SPONTANEOUS IGNITION OF PRESSURIZED HYDROGEN RELEASE

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We are at the dawn of a hydrogen economy.

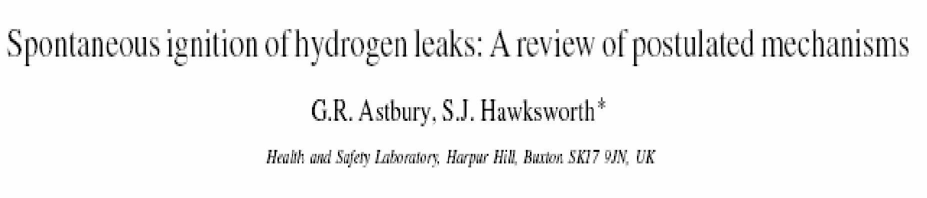
HYFIRE proposal for the EU Marie Curie Programme, Dec. 2004

Very High Pressure Hydrogen Storage

Vertical Flame
10-12 ft tall, 2-3 ft wide
(H_2 flame at SRI test site)

- The Fuel cell vehicles (FCV) currently in trial use are mounted with hydrogen containers pressurized up to 400 bar and yield a driving range of 300-350 km per filling - roughly half of the gasoline vehicle's driving range.
- Industry is developing containers for up to 1000 bar pressurization.

Safety Implications



Spontaneous ignition of hydrogen leaks: A review of postulated mechanisms

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Health and Safety Laboratory, Harpur Hill, Buxton SK17 9JN, UK

Analysis of Hydrogen Accidental Database Compiled by Kingston University

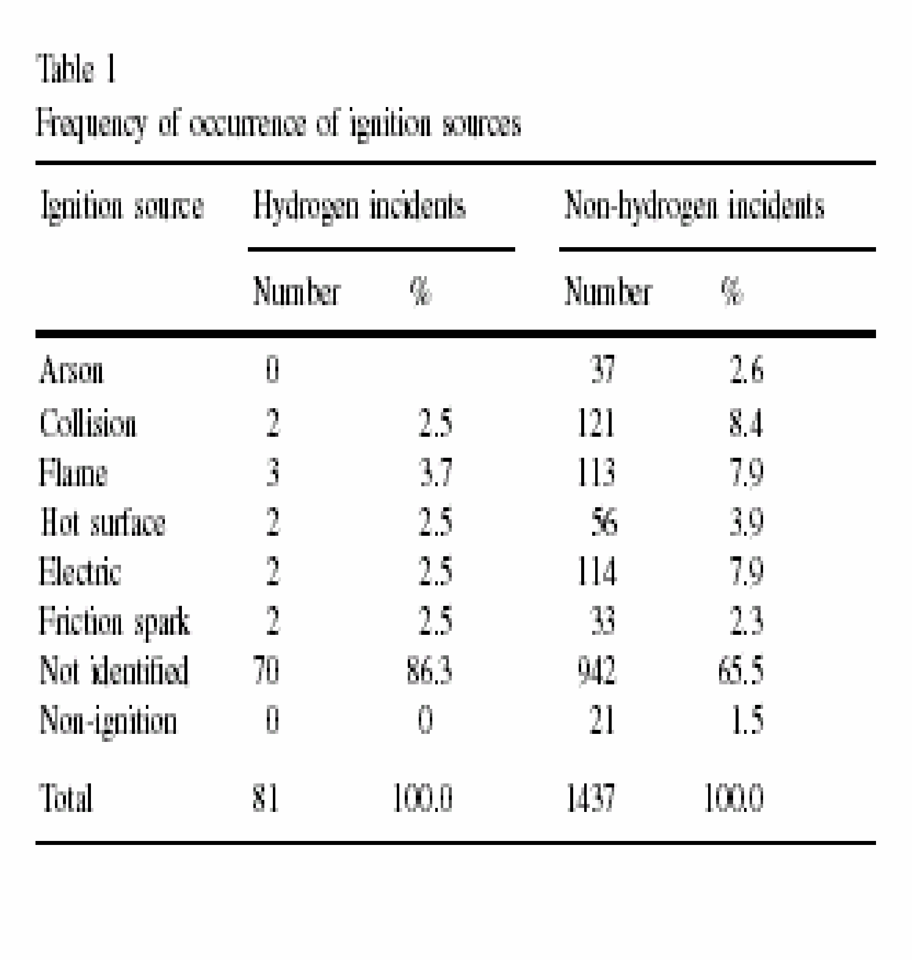


Table 1

Frequency of occurrence of ignition sources

Ignition source	Hydrogen incidents		Non-hydrogen incidents	
	Number	%	Number	%
Arson	0		37	2.6
Collision	2	2.5	121	8.4
Flame	3	3.7	113	7.9
Hot surface	2	2.5	56	3.9
Electric	2	2.5	114	7.9
Friction spark	2	2.5	33	2.3
Not identified	70	86.3	942	65.5
Non-ignition	0	0	21	1.5
Total	81	100.0	1437	100.0

Table 2 Frequency of occurrence of ignition sources

Ignition source	Hydrogen incidents	
	Number	Percentage
Arson	3	0.44%
Collision	29	4.29%
Flame	58	8.58%
Hot surface	57	8.43%
Electric	44	6.51%
Not identified	419	59.98%
No ignition	66	9.76%
TOTAL	**676**	

Postulated Ignition Mechanisms

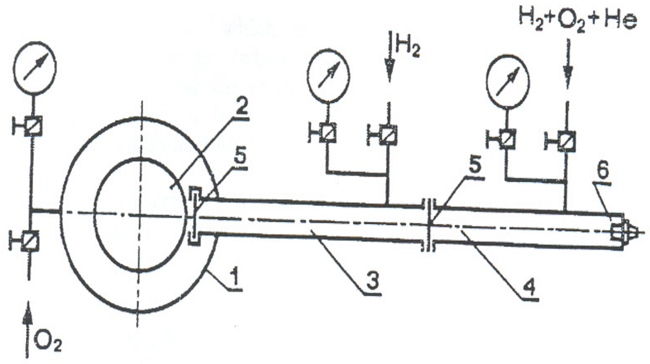
(Astbury & Hawksworth, 2005)

- ~~Reverse Joule-Thomson effect~~
- Static electricity
- Sudden adiabatic compression
- Hot surface ignition
- Mechanical friction and impact
- ***Diffusion ignition***

Self-ignition and explosion during discharge of high-pressure hydrogen, Toshio Mogi, Dongjoon Kim, Hiroumi Shiina, Sadashige Horiguchi, J of Loss Prevention, 2007.

Wolanski, P. and Wojcicki, S., Investigation into the Mechanism of the Diffusion Ignition of a Combustible Gas Flowing into an Oxidizing Atmosphere. Proc. Combust. Instit., 14, 1972.

FIRE AND EXPLOSION



Test stand for model tests. 1, spherical chamber; 2, w
section; 5, membrane; 6, ignitio

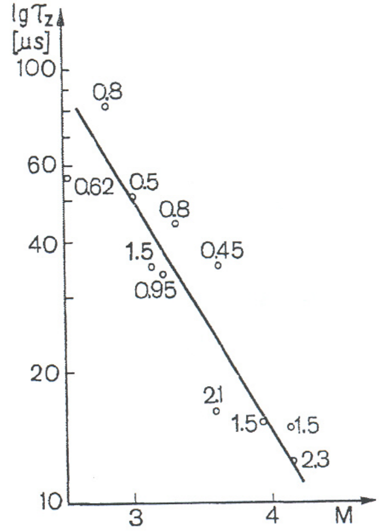
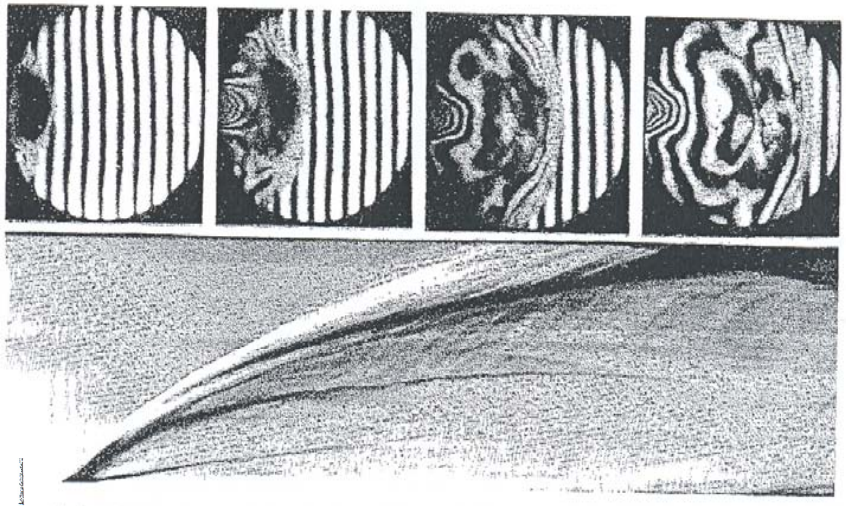


