

# Cummins/ORNL-FEERC CRADA: NOx Control & Measurement Technology for Heavy-Duty Diesel Engines

(Agreement #: 10030)\*

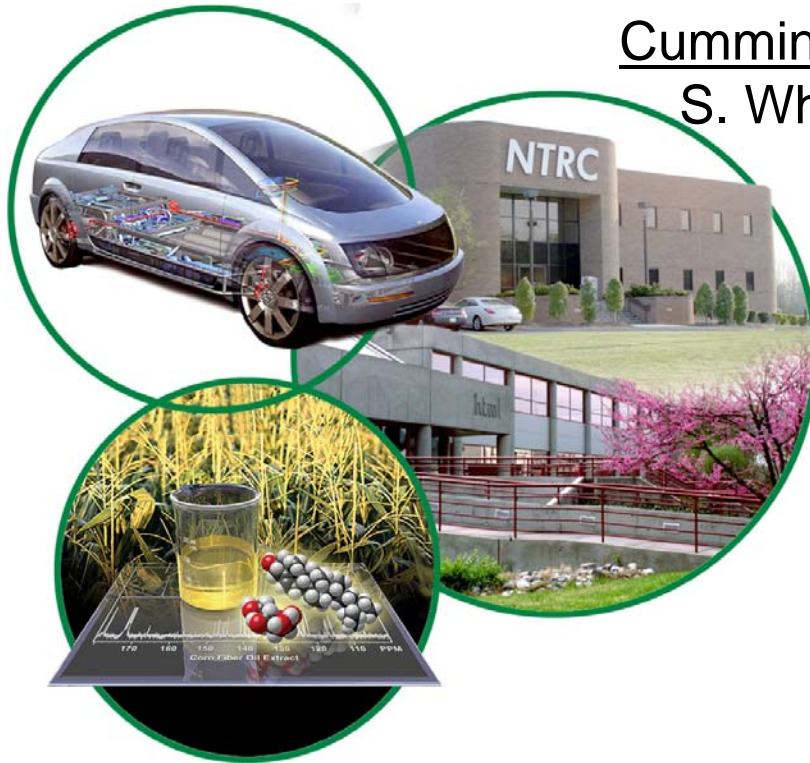
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Vehicle Technologies Program Annual Merit Review  
February 26, 2008, Bethesda, MD

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# Purpose of Work

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**Assist Cummins in addressing barriers  
to transportation-market penetration  
of fuel-efficient diesel engines**

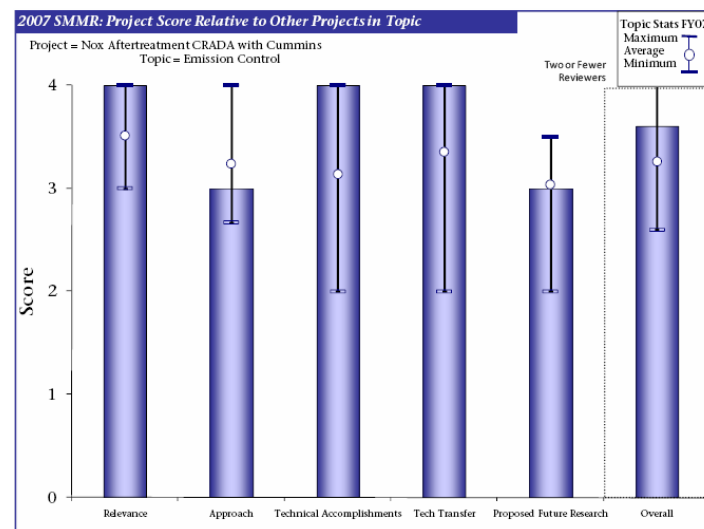
**& by doing so  
generate useful knowledge  
and enable products  
with broad public benefit**

Major Focus for FY2008:

- Oil Dilution (from engine-managed catalyst regeneration)
- LNT-Catalyst Ammonia Chemistry

