Flammability of Hydrocarbon/CO_2 Mixtures: Part 2. Predictive Models for Gas Jet Ignition

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Abstract

The present work examines predictive models for the flammability of hydrocarbon and CO_2 gas mixtures in jet releases. The extent of a flammable gas cloud from a jet release is often defined in terms of the location of the mean 50% Lower Flammable Limit (LFL) contour. Here, the use of 50% LFL rather than 100% LFL is to account for turbulent fluctuations above and below the mean gas concentration, which can produce pockets of flammable gas even where the mean mixture concentration is below the LFL.

Rather than focus on mean gas concentrations, which provide only an indirect indictor of flammability, the present work examines the flammability of gas jets using the concept of the 'flammability factor'. This field variable provides essentially a prediction of the ignition probability, i.e. the likelihood of the gas mixture being ignitable at any particular location and time.

Following the pioneering work undertaken at British Gas in the 1980's and using a combination of empirical relations taken from the literature, a simple predictive model is presented for the flammability factor in free, unobstructed, subsonic gas jets. The model is compared to previously published measurements of ignition probabilities and recent experiments conducted at the Health and Safety Laboratory (HSL). Good agreement between the model predictions and the previously published measurements is obtained. For the HSL experiments, the agreement between the model predictions and the measured ignition probability is reasonably good in the near-field of the jet but it deteriorates further downstream. The differences here are attributed to the effect of the wind in the experiments, which may have disturbed the downstream portion of jet, due to its relatively low momentum. The study demonstrates that even low wind speeds can have a significant influence on the dispersion behaviour of subsonic gas jets, and hence their ignition characteristics.

1. Introduction

This paper forms the second part of a study undertaken to investigate the hazards posed by mixtures of hydrocarbon and inert gases (see also Pursell *et al*., 2011). The present work examines predictive models for the flammability of hydrocarbon and CO_2 gas mixtures in jet releases.

A classical representation of a turbulent gas jet is shown in Figure 1. A virtual point origin for the jet is located a distance x_o upstream of the orifice, where the spreading jet converges to a point. As the jet evolves with distance downstream, the velocity on the centreline of the jet

gradually decays and the jet continually increases in width, due to the entrainment of ambient air as a result of shear-generated turbulence.

In free jets, sufficiently far downstream from the point of release, the cross-stream profiles of mean velocity and mean concentration adopt a Gaussian profile, i.e. the familiar bell-shaped curve indicated in Figure 1. Profiles of mean and Root-Mean-Square (RMS) velocity and concentration in this region are 'self-similar' in that the shape of the distributions remains the same at different axial positions.

This classical description of a turbulent jet gives the impression that velocity and concentration vary smoothly in gas jets, decaying gradually from maximum values on the jet centreline to zero in the far field. Whilst this is true for the *average* behaviour over a long period of time, the instantaneous structure of a turbulent jet exhibits large temporal and spatial variations. These fluctuations are of crucial significance when analysing the likelihood of the gas being within the flammable range, and therefore ignitable.

A gas detector (or point source of ignition) located close to the boundary of the jet is exposed to wide variations in gas concentration over time, including periods when the concentration is zero. To analyse these variations, a time-dependent variable can be defined which identifies periods when the detector is located in the turbulent fluid, when it is given a value of one, and periods in which it is located in the non-turbulent ambient fluid, when it is given a value of zero. Averaged over time, this measure represents the fraction of time that the detector is in the turbulent flow, and this is termed the turbulence intermittency, *I*. In practice, turbulence intermittency is measured by setting a very small threshold for concentration. Any concentration measurements larger than the threshold are given an intermittency indicator value of one, whilst those below are given a value of zero. In the jet flammability model, presented below, the turbulence intermittency is one of the key parameters used to characterise the flow.

The fraction of time any particular gas concentration exists at a point in a flow can be expressed as a Probability Density Function (PDF). This function, $P(f)$ describes the likelihood of the concentration taking a particular value. PDFs for turbulent natural gas jets have been measured by, for example, Birch *et al.* (1978). Near the centreline of a free jet, the shape of the PDF is nearly Gaussian, whilst on the periphery of the jet the PDF develops into a delta function, as more of the time is spent with a concentration close to zero.

To be able to predict the probability of ignition at any point in the flow, it is necessary to know the fraction of time that a source of ignition encounters gas concentrations between the upper and lower flammability limits. The fraction of time that the gas mixture is flammable is termed the 'Flammability Factor', *F*, and is related to the PDF of concentration at the ignition location as follows (Birch *et al*., 1981):

$$F = \int_{c_L}^{c_U} P(\tilde{c})\,d\tilde{c} \qquad (1)$$

This is equivalent to the area under the curve of the PDF for concentration, $P(\tilde{c})$, between the upper and lower flammability limits of c_U and c_L. The tilde symbol is used here to signify the time-varying instantaneous concentration at any point in space. Following the standard convention for Reynolds decomposition, the instantaneous concentration, $\tilde{c}$, is taken to comprise two parts: a mean concentration, *C*, plus a time-varying fluctuation, *c*. Similarly, the instantaneous, mean and fluctuating values of velocity are denoted as $\tilde{u}$, *U* and *u*, respectively.

The usefulness of the flammability factor measure was clearly established by Birch *et al*. (1981), who demonstrated that it correlated closely to the ignition probability. In their

experiments, the ignition probability was measured by recording the proportion of successful attempts to obtain ignition. A spark igniter was used with a spark gap of 3 mm, i.e. approximating a point source of ignition. To ensure that statistical errors were small, 400 ignition attempts were made at each measurement location. Their results showed that at various positions in a turbulent jet where the time-averaged mean concentrations were below the lower flammability limit, it was still possible to ignite the jet due to the presence of turbulent fluctuations, which increased the instantaneous concentration above the lower flammability limit. On the centreline of free jets, downstream of the point where the mean gas concentration fell below 50% LFL, the ignition probability was found to fall essentially to zero. At the boundary of turbulent jets, however, they showed that it was possible for the mean concentration to be as low as 10% LFL and yet for the mixture to still be ignitable at times.

Flammability factors have also been computed and compared to measurements of ignition probability for propane jets by Smith *et al.* (1986) and recently for hydrogen jets by Schefer *et al.* (2010). In both cases, there was good agreement between the predicted flammability factor and the measured ignition probability. In the propane jet measurements of Smith *et al*. (1986), at positions where the mean concentration was equal to 100% LFL it was found that there was a 50% probability of ignition.

The ignition probability is also affected by the chemical ignition delay period. This matter was investigated by Birch *et al*. (1979), who showed that the ignition probability increased as the temperature of the ignition source was increased. However, the ignition probability was found to become independent of the ignition source temperature if it was above 1400 K, and this condition will apply for electrical sparks of sufficient energy.

Following ignition at a point in a gas jet, a flame kernel may be convected downstream and eventually be extinguished, or alternatively it may propagate both downstream and upstream to light-up the whole jet. The probability that full light-up occurs, rather than just a localised ignition, can be very different. Localised ignition only requires instantaneous gas concentrations to be within the flammability limits and for there to be an ignition source present of sufficient energy. However, light-up of the whole jet depends on other factors, such as the existence of a pathway for the flame to propagate from one flammable region to another, and for the local flame speed to exceed local flow speeds.

