Ammonia generation over TWC for passive SCR NO\textsubscript{x} control in lean gasoline engines

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Gurpreet Singh, Ken Howden, Leo Breton

2014 CLEERS WORKSHOP
Gasoline engines represent the largest opportunity for reducing petroleum consumption in the U.S.

Reference: Transportation Energy Data Book, Ed. 29
Lean operation of gasoline engines improves efficiency, but creates emissions challenges.

BMW 120i lean gasoline vehicle on chassis dynamometer at ORNL

**Fuel economy improvement**

Fuel economy improvement with lean operation enabled relative to stoichiometric:

- FTP: 10%
- HFET: 14%
- US06: 4%

**NO\textsubscript{X} emissions with lean operation enabled**

Tier 2 Bin 2:

- FTP: 0.35 g/mi
- HFET: 0.35 g/mi
- US06: 0.35 g/mi

NOTE: fuel economy and emissions measurements included effects of lean NO\textsubscript{X} trap operation (SAE2010-01-2267, SAE2011-01-1218)
Passive SCR is a potential low cost strategy for reducing lean gasoline NO\textsubscript{x} emissions

Periodic excursions to slightly rich AFR: 
NH\textsubscript{3} generated from NO over TWC, stored on SCR

- Eliminates need for urea tank, injector, refills
- Reduces PGM loading relative to TWC+LNT
- Could reduce fuel penalty relative to LNT
  - TWC NH\textsubscript{3} generation: \( \lambda = 0.96 - 0.98 \)
  - LNT regeneration: \( \lambda = 0.8 \)

Normal lean operation: 
NO\textsubscript{x} reduced by NH\textsubscript{3} stored on SCR

SAE2010-01-0366, SAE2011-01-0306
Approach: Studies on Bench Reactor and Engine

- **Studies on Bench Flow Reactor**
  - Commercial, prototype, and model catalysts
  - Study of chemistry and mechanisms under simulated exhaust conditions
  - Two reactors simulate two catalysts in close coupled and underfloor positions

- **Studies on BMW 120i lean gasoline engine platform with Drivven open controller**
  - Realistic exhaust conditions
  - Full control of rich AFR for catalyst regeneration and reductant production/control
  - Scope does not include lean combustion optimization

Data supplied to modeling community via CLEERS
Ammonia generation over TWC for passive SCR NO\textsubscript{x} control on lean BMW 1-series engine (N43B20): catalyst and engine details

<table>
<thead>
<tr>
<th>Number of Cylinders</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement, cc</td>
<td>1995</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>12.0</td>
</tr>
<tr>
<td>Bore, mm</td>
<td>84</td>
</tr>
<tr>
<td>Stroke, mm</td>
<td>90</td>
</tr>
<tr>
<td>Rated Power</td>
<td>125 kW @ 6700 rpm</td>
</tr>
<tr>
<td>Torque</td>
<td>210 Nm @ 4250 rpm</td>
</tr>
<tr>
<td>OEM Emission Control</td>
<td>TWC and LNT</td>
</tr>
</tbody>
</table>

1.3 L TWC from PZEV 2009 Chevy Malibu

<table>
<thead>
<tr>
<th>formulation</th>
<th>Pt (g/l)</th>
<th>Pd (g/l)</th>
<th>Rh (g/l)</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>TWC combo</td>
<td>0</td>
<td>4.0</td>
<td>0.16</td>
<td>Y</td>
</tr>
</tbody>
</table>
Ammonia generation over TWC for passive SCR NO\textsubscript{X} control on lean BMW 1-series engine (N43B20): analytical details

2.0-liter lean GDI with Pd/Rh TWC at Oak Ridge National Laboratory

MKS FTIR: NH\textsubscript{3}, N\textsubscript{2}O, NO, NO\textsubscript{2}, CO etc.
FID: THC
SpaciMS: H\textsubscript{2} & O\textsubscript{2}

