Final Report: 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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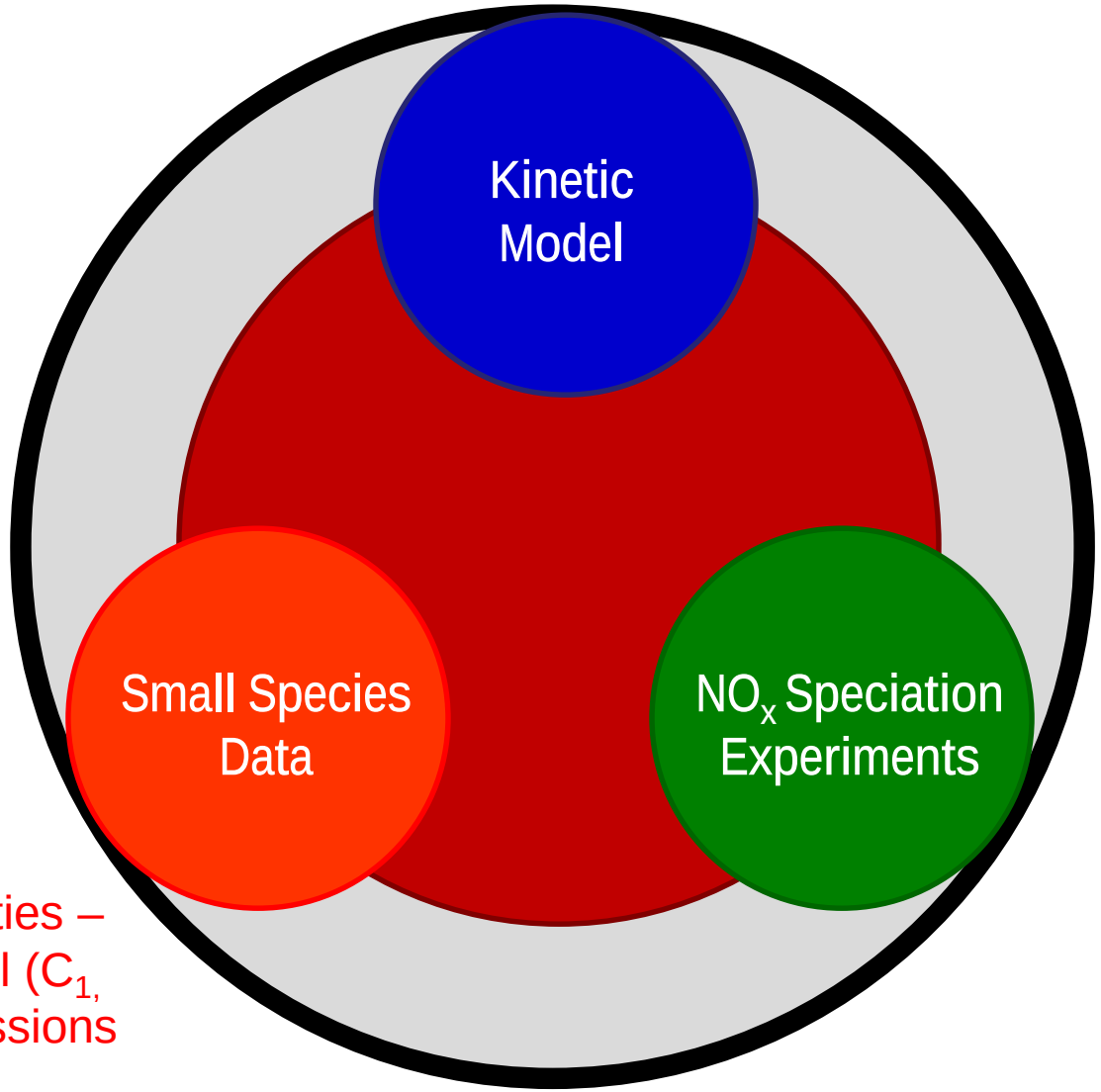
- Predictions of NO_x to address strict emission standards

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

- Fuel impurities – source of fuel (C_1, C_2 …) – 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

Objectives

- **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 NO_2 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!

Tasks

- Project management and planning

- Study of reactivity and speciation data for NO_x under various conditions in a high pressure McKenna burner – flow tube arrangment

- 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

Project Participants

University of South Carolina and Princeton University

PI: **Dr. Tanvir Farouk**, Assistant Professor
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

Presentation Outline

- **Project Objectives**
- **Research Tasks**
- **Research Team Members**
- **Final Report**
  - ❑ **Kinetic model for NO_x formation in HHC fuels**
  - ❑ **Measurement of NO_x perturbed oxidation experiments**
  - ❑ **Experiments for speciation measurements**
  - ❑ **Multi-dimensional CFD + Kinetics modeling and simulations**
- **Summary**

Kinetic model for NO_x formation in HHC fuels

Mechanisms

Saudi Aramco C_1-C_4 Mechanism (2012)
- 253 species
- 1536 reactions

Princeton C_0 Mechanism (2011)
- 13 species
- 27 reactions

USC C_1-C_4 Mechanism (2007)
- 111 species
- 784 reactions

SanDiego C_1-C_3 Mechanism (2002)
- 21 species
- 93 reactions

GRI Mechanism (1999)
- 53 species
- 325 reactions

$C_0 - C_4$ Models

Konnov NO_x Mechanism (2009)
- Fenimore
- N_2O

Dagaut NO_x Mechanism (2006)
- N_2O
- Limted C_xN_y

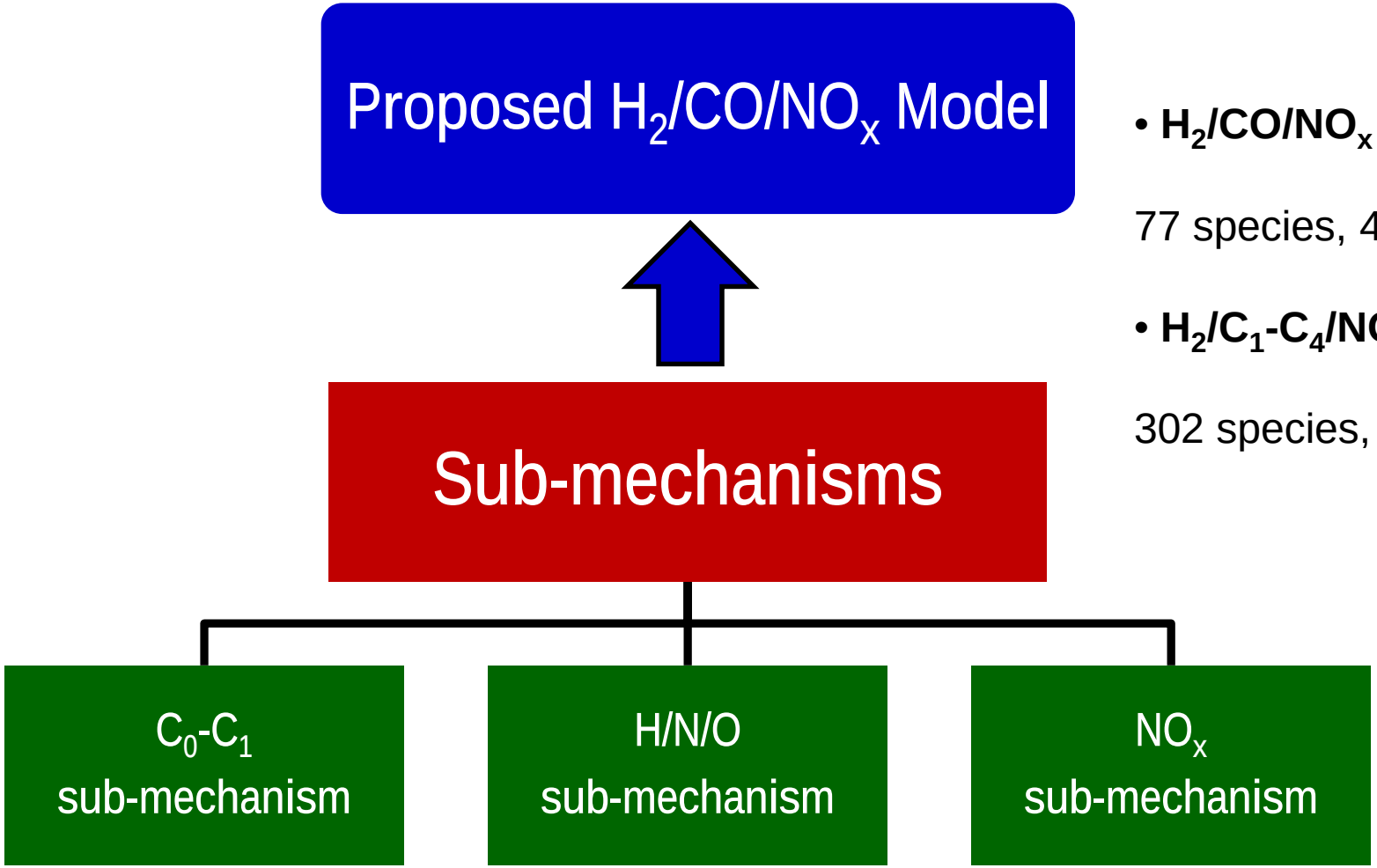
Rasmussen NO_x Mechanism (2008)
- N_2O absent
- N_xH_y absent

NO_x Models

Global combustion targets (e.g. ignition delay time and reactivity) are insufficient to provide the necessary constraining conditions for assessment and model development of NO_x interactions with Hydrogen and Syngas Oxidation.

Considerable differences in even qualitative behavior among popular literature models → improvements are possible.

$H_2/CO/NO_x$ Model



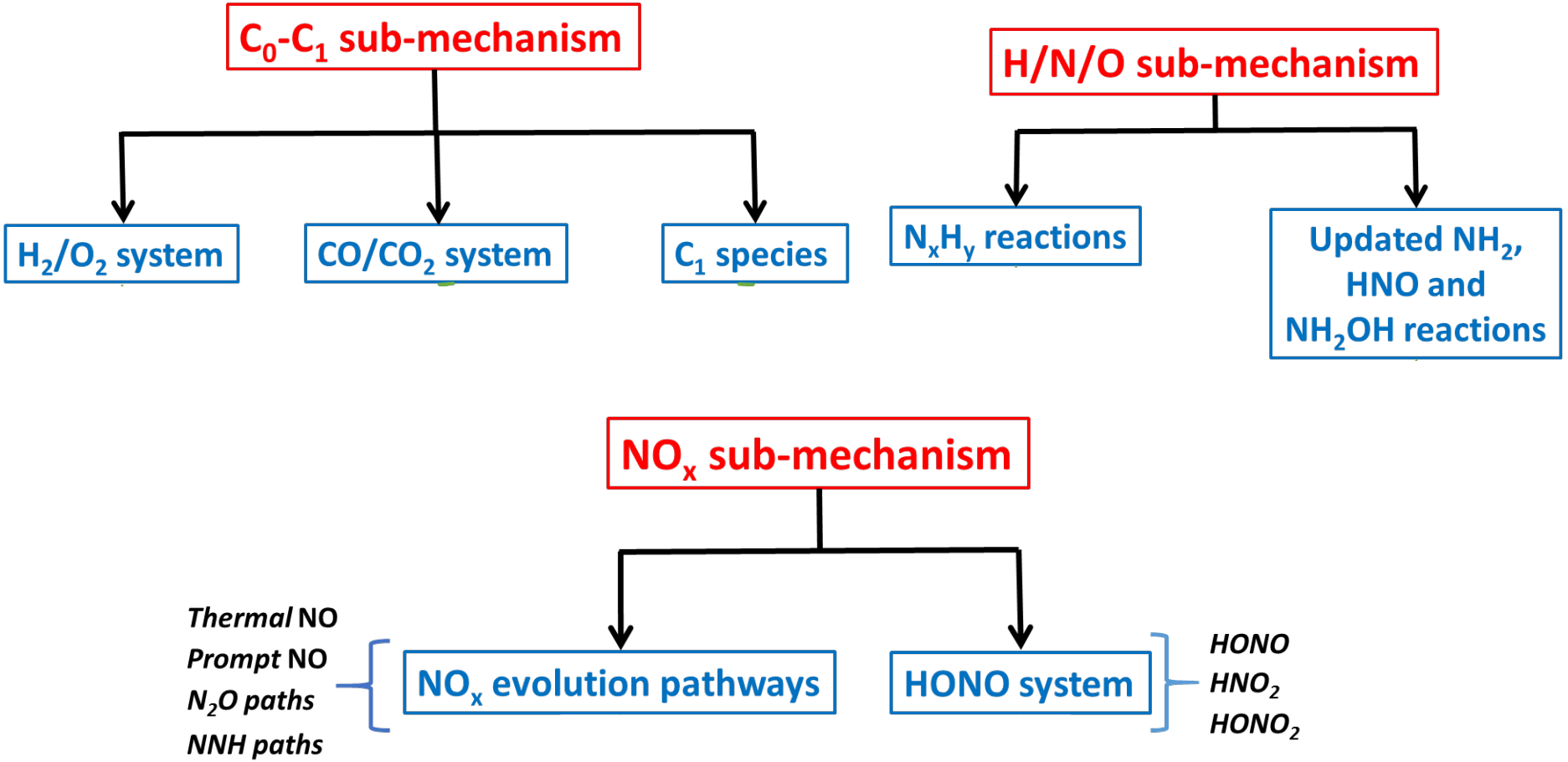
- **$H_2/CO/NO_x$ Model**

77 species, 442 reactions

- **H_2/C_1-C_4/NO_x Model**

302 species, 1952 reactions

Model Elements



[1]*Burke et al., Int. J. Chem. Kinet. 44 (2012)*
[2]*Metcalfe et al., Int. J. Chem. Kinet. 45 (2013)*
[3]*Skreiberg et al., Combust. Flame 136 (2004)*
[4]*Klippenstein et al., Combust. Flame 158 (2011)*

Prompt-NO Route Updates

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

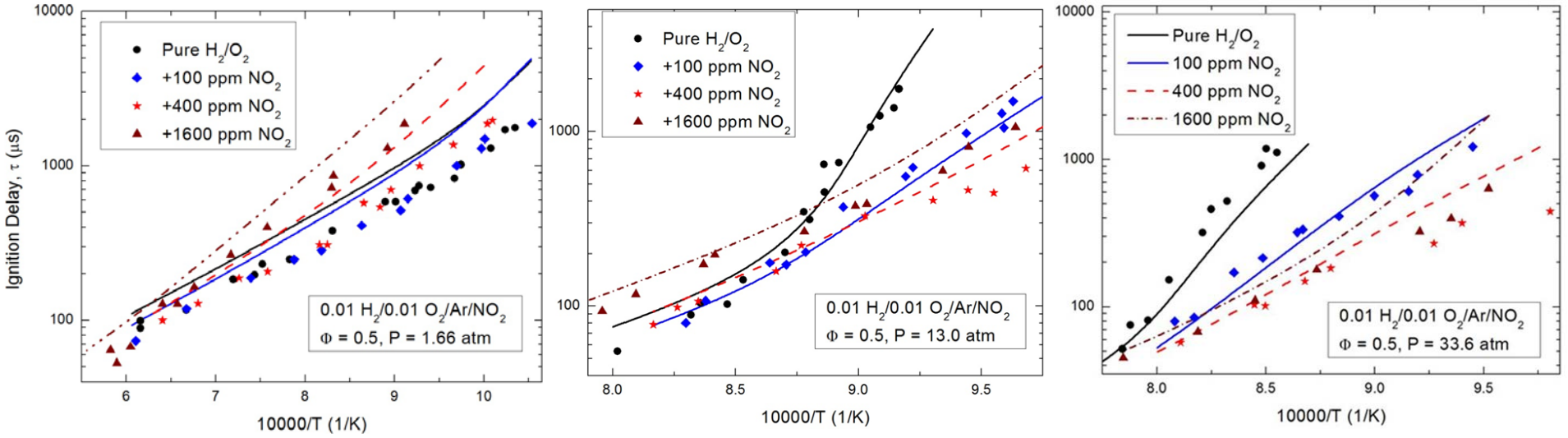
	Reactions	A	b	E (cal/mole)
1.	CN + HNO = HCN + NO	1.80E+13	0.0	0
2.	CN + CH_2O = HCN + HCO	4.20E+13	0.0	0
3.	HCN + N_2 = H + CN + N_2	3.60E+26	-2.60	124890
4.	HCN + M = HNC + M AR/0.7/ H_2O/7.0/ CO_2/2.0	1.60E+26	-3.23	54600
5.	HCN + OH = HNCO + H	2.80E+13	0	3700
6.	HNCO + O2 = HNO + CO_2	1.0E+12	0.0	35000
7.	NCO + NO = N_2O + 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_2O	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_2O/10.0	6.50E+12	0.0	0
14.	HOCN + O = NCO + OH	1.70E+08	1.50	4133
15.	HOCN + OH = HCO + H_2O	1.20E+06	2.0	-248
16.	H_2CN + OH = HCN + H_2O	1.50E+19	-2.18	2166
17.	HCNO + H = HCH + OH	7.20E+10	0.841	8612.0
18.	CN + H_2O = 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

