CAN THE ADDITION OF HYDROGEN TO NATURAL GAS REDUCE THE EXPLOSION RISK?

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ABSTRACT

One of the main benefits sought by including hydrogen in the alternative fuels mix is emissions reduction – eventually by 100%. However, in the near term, there is a very significant cost differential between fossil fuels and hydrogen. Hythane (a blend of hydrogen and natural gas) can act as a viable next step on the path to an ultimate hydrogen economy as a fuel blend consisting of 8−30 % hydrogen in methane can reduce emissions while not requiring significant changes in existing infrastructure.

This work seeks to evaluate whether hythane may be safer than both hydrogen and methane under certain conditions. This is due to the fact hythane combines the positive safety properties of hydrogen (strong buoyancy, high diffusivity) and methane (much lower flame speeds and narrower flammability limits as compared to hydrogen). For this purpose, several different mixture compositions (e.g. 8 %, 20 % and 30 % hydrogen) are considered. The evaluation of (a) dispersion characteristics (which are more positive than for methane), (b) combustion characteristics (which are closer to methane than hydrogen), and (c) Combined dispersion + explosion risk is performed. This risk is expected to be comparable to that of pure methane, possibly lower in some situations, and definitely lower than for pure hydrogen.

The work is performed using the CFD software FLACS that has been well-validated for safety studies of both natural gas/methane and hydrogen systems. The first part of the work will involve validating the flame speeds and flammability limits predicted by FLACS against values available in literature. The next part of the work involves validating the overpressures predicted by the CFD tool for combustion of premixed mixtures of methane and hydrogen with air against available experimental data. In the end, practical systems such as vehicular tunnels, garages, etc. is used to demonstrate positive safety benefits of hythane with comparisons to similar simulations for both hydrogen and methane.

1.0 INTRODUCTION

One of the main benefits sought by including hydrogen in the alternative fuels mix is emissions reduction – eventually by 100 %. However, in the near term, there is a very significant cost differential between fossil fuels and hydrogen. Hythane (a blend of hydrogen and natural gas) can act as a viable next step on the path to an ultimate hydrogen economy as a fuel blend consisting of 8−30 % hydrogen in methane by volume can reduce emissions of pollutants such as NO_x (and greenhouse gases such as CO_2) while not requiring significant changes in existing infrastructure [1−2]. The use of hythane is able to provide the immediate emissions benefits that can justify the required investment in infrastructure. Depending upon the blend, many of the vehicles currently running on Compressed Natural Gas (CNG) will not have to have any modifications to run on hythane. It also does not lead to a significant loss of range as the blend only corresponds to 5−7 % hydrogen by energy.

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There may be several additional advantages of using a mixture of hydrogen and natural gas as compared to pure natural gas. It is well-known that lean operation reduces the NOx emissions significantly. The use of hydrogen increases the flame speed at lean conditions significantly making that regime practically accessible. It also reduces the ignition energy of the fuel (the ignition energy of hydrogen is an order of magnitude smaller than methane while the laminar burning velocity is an order of magnitude larger). The use of hydrogen also accelerates the methane combustion and increases the efficiency of catalysis at lower exhaust temperatures.

There is much focus on the promoting the use of Hythane in public transport infrastructure around the world for the last 20 years [1]. Studies and demonstrations were carried out in the 1990s. Extensive testing and optimization was used to determine the volume fraction of hydrogen that should be used. Several hythane-based transport fleets are in use around the world, including airport shuttles in San Francisco and buses in Beijing. The use of hythane is the most "cost-effective" use of hydrogen that is available today. It uses infrastructure that builds on and co-exists with natural gas stations. This infrastructure will continue to be useful in the ultimate hydrogen economy and a pre-approval of "hythane" is a good way to satisfy all regulatory and public perception requirements.

However, the authors have not been able to find many safety studies on the use of hythane in literature. Some work has been carried out as a part of the EC-supported NaturalHy project (www.naturalhy.net). These included experiments carried out in a congested rig [6] and also a chamber open at one end with and without obstacles. However, we are not aware of studies looking into the combined dispersion and explosion phenomena. This work seeks to investigate some of the safety features of hythane. In particular, it seeks to show that hythane may also be safer not only than hydrogen but also than methane. This is due to the fact hythane combines the positive safety properties of hydrogen (strong buoyancy, high diffusivity) and methane (much lower flame speeds and narrower flammability limits as compared to hydrogen). For this study, a typical hythane mixture with 20 % hydrogen is considered. The evaluation of (a) dispersion characteristics (which may be more positive than for methane), (b) combustion characteristics (which are closer to methane than hydrogen), and (c) Combined dispersion + explosion modelling is performed for some representative scenarios where gas-fuelled vehicles may be present.

The work is performed using the CFD software FLACS that has been well-validated for safety studies of both natural gas/methane and hydrogen systems, as well as some mixtures involving hydrogen/CO. The first part of the work will involve validating the flame speeds and flammability limits predicted by FLACS against values available in literature [3–5]. The next part of the work involves validating the overpressures predicted by the CFD tool for combustion of premixed mixtures of methane and hydrogen with air against available experimental data [6]. In the end, practical systems such as vehicular tunnels, garages, etc. are used to evaluate relative safety of hythane compared to similar simulations for both hydrogen and methane.

2.0 BRIEF DESCRIPTION OF FLACS

All the simulations have been carried out using the CFD tool FLACS. FLACS is a computational fluid dynamics (CFD) tool that solves the compressible Navier-Stokes equations on a 3-D Cartesian grid. The tool is used extensively for simulating problems relevant to process safety. It has specifically been designed for modelling the consequences of a flammable gas release in a semi-confined and/or congested region. The software consists of a pre-processing module (CASD) that is used to build 3D models for complex geometries and define the simulation grid and scenario parameters. Due to the use of a distributed porosity concept, FLACS can therefore be used to simulate most kinds of complicated geometries using a Cartesian grid. A good description of geometry and the coupling of geometry to the flow, turbulence, and flame are key elements in the modelling. The core simulator includes conservation equations for mass, momentum, enthalpy, mass fraction of chemical species, turbulent kinetic energy, and dissipation rate of turbulent kinetic energy. The SIMPLE method for pressure correction is used [7]. FLACS uses a standard k-ε model for turbulence with some modifications including a model for generation of turbulence behind sub-grid objects and turbulent wall functions [8]. The post-processing module Flowvis can be used to visualize the calculation results (in terms of several physical variables) as scalar-time curves, 2D contour plots, 3D plots, or volume plots in a static/dynamic form as required. Several explosion experiments used to develop and validate FLACS have been published [9–11]. In addition, a number of validation reports and more details about the software are available at GexCon's web pages [12,13].

