Characterizing NOx Adsorber Regeneration and Desulfation

Presented by Shean Huff

Oak Ridge National Laboratory
Fuels, Engines, Emissions Research Center

2005 Advanced Combustion Engines Merit Review
April 19-21, 2005

Sponsor: U.S. Department of Energy, OFCVT
Program Managers: Ken Howden, Gurpreet Singh, Kevin Stork

Diverse ORNL Team Working on This Project

- Engine system management, experiment design, data collection and analysis
  - Shean Huff
  - Brian West
  - Jim Parks
- Analytical chemistry
  - John Storey
  - Sam Lewis
  - Bill Partridge
- Bench reactors
  - Todd Toops
  - Jae-Soon Choi
  - Josh Pihl (University of Wisconsin)
- Modeling (CLEERS interaction)
  - Stuart Daw
  - Kalyan Chakravarthy

Project Overview

Motivation

- Energy-efficient aftertreatment will enable light-duty diesel market penetration

Project Objectives and Approach

- Characterize H_2, CO, and HC's generated by the engine
  - FTIR, GC/MS, SpaciMS to characterize engine strategies
- Characterize candidate NOx adsorbers for performance and degradation
  - Correlate various reductants with catalyst performance
  - Characterize fresh, sulfated, and de-sulfated catalysts
- Develop stronger link between bench and full-scale system evaluations
  - Provide data through CLEERS to improve models. Use models to guide engine research

Research consistent with OFCVT Multi-Year Program Plan

- Experimental data and validated computer simulation models will be developed to provide a more definitive understanding of the … evolution of emissions in the aftertreatment systems.
- … enable rapid and effective optimization of the … aftertreatment devices for maximum overall system efficiency, compliance with emissions standards, and cost-effectiveness.
- … enhance the knowledge base that can be used by industry partners and suppliers… to develop energy-efficient, cost-effective advanced engine/emission control systems.
- …Improve the scientific foundation of NOx adsorber–catalyst performance and degradation mechanisms to mitigate the trend of greater efficiency loss as catalyst ages
- … sulfur effects on aftertreatment, including catalyst tolerance, regeneration methods, and further reduction of sulfur sources (lubricants) Improve the catalyst materials and systems for lean NO catalysis with urea and alternative reductants for performance over wider temperature range
- Improve the simulation capability for exhaust aftertreatment devices to accelerate the design of the most efficient and effective emission control systems

2004 Reviewer Comments (1/2)

(underlined comments specifically being addressed)

- **Excellent experimental facilities and tools to carry out characterization of NOx adsorbers and exhaust HC chemistry.**
- Solid team and process.
- Combines engine, bench & basic core competencies available at ORNL. **Excellent team.**
- The frame of work is within the practical domain of engine operation, albeit fairly fundamental.
- **Excellent utilization of one-of-a-kind instrumentation**. Thoughtful selection of areas to investigate such as desulfation and effects of fuel components. Also **coordination with CLEERS enhances the impact of the work**.
- Chemical speciation capability and SpaciMS set-ups are excellent. This facility should be able to generate **extremely useful information** in understanding the NAC transient behavior.
- This work is providing very useful information on NOx trap regeneration.
- **Excellent application of tools** (Spaci- MS) showing the effect of hydrogen on NOx adsorber performance.
- Keep improving the industry connections.
- Important to evaluate at HD not-to-exceed point to demonstrate space velocity limitations on this technology.
- scope is so broad,… many fundamental questions…not addressed – for instance, why were PM emissions…lower for Post80 [than DEM]? [need to] spin off smaller investigations to pinpoint questions that main program cannot address

2004 Reviewer Comments (2/2)

(underlined comments specifically being addressed)

- Frank presentation of need for engine replacement with additional details in the appendix was greatly appreciated and further demonstrated the vigor of the research.
- Better selection of injection strategies and more evaluation of the effects of EGR on the engine out compositions.
- Missing latest industry LNT desulfation/regeneration strategies – but probably no way to get them…
- Must not let CLEERS modeling efforts drive the practical exploration of system performance limits
- Limited to one catalyst… Do these results hold true for different catalyst formulations?
- How do results compare to reactor data?
- Is H2S formed directly, or is it actually from the SO2 released from the catalyst that further reacts with reductants at the back of the catalyst?
- Information on unregulated compounds, such as NH3, N2O, H2S, SO2, during regeneration is valuable as well.
- Discuss the experimental approach to desulfation. Calculate the effect on BSFC for each strategy (delayed and post).
- . . . They need to also look at adding EGR to get to rich conditions for NOx trap regeneration instead of increasing fueling.
- Keep improving the industry connections.

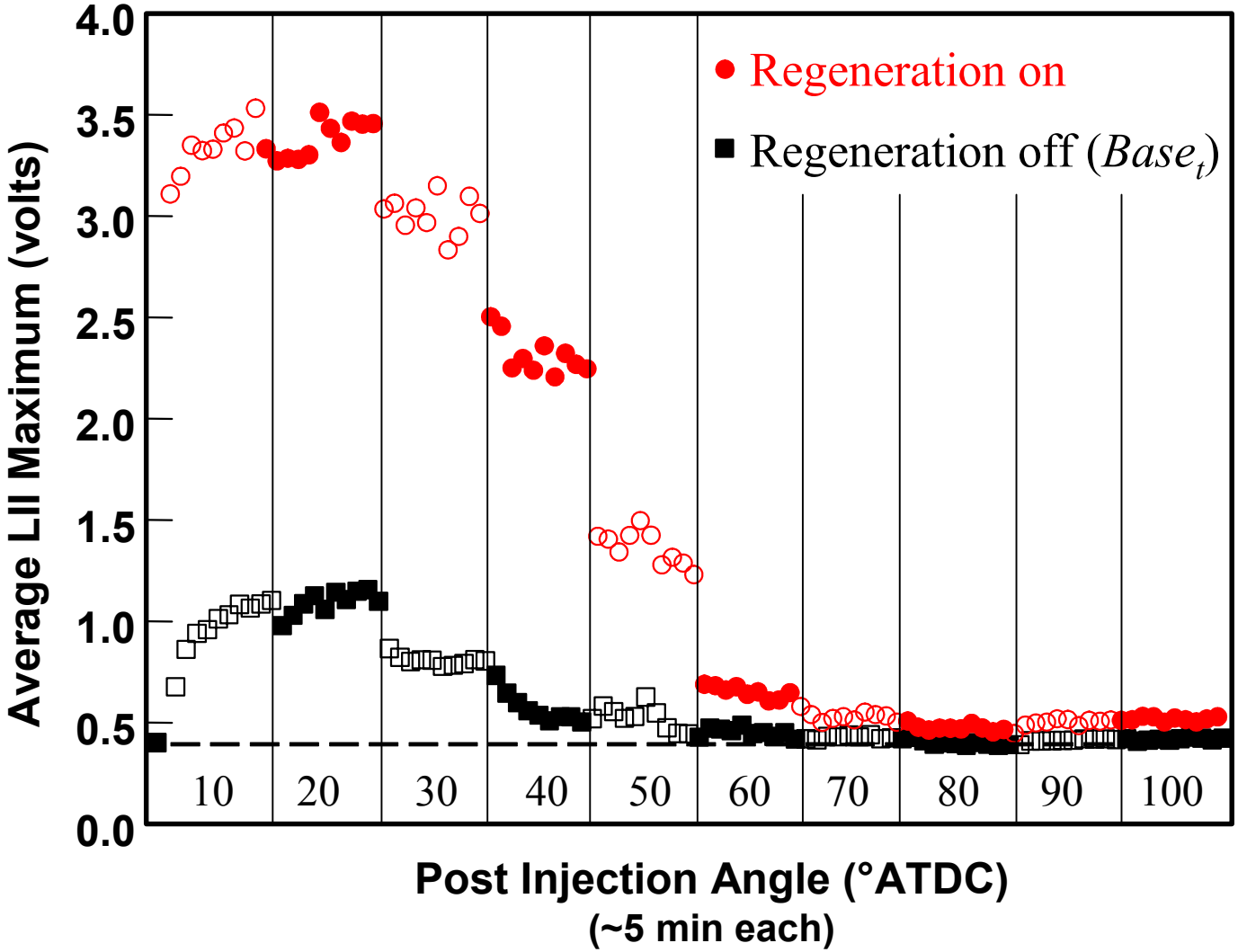
Summary of 2005 Objectives and Accomplishments

- ✓ Present reductant chemistry paper (SAE 2004-01-3023) at Tampa F&L
- ✓ Conduct detailed PM investigation with LII (and Witze)
  - Paper presented at SAE Congress (SAE 2005-01-0186)
- ✓ Conduct reductant utilization study
  - *in-situ* measurements
  - Varied: strategy, lean loading period, min AFR, catalyst configuration
- ✓ Continue to collaborate through CLEERS
- ✓ Investigate nitrogen selectivity (ammonia formation)
- ✓ Characterize LTC-based regeneration
- ✓ Investigate temperature effects
- ✓ Develop rapid sulfation protocol
- ✓ Develop improved desulfation control
  - Strategies for stable control of 550-850°C LNT temperature
- Examine other LNT formulations

