

CONDENSED PHASE EXPLOSIONS INVOLVING LIQUID HYDROGEN

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ABSTRACT

Liquid hydrogen may have an important role in the storage and transportation of hydrogen energy. It may also provide the best option for some users of hydrogen energy, notably the aviation sector.

In the 1960's liquid hydrogen spillages in open, uncongested conditions sometimes produced violent condensed phase explosions as well as the familiar gas phase flash and sustained pool fire. Testing showed that burning mixtures of LH2 and solid oxygen/nitrogen readily transitioned to detonation for oxygen concentrations in the solid phase at or above 50%.

Such explosive events have been observed in more recent research work on LH2 spillage and the pressure effects could be significant in some accident scenarios. There is a need to understand how solids are produced following spillage and what factors determine the level of oxygen enrichment.

This paper describes the physical processes involved in the accumulation of solids during a horizontal discharge at ground level, based on observations made in a recent HSE test that led to a condensed phase explosion. Areas where solids accumulated but remained in intimate contact with LH2 are identified.

The paper also includes a thermodynamic and fluid mechanical analysis of the condensation process that includes the calculation of densities of mixtures of LH2 and air in different proportions. When the difference in flow speed between air and underlying LH2 is low, a stable condensation layer can develop above the liquid where the temperature is just under the initial condensation point of air, allowing sustained oxygen enrichment of condensate.

INTRODUCTION

The explosive behaviour of liquid hydrogen when mixed with liquid oxygen and diluents was first of practical interest in the 1960's when liquid hydrogen was used as the fuel in all or some of the stages of the Saturn IV and Saturn V rockets. It was established that the explosive yield of hydrogen(1)-oxygen(s) mixtures was between 60 and 200% of that TNT (on a mass basis) in ideal conditions (Litchfield and Perlee, 1965) but could be significantly lower in the conditions of an open spill (Gayle et al., 1965). Detonation of hydrogen-oxygen mixtures could be triggered by an impulse of 1-2.5 kbar. Deflagration to detonation (DDT) transition also occurred rapidly if the surface of the mixtures was ignited (Litchfield and Perlee, 1965).

Further work was carried out on mixtures diluted with various materials including nitrogen, methyl chloride and sodium chloride. These substances desensitised the mixture to ignition by impact or explosives but did not affect the yield when detonation did occur (Litchfield and Perlee, 1965).

Of more significance to the potential use of liquid hydrogen as a low carbon fuel, it was established that for larger samples (more than a few tens of grams) DDT still occurred if the solid oxygen was diluted with nitrogen to around 50% (wt/wt) (Litchfield and Perlee 1965). For higher nitrogen concentrations (e.g. that of solidified air) the mixtures burned steadily to completion (as deflagrations) without exploding.

This means that if air condenses on the surface of a spill of liquid hydrogen the resulting hydrogen(1)-air(s) mixture may or may not pose a risk of condensed phase explosion if it is ignited. The outcome depends on the composition of the solidified air and the extent to which it has been enriched by oxygen.

More recent studies involving large outside spills onto concrete and onto large pebbles have sometimes shown significant condensed phase explosions just after ignition (Veser et al. 2021). It appears therefore that there are some flow conditions of practical significance that lead to oxygen enrichment and allow DDT - in a number of important spill scenarios. This suggests that the potential for condensed phase explosions should form part of an overall risk assessment for use of liquid hydrogen (LH2) – in additional to the obvious risks associated with pool fires and gas phase explosions.

This paper focusses on the case where a LH2 jet is discharged horizontally across a concrete surface. This might correspond to the flow out of an LH2 filling hose that becomes detached and falls to the ground. Hall (2014). reported a significant condensed phase explosion in this scenario for a 1 inch diameter outlet and release rate of around 135 g/s. The LH2 was close to its boiling point and the driving pressure was about 1 bar.

YIELD AND PHYSICAL FORM OF SOLID AIR DEPOSITS

Figure 1 shows one of the *unignited*, ground-level, horizontal liquid hydrogen jets studied by Royle and Willoughby (2014) and Hall (2014) in progress. The equivalent liquid volume flow rate was 1.9 litres/second, but vaporisation in the final section of the delivery system reduced the density of the two-phase release to 10-20 kg/m³, corresponding to a total volume flow rate at the nozzle of about 6.5 – 13 litres /second and a nozzle velocity of 13-26 m/s.



