Safety of Hydrogen

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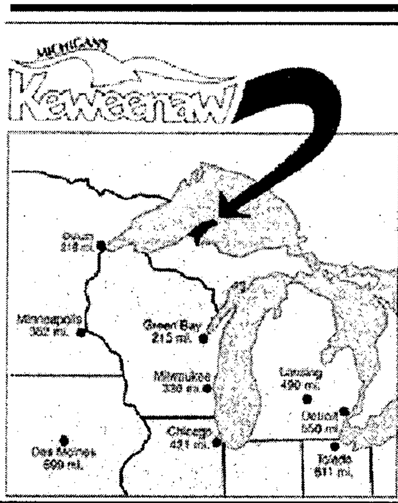
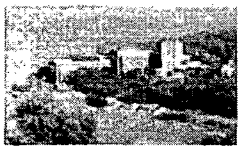
MichiganTech

The Upper Peninsula of Michigan



The Keweenaw ("portage" in Objibwa Indian) peninsula is a peninsula jutting out into Lake Superior.

Michigan Technological University



Total Enrollment:	6,536
Undergraduates:	5,705
Grad. Students:	831
Research Expenditures:	$28 million
College of Engineering:	3,705 (57%)

Chemical Engineering:
- 300 undergraduates (12th rank)
- 15 Faculty
- 34 Graduate Students
- $1 million research expenditures
- "Industrially relevant students"

Winter Carnival

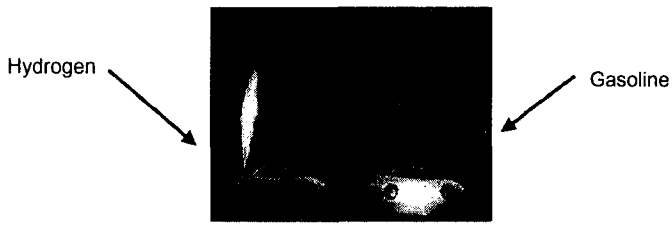
Outline of Talk

- Definitions
- Flammability data for hydrogen
- Hazards of hydrogen
- Risks of hydrogen
- Prevention of hydrogen fires / explosions

Questions of Interest for Hydrogen

If we use hydrogen as a fuel, what are:

1. **The hazards of hydrogen? Is hydrogen more hazardous than existing fuels?**
2. **The risks of using hydrogen? Does hydrogen use increase the risk over existing fuels?**



Definitions

Accident:	**The occurrence of a sequence of events that produce unintended injury, death or property damage.**
Safety:	**Strategy of accident prevention.**
Loss prevention:	**Prevention of injury to people, damage to environment, loss of equipment, inventory or production.**
Hazard:	**A chemical or physical condition that has the potential to cause an accident.**
Risk:	**Probability and consequence of an accident.**

Safety is not very well defined – hazard and risk are better concepts to use.

Hazard

A *chemical or physical condition* that has the potential to cause an accident.

If a chemical is present in a chemical plant, that chemical brings hazards into the plant. These hazards could include:

- **Flammability**
- **Toxicity**
- **Reactivity**
- **Explosivity**
- **Others**

Hazard

If a chemical is present, the hazards are always present.

An accident occurs when we lose control of the energy or mass of the chemical. For instance, an accident results if the chemical leaks out of a process.

However, if you use the chemical properly ("safely") an accident will not result.

Major hazard of gasoline and hydrogen: flammability

Risk

Probability and consequence of an accident,
i.e. likelihood of an accident and the severity of the accident.

Example: Seatbelt use is based on a reduction in the consequence of an accident, rather than the probability.

Physical Properties

1. **Physical state (solid, liquid, gas) under usage conditions.**
2. **Vapor pressure (liquid)**
3. **Flash point temperature (liquid)**
4. **Auto-ignition temperature (liquid)**
5. **Flammability zone, including flammability limits in air, limits in pure oxygen, limiting oxygen concentration**
6. **Ignition energy**
7. **Heat of combustion**
8. **Maximum pressure during combustion**
9. **Deflagration index**

Note: Toxic hazards not considered.