Collaboration and Interactions

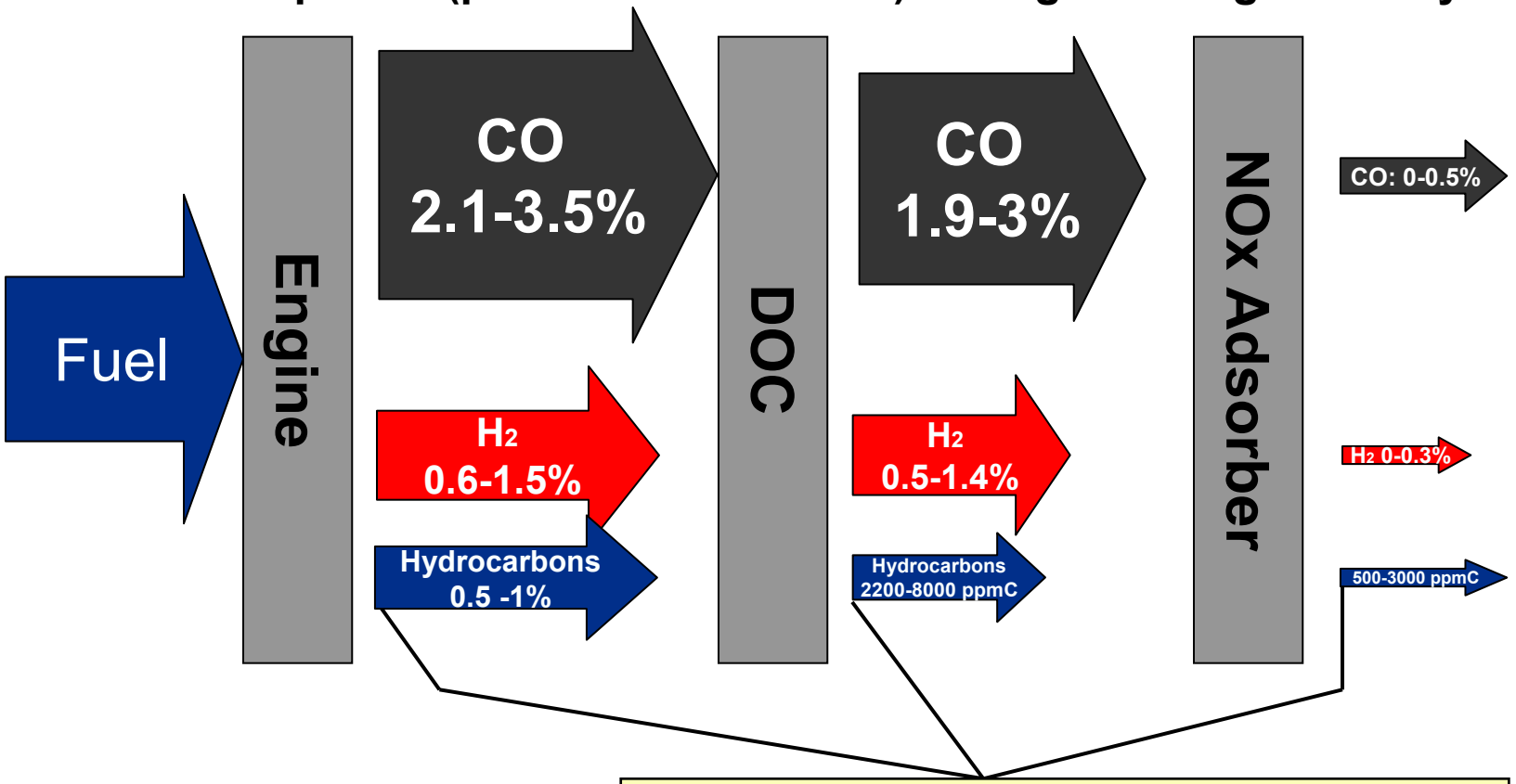
- Presented progress at DEER 2004, Diesel Cross-cut Team, and CLEERS meetings
- Collaboration with CLEERS LNT focus group
- Presented to industry peers in multiple settings
- Discussions with MECA partner(s)
- Papers presented at 2004 SAE Fall F&L, 2005 Congress
  - Reductant Chemistry – West et al, 2004-01-3023
  - PM study in collaboration with SNL – Witze et al, 2005-01-0186
- Abstract for 2005 Fall F&L

Work with SNL's LII allowed study of relationship between post injection timing and soot production



Approach Summary: vary strategy or fuel to change reductant chemistry

Reductant Species (peak concentrations) through the engine/catalyst system

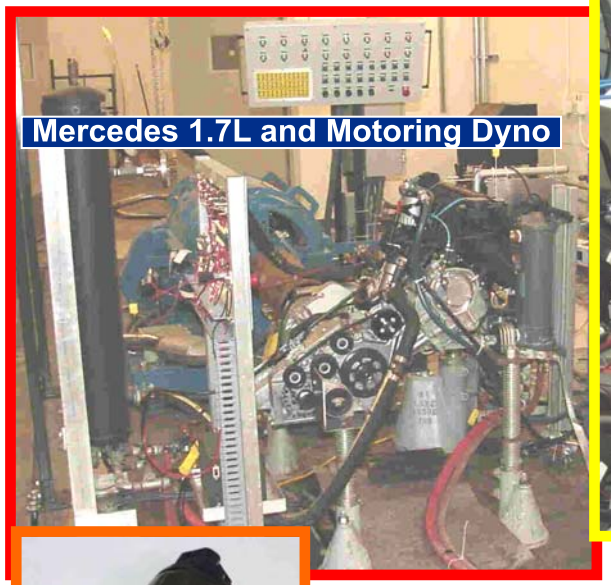


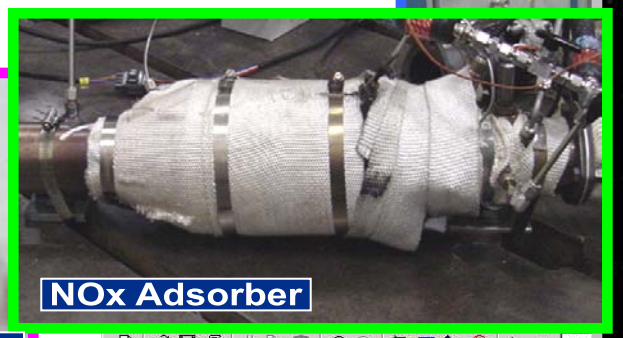
Other species measured:
Nitro-organics
Ammonia
N2O

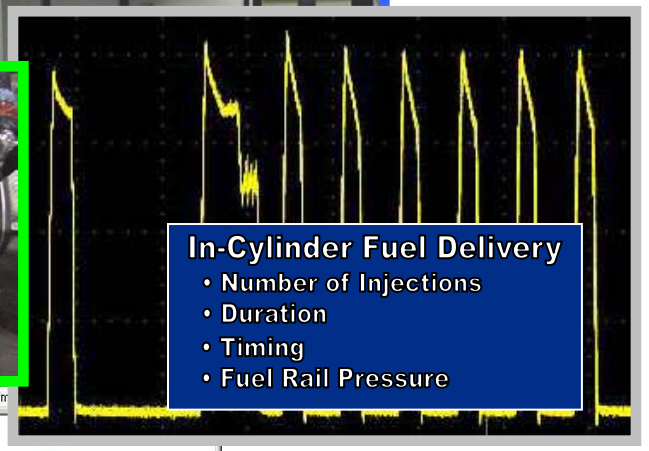
methane	ethane	ethyne	propene
butene	formaldehyde	acetaldehyde	benzaldehyde
toluene	benzene	napthalene	
tridecane	indene	styrene	
benzofuran	phenol	methyl napthalene	
acenathalene	diphenylethene		…many others

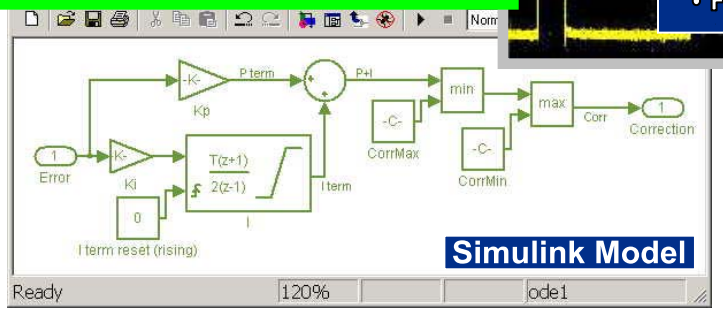
H2 and O2 transients measured using SpaciMS (SAE 2000-01-2952)

Common Rail Engine and Motoring Dynamometer at ORNL's Fuels, Engines, and Emissions Research Center dedicated to this activity



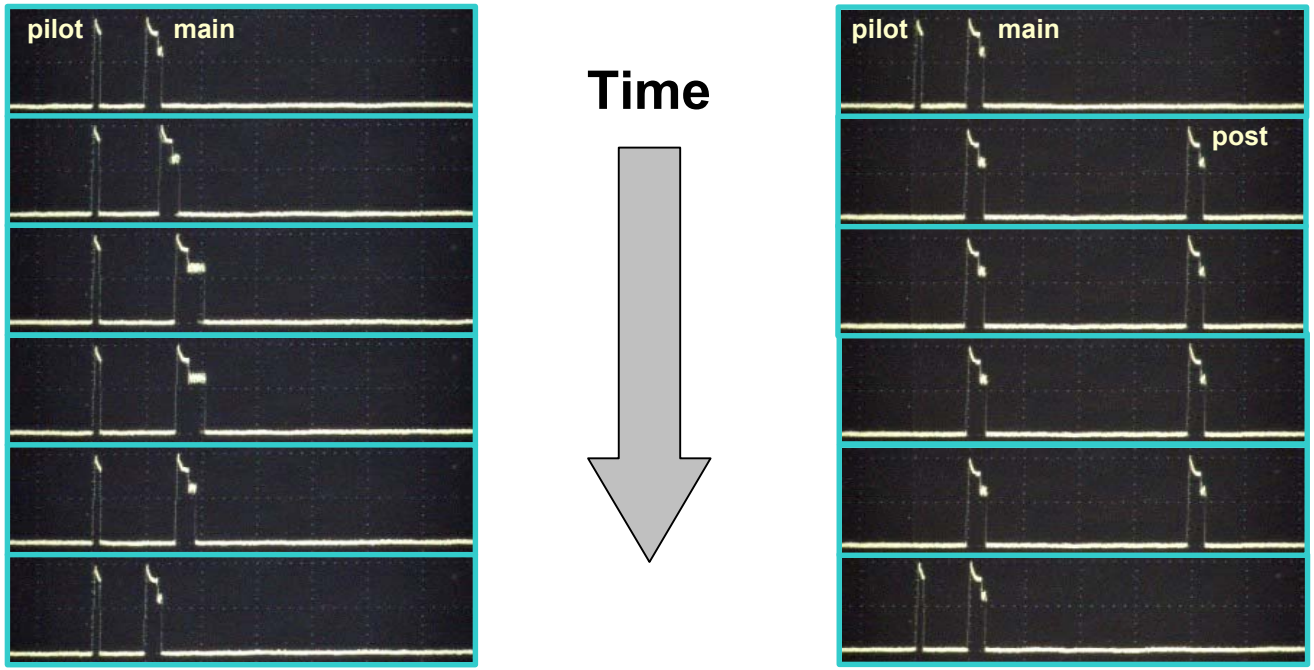






Three strategies for achieving intermittent rich combustion are focus of today's review

- Two strategies employ no EGR for highest engine-out NOx (fastest adsorber loading)
- Rich excursion is achieved by a combination of intake throttling and the following injection strategies:



