Characterizing NOx Adsorber Regeneration

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Fuels, Engines, Emissions Research Center

2004 Advanced Combustion Engines Merit Review
May 18-20, 2004

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

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 testing
  - Todd Toops
  - Jae-Soon Choi
  - Katey Lenox
- Modeling (CLEERS interaction)
  - Stuart Daw
  - Katey Lenox
  - 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
- Develop stronger link between bench and full-scale system evaluations
  – Provide data through CLEERS to improve models. Use models to guide engine research

Reviewer Comments- 2003

Relevance

- …understanding what happens during regeneration of NOx adsorber is very important….work done is directly relevant to this DOE program

Approach

- …experimental facility developed for this program is excellent
- …great combination between engine L/R modulation, calibration, and exhaust species analysis
- …answer question of oil dilution through late post injection would be valuable…
- …add smoke measurements

Technical Accomplishments

- …generated valuable information to improve understanding of regeneration process
- …opacity trace is missing, but accomplishments are good…
- …work is done on crucial points and is excellent
- …analysis with GC/MS and H2-SpaciMS is very revealing to understanding chemistry
- …need to move to testing of actual hardware and reporting results

Tech Transfer

- …Users for this work include the OEMS and CLEERS
- …collaboration should be widened….get more inputs from industry
- …very good collaboration with industry

2003 Reviewer Comments (cont)

Future work

- …benefit from modeling effort to complement experiments,…through CLEERS
- …[anxious] to see desulfation experiment results

Strengths

- …Complete program, well thought out
- Excellent work! …results on catalyst behavior would have improved the presentation…
- Exhaust speciation provided extremely important information for catalyst design
- Good to understand HC speciation at various conditions, but are some impractical for engine durability?...washing cylinder walls?

Weaknesses

- …Discussion on A/F ratio measurement with sensors points out a potential problem

Recommendations

- Link to modeling effort

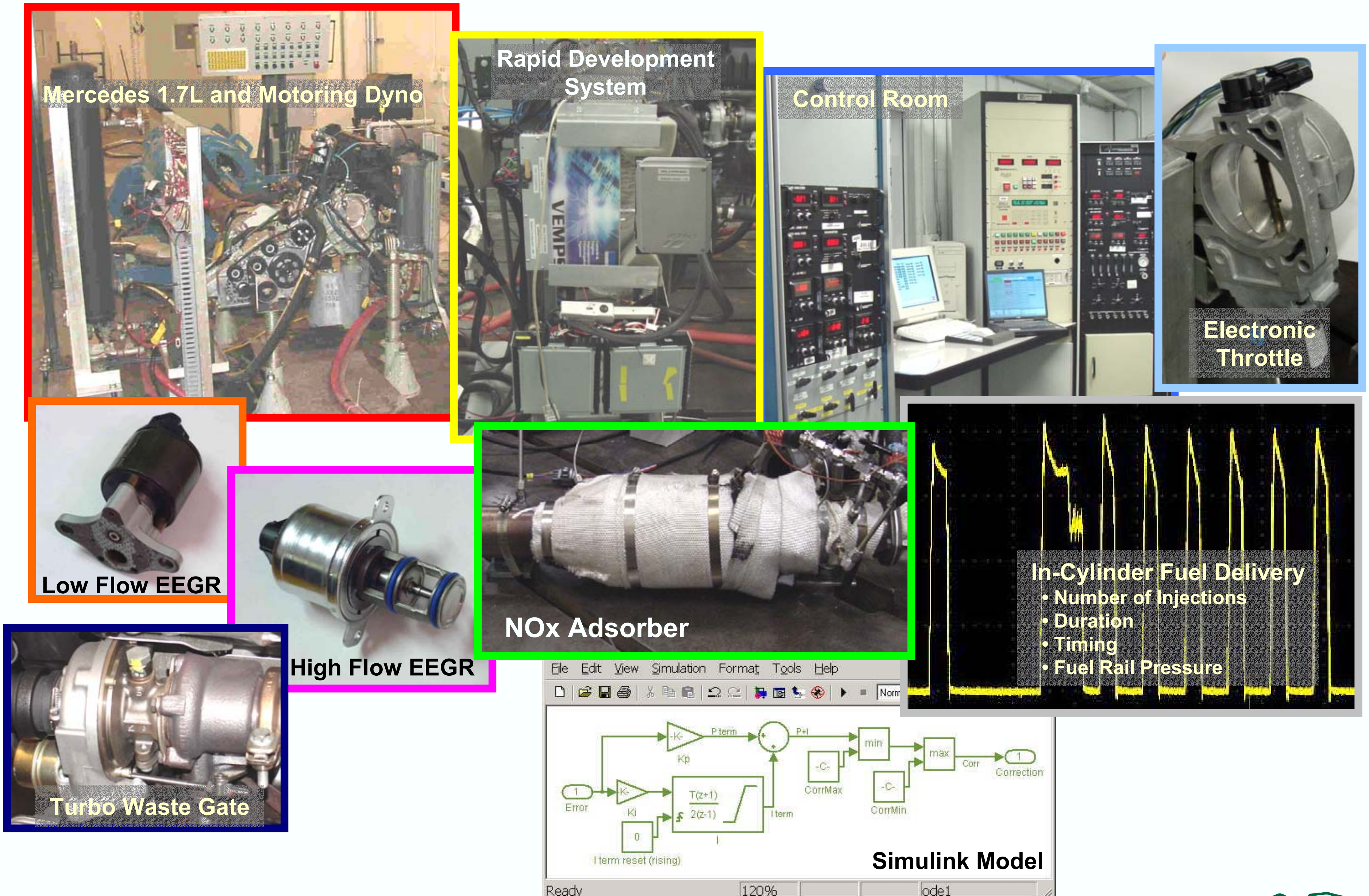
2004 Objectives and Accomplishments

- **Received full-size MECA catalysts (DOC and NOx Ads) in August 2003**
  - **NOx Adsorber cores for bench flow – 10/03 (same formulation)**
- **Defined and procured 2 “model catalysts”** (via CLEERS & Emerachem)
  - **Engine and bench samples**
- **(unplanned) Diagnosed engine problem, replaced engine** (see appendix)
- **Investigate Effects of**
  - **fuel chemistry and regeneration strategy on exhaust species**
  - **exhaust species on adsorber performance**
  - **regeneration strategy on PM**
- **Examined 3 fuels, 2 strategies with full speciation, SpaciMS**
  - **Further examine other temperatures**
  - **Examine Regeneration in the midst of LTC operation**
- **Developed desulfation strategy, desulfurized NOx adsorber**
- **Coordinating experimental plans with CLEERS and bench reactor teams**

Collaboration and Interactions

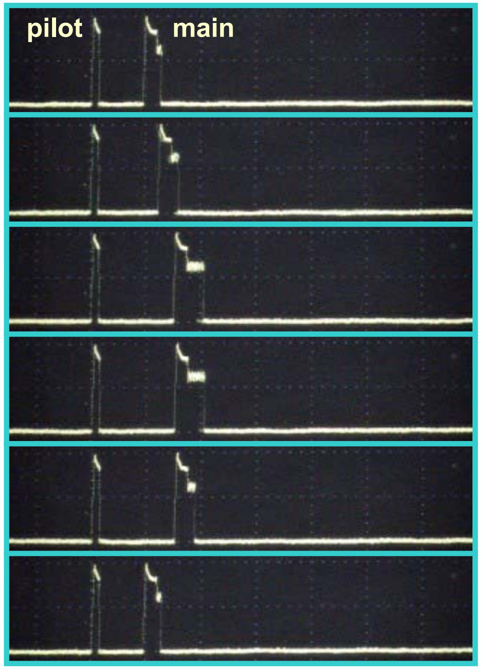
- Presented progress at DEER 2003, Cross-cut, National Lab-Catalysis (NL-Cat), and CLEERS meetings
- Met with LEP (Ford, GM, DCC)
  - DOE approved CRADA w/Ford
    - Working closely with LEP members (MOU pending) and through CLEERS in lieu of CRADA
- Discussions with MECA partner
- P. Witze visit, loan LII for measurements at ORNL
- Abstract submitted for SAE fall F&L

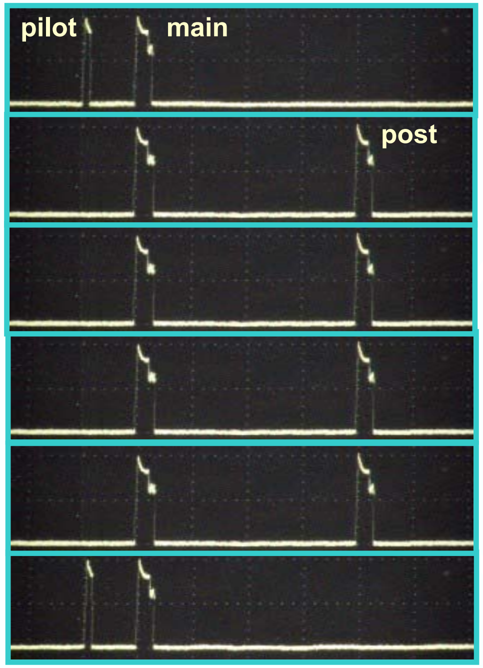
Common Rail Engine and Motoring Dynamometer dedicated to this activity



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

- Both 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:

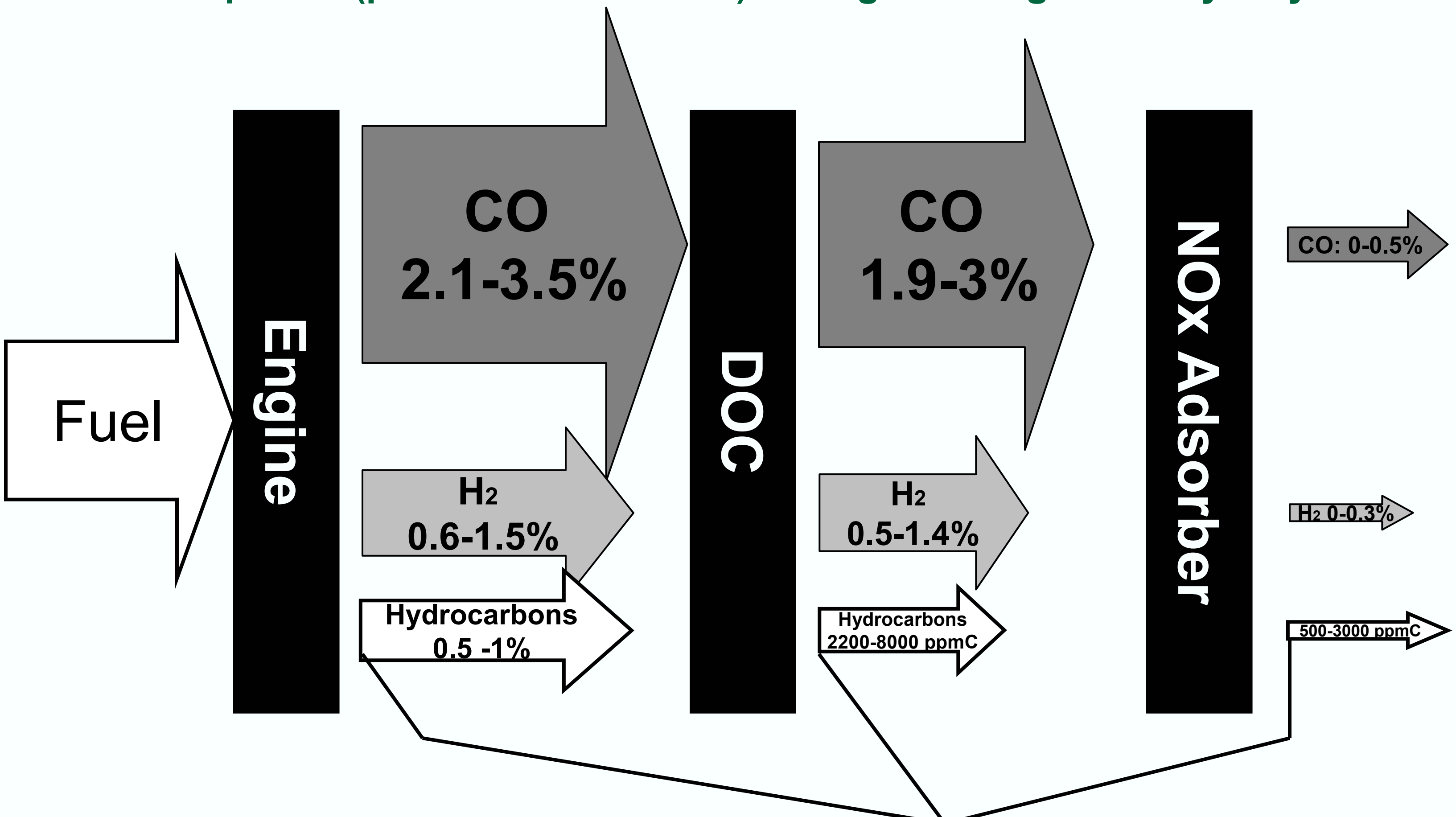




- 3rd strategy investigated uses high EGR to enter lean LTC mode prior to rich excursion
  - "LTC Regen" will be examined with both DEM and Post injection strategies to assess any differences in exhaust species