Measurements of ignition and light-up probability were examined by Birch *et al*. (1981) and Smith *et al*. (1986). On the axis of a turbulent jet, they found that the probability of light-up decreased much more quickly than that of localised ignition. At the maximum downstream location where light-up was found to be possible, the mean gas concentrations were above the 100% LFL.

The flammability factor predicts the probability of only a flame kernel being produced. Subsequently, this kernel may or may not lead to light-up of the jet. Model predictions of the flammability factor should therefore be compared to measured probabilities of the production of a flame kernel, rather than jet light-up.

It is very difficult to predict jet light-up, rather than localised ignition. To do so requires the prediction of the time-varying ‘connectedness’ of flammable regions in a turbulent flow, such that flame propagation can occur. This is possible in principle, using Computational Fluid Dynamics (CFD) methods based on Large Eddy Simulation (LES), as shown by Triantafyllidis *et al.* (2009), but it requires significant computing resources.

The two major studies by Birch *et al.* (1981) and Smith *et al.* (1986) examined relatively low-speed turbulent jets, with release velocities typically between 20 m/s and 30 m/s in quiescent air that was undisturbed by crosswinds. Subsequent experiments were performed by Birch *et*

al. (1988) on high-pressure releases where the flow was sonic at the source. These indicated that the flammability factor should also be a valid indicator of ignition probability for high-speed releases once the jet has decelerated to sub-sonic flow. Birch *et al*. (1989) also later investigated the ignition behaviour of jets in a cross-flow.

The addition of carbon dioxide, nitrogen or any other inert gas to a fuel does not affect the validity of the flammability factor concept for predicting ignition probability. The same physics applies and all that is required is to modify the upper and lower flammability limits for the particular gas mixture.

2. Jet Ignition Experiments

The companion paper by Pursell *et al*. (2011) describes a series of bulk ignition tests performed on gas jets comprising mixtures of methane (CH_4) and CO_2. In addition to these tests, ignition probability measurements were performed using the spark ignition system shown in Figure 2. Mean gas concentrations were recorded using a portable gas analyser at the positions where the ignition probability was measured. Tests were performed using pure CH_4 and a mixture comprising 80% CH_4 and 20% CO_2, by volume. The experiments were conducted using the same gas supply, metering and shut-off systems as described by Pursell *et al*. (2011). The release pipe had an internal diameter of 6 mm and was 400 mm in length. It was oriented vertically such that the gas issued upwards.

The ignition probability was measured using a sparking system which comprised a variable voltage power source, two 1 GOhm resistors, a 2 nF capacitor, high tension wires and tungsten electrodes. The power source was set to 16 kV, allowing the capacitor to be charged to 15 kV. The combination of resistors and capacitor dictated the capacitor charge time, and this was chosen to produce a spark every four seconds. The tungsten electrodes of diameter 1.6 mm and length 150 mm were positioned in the jet with a separation distance of 2 mm.

Ignition tests were performed in batches, with the gas shut off for a period of 20 to 30 seconds between each batch to avoid the build up of combustible gases, or to allow venting of combustion products when ignition had occurred. Each batch consisted of a maximum of ten sparks. However, when ignition occurred the batch was terminated. For each ignition location, a total of 100 batches were performed. In many cases, ignition occurred before the maximum of ten ignition attempts had been reached. On average 250 ignition attempts were performed at each location.

The mean concentrations of CH_4 and CO_2 in the unignited gas jet were determined prior to conducting ignition tests using a GA 2000 Portable Gas Analyser (Geotechnical Instruments, UK). The accuracy of the analyser was ±0.5% over the range 0% to 15%, ±1.0% over the range 15% to 30%, and ±3.0% over the range 30% to 100%. Gases were sampled via a stainless steel tube of internal diameter 4 mm and length 300 mm that was positioned in the gas jet and connected to the analyser by 5 meters of flexible tubing. The internal pump of the gas analyser operated at a flow rate of 620 ml/min, giving a residence time in the sampling tube of roughly 16 s. The gas jet was therefore sampled for 60 s prior to readings being taken, and an average reading was calculated over a further 60 s using values recorded at a rate of 1Hz. The standard deviation of the reported reading was ±0.8% for CH_4 and ±0.1% for CO_2.

All of the ignition experiments were performed in a sheltered courtyard that was walled on four sides and open to the atmosphere. This location allowed experiments to be performed in moderate weather conditions, but tests could only be performed in low to moderate wind speeds since higher wind speeds clearly affected the gas jet dispersion behaviour.

The gas release rate was 90 litres/min, the jet exit velocity 53.1 m/s and the Reynolds number 19,359, based on the pipe diameter, exit velocity and the viscosity of pure CH_4. This condition was chosen so as to be comparable with the previous work of Birch *et al.* (1981) and Smith *et al.* (1986) who used similar Reynolds Numbers of between 12,500 and 22,000.

3. Empirical Jet Ignition Model

The proposed model determines the flammability factor from various empirically-based correlations of mean and RMS gas concentration, turbulence intermittency and concentration PDFs. The following list provides a summary of the sources of empirical data:

- The mean velocity and mean concentration along the centreline of the subsonic jet are determined from empirical profiles from Chen & Rodi (1980), with some minor changes (described below);
- In the radial direction, Gaussian profiles are assumed for the mean velocity and mean concentration, using spreading rates given by Chen & Rodi (1980) and Birch *et al*. (1978);
- The RMS concentration fluctuation is determined using the *α-β* model of Chatwin & Sullivan (1990);
- The turbulent intermittency in the jet is determined using the empirical model of Kent & Bilger (1976);
- A two-part PDF is used for the concentration fluctuations, comprising the sum of a delta function and a truncated Gaussian, using conditionally sampled mean and RMS values, based on the model of Birch *et al*. (1981);
- The two-part PDF is integrated using error functions between upper and lower flammability limits which are calculated for the CH_4 and CO_2 mixtures using a modified Le Chatelier's law developed by Kondo *et al*. (2006).

The model has many similarities to that presented by Birch *et al*. (1981), except that they did not describe the profiles used for intermittency, and mean and RMS concentration[1].

