Catalytic Solutions to Achieve Clean Diesel Power

Mike Harold
University of Houston
Dept. of Chemical & Biomolecular Engng.

Seminar presented at
AIChE South Texas Section

September, 2009

Motivation

A good air day in Houston …………….. and a bad air day.

http://www.nasa.gov/vision/earth/everydaylife/archives/HP_ILP_Feature_03.html

The Energy & Environment Challenge

- Energy supply-demand imbalance
  - World-wide production of petroleum will peak in next 20-50 years
  - World-wide consumption of energy is accelerating
- Combustion of fossil fuels
  - Produces NOx, particulates, VOCs, CO_2

The Energy & Environment Challenge

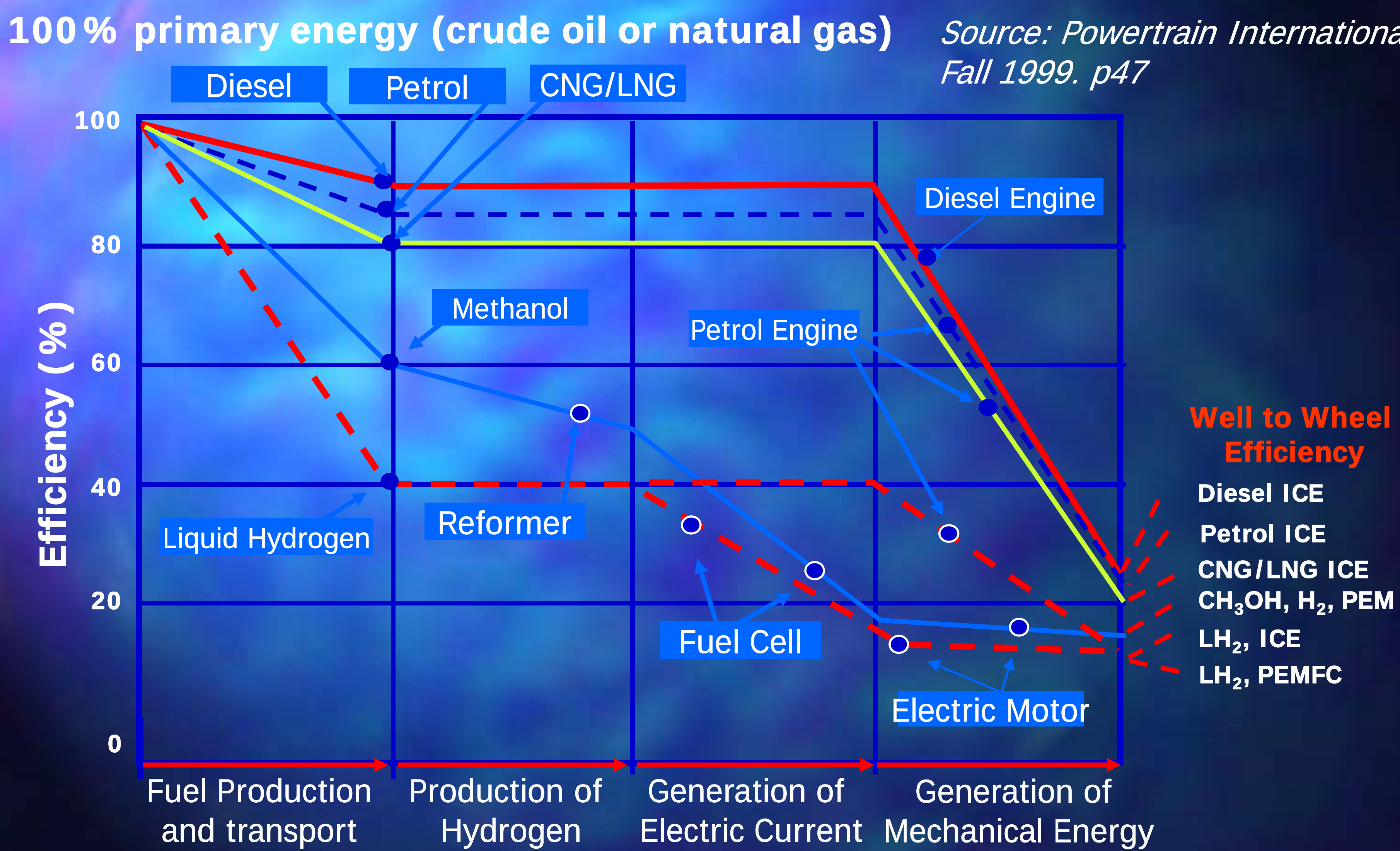
- Energy supply-demand imbalance
  - World-wide production of petroleum will peak in next 20-50 years
  - World-wide consumption of energy is accelerating
- Combustion of fossil fuels
  - Produces NOx, particulates, VOCs, CO_2

How do we meet the energy demands, clean the air, and address climate change?

Well to Wheel Efficiency:

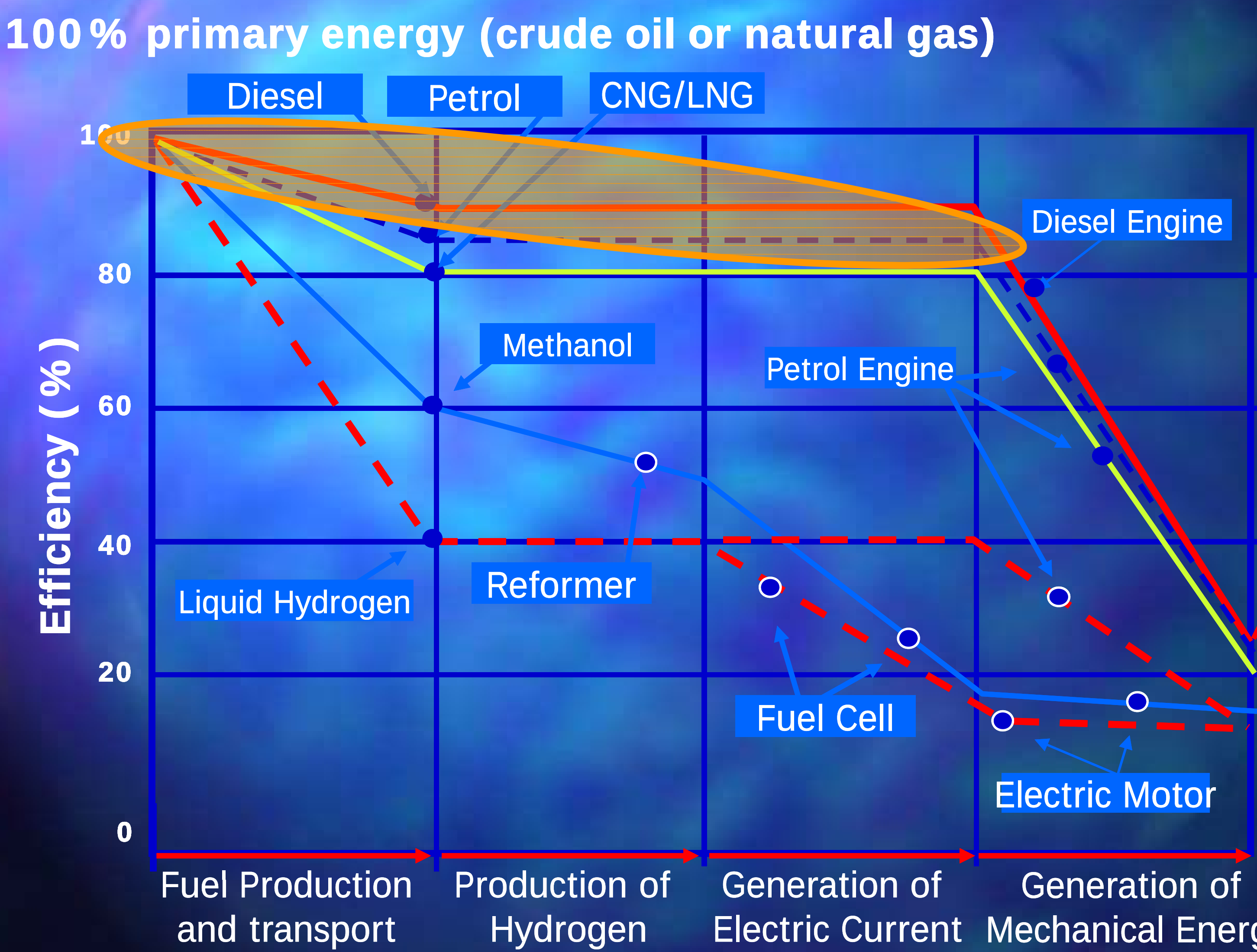
Petroleum/natural gas in fuel cells and combustion engines

Source: Powertrain International, Fall 1999. p47



Well to Wheel Efficiency:

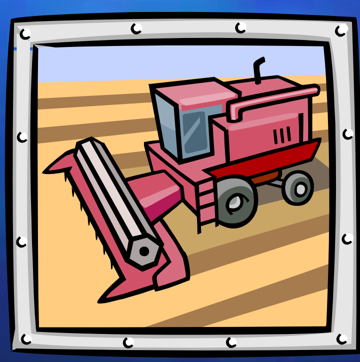
Petroleum/natural gas in fuel cells and combustion engines



Rudolph Diesel

Diesel Power: Exhaust Pollutants

POLLUTANT	ABATEMENT
Particulate Soot	Particulate Filter
VOCs	Oxidation Catalyst
CO	Oxidation Catalyst
NOx	SCR, NSR
SO_2	NONE



Diesel NOx Reduction Challenge

Diesel Power

- Large contributor to NOx
- Increased Durability
- Improved Fuel Efficiency
- Lean Combustion exhaust:

  Exhaust NO_X –> N_2 difficult

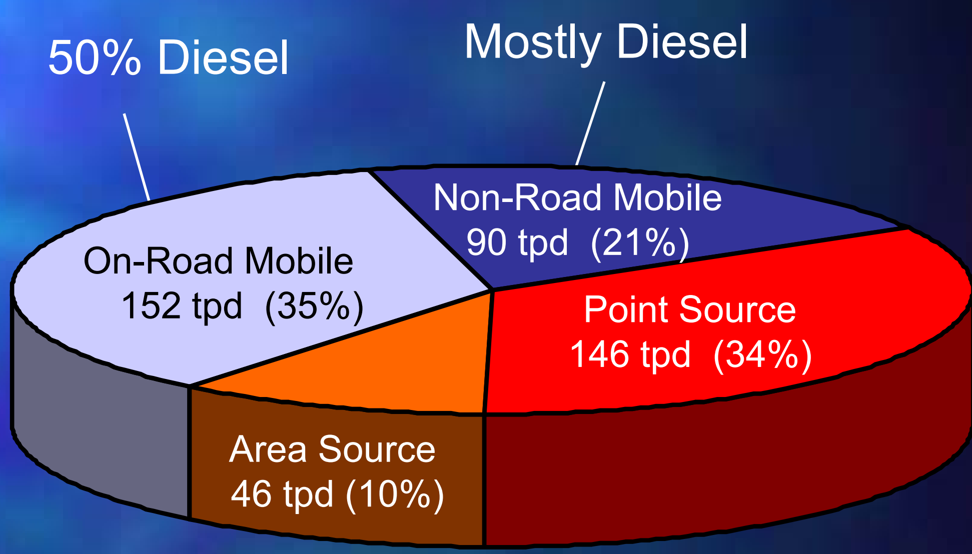
Challenge: Reduce diesel NO_X emissions* with cost effective & reliable technology

**EPA Target for Houston area:*

80% reduction in NOx emissions by 2018

Houston/Galveston Area

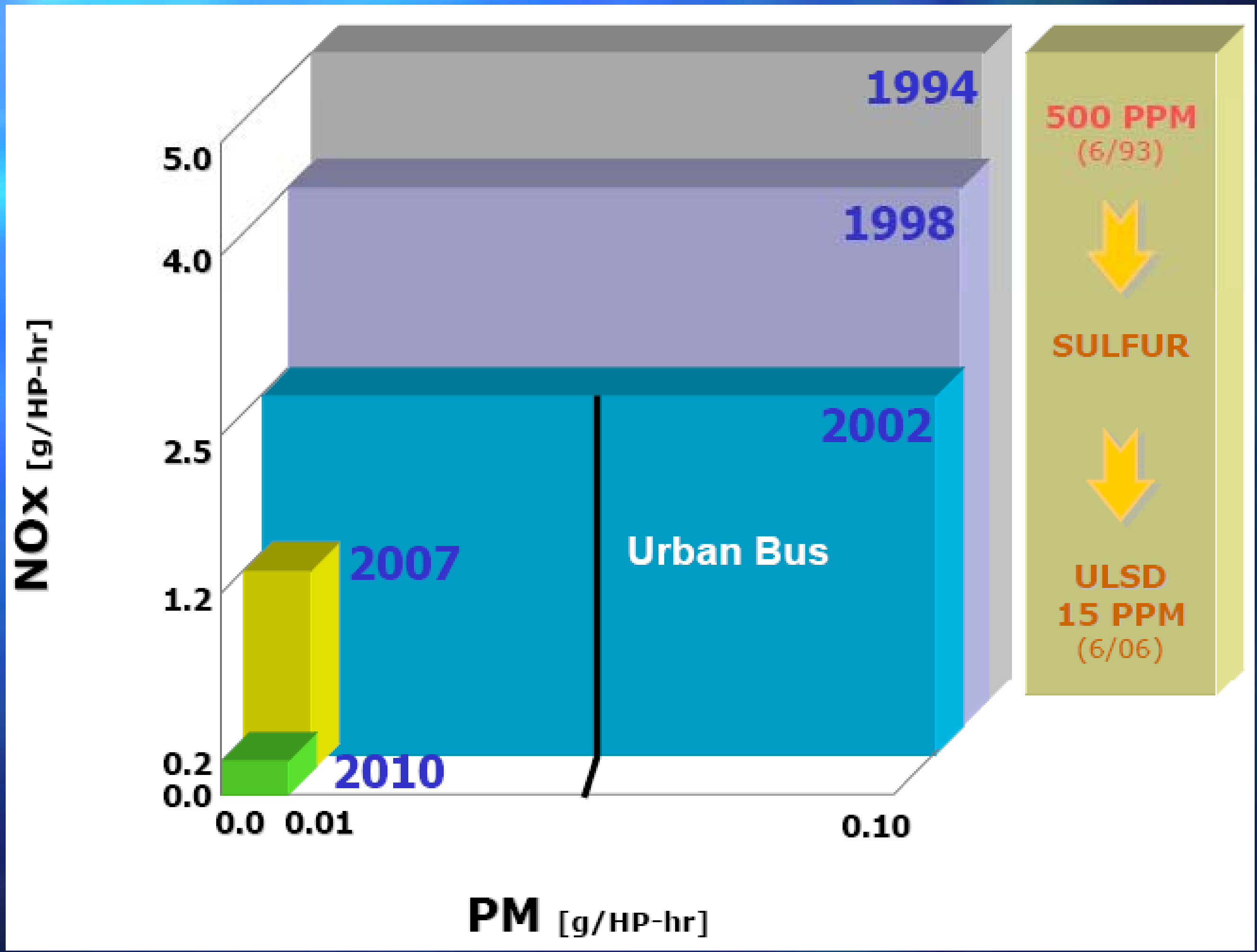
NOx Emission Sources**



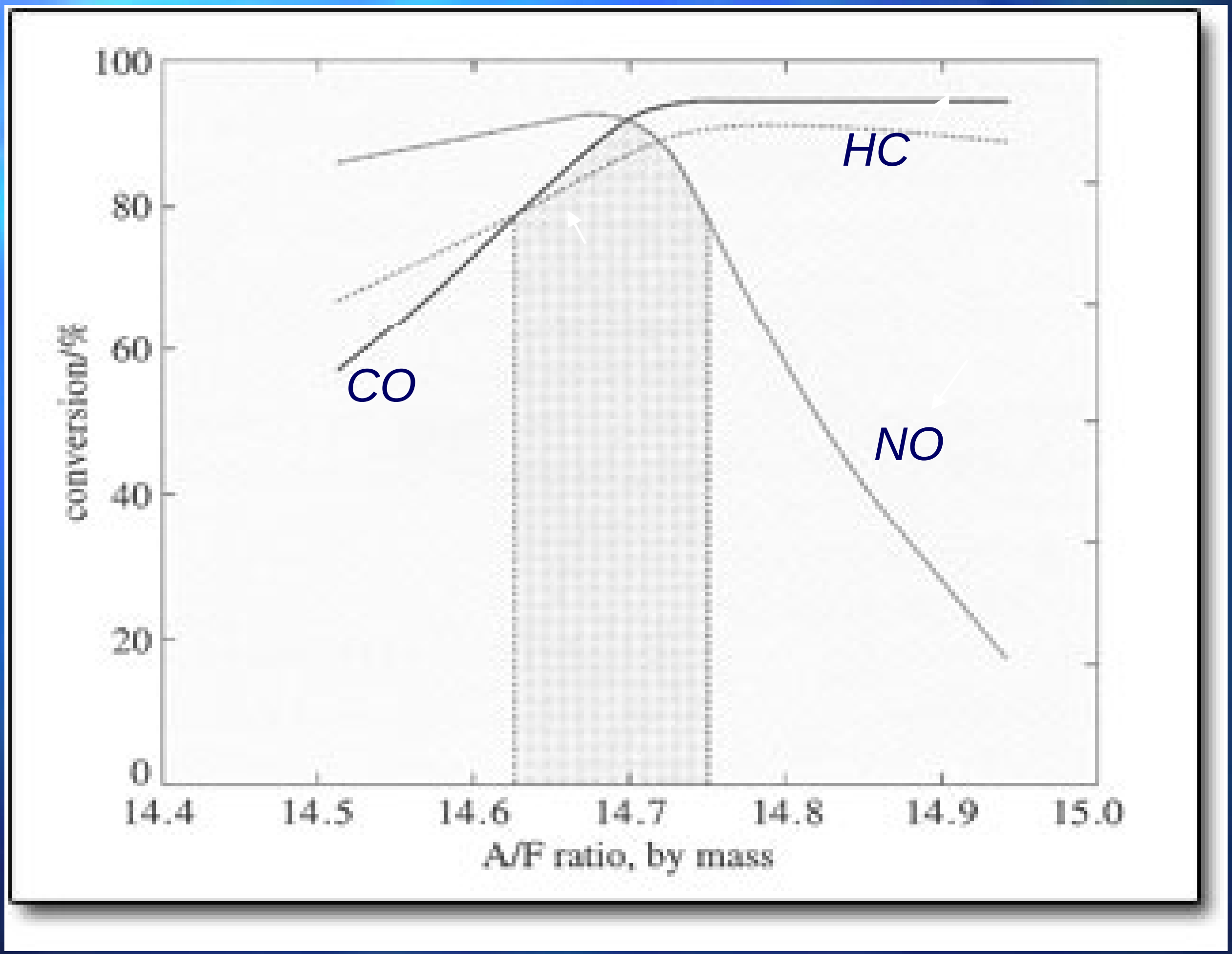
Total NOx: 434 tons NOx/day**

***Source: TCEQ Website*

US Heavy Duty Diesel Emissions Standards



Three-Way Catalytic Converter



www.openlearn.open.ac.uk

What is Clean Diesel?

- It is NOT a special type of diesel that does not produce pollutants when burned
- It is NOT Ultra Low Sulfur Diesel (ULSD)
- It is NOT “biodiesel” or “renewable diesel”
- It is NOT “gas-to-liquids” (GTL) diesel

What is Clean Diesel?

- It is NOT a special type of diesel that does not produce pollutants when burned
- It is NOT Ultra Low Sulfur Diesel (ULSD)
- It is NOT "biodiesel" or "renewable diesel"
- It is NOT "gas-to-liquids" (GTL) diesel
- Instead.....

  it is a system that combines low sulfur diesel (one of the above) with advanced engine and aftertreatment technologies to produce an exhaust with significantly lower NOx and PM emissions

Why is Clean Diesel Important?

- Diesel vehicles are more fuel efficient than gasoline vehicles (15-30%)
- Diesel vehicles have the highest "well-to-wheels" efficiency; i.e. efficiency of converting energy content of energy of petroleum in the ground into mechanical energy of the vehicle
- Clean diesel is a way to meet the challenge of reducing energy consumption in transportation and CO_2 emissions

The "Clean Diesel" Issue is Pervasive

Energy

Economics

Environment

Public Policy

Health

Technology

California proposes rules limiting pollution from nearly all diesel trucks

By Paul Rogers   Mercury News

Posted: 12/10/2008 06:56:32 PM PST

The black soot that big-rig trucks belch from their chugging **diesel engines** may soon become a thing of the past.

In one of the more far-reaching **smog** regulations that California has ever proposed, state air regulators are considering a first-in-the-nation plan that would require nearly every privately owned heavy diesel truck in the state to install a **filter that would reduce emissions of soot from their rigs by 85 percent**.

The new **regulation** would affect 1 million truckers, half of them registered out of state who regularly drive on California freeways. If approved by the California Air Resources Board at its meeting Friday, it would take effect in 2010, with nearly all trucks required to be retrofitted by 2014.

The filters — stainless steel and three feet long — attach to exhaust pipes and **cost $15,000 to $20,000 per truck**. Those who back the proposal point to massive public health benefits. Opponents call the **costs prohibitive**, especially during a time of **economic crisis**.

Supporters note that medical research over the past decade shows that microscopic diesel particles are among the most harmful type of air pollution. Not only can they lodge deep in the lungs during regular exposure, but also they can penetrate the walls of blood vessels, causing inflammation that can lead to strokes and heart attacks.

"This is a very big deal. **Particulate matter from diesel engines is one of the most toxic substances that we have found**," said Dr. Thomas Dailey, chief of pulmonary medicine at Kaiser Permanente Medical Center in Santa Clara.

Diesel soot contains more than **40 cancer-causing chemicals**, including formaldehyde and benzene. The elderly and children are considered most at risk, particularly in urban areas.

