INVESTIGATIONS INTO THE EFFECTS OF CARBON DIOXIDE AND NITROGEN ON THE FLAMMABILITY LIMITS OF GAS MIXTURES†

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The wider use of new technologies and initiatives such as cleaner-burning power stations and carbon sequestration brings new challenges for hazard assessment. One particular challenge is the need to understand the hazards presented by use of large inventories of often pressured mixtures of fuel gases and inerts, such as CO_2 or nitrogen.

This paper summarises the findings of a joint programme of CFD modelling and experimental tests which studied the combustibility of jet releases of mixtures of propane/CO_2, hydrogen/CO_2 and hydrogen/N_2 to determine flammability limits, flame length, and combustion stability.

PUBLISHED FLAMMABILITY LIMITS OF GASES AND THE INFLUENCE OF CO_2

Carbon dioxide has long been used in fire fighting and explosion suppression. As a result, a large amount of information exists on the mechanisms by which combustion is affected, as well as on the concentrations required to prevent ignition. Table 1 shows the flammable limits for the gases of interest to this study and the minimum CO_2 concentrations required to prevent the ignition.

Examination of the data listed above for hydrogen shows that carbon dioxide is a more effective suppressant than nitrogen. This is primarily a function of its specific heat, which gives greater flame cooling than for nitrogen.

The effectiveness of a number of different extinguishing media in suppressing the ignition of a methane/air mixture are ranked below.

$$\text{Halon} > CO_2 > H_2O > N_2 > \text{He} > \text{Ar}$$

Halons, the most effective of these gases, act through a combination of chemical inhibition through the trapping of free radicals created during combustion, as well as simple heat absorption and oxygen depletion.

INTRODUCTION TO THE BEHAVIOUR OF JET RELEASES

UNDERLYING PRINCIPLES

In an industrial situation it is foreseeable that releases will take the form of leaks from pressurised vessels or pipelines. The study of pressurised releases is a complex field with many factors influencing the behaviour of the release and its subsequent dilution.

For low velocity releases or leaks, dispersion/dilution will be dominated by buoyancy effects of the gas, which will govern its rate of entrainment into the surrounding atmosphere. For higher velocity releases from pressurised systems, the dilution/entrainment phenomena are driven more by the momentum of the gas jet, at least in the initial stages of the release. These momentum-dominated releases are characterised by high degrees of turbulent shear, which gives rise to rapid mixing and entrainment of fresh air on the periphery of the jet.

To help illustrate this phenomenon, a CFD simulation was undertaken of the release of a mixture containing 30% CO_2 and 70% methane at a pressure of 5 bar for a hole size of 2.5 mm^2. At this pressure, the release is choked. Rather than try to resolve the complex shockwave structures near the release point, the "resolved sonic source" approach was adopted (see Ivings et al., 2004). This involved only modelling the flow downstream of the sonic point, using the pseudo-source approach of Ewan & Moodie (1986). The jet was resolved using an unstructured grid and turbulence was modelled using the standard k-ε model. For validation of this approach, see Ivings et al. (2004). The simulation was performed using ANSYS-CFX version 10.

The coloured blocks at the bottom of the Figure 1 represent bodies of gas sampled along the length of the plume. These bodies could equally be propane, rather than methane as in the example, as no difference in behaviour would be observed in the near-field case modelled in this simulation. The output shows that the ratio of CO_2 to CH_4 concentration remains constant as the original mixture becomes more dilute, and that close to the point of release the degree of entrainment of air is low.

It can be seen that at the point of release the gas mixture will be unable to burn, as insufficient air has been entrained and the mixture is above its upper flammable limit. As one moves along the length of the jet, first a point will be reached where the methane/CO_2/air mixture reaches the upper flammable limit. Eventually, towards the end of the jet, a point will be reached where the mixture falls below the flammable limit. These regions characterise the portion of the mixture that is within the flammable envelope and is able to support combustion.

EXPERIMENTAL PROGRAMME

RELEASE APPARATUS

For ease of use, and comparison with other data on inerted mixtures, propane was chosen as the flammable gas for

Table 1. Published flammability limits for gases

Gas	LFL % volume	UFL % volume	Stoichiometric concentration % volume	Limiting inerting gas concentration % volume (Balance is air)
Methane	4.4	17.0	9.5	25% CO_2 *
Propane	1.7	10.9	4.0	32% CO_2 *
Hydrogen	4.0	77.0	29.6	60–62% CO_2 * 75% N_2 **

*Menon and Vakil, 2005
**IAEA, 2001

this experimental study, rather than methane as previously modelled.