The mean velocity and concentration profiles along the centreline of the jet from Chen & Rodi (1980) consist of two equations which are valid in separate regions of the flow: the momentum-dominated region near the jet orifice and an intermediate region further downstream where inertial forces are weaker and buoyancy forces start to become important. The boundary between these two regions is defined using a dimensionless axial distance, x^*:

$$x^* = Fr^{-1/2}\left(\frac{\rho_0}{\rho_a}\right)^{-1/4}\left(\frac{x'}{D}\right) \tag{2}$$

where x' is the axial distance from the virtual origin of the jet (see Figure 1), D is the orifice diameter, ρ the density and subscripts "a" and "0" refer to ambient and jet orifice values respectively. The Froude number, Fr, is given by:

$$Fr = \frac{U_0^2}{gD(\rho_a - \rho_0)/\rho_0} \tag{3}$$

where U_0 is the velocity at the jet orifice and g is the acceleration due to gravity. In the momentum-dominated region near the jet, where $x^* < 0.5$, the mean centreline velocity, U_{cl}, and centreline concentration, C_{cl}, are given by:

[1] *These were probably taken from unpublished experimental measurements (M. Fairweather, Private Communication, 2010)*

$$U_{cl} = 6.2U_0\left(\frac{\rho_0}{\rho_a}\right)^{1/2}\left(\frac{x'}{D}\right)^{-1} \tag{4}$$

$$C_{cl} = 5C_0\left(\frac{\rho_0}{\rho_a}\right)^{-1/2}\left(\frac{x'}{D}\right)^{-1} \tag{5}$$

whilst in the intermediate region, where x^* is between 0.5 and 5.0, they are given by:

$$U_{cl} = a_U U_0 Fr^{-1/10}\left(\frac{\rho_0}{\rho_a}\right)^{9/20}\left(\frac{x'}{D}\right)^{-4/5} \tag{6}$$

$$C_{cl} = a_C C_0 Fr^{1/8}\left(\frac{\rho_0}{\rho_a}\right)^{-7/16}\left(\frac{x'}{D}\right)^{-5/4} \tag{7}$$

Further downstream from the intermediate region, where x^* is greater than 5.0, buoyancy forces become dominant and the flow exhibits plume-like behaviour. However, since the fluctuating gas concentrations in this region of the flow are below the LFL, it is only necessary here to consider the momentum-dominated and intermediate regions.

Values of 7.1 and 4.2 are taken for the constants a_U and a_C in Equations (6) and (7), respectively. These differ slightly from the values given by Chen & Rodi (1980) and Smith *et al*. (1986) who used, respectively, a_U = 7.26 and a_C = 0.44, and a_C = 4.4. The values have been chosen in the present study to produce smooth transitions in velocity and concentration between the momentum-dominated and intermediate regions (see Gant *et al*., 2010, for further details).

In the radial direction, the mean velocity and mean concentration are approximated using Gaussian profiles:

$$\frac{U}{U_{cl}} = \exp\left[-K_U\left(\frac{r}{x'}\right)^2\right] \tag{8}$$

$$\frac{C}{C_{cl}} = \exp\left[-K_C\left(\frac{r}{x'}\right)^2\right] \tag{9}$$

where constants K_U and K_C are given values 94.0 and 73.6, based on values given by Chen & Rodi (1980) and Birch *et al*. (1978), respectively.

The RMS concentration is determined using the α-β model of Chatwin & Sullivan (1990):

$$\overline{c^2} = \beta C\left(\alpha C_{cl} - C\right) \tag{10}$$

where constants α and β are given values of 1.27 and 0.14, respectively, based on Chatwin & Sullivan's (1990) analysis of the methane jet experiments of Birch *et al*. (1978).

The turbulent intermittency, I, is calculated using the empirical formula of Kent & Bilger (1976):

$$I = \frac{K+1}{\left[\left(\frac{\overline{c^2}}{C^2}\right)+1\right]} \tag{11}$$

where K is a constant given a value of 0.25 by Kent & Bilger (1976).

To account for the change in shape of the concentration PDF with radius, the present model adopts the two-part PDF proposed by Birch *et al*. (1981) which smoothly varies between a truncated Gaussian distribution and a delta-function, based on the intermittency:

$$P(\tilde{c}) = \underbrace{(1-I)\delta(\tilde{c})}_{} + \frac{IA}{\sqrt{2\pi\overline{c_c^2}}} \exp\left[-\frac{(\tilde{c}-C_c)^2}{2\overline{c_c^2}}\right] \tag{12}$$

where the subscript 'c' denotes conditionally sampled values, which are calculated as follows:

$$C_c = \frac{C}{I} \tag{13}$$

$$\overline{c_c^2} = \frac{\overline{c^2}}{I} - \frac{C^2(1-I)}{I^2} \tag{14}$$

and scaling factor, A, is given by:

$$A = \frac{2}{ERF\left(\frac{1-C_c}{\sqrt{2\overline{c_c^2}}}\right) - ERF\left(\frac{-C_c}{\sqrt{2\overline{c_c^2}}}\right)} \tag{15}$$

where $ERF()$ denotes the error function.

To calculate the flammability factor requires the integration of Equation (12) between the upper and lower flammability limits. Since the delta function only has finite amplitude at concentrations approaching zero (i.e. well below the LFL) the underbraced term in Equation (12) can effectively be ignored. The remaining part is integrated using error functions as follows:

$$F = \frac{IA}{2}\left[ERF\left(\frac{c_U - C_c}{\sqrt{2\overline{c_c^2}}}\right) - ERF\left(\frac{c_L - C_c}{\sqrt{2\overline{c_c^2}}}\right)\right] \tag{16}$$

To account for the presence of carbon dioxide in the gas mixtures, the upper and lower flammability limits (c_U and c_L) are determined here using a modified version of Le Chatelier's law developed by Kondo *et al*. (2006):

$$c_L = \frac{\sum_i c_i}{\sum_i \frac{c_i}{L_i} - 0.01094 c_{co2}} \tag{17}$$

$$c_U = \left(\sum_i c_i \right) \left[100 - \frac{\left(\sum_i c_i n_i \right)}{B} \right] \tag{18}$$

where B is given by:

$$B = \sum_i \frac{c_i n_i}{100 - U_i} + 0.00105 c_{CO2} + 0.00106 c_{CO2}^2 - 0.00106 c_{CO2}^3 \tag{19}$$

The concentrations of each of the flammable gases, c_i, have lower and upper flammable limits of L_i and U_i respectively, and c_{CO2} is the concentration of carbon dioxide. The parameters c_i, L_i, U_i and c_{CO2} are all expressed in terms of percentage by volume in Equations (17) to (19), i.e. the LFL of methane is included in the equations as L_i = 5.0, not 0.050. The parameter n_i is the number of moles of oxygen consumed by one mole of fuel when the mixture is at the upper flammability limit. Assuming the combustion takes place in air, this is given by:

$$n_i = \frac{(100 / U_i) - 1}{1 + (79 / 21)} \tag{20}$$

4. Model Validation

To validate the new model for the flammability factor of subsonic free jets, it has been used to reproduce the results of Smith *et al*. (1986). Predictions of the mean gas concentration and flammability factor along the centreline of jets of natural gas and propane are presented in Figures 3 and 4, respectively. For the natural gas jet, the release velocity was 50 m/s whilst for the propane tests it was 20 m/s. In both cases, the orifice diameter was 6.35 mm. Smith *et al*. (1986) assumed that the virtual source of the gas jet was located four diameters upstream of the orifice. The same offset is used in the present model results, and the results are given in Figures 3 and 4 with the axial displacement measured from the virtual jet origin rather than the orifice. Despite this, the model of Smith *et al*. (1986) predicted the potential core of the jet, where the gas concentration has a volume fraction of one, to extend nearly twice as far in the axial direction as the present model predictions. The source of discrepancy between the predictions is unclear. However, these differences are limited to the region very close to the orifice where the gas concentrations are well above the upper flammability limit, and so they have little bearing on the flammability factor. Further downstream, the agreement between the model predictions of the mean gas concentration is good.

