# Emissions Control for Natural Gas Fueled Trucks

Jim Parks
Email: parksjeii@ornl.gov
**Oak Ridge National Laboratory**
**National Transportation Research Center**

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# Emission Regulations

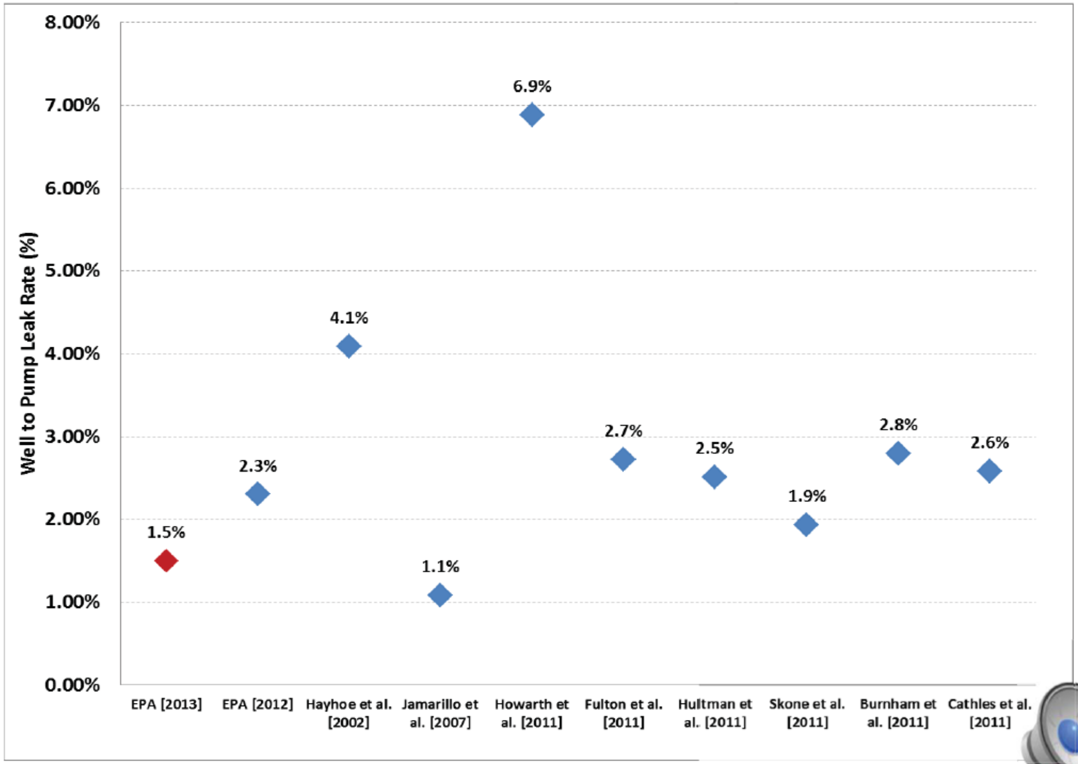
- **"Emissions"** can mean…
  - **Greenhouse Gas Emissions**
  - **Criteria Emissions** that affect air quality
    - Of which, criteria emissions include: oxides of nitrogen (NOx), non-methane hydrocarbon (MMHC), carbon monoxide (CO), particulate matter (PM)
    - Also, evaporative emissions, ammonia ($NH_3$), 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 $CO_2$ as well as $N_2O$ and $CH_4$
  - Exhaust Emission Standards for Heavy-Duty Highway Spark-Ignition and Compression-Ignition Engines
    - Includes NOx, NMHC, CO, and PM

***"Greenhouse Gas Emissions and Fuel Efficiency Standards for Medium- and Heavy-Duty Engines and Vehicles—Phase 2", Federal Register, Vol. 81, No. 206, pp. 73478-74274 (2016).***
***"Greenhouse Gas Emissions Standards and Fuel Efficiency Standards for Medium- and Heavy-Duty Engines and Vehicles (Phase 1)", Federal Register, Vol. 76, No. 179, pp. 57106-57513 (2011).***
***"Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements", Federal Register, Vol. 66, No. 12, pp. 5002-5193 (2001).***

# 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

## Leak Rates are Uncertain




Source: EPA and Howarth *et al.* (2012), Venting and Leaking of Methane from Shale Gas Development: Response to Cathles *et al.*

***Jason Mathers, "Minimizing methane emissions", Diesel Emissions Conference and Diesel Exhaust Fluid (2013).***

# Variations in upstream chemistry/processes affect tailpipe emissions

**NG Source**

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

**Distribution**

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

**NG Engine**

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

**Engine Emissions**

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

**Aftertreatment**

NG engine aftertreatment shares similar components to gasoline/diesel engines, but application design differs (for $CH_4$, etc.)

