TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2022 SUMMER SCHOOL ON COMBUSTION

# CURRENT STATUS OF AMMONIA COMBUSTION

William Roberts

King Abdullah University of Science and Technology

July 14-15, 2022

# TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

# 2022 SUMMER SCHOOL ON COMBUSTION

<table>
<tr><th colspan="6">Schedule</th></tr>
<tr><td>Beijing Time</td><td>July 11 (Mon.)</td><td>July 12 (Tue.)</td><td>July 13 (Wed.)</td><td>July 14 (Thu.)</td><td>July 15 (Fri.)</td></tr>
<tr><td>08:00 ~ 11:00</td><td></td><td></td><td>Mechanism Reduction and Stiff Chemistry Solvers<br>Tianfeng Lu<br>VMN: 52667557219</td><td></td><td>Mechanism Reduction and Stiff Chemistry Solvers<br>Tianfeng Lu<br>VMN: 52667557219</td></tr>
<tr><td>*10:00 ~ 12:00</td><td></td><td>Virtual Poster Session<br>10:00~12:00<br>VMN: 388239275</td><td></td><td>Virtual Lab Tour<br>10:00~12:00<br>VMN: 231842246</td><td></td></tr>
<tr><td>14:00 ~ 17:00 Session I</td><td colspan="3">Fundamental of Flames<br>Suk Ho Chung<br>VMN: 42399313194</td><td colspan="2">Combustion in Microgravity and Microscale<br>Kaoru Maruta<br>VMN: 71656262918</td></tr>
<tr><td>14:00 ~ 17:00 Session II</td><td colspan="2">Soot<br>Markus Kraft<br>VMN: 39404905340</td><td></td><td colspan="2">Current Status of Ammonia Combustion<br>William Roberts<br>VMN: 80506726244</td></tr>
<tr><td>19:00 ~ 22:00 Session I</td><td colspan="5">Combustion Chemistry and Kinetic Mechanism Development<br>Tiziano Faravelli<br>VMN: 35989357660</td></tr>
<tr><td>19:00 ~ 22:00 Session II</td><td colspan="4">Combustion Fundamentals of Fire Safety<br>José Torero<br>VMN: 57002781862</td><td></td></tr>
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Note:

[1]Session I and Session II are simultaneous courses.

[2]VMN: Voov Meeting Number

**Guidelines for Virtual Participation**

## 1. General Guidelines

- Tencent Meeting software (腾讯会议) is recommended for participants whose IP addresses locate within Mainland China; Voov Meeting (International version of Tencent Meeting) is recommended for other IP addresses. The installation package can be found in the following links:

  a) 腾讯会议
  https://meeting.tencent.com/download/

  b) Voov Meeting
  https://voovmeeting.com/download-center.html?from=1001

- All the activities listed in the schedule are "registrant ONLY" due to content copyright.
- To facilitate virtual communications, each participant shall connect using stable internet and the computer or portable device shall be equipped with video camera, speaker (or earphone) and microphone.

## 2. Lectures

- The lectures are also "registrant ONLY". Only the students who registered for the course can be granted access to the virtual lecture room.
- To enter the course, each registered participant shall open the software and join the conference using the corresponding Voov Meeting Number (VMN) provided in the schedule; only participants who show unique identification codes and real names as "**xxxxxx-Last Name, First Name**" will be granted access to the lecture room; the identification code will be provided through email.
- During the course, each student shall follow the recommendation from the lecturer regarding the timing and protocol to ask questions or to further communicate with the lecturer.
- For technical or communication issues, the students can contact the TA in the virtual lecture or through emails.
- During the course, the students in general will not be allowed to use following functions in the software: 1) share screen; 2) annotation; 3) record.

## 3. Lab Tour

- The event will be hosted by graduate students from Center for Combustion Energy, Tsinghua University and live streamed using provided Voov Meeting Number.
- During the activity, the participants will not be allowed to use following functions in the software: 1) share screen; 2) annotation; 3) record.
- Questions from the virtual participants can be raised using the chat room.

## 4. Poster Session

- The event will be hosted by the poster authors (one Voov Meeting room per poster) and live streamed using provided Voov Meeting Number.
- During the activity, the participants will not be allowed to use following functions in the software: 1) share screen; 2) annotation; 3) record.
- Questions from the virtual participants can be raised using the chat room or request access to audio and video communication.

## Teaching Assistants

- **Fundamentals of Flame (Prof. Suk Ho Chung)**

  TA1: Hengyi Zhou (周恒毅); zhouhy19@mails.tsinghua.edu.cn

  TA2: Xinyu Hu (胡馨予); hxy21@mails.tsinghua.edu.cn

- **Combustion Chemistry and Kinetic Mechanism Development (Prof. Tiziano Faravelli)**

  TA1: Shuqing Chen (陈舒晴); chen-sq19@mails.tsinghua.edu.cn

  TA2: Jingzan Shi (史京瓒); sjz21@mails.tsinghua.edu.cn

- **Current Status of Ammonia Combustion (Prof. William Roberts)**

  TA1: Yuzhe Wen (温禹哲); wyz20@mails.tsinghua.edu.cn

  TA2: Haodong Chen (陈皓东); chd20@mails.tsinghua.edu.cn

- **Soot (Prof. Markus Kraft)**

  TA1: Yuzhe Wen (温禹哲); wyz20@mails.tsinghua.edu.cn

  TA2: Haodong Chen (陈皓东); chd20@mails.tsinghua.edu.cn

- **Combustion Fundamentals of Fire Safety (Prof. José Torero)**

  TA1: Xuechun Gong (巩雪纯); gxc19@mails.tsinghua.edu.cn

  TA2: Weitian Wang (王巍添); wwt20@mails.tsinghua.edu.cn

- **Combustion in Microgravity and Microscale (Prof. Kaoru Maruta)**

  TA1: Hengyi Zhou (周恒毅); zhouhy19@mails.tsinghua.edu.cn

  TA2：Xinyu Hu (胡馨予); hxy21@mails.tsinghua.edu.cn

- **Mechanism Reduction and Stiff Chemistry Solvers (Prof. Tianfeng Lu)**

  TA1: Shuqing Chen (陈舒晴); chen-sq19@mails.tsinghua.edu.cn

  TA2: Jingzan Shi (史京瓒); sjz21@mails.tsinghua.edu.cn

# Ammonia Combustion

William L. Roberts
Director, Clean Combustion Research Center

Tsinghua Summer School
Center for Combustion Energy
Tsinghua University, Beijing
14-15 July 2022

Clean Combustion Research Center

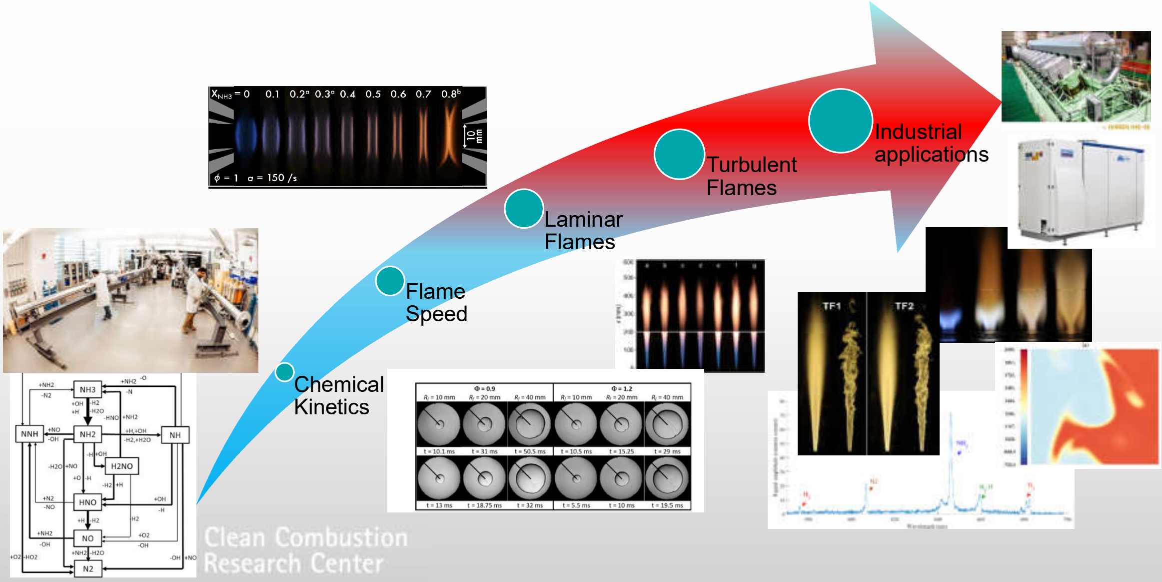


# Outline of Lecture Series

- Lecture 1: Introduction to ammonia
- Lecture 2: Ammonia combustion kinetics
- Lecture 3: Premixed ammonia flames
- Lecture 4: Non-premixed flames and Diagnostics
- Lecture 5: Sooting flames with ammonia
- Lecture 6: Practical considerations

Clean Combustion Research Center

# Ammonia Research in the CCRC

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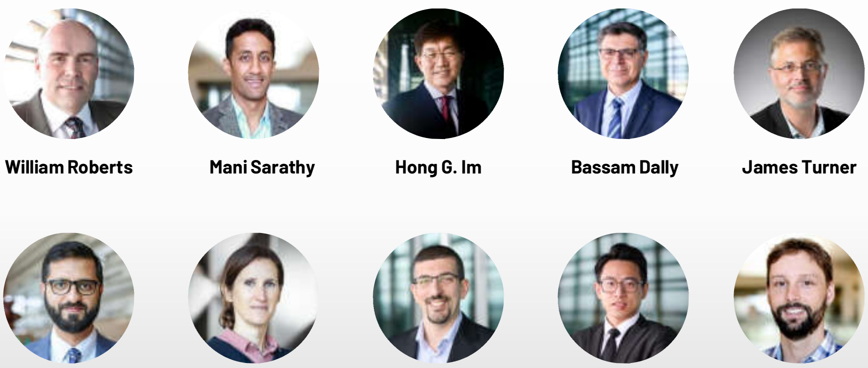
# The CCRC Ammonia Team



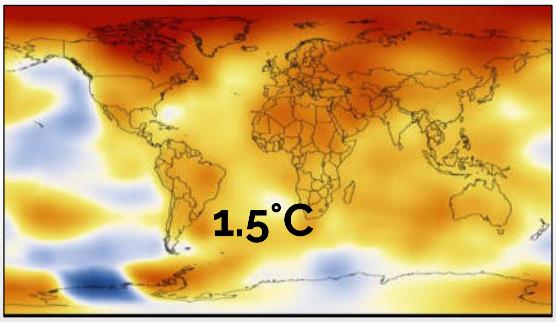
William Roberts | Mani Sarathy | Hong G. Im | Bassam Dally | James Turner

Aamir Farooq | Deanna Lacoste | Gaetano Magnotti | Xu Lu | Thibault Guiberti

Clean Combustion Research Center

# Climate Change and Paris Accords

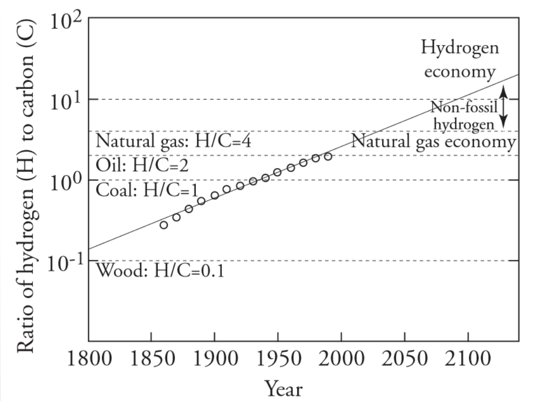
The race to zero carbon emissions…



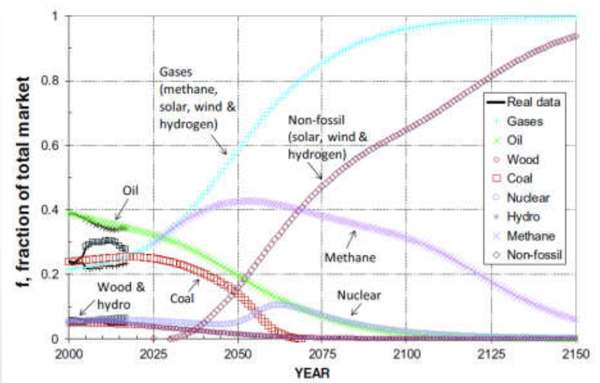

Global carbon emissions need to drop to zero by 2050!



# Age of Decarburization of Energy: Evolutionary transition



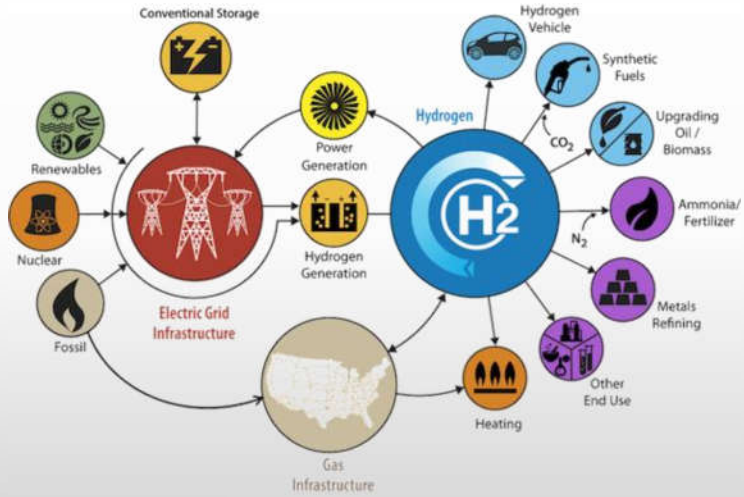

"Freeing Energy from Carbon." Technological Trajectories and the Human Environment. National Academic Press, Washington (1997)




Projected energy mix until 2150. Non-fossil energy becomes the market leader around 2070. Real data to 2017 (BP, annual),
Aguilera, Roberto F., and Roberto Aguilera. "Revisiting the role of natural gas as a transition fuel." Mineral Economics (2019): 1-8.

Primary energy mix transformation has been happening for a long time; rate is accelerating

# The Hydrogen Economy




−253 °C at 1 atm

700 bar at 23 °C

(Source: Triplepundit.com)



# Hydrogen colors

| Color | Primary Feedstock | Primary Energy Source | Primary Poduction Process | Carbon Impact (kg $CO_2$/kg $H_2$) |
|---|---|---|---|---|
| Brown | Coal or Lignite | Chemical Energy in Feedstock | Gasification & Reformation | 18 to 20 |
| Gray | Natural Gas | Chemical Energy in Feedstock | Gasification (SMR) | 10 to 12 |
| Blue | Coal, Lignite, or Natural Gas | Chemical Energy in Feedstock | Gasification with Carbon Capture and Sequestration | 0.6 to 3.5 |
| Green | Biomass or Biogas | Chemical Energy in Feedstock | Gasification and Reformation | 0 |
| | Water | Electricity | Electrolysis | |
| Pink | Water | Nuclear Power | Electrolysis | |

# Green Hydrogen

Renewable Energies

## Green Hydrogen

*A path to decarbonize heavy polluting sectors, including the chemical, steel, and iron industries, as well as the transportation sector…*

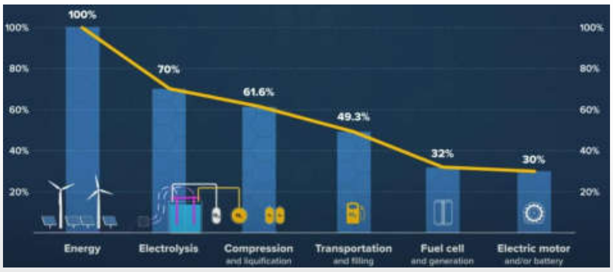
*More than 350 large scale projects are underway right now…*

*The investment in the hydrogen sector is around 500 billion USD…*



# Efficiency and transportation

*Challenges associated with hydrogen…*




Hydrogen Efficiency Rate

## Hydrogen Carriers

- Liquid organic carriers (Methylcyclohexane-Dibenzyltoluene)
- Metal alloy hydrides
- Liquid ammonia ($NH_3$)

Among these alternatives, liquid $NH_3$ is currently seen as the path towards transporting zero-carbon energy by road, rail, ship, or pipeline!



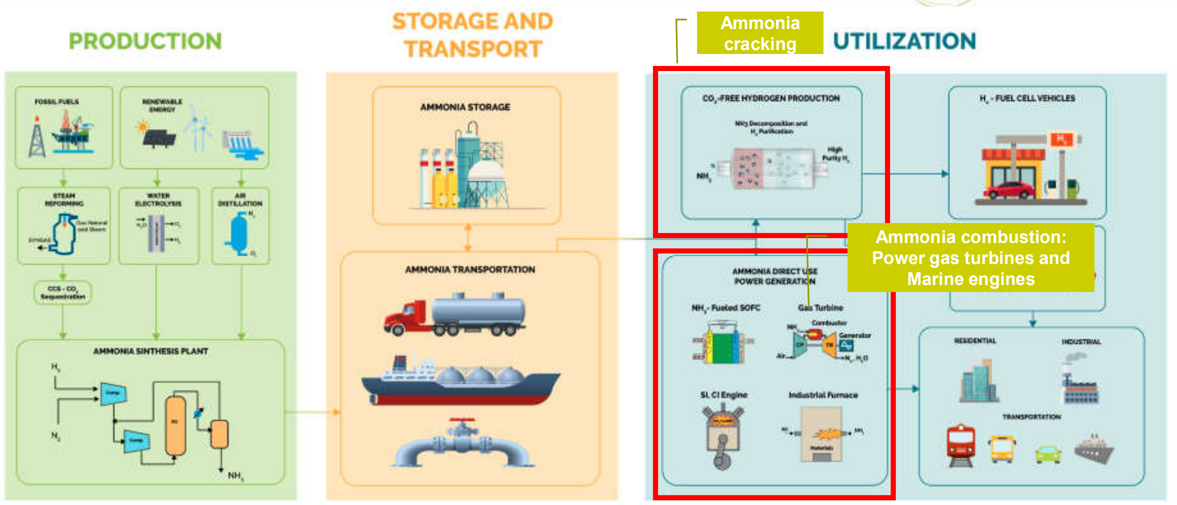
**Source:** *F. Bird, et al., Ammonia: Zero-carbon fertiliser, fuel and energy store, 2020*

# Low-carbon fuels

- GHG emission reductions are driven by renewables-based electricity, energy efficiency, electrification of transportation across key sectors
- Over 40% of end-uses can not be decarbonized easily or cost-effectively via electrification: Hard-to-abate sectors include Marine, Aviation, Long-haul and heavy duty transport, High-temperature heat for industry etc..
- Zero or low-carbon fuels offer opportunity for decarbonization of these hard-to-abate sectors.  These fuels or energy carriers include:
  - Hydrogen
  - Ammonia
  - Bio-fuels and
  - Synthetic fuels
- Carbon capture and utilization (CCUS) technologies are essential to enable cost-effective decarbonization effort



# The Blue and Green Ammonia Energy Economy



# Ammonia as a Transportation Fuel

2012-2015 KIER:
NH3/gasoline dual Fuel
10L/100 km

1960-1966: US Army
X-15 rocket plane powered by NH3 set speed and altitude records

2007-2012: Michigan University
NH3 - gasoline dual Fuel
3800 km

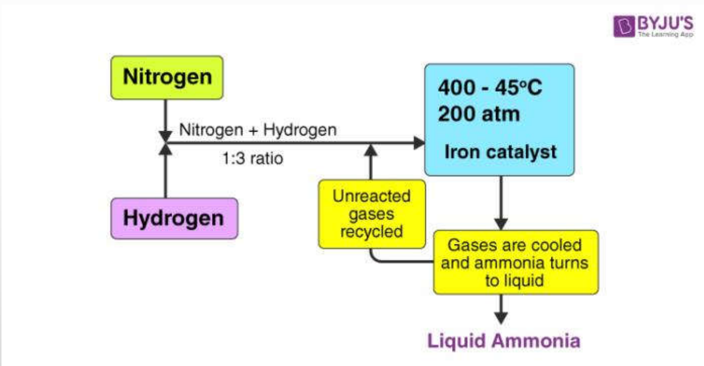
1940: Belgium
NH3/coal gas
100000 miles



# Ammonia Production

- Haber Process (Haber-Bosch) Germany, WW-II

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92\ kJ\ mol^{-1}$$




Only about 15% is converted in each pass

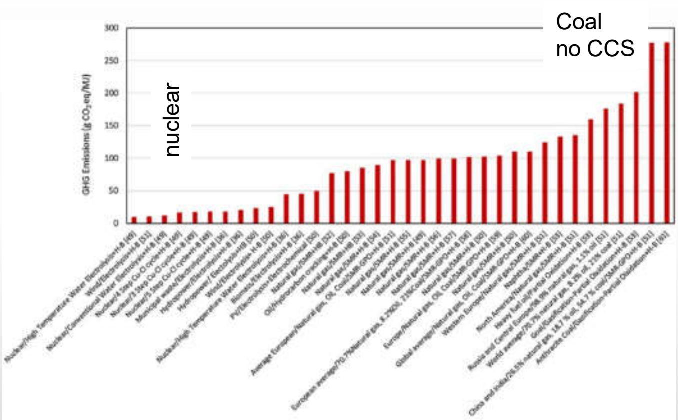
# Steam Methane Reformer

- 99% of Hydrogen is from SMR of natural gas
- ***Steam-Methane Reforming Reaction***
  $CH_4 + H_2O \text{ (+heat)} \rightarrow CO + 3H_2$ (syn gas)

  ***Water-Gas Shift Reaction***
  $CO + H_2O \rightarrow CO_2 + H_2$ (+small amount of heat)
- Uses high temperatures (700-1000 C) and pressures (25bar)
- Requires a catalyst



# Life cycle $CO_2$ emissions ammonia production options




**Major source of emissions:**
For grey ammonia: Hydrogen production via SMR, Fossil based electricity for Compressors, Air separation unit (ASU), Fugitive methane
For blue ammonia: extent of CCUS; fugitive methane;
Green ammonia: Solar/wind turbine manufacturing;
Pink ammonia: Uranium enrichment (nuclear)

Al-Aboosi, Fadhil Y., et al. "Renewable ammonia as an alternative fuel for the shipping industry." *Current Opinion in Chemical Engineering* 31 (2021): 100670.

# Ammonia usage

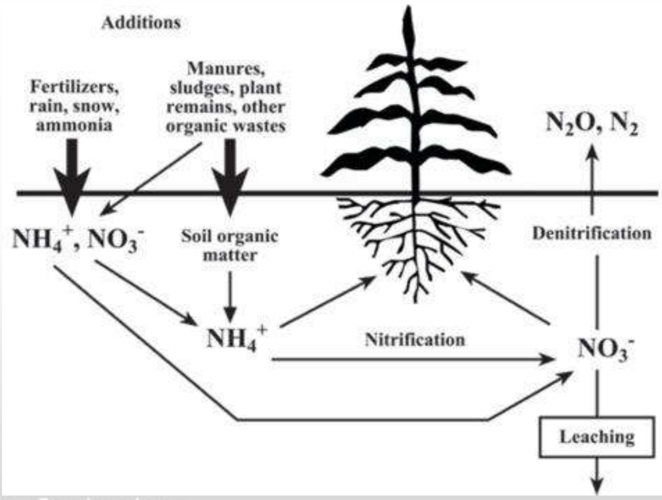
- Global production of ammonia is approx. 250 m tpa
- Mostly used for production of fertilizer
- Ostwald Process (1902)
- Convert ammonia to nitric acid
  - Primary oxidation
    - $4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O$ | H -24.8 Kcal/mol
    - 600 C, platinum or nickel
  - Secondary oxidation
    - $2NO + O_2 \leftrightarrow 2\, NO_2$
    - Lower temperature, 150 C
  - Absorption of $NO_2$
    - $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$



# Ammonium Nitrate

- Convert ammonia and nitric acid
- $HNO_3 + NH_3 \rightarrow NH_4NO_3$
- Primarily used as a fertilizer
- Decomposition is very exothermic and converts liquid to gas
  - At low temperatures: $NH_4NO_3 \rightarrow N_2O + 2H_2O$
  - At high temperatures: $2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O$
  - Regulated as an explosive

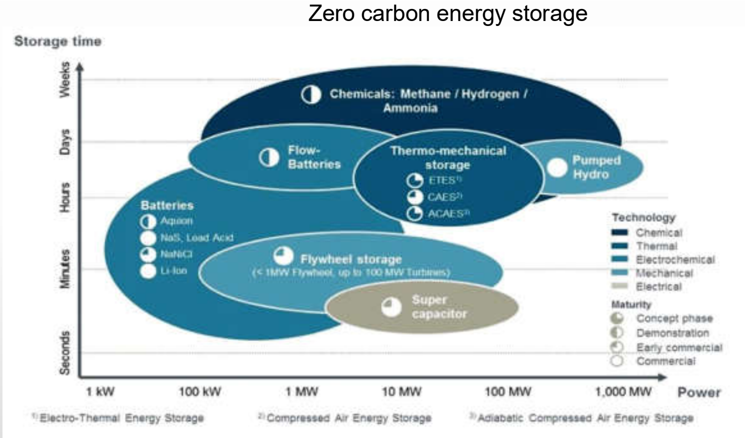
# Nitrogen uptake




https://nevegetable.org/book/export/html/31

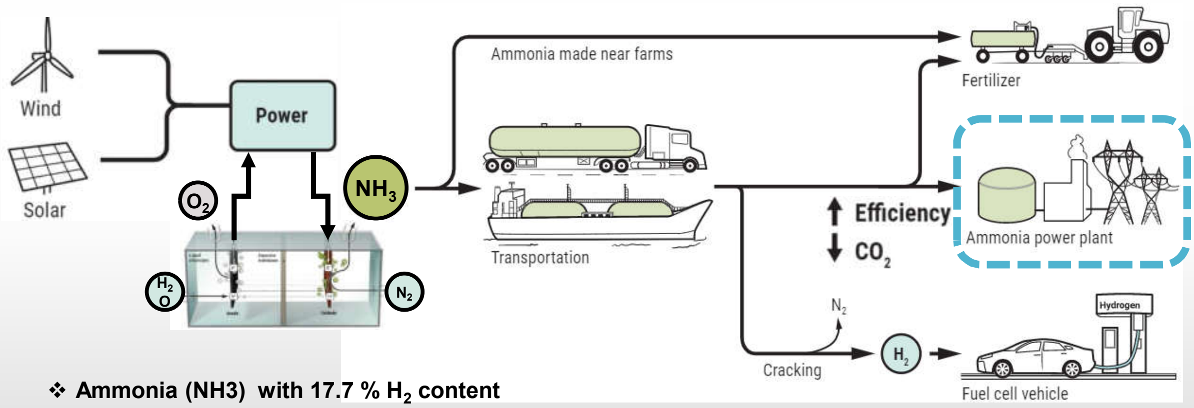
# Ammonia advantages

Zero carbon energy storage




Valera-Medina, Agustin, et al. "Ammonia for power." *Progress in Energy and Combustion Science* 69 (2018): 63-102.

# Carbon-free Ammonia Energy



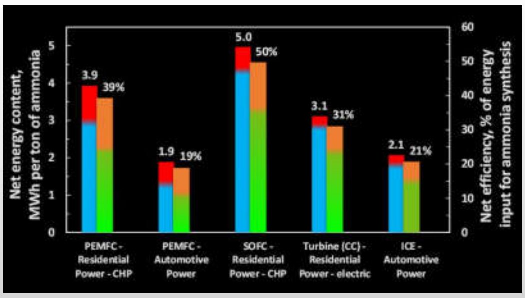

❖ **Ammonia (NH3) with 17.7 % $H_2$ content**
- Is regarded as carbon-free hydrogen carrier.
- Low cost of storage and transport.
- Can be produced from renewable resources.



# Round trip efficiencies (RTE)

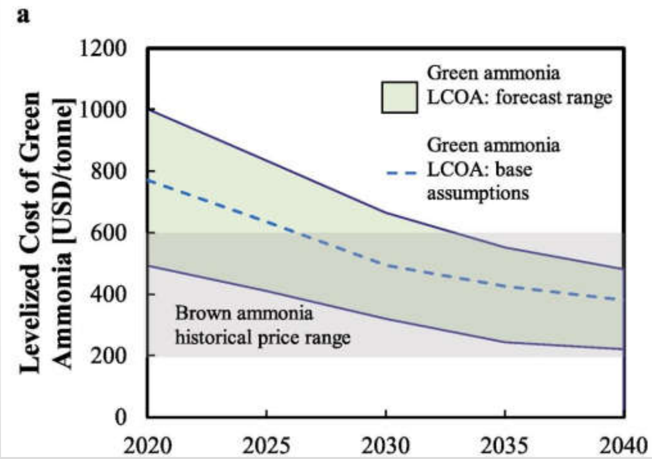
- Net energy required for the ammonia cracking between 0.28 and 0.30 MWh per ton ammonia
- The ammonia cracker leads to total losses “estimated to be 1.41 MWh per ton (equates to overall ammonia cracker efficiency 76%) for best case scenario.
- The hydrogen compression technologies: mechanical compression (40-50% efficient), electrochemical compression (potentially 70-80% efficient), and chemical compression using metal hydrides (less than 30% efficient)
- Overall efficiency for ammonia best- and worst-case RTE values range from 15-21% in ICEs and, in turbines, 24 to 31% of the input renewable energy.

| Process | Liq. $NH_3$ from RE sources | $NH_3$ cracker / $H_2$ separator | $H_2$ Comp. (880 bar) | PEM Fuel Cell Car |
|---|---|---|---|---|
| Process Efficiency (%) | 58.8 | 75.9 | 88.0 | 48.0 |
| $H_2$ content (MWh) | 5.88 | 4.46 | 3.93 | 1.89 |

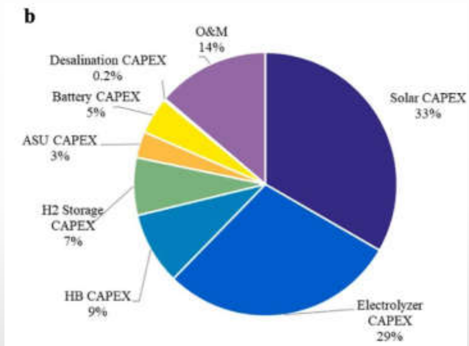



When possible burn ammonia directly

# Ammonia costs projected out to 2040




Green ammonia production cost forecasted 2020 to 2040

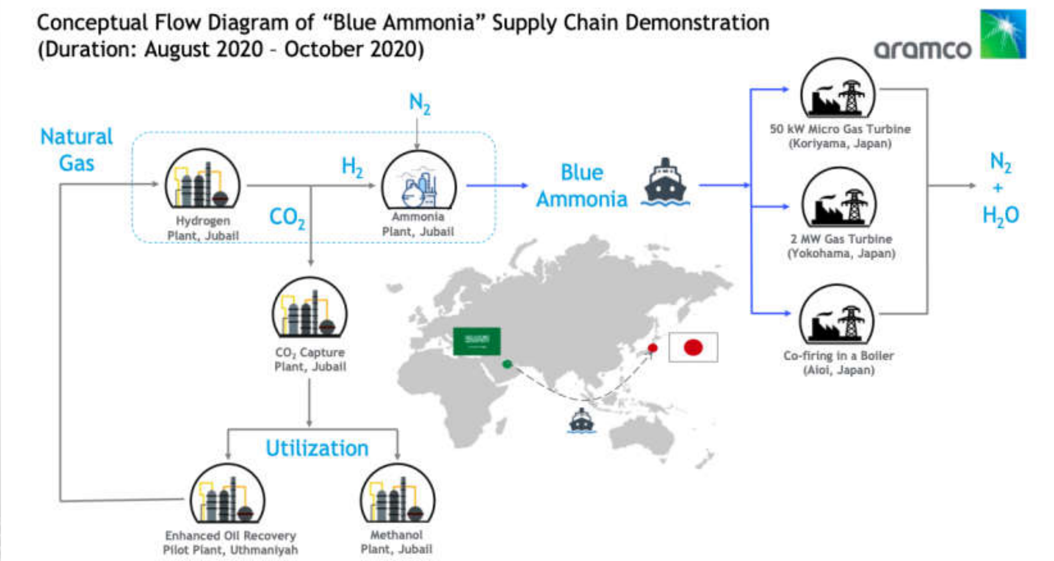



Cost-breakdown in 2040

Cesaro, Zac, et al. "Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants." Applied Energy 282 (2021): 116009.



# Blue Ammonia to Japan



# It's happening now!

Energy & Science

**Saudi Arabia Sends Blue Ammonia to Japan in World-First Shipment**

**Air Products, ACWA Power and NEOM Sign Agreement for $5 Billion Production Facility in NEOM Powered by Renewable Energy for Production and Export of Green Hydrogen to Global Markets**

The World's Largest Green Hydrogen Project Will Supply 650 Tons Per Day of Carbon-Free Hydrogen for Transportation Globally and Save the World Three Million Tons Per Year of CO2


ARTICLE

**OCP's Green Ammonia pilot plant, and the African Institute for Solar Ammonia**

By Trevor Brown on August 17, 2018

Last week, OCP Group announced plans to develop green hydrogen and green ammonia as sustainable raw materials for use in fertilizer production. This includes building pilot plants in both Germany, already under construction, and Morocco, yet to begin construction, as well as "the possible establishment of an African Institute for Solar Ammonia."



# First shipment of blue ammonia

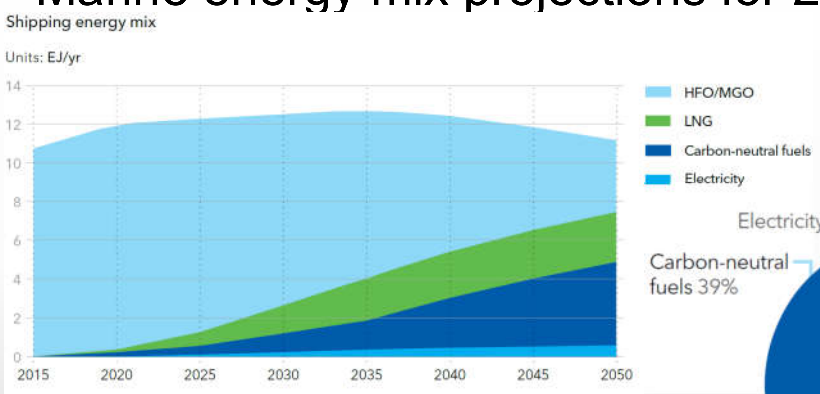
28 Sept 2020, SA ships 40 tones of blue ammonia to Japan

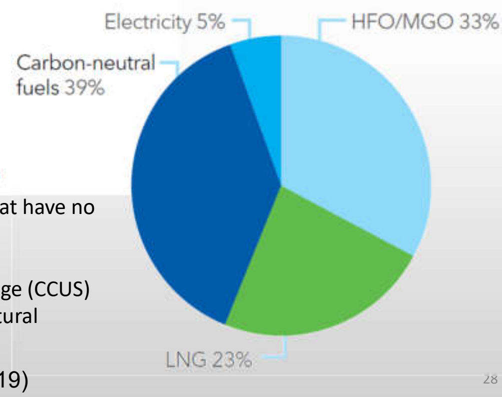
# Technological challenges for ammonia combustion

- Low burning velocity leads to stability issues
- High NOx
- Ammonia cracking not at commercial scale currently
- Material compatibility issues for Ammonia cracker and combustor components (Nitridation corrosion; Hydrogen embrittlement)
- High-Ammonia combustion for gas turbines; Ammonia co-firing with coal/HFO at low-TRL
- Low round trip efficiency (however, still better than liquid hydrogen or methanol!)



# Marine energy mix projections for 2050



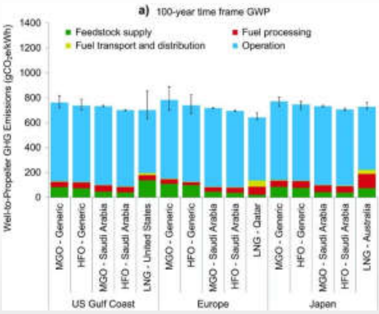




**Carbon-neutral fuels:** A variety of energy fuels or energy systems that have no net GHG or carbon footprint

- Hydrogen/Ammonia
- Nuclear, renewables or fossil fuels with carbon capture and storage (CCUS)
- Bio-fuels, if fuel carbon is sustainably sourced and part of the natural carbon cycle

Source: DNV-GL report (2019)

# Well-to-propeller GHG emissions

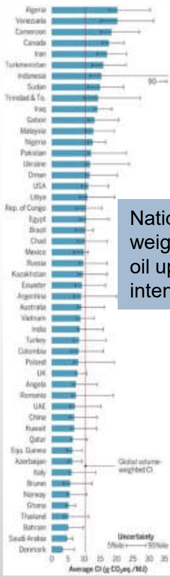



Total life cycle GHG emissions of different marine fuels in different regions.

The LNG benefits of higher engine efficiency and lower carbon content compared to HFO and MGO are generally offset by the disadvantages of methane losses in the LNG supply chain, including: fugitive emissions from upstream well activities, methane loss in LNG transmission and loading, and methane slip in marine engine

Conventional marine fuels produced from Saudi crude can have lower life cycle GHG emissions compared to U.S. Gulf Coast LNG depending on the U.S. gas production region.

Can Green ammonia replace HFO ?



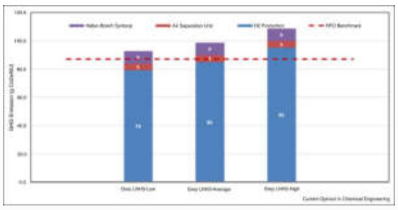
National volume-weighted average crude oil upstream GHG intensities (2015).

Science 361.6405 (2018): 851-853.

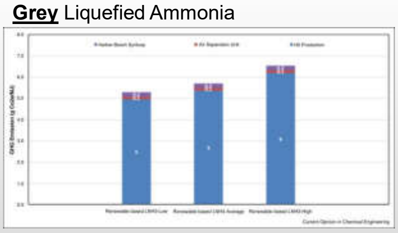


# Renewable Ammonia for Marine sector

- High carbon footprint & emission (SOx, Carbon black) reduction potential over convectional marine fuels (Heavy fuel oil)
- Existing supply chain need expansion: Manufacturing, Storage, Transportation technologies, Bunker ports
- Most significant cost-Electrolysis and Renewable energy: can be built near RE sites and Bunkering ports (for green ammonia); Carbon capture (for blue ammonia)
- Engine retrofitting or modification needed
- Staged replacement of HFO/MGO from marine engines possible (Grey➔Blue➔ Green)
- No need for Ammonia cracking (direct combustion)➔ high round trip efficiency



Breakdown of Life cycle GHG emissions for **Grey** Liquefied Ammonia



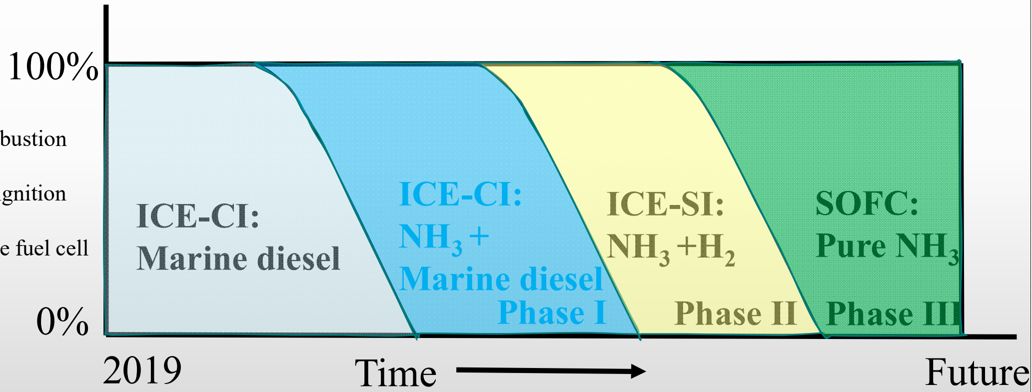
Breakdown of Life cycle GHG emissions for **Green** Liquefied Ammonia

Green ammonia offers > 10X $CO_2$ reduction potential over HFO

Al-Aboosi, Fadhil Y., et al. "Renewable ammonia as an alternative fuel for the shipping industry." *Current Opinion in Chemical Engineering* 31 (2021): 100670.

# The $NH_3$-hydrocarbon combustion becoming important in marine industry

**ICE**: internal combustion engine
**CI**: Compression ignition
**SI**: Spark ignition
**SOFC**: Solid oxide fuel cell




Pathway to zero emission shipping using ammonia as a fuel.



[1]. https://thrust.enviu.org/2020/03/19/7-reasons-why-ammonia-is-a-game-changer-for-the-maritime-industry/



شكرا

THANK YOU!

