



An Experimental and Modeling Study of NO_x- CO Formation in High Hydrogen Content (HHC) Fuels Combustion in Gas Turbine Applications (DE-FE0012005)

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Project Participants



University of South Carolina and Princeton University

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University of South Carolina– Mechanical Engineering

- **Sheikh Farhan Ahmed** – Graduate Student
- **Fahd Ebna Alam** – Graduate Student

Co-PI: Dr. Bihter Padak, Assistant Professor

University of South Carolina– Chemical Engineering

- **Nazli Asgari** – Graduate Student



Co-PI: Dr. Frederick Dryer, Professor

Princeton University – Mechanical and Aerospace Engineering

- **Mac Haas** – Technical Staff



- Detailed and validated coupled HHC + NO_x kinetic model
- New experimental speciation data for the oxidation kinetics of HHC fuel compositions in presence of impurities.
- Understanding of CO, NO and NO₂ formation and interactions in hot and cold flow interactions.
- Detailed and reduced kinetic models for HHC fuels including detailed fuel compositions and NO_x.



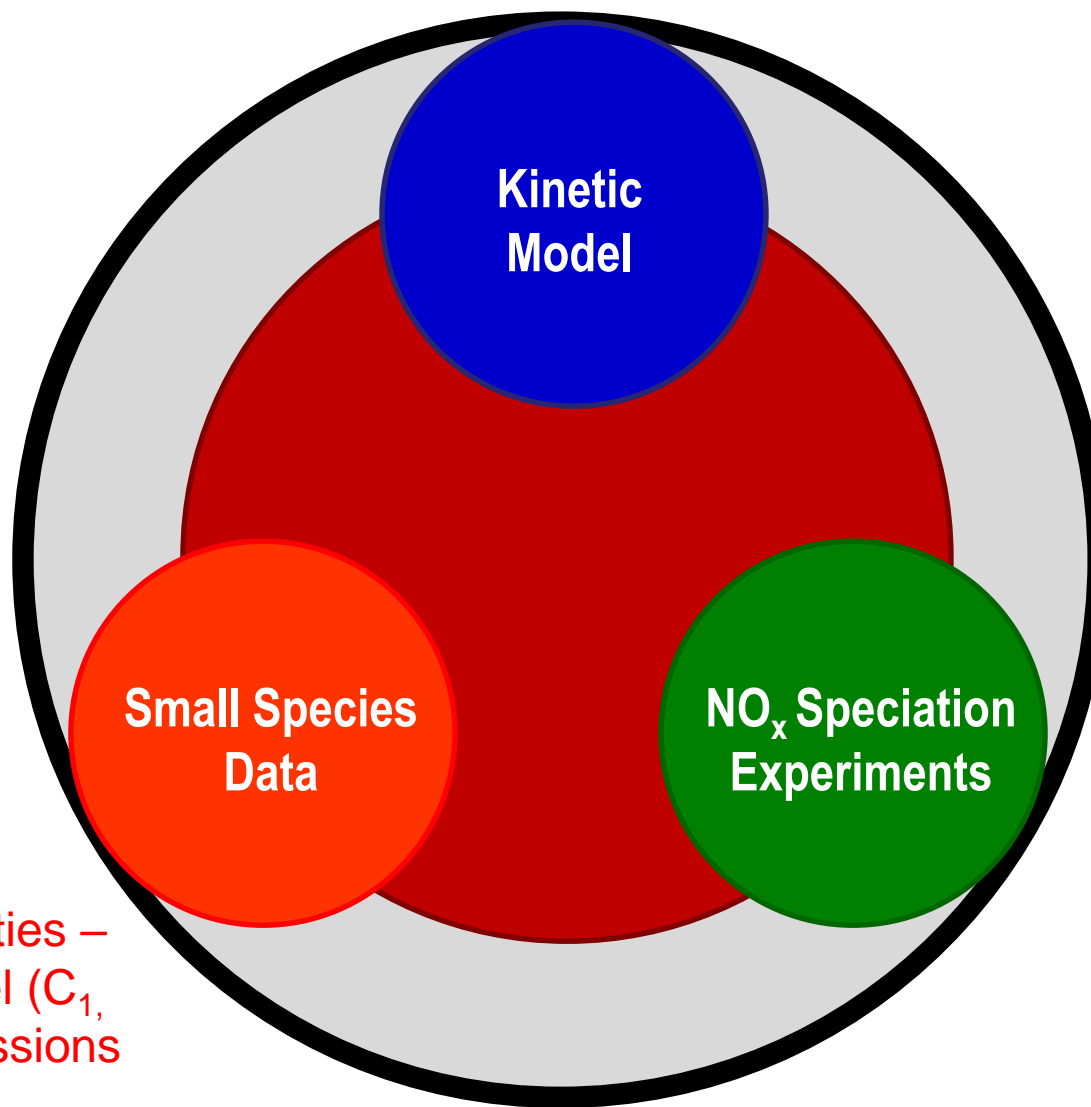
Improved, higher fidelity tools for engineering design!

- Study of reactivity and speciation data for NO_x under various conditions
- Studies of CO , NO , NO_2 formation and conversion for $\text{NO} - \text{NO}_2$ in mixing layers
- Studies of high pressure HHC fuel kinetics using a High Pressure Laminar Flow Reactor (HPLFR)
- Kinetic assessment, validation and development of a comprehensive HHC fuel + NO_x kinetic mechanism

Presentation Outline



- Research Team Members
- Project Objectives
- Research Tasks
- Year 3 progress
 - ☐ Measurement of NO_x Perturbed Oxidation Experiments
 - ☐ Kinetic Modeling of NO_x formation in HHC Fuels
 - ☐ Coupled CFD + Kinetics Modeling and Simulations
 - Tanvir Farouk (Fred Dryer)
 - ☐ Experiments for Speciation Measurements
 - Bihter Padak
- Summary



- Predictions of NO_x to address strict emission standards

- Trace emittents – NO_x influences the global and intricate combustion dynamics

- Fuel impurities – source of fuel (C₁, C₂ ...) – emissions

Unless one considers the **interactions of small species and emittents**, particularly on natural gas combustion the resulting model will likely have poor fidelity to be considered for engineering applications



Measurement of NO_x perturbed oxidation experiments

Influence of Trace Nitrogen Oxides on Natural Gas Oxidation



Nominal Feed Condition

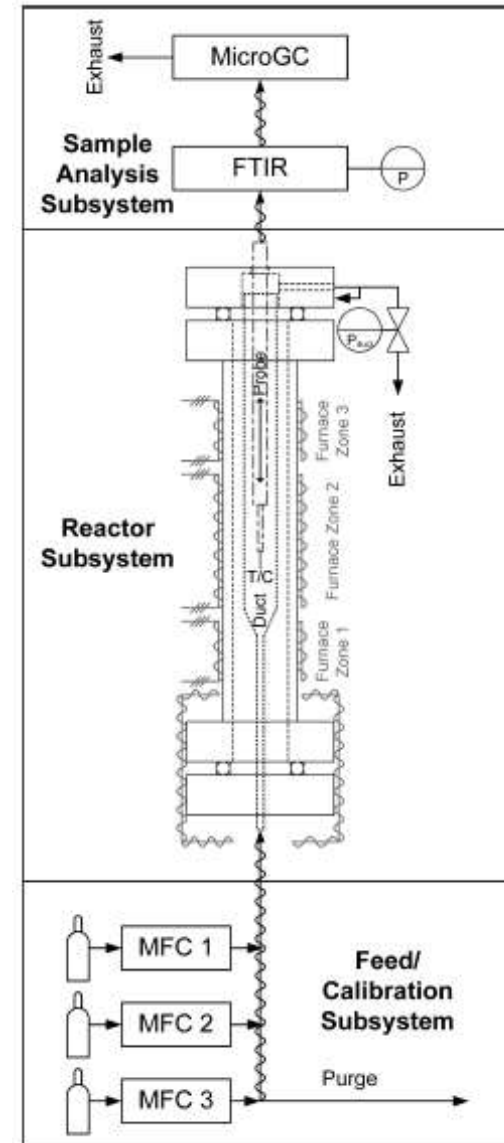
CH_4	= 9800 ppm ($\pm \sim 2\%$)
C_2H_6	= 200 ppm ($\pm \sim 4\%$)
O_2	= 10150 / 20300 / 40600 ppm ($\pm \sim 2\%$)
ϕ	= 2.0 / 1.0 / 0.5
Ar	= Balance
Q_{total}	= 1300 sccm
NO	= 25 ppm (± 1 ppm)
T	= 819 ± 5 K

P = 10 atm
T = 820 K

**BUT WHY
THESE
MODELS ?**

Kinetic Models

Model	# of Species	# of Elementary Rxn
GRI MECH 3.0 (2000)	54	325
Dagaut et al. (CST 2005)	148	1084
Konnov (C&F 2009)	129	1231
Gersen et al. (PROCI 2011)	136	979
Mathieu et al. (Fuel 2016)	166	1204



Non-NO_x Perturbed case ($\phi = 1.0$)

Simulation Initial Condition:

$X_{\text{CH}_4} = 9763 \text{ ppm}$

$X_{\text{C}_2\text{H}_6} = 204 \text{ ppm}$

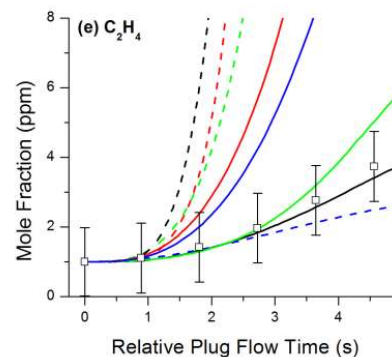
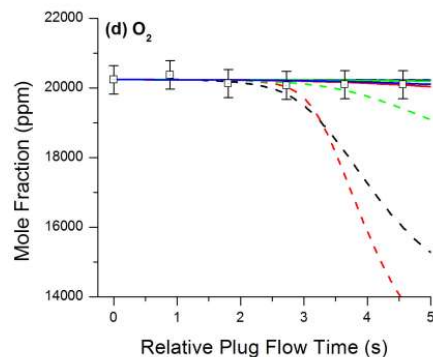
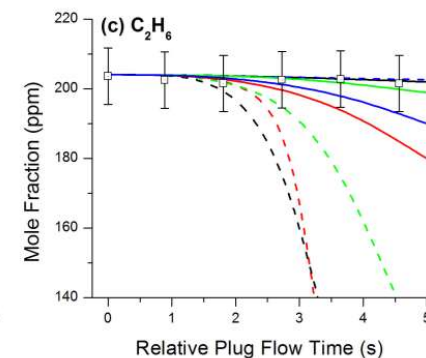
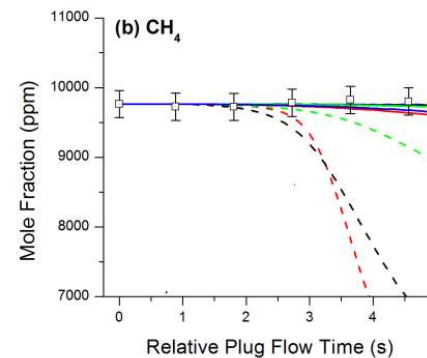
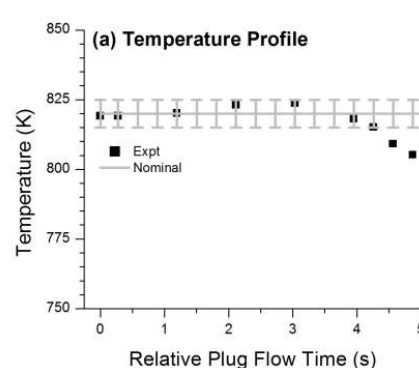
$X_{\text{C}_2\text{H}_4} = 1 \text{ ppm}$

$X_{\text{O}_2} = 20238 \text{ ppm}$

Balance Ar

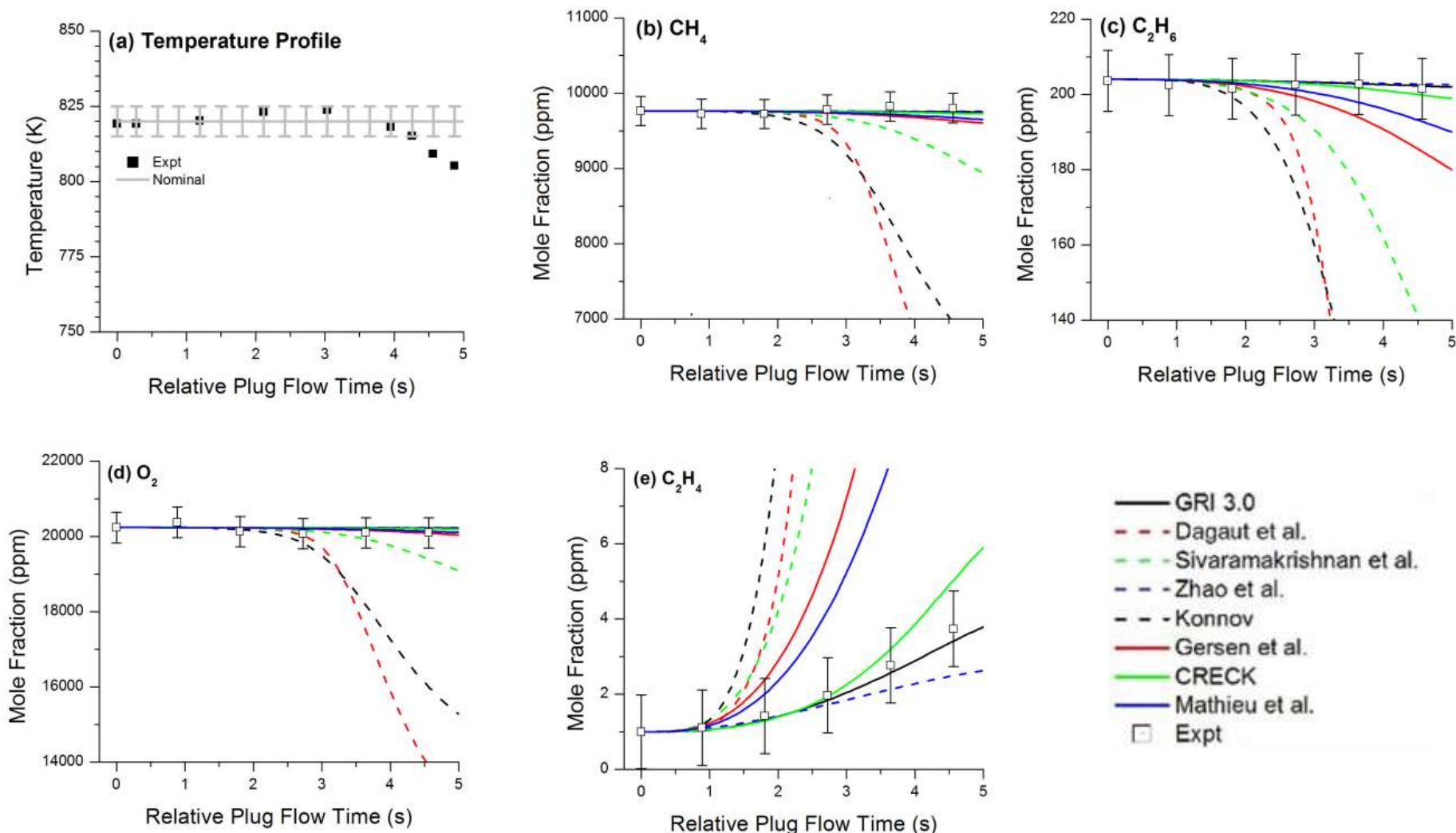
Simulation strategy: Experimentally acquired initial conditions + experimentally measured temperature imposition (CHEMKIN-PRO®). No time-shift is applied.

- ❑ No evidence of reaction for measured profiles of CH₄, O₂ and C₂H₆.
- ❑ Few ppm of C₂H₄ quantified @ distinct 950 cm⁻¹ FTIR wave number.
- ❑ Conditions of incipient of reactions. C₂H₆ oxidation via flux through C₂H₅ ⇌ C₂H₄.
- ❑ GRI 3.0, CRECK & Zhao et al. is predicting reasonable @ 4.0s Rel. Plug Flow Time.



