Joint Development and Coordination of Emissions Control Data and Models (CLEERS Analysis and Coordination)

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Oak Ridge National Laboratory
National Transportation Research Center

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    Charles Finney, Jae-Soon Choi, Bill Partridge

• Catalyst samples & guidance from Johnson Matthey:
  – Haiying Chen

• Guidance from CLEERS Advisory Committee members:
  – Wei Li, Christine Lambert, Craig Dimaggio, Neal Currier,
    John Kirwan, Balaji Sukumar, Louise Olsson, Mike Harold,
    Dick Blint, Stuart Daw

• Collaboration with partners at PNNL:
  – Mark Stewart, Ken Rappé, Yong Wang, Jamie Holladay
Overview

Timeline
Project start date: FY2016
Project end date: FY2018
• included in ORNL response to 2015 VTO “Lab Call”
• core activity since FY2000
• supports and coordinates emissions control research
• evolves with DOE priorities and industry needs

Budget

<table>
<thead>
<tr>
<th></th>
<th>FY17</th>
<th>FY18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination</td>
<td>$250k</td>
<td>$250k</td>
</tr>
<tr>
<td>Analysis</td>
<td>$400k</td>
<td>$325k</td>
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Barriers

U.S. DRIVE Advanced Combustion & Emission Control 2018 Roadmap Barriers & Targets:
• U.S. EPA Tier 3 Bin 30 emission standard
• 90% conversion of criteria pollutants (NOx, CO, HCs) at 150°C for the full useful life of the vehicle
• “Development of models and simulation tools… to predict performance and better understand catalytic processes”

Partners
• DOE Advanced Engine Crosscut Team
• U.S.DRIVE ACEC Tech Team
• CLEERS Focus Group members
  – 10 engine/vehicle manufacturers
  – 11 component and software suppliers
  – 13 universities
  – 4 national labs
• PNNL, Johnson Matthey
U.S. DRIVE ACEC Roadmap emphasizes the need for advanced aftertreatment research to ensure emissions compliance for high efficiency combustion engines.

“Compliance with exhaust emission regulations will be mandated and requires aftertreatment technologies integrated with the engine combustion approaches.”

“The overarching emissions goal for the powertrain technologies shown in Table 3 is the U.S. EPA Tier 3 Bin 30 emission standard...”

“...a principal goal of future low temperature aftertreatment technologies, embraced by the ACEC Technical Team, is to achieve greater than 90% conversion of criteria pollutants (NOx, CO, HCs) at 150°C for the full useful life of the vehicle.”

“...development of models and simulation tools ranging from the molecular level to the system level to predict performance and better understand catalytic processes”

“Understand the state of the PNA/HC Trap for shutdown/restart optimize restart/cold start performance”

“Characterize and understand PNA/HC Trap durability”
CLEERS provides a key stepping stone on the path to reduced petroleum consumption

- CLEERS = Crosscut Lean (Low-temperature) Exhaust Emissions Reduction Simulations

- Mission: accelerate development of emissions control technologies for high efficiency advanced combustion engines by improving accuracy of aftertreatment system simulations

- Objectives:
  - develop and disseminate pre-competitive data, parameters, and models
  - support collaborations among industry, university, national lab partners
  - gather feedback from industry on critical emissions control research needs
  - coordinate DOE National Laboratory research efforts

\[ \theta_1 = \frac{K_{NOx}}{1 + K_{NOx}P_{NO}} \]

\[ K_{I} = K_{I}e^{-\frac{\Delta H_{I}}{RT}} \]

- High NOx/HC+CO
- Low T

Goal: reduce petroleum consumption

component models

advanced system simulations

strategies for high efficiency

NH_3 + S_2 \rightarrow S_2NH_3
H_2O + S_2 \rightarrow S_2H_2O
Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)

ACEC Roadmap
Combustion Strategies

- Low Temperature Combustion
- Dilute Gasoline Combustion
- Clean Diesel Combustion

CLEERS (ACS022)
Coordination
Experiments, Analysis, Modeling

Low Temperature Catalysis (ACS085)

Lean Gasoline Emissions Control (ACS033)

Heavy Duty Emissions Control (ACS032)
Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)