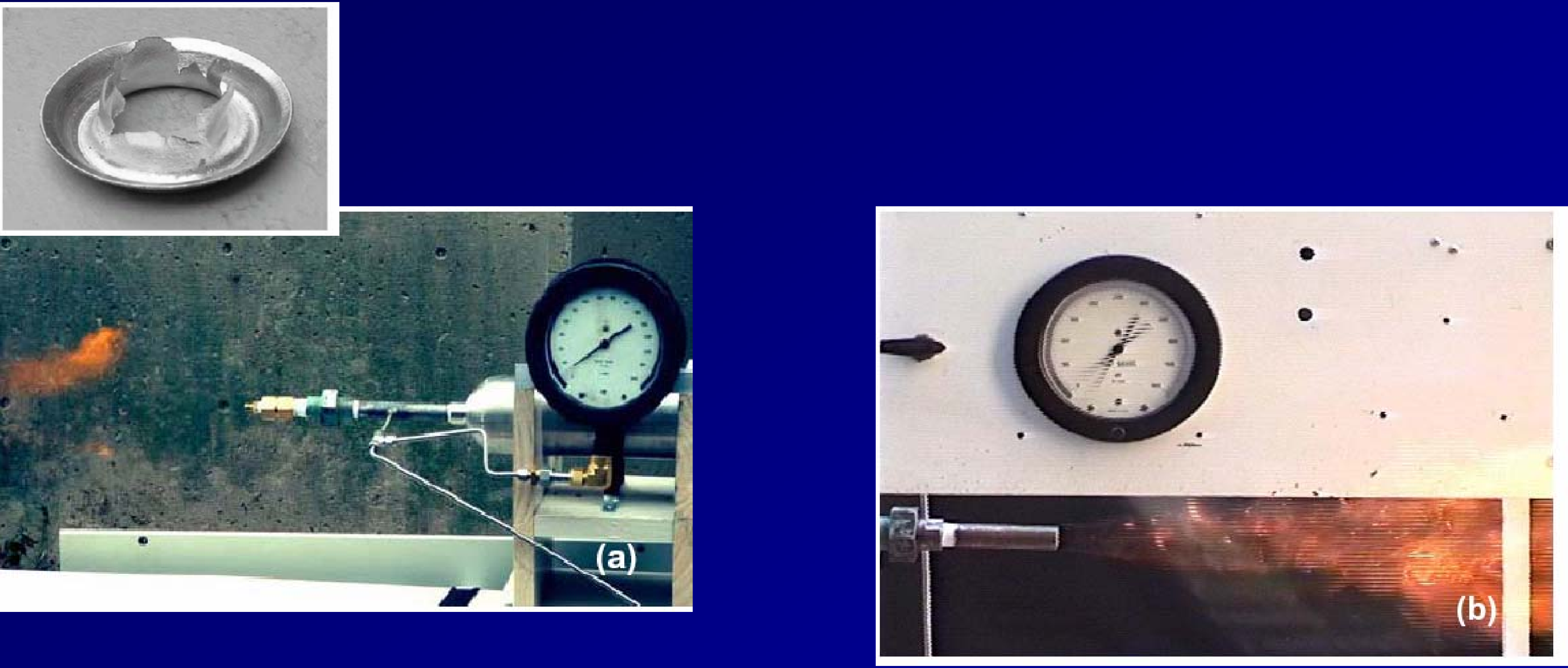
FIG. 4. Relation between the ignition delay and the Mach Number of the shock wave produced in oxygen by hydrogen emission. The numbers represent the values of the pressure behind the wave. The solid line shows the theoretical relation.



G. 2. Interferometric frame photographs of hydrogen flow into an atmosphere of oxygen (top) and
eren streak photograph of the same process (bottom). Frame rate, 312,500 frames per second (every
picture is shown).

Spontaneous Ignition of Pressurized Releases of Hydrogen and Natural Gas into Air

Frederick L. Dryer[1], Marcos Chaos, Zhenwei Zhao, Jeffrey N. Stein, Jeffrey Y. Alpert, and Christopher J. Homer



Sustained turbulent diffusion flame of hydrogen and air ignited by failure of a burst disk at (a) 43.1 atm (618 psig) using the downstream geometry shown in Figure 4 and (b) 86.1 atm (1250 psig) with a short length of unrestricted, constant diameter pipe (12.7 cm, 5”)

Self-ignition and explosion during discharge of high-pressure hydrogen

Toshio Mogi*, Dongjoon Kim, Hiroumi Shiina, Sadashige Horiguchi

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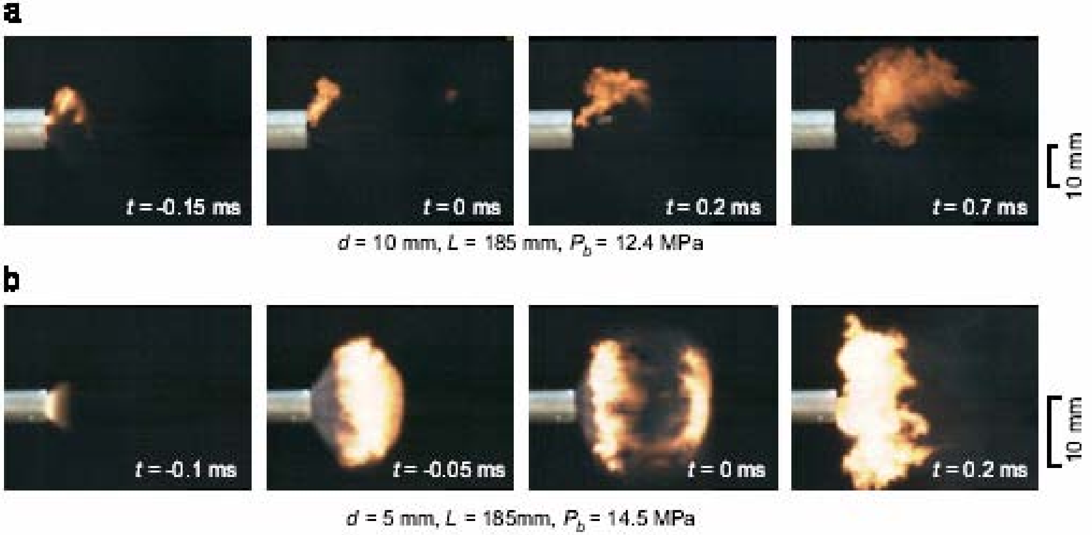
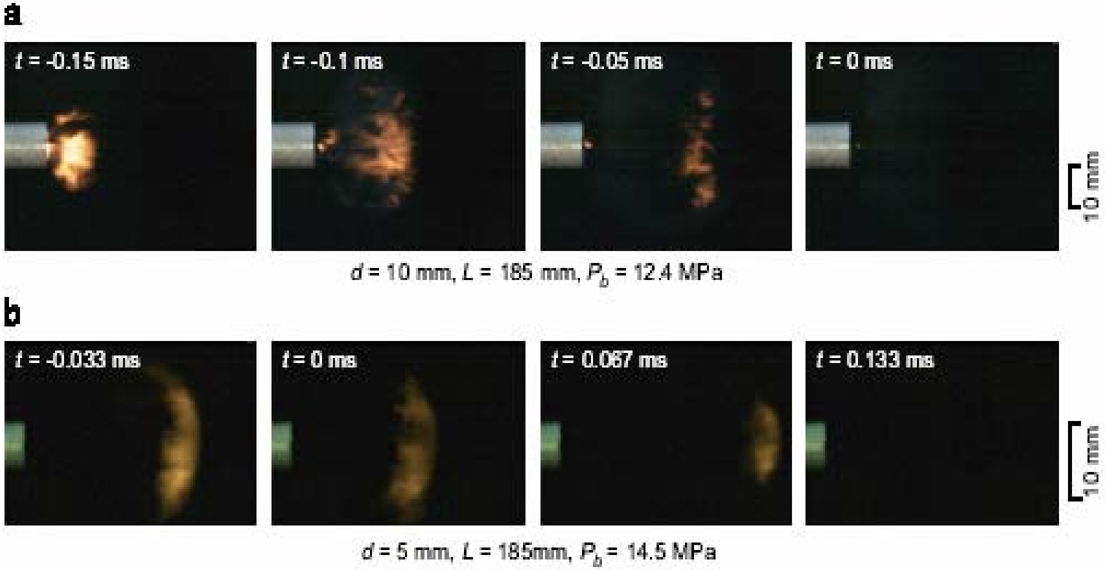


d = 10 mm, L = 185 mm, P_b = 12.4 MPa

d = 5 mm, L = 185mm, P_b = 14.5 MPa

Fig. 4. Example of successful ignition of hydrc



d = 10 mm, L = 185 mm, P_b = 12.4 MPa

d = 5 mm, L = 185mm, P_b = 14.5 MPa

Fig. 5. Example of failed ignition of hydrogen jet flow.

Shock-induced ignition of hydrogen gas during accidental or technical opening of high-pressure tanks

V.V. Golub*, D.I. Baklanov, T.V. Bazhenova, M.V. Bragin, S.V. Golovastov, M.F. Ivanov, V.V. Volodin

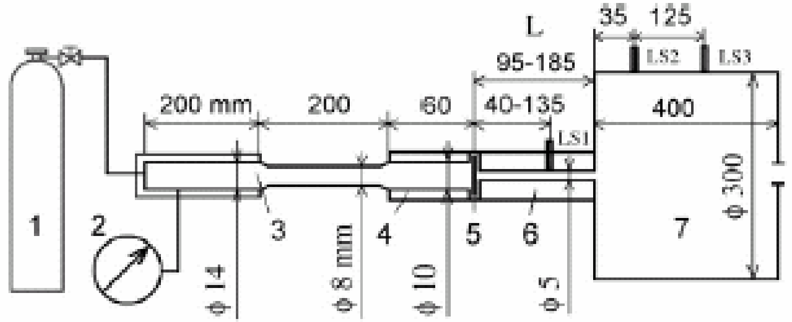


Fig. 8. Schematic of experimental setup. (1) hydrogen cylinder, (2) manometer, (3) high-pressure chamber, (4) diaphragm block, (5) diaphragm, (6) low-pressure chamber; (7) buster chamber; *L*—low-pressure chamber length; *d*—low-pressure chamber diameter; LS1–LS3—light gauges.

- Unlike in the case of Mogi et al. (2006), self-ignition was observed at a pressure of less than 50 bar in the tube under investigation (diameter 5mm and length 185 mm).