Approach Summary: vary strategy or fuel to change reductant chemistry

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

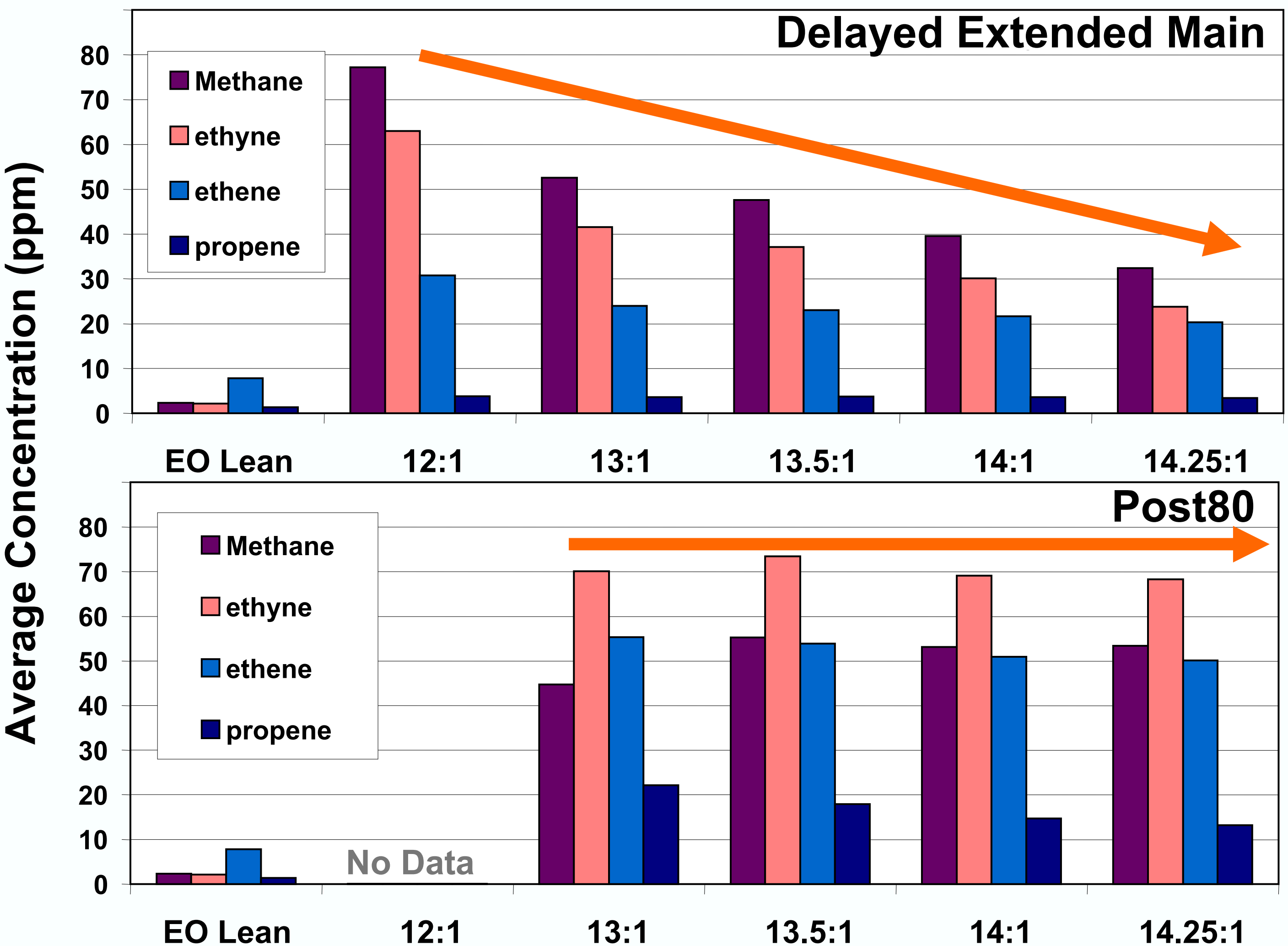


methane	ethane	ethyne	propene
butene	formaldehyde	acetaldehyde	benzaldehyde
toluene	benzene	napthalene	
tridecane	indene	styrene	
benzofuran	phenol	methyl napthalene	
acenathalene	diphenylethene		…many others

Other species measured:
Nitro-organics
Ammonia
N2O

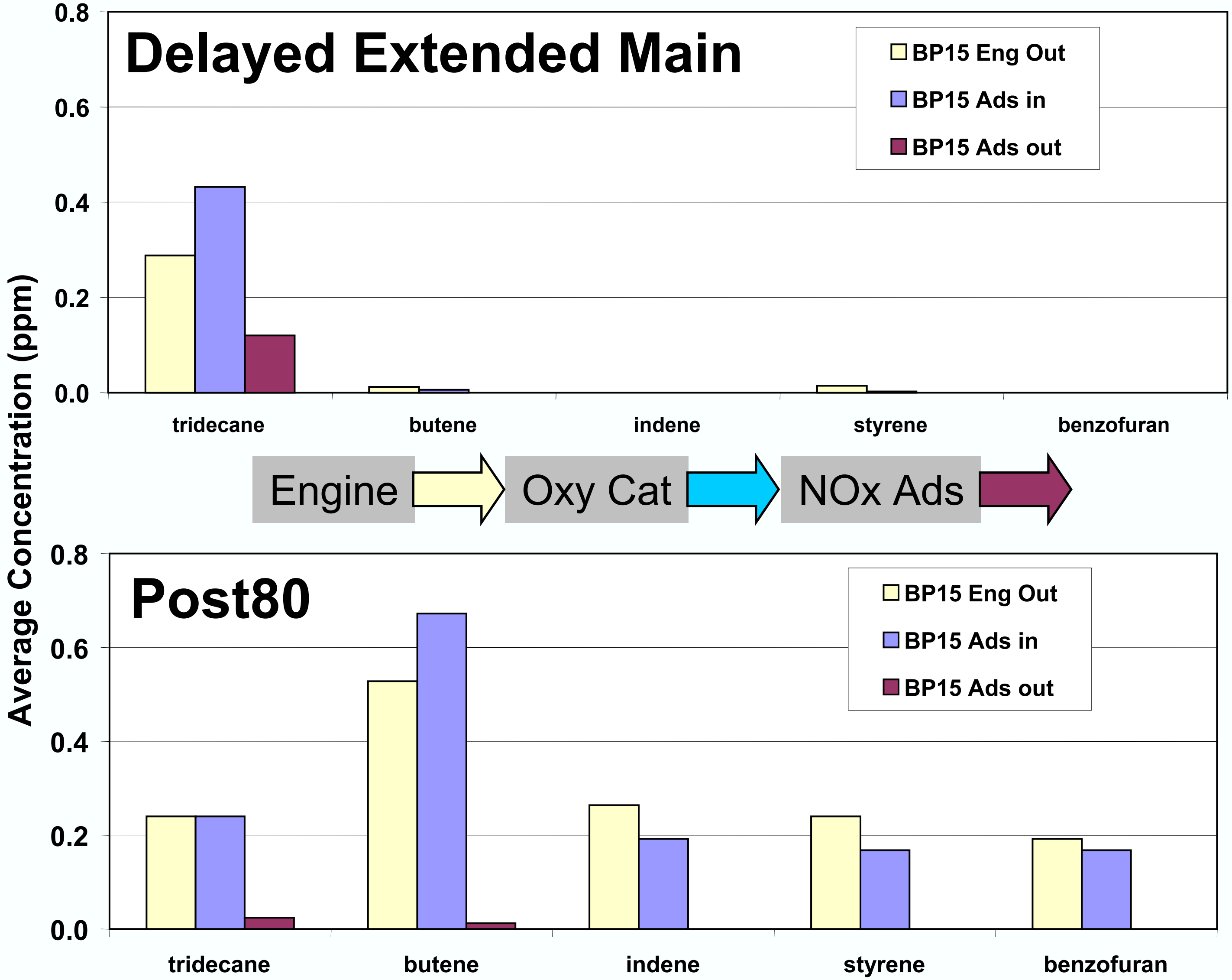
How does Regeneration strategy affect exhaust species?

Light HC species decrease with increasing air:fuel for DEM strategy, remain relatively flat for 80° post injection (Engine-out data, BP15 fuel)



- Engine Out Lean baseline shows moderate levels for normal combustion
- Air:Fuel ratio (x-axis) is target minimum A:F during rich regeneration
- Average species concentrations from FTIR (3s rich/ 60s cycle; Peaks approx 19x higher)
- None of compounds shown are present in raw fuel, all are indicators of in-cylinder fuel cracking
  - Alkenes and alkynes are reactive compounds, potential reductant species

