# 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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**Bihter Padak**

University of South Carolina, Columbia, SC 29208, USA

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Princeton University, Princeton, NJ 08544, USA

**2015 University Turbine System Research Workshop**

**Atlanta, GA**

**November 3rd – 5th, 2015**

# 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
- Fahd Ebna Alam – Visiting Researcher (8 mos)

# 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 shear layer flow regimes (hot and cold flow interactions). NO - $NO_2$ conversion in hot-cold shear layer interaction and EGR.

- Detailed and reduced kinetic models for HHC fuels including detailed fuel compositions and $NO_x$.

***Improved, higher fidelity tools for engineering design!***

# Tasks

- Study of reactivity and speciation data for $NO_x$ under various conditions

- Studies of CO, NO, $NO_2$ formation and conversion for NO → $NO_2$ in shear/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

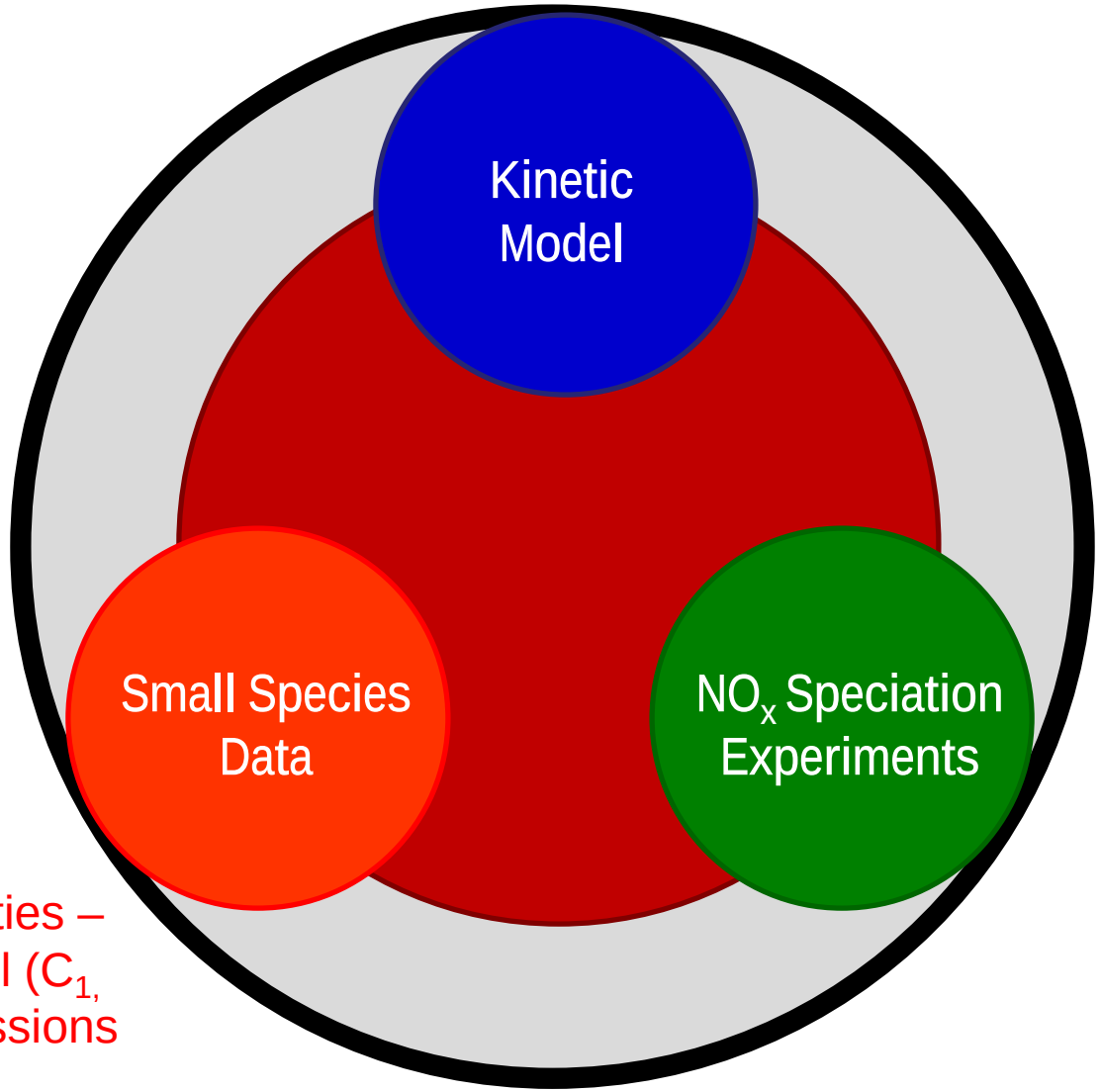
# Presentation Outline

- Research Team Members
- Project Objectives
- Research Tasks
- Year 2 progress
  - ❑ Kinetic Modeling of $NO_x$ formation in HHC Fuels
    - – Tanvir Farouk
  - ❑ Experiments for Speciation Measurements
    - – Bihter Padak
  - ❑ Measurement of Small Species Data and Modeling Implications
    - – Frederick Dryer (presented by Tanvir Farouk)
- Summary

- Predictions of $NO_x$ to address strict emission standards

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

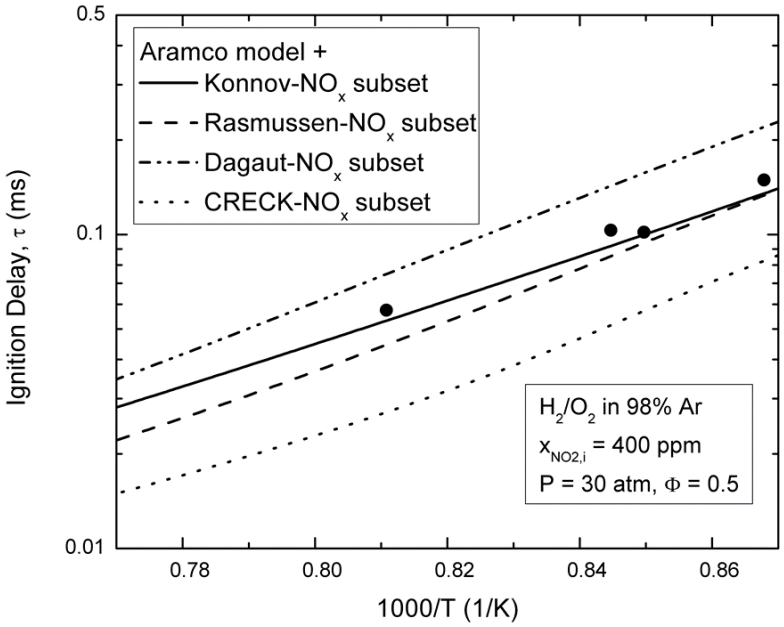
- Fuel impurities – source of fuel ($C_1$, $C_2$ …) – emissions

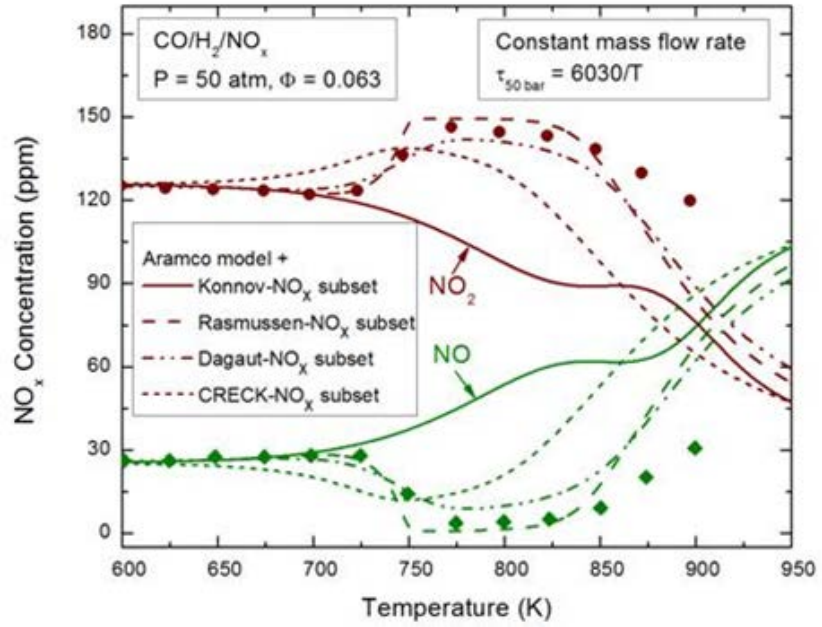



Unless one considers the ***interactions of small species and emittents***, particularly on natural gas combustion the resulting model will likely have poor fidelity to be considered for engineering applications

# Kinetic Modeling

# Current Predictive Models of $NO_x$ Formation




Global combustion targets are insufficient to provide the necessary constraining conditions for assessment and model development of $NO_x$ interactions with Hydrogen and Syngas Oxidation.

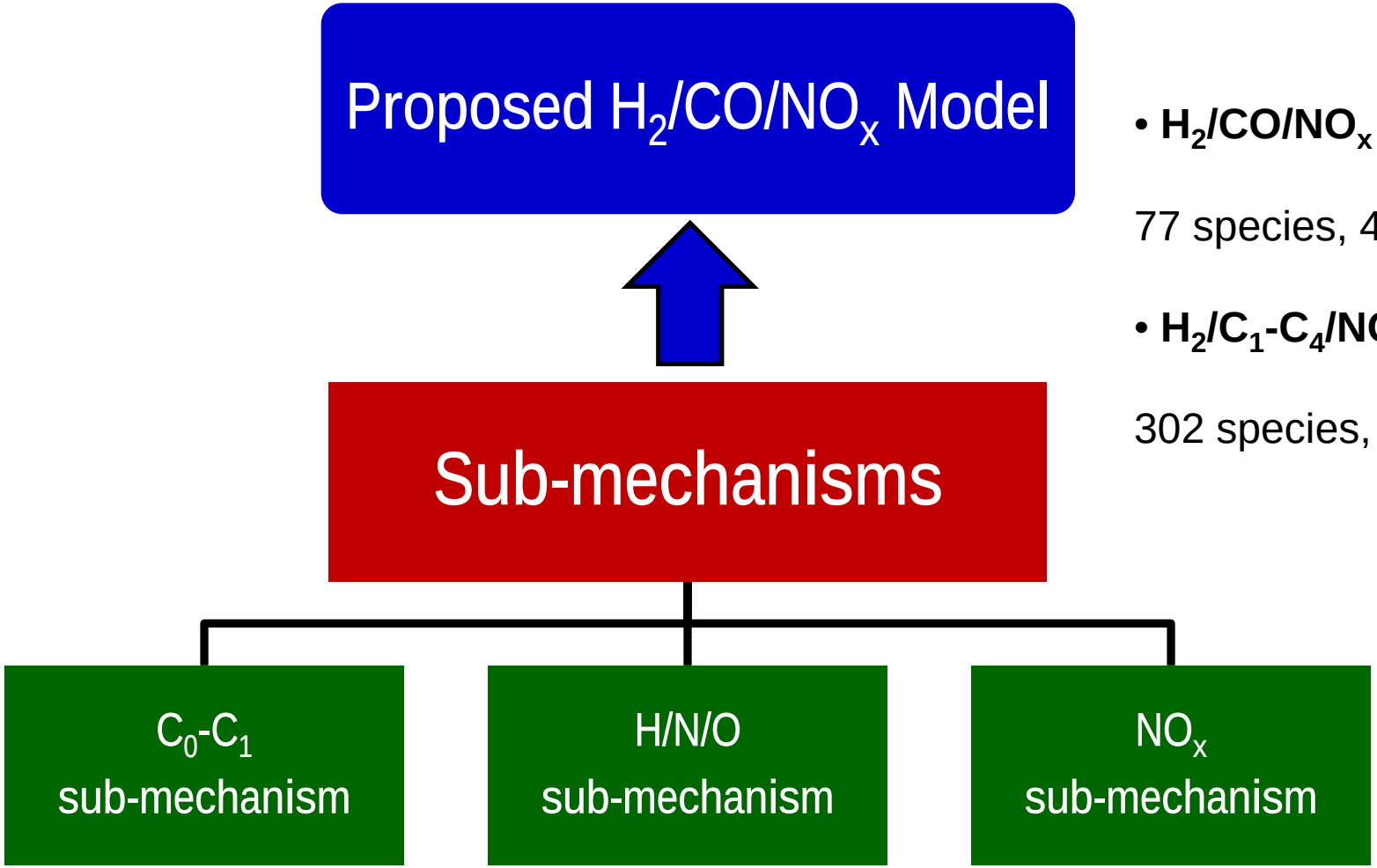
Detailed species evolution measurement necessary

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

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

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

# Proposed $H_2/CO/NO_x$ Model



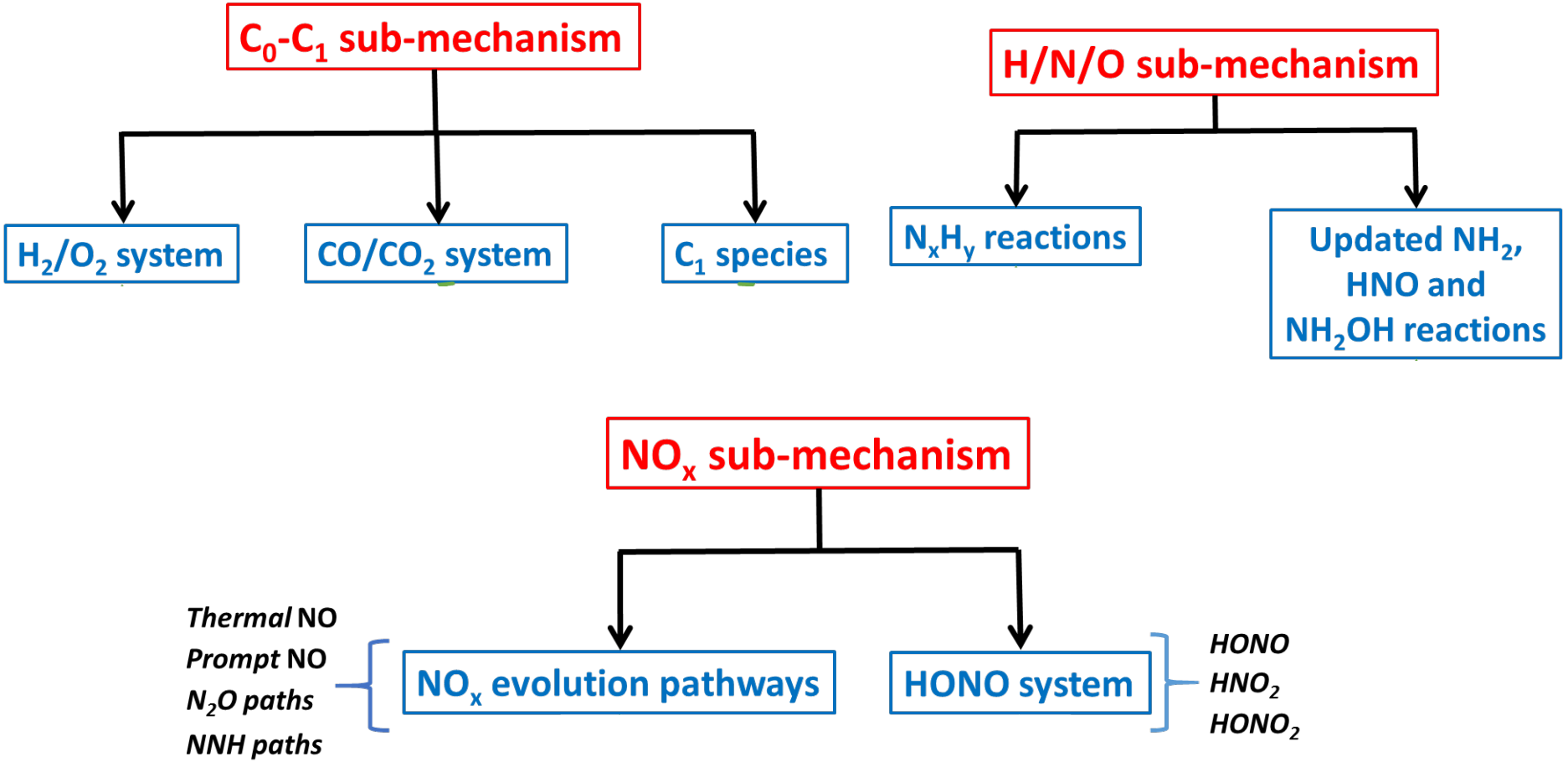

- **$H_2/CO/NO_x$ Model**

77 species, 442 reactions

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

302 species, 1952 reactions

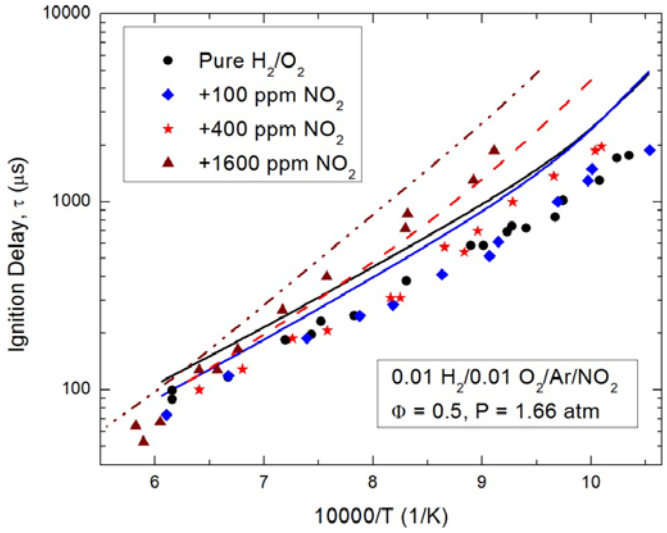
# Model Elements




[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)*

# Proposed Model Performance: Ignition Delay

## Dependence of $\tau_{ig}$ on initial $NO_2$ doping for $H_2/O_2$ system




100 ppm → insignificant

400 ppm or higher → reactivity decreases

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

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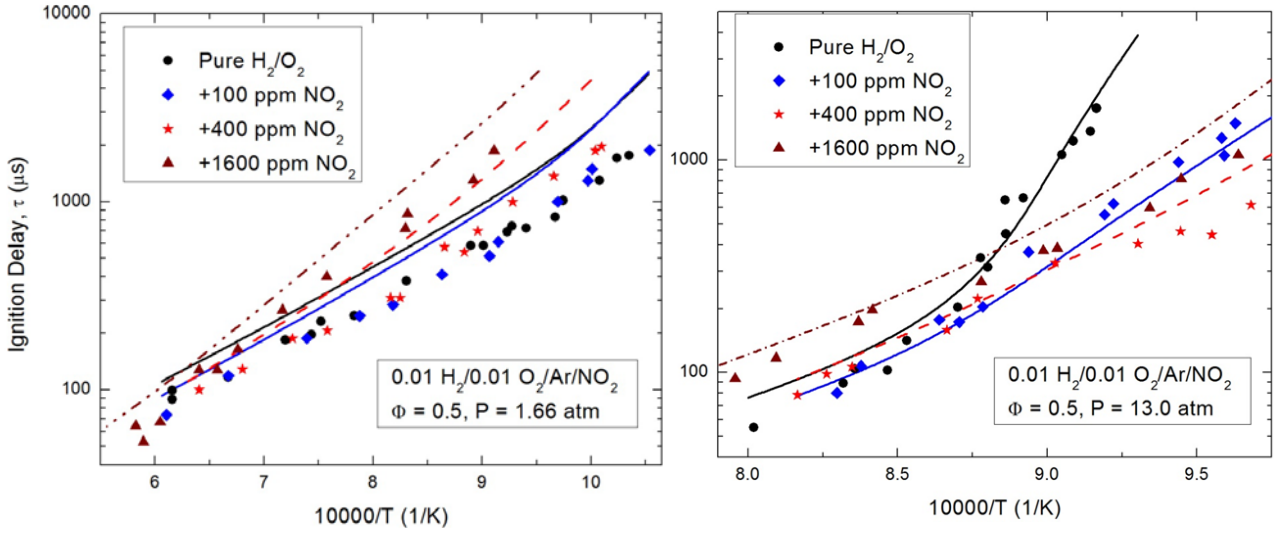


**Pressure** →

100 ppm → insignificant

400 ppm or higher → 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)*

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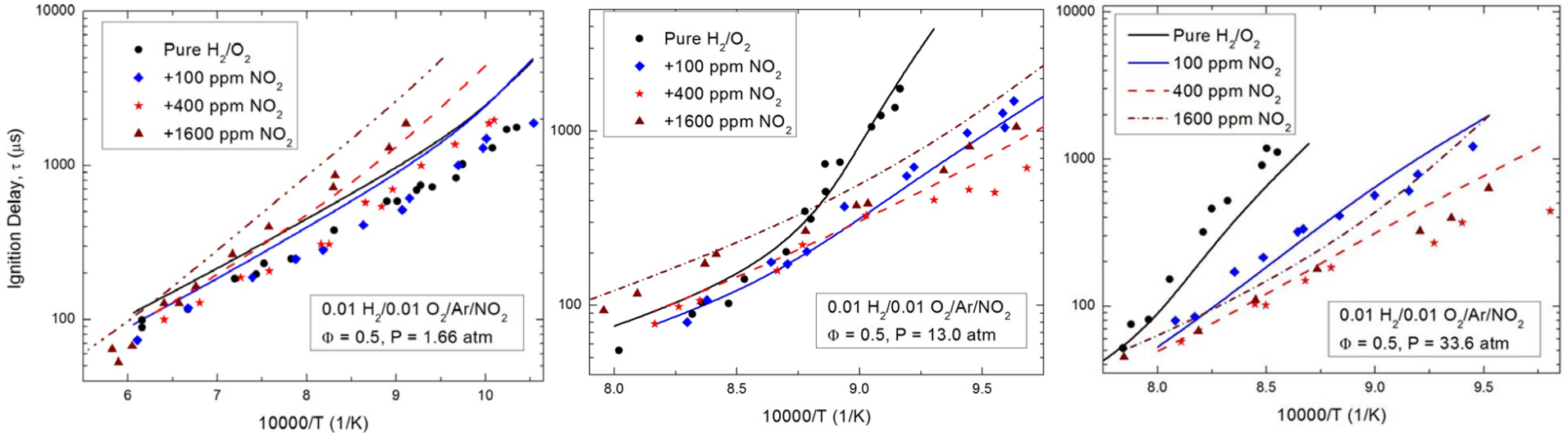


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**High pressure non-monotonic behavior captured by the model**

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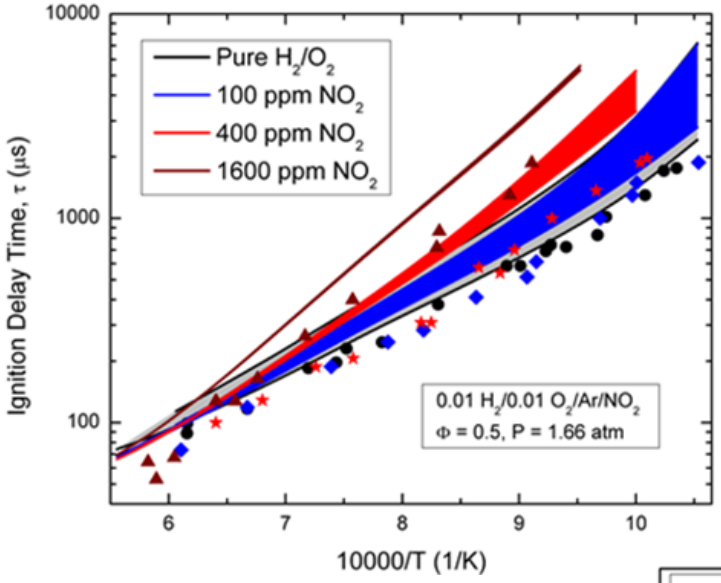
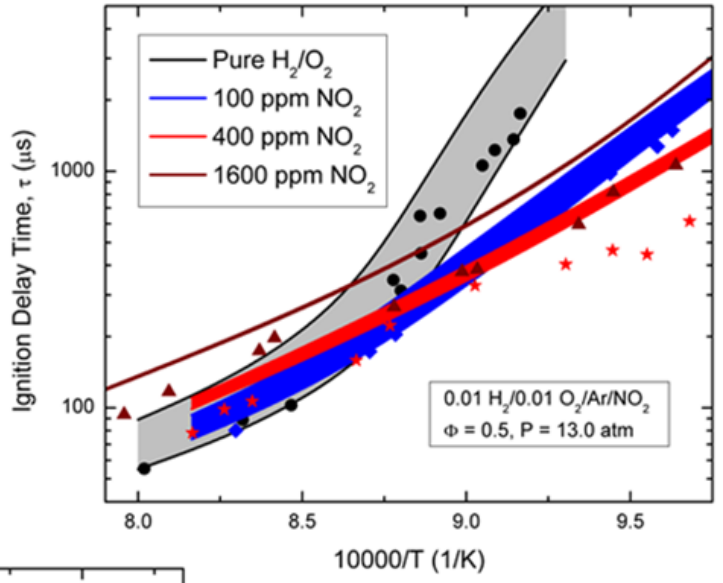
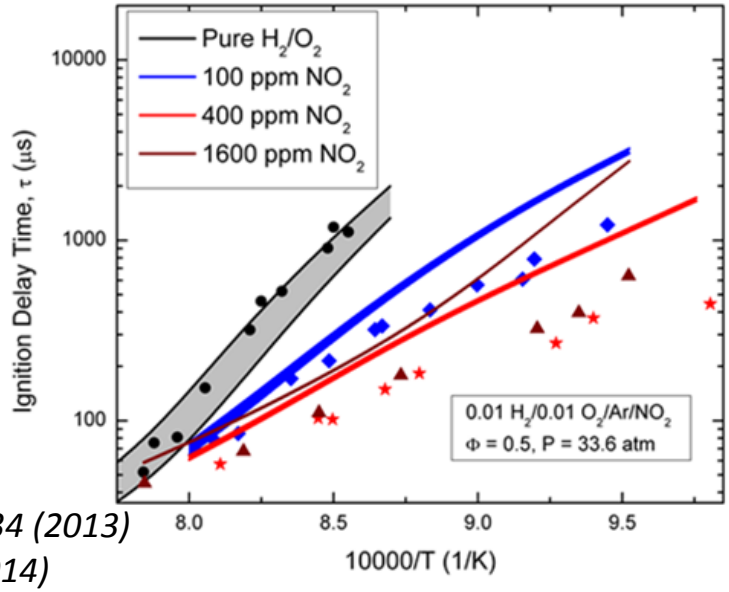
# Proposed Model Performance: Ignition Delay

