

Liquid Hydrogen Condensed Phase Experimentation & Interpretation

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Liquid hydrogen (LH2) has been identified as a carbon-free fuel in the transition to Net Zero. The transport sector has a particular interest in LH2 due to its increased density (71 kg/m³ at -253 °C, 1 barg) compared to pressurised gaseous hydrogen (24 kg/m³ at 20 °C, 350 barg). The Health and Safety Executive's (HSE) Science Division has been researching and assessing LH2 transport hazards for over a decade with supporting UK Safe Net Zero as one of the organisations key objectives.

Previous experiments have shown that large LH2 releases can condense the air around them, forming solidified deposits. One ignited release test exhibited evidence of a higher order explosion equivalent to ~2.7 kg of TNT, a far higher yield than other similar LH2 release ignitions. Several potential mechanisms for this larger explosion have been theorised, with one such mechanism being the 'oxygen enrichment' of condensed air deposits which would lead to a much more severe explosion when LH2 and an ignition source are introduced.

The experiments presented in this paper examine the condensation of air at a LH2 surface in conditions where the relative buoyancy of the hydrogen gas and air can have a significant effect on the mass transfer to the surface i.e. low airflow conditions. The extent of oxygen enrichment of the condensed air was assessed by measuring the composition of venting gas during the build-up of condensate and subsequent evaporation.

Experimental results showed that no oxygen enrichment occurred during formation of the condensate as oxygen and nitrogen condensed in the same ratio as air (1:3.7 O₂:N₂).

It was observed that an air condensate can become oxygen-enriched as nitrogen evaporates preferentially from the condensate.

1. Introduction

Due to the low boiling point at atmospheric pressure (20 K), there is the potential for LH2 to condense air during a spill, forming an air condensate which can increase its relative oxygen (O₂) content via preferential boil-off of nitrogen (N₂). Research into the explosibility of LH2 dates back to the 1960s (Litchfield and Perlee, 1965), where experiments demonstrated that air condensate with oxygen enrichment levels over 50 wt% O₂ (46.5 mol% O₂) could be detonated in a mixture with LH2. Therefore, it is important to understand the extent of O₂ enrichment in air condensate during practical applications where LH2 spills may occur, and the increased risks posed by this enrichment.

Recent work undertaken by the HSE has investigated the propensity of LH2 releases to condense air and induce O₂ enrichment of the condensed phase by the preferential evaporation of N₂.

These experiments were part of the Enhancing Safety of Liquid and Vaporised Hydrogen Transfer Technologies in Public Areas for Mobile Applications (ELVHYS) project, conducted by an international consortium and co-funded by the European Commission, the Clean Hydrogen JU under the Horizon Europe programme, and UKRI.

2. Previous Work

LH2 experimentation conducted by the HSE (Hall, 2014) investigated hazards associated with LH2 transportation and storage.

During one test, LH2 was released at low pressure (0.2 barg) onto the test pad and allowed a small pool to form for 250 s. The resulting vapour cloud was then ignited and burned back to the release point and continued burning as a jet fire for 3.6 s before a much larger explosion occurred. Figure 1 (left) shows the heat flux measurements from this test, and a second much higher peak, highlighted by the red circle, corresponding to the secondary explosion. Infrared camera footage in Figure 1 (right) shows a large fireball which was associated with the secondary explosion. No pressure measurements were made but models of the blast through the observed pressure effects and radiative fraction estimated a TNT equivalence of ~ 2.7 kg (12.5 MJ).

