Emissions Control for Lean Gasoline Engines
Project ID: ace033

Oak Ridge National Laboratory
National Transportation Research Center

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  - *Ken Price, Ryan Day, David Moser, Sanket Nipunage, Thiago Affonso, Sanket Nipunage, Tom Pauly*

Overview

Timeline

- Year 2 of 3-year program

  Project start date: FY2019

  Project end date: FY2021
- Builds on previous R&D in FY16-FY18
- Task 3 of larger ORNL project "Controlling Emissions from High Efficiency Combustion System" in response to 2018 VTO Lab Call

Barriers Addressed

U.S. DRIVE Advanced Combustion & Emission Control 2018 Roadmap Barriers & Targets:

- Lack of cost-effective aftertreatment for lean-burn systems
- Compliance with U.S. EPA Tier 3 Bin 30 emission standard
- Efficiency, durability, sulfur tolerance of aftertreatment systems

Budget

FY19	FY20
$500k	$500k

Collaborators & Partners

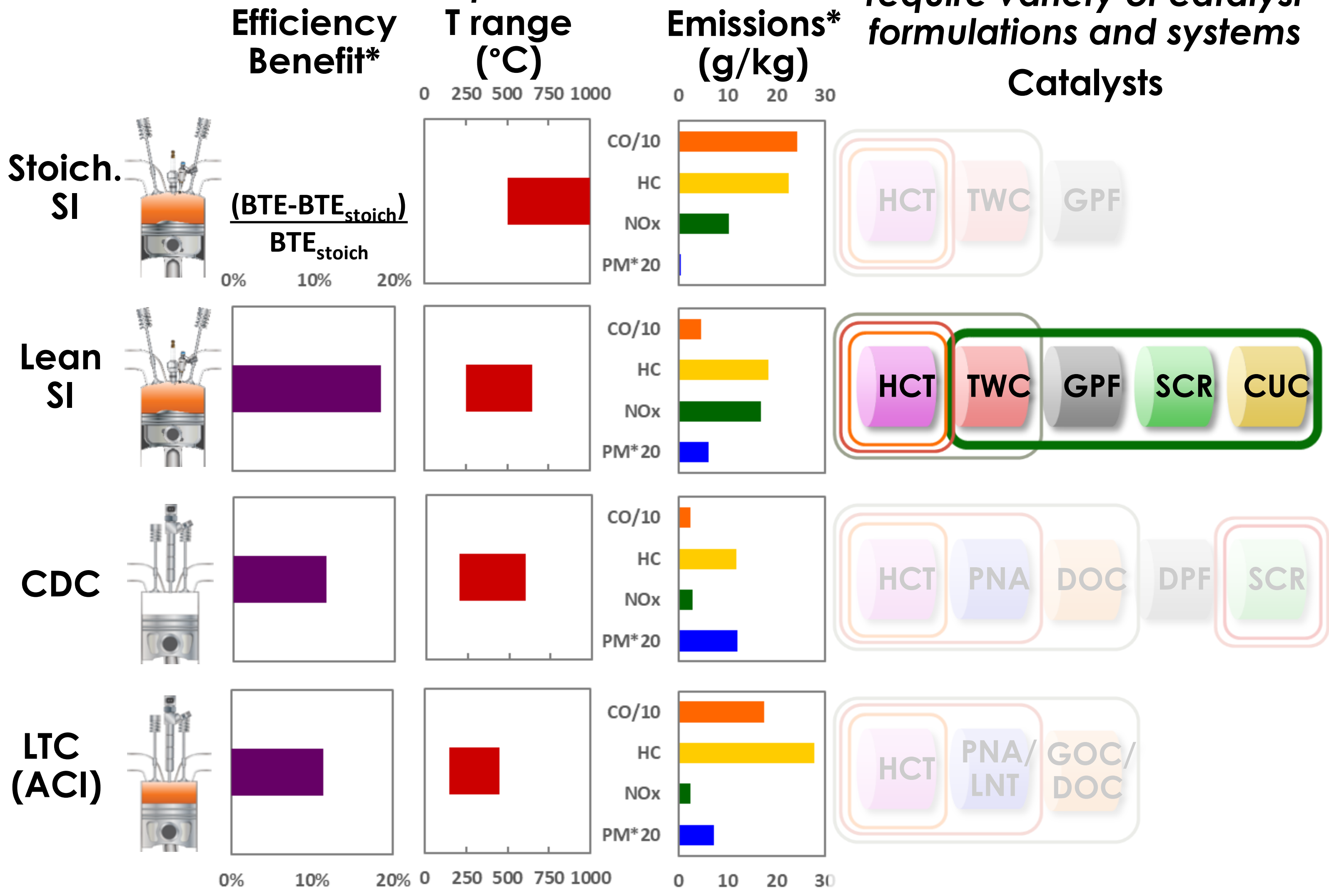
- General Motors
- Umicore
- Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS)

Advanced combustion technologies improve efficiency, but lean low temperature exhaust creates emissions challenges that must be addressed before commercialization

Higher fuel efficiency = lower exhaust temperatures

Unique emissions profiles require variety of catalyst formulations and systems

ORNL R&D portfolio spans wide range of applications, technologies, size scales, commercial readiness



Projects

CLEERS (ACE022)
Model new trap materials and aging effects on SCR catalysts

Low Temperature Emissions Control (ACE085)
Discover new low T catalysts & traps

Lean Gasoline Emissions Control (ACE033)
Develop pathways for lean gasoline engines to meet emissions with minimum fuel penalty

Chemistry & Control of Cold Start Emissions (ACE153)
Understand how exhaust chemistry impacts device performance & design

Cummins Emissions Control CRADA (ACE032)
Understand how aging affects properties and performance of SCR catalysts

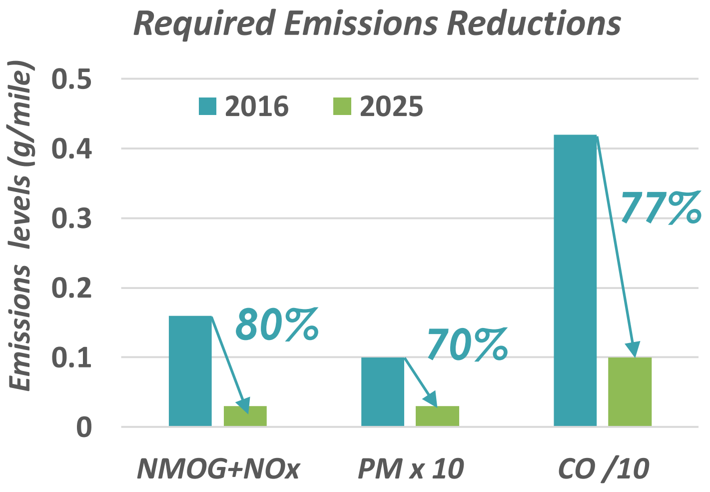
*(efficiency and emissions at 2000 rpm, ~2 bar BMEP)

see backup slide for abbreviations

Objectives and Relevance

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

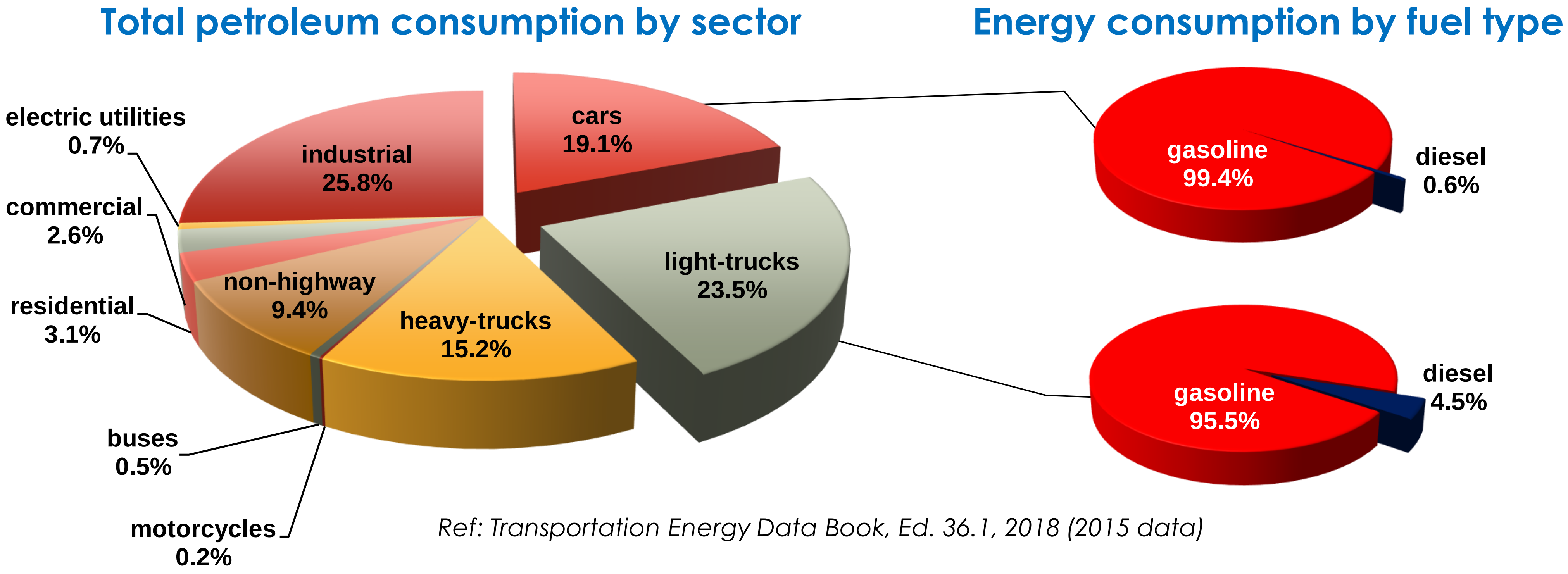
- Objective:
  - Demonstrate technical path to emission compliance that would allow the implementation of lean gasoline vehicles in the U.S. market
    - Lean vehicles offer 5–15% increased efficiency over stoichiometric-operated gasoline vehicles
    - Compliance required: U.S. EPA Tier 3
  - Investigate strategies for cost-effective compliance
    - Minimize precious metal content while maximizing fuel economy