# Lecture 2: Ammonia combustion kinetics

William L. Roberts
Director, Clean Combustion Research Center

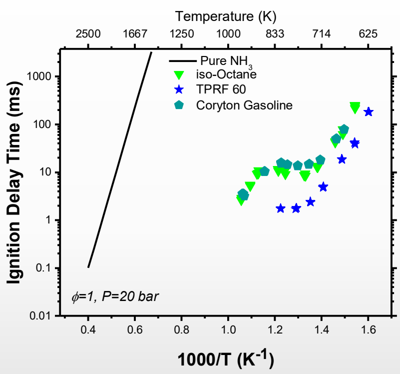
Tsinghua Summer School
Center for Combustion Energy
Tsinghua University, Beijing
14-15 July 2022

Clean Combustion Research Center



# Limitations of Ammonia as a Fuel

- Narrow flammability limits (18% to 28% of fuel mole fraction) and low flame speed
- High heat of vaporization (1371 kJ/kg vs. 271 kJ/kg of gasoline)
- High autoignition temperature (930 K vs.859 K for methane) and ON ~ 130
- Incomplete combustion: $NO_x$, $NH_3$ emissions
- Ammonia is toxic: exposure limit 25-50 ppm with fatal consequences above 300 ppm




- **Solution**: Blending of ammonia with suitable additives (H2, HCs, e-fuels)

Clean Combustion Research Center

## Outline of this lecture

- **Basic structure to model development**
- Ammonia thermal decomposition
- Ammonia oxidation
- Ammonia and Hydrogen
- Ammonia and DME, DEE
- Ammonia and higher hydrocarbons
- DeNOx mechanisms
- Pyrolysis of ammonia



## Mechanism development

- Considerable development ongoing to improve the Ammonia-$H_2$ mechanisms
- Need to enhance mechanisms with better CN chemistry
- Fold this into a more complete Ammonia-HC mechanism

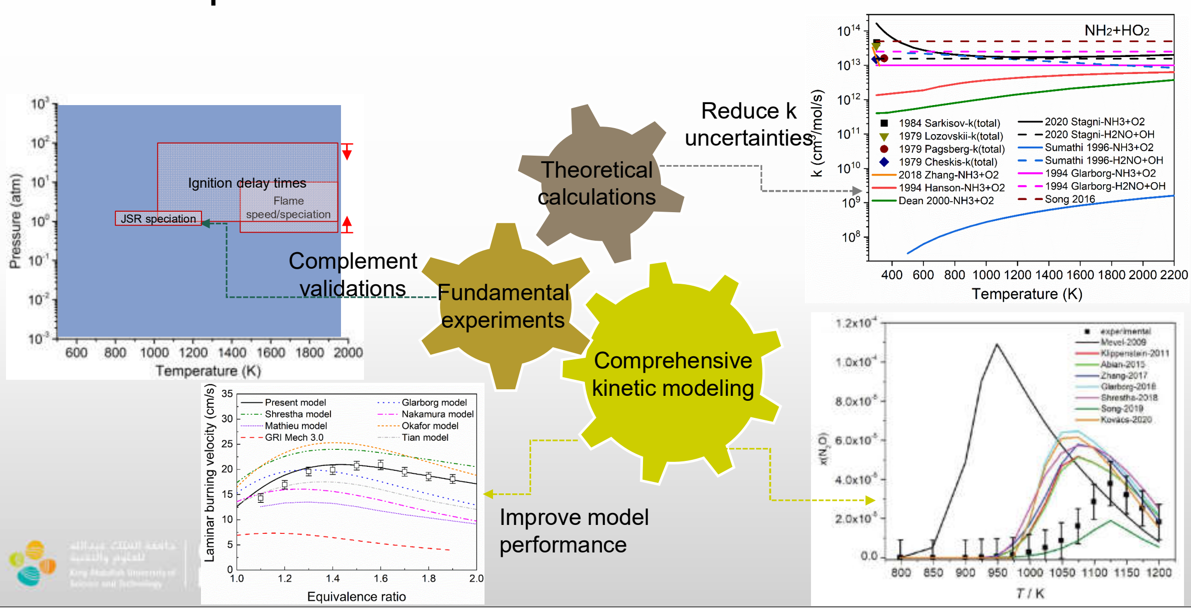
# Overview and comparison of four different ammonia oxidation mechanisms

| Mechanism | #species/ reactions | Subsets | Experiment type[a] | Mixtures | T (K) | P (bar) | Φ |
|---|---|---|---|---|---|---|---|
| Glarborg-Mech | 151/1395 | $H_2$/CO, C1-C2 hydrocarbon, amine and nitrogen | Flame spec [82] | $NH_3/O_2/Ar$ | Room temp | 0.046 | 0.71 |
| | | | FR spec [83] | $NH_3/CH_4/O_2$ | 900-1800 | 1.06 | 0.13, 1.07,1.55 |
| | | | ST IDT [81] | $NH_3/O_2/Ar$ | 1560-2500 | 1.4,10,30 | 0.5, 1.0, 2.0 |
| | | | RCM IDT [84] | $NH_3/CH_4/O_2/Ar/N_2$ | 900-1100 | 20, 40 | 0.5, 1.0, 2.0 |
| Stagni-Mech | 31/203 | Hydrogen/ amine | JSR/FR spec [74] | $NH_3/O_2/He$ | 500-2000 | 1 | 0.01-0.375 |
| | | | ST IDT [81] | $NH_3/O_2/Ar$ | 1560-2500 | 1.4, 10, 30 | 0.5, 1.0, 2.0 |
| | 156/2437 | C0-C3 Hydrocarbon/ amine | ST IDT [70] | $NH_3/O_2/N_2$ | 1100-1600 | 20-40 | 0.5-2.0 |
| | | | RCM IDT [62] | $NH_3/O_2/Ar$ | 1000-1130 | 40-60 | 0.5-2.0 |
| | | | JSR/FR spec [76] | $NH_3/CH_4/O_2/He$ | 500-2000 | 1 | 0.5, 1.0, 2.0 |
| Shrestha-Mech | 125/1099 | $H_2$, $H_2$/CO, $CH_4$/NOx/amine | FR spec [86] | $H_2/N_2O/NH_3/N_2$ | 995 | 3 | 2.2 |
| | | | Flame spec [87] | $NH_3$/NO/Ar | 298 | 0.07 | 1.46 |
| | | | Flame spec [88] | $NH_3/H_2/O_2/Ar$ | 298 | 0.05 | 1.0 |
| | | | ST IDT [81] | $NH_3/O_2/Ar$ | 1560-2500 | 1.4, 10, 30 | 0.5, 1.0, 2.0 |
| | | | $S_L$ [85] | $NH_3/O_2/He/N_2$ | 298, 323, 373 | 1 | 0.8-1.3 |
| | | | $S_L$ [35] | $NH_3/H_2$/air | 298, 473 | 1,3 | 0.8-1.4 |
| CEU-NH3 Mech | 91/445 | $H_2/CO/CH_4/CH_3OH/C_2H_5OH$/ amine | ST IDT [89] | $NH_3/CH_4$/air | 1400-1800 | 2, 5 | 0.5,1.0,2.0 |
| | | | ST IDT [81] | $NH_3/O_2/Ar$ | 1560-2500 | 1.4,10,30 | 0.5,1.0,2.0 |
| | | | $S_L$ [14, 37, 40] | $NH_3/H_2/CO/CH_4$/air | 298,348,398 | 1,3,5 | 0.7-1.5 |
| | | | Flame spec [90] | $NH_3$/NO/Ar | 298 | 0.07 | 1.46 |
| | | | FR spec [83] | $NH_3/CH_4/O_2$ | 900-1800 | 1.06 | 0.13, 1.07,1.55 |

ST: shock tube;
RCM: rapid compression machine;
JSR: jet-stirred reactor;
FR: flow reactor;
IDT: ignition delay time;
spec: speciation;
$S_L$: laminar burning velocity.

Elbaz, A.M., Guiberti, T., Wang, S., and Roberts, W.L., FUELCommunications 10 Mar 2022

# Development and refinement of mechanism

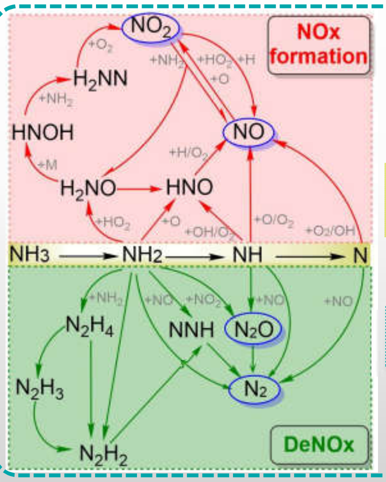


# Methods for Kinetic Model Development

**Base model**

- $H+O_2+R$=>Products: Burke and Klippenstein 2017
- $H_2$ model: Glarborg 2015
- Thermodynamic data: Active Thermochemical Table; Glarborg 2018

**Sub-mechanism of $NH_3$**




Evaluate the rate coefficient involved in N-related reactions

Recent progress in literature

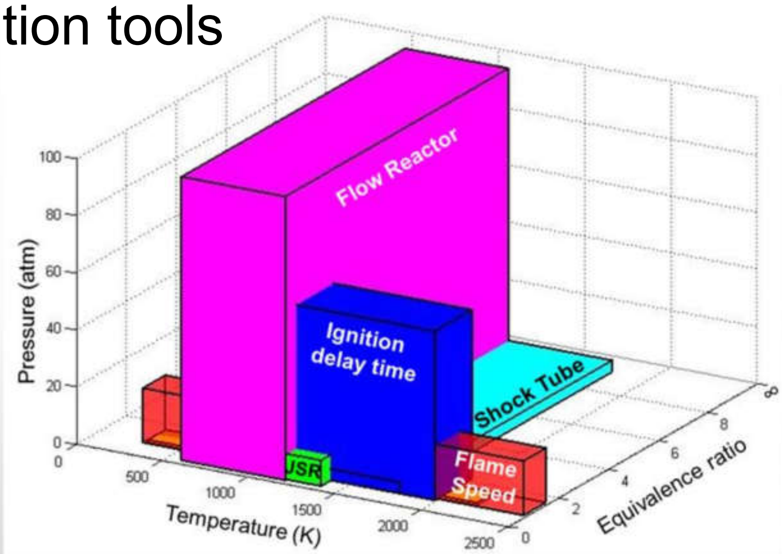
+

Comprehensive validation

Exp. data in literature



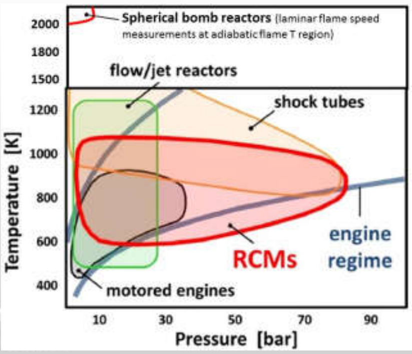
# Validation tools




Validation conditions

# Experimental Methodologies

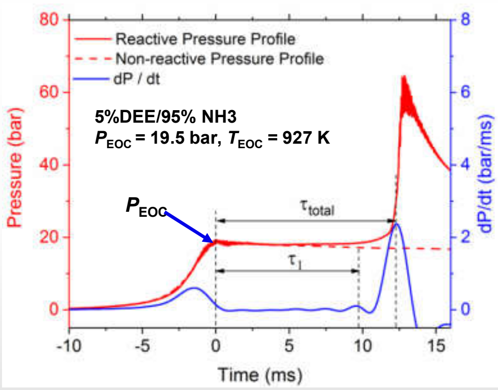
- **R**apid **C**ompression **M**achine (**RCM**):
  $T$ = 620 K – 942 K, $P$ = 20 and 40 bar, Φ = 0.5 and 1 for various ammonia ($NH_3$) and diethyl ether (DEE) blends
- **C**onstant **V**olume **S**pherical **R**eactor (**CVSR**):
  $T_i$ = 300 K, $P_i$ = 1, 3 and 5 bar and Φ = 0.8 to 1.3 for various $NH_3$/DEE blends




From Goldsborough et al, 2017



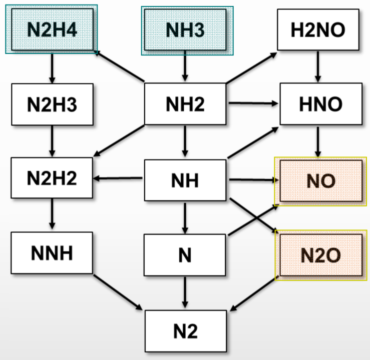
# A Typical Pressure Trace in RCM




- Ignition delay times (IDT) is defined as the time between end of compression and the maximum value of pressure derivative
- Uncertainty in compressed temperature ± 1 % → IDT = ±15 – 20 %

# Data for Model Validation

- ✓ Pyrolysis: $NH_3$ and $N_2H_4$
- ✓ $H_2/N_2O$; $H_2/NO$
- ✓ DeNOx mechanism: $NH_3/NO$; $NH_3/NO_2$
- ✓ $NH_3$ Oxidation
- ✓ $NH_3/H_2$ Oxidation






# Theoretical Studies of Ammonia Reactions

**Motivation**

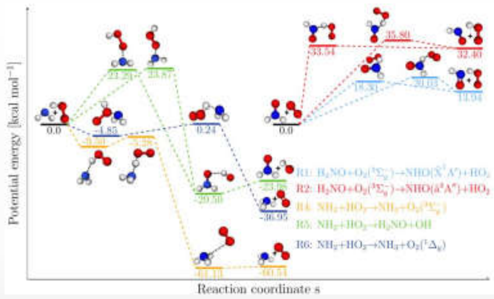
- Calculation of accurate rate constants and branching ratios for kinetic modeling of $NH_3/H_2$ oxidation

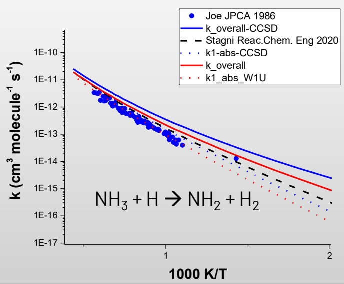
**Procedure**

- Geometry optimization at MP2/cc-pVTZ level of theory
- Single point calculation using G3, G4 and W1U composite methods and CCSD(T)/CBS level of theory
- Statistical rate theory for k(T)

**Results and Findings**

- Improved rates and branching ratios obtained for key $NH_3$ related reactions



# Outline of this lecture

- Basic structure to model development
- **Ammonia thermal decomposition**
- Ammonia oxidation
- Ammonia and Hydrogen
- Ammonia and DME, DEE
- Ammonia and higher hydrocarbons
- DeNOx mechanisms
- Pyrolysis of ammonia



# Decomposition of NH3

$$NH_3 \rightleftharpoons \frac{1}{2}H_2 + \frac{3}{2}N_2; \quad \Delta H = +45.6\ kJ/mol$$

$$R = A \times \exp\left[\frac{-E}{RT}\right] \times (P_{NH_3})^a (P_{H_2})^b \times (1-\beta^2) \rightarrow Temkin-Pyzhev\ Model$$

$$\beta = \frac{1}{K_{eq}} \times \frac{(P_{H_2})^{1.5}(P_{N_2})^{0.5}}{(P_{NH_3})}$$

$$K_{eq} = \left(\frac{p_{N_2} p_{H_2}{}^3}{p_{NH_3}{}^2}\right) = \frac{\Delta G}{RT}$$

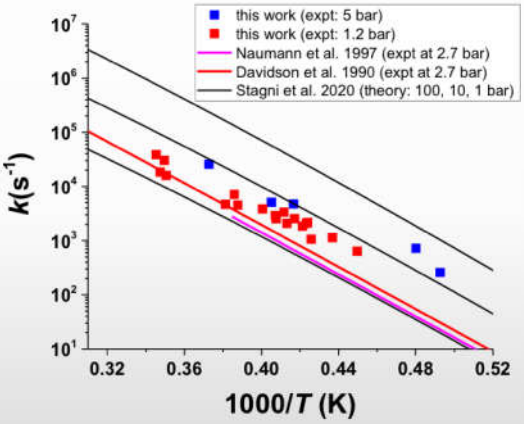
$$\Delta G = 95117 - 193.67T - 0.035293T^2 + 9.22e^{-6}T^3$$

***Source:***
*K. Lamb, S. S. Hla, and M. Dolan, "Ammonia decomposition kinetics over LiOH-promoted, A-Al2O3-supported Ru catalyst," Int. J. Hydrogen Energy, vol. 44, pp. 3726–3736, 2019.*

*S. Armenise, E. García-Bordejé, J. L. Valverde, E. Romeo and A. Monzón, "A Langmuir–Hinshelwood approach to the kinetic modelling of catalytic ammonia decomposition in an integral reactor" Phys. Chem. Chem. Phys., vol. 15(29), pp. 12104–12117, 2013.*

# Thermal Decomposition of Ammonia

- Rate coefficient of $NH_3 + M \rightarrow NH_2 + H + M$ experimentally measured using shock tube and UV laser diagnostic
- Rate coefficients will be further refined by considering the secondary chemistry (e.g., $NH_3 + H \rightarrow NH_2 + H_2$) and rationalized using high level ab initio/RRKM-ME calculations.
- <u>Future work</u>: unimolecular decomposition of $NH_2$ and $N_2H_x$ will be investigated.

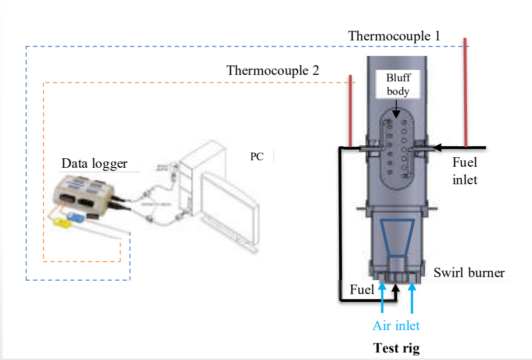


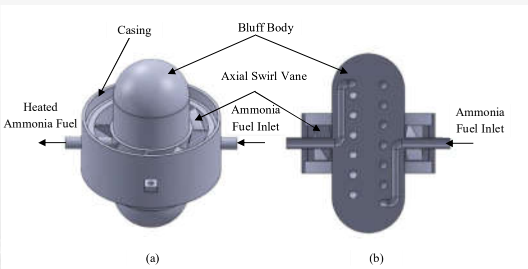

Clean Combustion Research Center



# Thermal Hydrogen Cracking

- Novel cracker system that employs energy from the combustion process to pre-crack ammonia.
- Reduced NOx emission levels by injecting a small percentage of the fuel mix into the region upstream of the cracker and downstream of the burner.




**N. Alboshmina, PhD Thesis, Cardiff Univeristy, 2019**

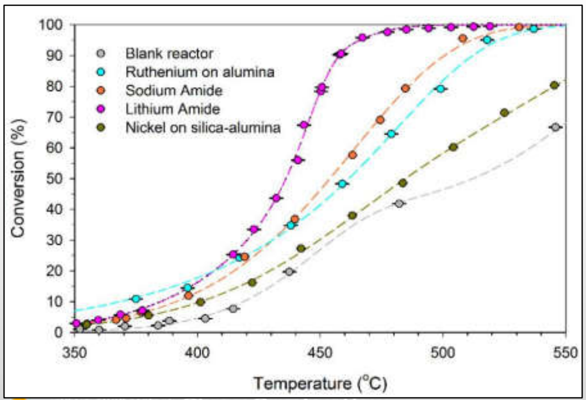
CARDIFF UNIVERSITY PRIFYSGOL CAERDYDD

# Ammonia Decomposition

$$NH_3 \rightleftharpoons \frac{1}{2}H_2 + \frac{3}{2}N_2; \quad \Delta H = +45.6\ kJ/mol$$

Thermodynamically favorable above 190°C at atmospheric pressure.

Significantly kinetically hindered, meaning that catalysts are required to promote the production of hydrogen.




However…

The immaturity of the ammonia decomposition technology is currently a limiting factor…

**Source:** *Siemens, "Ammonia to Green Hydrogen Project Feasibility Study"*



# Outline of this lecture

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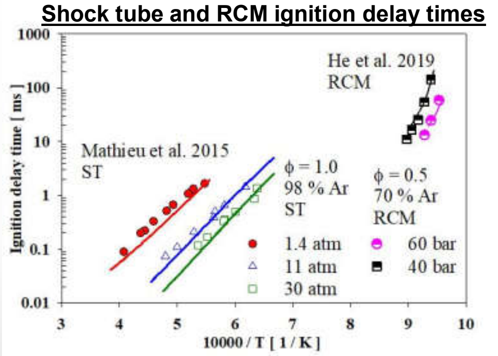
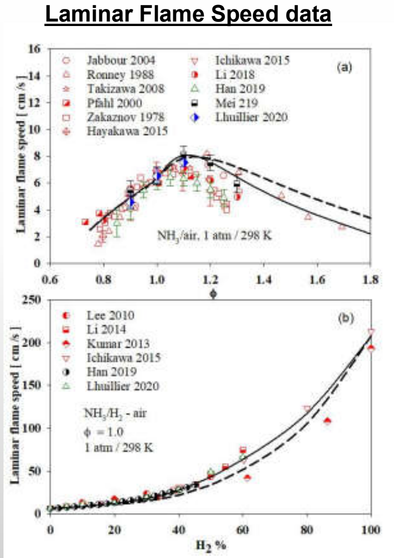
- Pyrolysis of ammonia

# Oxidation of Neat Ammonia ($NH_3$)

**Shock tube and RCM ignition delay times**




**Laminar Flame Speed data**



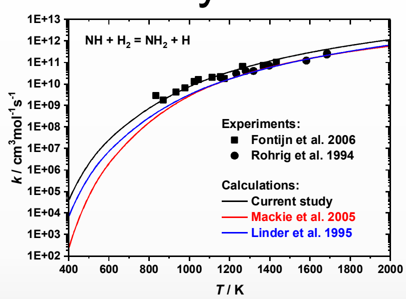

- Model prediction of ammonia ignition delay agree nicely with shock tube or rapid compression machine data
- Laminar flame speeds predictions, dashed line previous model (Shrestha et al. 2018) and solid line (current model) nicely capture experimental data from the literature.

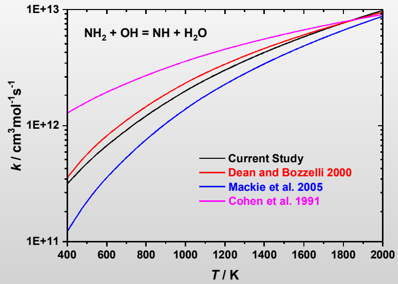


# $NH_3$ oxidation: High-temperature chemistry

**Validation**

| Fuel | Data type | T (K) | P (atm) | $\phi$ |
|---|---|---|---|---|
| NH3 | Flame speed | 298 | 1-5 | 0.6-1.5 |
| NH3 | Flame speed | 298-473 | 1 | 0.8-1.4 |
| NH3 | Flame speed | 298-473 | 1-10 | 0.8-1.3 |
| NH3 | Ignition delay | 1560-2455 | 1.4-30 | 0.5-2.0 |
| NH3 | Flow reactor | 1100-2000 | 1.25 | 0.375 |
| NH3 | Premixed Flame | 1500-2256 | 0.046 | 0.706 |

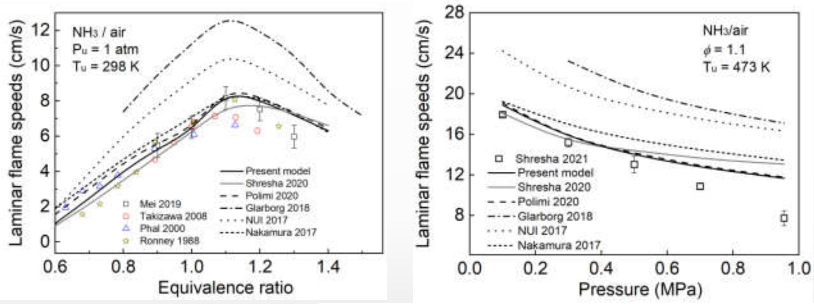




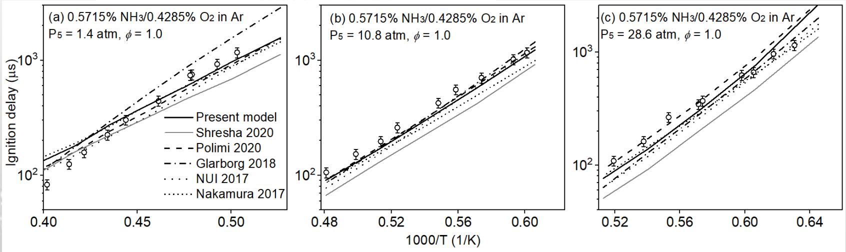
Y. Li et al., Int. J. Hydrog. Energy 45 (2020) 23624-23637.
B. Mei et al., Combust. Flame. 210 (2019) 236-246.
C. Lhuillier et al., Fuel 263 (2020) 116653.
K.P. Shrestha et al., Proc. Combust. Inst. 38 (2021).
O. Mathieu et al., Combust. Flame 162 (2015) 554-570.
A. Stagni. et al., React. Chem. Eng. 5 (2020) 696-711
J. Bian et al., Proc. Combust. Inst. 21 (1986) 953-963.

# $NH_3$ oxidation: High-temperature chemistry



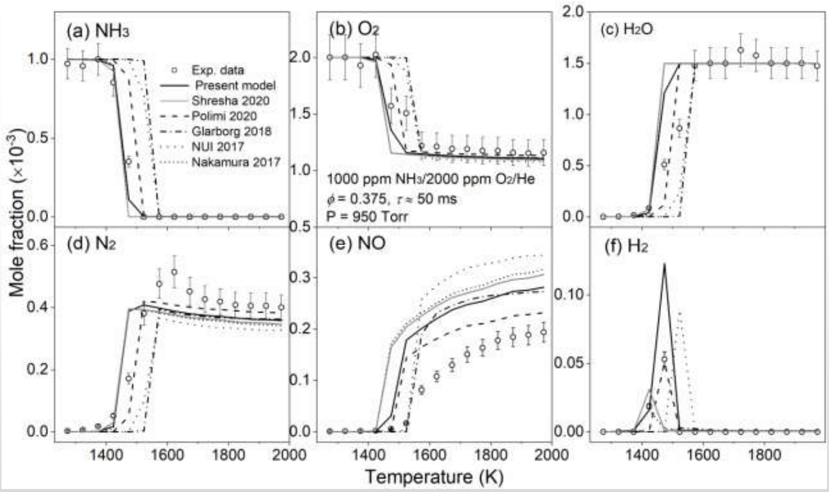
**Flame speed:**
KAUST, Shrestha, and Polimi models reasonably predict the experimental data

**Ignition delay:**
KAUST, Glarborg, Polimi, NUI, Nakamura models reasonably predict the experimental data



B. Mei et al., Combust. Flame. 210 (2019) 236-246.
K.P. Shrestha et al., Proc. Combust. Inst. 38 (2021).
O. Mathieu et al., Combust. Flame 162 (2015) 554-570.

# $NH_3$ oxidation: High-temperature chemistry



**Flow reactor oxidation:**
**Present**, Shresha 2020, **Polimi 2020** models reasonably predict the speciation data

A. Stagni. et al., React. Chem. Eng. 5 (2020) 696-711

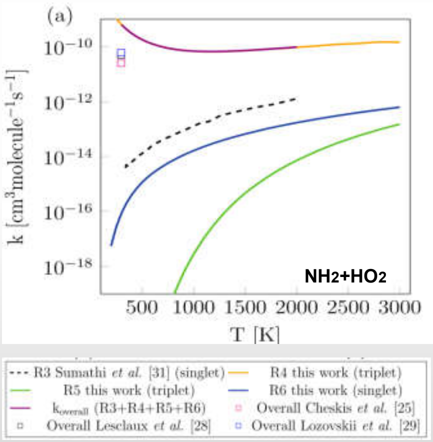
# $NH_3$ oxidation: Low- and intermediate-temperature chemistry

**Validation**

| Fuel | Data type | T (K) | P (atm) | $\phi$ |
|---|---|---|---|---|
| NH3 | JSR | 1100-1450 | 1 | 0.1-2.0 |
| NH3 | JSR | 500-1200 | 1.03 | 0.009-0.019 |
| NH3 | Flow reactor | 450-925 | 30-100 | 0.22-1.04 |
| NH3 | Ignition delay | 1100-1600 | 20-40 | 0.5-2.0 |
| NH3 | Ignition delay | 950-1150 | 20-60 | 0.5-2.0 |

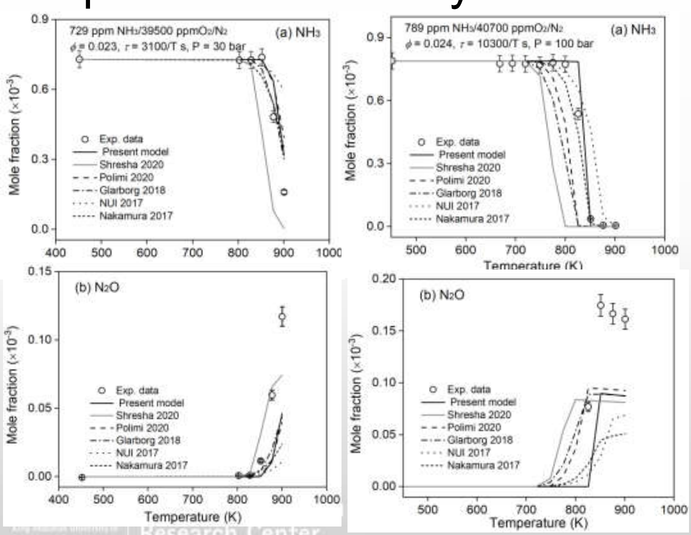
- R4 (triplet)/R6 (singlet): $NH_2 + HO_2 \rightarrow NH_3 + O_2(^3\Sigma_g^-)/O_2(^1\Delta_g)$
- R5 (triplet): $NH_2 + HO_2 \rightarrow H_2NO + OH$, excited PES but $H_2NO$ is ground state

P. Dagaut, Combust. Sci. Technol. (2019) 1-13.
A. Stagni. et al., React. Chem. Eng. 5 (2020) 696-711.
Y. Song et al., Fuel 181 (2016) 358-365.
B. Shu, et al., Proc. Combust. Inst. 37 (2019) 205-211.
X. He et al., Combust. Flame 206 (2019) 189-200.




J.E. Chavarrio et al., Combust. Flame, (2021) 111708.

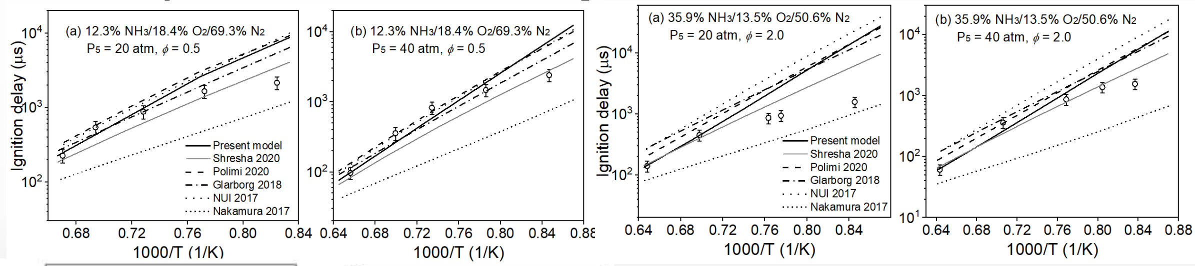
# $NH_3$ oxidation: Low- and intermediate-temperature chemistry

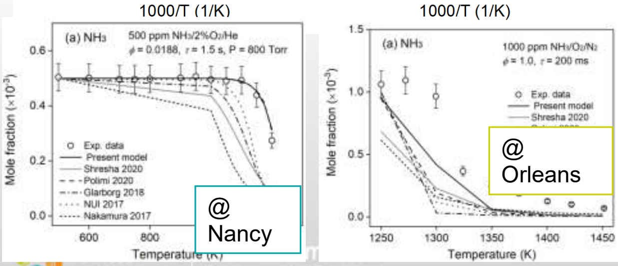



**Flow reactor oxidation:**
**Present** and **Nakamura 2017** models reasonably predict the oxidation rate of fuel at 30 and 100 bar;
All the models under-predict the formation of N2O

Y. Song et al., Fuel 181 (2016) 358-365.

# $NH_3$ oxidation: Low- and intermediate-temperature chemistry




**IDT:**
Except Nakamura model, other models can reasonably predict the exp. data
**JSR oxidation:**
KAUST model has good performance

P. Dagaut, Combust. Sci. Technol. (2019) 1-13; A. Stagni. et al., React. Chem. Eng. 5 (2020) 696-711.
B. Shu, et al., Proc. Combust. Inst. 37 (2019) 205-211.

# Outline of this lecture

- Basic structure to model development
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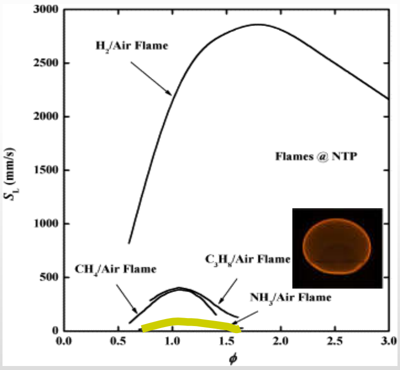
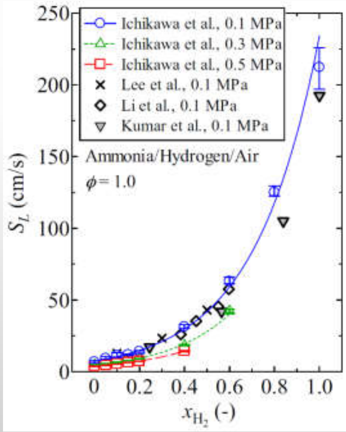
# Why blend?

- $NH_3$ (low reactivity) : low laminar flame speed, a narrow flammability range




- $H_2$ (high reactivity) : high laminar flame speed, wide flammability range, safety concerns

- Blending $NH_3/H_2$ mixtures
  - ✓ produce zero carbon emissions
  - ✓ enhances the intensity of NH3 combustion
  - ✓ diminishes safety concerns of H2




# $NH_3/H_2$ Kinetic Modeling

**Model validation**

- Validated against comprehensive data involved in $NH_3$, $N_2H_4$, $H_2/N_2O$, $H_2/NO$, $H_2/NH_3$
- New Jet Stirred Reactor at intermediate temperatures
- Better performance against present data

**Model development**

- Evaluate the source of rate constants
- Examine the agreements among different sources
- Evaluate/estimate the uncertainties of kinetic data

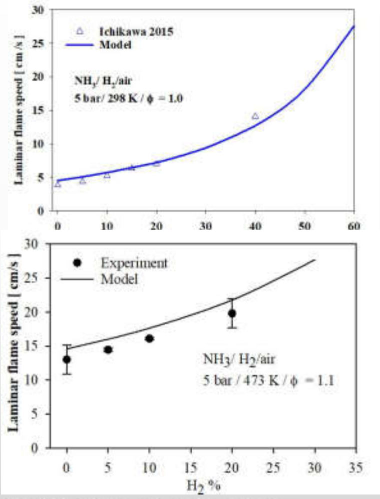
# $NH_3/H_2$ oxidation Validation

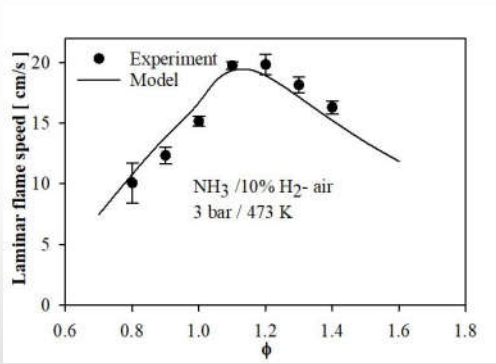
**Validation**

| Fuel | Data type | T (K) | P (atm) | $\phi$ |
|---|---|---|---|---|
| NH3/H2 | Flame speed | 298-473 | 1 | 0.8-1.4 |
| NH3/H2 | Flame speed | 298 | 1-5 | 1.0 |
| NH3/H2 | Flame speed | 473 | 1-10 | 0.8-1.4 |
| NH3/H2 | Flame speed | 298 | 1-5 | 0.7-1.6 |
| NH3/H2 | Ignition delay | 950-1150 | 20-60 | 0.5-2.0 |
| NH3/H2 | JSR | 800-1280 | 1 | 0.25-1.0 |
| NH3/H2 | Premixed flame | 400-2000 | 0.05-0.12 | 0.9-1.1 |

C. Lhuillier et al., Fuel 263 (2020) 116653.
K.P. Shrestha et al., Proc. Combust. Inst. 38 (2021).
A. Ichikawa et al., Int. J. Hydrog. Energy 40 (2015) 9570-9578.
S. Wang et al., Combust. Flame 221 (2020).
X. He et al., Combust. Flame 206 (2019) 189-200.
X.Y. Zhang et al., Combust. Flame 2021. 111653.
C. Duynslaegher et al., Proc. Combust. Inst. 32 (2009) 1277-1284.

# Model Predictions of $S_L$ of Various $NH_3/H_2$ Blends

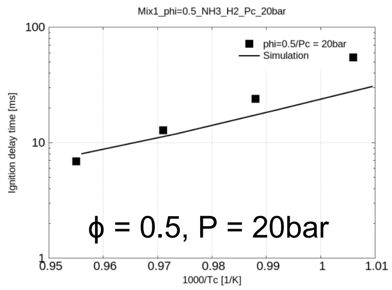


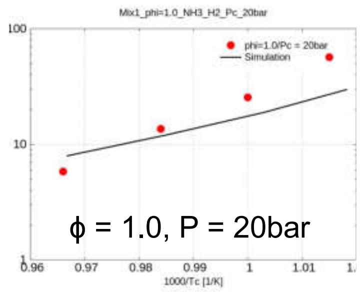



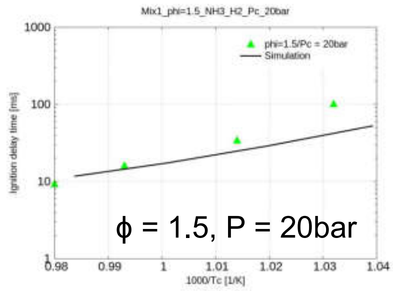

- fuel equivalence ratios dependence at elevated pressure and temperature.

- **Elevated pressure, temperature and different $H_2$ content**

## Model Predictions of IDT of Various $NH_3/H_2$ Blends



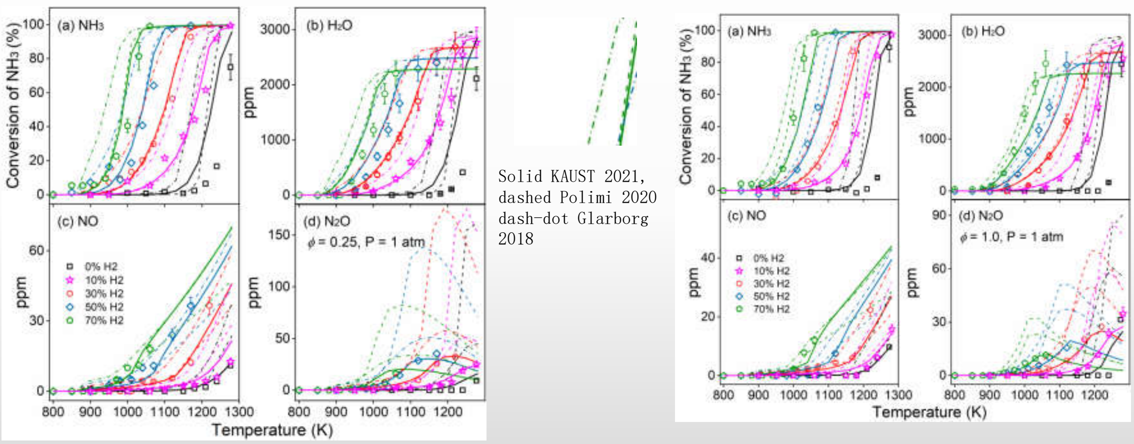




- Model captures nicely the ignition delay times of $NH_3/H_2$ blends measured in RCM by He et al. 2019 for different equivalence ratio.

## $NH_3/H_2$ oxidation Validation

JSR oxidation of NH3/H2 mixtures with various H2 content at eq rat 0.25, 1 s, and 1 atm.

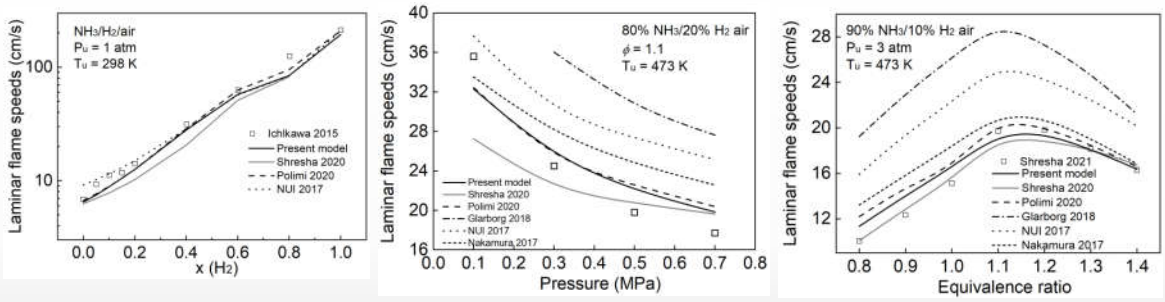



Solid KAUST 2021,
dashed Polimi 2020
dash-dot Glarborg 2018

**JSR oxidation:**
KAUST 2021 model has good performance

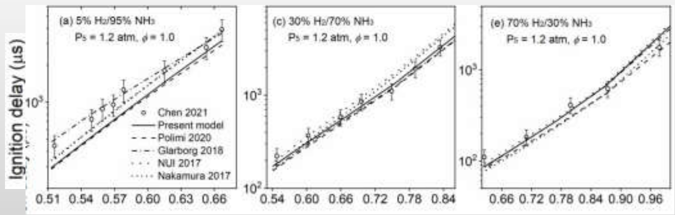
X.Y Zhang et al., Combust. Flame 234 (2021) 111653.

# NH$_3$/H$_2$ oxidation



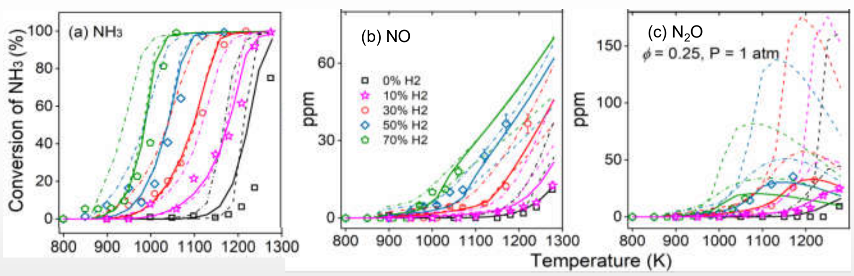

**Flame speed:**
**Present** and **Polimi 2020** models reasonably predict the exp. data

**IDT:**
All the models can predict the ignition delay of NH3/H2 mixture




K.P. Shrestha et al., Proc. Combust. Inst. 38 (2021).
A. Ichikawa et al., Int. J. Hydrog. Energy 40 (2015) 9570-9578.

# JSR data, NH$_3$/H$_2$ mixtures




Symbols: Present experimental data
Solid lines: Present model, broken lines: literature models

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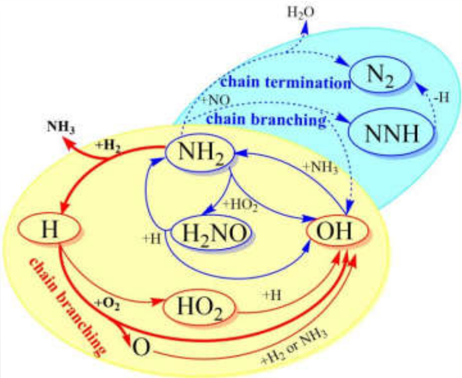
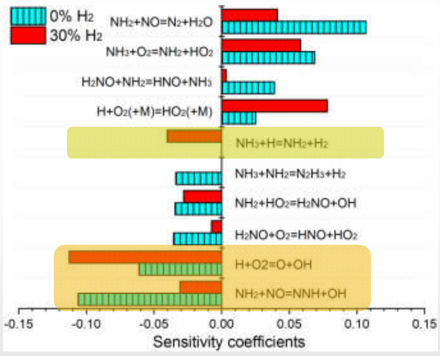
# Effects of $H_2$ blending on $NH_3$ conversion

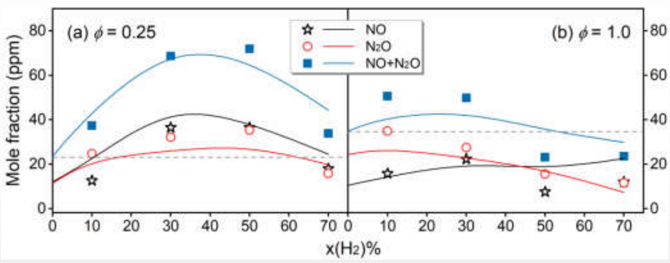


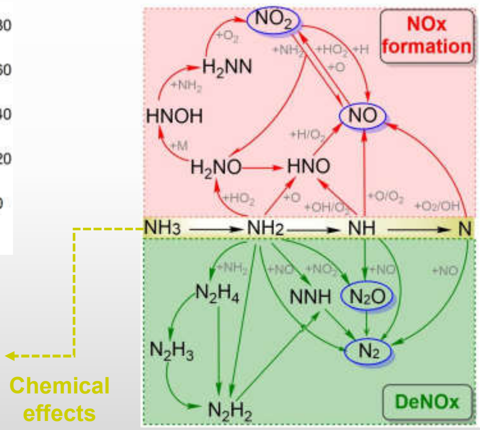




- ✓ Enhance $NH_2+H_2=NH_3+H$, $H+O2=O+OH$, $H+O_2(+M) = HO_2(+M)$, $NH_2+HO_2=H_2NO+OH$, $H_2NO+H=NH_2+OH$
- ✓ Inhibit $NH_2+NO=NNH+OH/N_2+H_2O$
- ✓ Chain-branching reaction is changed

X.Y Zhang et al., Combust. Flame 234 (2021) 111653.