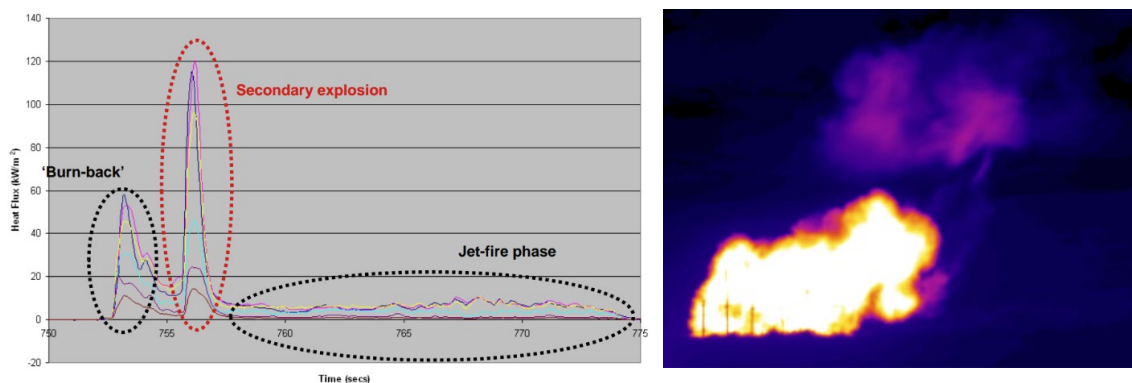


Figure 1: (Left) Heat flux recorded during experiment where LH2 was released at low pressure and ignited after a 250 s delay. Trace indicates that a secondary explosion occurred following the initial delayed ignition burn back period. (Right) Infrared video still of secondary explosion taken at the point of maximum radiative heat flux.

The experiment occurred during high wind conditions and subsequently it was not possible to recreate the event, potentially indicating a combination of contributing factors which are not fully understood. (Hall, 2014)

The explosion originated close to a pool of material which had been condensed by the unignited hydrogen jet. This indicates that the pool of condensed material may increase the severity of an explosion, which is theorised to be due to O₂ enrichment of the condensate.

Experiments performed by Karlsruhe Institute of Technology (Kotchourko, 2021) spilled LH₂ onto different substrates to characterise LH₂ pool formation. During one test where LH₂ was released onto gravel, an explosion occurred which caused significant damage to the experimental facility. Kotchourki proposes that this event may be caused by condensed O₂ forming between stones in the substrate.

Oxygen enrichment of condensed phases of air may be caused by the difference in the temperatures of phase changes of O₂ and N₂. As the LH₂ evaporates, and cryogenic temperatures are no longer sustainable, the solid air condensate will start to warm. The melting points of O₂ and N₂ are 55 K and 63 K respectively (Span et al., 2000; Schmidt and Wagner, 1985), meaning O₂ will melt first. As the condensate starts to melt, it may be possible for the condensate to become non-homogeneous and regions of the condensate could become significantly oxygen-rich, where pools of liquid O₂ form adjacent to blocks of solid N₂. The phase diagram indicates that, upon melting, the first liquid formed from the solid mixture will have a eutectic composition of 77% O₂ (Kochenburger, 2015) and therefore will be highly O₂ enriched. A fully eutectic composition is unlikely to be achieved as it would require a very slow rate of temperature increase, but it is assumed that the composition of the liquid will have an increased O₂ content.

As the liquid air condensate warms further it will start to vaporise. The boiling points of O₂ and N₂ are 90 K and 77 K respectively (Span et al., 2000; Schmidt and Wagner, 1985), meaning the N₂ will evaporate first. As the condensate starts to vaporise, it again may be possible for the condensate to become non-homogeneous and the condensate could become significantly oxygen-rich. In this case O₂ enrichment is achieved by the evolution of a N₂ enriched vapour. If the air is still, and dispersion of this cold N₂ enriched vapour is buoyancy dependant, it will stay close to the surface of the O₂ enriched liquid until it has warmed sufficiently. This N₂ enriched blanket may act to suppress the interaction of the O₂ enriched liquid with any nearby flammable substances.

During the formation of condensed air products from the atmosphere, Atkinson (2021) suggests that O₂ enrichment will only occur in a small range of LH₂/air molar ratios. If the ratio is too high (> 7), the temperature is too low, air is fully condensed and the resulting liquid phase will have the same composition as air and therefore will not be O₂ enriched. Conversely, if the ratio is too low (< 3), no condensation of air occurs. For turbulent exchange of heat to occur, the density of the cold gas at the surface of LH₂ must be between the density of ambient air and H₂ at the boiling point. This allows air to cross the layer of cold H₂ gas and come into contact with the liquid surface.