Non- NO_x Perturbed case ($\phi = 1.0$)

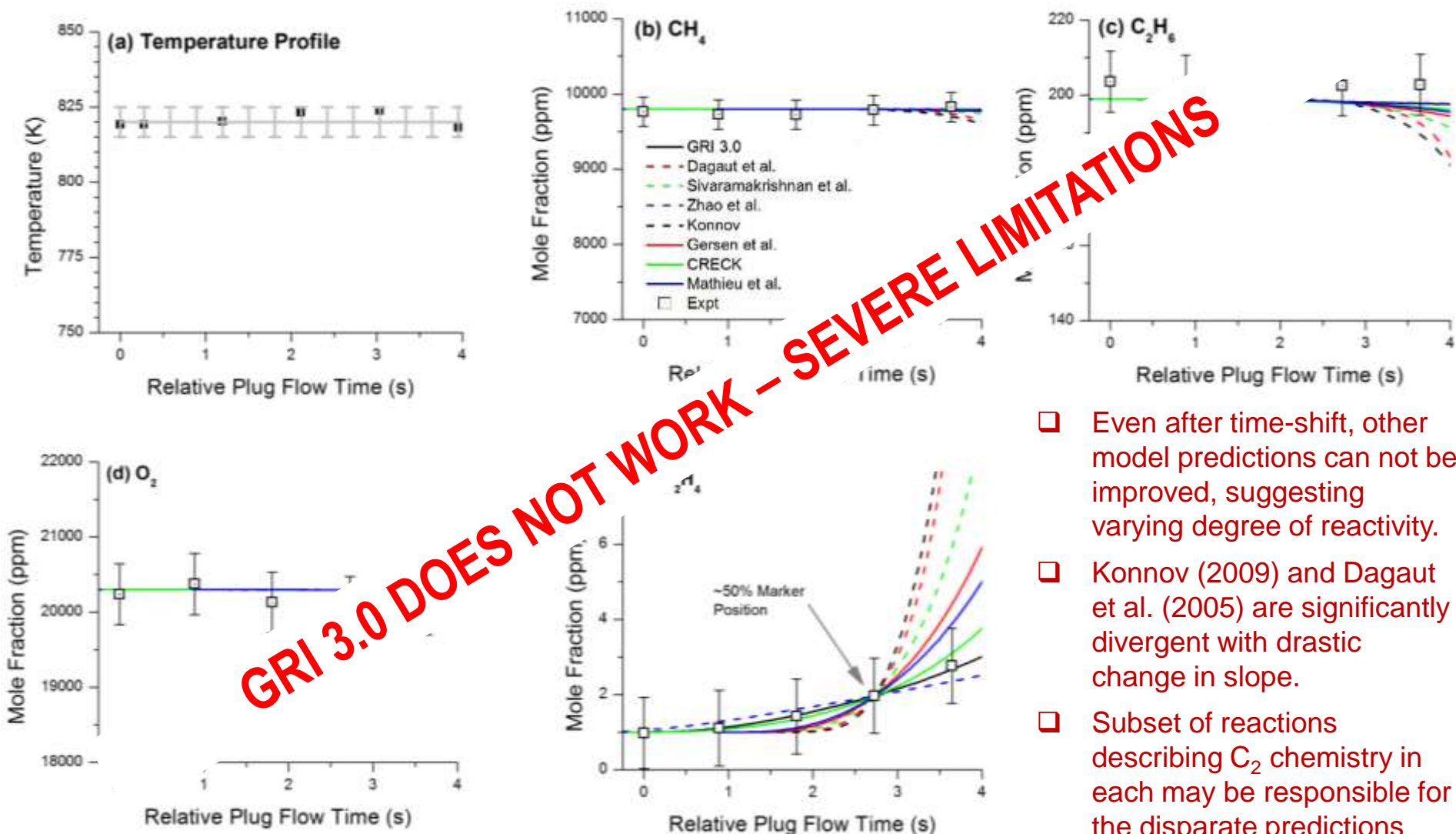
Can time-shift improve the model predictions?



□ GRI 3.0, CRECK & Zhao et al. is predicting reasonable @ 4.0s Rel. Plug Flow Time.

Time-shifted Analysis of Non-NOx Perturbed Case ($\phi = 1.0$)

~50% evolution of C_2H_4 is considered as marker for time-shift.



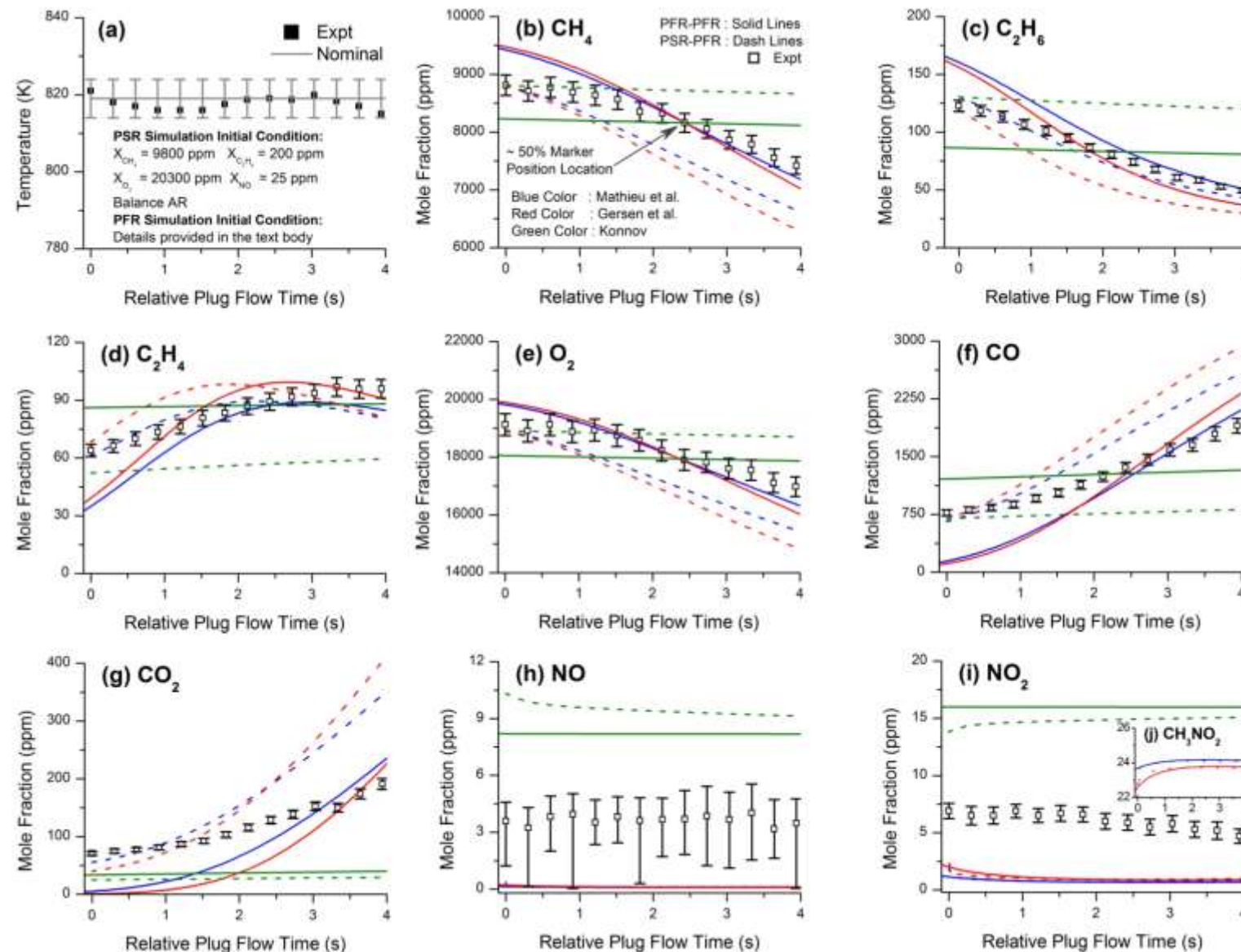
- Even after time-shift, other model predictions can not be improved, suggesting varying degree of reactivity.
- Konnov (2009) and Dagaut et al. (2005) are significantly divergent with drastic change in slope.
- Subset of reactions describing C_2 chemistry in each may be responsible for the disparate predictions

GRI 3.0 is non-reactive, like this case, for NOx perturbed reactive cases → Thus, neglected altogether.

Trace NO_x Perturbed Case ($\phi = 1.0$)

PFR-PFR Analysis (Solid Line): PFR Simulation with time-shift @ 50% CH_4 depletion

PSR-PFR Analysis (Dash Line): Adiabatic PSR targeting 1st data point matching, followed by PFR simulation.



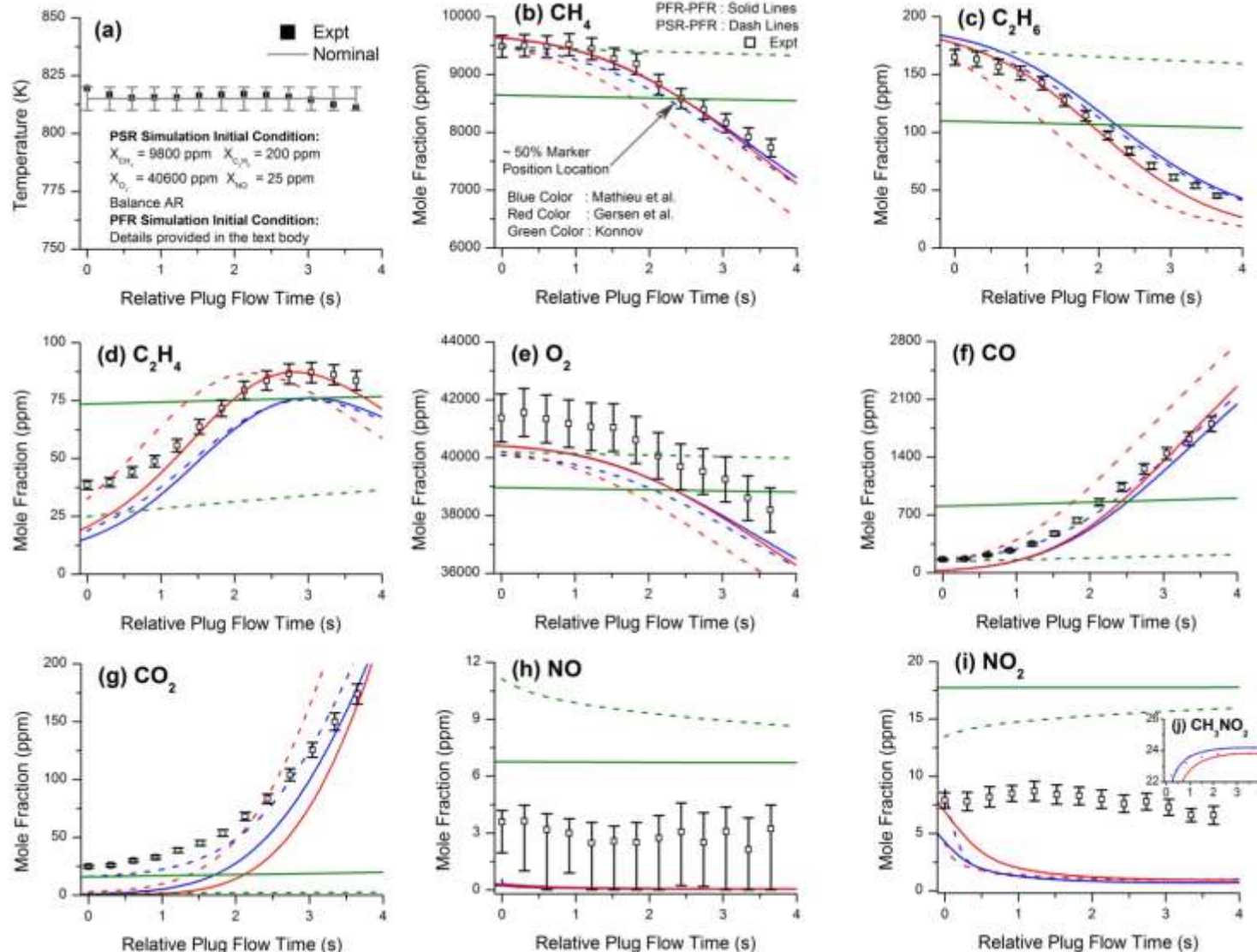
□ Gersen and Mathieu models essentially bound profiles of all of the experimentally measured major species.

□ However, NO_x mole fraction predictions indicate near-complete destruction of NO_x ($\text{NO} + \text{NO}_2$) $\rightarrow \text{CH}_3\text{NO}_2$

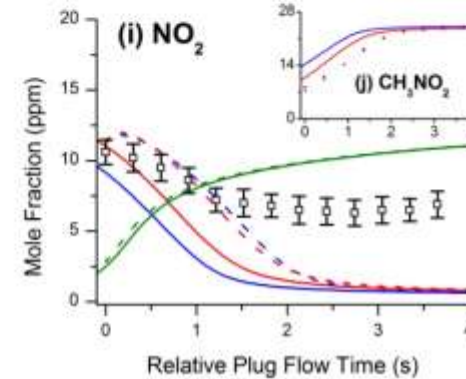
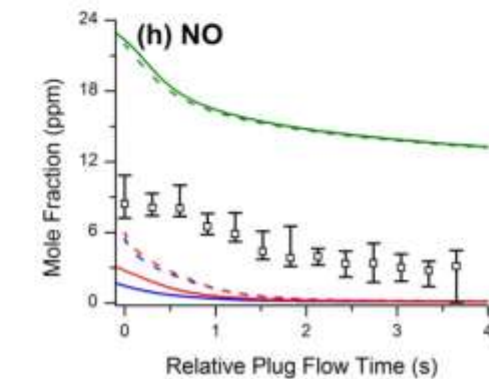
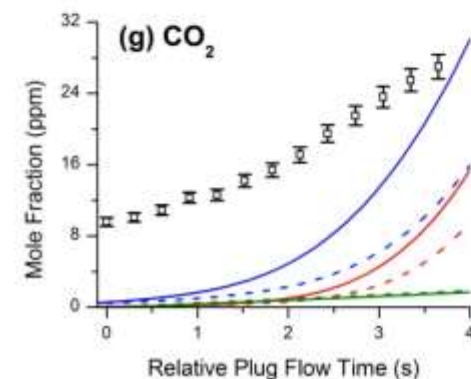
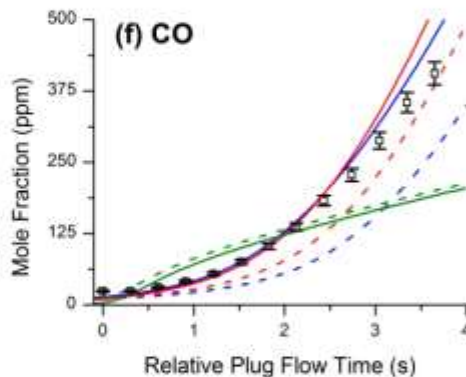
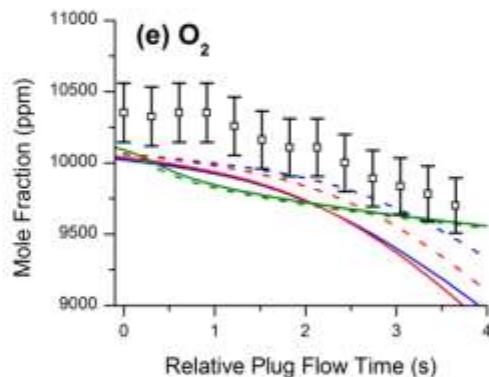
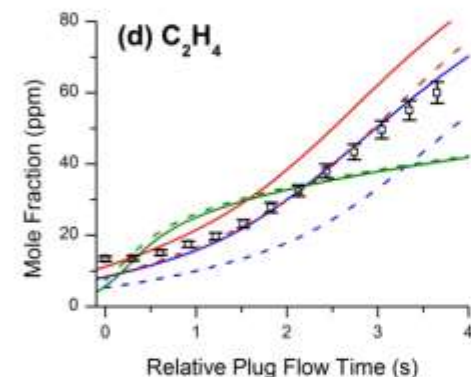
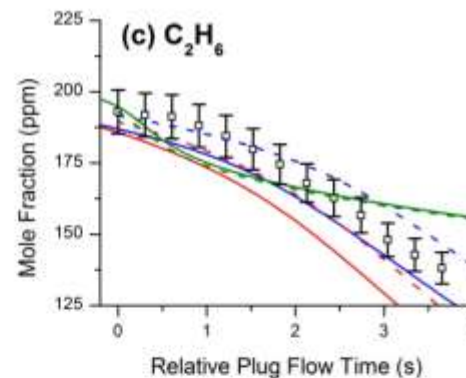
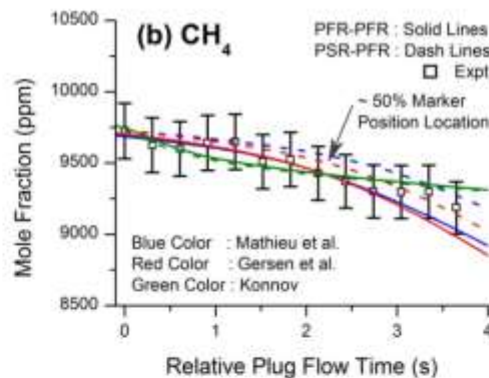
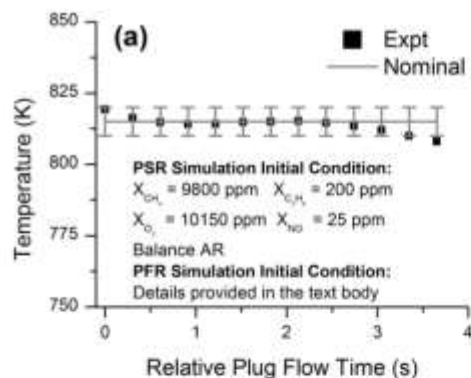
Trace NO_x Perturbed Case ($\phi = 0.5$)

PFR-PFR Initialization: Experimentally measured input at relative time, $t = 0$

PSR-PFR Initialization: Nominal condition as input to PSR. Vary residence time, τ_{PSR} to match experimentally measured input at relative time, $t = 0$.