# Effects of $H_2$ blending on $NO_x$ formation



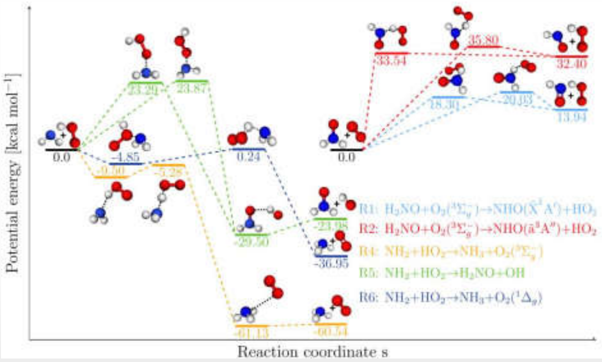




Dilution effects reduce $NO_x$ formation thermal effects are neglected

- ✓ More oxygenated radicals inhibit $NH_2+NO=NNH+OH/N_2+H_2O$, i.e. $DeNO_x$ paths, while enhance the $NH_2+O/HO_2$, $NH+OH/O$, i.e. $NO_x$ formation paths
- ✓ More NO can enhance the formation of $N_2O$ via $NH+NO=N_2O+H$

X.Y Zhang et al., Combust. Flame 234 (2021) 111653.

# Theoretical calculations




**Target reactions**

| |
|---|
| $NNH \leftrightarrow N_2 + H$ |
| $N_2H_2 + H \leftrightarrow NNH + H_2$ |
| $N_2H_2 + O \leftrightarrow NNH + OH$ |
| $NH_2 + H \leftrightarrow NH + H_2$ |
| $NH_2 + OH \leftrightarrow NH + H_2O$ |
| $NH_2 + OH \leftrightarrow NH + H_2O$ |
| $H_2NO + O_2 \leftrightarrow HNO + HO_2$ |

Multi-reference character: CCSDT(Q) and W3X-L methods;
Spin contamination: ROCCSD and ROCCSD(T)
Kinetic rate constant: VTST + tunneling + multi-structural anharmonicity corrections

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Y. Li et al., Int. J. Hydrog. Energy 45 (2020) 23624-23637.
J.E. Chavarrio et al., Combust. Flame, (2021) 111708.

# Ammonia Mechanism Reduction

Original mechanism
Zhang et al., 38 species and 263 reactions

Skeletal mechanism developed via CSP analysis
Khamedov et al., 26 species and 175 reactions

Coverage: blends of $NH_3$ and $H_2$ at a wide range of $P$, $T$, and $\varphi$

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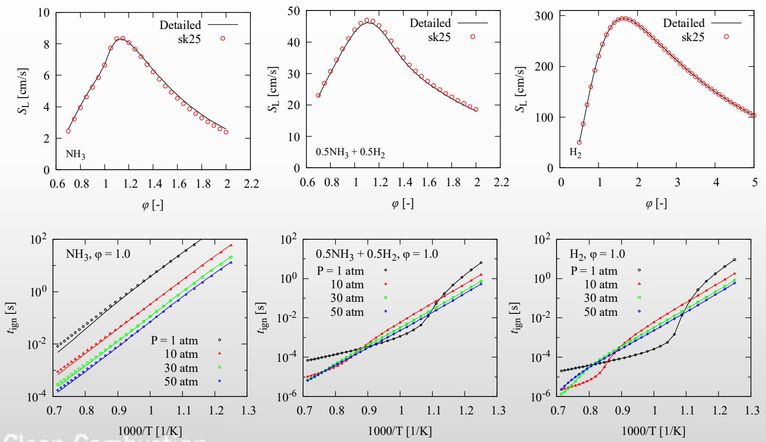
# Mechanism reduction, validation

Validation of laminar flame speed ($S_L$) and ignition delay time ($t_{ign}$)

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# Outline of this lecture

- Basic structure to model development
- Ammonia thermal decomposition
- Ammonia oxidation
- Ammonia and Hydrogen
- **Ammonia and DME, DEE**
- Ammonia and higher hydrocarbons
- DeNOx mechanisms
- Pyrolysis of ammonia

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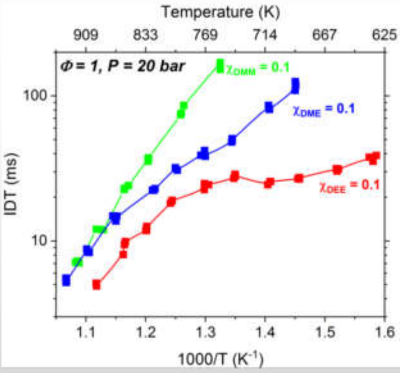
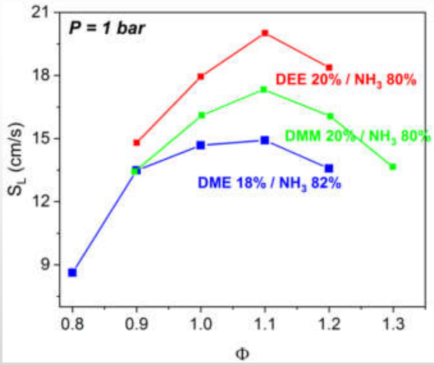
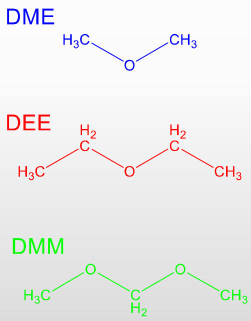
# Reactivity Enhancement of Various Ethers

- Among the three ethers, DEE is found to be the most effective in promoting the reactivity of ammonia. $\chi_{DEE} = 0.1$ blend exhibited similar reactivity as a representative gasoline

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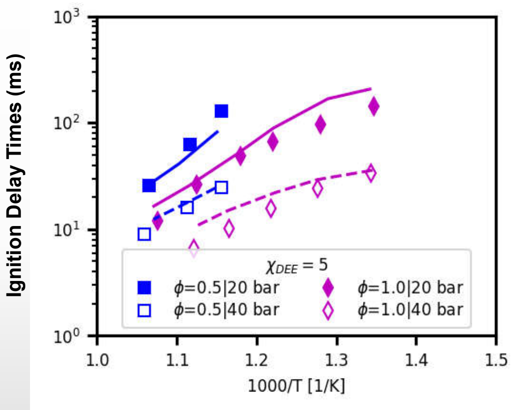
G. Issayev, PhD Thesis, KAUST 2021



# IDTs($P, \phi$) for higher $\chi_{DEE}$ Blends




- Our IDTs data exhibits strong ***P***, **$\phi$** dependence.
- IDTs shortened by a factor of ~5 by increasing pressure from 20 bar to 40 bar for a given **$\phi$** and ***T***; however, the effect of **$\phi$** is not as strong as ***T***.
- Our model remarkably captures the ***P***, **$\phi$** dependence of the IDTs of $NH_3$-DEE blends.

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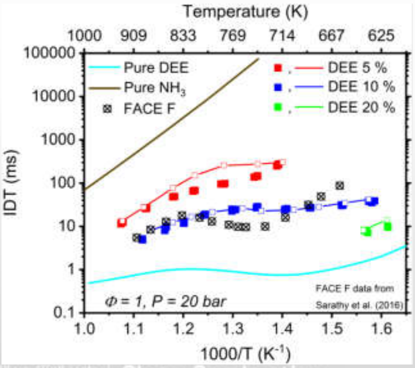
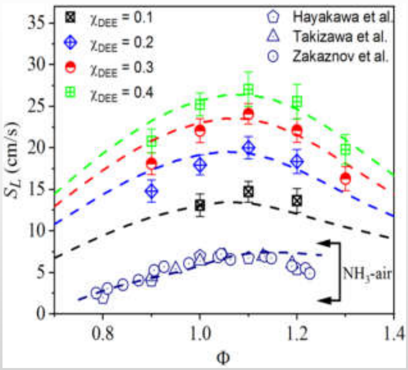
# Blending of NH3 with Diethyl Ether (DEE)

- IDTs of $NH_3$ are greatly enhanced by the addition of DEE as small as $\chi_{DEE} = 0.05$
- The decrease in IDTs with increasing DEE content is mainly due to the promotion of OH, H and $HO_2$ radicals coming from DEE chemistry
- Burning velocities ($S_L$) of the $NH_3$/DEE blends increase with increasing $\chi_{DEE}$ for a given $\Phi$

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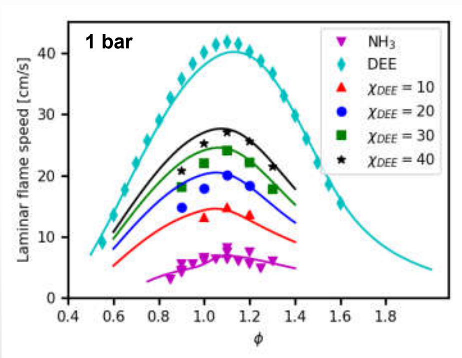
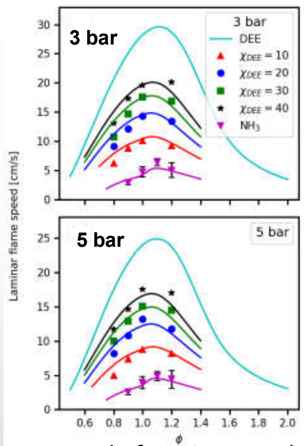
Issayev et al., PROCI, 2021



# Laminar Flame Speed (LFS) of Various $\chi_{DEE}$

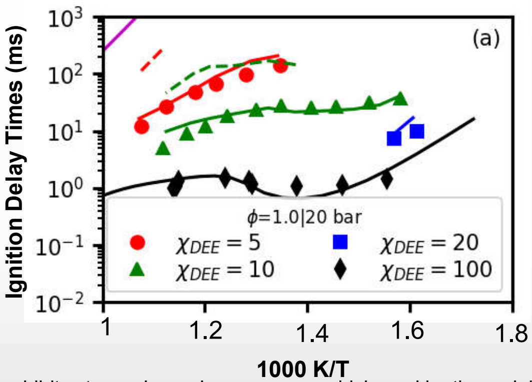



- ➢ As expected, DEE addition increases the flame speed of neat ammonia → higher the $\chi_{DEE}$ more the LFS of $NH_3$/DEE blends.
- ➢ Even $\chi_{DEE}$ = 10 enhances the LFS of $NH_3$ by a factor of 2 at 1 bar and 298 K. Our kinetic model captures the experimental data reasonably well.

Research Center

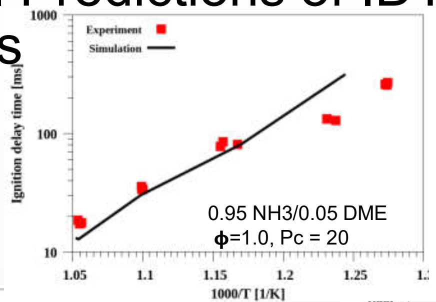
# Ignition Delay Times (IDTs) of $NH_3$/DEE Blends

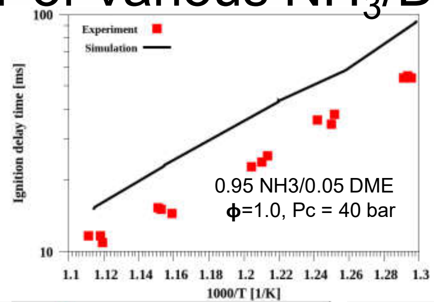


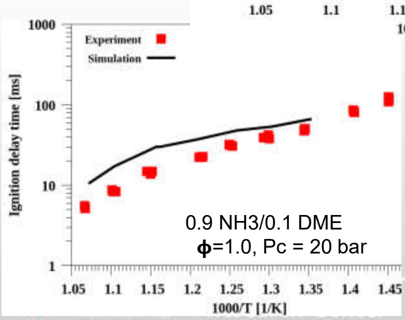

- Our data exhibits strong dependence on $\chi_{DEE}$ which our kinetic model captures satisfactorily.
- Cross-reactions are critical to accurately predict IDTs.
- The decrease of IDTs with increasing DEE is mainly due to the promotion of OH, H and $HO_2$ in the system.
- IDTs of $\chi_{DEE} = 20$ is marginally longer than neat DEE.

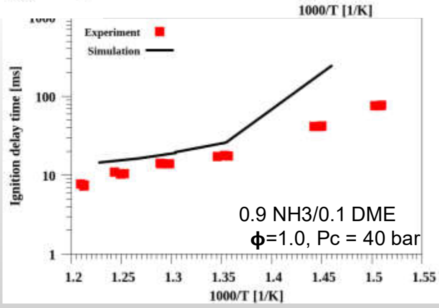


# Model Predictions of IDT of Various $NH_3$/DME Blends

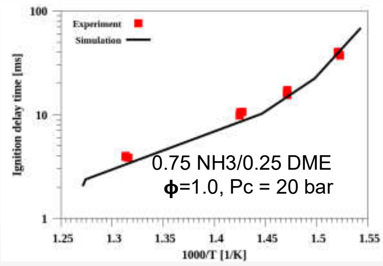


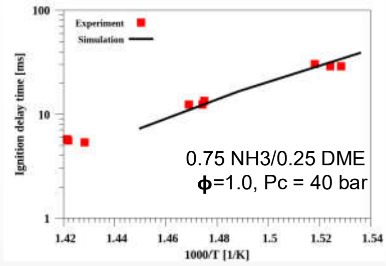



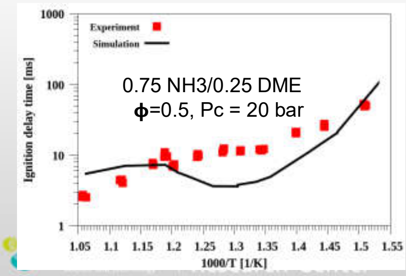



# IDT at higher DME fractions

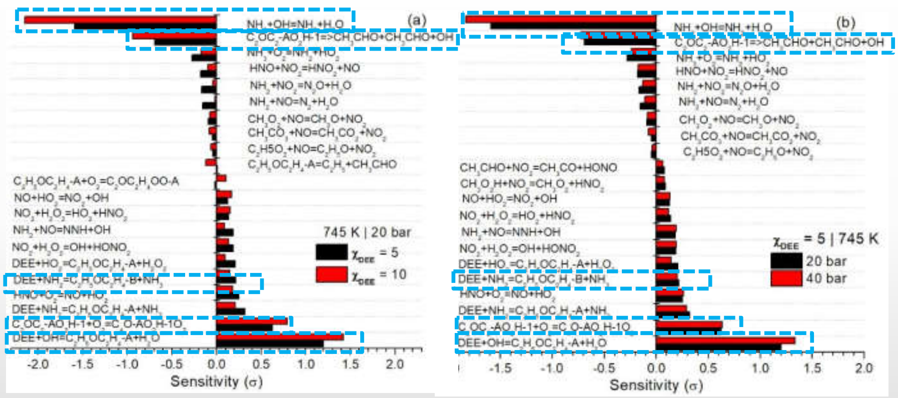



- Some experiment may need to be repeated. Modeling results reveal a clear NTC behavior in contrast to the experimental data.

# Low-*T* Reaction Sensitivity Analyses



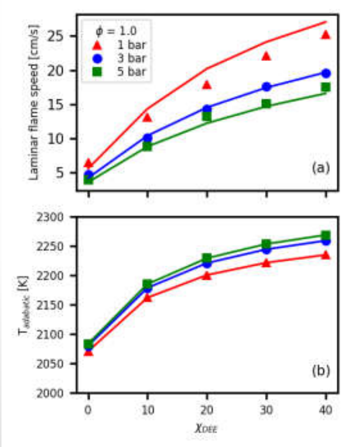

- The reactions of OH radicals with DEE and $NH_3$ are the topmost sensitive. The former promotes the reactivity while the latter retards it.
- The sensitivity of these reactions increases with $\chi_{DEE}$ **and *P*.**

# Pressure Dependence of LFS of Various $\chi_{DME}$

$$\mathbf{LFS} \propto \sqrt{\alpha \times RR}$$

Thermal diffusivity

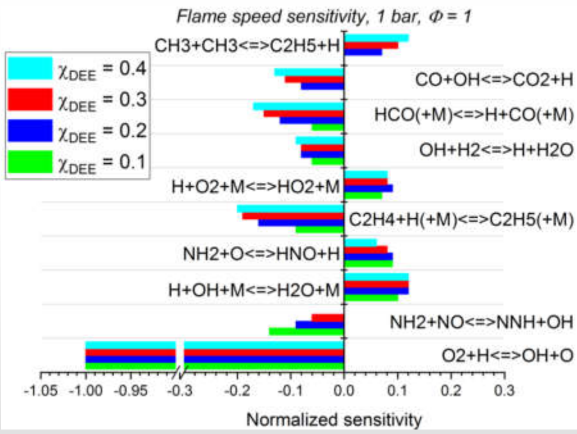
Rate of Reaction




- As expected, DEE content strongly impact the flame temperature ($T_{ad}$), hence the laminar flame speed (LFS).
- Clearly, LFS is greatly reduced by increasing initial pressures which our kinetic model captures reasonably.

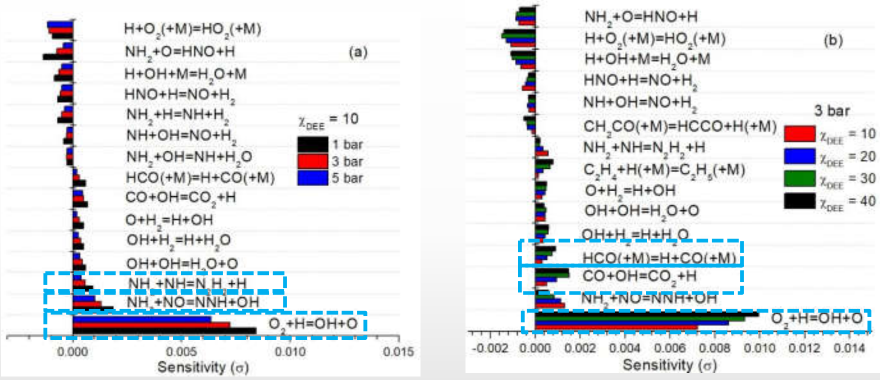


# Sensitivity Analysis




- The DEE related radicals were found to increase the reactivity, whereas $NH_3$ related radicals inhibit the overall reactivity.
- Flame speed is mainly governed by OH, C0-C2 and NH2 species.

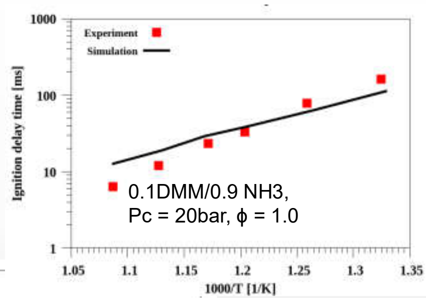
# Reaction Sensitivity Analyses of Various $\chi_{DEE}$

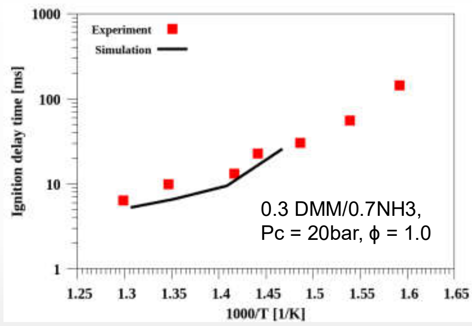


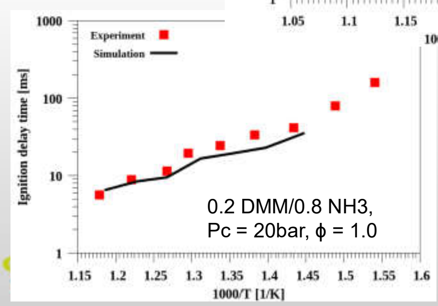

- The main H and OH producing channels are enhanced with higher $\chi_{DEE}$ .
- H and OH forming channels are suppressed at higher pressures.
- $H_2$/CO core mechanism show increasing dominance with increasing $\chi_{DEE}$.



# Model Predictions of IDT of Various $NH_3$/DMM Blends




- Symbols (current experimental data); lines (current model predictions)
- Model does a decent job; however, more data are needed for further model validation.

# Outline of this lecture

- Basic structure to model development
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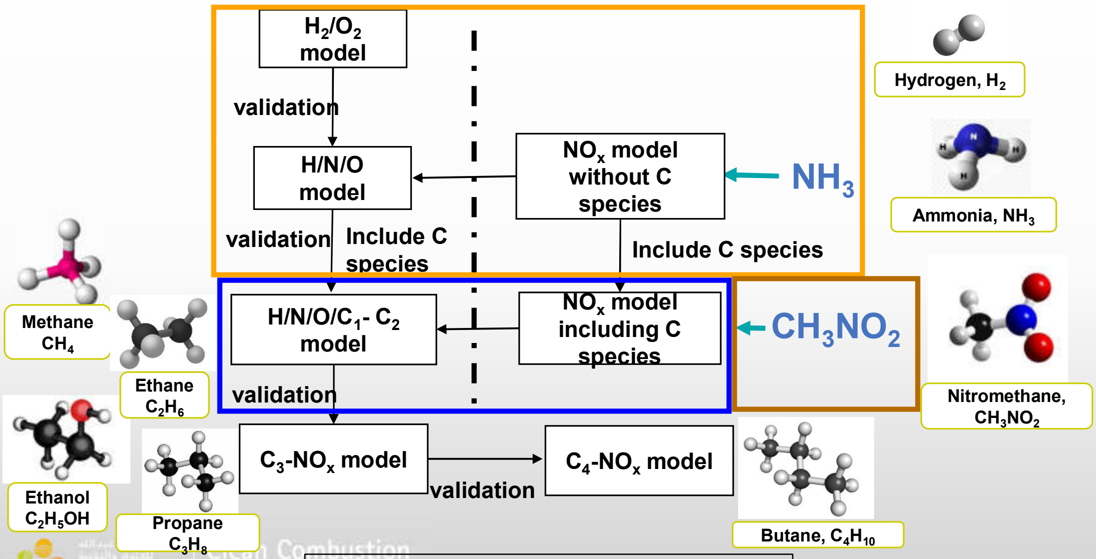
- Ammonia and DME, DEE
- **Ammonia and higher hydrocarbons**
- DeNOx mechanisms
- Pyrolysis of ammonia

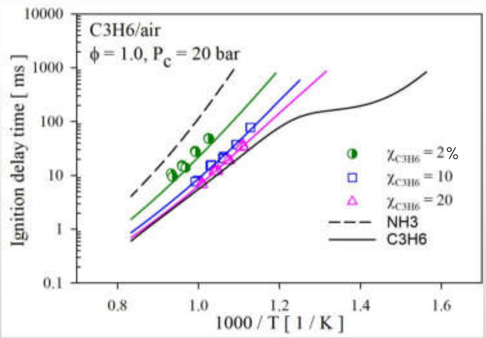
# Detailed Chemical Kinetic Model Development

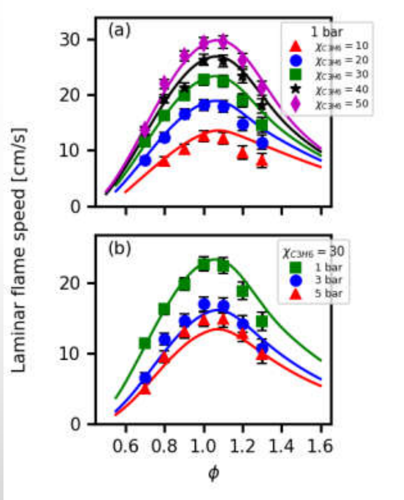



Shrestha et al. *Combustion & Flame 218 , 2020, 57- 74*

# Blending of Ammonia with Propene

- Propene ($C_3H_6$) is found found to be a very effective additive
- As low as 2% propene accelerates the ignition behavior of $NH_3$ by roughly three times

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- Basic structure to model development
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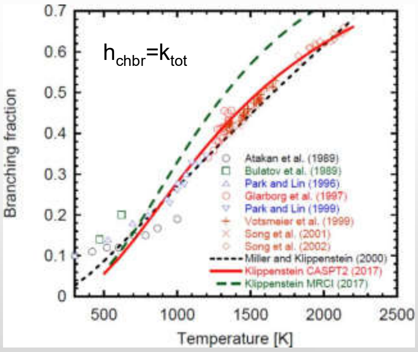
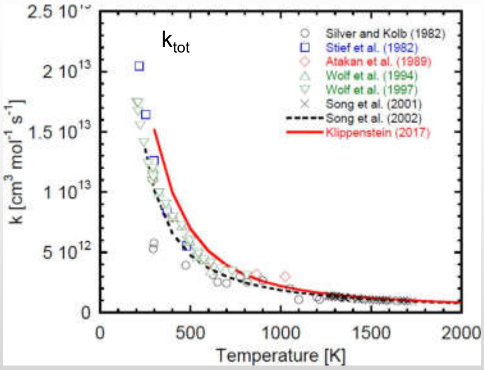
# DeNOx mechanism: $NH_3$/NO

Critical reactions

NH2+NO = NNH+OH chain branching reaction
NH2+NO = N2+H2O chain termination reaction





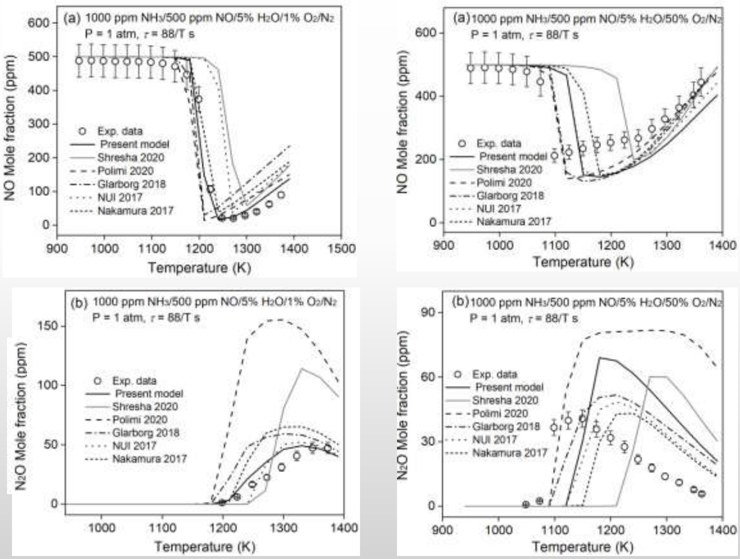

# DeNOx Targets

| Fuel | Data type | T (K) | P (atm) | $\phi$ |
|---|---|---|---|---|
| NH3/NO | Flame speed | 298 | 1 | 1.0-2.0 |
| NH3/NO | Flame speed | 298 | 1 | 0.1-4.0 |
| NH3/NO | JSR | 1100-1450 | 1 | 0.1-2.0 |
| NH3/NO | JSR | 1000-1400 | 1 | 0.016 |
| NH3/NO | Flow reactor | 920-1380 | 1 | 0.002 |
| NH3/NO | Flow reactor | 940-1400 | 1 | 0.0016-0.08 |
| NH3/NO | Premixed Flame | 1500-2100 | 0.071 | 1.46 |


P. Glarborg et al, Prog. Ener. Comb. Sci., (2018)
B. Mei et al., Proc. Combust. Inst. 38 (2021).
M.D. Checkel et al., Journal of Loss Prevention in the Process Industries 8 (1995) 215-220.
P. Dagaut, Combust. Sci. Technol. (2019) 1-13.
R. Rota et al., Combust. Sci. Technol. 163 (2001) 25-47.
F. Kasuya et al., Chemical Engineering Science 50 (1995) 1455-1466.
J. Vandooren et al., Combust. Flame 98 (1994) 402-410.

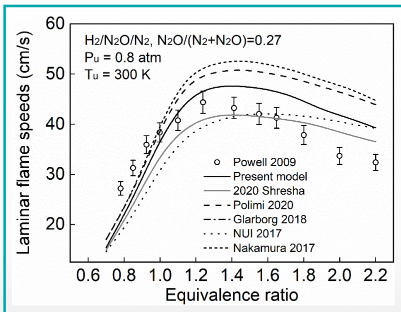
# DeNOx mechanism: $NH_3$/NO

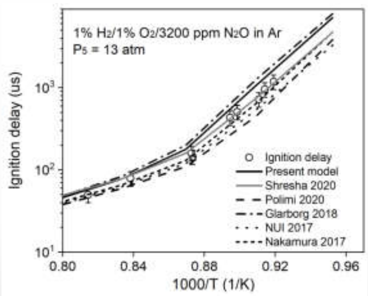
Glarborg 2018 model has the best performance;
KAUST 2021 model performs reasonably well;
Shrestha 2021 model predicts a lower oxidation reactivity



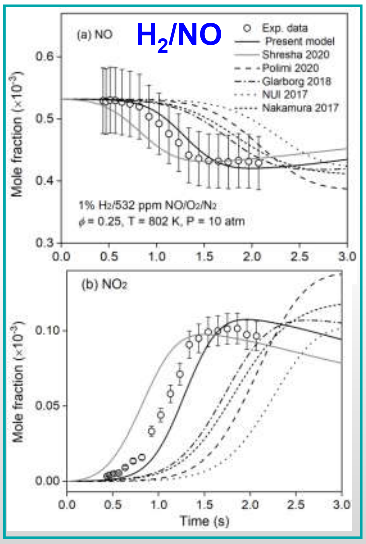

B. Mei et al., Proc. Combust. Inst. 38 (2021).
F. Kasuya et al., Chemical Engineering Science 50 (1995) 1455-1466.

# Submechanisms of $N_2O$ and NO




$H_2$/N2O




Present and Shrestha 2020 models reasonably predict the experimental data.

O.A. Powell et al., Combust. Sci. Technol. 181 (2009) 917-936.
O. Mathieu et al., Int. J. Hydrog. Energy., 37 (2012) 15393-15405.
M.A. Mueller et al., Int. J. Chem. Kinet. 31 (1999) 705-724.

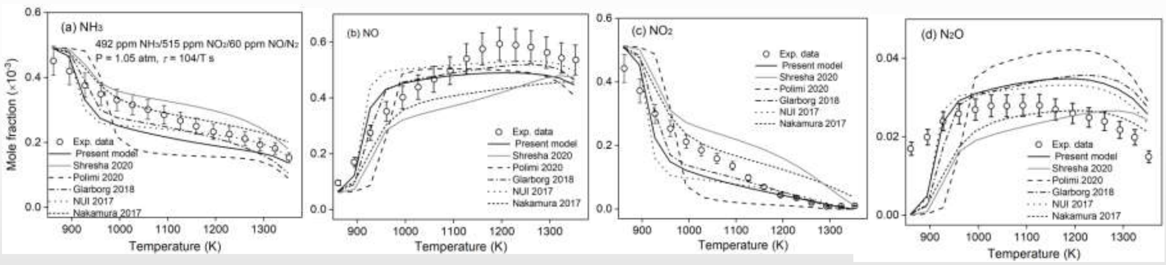
# DeNOx mechanism: $NH_3/NO_2$

## Validation

| Fuel | Data type | T (K) | P (atm) | $\phi$ |
|---|---|---|---|---|
| NH3/NO2 | Flow reactor | 850-1350 | 1 | ∞ |

## Critical reactions

NH2+NO2 = H2NO+NO
NH2+NO2 = N2O+H2O



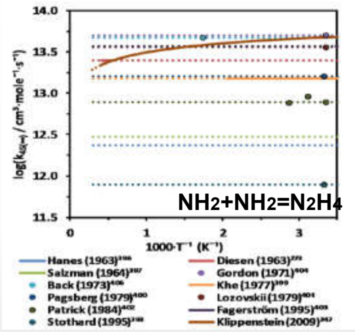

Glarborg 2018 model has the best performance;
Present, NUI 2017, Nakamura 2017 model perform reasonably well;
Shresha 2020 model predicts a slightly lower oxidation reactivity;
Polimi 2020 model predicts a higher oxidation reactivity

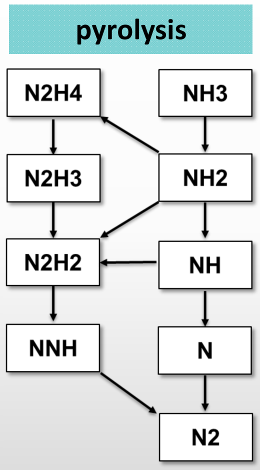
P. Glarborg et al., Int. J. Chem. Kinet. (1995) 1207-1220

# Pyrolysis of $NH_3$ and $N_2H_4$

## Critical reactions

**NH3+M = NH2+H+M**
**NH2+NH2+M=N2H4+M** hydrazine
**NH2+NH = N2H2+H** diazine



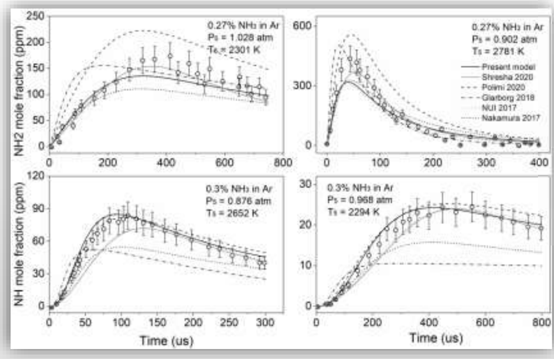



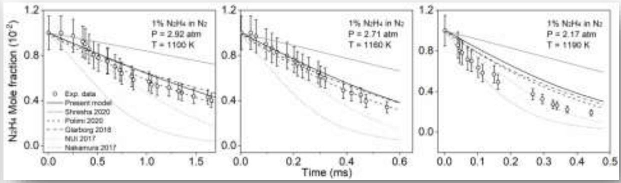

## Validation

| Fuel | Data type | T (K) | P (atm) | $\phi$ |
|---|---|---|---|---|
| NH3 | Pyrolysis | 2300-2800 | 1 | ∞ |
| N2H4 | Pyrolysis | 1100-1190 | 2-3 | ∞ |

D.F. Davidson et al., Int. J. Chem. Kinet. 22 (1990) 513-535.
C. Halat-Augier et al., Abstr. Symp. Pap., (1994).

# Pyrolysis of $NH_3$ and $N_2H_4$

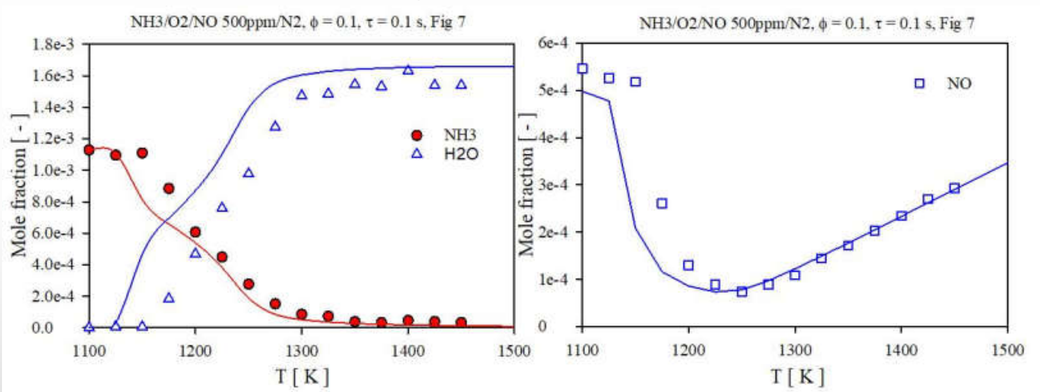



**N2H4 Pyrolysis:**
KAUST 2021, Polimi 2020, Glarborg 2018, and NUI 2017 models reasonably predict the speciation data.

**NH3 Pyrolysis:**
KAUST 2021, Shrestha 2021, and NUI 2017 models reasonably predict the speciation data.

# Oxidation of $NH_3$ in Presence of NO: Jet Stirred Reactor Experiments vs. Modeling




- ➢ Symbols: experimental data from Dagaut 2019; lines: current model prediction
- ➢ It will be interesting to validate the engine data (e.g., EGR process).

# Conclusions

- Significant advances have been made in studying ammonia combustion chemistry
- Various kinetic models provide good predictions for $NH_3$ pyrolysis and oxidation. Focus on $H_2$ blending needs attention.
- $H_2$ blending promotes the conversion of $NH_3$ at given temperatures
- Effects of blending $NH_3$ and $H_2$ with hydrocarbon fuels warrants further investigation

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شكرا

THANK YOU!

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# Lecture 3: Premixed ammonia flames

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Tsinghua Summer School
Center for Combustion Energy
Tsinghua University, Beijing
14-15 July 2022



# Outline of L-3

- **Laminar flame speeds**
  - **Methods**
  - **Cellularity**
- Swirl flames of $NH_3$ mixtures
  - Stability limits
  - NOx
- Gas Turbine combustors
  - Ansaldo mGT
  - Double Swirl Burner

# Combustion properties

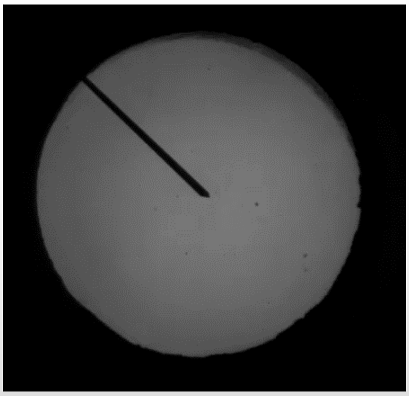
| | | | | |
|---|---|---|---|---|
| Fuel | $NH_3$ | $H_2$ | $CH_4$ | $C_3H_8$ |
| Maximum burning velocity (cm/s) | 7 | 291 | 37 | 43 |
| Lower calorific value (MJ/kg) | 18.6 | 120 | 50 | 46.4 |
| Flammability limit (in terms of $\Phi$) | 0.63-1.4 | 0.1-7.1 | 0.5-1.7 | 0.51-2.5 |
| Auto-ignition temperature (K) | 924 | 844 | 813 | 739 |
| Adiabatic flame temperature (K) | 2073 | 2383 | 2223 | 2273 |

Kobayashi H, Hayakawa A, Somarathne KDKA, Okafor EC. Science and technology of ammonia combustion. Proc. Combust. Inst. 2019;37(1):109-33



# Laminar flame speed

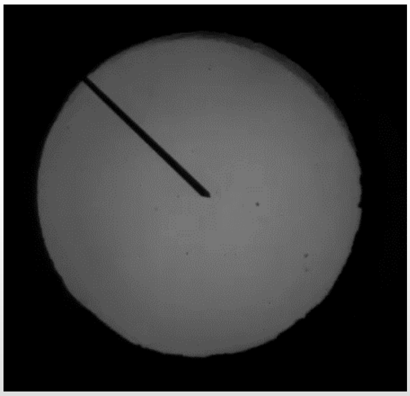
- The speed at which the flame propagates through the unburned premixed reactant mixture in a combustion process
- Important parameter in understanding chemical kinetics mechanisms in combustion



100% C3H8, $\varphi$ = 1, 1 bar

# Laminar flame speed

- Directly affects many combustion applications
- e.g., in an ICE, the flame speed directly influences knocking events, emissions, and efficiencies
- An important parameter in formulating new fuels



100% C3H8, φ = 1, 1 bar

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# Laminar flame speed

- To measure laminar flame speed, the flame must be:
  - One dimensional
  - No heat loss
  - No stretch
- Multiple experiments can measure flame speed:
  - Bunsen burner
  - Counterflow burner
  - Flat flame burner
  - Constant-volume combustion chamber (CVCC)

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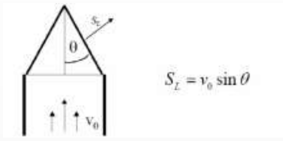
# Laminar flame speed methods

- Bunsen burner:
  - 1-D, no stretch, but loses heat to the burner
- Counterflow burner:
  - 1-D, no heat loss, but flame undergoes stretch




Credit: Min Suk Cha



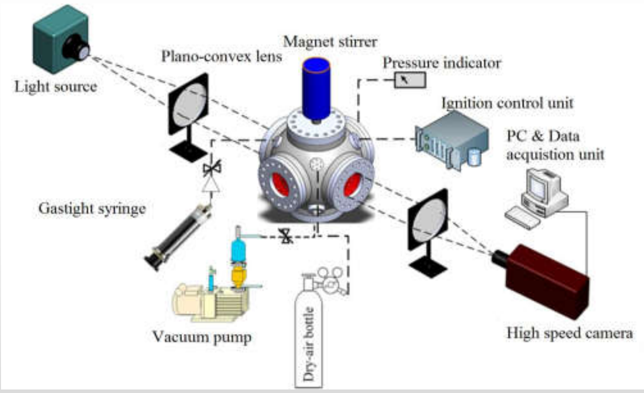
# Laminar flame speed methods

- Flat flame burner:
  - 1-D, no stretch, but loses heat to the burner
- Constant-volume combustion chamber (CVCC):
  - 1-D with no heat loss, but flame undergoes stretch

Credit: flatflame.com

# CVCC data acquisition

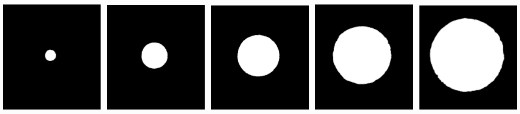
- Schlieren photography is used to capture the flame propagation
- The propagation is captured using a high-speed camera (4000 fps)
- MATLAB code is used to measure the flame displacement with time



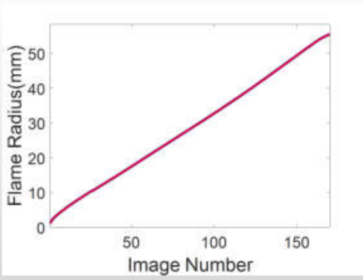



# Constant-volume combustion chamber (CVCC)

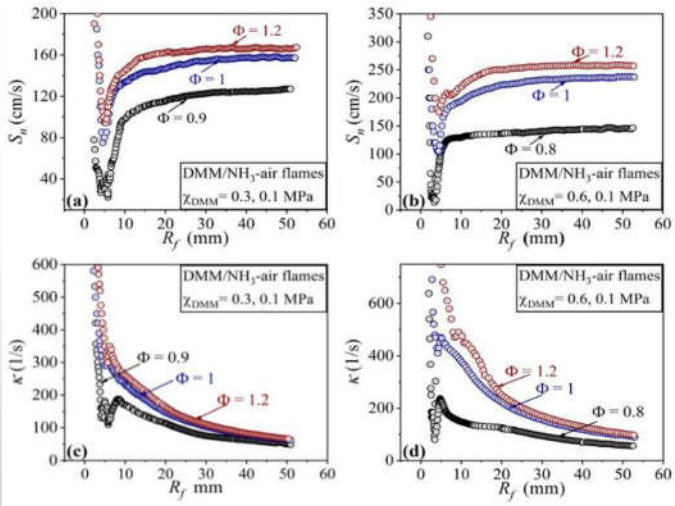
- 1-D with no heat loss, but flame undergoes stretch
- Displacement speed of the flame front is measured using MATLAB to estimate the burning velocity with time



Binary images produced using MATLAB
100% C3H8, φ = 1, 5 bar



# Flame speed and flame stretch




Stretch rate: the rate at which the flame area changes with time

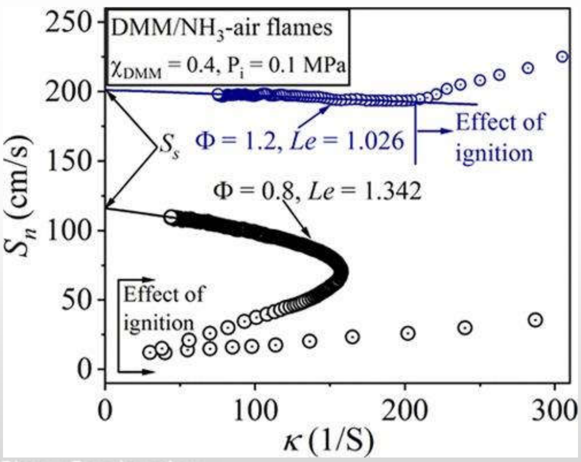
$$k = \frac{1}{A_f}\frac{dA_f}{dt},$$

$$A_f = 4\pi R_f^2$$

Elbaz et al. Energy & Fuels (11) 2020



# Extracting $S_n$ vs stretch rate

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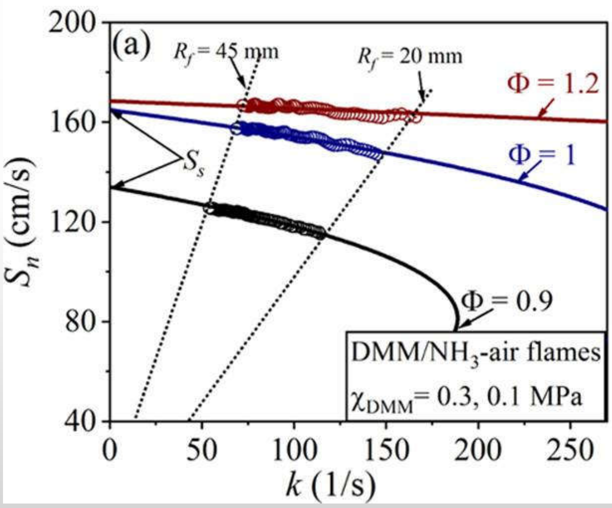
## Unstretched laminar burning velocity

- Extrapolating to zero stretch gives the laminar flame speed

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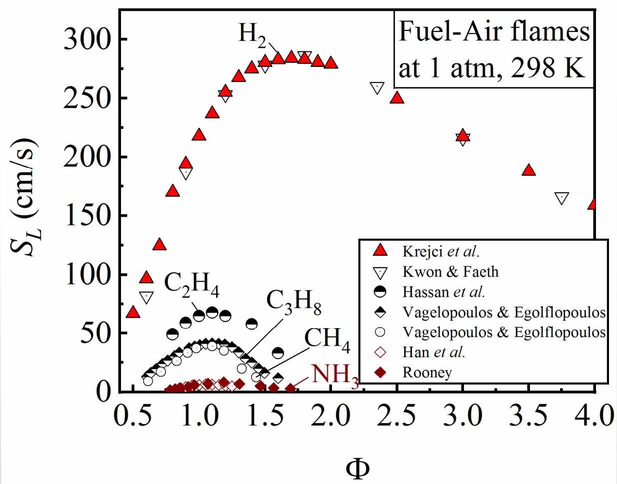
## $S_L$ for various HCs, $H_2$, $NH_3$

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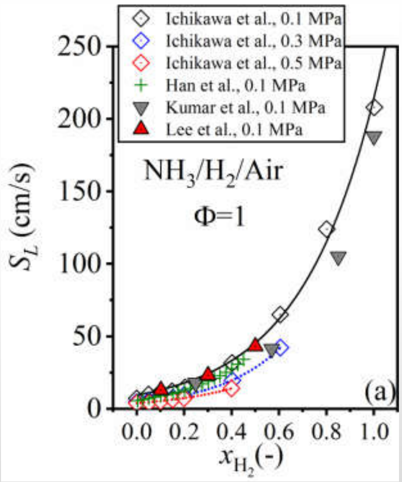
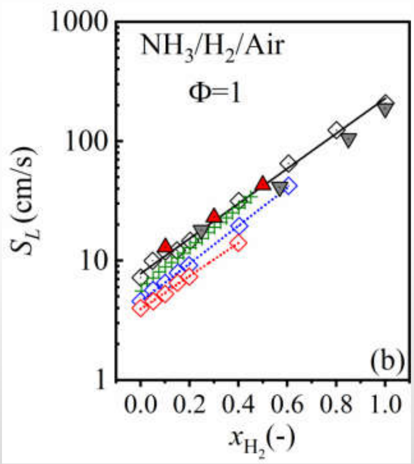
# Ammonia $H_2$ flames

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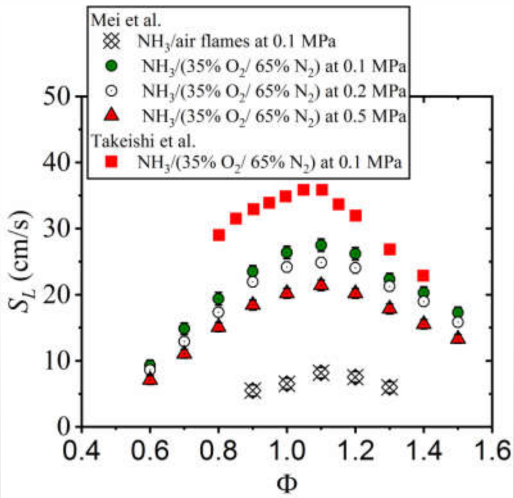
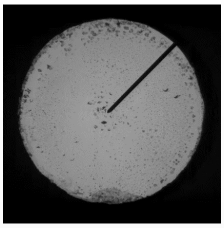
# Oxygen enrichment




Mei BW, Zhang XY, Ma SY, Cui ML, Guo HW, Cao ZH, et al Combust. Flame 2019;210:236-46
Takeishi H, Hayashi J, Kono S, Arita W, Iino K, Akamatsu F. Transactions of the JSME (in Japanese) 2015;81(824):14-00423.

