

# LEAN NOX TRAP MODELING BASED ON NOVEL MEASUREMENT TECHNIQUES

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Shawn Midlam-Mohler and Yann Guezennec

Ohio State University

Center for Automotive Research

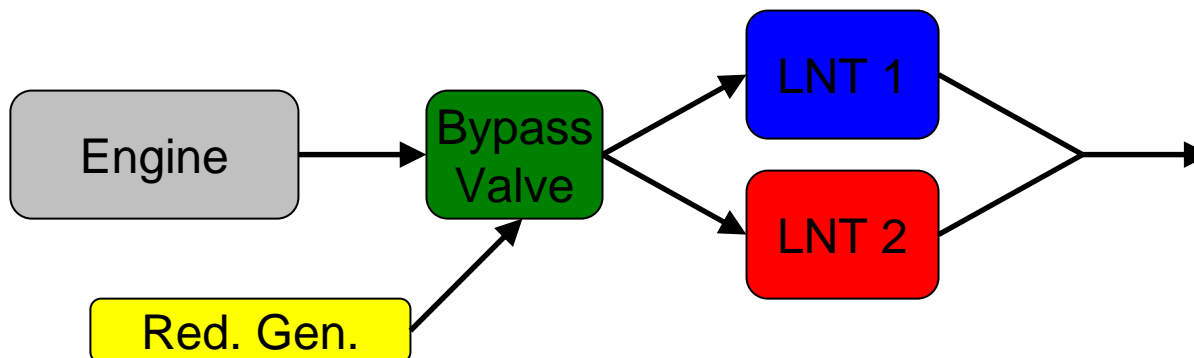
# Motivation

- During operation, an LNT has important spatial variations along its length:
  - The mass of  $\text{NO}_x$  stored under non-saturated conditions is generally higher at the front of the catalyst
  - Regeneration gasses reach and react at the front part of the catalyst before reaching the rear
  - Sulfur poisoning is more pronounced at the front of the catalyst
- All of the above effects are important to LNT modeling, regardless of the type of modeling (low-fidelity control models or high-fidelity kinetic models)
- Making simultaneous, distributed measurements using conventional techniques is generally both complicated and costly
- The following presentation outlines a technique that uses inexpensive sensors to infer spatial information from the catalyst
- This information is used to derive a low-fidelity control model of the regeneration process

This work was sponsored through Ford's URP program

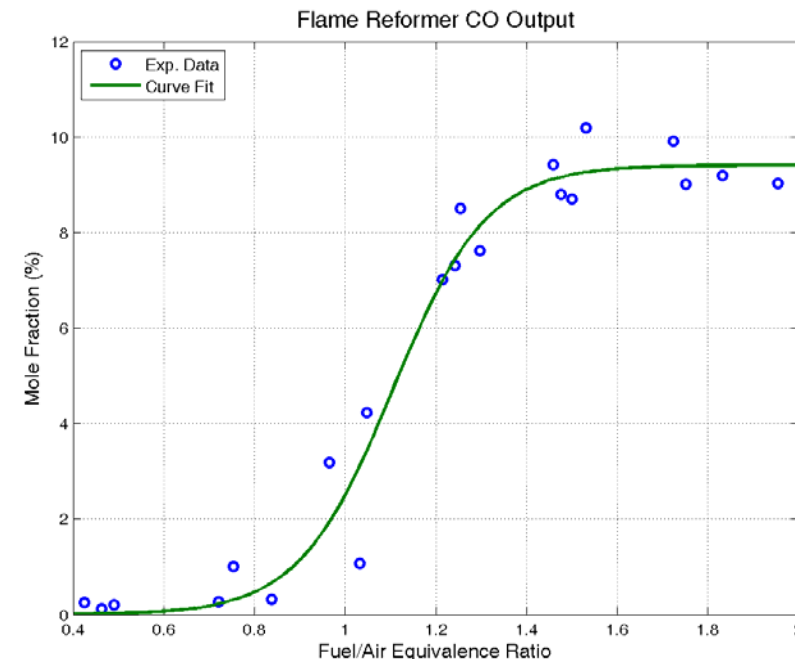
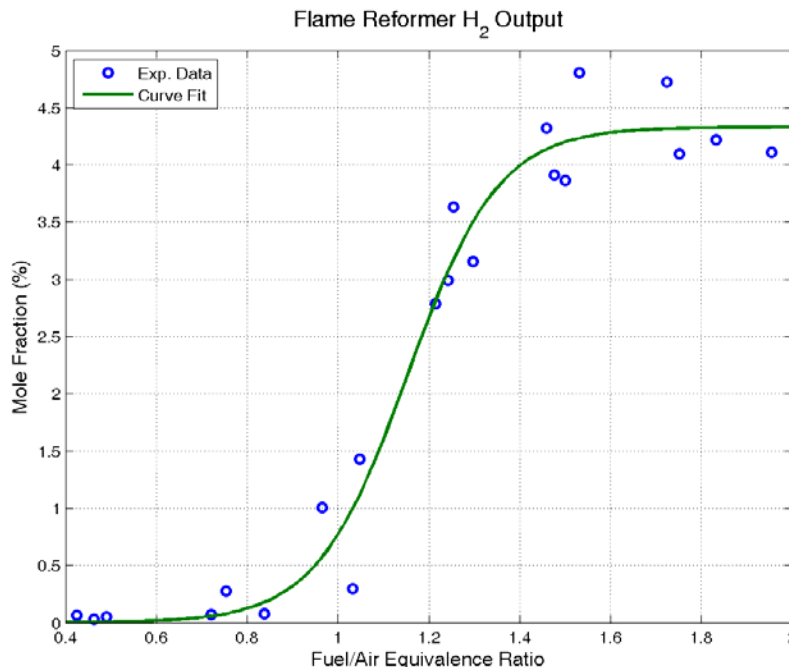
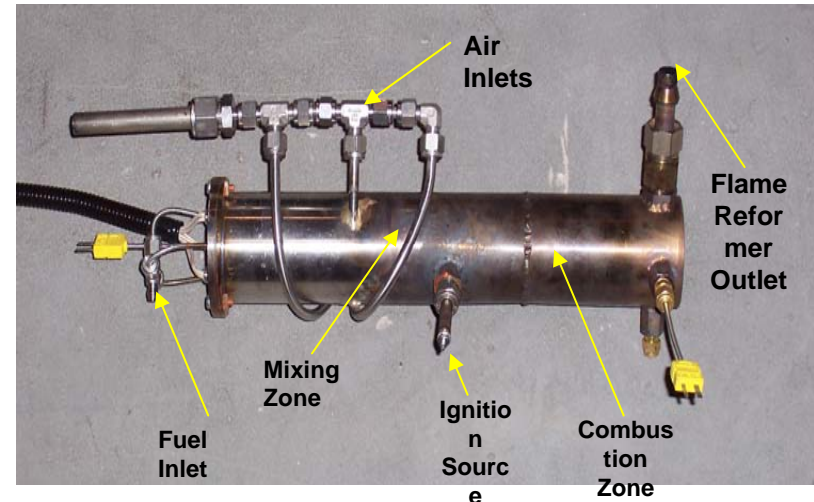
# System Under Investigation

- Work done on a total bypass regeneration system
  - During regeneration, all exhaust gas is diverted away from the catalyst
  - Reductant is supplied locally via an external device
- 2.5 L Euro 3, CR Diesel engine
- Reductant supplied from either bottled CO or from a “flame reformer” (equivalent results for both)
- Measurements include: two line gas bench, UEGO sensors, multiple gas and substrate temperature measurements



# Flame Reforming Basics

- Use rich combustion of Diesel fuel to produce ~4% H<sub>2</sub> and ~10% CO
- Pro: Non-catalytic, rapid response, simple, inexpensive
- Con: Moderate efficiency (but probably good enough)



# Theoretical Basis – 1/3

- A simple LNT reaction scheme is used to explain the measurement technique
- The key reactions used occur during the regeneration phase, which are lumped into the following:
  - Stored NO<sub>x</sub> depletion (includes release and reduction)
  - Stored Oxygen depletion (includes release and reduction)
  - Oxygen adsorption
- Catalyzed reactions of species in the gas phase are also important to the method

# Theoretical Basis – 2/3

- Looking at a small section of the catalyst substrate, the energy balance to the right can be written:
  - Mass entering and leaving the system carries energy
  - The substrate and gas can act as sinks to thermal energy
  - Conduction can remove energy from the system
  - Heat can be generated from within the control volume through chemical reactions

$$\dot{m}_{in} h_{in} + \dot{Q}_{reac} = \dot{m}_{out} h_{out} + \dot{Q}_{cond} + m_s c_s \frac{dT_s}{dt} + m_g c_g \frac{dT_g}{dt}$$

Where:

$\dot{m}_{in}$  = mass flow rate of gas into the catalyst section

$h_{in}$  = enthalpy of gas entering the catalyst section

$\dot{Q}_{reac}$  = rate of heat release due to chemical reactions in the cell

$\dot{m}_{out}$  = mass flow rate of gas out of the section

$h_{out}$  = enthalpy of gas exiting the catalyst section

$\dot{Q}_{cond}$  = rate of heat loss of the catalyst section to the surrounding substrate