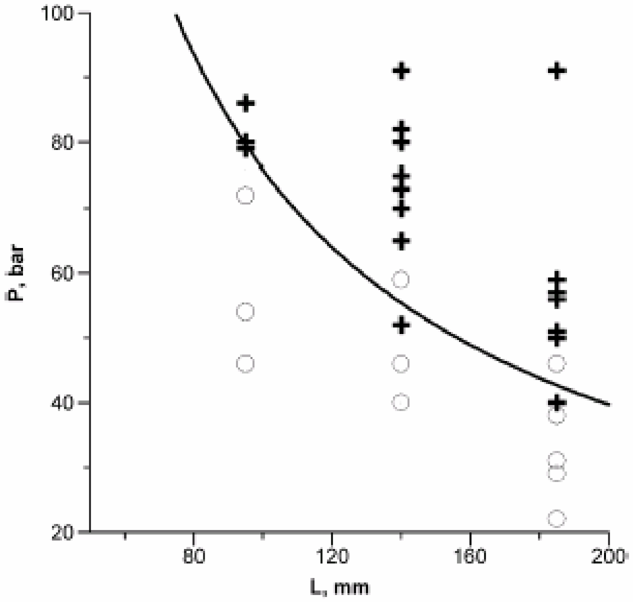


Fig. 10. Experimental results showing dependence of minimal reservoir pressure on the external tube length when self-ignition occurs. ○—self-ignition did not occur, +—self-ignition occurred.

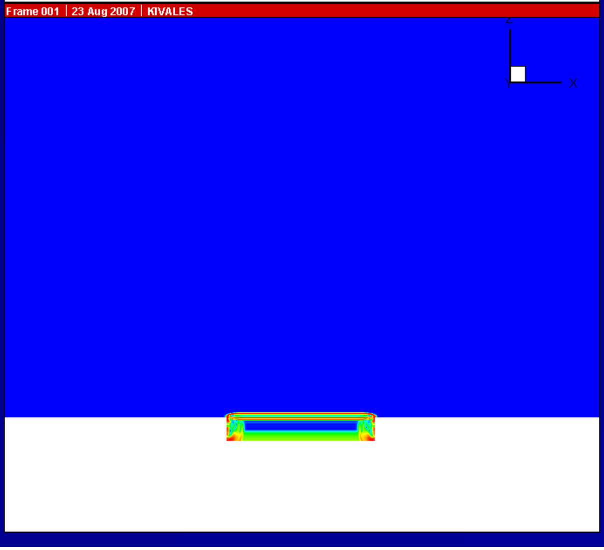
The importance of hole size/pipe diameter

Diffusion Ignition

(Wolanski and Wojcicki, 1973)

- ***<u>Sudden</u>*** **rupture of a pressure boundary**
- **Shock wave (primary)**
- **Shock-heated air or oxidizer (behind the shock wave)**
- **Cooling hydrogen – flow acceleration or divergence**
- **Formation of combustible mixture at contact surface – molecular diffusion**
- **Ignition (after a delay time)**

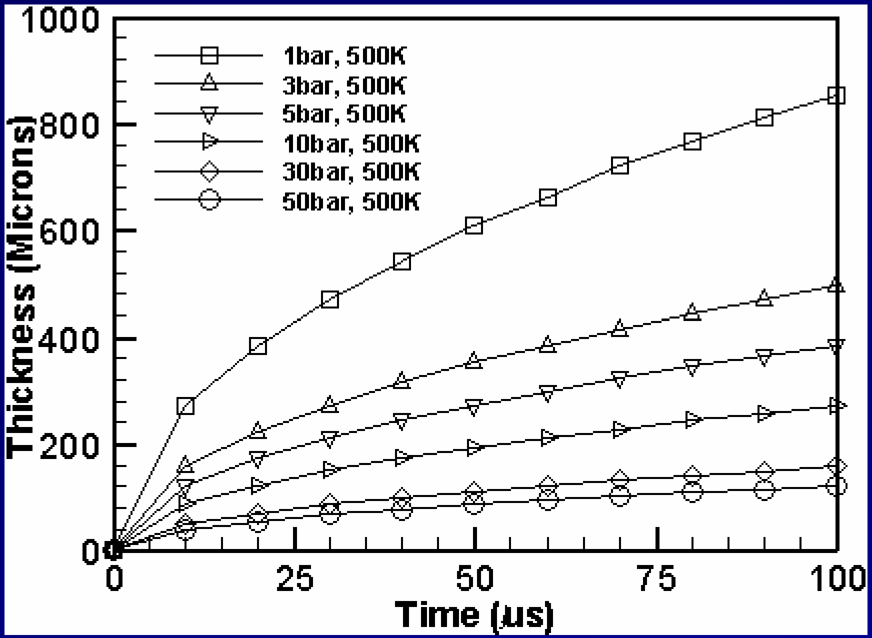
Temperature

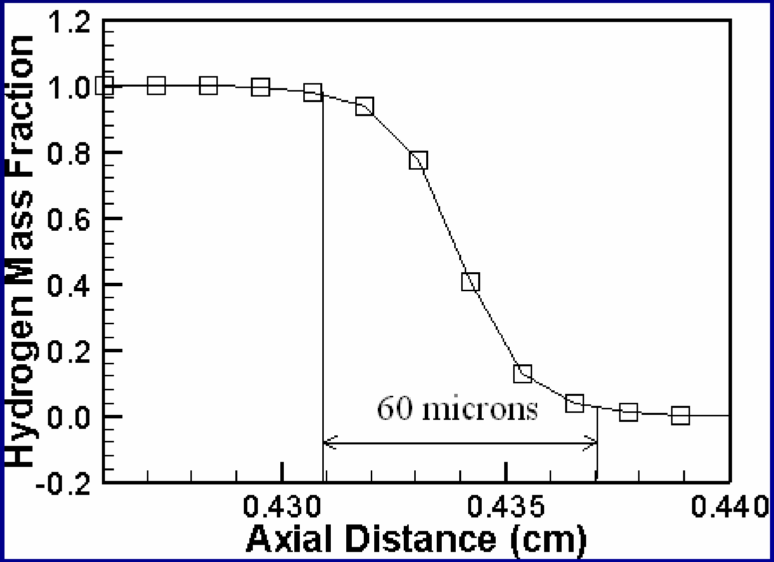


Schlieren Density

Mixing at Contact Surface

- Mass and energy exchange between shock-heated air and cooled hydrogen through ***molecular diffusion***





1-D diffusion computation for the release case of 100 bar through a 1mm hole at t=3us

Ignition & its Delay Time

- ***Mixing time***

  the time for the temperature of the mixture to reach the autoignition temperature

- ***Chemical delay time***

  due to the slow hydrogen combustion rate under low temperature

(Wolanski and Wojcicki, 1973)

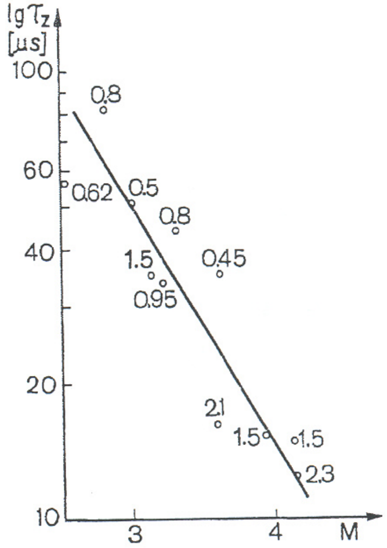


Fig. 4. Relation between the ignition delay and the Mach Number of the shock wave produced in oxygen by hydrogen emission. The numbers represent the values of the pressure behind the wave. The solid line shows the theoretical relation.

An increase in the release pressure leads to a rapid decrease in both mixing time and chemical delay time

Numerical Methods

- ***2-D*** **Unsteady Compressible Navier-Stokes equations solved with an** ***ILES*** **method**

- ***Detailed*** **chemical-kinetic scheme - 8 reactive species and 21 elementary steps –third body and "fall off" behavior considered (Williams 2006)**

- ***Multi-component*** **diffusion approach for mixing - thermal diffusion**

- ***ALE*** **numerical scheme: convective term solved separately from diffusion terms**

