Chemistry of Cold-Start Emissions and Impact of Emissions Control
Project ID: ace153

Oak Ridge National Laboratory
National Transportation Research Center

PI: Melanie Moses-DeBusk
Email: mosesmj@ornl.gov
Phone: 865-341-1338

2020 DOE Vehicle Technologies Office
Annual Merit Review

June 3, 2020

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
Acknowledgements

• Funding & guidance from DOE VTO Program Managers:
  – Siddiq Khan, Ken Howden, Gurpreet Singh, Mike Weismiller

• Contribution from the ORNL Team:
  – Shannon Mahurin, John Storey, Sam Lewis, Maggie Connatser, Larry Moore, Shean Huff

• Supply of HC-traps and Advisors at Umicore:
  – John Nunan, David Moser

• Guidance from Advisors at Ford Motor Company:
  – Jason Lupescu, Christine Lambert
Overview

Timeline

Project start date: FY2019
Project end date: FY2021

Barriers

U.S. Drive Advanced Combustion & Emissions Control Roadmap Barriers & Targets

• U.S. EPA Tier 3 Bin 30 emissions
• Reduced cold start emissions
• “..HC Traps must be designed for effective control of specific HC species that are present in gasoline engine exhaust.”

Collaborations

• Umicore: advisory role & supply HC-traps and GPFs
• Ford Motor Company: advisory role
• Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS)

Budget

<table>
<thead>
<tr>
<th>Task 4*: Chemistry and Control Cold-Start Emissions</th>
<th>FY19</th>
<th>FY20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$500k</td>
<td>$500k</td>
</tr>
</tbody>
</table>

• *New ORNL task in FY2019
• Part of larger ORNL response to 2018 VTO AOP Lab Call “Controlling Emissions from High Efficiency Combustion System”
Milestones: task specific over 3-year project

- **FY2019, Q1**: Define the different engine platforms to be tested
- **FY2020, Q1**: Completed a statistically significant LD gasoline campaign on gaseous HC emissions and PM focused on cold-start
- **FY2020, Q3**: Complete HC speciation analysis of LD HC speciation emissions and aftertreatment impacts on PM emissions and compositions
- **FY2021, Q1**: Complete a statistically significant LD cold-start sampling campaign focused on HC emissions changes over HC-Trap
- **FY2021, Q3**: Submit a manuscript on LD cold-start emissions
- **FY2021, Q4**: Completed a statistically significant hybrid cold-start campaign on gaseous HC emissions and PM
Why study the chemistry of cold-start emissions?

**Barrier**

U.S. EPA Tier 3 Bin 30 emissions (NMOG + NOx)

<table>
<thead>
<tr>
<th>Tier 3 Certification Bin Standards (FTP, 150,000 mi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bin 160</td>
</tr>
<tr>
<td>Bin 125</td>
</tr>
<tr>
<td>Bin 70</td>
</tr>
<tr>
<td>Bin 50</td>
</tr>
<tr>
<td>Bin 30</td>
</tr>
<tr>
<td>Bin 0</td>
</tr>
</tbody>
</table>


**Relevance**

- Cold-start emissions must be addressed to meet increasingly stringent emissions regulations (90% of emissions from cold-start (Bag 1))

**Objective/Approach**

- HC-Traps are a potential emissions control solution option for reducing cold-start hydrocarbon emissions
  - All traps not uniformly effective for all HC
- Target speciation of cold-start HC emissions from consumer, on-road vehicles
  - Specifically during first 250s of FTP-75 cold-start
  - Impact of aftertreatment catalysts on speciation

NMOG (non-methane organic gases); LDV (light duty vehicle); LDT (light duty truck); MDPV (Medium duty passenger vehicle); HCT (hydrocarbon trap); HC (hydrocarbon).
Low temperature emissions control challenges affect multiple platforms

**ORNL R&D portfolio spans wide range of applications, technologies, size scales, commercial readiness**

**ORNL Projects**

- **CLEERS (ACE022)**
  Model new trap materials and aging effects on SCR catalysts

- **Low Temperature Emissions Control (ACE085)**
  Discover new low T catalysts & traps

- **Lean Gasoline Emissions Control (ACE033)**
  Develop pathways for lean gasoline engines to meet emissions with minimum fuel penalty

- **Chemistry & Control of Cold Start Emissions (ACE153)**
  Understand how exhaust chemistry impacts device performance & design

