# FLAMMABILITY OF HYDROCARBON/$CO_2$ MIXTURES: PART 1. IGNITION AND EXPLOSION CHARACTERISTICS[†]

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The next decade is likely to see a rapid increase in the transport offshore of carbon dioxide ($CO_2$) for enhanced oil recovery and sequestration of the material into depleted oil and gas fields. As a result hydrocarbon gas streams may become increasingly contaminated by $CO_2$, and indeed, it may even sometimes be advantageous to mix the two streams to reduce the hazard posed by fires and explosions from unintended releases. As a result, risk assessments may therefore need to incorporate consequence modelling which takes into account the presence of $CO_2$ and the new/modified hazards including changes in fire and explosion properties, and the risk of asphyxiation. The present work examines the effect of $CO_2$ concentration on the ignition of hydrocarbon and $CO_2$ gas mixtures in jet releases and explosions in confined spaces.

A previous study investigated the inerting potential of $CO_2$ and $N_2$ with respect to propane and hydrogen gas releases (Thyer *et al.*, 2009). The present work extends that study to examine the effect of release velocity and $CO_2$ concentration on the ignition of methane releases. Additionally the explosivity of $CO_2$/methane mixtures was examined in a 20 litre explosion sphere and an 8 m long section of 1.04 m diameter pipeline.

Increasing concentrations of $CO_2$ were found to reduce the likelihood of ignition of a methane jet release. Up to $CO_2$ concentrations of 22–40% (v/v) it was possible for a self-sustaining flame to exist, but beyond these concentrations a pilot flame was required to aid combustion. Beyond 60% $CO_2$ the pilot flame had no effect and the mixture was completely inert. The release velocity was also found to influence the ignition characteristics, with high-velocity releases requiring a lower concentration of $CO_2$ to affect the ignition behaviour. This is due to the effect of $CO_2$ on reducing the flame front speed leading to flame blow out.

Explosion tests performed in the small explosion sphere and a larger 8 m section of pipeline displayed similar characteristics. In both situations increasing the concentration of $CO_2$ led to a reduction in the explosion overpressure. In the explosion sphere the $CO_2$/methane mixtures were found to be ignitable up to a $CO_2$ feed concentration of 60%. In the pipeline explosions, mixtures of 28.2% and 40% $CO_2$ were ignitable, whereas at 59% $CO_2$ ignition did not occur.

## INTRODUCTION

The next decade is likely to see a rapid increase in the transport offshore of carbon dioxide ($CO_2$) for enhanced oil recovery and sequestration into depleted oil and gas fields. As a result, hydrocarbon gas streams may become increasingly contaminated by $CO_2$, and indeed it may sometimes be advantageous to mix the two streams to reduce the hazard posed by fires and explosions from unintended releases. Risk assessments may therefore need to incorporate consequence modelling that takes into account the presence of $CO_2$ and the new or modified hazards, including changes in fire and explosion properties. In addition to these considerations, ageing offshore installations are also now being decommissioned or dismantled at an increasing rate. Dismantling of poorly-inerted former hydrocarbon processing plant has been known to cause fires and explosions resulting in fatalities. To help provide information to both regulatory bodies and industry on the hazards posed by mixtures of hydrocarbon and inert gases, the present work examines the flammability of premixed and non-premixed hydrocarbon and $CO_2$ gas mixtures.

Premixed explosion tests were performed on two scales. The first being on a smaller scale in a 20 litre explosion sphere that is a standard test used to assess the explosion properties of materials. The second type were larger tests performed in a 8 m section of 1.04 m diameter pipe, which had a total volume of 6.8 $m^3$. In both cases the mixtures of methane ($CH_4$) and carbon dioxide ($CO_2$) were examined with the methane concentration in the region of the stoichiometric concentration (9.5%) and overall $CO_2$ concentrations varying between 0 and 20%. Additionally mixtures of propane and $CO_2$ were examined in the smaller 20 litre sphere.

Two categories of diffusion flame (non premixed) ignition tests were performed. The first were bulk ignition tests using a large ignition source (propane blow torch). These were done to assess the limits of the $CO_2$ inerting effect on methane. The second category of tests were detailed ignition probability tests performed on a 100% v/v $CH_4$ and a 80/20% v/v $CH_4$/$CO_2$ non premixed gas jet mixtures. The results from these tests are presented in a companion paper that investigates an empirically-based

mathematical model for the ignition probability in free-jets (Gant *et al.*, 2011).

## BACKGROUND

There are numerous studies on the effect of inerting gases on the flammability envelope for fuel gases. Generally these studies have used one of the standard test procedures (ASTM, ISO or DIN) and the prescribed apparatus to determine the upper and lower concentrations where flame propagation will occur. When determining the role of $CO_2$ (or other additives) in inerting hydrocarbon mixtures the experimental mode of investigation can have a significant bearing on the observed flammability behaviour, with different flammability limits being observed when experiments were conducted with premixed flames or diffusion jet flames (Beyler, 1988). Furthermore there can be significant differences in behaviour when considering gas cloud combustion versus a jet or pressurised release. In the later case the mixing of the release with atmosphere will result in an oxygen gradient through the release, giving rise to a flammable/ignitable zone.

