Engine and Reactor Evaluations of HC-SCR for Diesel NOx Reduction

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Background:

Hydrocarbon assisted NOx SCR for automotive catalysis

- Copper zeolites late 80’s early 90’s
- Supported catalysts (PGMs and base metals) early 90’s
  - Bethke, Alt and Kung, Catalysis Letters, 1994
- Ag/alumina
  - Burch and Millington, Catalysis Today, 1996.
  - Shimizu et al., Applied Catalysis B: Environmental, 2000.
- DOE NOx Discovery Project
  - Initiated in August of 2002, completed end of 2007
  - Over 16,000 materials synthesized and evaluated
  - Ag/alumina selected as optimum material
Lean NOx Aftertreatment

Light Duty Diesel

US06 Catalyst Temp

Limited low temperature activity

Catalyst Operating Temperature (degrees C)

NOx Conversion Efficiency (%)

1 Aged 120 k mi
2 Aged 120 k mi

SV~12,500 h⁻¹
10% O₂
5% H₂O
5% CO₂
750 ppm CO
250 ppm H₂
100 ppm NO
sim-diesel #1
HC₁::NOₓ ~ 8

Ag/alumina catalyst
Cu-ZSM-5

SCR-Urea

SCR-HC

LNT

Pt/Alumina
Engine Results

Focus is the heavy duty, US dynamometer certification using the Duramax 6.6 liter diesel

• Catalyst volume:
  – Four, 5.0 liter bricks (20.0L total vol.)
  – emission measurements are after brick 3 and brick 4

• Reductant by in-exhaust injection:
  – diesel fuel
  – ethanol

• Federal test cycles:
  – Heavy duty FTP (HDFTP),
  – Cold-start HDFTP (CHDFTP)
  – Set 13 (Supplemental Emission Test)
Supplemental Emission Test (SET)

(aka Steady State Test / 13 Mode Test, Euro III - European Stationary Cycle / ESC)

Where:
- $n_{hi} =$ High speed as determined by calculating 70% of the maximum power. The highest engine speed where this power value occurs on the power curve is defined as $n_{hi}$.
- $n_{lo} =$ Low speed as determined by calculating 50% of the maximum power. The lowest engine speed where this power value occurs on the power curve is defined as $n_{lo}$.
- Maximum power = the maximum observed power calculated according to the engine mapping procedures defined in §86.1332.

\[
\text{Speed A} = n_{hi} + 0.25 \times (n_{hi} - n_{lo})
\]
\[
\text{Speed B} = n_{lo} + 0.50 \times (n_{hi} - n_{lo})
\]
\[
\text{Speed C} = n_{lo} + 0.75 \times (n_{hi} - n_{lo})
\]

\[
A_{WA} = \frac{\sum_{i=1}^{n} \left[ A_{Mi} \times WF_i \right]}{\sum_{i=2}^{\infty} \left[ A_{Pi} \times WF_i \right]}
\]

Where:
- $A_{WA} =$ Weighted average emissions for each regulated gaseous pollutant, in grams per brake horse-power hour.
- $A_{M} =$ Modal average mass emissions level, in grams per hour. Mass emissions must be calculated as described in §86.1342.
- $A_0 =$ Modal average power, in brake horse-power. Any power measured during the idle mode (mode 0) is not included in this calculation.
- $WF =$ Weighting factor corresponding to each mode of the steady-state test cycle, as defined in paragraph (b)(1) of this section.
- $l =$ The modes of the steady-state test cycle, as defined in paragraph (b)(1) of this section.
- $n =$ 13, corresponding to the 13 modes of the steady-state test cycle, as defined in paragraph (b)(1) of this section.

- rpm/load changes complete within first 20 sec of each mode
- 2 minutes at each non-idle mode, 4 minutes at idle
- 1 PM filter for over 13 modes
Diesel Aftertreatment testing architecture using 6.6 Duramax engine

- Diesel fuel
- Ethanol
Minimum temperature diesel fuel injection point

- Exhaust temperatures vary from 150 °C to 500 °C
- First 600 seconds show catalyst in temperatures no higher than 250 °C
- Conclusion: Almost half the HDFTP is completed before the exhaust reaches the optimum NOx conversion temperature
Low NOx efficiency because diesel fuel not injected below 280°C

EO NOx

NOx Std = 0.20 g/HP-hr

0.74 g/HP-hr 15L HC-SCR
0.59 g/HP-hr 20L HC-SCR

3.0 % Fuel economy penalty

15.6L UREA-SCR 82% NOx efficiency
Space velocity, oxygen concentration and gas temperature each contribute to the NOx conversion at a give engine operating point.
HDFTP NOx Emissions Results with EtOH

Minimum temperature ethanol injection point
HDFTP NOx Emissions EtOH

Start dosing 200°C

High NOx conversion at start-up

10L and 15L Instantaneous NOx Efficiency

Cumulative NOx g/NOx Eff.