Model Performance: Ignition Delay

Dependence of τ_{ig} on initial NO_2 doping for H_2/O_2 system



Pressure →

100 ppm → insignificant
400 ppm or higher → reactivity decreases

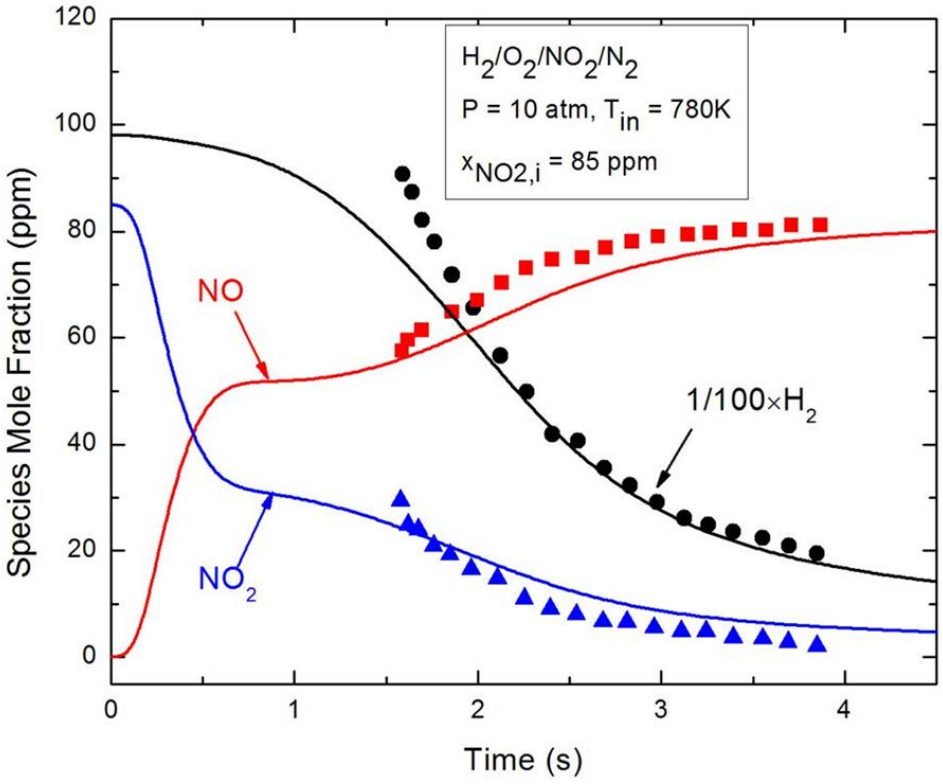
100 - 400 ppm → reactivity increases
1600 ppm → reactivity decreases

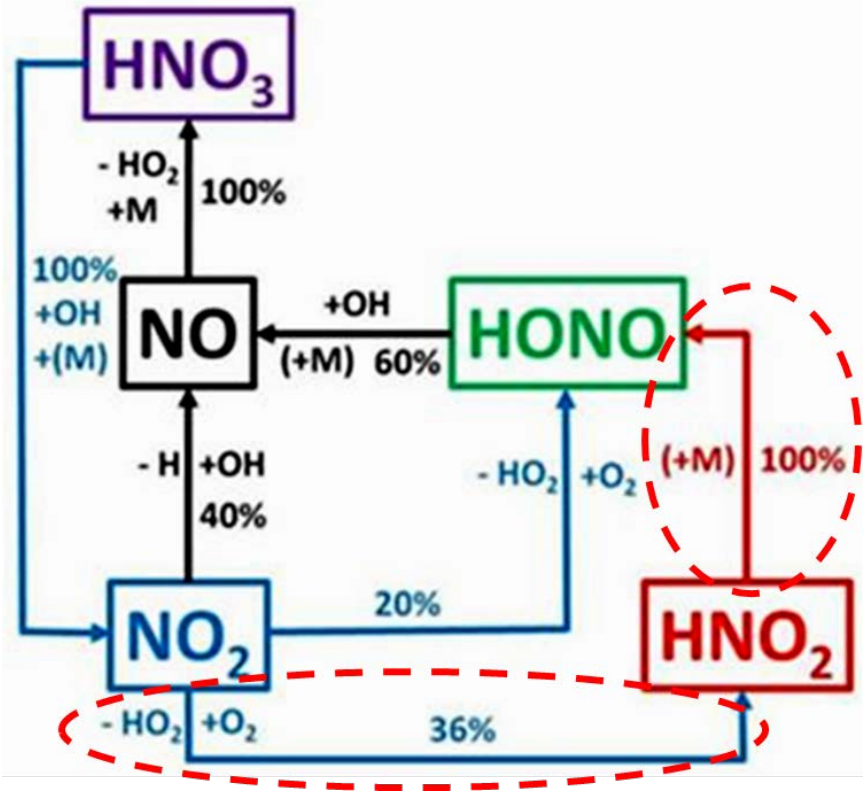
100 - 400 ppm → reactivity increases
1600 ppm → reactivity decreases

High pressure non-monotonic behavior captured by the model

Mathieu et al., Proc. Combust. Inst. 34 (2013)

Model Performance: PFR Speciation for $H_2/O_2/NO_2/N_2$ System





Reasonable model prediction of fuel consumption and NO-NO_2 conversion

NO → NO_2 conversion: through intermediate HNO_3

NO_2 → NO conversion: *(i)* direct

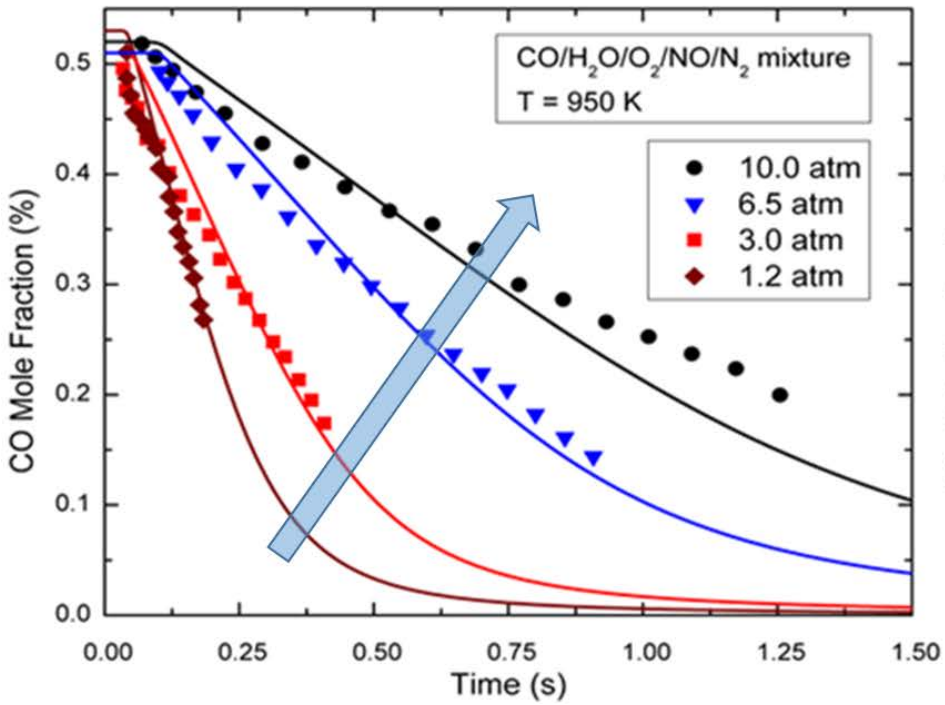
(ii) through intermediate HONO

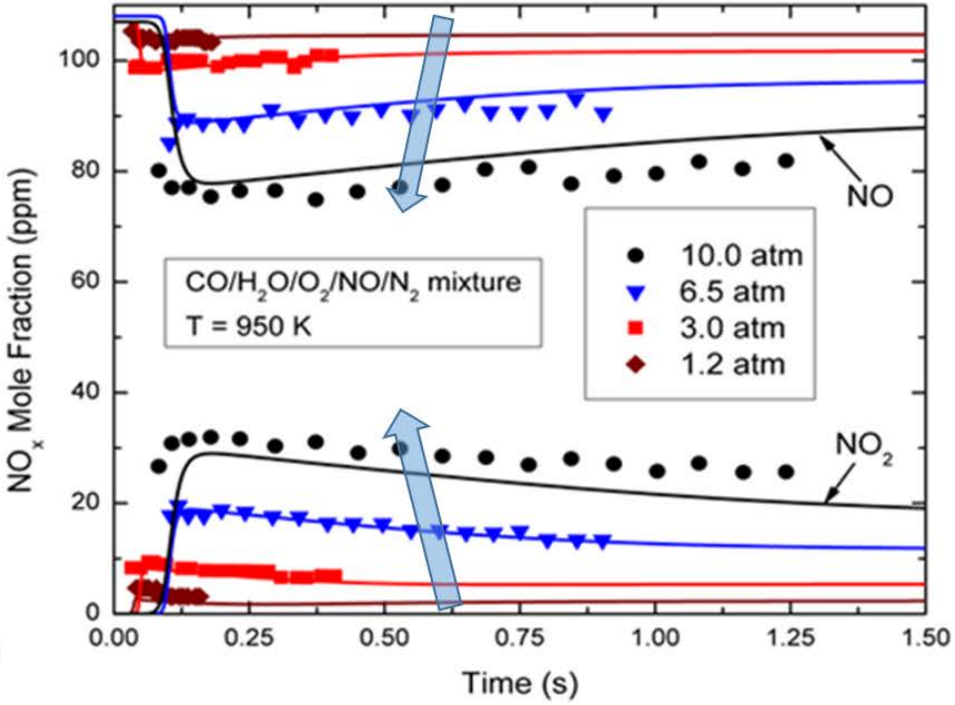
***(iii)* through intermediate HNO_2**

Mueller et al., Int. J. Chem. Kinet. 31 (1999)

Model Performance: Variable Initial Conditions for $CO/H_2O/O_2/NO$ System

Variable Initial Pressure

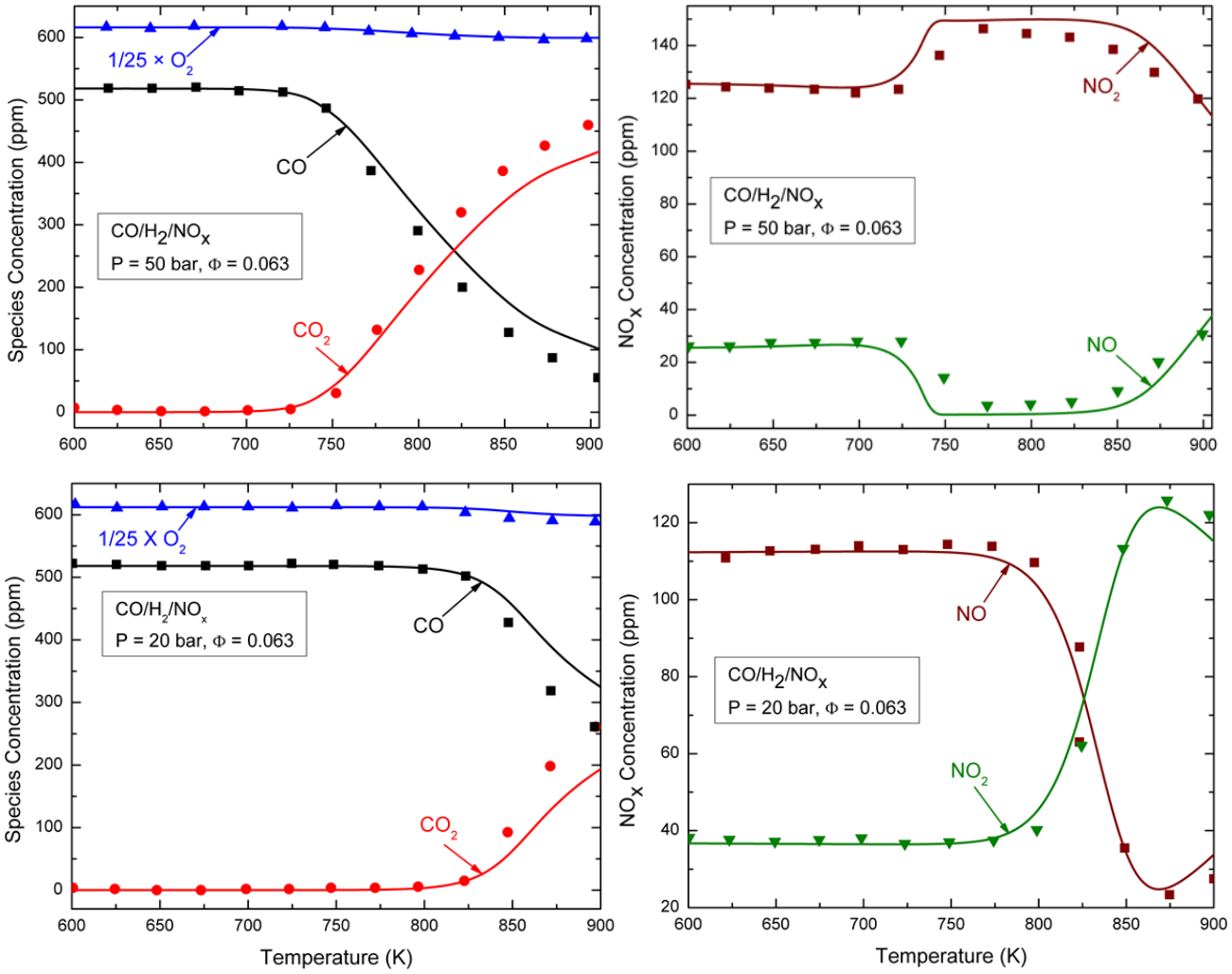




- ✓ Model reasonably predicts the experimental trends with variable initial pressure
- ✓ Complete NO-NO_2 interconversion without any formation of molecular nitrogen

Mueller et al., Int. J. Chem. Kinet. 31 (1999)

Model Performance: PFR Species Evolution for $CO/H_2/NO_x$ Oxidation System



- ✓ Flow reactor experiments at constant mass flow rate with temperature dependent residence time[1]

