Passive SCR for Lean Gasoline Emissions Control

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Sponsors: Gurpreet Singh and Ken Howden
Advanced Combustion Engines Program
U.S. Department of Energy

Lean gasoline project aimed at identifying technologies to overcome emission control barriers

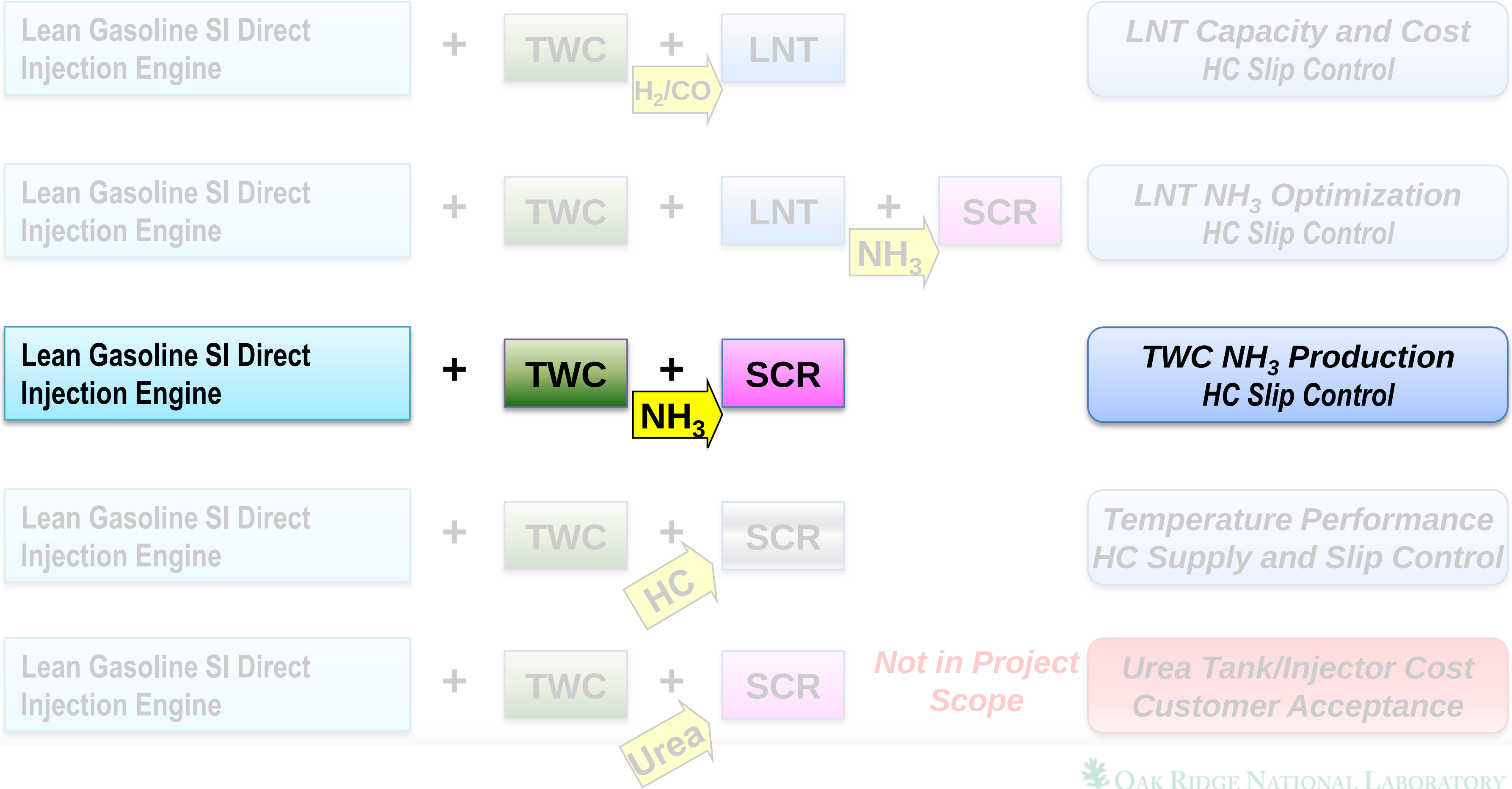
Enabling lean-gasoline vehicles to meet emissions regulations will achieve significant reduction in petroleum use

- Relevance:
  - U.S. passenger car fleet is dominated by gasoline-fueled vehicles.
  - Lean vehicles offer 5–15% increased efficiency over stoichiometric-operated gasoline vehicles
- Project scope:
  - Overall study will utilize flow reactors, lean gasoline engine cell, and lean gasoline vehicle
    - 2009 BMW 120i lean gasoline engine and vehicle at ORNL with full DRIVVEN control
  - Focusing on main barrier: lean emissions control
    - NOT combustion focused-project
  - Investigate strategies to achieve cost-effective compliance
    - Minimize precious metal content while maximizing fuel economy (FE)
- Current Focus:
  - Flow reactor analysis of relevant technologies from commercial catalyst supplier

Technology Options and Critical Issues Related to Cost and Performance

- **Goal: Enable Tier 2 Bin 2 Emission Compliance for Lean Gasoline Engine Vehicle**
- Focus on NOx, CO, HC (PM may be issue for DI engines, but outside of project scope; new project starting)
- Technologies:
  TWC = Three-Way Catalyst
  LNT = Lean NOx Trap
  SCR = Selective Catalytic Reduction

Specific Key Issues:
Cost, Durability, Fuel Penalty, Operating Temp.,+…



Lean Gasoline SI Direct Injection Engine + TWC + LNT (H_2/CO) — *LNT Capacity and Cost* / *HC Slip Control*

Lean Gasoline SI Direct Injection Engine + TWC + LNT + SCR (NH_3) — *LNT NH_3 Optimization* / *HC Slip Control*

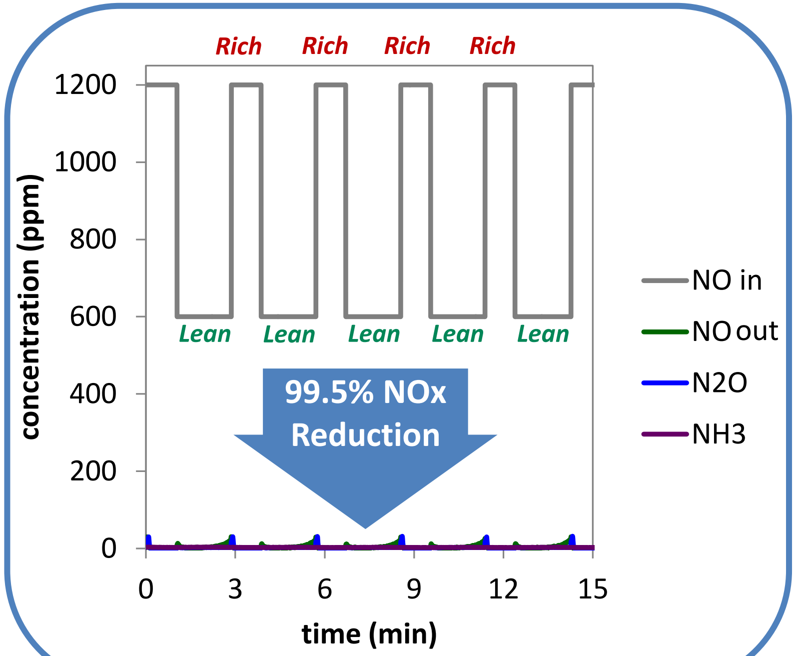
Lean Gasoline SI Direct Injection Engine + TWC + SCR (NH_3) — ***TWC NH_3 Production*** / ***HC Slip Control***

Lean Gasoline SI Direct Injection Engine + TWC + SCR (HC) — *Temperature Performance* / *HC Supply and Slip Control*