$m_s$  = mass of the catalyst section

$c_s$  = specific heat of the catalyst substrate

$T_s$  = temperature of the catalyst section

$m_g$  = mass of the gas in the catalyst section

$c_g$  = specific heat of the gas in the catalyst section

$T_g$  = average temperature of the gas in the catalyst section

# Theoretical Basis – 3/3

- Several simplifying assumptions can be used to arrive a workable form:
  - Conduction term is negligible (catalyst substrate has low thermal conductivity, temperature gradient is low, time for conduction is relatively small)
  - Enthalpy terms are negligible (small dT, low gas flows)
  - Thermal storage elements can be lumped together (thermal mass of substrate much larger than that of gas)

- Based on the above assumptions:

$$\dot{Q}_{reac} = m_s c_s \frac{dT_s}{dt}$$

- The implications of this is that the rate of temperature rise of the substrate (to the extent that the assumptions are true) is proportional to the heat released from the chemical reactions

# Reactions Considered for the Temperature Rise

The four lumped reactions responsible for the temperature rise are the following:

1. Reduction of free oxidizers
2. Reduction of stored oxygen
3. Reduction of stored NO<sub>x</sub>
4. Readsorption of oxygen



# Heating Value for the Reactions

- For each of the four reactions listed previously, heating values can be assigned
- Here, it is assumed that only CO is the reducer; it can also be used to account for a mixture of gasses

$$\dot{m}_{O_2,g} \cdot H_{rxn}^{O_2,g} = C_s \frac{dT_{s,O_2,g}}{dt}$$

$$\dot{m}_{O_2,des} \cdot H_{rxn}^{O_2,des} = C_s \frac{dT_{s,O_2,des}}{dt}$$

$$\dot{m}_{NO_x,des} \cdot H_{rxn}^{NO_x,des} = C_s \frac{dT_{s,NO_x,des}}{dt}$$

$$\dot{m}_{O_2,ads} \cdot H_{rxn}^{O_2,ads} = C_s \frac{dT_{s,O_2,ads}}{dt}$$

Where:

$\dot{m}_{O_2,g}$  = mass flow rate of gaseous oxygen reduced

$H_{rxn}^{O_2,g}$  = heating value of gaseous oxygen reduction

$\dot{m}_{O_2,des}$  = mass flow rate of oxygen desorbed

$H_{rxn}^{O_2,des}$  = heating value of oxygen desorption reaction

$\dot{m}_{NO_x,des}$  = mass flow rate of NO<sub>x</sub> desorbed

$H_{rxn}^{NO_x,des}$  = heating value of oxygen desorption reaction

$\dot{m}_{O_2,ads}$  = mass flow rate of oxygen readsorbed

$H_{rxn}^{O_2,ads}$  = heating value of oxygen readsorption reaction

# Temperature Rise Expression

- With the heating values, and the  $dT/dt$  expression, it is possible to link the total temperature rise to each of the four reactions
- With constant heats of reaction and heat capacity, the mass rate of oxidizer used in each reaction is related linearly to the rate of temperature rise

$$\frac{dT_s}{dt} = \frac{dT_{s,O2,g}}{dt} + \frac{dT_{s,O2,des}}{dt} + \frac{dT_{s,NOx,des}}{dt} + \frac{dT_{s,O2,ads}}{dt}$$

$$\frac{dT_{s,O2,g}}{dt} = \frac{\dot{m}_{O2,g} \cdot H_{rxn}^{O2,g}}{C_s}$$

$$\frac{dT_{s,O2,des}}{dt} = \frac{\dot{m}_{O2,des} \cdot H_{rxn}^{O2,des}}{C_s}$$

$$\frac{dT_{s,NOx,des}}{dt} = \frac{\dot{m}_{NOx,des} \cdot H_{rxn}^{NOx,des}}{C_s}$$

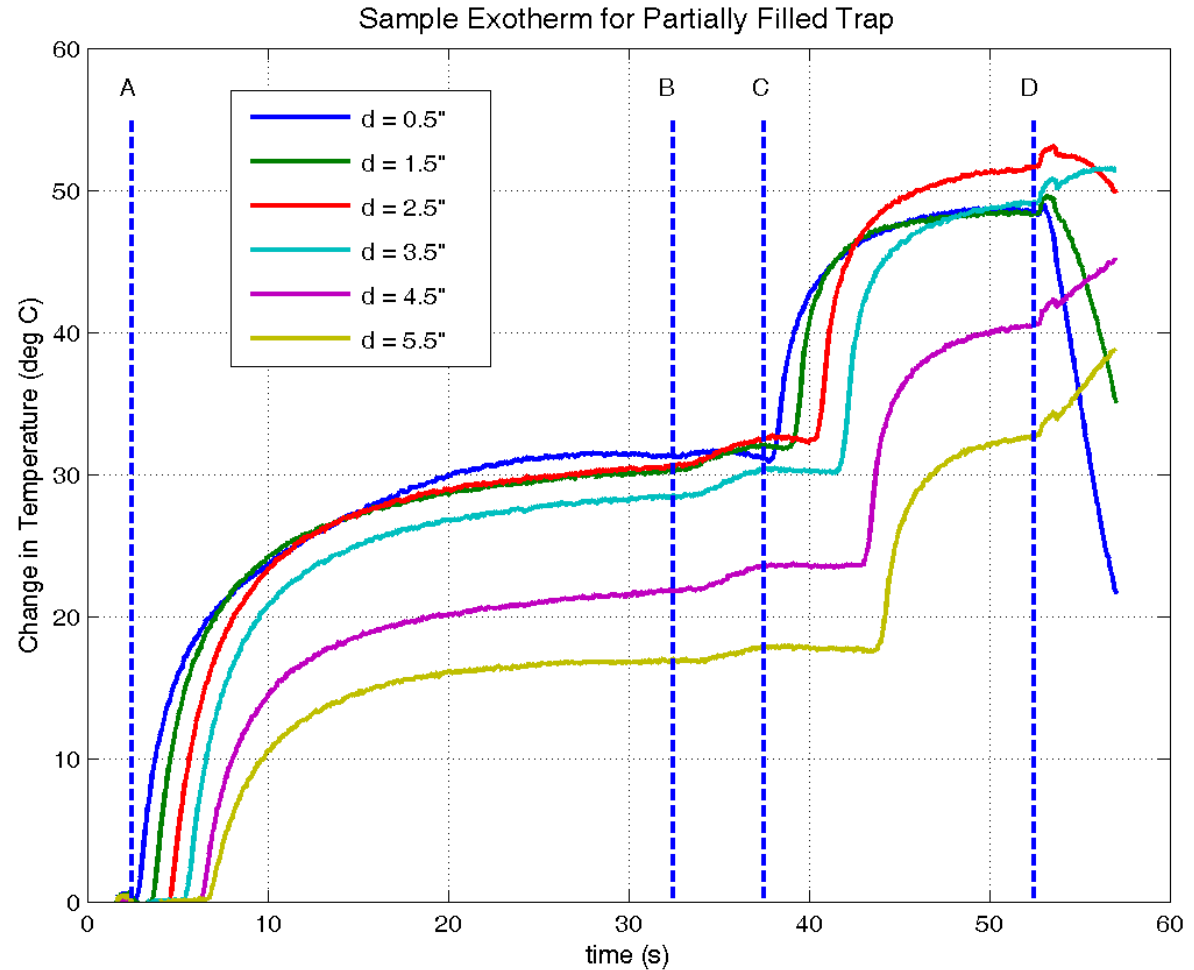
$$\frac{dT_{s,O2,ads}}{dt} = \frac{\dot{m}_{O2,ads} \cdot H_{rxn}^{O2,ads}}{C_s}$$

# Isolation of Reactions

- From the temperature data alone, it is not possible to determine which reaction is responsible for the temperature rise
- Fortunately, there are distinguishing characteristics to each source of temperature rise:
  - Reduction of free oxidizers: Localized temperature rise at front of catalyst
  - Reduction of stored oxygen: Occurs during net-rich phase
  - Reduction of stored NO<sub>x</sub>: Occurs during net-rich phase
  - Readsorption of O<sub>2</sub>: Occurs during net-lean phase immediately after net-rich phase
- It is not possible to isolate the temperature rise due to the reduction of stored oxidizers since they occur at the same time and location
  - As shown later, this is problem can be overcome

# Sample Exotherm

- A to B: CO passed through catalyst (net-rich)
- B to C: CO<sub>2</sub> passed through catalyst (AFR neutral)
- C to D: air passed through the catalyst (net-lean)
- The two distinct exotherms are referred to as the *rich exotherm* and the *lean exotherm*

