THE MITIGATION OF HYDROGEN EXPLOSIONS USING WATER FOG, NITROGEN DILUTION AND CHEMICAL ADDITIVES

Battersby, P., Holborn, P.G., Ingram, J.M., Averill, A.F. and Nolan, P.F.
Hydrogen Hazards Unit (CERC), London South Bank University, 103 Borough Rd, London, SE1 0AA, United Kingdom, holborpg@lsbu.ac.uk

ABSTRACT

This paper describes research work that has been performed at LSBU, using both a laminar burning velocity rig and a small scale cylindrical explosion vessel, to explore the use of very fine water fog, nitrogen dilution and sodium hydroxide additives in the mitigation of hydrogen deflagrations. The results of the work suggest that using a combination of the three measures together produces the optimal mitigation performance and can be extremely effective in: inhibiting the burning velocity, reducing the rate of explosion overpressure rise and narrowing the flammability limits of hydrogen-oxygen-nitrogen mixtures.

1.0 INTRODUCTION

The explosion hazard posed by hydrogen is a concern, both as a potential barrier to its widespread adoption as a clean energy fuel source (e.g. in fuel cells, hydrogen powered vehicles etc.) and in the nuclear industry where it can be generated during the course of normal operations (e.g. in waste storage as a consequence of radiolysis and corrosion) or under loss-of-cooling accident conditions (such as occurred at Three Mile Island and Fukushima). Such an explosion could obviously pose a serious risk to safety. The risk is particularly acute in nuclear plants where an explosion could threaten containment, leading to radioactive contamination of the surrounding environment, with potentially very serious consequences. Techniques for either preventing or mitigating hydrogen explosions are therefore of obvious interest.

A great deal of work has been done to examine hydrogen explosions and their mitigation, particularly in regard to nuclear safety [1, 2] and the HySafe project [3]. The most frequently used methods to either prevent or mitigate such explosions are through the use of venting systems or total inerting with a suitable agent (e.g. nitrogen, carbon-dioxide or argon). However, in some circumstances explosion venting and total inerting may be impractical or difficult to put into practice, either because of the nature of the plant or containment or because the inerting process itself may pose a safety hazard to operators. Attention has therefore been given to exploring the possibility of using other methods for the prevention or mitigation of hydrogen deflagrations in an enclosure.

One such mitigation technique is the dilution of the hydrogen-air mixture with nitrogen or steam, where the added diluent acts to reduce the oxygen content and introduces additional thermal ballast into the flame reaction zone [4]. Thus, although the concentration of diluent may be insufficient to render the flammable hydrogen mixture totally inert, it is still able to reduce the rate of reaction and burning velocity at which the flame propagates and hence the rate of pressure rise and maximum overpressure reached, allowing the explosion to be more readily contained (e.g. by using a smaller vent area).

There is also evidence to suggest that when certain chemical additives (e.g. alkali metal compounds such as sodium hydroxide) are introduced into a flame they have the ability to disrupt the chain-branching of free radicals (a process known as radical scavenging) in the flame that occurs during combustion, as part of the underlying chemical reaction mechanism [5, 6]. Under the right conditions such additives therefore have the potential to inhibit the combustion process, reducing the burning velocity of the flame and mitigating the overpressure in a vented explosion.

Water mist also has the potential to mitigate the effects of an explosion. When transported into the flame reaction zone water mist droplets will evaporate extracting heat from the flame, reducing the

rate of reaction and the burning velocity at which the flame propagates [7-9]. However, only a very limited amount of previous work has looked specifically at the application of water mist to the mitigation of hydrogen deflagrations (e.g. [10]) and the consequent effect upon the burning velocity of a hydrogen flame. There is also relatively little information about how the mitigation performance of fine water mist might be augmented through the additional use of nitrogen dilution and fogs containing chemical additives such as sodium hydroxide.

This paper provides an overview of work that has recently been carried out at London South Bank University (LSBU) to help address this knowledge gap using both a burning velocity rig [11] and a small scale cylindrical explosion vessel [12], to explore and obtain data to characterise the performance of very fine water fog, both alone, and in conjunction with nitrogen dilution and sodium hydroxide additives, in the mitigation of hydrogen deflagrations.