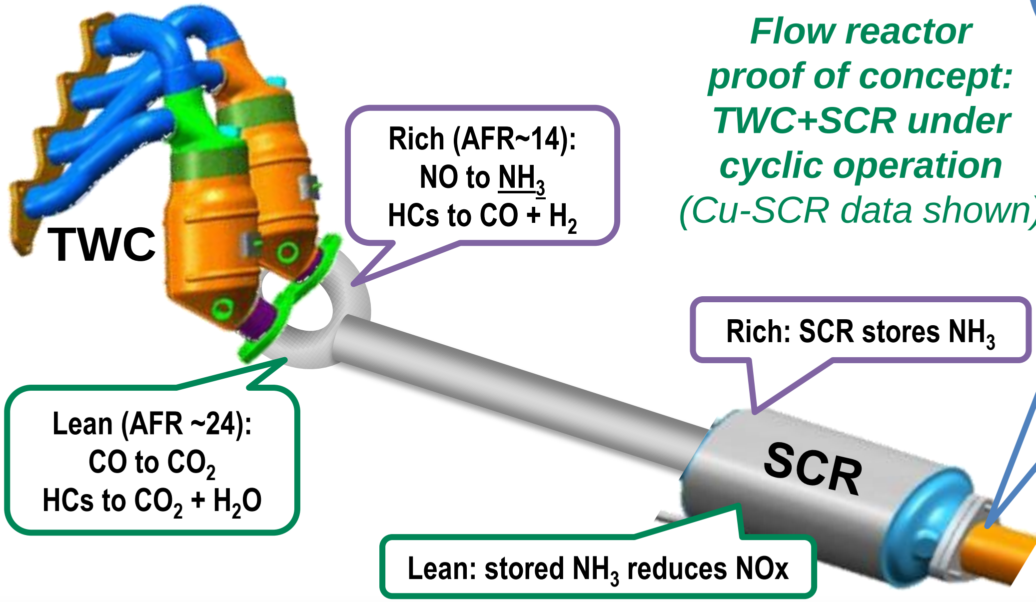
Lean Gasoline SI Direct Injection Engine + TWC + SCR (Urea) — *Not in Project Scope* — *Urea Tank/Injector Cost* / *Customer Acceptance*

Passive SCR approach and its potential

- "Passive SCR" relies on existing three-way catalyst (TWC) in combination with a SCR catalyst without urea dosing system
  - During mild rich period NOx is converted to NH_3 over TWC
  - NH_3 stored on downstream SCR; reduces NOx in lean period
- As high as 99.5% reduction in NO_x demonstrated with bench flow reactor under realistic engine exhaust conditions



Flow reactor proof of concept: TWC+SCR under cyclic operation
(Cu-SCR data shown)



Rich (AFR~14):
NO to NH_3
HCs to CO + H_2

Rich: SCR stores NH_3

Lean (AFR ~24):
CO to CO_2
HCs to CO_2 + H_2O

Lean: stored NH_3 reduces NOx

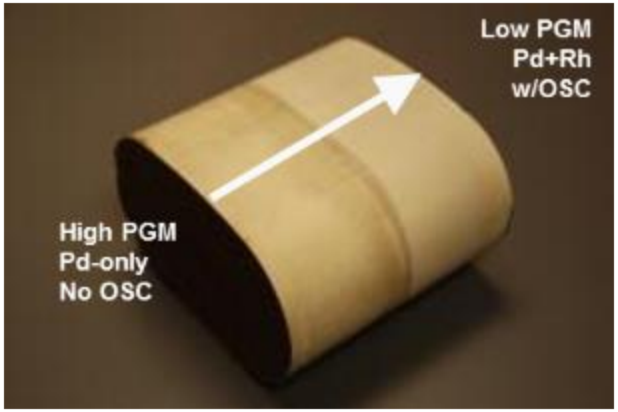
Tailpipe	Avg (ppm)	Max (ppm)
NO	4	31
NH_3	3	4
CO	*1200*	*3900*
N_2O	*2*	*32*

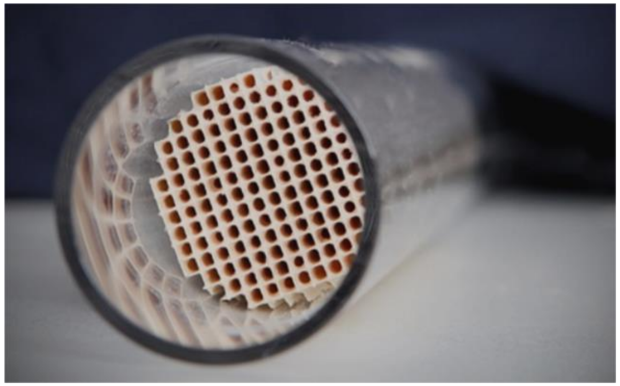
TWC and LNT studied in bench-core reactor with varying PGM content

- For bench reactor, focusing on modern TWC technology (Umicore recommended formulations representative of SULEV emission level technology)
- All catalysts degreened for 16 hr at 700ºC in humidified air (2.7% H_2O)

Catalyst Matrix

Catalyst	Description	Pt/Pd/Rh (g/L)
Pd-only	High Pd-only	0/6.7/0
Pd/Rh+Ce	Pd/Rh with O_2 storage	0/1.1/0.3
Combo	Combination of 2 above (as designed for SULEV vehicle, Pd-only upstream)	0/4.0/0.16
Pt/Pd/Rh+Ce+Ba	BMW LNT formulation (with NOx storage)	7/3/1



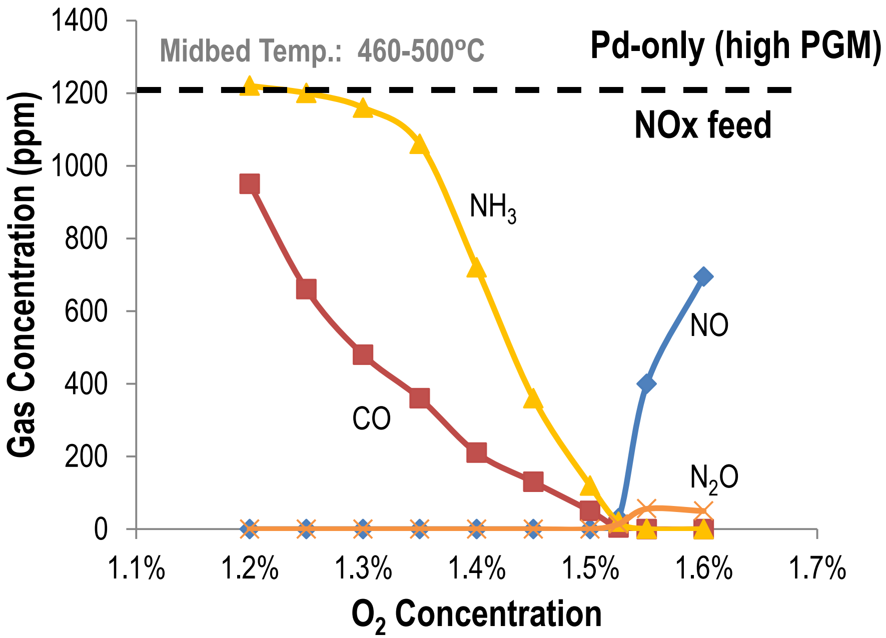


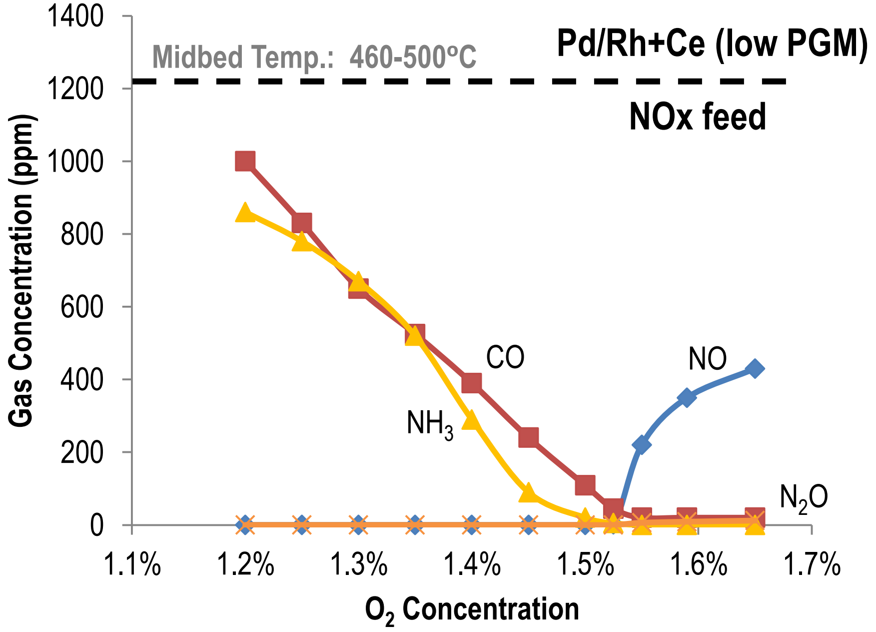
TWC is effective and tunable NH_3 generator

