

Presentation Start

Hydrogen Behavior – Myth Busting



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Safety

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Hydrogen Myths

- ⇒ Hindenburg
 - Hydrogen Caused the Disaster
- ⇒ Hydrogen Molecular Diffusivity is 3.8 times that of CH₄
 - Therefore it diffuses rapidly and mitigates any hazard
- ⇒ Hydrogen is 14.4 times lighter than air
 - Therefore it rapidly moves upward and out of the way
- ⇒ We do not know the flammability limits for H₂





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- ⇒ We just do not understand hydrogen combustion behavior
 - Hydrogen release is different than other fuels
 - Radiation is different than other fuels
- ⇒ Hydrogen hazards can be compared favorably to experiences with other hydrocarbon fuels
 - Less dangerous than gasoline, methane ...
- ⇒ Hydrogen is toxic and will cause environmental harm
 - “... We need to be indemnified against a hazardous toxic hydrogen spill ...” – Generic Insurance Company





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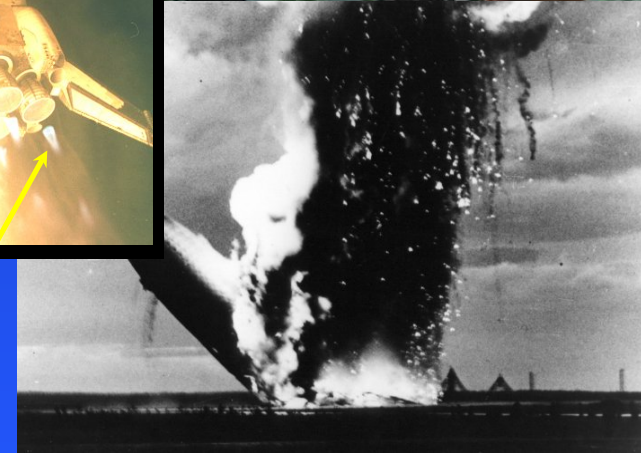
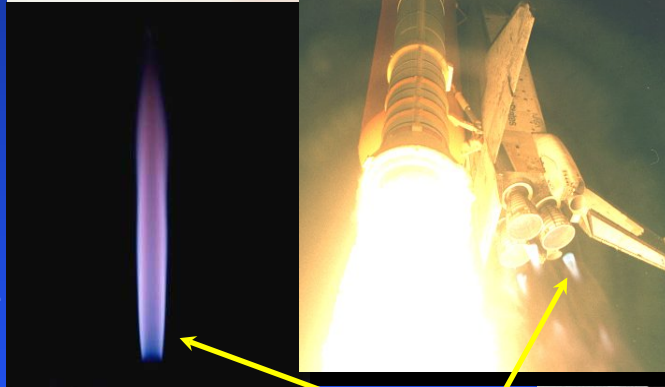




Lets get this out of the way!

Hindenburg Disaster

- 36 out of 97 died mostly trapped by the fire of fabric, diesel fuel, chairs, tables ... (not hydrogen)
- The craft did not explode but burned – and while burning stayed aloft (Hydrogen was still in the nose)
- The craft fell to the ground tail first – the nose was still full of hydrogen
- Radiation from the flame was red and orange – hydrogen flames emit in the near UV ~ 304 to 350 nm (OH^* lines), 680 nm to 850 nm (vibrationally excited H_2O), and ~ 0.5 to 23 μm (water bands)



Lets get this out of the way!

Hindenburg Disaster (Cont'd)



- ⇒ The covering was coated with cellulose nitrate or cellulose acetate -- both flammable materials. Furthermore, the cellulose material was impregnated with aluminum flakes to reflect sunlight. -- Dr. Addison Bain
- ⇒ A similar fire took place when an airship with an acetate-aluminum skin burned in Georgia – **it was full of helium!**
- ⇒ “I guess the moral of the story is, don’t paint your airship with rocket fuel.”
-- Dr. Addison Bain



Courtesy of *Dr. Addison Bain and the National Hydrogen Association*





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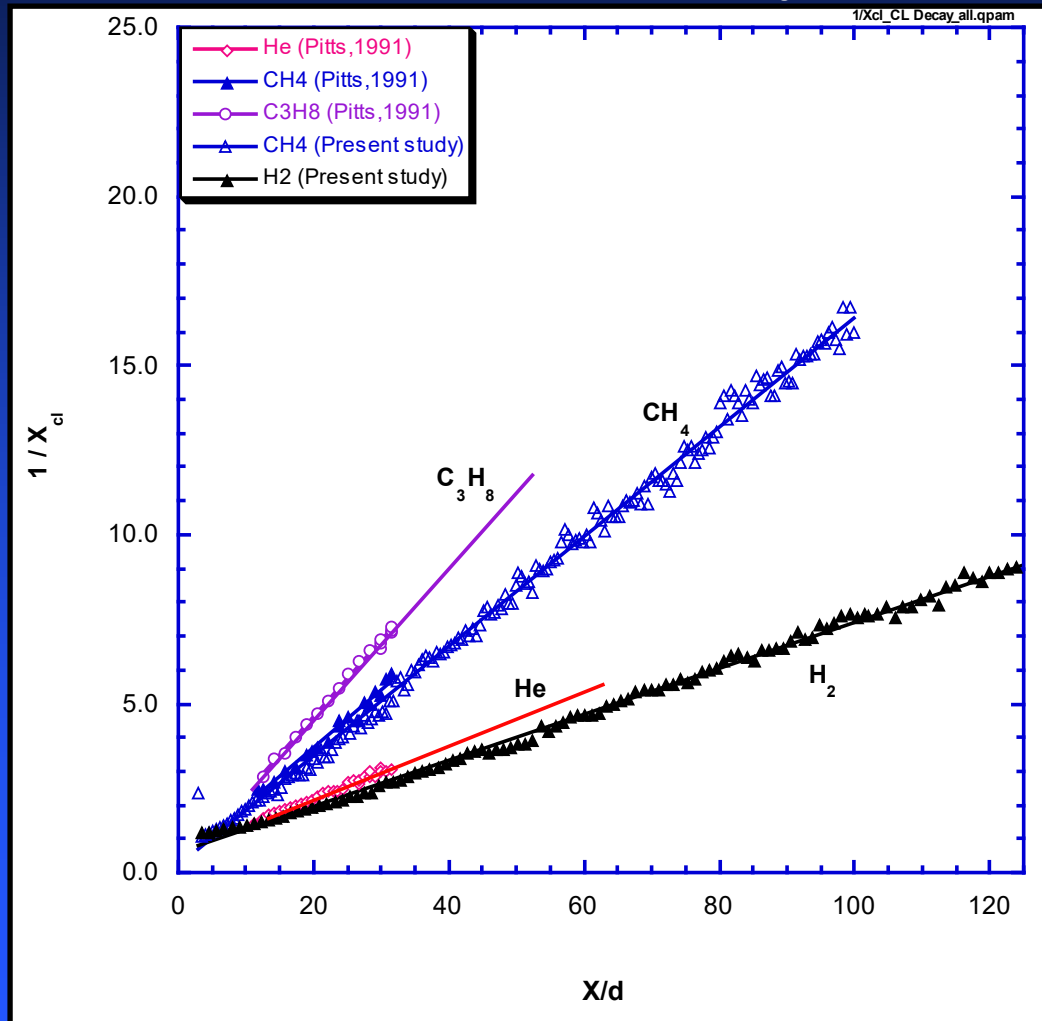
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Small Unignited Releases: Momentum-Dominated Regime