3rd strategy investigated uses high EGR to enter LTC during rich excursion

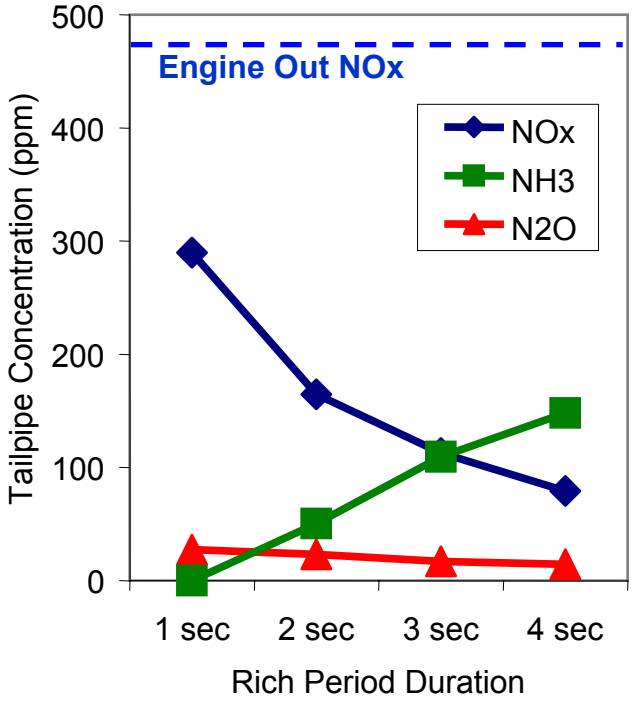
Topic #1

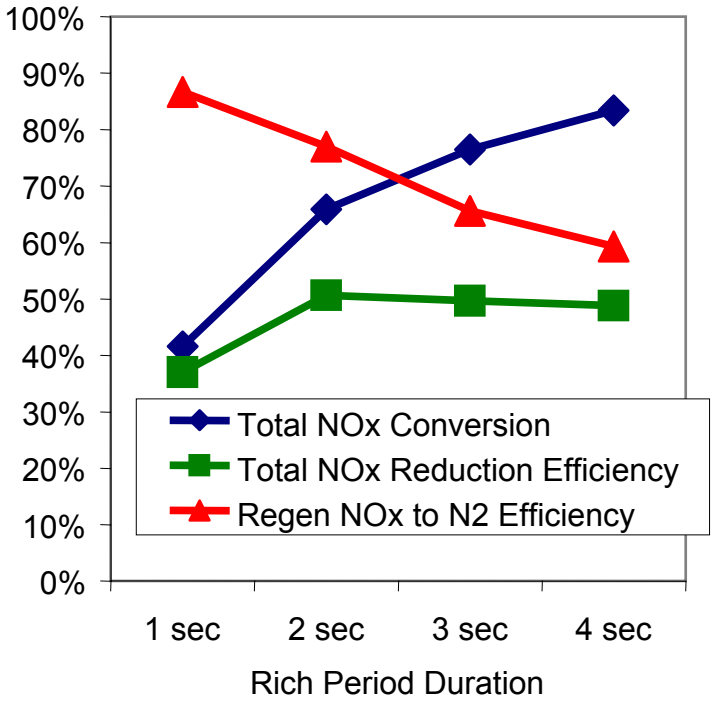
Nitrogen Selectivity:
Investigating Products of NOx Conversion

- Initial *experimental* strategies engineered for high ammonia production to facilitate study

N_2 Selectivity: General Observations

- **NH_3 and N_2O measured at tailpipe via FTIR (cycle averaged analysis)**
- **Experimental parameters chosen to enhanced NH_3**
  - DEM, 13:1, 300ºC, 60s Cycle
  - "Over-regeneration" with high NOx saturation of LNT



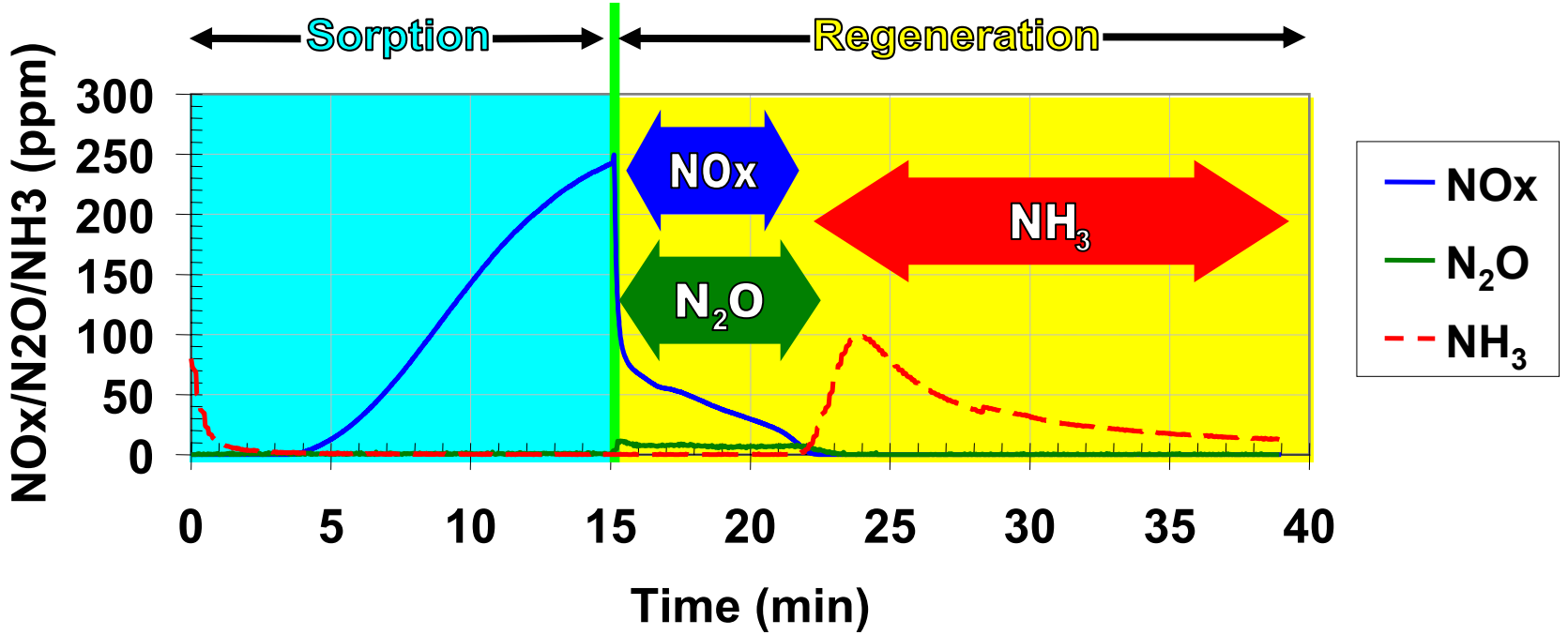


- **Excess reductant leads to high NH_3 emissions and reduced NOx to N_2 reduction efficiency**

Proposed Theory for NH_3 Formation (One of Many)

Lesage et.al., *Phys. Chem, Chem. Phys.*, **5**, pp. 4435-4440 (2003).

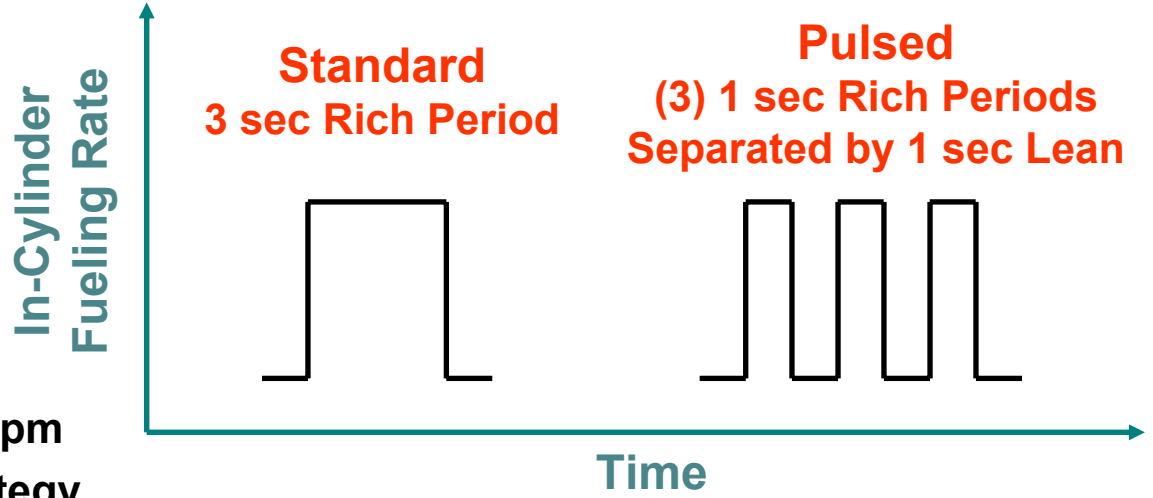
- **Isocyanate surface species formed on Pt plays role in NH_3 formation**
  - $2\ NCO + 3\ H_2O \rightarrow 2\ NH_3 + 2\ CO_2 + 0.5\ O_2$ **[Rich: NCO → NH_3]**
  - $2\ NCO + O_2 \rightarrow N_2 + 2\ CO_2$ **[Lean: NCO → N_2]**
- **ORNL bench reactor results for engine-aged core sample shown**



- **NH_3 formed <u>after</u> initial main NOx release/reduction spike**
  - only when NOx has been stored on catalyst

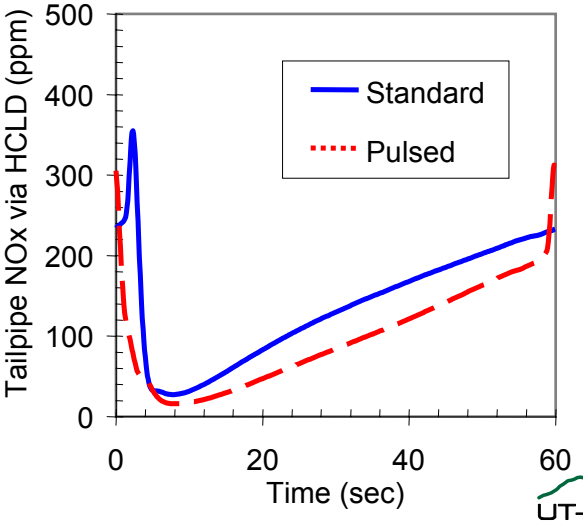
One Highlight of N_2 Selectivity Studies

- Comparison for (2) regeneration strategies
  - Same fuel penalty
  - Same base parameters
    - Temperature=300ºC
    - Cycle period=60 sec
    - Engine Out NOx~500 ppm
    - DEM regeneration strategy
    - 13:1 A/F target



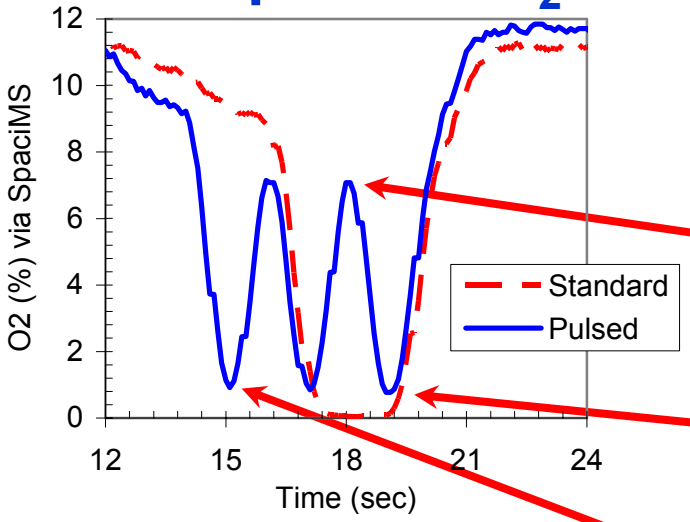
Pulsed Strategy Gives Lower NH_3 *AND* Equivalent NOx Reduction