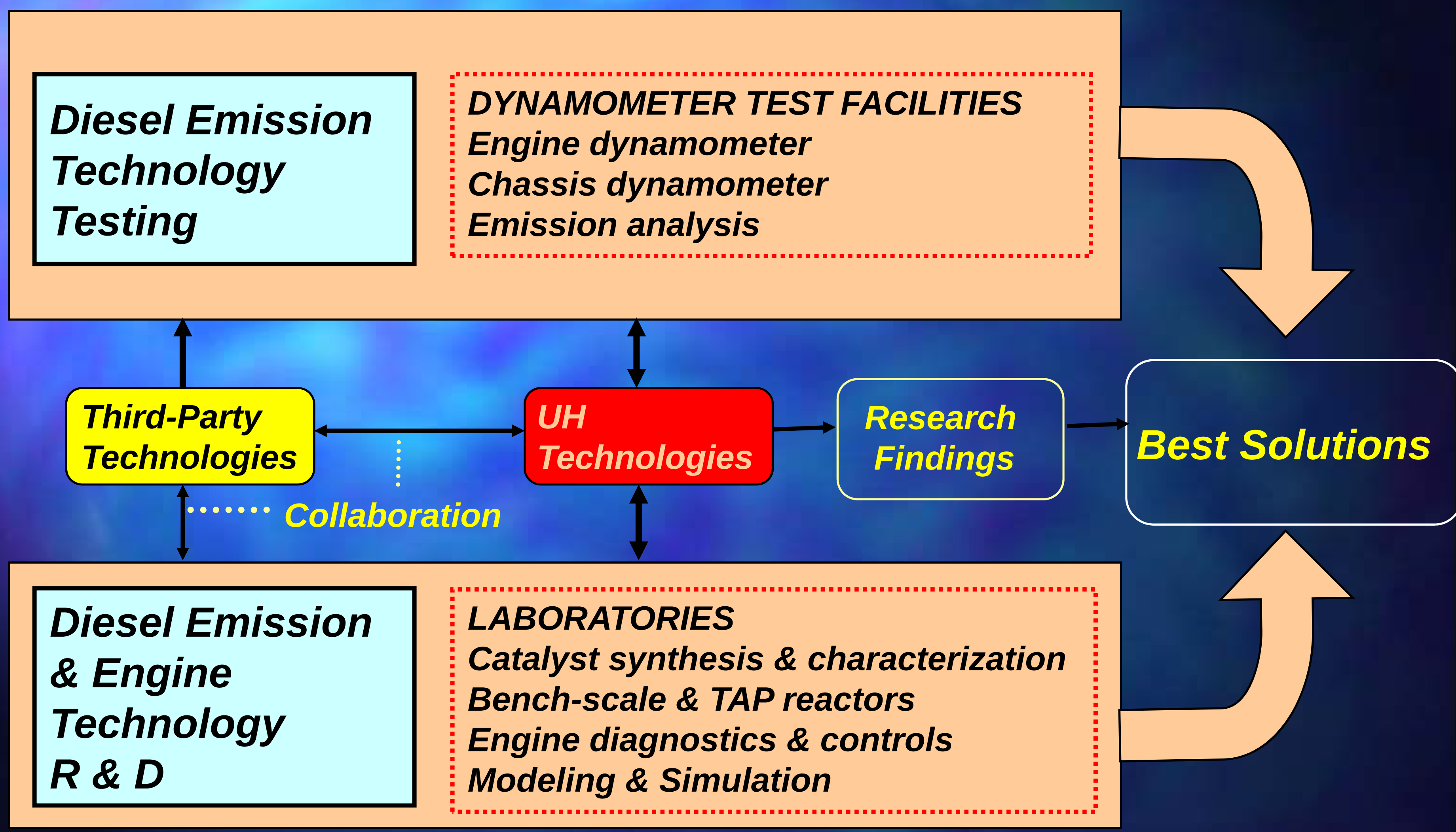
Clean Diesel Emission Technology

Evolving **New Fuels** →

Diesel Oxidation Catalyst	→	Diesel Particulate Filter	→	NOx Reduction Reactor	→ *Clean Exhaust*
Abatement: VOCs & CO		Soot & Solids		NO & NO_2	
Status: *Implemented*		*In Progress*		*Under Development*	

Message: The "clean diesel" vehicle is a sophisticated unit.

UH Clean Diesel Research

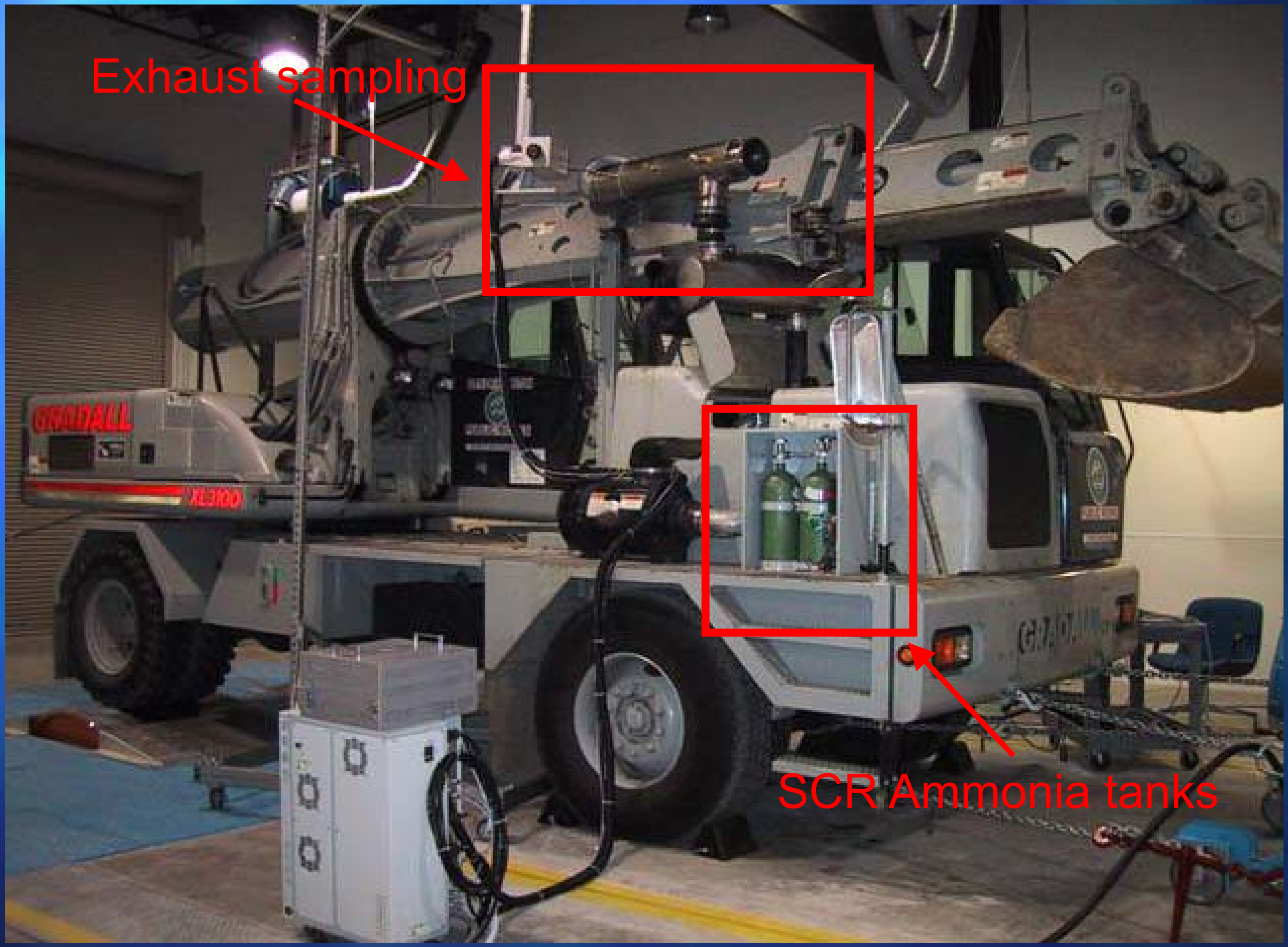


Technology Targets For Development & Testing

- Incremental
  - Fuels: Biodiesel, Fuel additives
  - Exhaust gas recirculation (EGR)
- "Step Change"
  - Selective catalytic reduction with urea/NH_3 (SCR)
  - Lean NOx traps (LNT)
  - SCR/LNT systems
  - Continuously regenerating soot filters
  - Integrated NOx & soot systems
  - Integrated biodiesel solutions (e.g. BD + EGR)

Texas Diesel Testing & Research Center

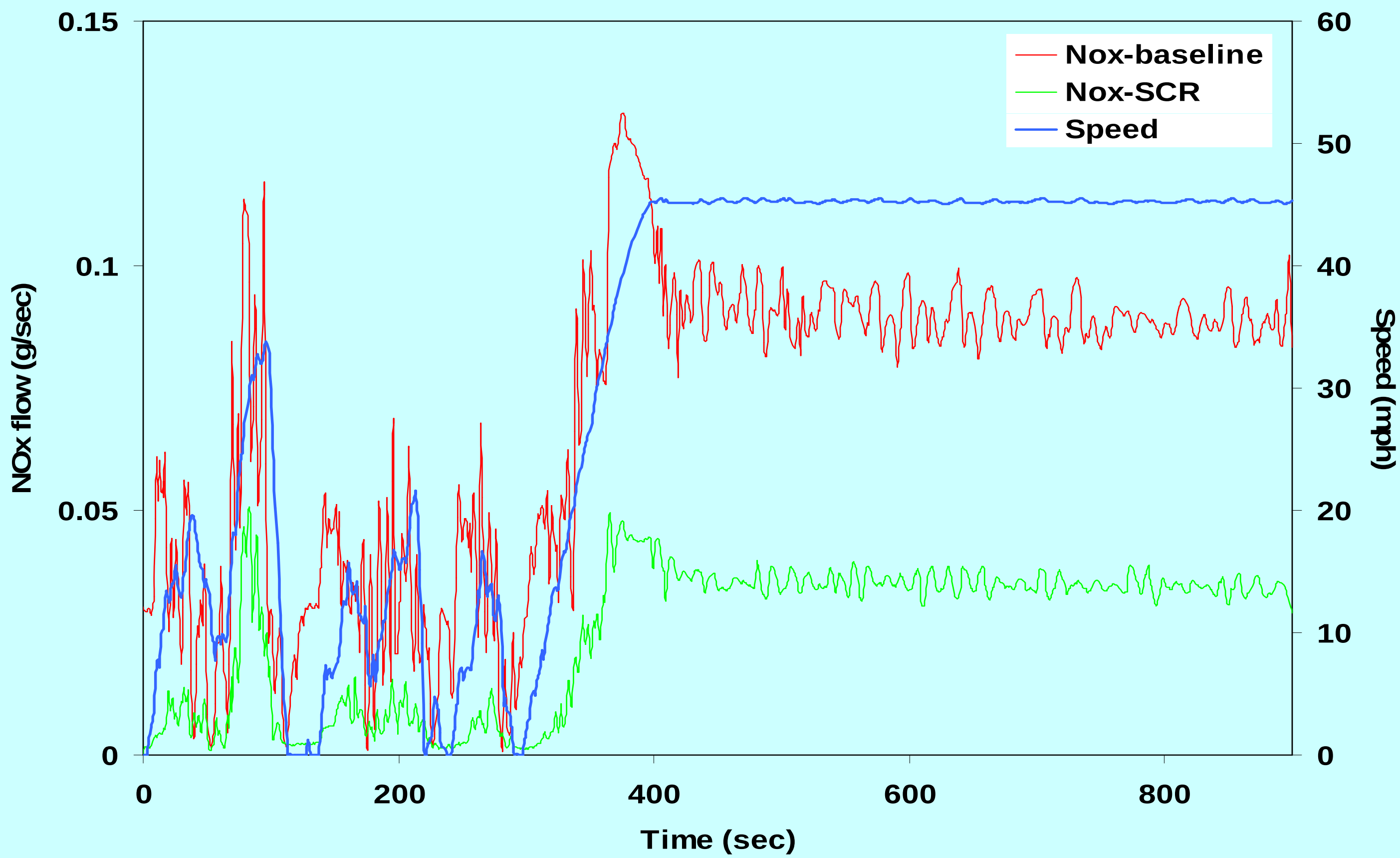
Heavy-Duty Chassis Dynamometer



SCR (Anhydrous NH_3): Typical Results

	% Reduction	g/mile(Baseline)	g/mile(SCR)
NOx	64.90	8.13	2.86

Equipment Type: 1992 Gradall, G3WD
Engine: Cummins 6BT 5.9
Baseline Test Date: 11/22/04
Retrofit Test Date: 11/23/04
Drive Cycle: "Off Road Excavator"
SCR: Extengine Inc.



Synergistic Technology: Biodiesel + EGR

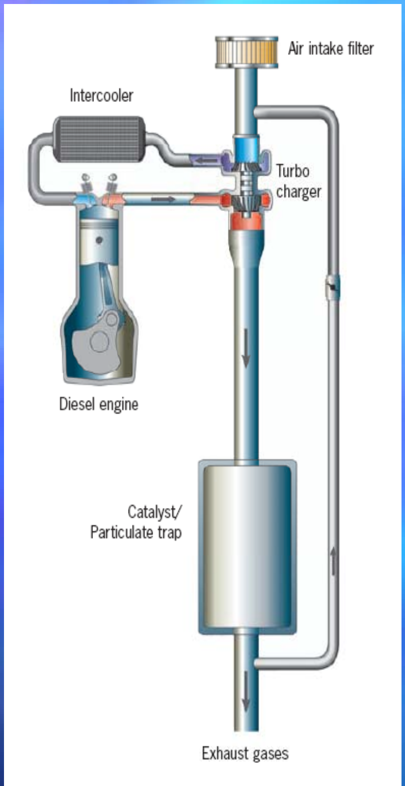
Biodiesel + EGR

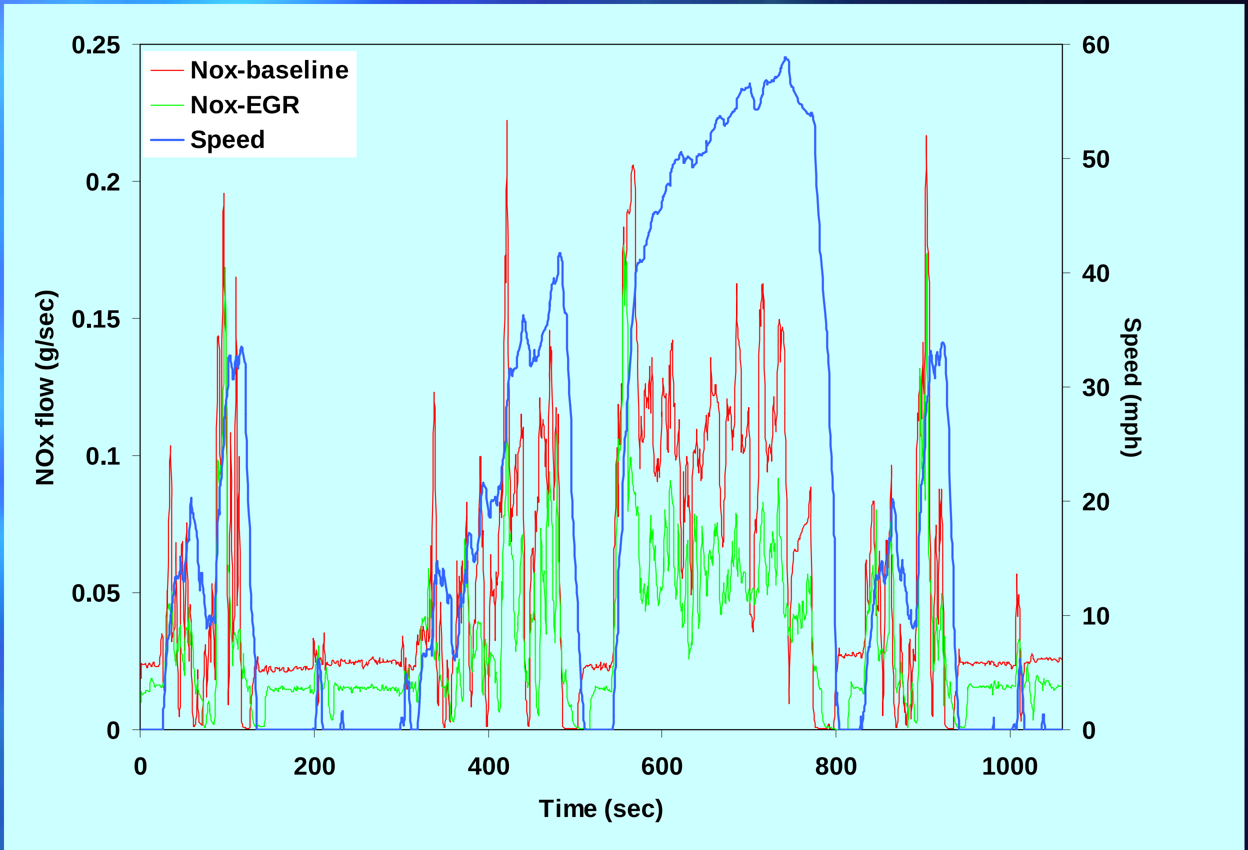
- Reduced particulates & HCs
- Reduced NOx

→ Reduced PM & NOx

An attractive retrofit solution!

EGR: Dynamometer Results



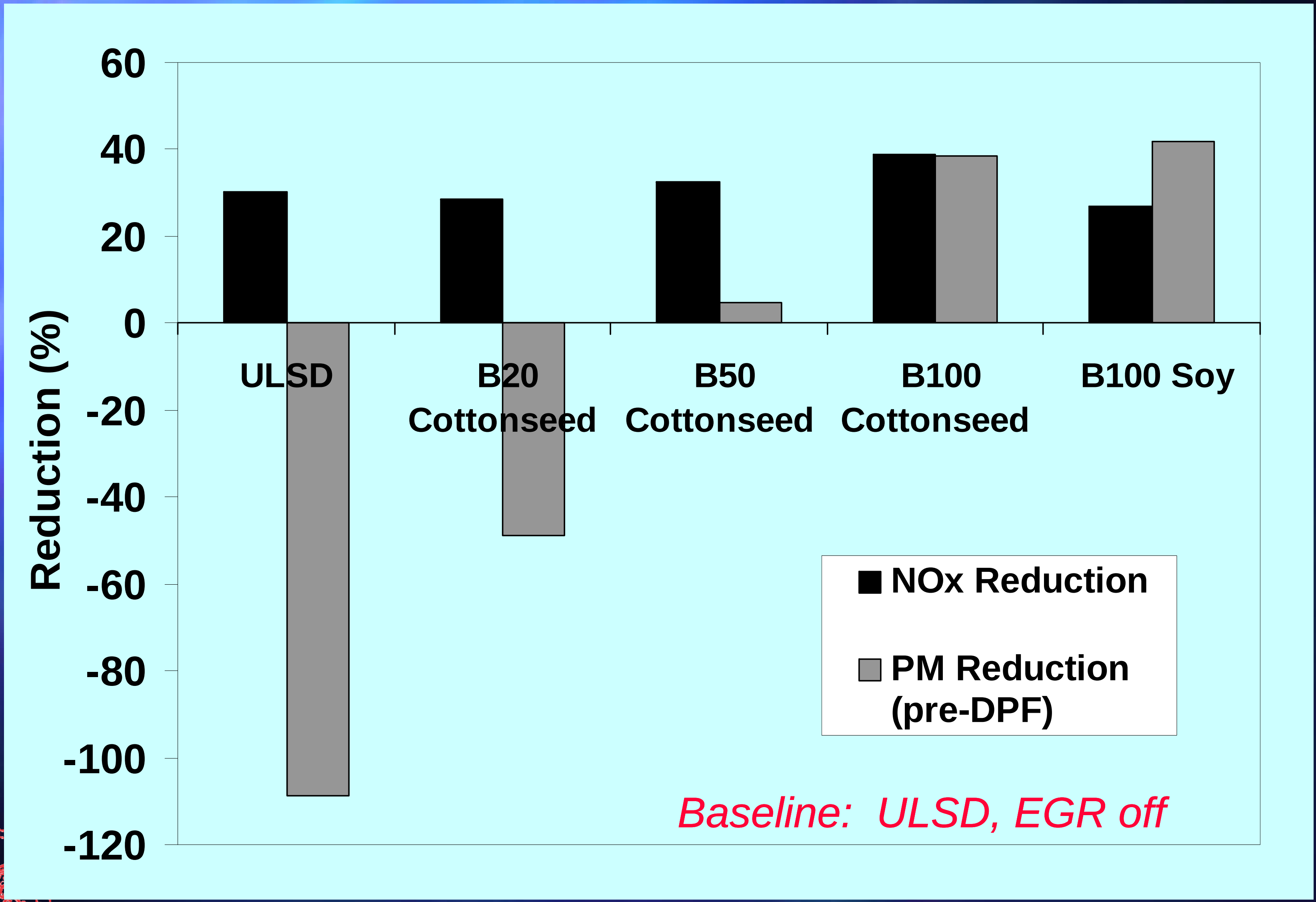


EGR System:

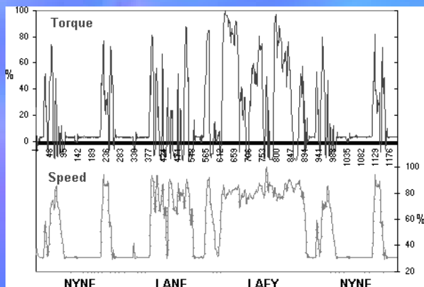
STT Emtec Inc.