3.0 HYTHANE FLAMMABILITY LIMITS AND REACTIVITY

As described above, the first step involved the validation of flammability limits and laminar burning velocities for hydrogen/methane mixtures. No data was found for the lower flammability limits (LFL) of hydrogen/methane mixtures. However, since the LFL values for the pure gases are quite close to each other (4 % vs. 5 %), it was assumed that the Le-Chatelier's law to calculate the flammability limits would give reasonable results.

The corresponding difference in upper flammability limits (UFL) is much larger. The UFL of methane-air mixtures is around 14 % methane in air while the UFL of hydrogen-air mixtures is around 75 % hydrogen in air. Therefore, the applicability of Le-Chatelier's formula was investigated. Wierzba and Ale [3] have experimentally determined the UFL of hydrogen/methane blends in air. Their results are compared with those obtained using Le-Chatelier's formula and a very good agreement is obtained. Thus, Le-Chatelier's law is applicable in this case for the calculation of both LFL and UFL and was implemented in FLACS for simulations involving hythane.

The laminar burning velocities calculated by FLACS were compared to data obtained experimentally by Ilbas et al. [4] and that obtained using numerical simulations with a detailed reaction mechanism by Di Sarli and Di Benedetto [5]. It was found that the predictions using the mixing rules available in FLACS based on oxygen consumption for each fuel were reasonable. In particular, FLACS predicts an increase of 10 % in the laminar burning velocity of methane-air mixture with the addition of 8 % hydrogen while the increase becomes 30 % with the addition of 20 % hydrogen. Thus, the laminar burning velocity values were used as such and no modifications were carried out.

The next step involved validation against available experimental data. For that purpose, recent experiments carried out by Shell in a congested rig were used [6]. These were presented in the 2nd International Conference of Hydrogen Safety in September, 2007.

4.0 VALIDATION AGAINST LARGE-SCALE EXPLOSION TESTS

Shell and HSL [6] have performed large-scale explosion experiments with mixtures of hydrogen and methane in a congested volume as part of the NaturalHy project. The geometry is shown in Figure 1. The pipe array has dimensions 3 m × 3 m × 2 m. In the lower 1 m there are 9 rows of vertical pipes (26 mm diameter) in each direction outwards (typical spacing 0.15 m), whereas in the upper 1 m there were 7 layers of horizontal pipes of the same diameter and spacing. More details can be found in [6]. Five different methane/hydrogen gas mixtures were applied in the tests, these were 0 %, 25.5 %, 51 %, 75 % and 100 % hydrogen. The pure hydrogen-air mixture had an equivalence ratio of 1.28 (fuel-rich), while the other mixtures were closer to stoichiometry (ER = 1.06–1.09). The ignition source was placed in the middle of the lower part (0.5 m above ground). The validation results are shown in Figure 2 where the pressure decay with distance for various sensors is shown. The top plot shows the results for sensors placed parallel to the wall (see Figure 1) and the bottom plot presents the results for sensors placed perpendicular to the wall at different distances.

Figure 1 Overview of the pipe array, vertical wall to the right, and monitor arrays parallel (M1–M7) and perpendicular (M8–M10, M15) to the wall.

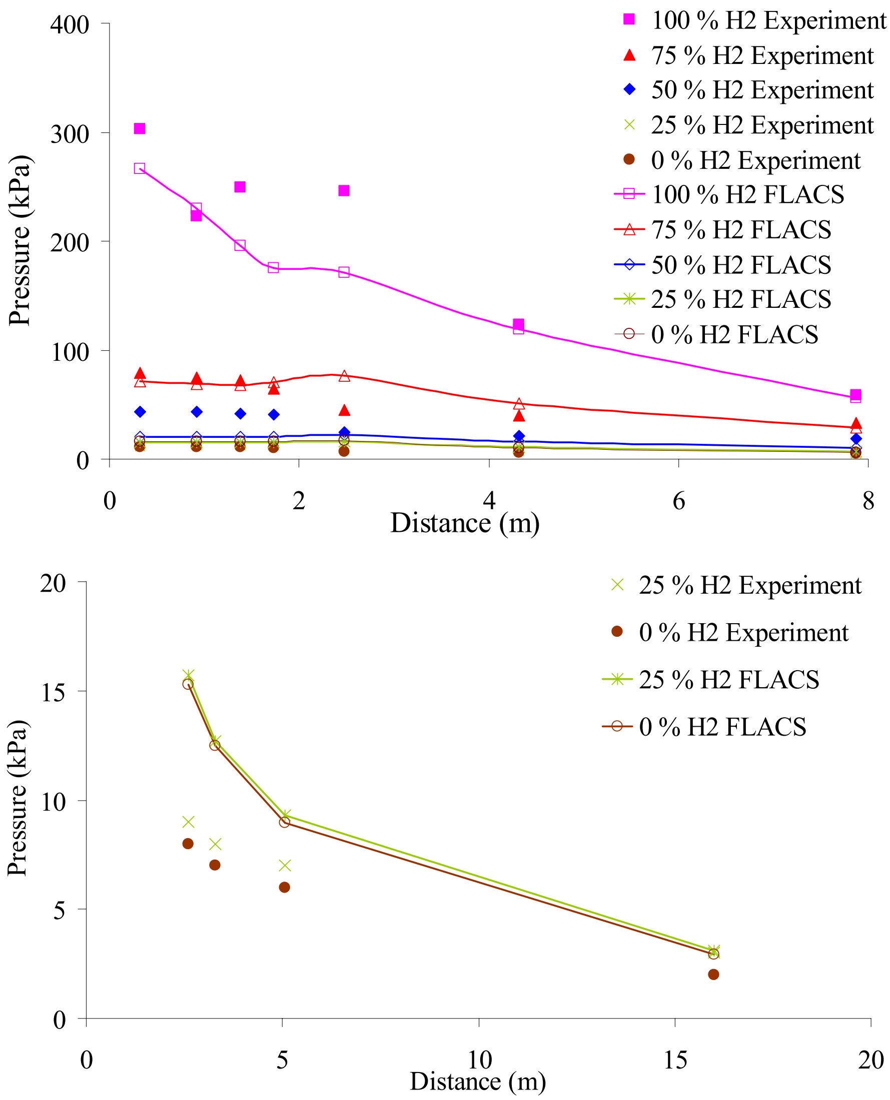

Figure 2 Pressure recordings (filled markers) versus FLACS simulations (lines) in monitor arrays parallel (M1-M7) parallel to the wall (top) and sensors away from wall (M8, M9, M10 and M15) (bottom) for methane- and hythane-air mixtures. Experimental observations are found in [6].

