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Presentation Start

Hydrogen Behavior – Myth Busting

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Hydrogen Myths

- Hindenburg
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  - Radiation is different than other fuels
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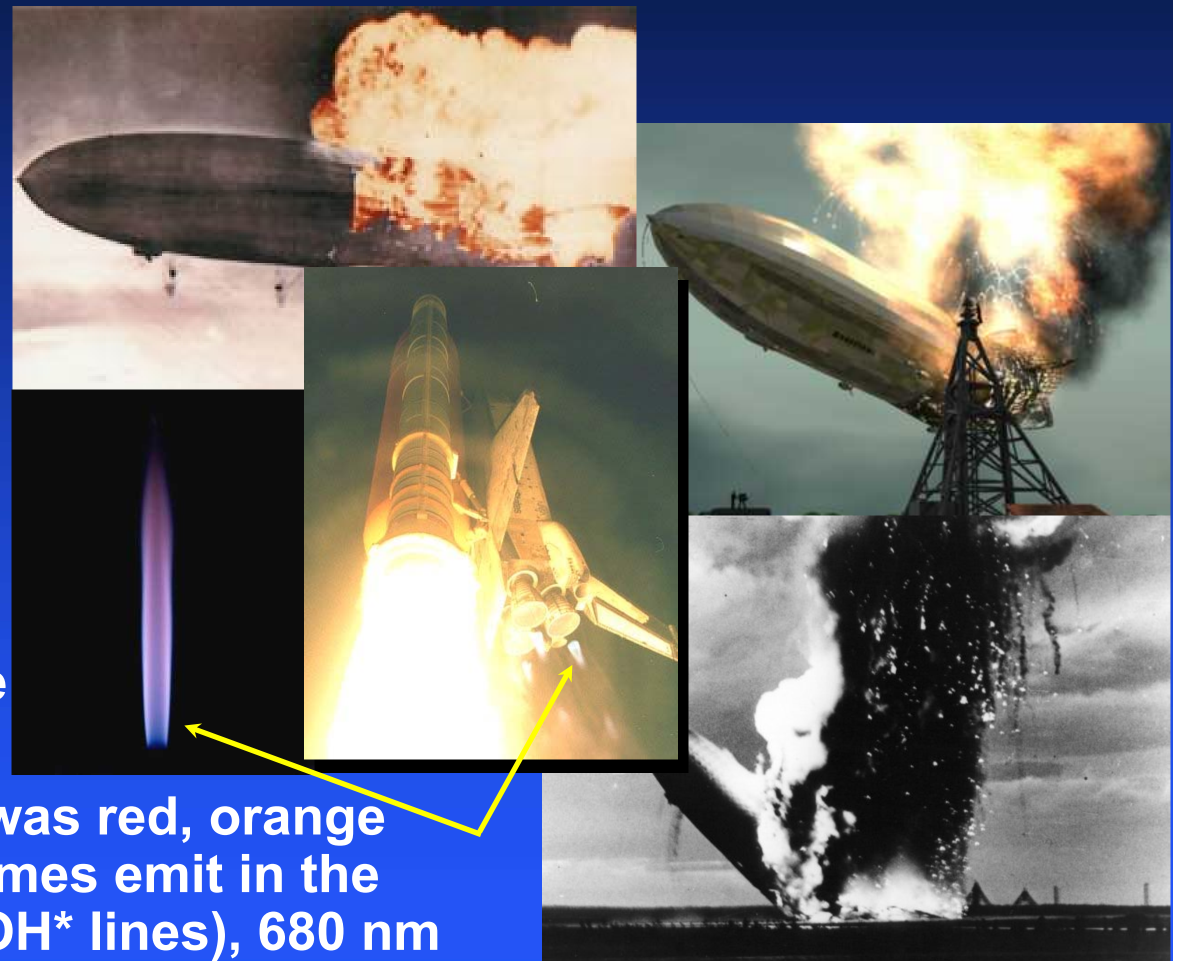
Lets get this out of the way! Hindenburg Disaster

- **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, orange and yellow – 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 mm (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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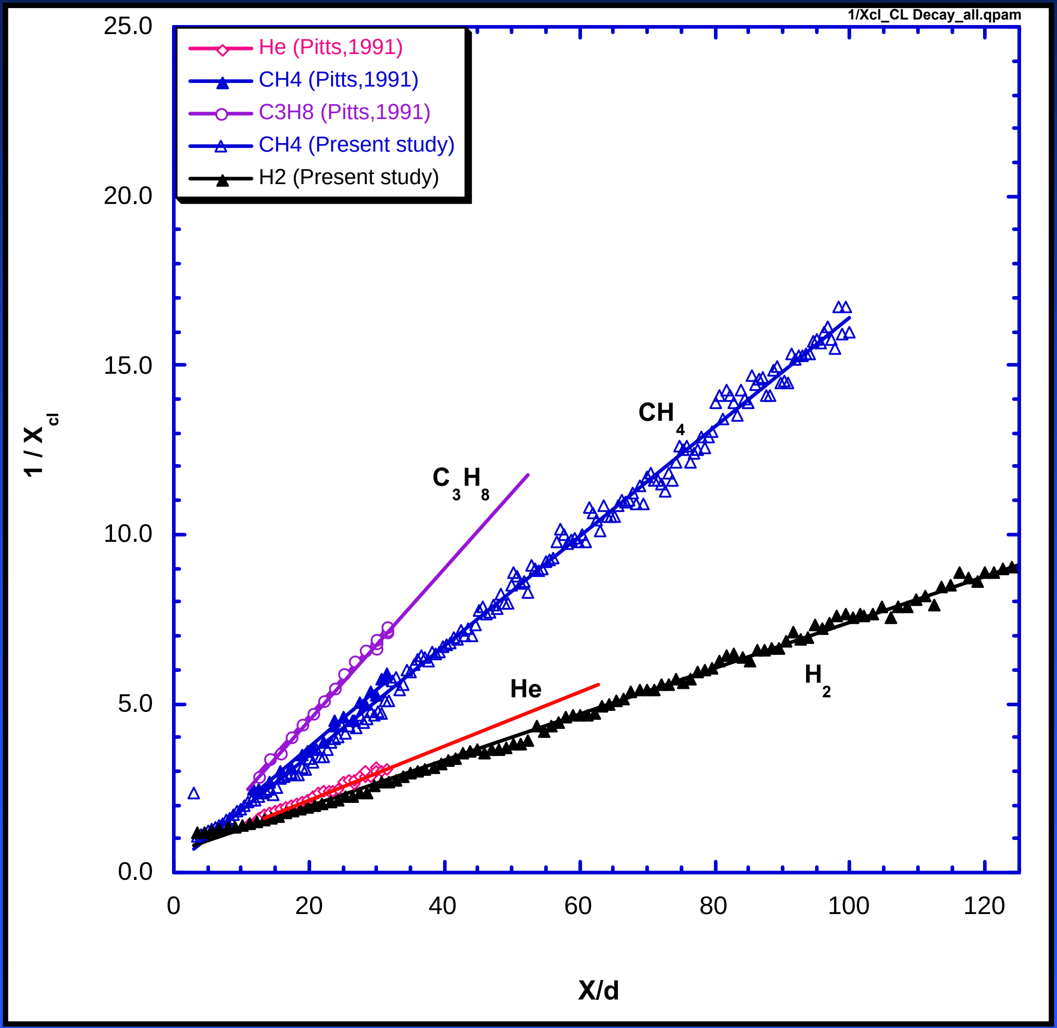
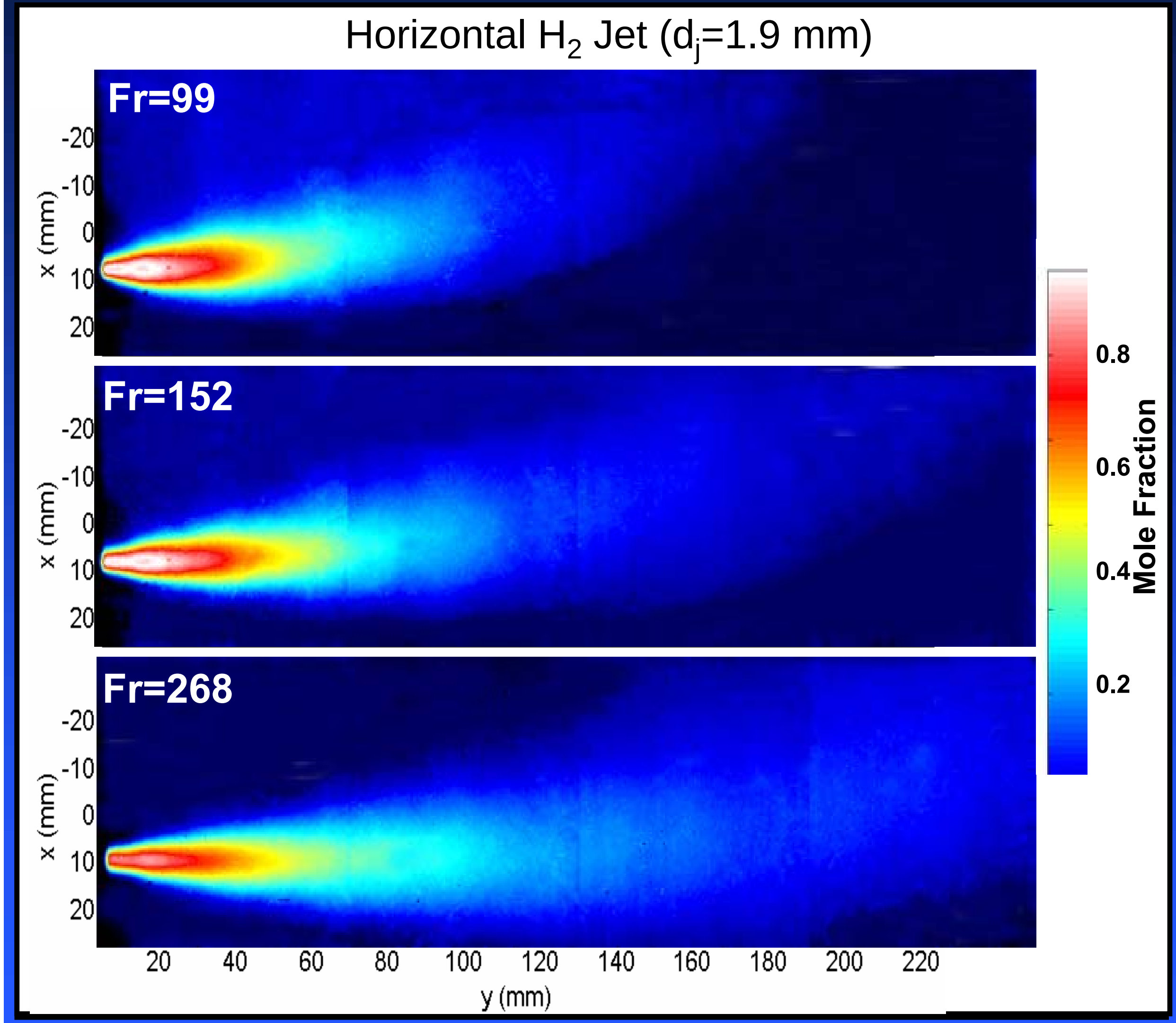
Small Unignited Releases: Momentum-Dominated Regime

