2.5	3.9	2.0	0.3	0.05

Flammability Behaviour in Unconfined Conditions

The last section dealt with flammability in confined conditions. It is pleasing to be able to record that removing the confinement considerably simplifies matters. In totally unconfined conditions, only two types of limit behaviour can occur. These are upward propagation (designated ↑) and direct propagation in all directions (designated ✥). The intermediate forms of combustion cannot happen when there is no roof for the initial flame to impinge upon.

The initial upward flame propagation creates such small pressure rises in the enclosed vessel that combustion is taking place essentially at constant pressure. Thus we consider that the absolute limits measured in the spherical vessel also apply to unconfined conditions. In confined conditions, this *limit may represent an intermediate form of combustion. In unconfined* conditions, this becomes restricted to upward propagation alone.

Direct combustion in all directions in the enclosed vessel is strongly influenced by confinement. This can be illustrated by considering the burning of methane-air mixtures containing 6.4 to 6.5% fuel. In the spherical vessel, the flame propagated in all directions throughout the whole volume. In soap bubbles, on the other hand, complete combustion did not occur. The flame expanded approximately spherically for 30 to 40 mm. The base then flattened and no further downward propagation occurred. Instead the flame and hot products rose bodily due to buoyancy effects. As combustion continued at the top and sides, this behaviour constitutes a limit for downward propagation. From this type of comparison, we conclude that limits for downward propagation obtained in confined conditions cannot sensibly be used when the mixture is unconfined.

Buoyancy forces have long been known to be important in flammability behaviour (see for example the review by Lovachev et al (10)). We consider that in unconfined conditions the limit for direct downward propagation as defined above is governed entirely by buoyancy. This in turn means that this limit has no fundamental significance. It arises simply from the opposition of buoyancy forces tending to lift the hot gases and combustion processes tending to expand the flame in all directions, including downwards. When the buoyant rise equals the flame speed, no further downward propagation is possible. Since the buoyant velocity increases with size whereas flame speed does not, the limit condition can be satisfied for any flame speed, provided the cloud is sufficiently large. Thus, when the mixture is unconfined, it becomes meaningless to talk in terms of a particular downward limit. Instead, we need some knowledge of how far a flame will propagate downwards before it becomes buoyancy limited. This is considered in the later section dealing with buoyancy effects.

Flammability Behaviour in Partially Confined Conditions

Having discussed flammability in totally confined and totally unconfined conditions, we now turn to the intermediate case of partial confinement. This is the most difficult and complex case, and few definite conclusions can be reached. The flammability behaviour will be intermediate between the extremes of confinement and unconfinement, and the extent of confinement will determine which extreme is more closely approached.

The limits for upward propagation alone ($\uparrow$) should be the same as for confined conditions, whatever the nature or extent of the confinement. The circumstances which cause the upward flame to be followed by downward propagation (combustion designated by $\updownarrow$ and $\updownarrow$) are unknown. This is probably the most crucial gap in our understanding, since this type of combustion can produce substantial overpressures. Clearly some sort of roof is needed for the upward flame to impinge upon. But the reasons for the onset of the downward moving flames are not understood. It is possible that the initial upward propagation can increase the pressure and temperature of the gas in a fully enclosed vessel to a sufficient extent for downward propagation to become possible. This process is almost certainly aided in a spherical vessel by the movement of hot burned gases down the walls. Such effects would be different in, say, a cuboid container, though downward propagation has been observed in such an enclosure by Krivulin et al (11). The distance the downward moving flames can travel before extinction is also unknown. We have tried in our soap bubble experiments to impose a form of partial confinement to see if downward propagation occurred. Solid roof sections, flat, cylindrical and spherical in shape, have been used. So far, we have obtained no real evidence of downward propagation.

Clearly, more work is needed on flammability in partially confined conditions to resolve these uncertainties. In the meantime, it is probably necessary for maximum safety to use information on flammability behaviour that is relevant to confined conditions.

Combustion in Large Volumes : Buoyancy Effects on Flammability

We have previously stated that in unconfined conditions, the limit for direct downward propagation is governed by buoyancy. In this section, we develop a simple model of the interaction of buoyancy and combustion; test its validity with data from soap bubble experiments, and examine its implications for the burning of large volumes of gas.