Figure 1: Spill onto concrete in progress

Unfortunately the flow of liquid along the ground is obscured by a thick cloud of condensed air. A purely liquid layer would have rained out from the two-phase mixture and it is likely that at some point the supercritical (shooting) liquid flow over the surface would have decreased in speed and increased in depth through a hydraulic jump.

The majority of the solid is at a range of about 2.7 to 3.5 m from the nozzle – extending to a width of about 0.5 m (Figure 2a and 2b). There is a smaller amount of solid material deposited on one edge of the jet. Although the wind was roughly aligned with the jet direction, the asymmetry in deposition

was presumably caused by a small component of the average wind perpendicular to the jet. Entrained air imparts transverse momentum to the flow of cold hydrogen and condensed air.

The total volume of the solid deposited (on partially pre-cooled ground) over a 7 minute period in the unignited test shown in Figures 1 and 2 was around 40 litres, which would amount to approximately 36 kg - assuming the deposit had the same density as nitrogen frost (Satorre et al. 2004).

The flow of LH2 would have vaporised as it moved away from the nozzle because of thermal contact with the ground and entrained air. As the heat transfer from the ground slackened, the primary source of heat to the LH2 flow at ground level must have been entrained condensing air. Examination of the yield of solid, and comparison with the maximum potential yield based on the LH2 supply and expected losses through heat transfer from the ground, suggests that a high proportion of the initially entrained air was locally deposited (Atkinson 2020). This suggests that the droplets/crystals of air components were large enough that they fell out rapidly rather than being carried away and further diluted with air. Note this was an approximate analysis; the maximum yield of solids depends on their average temperature and composition which was not known. The potential yield of oxygen enriched solid is much less than that possible for frozen air – because of the enthalpy carried away by the excess nitrogen.



Figure 2a: Solid deposits accumulated after 7 minutes



Figure 2b: Close-up of solid deposits accumulated after 7 minutes

Figure 3 shows schematically how the growth of a solid deposit might have proceeded.

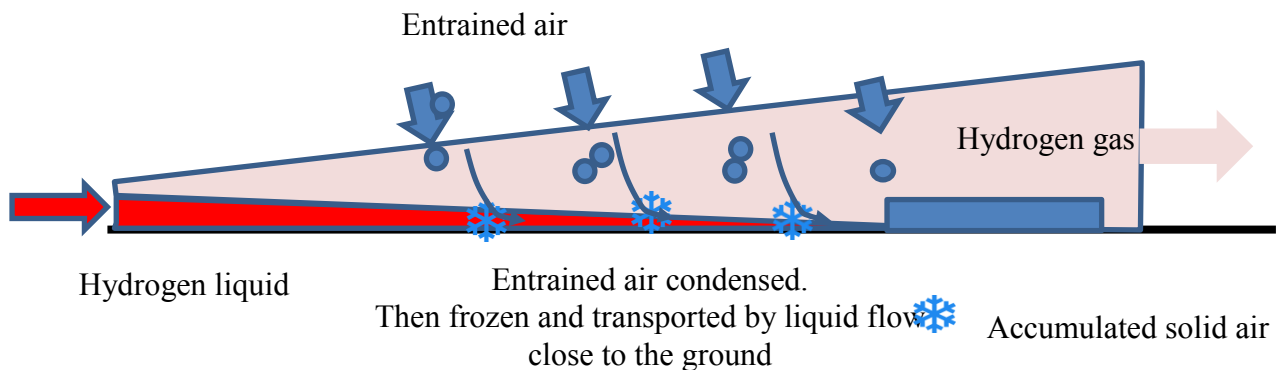


Figure 3: Schematic showing how solid deposits may accumulate

The final resting place of deposited frozen air droplets falling into the liquid would be at the limit of the rapid liquid flow and this seems to correspond to the distribution of solid shown in Figure 2. The accumulation of solids itself would eventually impede the flow of liquid along the ground and it may be that backing up of LH2 led to a widening of the area where solid was distributed and a gradual shift in the front edge of the deposit closer to the source.

Not all of the droplets of condensed air would fall on the liquid; some would fall out beyond this point, especially as extent of the liquid flow was restricted. In this case condensed air (potentially above the BP of hydrogen) would fall out on previously deposited material. This would finally produce a larger amount of solid deposit, at a temperature above the BP of hydrogen. There would also be ongoing heat transfer from overlying gas and the ground to the solids. Overall, only a proportion of the deposited material would have been cooled to LH2 temperatures.

Towards the end of the period of accumulation the majority of the solid mass would have been somewhat above the boiling point of hydrogen and therefore could not be in contact with LH2. However, solids right at the front of the mass would have still been in contact with liquid hydrogen. This is significant because it means that only a proportion of the observed solid deposit could potentially form detonable mixtures with LN2.