**NMOG** | **$CH_4$ $N_2O$** | **CO** | **NOx** | **PM**

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

$CH_4$ and $N_2O$ impact Greenhouse Gas emissions requirements; oxidation of $CH_4$ 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 $lb_m/MM_{scf}$]
  - **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 $H_2S$)

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 | |

- Stoichiometric Spark Ignition: Cold Start; $CH_4$ Control; $NH_3$ Control
- Lean Premixed Spark Ignition: Lean NOx; $CH_4$ Control; Low Temps
- Lean Premixed Diesel Pilot / Direct Injection Diesel Pilot: Lean NOx; $CH_4$ Control; Low Temps; PM Filters; NMHC Control

**Common Need #1: Efficient Catalytic Conversion of $CH_4$ at Low Temperatures**

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

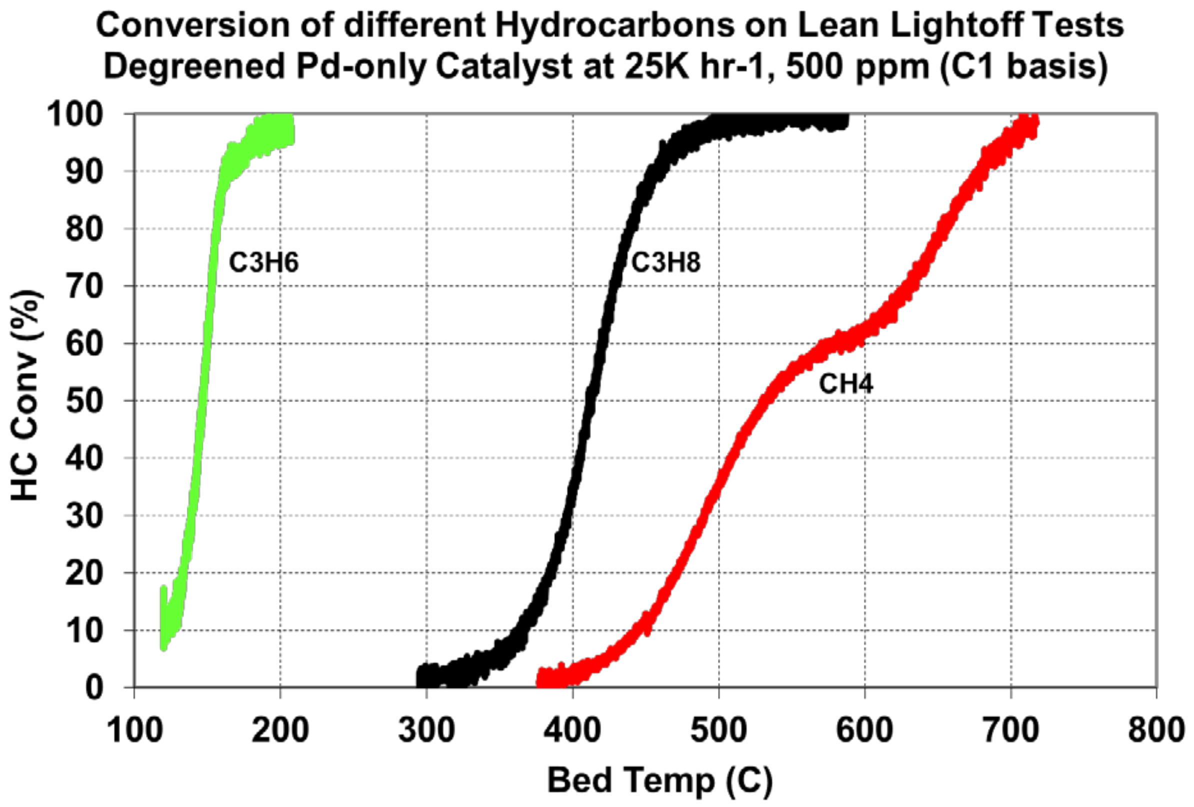
**Common Need #3: Cost- and Size-Effective and Durable Aftertreatment**

