

# Domestic and Industrial Hydrogen

Relevant Phenomena for Safety

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#### Introduction

#### **Hydrogen Safety Research**

- Specific properties of Hydrogen and comparison to Natural Gas / LPG
- How the change in properties can effect safety
- Work to be done





#### DNV Spadeadam Engineering, Research and Development



Effects will be illustrated using pictures and video from tests at Spadeadam

Located in the North of England within a MOD facility

MOD Range 5 leased in 1977 - continuously manned since that date

Remote & secure site for studying major accident hazards

- 22.7Te high pressure gas storage
- Cryogenic storage for 33Te LNG or 30Te LiN
- 47.5Te LiN storage

# Properties of Hydrogen

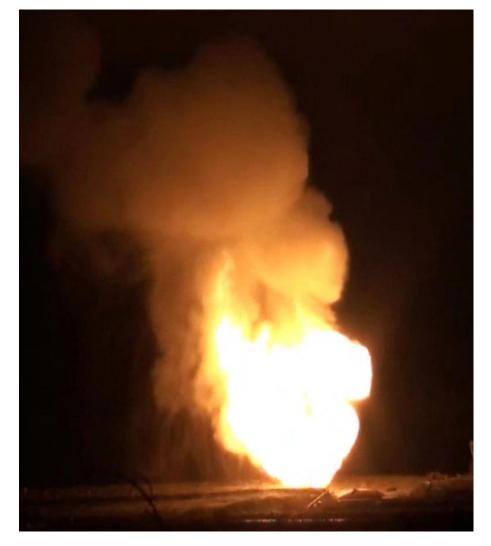


### Properties of Hydrogen

- Some past work in the public domain
- Current work only partly in public domain full publications are imminent.
- Focus on gaseous and liquid H<sub>2</sub> Note: Liquid research at scale not particularly mature.
- For comparisons, we assume a conversion scenario with same hole sizes and same operating pressure
- Topics
  - Introduce Projects
  - Outflow and Energy Content
  - Flammability, Dispersion and Accumulation
  - In-ground migration
  - Ignition
  - Fire
  - Explosion / Detonation



### Air Products / NaturalHy Transmission Fires

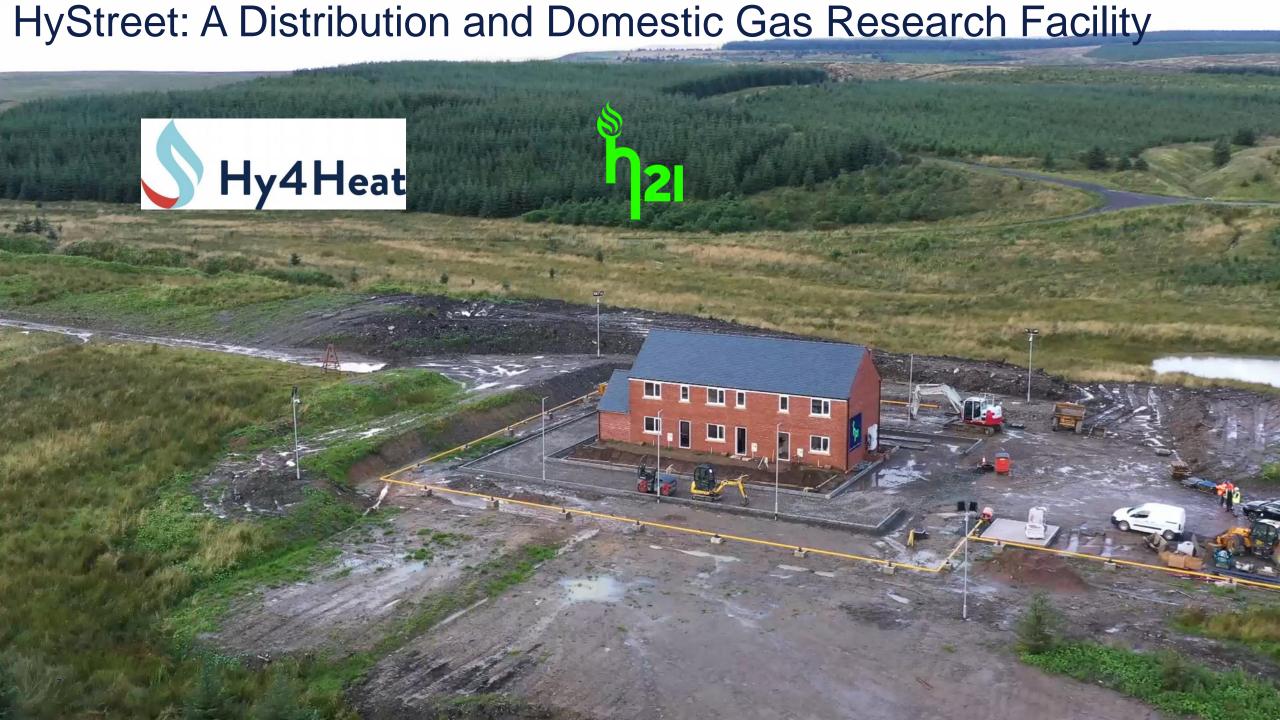




- Transmission releases up to 150mm double ended @ 70bar
- Outflow, thermal and overpressure measurements







### NPRA (via FFI): LH<sub>2</sub> Research



- Project relating to LH<sub>2</sub> bunkering
- Need for large scale data on LH2 release phenomena for model development and validation
  - 'Outdoor Releases'
    - · Including preliminary modelling exercise
  - 'Closed Room Releases'