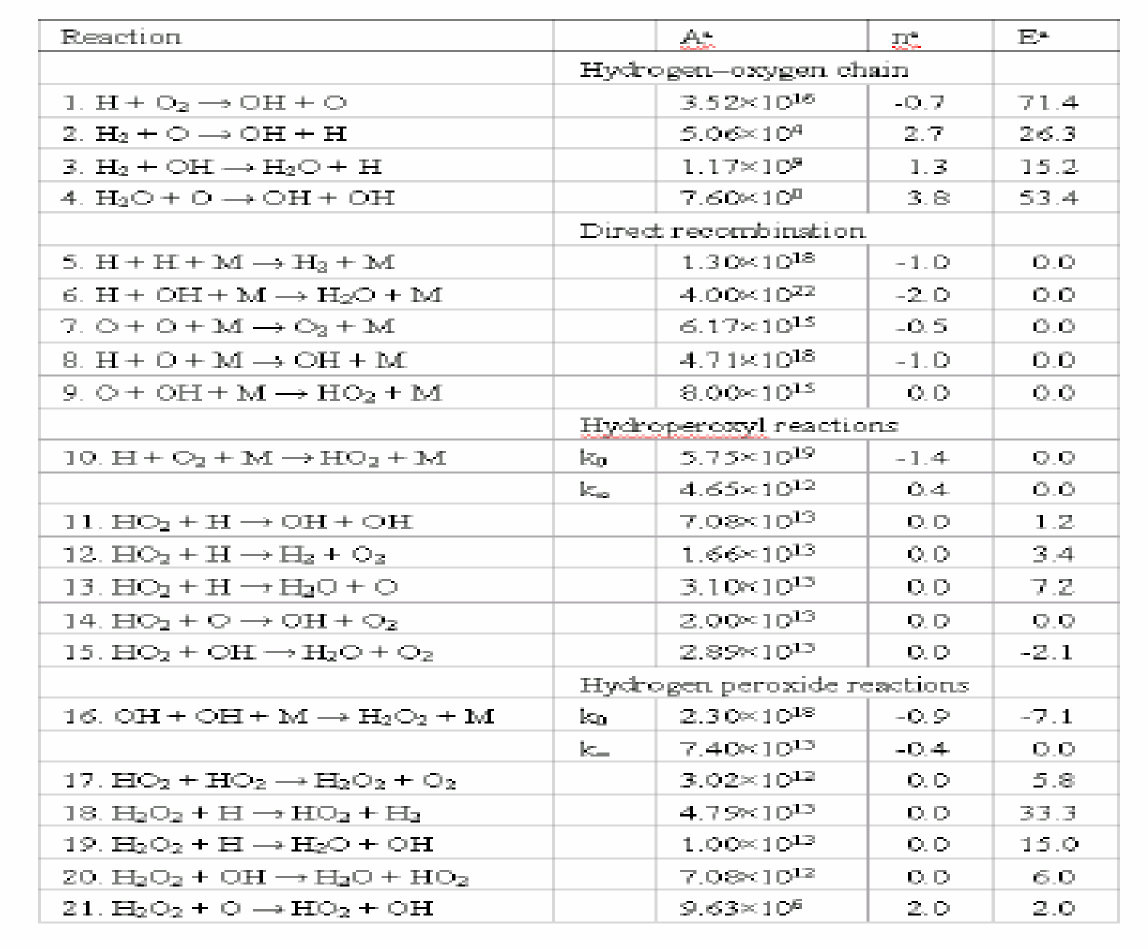
- **In Lagrangian stage,** ***2nd-order Crank-Nicolson*** **scheme +** ***2nd-order central differencing***

- **In rezone phase,** ***3rd-order Runge-Kutta method*** **+** ***5th - order upwind WENO scheme***

Numerical diffusion resulting from the use of lower order schemes could lead to overprediction of the contact surface thickness, and hence artificially increase the chance of autoignition.

THE DETAILED SAN DIEGO MECHANISM AND THE ASSOCIATED RATE PARAMETERS

(Williams 2006)



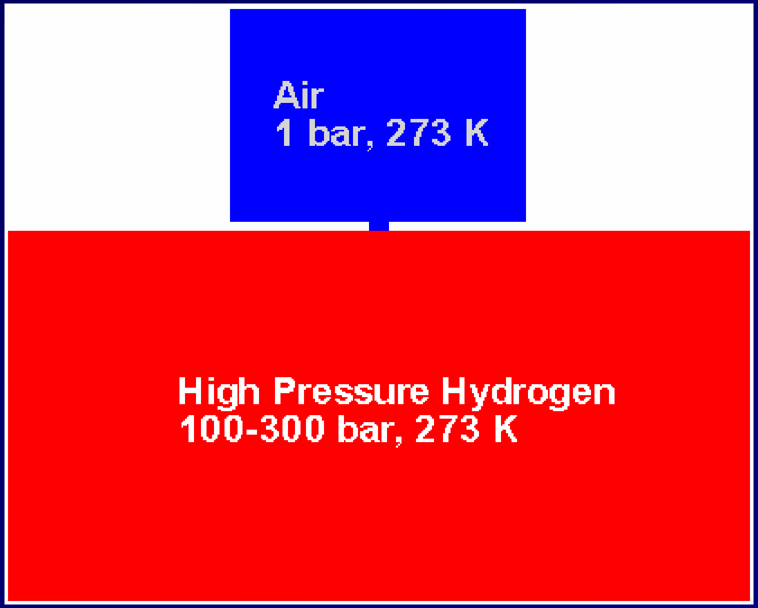
Reaction		A^a	n^a	E^a
	Hydrogen–oxygen chain			
1. $H + O_2 \rightarrow OH + O$		3.52×10^{16}	-0.7	71.4
2. $H_2 + O \rightarrow OH + H$		5.06×10^{4}	2.7	26.3
3. $H_2 + OH \rightarrow H_2O + H$		1.17×10^{9}	1.3	15.2
4. $H_2O + O \rightarrow OH + OH$		7.60×10^{0}	3.8	53.4
	Direct recombination			
5. $H + H + M \rightarrow H_2 + M$		1.30×10^{18}	-1.0	0.0
6. $H + OH + M \rightarrow H_2O + M$		4.00×10^{22}	-2.0	0.0
7. $O + O + M \rightarrow O_2 + M$		6.17×10^{15}	-0.5	0.0
8. $H + O + M \rightarrow OH + M$		4.71×10^{18}	-1.0	0.0
9. $O + OH + M \rightarrow HO_2 + M$		8.00×10^{15}	0.0	0.0
	Hydroperoxyl reactions			
10. $H + O_2 + M \rightarrow HO_2 + M$	k_0	5.75×10^{19}	-1.4	0.0
	k_∞	4.65×10^{12}	0.4	0.0
11. $HO_2 + H \rightarrow OH + OH$		7.08×10^{13}	0.0	1.2
12. $HO_2 + H \rightarrow H_2 + O_2$		1.66×10^{13}	0.0	3.4
13. $HO_2 + H \rightarrow H_2O + O$		3.10×10^{13}	0.0	7.2
14. $HO_2 + O \rightarrow OH + O_2$		2.00×10^{13}	0.0	0.0
15. $HO_2 + OH \rightarrow H_2O + O_2$		2.89×10^{13}	0.0	-2.1
	Hydrogen peroxide reactions			
16. $OH + OH + M \rightarrow H_2O_2 + M$	k_0	2.30×10^{18}	-0.9	-7.1
	k_∞	7.40×10^{13}	-0.4	0.0
17. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$		3.02×10^{12}	0.0	5.8
18. $H_2O_2 + H \rightarrow HO_2 + H_2$		4.79×10^{13}	0.0	33.3
19. $H_2O_2 + H \rightarrow H_2O + OH$		1.00×10^{13}	0.0	15.0
20. $H_2O_2 + OH \rightarrow H_2O + HO_2$		7.08×10^{12}	0.0	6.0
21. $H_2O_2 + O \rightarrow HO_2 + OH$		9.63×10^{6}	2.0	2.0

Two release scenarios

– *Numerical Simulation at Kingston University*

- **Direct release of pressurised hydrogen into air**
- **Release of pressurised hydrogen through a tube**

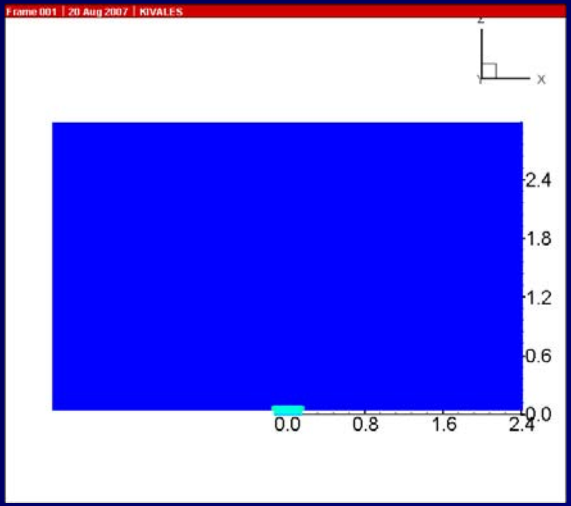
Problem Description



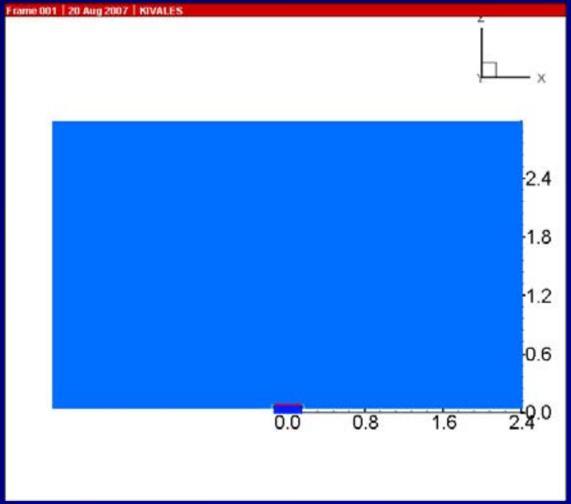
- Three hole sizes:
  1mm, 3mm, 5mm
- Three release Pressures:
  100 bar, 200 bar, 300 bar
- Non-slip and adiabatic wall boundary
- Minimum cell size:
  10 microns
- Only *early stage* of release simulated