3. Methodology

The experimental rig, which is shown in Figure 2, comprised a 100 L container which was filled from a LH2 tanker. LH2 was released at low pressure to encourage pool formation. While filling, a large diameter vent (path indicated by green arrows in Figure 4) was open to avoid over-pressurising the container. The LH2 level is determined using thermocouples at set heights in the container, which show a constant temperature when submerged and a thermocouple which is out of the liquid, which is approximately equivalent to a difference of 3 litres.

Air was injected into the container and metered using a flow controller. Air impinged on the top face of the container to minimise disturbance of the LH2 surface. This simulated low air flow conditions and maximised the amount of condensation by encouraging turbulent exchange of heat between the air and H₂ at the liquid surface. The vaporised gas was diverted (path indicated by blue arrows in Figure 4) so that it passed through a conditioning bath and to the vent from which samples were drawn to H₂ and O₂ sensors and a gas chromatograph. A differential pressure meter, orifice plate and temperature probe were used to calculate the mass flow rate through the vent so that a mass balance can be determined and the accumulation of condensate can be calculated. When all LH2 was vaporised (shown by H₂ concentrations at the vent falling to zero), the container was warmed using a 140 W heat trace cable to evaporate the remaining air condensate.

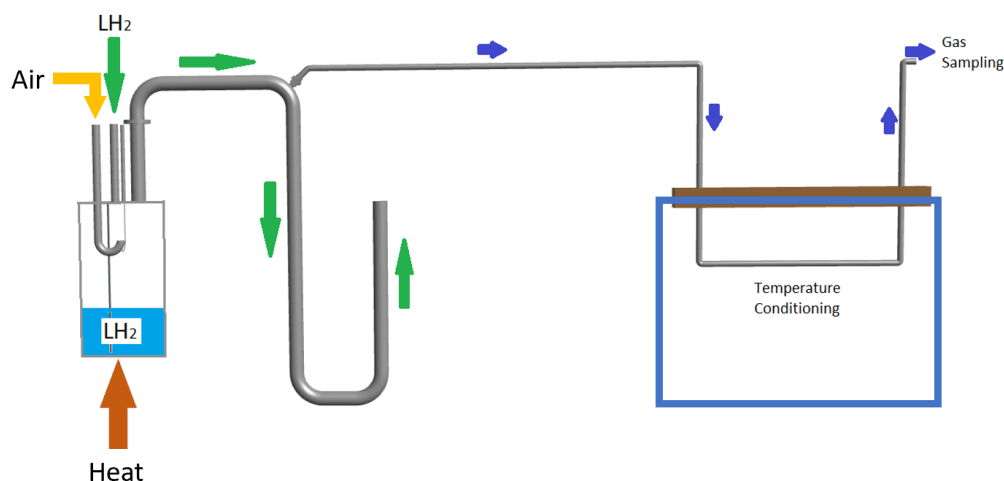


Figure 2: Diagram of the experimental setup. The container has LH₂ and air connections and sits on heat trace cable which can be activated to warm the container. Gas evolving from the container passes through a conditioning bath to warm it before being sampled for analysis.

Table 1: Ranges and accuracies for experimental measurements.

