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Properties of laminar premixed hydrogen-added ammonia/air flames

J.H. Lee, J.H. Park and O.C. Kwon*
School of Mechanical Engineering
Sungkyunkwan University
Suwon, Kyunggi-do, Korea

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Sungkyunkwan University & ME

- **Sungkyunkwan Univesity:**
  - The oldest university in Korea, founded in 1398.
  - One of the leading universities, among the top 5 in Korea.
  - Private university strongly supported by Samsung.
- **School of Mechanical Engineering:**
  - Established in 1967.
  - Natural sciences campus.
  - Faculties: 32.
  - Undergraduate students: 727.
  - Graduate students: 135.

Global warming

CO_2 emissions in Korea

- **Korea Metrological Administration report (July 2007): the average amount of CO_2 at the national air monitoring station in Anmyeondo, Chungcheong Province, in 2006 was 388.9 ppm:**
  - Korea's CO_2 level has been on the rise for seven straight years since 1999 when the amount was 370.2 ppm.
  - The U.S. Center for Global Development (2007): Korea ranked 10th among the world's greenhouse gas emitters by emitting 185 million tons of such gases annually.
  - The average temperature in Korea has risen by 1.5 degrees over the last 100 years.

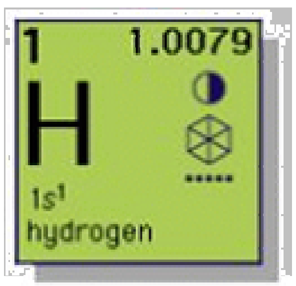
- **The Kyoto Protocol in 1997:**
  - Under the second phase of the Protocol, Korea may be required to reduce greenhouse gas emissions between 2013 and 2017.
  - In order to reduce 5% of greenhouse gas emissions in 1995, the estimated cost is 8 billion US dollars.

Hydrogen (H_2)

Clean
(Only NOx)

Energetic
(120 MJ/kg)

Abundant
(Renewable)



Hydrogen Fuel

Wide flammable limit

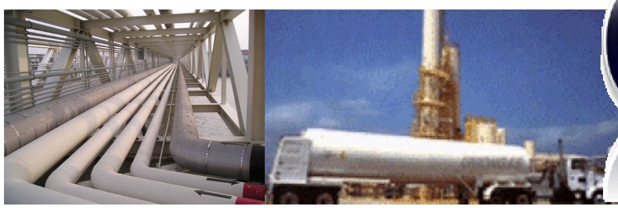
Low ignition energy

Fast burning velocity

High specific heat

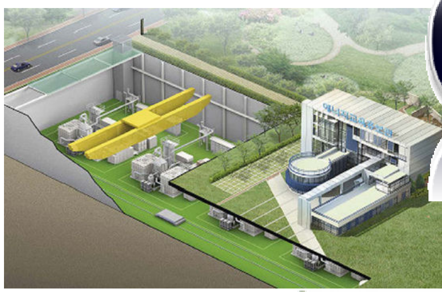
Hydrogen (H_2)

Mass production



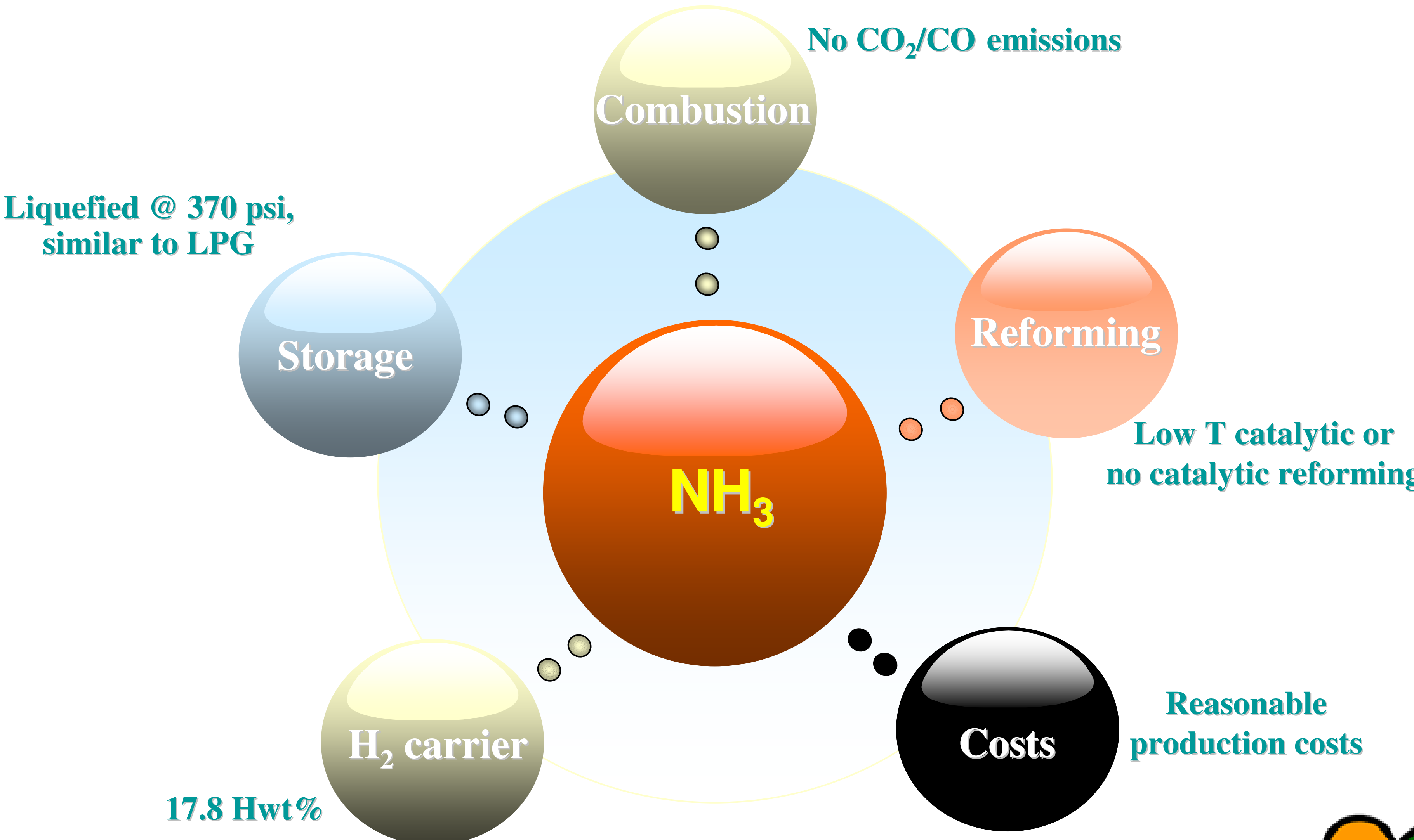
Difficulties of transport/storage
Pipelines: infrastructure needed

On-site production



No transport problem if hydrocarbons used
But CO_2/CO emitted

Ammonia (NH_3)



NH_3
Combustion
No CO_2/CO emissions
Reforming
Low T catalytic or
no catalytic reforming
Costs
Reasonable
production costs
H_2 carrier
17.8 Hwt%
Storage
Liquefied @ 370 psi,
similar to LPG

Ammonia in Korea

No earlier works for use of ammonia as a fuel

- Ammonia has been used for various fields during the last 50 years in Korea:
  - Fertilizers, refrigerants, catalysts and process chemicals.
  - Safety issues associated with handling of ammonia resolved.
  - Related regulations: industrial safety and health regulations and high pressure gas safety regulations.

