

# Flammability of Hydrocarbon/CO<sub>2</sub> Mixtures: Part 1. Ignition and Explosion Characteristics

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## Abstract

The next decade is likely to see a rapid increase in the transport offshore of carbon dioxide (CO<sub>2</sub>) 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<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> concentration on the ignition of hydrocarbon and CO<sub>2</sub> gas mixtures in jet releases and explosions in confined spaces.

A previous study investigated the inerting potential of CO<sub>2</sub> and N<sub>2</sub> 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<sub>2</sub> concentration on the ignition of methane releases. Additionally the explosivity of CO<sub>2</sub> / methane mixtures was examined in a 20 litre explosion sphere and an 8m long section of 1.04m diameter pipeline.

Increasing concentrations of CO<sub>2</sub> were found to reduce the likelihood of ignition of a methane jet release. Up to CO<sub>2</sub> 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<sub>2</sub> the pilot flame had no effect and the mixture was completely inert. The release velocity was also found to affect the ignition characteristics, with high-velocity releases requiring a lower concentration of CO<sub>2</sub> to affect the ignition behaviour. It is believed that this is due to the effect of CO<sub>2</sub> on reducing the flame front speed leading to flame blow out.

Explosion tests performed in the small explosion sphere and the larger 8m section of pipeline displayed similar characteristics. In both situations increasing the concentration of CO<sub>2</sub> led to a reduction in the explosion overpressure. In the explosion sphere the CO<sub>2</sub> / methane mixtures were found to be ignitable up to 15% CO<sub>2</sub>. In the pipeline explosions, mixtures of 3.7 % and 7% CO<sub>2</sub> were ignitable, whereas at 12% CO<sub>2</sub> ignition was not possible.

## 1. Introduction

The next decade is likely to see a rapid increase in the transport offshore of carbon dioxide (CO<sub>2</sub>) for enhanced oil recovery and sequestration into depleted oil and gas fields. As a result, hydrocarbon gas streams may become increasingly contaminated by CO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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 8m section of 1.04m diameter pipe, which had a total volume of 6.8m<sup>3</sup>. In both cases the mixtures of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) were examined with the CH<sub>4</sub> concentration in the region of the stoichiometric concentration (9.5%) and CO<sub>2</sub> concentration varying between 0 and 20%. Additionally mixtures of propane and CO<sub>2</sub> 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<sub>2</sub> inerting effect on methane. The second category of tests were detailed ignition probability tests performed on a 100% v/v CH<sub>4</sub> and a 80/20% v/v CH<sub>4</sub>/CO<sub>2</sub> 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).

## 2. Background

There are numerous studies on the effect of inerting gases on the flammability of 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<sub>2</sub> (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. 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<sub>2</sub> present. In 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<sub>2</sub> concentration decreased the flammability window, and it was projected that at a mole fraction of CO<sub>2</sub> of 0.8 (which corresponds to ca 25% v/v) ignition of the methane would not be possible.

Thyer *et al.* (2008) investigated the inerting effect of CO<sub>2</sub> and N<sub>2</sub> 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<sub>2</sub>. Based on the trend of the experimental results it was estimated that complete inerting would occur in the region of 90% CO<sub>2</sub>.

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. The premixed combustion scenario required a much lower concentration of inerting component to prevent ignition (25% v/v) compared to the diffusion jet (90% v/v). 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.

### **3. Experimental Setup**

#### **3.1. Explosion Studies**

##### **3.1.1 20 Litre Explosion Sphere**

A series of small-scale explosion experiments were carried out to determine the explosion behaviour of mixtures of hydrocarbon (methane or propane) with carbon dioxide 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 ~100 mbar absolute before the hydrocarbon, CO<sub>2</sub> 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°C 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. Methane and propane concentrations were 10% and 5% respectively, with the CO<sub>2</sub> concentration being varied between 0% and 20%

### 3.1.2 1.04m 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 1m<sup>2</sup> 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<sub>2</sub> 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 CO<sub>2</sub> 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. The overpressure generated by the explosion was monitored using four pressure transducers (model: ETS-IA-375, Kulite 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.

## 3.2. Ignition Study

CH<sub>4</sub> and CO<sub>2</sub> 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 6mm ID, 8mm OD, and 400mm 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, however more windy days affected the gas jet stability so tests were not performed. 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<sub>2</sub> with a release velocity of 53.1m/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.

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

## 4. Results & Discussion

### 4.1. Explosion Studies

#### 4.1.1 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. It was found for both gases that increasing the CO<sub>2</sub> 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<sub>2</sub> was present. For methane the maximum ignitable concentration was 15%, and for propane the concentration was 17.5%, 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<sub>2</sub> may be due to a reduction in the flame speed.