SCALE OF THE OBSERVED CONDENSED PHASE EXPLOSION

The condensed phase explosion occurred about 4 seconds after the initial ignition and vapour flash – a jet fire and pool burning were still in progress at this stage. Following the condensed phase explosion, the resulting fireball expanded to a volume approximating to a hemisphere of diameter 8 m - in less than 100 ms. As it lifted off, this fireball appeared to be at least as large as that associated with the initial flash fire following ignition (Figure 4). Higher radiant intensities were also observed. A cautious interpretation of the data available (as input to risk assessment) would be that the explosive power was similar to that of about 2 kg TNT (Hall, 2014).

The approximate hydrogen consumption necessary to fuel such a fireball can be estimated from its volume.

$$\text{Volume of combustion products} = 134 \text{ m}^3$$

Volume of stoichiometric STP hydrogen required = 19 m^3 (Assuming an expansion ratio of 7 for such a mixture). In this case the initial state of the fuel and oxidant may not have been gaseous and certainly not at STP but the final state in the fireball would have been fairly similar.

Volume of hydrogen required = $0.29 \times 19 = 5.5 \text{ m}^3$

Mass of hydrogen required = $5.5 \times .085 = 0.46 \text{ kg}$

It likely that only a proportion of this hydrogen was involved in the detonation – the remainder might be hydrogen liquid pooled close by, that was dispersed by the explosion and rapidly mixed with either solid air deposits or ambient air to further contribute to the fireball.

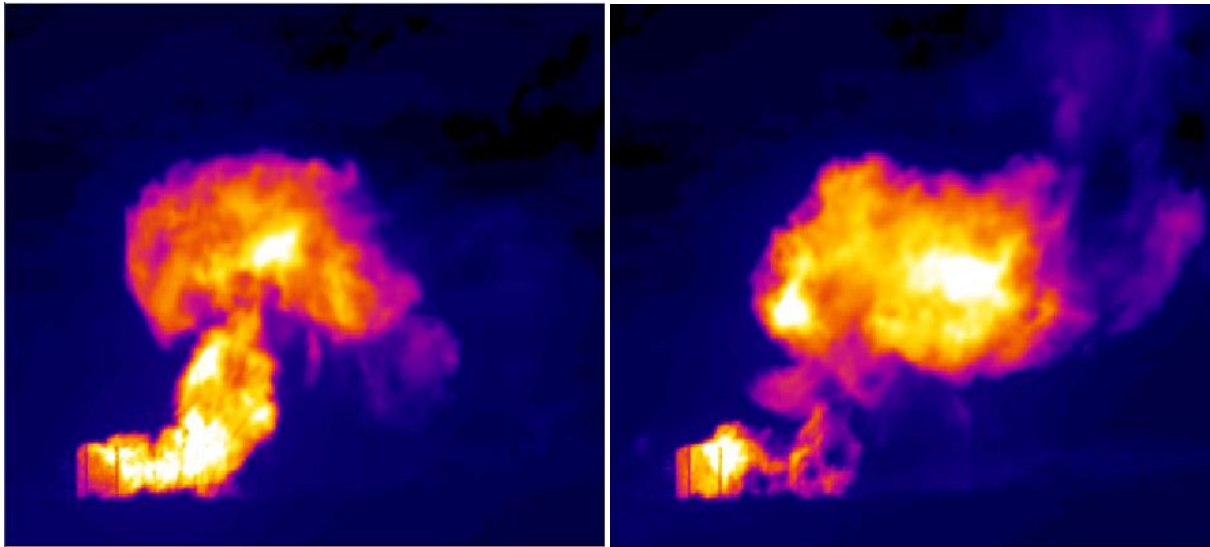


Figure 4: Comparison between fireball caused by the initial flash fire (left) and the secondary condensed phase explosion (right)

Approximately 3.7 kg of oxygen would also have been required. This would have corresponded to about 18 kg of air or a smaller quantity of oxygen-enriched material. Some of the oxidant may have come from rapid afterburning at the edge of a hydrogen-rich cloud in surrounding air.

The total mass of hydrogen and oxygen involved and the TNT equivalence based on observation of explosion effects are roughly consistent with reported equivalence data (Litchfield and Perlee, 1965). But it is likely that a significant fraction of the hydrogen was entrained by the detonation rather than being directly involved in the detonation.