	Standard	Pulsed	Difference
Engine Out NOx (ppm)	472.1	457.3	-3.1%
Avg. Tailpipe NOx (ppm)	138.7	98.6	-29.0%
Avg. Tailpipe NH3 (ppm)	217	73	-66.4%
NOx Capacity (g/l)	0.311	0.317	2.2%
BSFC (lb/bhp-hr)	0.381	0.390	2.3%
Catalyst Temperature (C)	331.5	342.6	3.4%



Tailpipe O_2 Analysis Supports Isocyanate Theory

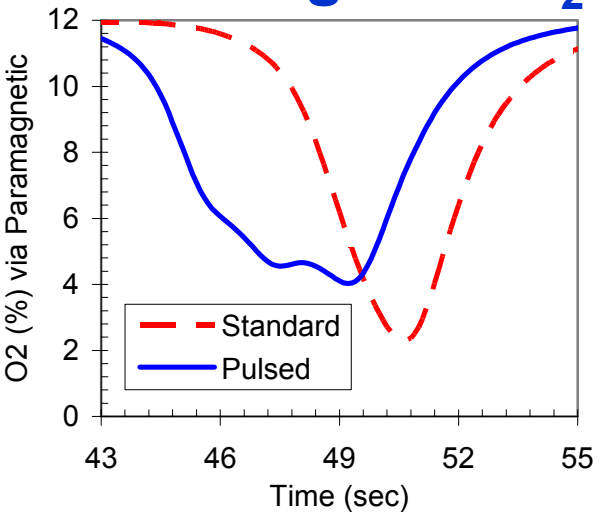
SpaciMS O_2



Standard

Pulsed

Paramagnetic O_2

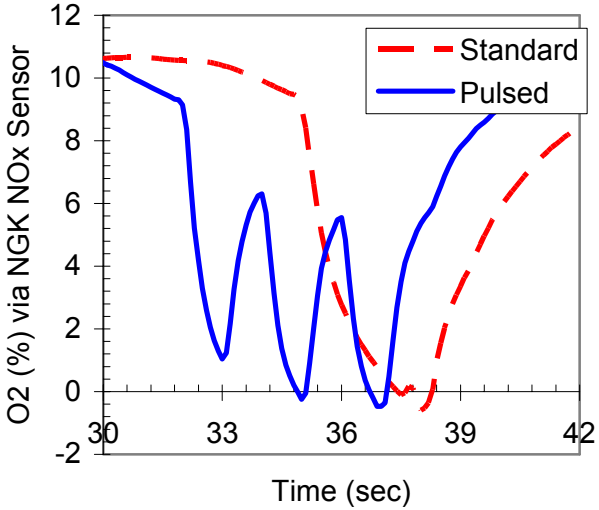


O_2 purge during Pulsed strategy

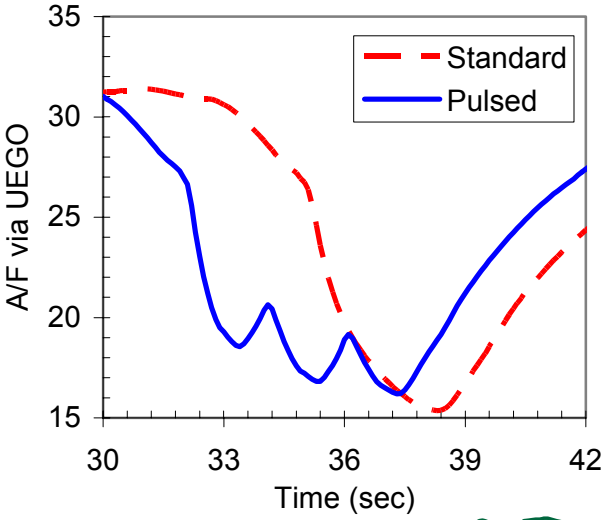
Zero O_2 during Standard strategy

Non-Zero O_2 minimum during Pulsed strategy ???

NGK Sensor O_2



UEGO A/F



Note:
Assuming no mixing, catalyst residence time is ~0.1s

Interim Summary 1: Strategy Dictates N_2 Selectivity

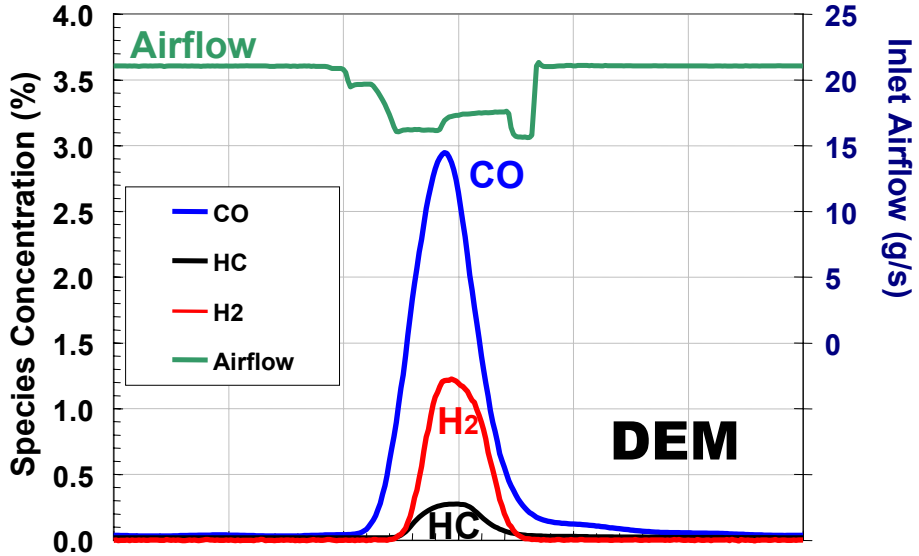
- NH_3 and N_2O can be formed during LNT regeneration
  - Proposed theory (Lesage, *et. al.*) suggests isocyanate formation on catalyst surface root cause of NH_3 formation
- Lean-rich pulsing during regeneration gives lower NH_3 formation ***AND*** Equivalent NOx reduction
  - Transient analysis of tailpipe O_2 with SpaciMS shows:
    - O_2 purge during regeneration (supports isocyanate theory)
    - Non-zero O_2 minimum: NH_3 oxidation potential
- Strategy details critical for minimal fuel penalty and optimal NOx reduction to N_2
- More results acquired…abstract submitted for SAE Fall Powertrain & Fluids conference…stay tuned

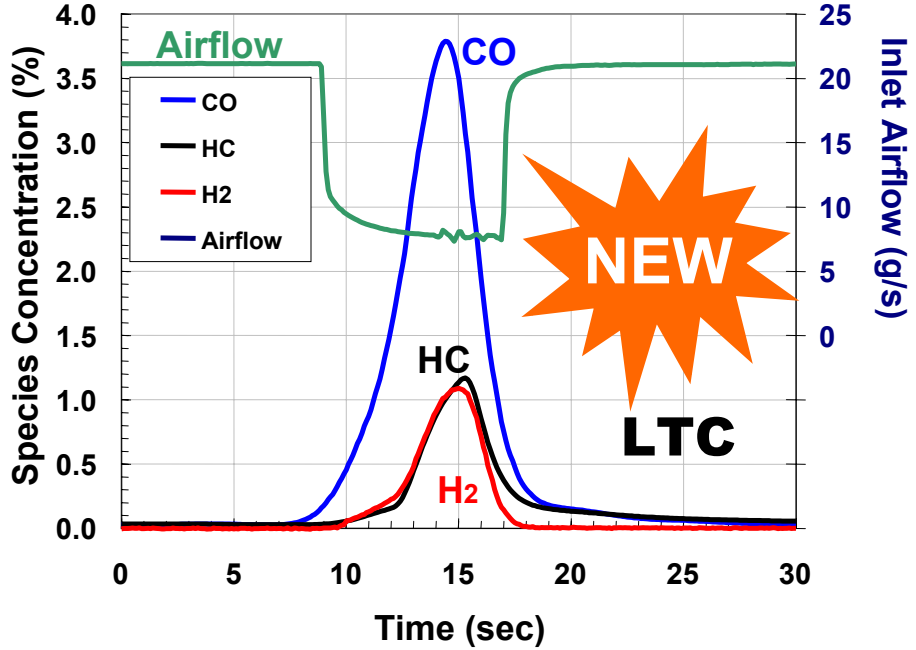
Topic #2

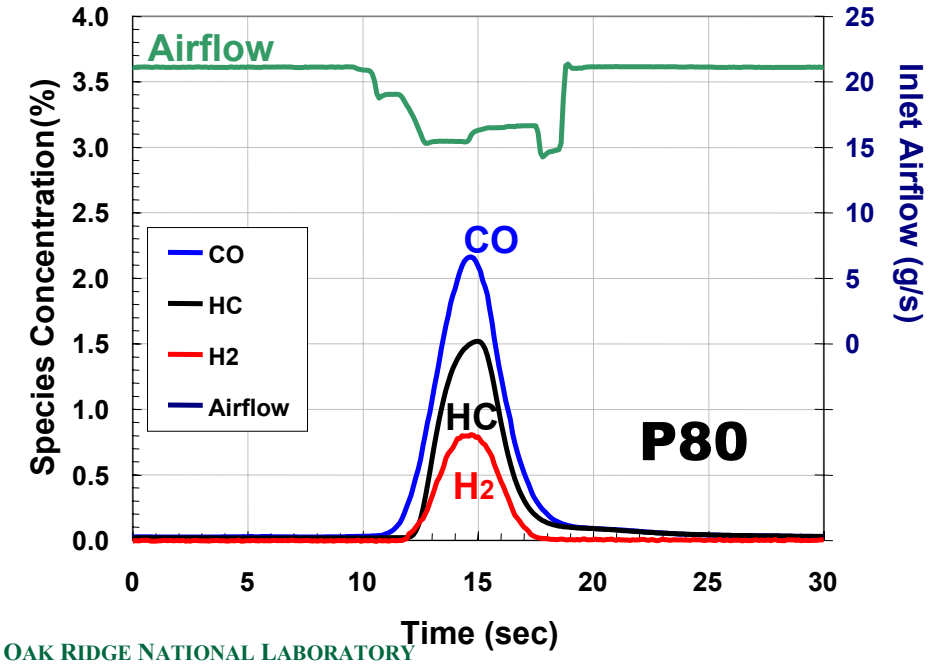
Characterizing LTC regeneration

- Recall "regeneration in the midst of LTC" from last year
  - Extremely low engine-out NOx and PM in lean LTC mode
  - Rich transition (DEM regeneration) caused high PM emissions
- New data: Examine LTC regen at higher engine load, principally using EGR for lean-rich transition