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 H_2 is significantly slower than methane and propane.

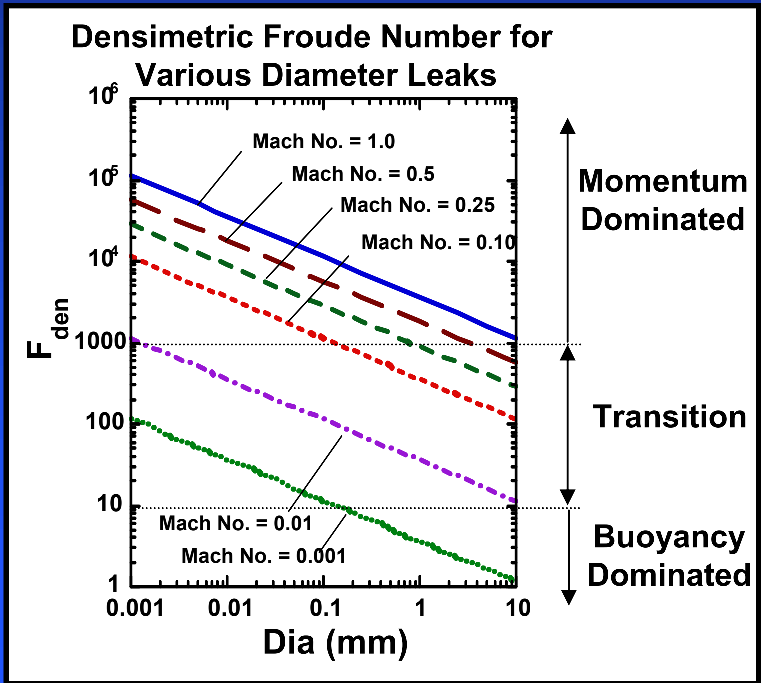
Buoyancy effects are characterized by Froude number



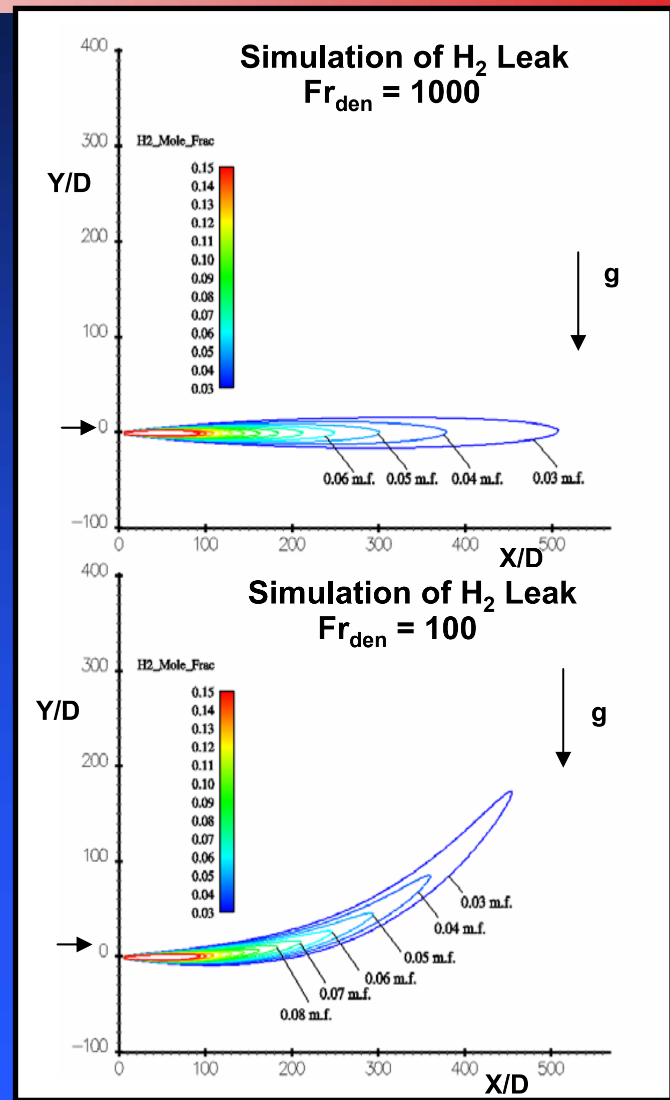
- Time-averaged H_2 mole fraction distributions.
- Froude number is a measure of strength of momentum force relative to the buoyant force
- Increased upward jet curvature is due to increased importance of buoyancy at lower Froude numbers.

Influence of buoyant force is quantified by the dimensionless Froude number

- Jets from choked flows (Mach 1.0) are typically momentum-dominated.
- Lower source pressures or very large pressure losses through cracks lead to subsonic, buoyancy-dominated plumes.



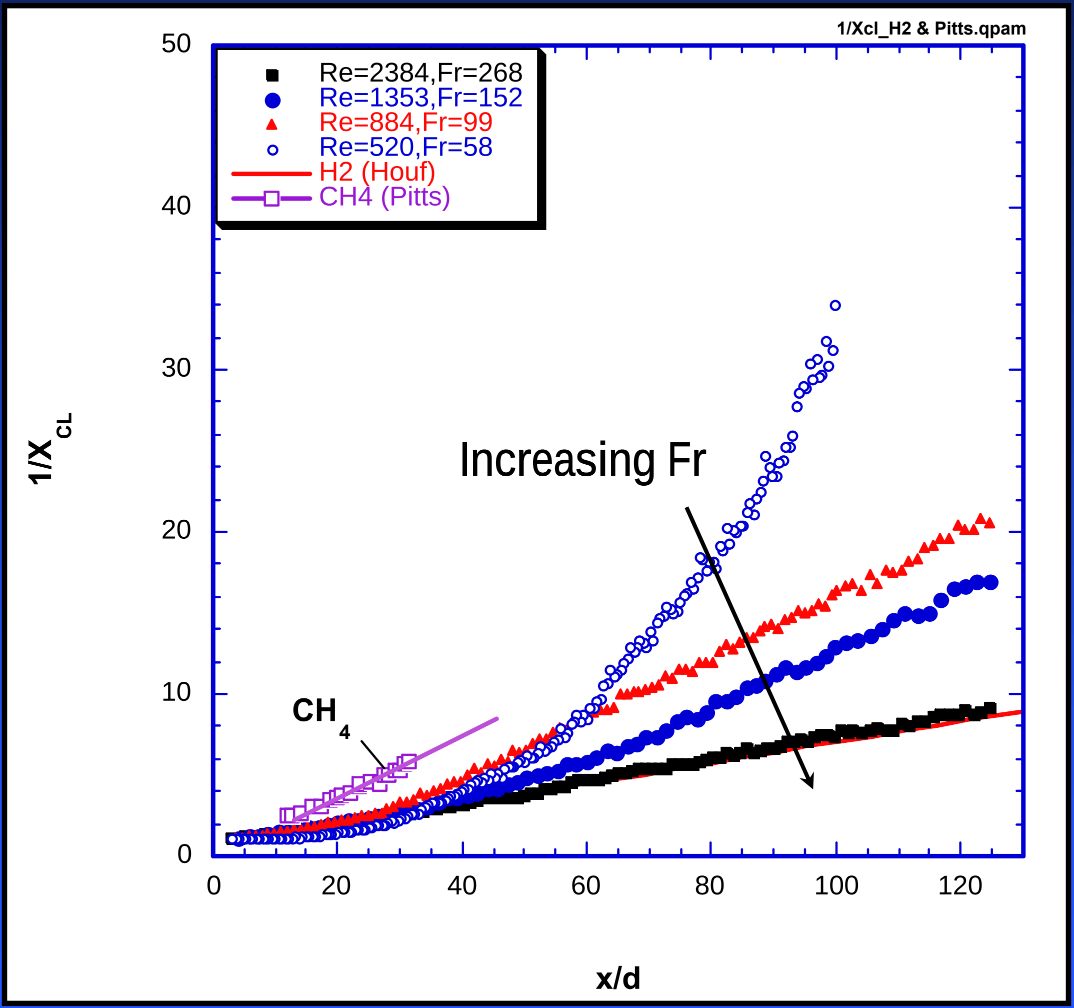
$Fr_{den} = U_{exit}/(gD(\rho_{amb} - \rho_{exit})/\rho_{exit})^{1/2}$



Ricou and Spalding entrainment law (J. Fluid Mechanics, 11, 1961)

Small Unignited Releases: Buoyancy Effects

- Data for round H_2 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.