- **Cummins Emissions Control CRADA (ACE032)**
  Understand how aging affects properties and performance of SCR catalysts

---

### Unique emissions profiles require variety of catalyst formulations and systems

<table>
<thead>
<tr>
<th>Efficiency Benefit</th>
<th>T range (°C)</th>
<th>Emissions* (g/kg)</th>
<th>Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoich. SI</td>
<td></td>
<td></td>
<td>HCT</td>
</tr>
<tr>
<td>Lean SI</td>
<td></td>
<td></td>
<td>TWC</td>
</tr>
<tr>
<td>CDC</td>
<td></td>
<td></td>
<td>GPF</td>
</tr>
<tr>
<td>LTC (ACI)</td>
<td></td>
<td></td>
<td>HCT</td>
</tr>
</tbody>
</table>

*(efficiency and emissions at 2000 rpm, ~2 bar BMEP)*

---

**See Backup Slide for abbreviations on this slide**
How to study the chemistry of cold-start emissions

Vehicle Platforms on Chassis Dynamometer

Truck A and Truck B: MY18, GDI pick-up trucks (25-30k on-road miles)

<table>
<thead>
<tr>
<th>Engine</th>
<th>Exhaust Modifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Truck A 2.7L Turbo (V6)</td>
<td>Removed: muffler, resonator</td>
</tr>
<tr>
<td>Truck B 5.3L NA (V8)</td>
<td>Removed: UB catalyst, muffler, resonator</td>
</tr>
</tbody>
</table>

Cold-Start:
- 1 cold-start/truck per day
  - Cold-start = 12 hour soak
- 1st, 250s of FTP-75

Sampling:

<table>
<thead>
<tr>
<th></th>
<th>Time Resolved</th>
<th>Cumulative 250s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FTIR</td>
<td>EEPS</td>
</tr>
<tr>
<td>Engine Out</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>ccTWC Out</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>HCT out</td>
<td>FY20</td>
<td>FY20</td>
</tr>
<tr>
<td>HCT+GPF Out</td>
<td>FY20</td>
<td>FY20</td>
</tr>
</tbody>
</table>

UB (underbody); MY (model year); NA (naturally aspirated); cc (close coupled)
**Cold-start emission Sampling Approach**

**TWC Out Sampling**

- **TWC** (three-way catalyst); **EC/OC** (elemental carbon/organic carbon); **DNPH** (2,4-dinitrophenylhydrazine); **LFE** (laminar flow element); **EEPS** (Engine Exhaust Particle Sizer); **FTIR** (Fourier-transform infrared spectroscopy)

**Engine Out/TWC In Sampling**

**Relevance**
- Technical

**Approach**
- Collaborative

**Future Work**
- Technical

**Technical Details**

- **Venturi Meter**
- **Tunnel Flow Out**
- **Filters**
  - Gravimetric, EC/OC
  - Empore, DNPH
  - Tedlar bags
- **Hydrocarbon Speciation**
- **EEPS**
- **FTIR**
- **Pump**
- **Heated filter**
- **Double Dilution**
  - w/ Thermal Denuder
- **TWC** (three-way catalyst)
Most Cold-Start (bag 1, 505s) HCs generated in 1st 250s

**Relevance**

**Approach**

**Technical**

**Collaboration**

**Future Work**

**TWC out Hydrocarbons**

**FID analysis**

**FTIR analysis: Truck A TURBO**

**FTIR analysis: Truck B NA**

- HC-traps will be located downstream of ccTWC in an underfloor location
- Cold-start HC emission at ccTWC out needed to study HC speciation impact on HC-trap effectiveness
- Greater than 85% of cold-start (bag 1, 505s of FTP-75) HCs in the first 250s
- Effectiveness of HC-traps is not a linear relationship with C1 HC emissions
  - Exhaust HCs more complex than C1 quantity

Ethanol
NM Paraffins
Methane
Olefins
Aldehydes
Aromatics
Alkynes

FID (flame ionization detector); THC (total hydrocarbons); HC (hydrocarbon); NM (non-methane)
Distribution of cold-start HC species change across ccTWC

- Significant drop in HC emission across TWC even during Cold-Start
- Both trucks had similar compositional distribution of HC C1 mass emissions at each location
- Distribution of HC species changes across ccTWC out: not just passing through
- Feed composition for development of ccTWC and HC-trap low temperature activity need to be different
- Cold-start THC at TWC out greater than full FTP targeted Tier 3 Bin 30 target (NMOG + NOx)
Detailed HC speciation by GC-MS provides identification of HC ≥ C5

