FUNDAMENTALS OF HYDROGEN IGNITION
and
HIGH PRESSURE HYDROGEN JET AUTO-IGNITION

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The 3rd European Summer School on Hydrogen Safety
Belfast, 21st July – 30th July 2008
Thanks

For Invitation
Prof. Vladimir Molkov

For taking care of management
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High Pressure Hydrogen Leak Issues

- Old story and still new: Chemical factory, refinery, etc. have hydrogen ignition caused by leaking. In many cases ignition occurs when it leaks from a tube.
- New story: Fuel cell system will use a high pressure hydrogen. By accident hydrogen may leak and auto-ignite. We need a regulation for high pressure hydrogen uses.
- We still do not know in detail in which case hydrogen auto-ignites.
High pressure hydrogen was mixed with air and detonates. The original mixture pressure was assumed to be 5-8 MPa and the pipe received a combustion pressure (most probably detonation) of 180-300 MPa.
Fundamentals of Hydrogen Ignition

The First Part of Lectures
Why the hydrogen ignition fundamentals?

Because we use the hydrogen data for low pressure case in most cases.
This part of my lecture will show you how much the low pressure chemistry does not agree with the high pressure chemistry using a detonation calculation.
Fundamentals of Hydrogen Ignition (1)
Present Status of Hydrogen Combustion Model and Its Issues

[Graph showing rate coefficients and pressure dependence]
Fundamentals of Hydrogen Ignition (2)

Numerical Analysis

- 1D compressible Euler equations
- Fuel \( \rightarrow \) hydrogen, Oxidizer \( \rightarrow \) oxygen or air
- The convective terms: 2\textsuperscript{nd} order Harten-Yee type TVD scheme
- The unsteady terms: Strang type fractional step method
- Axisymmetric flow
- Chemical reactions: Petersen & Hanson model, Koshi model
- Computational grids: decided by having 33 points in a half reaction length
- Initial pressures: 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 MPa
- Initial temperature: 298.15 K
- The computer used: NEC SX-6 (Max 8CPU) at JAXA/ISAS
Fundamentals of Hydrogen Ignition (3)
-Effects of initial pressure on detonation initiation-

<table>
<thead>
<tr>
<th>Initial pressure $P_0$[MPa]</th>
<th>Grid size [m]</th>
<th>Ignition pressure $P_i$[times]</th>
<th>Ignition temperature $T_i$[K]</th>
<th>Ignition area $A_i$ [points]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.71</td>
<td>38</td>
<td>1400</td>
<td>1000</td>
</tr>
<tr>
<td>0.2</td>
<td>0.51</td>
<td>38</td>
<td>1400</td>
<td>4500</td>
</tr>
<tr>
<td>0.5</td>
<td>0.275</td>
<td>38</td>
<td>1600</td>
<td>3000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.16</td>
<td>20</td>
<td>1400</td>
<td>9000</td>
</tr>
<tr>
<td>2.0</td>
<td>0.12</td>
<td>20</td>
<td>1400</td>
<td>9000</td>
</tr>
<tr>
<td>3.0</td>
<td>0.09</td>
<td>20</td>
<td>1400</td>
<td>9000</td>
</tr>
<tr>
<td>4.0</td>
<td>0.12</td>
<td>40</td>
<td>2000</td>
<td>1000</td>
</tr>
<tr>
<td>5.0</td>
<td>0.06</td>
<td>40</td>
<td>2000</td>
<td>3000</td>
</tr>
<tr>
<td>6.0</td>
<td>0.05</td>
<td>40</td>
<td>2000</td>
<td>4500</td>
</tr>
<tr>
<td>7.0</td>
<td>0.044</td>
<td>40</td>
<td>2000</td>
<td>3000</td>
</tr>
<tr>
<td>8.0</td>
<td>0.038</td>
<td>40</td>
<td>2000</td>
<td>1000</td>
</tr>
<tr>
<td>9.0</td>
<td>0.032</td>
<td>40</td>
<td>2000</td>
<td>1000</td>
</tr>
<tr>
<td>10.0</td>
<td>0.03</td>
<td>40</td>
<td>2000</td>
<td>3000</td>
</tr>
</tbody>
</table>

- Ignition pressure is very high for the case of the initial pressures higher than 5 MPa probably due to near supercritical conditions.