The hydrogen-oxygen-nitrogen mixtures used in the experimental work were defined in terms of the equivalence ratio, ϕ, and the oxygen index, Ω. The equivalence ratio, ϕ, is defined as the ratio of hydrogen to oxygen in the mixture relative to that found under stoichometric conditions. For stoichiometric hydrogen mixtures $\phi = 1$. For lean hydrogen mixtures $\phi < 1$, whilst for hydrogen rich mixtures $\phi > 1$. The oxygen index (or fuel-free oxygen fraction), Ω, is defined as the ratio of oxygen to oxygen and nitrogen in the mixture (i.e. $O_2/(O_2 + N_2)$ – expressed here as a percentage - and provides a measure of the nitrogen dilution level and the extent to which the oxygen level has been reduced. For air, $\Omega = 21\%$. For $\Omega < 21\%$ (i.e. with increased levels of nitrogen present) the level of oxygen in the gas mixture is depleted).

2.0 BURNING VELOCITY INHIBITION

2.1 Experiment

Fig. 1 shows a diagram of the fog generation and burner system used to determine the burning velocity [11]. To help stabilise the flame front a Mache-Hebra type nozzle was used and a flow-straightener was inserted into the widest part of the nozzle. The burner nozzle was mounted directly on top of a small chamber housing the ultrasonic fog generator and supplied with premixed H_2-O_2-N_2 gas mixtures from a blending panel. The chamber apparatus was mounted on a balance so that the mass loss rate and fog density could be determined. A small fan was used to ensure the fog and gases were adequately mixed. The water fog in the chamber was generated using a commercial fogger unit. The fogger unit in-turn was comprised of five discrete piezoelectric discs which were driven by a high frequency power supply operating at 1.65 MHz. The droplet size distribution of water fog generated by the 5-disc ultrasonic unit was determined using a Malvern Spraytech laser diffraction particle sizer unit. The water fog produced was very fine and approximately monodisperse in nature with a Sauter Mean of around 5 to 6 μm and a $D_{V,90}$ around 10 μm. In some experiments, when required, NaOH up to 5% by mass could also be added to the water being fogged.

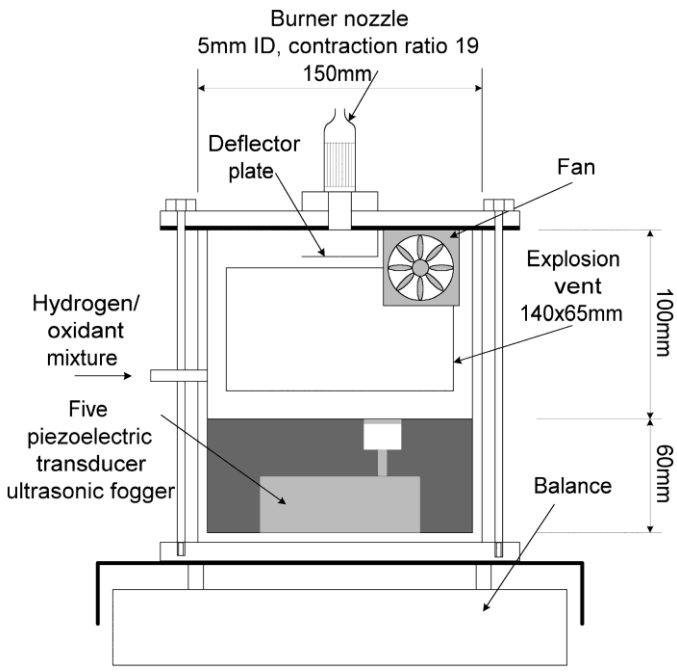

Figure 1. The burning velocity measurement rig

2.2 Results

A series of experiments was carried out to characterise the burning velocity for H_2-O_2-N_2 mixtures with equivalence ratios ranging between 0.6 and 3, water fog densities varying between 0 and 250 mg/l and oxygen index levels set at 21%, 16% and 10%, An additional series of experiments was also conducted using water fog containing a 0.5 M NaOH solution.

Fig. 2(a) shows an example of a schlieren image of the typical stable hydrogen flame cone formed for a fuel rich H_2-O_2-N_2 mixture with no water fog present. Fig. 2(b) illustrates the inhibiting and de-stabilising effect of the water fog upon the flame cone (which was worse for lean mixtures), causing it to become stretched and extended, forming a long and relatively thin "tail" at a reduced burning velocity.