**TWC out Hydrocarbons**

**FTIR HC Speciation**
- ethane (C2)
- isopentane (C5)
- cyclohexane (C6)
- ethylene (C2)
- propylene (C3)
- 1,3 butadiene (C4)
- isobutylene (C4)
- formaldehyde (C1)
- acetaldehyde (C2)
- acrolein (C3)

**Analytical HC Speciation**
- pentane (C5)
- octane (C8)
- 13-25 other (≥C5)
- 1-pentene (C5)
- 1-hexene (C6)
- formaldehyde (C1)
- acetaldehyde (C2)
- acrolein (C3)
- propionaldehyde (C3)
- crotonaldehyde (C4)
- butyaldehyde (C4)
- valeraldehyde (C5)
- benzaldehyde (C7)
- propionaldehyde (C3)
- crotonaldehyde (C4)
- tolualdehyde (C8)
- dimethyl benzaldehyde (C9)

- C6-C11 (next slide)

**Key Points**
- FTIR is ideal for small chain HC up to ~C4 (Distinct stretching regions)
- Analytical separation and identification by GC-MS provides more detail on species in exhaust
  - Major NM Paraffins: ethane and unbranched pentane and octane only account for ~31% of total TWC out

Total regulator C1 Mass (FID) → Compositional Distribution (FTIR major + Analytical minor) → Full HC Speciation (combination of FTIR + Analytical speciation)
Cold-start aromatics predominately larger, semi-volatile species

- Aromatics measured by FTIR method are “as C7” or toluene, measure stretch of the aromatic ring
- FTIR aromatic mass accounts for ~80% of total aromatics by analytical speciation (GC-MS)
  - GC-MS only identifies 9% of speciated aromatics as toluene
- TWC out aromatics are mix of fuel species other partial combustion products
- Only one species seen in Engine out speciation not seen at TWC out: tetramethyl benzene
Elemental carbon accounts for ~90% of total PM mass over first 250s.

Equates to nearly half of Tier 3 Bin 30 limit of 3mg total PM over entire FTP drive cycle.

Particle Number correlates to acceleration events in FTP.
- 76-95% of PN in 1st 250s

TWC reduces particle PN by 40-44%
Response to 2019 Reviewers’ Comments

• New Task in FY19;
• No previous reviewer response because 2020 AMR is first review
Collaborations and Coordination

**Collaborations**
- Umicore supplying HC-traps and GPFs for FY20 study
- Umicore and Ford technical staff acting as informal advisors on technical set-up of HC-trap vehicle testing
  - Umicore: John Nunan and David Moser
  - Ford Motor Co.: Jason Lupescu and Christine Lambert

**Coordination:**
- Share results CLEERS community

**HC-traps aged by SGS**
- according US Drive storage protocol

stoich/rich/lean cycling for 50 hr at 700 °C inlet temperature
Remaining Challenges

• Cold-start HC emission need to be reduced to meet future emission standards
  • HC-traps efficiency can vary by HC species

• Hybridization may reduce catalyst activity beyond vehicle cold-start due to drop in exhaust temperatures when engine is off

Future Work*  
(subject to change with funding levels)

• Measure detailed HC speciation after under floor HC-trap (FY20)
• Study impact HC-trap + GPF on HC speciation during cold-start (FY20)

• Evaluate the impact of hybridized vehicle on HC emissions (FY21)
• Measure the HC-trap trapping efficiency and speciation effectiveness from hybridized vehicle (FY21)
Summary

• Relevance
  – Hydrocarbon reduction during cold-starts when oxidation catalysts are not active will be needed to meet the more stringent HC emission standards for Tier 3 Bin 30 and beyond. HC-traps offer a potential solution but do not work uniformly for all hydrocarbon species.

• Approach
  – Use a chassis dynamometer to collect cold-start exhaust samples over the first 250s of FTP-75 drive cycle from consumer light-duty GDI pick-ups and collect analytical samples for detailed HC speciation by GC-MS
  – Evaluate which specific HC species are effectively trapped on a supplier developed HC-trap during cold-start

• Technical Accomplishments
  – Detailed speciation of HCs during first 250s of FTP cold-start at engine out and close-coupled TWC out. TWC out will be used as HC-trap In during FY20 study of HC-traps.