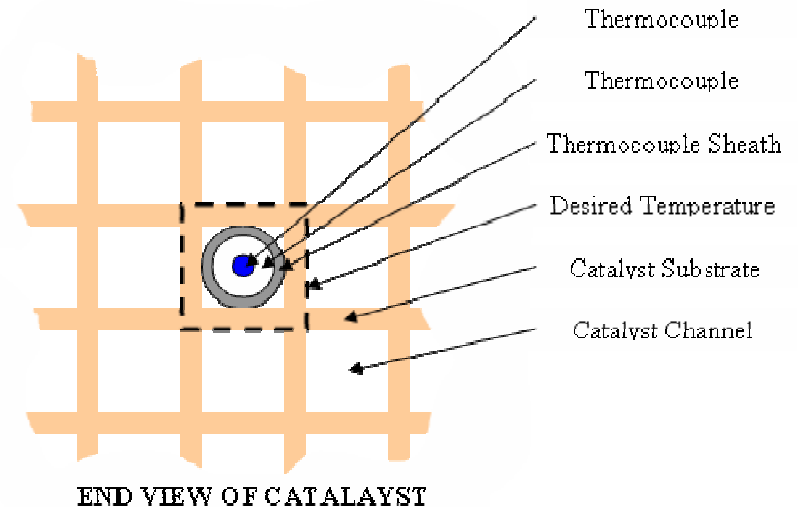


# Separation of NO<sub>x</sub> from Oxygen

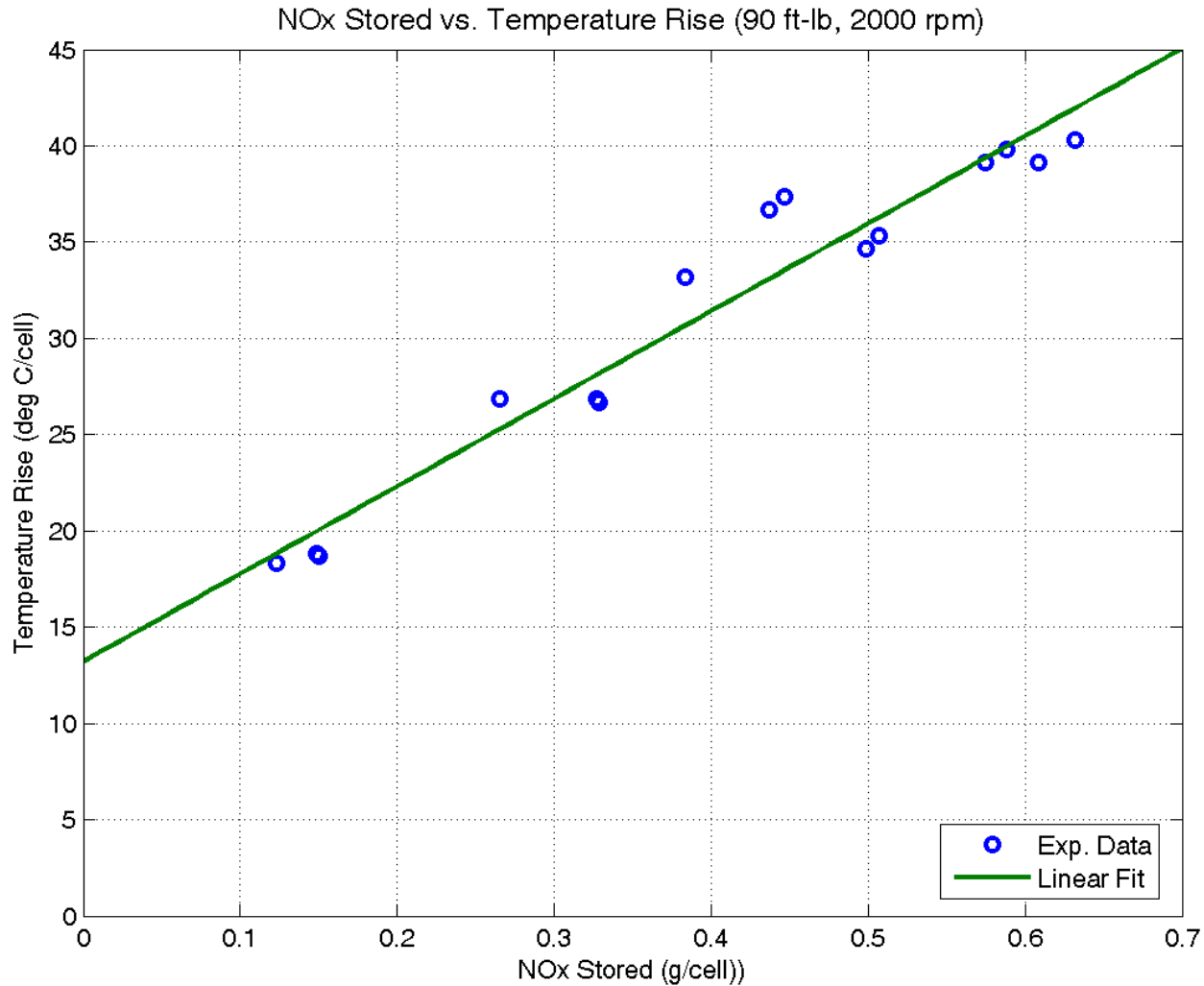
- During the rich phase, stored NO<sub>x</sub> and O<sub>2</sub> are reduced simultaneously, this makes them indistinguishable from temperature alone
- During the lean phase, there is an exotherm due solely to oxygen uptake:
  - From the lean exotherm, it is possible to determine the amount of oxygen readsorbed
  - This can be used to estimate the temperature rise contribution off the oxygen during the rich phase, leaving only the temperature rise from the NO<sub>x</sub>
  - With the estimate of the temperature rise due to NO<sub>x</sub>, it is possible to determine the mass of NO<sub>x</sub> reduced.

# Catalyst Instrumentation

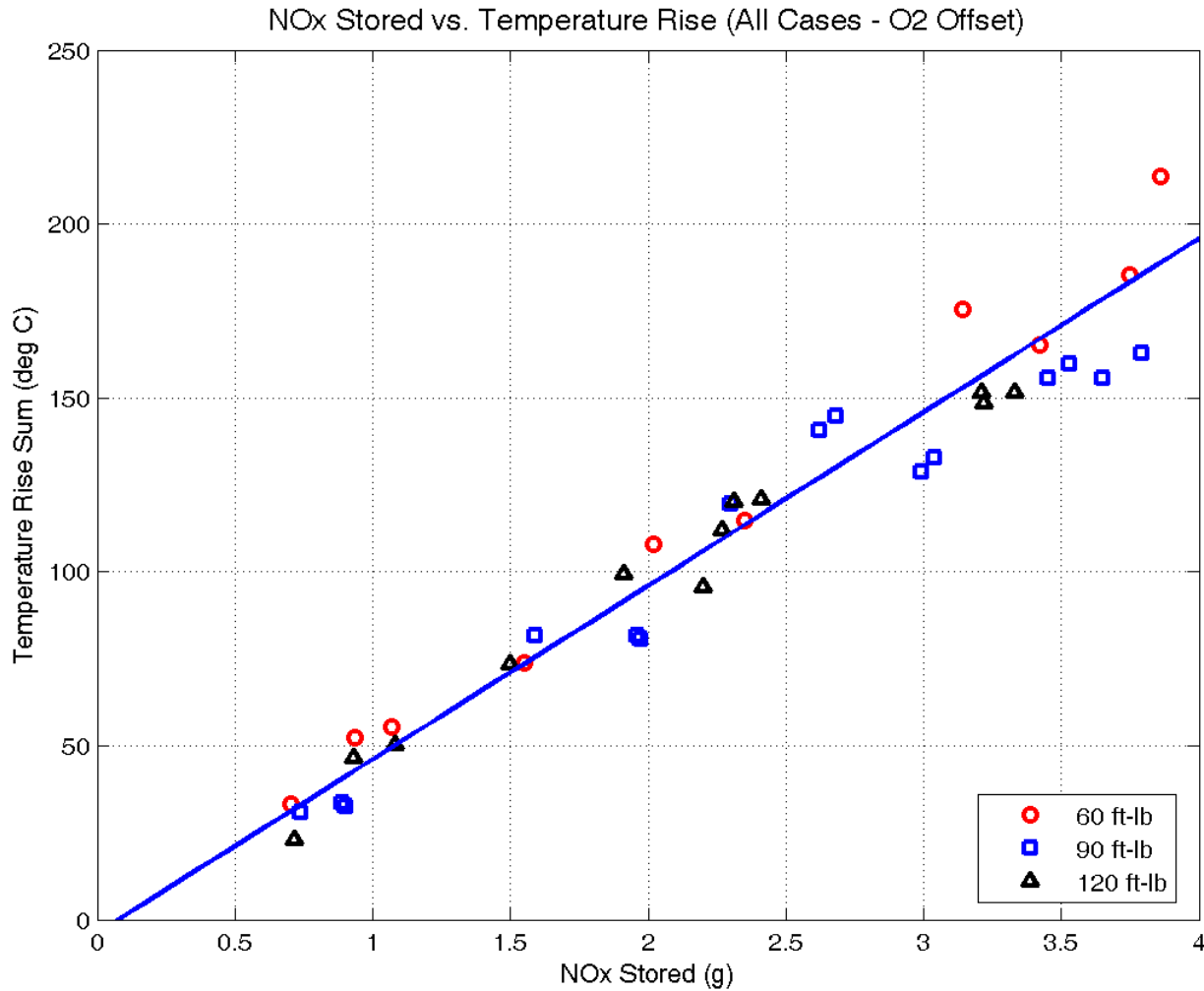
- At left, a 400 cpsi LNT substrate is shown
- 0.050" diameter sheathed thermocouples are inserted down the channels at various radial and axial locations
- Does not damage the catalyst
- Gas flow through the channels is greatly restricted