Data for round turbulent jets



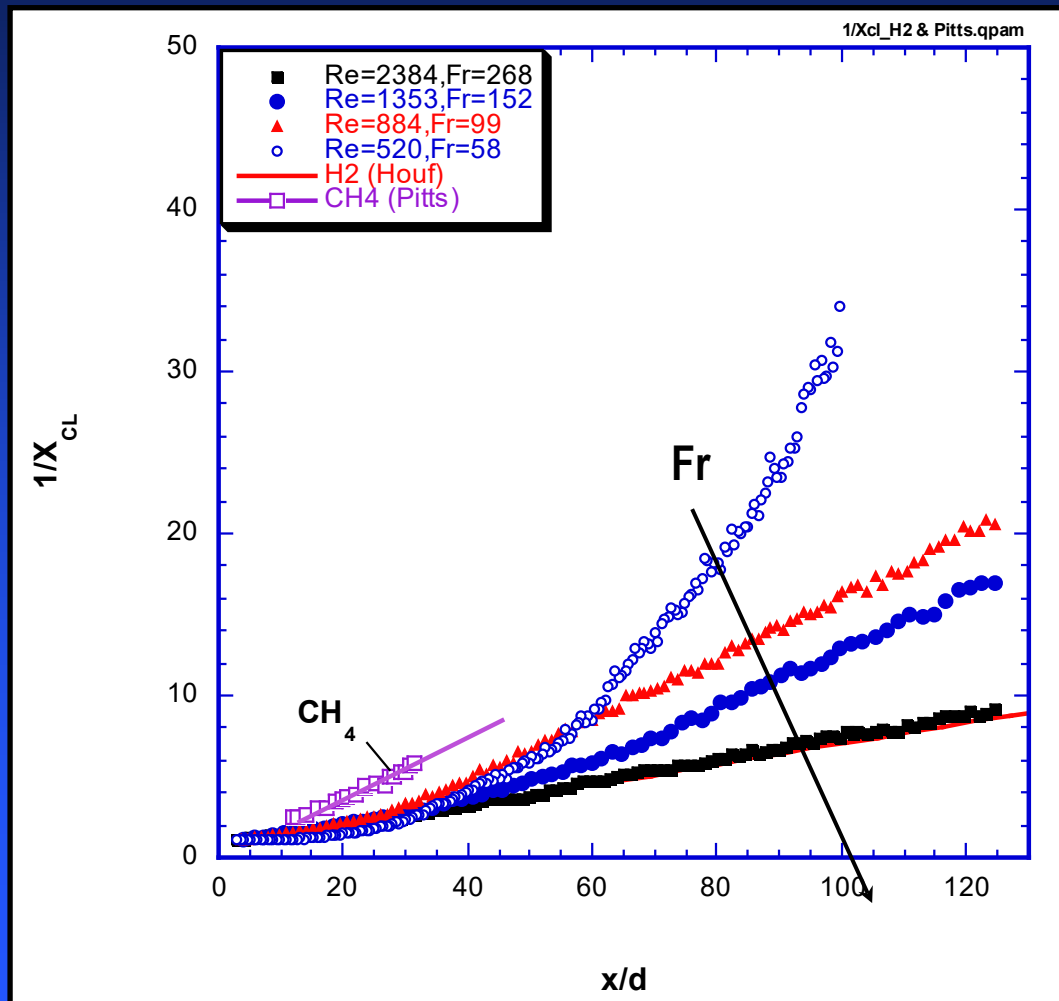
- ⇒ In momentum-dominated regime, the centerline decay rate follows a $1/x$ dependence for all gases.
- ⇒ The centerline decay rate for mole fraction increases with increasing gas density.
- ⇒ The decay rate for H₂ is significantly slower than methane and propane.





Small Unignited Releases: Buoyancy Effects

⇒ Data for round H₂ Jets (d_j=1.91 mm)



- ⇒ At the highest Fr, 1/X_{CL} increases linearly with axial distance, indicating momentum dominates.
- ⇒ As Fr is reduced buoyancy forces become increasingly important and the centerline decay rate increases.
- ⇒ The transition to buoyancy-dominated regime moves upstream with decreasing Fr.





Hydrogen Myths

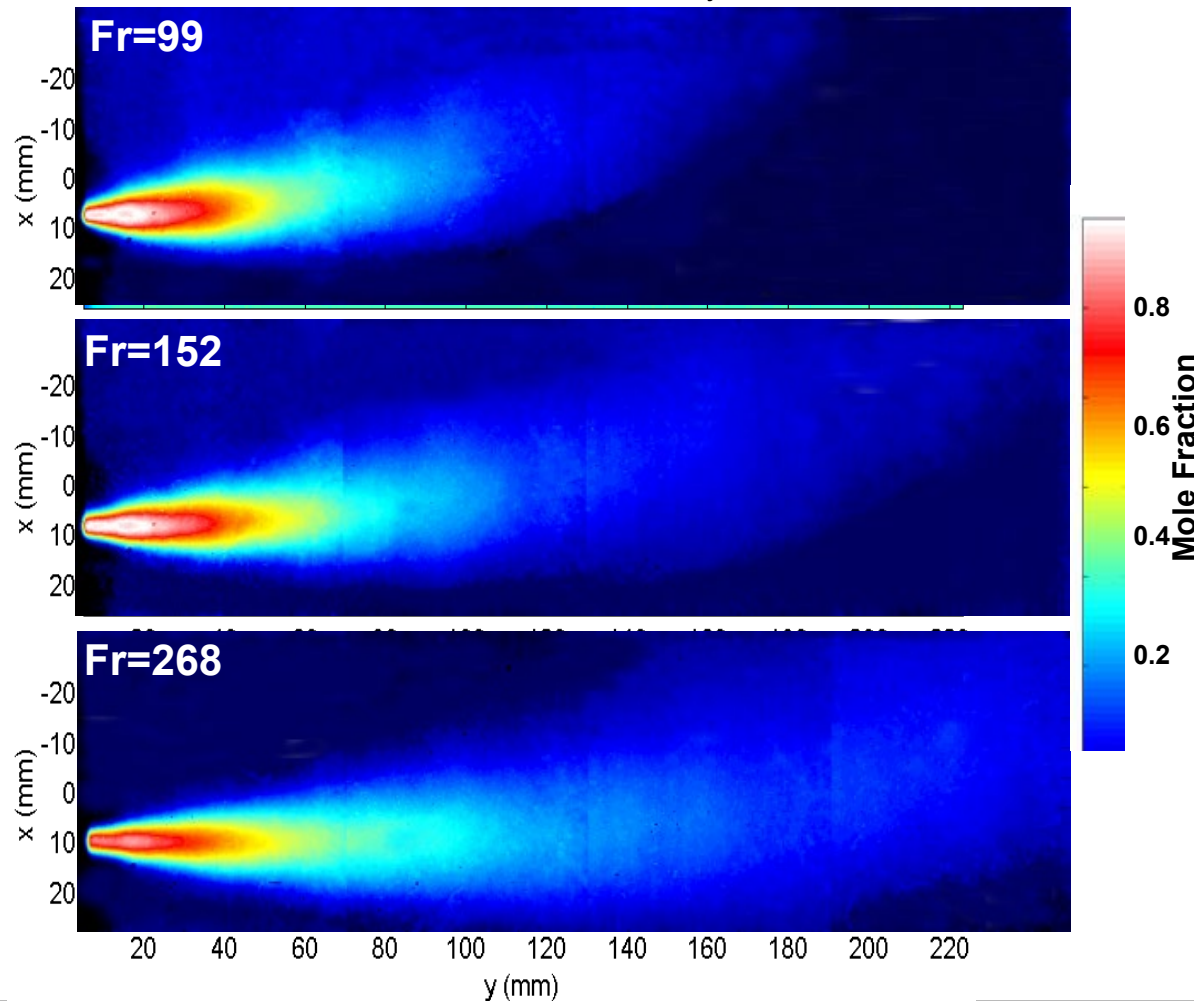
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Buoyancy effects are characterized by Froude number



Horizontal H₂ Jet ($d_j=1.9$ mm)



- ⇒ Time-averaged H₂ mole fraction distributions.
- ⇒ Froude number is a measure of strength of momentum force relative to the buoyant force
- ⇒ Increased upward jet curvature is due to increased importance of buoyancy at lower Froude numbers.