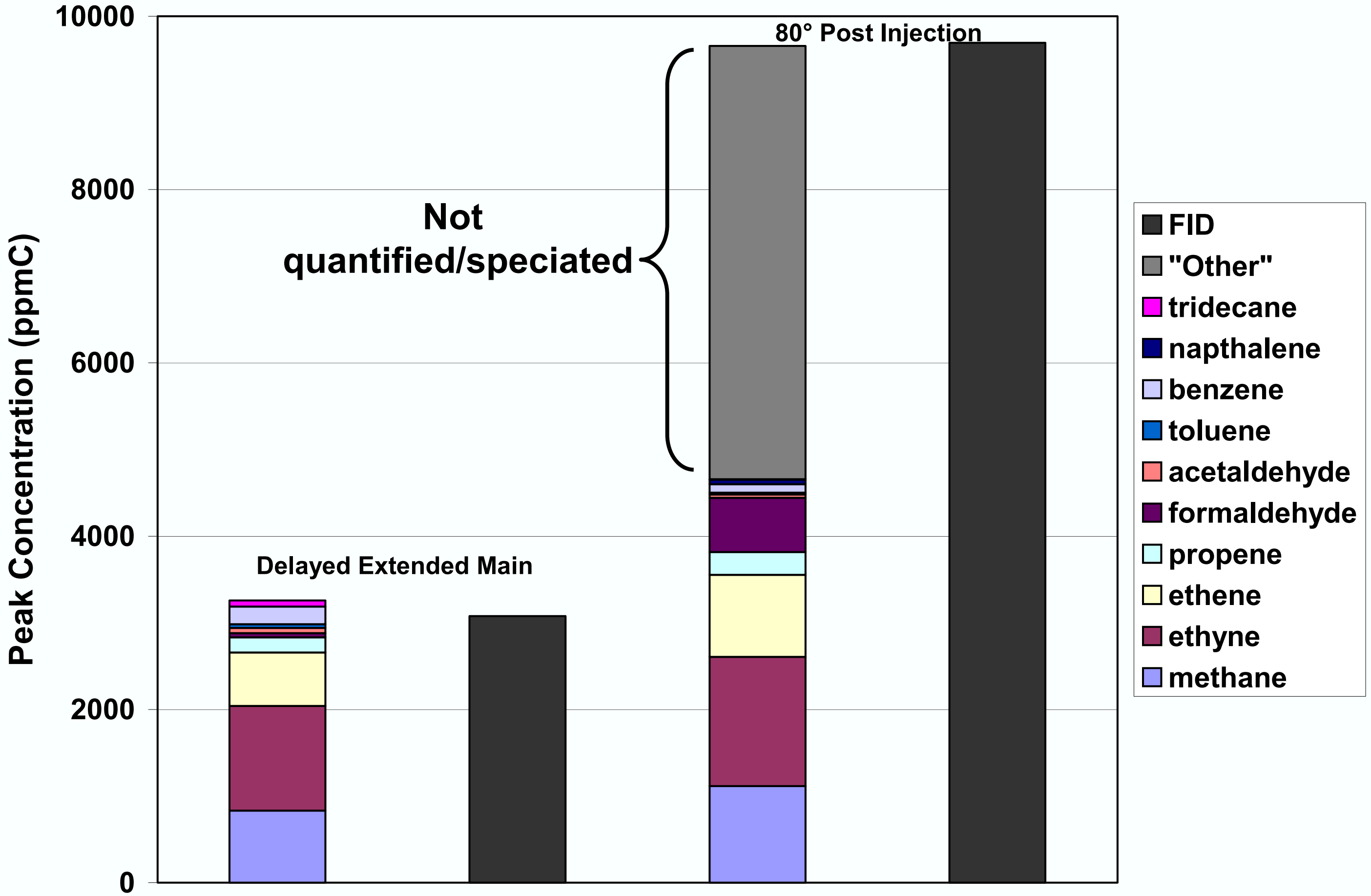
Post80 strategy yields much broader range of HC species than DEM



- Species measured with GC/MS
- Only tridecane is abundant in raw fuel, all other species are cracking products
- Most HCs consumed across NOx adsorber

Post 80 Strategy yields more total hydrocarbons and broader range of species than DEM

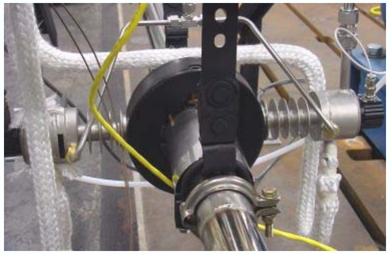
- Sum of 10 species accounts for bulk of the FID THC for DEM
- Same 10 species only account for half of FID THC for Post 80



How does Regeneration strategy affect Particulate Mass?

Several methods used to assess PM emissions during regeneration

- **TEOM (mass)**
  - similar to filter but gives more real-time information



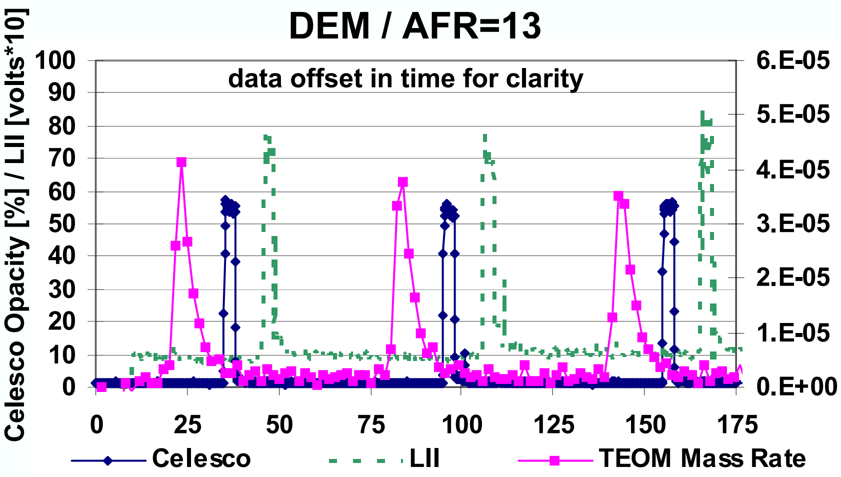
- **Celesco (opacity)**
  - measures raw exhaust

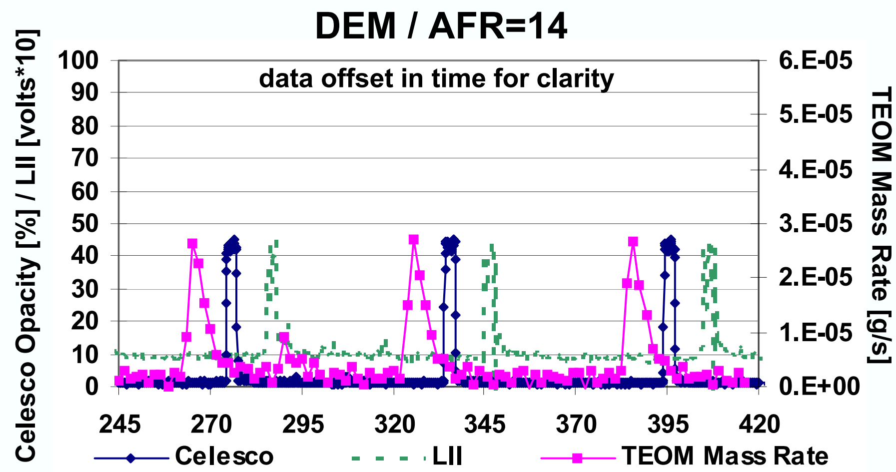
- **LII (Laser Induced Incandescence)**
  - Real-time soot measurement
  - collaboration with P. Witze, SNL

- **AVL smoke meter (BOSCH smoke number)**
  - fixed flow rate prevents reliable numbers during regeneration

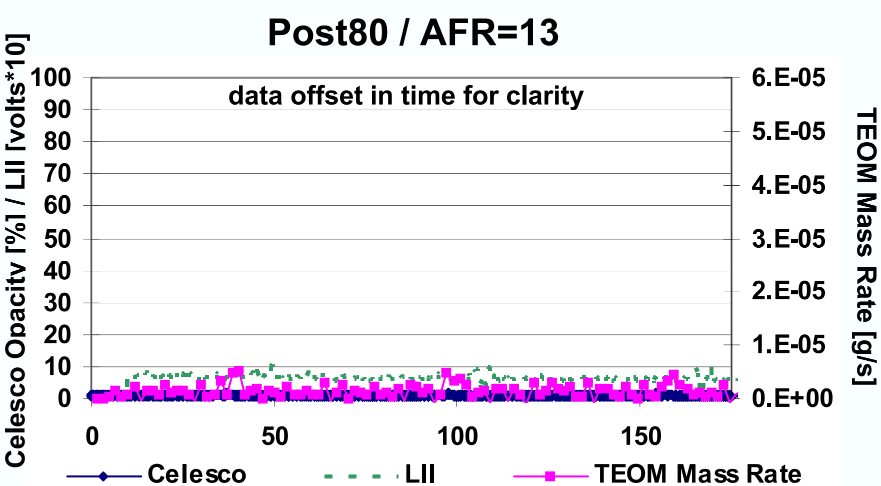
PM mass rate affected by strategy

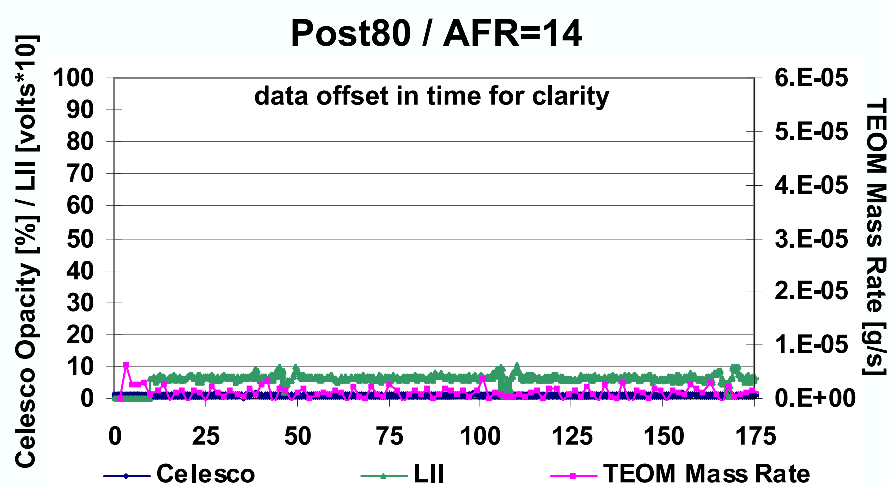
- PM increases sharply during the DEM regeneration.