# Evidence of the Method – 1/3

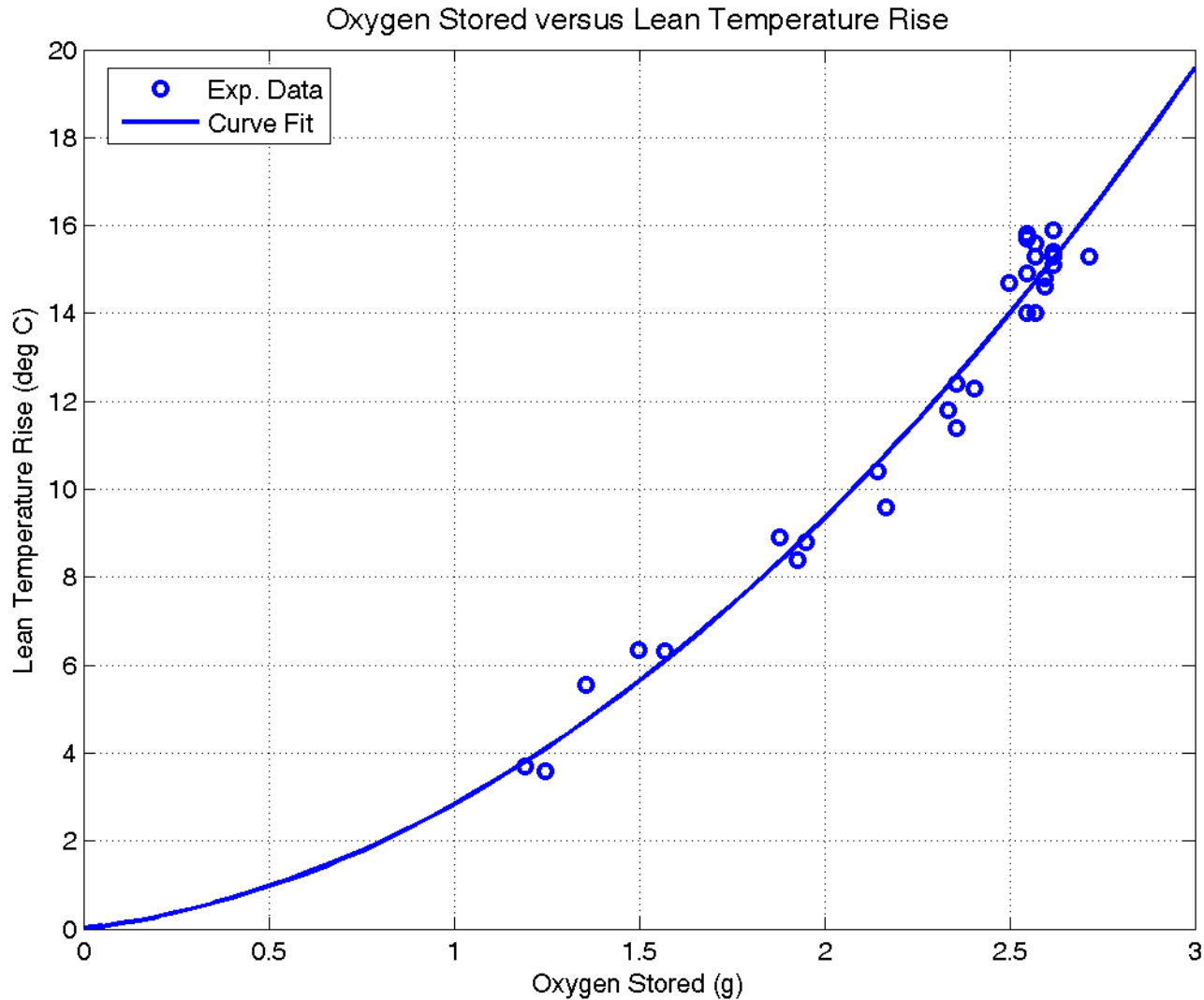


# Evidence of the Method – 2/3



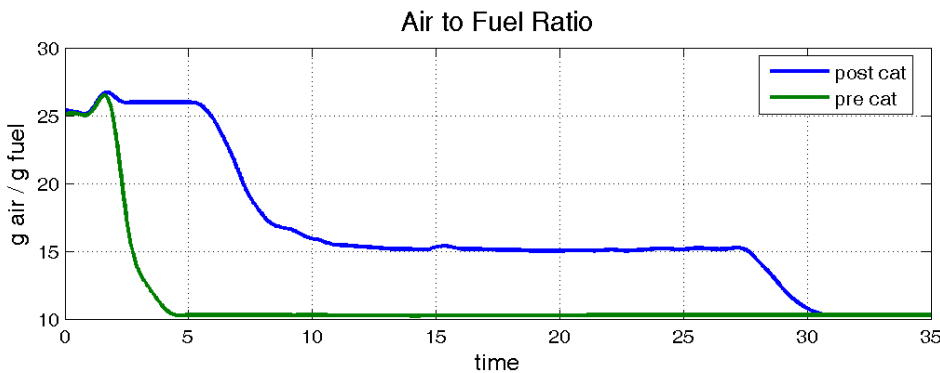
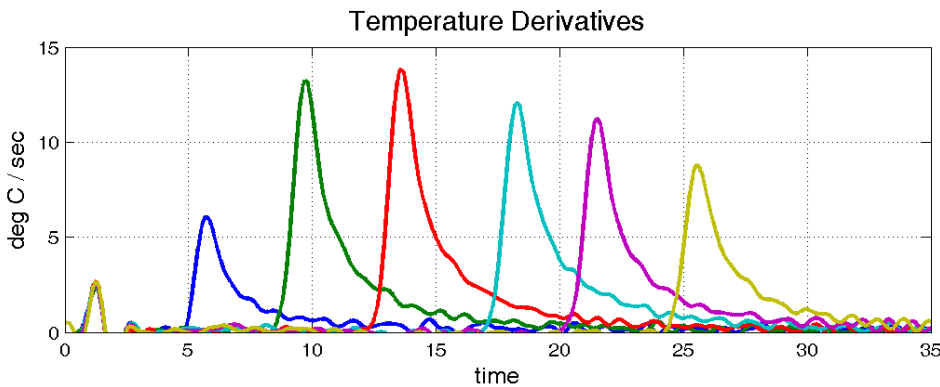


# Evidence of the Method – 3/3

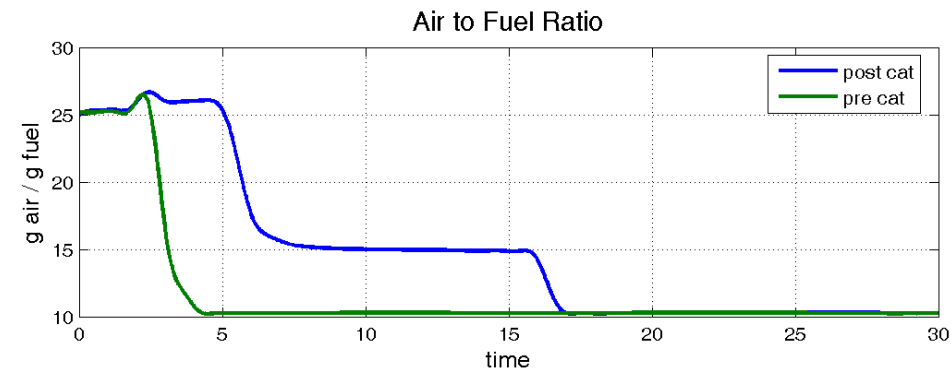
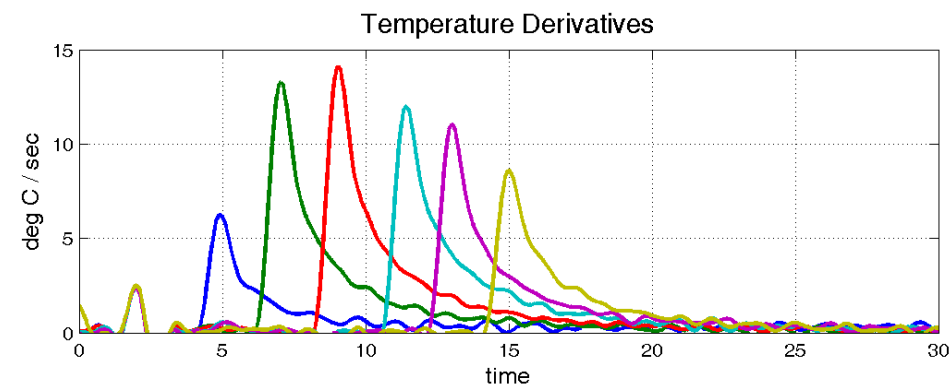


# Reaction Rates

- The derivative of temperature is linearly related to the reaction rate:



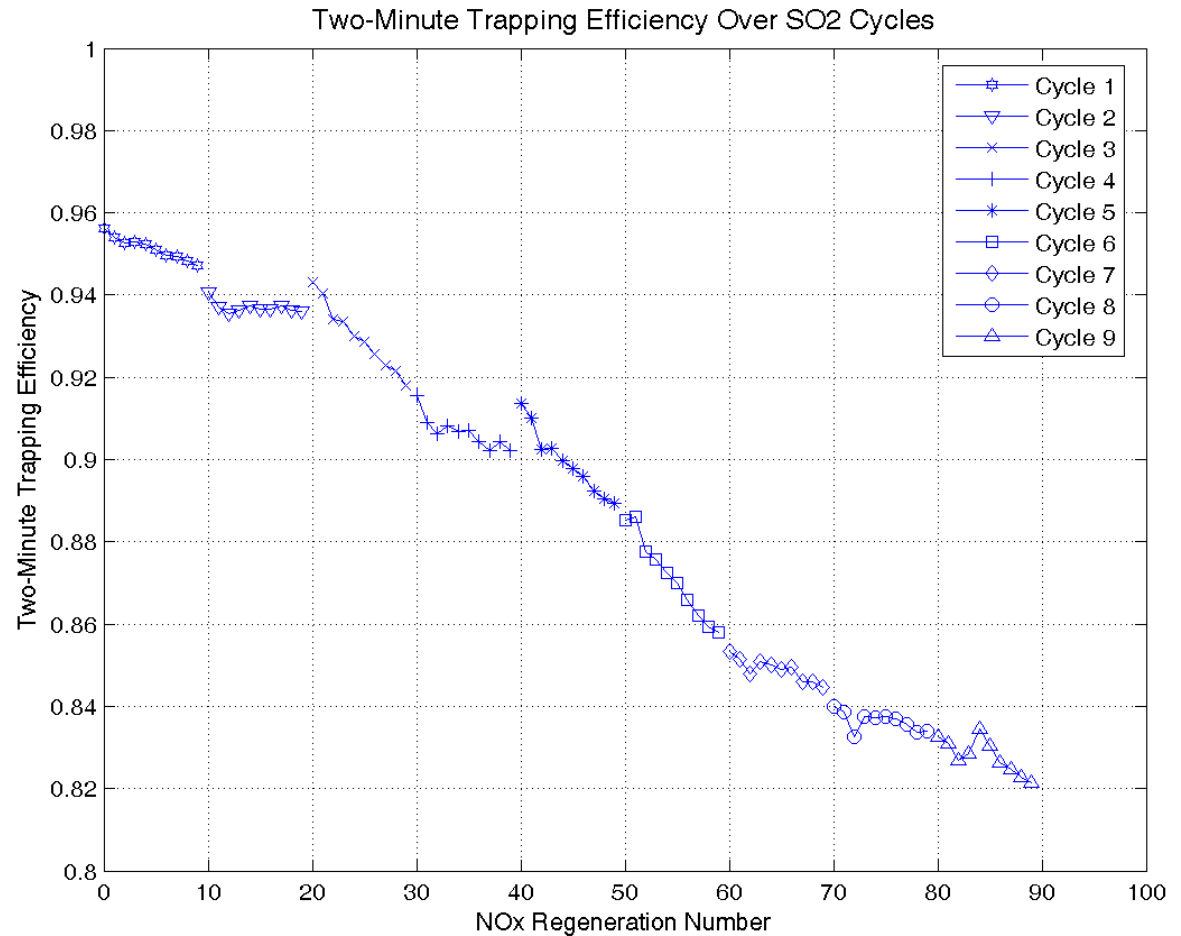
0.8 g/s CO



1.2 g/s CO

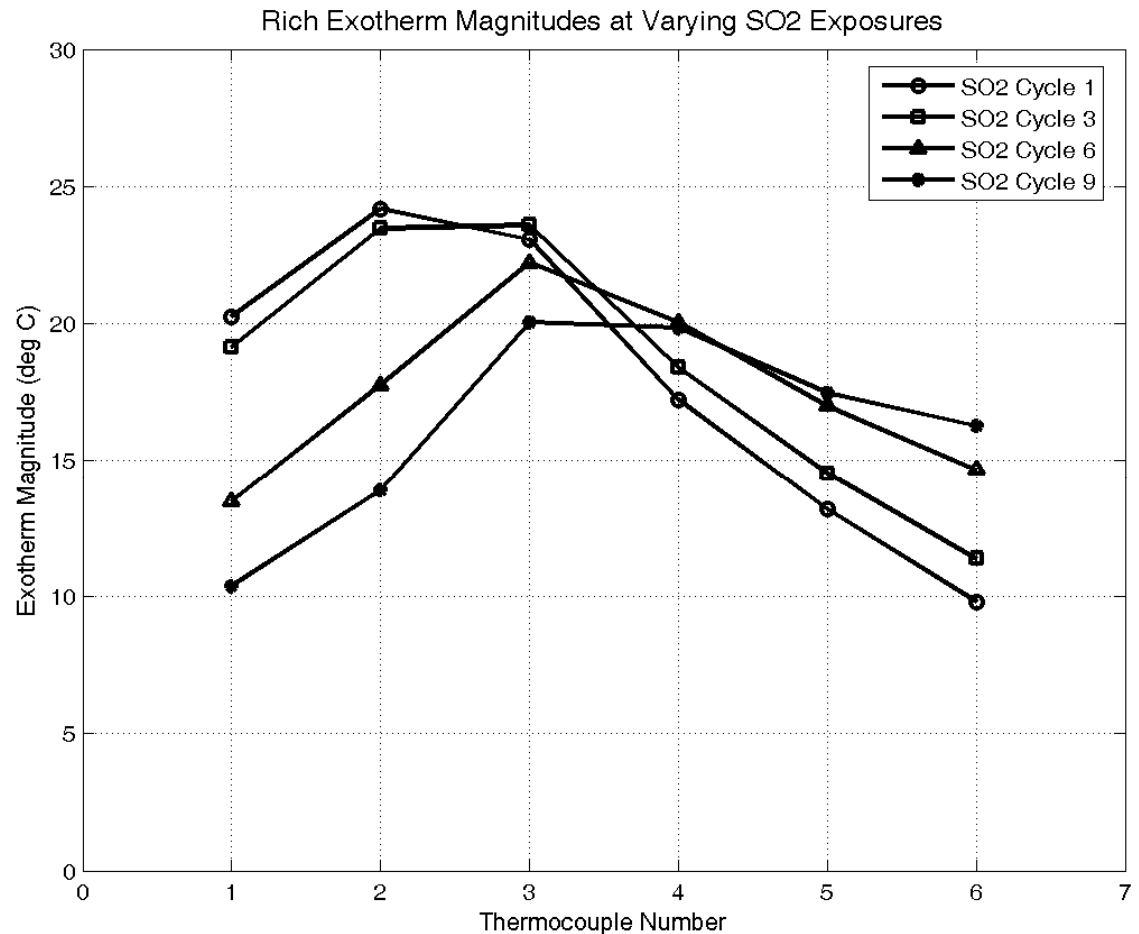
# Application to Sulfur Poisoning - 1/2

- Accelerated  $\text{SO}_2$  poisoning was conducted to gather experimental data for simulation, diagnostics, and modeling



# Application to Sulfur Poisoning - 2/2

- The exotherms detect the distribution of  $\text{NO}_x$  in the catalyst
- Sulfur poisoning manifests itself as a change in distribution
- Poisoning happens from the front of the catalyst back
- Depression of front exotherms
- Increase in rear exotherms

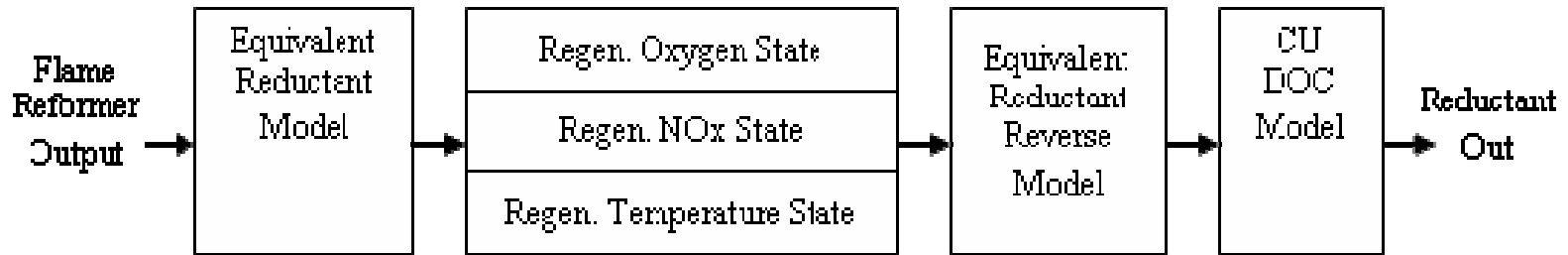


# LNT Regeneration Model

# Regeneration Model

- Model goals:
  - Accurate enough to serve as the plant in simulation studies
  - Accurate enough to validate control strategies in simulation
  - Regeneration model is not intended to be imbedded in PCM
- Model Structure:
  - Six-lump non-linear model, 18 total states
- Model Inputs:
  - Reductant inlet mass flow rate, oxygen mass inlet flow rate
- Model States:
  - Temperature, Oxygen Mass Stored, NO<sub>x</sub> Mass Stored
- Model Outputs:
  - Reductant outlet mass flow, oxygen outlet mass flow, temperature

# Regeneration Model with Support Models



- Equivalent Reductant – Transforms all reductants into equivalent reductant based on CO
- Equivalent Reductant Reverse – Transforms equivalent reductant back to hydrocarbons, then CO
- Clean-Up Catalyst Model – Oxidation catalyst model calibrated specifically for Flame Reformer emissions

# Regeneration Model – Verbal Description

- When reductant enters a lump, it first goes towards reducing stored oxygen
- Reductant that is unused by the oxygen storage is available for reducing stored  $\text{NO}_x$
- Reductant not used by either storage elements exits the lump
- When oxygen is introduced, it refills the oxygen mass state, unused oxygen exits the lump
- Constants relate the mass of reductant to mass of oxygen or  $\text{NO}_x$  reduced
- Temperature rise is related to CO consumption and  $\text{O}_2$  adsorption via constants
- Maximum reductant consumption is limited by a function that depends on the mass of stored oxidizer