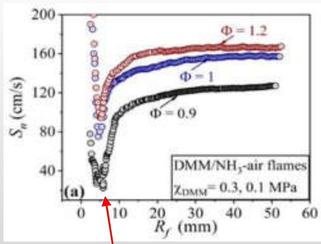
# Limitations

- Buoyancy is a significant limitation with slow flames, such as pure ammonia or at high pressures
- Early on, flame is affected by ignition effects—abnormal flame speed
- In the final stages, the flame is affected by chamber confinement



(note slower framing rate)

50% NH3/CH4, φ = 1.2, **7.5 bar**




Ignition effects at early stages

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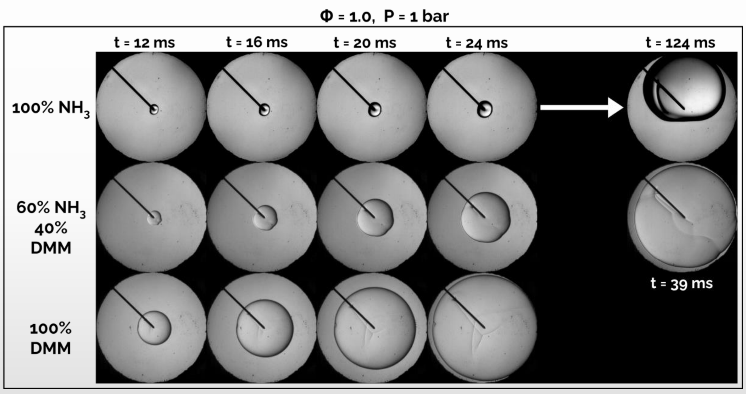
# Laminar flame speed

- New fuels (like ammonia) suffer from slow flame speeds
- Traditional fuels (like dimethoxymethane, DMM) have fast flame speeds
- The addition of DMM to ammonia increases flame speed and reduces buoyancy




Elbaz et al Energy & Fuels 34(11), 14726-14740

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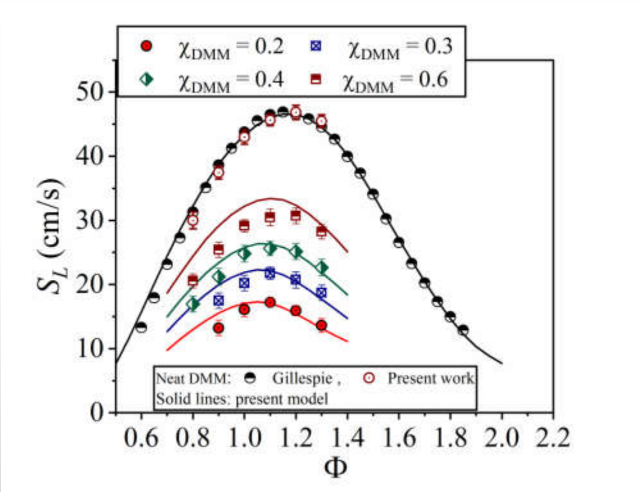
# Ammonia DMM blends



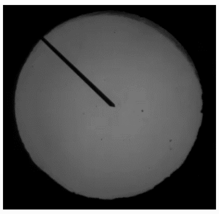



Elbaz AM, Giri BR, Issayev G, Shrestha KP, Mauss F, Farooq A, et al. Energy & Fuels 2020;34(11):14726-40.

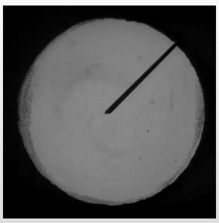
# Flame cellularity

- The thermal expansion of the flame results in hydrodynamic instability
- In common hydrocarbons (Le > 1) at 1 atm, molecular diffusion suppresses hydrodynamic instabilities
- Under high pressures, the flame thickness is significantly reduced, and diffusion effects are minimized
- Instability occurs in form of cellularity

100% C3H8, φ = 1



P = 1 bar



P = 5 bar

# Typical HC flame instability

- For Le > 1, hydrodynamic instability is directly proportional with equivalence ratio and pressure

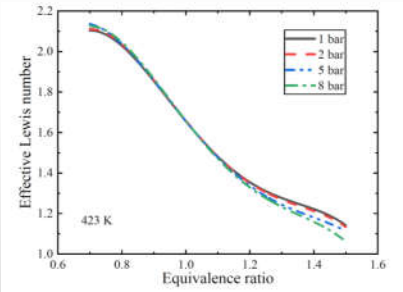



Fig. 10. Effective Lewis number ($Le_{eff}$) of 2-butanone-air flames at 423 K and 1–8 bar.

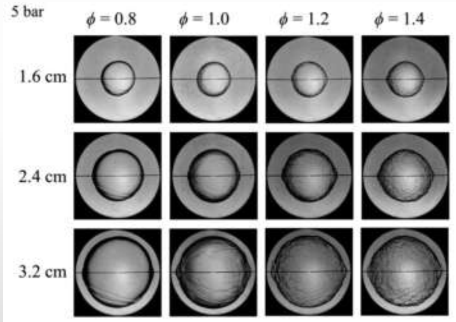



Fig. 11. Images of 2-butanone-air flames with varying equivalence ratios under 423 K and 5 bar.

Li, Ya, et al. "Laminar Burning Velocity and Cellular Instability of 2-Butanone-Air Flames at Elevated Pressures." *Fuel*, vol. 316, 2022, p. 123390.

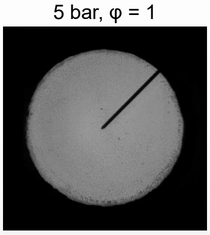


# Propane with ammonia

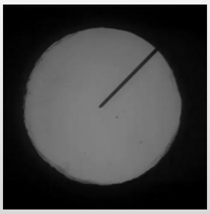
- The addition of ammonia was found to delay the flame cellularity

- Critical radius ($R_c$) at which cellularity occurs increases with ammonia addition

5 bar, φ = 1



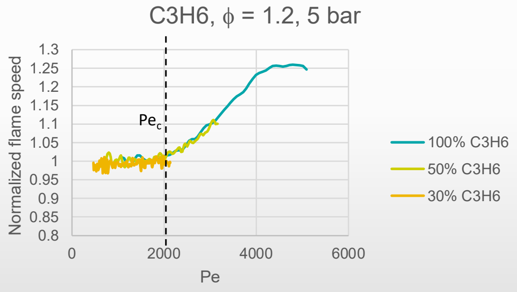
100% C3H8



50% C3H8
50% NH3

# Ammonia propene blends

- Cellularity accelerates flame propagation
- Peclet number (Pe) measures the extent of hydrodynamic instability intensity
- $Pe = \frac{R_f}{\delta}$,  $\delta$ = flame thickness
- Critical Pe ($Pe_c$) does not change with ammonia addition




To be submitted

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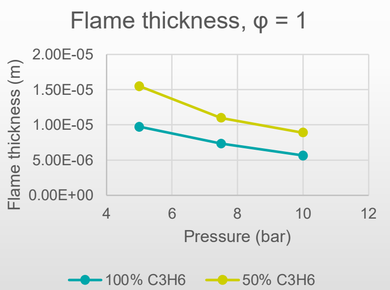
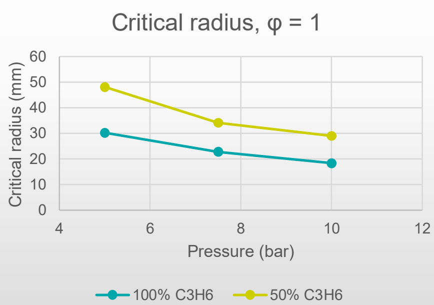
# Ammonia/propene, flame stability

- Flame thickness significantly increases with ammonia addition
- End result is that $R_c$ increases
- Flame is stable for longer

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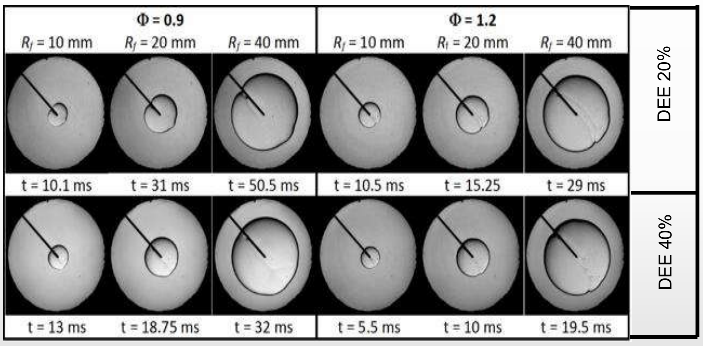
# Schlieren Images Recorded for Ammonia / Diethyl ether Air Premixed Flames




- The images show no indication of any flame instability - true for all cases

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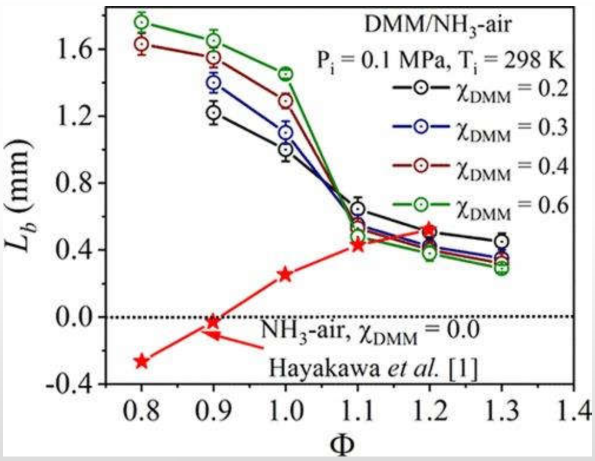
# Effect of DMM on Markstein length

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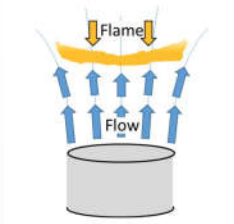
# Outline of L-3

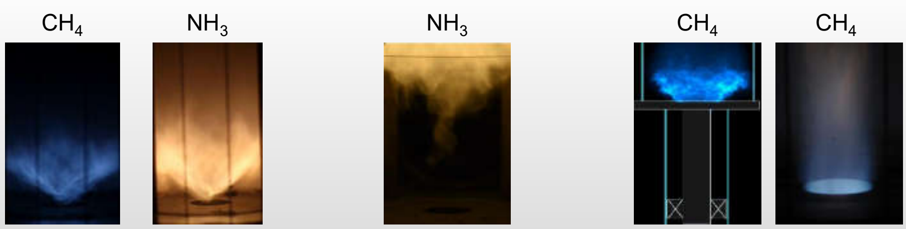
- Laminar flame speeds
  - Methods
  - Cellularity
- **Swirl flames of $NH_3$ mixtures**
  - **Stability limits**
  - **NOx**
- Gas Turbine combustors
  - Ansaldo mGT
  - Double Swirl Burner



# Flame stability

1. **Stable flame**: flame propagation speed = flow velocity.
2. **Flame blowout**: flame propagation speed < flow velocity.
3. **Flame flashback**: flame propagation speed > flow velocity.



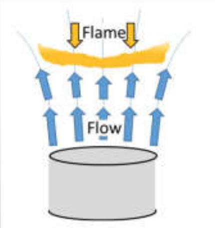

1. Stable flame

2. Flame blowout

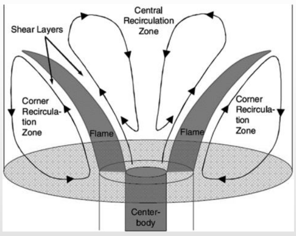
3. Flame flashback

# Swirl flow improves flame stability

As swirl added, the flame becomes **5 times** more stable.

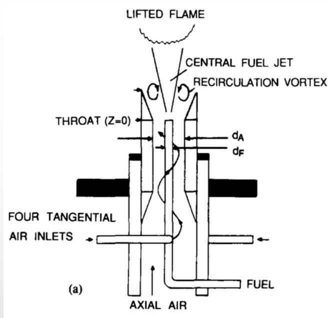



Jet flow




Swirl flow

Swirl burner

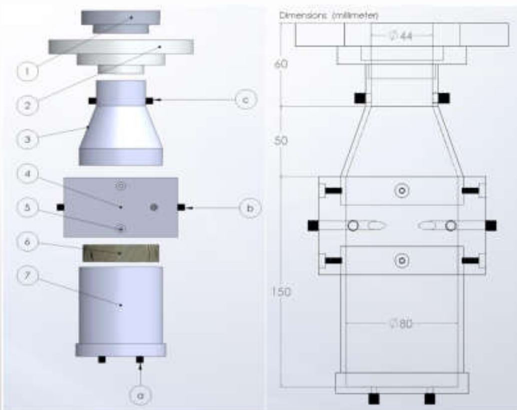



$$S_g = \frac{\pi r_0 d_A}{2A_t}\left(\frac{m_\theta}{m_\theta + m_A}\right)^2$$


Feikema, Douglas, Ruey-Hung Chen, and James F. Driscoll. *Combustion and Flame* 80.2 (1990): 183-195.



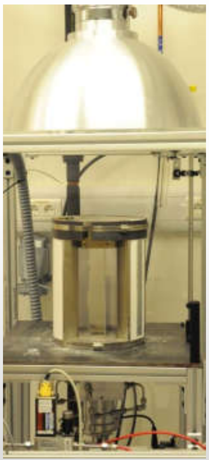

# KAUST ammonia swirl burner

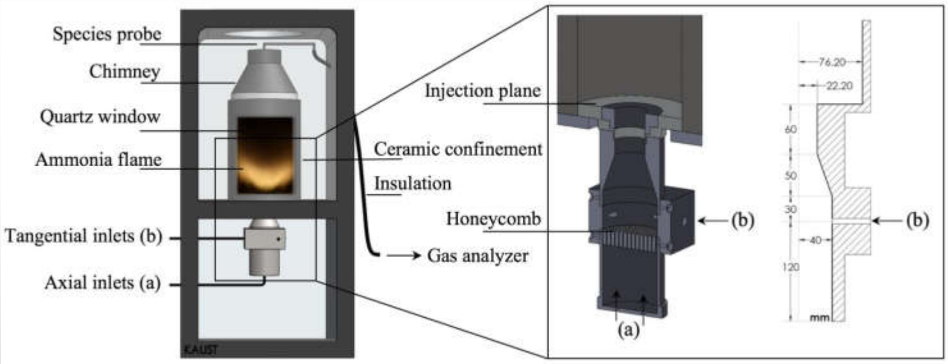



**Specifications:**
- Generic swirl burner.
- Three main body parts (3, 4, 7).
- Two axial inlets (a).
- Four tangential inlets (b).
- Honeycomb (6).
- Removable outlet (1).

# Experimental setup

Atmospheric pressure

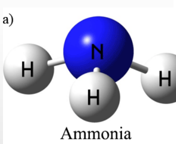


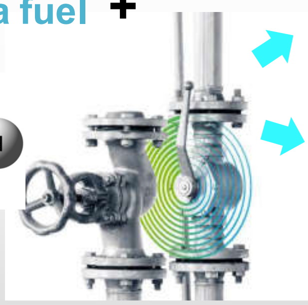





# Three ammonia fuel mixtures

**Ammonia fuel +**



**01 Methane:**

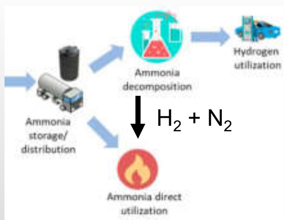
- Utilize current gas turbines systems.
- Enhance the chemical reactivity.

**02 Hydrogen:**

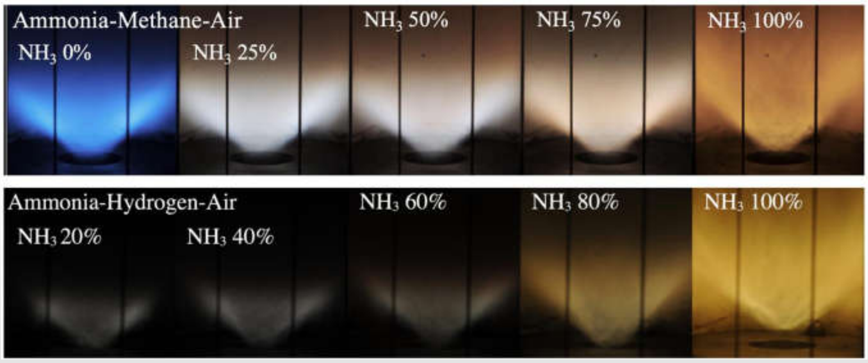
- Carbon free.
- Enhance chemical reactivity.

**03 Ammonia decomposition = hydrogen:nitrogen in 3:1 ratio:**

- Carbon free.
- Enhance chemical reactivity.
- Better storage flexibility.
- Avoid $N_2$ separation cost.

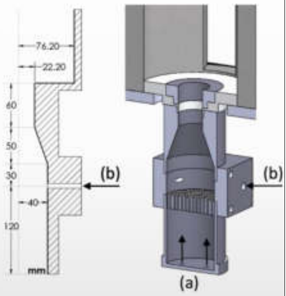


# Swirl Flames at 1 bar




Pictures of swirl flames for different fuel blends

(~ 5 kW)




Schematic of the swirl burner

Khateeb et al. Int. J. Hydrogen Energ. 2020
Khateeb et al. Exp. Therm. Fluid. Sci. 2020

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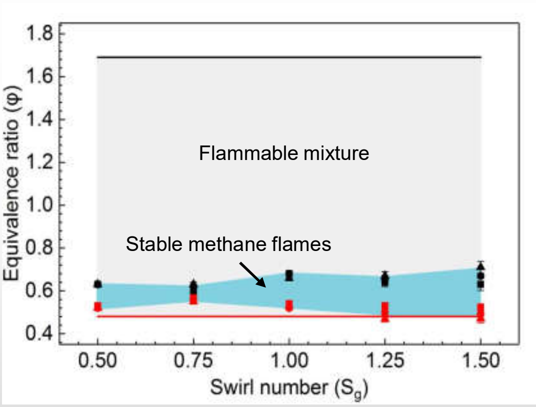
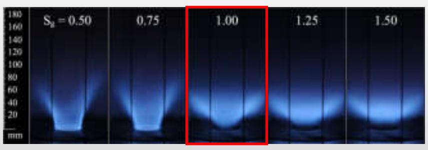
# Reference baseline

Methane-air flames




- Mixtures of methane and air, that do not include ammonia, are used as a reference baseline.
- Narrow range for stable methane flames (blue area).
- **$S_g$ = 1, Re = 5000** for other experiments.

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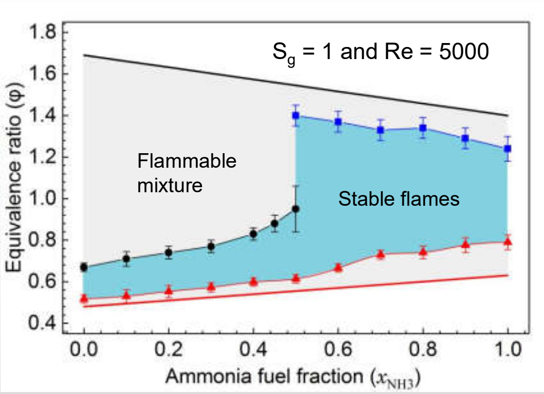
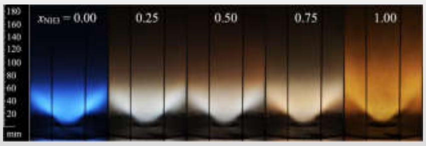
# Ammonia addition to methane flames



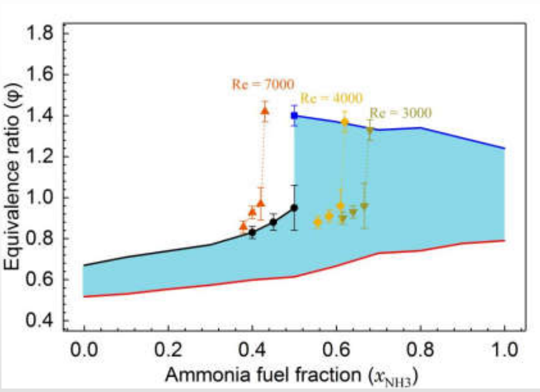

- Gradually replacing methane with ammonia increases the equivalence ratio leading to lean blowout or to flashback.
- At a critical ammonia addition the most reactive mixture does not yield conditions suitable for flashback.



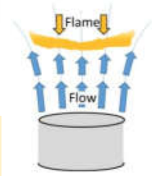



# Reynolds number

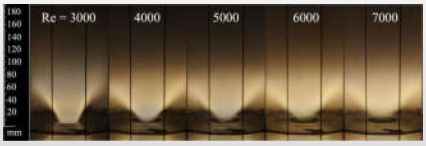
Ammonia-methane-air flames




$$Re = \frac{\rho u L}{\mu}$$



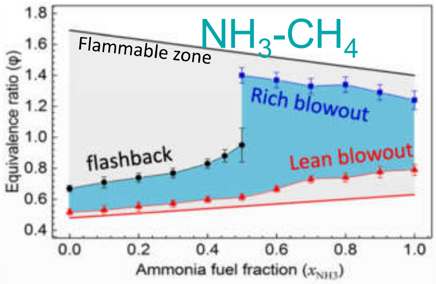

- Flame stability is a function of Re number.
- Fuel mixture reactivity reduces with ammonia additions.
- Proportional relation between Re and *u*.



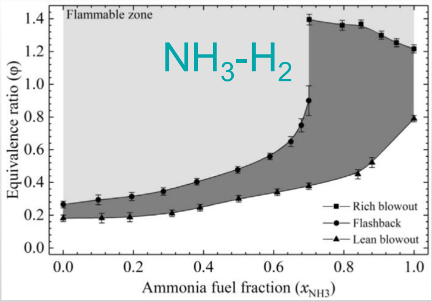

φ = 1.00, and $x_{NH3}$ = 0.80

# $CH_4$ and $H_2$ blends

- Stability is bounded by flashback and lean/rich blowout
- Adding ammonia widens the stable range for this burner
- Consistent with extinction measurements, $NH_3$-$H_2$ flames are less susceptible to blowout than $NH_3$-$CH_4$ flames



Stability limits of $NH_3$-$CH_4$ swirl flames



Stability limits of $NH_3$-$H_2$ swirl flames

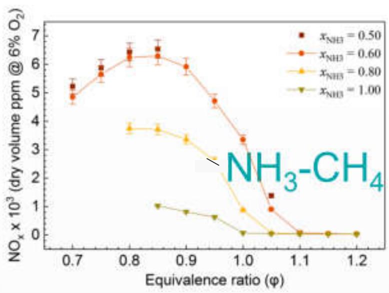
Clean Combustion Research Center

Khateeb et al. Exp. Therm. Fluid. Sci. 2020
Khateeb et al. Int. J. Hydrogen Energ. 2020

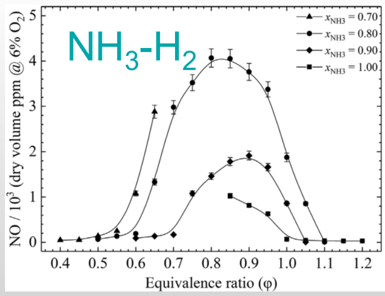


# NO emissions of blends

- Only rich $NH_3$-$CH_4$ swirl flames yield acceptable NO performance
  - A 2-stage combustor is required to avoid unburned $NH_3$ emissions
- Due to enhanced reactivity, very lean $NH_3$-$H_2$ flames can be stabilized and yield good NO performance



NO mole fraction in the exhaust of $NH_3$-$CH_4$ swirl flames

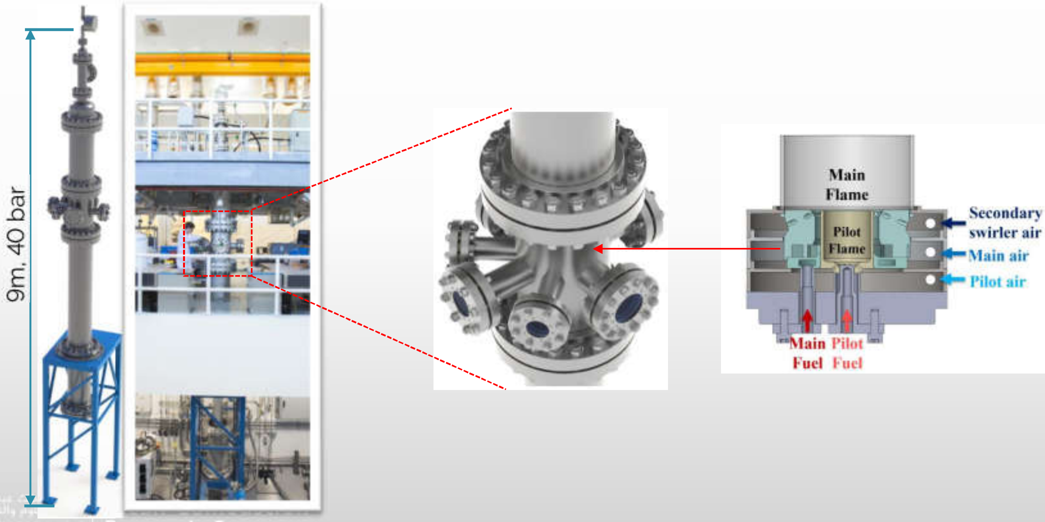


NO mole fraction in the exhaust of $NH_3$-$H_2$ swirl flames

Clean Combustion Research Center

Khateeb et al. Exp. Therm. Fluid. Sci. 2020
Khateeb et al. Int. J. Hydrogen Energ. 2020

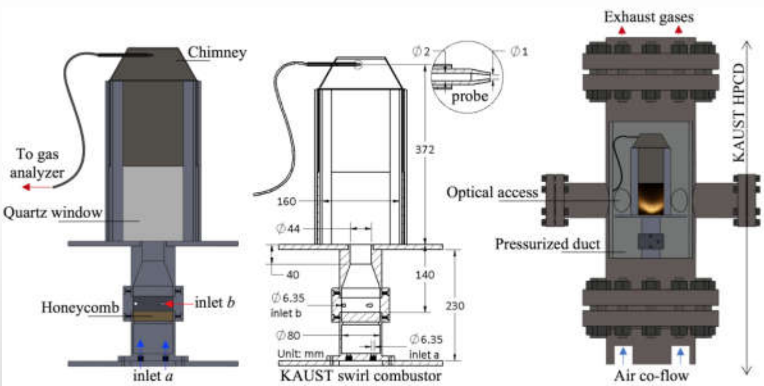
# High pressure combustion duct





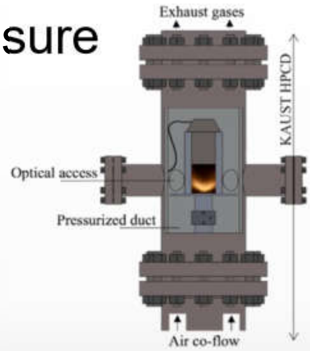

# Experimental setup - HPCD

Elevated pressures

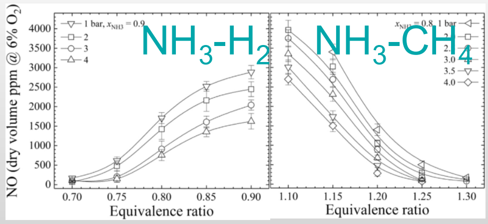


# NO Emissions at pressure

- Measurements were also done at elevated pressures relevant to the mGT (up to 5 bar)
- Trends of NO are not modified by pressure
- But increasing pressure decreases the NO mole fraction in the exhaust




High Pressure Combustion Duct (HPCD)



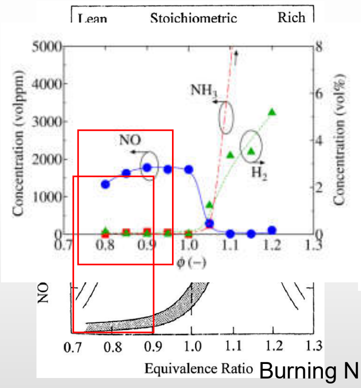

Khateeb et al. Int. J. Hydrogen Energ. 2021

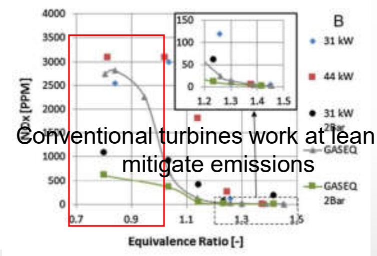


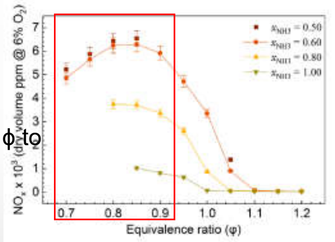
# Outline of L-3

- Laminar flame speeds
  - Methods
  - Cellularity
- Swirl flames of $NH_3$ mixtures
  - Stability limits
  - NOx
- **Gas Turbine combustors**
  - **Ansaldo mGT**
  - **Double Swirl Burner**

# Lean $NH_3$ combustion




Conventional turbines work at lean ϕ to mitigate emissions

Burning $NH_3$ or $NH_3$-$CH_4$ at the lean ϕ at which GTs typically works produce high NO emissions


- Hayakawa, A. et al. 2017: 10.1016/j.ijhydene.2017.01.046
- Valera-Medina, A. et al. 2017: 10.1016/j.apenergy.2016.02.073
- Khateeb, A. et al. 2020: 10.1016/j.expthermflusci.2020.110058
- Çeper, B. A. 2012. DOI: 10.5772/50597


# $NH_3$ fueling gas turbines

**1960's**
US Berkeley
- Poor combustion

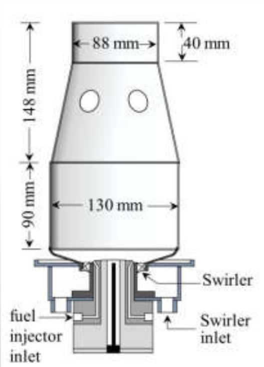
**2013**
University of Iowa
- Promising results.

Italian ENEL
- High NO emissions

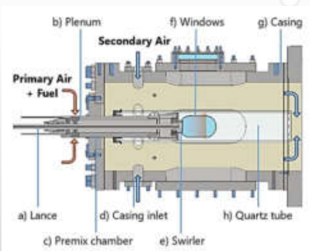
**1991**

Tohoku, Japan.
Cardiff, UK.
**2015 - present**

**Research focus:**
- Improve combustion efficiency.
- Reduce harmful emissions.



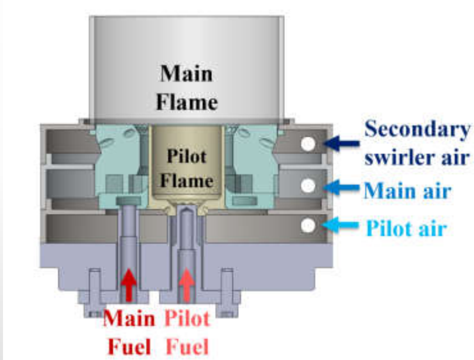

Tohoku $NH_3$ burner




Cardiff $NH_3$ burner


- Kurata O et al. Performances and emission characteristics of NH3-air and NH3-CH4-air combustion gas-turbine power generations. Proc Combust Inst **2017**;36:3351–9.
- Valera-Medina A et al. Premixed ammonia/hydrogen swirl combustion under rich fuel conditions for gas turbines operation. Int J Hydrogen Energy **2019**;44:8615–26.

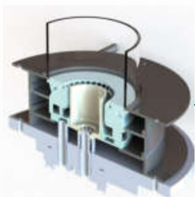
# Converting mGT to run on NH3 blends

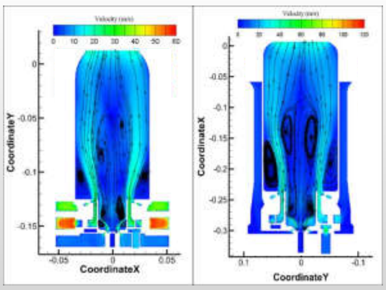



# Reduced-Scale mGT Burner

- A new burner was manufactured that retains features of the mGT burner but fits in the HPCD *(50 kW instead of 330 kW)*
- RANS simulations were used to ensure that full- and reduced-scale burners exhibit similar behavior



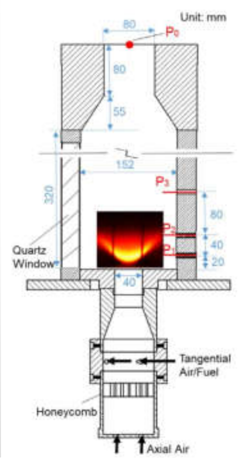
HPCD



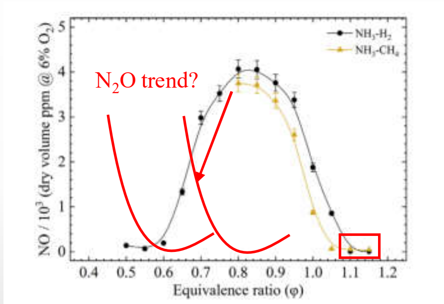

Simulated velocity fields

Reduced-scale burner

# $NH_3$ combustion for mGTs at KAUST



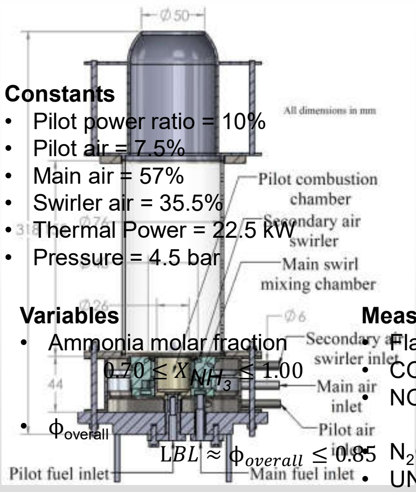

Trends are similar because, in both cases, NO is mainly produced via fuel-$NO_x$ pathways




Very lean flames could entail high $N_2O$ emissions (GWP 270 times that of $CO_2$)

- Zhu, X., et al. 2020: 10.1016/j.proci.2020.06.275
- Khateeb, A. et al., 2020: 10.1016/j.ijhydene.2020.05.236

# Reduced-scale burner setup and test plan




**Constants**

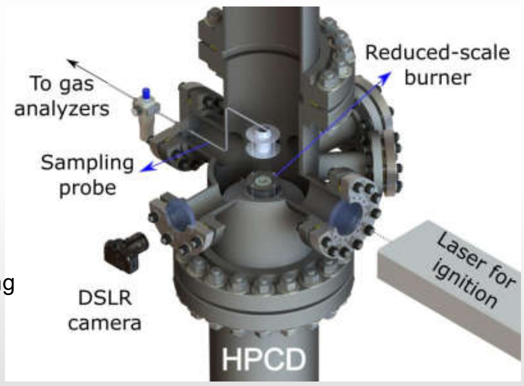
- Pilot power ratio = 10%
- Pilot air = 7.5%
- Main air = 57%
- Swirler air = 35.5%
- Thermal Power = 22.5 kW
- Pressure = 4.5 bar

**Variables**

- Ammonia molar fraction $0.70 \le X_{NH_3} \le 1.00$
- $\phi_{overall}$ $LBL \approx \phi_{overall} \le 0.85$

**Measured**

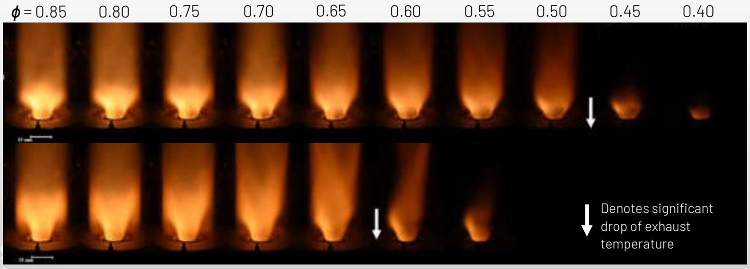
- Flame imaging
- $CO_2$
- NO
- $N_2O$
- $UNH_3$
- $O_2$



# Scaled mGT burner stability

- Very lean $NH_3$-$H_2$ swirl flames can be stabilized thanks to a pilot flame
- But a significant drop of combustion efficiency is observed if equivalence ratio is too low

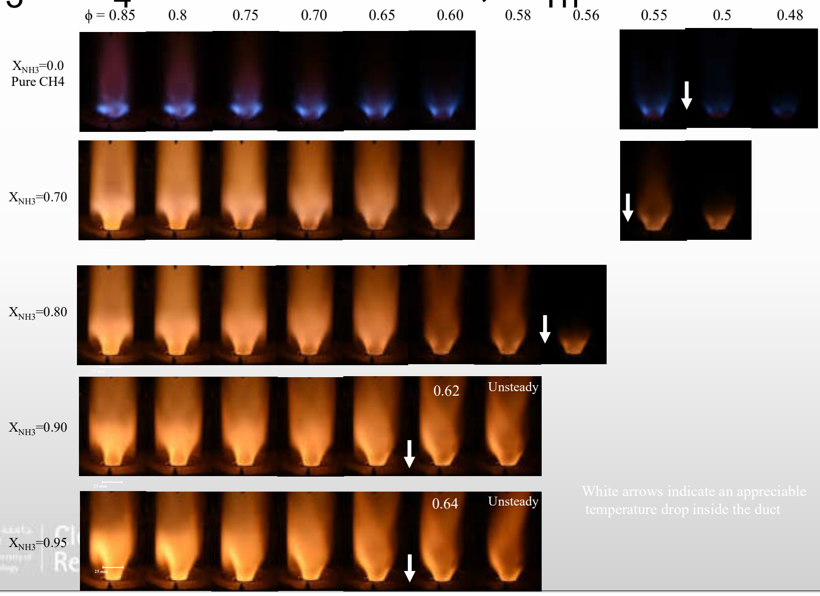
Lean ($\phi$ = 0.6) $0.7NH_3$-$0.3H_2$–air flame at 4.5 bar




Pictures of practical swirl flames for different ammonia fractions and equivalence ratios (22.5 kW)

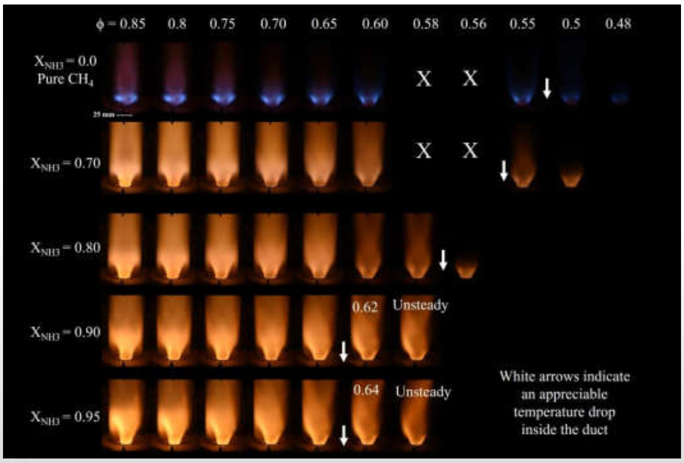


# $NH_3$-$CH_4$ Flames 4.5 bar, $P_{Th}$ = 22.5 kW




White arrows indicate an appreciable temperature drop inside the duct

# Flame imaging – Lean Cases



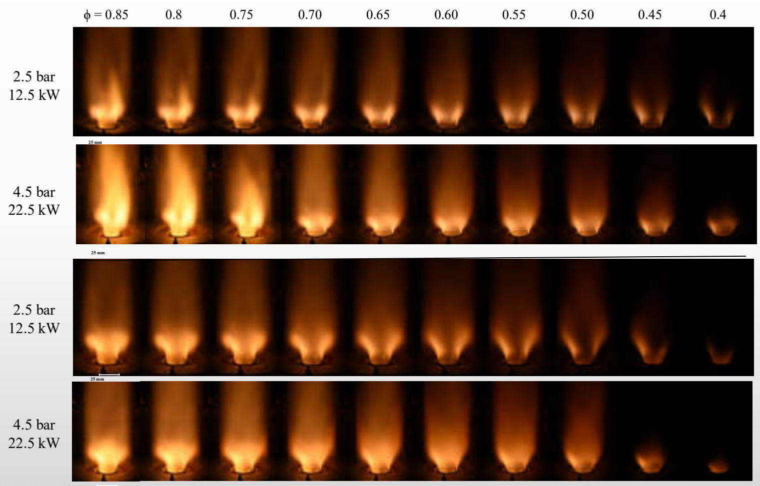

- The lower the ammonia fraction, the leaner the flame could burn stably
- The flames became unsteady and lost symmetry at higher equivalence ratios, for the highest ammonia fractions tested



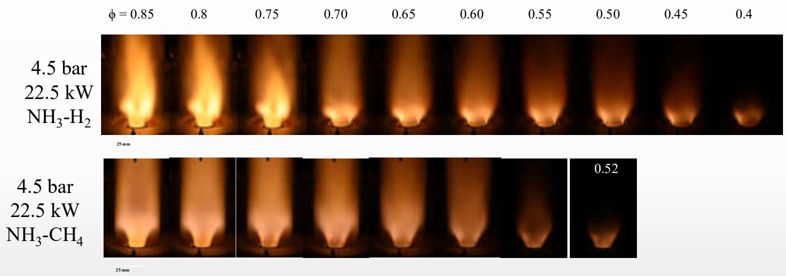
# Effect of pressure, $NH_3$-$H_2$

$X_{NH3}$=0.70

$X_{NH3}$=0.80

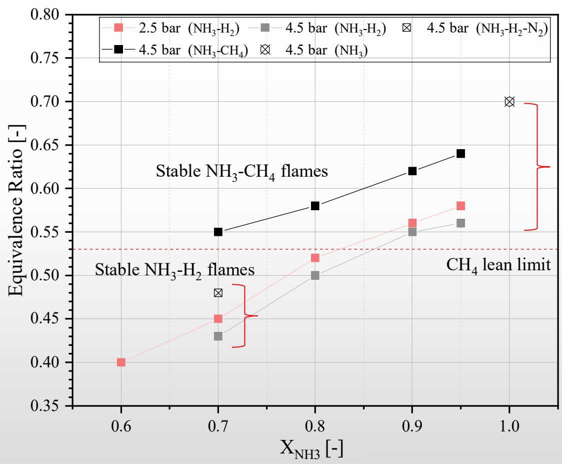


# Effect of equivalence ration at $X_{NH3}$ = 0.70






# Lean stability limits

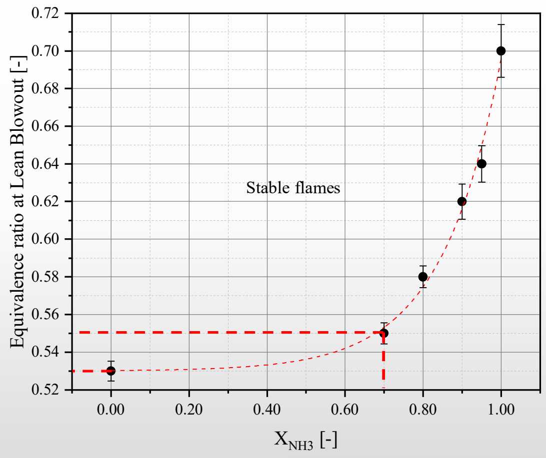



Just 5% of $CH_4$ or $H_2$ improves the lean stability limit of $NH_3$ combustion

The higher the pressure, the leaner the stable limit.