- Post 80 regeneration has little effect on PM

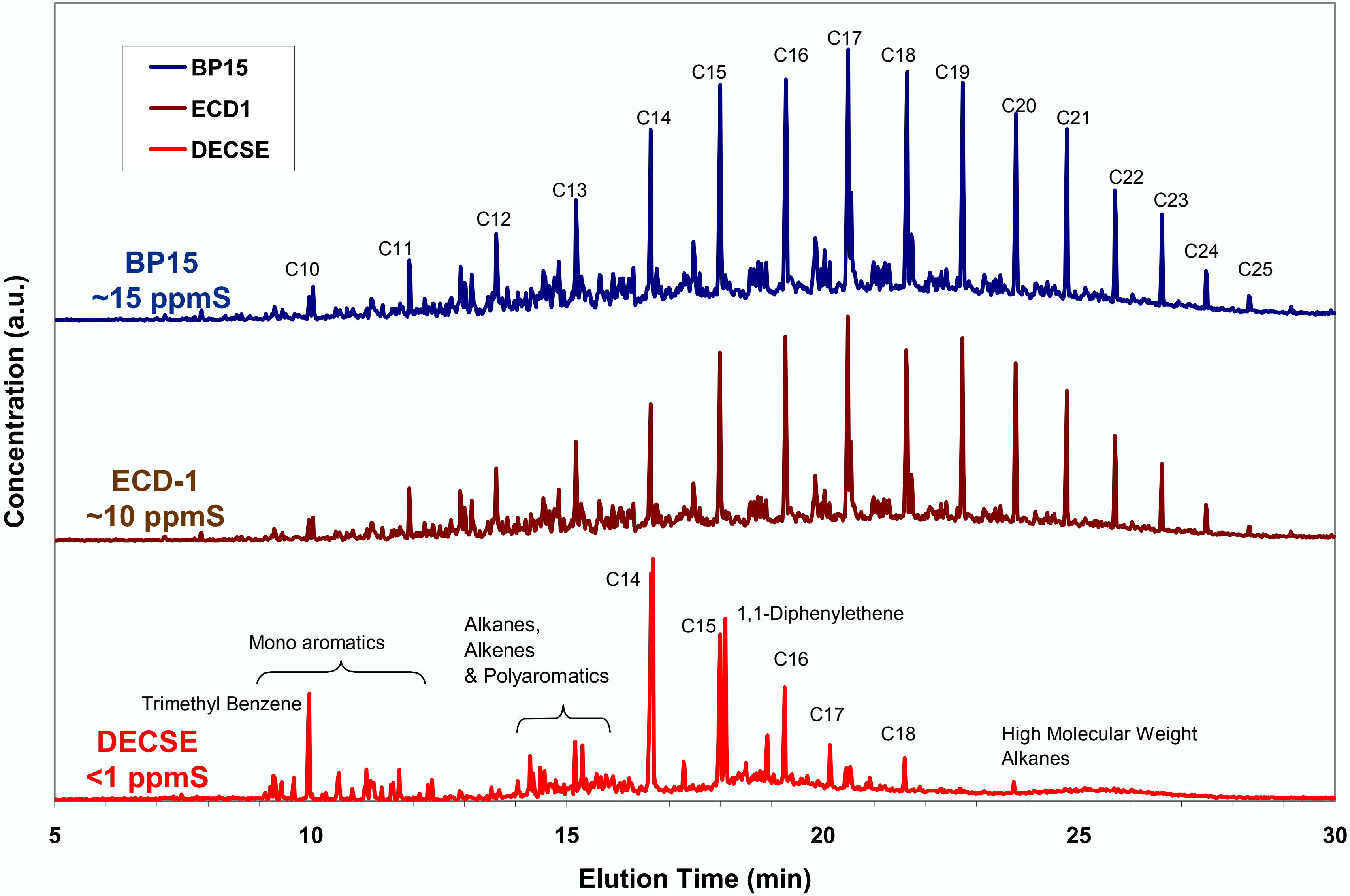




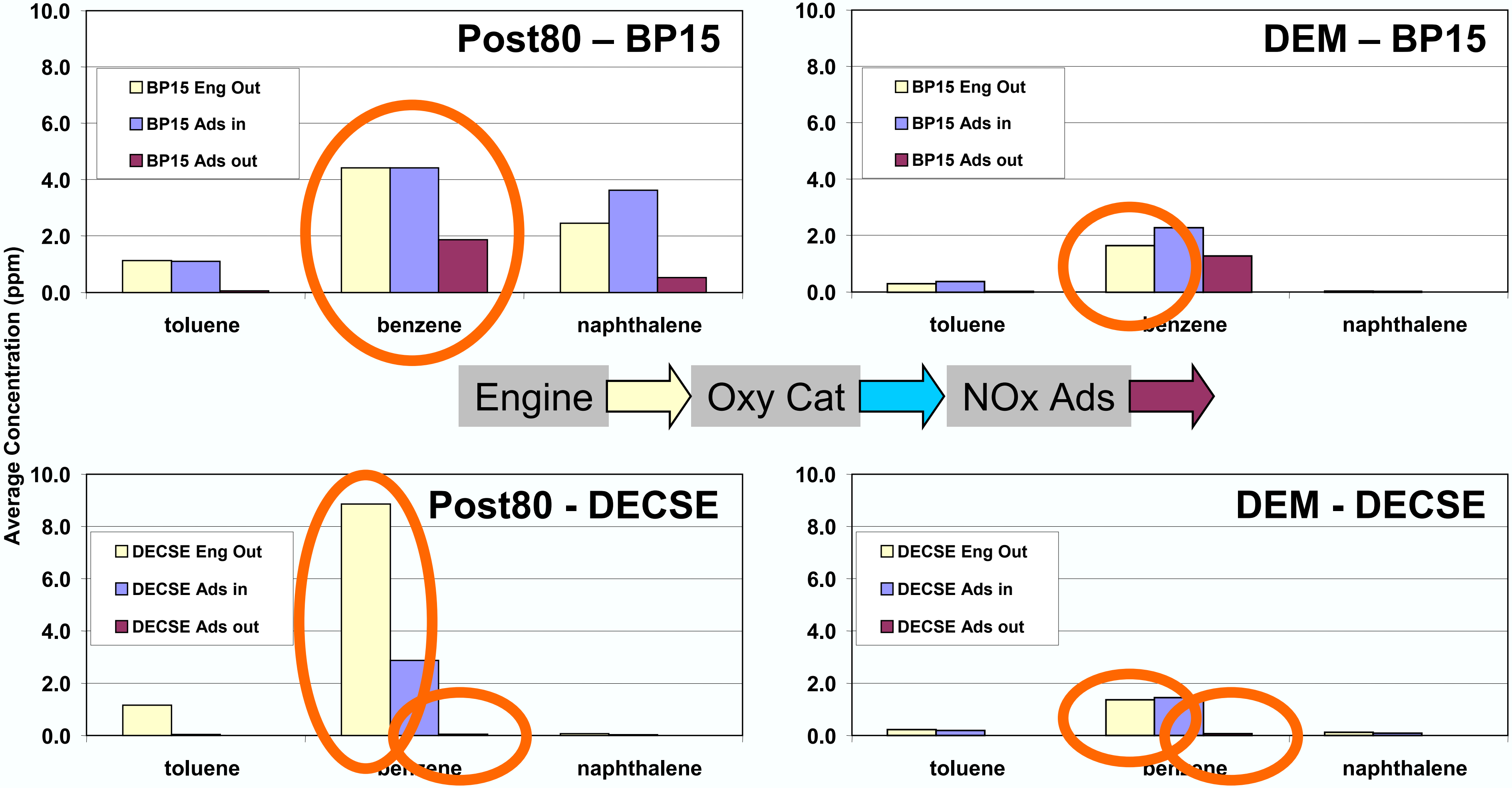
How does Fuel Chemistry affect exhaust species?

While DECSE fuel meets 2007 specs, it does not contain breadth of HC species in ECD1 and BP15.

BP15 and ECD1 are virtually identical except for sulfur, aromatics, and CN

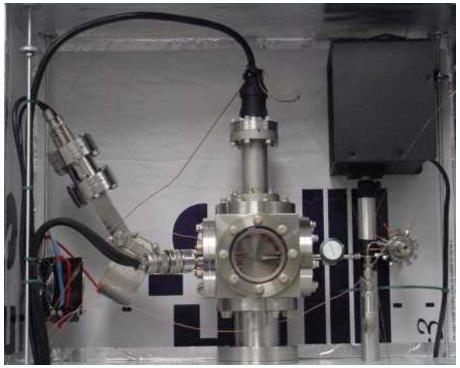


Benzene consumed in DECSE case due to less competition

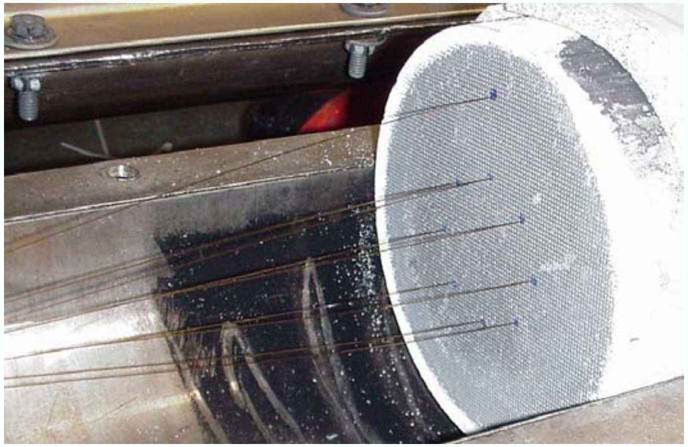


SpaciMS measurements enable tracking NOx, H_2, and other species through the catalyst system

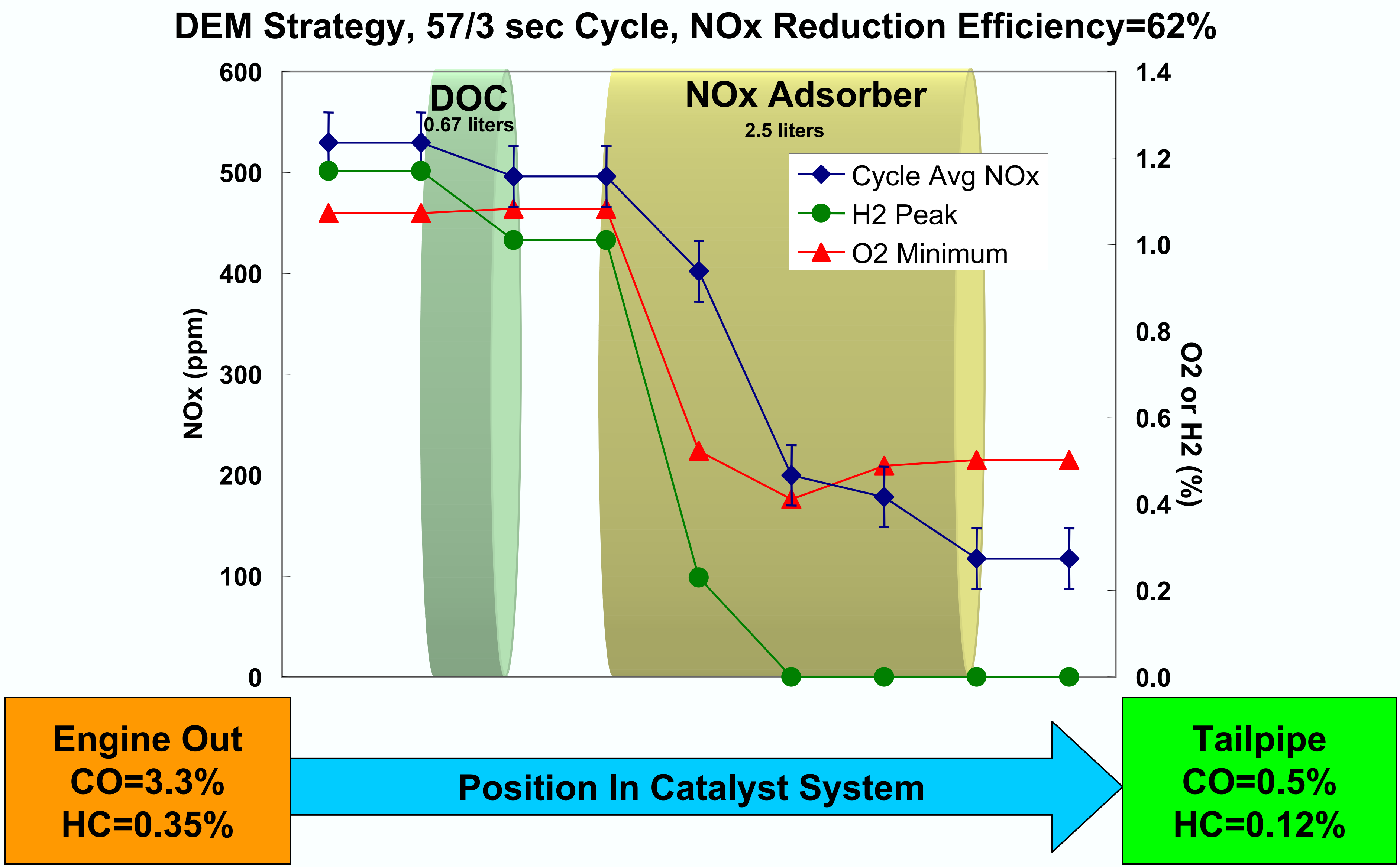
- Based on magnetic sector mass-spectrometer
- Capable of quantifying
  - H_2
  - H_2S
  - NOx
  - HC fragments
  - CO_2
  - SO_2
  - O_2



- Six capillaries were used for experiments
  - Engine-out
  - Adsorber in (DOC out)
  - Adsorber ¼, ½, ¾
  - Adsorber out
- Minimally invasive
  - Sample rate ~10 μL/min
  - Probe diameter 200 μm