- The cases of the initial pressures; 1.0, 2.0, and 3.0 MPa, need less ignition pressure due to high sensitivity for such cases.
Fundamentals of Hydrogen Ignition (4)
-Effects of initial pressure on detonation initiation-

- Detonation velocity profiles for the cases of the initial pressures of 1.0, 2.0, 3.0 MPa. 1D calculation of detonation gives typically such velocity profile.
The “present” includes an expansion region and damping region of velocity for average calculation and “present (modified) does not an expansion region.
Fundamentals of Hydrogen Ignition (6)
-High pressure chemical reaction model (1)-

• Ignition delay time using CHEMKIN 4.1: in these results both model gives good results and it is difficult to see the difference in the results.

Petersen & Hanson model

Koshi model
Koshi model gives shorter delay time than P-H model at higher temperature.
Fundamentals of Hydrogen Ignition (8)
-High pressure chemical reaction model (3)-

- P-H model shows H+O2+M->HO2+M sensitivity is much larger than that of Koshi model. Koshi model produces more radicals than P-H model.
Koshi model produces more radicals than P-H model.
Koshi model provides a stable calculation, while P-H model does not.

### Fundamentals of Hydrogen Ignition (10) - High pressure chemical reaction model (5) -

<table>
<thead>
<tr>
<th>Reaction model</th>
<th>Grid size [ m]</th>
<th>Ignition pressure $P_i$ [times]</th>
<th>Ignition temperature $T_i$ [K]</th>
<th>Ignition area $I_a$ [points]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-H model</td>
<td>0.16</td>
<td>20</td>
<td>1400</td>
<td>9000</td>
</tr>
<tr>
<td>Koshi model</td>
<td>0.16</td>
<td>50</td>
<td>2000</td>
<td>9000</td>
</tr>
</tbody>
</table>

- Koshi model provides a stable calculation, while P-H model does not.
Koshi model gives a stable detonation velocity profiles, while P-H model does less stable ones.
Fundamentals of Hydrogen Ignition (12)

Summary

• The pressure dependent chemical reaction model is important to solve the high pressure hydrogen auto-ignition problems.

• This part shows that we needs such pressure dependent reaction mechanism provides the better explanation of experimental data at high pressure atmosphere.
High Pressure Hydrogen Jet Auto-Ignition

The Second Part of Lectures
Background

Experimental findings

• Wolanski & Wojicicki (1973): High pressure H2 jet auto-ignition was found.
• Hayashi et al. (2004): High pressure He jet hitting a wall.
• Bazhenova et al. (2005): Similar High Pressure H2 jet from a hole.
• Dryer et al. (2006): High pressure H2 jet auto-ignition from a tube.
• Mogi et al. (2006): High pressure H2 jet auto-ignition from a hole.
• Pinto et al. (2007) & Aizawa et al. (2007): High pressure H2 jet auto-ignition from a hole and a tube.
• Mogi et al. (2008): High pressure H2 jet auto-ignition from a tube.

Numerical findings

• Hayashi et al. (2004): High pressure He jet hitting a wall.
• Liu et al. (2005): High pressure H2 jet leak from a hole.
• Yamada et al. (2008): High pressure H2 jet leak from a tube.
• Xu et al. (2008): High pressure H2 jet released from a tube.
High Pressure Hydrogen jetted to an obstacle
High Pressure Hydrogen jetted to an obstacle

**Experimental set-up**

<table>
<thead>
<tr>
<th>Reservoir tank pressure [MPa]</th>
<th>Reservoir tank temperature [K]</th>
<th>Distance between the nozzle exit and the plate [mm]</th>
<th>Nozzle exit initial pressure [MPa]</th>
<th>Nozzle exit initial temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>300</td>
<td>10, 30, 50</td>
<td>0.1 (air)</td>
<td>300 [K]</td>
</tr>
</tbody>
</table>
High Pressure Hydrogen jetted to an obstacle(2)