The flammability factor predicted by the present model shows some small differences compared to the previous results of Smith *et al*. (1986). For both the natural gas and propane jets, it predicts the flammability factor to decay more rapidly to zero than the model of Smith *et al*. (1986) in the far field, where mean concentrations fall below the LFL. In the natural gas jet, the results are therefore in slightly better agreement with the experiments, whilst in the propane jet they are slightly worse. These differences are fairly minor, however, and overall

the predicted flammability factor is in good agreement with the measured ignition probabilities.

Additional comparisons of the model's performance against the predictions and measurements of Birch *et al.* (1981) are given by Gant *et al.* (2010). Overall, these comparisons show a similar level of agreement to that shown in Figures 3 and 4. The results of this short validation study indicate that the model provides reliable predictions of the flammability factor for sub-sonic free jets in a quiescent environment.

5. Results & Discussion

The predicted and measured mean centreline concentrations of CH_4 and CO_2 are compared in Figures 5 and 6 for the pure CH_4 and CH_4-CO_2 mixture, respectively. The upper and lower flammability limits shown in these graphs are 15% and 5% for pure CH_4, and 13.4% and 5.1% for the CH_4-CO_2 mixture, as determined by the model of Kondo *et al.* (2006). Comparing the two figures, the presence of the CO_2 reduces slightly the axial extent of the region between the upper and lower flammable limits.

The agreement between the measured and predicted gas concentrations is generally good, although at an axial distance greater than 25 cm the model predicts consistently higher concentrations than those measured for the pure CH_4 jet. This may have resulted from the mean centreline of the jet deviating slightly from the axis along which the measurements were taken. For the CH_4-CO_2 mixture, the model agrees with the measurements to within 3% vol/vol for all but the first two measurement positions at 5 cm and 10 cm from the release point, where the gas concentrations are under-predicted by around 20% in relative terms.

The measured probability of ignition is compared to the predicted flammability factor at different axial positions in Figures 7 and 8. There is reasonable agreement between the measured and predicted ignition probabilities up to a distance of around 30 cm from the nozzle. Further downstream, the model produces significantly higher values than were measured experimentally. The experiments measured practically zero ignition probability at distances more than 70 cm and 50 cm for the pure CH_4 and CH_4-CO_2 jets, respectively, whilst the model predicted the jet to be ignitable up to a distance of 100 cm downstream from the source in both cases.

To try to account for the discrepancies in predicted and measured mean concentration, shown in Figures 5 and 6, the ignition probability data along the centreline of the jet are plotted against the mean concentration, instead of the axial displacement, in Figures 9 and 10. When the data are presented in this way, the measured ignition probabilities span a similar range of mean concentration to that predicted by the model. This highlights that even relatively small changes in mean concentration can have a significant affect on the ignition probability, particularly in regions where the gas concentration is close to the LFL. Despite these improvements in agreement between the measured and predicted values, the measured ignition probabilities remain much lower than those predicted by the empirical model. All of the measured ignition probabilities are less than 60% whereas they are predicted to reach nearly 100% in places.

One of the possible explanations for the low ignition probability measured in the experiments is that not all of the ignitions were detected. Very small pockets of gas could have been ignited that were too small to be visible. However, this is not considered to offer a plausible explanation for the discrepancy of 40% in the ignition probability. Ignitions were detected both audibly and visibly and there is confidence that the vast majority of ignitions were detected. In those cases where bright sunshine partially obscured the directly visible flame, its

presence was detected by the shadow produced on an adjacent wall, from the Schlieren effect. A similar approach appears to have been taken by Birch *et al*. (1981) who described ignitions as simply being "observed" in their experiments. In the more recent work of Schefer *et al.* (2010), thermocouples downstream of the ignition location were used to determine the presence of a flame kernel.

A more likely explanation of the discrepancy between the model predictions and measurements is that in the experiments gusts of wind disturbed the jet and led to gas concentrations varying more over time. The test area used in the experiments was open to the atmosphere and although tests were conducted in low to moderate wind speeds in a sheltered area to minimise its effect, some disturbances still occurred. These would have been more significant in the far-field of the jet, where its momentum diminished. Beyond a distance of 30 cm, the maximum velocity on the centreline of the jet was predicted to fall below 5 m/s. Although the results presented in Figures 9 and 10 account for the reduction in mean gas concentration due to these disturbances, the turbulent fluctuations in the jet will also have been affected. The same mean gas concentration can be produced by varying the gas concentration between wider limits, which could reduce the proportion of time the mixture spends within the flammable range, and hence lower its likelihood of ignition.

In realistic release conditions, following a failure on an offshore platform for example, it is unlikely that the flow around the release point will be quiescent. The results presented here are useful in demonstrating that even relatively small gusts of wind may have a significant effect on the dispersion of the gas and its chances of igniting in such cases. The results also suggest that the flammability factor model will tend to predict higher ignition probabilities along the axis of the jet than will occur in practice under these conditions. However, further work is necessary to establish whether the flammability factor model will provide conservative predictions under all circumstances, including those where the wind is directed along the axis of the jet (i.e. co-flowing).

Contours of the predicted flammability factor for the pure CH_4 and CH_4-CO_2 jets, are shown in Figures 11 and 12, respectively. In these plots, the bold red lines indicate the position of the LFL and UFL, based on the predicted mean gas concentration, and symbols show the locations where the ignition probability was measured in the experiments. The results show that the addition of CO_2 decreases the area over which the gas mixture can be ignited. Where the mean gas concentration is at the LFL or UFL, the predicted flammability factor is around 50%, which is in agreement with the previous findings of Smith *et al*. (1986).

The flammability factor model presented here is based on empirically-derived correlations and is valid only for free-jets in a quiescent atmosphere. The feasibility of using CFD to extend predictions of the flammability factor beyond such simple flows is examined in detail by Gant *et al*. (2010). Previous work in this field, such as that by Alvani and Fairweather (2008), is reviewed and a simplified methodology is proposed which retains many of the benefits of more sophisticated approaches.

The same fundamental principles of the flammability factor can also be used to analyse the toxic load a person may receive from atmospheric exposure to fluctuating concentrations of toxic gas, aerosol or dust. The techniques could be useful for those chemicals for which the Specified Level of Toxicity (SLOT) and Significant Likelihood of Death (SLOD)[2] are highly sensitive to the concentration of the toxic substance, such as CO_2.

[2] http://www.hse.gov.uk/hid/haztox.htm, *accessed July 2010.*

6. Conclusions

A brief introduction has been provided to analytical techniques that have been used to assess the flammability of non-premixed gas jets. A new empirically-based model has been presented and validated against the previously published work of Smith *et al*. (1986). It has then been applied to study jets of pure CH_4 and a CH_4-CO_2 mixture, for which new experimental data has also been presented.

The results showed that the ignitable region in a jet of CH_4 containing 20% CO_2 by volume was smaller than that in the equivalent pure CH_4 release, as expected. The model and the experiments demonstrated that it is possible to ignite gas jets at points in the flow where the mean concentration was either below the LFL or above the UFL.

