Cummins-ORNL\FEERC Emissions CRADA: NO\textsubscript{x} Control & Measurement Technology for Heavy-Duty Diesel Engines

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2013 DOE Vehicle Technologies Program
Annual Merit Review
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U.S. DOE Program Management Team:
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Overview

**Timeline**
- Current end date: Sept. 2015
- ~13% Complete

**Budget**
- 1:1 DOE:Cummins cost share
- DOE Funding:
  - FY2012: $450k
  - FY2013: $400k

**Barriers**
- *Emissions controls*
  - Catalyst fundamentals,
  - Reactions & mechanistic insights
  - Catalyst models (design tools & imbedded)
  - Control strategies & OBD
- Combustion Efficiency
  - Shift emissions tradeoff to fuel efficiency
- *Durability*
  - Enhanced durability via knowledge-based controls
- *Cost*
  - Lower catalyst & sensor costs
  - Lower development costs

**Partners**
- ORNL & Cummins Inc.
- Several informal collaborators
Objectives & Relevance

**Elucidate Practical & Basic Catalyst Nature**
for enabling improved Modeling, Design & Control

Objectives
- Develop diagnostics to advance applied & basic catalyst insights
- Understand parameters controlling distributed NH$_3$ storage
- Model distributed steady state SCR performance

Relevance – Detailed Catalyst Insights impact:
- Design models
- Control strategies & models
- NH$_3$ dosing control
- Required engineering margins (engine-efficiency vs. -emissions tradeoffs)
- System capital & operation costs
Milestones

2012 Milestones:
• Improve instrumental methods for transient analysis of catalyst state
  – Instantaneous NH\(_3\) coverage & loading rate, instantaneous conversion

2013 Milestone (on target for Sept. 2013 completion):
• Assess distributed performance of degreened & field-aged commercial 2010 Cummins SCR catalyst samples with focus on mechanistic understandings
• Extend steady state distributed SCR model
  – Include transient & inhibition behavior
• Demonstrate & characterize NH\(_3\) & Cu-oxidation-state sensor
Global Approach for Improving Energy Security

Develop & apply advanced diagnostics for catalyst characterization to improve: catalyst models, design, state assessment & controls for fuel-efficient engine systems

Clean, Fuel-Efficient, Durable Engines in the Marketplace

Catalyst Functional Behavior

Control & OBD Strategies

Proprietary Models
- For development
- For OBD

Diagnostics & Method Development

Catalyst Insights
- Reaction network
- Mechanisms
- Catalyst state & control measures

Improve Models
- With collaborators
- Kinetic parameters
- Use models to study catalysis

Focus
- Goals
- Strategy
- Analysis

Cummins 2007 6.7L ISB
Detailed Approach for 2013 Objectives

**Spatiotemporal Intra-Catalyst Characterization**

to Enhance Performance, Control, Cost & Durability

- Cummins-ORNL CRADA Team identifies catalyst-performance barrier
  - Distributed NH$_3$ capacity is not well understood & impacts performance
- Develop procedures to measure intra-SCR distributed NH$_3$ capacity
- Apply diagnostics to characterize distributed SCR performance
  - NH$_3$ capacity, SCR, parasitic NH$_3$ oxidation, NO & NH$_3$ oxidation
- Correlate distributed NH$_3$ capacity with other performance parameters
  - Compare insights with SpaciFTIR results from other DOE project
- Model distributed SCR behavior in collaboration with Chalmers partners
  - Based on AVL Boost
  - Determine kinetic parameters from SpaciMS data
  - Precompetitive model of distributed steady state SCR performance
- Incorporate insights into Cummins’ proprietary models
- Enable clean, fuel-efficient engine-catalyst systems
Technical Progress: **Summary**

- **Nature of Distributed NH₃ Capacity** *(New Insights)*
  - Correlating with distributed SCR conversion
  - on Model Cu-Beta Zeolite catalyst
  - on Commercial 2010 Cummins SAPO 34 catalyst
  - Control by Adsorption Isotherm

- **Modeling Distributed Steady State SCR Performance**
  - Determining kinetic parameters from SpaciMS data
  - Precompetitive AVL Boost distributed SCR model

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**Fractional NH₃ Coverage**

<table>
<thead>
<tr>
<th>Location</th>
<th>Inlet NH₃</th>
<th>Outlet NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCR Zone Back</td>
<td>DC &lt; TC</td>
<td>SCR Zone Front</td>
</tr>
</tbody>
</table>

**Langmuir isotherm** \( \Delta G \approx -40 \text{kJ/mol} \)

**SCR Zone**

- **Separation**

**SS NH₃ concentration (ppm)**

- **location in the catalyst (fraction of total length)**
Standard Protocols Resolve SCR Reaction Parameters

**NH₃ Saturation**
- **Total NH₃ Capacity (TC)**
- Coverage at inlet conditions
  - Maximum NH₃ at inlet conditions
  - i.e., inlet NH₃ concentration & Temp.