- Relevance:
  - 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

NMOG=non-methane organic gases; PM=particulate matter

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



Ref: Transportation Energy Data Book, Ed. 36.1, 2018 (2015 data)

- U.S. 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 <u>~13 billion gal/year</u>

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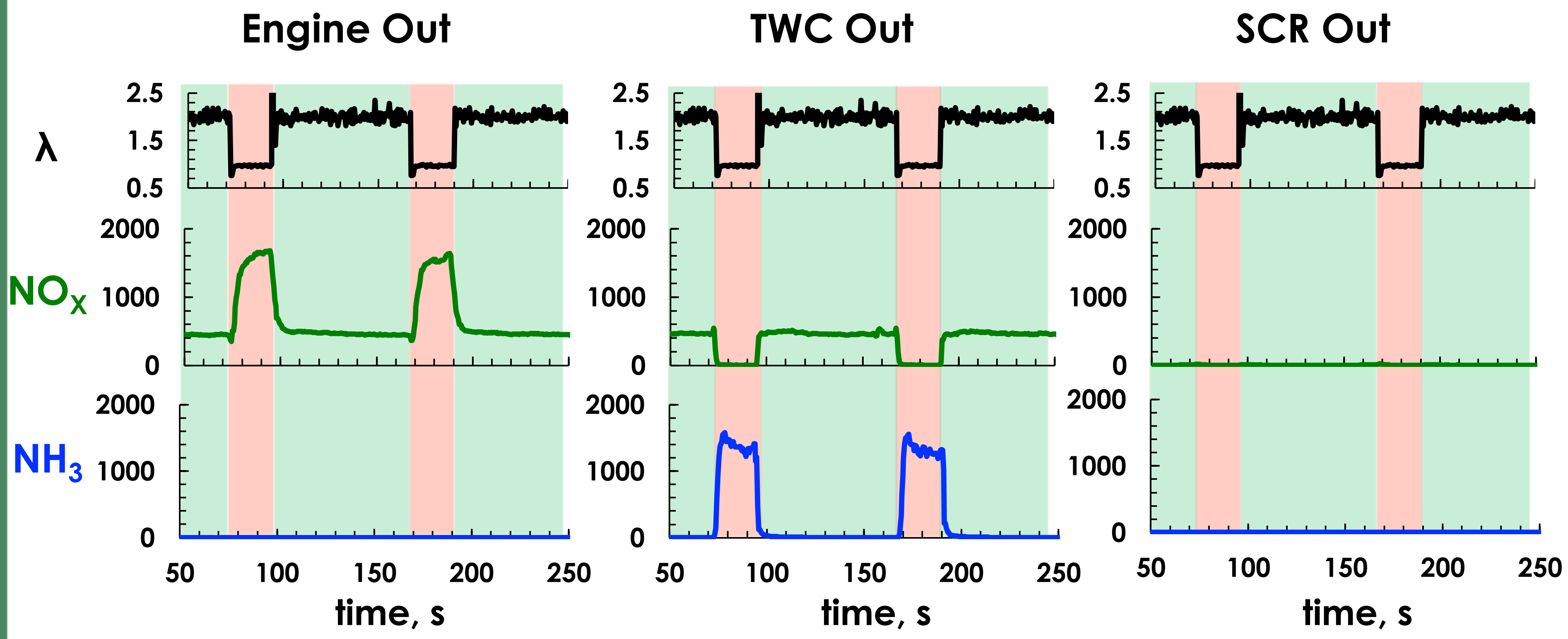
Passive SCR is non-urea approach to lean gasoline NOx control



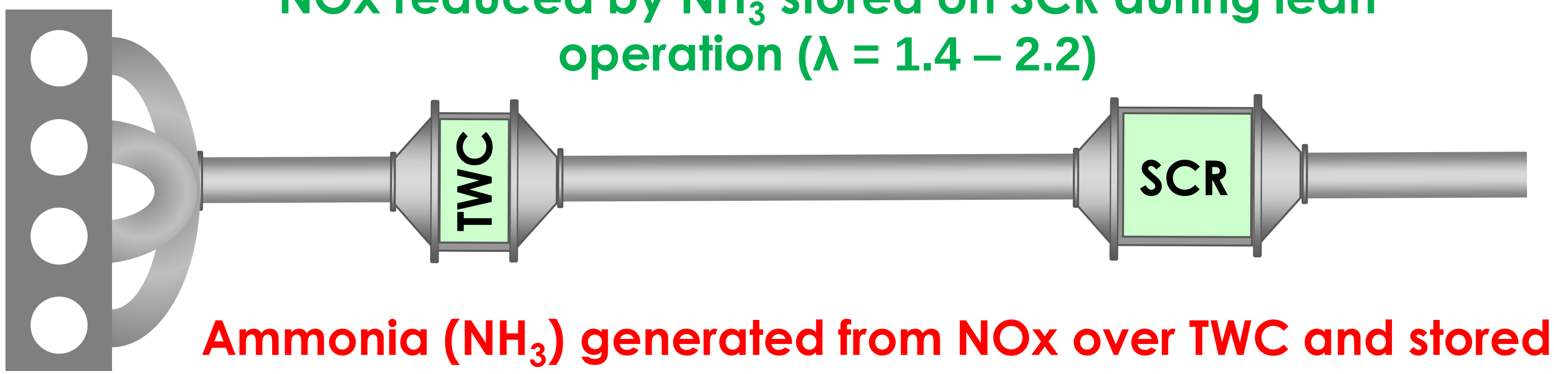
Passive SCR is a potential low cost strategy for reducing lean gasoline NOx emissions

- Makes use of TWC already onboard to generate NH_3
- Eliminates urea tank, injector, refills
- Potentially reduces PGM relative to TWC+LNT

$$\lambda = \frac{AFR}{AFR_{stoich}}$$

AFR = air/fuel ratio
λ <1: excess fuel
λ =1: stoichiometric
λ >1: excess air

NOx reduced by NH_3 stored on SCR during lean operation (λ = 1.4 – 2.2)



Ammonia (NH_3) generated from NOx over TWC and stored on SCR during rich phase (λ = 0.96 – 0.99)

SAE2010-01-0366, SAE2011-01-0306, SAE2011-01-0307

PGM=platinum group metals

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Approach focuses on engine and catalyst optimization of passive SCR

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

Lean

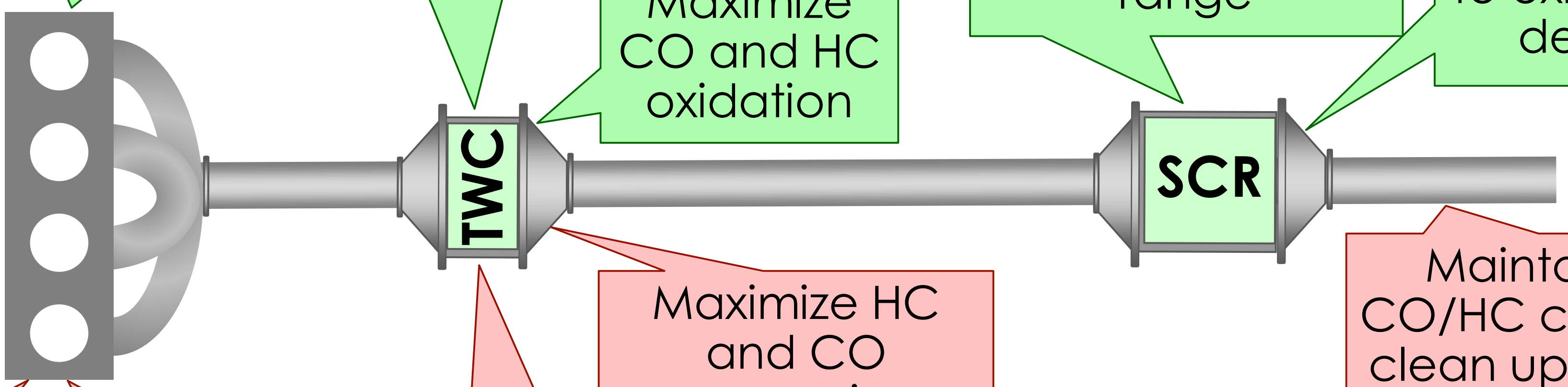
Minimize engine out Lean NOx emissions

Add NOx storage to extend lean operation

Maximize CO and HC oxidation

Maintain high NOx conversion over wide temperature range

Minimize NH_3 lost to oxidation and desorption



Rich

Maximize engine out Rich NOx emissions

Control emissions during lean-rich transitions

Maximize NO_X to NH_3 conversion efficiency

Maximize HC and CO conversion

Maintain high CO/HC conversion; clean up CO/HC if needed

Other Core Principles:

- Expand operating temperature range
- Evaluate durability to aging and sulfur
- Understand precious metal utilization to minimize cost

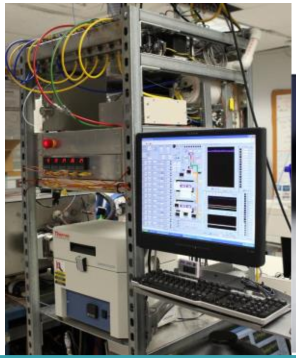
Refs: SAE2010-01-0366, SAE2011-01-0306

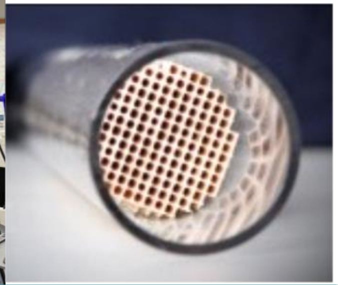
HC=hydrocarbon

Iterative Flow Reactor + Engine Study Approach

BMW 120i lean gasoline engine platform with open controller

- Define relevant exhaust conditions
- Evaluation of selected catalyst components, system integration and optimization
- Measurement of fuel economy and emissions over pseudo-transient cycle
- Optimize combustion parameters for fuel efficiency and emissions