It can be seen that the pressure levels in the explosion are well reproduced for most mixtures. For the pure hydrogen mixture very high pressures were seen at when the flame exited the pipe array (due to deflagration-to-detonation transition DDT). Also the simulation gave very high pressures at the edge of the pipe-array, but since DDT is not modelled this did not give the observed local pressure increase at the sensor array parallel to the wall. In general simulated pressure levels correspond well to the experimental curves, however, in the case with 50 % hydrogen the pressure level seen in the experiment is almost a factor of 2 higher inside the pipe array (less deviation outside).

The second plot in Figure 2 shows the pressure decay up to 16 m away from the wall for the cases with pure methane and hythane with 25 % hydrogen. The FLACS simulations predicted somewhat higher pressures than seen in the experiments for both cases, but the relative effect of the addition of 25 % hydrogen is very similar to observed giving only a marginal pressure increase.

It may therefore be concluded that most experiments are reproduced reasonably well with FLACS, and that the relative effect of adding 25 % hydrogen to methane seems to be well predicted.

5.0 SIMULATIONS IN PRACTICAL SYSTEMS

A simulation study has been performed in order to evaluate comparative risk for hythane relative to methane and hydrogen. Three different release scenarios were evaluated, all originating from a pressure relief device (PRD). These are:

1. Gas release from a car in a private garage
2. Gas release from a car in a public parking garage (two release locations)
3. Gas release from a bus in a typical US tunnel

The simulations were preformed to evaluate potential worst-case scenarios. However, it must be pointed out that an explosion after a PRD release is considered to be a very low probability event, since the PRD is designed only to activate during fire. Many industry representatives therefore are of the opinion that PRD releases will ignite immediately, and that explosions as a result of delayed ignition cannot happen. Other release scenarios (excluding tank failure which is also considered unlikely) are much less severe, and we would only expect these to be of concern for the private garage scenario due to a low room volume. Due to incidents and testing in the past, and the fact that unexpected failures are often the cause of major accidents, we think it is relevant nonetheless to study PRD releases with late ignition. This may also be supported by the US Hydrogen Research Advisory Council [15] which has prioritized further work on PRD reliability as one of 6 high priority topics for future research within hydrogen safety.

The release rates are shown in Figure 3. The PRD system configuration is assumed similar to those used in a previous study [16]. Hythane is assumed to be using methane storage systems, with 20 % of the natural gas replaced with hydrogen. The two kinds of vehicles (with the respective fuel amounts) considered are:

1. Car: 4 kg hydrogen (700 bar) or 26 kg methane (200 bar)
2. City bus 20 kg hydrogen (350 bar) or 104 kg methane (200 bar)

It must be mentioned that the hydrogen city bus release scenario only releases gas from one of the two PRD-systems, and a worst-case scenario could release another 20 kg hydrogen.

When comparing methane and hythane (20 % hydrogen) the mass of hythane is only 82 % of that of a methane tank and the energy content 95 % of a methane tank. Still, due to a higher flow velocity through the nozzle, the potential combustion energy for the released hythane is initially 5 % higher than for methane.

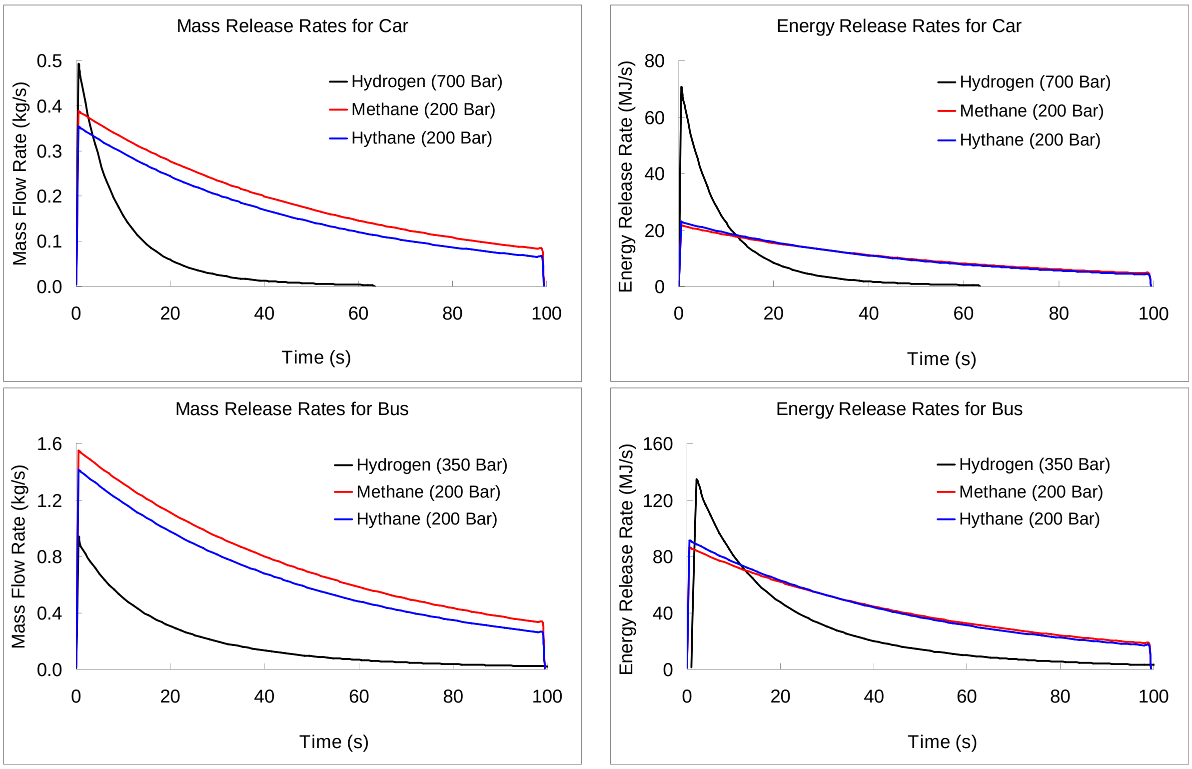

Figure 3 Mass release rates (left) and potential combustion energy release rate (right) for PRD releases from cars (upper plots) and buses (lower plots). It can be seen that even if less mass of hythane is released, the potential combustion energy of the released hythane is marginally higher initially.

