LOAD-Z

Low-NOx, **O**perable **A**mmonia Combustor **D**evelopment for **Z**ero-Carbon Power

RTX Technology Research Center

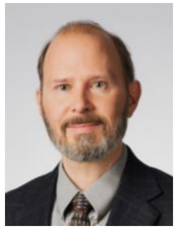
University Turbine Systems Research (UTSR) & Advanced Turbines Program Review 2023 Meeting, State College, PA
30 Oct. – 1 Nov. 2023

Prime Contractor: RTX Technology Research Center (RTRC)
Subcontractor: University of Connecticut (UConn)

LOAD-Z Project Team

Organization	Role in project
RTX Technology Research Center (RTRC)	- Project lead (prime). - Experiments in high-pressure staged combustion & swirl-stabilized combustion of NH_3. - Modeling, design, & testing of low-NOx gas turbine combustor for NH_3.
University of Connecticut (UConn)	- Fundamental NH_3 combustion experiments: • counterflow (strained) laminar flames • turbulent flame speed & structure - Development of chemical kinetic models/mechanisms.

Technology
Research Center



Lance Smith (PI)
Gas turbine combustor design & test

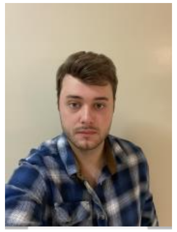
Paul Papas (co-PI)
Combustion experiments & modeling

Jordan Snyder
Combustion diagnostics & measurements

Steve Zeppieri
Combustion kinetics & modeling

Chih-Jen (Jackie) Sung (UConn lead)
Flame structure, emissions, and chemical kinetic models

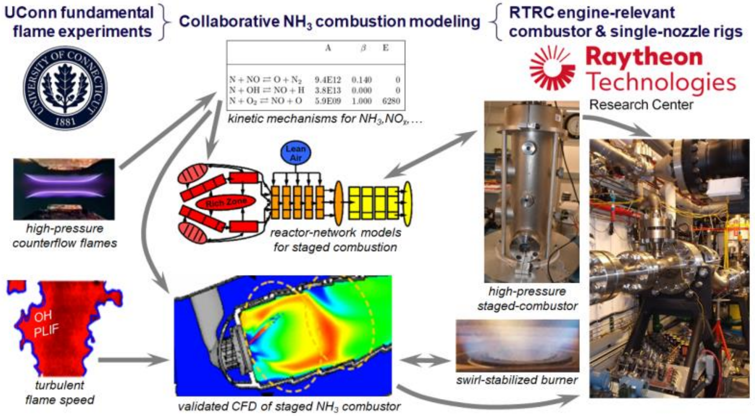
Baki Cetegen
Turbulent combustion and diagnostics



James Stevens
Combustion experiments & diagnostics

Outline

- Project Objectives & Partnership
- Counterflow Flame Studies – Reaction Rates for NH_3 Combustion
  - Experiments at 1 – 6 atm pressure (UConn)
  - Kinetic modeling in 1-D flames w/ radiation (RTRC)
- Burner Studies – NOx Emissions
  - Flat-flame burner experiments (30 atm pressure staged reactor rig)
  - Chemical Reactor Network (CRN) modeling of GT combustor
- Next Steps – Year-2 plans
  - UConn experiments incl. new rig
  - RTRC high-pressure experiments & modeling



	A	β	E
$N + NO \rightleftharpoons O + N_2$	9.4E12	0.140	0
$N + OH \rightleftharpoons NO + H$	3.8E13	0.000	0
$N + O_2 \rightleftharpoons NO + O$	5.9E09	1.000	6280

LOAD-Z Project – Objectives & Partnership

Low-NOx, Operable Ammonia Combustor Development for Zero-Carbon Power

- ***End Goal:*** Demonstrate performance of gas-turbine-capable NH_3-fuel combustor, at single-nozzle scale.
- ***Go Get:*** Obtain fundamental **&** engineering NH_3-flame data at gas-turbine-relevant conditions → P_{inlet} , T_{inlet} .

Year-4

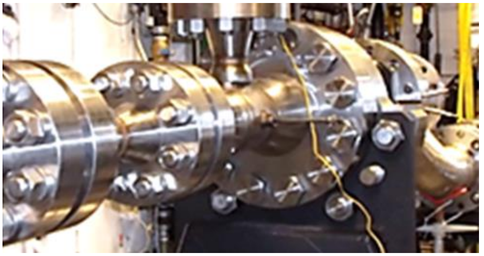
Year-3

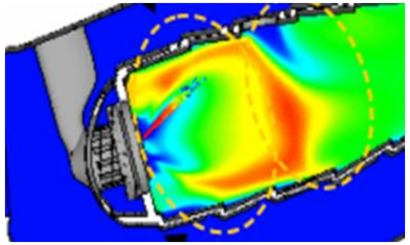
Year-2

Year-1

Time

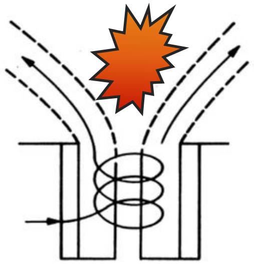
RTRC





- Single-nozzle high-pressure combustor, fired w/NH_3 fuel
- Measure emiss. & performance: NOx, efficiency, stability

- Flat-flame high-P burner (>>1-atm) for NOx evaluation



- 1-atm swirl-stab. burner
- Piloting studies w/ H_2

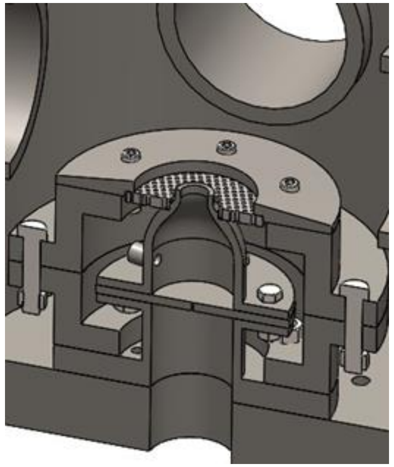
Modeling:

- CFD for design
- Kinetic improve. w/ exp. data

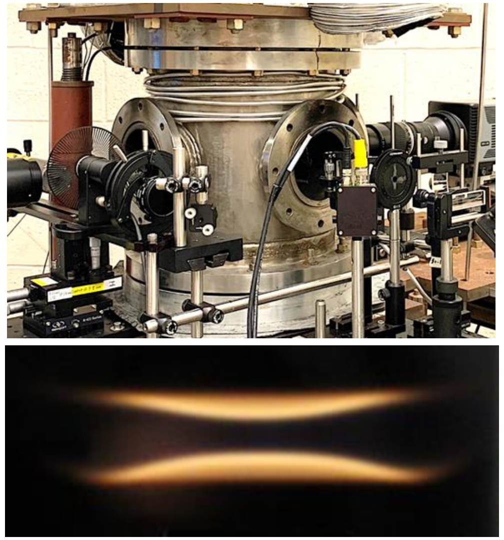
- CFD & validation
- Turb. models for NH_3 comb. & NOx (no post-process.)

- CRN modeling
- Counterflow
- Kinetic mechanisms

UConn



- Turbulent S_L rig, for NH_3 @ P, T > ambient (~20% turb. intensity)



- Counterflow flame rig, compatible w/NH_3 fuel
- Measure strained flames w/ inlet P, T > ambient

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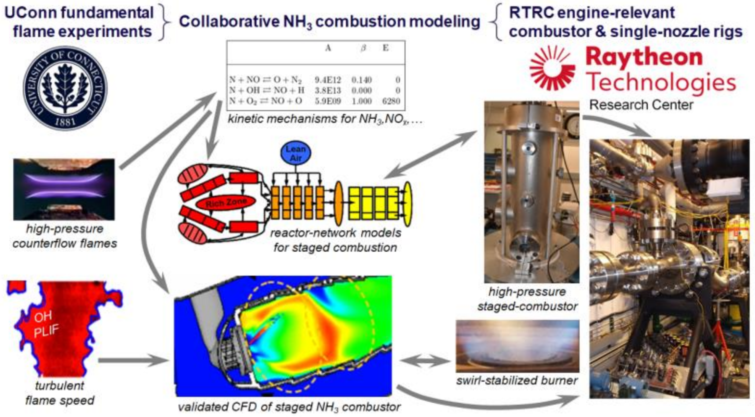
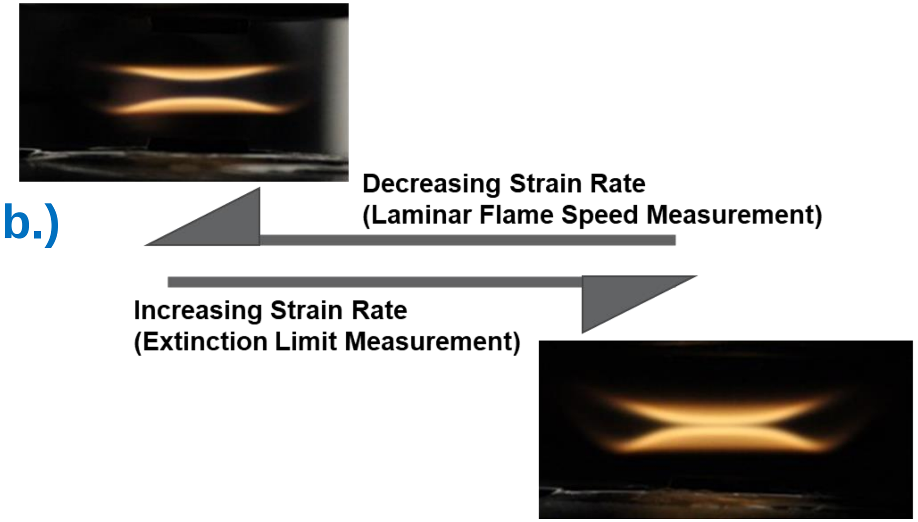