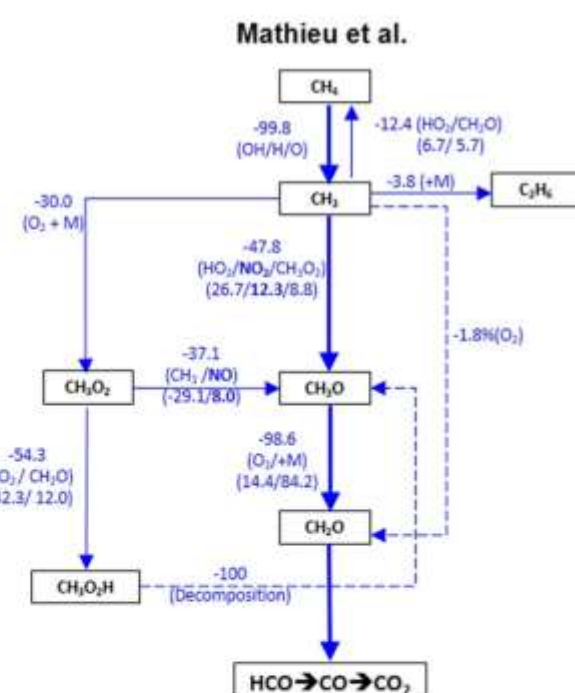
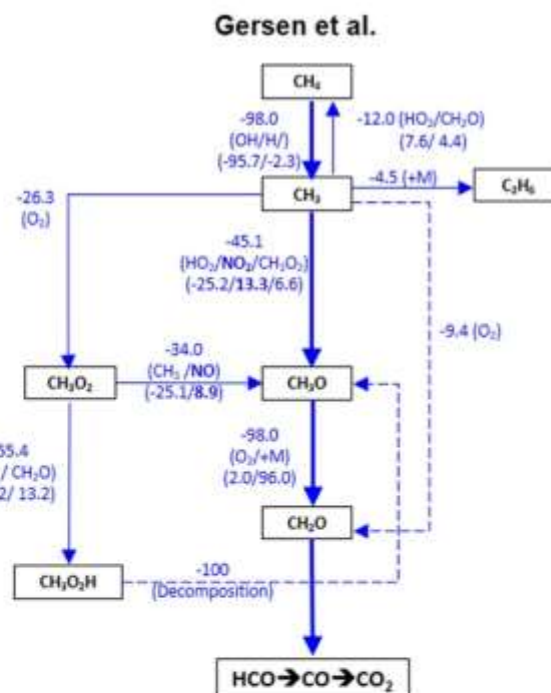
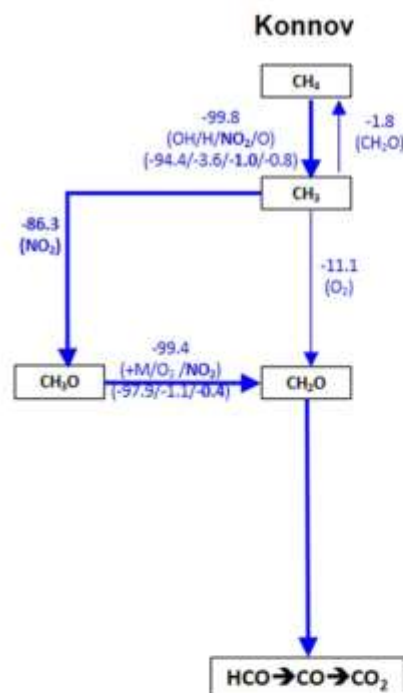


Trace NO_x Perturbed Case ($\phi = 2.0$)

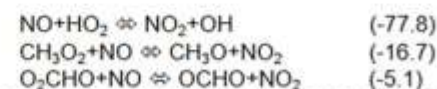
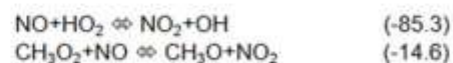


Similar model predictions as stoichiometric and lean case.

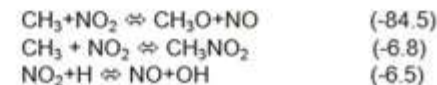
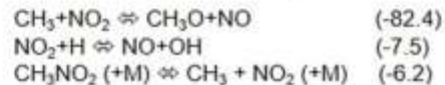
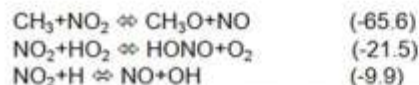
Kinetic Analysis thru Flux Analysis ($\phi = 1.0$, PSR-PFR Approach)



Dominant NO Consumption Pathways

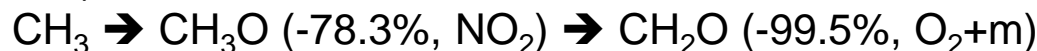


Dominant NO₂ Consumption Pathways



Kinetic Analysis # Konnov Model

- In Konnov (2009) model, there is no flux through the channel of CH_3O_2 (both NO_x perturbed and non-perturbed case)



- Interestingly, CH_3O_2 species is included in the model !

Unperturbed Condition

- Following reactions are known to consume CH_3



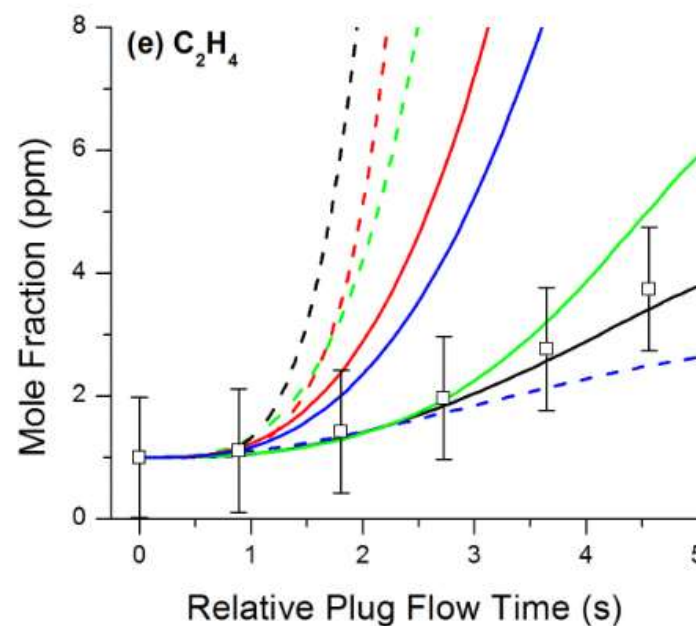
& this reaction is not competitive with either



and/or



- Eventually, the model predicts significant CH_3 consumption via CH_2O & CH_3O formation
- Both these reactions (R2 & R3) convert slowly reacting CH_3 to fast reacting species (CH_2O & CH_3O) plus OH radicals. This explains why the model shows reactivity !



RECAP:

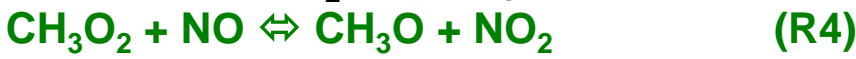
Non-perturbed ($\phi = 1.0$)
Konnov Model: Black Dash



Kinetic Analysis # Konnov Model

NO_x Perturbed Case

❑ An important NO ⇌ NO₂ recycling reaction



& the above reaction will be compared to



BUT, “CH₃O₂” Chemistry is found to be Questionable !!!

Thus, CH₃O₂-mediated NO_x recycling loop presents a potential bottle-neck. This leads to accumulation of NO via R5.

❑ Remaining NO_x cycling channel

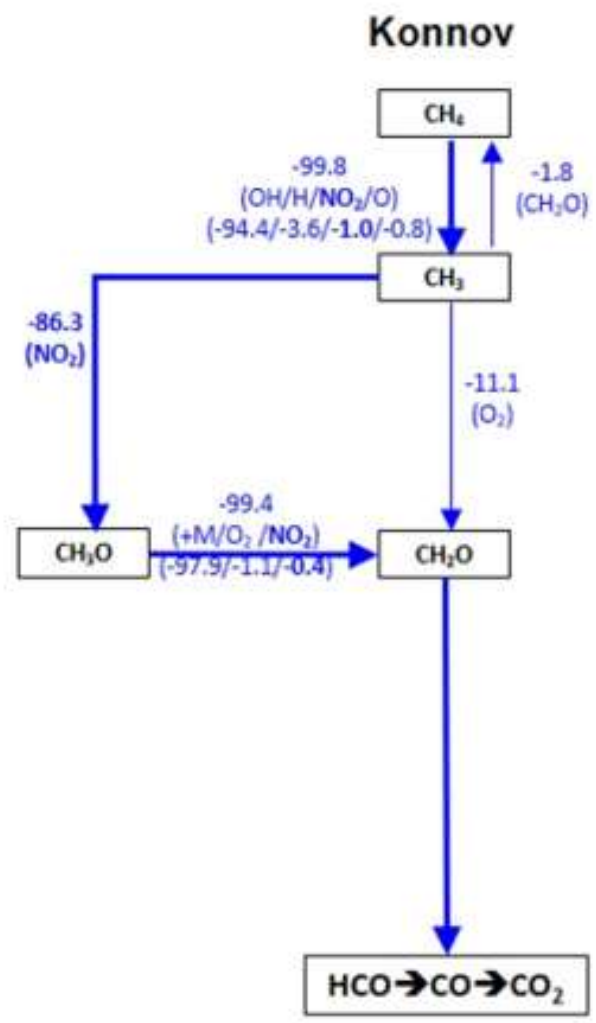


❑ Konnov model also lacks

The formation & destruction of Nitro-Alkyl
(Particularly, CH₃NO₂)



HONO Reaction



Kinetic Analysis # Mathieu and Gersen Model



Flux Analysis of Unperturbed Case ($\phi = 1.0$)

#1

- Qualitatively similar C_0 - C_2 + NO_x coupling pathways.
- Predict similar profiles of NO , NO_2 , and CH_3NO_2 evolution.

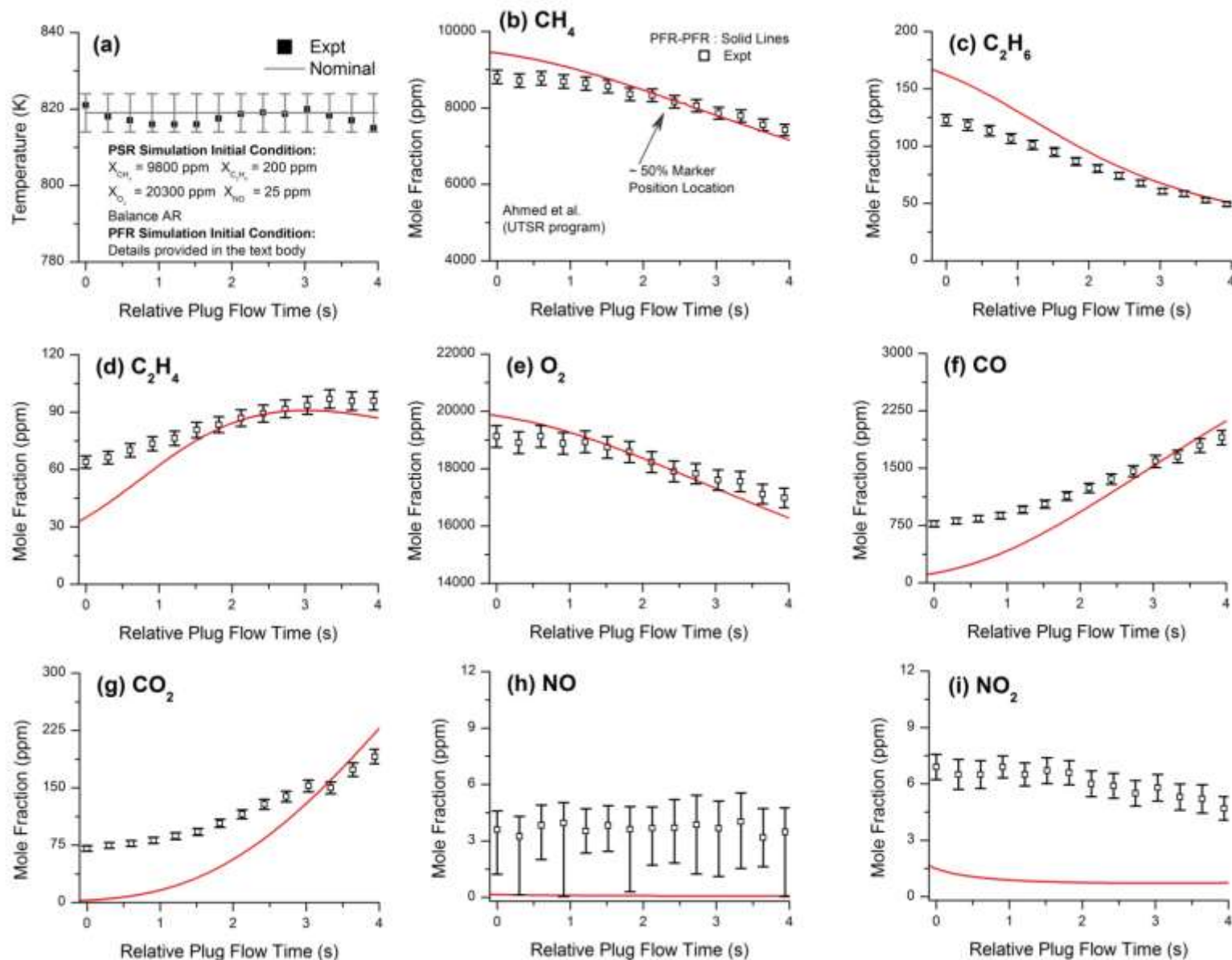
#2

- Exists discrepancy, particularly at longer residence time.
- At longer residence time, NO_x species equilibrates.
- Continuing need to study the coupling of NO_x chemistry to the chemistry of small reactive species generated from methane/natural gas oxidation

#3

- Unclear whether the predicted net sequestration of NO_x into CH_3NO_2 is due to chemistry directly linked to CH_3NO_2 , or
- An imbalanced NO_x flux through other reactions (such as R5 & R6)