Repeat tests did not reproduce the secondary explosion. Probably this means that wind conditions (which varied in subsequent tests) are important in allowing the accumulation of solid air with the necessary degree of oxygen enrichment.

Other tests were carried out on samples of solid ignited after the LH2 supply was removed and hydrogen vapour had cleared – so that the burning of the solid was not obscured by a pool fire (Royle and Willoughby 2014). In this case the solid burned steadily with a low flame – indicating the presence of at least some LH2.

CONDENSATION OF AIR WHEN MIXED WITH LIQUID HYDROGEN

Calculations in this section have been made on the assumption that the components of the nitrogen-oxygen-hydrogen system behave ideally i.e. the equilibrium vapour pressure of air components is determined only by the mole fraction in the liquid phase. It has also been assumed for simplicity that air contains only nitrogen and oxygen and water; minor components apart from water (e.g. argon) are counted as nitrogen. This is not likely to make a significant difference to the assessment of the properties of the solid deposit compared with uncertainties in the statistics of entrainment, i.e. the range of air to hydrogen ratios.

Figure 5 a-c shows the results of analysis of the equilibrium state for the adiabatic mixing of **liquid** hydrogen (at the boiling point) with air at 288 K (RH 0%).

Air (initially at 288 K) is fully condensed if the hydrogen to air (molar) ratio exceeds about 7 (Figure 5a). This corresponds to temperatures less than about 64 K. Liquid fully condensed by contact with such a large amount of hydrogen clearly has the same composition as air, i.e. there is no oxygen enrichment.

If more air is present, the proportion of air as a condensed liquid phase falls. If the hydrogen to air ratio is about 3 or less there is no condensation of air (it all remains in the gas phase). For hydrogen to air ratios between 3 and 7 there is a varying degree of oxygen enrichment. The first liquid formed as more hydrogen is mixed in with air has an oxygen mole fraction of around 60% and this is at a temperature of around 72 K.

All of the results in Figure 5(a-c) vary slightly if the air is moist, for example at 100% relative humidity (288 K) the limiting molar ratio at which condensation is complete increases by about 10%. Condensation of water vapour releases heat that must be offset by additional LH2.

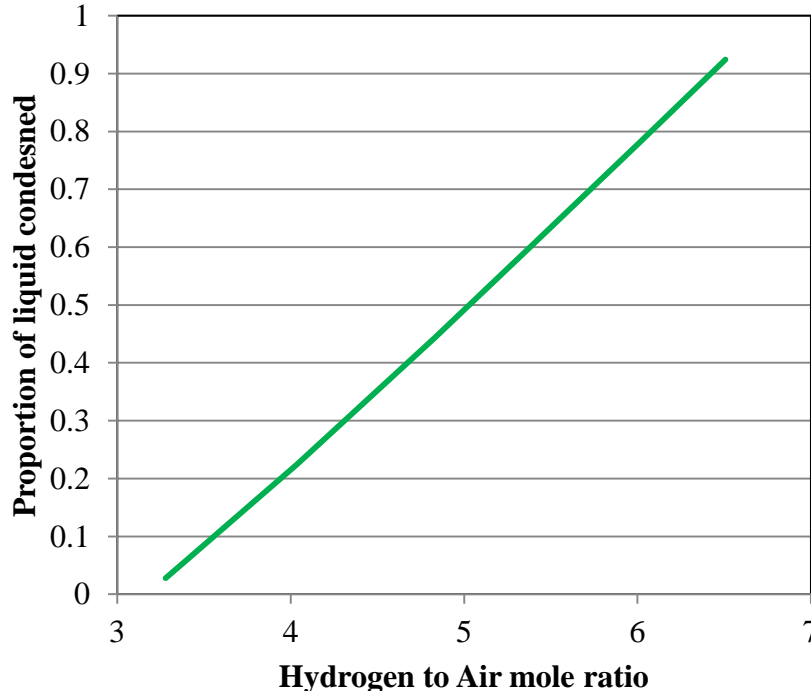


Figure 5a: Equilibrium state of **liquid** hydrogen and air mixed in different proportions - Molar proportion of air condensed.