Current Gaps for Understanding Ammonia Combustion

Combustion Challenges

- Low overall reaction rate
  - Relatively low flame speed & **extinction strain rates**
- Flame stabilization & efficiency in **highly turbulent flow (GT comb.)**
- Quantifying NOx formation & emissions

Counterflow NH_3/Air Premixed Flames

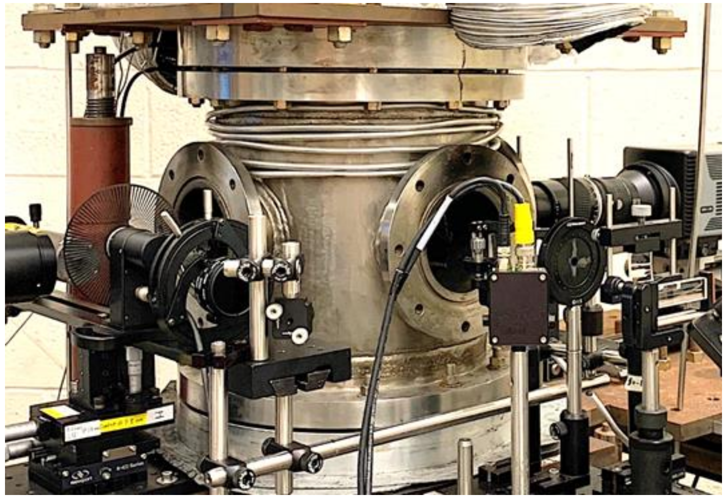


What is needed for improving ammonia models?

- Data at elevated pressure and temperatures relevant to gas turbines
- Extinction strain rate measurements for **both** premixed and non-premixed counterflow flames
  - ✓ Local velocity field measurements needed to determine ***local*** strain rate
  - ✓ Quantitative speciation (temperature) profiles (e.g., NO) at elevated pressures and temperatures
- Other data sets (shock tube, etc.) to better constrain reaction rate constant definitions

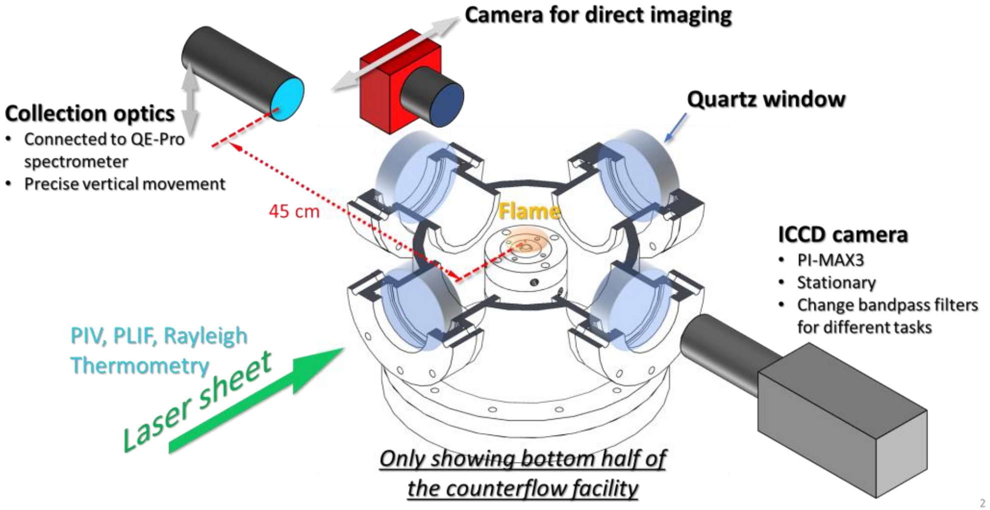
What are highly sensitive reactions with large specific rate constant uncertainty?

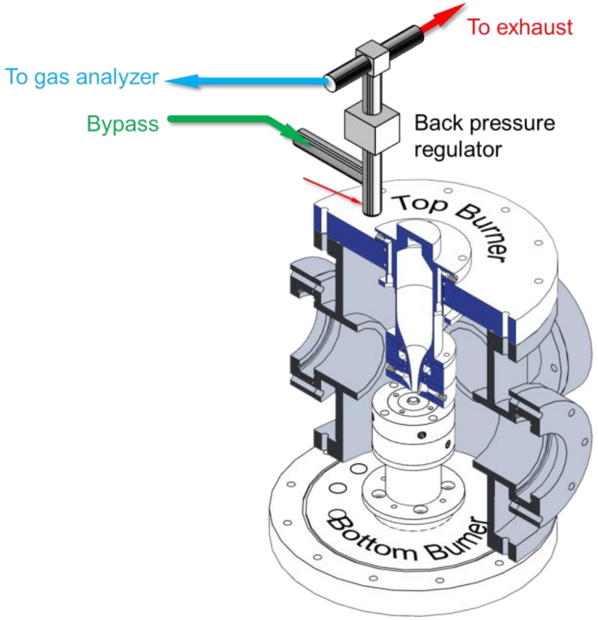
UCONN Counterflow Strained Flame Rig with Diagnostics



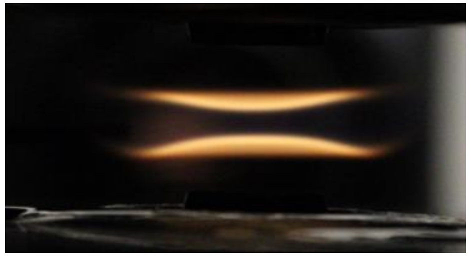
Capability of Counterflow Flame Rig

- *Ammonia compatible*
- *8+ atm*
- *200 ºC (now) → 500 ºC (later)*
- *Premixed, non-premixed, and partially-premixed combustion*





Premixed NH_3 Counterflow Flames



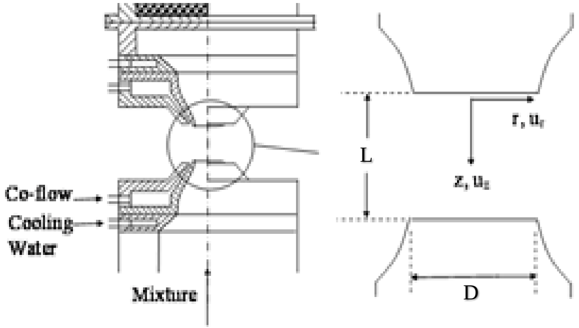
Premixed NH_3 –Air Flames, ϕ=1

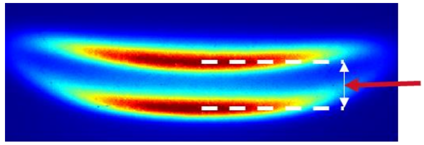
Decreasing Nozzle Exit Velocity

Decreasing Strain Rate (Laminar Flame Speed Measurement)

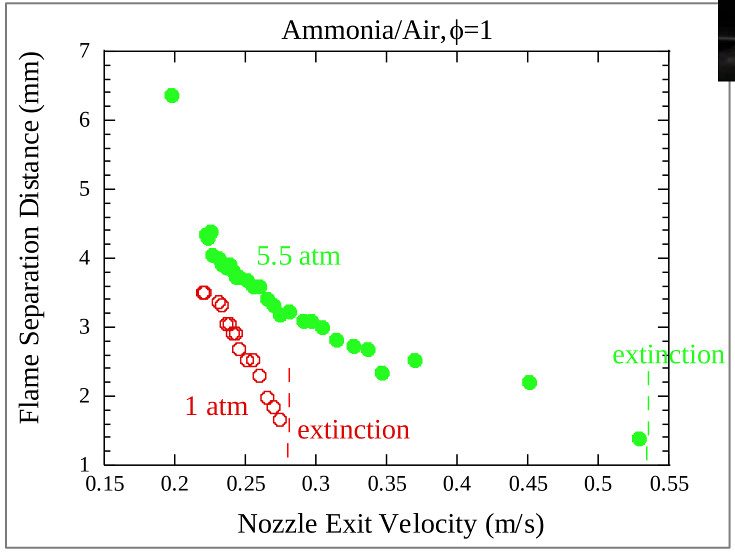
Increasing Strain Rate (Extinction Limit Measurement)

Increasing Nozzle Exit Velocity





Flame Separation distance

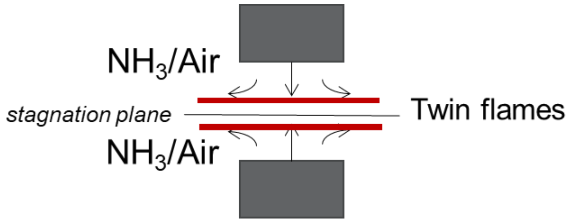


Global Strain Rate:

$$\kappa_G = \frac{4U_{ext}}{L}$$

Flame strain (stretch) rate is represented by the velocity gradient ahead of the flame and is proportional to nozzle exit velocity.