The flammability limits of methane and the effect of inert gases have been studied on many occasions (e.g. Zabetakis, 1965). A recent example is the study of Kondo *et al.* (2006) which examined flammability limits a number of hydrocarbons (methane, propane, ethylene, propylene, methyl ether, methyl formate, 1,1-difluoroethane, and ammonia) with different quantities of $CO_2$ present. It that work they used an explosion bomb similar to that described in ASTM E681 for determination of the concentration limits of flammability. It was found that increasing the $CO_2$ concentration decreased the flammability window, and it was projected that the inertisation point occurred at a $CO_2$ feed mole fraction of 0.794 (which corresponds to ca 25% v/v in the stoichiometric air/fuel/inert mixture). Thyer *et al.* (2008) investigated the inerting effect of $CO_2$ and $N_2$ on the ignition behaviour of propane and hydrogen for diffusion jets. Figure 1 (taken from Thyer *et al.*, 2008) shows the results obtained for experiments with propane

and $CO_2$. Based on the trend of the experimental results it was estimated that complete inerting would occur in the region of 90% $CO_2$ feed concentration. A detailed study of the ignition probability of diffusion flames was undertaken by Birch and co-workers at the British Gas research station (Birch *et al.* 1981, Smith *et al.* 1988, Birch *et al.* 1989). They studied the effect of ignition location on the probability of ignition for turbulent jets of methane, town gas and propane. The ignition source was an inductive spark system. The ignition probability was highest in regions corresponding to the stoichiometric concentration, however ignition was still possible in regions outside the mean flammability limit window due to turbulent fluctuations in the local fuel concentration. Birch *et al.* (1981) produced contour maps showing regions of ignition probability. Ahmed and Mastorakos (2006) examined spark ignition of turbulent methane diffusion jets, characterising the factors that affect ignition. High jet velocities were found to reduce the ignition probability due to convective heat loss from the spark in the early stages of the ignition process.

These studies highlight the difference in behaviour when examining ignition via different methods. When considering the flammability of jet releases of hydrocarbon/inert mixtures the limits determined in a static combustion test may not give complete guidance on the potential behaviour. In static tests adequate reduction of the oxygen content/ratio may render the system inert, however during release into the atmosphere the subsequent addition of air to the system may result in a flammable mixture. The release properties, the ignition source and its location relative to the release point will have important consequences on the flammable region.

## EXPERIMENTAL SETUP
### EXPLOSION STUDIES
20 Litre Explosion Sphere
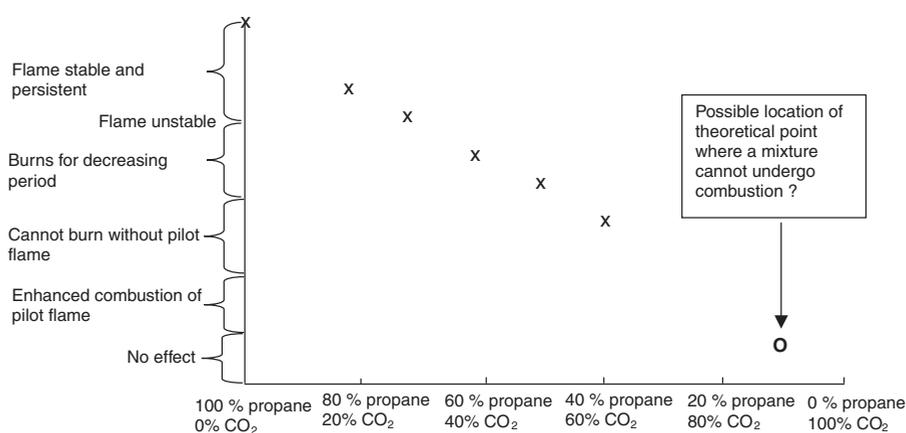A series of small-scale explosion experiments were carried out to determine the explosion behaviour of mixtures of



**Figure 1.** Illustrative graph showing changes in combustion stability as a function of propane/$CO_2$ concentrations (from Thyer *et al.*, 2008)

**Figure 2.** Photograph of (a) the 1.04 m diameter explosion vessel and (b) the $\frac{3}{4}$ open relief vent

hydrocarbon (methane or propane) with $CO_2$ and air. The tests were performed in a standard 20 litre explosion sphere in accordance with the principles of British Standard, BS EN 1839:2003 Determination of explosion limits of gases and vapours. The vessel was first evacuated to $\sim$100 mbar absolute before the hydrocarbon, $CO_2$ and air gases were introduced to the vessel via a manifold. The quantities of each substance were measured by partial pressure readings using a high precision digital pressure gauge. The vessel temperature was maintained at $25^oC$ by using heating fluid around the vessel jacket. The ignition of the atmosphere was effected using a 10 kV spark generator across two stainless steel electrode tips. Control of the ignition system was via a computer linked to the spark generator unit, an interlock on the fume cupboard sash preventing accidental activation of the spark generator. The explosion overpressures was recorded using two calibrated Kistler (type 701A) pressure transducers; the data logged at 50 kHz. Overall methane and propane concentrations were 10% and 5% respectively, with the $CO_2$ concentration being varied between 0% and 20%. This corresponds to $CO_2$/fuel feed concentrations of 0 to 80%.