- **Example steady-state feed conditions:**

~AFR	O_2	NO	CO	H_2	C_3H_6
14.6	**1.59%**	0.12%	1.80%	0.60%	0.10%
14.4	**1.34%**	0.12%	1.80%	0.60%	0.10%
14.2	**1.06%**	0.12%	1.80%	0.60%	0.10%

- NH_3 readily generated; varies with PGM
  - For Pd-only TWC with high PGM:
    - All NO converted to NH_3 at AFR ~14.2
  - For Pd/Rh+Ce (low PGM) TWC:
    - NH_3 production is still significant but reduced
    - Most likely Rh related…confirmation ongoing
- Steady-state N_2O formation observed under lean conditions and varies with PGM content
  - Up to 56 ppm with high PGM (Pd-only) TWC
  - Less than 10 ppm with low PGM (Pd+Rh) TWC
- At all conditions, >95% CO conversion
  - C_3H_6 not observed in effluent

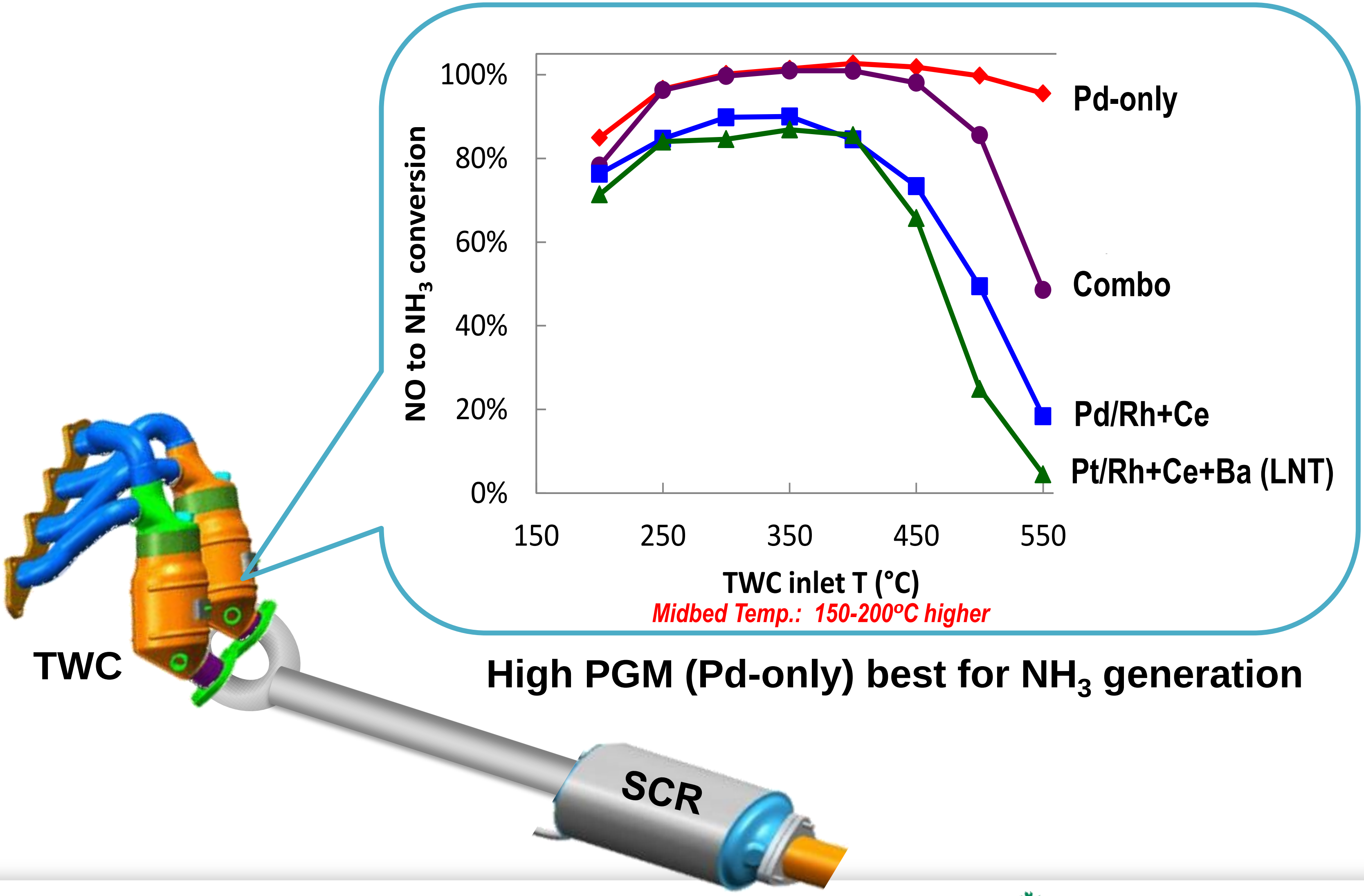




Passive SCR References: SAE2010-01-0366, SAE2011-01-0306, SAE2011-01-0307

PGM content and Pt/Pd/Rh ratios impact NH_3 selectivity

Evaluated multiple upstream catalyst formulations for NH_3 generation

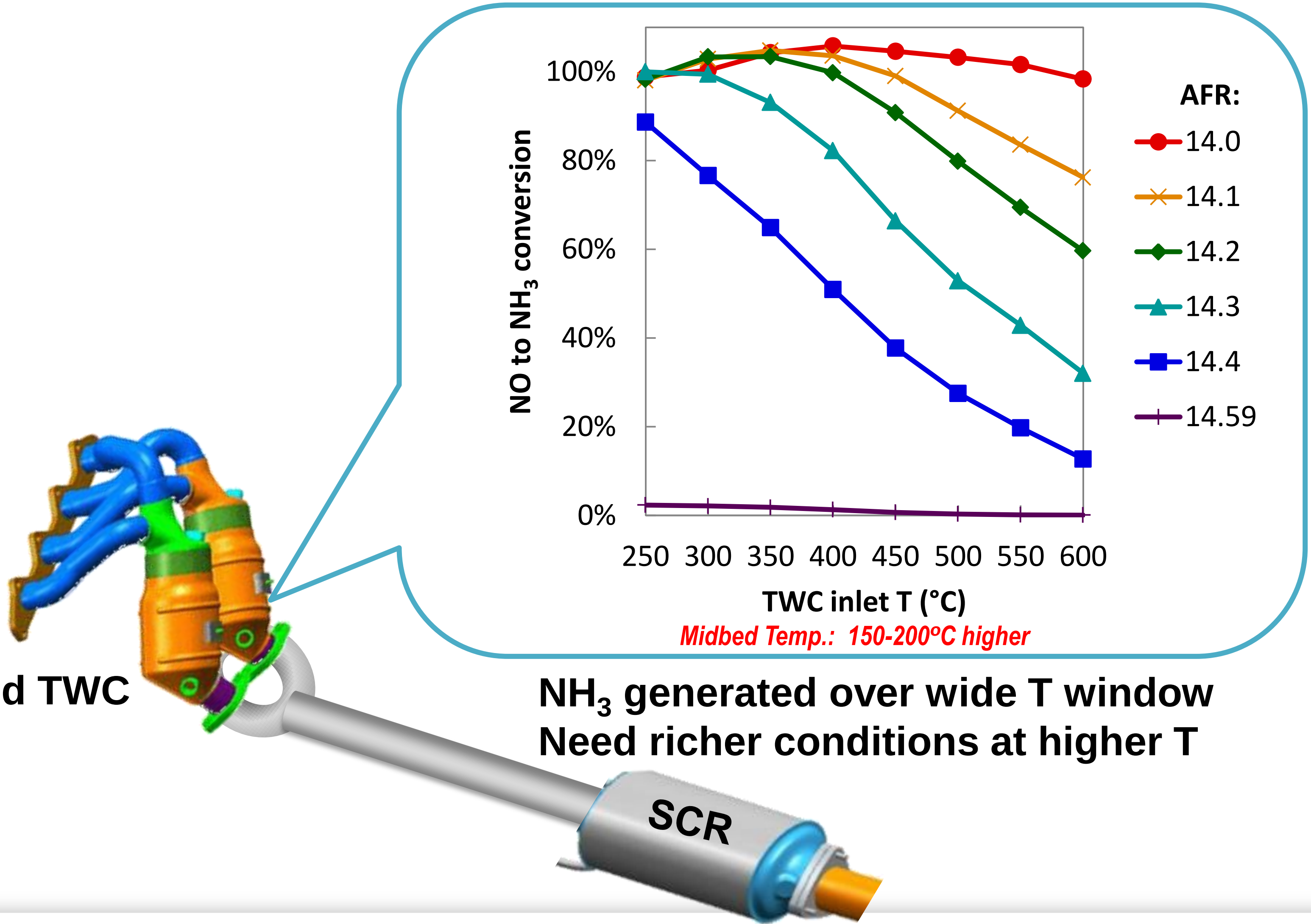


Midbed Temp.: 150-200°C higher

High PGM (Pd-only) best for NH_3 generation

AFR and temperature dictate NH_3 selectivity

Quantified NH_3 generation over Pd-only TWC