# Model Description – Equations 1

State Equations:

$$\begin{aligned} \dot{m}_{O_2} &= B_1 \cdot \dot{m}_{red,O_2} && \text{if } \dot{m}_{O_2,in} = 0 \\ \dot{m}_{O_2} &= B_3 \cdot \dot{m}_{ads,O_2} && \text{if } \dot{m}_{O_2,in} > 0 \\ \dot{m}_{NOx} &= B_2 \cdot \dot{m}_{red,NOx} \end{aligned}$$

$$\dot{T} = C_1 \cdot (B_1 \cdot \dot{m}_{red,O_2}) + C_2 \cdot (B_3 \cdot \dot{m}_{ads,O_2}) + C_3 \cdot (B_2 \cdot \dot{m}_{red,NOx})$$

Supporting Equations:

$$\begin{aligned} \dot{m}_{red,O_2} &= \dot{m}_{red,in} && \text{if } \dot{m}_{O_2,in} = 0 \text{ and } \dot{m}_{red,in} < A_1(T) \cdot m_{O_2} \\ \dot{m}_{red,O_2} &= A_1(T) \cdot m_{O_2} && \text{if } \dot{m}_{O_2,in} = 0 \text{ and } \dot{m}_{red,in} \geq A_1(T) \cdot m_{O_2} \\ \dot{m}_{ads,O_2} &= \dot{m}_{O_2,in} && \text{if } \dot{m}_{O_2,in} > 0 \text{ and} \\ &&& \dot{m}_{O_2,in} < A_3(T) \cdot (M_{O_2,max}(T) - m_{O_2}) \\ \dot{m}_{ads,O_2} &= A_3(T) \cdot (M_{O_2,max}(T) - m_{O_2}) && \text{if } \dot{m}_{O_2,in} > 0 \text{ and} \\ &&& \dot{m}_{O_2,in} \geq A_3(T) \cdot (M_{O_2,max}(T) - m_{O_2}) \\ \dot{m}_{red,NOx} &= \dot{m}_{red,in} - \dot{m}_{red,O_2} && \dot{m}_{red,in} - \dot{m}_{red,O_2} < A_2(T) \cdot m_{NOx} \\ \dot{m}_{red,NOx} &= A_2(T) \cdot m_{NOx} && \dot{m}_{red,in} - \dot{m}_{red,O_2} \geq A_2(T) \cdot m_{NOx} \end{aligned}$$

# Model Description – Equations 2

$m_{O_2}$  = mass of stored oxygen (state variable)

$B_1$  = stoichiometric constant for reductant to stored oxygen

$\dot{m}_{red,O_2}$  = mass flow rate of reductant used for O<sub>2</sub> reduction

$B_3$  = stoichiometric constant for free oxygen to stored oxygen

$\dot{m}_{ads,O_2}$  = mass flow rate of free oxygen used of O<sub>2</sub> readsorption

$m_{NO_x}$  = mass of stored NO<sub>x</sub> (state variable)

$B_2$  = stoichiometric constant for reductant to stored NO<sub>x</sub>

$\dot{m}_{red,NO_x}$  = mass flow rate of reductant used for stored NO<sub>x</sub> depletion

$T$  = temperature of catalyst element (state variable)

$C_1$  = temperature rise coefficient for stored oxygen reduction

$C_2$  = temperature rise coefficient for oxygen readsorption

$C_3$  = temperature rise coefficient for NO<sub>x</sub> reduction

$\dot{m}_{red,in}$  = mass flow rate of reductant into the element

$\dot{m}_{O_2,in}$  = mass flow rate of oxygen into the element

$A_1(T)$  = reductant limit constant for O<sub>2</sub> reduction,

$A_2(T)$  = reductant limit constant for NO<sub>x</sub> reduction

$A_3(T)$  = oxygen limit constant for O<sub>2</sub> adsorption

$M_{O_2,max}(T)$  = maximum mass of stored oxygen

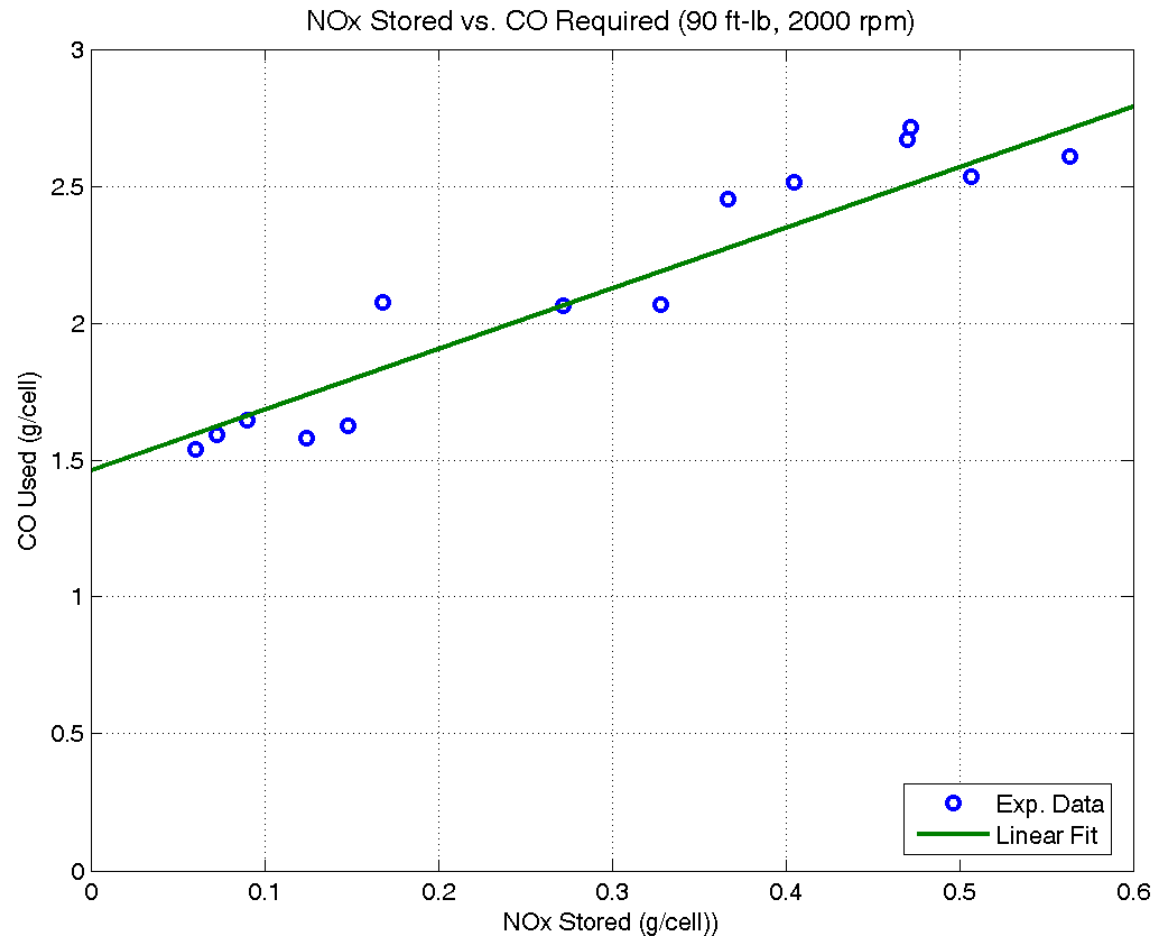
# Model Calibration Methodology

- The model, since it is distributed, requires “seeing” chemical reactions inside the catalyst
- This is accomplished through the use of exotherms
- All model calibration is performed using standard test cell equipment:
  - Thermocouples
  - UEGO sensors (2)
  - Upstream and Downstream NO<sub>x</sub> measurements
- With an understanding of exotherm behavior, model calibration is intuitive