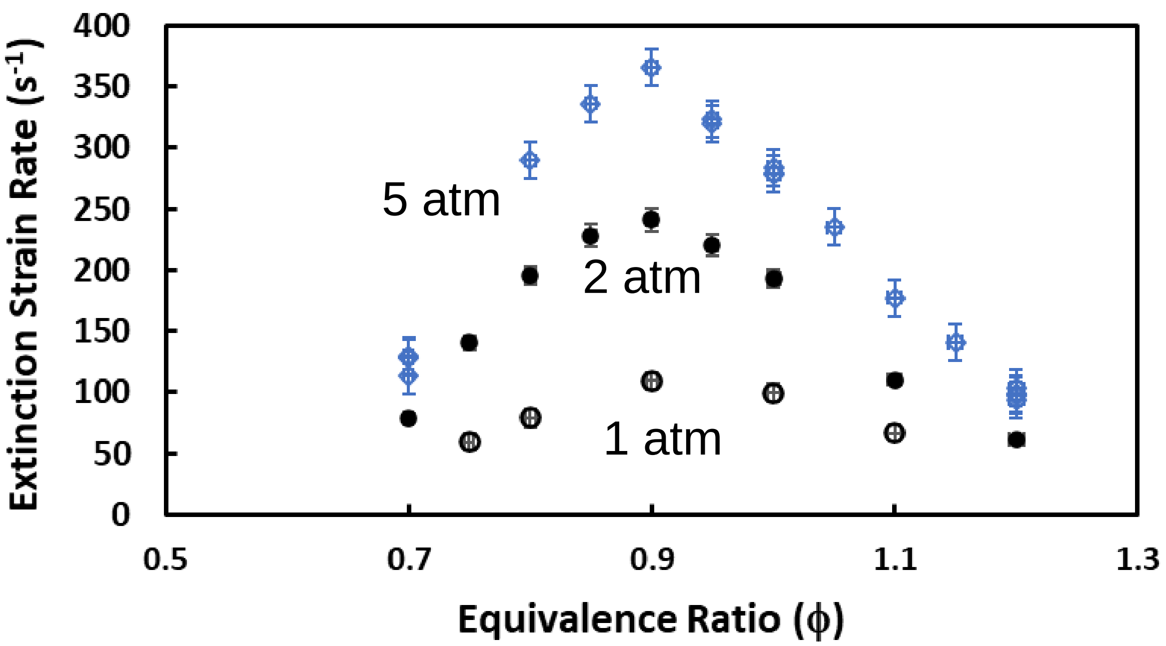
Premixed Counterflow NH_3/Air Flames: Effect of Pressure and Equivalence Ratio



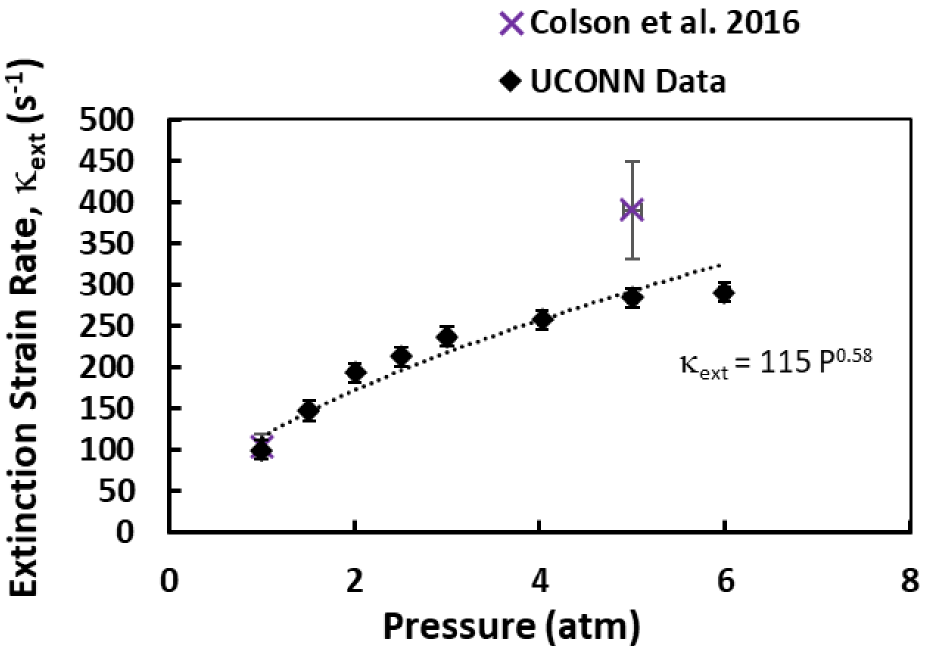
UCONN Counterflow Extinction Experiments

- Initial reactant temperature T_i = 294 – 298 K

Effect of Equivalence Ratio on Extinction Strain Rate



Effect of Pressure on NH_3-Air Flame Extinction (ϕ = 1)



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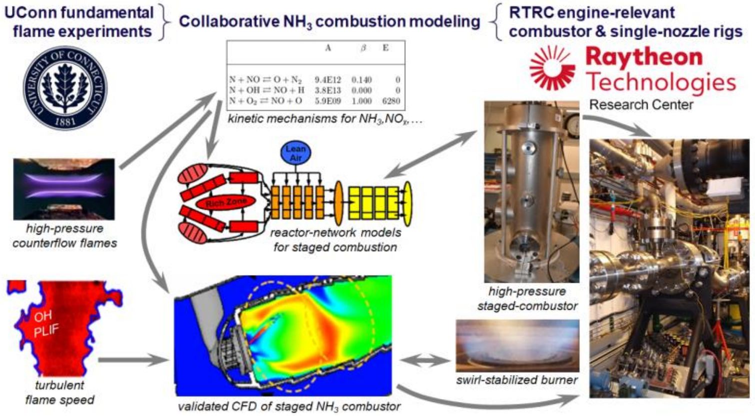


Chemical Kinetic Mechanisms

Selected published, comprehensive N/H chemical mechanisms

- Open-source computational framework developed by Dave Goodwin at Caltech Cantera

- **Glarborg et al. Mechanism (2018 and 2022 versions)**

  [Glarborg, Miller, Ruscic, Klippenstein: Modeling nitrogen chemistry in combustion, Prog. Energy Combust. Sci. (2018) 31-68]
  [Glarborg: The NH_3/NO_2/O_2 system: Constraining key steps in ammonia ignition and N_2O formation, Combust. Flame, Vol. 257 (2023)]

- **Stagni et al. Mechanism**

  [Stagni, Cavallotti, Arunthanayothin, Song, Herbinet, Battin-Leclerc, Faravelli: React. Chem. Eng. 5 (2020) 696–711]

- **Powell et al. Mechanism- (Referred to as "RTRC")**

  [Powell, Papas, Dreyer: Hydrogen- and C_1-C_3 Hydrocarbon-Nitrous Oxide Kinetics in Freely, Propagating and Burner Stabilized Flames, Shock Tubes, and Flow Reactors, Combust. Sci. Tech. 182 (2010) 252-283]
  [Powell, Papas, Dreyer: Flame Structure measurements of NO in Premixed Hydrogen-Nitrous Oxide Flames, Proc. Combust. Inst. 33 (2011) 1053-1062]

  - Two "RTRC" mechanisms differ by only 3 different rate expressions for amine radical reactions:

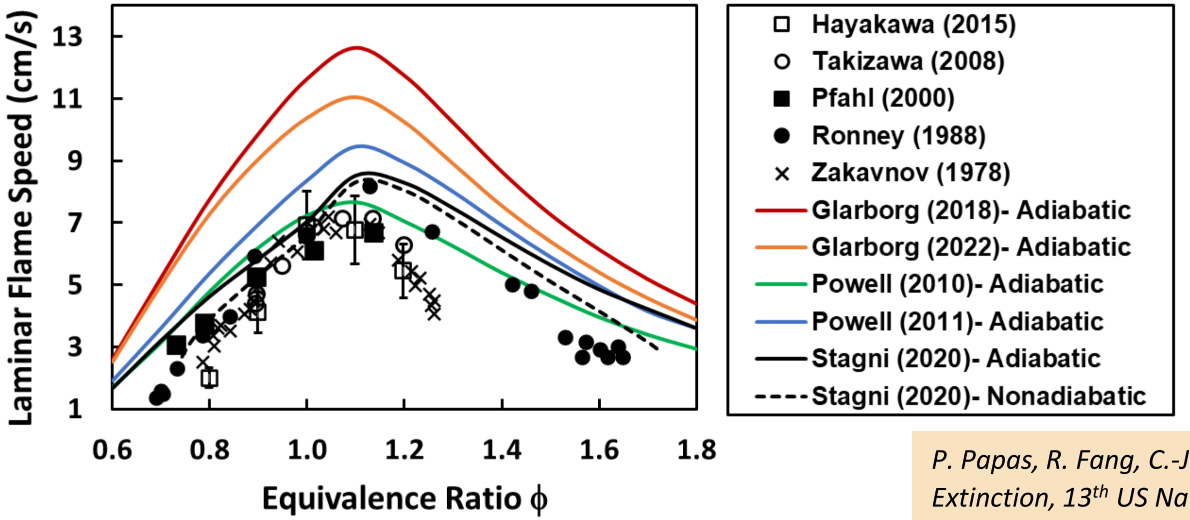
$$(1)\ NH_2 + NO \leftrightarrow N_2 + H_2O$$

