Emissions Control for Lean Gasoline Engines

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U.S. Department of Energy

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Project Overview

Timeline

- Year 1 of 3-year program
- Builds on previous R&D in FY13-FY15

Budget

- FY16: $400k (Task 2*)

*Task 2: Lean Gasoline Emissions Control

Part of large ORNL project "Enabling Fuel Efficient Engines by Controlling Emissions" (2015 VTO AOP Lab Call)

Barriers Addressed

- Barriers listed in VT Program Multi-Year Program Plan:
  - 2.3.1B: *Lack of cost-effective emission control*
  - 2.3.1C: *Lack of modeling capability for combustion and emission control*
  - 2.3.1.D: *Emissions control durability*

Collaborators & Partners

- General Motors
- Umicore
- University of South Carolina
- Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS)

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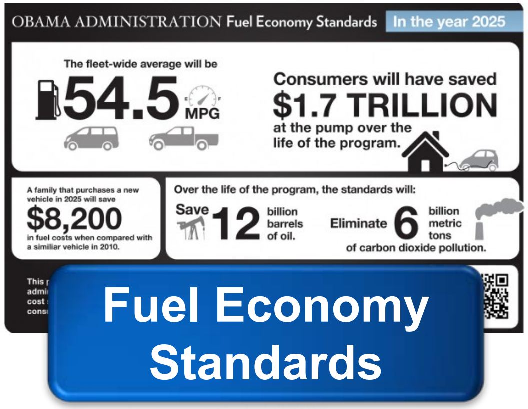
Objectives and Relevance

Enabling lean-gasoline vehicles to meet emissions regulations will achieve significant reduction in petroleum use

- Objective:
  - Demonstrate technical path to emission compliance that would allow the implementation of lean gasoline vehicles in the U.S. market.
    - Lean vehicles offer 5–15% increased efficiency over stoichiometric-operated gasoline vehicles



54.5 mpg CAFE by 2025

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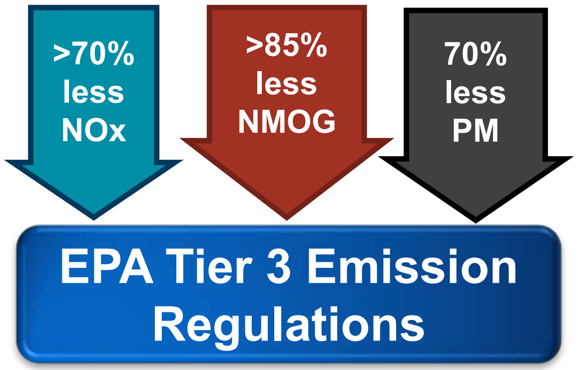
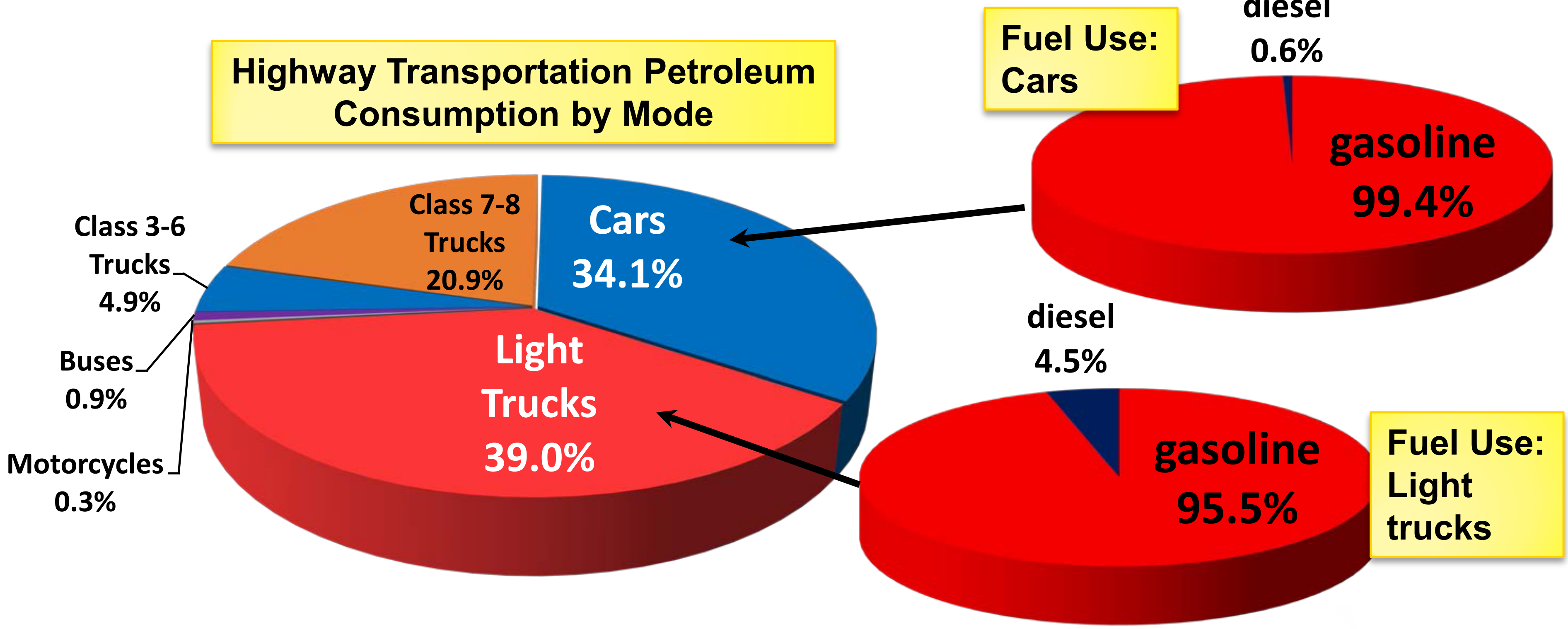
    - Lean vehicles offer 5–15% increased efficiency over stoichiometric-operated gasoline vehicles
    - Compliance required: U.S. EPA Tier 3
  - Investigate strategies for cost-effective compliance
    - minimize precious metal content while maximizing fuel economy



- <u>Relevance:</u>
  - U.S. passenger car fleet is dominated by gasoline-fueled vehicles.
  - Enabling introduction of more efficient lean gasoline engines can provide significant reductions in overall petroleum use
    - thereby lowering dependence on foreign oil and reducing greenhouse gases

Relevance: small improvements in gasoline fuel economy significantly decreases fuel consumption



- US car and light-truck fleet dominated by gasoline engines
- 10% fuel economy benefit has significant impact
  - Potential to save 13 billion gallons gasoline annually
- HOWEVER…emissions compliance needed!!!

Lean gasoline vehicles can decrease US gasoline consumption by ~13 billion gal/year

References: Transportation Energy Data Book, Ed. 34 (2013 petroleum/fuel use data)

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Milestones

Quarterly Milestones

Complete

- **FY2015, Q4:** Simulate transient load/speed operation of passive SCR on BMW lean gasoline engine platform *Further studies ongoing*

Complete

- **FY2016, Q1:** Complete bench flow reactor assessment of Pd-only and TWC/NSC formulations for NH_3 production during Passive SCR

Annual SMART Milestones

Complete

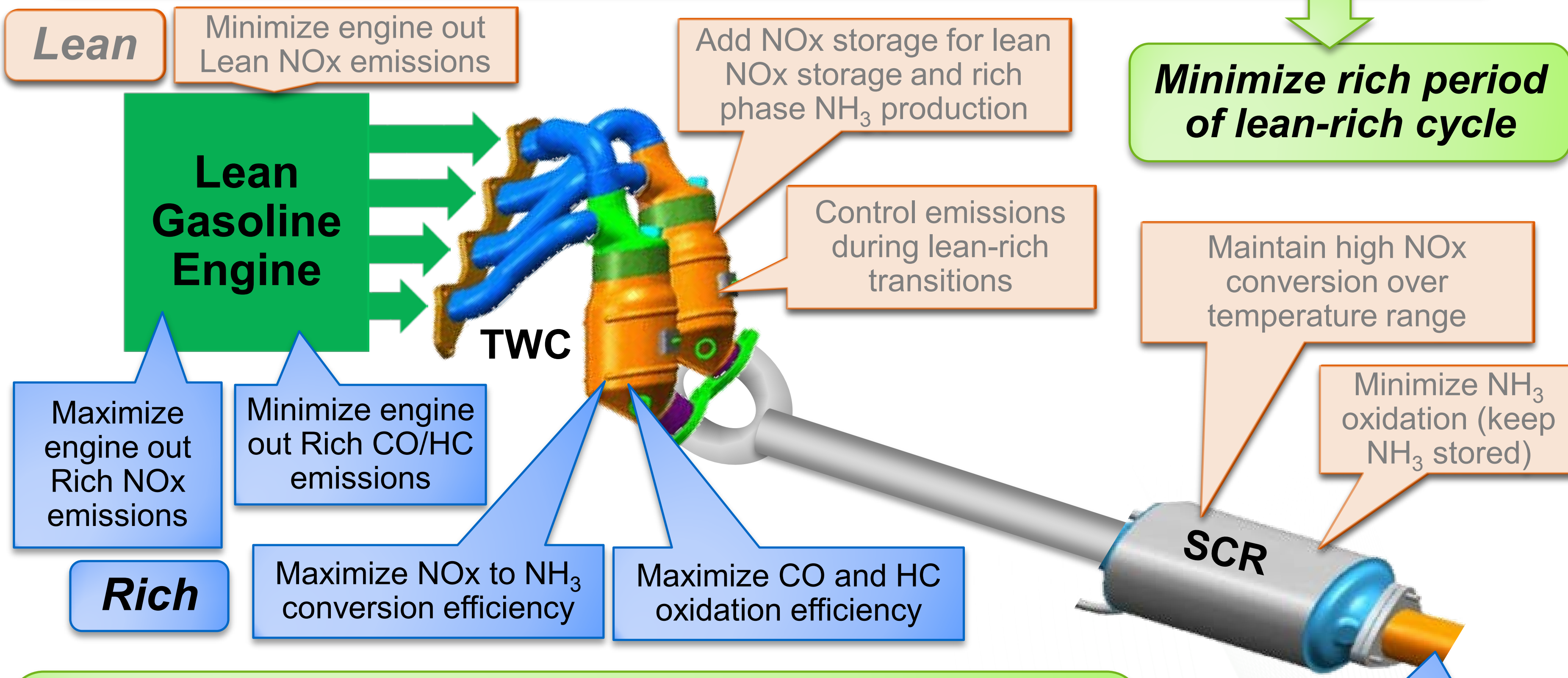
- **FY2015:** Determine effect of aging and/or poisoning on TWC NH_3 formation through flow reactor experiments *Further studies ongoing*
- **FY2017:** Achieve EPA Tier 3 level emissions with 15% fuel economy gain vs. stoichiometric operation and less than 4 g Pt-equivalent per liter engine with commercial feasibility assessment including material costs

