Emissions Control for Natural Gas Fueled Trucks

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Natural Gas Workshop at NREL
July 25, 2017
Emission Regulations

• “Emissions” can mean…
  – **Greenhouse Gas Emissions**
  – **Criteria Emissions** that affect air quality
    • Of which, criteria emissions include: oxides of nitrogen (NOx), non-methane hydrocarbon (MMHC), carbon monoxide (CO), particulate matter (PM)
    • Also, evaporative emissions, ammonia (NH₃), and Mobile Source Air Toxics are of concern

• EPA Federal regulations for Medium-Duty and Heavy-Duty trucks:
  – Greenhouse Gas Emissions Standards and Fuel Efficiency Standards for Medium- and Heavy-Duty Engines and Vehicles (Phase 1 and Phase 2)
    • Includes emission regulations for CO₂ as well as N₂O and CH₄
  – Exhaust Emission Standards for Heavy-Duty Highway Spark-Ignition and Compression-Ignition Engines
    • Includes NOx, NMHC, CO, and PM

Leakage of CH$_4$ is a critical factor in Well-to-Wheels Greenhouse Gas emission analysis of NG for transportation

- Concern over NG leakage as GHG problem has been expressed in multiple publications
- Leak rates uncertain but can easily overwhelm contribution from tailpipe emissions

Variations in upstream chemistry/processes affect tailpipe emissions

Increased availability of NG via tight gas production from shale enables low cost fuel potential

Variations in NG composition and contaminants at end use point (engine/vehicle) exist and are a concern

NG variability that affects combustion will affect exhaust composition; if controls mitigate effects, emissions changes mitigated too

Engine emissions (species and temperature) depend on combustion (lean vs. stoich) and inlet fuel chemistry

NG engine aftertreatment shares similar components to gasoline/diesel engines, but application design differs (for CH₄, etc.)

Regulated species: need to assess sulfur impacts and define hydrocarbon chemistry; PM also a potential concern

CH₄ and N₂O impact Greenhouse Gas emissions requirements; oxidation of CH₄ notoriously difficult for catalysts
Natural Gas fuel variation characterized in CRC Report

- **NG Characteristics that Vary (as function of time and region)**
  - **Methane Number** [89.5-103] (higher value means more CH4 content)
  - **Moisture content** (due to compression/handling at distribution end) [0-11 lbm/MMscf]
  - **Wobbe index** (higher heating value/square root of specific gravity)
  - **Heavy HC** ($C_{12+}$) content [impurity levels, varies site to site, zero some sites] (from compressor oil)
  - **Sulfur content** [0-8 ppmw]
    - Includes carbonyl sulfide, alkane sulfides, mercaptans, and disulfides (but **not** H$_2$S)

Variations on these scales will minimally affect aftertreatment if simply passed through to exhaust, **but**…if variations cause control issues, criteria pollutant levels could change and affect aftertreatment.

Sulfur always an issue for catalysts.

“Natural Gas Vehicle Fuel Survey”, CRC Project No. PC-2-12, June 2014
Emissions control challenges differ with combustion strategy, but common fundamental challenges emerge.

**Efficiency Increases, BUT...Exhaust Temperatures Decrease**

Stoichiometric Spark Ignition

Lean Premixed Spark Ignition

Lean Premixed Diesel Pilot

Direct Injection Diesel Pilot

Three-Way Catalyst (TWC)

Lean Aftertreatment w/ NG, Urea

Lean Aftertreatment w/ NG, Diesel, Urea

Cold Start  | CH₄ Control  | NH₃ Control  | Lean NOx  | CH₄ Control  | Low Temps  | Lean NOx  | CH₄ Control  | Low Temps  | PM Filters  | NMHC Control

**Common Need #1:** Efficient Catalytic Conversion of CH₄ at Low Temperatures

**Common Need #2:** Efficient Reductant/Fuel Utilization (and choice)*

**Common Need #3:** Cost- and Size-Effective and Durable Aftertreatment

*Note: Greenhouse Gas Emissions resulting from urea production are now common in regulatory analysis of overall vehicle Greenhouse Gas Emissions*
Common Need #1: Efficient Catalytic Conversion of CH₄ at Low Temperatures
CH$_4$ oxidation “light-off” over oxidation catalysts occurs at higher temperatures than HCs with C-C bonds

- CH$_4$ oxidation fundamentally more challenging than other HCs

Many challenges are associated with catalytic conversion of CH\textsubscript{4}

- Platinum Group Metal (PGM) catalysts are needed for CH\textsubscript{4} oxidation with Pd giving the best CH\textsubscript{4} oxidation performance
- Low temperature CH\textsubscript{4} conversion is extremely difficult
- Oxidative state of active site (Pd vs. PdO) affects CH\textsubscript{4} conversion
- Short-term thermal exposure history affects CH\textsubscript{4} conversion
- CH\textsubscript{4} conversion sensitive to poisoning by Sulfur and other impurities
CH$_4$ conversion has multiple impacts on efficiency and emissions of the system

