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A REVIEW OF THE EXTINCTION MECHANISMS OF DIFFUSION FLAME FIRES

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ABSTRACT

This report is the first submission by the University of Edinburgh (Fire Safety Engineering Group) within the project "A Study of the Science of Fire Suppression and Extinction". The main objectives of the study are to survey the field of fire suppression and extinction, to determine the true state of knowledge and understanding of the subject and to highlight important gaps in the current knowledge which may form topics suitable for future research. The report gives an overview of fundamental studies of flaming combustion and the techniques employed for assessing the suppression effectiveness of extinguishants. The major mechanisms of fire suppression and extinction are described and practical definitions of these terms are proposed. The report reflects the current state-of-the-art of research into fire suppression and extinction.

MANAGEMENT SUMMARY

Introduction

This report is the first submission by the University of Edinburgh (Fire Safety Engineering Group) within the project "A Study of the Science of Fire Suppression and Extinction". The main objectives of the study are to survey the field of fire suppression and extinction, to determine the true state of knowledge and understanding of the subject and to highlight important gaps in the current knowledge which may form topics suitable for future research. It is also intended to produce a comprehensive description of the suppression process from a fully developed fire to the point of extinction. The Home Office Fire Research and Development Group (FRDG) gave the following guidelines in relation to the work:

- Water is the main extinguishing agent used by the Fire Service.
- The Fire Service is concerned with large fires, much larger than those controlled by sprinklers.
- Class A fires are the most common but other types should also be considered.
- This work is not concerned with searching for a Halon replacement.

The present report introduces the various stands of scientific research which have been employed in the study of fire suppression. The topics covered include: a description of the combustion process, the classification of flames and a review of the literature on combustion suppression. The report concludes with a discussion of the mechanisms of fire suppression and extinction.

Literature Search

An extensive literature search programme was initiated at the outset of the project; the objectives were twofold:

- To source and collect copies of relevant journal articles and other publications
- To identify prominent research centres and individuals in the field of fire suppression and extinction

The scope of the initial search was kept deliberately wide to ensure that a comprehensive database was established. Four computer-based systems were interrogated using "keyword" searches. An initial set of some 5500 references was refined somewhat by subtracting duplicates and other spurious material; nevertheless a substantial amount of potentially useful material remained. This rapidly-expanding bibliography has been further augmented by the Fire Safety Engineering Group's own reference material. Reference material drawn upon for this initial report has been restricted to publications which provide a fairly broad treatment of fire suppression and extinction.

The abundance of published information on the suppression and extinguishment problem has not been reflected proportionately in the contents of recent general conferences on fire safety science, where there has been a considerable bias towards *fire dynamics* topics (i.e. the quantification of fire spread and smoke movement). Evidence of renewed activity in the fire suppression area is provided however, by an increasing number of specialised conferences whose contributors have been motivated to some degree by the search for "Halon replacements".

Class A Fires as Turbulent Diffusion Flames

Two types of flame are described in this report, the *premixed* flame and the *diffusion* flame. It is shown that the fires of practical concern to the Fire Service are *turbulent diffusion flames* rather than the *premixed* variety. Notwithstanding this important distinction, experimental studies on both types of flame have been used extensively to improve our understanding of the suppression process.

Published Work on Combustion Suppression

This report contains a wide-ranging review of the literature on combustion suppression, from the 1950s to the present day. The articles include small-scale and large-scale experimental studies as well as theoretical analyses of the problem (including computer simulations). Some studies were designed to quantify the relative effectiveness of novel suppressants while others were clearly aimed at obtaining more fundamental data on some aspects of fire suppression (such as the details of the chemical interaction between the fire and a chemically-active suppressant). The report includes details of the methods used to measure the suppression effectiveness (e.g. measurement of the flame burning rate, or changes in the limits of flammability) and the various experimental configurations are described.

The computer simulation of combustion processes is a vast and highly complex area which cannot be fully addressed in the current wide-ranging review document. Nevertheless, articles on the computer simulation of fire problems are becoming increasingly more common in the literature, reflecting their growing contribution to fire science; some idea of the potential application of this technique to combustion suppression problems emerges from this report.

Practical Definitions of Suppression and Extinction

"Fire extinguishment is the application of the agent at any level high enough and for long enough so that no burning of any kind continues. In fire suppression, open flaming is stopped, but a deep seated fire condition will require additional steps to assure total extinguishment."

The Mechanisms of Fire Suppression

There appears to be a general consensus in the literature as to the major physical and chemical mechanisms which can effect fire suppression:

- *Cooling* of the combustible fuel surface which in a liquid reduces the vapour pressure and in a solid reduces the rate of pyrolysis.
- *Covering* (or *blanketing*) the fuel surface with a barrier to reduce the emission of fuel vapour; this method also interrupts thermal feedback from the flame and therefore also contributes to fuel cooling.
- *Cooling* the flame zone itself; this reduces the concentration of free radicals (the chain-branching initiators of the combustion reaction). Some proportion of the heat of reaction is taken up by heating an inert substance (such as water) and therefore less thermal energy is available to continue the chemical break-up of compounds in the vicinity of the reaction zone.
- *Inhibiting* the flame zone by the introduction of a material which acts as a "sink" for free radicals (i.e. *free radical quenching*). This method removes the highly reactive free radicals from the combustion zone by introducing a chemical (e.g. a Halon) which is effectively more chemically attractive to the radicals, but which forms stable products which do not contribute to the combustion reaction.
- *Inerting* the air feeding the flame by reducing the oxygen partial pressure by the addition of an inert gas (e.g. N_2, CO_2, H_2O vapour). Again this is equivalent to the removal of the oxidiser supply to the flame.
- *Dilution* of a flammable liquid with a non-combustible liquid to reduce the partial pressure of flammable vapours. This is equivalent to the removal of the fuel supply.
- *Quenching* effects caused by the introduction of small particles in high concentrations (e.g. dry powder stream); flames cannot propagate between solid surfaces at close separations due to the loss of thermal energy by conduction to these surfaces.
- *Flame blow-off* caused by a high extinguishant stream velocity; if the characteristic transport time of the reactants is shorter than the chemical time, combustion is not possible.

Summary

Fundamental studies of flaming combustion and suppression have been reviewed and scientific methods for assessing the suppression effectiveness of extinguishants are described. The report accurately reflects the general state-of-the-art of current research into fire suppression and extinction. The specific case of the application of water sprays and mists to Class A fires will be the subject of future work.

CONTENTS **Page No.**

FIGURES

APPENDICES

1. INTRODUCTION

1.1 Terms of Reference

This report has been written under the terms of the *Agreement for the Study of the Science of Fire Suppression and Extinction* between the University of Edinburgh and the Home Office Fire Research and Development Group (Fire and Emergency Planning Department).

1.2 Objectives

The broad objective of this three-year study is to survey the field of fire suppression and extinction in order to determine the true state of knowledge and understanding of the subject. It is also envisaged that the review will highlight important gaps in the current knowledge; therefore a secondary objective of the project is to identify topics suitable for future research initiatives. The objective of the project is to produce a comprehensive description of the suppression process from a fully developed fire to the point of extinction. The Home Office Fire Research and Development Group gave the following guidelines in relation to the work:

- Water is the main extinguishing agent used by the Fire Service.
- The Fire Service is concerned with large fires, much larger than those controlled by sprinklers.
- Class A fires are the most common but other types should also be considered.
- This work is not concerned with searching for a Halon replacement.

The use of sprinklers is not a major concern of this work although there has been much relevant research in this area. The main objective of this initial document is the development of a concise, practical description of the interactions between fires and various active methods of fire extinguishment; in particular the physical and chemical mechanisms exploited by extinguishants are examined. The discussion is centred on the general mode of action of suppressants/extinguishants; the effectiveness of specific media will be considered in detail at a later stage.

1.3 Methodology

This report is intended to provide a tractable discussion of the physical and chemical mechanisms which can effect the extinguishment of fire. The level of detail has been kept to a minimum while still permitting a comprehensive explanation of the processes involved; several appendices are included together with an extensive list of references. The sections are intended to proceed in a logical manner, beginning with the introduction of some combustion fundamentals. The structure of flames and flame stability are then discussed with particular reference to the mode of action of suppressants. Proposals for a "unified theory of fire suppression" are assessed and suggestions for practical definitions of "fire suppression" and "fire extinction" are advanced. The state-of-the-art of mathematical modelling of the dynamics of fire-suppressant interaction is discussed in the context of the possible application of this technology to the problem of fire extinguishment. The report concludes with a summary section and some proposals for the future direction of the current project.

2. AN OVERVIEW OF FLAMING COMBUSTION

2.1 General

A great deal has been written on the many and varied aspects of flaming combustion, each author preferring to stress in varying degrees the chemical or physical nature of the subject (References 1-6). While it is not the intention to reproduce such texts here, some discussion of the nature of flaming combustion is unavoidable, and indeed indispensable, if the mechanisms of flame extinction and suppression are to be subsequently understood. The discussion focuses on some characteristics of flames which are readily measurable and which have consequently proved useful in the assessment of various flame inhibitors and extinguishants. The approach adopted is very much in the spirit of Gaydon and Wolfhard (Reference 5) who preferred the development of a simple physical understanding of flame processes and had "...little enthusiasm for abstract mathematical treatments of combustion, these usually involving many unknown and often unknowable parameters." Nevertheless, the current proliferation of computer modelling techniques is extremely important and cannot be ignored and so references to more mathematical treatments have also been included; where relevant, some theoretical aspects have been expanded in the Appendices.

2.2 The Combustion Process

Combustion has been defined as (Reference 7):

The rapid, high-temperature oxidation of fuels, converting carbon to carbon dioxide (or carbon monoxide) and hydrogen to water vapour. Any sulphur in the fuel is oxidised to sulphur dioxide or trioxide...while nitrogen either remains unreacted or is converted to nitrogen oxides. Most combustion reactions occur in the gas phase.... The release of chemical energy during combustion of gases produces a luminous, radiating zone which is seen as the flame or flame front.

In chemical terms, *oxidation* is merely the process whereby electrons are transferred from the fuel (or *reducing agent*) to the *oxidising agent*; the result of this interaction is that the fuel becomes *oxidised* while the oxidiser is simultaneously *reduced*. Oxidation is a very common phenomenon, everyday examples occurring at room temperature include the rusting of metals, the drying of paint and the souring of wine etc. At elevated temperatures the rate of oxidation increases rapidly, with a correspondingly increased rate of heat liberation per unit time; eventually a point is reached where the reaction is able to sustain itself from its heat of reaction (i.e. *combustion* has been initiated). The process attains a steady-state when the rate of chemical heat generation is equal to the rate of heat dissipation to the surroundings. The foregoing discussion applies equally to oxidising reactions in oxygen-free atmospheres, such as the burning of calcium and aluminium in nitrogen, the combustion of phosphorous, carbon and other elements in nitrous oxide and the chemical reactions involving fluorine and other halogens with hydrogen and hydrocarbons. These reactions are rare however, and the most common form of combustion (whether "wanted" or "unwanted") involves the reaction of oxygen in the air with various solid, liquid and gaseous fuels. Cox (Reference 4) has suggested that one essential feature of "unwanted" fire distinguishes it from other forms of combustion; *the rate of fuel supply to the fire is controlled by the positive feedback of heat from the products of its own combustion.*

The latter statement holds for both of the "condensed phases" of combustible material (i.e. solid or liquid); the heat feedback always drives the supply of gaseous volatiles and thermal radiation is usually the dominant heat transfer mechanism in fire scales greater than around 0.3 m. (In the case where the fuel is initially gaseous, the supply rate is determined by fluid dynamic principles rather than thermal feedback effects.) Drysdale (Reference 2) described 'fire' as a manifestation of a chemical reaction but emphasised that the mode of burning may be more dependent on the physical nature of the fuel and its environment than on the fuel chemistry. Notwithstanding this observation, a rational study of the action of fire extinguishants must include at least a qualitative discussion of basic combustion chemistry principles; the familiar candle flame has frequently been used for this purpose in the literature (References 3, 5, 8). The candle flame is an example of a *diffusion flame*, a small scale version of the flame type most often encountered by the Fire Service; the following section considers flame phenomena in more detail.

2.3 Classification of Flames

A crude physical description of a flame might be *a region of burning gas which emits heat and light*; this agrees with a typical dictionary definition: *a hot usually luminous body of burning gas often containing small incandescent particles, typically emanating in flickering streams from burning material or produced by a jet of ignited gas.* Intricate and ingenious experimental methods have been developed to facilitate the detailed study of flames in terms of both the light and heat emitted; specific references to some of these research techniques appear throughout this report.

Having introduced a general physical description of a flame, some sub-categories may be briefly mentioned in the context of their relevance to the current study of extinction and suppression;

- *Stationary flames*
- *Propagating flames*
- *Premixed flames*
- *Diffusion flames*

Stationary flames will be arbitrarily defined as those in which the location of the flame does not change significantly over the course of time; thus a candle flame is *stationary* since the source of light and heat referred to above is always located at the top of the candle. Similarly, a lighted Bunsen burner placed on a laboratory bench is an example of a stationary flame, and on a larger scale a burning house could be considered as containing a more or less infinite number of stationary flames. In the latter case it might be argued that the location of the flame does in fact change, especially during the early phases of fire growth as new fuel sources become involved; i.e. the fire spreads (or moves) through the house. The classification is justified, however as the individual flames do remain associated with an essentially fixed fuel bed and so do not constitute a *propagating flame* in the strict sense of the term.

True *propagating flames* are characterised by rapid combustion events occurring in homogeneous fuel/oxidiser mixtures where the flame front passes through the mixture, away from the ignition source; this process is more commonly known as an *explosion*. The study of such events may be made either at constant volume, as in the case of expanding spherical explosion waves generated in closed vessels, or at constant pressure where for example a flame front may be allowed to propagate at high speed down a tube filled with the combustible mixture. The latter configuration may be adapted to permit the physical measurement of *flame speed* (see Section 3.2) while explosions within closed volumes are harnessed in the internal combustion engine in order to perform mechanical work. Large scale explosions of either configuration may be extremely destructive and will be considered within the current project in the context of the *backdraught* phenomenon. It should perhaps also be mentioned that a *detonation* is an explosion where the reaction rate is increased locally due to high temperatures induced by the formation of a shock wave; once the initial detonation has occurred, the flame front is subsequently propagated by the shock wave at speeds of up to 3000 m/s (i.e. approximately 10 times the speed of sound in air); the exact velocity is dependent upon the characteristic sonic velocity for the gas mixture.

Propagating flames occurring in homogeneous fuel/oxidiser mixtures are also examples of *premixed flames*; by definition a premixed flame is one which is established in an intimate combustible mixture of fuel and oxidiser. In theory it is possible to produce a stationary premixed flame by maintaining a supply of the combustible mixture in the direction opposite to that of flame front propagation. In practice, for the simple configuration where a flame is propagating within a tube of flammable mixture (the constant pressure scenario), a stationary flame may only be established at the tube exit when the gas mixture is supplied at a mean velocity slightly in excess of the characteristic flame speed (S_u); this is the operating principle of the Bunsen burner.

Diffusion flames differ from their premixed counterparts in that the fuel and oxidiser "reservoirs" are initially separate; after combustion is initiated, it is subsequently maintained by the continuous inter-mixing of fuel and oxidiser into the combustion (or *reaction*) zone. Since this process is actually the merging of two initially chemically distinct masses of gas, it is also apparent that there must be a gradual change in chemical composition normal to the "flame sheet" wherein the chemical reactions are occurring. In small scale flames, such as a candle, this process is controlled by *molecular diffusion*; the mixing in larger flames is induced by macro-scale aerodynamic effects which produce *turbulent diffusion*. Therefore, in contrast to *premixed flames*, the notion of a burning velocity is not relevant in the case of *diffusion flames* since the rate of combustion is controlled by the rates of diffusion and mixing.

Gaydon and Wolfhard (Reference 5) reported that premixed flames had attracted much more scientific study than diffusion flames because the former yielded information on fundamental properties of the gas mixture such as its burning velocity and temperature. Cox's "wanted" fires (Reference 4) are almost exclusively of the premixed variety, where research goals include increasing combustion efficiency and reducing noxious exhausts (for example in power stations, industrial furnaces, internal combustion engines etc.); this work has exploited novel experimental and theoretical techniques and has led to an improved understanding of many aspects of combustion. 'Unwanted' fires, predominantly of the diffusion flame variety, are the province of Fire Safety specialists; the behaviour of diffusion flames (whether during growth or extinction) is more complex than their premixed counterparts, involving the turbulent transfer of heat and mass in addition to chemical interactions. Although it has long been realised that large-scale turbulent diffusion flames correspond to the "real situation" of practical importance in fire safety problems, many aspects of their nature are still not completely understood and so their detailed behaviour cannot be predicted with any degree of accuracy at the present time.

In the following discussion it will be seen that the study of premixed flames continues to figure prominently in contemporary studies of combustion, and therefore fire suppression, whether these studies be experimental or theoretical. The structure and stability of diffusion flames is also addressed in more detail and compared with that of premixed flames; in both cases the purpose is to define those measurable parameters which have been used to assess the effectiveness of flame inhibitors and extinguishants. Again, the narrative is based on the physical aspects of flames; a succinct discussion of flame chemistry follows in Section 4, and the computer analysis of a simple stoichiometric chemical reaction is considered briefly in Appendix B.

3. COMPARISON OF PREMIXED FLAMES AND DIFFUSION FLAMES

3.1 General

Throughout Section 3, reference will be made to Figures 1 and 2. The lower part of Figure 1 shows schematic diagrams of premixed and diffusion flames while the upper region consists of the corresponding qualitative concentration and temperature distributions through the reaction zone and beyond. Figure 2 comprises a sequence of computer-processed video frames obtained from a series of visualisation experiments using propane-air flames at the Fire Safety Laboratory in Edinburgh.