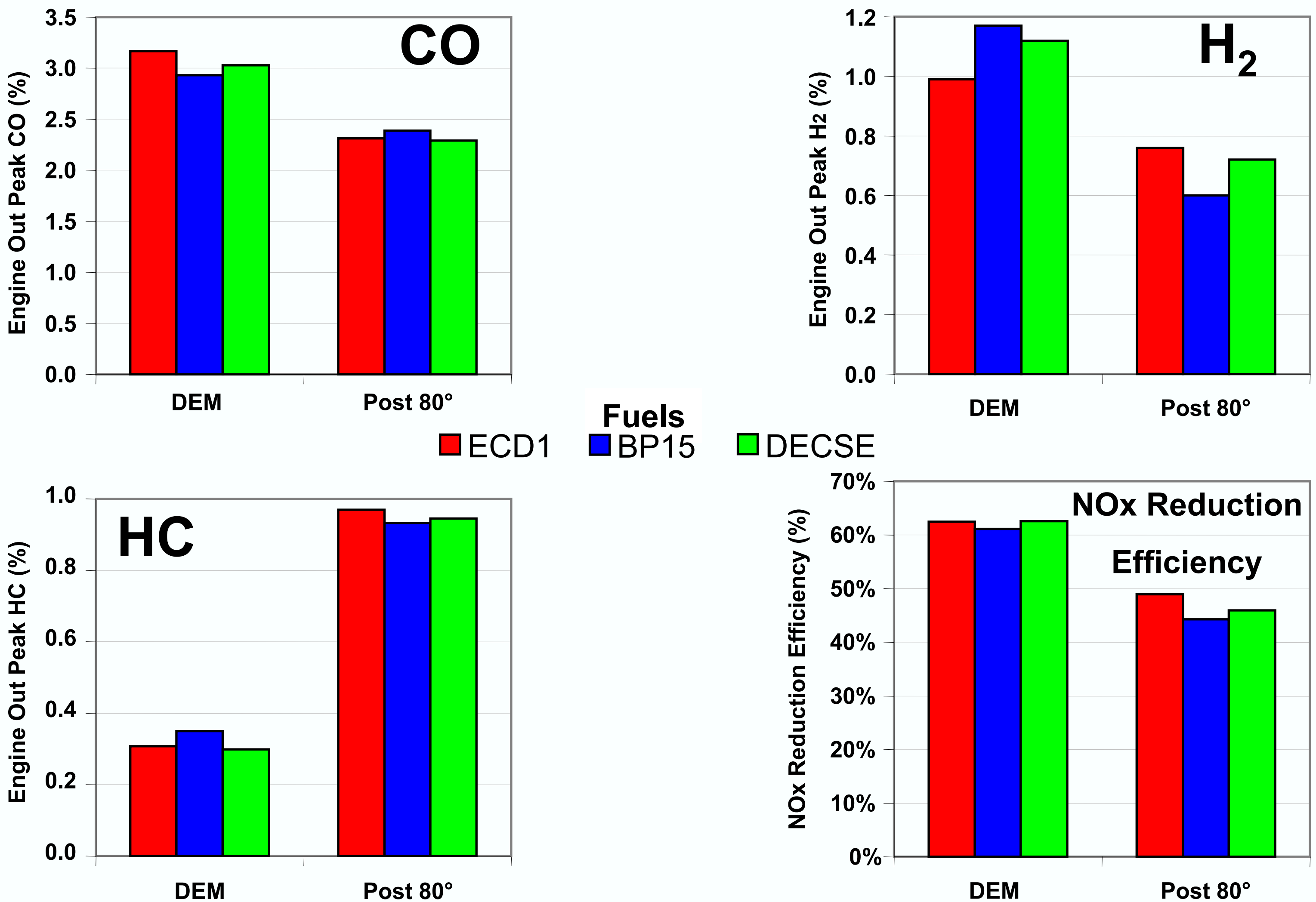


Regeneration of NOx sites less effective when intra-catalyst hydrogen is depleted



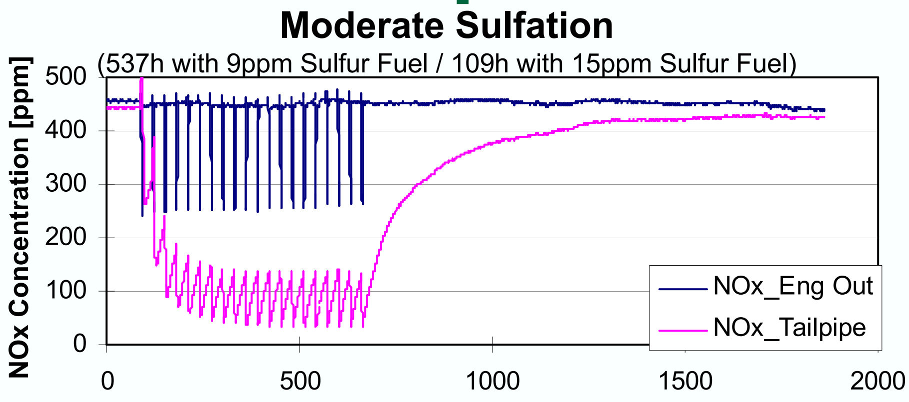
H_2 and CO have strongest effect on catalyst efficiency

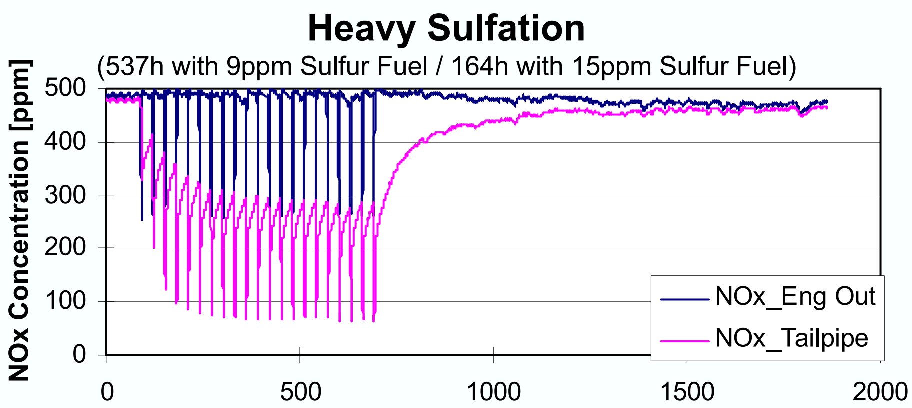
- DEM strategy makes more CO/H_2, and has lower total HC.
- DEM yields better NOx reduction.
- Engine Out HC species effects on NOx performance appear secondary
- Fuel chemistry has little effect on peak CO, H_2, or HC concentration

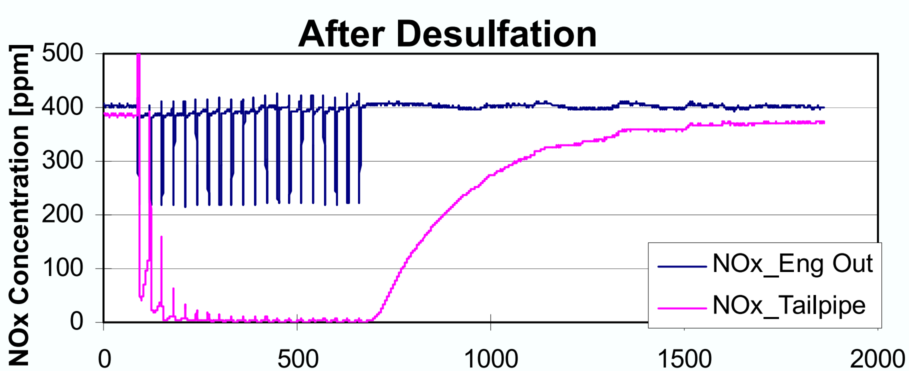


Desulfation

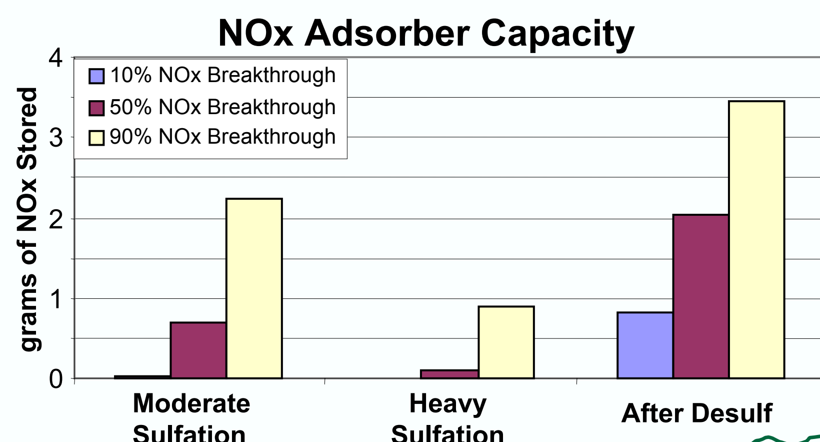
The level of catalyst sulfation determined using saturation experiment





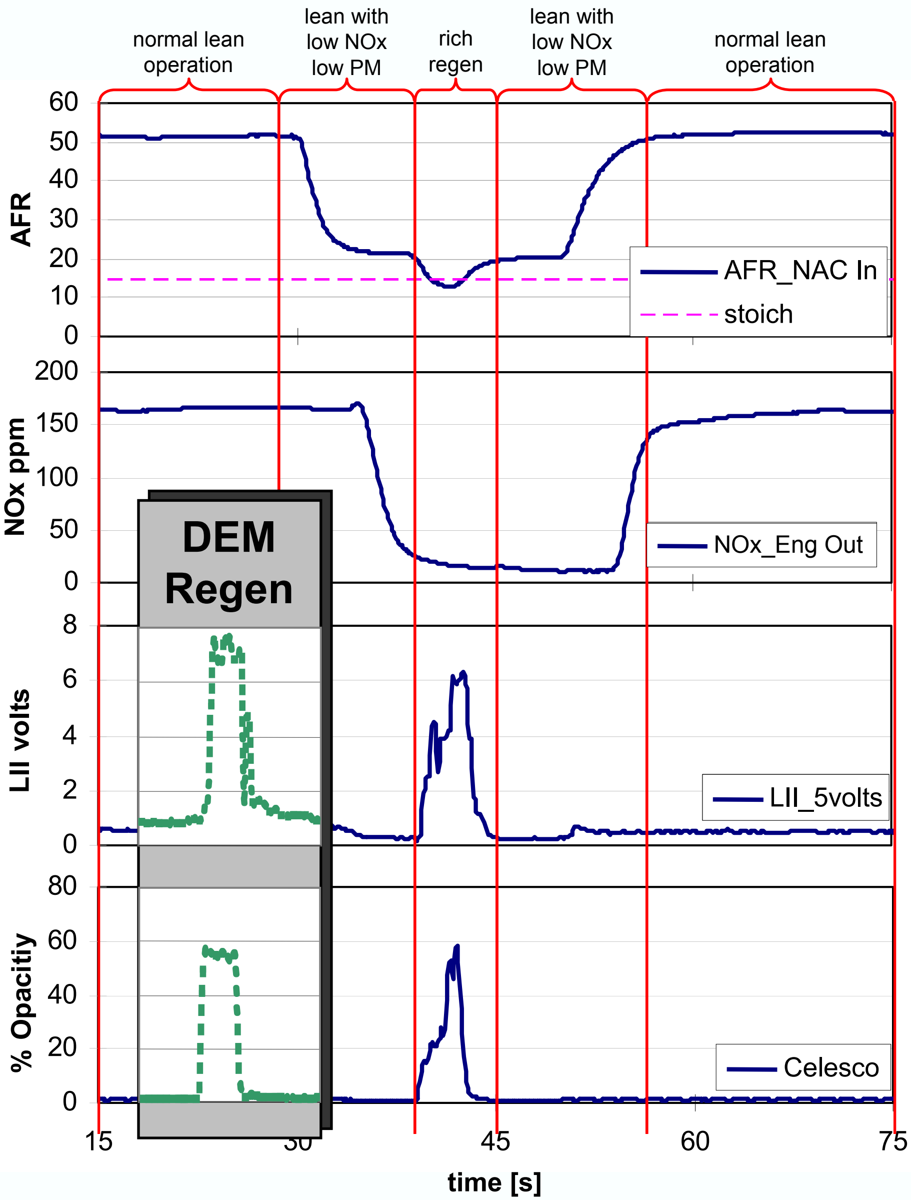


- Perform a repeatable experimental cycle
  - allow the catalyst to saturate
  - perform 20 regenerations
    - AFR~13
    - NO EGR (Engine Out NOx 400-500ppm)
    - 30 second regeneration loop time
  - disable regeneration and allow catalyst to saturate with NOx by running lean for 20 minutes
- Compare NOx conversion efficiency from regenerations
- Compare NOx storage capacity from lean saturation