#### 4.1.2 1.04m Diameter Pipeline

The effect of CO<sub>2</sub> concentration on the large-scale gas explosions are presented in Figure 7. Increasing the CO<sub>2</sub> concentration caused a decrease in the maximum overpressure recorded. At 12% CO<sub>2</sub> no ignition of the gas mixture occurred. These results are comparable to results obtained for CH<sub>4</sub> ignitions in the smaller 20 litre explosion sphere where a reduction in overpressure was recorded with increasing CO<sub>2</sub> concentration. However, in the 20 litre explosion sphere ignition was detected at slightly higher CO<sub>2</sub> 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 1.04m pipe tests (8.3m<sup>3</sup>) 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.

### 4.2. Ignition Characteristics of CH<sub>4</sub>/CO<sub>2</sub> Mixtures

The bulk ignition behaviour of CH<sub>4</sub> /CO<sub>2</sub> gas mixtures was examined at 3 different exit velocities, and at CO<sub>2</sub> concentrations up to 70%. The response was classified according to Table 2. Figure 8 shows a plot of the change in the ignition response class with changing CO<sub>2</sub> concentration, for the 3 different exit velocities. For all the gas velocities examined, the ignition response decreased with increasing CO<sub>2</sub> concentration. For gas velocities of 29.5 m/s and 17.7 m/s the methane was completely inerted at CO<sub>2</sub> concentrations above 60%. Due to the limited range of the gas flow meters it was not possible to explore CO<sub>2</sub> 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 be completely inerted in the region of 50 to 60% CO<sub>2</sub>.

Figure 8 also shows that the lower velocity gas jets maintained a higher ignition class over a wider range of CO<sub>2</sub> concentration. In these circumstances a lower flame front speed would be required to maintain a stable flame. Figure 9 shows a comparison of a pure methane flame at each exit velocity examined. Using image analysis the flame stand off position was determined. At the lowest velocity (17.7m/s) the flame stand off was 0.8cm; at the intermediate velocity (29.5m/s) it was 4.1cm; and at the highest velocity (53.1m/s) the stand off was 8.3cm. This 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 17.7, 29.5 and 53.1 m/s the gas velocity at the flame stand of distances are 15.3, 12.5, 13.7 m/s respectively.

Thus the flame front stabilises in the same velocity region irrespective of the initial exit velocity.

Figures 10, 11 and 12 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 stand off distance increases with an increase in the CO<sub>2</sub> concentration. Thus the flame front velocity decreases as the concentration of CO<sub>2</sub> 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.

The addition of CO<sub>2</sub> to the fuel mixture will have the effect of changing the calorific value of the fuel mixture. 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.

The current results demonstrate that hydrocarbon lines containing some CO<sub>2</sub> can still give rise to combustible mixtures, particularly where the released gas can be freely mixed with air. In such situations, ignition could still occur with CO<sub>2</sub> concentrations above “inerting” levels determined from standard flammability tests. Furthermore, even beyond the concentrations where ignition is not sustained, the CO<sub>2</sub> /gas mixture may still promote combustion. Thus if a partially inerted mixture was released onto a continuous ignition source, such as an on-going hydrocarbon fire, it could add to the severity of the fire.

## **5. Conclusions**

It has been shown that the addition of CO<sub>2</sub> 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<sub>2</sub> reduces the overpressure obtained from explosion tests. In well-controlled small-scale explosions methane was inerted at a CO<sub>2</sub> concentrations above 17.5%, and for propane above 20%. In larger scale methane explosion tests the limiting CO<sub>2</sub> concentration was found to be 12%. Investigations of ignition of diffusing methane and CO<sub>2</sub> mixtures showed that stable combustion was possible up to CO<sub>2</sub> 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<sub>2</sub> concentration reached 60-70%. In relation to process safety, care should be taken when inerting hydrocarbons lines as accidental release may still result in combustible mixtures.