# Outflow of Hydrogen



www.hy4heat.info



#### Steer Theory and practice

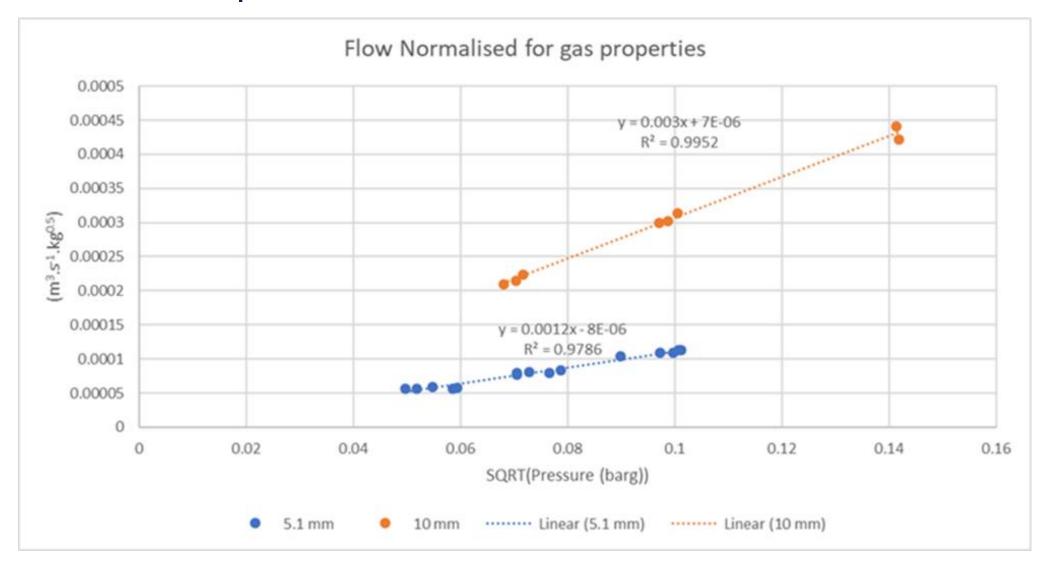
- Pretty ideal gas, expect to behave as theory.
- So for comparison with methane:
  - i.e. Laminar flow through same hole function of pressure and viscosity so at equal pressure will differ by ratio of viscosities (friction inhibited) **OBSERVED**
  - i.e. Turbulent flow through same hole function of root pressure and density so at equal pressure will differ by ratio of root densities (momentum driven)

**OBSERVED** 

Model			H <sub>2</sub>	Ratio	CH₄
			μ = 0.87 x 10 <sup>-5</sup> Pa.s	1:1.24	μ = 1.08 x 10 <sup>-5</sup> Pa.s
			P = 0.0852 kg/m <sup>3</sup>	1:7.98	P = 0.6681 kg/m <sup>3</sup>
w ks)	High Reynolds	ch	$Q \propto \sqrt{\frac{\Delta P}{\rho}}$	2.82 : 1	$Q \propto \sqrt{\frac{\Delta P}{\rho}}$
Turbulent flow (significant leaks)	Momentum dominates	Darcy- Weisbach			
	(High speed, unchoked)				
small	Low Reynold	uille	$Q \propto \frac{\Delta P}{\mu}$		
Laminar flow (small leaks)	Friction Dominates	Hagen-Poiseuille		1.24 : 1	$Q \propto \frac{\Delta P}{\mu}$
	(Low Speed)	Hage			

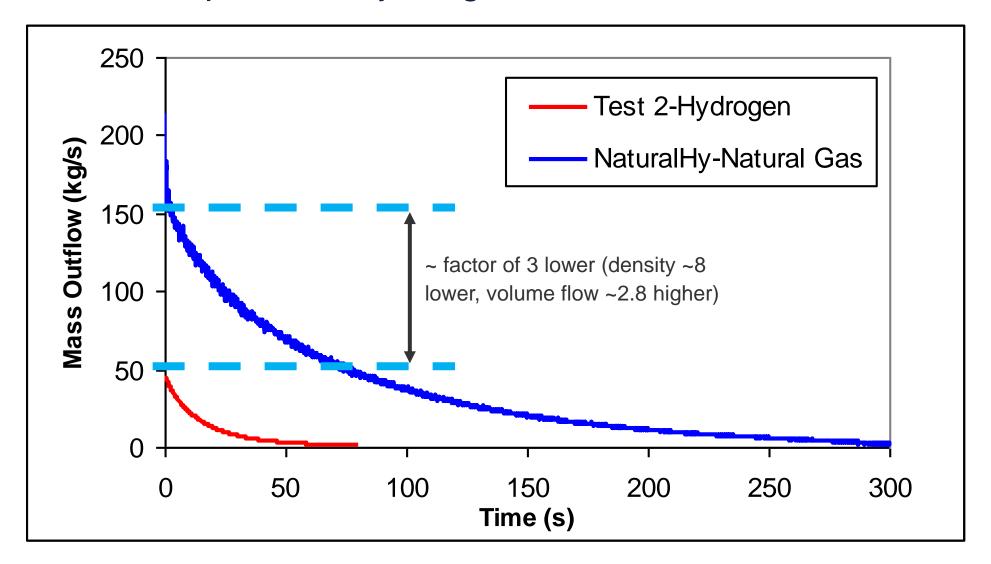


#### Outflow to atmosphere: Gaseous: DNV measurements





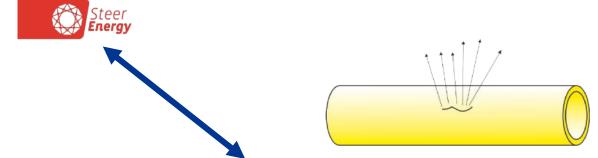
#### Outflow to atmosphere: Very Large Gaseous Releases





#### Leakage to Atmosphere: Conclusions (low pressure at least)

- Considering risk, nearly all leaks to atmosphere with the potential to cause harm are turbulent
- Considering conversion of gas networks, operating pressures will be similar to today
  - => leaks will produce a factor of 2.8 more gas per second on volumetric basis
- Conclusion of Hv4Heat WP7 Lot1 (for low pressure leaks):



Non-leaking in Methane = Non-leaking in Hydrogen Leaking in Methane = Leaking in Hydrogen





#### Energy Content: How much GH<sub>2</sub> do we need to replace methane?

- Heat of Combustion (HHV):
  - Methane = 55.5 MJ/kg
  - Hydrogen = 142 MJ/kg





- Heat Energy per Litre
  - Methane = 40 kJ/litre
  - Hydrogen = 13 kJ/litre
- Ratio = 3.2
  - i.e. three times the velocity in the pipe for the same energy flux (power)
  - Density considered → lower momentum for H<sub>2</sub>

- Density (@1bara):
  - Methane = 0.717 kg/m<sup>3</sup>
  - Hydrogen = 0.089 kg/m<sup>3</sup>
- Ratio = 8.1

- 30kW appliance will require approx. 3 litres per second,
   180 SLPM
- Boil 1 litre of water from 10°C to 100°C will require 90
   (K) x 4.2 (kJ.K<sup>-1</sup>.kg<sup>-1</sup>) x 1 (kg) / 13 (kJ/litre) = 30 litres
  - ....@ 100% efficiency...