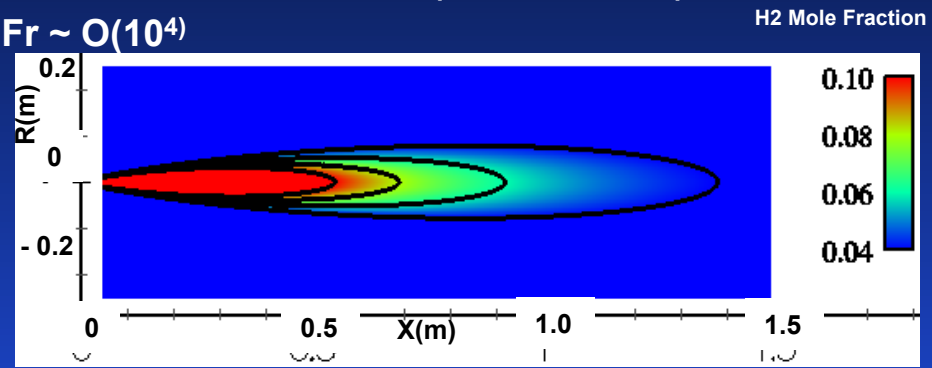


Choked & Unchoked Flows at 20 SCFM

Tank Pressure = 3000 psig, Hole Dia. = 0.297 mm

Exit Mach Number = 1.0 (Choked Flow)

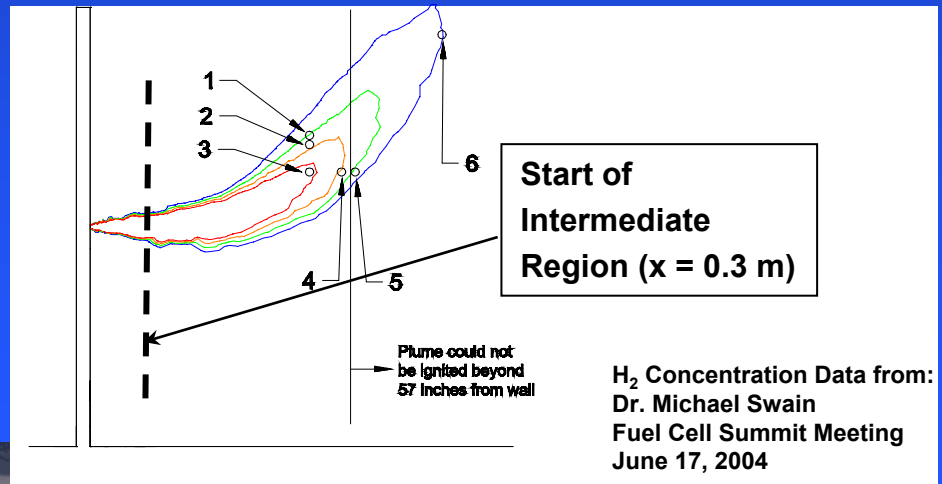
Fr ~ O(10⁴)



Flowrate = 20 scfm, Hole Dia. = 9.44 mm

Exit Mach Number = 0.1 (Unchoked Flow)

Fr ~ O(100)



- ⇒ Correlations based on experimental data
- ⇒ Start Intermediate Region
 - $x/D = 0.5 F^{1/2} (\rho_{\text{exit}}/\rho_{\text{amb}})^{1/4}$
- ⇒ End Intermediate Region
 - $x/D = 5.0 F^{1/2} (\rho_{\text{exit}}/\rho_{\text{amb}})^{1/4}$
- ⇒ F = Exit Froude No.
 - = $U_{\text{exit}}^2 \rho_{\text{exit}} / (gD(\rho_{\text{amb}} - \rho_{\text{exit}}))$

Start Intermediate Region - x = 6.3 m

- ⇒ Assuming gases at 1 Atm, 294K (NTP)
 - Red – 10.4%
 - Orange – 8.5%
 - Green – 5.1%
 - Blue – 2.6%

*(Chen and Rodi, 1980)



Momentum-Dominated Jets are within the Ignition Region



Flow between exit and 4% mole fraction (LFL) remains in jet momentum dominated regions
Choked flow conditions

Unignited Jet Separation Distance Length Scales

Pressure = ~20 MPa (~3000 psig)

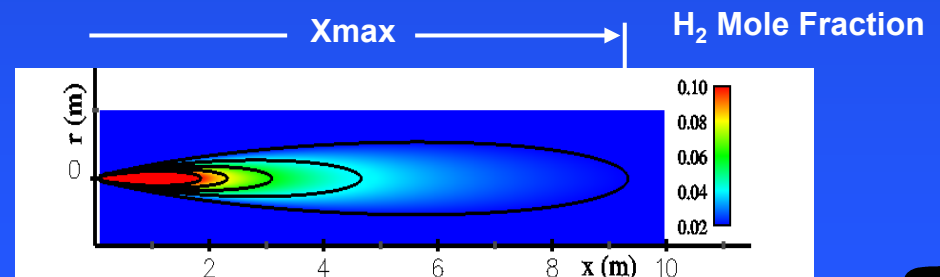
Hole Diameter	Flowrate	Xmax - Distance to 4% mole fraction	Start of Intermediate Region
3.175 mm (1/8 inch)	9.718x10 ⁻² Kg/sec (2,463 ft ³ /min)*	14.80 m (48.55 ft)	20.7 m (67.9 ft)
1.5875 mm (1/16 inch)	2.430x10 ⁻² Kg/sec (615.9 ft ³ /min)*	7.40 m (24.28 ft)	14.6 m (48.0 ft)
0.794 mm (1/32 inch)	6.075x10 ⁻³ Kg/sec (154.1 ft ³ /min)*	3.70 m (12.14 ft)	10.3 m (33.9 ft)

*@NTP = 21° C (70° F), 101 kPa (14.7 psia)

- Start Intermediate Region

$$x/D = 0.5 F^{1/2} (\rho_{\text{exit}} / \rho_{\text{amb}})^{1/4}$$

$$F = \text{Exit Froude No.} = U_{\text{exit}}^2 \rho_{\text{exit}} / (gD(\rho_{\text{amb}} - \rho_{\text{exit}}))$$





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Flammability Limits for H₂

Upward Flame Propagation

Tube Dimensions, cm		Firing end	Limits, percent		Water Vapor Content	Reference
Diameter	Length		Lower	Higher		
7.5	150	Closed	4.15	75.0	Half-saturated	356
5.3	150					
5.3	150					
5.3	150					
5.0	150					
5.0	150					
4.8	150					
4.5	80					
4.5	80					

Horizontal Flame Propagation

Tube Dimensions, cm		Firing end	Limits, percent		Water Vapor Content	Reference
Diameter	Length		Lower	Higher		
7.5	150	Closed	6.5	-----	Half-saturated	356
5.0	150		N			
2.5	150		N			

Propagation in a Spherical Vessel

Capacity, cc	Firing end	Limits, percent		Water Vapor Content	
		Lower	Higher		
Not stated	Closed	9.2	----	Saturated	
Not stated		N	8.5	67.5	N
1,000		N	8.7	75.5	N
810		N	5.0	73.5	N
350		N	4.6	70.3	N
35		N	9.4	64.8	N

Downward Flame Propagation

Tube Dimensions, cm		Firing end	Limits, percent		Reference
Diameter	Length		Lower	Higher	
21.0	31	Open	9.3	----	N
8.0	37	Closed	8.9	68.8	
7.5	150	N	8.8	74.5	
7.0	150	N	-----	74.5	
6.2	33	Open	8.5	----	
6.0	120	N	9.45	----	





Flammability Limits for H₂

Upward Flame Propagation

Tube Dimensions, cm		Firing end	Limits, percent		Water Vapor Content	Reference
Diameter	Length		Lower	Higher		

⇒ **Seventy-eight investigations of hydrogen flammability limits were identified between 1920 and 1950.**

⇒ **Hydrogen flammability limits are well established.**

cm		end			1,000	N	8.7	75.5	N
Diameter	Length		Lower	Higher	810	N	5.0	73.5	N
21.0	31	Open	9.3	----	350	N	4.6	70.3	N
8.0	37	Closed	8.9	68.8	35	N	9.4	64.8	N
7.5	150	N	8.8	74.5					
7.0	150	N	----	74.5					
6.2	33	Open	8.5	----					
6.0	120	N	9.45	----					