### 1.04 m Diameter Pipeline

Larger gas explosions were conducted in a facility designed to test the explosion resistance of passive fire protection materials. The facility was constructed from a number of 1.04 m internal diameter steel pipe sections, as shown in Figures 2 and 3. The gas was ignited at one end of the pipe and the explosion was allowed to propagate along the pipe and exit at the opposite end of the pipe incident on to a 1 $m^2$ test piece. The overpressure of the explosion exiting the pipe end could be controlled by varying the coverage of the top vent – for all tests conducted 3 quadrants were left open (see Figure 2b). Methane and $CO_2$ were introduced into the vessel from remotely controlled gas bottles. Polythene sheets were placed over the top vent and the open end to retain the gas during filling, with the contents of the pipe being mixed using an electrically driven fan. Ignition was effected using a 5 grain blackpowder fuse. The gas concentration was monitored using a GA 94A Landfill Gas Analyser (Geotechnical Instruments). The target methane concentration was the stoichiometric value for methane, 9.5%. However, due to the response time of the gas analyser the final gas concentrations varied from the target by a small margin. Four tests were performed with overall $CO_2$ concentrations of 0, 3.7, 7 and 12% v/v, with corresponding methane concentrations of 9.3, 9.4, 10.5 and 8.2% v/v (therefore the $CO_2/CH_4$ feed concentrations were 0, 28.2, 40 and 59.4%). The overpressure generated by the explosion was monitored using four pressure transducers (model: ETS-IA-375, Kulite
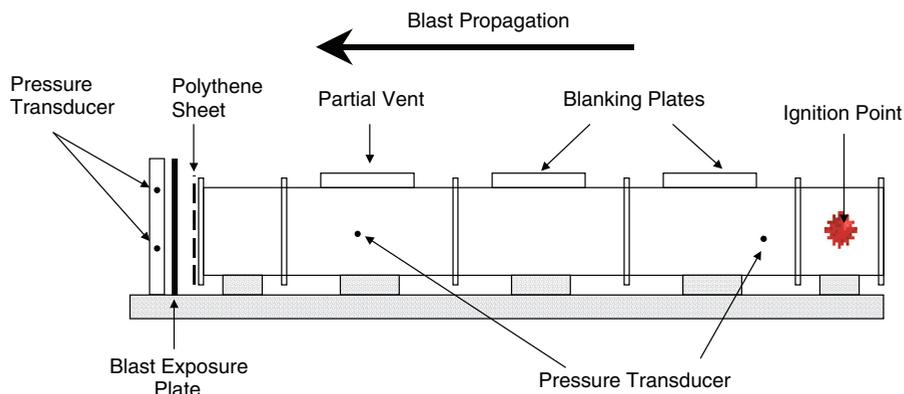


**Figure 3.** Schematic of the pipeline explosion vessel

**Table 1.** Experimental release conditions

| Volumetric flow rate (l/min) | 30 | 50 | 90 |
|---|---|---|---|
| Exit velocity (m/s) | 17.7 | 29.5 | 53.1 |
| Reynolds number* | 6453 | 10755 | 19359 |

*For 100% $CH_4$

Semiconductor Products). Two 0–17 barg pressure transducers were mounted at either end of the pipe, and two 0–7 barg pressure transducers were mounted in the test plate. Data was logged using a high speed data logger (DewiSoft v7.0) at a sampling rate of 50 kHz.

IGNITION STUDY
Methane and $CO_2$ gases were provided from gas cylinders regulated to 3 bar. Each gas was connected through a rotameter with a manual flow controller allowing flowrates between 10 and 90 l/min. Following the rotameters the gases were combined at a T-junction, and then a shut off valve. The shut off valve allowed the total gas flow to be stopped immediately without adjusting the flow settings. The shut off valve was connected to the release nozzle via 5 metres of fire resistant gas tubing. The release nozzle had dimensions of 6 mm ID, 8 mm OD, and 400 mm length. The nozzle was attached vertically to a metal frame. Ignition was effected using a propane blowtorch. All experiments were performed in a sheltered courtyard that allowed experiments to be performed in moderately still weather conditions. The bulk ignition characteristics were examined at 3 different total flowrates (30, 50 and 90 l/min), details of the corresponding exit velocities and Reynolds numbers are given in Table 1.

The tests were categorised based on the response of the gas mixture to the ignition flame, in a similar manner to the study of Thyer *et al.* (2009), see Table 2. For Classes 1, 2, and 3 the blowtorch flame was kept in the gas jet, whereas for Classes 4 and 5 the flame was removed as soon as ignition occurred. Figure 4 shows an example of a Class 3 ignition for a gas mixture containing 16.7% v/v $CO_2$ with a release velocity of 53.1 m/s. Each image is a sequential frame recorded at 25 frames per second. In the initial frames it is seen that the gas burns in the presence of the pilot flame, however once this is removed the flame front is blown downstream and extinguished.

**Table 2.** Ignition response classifications

| Class | Ignition response |
|---|---|
| 1 | No effect on pilot flame |
| 2 | Enhances combustion of pilot flame |
| 3 | Burns only in the presence of the pilot flame |
| 4 | Burns for a short period |
| 5 | Stable combustion, burns continuously |

Ignition tests were recorded using a HDC-SD10 video camera (Panasonic) that recorded at 25 fps. Individual frames/images were captured using the HD Writer AE v1.5 (Panasonic). The image analysis software ImageJ was used to determine the flame lift off distances.