$N_2$ in cracked $NH_3$ reduces the mixture reactivity and narrows the LSL

# Lean stability limits, $NH_3+CH_4$




- Lean blowout of $CH_4$-air and $NH_3$-air flames occur at $\phi$=0.53 and $\phi$=0.70, respectively
- Decreasing $X_{NH3}$ reduces the equivalence ratio at the lean blowout
- Ammonia addition up to $X_{NH3}$ = 0.70 does not drastically modify the stability

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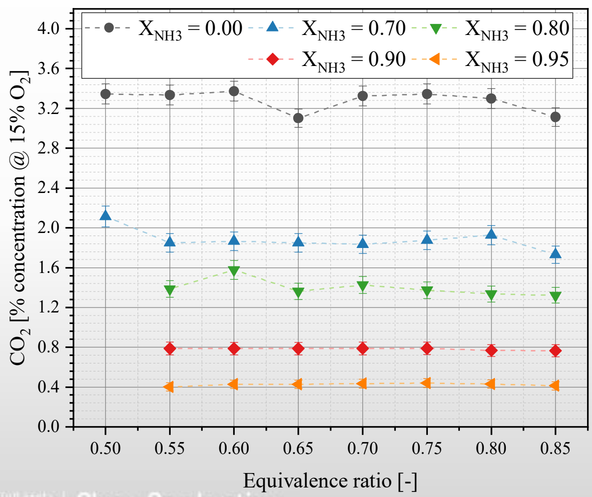
# $CO_2$ emissions




- $CO_2$ concentration monotonically decreases as $X_{NH3}$ increases regardless of the equivalence ratio
- Comparing the $CO_2$ concentrations at $\phi$=0.85 for pure methane and $X_{NH3}$=0.70, there is a substantial $CO_2$ reduction of 40%
- Lean $NH_3$-$CH_4$-air flames can be stabilized with a non-marginal $NH_3$ concentration

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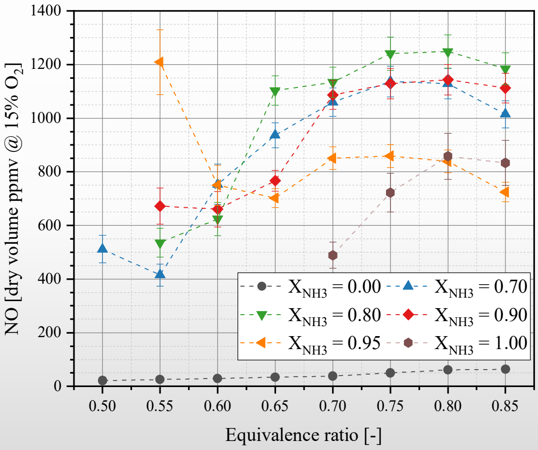
# NO Emissions




- NO emission peaks around ϕ=0.75 or 0.80

*“...an ammonia flame with around 240 ppm of $N_2O$ in the exhaust would have roughly the same global warming impact than a methane-air flame with an equivalence ratio of φ=0.60.”*

Khateeb, A. et al., 2020: 10.1016/j.ijhydene.2020.05.236

- No lean $NH_3$-$CH_4$-air flames were found that yield competitively low NO emissions

70 ppmv (at 16% $O_2$ basis) is required for the Japanese regulation

42 ppmv (at 15% $O_2$ basis) is required for new turbines firing natural gas for the Environment Protection Agency from the U.S

- However, coupling an SCR unit downstream of the turbine could allow for meeting the local regulation

Nitrous Oxide ($N_2O$) has a GWP 265–298 times that of $CO_2$ for a 100-year timescale.

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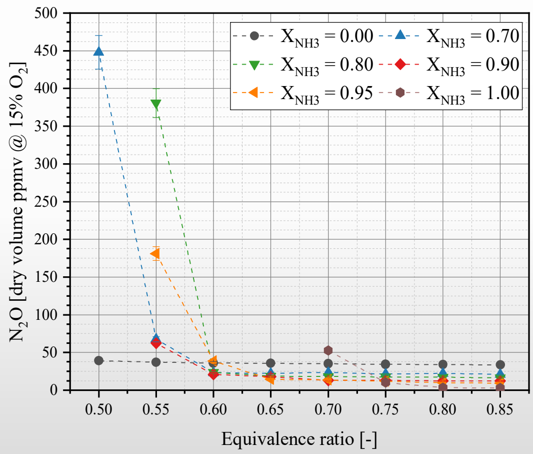
# $N_20$ emissions




- $N_2O$ emissions are almost negligible for most of the conditions tested except for very lean conditions

- $NH_3$-$CH_4$-air flames produce about the same $N_2O$ emissions than pure $CH_4$–air flames for ϕ>0.60

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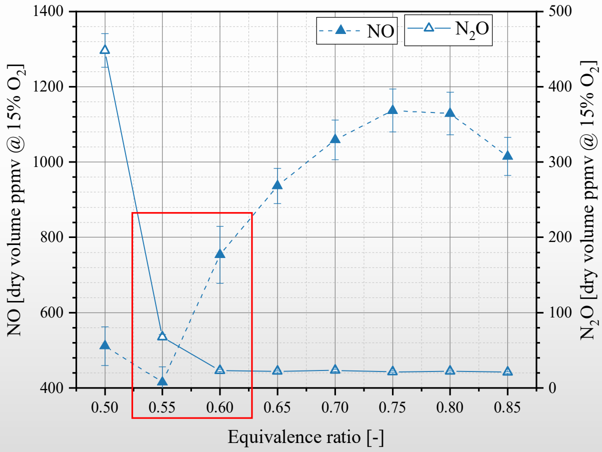
# NO-$N_2O$ trade-off ($X_{NH3}$ = 0.70)




- NO-$N_2O$ trade-off has been recognized
- $NH_3$-$CH_4$-air combustion with an ϕ = 0.60 and $X_{NH3}$ ≈ 0.70 is an appropriate candidate to explore in our mGT

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# Conclusions – Lean mGT scale burner

- Lean to far lean $NH_3$-$CH_4$ flames can be stabilized
- $NH_3$-$CH_4$ mixtures up to an $X_{NH3}$ = 0.70 produce flames with similar stability to pure $CH_4$.
- Far lean $NH_3$-$CH_4$ mixtures exhibit NO emissions that are much reduced compared to that found for lean equivalence ratios typically associated with lean premixed combustors (ϕ ~ 0.70 or 0.80)
- $N_2O$ emissions are negligible, except for very lean equivalence ratios.

We need to explore another strategy!

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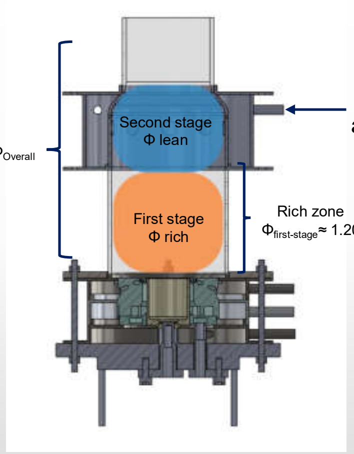
# Two-stage Rich-Lean

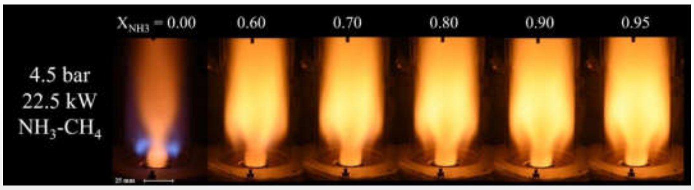



- Hayakawa, A. et al. 2017: 10.1016/j.ijhydene.2017.01.046
- Valera-Medina, A. et al. 2017: 10.1016/j.apenergy.2016.02.073
- Khateeb, A. et al. 2020: 10.1016/j.expthermflusci.2020.110058

- Rich $NH_3$-air and $NH_3$-$CH_4$-air premixed flames for low NO emissions
- Unburnt fuel, either $NH_3$, $H_2$, and/or $CH_4$
- Additional air is injected to oxidize all the remaining fuel
- The reduced-scale burner is considered in this study as a candidate for the first stage combustor

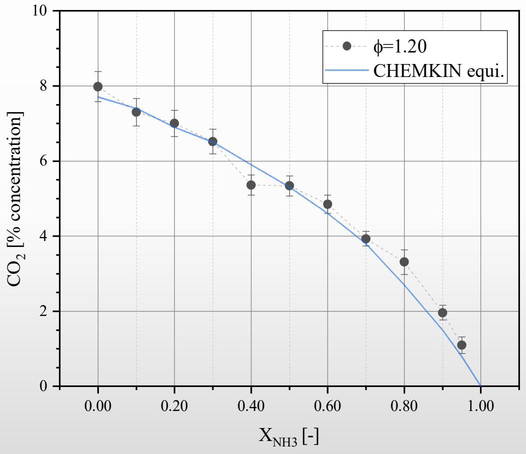


# Flame imaging – Rich Cases (ϕ = 1.20)




- $CH_4$–air flame presents a premixed outer reaction zone and a brighter sooty central jet issuing from the pilot.
- The flames with ammonia in the fuel blend exhibit the typical orange-yellow hue attributed to the $NH_2$ alpha band
- The lower the ammonia fraction, the more compact the main reaction zone is

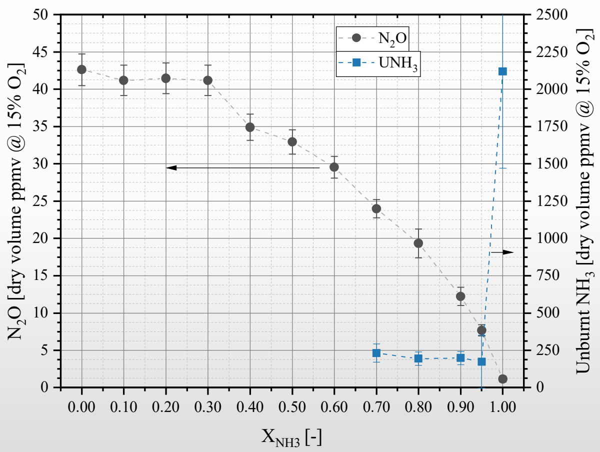
# $CO_2$ – Rich Cases (ϕ = 1.20)




- $NH_3$ addition monotonically reduces $CO_2$ emissions by reducing the concentration of $CH_4$ in the fuel mixture
- The minimum $CO_2$ concentration recorded was 1.20% for $X_{NH3}$ = 0.95
- Chemkin equilibrium simulations suggested that there is no $O_2$ selectivity for $NH_3$-$CH_4$-air combustion as a function of the ammonia fraction for ϕ = 1.20



# $N_2O$– Rich Cases (ϕ = 1.20)




- Ammonia additions up to $X_{NH3}$ = 0.30 do not influence the $N_2O$ emissions
- Beyond this threshold, $N_2O$ emissions monotonically decrease by increasing the $X_{NH3}$
- The $X_{NH3}$ concentration was constant from fuels blends with $X_{NH3}$ = 0.70 up to 0.95
- $NH_3$-air combustion entails ten times larger $U_{NH3}$ emissions compared with $NH_3$-$CH_4$-air flames.

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# Conclusions

- $NH_3$-$CH_4$ mixtures up to an $X_{NH3}$ = 0.70 produce flames with similar stability to pure $CH_4$.
- NO concentration is still too high to satisfy current regulations.
- $N_2O$ emissions are negligible, except for very lean equivalence ratios where it reaches unacceptably high values.
- The reduced-scale burner has demonstrated to be a suitable candidate as the first stage of a two-stage rich-lean combustor.
- More work is needed to implement the rich-lean combustion concept for the studied burner.

# KAUST Double Swirl Burner

Innovative design for double stream burner to:

- Study flame behavior of $NH_3$ Studies NO emissions
- Studies the practicality of using KDSB as a combustion device for several applications such as gas turbines.

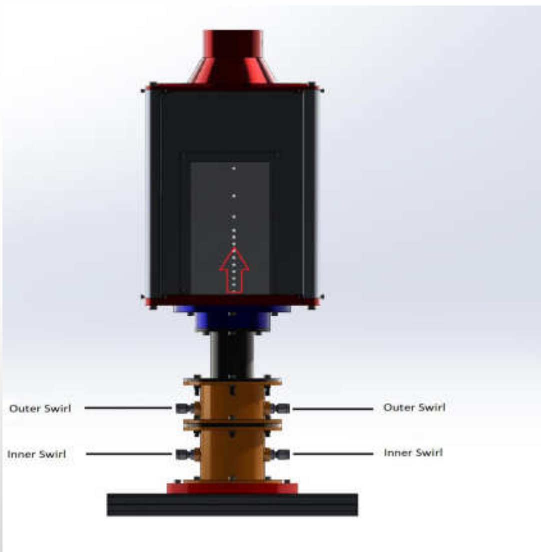
# KDSB Main Parts

- ❑ Co-axially positioned
  i. Inner stream
  ii. Outer stream
- ❑ Swirlers (30/45/60)
  i. Inner
  ii. Outer
- ❑ Central Bluff body
- ❑ Large Square Combustor



# Burner Details

- ❑ Inner Stream: $NH_3$/$CH_4$/Air mixture.
- ❑ Outer Stream: $CH_4$/Air mixture.
- ❑ Quartz windows for optical access.

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# Burner in action



# Flame Measurements

- ❑ Gas analyzer_Testo350
- ❑ Detects: NO, $O_2$, and CO, $CO_2$
- ❑ Water cooled sampling probe to quench the chemical reaction.

Testo.com

- ❑ In-flame temperature
- ▪ Type-S Thermocouple:

Measures temperature distribution radially and axially.

- ❑ Emission temperature
- ▪ Type- K Thermocouple:

Measures exhaust gas temperature

# NH3 addition to the burner

- ❑ Incremental increase of $xNH_3$

Prevents sudden blowout due to the flame velocity of $NH_3$

- ❑ Initially, pure methane in both annuli

- ❑ Pure ammonia in the inner annulus

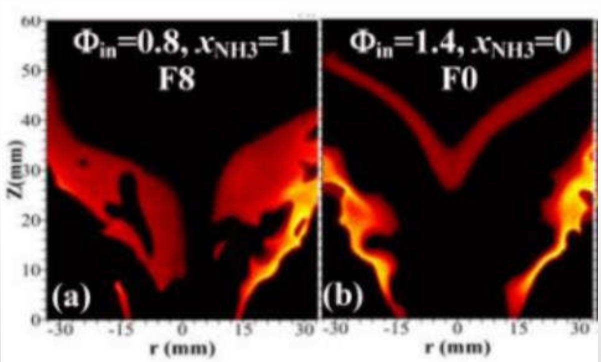
Direct imaging of swirl flame: $xNH_3$ increases from 0 to 1 at $Re_{out}$=4350, $\phi_{out}$=0.7, $Re_{in}$=4250, $\phi_{in}$=1.2, outer swirl number=0.49, and inner swirl number=0.72



# OH-PLIF

- ❑ Planar Laser-Induced Fluorescence Laser was used to:

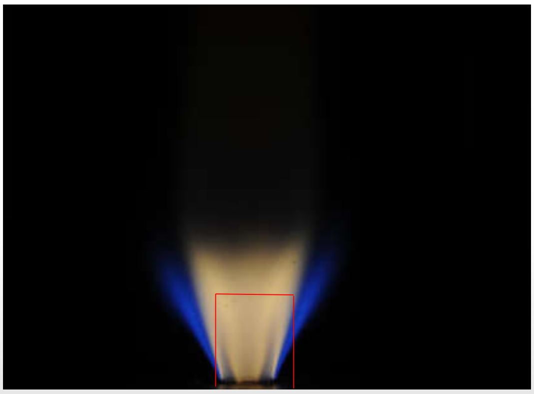
- Detects and measures OH concentration
- Measuring OH level helps understanding NO formation
- Effect of ammonia addition




Direct imaging of OH distribution: $\phi_{out}$ kept constant (0.6) to observe OH distribution at $Re_{out}$=4350, $Re_{in}$=4250, $\phi_{out}$=0.6, and $\phi_{in}$=0.8, and $\phi_{in}$=1.4

# Bluff-Body Aerodynamics

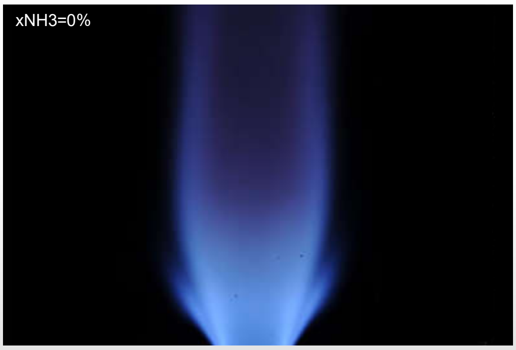
- Flow separation
  - Improves flame stability
  - Provides recirculation zones



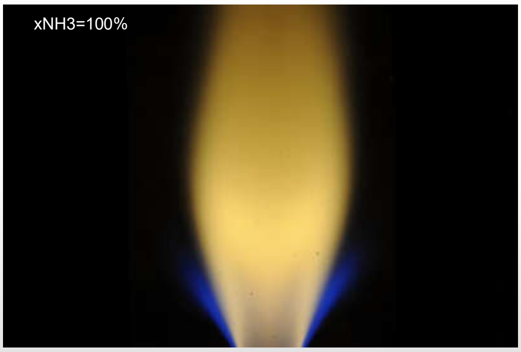
Direct imaging of swirl flame: Circulation zone created by the bluff body at $Re_{out}$=4350, $Re_{in}$=4250, $\phi_{out}$=0.7, and $\phi_{in}$=0.8



# Flame structure from pure methane to pure ammonia




Direct imaging of swirl flame: Both annuli are pure $CH_4$ at $Re_{out}$=4350, $\phi_{out}$=0.7, $Re_{in}$=4250, and $\phi_{in}$=1.4




Direct imaging of swirl flame: Inner annulus is pure $NH_3$, and outer annulus is pure $CH_4$ at $Re_{out}$=4350, $\phi_{out}$=0.7, $Re_{in}$=4250, and $\phi_{in}$=1.4

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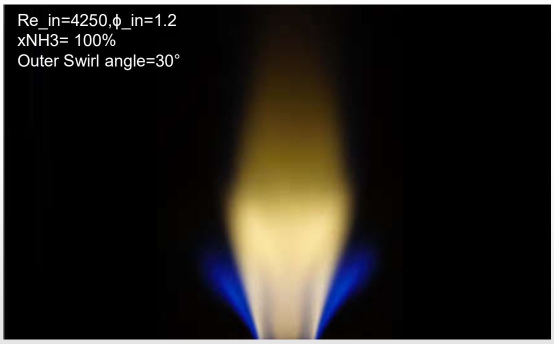
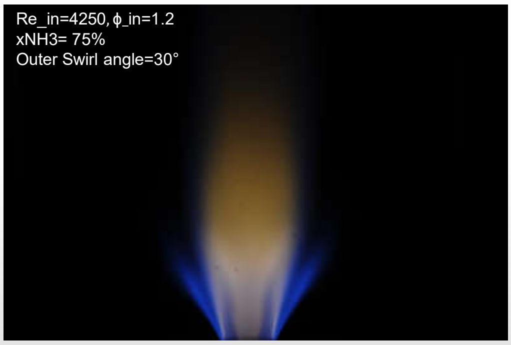
# Effect of increasing Ammonia percentage




Direct imaging of swirl flame: Effect of $xNH_3$ on NO emissions at $Re_{out}$=4350, $Re_{in}$=4250, $\phi_{out}$=0.7, and $\phi_{in}$=1.2




Direct imaging of swirl flame: Effect of $xNH_3$ on NO emissions at $Re_{out}$=4350, $Re_{in}$=4250, $\phi_{out}$=0.7, and $\phi_{in}$=1.2

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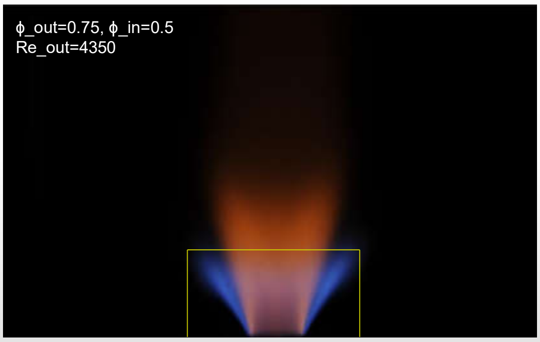
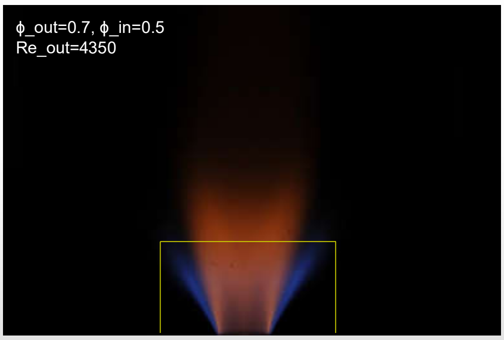
# Effect of outer stream equivalence ratio




Direct imaging: Outer annulus stream equivalence ratio increased from 0.7 to 0.75 to observe flame stability at $Re_{out}$=4350, $\phi_{out}$=0.75, $Re_{in}$=4250, and $\phi_{in}$=0.5




Direct imaging: Outer annulus stream kept at $Re_{out}$=4350, $\phi_{out}$=0.7, $Re_{in}$=4250, and $\phi_{in}$=0.5

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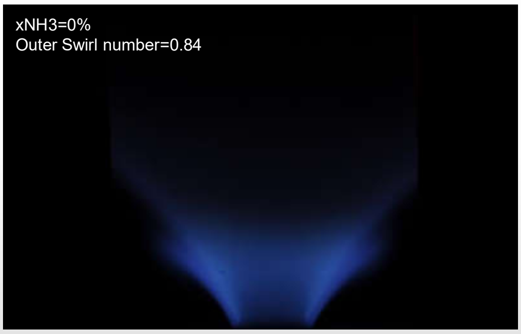
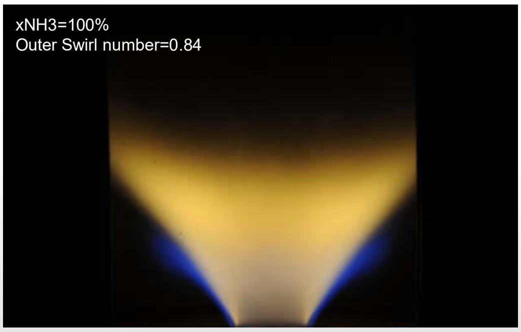
# Effect of increasing swirl number




Direct imaging: Effect of outer swirl on the emissions, pure $CH_4$ in both annuli at $Re_{out}$=4350, $\phi_{out}$=0.7, $Re_{in}$=4250, $\phi_{in}$=1.4, and inner swirl number=0.72




Direct imaging: Effect of outer swirl on the emissions at $Re_{out}$=4350, $\phi_{out}$=0.7 ,$Re_{in}$4250, $\phi_{in}$=1.4, and inner swirl number=0.72

# Effect of inner stream equivalence ratio

Direct imaging of swirl flame: Effect of inner annulus equivalence ratio at $Re_{out}$=4350, $\phi_{out}$=0.7, $Re_{in}$=4250, outer swirl number=0.49 , and inner swirl number=0.72

# Future Work with KDSB

- Effect of pressure on NO emissions and flame stability.
- Flow field measurements using PIV.



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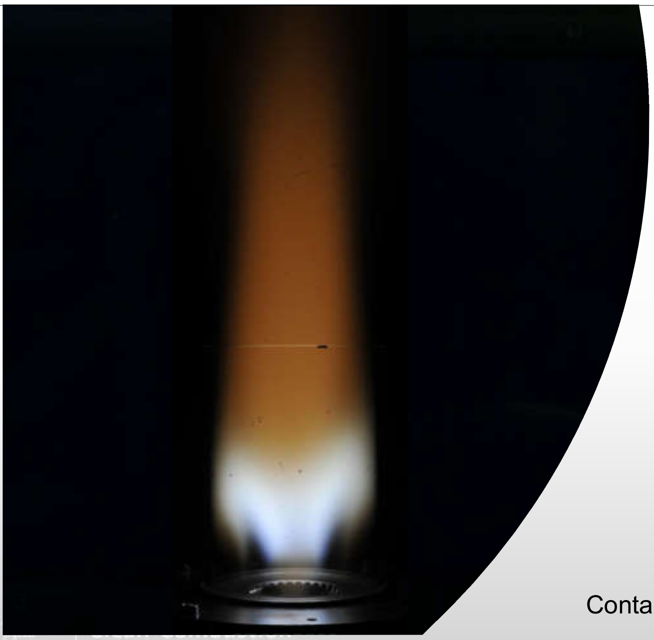
THANK YOU!

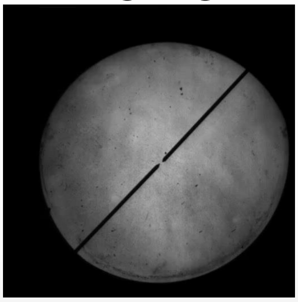


# Thank you

Q&A session

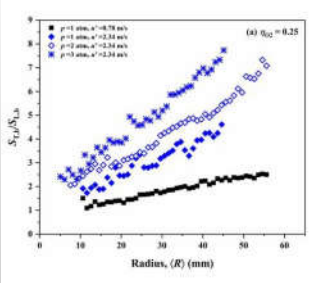
Contact: cristian.avilajimenez@kaust.edu.sa

# Turbulent Flame Speeds of Ammonia



- Experiment: propagating spherical flames in a high pressure high temperature turbulent constant volume combustion chamber
- The normalized turbulent flame speed, $S_{T,b}/S_{L,b}$ decreases with increasing the $O_2$ content. This is mainly due to increasing $S_{L,b}$ with $O_2$ content
- $O_2$ content is defined as: $\eta_{O2} = X_{O2}/(X_{O2}+X_{N2})$

| Flame conditions | | | | |
|---|---|---|---|---|
| $\eta_{O2}$ | 0.25 | 0.3 | 0.35 | 0.4 |
| Pi (bar) | 1 to 3 | | | |
| u'(m/s) | 0.78 to 2.34 | | | |
| Φ | 1 | | | |



# Lecture 4: Non-premixed ammonia flames

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Director, Clean Combustion Research Center

Tsinghua Summer School
Center for Combustion Energy
Tsinghua University, Beijing
14-15 July 2022

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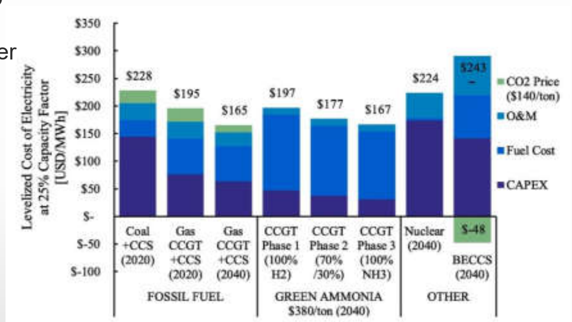
# 100% Green ammonia combustion in CCGT

- LCOE of Ammonia direct firing in CCGT (167 USD/MWh) on par with NG CCGT with CCS in 2040
- Coal+CCS, Bio-energy+CCS and Nuclear are costlier
- The additional costs of 30 USD/MWh for Ammonia cracking to produce Hydrogen➔ Gas turbine OEMs should prioritize achieving a more ammonia compatible turbine technology in the long term




Projected costs in 2040

Cesaro, Zac, et al. "Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants." Applied Energy 282 (2021): 116009.

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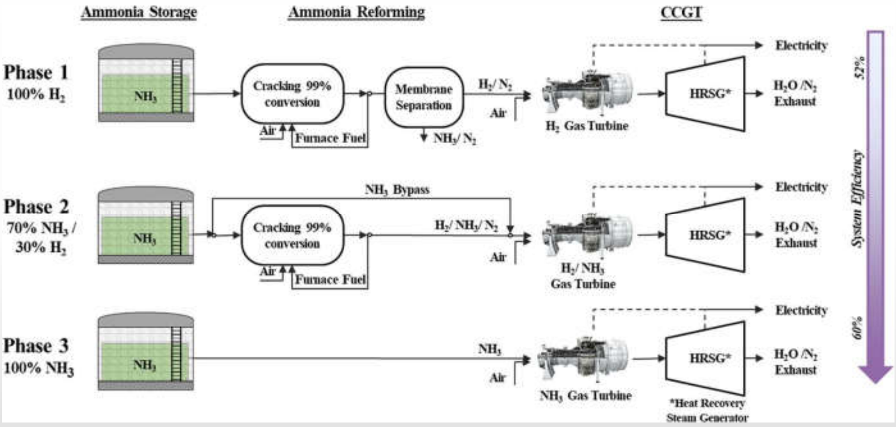
# Ammonia combustion in CCGT

2040




Ammonia fueled CCGT configurations as modelled in three cases of 100% H2, 70% NH3 / 30% H2, and 100% NH3

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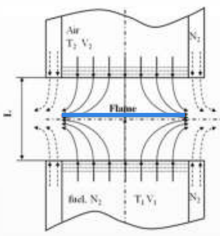
Cesaro, Zac, et al. "Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants." Applied Energy 282 (2021): 116009.



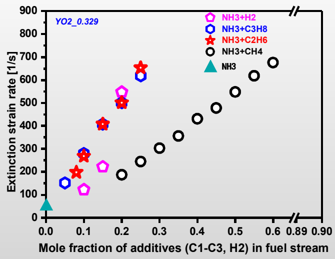
# Extinction Strain Rate

- Subjecting flames to strain mimics some of the effects of turbulence
- The extinction strain rate is useful to predict the stability of swirl flames
- Blending $NH_3$ with a more reactive fuel allows to boost resistance to extinction




Schematic of a counterflow flame

Picture of a counterflow flame




Measured extinction strain rates

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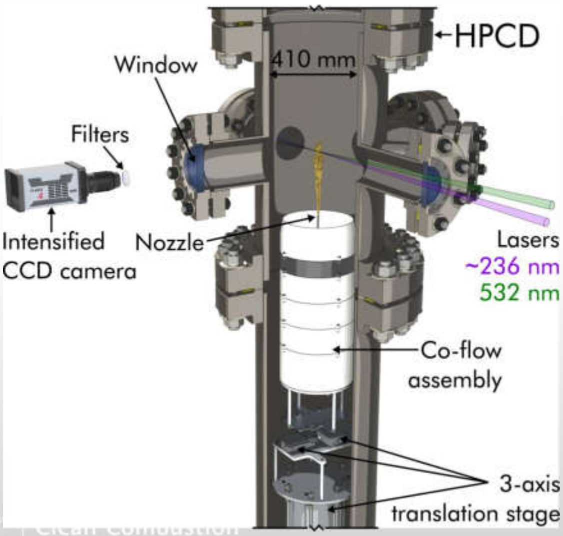
# Ammonia Turbulent Diffusion Flame




Cracked NH3 flames

| Flame conditions | TF1 | TF2 |
| --- | --- | --- |
| $NH_3$ Crack ratio | 14% | 28% |
| Re @Blowoff | 28000 | >33500 |
| Re @Setpoint | 11200 | 11200 |

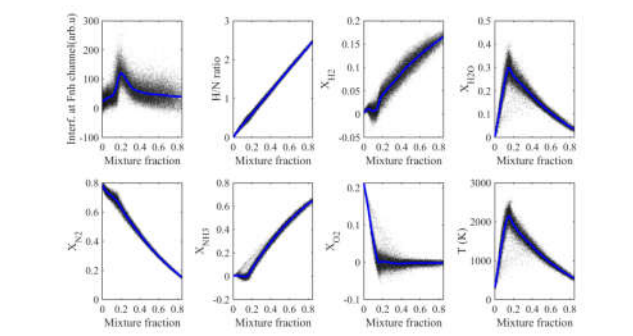
Raman for major species and temperature
LIF for radical species

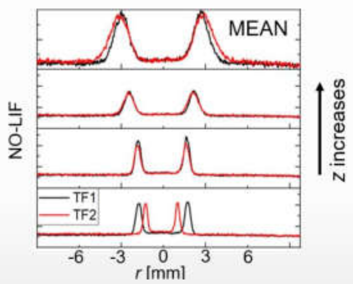


# Laser based measurements

- First simultaneous Raman measurements of temperature and major species, and quantitative NO-LIF in $NH_3/H_2/N_2$-air flames at 5 bar
- Ultrafast optical shutter to suppress flame luminosity

# Ammonia Turbulent Diffusion Flame




Excellent data for code and kinetic mechanism validation

| Flame conditionsv | TF1 | TF2 |
|---|---|---|
| $NH_3$ Crack ratio | 14% | 28% |
| Re @Blowoff | 28000 | >33500 |
| Re @Setpoint | 11200 | 11200 |



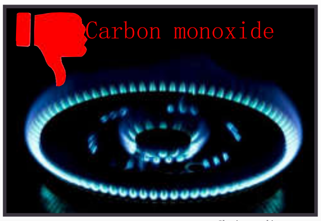
# Flame spectroscopy

- We can learn a great deal from the natural emissions from flames
- Two sources: excited species (chemiluminescence) and thermal radiation
- Blue emissions at 430 nm comes from CH*
- OH* easily detected with UV sensitive cameras
- Faint red color from hydrogen flames comes from hot water bands
- Yellow from sooting flames is broad band black body radiation
- Ammonia flames offer opportunity to investigate new excited species

# Flame emissions

On a stove, natural gas-air flames can exhibit different colors

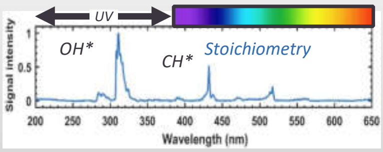
Architecturelab.net

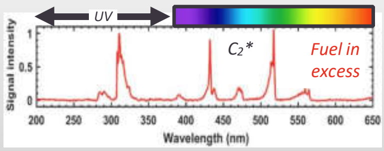



flamingoappliance.com


homeguides.sfgate.com

These colors are the signature of excited combustion radicals and soot




*Methane-air flame spontaneous emission flame spectrum*

Adapted from Oh et al. *Int. J. Heat Mass Transf.* 2020

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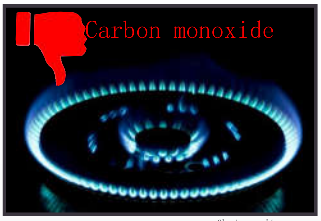
# Flame emissions

On a stove, natural gas-air flames can exhibit different colors

Architecturelab.net




flamingoappliance.com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Monitoring the color of a flame allows us to infer many of its important properties

*harmful emissions, reactivity, temperature, fuel blend composition*

There are many other practical applications
(incinerators, boilers, gas turbines, engines, etc.)

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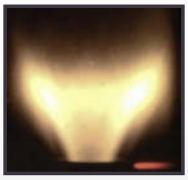
# Ammonia Chemiluminescence

The spontaneous emission of light by flames is now well understood for hydrocarbon and hydrogen fuels.

This is not the case for ammonia and its blends!