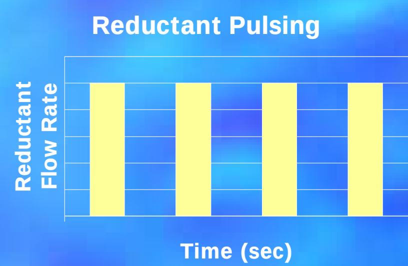
	% Reduction
NOx	42
CO	83
HC	92

EGR + Biodiesel: Summary of Effects

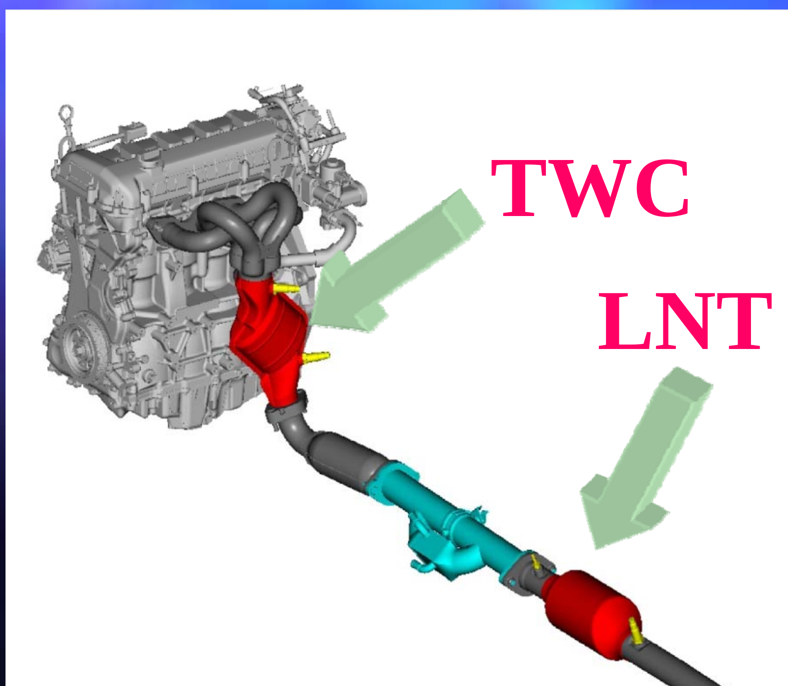


Lean NOx Trap: Adsorptive Catalytic Reactor



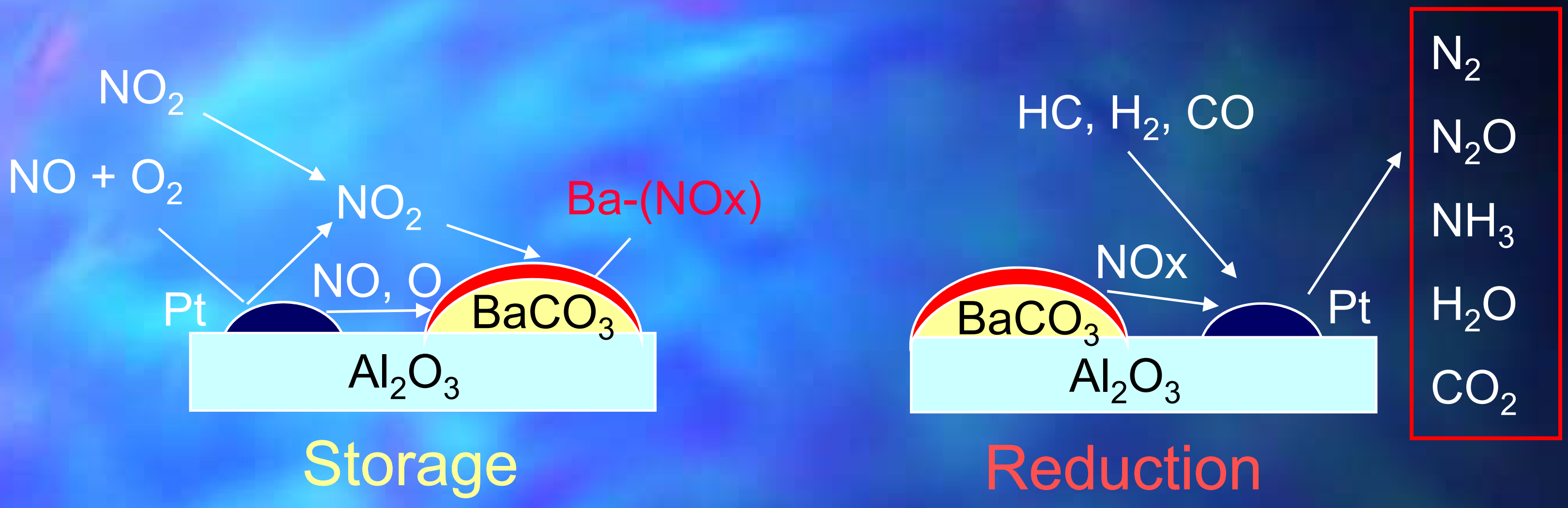


Engine Exhaust → LEAN NOx TRAP → Clean Exhaust



- Challenges
  - Maximize NOx conversion
  - Maximize reductant conversion
  - Minimize fuel penalty
  - Minimize deactivation
  - Achieve robust control

NOx Storage & Reduction (NSR)



- NOx Storage
  - Trap NO/NO_2 as surface species, nitrite, nitrate
  - Need high trapping efficiency (> 95%)
  - Catalytic adsorbent: Pt/Rh/Alkali Earth Oxide/Support
- NOx Reduction
  - Reduce NOx on Pt/Rh during rich purge
  - Need high conversion of NOx to N_2 (> 90%)
  - Ensure high conversion of reductant via oxidation

What is "Optimal LNT Operation"?

- LNT design: A multi-objective task
  - Maximize NOx & reductant conversion
  - Maximize N_2 selectivity (eliminate NH_3)
  - Minimize fuel penalty
  - Maintain high catalyst activity
  - Achieve robust on-board control
- Hybrid LNT-SCR application:

$$H_2, NO \longrightarrow \boxed{LNT} \xrightarrow{NH_3,\ NO} \boxed{SCR} \xrightarrow{N_2,\ H_2O}$$

  - Promote interstage ammonia production

Objective: *Move towards "optimal LNT operation" by…..*

- Elucidate spatio-temporal behavior of LNT with H_2 as reductant
- Understand differences in steady-state & cyclic product distributions; e.g., N_2 vs. NH_3
- Formulate phenomenological picture of LNT
- Develop quantitative reactor model to guide optimization

LNT Research Approach

Experiments ↔ ***Modeling & Simulation***

- Lean NO_X Storage
- Steady-state lean NO_X reduction
- NO_X storage & reduction (cycling)

Transient kinetics studies (TAP)

Bench-scale Reactor Studies

Vehicle Dynamometer Testing

Implementation / Optimization of LNTs

- Develop predictive LNT models
- Optimize LNT design
- Integrate into onboard control system

Kinetic Modeling

- Micro-kinetics
- Global kinetics

Reactor Modeling

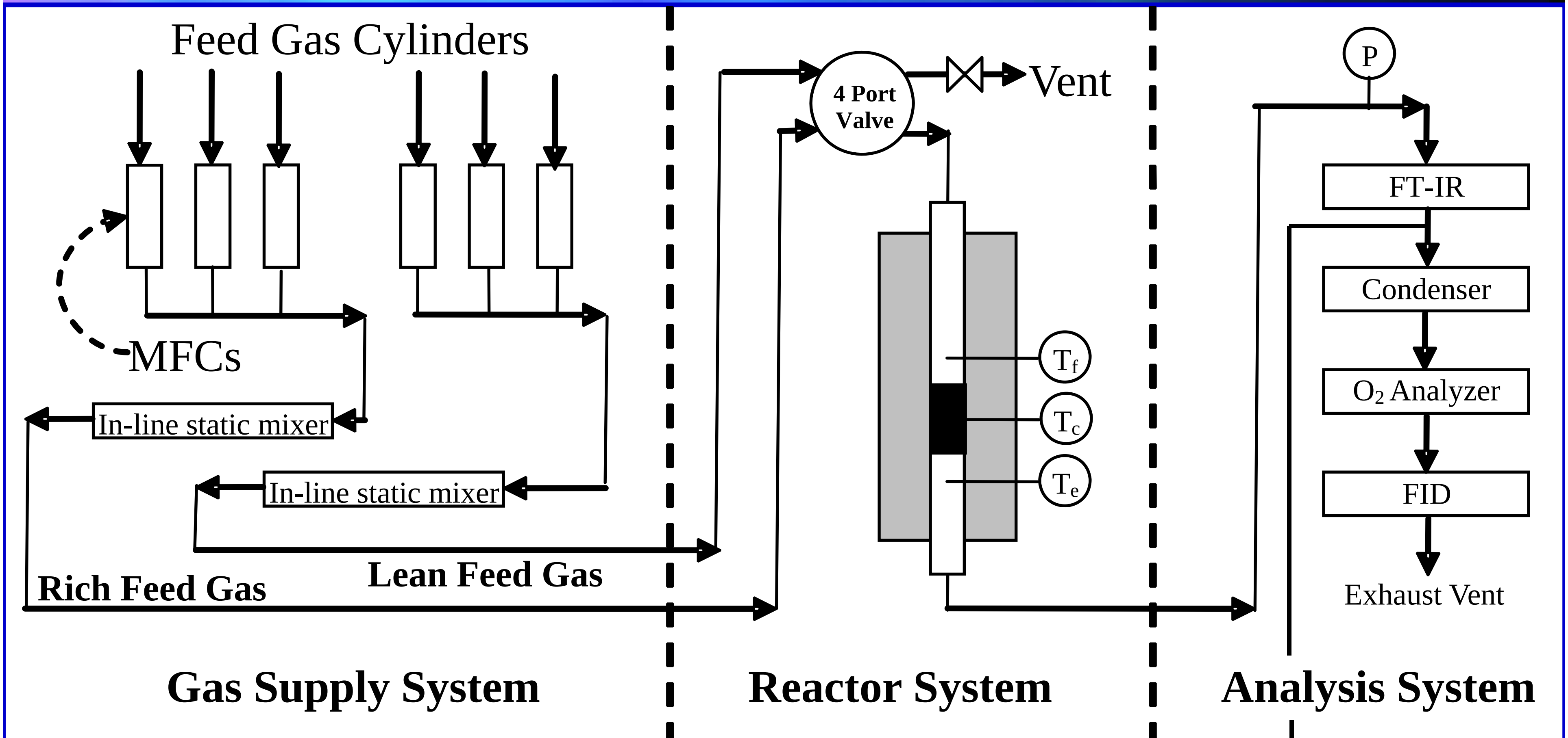
- Isothermal / short monoliths
- Non-isothermal integral monoliths

Activities

- Elucidation of data
- Bifurcation analysis

Low-dimensional models for optimization & control

Bench-Scale Monolith Reactor System



Mass Spec

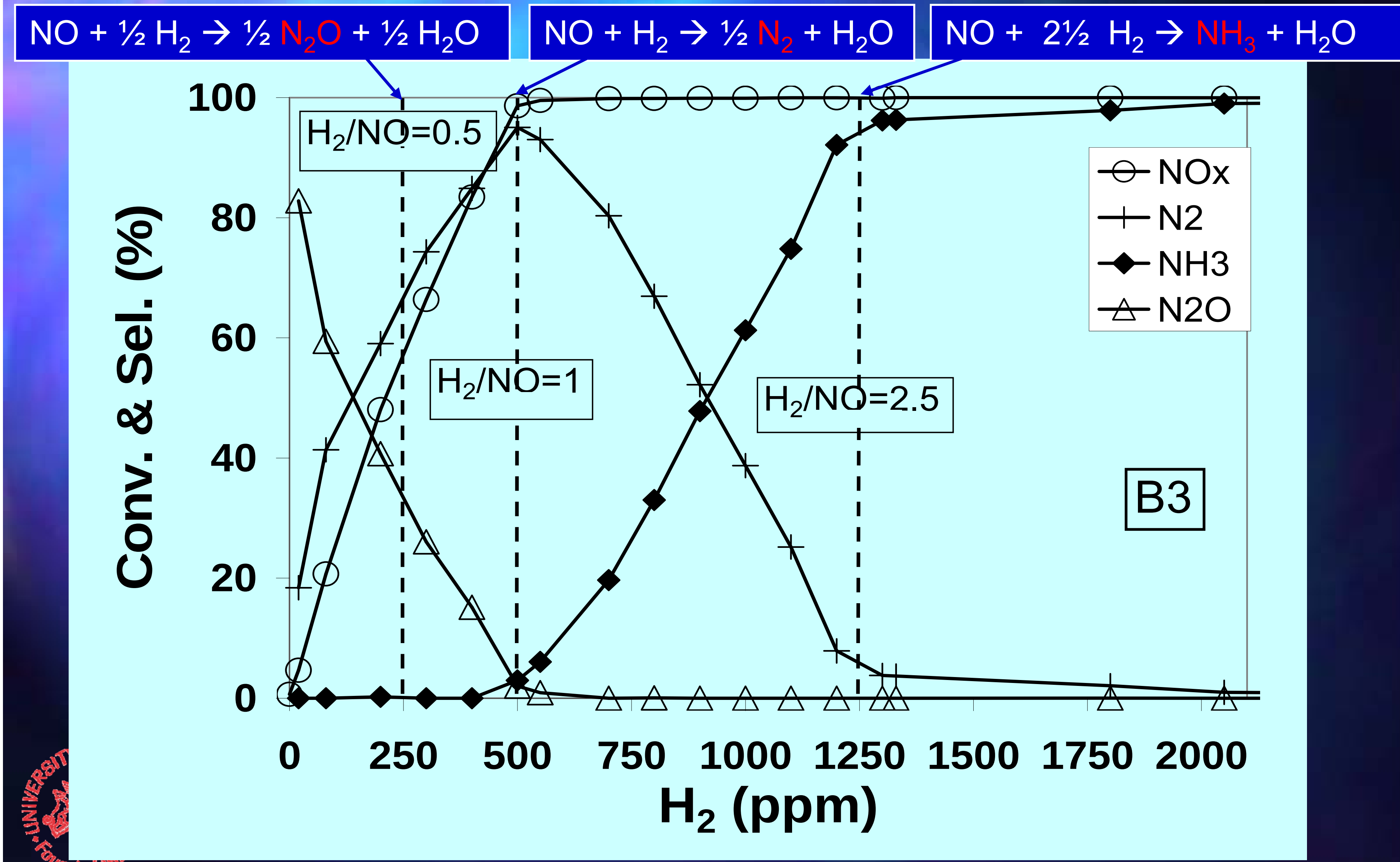
Catalysts Used in Study: "B" Series

Sample	Pt (wt. %)	BaO (wt. %)	Pt Dispersion (%)	Pt Area (m^2/g)	Pt Particle Size (nm)	BET Area (m^2/g)
B0	0.00	16.7	N/A	N/A	N/A	107
B1	0.32	16.6	39.8	0.31	2.85	111
B2	1.27	16.5	33.0	1.04	3.43	109
B3	2.20	16.3	21.9	1.19	5.18	116
B4	3.71	16.0	34.7	3.18	3.26	107

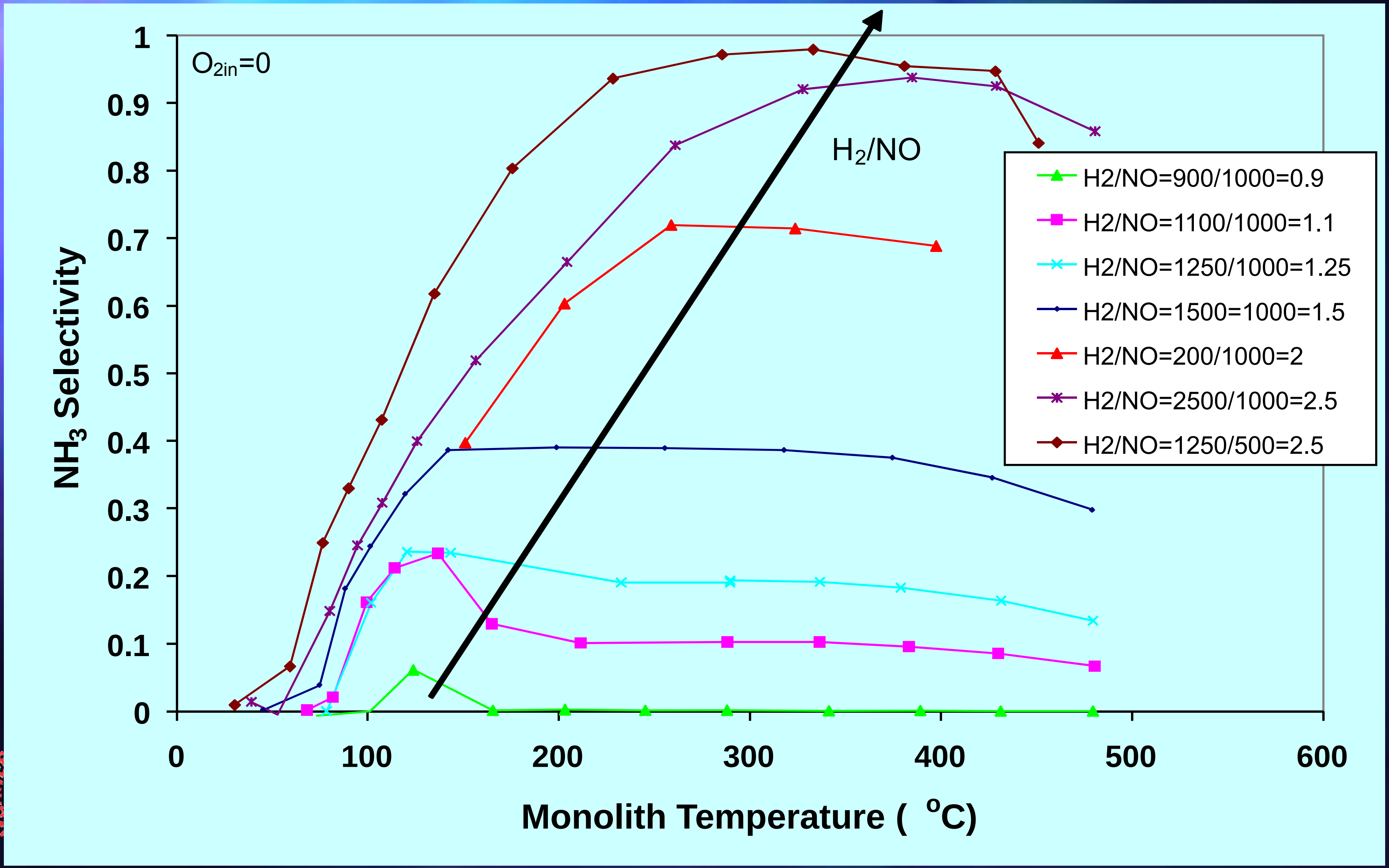
Monolith dimensions: 0.8 cm diameter, 2 cm length

Steady-State NO + H_2 on Pt

Steady-State NO + H_2 on Pt/BaO: Effect of Feed Ratio on Selectivity (300 ºC)

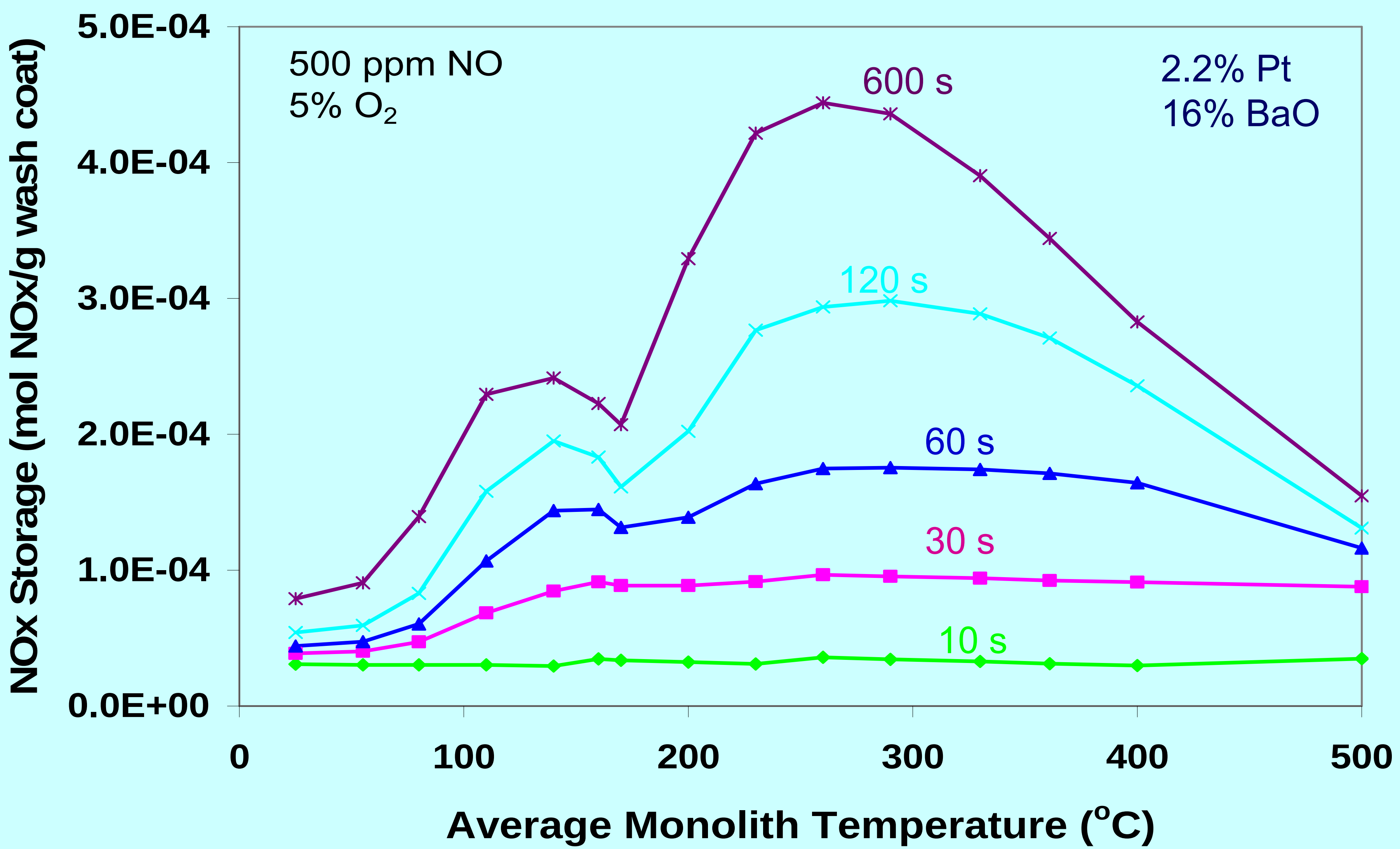


Steady-State NO + H_2 on Pt/BaO: Effect of Temperature on Selectivity



NOx Storage

NOx Storage on Pt/BaO



NO_x Storage Pathways

SHORT TERM STORAGE

$NO + 0.5\ O_2 \overset{Pt}{\leftrightarrow} NO_2$

Pt, BaO

Pt, BaO

BaO

NITRITE PATHWAY

$BaO + 0.5\ O_2 \overset{Pt}{\leftrightarrow} BaO_2$

$BaO_2 + NO \overset{Pt}{\leftrightarrow} BaONO_2$

$BaONO_2 + NO \overset{Pt}{\leftrightarrow} Ba(NO_2)_2$

$Ba(NO_2)_2 + O_2 \overset{Pt}{\leftrightarrow} Ba(NO_3)_2$

$BaO + 2\ NO + 1.5\ O_2 \leftrightarrow Ba(NO_3)_2$

$BaO + 2\ NO_2 + 0.5\ O_2 \leftrightarrow Ba(NO_3)_2$

NITRATE PATHWAY

$NO_2 + BaO \leftrightarrow BaONO_2$

$BaONO_2 \leftrightarrow BaO_2 + NO$

$BaO_2 + NO_2 \leftrightarrow BaO\text{-}NO_3$

$BaO\text{-}NO_3 + NO_2 \leftrightarrow Ba(NO_3)_2$

$BaO + 3\ NO_2 \leftrightarrow Ba(NO_3)_2 + NO$

NOx Storage & Reduction

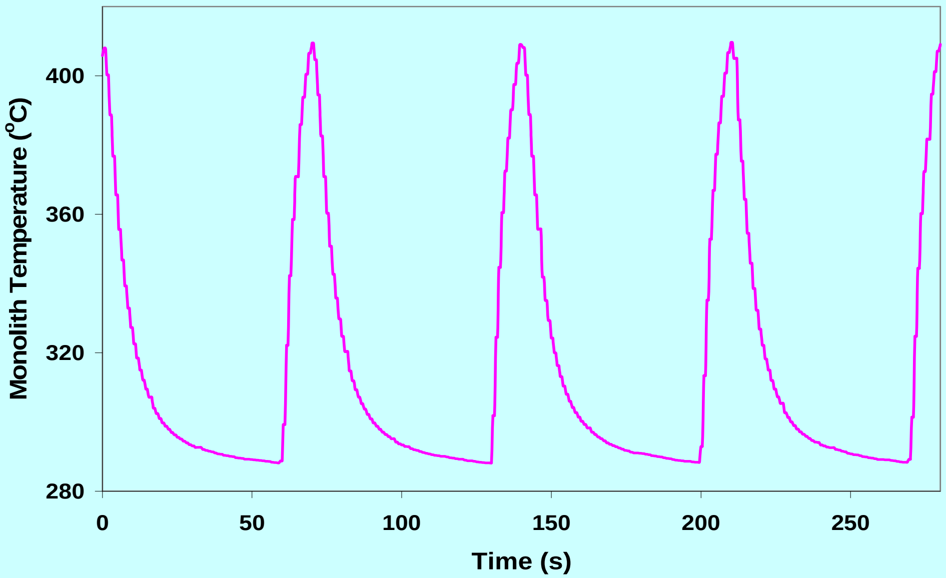
NSR With H_2: Lean-Rich Cycling Protocol