5.1 Private garage release scenario

The first scenario is a two-car private parking garage attached to a house, with a floor area of 35 m^2. Two passive vent openings of 0.16 m^2 each (one near floor and one near ceiling) are defined with the purpose of removing dense or buoyant gases being released. Dispersion simulations were performed for methane, hydrogen and hythane PRD releases. The development of the simulated releases can be seen in Figure 4.

These simulations clearly showed how the PRD release would quickly fill up the available volume. The concentration in the room is almost uniform due to a high flow velocity. For hydrogen after less than 5 s the mixture is close to stoichiometric, after 20 s the hydrogen concentration is around 60 % by volume. When the release is stopped, hydrogen gradually flows out of the upper vent opening and replaced by air (after 500 s half the volume is still flammable). Because of the very wide flammability limits for hydrogen, practically all of the room is within the flammability limits the first 4 minutes, and thereafter cold air is coming in near the floor and pushing the buoyant hydrogen out of the upper vent opening over the next 10 minutes.

For the methane and hythane scenarios the development is different. These two gases have a much more limited flammable range (LFL:UFL), and within roughly 30s the whole garage ends up at concentrations above the upper flammable limit (UFL) and can not be ignited. Before this, after around 15 s, very reactive concentrations of gas can be seen in most of the room. When the release is stopped, the venting mechanism is similar to that of hydrogen, where a too rich (to burn) concentration of gas is lifted by cold air coming in near the floor. During this venting process, there is only a thin layer of gas which has been diluted by air to become flammable (in the simulations this represent around 20–25 % of the garage volume). It can be seen that from Figure 5 that the flammable cloud for resulting from a hythane release is initially larger than that from a methane release, whereas the values are very similar during the venting process afterwards.

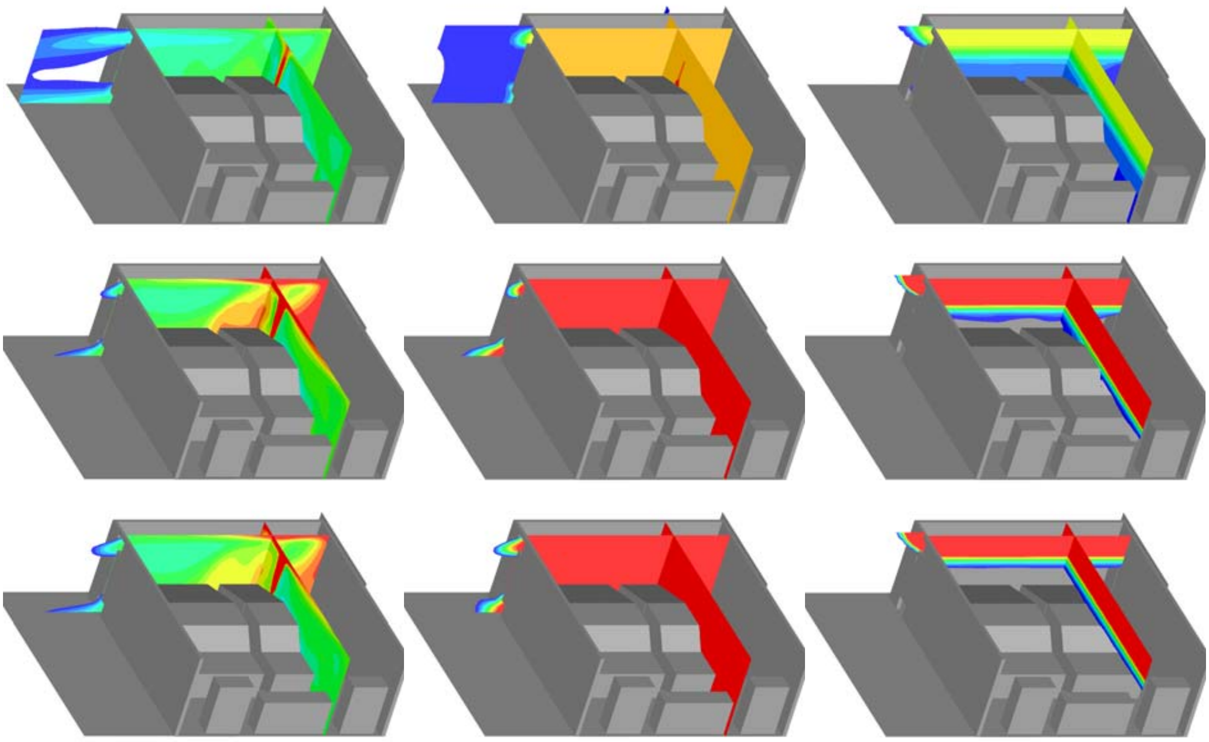

Figure 4 Simulated hydrogen gas clouds 4 s, 20 s and 200 s after start of release (top), methane gas cloud 14 s, 26 s and 500 s after start of release (middle), and hythane gas cloud 14 s, 30 s and 500 s after start of release (bottom). Red colour indicates concentrations at or above the upper flammability limit UFL, whereas green colour is around stoichiometry (most explosive concentration).

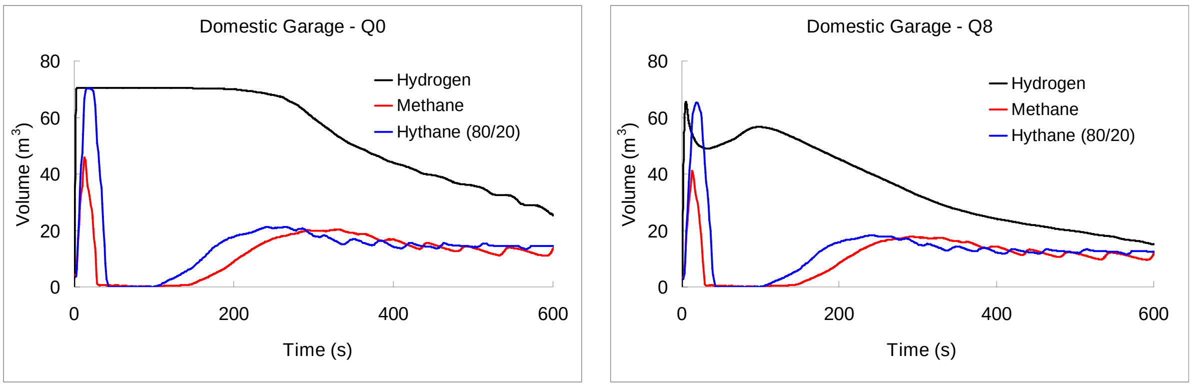

Figure 5 Flammable gas cloud volume (left) and expansion based equivalent stoichiometric cloud (right) for hydrogen, methane and hythane.