**SCR Conditions**
- SS Conversion & NH₃ slip
- **Dynamic NH₃ Capacity (DC)**
- **DC**: fraction of TC used for SCR
- Unused Capacity (UC) = TC-DC

We will focus on: **Total & Dynamic NH₃ Capacity**
NH₃ Coverage Distribution Imposed by Gas-Phase NH₃ Distribution

- Cu-Beta Zeolite catalyst, Standard SCR
- SCR zone shifts to catalyst front at higher temperatures
  - high NH₃ concentrations exist deeper into catalyst at lower temperature
- High NH₃ coverage at catalyst front where gas-phase NH₃ is high
  - Dynamic = Total capacity in high NH₃ concentration front section
- Dynamic-Total separation occurs at a common NH₃ level (ca. 50ppm NH₃)
- NH₃ coverage distribution changes with temperature
  - but Dynamic-Total capacity separation imposed by local gas-phase NH₃
  - & gas-phase NH₃ distribution is imposed by SCR conversion distribution
Cu-SAPO-34 Catalyst Shows Similar NH₃ Coverage Behavior

- Comparing CRADA insights to commercial catalyst behavior
  - Very different Model Cu-Beta-Zeolite & Commercial Cu-SAPO-34 catalysts
  - Validate & expand applicability of CRADA findings

- Dynamic = Total capacity above *same NH₃ level* for all conditions!
  - Separation at ~175ppm NH₃ for commercial catalyst (vs. ~50ppm for Cu-Beta-Z)
  - A case where Standard & Fast SCR are similar!
  - NH₃ coverage equilibrium reactions much faster than even Fast SCR

- **Local gas-phase NH₃ & Adsorption Isotherm control local NH₃ coverage**
  - SCR imposes gas-phase NH₃ distribution & local NH₃ concentration
  - Local gas-phase NH₃ & adsorption isotherm dictate local NH₃ coverage
  - NH₃ coverage distribution specified by gas-phase NH₃ distribution & isotherm

**Standard: NO SCR**

**Fast: NO+NO₂ SCR**

*SpaciFTIR data from Michigan Tech DOE Project*
• Adsorption isotherm indicates equilibrium-coverage variation with NH₃
  – Total capacity measured at inlet NH₃, and decreases at higher temperatures

• Coverage variation is relatively flat in high-NH₃ region
  – practically: Dynamic ≈ Total capacity in this region

• Dynamic & Total capacity should separate around the isotherm knee

• SCR reduces the gas-phase NH₃ concentration along the catalyst length
  – lower local coverage equilibrium, Dynamic < Total capacity

• Specific SCR reaction does not change the isotherm
  – only changes where these zones occur spatially within the catalyst

• Adsorption isotherm shape varies with catalyst formulation
  – E.g., different NH₃ site types, coverage dependence,..
Intra-Catalyst Measurements Enable Calculation of Kinetic Parameters under Realistic Operating Conditions

- Based on KCK Cu-Beta-Zeolite catalyst & Standard SCR
- Kinetic parameters determined from steady state Intra-SCR SpaciMS data
  - NO oxidation, NH$_3$ oxidation, NH$_3$ Standard SCR (published in Coelho thesis)
  - Further demonstrates rich nature of intra-catalyst distributed (SpaciX) analysis
  - *Enables determining kinetic parameters under realistic conditions*
  - Avoids unrealistic temperatures &/or space velocity where chemistry may differ
- AVL BOOST model in good agreement with experimental measurements
  - Distributed NO & NH$_3$ oxidation, & SCR
  - Kinetic & equilibrium controlled temperature regimes
  - Zero Parasitic Oxidation despite significant neat NH$_3$ oxidation

**Graphs**

- **200°C**
  - NH$_3$-sim, NH$_3$-exp, NH$_3$ inlet

- **400°C**
  - NH$_3$-sim, NH$_3$-exp, NH$_3$ inlet

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*Modeling performed at Chalmers KCK in Louise Olsson Group*

