Update on Engine Technologies and Emissions

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HEI Fuels Workshop
Chicago
Summary

• There are several low-CO$_2$ engine strategies being developed that can drop emissions by up to 40%.
  – Emissions and development challenges are summarized – LT, HC, lean NOx, PN

• Gasoline particulates are emerging as a major emissions issue
  – Difficult to remediate without filters
    • Rich zones during cold start, hot starts, accelerations, and LT ambient conditions
  – High PAH emissions
  – GPF solution

• Lean NOx solutions are focusing on lower-temperature and cold start

• LT oxidation catalysts are evolving – CH$_4$, HC, CO
Engines
<table>
<thead>
<tr>
<th>Technology</th>
<th>CO₂ Benefit*</th>
<th>Challenges</th>
<th>Penetration</th>
<th>Implications for emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDI</td>
<td>~ 3 – 5%</td>
<td></td>
<td>98% by 2022</td>
<td>PN</td>
</tr>
<tr>
<td>Atkinson cycle (+VVT)</td>
<td>3 – 10%</td>
<td>↓ peak power &amp; torque</td>
<td>Primarily in hybrids</td>
<td>Cooler exhaust</td>
</tr>
<tr>
<td>Adv. start-stop</td>
<td>2 – 5%</td>
<td>Consumer acceptance</td>
<td>45% by 2025</td>
<td>Warm start PN</td>
</tr>
<tr>
<td>Dynamic cyl. deactivation (+ VVL)</td>
<td>2 – 10%</td>
<td>Noise &amp; vibration</td>
<td>50% in 2025</td>
<td>Reduced idle emissions.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hotter exhaust Faster heat up for DPF regen</td>
</tr>
<tr>
<td>Lean-burn gasoline</td>
<td>15 – 25%</td>
<td>NOx, pSCR controls</td>
<td>Implemented EU</td>
<td>PN, NOx control, LT exhaust</td>
</tr>
<tr>
<td>2-stroke opp. piston Diesel</td>
<td>30 – 40%</td>
<td>Boost; new design</td>
<td>Development</td>
<td>Conventional DPF+SCR</td>
</tr>
<tr>
<td>Dedicated-EGR</td>
<td>20 – 25%</td>
<td>Durability</td>
<td>Development</td>
<td></td>
</tr>
<tr>
<td>GDCI</td>
<td>20-30%</td>
<td>Transient control</td>
<td>Research</td>
<td>Lean NOx; High HC (→ adv. ox. Cat, HC trap)</td>
</tr>
<tr>
<td>Pre-chamber combustion</td>
<td>15 – 20%</td>
<td>Complexity (2 chambers),</td>
<td>Research</td>
<td>Lean NOx</td>
</tr>
<tr>
<td>LTC (HCCI, RCCI)</td>
<td></td>
<td>Complexity – dual fuels</td>
<td>Research</td>
<td>Low NOx and PM emissions. LT and high HC emissions.</td>
</tr>
</tbody>
</table>

*Compared to NA PFI engines
Gasoline particulates
Achieving PN reductions across all real world conditions and over vehicle lifetime is challenging

Progress made on in-cylinder particulate formation minimized via optimization of:

- Injection parameters (# injectors, timing, spray pattern, pressures, etc.)
- Combustion chamber geometry
- Valve events
- Charge motion, etc.

Challenge is to maintain sustainable low PN over real world conditions

- Variation in speed/load
- Ambient temperature
- Deposits – Injectors, combustion chamber, valves
- Production tolerances
- Wear, aging
- Variation of fuel, lube oil quality
- Variability across fleet
- Measurement challenges
- …

Fraidl et al. (AVL, 2012)
Test drive cycle has a significant impact on tailpipe emissions

Particulates driven mostly by cold start and hard acceleration events

- High particle conc. for $t < 250$ s
- Unimodal, nucleation mode
  - Order of mag. higher conc.