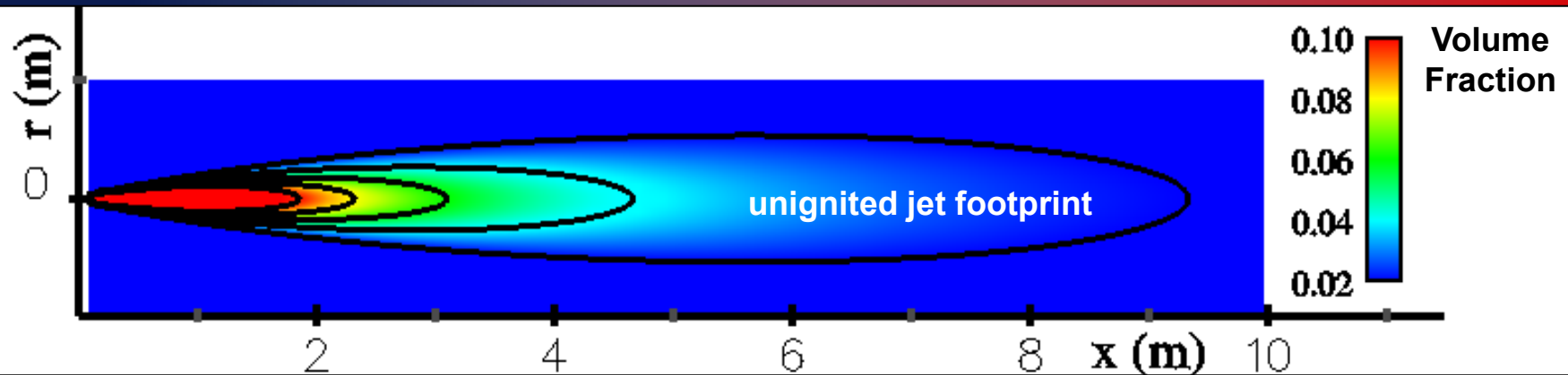
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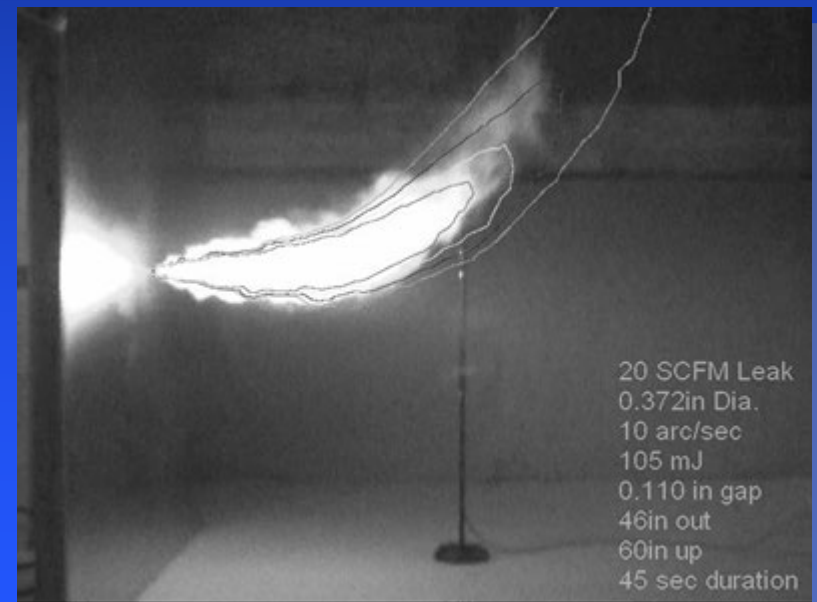




What is a Reasonable Flame Stabilization Limit?



- ⇒ Which volume fraction contour is relevant:
 - lean flammability limit? ... 4% or 8%
 - detonation limit? ... 18%
 - a fraction of the lowest lean flammability limit? ... 1%
- ⇒ **Ignition of hydrogen in turbulent jets occurs around 8% as measured by Swain.**
 - This is consistent with the downward propagating limit of 8%



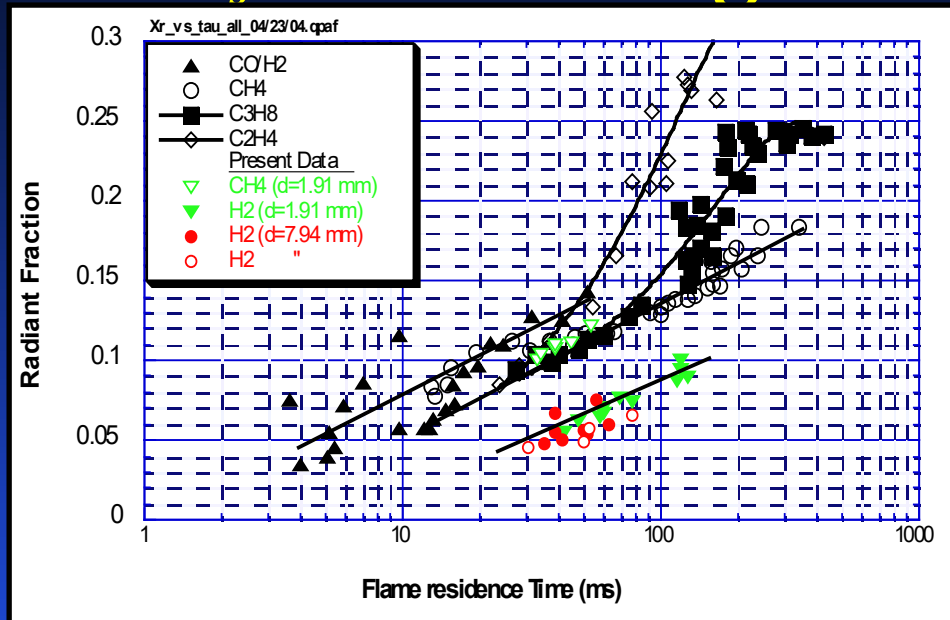


Hydrogen Myths

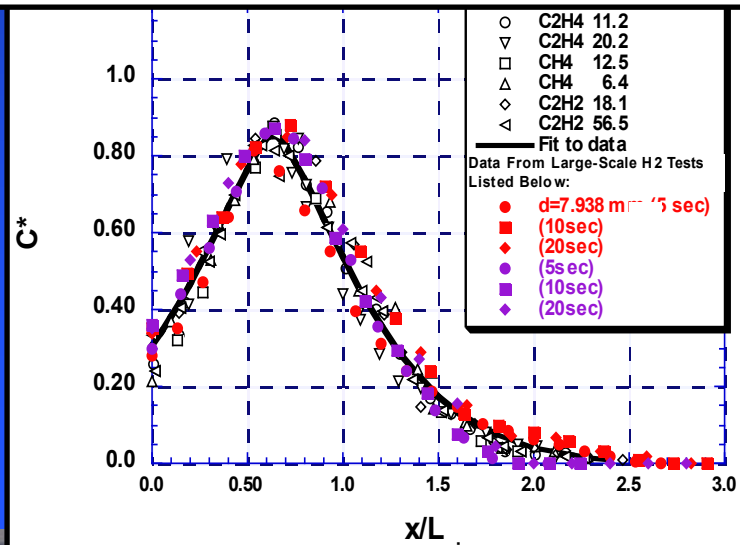
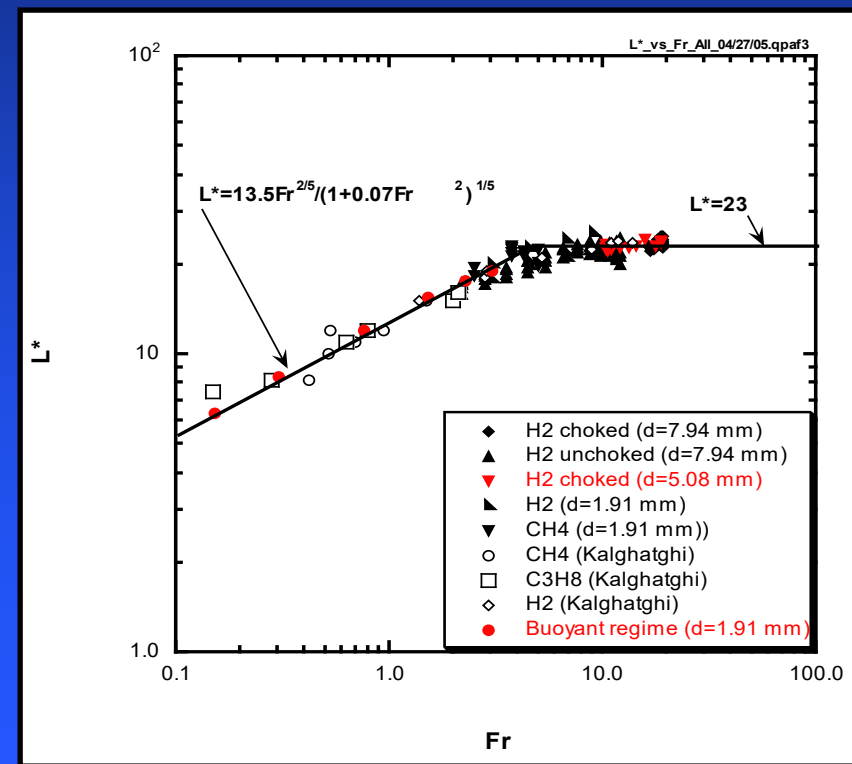
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Hydrogen jets and flames are similar to other flammable gases