Measurement	Instrument	Range	Accuracy
LH ₂ Level	Thermocouple rake (Type T)	0 – 100 L	+/- 3 L
Vent Temperature	Thermocouple (Type T)	77 – 400 °C	+/- 1 °C
Gas Concentration (all gases)	H ₂ : XEN-5320 O ₂ : Pyroscience FDO2	0 – 100 vol%	+/- 1 vol% H ₂ +/- 2 vol% O ₂
Air Inlet	Bronkhorst IN-FLOW	0 – 500 L/min	+/- 3 L/min

4. Results

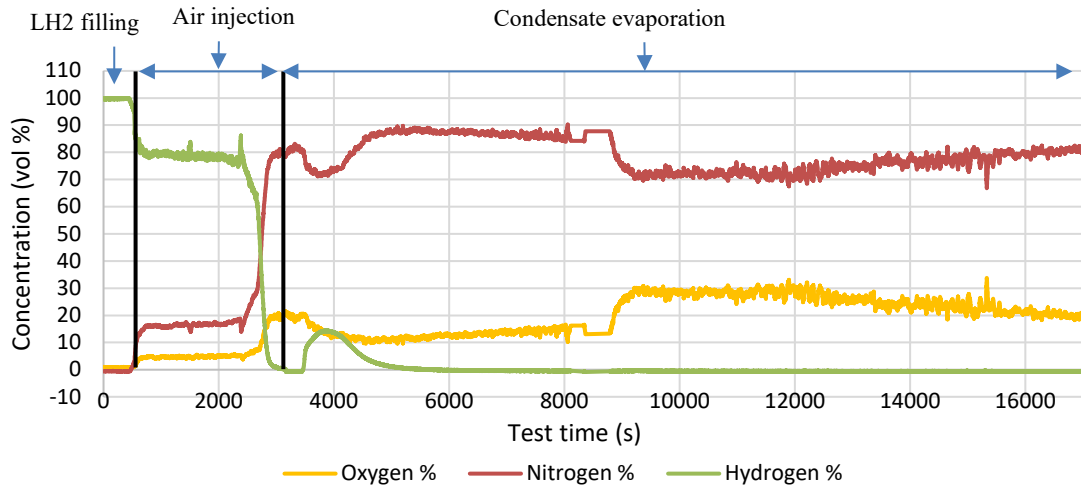


Figure 3: Volumetric concentration of gaseous O_2 , N_2 and H_2 measured at the vent of the experimental container for the 16 litre LH2 test. Black vertical lines separate the test phases. Note that N_2 concentration is not directly measured but determined as the only other component in the tertiary system. The LH2 filling, air injection and condensate evaporation phases of the experiment are indicated.

Figure 3 shows the concentrations of O_2 , N_2 and H_2 at the vent of the experimental rig over the period of Test 1. The rig was filled with 16 litres of LH2 at the start of the test.

The first 500 s show the end of the LH2 filling stage, hence the concentration of H_2 is 100 vol%. When air is introduced at 500 s, the concentration of H_2 drops to around 78 vol% and remains steady until the H_2 has evaporated at 3100 s. During this time, O_2 and N_2 concentrations are approximately constant at 5 vol% and 17 vol% respectively, which is close to the ratio of O_2 and N_2 in atmospheric conditions. This indicates that neither oxygen nor nitrogen is condensing preferentially.

After 3,100 s, the air supply was stopped and the condensed phase warmed. At this point, O_2 and N_2 concentrations are approximately 20 vol% and 80 vol% respectively. O_2 concentrations begin to fall to a minimum of 10.5 vol% and N_2 concentrations rise to 88 vol%. As the concentration of nitrogen is higher than the atmospheric composition, this indicates that N_2 is evaporating preferentially, due to its lower boiling point and therefore the condensate is becoming enriched with O_2 .

At 8,800 s, O_2 concentrations begin to increase, to a maximum of 29 vol% at 9,600 s, which indicates that the condensate has become enriched with O_2 and is now evaporating and causing O_2 concentrations at the vent to rise. By the end of the test, O_2 and N_2 concentrations have returned to an atmospheric composition, indicating that there is no longer an O_2 enriched atmosphere in the container.