- Ammonia is cheaper than other fuels; however, 100% imported due to low demand in Korea.

SWOT of use of ammonia as a fuel in Korea

Strengths

- CO/CO_2 free
- High hydrogen density: transport and storage
- Established infrastructure

Weaknesses

- Public concern over toxicity
- 100% imported
- No earlier works for ammonia as a fuel

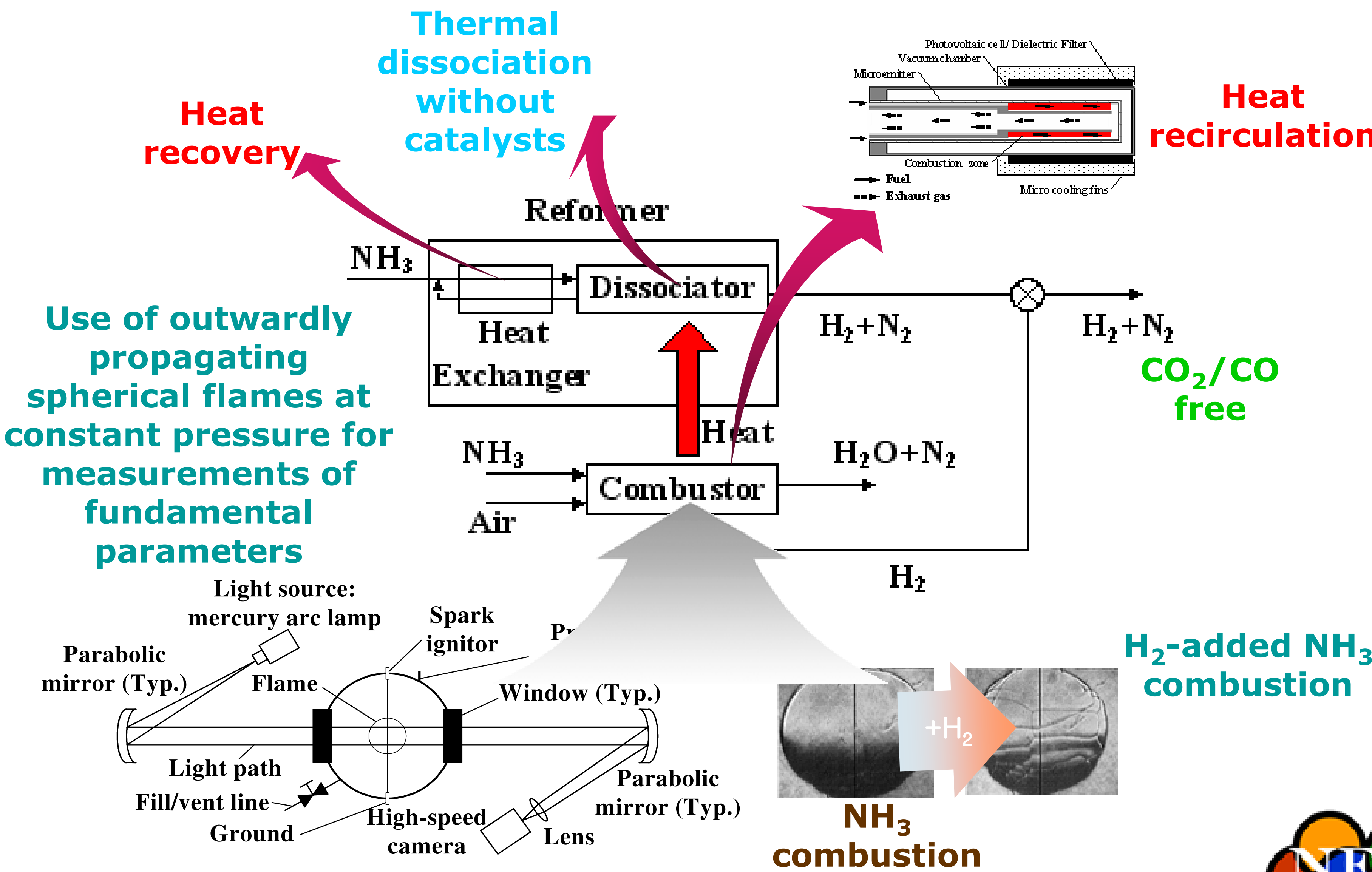
Opportunities

- Initial stage of research on ammonia as a fuel even in advanced countries
- Increasing public concern on the environment: the Kyoto protocol

Threats

- Price increase of ammonia
- Development first, the environment later policies

Use of ammonia as a fuel: the present project



Originalities of the present project

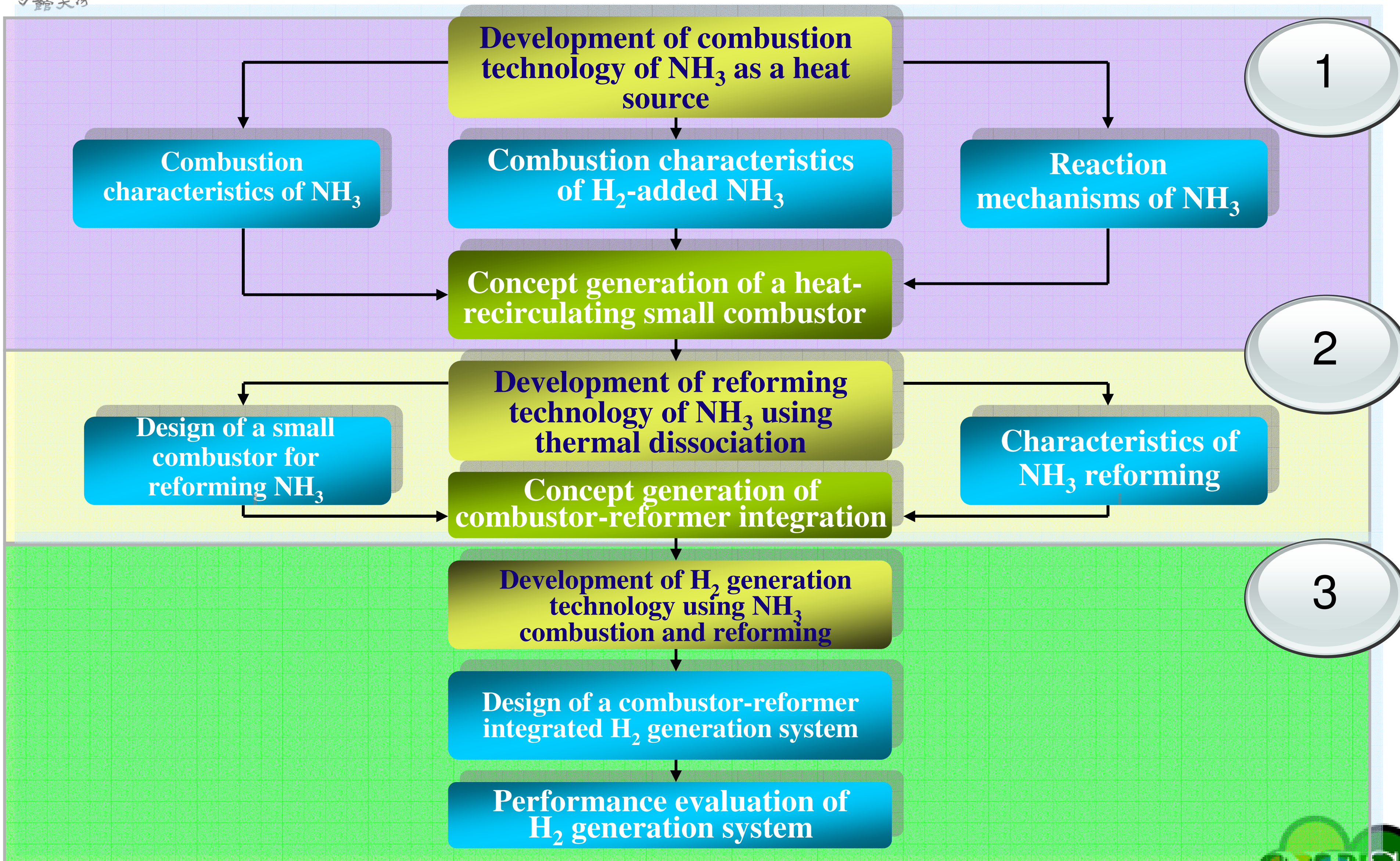
1. Use of ammonia as a fuel
2. Combustion characteristics of ammonia as a fuel
3. Combustion characteristics of hydrogen-added ammonia
4. No catalytic, thermal dissociation of ammonia
5. Use of ammonia for both combustion and reforming
6. Accurate measurements of burning velocities of ammonia