## Effect of initial H-atom impurities on the ignition delay of $H_2/O_2$ system



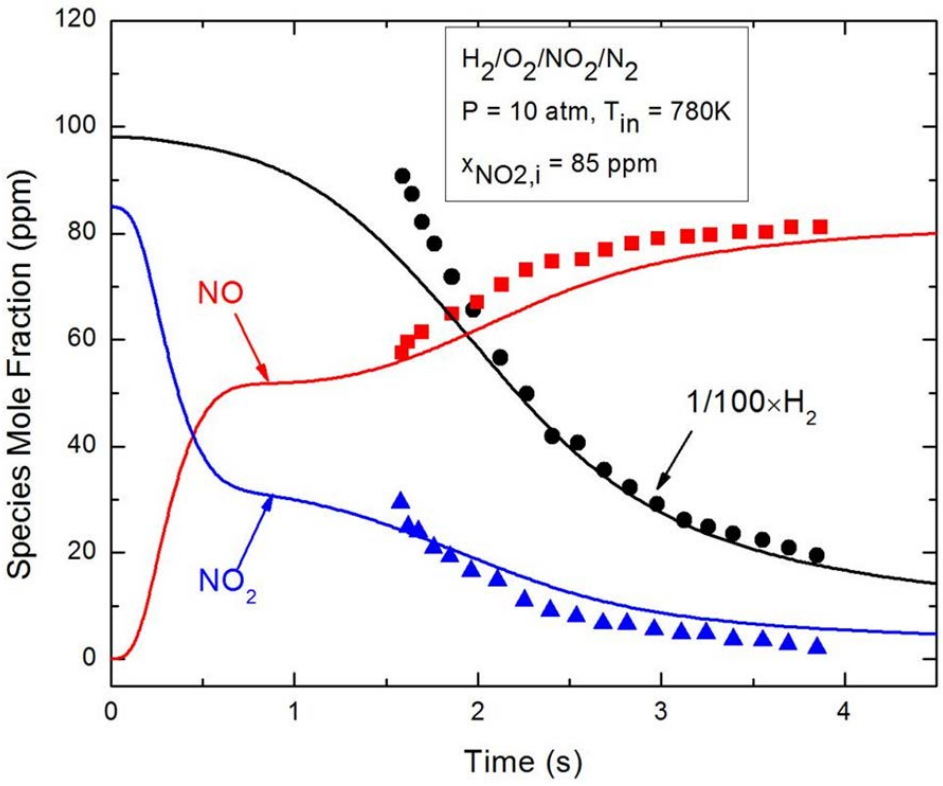

350 ppb of H-impurity

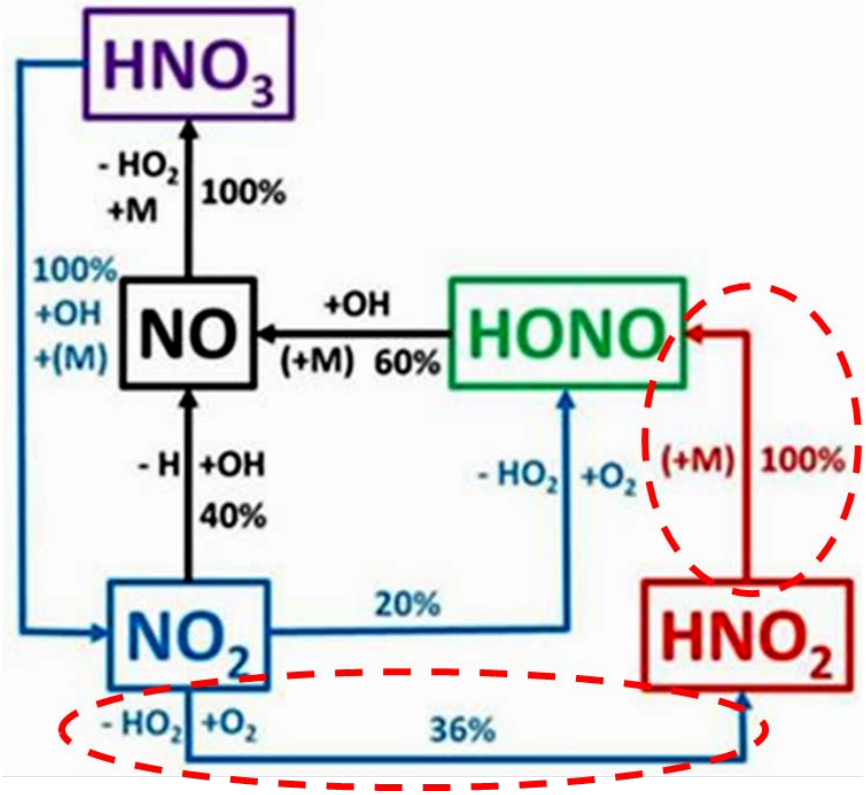



Impurity effects change with-
- ✓ pressure
- ✓ initial $NO_2$ doping

*Mathieu et al., Proc. Combust. Inst. 34 (2013)*
*Urzay et al. Combust. Flame 161 (2014)*

# Proposed 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

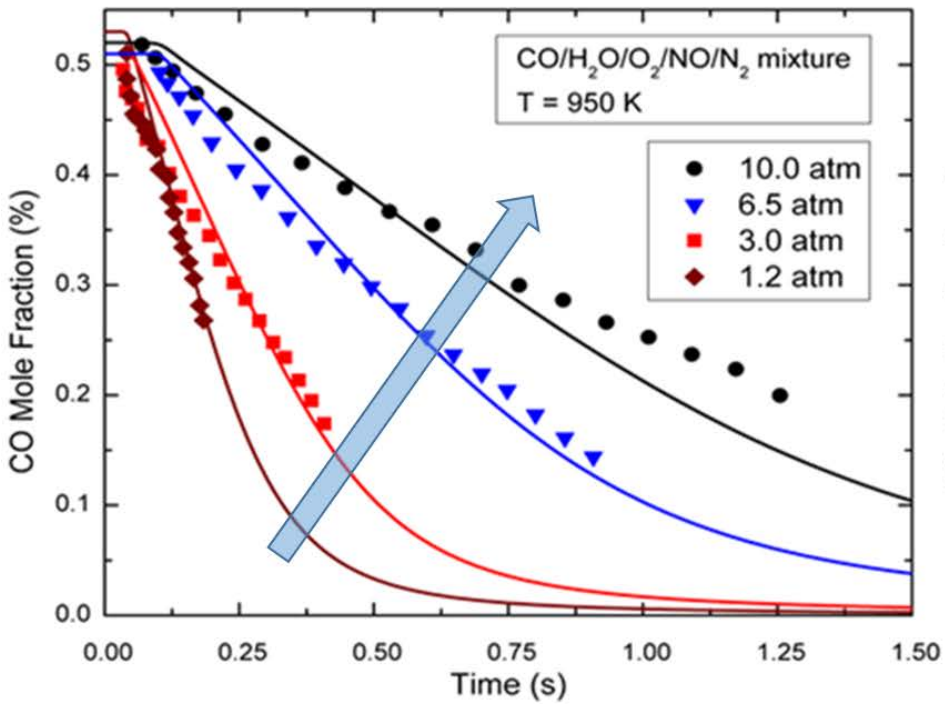
*(ii)* through intermediate HONO

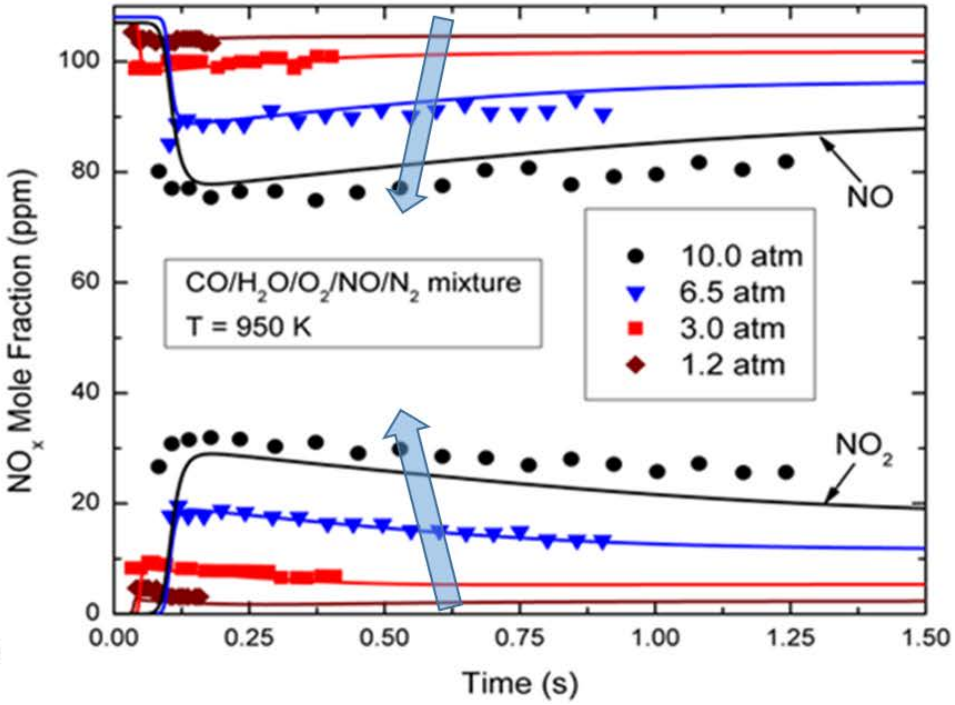
***(iii)* through intermediate $HNO_2$**

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

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

## Variable Initial Pressure



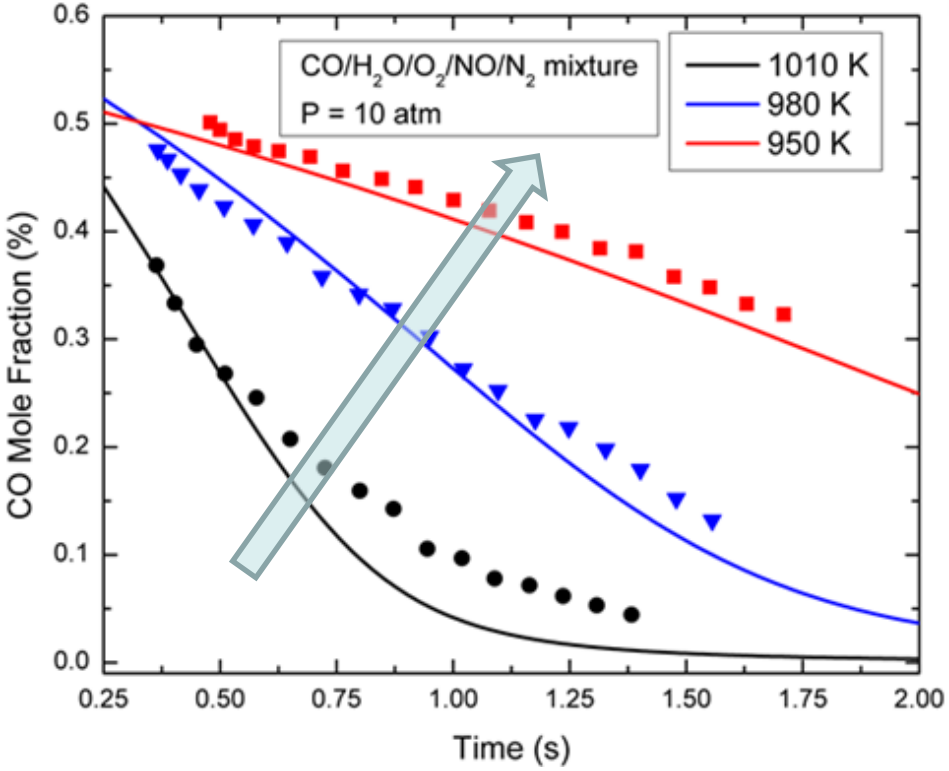



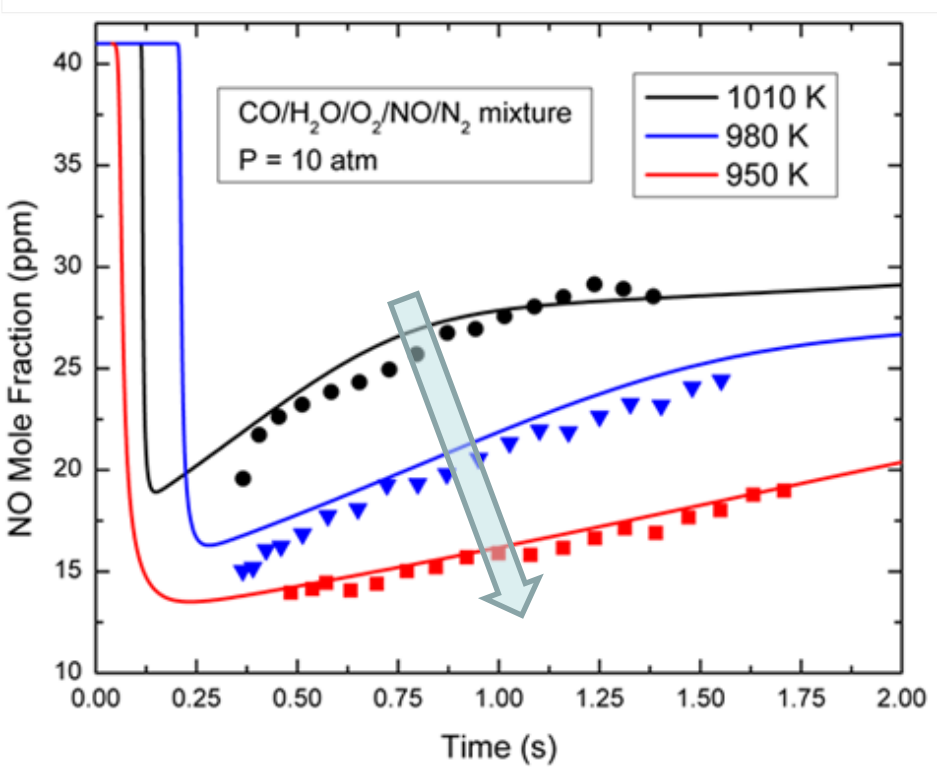

- ✓ **Model reasonably predicts the experimental trends with variable initial pressure**
- ✓ **Complete $NO$-$NO_2$ interconversion without any formation of molecular nitrogen**

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

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

## Variable Initial Temperature

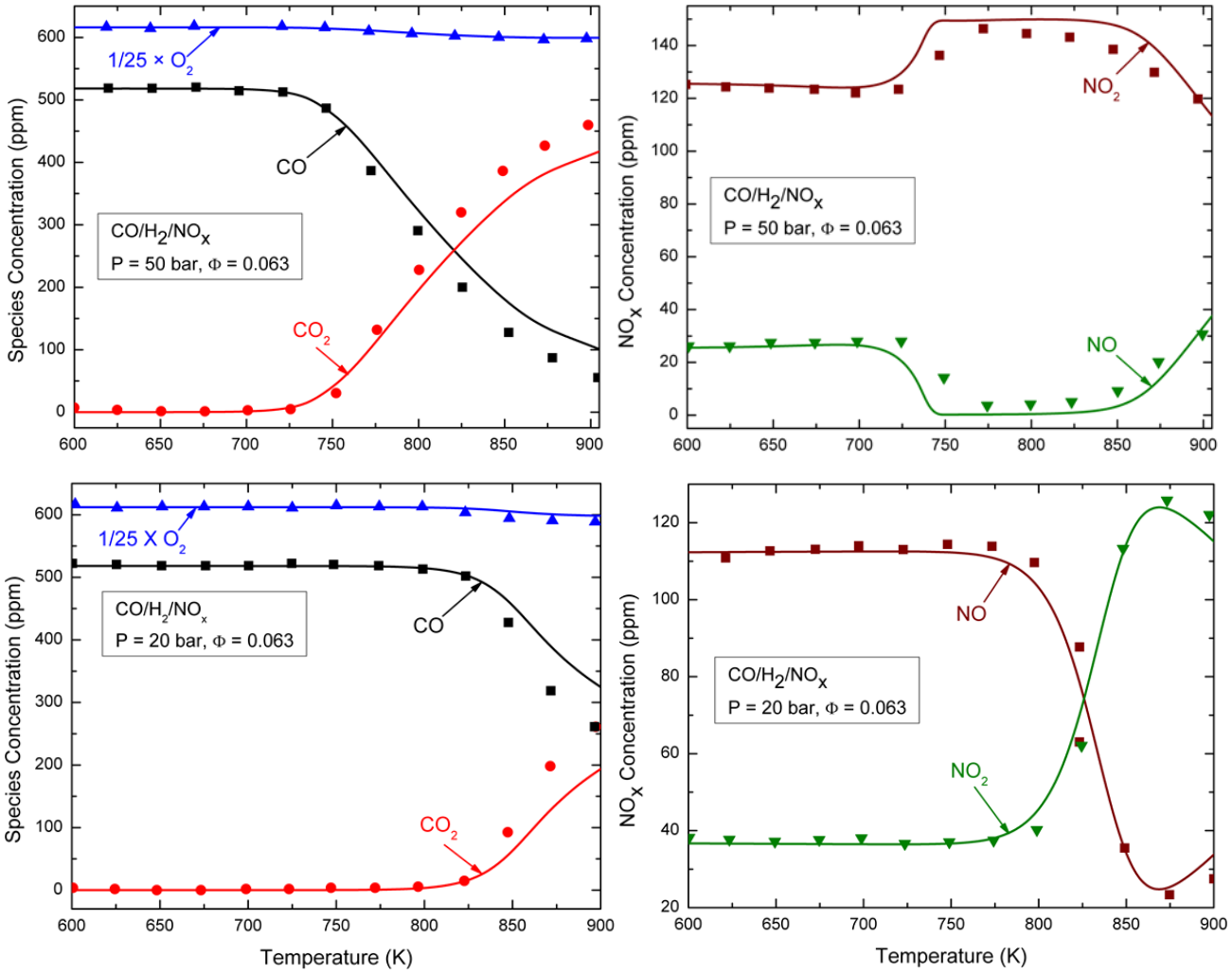



✓ **Model reasonably predicts the experimental trends with variable initial Temperature**

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

# Proposed 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

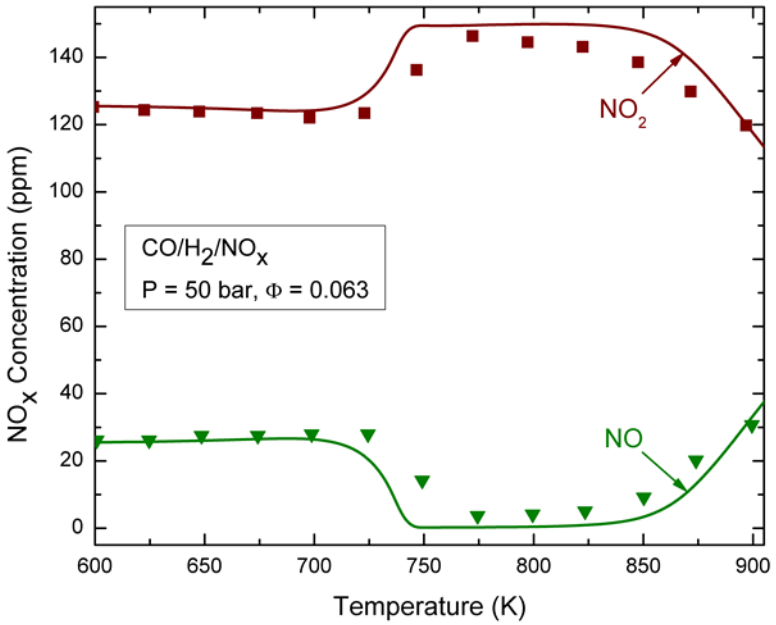
$$\tau_{20\ bar} = 2350/T$$

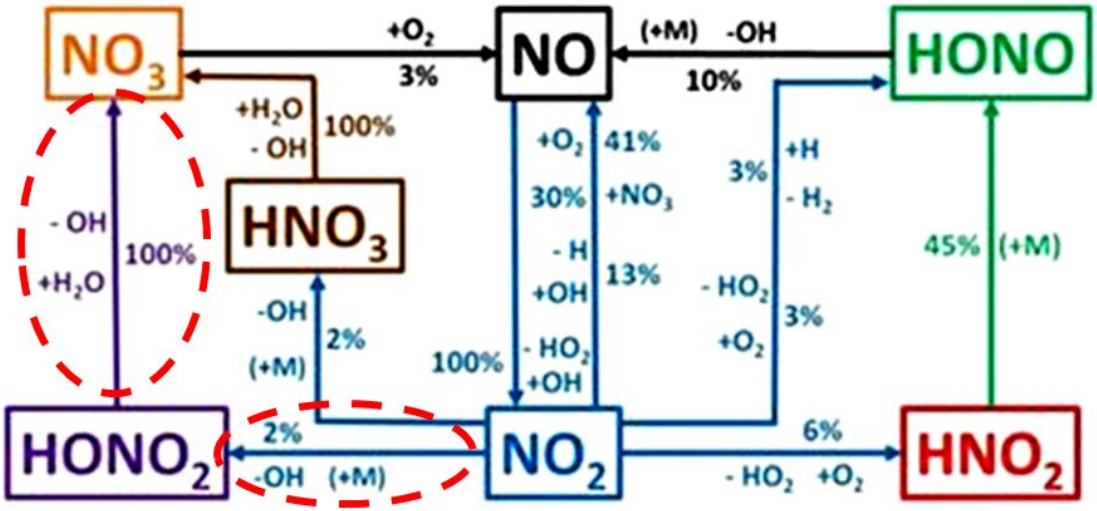
$$\tau_{50\ bar} = 6030/T$$

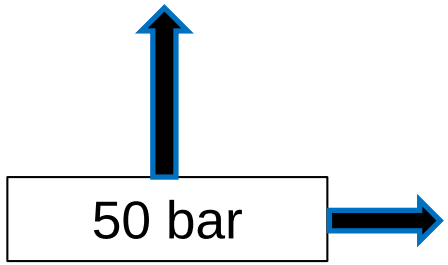
- ✓ Reasonable predictions for $CO$-$CO_2$ and $NO$-$NO_2$ conversion

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

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



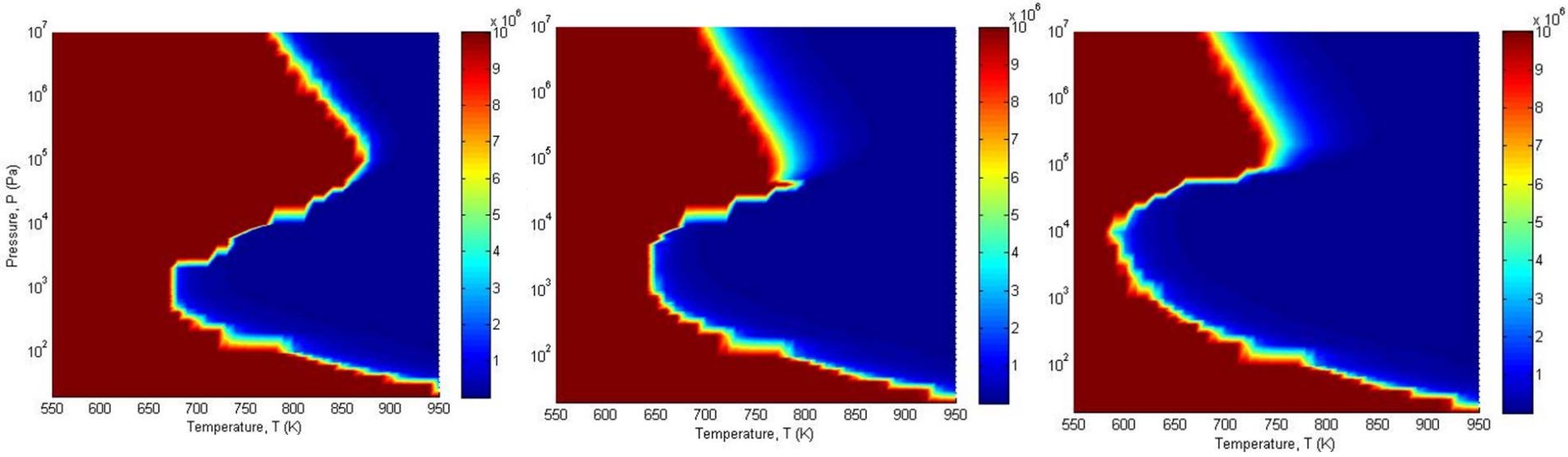

**Dominance of pressure-dependent reactions: two additional NO ↔ $NO_2$**

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

# Effect of Physical and Chemical Perturbations on the Explosion limit and Ignition Delay Time of $H_2/O_2$

**Physical and chemical perturbation effects on the explosion limit as well as the ignition delay time of hydrogen**

## Chemical Perturbation- initial NO doping




Base case

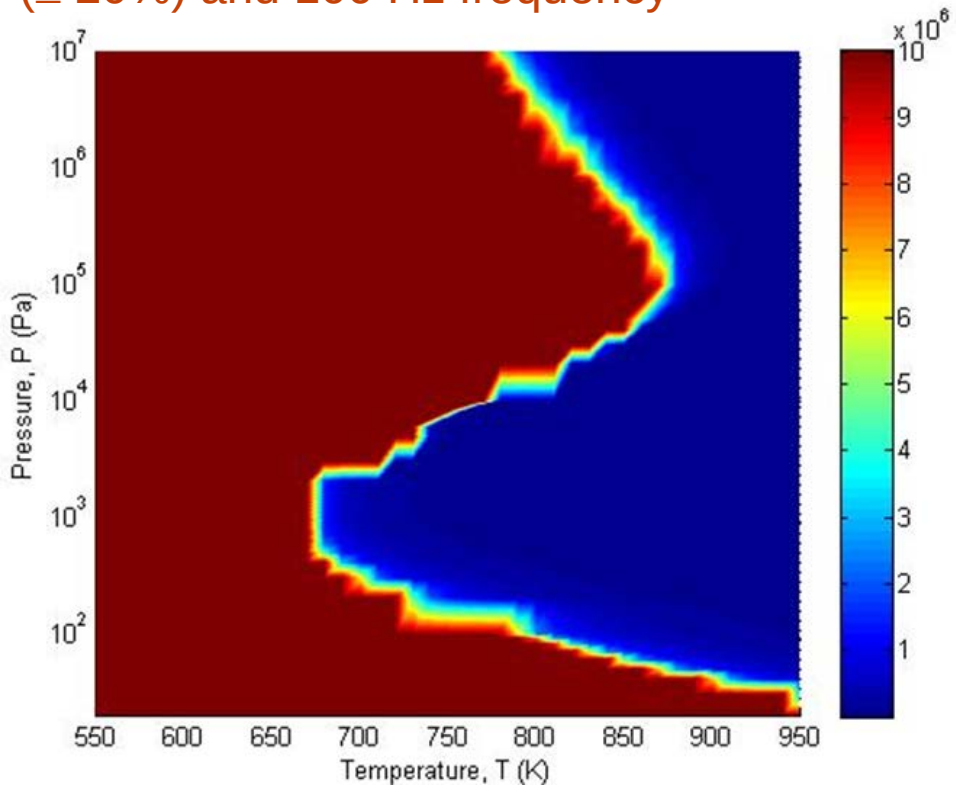
50 ppm NO

200 ppm NO

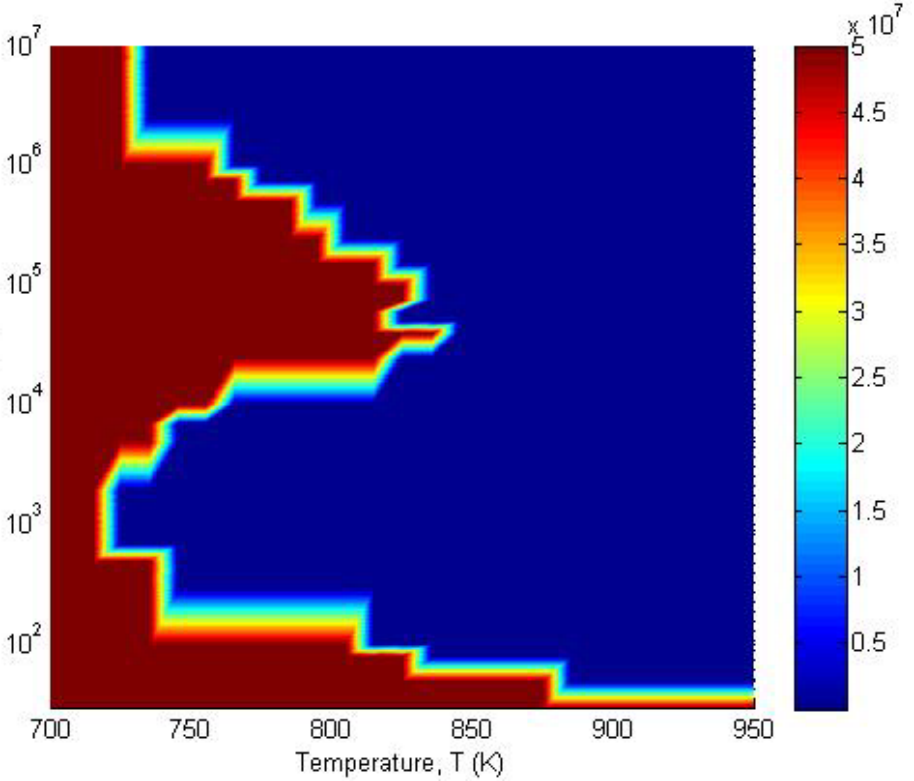
- ✓ With an increase in initial NO concentration, the initiation point of the second explosion limit moves towards higher pressures and lower temperatures
- ✓ The second explosion limit demarcation line becomes more and more flat with an increase in initial NO concentration
- ✓ The initiation point of the third explosion limit shifts toward lower pressures and higher temperatures with an increase in initial NO concentration

# Effect of Physical and Chemical Perturbations

Physical Perturbation- Fluctuating pressure with Gaussian random amplitude (± 20%) and 100 Hz frequency




Base case




**Sinusoidal Pressure Perturbations**

$P = P_0 + A_{rand} * \sin(2\pi f t)$

- ✓ With pressure perturbation, the initiation point of the second explosion limit moves towards higher temperatures and the initiation point of the third explosion limit moves towards lower temperatures
- ✓ The third explosion limit demarcation line becomes less steep with pressure perturbation

# Summary

- $C_0$ – $C_4$/$NO_x$ model has been assembled
- $H_2$/CO/$NO_x$ model has been validated
- Influence of trace impurities on combustion characteristics
- Chemical and physical perturbation effects on ignition delay and explosion limits for $H_2$/$O_2$ systems
- Trace $NO_x$ – emittents can alter the combustion behavior, global/optimized models can not capture intricate features

# Experimental Setup for Speciation Measurements

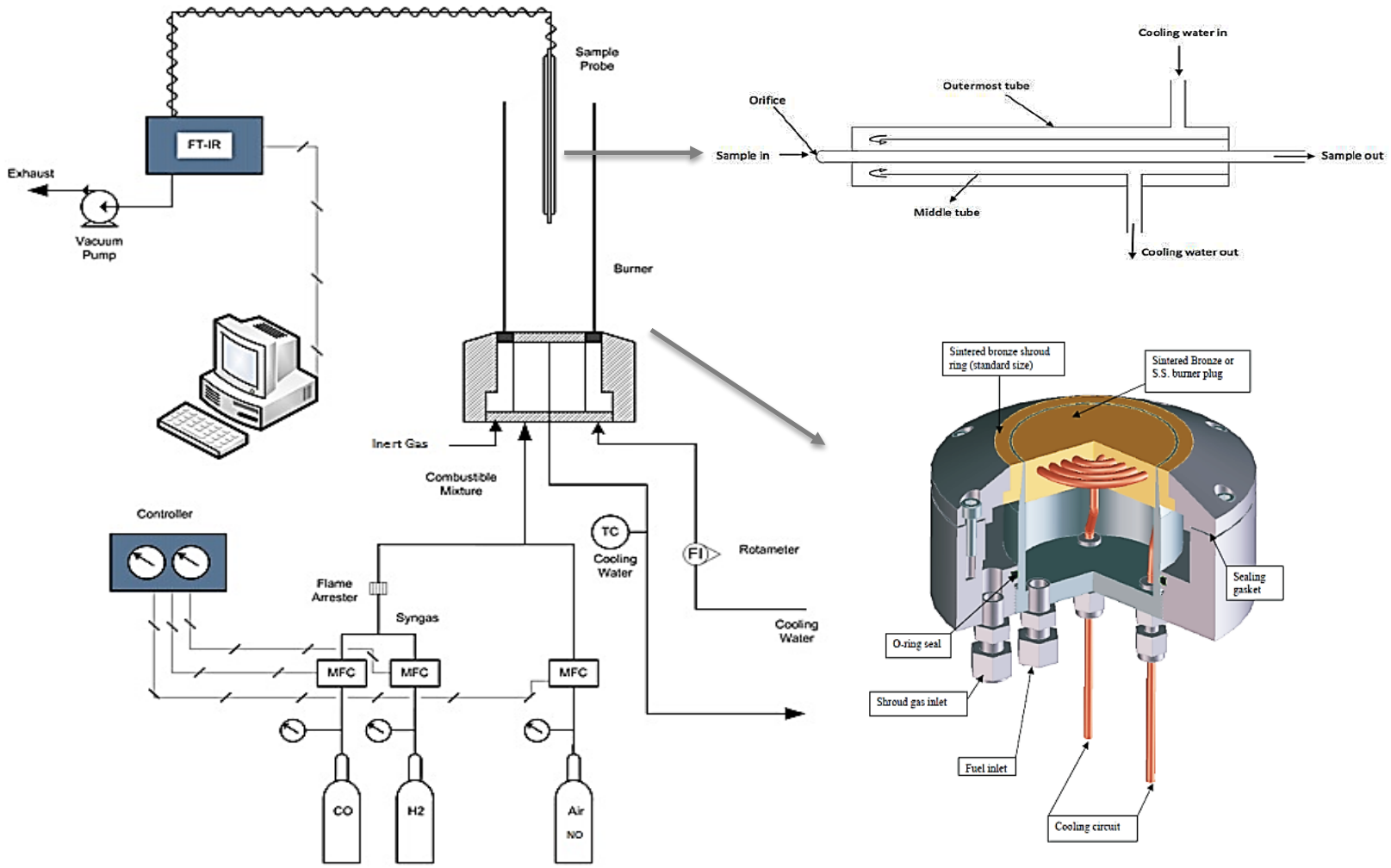
# Scope of Work

The presented work is focusing on $NO_x$ formation in a syngas/air combustion system at atmospheric pressure.