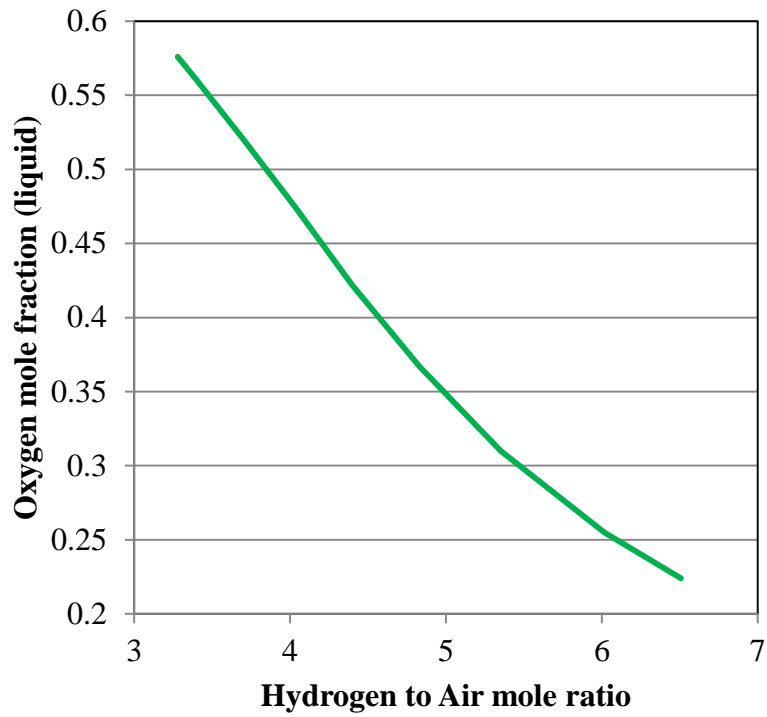


Figure 5b: Equilibrium state of **liquid** hydrogen and air mixed in different proportions –Oxygen mole fraction in the liquid phase.

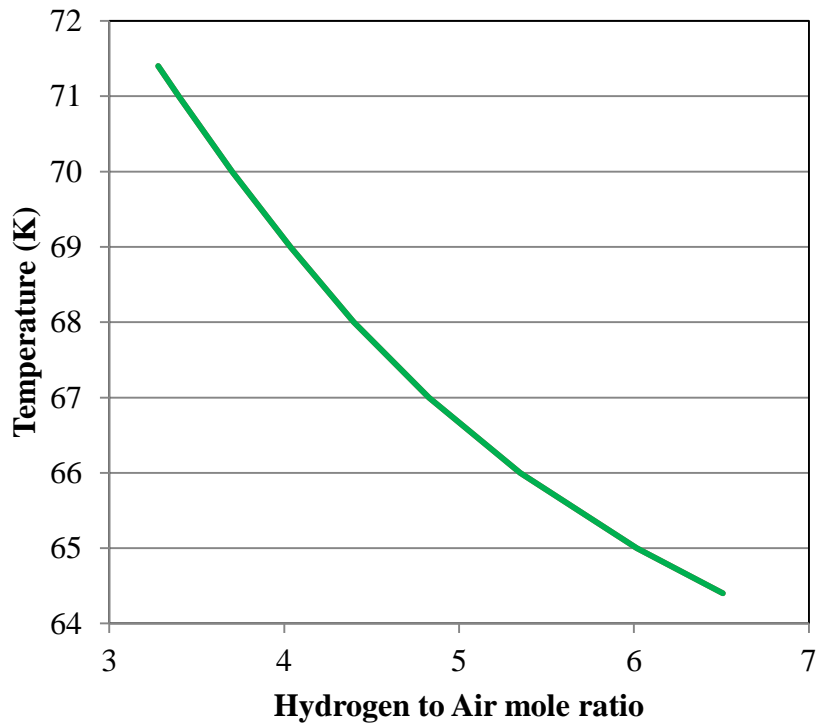


Figure 5c: Equilibrium state of **liquid** hydrogen and air mixed in different proportions – Final temperature.

Figure 6 shows the density of mixtures - relative to air and to hydrogen gas given off from the liquid surface - at the boiling point. The plot also show the density of the gas phase left if there is deposition of condensed components.

Density is important in modulating heat and mass transfer for cases where there is limited movement between the liquid LH2 and overlying ambient air. If the liquid is stationary this would correspond to low air velocities. If the liquid is moving it would correspond to wind directions and speeds that roughly matched the liquid movement. The relative velocity at which density stratification strongly influences the mixing process depends on the gradient Richardson number (Turner 1973) which is a function of the characteristic differences in density, the velocity difference and the depth of the flow. In this case the velocity difference would have to be about 1 m/s or less for stabilising density differences of order 0.1 kg/m³ to suppress mixing. For much larger relative velocities, turbulent transport of heat and mass would progress in a way that was not affected by density.