<u>Lean:</u>
5% O_2
500 ppm NO
t_l=60 s

<u>Rich:</u>
500 ppm NO
5.1% H_2
1.5% O_2
t_r=10 s

GHSV = 60K hr^{-1}

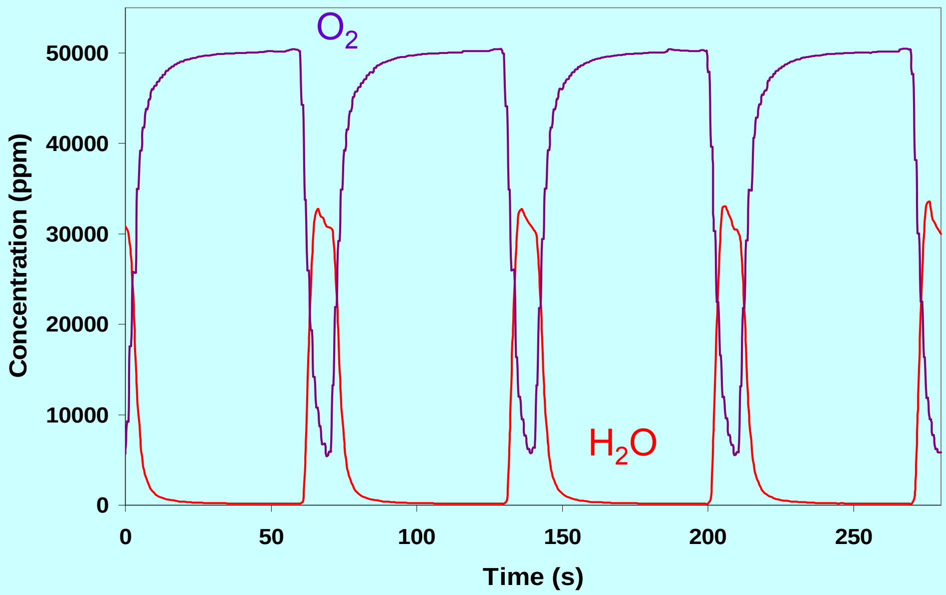
NSR With H_2: Cycling Profiles

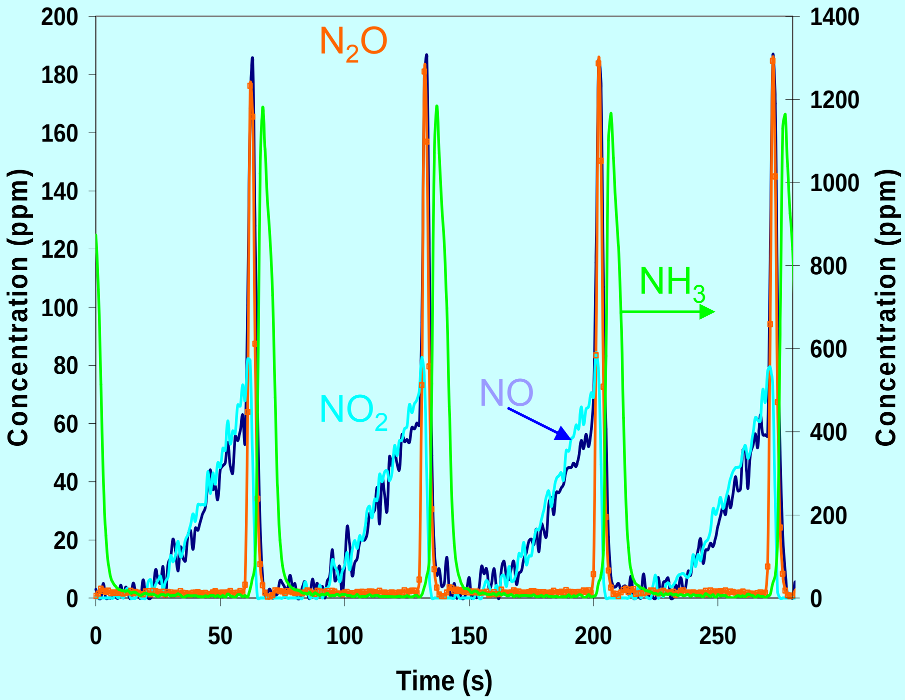


$5\%\ O_2$ (lean)
$1.5\%\ O_2$ (pulse)
NO = 500 ppm
$5.1\%\ H_2$ (pulse)
$S_{N,p} = 0.6$
$T_{m,avg} = 340\ ^oC$

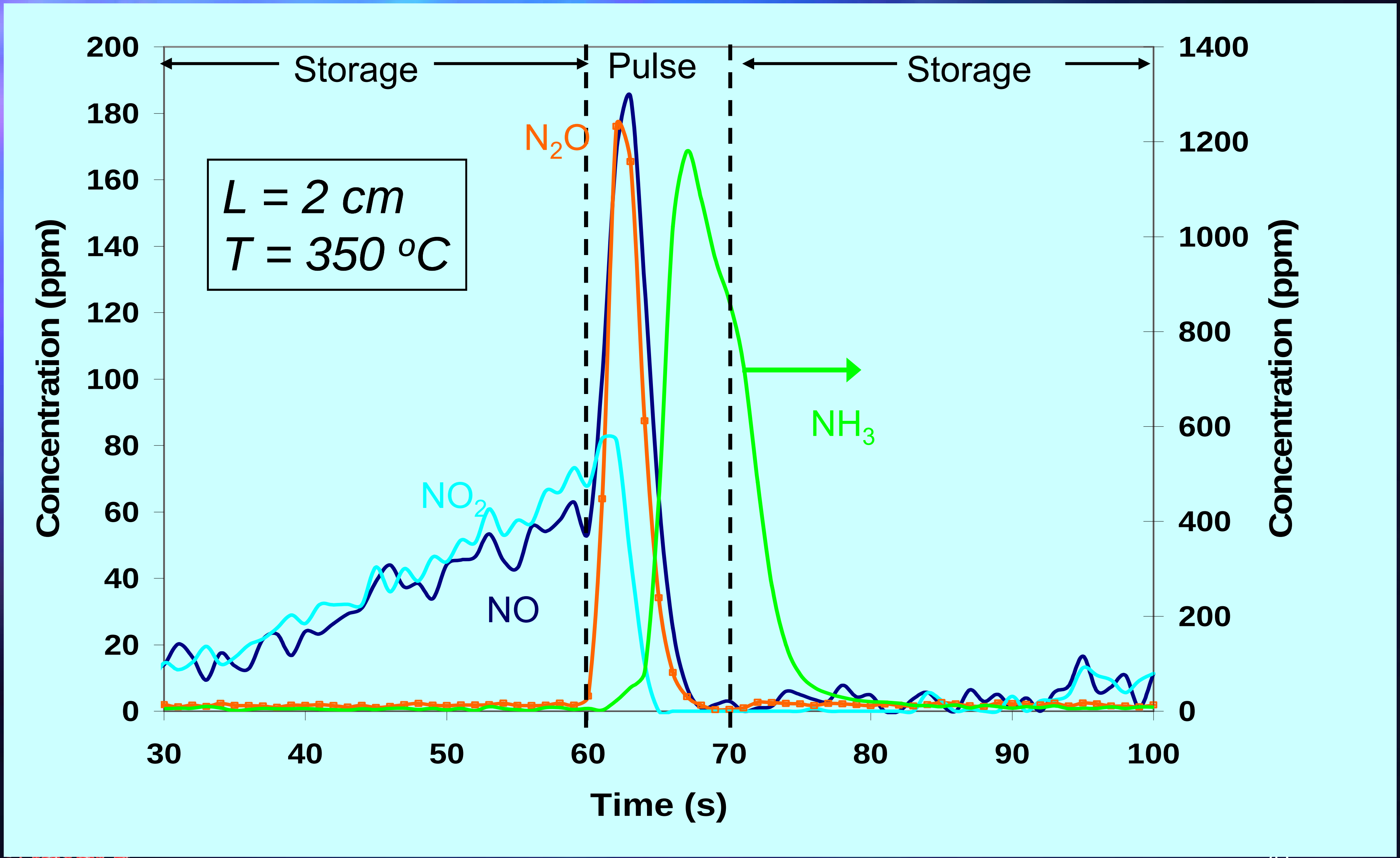
2.2% Pt
16% BaO

60 s lean time
10 s pulse

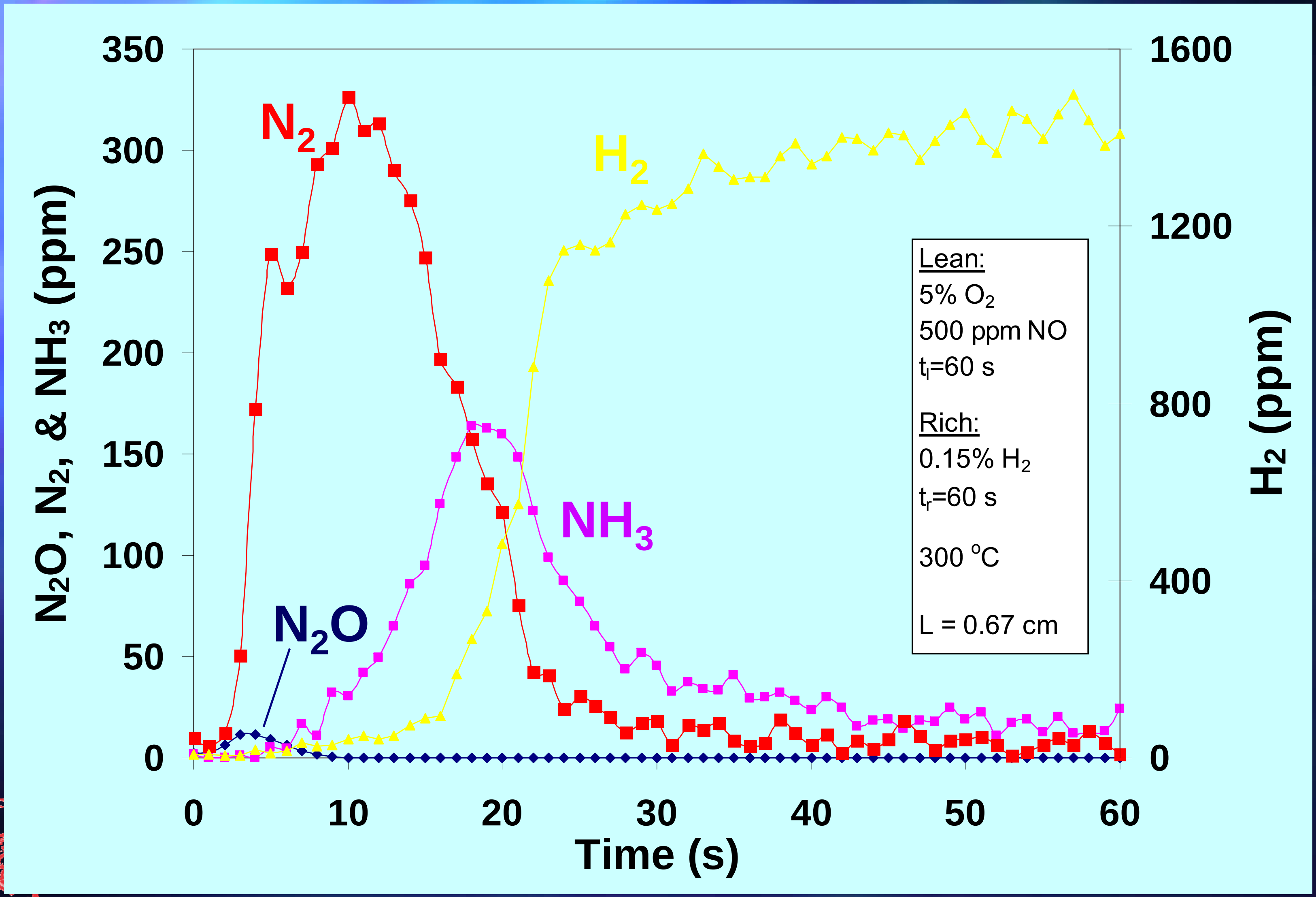




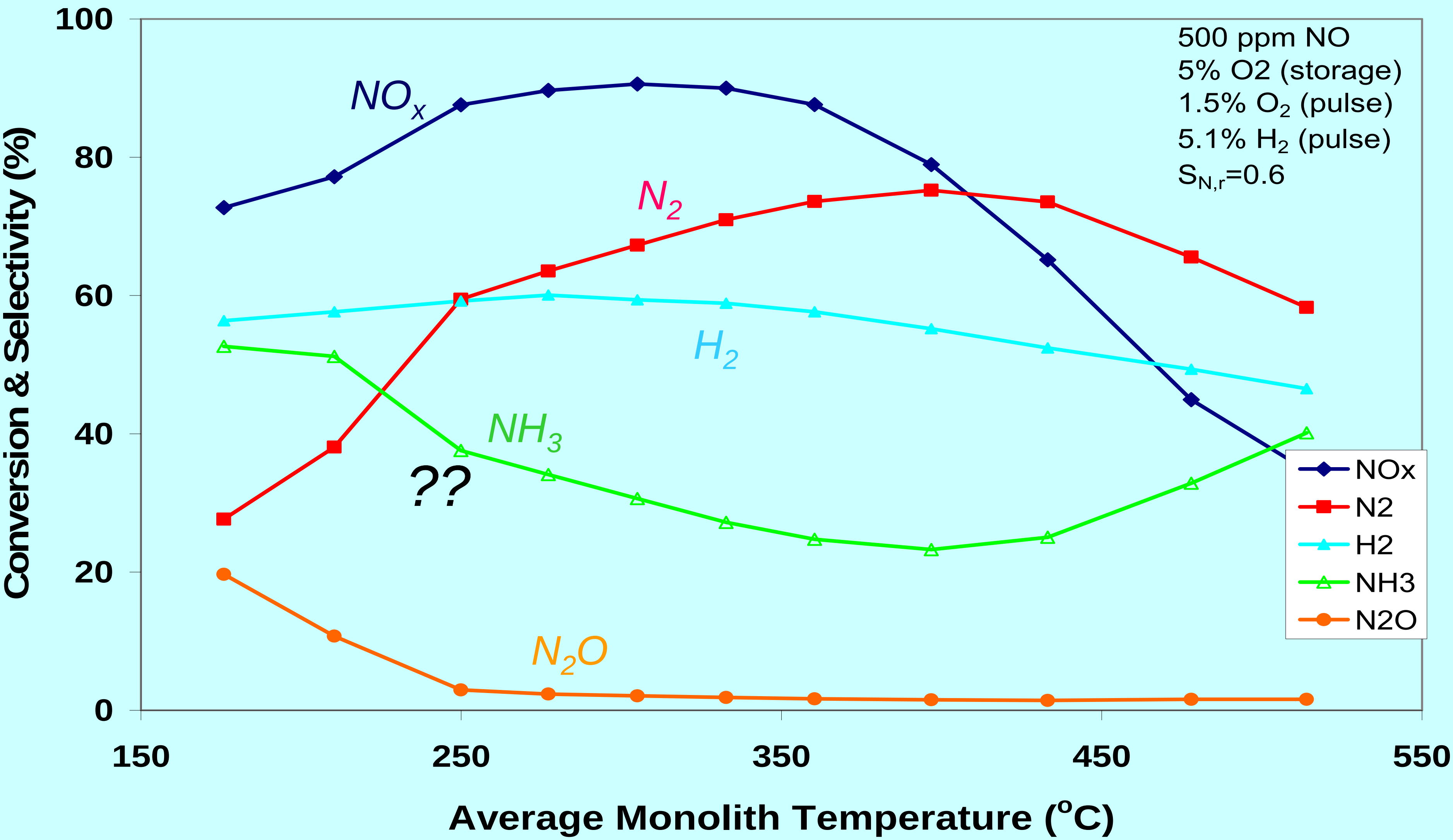
NSR With H_2: Transient Product Distribution