3.2 Premixed Flames

Figure1(a)(lower) illustrates the propagation of a spherical combustion wave away from an ignition source in an intimate premixture of fuel and oxidiser. The case shown corresponds to the constant pressure propagating premixed flame described in Section 2.3 (i.e. an explosion), where the flame front travels at S_u the characteristic *flame speed* for the particular mixture. The laboratory study of such flames is made easier if they are stationary and it was suggested in Section 2.3 that this could be achieved by supplying a stream of the premixture at a mean velocity equal to S_u in the direction opposite to flame propagation. In practice, this arrangement would produce a flame possessing only *neutral stability* (Reference 1) and its position would shift in a random manner due to small perturbations within the flow; fortunately flames can be effectively stabilised by attaching them to a *burner*. In the case of a typical laminar premixed flame, the burner fulfils three functions: it facilitates the mixing of fuel and oxidant, it provides a suitable conduit for the establishment of laminar flow and its edges provide a heat sink which restricts movement of the flame. The stabilising effect is localised at the burner rim, in fact a simple metal ring can perform the same function; the *quenching* effect is primarily due to heat removal although it has also been suggested that active species are *quenched* (References 1, 5) as well (flame quenching is discussed in Section 5.2).

Gaydon and Wolfhard (Reference 5) have described the introduction of the Bunsen burner around 1855, and its subsequent adoption by industry, in preference to the conventional diffusion flame burners whose simple design produced very inefficient combustion (see also Reference 4). The industrial advantages of premixed flames were those of increased temperature and improved heat transfer which resulted from the more intense combustion; in addition, the virtually transparent flame region contained very little carbon and so the problems associated with sooting were greatly reduced. This familiar design of premixing burner entrains air laterally through apertures at the base, by virtue of the upward motion of the gas supply issuing from a small nozzle located on the axis of the burner tube, adjacent to the apertures. It has been found that, even with the air holes fully open, the amount of air entrained initially is usually well below that required for complete combustion of the gas (i.e. less than the *stoichiometric* value where sufficient oxygen is present to permit, in theory at least, complete combustion to the products described in the introduction of Section 2.2); in some instances less than half the required amount of air is entrained (Reference 5).

The combustion of the mixture at the top of the burner is aided by the subsequent entrainment of additional (or secondary) air local to the flame; this mechanism tends to have a stabilising effect on the inner premixed flame, which displays a characteristic cone-shaped luminous inner zone surrounded by a paler sheath of flame (the so-called *outer-cone*). Without this outer region, the combustion would otherwise be supported between only a relatively narrow range of gas flow rates. At low gas flow rates the flame is liable to propagate (*strike-back*) down the tube, while high gas flows can result in *blow-off* (extinguishment) of the flame; these critical design aspects of premixed burners have been analysed in detail by Lewis and von Elbe (Reference 6). Gaydon and Wolfhard (Reference 5) stress that the gas velocity at all points in the tube must be sufficient to prevent strike-back; consequently, burner design is somewhat dependent upon the fuel gas envisaged, since different gases have different characteristic flame speeds (S_u). Figure 2(g) depicts the streamlines through the reaction zone of a laminar premixed burner flame (e.g. Figure 2(d) above); the expansion of the gas stream exiting the burner and the gap between the flame base and the burner rim are both evident in this diagram.

The laboratory study of laminar premixed flames requires the establishment of a steady flame whose constituent mixture is ideally variable over a wide range, from fuel-lean to fuel-rich; Gaydon and Wolfhard (Reference 5) advocated a burner tube at least 300 mm long with a T-piece at the base for the introduction of accurately-metered fuel and air flows. The flow régime in the tube is characterised by the Reynolds' number,

$$\mathrm{Re} = \frac{\rho v d}{\mu} \tag{3.1}$$

where,

ρ = density of the gas mixture (kg/m^3)
v = mean velocity of the mixture (m/s)
d = diameter of the burner tube (m)
μ = absolute viscosity of the gas mixture (Pa.s)

For Re < 2300, the flow is laminar in character; in this state the direction of motion of all the fluid particles is always parallel with the tube axis, with no "sideways" (lateral) excursions of velocity. The gas mixture may be visualised as flowing in concentric cylindrical sheets or "laminae", each associated with a particular instantaneous value of velocity; the velocity of the laminae increases from the wall of the tube, reaching a maximum at the centre. Beyond some critical Reynolds' number, and in general at all Re > 3200, the gas flow becomes turbulent; the fluid particles now exhibit random fluctuations in velocity in all directions, accompanied by rapid interchanges of momentum, the formation of eddies and a dramatic increase in the resistance to flow. Regardless of whether the flow is laminar or turbulent, a certain length of pipe is required before the flow is *fully developed*; beyond this point, the shape of the velocity profile across the pipe remains constant. Various empirical relationships have been devised to express the length of pipe required (L), for example

$$L = 0.05\mathrm{Re}.d \qquad (3.2)$$

as given by Gaydon and Wolfhard (Reference 5). Thus, in either case (laminar or turbulent) a long burner promotes the establishment of a well mixed and fully developed flow although the exact length required will be proportional to the Reynolds' number of the flow. The video images of Figure 2 were obtained using a steel burner tube approximately 1 metre in length and of 10 mm internal diameter; propane and air were introduced to the base of the burner via a T-piece as described above. In the lower sequence of four images, the gas flow rates in this simple burner are relatively high and consequently the flames are turbulent.

In the upper sequence the flow rates are much lower and the flames are laminar in nature; in addition the top of the burner has been fitted with a *Smithells separator* to aid the visualisation of the true premixed flame. This consists of a "pyrex" tube of 20 mm internal diameter fitted concentric to the steel burner tube and with its rim located some 30 mm above the former's rim; a good seal exists where the two tubes are connected to eliminate unwanted entrainment of air from below. The arrangement is shown schematically in the left uppermost image and the flame shown here is a laminar propane diffusion flame; there is zero airflow into the T-piece and combustion proceeds using air which diffuses towards the reaction zone from the laboratory atmosphere. The high luminosity is characteristic of diffusion flames and is due to optical radiation from incandescent carbon particles. As the sequence progresses from left to right, the propane flow is constant but the premixed airflow is increased; as more air is added the luminous yellow-white region contracts and an outer blue-violet sheath becomes evident. Fully developed laminar pipe flow displays a characteristic parabolic velocity profile and a thin flame front which is conical to slightly bell-shaped in profile; this is well seen in the image of Figure 2(d) and the schematics of (g) and (h). The onset of instability is observed in (e), where the inner cone has become detached from the upper "pyrex" rim and is *striking back* against the premixed gas flow because the flame speed has exceeded this flowrate. In (f), stability is regained with the inner cone (the true premixed flame) supported by the smaller diameter steel burner rim and the pale outer cone (a diffusion flame) stabilised by the Smithells separator above. Chemical analysis of the (non-luminous) interconal gases reveals a mixture of CO, H_2, CO_2, H_2O and N_2 (Reference 5); the hydrocarbons are usually completely broken up during their passage through the inner cone. In general the amount of CO and H_2 decreases and the amount of CO_2 and H_2O increases in the interconal region as the proportion of air in the premixture is increased.

Again in the lower sequence, the leftmost image is a pure propane diffusion flame; however the initial flowrate of propane is higher than above and lateral excursions of the flame are indicative of turbulent behaviour. Once again the premixed airflow is increased from left to right while the propane flow is constant; the centre of the flame becomes blurred while the outer regions retain their sharpness. Further increase in turbulence leads to a general thickening of the entire flame front; this relatively large volume which now contains the primary chemical reactions is commonly referred to as the *flame brush* Figure 2(k). The final image (l) shows the moment of *blow-off* where the loss of stability results in flame extinguishment. With high gas flowrates, the flame is lifted higher above the burner rim; there are two consequences, firstly the quenching effect (heat transfer) to the rim is reduced and secondly there is an increase of secondary air entrainment at the burner rim. The former tends to increase the flame speed S_u while the latter tends to reduce S_u near the rim; if the latter effect is dominant then the flame continues to rise (away from the fuel source and into the ambient atmosphere) and is extinguished; the *blow-off* limit has been reached.

Hirst (Reference 8) summarises the main characteristics of premixed flames thus:

- The reactants are gaseous.
- The reactants have already been mixed prior to ignition.
- Heat transfer and the diffusion of active species are rate-controlling.
- Reaction can occur in any mixture which is within the lower and upper limits of flammability: typically these limits are respectively from 0.5 to 2.5 of the stoichiometric ratio.
- The flames are generally coloured blue.
- The flames propagate freely throughout the premixed volume at a velocity which is a characteristic of the particular mixture.
- The occurrence of premixed combustion in a closed vessel results in an increase of pressure which may rupture the vessel.
- Under normal conditions a premixed flame is an explosion.
- Under exceptional circumstances a premixed flame will propagate as a detonation at supersonic velocity.

Some fundamental data for several premixed flames are given in Table 3.1 below. The use of these and other premixed flame characteristics in the study of fire suppression is described in Section 5.

Table 3.1

Flammability limits and flame properties for some common gases at atmospheric pressure (adapted from Reference 1)

	Flammability limits	(% by volume)	Flame temperature	Maximum burning velocity
Reactants	Lower	Upper	(K)	S_u (m/s)
$H_2 + O_2$	4.0	94	3083	11.0
$C_2H_2 + O_2$			3431	11.4
H_2+ air	4.0	75	2380	3.1
C_2H_2 + air	2.5	80	2513	1.58
CH_4 + air	5.3	15	2222	0.45
C_3H_8 + air	2.2	9.5	2250	0.43

3.3 Diffusion Flames

Cox (Reference 4) considers that the essential feature of an "unwanted fire" is the control of the fuel supply by the positive feedback of heat from the products of its own combustion. Irrespective of whether the fuel is initially solid or liquid, the supply of gaseous volatiles is produced via this feedback of thermal energy; in fires of dimension >0.3 m, the feedback is dominated by thermal radiation. Such fires are predominantly of the diffusion flame variety (although premixing can occur in exceptional circumstances), and are usually turbulent in character. The more products of combustion that are released, the greater is the radiative heat feedback and the consequent rate of release of volatiles; the latter then burn and release an even greater quantity of products and so on.

A candle flame provides a convenient example of diffusion-controlled combustion on a small scale (Reference 8). Once lit, the flame transfers heat energy back to the wax surrounding the wick. The molten wax is subsequently drawn up the wick by capillary action, whereupon it is subjected to further heating causing it to vapourise. The vapour is raised to still higher temperatures as it approaches the reaction zone (pale blue boundary in Figure 1(b)(lower)); this zone contains all the active (heat-producing) combustion processes and is only some 1-2 mm thick (Reference 8). The candle flame is an example of a slow-burning diffusion flame since the rate of fuel supply is relatively slow and the flow régime is laminar. The mixing process occurs solely by molecular diffusion and therefore the flame properties are determined by molecular properties; in contrast, large-scale diffusion flames generate strong buoyancy forces and correspondingly high local velocities. The turbulence associated with such velocity fields dominates the molecular effects and the character of large diffusion flames is consequently governed by the fluid dynamics of the system.

Figure 1(b)(upper) shows that the fuel concentration has a maximum on the flame axis but falls away rapidly towards the reaction zone; this behaviour is mirrored by the depletion of oxygen concentration on the other side (ambient atmosphere) of the flame front. The concentration of products, on the other hand, peaks inside the reaction zone and drops rapidly both towards the flame axis and into the ambient region. The flame boundary represents the position at which the fuel:oxygen ratio becomes *stoichiometric* and since the fuel concentration reduces with height, this boundary moves towards the axis and finally converges at the tip where all the fuel is consumed (Reference 1). The assumption of a thin reaction zone is highly idealised since heat and mass transfer effects produce significant reactions on either side of the "true" reaction zone. In general the fuel is pyrolysed and the oxidant broken into reactive radicals (see Section 4); thus the reactants entering the "true" reaction zone are not the original chemical species. Hirst (Reference 8) invokes the candle flame example to describe the pyrolysis (or "loosening by fire") of long chain paraffin wax molecules into smaller molecules. This process leads to molecular fragments which combine to form carbonaceous species, leading to the formation of minute soot particles. Highly reactive hydrogen atoms are also produced which are extremely mobile and diffuse rapidly into the reaction zone where they combine with oxygen to form (ultimately) water vapour.

The carbon particles are heated almost to reaction zone temperatures before they break down into carbon atoms which also react with oxygen to form carbon dioxide. The luminosity of the candle flame (and other diffusion flames) is due to radiation from white hot carbon particles within the fuel-rich region.

In small-scale diffusion flames, the reactions are almost invariably stoichiometric, and Hirst (Reference 8) has described how stoichiometry is preserved by the automatic adjustment of the size of a candle flame even when a particularly volatile region of wax undergoes pyrolysis. The candle flame remains just the right size to ensure complete combustion, but if it were larger then some of the carbon particles would fail to react and an open flame would result, with the unburned carbon being released as smoke. Most flames encountered during well-developed fires are large turbulent diffusion flames which are open and therefore produce large volumes of hot smoke (References 8, 9). In addition, the presence of turbulence in large-scale fires produces random local motions superimposed on the otherwise uniform motion of the fluid; these random features have been described variously as *eddies*, *vortices*, *turbulent spheres* and *turbulent balls*.

The formation of eddies is due to the transfer of momentum between the rapidly rising hot gases and the stagnant ambient atmosphere. An eddy of combustion products results in the increased separation of the fuel and oxidiser streams thus decreasing the local diffusion rate; as a result the flame height is increased. When the eddy eventually breaks away, the fuel and oxygen are brought into more intimate contact, the burning rate increases and the flame height is reduced; these eddy effects produce the "flickering" commonly associated with diffusion flames. Some combinations of boundary conditions and aerodynamic effects can produce *flame stretch*, where the area (A) of an element of the flame front increases with time (Reference 3). During the study of turbulent burner flames, Karlovitz *et al* (Reference 10) noticed that the reaction zone near the burner rim got thinner as the gas flow was increased; at higher flows, holes were observed in the flame surface at the rim prior to lifting of the flame. The Karlovitz number K was introduced to nondimensionalize flame stretch by multiplying it by the characteristic time required for the flame to burn through its *preheat zone* (of thickness η_0).

$$K = \frac{\partial(\ln \Delta A)}{\partial t}\frac{\eta_0}{S_u} \tag{3.3}$$

Another related dimensionless quantity is the Damköhler number (References 2, 3),

$$\mathrm{Da} = \frac{\tau_f}{\tau_r} \tag{3.4}$$

which is the ratio of a characteristic flow time (τ_f) to a characteristic chemical reaction time (τ_r). When Da → 0 the flow is inert and when Da → ∞ the reaction occurs quickly relative to the specified length scale of the problem (this is known as the *flame sheet* approximation). The Karlovitz and Damköhler numbers are relevant to the phenomenon of flame blow-off (or blow-out), previously discussed in Section 3.2 for the case of premixed flames. According to Hirst (Reference 8), during blow-out the reaction zone is distorted and stretched which results in it becoming thinner. Consequently, the residence time of the reactants is reduced and the reactions are incomplete. There is a reduction in the amount of heat liberated and the local flame temperature drops below the critical value required to maintain combustion. In addition, the reaction zone is shifted somewhat into regions either fuel-rich or fuel-lean, with the result that the reactions are no longer stoichiometric. Barnard and Bradley (Reference 1) have also described how the entrainment of cold air is possible through holes created by flame stretch; this results in further reduction of temperature and reaction rate until the flame is finally extinguished.

Fristrom (Reference 11) suggested that more fires are extinguished by blow-off than by all other mechanisms since this is the usual method by which matches and candles are extinguished. It was conceded however, that larger fires are increasingly more difficult to extinguish by this method (References 8, 12); the exception is for oil well fires which are routinely blown out by the detonation of a high explosive charge. Fristrom (Reference 11) quoted some authorities as suggesting that in reality all flames are ultimately extinguished by the blow-off which follows primary suppression techniques; indeed it has been postulated that an examination of the local Damköhler number is sufficient to predict the occurrence of flame extinction (References 3, 12).

Gaydon and Wolfard (Reference 5) discussed several reasons for the lack of basic research on diffusion flames, identifying in particular the absence of a fundamental characteristic such as a burning velocity or flame temperature. Two historically important assumptions in the theoretical analysis of diffusion flames were described:

- The reaction zone is assumed to be located at the position where air and fuel are in stoichiometric proportions.

- The rate of diffusion alone is assumed to be the rate-determining process.

The problem with the first of these is that chemical reactions occur over a wide range of fuel:oxygen ratios, particularly at high temperatures when virtually any proportions will support combustion. The second assumption requires the prescription of an independent fundamental parameter, the *diffusion coefficient*; in practice however, this is found to vary with both temperature (approximately as $T^{1.75}$) and mixture composition. However, recent advances in the general area of fire dynamics, coupled with novel computational techniques and the availability of parallel computing technology have provided some new insights to flame behaviour.

Cox (Reference 5) has discussed how the extreme complexity of the fire problem led to fire science's historical reliance upon empirically-based solutions. This traditional approach is changing however, as the subject becomes more mature and powerful computing facilities become more commonplace. A good review of the current state-of-the-art for turbulent diffusion flames is given in a recent article by Moss (Reference 13). An example of the application of "laminar flamelet" theory and the prediction of turbulent diffusion flame extinction by hole production is given by Green (Reference 14). Finally a recent account of developments in parallel computing, applied to the Direct Numerical Simulation (DNS) of "controlled" and "uncontrolled" turbulent combustion is included as Appendix D of this report.

In conclusion, Hirst (Reference 8) has summarised the characteristic properties of diffusion flames thus:

- The reactants are gaseous.
- The reactants are mixed by diffusion.
- Diffusion is rate-controlling.
- The reaction is usually stoichiometric.
- The flames are luminous due to the presence of carbon particles.
- Large flames are open at the top and unburned carbon is released as smoke.
- The flame must always be located close to the source of fuel.
- Most fires comprise large turbulent diffusion flames.