## RESULTS & DISCUSSION
### EXPLOSION STUDIES
#### 20 Litre Explosion Sphere
Figures 5 and 6 present the results of the explosions tests performed in the 20 litre explosion sphere, for methane and propane respectively. To allow comparisons with the non premixed ignition tests the results are present in terms of a 'feed' concentration of $CO_2$ and fuel gas. It was found for both gases that increasing the $CO_2$ concentration caused a decrease in both the maximum overpressure ($P_{Max}$), and the rate of change of pressure ($dP/dt$). It is notable for both gases that the rate of change of pressure was greatly reduced in all tests where $CO_2$ was present. For methane the maximum ignitable concentration was 60%, and for propane the concentration was 78%, however at this level only a slight overpressure was recorded. The reduction in the $P_{Max}$ and $dP/dt$ due to the addition of $CO_2$ will be due to a reduction in the flame speed.

#### 1.04 m Diameter Pipeline
The effect of $CO_2$ feed concentration on the large-scale gas explosions are presented in Figure 7. Increasing the $CO_2$ concentration caused a decrease in the maximum overpressure recorded. At a $CO_2$ feed concentration of 59.4% no ignition of the gas mixture occurred. These results are comparable to results obtained for methane ignitions in the smaller 20 litre explosion sphere where a reduction in overpressure was recorded with increasing $CO_2$ concentration. However, in the 20 litre explosion sphere ignition was detected at slightly higher $CO_2$ concentrations. The tests conducted in the 20 litre explosion sphere were more controllable with more certain mixing of the gas prior to ignition. Given the larger volume involved in the 1.04 m pipe tests (8.3 $m^3$) there is the possibility of incomplete mixing. Thus there is the possibility of failed ignition even though the mean concentration in the pipe was ignitable.

#### IGNITION CHARACTERISTICS OF $CH_4/CO_2$ MIXTURES
The bulk ignition behaviour of $CH_4/CO_2$ gas mixtures was examined at three different exit velocities, and at $CO_2$ concentrations up to 70%. Still images for each condition are presented in Figures 8, 9 and 10. The ignition response was classified according to Table 2. Figure 11 summarises the change in the ignition response class with changing $CO_2$ concentration, for the three different exit velocities. For all the gas velocities examined, the ignition response decreased with increasing $CO_2$ concentration. For gas velocities of 29.5 m/s and 17.7 m/s the methane was completely inerted at $CO_2$ concentrations above 60%. Due to the
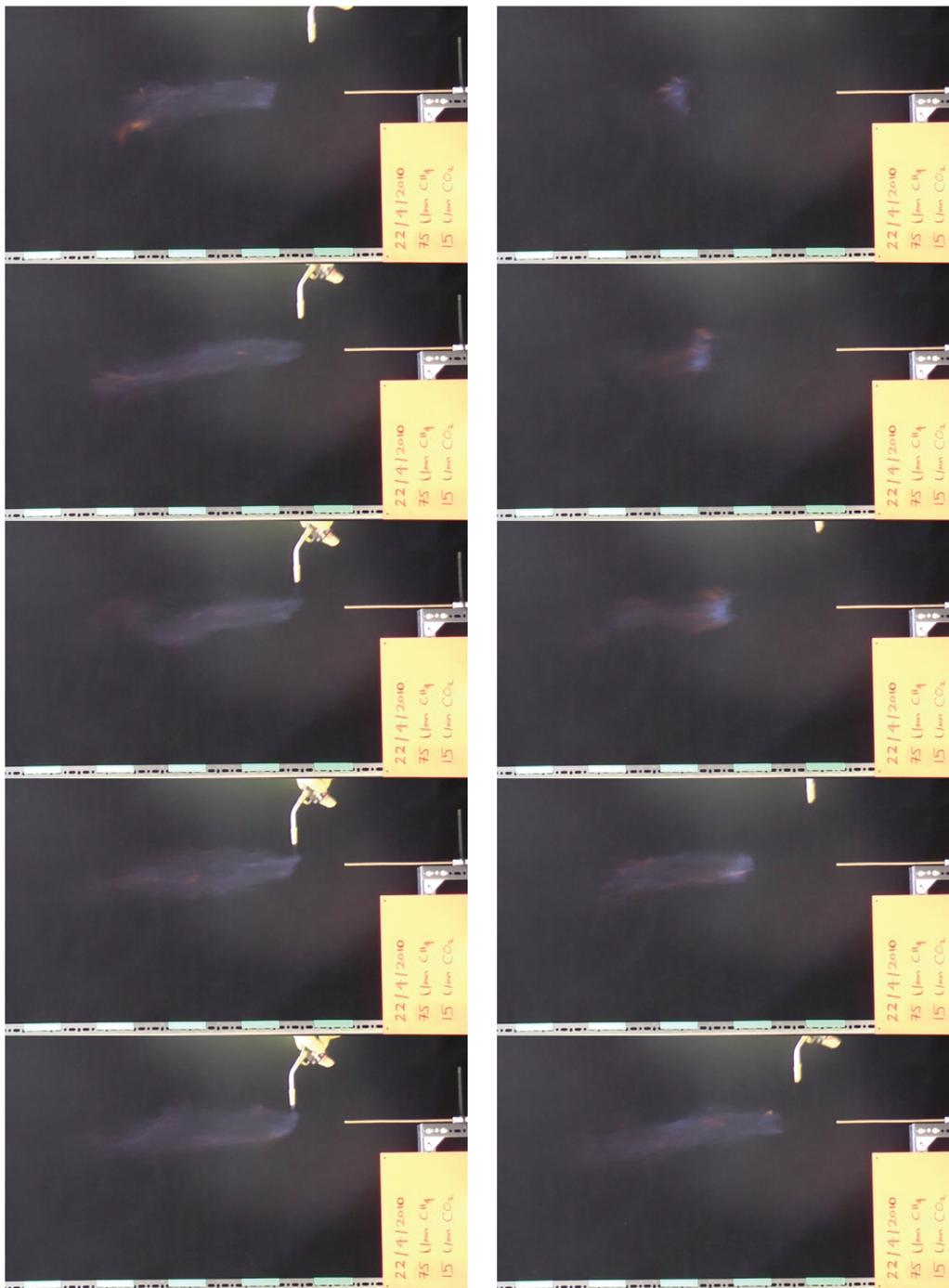
**Figure 4.** Unstable composition, 16.7% $CO_2$, 53.1 m/s. Image time step = 1/25 second