Numerical Analysis

- 2D compressible Euler equations
- Fuel: hydrogen, Oxidizer: air
- The convective terms: Harten-Yee type TVD scheme
- The unsteady terms: Strang type fractional step method
- Axisymmetric flow
- No chemical reactions due to a use of He as a fuel
- No viscous and thermal conductivity effects
- Specific heats are a function of temperature.
- No bulk viscosity, no Soret effects, no Dufour effects, no pressure gradient diffusion, no gravity effects.
- The boundary condition at the wall is adiabatic and slip.
The slight difference comes from He (experiments) and H2 (computations).

Temperature and pressure become constant being longer between the nozzle exit and the plate surface.
High Pressure Hydrogen jetted to an obstacle (4)
-Temperature and pressure profiles between the nozzle exit and the plate surface (Reservoir pressure at 10 MPa)-

- The distance between the nozzle exit and the plate surface: 30 mm
- The hole diameter: 1 mm
- The max temp.
- Jet flows
High Pressure Hydrogen jetted to an obstacle

-Temperature and pressure profiles at the center axis of the jet between the nozzle exit and the plate surface (Reservoir pressure at 10MPa)-

• The base shock is somewhat strong (0.38 MPa), but the temperature there is about 303 K.
High Pressure Hydrogen jetted to an obstacle(6)

- Temperature and pressure profiles between the nozzle exit and the plate surface (Reservoir pressure at 100MPa)

- The temperature at the separation bulb is 386 K not to ignite H2.
High Pressure Hydrogen jetted to an obstacle

-Temperature and pressure profiles on the plate (Reservoir pressure at 100MPa)-

- Temperature profiles do not change much to reservoir pressure.
- But pressure profiles do change much especially for the short distance between the nozzle exit and the plate.
High Pressure Hydrogen jetted to an obstacle (8)

Max temperature profiles in the jet (Reservoir pressures from 5 to 100 MPa)

Max temperature profiles increase as the reservoir pressure increase.
But temperature is still lower than ignition temperature.
Summary

• The numerical temperature agrees well with the experimental one on the surface of the flat plate.

• The temperature profiles on the flat plate for the case of the reservoir pressure of 100 MPa are within 350 K, which does not give the ignition to hydrogen.

• Just only for the case of 10 mm distance between the nozzle exit and the flat plate surface, the maximum temperature shows a linear increase of temperature to the increase of reservoir pressure.
High Pressure Hydrogen Leak from a small Hole
High Pressure Hydrogen Leak from a small Hole(1)

Numerical Analysis

- 2D axisymmetric Euler equations with the detailed chemical reaction mechanism.
- Hydrogen reaction mechanism of 9 species and 18 reactions.
- The convection terms are integrated by Harten-Yee type non-MUSCL TVD scheme.
- The time discretization is performed by Strang-type fractional step method.
- Chemical reactions are treated by a point implicit way to avoid stiffness.
High Pressure Hydrogen Leak from a small Hole(2)

Numerical Conditions

- Reservoir tank pressures are 10, 40, 70 MPa.
- Reservoir tank temperature is 300 K.
- The computational domain is rectangular.
- The left boundary condition is a solid wall and other boundaries are free stream conditions.
- A small hole of 1, 3, 5 mm diameter is located at the center of the left wall.
- The H2 jet is choked at the hole and the Mach number there is unity.
- The initial ambient air is at 0.1 MPa, 300 K, and at rest.
- The uniform grid size of $dx=dy=10$ or 20 μm.
The max temperature is 450 K at the jet front. No OH molecules appear in this case.
High Pressure Hydrogen Leak from a small Hole(4)
-The case of the reservoir pressure of 40 MPa-

Temperature profiles

The time is at 2 s.

- The max temperature is 1750 K at the contact surface (t=10 s).

The time is at 10 s.
High Pressure Hydrogen Leak from a small Hole(5)
- The case of the reservoir pressure of 40 MPa -

• A large number of OH molecules are found at the contact surface region.