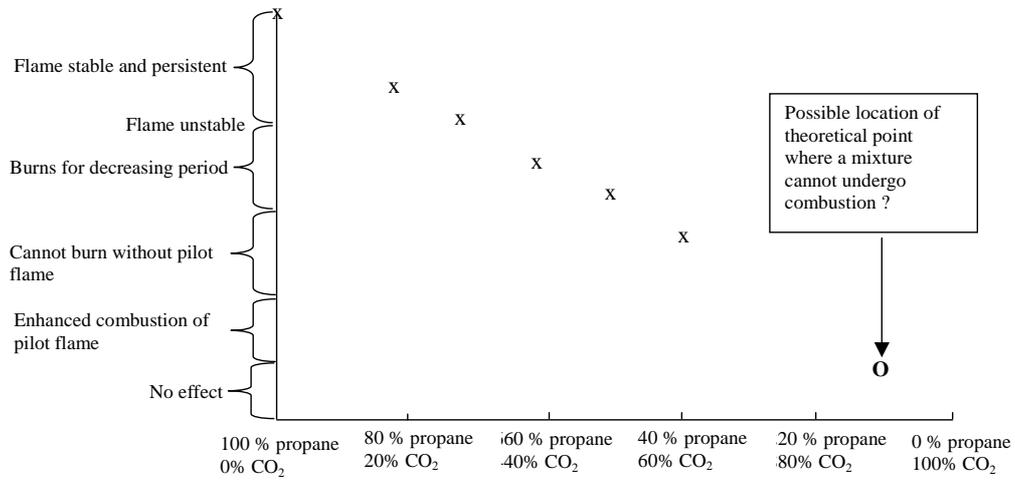
## **6. Acknowledgements**

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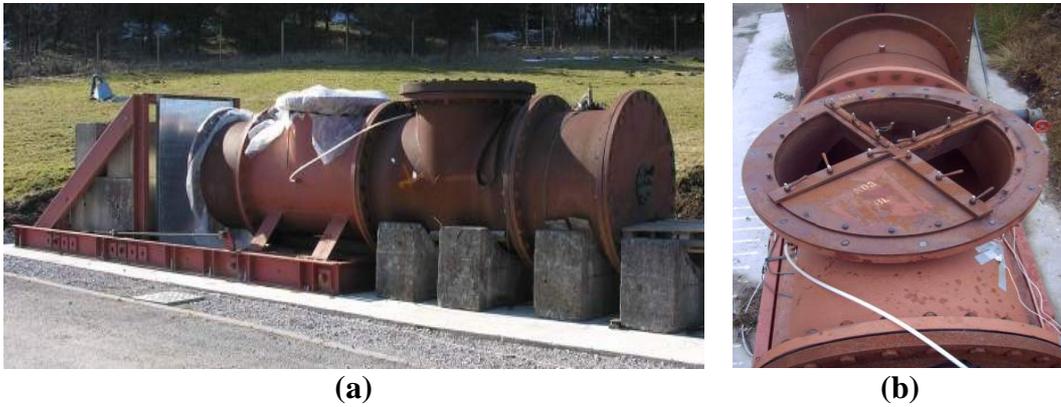
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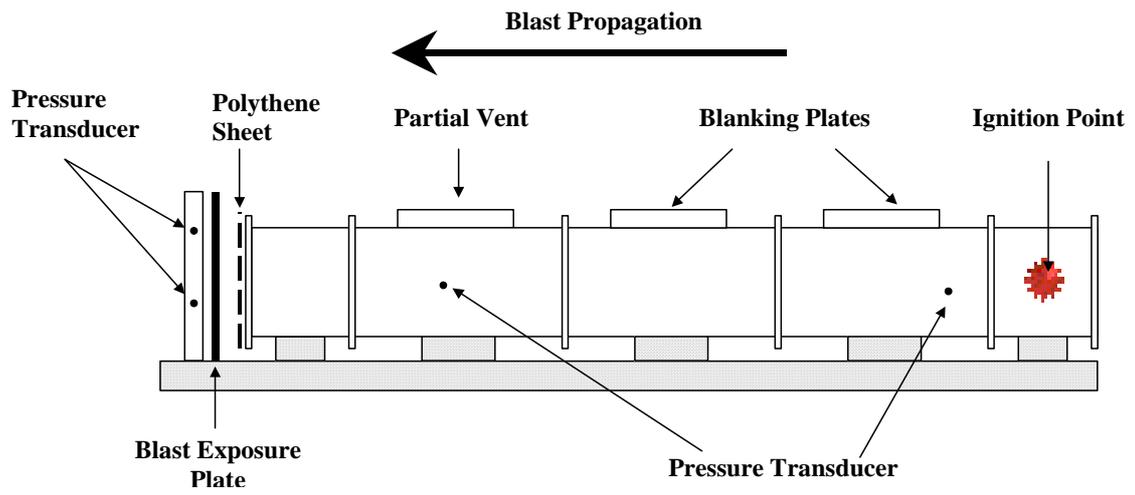
# Figures