The agreement between the flammability factor predicted by the empirical model and the ignition probability measured in the experiments was reasonably good in the near-field of the jet but was found to deteriorate further downstream. Generally, the model predictions were significantly higher than those measured, with the measured ignition probabilities remaining below 60% even where it was predicted for gas concentrations to be within the flammable range for the vast majority of the time. The difference between modelled and measured behaviour was attributed to the effect of the wind in the experiments. The results provide an important lesson and demonstrate that care should be exercised in applying free-jet flammability factor models to assess hazards in realistic environments, where the effects of even moderate winds may be significant.

The flammability factor model presented here can easily be extended to consider other gas mixtures. Applications include discharges from oil storage tanks with nitrogen-inerting or flue gas systems, and hydrogen and inert gas mixtures used in pre-combustion CO_2-capture power stations. The same fundamental principles of the flammability factor can also be used to analyse the toxic load a person may receive from atmospheric exposure to fluctuating concentrations of a toxic gas, aerosol or dust.

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8. References

Alvani, R.F. and Fairweather, M., 2008, Prediction of the ignition characteristics of flammable jets using intermittency-based turbulence models and a prescribed PDF approach, *Computers and Chemical Engineering*, **32**: 371-381.

Birch, A.D., Brown, D.R., Dodson, M.G. and Thomas, J.R., 1978, The turbulent concentration field of a methane jet, *J. Fluid Mech*., **88**: 431-449.

Birch, A.D., Brown, D.R., Dodson, M.G. and Thomas, J.R., 1979, Studies of flammability in turbulent flows using laser Raman spectroscopy, *17th Symposium (International) on Combustion*, The Combustion Institute, 301-314.

Birch, A.D., Brown, D.R. and Dodson, M.G., 1981, Ignition probabilities in turbulent mixing flows, *18th Symposium (International) on Combustion*, The Combustion Institute, 1775-1780.

Birch, A.D., Brown, D.R., Cook, D.K. and Hargrave, G.K., 1988, Flame stability in under-expanded natural gas jets, *Combust. Sci. and Tech*., **58**: 267-280.

Birch, A.D., Brown, D.R., Fairweather, M. and Hargrave, G.K., 1989, An experimental study of a turbulent natural gas jet in a cross-flow, *Combust. Sci. and Tech*., **66**: 217-232.

Chatwin, P.C. and Sullivan, P.J., 1990, A simple and unifying physical interpretation of scalar fluctuation measurements from many turbulent shear flows, *J. Fluid Mech*., **212**: 533-556.

Chen, C.J. and Rodi, W., 1980, *Vertical turbulent buoyant jets: a review of experimental data*. Pergamon Press.

Gant, S.E., Lea, C.J, Pursell, M., Rattigan, W. and Thyer, A., 2010, Flammability of hydrocarbon and carbon dioxide mixtures: experiments and modelling, Health & Safety Laboratory Report MSU/2010/21.

Kent, J.H. and Bilger, R.W., 1976, The prediction of turbulent diffusion flame fields and nitric oxide formation, *16th Symposium (International) on Combustion*, The Combustion Institute, 1643-1656.

Kondo, S., Takizawa, K., Takahashi, A. and Tokuhashi, K., 2006, Extended Le Chatelier's formula for carbon dioxide dilution effect on flammability limits, *J. Hazardous Mater*., **A138**: 1-8.

Pursell, M.R., Gant, S.E., Fletcher, J., Rattigan, W., Thyer, A.M. and Connolly, S., 2010, Flammability of Hydrocarbon/CO_2 Mixtures: Part 1. Ignition and Explosion Characteristics, Submitted to *IChemE Hazards XXII Conference*, Liverpool, UK, 11-14 April 2011.

Schefer, R.W., Evans, G.H., Zhang, J., Ruggles, A.J. and Greif, R., 2010, Ignitability limits for combustion of unintended hydrogen releases: experimental and theoretical results, *Int. J. Hydrogen Energy*, Article in Press, doi:10.1016/j.ijhydene.2010.04.004.

Smith, M.T.E., Birch, A.D., Brown, D.R. and Fairweather, M., 1986, Studies of ignition and flame propagation in turbulent jets of natural gas, propane and a gas with a high hydrogen content, *21st Symposium (International) on Combustion*, The Combustion Institute, p1403-1408.

Triantafyllidis, A., Mastorakos, E. and Eggels, R.L.G.M., 2009, Large eddy simulation of forced ignition of a non-premixed bluff-body methane flame with conditional moment closure, *Combust. Flame*, **156**: 2328-2345.

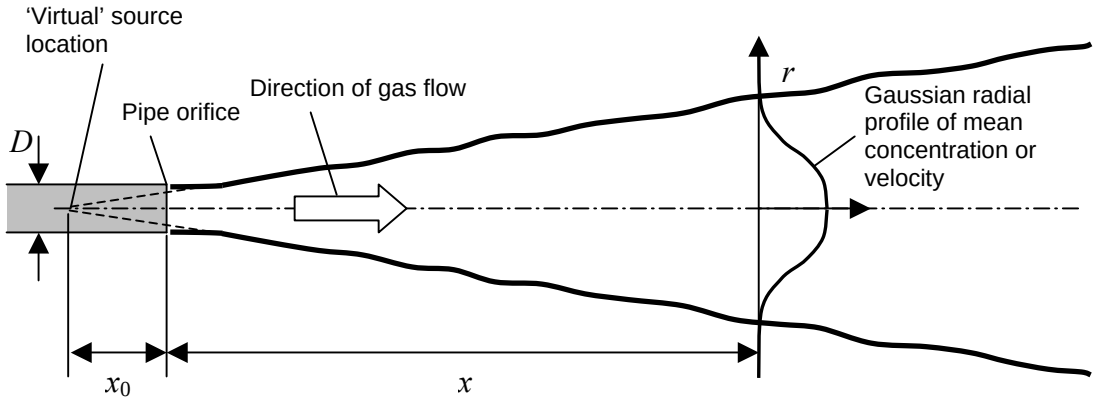

Figure 1 Schematic of a gas jet

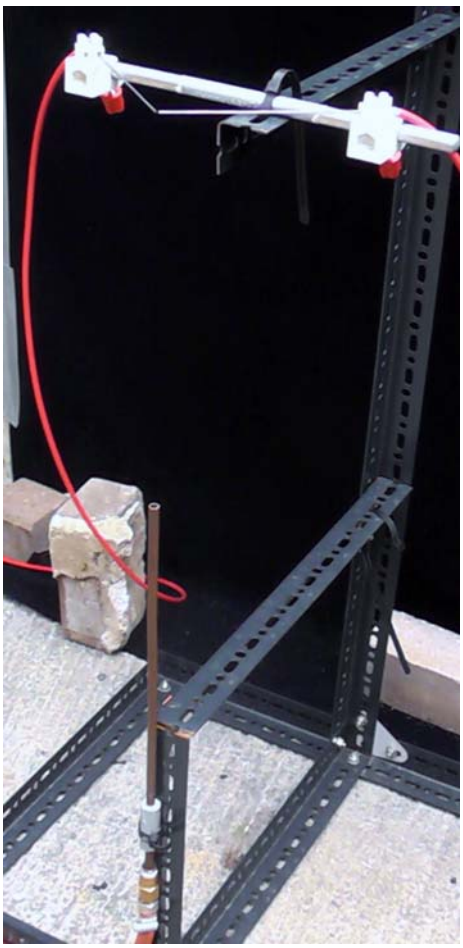

Figure 2 Experimental apparatus showing the release pipe and the spark electrodes attached to the supporting frame