In the early stages of combustion from a point source of ignition, the flame expands spherically. The rate of expansion is determined by the flame speed of the mixture. As the size of the hot gas ball increases, buoyancy forces become significant, causing changes in the flame shape. Initially the base of the sphere flattens and no further downward propagation occurs. Subsequently, the whole ball rises in space, in the shape of an oblate spheroid. or, with greater deformation, "kidney-shaped" with a hollowed out base. Here we are concerned only with the first of these stages - the flattening of the sphere.

The equation of motion for the process is :

$$\frac{d(Mv)}{dt} = (\rho_u - \rho_b)\ g\ V$$

The equation should also include a drag term. But during the early stages of combustion, this will be very small and can safely be ignored.

The mass M is given by

$$M = (\rho_b + k\ \rho_u)\ V$$

with $k\ \rho_u\ V$ representing the virtual mass. The value of k ranges from 0.5 to 0.6 (7) and here is given a value of 0.5. For a spherical case, the equation of motion becomes :

$$\frac{d(r^3\ v)}{dt} = B\ g\ r^3$$

where $B \equiv (\rho_u - \rho_b)/(k\ \rho_u + \rho_b)$

We also have the definition of flame speed :

$$dr/dt \equiv S_s$$

where S_s is the velocity of the sideways motion, assumed to be free from buoyancy effects.

The model produces the following expression for the buoyant velocity :

$$v = \tfrac{1}{4}\ B\ g\ t$$

The velocities of the top and bottom of the flame front, S_T and S_B, respectively, are given by :

$$S_T = S_s + v$$

$$S_B = S_s - v$$

The model has been tested against data from the soap-bubble experiments. Burnt gas densities were determined assuming adiabatic combustion. An example is shown in Figure 5 for the positions of the top and bottom of the flame. Agreement with experiment is good. This simple model was not designed to account for buoyant rise in very slow burning clouds, where the flame shape is highly distorted. In these cases, it over-estimated the buoyant rise. More sophisticated models, (for example, see (7)), are needed to describe these flames.

Our soap-bubble experiments are small scale and by themselves do not constitute a sufficiently rigorous test of the model. Experiments on flame propagation in large clouds of 10 m diameter have been performed by Lind (12). The model successfully predicts the buoyant rise of these flames which are burning for periods of more than a second. Thus we are confident that the model is accurate for near-spherical flames. Fuller justification for the model is given in another paper by Smith and Ward (13).

We have earlier stated that the condition for the limit of direct downward propagation is that S_B is zero. This occurs when $v = S_S$. The extent of downward propagation predicted in this way for lean methane-air mixtures is shown in Figure 6. The positions of the side and top of the flame at the instant the downward propagation ceases, are also shown, though these will increase with subsequent development. It can be seen that a 6.4% mixture will burn down only about 40 mm, whereas the same mixture burns out completely in the enclosed vessel. Similarly a stoichiometric mixture, when completely unconfined, will burn down for a distance of only 0.85 m before stopping. The corresponding side and top dimensions are 1.7 and 2.55 m.

Flammability Behaviour for Mixed Fuels

In addition to the work involving pure fuels in air, some experiments were performed in the closed vessel using multi-component fuels, to test the validity of le Chatelier's rule under these conditions. In its simplest form, this rule states that if any two fuel-air mixtures, which are both at the lower limit of flammability, are mixed together in any proportions, the resulting mixture will also be at the lower limit. The rule can be extended to apply to upper limits; it can also be used in principle for fuels with three or more components. It does not hold for all fuels, but it does seem valid for simple hydrocarbons. The rule and its application are explained in detail elsewhere (1). Although it has been tested thoroughly at the absolute flammability limits of binary fuel mixtures in standard tube apparatus, there is little experimental evidence to support its application to mixtures of three or more fuels. Furthermore, it has not previously been tested on the different modes of combustion occurring in near-limit mixtures.