- CH$_4$ (Greenhouse Gas) Control
- Thermal Management (exotherm from CH$_4$ oxidation)
- Low Fuel Penalty for Lean NOx Reduction
- Efficient Stoichiometric NOx Reduction with TWC
- Utilization (reforming) of CH$_4$ to enable higher combustion efficiency and lower emissions
Common Need #2: Efficient Reductant/Fuel Utilization (and choice)*
**CH₄ control for lean engines presents challenge for Greenhouse Gas Emissions (ARPA-E example shown)**

- **ARPA-E GENSETS program** aimed at developing high efficiency natural-gas-fueled CHP generators for residential applications

- Team led by Mahle Powertrain developing an ultra-lean-burn genset
  - uses Mahle Jet Ignition (fueled pre-chamber)

- Project currently on track to meet GENSETS program goals except GHG emissions
  - CH₄ accounts for ~1/3 of GHG emissions (high GWP multiplier)
  - state-of-the-art methane oxidation catalyst (MOC) unable to convert CH₄ under anticipated engine exhaust temperatures and compositions (lean conditions, T < 350 °C)
  - Lean-rich cycling required for LNT (Lean NOx Trap)

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**Estimated GHG Emissions**

![Graph showing GHG emissions for CH₄ and CO₂ at different lambda values](https://arpa-e.energy.gov/?q=programs/gensets)

**CH₄ conversion over MOC in synthetic exhaust mixtures**

![Graph showing CH₄ conversion with different lambda values](https://arpa-e.energy.gov/?q=programs/gensets)

**MOC, LNT, HX**

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*https://arpa-e.energy.gov/?q=programs/gensets*
CH₄ conversion to CO/H₂ can enable higher engine efficiency via thermochemical recuperation

- GTI (Gas Technology Institute) and Cummins collaborated on a CEC project for stationary NG engines
- Thermochemical recuperation was utilized to reform CH₄ to CO/H₂ and increase engine efficiency
- Durability issue in the reforming catalyst were cited as problematic in maintaining engine efficiency gains
- Durable NG reforming catalysts are needed to enable combustion improvement

CEC Final Report by GTI, Report# CEC-500-2013-106
Common Need #3: Cost- and Size-Effective and Durable Aftertreatment
Three-Way Catalysis for NG Trucks Shown Effective in CARB Project

- Goal of 0.02 g/bhp-hr NOx demonstrated on Cummins ISX12G (12-liter) engine with 9-liter close coupled and 20-liter underfloor Three-Way Catalysts (TWCs)
- Durability and NH₃ control also demonstrated
- Cost and size reductions and CH₄ control can improve commercial outlook

CNG Final Results over FTP and RMC-SET Cycles

Well below the project target of 0.02 g/bhp-hr over FTP cycle

Seungju Yoon (CARB), www.arb.ca.gov/research/veh-emissions/low-nox/lownox-cleers.pdf
Fuel impurity and lubricant component can impact emissions control systems over lifetime of vehicle

- High durability requirements of emissions control; poison effects on degradation important

- Biodiesel compatibility study has shown how a 1 ppm impurity can impact catalysts
  - Study by collaborators NREL, ORNL, NBB, MECA, and Ford investigated potential harmful effects of Ca, Na, and K on catalysts
  - Trace impurities NaOH/KOH from biodiesel production process can build-up and have big impact
  - Na and K displace Cu in zeolite framework
  - Results in Cu-oxide on surface of washcoat

- As NG feed streams and lubricant formulations change, it is important to understand what impurities are prevalent and how to minimize
  - Na + K come from biodiesel synthesis process and are regulated by producers
Particulate Matter (PM) from NG Engines

PM related Natural Gas Exhaust Constituents

- Mechanical wear produces small metal particles
- High Lubricant use generates organic hydrocarbon (HC) aerosols
- Organic HC from lubricant can condense on metal particles facilitating distribution from exhaust to external environment
- Small particle size + OC and Metal content creates potential health concerns

Fuel composition and Engine operation influence

- Particles size distribution
- Quantity of particles (#/kWh)

Figure 5. Bus-type average concentrations of V, Al, P, Zn, Na, Sr, K, Ba, Fe, Cu, organics (Org), and rBC for the EURO III, hybrid, ethanol, and CNG buses at the depot and on-road. For K the concentrations are divided by 100 and for Sr and Ba multiplied by 100 in order to get them to the same scale.