GO/NO-GO Decisions

- **FY2017, Q2:** criteria based on FY2017 SMART Milestone

Approach focuses on catalyst and system optimization of Passive SCR (and LNT+SCR)

Key Principle: system fuel efficiency gain depends on optimizing NH_3 production during rich operation and NOx reduction during lean operation



Other Core Principles:

- Expand range of temperature operation
- Materials must be durable to temperature and poisons (S)
- Understand Pt group metals utilization to minimize cost

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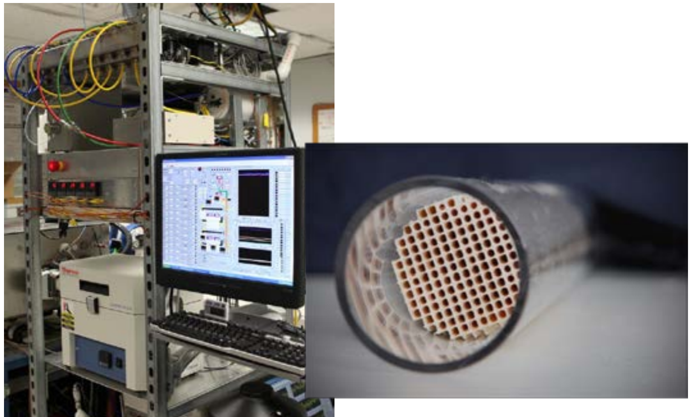
Iterative Bench Reactor + Engine Study Approach



Bench Flow Reactor with cycling and multi-catalyst (close-coupled and underfloor) capabilities

BMW 120i lean gasoline engine platform with National Instruments (Drivven) open controller

Define exhaust conditions

Formulation-dependent TWC performance

TWC performance vs. AFR with realistic HC and H_2 characterization

System study guidance

Controlled TWC+SCR system performance

Realistic TWC+SCR system performance with fuel efficiency measurement

umicore Automotive Catalysts

Prototype catalysts

TWC+SCR performance with refined load step cycle

Combustion parameter optimization to maximize NH_3 production

Collaborations with modeling community and CLEERS

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Collaborations and Partners

Primary Project Partners

- **GM**
  - guidance and advice on lean gasoline systems via monthly teleconferences
- **Umicore**
  - guidance (via monthly teleconferences) and catalysts for studies (both commercial and prototype formulations)
- **University of South Carolina (Jochen Lauterbach)**
  - Catalyst aging studies with student Calvin Thomas

Additional Collaborators

(3) Lean GDI PM Projects

- **CDTi:** catalysts for studies
- **CLEERS:** Share results/data and identify research needs
- **LANL:** Engine platform used for NH_3 sensor study (M. Mukundan, E. Brosha, C. Kreller)
- **MECA:** GPF studies via Work For Others contract
- **University of Minnesota:** Collaboration on DOE funded project at U of Minn. related to lean GDI PM (PI: Will Northrop)
- **CTS (Filter Sensing Technologies):** Small business technical assistance on RF sensors for GPF on-board diagnostics
- **DOE VTO Fuel and Lubricant Technology Program:** Engine platform used for ethanol-based HC-SCR studies

Responses to 2015 Reviewers

FY2015 AMR Review
(5 Reviewers)
[scores: 1 (min) to 4 (max)]

Category	Score
Approach	3.50
Tech Accomplishments	3.50
Collaboration	3.50
Future Research	3.50
Weighted Average	**3.50**

Relevant to DOE Objectives?
YES (100%)

Sufficiency of Resources	
Insufficient (40%)	Sufficient (60%)

Summary of Reviewers' Feedback:

- Generally positive feedback on:
  - Approach (bench+engine)
  - Collaborations with industry
  - Project design, relevance, future plans
  - Inclusion of S, aging effects
- More interest in OEM perspectives
- Consider deS and desoot fuel penalties and CO/HC emissions
- Consider N_2O (relative to GHG* standard)
- Fundamental questions on ceria, Rh effects
- Want more soot and modeling R&D

*N_2O Greenhouse Gas (GHG) cap is 10 mg/mile

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Suffi
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Summary of Reviewers' Feedback:

"…feedback from OEMs on value of passive systems, lessons learned and technical challenges would improve rating to outstanding. Several OEMs indicate passive system challenges are constraining use especially predictability of efficiently producing NH_3."

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Project Adjustments/Responses:

- Project directly addressing OEM concerns

Project results shared with Ford and FCA. Lots of questions on feasibility, transient control, and net fuel efficiency gain.
References: J. Theis et al. CLEERS 2015, SAE 2015-01-1004, SAE 2015-01-1006; Doornbos et al. SAE 2015-01-0776, SAE 2015-24-2504, SAE 2016-01-0935

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- Project directly addressing OEM concerns
- Will calculate deS/desoot effects
- N_2O data collected; more analysis occuring
- Surface science studies (DRIFTS/XPS)
- Resource limited, but project leveraged for (3) PM/GPF projects & CLEERS database

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Summary of Technical Accomplishments

- **Bench Reactor Studies:**
  - Cold start selectivity as a function of λ defined for catalyst sample matrix
- **Engine Studies:**
  - Completed study of effects of NH_3:NOx on fuel efficiency and NOx/NH_3/N_2O slip
- **Aging and S Effects:**
  - Materials characterization conducted on Malibu-1 catalyst (PGM size) after aging
  - S exposure study during lean-rich cycling completed (data analysis ongoing)

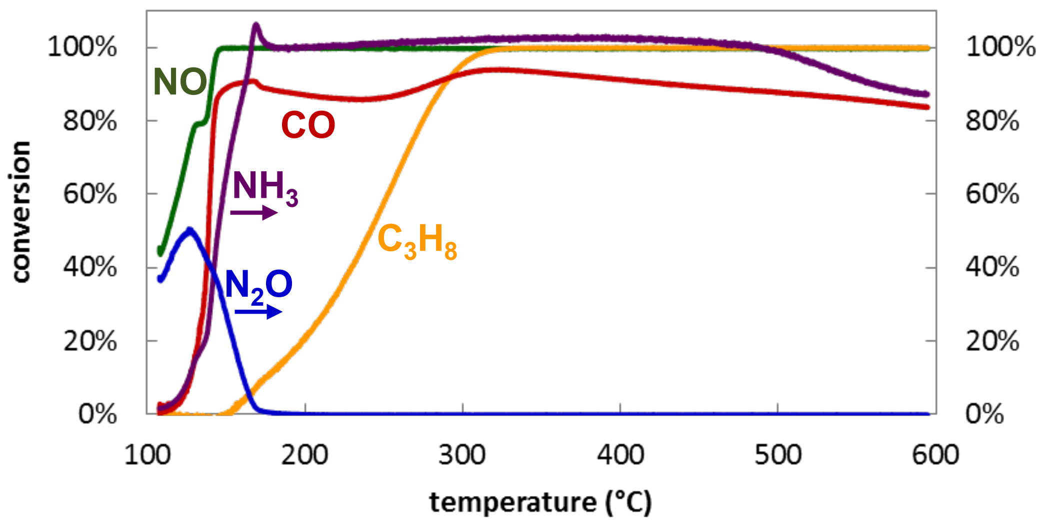
Catalyst Sample Matrix [OSC=oxygen storage capacity; NSC=NOx storage capacity]