# Guidance from FY 2007 Review

- Feedback was very positive
- Highest score achieved in three areas
  - Relevance
  - Technical Accomplishments
  - Tech Transfer
- “A useful industry partnership that has shown good progress and results.”
- No weaknesses or recommendations were cited.
- Previous review recommendations:
  - Using fully formulated catalyst (*implemented in '07*)
  - Quantifying H<sub>2</sub>S, NH<sub>3</sub>, N<sub>2</sub>O and SO<sub>2</sub> distributions (*implemented in '07 except NH<sub>3</sub>*)
  - **Major effort in FY2008 to quantify NH<sub>3</sub> chemistry**



# CRADA Addresses Multiple DOE\VT Barriers

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## Oil Dilution (Engine System Section)

- Can result from emissions control system management and operation
- Oil dilution can cause durability issues
- Conventional methodologies slow development

## LNT Ammonia Chemistry (Instrumentation & Bench Section)

- $\text{NH}_3$  must be controlled in viable catalyst systems:
  - Avoid  $\text{NH}_3$  slip
  - Manage generation and utilization in LNT and hybrid LNT-SCR systems

## Specific DOE\VT Multi-Year Program Plan Barriers Addressed :

- ‘*Emissions.* The key barriers ... incomplete development of aftertreatment technology, especially for  $\text{NO}_x$ ;..’
- ‘*Durability.* .. system has to perform effectively for 120,000 miles...’

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# Oil Dilution Research

# Performance Measures – Oil Dilution

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## Conventional methodologies:

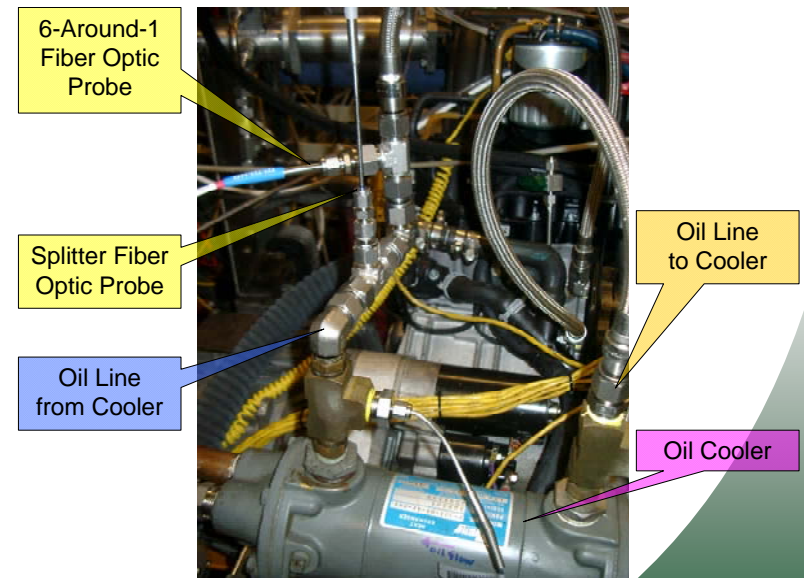
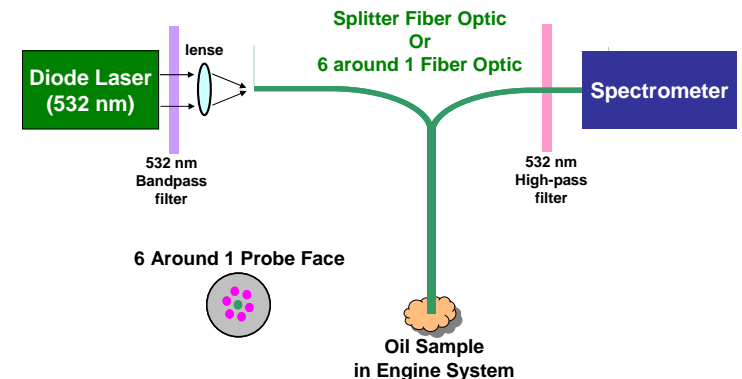
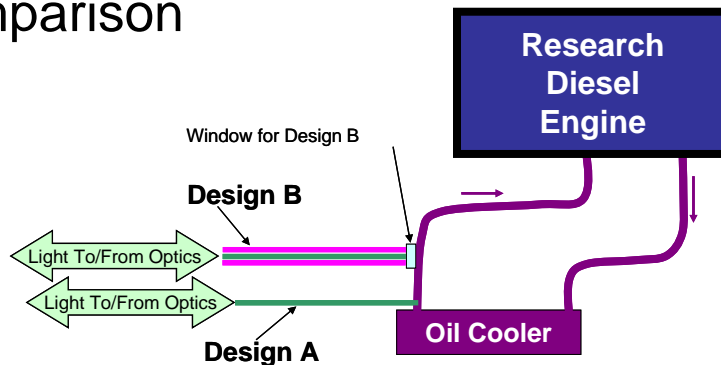
- bottleneck development
- require extractive sampling
- off-line (often off-site) analysis