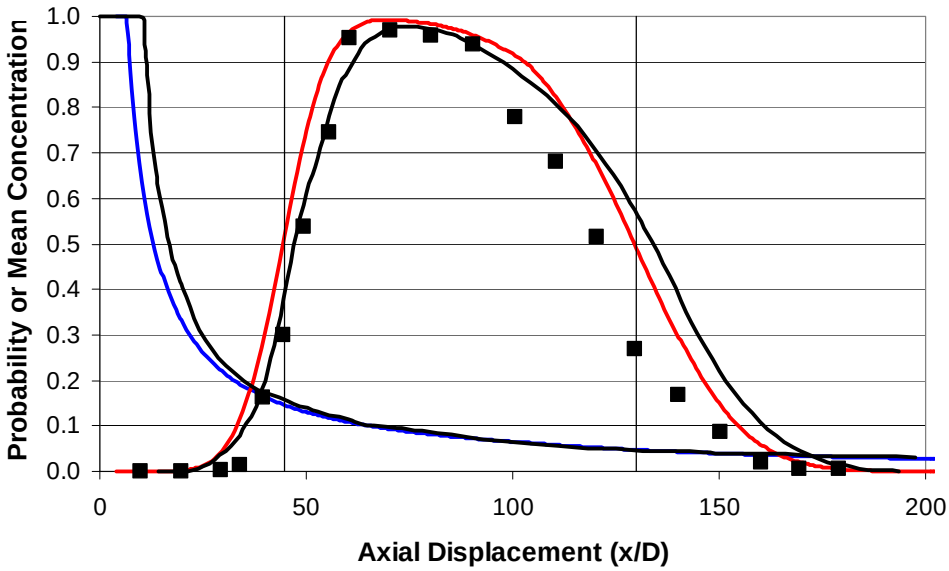

Figure 3 Comparison of flammability factor predictions and mean concentrations to ignition probability measurements for the natural gas jet studied by Smith *et al*. (1986). The black lines are the previous prediction of Smith *et al*. (1986) and coloured lines are the present model predictions. Symbols indicate measured values and the vertical lines indicate the positions of the mean UFL and LFL.

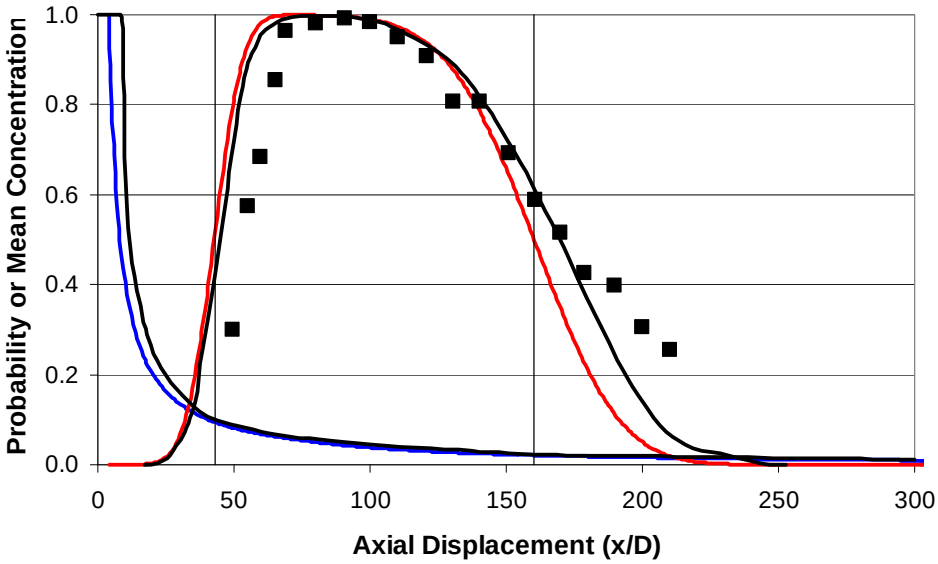

Figure 4 Comparison of flammability factor predictions and mean concentrations to ignition probability measurements for the propane gas jet studied by Smith *et al*. (1986). The black lines are the previous predictions of Smith *et al*. (1986) and coloured lines are the present model predictions. Symbols indicate measured values and the vertical lines indicate the positions of the mean UFL and LFL.

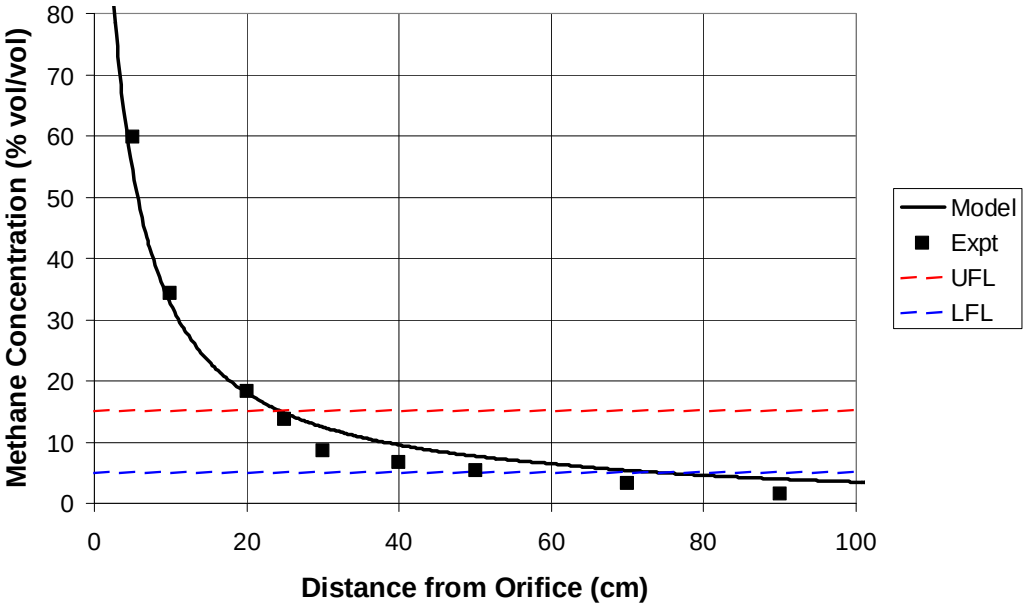

Figure 5 CH_4 concentrations along the jet axis for the pure CH_4 release.