limited range of the gas flow meters it was not possible to explore $CO_2$ mixture concentrations above 45% when examining the highest gas velocity (53.1 m/s), however it is expected that it would follow a similar trend to the other two conditions, and thus be completely inerted in the region of 50 to 60% $CO_2$.

Figure 11 also shows that the lower velocity gas jets maintained a higher ignition class over a wider range of $CO_2$ concentration. In these circumstances a lower flame front speed would be required to maintain a stable flame. Figure 12 shows a comparison of a pure methane flame at each exit velocity examined, where it can be seen that
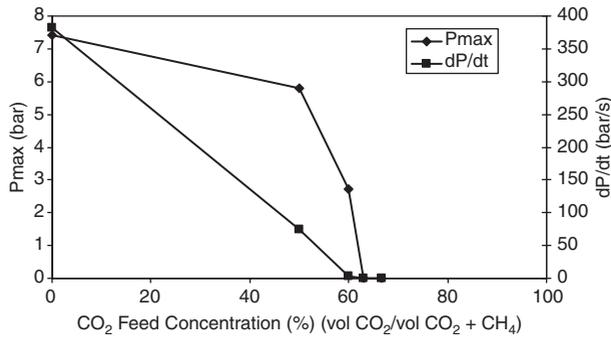
**Figure 5.** The effect of $CO_2$ concentration on the maximum overpressure ($P_{max}$) and the maximum rate of change of pressure ($dP/dt$) for $CH_4$ ignition performed in the 20 litre explosion sphere
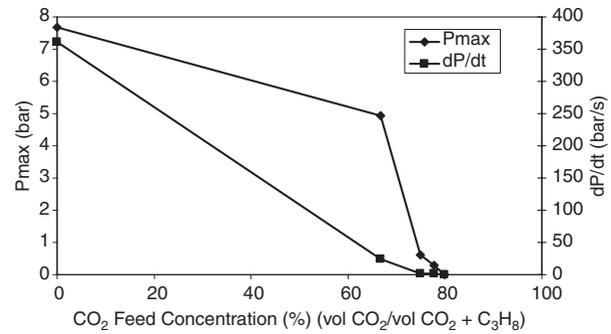


**Figure 6.** The effect of $CO_2$ concentration on the maximum overpressure ($P_{max}$) and the maximum rate of change of pressure ($dP/dt$) for $C_3H_8$ ignition performed in the 20 litre explosion sphere

with increasing initial velocity the flame lift off position increases. Using image analysis the flame lift off position was determined; at the intermediate velocity (29.5 m/s) it was 6.9 cm, however at the highest velocity (53.1 m/s) the lift off was nearly twice that value at 12.8 cm. This
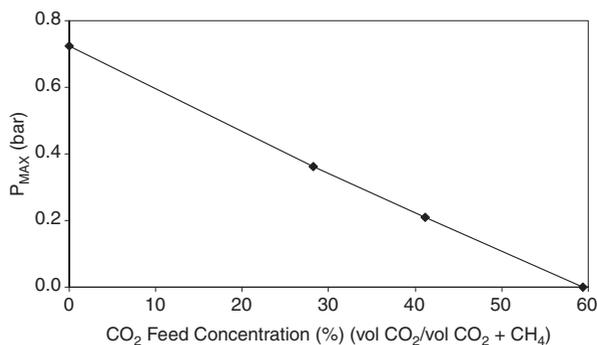


**Figure 7.** The effect of $CO_2$ concentration on the maximum overpressure ($P_{max}$) for $CH_4$ ignitions performed in the 1.04 m diameter pipeline