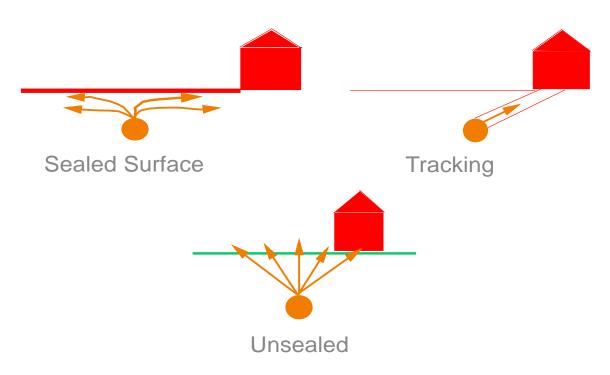


#### Outflow Underground

- Idealised leakage into ground should be laminar Darcy flow and only dependent on pressure, permeability of soil and viscosity of fluid
- => flow into soil higher by ratio of viscosities when compared to methane (i.e. factor 1.2 higher)
- Reality includes tracking so likely flow rates are between factor 1.2 and 2.8 higher
- Darcy (laminar) flow:

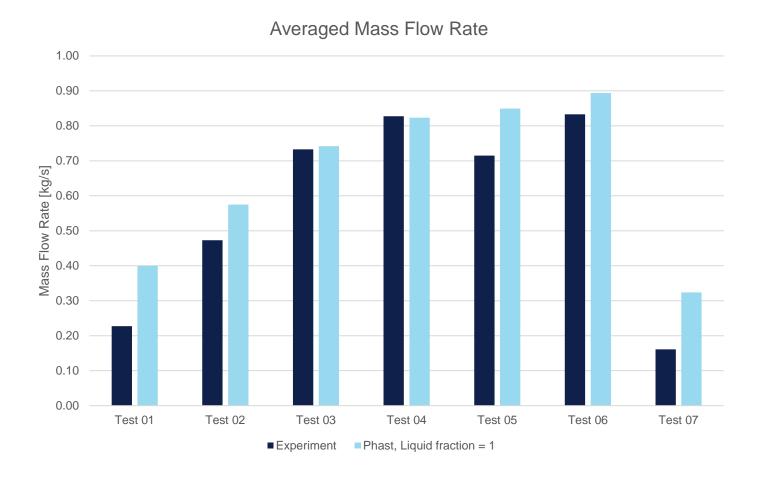
$$Q = \frac{kA}{\mu L} \Delta p$$

- · k is the absolute permeability
- µ is viscosity

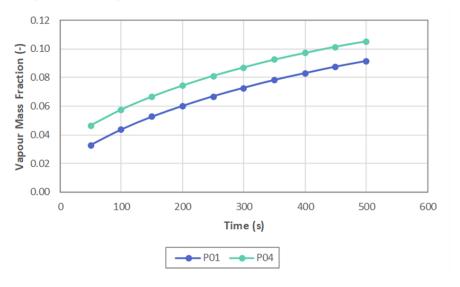




#### LH<sub>2</sub> Flow rates: experiments vs Phast predictions



- Standard Phast leak model
- Averaged pressure at Orifice
- Saturation temperature
- Assume liquid fraction 1.0
- Flow rate predictions: Generally good agreement

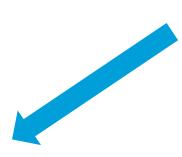




#### Energy Content: How much LH<sub>2</sub> do we need to replace LNG?

- Heat of Combustion (HHV):
  - Methane = 55.5 MJ/kg
  - Hydrogen = 142 MJ/kg





- Density (@1bara):
  - Methane = 500 kg/m<sup>3</sup>
  - Hydrogen = 70 kg/m<sup>3</sup>
- Ratio = 7.1

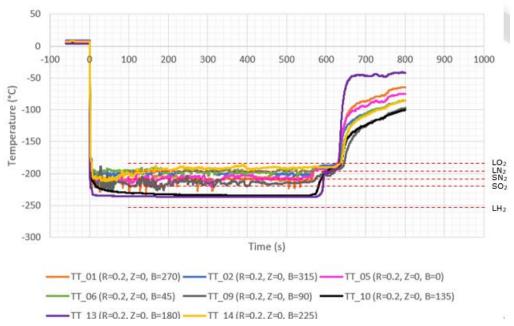
- Heat Energy per unit volume
  - Methane = 28 GJ/m<sup>3</sup>
  - Hydrogen = 10 GJ/m<sup>3</sup>
- Ratio = 2.8
  - i.e. three times the volume for the same energy store
  - But only 0.4 x mass



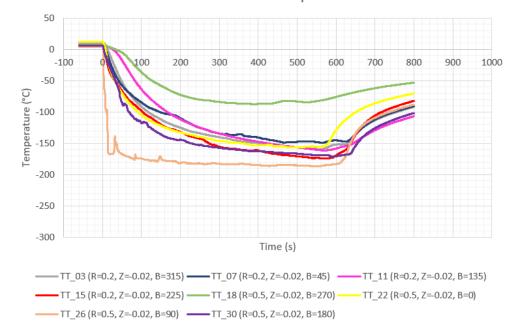
### From LH<sub>2</sub> experiment: Pooling / Rainout

- Surface temperature measurements show evidence of LH<sub>2</sub>
  - Difficult to distinguish between 2-phase and actual pool
  - Release in this example (Test02) stops circa 560 seconds
    - Enduring L-Air components ~80 seconds after release
  - No LH<sub>2</sub> evidence beyond 0.5m from release
- No evidence of rainout in horizontal releases
- NOTE: Models do predict presence of LH<sub>2</sub> pools

#### Surface Temperature@ 0.2m Radius



#### -20mm Concrete Temperature



# Dispersion of Hydrogen



### Flammability in Air

Fuel	LFL (%vol)	UFL (%vol)	Stoichiometric (%vol)
Hydrogen	4	75	30
Methane	5	14	10
Propane	2.1	9.5	4.0