Physical Properties

Hazard: Based on all of the physical properties

Physical state (solid, liquid, gas) under usage conditions.
Vapor pressure (liquid)
Flash point temperature (liquid)
Auto-ignition temperature (liquid)
Flammability zone, including flammability limits in air, limits in pure oxygen, limiting oxygen concentration
Ignition energy
Heat of combustion
Maximum pressure during combustion
Deflagration index

Physical Properties

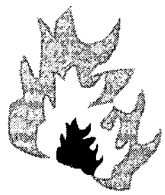
Risk is based on probability and consequence. This is highly dependent on the particular hardware design and application. However, a number of properties are related to risk and these can be used to make some initial estimates of risk.

Probability: (probability of fire / explosion)
- **Physical state**
- **Vapor pressure**
- **Flash point temperature**
- **Auto-ignition temperature**
- **Flammability zone size**
- **Ignition energy**

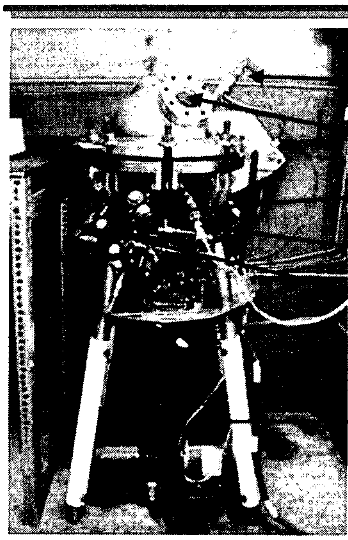
Consequence: (What happens after it ignites)
- **Heat of combustion**
- **Max. pressure during combustion**
- **Deflagration index**

Combustion Characterization

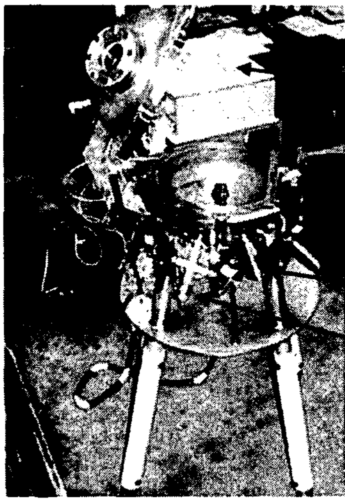
Question: How do we characterize combustion and what experimental apparatus is used to achieve this?