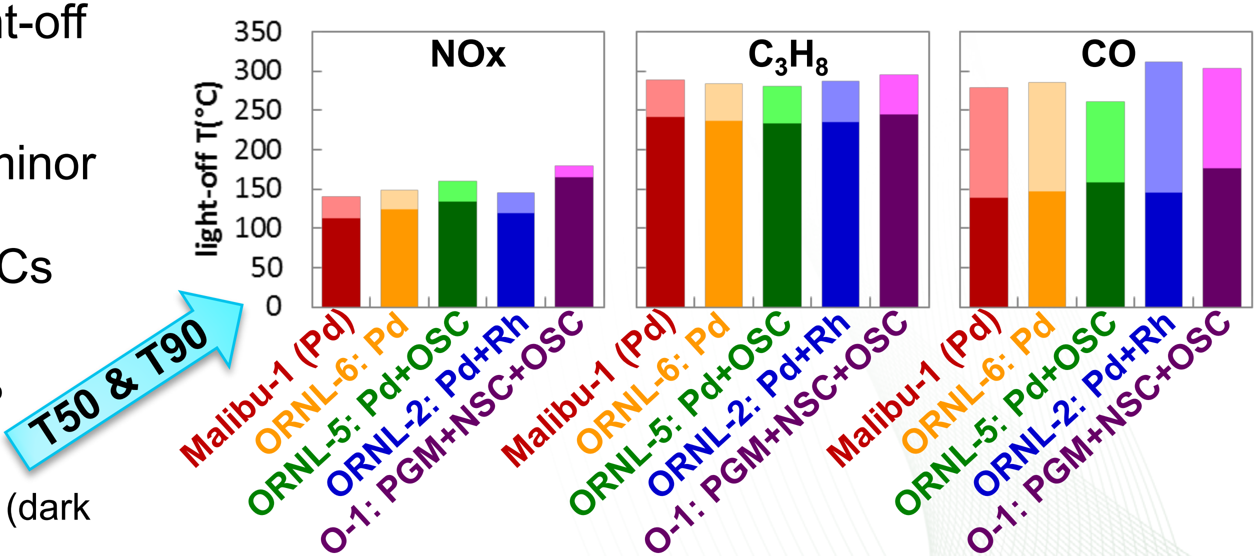
sample ID	Description	Pt (g/l)	Pd (g/l)	Rh (g/l)	OSC	NSC
Malibu-1	Front half of TWC	0	7.3	0	N	N
Malibu-2	Rear half of TWC	0	1.1	0.3	Y	N
Malibu-combo	Full TWC	0	4.0	0.16	Y	N
ORNL-1	Pt + Pd + Rh	2.47	4.17	0.05	Y	Y
ORNL-2	Pd + Rh	0	6.36	0.14	N	N
ORNL-6	Pd	0	6.50	0	N	N
ORNL-5	Pd + OSC high	0	6.50	0	H	N
ORNL-4	Pd + OSC med	0	4.06	0	M	N
ORNL-3	Pd + OSC low	0	1.41	0	L	N

Extensive flow reactor investigations show impact of TWC formulation, λ on light-off performance for passive SCR

- Gas composition has a large effect on light-off performance
  - best combination of NOx reduction, NH_3 production, and HC conversion achieved at λ 0.97 for all 5 TWCs evaluated
  - same as optimum rich λ for passive SCR operation
- Conversion of NO and CO, production of NH_3 all light-off at around 150°C
- Formulation has only a minor influence on light-off performance among TWCs tested
  - T50 (Temperature at >50% conversion) and T90 (Temperature at >90% conversion) shown at right (dark bars=T50; light bars=T90)

Malibu (Pd) TWC catalyst light-off at λ=0.97





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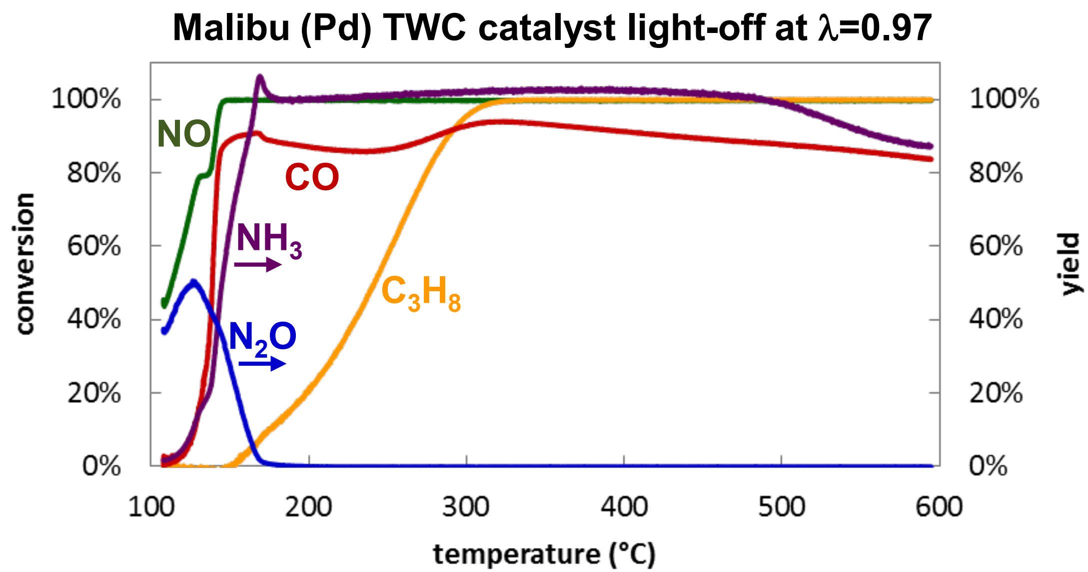
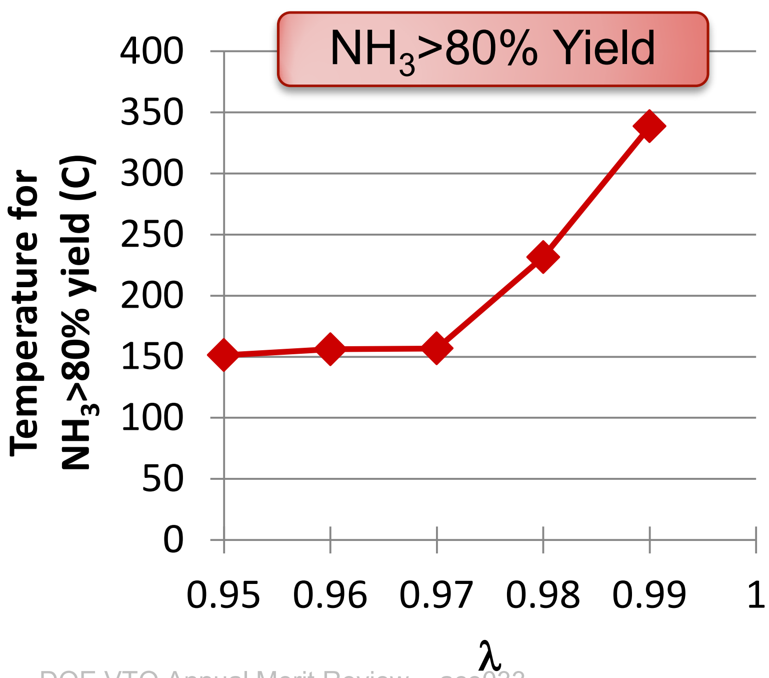
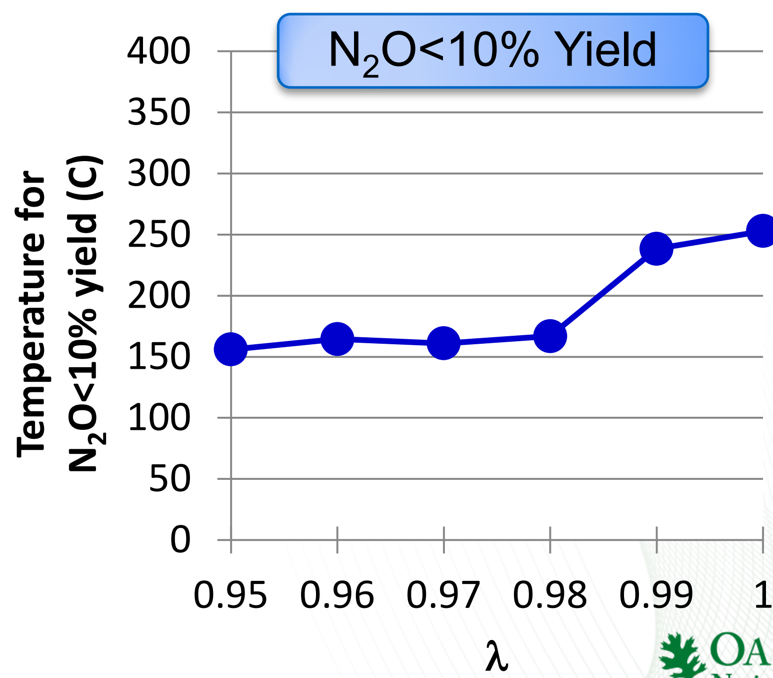
λ affects NH_3 and N_2O formation during light-off as well

- NH_3 formed at >80% yield starting at ~150°C for Malibu-1 catalyst (Pd)
- Temperature for N_2O to decrease to <10% yield a function of λ
- Note: ***inlet temperature*** shown







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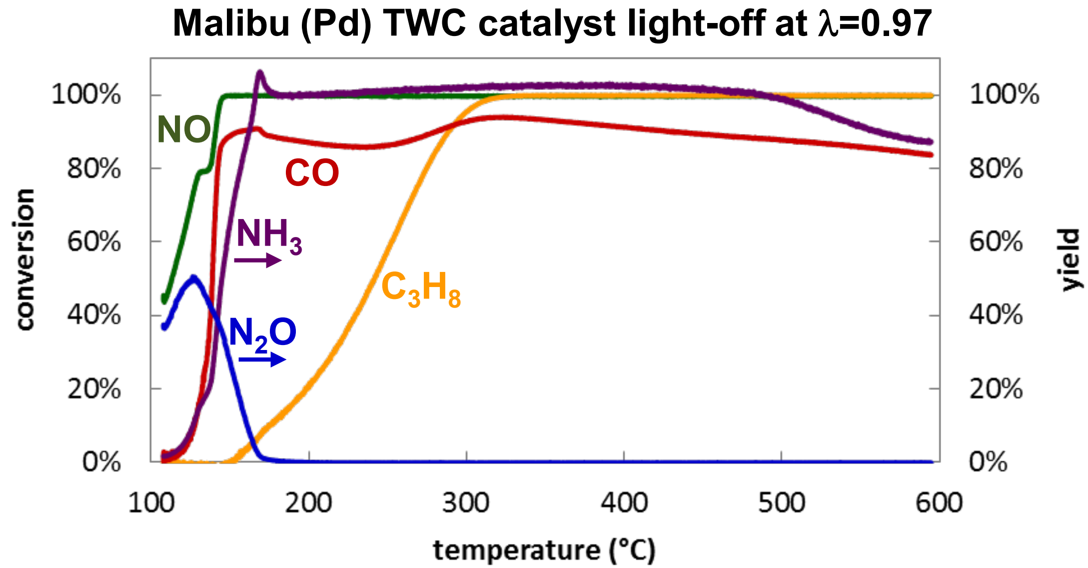