ACEC Roadmap
Combustion Strategies

Low Temperature Combustion

Dilute Gasoline Combustion
CLEERS (ACS022) Coordination, Analysis, Modeling

Clean Diesel Combustion

Guidance from Industry Priorities Survey and CLEERS Participant Interactions
Presentations to CLEERS Workshop & Telecons
Data sharing through website

Low Temperature Catalysis (ACS085)
Lean Gasoline Emissions Control (ACS033)
Heavy Duty Emissions Control (ACS032)

relevance approach accomplishments collaborations future work
Enabling Fuel Efficient Engines by Controlling Emissions
(ORNL FEERC response to 2015 VTO AOP Lab Call)

ACEC Roadmap
Combustion Strategies

Low Temperature Combustion

Dilute Gasoline Combustion

Clean Diesel Combustion

CLEERS (ACS022)
Coordination
Experiments, Analysis, Modeling

Low Temperature Catalysis
(ACS085)

NH₃ formation on PGM catalysts
NH₃ storage/release on SCR catalysts

Lean Gasoline Emissions Control
(ACS033)

NH₃ storage/release on SCR catalysts
Aging effects on SCR catalysts

Heavy Duty Emissions Control
(ACS032)

Adsorption, desorption, reaction on low T traps
ORNL coordinates CLEERS activities and conducts focused R&D in support of CLEERS objectives

ORNL CLEERS Coordination
- Telecons*
- Website
- CLEERS Advisory Panel
- Workshops
- Data Sets
- Device Parameters
- Reaction Mechanisms
- Modeling Strategies
- Surveys
- Newsletter
- Experiment Protocols
- LTAT*

ORNL CLEERS Analysis
- Flow reactor experiments*
- Catalyst property measurements
- Protocol development
- Calibration & validation data sets
- Specialized diagnostics
  - in situ DRIFTS
  - Spaci-MS, Spaci-IR
- Characterization
  - microscopy
  - XRD
  - BET
  - Chemisorption
- Analysis*
  - thermodynamics
  - Parameter estimation
- Modeling*
  - micro-kinetic, global
  - Chemkin, Autonomie
  - Custom codes
  - = collaboration with PNNL
## Milestones

<table>
<thead>
<tr>
<th>FY</th>
<th>Qtr</th>
<th>Milestone</th>
<th>Status</th>
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<tbody>
<tr>
<td>2017</td>
<td>4</td>
<td>Organize 2017 CLEERS Workshop</td>
<td>complete</td>
</tr>
<tr>
<td>2018</td>
<td>4</td>
<td>Organize 2018 CLEERS Workshop</td>
<td>on schedule</td>
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CLEERS is an efficient means for communicating pre-competitive information

- Workshop #20, Oct 3-5, 2017, Ann Arbor, MI
  - 162 attendees representing OEMs, component & software suppliers, national labs, universities, government agencies
  - 39 presentations (4 invited), 23 posters
  - Panel discussion on emerging low temperature aftertreatment modeling needs

- Focus Group teleconferences:
  - Technical presentations of latest results
  - 40-80 invited participants from around globe
  - Typically >50% industry representatives

- 2017 Industry Priorities Survey:
  - Industry guidance on CLEERS activities and R&D priorities
  - Results presented to DOE Advanced Engine Crosscut Team
  - Report posted to CLEERS Website
Supported the U.S.DRIVE ACEC LTAT team in developing and testing experimental protocols for low T catalysts

**U.S.DRIVE ACEC Tech Team Low Temperature Aftertreatment Working Group**

<table>
<thead>
<tr>
<th>Org.</th>
<th>Representatives</th>
</tr>
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<tbody>
<tr>
<td>FCA</td>
<td>Craig DiMaggio</td>
</tr>
<tr>
<td>Ford</td>
<td>Joe Theis</td>
</tr>
<tr>
<td>GM</td>
<td>Se Oh Ming Yang</td>
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<tr>
<td>PNNL</td>
<td>Ken Rappe Mark Stewart</td>
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<tr>
<td>ORNL</td>
<td>Jim Parks Josh Pihl</td>
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<tr>
<td>UM</td>
<td>Galen Fisher</td>
</tr>
<tr>
<td>DOE</td>
<td>Ken Howden</td>
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</table>