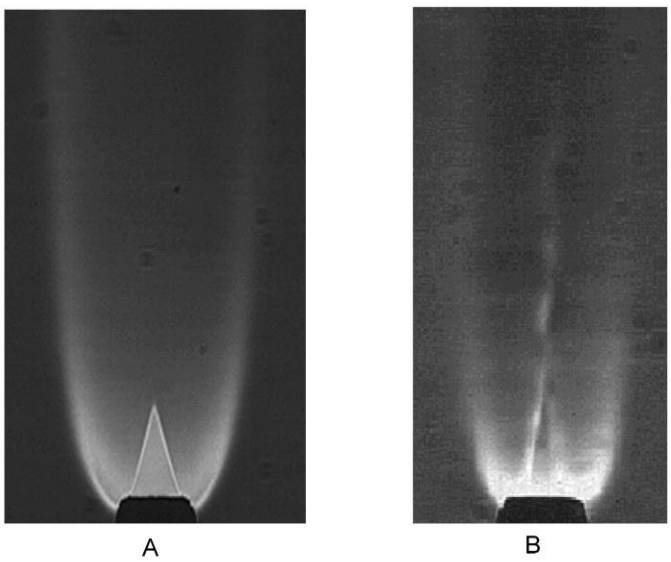

Figure 2. Schlieren images of the H_2-air burner flame: (a) without fog, (b) with fog

Figs. 3 and 4 summarise the effect of increasing water fog density upon the variation in the burning velocity with the equivalence ratio of the H_2-O_2-N_2 mixture, for O_2 index = 21% (air) and 16% respectively.

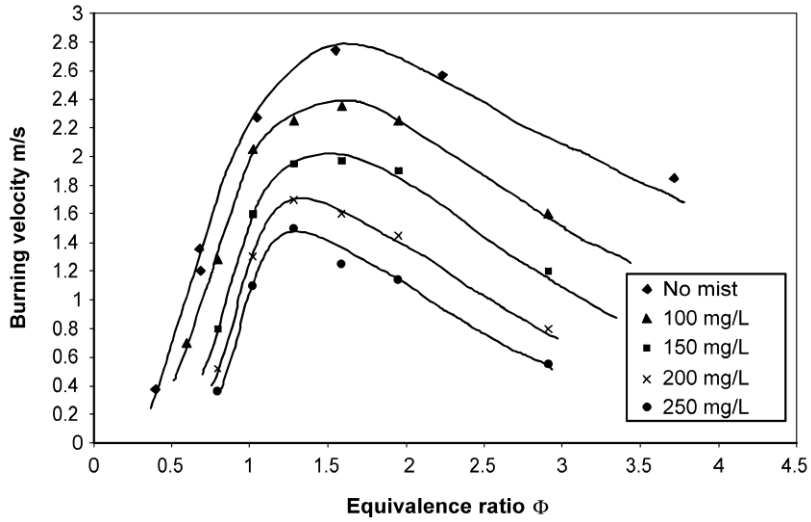

Figure 3. The effect of increasing fog density on the variation of burning velocity with equivalence ratio for H_2-air flames (Ω = 21%).

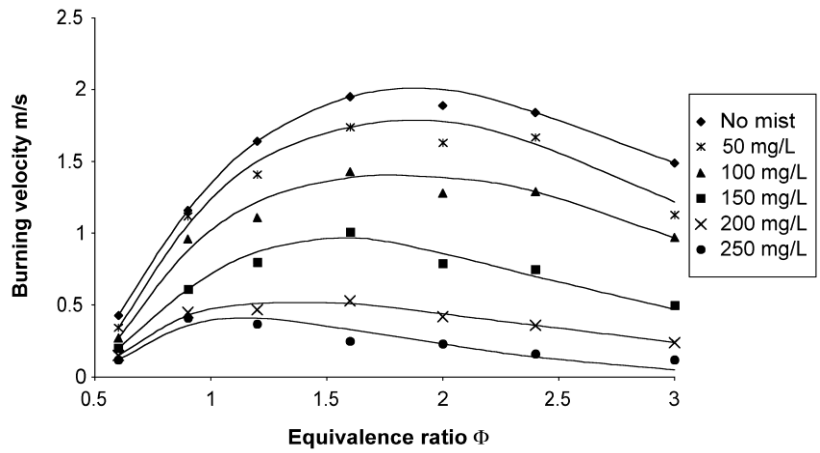

Figure 4. The effect of increasing fog density upon the variation of burning velocity with equivalence ratio for nitrogen diluted H_2-O_2-N_2 flames (Ω = 16%)