Pressure

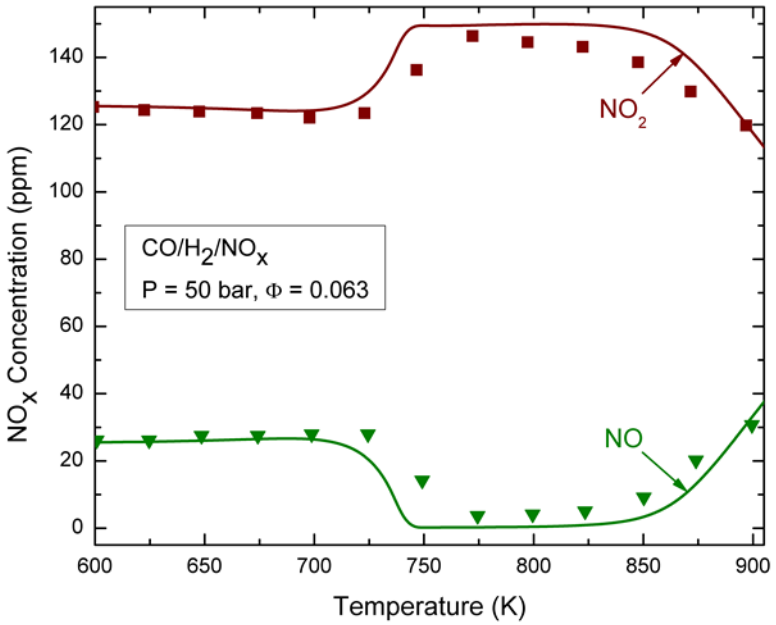
$$\tau_{20\ bar} = 2350/T$$

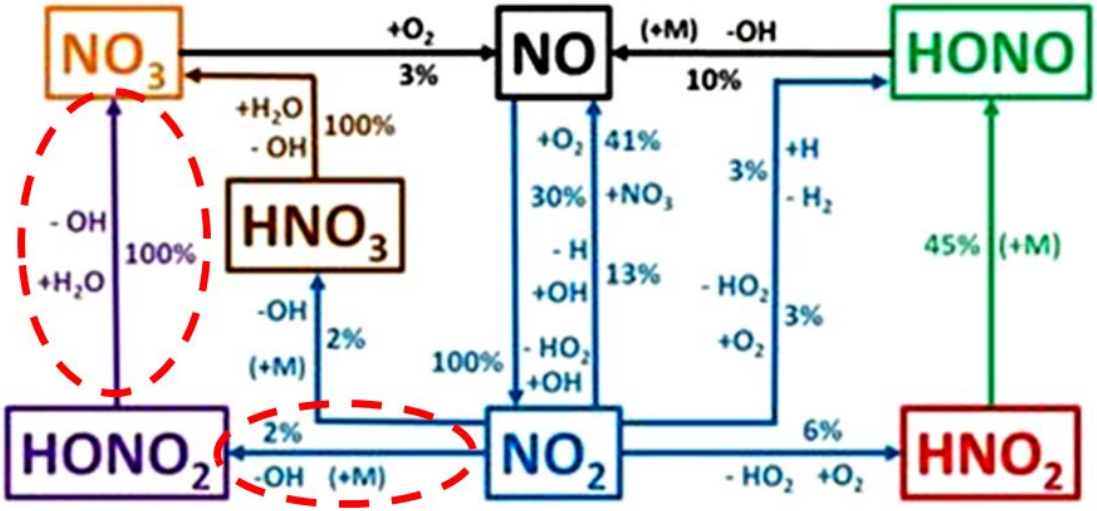
$$\tau_{50\ bar} = 6030/T$$

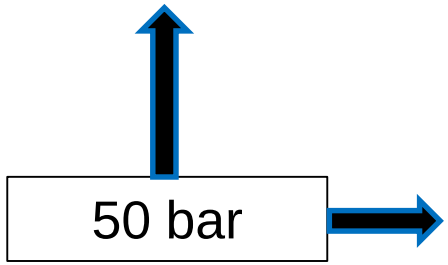
- ✓ Reasonable predictions for CO-CO_2 and NO-NO_2 conversion

Rasmussen et al., Int. J. Chem. Kinet. 40 (2008)

Proposed Model Performance: PFR Species Evolution for $CO/H_2/NO_x$ Oxidation System







Dominance of pressure-dependent reactions: two additional NO ↔ NO_2

Rasmussen et al., Int. J. Chem. Kinet. 40 (2008)

Summary

- $C_0 – C_4/NO_x$ model has been developed
- $H_2/CO/NO_x$ model has been validated
- Influence of trace impurities on combustion characteristics
- Trace NO_x – emittents can alter the combustion behavior, global/optimized models can not capture intricate features

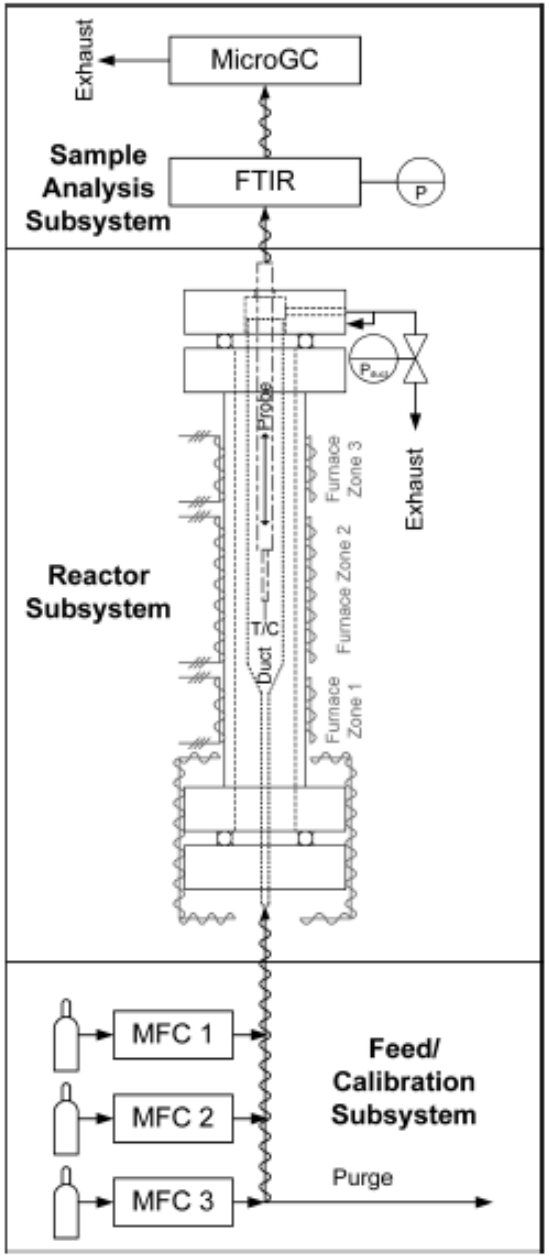
Measurements of NO_x perturbed oxidation experiments

Influence of Trace Nitrogen Oxides on Natural Gas Oxidation

Nominal Feed Condition

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

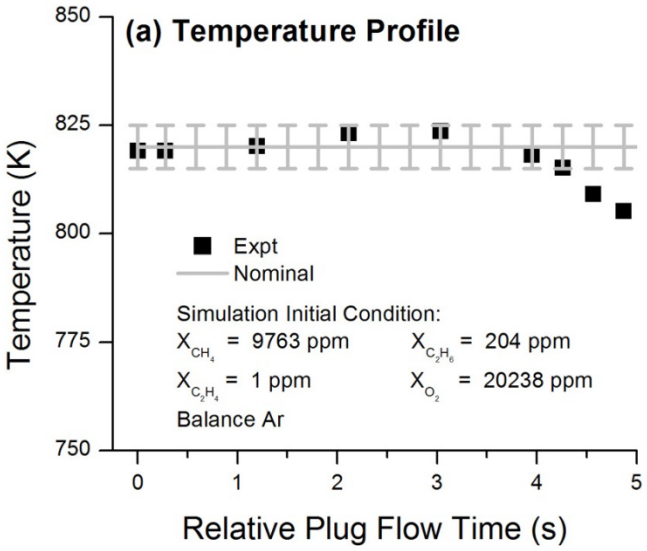
P = 10 atm
T = 820 K

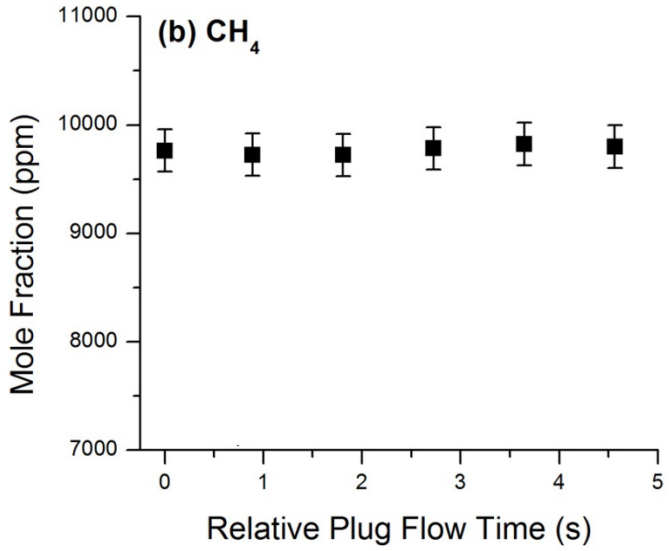


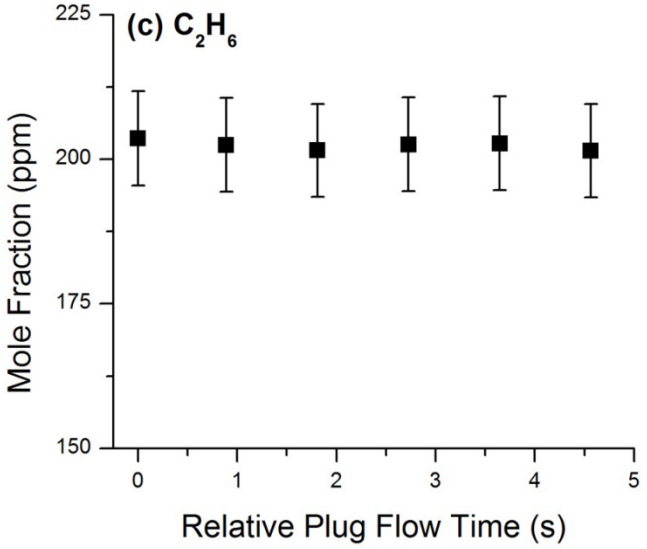
(Haas & Dryer, JPC-A 2014)

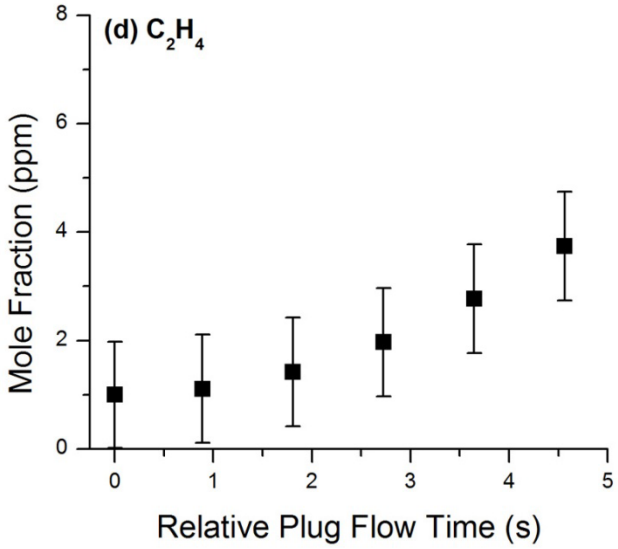
Non-NO_x Perturbed case (φ = 1.0)

- No evidence of reaction for measured profiles of CH_4, and C_2H_6.
- Few **ppm** of C_2H_4 quantified @ distinct 950 cm^{-1} FTIR wave number.
- Conditions of incipient of reactions. C_2H_6 oxidation via flux through $C_2H_5 \Leftrightarrow C_2H_4$.



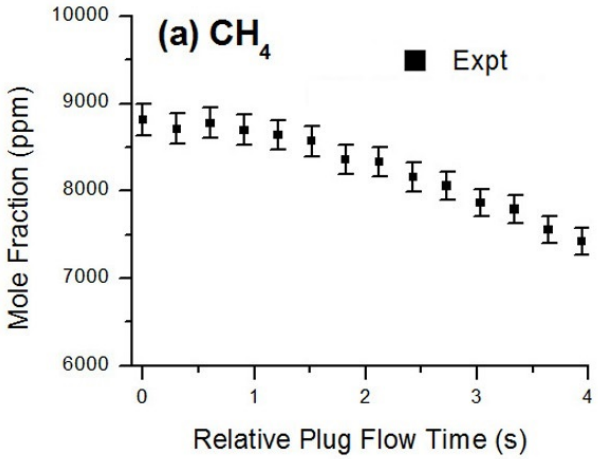


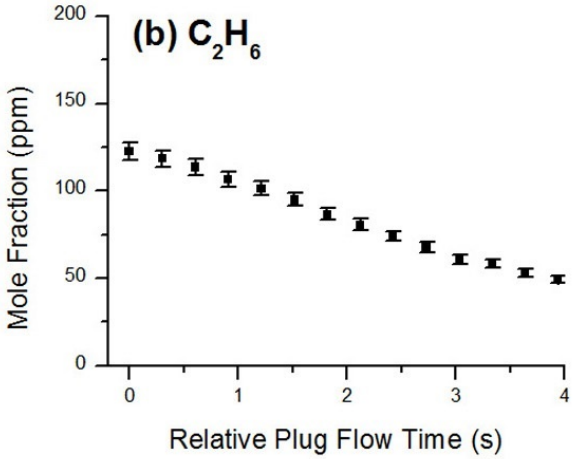


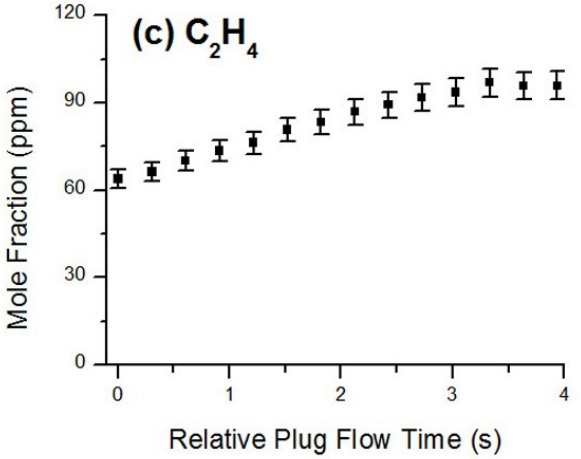


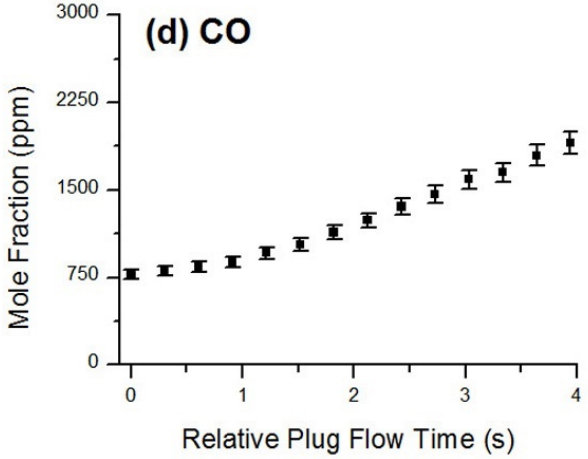
Trace NO_x Perturbed Case (φ = 1.0)

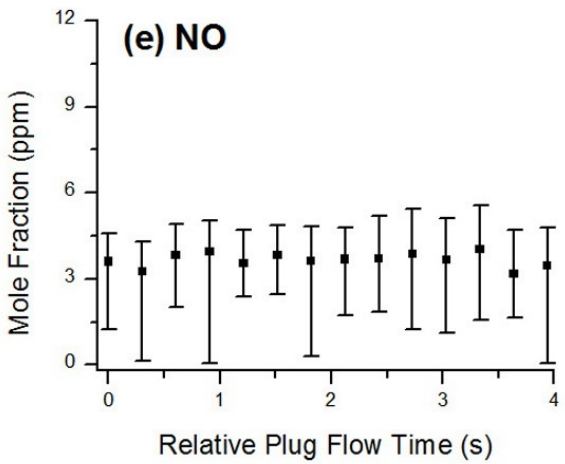
Reactivity induced due to trace NO_x (~ 25 ppm)