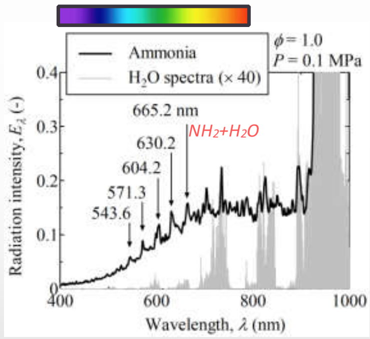
*Real color picture of a pure ammonia-air flame*

Adapted from Hayakawa et al. *Int. J. Hydrogen. Energ.* 2017



*Real color picture of an ammonia-hydrogen-air flame*

Adapted from Valera-Medina et al. *Int. J. Hydrogen. Energ.* 2019




*Chemiluminescence spectra of a pure ammonia-air flame*

Adapted from Hayakawa et al. *Mech. Eng. J.* 2015


*Real color pictures of ammonia-methane-air flames*

Adapted from Ku et al. *Energy* 2018

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# Objectives of this study

Measure a large database of chemiluminescence in $NH_3$-$CH_4$ flames

Identify promising excited radicals for $NH_3$-$CH_4$ flame sensors

*Experimental setup*

*Data post-processing*

*Results and discussion*

*Conclusions*

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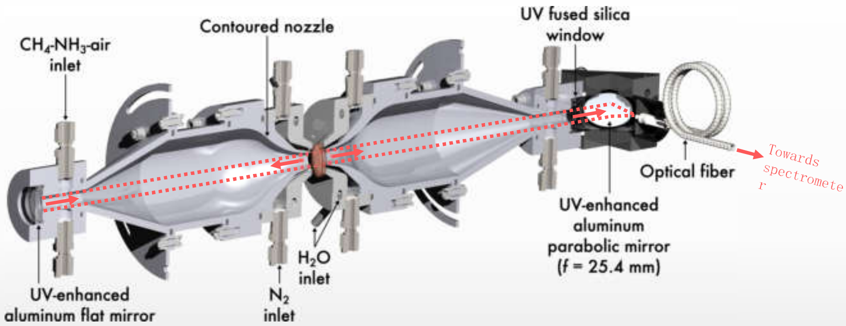
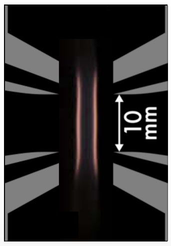
# Experimental setup




*Stoichiometric 0.5$CH_4$-0.5$NH_3$ (by vol.)*

Custom counterflow burner:

- stabilizes laminar premixed twin flames
- features optical access along its centerline
- is coupled to a spectrometer

The light emitted by two 10-mm flame discs was analyzed quantitatively for many flame conditions

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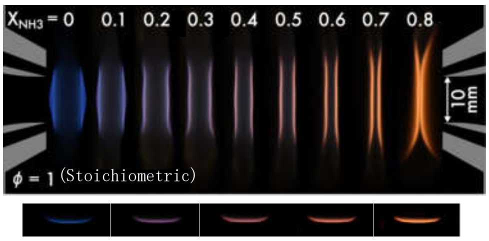
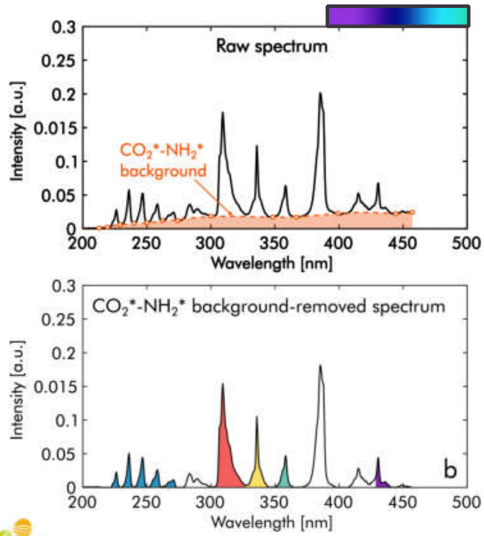
# Experimental setup




Adapted from Ku et al. *Energy* 2018

- Ammonia volume fraction in the fuel blend was varied ($X_{NH3}$)

# Data post-processing

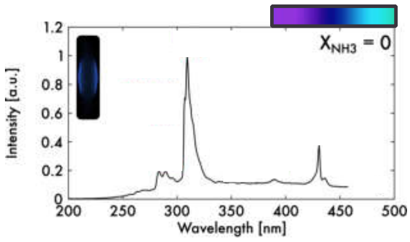



An example of flame chemiluminescence spectra

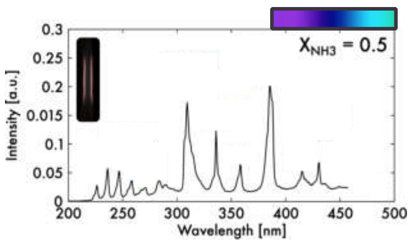
The broadband contribution from "large" species can be identified by interpolation

The chemiluminescence intensity from each species can be obtained by integration

# Results and discussion




*Spectrum measured in a pure $CH_4$ flame*

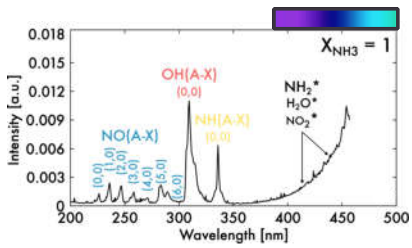



*Spectrum measured in a 0.5$CH_4$-0.5$NH_3$ flame*

Expected features of a methane flames are found

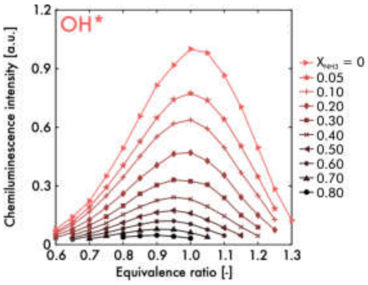
Adding ammonia yields contributions from additional excited radicals (NO*, NH*, and CN*)

Contributions from C-containing excited radicals disappear for pure ammonia

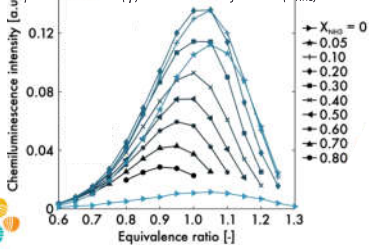



*Spectrum measured in a pure $NH_3$ flame*

## OH* and NO*




OH* chemiluminescence intensity as a function of equivalence ratio ($\phi$) and ammonia fraction ($X_{NH3}$)

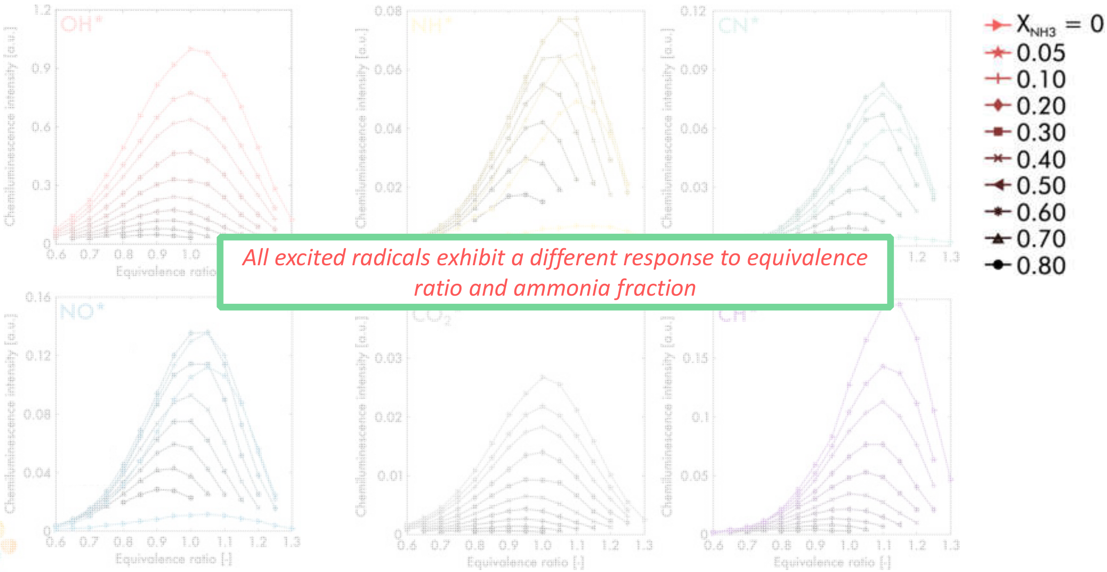



OH* intensity peaks near stoichiometric and decreases with ammonia addition

➡ OH* intensity correlates well with heat-release rate

NO* intensity first increases rapidly but then decreases with ammonia addition

## Intensity vs ammonia fraction




*All excited radicals exhibit a different response to equivalence ratio and ammonia fraction*

# Implications

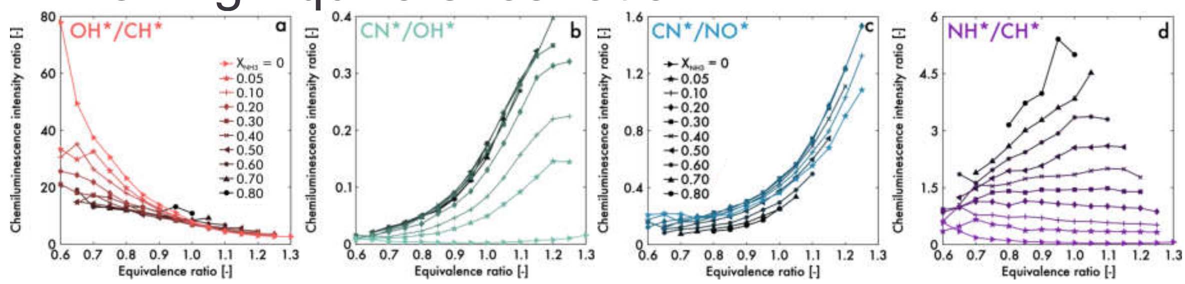
The chemiluminescence intensity also scales with the flame's surface area

Unfortunately, in most practical applications, the flame's surface area is not known and/or varies with time (turbulence)

➡ One should rely on intensity ratios to cancel effects of the flame's surface area

*6 excited radicals, leading to 15 possible ratios*

# Inferring Equivalence ratio




Except for pure $CH_4$, OH*/CH* cannot be used to infer equivalence ratio

If $X_{NH3} > 0.2$, CN*/OH* can be used to infer equivalence ratio

If $X_{NH3} < 0.5$, CN*/NO* can be used to infer equivalence ratio

*Very important for NO mitigation!*

If $X_{NH3} < 0.4$ and $\phi > 0.7$, NH*/CH* can be used to infer ammonia fraction

There is a great potential for chemiluminescence-based sensors in ammonia-methane-air flames!

# Observations

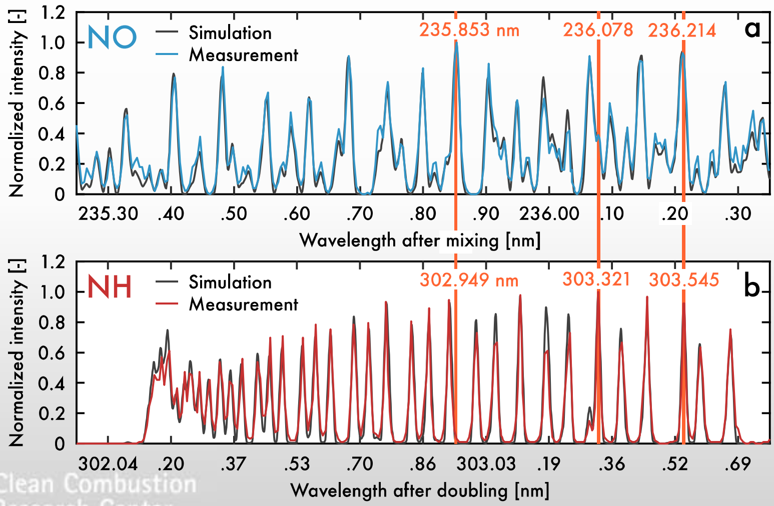
The light signature of laminar ammonia-methane-air flames was examined in details

- In addition to $NH_2$* (yellow/orange hue), 6 excited radicals contribute to the chemiluminescence in the UV-blue region
  - Such richness is a blessing for the development of chemiluminescence-based flame sensors

- Potential applications include the detection of harmful emissions (NO, $NH_3$, CO), fluctuations of fuel blend composition, and flame instabilities

For more details, see Zhu et al. *Combustion and Flame* 2021 (in press) https://doi.org/10.1016/j.combustflame.2021.111508

# Measured and simulated excitation scans

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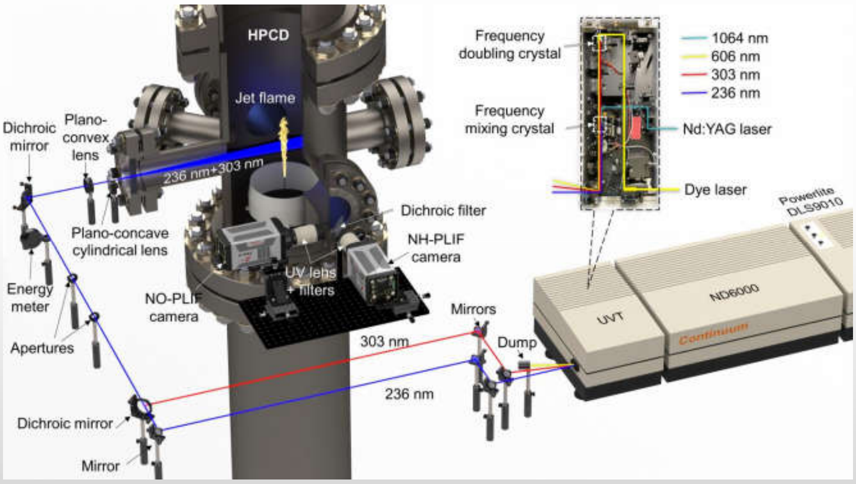
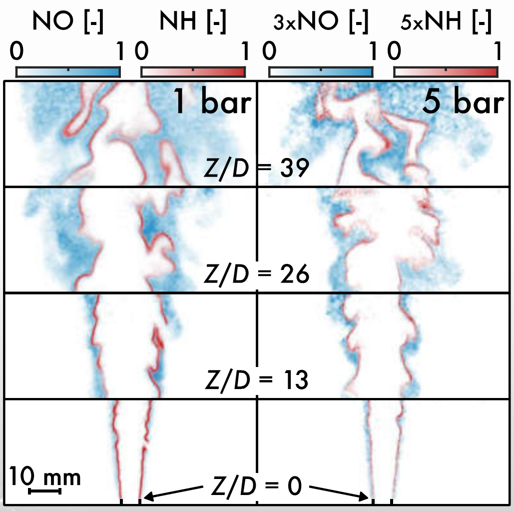
# New NO+HN diagnostics






# NO and NH in turbulent $NH_3/H_2/N_2$ flame

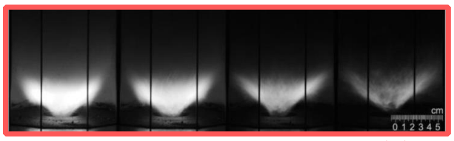



Blue is NO
Red is NH

NO: $Q_1(0)$ and $Q_{21}(1)$ transitions

NH: $R_1(4)$ transition

# Questions?

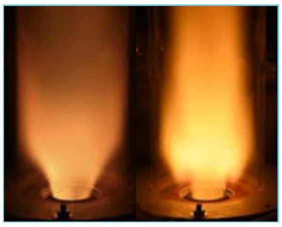



$H_2$-$NH_3$ swirl 1 bar

$CH_4$-$NH_3$ laminar 1 bar

$CH_4$-$NH_3$ swirl 1 bar

$H_2$-$NH_3$ jet 5 bar



$H_2$-$NH_3$ swirl 5 bar

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THANK YOU!

# Lecture 5: Sooting flames with ammonia

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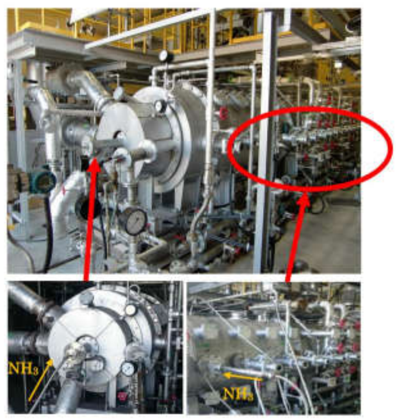
# $NH_3$-hydrocarbon applications

An intermediate step in the transition to hydrogen and ammonia is the blending of these fuels with hydrocarbons.


Ammonia engine (left); mixing system of ammonia and dimethyl ether (right).

$NH_3$ and secondary fuel engine [1-2]




$NH_3$-coal furnace [3-4]

1. A.J. Reiter, S.-C. Kong. Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. Fuel, 90 (2011), pp. 87-97
2. https://www.me.iastate.edu/song-charng-kong/research/
3. S.H. Crolius, IHI First to Reach 20% Ammonia-Coal Co-Firing Milestone, (2018).
4. C.R.I. of E.P.I. (CRIEPI), Heading towards implementation to use Ammonia for coal power plant: developing a technology to create pulverized coal to reduce the discharge of nitrogen oxides, (2017).

# $NH_3$-hydrocarbon emission

## Diversification of pollutants:

1. **Soot**: having negative effect on combustion efficiency, human health, and the environment.
2. **Polycyclic aromatic hydrocarbon (PAH)**: can react with DNA, increase the risk of cancer in humans.
3. **Nitro-PAH**: are more toxic than PAH.
4. **NOx and $N_2O$**: Harmful for human and environment (eg: Photochemical smog in Los Angeles in 1944).
5. **HCN**: concentration of 100–200 ppm in breathing air will kill a human within 10 to 60 minutes.
6. **$NH_3$**: Toxic gas.
7. **$CO_2$**: greenhouse gas





# $NH_3$-hydrocarbon research trend

**The data is collected from the below journals:**
1) Combustion Flame
2) Proceedings of the Combustion Institute
3) Fuel
4) Energy
5) Energy & Fuel
6) International Journal of Hydrogen Energy

**Search keywords: $NH_3$ soot/PAH; $NH_3$/NO; $NH_3$/HCN;**
**Year**: 2017-2022.
**Careful attention is paid to check if the work uses NH3-HC blending as fuel.**

Publication number:

**Soot/PAH 11** **VS** **HCN 1** **$NO_X$ 33**

**1. Most focus has been paid to $NO_X$.**
**2. Less attention was given to soot in $NH_3$-HC blends.**
**3. Only one paper reported the qualitative HCN concentration measurements.**

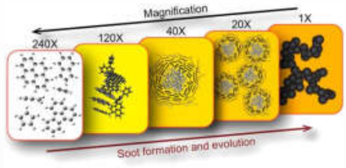
# Soot and PAHs formation in flame

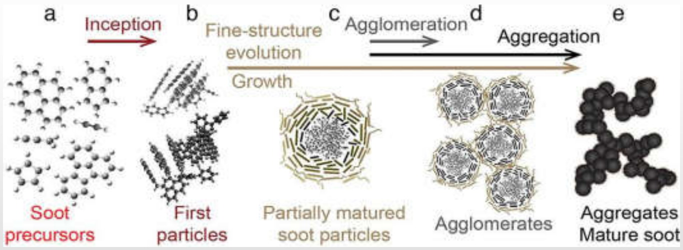
In flames, the general steps of the formation of PAHs and soot particles：

a. Formation of soot precursors --- PAHs (polycyclic aromatic hydrocarbons)

b. Soot inception from PAHs --- first particles

c-e Particle growth through surface reaction, agglomeration, and aggregation --- mature soot




The soot and PAH formation will be discussed for $NH_3$-HC combustion.

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HA Michelsen, et al, *ACS nano* 14 (2020): 12470-12490.



# Outline

1. $NH_3$-hydrocarbon application
2. **Soot formation**
3. PAH formation
4. Kinetic modeling
5. Role of HCN in PAH formation
6. Future work

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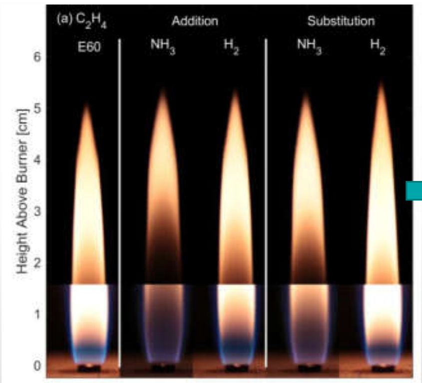
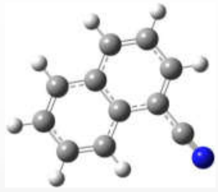
# Methodology for $NH_3$-HC combustion




Flame observation
(LII and LIF)

Pyrolysis experiment
(GCMS)

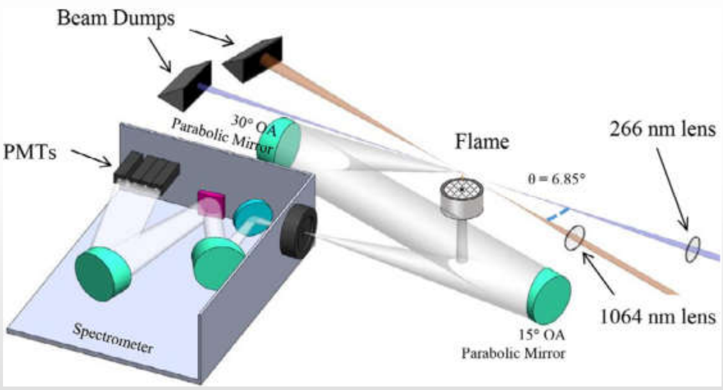


Kinetic study
(Quantum chemistry)

*Anthony M Bennett, Peng Liu, Zepeng Li, Najeh M Kharbatia, Wesley Boyette, Assaad R Masri, William L Roberts. Soot formation in laminar flames of ethylene/ammonia. Combustion and Flame, 220, 210-218.*

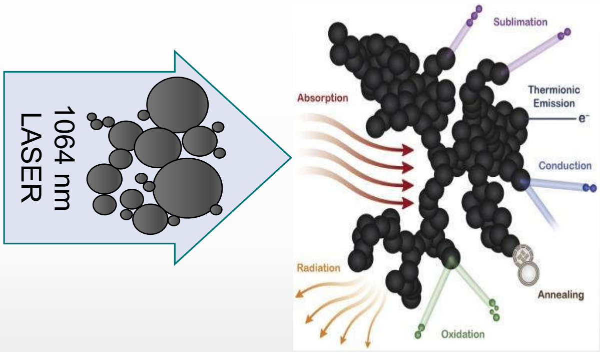


# Laser Induced Emissions




- 266 nm for LIF, 80 ps pulse duration
- UV and Vis PMTs
- 1064 nm for LII, 8 ns pulse duration
- Fluence of 0.23 J/cm2, plateau region
- Temporal offset of 900 ns

# Laser Induced Incandescence




→ Soot volume fraction

Principle: A short, energetic laser pulse is used as the illumination source. The illuminated soot particles absorb the light and are heated up by the laser pulse to very high temperatures (~4000 K).

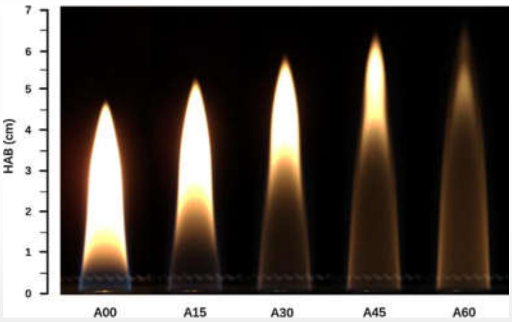
As a consequence of the increased temperature, the soot particles emit increased levels of black body (Planck) radiation, Incandescence. The Incandescence is in turn related to the soot volume fraction, and with a proper calibration quantitative soot volume fraction measurements can be made.



*Michelsen, H. A., C. Schulz, G. J. Smallwood, and S. Will. "Laser-induced incandescence: Particulate diagnostics for combustion, atmospheric, and industrial applications." Progress in Energy and Combustion Science 51 (2015): 2-48.*



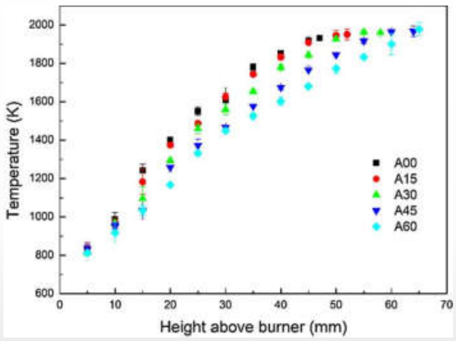
# Visible flame & T, $NH_3$-$C_2H_4$ coflow flame




| A00 | A15 | A30 | A45 | A60 |
|---|---|---|---|---|
| 60% Ar+ 0%$NH_3$+ 40%$C_2H_4$ | 45% Ar+ 15%$NH_3$+ 40%$C_2H_4$ | 30% Ar+ 30%$NH_3$+ 40%$C_2H_4$ | 15% Ar+ 45%$NH_3$+ 40%$C_2H_4$ | 0% Ar+ 60%$NH_3$+ 40%$C_2H_4$ |

Visible flame appearances with various levels of $NH_3$ addition.

**The yellow luminescence region in the flame gradually shrinks with $NH_3$ addition, indicating that $NH_3$ dramatically inhibits soot formation.**



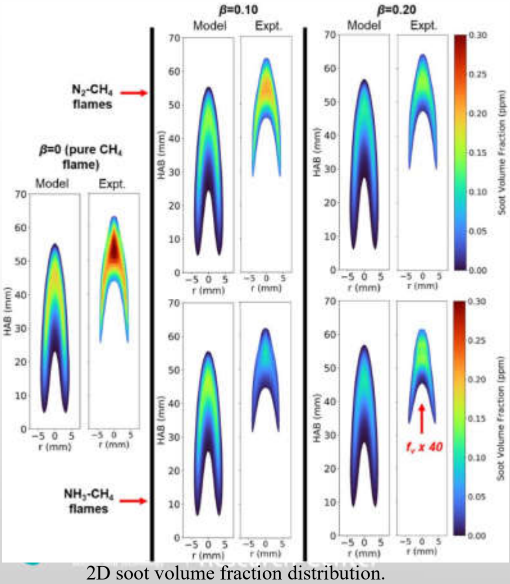

Measured flame temperature profiles along the centerline.

**Flame temperature decreases with $NH_3$ addition.**



*Liu, Yang, et al. "Effects of ammonia addition on soot formation in ethylene laminar diffusion flames." Fuel 292 (2021): 120416.*

# Soot volume fraction, $NH_3$-$CH_4$ coflow flame



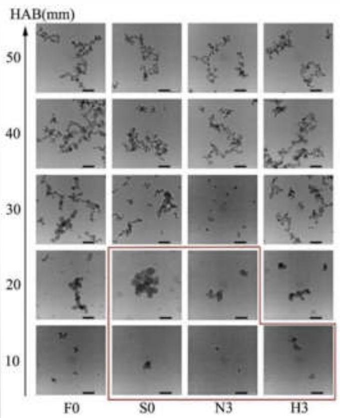

2D soot volume fraction distribution.

- Adding either $N_2$ or $NH_3$ to the flame lowers overall soot concentrations.
- $NH_3$ addition demonstrates a much stronger soot suppression.
- The stronger soot reduction by $NH_3$ flames is not captured by model, indicating a significant lacking in C-N chemistry.

*Montgomery, Matthew J., et al. "Effect of ammonia addition on suppressing soot formation in methane co-flow diffusion flames." Proceedings of the Combustion Institute 38.2 (2021): 2497-2505.*



# Soot morphology in $NH_3$-$C_2H_4$ coflow flame



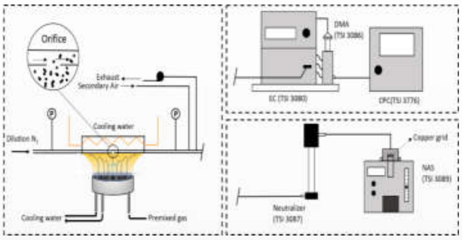

Pure $C_2H_4$ | 30%$N_2$+ 70% $C_2H_4$ | 30%$NH_3$+ 70% $C_2H_4$ | 30%$H_2$+ 70% $C_2H_4$

Soot morphology evolution along the centerline of $C_2H_4$/$NH_3$/$H_2$ flames.

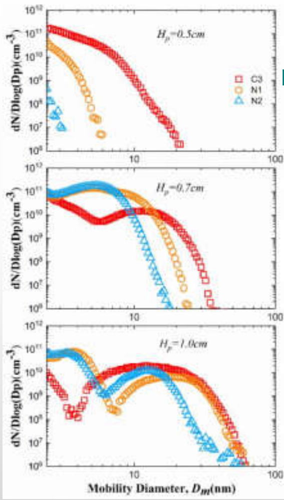
- The addition of different additives all lead to the reduction of the soot formation at each sampling point.
- The effect of $NH_3$ addition is the most significant.
- Few soot particles can be observed from the image at HAB of 10 mm, suggesting a low nucleation rate near the burner.

*Li, Qianqian, Chen Song, Zhiyu Yan, Xun Cao, Jinhua Wang, and Zuohua Huang. Effects of NH3/H2/N2 addition on soot morphology and nanostructure in laminar co-flow ethylene diffusion flame. International Journal of Hydrogen Energy 47. 36 (2022): 16321-16334*

# Soot size distribution, $NH_3$-$C_2H_4$ premix flame




Experiment setup.




Higher ammonia concentrations result in fewer small particles. This indicates the addition of **ammonia suppresses soot nucleation**.

The bimodal curve appears latter in $NH_3$ addition flame, indicating the addition of **ammonia slows down soot grow**.

Carbon flowrate in fuel keeps unchanged.

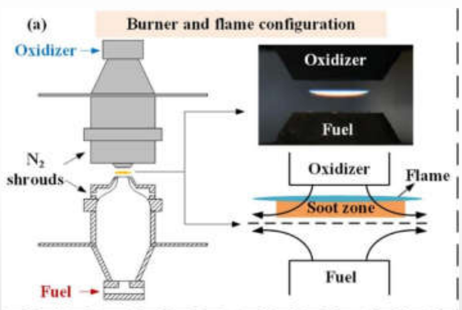
**C3: 0% $NH_3$** molar doping ratio in $C_2H_4/O_2/NH_3$/Ar flame.
**N1: 10% $NH_3$** molar doping ratio in $C_2H_4/O_2/NH_3$/Ar flame.
**N2: 20% NH3** molar doping ratio in $C_2H_4/O_2/NH_3$/Ar flame.



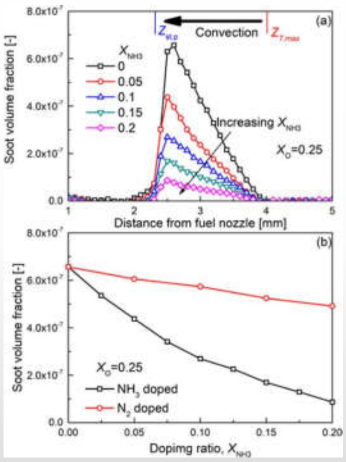
*Shao, Can, Felipe Campuzano, Yitong Zhai, Haoyi Wang, Wen Zhang, and S. Mani Sarathy. "Effects of ammonia addition on soot formation in ethylene laminar premixed flames." Combustion and Flame 235 (2022): 111698.*



# Soot formation, $NH_3$-$C_2H_4$ counterflow flame




Experiment setup.



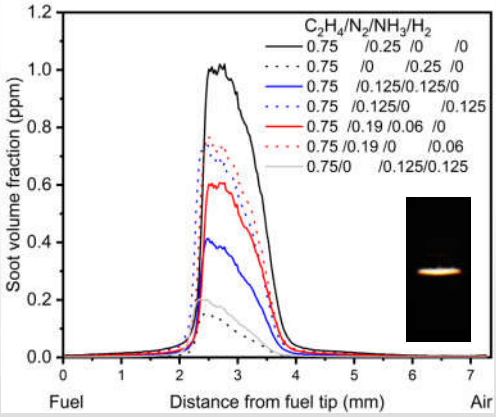

The profile of soot volume fraction with different doping ratio of in $NH_3$-doped flames.

The suppression effect is roughly proportional to the fraction of $NH_3$ introduced.



*Zhou, Mengxiang, Fuwu Yan, Liuhao Ma, Peng Jiang, Yu Wang, and Suk Ho Chung. "Chemical speciation and soot measurements in laminar counterflow diffusion flames of ethylene and ammonia mixtures." Fuel 308 (2022): 122003.*

# Soot formation, $NH_3$-$C_2H_4$ counterflow flame




SVF profiles as a function of distance from the fuel tip. *Data from KAUST soot lab.*

In experiments, flowrate of $C_2H_4$ keeps constant, $NH_3$ or $H_2$ is used to replace diluent $N_2$ (unit is mole fraction).

1. The suppression effect by $NH_3$ is more stronger than $H_2$ (see solid blue line and dot blue line, where the addition content is same).

2. The suppression effect could not be fully explained by the H atom concentration in fuel flow (compare the blue dot line and the solid red line, where the former contains more H atom)

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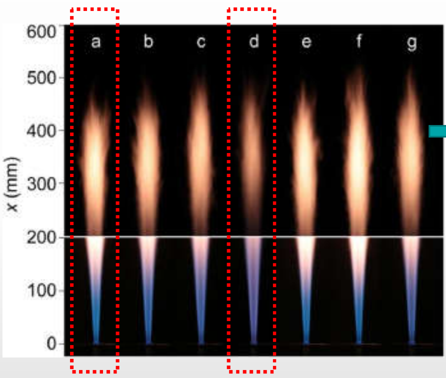
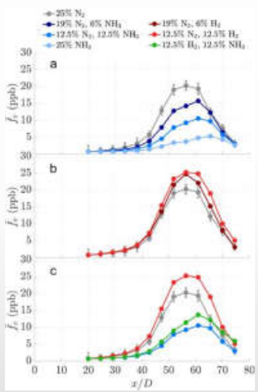
# Soot formation, turbulent $NH_3$-$C_2H_4$ jet flame




The substitution of ammonia for nitrogen has a noticeable effect on the color of the base of the flame, going from bright blue with no ammonia to dark violet with 25% ammonia.

DSLR photos of turbulent flames (U = 30 m/s) with varying levels of $H_2$ & $NH_3$. Compositions are 75% $C_2H_4$ with **(a) 25% $N_2$**; (b) 19% $N_2$, 6% $NH_3$; (c) 12.5% $N_2$, 12.5% $NH_3$; **(d) 25% $NH_3$**; (e) 19% $N_2$, 6% $H_2$; (f) 12.5% $N_2$, 12.5% $H_2$; (g) 12.5% $NH_3$; 12.5% $H_2$.




$NH_3$ addition suppress soot Formation

$H_2$ addition promotes soot formation.

Mean soot volume fraction along the flame's centerline for the 25% $N_2$ condition and (a) $N_2$/$NH_3$ variants; (b) $N_2$/$H_2$ variants; (c) 12.5% variants.

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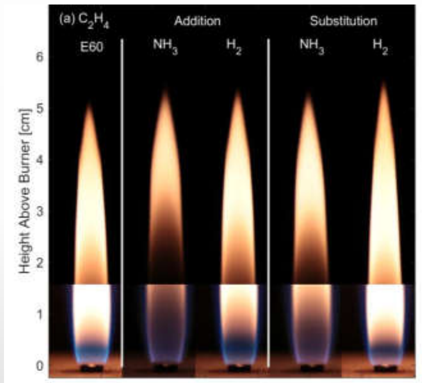
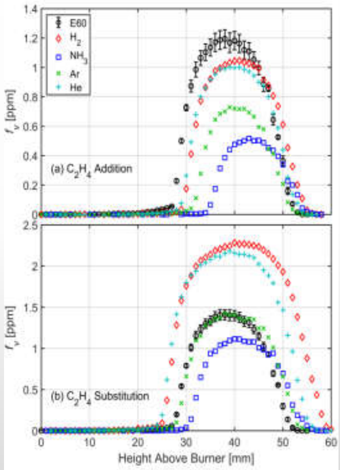
*Wesley Boyette, Scott A. Steinmetz, Thibault F. Guiberti, Matthew J. Dunn, William L Roberts, Assaad R Masri. Soot formation in turbulent flames of ethylene/hydrogen/ammonia. Combustion and Flame, 226, 315-324.*

# Soot formation, laminar $NH_3$-$C_2H_4$ coflow flame




For the **substitution method**, a certain percentage (of total reference volume) of the $N_2$ is substituted with a different diluent.
For the **addition method**, diluents are added to the reference case in a certain percentage of the total reference volume.




Centerline profiles of $f_v$.

Introduction of additional diluents suppress soot formation.

$H_2$ and He promotes soot formation, Ar presents unremarkable effect, $NH_3$ suppress soot formation

Dilution, thermal, and chemical effects are accounted for the observations

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*S.A. Steinmetza, H.A. Ahmeda, W.R. Boyettec, M.J. Dunna, W.L. Roberts, and A.R. Masria. Effects of ammonia and hydrogen on the sooting characteristics of laminar coflow flames of ethylene and methane. Fuel, 2022.*



# Soot formation in $NH_3$-HC flames

- $NH_3$ chemically inhibits soot formation both in $CH_4$ and $C_2H_4$ flames. The suppression effect is roughly proportional to the fraction of $NH_3$ introduced.
- Soot inception and growth are both slowed down with $NH_3$ addition.
- The soot reduction by $NH_3$ addition is insensitive to the burner type (Premix, counterflow, and coflow) and hydrodynamic (laminar and turbulent).
- The soot reduction by $NH_3$ introduction can not be fully explained by the higher $H/H_2$ concentrations.

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# Outline





# Laser Induced Fluorescence

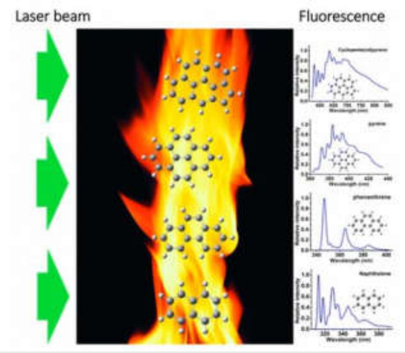
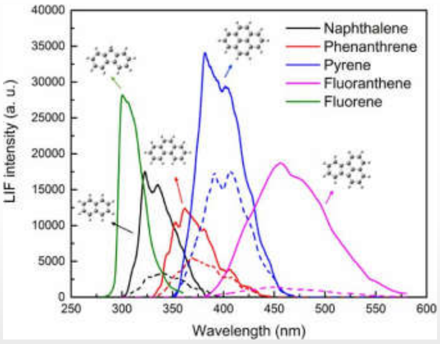



Illustration of LIF principle [1].




Normalized fluorescence spectra of PAH at 673 K (solid lines) and 1073 K (dashed lines) [2].

The PAH fluorescence spectra is greatly sensitive to its structure.


[1] Peng Liu, Zhenwu He, Gao-lei Hou, Bin Guan, He Lin, Zhen Huang. The Diagnostics of Laser-Induced Fluorescence (LIF) Spectra of PAHs in Flame with TD-DFT: Special Focus on Five-Membered Ring. J. Phys. Chem. A 2015, 119, 13009-13017.
[2] Yiran Zhang, Bang Xiao, Youping Li, Peng Liu, Reggie Zhan, Zhen Huang, He Lin. LIF diagnostics for selective and quantitative measurement of PAHs in laminar premixed flames. Combustion and Flame, 2020, 222, 5-17.

# PAH, $NH_3$-n-heptane premix flame

Experimental conditions of tested flames.

| Equivalence ratio, (Φ) | $NH_3$ blending ratio (mol.%) | $N\text{-}C_7H_{16}$(g/min) | $NH_3$(L/min) | $O_2$(L/min) | Ar(L/min) | Total flow(L/min) | $T_{max}$ (K) |
|---|---|---|---|---|---|---|---|
| 2.2 | 0 | 1.434 | 0.000 | 1.750 | 4.900 | 7.000 | 1735.8 (±70.0) |
| 2.2 | 10% | 1.399 | 0.038 | 1.721 | 4.900 | 7.000 | 1733.4 (±72.5) |
| 2.2 | 20% | 1.358 | 0.083 | 1.686 | 4.900 | 7.000 | 1729.7 (±70.5) |
| 2.2 | 30% | 1.308 | 0.137 | 1.644 | 4.900 | 7.000 | 1726.9 (±70.5) |

Carbon flow decreases to keep constant equivalence ratio.

Flame peak temperatures are close.

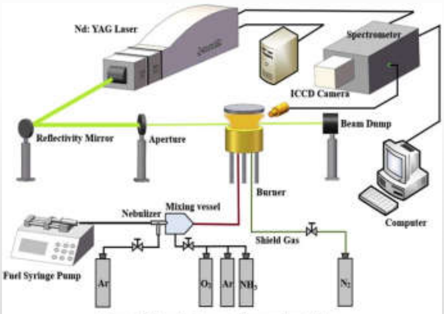
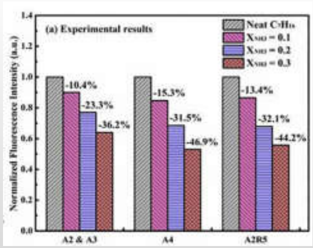



Figure 1: Schematic diagram of the experimental setup

Experiment setup.




Higher ammonia concentrations result in weaker PAH signal. This indicates the addition of **ammonia suppresses PAH formation**.



*Li, Youping, Yiran Zhang, Reggie Zhan, Zhen Huang, and He Lin. "Experimental and kinetic modeling study of ammonia addition on PAH characteristics in premixed n-heptane flames." Fuel Processing Technology 214 (2021): 106682.*

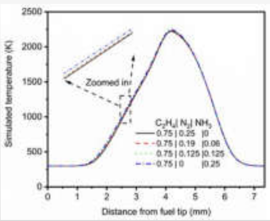


# PAH, $NH_3$-$C_2H_4$ counter-flow flames

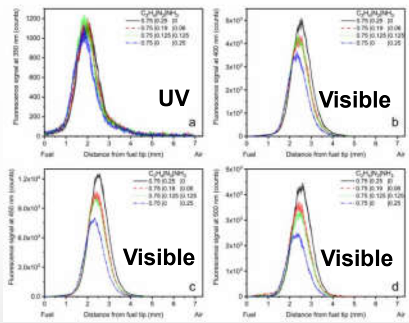
| Condition | Ethylene | Nitrogen | Ammonia | Zst |
|---|---|---|---|---|
| 1 | 75% | 25% | 0% | 0.0968 |
| 2 | 75% | 19% | 6% | 0.0964 |
| 3 | 75% | 12.5% | 12.5% | 0.0957 |
| 4 | 75% | 0% | 25% | 0.0939 |

Carbon flows keep constant.

$N_2$ is substituted by $NH_3$.




The temperature profiles are highly overlapping, ruling out the thermal effect.




PAH-LIF signal in laminar counter-flow flame.

The changes is likely from the chemical effect from $NH_3$ addition.

1): UV signal (PAH with 2-3 ring) is marginally sensitive to $NH_3$ addition.

2): Visible signal (PAH with at least 4 rings) decreases as $NH_3$ addition



*Bennett, Anthony M., Peng Liu, Zepeng Li, Najeh M. Kharbatia, Wesley Boyette, Assaad R. Masri, and William L. Roberts. "Soot formation in laminar flames of ethylene/ammonia." Combustion and flame 220 (2020): 210-218.*

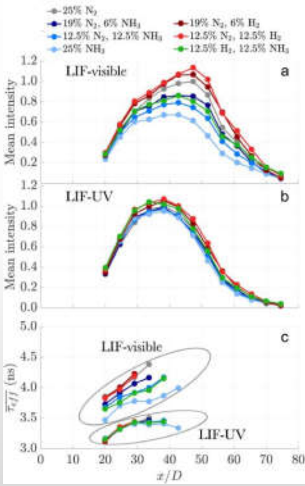
# PAH, turbulent $NH_3$-$C_2H_4$ jet flame

Details of all operating condition parameters for the pointwise LIF and LII experiments.

| $C_2H_4$ % | $N_2$ % | $NH_3$ % | $H_2$ % | $V_a/V_f$ – | $\phi_j$ – | $\xi_j$ – | $U$ (m/s) | $Re$ – |
|---|---|---|---|---|---|---|---|---|
| 75 | 25 | – | – | 2 | 5.3 | 0.32 | 30 | 12,400 |
| 75 | 19 | 6 | – | 2 | 5.4 | 0.32 | 30 | 12,400 |
| 75 | 12.5 | 12.5 | – | 2 | 5.5 | 0.31 | 30 | 12,400 |
| 75 | – | 25 | – | 2 | 5.8 | 0.30 | 30 | 12,500 |
| 75 | 19 | – | 6 | 2 | 5.4 | 0.31 | 30 | 12,200 |
| 75 | 12.5 | – | 12.5 | 2 | 5.5 | 0.30 | 30 | 12,000 |
| 75 | – | 12.5 | 12.5 | 2 | 5.7 | 0.29 | 30 | 12,100 |

Flowrate of $C_2H_4$ keeps unchanged.

$N_2$ is substituted by $NH_3$ or $H_2$.




LIF-visible signal (PAH with at least 4 rings) decreases with $NH_3$ addition, and increases with $H_2$ addition.

LIF-UV signal (PAH with 2-3 rings) is not sensitive to $NH_3$ addition.

Centerline profiles of (a) point-LIF-visible normalized mean integrated intensity; (b) point-LIF-UV normalized mean integrated intensity; (c) conditioned τeff for point-LIF-visible & point-LIF-UV.



*Wesley Boyette, Scott A. Steinmetz, Thibault F. Guiberti, Matthew J. Dunn, William L Roberts, Assaad R Masri. Soot formation in turbulent flames of ethylene/hydrogen/ammonia. Combustion and Flame, 226, 315-324.*



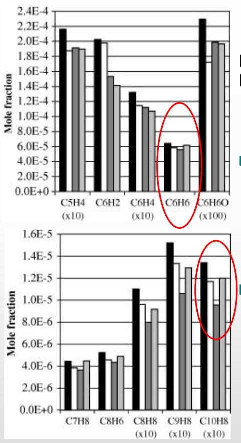
# PAH, $NH_3$-$C_2H_4$ premix flames

Table 1
Flames inlet compositions ($\phi$: equivalence ratio)

| Flames | F2.50 | F2.50C | F2.50N | F2.50H |
|---|---|---|---|---|
| $X(C_2H_4)$ | 0.33 | 0.33 | 0.33 | 0.33 |
| $X(O_2)$ | 0.40 | 0.40 | 0.40 | 0.40 |
| $X(Ar)$ | 0.27 | 0.12 | 0.237 | 0.14 |
| $X(CO_2)$ | – | 0.15 | – | – |
| $X(NH_3)$ | – | – | 0.033 | – |
| $X(H_2O)$ | – | – | – | 0.13 |
| $\phi$ | 2.50 | 2.50 | 2.54 | 2.50 |

The flowrate of $C_2H_4$ and $O_2$ kept constant.

The diluent Ar is substituted by $NH_3$.