Objective (within 3 years)

Goal

Development of CO_2/CO-free hydrogen generation technology using combustion and reforming of ammonia (miniature/portable size of efficiency of 10-30% and power of 5-30 W)

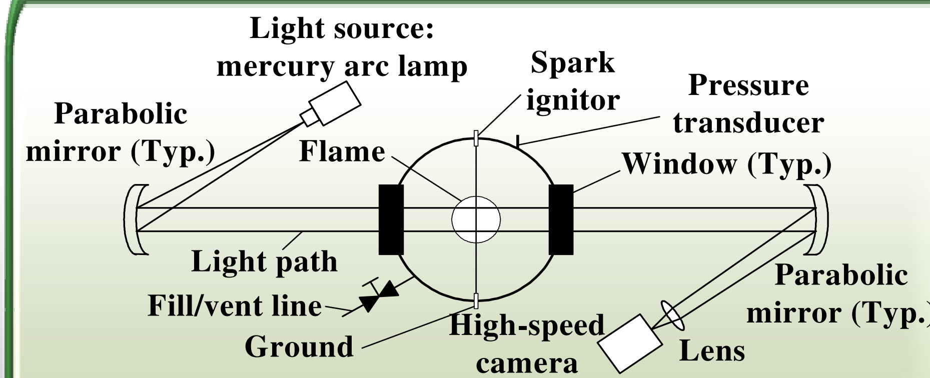
Research plan



Research Years 1-2

Studies on combustion characteristics of ammonia

- Setup of experimental apparatus
- Measurements/predictions of combustion characteristics of hydrogen-added ammonia
- Understanding of reaction kinetics of ammonia-air via numerical simulations



$$S_{L\infty}/S_L = 1 + MaKa$$

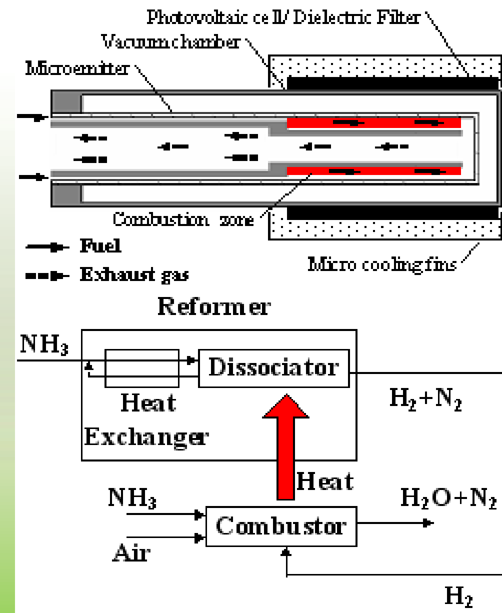
$$S_L = (\rho_b/\rho_u)dr_f/dt \qquad Ka = K/(S_L/\delta)$$

$$K = (2/r_f)dr_f/dt \qquad \delta = D/S_L$$

Research Years 2-3

Studies on reforming characteristics of ammonia

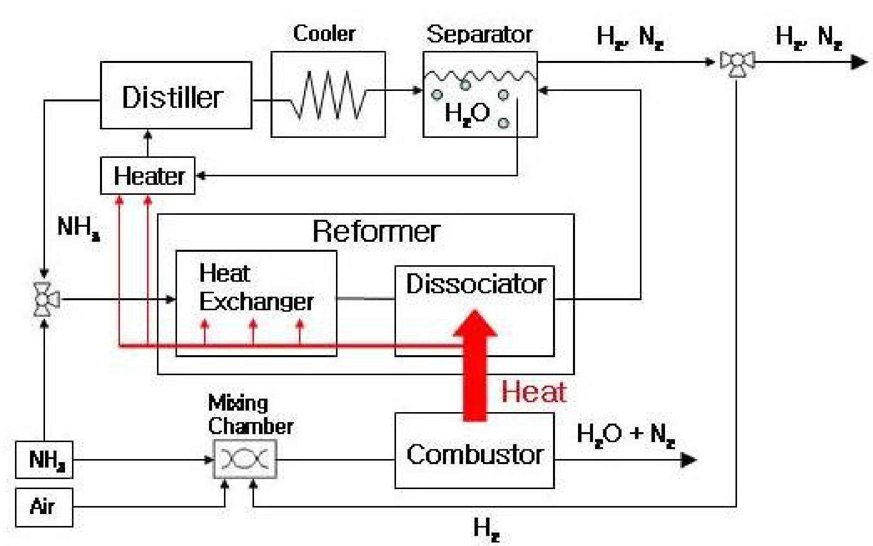
- A study on combustion and heat transfer characteristics in a small combustor via 2/3-D numerical simulations
- Setup of a small heat-recirculating combustor
- Setup of experimental apparatus for ammonia reforming



Research Year 3

Studies on hydrogen generation technology using ammonia

- Setup of a combustor-reformer integrated hydrogen generation system
- Performance evaluations of hydrogen generation system
- Demonstration of hydrogen generation technology using ammonia



Technological challenges to overcome

- **Combustor:**
  - Burning temperature high enough for combustion stability and performance but suppressing NOx formation
  - Heat losses quenching flames
  - Ignition (delay)
  - Maintenance: no catalyst → heat recirculation concept applied but with NH_3

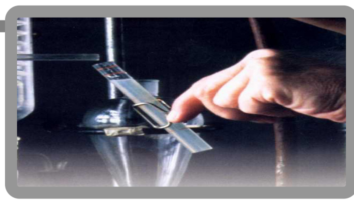
- **Reformer:**
  - Uniform and steady heating: residence time and array
  - Erosive to some materials such as metals

- **Combustor-reformer integrated system:**
  - Effective heat transfer between a combustor and a reformer
  - Simple structure with heat recirculation