Reference: Koczak, J. et al. / SAE 2016-01-0992

- GDI engines emit large # of very fine particles!
- Mass-based emissions are low (but still above CA limit of 1 mg/mi)
Soot composition & reactivity depend on fuel type and engine load

U. Birmingham, 2014 Cambridge Particle Meeting

<table>
<thead>
<tr>
<th>PM composition</th>
<th>Impact of fuel</th>
<th>Impact of engine load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed=1500 rpm; load=8.5 bar IMEP; λ=0.9; SOI=100° bTDC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ULG</td>
<td>Soot 35%</td>
<td>Volatility 65%</td>
</tr>
<tr>
<td>E25</td>
<td>Soot 36%</td>
<td>Volatility 64%</td>
</tr>
<tr>
<td>ETH</td>
<td>Soot 6.4%</td>
<td>Volatility 93.6%</td>
</tr>
<tr>
<td>DMF</td>
<td>Soot 29%</td>
<td>Volatility 71%</td>
</tr>
<tr>
<td>ULG 5.5 bar</td>
<td>Soot 9%</td>
<td>Volatility 91%</td>
</tr>
<tr>
<td>ULG 8.5 bar</td>
<td>Soot 36%</td>
<td>Volatility 64%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PM Reactivity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ULG</td>
<td>153</td>
</tr>
<tr>
<td>E25</td>
<td>124</td>
</tr>
<tr>
<td>ETH</td>
<td>83</td>
</tr>
<tr>
<td>DMF</td>
<td>114</td>
</tr>
</tbody>
</table>

|  |
|----------------|---|
| ULG 5.5 bar | 131 |
| ULG 8.5 bar | 153 |
GDI PN is characterized, and somewhat different from diesel. Smaller primary and aggregate size; less chrystalline. Oxidation catalyzed by ash.

GDI PN aggregate size is bi-modal and much smaller than for diesel. Primary particle size is also ~10nm smaller.

**GDI PN oxidation rates depend on ash content.**

$t_{80}$ is time to 80% oxidation.

Gasoline-derived GDI soot appears to be graphitic similar to diesel soot in TEM observation.

PDF data verify Raman results:
- Degree of crystalline structures: GDI soot < Diesel soot
- GDI soot shows no distinct change with engine conditions.

ANL, CLEERS, 5-14
GDI engines have high PAH emissions.

2013 Ford Focus GDI has PAH emissions in the upper percentiles of the whole Toronto fleet.

Univ Toronto, Environ Sci and Techn, 1/16

PAHs are soot precursors, so GDI soot may be “immature”.

E10 GDI PAH emissions ~4X higher on FTP-75 than for similar PFI pick-up truck. PM-based PAHs 14X higher. Large PAHs 35-135X higher.

<table>
<thead>
<tr>
<th>2012 MY Mazda 3</th>
<th>2013 MY Ford F150</th>
<th>2014 MY Chevrolet Silverado</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0L Wall-guided, DI</td>
<td>3.7L Wall-guided, DI</td>
<td>5.3L Wall-guided, DI</td>
</tr>
<tr>
<td>Inline, 4 cylinders</td>
<td>V6</td>
<td>V8</td>
</tr>
<tr>
<td>115 kW at 8000 rpm</td>
<td>225 kW at 6500 rpm</td>
<td>285 kW at 5800 rpm</td>
</tr>
<tr>
<td>203 Nm at 4000 rpm</td>
<td>377 Nm at 4000 rpm</td>
<td>519 Nm at 4100 rpm</td>
</tr>
<tr>
<td>13:0.1</td>
<td>10.5:1</td>
<td>11:0:1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>California LEVII, SULEV</th>
<th>California LEV II, ULEV</th>
<th>California LEV II, ULEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>18,851</td>
<td>13,700</td>
<td>2,649</td>
</tr>
</tbody>
</table>

UC-Riverside, SAE PF&L, 10/16

E10: GDI has up to 14X more PM-PAHs than similar PFI vehicle. Mazda GDI car has 2.7X more PM-PAHs than large PFI pick-up truck.