The formation of $C_6H_6$ is marginally sensitive to $NH_3$ addition.

The formation of $C_{10}H_8$ is significantly sensitive to $NH_3$ addition.

Mole fraction profiles in rich premix flames



*Renard, C., Véronique Dias, P. J. Van Tiggelen, and Jacques Vandooren. "Flame structure studies of rich ethylene–oxygen–argon mixtures doped with CO2, or with NH3, or with H2O." Proceedings of the Combustion Institute 32, no. 1 (2009): 631-637.*

# PAH, $NH_3$-$C_2H_4$ coflow flames

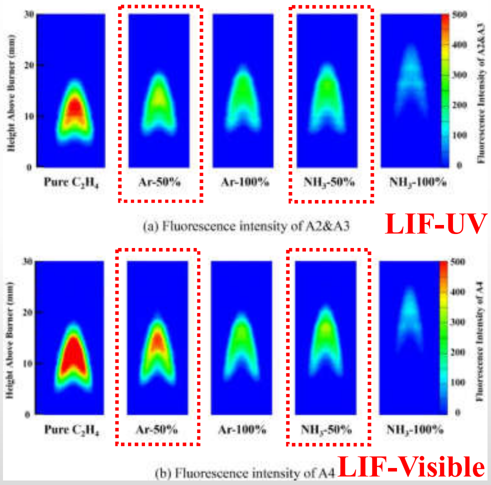
Experimental conditions of five test fuels (1 atm, 293 K).

| Cases | $NH_3$(L/min) | Ar(L/min) | $C_2H_4$(L/min) | $\alpha$(%) |
|---|---|---|---|---|
| Pure $C_2H_4$ | / | / | 0.12 | 0 |
| Ar-50% | / | 0.06 | 0.12 | 50 |
| Ar-100% | / | 0.12 | 0.12 | 100 |
| $NH_3$-50% | 0.06 | / | 0.12 | 50 |
| $NH_3$-100% | 0.12 | / | 0.12 | 100 |

Dilution ratio of the reference flame is 0 %. Comparing Ar-50% (Ar-100%) and $NH_3$-50% ($NH_3$-100%) is more meaningful.

The LIF-UV signal from Ar-50% flame is marginally higher than $NH_3$-50% flame, the signal difference increases significantly for LIF-Visible signal.

The LIF-UV signal from Ar-100% flame is notably higher than $NH_3$-100% flame, indicating the importance of flame temperature and dilution ratio effects on soot formation.




(a) Fluorescence intensity of A2&A3

(b) Fluorescence intensity of A4



Ren, Fei, Xiaogang Cheng, Zhan Gao, Zhen Huang, and Lei Zhu. "Effects of NH3 addition on polycyclic aromatic hydrocarbon and soot formation in C2H4 co-flow diffusion flames." Combustion and Flame 241 (2022): 111958.



# PAH formation in $NH_3$-HC flames

- The formation of 1-2 ring aromatic species (LIF-UV) is marginally sensitive to $NH_3$ chemistry
- The formation of large aromatic species (LIF-Visible) is greatly suppressed by $NH_3$ chemistry.
- The PAH reduction by $NH_3$ addition is very sensitive to flame temperature and dilution ratio.

# Outline

1. $NH_3$-hydrocarbon application
2. Soot formation
3. PAH formation
4. **Kinetic modeling**
5. Role of HCN in PAH formation
6. Future work



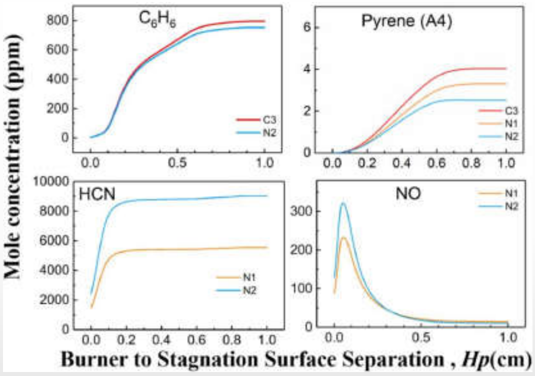
# CN chemistry in $NH_3$-HC combustion

The most applied CN chemistry used to explain PAH reduction is from *P. Glarbort et al*. 2018, Which is limited to $C_2$ species.

[HTML] **Modeling nitrogen chemistry** in **combustion**
P Glarborg, JA Miller, B Ruscic… - … in energy and **combustion** …, 2018 - Elsevier
… **nitrogen** species (amines, cyanides, etc.), and interactions between the hydrocarbon and **nitrogen chemistry** (… review is based on work on **nitrogen chemistry** published over the last 40 …
Save Cite Cited by 603 Related articles All 7 versions Web of Science: 395

For example:
1) ABF-PAH mechanism + P. Glarbort mechanism for modeling $NH_3$-$C_2H_4$-$O_2$-Ar premix flame (*Combustion and Flame 235 (**2022**): 111698*)
2) KM2 hydrocarbon-PAH mechanisms + P. Glarbort mechanism for modeling $NH_3$-$C_2H_4$-$O_2$-$N_2$ counterflow flame. (*Fuel 308 (**2022**): 122003*)
3) n-heptane mechanism + P. Glarbort mechanism for modeling premixed n-heptane-$NH_3$ blending flames. (*Fuel Processing Technology 214 (**2021**): 106682.*) and ethylene-ammonia coflow flame (*Fuel 307 (**2022**): 121914*)

# Kinetic modeling of $NH_3$-$C_2H_4$ premix flame




The computed mole fraction of benzene, pyrene, hydrogen cyanide, and nitrogen monoxide in targeted flames.

**C3: 0% $NH_3$** molar doping ratio in $C_2H_4/O_2/NH_3/Ar$ flame.
**N1: 10% $NH_3$** molar doping ratio in $C_2H_4/O_2/NH_3/Ar$ flame.
**N2: 20% NH3** molar doping ratio in $C_2H_4/O_2/NH_3/Ar$ flame.

- The computed mole fraction of benzene is close for reference flame and 20% $NH_3$ doping flame.
- The computed mole fraction of pyrene decreases significantly with $NH_3$ doping.
- The reduction of pyrene concentration is linked to the enhanced formation of HCN.

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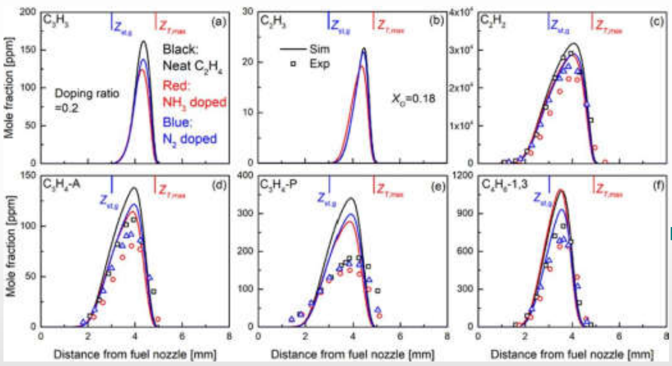
*Shao, Can, Felipe Campuzano, Yitong Zhai, Haoyi Wang, Wen Zhang, and S. Mani Sarathy. "Effects of ammonia addition on soot formation in ethylene laminar premixed flames." Combustion and Flame 235 (2022): 111698.*



# Kinetic modeling of $NH_3$-$C_2H_4$ counterflow flame




Concentration of important intermediate species in neat $C_2H_4$, $NH_3$– and $N_2$-doped flames.

The inhibiting effect of $NH_3$ addition on $C_2H_2$ formation was not captured by simulation (Fig. c) .

Trend of 1,3-butadiene ($C_4H_6$-1,3) mole fraction in the $NH_3$– and $N_2$– doped flames was not captured by the present mechanism (Fig. f).

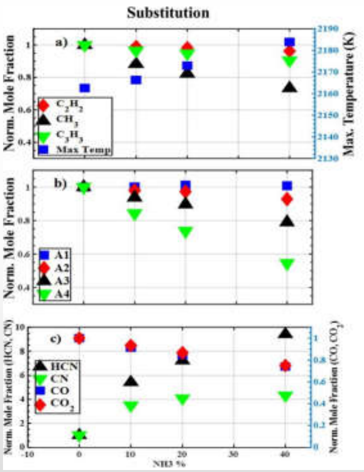
Further investigations about the chemical interactions between larger hydrocarbons and N-containing radicals are required.

Clean Combustion Research Center

*Zhou, Mengxiang, Fuwu Yan, Liuhao Ma, Peng Jiang, Yu Wang, and Suk Ho Chung. "Chemical speciation and soot measurements in laminar counterflow diffusion flames of ethylene and ammonia mixtures." Fuel 308 (2022): 122003.*

# $NH_3$-$C_2H_4$ counterflow flame, cont.

A certain percentage of the $N_2$ is substituted with $NH_3$.



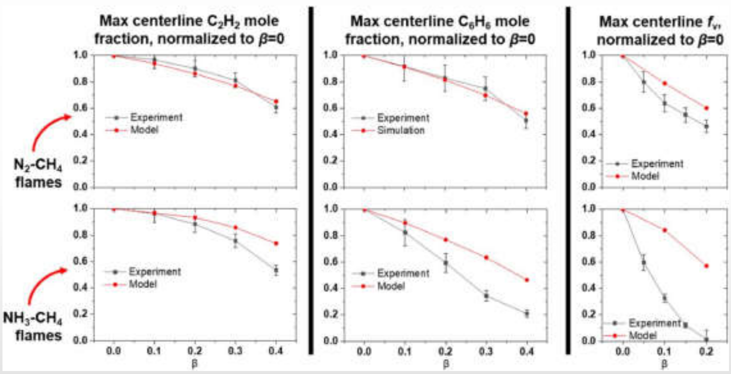

Chemical kinetics calculations for laminar counterflow flames of $C_2H_4$ mixed with varying amounts of $NH_3$.

- The introduction of ammonia causes reductions in the peak concentrations of all hydrocarbon species, with higher effects on the larger species (such as $A_4$) compared to the smaller ones.
- The almost constant $A_1$ peak concentrations for the ammonia-substitution flames can be linked to possible competing effects of reduced $C_3H_3$ concentrations and the slight temperature increase.
- The introduction of ammonia causes large increases in the peak concentrations of both HCN and CN.
- A detailed mechanism describing the nitrogen-fuel interactions with higher hydrocarbons, C3 and higher, and PAHs is required to be explored in future studies.



S.A. Steinmetza, H.A. Ahmeda, W.R. Boyettec, M.J. Dunna, W.L. Roberts, and A.R. Masria. *Effects of ammonia and hydrogen on the sooting characteristics of laminar coflow flames of ethylene and methane. Fuel, 2022.*

# Kinetic modeling of $NH_3$-$C_2H_4$ coflow flame




Normalized centerline maximum $C_2H_2$ mole fraction (left column), $C_6H_6$ mole fraction (middle column), and fv (right column) versus β.

- The model **was able** to capture changes in $C_2H_2$, $C_6H_6$, and $f_v$ with increasing **$N_2$ addition** to the fuel.
- The model **was unable** to capture changes in $C_2H_2$, $C_6H_6$, and $f_v$ with increasing **$NH_3$ addition** to the fuel.
- This disagreement is attributed to a lack of chemical pathways in the underlying mechanism that describe the interaction of $NH_3$ and its decomposition products with $C_3$ or greater hydrocarbons.

Montgomery, Matthew J., et al. *"Effect of ammonia addition on suppressing soot formation in methane co-flow diffusion flames." Proceedings of the Combustion Institute 38.2 (2021): 2497-2505.*

## Kinetic modeling of $NH_3$-HC flames

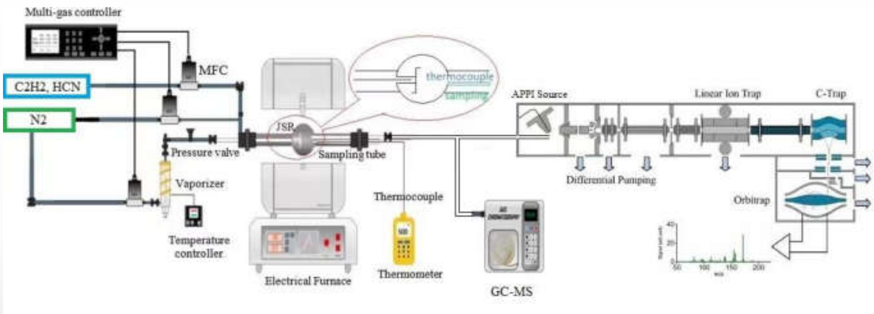
- The inhibiting effect of $NH_3$ addition on $C_2H_2$, $C_6H_6$ and some important HC species can not be captured by current mechanism.
- The reactions of $C_6H_6$ formation are inhibited due to the decreased concentrations of $C_2H_2$, $CH_3$, and $C_3H_3$.
- The reductions of large PAHs and $C_2H_2$ will inhibit soot nucleation and surface growth processes, resulting in reduction of the total loading of soot.
- A detailed mechanism describing the nitrogen-fuel interactions with higher hydrocarbons, C3 and higher, and PAHs is required to be explored in future studies.



## Outline

1. $NH_3$-hydrocarbon application
2. Soot formation
3. PAH formation
4. Kinetic modeling
5. **Role of HCN in PAH formation**
6. Future work

# Pyrolysis experiment for HCN-$C_2H_2$-$N_2$




Schematic of apparatus for JSR experiments.

Experiment conditions

| C2H2 (%) | HCN (ppm) | N2 (%) |
|---|---|---|
| 1% | 0 | 99 |
| 1% | 1000 | 98.9 |
| 1% | 5000 | 98.5 |

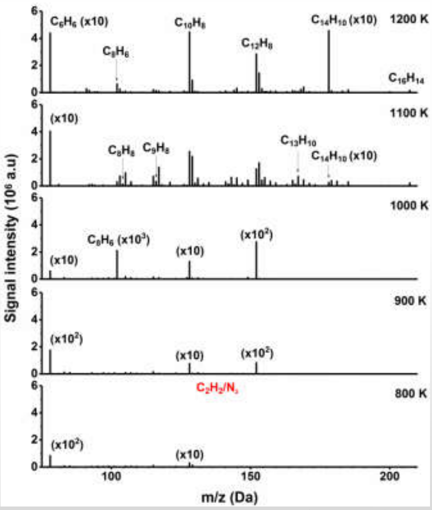
Temperature range: 800-1200 K.
Residence time: 1 s.
Heating temperature for sampling tube: 200 ºC.
Heavier species: Orbitrap MS (signal fluctuation: 6.6%)
Lighter species: GC-MS (signal fluctuation: 20%)

Research Center

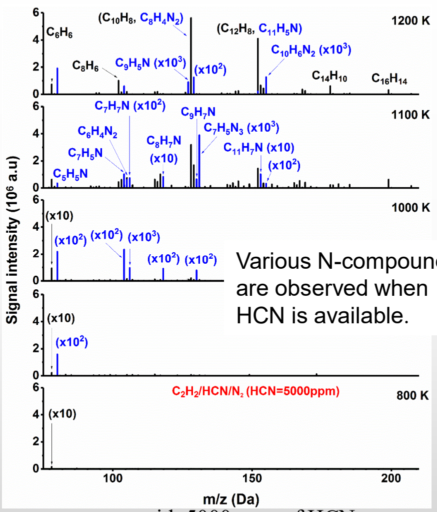
Peng Liu, Bingjie Chen, Anthony Bennett, Heinz Pitsch, William L. Roberts. Probing the influence of hydrogen cyanide on PAH chemistry. Accepted for 39th combustion symposium.



# $C_2H_2$-HCN-$N_2$ pyrolysis experiments




mass spectra observed in $C_2H_2$/$N_2$ pyrolysis



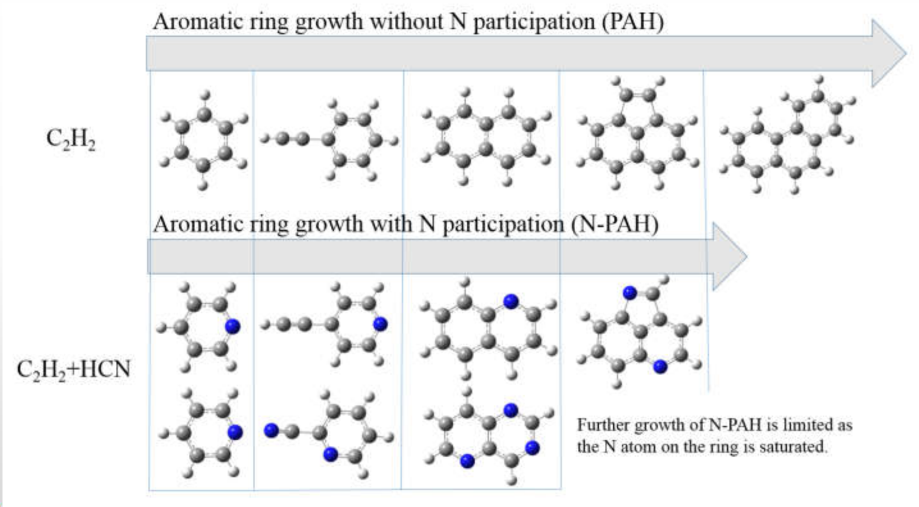

Various N-compounds are observed when HCN is available.

now with 5000 ppm of HCN

Research Center

Peng Liu, Bingjie Chen, Anthony Bennett, Heinz Pitsch, William L. Roberts. Probing the influence of hydrogen cyanide on PAH chemistry. Accepted for 39th combustion symposium.

# PAH vs N-PAH growth

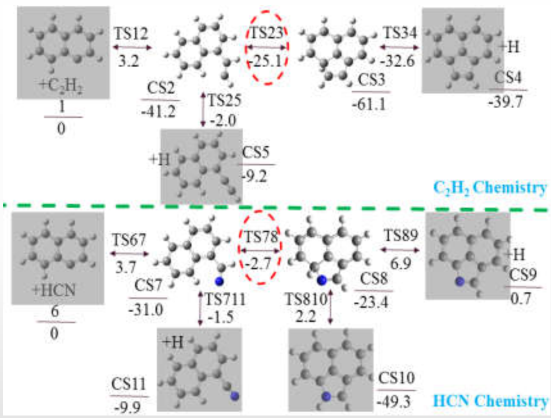



The possible growth sequence for the observed mass peak.

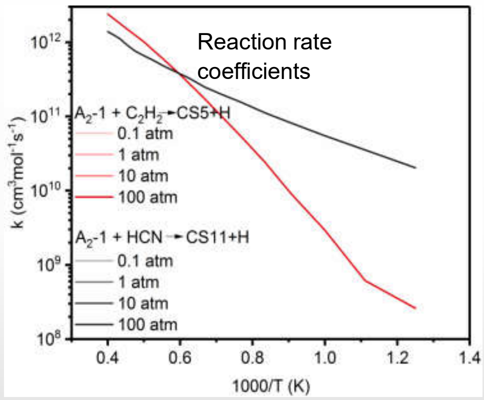
*Peng Liu, Bingjie Chen, Anthony Bennett, Heinz Pitsch, William L. Roberts. Probing the influence of hydrogen cyanide on PAH chemistry. Accepted for 39th combustion symposium.*



# $C_2H_2$ vs HCN reactivity on $A_2$-1



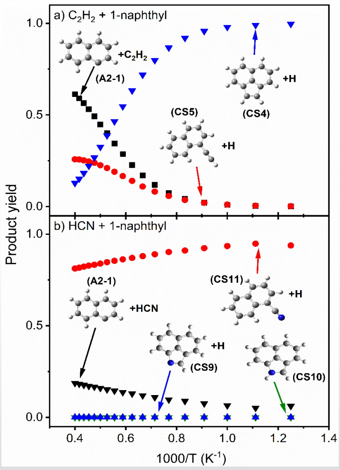

The reaction pathway energies calculated using CCSD-pVDZ (t) method




The addition of HCN to PAH radical is comparable to that of $C_2H_2$ at flame temperatures and high P

*Peng Liu, Bingjie Chen, Anthony Bennett, Heinz Pitsch, William L. Roberts. Probing the influence of hydrogen cyanide on PAH chemistry. Accepted for 39th combustion symposium.*

# Reaction characteristic of HCN and $C_2H_2$ with PAH



Product yields at 1 atm for a) $A_2$-1 + HCN pathway, b) $A_2$-1 + $C_2H_2$ pathway by RRKM-ME simulations.

In RRKM-ME simulation, the mole fraction of the excited well (CS2 or CS7) is assigned to be 1 as the input of simulations. The excited well can return to the reactants or go forward to the products, depending on channel competition at different temperatures.

In the $A_2$-1 + $C_2H_2$ system, CS4 (acenaphthylene) is the dominant product in the temperature range of 800-2100 K. (**Aromatic ring increases**)

In the $A_2$-1 + HCN system, the dominant product is 1-naphthalenecarbonitrile (CS11). (**Aromatic ring does not increase**)



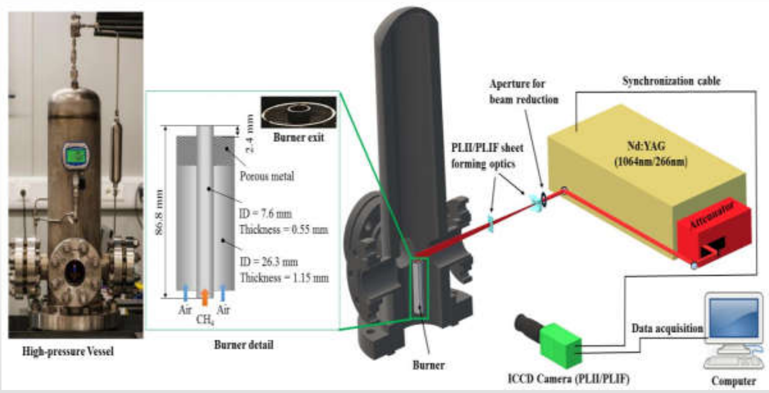
*Peng Liu, Bingjie Chen, Anthony Bennett, Heinz Pitsch, William L. Roberts. Probing the influence of hydrogen cyanide on PAH chemistry. Accepted for 39th combustion symposium.*



# Outline

1. $NH_3$-hydrocarbon application
2. Soot formation
3. PAH formation
4. Kinetic modeling
5. Role of HCN in PAH formation
6. **Future work**

# HCN and $NH_3$ addition in pressurized laminar diffusion flame



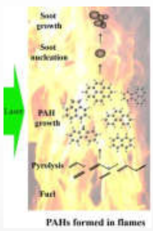

Experimental setup

**Scheduled experimental plan.**
1) HCN concentration: 0 / 1000 / 5000 ppm.
2) Pressure: 1-10 bar.
3) Fuel: ethylene and methane.
4) Test targets: PAH and soot.
5) Method: PLIF and LII.
6) Burner: co-flow and counter-flow burners.



# Full evaluation of various emissions for $NH_3$-HC combustion

Soot (LII and SMPS)



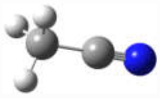

PAH (LIF and GCMS)

HCN and $CO_2$ (GCMS)


$NH_3$ and NOx (FTIR)

**Scheduled experimental plan.**
1) HCN and $NH_3$ addition content.
2) Fuel: ethylene and methane.
3) Test targets: Pollutants concentration.
4) Burner: co-flow, counter-flow, and swirling burners.

# Detect large CN species for $NH_3$-HC combustion



C2H3N

C3H3N

C4H5N

C5H5N

JSR

Counterflow flame

Coflow flame

Experimental data for the development of better CN mechanism



# Mechanism development

- Considerable development ongoing to improve the Ammonia-$H_2$ mechanisms
- Need to enhance mechanisms with better CN chemistry
- Fold this into a more complete Ammonia-HC mechanism

شكرا

THANK YOU!



# Lecture 6: Practical considerations

William L. Roberts
Director, Clean Combustion Research Center

Tsinghua Summer School
Center for Combustion Energy
Tsinghua University, Beijing
14-15 July 2022

# outline

- **Decomposition**
  - **Thermal/catalytic**
  - **Exploiting plasma**
- Nitridation
  - Experimental design
- Thermoacoustic Instabilities
- General conclusions

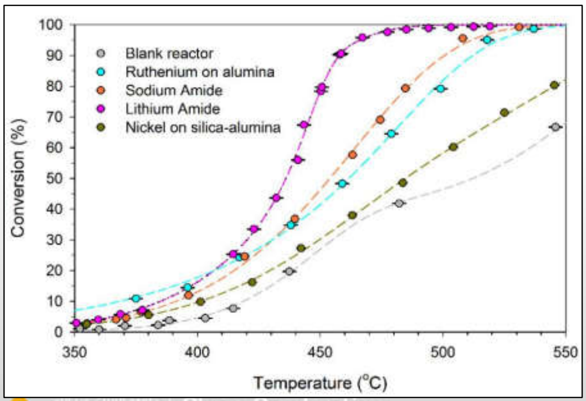


# Ammonia Decomposition

$$NH_3 \rightleftharpoons \frac{1}{2}H_2 + \frac{3}{2}N_2; \quad \Delta H = +45.6\ kJ/mol$$

Thermodynamically favorable above 190°C at atmospheric pressure.

Significantly kinetically hindered, meaning that catalysts are required to promote the production of hydrogen.



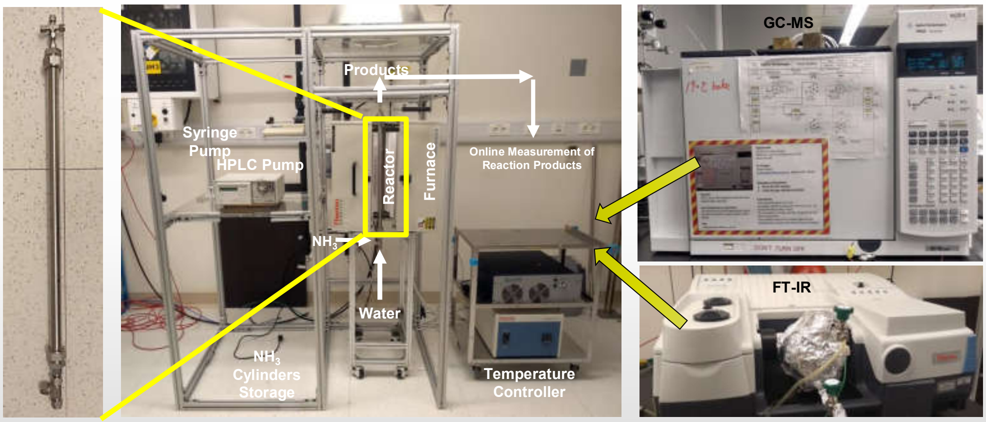

However…

The immaturity of the ammonia decomposition technology is currently a limiting factor…



***Source:** Siemens, "Ammonia to Green Hydrogen Project Feasibility Study"*

# Ammonia Cracking Rig




- Temperature → 300 – 700 °C • Pressure → 1 – 40 bar • Water content → 0 – 0.5 wt.%

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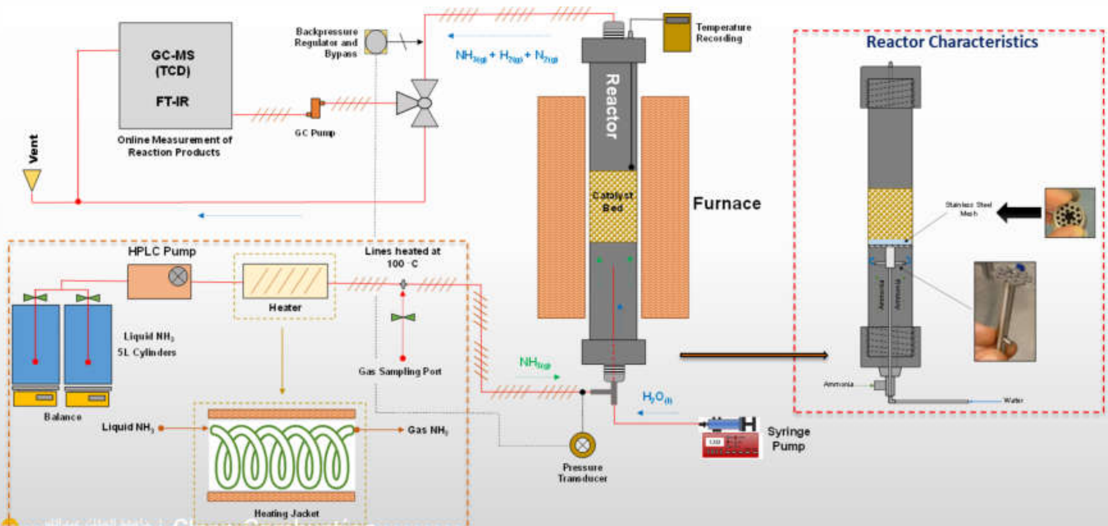
# Experimental Setup – High Pressure

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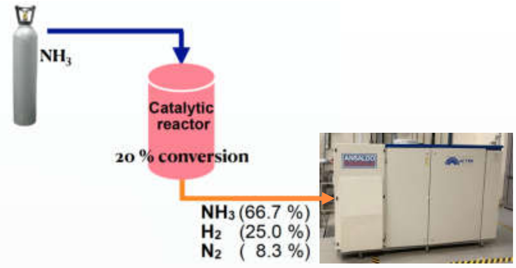
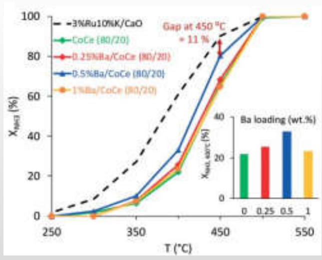
# In-Situ $NH_3$ Cracking

- Once the optimal $NH_3$-$H_2$ blend has been identified, an online catalytic $NH_3$ cracker will be connected to the mGT
- The catalytic $NH_3$ cracker is developed by Prof. Gascon at the KAUST Catalysis Center




Example of implementation for a 20% $NH_3$ cracking target




Conversion profiles vs. reaction temperature

*Reproduced from Morlanes et al. Catal. Sci. Technol. 2021*



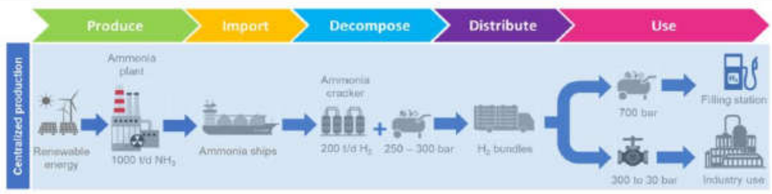
# Low-temperature plasma-chemical kinetic study for ammonia

Min Suk Cha

# New energy system with $NH_3$

- $NH_3$ : a medium for the $H_2$ storage and transportation

**7.5 bar at 23 °C** | **−33 °C at 1 atm**




(Source: Makhloufi et al 2021)

- Thermal ammonia cracker

- General decomposition process: Inversion of Haber-Bosch process

$2NH_3 + \Delta H$ (45.6 kJ/mol) $\rightarrow N_2 + 3H_2$ above 600 °C w/o catalysis ($T > 450$ °C *w/ catalysis*)

**Issues: energy consumption, limitation for different scale**

# Importance of plasma chemistry

- Plasma chemistry will play a role in the electrified future for various applications.

- **Electric-to-chemical**
  - To store intermittently generated (or surplus) electricity
  - Chemical production
    - hydrogen, methanol, ammonia, or formic acid

**HCs**

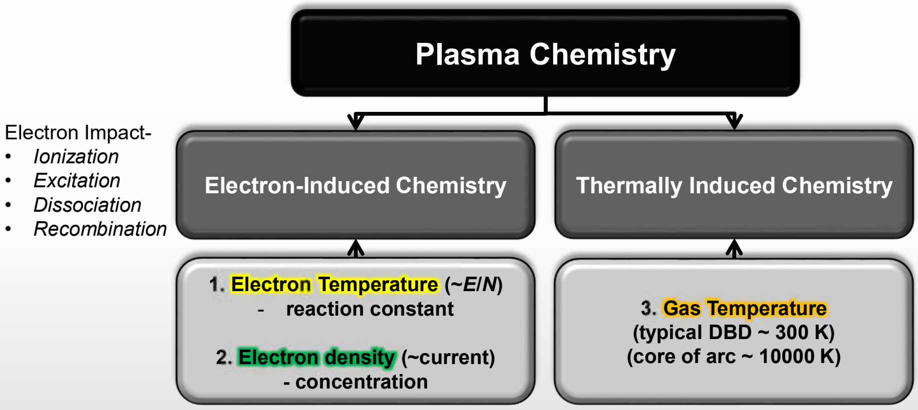
**$O_2$**
**$H_2O$**
**$CO_2$**

**+**

**$N_2$**
**(air)**

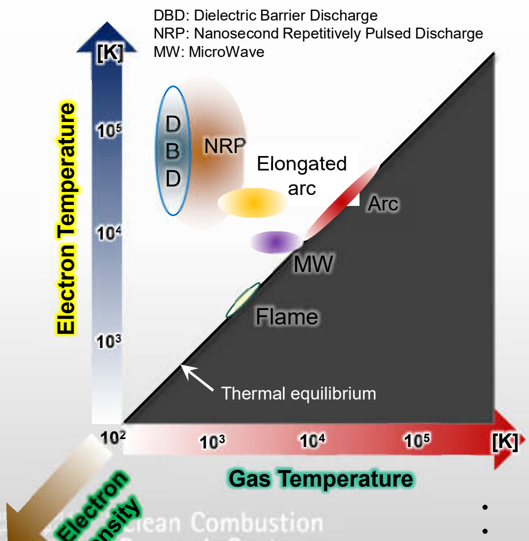
- **Fuel reforming**
  - Partial oxidation
    - $CH_4 + 1/2O_2 \rightarrow 2H_2 + CO$
  - Steam reforming
    - $CH_4 + H_2O \rightarrow 3H_2 + CO$
  - Dry reforming
    - $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$
- **Plasma-assisted combustion**
  - HCs, $O_2$: reactants
  - $CO_2$, $H_2O$: products

# Chemical reactions in plasmas

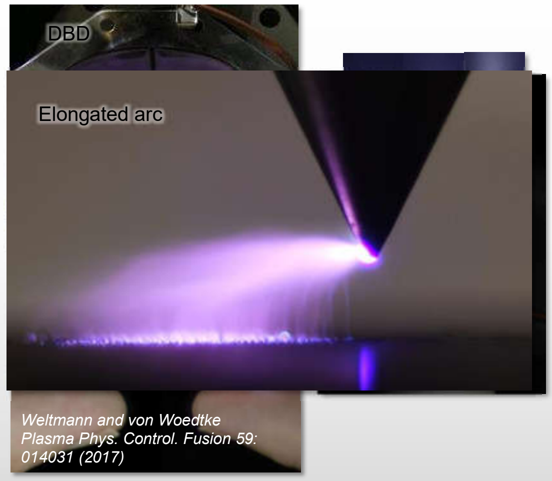



- What are the respective roles of electrons and gas temperature on the plasma chemistry?
- Can we tailor a plasma source and an operating condition for a specific application?
- Necessity to have a predictive capability for the plasma-chemical reaction

# Plasmas at atmospheric pressure




Cha and Ramses, *Frontiers Mech. Eng.* 8:903379 (2022)




- Room to optimize a specific chemical process
- Trade-off between electron T and gas T

# Kinetic simulation: KAUSTKin

- Essential predictive tool toward the knowledge-based approach

**ZDPlasKin**
Zero-dimensional plasma kinetic solver
Electron induced reactions

*E*/*N*; EEDF

Species equation
Energy equation
Bolsig+: reaction rates

**ChemKin**
Zero-dimensional chemical kinetic solver
Thermally induced reactions

$T_g$; Arrhenius form

Species equation
Energy equation

**KAUSTKin**
*Moderator*
between ZDPlasKin and ChemKin

- Providing zero-dimensional plasma-chemical kinetic solving strategy
- Physical modeling of DBD



# Experimental conditions for validation

**Common practice**

Highly diluted mixture with the noble gases (He or Ar)

Highly diluted: to minimize a temperature variation due to the reaction

Noble gas: to facilitate electrical discharges

- Effects of a balance gas on the plasma chemistry?
- Effects of gas composition on the validation of a reaction mechanism?

# Numerical conditions

| Parameter | Conditions |
|---|---|
| **Reduced electric field (*E*/*N*)** | 100–1000 Td, 100 Td-interval<br>Covering a normal range of NTP |
| **Gas temperature ($T_g$)** | 300–1000 K, 100 K-interval<br>Full conversion between 900–1000 K |
| **Gas composition ($Y_i$)** | $NH_3$ 100, 75, 50, 25 vol%<br>replacing with $N_2$, $H_2$ |



# Reaction mechanism

**Electron reaction** (electron, ion, excited species)

Plasma $NH_3$ synthesis mechanism

Ref: TRINITI, Morgan (LXCat database), van'tVeer Plasma.Sci.Tech. 2020.

+

**Thermal reaction** (neutral, excited species)

$NH_3$ pyrolysis mechanism

Ref: Combustion mechanisms
Zhang. C&F. 2021, Osipova. C&F. 2022.

**Total 66 species, 222 reactions**

(162 electron reactions + 60 thermal reactions)

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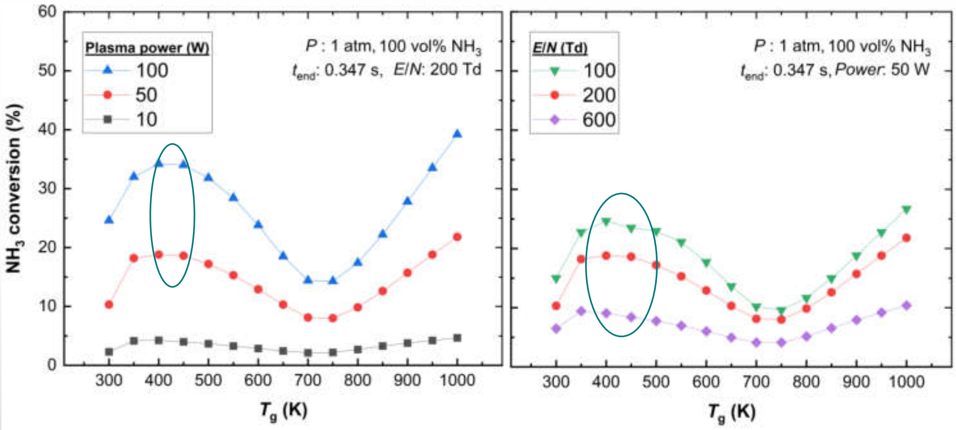
# Preliminary result from simulation




- Local maximum conversion at around 400 K
- Higher conversion at lower *E*/*N*
- Both positive toward high efficiency cracking system



# Ongoing works

- Validation of the proposed mechanism of $NH_3$ cracking with the experiment.

# outline

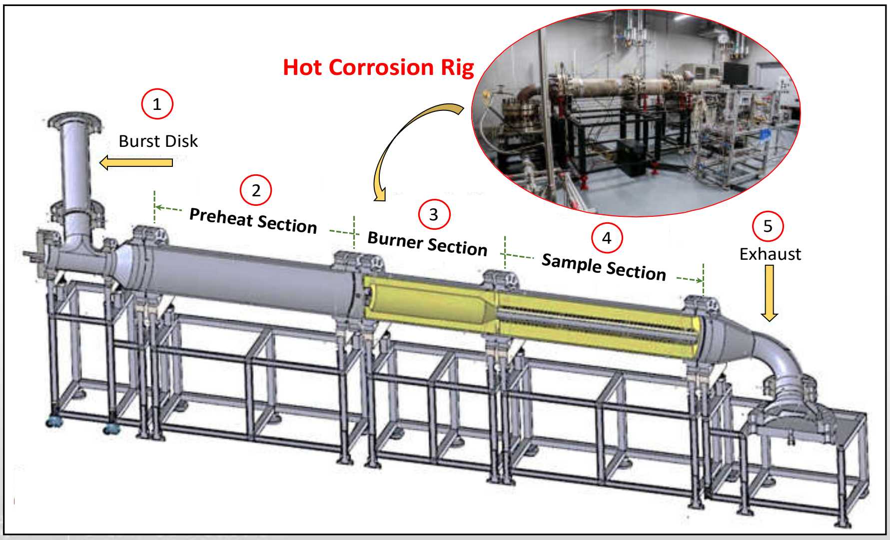
- Decomposition
  - Thermal/catalytic
  - Exploiting plasma
- **Nitridation**
  - **Experimental design**
- Thermoacoustic Instabilities
- General conclusions



# Objective of the Nitridation Project

Ammonia metal compatibility studies at elevated pressures and temperatures

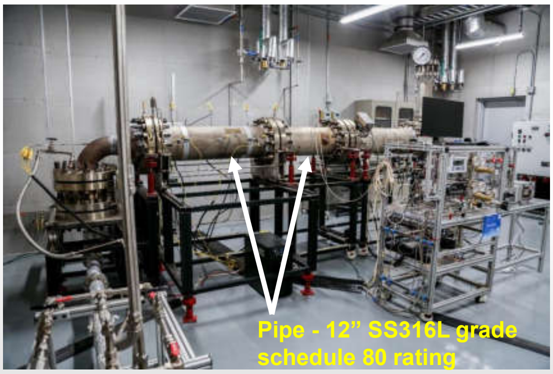
# Initial Design (First Iteration)






# Corrosion Rig

## Operated for extended hours at high temperatures & pressures

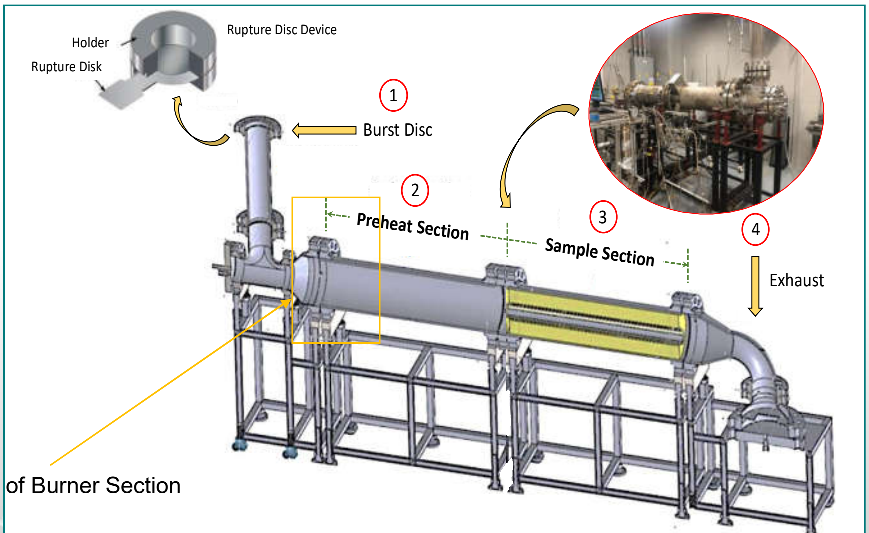




- Tested up to 700-1000 °C
- Tested up to 15 bar (Design - 40 bar)
- Low velocity (~1 m/s)

- Spray combustion of AXL (crude oil)
- Temperature control (heaters along section)
- Operate continuously for extended amount of time

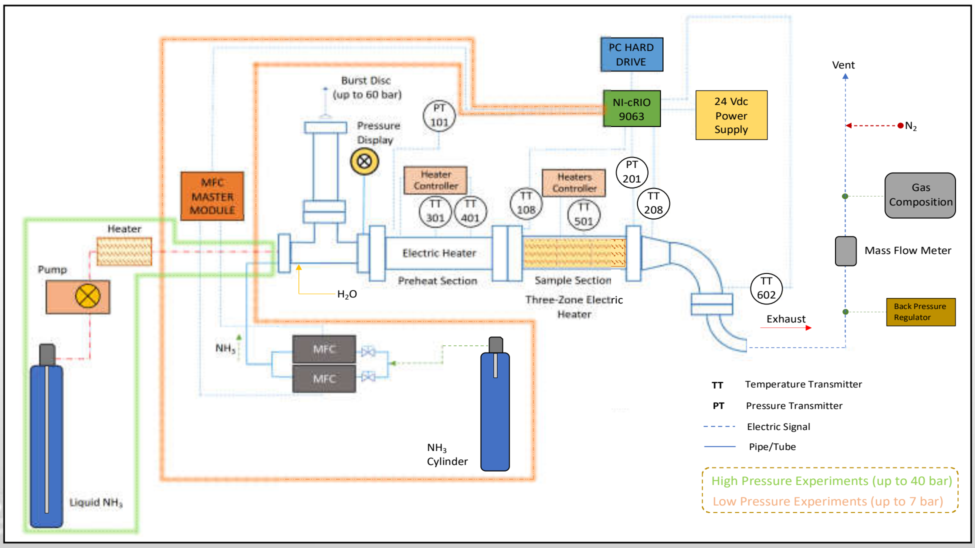
# Moving Towards Nitridation Studies

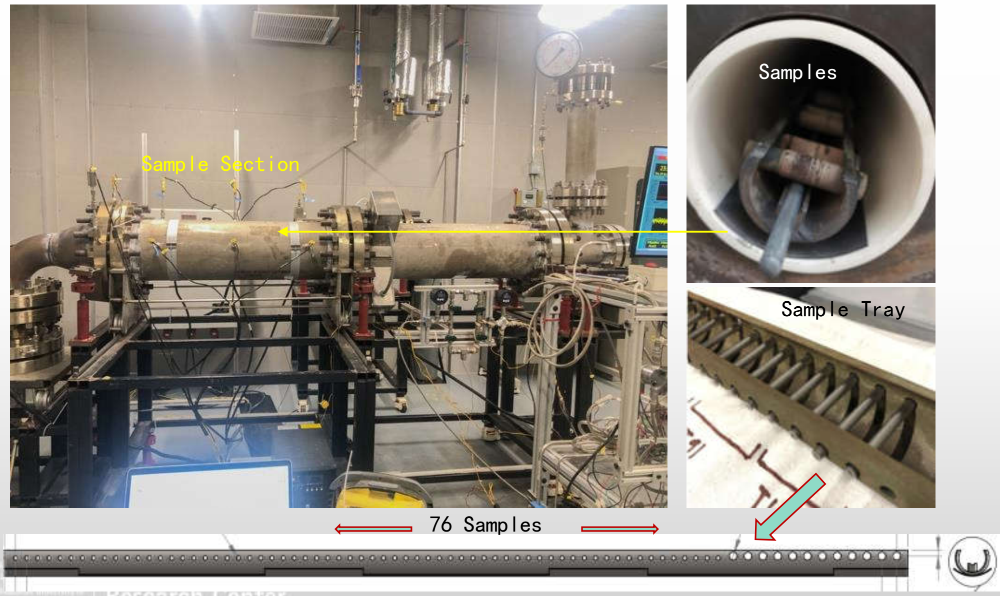



Modified Hot Corrosion Rig



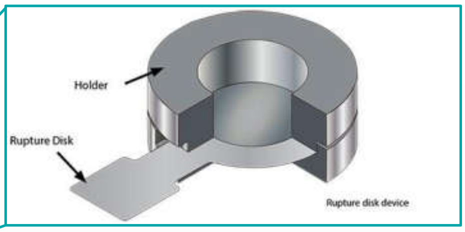
# Experimental Layout

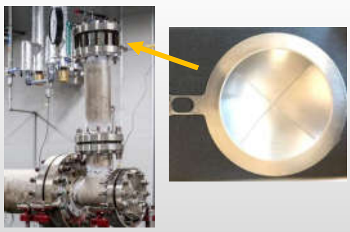



Sample Section
Samples
Sample Tray
76 Samples

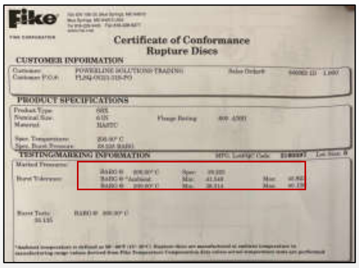


# Burst Disk


Holder
Rupture Disk
Rupture disk device



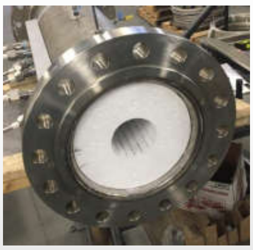
# Burst disk rupture




Spec. min at atmospheric pressure was 41.5 bar
Disk ruptured at 38 bar!