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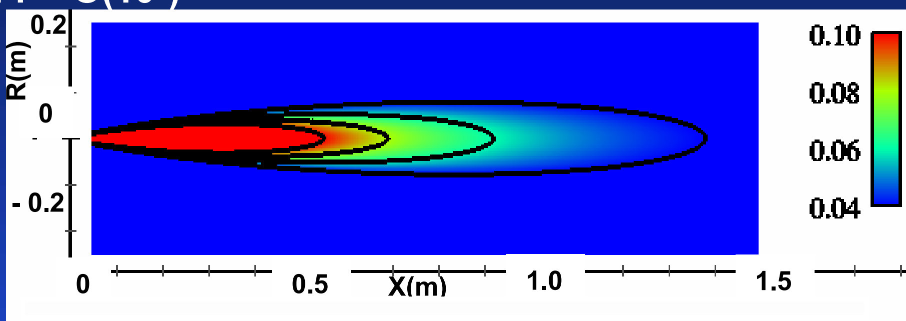
Choked & Unchoked Flows at 20 SCFM

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

Exit Mach Number = 1.0 (Choked Flow)

Fr ~ O(10^4)

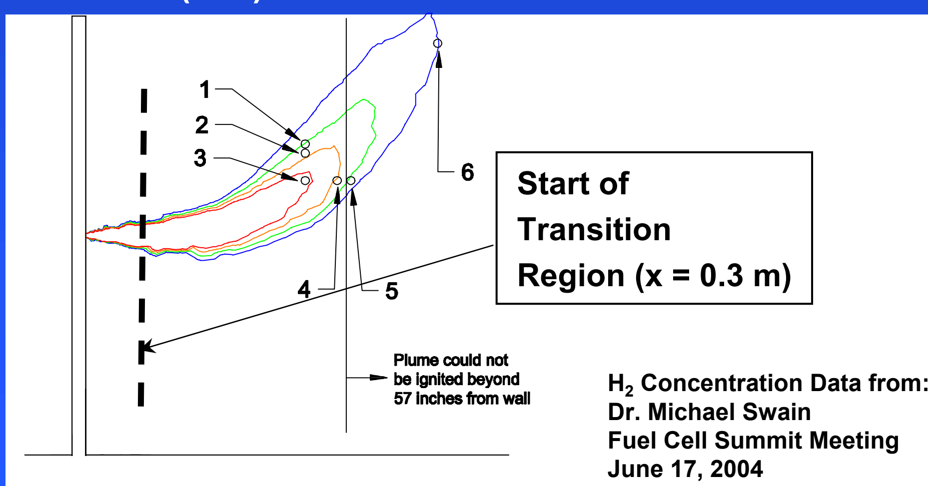
H2 Mole Fraction



Flowrate = 20 scfm, Hole Dia. = 9.44 mm

Exit Mach Number = 0.1 (Unchoked Flow)

Fr ~ O(100)



H_2 Concentration Data from:
Dr. Michael Swain
Fuel Cell Summit Meeting
June 17, 2004

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

Start Transition 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)

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Flammability Limits for H_2

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	Ņ				
2.5	150	Ņ				

Downward Flame Propagation

Tube Dimensions, cm		Firing end	Limits, percent		Water Vapor Content	Reference
Diameter	Length		Lower	Higher		
21.0	31	Open	9.3	----		
8.0	37	Closed	8.9	68.8		
7.5	150	Ņ	8.8	74.5		
7.0	150	Ņ	-----	74.5		
6.2	33	Open	8.5	----		
6.0	120	Ņ	9.45	----	Ņ	325

Propagation in a Spherical Ves

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

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Tube Dimensions, cm		Firing end	Limits, percent		Water Vapor Content	Reference
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- ***78 investigations of hydrogen flammability limits were identified between 1920 and 1950.***
- ***Hydrogen flammability limits are well established.***

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Diameter	Length		Lower	Higher
21.0	31	Open	9.3	----
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N̦ 325

Ves

	Firing end	Lower	Higher	Water Vapor Content
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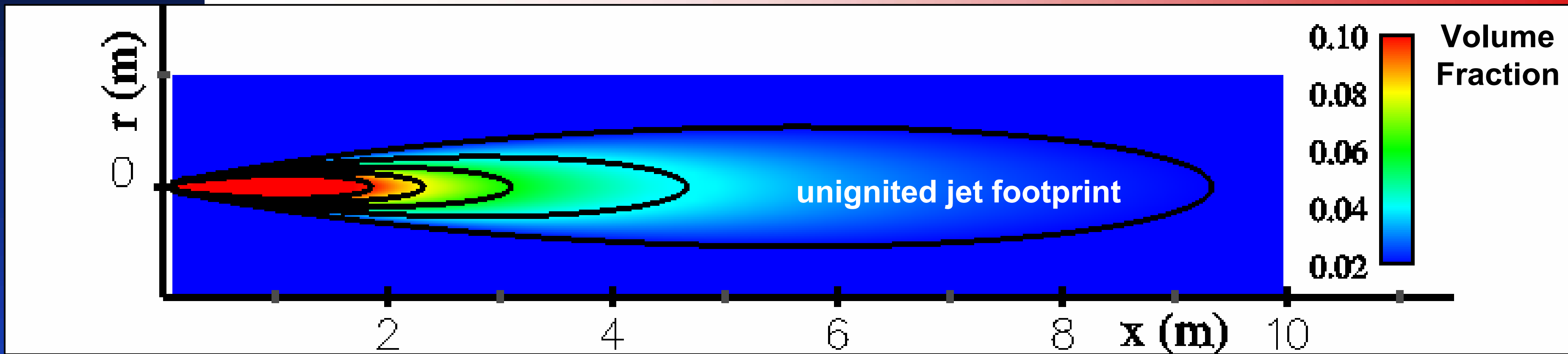
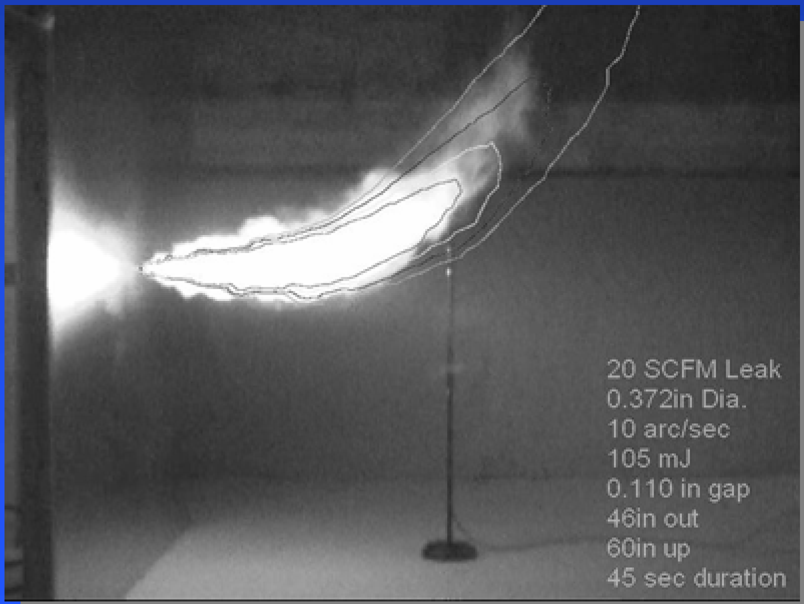
350	N̦	4.6	70.3	N̦
35	N̦	9.4	64.8	N̦

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%



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Joule-Thomson Effect

High-pressure H_2 Jet

- A rapidly expanding gas can increase or decrease in temperature.
- The direction and magnitude of temperature change is determined by the Joule-Thomson coefficient.
- Definition:

$$\mu_{JT} = (\delta T / \delta P)_H = (\Delta T / \Delta P)_H$$

- Above the inversion temperature, the expanding gas temperature rises.
- The inversion temperature of H_2 is between 28 and 200 K (depending on pressure); at ambient temperature the expanding H_2 increases in temperature.

- For initial compressed gas pressure of 14 MPa, the estimated temperature rise is approximately 6 C.
- At pressures up to 250 MPa, the maximum estimated coefficient is 0.53 K/MPa. Thus, at H_2 storage pressures of 100 MPa, the maximum temperature rise would be 53 C, (gas temperature is only ~75C).