Gas PAHs: GDI 4.3X higher than PFI
Particulates during cold-cold start (7 °C) shown to exceed limits even for PFI vehicles


- PN from GDI mostly in accumulation > 50nm mode
  - Enrichment at low T, wall & piston wetting
- PN from PFI mostly < 50nm mode
- Particulates mostly “solid”
- Average PN over 180s: $3.1 \times 10^{13}$ for GDI & $2.1 \times 10^{13}$ for PFI
- Almost all vehicles exceed limit
  - DPF seen to be very effective for Diesels

PN for different vehicles 180s after cold start at 7C.
PN exposures can be high in parking garages.

PN emissions from modern GDI car as measured by the trail car in a parking facility. 150,000 to 700,000/cm$^3$. Outside background is 3000/cm$^3$. Timeframe here is 100 sec.
Due to high hot-start PN emissions, an HEV might have higher PN emissions than a conventional vehicle.

- Engine bench simulation of D-segment HEV with 50 kW electrical system, 1.3 kW-hr battery
- Engine used only 28% of time during transients and high load.
- “HEV” on NEDC has 4.6X PN vs. conventional operation.
- **Caution:** Not calibrated nor optimized for HEV

**Comparison of conventional and hybrid driving operation at the engine test bench on NEDC cycle**

- B-segment vehicle
- 1.6 liter GDI
- Euro 5b
- Two close coupled TWC
- Uncoated GPF
- Fuel: EN 228, 4.8% EtOH, 31.7% aromatics, research octane 97.2, 3 ppm sulfur

\[ \text{Tot. PN} = 2.6 \times 10^{12} \text{ part / km} \]

\[ \text{Tot. PN} = 1.2 \times 10^{13} \text{ part / km} \]

**IFP, SAE 2016-01-2283**
Across engine types, PM may not be a good indicator of PN. At any given PM level, PN can vary up to 1.5 orders of magnitude.
Evolution of light duty GPF architectures to meet particulate regulations

Broad introduction of GPF (uncoated and coated) – EU, Beijing and CARB

EU5/6b / LEV II/III (@3-6mg/mi)

EU6c/7 / Beijing 6 / LEV III (@1-3mg/mi)

TWC Integration into GPF

GPF for Filtration only
Comparison of soot oxidation on bare and coated GPF


<table>
<thead>
<tr>
<th>Bare GPF</th>
<th>Coated GPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2”x5.5”, soot load ~ 0.52g</td>
<td>2”x4.5”, soot load ~ 0.52g</td>
</tr>
</tbody>
</table>

Complete oxidation to CO$_2$ on coated GPF due to PGM
PM characteristics from Lean GDI engines depends on combustion mode. GPFs effective for all conditions

**Reference:** Parks J. et al. (ORNL), SAE 2016-01-0937

| Engine | 2008 BMW 1-series 120i, 2.0L, 4-cyl., naturally aspirated |
| Combustion modes | Lean stratified, Lean homogenous, Stoichiometric |
| GPFs | 200/12, 5.66”x6”, Bare, Underfloor |

**PM depends on combustion mode**
- Order of magnitude higher for lean stratified mode
- Mean particle size smaller for stoichiometric
- Organic C content PM: Lean stratified < stoichiometric < Lean homogenous

**GPFs capture most particles in all cases**
- Filtration efficiency > 95% over wide operating range

**PM depends on NOx control strategy**
- LNT cycling produced higher PM than lean-rich cycling for passive SCR
- GPFs highly effective even during transients

**Passive SCR**
- Lean Stratified

**LNT**
- Lean Stratified

**Organic content of PM primarily paraffins from engine oil**
- Little/no PAHs found as reported in stoich. GDI engines
Lean NOx Control
Passive SCR with lean gasoline engines shown to achieve > 99% deNOx and 11.5% fuel consumption benefit