Real-time data highlights approach of strategies

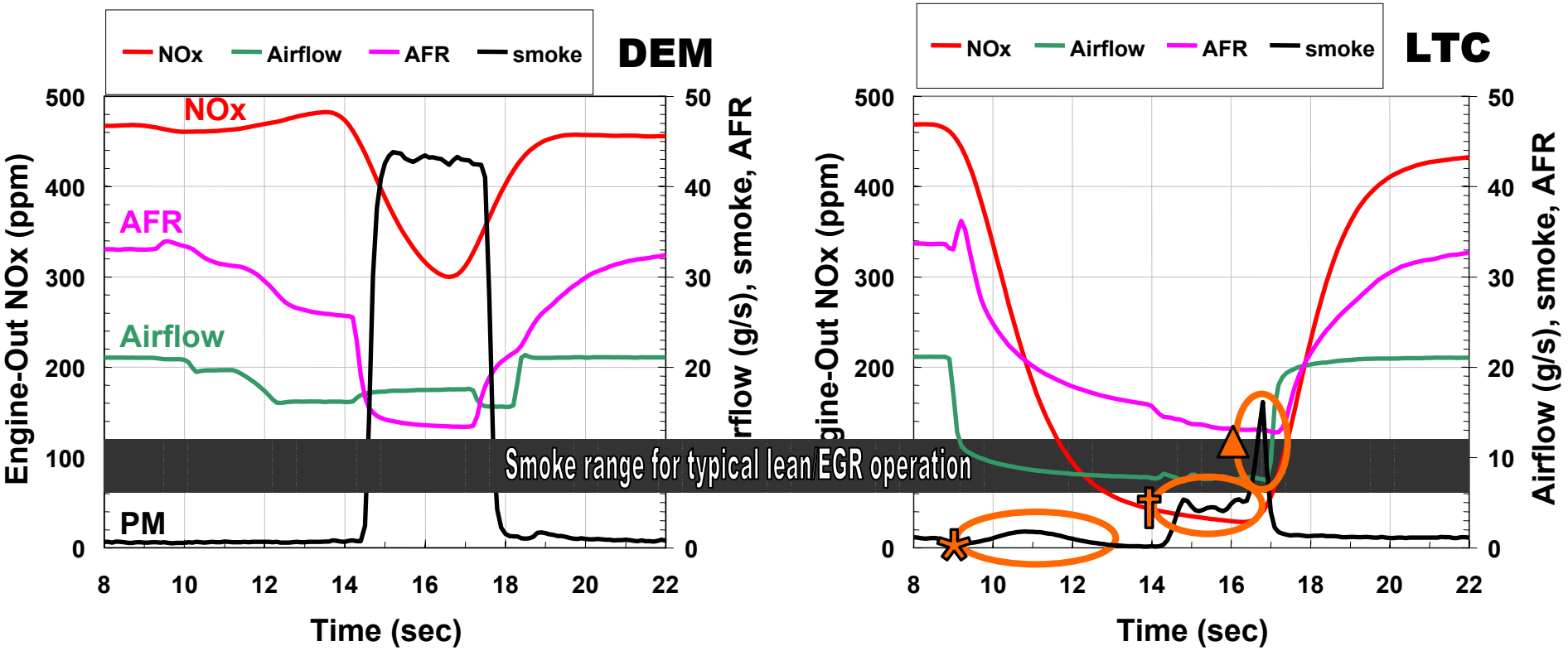






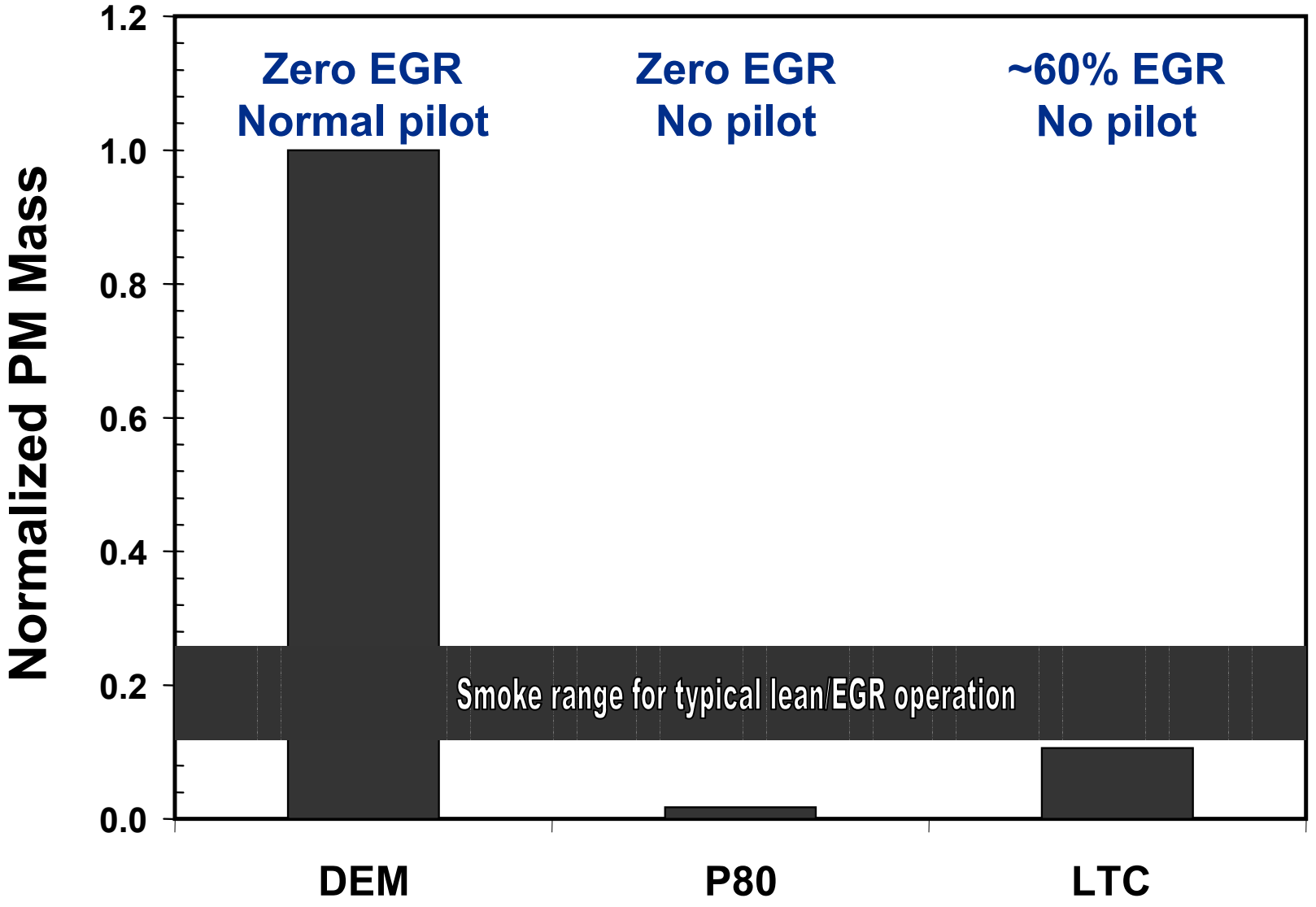
- DEM and P80 strategies employ identical throttling schedule, similar reduction in intake air mass (reduction of AFR)
  - Approach to excess fuel addition affects reductant species formed, concentrations
- "LTC" strategy uses EGR and nominal injection control for rich transition

Close look at EGR-induced regeneration shows traits of LTC (low-NOx, low PM)

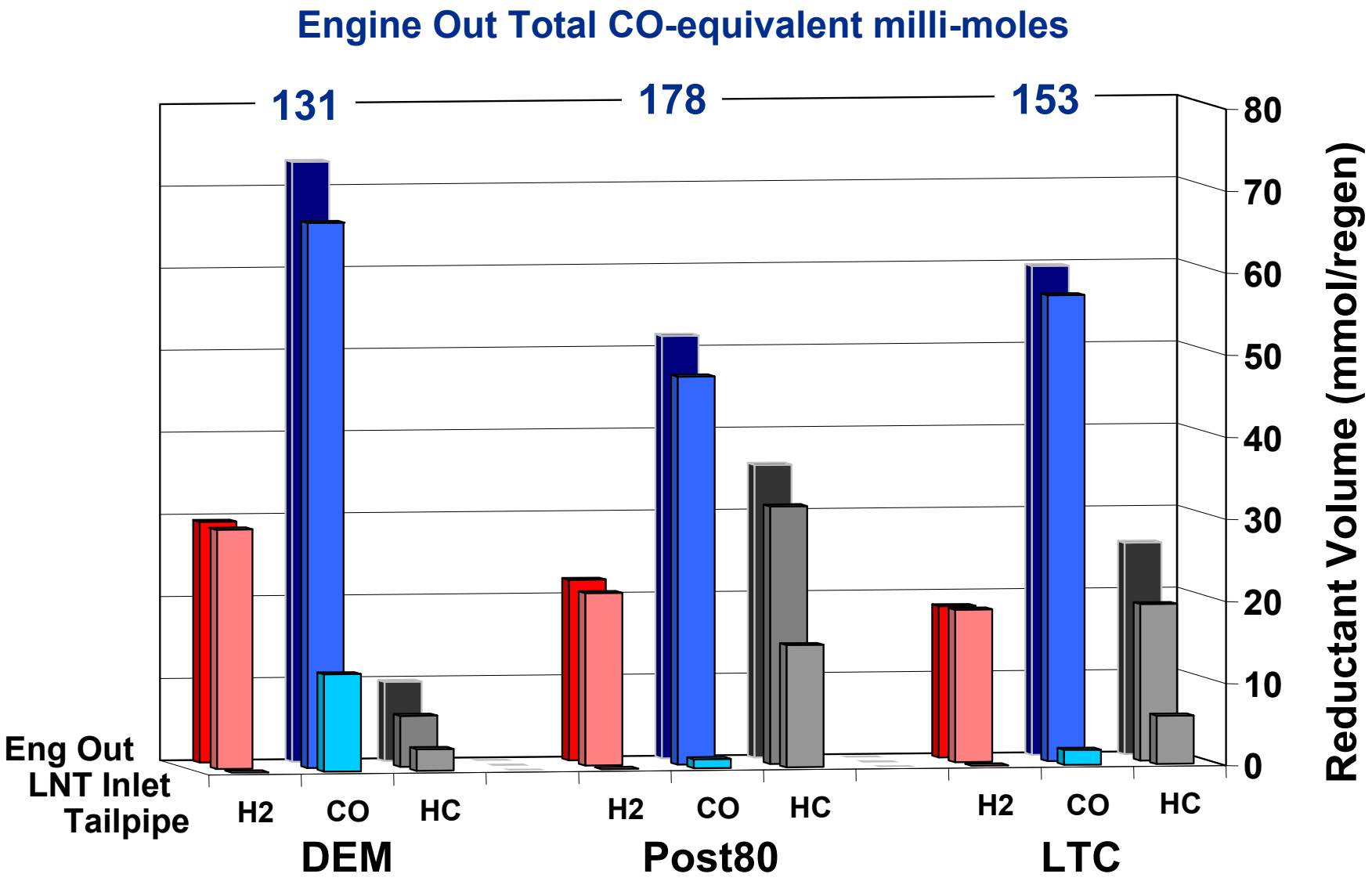


- Intake airflow decreased via EGR in lieu of throttle
- PM "hump" discernible as EGR increases (✱)
- Small PM increase with 15% increase in main fuel pulse (†)
- PM spike at end due to rapid transition back to zero EGR (▲)