Syngas tests were carried out with Φ:0.5-1, $H_2$/CO from 1:1 to 1:4, total flow rate of 3-6 slpm.

The first set of experiments were conducted at atmospheric pressure and the second part is going to be done at elevated pressures.

# Schematic of Experimental Setup



# Experimental Plan

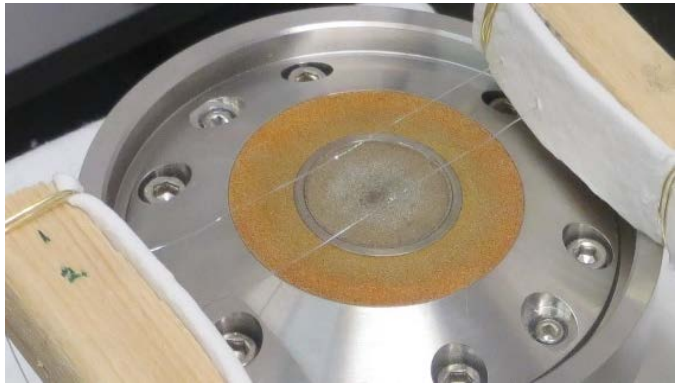
- Burner stability tests

- Temperature measurements
  - Flame temperatures
  - Radial temperature profile
  - Axial temperature profile

- Speciation data
  - NO, $NO_2$ and $N_2O$ concentration profiles
  - CO concentration profile

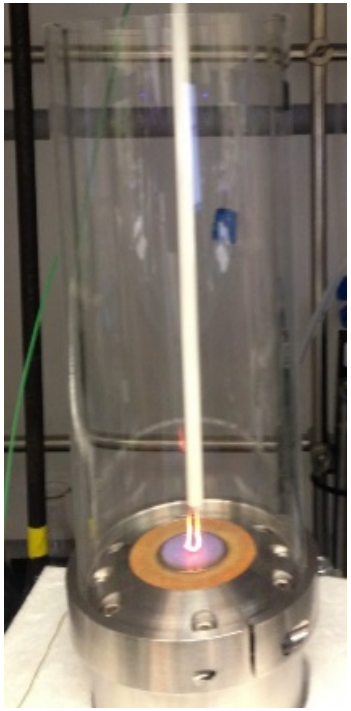
# Temperature Measurements

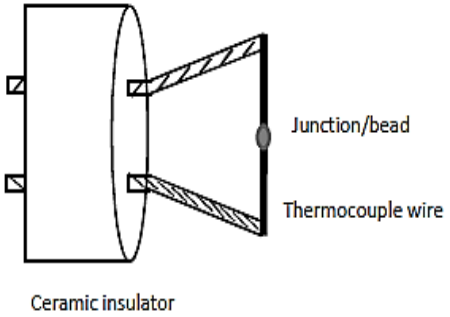
## Flame T measurements



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

## Radial and axial T profile measurements

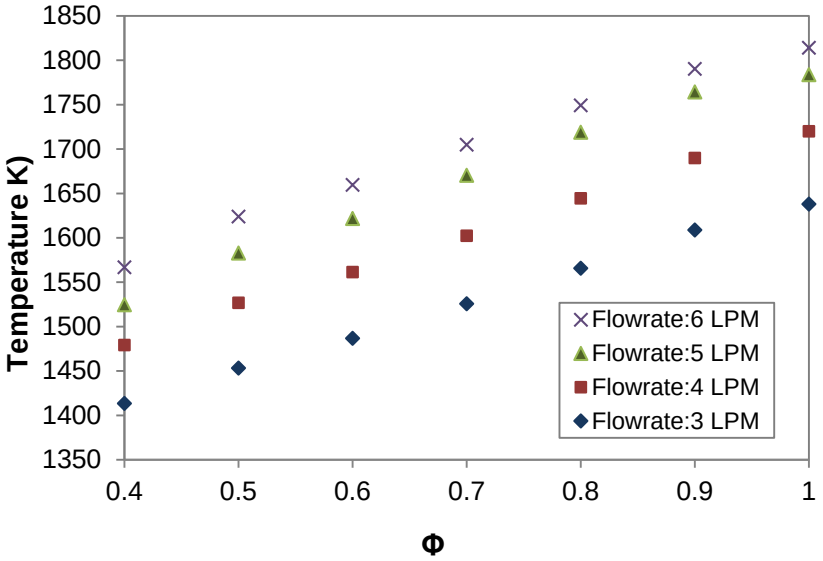




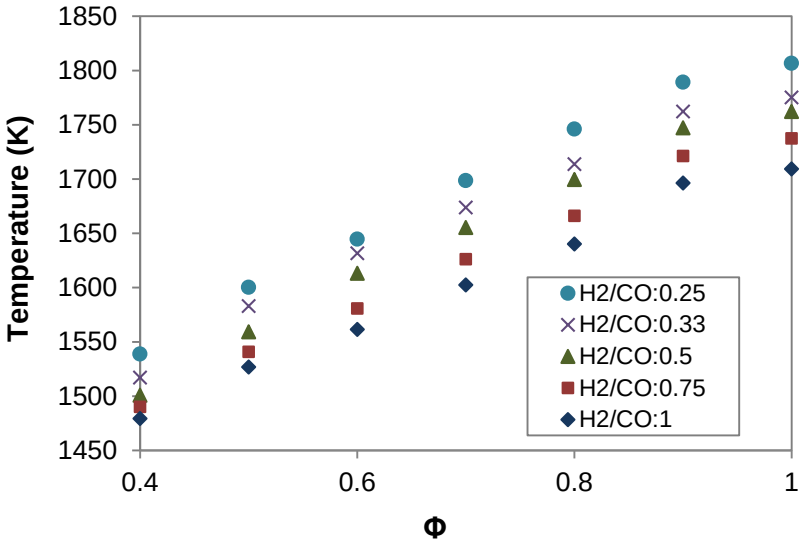

**Thermocouple diagram**

# Flame Temperature Measurements

## Different flow rates at $H_2$/CO: 1




## Different $H_2$/CO ratios at 4 LPM

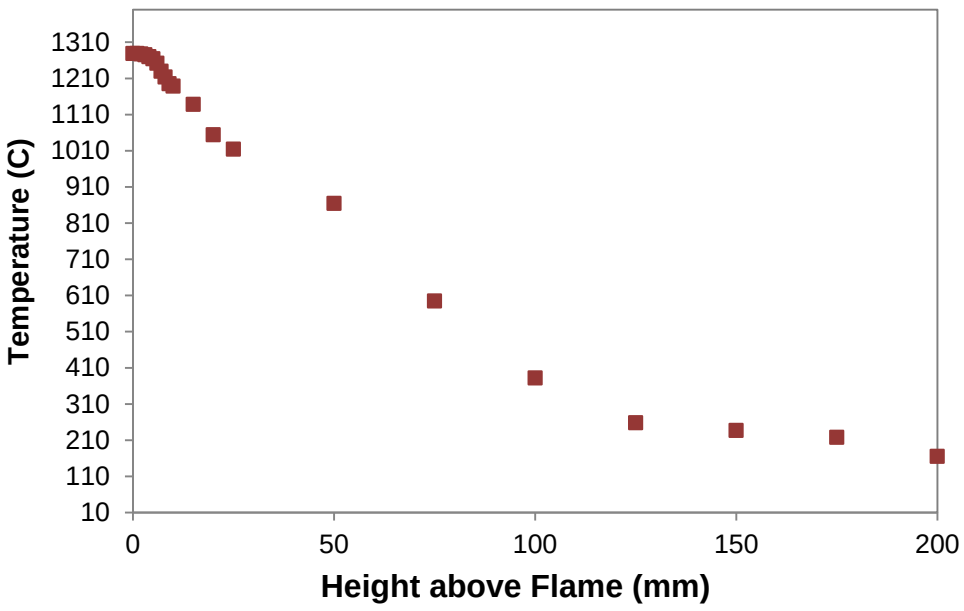



- With increasing the flow rate the distance between the burner plate and the reaction zone grows and heat transfer is reduced.
- Decreasing the $H_2$/CO ratio results in an increase in the flame temperature due to increased heat release by the CO+OH reaction.

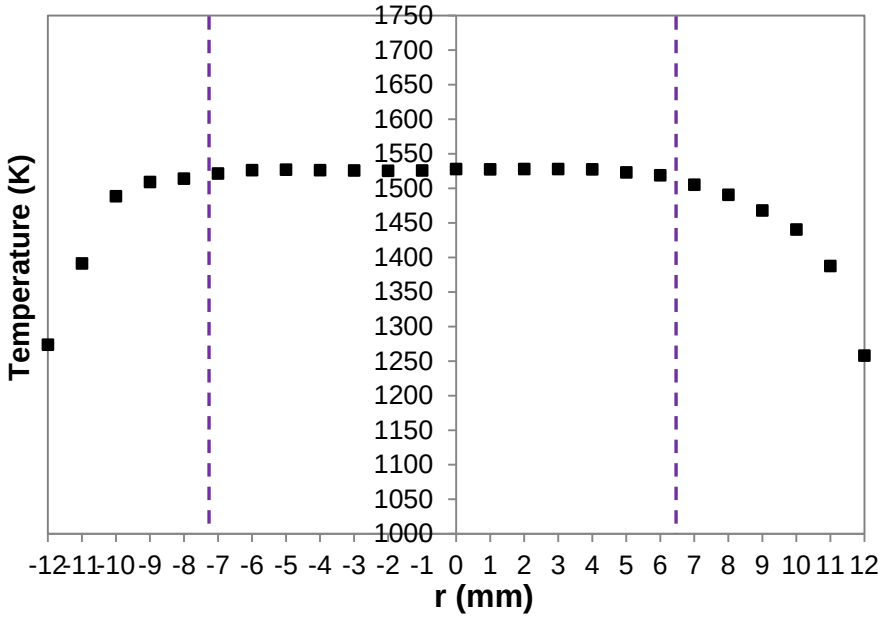
# Temperature Profiles

**$H_2$/CO:1  Φ: 0.5**

## Axial temperature profile



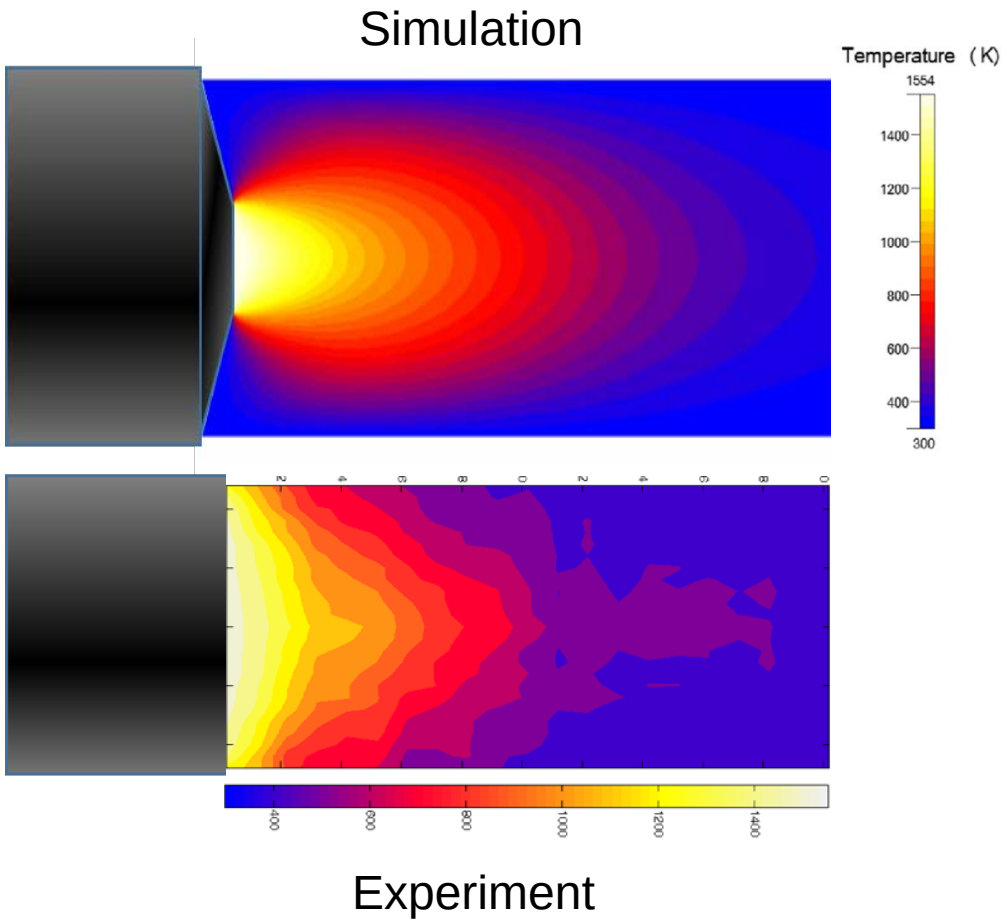

## Radial temperature profile



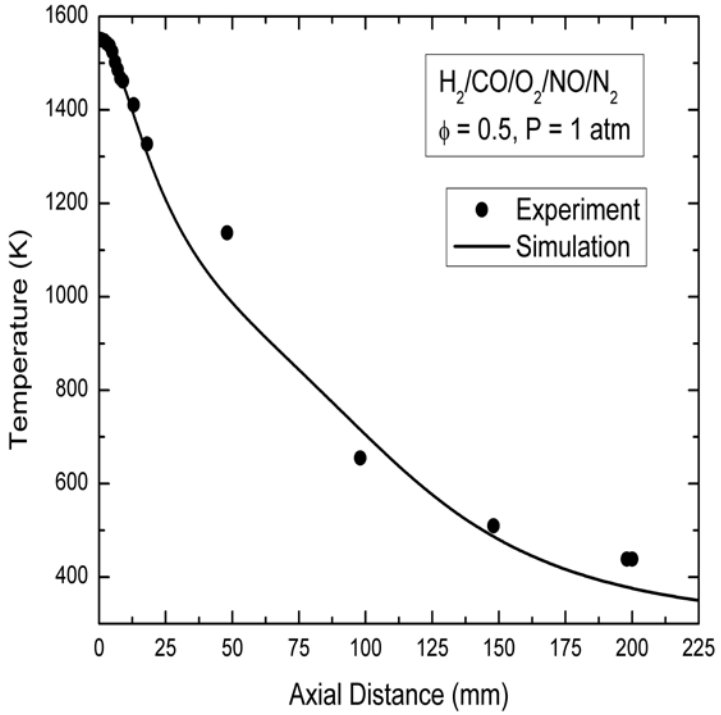

- Temperature decreases as going away from the burner.
- A uniform temperature profile was obtained for a radius of 7mm.

# Temperature Predictions with CFD Modeling

## 2-D Temperature Profile



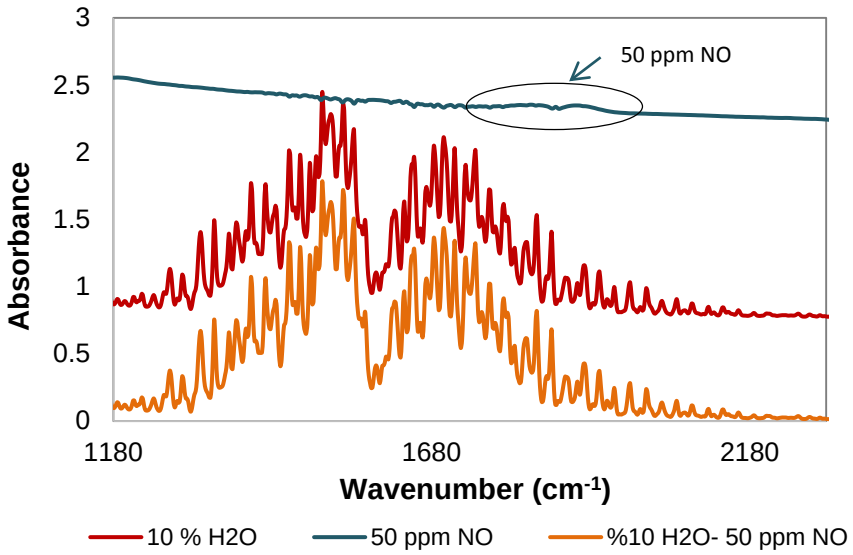

## Centerline Temperature Profile




- CFD simulations reasonably predicts the experimental temperature distribution

# $NO_x$ Measurements with FTIR Spectroscopy

- FTIR spectroscopy is employed for speciation measurements.
- Overlapping peaks for the gases of interest.

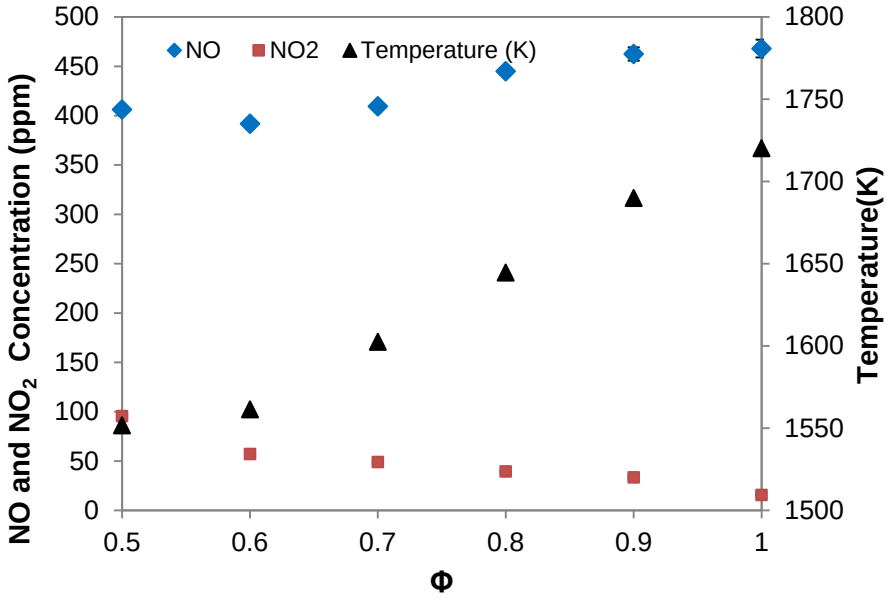


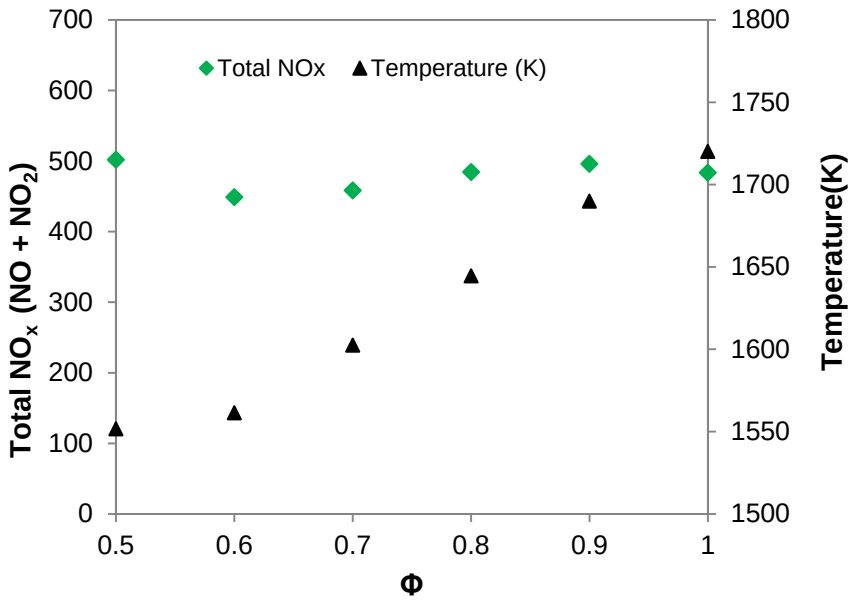

- To deconvolute the overlapping peaks, multivariate calibration was conducted.

| Species | $NO$-$H_2O$ | $NO_2$-$H_2O$ | $N_2O$-$H_2O$ |
|---|---|---|---|
| Experimental sets | 36 | 36 | 36 |