Experimental Apparatus – Flammability Limits



Experimental Apparatus



Not visible: gas mixer

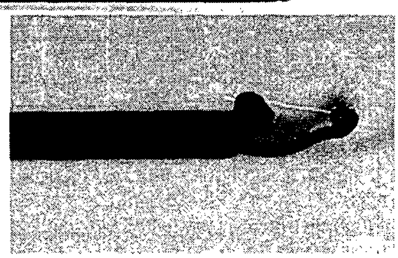
Control / computer interface

Pressure transducer for gas mixing

Pressure transducer to follow combustion pressure

Rupture disk

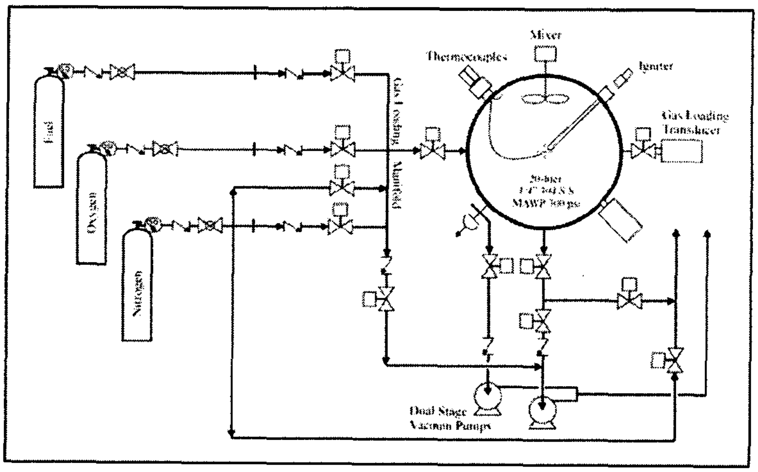
Igniter – 10 cm 40 Gauge



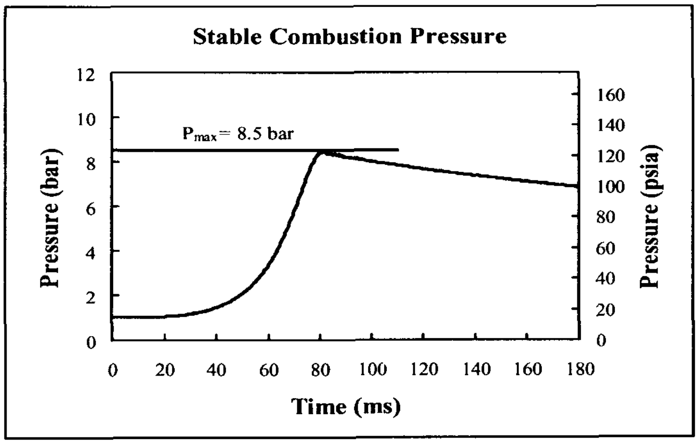
Experimental Apparatus

- 20 Liter sphere
- 1 cm fuse wire igniter (10 J)
- Gases mixed from pure components
- Computer control and data acquisition
- High precision pressure transducer to mix gases
- High speed data acquisition on pressure vs. time.

Experimental Apparatus

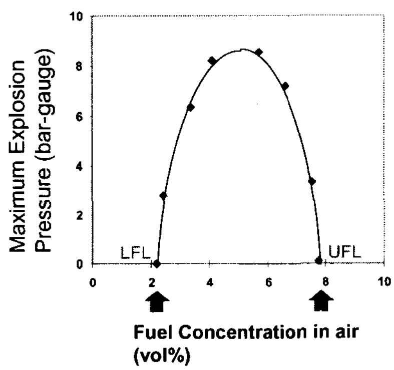


P_{max} Determination



Experimental Determination - LFL, UFL

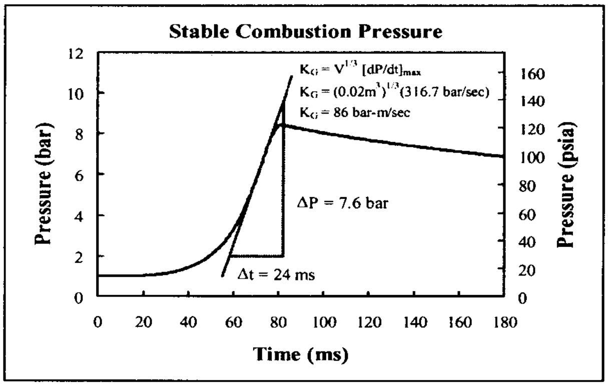
Run experiment at different fuel compositions with air:



Need a criteria to define limit - use 7% abs. pressure increase. Other criteria are used - with different results!

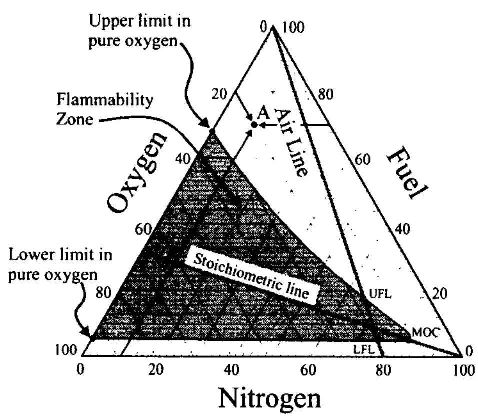
Flammability limits are an empirical artifact of experiment!

Deflagration Index, K_G



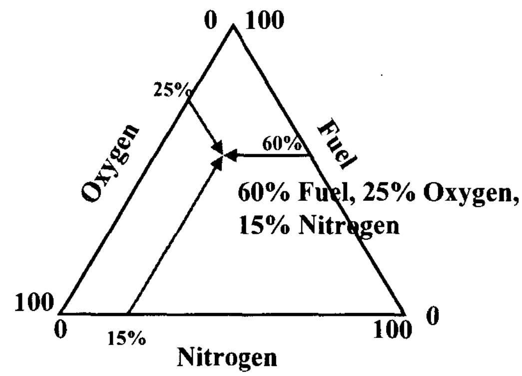
The higher the value of K_G, the more robust the explosion!