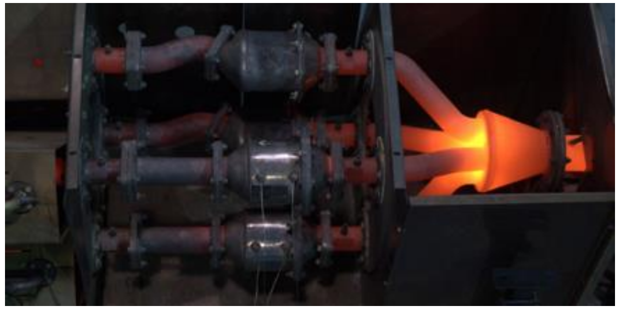




Automated Flow Reactor with feedback control and tandem catalysts

- Detailed characterization and screening of catalysts in simulated exhaust
- Investigation of alternative catalyst configurations and operating strategies
- Age and characterize selected catalyst formulations

Collaborations with modeling community and CLEERS



C-FOCAS Burner at SGS full scale catalysts aging

- Age selected TWC, SCR and CUC catalysts for engine and flow reactor evaluations
- Air-fuel ratio, temperature and flow rate control

umicore Automotive Catalysts

Prototype Catalysts & Insights

GM

Technical Guidance

Collaborations and Partners

Primary Project Partners *(regular monthly teleconferences)*

- **GM:** guidance and advice on lean gasoline systems
- **Umicore:** guidance and catalysts (commercial and prototype formulations)

umicore
Automotive
Catalysts

Additional Collaborators/Partners on Project/Engine Platform (since project inception)

- CLEERS: share results/data and identify research needs
- LANL engine platform used for NOx/HC/NH_3 mixed-potential sensor research
- PNNL detailed PM characterization from lean gasoline engines using SPLAT
- DOE Co-Optima: engine platform used for biofuel-based HC-SCR studies
- U. of Minnesota: collaboration on DOE funded project at U. of Minn. related to lean GDI PM
- U. of Kentucky: FOA project on HC/NOx trap catalysts for gasoline applications
- Tennessee Tech U.: project data being used for lean gasoline emission control system modeling
- CDTi: catalysts for studies
- MECA: GPF studies via NTRC User-Facility contract
- CTS: FOA project on radio-frequency (RF) sensors for GPF, SCR, TWC diagnostics
- SGS full scale catalyst aging
- Hyundai: engine platform used for Proprietary User Agreement Project
- MAHLE: new advanced pre-chamber ignition ultra lean gasoline engine

R&D Expanded Coverage via Collaborations:

- PM Emissions
- Sensors
- Modeling
- Fuels
- Aging

Milestones

Quarterly Milestones

Complete

- **FY2019, Q3:** Complete evaluation of 5-function emissions control system with cleanup catalyst

On Track

- **FY2020, Q4:** Complete measurement of fuel economy benefit and emissions using transient drive cycle on the newly installed MAHLE Jet Ignition engine

On Track

- **FY2021, Q4:** Tier 3 Bin 30 level emissions with an advanced engine platform with less than 4 g Pt-equivalent per liter engine displacement

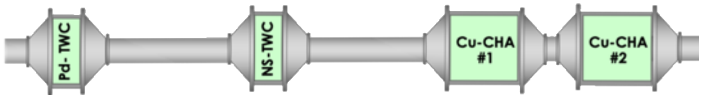
GO/NO-GO Decision

Complete

- **FY2019, Q4:** Install MAHLE Jet Ignition engine at ORNL with full controls which will expand lean operation map for higher fuel efficiency and lower engine out emissions

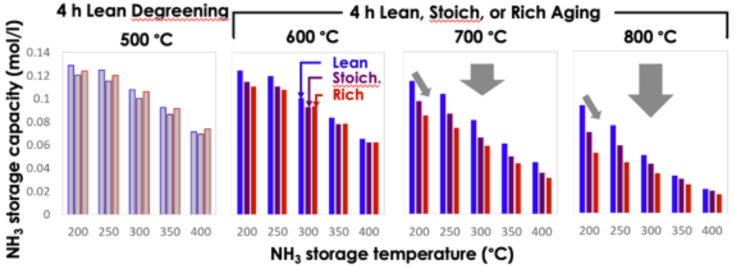
Summary of Technical Accomplishments

- Evaluated passive SCR performance with aged production Cu-chabazite SCR catalysts on engine over pseudo-transient cycle



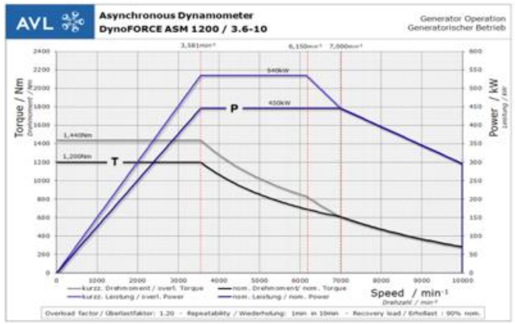
All catalysts aged using Advanced Combustion and Emission Control (ACEC) aging protocol

- Preliminary results of SCR aging effects obtained on synthetic exhaust flow reactor under relevant passive SCR operating conditions



- Installed and instrumented MAHLE Jet Ignition (MJI) engine in the test cell at ORNL with full controls

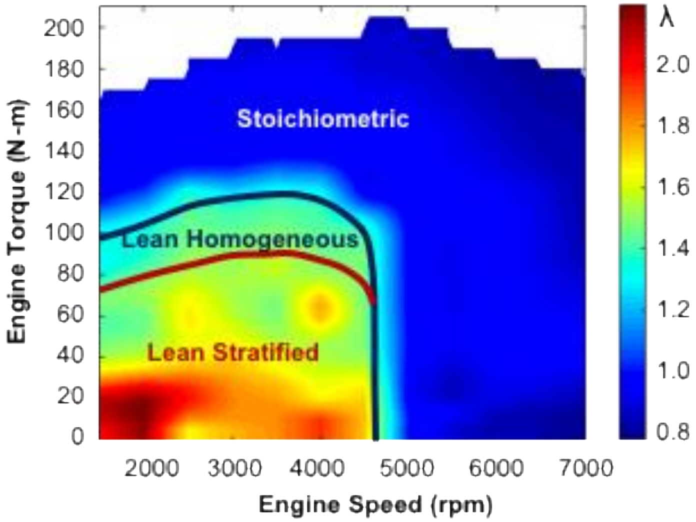
- Procured 400 hp AVL Alternating Current (AC) Dynamometer suitable for wide range of applications

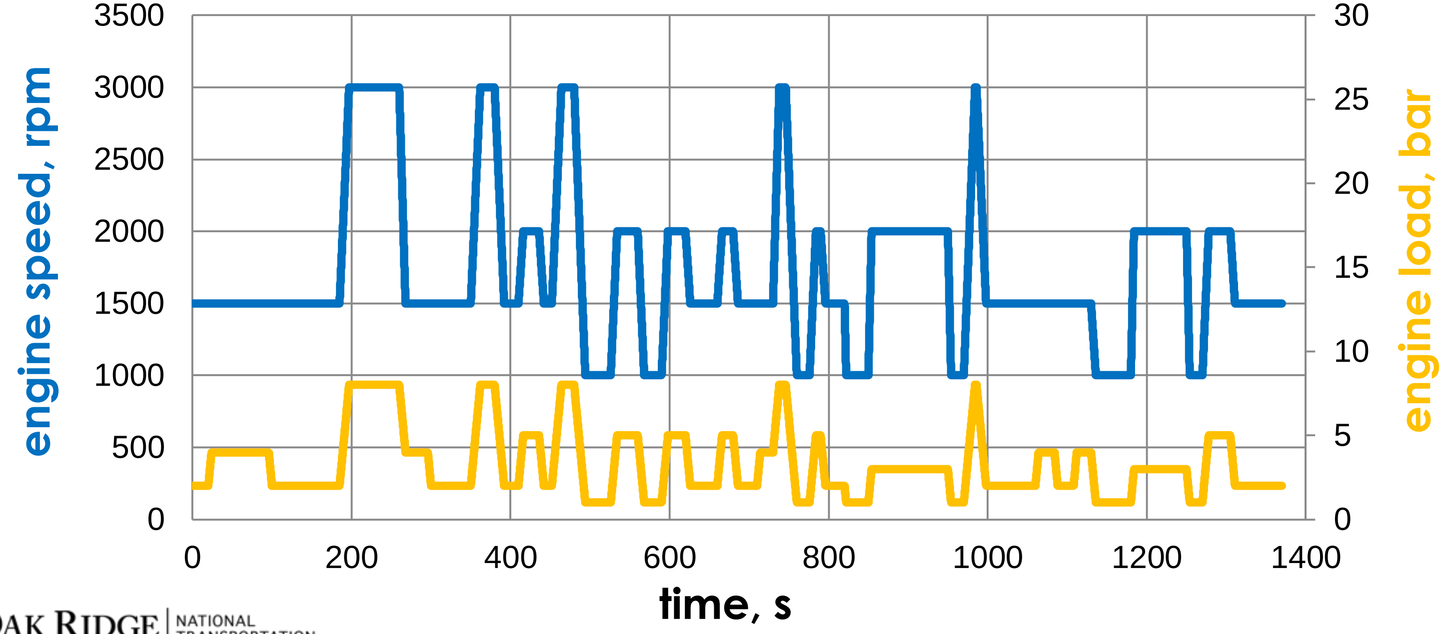


To simulate drive cycle, GM provided 6-mode pseudo-transient cycle utilized for on-engine passive SCR evaluations