# $NO_x$ Speciation Data

## $NO_x$ vs. Φ with $H_2$/CO:1 and 500 ppm NO in the feed




As Φ increases ➡

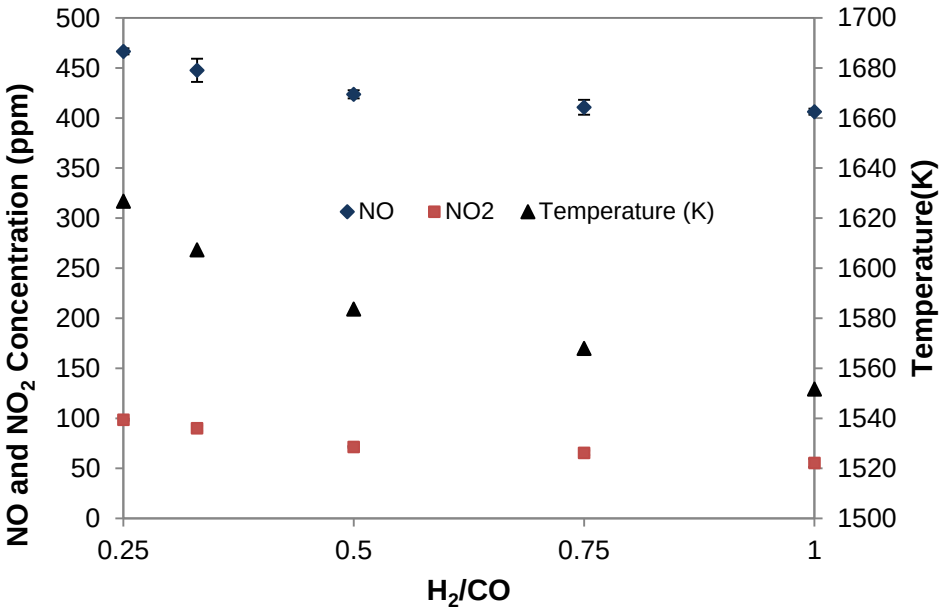
NO concentration ↑

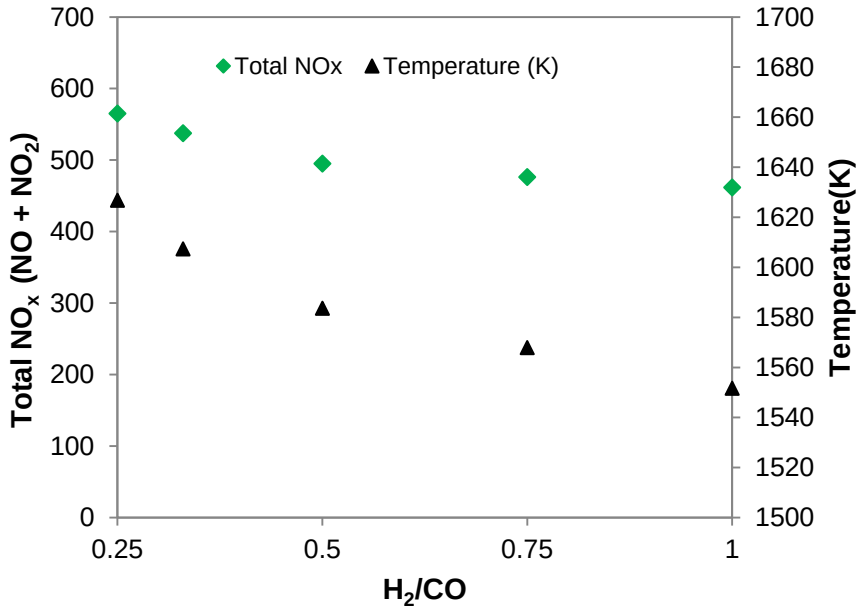
$NO_2$ concentration ↓

Total $NO_x$ does not change much

# $NO_x$ Speciation Data

## $NO_x$ vs. $H_2$/CO with Φ =0.5 and 500 ppm NO in the feed



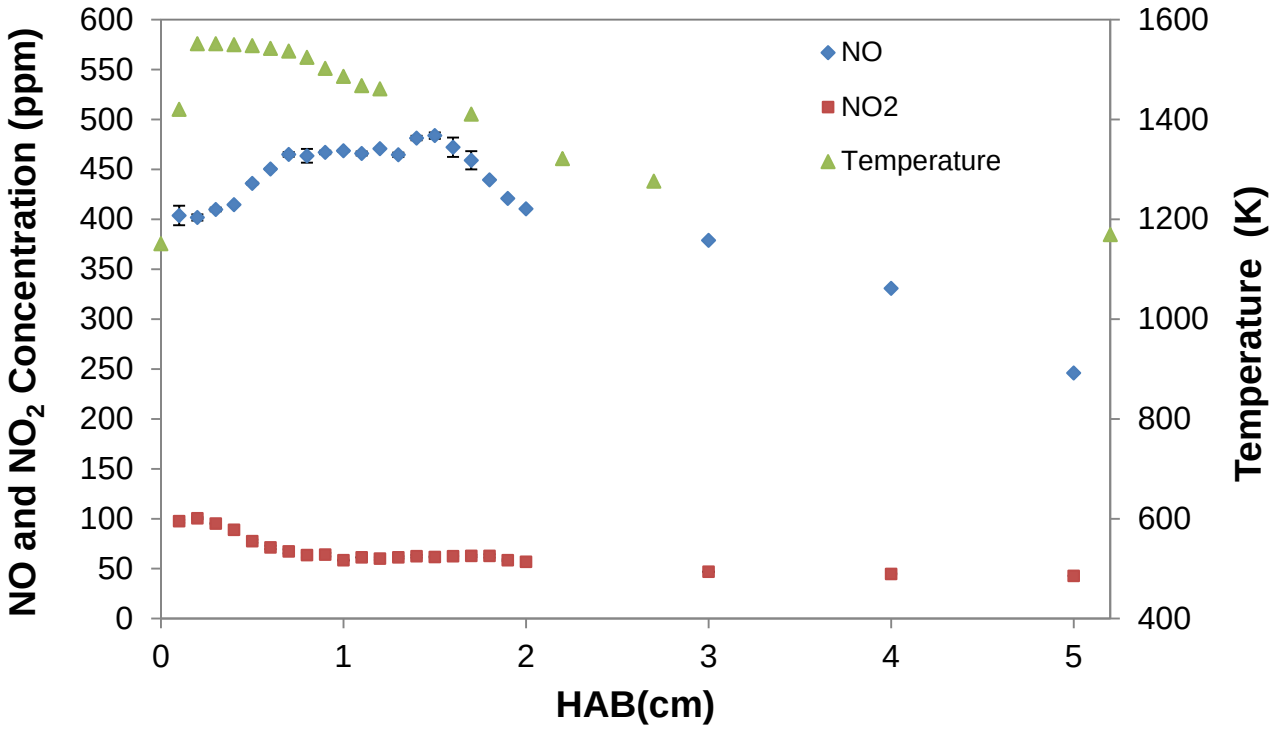

As $H_2$/CO increases ➡

- NO concentration ↓
- $NO_2$ concentration ↓
- Total $NO_x$ ↓

# $NO_x$ Speciation Data

**NO, $NO_2$ profiles at different heights above burner (HAB)**

**$H_2$/CO=1, Φ=0.5 and 500 ppm NO in the feed**

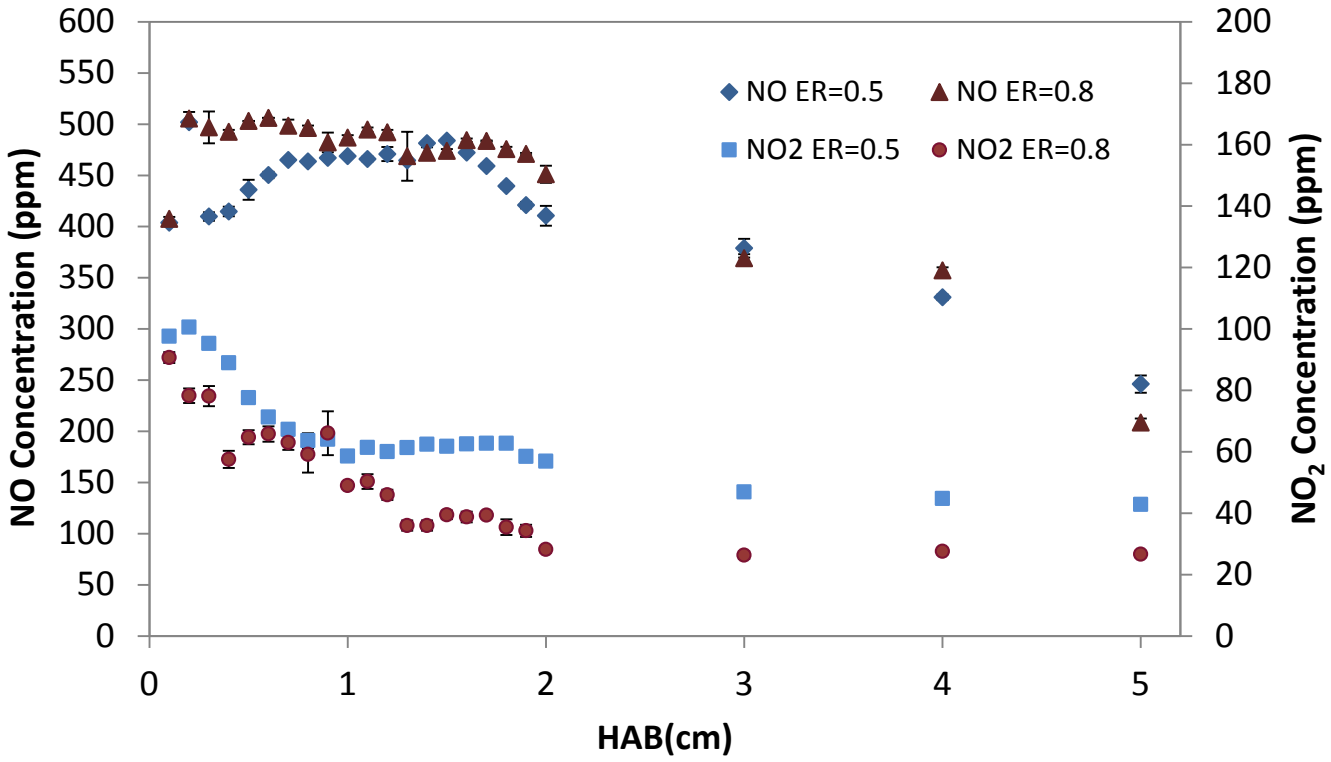



- Initially NO concentration increases due to $NO_2$ to NO conversion
- At lower T NO decreases due to NO to $N_2$ conversion
- No $N_2O$ was observed.

# $NO_x$ Speciation Data

**NO, $NO_2$ profiles at different heights above the burner (HAB)**

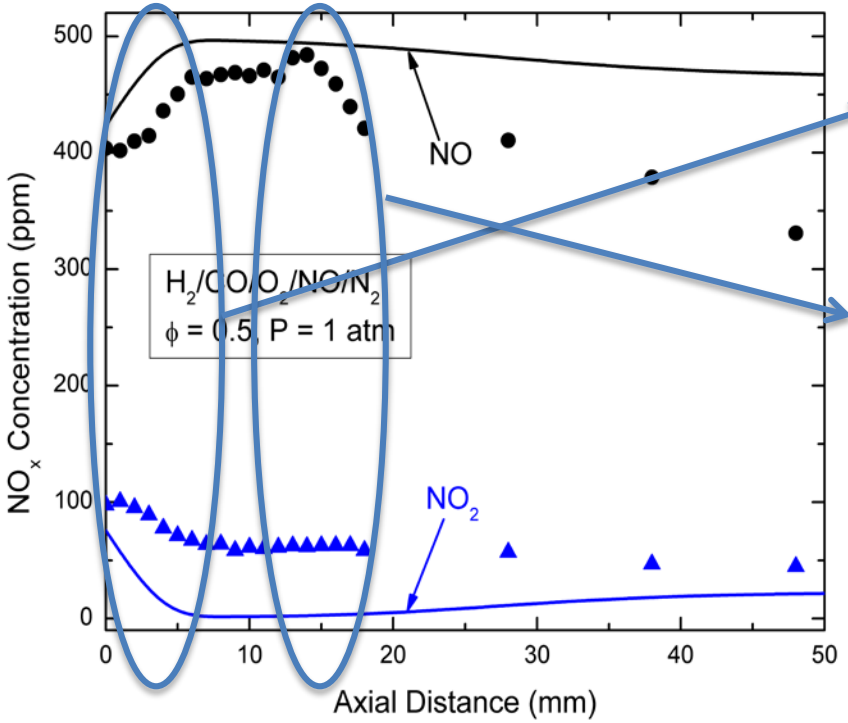
**Φ=0.5 and 0.8, $H_2$/CO=1 and 500 ppm NO injection**




As Φ increases ➡ NO concentration ↑

$NO_2$ concentration ↓

# $NO_x$ Speciation with CFD Modeling



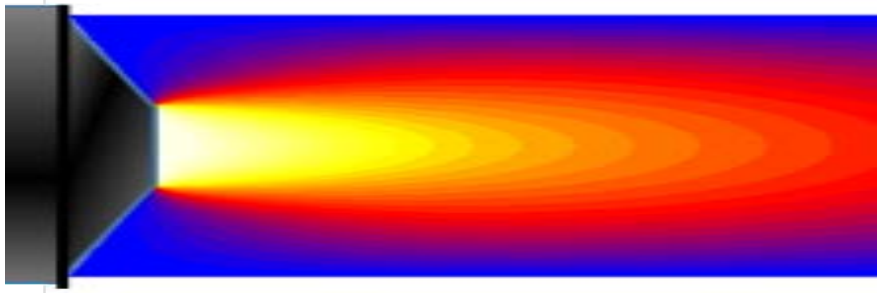

$NO_2$ to NO conversion

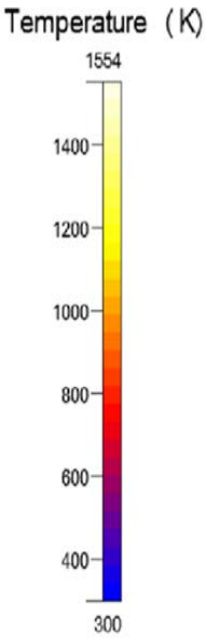
**$NO_2 + H = NO + OH$ (R1)**

NO to $N_2$ conversion

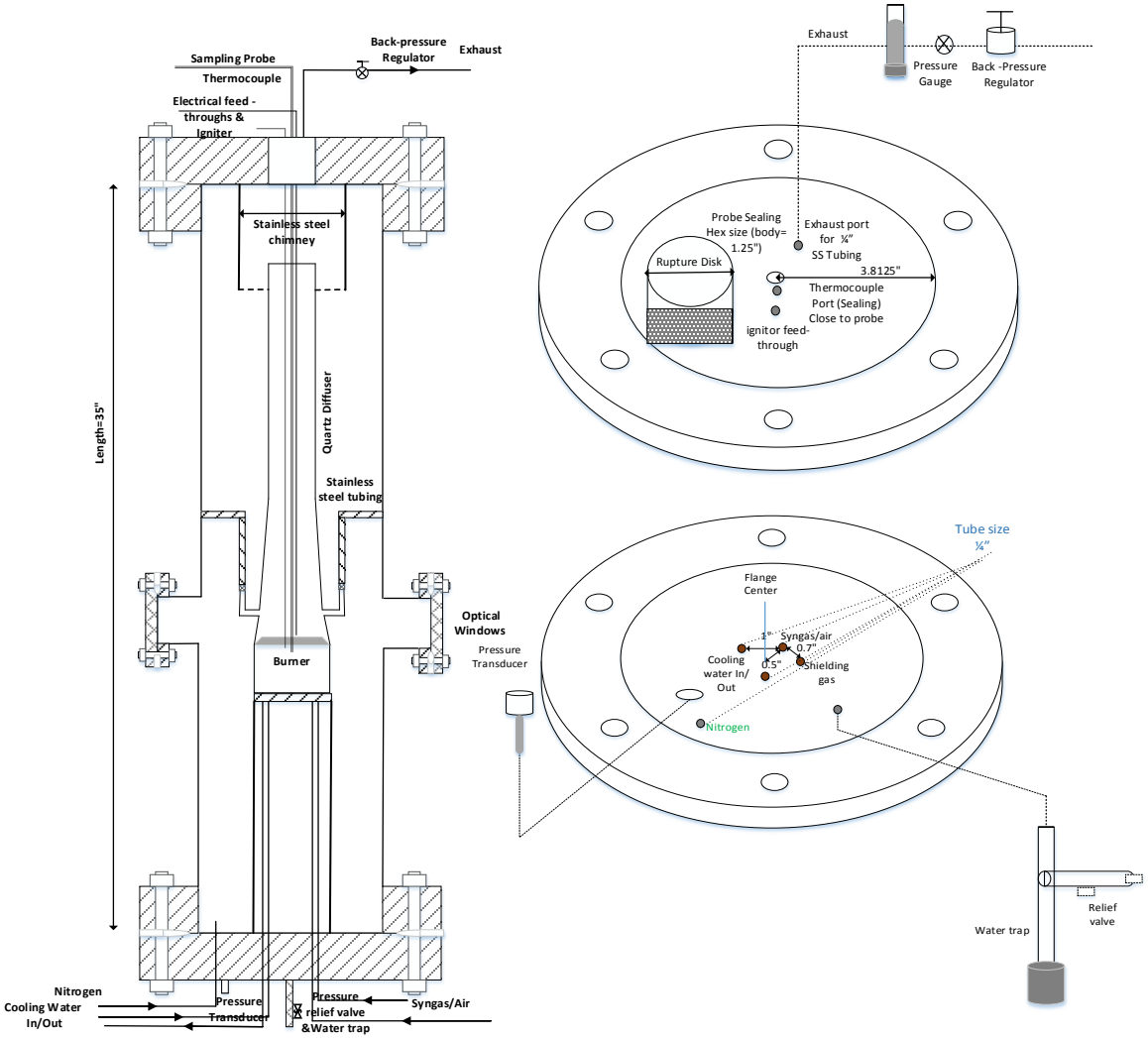
**$NO + N = N_2 + O$ (R2)**

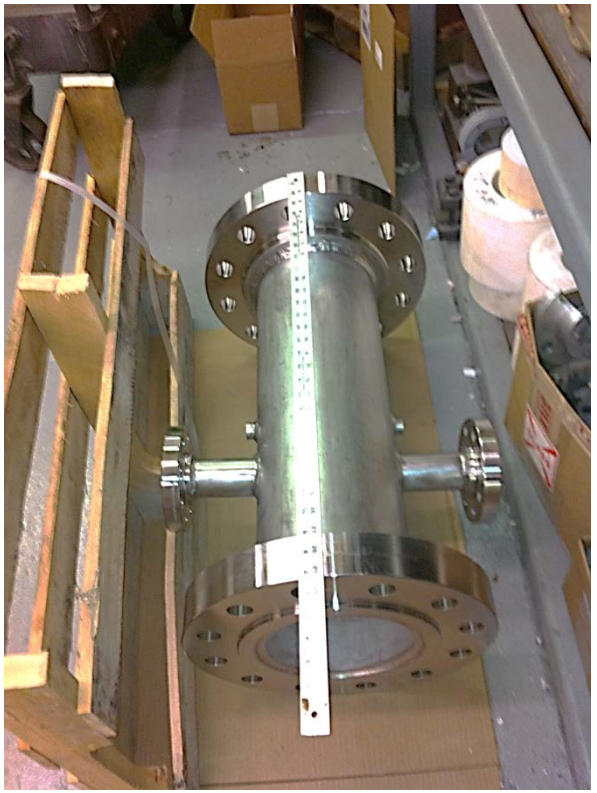
**$NO + H = N + OH$ (R3)**





# High Pressure System



# Summary

- Axial and radial temperature profiles has been measured – temperature of the reacting zone.
- $NO_x$ speciation data at atmospheric pressure was collected at different conditions.
- There was a reasonable agreement between experimental data and simulations.

## ***Future Work***

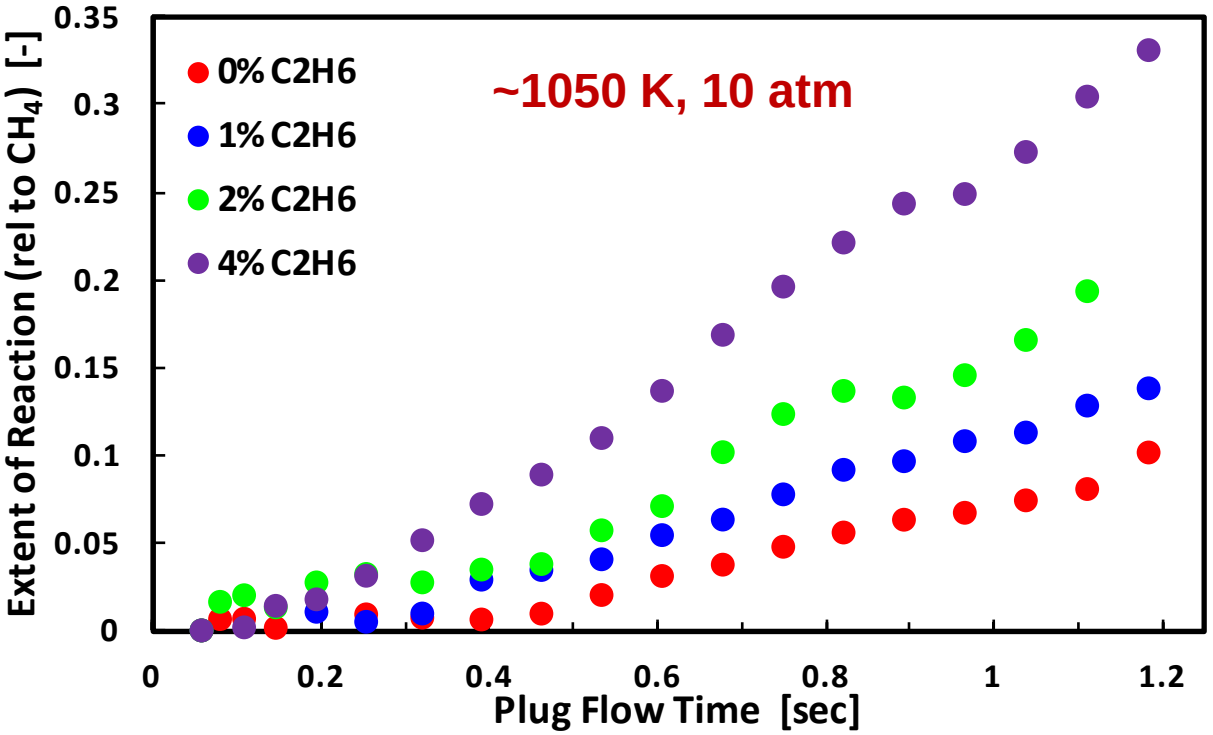
- $NO_x$-CO speciation data will be collected at higher pressures (1-15atm), considering the effect of different parameters such as hydrocarbons and diluents.
- Effect of exhaust gas recirculation will be investigated.

# Small Species Flow Reactor Pyrolysis/Oxidation Database

# $NO_x$-perturbed $CH_4$ + 2 % $C_2H_6$ "natural gas" oxidation

## Effect of increased $C_2H_6$ doping in $CH_4$ (without $NO_x$ addition)

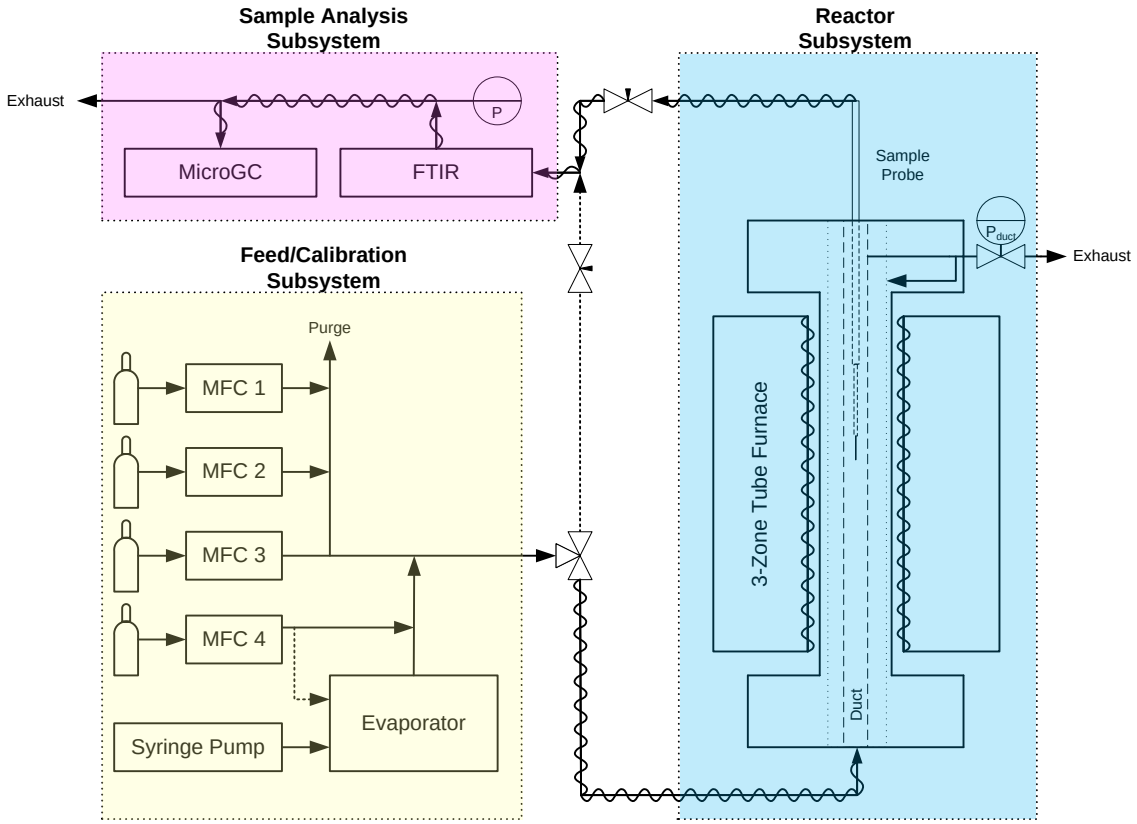
(recap from last UTSR review meeting)



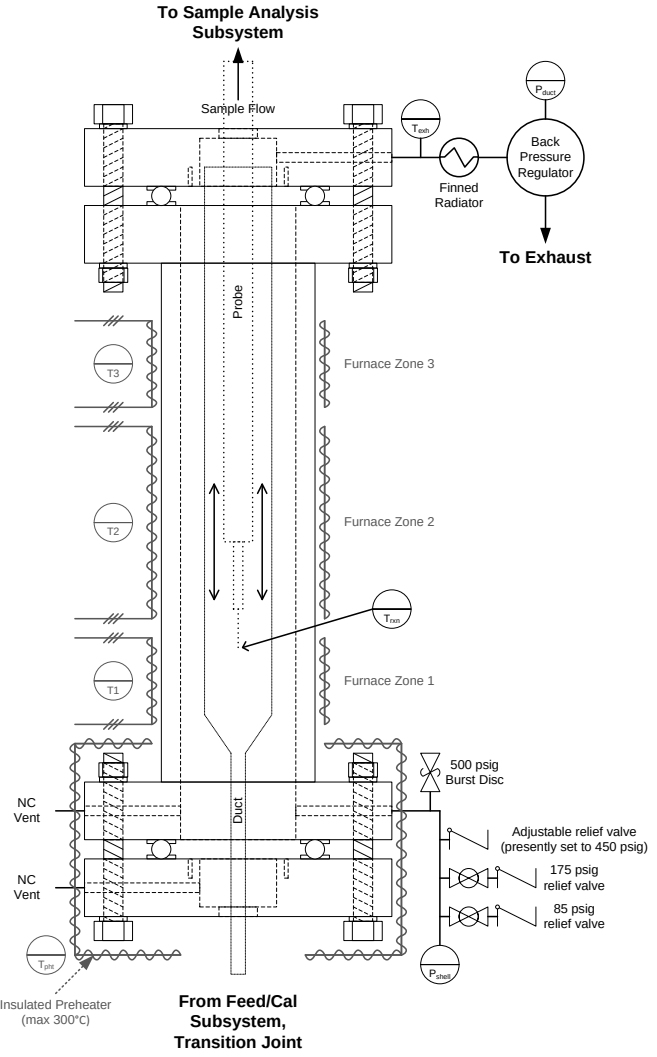

- Overall initial reactivity increases *threefold* for just 4% $C_2H_6$ in $CH_4$
- Additional reactivity expected with small (< 100 ppm) $NO_x$ addition
- $NO_x$ perturbed experiments use 2% $C_2H_6$ in $CH_4$ as a representative "natural gas"

# Experimental Setup: HPLFR Schematics

## Facility Overview




## Reactor Subsystem Detail



# $NO_x$ Perturbed Methane/Ethane Blend Study in High Pressure Laminar Flow Reactor

- Exploration of intricate interactions between $C_{1-2}$ and $NO_X$ kinetics.

- Constrain/further validate the Fenimore $NO_x$ mechanism.

- $NO_x$ kinetics for “Shale Gas” (near-future potential as stationary power generation gas turbines).