• Collaborations
  – Umicore and Ford technical experts are providing guidance on proper HC-trap testing on vehicles
  – Umicore supplying HC-traps and catalyzed GPFs

• Future Work
  – Vehicle evaluation of HC-trap and a HC-trap + GPF impact on the detail HC speciation of the cold-start emissions
  – Investigate the use of HC-traps for control of hydrocarbon emissions from hybridized vehicles.
# How to study the chemistry of cold-start emissions

**Vehicle Platforms on Chassis Dynamometer**

Truck A and Truck B: MY18, GDI pick-up trucks (25-30k on-road miles)

<table>
<thead>
<tr>
<th>Engine</th>
<th>Exhaust Modifications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Truck A</strong></td>
<td>2.7L Turbo (V6) Removed: muffler, resonator</td>
</tr>
<tr>
<td><strong>Truck B</strong></td>
<td>5.3L NA (V8) Removed: UB catalyst, muffler, resonator</td>
</tr>
</tbody>
</table>

**Sampling:**

<table>
<thead>
<tr>
<th>P</th>
<th>Time</th>
<th>Engine Out</th>
<th>TWC Out</th>
<th>HC-trap Out</th>
<th>HC-trap + GPF Out</th>
<th>Speciation/Analyzed</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bag</td>
<td>250s/505s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>Total HC, NOx, CO, CO2 (ppm)</td>
<td>FID, [CAI emissions analyzers]</td>
</tr>
<tr>
<td>Canister</td>
<td>250s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>C_5^-C_8 Hydrocarbons (ng/L)</td>
<td>GC-MS</td>
</tr>
<tr>
<td>Empore</td>
<td>250s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>C_9^-C_18 Hydrocarbons (ng/L)</td>
<td>Extraction + GC-MS</td>
</tr>
<tr>
<td>DNPH</td>
<td>250s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>Aldehydes (ng/L)</td>
<td>Extraction + HPLC-MS or HPLC-UV-Vis</td>
</tr>
<tr>
<td>PM mass</td>
<td>250s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>Particulate Matter (mg/L)</td>
<td>Gravimetric</td>
</tr>
<tr>
<td>PM EC/OC</td>
<td>250s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>Elemental &amp; Organic Carbon (mg/L)</td>
<td>Thermal-Optical</td>
</tr>
<tr>
<td>EEPS</td>
<td>250s/505s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>PN (#/s) and Size Distribution (nm)</td>
<td>Array of Electrometers (electrical mobility)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>time resolved (10Hz)</td>
<td></td>
</tr>
<tr>
<td>FTIR</td>
<td>250s/505s</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>FY20</td>
<td>Gaseous Concentrations (ppm)</td>
<td>IR (stretching frequency)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>time resolved (5Hz)</td>
<td></td>
</tr>
</tbody>
</table>

**Cold-Start:**
- 1 cold-start/truck per day (cold-start = 12hr soak)
- 1st, 250s of FTP-751
### ABBREVIATIONS for Slide 6

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUC</td>
<td>Clean-up catalyst</td>
</tr>
<tr>
<td>DOC</td>
<td>Diesel oxidation catalyst</td>
</tr>
<tr>
<td>DPF</td>
<td>Diesel particulate filter</td>
</tr>
<tr>
<td>GOC</td>
<td>Gasoline oxidation catalyst</td>
</tr>
<tr>
<td>GPF</td>
<td>Gasoline particulate filter</td>
</tr>
<tr>
<td>HCT</td>
<td>Hydrocarbon trap</td>
</tr>
<tr>
<td>LNT</td>
<td>Lean NOx trap</td>
</tr>
<tr>
<td>PNA</td>
<td>Passive NOx adsorber</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>TWC</td>
<td>Three-way catalyst</td>
</tr>
<tr>
<td>Stoich</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>SI</td>
<td>Spark ignited</td>
</tr>
<tr>
<td>CDC</td>
<td>Conventional diesel combustion</td>
</tr>
<tr>
<td>LTC</td>
<td>Low temperature combustion</td>
</tr>
<tr>
<td>ACI</td>
<td>Advanced compression ignition</td>
</tr>
<tr>
<td>PNA</td>
<td>Passive NOx adsorber</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>BMEP</td>
<td>Brake mean effective pressure</td>
</tr>
</tbody>
</table>