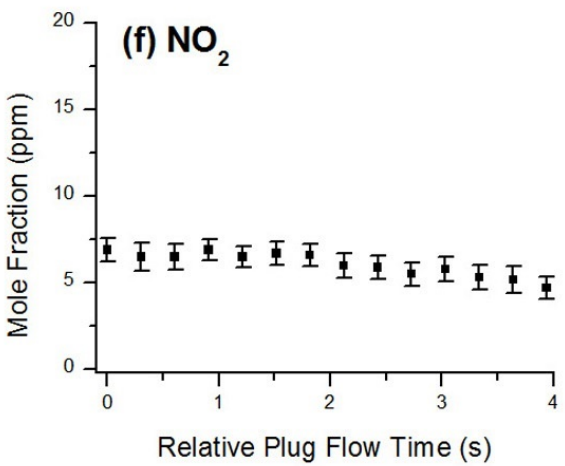






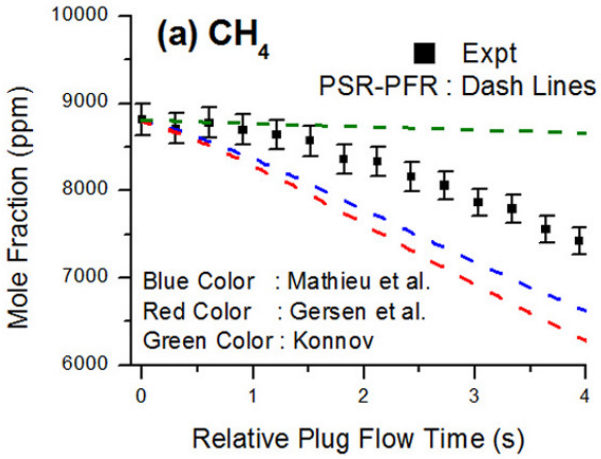


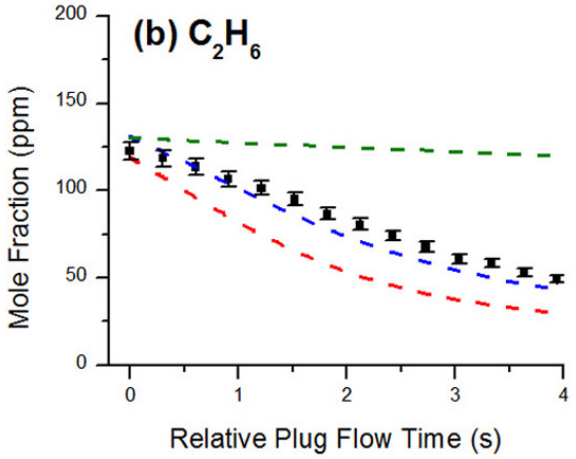


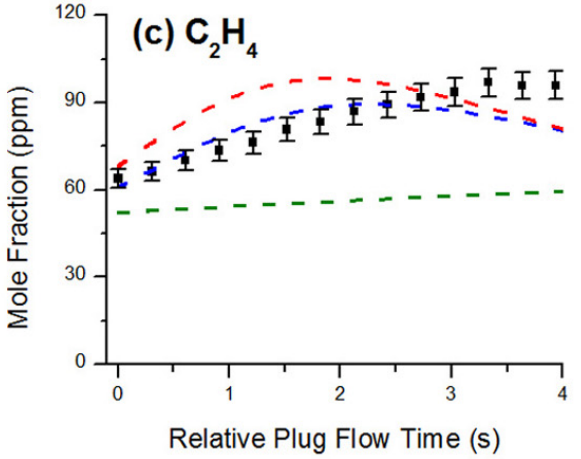


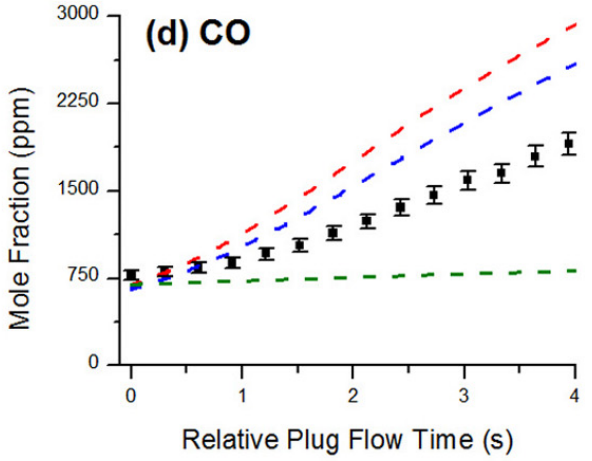
Trace NO_x Perturbed Case (φ = 1.0)

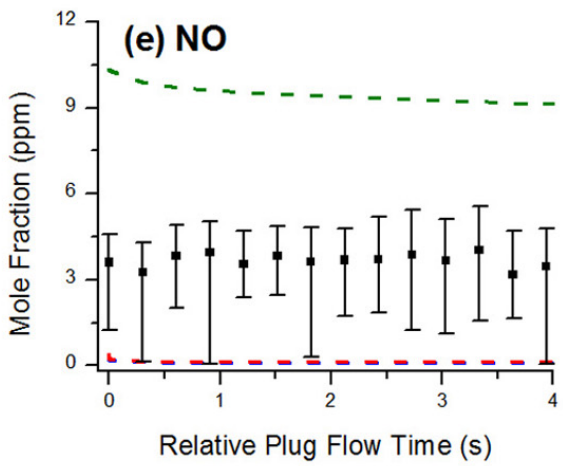
- NO_x mole fraction predictions indicated near-complete destruction of NO_x ($NO+NO_2$) ➔ CH_3NO_2

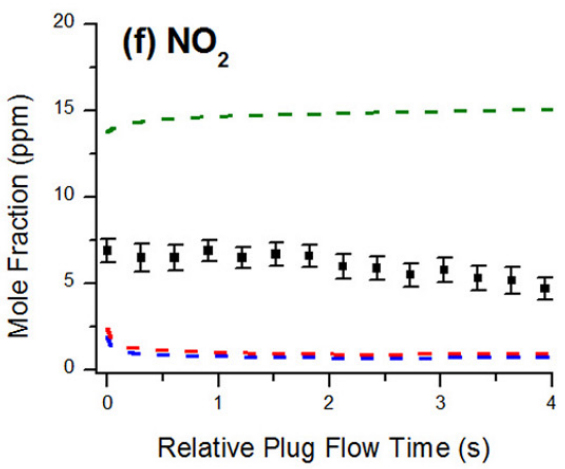




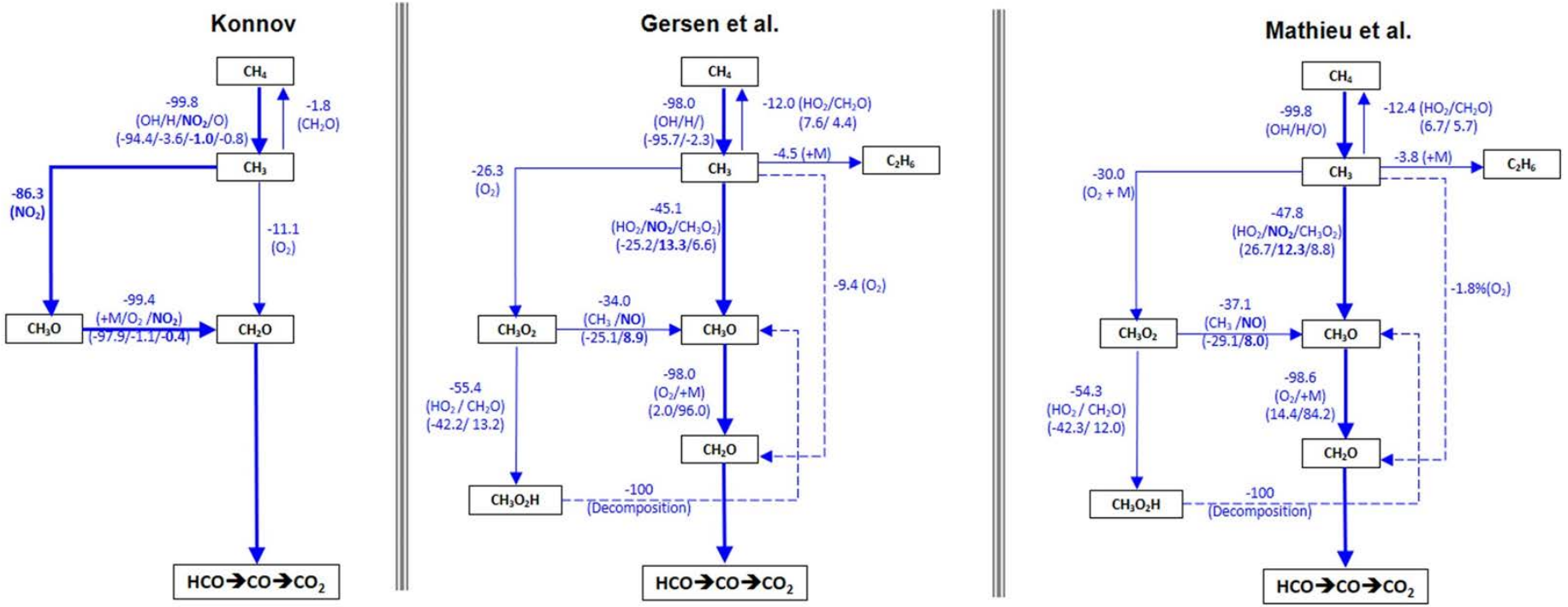








Kinetic Analysis – Path Flux (φ = 1.0)



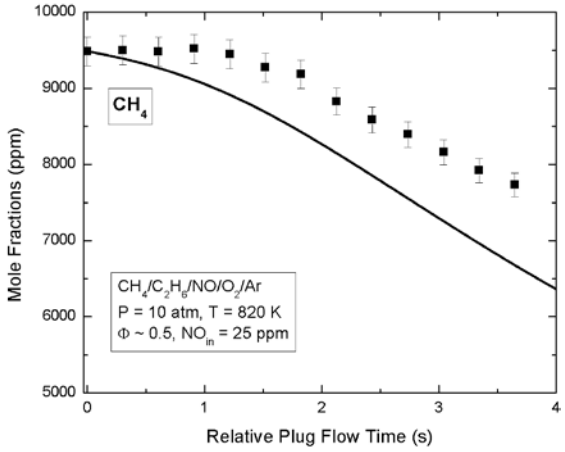
Dominant NO Consumption Pathways

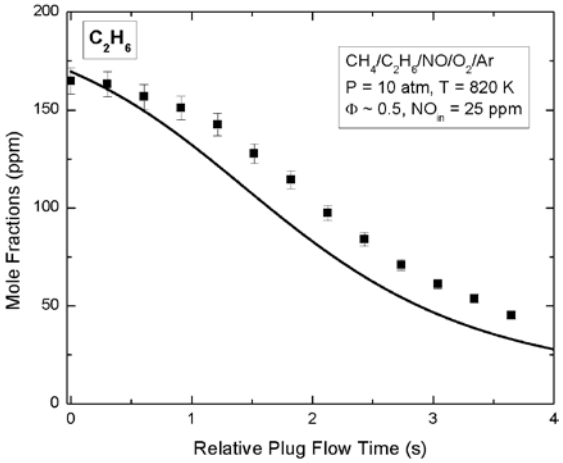
$NO+HO_2 \Leftrightarrow NO_2+OH$	(-99.8)	$NO+HO_2 \Leftrightarrow NO_2+OH$	(-85.3)	$NO+HO_2 \Leftrightarrow NO_2+OH$	(-77.8)
		$CH_3O_2+NO \Leftrightarrow CH_3O+NO_2$	(-14.6)	$CH_3O_2+NO \Leftrightarrow CH_3O+NO_2$	(-16.7)
				$O_2CHO+NO \Leftrightarrow OCHO+NO_2$	(-5.1)

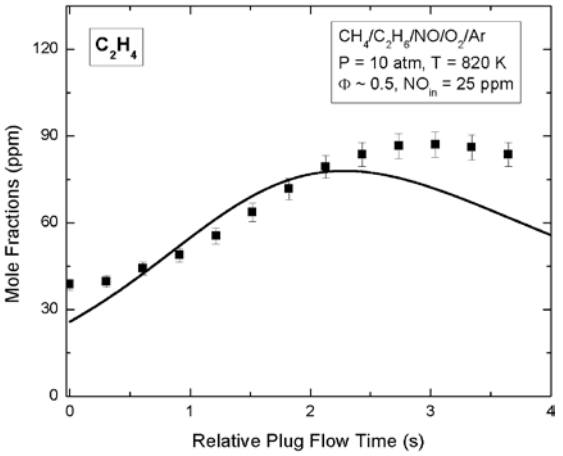
Dominant NO_2 Consumption Pathways

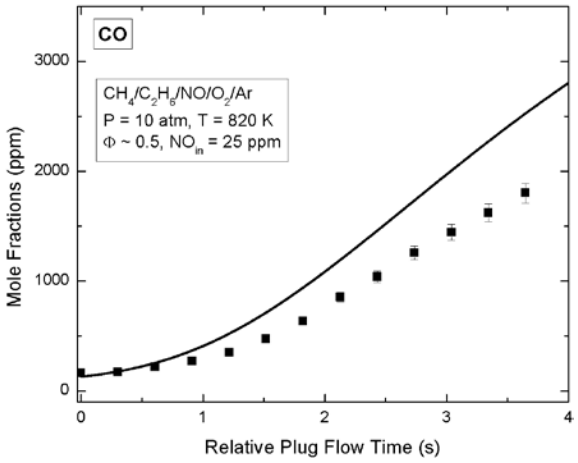
$CH_3+NO_2 \Leftrightarrow CH_3O+NO$	(-65.6)	$CH_3+NO_2 \Leftrightarrow CH_3O+NO$	(-82.4)	$CH_3+NO_2 \Leftrightarrow CH_3O+NO$	(-84.5)
$NO_2+HO_2 \Leftrightarrow HONO+O_2$	(-21.5)	$NO_2+H \Leftrightarrow NO+OH$	(-7.5)	$CH_3 + NO_2 \Leftrightarrow CH_3NO_2$	(-6.8)
$NO_2+H \Leftrightarrow NO+OH$	(-9.9)	CH_3NO_2 (+M) $\Leftrightarrow CH_3 + NO_2$ (+M)	(-6.2)	$NO_2+H \Leftrightarrow NO+OH$	(-6.5)

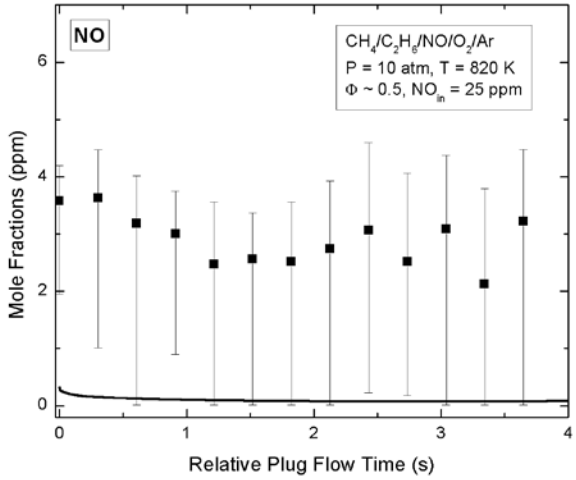
Current Model Predictions
Trace NO_x Perturbed Case (φ = 0.5)