4. FLAME CHEMISTRY

It will be apparent even from the fairly simple discussion in the preceding sections that a fire represents a highly complex combustion system. The picture is especially complicated when the original fuel is a solid; the extensive thermal decomposition associated with combustion in this case results in the release of complex gaseous fuel mixtures (Reference 15). Despite this undoubted complexity, a "feel" for the more important chemical interactions (or *kinetics*) in the main reaction zone can be gleaned from two fairly simple concepts, namely;

- Free radical formation.
- Chemical chain reactions.

Free radicals are defined as "molecules or ions with unpaired electrons and hence generally exceedingly reactive" (Reference 7) and have a complete range of stability (or longevity), some having a relatively long life and others only having transient existence as intermediates in chemical reactions. The most important radicals in hydrocarbon combustion are H, O, OH, CH_3 and CHO; the H radical is the most important component in so-called branching chain reactions.

Chemical chain reactions are of two types, linear chain reactions and branching chain reactions; although the former are more normal, the latter are extremely important in many combustion reactions (Reference 1). The general process for a chain reaction is that an active species (usually a free radical or atom) reacts with a stable molecule to give a stable product molecule plus another active species which can propagate the chain. For example, the reaction between hydrogen and chlorine is propagated by the cycle:

$$Cl + H_2 \rightarrow HCl + H \qquad (4.1)$$

$$H + Cl_2 \rightarrow HCl + Cl \qquad (4.2)$$

which is a linear chain because each propagation step leaves the total number of active centres unchanged. In the case of chain-branching reactions, one active centre reacts and produces more than one new centre which can continue the chain. A simple example of this case is the reaction between the hydrogen atom and the oxygen molecule:

$$H + O_2 \rightarrow OH + O \qquad (4.3)$$

where the reaction of the single active centre (H) produces the radical OH and the diradical O (2 unpaired electrons) which can subsequently react with hydrogen molecules to continue the chain. The subject of flame chemistry is covered in more detail in Reference 15 while examples of the experimental determination of free radical populations in flames are given by Burke *et al* (Reference 16) and by Masri *et al* (Reference 17). These data are fundamental to some of the combustion suppression research reported in Section 5; a particular case is the theoretical work on the extinction of premixed methane-air flames by thermally stable gases (Reference 18) (see also Appendix B).

5. A REVIEW OF PUBLISHED WORK ON COMBUSTION SUPPRESSION

5.1 Introduction

Fristrom's review of combustion suppression (Reference 11), in 1967, identified several techniques which could be used for the quantitative study of fire suppression. Pitts *et al* (Reference 19) published a more recent review of the subject in 1990 and the following list is compiled from these two reports. These two articles, separated by 23 years, provide convenient benchmarks against which the progress of the science may be judged; in general the experimental methods have remained similar (although contemporary instrumentation is far superior), while the advent of computer technology has spawned the new theoretical modelling techniques which were absent in the 1960s. The motivation for the review of Reference 19 was the initiation in the U.S. of a systematic search for optimal Halon replacements in response to the Montreal Protocol which limits the production of commercial firefighting halons (Appendix C). The ultimate test for an agent is its ability to extinguish large, turbulent diffusion flame fires; however cost, material and time factors preclude the testing of every possible agent on a full-scale fire. These practical aspects have resulted in the development of a range of laboratory scale tests designed to provide guidance for researchers in characterising fire suppression behaviour. The list of methods in Section 5.2 is assembled according to the logic of Pitts *et al* (Reference 19), so that the relevance of the test to actual fire situations is increasing.

5.2 Methods for Evaluating Combustion Suppression

5.2.1 Flame Chemistry and Flame Structure of Premixed Flames

Flame structure refers to the detailed velocity, temperature and chemical species concentration fields local to the *reaction zone* (or *flame front*). These experiments consist of burning a premixture of fuel and oxidiser in the presence and absence of an added agent. Interpretations can be made in terms of the elementary physical and chemical processes; the dominant elementary reactions may often be identified and quantitative measurements made of the rates. This powerful technique is thus able to provide crucial information for any basic theory of flame extinction problems. Fristrom (Reference 11) noted that although the potential of the approach was high, experimental difficulties had limited the use of the technique. Pitts *et al* (Reference 19) quoted work performed in the 1970s where the observation of concentration profiles in low pressure premixed flames of methane, oxygen and argon provided important insights into the chemical mechanism of flame suppression by CF_3Br (Halon 1301).

5.2.2 Agent Effects on Flame Speed S_u of Premixed Flames

The concept of flame speed was introduced in Section 2.3 and its relevance to flame stability on burners discussed in Section 3.2. There are a variety of methods for measuring flame burning velocity (Reference 5) but one of the simplest, at least in theory, can be explained with reference to a laminar premixed flame (Figure 2(d) and (h)). Since S_u is the velocity with which a plane flame front moves normal to its surface through the unburned gas, it can be shown, with reference to Figure 2(h), that

$$S_u = U \sin \alpha \tag{5.1}$$

where α is the cone half-angle. The velocities observed are sensitive to parameters such as the fuel/air ratio, temperature and pressure; the presence of fuel additives also modifies the burning velocity. A decrease in the burning velocity with the addition of varying amounts of flame suppressants gives a measure of suppression capability. The justification for such tests is that firstly there is a reasonable correlation between these tests and the ability of the agent to put out real fires. Secondly, these tests can provide important chemical kinetic data of the type discussed in Section 4. References to such work are given by Fristrom (Reference 11) and by Pitts *et al* (Reference 19); the latter study includes references to pioneering work in this area which classified the inhibition effectiveness of chlorine, bromine and iodine atoms (the ratios of effectiveness were given as 1:7:7 respectively).

5.2.3 Agent Effects on Various Premixed Flame Limits

i) General

It is common practice to express the results of flame inhibition studies in the form of limits, expressed as a function of the composition of the flame system. Fristrom (Reference 11) described the various limits (ignition, flammability, quenching, pressure, blow-off and detonation) and noted that although the various limits are related, they cannot in general be deduced from each other.

ii) Ignition limit

The limit beyond which it is not possible to ignite a premixed system, the ignition source commonly being an electric spark (although pilot flames and hot surfaces have also been used). Ignition limits correspond approximately to the flammability limits, since a flame which cannot propagate certainly cannot be ignited. If any method of ignition can be employed then the reverse is also true, i.e. any flame which can propagate can be ignited. However, for a particular source and strength of ignition it may be that ignition is not possible, even though a flame can propagate. Fristrom (Reference 11) cites mine fires as problem where these considerations apply.

iii) Flammability limits

The relative amounts of fuel and oxidiser in the mixture necessary to sustain combustion; outside these composition limits, flame propagation in premixed gas systems cannot occur. These measurements are commonly made in a device called an explosion burette (Reference

19). The test mixture is placed in a long tube, open to the atmosphere and of sufficient diameter to ensure that the tube walls have negligible effect. A spark or small pilot flame is used to ignite the gases and the progress of the flame front is observed. The mixture is considered flammable if the flame propagates to the end of the tube and nonflammable when this does not occur. The effect of an agent on combustion behaviour is often characterised in terms of the lean and rich flammability limits as the concentration of the additive is increased; usually the concentration range of the mixture which supports combustion is decreased as the agent is added. As the agent concentration is increased, a point is reached where the lean and rich limits coincide; at this point the agent concentration is termed the *flammability peak concentration*, or more simply the *peak concentration*. Further increases in agent concentration result in the situation where the fuel and air will not support combustion for any fuel/air ratio. The peak concentrations are commonly used to rate the effectiveness of suppression agents.

iv) Quenching limits

As a flame front approaches a solid surface, heat is extracted from the reaction zone by thermal conduction; this effect produces a drop in the burning velocity of the flame front in the vicinity of a solid heat sink. The quenching distance is defined as the minimum burner diameter or hole through which a flame will propagate. From the discussion in Section 3.2 and the variation in flame speeds illustrated in Table 3.1, it can be appreciated that the quenching distance will be inversely proportional to S_u and therefore depends on the properties of the flammable mixture in question. Hirst (Reference 8) gives the quenching distance for a hydrogen/air mix as 0.5 mm compared with a range of 1.8 to 3 mm for most hydrocarbons. Flame quenching is important in the design of flame traps (Reference 1), where the object is to prevent flame propagation (e.g. a miner's safety lamp in which the flame is surrounded by a fine copper gauze). In industrial applications, flame traps frequently comprise an assembly of narrow-bore, thin-walled tubes which have minimal resistance to gas flow while preventing flame propagation. In the study of suppression agent effectiveness, variations in the quenching distance are studied; increasing the concentration of agent will tend to increase the minimum quenching distance as S_u is progressively reduced.

v) Pressure limits

Pressure limits simply represent the pressure dependence of either ignition or quenching limits and are expressed in this manner because the independent experimental variable was pressure. The investigation of suppression agent effectiveness is conducted in the manner described in the previous paragraphs.

vi) Blow-off limits

The stabilisation of a flame on a burner was discussed in Section 3.2 and the notions of flame blow-off and strike-back were introduced. It was shown that a stable flame occurs only when the heat transfer effects and the gas flow velocity profile satisfy certain critical conditions. In particular, as the flame front approaches the solid boundary there is a local reduction in S_u (see *Quenching limits* above). Simultaneously the local flow velocity tends to zero at the solid boundary and therefore the flame is stabilised only at some distance from the burner rim where these two effects are balanced. If the burning velocity drops more rapidly than the gas flow velocity, a balance is not achieved and the flame will *blow-off*; conversely if the local S_u is greater than the flow velocity the flame will *strike-back* down the burner tube, again resulting in flame extinguishment. The critical blow-off velocity for the flame can be correlated with the ratio of boundary layer thickness to flame front thickness (i.e. if the latter ratio is high, then the blow-off velocity will also be high). Flame thickness varies inversely with burning velocity (Reference 11); therefore, a greater S_u results in a more stable flame. The flame front thickness also varies inversely with thermal conductivity; hence a helium diluted flame is more difficult to stabilise than its argon diluted counterpart. In addition, if the burner is warmed, the heat transfer rate is reduced and the flame is more easily stabilised. Also, if diffusion from the ambient atmosphere tends to increase S_u then the flame will be more easily stabilised. Therefore a rich flame will be stabilised by the diffusion of oxygen from an air atmosphere and will be more stable than a fuel lean flame of the same nominal S_u. If the surrounding atmosphere were fuel however, then the opposite would be true (Reference 11). Regarding turbulent flames, Fristrom (Reference 11) observed that these may be stabilised by continuous re-ignition of the system from a laminar flame within the boundary layer or by hot reactive gas originating from a recirculating burning region in the wake of a bluff object. A similar blow-off correlation can be found for the case of turbulent flames; in this case the characteristic parameter is the ratio of the stream velocity to the characteristic length of the bluff body stabiliser. This ratio is proportional to the residence time in the turbulent eddy; if the latter is short compared with the initial flame reaction time then no reservoir of hot reactive gas exists to ignite the main turbulent gas stream. Since the main stream velocity is far in excess of S_u then blow-off should occur; it is also known that high shear stresses generated by turbulence can disrupt the reaction zone sufficiently to extinguish a flame. Finally, it is perhaps worth repeating here the view held by some and previously stated in Section 3.3, that all fires are ultimately extinguished by the blow-off which follows primary suppression techniques.

vii) Detonation limits

The concept of a detonation was introduced in Section 2.3 and the limits of detonation are analogous to the flammability limits discussed above. Despite similar chemistry however, the detonation limits are found to be different from the flammability limits for a given system. Some systems which will burn will not detonate and some systems which detonate will not support stable burning (Reference 11). It has also been found that detonation inhibitors differ from flame inhibitors despite the apparent physical and chemical similarity of the processes. It is suspected that major differences in the time-temperature histories of flame and detonation processes give rise to differences in the dominant chemical reactions. For example, many halogen compounds which are effective flame inhibitors appear to be accelerators for detonations. Conversely it is found that many fuels which support combustion, such as ethane or ethylene, inhibit the hydrogen-oxygen detonation.

5.2.4 Full Kinetic Modelling of Premixed Flames

The use of this fairly novel technique has previously been discussed in Section 4 in relation to studies of premixed methane-air flame inhibition by thermal mechanisms (Reference 18); Section 5.4 and Appendix B contain more details concerning the application of this method to fire suppression studies. Pitts *et al* (Reference 19) report that in recent years it has become possible to model important aspects of laminar flames but that the complete modelling of complex combustion systems remains an intractable problem. The conservation equations for mass, momentum and energy are now routinely solved by *Computational Fluid Dynamics* (CFD) computer codes; it is now possible to add chemical kinetics routines which model combustion reactions. Such models require the input of empirical data (e.g. thermal conductivities and rate constants for individual reaction steps (Appendix B)) and are usually simplified by considering only one- or two-dimensional flames. Reference 19 contains several examples of this type of theoretical investigation, designed primarily to study the chemical suppressant action of Halon compounds. Pitts *et al* (Reference 19) identified some serious deficiencies regarding the empirical data used in such models but concluded that state-of-the-art calculations are currently capable of modelling simple diffusion flames; it was considered that future studies of suppression behaviour using these models would be particularly illuminating. The current state-of-the-art is not sufficiently mature however, to permit the theoretical modelling of the suppression and extinction of large-scale three-dimensional turbulent diffusion flames which are of most practical importance. The emerging technology of Direct Numerical Simulation (DNS) has the potential to model the fundamental chemical and physical phenomena associated with such complex combustion systems (Appendix D). The advantage of DNS is that the governing equations of turbulent combustion are solved without the approximations used in conventional CFD models. The drawback of the technique is that it relies on the availability of massive computing resources; the research initiative described in Appendix D requires the Massively Parallel Processing (MPP) capability of Edinburgh University's Cray T3D super computer. The initial aim of the research is to model the dynamics of the flame-turbulence interaction, therefore the chemistry is of secondary importance and is modelled using the simple one-step reaction approximation. In the future, DNS may provide the means of simulating turbulent diffusion flames while retaining all of the important intermediate reaction steps. At present however, it must be conceded that an accurate theoretical representation of the extinguishment (by any means) of a large turbulent diffusion flame remains some years away.

5.2.5 Flame Chemistry and Flame Structure of Inhibited Diffusion Flames

Two configurations have been used to study the structure of inhibited diffusion flames; these are the *coflow* system and the *counterflow* system. In the former, a diffusion flame is established when the fuel flows into either a stagnant or a coflowing oxidising atmosphere (e.g. using the cup-burner shown in Figure 3). Pitts *et al* (Reference 19) described cup-burners of diameters 25.4 mm and 28 mm used for burning flammable liquids in oxidising atmospheres containing variable concentrations of extinguishing agents. It was suspected that the diffusion flames established in these devices were neither truly laminar nor truly turbulent in nature.

In the counterflow arrangements shown in Figure 4 (Reference 20), the burner design is arranged so that the flame is formed between opposing streams of fuel and oxidiser. Four distinct burner configurations have been used: (I) the three-dimensional or flat counterflow diffusion flame established between two opposed jets from circular tubes or rectangular nozzles, (II) the flat counterflow diffusion flame established between two opposed matrix burners ejecting individual reactants, (III) the counterflow diffusion flame established in the forward stagnation region of a spherical or hemispherical porous burner and (IV) the counterflow diffusion flame established in the forward stagnation region of a cylindrical porous burner. The flow velocity (or more accurately the mass flux) of fuel and oxidiser are monitored with and without the presence of inhibitor. At some critical mass flux, a hole is seen to develop at the centre of the flame region and this increases in area with increasing mass flux; this is taken as a measure of *flame strength* and variations in this quantity are indicative of flame suppression effectiveness. The production of a hole at the centre of the flame is due to the *flame stretch* and *blow-off* effects discussed earlier in Section 3.2. The blow-off flux is found to be proportional to the reaction rate and jet diameter but independent of the transport coefficients (Reference 11). Furthermore, the effectiveness of an extinguishant depends on whether it is introduced on the fuel or oxidiser side of the flame front. The efficacy of a diluent such as nitrogen is highest when introduced on the fuel side while a chemical inhibitor (such as a volatile halogen compound) is most effective on the oxidiser side.

All four types of counterflow configuration have been used for the study of the suppression effectiveness of the various halogenated compounds such as carbon tetrachloride and methyl bromide (Reference 20). A study of the inhibition of the methane-air diffusion flame showed that inert diluents (argon and nitrogen) had little effect while organic halides were ranked in effectiveness as $CH_3Cl < CCl_4 < CH_3Br \sim CF_3Br$. The method was also shown to be effective in the assessment of powdered agents against methane-air, propane-air and *n*-butane-air flames; the main problem involved achieving a steady powder loading of the air stream.

The burner configurations of Figure 4 may only be used to study stationary diffusion flames produced by gaseous fuel streams, however the establishment of a stationary counterflow diffusion flame above a *condensed* fuel is also mentioned in Reference 20. This is achieved by directing an oxidising gas stream downward onto the surface of a liquid or solid fuel. Experiments were reported which used this technique to investigate the various combustion characteristics of liquid or solid fuels, e.g. the linear regression rate, the extinction limit and the structure of diffusion flames above the condensed fuels and the effects of a flame retardant on diffusion flames. One particular study examined the structure and extinction of laminar diffusion flames above liquid fuels and wood, when subjected to nitrogen or water. It was found that the dominant extinguishing mechanism for water was thermal (i.e. heat removal from the fuel and flame) and that a critical Damköhler number could be derived to predict the extinction point of the flame (Section 3.3).