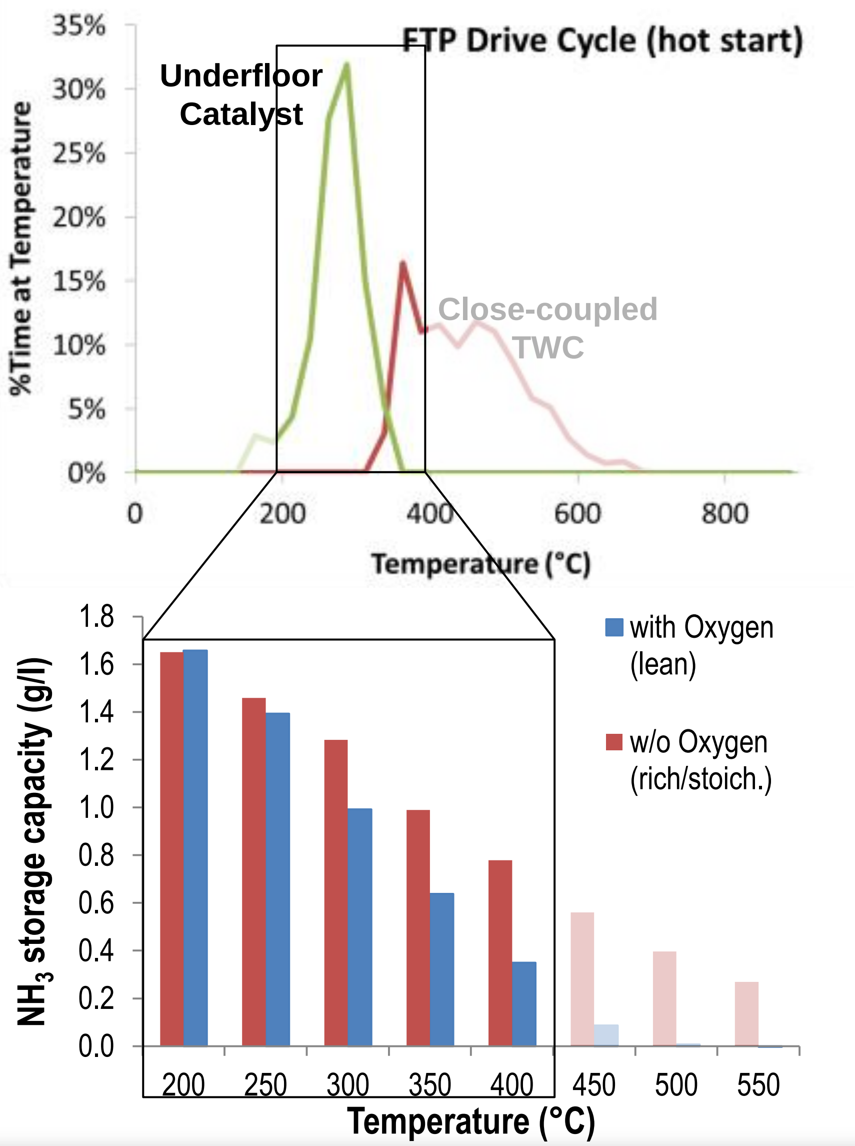


Midbed Temp.: 150-200°C higher

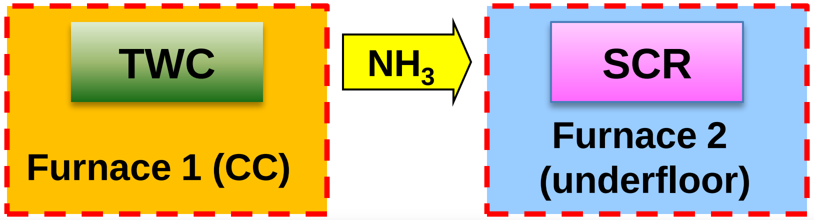
NH_3 generated over wide T window
Need richer conditions at higher T

NH_3 production over TWC occurs at temperatures relevant to vehicle operation and NH_3 storage on SCR

- Histogram of catalyst temperatures during drive cycle (Hot LA4) with BMW 120i
  - 200-350ºC for underfloor catalyst
  - 350-600ºC for close-coupled (CC) TWC
- TWC: tunable NH_3 production 250-600ºC @ inlet
- NH_3 storage temperatures in SCR significant between 200 and 400°C
  - More NH_3 storage occurs under rich/stoichiometric conditions
  - BUT, switching from rich to lean will result in NH_3 release and possible oxidation if over-saturated
- CC-TWC NH_3 production temperatures mesh well with underfloor temperatures for storage on SCR



Separate furnaces on bench flow reactor mimic CC and underfloor locations



Experiments run on automated flow reactor with two furnaces in series

- Catalysts:

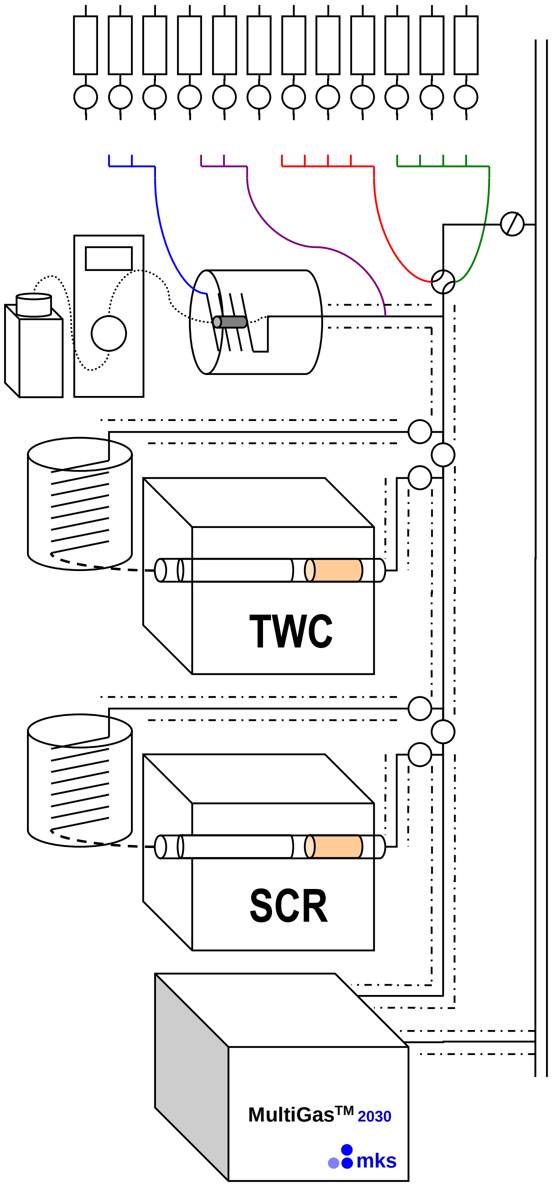
	TWC	SCR
formulation	**Pd-only**	Cu or Fe zeolite
SV (hr^{-1})	70k	28k
T (°C)	300, 450, 600	200, 250, 300, 350, 400, 450

- Gas compositions:

Max lean time:
2x rich time or 67%

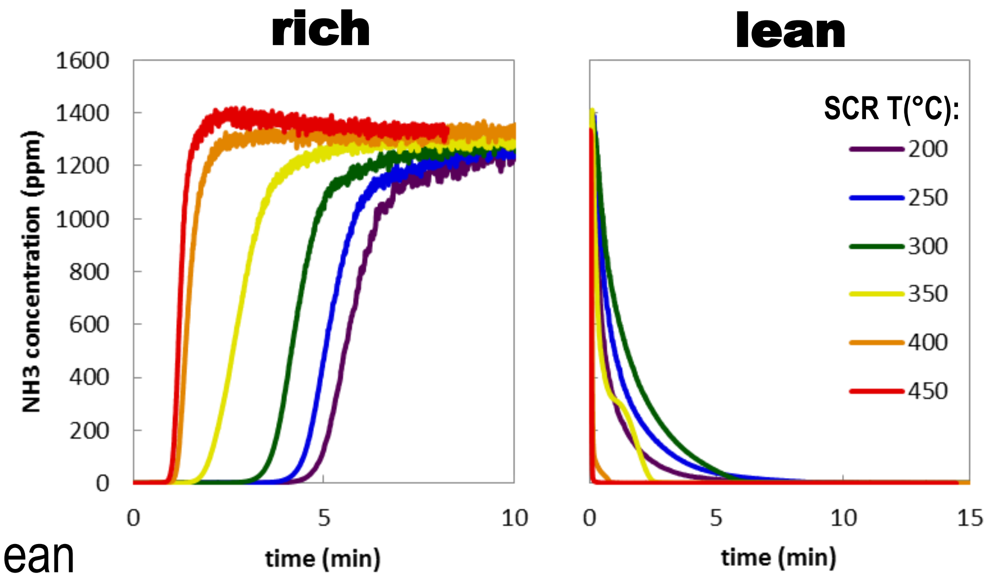
	Lean	Rich			
AFR	24	14.0	14.1	14.2	14.3
O_2 (%)	8	0.79	0.98	1.08	1.20
NO (ppm)	**600**	**1200**			
CO (%)	0	1.8			
H_2 (%)	0	0.6			
C_3H_6 (%)	0	0.1			
H_2O (%)	5	5			
CO_2 (%)	5	5			

- Switch conditions:
  - lean to rich: >20 ppm NOx at SCR out
    - had to increase threshold for Fe zeolite
  - rich to lean: fixed rich time based on empirical optimization to achieve ~ 10 ppm NH_3 slip at SCR out

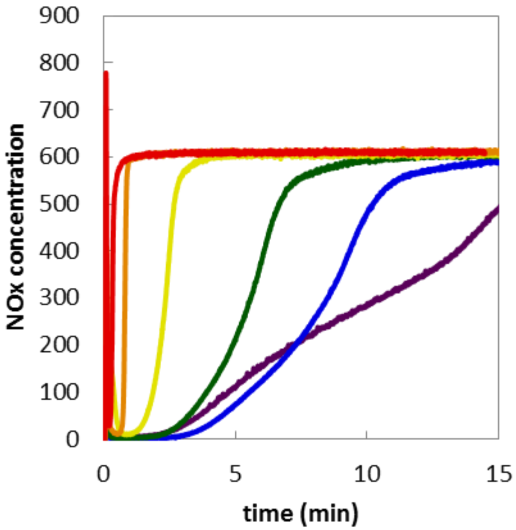


Cu SCR: saturation experiments illustrate NH_3 storage capacity limitations

- Experiment protocol:
  1. lean ~10 min
  2. switched to rich at start of run
  3. switched back to lean after NH_3 reached steady state



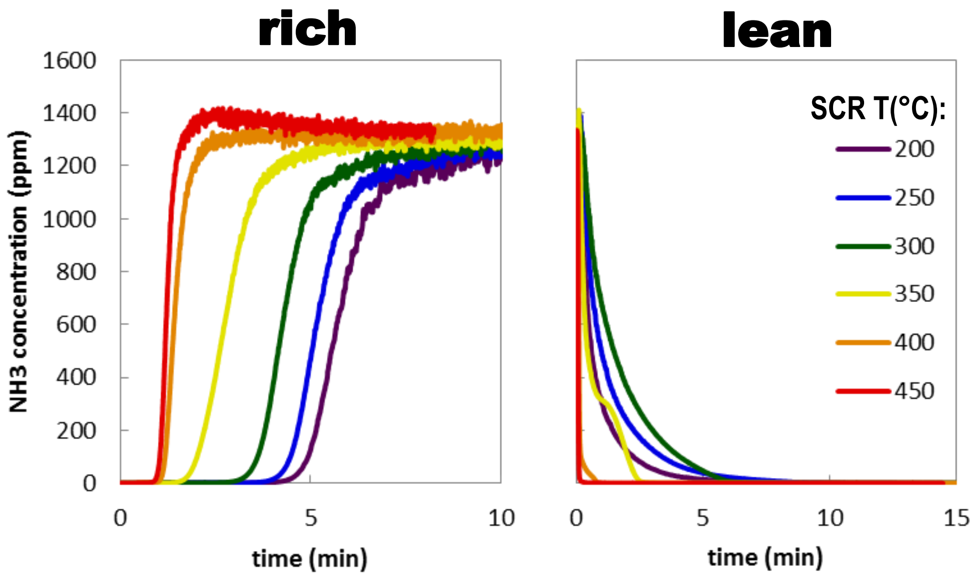
- NH_3 desorbs immediately upon switch to lean
  - surface NH_3 in equilibrium with gaseous NH_3; remove NH_3 from gas, surface NH_3 desorbs
  - NH_3 toward back of catalyst desorbs and slips before NOx can reach it
  - need to leave unused capacity in back of catalyst while cycling to buffer desorbed upstream NH_3
- Cycle times must be optimized to maximize NOx conversion and fuel economy while minimizing NH_3 slip

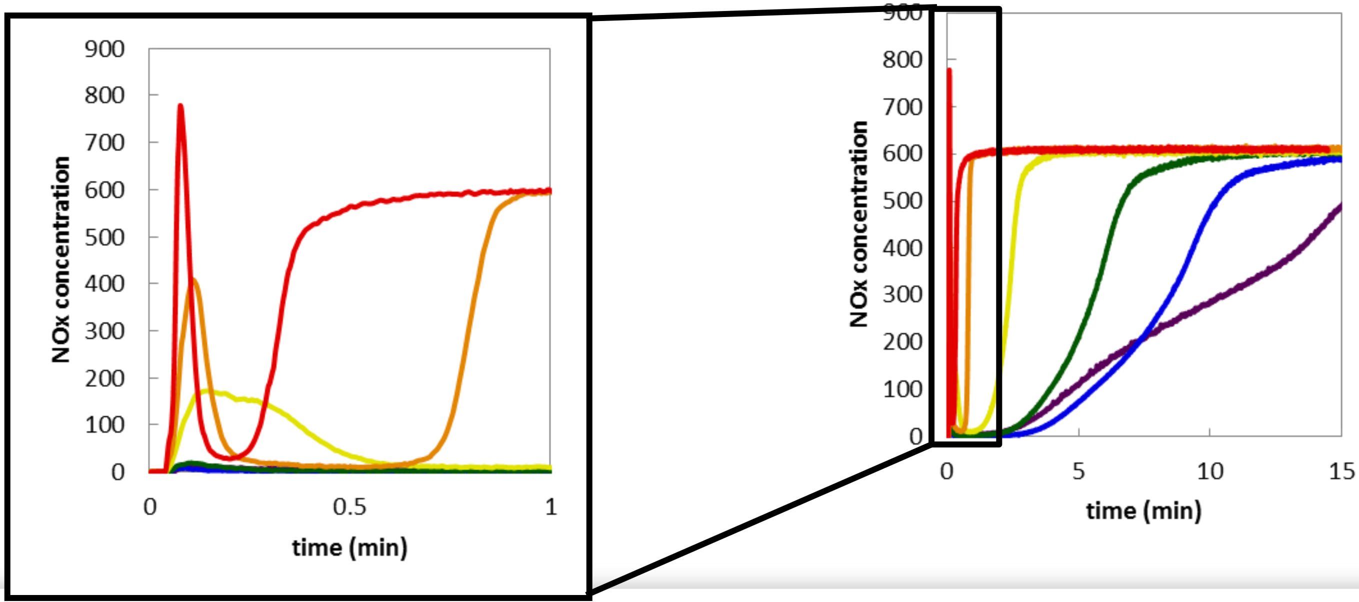


TWC: 450 °C **Rich AFR: 14.0**

Cu SCR: saturation experiments reveal NH_3 oxidation to NO over SCR

- NOx spike upon switch from rich to lean:
  - not observed at TWC out
  - NH_3 oxidation to NO over Cu SCR
  - decreases NH_3 inventory
  - increases NOx slip