## Performance measures designed to streamline development:

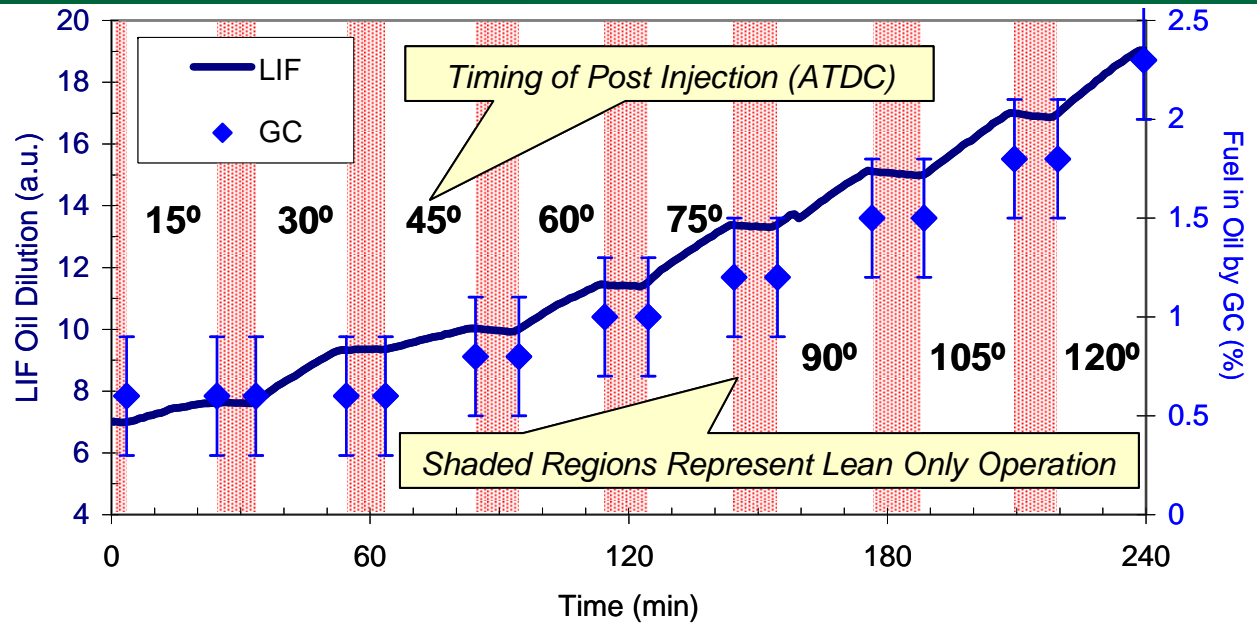
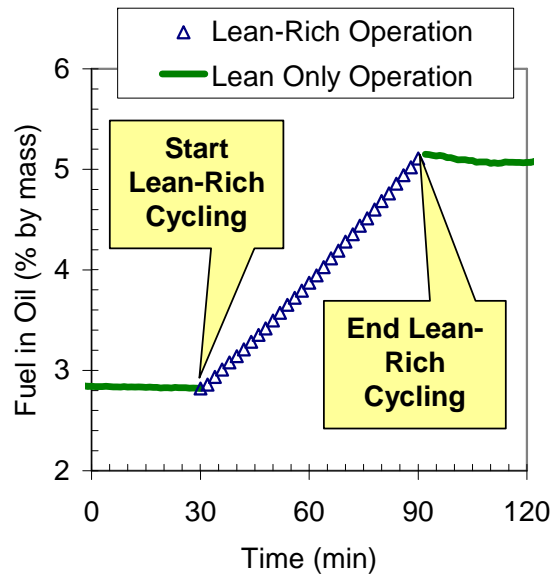
- Fast measurement ~15 min
- On-engine measurements
- Real-time feedback