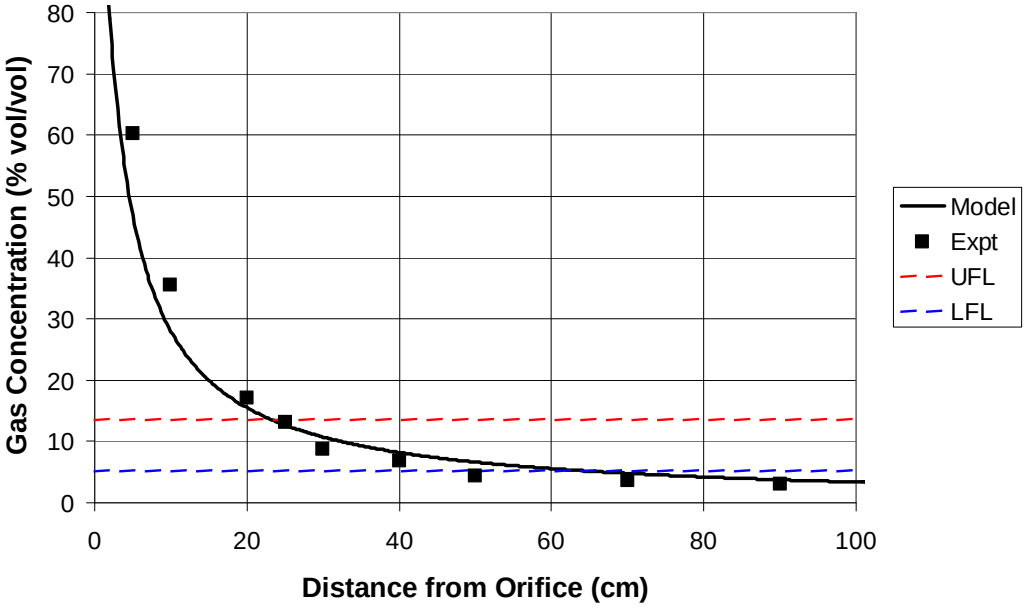

Figure 6 Combined CH_4 plus CO_2 concentrations along the jet axis for the CH_4-CO_2 release.

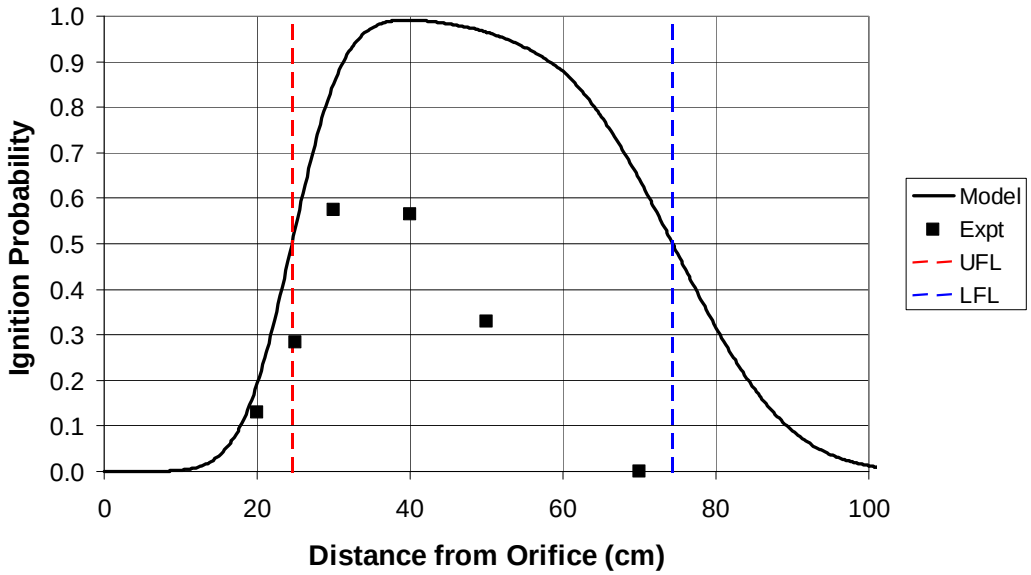

Figure 7 Measured ignition probability (symbols) and predicted flammability factor (solid line) along the centreline of the pure CH_4 release.

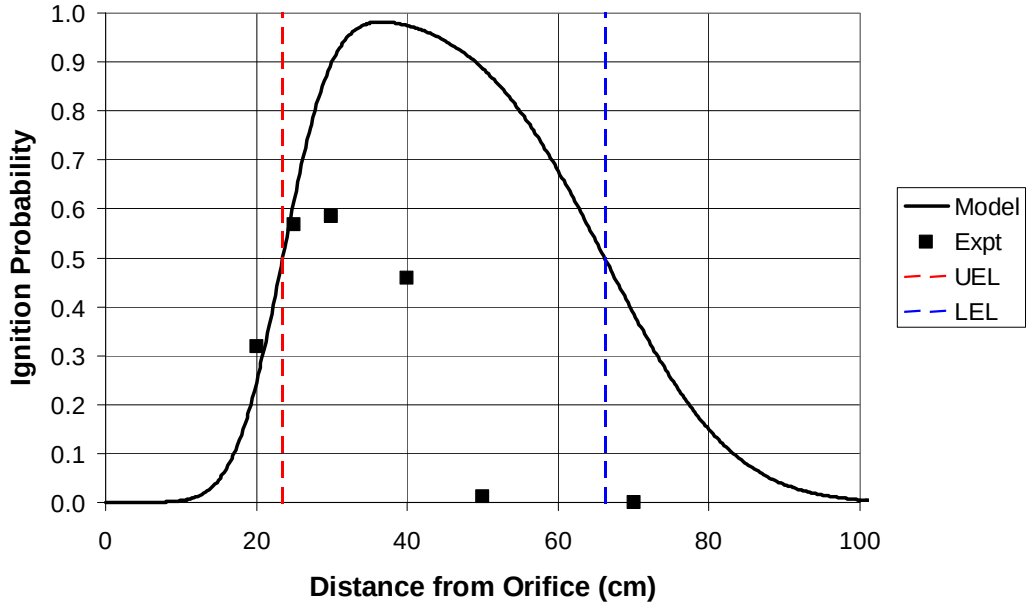

Figure 8 Measured ignition probability (symbols) and predicted flammability factor (solid line) along the centreline of the CH_4-CO_2 mixture.

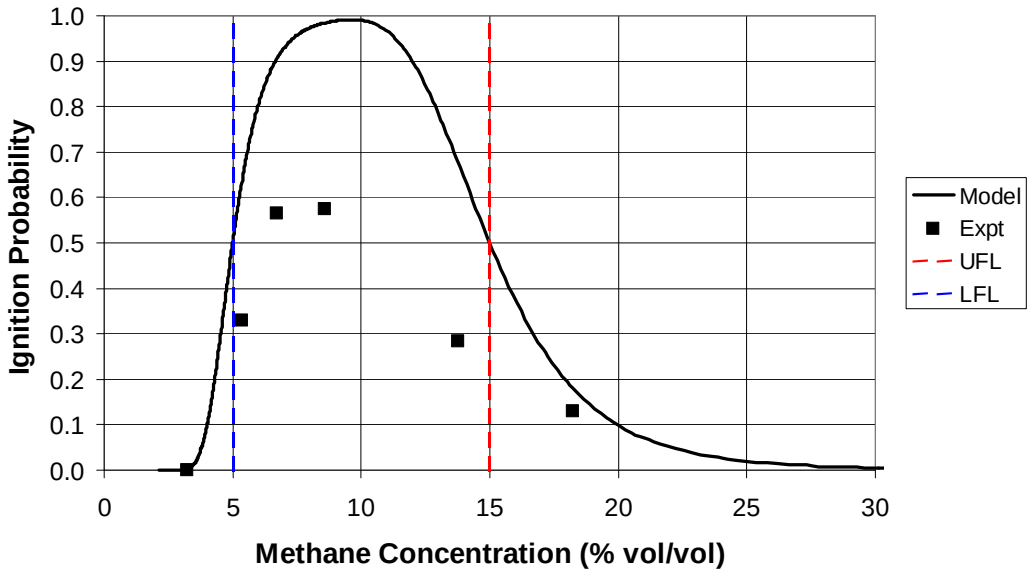

Figure 9 Measured ignition probability (symbols) and predicted flammability factor (solid line) along the centreline of the pure CH_4 release.