Overview of the Under-expanded jet

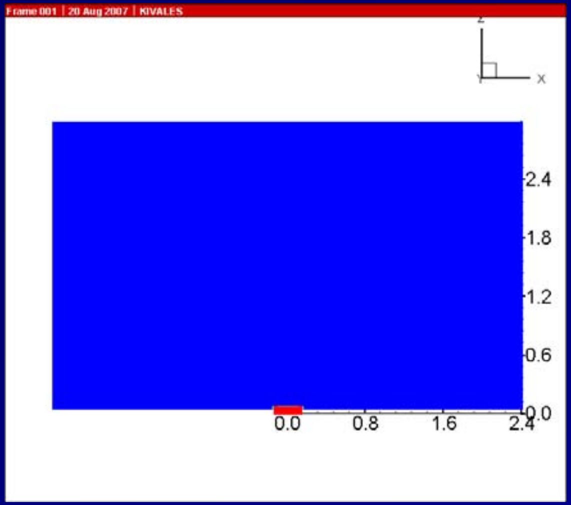
1. Mach Number



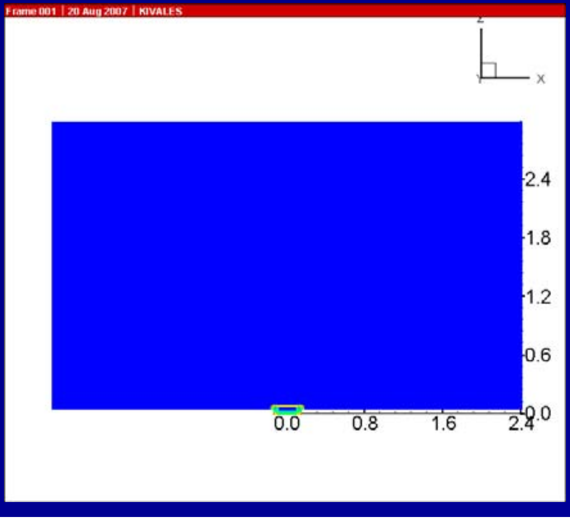
2. Temperature



3. Mass Fraction

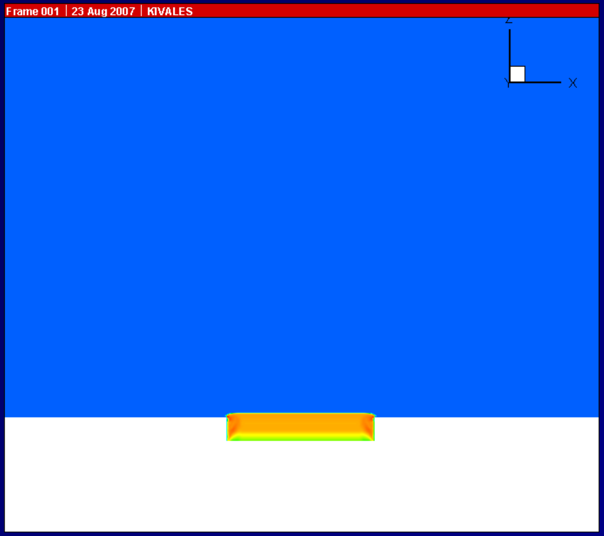


3. Density Schlieren



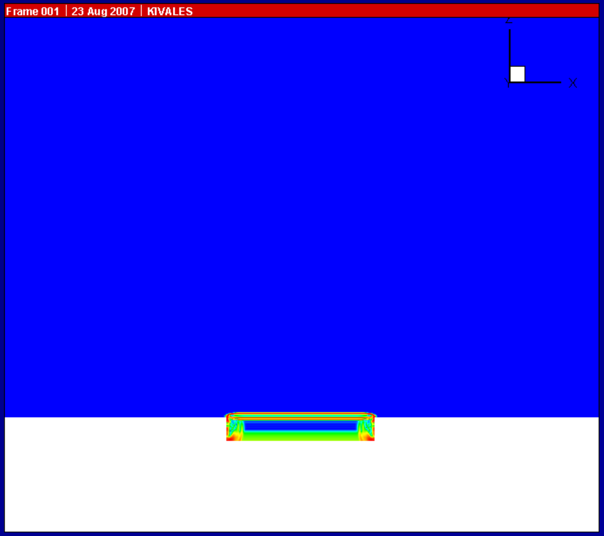
The Very Early Release Moment

1. Axial Velocity

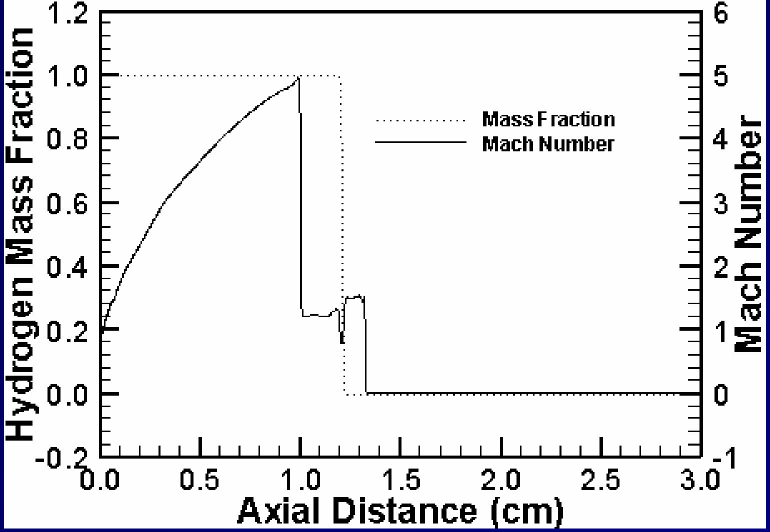


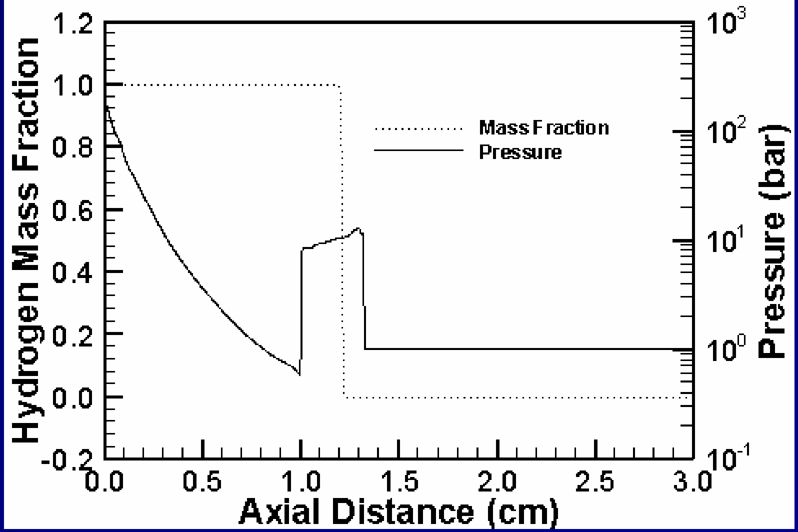
2. Temperature

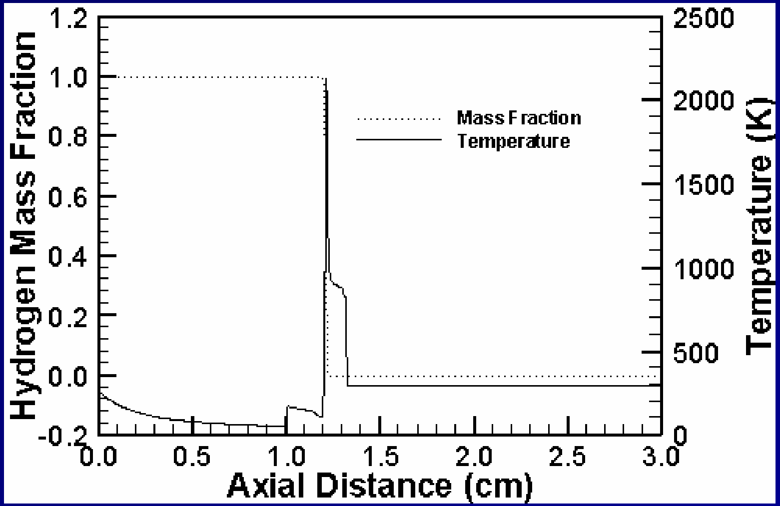
3. Density Schlieren

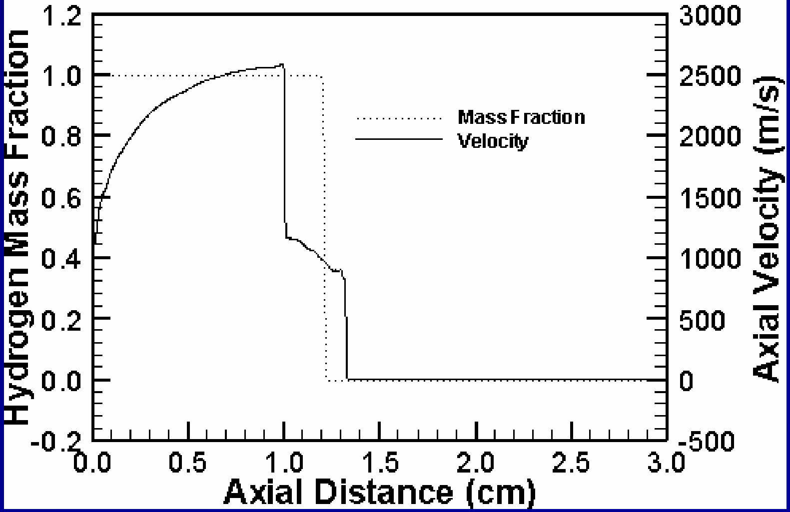


Changing Patterns



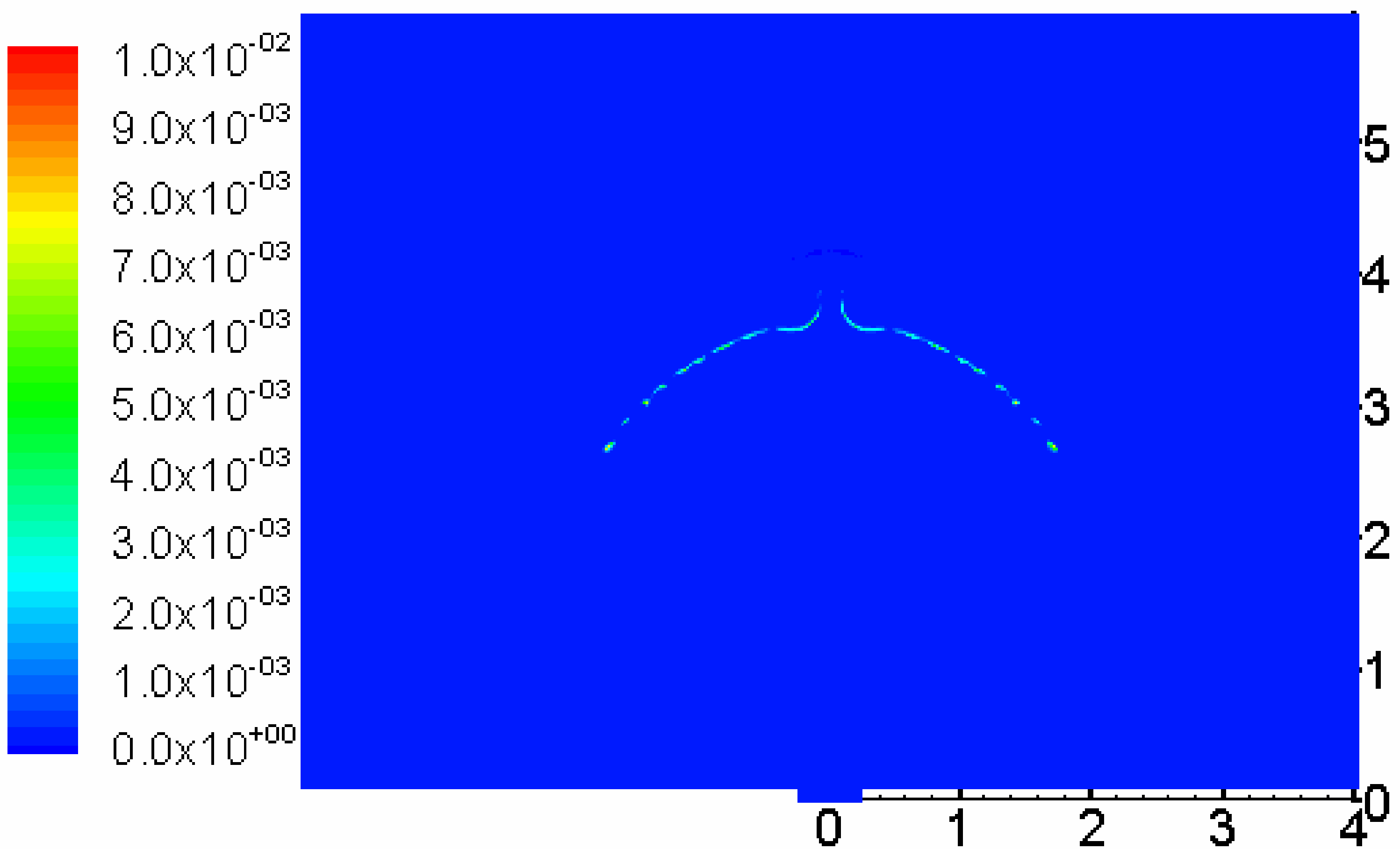