LTC-based regeneration produces very low PM

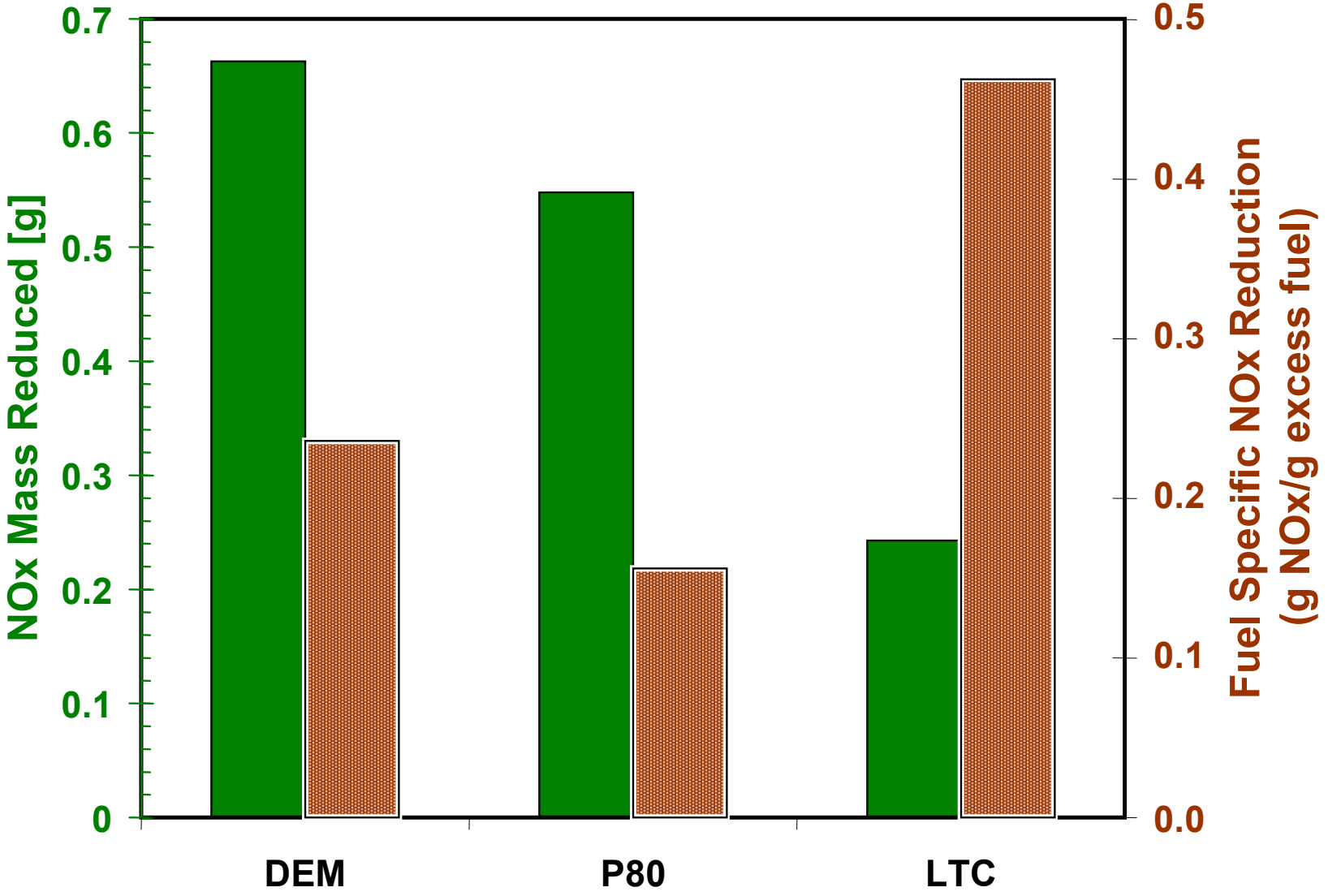


Integration of reductant produced shows similar total mole count for LTC case



LTC strategy has potential for lower overall fuel penalty, despite lower average NOx conversion

Strategies not optimized for FEP, NOx, torque, etc.



Interim Summary 2: Preliminary LTC Regeneration Strategy Has Many Benefits

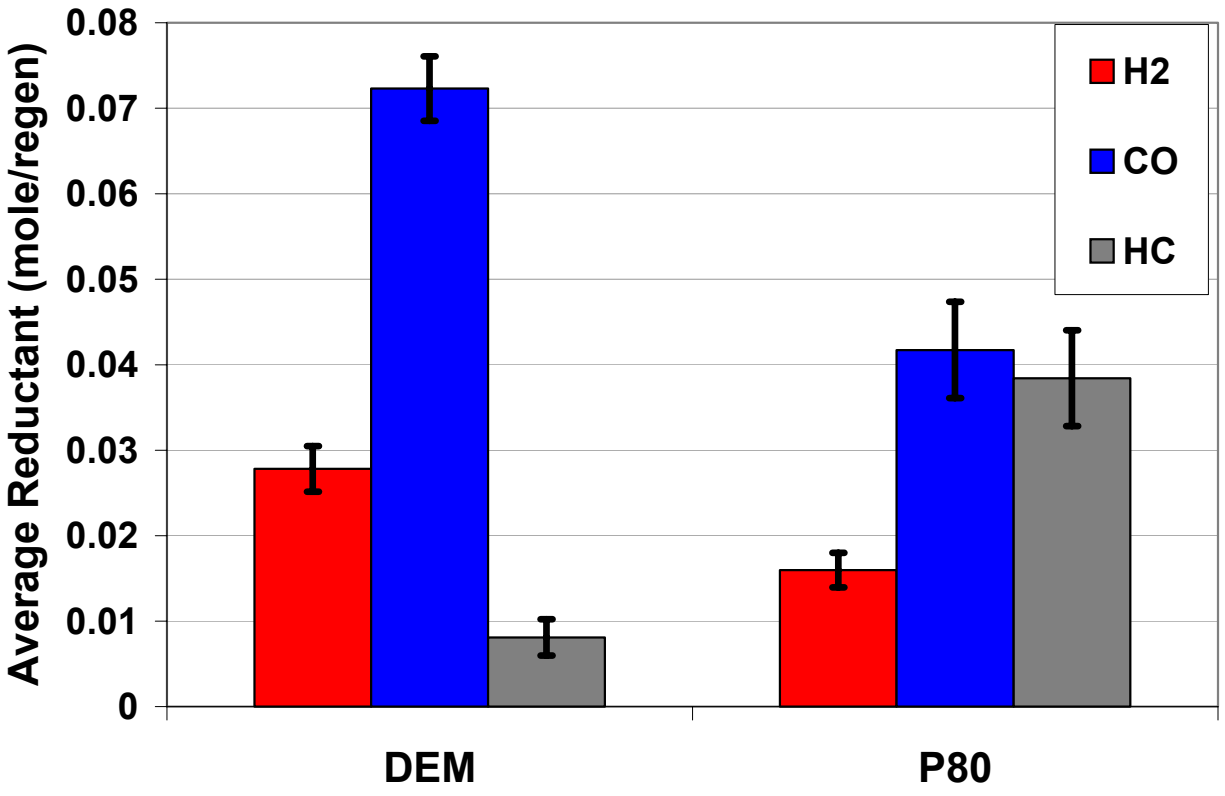
- LTC regeneration produces PM levels less than typical lean/EGR operation
- Fuel consumption for LTC less than DEM/P80 leading to better fuel specific NOx reduction for LTC
  - LTC: 0.54g NOx/g excess fuel
  - DEM: 0.28g NOx/g excess fuel
  - P80: 0.18g NOx/g excess fuel
- Mass of NOx reduced lowest for LTC, but LTC is most fuel efficient
- Demonstrated low fuel requirement suggests LTC strategy may be more fuel efficient means of LNT regeneration compared to DEM/P80
  - potential for improving NOx conversion and torque smoothing with further tuning

Topic #3

Examining Temperature Effects on Regeneration

- 200°C, 300°C, 400°C LNT ¼ length core temperature at the start of the regeneration

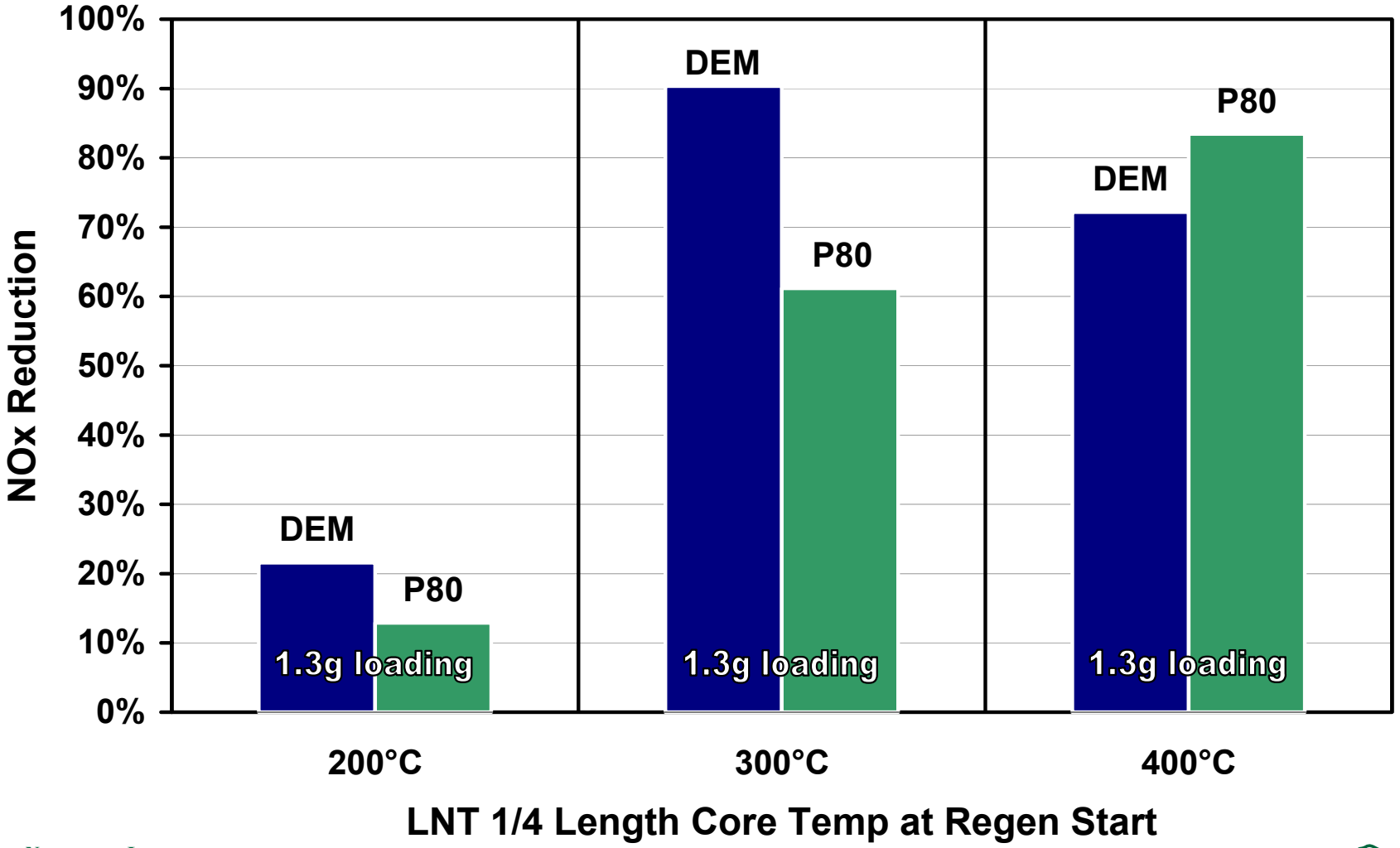
Engine-out reductant production for each strategy held constant for temperature effects study