NOx Std = 0.20 g/HP-hr

0.24 g/HP-hr 10L HC-SCR
0.13 g/HP-hr 15L HC-SCR

5.0% F.E. penalty Diesel Equivalent

Seconds
SET 13 NOx Emissions Results with EtOH

Conversions uniformly higher at each engine operating point
NOx conversions for cold start HDFTP are reasonable
### Engine Dynamometer Test Results

<table>
<thead>
<tr>
<th>Light-Duty w/ ULSD</th>
<th>Catalyst Volume</th>
<th>NOx Conversion</th>
<th>Fuel Economy Penalty</th>
<th>Weighted Emissions</th>
<th>Emission Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTP75</td>
<td>20L</td>
<td>60%</td>
<td>3.1%</td>
<td>0.640 g/mi</td>
<td>0.070 g/mi</td>
</tr>
<tr>
<td>US06</td>
<td>20L</td>
<td>76%</td>
<td>2.6%</td>
<td>0.149 g/mi</td>
<td>0.400 g/mi</td>
</tr>
<tr>
<td>HWYFET</td>
<td>20L</td>
<td>92%</td>
<td>2.4%</td>
<td>0.024 g/mi</td>
<td>0.070 g/mi</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heavy-Duty w/ ULSD</th>
<th>Catalyst Volume</th>
<th>NOx Conversion</th>
<th>Fuel Economy Penalty</th>
<th>Weighted Emissions</th>
<th>Emission Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot HDFTP</td>
<td>20L</td>
<td>60%</td>
<td>3.0%</td>
<td>0.59 g/BHP-h</td>
<td>0.20 g/BHP-h</td>
</tr>
<tr>
<td>SET 13-Mode</td>
<td>20L</td>
<td>65%</td>
<td>2.7%</td>
<td>0.63 g/BHP-h</td>
<td>0.20 g/BHP-h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heavy-Duty w/ Ethanol</th>
<th>Catalyst Volume</th>
<th>NOx Conversion</th>
<th>Fuel Economy Penalty</th>
<th>Weighted Emissions</th>
<th>Emission Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot HDFTP</td>
<td>15L</td>
<td>82%</td>
<td>4.3% (diesel eq.)</td>
<td>0.13 g/BHP-h</td>
<td>0.20 g/BHP-h</td>
</tr>
<tr>
<td>SET 13-Mode</td>
<td>15L</td>
<td>91%</td>
<td>4.7% (diesel eq.)</td>
<td>0.16 g/BHP-h</td>
<td>0.20 g/BHP-h</td>
</tr>
<tr>
<td>HDFTP (wtd. hot+cold)</td>
<td>15L</td>
<td>86%</td>
<td>4.7% (diesel eq.)</td>
<td>0.20 g/BHP-h</td>
<td>0.20 g/BHP-h</td>
</tr>
</tbody>
</table>

Light-Duty:  SAE 2008-01-2487 (M.B. Viola)

Heavy-Duty: submitted SAE 2009 (M.B. Viola)
### Dual-Catalyst Concept: HC-SCR + NH₃-SCR

**SOLUTION:**

- NOₓ + C₂H₅OH → N₂ + NOₓ + NH₃ → N₂

#### HC-SCR
- HC-SCR @ SV ~ 25,500 h⁻¹ +/- NH₃-SCR @ SV ~ 60,000 h⁻¹
- 6% O₂ / 5% H₂O / 5% CO₂ / 750 ppm CO / 250 ppm H₂
- 400 ppm NO / 431 - 1724 ppm C₂H₅OH (HC₁:NOₓ ~ 2.2 to 8.6)

#### NH₃-SCR
- 3.0 wt.% Ag₂O/Al₂O₃ + Cu-zeolite

- **Tune ethanol injection amount to “balance” NOₓ and NH₃ breakthrough**
- **High NOₓ conversion levels maintained while lowering amount of ethanol injected**
- **System optimization still required**

#### Dual-Catalyst Concept

- HC-SCR + NH₃-SCR
- Solution: NOₓ + C₂H₅OH → N₂ + NOₓ + NH₃ → N₂
- “fixed” HC₁:NOₓ ~ 8.6
- “variable” HC₁:NOₓ ~ 2.2  2.2  3.2  2.7  3.2  4.3  8.6
Engine Results Status

• With diesel as a reductant
  – HDFTP: 60% NOx reduction using 3x engine displacement (ED)
  – SET 13-Mode: 65% NOx reduction using 3x ED

• With EtOH as a reductant
  – HDFTP: 84% (1.5 ED), 91% (2.3 ED) NOx reduction
  – SET 13-Mode obtained 90% (1.5 ED) NOx reduction
  – Cold start HDFTP: 82% (2.3 ED)

• Poisoning and aging evaluations
  – Sulfur does poison, but is regenerable
  – Phosphorous does deposit, but does not appear to degrade performance abnormally
  – Heavy HC’s do poison, but are also regenerable
Summary

- **Accomplishments**
  - High-throughput technology has optimized the HC-SCR catalyst formulation
  - Effectiveness of diesel fuel and ethanol demonstrated in both reactor and engine testing
  - HC-SCR control strategy has been developed
  - Dual bed technology demonstrated
  - All degradation mechanisms identified and redaction schemes devised

- **Drawbacks**
  - High SV significantly reduces the NO\textsubscript{x} conversion efficiency
  - Poor diesel fuel vaporization at low T can limit reductant delivery
  - Degradation modes require close engine control
  - Hydrocarbon slip