0% $CO_2$: Class 5        16.7% $CO_2$: Class 5

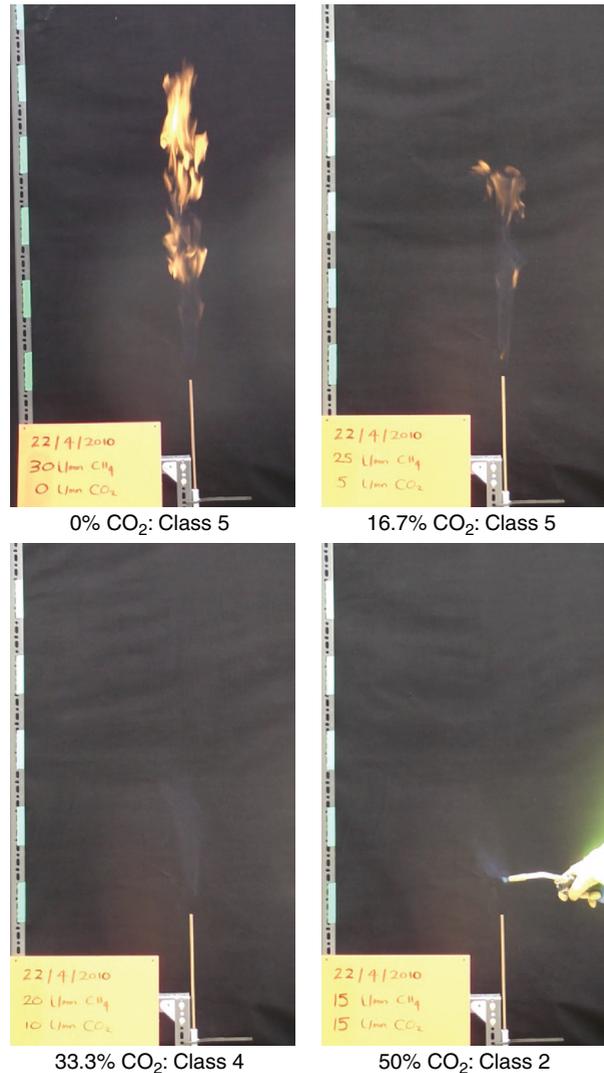33.3% $CO_2$: Class 4        50% $CO_2$: Class 2

**Figure 8.** Images from ignition class tests for an exit velocity of 17.7 m/s and $CO_2$ concentrations from 0% to 60%

demonstrates the competition between the advancing gas velocity and the flame front speed in determining the stability of the flame. The decay of the gas velocity with distance from the release point can be calculated using the mathematical models presented in the companion paper (Gant *et al.*, 2011). For exit velocities of 29.5 and 53.1 m/s the gas velocity at the flame lift off distances was 8.77 and 9.64 m/s respectively. Thus the flame front stabilises in the same velocity region irrespective of the initial exit velocity.