- Much wider flammable range for hydrogen
- Stoichiometric ratio is higher discuss later but can be an advantage as higher fuel ratios required for very reactive mixtures
- Slightly narrower for cold H2 (see <a href="http://www.hysafe.net/wiki/BRHS/ChemicalPropertiesOfHydrogen">http://www.hysafe.net/wiki/BRHS/ChemicalPropertiesOfHydrogen</a>):

$$c_{LFL} = c_{LFL}(300K) - \frac{3.14}{\Delta H_c}(T - 300) = 4.0 - 0.013 (T - 300) [vol\%]$$
 For T = 90 K (O<sub>2</sub> b.p.):  
 
$$LFL = 6.7 \text{ %vol}$$
 
$$c_{UFL} = 74.0 + 0.026 (T - 300) [vol\%]$$
 UFL = 68.5 %vol



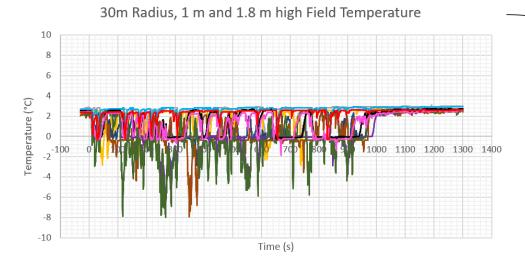
### Vapour Releases: Dispersion

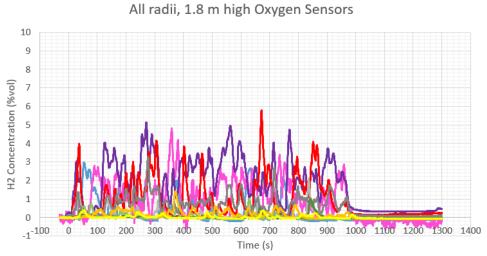
- Dispersion in open releases is determined by turbulence, buoyancy and momentum
- Higher buoyancy of hydrogen would imply shorter dispersion distances for same volumetric flow (i.e. distance to flammable limits will be less)
- Not necessarily true for like hole-size / pressure combination where higher volumetric flow is expected

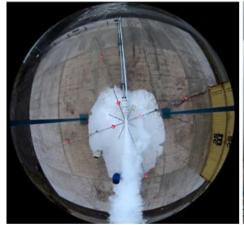
Fuel	Density (kg/m³)
Hydrogen	0.089
Methane	0.717
Propane	1.808



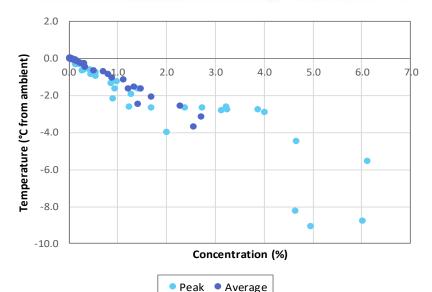
### From LH<sub>2</sub> experiment: Dispersion, LFL Limits







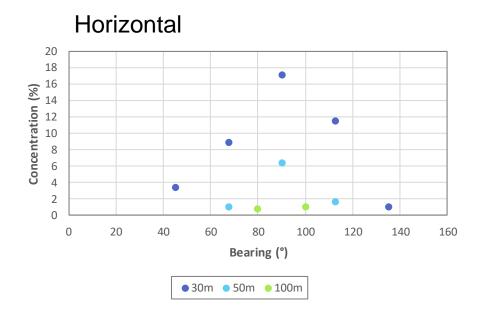


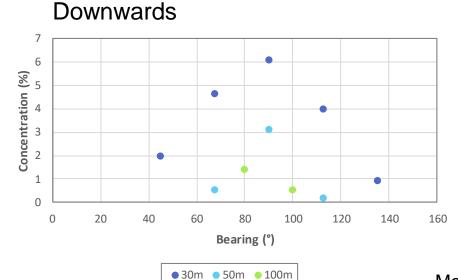


- Generally:
  - Increased concentration → decreased temperature



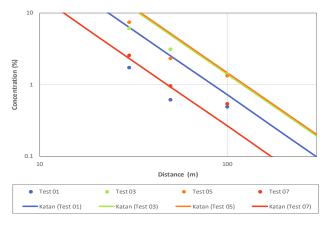
#### From LH<sub>2</sub> experiment: Dispersion, LFL Limits





- Generally (all near ground level):
  - Decaying concentrations with distance
  - Centred on downwind bearing
  - Greater concentrations for horizontal than downwards
  - LFL farther reaching in horizontal

#### Models seem conservative:





# Accumulation of Hydrogen

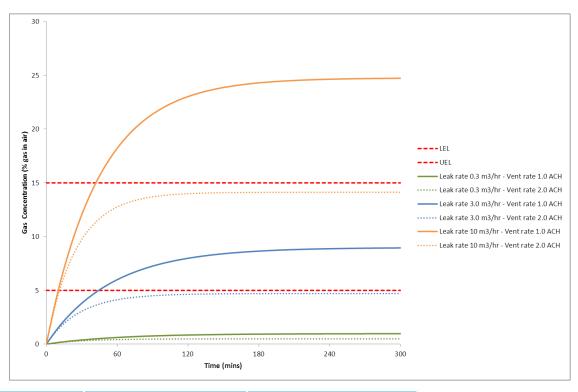


#### Accumulation

- Accumulation in enclosed spaces determined by volume of enclosed space, buoyancy of gas, gas ingress rate, air change rate and time since release
- Generally:
  - Buoyant gases accumulate above the release point, mixing into the layer according to:

$$C = \left(\frac{100Q_g}{Q_a + Q_g}\right) \left\{1 - \exp\left[-\left(Q_a + Q_g\right)t/V\right]\right\}$$

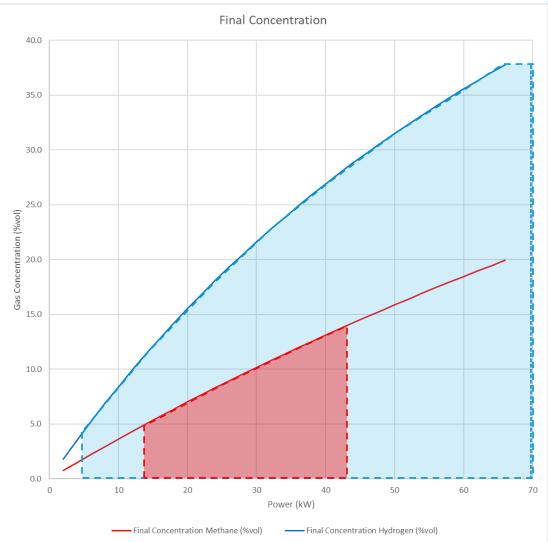
- Meaning that for like-for-like H<sub>2</sub> and CH<sub>4</sub> releases, one could expect that the concentration at any one time being higher
- At higher concentrations, buoyancy driven ventilation could be an issue



