Introduction to Hydrogen Explosion Events and Comparison with Methane

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Introduction

The use of hydrogen as a replacement for natural gas presents all of the hazards we associate with natural gas although the extent of the hazards can be greater for hydrogen; the flammability ranges in air for hydrogen are 4 % to 75 % by volume, high pressure releases of hydrogen can auto-ignite and hydrogen explosions can be more severe as hydrogen is more prone to detonation.

This paper provides background and insight into the potential for the ignition of a hydrogen in air mixture to reach detonation in comparison with methane, and the impact that can have on structures.

Background

The ignition of a mixture of gas and air can result in a vapour cloud explosion. After ignition occurs, combustion of the gas/air mixture creates a flame front that propagates through the gas/air mixture. As the flame front advances, the available fuel is oxidised and hot, gaseous reaction products are produced. This input of heat energy and evolution of products give rise to a rapid increase in pressure, generating a pressure gradient, which in turn drives the resulting blast wave. A number of factors dictate the rate at which the flame front advances, and thus the rate at which energy is released into the environment. The rate and amount of energy released is also a function of the fuel and its concentration within the cloud.

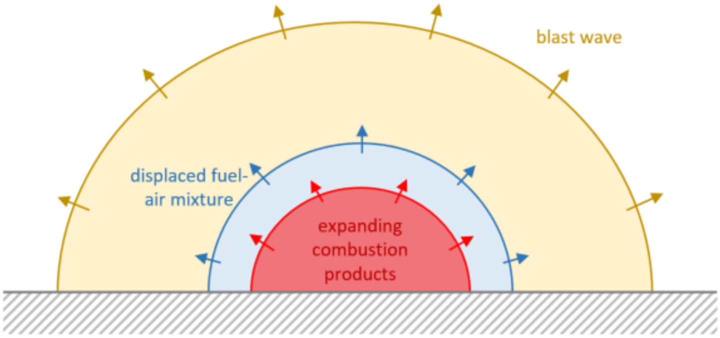

Figure 1: Schematic of a Deflagration

Deflagration describes the rapid combustion of a flammable mixture during which the velocity of the advancing flame front (reacting zone) does not exceed the velocity of sound in the uncombusted mixture. Under certain, more severe conditions, the velocity of the advancing flame front can accelerate up to and even exceed the velocity of sound in the uncombusted mixture, yet remain below a critical threshold, described below. These “fast” deflagrations present higher overpressures, characterised by a steeper, shorter rise time, which can tend towards a shock wave.

Ultimately, if the required conditions prevail, the velocity of the advancing flame front can accelerate to become super-sonic, achieving a relatively very high, steady state velocity, resulting in detonation. Explosions during which detonation occurs give rise to comparatively very high overpressures and associated shock waves which can be extremely damaging to affected structures and plant.

Detonations have occurred in a number of serious accidental industrial explosions such as the incident at Flixborough in 1974 and Buncefield in 2005.

Parameters Governing Vapour Cloud Deflagrations

A range of physical parameters interact to determine the likelihood of a vapour cloud deflagration, and its subsequent intensity. These parameters and influences are discussed below.

Cloud Concentration

For combustion to occur for a gas/ air mixture it is necessary for the volume of fuel within a given volume to lie within a well defined range, bounded by the lower and upper flammability limits. In the case of hydrogen-air mixtures, this range is particularly wide with a LFL of 4% by volume and an UFL of 75% by volume.

The concentration of fuel in oxidiser at which combustion is completed with no excess of either component is known as the stoichiometric concentration. In the case of hydrogen-air mixtures this concentration is 29.5 % by volume and for methane it is 9.5 %.

Rate of Combustion

Stoichiometric concentrations of hydrogen in air and methane in air possess a very similar energy content, with values in the range 3.2 – 3.7 MJ per m^3 of mixture. This means that under totally confined conditions ignition of the mixture will generate approximately the same maximum pressure. However, the time to reach the maximum pressure will be different due to the different burning velocity, the burning velocity being the velocity that the flame front moves relative to the unburnt mixture ahead of it, and is related to the laminar flame speed. In reality the maximum potential pressure in a confined volume is seldom reached due to failure or planned venting from the confining structure relieving the pressure build up.