$$(2)\ NH_2 + NO \leftrightarrow NNH + OH$$

$$(3)\ NH_3 + NH_2 \leftrightarrow N_2H_3 + H_2$$

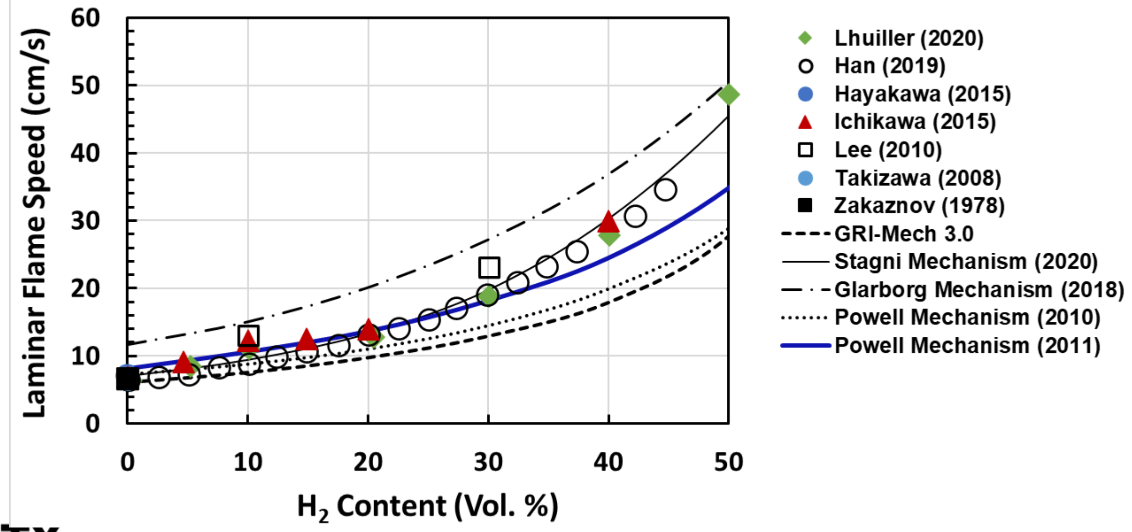
N/H Chemical Kinetic Mechanisms

Comparison of selected published N/H chemical mechanisms with laminar flame speed data

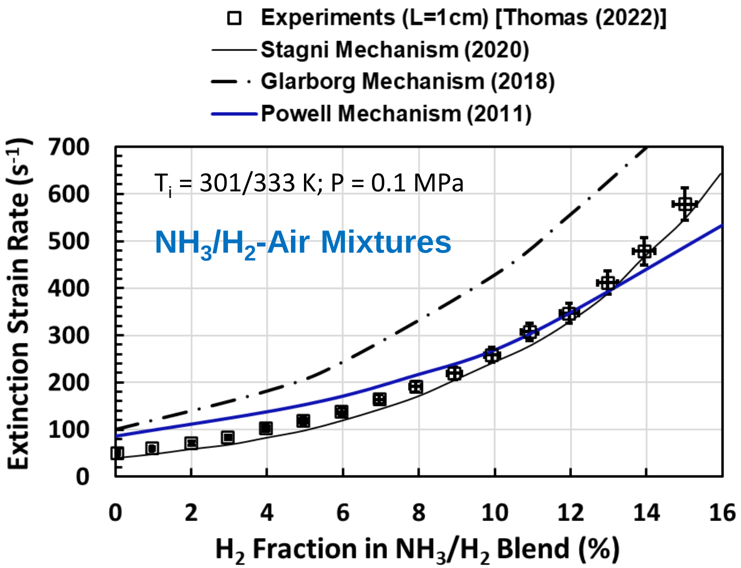


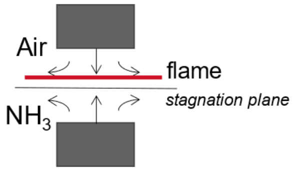
P. Papas, R. Fang, C.-J. Sung, L. L. Smith, J. F. Stevens, An Assessment of Kinetic Models for Ammonia Flame Extinction, 13th US National Combustion Meeting, College Station, TX, March 19-22, 2023.

Premixed NH_3 Flame Speed: Effect of added H_2



Non-Premixed NH_3 Extinction Strain Rate



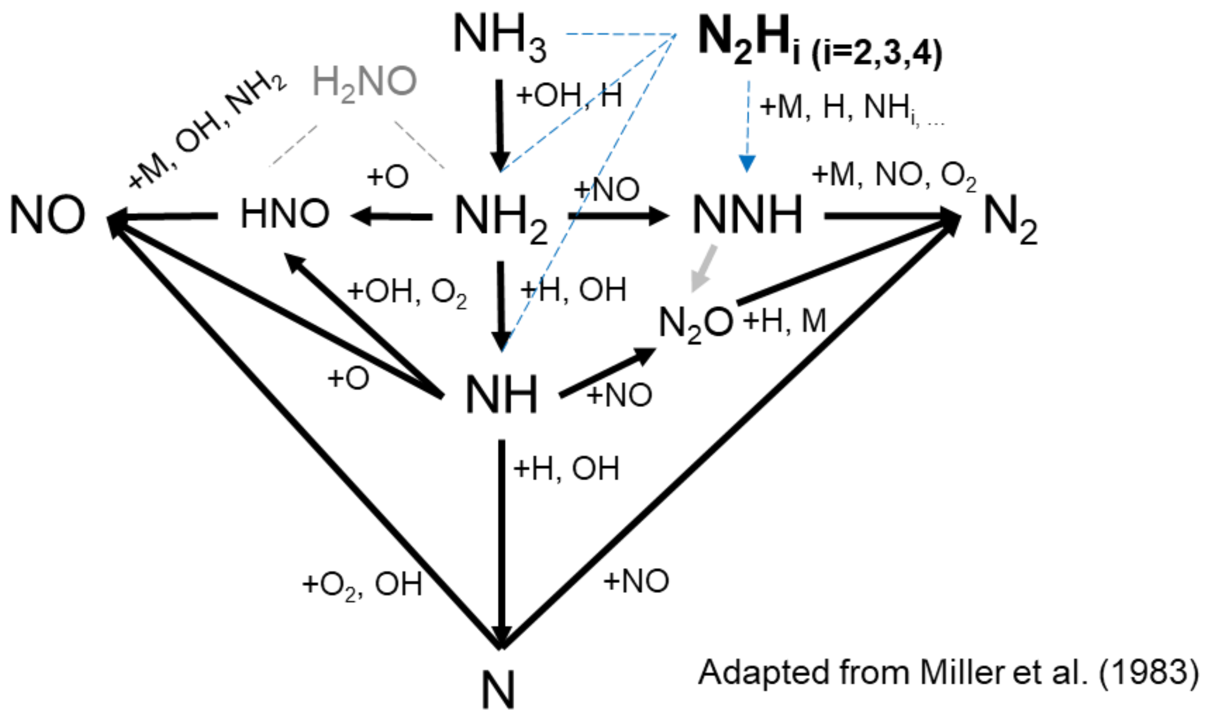


Chemical Kinetic Mechanisms

Example Data Sets used for “RTRC” N/H Mechanism Validation

Experiment	References
Flow reactor studies	
N_2O decomposition	Allen et al. (1995)
H_2/ N_2O/ H_2O/ N_2	Allen et al. (1998)
Flame speed studies	
H_2/ N_2O/ N_2	Powell et al. (2009)
CH_4, C_2H_2, C_3H_8/ N_2O/ N_2	Powell et al. (2009)
NH_3/ NO/ N_2	Mei et al. (2020)
NH_3/ H_2	Lhuiller (2020); Han (2019); Ichikawa (2015)
NH_3/ Air	Hayakawa (2015); Takizawa (2008)
Flame structure studies	
H_2/ N_2O/ CO/ Ar	Vandooren et al. (1997)
NH_3/ N_2O/ Ar	Venizelos and Sausa (1998; 2002)
Shock tube and induction time studies	
H_2/ N_2O/ Ar	Hidaka et al. (1985); Mével et al. (2009)
CH_4/ N_2O/ Ar	Drummond (1969); Soloukhin (1971)
N_2O/ CH_4/ CO/ Ar	Dean and Johnson (1980)
Counterflow studies	
NH_3/H_2 (Air)- Extinction	Thomas et al. (2022)

Ammonia Oxidation Pathway Schematic



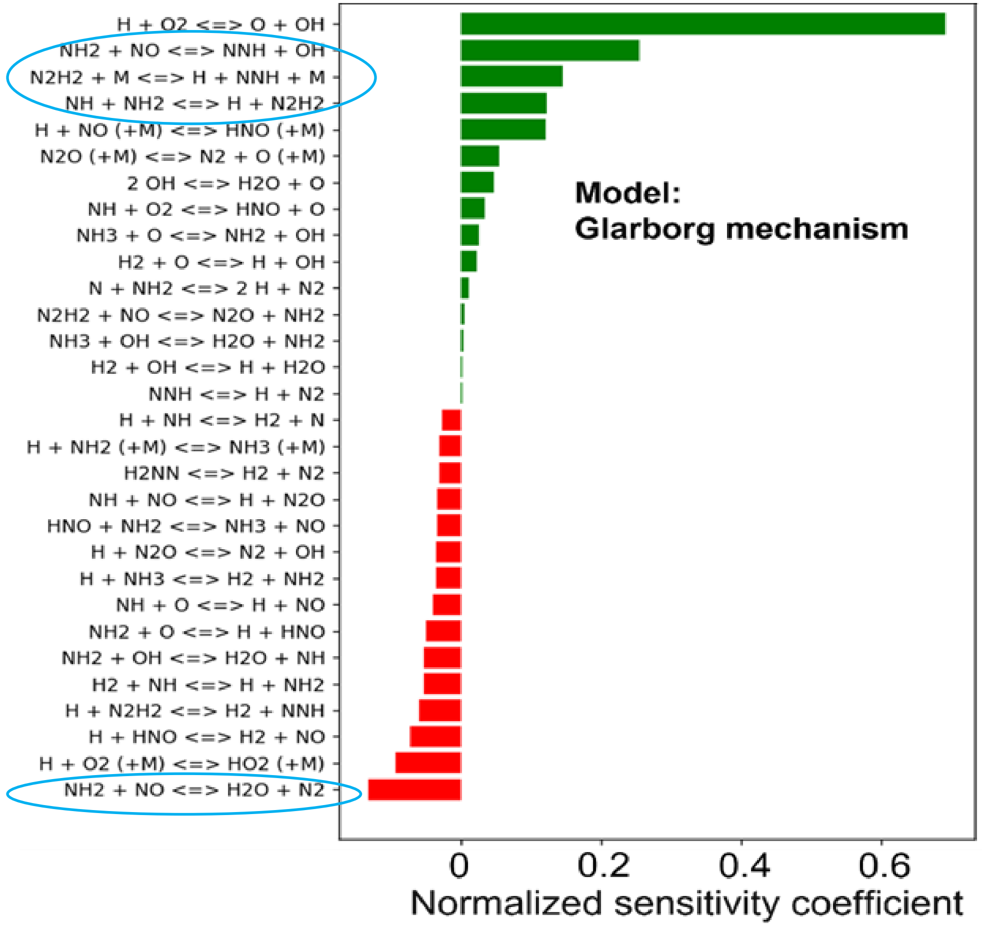
Adapted from Miller et al. (1983)