*OH molecule profiles*  
The time is at 10 s.
High Pressure Hydrogen Leak from a small Hole(6) -The case of the reservoir pressure of 40 MPa-

Temperature profiles

The time is at 100 s.

• When the jet propagates further, temperature goes down to extinguish the local flame.
High Pressure Hydrogen Leak from a small Hole(7) -The case of the reservoir pressure of 70 MPa-

Temperature profiles

The time is at 10 s.

The time is at 100 s.

- The over-expansion situation gives such quenching phenomena to the jet flame.
High Pressure Hydrogen Leak from a small Hole(8)
-The case of the reservoir pressure of 70 MPa-

- H2O stays between hydrogen and air and propagates together with the jet. H2O prevents H2 and air mixing.

H2O mass fraction profiles

The time is at 60 s.

H2O and H2 mass fraction profiles

The time is at 60 s.

Color: H2
Black: H2O
Summary

• For 40 and 70 MPa cases the local combustion occurs at the early stage of H2 jet propagation. The high temperature region behind the leading shock wave provides such local ignition.

• In all cases the max temperature decreases below 1000 K at t=100 s. H2O prevents the well mixing of H2 and air.

• The local combustion does not stay and moves together with the jet not to keep such ignition source.
High Pressure Hydrogen Leak from a Tube
High Pressure Hydrogen Leak from a Tube(1)

Experimental set-up

Small shock tube system

<table>
<thead>
<tr>
<th>High pressure section (N2)</th>
<th>Low Pressure section (H2)</th>
<th>Hydrogen jet pressure [MPa]</th>
<th>Tube 1</th>
<th>Tube 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_H$ [MPa], $T_H$ [K]</td>
<td>$P_L$ [MPa], $T_L$ [K]</td>
<td></td>
<td>$d_i$</td>
<td>$d_i$</td>
</tr>
<tr>
<td>8 , 300</td>
<td>0.9, 300</td>
<td>3.8, 6.8</td>
<td>$L=48$, 71, 113</td>
<td>$L=50$, 100, 180</td>
</tr>
</tbody>
</table>

Dump tank pressure= 0.1 MPa
High Pressure Hydrogen Leak from a Tube (2)

<table>
<thead>
<tr>
<th>Tube 1</th>
<th>Tube 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>di inner diameter [mm]</td>
<td>di inner diameter [mm]</td>
</tr>
<tr>
<td>L tube length [mm]</td>
<td>L tube length [mm]</td>
</tr>
<tr>
<td>d_i=4.8, L=48, 71, 113</td>
<td>di=10.0, L=50, 100, 180</td>
</tr>
</tbody>
</table>

Diaphragm: 50 mm thickness

Tube configuration

H₂

Diagram showing the configuration of high pressure hydrogen leak from a tube with dimensions and diaphragm thickness.
Numerical Analysis

- 2D axisymmetric Euler equations with the detailed chemical reaction mechanism.
- Hydrogen reaction mechanism of 9 species and 18 reactions.
- The convection terms are integrated by Harten-Yee type non-MUSCL TVD scheme.
- The time discretization is performed by Strang-type fractional step method.
- Chemical reactions are treated by a point implicit way to avoid stiffness

- Petersen & Hanson model (High pressure model)
High Pressure Hydrogen Leak from a Tube (4)

Numerical Conditions

• Reservoir tank pressures are 3.8, 6.8 MPa.
• Reservoir tank temperature is 300 K.
• The computational domain is rectangular.
• The left boundary condition is a solid wall and other boundaries are free stream conditions.
• A small hole of 10 mm diameter is located at the center of the left wall or tube inner diameter of 10 mm.
• The H2 jet is choked at the hole and the Mach number there is unity.
• The initial ambient air is at 0.1 MPa, 300 K, and at rest.
• The uniform grid size of dx=dy= 20 μm.
High Pressure Hydrogen Leak from a Tube (5)