# Model

## Parameter Identification - 1

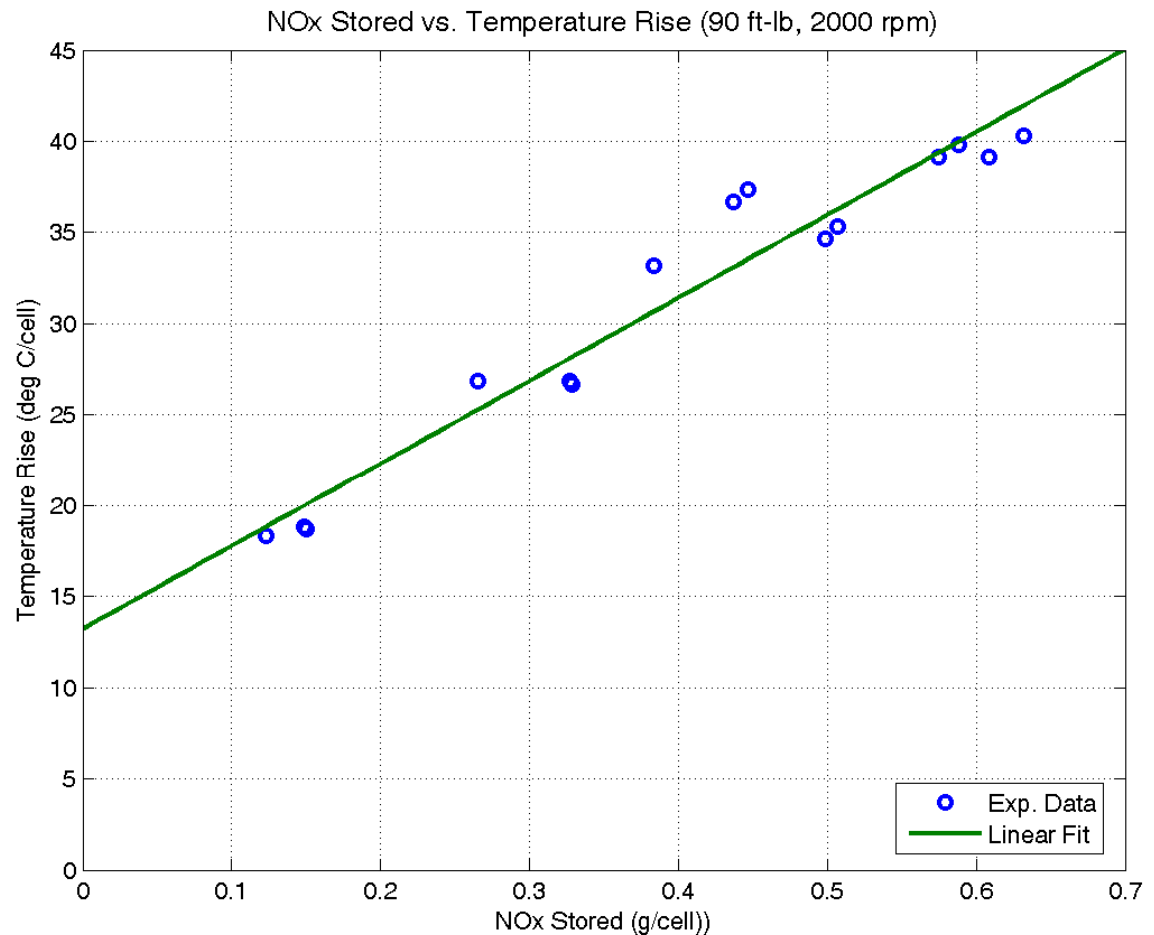
- Data from varying length storage cycles
- Slope of curve is  $[g \text{ CO}] / [g \text{ NO}_x] = 1 / B_3$
- Y-intercept can be used to get  $[g \text{ CO}] / [g \text{ O}_2] = 1 / B_1$  after the oxygen storage at this condition is measured



# Model

## Parameter Identification - 2

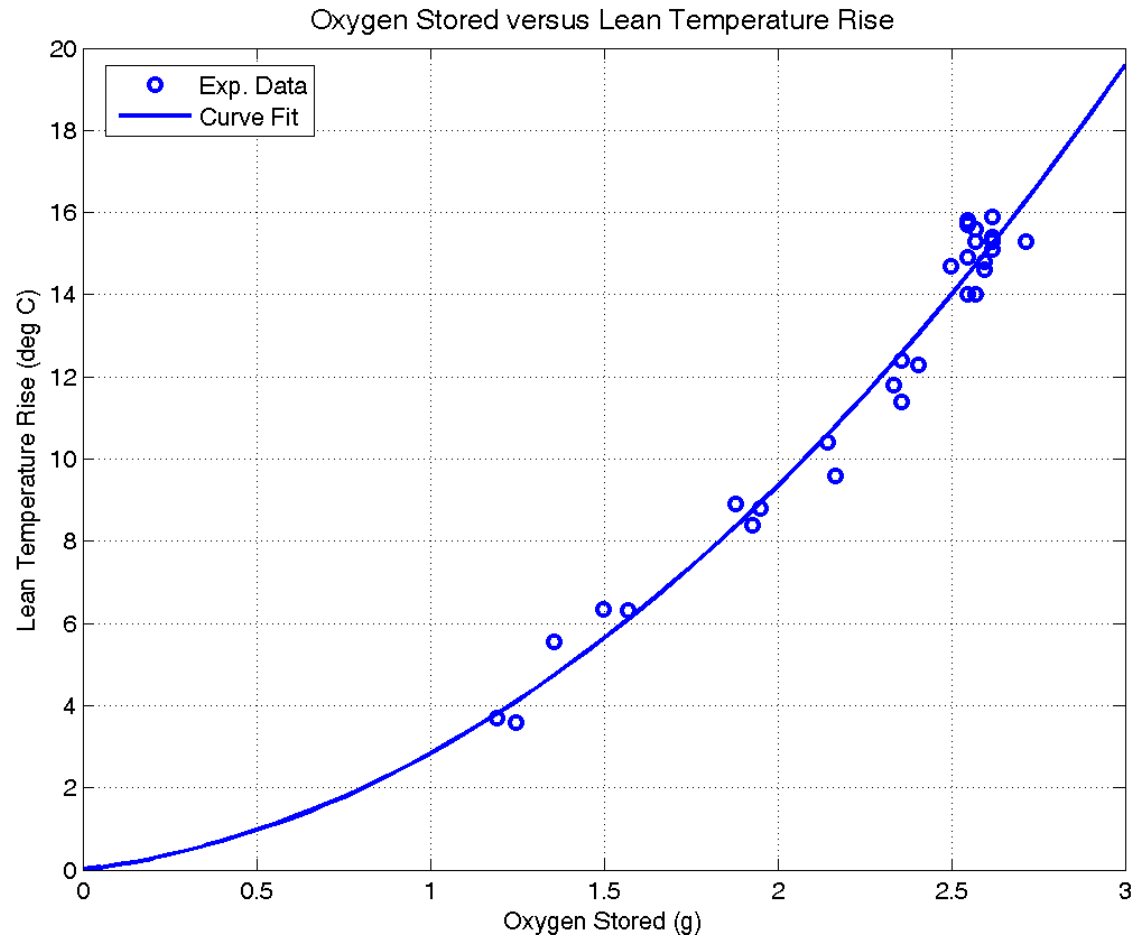
- Data from varying length storage cycles
- Slope of curve is  $[\text{deg C}] / [\text{g NOx}] = C_3$
- Y-intercept can be used to get  $[\text{deg C}] / [\text{g O}_2] = C_1$  with the oxygen storage mass at this condition



# Model

## Parameter Identification - 3

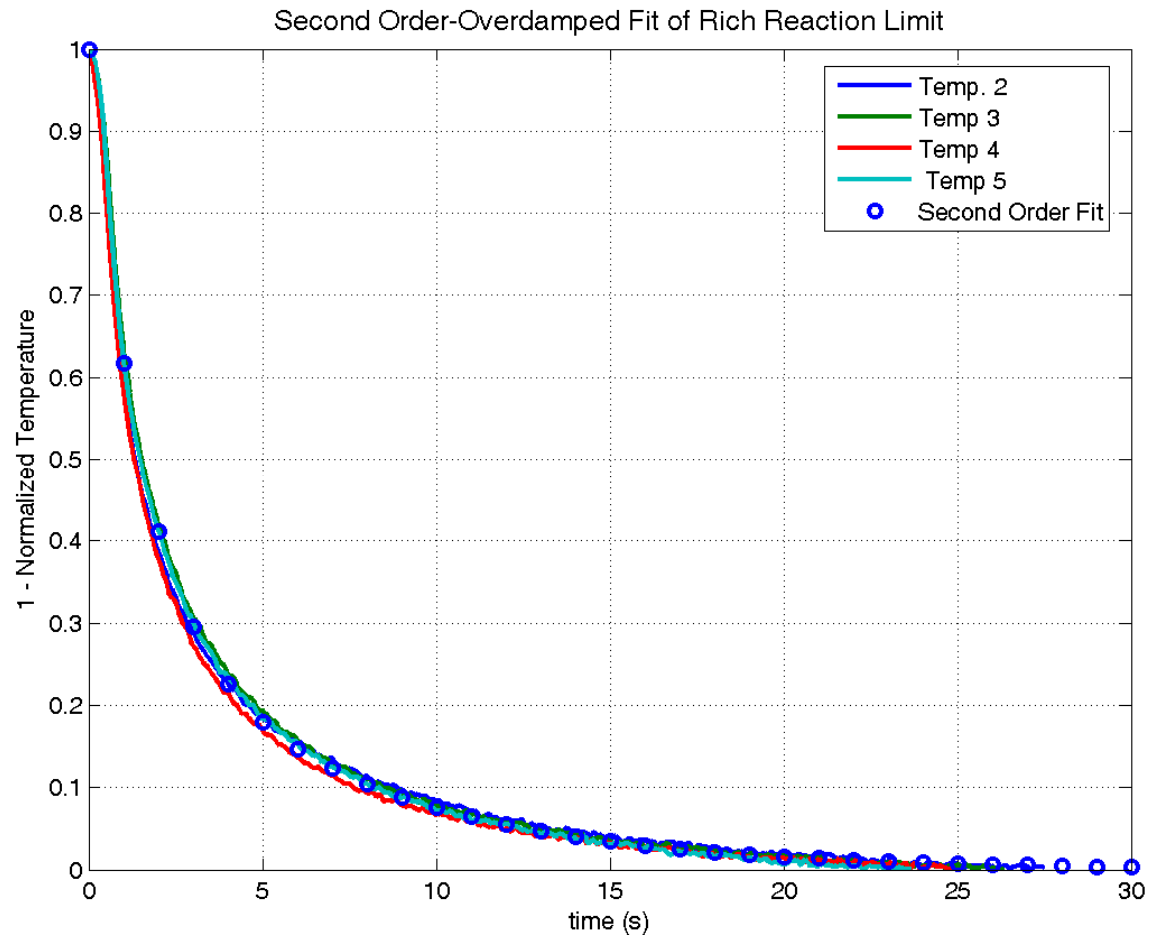
- Slope of this curve has units of  $[\text{deg C}] / [\text{g O}_2] = C_2$
- $B_2 = 1$ , since it is relating grams of  $\text{O}_2$  to grams of  $\text{O}_2$
- Multiple mechanism for  $\text{O}_2$  storage are suspected to be the cause the nonlinearity