# Approach – Oil Dilution

- Inexpensive & compact laser-pointer sources
- Fluorescence of commercial diesel-fuel dye
- Two fiber-based designs implemented
- Sample-point agile optical fiber design
- Engine-cell safe closed system design
- Demonstrate on ORNL research diesel
  - Flexible engine control system
- Extract samples for ASTM method comparison



# Results - Oil Dilution



- Slope indicates relative oil dilution rate
- Real-time on-engine feedback of oil dilution
  - ~ <15 min feedback time
- Laser-Induced Fluorescence (LIF) method
  - trends with ASTM
  - more sensitive than ASTM
- LIF Oil Dilution diagnostic realizes performance measures



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# LNT Ammonia Chemistry Research

# Performance Measures – LNT Ammonia Chemistry

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## Ammonia is relevant to diesel product development:

- $\text{NH}_3$  slip management
- System design & calibration
- On-board detection of system state
- Cummins development emphasizes fundamental knowledge

## Ammonia is difficult to measure w/ SpaciMS:

- Interferences with  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_x$
- $\text{NH}_3$  is sticky
- Variable and different elution times

## Performance Measures address diagnostic and information needs:

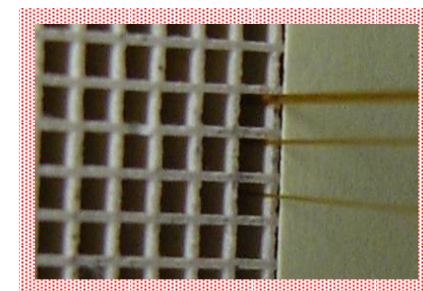
- Enable SpaciMS measurement of  $\text{NH}_3$  inside operating LNT catalysts
- Map transient  $\text{NH}_3$  distribution through catalyst
- Clarify  $\text{NH}_3$  formation and utilization in LNT chemistry