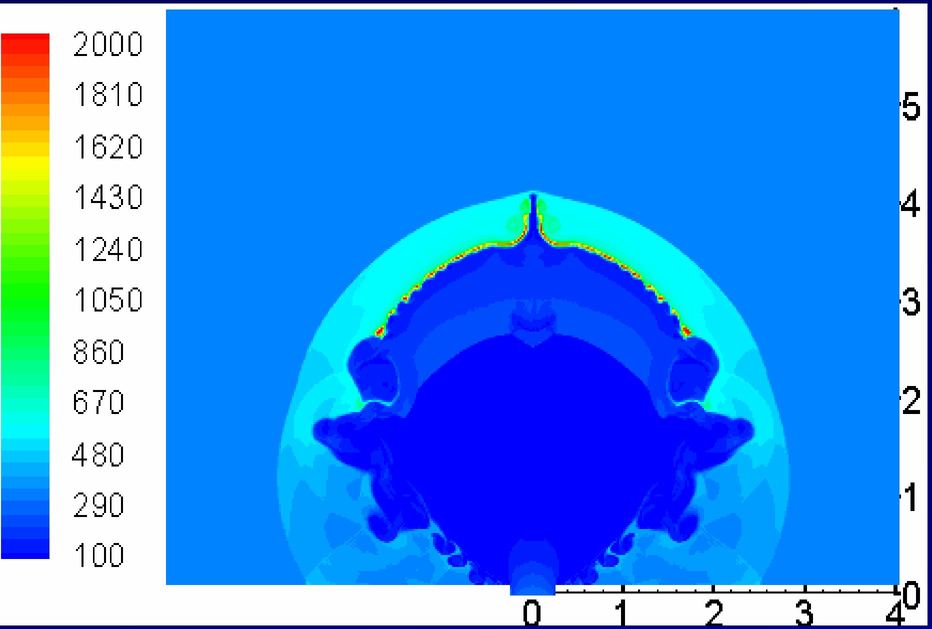
For the release case

Contour of OH

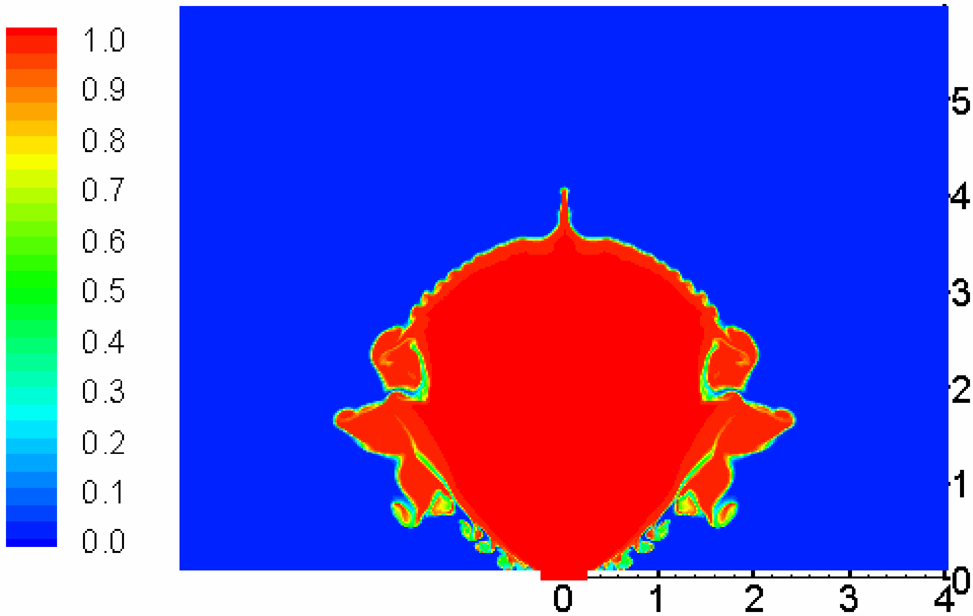


<u>*For the release case of 300 bar through a 5mm hole at t=35us*</u>

Contour of Temperature



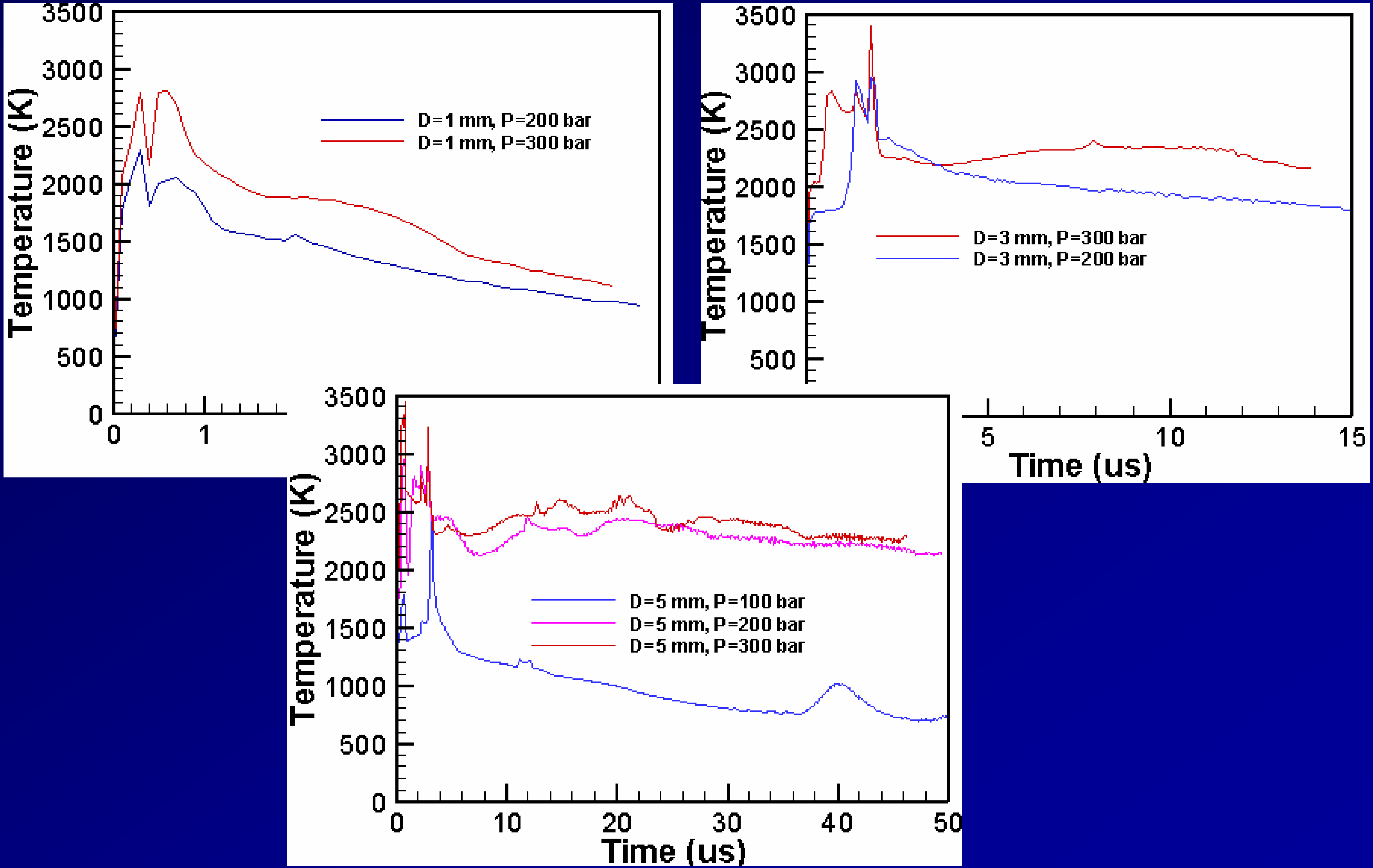
Contour of Mass Fraction



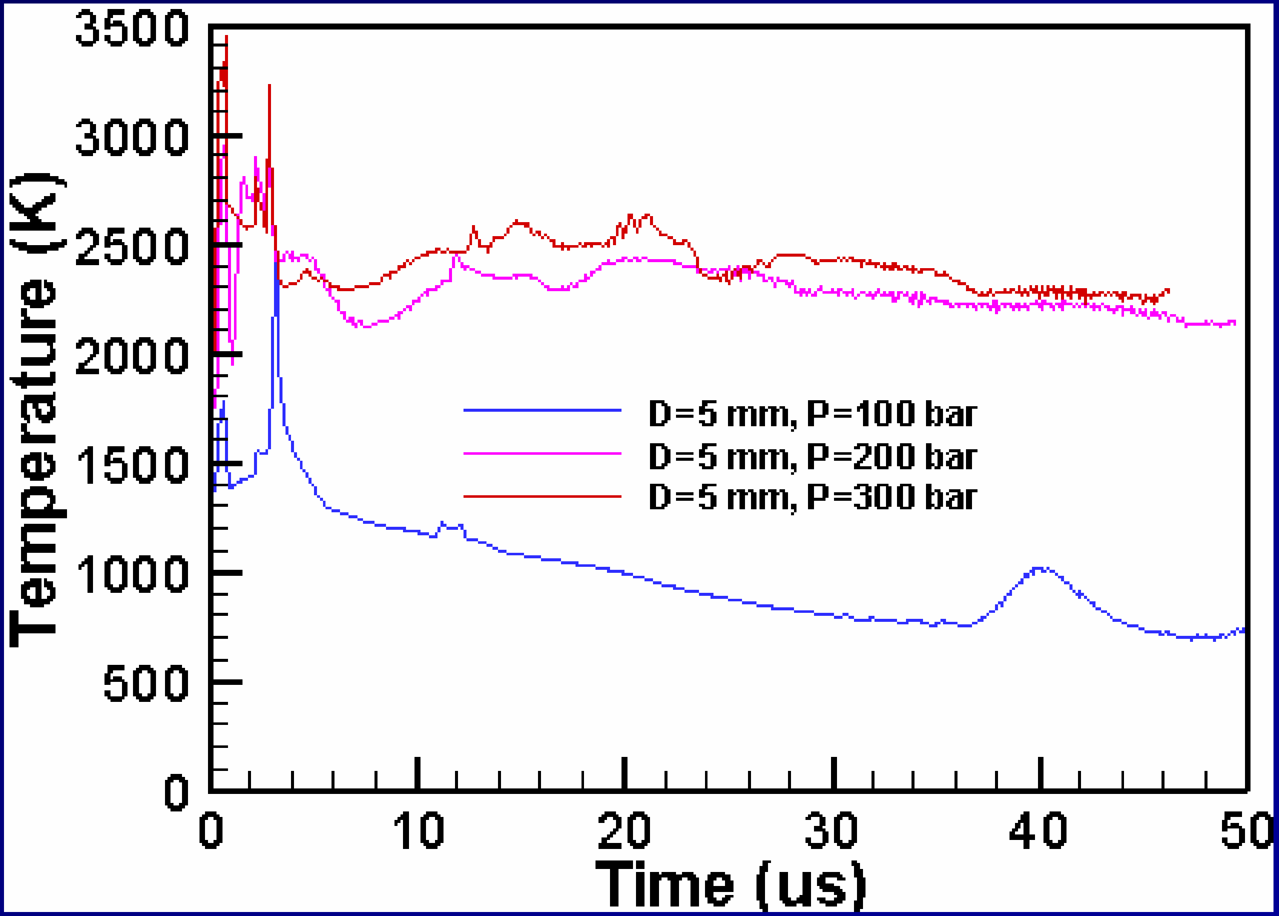
Wrinkling of the contact surface due to Richtmyer-Meshkov instability

For the release case of 300 bar through a 5mm hole at t=35us

Release through a 1mm, 3mm and 5mm holes



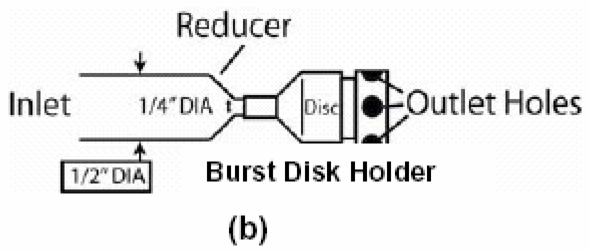
Release through a 5 mm hole

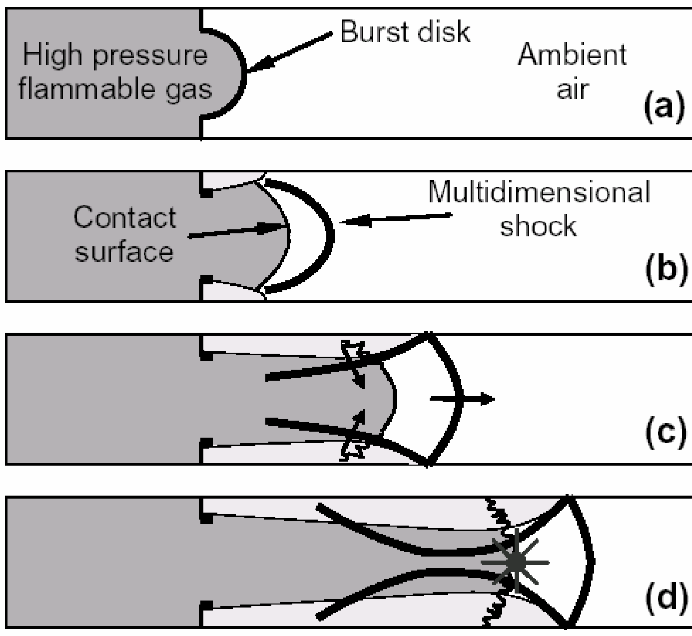