Hydrogen gas at its boiling point is lighter than ambient air, so the overall density difference between hydrogen gas and ambient air promotes mixing and hence heat transfer from the air to LH2 and consequent condensation of air (Figure 6). However this will only apply if the unstable density gradient extends across the full depth of the flow.

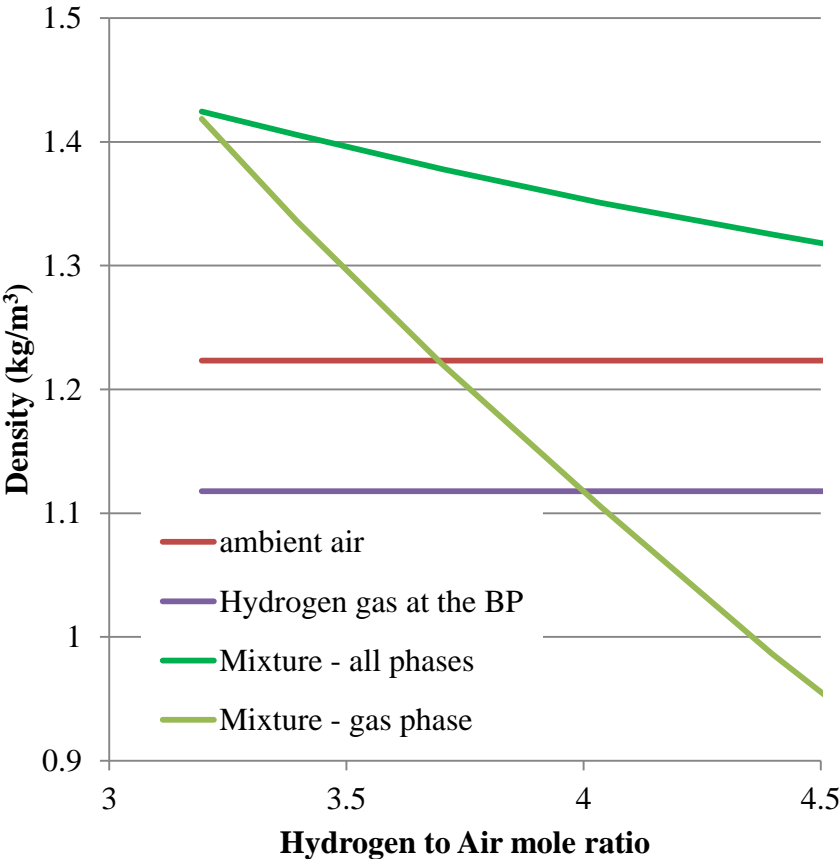


Figure 6: Density of a mixture of air (initially at 288K) and LH2 (at BP).

If there was a very light gas phase layer (corresponding to a high LH2/air ratio) above the liquid surface, mixing with overlying air would proceed – introducing warmer, air-rich gas - but mixing with

hydrogen gas at the surface of the liquid would be inhibited. The suppression of turbulent transport of heat down to the LH2 surface and cold hydrogen upwards would cut off the supply of cold hydrogen to the lowest layer. Hydrogen mole fractions would drop and the density would tend to increase until it was comparable with hydrogen gas at the BP.

Conversely, if the gas layer above the liquid surface had too low a LH2/air ratio (and consequently too high a density) mixing with hydrogen gas at the surface of the liquid would be supported but mixing with overlying air would be inhibited. Again the changes in rates of mass transport would tend to return the condensation layer to a density somewhere between that of hydrogen gas and ambient air.

These arguments and the gas phase density results shown in Figure 6 suggest that, in low shear conditions, the condensation layer separating ambient air from underlying LH2 will tend to contain gas with a density somewhere between that of hydrogen and air, which corresponds to a LH2/air ratio of around 3.75.

The temperature would be around 70 K and the oxygen fraction in the liquid condensate would be around 50% mole/mole. The gas phase would be considerably nitrogen rich.

Heat transfer to the LH2 surface would proceed by direct turbulent mixing of the gas phase (which would be dense enough to displace hydrogen gas formed) and by heat transfer from droplets of oxygen-enriched liquid air that fell out onto the LH2 surface. There is also a small contribution from the heat of fusion of droplets.

Turbulent exchange between this condensation layer and the overlying air would carry away excess nitrogen left by oxygen enrichment of the condensate.

This conceptual model of mass transport is shown in Figure 7.