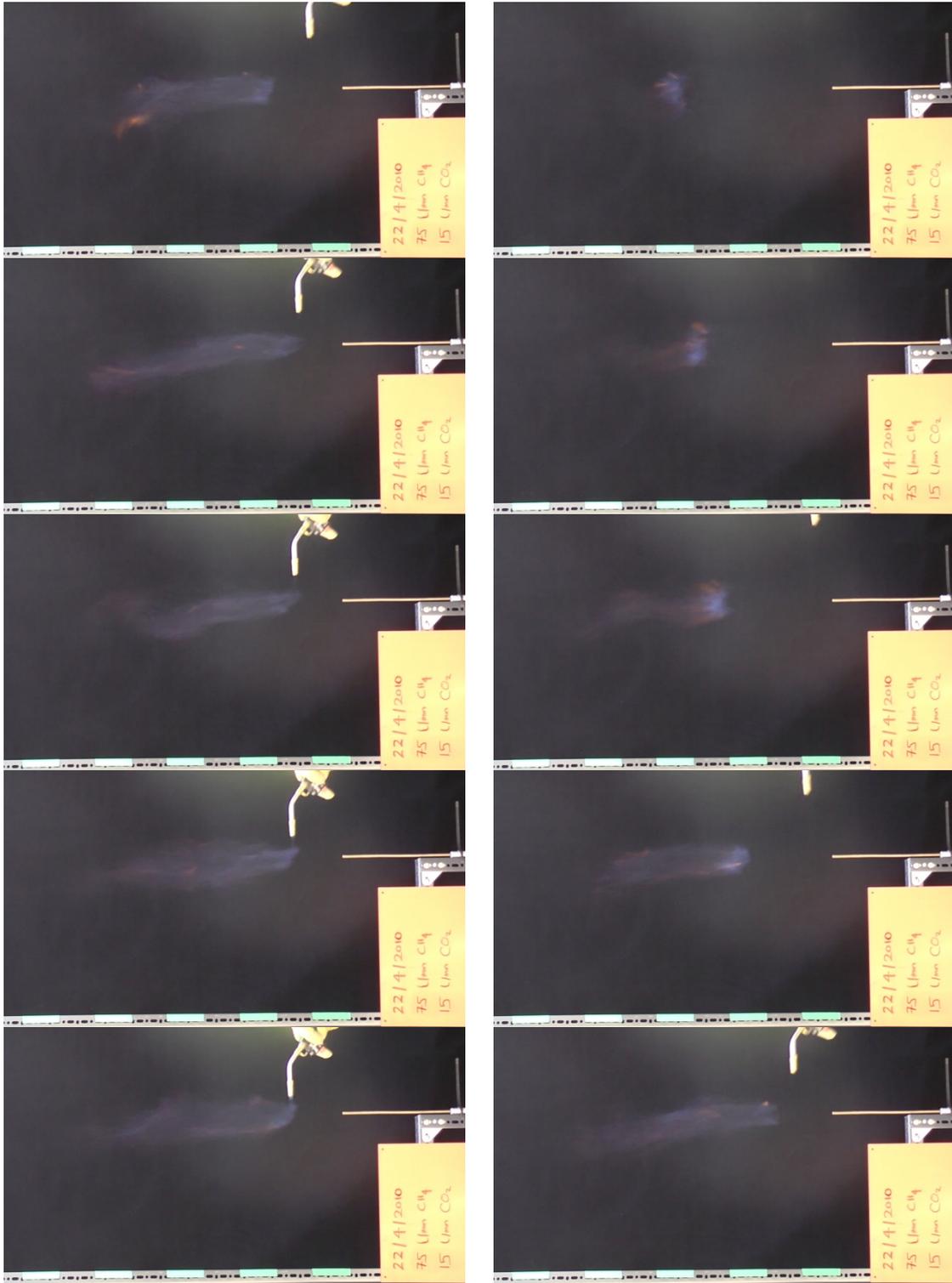
**Figure 1** Illustrative graph showing changes in combustion stability as a function of propane/CO<sub>2</sub> concentrations (from Thyer *et al.*, 2008).



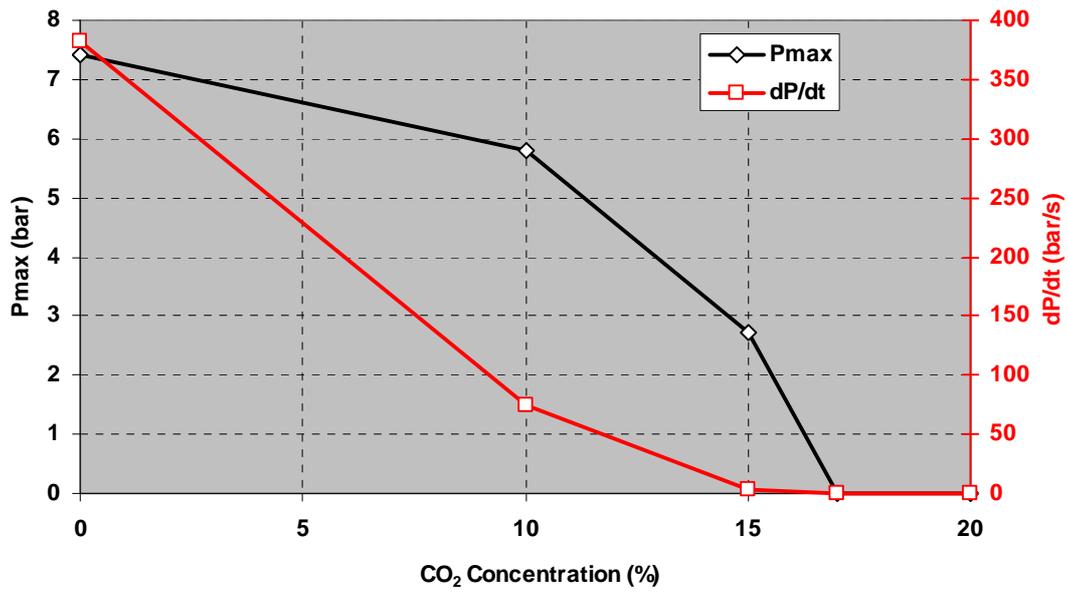
**Figure 2** Photograph of (a) the 1.04 m diameter explosion vessel and (b) the 3/4 open relief vent