Delivery pressures for all gases were set at approximately 2 barg and flow rates controlled using rotameters calibrated for the gases in question. Gas streams exiting the rotameters were combined and delivered to a simple release nozzle comprising a length of 7 mm internal diameter stainless steel tube.

Flame lengths and stand-off from the release nozzle were assessed by mounting a blackboard marked with vertical lines at 10 cm intervals behind the flame, to allow the comparison of relative, rather than absolute, lengths from video records.

For those tests involving flame impingement onto a target, a rectangular section of insulating ceramic board was mounted at 90º to the flame axis at a known distance from the

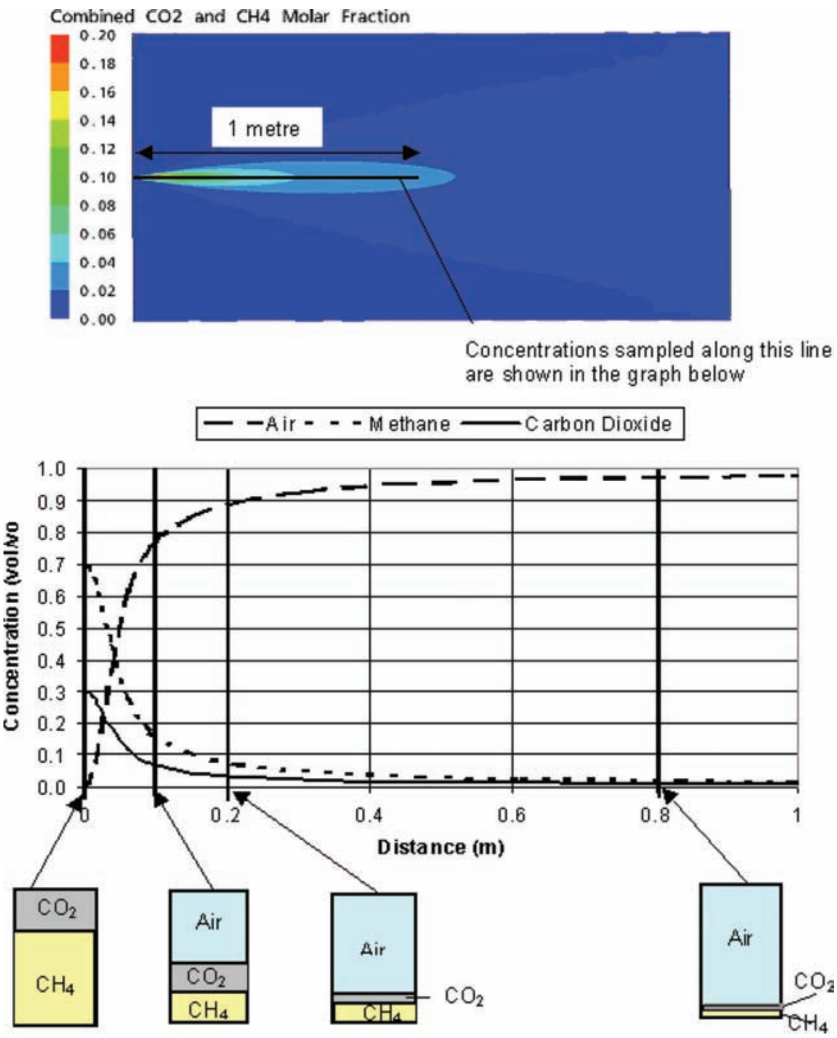


Figure 1. Concentrations of air, CO_2 and methane in the jet

Table 2. Flame stability and test conditions for unimpeded propane/CO_2 releases

	Flow rate $l.min^{-1}$		
Gas mixture (propane:CO_2)	50	79	127
100 % propane	Combustion stable	Combustion stable	Combustion stable
80:20	Combustion less stable	Combustion unstable	Not studied
70:30	Combustion unstable	Not studied	Not studied
69:31	Not studied	Not studied	Longest burning time 10 s
60:40	Longest burning time 20 s	Longest burning time 30s	Not studied
55:45	Longest burning time 15 s	Not studied	Not studied
50:40	Longest burning time 6 s	Not studied	Not studied

release nozzle. This would allow an understanding of the effects obstacles would have on flame stability and behaviour.