Expected benefits

Technological

- Combustion and reforming technologies for using ammonia as a fuel
- Technologies for portable H_2 and power generation systems with rapid response time

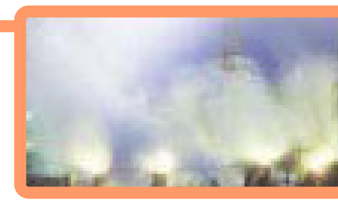


Environmental

- Reduction of carbon dioxide to prevent global warming

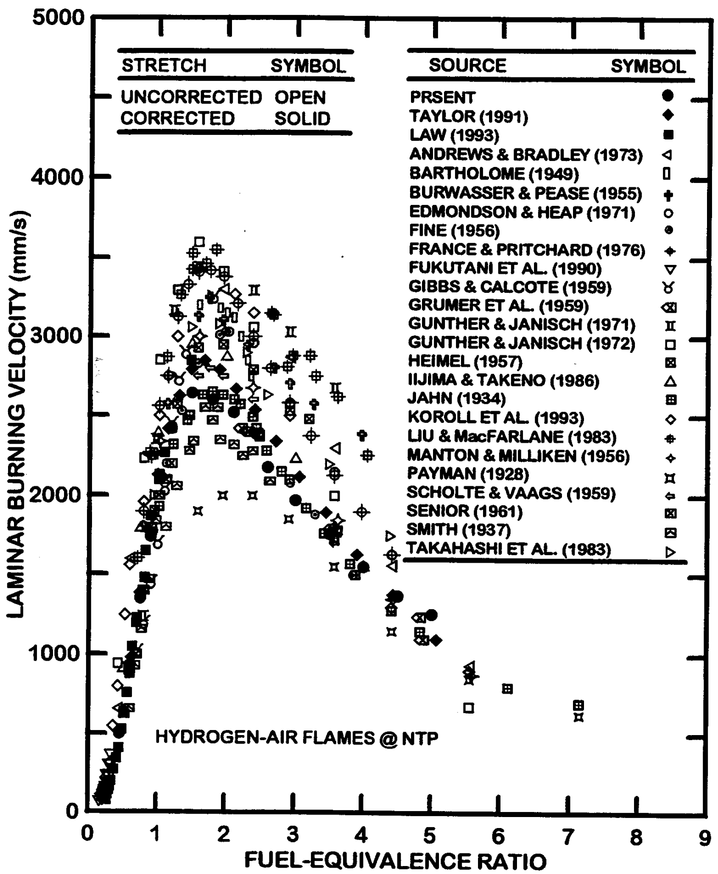
Economic

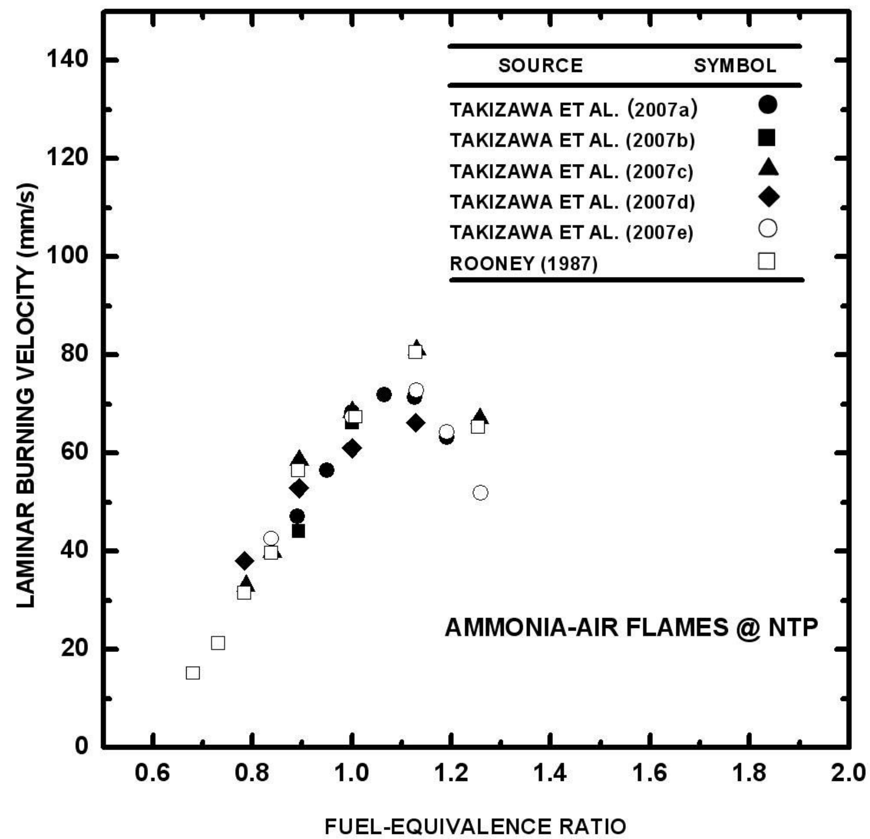
- Replacement of fossil fuels by ammonia, reducing costs to remove greenhouse gases
- CO_2 credit price of 3 cents/kg (2005)