The effect of using a NaOH additive in the water fog upon the burning velocity of the flame was also examined. Fig. 5 shows a comparison of the variation in the burning velocity observed for a H_2-air flame with ϕ = 2 using water fog only, with that found using fog containing 0.5M NaOH. For fog densities less than about 170 mg/l the burning velocity obtained using NaOH solution is similar to that found for fog. However above this density the NaOH solution produces an abrupt reduction in the burning velocity (i.e. a sharp downward transition to a low burning velocity) that is not observed when using water fog alone. Similar sharp transition behaviour was also observed across the range of (hydrogen rich) equivalence ratios (ϕ = 1.2, 1.6, 2.0) and nitrogen dilution levels (oxygen index, Ω = 21%, 16%, 10%) examined.

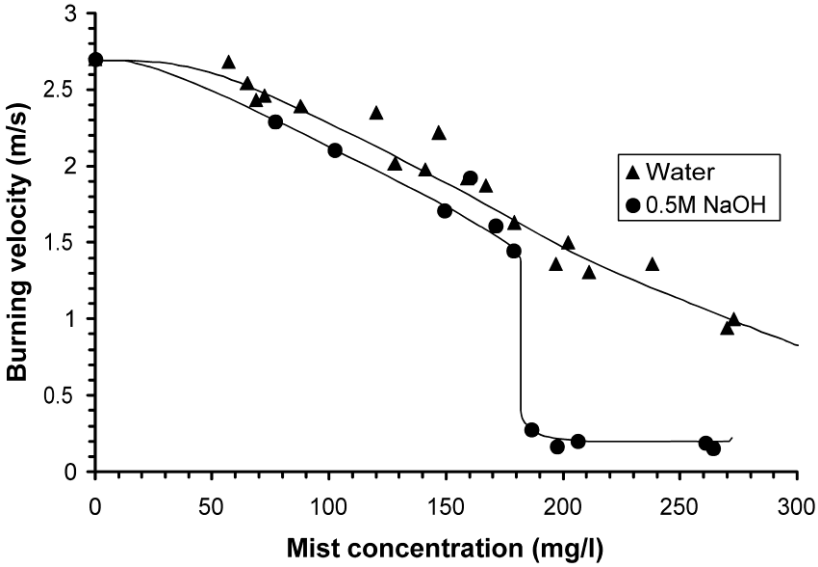

Figure 5. The effect of using water and 0.5 M NaOH fog upon the burning velocity of a H_2-air flame with $\phi = 2$.

3.0 OVERPRESSURE MITIGATION AND NARROWING OF FLAMMABILITY LIMITS

3.1 Experiment

A series of experiments were performed to determine the rise in overpressure for different H_2-O_2-N_2-fog mixtures and vent sizes. A detailed description of the cylindrical explosion vessel apparatus and the experimental test results obtained for the mitigation of hydrogen deflagrations is given in Battersby et al. [12]. The vented cylindrical explosion rig chamber (approximately 0.8 m high, with diameter 0.45 m), was filled with a pre-specified mixture of hydrogen-oxygen-nitrogen. Three different diameter vent sizes were employed in the tests: 300 mm, 200 mm and 100 mm, with two different foil thicknesses (0.015 mm and 0.025 mm). In addition a very fine water mist fog, of adjustable density, could also be generated inside the rig chamber using a (variable) number of 5-disc ultrasonic fogging units placed beneath the surface of water (or in some tests NaOH solution) filling the lower part of the chamber. The water fog density present in the vessel was determined on the basis of the number of 5-disc fogger units operating in the chamber. Fog density measurements for samples extracted from the vessel chamber were used to test the uniformity of the fog produced in the rig chamber and an empirical correlation between the stable water fog concentration developed in the chamber and the number of fogger units in operation obtained. An air driven fan (running at 750 rpm) was used to ensure adequate mixing and homogeneity of the hydrogen, nitrogen and water fog introduced into the vessel chamber atmosphere. The hydrogen and nitrogen was added over a period of around 3 minutes to ensure adequate mixing and was sufficient to allow the water fog to build up and reach a steady state concentration. A high energy 9 J exploding wire ignition source was then used to try to ignite the combined H_2-O_2-N_2 and water fog mixture and the resulting overpressure rise recorded using a pressure transducer mounted in the wall of the cylindrical vessel. The experimental test data obtained was also used to determine the flammability limits of the mixtures tested [13]. A schematic diagram and photograph of the cylindrical explosion rig chamber used to obtain the pressure rise data is shown in Fig. 6.