Pseudo-transient cycle is simplified modal engine test cycle representative of "hot" FTP cycle

- six speed and load points with constant acceleration during transitions
- cycle closely captures fuel consumption benefit relative to stoichiometric operation observed in vehicle study*
  - 9.6% with pseudo-transient cycle (baseline for comparing fuel penalties)
  - 10% with FTP vehicle study





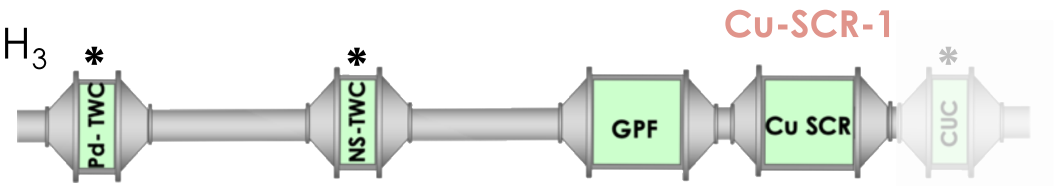
Speed [rpm]	Load [bar]	Default Mode
1000	1.0	LS
1500	2.0	LS
1500	4.0	LS
2000	3.0	LS
2000	5.0	LH
3000	8.0	Stoich

LS=lean stratified; LH=lean homogeneous

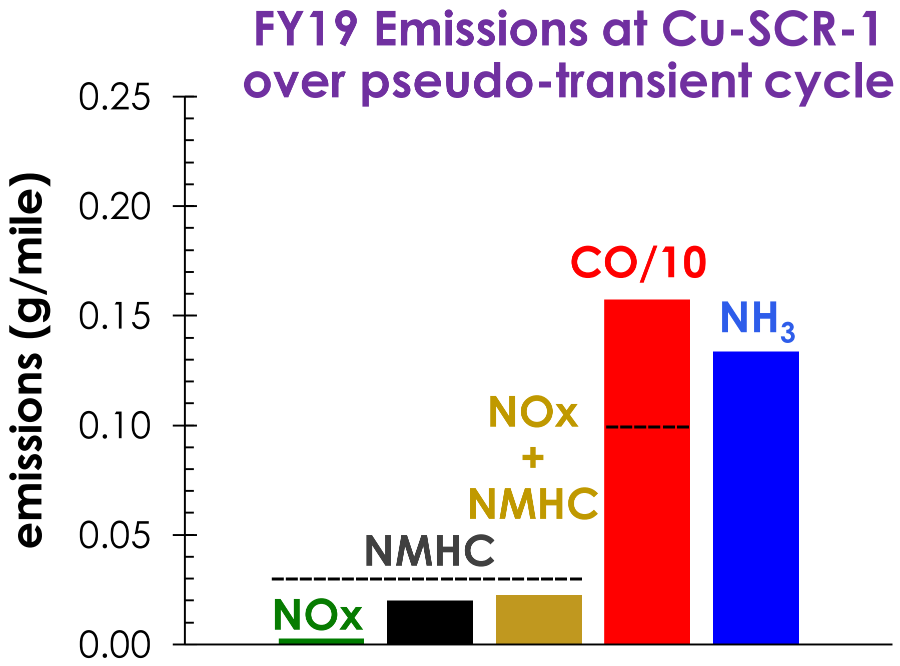
** - SAE2010-01-2267, SAE2011-01-1218*

FY19 results: improved system architecture demonstrated higher fuel efficiency and lower emissions; challenges and opportunities remain

- FY19: Pd-TWC and NS-TWC combination enabled more efficient NH_3 generation and provided a pathway for increasing fuel economy benefit from 5.9% (with Pd-TWC only) to 8.3%
- Remaining challenges
  - <u>CO control during rich operation</u>
    - clean-up catalyst
    - secondary air injection
  - <u>Increase fuel efficiency</u>
    - improve control strategies for better NH_3 utilization
    - additional catalyst formulations/architectures
    - advanced pre-chamber ignition system (MJI engine) for higher fuel efficiency and lower engine out emissions
  - <u>SCR durability under relevant passive SCR conditions</u>
    - **early generation Cu-SCR-1 used in all prior studies, not aged**
    - age, analyze and characterize new SCR formulations supplied by Umicore (ongoing studies)



* catalysts aged using ACEC aging protocol (see backup slides)



------ Tier 3 bin 30: 0.03 g/mi of NOx+NMOG,1.0 g/mi of CO

NMHC=non-methane hydrocarbon; NMHC~NMOG for gasoline engines

New catalyst formulations supplied by Umicore specifically for this project

- **Clean-Up Catalysts (CUC):**
  - Four unique Pt/Pd ratio prototype formulations with high OSC levels
- **Ammonia Slip Catalysts (ASC):**
  - Two SCR + Pt-based ASC combo formulations
- **Selective Catalytic Reduction (SCR) catalysts:**
  - Two new formulations for durability studies
  - Permission from Umicore to analyze to determine aging mechanisms

Sample ID	Description	Cell Density (cpsi)
Cu-SCR-1	early generation Cu SCR	400
Cu-SCR-2	production Cu-chabazite SCR	400
Cu-SCR-3	next generation Cu-chabazite SCR	600

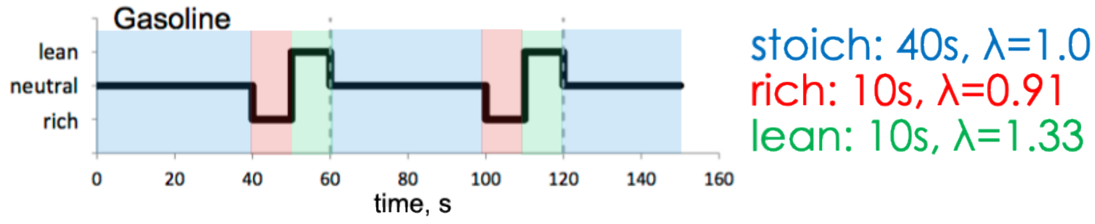
used in all prior studies

new formulations

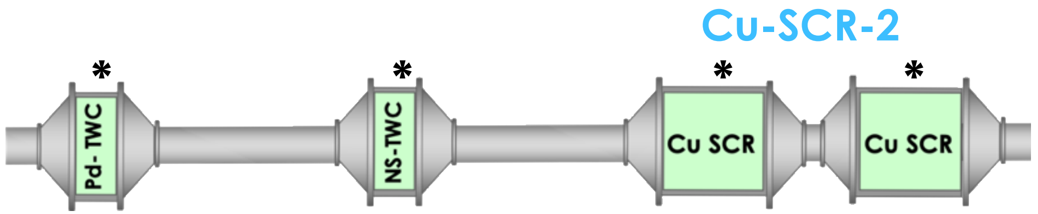
OSC=oxygen storage capacity

Lower NH_3 storage capacity of aged Cu-SCR-2 affects overall NOx reduction efficiency and fuel consumption

- For engine studies, production Cu-SCR-2 catalysts were aged at SGS using ACEC aging protocol:



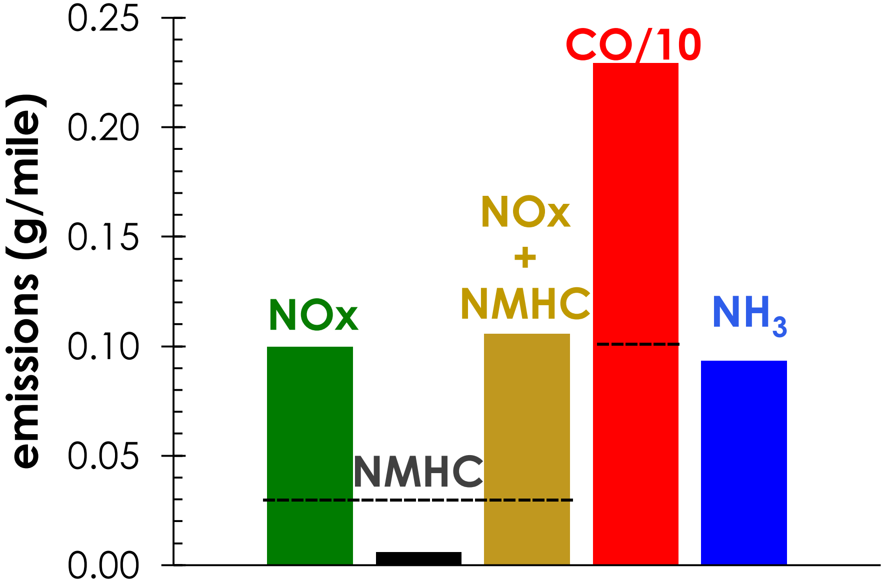
stoich/rich/lean cycling for 50 hr at 700 °C inlet temperature



* catalysts aged using ACEC aging protocol

- Increase in NOx emissions with aged Cu-SCR-2 when using the same operating strategy as with degreened Cu-SCR-1
- NOx and NH_3 slip indicative of lower NH_3 storage capacity of aged Cu-SCR-2

Emissions at aged Cu-SCR-2 over pseudo-transient cycle

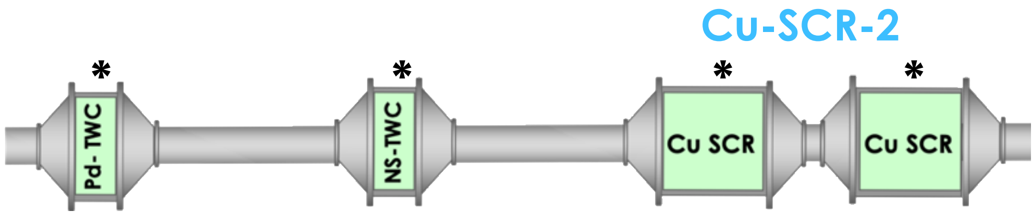


------ Tier 3 bin 30: 0.03 g/mi of NOx+NMOG,1.0 g/mi of CO

Sample ID	Description
Cu-SCR-1	early generation Cu SCR
Cu-SCR-2	production Cu-chabazite SCR
Cu-SCR-3	next generation Cu-chabazite SCR