Regeneration in the midst of low-NOx, low-PM operation

Rich excursion during "LTC" produces high levels of PM like DEM strategy



- Preliminary development
  - operate at light load cruise condition
  - transition into low NOx/low PM operation
    - open EGR to 50%-55%
    - disable pilot
    - advance main timing
  - force rich by increasing the main fuel pulse width
- Noteworthy observations
  - engine out NOx remains low during rich operation
  - comparable soot levels to DEM regeneration strategy
  - not able to evaluate NOx reduction efficiency due to sulfur poisoned catalyst state
- Future Plans
  - compare soot/PM for various enrichment methods
  - evaluate soot/efficiency trade off
  - perform detailed characterization

Summary and Conclusions

- H_2 and CO appear to be the key reductants for conditions investigated
- Fuel chemistry has little effect on hydrogen/CO production (for fuels and strategies studied)
  - Larger effect on some HC species
  - Importance of these species as yet undetermined
- Regeneration strategy affects HC species, CO/H_2 production, PM emissions
  - DEM makes more PM, more CO and H_2
  - At ~300C, with sulfated catalyst
    - DEM better than Post80
    - CO and H_2 are key reductants, HC influence appears secondary
- DEM regeneration in the midst of LTC is "low NOx" but is not "low PM, low NOx"
  - Will investigate this further
- This information is critical to improving system efficiency and reducing cost

Future Plans

- Complete experiments at other NOx adsorber temperatures (~200C and 400C)
- Further investigate regeneration during “LTC”
- Rapid sulfation/desulfation with speciation and SpaciMS
- Examine model catalysts and other MECA catalysts
- Share results and coordinate research plans through CLEERS LNT focus group

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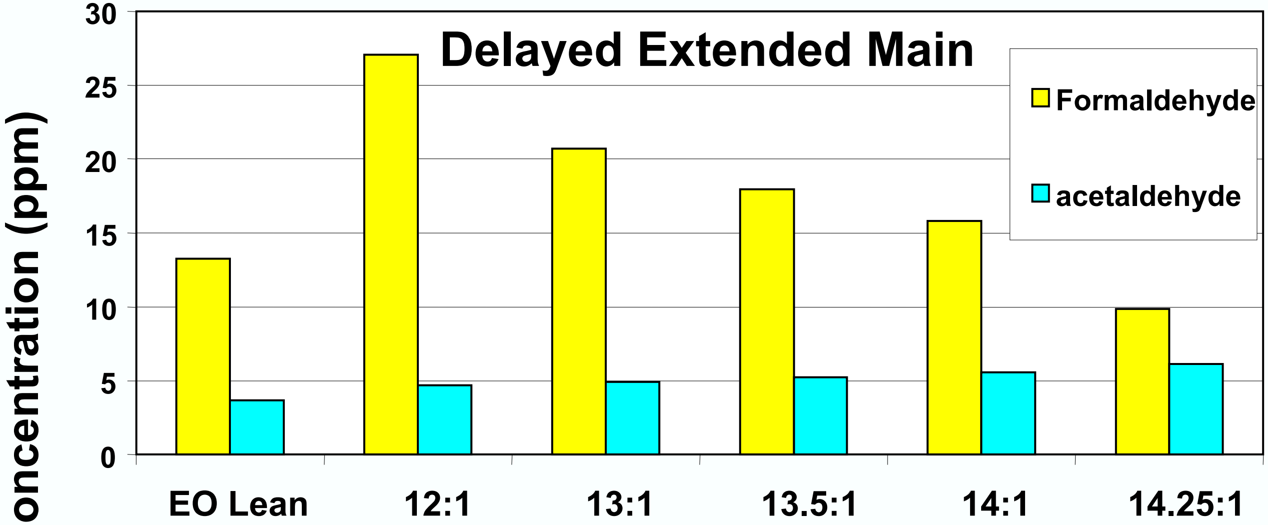
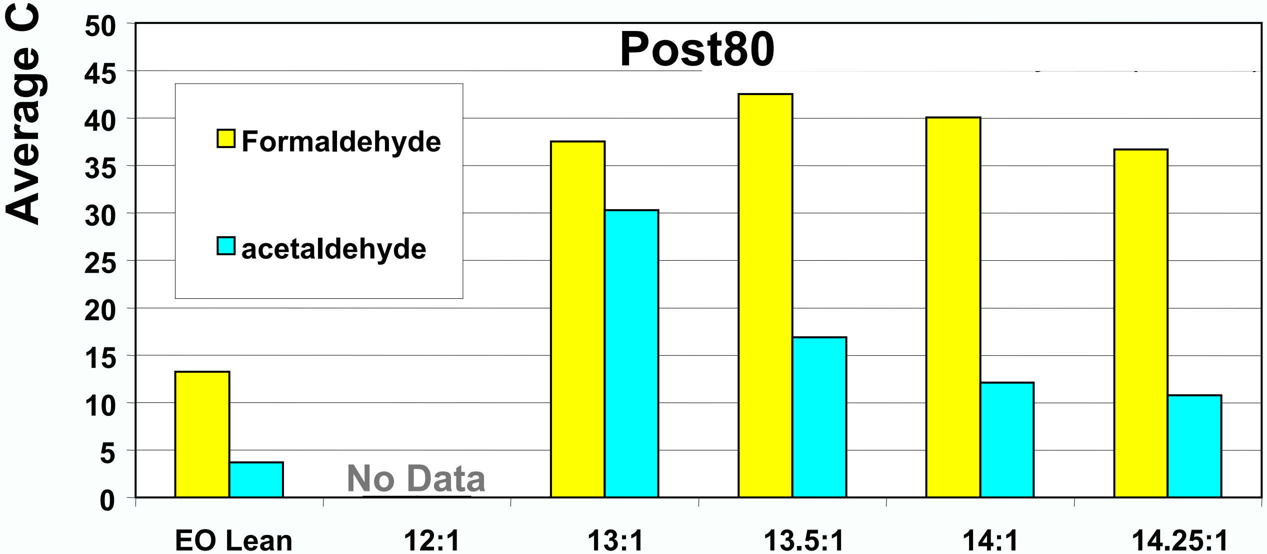
Appendix

- Additional HC species information
- Desulfation
- Air:Fuel ratio sweep
- Engine replacement
- UEGO biasing

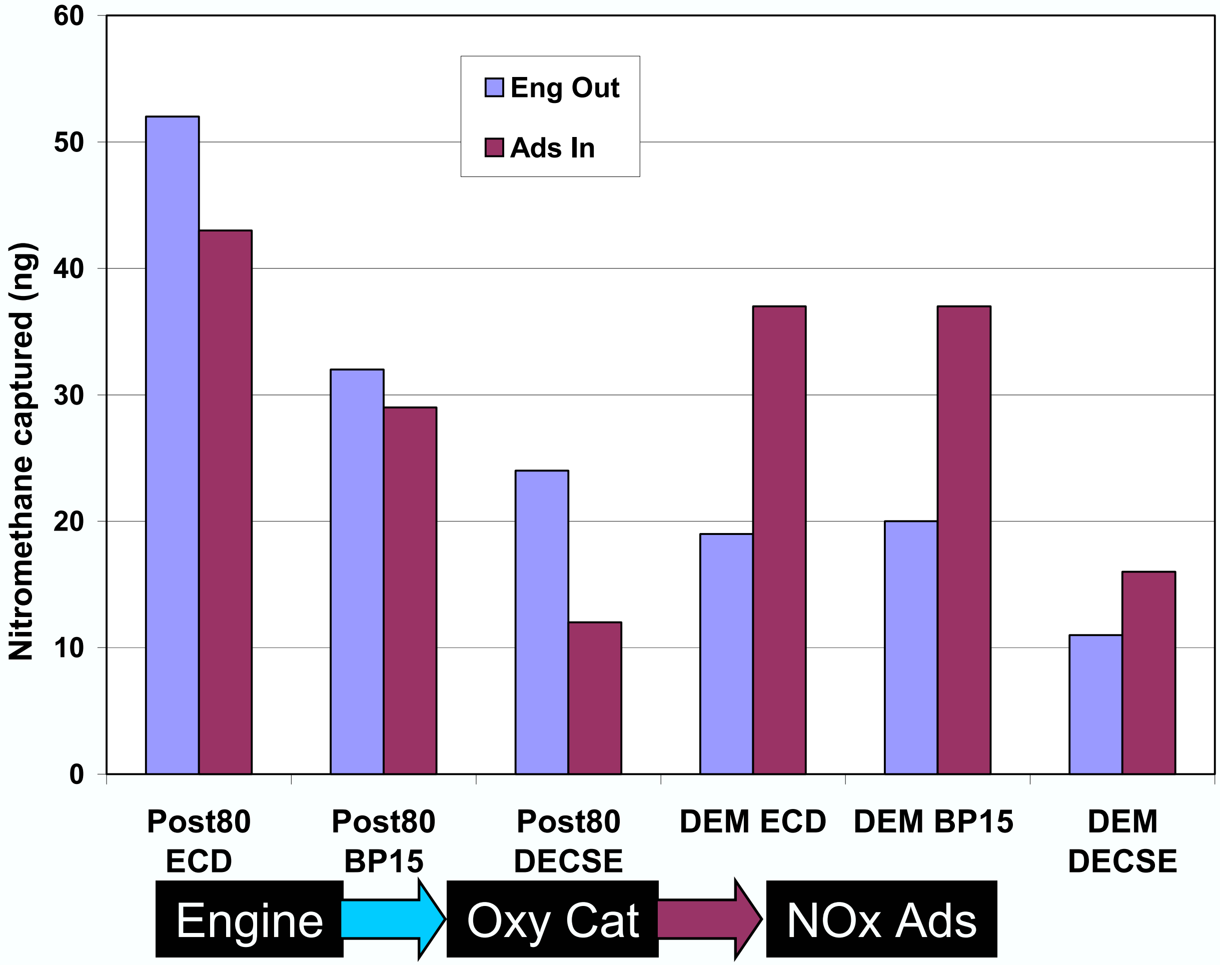
Formaldehyde decreases with increasing A:F for DEM strategy, while acetaldehyde is flat. Opposite is true for 80° post injection. (Engine-Out data, BP15 fuel)