**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 $CH_4$ 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

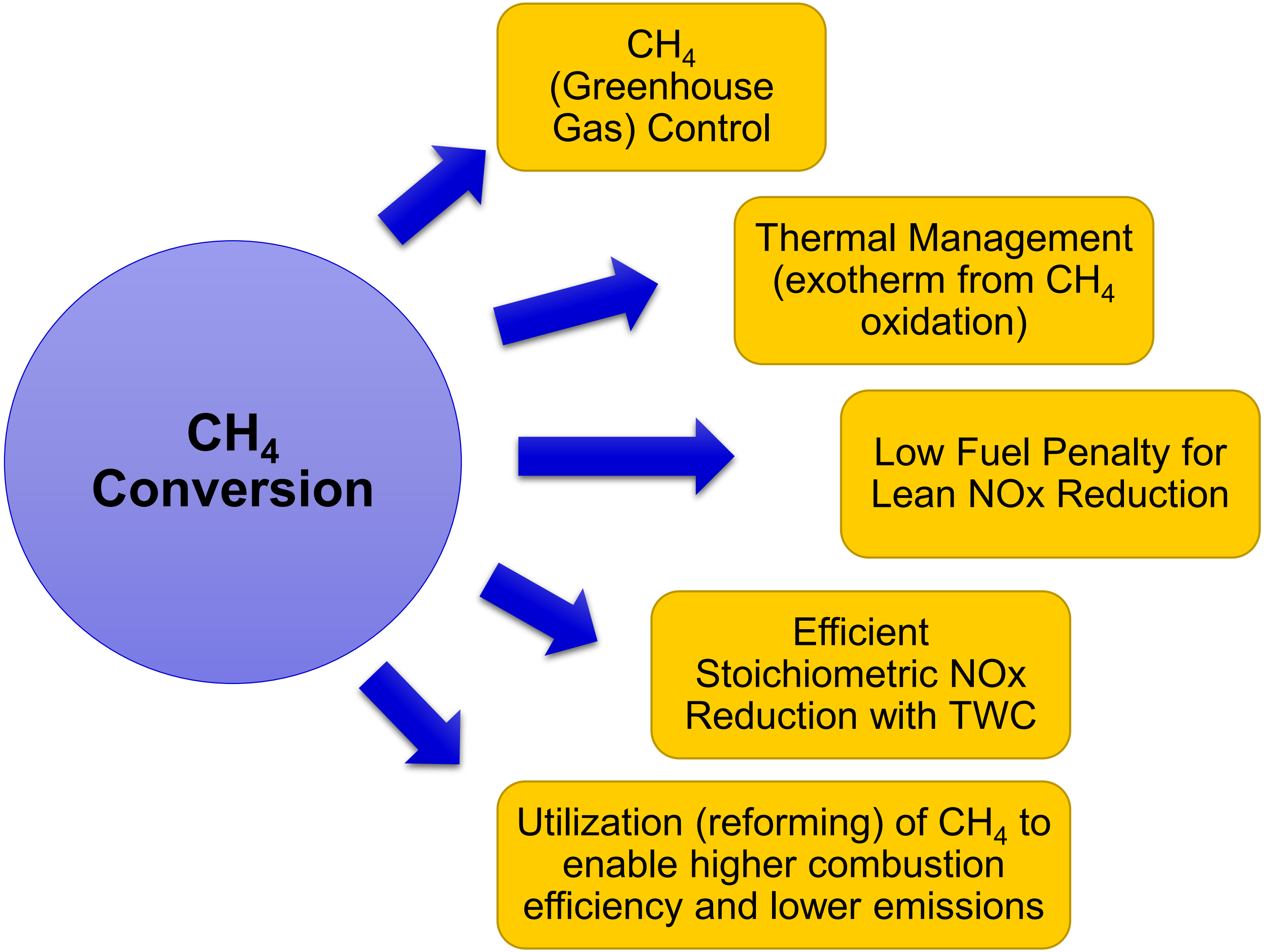



***Joseph R. Theis, Robert W. McCabe, "The effects of high temperature lean exposure on the subsequent HC conversion of automotive catalysts", Catalysis Today 184 (2012) 262-270.***

## Many challenges are associated with catalytic conversion of $CH_4$

- Platinum Group Metal (PGM) catalysts are needed for $CH_4$ oxidation with Pd giving the best $CH_4$ oxidation performance → **Cost**
- Low temperature $CH_4$ conversion is extremely difficult → **Efficiency**
- Oxidative state of active site (Pd vs. PdO) affects $CH_4$ conversion → **Controls**
- Short-term thermal exposure history affects $CH_4$ conversion → **Controls**
- $CH_4$ conversion sensitive to poisoning by Sulfur and other impurities → **Durability**

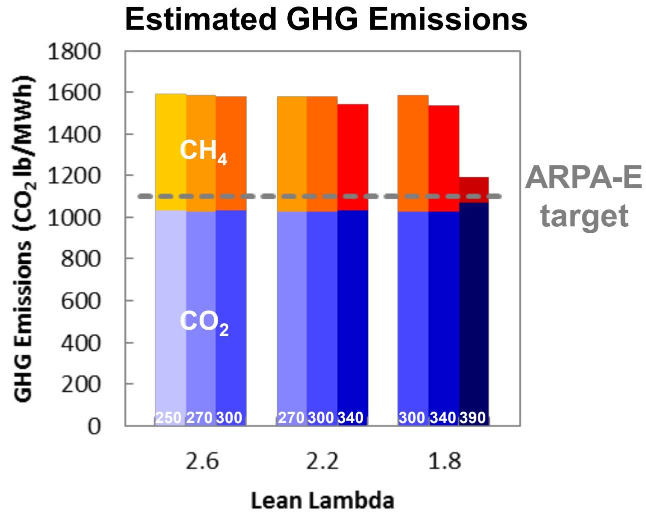
# $CH_4$ conversion has multiple impacts on efficiency and emissions of the system