Trace NO_x Perturbed Case ($\phi = 1.0$): Present Model



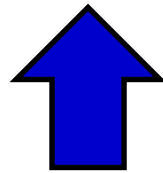


Kinetic Modeling of NO_x

Proposed H₂/CO/NO_x Model



Proposed H₂/CO/NO_x Model



Sub-mechanisms

C₀-C₁
sub-mechanism

H/N/O
sub-mechanism

NO_x
sub-mechanism

- H₂/CO/NO_x Model

77 species, 442 reactions

- H₂/C₁-C₄/NO_x Model

302 species, 1952 reactions

Prompt-NO Route Updates

Table I Reactions and forward rate parameters for the modified Fenimore reaction pathways

	Reactions	A	b	E (cal/mole)
1.	CN + HNO = HCN + NO	1.80E+13	0.0	0
2.	CN + CH ₂ O = HCN + HCO	4.20E+13	0.0	0
3.	HCN + N ₂ = H + CN + N ₂	3.60E+26	-2.60	124890
4.	HCN + M = HNC + M AR/0.7/ H ₂ O/7.0/ CO ₂ /2.0	1.60E+26	-3.23	54600
5.	HCN + OH = HNCO + H	2.80E+13	0	3700
6.	HNCO + O ₂ = HNO + CO ₂	1.0E+12	0.0	35000
7.	NCO + NO = N ₂ O + CO	4.00E+19	-2.16	1743
8.	NCO + NO = N ₂ + CO ₂	1.50E+21	-2.74	1824
9.	HCNO + OH = NCO + H + OH	4.5E+12	0.0	0
10.	HCNO + OH = NCO + H ₂ O	3.50E+12	0.0	0
11.	HCNO + OH = HCO + HNO	4.50E+12	0.0	0
12.	HCNO + OH = NO + CO + H ₂	1.42E-07	5.64	9220
13.	NO ₂ + HCO = HONO + CO N ₂ /0.0/ O ₂ /1.5/ H ₂ O/10.0	6.50E+12	0.0	0
14.	HOCN + O = NCO + OH	1.70E+08	1.50	4133
15.	HOCN + OH = HCO + H ₂ O	1.20E+06	2.0	-248
16.	H ₂ CN + OH = HCN + H ₂ O	1.50E+19	-2.18	2166
17.	HCNO + H = HCH + OH	7.20E+10	0.841	8612.0
18.	CN + H ₂ O = HCN + OH	3.90E+06	1.83	10300
19.	OH + HCN = HOCN + H	5.90E+04	2.40	12500
20.	OH + HCN = HNCO + H	2.00E-03	4.0	1000
21.	HOCN + H = HNCO + H	3.10E+08	0.84	1917

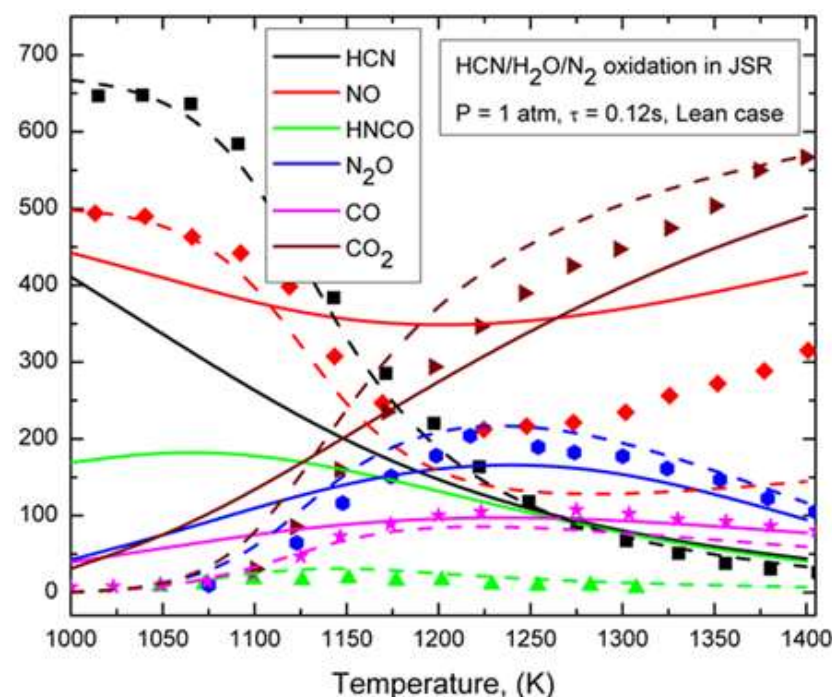
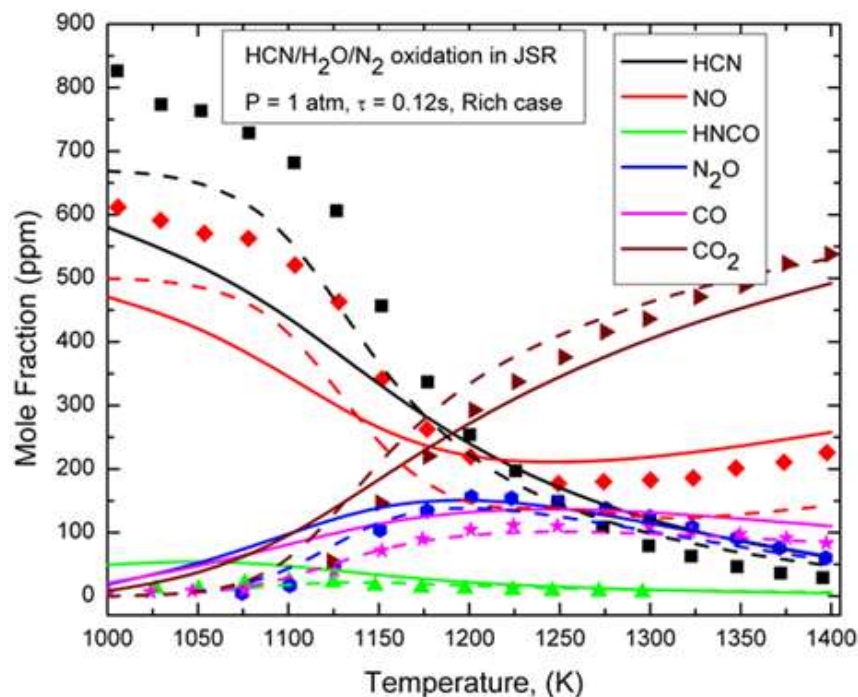
HCN → one of the major intermediates in prompt-NO kinetics

12 additional reactions and 9 rate updates are proposed based on the path flux comparisons of the NO_x model of Dagaut et al. (2008) and the proposed model

Prompt-NO Route Updates

HCN \longrightarrow one of the major intermediates in prompt-NO kinetics

Dagaut et al. (2000) JSR data for HCN/H₂O/N₂ oxidation used to compare performance of the proposed model



Solid line: w/o updates
Dashed line: w updates

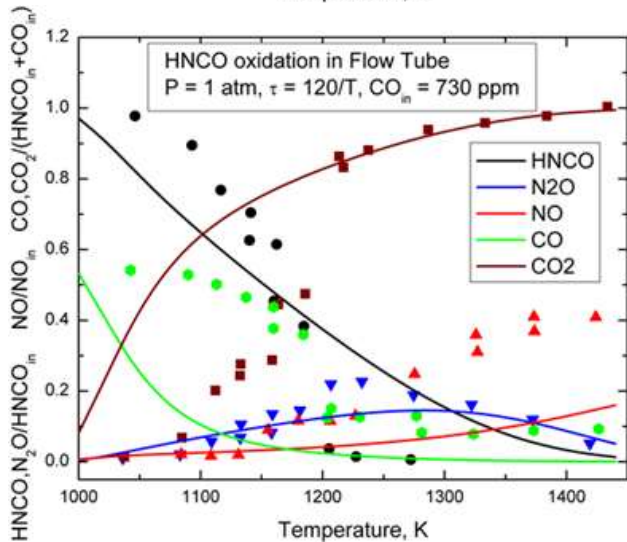
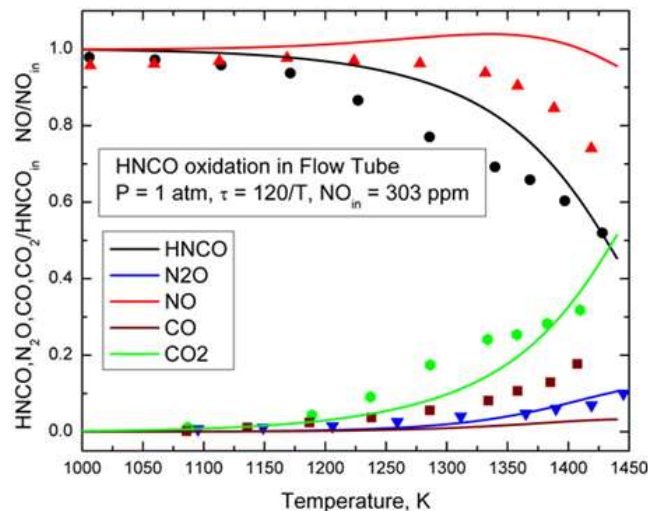
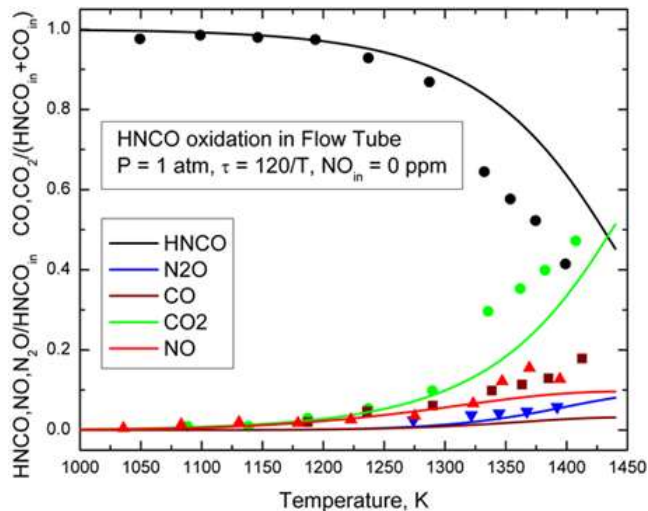
Dagaut et al., *Combust. Sci Tech* 155 (2000)

Dagaut et al., *Prog Energy Combust Sci* 34 (2008)

Prompt-NO Route Updates

HNCO \longrightarrow a significant intermediate in fuel-nitrogen oxidation

Flow tube experiments of Glarborg et al. (1994) on the effects of NO and CO on HNCO oxidation used to check the updated model performances



Reasonable agreements with the experimental findings are observed with the updated model



Multi-dimensional Laminar Reacting Flow Modeling

- Experiments were simulated using an in-house multi-dimensional laminar reacting flow model which solves the conservation equations.
- Two-dimensional axi-symmetric analysis of syngas/ NO_x oxidation in the McKenna burner and its associated tube arrangement was performed adopting the open-source OpenFOAM® framework.
- Detailed syngas/ NO_x oxidation chemistry of Ahmed et al.¹ was employed in the simulation which includes 77 species and 442 elementary reactions.

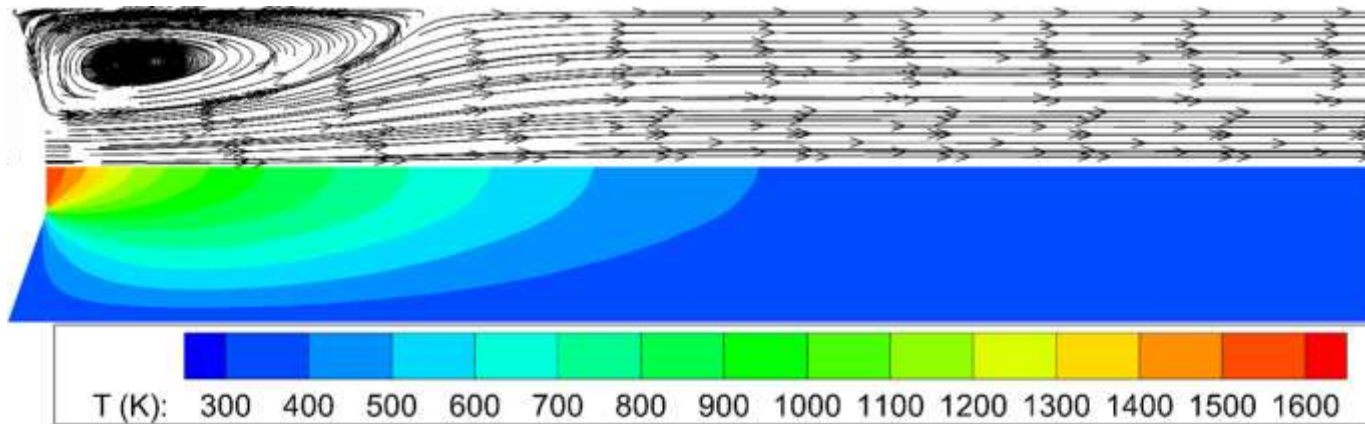
POST FLAME MODEL - REACTIVITY

- The McKenna burner itself is not computationally resolved instead the post flame reactivity is modeled.
- The post flame combustion products obtained from the CHEMKIN PRO burner stabilized module were provided as the inlet boundary conditions for this model.
- The wall temperature was prescribed to be room temperature (300 K).
- The experimental measurements of the centerline temperature and NO_x speciation were compared with the post flame modeling results.

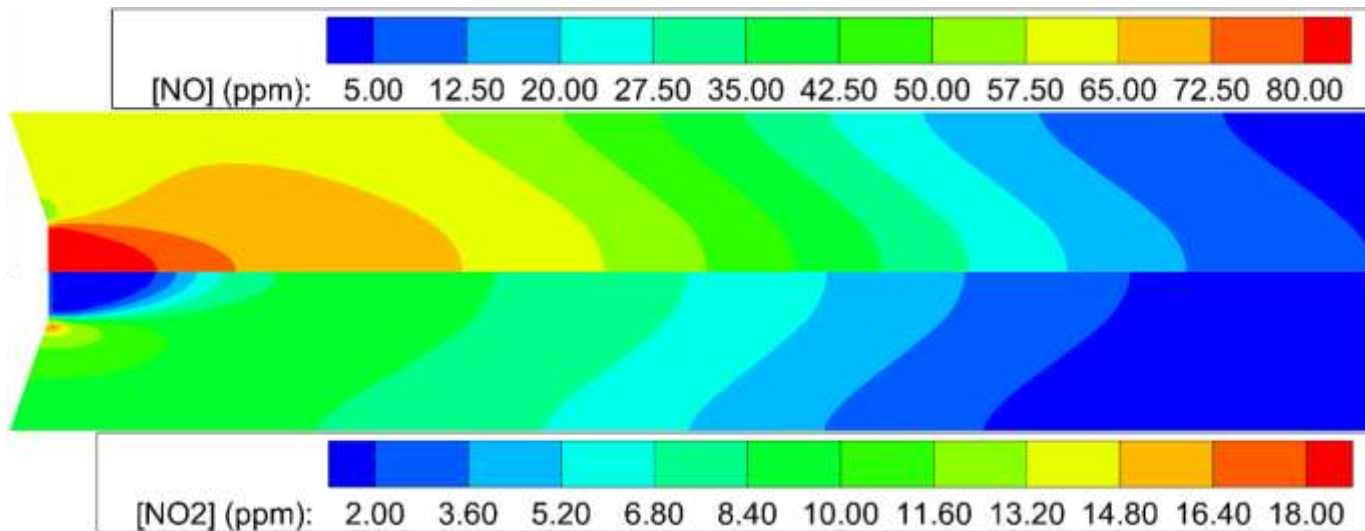
Multi-dimensional Laminar Reacting Flow Modeling: Post Flame Model