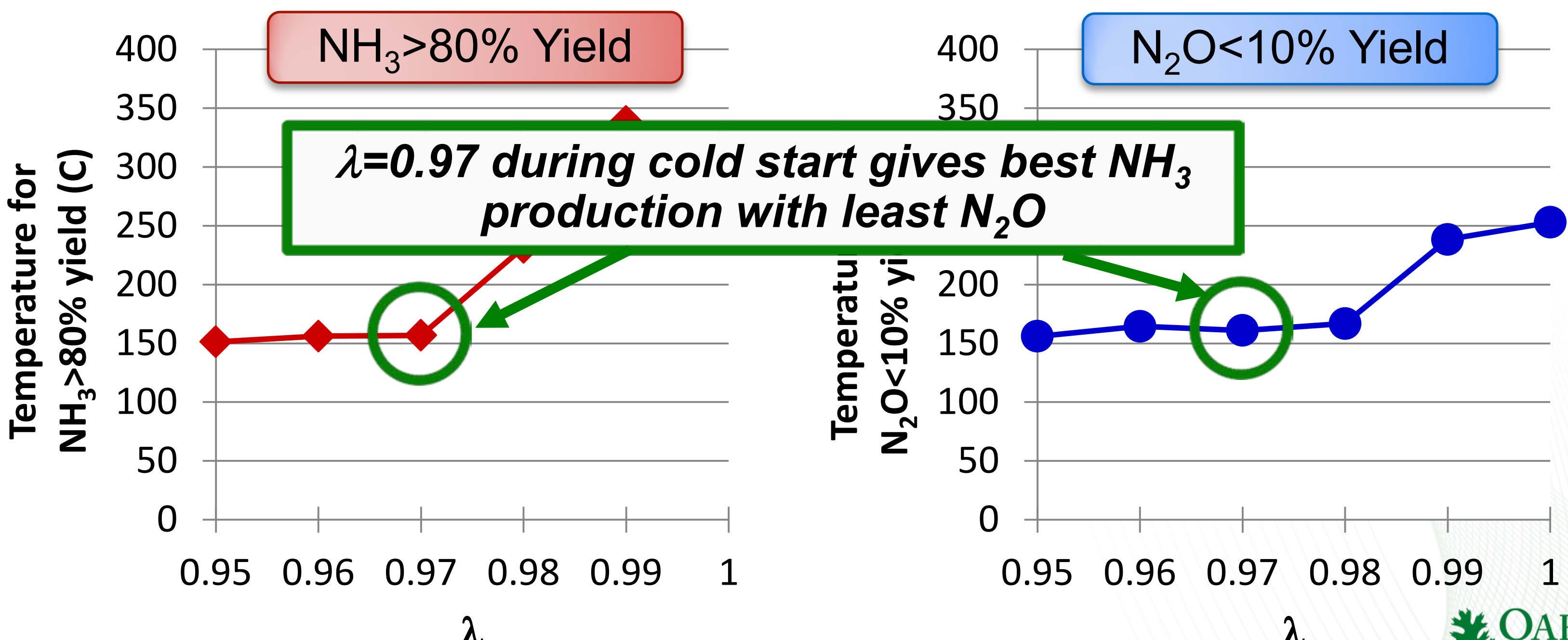

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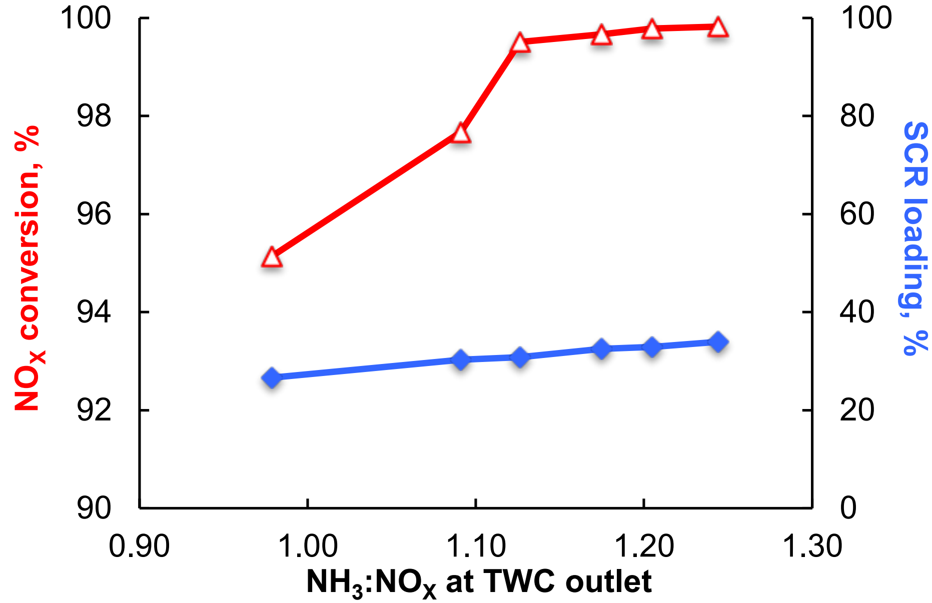
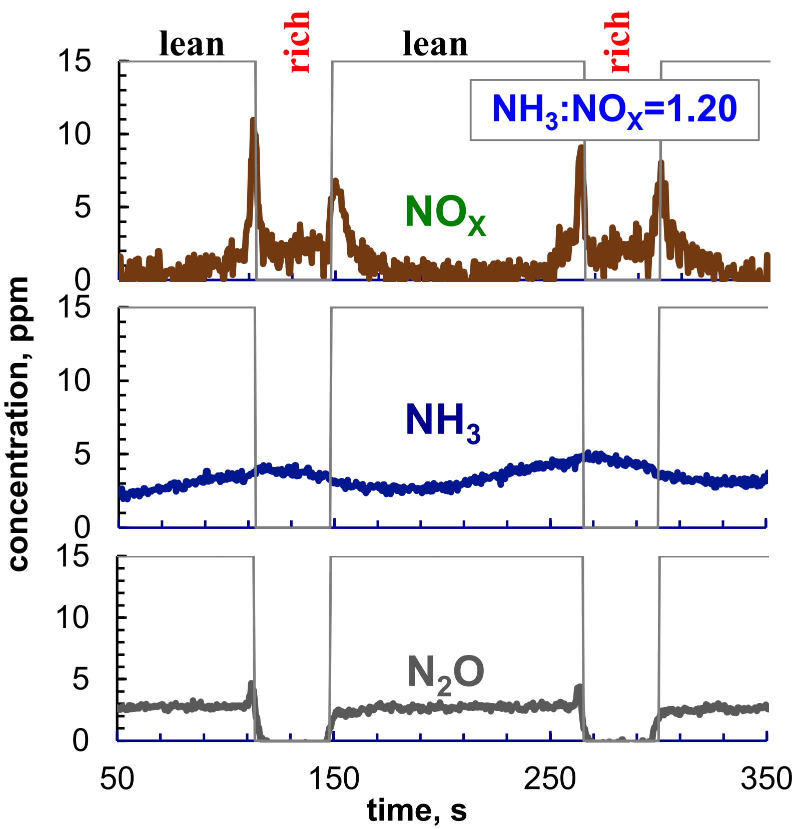
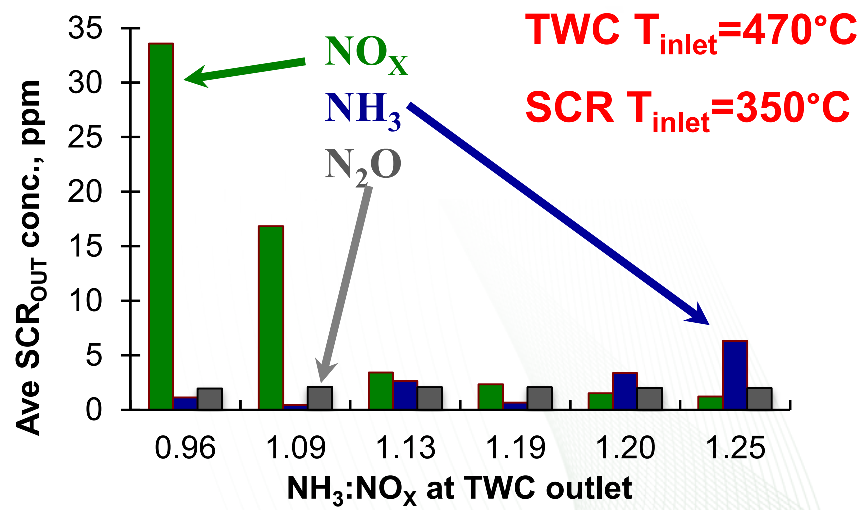
Engine-based studies show NH_3:NOx>1 critical to achieving highest NOx conversion