Volume (m³)	Air Flow Rate (m³/hr)	Methane Flow Rate (m³/hr)	Hydrogen Flow Rate (m³/hr)	1 Hour Concentration Methane (%vol)	1 Hour Concentration Hydrogen (%vol)		
1	1	0.1	0.28	6	15	9	22
1	1	0.2	0.56	12	25	17	36
1	1	0.3	0.84	17	33	23	46



#### Accumulation



Power (kW)	Volume (m³)	Air Change Rate (changes/ hr)	Methane Flow Rate (m³/hr)	Hydrogen Flow Rate (m <sup>3</sup> /hr)	1 Hour Concentration Methane (%vol)	1 Hour Concentration Hydrogen (%vol)	Final Concentration Methane (%vol)	Final Concentration Hydrogen (%vol)
2	30	1	0.2	0.6	0.5	1.1	0.7	1.8
4	30	1	0.5	1.1	0.9	2.3	1.5	3.5
6	30	1	0.7	1.7	1.4	3.3	2.2	5.2
8	30	1	0.9	2.2	1.9	4.4	2.9	6.9
10	30	1	1.1	2.8	2.3	5.4	3.6	8.4
12	30	1	1.4	3.3	2.8	6.4	4.3	9.9
14	30	1	1.6	3.9	3.3	7.4	5.0	11.4
16	30	1	1.8	4.4	3.7	8.4	5.7	12.8
18	30	1	2.0	5.0	4.2	9.3	6.4	14.2
20	30	1	2.3	5.5	4.6	10.2	7.0	15.5
22	30	1	2.5	6.1	5.1	11.1	7.7	16.8
24	30	1	2.7	6.6	5.5	12.0	8.3	18.1
26	30	1	2.9	7.2	6.0	12.9	8.9	19.3
28	30	1	3.2	7.7	6.4	13.7	9.6	20.5
30	30 1 3.4	3.4	8.3	6.8	14.5	10.2	21.6	
32	30	1	3.6	8.8	7.3	15.3	10.8	22.7
34	30	1	3.8	9.4	7.7	16.1	11.4	23.8
36	30	1	4.1	9.9	8.1	16.9	12.0	24.9
38	30	1	4.3	10.5	8.5	17.6	12.5	25.9
40	30	1	4.5	11.0	9.0	18.4	13.1	26.9
42	30	1	4.8	11.6	9.4	19.1	13.7	27.9
44	30	1	5.0	12.1	9.8	19.8	14.2	28.8
46	30	1	5.2	12.7	10.2	20.5	14.8	29.7
48	30	1	5.4	13.2	10.6	21.2	15.3	30.6
50	30	1	5.7	13.8	11.0	21.9	15.9	31.5
52	30	1	5.9	14.3	11.4	22.6	16.4	32.3
54	30	1	6.1	14.9	11.8	23.2	16.9	33.2
56	30	1	6.3	15.4	12.2	23.9	17.4	34.0
58	30	1	6.6	16.0	12.6	24.5	17.9	34.8
60	30	1	6.8	16.6	13.0	25.1	18.5	35.6
62	30	1	7.0	17.1	13.4	25.7	19.0	36.3
64	30	1	7.2	17.7	13.8	26.3	19.4	37.0
66	30	1	7.5	18.2	14.2	26.9	19.9	37.8



#### Accumulation in Practice (more later)



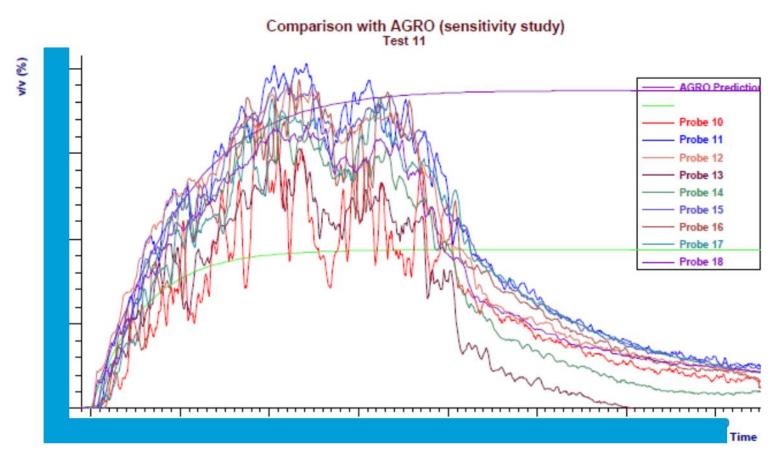
- Release pressure of 100bar, nozzle sizes up to 1.6mm (flow up to 20 g/s)
- Partially ventilated enclosure, monitored accumulation / venting

- Full scale filling station and plant room
- Culmination of more idealised explosion experiments





#### Accumulation in Practice



- Accumulation largely predictable by existing phenomenological models which have buoyancy terms and take into account vent openings, wind direction etc.
- No real surprises when compared to other buoyant gases (e.g. NG)



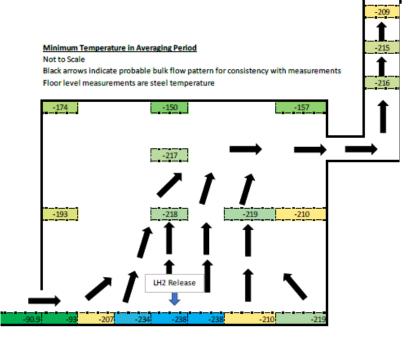
#### LH<sub>2</sub> Accumulation in Practice

- Only large leaks into small enclosure in NPRA works
- Pooling
- Temperatures below that of liquid air products
  - → Air entering chamber condenses / freezes