# Interior of rig post rupture

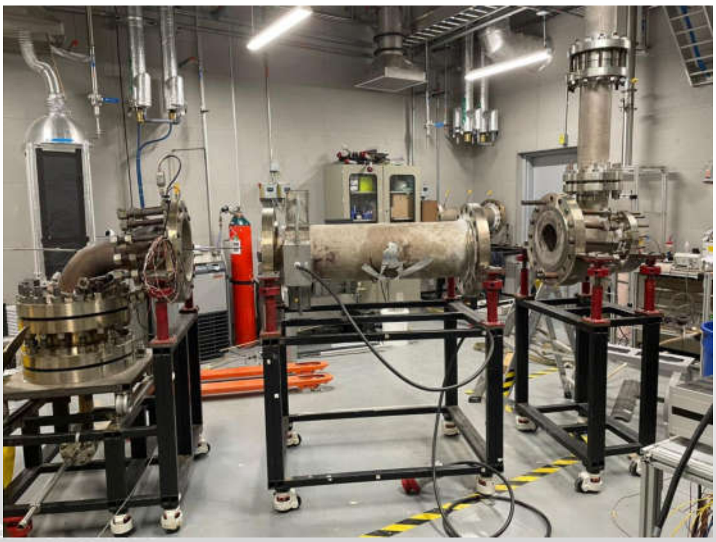


Sample Section before the welded nickel plate

# External ejecta→ Heater Coils



# Redesign (Third Iteration)



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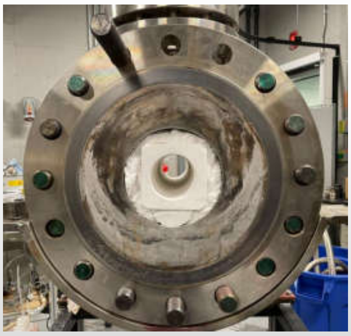
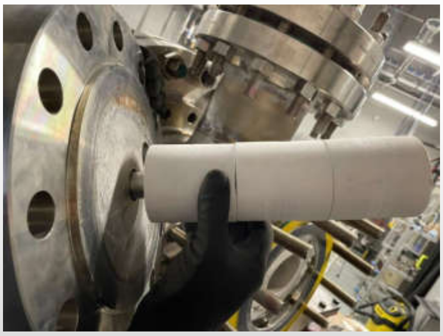
# New Ceramic in Sections

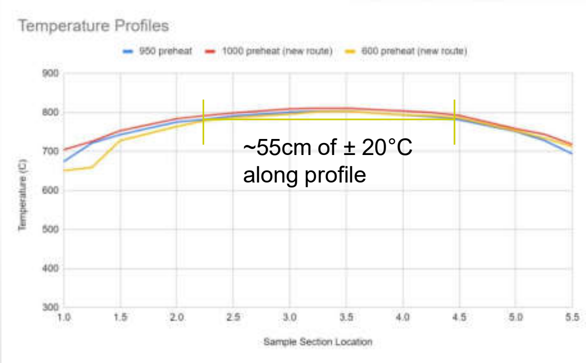


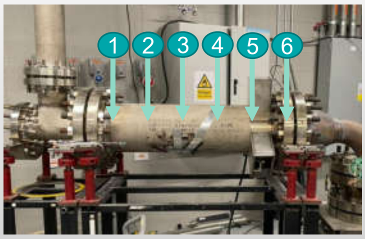
# Increasing Preheat





# New Sample Tray

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# High Flow/Higher Pressure

The tank did not provide enough pressure to continue testing.

Solution:

- Heated water bath

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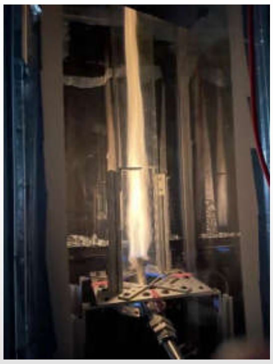
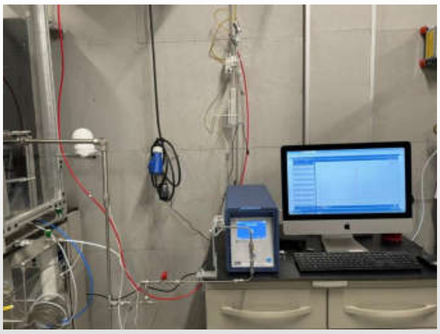
# Abatement System



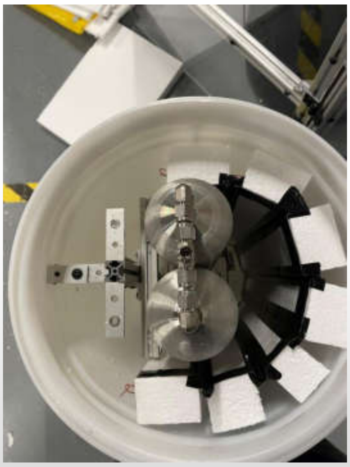





# Analytics

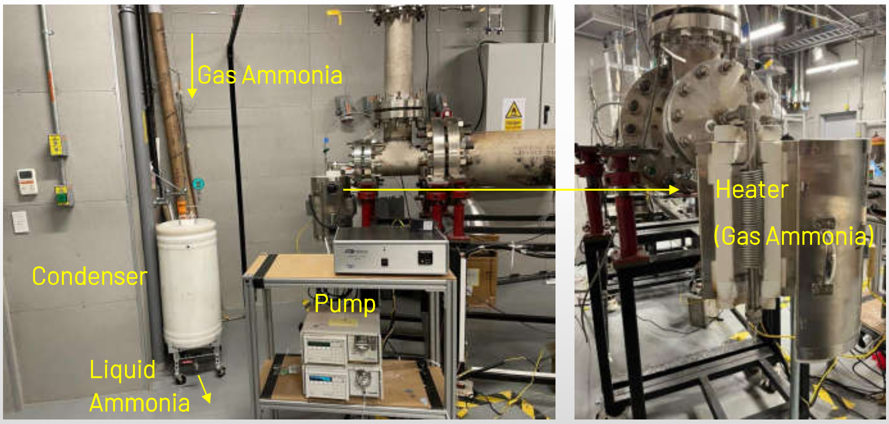



# Ammonia Condenser

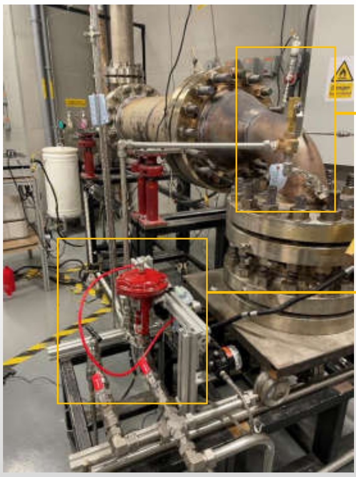




# Liquid ammonia supply system
# High pressure tests



## Safety Mechanisms



Relief valve set at 34 Bar

Badger valve set at 32 Bar

Target Pressure → 30 Bar

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## outline

- Decomposition
  - Thermal/catalytic
  - Exploiting plasma
- Nitridation
  - Experimental design
- **Thermoacoustic Instabilities**
- General conclusions

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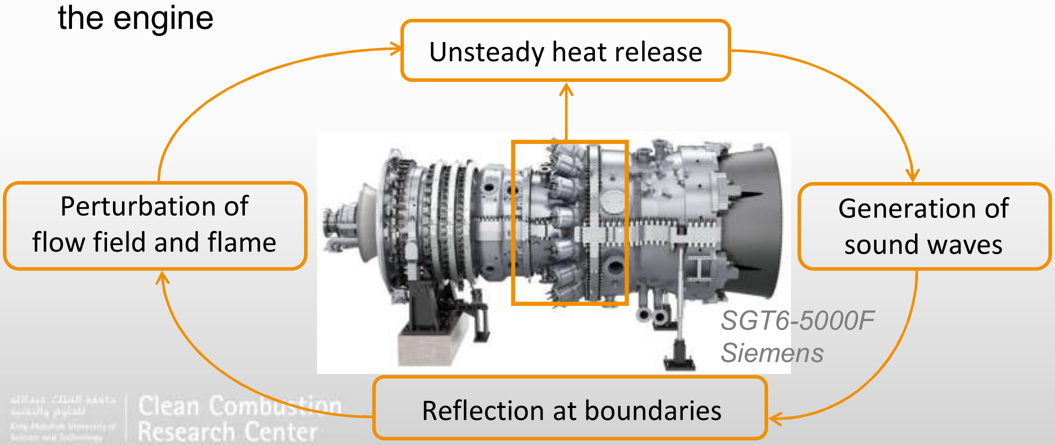
# Ammonia combustion in gas turbine engines

## Combustion instabilities

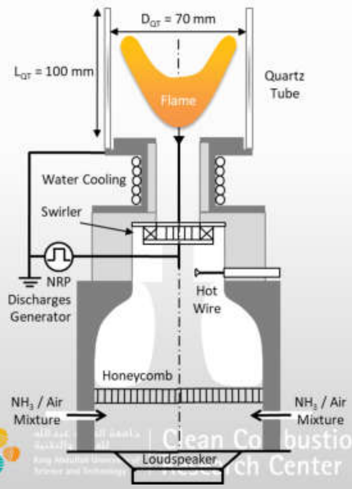
- Coupling between unsteady heat release rate and acoustic modes of the engine

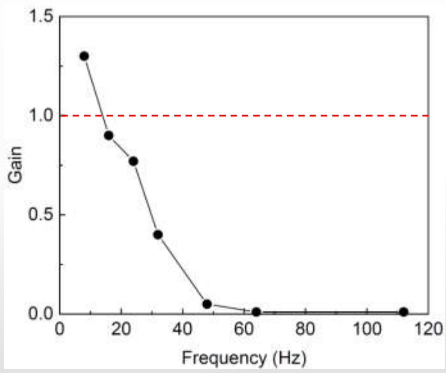





# Response of $NH_3$ flames to flow perturbations

## 4-kW atmospheric pressure swirl $NH_3$-air flame



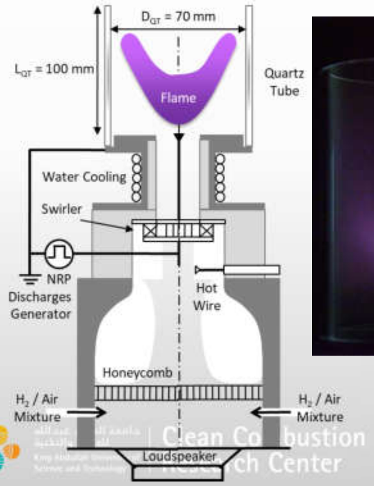



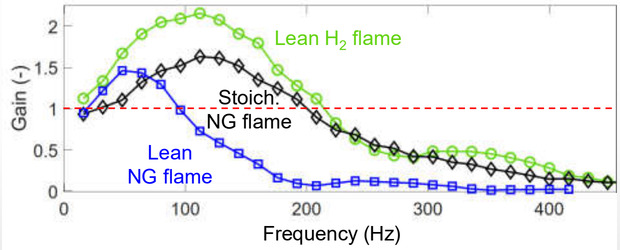

- $NH_3$ flames nonresponsive to acoustic perturbations

*Shohdy et al., WiP poster, 39th Int. Symp. Combust.*

# Response of $H_2$ flames to flow perturbations

## 3-kW atmospheric pressure swirl $H_2$-air flame



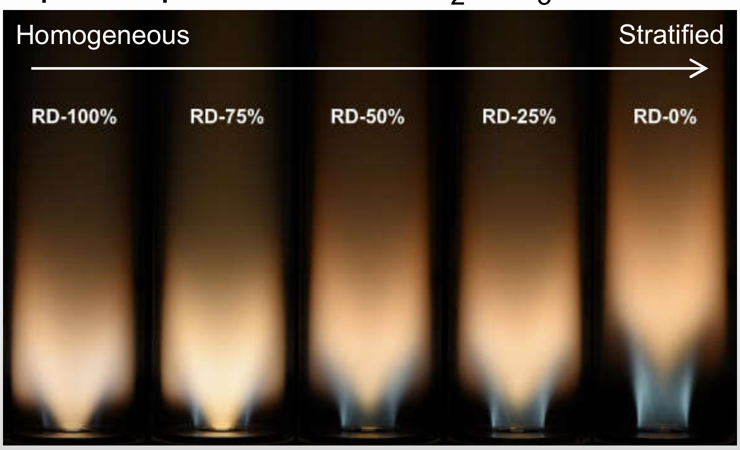

- $H_2$ flames strongly responsive to acoustic perturbations

*Amiralin and Lacoste, ASPACC 2021*



# Instabilities of $H_2$-$NH_3$ flames

## 5-kW atmospheric pressure swirl $H_2$-$NH_3$-air stratified flames



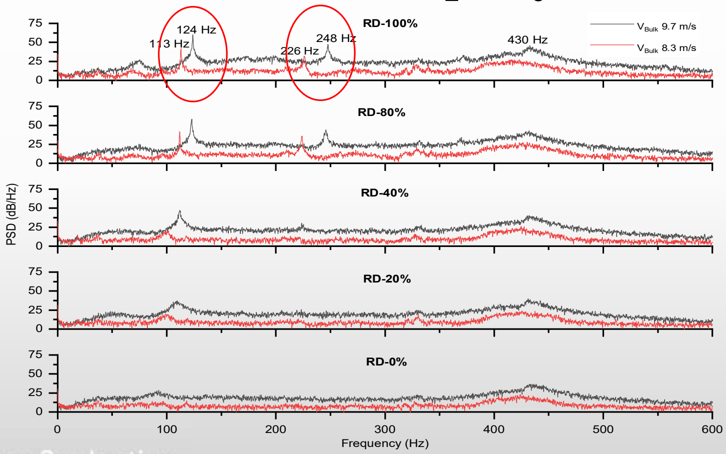

*Katoch et al., Submitted to Combust. Flame*

# Instabilities of $H_2$-$NH_3$ flames

## 5-kW atmospheric pressure swirl $H_2$-$NH_3$-air stratified flames

Homogeneous → Stratified

Unstable → Stable




*Katoch et al., Submitted to Combust. Flame*



# outline

- Decomposition
  - Thermal/catalytic
  - Exploiting plasma
- Nitridation
  - Experimental design
- Thermoacoustic Instabilities
- **General conclusions**

## Technological challenges for ammonia combustion

- Low burning velocity leads to stability issues
- High NOx
- Ammonia cracking not at commercial scale currently
- Material compatibility issues for Ammonia cracker and combustor components (Nitridation corrosion; Hydrogen embrittlement)
- High-Ammonia combustion for gas turbines; Ammonia co-firing with coal/HFO at low-TRL
- Low round trip efficiency (however, still better than liquid hydrogen or methanol!)



## Conclusion number 1

- The direct use of ammonia as a fuel in the combustion and energy system can be a reliable and efficient way of transporting and consuming hydrogen. However, care must be taken to overcome its poor combustion characteristics, such as low propagation speed, high ignition delay time, narrow flammability limits, and low flame radiation and temperature.

# Conclusion #2

- Dual-fuel combustion, or co-firing, is currently the more common strategy to enhance ammonia's slow chemistry and low reactivity. Literature is reviewed showing different combustion promoters blended with ammonia, such as hydrogen (pure, or partially cracked ammonia), methane, carbon monoxide, syngas, DME, DEE, and DMM. Hydrogen was found to be the most effective ammonia combustion promotor, and methane was found to be the least effective combustion promotor among the fuels tested in the literature.



# Conclusion #3

- Ammonia combustion chemistry differs significantly between lean and rich conditions. Burning ammonia under lean conditions feature a high O/OH radical pool, and HNO acts as an intermediate in fuel NOx production. Under rich combustion, abundant $NH_i$ radicals are formed with the H radical pool, producing NNH due to $NH_i$ recombination reaction. $N_2$ can be produced through the $N_2O$ and NNH intermediate channels, resulting in thermal De-NOx processes. In recently advanced mechanisms, the low-temperature favored $H_2NO$ pathway and the high-pressure favored $NH_i$ re-combination reactions are seen to play a vital role in ignition delay time and flame speed prediction, but still have undesirably high uncertainties. NO sensitivity is fuel composition-dependent, and the burning rate-sensitive reactions are also responsible for the NO production due to the enhancement or reduction of the O/H radical pool. Increasing the pressure is seen to decrease the O/H radical pool and thus the NO emissions.

# Conclusion #4

- In $NH_3$-$H_2$-air flames, hydrogen addition promotes a larger O/H radical pool without changing the oxidation pathway of ammonia. This leads to the observed higher burning velocity and $NO_x$ generation as compared to $NH_3$-air flames. Reactions between N-containing radicals and OH/NO and $H_2NO$ oxidation become more critical with $H_2$ substitution. $HO_2$ and $NO_2$ are more dominant than N-related small species during the low-temperature oxidation stage. Newly opened chain branching channels of NH, NNH, and $N_2O$ dominate at elevated temperatures. Methane addition plays a similar role to ammonia oxidation by enriching the O/H radical pool and $HO_2$. Reactions $CH_3 + NO_2 = CH_3O + NO$ and $NO + HO_2 = NO_2 + OH$ are seen to play a catalytic cycle role in methane oxidation, and they are the significant C-N interaction reactions in the ignition stage of ammonia-methane flames.

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# Conclusion #5

- Flame speed measurements in $NH_3$ blended with hydrocarbons, syngas, and oxygenated fuels show that the dual-fuel reaction can be understood as a parallel oxidation process of each fuel, but sharing the same radical pools of H and OH. The observed discrepancies in the prediction of laminar burning velocity are strongly related to the inaccuracy of the rate parameters of the critical nitrogen family reactions. Moreover, the key reactions in the models depend on the model itself and tested target conditions. This significantly differentiates the ignition delay time reaction sensitivity and those for the flame speed, and indicates the need to improve the capability of chemical kinetics model predictions by expanding their target flame conditions and investigating the C-N crossing reactions.

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# Conclusion #6

- Ammonia blend utilization in gas turbines and practical devices show continued attention and significant progress; however, the optimization of flame stability and NOx mitigation remains critical challenges. Two-stage combustion has received much attention recently for its ability to reduce NOx and its efficiency. This has been demonstrated over a wide range of operating conditions. Other NOx mitigation strategies continue to be explored, including very lean burning, flameless combustion, and humidification. Moreover, the ammonia spray flame is receiving close attention as a combustion system to reduce the cost and complexity associated with ammonia evaporation upstream of the combustors. A significant issue facing the ammonia spray flame is the fast cooling of the reactants in the vicinity of the injectors due to the large heat of vaporization of liquid ammonia.

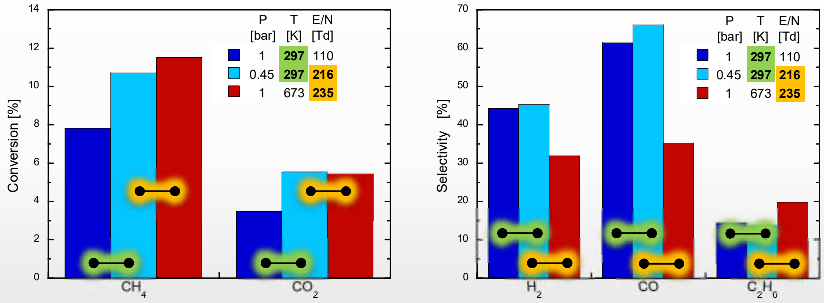


شكرا

THANK YOU!

# Respective role of electron and thermal reactions

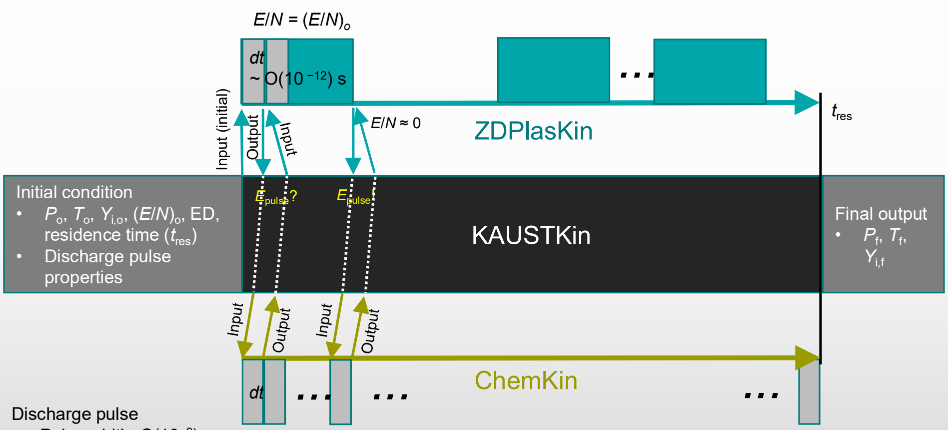
$CH_4$-$CO_2$ mixture: effect of plasma chemistry




- Experimental data using a temperature controlled DBD reactor
- Electron-impact reaction initiates the process by dissociating reactant (creating radicals).
- Thermo-chemistry controls the product distribution.

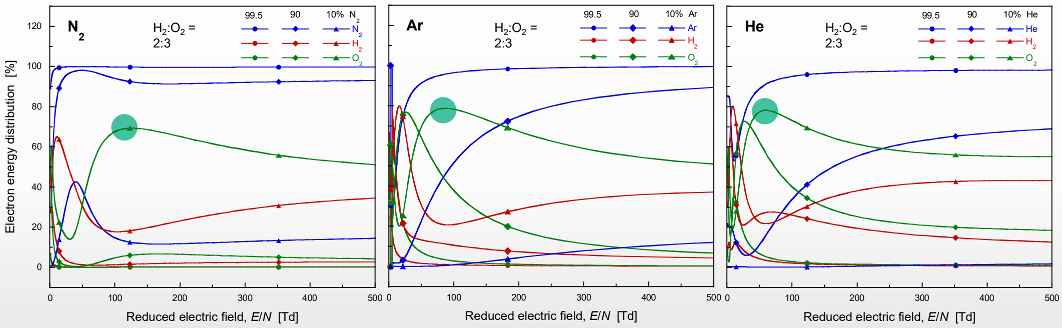
Zhang and Cha, *J. Phys. D.* 46:415205 (2013)

# Simulation scheme in KAUSTKin




Discharge pulse
- Pulse width: O($10^{-9}$) s
- Off-pulse duration: O ($10^{-3}$) s
- # pulse: 275/s
- Unit energy per pulse ($E_{pulse}$): predetermined based on overall energy density (ED)

# Importance of composition in plasma chemistry

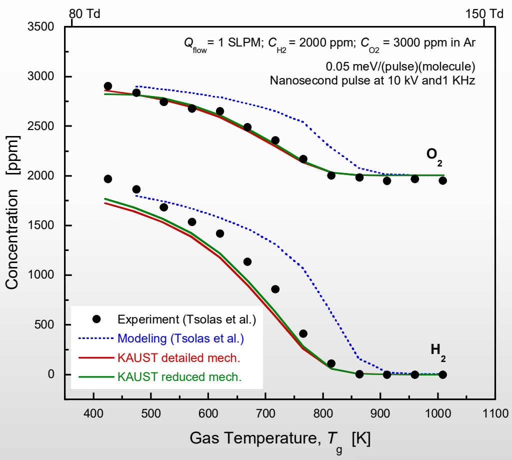



- Electron energy distribution to each gas component is significantly affected by
  - balance gas
  - and gas composition.

Snoeckx and Cha, *Combust. Flame 225:1* (2021)



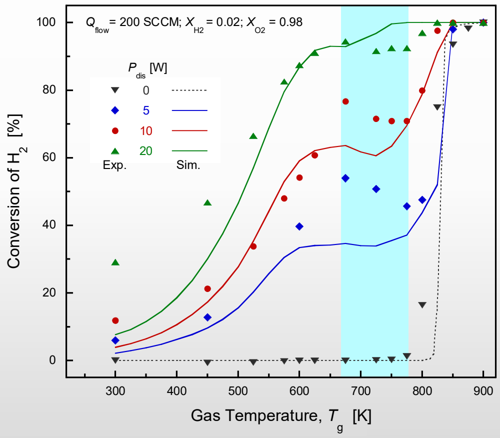
# Kinetic study for $H_2/O_2/Ar$ mixture




- Electron impact dissociation
  - $e^- + H_2 \rightarrow e^- + H + H$
  - $e^- + O_2 \rightarrow e^- + O + O$
- Excited metastable states of Ar (Penning dissociation)
  - $Ar^* + H_2 \rightarrow Ar + H + H$
  - $Ar^* + O_2 \rightarrow Ar + O + O$
- KAUST detailed mechanism
  - 33 species 221 reactions
- KAUST reduced mechanism
  - 16 species 75 reactions
  - Excluding electron impact reactions with $H_2$ and $O_2$
- **Almost identical result between reduced and detailed mechanism indicates**
  - **Electron impact reactions are not important in this mixture.**
  - **Penning dissociation prevails.**
  - ***Thus, no inert* gas in the plasma reaction**
- For the validation of kinetic mechanism, experimental conditions must be carefully selected based on a specific balance gas and mixture composition.

Snoeckx and Cha, *Combust. Flame 225:1* (2021)
Tsolas et al. *Combust. Flame 165:144* (2016)

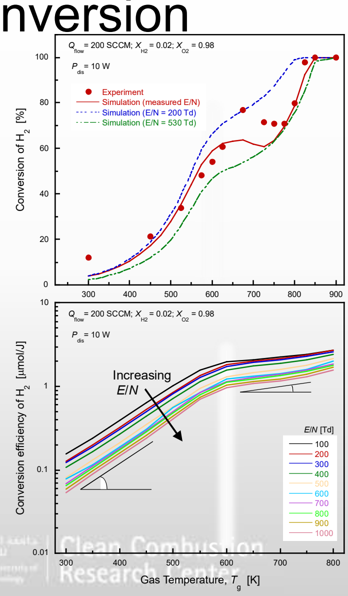
# $H_2/O_2$ system




- $H_2$ is a basic building block for HCs and $NH_3$.
- To develop a balance-gas-independent mechanism for the oxidation of hydrogen
- 21 species, 265 reactions
  - NUIGMech 1.1 thermal mechanism
  - Ozone reactions
  - Plasma $H_2/O_2$ mechanism was composed from various sources.
- Non-linear oxidation behavior
  - NTC-like behavior can be found for both experimental and numerical results.

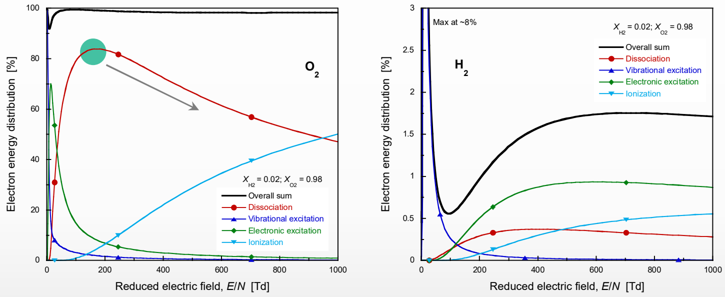
Snoeckx and Cha et al., *Combust. Flame 242*:112205 (2022)

# Effect of reduced field intensity on the conversion




- It is bounded by two predicted lines with fixed *E*/*N*.
  - *E*/*N* = 200 and 530 Td
  - Lower *E*/*N* shows a better conversion than higher one.
- Up to ~ 600 K
  - It follows *E*/*N* = 200 Td trend.
- 600 – 750 K
  - Significant transition toward the trend of *E*/*N* = 530 Td.
- The observed NTC-like behavior can be attributed to
  - the drastic change in the *E*/*N*,
  - the change in the overall reaction rate.

# Electron energy distribution (dissipation)

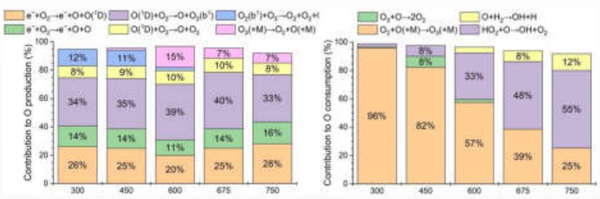



- Negligible electron impact dissociation of $H_2$
- Peak electron impact dissociation of $O_2$ at ~180 Td
  - Optimal *E*/*N* for the O radical generation
  - Higher *E*/*N* is not in favor of increase in the radical generation.
- The lower oxidation with higher *E*/*N* is due to the decreased $O_2$ dissociation resulting in less O radicals.



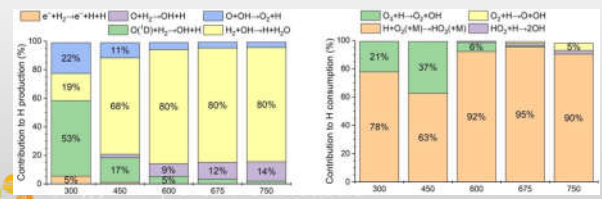
# Radical production and consumption

O radical




- O radical production
  - Mainly due to the discharge
  - Electron, quenching of O($^1$D), $O_3$ decomposition
- O radical consumption
  - $O_3$ generation in lower $T_g$
  - Increased consumption as $T_g$ increases via
    - $HO_2 + O \rightarrow OH + O_2$; $O + H_2 \rightarrow OH + H$

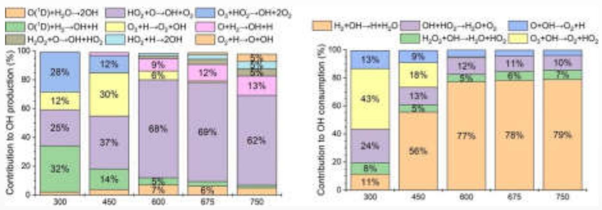
H radical



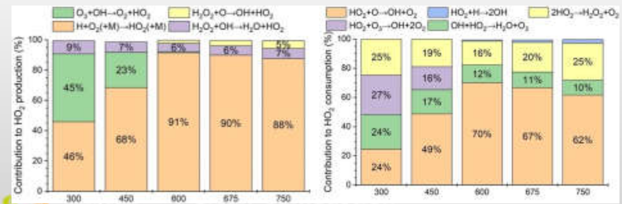

- H radical production
  - Negligible effect of the discharge
    - for lower $T_g$, O($^1$D) + $H_2 \rightarrow OH + H$, $O + OH \rightarrow O_2 + H$
  - As $T_g$ increases,
    - Main water formation route: $H_2 + OH \rightarrow H + H_2O$
    - main chain branching reaction becomes visible: $O + H_2 \rightarrow OH + H$
- H radical consumption
  - Mostly to produce $HO_2$
  - At lower $T_g$, $O_3 + H \rightarrow O_2 + OH$
  - As $T_g$ increases, main chain branching reaction becomes visible.
    - $O_2 + H \rightarrow O + OH$

# Radical production and consumption

OH radical



$HO_2$ radical



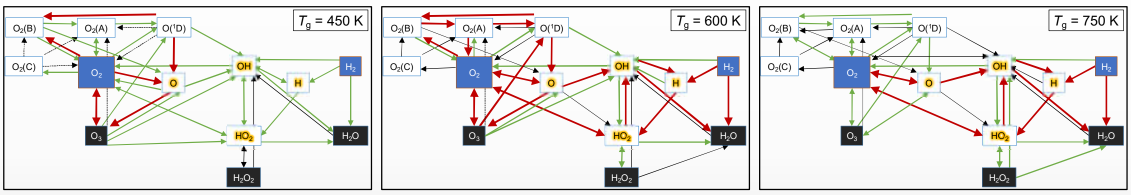
- OH radical production
  - At lower $T_g$,
    - $O(^1D) + H_2 \rightarrow OH + H$; $O_3 + HO_2 \rightarrow OH + 2O_2$; $HO_2 + O \rightarrow OH + O_2$
  - As $T_g$ increases
    - $HO_2 + O \rightarrow OH + O_2$
    - Main chain branching reactions become important
      - $O + H_2 \rightarrow OH + H$; $H + O_2 \rightarrow OH + O$
- OH radical consumption
  - At lower $T_g$
    - $O_3 + OH \rightarrow HO_2 + O2$; $OH + HO_2 \rightarrow H_2O + O_2$
  - As $T_g$ increases
    - Main water formation reaction becomes important.
    - Radical quenching due to $H_2O_2$ becomes visible
      - NTC-like behavior

- $HO_2$ radical production
  - Mostly $H + O_2 (+M) \rightarrow HO_2 (+M)$
  - Consistently $H_2O_2 + OH \rightarrow H_2O + HO_2$
  - At lower $T_g$ $O_3 + OH \rightarrow O_2 + HO_2$
- $HO_2$ radical consumption
  - To produce OH radicals, $H_2O_2$, and water



# Schematic reaction network

Time integrated production [cm$^{-3}$]: Red > $10^{17}$, Green ~$10^{16}$, Black ~$10^{15}$



**Radical initiation**

$e^- + O_2 \rightarrow O + O$

$e^- + O_2 \rightarrow O + O(^1D)$

**Oxidation limiting steps**

$O + O_2 (+M) \rightarrow O_3 (+M)$

$O_3 + OH \rightarrow O_2 + HO_2$

$O_3 + HO_2 \rightarrow OH + O_2 + O_2$

$H + O_2 (+M) \rightarrow HO_2 (+M)$

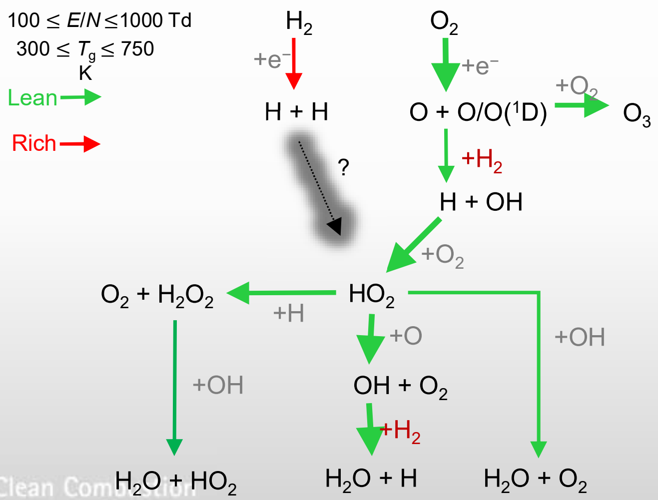
$H + O_2 \rightarrow O + OH$ at higher $T_g$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$H_2O_2 + O \rightarrow OH + HO_2$

$H_2O_2 + OH \rightarrow H_2O + HO_2$

# Schematic chemical pathway

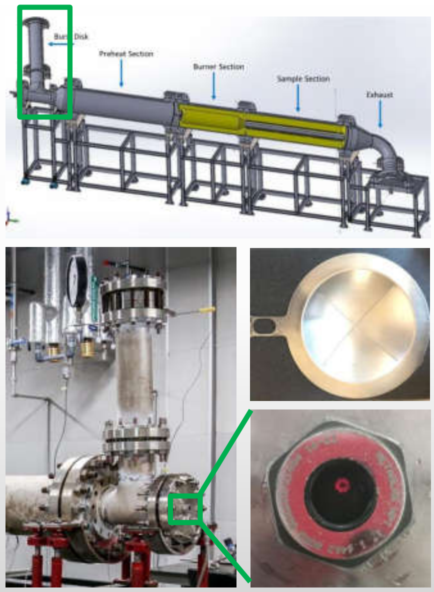





# Conclusion

- Plasma-chemical model and mechanism were developed for low-temperature oxidation of $H_2$ in a very lean mixture.
- $HO_2$ radical is the key intermediate species for the low-temperature oxidation of $H_2$.
- Role of *E*/*N*
  - Higher *E*/*N* was worse, because electron impact $O_2$ dissociation decreases as *E*/*N* increases.
  - NTC-like behavior was mainly due to the drastic change in *E*/*N* of the DBD reactor.
- Role of the gas temperature
  - Two distinctive overall reaction rates pivoting at ~600 K: contributing to the NTC-like behavior
  - At lower $T_g$:
    - O radicals are consumed to produce ozone.
  - As $T_g$ increases:
    - The negative ozone effect becomes weaker.
    - However, $HO_2$ formation (via $O_2$ + H: radical quenching) limits the oxidation rate.
    - $H_2O_2$ formation via radical quenching also contributes to the NTC-like behavior.
  - For further increased $T_g$ :
    - Full radical branching reactions ($H_2$ + O→OH + H; $O_2$ + H →OH + O) prevail over the electron induced reaction as well as $HO_2$ chemistry.

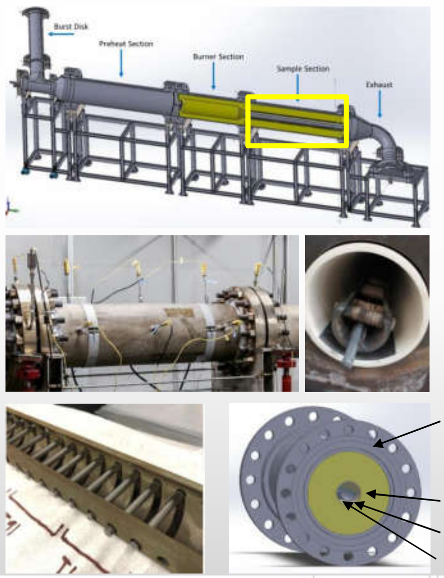
# Burst disk




- Safety Mechanism
  - The burst disk has pressure limitation (rated for 20 bar at 22°C)
- Dry air from lab supply line
- Eye piece to visually see flame stability



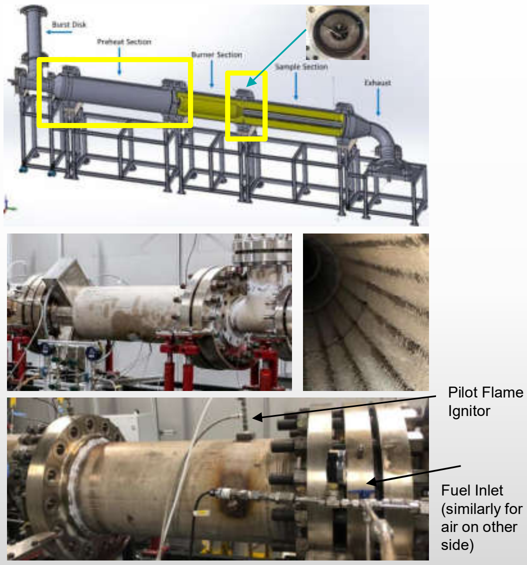
# Sample Section




- Alumina tube
- Alumina foam insulation
- 3-zone heater along length
- Lowest sustained temp = 750C
- Highest sustained temp = 900C

# Preheat & Burners

- Heating coils embedded in alumina foam
  - 30 kW, Tested to 800 F (425 C)
- Pilot flame
  - Ignite ethylene by spark
  - Diluted by preheated air
- Fuel and injector air Inlet
- Goes to a spray atomizer






# Exhaust Section

- Reduces to a 6" pipe to send to vertical exhaust line
- Elbow and piping is not internally insulated
- Needle valve is manually adjusted to maintain chamber pressure
- Need to check weld ratings for NH3
- Emergency Exhaust
  - In case the main line gets clogged