Given the H_2 auto-ignition temperature of 585 C, Joule-Thomson heating is insufficient to cause ignition

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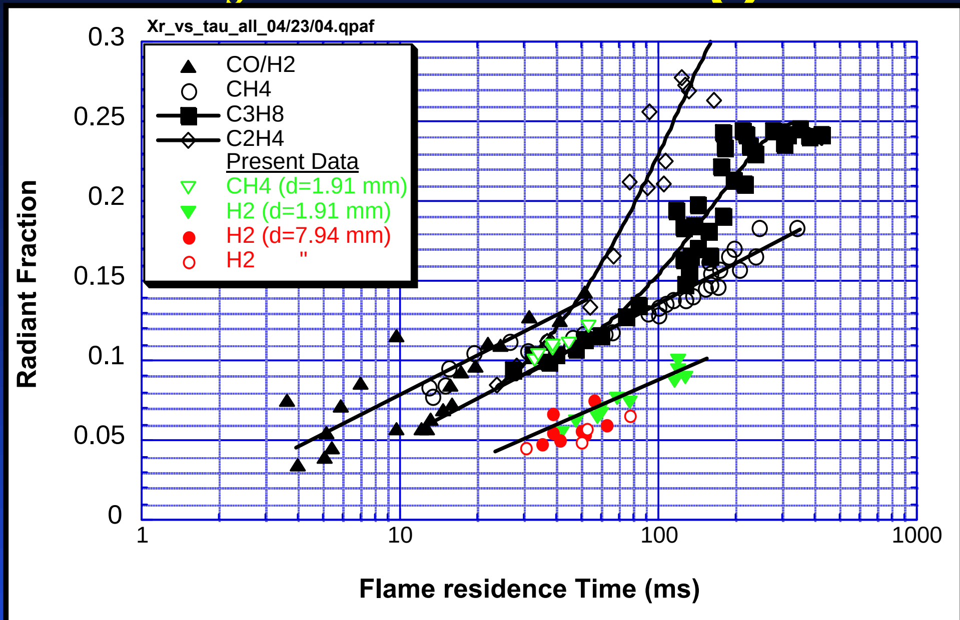
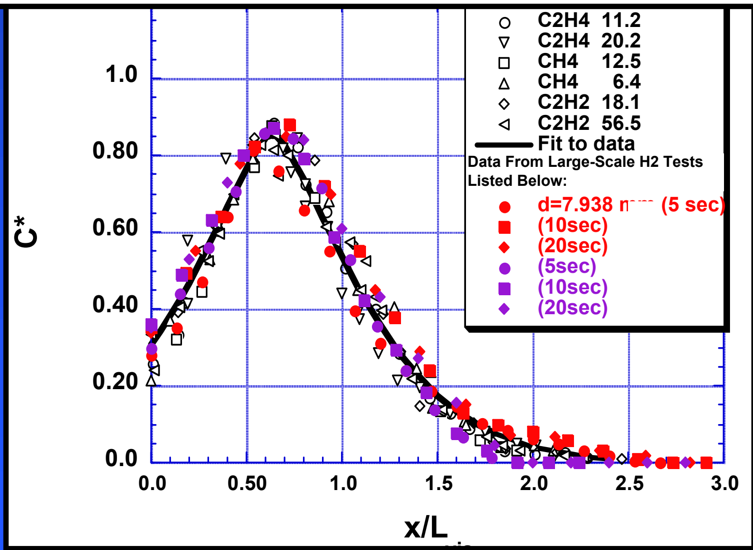
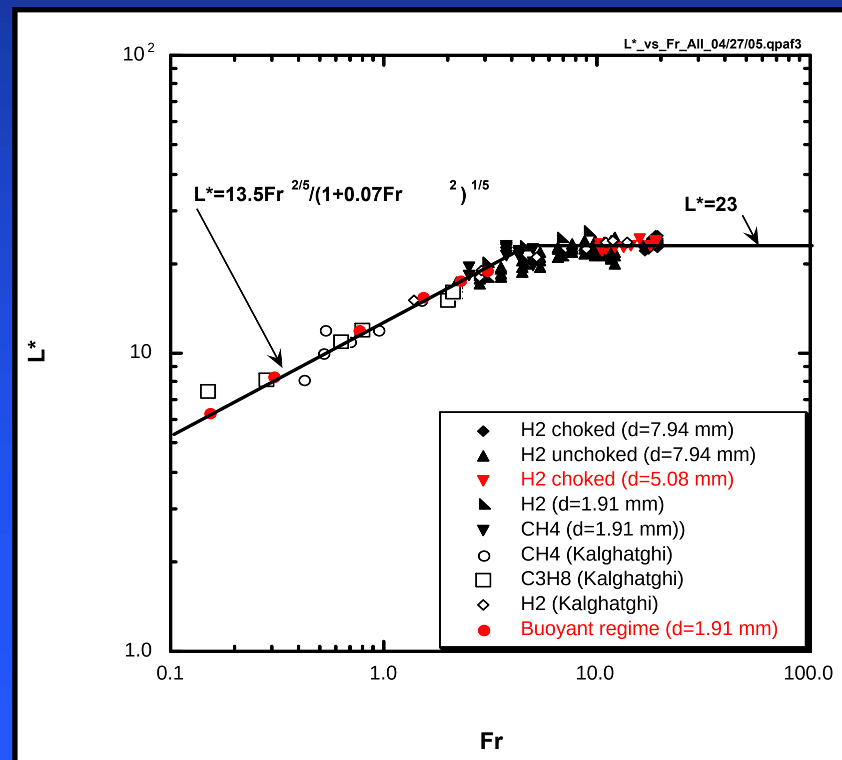
Hydrogen jets and flames are similar to other flammable gases

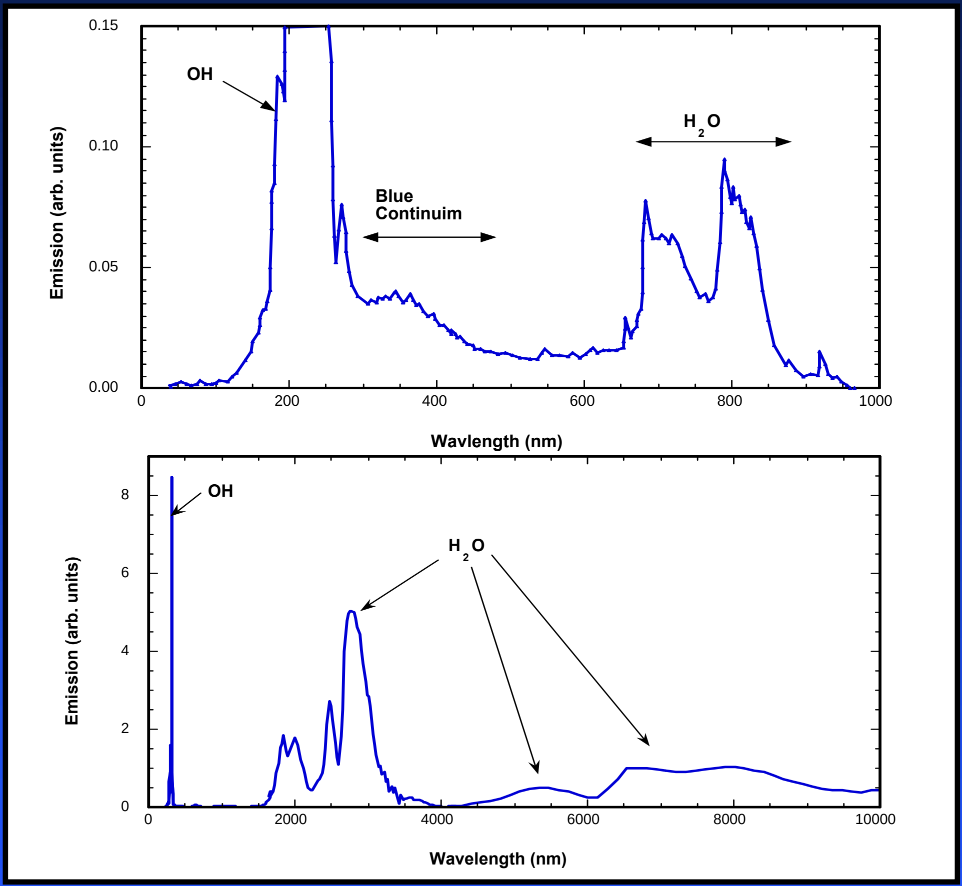




- Fraction of chemical energy
- Converted to thermal radiation
- Radiation heat flux distribution
- Jet length



H_2 Flame Radiation



- Orange emission due to excited H_2O vapor
- Blue continuum due to emission from OH + H => H_2O + hν
- UV emission due to OH*
- IR emission due to H_2O vibration-rotation bands

H_2O emission in IR accounts for 99.6% of flame radiation

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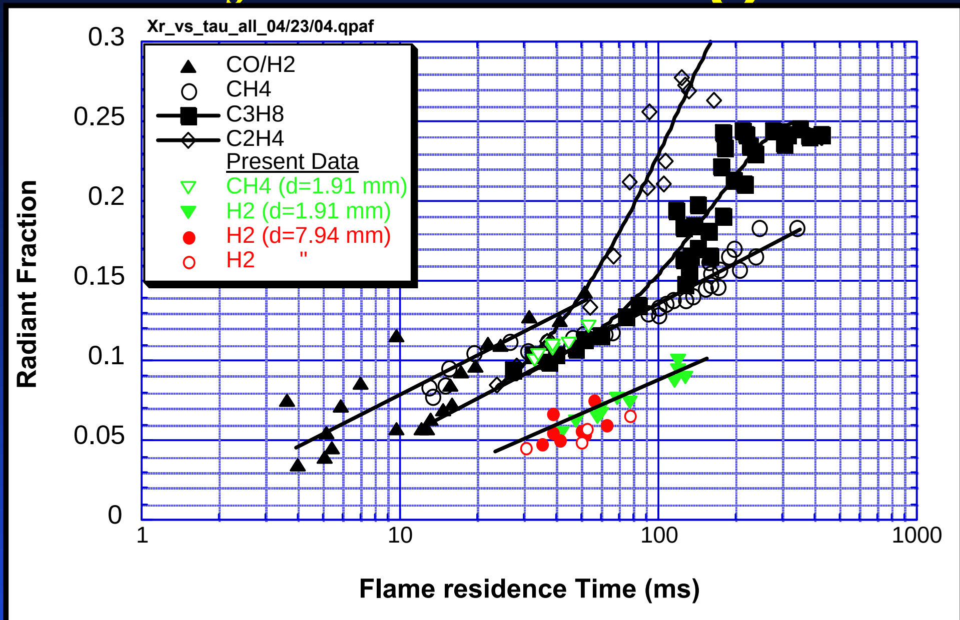