- Supported development of low T catalyst screening protocols for oxidation (2014-15), NOx+HC storage (2015-18), TWCs (2016-17), and NH₃ SCR (2018)
- Hosting protocols on CLEERS website
Core CLEERS organizational activities remain high priorities for industry participants

- Annual public workshop
- Monthly technical teleconferences
- Standard lab protocols for catalyst measurements
- Website
- Coordination of national lab emissions control R&D
- Access to unique DOE lab facilities
- Posting of device models & data from govt. projects
- CLEERS newsletter
- Restricted access repository for sharing
- Web collaboration tools
- Posting location for job openings and resumes
- Social media pages/groups for CLEERS participants

average priority score

<table>
<thead>
<tr>
<th>Fraction ranked:</th>
<th>low</th>
<th>medium</th>
<th>high</th>
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<tr>
<td>fraction ranked:</td>
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2017 CLEERS Industry Priorities Survey showed continuing interest in low temperature strategies

- As in the past, the survey revealed a diversity of opinions in industry
- Several R&D topics received high priority rankings across multiple technologies:
  - low temperature formulations
  - aging mechanisms
  - multifunctional filters
- Top ranked technologies varied by application:
  - gasoline: GPFs, HC traps
  - diesel: PNAs, urea SCR
- ORNL’s CLEERS R&D activities are currently focused on understanding and modeling the operation and aging of:
  - passive NOx adsorbers (PNA)
  - hydrocarbon traps (HCT)
Synthetic exhaust flow reactor experiments starting to reveal the chemistry underlying NO adsorption on a PNA

- Obtained catalyst core sample from Johnson Matthey
  - model dCSC™ component
  - Pd-exchanged ZSM-5
    - Pd loading: 50 g/ft³ (1.8 g/l)
    - washcoated on a 400 cells/in² cordierite monolith
- Loaded in automated synthetic exhaust flow reactor
- Degreened at 600 °C for 4 h under 10% O₂/7% H₂O/N₂
- Ran NO storage/release experiments:
  - isothermal NO adsorption
  - TPD
  - varied gas composition, storage T
PNA isothermal storage/TPD experiments enable reproducible measurements of capacity and stability.

<table>
<thead>
<tr>
<th>pretreat, cool conditions</th>
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<tbody>
<tr>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{T}$</td>
</tr>
<tr>
<td>$\text{SV}$</td>
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<table>
<thead>
<tr>
<th>NO exposure conditions</th>
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<tbody>
<tr>
<td>NO</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
</tr>
<tr>
<td>$\text{T}$</td>
</tr>
<tr>
<td>$\text{SV}$</td>
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</table>

Note: procedure focuses on reaction mechanism identification and model parameter estimation, and therefore differs from the ACEC LTAT protocol for storage catalyst performance evaluation.
CO$_2$ has no effect on PNA NO uptake/release or CO oxidation

**CO$_2$ (%)**:
- 0
- 5
- 7
- 9
- 11
- 13

**NO adsorption**

- NO (ppm)
- time (min)

**TPD**

- TPD
- T (°C)

**NO storage (mol/l)**

- adsorbed
- desorbed

**CO$_2$ (%)**:
- 0
- 5
- 7
- 9
- 11
- 13
Increasing $O_2$ has no effect on NO uptake, slightly decreases release $T$, inhibits CO oxidation.
Increasing $\text{H}_2\text{O}$ decreases NO uptake, increases CO oxidation.
Increasing NO increases rate of uptake (but not capacity) and inhibits CO oxidation.
Increasing CO increases NO uptake, decreases release temperature, and increases CO oxidation activity.