# Experimental Details

## ❑ Non-Reacting Cases (Nominal Values, ppm)

| | | |
|---|---|---|
| $CH_4$ | = | 9800 |
| $C_2H_6$ | = | 200 |
| $O_2$ | = | 20300 (ϕ=1.0) |
| NO | = | Nil |
| Ar | = | Balance |

%C ~ 1.02 %
Avoids excessive exothermicity

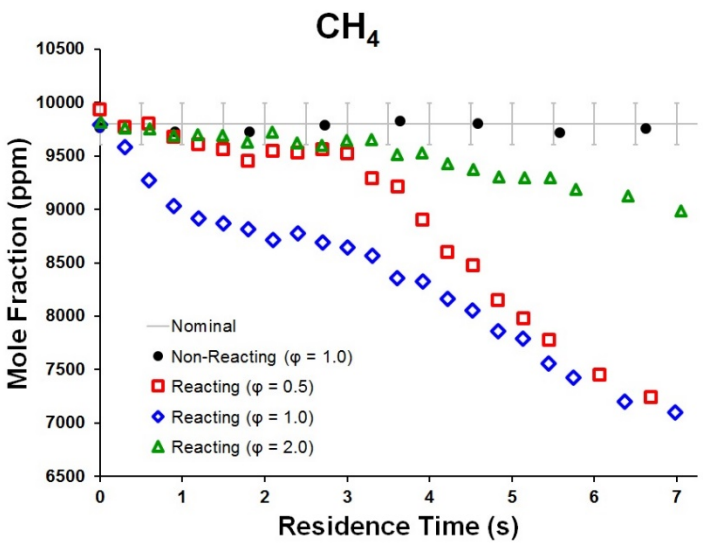
## ❑ Reacting Cases Run (Nominal Values, ppm)

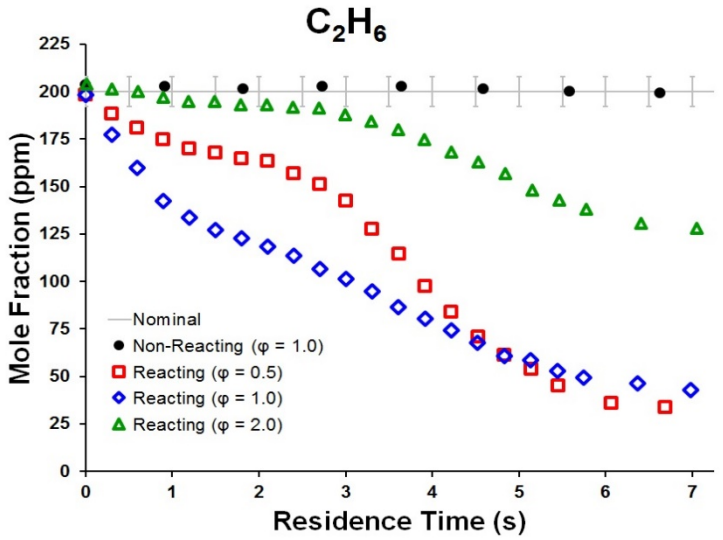
| | | |
|---|---|---|
| $CH_4$ | = | 9800 |
| $C_2H_6$ | = | 200 |
| $O_2$ | = | 20300 (ϕ=1.0) / 40600 (ϕ=0.5) / 10150 (ϕ=2.0) |
| NO | = | 25 |
| Ar | = | Balance |

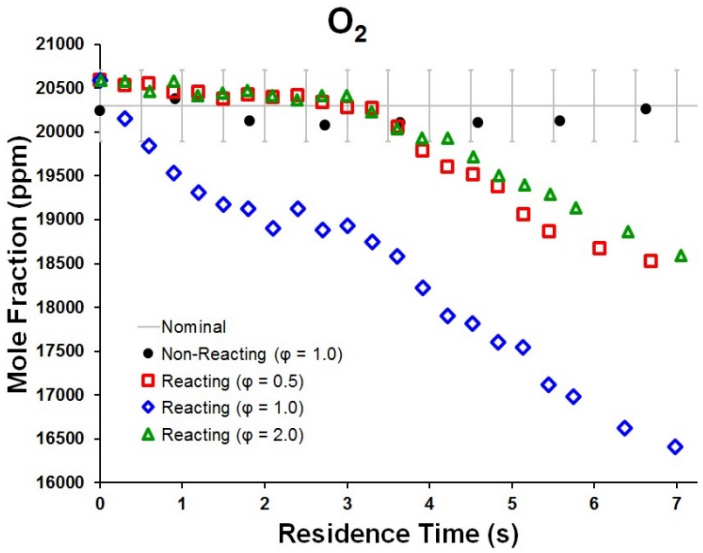
## ❑ P, T & $Q_{blend}$ (Nominal Values)

| | | |
|---|---|---|
| P | = | 5 & 10 atm |
| T | = | 820 K |
| $Q_{blend}$ | = | 650 sccm & 1300 sccm |

# HPLFR Experimental Measurements




- **Measurement Uncertainty**
  - $CH_4$ ~ 2%
  - $C_2H_6$ ~ 4%
  - $O_2$ ~ 2%
- **Illustration of $O_2$ measurement for rich & lean condition is scaled with respect to φ = 1.0 case**
- **Quantification in progress for**
  - CO $CO_2$ $C_2H_2$ $H_2O$

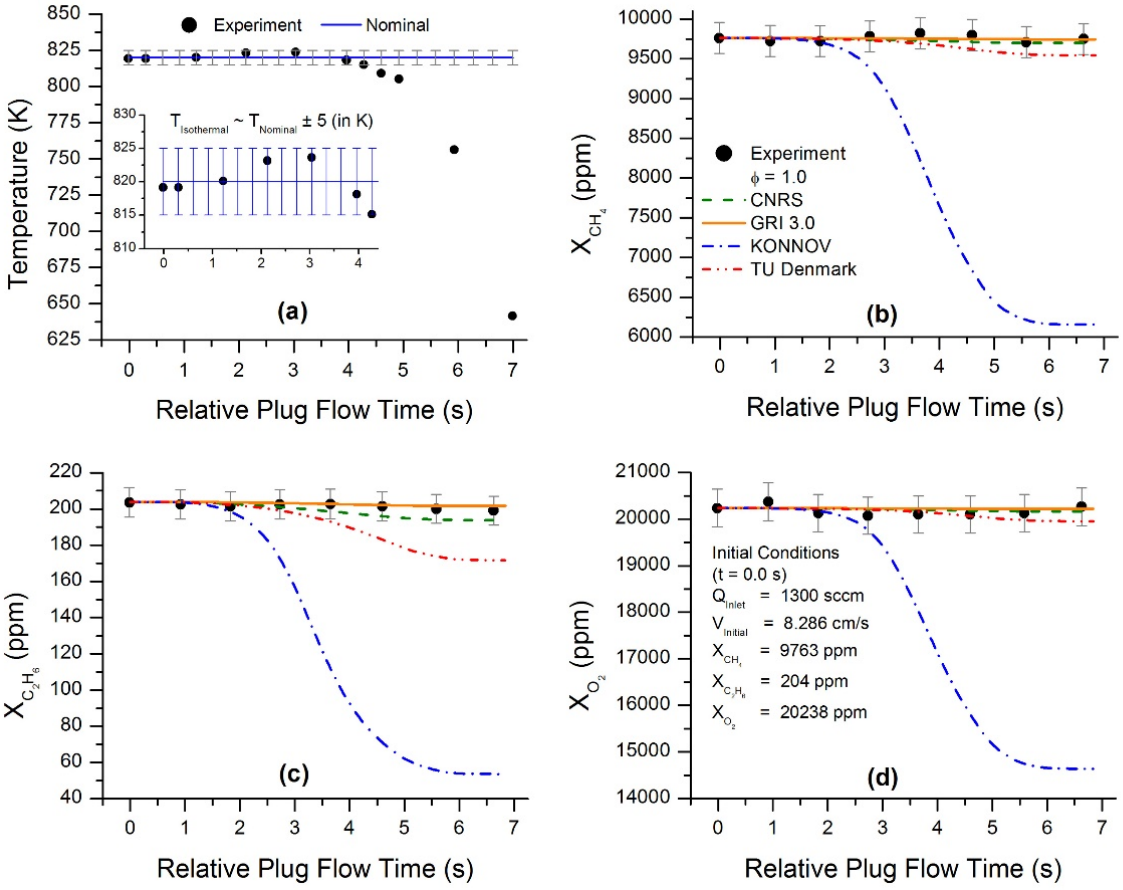
# Simulation # Non-Reacting Case

**P (Nominal) = 10 atm**
**T (Nominal) = 820 K**
**Φ = 1.0**

**$NO_x$ is not introduced**

**Fuel conversion is not observed.**

**Konnov et al. (2009) is particularly overly reactive under non-reacting condition !!!**




**GRI 3 # http://combustion.berkeley.edu/gri-mech/**
**CNRS # R. Sivaramakrishnan et al, PCCP (2007)**
**KONNOV # A.A. Konnov, C&F (2009)**
**TU Denmark # S. Gersen et al, POCI (2011)**

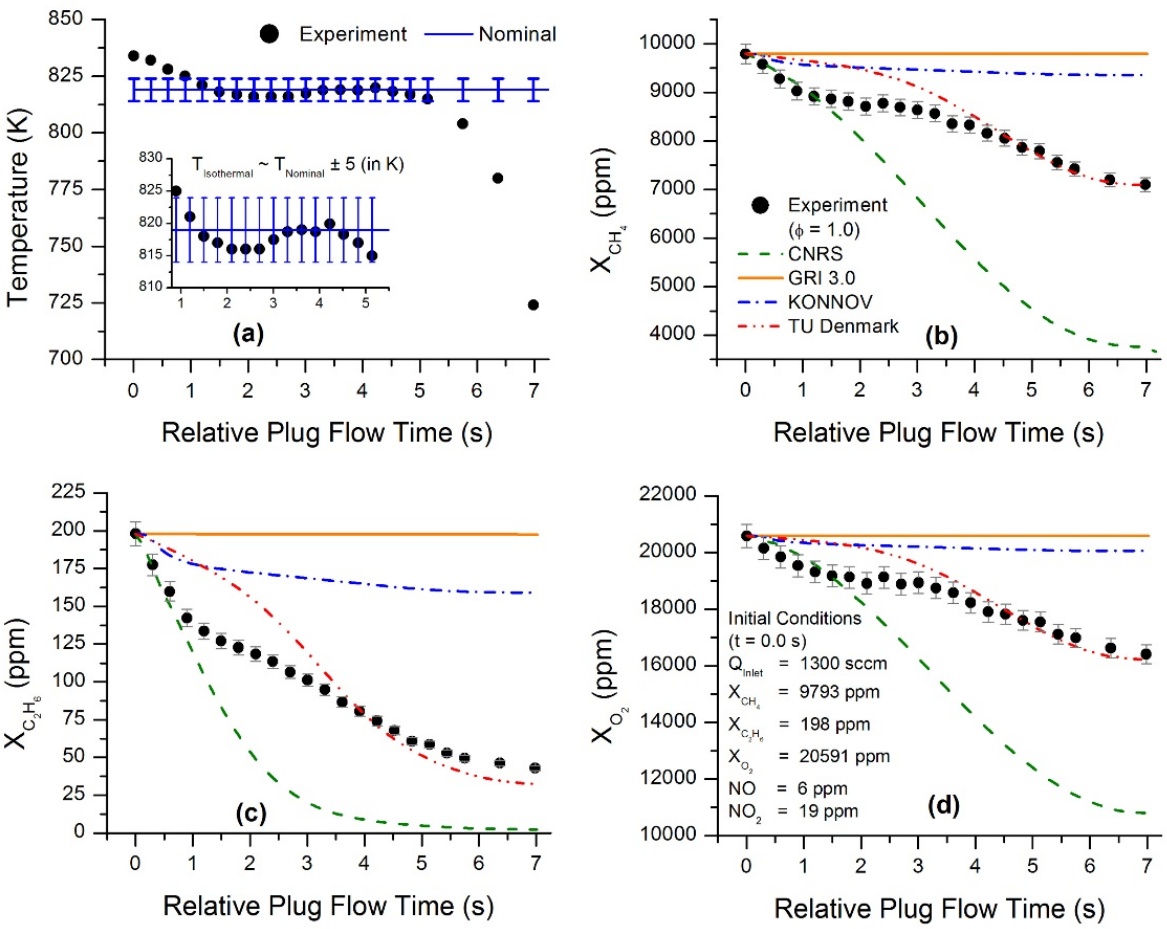
# Simulation # Reacting Case (with $NO_x$)

**P (Nominal) = 10 atm**
**T (Nominal) = 819 K**
**Φ = 1.0**
**NO = 25±1 ppm**

**Trace NO can enhance reactivity substantially !**

**CNRS is over-reactive whilst KONNOV mechanism is less reactive, even under reacting environment !!**

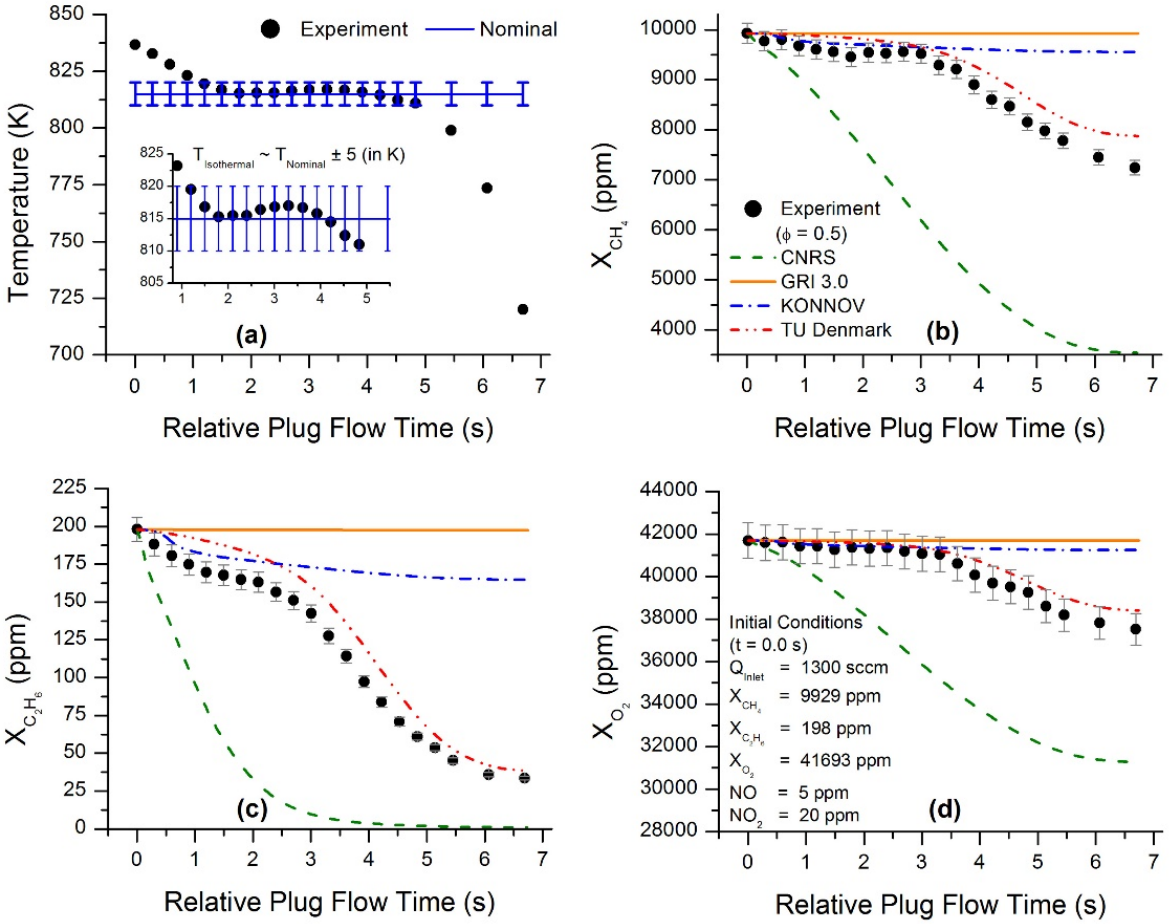
**TU Denmark predicts the best !!! Includes Nitro-methane/ethane chemistry.**



# Simulation # Reacting Case (with $NO_x$)

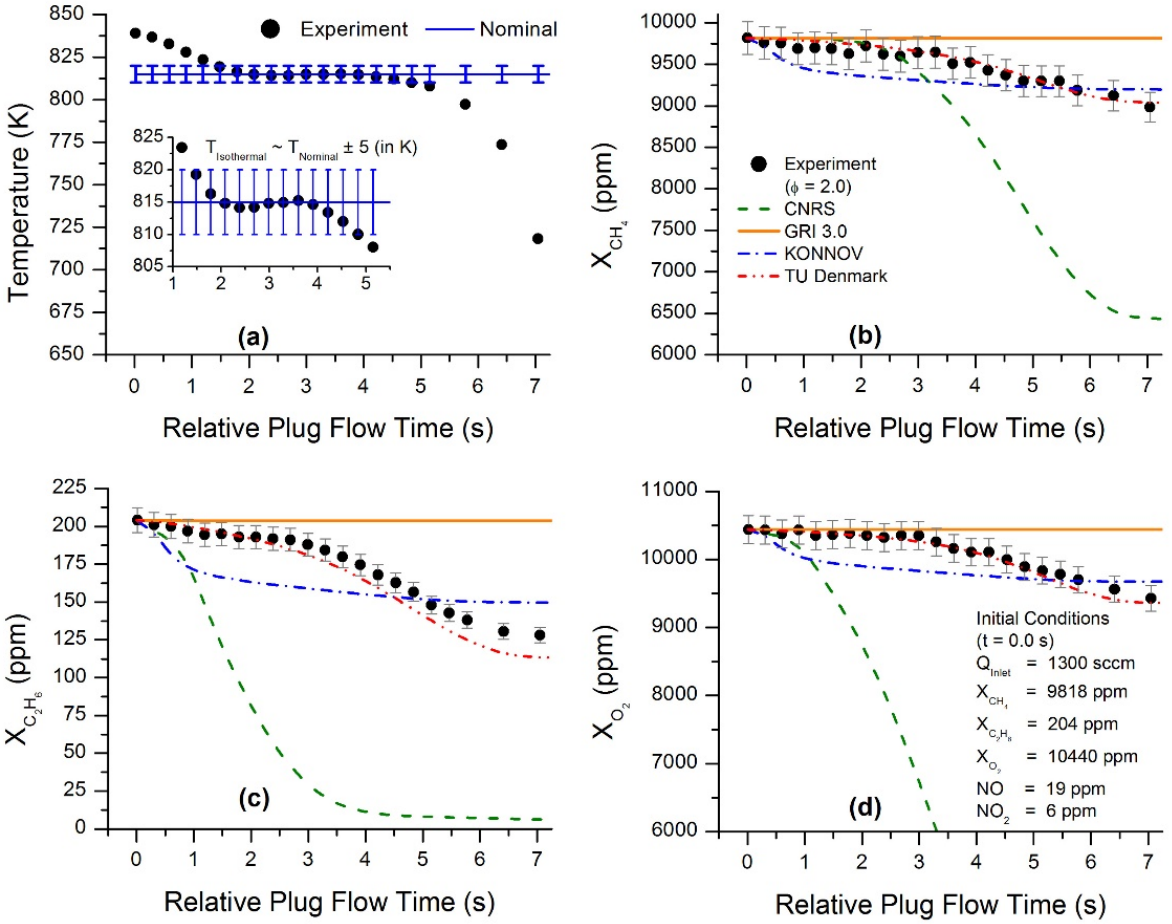
**P (Nominal) = 10 atm**
**T (Nominal) = 815 K**
**Φ = 0.5**
**NO = 25±1 ppm**

**Chemkin-Pro based imposed temperature profile Plug flow reactor (PFR) Model is used to simulate all three reacting cases**



# Simulation # Reacting Case (with $NO_x$)

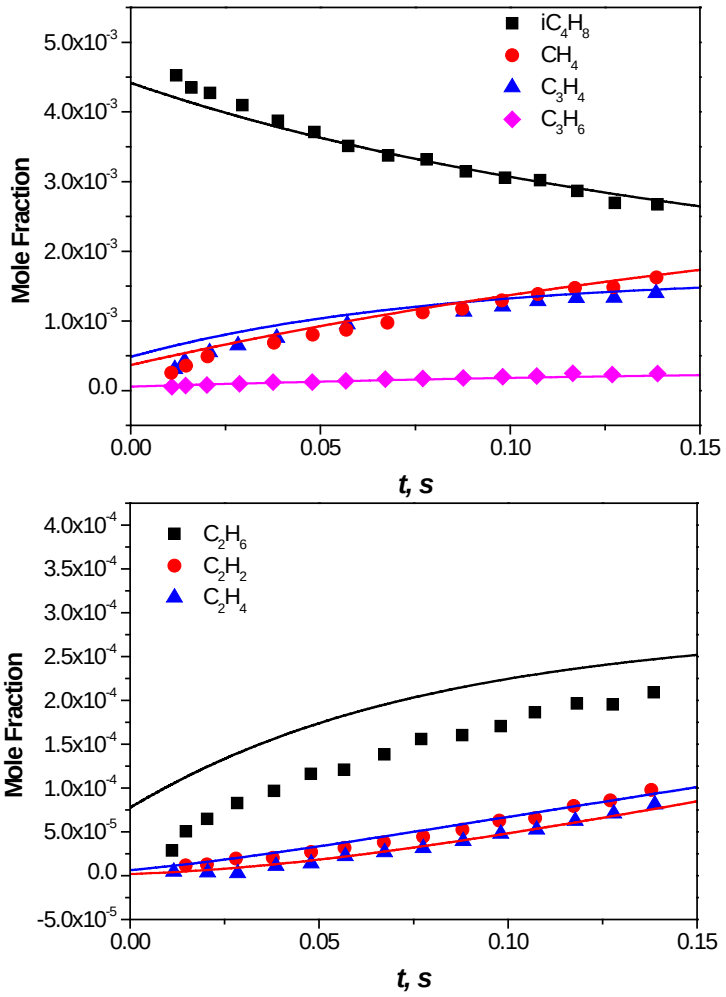
**P (Nominal) = 10 atm**
**T (Nominal) = 815 K**
**Φ = 2.0**
**NO = 25±1 ppm**



# Additional Small Species Database Efforts

## Isobutene pyrolysis/oxidation near 1145 K

### 5000 ppm $iC_4H_8$, φ = ∞




- Isobutene is a significant intermediate from isobutane oxidation
- Oxidation is relatively slow due to resonantly-stabilized isobutenyl radical
  - Pyrolytic pathways are competitive with oxidative ones
- Limited (reliable) pyrolysis data available in the literature
- Present flow reactor data motivated significant revisions to $iC_4H_8$ pyrolysis kinetics of previous model iteration
- Major/minor species generally predicted well, with some over prediction of $C_2H_6$ likely due to consumption pathways (i.e., not formation via $CH_3$ recombination)



1. Zhou, Li, O'Connor, Somers, Thion, Keesee, Mathieu, Petersen, DeVerter, Oehlschlaeger, Kukkadapu, Sung, Alrefae, Khaled, Farooq, Direnberger, Glaude, Battin-LeClerc, Santner, Ju, Held, Haas, Dryer, and Curran, submitted to *Combust Flame*

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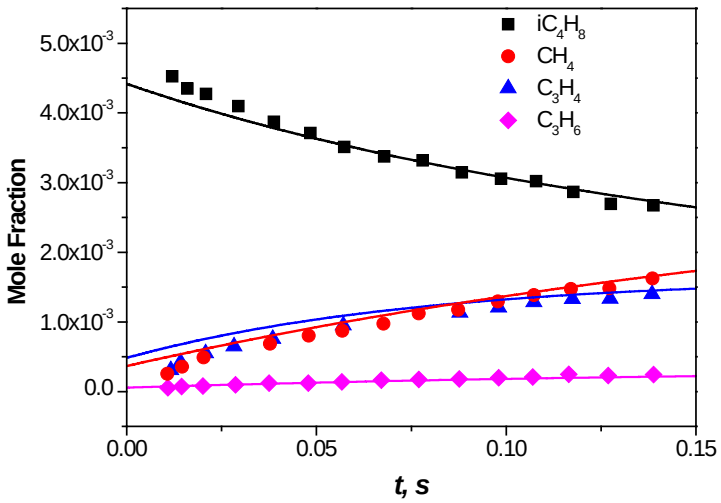
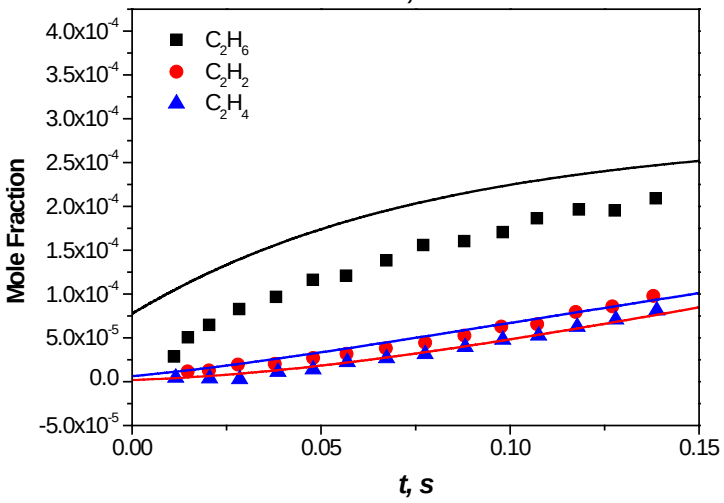
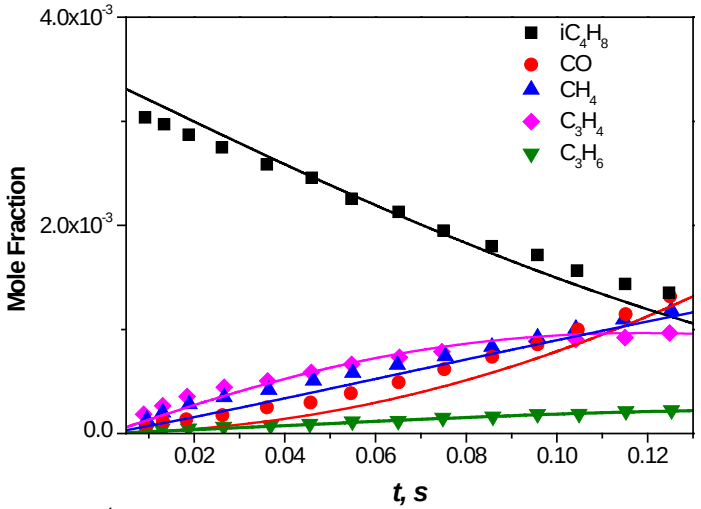
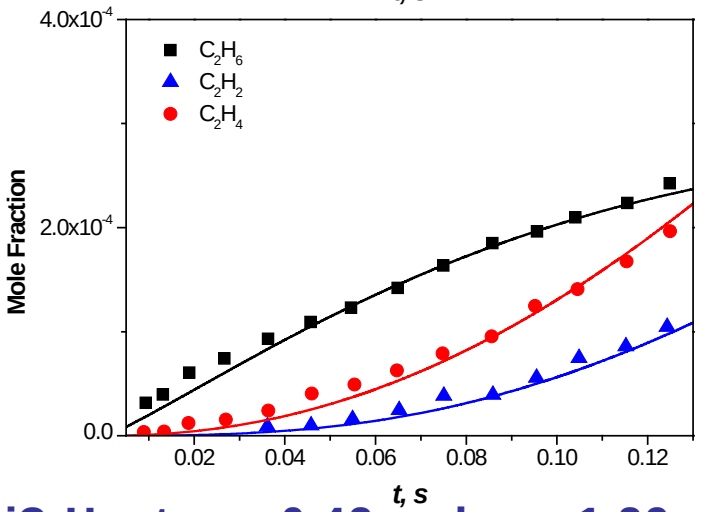



### 3400 ppm $iC_4H_8$, φ = 0.91




**Also measurements for ~3400 ppm $iC_4H_8$ at φ = 0.42 and φ = 1.29**



1. Zhou, Li, O'Connor, Somers, Thion, Keesee, Mathieu, Petersen, DeVerter, Oehlschlaeger, Kukkadapu, Sung, Alrefae, Khaled, Farooq, Direnberger, Glaude, Battin-LeClerc, Santner, Ju, Held, Haas, Dryer, and Curran, submitted to *Combust Flame*

# Experimental Measurements with (In-Progress) Modeling

## Isobutane oxidation

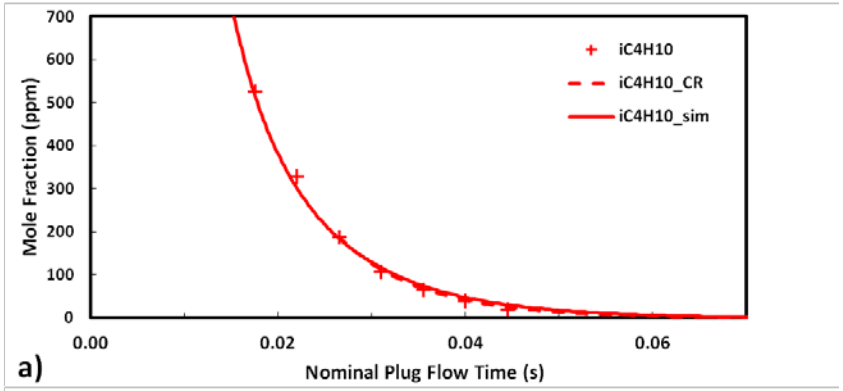
- Six speciated oxidation experiments at temperatures similar to isobutene experiments discussed:

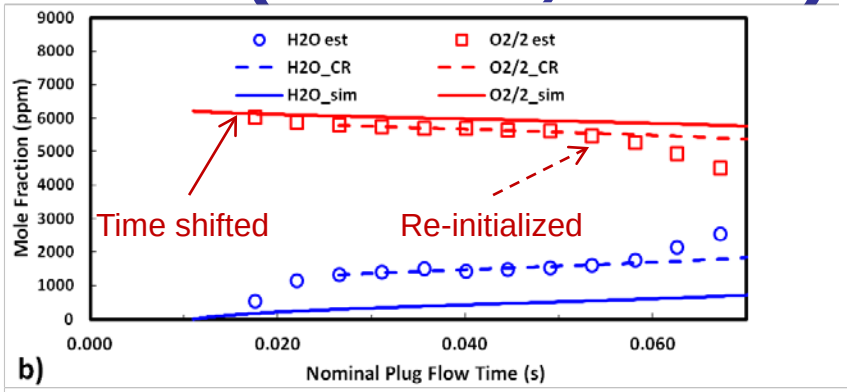
| Experiment Reference | Nominal Initial Conditions | | | |
|---|---|---|---|---|
| | Temperature (K) | iC4H10 (ppm) | O2 (ppm) | Nominal ϕ |
| IB1 | 1154 | 850 | 18100 | 0.3 |
| IB2 | 1191 | 1500 | 12400 | 0.8 |
| IB3 | 1184 | 2400 | 10400 | 1.5 |
| IB4 | 1110 | 1100 | 23900 | 0.3 |
| IB5 | 1152 | 1600 | 15100 | 0.7 |
| IB6 | 1225 | 1500 | 6050 | 1.6 |

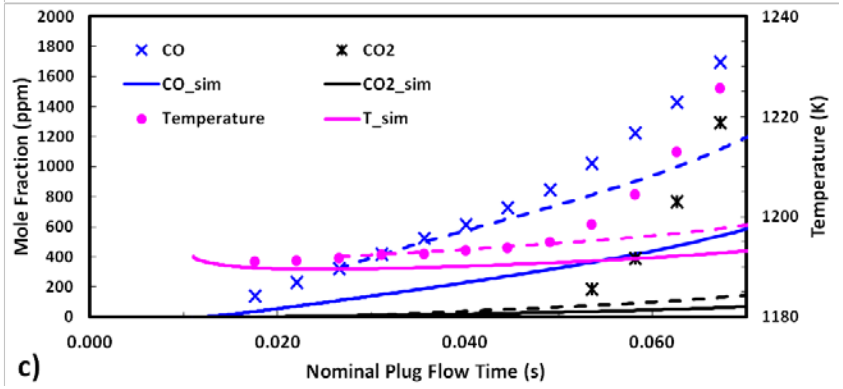
- Present modeling efforts focused on testing robustness of assumed initial conditions (ideal zero dimensional vs. time-shift vs. computational re-initialization vs. others)
- Updated kinetic sub-model for isobutene has yet to be tested against present flow reactor isobutane data

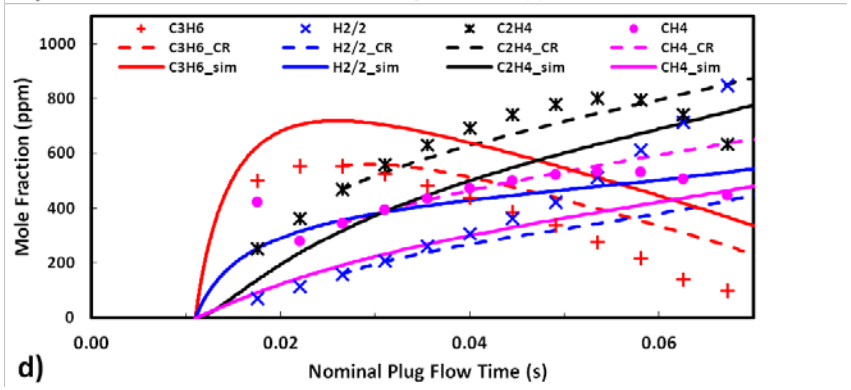
# Experimental Measurements with (In-Progress Modeling)

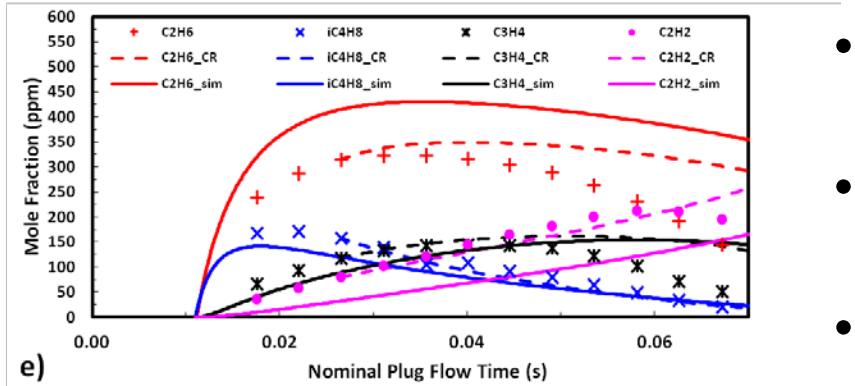
## Isobutane oxidation – Case IB2 (1191 K, 1 atm)



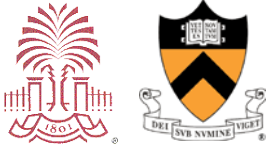

- Consumption of $iC_4H_{10}$ and daughter $iC_4H_8$ predicted well
- Discrepancies primarily due to under-predicted T evolution?
- Effect of updated $iC_4H_8$ sub-model?