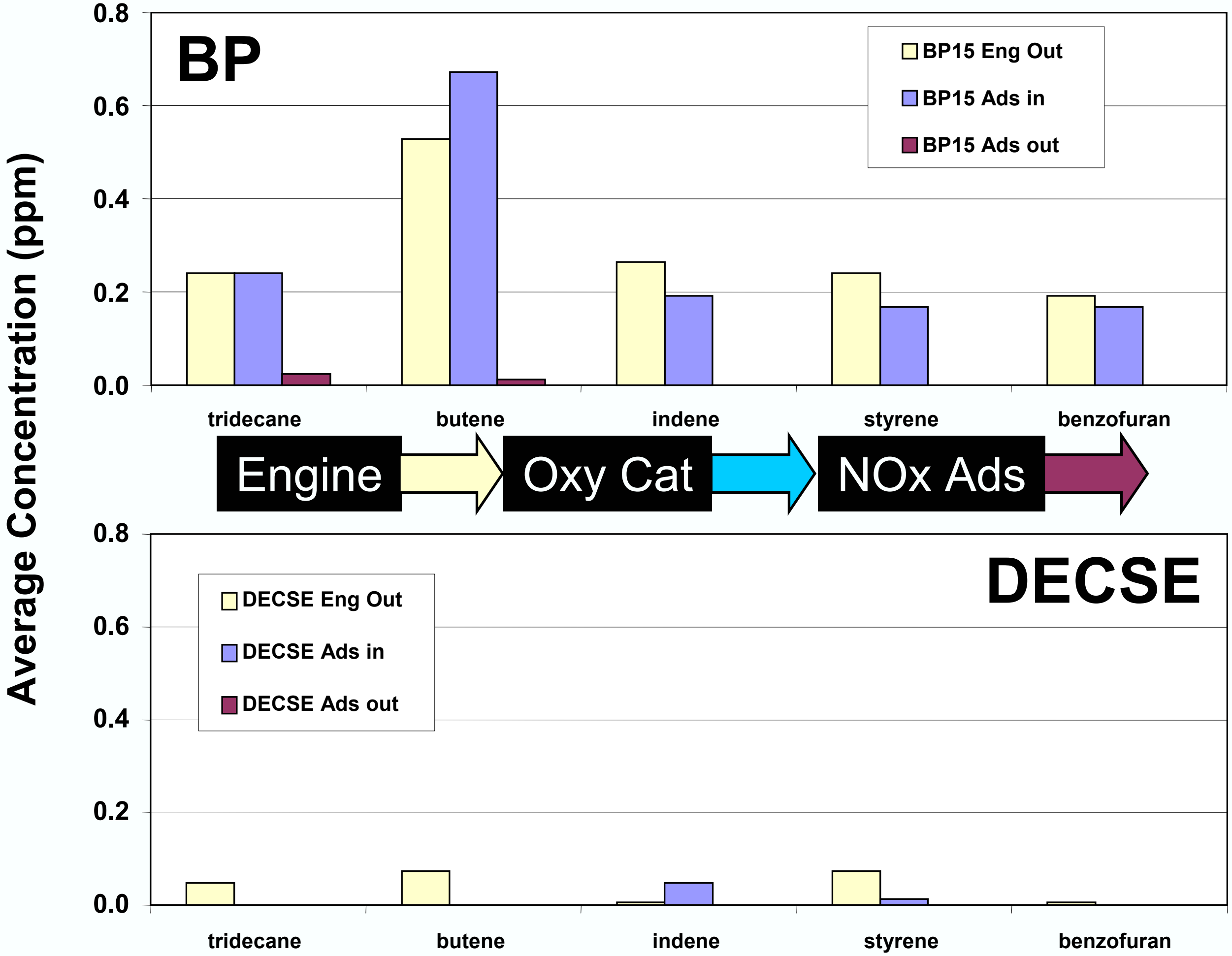
- Engine Out Lean baseline shows moderate levels for normal combustion
- Air:Fuel ratio is target minimum A:F during rich regeneration
- Average species concentrations from FTIR (3s rich/ 60s cycle; peaks approx 19x)
- Aldehydes are reactive compounds, indicators of extensive fuel cracking, partial oxidation

Nitromethane formation in engine and catalysts is indicator for differences in exhaust chemistry from fuel or regeneration strategy



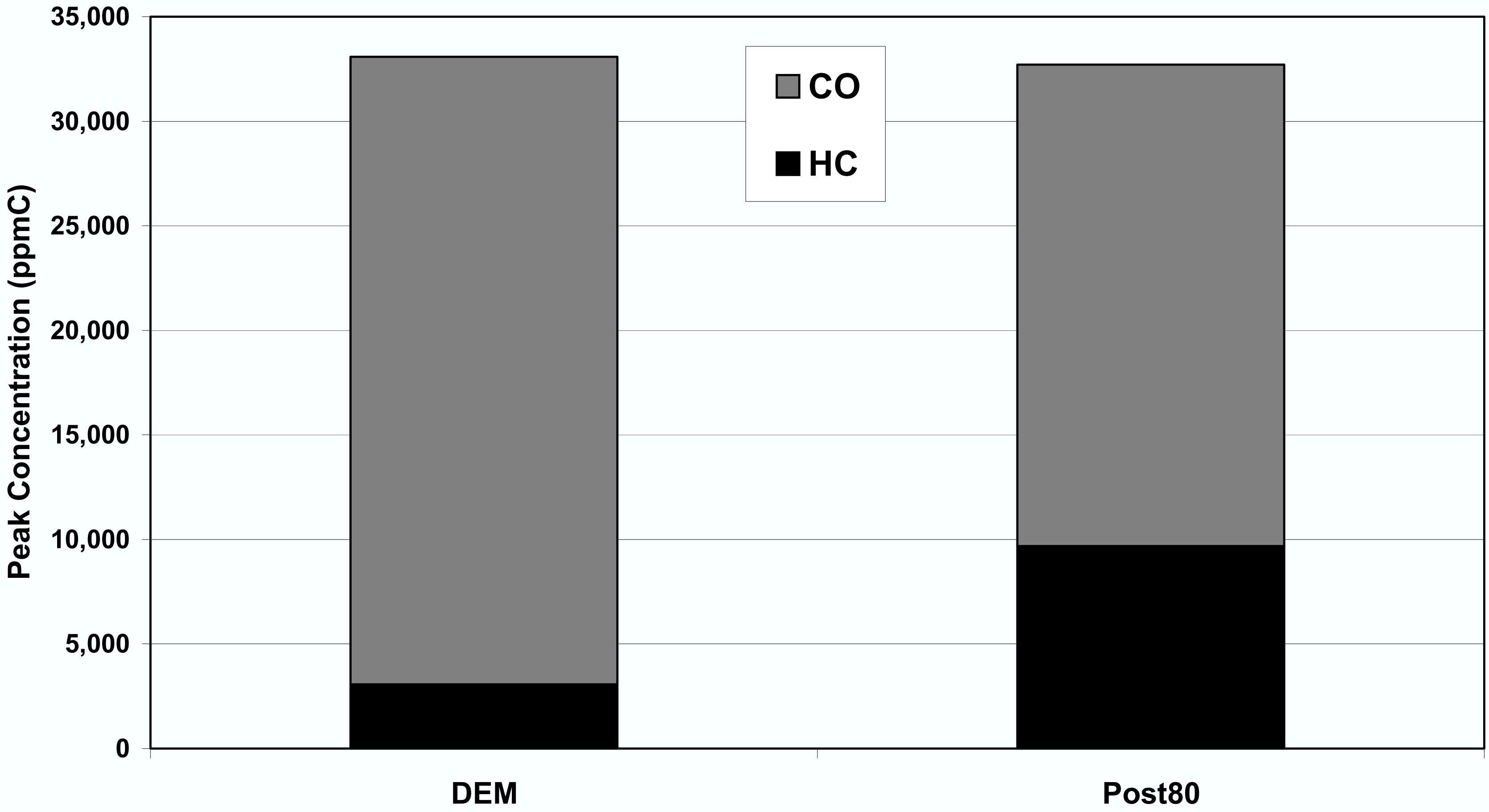
- Nitromethane and other organo-nitrates are collected and measured usng a unique ORNL method
- Note consistent *decrease* in NM across oxidation catalyst for Post80 strategy, *increase* for DEM strategy

BP15 generates broader range of HCs and higher concentrations of certain species than DECSE for Post80 strategy



- Data from 80° Post injection regeneration
- Average species concentrations from GC/MS (3s rich/ 60s cycle)

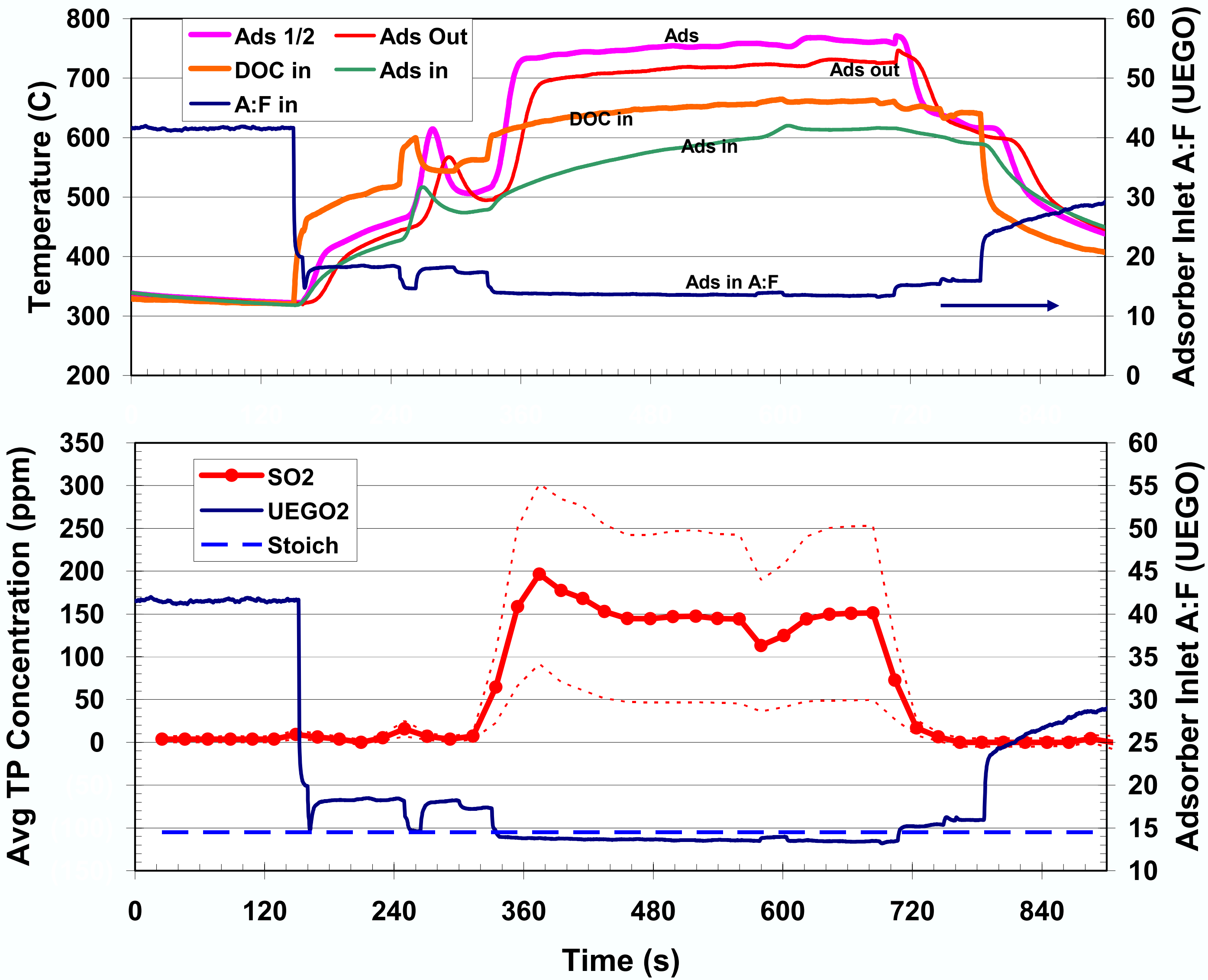
Total gaseous exhaust carbon (Peak HC+CO) concentration for DEM and Post 80 strategy are the same (14:1 indicated A:F)`