Anaerobic Pulse: Product Distribution

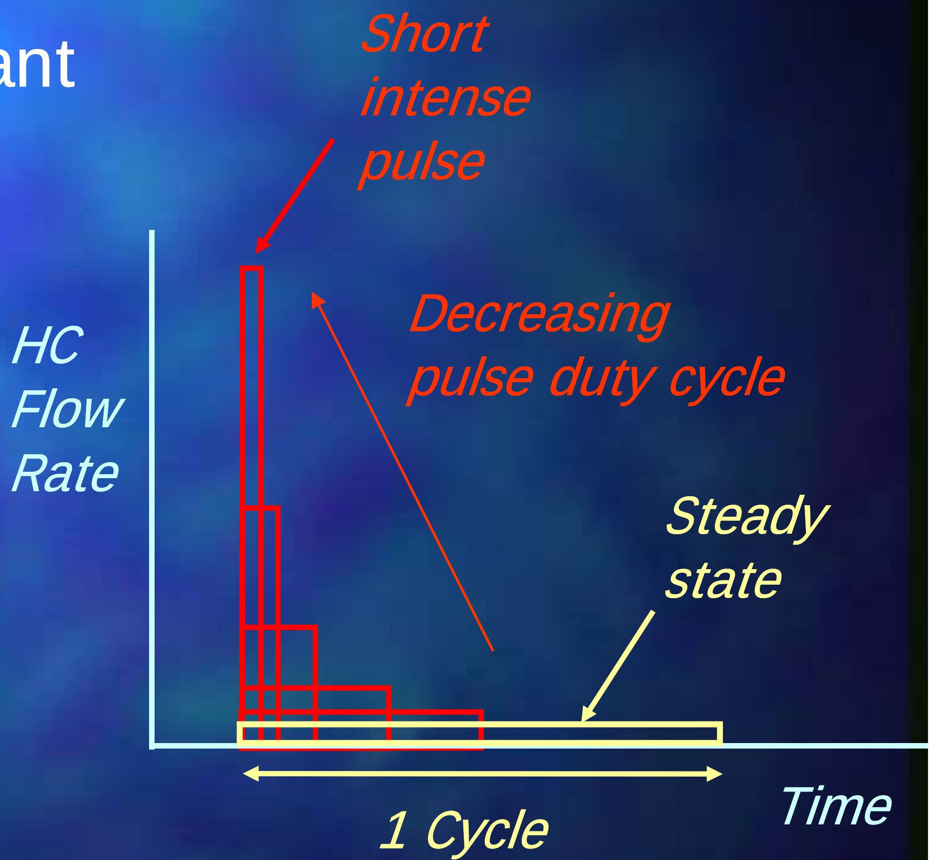


NSR With H_2: Cycle-Averaged Results

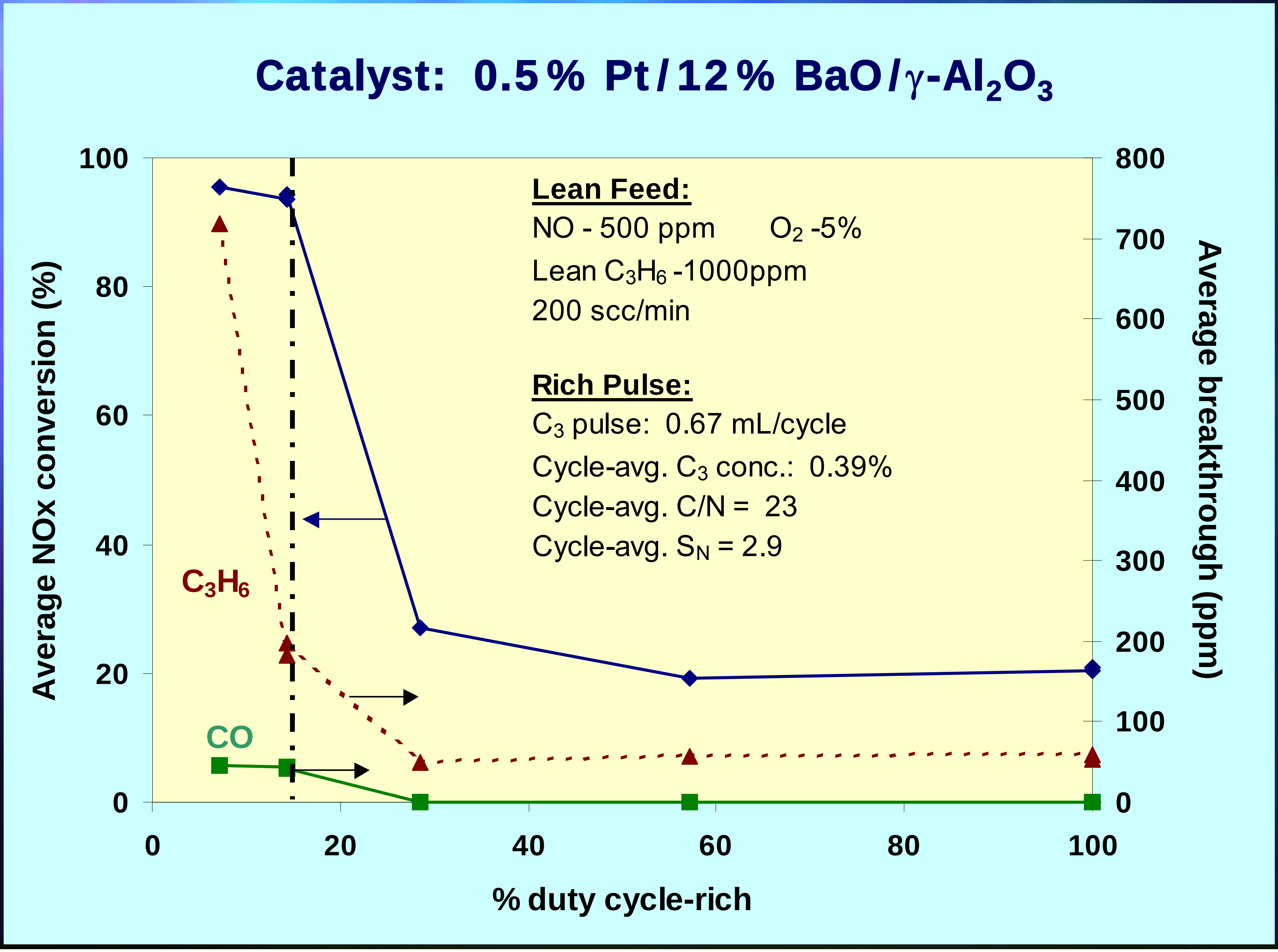


Fuel Injection Protocol

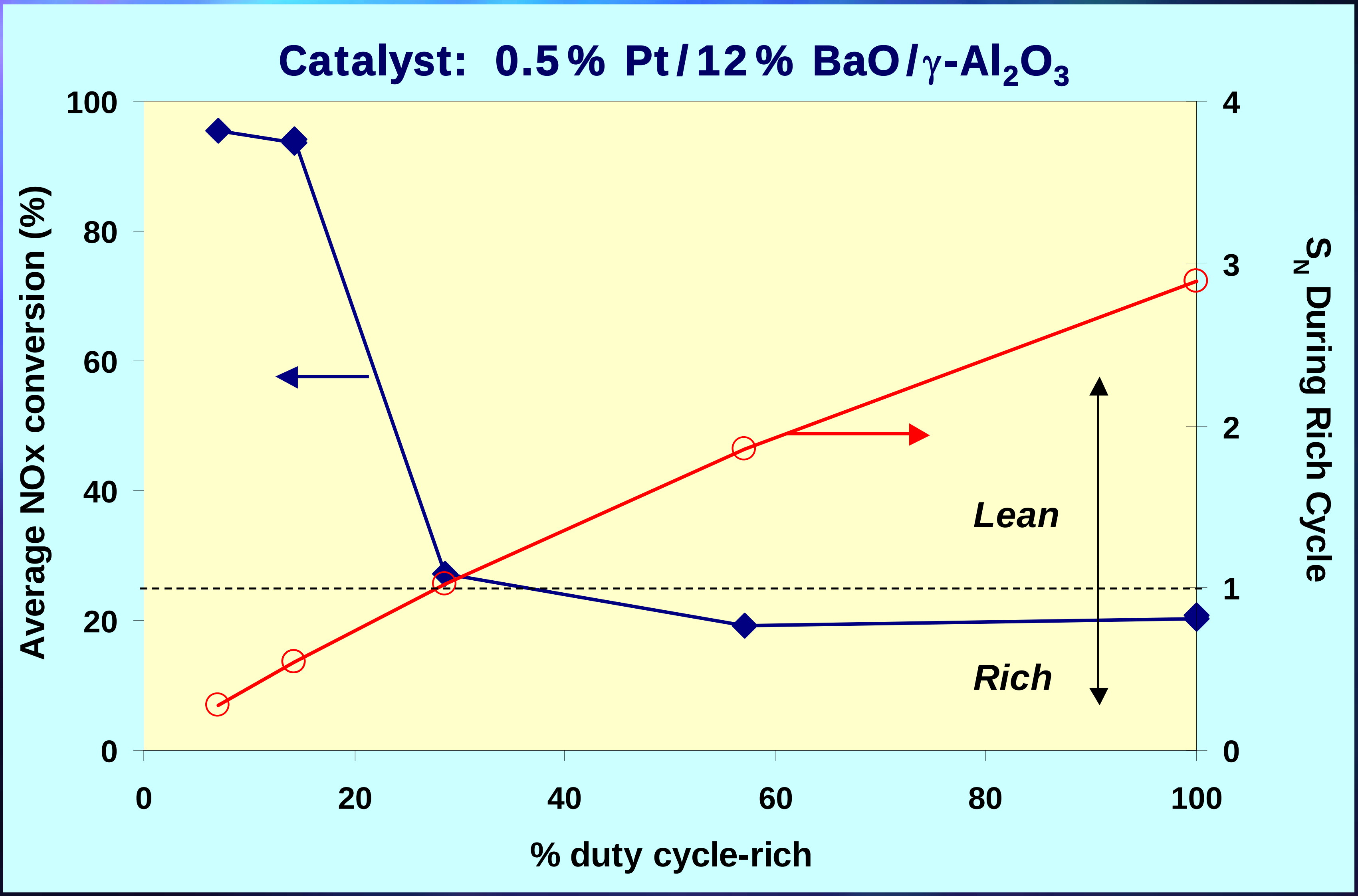
- Evaluate different reductant injection policies
- Determine optimal policy
  - High NOx conversion
  - Low fuel consumption
- Experiment:
  - Fix reductant (propylene) injected per cycle
  - Vary duty cycle of pulse
  - Fix total cycle time



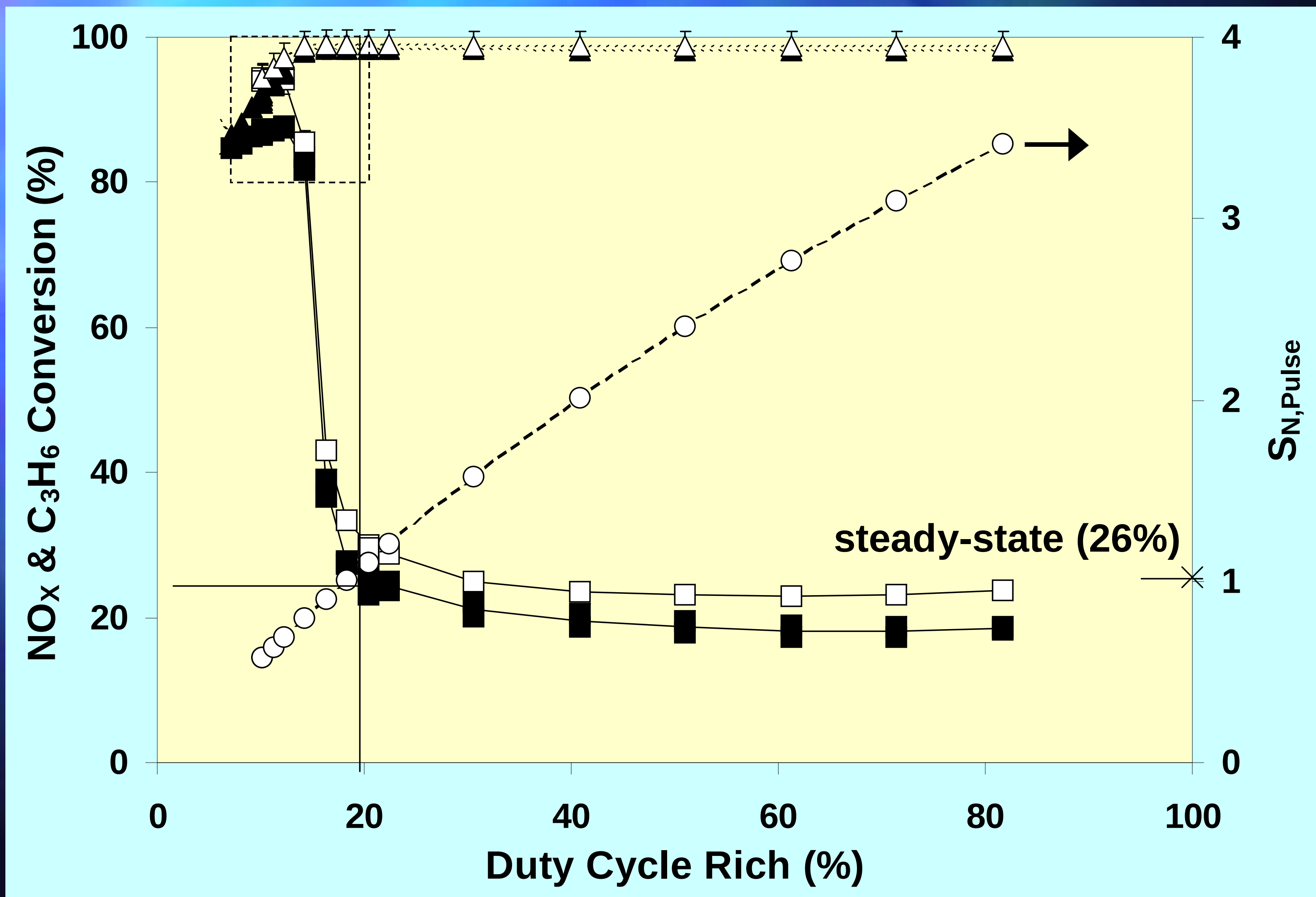
Effect of Propylene Duty Cycle



Effect of Propylene Duty Cycle



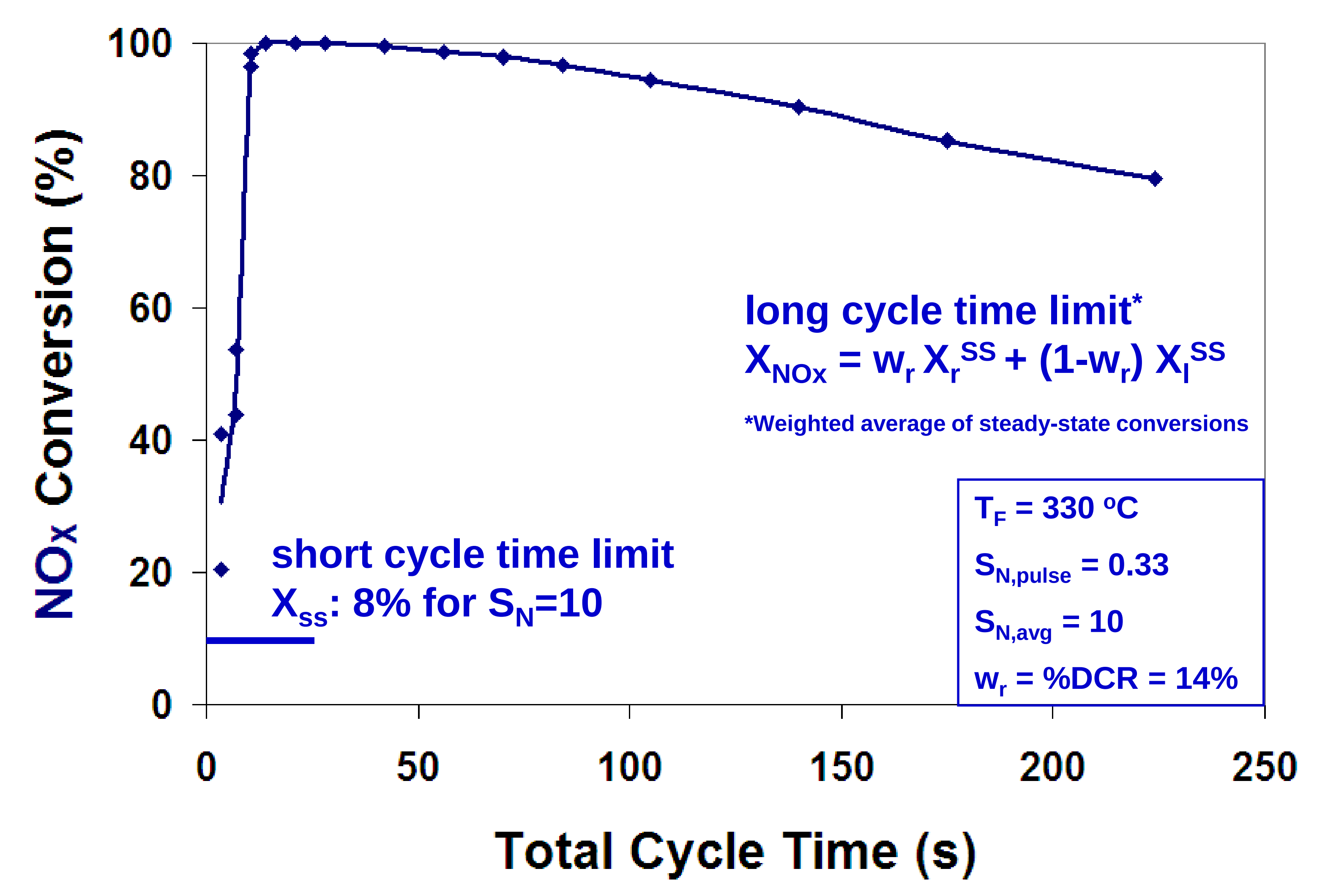
Effect of Propylene Duty Cycle (Monolith Catalyst C3)



$$\text{Duty Cycle Rich} = \frac{\text{Pulse Time}}{\text{Cycle Time}}$$

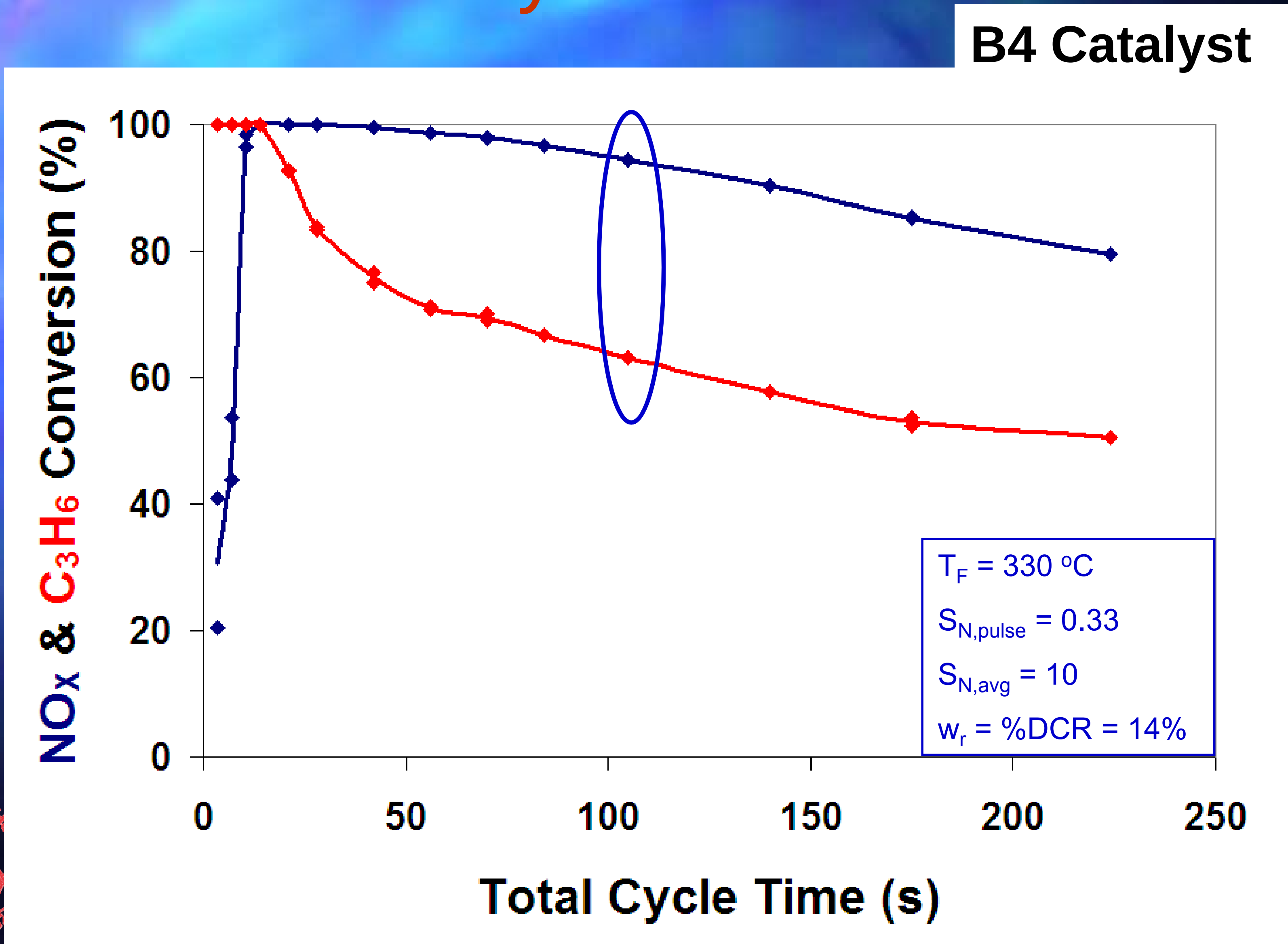
Effects of Total Cycle Time

B4 Catalyst



Duty Cycle Rich = $\frac{\text{Pulse Time}}{\text{Cycle Time}}$

Effects of Total Cycle Time



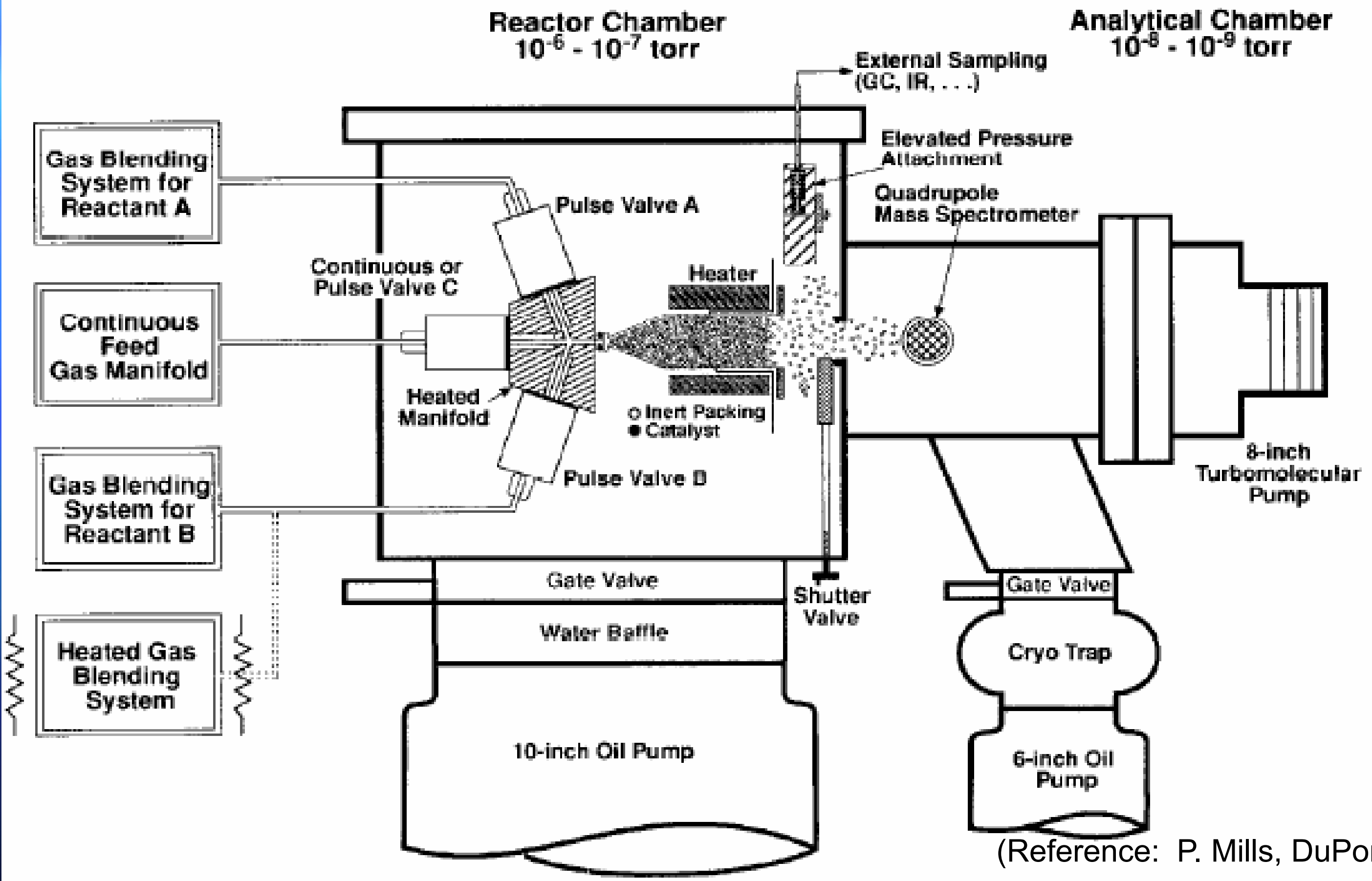
Complicating Issues

- Main routes to N_2
- Reaction between stored NOx and reductants (H_2 and NH_3)
- Role of NH_3 as intermediate reductant
- Reduction effectiveness of H_2 vs. NH_3

Complicating Issues

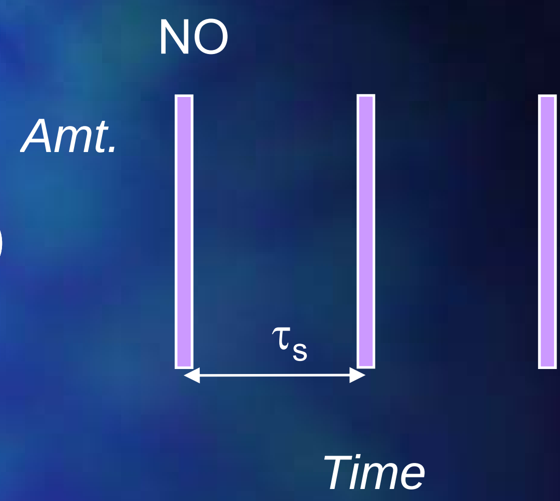
- Main routes to N_2
- Reaction between stored NOx and reductants (H_2 and NH_3)
- Role of NH_3 as intermediate reductant
- Reduction effectiveness of H_2 vs. NH_3

Temporal Analysis of Products (TAP)



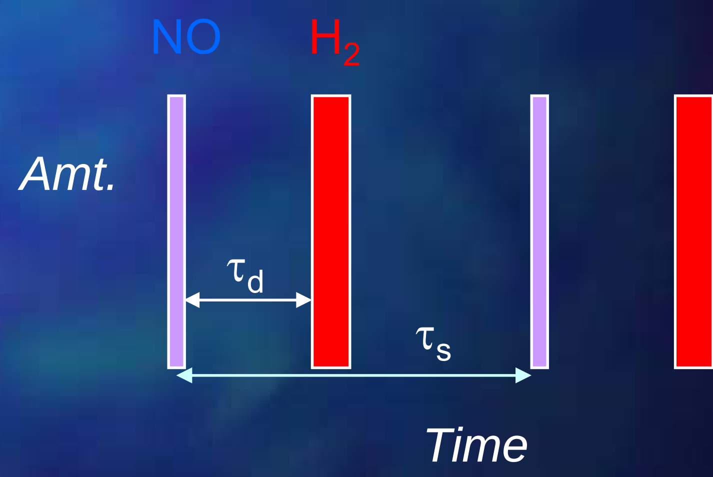
(Reference: P. Mills, DuPont)