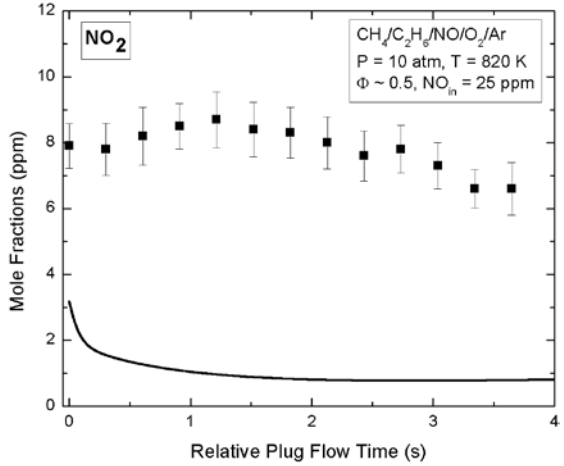




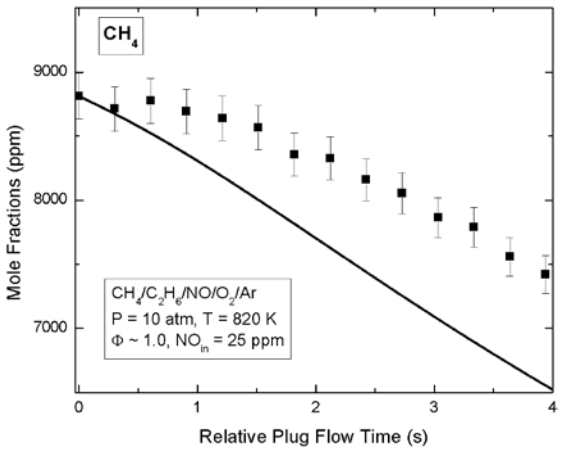


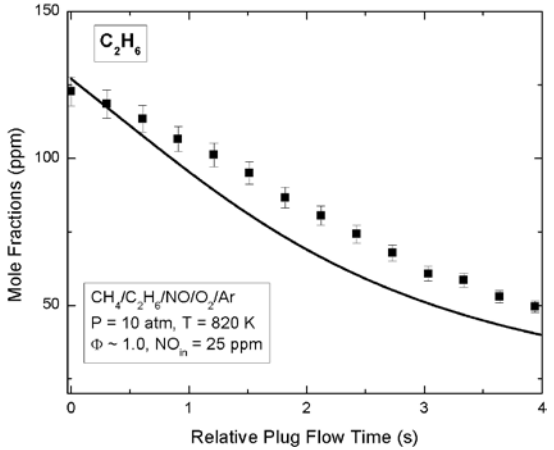


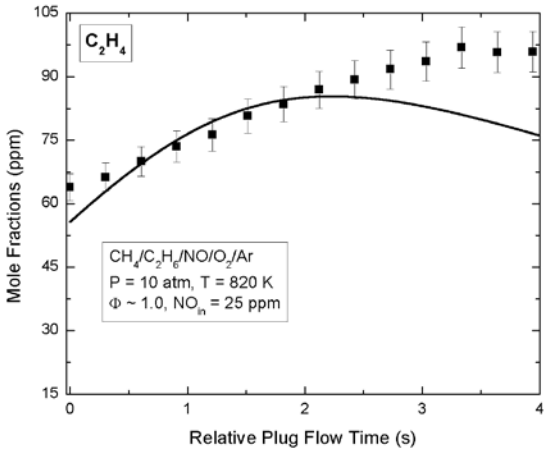


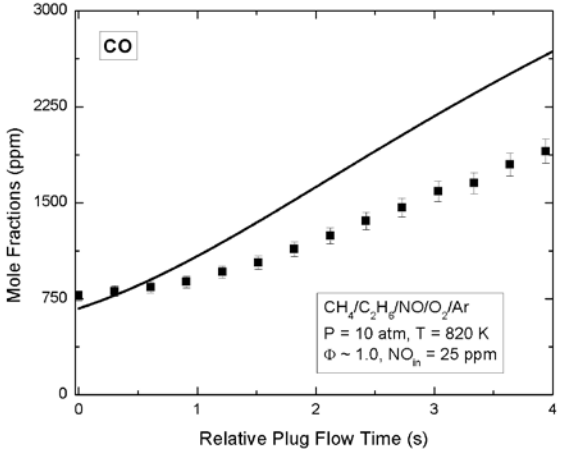


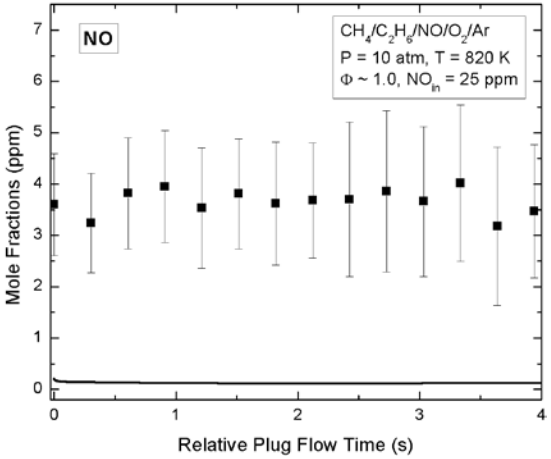
Current Model Predictions
Trace NO_x Perturbed Case (φ = 1.0)

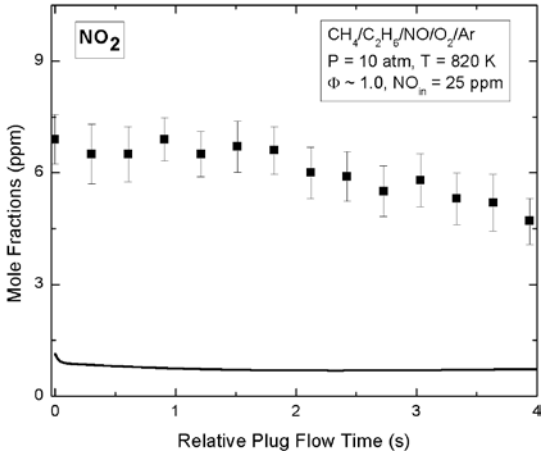












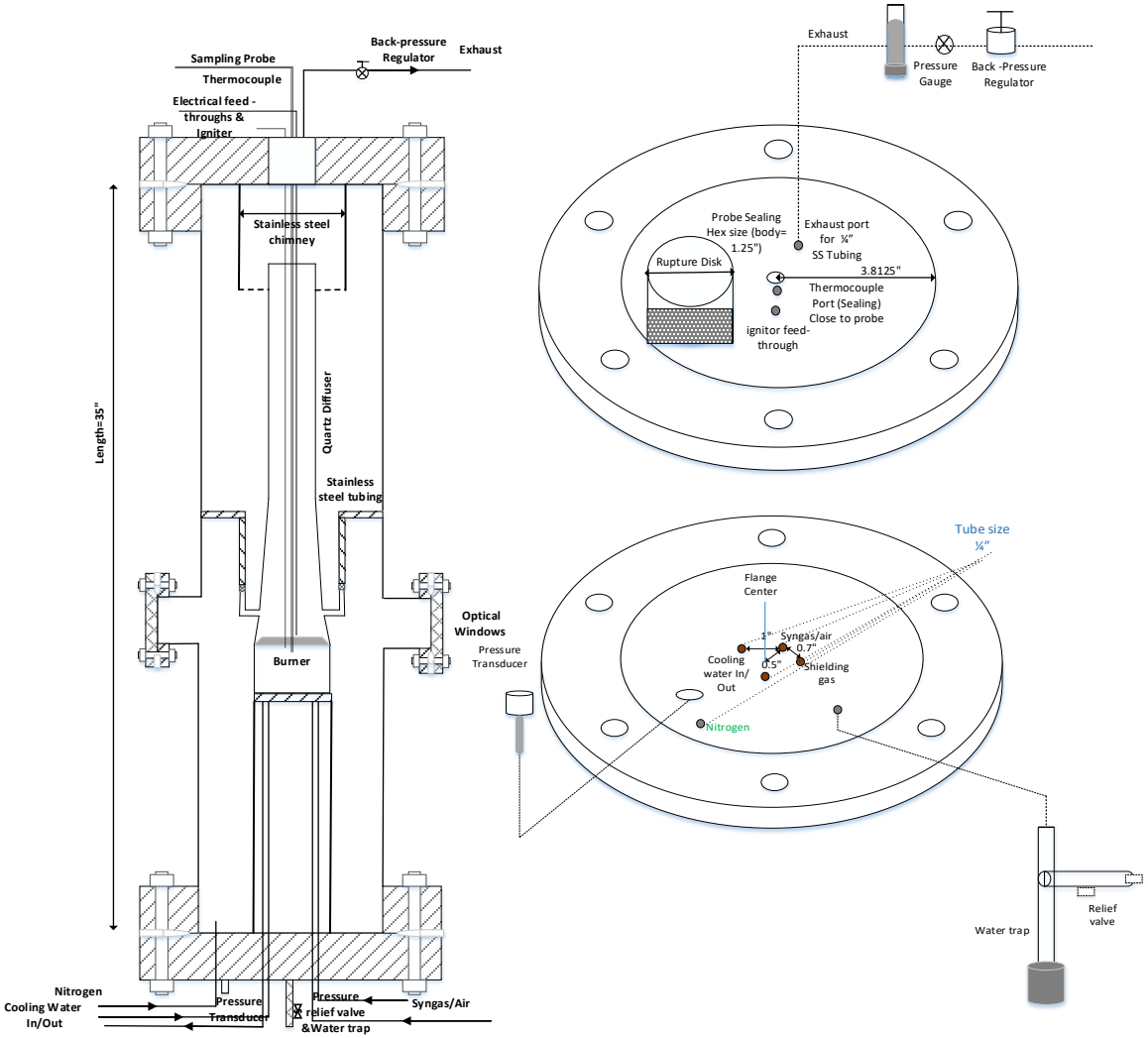
Summary

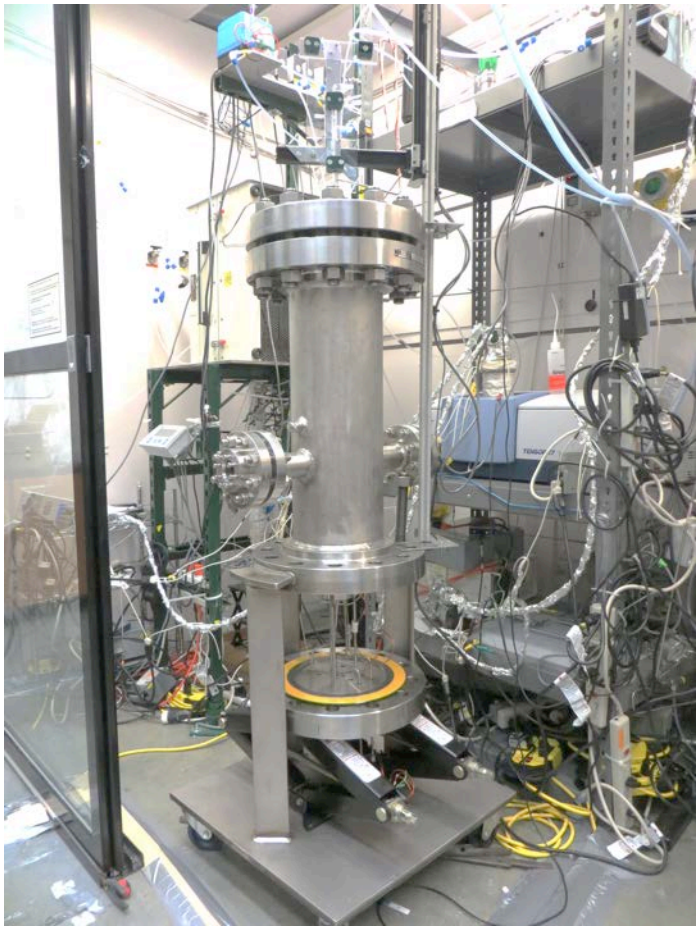
- Influence of trace impurities on combustion characteristics.

- Performance of existing model has been analyzed and inclusions were proposed and incorporated in the present model to include/predict the influence of trace emittents .

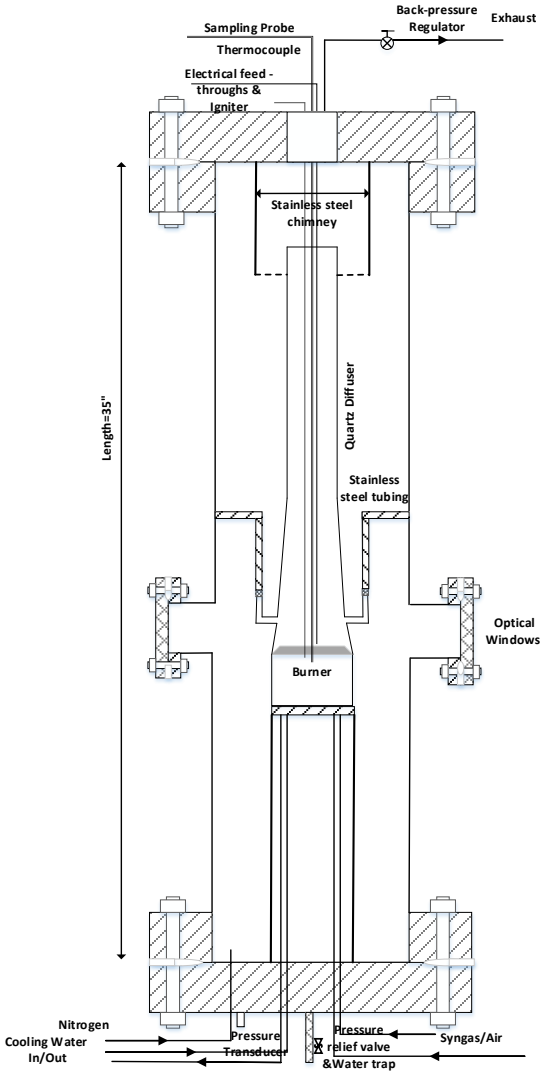
Experiments for Speciation Measurements and Multidimensional CFD Modeling