- Radical combinations involving NH_i to form N_2H_i important under fuel-rich conditions & not well characterized

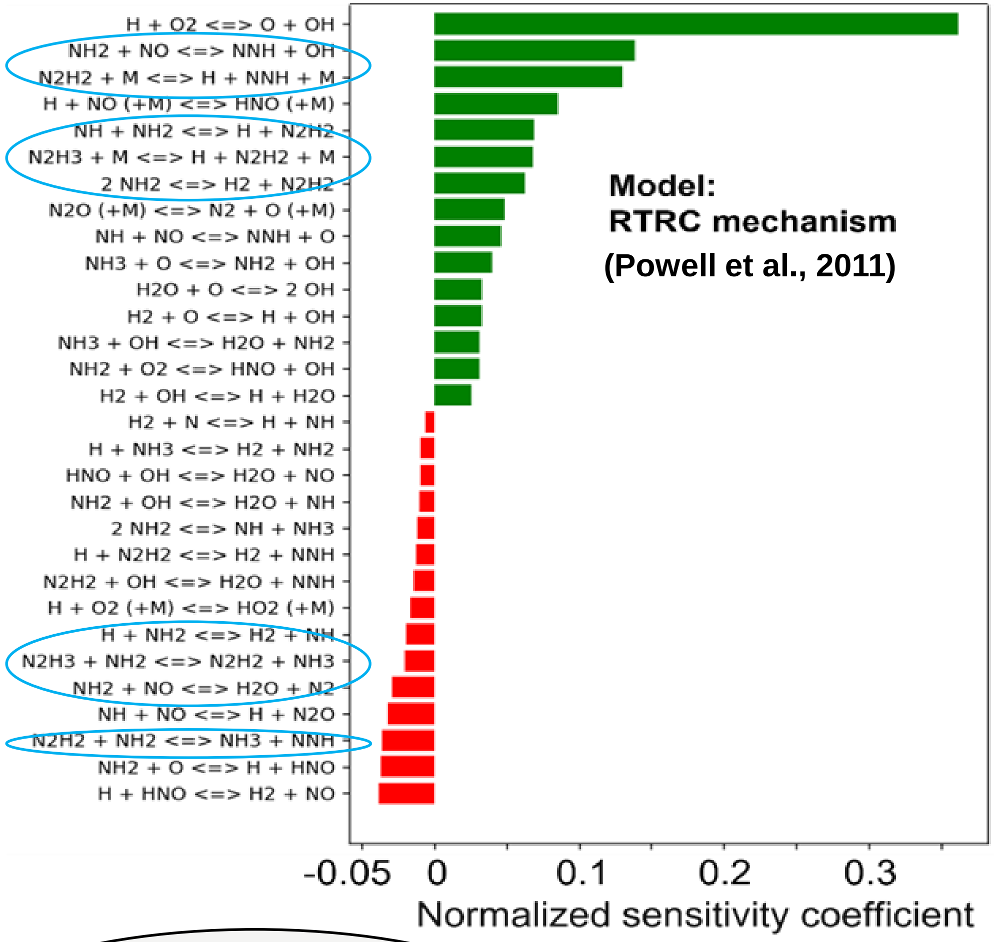
Feature Sensitivity to Extinction Strain Rate

NH_3/Air Counterflow Flame

T_i = 301/333 K; P = 0.1 MPa



T_i = 301/333 K; P = 0.1 MPa



Sensitive rate constants:

NH_2/NO Interactions

$(1a)\ NH_2 + NO \leftrightarrow N_2 + H_2O$

$(1b)\ NH_2 + NO \leftrightarrow NNH + OH$

NH_i/N_2H_i Reactions

$(2a)\ N_2H_2 + M \leftrightarrow NNH + H + M$

$(2b)\ N_2H_3 + M \leftrightarrow N_2H_2 + H + M$

Sensitive <u>and</u> Uncertain rate constants

Chemical Kinetic Mechanisms

Comparison of important N_2H_i/NH_i interactions between Glarborg, Stagni and RTRC mechanisms

Glarborg (2018)

$NH_2+NH_2 \leftrightarrow N_2H_2+H_2$
$NH_2+NH \leftrightarrow N_2H_2+H$
$NH_2+NH_2\ (+M) \leftrightarrow N_2H_4\ (+M)$
$N_2H_4+H \leftrightarrow N_2H_3+H_2$
$N_2H_4+H \leftrightarrow NH_3+NH_2$
$N_2H_4+NH_2 \leftrightarrow N_2H_3+NH_3$
$N_2H_3+H \leftrightarrow N_2H_2+H_2$
$N_2H_3+NH_2 \leftrightarrow N_2H_2+NH_3$
$N_2H_3+NH \leftrightarrow N_2H_2+NH_2$
$N_2H_2+M \leftrightarrow NNH+H+M$
$N_2H_2+H \leftrightarrow NNH+H_2$
$N_2H_2+NH_2 \leftrightarrow NNH+NH_3$
$N_2H_2+NH \leftrightarrow NNH+NH_2$
$N_2H_2+H \leftrightarrow N_2H_3$
$NH_2+NH_2 \leftrightarrow H_2NN+H_2$
$H_2NN \leftrightarrow NNH+H$
$H_2NN+H \leftrightarrow NNH+H_2$
$H_2NN \leftrightarrow N_2H_2$
$H_2NN+H \leftrightarrow N_2H_2+H$
$H_2NN+NH_2 \leftrightarrow NNH+NH_3$
$N_2H_4 \leftrightarrow H_2NN+H_2$
$N_2H_3+NH_2 \leftrightarrow H_2NN+NH_3$

Pros: - Comprehensive N kinetics for NOx
- Extended to low-temp. ignition chemistry

Cons: - Flame-speed predictions vs. data

RTRC

$NH_2+NH_2 \leftrightarrow N_2H_2+H_2$
$NH+NH_2 \leftrightarrow N_2H_2+H$
$N_2H_4+M \leftrightarrow NH_2+NH_2+M$
$N_2H_4+H \leftrightarrow N_2H_3+H_2$
$N_2H_4+H \leftrightarrow NH_2+NH_3$
$N_2H_4+NH_2 \leftrightarrow N_2H_3+NH_3$
$N_2H_3+H \leftrightarrow N_2H_2+H_2$
$N_2H_3+NH_2 \leftrightarrow N_2H_2+NH_3$
$N_2H_2+NH_2 \leftrightarrow NH+N_2H_3$
$N_2H_2+M \leftrightarrow NNH+H+M$
$N_2H_2+H \leftrightarrow NNH+H_2$
$N_2H_2+NH_2 \leftrightarrow NNH+NH_3$
$N_2H_2+NH \leftrightarrow NNH+NH_2$
$N_2H_3+M \leftrightarrow N_2H_2+H+M$
$N_2H_3+H \leftrightarrow NH_2+NH_2$
$NNH+NH_2 \leftrightarrow N_2+NH_3$
$NNH+NNH \leftrightarrow N_2H_2+N_2$
$NNH+NH \leftrightarrow N_2+NH_2$
$NNH+M \leftrightarrow N_2+H+M$
$N_2H_4+M \leftrightarrow N_2H_3+H+M$
$N_2H_3+M \leftrightarrow NH_2+NH+M$
$N_2H_2+M \leftrightarrow NH+NH+M$
$N_2H_3+H \leftrightarrow NH+NH_3$
$NH_3+NH_2 \leftrightarrow N_2H_3+H_2$
$N_2H_4+NH \leftrightarrow NH_2+N_2H_3$
$N_2H_4+N_2H_2 \leftrightarrow N_2H_3+N_2H_3$
$N_2H_3+N_2H_2 \leftrightarrow N_2H_4+NNH$
$N_2H_2+N_2H_2 \leftrightarrow NNH+N_2H_3$

Pros: - Validated N/ O/ H chemistry for NOx, N_2O
- Flame-speed predictions match existing data

TBD: - Counterflow predictions → **Newly added UConn data** (for all mechs.)