Smaller releases somewhere closer to vapour mixing /

accumulation

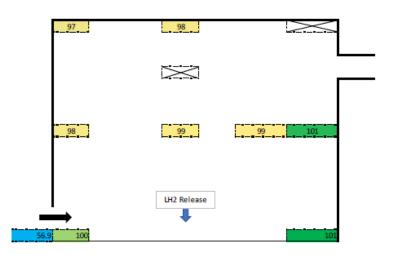




#### Hydrogen Concentration

Not to Scale

Uses maximum value before trace truncated for temperature effects



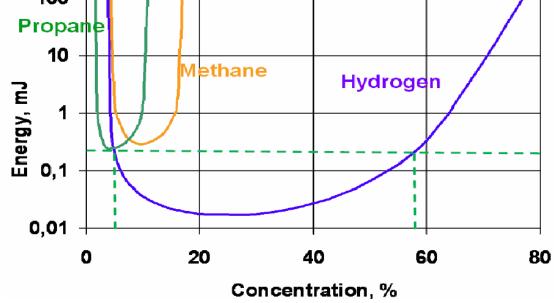


# Ignition of Hydrogen



#### Minimum Ignition Energy (MIE) and Autoignition

Fuel in Air	Minimum Ignition Energy (mJ)	Autoignition Temp (K)
Methane	0.30	813
Ethane	0.26	788
Propane	0.26	723
Butane	0.26	678
Propylene	0.28	733
Hydrogen	0.02	793 - 1023 (858)



http://www.hysafe.net/wiki/BRHS/MainCharacteristicDataOfHydrogen

- Full order of magnitude lower MIE
  - Not full story as many common ignition sources have abundant energy for ignition of other gases
- Higher autoignition temperature good news for hot surface ignition
- All of above at nominal standard conditions care around cryogenic temperatures

https://www.semanticscholar.org/paper/LECTURE.-Sources-of-hydrogenignition-and-

measures/65099ce728577093e3cc2f76b9ccc32d66b4df80/figure/2

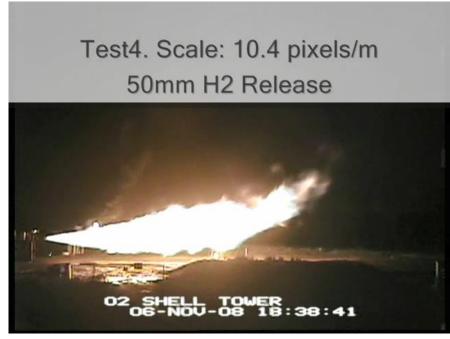


# Hydrogen Fires



#### Fires







- Transmission releases up to 150mm double ended @ 70bar
- Outflow, thermal and overpressure measurements



#### Fires (refresh from hydrocarbons)

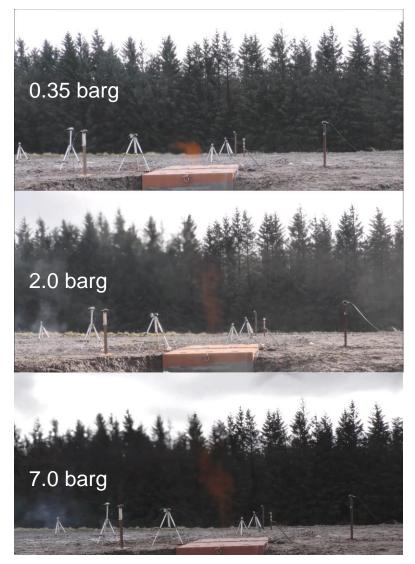
Parameter	Description	0.1 kg s <sup>-1</sup>	1.0 kg s <sup>-1</sup>	10 kg s <sup>-1</sup>	>30 kg s <sup>-1</sup>
Flame length (m)	Distance from release source to flame tip	5	15	40	65
Fraction of heat radiated, F  Proportion of the combustion energy of the released gas radiated		0.05	0.08	0.13	0.13
Total heat flux (kW m <sup>-2</sup> )	Total heat flux onto an object in the flame	180	250	300	350
Radiative flux (kW m <sup>-2</sup> )	Thermal load from flame radiation onto an object in the flame	80	130	180	230
Convective flux (kW m <sup>-2</sup> )	Thermal load from convective movement of hot gas over an object in the flame	100	120	120	120

- Heat applied to object within flame is sum of radiative and convective components
- No known measurements at large scale of total heat flux for hydrogen
  - Adiabatic flame temperature is higher so expect perhaps increase in convective heat



#### Fires

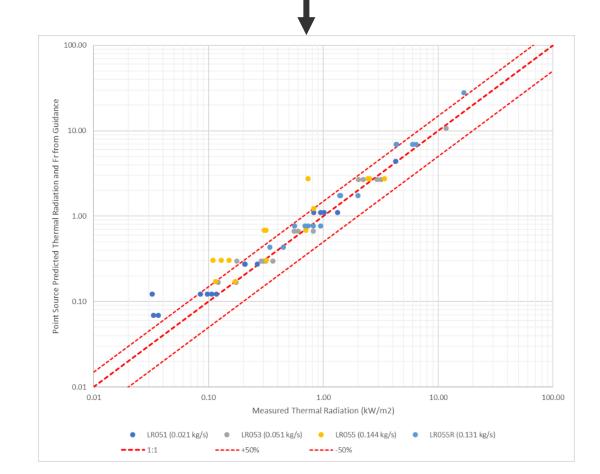




Generally: thermal field dependent on heat energy outflow (power),
 fraction of heat radiated and distance from fire

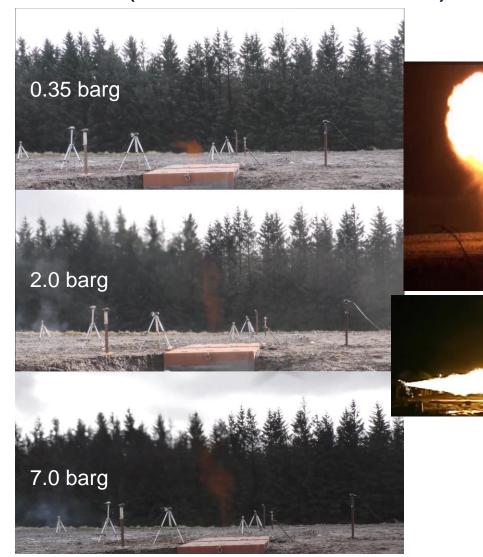
$$I = \frac{QF_r}{4\pi r^2}$$

Very simple point source check



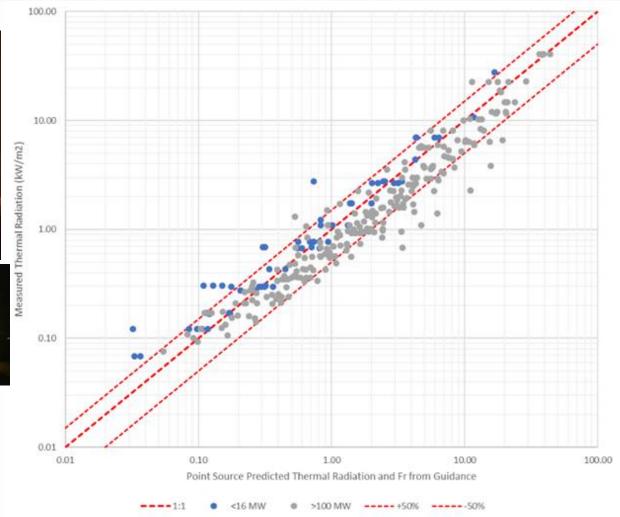
#### Fires (H21 + AirProducts)