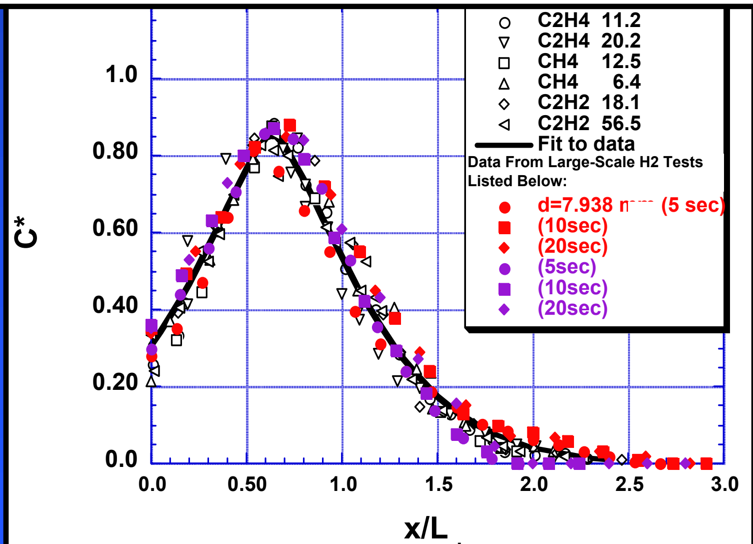

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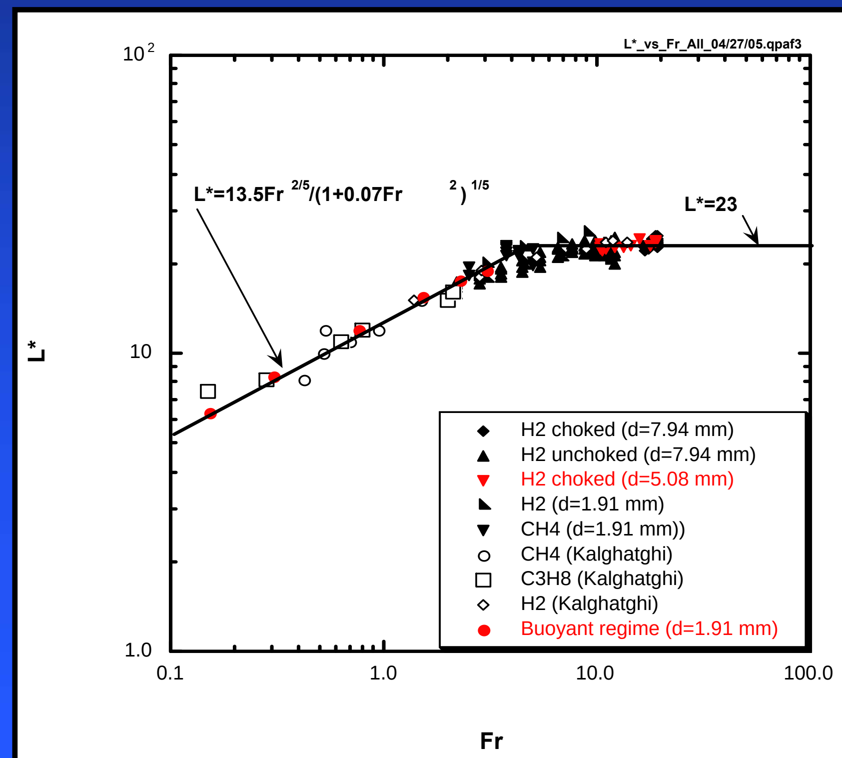
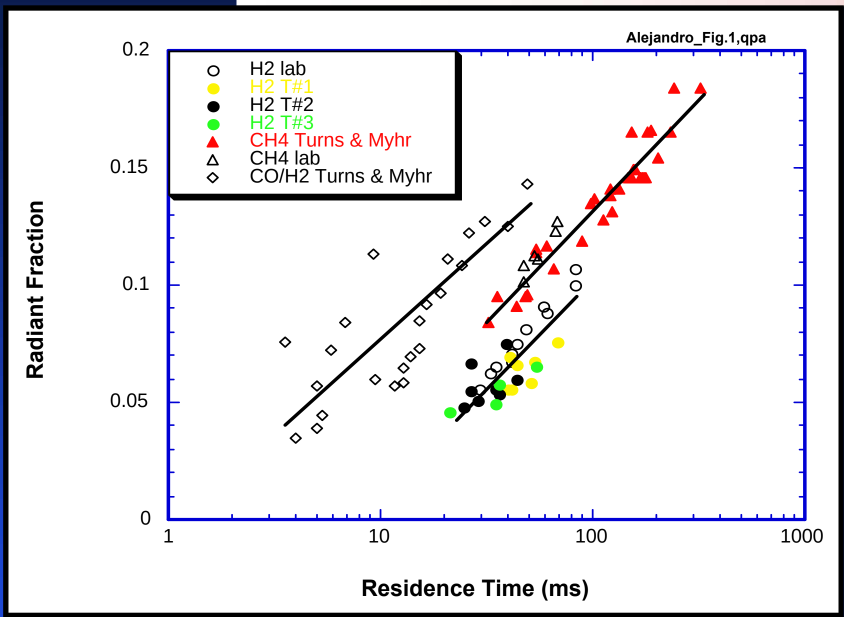
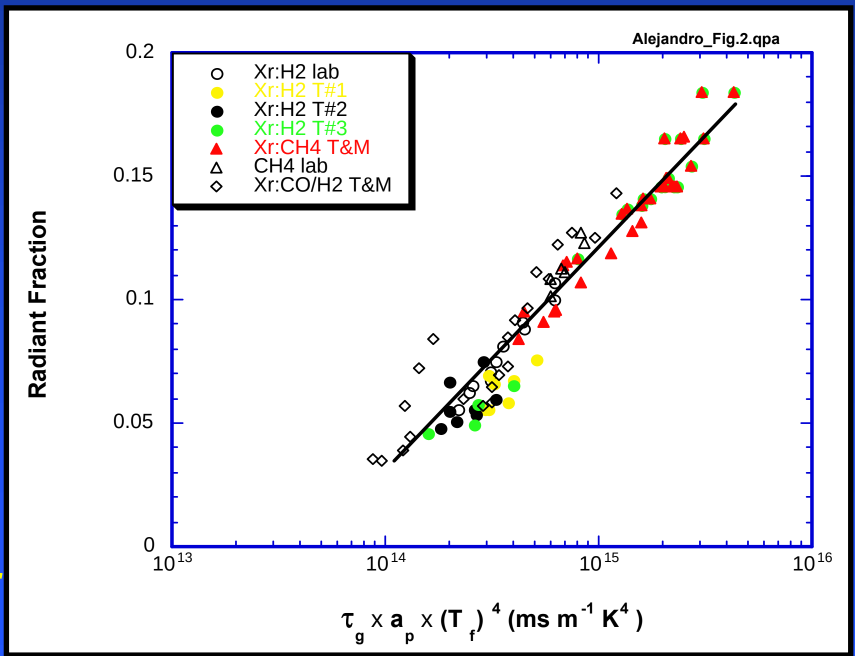


Thermal Radiation from Hydrogen Flames



- Previous radiation data for *nonsooting* CO/H_2 and CH_4 flames correlate well with flame residence time.
- Sandia's H_2 flame data is a factor of two lower than the hydrocarbon flame data.
- Radiation heat flux data collapses on singe line when plotted against product τ_G x a_p x 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***