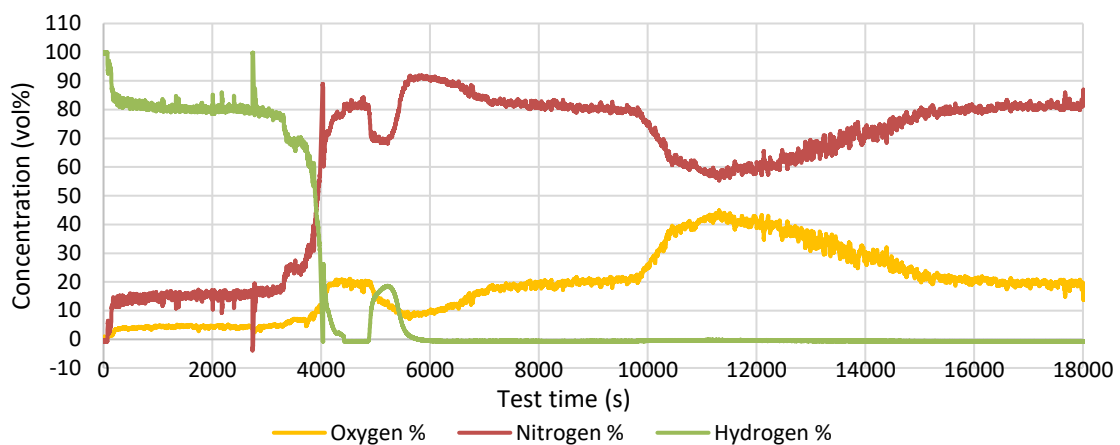


Figure 4: Volumetric concentration of O_2 , N_2 and H_2 measured at the vent of the experimental container for the 28 litre LH2 test. Air injection and condensate evaporation phases of the experiment are indicated.

Figure 4 shows the concentrations of O₂, N₂ and H₂ at the vent of the experimental rig over the duration of Test 2. The container was filled with 28 litres of LH₂ at the start of the test.

The concentration traces follow the same trend as the previous test. During the introduction of air, H₂ concentration remains steady at 80 %, while O₂ and N₂ concentrations remain around 4 vol% O₂ and 15 vol% N₂, again maintaining an approximately atmospheric ratio during this phase of the test. The air injection phase took longer than the previous test, which was expected due to the larger amount of LH₂ in the container. This indicates that a larger amount of air condensate was formed.

At 4,600 s, the air supply is stopped and the container is heated to evaporate the condensate. O₂ concentrations fall to a minimum of 9 vol% O₂ at 5,700 s, indicating that the air condensate is being enriched. This is followed by an increase in O₂ concentration to a maximum of 42 vol% O₂ at 11,300 s which is indicative of an evaporating oxygen enriched mixture.

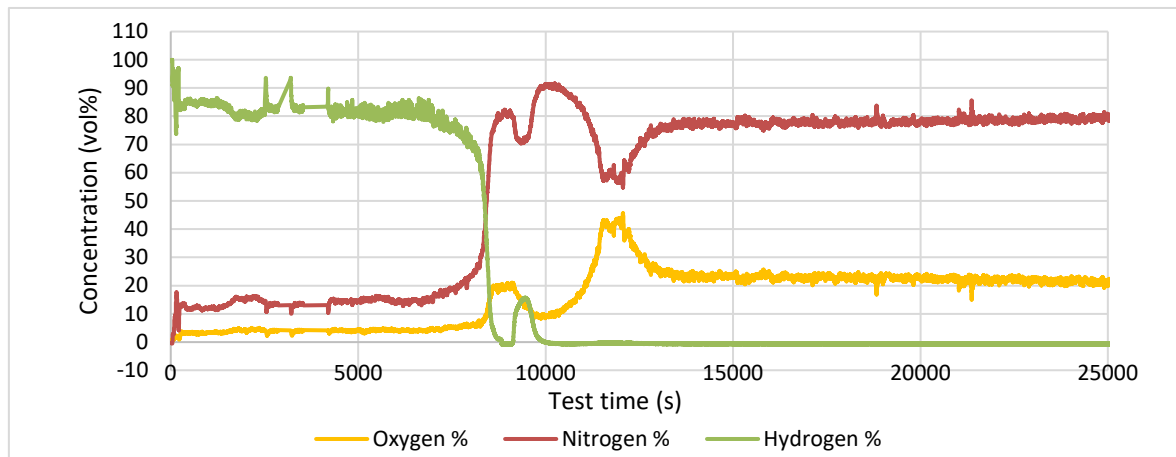


Figure 5: Volumetric concentration of O₂, N₂ and H₂ measured at the vent of the experimental container for the 57 litre LH₂ test. Air injection and condensate evaporation phases of the experiment are indicated.