Numerical Conditions

- Reservoir tank pressures are 10, 40, 70 MPa.
- Reservoir tank temperature is 300 K.
- The computational domain is rectangular.
- The left boundary condition is a solid wall and other boundaries are free stream conditions.
- A small hole of 1, 3, 5 mm diameter is located at the center of the left wall.
- The H2 jet is choked at the hole and the Mach number there is unity.
- The initial ambient air is at 0.1 MPa, 300 K, and at rest.
- The uniform grid size of $dx=dy=10$ or 20 μm.
High Pressure Hydrogen Leak from a Tube (6)
-The case of the small hole-

High speed movie

No ignition case

(a) 40 sec
(b) 72 sec
(c) 168 sec
(d) 248 sec
(e) 288 sec
(f) 328 sec

• The hole diameter is 10 mm. The hydrogen pressure is 2.3 MPa.
High Pressure Hydrogen Leak from a Tube (7)
-The case of the tube-

High speed movie

Ignition case

(a) 20 s
(b) 84 s
(c) 148 s
(d) 196 s
(e) 276 s
(f) 328 s

- The hole diameter is 4.8 mm. The tube length is 116 mm. The hydrogen pressure is 6.8 MPa. -
High Pressure Hydrogen Leak from a Tube (8)
-Comparison between experiments and numerical analysis-

- H2 temperature is 671 K. H2 pressure is 3.8 MPa. Calculation does not include chemical reactions. The computation explains the experimental results well.
High Pressure Hydrogen Leak from a Tube (9)
-OH emission pictures for the tube case-

Auto-ignition

(a) 125 s

(b) 150 s

(c) 175 s

(d) 200 s

- The tube diameter is 4.8 mm. The tube length is 115 mm. The flame (lifted flame) stays at the tube exit.
High Pressure Hydrogen Leak from a Tube (10)

-Comparison between the jet from a hole and that from a tube-

The leading shock decays quickly for both a hole case and a tube case.

(a) leading shock position  (b) leading shock velocity

The leading shock decays quickly for both a hole case and a tube case.
### High Pressure Hydrogen Leak from a Tube (11)

- Auto-ignition conditions for tube cases -

<table>
<thead>
<tr>
<th>Hydrogen pressure [MPa]</th>
<th>Tube diameter [mm]</th>
<th>Tube length [mm]</th>
<th>Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>4.8</td>
<td>71</td>
<td>no</td>
</tr>
<tr>
<td>3.8</td>
<td>4.8</td>
<td>48</td>
<td>no</td>
</tr>
<tr>
<td>3.8</td>
<td>4.8</td>
<td>71</td>
<td>yes</td>
</tr>
<tr>
<td>3.8</td>
<td>4.8</td>
<td>113</td>
<td>yes</td>
</tr>
<tr>
<td>6.8</td>
<td>4.8</td>
<td>48</td>
<td>no</td>
</tr>
<tr>
<td>6.8</td>
<td>4.8</td>
<td>71</td>
<td>yes</td>
</tr>
<tr>
<td>6.8</td>
<td>4.8</td>
<td>113</td>
<td>yes</td>
</tr>
<tr>
<td>6.8</td>
<td>10.0</td>
<td>118</td>
<td>no</td>
</tr>
<tr>
<td>6.8</td>
<td>10.0</td>
<td>180</td>
<td>yes</td>
</tr>
</tbody>
</table>

- The larger diameter tube and the higher hydrogen pressure conditions give hydrogen auto-ignition.
High Pressure Hydrogen Leak from a Tube (12)
-Auto-ignition conditions for tube cases-

- The longer tube length is also important factor for auto-ignition.
Hydrogen jet coming out of a hole does not auto-ignite at the reservoir pressures up to 70 MPa for any size of hole diameter.

Hydrogen jet coming out of a tube has a different story: hydrogen auto-ignites depending on the tube diameter, tube length, and reservoir pressure.

The hydrogen auto-ignites in the tube too.
Whole Summary

• Hydrogen leak from a hole may not auto-ignite for any reservoir pressure cases unless some special condition is set.

• However hydrogen leak will auto-ignite when it comes from a tube depending on tube diameter, tube length, and reservoir pressure.

• As far as we know, hydrogen auto-ignites inside of the tube if the tube has an oxidizer.