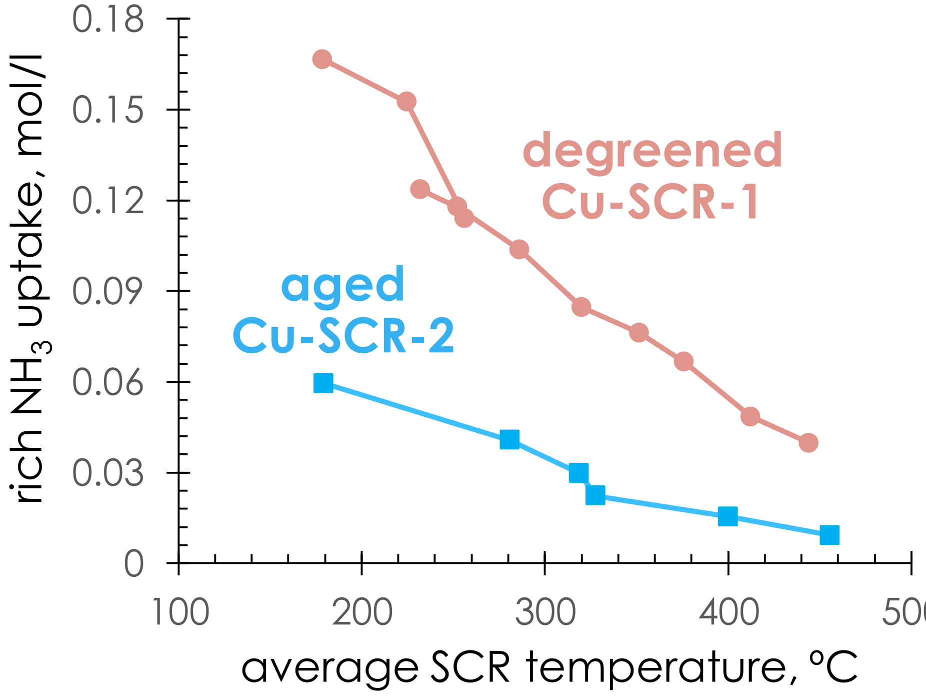
SCR activity and/or NH_3 storage capacity sensitive to aging air-fuel ratio and temperature

- SCR rich NH_3 uptake measured on engine (details in backup slides)
- Significantly lower rich NH_3 storage capacity measured on aged Cu-SCR-2
- SCR activity and/or NH_3 storage degrade after hydrothermal aging
  - Severity depends on catalyst formulation, aging temperature and air-fuel ratio
  - Potentially other aging mechanisms when exposed to rich



* catalysts aged using ACEC aging protocol

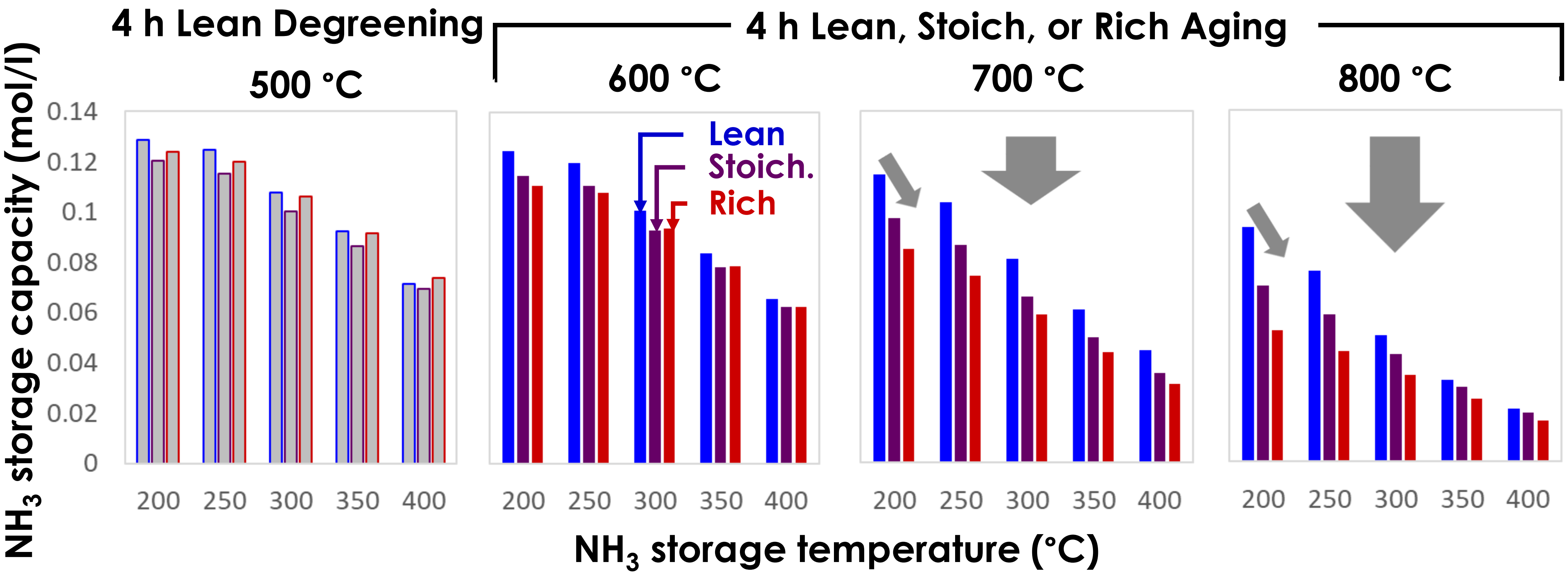
Passive SCR performance depends on absolute amount of stored NH_3 → important to understand aging mechanisms effecting NH_3 storage capacity and NOx reduction under relevant passive SCR conditions



References:
SAE2008-01-0811
SAE2016-01-0954
Catal. Sci. Technol., 2019, 9, 2152
Catalysts 2019, 9, 929

Sample ID	Description
Cu-SCR-1	early generation Cu SCR
Cu-SCR-2	production Cu-chabazite SCR
Cu-SCR-3	next generation Cu-chabazite SCR

Flow reactor aging study: loss of NH_3 storage sites depends on hydrothermal aging temperature and gas composition

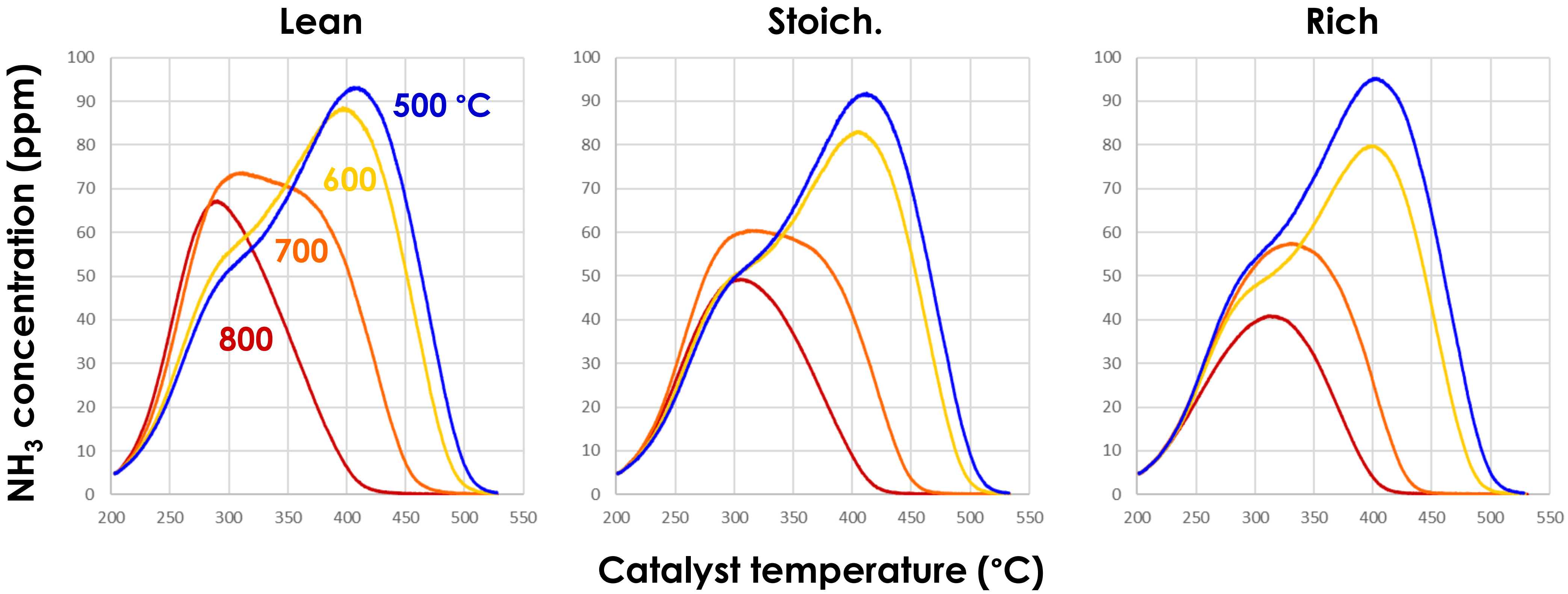


	Lean	Stoich	Rich
O_2	10%	0	0
CO	0	0	0.8%
H_2	0	0	0.4%
CO_2	6.6%	6.6%	6.6%
H_2O	6.6%	6.6%	6.6%