Figures 8, 9 and 10 show images from the flame stability tests for exit velocities of 17.7, 29.5 and 53.1 m/s respectively. For each exit velocity the first three images show flames that had either Class 5 or 4 stability, i.e. the flames did not require a pilot light to maintain the flame. In each series of photographs it is seen the flame front lift off distance increases with an increase in the $CO_2$
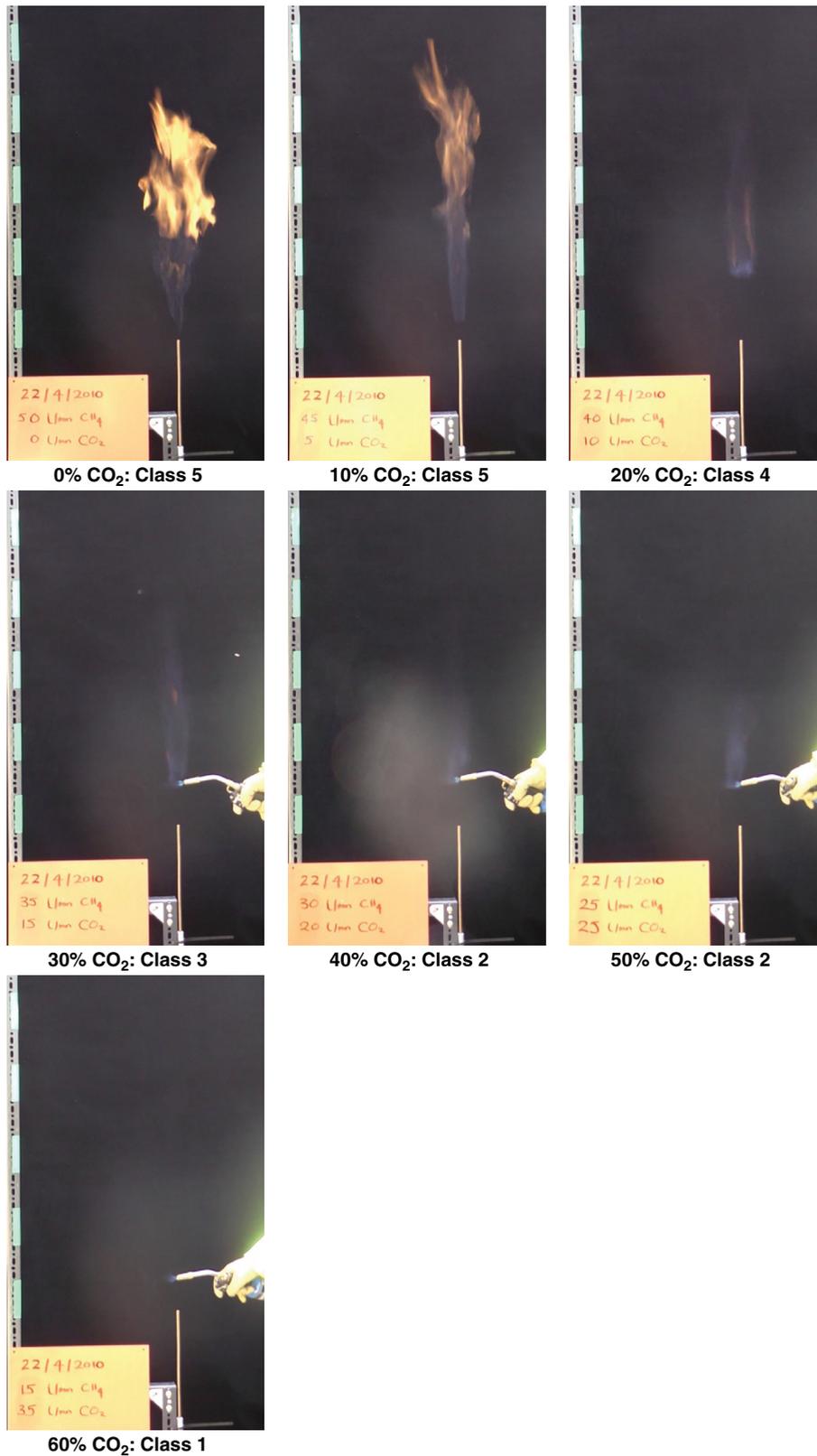
**Figure 9.** Images from ignition class tests for an exit velocity of 29.5 m/s and $CO_2$ concentrations from 0% to 60%
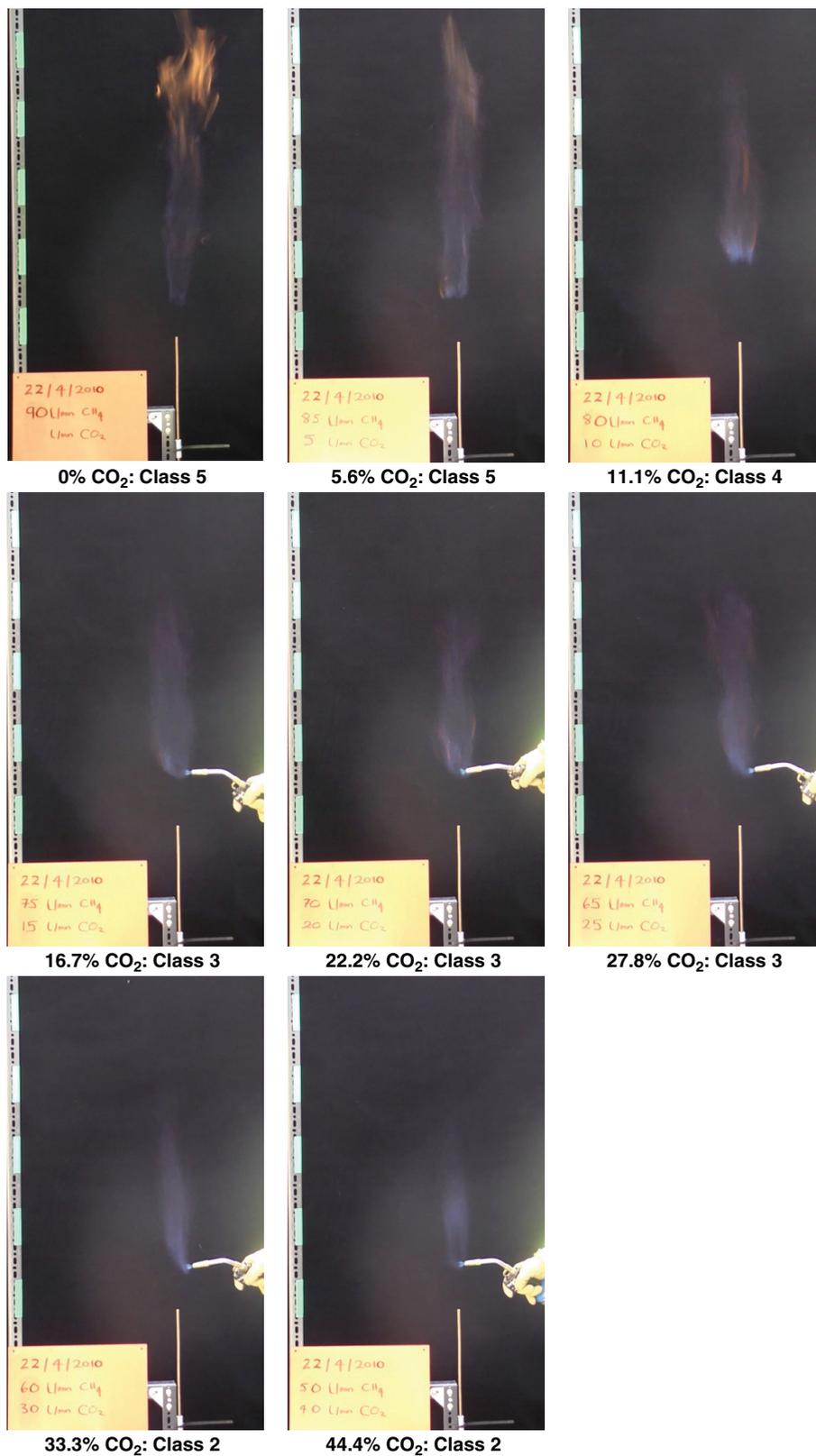
**Figure 10.** Images from ignition class tests for an exit velocity of 53.1 m/s and $CO_2$ concentrations from 0% to 44.4%
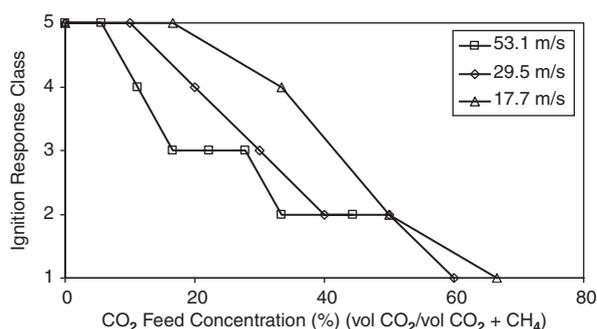
**Figure 11.** The change in ignition response class of gas mixtures with $CO_2$ over the range 0–70%, for exit gas velocities of 17.7, 29.5 and 53.1 m/s