- Same DEM and Post80 strategy used at 200, 300, and 400°C LNT temperature
- Error bars represent ± 1 standard deviation

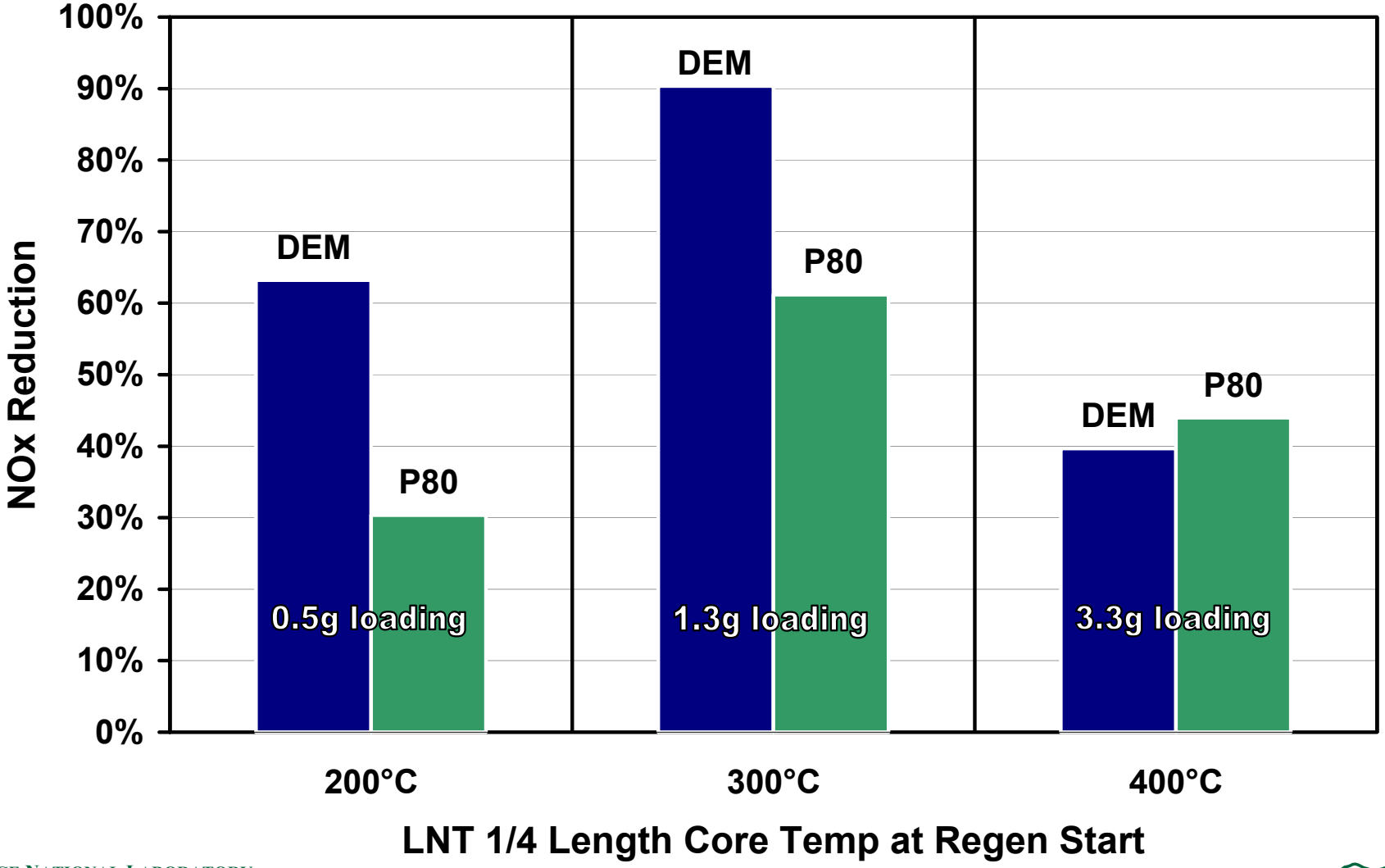
DEM is best strategy at 200 and 300°C, Post 80 slightly better at 400°C

Strategy engineered for constant NOx loading between regenerations



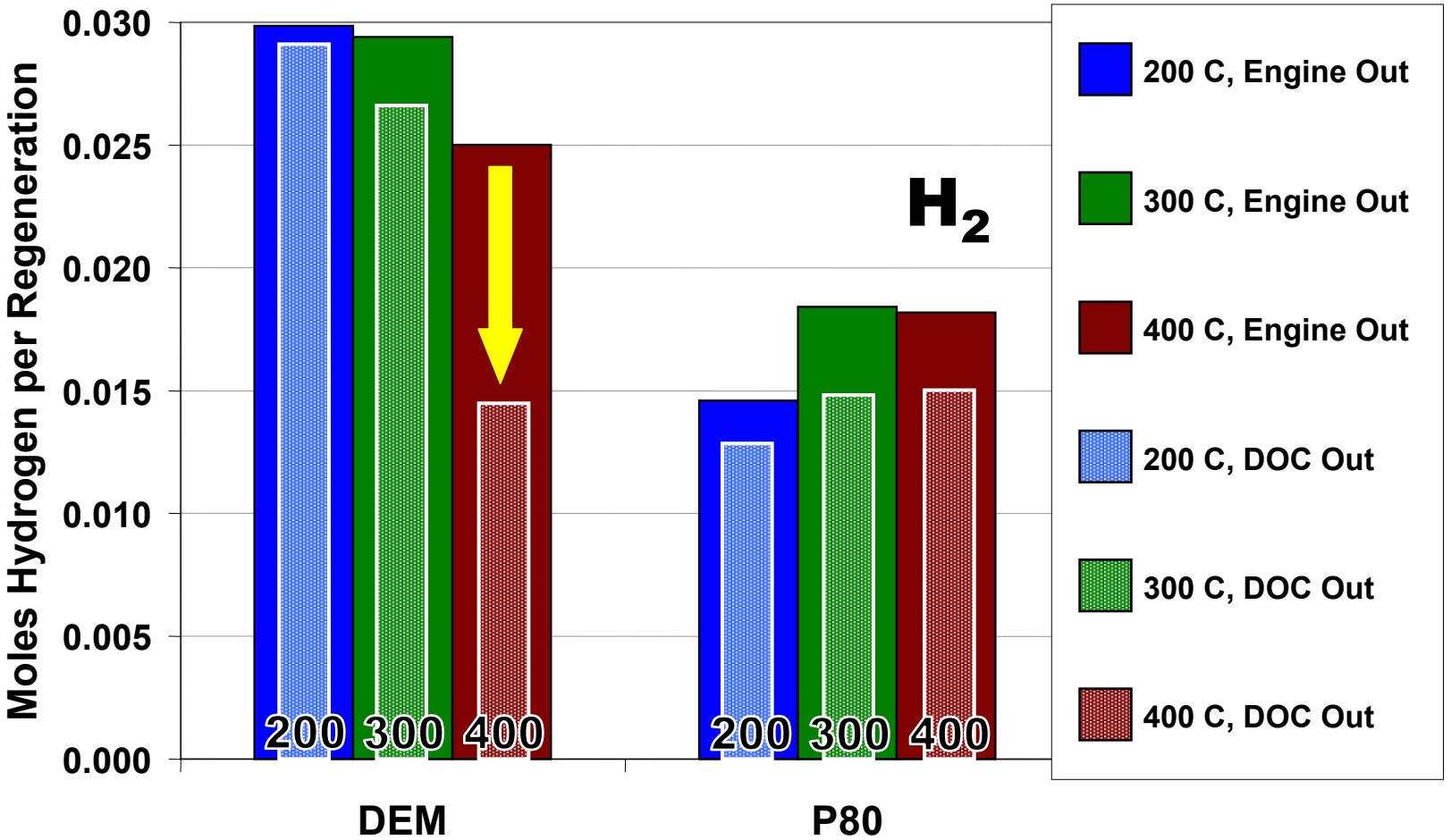
Post 80 still holds small performance margin at 400°C with various NOx loading.