In order to evaluate the hazard of a given gas cloud, methods have been developed that aim at estimating an equivalent stoichiometric gas cloud with comparable explosion consequences. The size of the equivalent stoichiometric cloud at the time of ignition is calculated as the amount of gas in the flammable range, weighted by the concentration dependency of the flame speed and expansion. For a scenario of high confinement, or a scenario where very high flame speeds (faster than speed of sound in cold air) are expected (either large clouds or very congested situations), only expansion based weighting is used (denoted as *Q*8). For most situations lower flame speeds are expected and the conservatism can be reduced. Here a weighting of reactivity and expansion is used (denoted as *Q*9). More details are given in [16].

Explosion calculations have been carried out for each of these scenarios in order to estimate the expected worst-case explosion loads that can be expected if such a scenario would occur. In this case, the cloud at the time of maximum estimated equivalent stoichiometric gas cloud (Q8 for high confinement scenarios like this) is ignited in the inner end of the garage near the floor (expected worst-case ignition location with long flame travel distance to the opening). The large garage gate is assumed to yield at 50 mbar. The explosion pressures are shown for the 3 cases are shown in Figure 6.

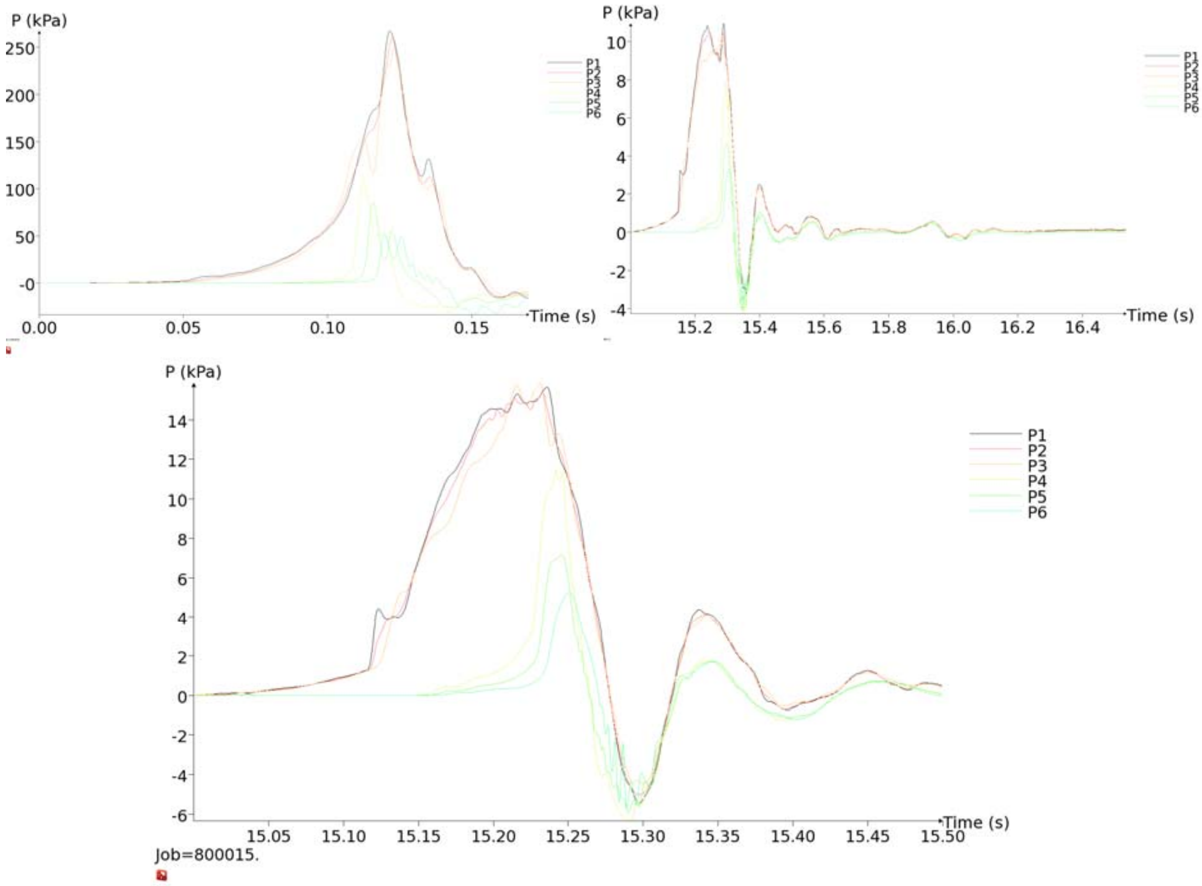

Figure 6 Explosion pressure for realistic worst-case hydrogen (top left), methane (top right) and hythane explosions (bottom). The various curves correspond to six different sensor locations placed inside the garage.

While the hydrogen overpressures (400 kPa) get very high, and would definitely destroy the adjacent house, the methane (11 kPa) and hythane (15 kPa) pressures should be less of a concern. These would probably destroy the garage, but the damage to the adjacent house would be much less extensive. The reason for the slightly higher pressure seen in the explosion with hythane compared to methane is mainly a larger gas cloud as seen in Figure 5, and to a less extent the higher reactivity of hythane.

5.2 Public parking garage release scenarios

Calculations have also been carried out for potential releases in a typical public parking garage. The model of such a garage can be seen in Figure 7. The garage has 3 underground levels. The release scenarios considered were PRD releases from a car either in the middle of the large open area with flat ceiling (2.75 m height) or in a more confined corner with lower ceiling (2.50 m height) in which some significant structural beams in the ceiling give some extra confinement. Both release scenarios were assumed to occur on the 2nd deck.