- Aging at 600 °C has minimal effect on NH_3 storage capacity regardless of composition
- Aging at 700 °C and 800 °C both significantly reduce NH_3 storage capacities, especially at higher storage temperatures
- Aging severity varies with gas composition: Rich > Stoich. > Lean

Sample ID	Description
Cu-SCR-1	early generation Cu SCR
Cu-SCR-2	production Cu-chabazite SCR
Cu-SCR-3	next generation Cu-chabazite SCR

NH_3 TPD results clearly indicate loss of high temperature storage sites with ≥700 °C aging



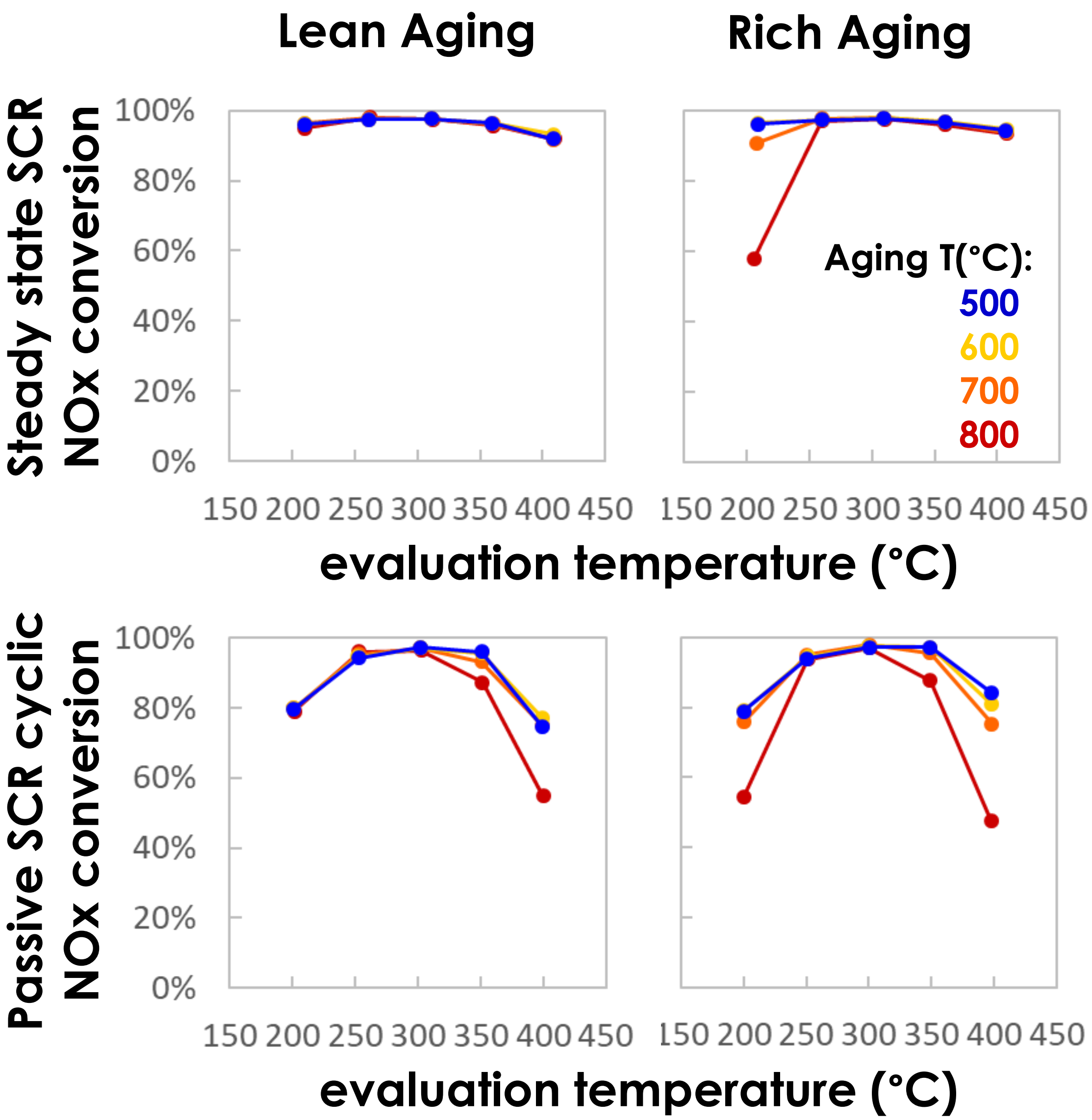
- High temperature NH_3 storage is degraded at 700 °C aging and eliminated at 800 °C
- Stoich. and (especially) Rich aging accelerate degradation

Sample ID	Description
Cu-SCR-1	early generation Cu SCR
Cu-SCR-2	production Cu-chabazite SCR
Cu-SCR-3	next generation Cu-chabazite SCR

TPD=temperature-programmed desorption

Passive SCR NOx conversion is more sensitive to aging than steady state SCR, and rich aging is worse than lean aging

- Steady State SCR:
  - Lean aging has no effect
  - Rich aging impacts low T NOx conversion
    - 700 °C: slight reduction
    - 800 °C significant degradation
- Passive SCR cycles:
  - Lean aging at 800 °C degrades high T NOx conversion
  - Rich aging progressively degrades high T NOx conversion
  - Rich aging at 800 °C also degrades low T NOx conversion



λ	2.0
NO	600 ppm
NH_3	600 ppm
O_2	10%
CO_2	6.6%
H_2O	6.6%
SV	25000 h^{-1}

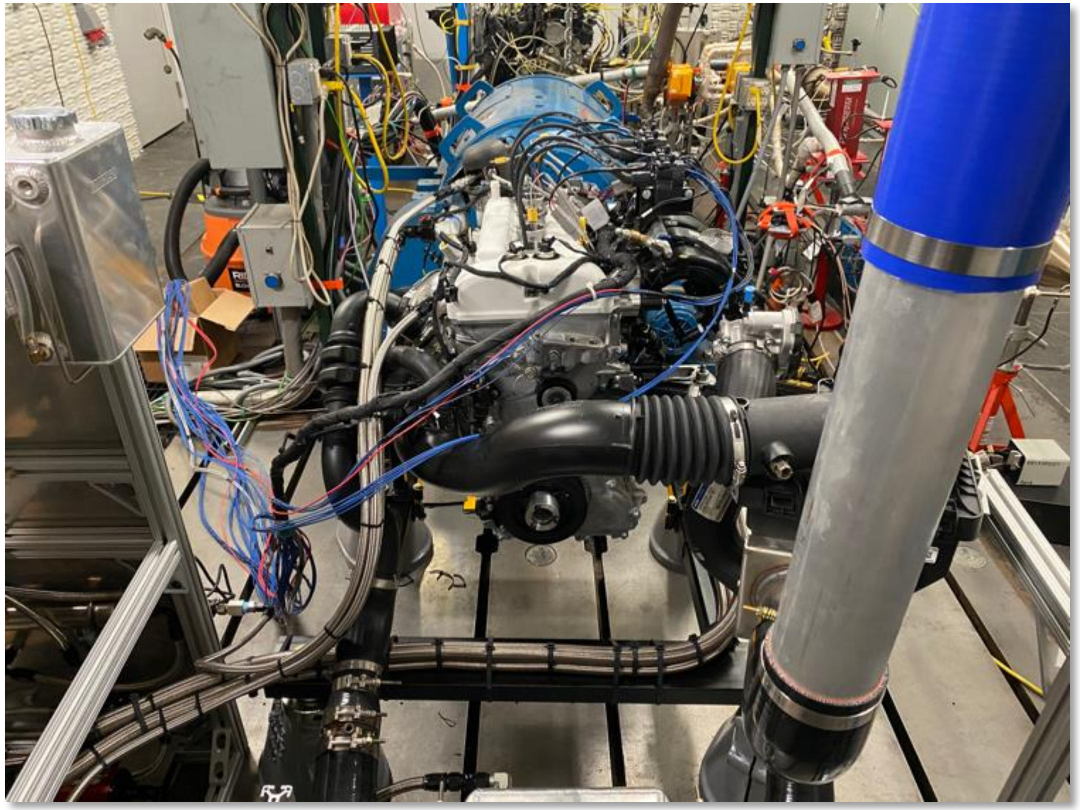
λ	2.0	0.97
NO	360 ppm	0
NH_3	0	600 ppm
O_2	10%	0
CO	0	0.8%
H_2	0	0.4%
CO_2	6.6%	11%
H_2O	6.6%	11%
SV	25000 h^{-1}	15000 h^{-1}

SV=space velocity

Advanced pre-chamber ignition system enables ultra-lean combustion for emissions controls research at ORNL