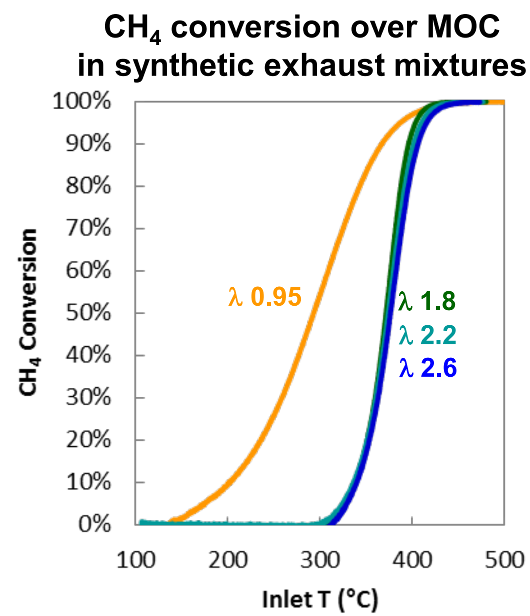


## Common Need #2: Efficient Reductant/Fuel Utilization (and choice)*

# $CH_4$ 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
  - $CH_4$ accounts for ~1/3 of GHG emissions (high GWP multiplier)
  - state-of-the-art methane oxidation catalyst (MOC) unable to convert $CH_4$ under anticipated engine exhaust temperatures and compositions (lean conditions, T < 350 °C)
  - Lean-rich cycling required for LNT (Lean NOx Trap)


https://arpa-e.energy.gov/?q=programs/gensets

# $CH_4$ conversion to $CO/H_2$ 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 $CH_4$ to $CO/H_2$ 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 (http://www.energy.ca.gov/2009publications/CEC-500-2009-011/CEC-500-2009-011.PDF)***

Figure 1: Simplified Flow Diagram of TCR System for Natural Gas Engine Configured for Stoichiometric Combustion with Cooled Exhaust Gas Recirculation

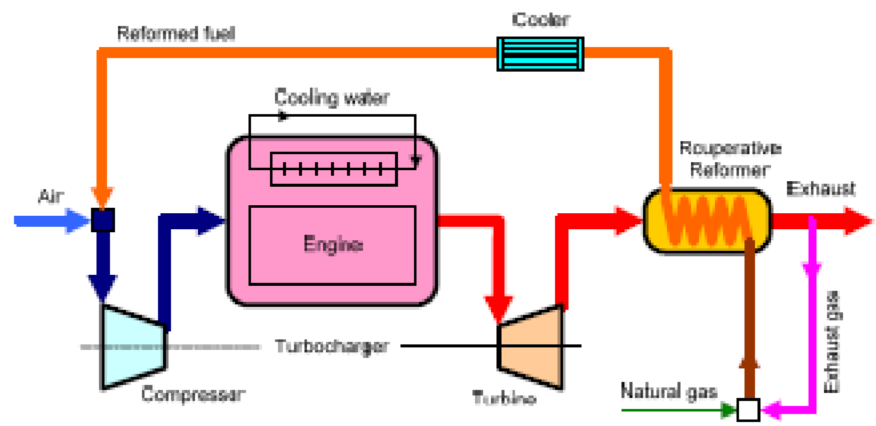
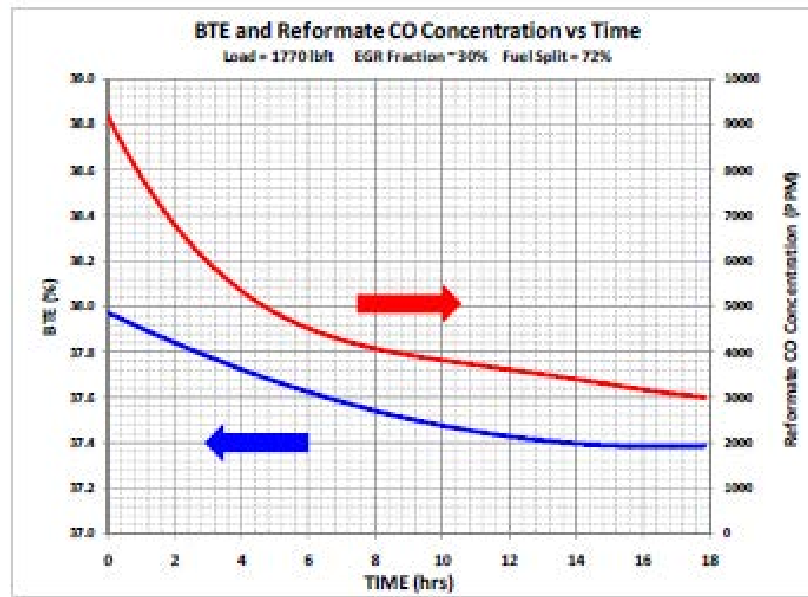