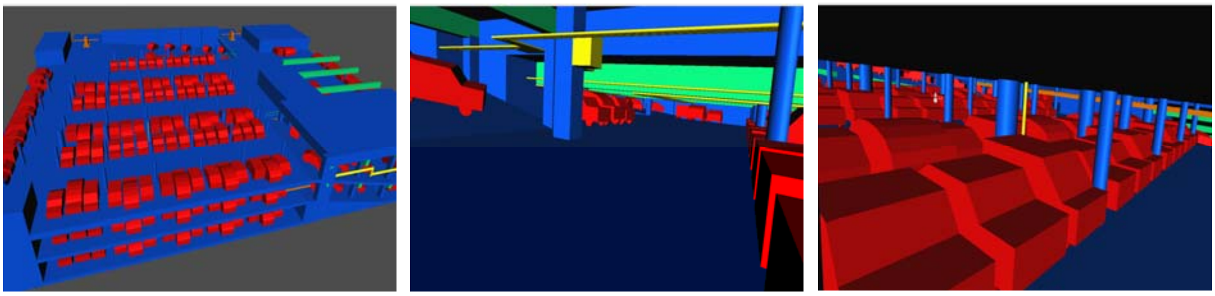

Figure 7 FLACS representation of a three-level underground public parking garage (left picture). The two right pictures show the two different release locations: middle of an open area with flat ceiling (middle) and corner with a lower ceiling and some significant structural beams (right).

The gas cloud development for the hydrogen release for the release in the open scenario with flat ceiling is shown in Figure 8. Initially, before the flow pattern has been established in the air, there is a gas pocket near the ceiling with concentration close to stoichiometric. However, this layer of gas with concentrations of significant concern disappears quickly due to an established flow field and a reduced release rate. The sizes of the flammable cloud and equivalent stoichiometric cloud (Q9) as a function of time for the both the release scenarios are shown in Figure 9. It can be seen that the maximum flammable clouds for hydrogen (200–500 m^3, the values being higher for the corner release) are much larger than that of methane and hythane (8–40 m^3). Most of the cloud volume is however quite dilute with concentrations near the lower flammable limit and is therefore of low reactivity. This can be seen by the fact that the estimated equivalent stoichiometric cloud is much smaller than the total flammable cloud. The maximum estimated equivalent cloud size for hydrogen is 5–8 m^3 while that for methane and hythane is 2–8 m^3. For the centre release scenario no accumulation of gas takes place, and the hazard quickly disappears. Due to increased confinement for the corner release scenario, it takes slightly longer for the gas to diffuse away.

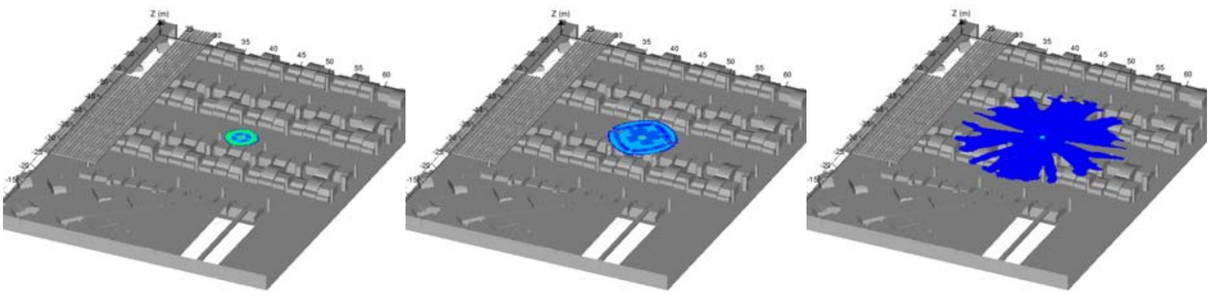

Figure 8 Hydrogen concentrations near the ceiling following a PRD release from a car 0.5s, 1s and 5s after the onset of the release. Vertical structural beams cause the non-circular pattern seen in the middle and in the right picture.

Due to a much higher reactivity of hydrogen than methane and hythane, significant explosion pressures can only be found for the hydrogen scenarios, where pressures of the order 0.5 bar were seen in the simulations (jet-induced turbulence contributes to flame acceleration). Since the energy in the small flammable cloud is very limited, the pressures quickly decay with distance. For the scenarios with methane and hythane, predicted explosion pressures are very low (less than 10 mbarg) and should be of no concern.