# Overall Summary

- $H_2$/CO/$NO_x$ model developed validated against a large dataset
- $C_0$ – $C_4$ $NO_x$ is being developed
- Chemical and physical perturbation effects on global combustion markers

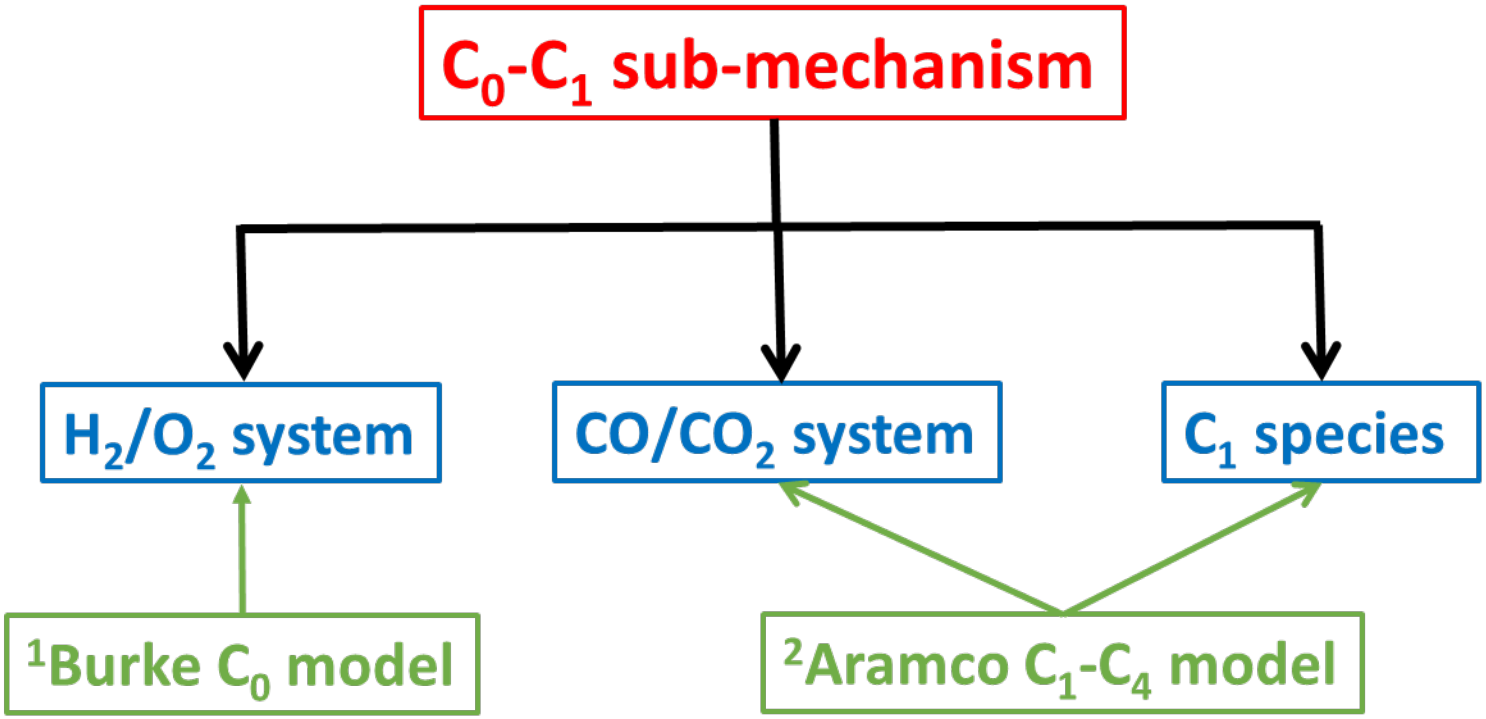
- Atmospheric pressure burner experiments, flame- post flame speciation, temperature measurements
- Multi-dimensional CFD model with detailed chemical kinetics

- Species-resolved measurements from flow reactor oxidation of small hydrocarbon species ($C_4$ and smaller) and $H_2$ add to the database of experimental measurements relevant to improving the fidelity of high hydrogen content (HHC) fuels and natural gas combustion predictions for gas turbine applications
- Present database considers fuels composed of $H_2$, $CH_4$, $C_2H_6$ (with significant $C_2H_4$ daughter intermediates), $C_3H_6$, $iC_4H_8$, and $iC_4H_{10}$. Oxidation may be in presence/absence of added trace $NO_x$
- Modeling efforts are ongoing and are considering not only different available kinetic models, but also assumptions regarding initial conditions
- Detailed and reduced model constructs will be available



# Thank You

# Model Elements: Proposed $H_2/CO/NO_x$ Model

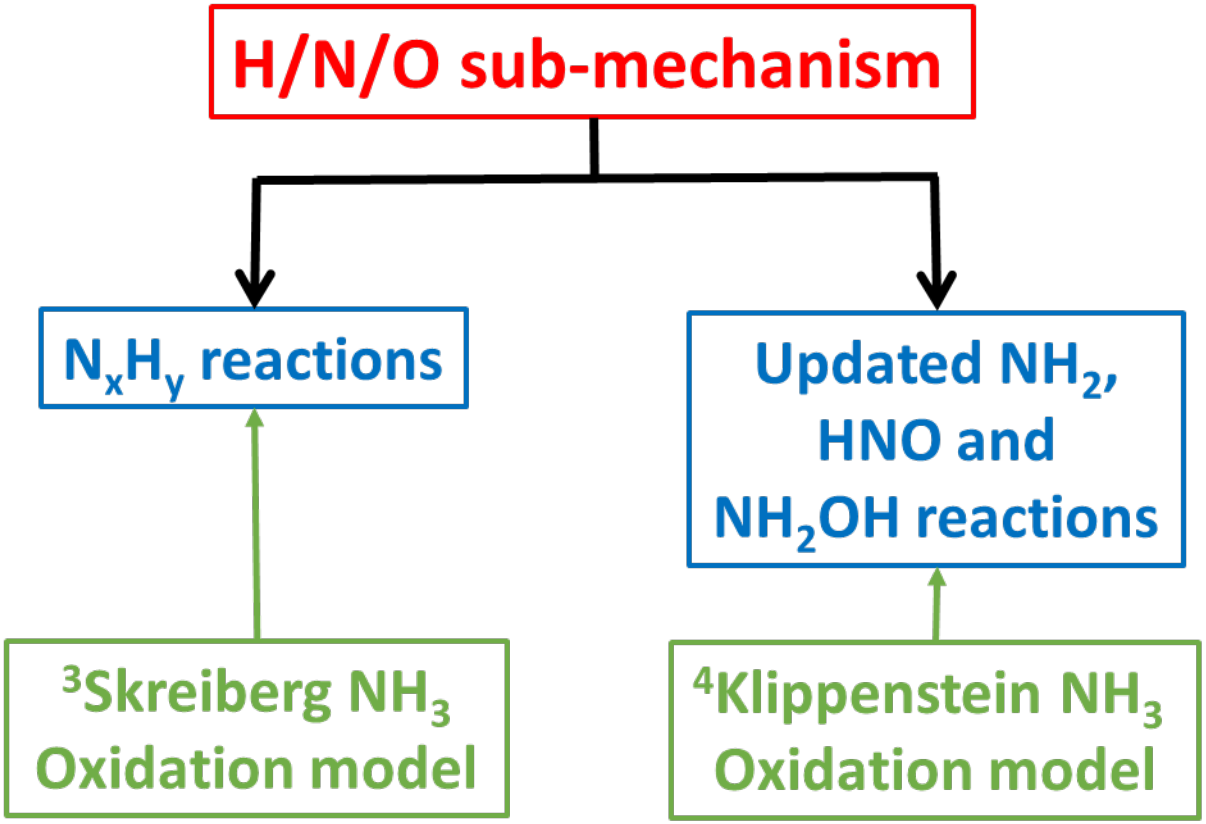



*No HOCO chemistry considered*

[1]Burke et al., Int. J. Chem. Kinet. 44 (2012)

[2]Metcalfe et al., Int. J. Chem. Kinet. 45 (2013)

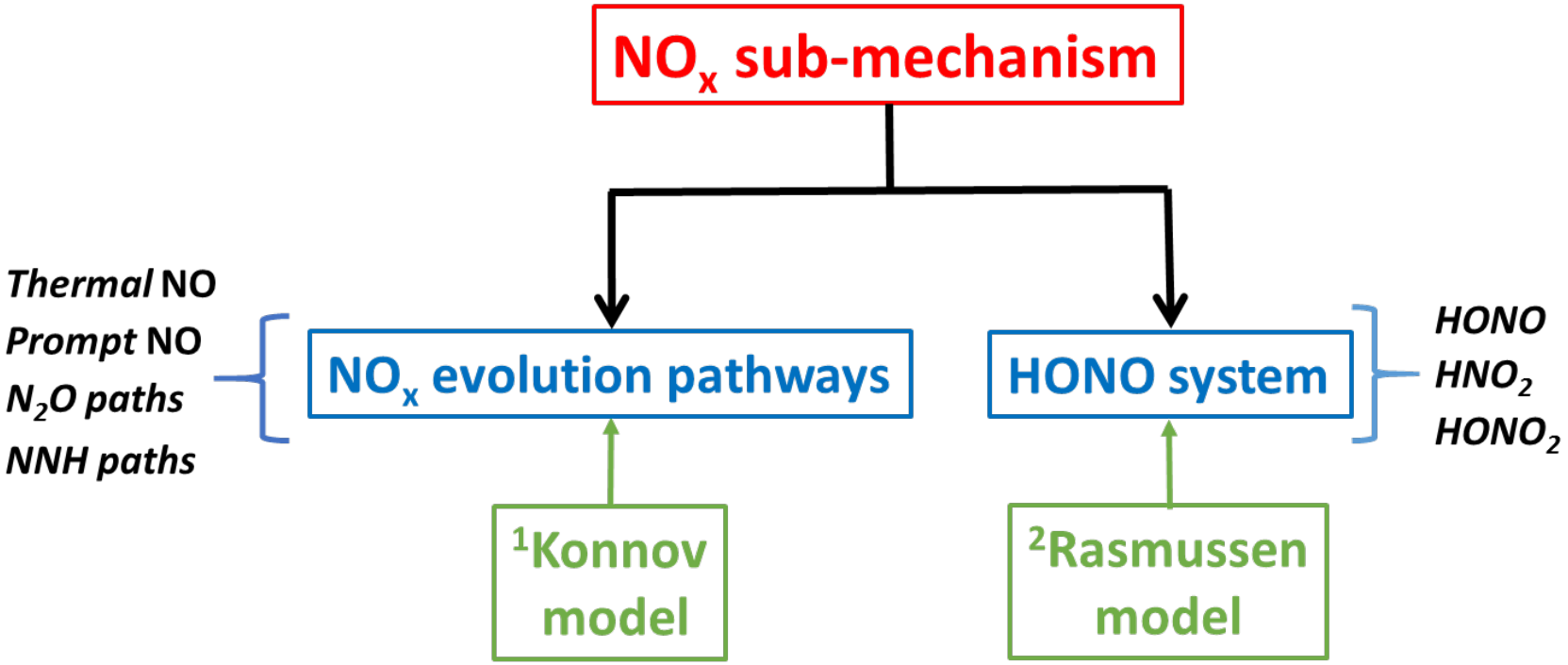
# Model Elements: Proposed $H_2/CO/NO_x$ Model




[3]Skreiberg et al., Combust. Flame 136 (2004)

[4]Klippenstein et al., Combust. Flame 158 (2011)

# Model Elements: Proposed $H_2/CO/NO_x$ Model

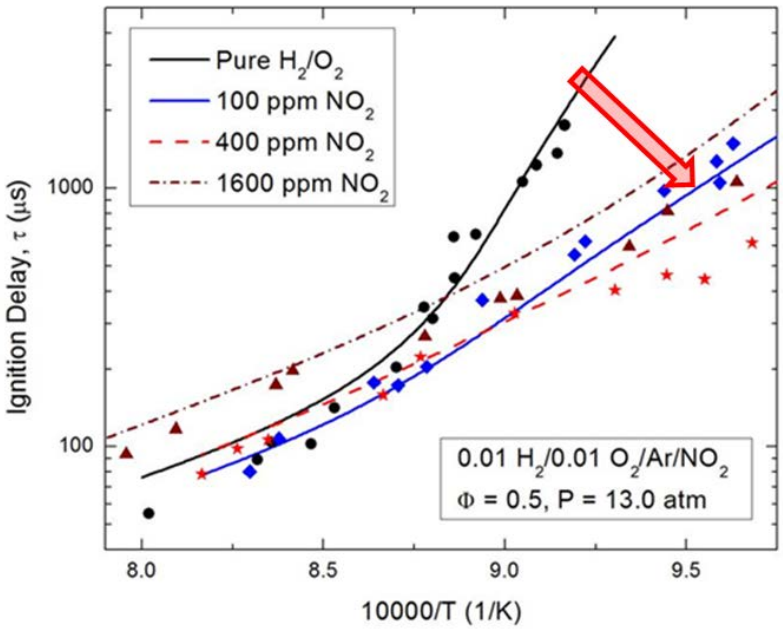


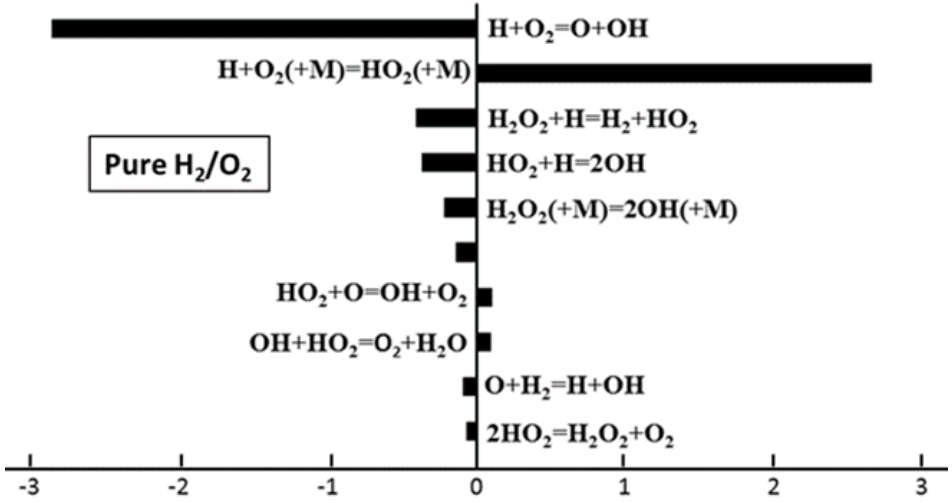

[1]Konnov et al., Combust. Flame 156 (2009)

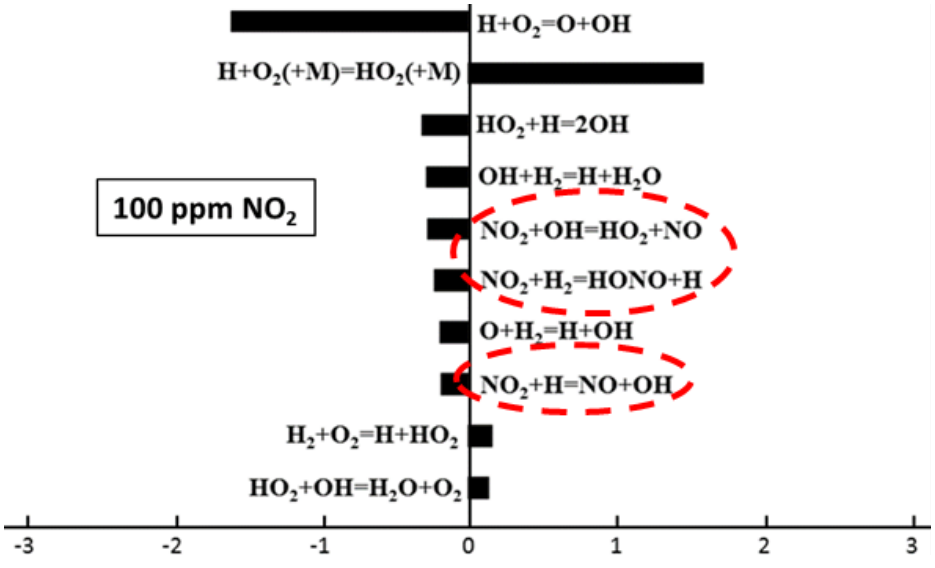
[2]Rasmussen et al., Int. J. Chem. Kinet. 40 (2008)

# Proposed Model Performance: Ignition Delay

## Dependence of $\tau_{ig}$ on initial $NO_2$ doping for $H_2/O_2$ system




**High pressure non-monotonic behavior captured by the model**

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

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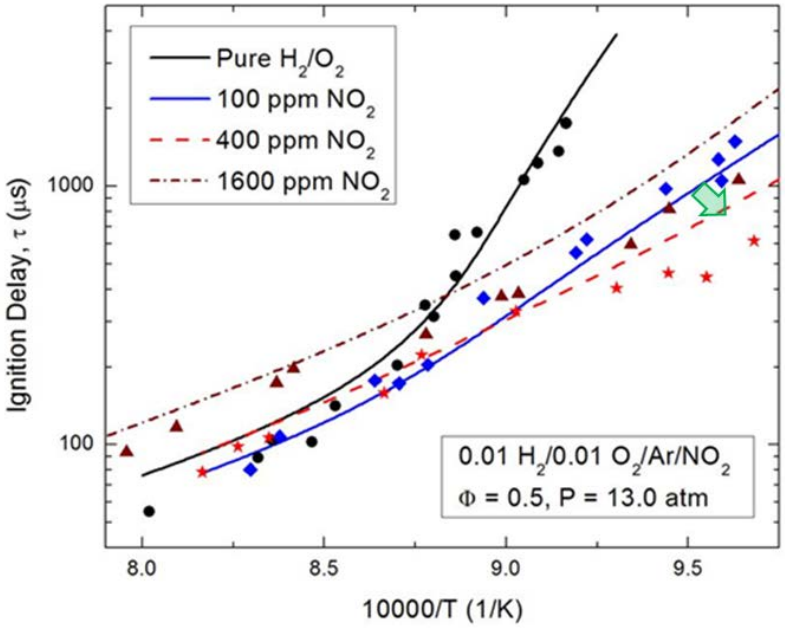


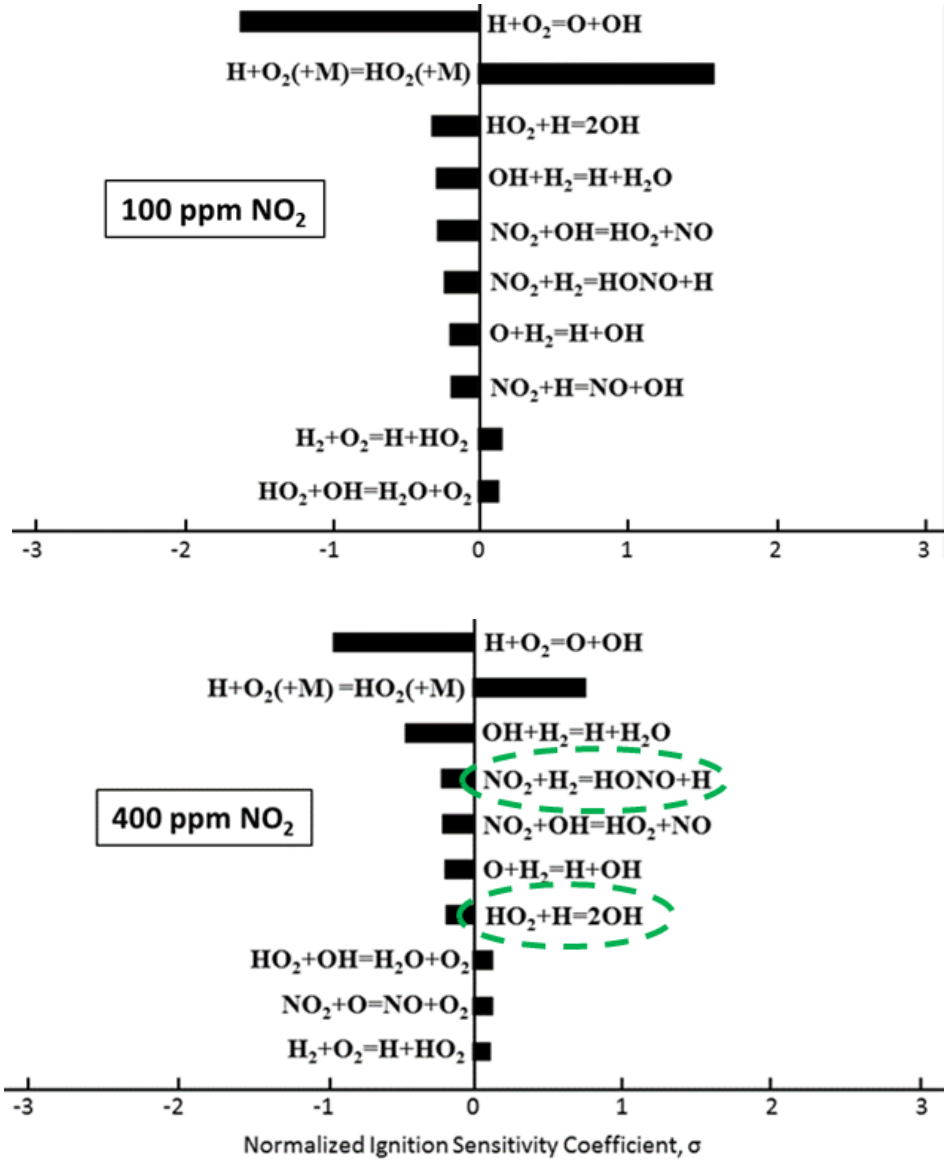


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*Mathieu et al., Proc. Combust. Inst. 34 (2013)*

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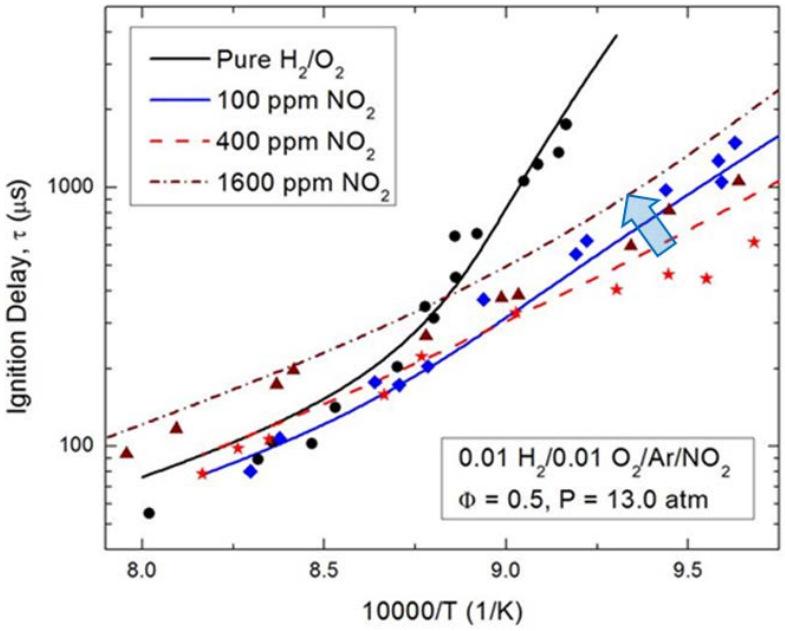
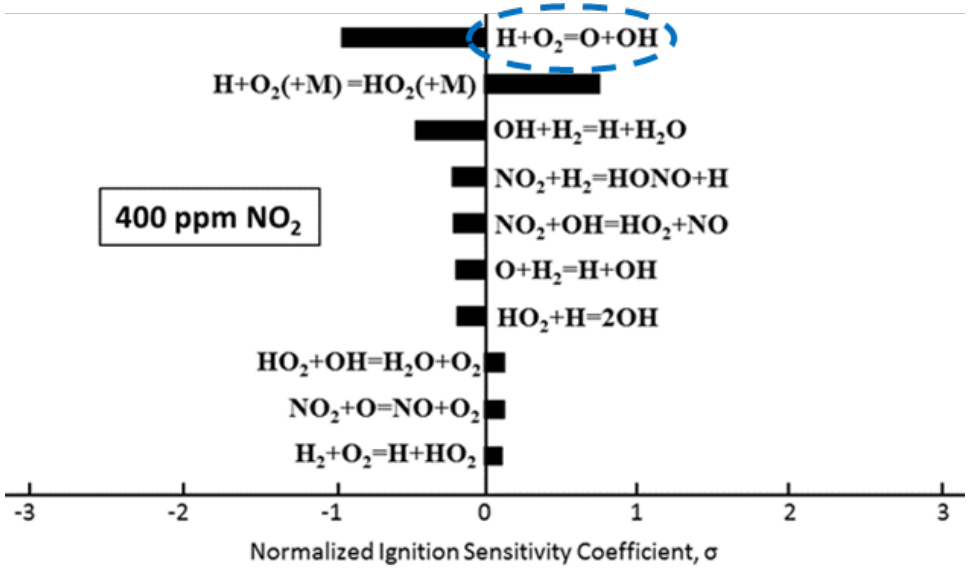
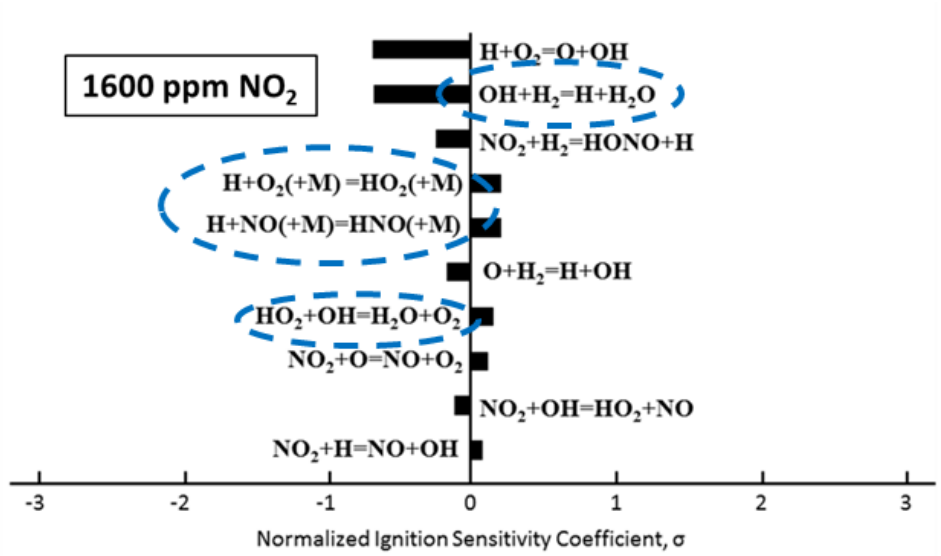