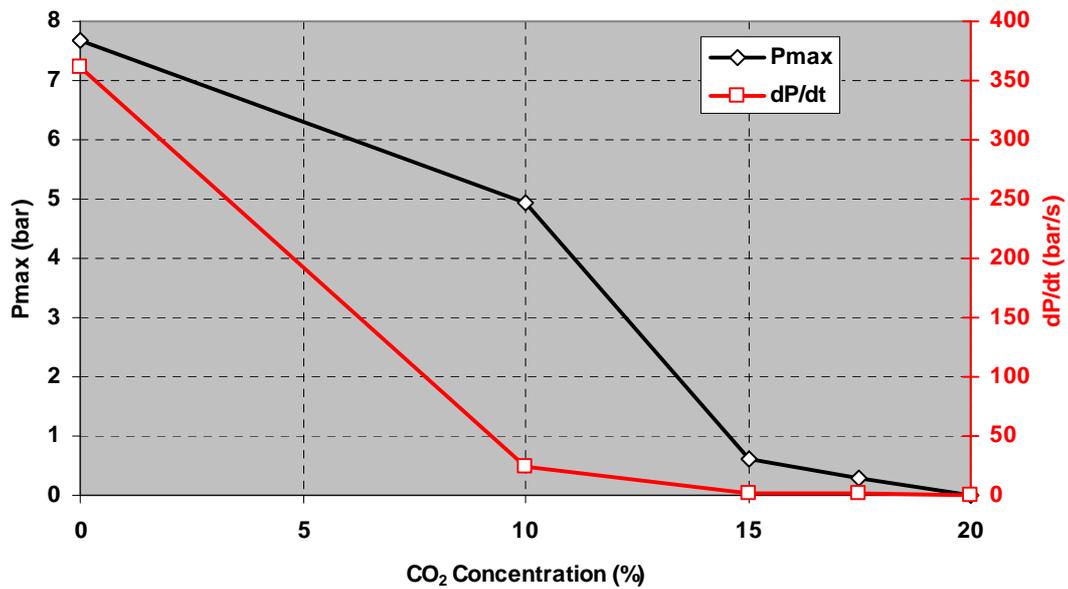
**Figure 3** Schematic of the pipeline explosion vessel



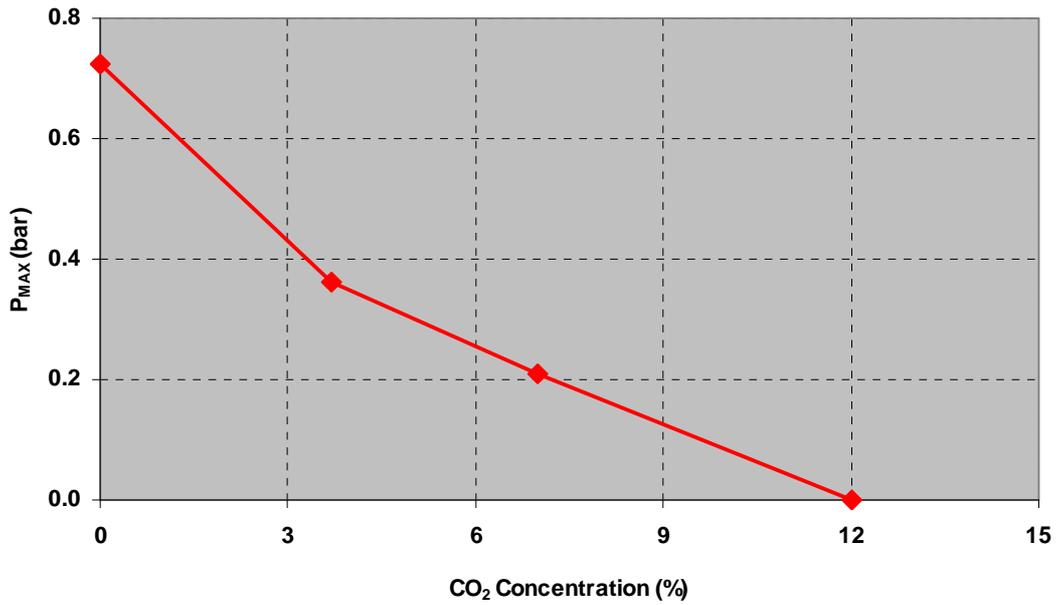
**Figure 4** Unstable composition, 16.7% CO<sub>2</sub>, 53.1 m/s . Image time step = 1/25 second.