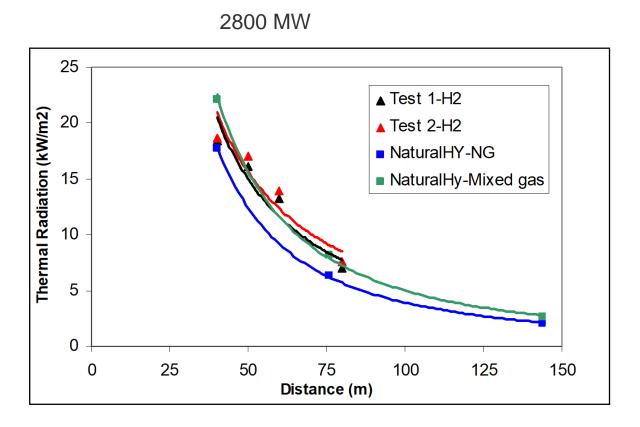


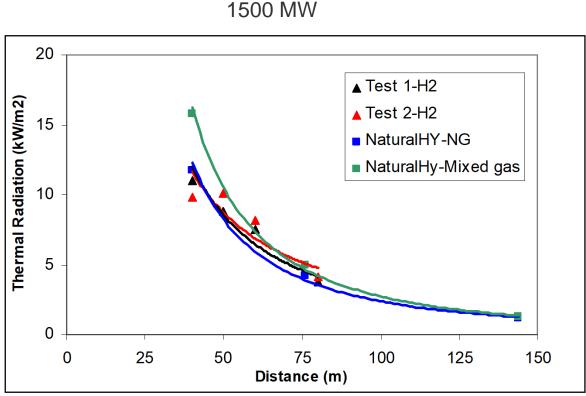




#### Fires: Air Products Hydrogen Transmission Fires: Key Findings

• Thermal field dependent on heat energy outflow (power), fraction of heat radiated and distance from fire

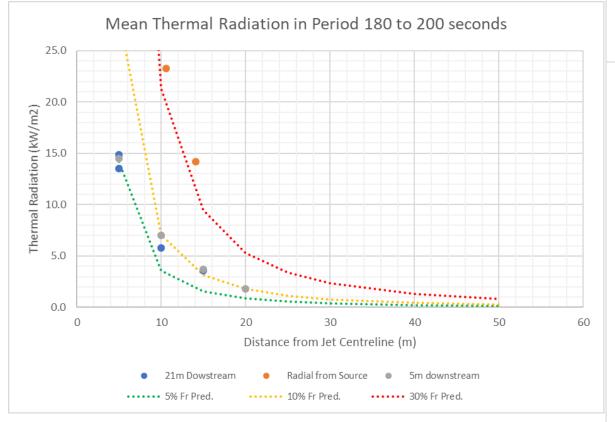


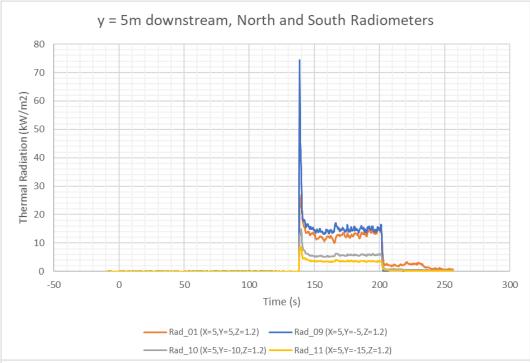


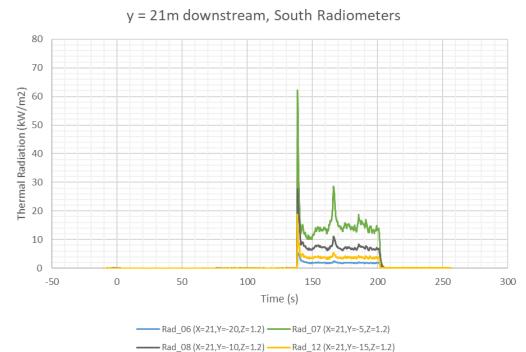


#### LH<sub>2</sub>: Thermal Radiation (delayed ignition)

- Seems to fall with r-2
- Initial fireball ~4-5 times higher flux than steady state
- Curious that radial sensors higher than normal sensors







#### Fires: Visual

- Difficult to assess visual comparison with limited data sets
- NG can be non-luminous and H2 can be highly luminous

Experiment 3, NG, 25 mm, 2 bar, upwards

LR053, H<sub>2</sub>, 20 mm, 2 bar, upwards





Experiment 8, NG, 75 mm, 0.5 bar, impacting

LR042, H<sub>2</sub>, 70 mm, 2 bar, horizontal







## LH<sub>2</sub> Fires: Visual

#### **Vertically Down**



#### **Horizontal (away from camera)**





# Hydrogen Explosions

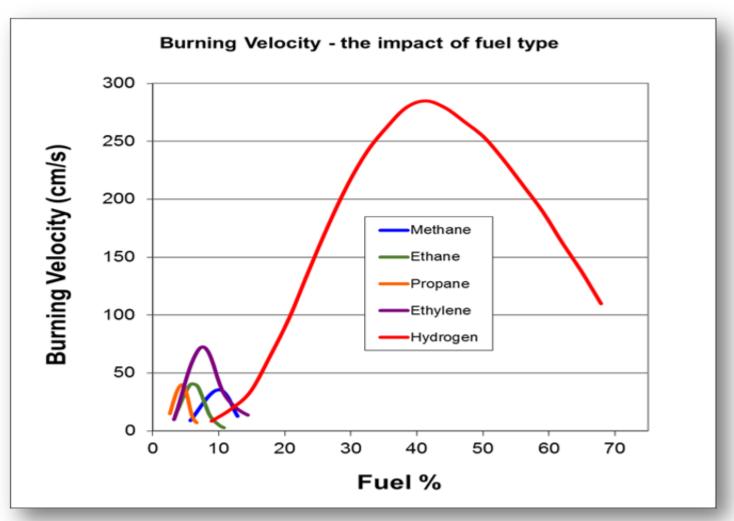


#### **Explosion: Expansion Ratio**

- Expansion ratio is ~ ratio of flame temperature and initial mixture temperatures
  - Max. theoretical from 300 K initial conditions and adiabatic flame
    - ~8.5 barg (hydrocarbons similar)
- Caution for cold mixtures from LH<sub>2</sub>: 90 K initial conditions  $\rightarrow$  >3x expansion ratio

