Fuel-Borne Reductants for NOx Aftertreatment: Preliminary EtOH SCR Study

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Caterpillar: Alexander Panov, Paul Park

Other contributors: Williams-Pekin: Fuel grade ethanol
GE Betz: Blending agent, blend testing
Gromark: Blended fuel
Illinois DOCCA: Coordinated delivery

Sponsor: US DOE, OFCVT, Team Leader: Steve Goguen

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Background Leading to Current Effort

1. Previous work: E-diesel, urea SCR, adsorber catalysts.
2. HC SCR receiving less attention than other aftertreatment technologies.
3. ORNL formulated concepts for fuel-borne reductant systems. EtOH seen as a removable fuel-borne reductant for HC SCR.
4. Caterpillar marketed an EtOH SCR system for stationary diesels. Co-operative effort developed between Caterpillar and ORNL.
# Comparison of Urea SCR to EtOH SCR

<table>
<thead>
<tr>
<th>Urea SCR</th>
<th>EtOH SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial technology for stationary engines</td>
<td>R&amp;D, utility being explored</td>
</tr>
<tr>
<td>NOx Reduction &gt; 90% achievable for 300-500°C</td>
<td>NOx Reduction ~ 80% thought to be possible for 400-500°C?</td>
</tr>
<tr>
<td>Uses ~ 1:1 NH₃/NOx mol ratio</td>
<td>Uses ≥ 3:1 C/NOx mole ratio</td>
</tr>
<tr>
<td>Aqueous solution injected into exhaust</td>
<td>Used undiluted, can be fuel-borne</td>
</tr>
<tr>
<td>32.5% urea freezes at 12°F</td>
<td>Freezing not an issue</td>
</tr>
<tr>
<td>Can produce/slip NH₃, N₂O, inert PM, reactive solids</td>
<td>Unwanted products/slip likely:, NH₃, N₂O, aldehydes, HC</td>
</tr>
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</table>
Initial Project Objectives:

- Evaluate performance of EtOH reductant, Ag-Alumina SCR catalyst system on diesel exhaust. Look at unregulated emissions
- Demonstrate EtOH stripping from E-diesel & its usefulness for NOx reduction.
- Later: consider other fuel-borne reductants, catalysts
Ethanol Was Stripped From 15% E-Diesel

Using “mild distillation” nearly all EtOH was removed and then recovered.
Experimental Configuration

- Donated 1999 Cummins ISB, 5.9 L, With Cummins provided cooled EGR, upgraded fuel system, turbo., controls. Configured for “Near-2004” emissions.
- 285 hp DC motoring dynamometer
- Measured gases in exhaust via standard benches
- FTIR and GC-MS used to look for specific HCs, N₂O, NH₃, Acetaldehyde
Cummins 5.9 L Engine
Reductant Injector and Catalyst in the Exhaust
ORNL/NTRC Cell 3

7 L catalyst located 1 m downstream of the injector.

Automotive EFI injector downstream of turbo outlet.
SCR Performance Experimental Methodology

- **Shakedown, de-green** catalyst for ~10 hours at 400°C.

- **Performance Investigation at Two Engine Conditions / Space Velocities:** compared conversion at a low & high space velocity while maintaining similar catalyst temperature and NOx flux.

<table>
<thead>
<tr>
<th>Test Setting</th>
<th>Speed RPM</th>
<th>Torque ft-lbs</th>
<th>SV 1/h</th>
<th>Cat T °C</th>
<th>NOx g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVL8-M3</td>
<td>1115</td>
<td>230</td>
<td>21000</td>
<td>360-400</td>
<td>~1.5</td>
</tr>
<tr>
<td>~AVL8-M6</td>
<td>2225</td>
<td>180</td>
<td>57000</td>
<td>360-400</td>
<td>~2.1</td>
</tr>
</tbody>
</table>

**Fuel-Reductant Combinations:**

1. ECD-1          fuel-grade EtOH
2. ECD-1         “stripped” fuel-grade EtOH
3. E-diesel       “stripped” fuel-grade EtOH
4. ECD-1          reagent grade EtOH
Excellent NOx Conversion Was Achieved at 21000/h, 360-400°C

NOx conversion vs C/N ratio, 1115 RPM

Space Velocity ~ 21,000 1/h
Catalyst temperature: 360-390°C

ECD1, fuel EtOH, test 1
Excellent NOx Conversion Was Achieved at 21000/h, 360-400°C