Flammability Diagram



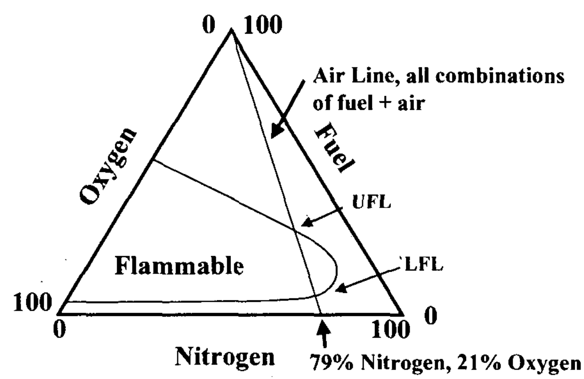
Flammability Diagram - 1

(1) Fuel + (z) Oxygen ---> Products



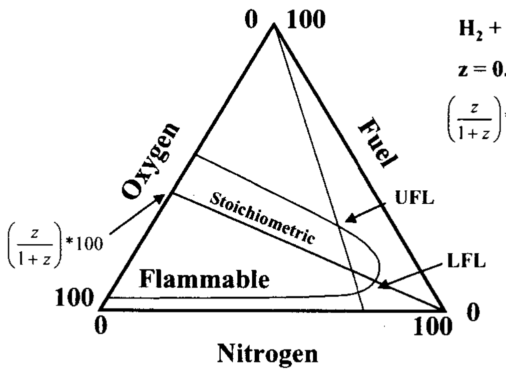
Flammability Diagram - 2

(1) Fuel + (z) Oxygen ---> Products



Flammability Diagram - 3

(1) Fuel + (z) Oxygen ---> Products



$H_2 + 1/2\ O_2 \dashrightarrow H_2O$

$z = 0.5$

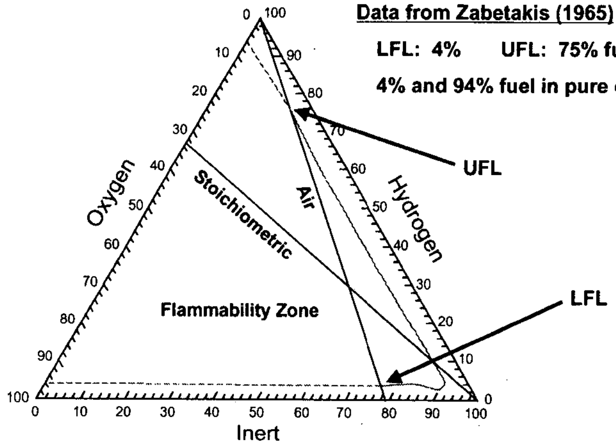
$$\left(\frac{z}{1+z}\right)*100 = \left(\frac{0.5}{1.5}\right)*100 = 33.3\%$$

Flammability Data for Hydrogen

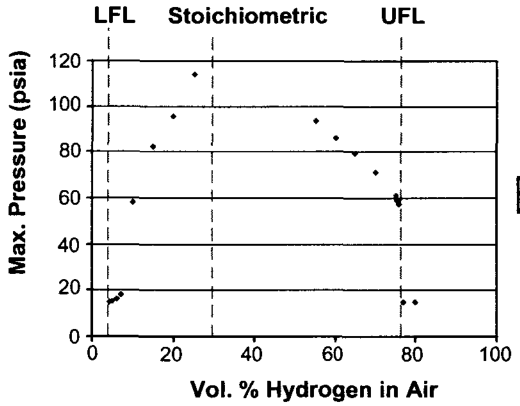
Data from Zabetakis (1965)

LFL: 4% UFL: 75% fuel in air

4% and 94% fuel in pure oxygen



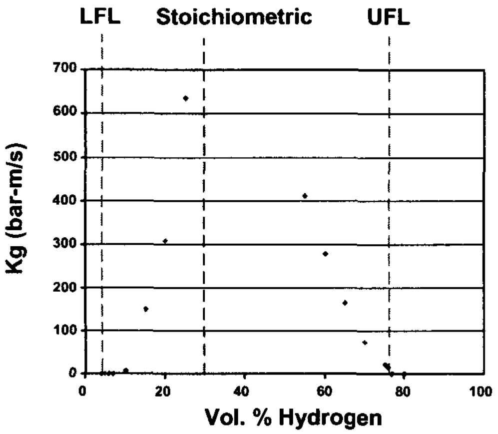
MTU Flammability Data for Hydrogen



Max. pressure =
114 psia
7.6 bar
(Literature = 6.9 bar)

Data not complete!