Stagni (2020)

$N_2H_4+H \leftrightarrow N_2H_3+H_2$
$N_2H_3+NH_2 \leftrightarrow N_2H_2+NH_3$
$N_2H_4+NH_2 \leftrightarrow N_2H_3+NH_3$
$N_2H_3+H \leftrightarrow N_2H_2+H_2$
$N_2H_2 \leftrightarrow NNH+H$
$N_2H_2+H \leftrightarrow NNH+H_2$
$N_2H_3 \leftrightarrow N_2H_2+H$
$N_2H_2+NH_2 \leftrightarrow NNH+NH_3$
$N_2H_2+NH \leftrightarrow NNH+NH_2$
$NNH+NH_2 \leftrightarrow N_2+NH_3$
$N_2H_2 \leftrightarrow H_2NN$
$H_2NN \leftrightarrow NNH+H$
$H_2NN+H \leftrightarrow N_2H_2+H$
$H_2NN+H \leftrightarrow NNH+H_2$
$H_2NN+NH_2 \leftrightarrow NH_3+NNH$
$N_2H_4 \leftrightarrow H_2NN+H_2$
$N_2H_3+NH_2 \leftrightarrow H_2NN+NH_3$

Pros: - Flame-speed predictions match existing data

Cons: - Limited NOx data validation

Common reaction steps in all mechanisms

Non-Adiabatic Premixed Ammonia Counterflow Flames

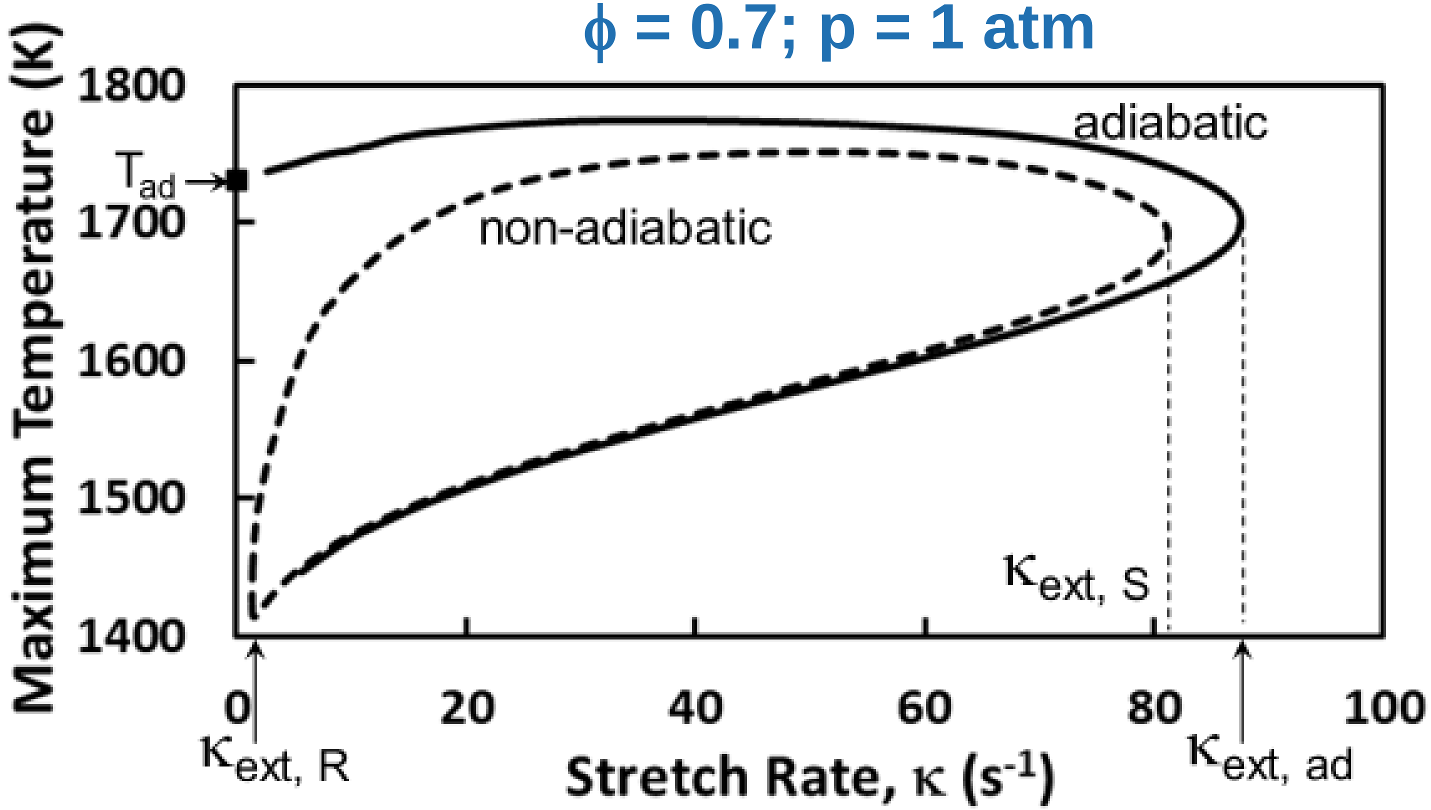
Modified Counterflow Model scripts to account for radiative heat loss

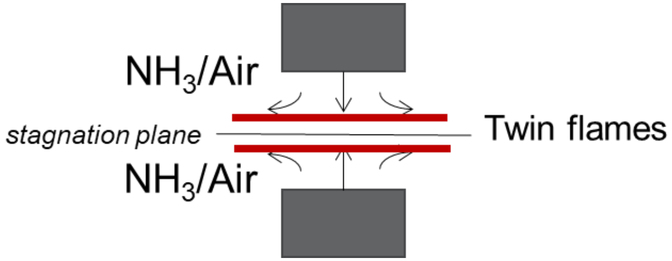
Radiative heat loss per unit volume

$$q_r = -4\sigma\kappa_p(T^4 - T_o^4)$$

(σ = Stefan-Boltzmann constant, κ_p is the Planck mean absorption coefficient; T_o = ambient unburnt reactant temperature, κ_p = total Planck's mean absorption coefficient)

$\phi = 0.7$; p = 1 atm





- Overall burning rate

$$S \sim (Le^{-1} - 1)\kappa$$

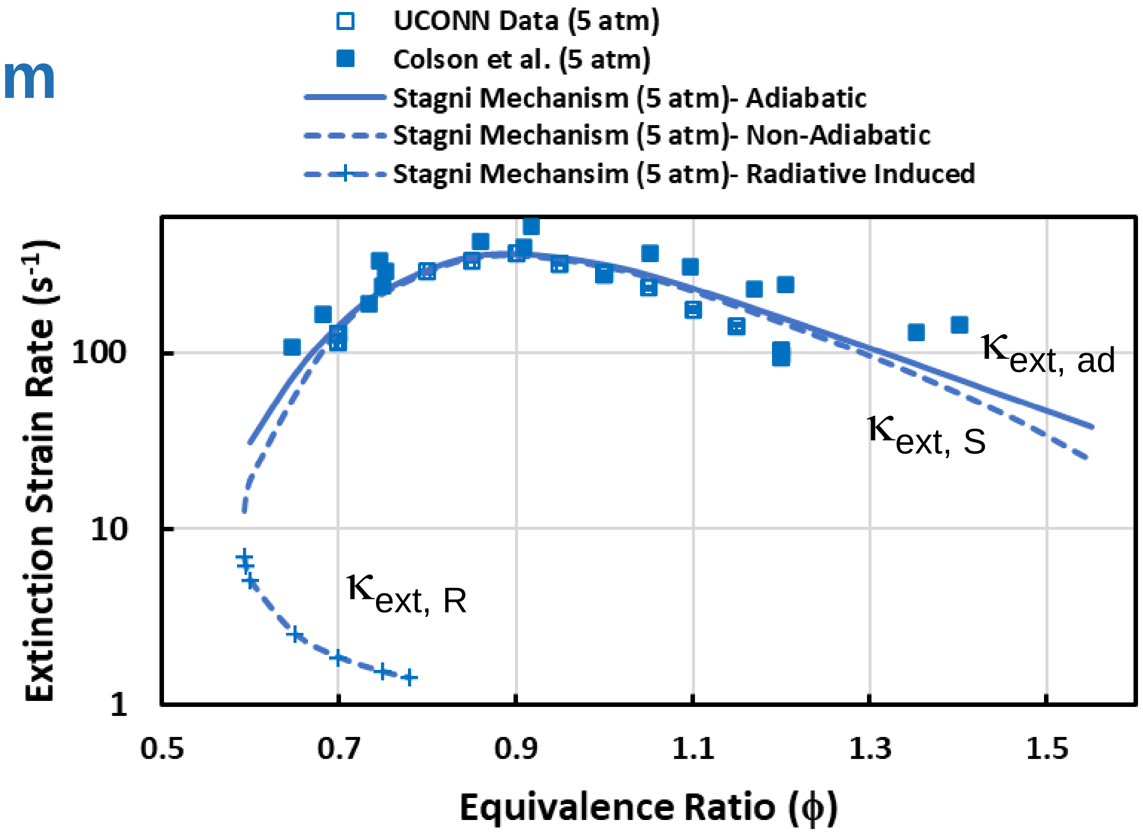
- NH_3 counterflow flames exhibit radiative-induced and stretch-induced extinction limits near lean flammability limit