Exhaust Analysis
Up to 18% improvement in BSFC/BTE by operating lean

Performance and emissions at 2000 rpm 2 bar

<table>
<thead>
<tr>
<th></th>
<th>Stoich</th>
<th>LeanS</th>
<th>LeanH</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ</td>
<td>1.00</td>
<td>2.00</td>
<td>--</td>
</tr>
<tr>
<td>Gas Temp. [°C]</td>
<td>677</td>
<td>489</td>
<td>--</td>
</tr>
<tr>
<td>BSFC [g/kWhr]</td>
<td>354.9</td>
<td>293.4</td>
<td>--</td>
</tr>
<tr>
<td>BTE [%]</td>
<td>23.7</td>
<td>28.8</td>
<td>--</td>
</tr>
<tr>
<td>BSNO\textsubscript{X} [g/kWhr]</td>
<td>4.3</td>
<td>3.2</td>
<td>--</td>
</tr>
<tr>
<td>BSHC [g/kWhr]</td>
<td>10.0</td>
<td>9.5</td>
<td>--</td>
</tr>
<tr>
<td>BSCO [g/kWhr]</td>
<td>67.8</td>
<td>16.6</td>
<td>--</td>
</tr>
</tbody>
</table>

**MULTIMODE**

**STOICH**

![Graph showing performance and emissions at 2000 rpm 2 bar]

Stoichiometric
Lean
Homogeneous
Lean
Stratified
**NH₃ production over TWC is tunable with extent of rich operation**

- Complete NOₓ conversion for λ rich of stoich
- Richer λ increases NOₓ to NH₃ selectivity reaching 100% at λ=0.96
- At λ<0.96, NH₃ is limited by NOₓ availability
- At λ>0.96, NOₓ reduction is more selective to N₂
  - Modifications to TWC formulation may push to higher NH₃ selectivity at λ>0.96

\[ CO + H₂O ⇌ H₂ + CO₂ \]
\[ CₓHᵧ + xH₂O ⇌ xCO + (x+y/2)H₂ \]
\[ 2NO + 5H₂ → 2NH₃ + 2H₂O \]
... and NH₃ production over TWC is tunable with combustion strategy

**OEM A** = injection parameters used for stoich engine operation

**OEM B** = injection parameters used for stock lean NOₓ trap regeneration (λ=0.81)

- Temperatures are similar (560-650°C)
- N₂O was not detected
- CO at TWC_{OUT} is similar (within 5%)
- NH₃_{OEM A} is 2x NH₃_{OEM B}

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2
\]
\[
\text{C}_x\text{H}_y + x\text{H}_2\text{O} \rightleftharpoons x\text{CO} + (x+y/2)\text{H}_2
\]
\[
2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}
\]
**OEM A at \( \lambda=0.96 \) selected for maximum \( \text{NH}_3 \) production**

<table>
<thead>
<tr>
<th>Speed</th>
<th>Load</th>
<th>OEM Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 rpm</td>
<td>1 bar</td>
<td>Lean Stratified</td>
</tr>
<tr>
<td>1000 rpm</td>
<td>5 bar</td>
<td>Lean Homogeneous</td>
</tr>
<tr>
<td>1000 rpm</td>
<td>6 bar</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>2000 rpm</td>
<td>2 bar</td>
<td>Lean Stratified</td>
</tr>
<tr>
<td>2000 rpm</td>
<td>4 bar</td>
<td>Lean Stratified</td>
</tr>
<tr>
<td>2000 rpm</td>
<td>6 bar</td>
<td>Lean Homogeneous</td>
</tr>
<tr>
<td>2000 rpm</td>
<td>8 bar</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>3000 rpm</td>
<td>2 bar</td>
<td>Lean Stratified</td>
</tr>
<tr>
<td>3000 rpm</td>
<td>7 bar</td>
<td>Lean Homogeneous</td>
</tr>
</tbody>
</table>

Selected steady-state engine operating points cover the majority of the engine operating range encountered during FTP.
TWC is effective in reducing $\text{NO}_x (>99.6\%)$ with higher selectivity toward $\text{NH}_3$ at $\lambda=0.96$

- Greater than 80% $\text{NH}_3$ selectivity at $\lambda=0.96$
- 7-40% $\text{NH}_3$ selectivity at $\lambda=1.00$ (no $\lambda$ dithering)
Higher engine-out H$_2$ concentration at $\lambda=0.96$ result in higher NH$_3$ yield

Dashed line represents $2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$

Much higher engine-out H$_2$ concentrations at $\lambda=0.96$ results in higher NH$_3$ yields

Engine out NO$_X$ level has large impact on NH$_3$ production
HC emissions are not sensitive to changes in $\lambda$, while CO emissions are significant with higher $\lambda$.