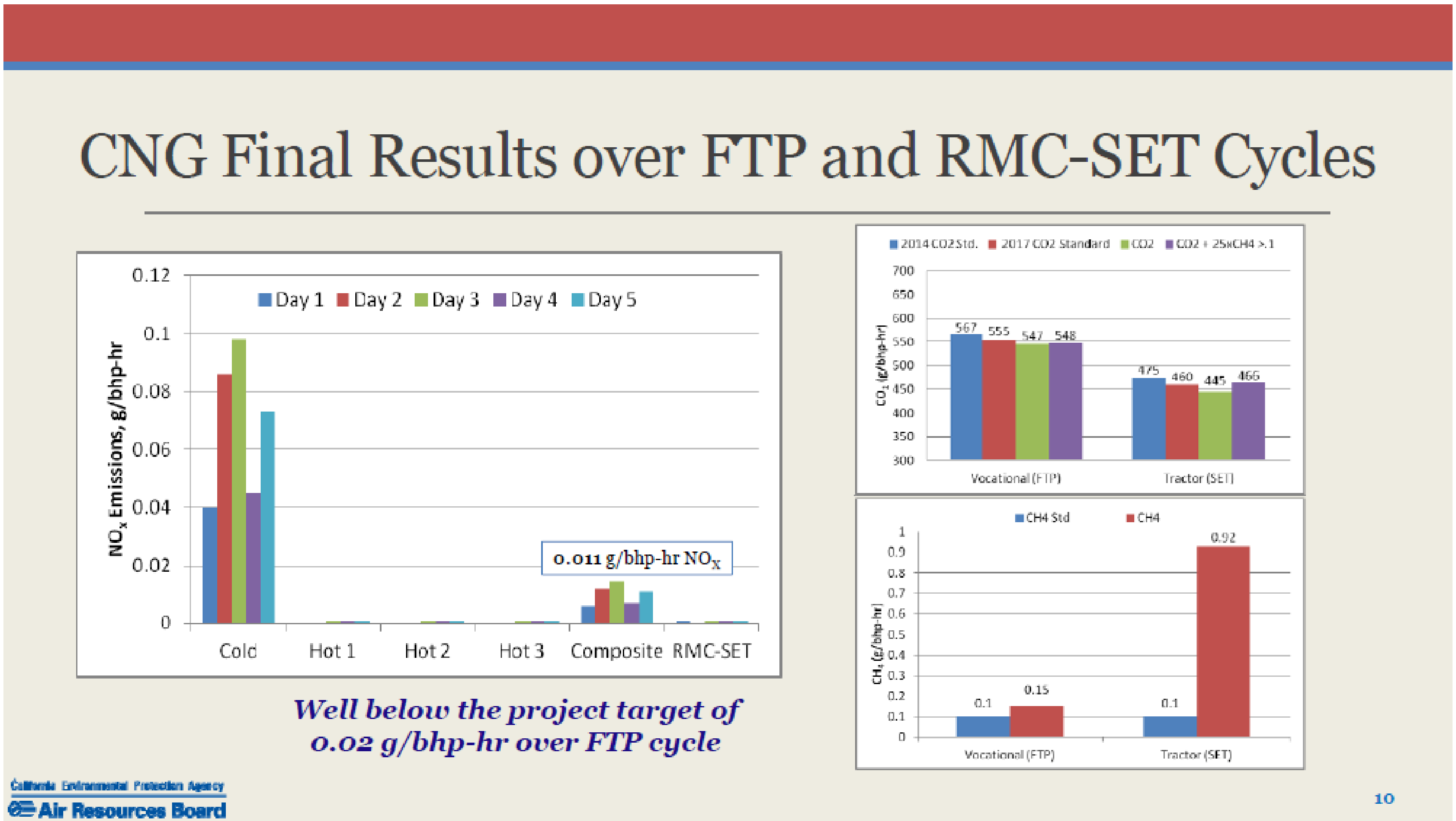

Figure 81: Reduction in System BTE and Reformate CO Concentration Versus Time



## 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 $NH_3$ control also demonstrated
- Cost and size reductions and $CH_4$ control can improve commercial outlook






*Seungju Yoon (CARB), www.arb.ca.gov/research/veh-emissions/low-nox/lownox-cleers.pdf*

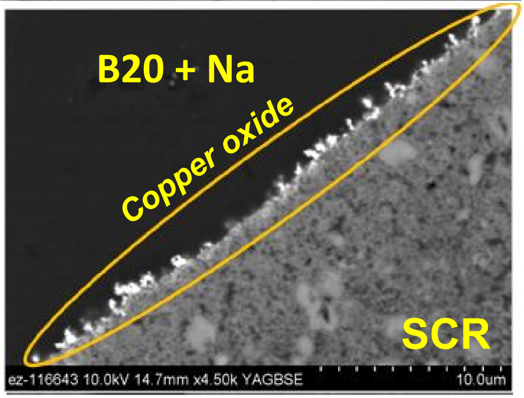
# Fuel impurity and lubricant component can impact emissions control systems over lifetime of vehicle

- 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

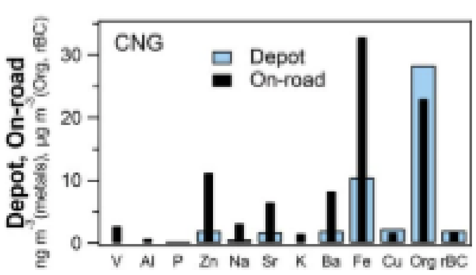



**Figure 5**. Bus-type average concentrations of V, Al, P, Zn, Na, Sr, K, Ba, Fe, Cu, organics (Org), and rBC for the EURO III, hybrid, ethanol, and CNG buses at the depot and on-road. For K the concentrations are divided by 100 and for Sr and Ba multiplied by 100 in order to get them to the same scale.