5.2.6 Extinction of Turbulent Diffusion Flames

These tests are designed to most closely resemble the agents' use in the field, however a major drawback is the lack of standardisation between tests and a lack of reproducibility within a given series of tests. Several test configurations are described in (Reference 19) but again the emphasis is on chemical suppressants (halons). Since halons are either used for *total flooding* or local application (*streaming*), it is obvious that there will be fundamental differences in the test methodology. Total flooding systems require to be tested against a fire in a relatively airtight enclosure so that the agent concentration can be maintained above a specified level for several tens of minutes; in this manner an atmosphere is created which does not sustain combustion. Local application involves spraying the agent directly on, or near, the fire in order to induce extinguishment. Fristrom (Reference 11) discusses the problems associated with defining an extinction parameter for such tests; it is concluded that even simply attempting to specify the time and rate of application to achieve extinction is not straightforward (e.g. because it is difficult to compare the *extinguishant mass rate per unit fire area* for media with different physical states, degrees of aggregation etc.). Hirst (Reference 8) has described the practical fire tests as "...often the only convincing way of comparing the effectiveness of extinguishing agents, or of different extinguisher designs." Although this is a desirable proposition, the practicalities of defining a "standard test fire" and a "standard method of application of the agent" etc. are not straightforward (Reference 11). It is considered that this is too large a subject area to be treated adequately in the present report which has been concerned with presenting some general concepts of extinction and suppression. There is no virtue in describing a few particular large-scale fire suppression tests at this stage; the important large scale data on water suppression of Class A fires will be the subject of future reports.

5.3 Experimental Studies of Suppression

This section comprises a brief summary of some of the experimental applications of the techniques described in Section 5.2. Tsuji (Reference 20) reported several studies of the inhibition of counterflow diffusion flames using various suppression agents, including halogenated compounds and alkali metal vapours (see also Section 5.2). Changes in flame speed (S_u) have been measured for various flames due to the presence of chlorine and bromine (Reference 21), metal salts (Reference 22) and various gases and vapourized liquids (Reference 23). Palmer and Seery (Reference 21) found that the addition of chlorine or bromine reduced the burning velocity of hydrogen-containing carbon monoxide flames in air, oxygen or nitrous oxide atmospheres. It was also found that if the hydrogen content was low, the effect of chlorine upon nitrous oxide-supported flames became acceleratory due to the chlorine catalysis of nitrous oxide decomposition. Rosser *et al* (Reference 22) studied the inhibition of hydrocarbon flames by finely divided (250-325 mesh) metal salts; sodium fluoride, sodium chloride, sodium bromide, cuprous chloride, potassium sulphate, sodium monohydrogen carbonate, potassium monohydrogen carbonate and sodium carbonate were all found to be very effective inhibitors of the premixed methane-air flame (indicative of chemical interference with the combustion process). Miller *et al* (Reference 23) examined the effect of eighty different compounds (gases and vapourised liquids) on the burning velocity of the premixed hydrogen-air flame. The most effective inhibitors were found to be the hydrocarbons as a group, bromine-substituted hydrocarbons, several metallic chlorides and iron pentacarbonyl. Chlorine and fluorine-substituted hydrocarbons were found to be relatively ineffective.

The detailed structure of flames has been studied (References 24-29) and the opposed-jet flame strength has frequently been measured in the presence of inhibitors (Reference 28, 29); measurement of various limits such as the blow-off limit (Reference 30) and flammability limits (Reference 31) is frequently used to assess flame inhibition. Fenimore and Jones (Reference 24) studied the inhibition of hydrogen-nitrous oxide flames by methyl bromide (CH_3Br); using a flame probing technique it was possible to determine the rate of reaction (Appendix B) and the inhibitory role of the methyl radical (CH_3). Ibiricu and Gaydon (Reference 25) performed spectroscopic studies of counterflow diffusion flames of ethylene, methane and hydrogen in air; the effect of adding various inhibitors (methyl bromide, bromine, carbon tetrachloride, chlorine or phosphorous oxychloride) to either the fuel or air stream was discussed. The inhibition effect was explained in terms of the removal of OH radicals which tended to slow the oxidation process, promoting polymerisation and carbon formation thereby increasing the radiation losses and cooling the flame. Melvin and Moss (Reference 26) performed an experimental investigation of the structure of flat diffusion flames of hydrogen, oxygen and nitrogen. The results were compared with theoretical predictions and it was found that close to flame extinction a significant increase in convective mass transfer occurred at the flame base; it was suggested that the consequent disruption of mixing in, or shielding of, the reaction zone made flame extinction a progressive process. Laminar counterflow diffusion flames of methyl chloride, trichloroethylene and methane mixtures were studied by Yang and Kennedy (Reference 27) in the context of the disposal of hazardous chlorinated wastes by incineration; once again the role of chlorine in flame extinction was highlighted. Mastorakos *et al* (Reference 28) generated a small-scale turbulent counterflow diffusion flame using opposing streams of natural gas (with various levels of initial premixing of air) and air. The extinction limits were measured and it was found that the bulk velocity for extinction increased with tube separation (Type I burner, Figure 4) and with initial premixing, but decreased with an increase in turbulence intensity of the flows. It was also shown that both the mean and turbulent flame stretch rates affect the extinction process and it was postulated that a critical strain rate could be used to predict the extinction of turbulent diffusion flames. However, in cases where re-ignition was possible after localised extinction, the criterion for global extinction is not so easily determined due to the increased complexity of the system.

Fristrom (Reference 11) also noted the problems associated with the extrapolation of laboratory data to full-scale fire suppression, particularly the problems associated with *scaling*. For example, scaling laboratory pool fires a few centimetres in diameter to hydrocarbon spill fires of the order of 100 metres diameter introduces a factor of 10^8 in area and burning rate. Care must be taken when extrapolating such data to ensure that any changes in mechanism (physical or chemical) associated with the changes in scale are taken into account. Fristrom (Reference 11) also emphasised the importance of conducting an economic appraisal in order to assess the practical benefits arising from the adoption of a particularly promising agent; it was suggested that factors such as ease of application, storage and cost should be included.

5.4 Theoretical Studies of Suppression

This section comprises a brief summary of some of the theoretical applications of the techniques described in Section 5.2 and Appendix B.

Ewing *et al* (Reference 32) developed an empirical relation in order to correlate the fire-suppression effectiveness of a variety of gaseous, liquid and solid agents. Their flame-extinguishment model was developed under the fire research program at the U.S. Naval Research Laboratory and tested against experimental data relating to the extinguishment of both premixed and diffusion flames by a wide range of agents. These workers concluded that a lack of standardisation in experimental methods and in the reporting of test results makes a meaningful inter-comparison very difficult. It was further concluded that the high extinguishing effectiveness of many "chemical inhibitors" can be predicted under ideal conditions from a simple flame heat balance incorporating heat-absorption sinks resulting from heat capacity, vaporisation, decomposition and dissociation of the inhibitor.

The suppression-effectiveness of the thermally-stable gases (CO_2, H_2O, N_2 and He) for the case of the methane-air premixed flame was studied by Tuovinen (Reference 14) using the "CHEMKIN" computer code developed by Sandia National Laboratory in the U.S. Although this model cannot simulate a turbulent diffusion flame, Tuovinen's results are nonetheless interesting; it was found that extinction of the mixture was predicted when a certain amount of heat was removed from the system. At this critical point, which corresponded to a premixed flame temperature between 1250 K and 1380 K, production of the highly reactive *free radicals* OH, O and H (see Section 4) ceased and led to flame extinction. The extinction concentrations for CO_2, H_2O, N_2 and He were about 30, 38, 45 and 54% by volume (air + diluent gas) for a slightly fuel-lean premixture. The "CHEMKIN" model used in this study required the provision of a suitable chemical reaction scheme at the outset; for methane-air reaction, the model contains data for 23 chemical species and 73 elementary reaction steps which are described in Appendix B of this report. A similar procedure, albeit with a different computer code, was adopted by Lee *et al* (Reference 33), initially using a scheme with 38 gas-phase species and 358 elementary reaction steps to model freely burning premixed flames in mixtures of methyl chloride and methane in air. It was found that a less computationally-intensive scheme consisting of only 25 species and 63 reaction steps was able to accurately predict the salient features of the simulated flames. The inhibitory effect of chlorinated compounds was described; these compounds hamper hydrocarbon combustion due to their low heats of combustion and by decreasing the frequency of the $H + O_2$ reaction through channelling H atoms to form HCl.

Other notable articles on theory of flame extinction include those of Abrams (Reference 34) (chemical quenching theory), Williams (References 12, 35), Ewing *et al* (References 36, 39) Beyler (Reference 37) and Chao and Law (Reference 38).

6. THE MECHANISMS OF THE SUPPRESSION AND EXTINCTION OF FIRE

6.1 General

In contrast to precise scientific definitions of combustion, the *fire triangle* (Figure 5a) has proved to be a successful educational tool because it provides a simple, pictorial explanation of the fire threat in terms of the requirements for uninhibited fire growth. The fire triangle has been used to represent the interaction between the three essential entities required to sustain the most common fires, namely a fuel, oxygen (or air) and a sufficiently high temperature to maintain the chemical reaction. However, the increasing awareness of the power of certain chemical flame inhibitors has led to the proposal of the "suppression pyramid" (or tetrahedron) (Figure 5b) as the fire-fighting analogue of the fire triangle; each of the 4 sides represents a key suppression mechanism.

There is at present however, some debate as to the accuracy of this simplistic model. It is natural that three elements of suppression (removal of fuel, removal of oxygen, removal of heat) are obtained by their removing their contribution to the fire triangle. The fourth suppression method relies on a form of chemical intervention, specifically on free radical quenching using an ionically active agent (Section 4). This latter effect was assumed to account for the disproportionate extinguishing capability of some compounds which was not attributable to any of the accepted mechanisms (References 34, 40, 41).

6.2 Proposed Mechanisms for Fire Suppression and Extinction Found in the Literature

Thorne (Reference 42) identified six mechanisms by which the combustion process could be interrupted, leading to flame extinguishment:

- *Cooling* of the combustible fuel surface which in a liquid reduces the vapour pressure and in a solid reduces the rate of pyrolysis. In both cases this is equivalent to reducing the supply rate of fuel to the fire which reduces the rate of heat release from the fire; consequently the thermal feedback from the flame is reduced and this augments the primary cooling effect of the suppression agent. The application of a water spray to the fuel bed is typical of this method.

- *Covering* (or *blanketing*) the fuel surface with a barrier to reduce the emission of fuel vapour; this method also interrupts thermal feedback from the flame and therefore also contributes to fuel cooling. This mechanism may be viewed either as removing the fuel supply or removing the oxidiser supply. The application of foam to hydrocarbon pool fires is an obvious example of the method.

- *Cooling* the flame zone itself; this reduces the concentration of free radicals (the chain-branching initiators of the combustion reaction). Some proportion of the heat of reaction is taken up by heating an inert substance (such as water) and therefore less thermal energy is available to continue the chemical break-up of compounds in the vicinity of the reaction zone. One function of the new water mist technology is to act in this manner, the fine droplets providing a very large surface area per unit mass of spray in order to increase the rate of heat transfer.

- *Inhibiting* the flame zone by the introduction of a material which acts as a "sink" for free radicals (i.e. *free radical quenching*). This method removes the highly reactive free radicals from the combustion zone by introducing a chemical (e.g. a Halon) which is effectively more chemically attractive to the radicals, but which forms stable products which do not contribute to the combustion reaction. Hence the vigorous chain-branching reactions, which are vitally important in promoting combustion, are starved of the free radicals which they require.

- *Inerting* the air feeding the flame by reducing the oxygen partial pressure by the addition of an inert gas (e.g. N_2, CO_2, H_2O vapour). Again this is equivalent to the removal of the oxidiser supply to the flame. This is another mechanism by which water mists can suppress large fires (by the production of steam).

- *Dilution* of a flammable liquid with a non-combustible liquid to reduce the partial pressure of flammable vapours. This is equivalent to the removal of the fuel supply.

Tuovinen (Reference 18) added the following mechanisms:

- *Quenching* effects caused by the introduction of small particles in high concentrations (e.g. dry powder stream); flames cannot propagate between solid surfaces at close separations due to the loss of thermal energy by conduction to these surfaces (Section 5.2 and Reference 43). Once again the result is that there is insufficient heat energy left to continue the chemical processes in the reaction zone.

- *Flame blow-off* caused by a high extinguishant stream velocity; if the characteristic transport time of the reactants is shorter than the chemical time, combustion is not possible (see Sections 3.2, 5.2, 5.3). In practice this effect may be exploited for practical firefighting, but only in the special case of oil well fires where the fuel supply is highly localised and there is a very low possibility of re-ignition.

- *Particle momentum effects*; it is stated that intensive turbulence may also cause extinction by increasing the particle momentum of the gases. In this case, extinction may occur in the absence of any extinguishant. This is in fact also flame blow-off and results from excessive rates of strain within the combustion zone (e.g. Reference 28).

Haessler (Reference 9) also offers two further possibilities for mechanisms of fire suppression:

- *Critical sound vibrations*; it is noted that a candle flame may be extinguished using a tuning fork coupled to a resonator tube. (It is also reported that sufficiently high frequencies can actually start fires.)

- *Ion separation*; this item is "purely speculative" but it relies on the separation of positive and negative ions known to be essential for the continued reaction within the combustion zone. (Some contemporary references to this method have been found during the present literature search, but no details have been obtained at the time of writing.)

While the main mechanisms described above are well known and accepted by fire safety scientists, the ability to translate this theory into efficient practical methods of firefighting is rare. The phenomenal suppression efficiency of the halons provided a means to engineer clean and economical suppression systems; however the phase-out of these materials has prompted a re-appraisal of the science of fire suppression including a search for "Halon replacements" (Appendix C). Even the latter example is really only applicable to the protection of equipment such as computers, which are routinely housed in sealed compartments and amenable to protection from fixed suppression systems. In the case of the Fire Service, who have to attend large post-flashover turbulent diffusion flame fires in compartments, the benefits of an increased understanding of the suppression and extinction processes have yet to be realised.

The authors have canvassed the opinions of several "experts" during the writing of the present report (including Fire Service professionals and Fire Scientists) and a range of opinions have been expressed as to the current thinking in tackling large diffusion flame fires. The most basic response (from an American fire-fighter) was "big fire:big hose, small fire:small hose", but this neglects the damage to property which over-application of water may cause. Others have commented that there has been a shift, in the UK at least, towards achieving an initial knock-down of fire with the use of high pressure hosereels delivering smaller quantities of water in small droplets. Due to the greater surface area and rapid cooling effect from vapourisation there is a fast knockdown and little water damage. However, the use of fine droplets in this manner does not directly cool the seat of the fire as a conventional water spray would, and consequently the initial attack must be followed up with other work (such as the application of larger water droplets from a jet, "turning over" etc.) to prevent re-ignition. There would appear to be scope for an in-depth review of the action of various water sprays and mists on typical Class A fires; this will be a major objective during the remainder of the current research contract. A prerequisite for assessing the various firefighting methods is to establish what is meant by "suppression" and "extinction" in terms which can be physically measured if possible; only then can it be said that one technique surpasses another. The following Section examines some definitions of fire extinction and suppression and discusses their practical application to the problem of large scale turbulent diffusion flame fires.

6.3 Practical definitions of suppression and extinction

In the small scale experiments described in Section 5, the point of flame extinction was determined by the disappearance of the visible flame and flame suppression was known to be taking place when there was an observed reduction in the burning velocity or some other comparable effect in the experimental data. The inhibitory effect of various agents could then be ranked according to the relative magnitudes of the latter effects. Williams (Reference 35) attempted to develop simplified descriptions of the extinction process involving a few chemical-kinetic parameters that could be readily measured in the laboratory. It was concluded that it should be possible to apply such ideas to large turbulent diffusion flames if these were considered to be composed of collections of laminar flamelets, but it was conceded that the development of criteria for the extinction of laminar flames contributed to only one part of the overall problem of fire suppression. The search for a so-called "unified theory" of flame extinction has been discussed in References 12 and 37. The motivation for Beyler's approach (Reference 37) was to derive a single mathematical expression with which to compare the suppression effectiveness of diverse fire extinguishing media.

In an earlier paper (Reference 12), Williams expounded a similar rationale based on a formula defining a "boundary" (or global) Damköhler number (Section 3.3) at extinction which was shown to be related in a purely qualitative manner to seven fire suppression mechanisms (similar to the list derived in Section 6.2). Such a "unified" analysis is difficult to apply in an overall manner to a large-scale turbulent fire since many local Damköhler numbers can be defined within the flame zone (based on local temperatures, chemical species concentrations etc.) and until all are reduced to below some critical value then re-ignition may occur. Williams' global definition (Reference 12) offered a solution to this problem by incorporating several well-defined variables such as ambient air temperature (and oxygen concentration), fuel bed temperature etc.; the final expression was shown to contain parameters pertaining to all the originally-postulated suppression mechanisms. The suppression criterion was given as: "Reduce the global Damköhler number below its critical value for extinction (D_E) and prevent it from rising again above its critical value for ignition (D_I)". It was concluded that the unified view of fire suppression had not been exploited in practical fire suppression activities but with adequate verification could be of potential value in improving fire suppression measures.

The best practical definition for real fires which has so far been found states: "Fire extinguishment is the application of the agent at any level high enough and for long enough so that no burning of any kind continues. In fire suppression, open flaming is stopped, but a deep seated fire condition will require additional steps to assure total extinguishment." (This was passed on to the authors as a result of an "Internet" enquiry, however an exact reference for the article is still being sought.) It can also be seen that this definition retains the essence of Williams' critical Damköhler numbers (extinction and re-ignition) argument, albeit in less mathematical language. The message is that effective fire suppression requires not only that the fire be extinguished but additionally that it not be re-kindled. The choice of suppression strategy has a significant impact on the probability of re-ignition. For example, the use of a suppression agent which results in the removal of the source of fuel vapour (e.g. water cooling of a solid fuel below its characteristic pyrolysis temperature) will automatically remove the possibility of re-ignition. On the other hand, if the primary suppression mechanism is chemical in nature it is more probable that re-ignition of flammable vapours may occur since cooling is either absent or greatly reduced.