# Approach – LNT Ammonia Chemistry

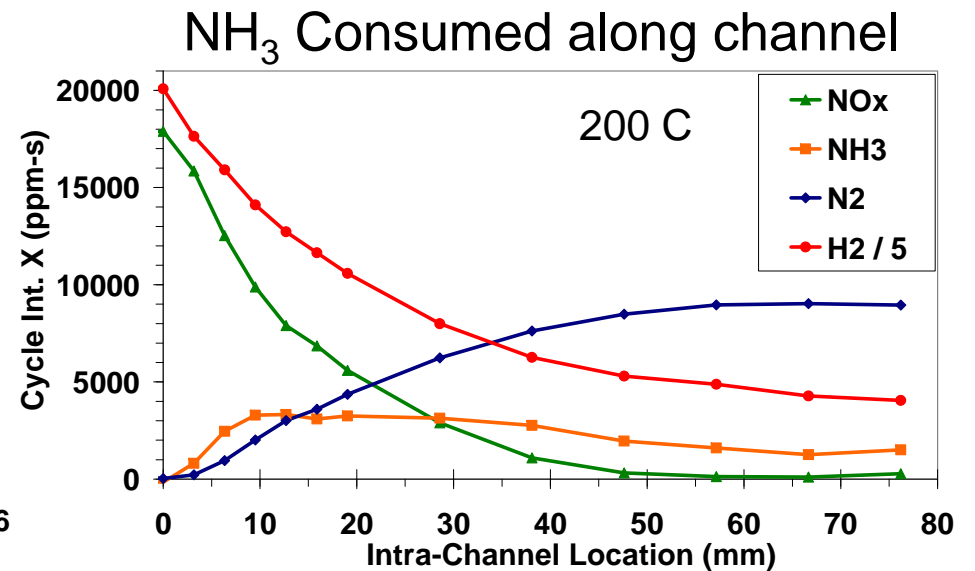
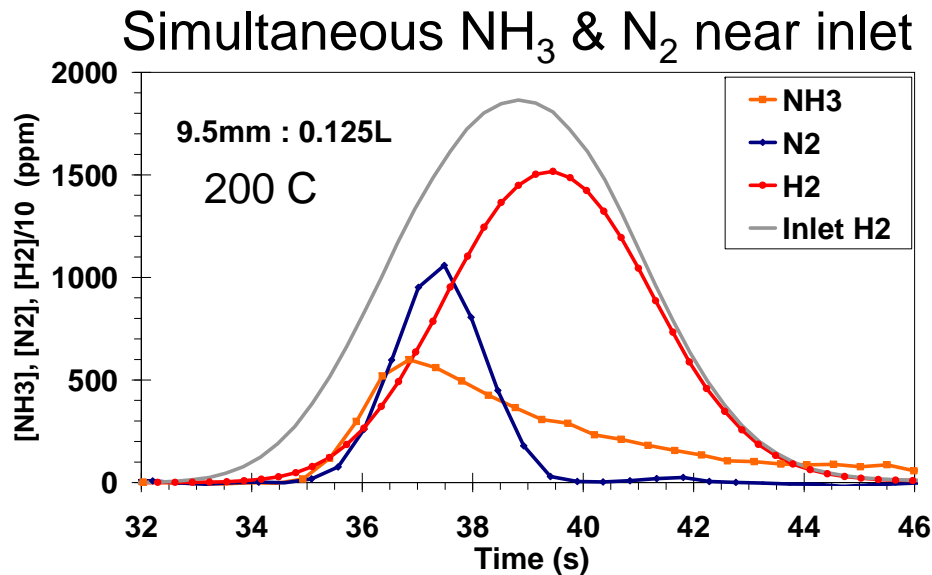
- Catalyst core (3/4" x 3") on bench reactor
- Washcoat: Pt/Ba/Al<sub>2</sub>O<sub>3</sub> model catalyst
  - No cerium – oxygen-storage component
- CLEERS standard short cycling:
  - 60-s lean: 300ppm NO + 10% O<sub>2</sub>
  - 5-s rich: 2% H<sub>2</sub>
  - Common: 5% H<sub>2</sub>O + 5% CO<sub>2</sub> + Ar balance



- ***Resolve species distributions along catalyst channel***
  - SpaciMS
  - NH<sub>3</sub> generation and utilization
  - NO<sub>x</sub>, N<sub>2</sub> and H<sub>2</sub>
- Analyze distributed performance
  - Phase/timing of species puffs
  - Selectivity