In the context of explosion hazards, it is the relatively high laminar flame speed (and subsequent turbulent flame speed) giving rise to rapid increases in pressure which result in the increased severity of hydrogen deflagrations. Stoichiometric hydrogen-air mixtures exhibit a laminar flame speed of the order of 30 cm/s, whereas stoichiometric mixtures involving methane have laminar flame speeds of the order of 3 – 4 cm/s.

Degree of Dispersion

Variations in concentration within the combusting media will influence the rate of energy release and, in bounding situations may prevent continued combustion as the mixture is pushed outside the flammability limits. The degree of dispersion and the manner in which the fuel is dispersed influence the mixture concentration prior to ignition.

Congestion

Congestion due plant and equipment provide obstacles for the propagating flame front and can result in turbulence in the flow field. The role of turbulence is highly influential in determining the intensity of any vapour cloud explosion. The propagating flame front, which represents the interface along which the combustion reactions take place, becomes accelerated as turbulence distorts and stretches the flame, exposing a greater surface area over which combustion reactions occur.

The process of flame front acceleration increases the rate at which energy is added to the system, thereby increasing pressure gradients which drive the blast wave.

As well as plant and equipment sources of turbulence in the flow field include the boundary layer friction along confining surfaces.

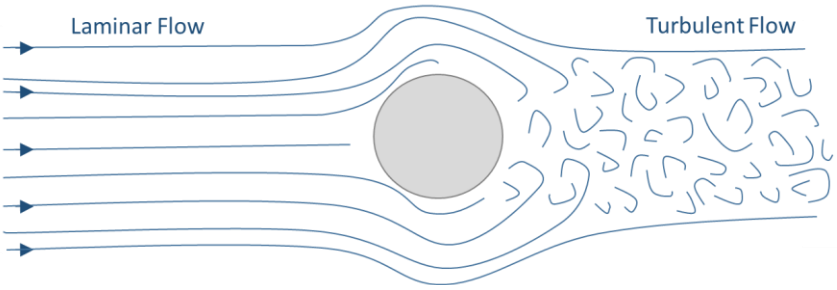

Figure 2: Schematic Showing the Development of Turbulent Flow Downstream of an Obstacle

Confinement

Physical restrictions on the expansion and flow of the blast wave have the effect of increasing peak overpressures. Thus, buildings or enclosures which are not provided with adequate vent paths will be subject to significantly enhanced blast loads during an internal vapour cloud explosion. Coal mines are a good example of confined explosions with methane as the fuel for explosion seeping into the mine from the coal faces.

Partial confinement may also be provided by densely populated pipe racks, large vessels and other major plant items.

Ignition Source – Energy

The occurrence of an explosion depends upon the existence of an ignition source with sufficient energy to initiate combustion within the cloud. The minimum ignition energy required for hydrogen-air mixtures is less than 20 μJ, whereas for methane this minimum ignition energy is 290 μJ and for propane 250 μJ. Increased amounts of energy above the minimum ignition energy can result in intensified explosions.

Ignition Source - Location

The location of the ignition source is a significant factor affecting explosion intensity. Elongated structures, with ignition occurring at one end and a vented opening at the other tend to suffer more vigorous explosions than those with central ignition location and symmetrical disposition of vent paths.

Flame Acceleration and Deflagration to Detonation Transition (DDT)

The detonation process involves the extremely rapid reaction of the flammable mass and is characterised by the supersonic propagation of a coupled shock-reaction front. Typical deflagrations propagate with at speeds typically 1 - 100 m/s whereas detonation waves propagate at speeds of the order 2000 m/s. However, in the context of accidental vapour cloud explosions, detonation is achieved only after a prerequisite sequence of combustion processes have been completed.