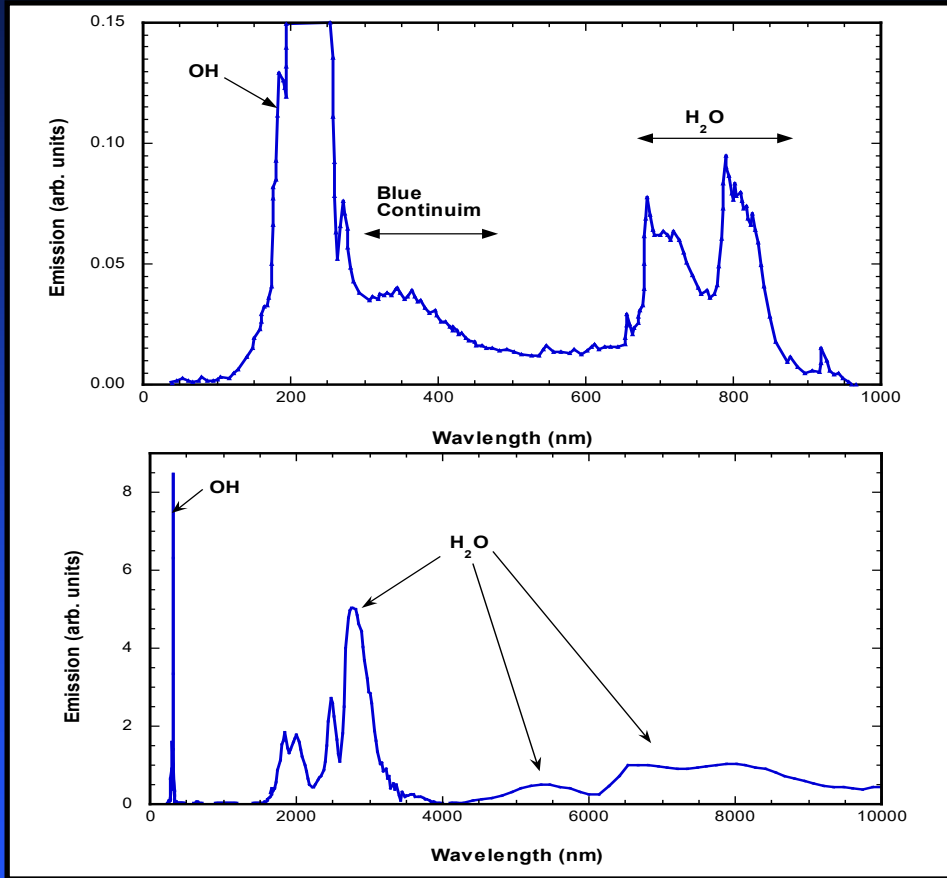


- ⇒ fraction of chemical energy
- ⇒ converted to thermal radiation
- ⇒ radiation heat flux distribution
- ⇒ jet length





H₂ Flame Radiation

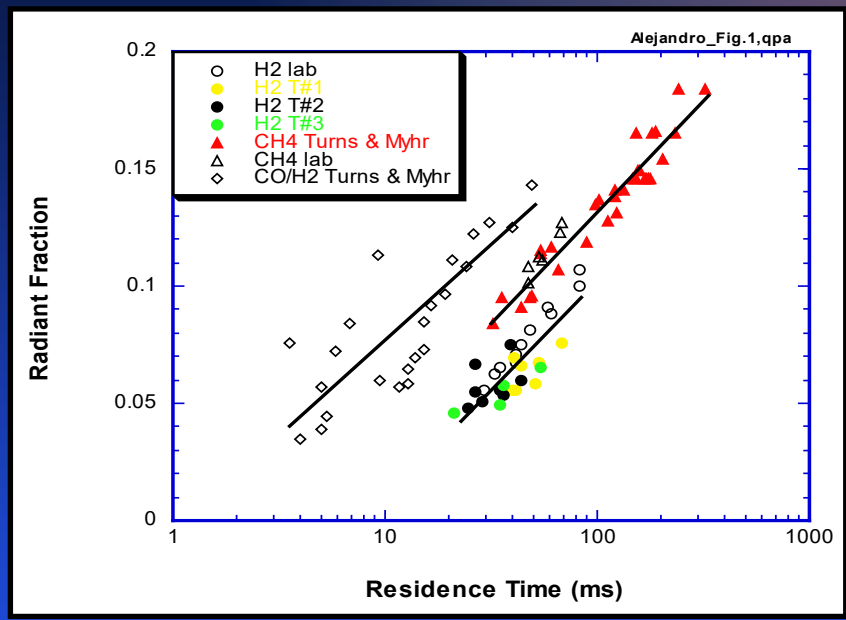


- ⇒ Orange emission due to excited H₂O vapor
- ⇒ Blue continuum due to emission from OH + H ⇒ H₂O + hν
- ⇒ UV emission due to OH*
- ⇒ IR emission due to H₂O vibration-rotation bands

H₂O emission in IR accounts for 99.6% of flame radiation

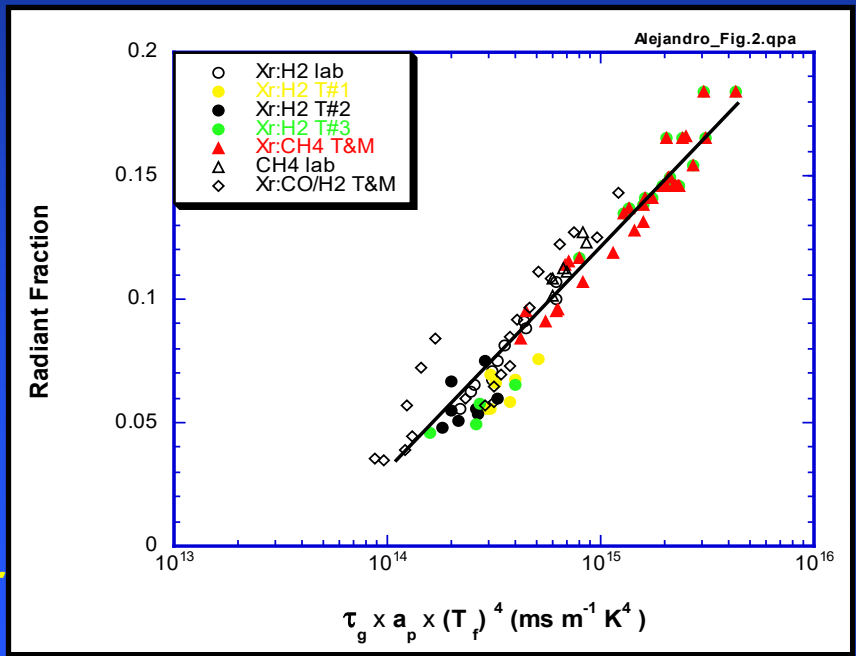


Thermal Radiation from Hydrogen Flames



- ⇒ Previous radiation data for *nonsooting* CO/H₂ and CH₄ flames correlate well with flame residence time.
- ⇒ Sandia's H₂ flame data is a factor of two lower than the hydrocarbon flame data.