7. CONCLUSIONS AND PROPOSALS FOR FUTURE WORK

The present report provides an overview of some important fundamental studies of flaming combustion; the development of technologies (both experimental and theoretical) to assess the suppression effectiveness of extinguishants has also been described. However, this brief overview has necessarily been based only on a relatively small proportion of the total information on all aspects of fire suppression yielded by the literature search initiated at the start of the project. Nevertheless, this report does accurately reflect the state-of-the-art of research into fire suppression and extinction in general terms. The specific case of the application of water sprays and mists to Class A fires will be the subject of future work. This area of work is particularly interesting since the interaction of a water spray and a large-scale turbulent diffusion flame is not entirely explained by small-scale experiments or by analytical theories of fire suppression. A reasonable amount of data exists on large scale tests involving water suppression of fires in diverse configurations. Large-scale tests have their own inherent limitations since one test is never enough to give definitive answers to a problem; the main advantage of large-scale experiments is that they should be indicative of the real behaviour and this is extremely valuable.

The following two suggestions are made for a logical progression of the work:

- A detailed report on the general topic of the *use of water sprays against Class A fires*. It is envisaged that this would include a thorough discussion of how fires are extinguished by the interaction between water sprays and Class A fires; emerging technologies in this area (e.g. computer modelling, water additives etc.) would also be assessed in greater detail than the present report has allowed. The report should also include a section on the practical techniques of water spray application, reviewing past and present practice. This work package would be expected to fulfil the main stated aims of the FRDG discussed in Section 1.2.

- A less detailed report, perhaps including a spreadsheet or database, which summarises the use of all known types of extinguishants (water spray & mist, halons & "replacements", foams, powders, etc.). This approach could include various inter-comparisons such as *effectiveness* and *cost*, based on published data; again the application methods would also be reported.

It is envisaged that either approach would allow the respective subjects to be studied in sufficient detail that gaps in the existing knowledge would be accurately "diagnosed" allowing detailed suggestions for future research to be advanced.

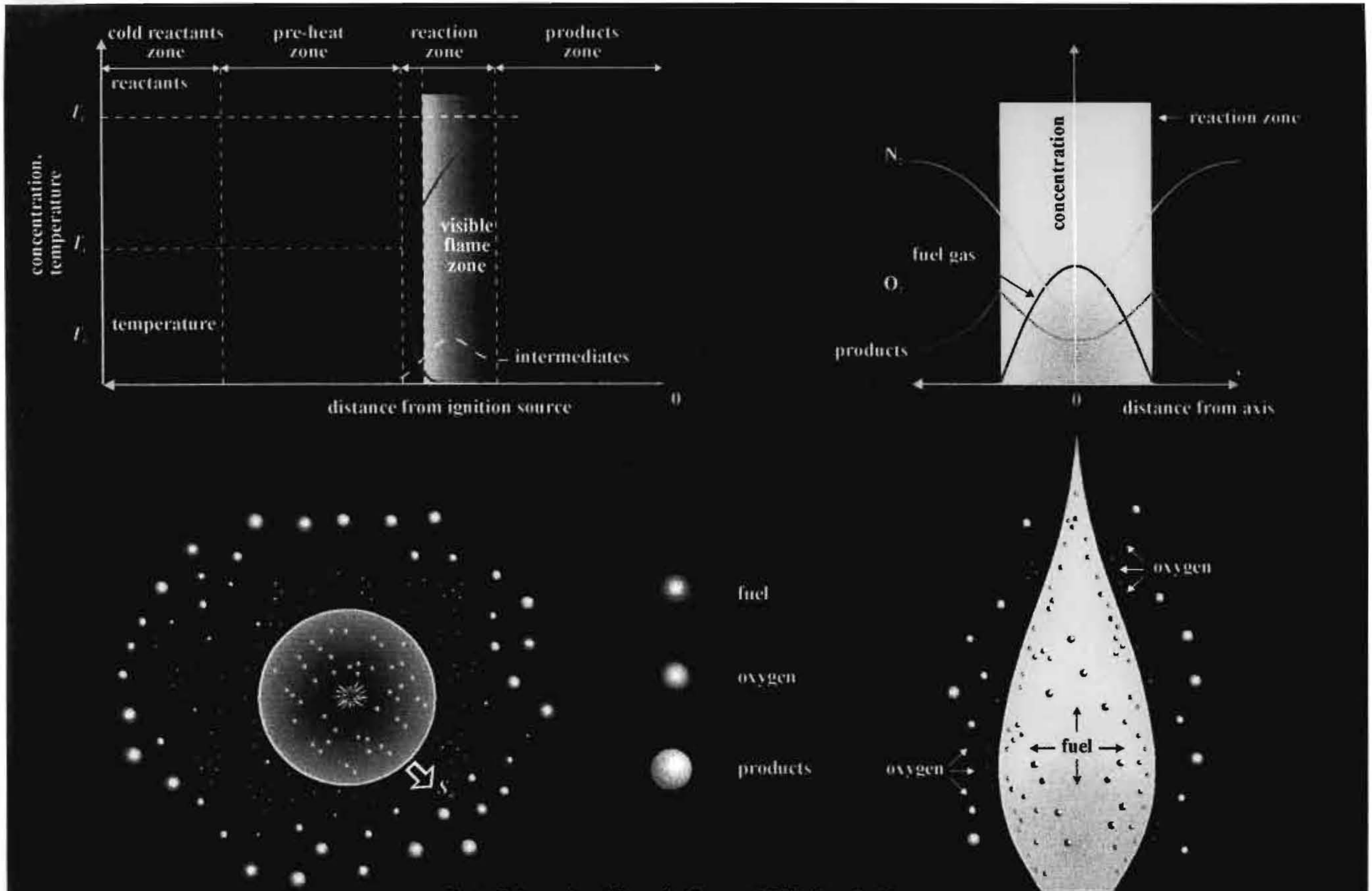

Fig.1 Schematics of Premixed (a) and Diffusion (b) flames

(a) (b)

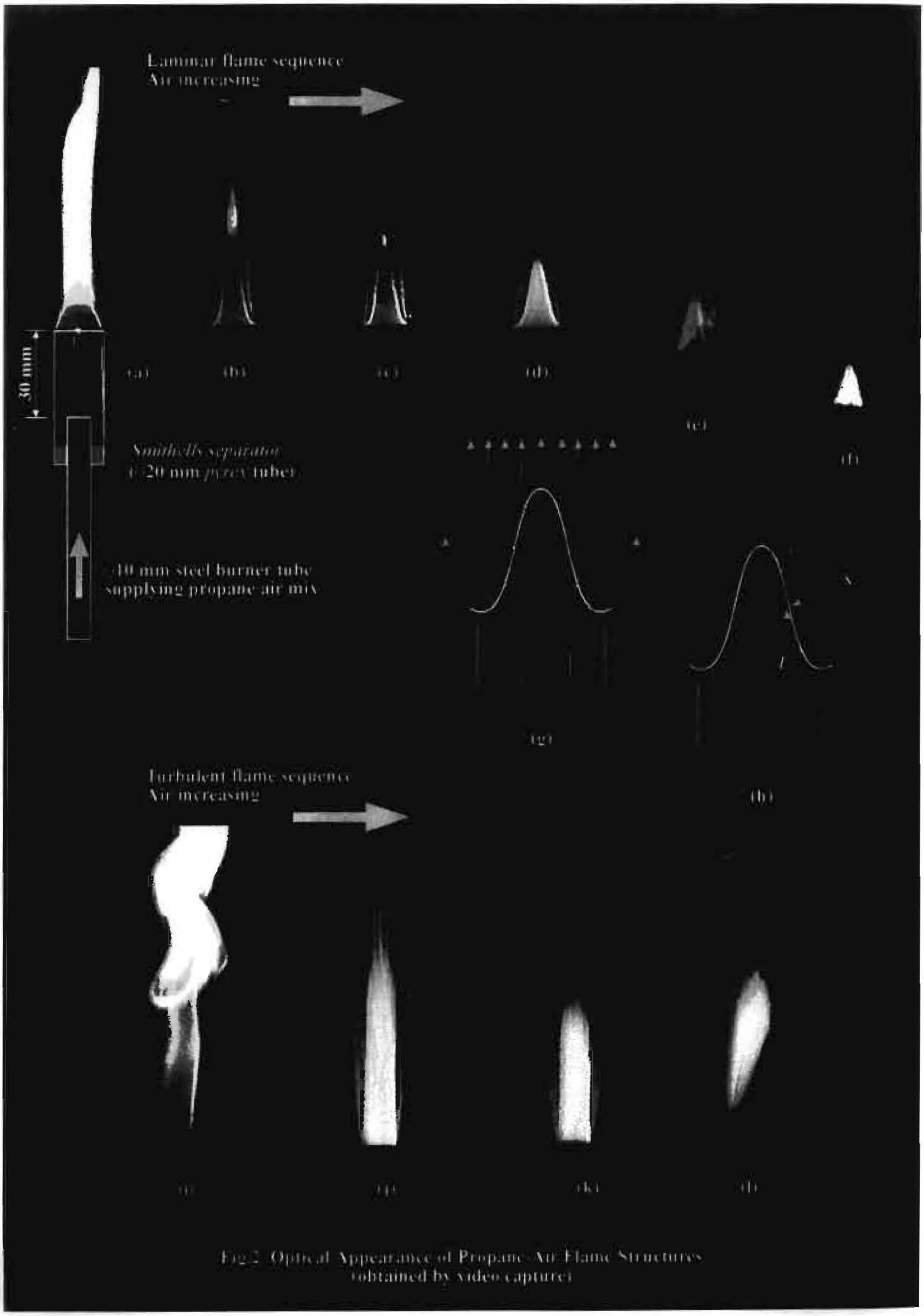

Fig.2 Optical Appearance of Propane-Air Flame Structures
(obtained by video capture)

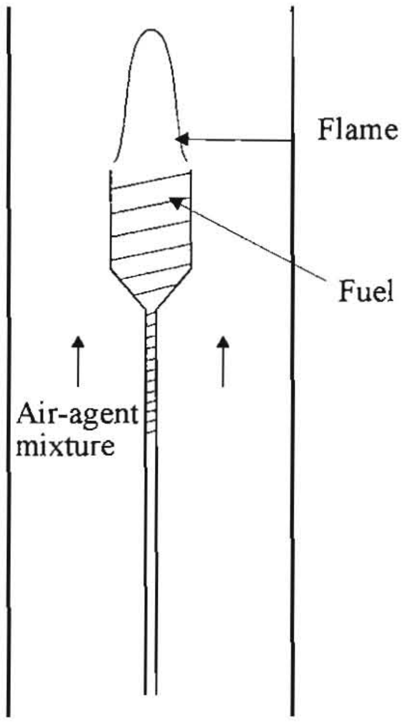

Figure 3
The Cup Burner - a *Coflow* Diffusion Flame Burner (after Hirst, Reference 8)

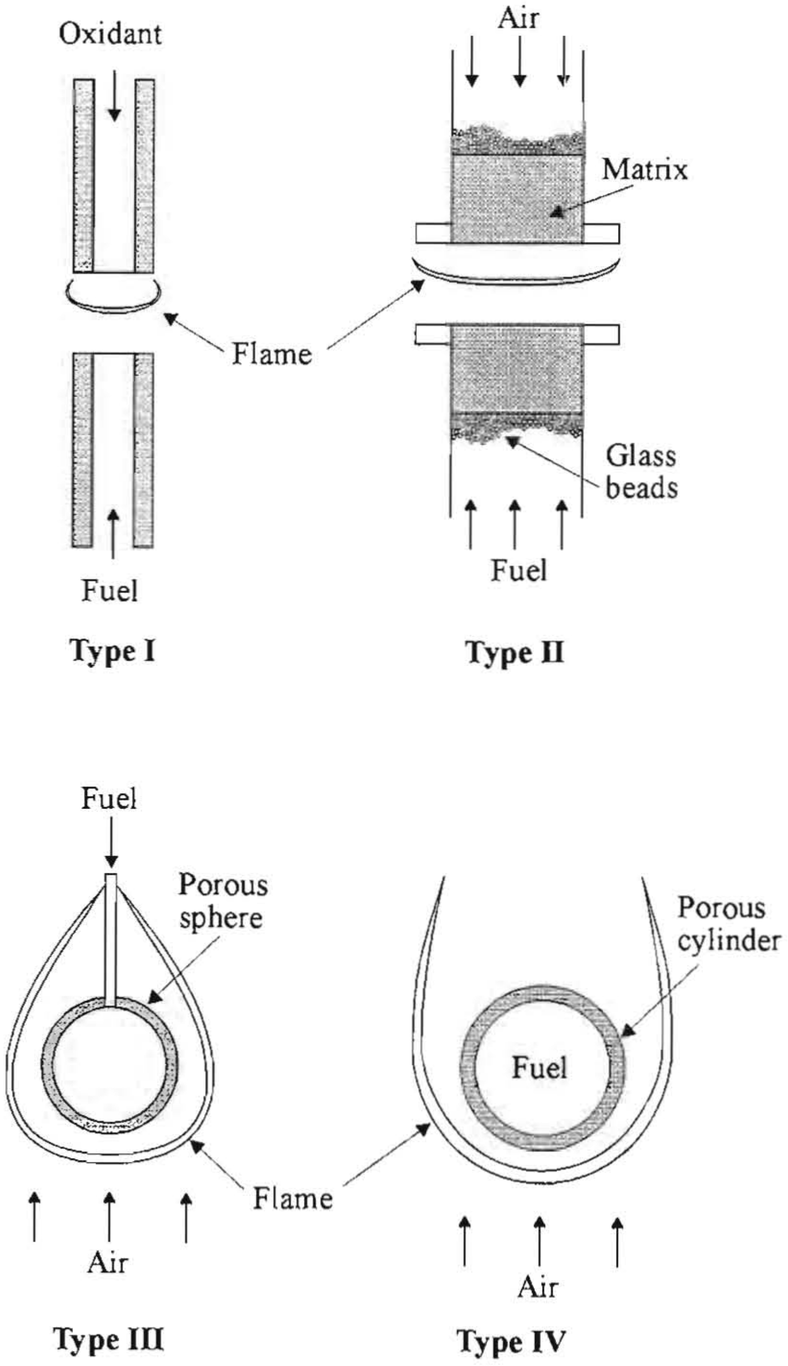

Figure 4
Four Types of *Counterflow* Diffusion Flame Burners (after Tsuji, Reference 20)

Figure 5a
The Fire Triangle

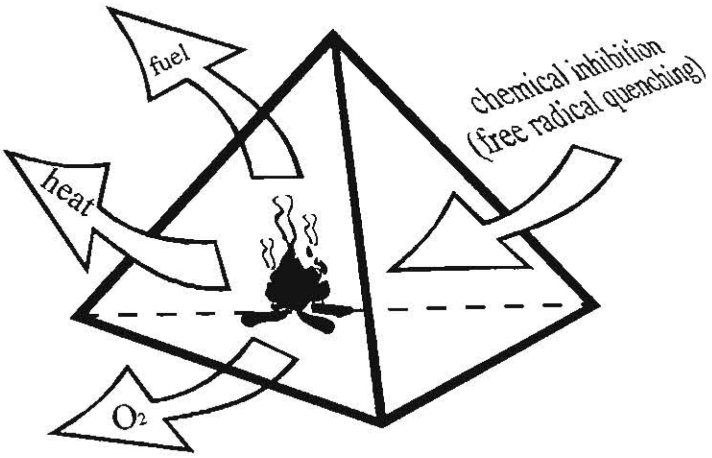

Figure 5b
The *Suppression Pyramid*

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APPENDIX A. LITERATURE SEARCH STRATEGY

An extensive literature search programme was initiated at the outset of the project; the objectives were twofold:

- To source and collect copies of relevant journal articles and other publications
- To identify prominent research centres and individuals in the field of fire suppression and extinction

The scope of the initial search was kept deliberately wide to ensure that a comprehensive database was established. Four computer-based systems were interrogated using "keyword" searches; the selected keywords were **EXTIN***, **SUPPRES***, **FOAM**, **SPRAY**, **DROP**, **MIST**, **FOG**, **CO2**, **DRY+CHEMICAL**, **DRY+POWDER** and **HALON*** (* is the "wildcard" character which represents any arbitrary following text). The total number of "hits" (i.e. successful matching of keyword to a database entry) achieved within the various databases are summarised in Table A1.1 below.

Table A.1
Keyword search of on-line databases

Database	Origin or location	Total hits
FIREDOC	Fire Research Information Services, National Institute of Standards & Technology, USA	2120
CARDBOX	Fire Experimental Unit (FEU), Moreton-in-Marsh, UK	1600
ISI/ISTP	Bath Information & Data Services (BIDS), Bath University, UK	650
BRIX-FLAIR	European Space Agency - Information Retrieval Service (ESA-IRS), Frascati, Italy	1200

This initial set of some 5500 references was refined somewhat by subtracting duplicates and other spurious material; nevertheless a substantial amount of potentially useful material remained. Many of these references are available in the Robertson (Engineering) Library collection at Edinburgh University and copies of other documents have been obtained through the inter-library loan procedure. This rapidly-expanding bibliography has been further augmented by the Fire Safety Engineering Group's own reference material. Reference material drawn upon for this initial report has been restricted to publications which provide a fairly broad treatment of fire suppression and extinction. The surprising abundance of published information on the suppression and extinguishment problem has not been reflected proportionately in the contents of recent general conferences on fire safety science (References 44a-d), where there is considerable bias towards *fire dynamics* topics (i.e. the quantification of fire spread and smoke movement). Evidence of renewed activity in the fire suppression area is provided however, by an increasing number of specialised conferences (Reference 45-48) whose contributors have been motivated to some degree by the search for "Halon replacements" (see Appendix C).