Present status of work

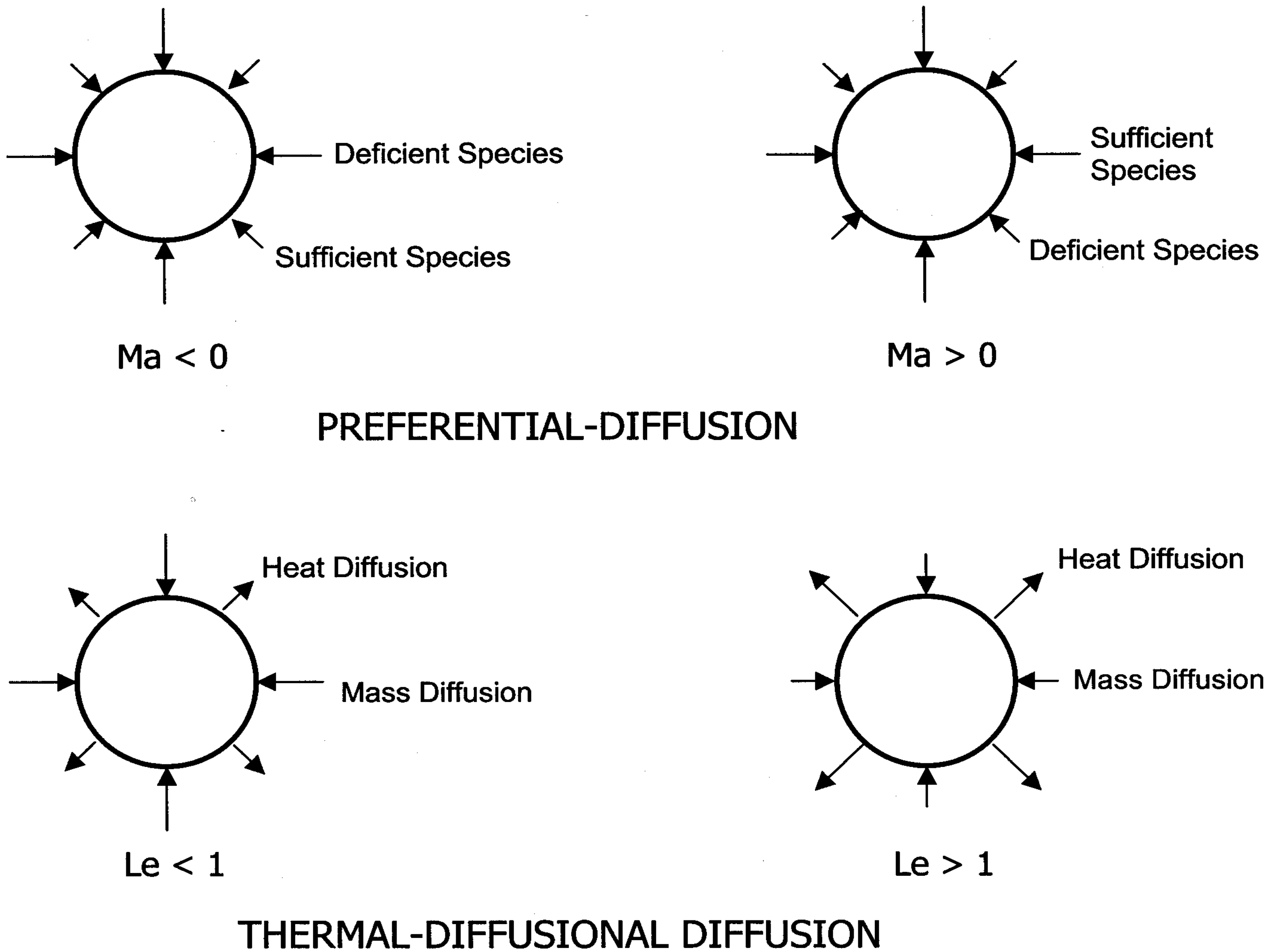
Laminar burning velocities





- **This provides strong motivation for accurate measurements of laminar burning velocities.**

Nonequidiffusion



Local-conditions hypothesis

- Laminar burning velocity/stretch interactions are related, following Markstein (1964):

$$S_L = S_{L\infty} - LK \qquad (1)$$

- Application of the local-conditions hypothesis of Kwon et al. (1992) then yields:

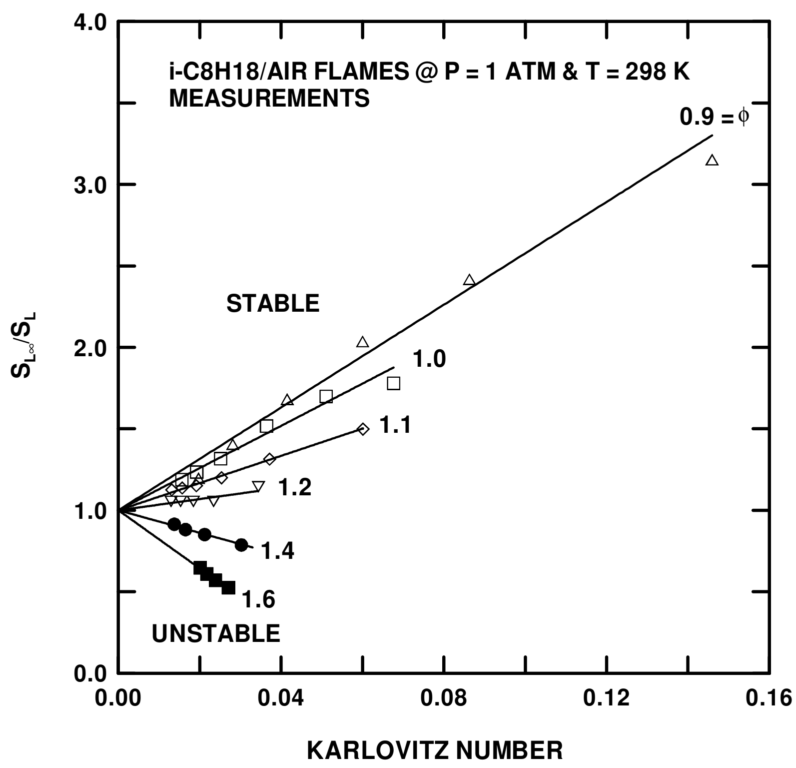
$$S_{L\infty}/S_L = 1 + Ma\,Ka \qquad (2)$$

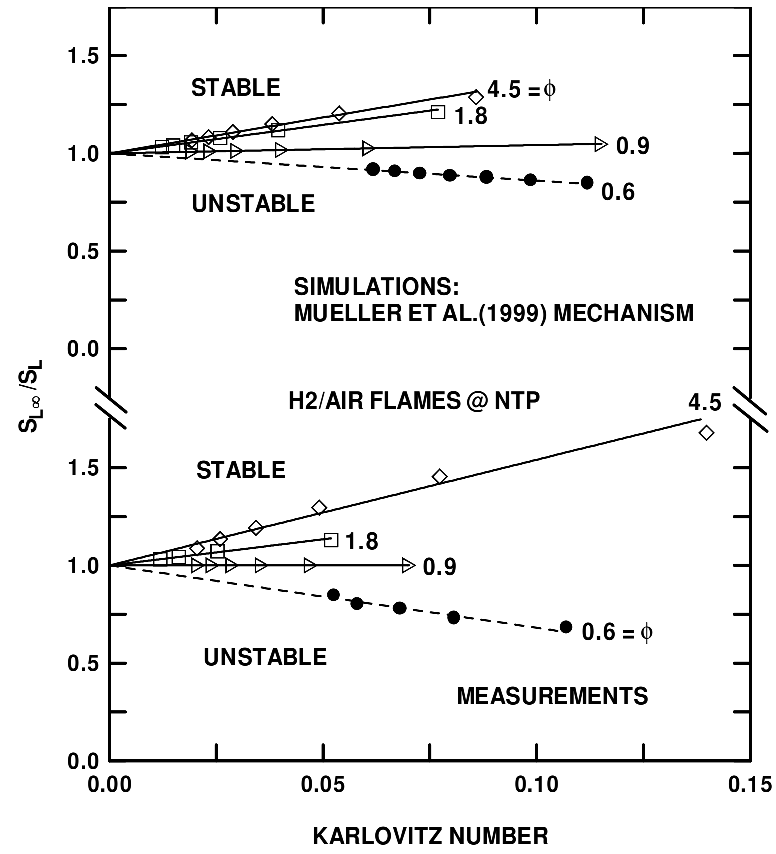
where

$$Ka = K\,\delta_D/S_L, \quad Ma = L/\delta_D, \quad \delta_D = D_u/S_L \qquad (3)$$