In this work, we have found that the rule could be used reliably to predict the lower and upper limits of any mixture of $C_1 - C_4$ paraffins in air. We also found that the rule could be used with equal confidence to predict the limits for direct downward propagation in the closed sphere (symbol ✥). Additionally, le Chatelier's rule could be used to calculate the limits for the intermediate types of combustion (symbols ↥ and ↕), but with slightly less accuracy. However, since the last three flame types are influenced by the vessel dimensions, care is needed to use the correct limits for the fuel constituents. This work is more fully described elsewhere (8).

CONCLUDING REMARKS

In this paper, we have tried to demonstrate that the flammability behaviour of fuels is more complex than is commonly supposed, but that, even so, we now have a fairly good understanding of many of its aspects, in the case of the simple paraffins, methane to butane.

For gases in closed spherical vessels, the composition limits and the transient overpressures produced by the different forms of limit combustion are well characterised. Our work and other similar studies present a consistent picture. We conclude that flammability behaviour with spherical confinement is now fairly well understood.

In other shaped vessels and more particularly in partially confined enclosures, the patterns of combustion are more complex and firm conclusions difficult to make. More work is needed to resolve these uncertainties.

When all confinement is removed, matters are considerably simplified. Buoyancy effects assume great importance and dictate the extent to which combustion is possible in the downward direction. Reasonable predictions of their magnitude are possible. However, a conceptual difficulty arises here, because in these circumstances, the idea of a "limit" of flammability has no real meaning.

When multicomponent fuels are considered, flammability behaviour can be predicted fairly well using le Chatelier's rule, provided data are available for the pure fuels.

We hope that the approach adopted in this paper is useful, and might provide a convenient framework for scientists and engineers to examine flammability characteristics over a wide range of circumstances.

Acknowledgement

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SYMBOLS USED

$B = (\rho_u - \rho_b) / (k\ \rho_u + \rho_b)$

M = mass of combustion products and corresponding virtual mass

r = radius of flame

ρ = density

S = flame speed

t = time

V = volume of combustion products

v = velocity of centre of gravity of combustion products; buoyant velocity

Subscripts

B = base of flame

b = burned gas

S = side of flame

T = top of flame

u = unburned gas

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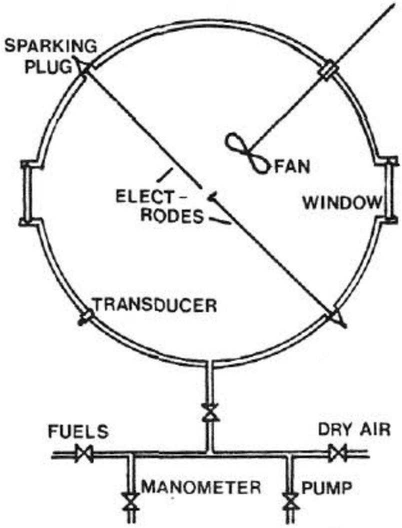