Flammability Data for Hydrogen



Kg = 636 bar-m/s
(Literature = 660)

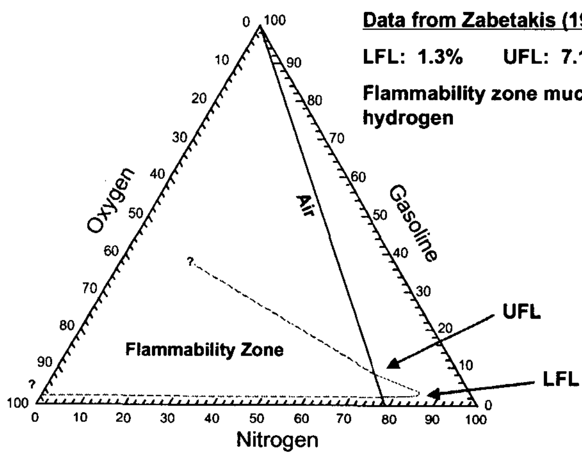
Data not complete!

Flammability Data for Hydrogen

Based on combustion in air

Physical State:	**Gas**
LFL:	**4%**
UFL:	**75%**
Limiting Oxygen Concentration:	**5%**
Auto-Ignition Temperature:	**572 °C**
Min. Ignition Energy:	**0.018 mJ**
Heat of Combustion:	**-285.8 kJ/mol**
Max. Pressure during Combustion:	**7 bar g**
Deflagration Index (Kg):	**636+ bar-m/s**

Flammability Data for Gasoline



Data from Zabetakis (1965)

LFL: 1.3% UFL: 7.1% fuel in air

Flammability zone much smaller than hydrogen

Flammability Data for Gasoline

Based on combustion in air

Physical State:	**Liquid**
LFL:	**1.3%**
UFL:	**7.1%**
Flash Point Temperature:	**-43 °C**
Limiting Oxygen Concentration:	**12%**
Auto-Ignition Temperature:	**260 °C**
Min. Ignition Energy:	**0.25 mJ (est.)**
Heat of Combustion:	**-5512 kJ/mol (octane)**
Max. Pressure during Combustion:	**8 bar g (est.)**
Deflagration Index (Kg):	**100 bar-m/s (est.)**

Comparison of Hazards

Based on combustion in air.

Property	Hydrogen	Gasoline
Physical State:	?	?
Flammability Zone Size:	*	
Auto-Ignition Temperature:		*
Min. Ignition Energy:	*	
Heat of Combustion:		*
Max. Pressure during Combustion:	-	-
Deflagration Index:	*	
TOTALS:	3	2

Comparison of Probability

Based on combustion in air.

Property	Hydrogen	Gasoline
Physical State:	*	
Flammability Zone Size:	*	
Auto-Ignition Temperature:		*
Min. Ignition Energy:	*	
TOTALS:	3	1

Comparison of Consequence

Based on combustion in air.

Property	Hydrogen	Gasoline
Heat of Combustion:		*
Max. Pressure during Combustion:	-	-
Deflagration Index:	*	
TOTALS:	1	1

For gasoline, the likely consequence is a fire, rather than an explosion.
For hydrogen, the likely consequences are fire and/or explosion.

Summary of Hazards / Risks

Based on combustion in air.

	Hydrogen	Gasoline
Hazards:	3	2
Probability:	3	1
Consequences:	1	1

Conclusion: Hydrogen poses increased hazard and increased risk over gasoline.

Note: A more detail risk analysis would require specifics on the pressure / temperature of storage and the specific hardware used to extract the energy. The hazards are mostly unchanged with application.

Comparison of Hydrogen and Gasoline

Source: Prof. Ralph Swain, University of Florida

Problem: This test uses two different failure scenarios. For hydrogen, the failure was through the normal relief system. For gasoline, the failure was due to a leak in the gas tank.

This test considers only the consequences of a release, not the probability – the risk for these two materials is not heavily dependent on the consequences but more on the probability. Furthermore, an ignition source was provided, so fire was the only possible outcome.

Comparison of Hydrogen and Gasoline

The hazards are mostly unchanged with application (although a new hazard might be introduced if the hydrogen is stored at high pressure).

The risks cannot be compared in this test since the failure mechanisms are very different.

A proper quantitative risk analysis requires:

1. Identification and tabulation of all incidents without regard to importance or initiating event.
2. Consequence estimation for all incidents and identification of all incident outcomes, i.e. jet fire, vapor explosion, pool fire, fireball, etc.
3. Likelihood estimation for all incidents.