- ⇒ Radiation heat flux data collapses on single line when plotted against product $\tau_G \times a_p \times T_f^4$.
- ⇒ a_p (absorption coefficient) is factor with most significant impact on data normalization
- ⇒ **Plank mean absorption coefficient for different gases must be considered**





Hydrogen Myths

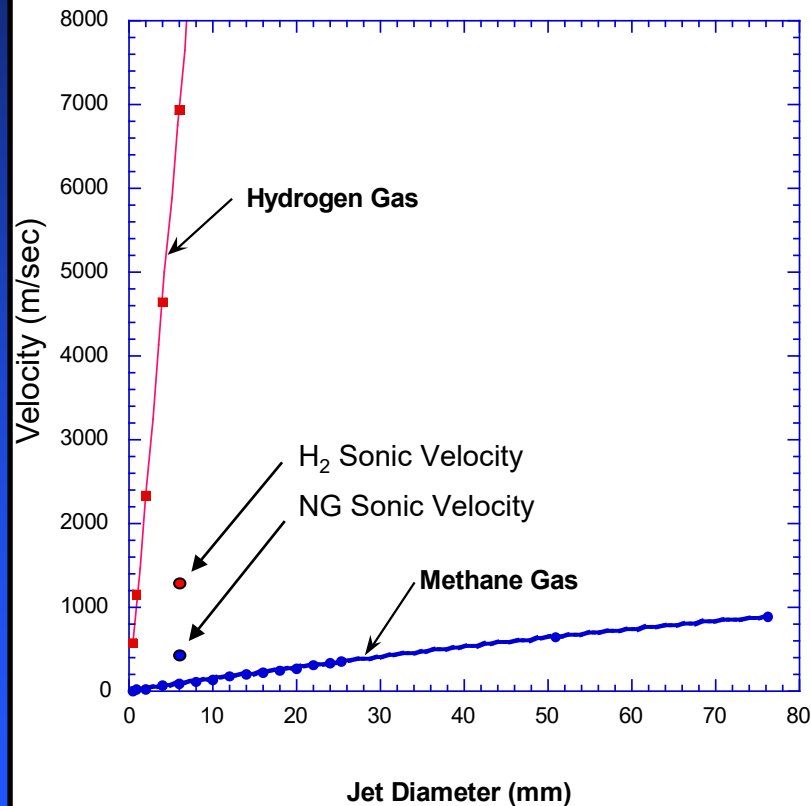
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Comparisons of NG and H₂ Behaviors

Comparison of Blow-Off Velocities
for Hydrogen and Natural Gas

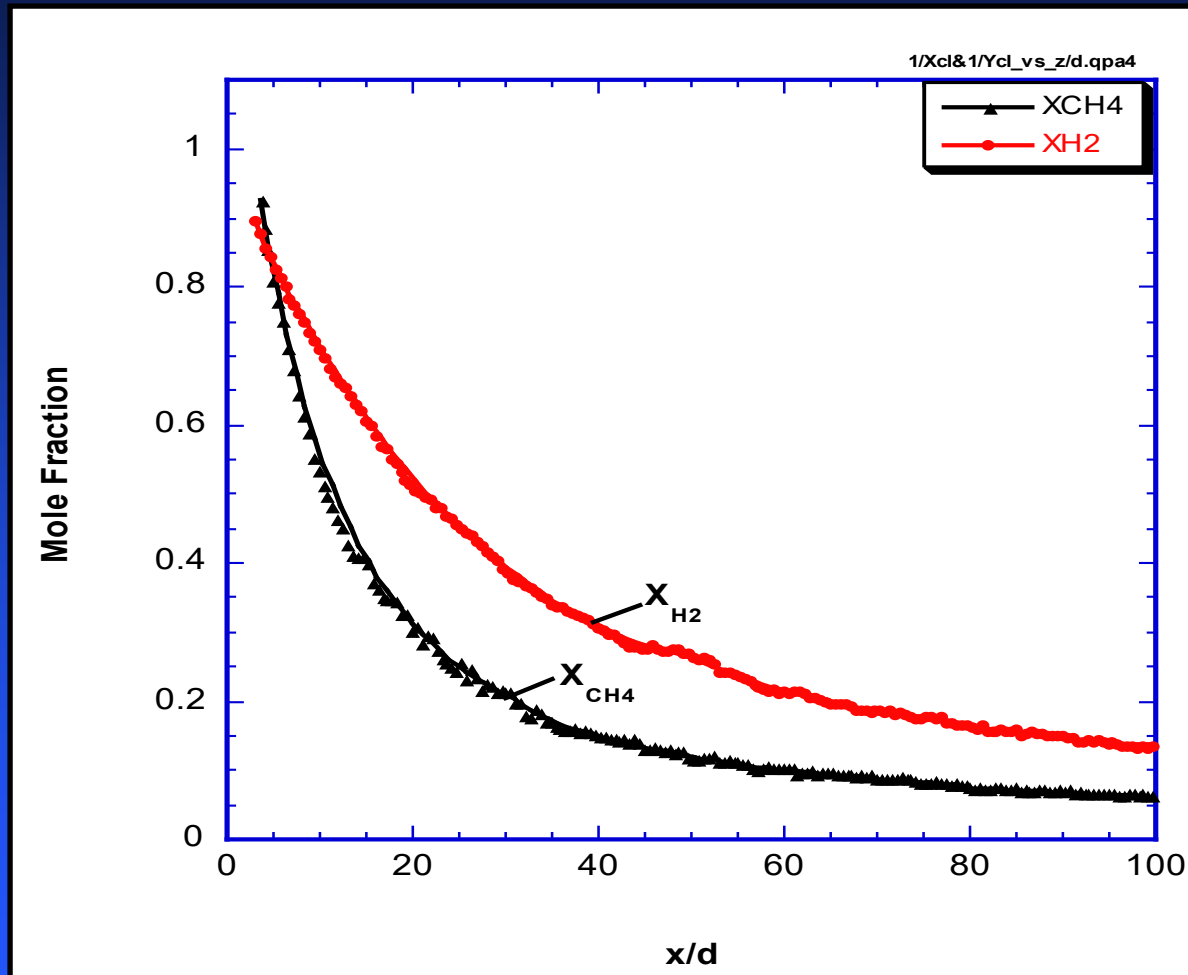


3.175 mm (1/8 inch) diameter hole

- ⇒ Assume 3.175 mm (1/8 inch) dia. hole
- ⇒ Unignited jet lower flammability limits
 - LFL H₂ - 4% mole fraction
 - LFL NG - 5% mole fraction
- ⇒ Flame blow-off velocities for H₂ are much greater than NG
- ⇒ Flow through 1/8" diameter hole is choked
 - $V_{\text{sonic}} = 450$ m/sec for NG (300K)
 - $V_{\text{sonic}} = 1320$ m/sec for H₂ (300K)
- ⇒ Hole exit (sonic) velocity for NG is greater than NG blow-off velocity
 - No NG jet flame for 1/8" hole
- ⇒ Hole exit (sonic) velocity for H₂ is much less than blow-off velocity for H₂
 - H₂ jet flame present for 1/8" hole



Small Unignited Releases: Momentum-Dominated Regime



⇒ Decay rate for H₂ mole fraction is slower than CH₄.



Unignited jet concentration decay distances for natural gas and hydrogen.