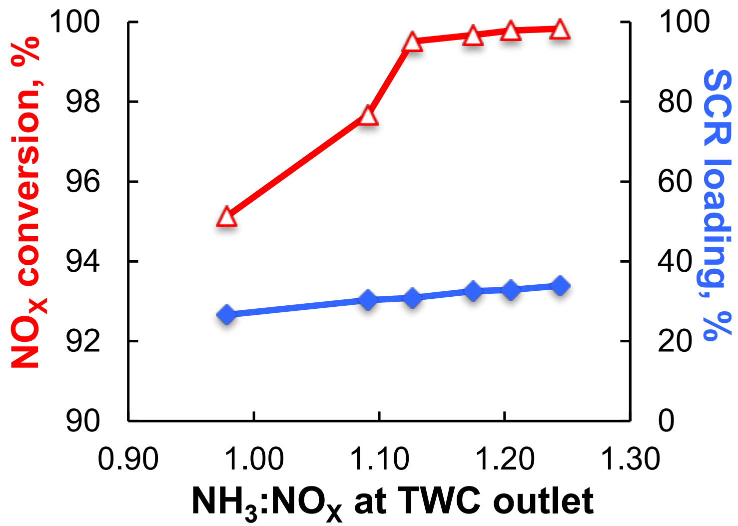
- NOx conversion reaches >99% at NH_3:NOx=1.13
- Increasing NH_3:NOx to 1.20 results in NH_3 slip
- N_2O primarily forms over SCR during lean phase (~2ppm) and not affected by NH_3:NOx
- N_2O spike over TWC observed at lean to rich transition (~8ppm)

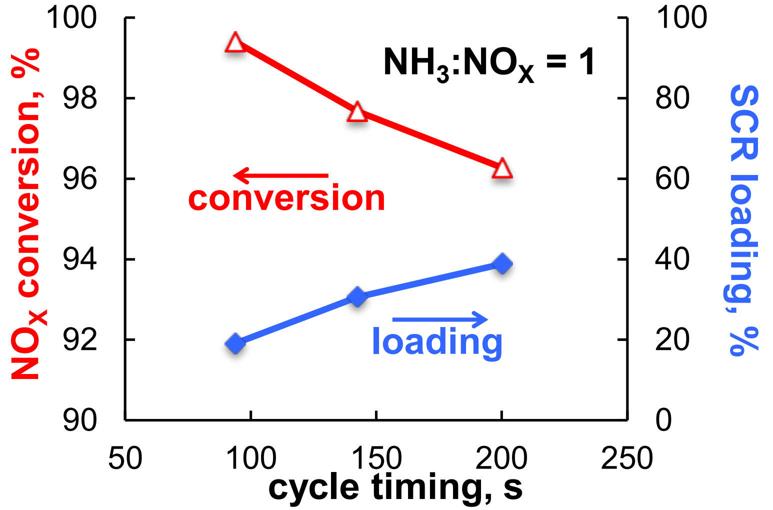


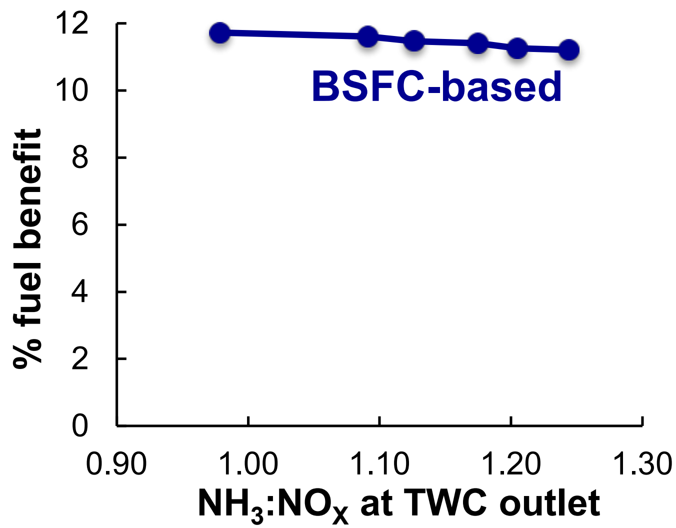


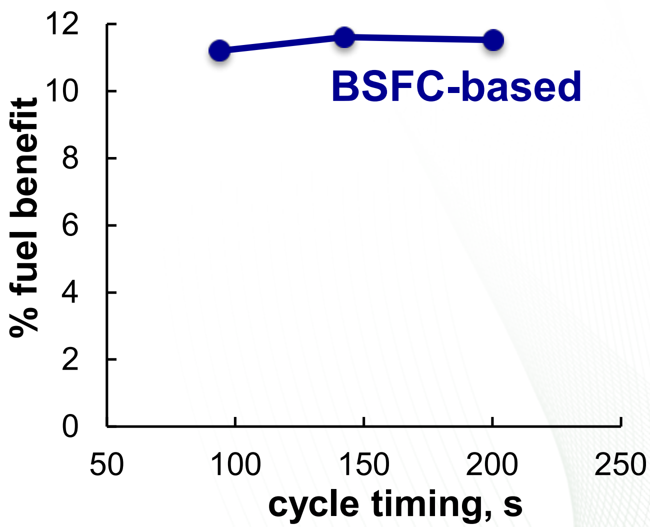


Reducing cycle timing enables >99% NOx conversion at NH_3:NOx=1 (engine studies)