Assuming that a flammable atmosphere has formed, and that the event is initiated by a “weak” ignition source, such as a small electrostatic discharge, the first phase of the explosion commences with laminar combustion. The flame front velocity at this stage is a function of the laminar flame speed and the density ratio across the flame front: i.e. the ratio of density of the reactants to that of the combustion products. In typical accidental explosion scenarios this phase is short lived as hydrodynamic instabilities start to distort the laminar flame into a “wrinkled” form. This second stage of combustion tends to persist over greater distances and is therefore more significant in determining the final form and magnitude of the explosion. The wrinkled profile of the advancing flame front now offers an increased surface area over which the combustion reactions may take place, accelerating the flame front velocity up to a value several times that of the laminar flame speed. Following this stage, the advancing flame front may be expected to commence interaction with obstacles in the field and/or boundary layers along confining surfaces, inducing further turbulence. This has the effect of transforming the wrinkled flame into a turbulent “flame brush”. The flame brush offers yet more surface area for combustion and further accelerates the flame front. If flame front acceleration and its underlying levels of turbulence continue to increase, the flame brush structure may break down into a distributed combustion zone structure in which separate pockets of turbulent combustion arise in the flammable mass.

The initial role of turbulence in the flow field is to accelerate the flame front and thus intensify the developing explosion. However, a point is reached at which turbulence also begins to have a negative contribution to the combustion process. This phase is characterised as the subsonic flame regime, in which turbulence can be seen to intensify combustion as described earlier, and also, to subdue it, by a mechanism known as "quenching". Quenching occurs when the hot turbulent jets of combustion products fail to ignite the reactants downstream of the advancing flame front due to the rapid, turbulent entrainment of cold unburned mixture with the hot products in the jets. In this way the propagation of the flame front is locally quenched or extinguished. These competing aspects of turbulent combustion interact to define the subsonic flame regime in the flame speeds range from several tens m/s up to around 200 m/s.

Where the conditions for quenching are not met, and adequate confinement exists around the advancing flame front, continued acceleration occurs until flame propagation enters the choking regime. At this stage in the explosion process the flame front velocity is broadly steady state, being limited by the combined effects of heat addition from combustion and friction at boundaries. Once this stage has been reached, the potential has been established for deflagration to detonation transition.

In the case of hydrogen-air mixtures, flame speeds in the choking regime are of the order of 1000 m/s. Under these conditions, localised explosions within the advancing flame system are capable of initiating detonation. This stage is described as the quasi-detonation regime. At this point, the obstacles (plant, structures, etc.) surrounding the explosion become critical. This influence derives from the relationship between the cellular structure of a detonation wave and the width of the gaps between obstacles providing local confinement. The cellular structure of the detonation arises from complex shock phenomena, and is a function of reactive mixture chemistry, pressure and temperature. In order for the quasi-detonation regime to become fully established as a true detonation mechanism, the local width of the bounding structure, D, must exceed, by a known critical ratio, the detonation cell width, λ. Only when D/λ exceeds the critical ratio will transition occur from deflagration, through quasi-detonation, to fully established detonation. This tells us that, for a given set of initial conditions, a given geometry will either permit or prevent the establishment and propagation of the cellular detonation structure.

It is also the case that a flame front advancing in the choking regime may be transitioned to detonation by its collision with a rigid obstacle, such as a step or ridge. This process is known as shock focusing, and is an important means by which a deflagration in a relatively open geometry could transition over to detonation.

Once established, the full detonation regime persists by means of a complex shock-induced combustion mechanism, where a narrow frontal zone exists, in which the coupled shock and reaction processes occur, characterised by the cellular structure noted above.

Blast Loading from Deflagrations & Detonations

Explosions give rise to a rapidly expanding blast wave and it is the interaction of this blast wave with structures which is the primary damage mechanism.

Blast loading from deflagrations and detonations generally comprises two main transient components; a positive phase overpressure pulse and a negative phase overpressure pulse. There is a degree of variability in the shape and duration of each pulse due to the influence of geometric and combustion factors. However, for the purposes of assessing structural response to deflagration blast loads, the pulses are often abstracted to a pair of isosceles triangles. Figure 3a illustrates a typical overpressure transient from a deflagration.