NO Pulse & NO/H_2 Pump-Probe Experiments



- NO pulsing probes uptake & decomposition
  - Variation of pulse intensity, spacing time (τ_s)

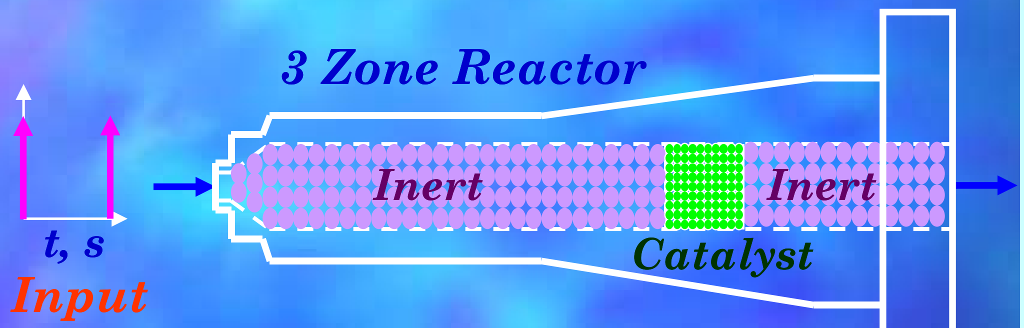
- NO and H_2 pump-probe
  - NO & H_2 pulsed alternately
  - Variation of pulse intensities, delay time (τ_d) , spacing time (τ_s)



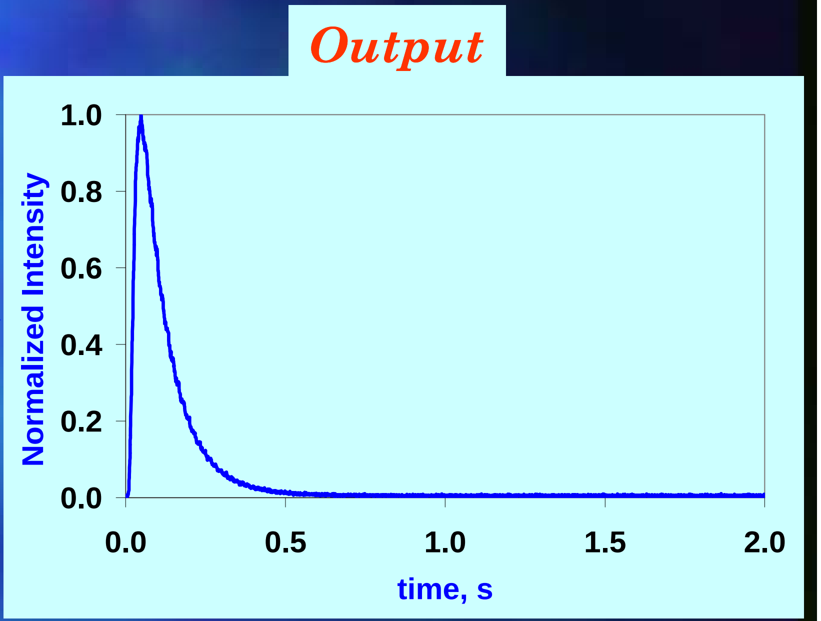
- Feed composition*
  - Excess NO
  - Excess H_2

*Basis: $NO + H_2 \rightarrow \frac{1}{2} N_2 + H_2O$

Reactor and Catalyst



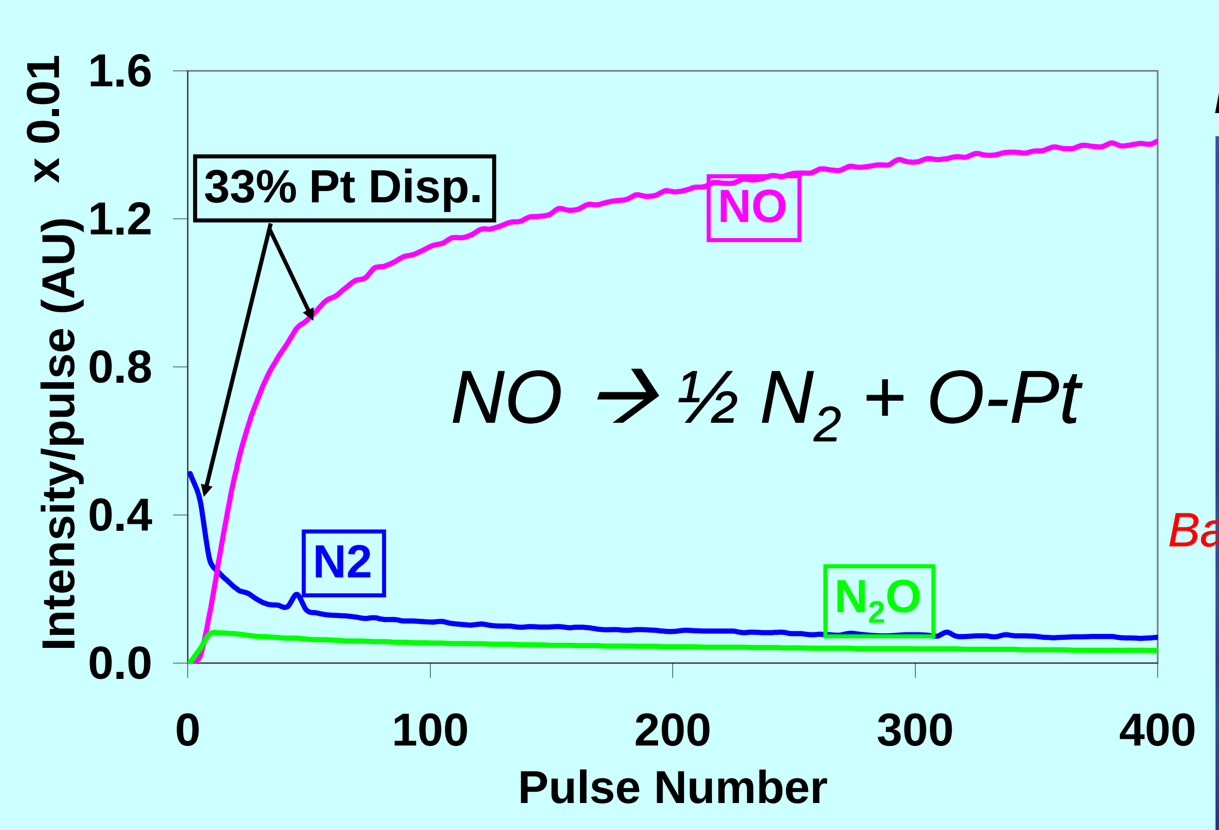
0.5 – 2.5 x 10^{16} molecules/pulse



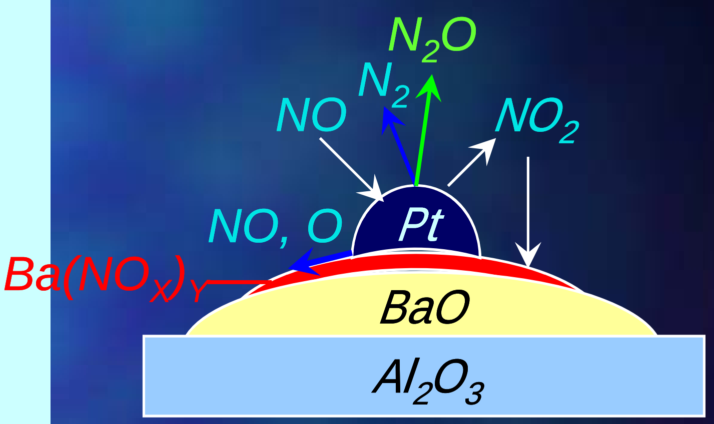
Catalyst Composition

Sample	Pt (wt. %)	BaO (wt. %)	Pt Dispersion (%)	Mass of Catalyst (mg)	Estimated Exposed Pt Sites
D3	2.36	12.7	3	110	2.4 x 10^{17}
B2M	0.28	16.6	33	21 (Pt/BaO) + 76 (BaO)	2.8 x 10^{17}

NO Storage on Pt/BaO/Al_2O_3

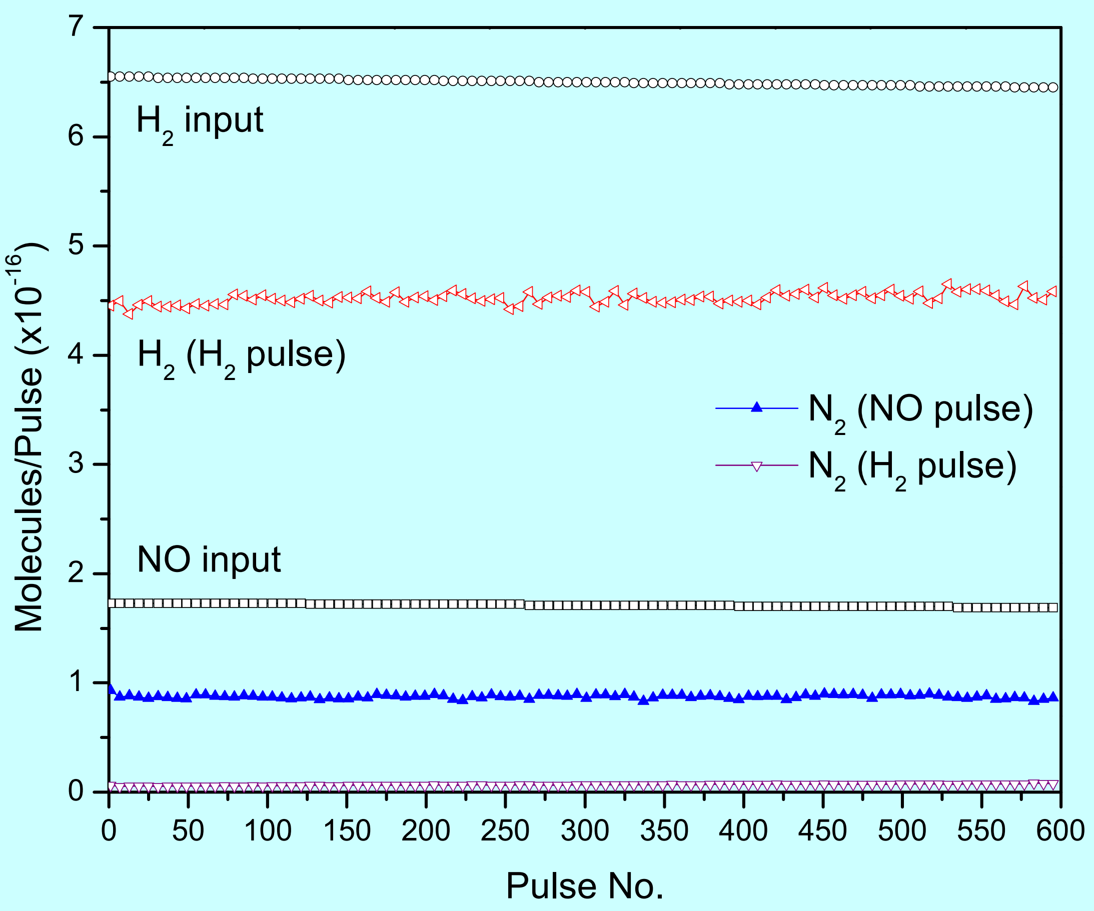


T = 250 °C
NO = 2.1 x10^16 molecs/pulse

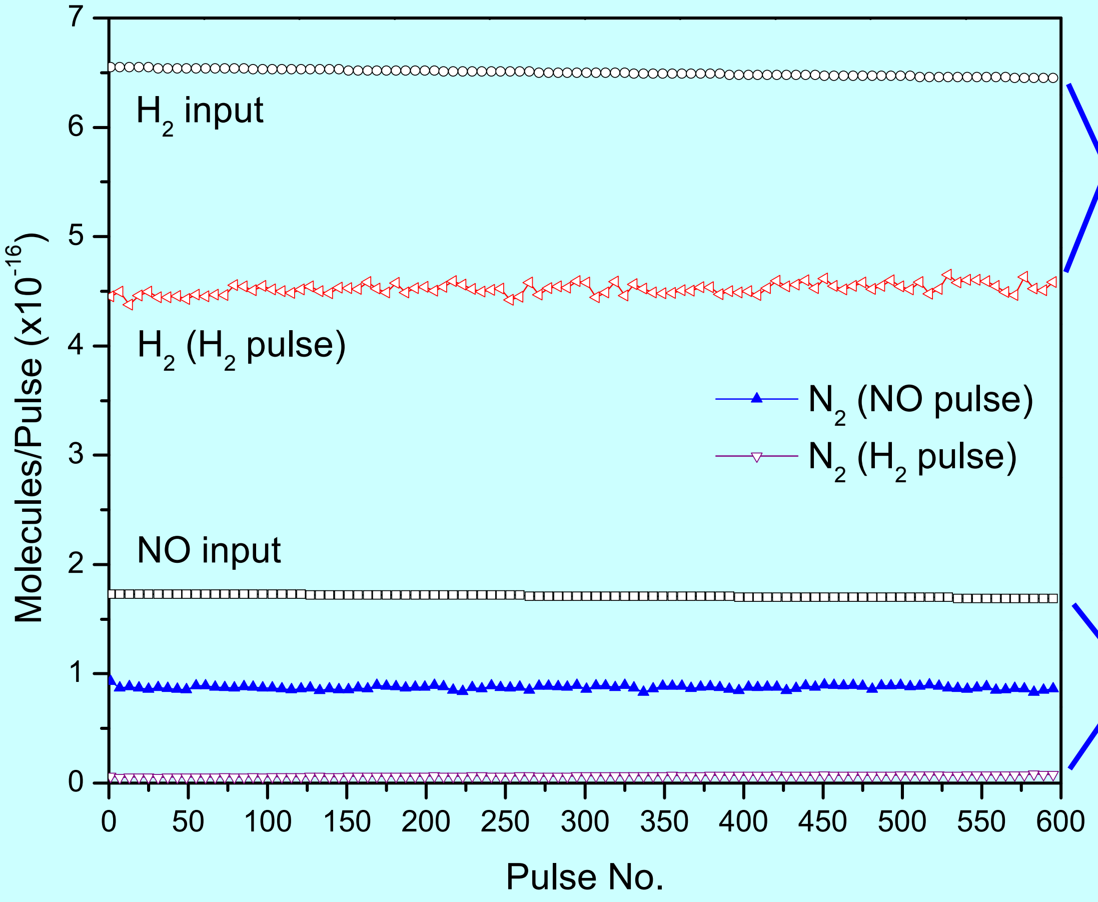


- Sustained N_2 production ⇨ Continuous spillover of NO & O from Pt to Ba ⇨ NO_2 formation

Pump/Probe on Pre-Reduced Pt/BaO: Excess H_2 ($NO : H_2 = 1 : 3.8$), 350 ºC



Pump/Probe on Pre-Reduced Pt/BaO: Excess H_2 ($NO : H_2 = 1 : 3.8$), 350 ºC

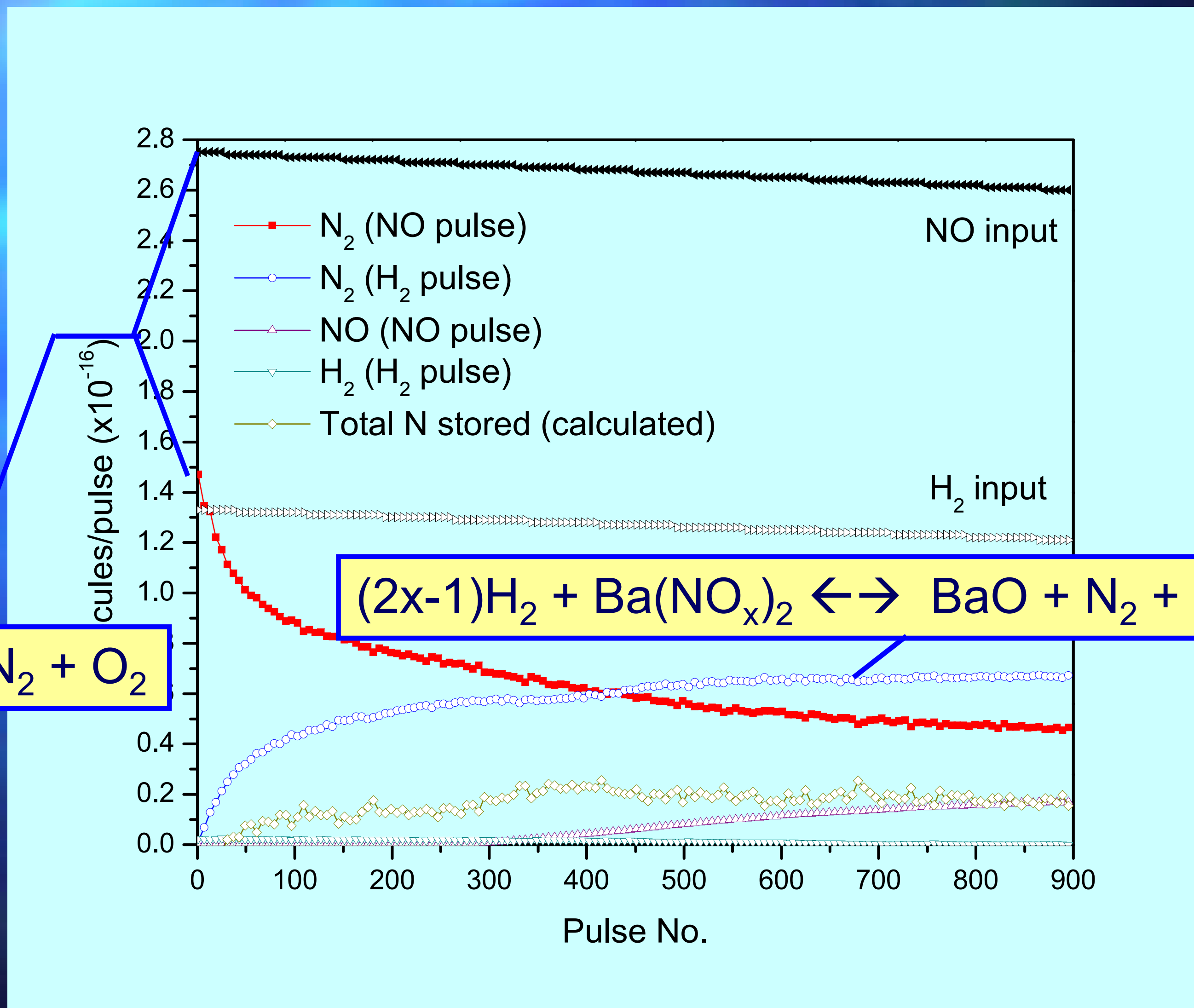


$2 H_2 + O_2 \leftrightarrow 2 H_2O$

H_2 consumed = $2 \times N_2$ produced

$2 NO \leftrightarrow N_2 + O_2$

Pump/Probe on Pre-Reduced Pt/BaO: Excess NO ($NO:H_2$ = 1 : 0.5), 350 °C



$2\,NO \leftrightarrow N_2 + O_2$

$(2x-1)H_2 + Ba(NO_x)_2 \leftrightarrow BaO + N_2 + (2x-1)H_2O$

NSR Reduction Chemistry with H_2

2 H-Pt + O-Pt $\leftrightarrow$ H_2O + 3 Pt …. H_2 reacts off O-Pt

NO – Pt $\leftrightarrow$ ½ N_2 + O-Pt …. Occurs on reduced Pt

2 NO – Pt $\leftrightarrow$ N_2O + O-Pt…. Occurs on O-poisoned Pt

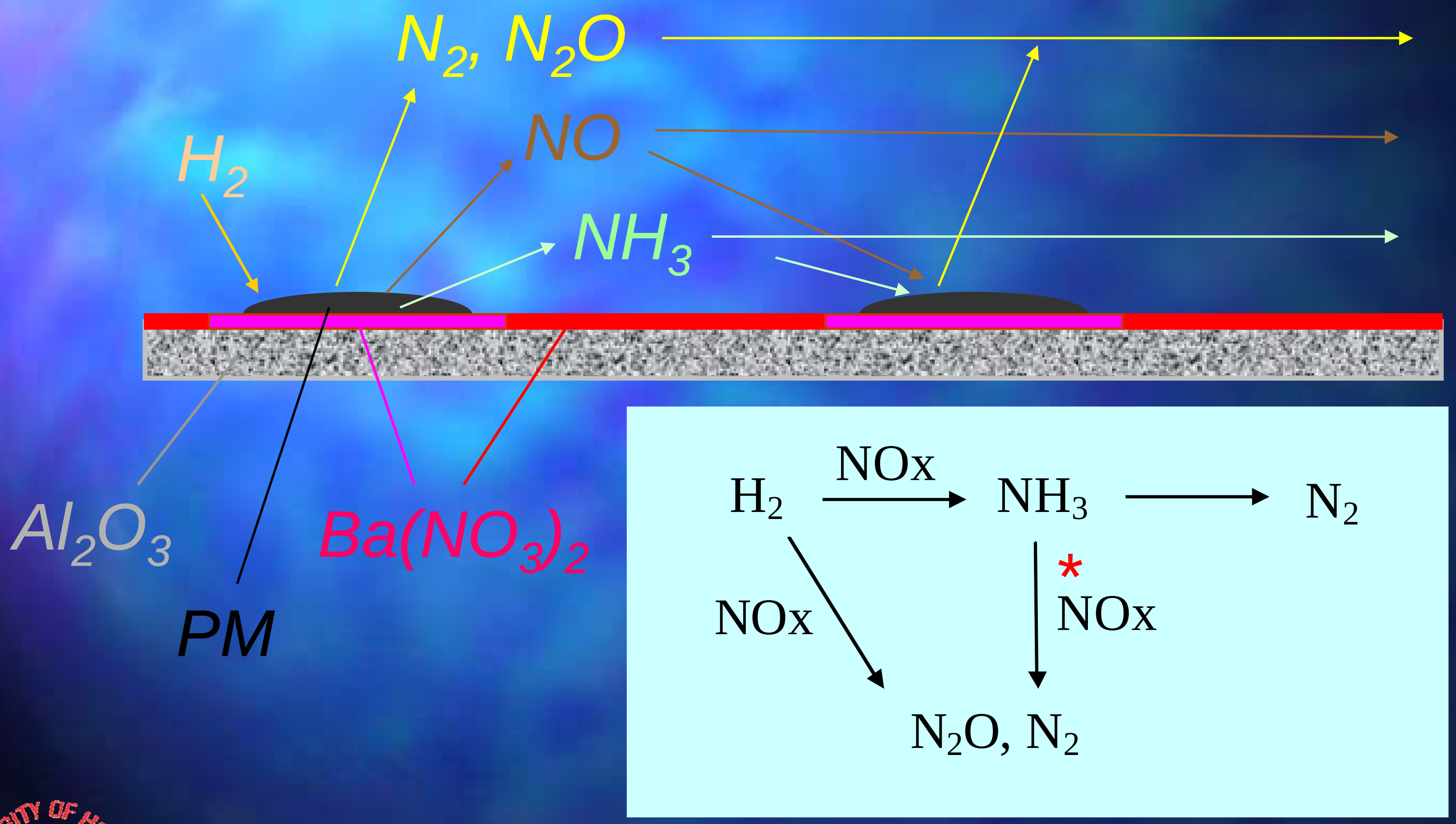
N-Pt + 3 H-Pt $\leftrightarrow$ NH_3 + 4 Pt … Occurs in rich conditions