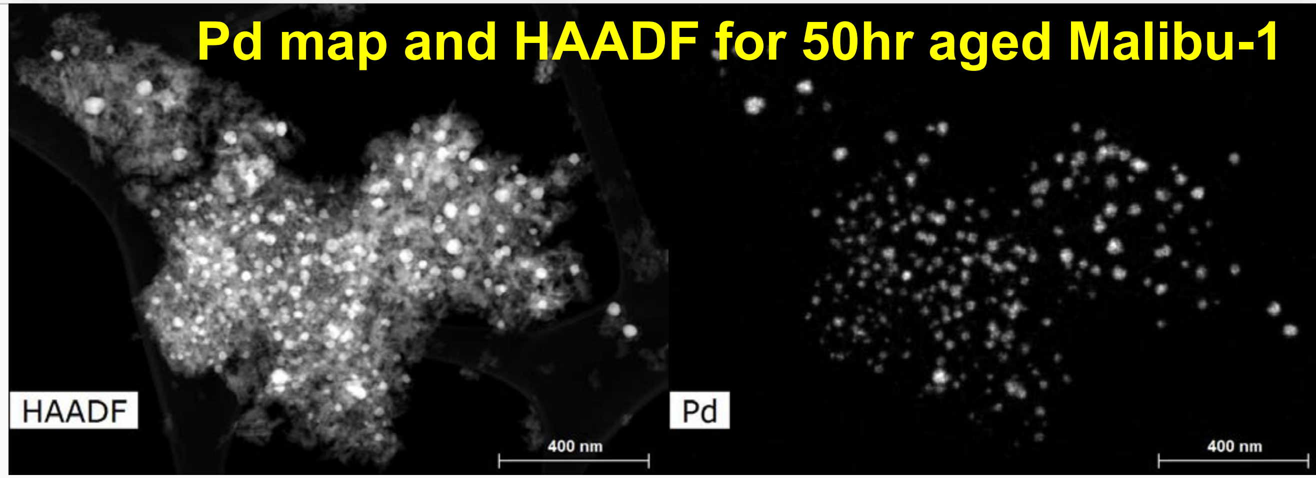


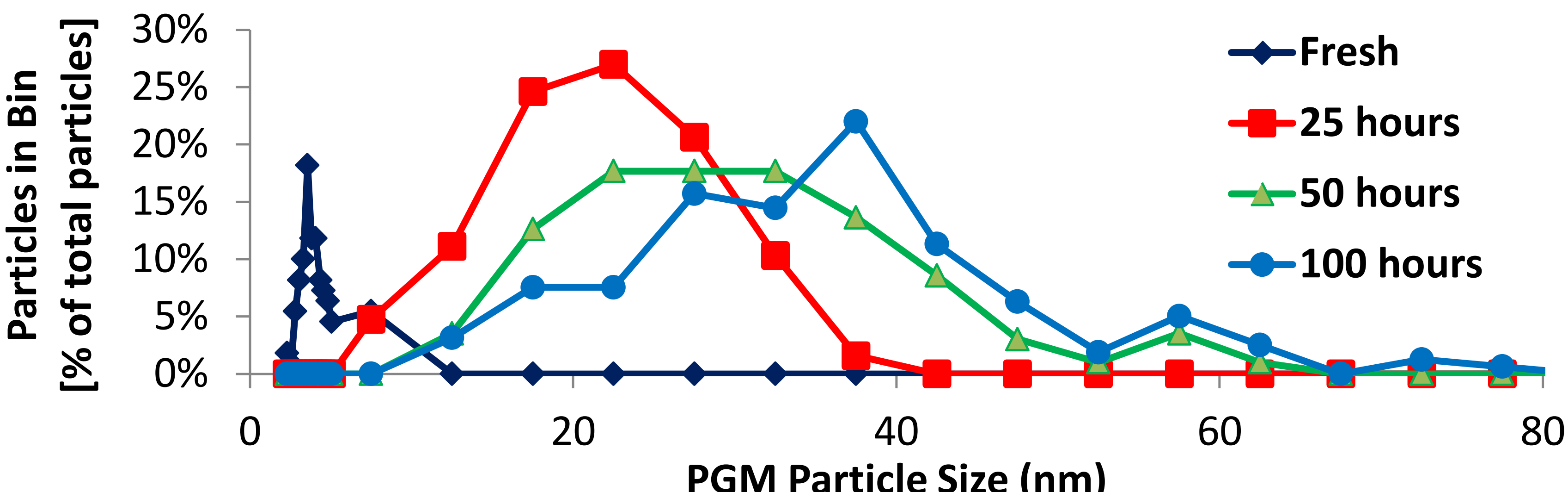




PGM sintering occurs mostly in early aging hours but continues to 100 hours

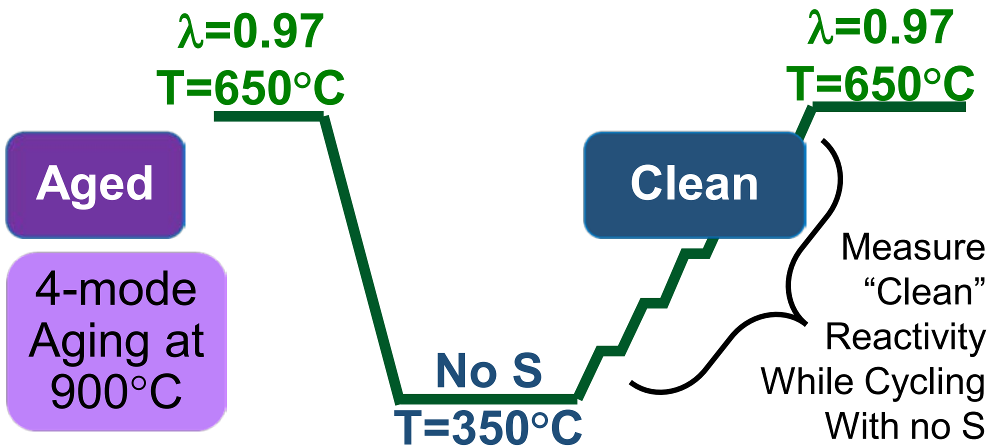
Recall FY15 Aging Data



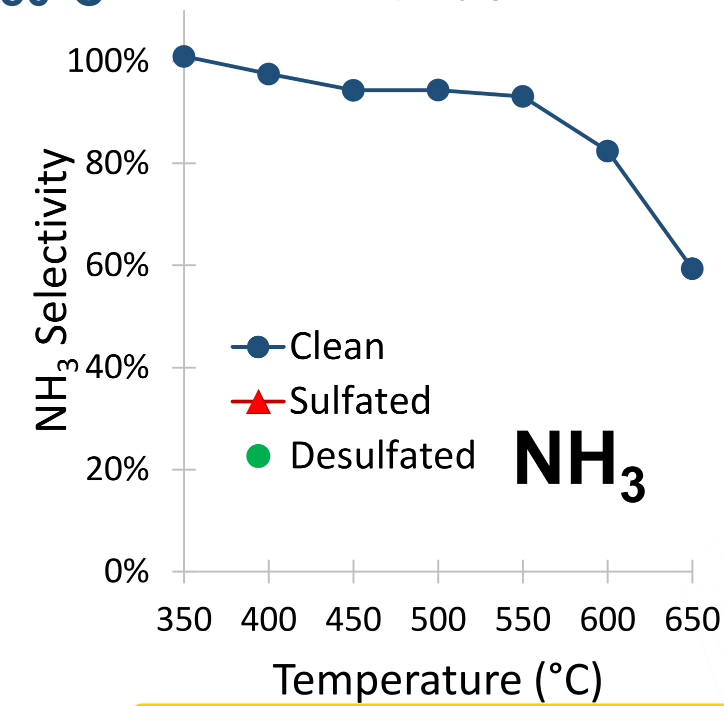


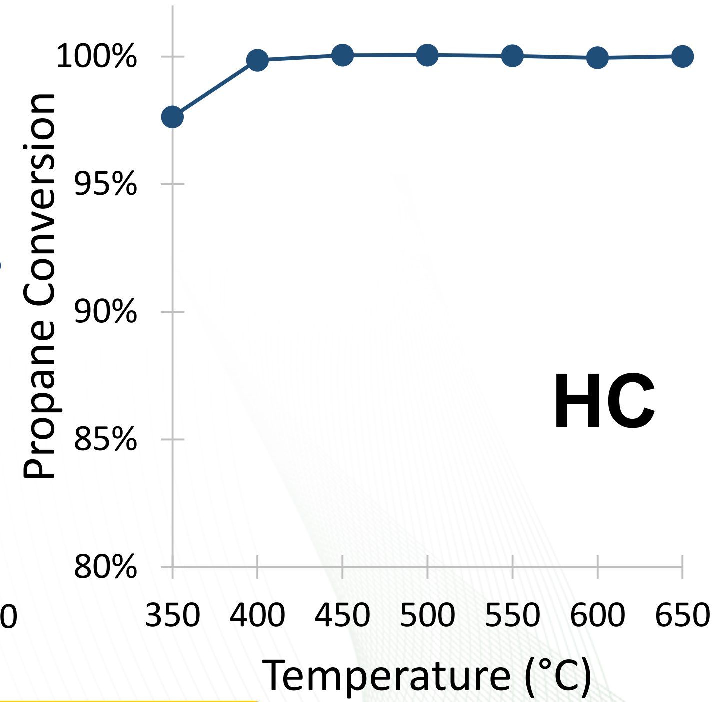
This research was performed, in part, using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities. STEM images collected by Michael Lance (ORNL).

Sulfur impact evaluated on hydrothermally aged TWC while cycling; some effects observed but recoverable



1. Began with Hydrothermally aged Pd TWC (Malibu-1)





Note: Preliminary Results Shown

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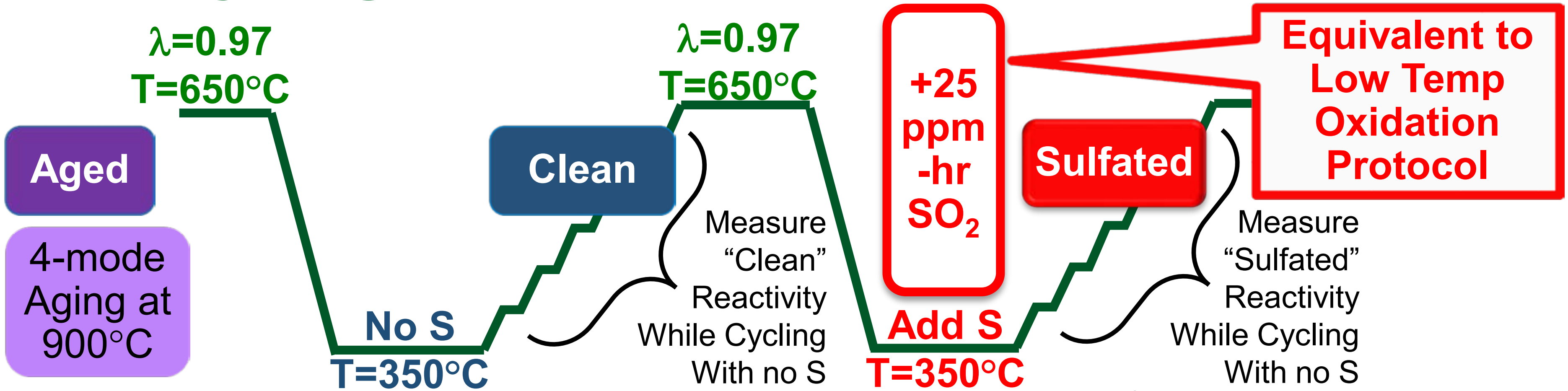

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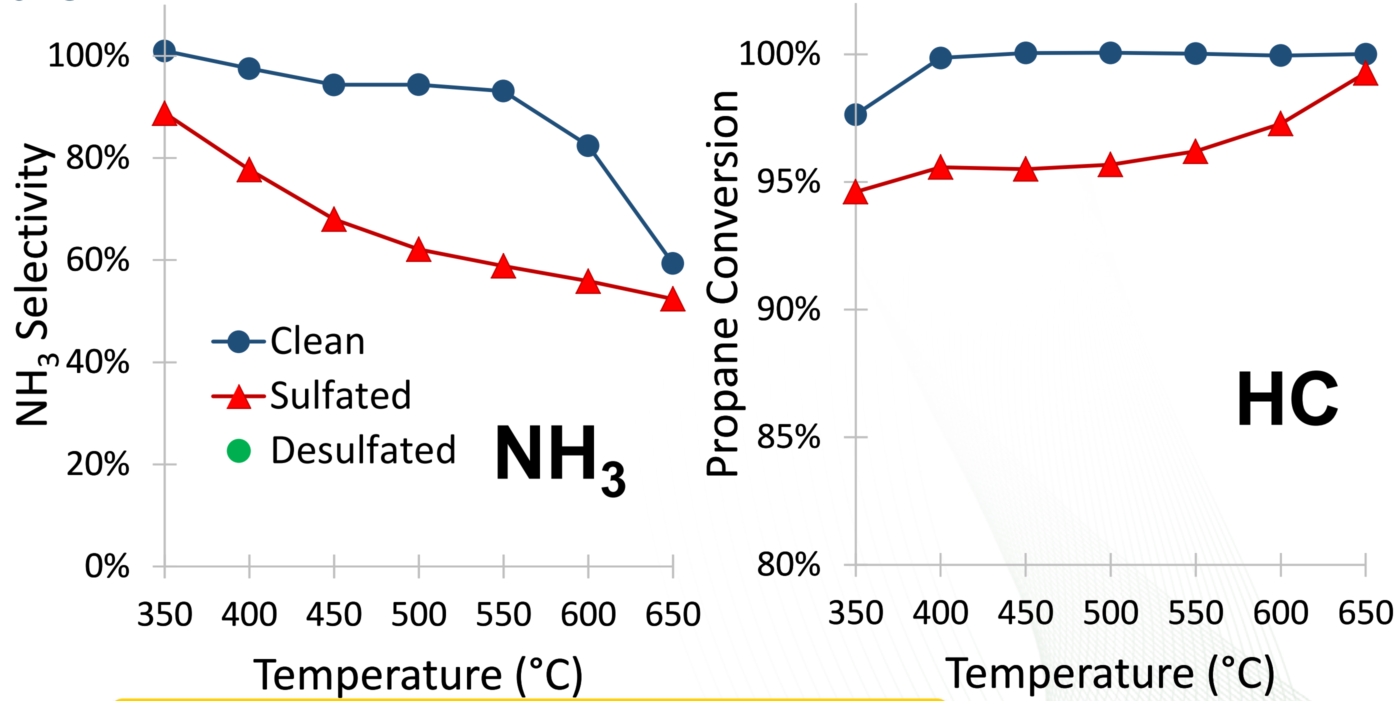
2. S aged TWC while lean-rich cycling (fixed load shown)