100 ppm initial NO doping



**Recirculation
bubbles
formed at the
dead zone**



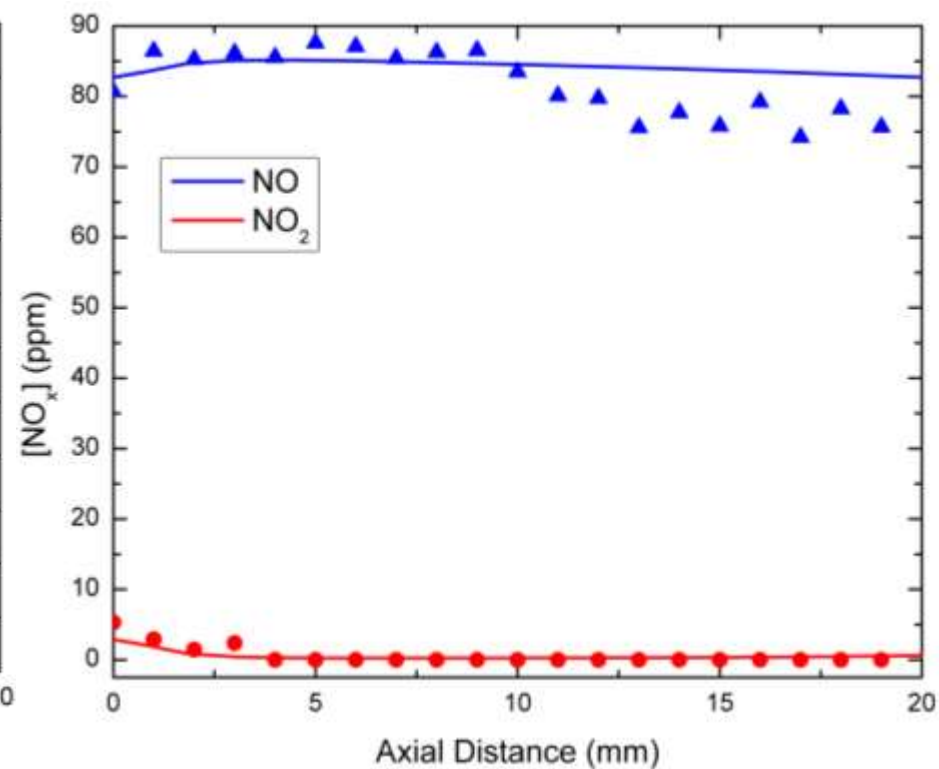
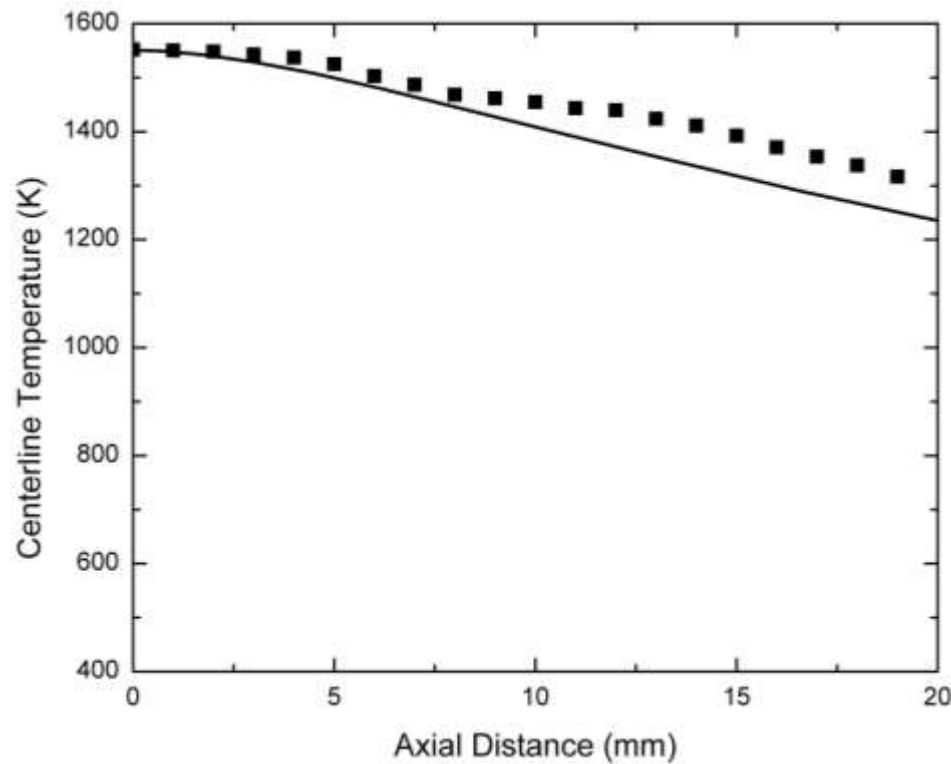
**NO & NO₂
concentration
contours**

$\text{H}_2:\text{CO} = 1$, $\phi = 0.5$, flow rate 4 slpm, 100 ppm NO feed, Air = 0.0713 kg/s, Fuel = 0.00858 kg/s

Multi-dimensional Laminar Reacting Flow Modeling: Post Flame Model

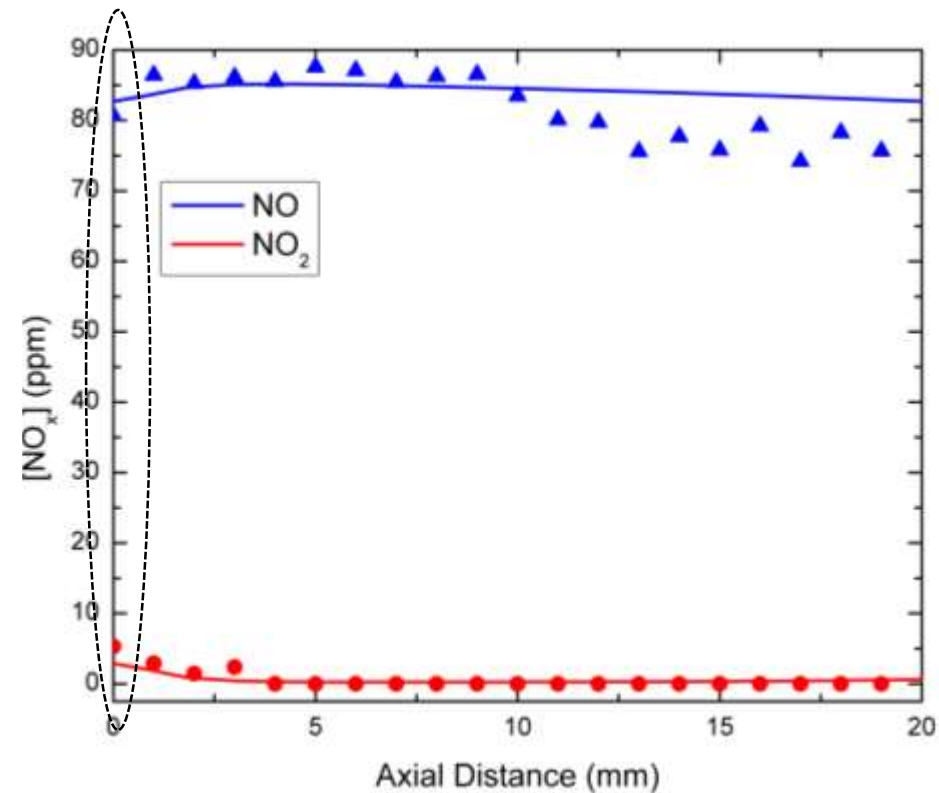
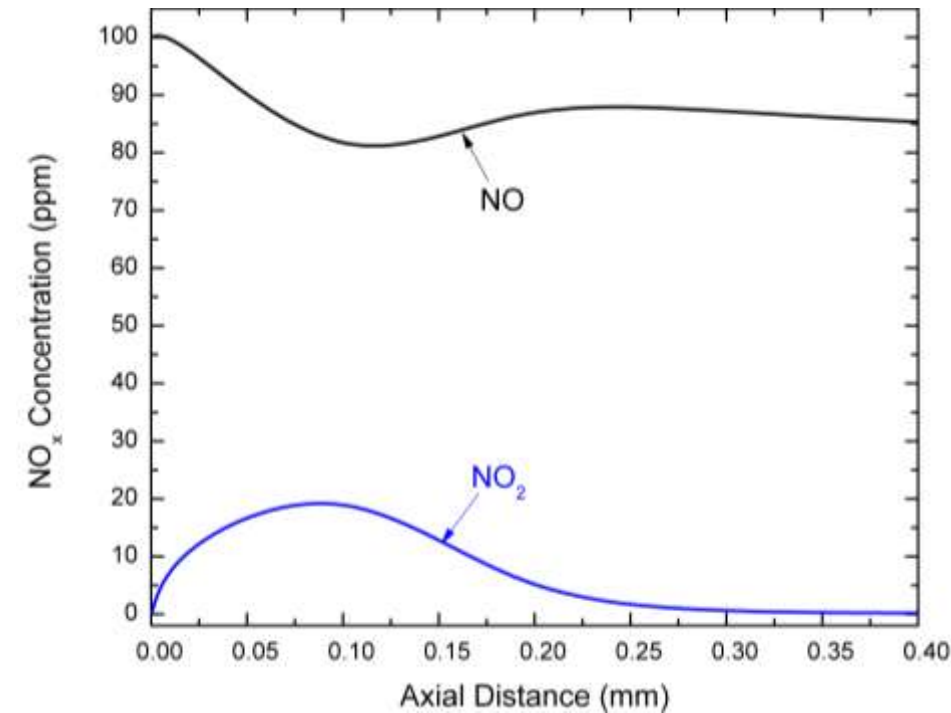
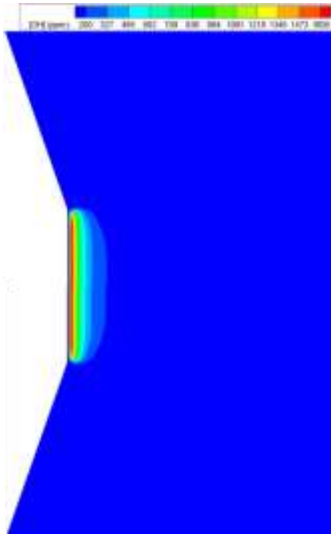


100 ppm initial NO doping



$\text{H}_2:\text{CO} = 1$, $\phi = 0.5$, flow rate 4 slpm, 100 ppm NO feed, Air = 0.0713 kg/s, Fuel = 0.00858 kg/s

Multi-dimensional Laminar Reacting Flow Modeling: Resolved Flame



Multi-dimensional simulations show an initial NO to NO₂ conversion very close to the inlet

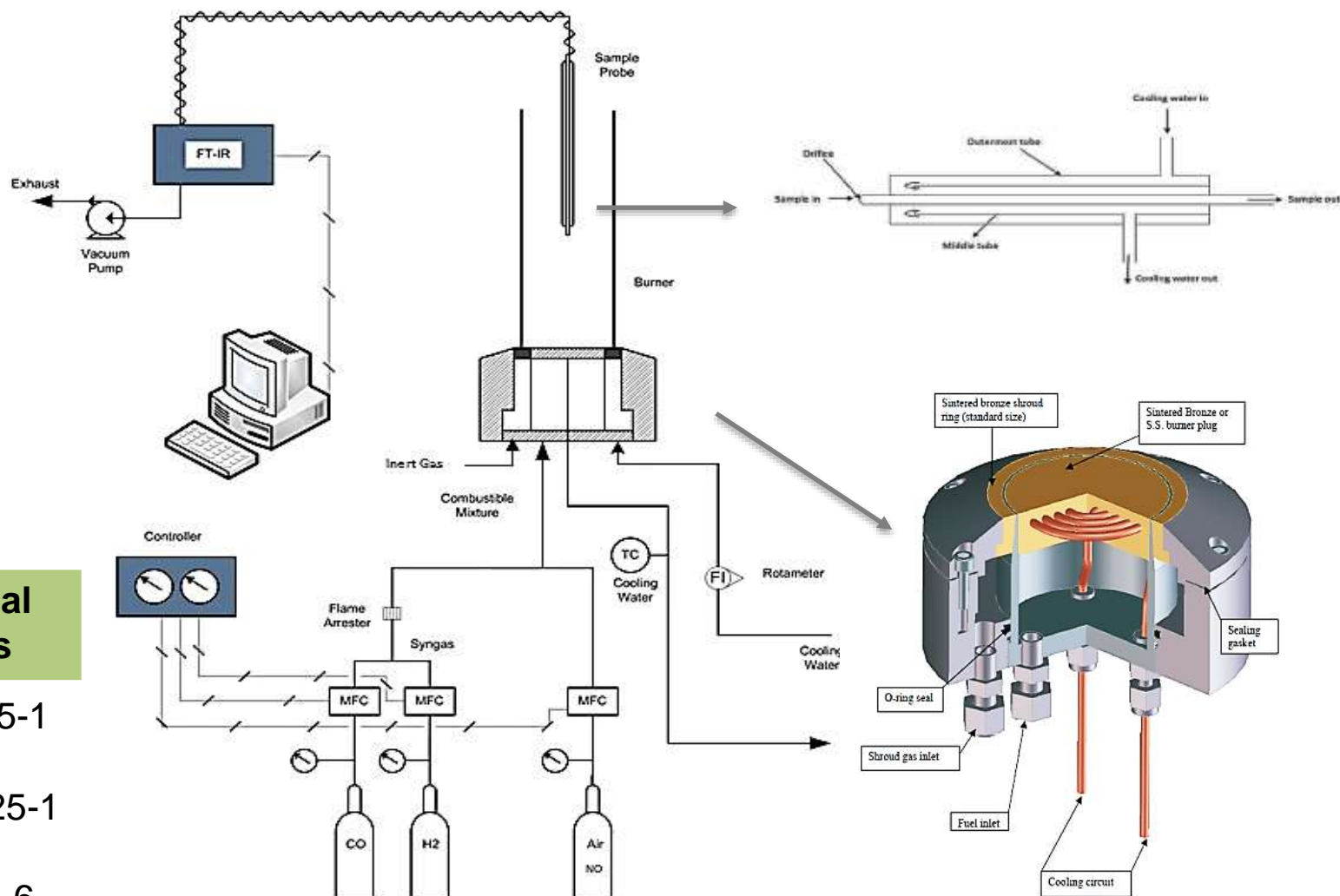


- Influence of trace impurities on combustion characteristics.
- Trace NO_x – emittents can alter the combustion behavior, global/optimized models can not capture intricate features. Performance of existing model has been analyzed and inclusions are proposed.
- The validated $\text{H}_2/\text{CO}/\text{NO}_x$ model has been updated to included HCN routes – prompt NO routes.
- Multi-dimensional CFD+Kinetic model/simulations conducted to investigate the NO_x speciation experiments.