$Ba(NO_3)_2$ + 4 Pt $\leftrightarrow$ BaO_2 + 2 O– Pt + 2 NO (– Pt)…
Occurs in vicinity of Pt/Ba interface

Complicating Issues

- Main routes to N_2
- Reaction between stored NOx and reductants (H_2 and NH_3)
- Role of NH_3 as intermediate reductant
- Reduction effectiveness of H_2 vs. NH_3

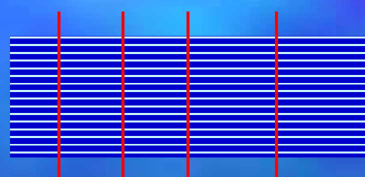
Upgraded Picture of NSR With H_2 as Reductant

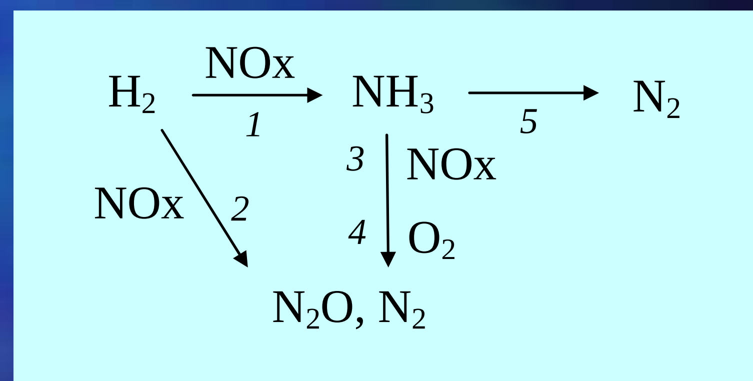


* <u>NH_3 as reductant:</u> *Pihl et al., SAE, 2006; Cumaranatunge et al., J. Catal.,* ***246****, 2007.*

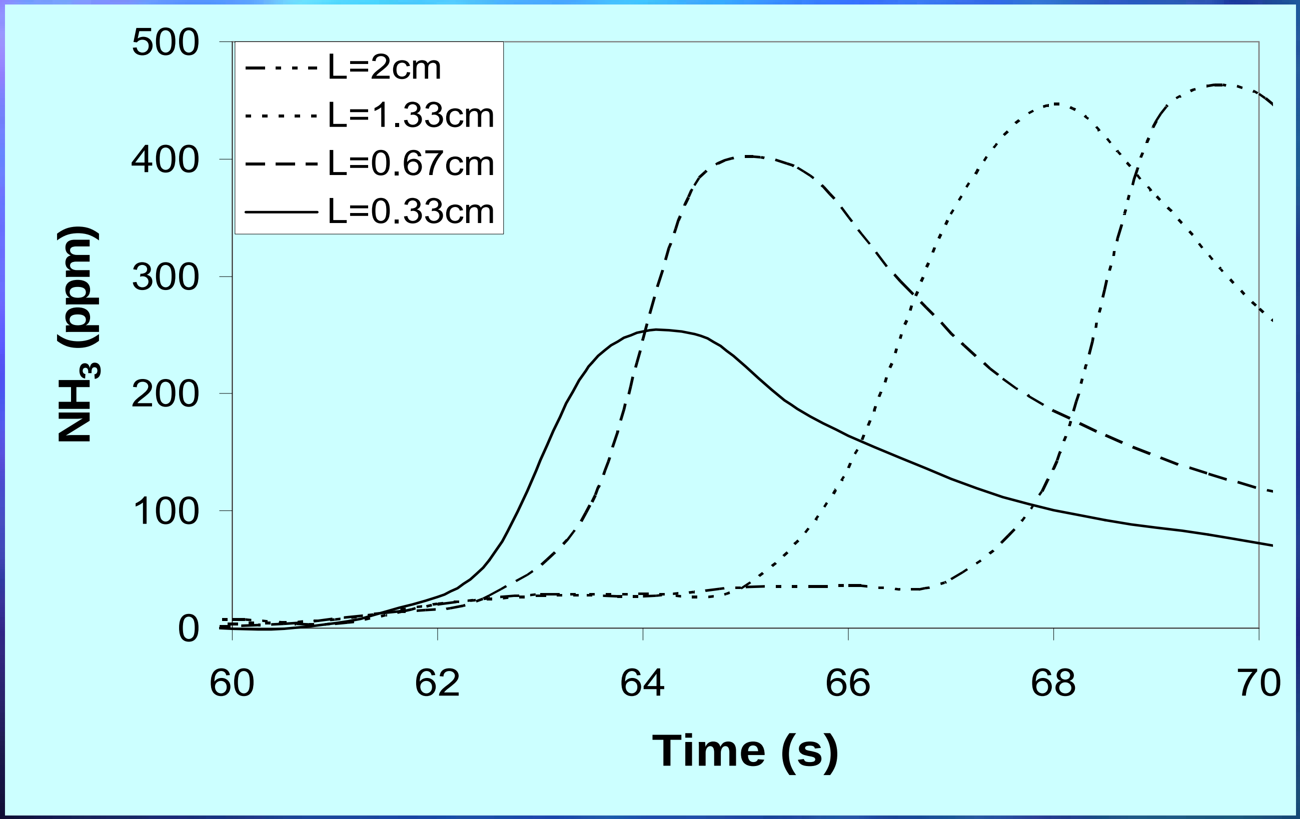
Varied Monolith Length Experiments

- Approach
  - Divide original monolith into progressively smaller sections
  - Replicate experiments to generate spatio-temporal concentration profiles

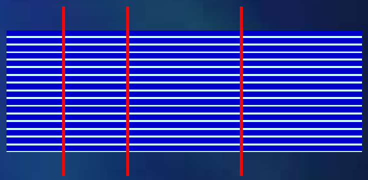




Effect of Length on Ammonia Production: Aerobic Pulse



(T_f = 320 ^oC)



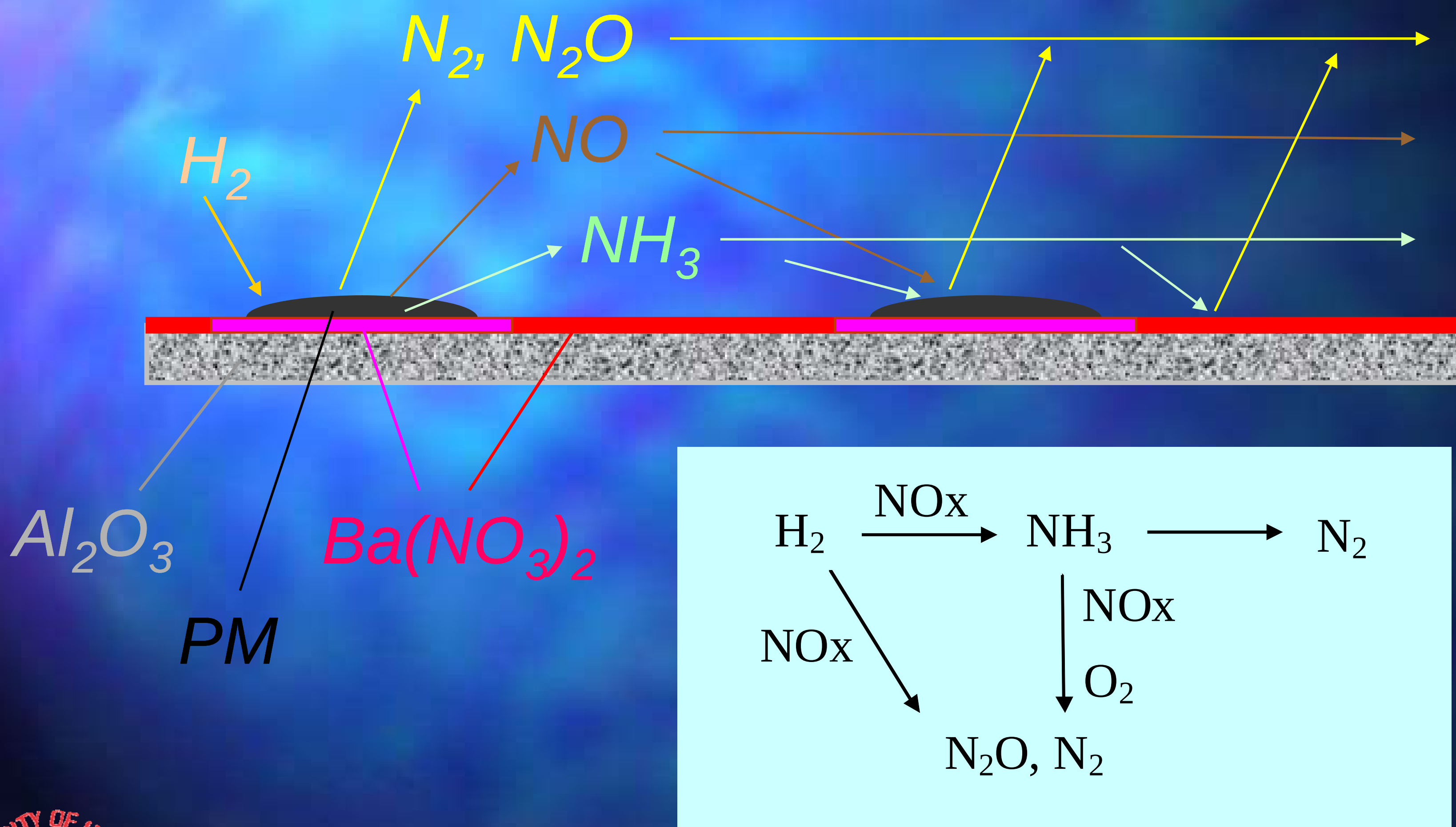
Lean: 500 ppm NO and 5% O_2 (60s);

Rich: 4.35% H_2 and 1.5% O_2 (10s); $S_{N,P}$=0.7

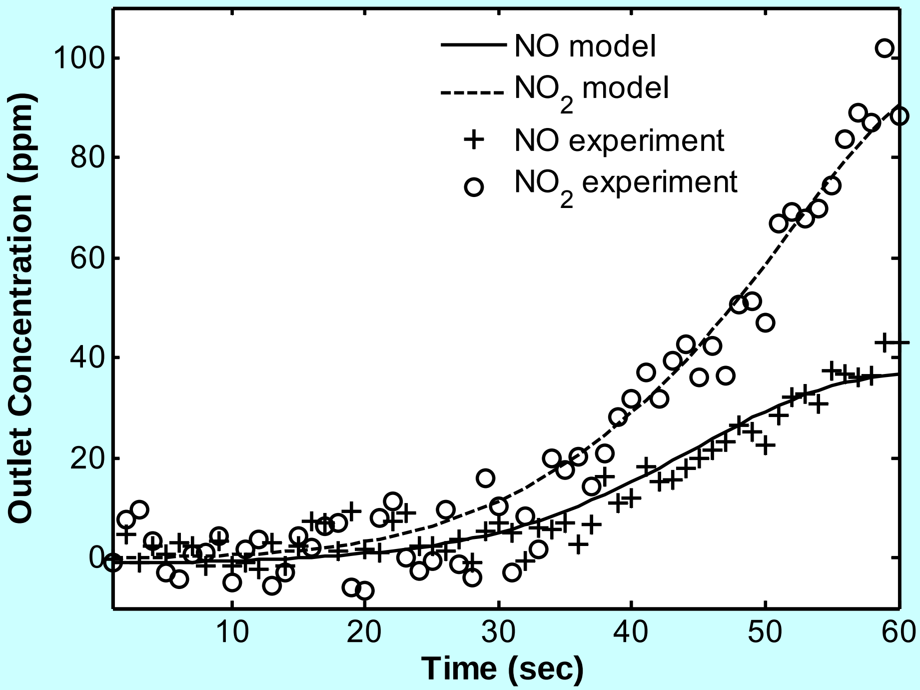
Summary ($NO/H_2/NH_3$ System)

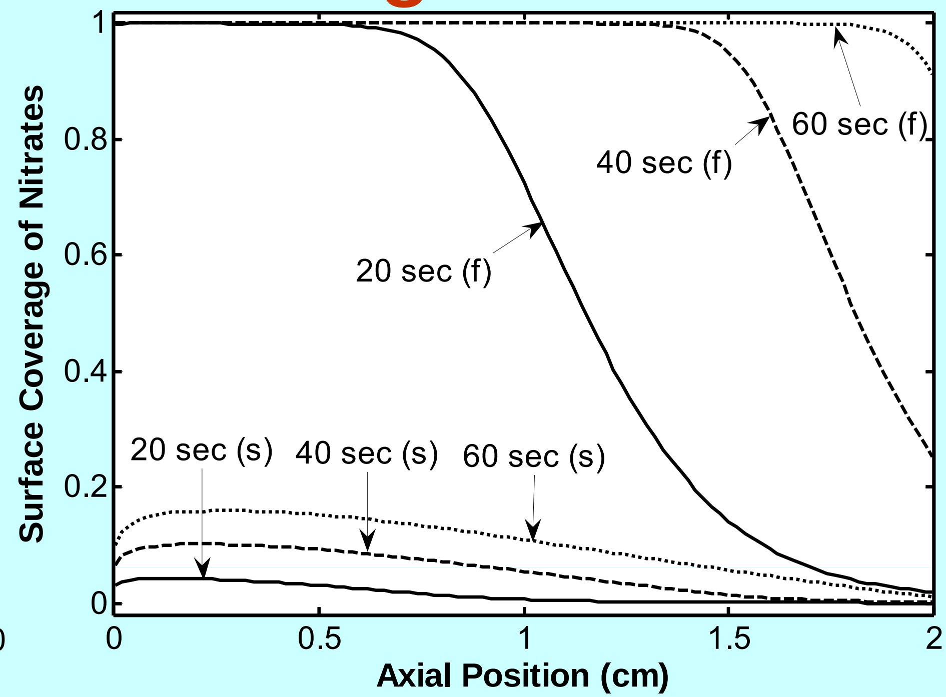
- H_2 and NH_3 serve as reductants during NSR
  - H_2 is a superior reductant under steady-state conditions and below 380 ºC during cycling
- Formation of N_2 can occur through four different reaction routes; two primary routes
  - Direct : $H_2 + NOx \rightarrow N_2$
  - Indirect: $H_2 + NOx \rightarrow NH_3$ and $NH_3 + NOx \rightarrow N_2$
- Regeneration initially feed rate limited by H_2
- Rate limiting step switches from a feed rate limited state to one in which the supply of NOx from the storage phase to Pt is limiting

Picture of NSR With H_2 as Reductant



Model vs. Experiment: Storage





Conditions: T = 275 ^oC
Lean: 500 ppm NO, 5% O_2
Rich: 1500 ppm H_2, balance Ar (100 s)
Pt, BaO: 2.70 wt.%, 14.6 wt.%

*Clayton, R.D., M.P. Harold, and V. Balakotaiah, "NOx Storage and Reduction with H_2 on Pt/BaO/Al_2O_3 Monolith: Spatio-Temporal Resolution of Product Distribution," Appl. Catal. B. Environmental, **84**, 616-630 (2008).*

Bhatia, D., M.P. Harold, and V. Balakotaiah, "A Global Kinetic Model for NOx Storage and Reduction on Pt/BaO/Al_2O_3 Monolithic Catalysts, Catalysis Today, under review (2009).

Global Kinetic Model for NOx Storage & Reduction: Regeneration

4. $8H_2 + Ba(NO_3)_2(f) \rightarrow 5H_2O + BaO(f) + 2NH_3$

$$R_{v4} = k_4 X_{H_2,wc} c_{BaO}(f)\theta_{Ba(NO_3)_2}(f)$$

5. $8H_2 + Ba(NO_3)_2(s) \rightarrow 5H_2O + BaO(s) + 2NH_3$

$$R_{v5} = k_5 X_{H_2,wc} c_{BaO}(s)\theta_{Ba(NO_3)_2}(s)$$

6. $\frac{10}{3}NH_3 + Ba(NO_3)_2(f) \rightarrow 5H_2O + BaO(f) + \frac{8}{3}N_2$

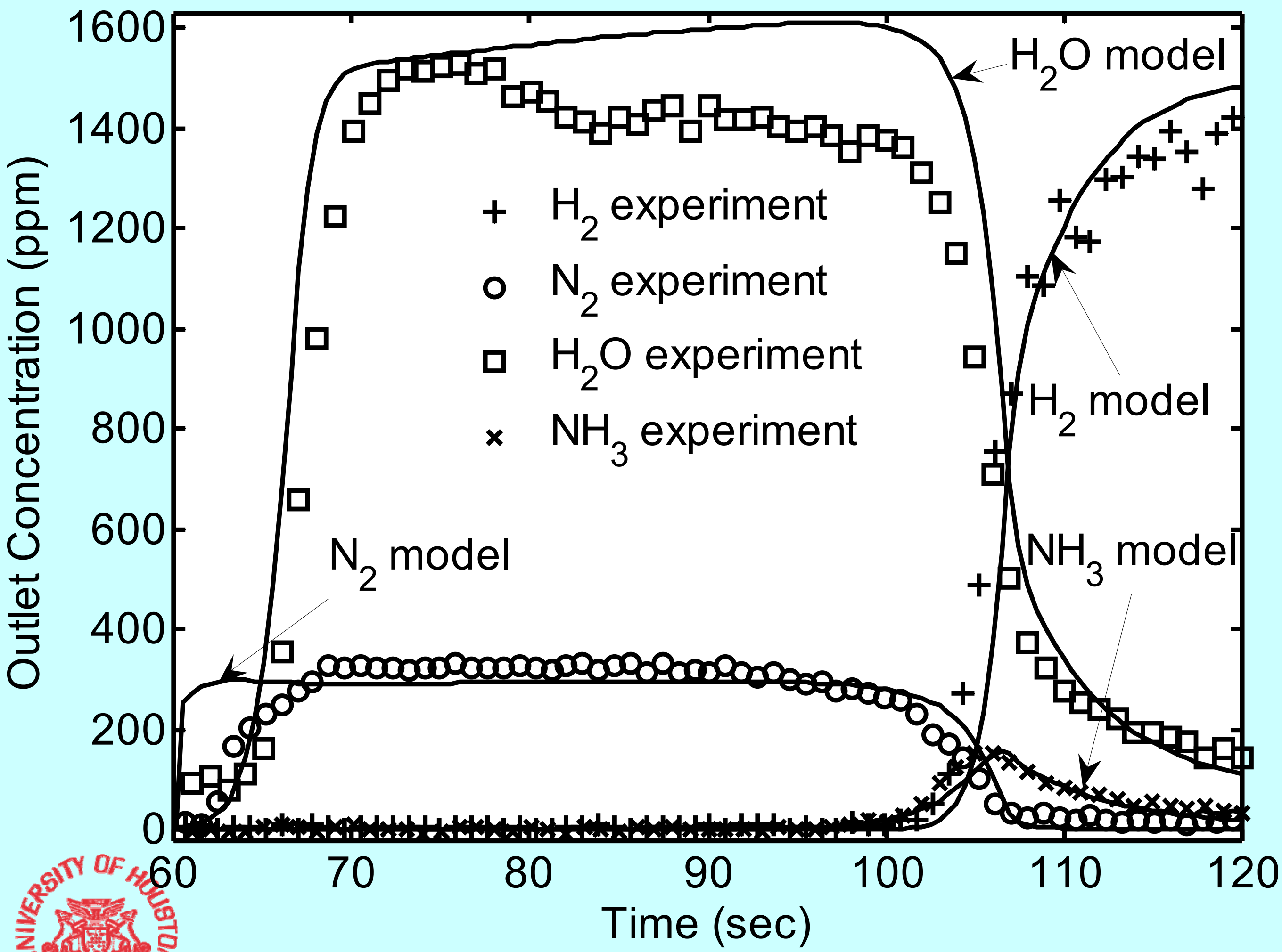
7. $\frac{10}{3}NH_3 + Ba(NO_3)_2(s) \rightarrow 5H_2O + BaO(s) + \frac{8}{3}N_2$

8. $H_2O + Al_2O_3 \Leftrightarrow H_2O - Al_2O_3$

9. $NH_3 + Al_2O_3 \Leftrightarrow NH_3 - Al_2O_3$

$$\begin{tikzcd} H_2 \arrow[r, "NOx"] & NH_3 \arrow[d, "NOx", "O_2"'] \\ & N_2 \end{tikzcd}$$

Model vs. Experiment: Regeneration

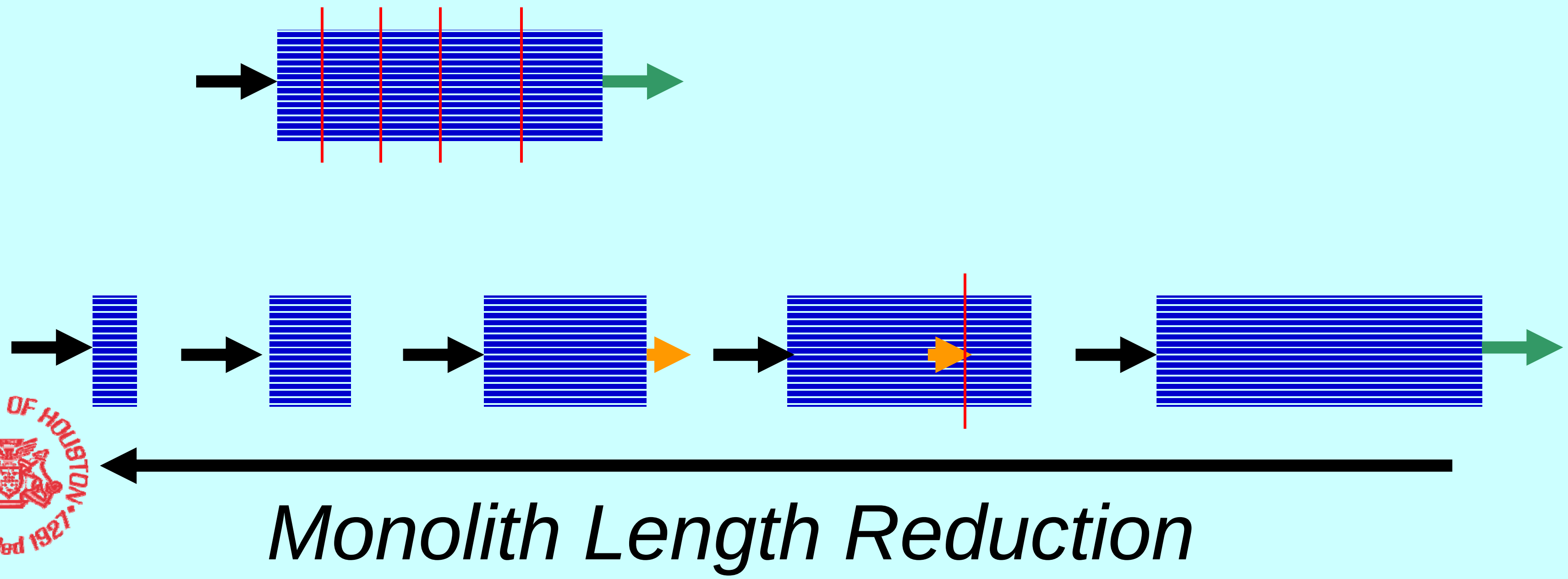


Conditions:
Lean: 500 ppm NO, 5%O_2
Rich: 1500 ppm H_2, balance Ar (100 s)
Pt, BaO: 2.70 wt.%, 14.6 wt.%
T = 275 ^oC