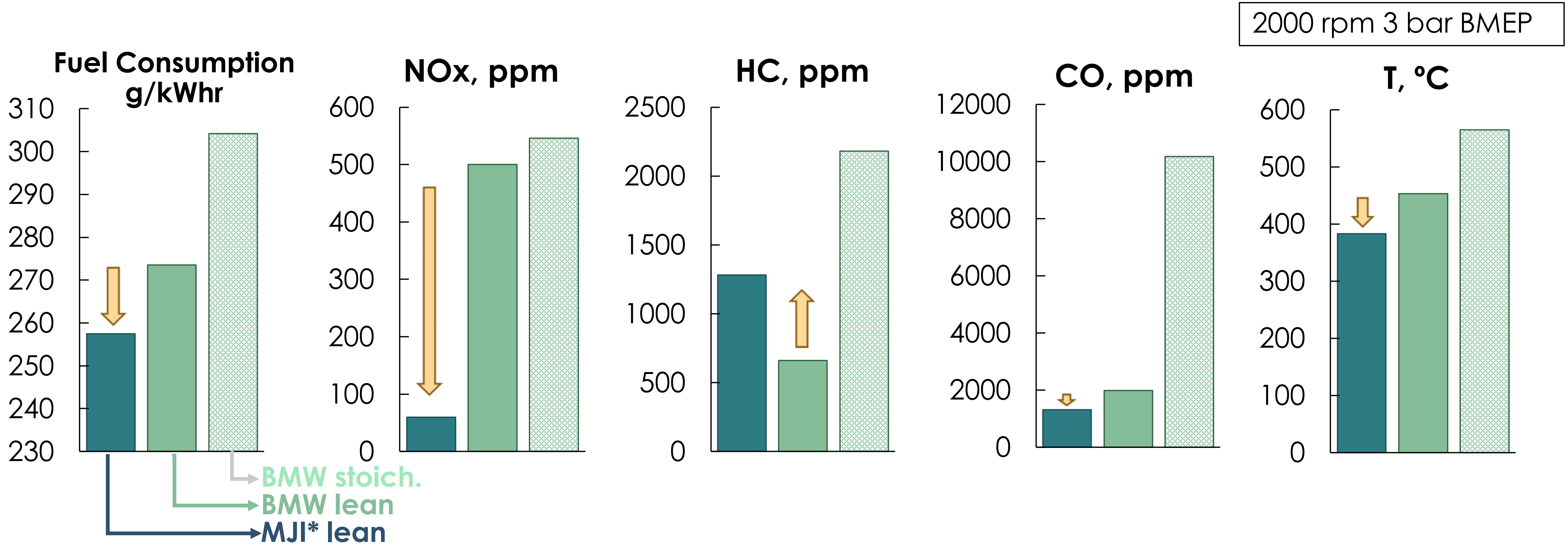
- ORNL procured MAHLE pre-chamber turbulent jet ignition combustion system for lean gasoline emission control research
  - installed and instrumented in the test cell with full controls
- Platform enables wider range of ultra lean operation
- Capable of better control over exhaust composition and temperatures than conventional lean systems
- Based on a 2.3L Ford EcoBoost engine platform, provides relevant turbo-boosted stoichiometric baseline for comparison

MAHLE Jet Ignition (MJI) engine in test cell at ORNL



Comparison with BMW lean engine indicates performance and emissions benefits

- MJI research engine offers performance and emissions benefits for passive SCR application
  - Lower fuel consumption
  - Lower NOx and CO emissions but higher lean HC emissions
  - Lower exhaust temperatures



*Note: data collected at MAHLE on MJI with 14:1 compression ratio

Remaining Challenges	Future Work*
• CO control during rich conditions	• Experiments planned on flow reactor and engine platform to evaluate impact of new clean-up catalysts supplied by Umicore • Potential addition of secondary air
• Maximize fuel efficiency while maintaining or further reducing emissions	• Utilize MAHLE Jet Ignition engine to expand lean operation map for higher fuel efficiency and lower engine out emissions • Flow reactor and engine evaluations of additional catalyst technologies and architectures • Improve control strategies and control emissions during engine mode transitions
• SCR durability under relevant passive SCR conditions	• Continue flow reactor and engine aging evaluations of new SCR catalysts supplied by Umicore

** - subject to change based on funding levels*

Responses to FY19 reviewer comments

Summary of Reviewer's Feedback:	Project Responses:
• …consider using a modern, bi-functional CUC that includes both oxidation catalyst and SCR functions…	• SCR + Pt-based ASC combo formulations were supplied by Umicore for flow reactor and engine studies
• …what is the strategy to mitigate CO during rich operation…	• Demonstrated CO reduction with addition of a clean-up catalyst • Experiments planned on flow reactor and engine platform to evaluate impact of new clean-up catalysts with varied Pt/Pd ratio and high OSC levels supplied by Umicore • Addition of secondary air is under consideration
• SCR durability under relevant passive SCR conditions	• Flow reactor and engine aging evaluations of new SCR catalysts supplied by Umicore are ongoing • Preliminary results showed that aging severity varies with aging temperature and gas composition (rich>stoich.>lean). But SCR is still active even after 800 °C rich aging.

Summary

- **Relevance**
  - Lean GDI engine emission control enables potential 10-15% fuel efficiency gain for gasoline-dominant U.S. light-duty fleet
- **Approach**
  - Engine, flow reactor, and aging studies are combined to study fuel efficiency and emissions relative to Tier 3 standard
- **Technical Accomplishments**
  - Evaluated passive SCR performance with aged production Cu-chabazite SCR catalysts on engine over pseudo-transient cycle
  - Preliminary results of SCR aging effects obtained on synthetic exhaust flow reactor under relevant passive SCR operating conditions
  - Installed and instrumented MAHLE Turbulent Jet Ignition engine in the test cell at ORNL with full controls
  - Procured 400 hp AVL Alternating Current (AC) Dynamometer suitable for wide range of applications
- **Collaborations**
  - GM and Umicore are primary partners
- **Future Work** *(subject to change based on funding levels)*
  - Evaluate effects of aging on SCR catalysts under passive SCR conditions
  - Measure fuel economy benefits and emissions on the MJI engine
  - Install the new transient dynamometer in the test cell
  - Flow reactor and engine evaluation of impacts of clean-up catalysts
  - Evaluate additional catalyst technologies and architectures

Technical back-up slides

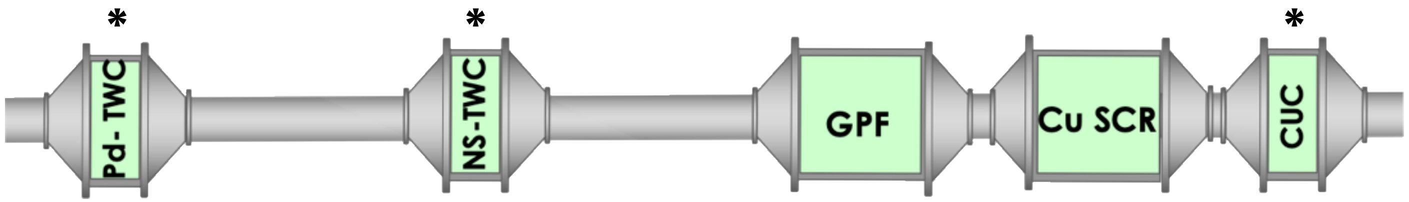
Abbreviations for slide #4

CUC	Clean-up catalyst
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
GOC	Gasoline oxidation catalyst
GPF	Gasoline particulate filter
HCT	Hydrocarbon trap
LNT	Lean NOx trap
PNA	Passive NOx adsorber
SCR	Selective catalytic reduction
TWC	Three-way catalyst

Stoich	Stoichiometric
SI	Spark ignited
CDC	Conventional diesel combustion
LTC	Low temperature combustion
ACI	Advanced compression ignition
PNA	Passive NOx adsorber
rpm	Revolutions per minute
BMEP	Brake mean effective pressure

FY19: Five-function passive SCR system

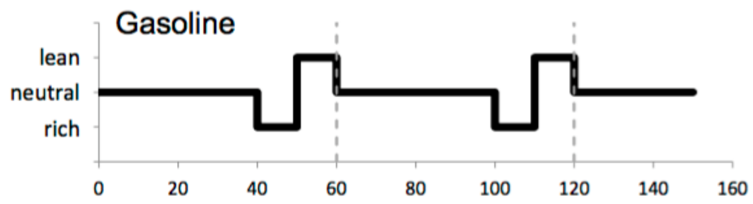
- **TWCs and CUC aged at SGS using ACEC aging protocol**
- **Cu SCR degreened on engine**



** catalysts aged using ACEC aging protocol*

Catalyst ID	Description	Pt (g/l)	Pd (g/l)	Rh (g/l)	OSC/NSC (Yes/No)	Volume (l)
Pd-TWC	Pd-only TWC utilized for NH_3 generation	0	7.3	0	No/No	0.62
NS-TWC	TWC with oxygen and NOx storage components utilized for NH_3 generation and lean NOx storage	2.47	4.17	0.05	Yes/Yes	0.82
GPF	Uncatalyzed GPF utilized as a heat sink and particulate matter (PM) control	-	-	-	-	2.47
Cu-SCR	Early generation Cu SCR (Cu-SCR-1) utilized for lean NOx reduction	-	-	-	-	2.47
CUC	High OSC containing catlyst utlized for rich CO and HC control and NH_3 slip	0	6.5	0	Yes/No	1.00