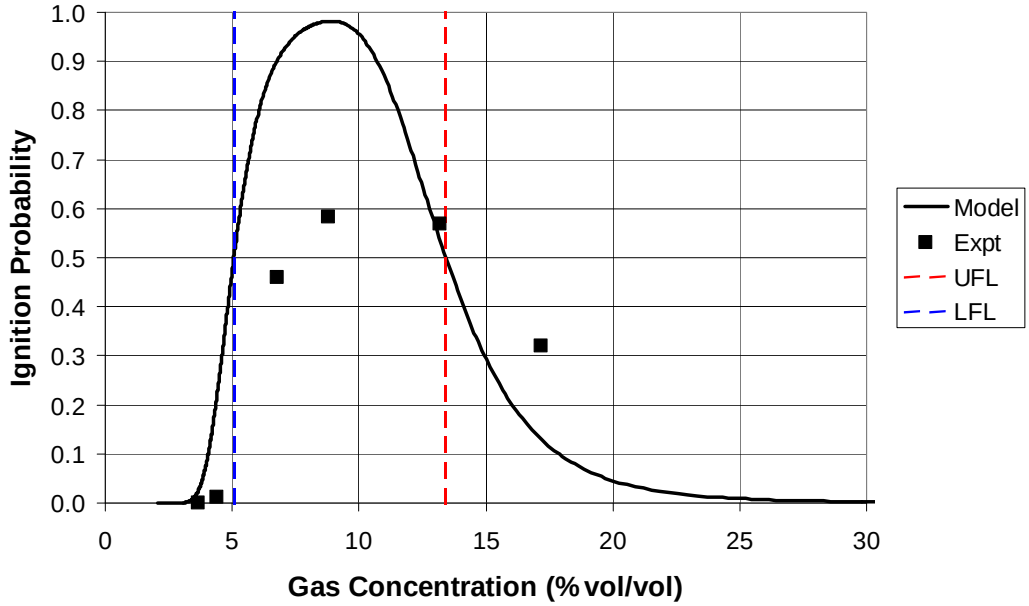

Figure 10 Measured ignition probability (symbols) and predicted flammability factor (solid line) along the centreline of the CH_4-CO_2 mixture.

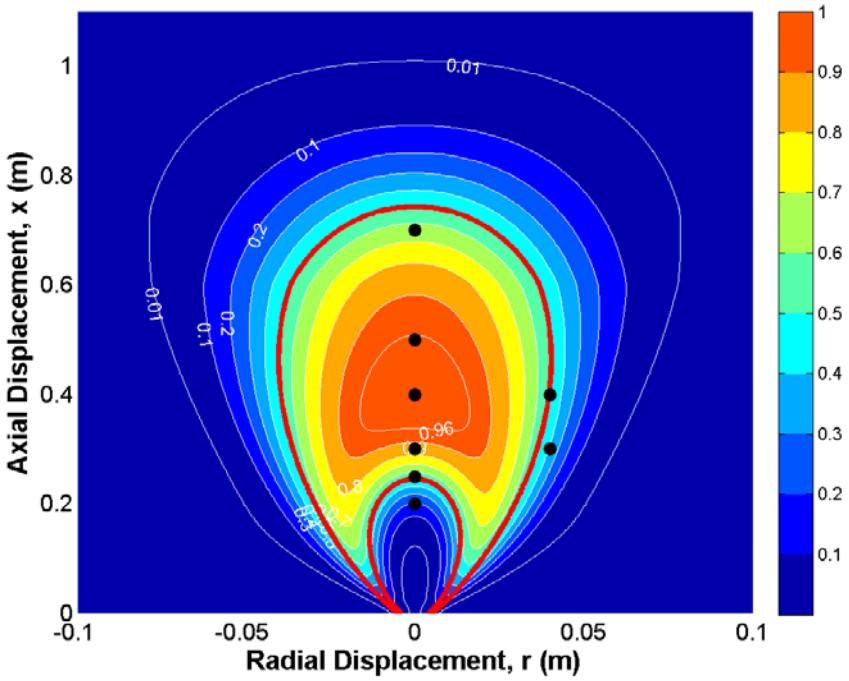

Figure 11 Predicted flammability factor for the pure CH_4 release.

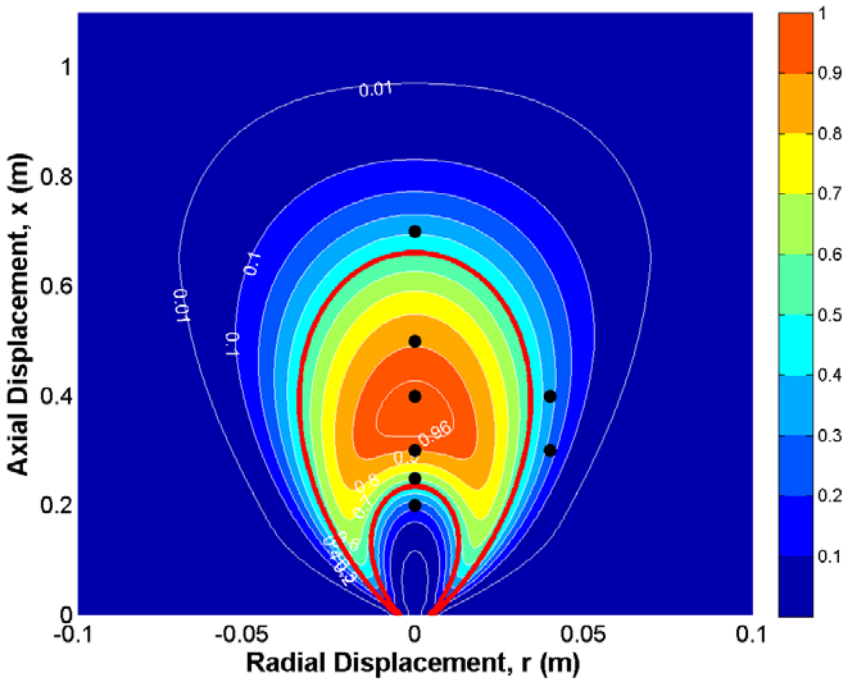

Figure 12 Predicted flammability factor for the CH_4-CO_2 mixture.