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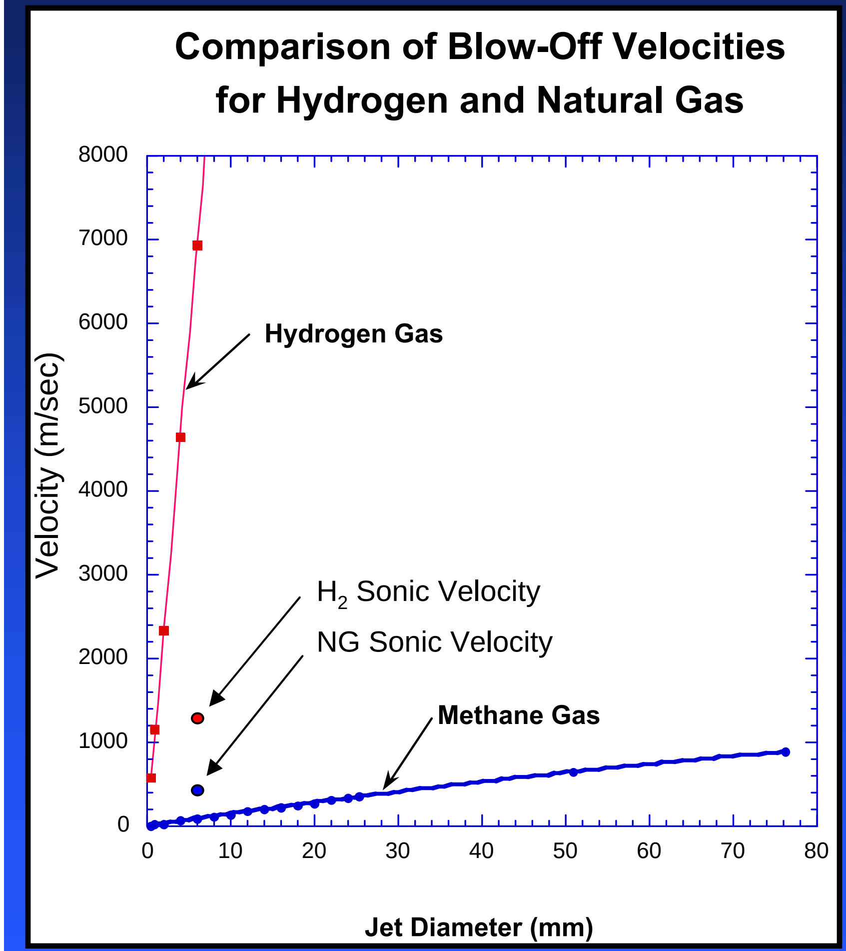
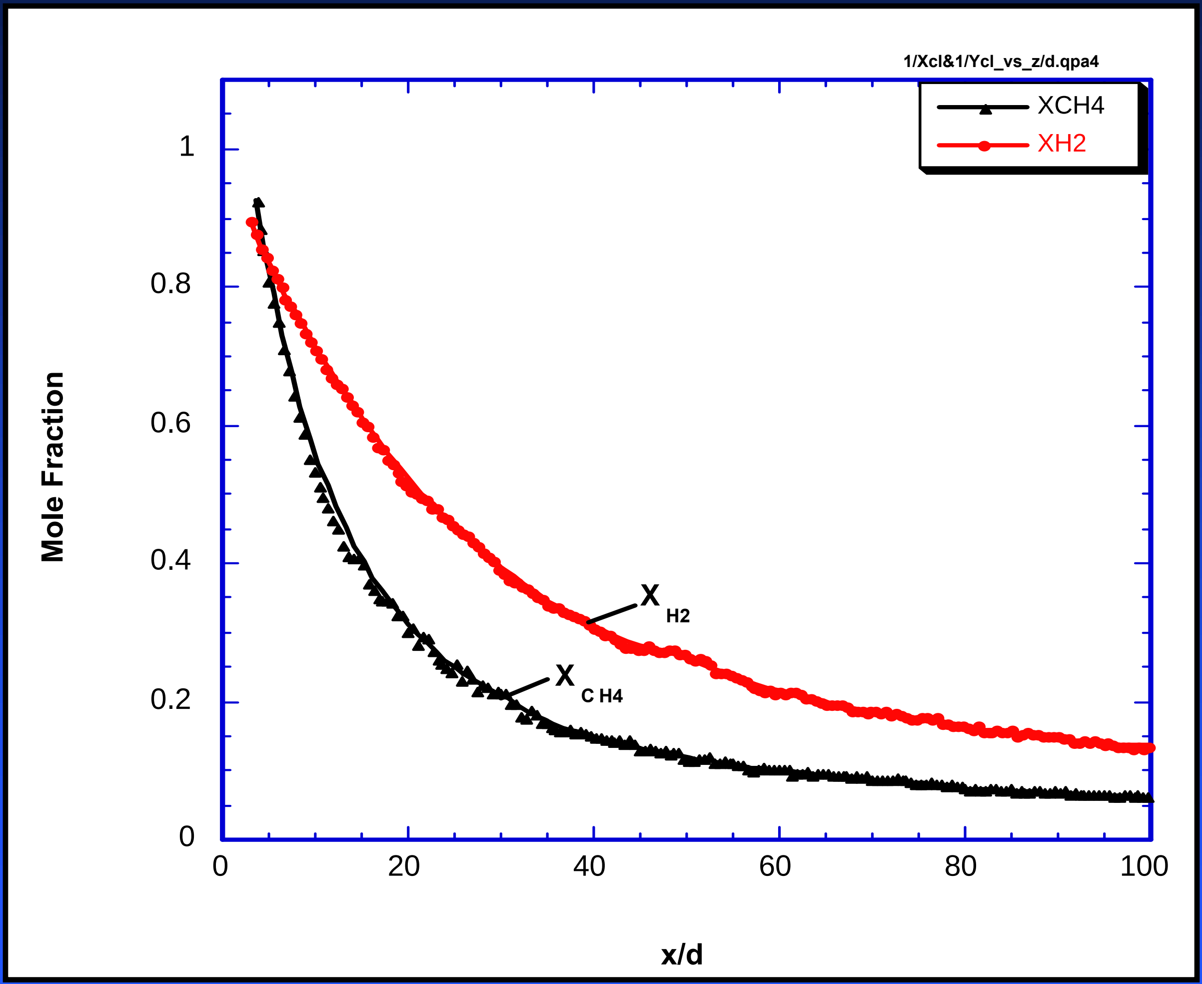
Comparisons of NG and H_2 Behaviors



3.175 mm (1/8 inch) diameter hole

- Assume 3.175 mm (1/8 inch) dia. hole
- Unignited jet lower flammability limits
  - LFL H_2 - 4% mole fraction
  - LFL NG - 5% mole fraction
- Flame blow-off velocities for H_2 are much greater than NG
- Flow through 1/8" diameter hole is choked
  - V_{sonic} = 450 m/sec for NG (300K)
  - V_{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 H_2 is much less than blow-off velocity for H_2
  - H_2 jet flame present for 1/8" hole

Small Unignited Releases: Momentum-Dominated Regime



- Decay rate for H_2 mole fraction is slower than CH_4.

Unignited jet concentration decay distances for natural gas and hydrogen.

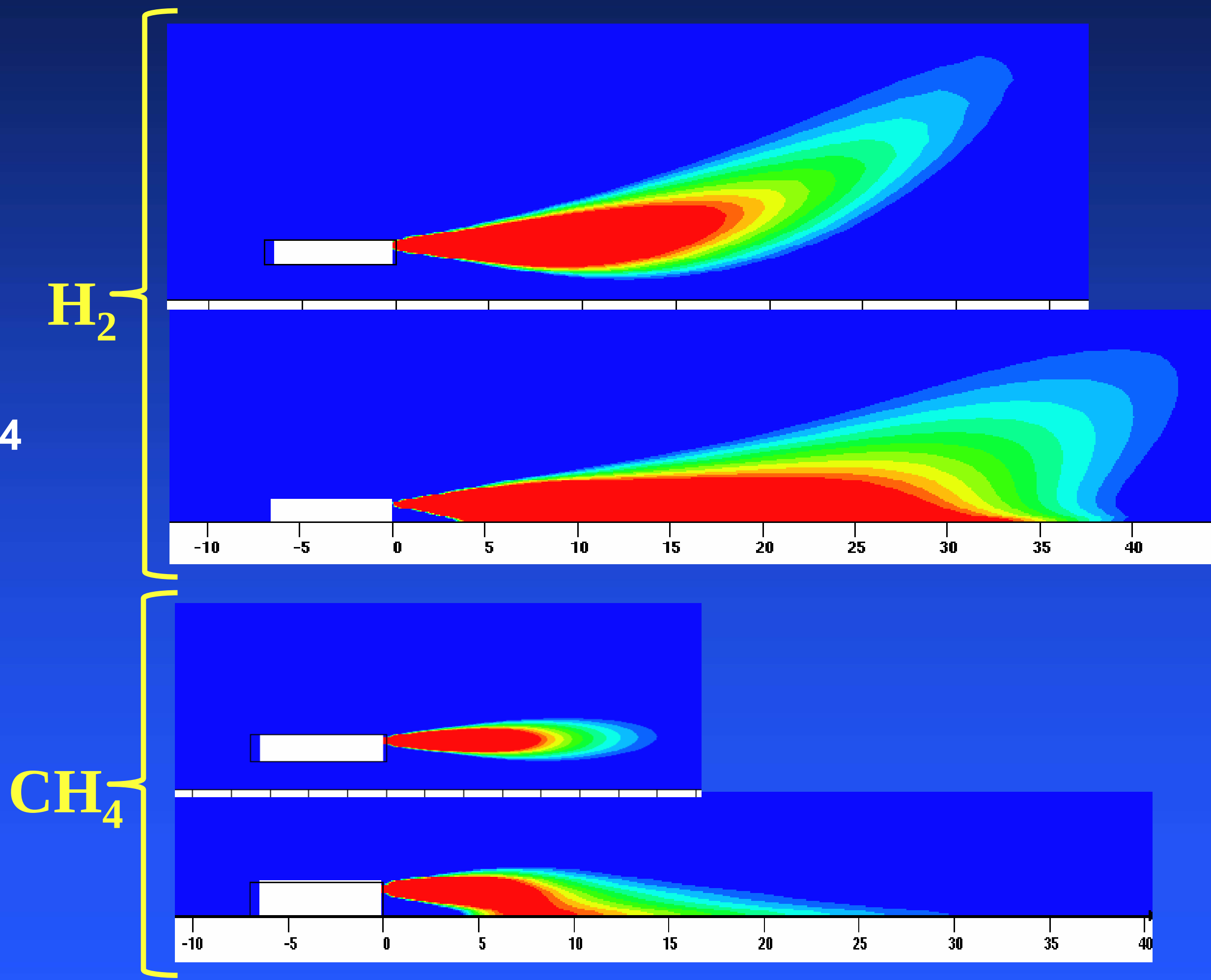
Distance on Jet Centerline to Lower Flammability Limit for Natural Gas and Hydrogen