# Results - LNT Ammonia Chemistry

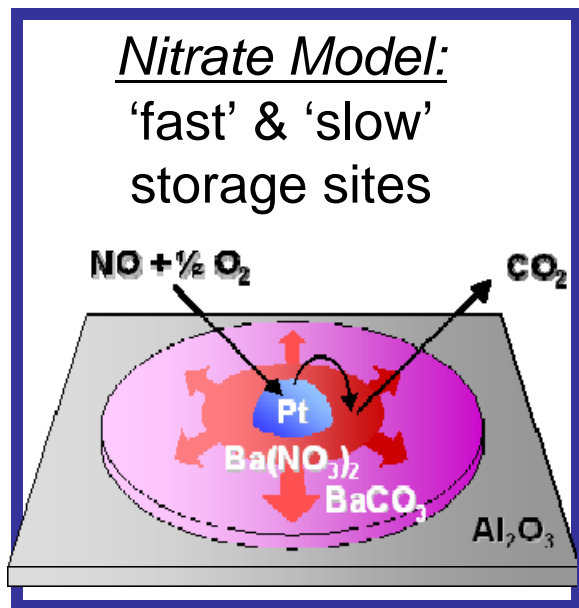


- Simultaneous  $\text{N}_2$  &  $\text{NH}_3$  generation at catalyst front
- $\text{NH}_3$  shifts to later times along catalyst length
- $\text{NH}_3$  consumed along catalyst length along with  $\text{H}_2$

**SpaciMS  $\text{NH}_3$  measurements demonstrated**

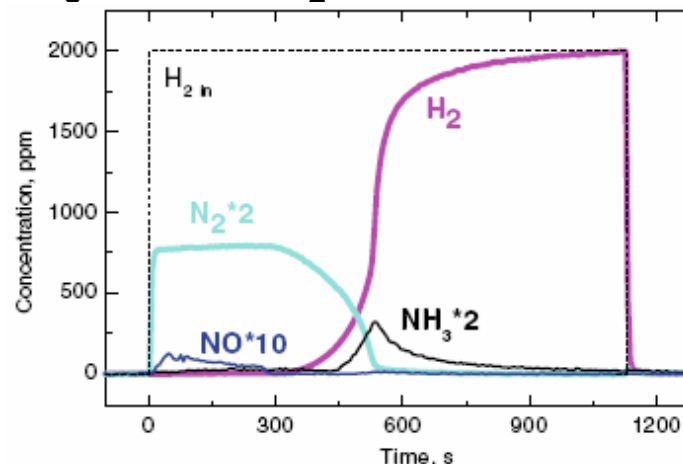
**Must account for  $\text{NH}_3$  regeneration role**

# Results – Vis-à-vis Literature Ammonia Chemistry



## Dominant Literature NH<sub>3</sub> Theory:

NH<sub>3</sub> created at 'slow' sites, &  
NH<sub>3</sub> follows N<sub>2</sub> and reductant slip



Nova et al. (2007) Topics in Catalysis

- Our measurements show same sequence at outlet
- But simultaneous NH<sub>3</sub> and N<sub>2</sub> inside catalyst

**NH<sub>3</sub> doesn't always follow N<sub>2</sub>**

**Literature NH<sub>3</sub> model incomplete**

**NH<sub>3</sub> not always from 'slow' sites**

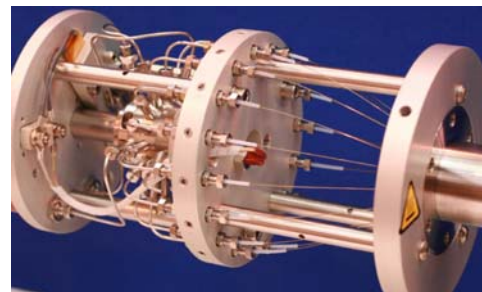
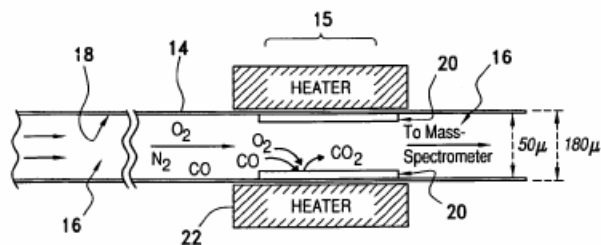
# Technology Transfer

## Via CRADA:

- All CRADA activities impact Cummins' product development
- CRADA instrumental in the commercialization of the 2007 Dodge Ram engine-catalyst system