- Overall, need to study PM emissions and design specific control approaches
- Note: for diesel+NG fuel engines, optimal PM control approach needs exist

Considerations relative to other emission control R&D

- **Modeling** of specific NG processes can enable improvements in emission control system design and controls optimization
  - CLEERS (Crosscut Lean Exhaust Emissions Reduction Simulations) is a DOE-supported initiative to simulate emission control devices
    - www.cleers.org

- **Thermal management** may aid in keeping catalysts at optimal temperature conditions

- **Sensors** can assist in the control of emission control systems (and engines)

- **Controls** enable emission control over a wide range of transient operating conditions

- **Low Temperature Aftertreatment Protocols** are being utilized in DOE Vehicle Technology Office programs to provide a common metric for catalyst performance assessment under conditions relevant to industry stakeholders
  - Protocols defining exhaust compositions for NG engines will be beneficial
Low Temperature Aftertreatment Protocol Performance: CH$_4$ is difficult to control using commercially available emissions control catalysts, including three-way catalysts.

Chevy Malibu TWC aged* 50 h 800 °C

simulated exhaust*:
\[ \lambda = 0.999 \]
13% H$_2$O
13% CO$_2$
1670 ppm H$_2$
5000 ppm CO
1000 ppm NO
3000 ppm C$_1$ HC
0.70-0.86% O$_2$
SV = 30,000 h$^{-1}$

"E10":
65% i-C$_8$H$_{18}$
25% C$_6$H$_5$CH$_3$
10% C$_2$H$_5$OH

*aging and experiments conducted according to the U.S.DRIVE LTAT Low Temperature Oxidation Catalyst Test Protocol
Summary of Potential Research Needs

• Efficient CH$_4$ conversion at low temperatures
• Efficient utilization of CH$_4$ for emission control and efficient combustion
• Sensors to enable optimal control of emission control system
• Control strategies to optimize emission control performance during transient vehicle operation
• Thermal management strategies for optimal emissions control
• Assessment of durability implications from fuel composition and lubricants
• Assessment and mitigation of particulate matter emissions
• Models that capture specific NG catalyst performance
• Reduced fuel/reductant use for emissions control (reduce “fuel penalty”)
Backup Slides
CH₄ oxidation via catalysis is fundamentally difficult

- A lot of what we know comes from producing energy more efficiently than traditional thermal combustion in gas-turbine combustors via catalytic combustion.

- Abatement of CH₄ emissions is, of course, much more difficult than NMHCs because the methane’s greater stability (stronger C-H bonds which are, thus, more difficult to activate).

- Difficulties for methane emission control from CNG vehicles enumerated as:
  - Fairly low (500-550 °C) operating temperatures
  - Fairly low (500-1000 ppm) methane concentrations
  - Presence of water vapor and CO₂
  - Presence of SOx (~1 ppm) and NOx

- Primary catalyst families are noble metals (primarily Pt and Pd) and, perhaps transition metal oxides for lean operation
Characteristics of precious metal-based catalysts for methane oxidation

- For all of these PM-based catalysts, optimum performance is achieved at λ’s slightly less than 1
  - More fuel efficient lean operation probably will require a different class of catalyst materials
- Higher temperatures are required compared to oxidation of other HCs, so aging (including PM sintering) can be an even more significant issue.
- Water and sulfur are potent inhibitors of the CH$_4$ oxidation reaction.
- Light-off curves display unusual hysteresis that might effect control strategies (figure from Bill Epling).
Oxidative state of active site affects CH₄ conversion

- Amount of PdO vs. Pd on catalyst surface has significant effect on CH₄ conversion efficiency vs. temperature

- Surface chemistry effect has implications for engine air-to-fuel ratio control and control optimization of catalyst conversion efficiency

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**Fig. 6.** Methane conversion by 4% PdO/Al₂O₃ as a function of temperature from 300 to 900°C; (—) heating, (---) cooling, (-----) baseline.

**Fig. 7.** Methane conversion by 4% PdO/Al₂O₃ as a function of temperature not exceeding 770°C; (—) heating, (---) cooling, (-----) baseline.

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Impact of Pd oxide state on “light-off” temperature dramatic

- A wide range of light-off temperatures result from the PdO vs. Pd state on catalyst surface as controlled by lean vs. rich conditions and temperature.

"CH₄ Conversion on Successive Lean Lightoff Tests"

Pd-Rich Trimetal Catalyst

Performance recovers after catalyst exposed to 800°C lean where Pd oxide decomposes back to metallic Pd.

CH₄ lightoff performance gradually degrades as Pd is increasingly oxidized during successive lean temperature ramps to higher temperatures.