APPENDIX B. THERMOCHEMISTRY AND MODELLING THE PREMIXED METHANE/AIR REACTION

According to Barnard and Bradley (Reference 1): "While all combustion processes depend on the total amount of energy released by chemical reaction, not all depend on the *rate of reaction*, provided it exceeds some minimum value." The gross behaviour of detonation waves, diffusion flames (laminar), burning droplets and liquid propellant rocket engines are virtually independent of chemical kinetics; on the other hand chemical kinetics effects are relevant to the cases of pre-mixed flames, fires (turbulent diffusion flames) and internal combustion engines. The "CHEMKIN" computer code, used in Reference 18 to study the extinction of pre-mixed methane-air flames, requires as input data the specification of a valid *elementary reaction* scheme describing the details of the overall *stoichiometric* methane-oxygen reaction,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{B1}$$

Whilst the *overall* or *global* expression represents the stoichiometry of the reaction, it does not necessarily reflect the discrete chemical events which occur as the chemical species react. This distinction assumes great importance in the study of fire suppression when the dominant mechanisms of combustion inhibition are associated with the elementary chemical reaction steps; in these cases, sufficient chemical kinetics detail must be retained in order to explain the suppression process. The quantitative behaviour of a chemical reaction is more formally represented by a *rate law*, which specifies the time rate of change of the concentration of chemical species in terms of a product of species concentration terms and a *rate constant* (Reference 1). Thus for the general stoichiometric reaction,

$$\nu_R R + \nu_S S + \cdots \rightarrow \nu_P P + \nu_Q Q + \cdots \tag{B2}$$

where chemical combination of the reactants R and S gives rise to the products P and Q the rate law is given by,

$$-\frac{1}{\nu_R}\frac{d[R]}{dt} = -\frac{1}{\nu_S}\frac{d[S]}{dt} = +\frac{1}{\nu_P}\frac{d[P]}{dt} = +\frac{1}{\nu_Q}\frac{d[Q]}{dt} = k[A]^i[B]^j$$

where k is the rate constant and the powers i and j are known as the *order of reaction* with respect to the reactants R and S and the overall order is $(i+j)$ (Reference 1). In the particular case of the process,

$$H + O_2 \rightarrow OH + O \tag{B3}$$

which is an elementary step (no. 68) in the methane-oxygen reaction shown in Table B.1, a hydrogen atom collides with an oxygen molecule and the three atoms rearrange to produce a hydroxyl radical (OH) and an oxygen atom.

The corresponding rate law may be written as,

$$-\frac{d[\mathrm{H}]}{dt} = -\frac{d[\mathrm{O_2}]}{dt} = +\frac{d[\mathrm{OH}]}{dt} = +\frac{d[\mathrm{O}]}{dt} = k[\mathrm{H}][\mathrm{O_2}] \qquad \text{(B4)}$$

where the rate of reaction is directly proportional to the concentration of hydrogen atoms and oxygen molecules and the *order of the reaction* is two. Such a rate law for an individual elementary step is valid over a very wide range of temperature and pressure in contrast to a rate law based on a global equation (e.g. the overall methane-oxygen reaction of equation B1) which has only a limited range of applicability. It would be preferable in combustion studies to deal only with elementary reactions and to dispense with global expressions altogether; however, it is often the case that the detailed reaction scheme is not completely understood, or its extreme complexity renders it unsuitable for computational analysis and in these cases a global (or *one-step*) reaction must be used. The one-step reaction assumption has often been preferred in Computational Fluid Dynamics (CFD) models of combustion problems since the codes are intended primarily to resolve the details of the fluid flow rather than the complex combustion chemistry. Computer programs which combine both these elements in great detail are being developed (Appendix D), but remain some years away from practical realisation.

Reaction kinetics are modelled using the *Arrhenius equation* which relates a rate constant (k) to the thermodynamic temperature (T),

$$k = AT^{\beta}\exp(-E/RT) \qquad \text{(B5)}$$

where the two *Arrhenius parameters*, A and E are independent of temperature. A is termed the *frequency factor* (or *pre-exponential factor*) and E is the *activation energy*. The frequency factor is related to the rate at which chemical bonds can rearrange in a molecule and is of the order of a vibrational frequency (i.e. 10^{13} s^{-1}); the activation energy is a measure of the energy barrier to reaction. The following table illustrates the 73 elementary reactions involving the 23 chemical species used in Tuovinen's calculations (Reference 18) (see also Figure B1). The symbol M which appears in the Table is used to denote any molecule present in the system and its function is to remove some of the energy released by the formation of the new chemical bond thereby preventing the product from immediately re-dissociating; M is termed a *third body* or *chaperon* (Reference 1).

Table B.1

List of 73 elementary reactions involved in the methane-oxygen reaction

	Reactions Considered			*A*	β	*E*
1	$C_2H_6 + H$	→	$C_2H_5 + H_2$	0.540D+03	3.5000	5207.0
2	$C_2H_6 + O$	→	$C_2H_5 + OH$	0.300D+08	2.0000	5111.0
3	$C_2H_6 + OH$	→	$C_2H_5 + H_2O$	0.630D+07	2.0000	645.00
4	$C_2H_6 + HO_2$	→	$C_2H_5 + H_2O_2$	0.600D+13	0.0000	19394.0
5	$C_2H_6 + CH_3$	→	$C_2H_5 + CH_4$	0.550D+00	4.0000	8288.0
6	C_2H_6	→	$CH_3 + CH_3$	0.240D+17	0.0000	87418.0
7	$C_2H_4 + H$	→	C_2H_5	0.100D+14	0.0000	1505.0
8	$C_2H_4 + H$	→	$C_2H_3 + H_2$	0.150D+15	0.0000	10199.0
9	$C_2H_4 + O$	→	$CH_3 + HCO$	0.160D+10	1.2000	740.00
10	$C_2H_4 + OH$	→	$C_2H_3 + H_2O$	0.300D+14	0.0000	2986.0
11	$C_2H_4 + CH_3$	→	$C_2H_3 + CH_4$	0.420D+12	0.0000	11106.0
12	C_2H_5	→	$C_2H_4 + H$	0.200D+14	0.0000	39648.0
13	$C_2H_5 + O_2$	→	$C_2H_4 + HO_2$	0.200D+13	0.0000	4992.0
14	$C_2H_5 + H$	→	$CH_3 + CH_3$	0.300D+14	0.0000	0.0000
15	$C_2H_5 + C_2H_5$	→	$C_2H_6 + C_2H_4$	0.140D+13	0.0000	0.0000
16	$C_2H_3 + O_2$	→	$C_2H_2 + HO_2$	0.100D+13	0.0000	0.0000
17	$C_2H_3 + H$	→	$C_2H_2 + H_2$	0.200D+14	0.0000	0.0000
18	$C_2H_3 + O$	→	$C_2H_2 + OH$	0.300D+14	0.0000	0.0000
19	$C_2H_2 + H$	→	C_2H_3	0.550D+13	0.0000	2412.0
20	$C_2H_2 + O$	→	$CH_2 + CO$	0.410D+09	1.5000	1696.0
21	$C_2H_2 + OH$	→	$CH_2 + HCO$	0.300D+13	0.0000	1099.0
22	$C_2H_2 + O_2$	→	$HCO + HCO$	0.400D+13	0.0000	28000.0
23	$CH_4 + H$	→	$CH_3 + H_2$	0.220D+05	3.0000	8742.0
24	$CH_4 + O$	→	$CH_3 + OH$	0.120D+08	2.1000	7619.0
25	$CH_4 + OH$	→	$CH_3 + H_2O$	0.167D+07	2.1000	2460.0
26	$CH_4 + HO_2$	→	$CH_3 + H_2O_2$	0.200D+12	0.0000	14940.0
27	CH_4	→	$CH_3 + H$	0.100D+16	0.0000	0.10032E+06
28	$CH_3 + O_2$	→	$HCHO + H + O$	0.150D+14	0.0000	28662.0
29	$CH_3 + H_2$	→	$CH_4 + H$	0.660D+03	3.0000	7739.0
30	$CH_3 + M$	→	$CH_2 + H$	0.100D+17	0.0000	90523.0
31	$CH_3 + H$	→	CH_4	0.600D+17	-1.000	0.0000
32	$CH_3 + O$	→	$HCHO + H$	0.700D+14	0.0000	0.0000
33	$CH_3 + CH_3$	→	C_2H_6	0.240D+15	-0.400	0.0000
34	$CH_3 + CH_3$	→	$C_2H_5 + H$	0.800D+15	0.0000	26512.0
35	$CH_3 + CH_3$	→	$C_2H_4 + H_2$	0.100D+17	0.0000	32005.0
36	$CH_2 + O_2$	→	$CO_2 + H + H$	0.130D+14	0.0000	1505.0
37	$CH_2 + O$	→	$CO + H + H$	0.500D+14	0.0000	0.0000
38	$CH_2 + CH_3$	→	$C_2H_4 + H$	0.400D+14	0.0000	0.0000
39	$HCHO + H$	→	$HCO + H_2$	0.250D+14	0.0000	3989.0
40	$HCHO + O$	→	$HCO + OH$	0.350D+14	0.0000	3511.0

	Reactions Considered (cont.)			A	β	E
41	$HCHO + OH$	→	$HCO + H_2O$	0.300D+14	0.0000	1194.0
42	$HCHO + HO_2$	→	$HCO + H_2O_2$	0.100D+13	0.0000	8000.0
43	$HCHO + CH_3$	→	$CH_4 + HCO$	0.100D+12	0.0000	6091.0
44	$HCHO + M$	→	$HCO + H + M$	0.500D+17	0.0000	76431.0
45	$HCO + O_2$	→	$CO + HO_2$	0.300D+13	0.0000	0.0000
46	$HCO + M$	→	$CO + H + M$	0.250D+15	0.0000	16791.0
47	$HCO + H$	→	$CO + H_2$	0.200D+15	0.0000	0.00000
48	$HCO + O$	→	$CO + OH$	0.300D+14	0.0000	0.00000
49	$HCO + O$	→	$CO + H$	0.300D+14	0.0000	0.00000
50	$HCO + OH$	→	$CO + H_2O$	0.500D+14	0.0000	0.00000
51	$CO + OH$	→	$CO_2 + H$	0.440D+07	1.5000	-740.00
52	$CO + HO_2$	→	$CO_2 + OH$	0.150D+15	0.0000	23574.0
53	$CO + O_2$	→	$CO_2 + O$	0.250D+13	0.0000	47769.0
54	$H_2O_2 + H$	→	$H_2 + HO_2$	0.170D+13	0.0000	3750.0
55	$H_2O_2 + H$	→	$H_2O + OH$	0.100D+14	0.0000	3583.0
56	$H_2O_2 + O$	→	$HO_2 + OH$	0.280D+14	0.0000	6401.0
57	$H_2O_2 + OH$	→	$HO_2 + H_2O$	0.700D+13	0.0000	1433.0
58	$H_2O_2 + M$	→	$2OH + M$	0.120D+18	0.0000	45381.0
59	$H_2 + O$	→	$OH + H$	0.150D+08	2.0000	7548.0
60	$H_2 + OH$	→	$H_2O + H$	0.100D+09	1.6000	3296.0
61	$H_2 + HO_2$	→	$H_2O_2 + H$	0.730D+12	0.0000	16854.0
62	$HO_2 + H$	→	$OH + OH$	0.150D+15	0.0000	1003.0
63	$HO_2 + H$	→	$H_2 + O_2$	0.250D+14	0.0000	693.0
64	$HO_2 + O$	→	$O_2 + OH$	0.200D+14	0.0000	0.0000
65	$HO_2 + OH$	→	$H_2O + O_2$	0.200D+14	0.0000	0.0000
66	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	0.200D+13	0.0000	0.0000
67	$H + H_2O$	→	$H_2 + OH$	0.460D+09	1.6000	18558.0
68	$H + O_2$	→	$OH + O$	0.120D+18	-0.910	16504.0
69	$H + O_2 + M$	→	$HO_2 + M$	0.200D+19	-0.800	0.00000
70	$OH + H$	→	$H_2 + O$	0.680D+07	2.0000	5570.0
71	$OH + OH$	→	$H_2O + O$	0.150D+10	1.1400	0.00000
72	$O + H_2O$	→	$OH + OH$	0.150D+11	1.1400	17245.0
73	$O + OH$	→	$O_2 + H$	0.180D+14	0.0000	0.0000

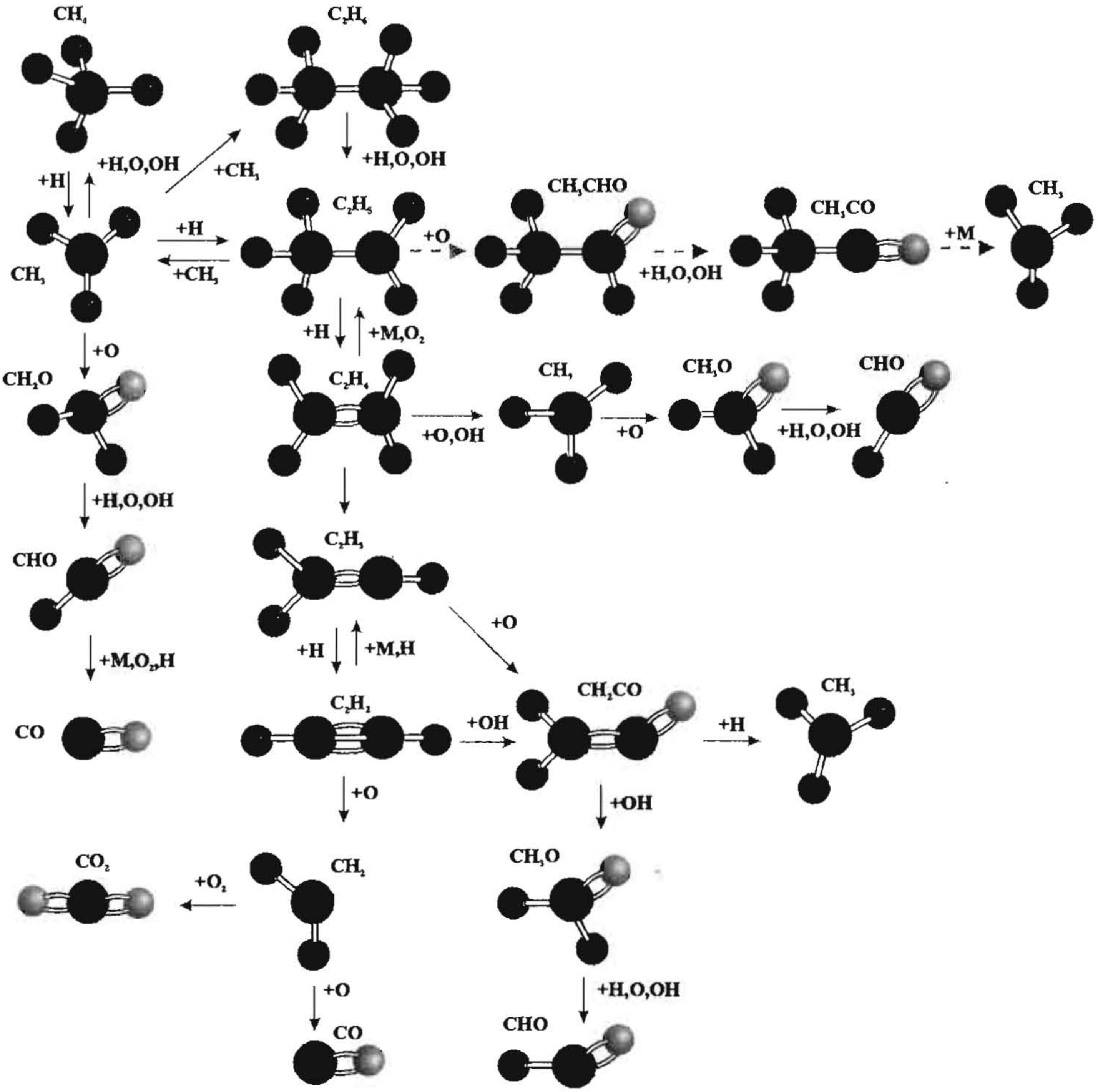

Fig.B1 Schematic of Premixed Methane-Air Reaction

APPENDIX C. OVERVIEW OF HALONS, THEIR SHORTCOMINGS AND REPLACEMENT CANDIDATES

The early development (1950s) of Halon (*halogenated hydrocarbon*) agents for firefighting use has been discussed by Guise (Reference 40), Friedman (Reference 41) and Abrams (Reference 34). Hirst (Reference 8, 1989) provides an overview of their chemical composition and stresses their impressive firefighting efficiency, "...a lot of firefighting potential can be contained in a small space." Hirst (Reference 8) also discusses the numbering system used for halons which describes the molecular structure of the agent, for example Halon 1211 is $CBrClF_2$. The first digit gives the number of carbon atoms, the second refers to fluorine atoms, the third is chlorine and the fourth is bromine atoms; sometimes a fifth number is present which represents the number of iodine atoms. Figure C1 shows the location of the halogens in Group VII of the Periodic Table (yellow column at right of Figure); element number 85, astatine, is also a member of the halogen family but does not feature in commercial halons (it is rare, expensive and also radioactive).

More recently, commercial Halon emission has been identified as contributing to the depletion of the earth's stratospheric ozone (Reference 19). The work described by Pitts *et al* (Reference 19) is typical of a wider research effort in the developed world, aimed at evolving a "new generation" of *Halon alternatives* (i.e. highly effective but environmentally benign firefighting agents). The remainder of this appendix consists of recently published information from the U.S. Environmental Protection Agency (EPA) which answers some frequently asked questions on the subject and gives an insight into the screening process required for alternative agents in U.S. Tables are included which provide details of some of the specific agents presently under consideration.