## Outside of CRADA:

- Coordination with CLEERS impacts broad range of DOE interests
- Delphi improved reformer-catalyst models based on SpaciMS analysis
- Multiple industry inquiries into Oil Dilution diagnostic
- Hiden Analytical marketing commercial SpaciMS
- 2007 Cummins patent expands SpaciMS capabilities



# Publications, Presentations, Patents

## 3 Publications:

- J.-S. Choi, W.P. Partridge, J.A. Pihl, and C.S. Daw, “Sulfur and temperature effects on the spatial distribution of reactions inside a lean NO<sub>x</sub> trap and resulting changes in global performance”, *Catalysis Today*, doi:10.1016/j.cattod.2008.01.008 (2008).
- J.-S. Choi, W.P. Partridge, and C.S. Daw, “Sulfur impact on NO<sub>x</sub> storage, oxygen storage and ammonia breakthrough during cyclic lean/rich operation of a commercial lean NO<sub>x</sub> trap”, *Applied Catalysis B: Environmental* 77, 145-156 (2007).
- Jim Parks, Bill Partridge and Shawn Whitacre "Rapid In Situ Measurement of Fuel Dilution of Oil in a Diesel Engine using Laser-Induced Fluorescence Spectroscopy," Society of Automotive Engineers paper 2007-01-4108, 2007.

## 4 Presentations:

- J.-S. Choi, W.P. Partridge, J.A. Pihl, and C.S. Daw, “Sulfur effects on spatiotemporal distribution of reactions in a commercial lean NO<sub>x</sub> trap”, *AIChE National Meeting*, Salt Lake City, UT, November 4-9, 2007.
- Jim Parks, Bill Partridge, and Shawn Whitacre, Rapid In Situ Measurement of Fuel Dilution of Oil in a Diesel Engine Using Laser-Induced Fluorescence Spectroscopy , presented at the SAE Powertrain and Fluid Systems Conference in Chicago, IL on October 29-31, 2007.
- J.-S. Choi, W.P. Partridge, and C.S. Daw, “Assessing a commercial lean NO<sub>x</sub> trap performance via spatiotemporal species profile measurements”, *North American Meeting (NAM) of the North American Catalysis Society*, Houston, TX, June 17-22, 2007.
- W.P. Partridge, J.-S. Choi, C.S. Daw "Distributed Impact of Sulfation on LNT Catalyst Reactions," 10th DOE Crosscut Workshop on Lean Emissions Reduction Simulation, University of Michigan, Dearborn, Michigan, May 2nd, 2007.

## 1 Patent:

- N.W. Currier, A. Yezerets, US Patent Number US 7,211,793 B2, Mass Spectrometry System and Method, May 1, 2007.

# Future Activities

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## **Engine-Systems Section:**

- Apply oil-dilution diagnostic on development V engine at Cummins (scheduled - March 2008)
- Develop and apply methods to quantify cylinder and cycle dispersion

## **Instrumentation & Bench Section:**

- Characterize  $\text{NH}_3$  chemistry in LNT with oxygen-storage component (Umicore, CLEERS reference catalyst)
- Characterize sulfation impact on LNT catalyst reactions, including  $\text{NH}_3$  formation and utilization and water-gas-shift



# Summary

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- **Relevance to DOE Objectives**
  - Reduce fuel consumption by enabling diesel market penetration
- **Approach**
  - Real-time on-engine measurement of oil dilution
  - Measure evolution of  $\text{NH}_3$  generation and utilization inside catalyst
- **Technical Accomplishments**
  - Streamline engine calibration
  - Enable SpaciMS  $\text{NH}_3$  measurements & clarify LNT catalyst reactions
  - Enable improved modeling of LNT and hybrid LNT-SCR systems
- **Technology Transfer**
  - Broad based transfer via Cummins products & outside CRADA
- **Future Plans**
  - Measure cylinder and cycle dispersion on development engines
  - Quantify distributed impact of sulfation on  $\text{NH}_3$  LNT reactions
  - Designed to address Cummins' technical barriers