Distance on Jet Centerline to Lower Flammability Limit for Natural Gas and Hydrogen

Tank Pressure	Hole Diameter	Distance to 5% Mole Fraction Natural Gas	Distance to 4% Mole Fraction. Hydrogen
18.25 bar (250 psig)	3.175 mm (1/8 inch)	1.19 m (3.90 ft)	4.24 m (13.91 ft)
	1.587 mm (1/16 inch)	0.59 m (1.93 ft)	2.12 m (6.95 ft)
207.8 bar (3000 psig)	3.175 mm (1/8 inch)	3.92 m (12.86 ft)	13.54 m (44.42 ft)
	1.587 mm (1/16 inch)	1.96 m (6.43 ft)	6.77 m (22.21 ft)

Distance to the lower flammability limit for hydrogen is about 3 times longer than for natural gas

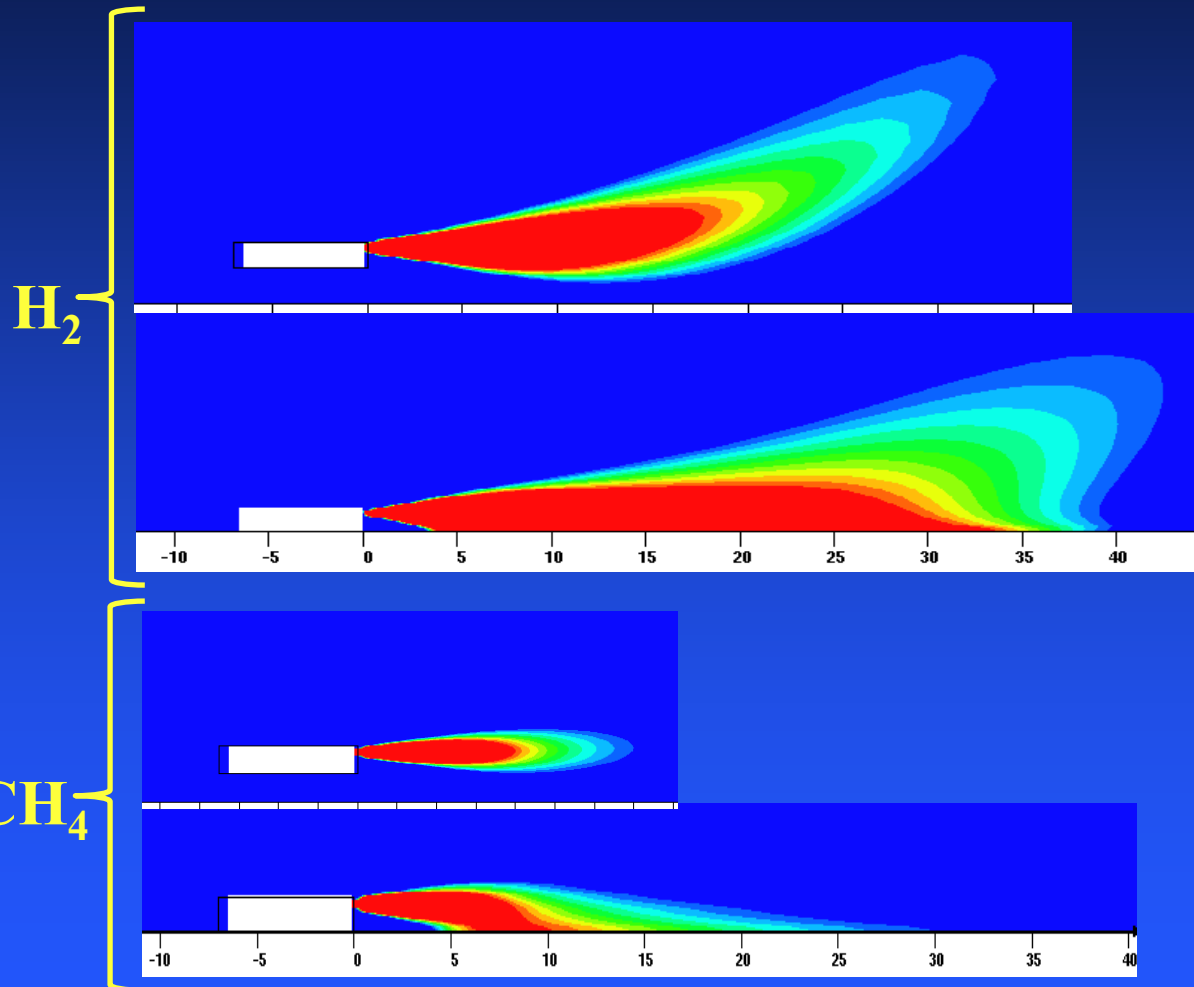




Effects of surfaces ?

⇒ Surfaces may result in a larger increase of the flammable extent of jets for CH₄ than H₂

⇒ “Transient puffs” seems to lead to a larger temporary increase of extent of **horizontal** hydrogen surface jets

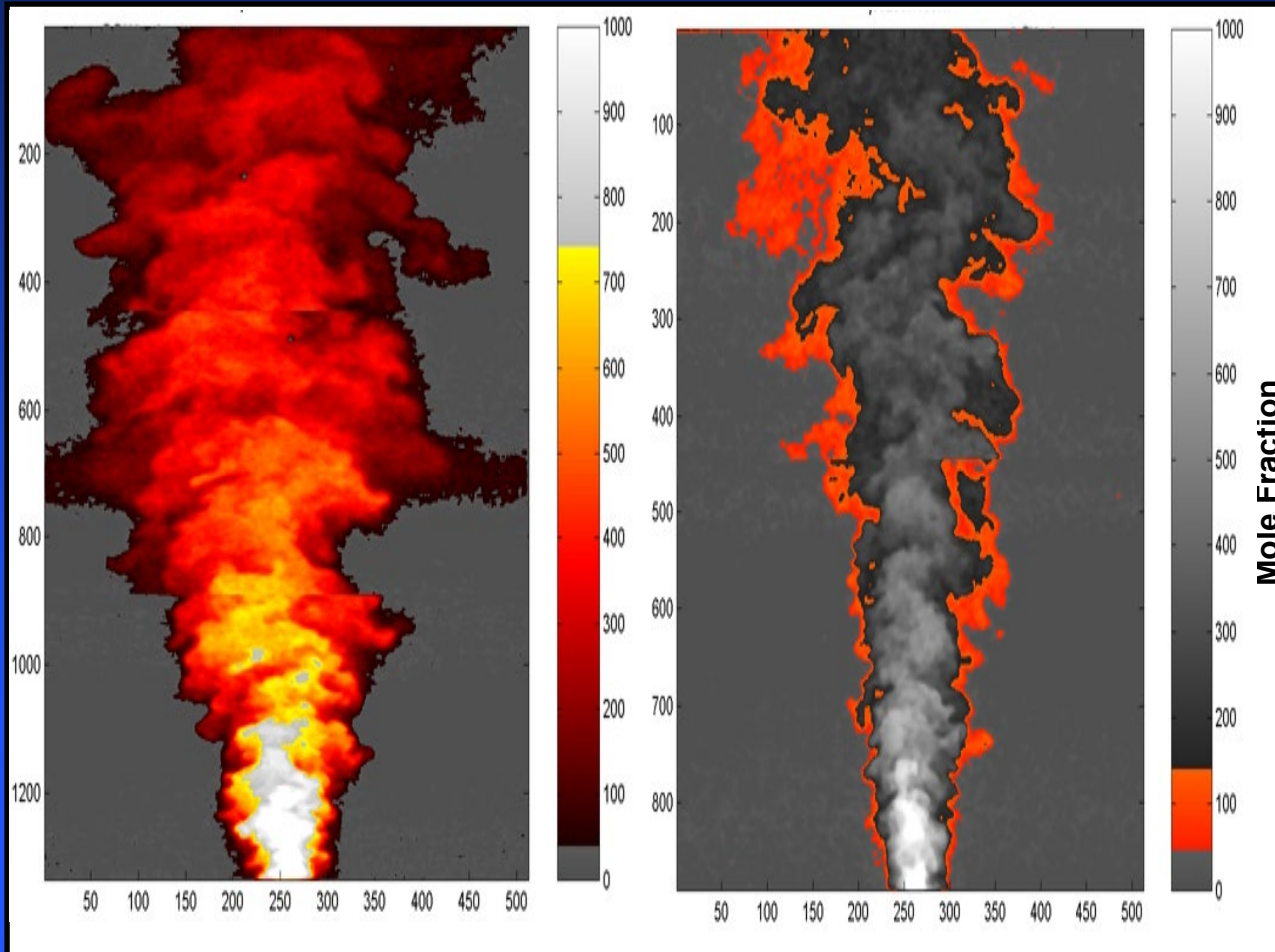


Small Unignited Releases: Ignitable Gas Envelope



H₂ Jet at Re=2,384; Fr = 268

CH₄ Jet at Re=6,813; Fr = 478



- H₂ flammability limits: LFL 4.0%; RFR 75%
- CH₄ flammability limits: LFL 5.2%; RFR 15%