*Filipa Coelho: Erasmus Programme MS Student*
Collaborations & Coordination

- **Cummins**
  - CRADA Partner, Neal Currier (Co-PI)

- **Chalmers (Prof. Olsson)**
  - SCR measurements, kinetic analysis & modeling (Xavier Auvray & Filipa Coelho)

- **Michigan Tech. University (Prof. Parker)**
  - SpaciFTIR analysis of Cummins 2010 SCR catalyst (Josh Pihl)

- **Politecnico di Milano (Profs. Tronconi & Nova)**
  - Precompetitive study of selected SCR mechanisms
  - Prof.s Tronconi & Nova to ORNL Oct. 15, 2012
  - PoliMi PhD student working at ORNL Oct.-March, 2012 (Maria Pia Ruggeri)

- **CLEERS (ACE022, Wednesday 2:15pm)**
  - Diagnostics, analysis & modeling coordination

- **Institute of Chemical Technology, Prague (Prof. Marek & Dr. Kočí)**
  - Precompetitive study of LNT N₂O chemistry (with CLEERS)
  - KONTAKT II Grant from Czech Republic Government
  - Dr. Kočí working at ORNL April 16-20, 2012
  - ICTP PhD student working at ORNL Oct.-Dec., 2012 (Šárka Bártová)

- **Dissemination via Publications & Presentations**
  - 1 Archival Journal Publication & 12 Presentations
Future Work

2013 Work:

- Measure distributed chemistry of commercial SCR
  - degreened & field-aged 2010 Cummins SCR samples
  - Standard & Fast SCR; 200, 300 & 400°C
- Extend steady state distributed SCR model (w/ Chalmers)
  - Include transient & inhibition behavior
- Investigate mechanistic aspects of selected SCR reactions (w/ PoliMi)
- Continue collaborations with CLEERS, PoliMi, ICT Prague & Chalmers
- Demonstrate & characterize NH$_3$ & Cu-oxidation-state sensor

2014 Work:

- Measurements to further understand commercial SCR performance
  - Alternate, incremental and various methods for ageing
  - Focus on insights for improved modeling, design and control
- Exercise SCR model to understand selected inhibition nature
Summary

• Relevance
  – CRADA work enables improved catalyst knowledge, models, design & control
  – This reduces catalyst system costs & required engine-efficiency tradeoffs
  – This in turn enables improved fuel economy

• Approach
  – Develop & apply diagnostics to characterize catalyst nature
  – Analyze data to understand mechanistic details of how the catalyst functions
  – Develop improved catalyst models based on improved catalyst knowledge

• Technical Accomplishments
  – New insights regarding parameters controlling distributed NH3 coverage
  – SpaciX data allows determining kinetic parameters under realistic operating conditions
  – Steady state distributed SCR model accurately predicts catalyst performance

• Collaborations
  – Numerous university collaborations resulting in presentations, publications and advances
  – Coordination & collaboration with other DOE projects to maximize benefit

• Future Work
  – Analysis & tuning of EGR mixing model – identify mixing and model-data difference origins
  – EGR Probe Improvements: interference identification & probe-to-probe variations
  – Diagnostic identification & development for addressing next-generation efficiency barriers
Technical Back-Up Slides
Cummins 4-Step Protocol Resolves Reaction Parameters

- **Step 1**: NO oxidation
- **Step 2**: SS NO$_x$ & NH$_3$ conversions, Parasitic NH$_3$ oxidation, Dynamic NH$_3$ capacity
- **Step 3**: NO$_x$-free NH$_3$ oxidation, Unused NH$_3$ capacity
- **Step 4**: NO oxidation, Total NH$_3$ capacity

**Table**

<table>
<thead>
<tr>
<th>[NO]</th>
<th>200 ppm</th>
<th>200 ppm</th>
<th>0</th>
<th>200 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NH$_3$]</td>
<td>0</td>
<td>200 ppm</td>
<td>200 ppm</td>
<td>0</td>
</tr>
</tbody>
</table>

**Graph**

1. **Step 1**: NO Oxidation
2. **Step 2**: NO Oxidation, NO$_2$, Parasitic NH$_3$ Oxidation
3. **Step 3**: NO$_x$-free NH$_3$ Oxidation
4. **Step 4**: NO Oxidation

**Equation**

Total = Dynamic + Unused