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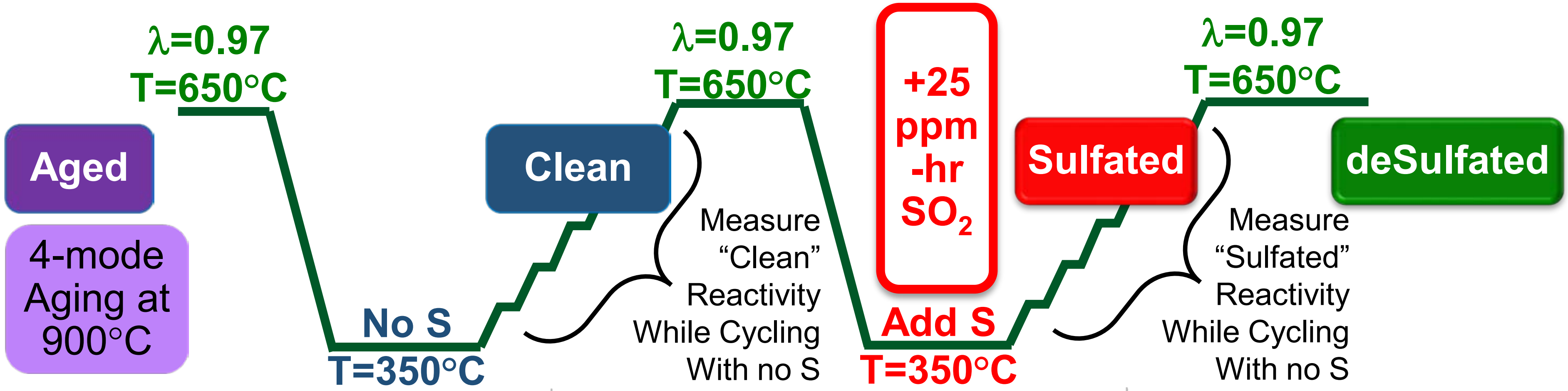
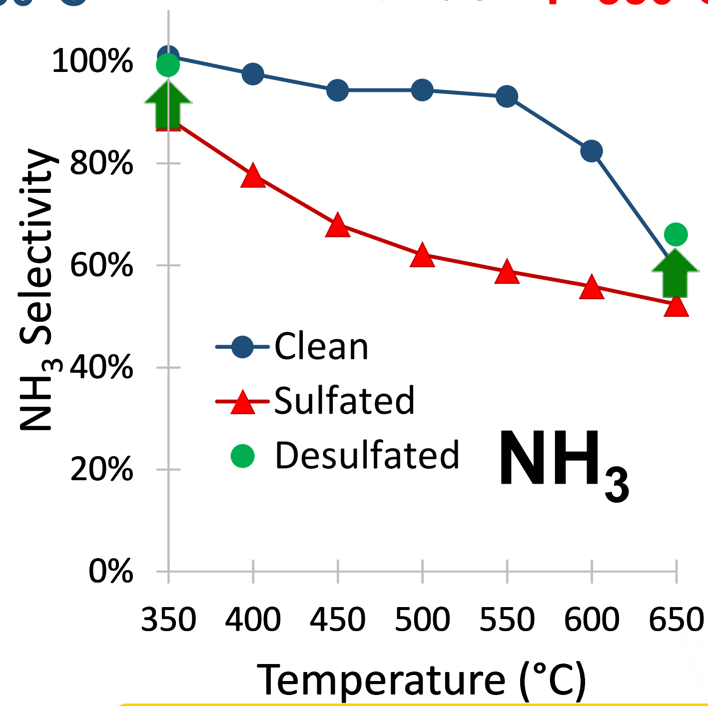
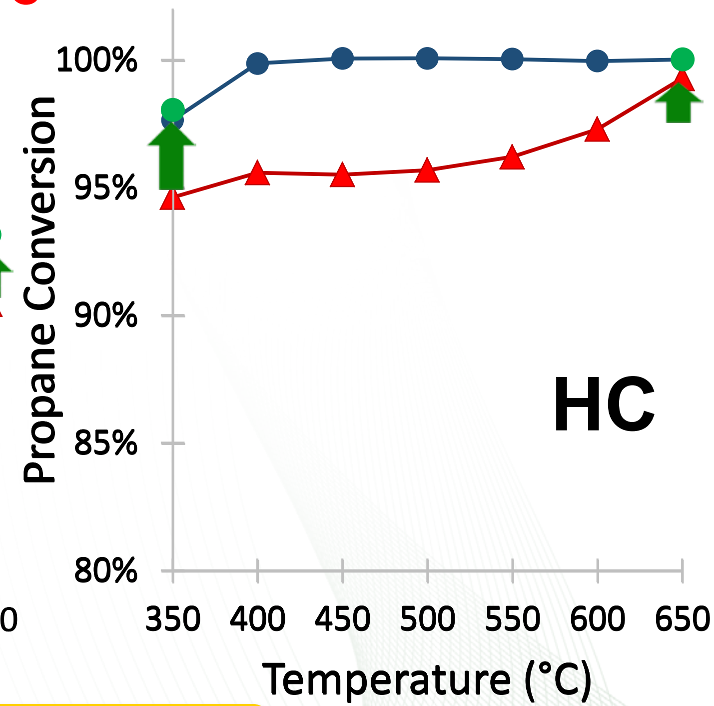


1. Began with Hydrothermally aged Pd TWC (Malibu-1)
2. S aged TWC while lean-rich cycling (fixed load shown)
3. After S aging, deS at 650°C and λ=0.97 while lean-rich cycling
4. After deS: 350°C and 650°C data show good performance recovery





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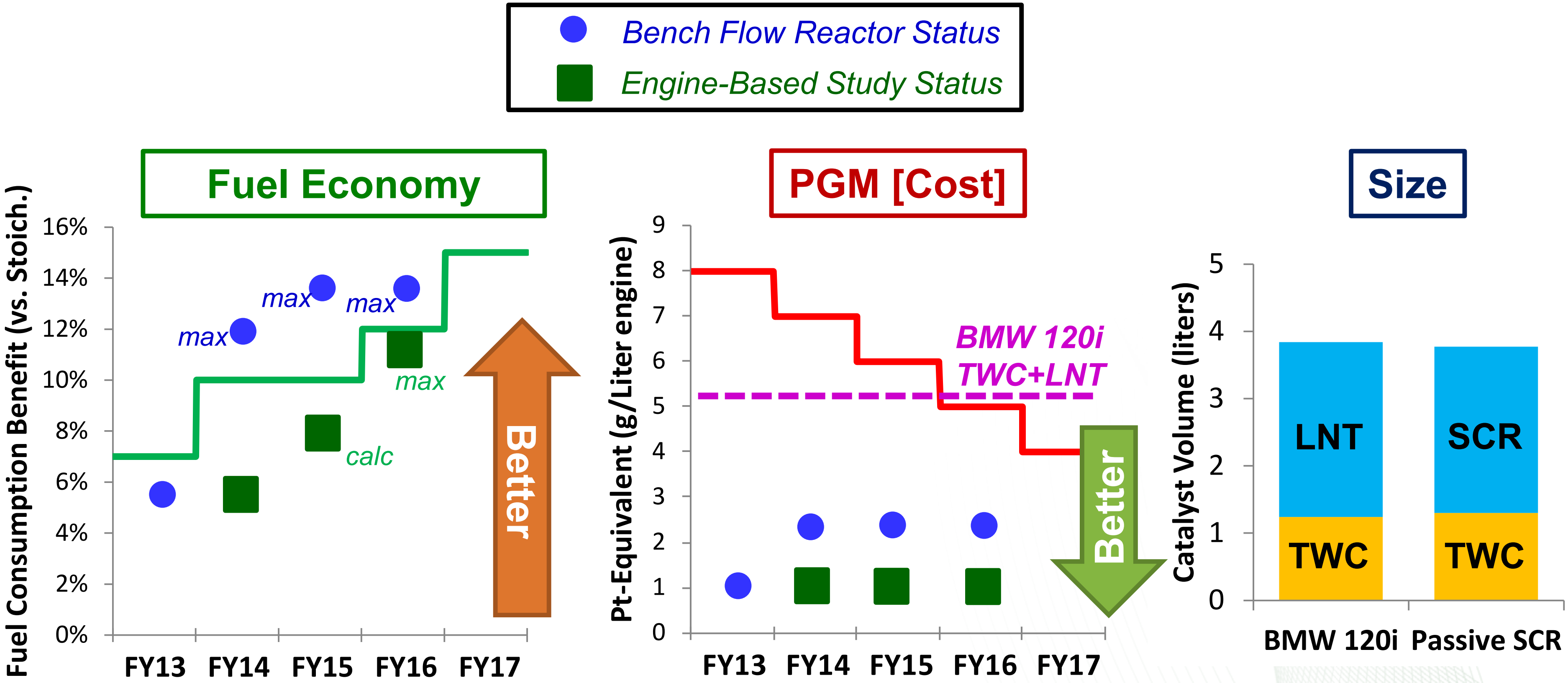
Remaining Challenges