# Model

## Parameter Identification - 4

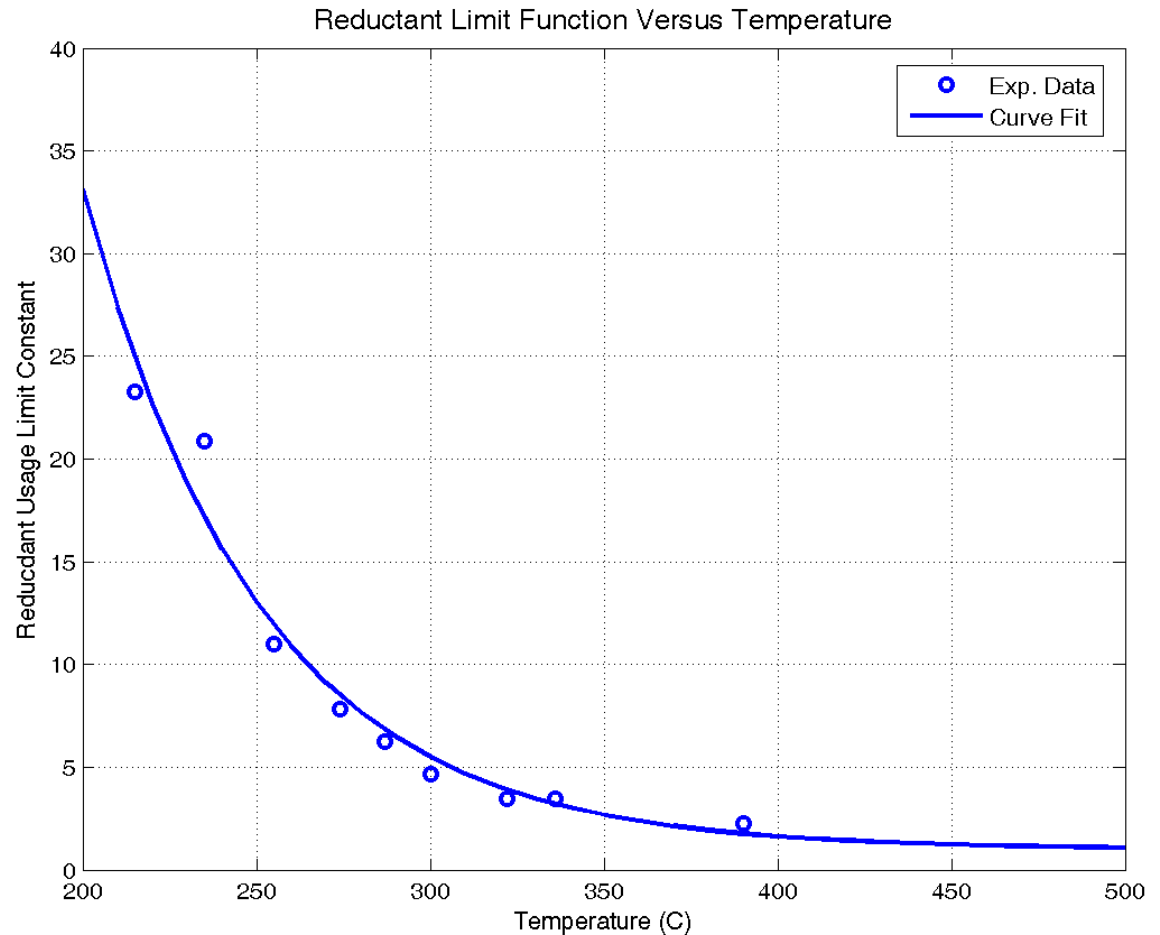
- “A” parameters require time-domain data
- Need to put the catalyst in state where it reveals only the sought after dynamics – CO oversupply
- The resulting exotherm can be used to determine the maximum reductant usage function or constant



# Model

## Parameter Identification - 5

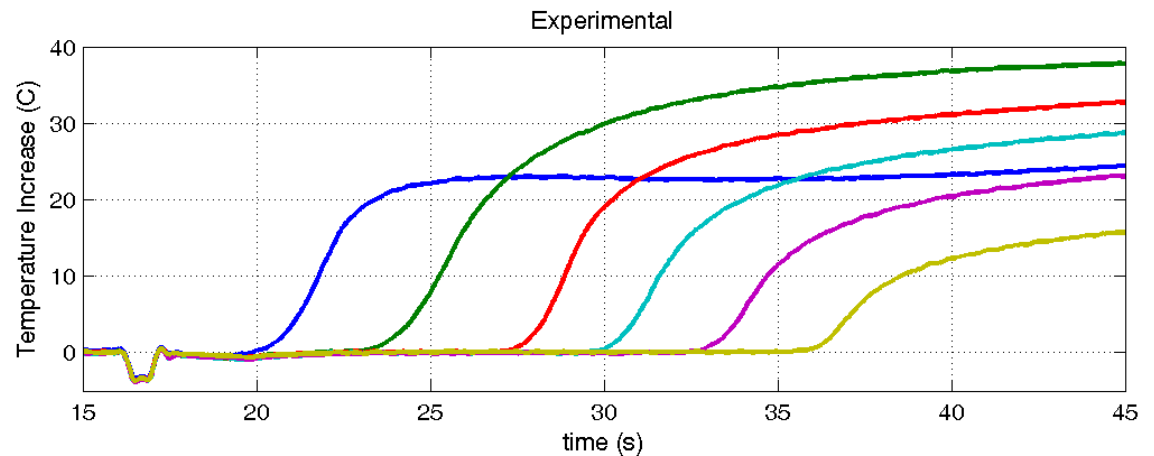
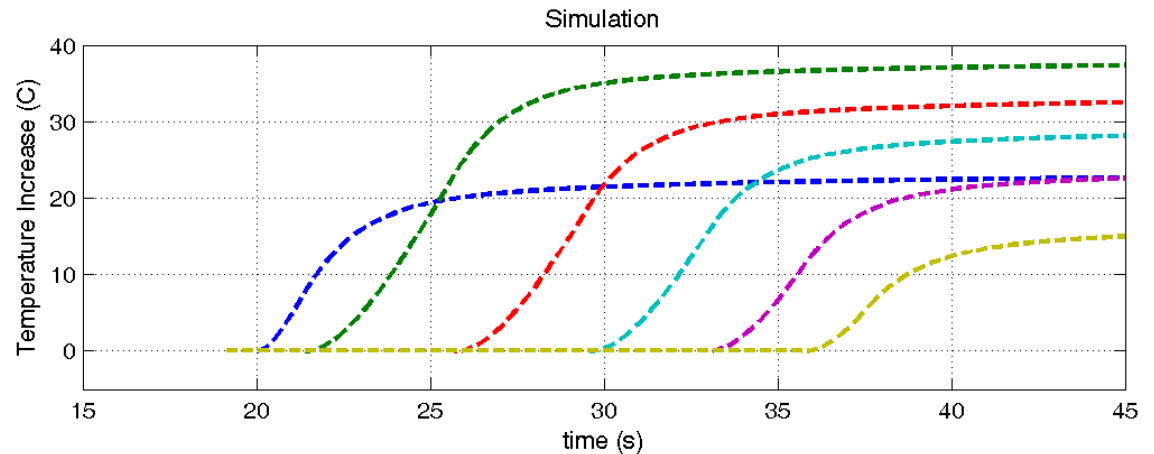
- A first-order reductant usage function fit well over typical operating conditions
- Strong dependence on catalyst temperature
- “Time-constant” depends on catalyst formulation





# Regeneration Model Validation

- The model demonstrates good agreement in magnitude with experimental data
- The time agreement is acceptable given the intended application



# Applications for the Model


- System performance simulation
- Develop temperature based controls
  - The ability to “see” inside the catalyst
  - Allows sensing impending reductant slip *before* it happens
- Formulate and solve an optimal control of reductant flow rate
  - Based on a linearized model, it is possible to solve for a control that minimizes regeneration time, minimizes reductant slip, and maximizes NO<sub>x</sub> reduction
  - A square pulse of reductant is far from the optimal shape
- All of the above were investigated

# Conclusions

- Inexpensive temperature measurements inside the catalyst substrate allow internal reactions to be observed with time and spatial resolution in an engine environment
- These measurements can be used to estimate the mass of  $\text{NO}_x$  and  $\text{O}_2$  reduced and the amount of  $\text{O}_2$  readsorbed
- This information has a variety of uses in modeling, control, fault detection, and catalyst evaluation

# Future Work

- Develop a more rigorous approach to using temperature measurements to infer reactions
- Look at applications to engine-based regeneration
- Explore the suitability of the method as a low cost sensor with additional function over UEGO and  $\text{NO}_x$  sensors

 This work is currently unfunded and proceeding slowly. If there is an interest in collaboration, contact: [midlam-mohler.1@osu.edu](mailto:midlam-mohler.1@osu.edu)