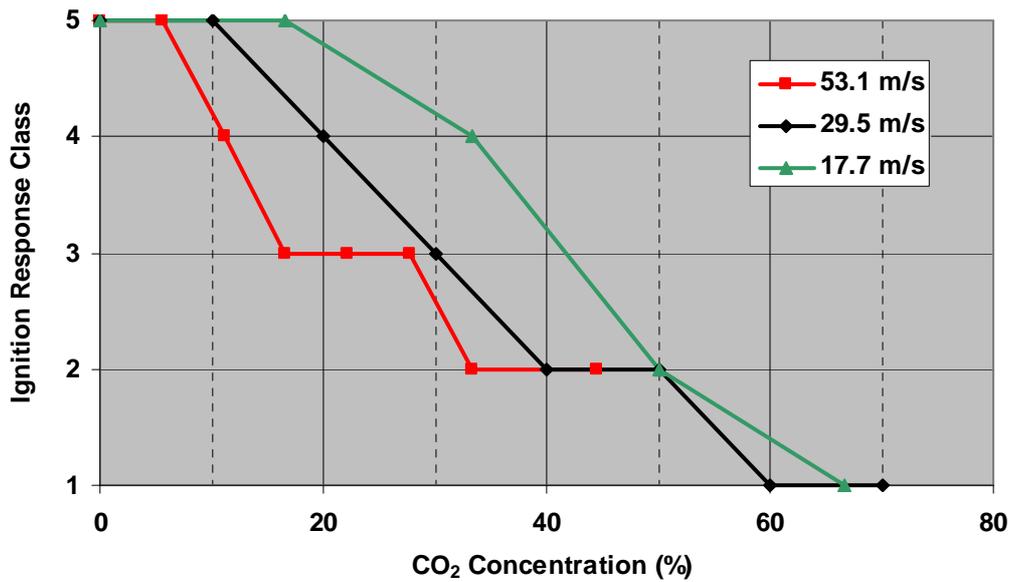
**Figure 5** The effect of CO<sub>2</sub> concentration on the maximum overpressure (P<sub>MAX</sub>) and the maximum rate of change of pressure (dP/dt) for CH<sub>4</sub> ignition performed in the 20 litre explosion sphere.



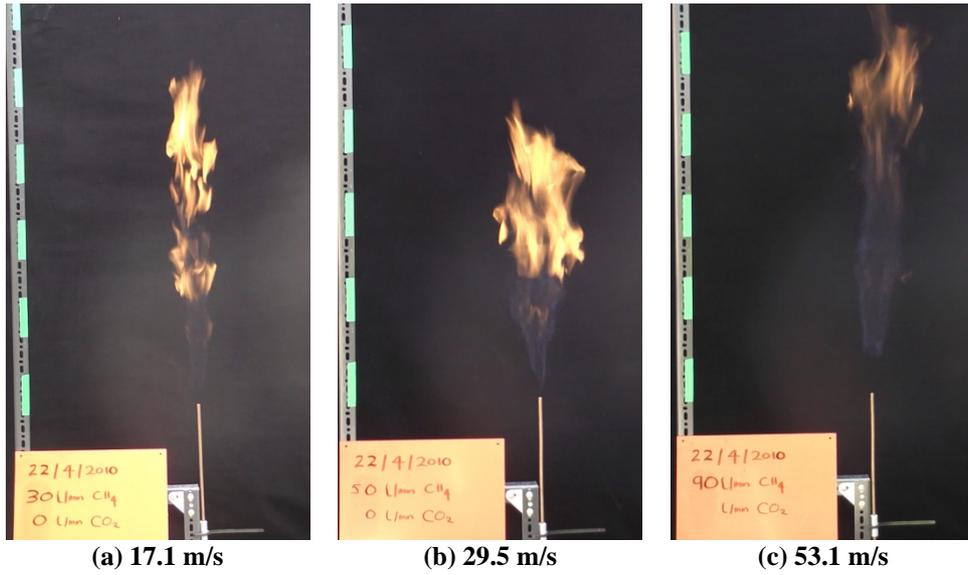
**Figure 6** The effect of CO<sub>2</sub> concentration on the maximum overpressure (P<sub>MAX</sub>) and the maximum rate of change of pressure (dP/dt) for C<sub>3</sub>H<sub>8</sub> ignition performed in the 20 litre explosion sphere.



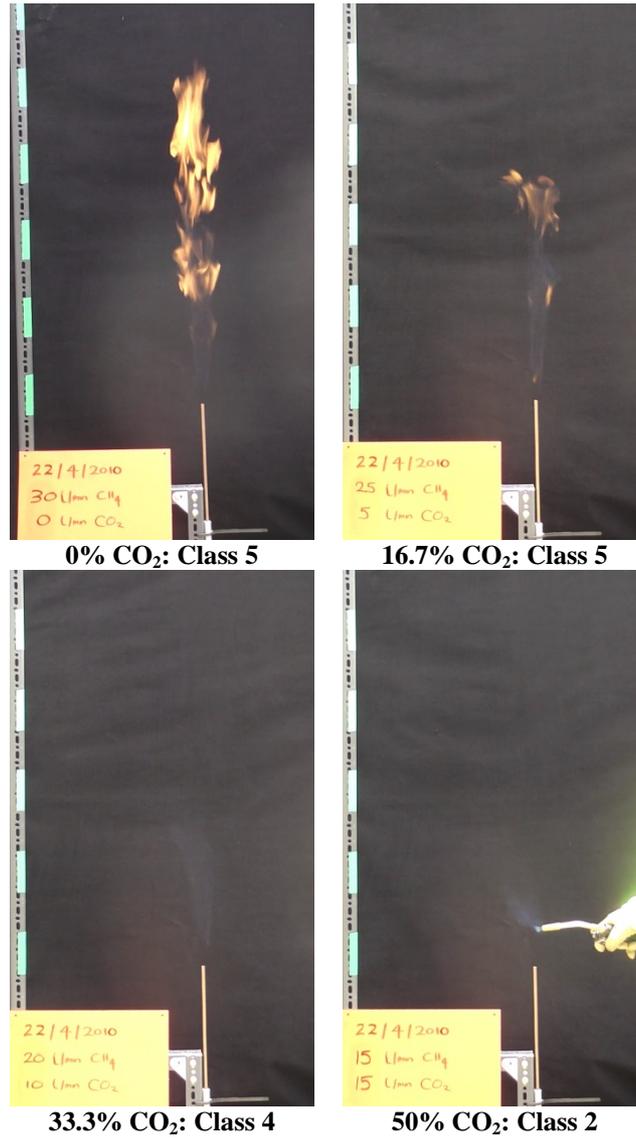
**Figure 7** The effect of CO<sub>2</sub> concentration on the maximum overpressure (P<sub>MAX</sub>) for CH<sub>4</sub> ignitions performed in the 1.04m diameter pipeline.



