Lean Gasoline Emissions Control: \(\text{NH}_3\) generation over commercial Three-Way Catalysts and Lean-NOx Traps

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Small improvements in gasoline fuel economy significantly decreases fuel consumption

• 132,000 million gallons of fuel used by cars and light trucks annually**
• New car and light-truck sales dominated by gasoline engines
• 10% fuel economy benefit † from base case of 22.6/18.1 mpg** has big impact
  – Saves >200,000,000 barrels gasoline annually
  – 5% of overall petroleum used
• HOWEVER...emissions control challenges exist

** - References: Transportation Energy Data Book, Ed. 29; *2009 data; **2008 data.
† - data from chassis dynamometer data at ORNL; see technical backup slides
Why NH$_3$-generation on TWCs?

- Zeolite-based NH$_3$-SCR has been shown to have very high NOx conversions over wide temperature window

- Urea injection systems are unlikely solution in lean gasoline systems
  - Significant additional cost would deter consumers
  - Higher engine out NOx will require more urea
    - introducing urea filling infrastructure issues on this scale
  - Other NH$_3$ introduction methods being studied

- Utilizing existing TWCs on gasoline vehicles is intriguing since they are already on the vehicle and will be needed on lean gasoline vehicles
  - NH$_3$ generation recently explored in “Passive SCR” approach*

- Goal is to investigate potential of using similar levels of PGM on TWC
  - while maximizing lean timing and minimizing fuel penalty

* - GM: SAE 2011-01-0306, SAE 2010-01-0366
“Passive” SCR for lean gasoline emissions control

- Slightly rich operation
  - AFR ≈ 14

TWC converts:
- NO to NH₃
- HCs to CO + H₂

SCR stores NH₃
"Passive" SCR for lean gasoline emissions control

lean operation
AFR ≈ 24

TWC converts:
CO to CO₂
HCs to CO₂ + H₂O

stored NH₃ reduces NOx
NH₃ GENERATION IN BENCH REACTORS
TWC and LNT studied in bench-core reactor with varying PGM content

- For bench reactor, focusing on modern TWC technology
  - 1.3L TWC is a 2 formulation combination (combo)
    - Total PGM: 0/4.0/0.16 g/L Pt/Pd/Rh (118 g/ft³ total PGM)
  - Front 0.6L of TWC is Pd-only no Ce
    - High PGM: 0/6.7/0 g/L Pt/Pd/Rh (190 g/ft³ total PGM)
    - No ceria-based OSC, but oxygen storage measured
      - Expected to proceed via Pd-O formation
  - Rear 0.7L of TWC is Pd/Rh+Ce w/ Ceria
    - Low PGM: 0/1.1/0.3 g/L Pt/Pd/Rh (40 g/ft³ total PGM)
  - Investigating each portion individually and in combined form
    - Degreened at 16h at 700°C in humidified air (2.7% H₂O)

- LNT is commercial formulation from lean gasoline BMW
  - 2.6L Pt/Pd/Rh = 7/3/1, 3.3 g/L-cat (94 g/ft³); Ba loading: 20 g/L (560 g/ft³); Ce: 56 g/L (1600 g/ft³)
  - Degreened at 16h at 700°C in humidified air (2.7% H₂O)
TWC is effective and tunable NH₃ generator

- **Example feed conditions:**
  - ~AFR | O₂ | NO | CO | H₂ | C₃H₆
  - 14.6 | 1.59% | 0.12% | 1.80% | 0.60% | 0.10%
  - 14.4 | 1.34% | 0.12% | 1.80% | 0.60% | 0.10%
  - 14.2 | 1.06% | 0.12% | 1.80% | 0.60% | 0.10%

- **NH₃ readily generated; varies with PGM**
  - For Pd-only TWC with high PGM:
    - All NO fed converted to NH₃ when very rich
  - For Pd/Rh+Ce (low PGM) TWC:
    - NH₃ production is still significant but reduced

- **At all conditions, >95% CO conversion**
  - C₃H₆ not observed in effluent

- **N₂O formation observed under lean conditions and varies with PGM content**
  - Up to 56 ppm with high PGM (Pd-only) TWC
  - Less than 10 ppm with low PGM (Pd+Rh) TWC

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Midbed Temperatures: 460-500°C
PGM content and Pt/Pd/Rh ratios impact NH$_3$ production

Evaluated multiple upstream catalyst formulations for NH$_3$ generation

High PGM (Pd-only) best for NH$_3$ generation
AFR and temperature dictate NH₃ production

Quantified NH₃ generation over Pd only TWC

- NH₃ generated over wide T window
- Need richer conditions at higher T

AFR:
- 14.0
- 14.1
- 14.2
- 14.3
- 14.4
- 14.59

TWC inlet T (°C)