Experiments for Speciation Measurements

Schematic of Experimental Setup



Experimental Conditions

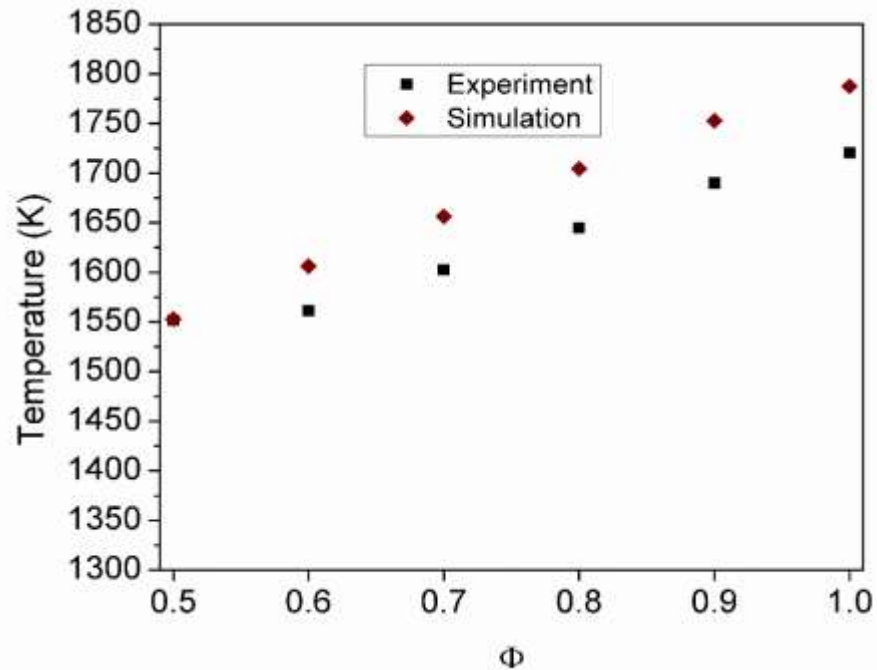
Φ	0.5-1
H ₂ /CO	0.25-1
Total Flow Rate	3-6 SLPM

Flame Temperature Measurement / Simulation

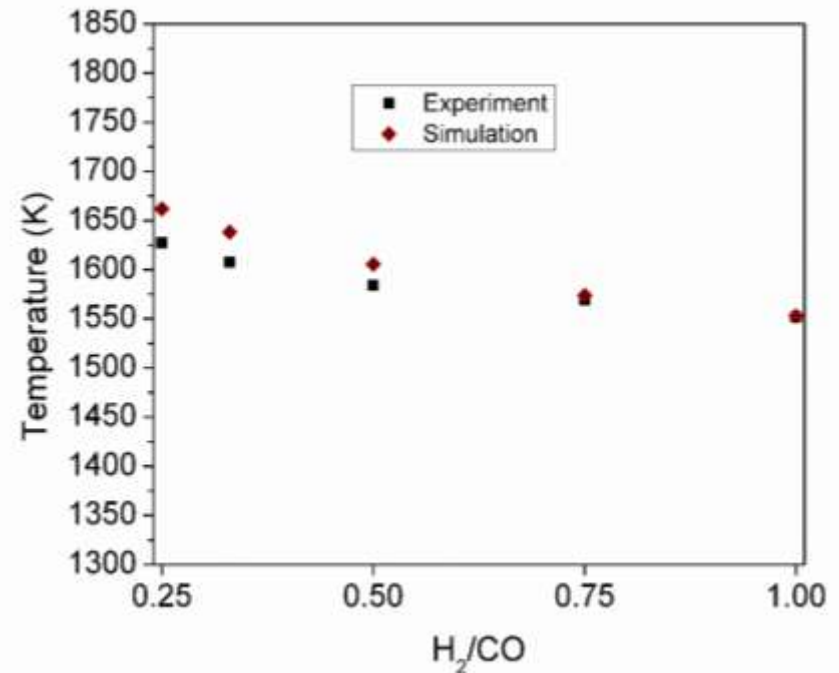


Temperature predictions with CHEMKIN PRO burner stabilized module simulations compared against experimental measurements

H_2/CO : 1 and 4LPM



Φ : 0.5 and 4LPM

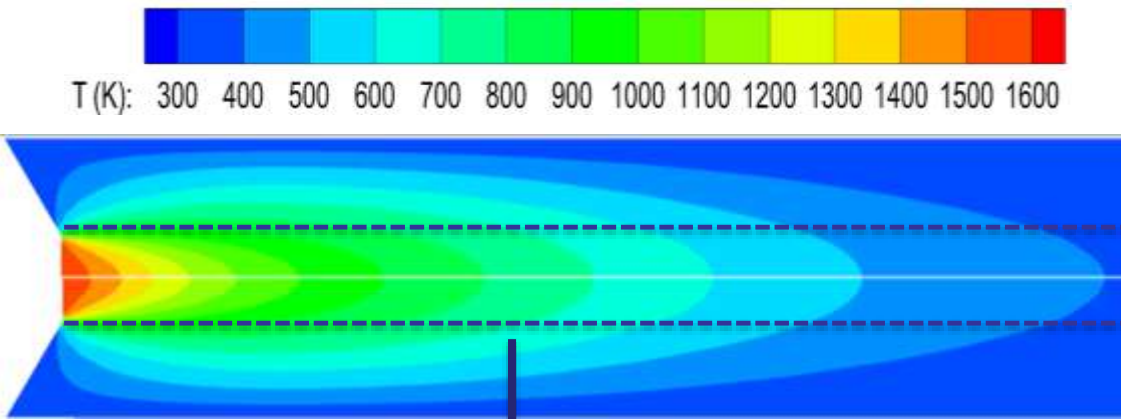


Multi-dimensional Temperature Measurements/Predictions

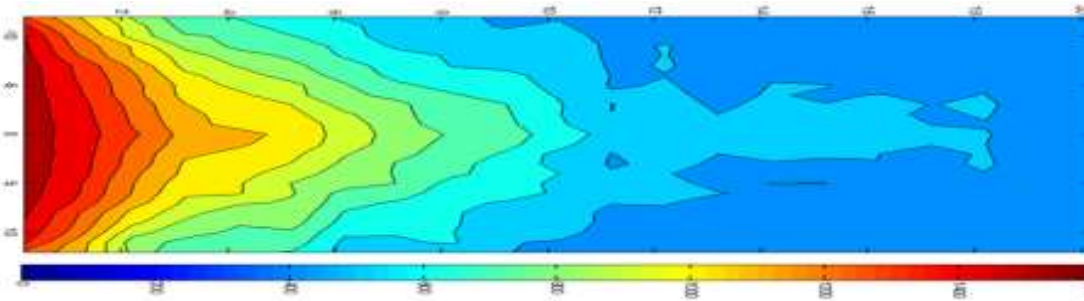
$H_2/CO:1$ $\Phi: 0.5$

2-D Temperature Profile

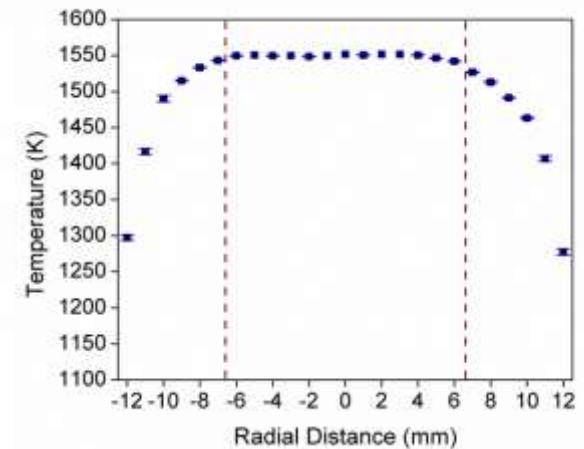
Simulation



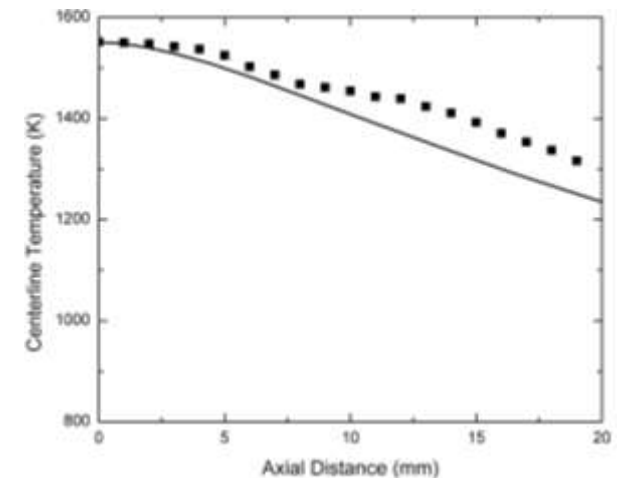
Experiment (525 points)



Radial Temperature Profile



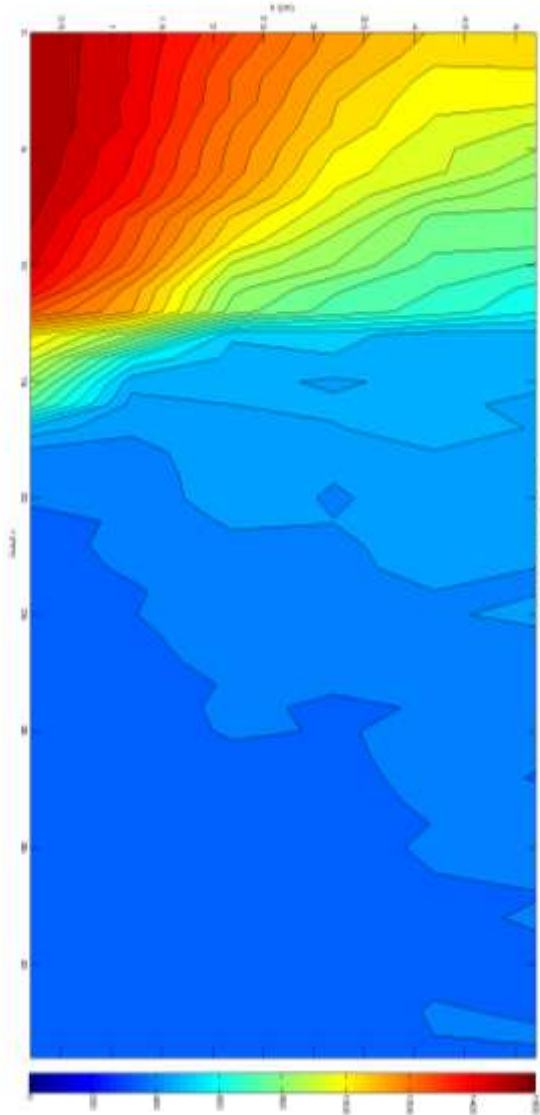
Centerline Temperature Profile



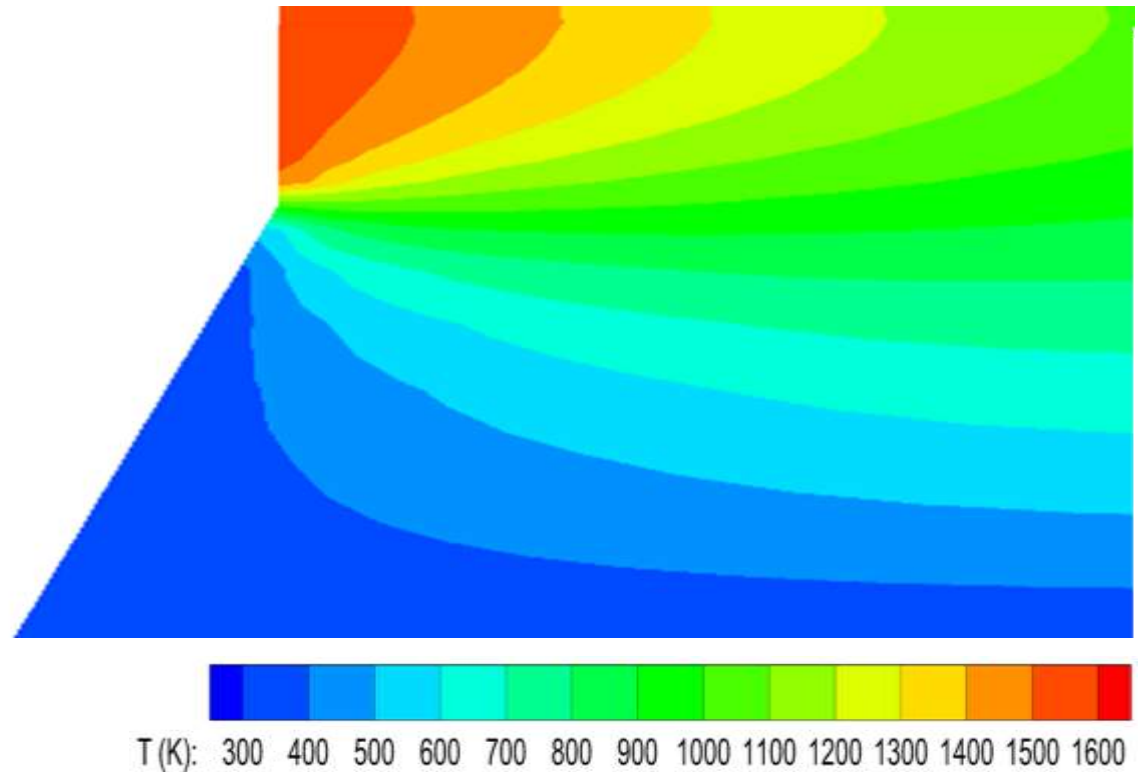
Multi-dimensional Temperature Measurements/Predictions



Experiment

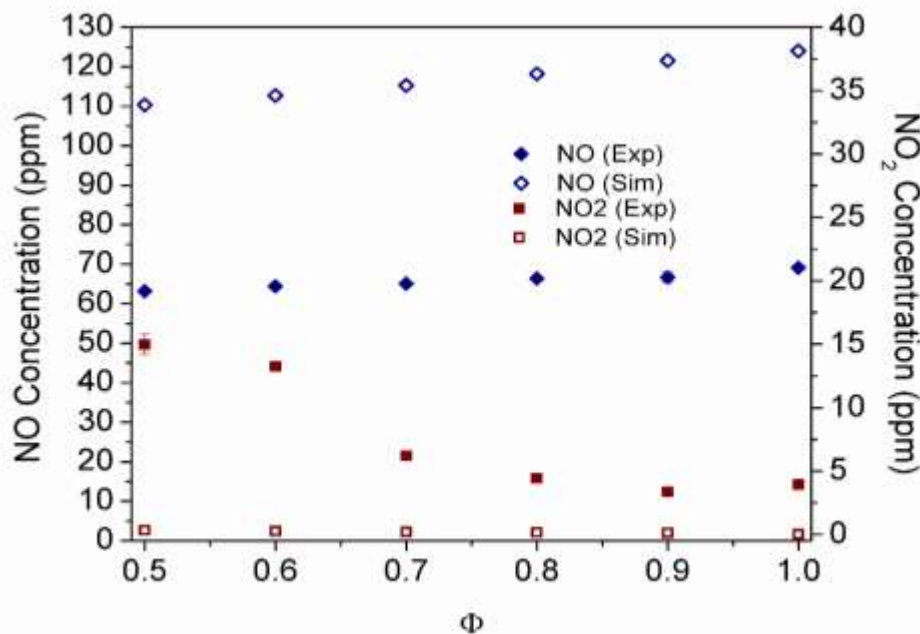


Simulation



NO_x Speciation Measurement/Prediction by Flame Simulation

H₂/CO:1 and 100 ppm initial NO doping



One of the dominant NO formation paths contributes more for $\Phi = 1.0$ (34%) than for $\Phi = 0.5$ (20%)



More dominant NO to HNO path through $\text{NO} + \text{H}(+\text{M}) = \text{HNO}(+\text{M})$ for $\Phi = 1.0$ (33%) than for $\Phi = 0.5$ (12%)

Less dominant NO to NO₂ path through $\text{NO} + \text{O}(+\text{M}) = \text{NO}_2(+\text{M})$ for $\Phi = 1.0$ (43%) than for $\Phi = 0.5$ (73%)

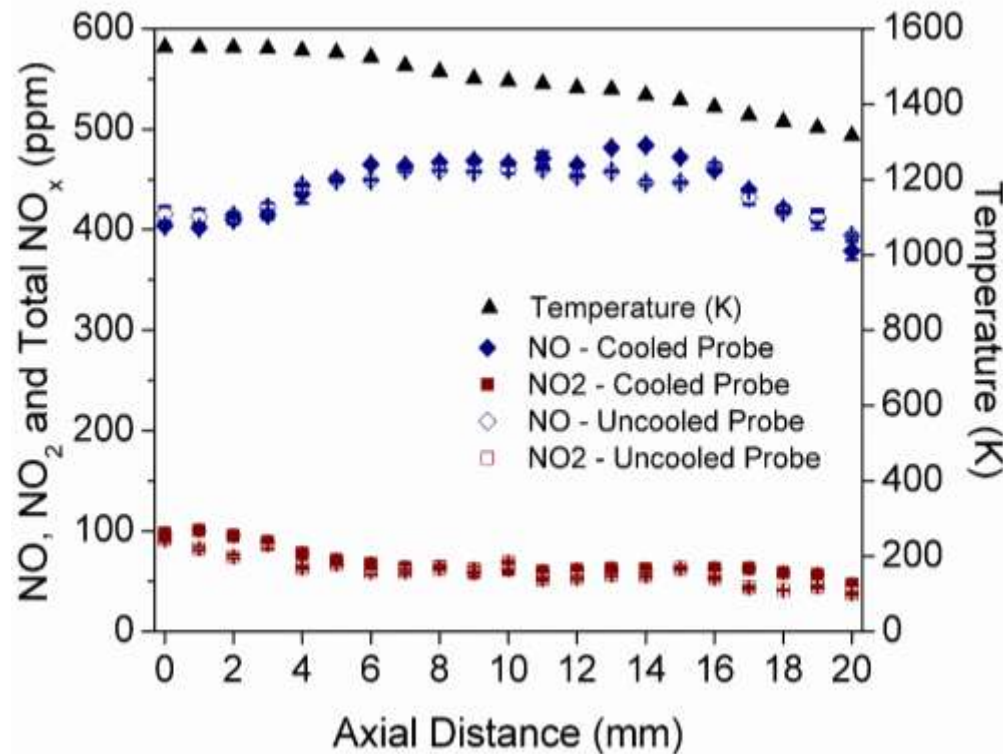
As Φ increases ➡ NO concentration ↑
NO₂ concentration ↓

- No N₂O was observed.