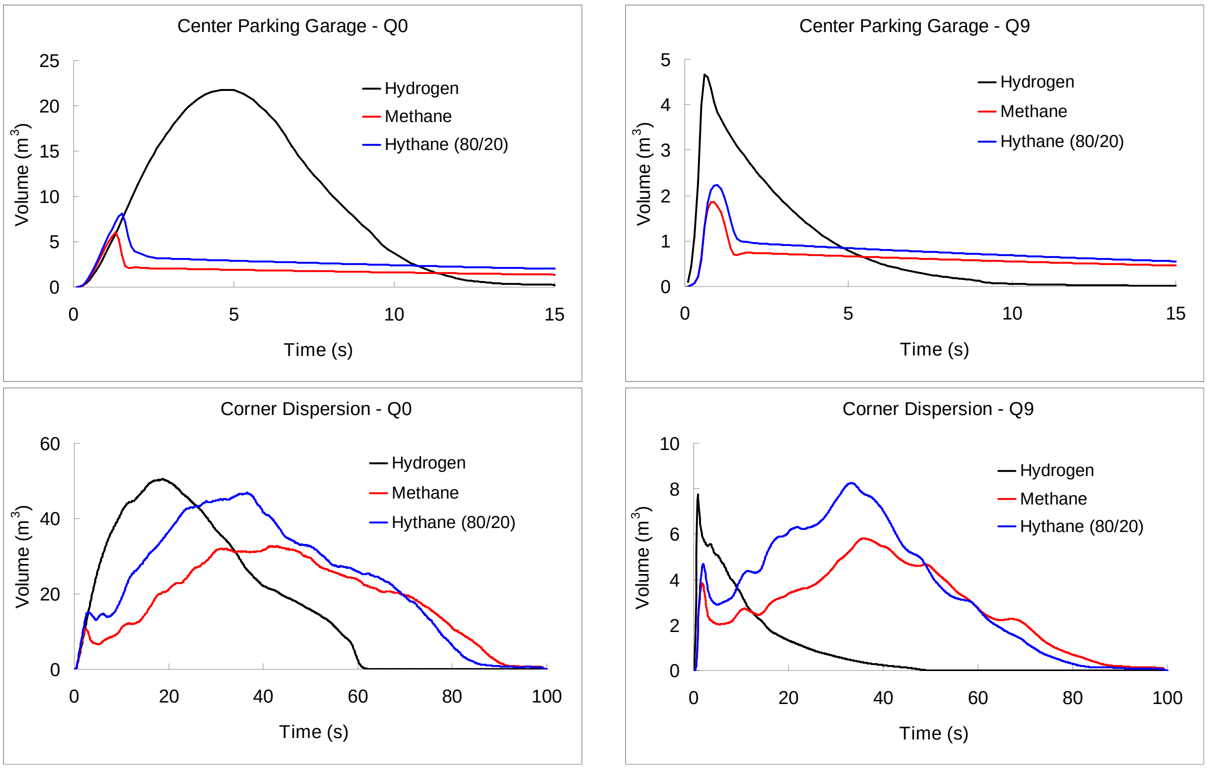

Figure 9 Total flammable volume (left) and equivalent stoichiometric gas cloud Q9 (right) for the centre (upper) and corner release scenario (lower). The total and equivalent Q9 flammable volumes for hydrogen are scaled down by a factor of 10 for both scenarios.

5.3 Tunnel release scenario

The third scenario evaluated is a typical US road tunnel. This is a one-directional tunnel with two lanes, and a cross section of about 6 m × 4 m, which is significantly smaller than used in a previous simulation study [16]. The tunnel is assumed full of vehicles (with a mix of cars, buses and trucks based on statistics) in a typical rush-hour situation (see Figure 10).

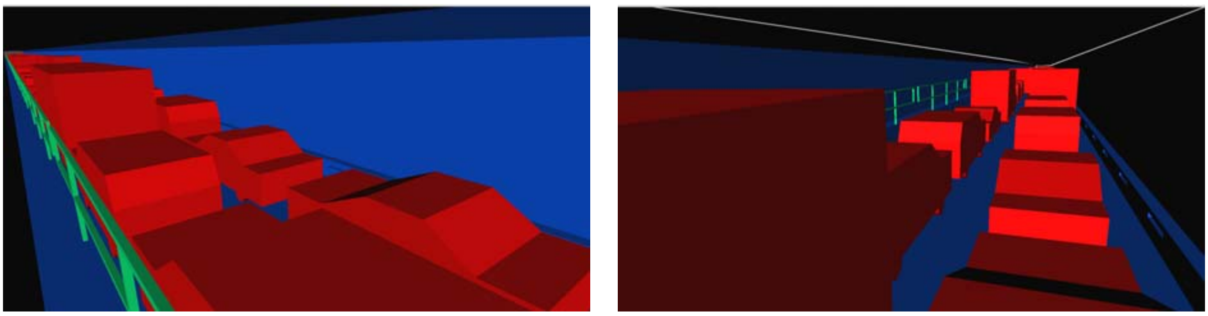

Figure 10 Tunnel geometry model with high traffic congestion

The release scenario is a PRD release from a city bus. The initial cloud development for the hydrogen cloud is seen in Figure 11. The predicted worst-case clouds for methane and hythane are shown in Figure 12 (see following). It can be seen from Figure 13 that the volume of the flammable cloud is twice as high for hydrogen as for methane or hythane, but the volumes near stoichiometry are much higher for methane and hythane (5 times higher Q9 equivalent stoichiometric cloud) than for hydrogen. Hydrogen reaches its estimated maximum severity after only 20 s, whereas methane and hythane may be at worst-case around 100 s. The main reasons for the differences may be that hydrogen leak profile decays faster, hydrogen disappears faster (due to higher release velocity and more buoyancy), and the lower buoyancy of methane and hythane makes it more likely to generate a dangerous gas cloud through the full cross-section.

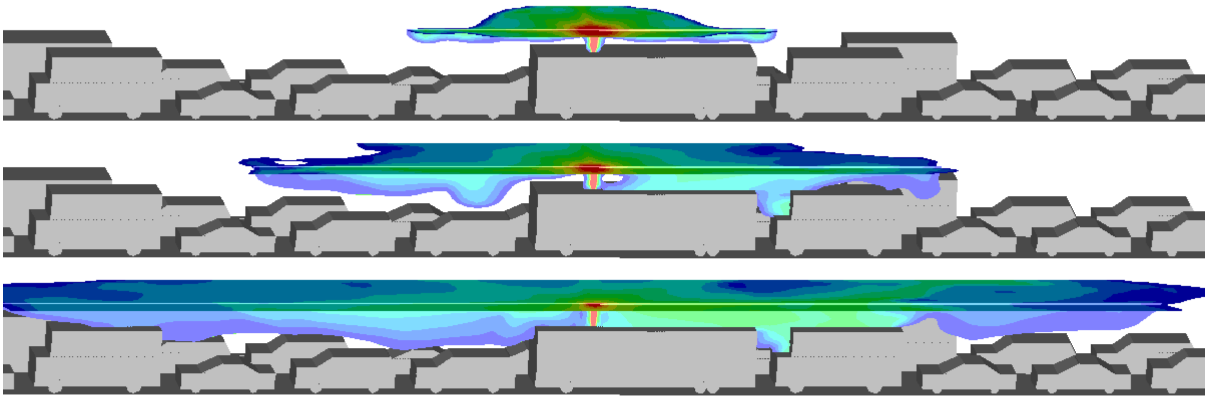

Figure 11 Hydrogen volume fractions in the tunnel geometry 1 s (top), 4 s (middle) and 12 s (bottom) after the beginning of the release. Concentrations around stoichiometry are shown in green.

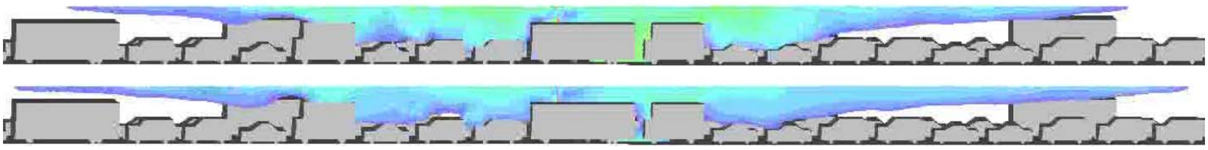

Figure 12 Methane (top) and hythane (bottom) flammable gas clouds 100 s after start of release in the tunnel geometry. The most reactive concentrations around stoichiometry are shown in green.