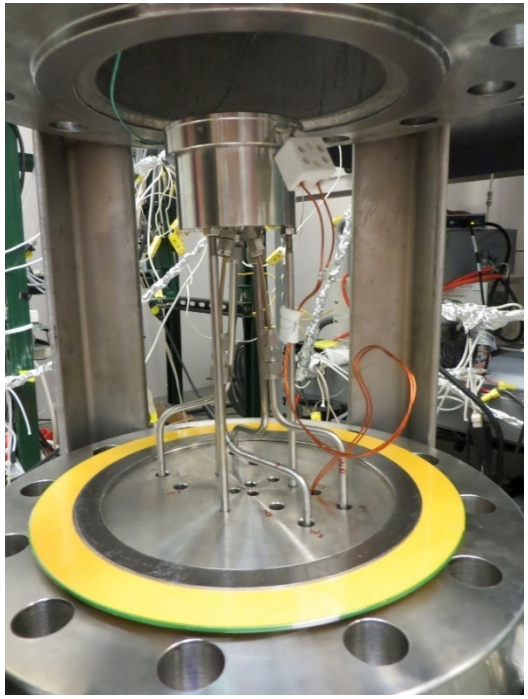
High Pressure Reactor System

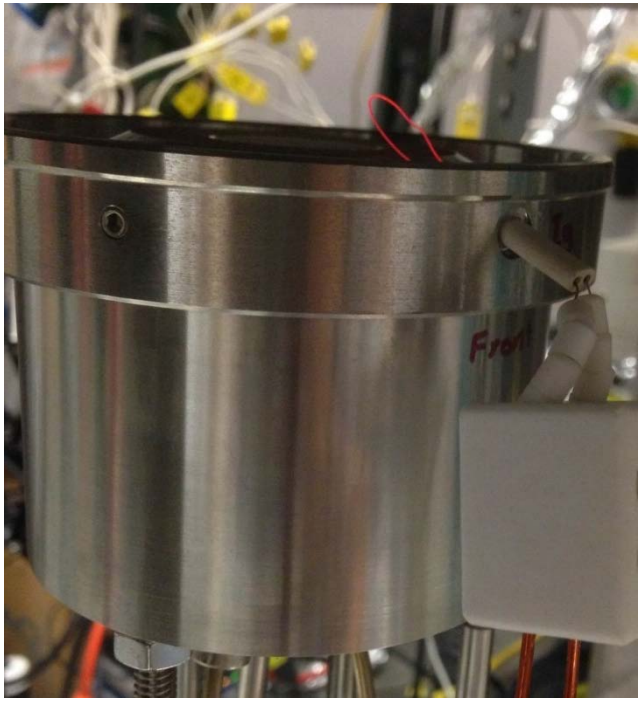




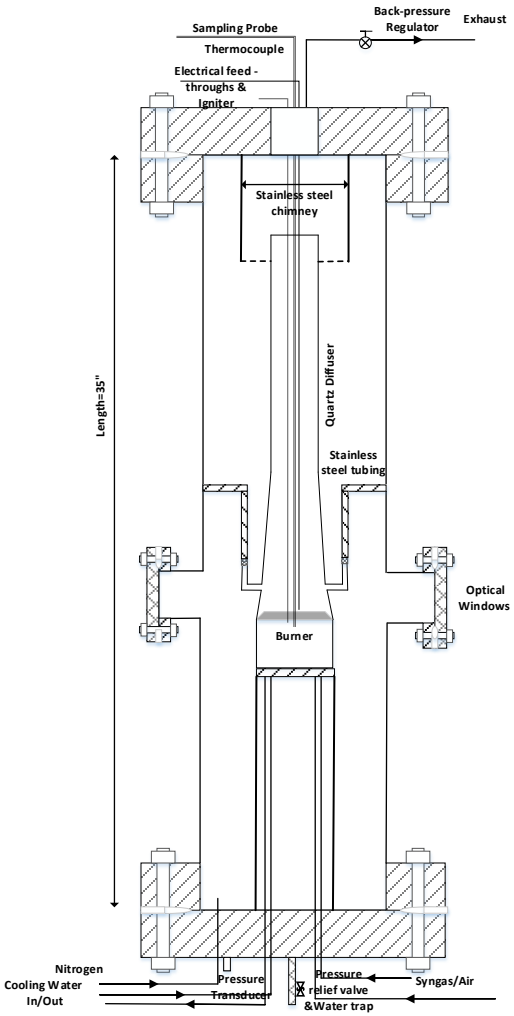
High Pressure Reactor System

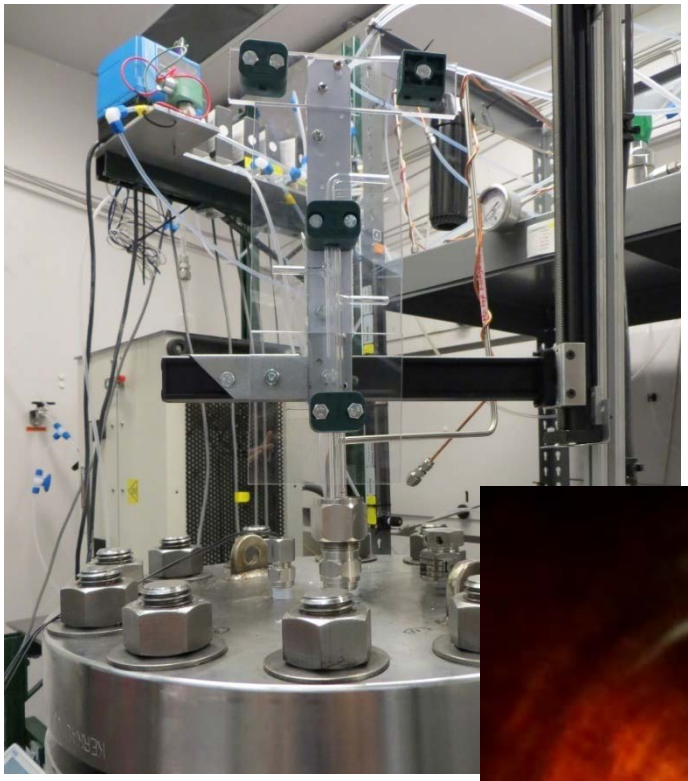


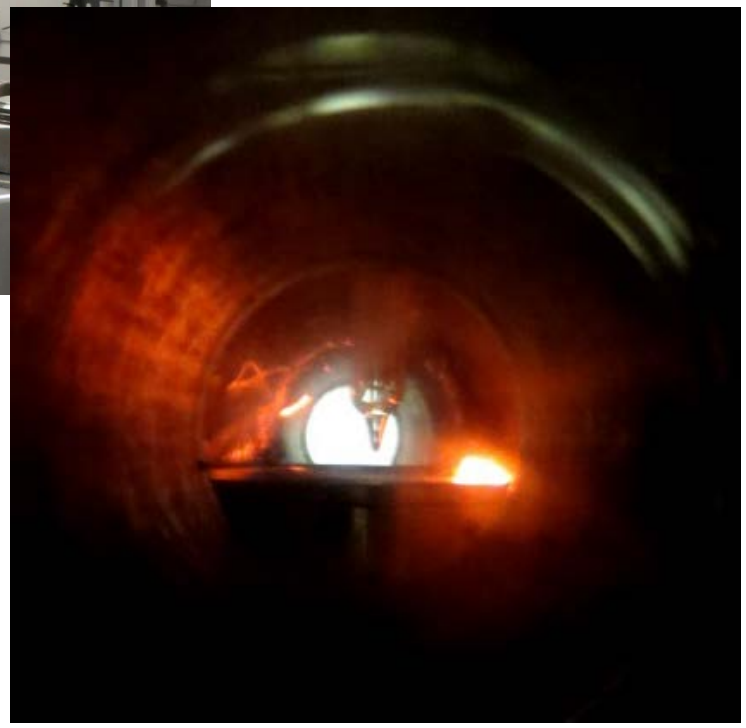




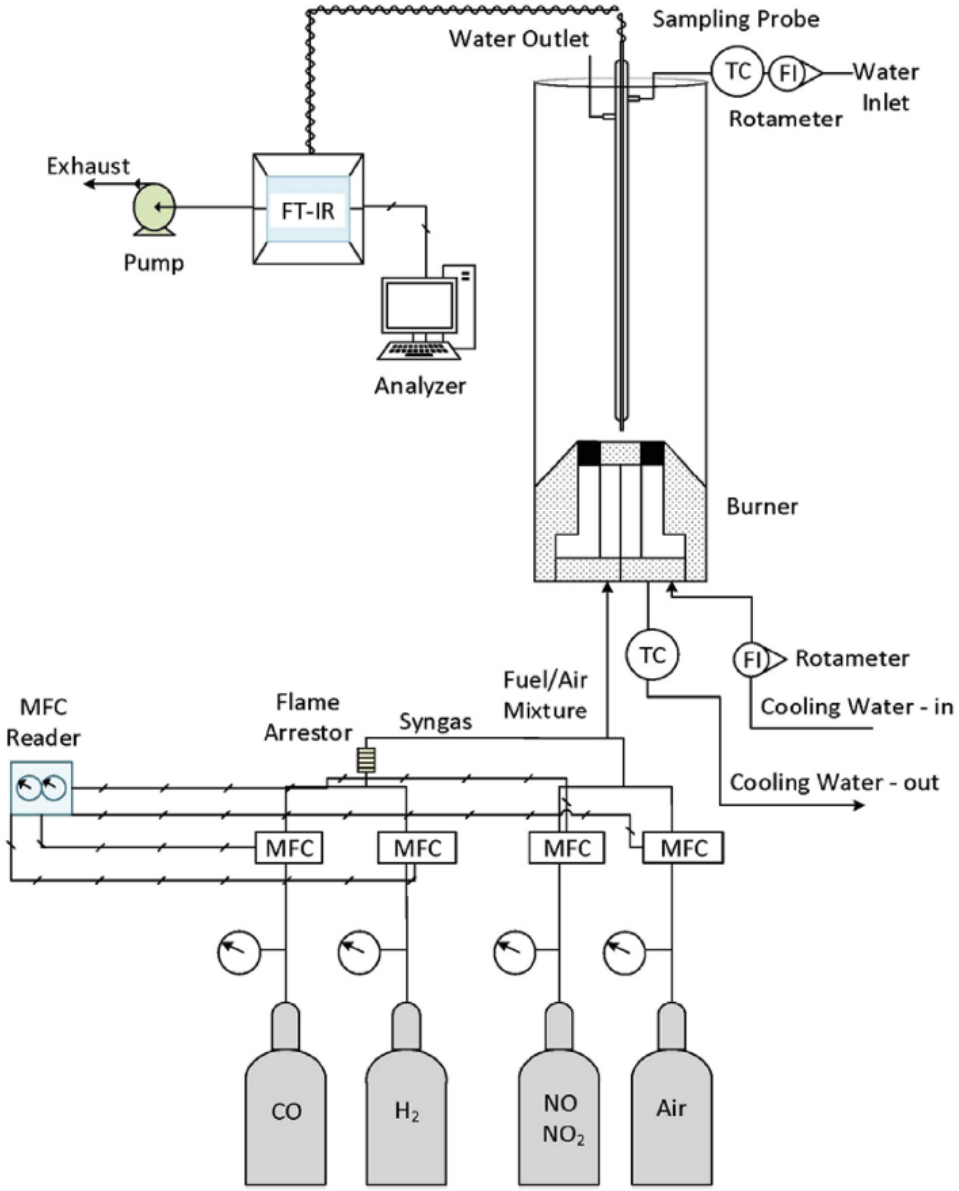
High Pressure Reactor System







Schematic of the Experimental Setup



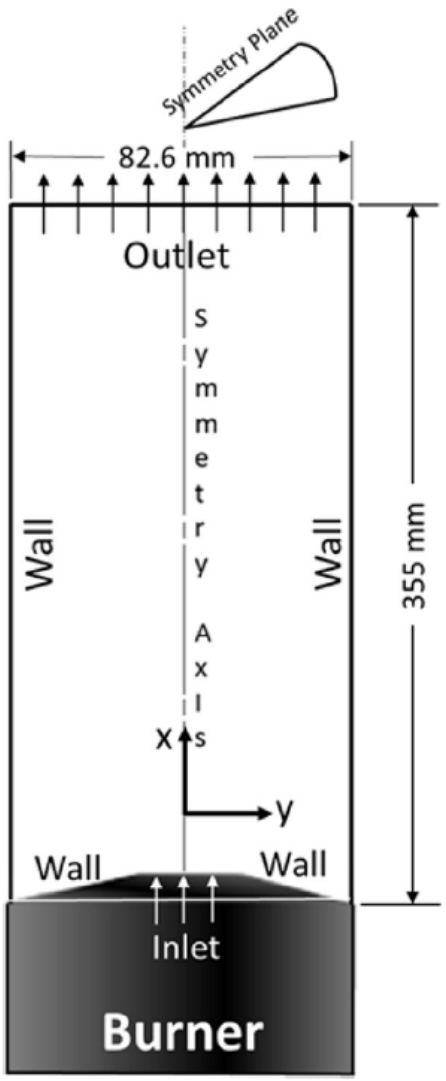
- Quartz glass probe for measuring species distribution in the reactor (axial and radial profiles)
- Thermocouple probe for measuring the temperature distribution

Multi-dimensional Laminar Reacting Flow Modeling

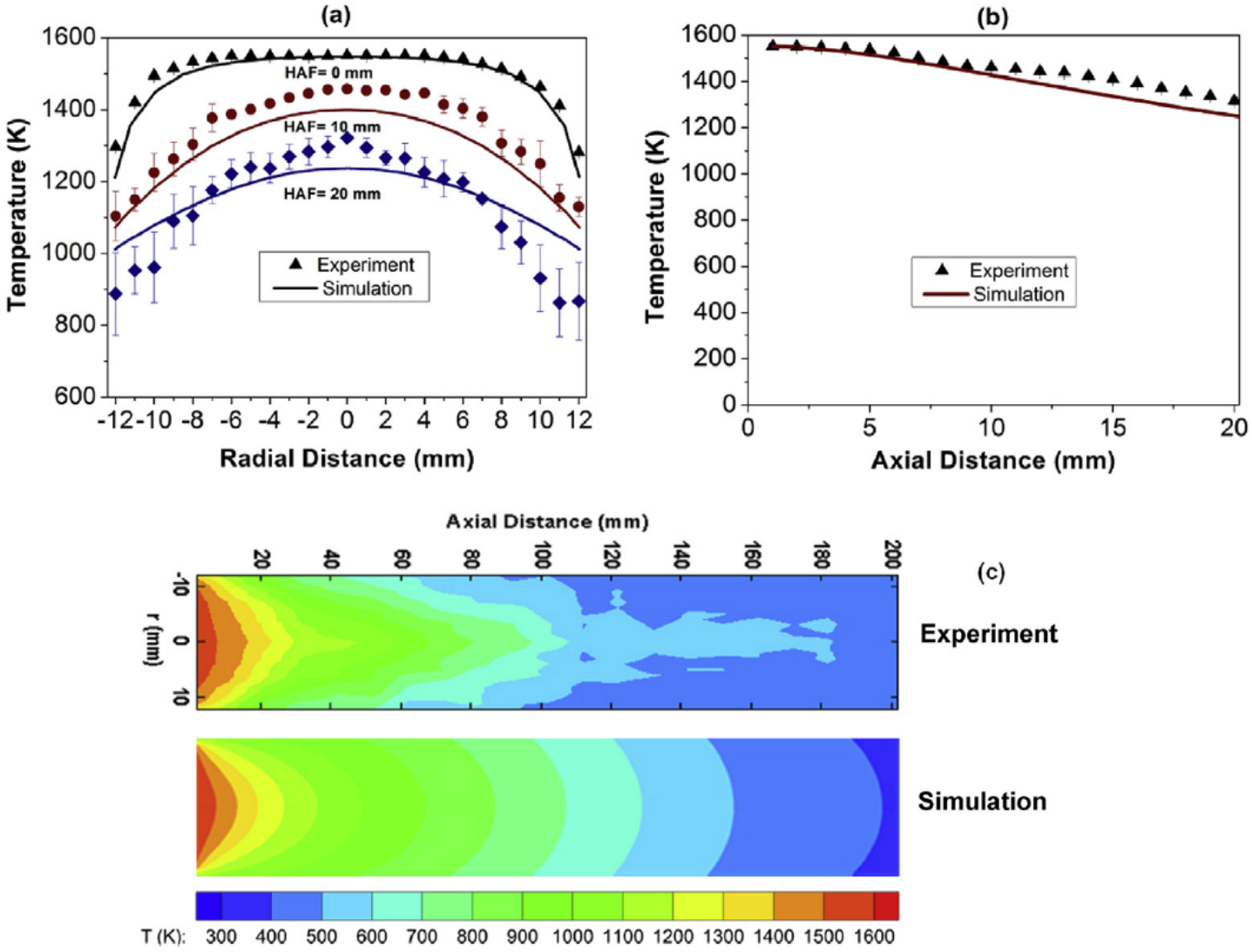
- Experiments were simulated using an in-house multi-dimensional laminar reacting flow model which solves the conservation equations.
- Two-dimensional axi-symmetric analysis of syngas/NO_x oxidation in the McKenna burner and its associated tube arrangement was performed adopting the open-source OpenFOAM® framework.
- Detailed syngas/NO_x oxidation chemistry 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.