Experimental NO_x Speciation Profile – Probe Effect

Sampling with cooled probe vs. uncooled probe

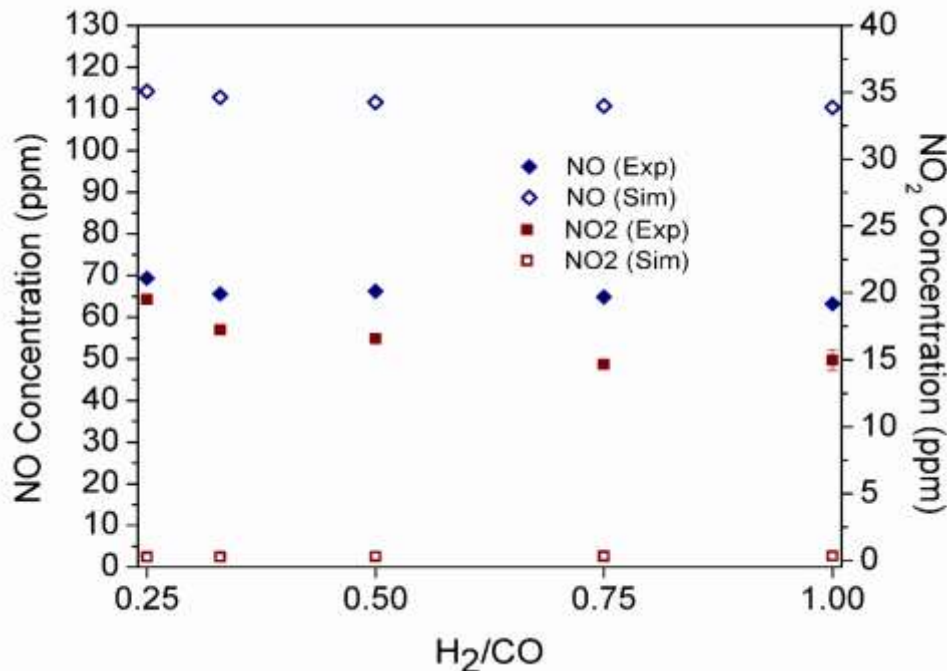
H₂/CO=1, Φ =0.5, 500 ppm initial NO doping



- ❑ Experiments were repeated with uncooled probe to see if there is any NO₂ formation in the sampling probe.
- ❑ Consistent results were obtained for both cooled and uncooled probes

NO_x Speciation Measurement/Prediction by Flame Simulation

$\Phi = 0.5$ and 100 ppm initial NO doping



HNO Source



15% (H₂/CO:0.25), 45% (H₂/CO:1)



6% (H₂/CO:0.25), 12% (H₂/CO:1)

More dominant for H₂/CO:1

Lower NO production for H₂/CO = 1



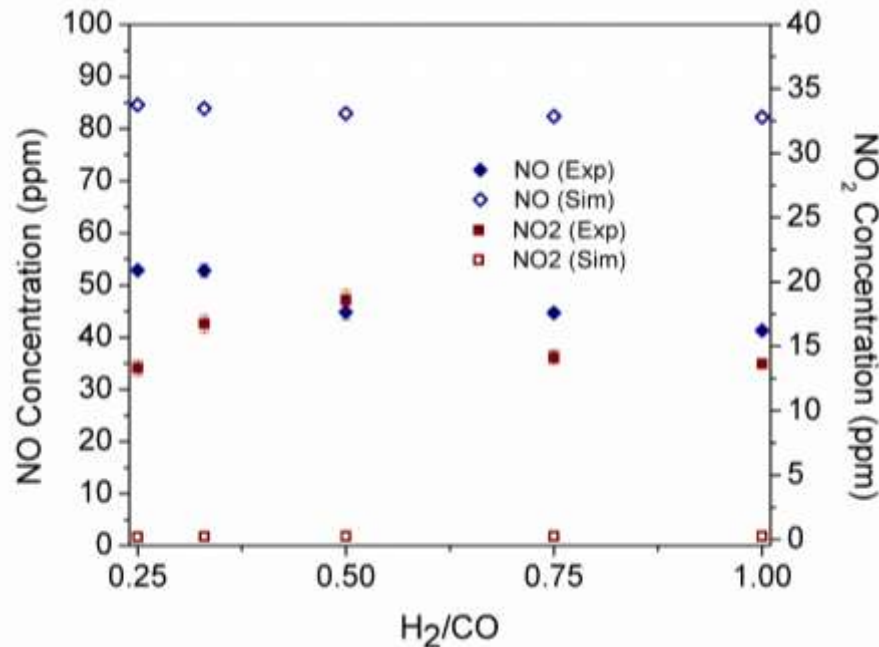
67% (H₂/CO:0.25), 55% (H₂/CO:1)

As H₂/CO increases → NO concentration ↓

NO_x Speciation Measurement/Prediction by Flame Simulation



$\Phi = 0.5$ and 75 ppm initial NO₂ doping



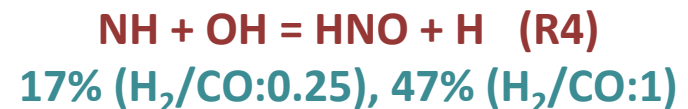
Overall contribution of NO to HNO formation ↓



Small percentage of NO comes from NO₂



Other HNO Sources are more dominant



More dominant for H₂/CO:1
Lower NO

As H₂/CO increases

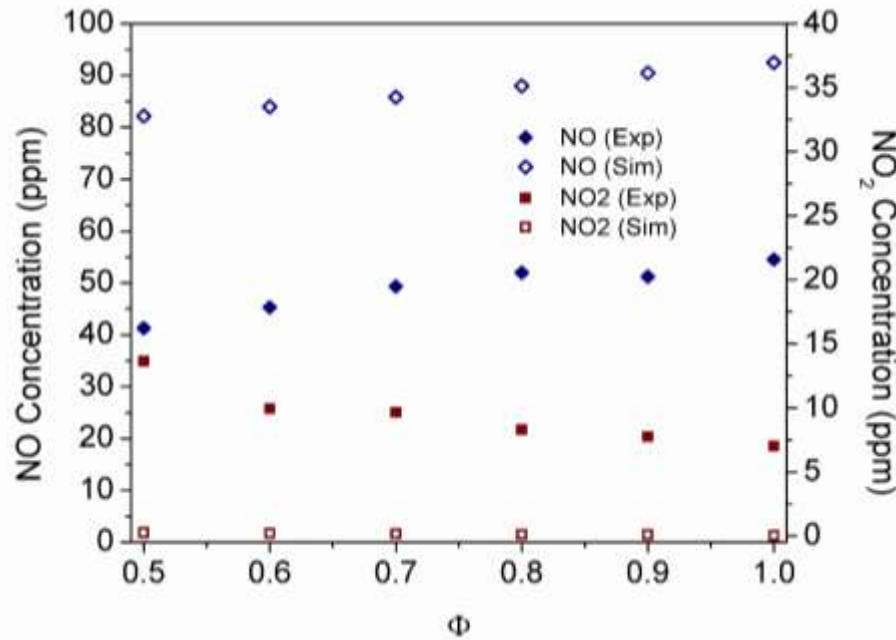



NO concentration ↓

NO_x Speciation Measurement/Prediction by Flame Simulation



H₂/CO:1 and 75 ppm initial NO₂ doping



As Φ increases  NO concentration \uparrow
NO₂ concentration \downarrow

One of the dominant NO formation paths contributes more for $\Phi = 1.0$ (33%) than for $\Phi = 0.5$ (18%)



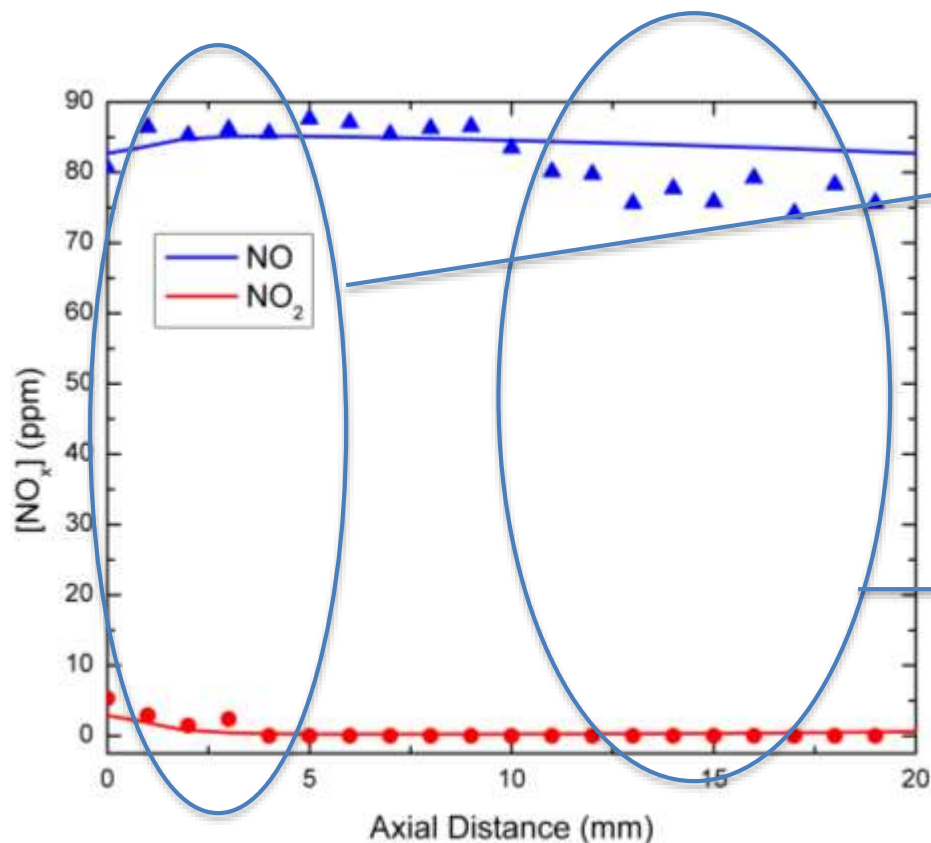
More dominant NO to HNO path through $\text{NO} + \text{H}(+\text{M}) = \text{HNO}(+\text{M})$ for $\Phi = 1.0$ (33%) than for $\Phi = 0.5$ (11%)

Less dominant NO to NO₂ path through $\text{NO} + \text{O}(+\text{M}) = \text{NO}_2(+\text{M})$ for $\Phi = 1.0$ (48%) than for $\Phi = 0.5$ (75%)

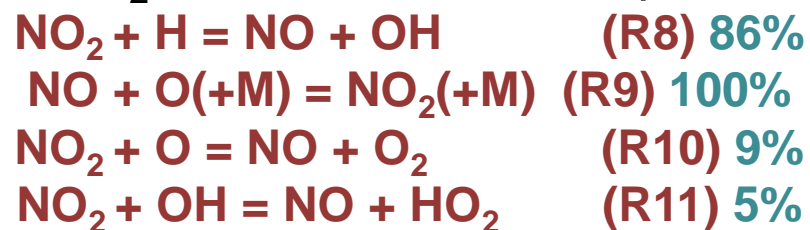
Qualitative trends are captured for speciation predictions but they are not in quantitative agreement due to possible multi-dimensional transport - possible axial and radial variation not captured in the model.

Centreline NO_x Speciation Profile with Multi-dimensional Laminar Reacting Flow Modeling

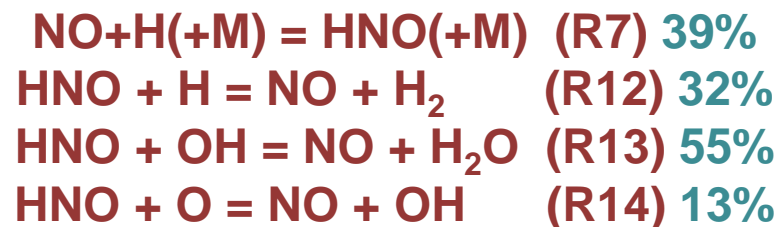
$\text{H}_2/\text{CO}=1$, $\Phi=0.5$ and 100 ppm initial NO doping



NO_2 -NO interconversion paths

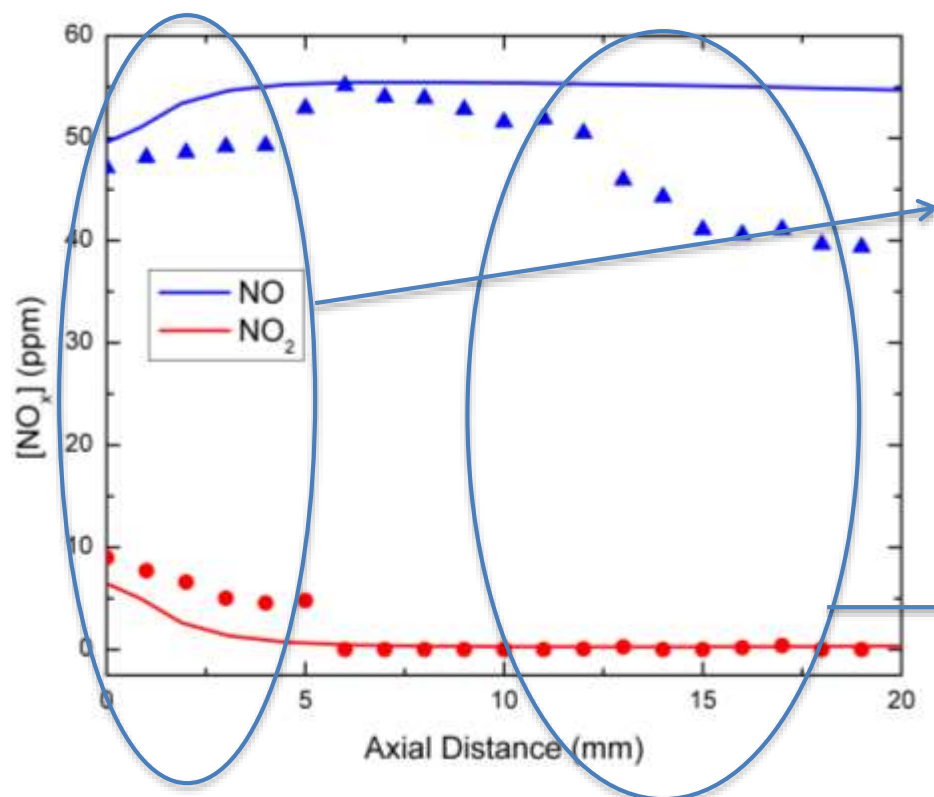


NO-HNO interconversion

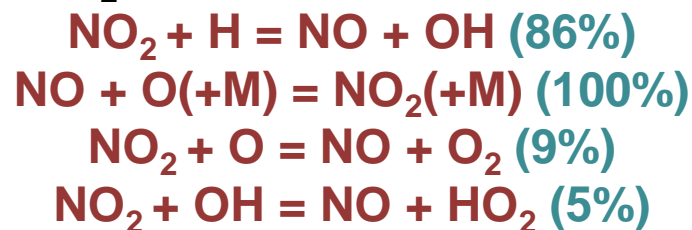


Centreline NO_x Speciation Profile with Multi-dimensional Laminar Reacting Flow Modeling

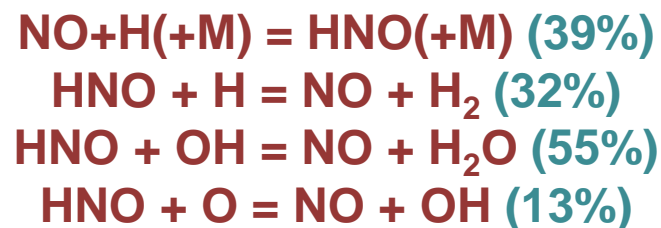
$\text{H}_2/\text{CO}=1$, $\Phi=0.5$ and 75 ppm initial NO_2 doping