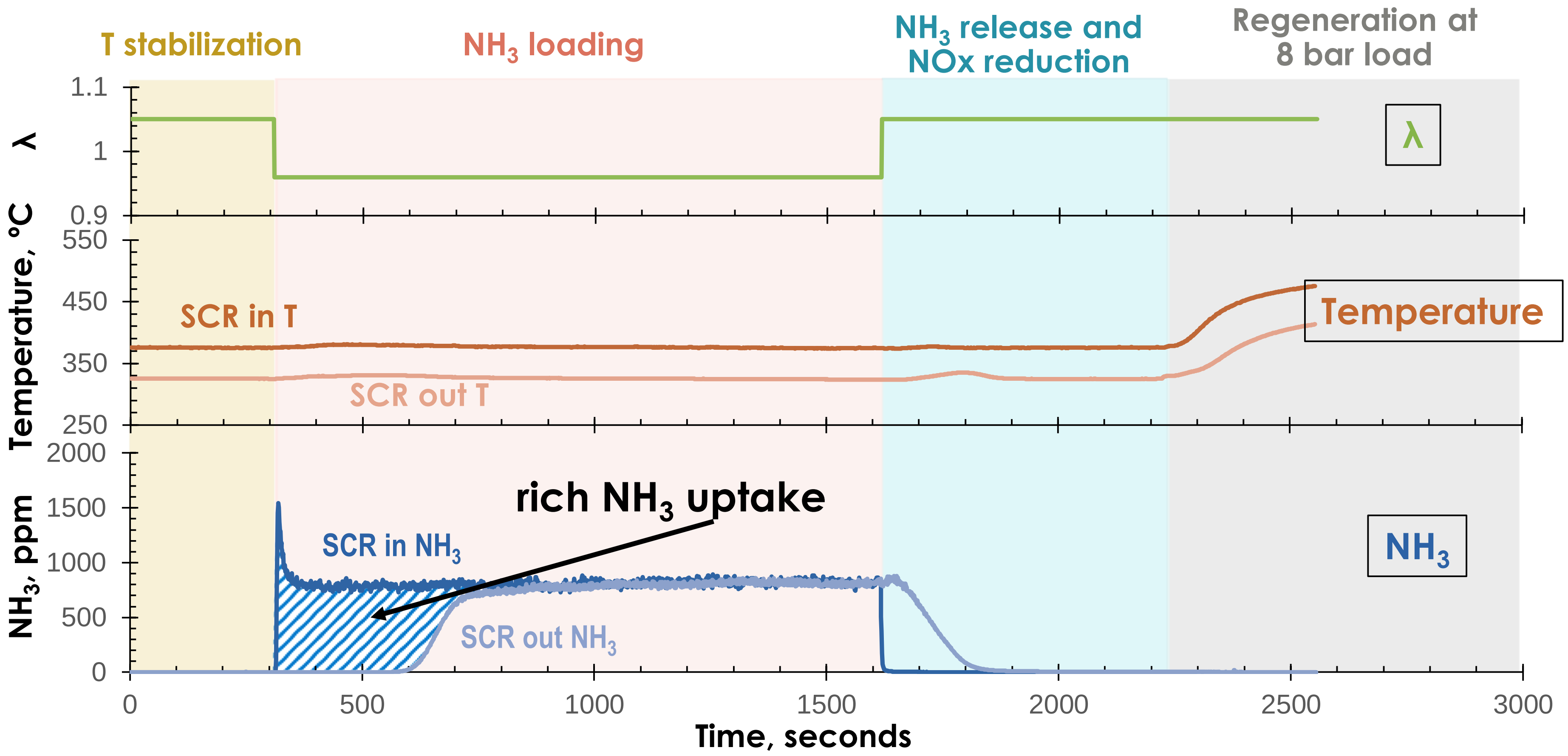
ACEC aging protocol used to age TWC and CUC at SGS

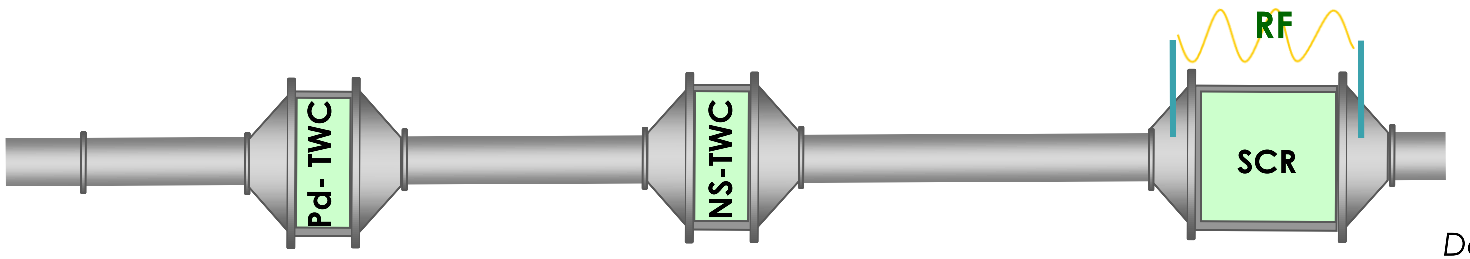


- Aging Cycle
  - Stoich: 40 seconds, lambda=1
  - Rich: 10 seconds, lambda=0.91
  - Lean: 10 seconds, lambda=1.33
- Aging inlet temperature
  - 800 °C for closed coupled
    - Pd-TWC and NS-TWC
  - 700 °C for underfloor
    - CUC
- Aging time = 50 hours
- Catalyst space velocity = 30K hr^{-1}

https://cleers.org/wp-content/uploads/2015_LTAT-Oxidation-Catalyst-Characterization-Protocol.pdf

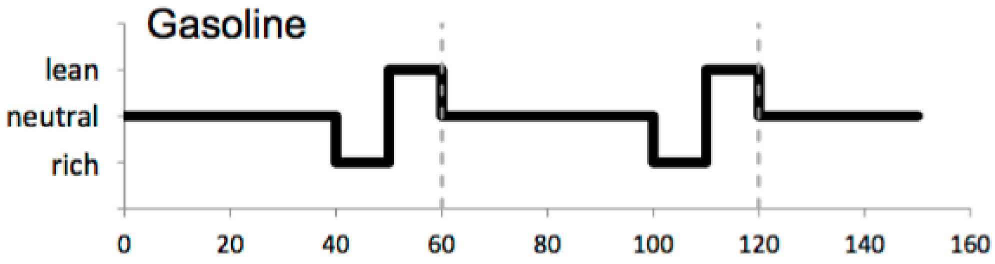
SCR rich NH_3 uptake measured on engine





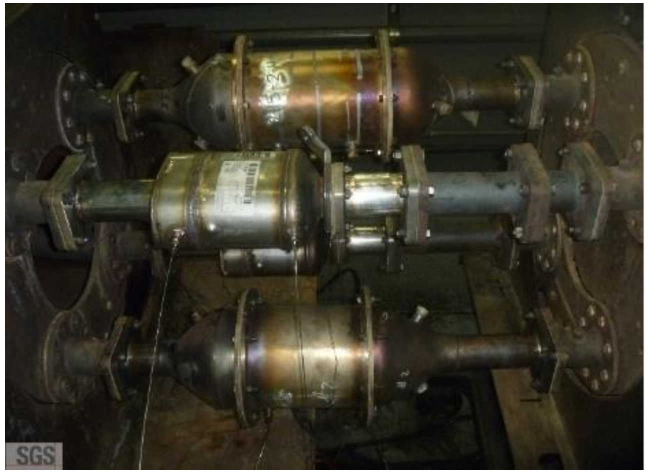
Data from 2000 rpm 5 bar, Cu-SCR-1

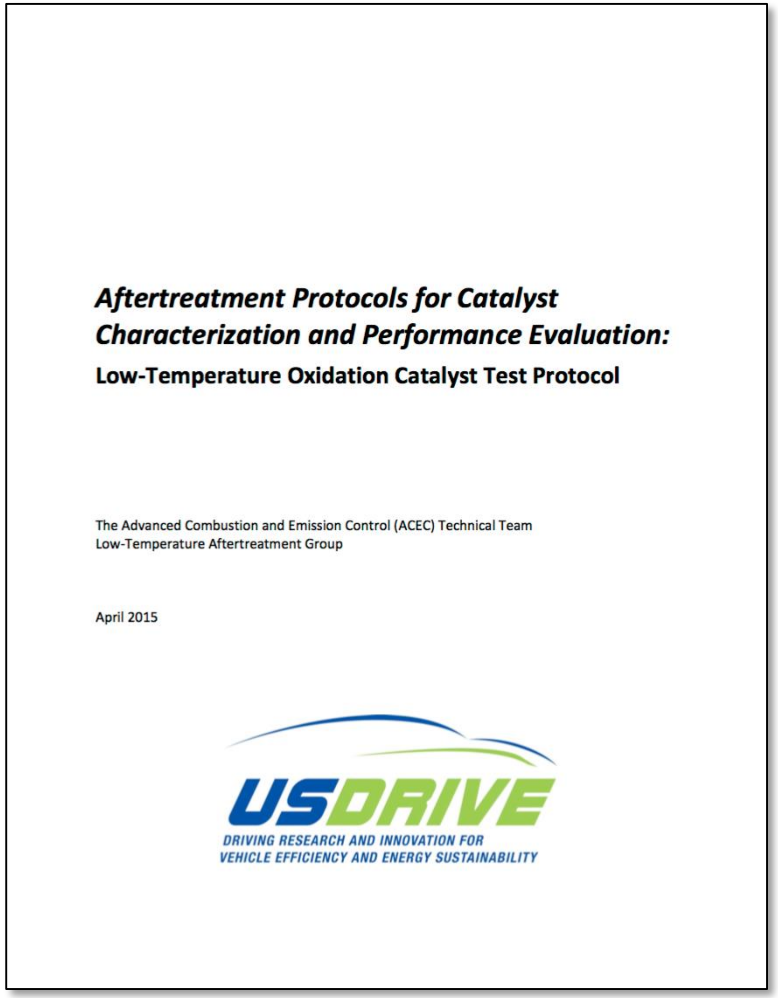
Cu-CHA SCRs aged at SGS using LTAT aging protocol for 50 hours at 700 °C inlet temperature



Thermally aged at SGS using LTAT aging protocol

- Aging Cycle
  - Stoich: 40 seconds, lambda=1
  - Rich: 10 seconds, lambda=0.91
  - Lean: 10 seconds, lambda=1.33
- Aging inlet temperature
  - **700 °C for underfloor**
- Aging time
  - 50 hours
- Catalyst space velocity
  - 30K hr^{-1}





Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:

Low-Temperature Oxidation Catalyst Test Protocol

The Advanced Combustion and Emission Control (ACEC) Technical Team
Low-Temperature Aftertreatment Group

April 2015

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Catalyst samples aged under lean, stoich and rich conditions in bench flow reactor

Aging Conditions	Lean & Degreen	Stoich	Rich
O_2 (%)	10	~	~
CO (%)	~	~	0.8
H_2 (%)	~	~	0.4
H_2O (%)	6.6	6.6	6.6
CO_2 (%)	6.6	6.6	6.6

Evaluation:

- NH_3 storage and passive SCR cycling activity:
  - 200 – 400°C
- NH_3 TPD: Adsorbed at 200°C, ramp to 550°C