Figure 1. Section of closed Sphere

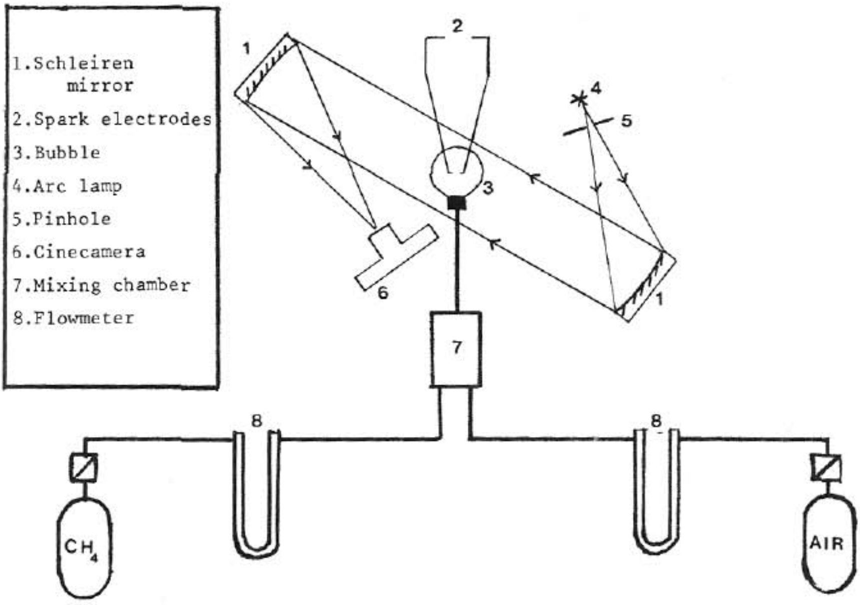

Figure 2. Diagram of Soap Bubble Apparatus

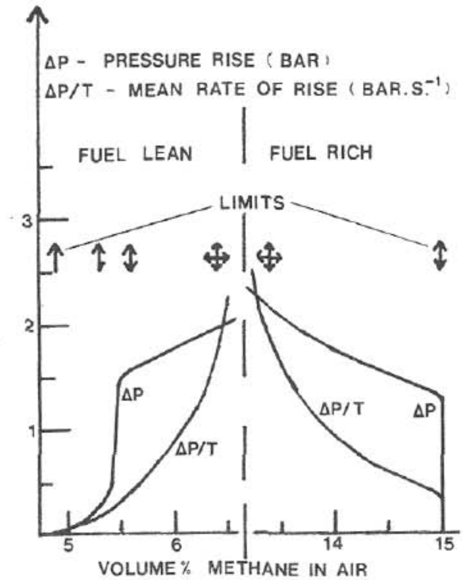

Figure 3. Pressure Rises in Closed Sphere for Methane

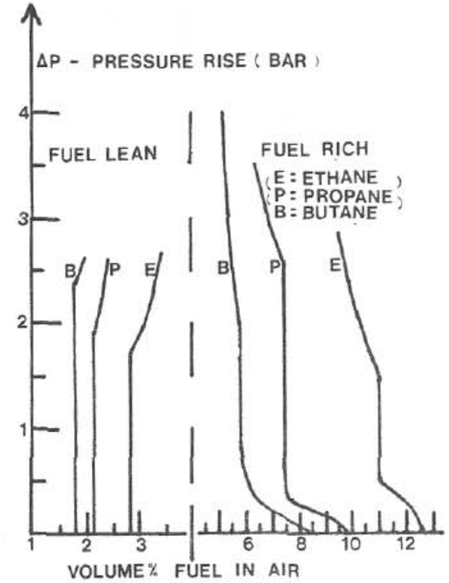

Figure 4. Pressure Rises in Closed Sphere for Ethane, Propane and Butane

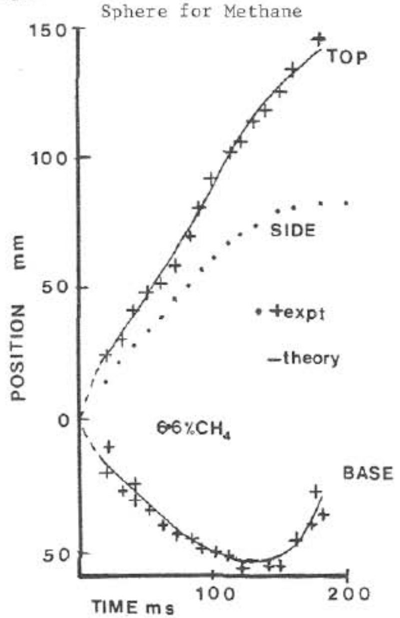

Figure 5. Predicted and Measured Positions of Top and Base of Flame

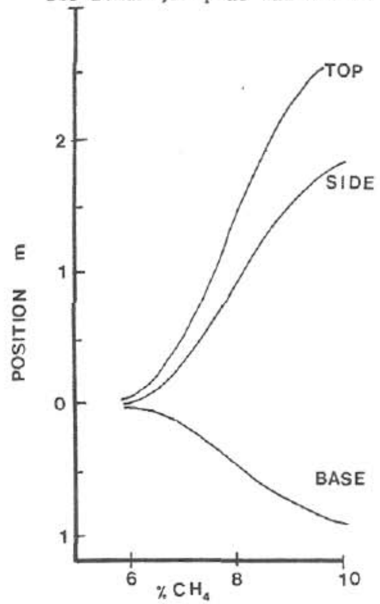

Figure 6. Flame Positions at end of downward Propagation in Unconfined mixture