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

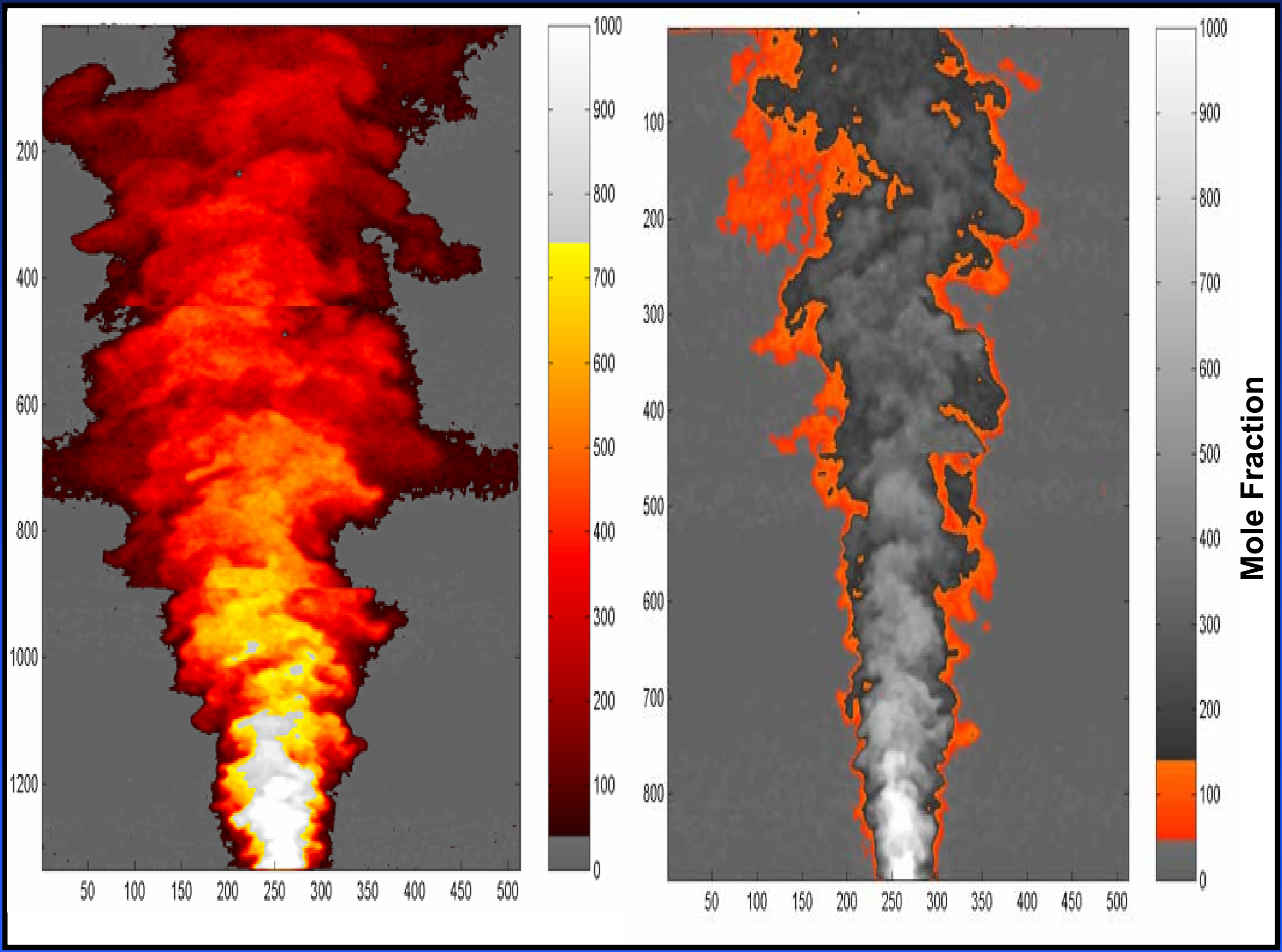
Effects of surfaces ?

- While both flammable envelopes lengths are increased, the increase is more pronounced for CH_4 jets than H_2 jets
- "Transient puffs" seems to lead to a larger temporary increase of extent of horizontal H_2 surface jets



Small Unignited Releases: Ignitable Gas Envelope

H_2 Jet at Re=2,384; Fr = 268 CH_4 Jet at Re=6,813; Fr = 478



- H_2 flammability limits: LFL 4.0%; RFR 75%
- CH_4 flammability limits: LFL 5.2%; RFR 15%

Radial profiles in H_2 jet, d = 1.91 mm, Re = 2384

Is there a myth about the minimum ignition energy?

- Lower ignition energy of H_2 is the lowest of the flammable gases at stoichiometry
  - Over the flammable range of CH_4 (~below 10%), however, H_2 has a comparable ignition energy.

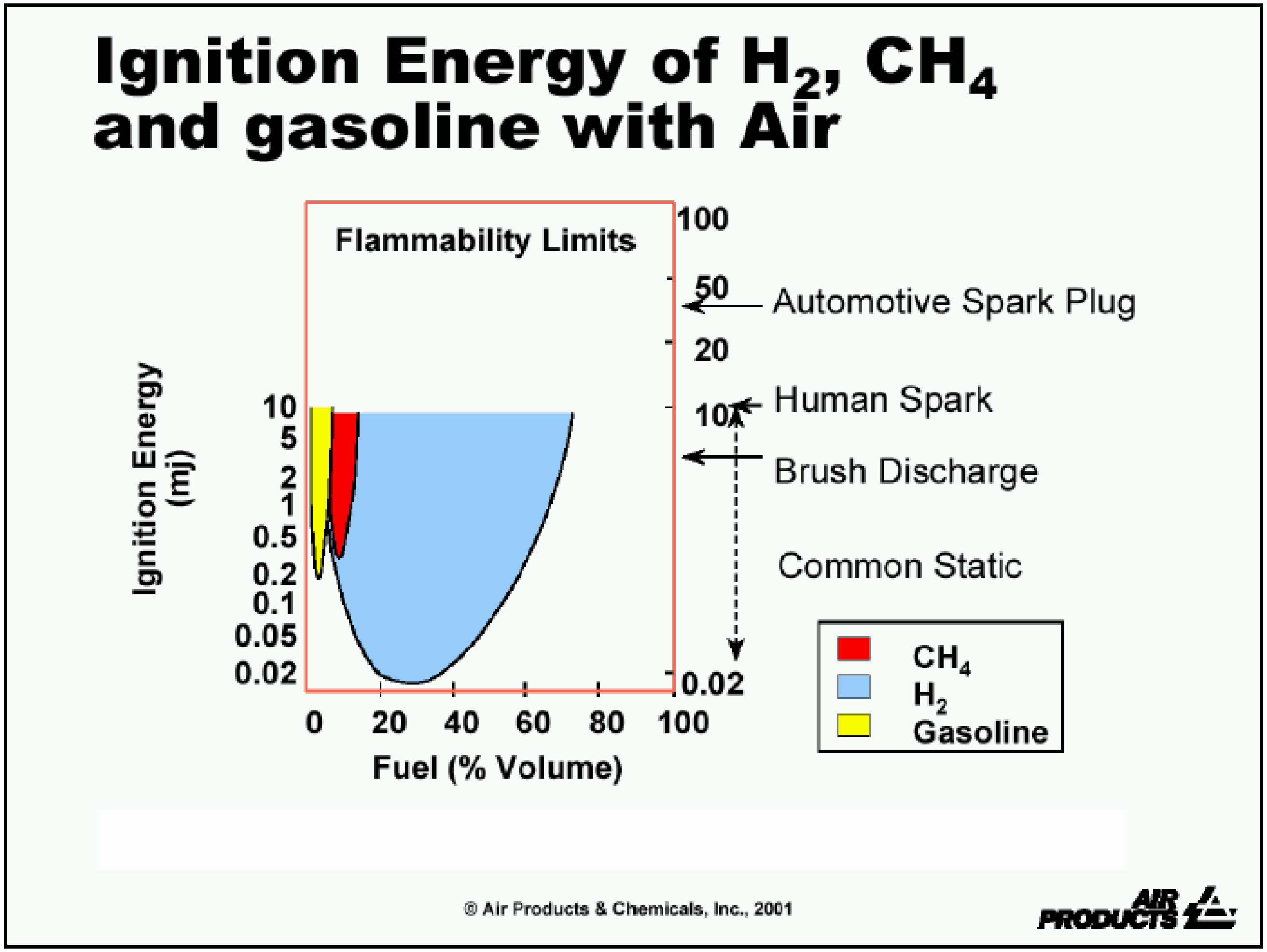


Figure 1: Flammability Limits vs. Ignition Energy of H_2, CH_4 and Gasoline in Air

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Some people just do not get it!

- ⇨ **H_2**
  - ➢ **is not toxic,**
  - ➢ **it is environmentally benign**
  - ➢ **We just borrow it -- ($2H_20 + E \rightarrow 2H_2 + O_2$; then $2H_2+O_2 \rightarrow 2H_2O + E$)**
- ⇨ **H_2 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 H_2 in the commercial setting just as we have for our hydrocarbon fuels.

Publication list

Nighttime photograph of ~40 MPa large-scale H_2 jet-flame test (d_j = 5.08mm, L_{vis} = 10.6 m) from Sandia/SRI tests.

(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 R. W., "Combustion Basics," in National Fire Protection Association (NFPA) Guide to Gas Safety, 2004.

(9) P. Bénard (2007), Chapter 3 – Hydrogen Release and Dispersion - Release of hydrogen - section a.1, , Biennial Report on Hydrogen Safety, HySafe.

(10) B. Angers, A. Hourri, P. Bénard, P. Tessier and J. Perrin (2005), "Simulations of Hydrogen Releases from a Storage Tank: Dispersion and Consequences of Ignition". International Conference on Safety 2005, Sept 8-10, 2005, Pisa, Italy.

(11) A.V. Tchouvelev, P. Bénard, V. Agranat and Z. Cheng (2005), "Determination of Clearance Distances for Venting of Hydrogen Storage". International Conference on Safety 2005, Sept 8-10, 2005, Pisa, Italy (NRCAN, AUTO 21).

(12) Tchouvelev A., P. Bénard, D. R. Hay, V. Mustafa, A. Hourri, Z. Cheng, Matthew P. Large, Quantitative Risk Comparison of Hydrogen and CNG Refuelling Options, Final Technical Report to Natural Resources Canada for the Codes and Standards Workshop of the CTFCA, August 2006 (194 pages).

(13) Bénard, P., Tchouvelev, A., Hourri, A., Chen, Z., Angers, B. High Pressure Hydrogen Jets in a Presence of a Surface. Proceedings of International Conference on Hydrogen Safety, San Sebastian, Spain, September 2007.