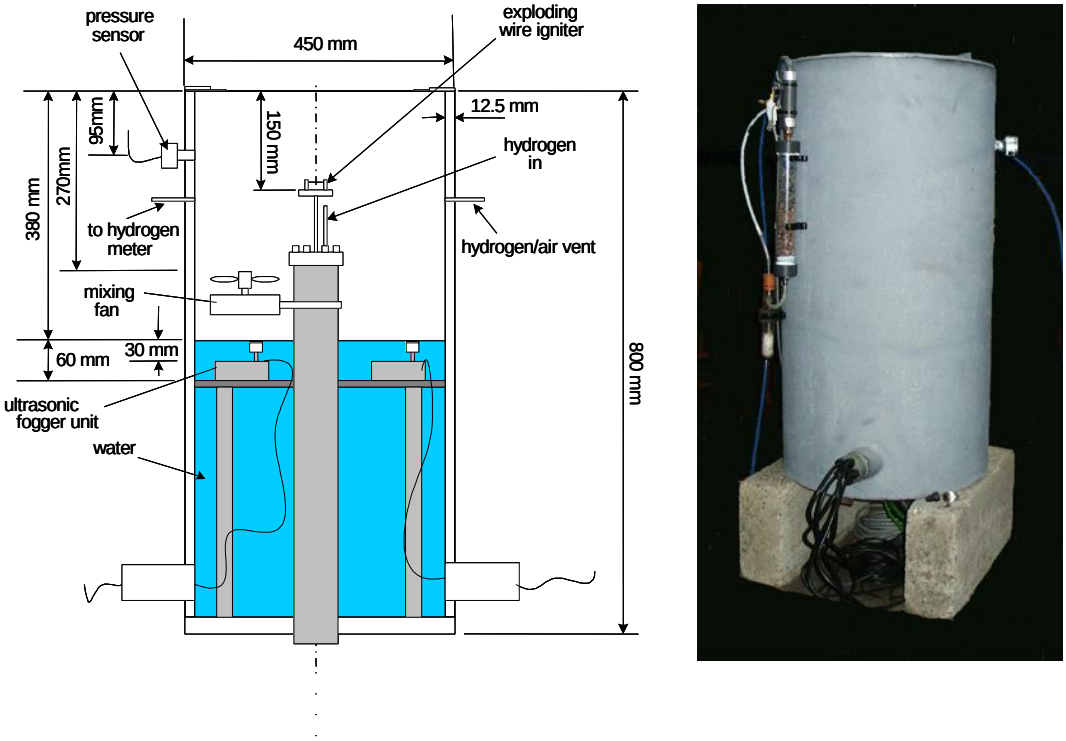

Figure 6. The LSBU cylindrical explosion rig.

3.2 Results

Some initial tests were conducted with a (nominally) unvented chamber using hydrogen-air mixtures (Ω = 21%) to show the effect of the water fog density upon the overpressures generated. Fig. 7 shows an example, illustrating the effect of increasing fog density upon the overpressure-time curve (ϕ = 0.39). It is evident that the presence of water fog at densities of 200 mg/l or more significantly reduces the rate of pressure rise and the magnitude of the peak overpressure obtained.