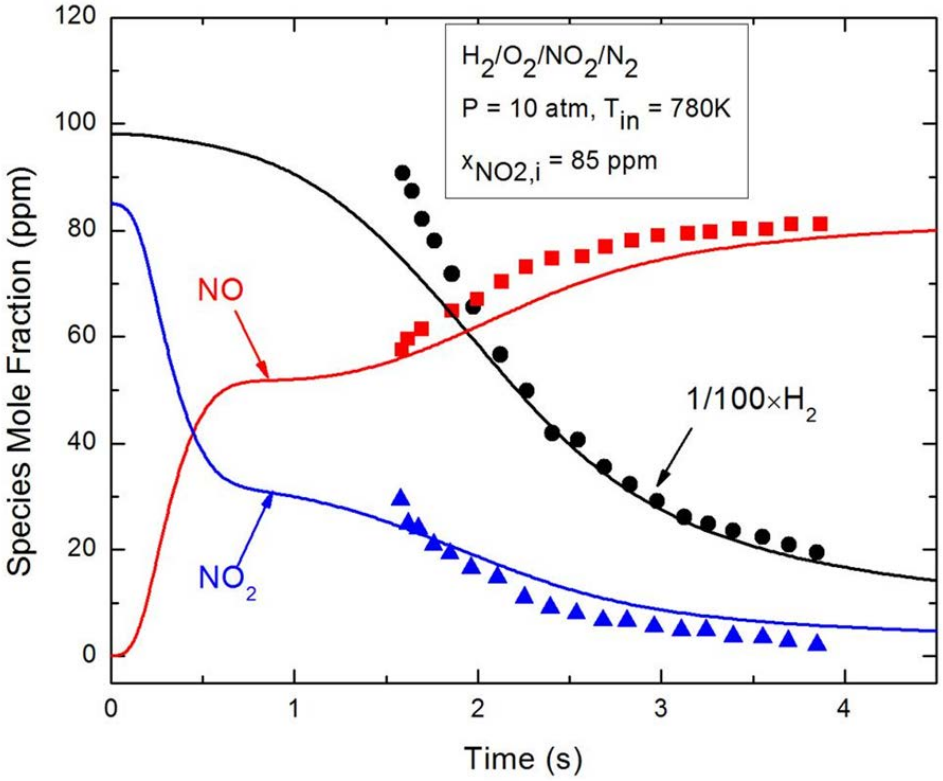



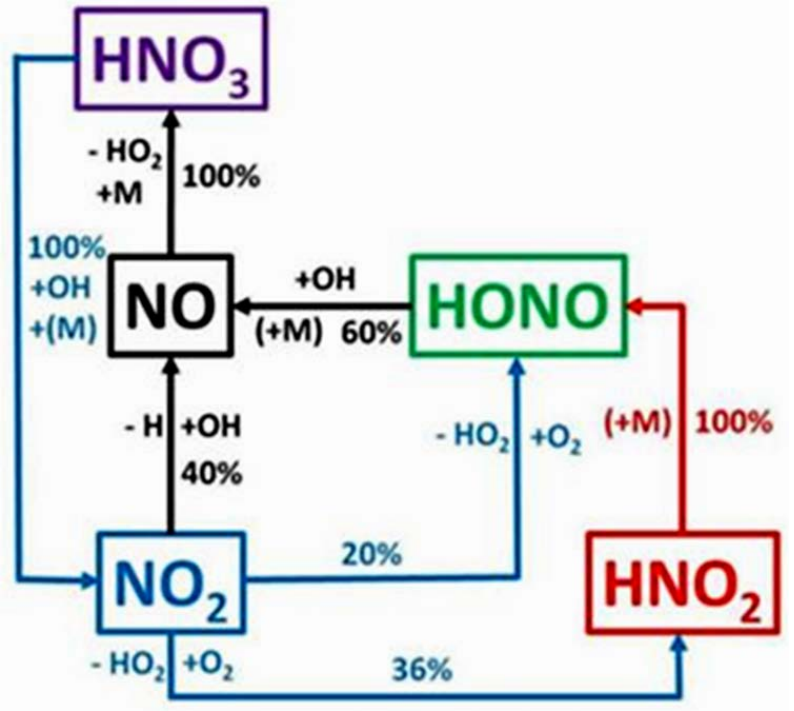




**High pressure non-monotonic behavior captured by the model**

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

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



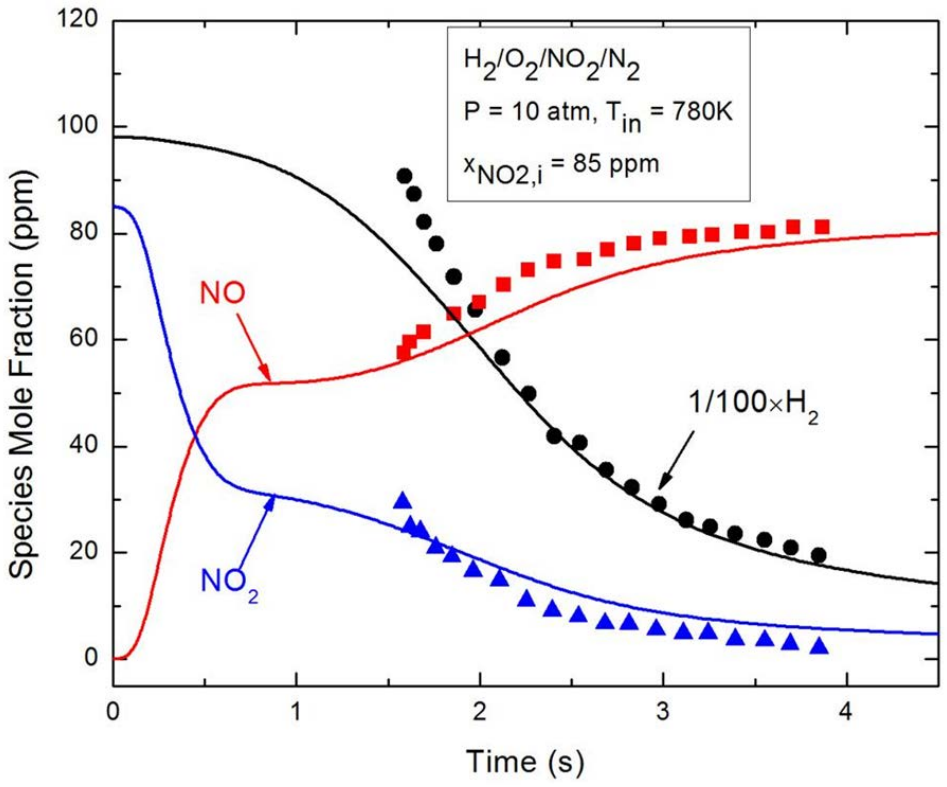



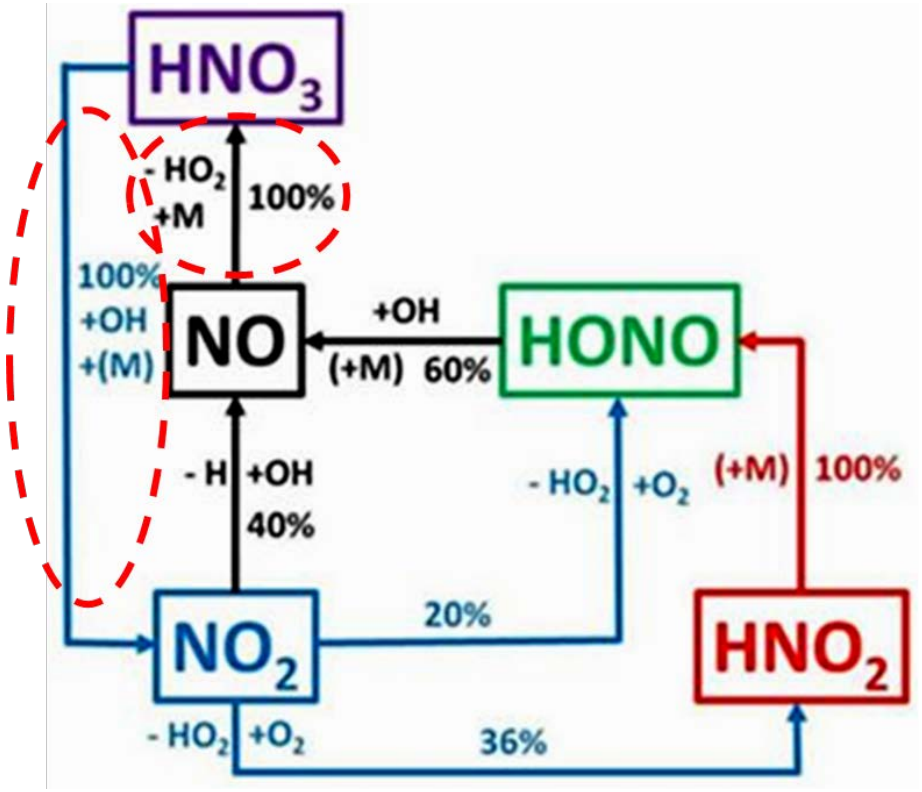

**Major reaction pathways of $NO-NO_2$ recycling process**

**Reasonable model prediction of fuel consumption and $NO-NO_2$ conversion**

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

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



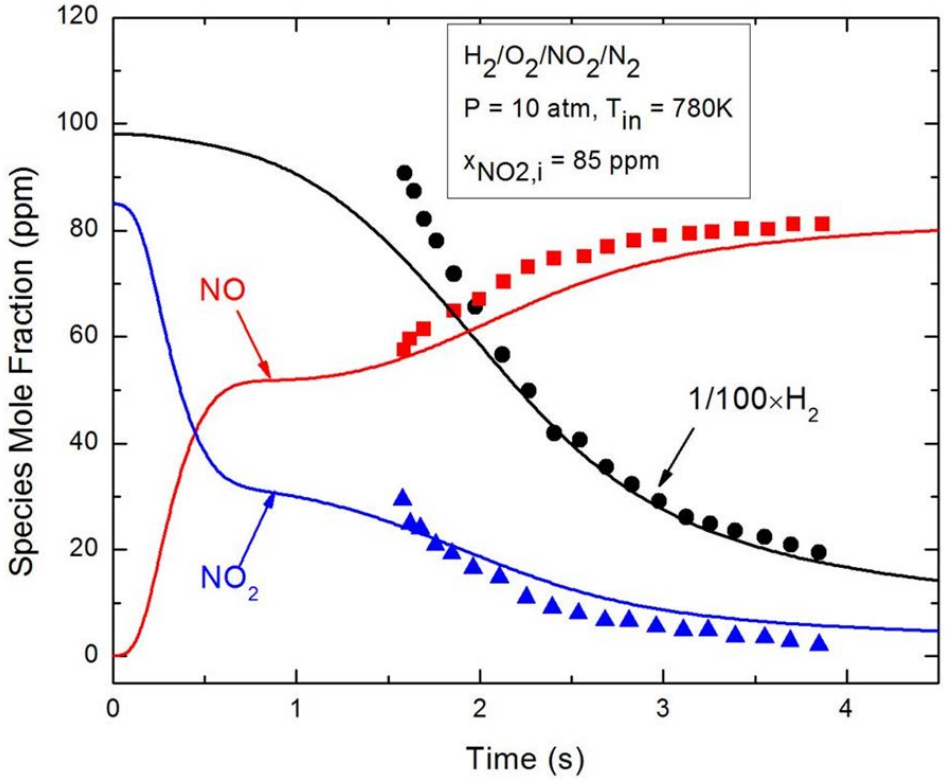



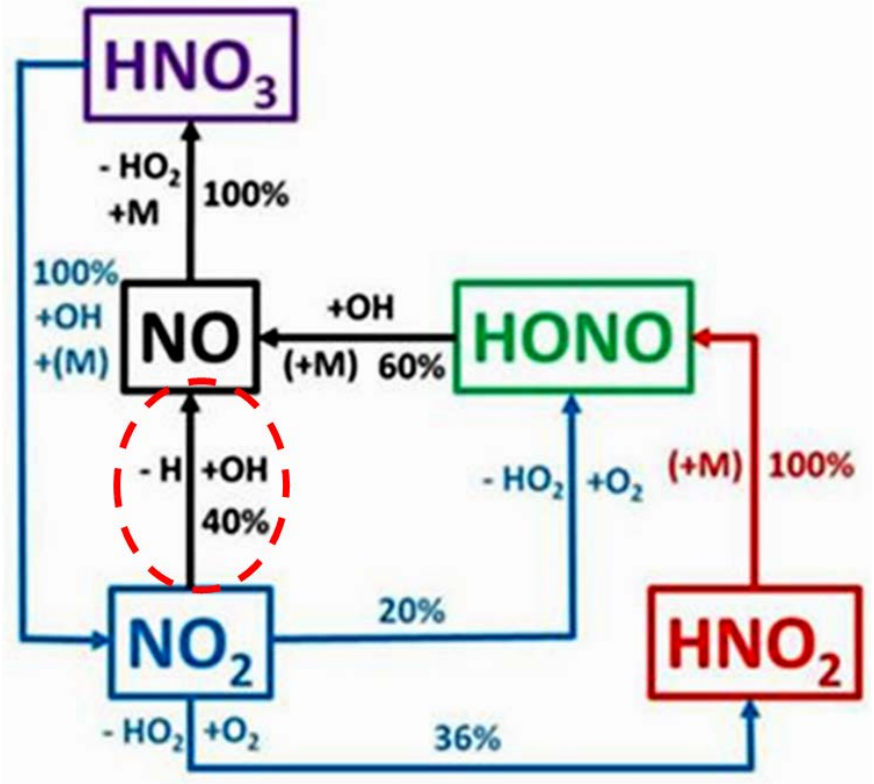

**Reasonable model prediction of fuel consumption and NO-$NO_2$ conversion**

$NO \rightarrow NO_2$ conversion: through intermediate $HNO_3$

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

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



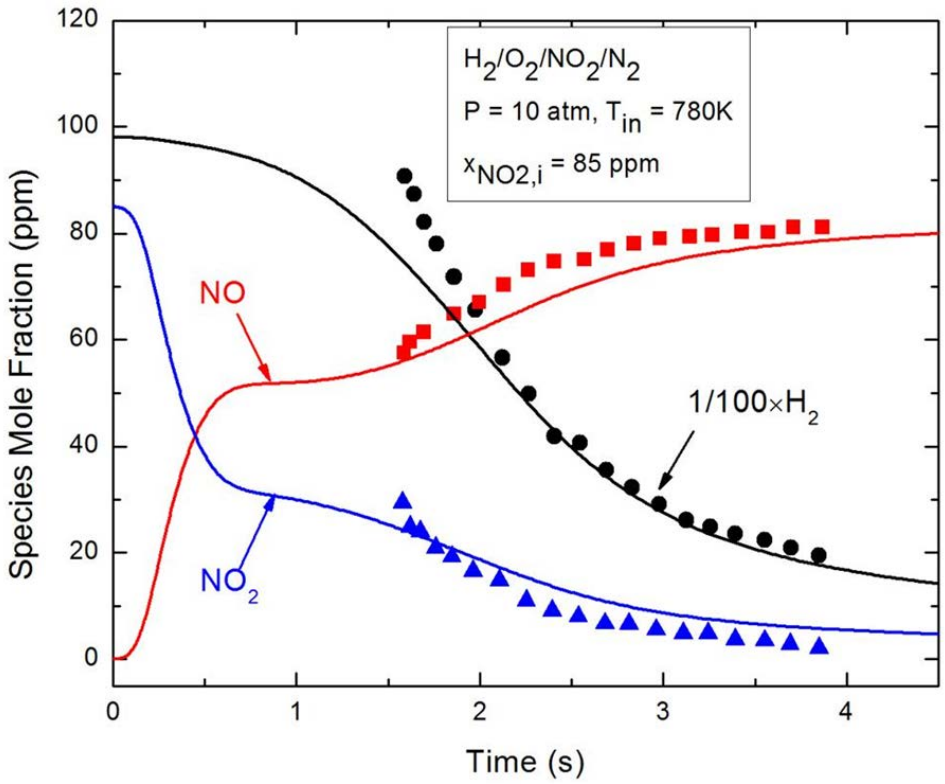

**Reasonable model prediction of fuel consumption and NO-$NO_2$ conversion**

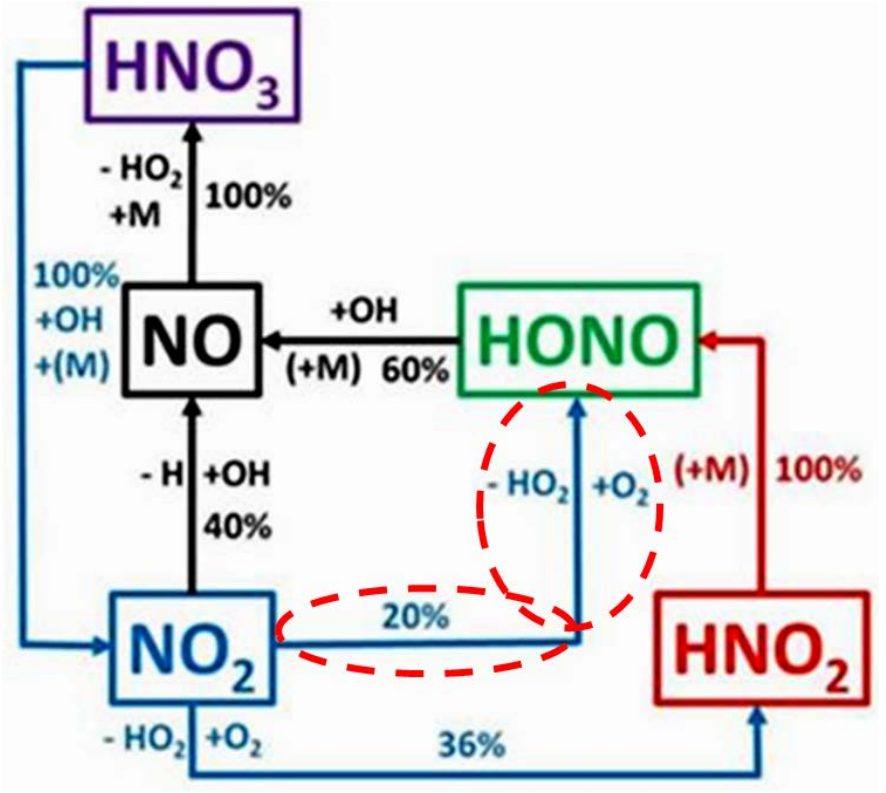
$NO \rightarrow NO_2$ conversion: through intermediate $HNO_3$

$NO_2 \rightarrow NO$ conversion: ***(i)*** **direct**

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

# Proposed 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**

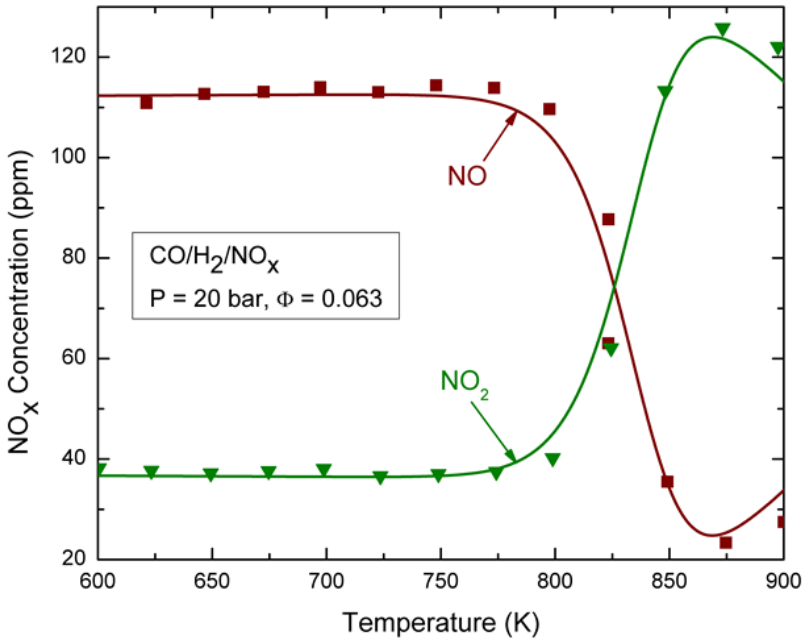
$NO \rightarrow NO_2$ conversion: through intermediate $HNO_3$

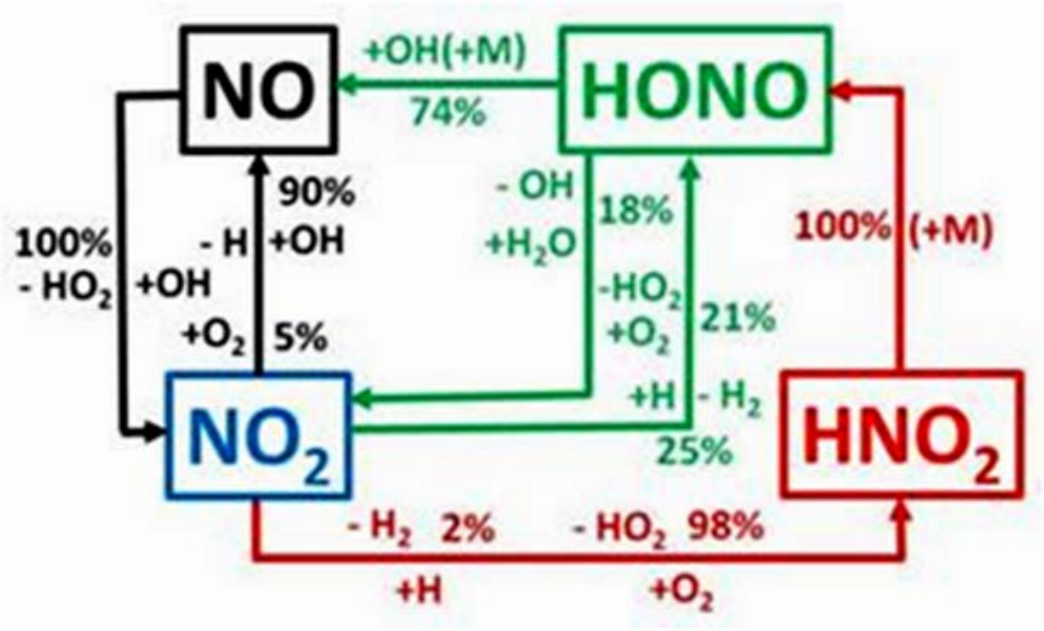
$NO_2 \rightarrow NO$ conversion: *(i)* direct

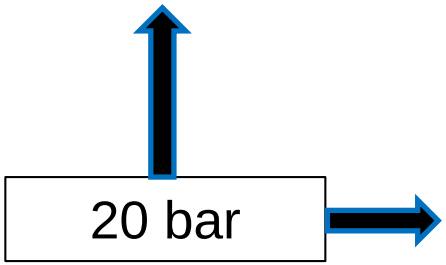
***(ii)* through intermediate HONO**

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

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



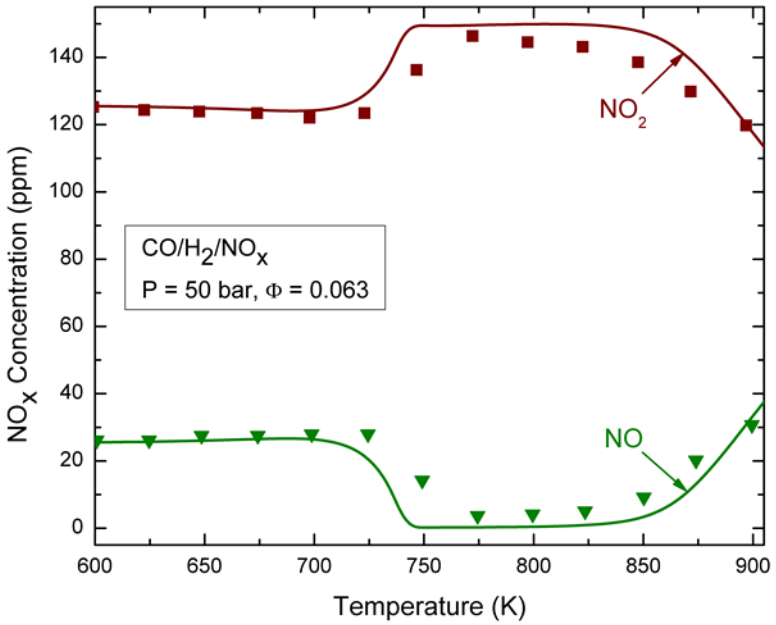

**$NO \leftrightarrow NO_2$: *(i)* direct**

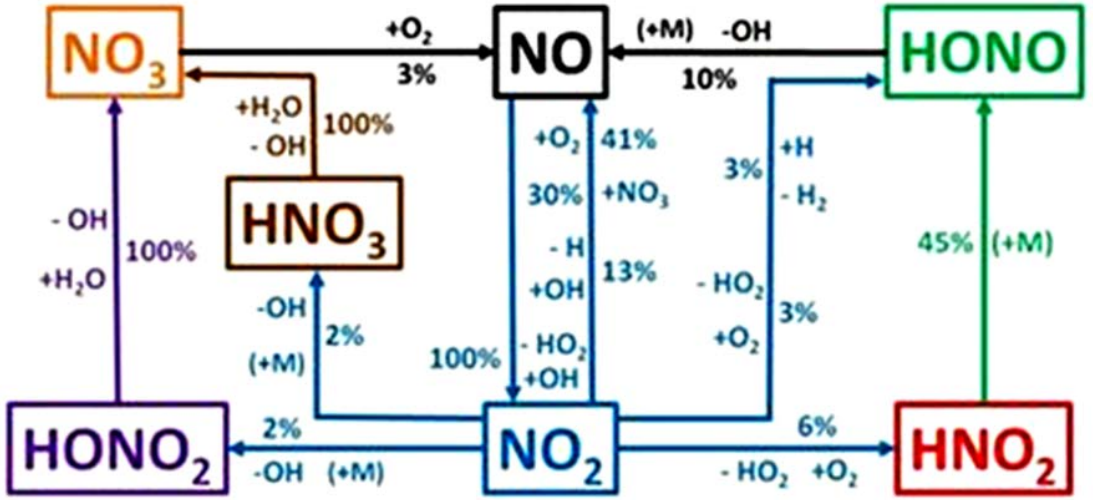
***(ii)* through intermediate HONO**

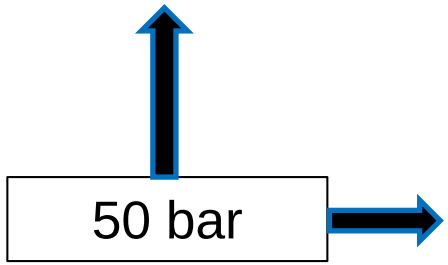
***(iii)* through intermediate $HNO_2$**