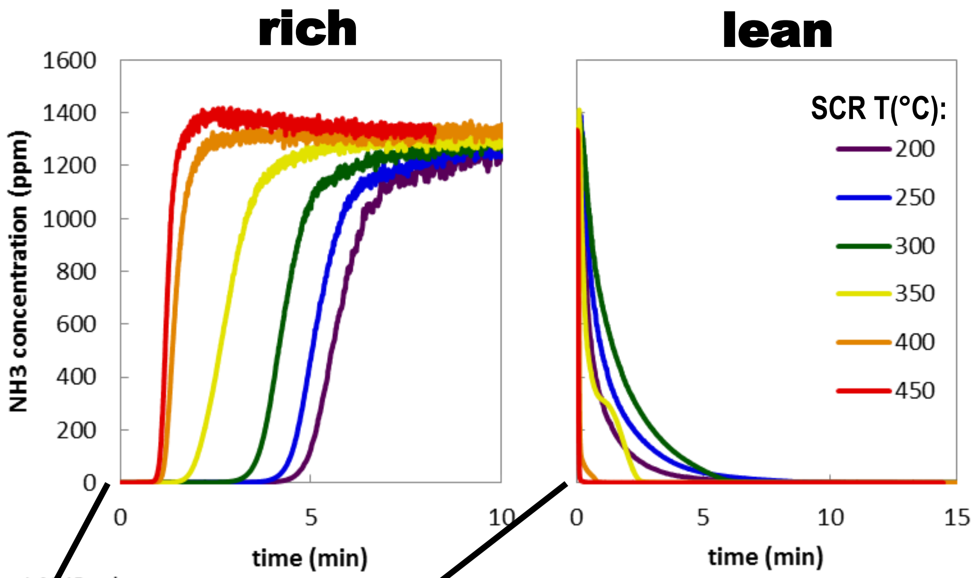


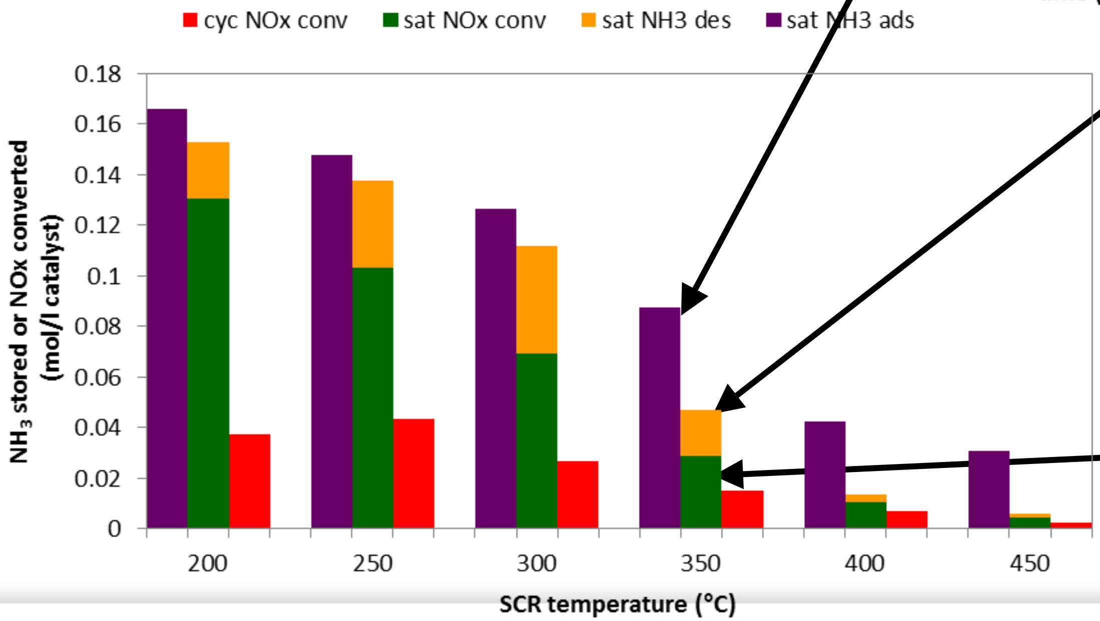


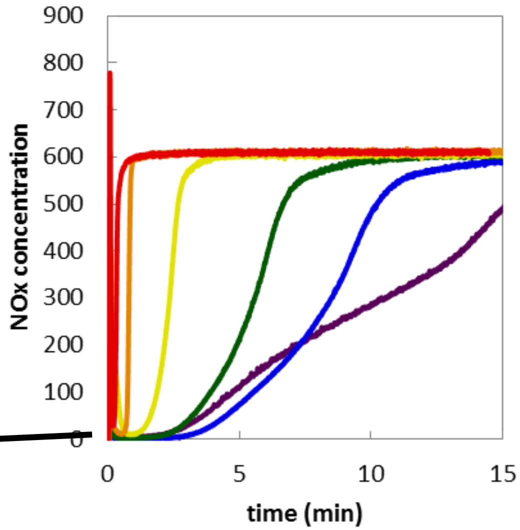
TWC: 450 °C **Rich AFR: 14.0**

Cu SCR: Comparison of NH_3 storage/utilization during saturation and cycle experiments

- Significant NH_3 capacity lost due to oxidation at high temperatures
- Only 20-50% of the remaining NH_3 capacity can be used during cycling
    - excess capacity needed to buffer desorption of upstream NH_3
    - modeling needed to guide optimization







TWC Midbed Temp.: 150-200°C higher **TWC: 450 °C** **Rich AFR: 14.0**

Cu SCR: Impact of SCR temperature

- SCR temperature = main factor determining NOx conversion efficiency and fuel penalty
- High temperatures:
  - increase NH_3 oxidation to NO (>=350 °C)

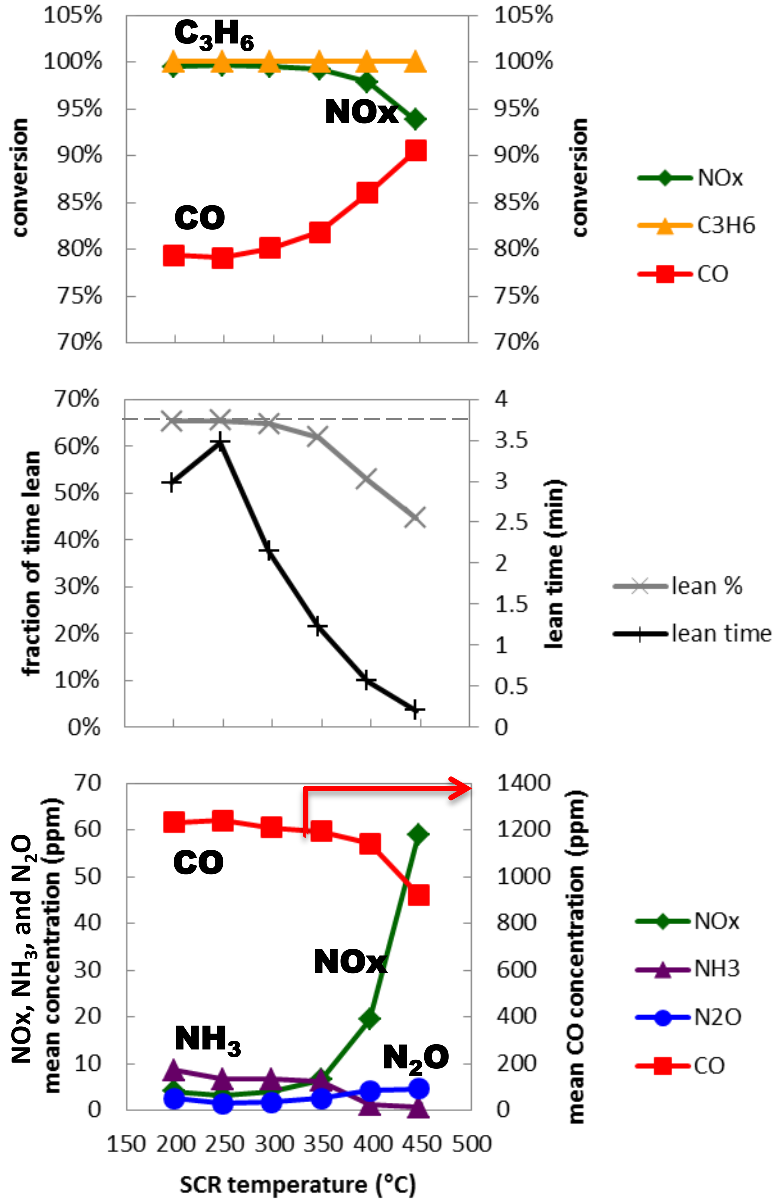
    NOx conversion ⬇

    lean time fraction ⬇
  - decrease NH_3 storage capacity and shorten cycle times
    - increase fraction of cycle under transient AFR (passing through stoich)