Measurements and Predictions

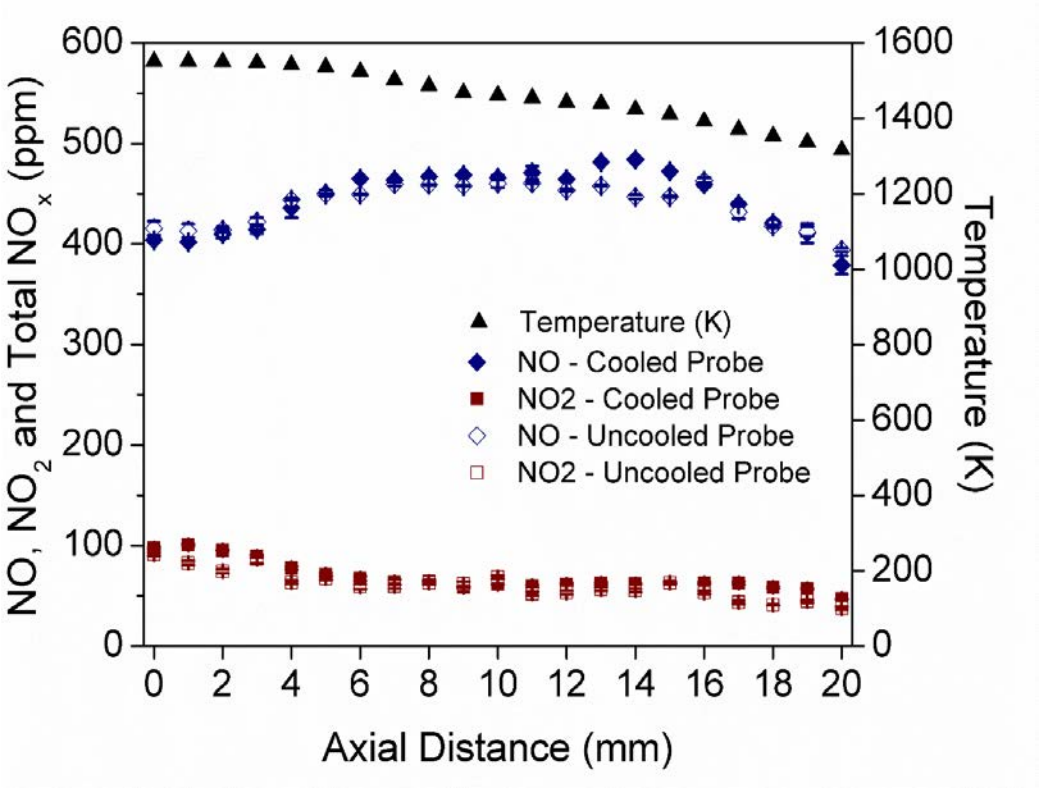


Measured and predicted a) radial temperature profiles at different height above the flame (HAF), b) centerline temperature profile and c) 2-D temperature contours for $H_2/CO = 1$ and $\varphi = 0.5$. The contour levels for the experiments and simulations are identical

Experimental NO_x Speciation Profile – Probe Effects

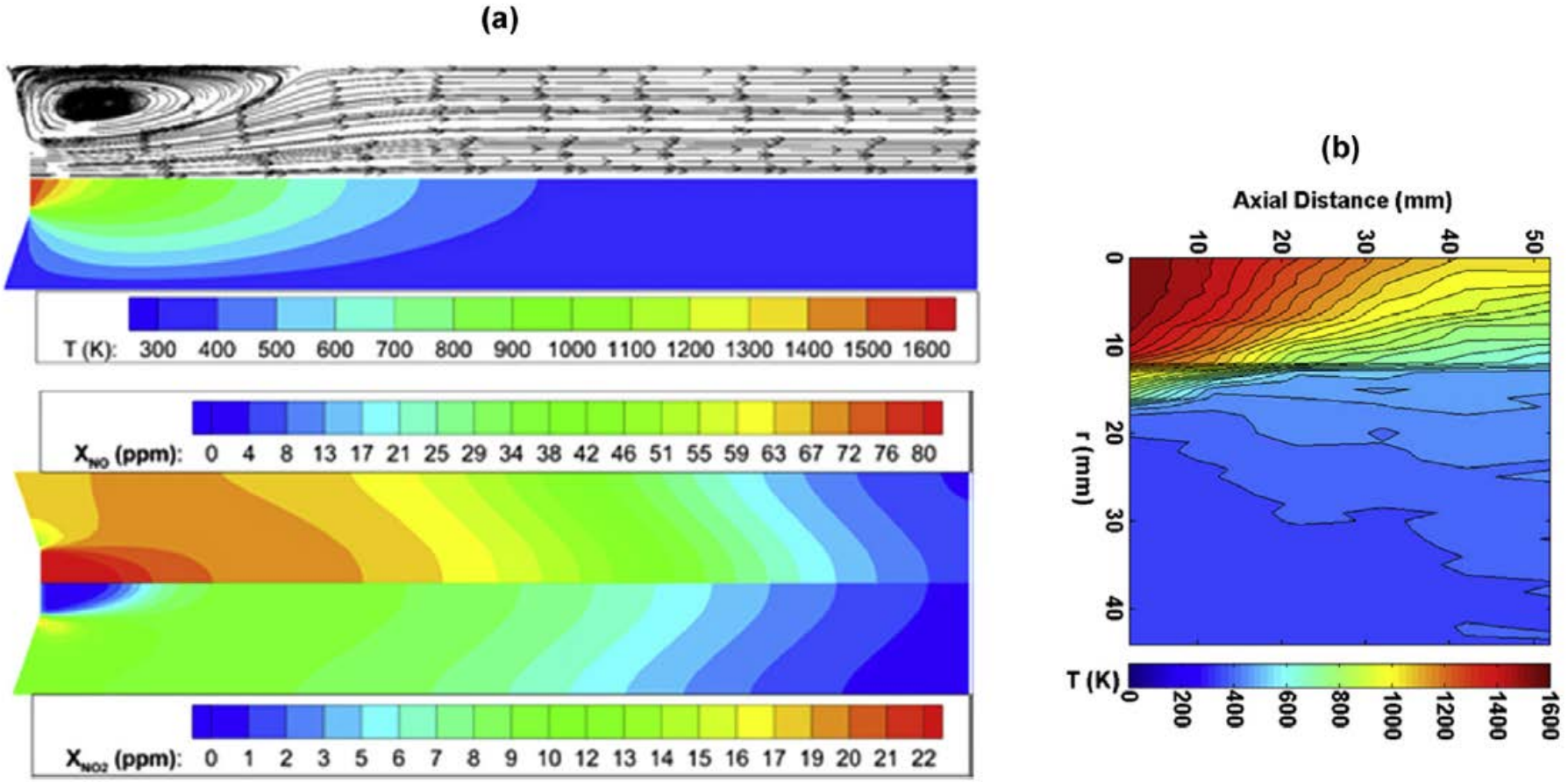
Sampling with cooled probe vs. uncooled probe

H_2/CO=1, Φ=0.5, 500 ppm initial NO doping



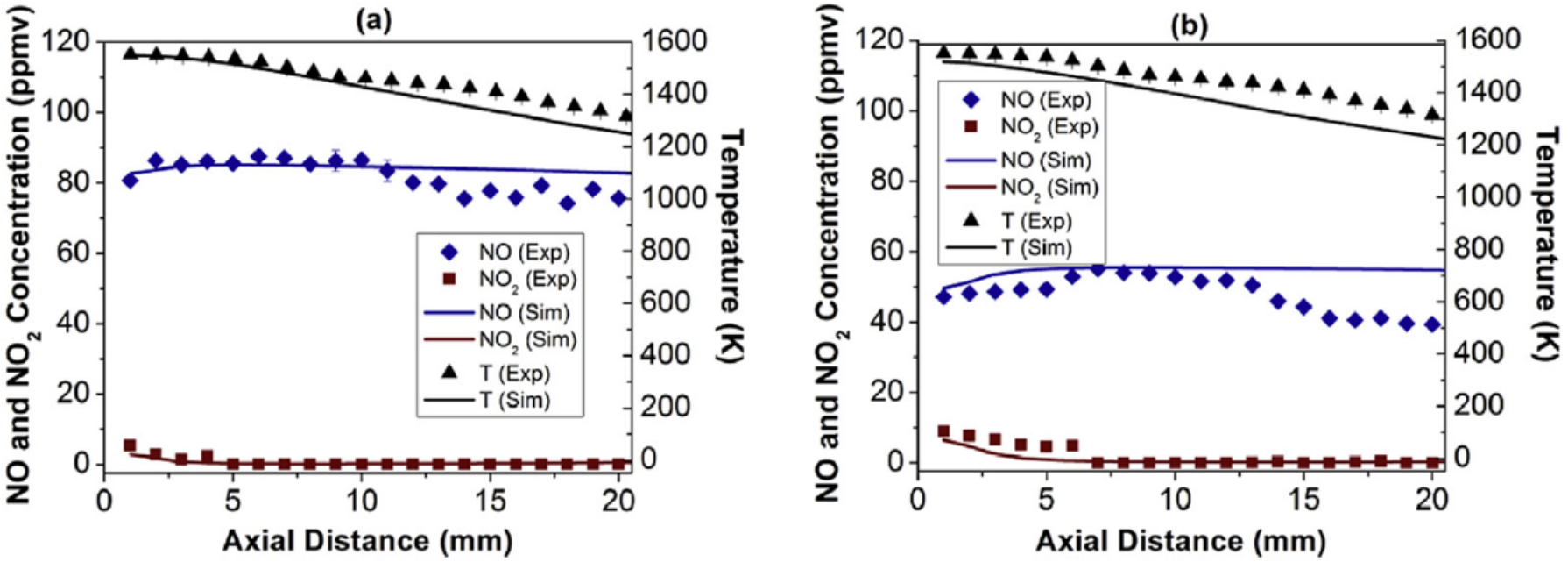
- Experiments were repeated with uncooled probe to see if there is any NO_2 formation in the sampling probe.
- Consistent results were obtained for both cooled and uncooled probes

Measurements and Predictions



a) Temperature and NO/NO_2 concentration contours obtained from multi-dimensional simulations, and b) measured temperature contour for H_2/CO = 1 and φ = 0.5.

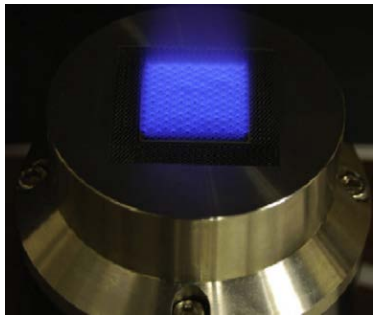
Measurements and Predictions



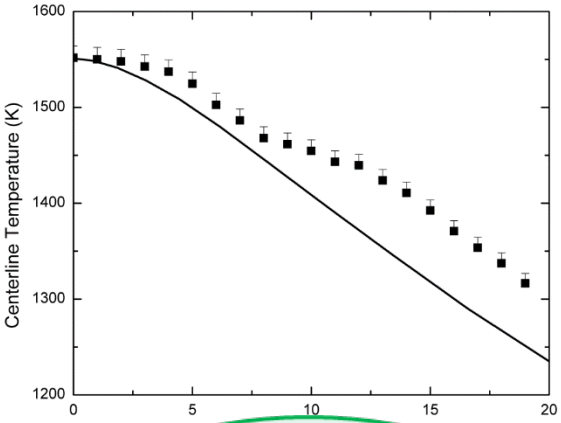
Measured NO_x speciation and temperature data with multidimensional simulation predictions for $H_2/CO = 1$ and and $\varphi = 0.5$ with a) 100 ppm NO doping and b) 75 ppm NO_2 doping.

The model is able to predict the NO-NO_2 speciation in the post flame and also provide insight on the reaction processes contributing to the inter-conversion.

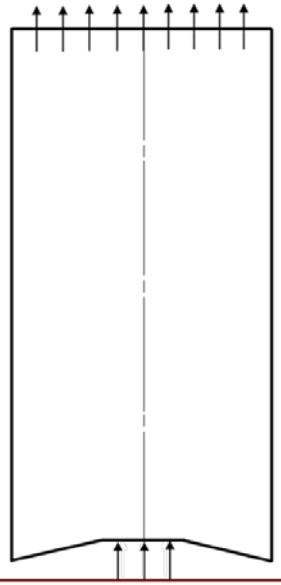
Resolving the Flame and Post Flame Simultaneously



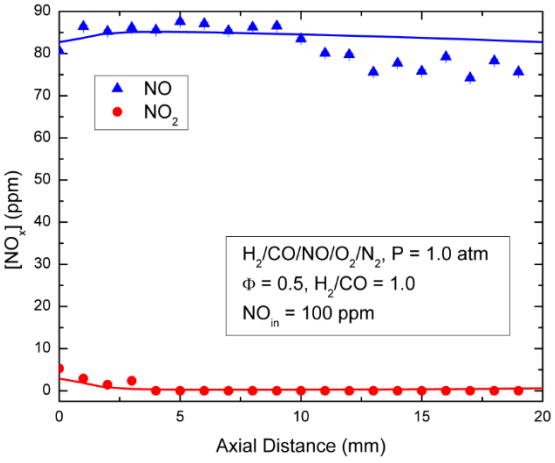
Post-flame simulation alone can not capture the initial NO_x recycling observed by the measurements



No initial NO-NO_2 conversion



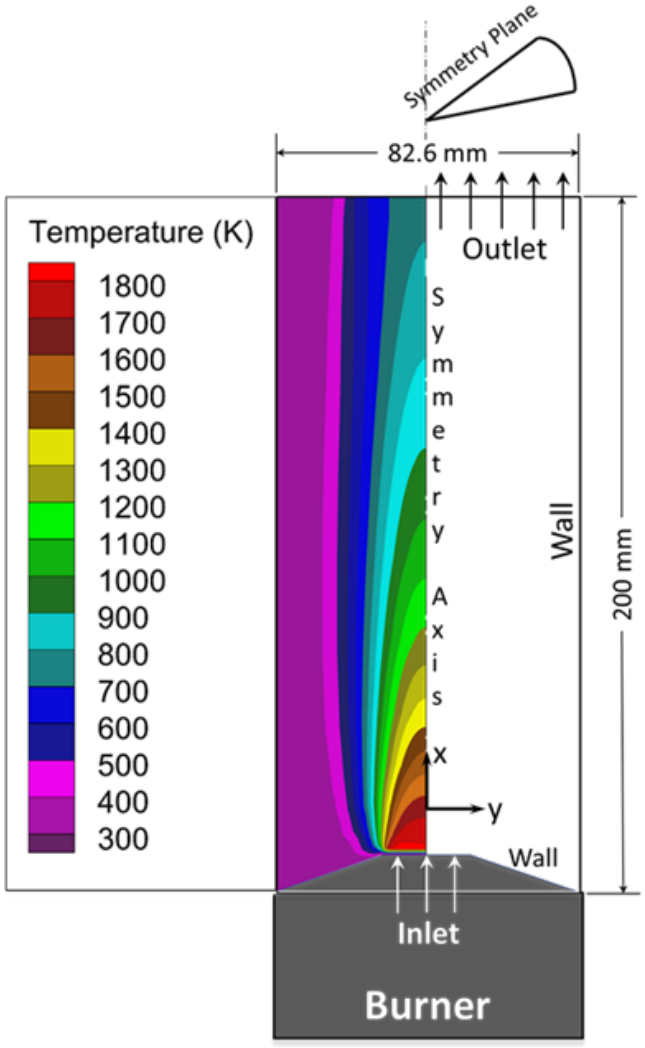
Premixed burner-stabilized flame solution for syngas/NO_x/air
T_{in} = flame temperature