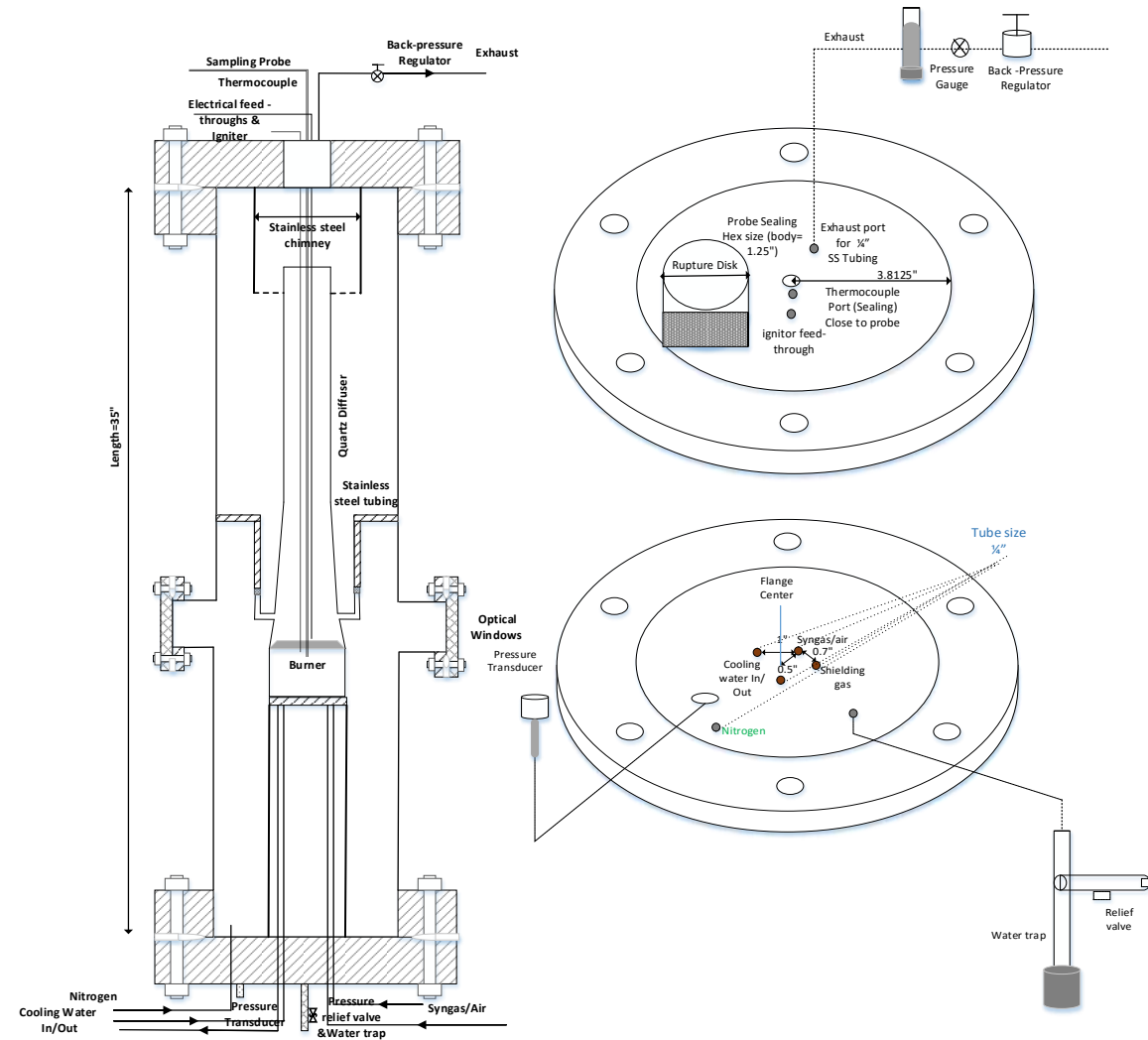
NO_2 -NO interconversion paths



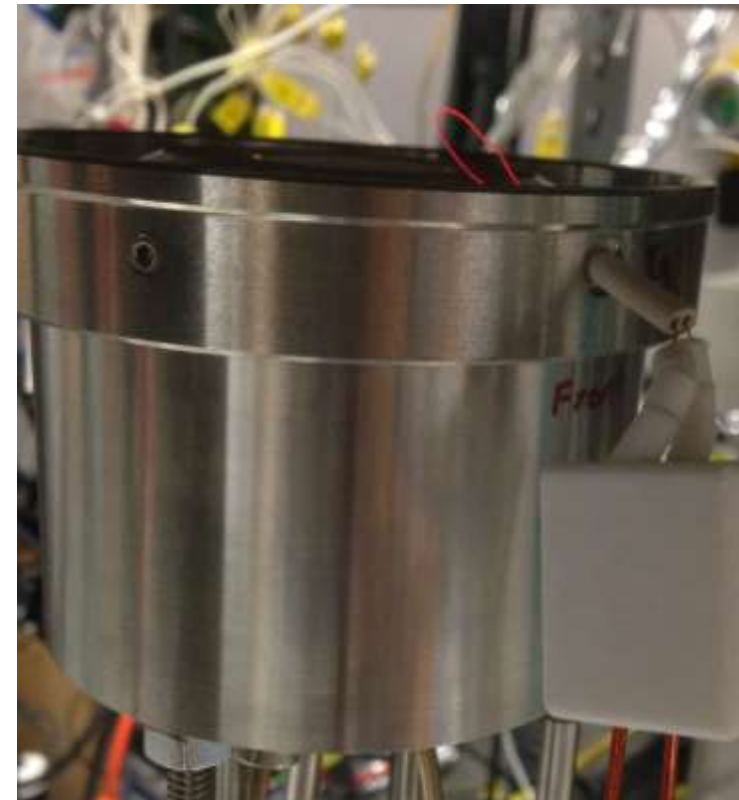
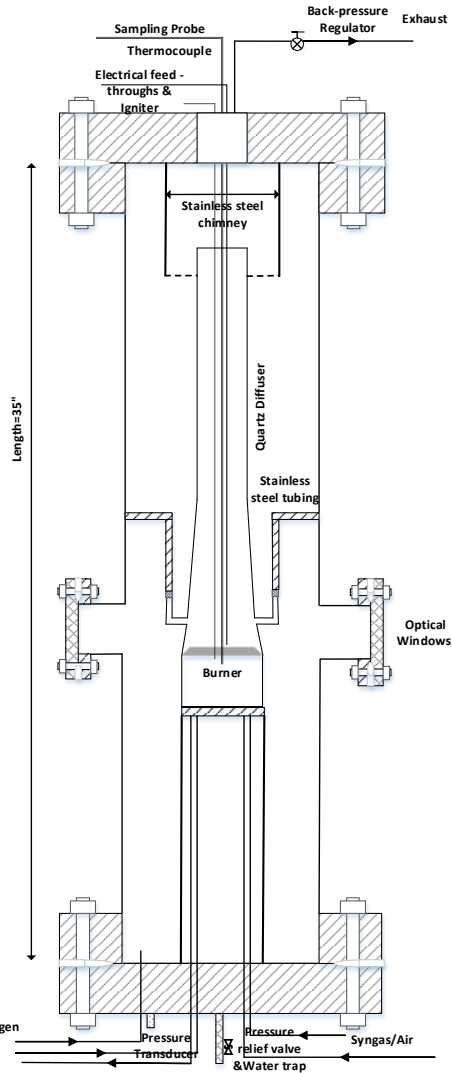
NO-HNO interconversion



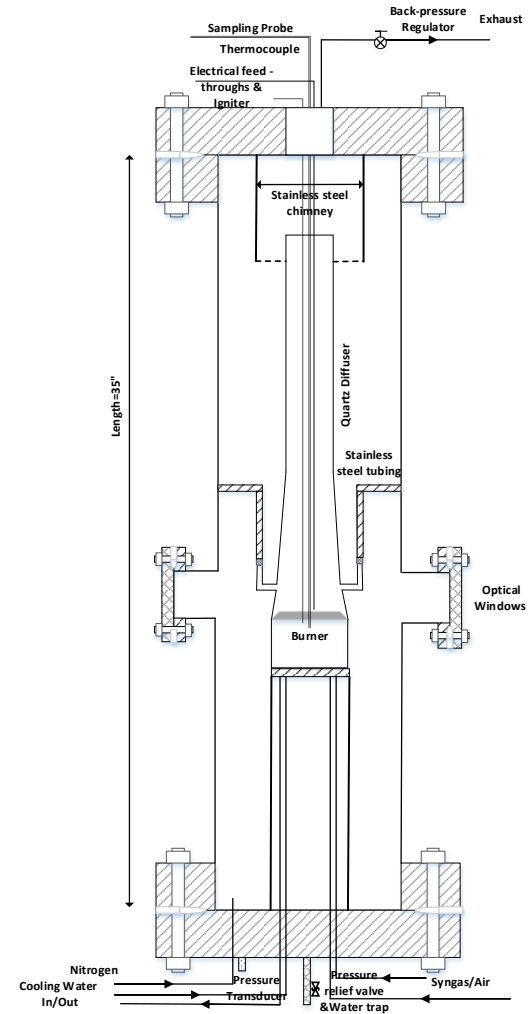
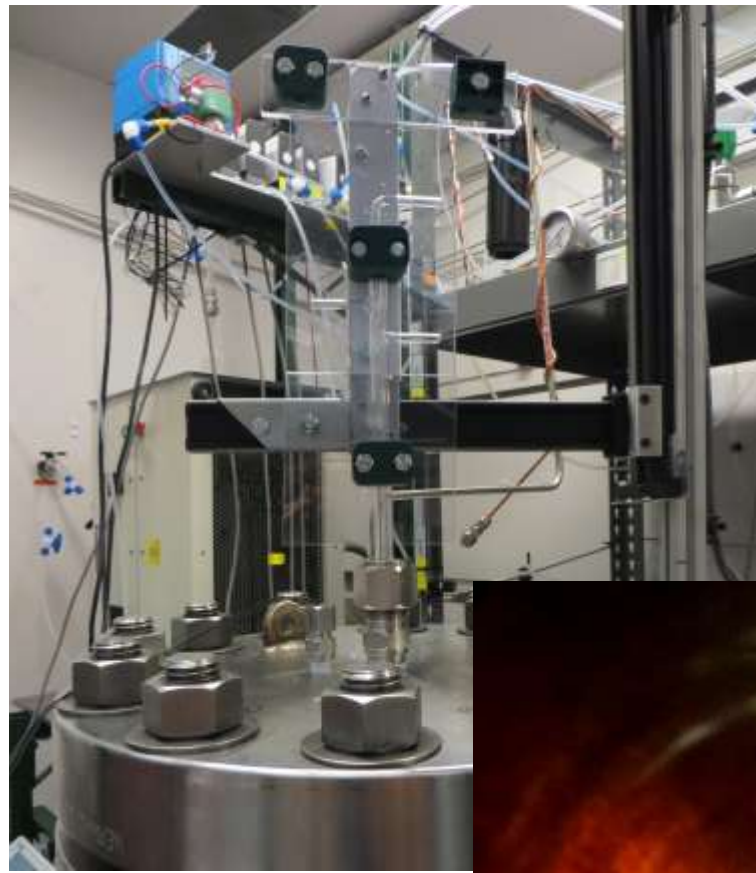
High Pressure System



High Pressure System



High Pressure System



Overall Summary



- NO_x model for high hydrogen content fuel; model has been validated against a wide range of targets. Prompt pathways have been revised and updated.
- NO_x perturbed natural gas oxidation experiments conducted in a flow reactor configuration. Presence of trace NO_x significantly alters the oxidation behavior.
- The performance of different models are compared and analyzed against the experimental data.
- Multi-dimensional post flame CFD simulations conducted. The model captures the post flame reactivity with the coupled transport and detailed kinetics.
- Flame needs to be resolved numerically to obtain the NO - NO_2 conversion occurring prior to the flame.
- Axial and radial temperature profiles were obtained
- NO_x speciation data at atmospheric pressure was collected at different conditions.
- There was a reasonable agreement between experimental data and simulations.

Future Work

- NO_x -CO speciation data will be collected at higher pressures considering the effect of different parameters such as hydrocarbons and diluents.
- Effect of exhaust gas recirculation will be investigated.



- Alam, F., Haas, M., Farouk, T., Dryer, F., “Influence of trace nitrogen oxides on natural gas oxidation: Flow reactor measurements and kinetic modeling” **Energy and Fuel** (In Review).
- Ahmed, S., Santner, J., Padak, B., Dryer, F., Farouk, T., “Computational study of NO_x formations at conditions relevant to gas turbine operation part II: NO_x in high hydrogen content fuel combustion at elevated pressure” **Energy and Fuel** (2016), 30, 7691 - 7703.
- Santner, J., Ahmed, S., Farouk, T., Dryer, F., “Computational study of NO_x formation at conditions relevant to gas turbine operation, part I” **Energy and Fuel** (2016), 30, 6745 – 6755.
- Alam, F., Haas, F., Farouk, T., Dryer, F., “Flow reactor measurements and kinetic modeling of nitrogen oxides (NO_x) perturbed synthetic natural gas oxidation ” *Spring Technical Meeting of the Eastern States Section of the Combustion Institute*, Princeton, New Jersey, March 13 – 16, 2016, Pages 1 – 6.
- Ahmed, S., Santner, J., Dryer, F., Farouk, T., “Comprehensive kinetic model for predicting NO_x during hydrogen content fuel combustion at elevated pressure” *9th U.S. National Combustion Meeting*, Cincinnati, Ohio, May 17 – 20, 2015.
- Santner, J., Ahmed, S., Farouk, T., Dryer, F., “Computational study of NO_x formation at conditions relevant to gas turbine operating conditions” *9th U.S. National Combustion Meeting*, Cincinnati, Ohio, May 17 – 20, 2015.

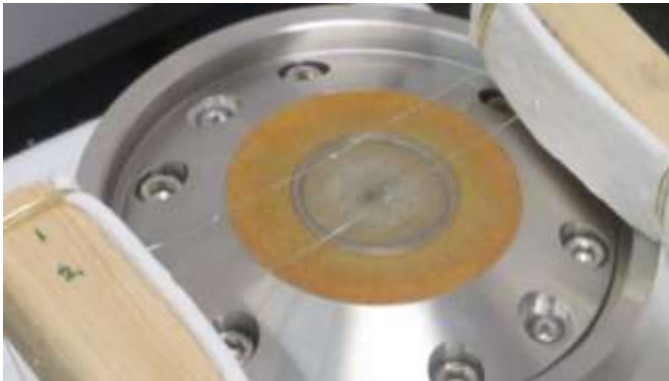


Thank You

Temperature Measurements

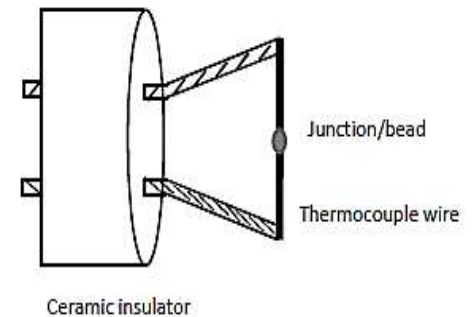
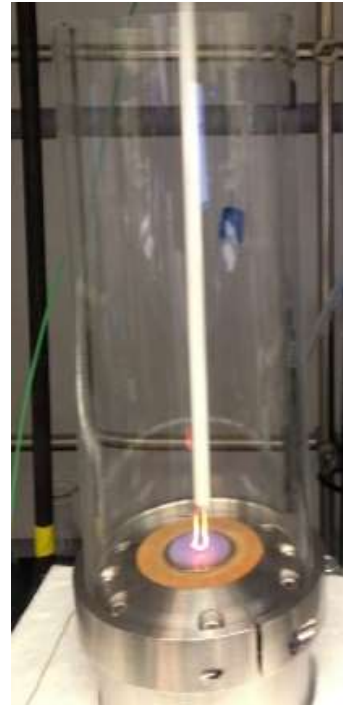


Flame T measurements



- Radiation correction was applied to T measurements
- Using the R-type thermocouple, the radiation loss was % 8

Radial and axial T profile measurements



Thermocouple diagram