    CO conversion ⬆

    NH_3 slip ⬇
- Low temperatures (<200 °C) limit reaction rates

  NOx conversion ⬇
- **Cu SCR operating window: 200-350 °C**

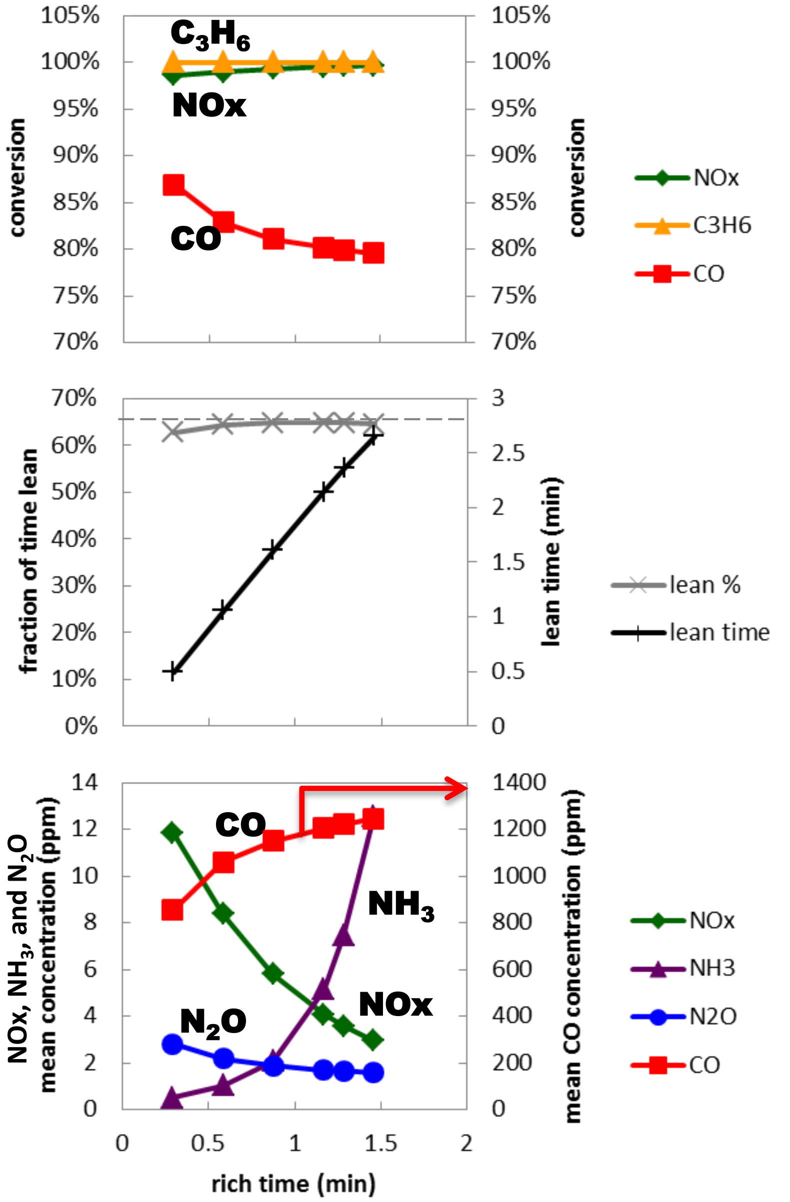


TWC Midbed Temp.: 150-200°C higher

TWC:	Rich AFR:	Rich time:
450 °C	14.0	varies

Cu SCR: Impact of rich time

- Long rich times increase NH_3 inventory on SCR catalyst
  - NOx conversion ⬆
  - NH_3 slip ⬆
- Short rich times increase fraction of cycle under transient AFR (passing through stoich)
  - NOx conversion ⬇
  - lean time fraction ⬇
  - CO conversion ⬆
- Optimal time window fairly small due to steep increase in NH_3 slip



	TWC:	SCR:	Rich AFR:
TWC Midbed Temp.: 150-200ºC higher	450 °C	300 °C	14.0

Cu SCR: Impact of AFR

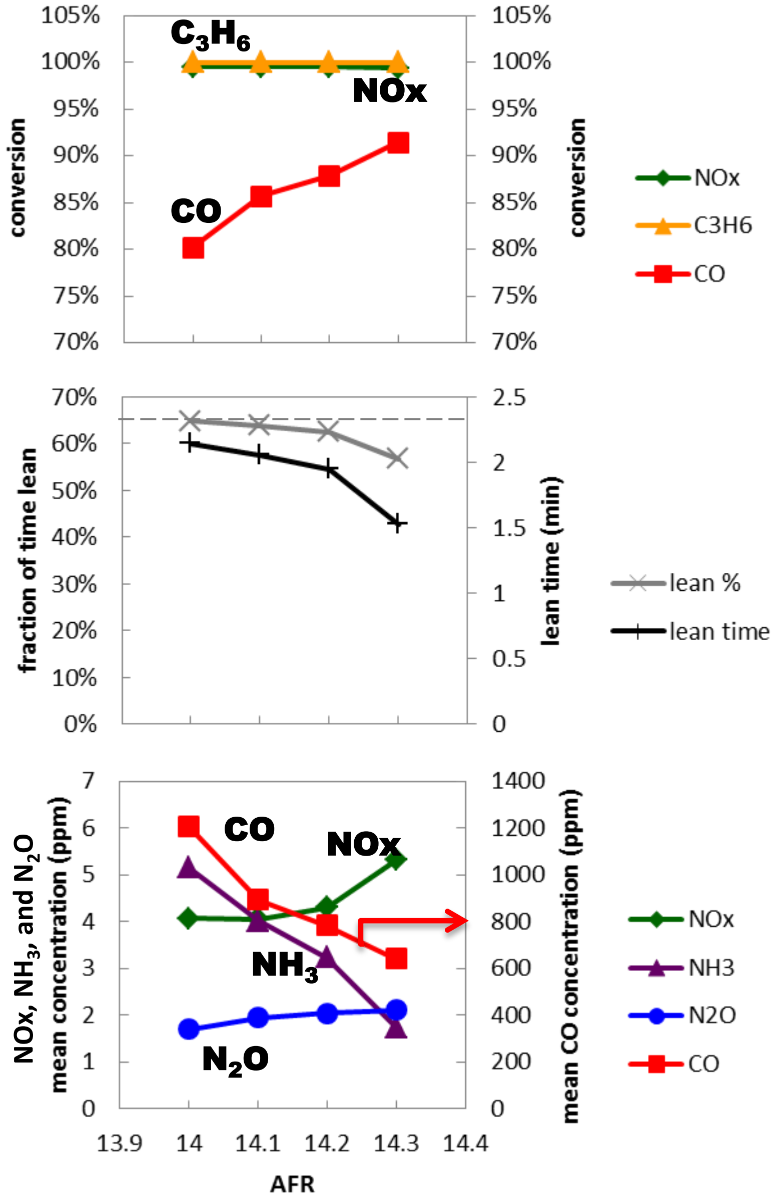
- Increasing AFR generates less NH_3 over TWC for a fixed rich time

lean time fraction ⬇

NH_3 slip ⬇

CO conversion ⬆

- AFR has less of an impact on overall performance (NOx conversion) compared to temperature or rich time
- Fuel penalty depends on both lean time fraction and AFR
  - AFR will need to be optimized for each set of operating temperatures
  - other strategies such as rich tip-in will be explored