United States Environmental Protection Agency (EPA)

Office of Air and Radiation: Stratospheric Protection Division
Revision 8: April 1995

U.S. EPA Questions and Answers on Halons and their Substitutes

This fact sheet provides an overview of regulations governing the production and use of halon and the development of substitute agents for fire suppression and explosion protection.

A. HALONS AND THE PHASEOUT OF OZONE-DEPLETING SUBSTANCES

1. Q: When was the production of halons banned?
   A: Under the Clean Air Act, the U.S. has banned the production and import of halons 1211, 1301, and 2402 beginning January 1, 1994 in compliance with the Montreal Protocol On Substances That Deplete The Ozone Layer.

2. Q. Must I now dismantle my halon fire protection system?
   A: No. It is legal to continue to use your existing halon system. It is even legal to purchase recycled halon to recharge your system.

3. Q: I have heard that not all halon production will cease after 1994. Is this the case?
   A: The Montreal Protocol does allow production exemptions for what are called "essential uses." Production allowed under the essential use exemption is likely to be very small, however. This issue is discussed below.

4. Q: Are there any laws on emissions of halons?
   A: Currently there are no laws prohibiting halon emissions. However, EPA, the National Fire Protection Association (NFPA), the National Association of Fire Equipment Distributors (NAFED), the Fire Suppression Systems Association (FSSA), and the Fire Equipment Manufacturers Association (FEMA) all discourage discharge testing of halon. Proper conservation of halon includes improving leak detection, preventing accidental discharge, and avoiding testing and training.

B. HALON RECYCLING AND BANKING

1. Q: Will there be enough recycled halon available for my use?
   A: The U.S. owns 40 percent of the world's supply of Halon 1301. Fire protection consultants and EPA believe that there will be enough of the chemical to service existing critical needs for several years. EPA is working with halon users to ensure that these needs are met with recycled halon.

2. Q: Where can I purchase recycled halon?
   A: Recycled halon can be purchased from many halon and fire protection equipment distributors or directly from owners who are decommissioning their halon systems. In addition, the Halon Recycling Corporation (HRC) may be able to provide information on such sellers.

3. Q: What is the HRC?
   A: The HRC is a non-profit information clearinghouse established to assist sellers wishing to dispose of Halon 1301 *in a responsible manner*, and to help buyers with *critical uses* locate supplies of Halon 1301 for recharging their existing systems.

4. Q: Who set up the HRC?
   A: The HRC was established by members of the fire protection community and by the Halon Alternatives Research Corporation (HARC), an industry consortium that promotes the research, development, and promotion of alternatives to halons for fire protection.

5. Q: What do you mean by the term "critical use"?

A: The term "critical use" is used by HRC to identify priority uses of recycled halon. A use is considered "critical" when a need exists "to minimise damage due to fires, explosions, or other extinguishing agents, which would otherwise result in serious impairment of an essential service to society or pose an unacceptable threat to life, the environment, or national security even though all other appropriate fire protection measures have been taken."

6. Q: Who determines that my use is critical?
   A: The HRC has established two ways to make this determination. To be "registered", a buyer must sign a self-evaluation form. To be "certified," a buyer must submit an application that will be reviewed by an independent review committee. The committee certifies that the user has a legitimate need to continue using halon, taking into account technological, economic, and legal considerations.

7. Q: Why do these distinctions matter?
   A: The HRC wishes to facilitate the trade of recycled halon. However, some sellers may want to ensure that their halon is sold only to users with the most critical value to society. The "certified" rating, which is granted by HRC's independent review committee, will provide this assurance.

8. Q: What are the terms of the contract if I want to buy or sell halons through the HRC?
   A: The terms of all transactions are completely between the buyer and the seller. HRC merely acts as a clearinghouse by putting buyers and sellers together. However, EPA has prepared a "Sample Agreement for the Sale of Halon 1301" which may be helpful to those writing such agreements. This document is available on either hard copy or electronic diskette by contacting the Stratospheric Ozone Information Hotline or HRC.

9. Q: How can I contact the HRC?
   A: You can phone the HRC at (800) 258-1283 or (703) 841-0626, or fax (703}243-2874.

10. Q: Are there standards for recycled halon?
    A: The military specification for Halon 1211 has been revised to allow the use of recycled halon. Also, ASTM has developed ES 24-93, an emergency specification for Halon 1301 for both commercial and military use.

11. Q: Is recycling equipment available?
    A: Yes. Several manufacturers have developed recycling equipment for both Halon 1301 and Halon 1211 that recovers almost 100% of the halon and reclaims it to meet specifications. Contact HRC for the list of vendors.

12. Q: Can I import halon?
    A: It is legal under the Montreal Protocol and the US Clean Air Act to import recycled halon, that is, halon that has been recovered from a fire suppression system. However, current U.S. tax code imposes a tax on imported ozone-depleting substances. In addition, all bulk imports must be reported to EPA. Unused or newly produced halon may not be traded across international borders. Contact the IRS for more information concerning the tax.

C. HALON DISPOSAL

1. Q: I am removing halon from my systems. How can I dispose of it?
   A: Your halon is valuable to society and has a market value. You can make it available to critical users through the HRC, you can sell or give it to the Department of Defense (DoD} halon bank, or you can return it to your halon distributor for resale.

2. Q: Will the HRC come to take my halon?
   A: No. The HRC is not a physical "bank," but is an information clearinghouse that will help you locate a buyer for your halon.

3. Q: What if I can't find anyone to buy my halon because I have too little for it to be of interest or because have Halon 1211 or Halon 2402?
   A: HRC and EPA can help you locate a regional organization that will take your halon as a service.

4. Q: Tell me more about the DoD bank.
   A: The Defense Logistics Agency (DLA) is coordinating the DoD bank for the U.S. military in order to maintain a reserve of ozone-depleting substances (ODSs) for supporting Mission Critical Requirements. DLA has a policy to rely on reclamation and recovery whenever possible. DLA is willing to purchase recycled ODSs from the public, particularly Halon 1301, CFC-11, CFC-12, and CFC-114.

5. Q: How can I contact someone at the DoD Bank?
   A: Phone DLA at {804) 279-4525.

D. THE MONTREAL PROTOCOL AND REQUIREMENTS FOR ESSENTIAL USE

1. Q: Is the term "critical use" the same as the term "essential use"?

   A: No. The term "critical use is being used by HRC as a broad screen to help channel stocks of halons to users with applications requiring halons at least for the near term. The term "essential use" has a specific meaning under the terms of the Montreal Protocol. Under the Montreal Protocol, it is possible for a national government to represent a particular use as essential to society and obtain permission to continue manufacturing new halon for that use.

2. Q: What are the criteria for essential use?
   A: The Montreal Protocol requires that: 1) the use is necessary for human health and safety or is critical for the functioning of society, and 2) there are no technically and economically feasible alternatives that are acceptable from the standpoint of the environment and health. Once an end use has been defined as essential two further criteria must be met in order to allow production. The applicant must show that: 1) all economically feasible steps have been taken to minimise emissions from the "essential use", and 2) sufficient supplies are not available from existing stocks of banked or recycled halon.

3. Q: How can I obtain halon under the "essential use" designation?
   A: To have your use designated as essential, you must submit a detailed application to EPA describing the use, why you consider it essential to society, why no alternatives are feasible, and what you have done to locate stocks of banked or recycled halon. If EPA accepts your application, EPA will nominate your use to the Parties to the Protocol. EPA believes, however, that it will be very difficult to obtain this designation.

4. Q: What happens then?
   A: EPA, working with the State Department, must submit the nomination to the United Nations Environment Programme (UNEP) six months before the Parties to the Protocol meet. UNEP's Halon Technical Options Committee (HTOC) will first determine whether there is sufficient recycled halon available to meet the need. Only then will the HTOC evaluate the technical merits of the nomination. The recommendation is then passed on to the Technology and Economics Panel, which in turn will make a recommendation to the Working Group of the Parties. Once a decision has been made by the Parties, EPA must review the decision to ensure that it complies with the Clean Air Act.

5. Q: Does this apply to Halon 1301 as well as to Halon 1211 ?
   A: While the Clean Air Act requires the phase out of Halons 1211, 1301, and 2402, only Halon 1301 is likely to be considered for an essential use nomination. There is an oversupply of Halon 1211 in the U.S. and it is unlikely that new production will be necessary. Halon 2402 is rarely used.

6. Q: I don't know if there are any suitable alternatives yet, and I don't know if there will be enough recycled halon for my needs. But I believe my use is essential to society. What should I do?
   A: Nominations for essential uses can be made annually for consideration by the Parties to the Montreal Protocol. EPA recommends that you research alternatives thoroughly,

search for recycled halon from both your internal stores of halon in non-essential systems and from other sources, and implement new risk management and conservation schemes to minimise halon emissions. If you still believe you need an essential use exemption, EPA would like to work with you as you develop your application in order to fully represent U.S. interests before the Parties.

7. Q: Are applications made on an industry-wide basis?
   A: No. Exemptions will only be granted to individual users. Therefore, each company within an industry must submit a separate application.

8. Q: Can I apply for an essential use exemption this year?
   A: EPA typically issues a Federal Register notice in the fall calling for nominations to be considered at the meeting of the Parties in the summer or fall of the following year. Call EPA for the current schedule.

9. Q: Is there anything else I should know?
   A: New production is still subject to the U.S. tax on newly produced halons ($53.50 per pound for Halon 1301 in 1995), and it may be very costly to manufacture halon in small quantities. After the year 2000, there may be no company in the world still producing halons. Further, after 1999, the Clean Air Act severely restricts uses for which halon may be produced.

E. SNAP STATUS AND REVIEW PROCESS

1. Q: What does SNAP stand for?
   A: EPA's Significant New Alternatives Policy program. The Agency set up the SNAP program under Section 612 of Title VI of the Clean Air Act Amendments (CAA) of 1990.

2. Q: What is EPA doing under the SNAP program?
   A: Under SNAP, EPA is evaluating substitute chemicals and alternative technologies that companies want to use in place of the ozone-depleting substances, to ensure that they won't cause greater damage to human health and the environment than the ozone depleters that are being replaced. Based on this evaluation, EPA maintains a list of acceptable substitutes and a list of unacceptable substitutes.

3. Q: When were the SNAP lists published in the Federal Register?
   A: 58 FR 13043, March 18, 1994 (Rule)
   59 FR 44240 August 26, 1994 (Notice)
   59 FR 49108 Sept. 26, 1994 (Proposed Rule)
   60 FR 3318 January 13, 1995 (Notice)

   A summary of substitutes is detailed in Exhibit 1.

4. Q: What is the difference between a 'Notice,' a 'Proposed Rule,' and a 'Final Rule'?
   A: A 'Notice' contains no regulatory controls and thus does not need to go through the notice-and-comment rulemaking process. It contains technical corrections to the original rule as well as listings of new agents which are 'Acceptable' without restrictions. It enters into force upon publication in the Federal Register.

   A 'Proposed Rule' contains proposed lists of agents deemed 'Acceptable' but which are subject to use restrictions or which are 'Unacceptable'. There is a 45-day public comment period beginning with the date of publication in the Federal Register.

   After the public has an opportunity to comment on EPA's proposed rules, a 'Final Rule' is published enacting the provisions into law.

5. Q: Will there be other agents available in the future?
   A: Yes. Manufacturers are continuing to develop new agents and technologies which EPA will review and which will be included on future SNAP lists. These updated lists will be published periodically in the Federal Register. Exhibit 1 lists agents which are

listed as pending because the evaluation of the product has not yet been completed.

6. Q: How does EPA decide whether a substitute is acceptable or unacceptable?
   A: EPA's decision on the acceptability of new substitutes proposed by manufacturers is based primarily on the potential human health and environmental risks posed by the substitutes as compared to (in the case of halons) the halon being replaced, as well as to other substitute fire-control agents. The screening of new substitutes is done separately for each specific application, such as for a total flood agent or for use as a streaming agent. A listing of 'acceptable' does not imply that the agent is necessarily effective for a particular fire hazard or site, and users are advised to consult with a fire protection professional for selection of appropriate agents.

7. Q: What are the most significant criteria for evaluating a halon substitute?
   A: The key factor in assessing the safety of a halocarbon fire agent is cardiotoxicity. The results of a standard protocol to determine an agent's cardiosensitization level is compared to the amount of agent required to extinguish a fire. We call this comparing the design concentration to the No Observed Adverse Effect Level (NOAEL) and the Lowest Observed Adverse Effect Level (LOAEL).

8. Q: Are there any restrictions on the use of these agents?
   A: Halocarbon substitutes being used as total flooding agents have conditions which must be observed. These conditions include:

   - Where egress from an area cannot be accomplished within one minute, the employer shall not use the agent in concentrations exceeding its cardiotoxic "No Observed Adverse Effect Level" (NOAEL).

   - Where egress takes longer than 30 seconds but less than one minute, the employer shall not use the agent in a concentration greater than its cardiotoxic "Lowest Observable Adverse Effect Level" (LOAEL).

   - Agent concentrations greater than the LOAEL are only permitted in areas not normally occupied by employees provided that any employee in the area can escape within 30 seconds. The employer shall assure that no unprotected employees enter the area during agent discharge.

   In addition, systems using agents which are safe in high concentrations must be designed to ensure a minimum of 16% oxygen.

   Please see the SNAP rule for complete details of the use conditions for each agent.

9. Q: I heard that HCFCs are not acceptable halon substitutes.
   A: Under section 610 of the CAA, Congress requires EPA to ban HCFCs in all 'pressurised dispensers'. Portable extinguishers fall under the definition of a pressurised dispenser, but total flooding systems and fixed streaming systems do not. However, EPA will allow the sale and distribution of HCFCs in portable extinguishers to commercial users and owners of marine vessels and aircraft, for uses where the HCFC is the most suitable agent for fire safety. The Final Rulemaking for the section 610 "nonessential products ban" for class II substances was published December 30, 1993. For more specific guidance, contact the Stratospheric Ozone Information Hotline or the 'Nonessential Products Ban' program coordinator at (202) 233-9729.

10. Q: What are the limitations on using a PFC (either C_4F_{10}, C_6F_{14} or C_3F_8)?
    A: PFCs may only be used where no other agent is technically feasible due to performance or safety requirements. The user must conduct an evaluation of the other alternatives and must determine that they either will not perform properly or that they will pose a risk to human health. In

addition, PFC use must meet the conditions discussed in question E.8 above.

11. Q: Do I have to obtain EPA approval to use a PFC?
    A: No approval is required from EPA However, the user must maintain documentation of the evaluation.

12. Q: What is the SNAP status of alternative technologies such as inert gases, water mist, and powdered aerosols?
    A: Non-halocarbon systems are considered "alternative technologies" and are subject to EPA SNAP review.

13. Q: What are the SNAP conditions on the use of inert gases, which work by lowering the oxygen level?
    A: Inert gas systems work by lowering the oxygen in a room to a level that will not sustain combustion, while remaining high enough to sustain human life. Three inert gases are being listed by SNAP. IG-541 is an inert gas blend which lowers the oxygen level and raises the CO_2 level. SNAP requires that the oxygen level must not fall below 10% and the CO_2 level must not exceed 5%. IG-01 and IG-55, which do not raise the CO_2 level, will be listed in a Final Rule in the near future. The design concentration of each of these agents must result in an oxygen level of at least 10%.

14. Q: Are there conditions on using water mist or water fog systems?
    A: EPA is proposing to list water mist systems that do not contain any additives as acceptable without use restrictions. However, any system with an additive must be reviewed by EPA on a case-by-case basis.

15. Q: Can I use a powdered aerosol in a total flood system in an occupied area?
    A: Powdered aerosol in total flooding systems have not undergone a medical panel peer review for physiological effects, and thus they have only been listed as acceptable in normally unoccupied areas.

16. Q: What alternatives are suitable for my particular end use?
    A: EPA maintains a list of acceptable substitutes, but it is up to manufacturers and users to assess their suitability for particular uses.

17. Q: How can I contact the vendors of these substitutes ?
    A: Exhibit 2 & 3 include lists of manufacturers and vendors of halon substitutes.

18. Q: How can I obtain copies of the SNAP rule?
    A: The SNAP rule can be ordered for a nominal fee from the Government Printing Office, (202) 783-3238. You must provide them with the date of publication of the rule you want (see question E.3).

19. Q: Is the Rule available electronically?
    A: Yes, the rule can be downloaded from the EPA OAQPS bulletin board service (Office of Air Quality Planning and Standards, Technology Transfer Network). The BBS modem number is (919) 541-5742, with modem settings of N, 8, I, Full Duplex, using a terminal type of VT100, VT102 or ANSI. For assistance in accessing this service, call (919) 541-5384 during normal business hours, EST.

    Internet users can use telnet to access this service interactively. However, as there is no FTP service, the Kermit protocol is required to download a file. The internet telnet address is: ttnbbs.rtpnc.epa.gov

20. Q: What other government regulations or industry standards concerning halons should I be aware of?
    A: The National Fire Protection Association (NFPA) has issued NFPA 2001 to address alternative total flooding agents and further work is underway to address water mist and other alternative systems. In addition, manufacturers of systems containing the new alternative agents typically obtain Underwriters Laboratories (UL) or Factory Mutual (FM) certification.