(14) Tchouvelev, A.V., Howard, G.W. and Agranat, V.M. Comparison of Standards Requirements with CFD Simulations for Determining of Sizes of Hazardous Locations in Hydrogen Energy Station. Proceedings of the 15th World Hydrogen Energy Conference, Yokohama, June 2004.

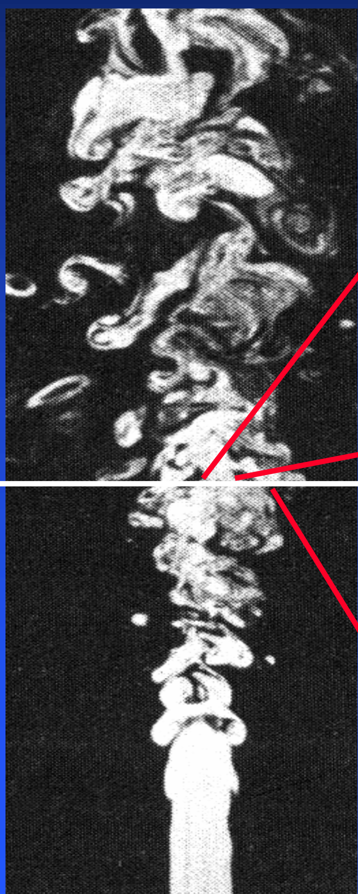
Presentation End

Toss-up

- In practice, most of a hydrogen jet close to the release point is ignitable, and significant regions of the jet have ignitable concentrations higher than 10%
  - A hydrogen jets thus remains more likely to ignite than natural gas.
- For a slow and uniform build-up of hydrogen, however, the risks remain comparable provided detectors are used, depending on the location of the ignition source with respect to the leak
  - The low minimum ignition energy issue remains, overall, a concern.

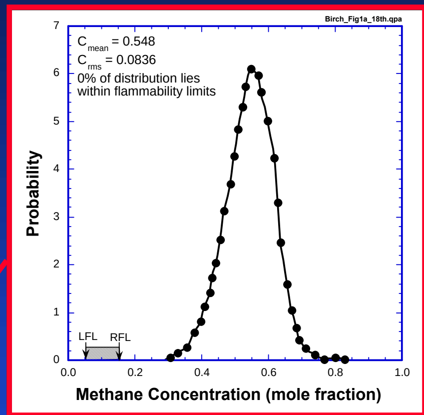
Jet Ignition Probability

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



-5 0 5
r/D

z/D=10



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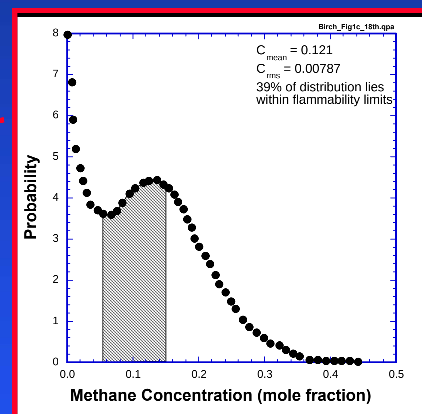
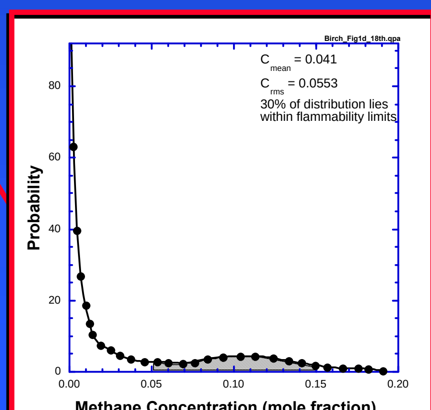


r/D=1.5



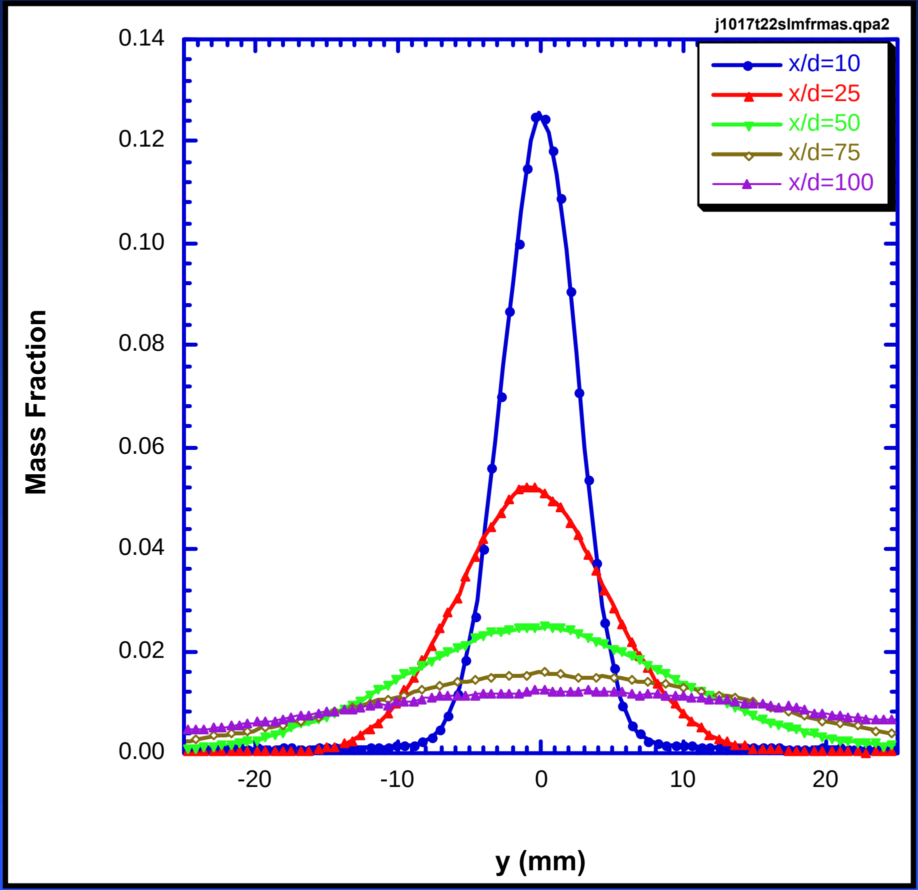
r/D=1.8

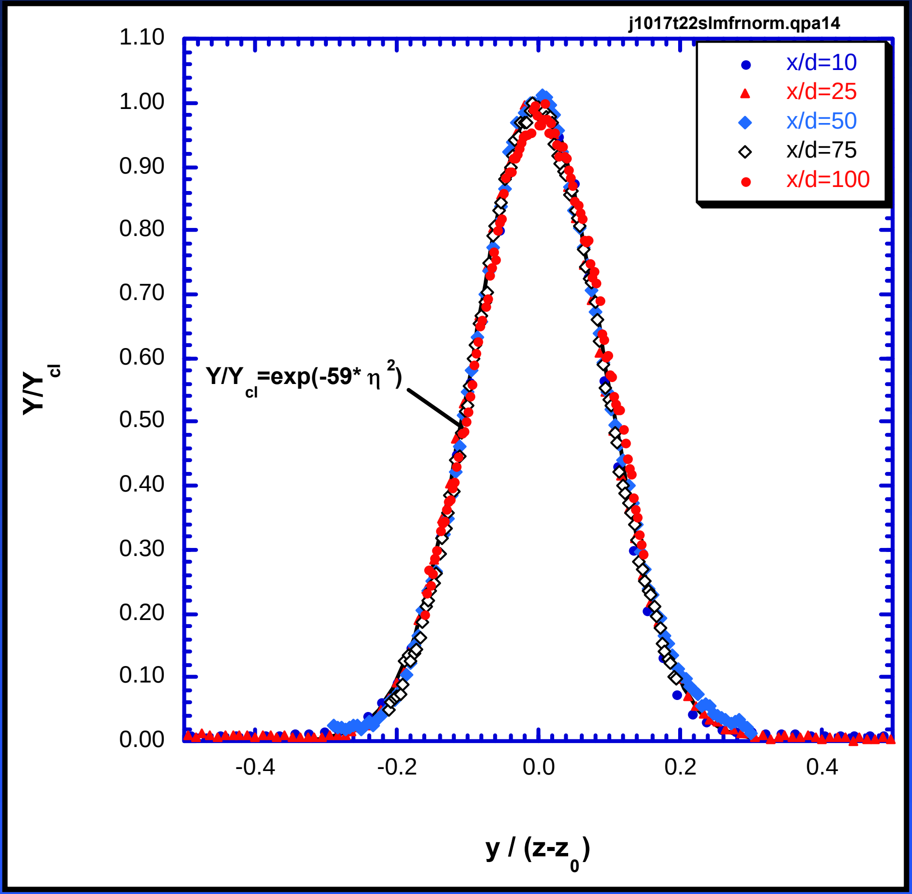
- **Probability distributions quantify intermittent nature of turbulent flows.**

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

Small Unignited Releases: Momentum-Dominated Regime

Radial profiles in H_2 jet, d=1.91 mm, Re = 2384





Radial profiles of H_2 mass fraction collapse onto a single curve in agreement with CH_4 jet data.

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

<u>Unignited Jet Separation Distance Length Scales</u>

Pressure = ~20 MPa (~3000 psig)

Hole Diameter	Flowrate	Xmax - Distance to 4% mole fraction	Start of Intermediate Region
3.175 mm (1/8 inch)	9.718×10^{-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)	2.430×10^{-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)	6.075×10^{-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**
  $$x/D = 0.5\, F^{1/2}(\rho_{exit}/\rho_{amb})^{1/4}$$

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