NOx conversion vs C/N ratio, 1115 RPM

Space Velocity ~ 21,000 1/h
Catalyst temperature: 360-390°C
NOx Conversion Was Excellent at 21000/h and 360-400°C

Selectivity appeared to improved as catalyst is exposed to more sulfur

NOx conversion vs C/N ratio, 1115 RPM

Space Velocity ~ 21,000 1/h
Catalyst temperature: 360-390°C

1.5% fuel penalty: energy basis
Good NOx Conversion Achieved at 57000/h and 360-400°C

NOx conversion vs C/N ratio, 2225 RPM

1.5% fuel penalty: energy basis

NOx conversion very similar for the different fuel-reductant combinations

Space Velocity ~ 57,000 1/h
Catalyst temperature: 360-390°C
HC Slip Changed with Progression of Experiments

HC slip vs C/N ratio, 1115 RPM

- ECD1, fuel EtOH
- ECD1, fuel EtOH
- ECD1, stripped EtOH
- E-diesel, stripped EtOH
- ECD1, fuel EtOH
- ECD1, high grade EtOH

Space Velocity ~ 21,000 1/h
Catalyst temperature: 360-390 C
HC slip at high SV was about the same ppm level, mass flux is ~2.7 times greater.

HC slip vs C/N ratio, 21,000 1/h & 57,000 1/h

Catalyst temperature: 360-390°C

~ 0.5 g/hp-h

~ 0.19 g/hp-h
FTIR Results: Ammonia Emissions

- NH$_3$ @ 21000/h
- NH$_3$ @ 57000/h

NH$_3$ (ppm) vs. C1:NOx Ratio
In the past, some catalyst formed large amounts of $\text{N}_2\text{O}$.
FTIR Results: \( \text{NO}_x \), Versus Acetaldehyde Emissions

- **Acet @ 21000/h**
- **Acet @ 57000/h**

- **Acetaldehyde (ppm)**
- **C1: NO\(_x\) Ratio**
We Have Begun to Look at Other Fuel-borne Reductants

Note: much higher SV and NOx flux

7 liter Ag alumina catalyst, 2225 rpm, 360 deg.C, 90000 SV,

% NOX conversion

ethanol flow, wt% of fuel flow

EtOH

Octanol

Heptane
## Reductant stripping experiments

<table>
<thead>
<tr>
<th>REDUCTANT</th>
<th>BOILING POINT, deg.C</th>
<th>% BLENDED IN ECD1 FUEL</th>
<th>% SEPARATED (rotovap, 100 CC, 10 minutes, 90 deg.C, 200 mm Hg vacuum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>78</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>1-propanol</td>
<td>97</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>1-butanol</td>
<td>117</td>
<td>20</td>
<td>17.5</td>
</tr>
<tr>
<td>n-hexane</td>
<td>69</td>
<td>20</td>
<td>4.9</td>
</tr>
<tr>
<td>n-heptane</td>
<td>98</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>1-octanol</td>
<td>196</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>
Low Temperature Effectiveness of Catalyst

Low Temperature Evaluation: For low SV, catalyst temperatures near 250°C, 300°C, 340°C and 370°C were examined at two C/N ratios.
GC-MS Results Clearly Show Different Nature of Slip HC for The 3 EtOH “Grades”

Reagent grade EtOH

E-diesel distilled, fuel grade EtOH: evidence of gasoline & diesel components

Denatured, fuel grade EtOH: gasoline components seen

SV = 21,000 1/h

C9

C10

Time-->
Observations & Conclusions

- Ethanol SCR effectively reduced NOx emissions of diesel exhaust for catalyst temperatures between 360-400°C
  - moderate C1/NOx ratios
  - 90% for 21000/h and 80% for 57000/h
  - Some conversion observed at 250°C
- Saw catalyst performance improve with sulfur exposure
- Low levels of N₂O (< 6 ppm) were produced
- Ethanol was converted to acetaldehyde: slipped at 57000 1/h
- Ammonia was produced (high C/N, low SV), but may not be problematic
- Fuel-borne feasibility was demonstrated by stripping EtOH from E-diesel – use as reductant in the SCR system
- Technology may show promise - examining a broader set of parameters/conditions is warranted