**CO (ppm):** □ 50 □ 100 △ 200 ○ 400 × 800

**NO adsorption**

**TPD**

**NO storage (mol/l)**

**relevance approach accomplishments collaborations future work**
NO uptake first increases, then decreases with increasing temperature, resulting in a "sweet spot" at 150 °C.
Experiments are starting to shed light on PNA chemistry, modeling approaches

<table>
<thead>
<tr>
<th>Storage Impact</th>
<th>Release Impact</th>
<th>Notes</th>
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</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>none</td>
<td>can remove CO₂ from experiments</td>
</tr>
<tr>
<td>O₂</td>
<td>none</td>
<td>high T O₂ required to recover capacity</td>
</tr>
<tr>
<td>H₂O</td>
<td>small decrease³</td>
<td>possible competition for surface sites</td>
</tr>
<tr>
<td>NO</td>
<td>none</td>
<td>lower T @ low NO not simple equil. adsorption/desorption</td>
</tr>
<tr>
<td>CO</td>
<td>increase²</td>
<td>partial Pd reduction required for NO storage?</td>
</tr>
<tr>
<td>T</td>
<td>increase, decrease¹</td>
<td>H₂O inhibition giving way to NO desorption?</td>
</tr>
</tbody>
</table>

Literature with similar observations: ¹Chen et al., Catal Lett 2016 146, 1706 (JM); ²Vu et al., Catal Lett 2017 147, 745 (UVA); ³Zheng et al., J. Phys. Chem. C 2017, 121, 15793 (PNNL)
Collaborations: 36 Industry, 27 Academic, 9 Natl. Labs/Govt.

### CLEERS Technology Focus Group
- **Adv. Eng. Crosscut**
  - ACEC TT
  - DOE VTO
- **LD OEMs**
  - FCA
  - Ford
  - GM
  - EPA
  - TARDEC
- **HD OEMs**
  - Caterpillar
  - Cummins
  - Daimler
  - Navistar
  - Paccar
  - Volvo
- **Suppliers**
  - BASF
  - Johnson-Matthey
  - Umicore
  - Corning
  - Delphi
  - Haldor Topsoe

### Universities
- Chalmers Univ.
- Michigan Tech. Univ.
- Pennsylvania State Univ.
- Politecnico di Milano
- Purdue Univ.
- Texas A&M Univ.
- UCT Prague
- Univ. of Houston
- Univ. of Kentucky
- Univ. of Notre Dame
- Univ. of Michigan
- Univ. of Virginia
- Univ. of Wisconsin

### Industry
- John Deere
- Bosch
- Tenneco
- IAV
- N2Kinetics
- Emissol

### Nat’l Labs
- ORNL
- PNNL
- ANL
- LANL

### CLEERS Industry Survey Recipients
- John Deere
- Bosch
- Tenneco
- IAV
- N2Kinetics
- Emissol

## CLEERS Participants
- Denso
- Aramco
- SwRI
- Hannam Univ.
- Univ. of Connecticut
- Eaton
- AVL
- NRCan
- Karlsruhe Inst. of Tech.
- Univ. of Kansas
- GE
- CD Adapco
- NREL
- Univ. of New Mexico
- Hyundai
- Converge
- CPERI/CERTH
- Michigan State Univ.
- Univ. Pierre & Marie Curie
- Hino
- Exothermia
- PSI
- Ohio State Univ.
- Univ. of Tennessee
- NGK
- Gamma
- TNO
- Queens Univ. Belfast
- West Virginia Univ.
- Toyota
- Ricardo
- PSI
- Seoul National Univ.
- Wayne State Univ.
## Responses to Comments from Reviewers (4)

### Reviewer Comments:
- “…project could be outstanding with a simple survey of participants for strengths, weaknesses, and solutions”
- “Continued research in the area of SCR characterization and performance prediction is very desirable from an OEM standpoint… the embracing of LT catalyst formulations is critical to helping enable future powertrains…”
- “…not clear how CLEERS is contributing to the lack of cost-effective emission control because it seems to be studying the same technologies as everyone else”
- “…continuing to provide understanding of the functionality and chemical state of copper (Cu) in SCR formulations is of value to the OEM community”
- “…reviewer was very tired of hearing about Cu/chabazite”
- “…more activities addressing catalyst aging/deactivation mechanisms”

### Responses:
- We conduct the CLEERS Priorities Survey every 2 years
- Our focus is guided by results of the Industry Priorities Survey as well as Merit Review comments
- We are developing models for PNA, HC Trap, and SCR catalysts because they have been identified as high priority technologies by survey participants and most reviewers
- Ongoing NH₃ SCR work has emphasized aging effects
- Aging will be included in future PNA, HC Trap efforts
CLEERS data sets, parameters, and modeling strategies are put to use by industry partners

- Reviewer comments:
  - “The reviewer questioned next steps once CLEERS has data and models.”
  - “The reviewer noted that there is no proof that the CLEERS mission of accelerating development of emission control technologies is being fulfilled. Rather, the development is led by suppliers and OEMs that do not share competitive information.”