RELEASES OF PROPANE/CO_2 MIXTURES

Non-impinging Releases

Test conditions, burning durations and comments on combustion stability for a range of propane/CO_2 mixtures are given in Table 2. The burning times quoted are the longest times observed before combustion ceased and were measured from the time of ignition to self-extinguishment.

In brief, these tests showed that CO_2 had the effect of decreasing combustion stability until, at a concentration somewhere between 30–40% CO_2, gas mixtures could no longer maintain selfsustaining combustion. Instead, the flame was unstable and the burning zone would progressively retreat along the jet release, until it suddenly died when the flame was 10 cm or so in length.

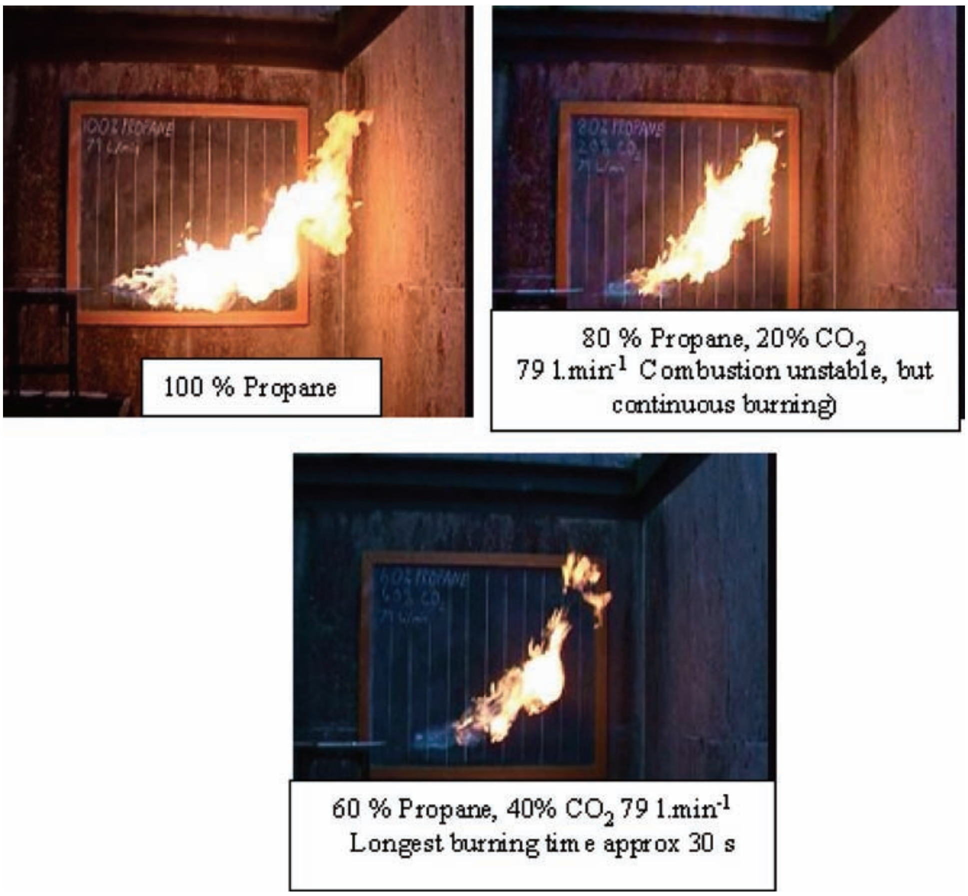


Figure 2. General appearance of flames from ignited propane/CO_2 mixtures of differing ratios. Flow rate 79 $l.s^{-1}$

Table 3. Flame behaviour for impinging jet releases of propane/CO_2 jets at a flow rate of 79 $l.min^{-1}$

Gas mixture (propane:CO_2)	Nozzle – plate separation 20 cm Flame behaviour	Nozzle – plate separation 50 cm Flame behaviour	No plate (Table 3 non-impinging test data) Flame behaviour
100% propane	Combustion stable	Combustion stable	Combustion stable
80/20 propane/CO_2	Combustion stable	Combustion less stable	Combustion unstable
60/40 propane/CO_2	Combustion less stable, but burning continuous	Combustion unstable, longest burning time 12 s	Longest burning time 30 s

The general appearance of flames seen in these tests is illustrated in Figure 2. In capturing these video stills, attempts have been made to obtain representative pictures showing 'average' behaviour over the duration of the test. The ignition source used for these tests was a propane blow torch, which was applied about 30 cm downstream of the release and was used to mimic a secondary fire through which the jet may pass.