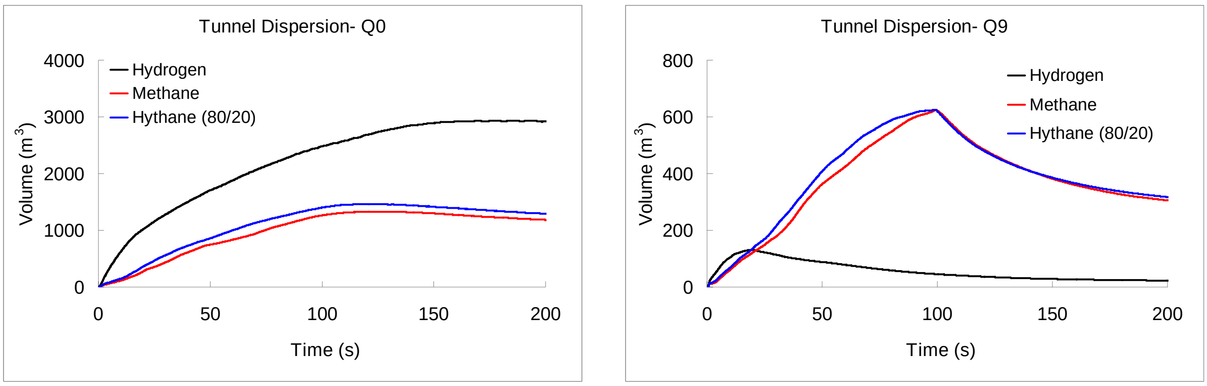

Figure 13 Flammable gas cloud volume (left) and Q9 equivalent stoichiometric gas cloud (right) for hydrogen, methane and hythane mixtures.

When igniting and exploding the dispersed clouds at the expected worst-case times (20 s for hydrogen and 100 s for methane and hythane), hydrogen still gives the highest overpressure due to a higher reactivity. But the methane overpressure is almost as high, and is in fact higher than the hythane pressure. These results are presented in Figure 14. In Figure 12 it can be seen that the hythane and methane gas clouds are of comparable size, but that the methane cloud seems to be somewhat closer to stoichiometry than hythane. Two possible explanations for this differences is that the hythane release rates decay somewhat towards the end of the release due to a higher flow rate initially, and also that the early jet momentum and thus mixing/dilution is somewhat higher for hythane than for methane.

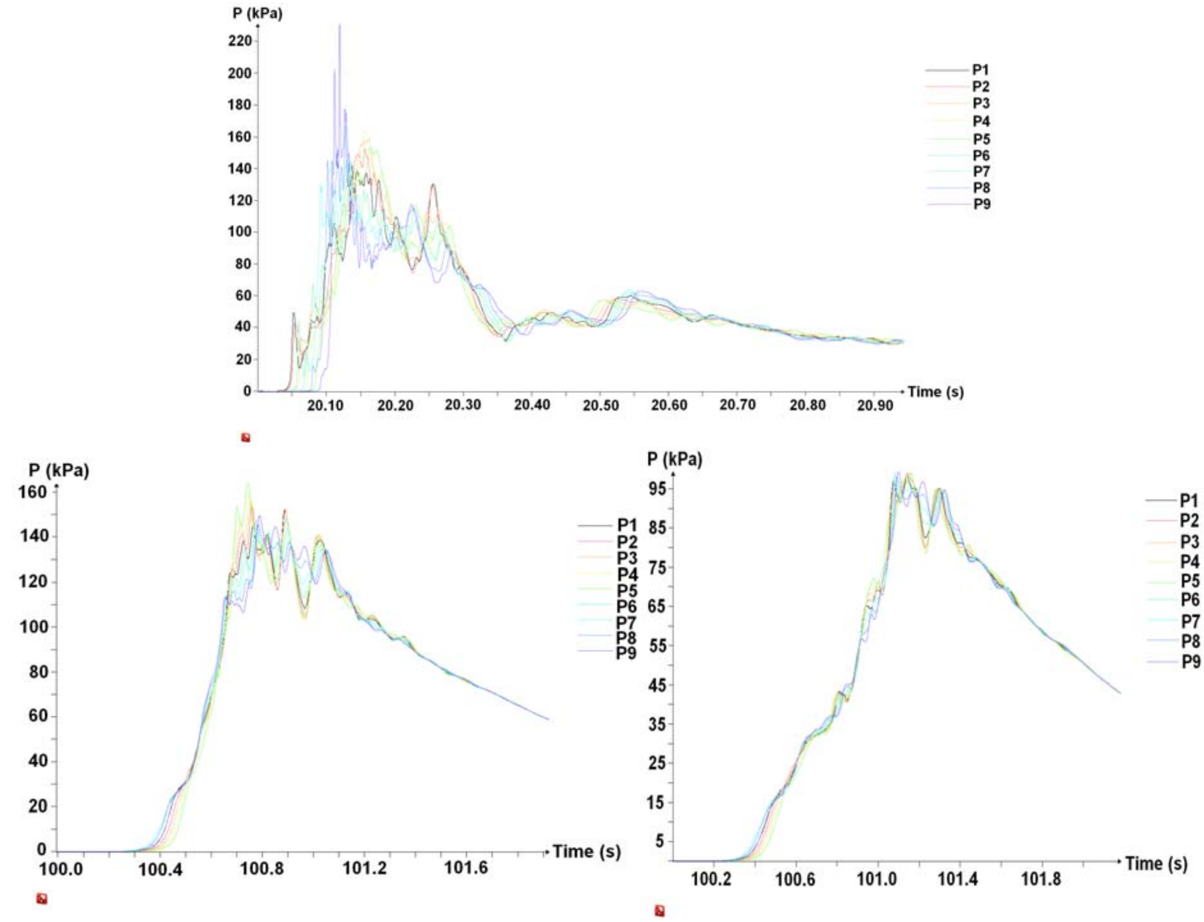

Figure 14 Worst-case explosion pressures with ignition at 20s for hydrogen (top) and at 100 s for methane (bottom left) and hythane (bottom right).

6.0. FINAL REMARKS

A simulation study has been performed in order to evaluate the safety aspects of hythane relative to methane and hydrogen. In general it was found that hythane explosions would be marginally stronger than methane explosions, and that both of these will give significantly lower pressures compared to pure hydrogen. In the tunnel case, however, somewhat higher pressures were seen with methane compared to hythane. The reason for this is probably that the methane gas cloud is closer to stoichiometry and more reactive than the hythane cloud. In this case, a methane release was seen to be more "dangerous" than a hythane release. However, no proper quantitative risk assessment has been carried out and the evaluations are only based on estimated worst-case cloud.

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