Manuscript to be submitted to PROCI

Non-Adiabatic Premixed Ammonia Counterflow Flames

Ammonia flames exhibit both stretch- and radiative-induced extinction states near lean flammability limit

p = 5 atm

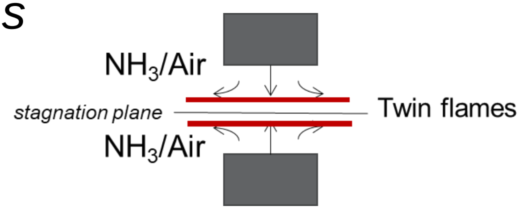


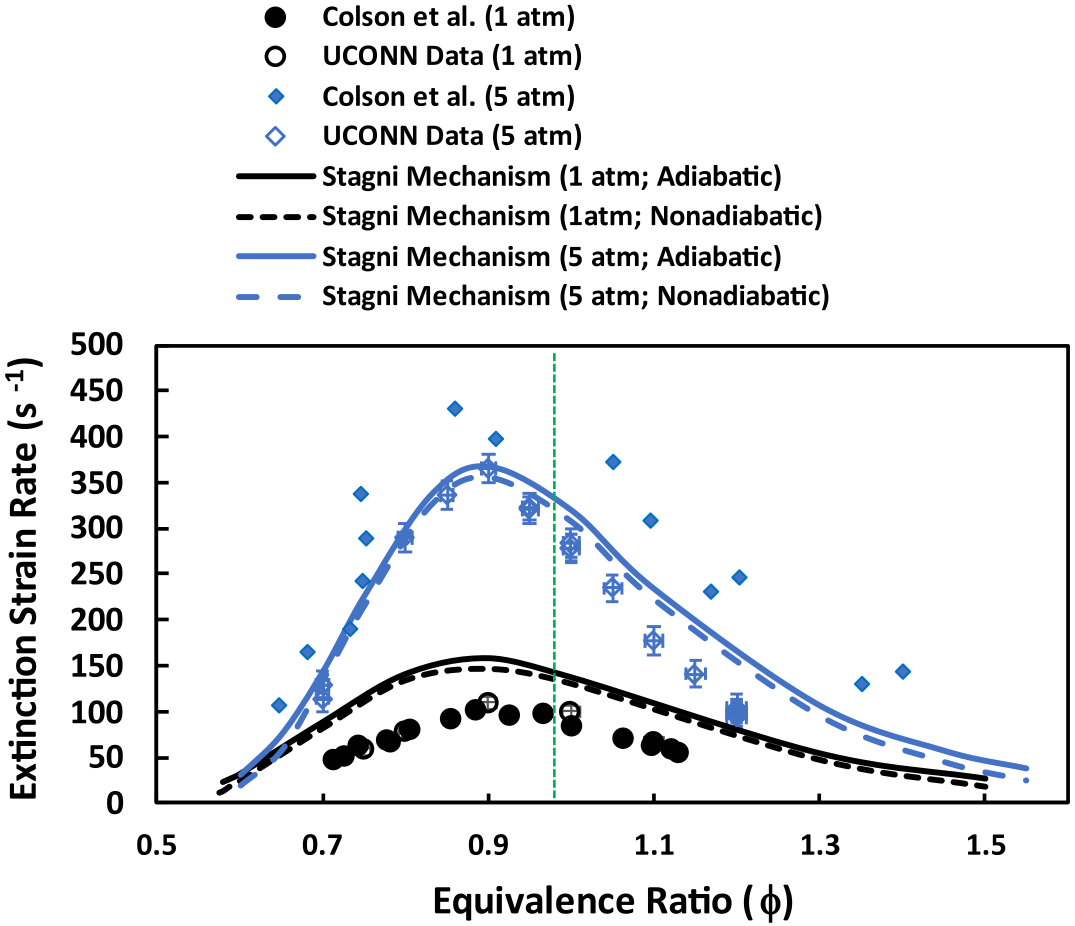
C-shaped curve for counterflow premixed fuel-lean, ammonia-air flames showing computed adiabatic stretch-induced stretch rate $\kappa_{ext,ad}$ (solid line) as well as non-adiabatic stretch-induced stretch rates $\kappa_{ext,S}$ (dashed line) and radiative-induced stretch rates $\kappa_{ext,R}$ (+ symbols).

Manuscript to be submitted to PROCI

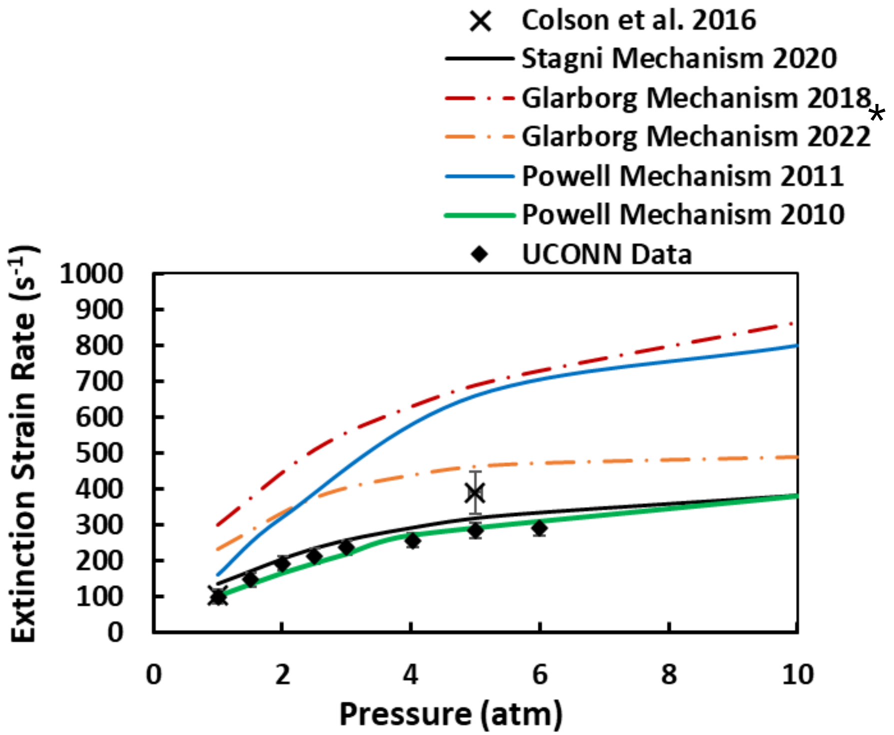
Premixed Counterflow NH_3/Air Flames: Effect of Pressure on Extinction Strain Rate

Comparison with available data from Colson et al. (2016) and N/H chemical mechanisms





Stoichiometric Premixed NH_3/Air Flames



* Glarborg, Combust. Flame, Vol. 257 (2023)

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- Counterflow Flame Studies – Reaction Rates for NH3 Combustion
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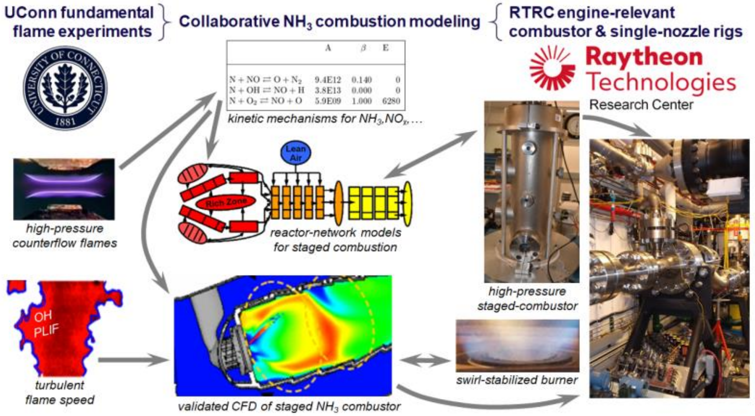


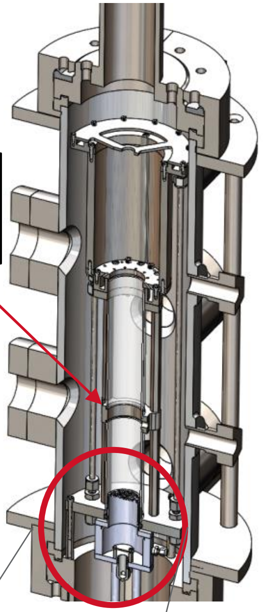
	A	β	E
$N + NO \rightleftharpoons O + N_2$	9.4E12	0.140	0
$N + OH \rightleftharpoons NO + H$	3.8E13	0.000	0
$N + O_2 \rightleftharpoons NO + O$	5.9E09	1.000	6280

High-Pressure Staged Reactor Rig (RTRC) – NOx Evaluations

Capability of High-Pressure Reactor

- *30+ atm*
- *Vessel shell rated >500 K*
- *Coflow / purge enables higher preheat & flame temperatures*
- *Staged reaction-zones for fuel-rich & fuel-lean measurements*

- Planned diagnostic techniques
  - Extractive probe with in-line analyzers for species measurements (NO, NH_3, …)