PROPANE/CO_2 IMPINGING JET RELEASES

In any industrial situation, there is a possibility of the escape of process materials into congested or confined areas. As a result, a small number of tests were conducted where a flat insulating sheet was placed at 90° to the flame to allow the study of combustion in impinging flames. The outcome of these tests is summarised in Table 3 and the general appearance of flames illustrated in Figure 3.

The limited number of tests undertaken makes it difficult to draw firm conclusions, however, it appears that combustion was more stable in tests where the plate was located close to the release. In order to understand this, it is necessary to consider the behaviour of non-impinging flames. For the tests involving freely burning flames it was seen that mixtures would be reached where combustion became unstable and the blowout stability limit was reached. At this point the flame would progressively retreat along the flame over a few seconds until it died out.

The results shown in Table 3 would appear to show that if an object is placed close to the jet release, then combustion becomes more stable. It is possible that this effect is caused by:

- the plate giving more rapid deceleration of the gas jet;
- affecting turbulence and entrainment of air into the jet;
- providing a feedback mechanism for a proportion of the heat back into the flame; and,
- providing a surface on which the flame could become attached.

Flame attachment to surfaces is suggested as it is widely known that flames can be drawn to objects, perhaps under the influence of local airflow, giving more persistent burning.

HYDROGEN/CO_2 MIXTURES

Tests undertaken to investigate the combustibility of hydrogen/CO_2 mixtures followed a similar format to those performed earlier for propane/CO_2 mixtures, except that the higher flow rate of 127 $l.min^{-1}$ was not studied due to difficulties in obtaining stable flow conditions through the rotameter for high deliveries of hydrogen. A summary of tests is given in Table 4.

Two major differences in flame appearance and stability were noted in these tests, compared to the behaviour of the propane/CO_2 tests.

1) There appeared to be a sharp dividing line between mixtures capable of supporting combustion and those which were not, with small changes in hydrogen concentration resulting in sudden loss of flame stability and hence combustion.
2) No difference was observed in flame length for different gas mixtures, in contrast to observations made with tests using the propane/CO_2 mixtures, but this may have been due to the almost invisible nature of the flames.

Generally, these flames appeared as a translucent orange/blue flames, which could only really be seen as a result of their movement. When CO_2 was introduced into the hydrogen, flames became more jet-like in nature and became pale blue.

HYDROGEN/NITROGEN MIXTURES

Having developed a reasonable understanding of combustion in fuel/inert gas mixtures in the previous sections, a narrower programme of work was undertaken for mixtures of hydrogen and nitrogen. This more limited study concentrated on releases having a combined flow rate of 79 $l.min^{-1}$.

No video or photographic records were made of these tests, as the flames formed during combustion were completely invisible.

The observation of stable combustion in a 40:60 hydrogen/nitrogen mixture agrees with operational experience, where this mixture is used as a fuel in large gas turbines. Here, the high nitrogen level helps prevent combustion moving towards detonation.