Release through a tube into an open space

Table 1 Computational parameters of release through a tube

	Case 1	Case 2	Case 3	Case 4
Release Pressure [bar]	40	70	100	70
Dimensions in Diameter [cm]	1(tube)/16(open space)			
Length of Tube [cm]	2	2	7	2
No. of Grids	1,600,000			800,000
Minimum Grid Spacing [μm]	20			40





Spontaneous Ignition of Pressurized Releases of Hydrogen and Natural Gas into Air

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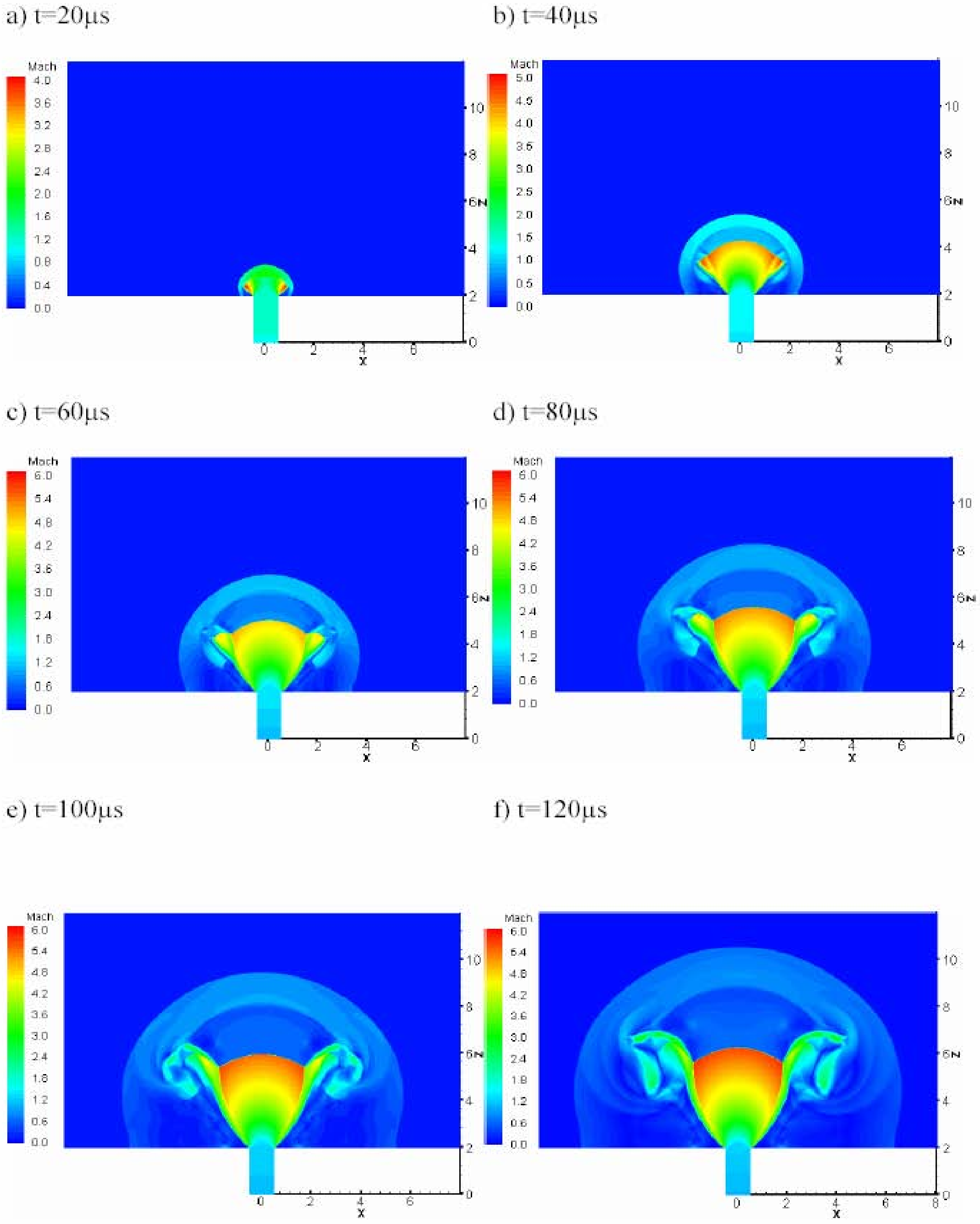
Simulation set up using the test configurations of Dryer et al. [2] as reference