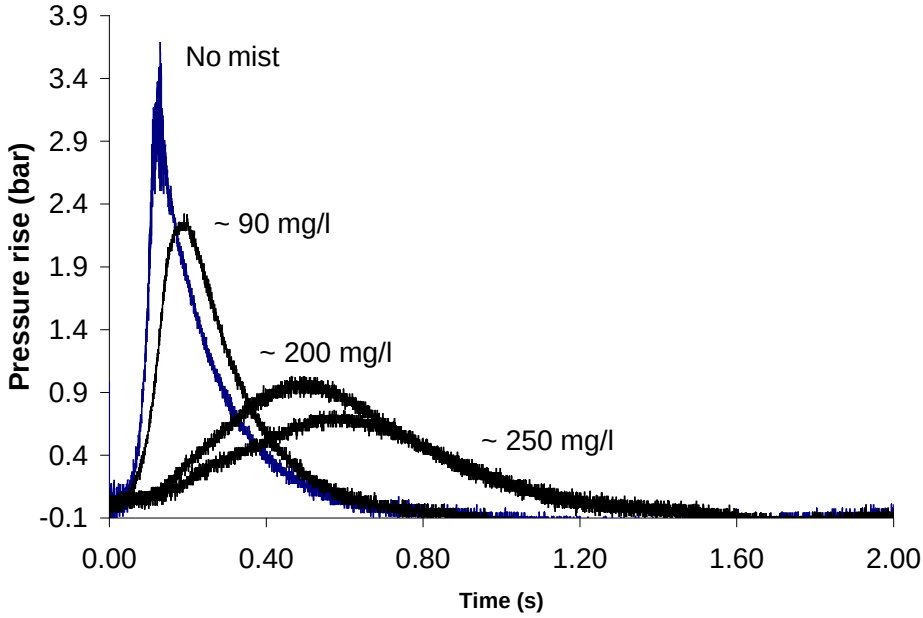

Figure 7. The effect of increasing water fog density upon the explosion overpressure versus time curves generated for H_2-air (ϕ= 0.39) ignitions in a nominally unvented chamber

A systematic test program was then performed to determine the effect of water fog density (ranging from 0 to 290 mg/l) upon the initial rate of pressure rise for general H_2-O_2-N_2-fog mixtures (in the vessel fitted with the 200 mm vent) with equivalence ratios of 0.35, 0.6, 1.2, 1.4, 1.6 and 2.4 and oxygen index values of 10%, 12.5%, 16% and 21%. When the maximum pressure rise produced in a given experimental test was less than 0.01 barg in magnitude the mixture tested was classified as being not flammable (to the 9 J exploding wire ignition source). Increasing the water fog density reduces the initial rate of pressure rise and narrows the flammability limits observed in H_2-O_2-N_2 mixtures. Fig. 8 shows the effect of varying water fog density upon the limits of flammability, suggested by the results of this test program. It is evident that both the upper flammability limit and total extent of the flammable region is reduced (in comparison with the fog-free limit obtained with nitrogen dilution alone) as the density of water fog is increased from 170 to 250 mg/l. The results also suggest that with a fog density above about 200 mg/l the location of the "nose" on the right hand side of the flammability curve is shifted from Ω = 7% to 10%, suggesting that a mixture with Ω less than 10% would then become inerted.

An additional series of experiments were then conducted to examine the effect of using a 0.5 M NaOH additive solution in the water fog upon the initial rate of pressure rise and location of the inerting (flammability) limits observed in the explosion vessel tests. The results of these tests indicate the existence of an inerting limit consistent with the location of the critical fog density behaviour observed in the corresponding burning velocity experiments performed with NaOH fog.

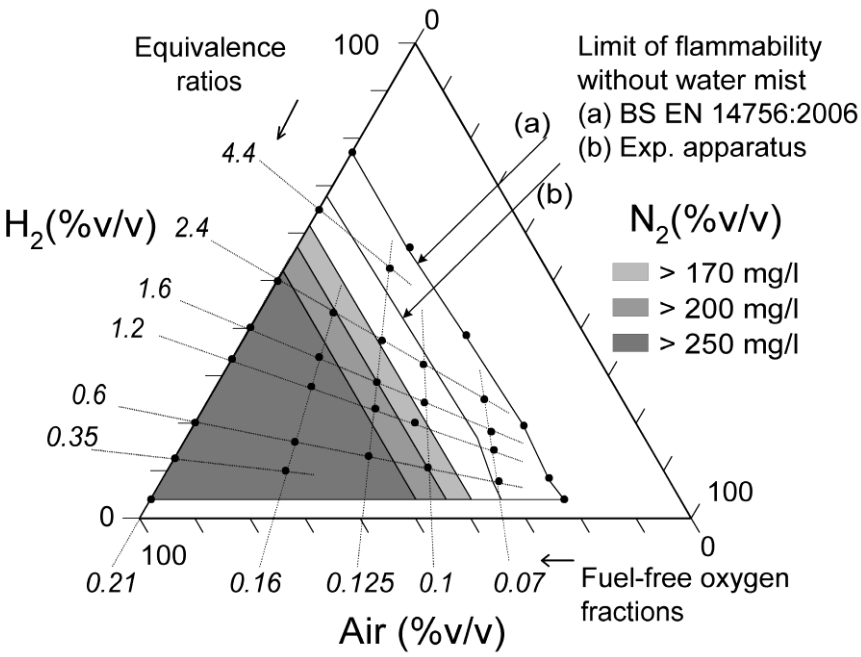

Figure 8. The effect of the water fog density upon the flammability limits for H_2-O_2-N_2 gas mixtures measured in the LSBU cylindrical rig

Fig. 9 shows the effect of 0.5 M NaOH fog upon the suggested limits of flammability of H_2-O_2-N_2 mixtures. By comparing it with Fig. 8 it can be seen that the effectiveness of the fog upon the flammability limits is considerably enhanced by the presence of NaOH additive, with significant relative reductions in both the size of the flammable region and the upper flammability limit.