Flame/stretch response

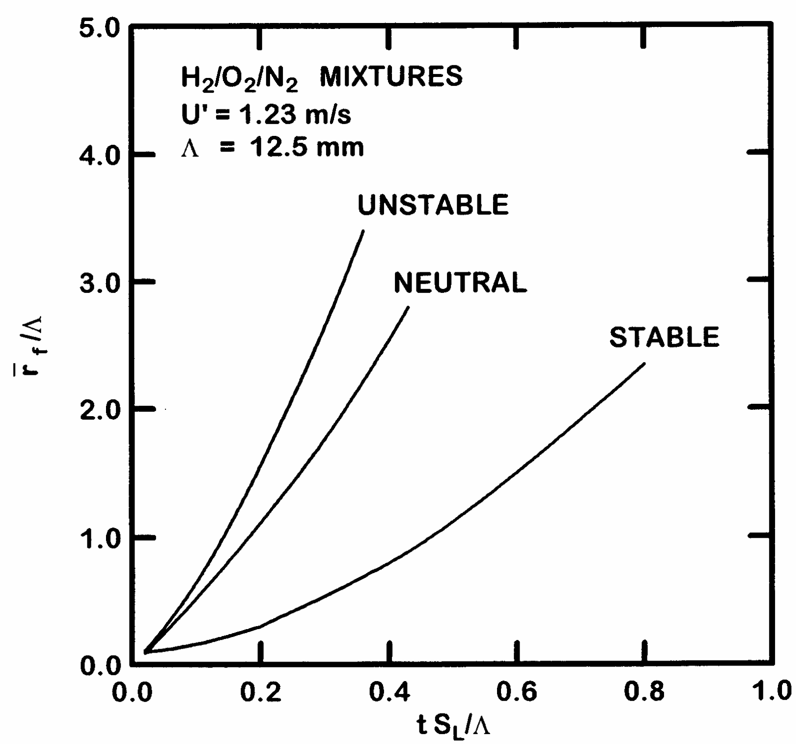
- Linear response conveniently yields constant Markstein numbers at each reactant condition:





Turbulent flame speed evolution

- Preferential diffusion affects even strongly turbulent premixed flames:



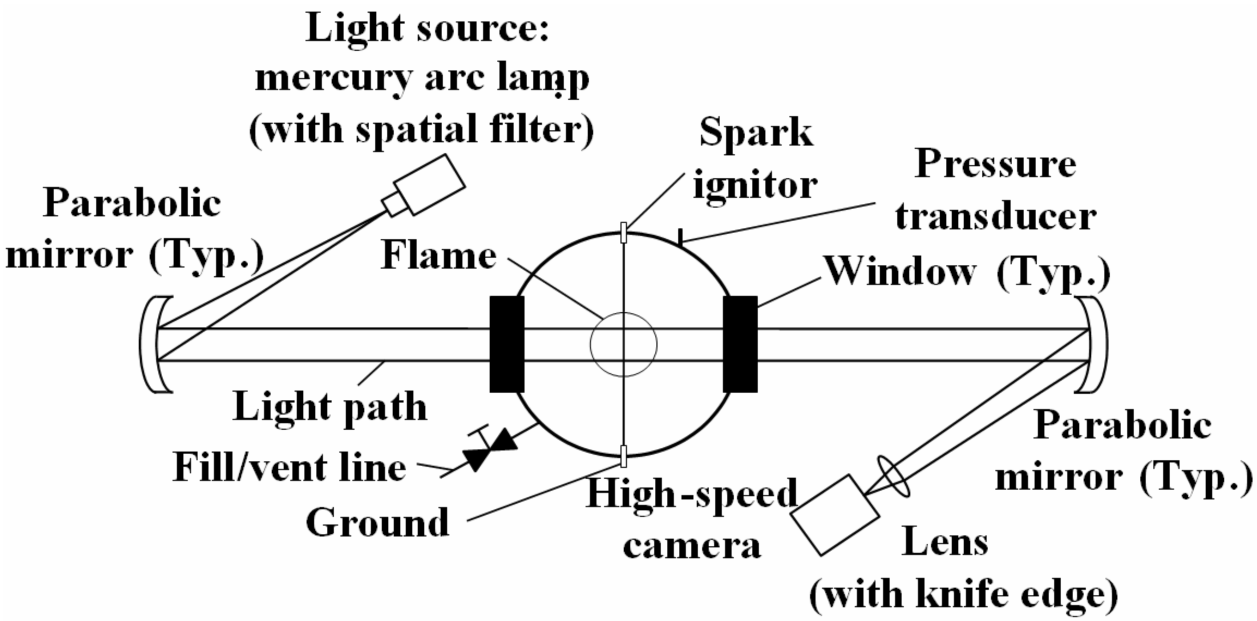
- This provides strong motivation to find laminar flame response to stretch.

Objectives

- **Study effects of H_2-addition on properties of laminar premixed NH_3/air flames:**
  - **Measure laminar burning velocities for various values of stretch, fuel-equivalence ratios and hydrogen concentrations.**
  - **Use the measurements to find fundamental unstretched laminar burning velocities and flame response to stretch (Markstein numbers).**
  - **Use the measurements to evaluate contemporary models of flame structure based on detailed chemical reaction mechanisms.**
- **These fundamental data can be used for designing ammonia-fueled hydrogen generation systems.**

Experimental methods

- Flames are spark ignited at the center of a 320 mm diameter spherical chamber:



- Motion picture Schlieren photographs indicate flame stability, rates of propagation and stretch.
- Measurements are limited to flame radii of 5-30 mm to provide thin, quasi-steady constant-pressure flames.

Data reduction

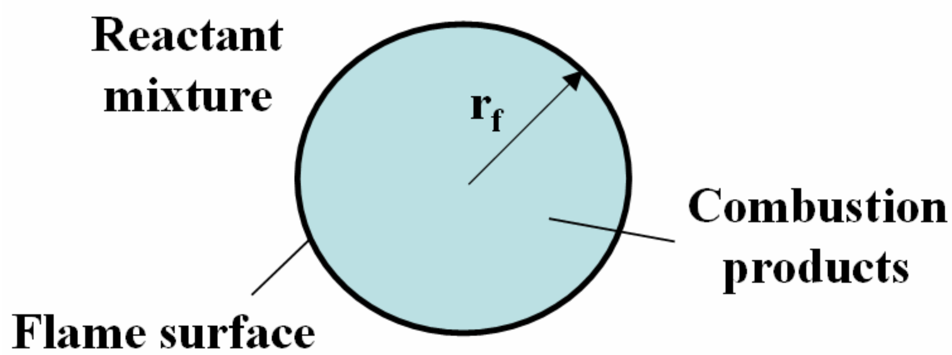
- Data is reduced where effects of curvature and unsteadiness are small ($\delta_D/r_f << 1$) and the following relationships apply:

  - Laminar burning velocity

    $$S_L = (\rho_b/\rho_u)\, dr_f/dt$$

  - Flame stretch

    $$K = (2/r_f)\, dr_f/dt$$



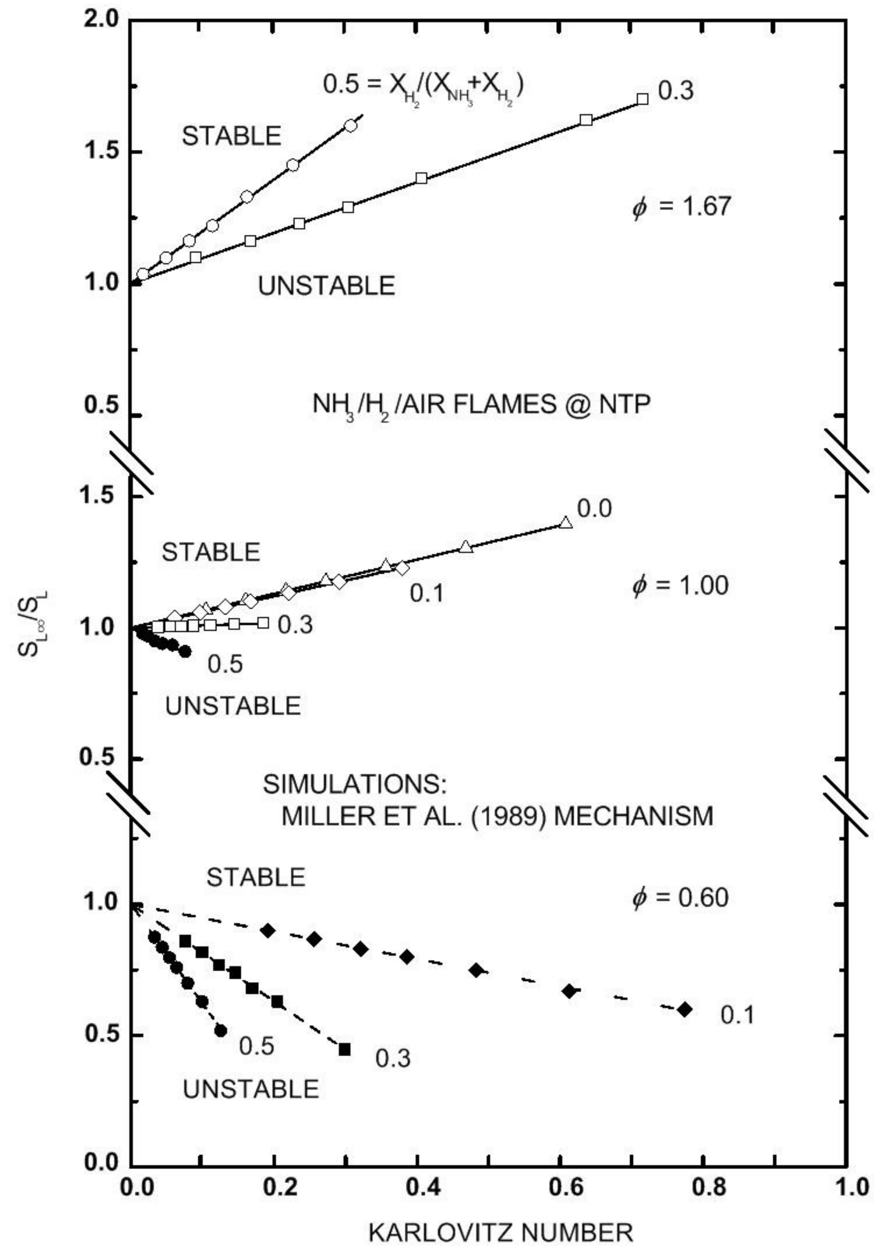
- Results are limited to unwrinkled flames where effects of ignition and buoyancy are small.

Numerical simulations

- Codes treating variable properties, multicomponent diffusion and thermal diffusion with detailed chemical kinetics are used:
  - PREMIX: steady laminar one-dimensional flame code developed by Kee at al. of Sandia National Laboratories.
  - COSILAB: steady and unsteady laminar one-dimensional flame code developed by Rogg of Ruhr-Universität Bochum.
- A detailed N/H/O reaction mechanism of Miller et al. (1989; 73 steps and 19 species) is considered.

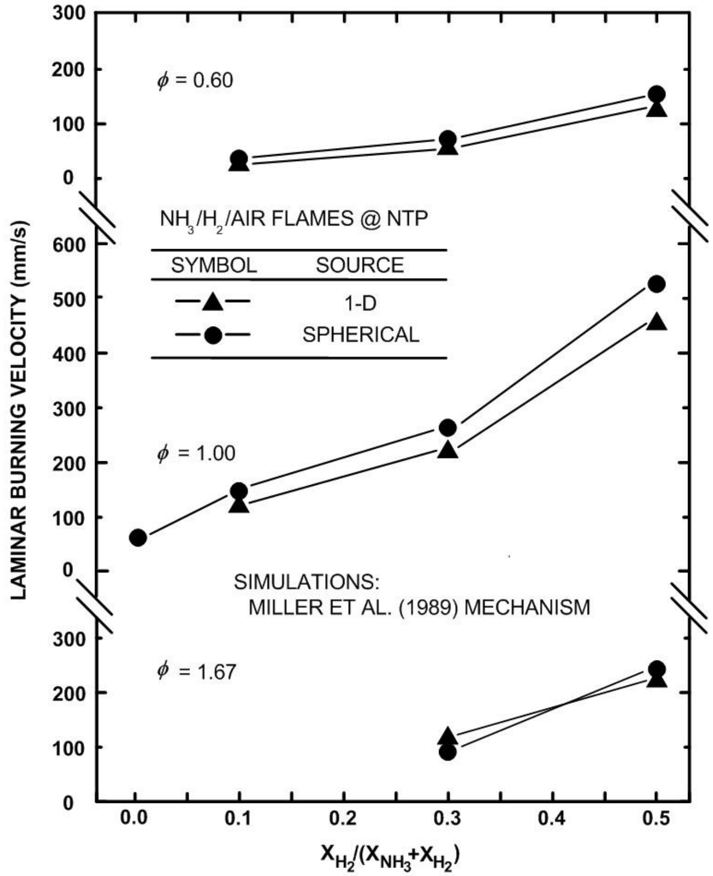
Flame/stretch response: NH_3/H_2/air flames

- **Linear response conveniently yields constant Markstein numbers at each reaction condition (predicted results only):**



Unstretched laminar burning velocities

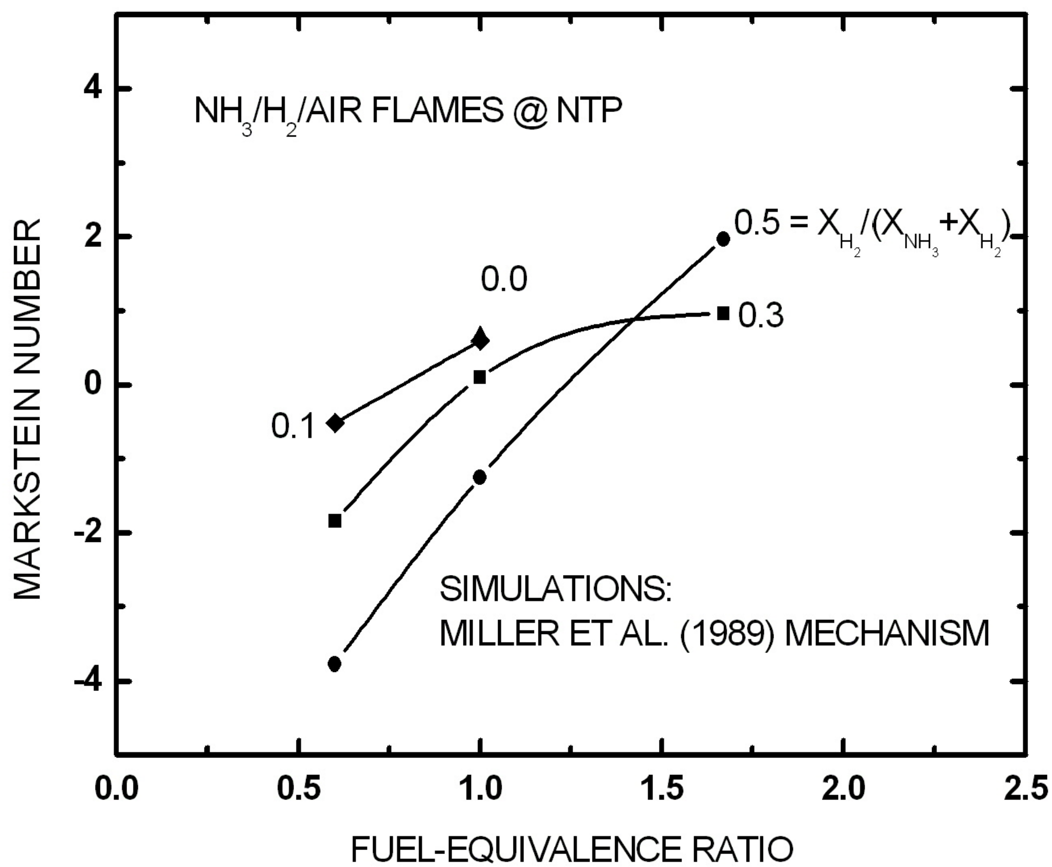
- Hydrogen functions by increasing light radical concentrations (predicted results only):