HC emissions are formed in crevices and oil film layer where flame cannot propagate.

CO emission form at the flame front zone by incomplete oxidation of HC compounds and are controlled by $\lambda$. 

![Graph showing HC and CO emissions vs. speed (rpm) and load (bar)]
High NH₃ yields through wide range of temperatures and space velocities

Complete NOₓ conversion at all conditions with complete NOₓ to NH₃ selectivity in 400-600°C and 20-60K h⁻¹ space velocity ranges.

HC emissions are similar to HC emissions at λ=1.00 with HC conversion >80% at temperatures above 500°C.

At high temperatures, O₂ is selectively reacting with HC compared to CO.

With TWC temperature ranging from 450-700°C during typical driving conditions, NH₃ can be generated without excessive HC emissions.
Less richer $\lambda$ may be desirable from fuel economy and HC/CO emissions consideration

"Ideal" passive SCR: all of $\text{NH}_3$ generated over TWC during rich is stored on SCR and subsequently reduces all of $\text{NO}_x$ that passes through TWC upon switching to lean

Note: calculations are based on steady-state emissions and fuel consumption data
Lean gasoline passive-NH₃ SCR demonstrates >99% NOₓ reduction

- >99% NOₓ reduction efficiency achieved by cycling between rich (NH₃ production) and lean (NH₃ consumption for NOₓ reduction) modes
- 5.4% Fuel Economy gain at 2000 rpm/2 bar (steady-state)

![Graph showing NOₓ reduction over time](image-url)

\[
2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}
\]

\[
\text{NH}_3 + \text{*} \rightleftharpoons \text{NH}_3^*
\]

\[
2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2
\]

\[
4\text{NH}_3^* + 4\text{NO} + \text{O}_2 \rightarrow 4\text{*} + 4\text{N}_2 + 6\text{H}_2\text{O}
\]
Transient drive cycle may enable better fuel economy gain

- Acceleration during transient drive cycle creates opportunity for high Engine Out NO\textsubscript{X}, and thereby, high TWC Out NH\textsubscript{3}

- Modeled results shown based on steady-state engine map and FTP drive cycle

- Over entire cycle, more NO\textsubscript{X} created during stoichiometric operation; thus, efficient NO\textsubscript{X} to NH\textsubscript{3} catalysis can enable greater vehicle fuel economy

- Estimated transient fuel economy gain = 10.8% (vs. ~5-6% observed for steady-state operation)
Summary/Conclusions

• NH$_3$ production over TWC is tunable with combustion strategy and extent of rich operation
• Higher engine-out H$_2$ concentration at $\lambda=0.96$ result in higher NH$_3$ yield
• Engine out NO$_X$ level has large impact on NH$_3$ production
• HC emissions are similar to HC emissions at $\lambda=1.00$ with HC conversion $>80\%$ at temperatures above 500°C
• At high temperatures, O$_2$ is selectively reacting with HC compared to CO
• $\lambda>0.96$ may be desirable from fuel economy and HC/CO emissions consideration
• $>99\%$ NO$_X$ reduction efficiency with TWC+SCR approach on engine with $>5\%$ fuel economy gain over stoich
• Transient drive cycle may enable better fuel economy gain
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QUESTIONS?

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BMW 120i engine features three main combustion modes

- Spray guided combustion system design
- Piezoelectric injectors operate at different voltages as well as different durations
- Multiple sparks enable ignition under lean operation
- In addition to three main combustion modes, there is also an OEM rich homogeneous mode for LNT control of NO$_x$ emissions to meet EURO V NO$_x$ emission standards