- One example of industry applying CLEERS data for model development:
  - ECS&T paper led by Gamma Technologies (makers of GT-POWER)
  - Development of LNT model
  - Based on ORNL CLEERS data

## Remaining Challenges & Barriers/Future Work

<table>
<thead>
<tr>
<th>Remaining Challenges:</th>
<th>Future Work: <em>(subject to change based on funding)</em></th>
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<tbody>
<tr>
<td>• Ongoing need for coordination and collaboration in developing simulation tools for next generation emissions control devices.</td>
<td>• Continue coordinating CLEERS activities: workshops, teleconferences, website, surveys</td>
</tr>
<tr>
<td>• Better NH₃ SCR models needed for design and control of aftertreatment systems with higher NOx conversion efficiencies over full vehicle life to meet Tier 3 regulations and beyond.</td>
<td>• Finish incorporating 2 site NH₃ storage model with aging adaptation into full SCR device model</td>
</tr>
<tr>
<td>• Decreasing exhaust temperatures from higher efficiency engines and advanced combustion modes.</td>
<td>• Measure NH₃ storage isotherms on model Cu-SSZ-13 materials to develop fundamental understanding of storage sites and aging effects</td>
</tr>
<tr>
<td>• 90% conversion of NOx and HCs at 150 °C</td>
<td>• Passive NOx Adsorbers:</td>
</tr>
<tr>
<td></td>
<td>- Develop model(s) for NO adsorption and estimate associated parameters from data</td>
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<tr>
<td></td>
<td>- Evaluate effectiveness of models for other PNA formulations</td>
</tr>
<tr>
<td></td>
<td>• Hydrocarbon traps:</td>
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<tr>
<td></td>
<td>- Measure adsorption isotherms for single HCs (ethanol, toluene, iso-octane, decane...)</td>
</tr>
<tr>
<td></td>
<td>- Develop preliminary model(s) for HC adsorption/desorption</td>
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Summary

- **Relevance**
  - CLEERS supports the development of simulation tools for the design, optimization, and control of next generation advanced combustion engine/aftertreatment systems that maximize efficiency while still meeting emissions standards

- **Approach**
  - Promote sharing of precompetitive information among the emissions control community through workshops, teleconferences, website, and surveys
  - Develop modeling strategies, reaction mechanisms, parameter estimates, experimental protocols, and data sets to support development of aftertreatment simulation tools, with a particular focus on catalysts for low temperature exhaust

- **Technical Accomplishments**
  - Maintained high levels of participation in CLEERS activities
  - Conducted detailed measurements of gas composition impacts on NO uptake on a PNA catalyst; began to develop conceptual model of NO adsorption/desorption

- **Collaborations**
  - PNNL; Johnson Matthey
  - Advanced Engine Crosscut Team, U.S.DRIVE ACEC Tech Team, CLEERS Participants

- **Future Work** *(subject to change based on funding levels)*
  - Continue coordination of CLEERS activities
  - Measure & model adsorption/desorption phenomena on PNAs and HC Traps
Technical Back-Up Slides
CLEERS is a team effort involving contributions from many people and organizations.
Proposed schedule for ORNL CLEERS activities shifts focus to adsorbers for low T applications

1. Coordination
   1.a. Workshop
   1.b. Telecons, website
   1.c. Priorities Survey

2. NOx storage/release on PNAs
   2.a. Protocol development
   2.b. NO adsorption/desorption
   2.c. Co-adsorption/inhibition
   2.d. PNA formulation effects

3. HC storage/release on traps
   3.a. Instrumentation & protocols
   3.b. Single HCs
   3.c. HC mixes
   3.d. Trap formulation effects

4. NH₃ storage/release on SCR
   4.a. commercial Cu-SSZ-13 aging
   4.b. commercial Cu-SAPO-34
   4.c. reaction & aging mechanisms
   4.d. model SSZ-13