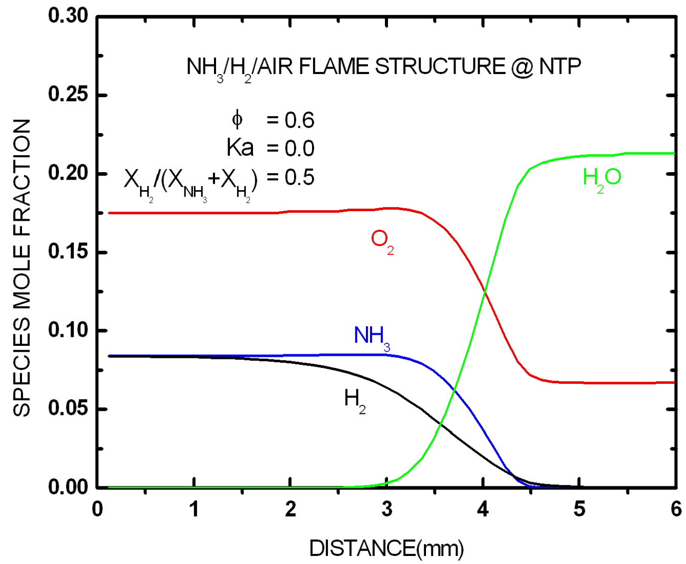
- Laminar burning velocities increase as hydrogen concentrations increase due to enhanced light radical concentrations.

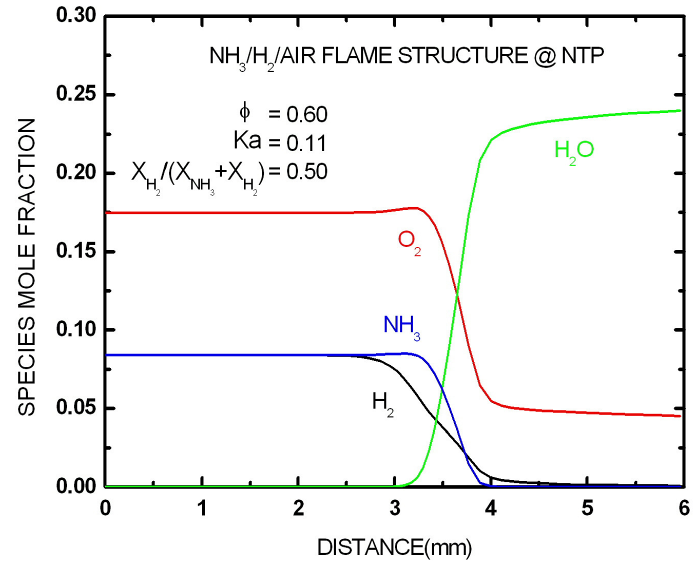
Markstein numbers

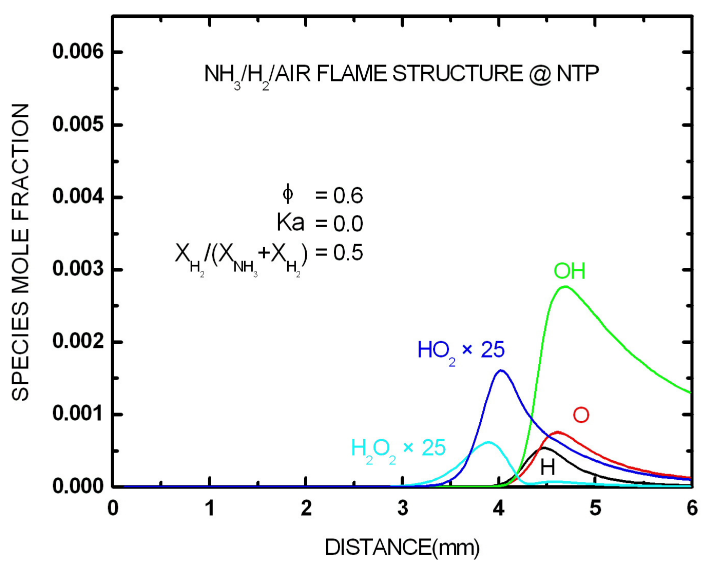
- **Increased hydrogen concentrations enhance unstable nonequidiffusion/stretch interactions for fuel-lean and stoichiometric conditions (predicted results only):**

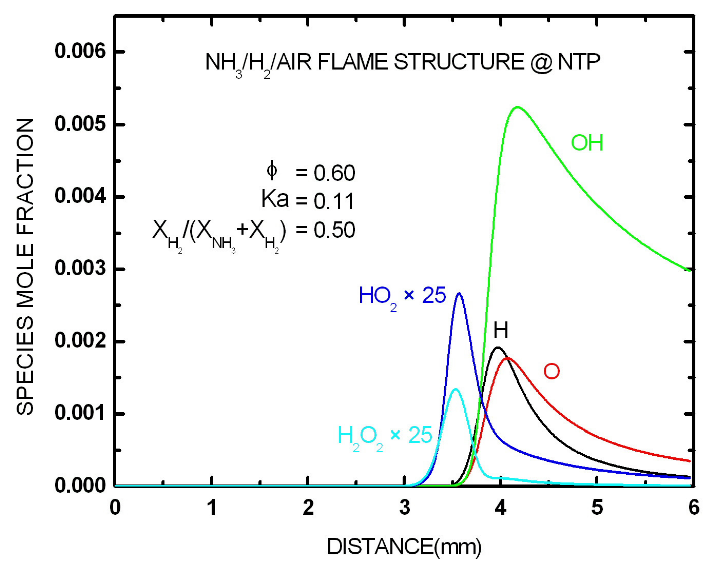


Predicted flame structure









Concluding remarks

- The local-conditions hypothesis yielded a simple correlation of flame/stretch interactions with Ma independent of Ka for moderate and even high levels of stretch.

- Flame/stretch interactions were substantial for hydrogen-added ammonia/air flames with laminar burning velocities varying in range 0.4-1.7 the unstretched value for Ka < 0.8.

- Hydrogen acts to increase light radical concentrations and thus laminar burning velocities, which is desirable for intensifying burning of pure ammonia.

- Once combustion characteristics of ammonia are investigated, a heat-recirculating ammonia-fueled combustor will be designed.