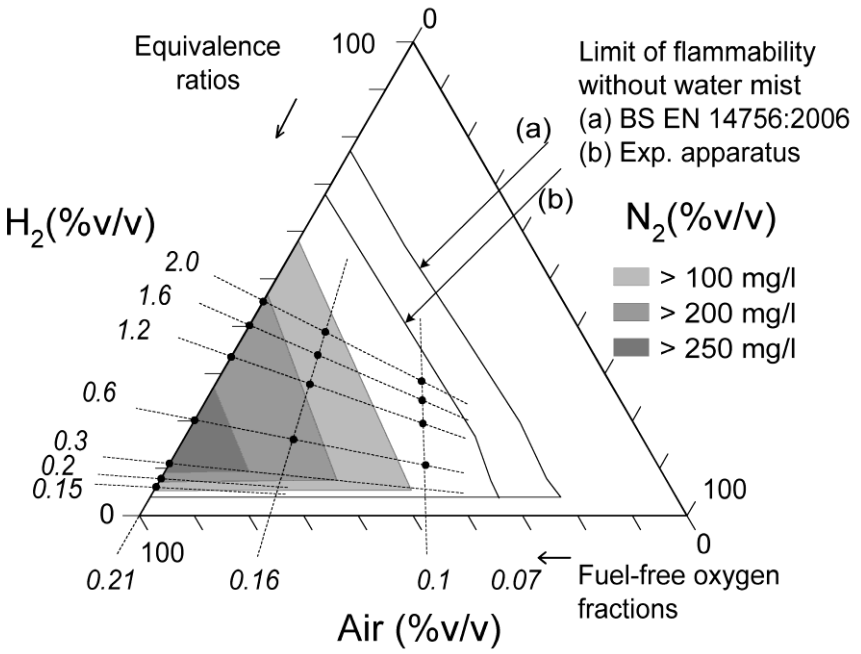

Figure 9. The effect of 0.5 M NaOH solution water fog upon the flammability limits of H_2-O_2-N_2 gas mixtures measured in the LSBU cylindrical rig

4.0 MODELLING STUDIES

The experimental data obtained using the burning velocity rig can be used to characterise the effect of water fog and nitrogen dilution upon the burning velocity of the hydrogen flames. This information was used as input to the FLACS CFD gas explosion code which was then used to numerically simulate the experimental explosion tests performed using the cylindrical explosion vessel. This has allowed the potential mitigating effect of nitrogen dilution (reduced oxygen) and very fine water fog, used both alone and in combination, to be explored and permitted their direct comparison with corresponding experimental test data. As an illustrative example, Fig. 10 shows a comparison of the simulated and experimental overpressure curves obtained for an 18% hydrogen-air (ϕ = 0.52) mixture with the 200 mm diameter vent and increasing number of fogger units operating. As the fog density is increased the rate of pressure rise is reduced and the secondary peak disappears, as does the slight over-shoot above the bursting pressure. Similar qualitative behaviour is also apparent in the corresponding experimental test data, with broadly similar times to the first pressure peak being displayed. For further details of the simulations performed and their comparison with the experimental pressure-time data see [14, 15].