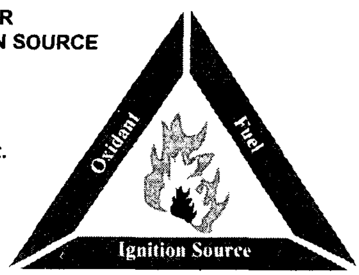
CCPS, *Guidelines for Quantitative Risk Analysis*, 2nd ed., 2000.

Prevention of Hydrogen Fires / Explosions

FIRE TRIANGLE

FUEL
OXIDIZER
IGNITION SOURCE

Fire will occur when all three legs of the triangle are present.

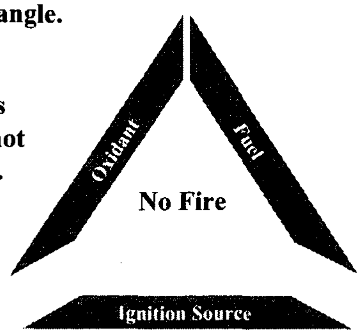


Oxidant may not be oxygen, i.e. chlorine.

Application of the Fire Triangle

Fires and explosions can be prevented by removing any single leg from the fire triangle.

Problem: Ignition sources are so plentiful that it is not a reliable control method.



Robust Control: Prevent existence of flammable mixtures.

Inherently Safer Design

Inherently safer designs

permanently and inseparably

reduce or eliminate process hazards

that must be contained and controlled to avoid accidents.

Inherently Safer Design

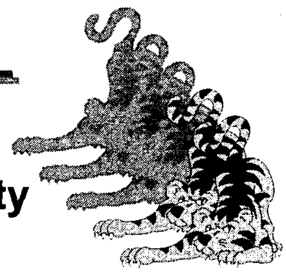
"The essence of the inherently safer approach to plant design is the avoidance of hazards rather than their control by added-on protective equipment."

T. A. Kletz, *Plant Design for Safety: A User-Friendly Approach* (NY: Hemisphere, 1991)

Inherently Safer Design Strategies

- **MINIMIZE**
- **SUBSTITUTE**
- **MODERATE**
- **SIMPLIFY**

Minimize



= Reduce hazardous material/energy quantity

- Reduces energy
- Reduces potential accident severity

Substitute

= Replace with a less hazardous material

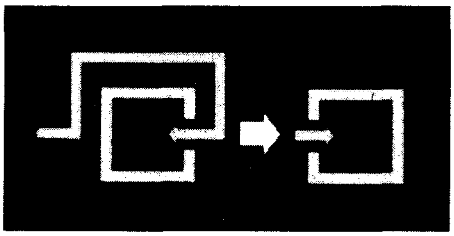
- Reduces/eliminates available chemical energy
- Reduces/eliminates potential accident severity

Moderate

- **Use under less hazardous conditions**
  - Available energy may be the same, but
  - Passively reduces potential loss event impacts
  - For chemical processes, this usually means lower temperatures, pressures, concentrations, etc.

Simplify

- **Reduce unnecessary complexity**
  - Reduces likelihood of an accident



Safe Usage of Hydrogen

- Hydrogen has been used safely for many years by chemical companies, gas suppliers, and NASA. However, it has not been used at the consumer level.
- Existing National Fire Protection Agency documents:
  1. 50A: Standard for Gaseous Hydrogen Systems at Consumer Sites
  2. 50B: Standard for Liquefied Hydrogen Systems at Consumer Sites
  3. 52: Compressed Natural Gas (CNG) Vehicular Fuel Systems Code.

A lot of technology already exists to use hydrogen safely.

Conclusions

- Hydrogen represents increased hazard and risk over gasoline fuels. However, a complete quantitative risk analysis, based on the actual hardware, has not been completed.
- Hydrogen hazards and risks are due to: increased size of flammability zone, very small min. ignition energy and very large deflagration index.
- Hydrogen can be handled safely, but to date this has been done mostly by industrial facilities, not consumers.

Recommendations

1. **Need significantly more data on hydrogen combustion:**
   - **Detailed pressure vs. time data.**
   - **Over a wide range of mixtures with hydrogen, oxygen, nitrogen.**
   - ***Effects of water, other inert gases.***
   - **Effect of increased pressure, temperature.**
2. **Need a complete quantitative risk analysis for hydrogen use in consumer vehicles, specific to the particular vehicle design.**

Thank You! Questions?