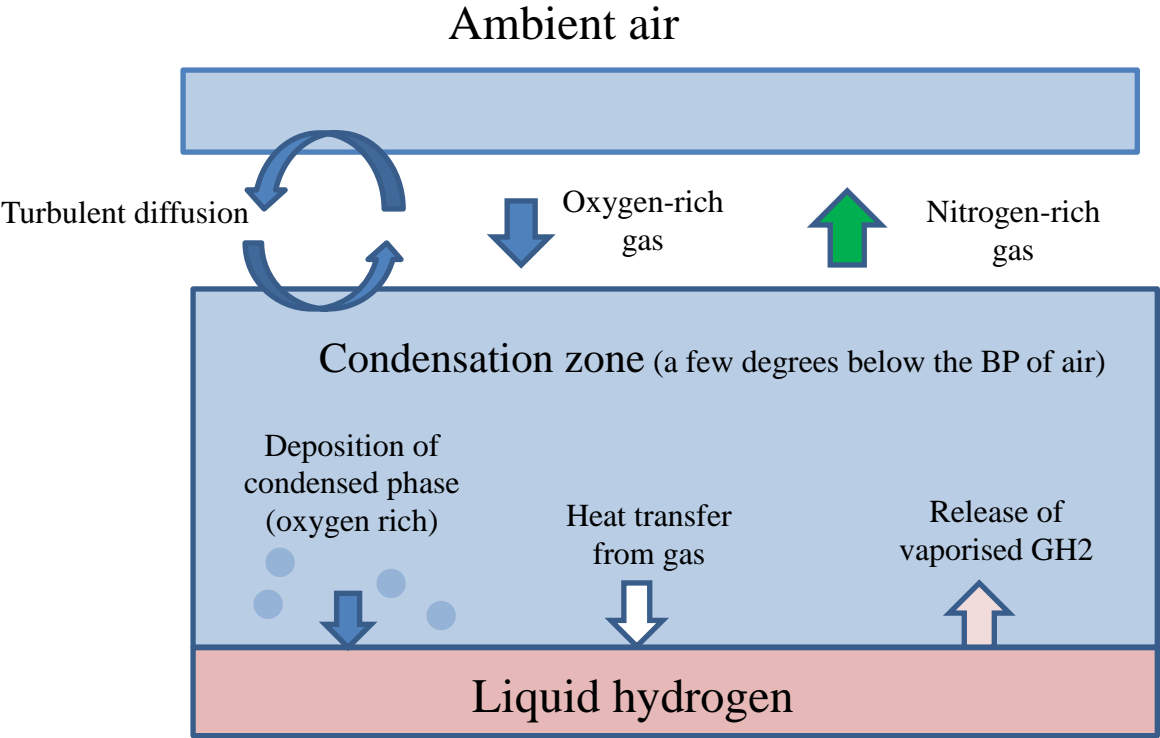


Figure 7: Schematic showing heat and mass transfer

SCALING

The accumulation of potentially oxygen-enriched solid increases with the time of the spill. However, in open geometries, like the one studied here, it is possible that only the most recently deposited solid will be cold enough to maintain contact with LH2 and contribute directly to a solid phase reaction. The quantity of accumulated hydrogen will also tend to a constant level. Consequently the severity of the worst case explosion is not likely to continue to increase with time after a certain stage. Based on observations in HSE tests the time scale required to develop the maximum explosive potential in this type of situation is probably a few minutes.

In circumstances where the amounts of LH2 and condensed air continue to accumulate e.g. pooling in a depression in the ground, then the potential for larger explosions may increase over longer periods of time.

The rate of accumulation of solid is also a function of the surface area of the spill. On level ground larger rates of LH2 spillage will correspond to larger pool areas and maximum accumulations of both LH2 and solids in a roughly proportional manner. An increase in horizontal extent of the spill is also likely to lead to a thickening of the mixing layers including the condensation layer. This will typically increase the gradient Richardson number and the upper limit on flow speeds that correspond to a very stable condensation layer and high levels of oxygen enrichment. The velocity limit will typically scale as the square root of the length-scale of the flow.

RISK ASSESSMENT

Further work on this issue is required to establish the dependency of explosion risk with release conditions – see below. However, significant explosions have occurred and the test described in Hall (2014) suggests that a 1 bar, 1 inch bore release at a rate of 135 g/s LH2 corresponds to a pool surface area of around 1 m². The TNT equivalence could be conservatively assumed to be of order 2 kg.