Desulfation

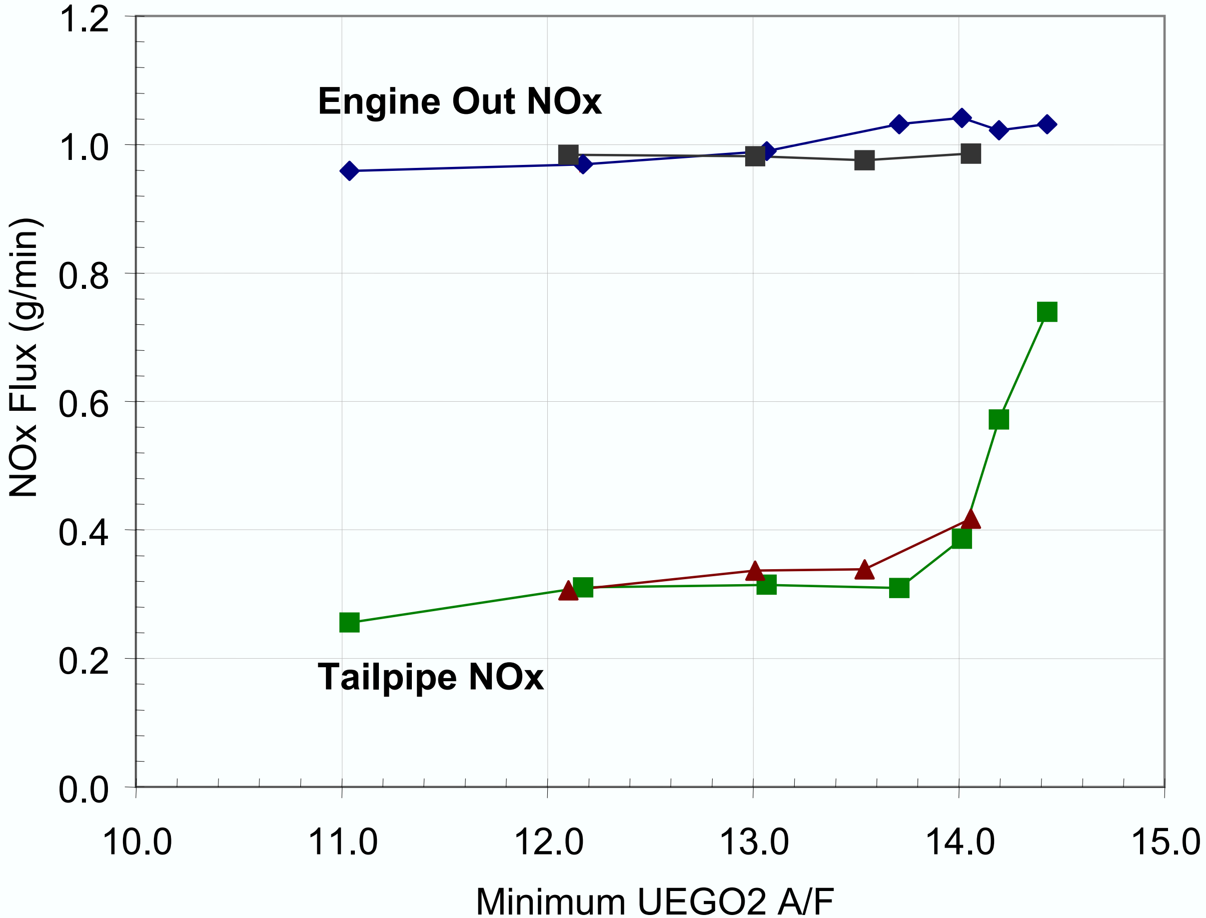
- NOx adsorber stores SOx, similar to NOx
- Periodically must remove SOx to restore performance
- Sulfates more stable than nitrates
  - Desulfation requires higher temperatures and longer times
  - Target 700C, 13.5-14:1 A:F, 6-8 minutes

Throttling and post injection used to effect desulfation



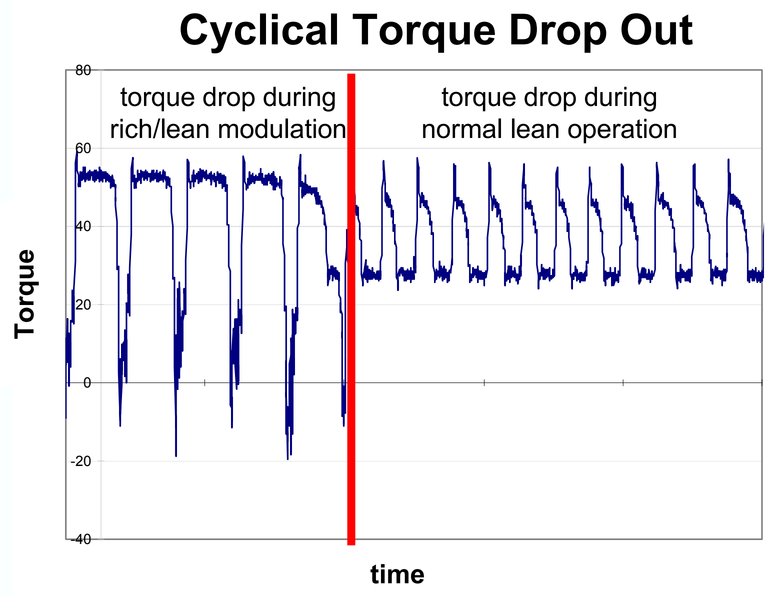
- Adsorber inlet temperature ranged 500-620C
- Adsorber midbed peaked at ~760C
- 3000 ppmC Average HC emissions during desulfation
- HC species included 50 ppm benzene
- No cleanup catalyst was used

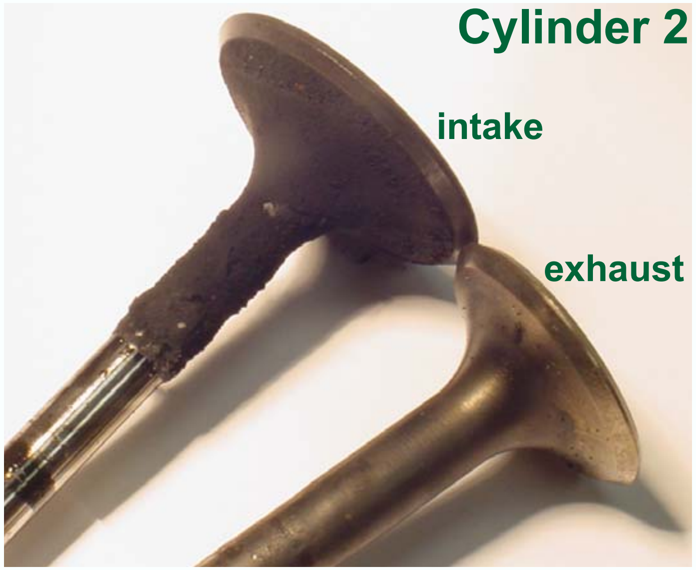
A:F sweep shows optimum use of reductant near 14:1 indicated A:F



- **Data from delayed extended main injection**
- **Data implies that regeneration is transport limited (more available reductant does not improve NOx reduction)**
  - **Catalyst sulfur poisoned**

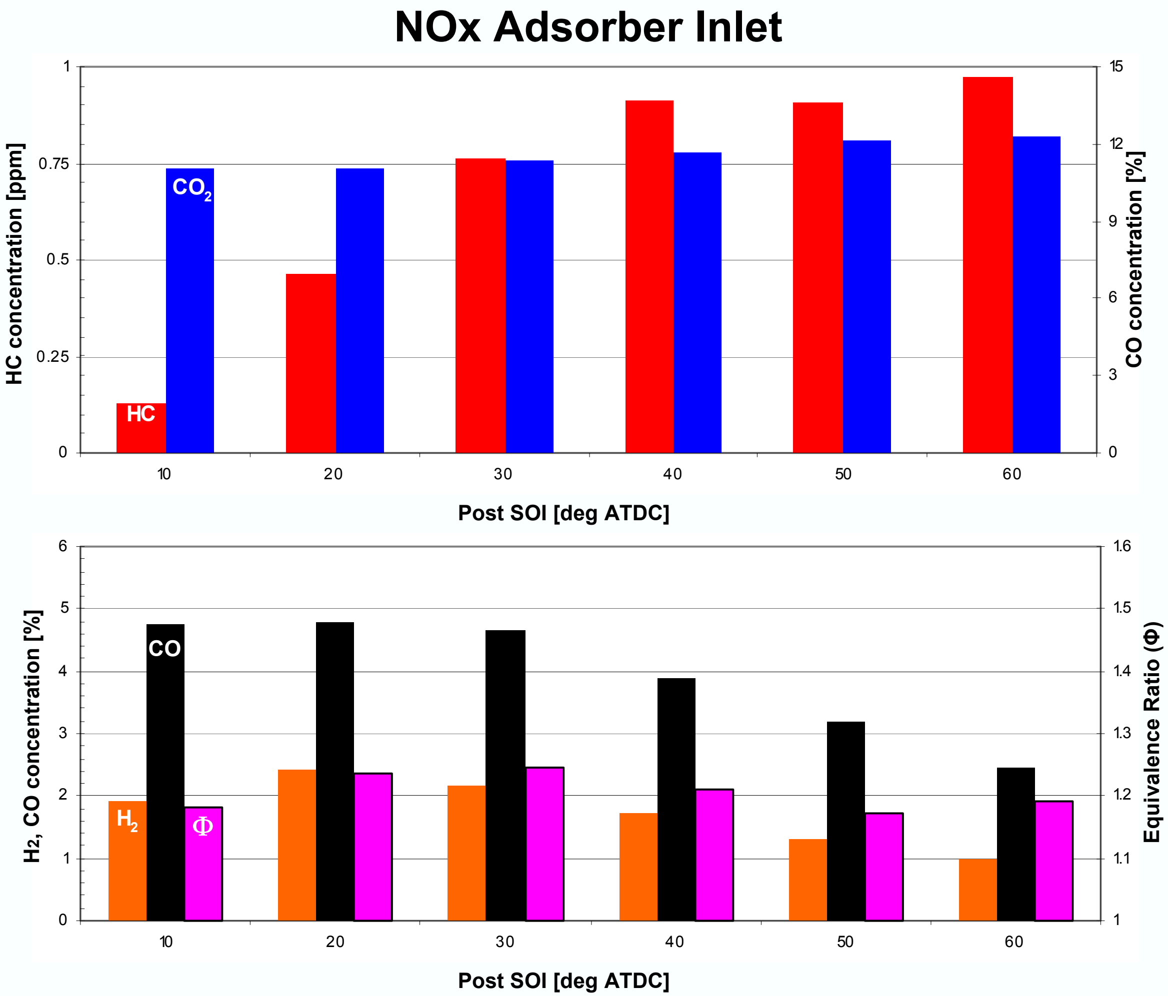
Engine was replaced after 850 hours due to intermittent cylinder 2 malfunction





- Performing post injection regenerations induced torque drop out
- cyclical drop out / recover
- pinpoint culprit cylinders (#2 mostly, occasionally #1)
- Swap of injector drivers and replacement of injectors had no benefit
- replaced engine to expedite project
- engine tear down indicates the following
  - No measured bore wear (850+ hours with 80%-90% of run time regenerating)
  - No valve leakage measured by vacuum
  - weak valve springs
  - excessive intake valve guide clearance
  - PM caked intake valve
- likely caused by “sticky” intake valve

Wide range O_2 sensor reading affected by exhaust species



- Post injection with same fuel delivered and timing sweep
- Indication that H_2 causes sensor to read richer
- Indication that high levels of unburned fuel cause sensor to read leaner
- Future Plans
  - new project to investigate species interaction