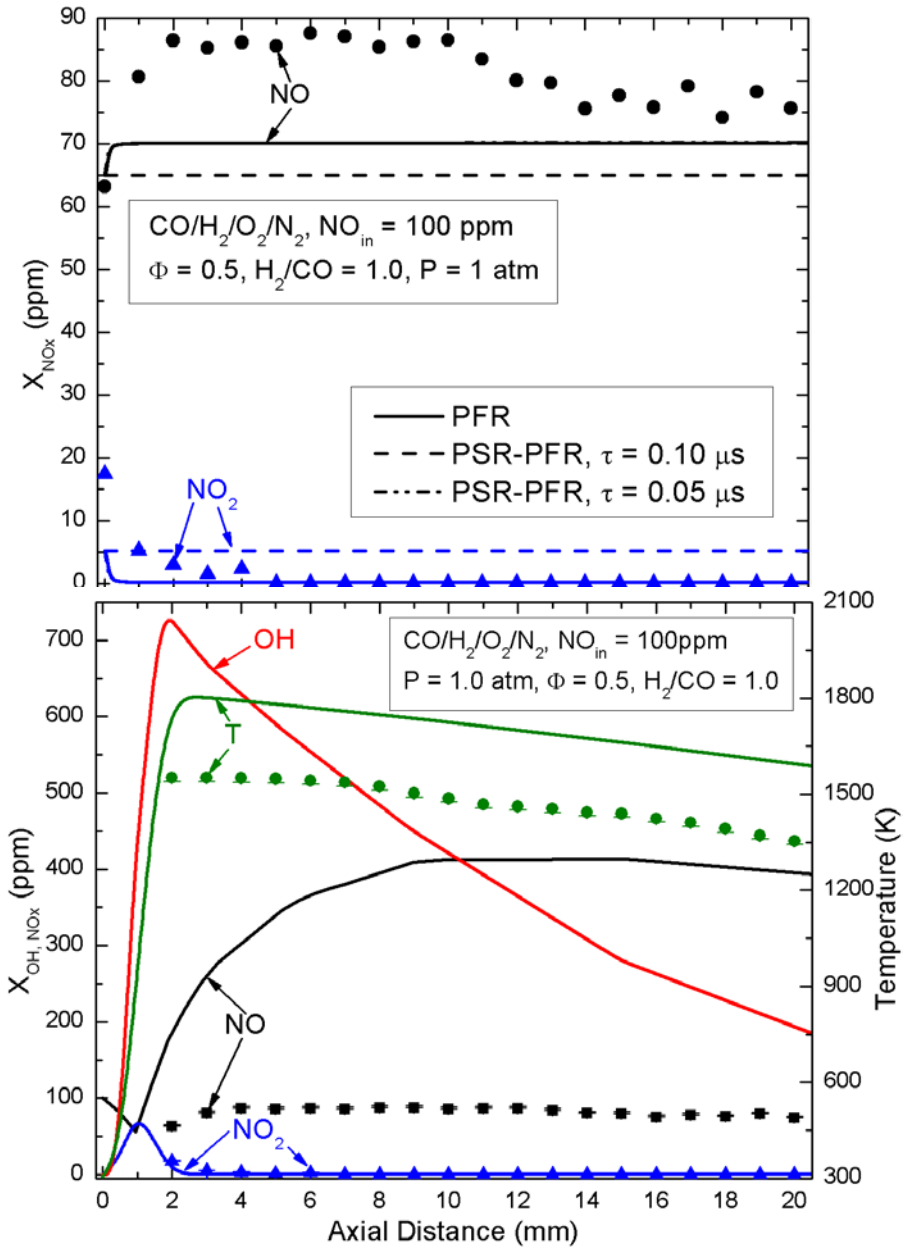
1-D flow reactor/tube modeling

- **Initializing with burner-stabilized flame solution**
- **Separate flame-post flame regimes of solution**

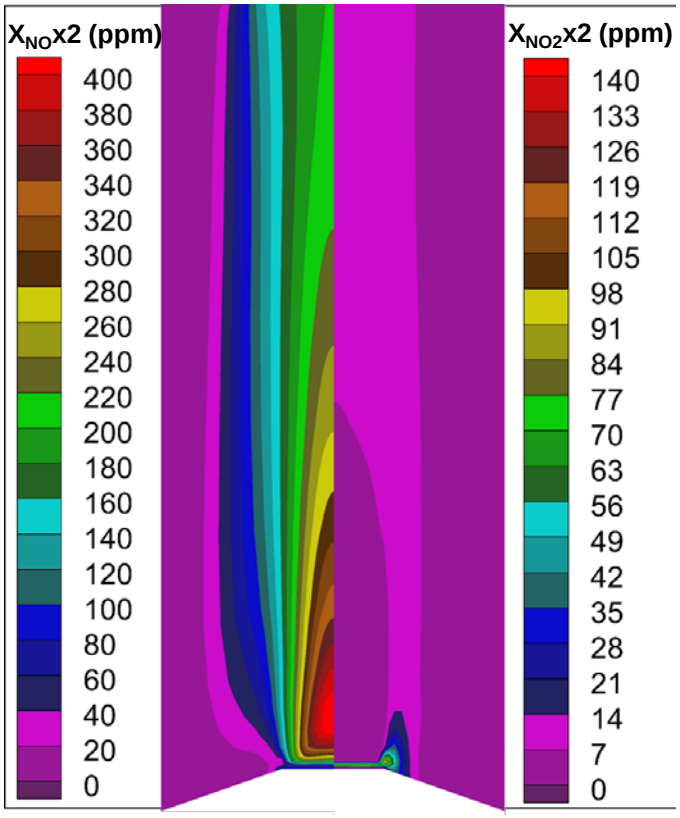
Resolving the Flame and Post Flame Simultaneously



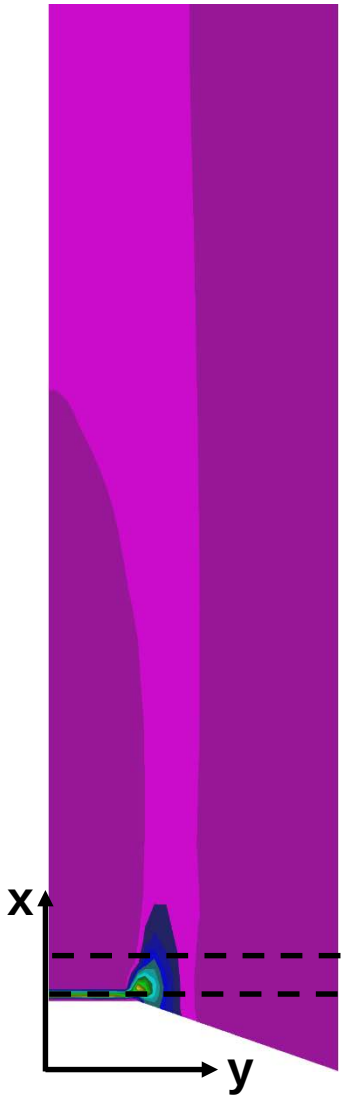
Schematic illustration of the computational domain of the burner-coupled model (right half) and the temperature field of the base case (NO_{in} = 100 ppm)



Resolving the Flame and Post Flame Simultaneously

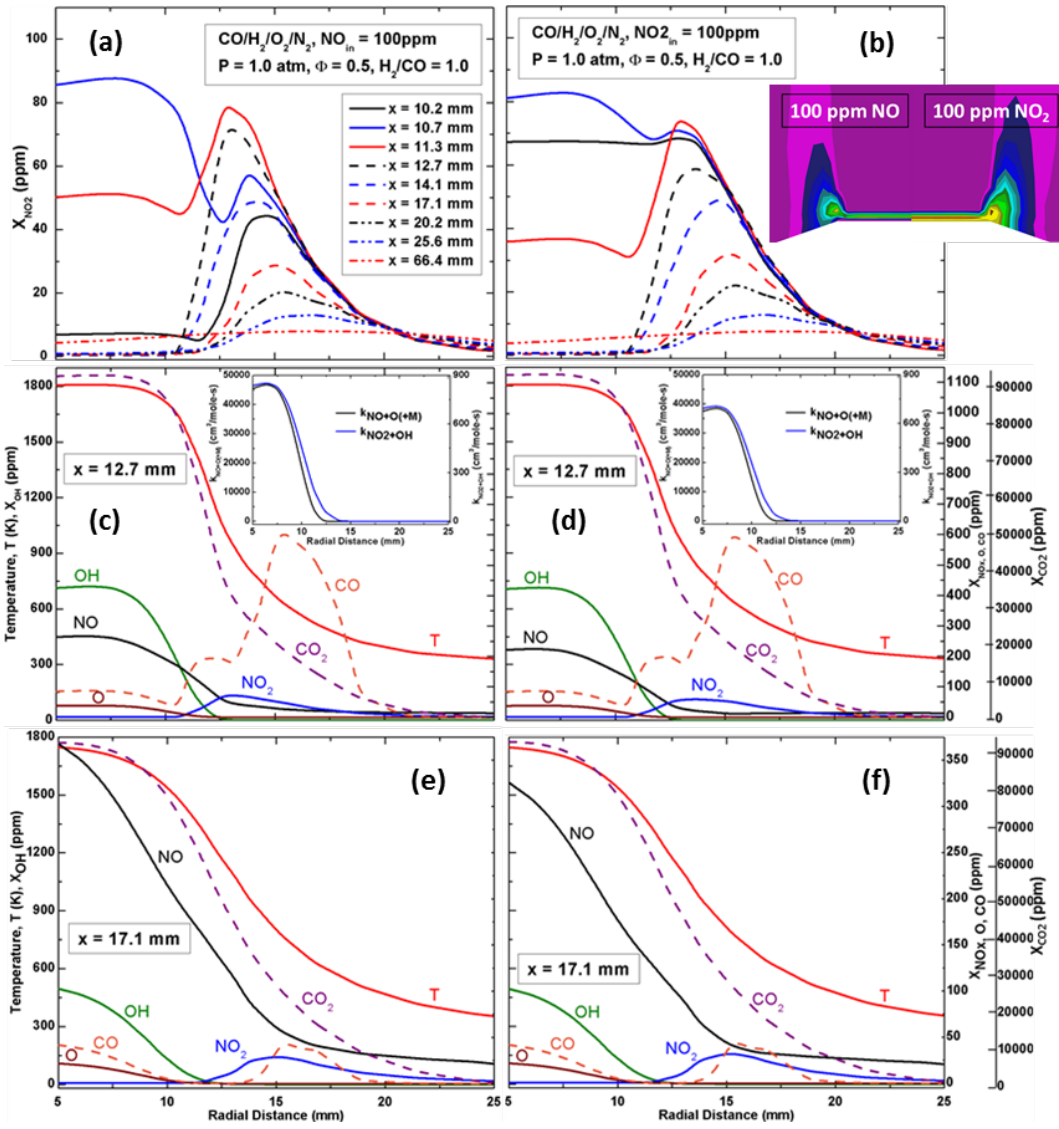


Resolving the Flame and Post Flame Simultaneously



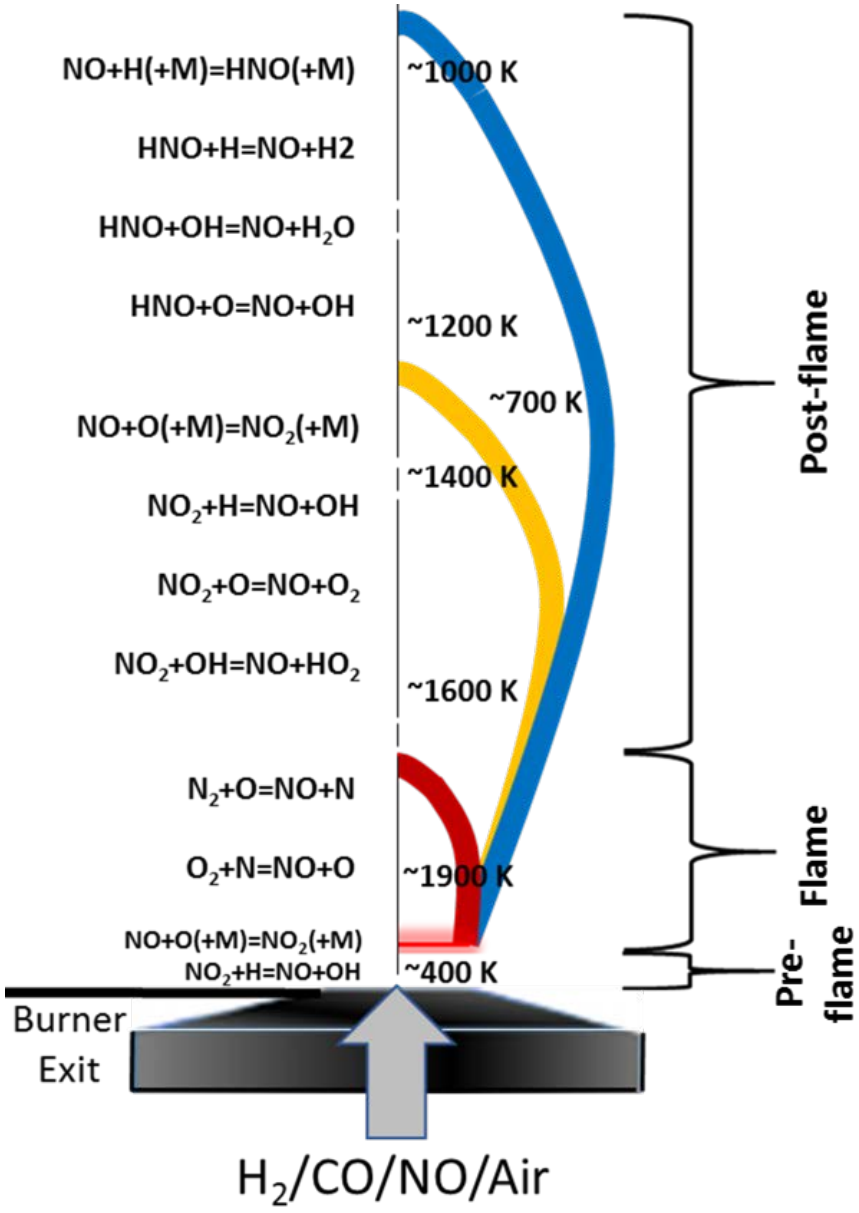
- NO-NO_2 partial equilibrium dominants at ≈850 K
- Presence of active radicals and non-participating wall

$NO + O(+M) \rightarrow NO_2(+M)$
$NO_2 + H \rightarrow NO + OH$



Summary

- High pressure reactor to obtain speciation data under a wide range of conditions
- Multidimensional reactive flow model with detailed NO_x chemistry
- Resolve McKenna flame along with the post combustion region
- Capability to analyze NO_x formation in pre, post and flame locations
- NO_x recycling not only a post flame phenomena
- Early NO_x recycling happens prior to the flame close to the inlet
- Reaction pathways vary for NO_x recycling at pre, post and flame locations



Overall Summary

- NO_x model for high hydrogen content fuel; model has been validated against a wide range of targets.

- NO_x perturbed natural gas oxidation experiments conducted in a flow reactor configuration. Presence of trace NO_x significantly alters the oxidation behavior.

- Speciation data over a wide range of conditions were obtained.

- Multi-dimensional post flame CFD simulations. The model captures the post flame reactivity with the coupled transport and detailed kinetics.

- Multi-dimensional CFD+Kinetic model resolving, pre, flame and post flame region in a self consistent fashion.

- Model and simulations data are compared against experiments to asses the model performance and fidelity.

Publications

• Asgari, N., Ahmed, S., Farouk, T., Padak, B., "NOx formation in post flame gases from syngas/air combustion at atmospheric pressure" ***International Journal of Hydrogen Energy*** (2017), 24569 – 24579.

• 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*** (2016), 31, 2360 – 2369.

• 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.

• Ahmed, S., Dasgupta, A., Dryer, F., Farouk, T., "Multidimensional numerical investigation of NOx formation in a burner coupled flow tube configuration: NOx kinetics in post, pre and flame locations " *10th U.S. National Combustion Meeting*, College Park, Maryland, April 23 – 26, 2017.

• 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