21. Q: Where can I obtain additional information about the SNAP program and likely alternatives for halon?

A: Please contact::

EPA's Stratospheric Ozone Information Hotline (800) 296-1996, (202) 775-6677

or

Karen Metchis
Halon Program Manager
Stratospheric Protection Division
U.S. EPA 6205J
Washington, DC 20460
(202) 233-9193
FAX (202) 233-9577
internet: Metchis.Karen@epamail.epa.gov

F. IMPORTANT PHONE NUMBERS

1. Q: Please repeat all the phone numbers again. What other phone numbers could be helpful?

A:

- **EPA Stratospheric Ozone Hotline**
  (800) 296-1996 or (202) 775-6677

- **EPA Halon Program Manager**
  (202) 233-9193

- **EPA Import and Production Regulation**
  (202) 233-9185

- **EPA Nonessential Products Ban Program Coordinator**
  (202) 233-9729

- **Halon Alternatives Research Corporation (HARC)**
  (703) 841-0626

- **Halon Recycling Corporation**
  (800) 258-1283 or (703) 841-0626

- **DLA/DoD Bank**
  (804) 279-45250

- **Internal Revenue Service (IRS)**
  (202) 622-313

- **National Fire Protection Association (NFPA)**
  (800) 344-3555

- **National Association of Fire Equipment Distributors (NAFED)**
  (312) 644-6610

- **Fire Suppression Systems Association (FSSA)**
  (410) 931-8100

- **Fire Equipment Manufacturers Association (FEMA)**
  (216) 241-7333

- **Underwriters Laboratories (UL)**
  (708) 272-8800

- **Factory Mutual (FM)**
  (617) 255-4773

EXHIBIT 1:
FIRE AND EXPLOSION PROTECTION AGENTS

STATUS OF SUBSTITUTES SUBMITTED UNDER EPA'S SNAP PROGRAM

ACCEPTABLE TOTAL FLOODING AGENTS*
(Feasible for Use in Occupied Areas)

Agent	Comment
C_4F_{10} (PFC-410 or CEA-410)	Allowed where no other agent is technically feasible. NOAEL 40%
C_3F_8 (PFC-218 or CEA-308)	Allowed where no other agent is technically feasible. NOAEL 30% (final listing forthcoming)
HCFC Blend A (NAF S-III)	NOAEL 10%; LOAEL 10%
HFC-23 (FE 13)	NOAEL 30%
HFC-227ea (FM-200)	NOAEL 9.0%; LOAEL 10.5%
IG-01 (Argon)	Minimum oxygen 10%. Proposed Acceptable. (forthcoming)
IG-55 (Argonite)	Minimum oxygen 10%. Proposed Acceptable. (forthcoming)
IG-541 (Inergen)	Minimum oxygen 10%; Maximum CO_2 5%
Water Mist with No Additives	Acceptable. (forthcoming)
Carbon Dioxide	Must meet NFPA 12 and OSHA 1910.162(b)5 requirements.
Water Sprinklers	

ACCEPTABLE TOTAL FLOODING AGENTS*
(Feasible for Use in Unoccupied Areas Only)

Agent	Comment
CF_3I	NOAEL 0.2%; LOAEL 0.4% (final listing forthcoming)
HBFC-22B1 (FM-100)	Class I Substances will be phased out by 1996. NOAEL 0.3%; LOAEL 1.0%
HCFC-22	NOAEL 2.5%; LOAEL 5.0%
HCFC-124	NOAEL 1.0%; LOAEL 2.5%
HFC-125	NOAEL 7.5%; LOAEL 10.0%
HFC-134a	NOAEL 4.0%; LOAEL 8.0%
Gelled Halocarbon/Dry Chem. Suspension (PGA)	(final listing forthcoming)
Inert Gas/Powdered Aerosol Blend (FS 0140)	(final listing forthcoming)
Powdered Aerosol A (SFE)	

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* Total flooding agents subject to use conditions. See fact sheet for details.7-

EXHIBIT 1: (CONTINUED)
FIRE AND EXPLOSION PROTECTION AGENTS

STATUS OF SUBSTITUTES SUBMITTED UNDER EPA'S *SNAP* PROGRAM

MISCELLANEOUS ACCEPTABLE TOTAL FLOOD LISTINGS

Agent	Comment
Sulphur Hexafluoride (SF_6)	(final listing forthcoming) Discharge test agent for new halon systems, allowed for military uses and civilian aircraft uses only.

ACCEPTABLE STREAMING AGENTS

Agent	Comment
C_6F_{14} (PFC-614 OR CEA-614)	Allowed where no other agent is technically feasible
HBFC-22B1 (FM-100)	Non-residential uses only. Will be phased out by 1996.
HCFC Blend B (Halotron I)	Non-residential uses only.
HCFC Blend C (NAF P-III)	Non-residential uses only.
HCFC Blend D (Blitz-III)	Non-residential uses only.
HCFC-123	Non-residential uses only.
HCFC-124 (FE-241)	Non-residential uses only.
Gelled Halocarbon/Dry Chem. Suspension (formerly Powdered Aersol B)	Allowable in the residential use market.
Water Mist with No Additives	Acceptable (forthcoming)
Carbon Dioxide	
Dry Chemical	
Water	
Foam	

PENDING

Agent	Comment
[HFC Blend] A	Total flooding agent for unoccupied areas.
Water Mist Systems with Additives	Streaming & total flooding applications. Must be individually submitted to EPA and reviewed on a case-by-case basis.

Exhibit 2:
FIRE AND EXPLOSION PROTECTION AGENT MANUFACTURERS

3M
John Schuster
(612) 736-6055
FAX (612) 736-7542
3M Center Building, 223-6S-04
St. Paul MN 55144 - 1000
C_6F_{14} *(CEA-614);* C_4F_{10} *(CEA-410)*

Allied Defense Industries, Inc.
Jerry Brown
(703) 734-9626
FAX (703) 448-8591
1487 Chain Bridge Road, Suite 304
McLean, VA 22101
Powdered Aerosol A (SFE Powdered Aerosol)

American Pacific Corporation
Halotron, Inc.
Fred Gibson. III
(702) 735-2200
FAX (702) 794-4463
3770 Howard Hughes Parkway, Suite 300
Las Vegas, NV 89109
HCFC Blend B (Halotron I); HFC Blend A (Halotron II)

Ansul Fire Protection
David Pelton
(708) 305-5700
FAX (708) 305-3360
1240 Iroquois Drive, Suite 102
Naperville, IL 60563-8537
IG-541, formerly [Inert Gas Blend] (Inergen)

DuPont Fluoroproducts
Daniel Moore
(302) 992-2177
FAX (302) 992-2836
Barley Mill Plaza 13-2150
P.O. Box 80013
Wilmington, DE 19880-0013
HFC-23 (FE-13); HFC-125 (FE-25); HFC-134a; HCFC-124 (FE-241); HCFC-123 (FE-232)

BioGenesis Engineering
Dr. Mehsen C. Amiran
(414) 768-2468
FAX (414) 571-2422
610 W. Rawson Avenue
Oak Creek, WI 53154
Surfactant Blend A (ColdFire 302; Fire Strike)

Ginge-Kerr as
Ole Bjarnsholt
111, Stamholmen
DK-2650 Hvidovre
Denmark
IG-55 (Argonite)

Great Lakes Chemical
Doug Register
(317) 497-6382
FAX (317) 463-2849
P.O. Box 2200
West Lafayette, IN 47906
HFC-227ea (FM-200); HBFC-22B1 (FM-100)

Minimax GmbH
Mr. Wolfgang Koch
(49) 4531 803-443
FAX (49) 4531 803-500
Industriestrasse 10/12
23840 Bad Oldesloe, Germany
IG-01 (Argon)

North American Fire Guardian
Elio Guglielmi
(604) 684-7374
FAX (604) 684-7415
Suite 304
700 West Pender St.
Vancouver, B.C. Canada V6C 1G8
HCFC Blend A (NAF S-III); HCFC Blend C (NAF P-III); HCFC Blend D (Blitz)

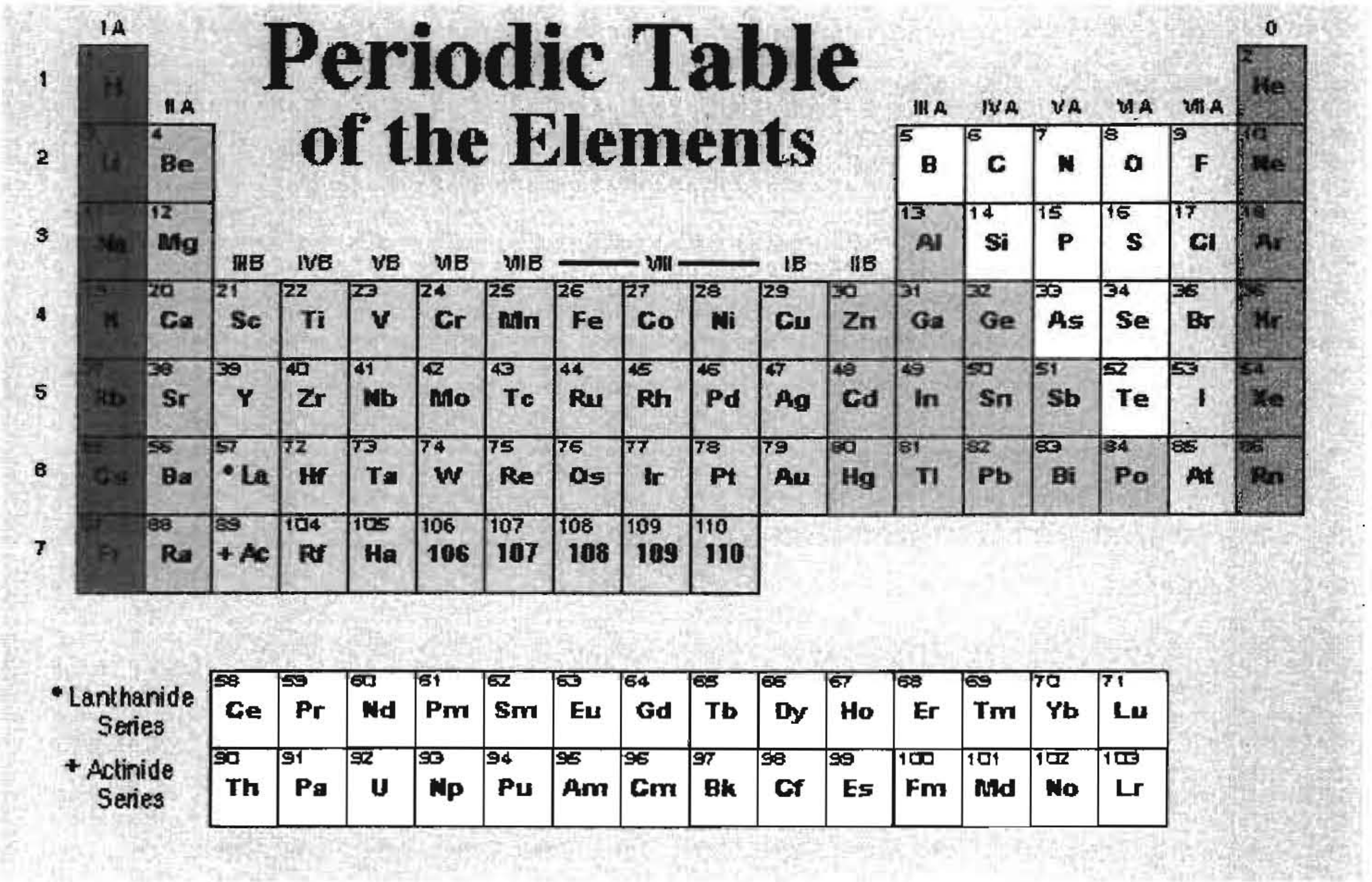
Olin Aerospace Co.
Gary Holland
(206) 885-5000
FAX (206) 882-5744
11441 Willows Rd., N.E.
Redmond, Washington 98073-9709
Inert Gas/Powdered Aerosol Blend

Pacific Scientific
Steve Newhouse
(818) 359-9317
FAX (818) 359-7013
HTL/KinTech Division
1800 Highland Avenue
Duarte, California 91010
CF_3I (Triodide)

Powsus, Inc.
Harry E. Stewart
(215) 647-2267
1178 Wisteria Drive
Malvern, Pennsylvania 19355
Powdered Aerosol B (PGA Powdered Aerosol Formulations)

Securiplex Technologies, Inc.
Victor Gameiro
(514) 633-1000
FAX (514) 633-8338
549 Meloche
Dorval (Quebec) Canada H9P 2W2
Water Mist A (Firescope 2000 Fine Water Spray System); IG-55 (Argonite)

Yates Fire Protection
H. James Yates
(804) 827-8696
FAX (804) 827-8697
PO Box 9206
Hampton, VA 23670
Water Mist B (Unifog Water Mist)



Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 • La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 + Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

• Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig.C1 Location of the Halogens within the Periodic Table

APPENDIX D. EXPLOITING MPP TECHNOLOGY FOR COMPUTATIONAL COMBUSTION

by

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Keckwick Lane
Daresbury
Warrington WA4 4AD

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Trumpington Street
Cambridge CB2 1PZ

1. Introduction

Combustion is widely accepted to be a "Grand Challenge" problem (Reference D1). The successful prediction of harmful pollutants from combustion processes requires a detailed understanding of many complex interactions. Other problems, such as the design of efficient lean-burn engines are equally challenging. In practice, the combustion chemistry and fluid mechanical processes of such problems are not well understood, particularly the small scale interactions, and many fundamental assumptions have to be made to enable the problem to be tractable. All Grand Challenge problems place enormous demands on conventional computing facilities and a cost effective approach that will enable large scale problems to be tackled is to employ the principles of parallel processing. In this approach, individual processors work simultaneously on a problem that may previously have been intractable. Current technology allows Massively Parallel Processing (MPP), where hundreds or thousands of processors are coupled together, to be a reality and the UK's flagship facility is a Cray T3D. This machine is located at the Edinburgh Parallel Computing Centre (EPCC) and has 320 processors. Projects are allocated on a "consortia" based approach whereby a group of leading researchers work together to exploit the facility. Computational Combustion for Engineering Applications (CCEA) is one such consortium (Reference D2). The project is led by Professor K. N. C. Bray (Cambridge) and managed by Dr. D. R. Emerson (Daresbury Laboratory) and involves fundamental calculations which will lead to a better understanding of many combustion processes and improvements in modelling capabilities. To illustrate some of the work being pursued by the CCEA consortium, one of the project highlights is presented in the following section.

2. Direct Simulation of Turbulent Combustion

Combustion in real systems is almost always turbulent, and the presence of turbulence has a profound effect on the rate of chemical reaction as well as on the transport of heat, chemical species and momentum. In most cases turbulence acts to increase the rates of reaction and of transport, but under more extreme circumstances turbulence can result in flame extinction. Despite the enormous technological importance of combustion, both controlled and uncontrolled, the underlying physics of these phenomena are not well understood. Thus the design of combustion equipment and the prevention or mitigation of fires and explosions has remained at a rather empirical level. Similarly, design tools based on the use of computational fluid dynamics (CFD) while reasonably successful in predicting "cold-flow" phenomena have proved less reliable when applied to combustion problems.

The ideal route to improved understanding and better combustion models is through the use of carefully-designed experiments. The use of laser diagnostics has revolutionised the science of combustion measurement and the quality of data obtained is excellent. Unfortunately, combustion in turbulence is a highly three-dimensional and time-dependent process, while current visualisation and measurement techniques are limited to two-dimensional snapshots.

A completely different approach which overcomes these limitations is the use of Direct Numerical Simulation (DNS). Recent advances in computer power have made it possible to solve the governing equations of turbulent combustion without modelling or approximation. The computational requirements are very severe since it is vital to resolve the smallest scales of turbulence and reaction. The largest problem that can be tackled is then set by the size of the available computer. In general, the larger the problem size, the more useful are the results of DNS in providing an insight into the full-scale process.

The present DNS work is being carried out with support from EPSRC and the High Performance Computing Initiative (HPCI) Centre at Daresbury and is intended to establish a capability within the UK. A code known as ANGUS has been developed by R. S. Cant to solve the Navier-Stokes equations for fluid flow augmented by additional equations to represent the conservation of energy and chemical species. At present the chemical reaction mechanism is represented by a one-step Arrhenius approximation, since the purpose is to look at the dynamics of the flame turbulence interaction rather than at the chemistry per se. Standard second-order central differences are employed, with second-order Adams-Bashforth time stepping. A low-Mach number limit is considered and the resulting Poisson equation for the pressure is then solved by using either Fourier analysis, multigrid or conjugate gradient methods. The final choice depending on the problem size and the computer system being used.

The initial test case consists of two flames placed back-to-back near the central plane of a computational box having periodic boundary conditions on all variables. Turbulence within the box is allowed to decay as the flames propagate outwards. In the initial configuration there is no heat release. Initial results have been obtained for turbulence decay and for early flame propagation and are very encouraging.

3. Concluding Remarks

The work being undertaken within the CCEA project is intended to lead to a better physical and chemical understanding of many fundamental combustion processes. It is recognised that these computations cannot, in general, be pursued by industry but the results obtained from the work will lead to improvements in modelling capabilities. This will then allow more realistic computations to be performed with improved predictive capabilities. The data collected from the DNS work will form part of a database and access to this data by the science and engineering communities will be encouraged.

It is clear from the work highlighted that supercomputing, and MPP technology in particular, is playing a vital role in encouraging scientific advances in the field of computational combustion. However, it should be noted that many combustion applications can be developed to exploit parallel computers and these systems can range from modest workstation clusters to MPP facilities. The benefits to the individual will range from increased realism, arising from better resolution or improved modelling, to improving the throughput and reducing the time to solution.

Acknowledgements

This work has been supported by EPSRC, Collaborative Computational Project 12 (CCP12), which is looking at high performance computing in engineering, and by the High Performance Computing Initiative.

References

D1. Grand Challenges 1993: High Performance Computing and Communications
The FY 1993 U.S. Research and Development Program.

D2. Computational Combustion on the Cray T3D by D. R. Emerson
EPCC Project Directory 1994-1995, p 58.