Release through a tube into an open space

Flow structure


a) t=20μs

b) t=40μs

c) t=60μs

d) t=80μs

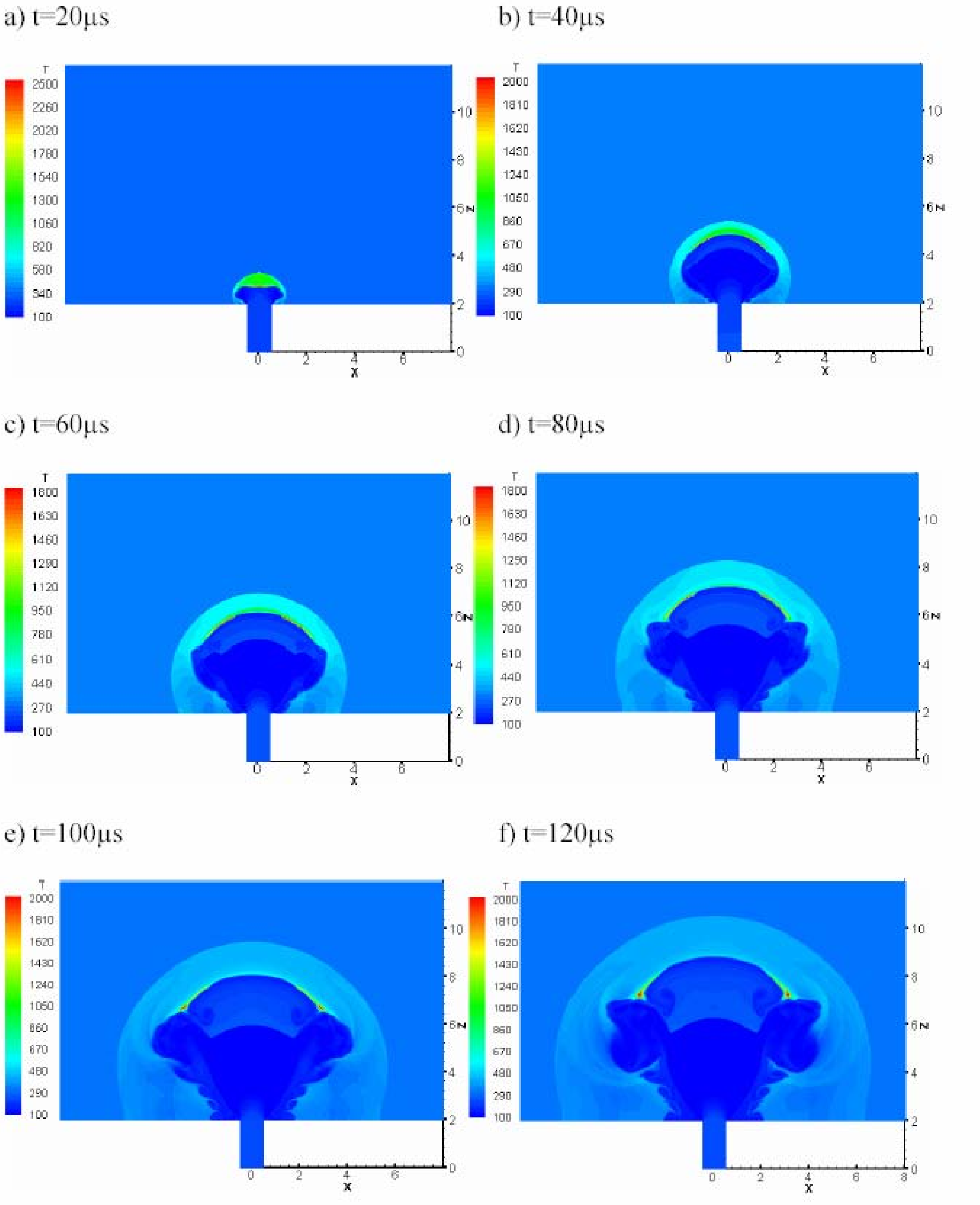
e) t=100μs

f) t=120μs

Fig. 2 Contours of Mach number at six different moments for a release pressure of 70 bar.

Release through a tube into an open space

Temperature contours


a) t=20μs

b) t=40μs

c) t=60μs

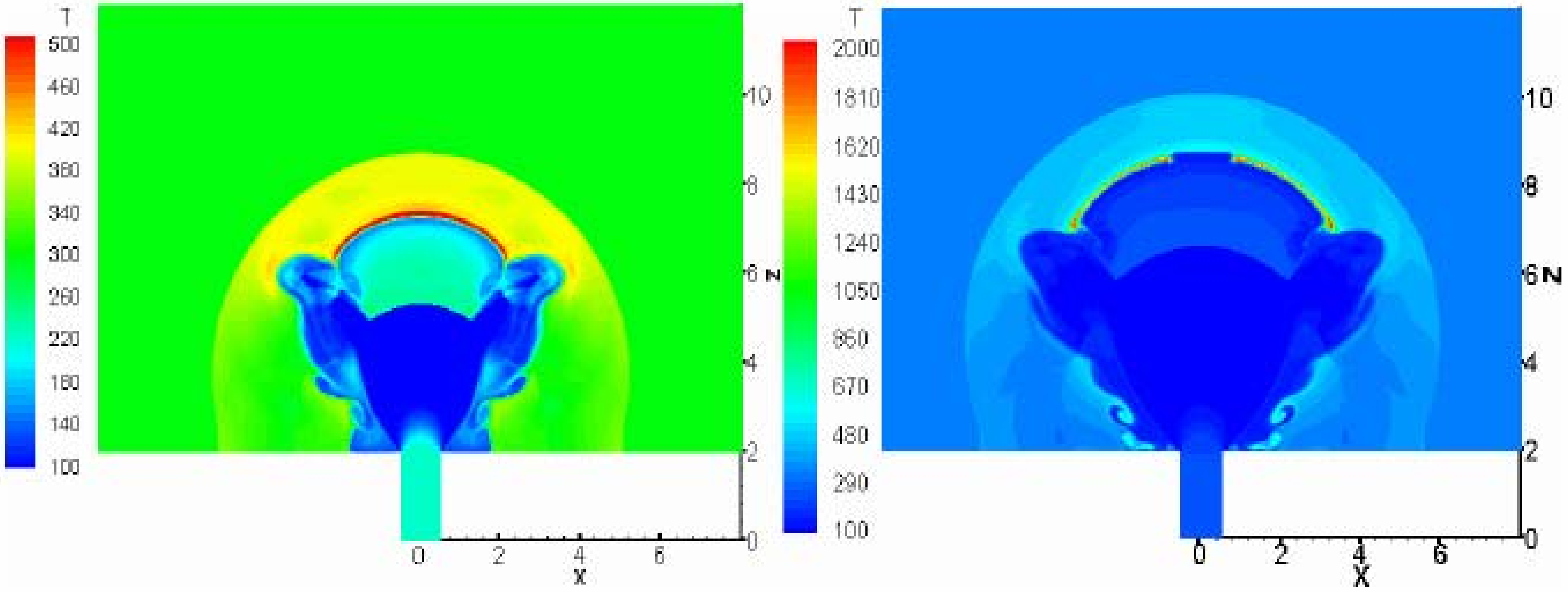
d) t=80μs

e) t=100μs

f) t=120μs

Fig. 3 Contours of temperature at six different moments for a release pressure of 70 bar.

Release through a tube into an open space – effect of release pressure



a) 40bar t=60µs

b) 100bar t=100µs

Fig. 6 Contours of temperature for two different release pressures.

Concluding Statement

The release of highly pressurised hydrogen into air could lead to spontaneous ignition depending on pressure, hole sizes, etc. Current work demonstrated the conditions leading to auto-ignition. A flame was found to be sustained over a period of 50 μs and still stable when the simulation was terminated due to limitation of computer power.

Further work is underway to establish whether this flame could be maintained, leading to a jet fire, fire ball or an explosion.

ACKNOWLEDGEMENT

- *B P XU's Post-doctoral Fellowship is funded by Kingston University.*
- *The authors would like to acknowledge EU FP6 Marie Curie programme for funding hydrogen research at Kingston University through the HYFIRE project (HYdrogen combustion in the context of FIRE and explosion safety).*
- *BP and HSL are supporting groups for HYFIRE.*