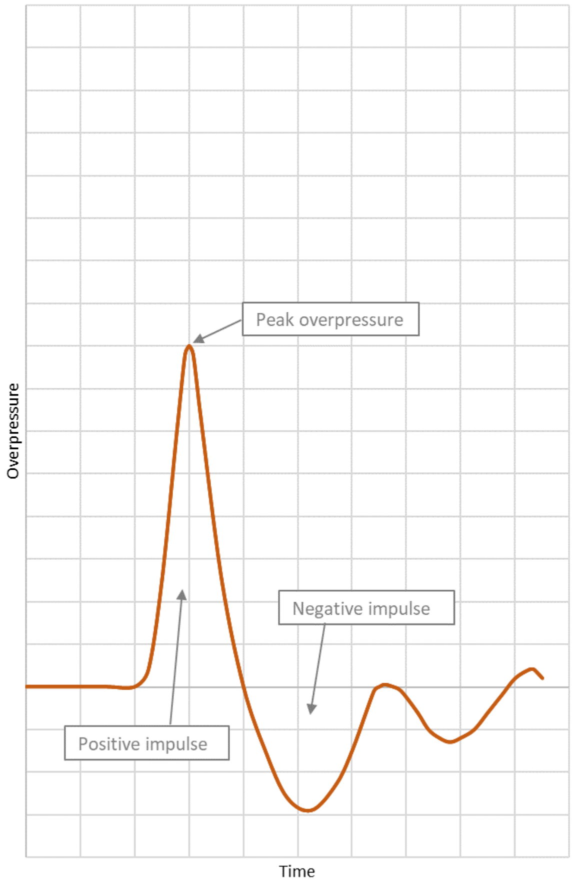

Figure 1a - Typical deflagration overpressure transient

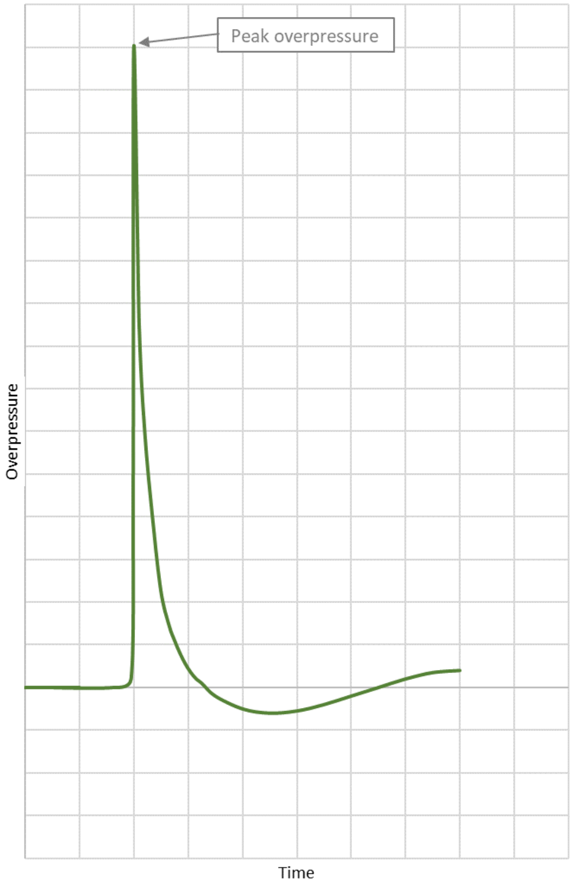

Figure 1b - Typical detonation overpressure transient

The key characteristics of the blast loading transient are its peak positive and negative overpressures, the duration of each phase and the area under each phase of the curve, known as the impulse. The loading transient from a detonation differs fundamentally in that the positive phase has virtually zero rise time, i.e. it is a shock wave in which loading is applied virtually instantaneously, Figure 3b. It is this feature which often makes detonation loading more severe.

The maximum pressure generated in a deflagration is around 8 barg for a fully confined explosion, however pressures of this magnitude are unlikely to be reached due to venting of the explosion either from an intentional vent or failure of the confining structure. In unconfined explosions the pressures generated will be lower than this maximum and are more likely to have a maximum of up to a few barg. The shock wave from a detonation can result in pressures of substantially greater magnitude of up to 20 barg.