- NOx loading reduced at 200°C via. retarded timing
- NOx loading increased at 400°C via. longer lean time



DOC has little effect on LNT inlet species except at 400°C

Dramatic drop in H_2 across DOC for 400°C DEM case



Engine → Engine-out → DOC → DOC-out → LNT

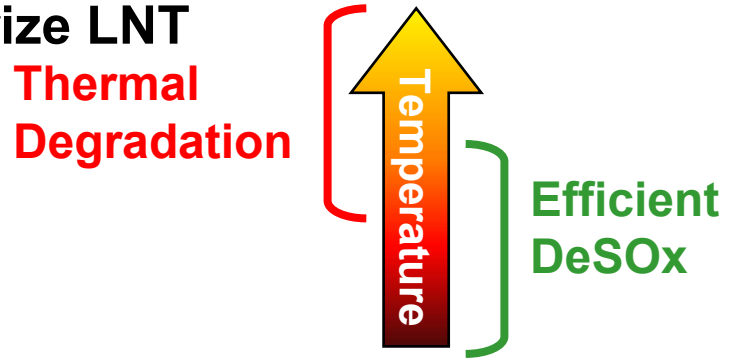
Interim Summary 3: Temperature Effects

- **DEM has better NOx Reduction Efficiency at 200°C and 300°C**
- **P80 has better NOx Reduction Efficiency at 400°C**
  - **Reasons unclear – intend to investigate further**
    - **possibly related to H2 depletion across DOC**

Topic #4

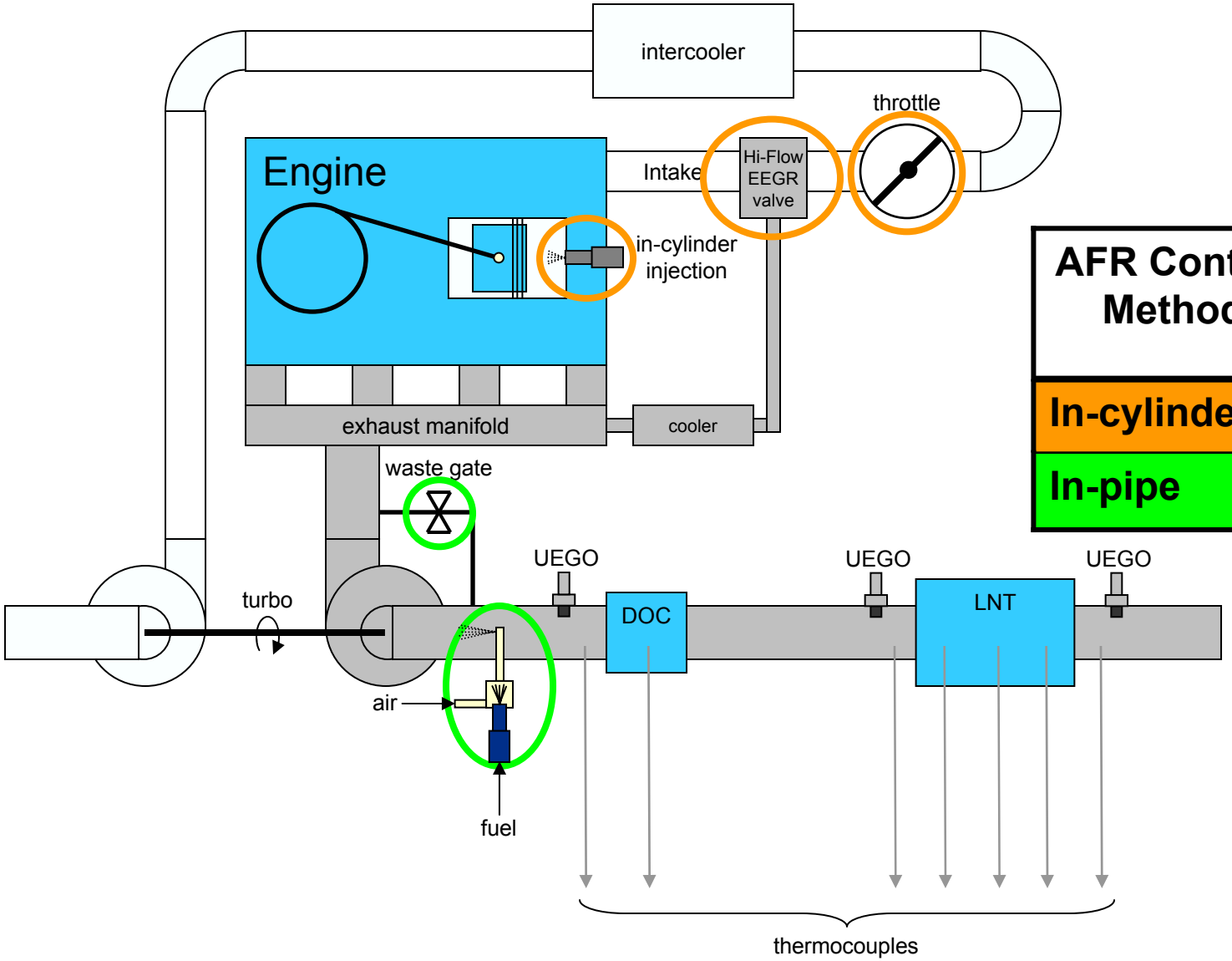
Rapid Sulfation and Desulfation

- LNTs store sulfates similar to nitrates
- Must periodically execute desulfation to remove S
- Challenge to consistently desulfurize LNT
  - Sulfur removal efficiency and thermal degradation both increase with increasing temperature



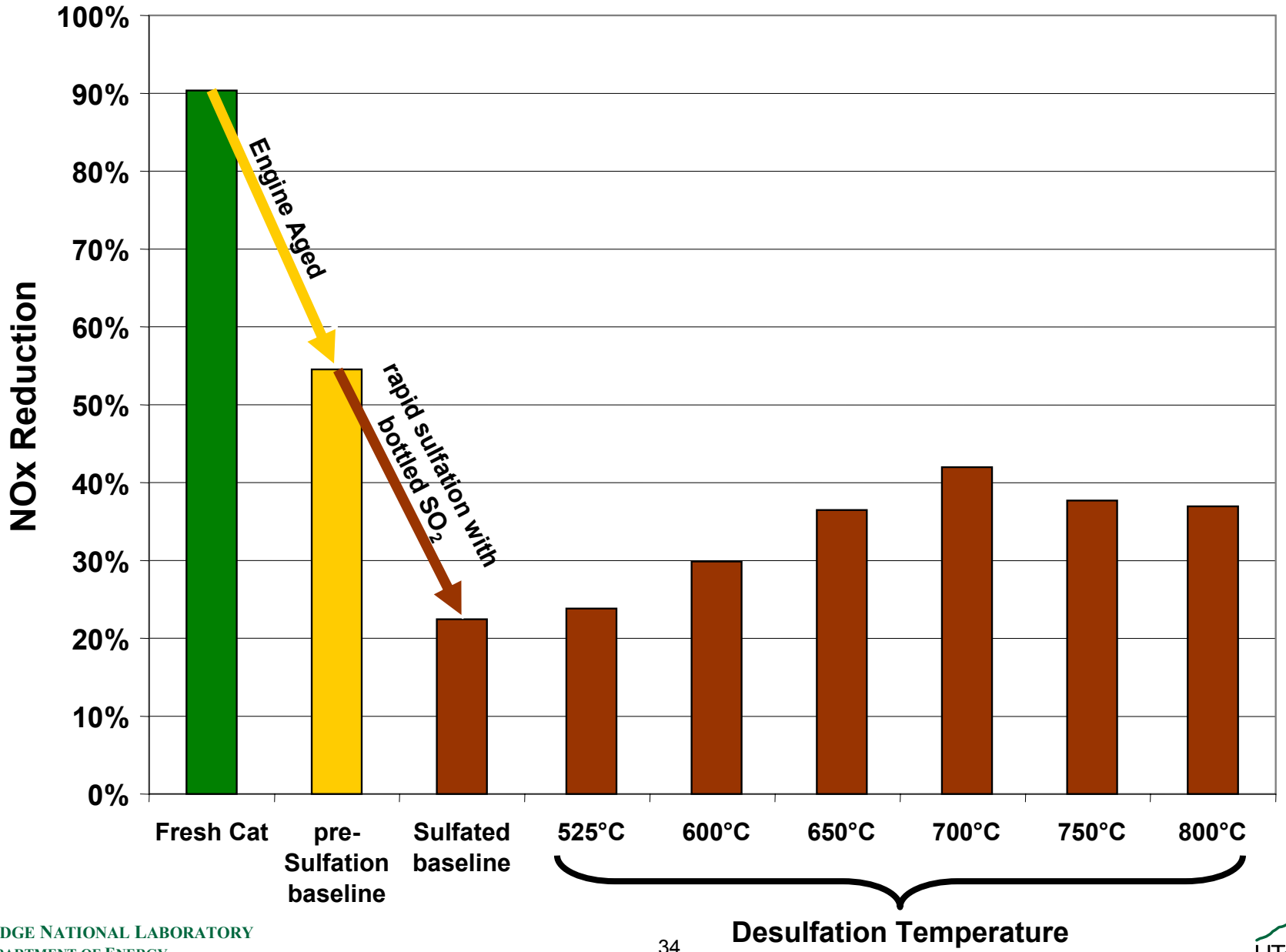
- Rapid sulfation allows repeated desulfations in controlled manner

For Improved Desulfation Control, In-pipe Fuel Injection Has Been Added



AFR Control Method	Torque COV (instability)
In-cylinder	15%
In-pipe	1%

Desulfation at Increasing Temperatures Elucidates Sulfur Removal vs. Thermal Degradation



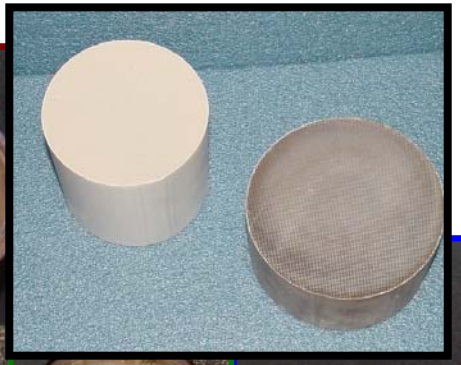
Interim Summary 4: Desulfation

- Investigated in-cylinder and in-pipe strategies for air-to-fuel and temperature control during deSulfation
  - In-pipe more stable and controllable than in-cylinder technique
- deSulfation with in-pipe strategy shows bulk of sulfur released between 600°C and 700°C
  - Control suitable for upcoming experiments

Future Plans

- Further investigate temperature dependence on strategy effectiveness (200, 300, and 400°C)
- Extend study to model catalysts, other MECA catalysts
- Investigate potential for improved NOx conversion of LTC regeneration, while targeting minimal fuel penalty
- Improve understanding of desulfation phenomena through engine-based rapid sulfation/desulfation experiments
- Continue to share results and coordinate research plans through CLEERS LNT focus group and other industry contacts

Model LNT Catalysts and Production LNT Catalysts Ready for Engine Cell



- All catalysts are 2.5 liter
- Two-piece assembly allows for midbed sampling without SpaciMS
  - Intra-channel sampling still possible
- Toyota D-CAT exhaust system (DPNR) on order
- Additional MECA catalysts requested…

Characterizing LNT Regeneration and Desulfation (Closing Summary)

- **Relevance**

  Improved understanding of LNT catalysts is critical to enabling greater use of high efficiency lean-burn engines

- **Approach**

  Engine-based experiments with advanced diagnostic tools, model and MECA-supplied catalysts

- **Accomplishments** – Important findings in

  1) Nitrogen selectivity
  2) LTC regeneration
  3) Temperature effects
  4) Rapid Sulfation/Desulfation

- **Collaboration**

  Working closely with industry, other labs, and CLEERS LNT focus group.

- **Future Research**

  Continue to elucidate LNT functions to enable mitigation of aging and fuel penalty issues

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