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

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



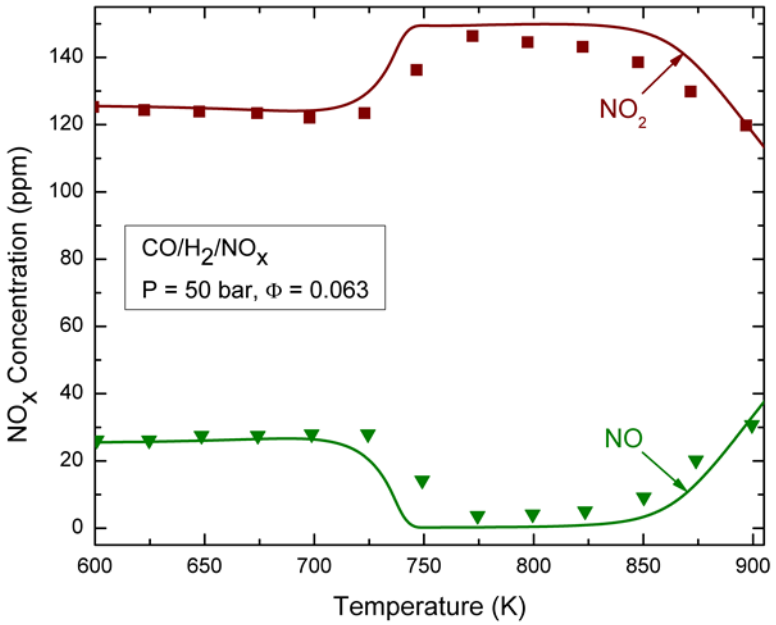



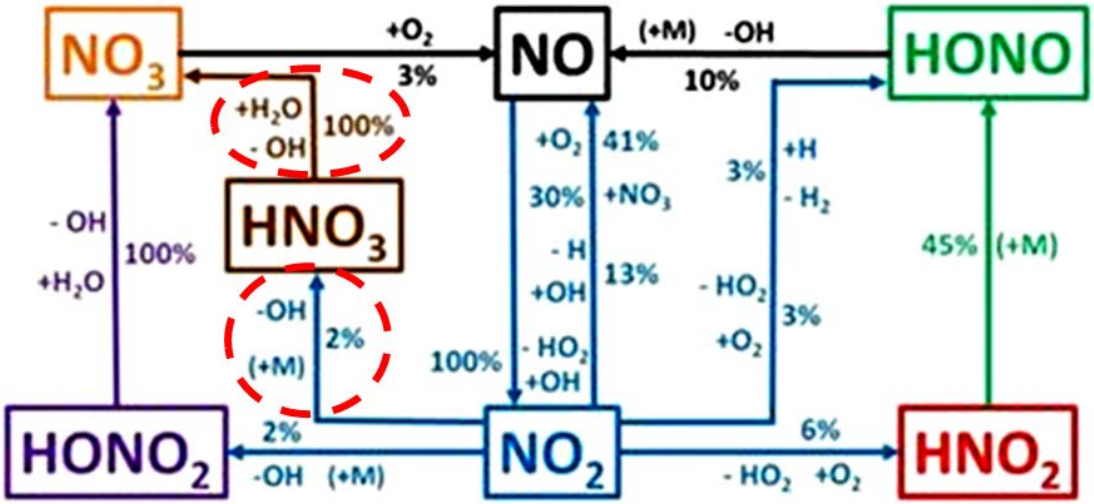



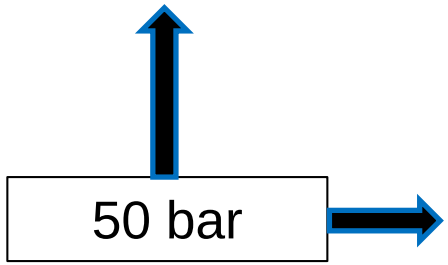

**Dominance of pressure-dependent reactions: two additional NO ↔ $NO_2$**

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

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



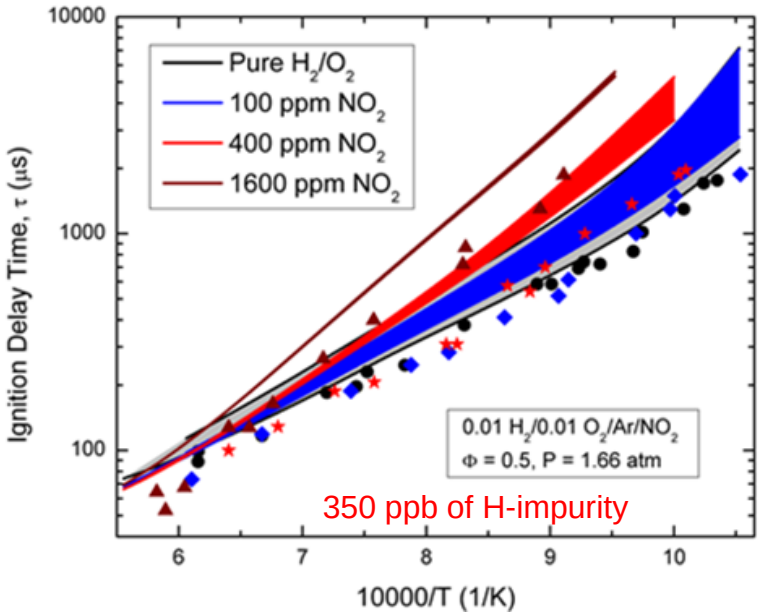



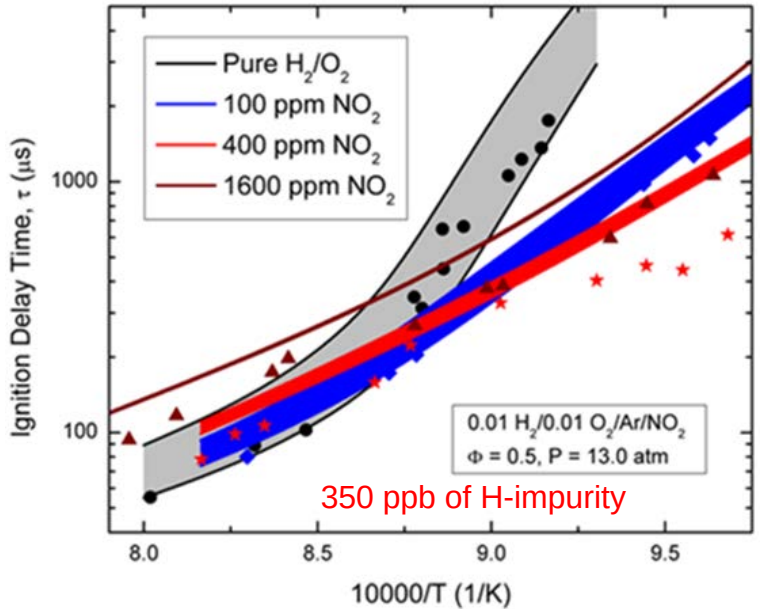




**Dominance of pressure-dependent reactions: two additional NO ↔ $NO_2$**

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

# Effect of Physical and Chemical Perturbations on the Explosion limit and Ignition Delay Time of $H_2/O_2$

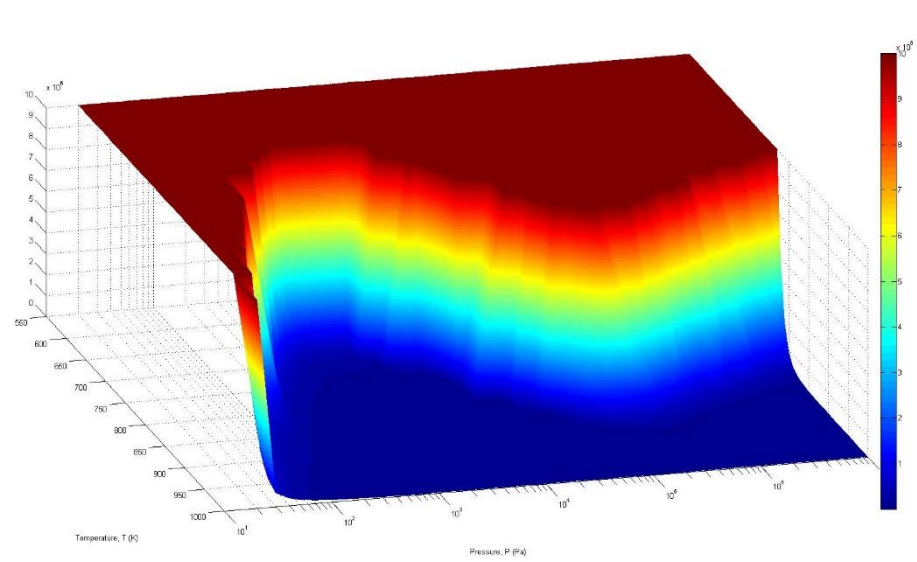


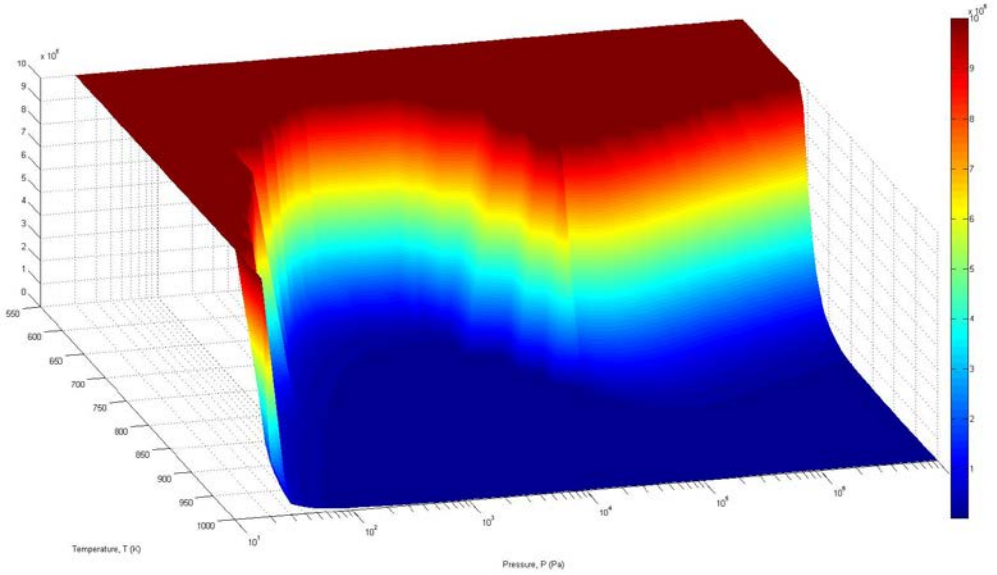

- ✓ Significant effects of impurities on the ignition delay time of $H_2$-oxidation
- ✓ The nature of variation also changes with pressure.

# Effect of Physical and Chemical Perturbations on the Explosion limit and Ignition Delay Time of $H_2/O_2$

## Chemical Perturbation- initial NO doping

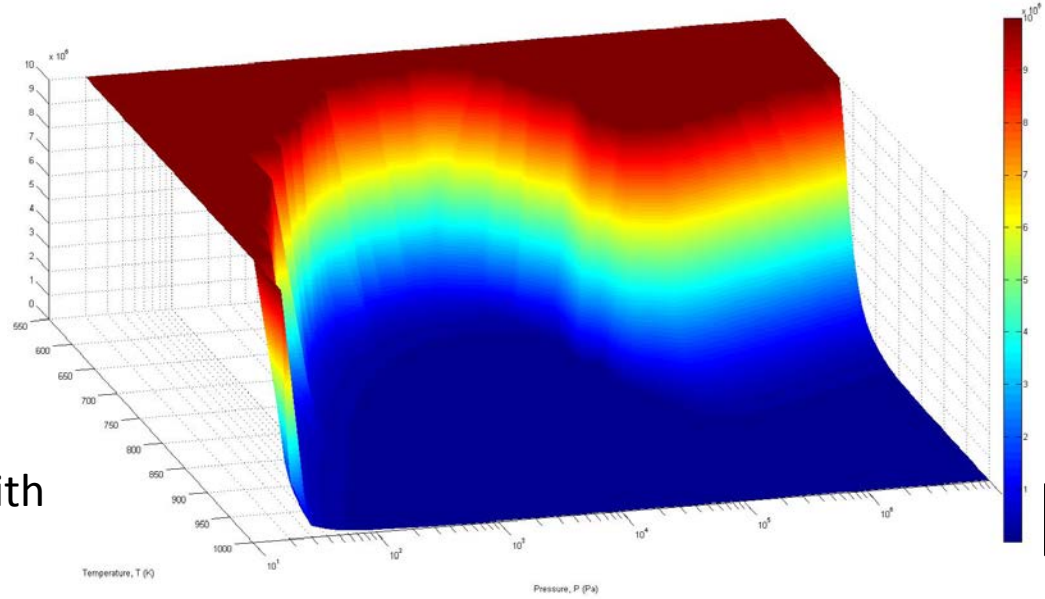



Base case




50 ppm NO

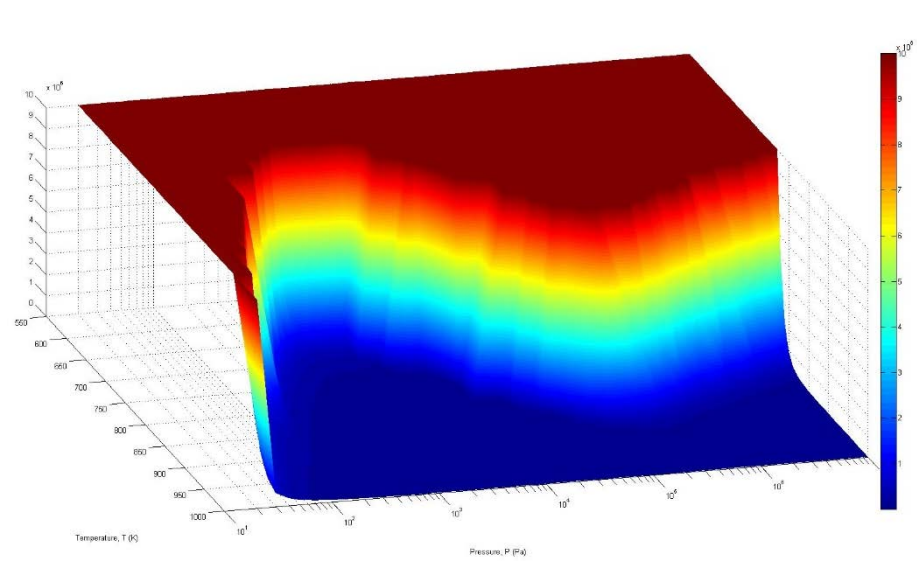
- ✓ τ changes more rapidly towards low T and high P along the 1st limit with a decrease in NO doping
- ✓ Change in τ along the 2nd limit becomes more rapid with an increase in NO doping



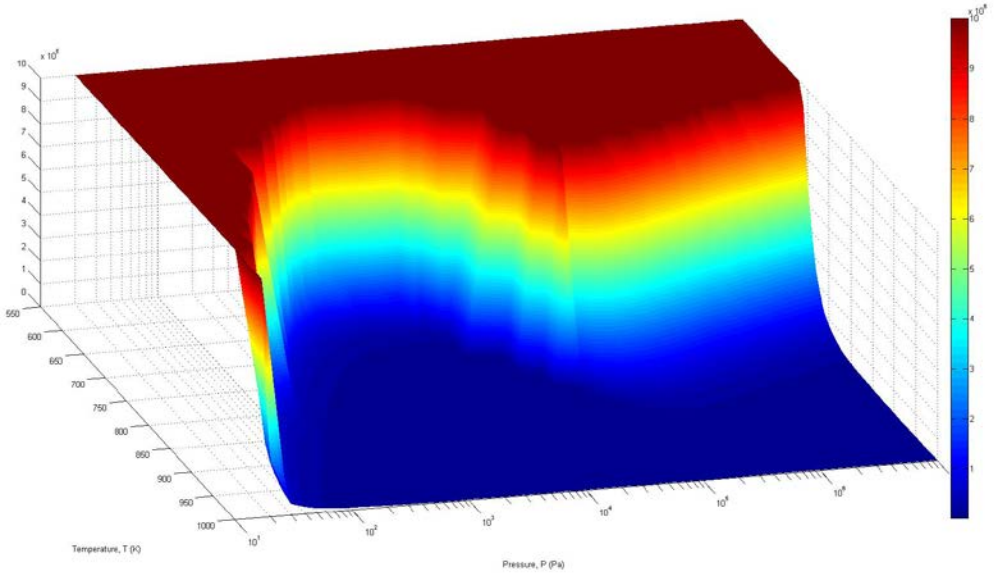

200 ppm NO

# Effect of Physical and Chemical Perturbations on the Explosion limit and Ignition Delay Time of $H_2/O_2$

## Chemical Perturbation- initial NO doping

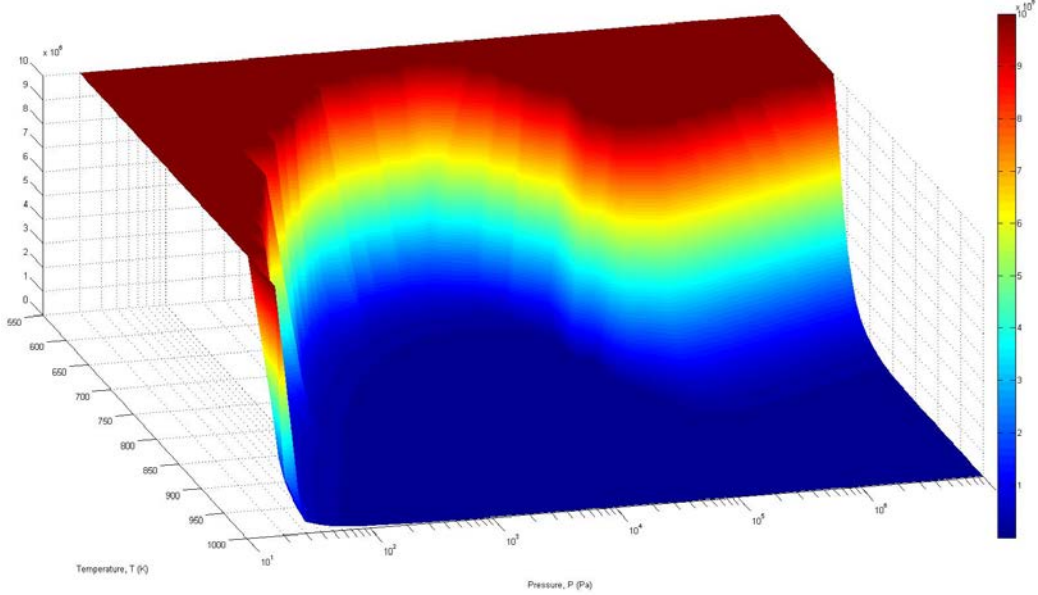



Base case



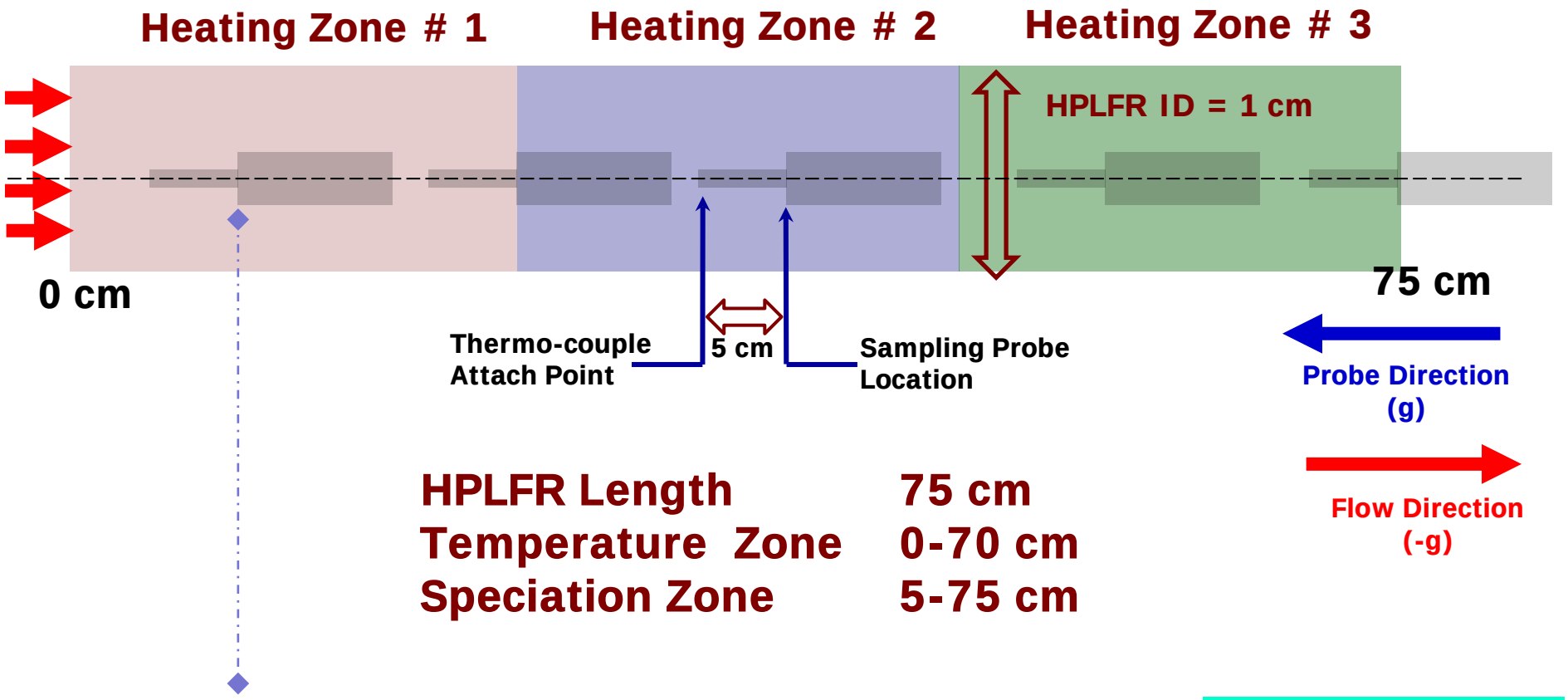

50 ppm NO

✓ τ changes more rapidly towards low T and high P along the 3rd limit with a decrease in NO doping




200 ppm NO

# Spatial ➔ Temporal Coordinate Transformation




| | |
|---|---|
| HPLFR Length | 75 cm |
| Temperature Zone | 0-70 cm |
| Speciation Zone | 5-75 cm |

Last Speciation Data Point (probe moving top-to-bottom). Declare this position as X (relative) = 0.0 cm

➔

Match the corresponding "T" for each location upward already measured

➔

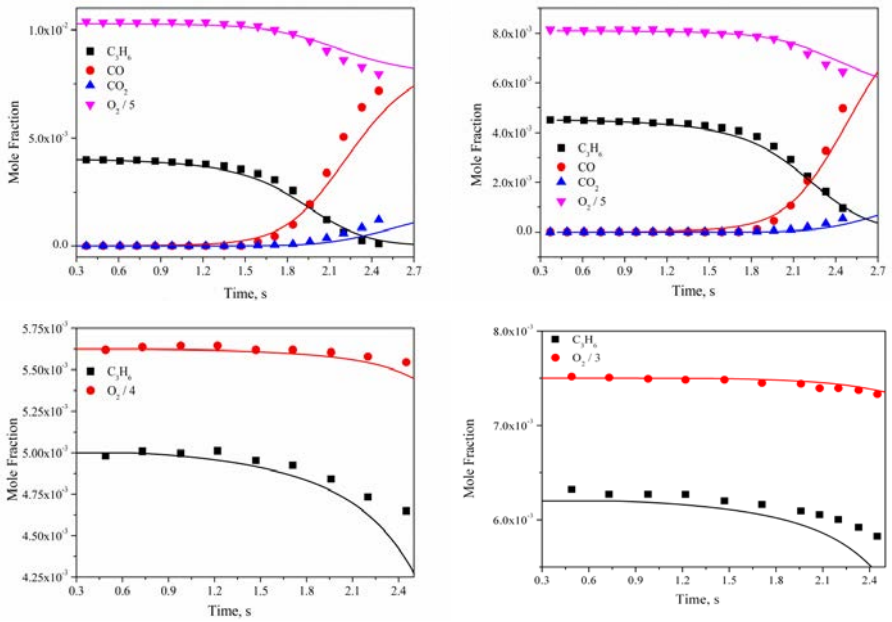
Redo this until the first temperature location which is X(end)

➔

Apply gas dynamics & Ideal Gas law. Get the velocity at particular location. and also get the "t"

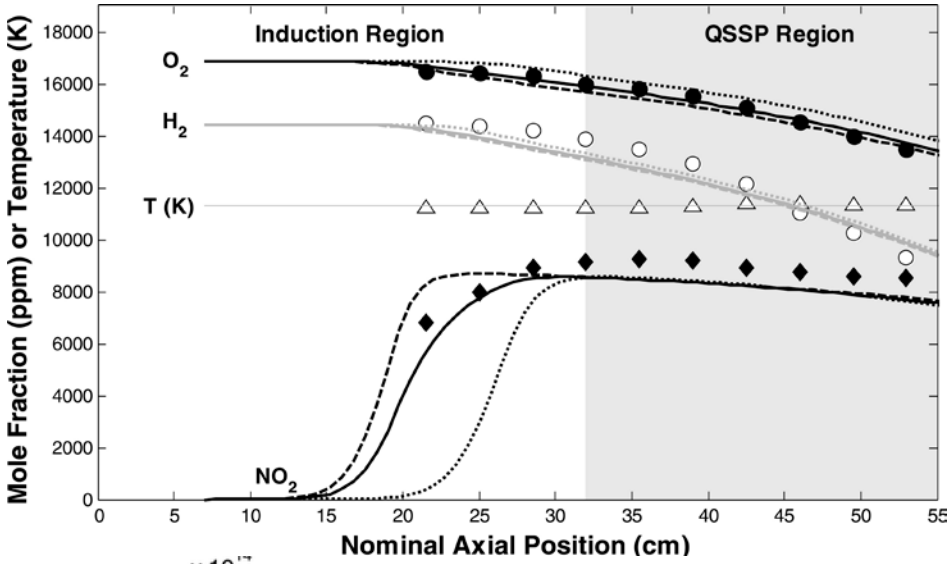
# Additional Small Species Database Efforts

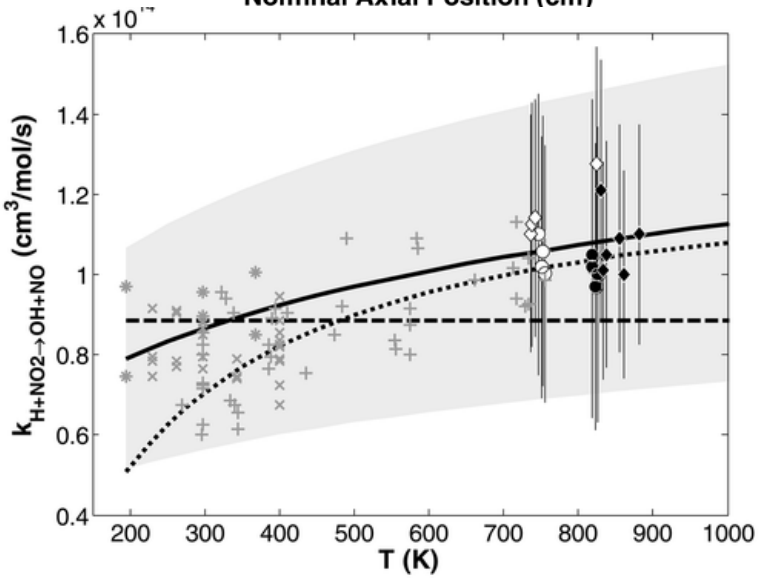
## Propene oxidation[1]




- Recap of $C_3H_6$ measurements/modeling presented at last UTSR review meeting
- Propene is an important intermediate in $C_3H_8$ oxidation, as well as for kinetics of higher hydrocarbons fraction of natural gas
- Previous models predicted substantial reactivity at the relatively low reactivity ~800 K, 15 atm conditions shown

## NOx-perturbed $H_2$ oxidation[2]




**Supported (in part) by Siemens Energy**

1. Burke et al. *Combust Flame.* 161:2765 (2014)
2. Haas & Dryer. *J Phys Chem A.* 119:7792 (2015)

1. Santner, J., Ahmed, S., **Farouk, T.,** Dryer, F., “Computational study of $NO_x$ formation at conditions relevant to gas turbine operation, part I” *Combustion and Flame (being submitted - November)*.

2. Ahmed, S., Santner, J., Dryer, F., Padak, B., **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” *Combustion and Flame (being submitted - November)*.