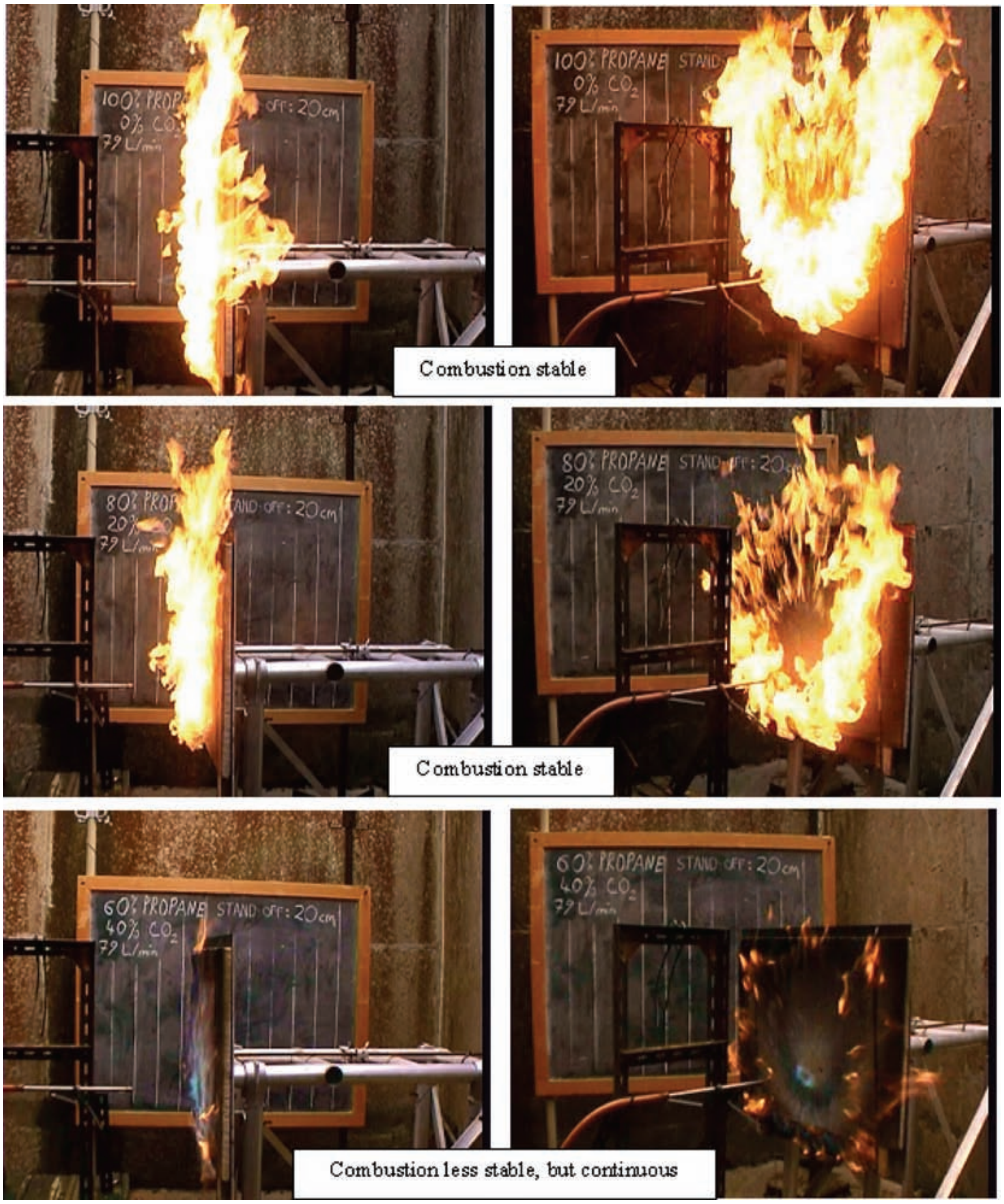


Figure 3. Effects of flame impingement on combustion in ignited propane/CO_2 mixtures of differing ratios. Nozzle – plate separation 20 cm, flow rate 79 $l.s^{-1}$

DISCUSSION/CONCLUSIONS

The aim of this work was to study the flammability of jet releases of propane and hydrogen mixed with either carbon dioxide or nitrogen inerting agents. This work builds upon the earlier study of Munteanu et al. (2002) who studied the ignitability of homogeneous mixtures of propane, carbon dioxide and air in a quiescent environment. Their work showed that the minimum concentration of CO_2 required to prevent ignition of a propane/air mixture was 32% CO_2.

The present work comprised of two parts – a theoretical part based on consideration of idealised jet releases, and an experimental part involving jet releases of propane/CO_2, hydrogen/CO_2 and hydrogen/nitrogen mixtures, either released into free space or impinging onto a target. The theoretical phase of the investigation involved a short

Table 4. Flame stability and test conditions for unimpeded hydrogen/CO_2 releases

	Flow rate $l.min^{-1}$	
Gas mixture (hydrogen:CO_2)	50	79
100% hydrogen	Combustion stable	Combustion stable
60:40	Combustion stable	Combustion stable
50:50	Combustion stable	Combustion stable
40:60	Combustion stable	Combustion stable
39:61	Not studied	Longest burning time 19 s
37:63	Not studied	Will not burn on removal of pilot flame
35:65	Longest burning time 40–45 s	Not studied
33:67	Burns for 1–2 s	Not studied
30:70	Will not burn on removal of pilot flame	Will not burn on removal of pilot flame
25:75	Not studied	Will not burn on removal of pilot flame
20:80	Not studied	Will not burn on removal of pilot flame

Table 5. Flame stability and test conditions for unimpeded hydrogen/nitrogen releases

Gas mixture (hydrogen/nitrogen)	Comments
40:60	Combustion stable
30:70	Burnt for several minutes
27:73	1–2 s burning
25:75	1–2 s burning
20:80	Would not remain ignited without pilot flame

programme of CFD simulations. The work provided information on a range of factors including:

- gas concentrations along the length of jet releases under various conditions;
- the predicted size of the flammable envelope for particular release conditions; and,
- an estimate of the concentrations of component gases in a propane/CO_2 mixture, which would not support combustion following escape.