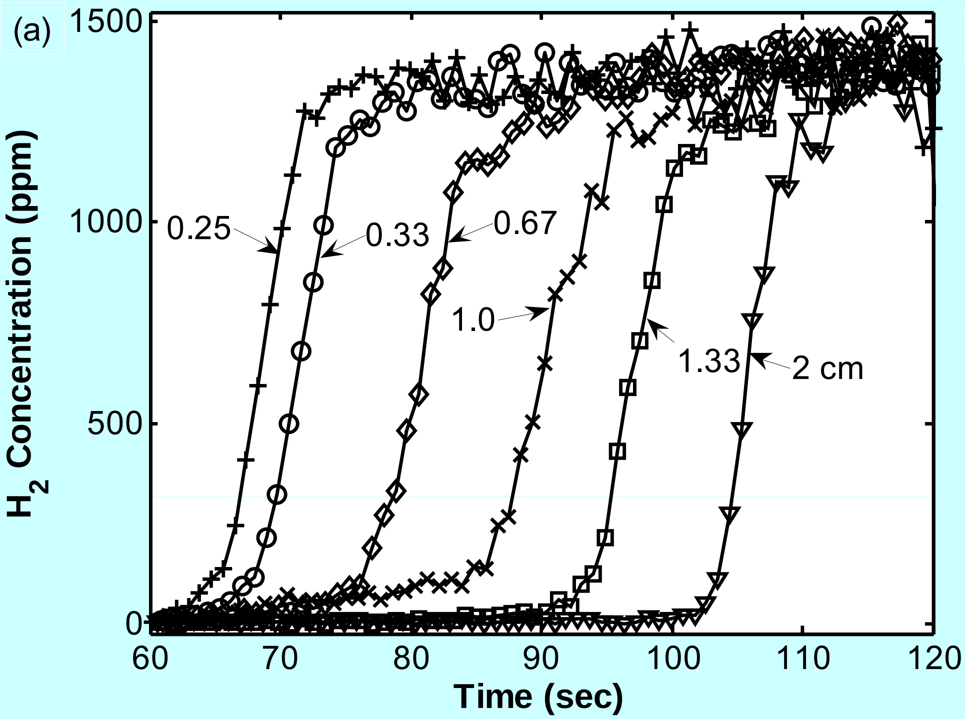
Varied Length Experiments

Approach:

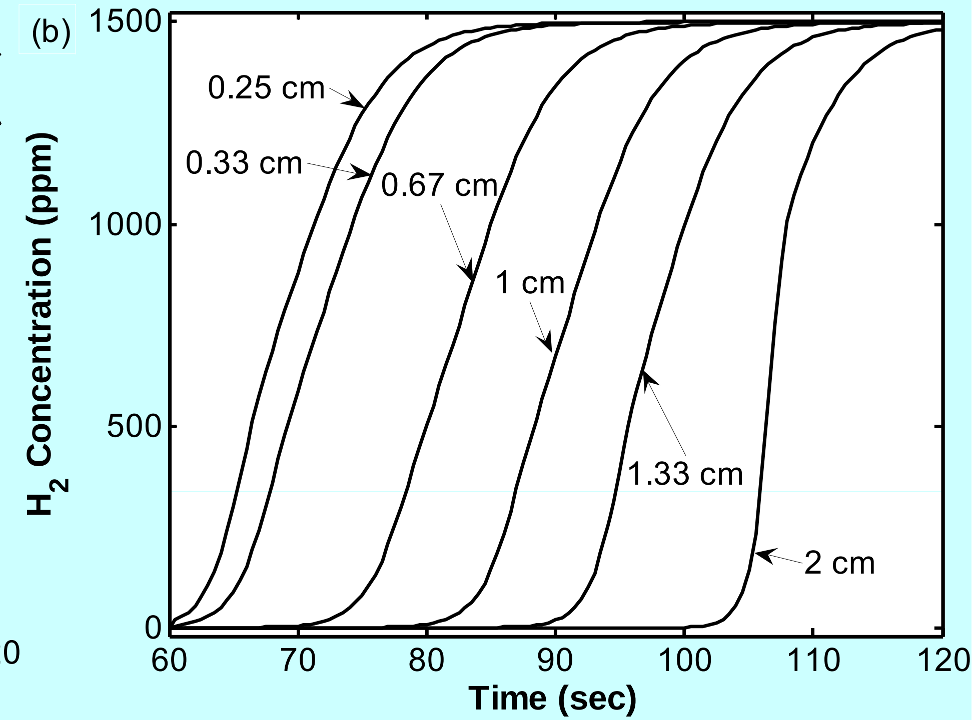
- Divide original monolith into progressively smaller sections
- Replicate experiments to generate spatio-temporal concentration profiles



Effluent H_2 Transient

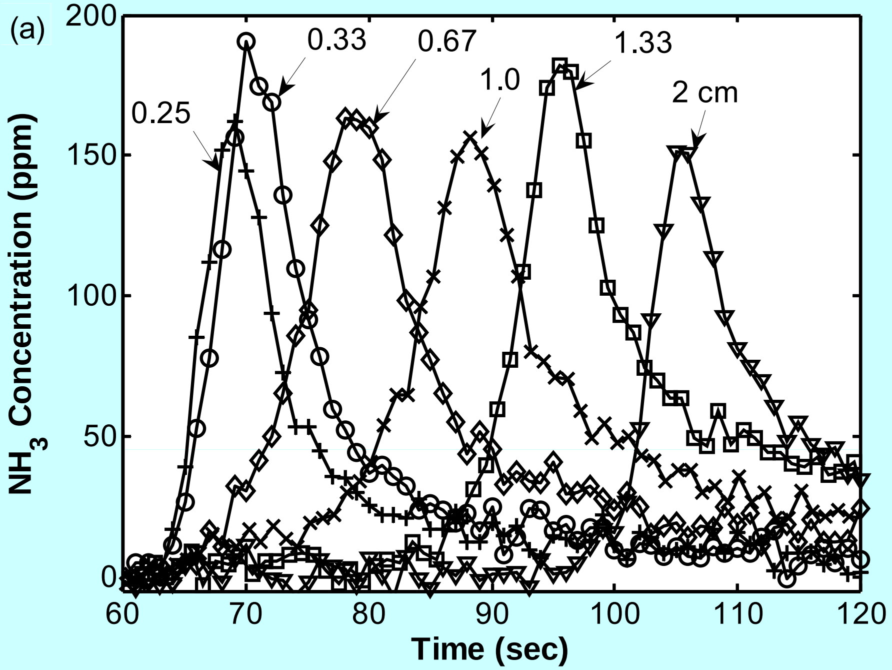


Experiment

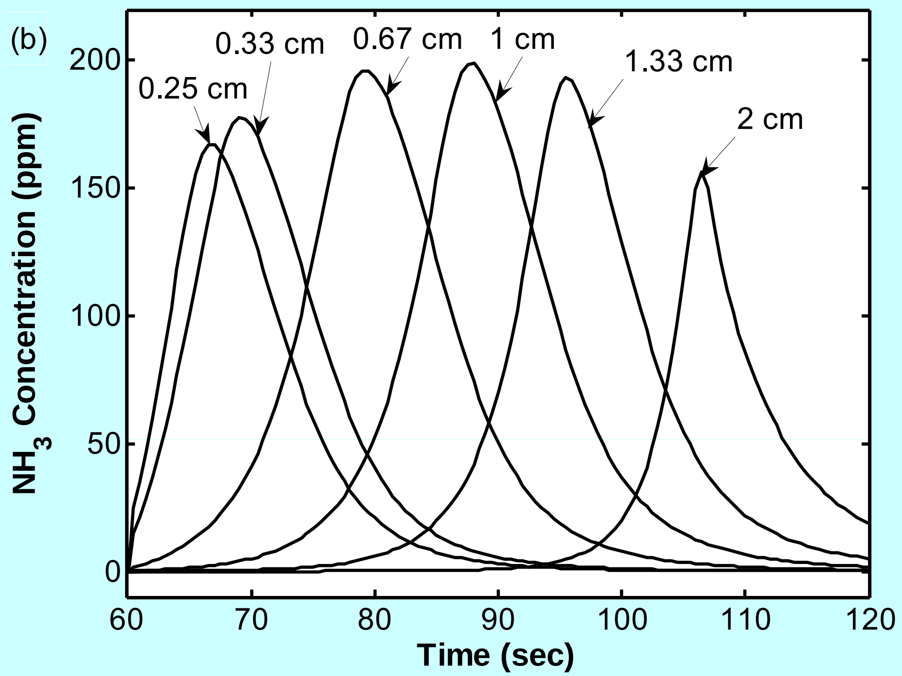


Model

Effluent NH_3 Transient

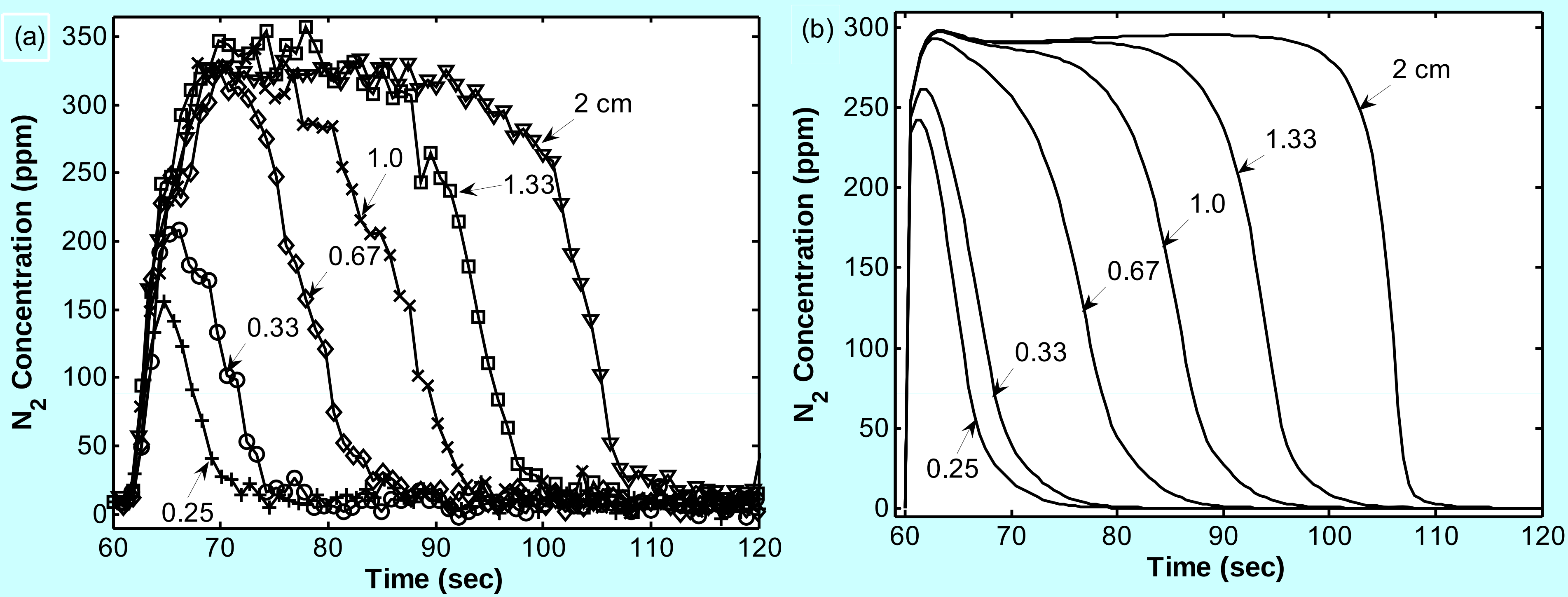


Experiment



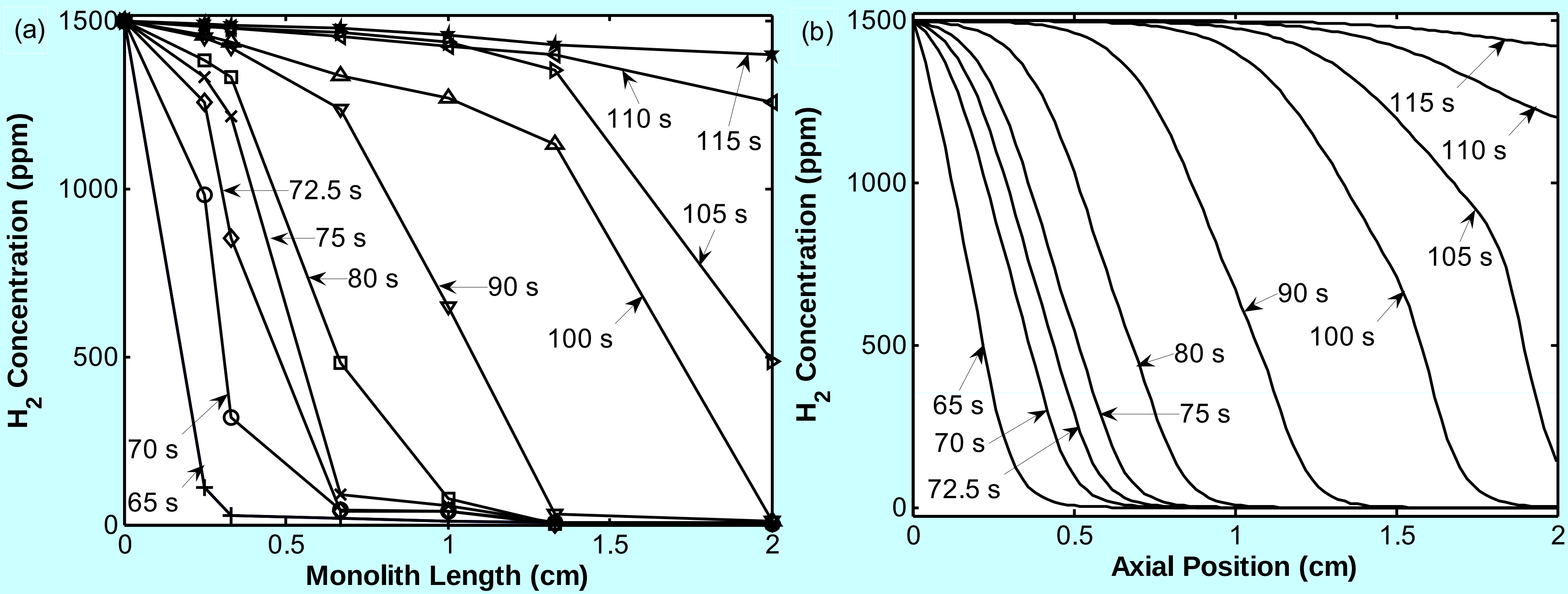
Model

Effluent N_2 Transient



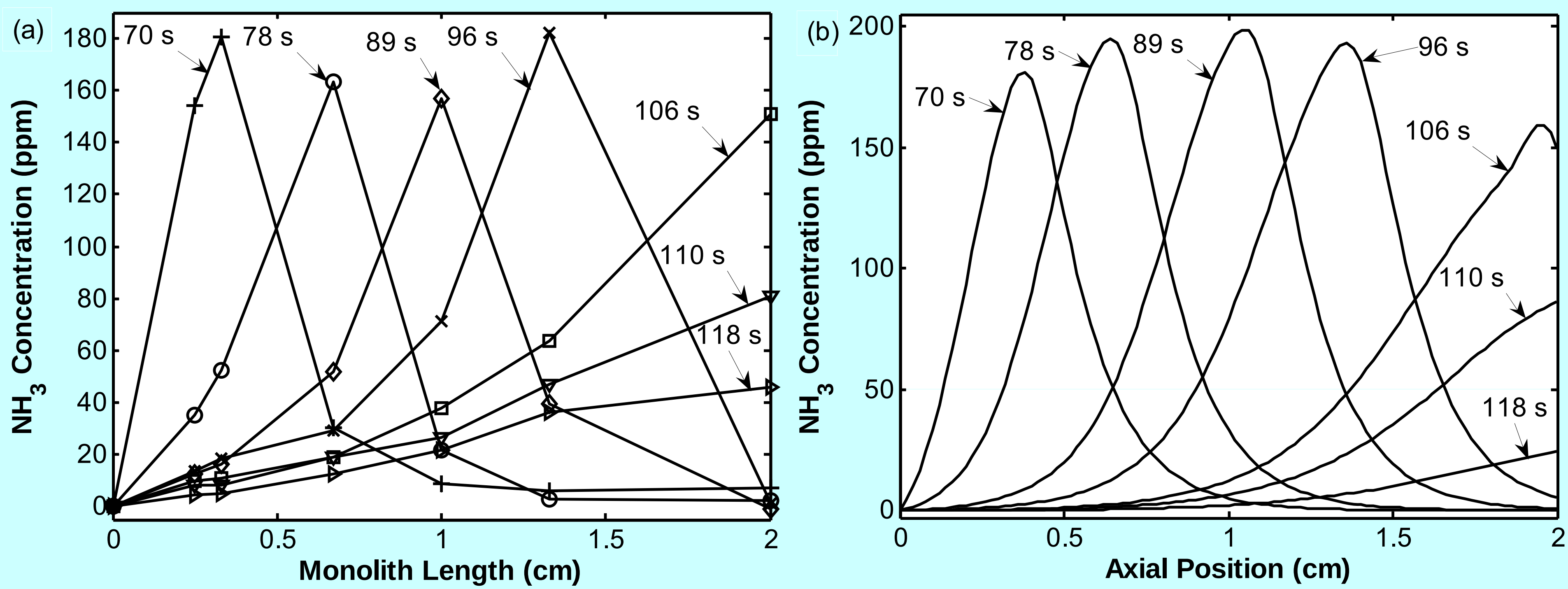
Experiment *Model*

Traveling H_2 Front



Experiment *Model*

Traveling NH_3 Front



Experiment

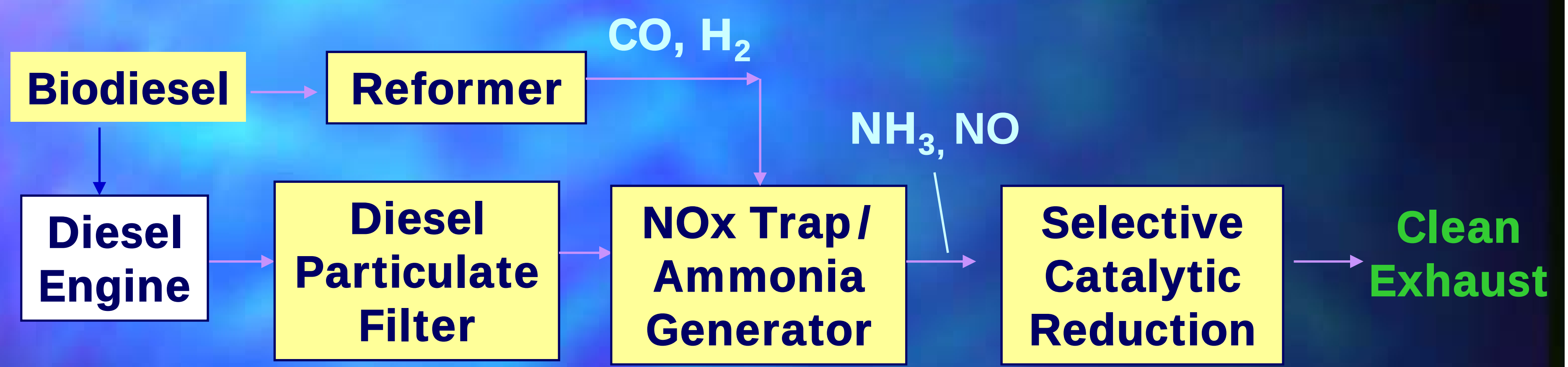
Model

Summary

- Growth of diesel-powered vehicles requires cost-effective & reliable lean NOx reduction
- NOx storage and reduction: Complexity is both its success and challenge
- Focus on building mechanistic understanding through bench-scale and TAP experiments
- On track towards predictive LNT reactor model with microkinetics
- Next steps
  - Catalysis:
    - Develop improved LNT catalysts
    - Elucidate chemistry/kinetics at Pt/Ba interface
  - Systems integration:
    - Link model with engine controls
    - Combine LNT with SCR

The Future Diesel Vehicle?

A Chemical Plant on Wheels.....



Abatement:

	VOCs, Soot	NOx	NOx
Concept:	***Filtration & Oxidation***	***NOx Adsorption & Reduction***	***NH_3 Adsorption & Reduction***

Acknowledgements

- Collaborators
  - Dr. Rachel Muncrief, Dr. Vinay Medhekar, Dr. Jun Choi
  - Karen Kabin, Manish Sharma, Pranav Khanna,
    Jim Lattner, Bala Nair, Madhu Bhattchacharya,
    Robert Clayton, Jin Xu, Divesh Bhatia, Saurabh Joshi,
    Yongjie Ren
  - Prof. Vemuri Balakotaiah, Prof. Mickey Rooks (CHBE)
  - Prof. Matt Franchek, Prof. Karolos Grigoriadis (ME)
  - Dr. Stan Roth, Dr. C.Z. Wan (BASF Catalysts Inc.)
  - Dr. Bob McCabe, Dr. Joe Theis (Ford)
- Funding
  - National Science Foundation
  - State of Texas Advanced Technology Program
  - DOE National Energy Technology Laboratory
  - City of Houston
  - Texas Commission on Environmental Quality (TCEQ)
  - BASF (Engelhard Inc.), Ford, Cummins Inc.