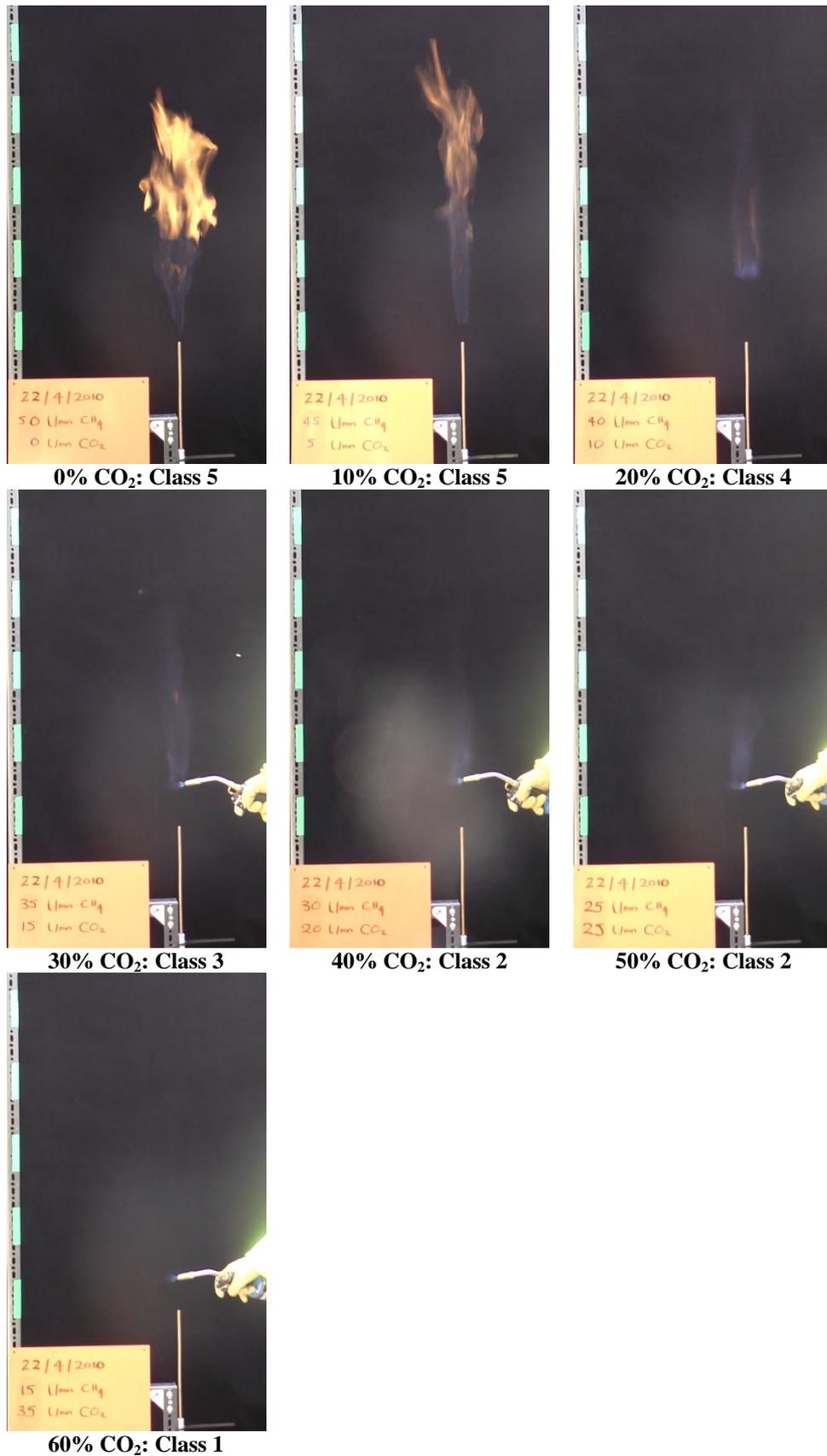
**Figure 8** The change in ignition response class of gas mixtures with CO<sub>2</sub> over the range 0 – 70%, for exit gas velocities of 17.7, 29.5 and 53.1 m/s.