#### **Explosion: Reactivity**

- Significantly higher burning velocity at higher concentrations
- Not all bad news below 15% or so, hydrogen less reactive than other fuels
- But increased reactivity will significantly enhance confined explosion





#### **Explosion: Reactivity**

Laminar burning velocity also has a temperature dependency:

- http://www.hysafe.org/img/hydrairarticle.pdf:
- $\beta_1 = 1.54$  at  $\Phi = 1.0$

• So @ 
$$T_u$$
 = 90 K ( $O_2$  b.p.),  $T_{u0}$  = 300 K,  $P = P_0$ 

• 
$$S_{uL} = 3.3^{1.54} \times S_{uL0} = 6.3 \times S_{uL0}$$

• So @ 
$$T_u$$
= 90 K ( $O_2$  b.p.),  $T_{u0}$  = 300 K,  $P = P_0$   $\frac{S_{uL}}{S_{uL}^o} = \left(\frac{T_u}{T_{u0}}\right)^{\beta_1} \left(\frac{P}{P_0}\right)^{\beta_2}$ , •  $S_{uL}$  = 3.3<sup>1.54</sup> x  $S_{uL0}$  = 6.3 x  $S_{uL0}$ 

#### Hydrogen Explosions in Practice

 Explosions range from benign to extreme for relatively minor changes in ventilation, outflow rate, confinement and congestion



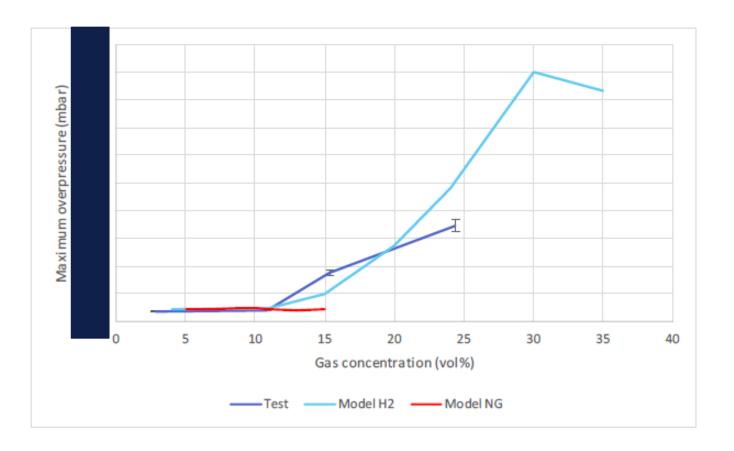


8% H<sub>2</sub> 26% H<sub>2</sub>



### Hydrogen Explosions in Practice – comparison with Methane

- Dynamic effects in explosion vs. inertial effects of venting mechanisms
  - CH4 often benefits from venting
  - ->~10% H2 the speed of reaction can begin to overcome the venting mechanisms
- Can mean greater damage e.g. wall failure instead of window failure.



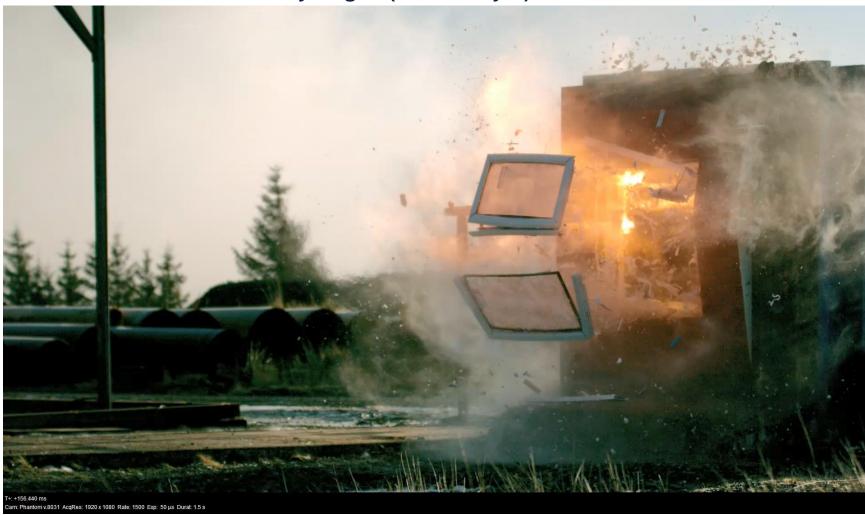


#### Hydrogen Explosions in Practice – comparison with Methane



#### Hydrogen Explosions in Practice – comparison with Methane





### LH<sub>2</sub>: Confined Vented Explosion



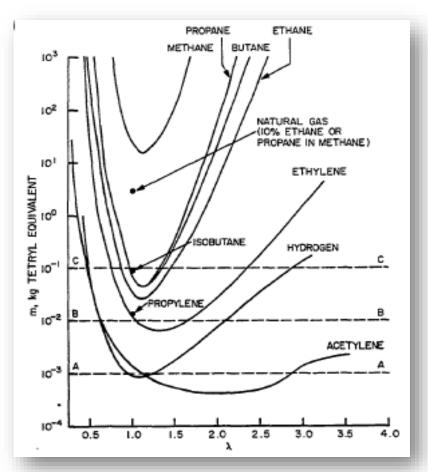
- Compared to gaseous release:
  - Greater expansion ratio
  - Embrittlement issues for steelwork
  - Presence of liquid / solid products of air

#### **Explosion Detonation Initiation**

- Detonability varies with fuel type and fuel concentration
- Initiation of detonation quantified by explosive mass required to initiate a detonation

Fuel	Minimum Mass tetryl (g)
Hydrogen	0.8
Methane	16,000
Propane	37
Ethylene	5.2
Acetylene	0.4

- Natural Gas detonations ~NEVER happen
- Hydrogen detonations are entirely credible



Concentration limits to the initiation of unconfined detonation in fuel/air mixtures, DC Bull, Transactions of the Institute of Chemical Engineers, Volume 57, Number 4, Pages 219-2271979 (λ indicates the concentration relative to stoichiometric)



## **Explosion Detonation Initiation**



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