The theoretical analysis estimated that to produce a propane/CO_2 gas mixture which would not support combustion following its release, it would be necessary to have a CO_2 concentration at or above 88%.

The ignition of the various mixtures in the jet release experiments showed behaviour broadly in agreement with the earlier work of Munteanu et al. (2002), and also appeared to support the earlier indications of the CFD/theoretical work. However, rather than observing a sharp cut-off in the ability of a mixture to support combustion, instead it was found that the published inerting limits

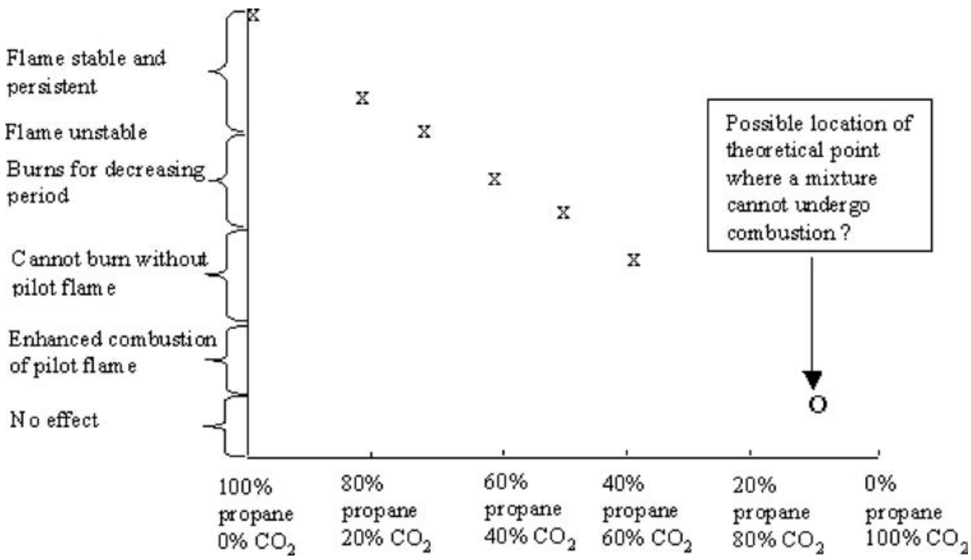
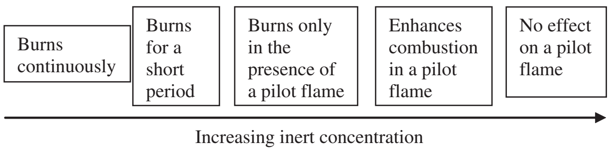


Figure 4. Illustrative graph showing changes in combustion stability as a function of propane/CO_2 concentrations

corresponded to mixtures which were unable to maintain self-sustaining combustion.

Increases in the inerting level beyond the published values led to changes in combustibility that can be described as ‘fuzzy bands’ of stability/behaviour. In these ‘fuzzy bands’, there was a progressive reduction in flame stability, which was manifested by increased flame lift-off and a flame that extinguished after a progressively shorter period as the concentration of the inerting agent was increased. For propane jets, the reduction in flame stability was observed even with a CO_2 concentration of 20% (the lowest CO_2 concentration tested). At a concentration above 40%, the mixture was only able to support combustion for six seconds. This behaviour is explained diagrammatically in Figure 4, which illustrates these progressive changes in combustion stability as a function of CO_2 and propane concentration for a flow rate of 50 l.min^{-1}.

Also shown in Figure 4 is another important finding from the present work, that the combustibility of the gas mixtures could be described as follows:



From this it can be seen that combustion undergoes a transition through mixtures able to burn continuously, to those which burn for a short period, and then moving into a region where combustion is only maintained while a pilot flame is present. After this, a region is reached where if the flame from a hand-held blow-torch was passed through the jet, the blow-torch flame was found to increase in length significantly. In many ways, this finding is not new, indeed the behaviour is identical to that observed in the operation of the mining safety (Davy) lamp, where flame elongation was used as a means of judging methane concentration. Examples also exist of how non-flammable mixtures ingested into the air intakes of gas turbines can affect their operation, or where the operation of vehicle engines has been affected on entering gas clouds. In practical terms, the behaviour implies that even though gas releases containing high concentrations of inerting agents may not present a direct fire or explosion hazard, they may contribute to the escalation of a separate incident.

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