concentration. Therefore the flame front velocity deceases as the concentration of $CO_2$ increases. Beyond the threshold concentrations of 33.3%, 20% and 11.1%, for exit velocities of 17.7, 29.5 and 53.1 m/s respectively, it was not possible to maintain a stable flame. Above these concentrations the flame front velocity that could have been generated anywhere in the gas stream will have been lower than the local velocity in the jet, thus blow out of the flame occurred. The addition of $CO_2$ to the fuel mixture will have the effect of changing the calorific value of the fuel mixture leading to a reduction in the reaction rate and flame speed. Ishizuka and Tsuji (1981) examined the effect of inert gases on flame stability in countercurrent diffusion flames. They found a limiting inert concentration beyond which a stable flame could not be maintained, which they attributed to chemical limitations on the combustion rate. They also observed that the flame temperature decreased as the inert concentration in the fuel mixture was increased. Similarly in the 20l explosion sphere tests presented earlier the

reduction in $P_{max}$ and dP/dt with increasing $CO_2$ concentration are indicative of a reduction in the flame speed.

The current results demonstrate that hydrocarbon lines containing $CO_2$ can still give rise to combustible mixtures when unintended releases occur. The concentrations identified in Figure 8 occur at levels at or below those determined in the explosions tests (Figure 5), therefore static tests provided conservative values that should be observed.

## CONCLUSIONS

It has been shown that the addition of $CO_2$ has an effect on the ignition of methane and propane when both premixed and diffusive fuel-air mixtures are considered. Increasing the concentration of $CO_2$ reduces the over-pressure obtained from explosion tests. In well-controlled small-scale explosions methane was inerted at a $CO_2$ feed concentrations above 60%, and for propane above 78%. In larger scale methane explosion tests the limiting $CO_2$ feed concentration was found to be 59.4%. Investigations of ignition of diffusing methane and $CO_2$ mixtures showed that stable combustion was possible up to $CO_2$ threshold concentrations of 33.3%, however the stability of the flame was also influenced by the fuel gas exit velocity. Above the stability threshold enhancement of the ignition source occurred and complete inerting did not occur until the mean $CO_2$ concentration reached 60–70%. In relation to process safety, care should be taken when inerting hydrocarbons lines as accidental releases may still result in combustible mixtures.
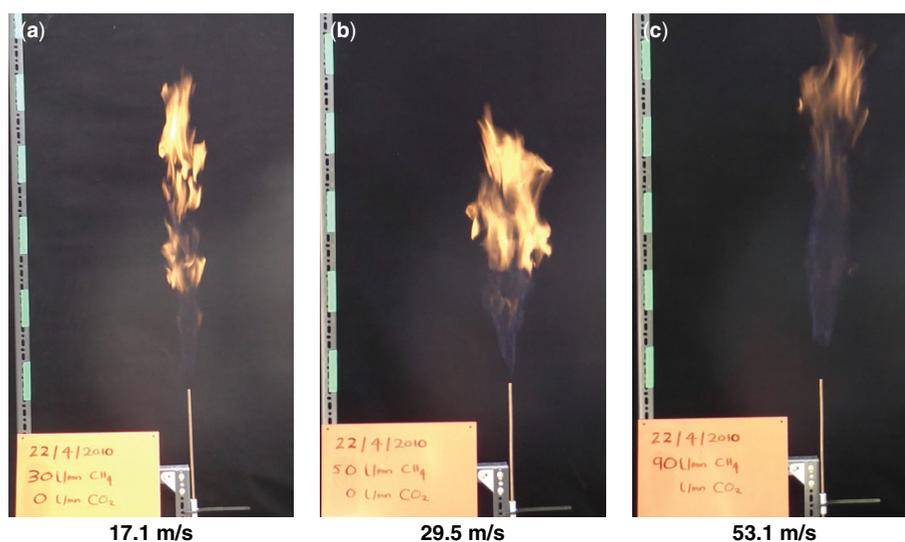
**Figure 12.** Comparison of the pure methane flames at different exit velocities

those of the authors alone and do not necessarily reflect HSE policy.

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