These characteristics determine how an affected structural component will respond when subjected to a given blast load. The relationship between the dynamic properties of the structure and the applied transient load determine how the structure responds.

Furthermore, the presence of the structure has an influence on the expanding blast wave. As the wave impinges upon walls, floors and other obstacles it becomes reflected, and thus the peak overpressure applied to the structure is amplified. The amplification for deflagration is typically a factor of 2 as the blast wave gets reflected from the obstacle. This factor can be higher for the shock wave from a detonation with factors in the range 5 to 10.

Comparison of Hydrogen and Methane to Result in Detonation

The increased hazard from the ignition of a flammable gas cloud of hydrogen in air compared to methane in air is primarily based on the increased reactivity of hydrogen giving rise to larger overpressures and a greater potential for detonation to occur. A prerequisite to an explosion event is the formation of a flammable gas cloud. There are a number of factors that affect the formation of a flammable gas cloud;

- Release of a flammable gas. Hydrogen is often stored at high pressure and is highly diffusive which can result in small leaks.
- Mixing of the flammable gas with air. Hydrogen is the most buoyant of gases at normal ambient temperatures. The high buoyancy can result in greater potential for the gas to disperse however, gaseous hydrogen is often stored at high pressure and a high pressure release can promote mixing with air.
- Flammability range. Hydrogen has a larger flammability range than methane, 4 % to 75 % by volume in air compared to 4.4% to 16.4% by volume in air.

Once a flammable gas cloud has been formed there are a number of prerequisites required to reach detonation. These are summarised as follows:-

- Ignition within flammability limits. The minimum ignition energy of hydrogen in air mixture is 20 μJ which is very low and compares with 290 μJ for methane. Typical energy sources that could result in ignition are electrical sources, such as arcs from switches, electrostatic discharge, mechanical sources such as friction or impact from dropped objects and hot surfaces. Increases in the ignition energy above the minimum ignition energy can result in a more energetic reaction and therefore faster initial flame speeds.
- Acceleration of flame front from laminar through subsonic to choking regimes and beyond; or collision of a shock wave with a suitable obstacle, causing shock focusing. The higher initial flame speed for a hydrogen in air mixture means that acceleration to subsonic speeds and beyond is more likely that for the slower flame speed for a methane in air mixture. Methane has a lower laminar flame speed, and while ignition of methane in air mixtures can reach greater than subsonic speeds, this is usually achieved within a confined system, such as a pipe or shock tube or with an increased initial ignition energy such as generated by high explosive.
- Sufficient geometric width to permit detonation cell formation. For hydrogen in air the detonation cell width, λ, varies from 10 mm to around 2 m depending upon the concentration, temperature and pressure of the vapour cloud prior to combustion. For methane the detonation cell width has a smaller range and is around 350 mm and only occurs around a stoichiometric mixture.

Table 1: Comparison of Selected Paramaters for Hydrogen and Methane

Parameter	Hydrogen	Methane
Molecular Weight	2	16
Flammability Range in Air	4% to 75%	4.4% to 16.4%
Stoichiometric concentration (by volume)	29.5%	9.5%
Ignition Energy	20 μJ	290 μJ
Maximum Laminar Flame Speed	28 m/s	3.5 m/s

Summary

The ignition of a flammable mixture of methane or hydrogen in air can result in a deflagation that can generate damaging overpressures. In comparison to methane, hydrogen has larger flammability limits and a lower ignition energy which means that a release has greater potential to result in a deflagration. This should be caveated by the greater potential for a hydrogen release to disperse when released.

The majority of vapour cloud explosion events result in a deflagation. The transition from a deflagration to detonation is complex and requires the correct conditions with a number of factors required to be in place. For mixtures of methane in air the transition to detonation is unlikely except in extreme circumstances such as a confined volume or with a large initial ignition energy. The increased reactivity of hydrogen and the associated initial flame speed means that hydrogen has greater potential for a deflagration to transition to detonation.