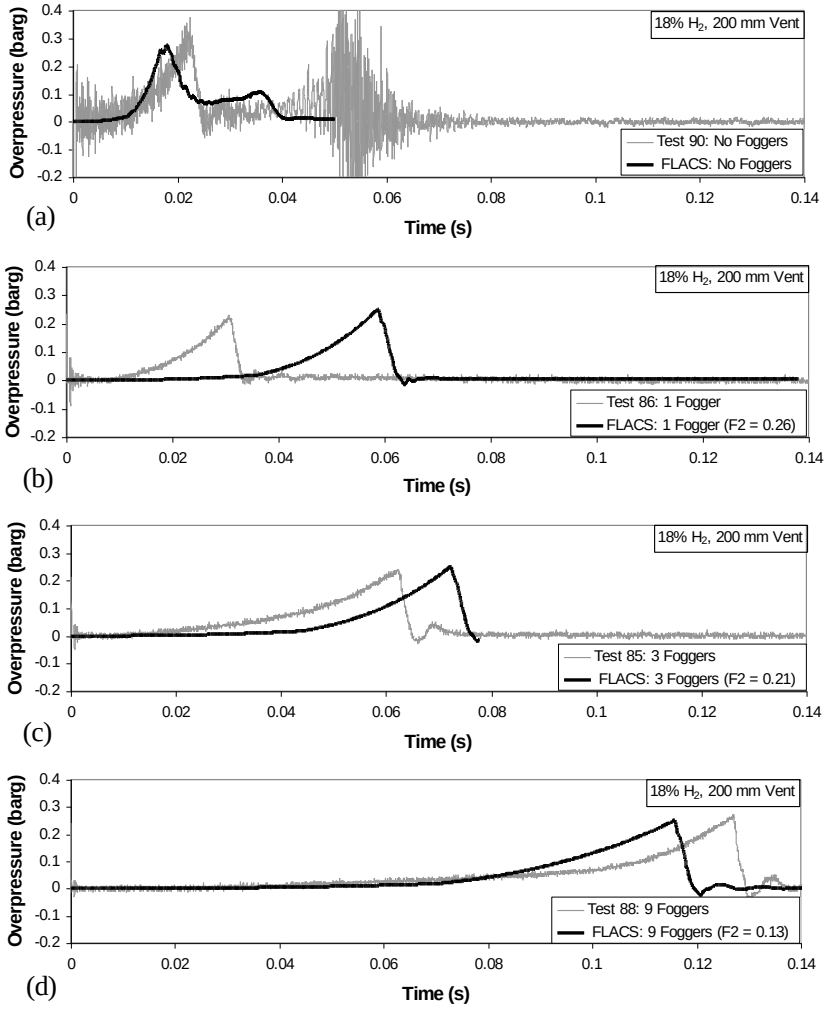

Figure 10. A comparison between the simulated and experimental overpressure-time curves obtained for H_2-air (ϕ = 0.52) explosions with an increasing number of fogger units operating

5.0 DISCUSSION

The results of this study suggest that using very fine water fog both alone and in combination with nitrogen dilution (reduced oxygen) can be effective in mitigating H_2-O_2-N_2 burning velocities and explosion behaviour. However, (relatively uniform) high fog densities may be difficult to achieve in larger spaces and could produce significant rain-out rates. It is also evident that higher fog densities become progressively harder to achieve as the number of ultrasonic units required increases. Measures that can lower the target fog density requirement (such as nitrogen dilution and sodium hydroxide additive) may therefore help to improve the practicality of this mitigation technology and widen the range of potential applications.

6.0 CONCLUSIONS

An experimental programme has been carried out at LSBU to explore and obtain data using both a burning velocity rig and a small scale cylindrical explosion vessel to characterise the performance of very fine water fog, both alone, and in conjunction with nitrogen dilution and sodium hydroxide additives, in the mitigation of hydrogen deflagrations. The study has shown that high density water fog (Sauter mean diameter 5 μm) can significantly reduce the burning velocity and rate of pressure rise of hydrogen-oxygen-nitrogen mixtures over a wide range of equivalence ratios and oxygen index levels.

Adding 0.5 M NaOH to water fog produces an abrupt reduction in the burning velocity of hydrogen rich mixtures above a critical fog density and significantly reduces the range of flammable H_2-O_2-N_2 mixtures. This transition point observed in the burner rig experiments was also shown to be in accordance with modified flammability/inerting limits that were determined for H_2-O_2-N_2 mixtures inhibited by water fog with NaOH additive in the cylindrical rig tests.

Water fog, nitrogen dilution and sodium hydroxide additive (to the fog) have complementary effects which serve to enhance their inhibitive capabilities. Hence, the results of the work suggest that using a combination of the three measures (water fog, nitrogen dilution and NaOH additive) together produces the optimal mitigation performance and can be extremely effective in: inhibiting the burning velocity, reducing the explosion overpressure and narrowing the flammability limits of hydrogen-oxygen-nitrogen mixtures.

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