S. Saarikoski, H. Timonen, S. Carbone, H. Kuuluvainen, J. V. Niemi, A. Kousa, T. Rönkkö, D. Worsnop, R. Hillamo & L. Pirjola (2017) Investigating the chemical species in submicron particles emitted by city buses, Aerosol Science and Technology, 51:3, 317-329, DOI: 10.1080/02786826.2016.1261992

## Fuel composition and Engine operation influence

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

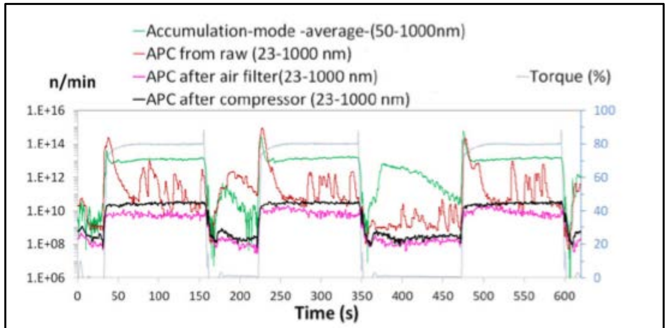



Figure 9. Comparison between DMS500 upstream turbine accumulation mode data and APC 489 measurements from the intake and exhaust flow during transient tests.

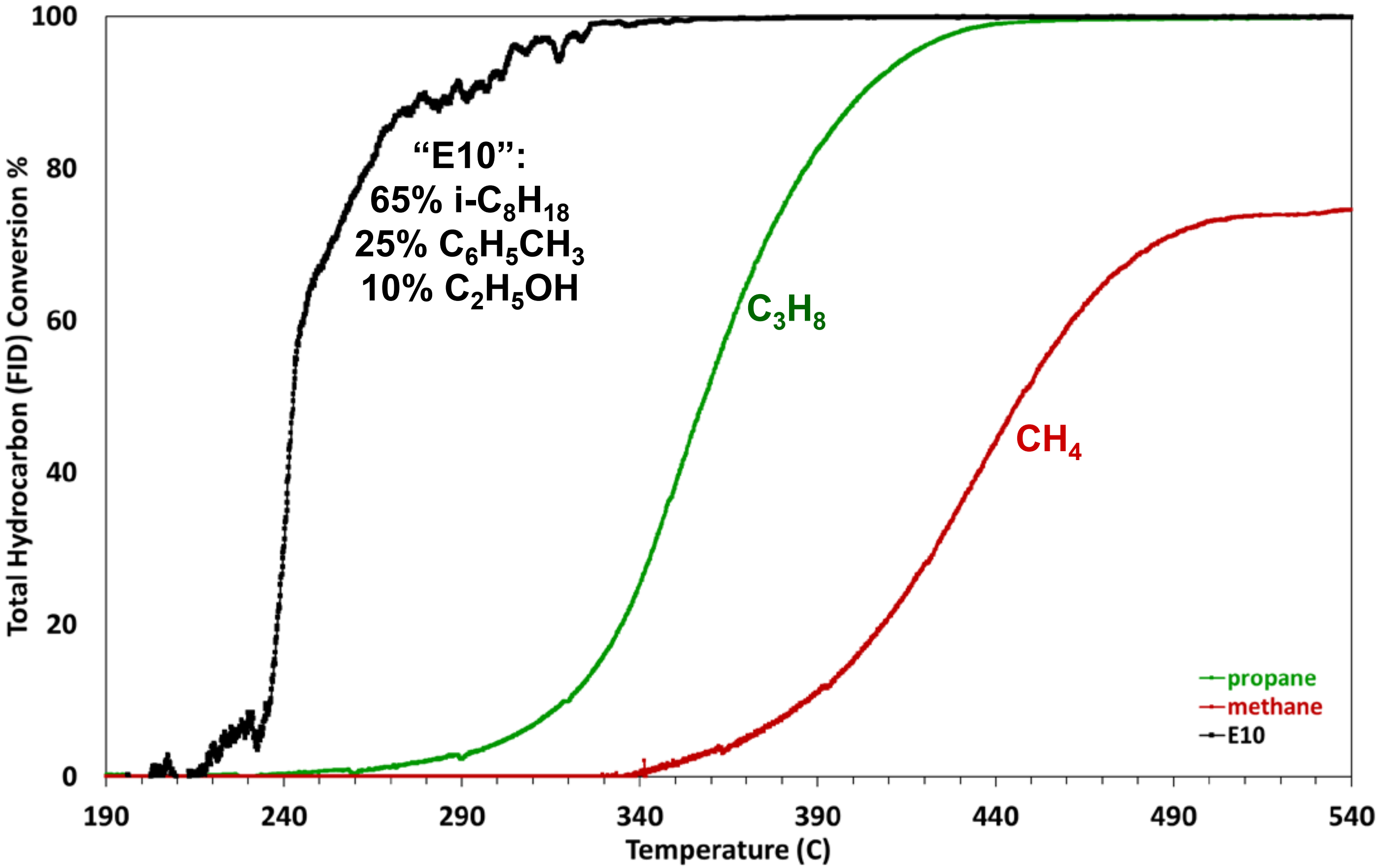
Amirante, R., Distaso, E., Tamburrano, P., and Reitz, R., "Measured and Predicted Soot Particle Emissions from Natural Gas Engines," SAE Technical Paper 2015-24-2518, 2015, doi:10.4271/2015-24-2518.

