Hydrocarbon fouling of SCR during Premixed Charge Compression Ignition (PCCI) combustion

Jim Parks, Vitaly Prikhodko, Josh Pihl, and Sam Lewis

*Oak Ridge National Laboratory*

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Advanced Diesel Engine Combustion Techniques Present Different Emissions Challenges

Conventional Diesel Combustion

Premixed Charge Compression Ignition (PCCI) Diesel Combustion

Catalytic Control Options

DOC +
DPF +
SCR or LNT

PCCI reduces burden of NOx and PM control on aftertreatment (thereby reducing cost and fuel penalty), but higher CO and HC emissions result.
Objective

- The goal of this study is to investigate the effect of HC emissions from conventional and advanced combustion modes on the performance of the Fe- and Cu-zeolite SCRs

  - Catalyst cores were exposed to a raw engine exhaust from conventional and PCCI combustion on slipstream setup
    - Cu-zeolite SCR
    - Fe-zeolite SCR
  - Exposed samples were characterized on bench flow reactor
    - SCR performance measured before and after temperature ramp (oxidizing conditions)
  - HC were extracted and analyzed by GC-MS

Catalysts Fouled in Engine Exhaust

Performance Studied on Bench Reactor

Extracted HC analyzed by GC-MS
Catalyst cores were exposed to a raw engine exhaust from conventional and PCCI combustion on slipstream

- **1.9-liter 4-cylinder GM CIDI**
  - Variable geometry turbocharger
  - High pressure common rail
  - Cooled high-pressure EGR
  - Full-pass Drivven engine control system

- **1x3 inch sample cores cut from a catalyst brick were hydrothermally degreened in a laboratory furnace for 12hr**
  - Cu-zeolite SCR from 2010 Ford F-series exhaust system
  - Fe-zeolite SCR donated by Umicore Autocat USA (CLEERS reference SCR)

- **Catalyst cores were exposed to a raw engine exhaust from conventional or PCCI combustion**
  - Aggressive conditions: 3 hours, 115°C, 30k 1/hr SV (via Vacuum Pump and 0.063 in. orifice), no DOC/DPF upstream

**Engine Condition: 1500 rpm, 2.6 bar BMEP**

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<thead>
<tr>
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<th>Conventional</th>
<th>PCCI</th>
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<tr>
<td>Engine Out $\text{NO}_x$</td>
<td>1.02 g/bhp-hr</td>
<td>0.24 g/bhp-hr</td>
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<tr>
<td>Engine Out HC</td>
<td>1.35 g/bhp-hr</td>
<td>2.19 g/bhp-hr</td>
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<tr>
<td>Engine Out CO</td>
<td>3.12 g/bhp-hr</td>
<td>11.70 g/bhp-hr</td>
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**Schematic of engine exhaust slipstream for catalyst exposure to hydrocarbons**
HC were extracted and analyzed by GC-MS

- Hydrocarbons were extracted from a loaded sample using 50/50 hexane/acetone solution in a microwave-assisted extractor

- Extracts were concentrated, spiked with an internal standard, and then analyzed by GC-MS
  » Diesel range organic components
Shift to lighter, more volatile HCs in PCCI

- Surface HC are different between conventional and PCCI combustion modes
  - More HC from PCCI exposure (consistent with CO+CO$_2$ release results)
  - Shift to lighter, more volatile HC in PCCI
- No apparent difference is observed between Cu- and Fe-SCR
DRIFTS analysis shows distribution of HCs along catalyst

- DRIFTS detects HC variation along length of catalyst
  - DRIFTS=Diffuse Reflectance Infrared Fourier Transform Spectroscopy
- Under current exposure parameters, HCs observed along entire catalyst length
  - Qualitative distribution of HCs may be useful for modeling of HC fouling effects

![Graph showing HC species as function of position along flow axis](image-url)

- DRIFTS HC Signal relative to Catalyst (a.u.)
- Length along flow axis (mm)

- Cu SCR exposed to PCCI
- Cu SCR with no HCs
SCR performance was characterized on a bench flow reactor

- **Bench flow reactor conditions**
  - Inlet: 350 ppm NO\textsubscript{X} + 350 ppm NH\textsubscript{3}, 14% O\textsubscript{2}, 4.5% H\textsubscript{2}O, SV=30K 1/hr
  - Temperature Ramp: 5°C/min, 150-600°C
    - Ramp1: exposed sample (straight from the engine with adsorbed HCs and soot)
    - Ramp2: cleaned sample (cool sample back to 150°C after Ramp1 and repeat ramp)
  - Gas analysis with MKS FTIR

**Ramp1: Cu-SCR exposed to conventional combustion exhaust**

![Graph showing concentration over time and temperature](image)
Cu-zeolite shows more tolerance to HC fouling (vs. Fe-), but fouling from PCCI HCs more severe (for Cu-case)

- HC/soot fouling impacts mainly low temperature NOx conversion
  - Fe much worse than Cu as expected
  - PCCI and Conventional similar for Fe
  - PCCI worse than Conventional for Cu

- Performance loss reversible via higher temperature exposure (see “Cleaned” data plots)

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<td>Engine Out NOx</td>
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<td>Engine Out HC</td>
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<td>Engine Out CO</td>
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Bench Flow Reactor Conditions:
Inlet: 350 ppm NOx + 350 ppm NH₃ (ANR=1)
SV=30k/hr, 14% O₂, 4.5% H₂O
Oxidation and Release of HCs differs for Cu- and Fe-SCR

- During temperature ramp, HCs, CO, and CO₂ are released by SCR catalysts
- More C species on surface of Fe-zeolite sample
- More C for PCCI than conventional
- Prominent low temperature CO+CO₂ peak for Cu-zeolite
- Much more HC on Fe-zeolite
Oxidation and Release of HCs differs for Cu- and Fe-SCR

- Integrated results for total moles of HC and CO+CO₂ show differences due to catalyst formulation and combustion type
  - More total C trapped on Fe-zeolite
  - More total C trapped during PCCI (vs. Conventional)

- Larger difference in C released from PCCI and Conventional for Cu SCR
  - Note that PCCI has higher HC emissions (same exposure time)
  - C release results consistent with NOₓ performance results
NH₃ storage is not affected by stored HC

- Integrated results for total moles of NH₃ stored during stabilization step (prior to ramp) does not appear to be affected by HC+Soot present of the surface of the catalyst
  - More NH₃ stored on Cu-SCR as expected
Standard SCR Reaction Impacted More by Fouling

- Measured steady state NOx conversions for “standard” and “fast” SCR reactions:
  - Standard:
    - $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$
  - Fast:
    - $4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$

- At 200 C, fouling by PCCI exhaust:
  - reduced standard SCR NOx conversion
  - had no impact on fast SCR activity

- For temperatures 250 C and above, hydrocarbons desorbed and did affect SCR performance
Conclusions

• Reversible HC fouling was observed on Cu- and Fe-SCR
  » Aggressive HC conditions based on low exhaust temperature exposure

• At low temperatures Cu-zeolite shows more tolerance to HC fouling compared to Fe-zeolite (as expected)

• Higher HC levels from PCCI led to more fouling of low temperature performance
  » HC fouling effect differences between conventional and PCCI combustion HCs were more noticeable on Cu-zeolite catalyst

• HC chemistry extracted from SCR cores shows lower molecular weight HCs on SCR from PCCI exhaust exposure (vs. diesel-like HCs form conventional exhaust)

• No effect from HC fouling on NH₃ storage capacity was observed

• The standard SCR reaction (NO only) was impacted by fouling more than the fast (NO+NO₂) SCR reaction