For the purposes of assessing the potential risks, larger pools could be assumed to develop in proportion to higher mass flow rates:

$$Pool\ size = \frac{mass\ flow\ (g/s)}{135} \times 1\ m^2$$

The potential TNT equivalence – assuming propagation is possible through the accumulated solid/liquid mixture – would be:

$$TNT\ equivalence = \frac{mass\ flow\ (g/s)}{135} \times 2\ kg$$

It seems likely that, for spills outdoors, the risk might be dominated weather conditions where the wind is very light. The probability of this occurring is <10% for most European locations but may be much greater in other parts of the world.

FURTHER WORK

A first priority for research effort is to develop an experimental system where the ventilation can be controlled and in which oxygen enrichment and DDT on ignition can be reproduced. The simplest candidate for such a system would be low pressure LH2 flow into a highly insulated well in a sheltered environment Figure 8a. After heat input from the container walls had dropped to a low level further vaporisation of LH2 would depend on convective heat transfer from overlying air in the manner illustrated in Figure 7.

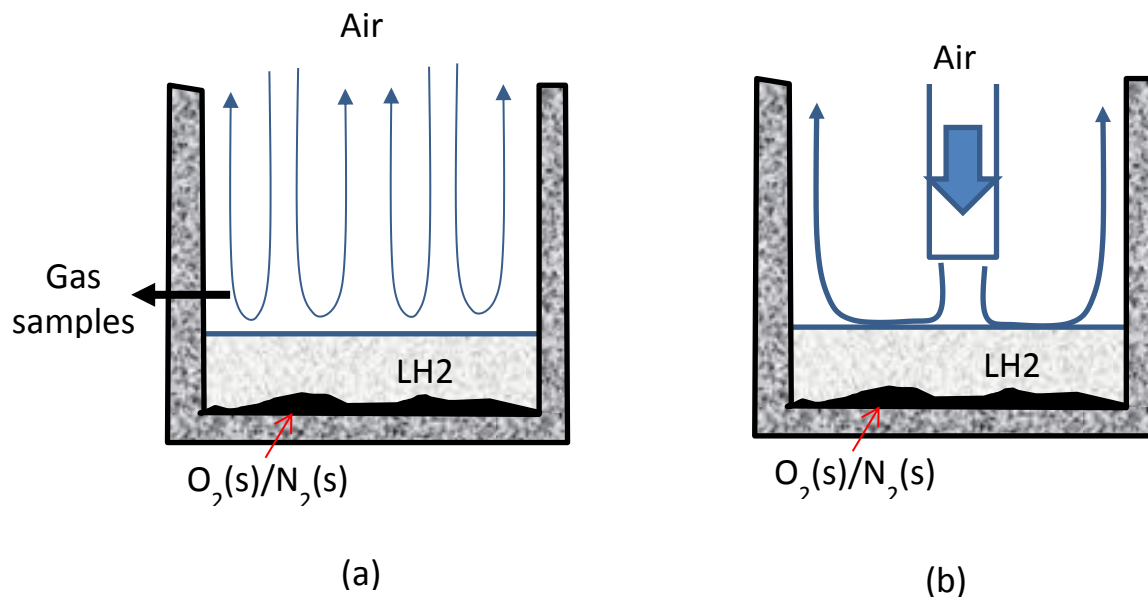


Figure 8: Schematics of experiments in which mass transport of air to the LH2 surface is by (a) density driven (natural) convection (b) forced convection

It is expected that denser, solidified air fractions would accumulate under the LH2. It might be possible to measure a shift towards oxygen enrichment as the distance to the LH2 surface decreased. The overall composition of accumulated solids could be determined by analysis of the outflow as they were vaporized – after the LH2 supply was cut off.

The potential for DDT could be investigated directly. Litchfield and Perlee (1965) observed a delay of about a minute before excess LH2 burned away – exposing the detonable liquid/solid mixture. For mixtures with high levels of nitrogen dilution $N_2(s) > 50\%$ wt/wt the mixture simply burned away steadily to completion.

Further experiments in which an airflow is induced over the surface could help to determine the limits on flow conditions in which enrichment occurs - Figure 8b.

Further large scale experimentation is also important because reliable risk assessment depends on an understanding of the quantity of detonable material accumulated in a given release scenario and the explosive power on ignition – both of which are uncertain and cannot be determined from smaller more controlled testing. The analysis presented here suggests that any large-scale, outdoor experiments to investigate this phenomenon should focus on low wind speed conditions. In marginal conditions may be possible to increase the probability of explosions by shielding the area where LH2 pools from the wind. Alternatively releases could be carried out in a tunnel-like geometry where the air flow can be controlled upstream of the developing spill.

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