NO to NH₃ conversion

0% 20% 40% 60% 80% 100%

250 300 350 400 450 500 550 600
NH₃ production over LNT and TWC occurs at temperatures relevant to vehicle operation and NH₃ storage on SCR

- Histogram of catalyst temperatures during drive cycle with BMW 120i
  - FTP (hot start)
  - 200-350°C for underfloor catalyst
  - 350-600°C for close-coupled (cc) TWC
- TWC: tunable NH₃ production 250-600°C

- NH₃ production temperatures over cc-TWC mesh well with NH₃ storage temperatures on underfloor SCR
  - More NH₃ storage occurs under rich/stoichiometric conditions
  - However switching from rich to lean will result in NH₃ release if over-saturated
PASSIVE SCR APPROACH IN BENCH REACTOR
Fully-automated two furnace bench reactor employed with TWC and SCR

**Lean**
- 600 ppm NO\(_x\)
- 8% O\(_2\)
- 5% H\(_2\)O, 5% CO\(_2\), Bal. N\(_2\)

- Switches from lean to rich when FTIR reads 20 ppm NO\(_x\)

**Rich**
- 1200 ppm NO\(_x\)
- 1.8% CO
- 0.6% H\(_2\)
- 0.1% C\(_3\)H\(_6\)
- 0.79%, 0.98%, 1.06%, 1.20% :O\(_2\)
- 14.0 14.1 14.2 14.3 :AFR
- 5% H\(_2\)O, 5% CO\(_2\), Bal. N\(_2\)

- Rich to lean when predicted NH\(_3\) storage is half filled
Manual optimization of cycling illustrates the potential of this approach

Flow reactor proof of concept: TWC+SCR under cyclic operation

- TWC inlet: 450 °C
- SCR inlet: 300 °C
- rich time: 60 s (AFR≈14)
- lean time: 110 s (AFR≈24)
- NOx conv.: 99.5%
- CO conv.: 93.9%

Estimated fuel economy gain: 5-6%

<table>
<thead>
<tr>
<th>Compound</th>
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<tbody>
<tr>
<td>NO</td>
</tr>
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<td>N₂O</td>
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<td>NH₃</td>
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<td>CO</td>
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<table>
<thead>
<tr>
<th>avg (ppm)</th>
<th>max (ppm)</th>
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<td>NO</td>
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<tr>
<td>NH₃</td>
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<tr>
<td>CO</td>
<td>1200</td>
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</table>
Fuel economy impacts of NOx emissions compliance with passive SCR

- Rich excursions to generate NH$_3$ increase fuel consumption due to:
  - temporary loss of lean operation
  - fuel economy boost (assumed 10%)
  - injection of excess fuel

- Overall impact on fuel economy depends on:
  - how long the engine can run lean
  - how rich it must go to generate NH$_3$
Fuel economy impacts of NOx emissions compliance with passive SCR

- Fraction of time lean depends on:
  - NH\textsubscript{3} yield during rich operation
    - decreases with TWC T and AFR
  - relative NOx flux (concentration and flow rate) during rich vs. lean
    - rich NOx = 2 x lean NOx here
- Exploiting flow changes during transient driving could increase lean operation time
- Higher than expected lean time at 300°C due to NOx storage over TWC during lean operation
  - possible formulation strategy
- For all conditions shown NOx conversion is > 99%
Fuel economy impacts of NOx emissions compliance with passive SCR

- Current implementation of passive SCR generates a net fuel economy benefit of 5-6% over a comparable stoich. engine
- Optimal AFR depends on TWC T

- Possibilities for reducing fuel penalty:
  - higher NOx flux ratios during transient operation on vehicle
  - addition of a NOx storage material
For a fixed cycle, addition of NOx storage significantly increases NH₃ formation

- Cycle Averaged Alpha is 3+ times higher than best TWC formulation
  - Alpha: NH₃ produced / NOx in effluent
Emissions other than NOx still present potential challenges

- Current operating strategies optimized for NOx reduction
- Minimal HCs observed with 0.1% $C_3H_6$ in feed
  - Consumed by reactions with NOx, O$_2$, or steam reforming
- Significant CO slips during rich operation
  - higher AFRs reduce but do not eliminate
  - CO slip a complicated function of TWC temperature due to water-gas shift kinetics and thermodynamics
  - downstream cleanup catalyst and secondary air may be required
- $N_2O$ may be problematic at low TWC temperatures
  - potential for mitigation by changes in formulation or operating strategy
Summary

- TWCs shown to be able to produce NH₃ over a broad temperature window
  - Key variables are PGM content, temperature and AFR

- Greater than 99% NOx conversion observed in passive approach
  - Lean-only conversion is >98%
  - CO slip is a concern and will need to be accounted for

- Significant fuel economy gain realized which could be improved with NOx storage on TWC
  - Future efforts exploring addition of NOx storage component on Pt-free TWC
Acknowledgements