- 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% $H_2O$
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 $h^{-1}$

*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

# $CH_4$ oxidation via catalysis is fundamentally difficult

ELSEVIER

Applied Catalysis B: Environmental 39 (2002) 1–37

APPLIED CATALYSIS
B: ENVIRONMENTAL

www.elsevier.com/locate/apcatb

Complete oxidation of methane at low temperature over noble metal based catalysts: a review

Patrick Gélin*, Michel Primet

*Laboratoire d'Application de la Chimie à l'Environnement, UMR CNRS 5634, Université Claude Bernard Lyon 1, Building Chevreul, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

Received 29 October 2001; received in revised form 20 March 2002; accepted 25 March 2002

- 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 $CH_4$ 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 $CO_2$
  - 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

- Pd > Rh > Pt, but ceria especially promotes Rh performance (Oh, et al., *J. Catal.* **132** (1991) 287 [10])
- 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).

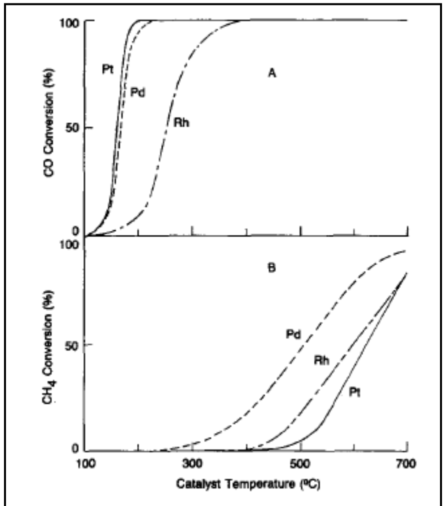
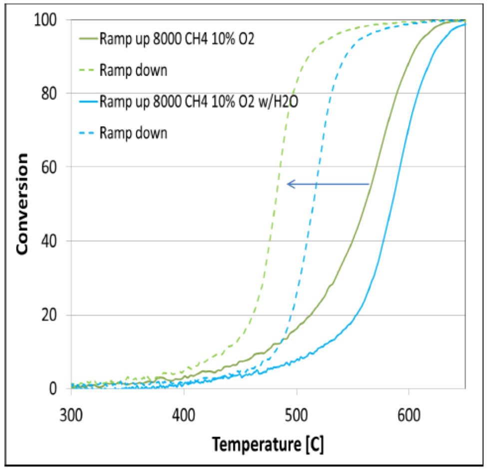



FIG. 1. Conversions of CO (A) and $CH_4$ (B) over the alumina-supported noble metal catalysts as a function of temperature in an oxidizing feedstream containing 0.2 vol% $CH_4$, 0.1 vol% CO, and 1 vol% $O_2$.



# Oxidative state of active site affects $CH_4$ conversion

- Amount of PdO vs. Pd on catalyst surface has significant effect on $CH_4$ conversion efficiency vs. temperature
- Surface chemistry effect has implications for engine air-to-fuel ratio control and control optimization of catalyst conversion efficiency