- Improve system level fuel economy (reduce NH_3 production fuel penalty)
- Address catalyst performance during transients and rich-lean transitions
- Determine technique to enable NSC functionality over temperature range
- Broaden aging studies to include SCR



Future Work: Addressing Remaining Challenges

- Catalyst formulation studies on bench flow reactor
  - Examine SCR formulations for NH_3 oxidation and compare resulting data with engine-based data
- Continue aging studies including studying select prototype formulations
  - Perform materials characterization [TEM, BET/Chemi, XRD]
  - Continue aging of TWC formulations with sulfur while cycling
  - Characterize aged SCR (aging complete)
- Continue engine-based studies to maximize system fuel efficiency
  - Repeat existing studies with TWC formulation that contains NSC
  - Understand transient and switching effects on Passive SCR/LNT+SCR
  - Define method to predict transient emissions and fuel efficiency

Summary

Relevance	Enabling lean gasoline vehicles will significantly reduce US petroleum use
Approach	Focus on non-urea Passive SCR and LNT+SCR
	Evaluate catalyst formulations on bench flow reactor for cost-effective emissions control
	Study fuel penalty and realistic performance on lean gasoline engine research platform
Collaborations	Primary: GM, Umicore, and Univ. of South Carolina
	Additional: CDTi, LANL, MECA, Univ. of Minnesota, CTS(FST)
Technical Accomplishments	**Characterized NOx/HC/CO light-off and NH_3/N_2O formation vs. temperature on bench flow reactor of Umicore catalyst matrix**
	Determined optimal NH_3:NOx of 1.13 for fuel efficiency and NOx/NH_3/N_2O slip performance
	Measured PGM peak size shift from 3.5 nm to ~37 nm with aging time
	99% NH_3 yield at 350°C after S during lean-rich cycling + deS
Future Work	Bench reactor, aging, and engine studies ongoing toward project goals of fuel efficiency and cost (Pt-equivalent)

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Technical Backup slides

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Project Goals Defined by Industry

In addition to milestones, a set of project goals has been adopted to ensure progression towards goal of low-cost emissions control solution for fuel efficient lean-burn gasoline vehicles

	FY13	FY14	FY15	FY16	FY17
Fuel economy gain over stoichiometric	7%	10%	10%	12%	15%
Total emissions control devices Pt* (g/L_{engine})	8	7	6	5	4

	5-year Average ($/troy oz.)	Pt-equivalent
Platinum	$ 1,504 /troy oz.	1.0
Palladium	$ 463 /troy oz.	0.3
Rhodium	$ 3,582 /troy oz.	2.4
Gold	$ 989 /troy oz.	0.7

* - will use Pt equivalent cost to account for different costs of Pt, Pd and Rh; 5-year average value fixed at beginning of project

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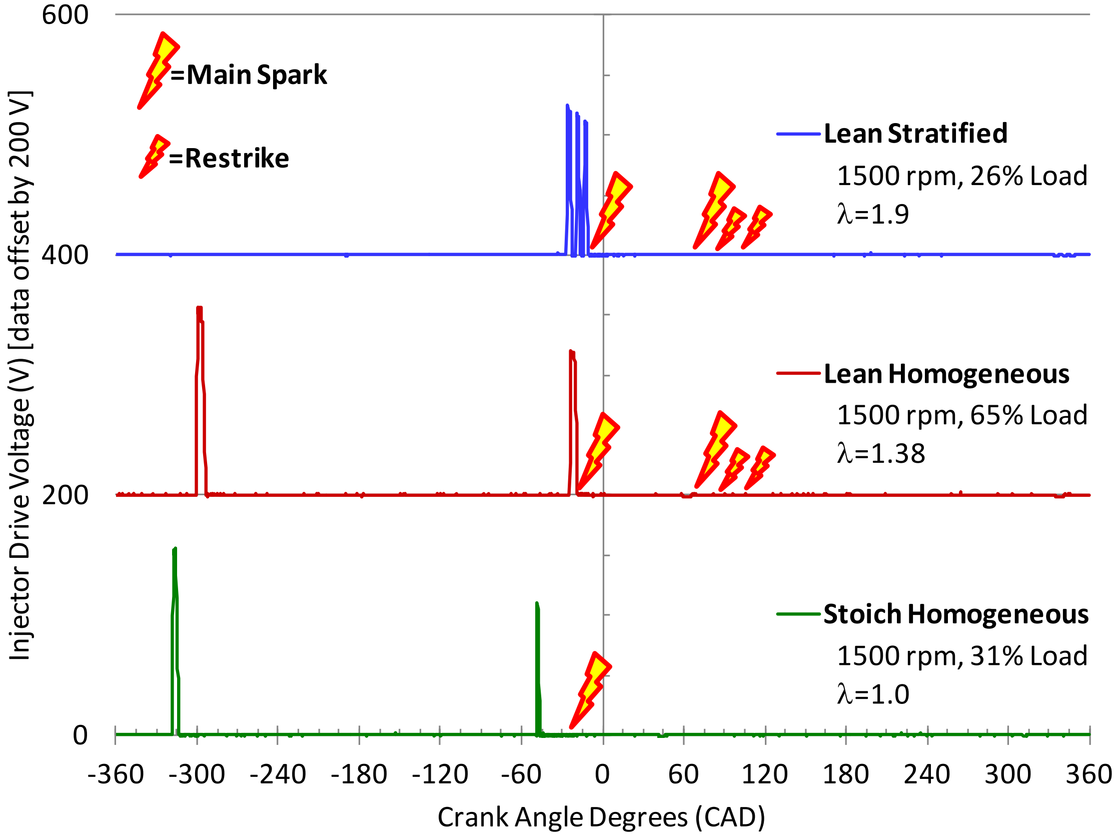
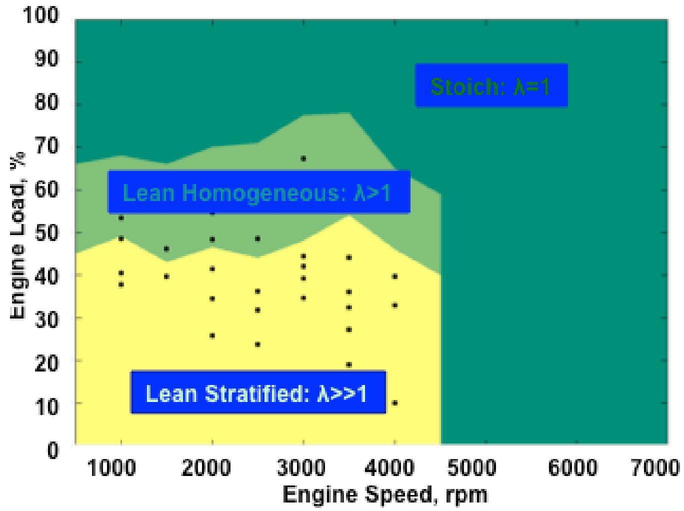
BMW 120i engine features three main combustion modes





- 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 combustions modes, there is also an OEM rich homogeneous mode for LNT control of NO_X emissions to meet EURO V NO_X emission standards

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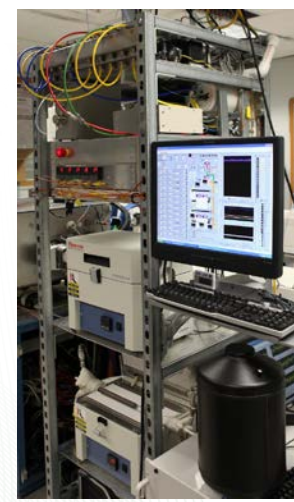
Conducted transient flow reactor experiments to estimate TWC effects on fuel consumption

- Used feedback-controlled cycles on flow reactor to evaluate dynamic TWC response in context of passive SCR
- Evaluated two different simulated engine cycles (fixed load, load step)

	fixed load		load step	
	rich	lean	rich	lean
load (BMEP)	2 bar	2 bar	8 bar	2 bar
SV (h^{-1})	**27000**	45000	**60000**	45000
NOx (ppm)	**600**	360	**1200**	360
max lean time	**50%**		**80%**	
simulates	cruise		"hill" transient	

	Rich						Lean
λ	0.95	0.96	0.97	0.98	0.99	1.00	2
O_2 (%)	0.96	1.02	1.07	1.13	1.17	1.22	10
CO (%)	2.0	1.8	1.6	1.4	1.2	1.0	0.2
H_2 (%)	1.0	0.9	0.8	0.7	0.6	0.5	0
NO (ppm)	600 (or 1200)						360
C_3H_8 (ppm C_1)	3000						1900
H_2O (%)	11						6.6
CO_2 (%)	11						6.6
TWC SV (hr^{-1})	27000 (or 60000)						45000

- Compositions & flows selected to mimic BMW GDI engine exhaust
- Space velocity changed with λ and load
- C_3H_8 chosen as challenging HC



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