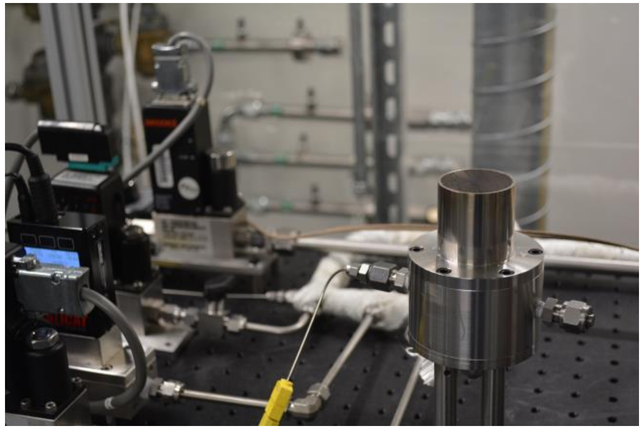
Secondary Air Addition

New NH_3 Flat Flame Burner

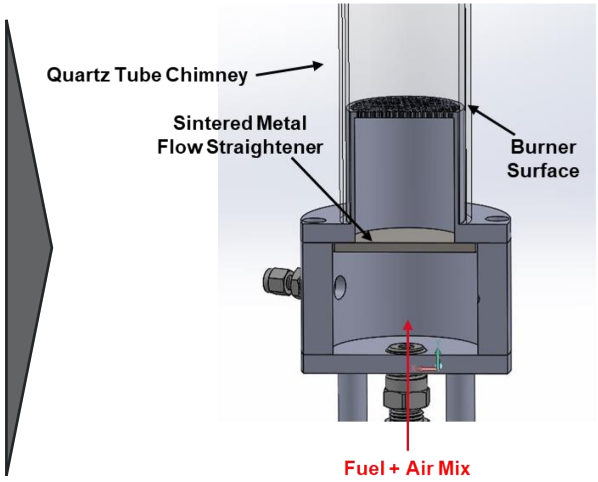
pump liquid NH_3 to >500psi

RTRC High-Pressure Staged Flame Reactor Rig

- High-pressure burner rig modifications for NH_3 compatibility
  - Removal of copper components from inside pressure vessel & burner
  - Modified burner insert for NH_3 operation
  - For staged-burner testing (RQL), chimney modification for staged air addition

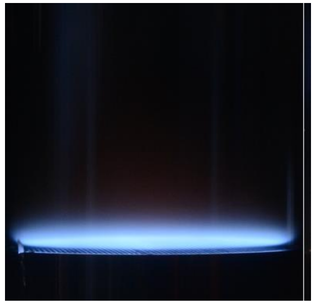


Shakedown Burner Testing Set-up



Flat Flame Burner

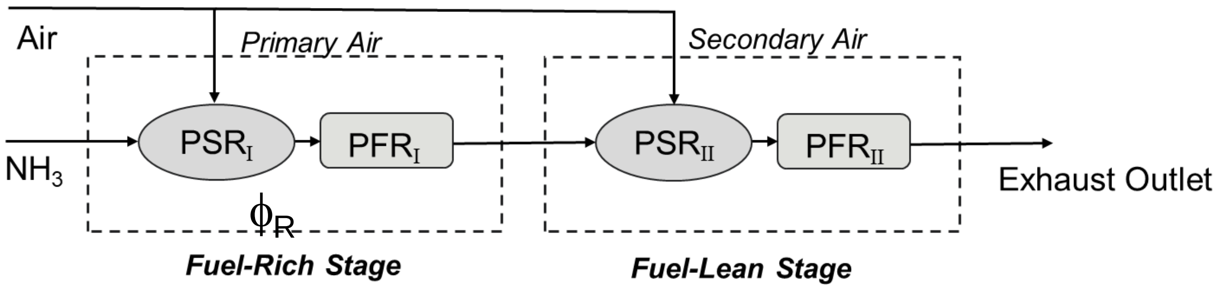
CH_4-Air



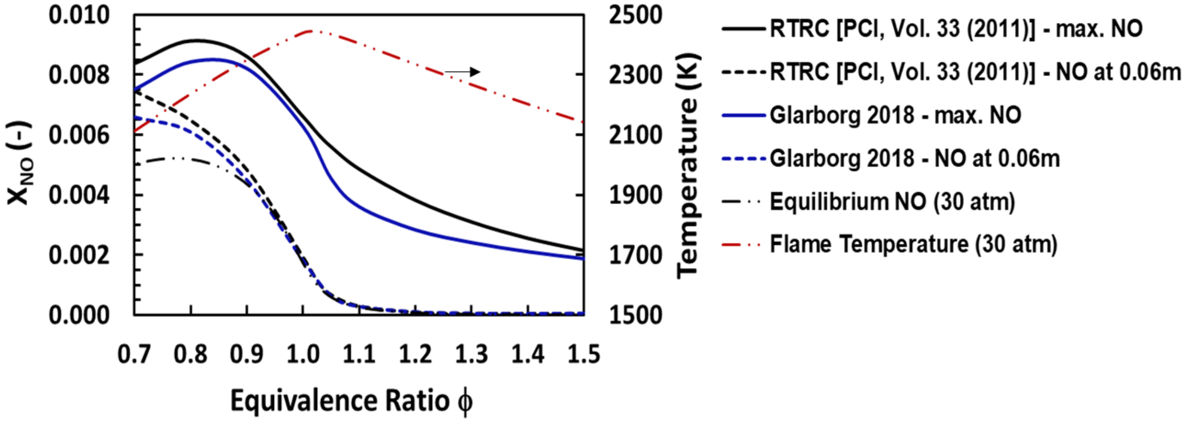
100% NH_3-Air

Chemical Reactor Network (CRN) Modelling

CRN Model Schematic for RQL Combustor



Premixed Flame (30 atm)



- Validation against available simulation data from Li et al., Fuel 355 (2024) 129509.
- **Overall "theoretical" NOx levels <30 ppm for a RQL architecture appear feasible**
- Established N/H mechanisms show wide variability for NOx

ϕ$_R$ = 1.25

Total Residence time τ (ms)	**τ_{PSR_I} (ms)**	**τ_{PFR_I} (ms)**	**τ_{PSR_II} (ms)**	**τ_{PFR_II} (ms)**	**Pressure (atm)**	**Inlet Temp. (K)**	**Outlet Temp. (K)**	**NOx* (ppm)**
20	3	14	2	1	12	600	1850	38.5
20	3	14	2	1	30	700	1850	30.1
30	3	24	2	1	30	700	1850	22.9

* 15% O_2 dry

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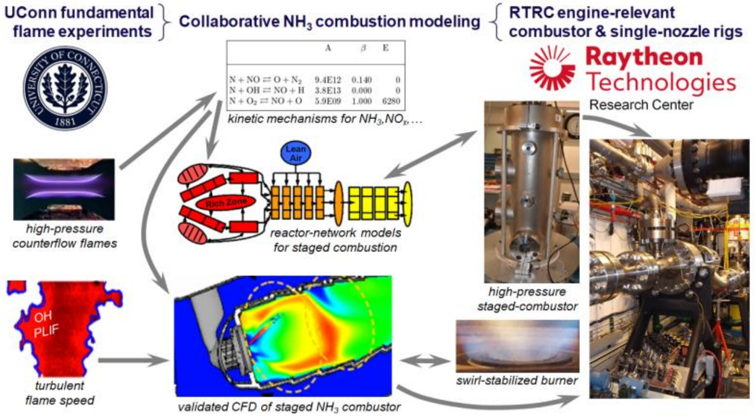
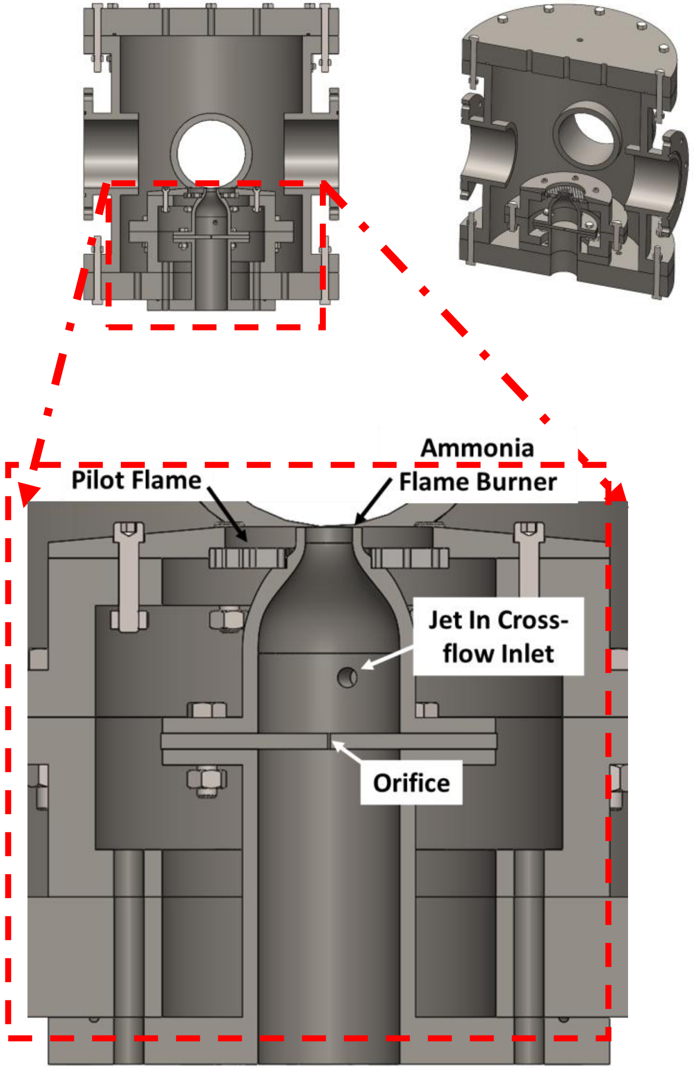


Next Steps: 2024 Experiments

- **UConn Counterflow testing continuing with preheat**
- **UConn Turbulent Flame Rig**
  - Turbulent flame speed measurements (NH PLIF for flame surface area)
  - Effects of pressure, equivalence ratio, and turbulent intensity (Turbulent intensity range: 15–25%)
  - Pressure range: 1–7 atm; up to 500 K preheat

UConn Turbulent Flame Rig



- **RTRC High-Pressure Staged Reactor Rig**
  - System pressure up to 30 atm
  - Air preheat up to 800K
  - NOx measurements using probe extraction technique
  - FTIR Analysis and other diagnostics

Questions?

Please e-mail any questions to:

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Paul Papas (paul.papas@rtx.com)

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