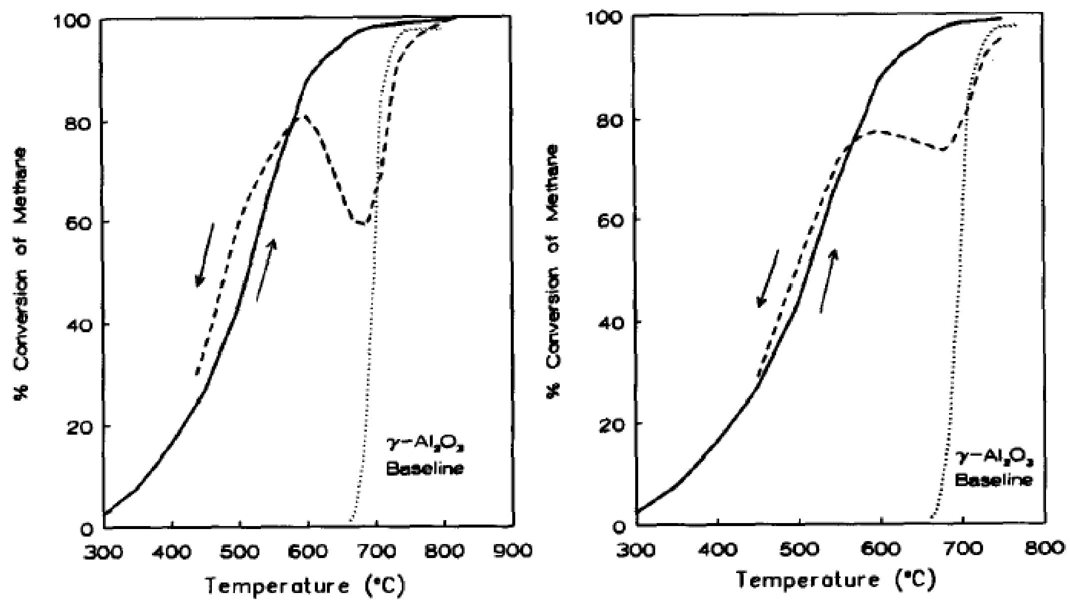


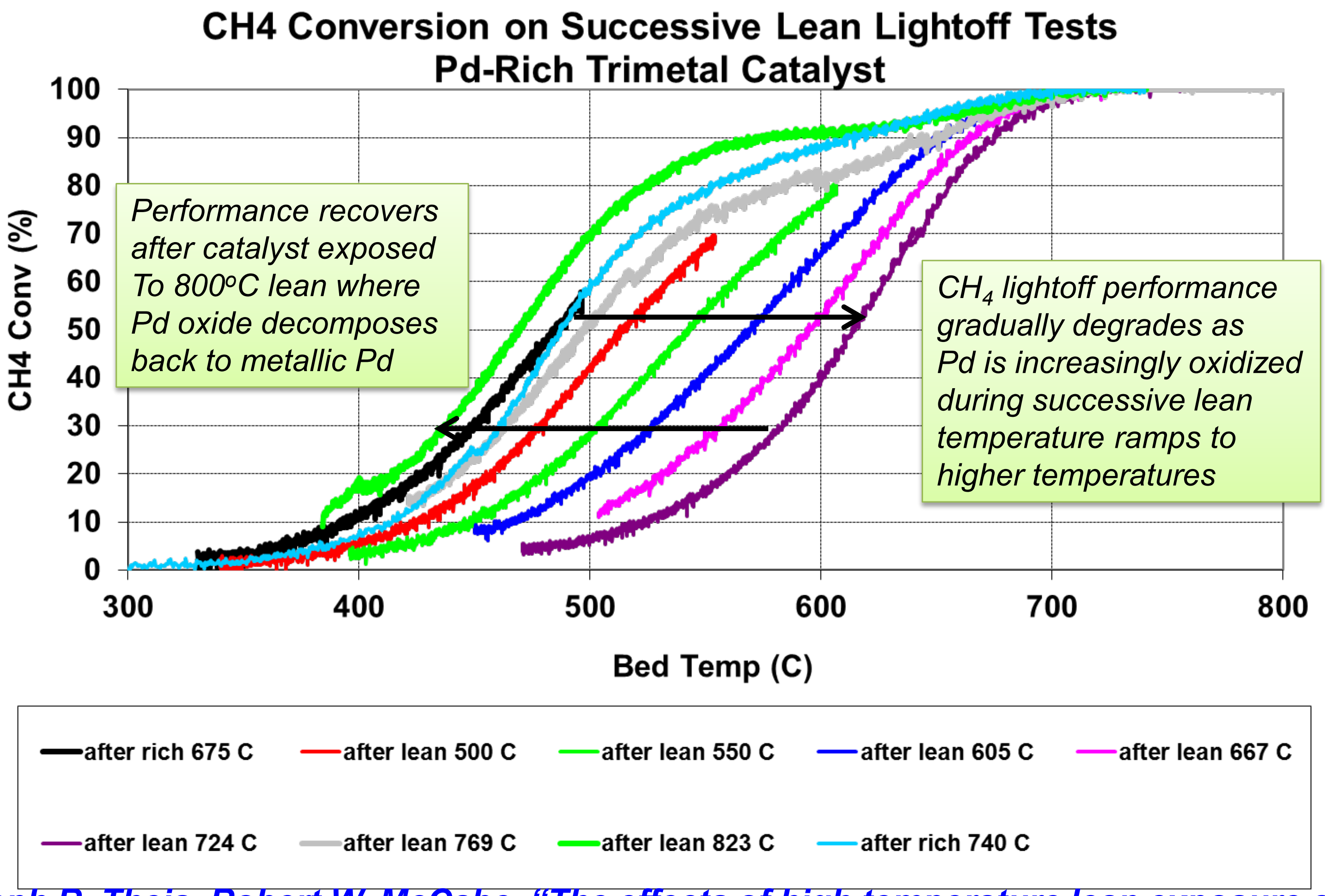

Fig. 6. Methane conversion by 4% $PdO/Al_2O_3$ as a function of temperature from 300 to 900°C; (—) heating, (- - -) cooling, (····) baseline.

Fig. 7. Methane conversion by 4% $PdO/Al_2O_3$ as a function of temperature not exceeding 770°C; (—) heating, (- - -) cooling, (····) baseline.

*R. J. Farrauto, M. C. Hobson, T. Kennelly, and E. M. Waterman, "Catalytic chemistry of supported palladium for combustion of methane", Applied Catalysis A: General, 81, (1992) 227-237.*

# 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




***Joseph R. Theis, Robert W. McCabe, "The effects of high temperature lean exposure on the subsequent HC conversion of automotive catalysts", Catalysis Today 184 (2012) 262-270.***