Reference: Prikhodko V. et al. (ORNL), SAE 2016-01-0934

Engine: 2008 BMW 1-series 120i, 2.0L, 4-cyl., GDI, naturally aspirated
Test conditions: Load step conditions - Engine alternated between lean ($\lambda = 2.0$, 2 bar BMEP) and rich ($\lambda = 0.97$, 8 bar BMEP) operation

1) At NH$_3$/NOx = 1.13:
   - NOx conversion = 99.5%
   - % fuel benefit = 11.5%

2) Higher NH$_3$/NOx: NH$_3$ slip and decreased fuel benefit

3) Increased cycle time leads to decreased NOx conversion (NH$_3$ oxidation during longer lean period)

4) Low CO conversion still a challenge
A new Pd-zeolite passive NOx adsorber has impressive cold-start NOx storage capacity. Desorbs at 250-400°C.
Urea dosing increases PN count by 3-5X. 80% of PN on WHTC from urea.

- DEF dosing increases particle count by 460% to 610% over the WHTC
- Propose HNCO polymerization, urea pyrolysis, and urea micro-explosions during evaporation as the leading causes
- Under normal urea dosing over 80% of the total particle count was found to be DEF-based.
- Increasing ET temperature from 300 to 400 °C decreased the DEF-based particle count by 15% for an ANR = 1.1.
- Coupled with the TGA results, it is plausible that this volatile fraction of the DEF-based particles were urea or biuret.
Oxidation Catalysts
DOCs and DPFs can capture LTC volatile PM via an adsorption mechanism. Lighter PM eventually breaks through. DOC efficiency also impacted by adsorption saturation.

DOC conversion efficiency in LTC mode drops with time from 85% to 40% then stabilizes after 80 minutes, despite T>190C. Zeolite HC adsorption and saturation.

LTC HC emissions over the duration of the test is ~30% higher than for conventional combustion (FTIR might be missing species).

Most of LTC PM is volatile. Nearly all soot is captured by DPF.

LTC DPF PM emissions increase but with delay as it also becomes HC-saturated. DPF can remove LTC non-soot particles via adsorption.
Bimetallic catalysts on dual component support shows improved low-T CH$_4$ oxidation

Reference: A.I. Osman et al. / Applied Catalysis B: Environmental 187 (2016) 408–418

Context
Natural gas is attractive as abundant and clean burning fuel but total combustion important due to global warming potential

Background
Pd known to be most effective for catalytic CH$_4$ combustion -
- Proceeds through (a) dissociation & (b) oxidation via PdO
For enhanced activity:
1) Addition of an O$_2$ carrier $\rightarrow$ TiO$_2$
2) Support acidity $\rightarrow$ η-Al$_2$O$_3$ or H-ZSM-5
3) Reduced deactivation/sintering $\rightarrow$ CeO$_2$
4) Use of bimetallic catalyst $\rightarrow$ Pt

Improved low T activity achieved
- Optimized combination of four components – Pd, Pt, acidic support & O$_2$ carrier – shown to enable highly active and stable catalyst
  - Optimum at 17.5% TiO$_2$ on ZSM-5(80)
  - T$_{10}$ was observed at only 200 °C
- Role of bimetallic catalyst in improving catalyst stability confirmed
  - On addition of platinum, no decrease in the catalyst activity over 50 h at 250 °C

T$_{10}$ achieved at 200 °C
17.5%TiO2(5 wt% Pd, 2 wt% Pt, H-ZSM-5(80)
Summary

• There are several low-CO₂ engine strategies being developed that can drop emissions by up to 40%.
  – Emissions and development challenges are summarized – LT, HC, lean NOx, PN

• Gasoline particulates are emerging as a major emissions issue
  – Difficult to remediate without filters
    • Rich zones during cold start, hot starts, accelerations, and LT ambient conditions
  – High PAH emissions
  – GPF solution

• Lean NOx solutions are focusing on lower-temperature and cold start

• LT oxidation catalysts are evolving – CH₄, HC, CO
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