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  — Catalysts and Monthly teleconferences
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• University of Wisconsin
  — Modeling (not discussed here) and Monthly teleconferences
  — Chris Rutland and Jian Gong
ADDITIONAL SLIDES
## Reaction Conditions

<table>
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<tr>
<th>Lambda</th>
<th>AFR</th>
<th>$O_2$</th>
<th>NO</th>
<th>CO</th>
<th>$H_2$</th>
<th>$C_3H_6$</th>
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<tr>
<td>1.000</td>
<td>14.59</td>
<td>1.59%</td>
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<td>1.80%</td>
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<td>0.996</td>
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<td>0.995</td>
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<td>0.12%</td>
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<td>0.987</td>
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<td>0.973</td>
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<td>1.80%</td>
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<td>0.960</td>
<td>14.00</td>
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<td>0.12%</td>
<td>1.80%</td>
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BMW lean GDI LNT benchmarking against CLEERS reference

CLEERS reference
Lean GDI, 2004, provided by Umicore

New LNT
Lean GDI, 2009, from BMW 120i vehicle

<table>
<thead>
<tr>
<th></th>
<th>CLEERS reference</th>
<th>New LNT</th>
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<tbody>
<tr>
<td>Cell density (cpsi)</td>
<td>625</td>
<td>413</td>
</tr>
<tr>
<td>Ba loading (g/ft³)</td>
<td>442</td>
<td>565</td>
</tr>
<tr>
<td>PGM loading (g/ft³)</td>
<td>103</td>
<td>94</td>
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<tr>
<td>Pt/Pd/Rh ratio</td>
<td>8/3/1</td>
<td>7/3/1</td>
</tr>
</tbody>
</table>

- Responsive to FY10 review comments
- Initial characterization indicates similar basic components in both LNTs
  - Reactor evaluation planned
  - Catalyst used in an ORNL lean gasoline engine-based project (see ACE033 talk)
Detailed elemental analysis of different LNT technologies on hand

**New LNT**
Lean GDI, 2009, from BMW 120i vehicle

<table>
<thead>
<tr>
<th>Element</th>
<th>Loading (g/ft³)</th>
<th>Loading (g/in³)</th>
<th>Loading (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>565</td>
<td>0.33</td>
<td>19.9</td>
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<tr>
<td>Ce</td>
<td>1572</td>
<td>0.91</td>
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<tr>
<td>Zr</td>
<td>122</td>
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<tr>
<td>La</td>
<td>69</td>
<td>0.04</td>
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<tr>
<td>Pt</td>
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<td>0.04</td>
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<tr>
<td>Pd</td>
<td>24</td>
<td>0.01</td>
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<tr>
<td>Rh</td>
<td>8</td>
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<td>0.3</td>
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</tbody>
</table>

PGM loading: 94 g/ft³ (0.05 g/in³, 3.3 g/L)

**CLEERS reference**
Lean GDI, 2004, provided by Umicore

<table>
<thead>
<tr>
<th>Element</th>
<th>Loading (g/ft³)</th>
<th>Loading (g/in³)</th>
<th>Loading (g/L)</th>
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<td>Ba</td>
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<td>0.256</td>
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<tr>
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<tr>
<td>Pt</td>
<td>72</td>
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<tr>
<td>Pd</td>
<td>23</td>
<td>0.013</td>
<td>0.8</td>
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<tr>
<td>Rh</td>
<td>9</td>
<td>0.005</td>
<td>0.3</td>
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</tbody>
</table>

PGM loading: 103 g/ft³ (0.06 g/in³, 3.6 g/L)
$\text{N}_2\text{O}$ formation can be significant on all catalysts and under lean or rich operation
**TWC (high PGM Pd-only) transients**

- **NH₃ profiles during lean to rich transitions:**

  ![NH₃ concentration at 300°C](image1)
  ![NH₃ concentration at 450°C](image2)
  ![NH₃ concentration at 600°C](image3)

- **CO profiles during lean to rich transitions:**

  ![CO concentration at 300°C](image4)
  ![CO concentration at 450°C](image5)
  ![CO concentration at 600°C](image6)
TWC (high PGM Pd-only) transients

- NO profiles during lean to rich transition illustrate some storage at low temperature:

  - 300°C
  - 450°C
  - 600°C

- N₂O profiles during lean to rich transitions:
SCR Screening:

NH₃–SCR Storage/Reaction:
SV = 30,000 hr⁻¹

Storage:
500 ppm NH₃
5% H₂O, bal. N₂

Reaction:
500 ppm NO
10% O₂
5% H₂O, bal. N₂

Steady-State NH₃–SCR:
SV = 30,000 hr⁻¹

500 ppm NO
500 ppm NH₃
10% O₂
5% H₂O