Radial profiles in H₂ jet, d = 1.91 mm, Re = 2384

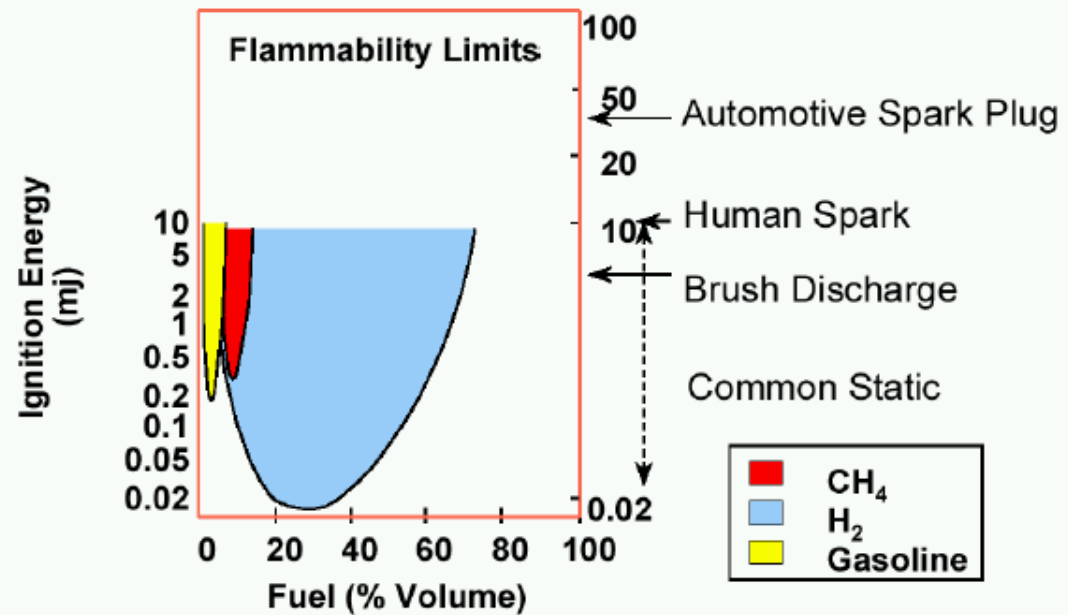


Is there a myth about the minimum ignition energy?



- ⇒ Lower ignition energy of H₂ is the lowest of the flammable gases at stoichiometry
 - Over the flammable range of natural gas (~below 10%), however, H₂ has a comparable ignition energy.

Ignition Energy of H₂, CH₄ and gasoline with Air



Flammability Limits of H₂ Are Seven Times Wider Than CH₄

© Air Products & Chemicals, Inc., 2001



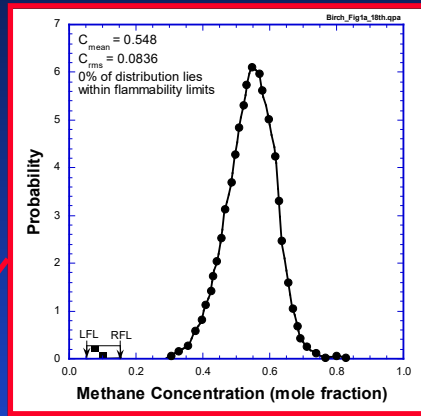
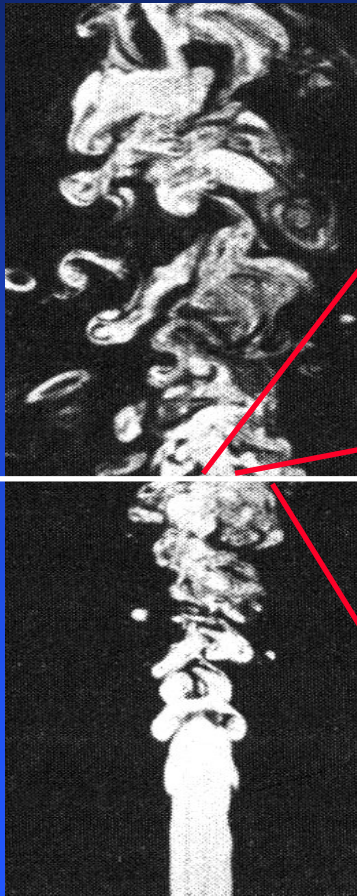
Figure 1: Flammability Limits vs. Ignition Energy of H₂, CH₄, and Gasoline in Air



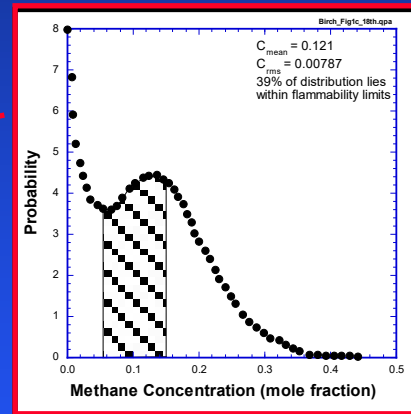


Jet Ignition Probability

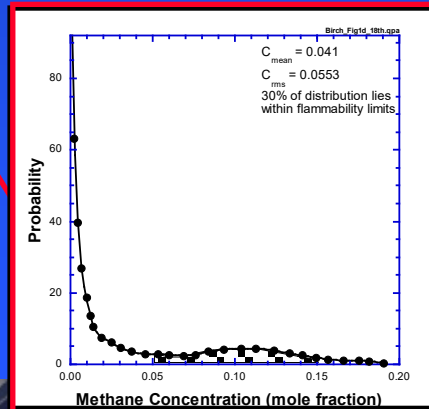
- Methane jet into ambient air (Birch et. al., 1981)



- Probability distributions quantify intermittent nature of turbulent flows.



$z/D=10$



Flammability Factor is defined as the cumulative probability of a potentially flammable mixture occurring at a given point.





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Some people just do not get it!

⇒ H₂

➤ is not toxic,

➤ it is environmentally benign

➤ We just borrow it -- ($2\text{H}_2\text{O} + \text{E} \rightarrow 2\text{H}_2 + \text{O}_2$; then $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{E}$)

⇒ H₂ is a fuel and as such has stored chemical energy

➤ It has hazards associated with it

• It is no more dangerous than the other fuels that store chemical energy

• IT IS JUST different; -- **WE UNDERSTAND THE SCIENCE**

We will learn how to safely handle H₂ in the commercial setting just as we have for our hydrocarbon fuels.



Publication list



11.3 m

- (1) Houf and Schefer, "Predicting Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen," accepted for publication *Int. Jour. of Hydrogen Energy*, Feb. 2006.
- (2) Schefer, Houf, San Marchi, Chernicoff, and Englom, "Characterization of Leaks from Compressed Hydrogen Dispensing Systems and Related Components," *Int. Jour. of Hydrogen Energy*, Vol. 31, Aug. 2006.
- (3) Molina, Schefer, and Houf, "Radiative Fraction and Optical Thickness in Large-Scale Hydrogen Jet Flames," *Proceedings of the Combustion Institute*, April, 2006.
- (4) Houf and Schefer, "Rad. Heat Flux & Flam. Env. Pred. from Unintended Rel. of H₂," *Proc. 13th Int. Heat Tran. Conf.*, Aug., 2006.
- (5) Schefer, Houf, Williams, Bourne, and Colton, "Characterization of High-Pressure, Under-Expanded Hydrogen-Jet Flames," submitted to *Int. Jour. of Hydrogen Energy*, 2006.
- (6) Houf and Schefer, "Predicting Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen," 16th NHA Meeting, Washington, DC, March 2005.
- (6) Schefer, R. W., Houf, W. G., Bourne, B. and Colton, J., "Turbulent Hydrogen-Jet Flame Characterization", *Int. Jour. of Hydrogen Energy*, 2005.
- (7) Schefer, R. W., Houf, W. G., Bourne, B. and Colton, J., "Experimental Measurements to Characterize the Thermal and Radiation Properties of an Open-flame Hydrogen Plume", 15th NHA Meeting, April 26-30, 2004, Los Angeles, CA.
- (8) Schefer, "Combustion Basics," in *National Fire Protection Association (NFPA) Guide to Gas Safety*, 2004.

Nighttime photograph of ~40 MPa large-scale H₂ jet-flame test ($d_j = 5.08\text{mm}$, $L_{\text{vis}} = 10.6\text{ m}$) from Sandia/SRI tests.