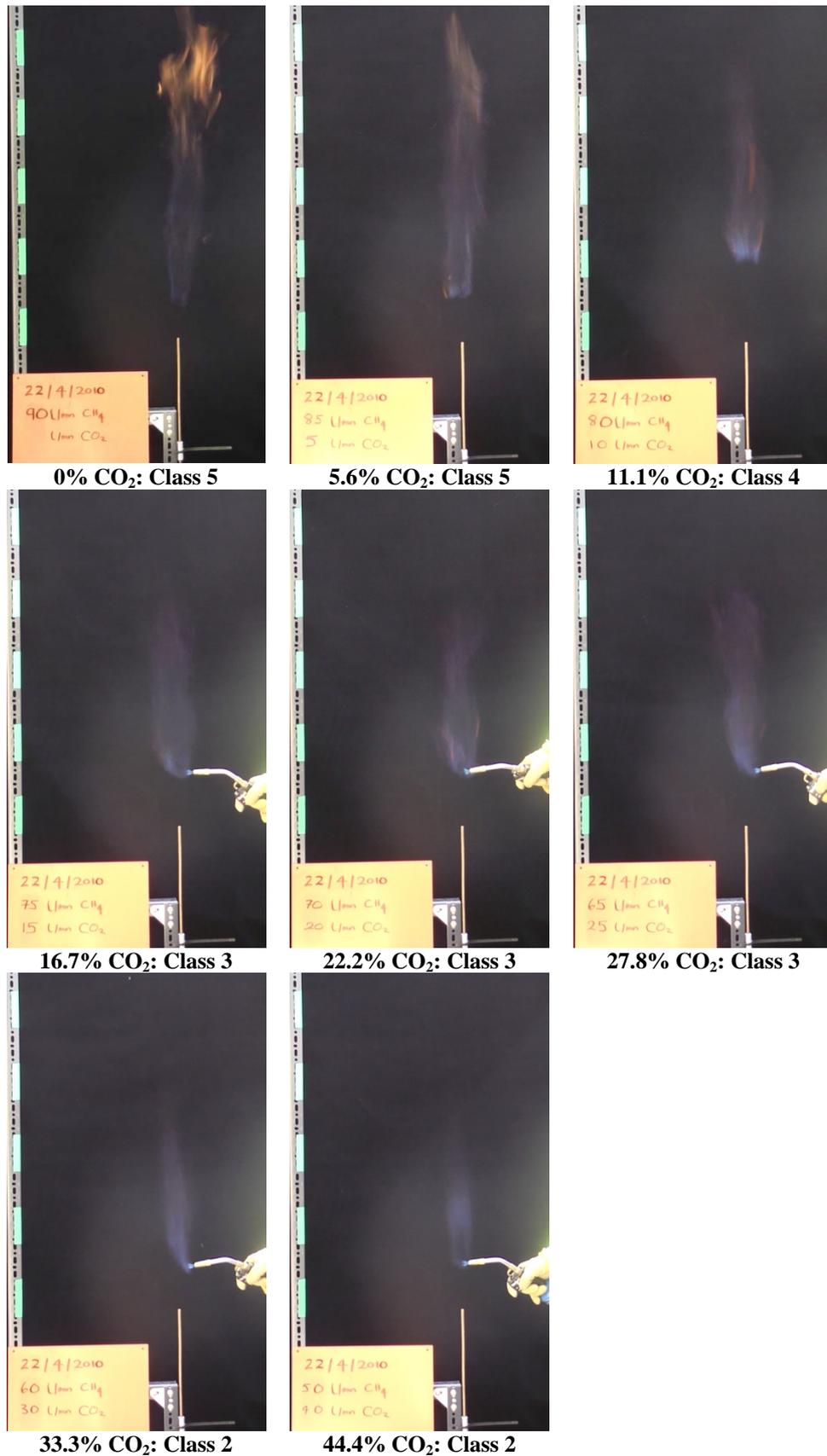
**Figure 9** Comparison of the pure methane flames at different exit velocities



**Figure 10** Images from ignition class tests for an exit velocity of 17.7m/s and CO<sub>2</sub> concentrations from 0% to 60%



**Figure 11** Images from ignition class tests for an exit velocity of 29.5m/s and CO<sub>2</sub> concentrations from 0% to 60%



**Figure 12** Images from ignition class tests for an exit velocity of 53.1m/s and CO<sub>2</sub> concentrations from 0% to 44.4%

## Tables

**Table 1 Experimental Release Conditions**

<b>Volumetric Flow rate (l/min)</b>	30	50	90
<b>Exit velocity (m/s)</b>	17.7	29.5	53.1
<b>Reynolds number*</b>	6453	10755	19359

\*for 100% CH<sub>4</sub>

**Table 2 Ignition Response Classifications**

<b>Class</b>	<b>Ignition response</b>
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