Figure 5 shows the concentrations of O₂, N₂ and H₂ at the vent of the experimental rig over the duration of Test 3. The container was filled with 57 litres of LH₂ at the start of the test.

The concentration traces exhibit the same behaviour as the previous two tests. When air is introduced to the container, H₂ concentration reaches a steady state at 81 vol% H₂. During this time, O₂ and N₂ concentrations are 5 vol% O₂ and 15 vol% N₂. This is a slightly higher ratio of O₂ compared to atmospheric, indicating that slightly less O₂ is being condensed compared with N₂. As expected, the time (and therefore amount of air) required to evaporate all the LH₂ was significantly longer than for the previous tests.

At 9,000 s, O₂ concentration begins to drop as N₂ evaporates preferentially from the condensate. O₂ concentration reaches a minimum of 10 vol% at 10,100 s before rising to a maximum of 43 vol% at 12,000 s when the additional O₂ in the condensate begins to evaporate. The peak O₂ concentration is reached much faster, within 3,000 s of heating the container, than the previous two tests which took over 6,000 s to achieve maximum O₂ concentration. However, in test 3 O₂ and N₂ concentrations took much longer to return to ambient compared to the previous tests.

In all tests, hydrogen levels increase temporarily when the container is heated. This may be due to a layer of cold hydrogen gas remaining above the condensate which cannot be flushed by injecting air into the container, but the exact mechanism for this behaviour is not fully understood at this time.

5. Conclusion

Experiments were conducted to investigate the extent of O₂ enrichment of air condensates formed by LH₂ spills. A container was filled with LH₂ and air was condensed into the LH₂ pool. The condensate was then evaporated and the composition of the gas leaving the container was measured.

When exposed to LH₂, components of air condense equally, shown by the ratio of O₂ to N₂ leaving the container being approximately equal to the atmospheric composition of air during the H₂ evaporation phase. This indicates that the condensate also forms with atmospheric concentrations of O₂ and N₂.

Condensed air can become enriched with O₂ via the preferential evaporation of N₂. This is shown by an increase in N₂ concentration at the vent of the container. Therefore, the condensate must be enriched with O₂ as a higher proportion of O₂ remains in the container. This is further evidenced by a later increase in O₂ concentration when

the oxygen-enriched condensate begins to evaporate. Larger amounts of LH2 result in higher O₂ concentrations observed in the gaseous phase when the oxygen-enriched condensate evaporates. However, further analysis is required to determine whether this results in significantly higher O₂ concentrations in the condensate, which will be presented in the experimental report of the ELVHYS Project.

Conditions in these experiments were optimised to form significant amount of condensed air in a very still environment. This maximises the amount of condensate by promoting the turbulent exchange of heat between the air and cold H₂ gas due to their densities. Further studies may wish to investigate the extent of O₂ enrichment from LH2 releases under various wind conditions and in different pool geometries.

To obtain a method reliable method for quantifying the expected amount of oxygen enrichment and explosibility of oxygen-enriched mixtures, further experimentation is required to investigate factors affecting the phenomenon of O₂ enrichment and to ensure reliability of the estimation technique so that it can be used as effective guidance. To extrapolate the experimental data to other tests cases, a numerical model of the formation and evaporation of the condensate could be created, which considers the heat input to the container and the amounts of each component in the condensed and gaseous phases.

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Disclaimer

This report and the work it describe were undertaken by the Health and Safety Executive (HSE). Its contents, including any opinions and/or conclusions expressed or recommendations made, do not supersede current HSE policy or guidance.

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