TWC Midbed Temp.: 150-200°C higher

TWC: 450 °C

SCR: 300 °C

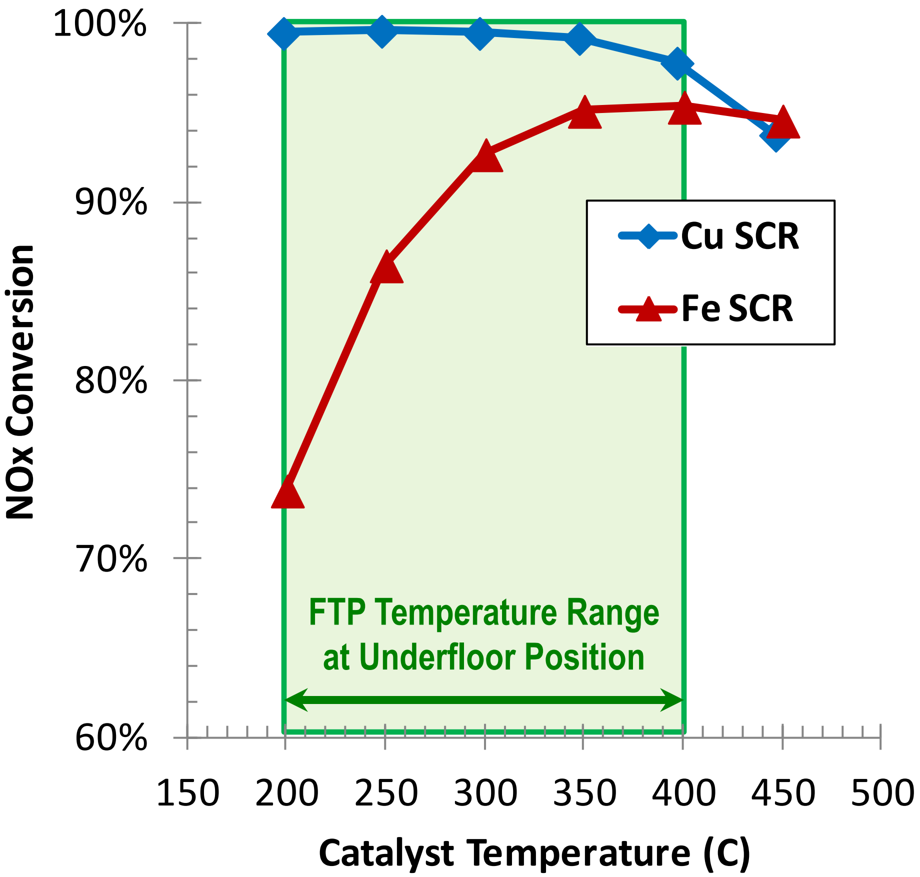
Rich time: 70 s

Higher storage capacity of Cu-SCR gives better NOx conversion than Fe-SCR

- Fe zeolite has much lower NH_3 storage capacity than Cu, limiting lean operating time and high temperature NOx conversion
- Fe zeolite is less active in SCR reactions, resulting in much lower NOx conversions, particularly at low temperatures
- Relation of NH_3 storage and oxidation temperature profiles to NOx conversion activity critical for achieving high NOx conversion

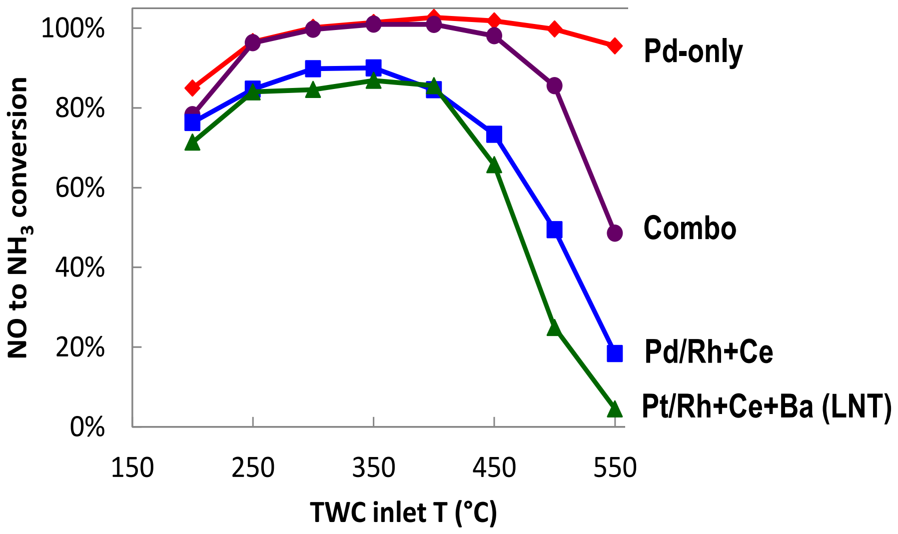
TWC (CC Position)=450°C
Rich AFR=14.0
Rich time varies

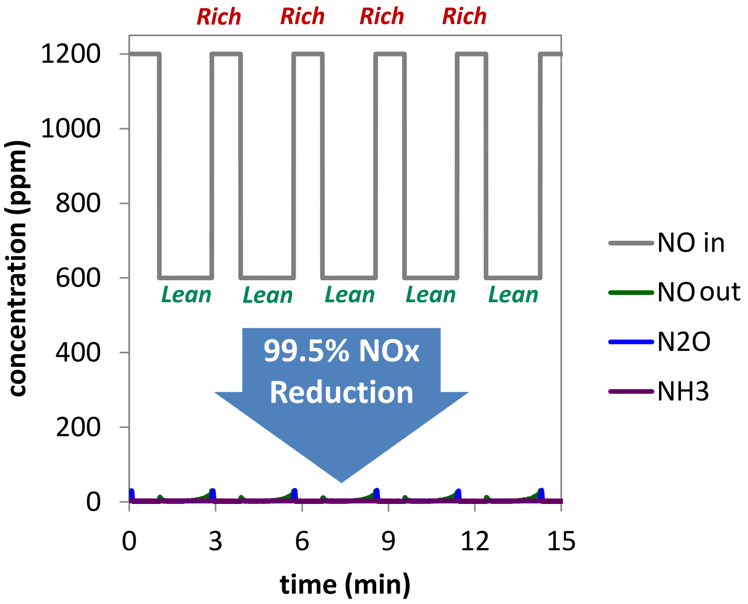
TWC Midbed Temp.: 150-200°C higher



Summary

- **NH_3 production readily occurs at close-coupled relevant temperatures**
  - Occurs with a range of catalysts
  - Pd-only w/o Ce was best evaluated TWC
- **NH_3 storage in SCR occurs at underfloor-relevant temperatures**
  - More storage occurs under rich conditions,
    but only lean storage capacity useable
- **>99% NOx reduction efficiency achievable with TWC+SCR approach**
  - Identified limitations at higher underfloor temperatures and AFRs
- **Future direction will include NOx storage component to TWC and engine operation**





Collaborations and partners

- **General Motors, Ford, Chrysler**
  - Teleconferences and on-site visits to share/discuss results
- **Umicore**
  - Catalyst supplier for the commercial LNT and TWCs
  - Facilitating range of catalysts with varying PGM and functionality
- **University of South Carolina (Michael Amiridis)**
  - Visiting graduate student Chris DiGiulio collaborated on bench reactor studies (Dr. Chris DiGiulio received his Ph.D. in Dec. 2012 and is now employed with UOP)
- **University of Wisconsin (Chris Rutland)**
  - Monthly teleconferences focused on sharing data for modeling of lean emission control systems
  - Jian Gong Ph.D. candidate
- **CLEERS**
  - share results/data and identify research needs

umicore Automotive Catalysts

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8th International Conference on Environmental Catalysis

Asheville, North Carolina

August 24-27, 2014

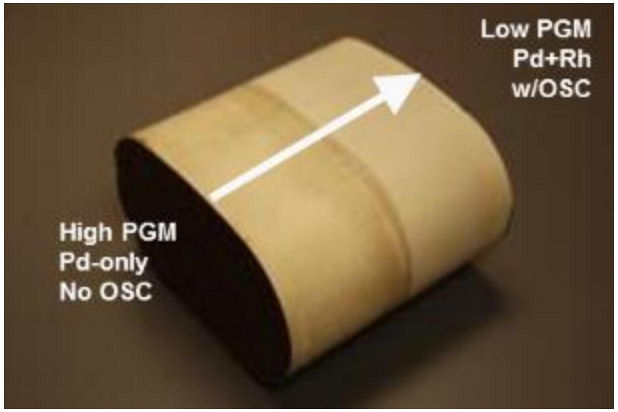
- ICEC returns to US soil for the first time since 1998
  - To be held at the Grove Park Inn Resort & Spa
- **Sessions:**
  - *Catalytic Materials*
  - *Emission Control*
  - *Indoor Air Cleaning*
  - *Water Treatment*
  - *Sustainable/Clean Energy Production*
  - *Green Chemistry*
- Contacts:
  - Todd Toops – Chairman (ORNL): toopstj@ornl.gov
  - Jerry Spivey – Technical Director (LSU): jjspivey@lsu.edu
- Asheville is an award winning tourist destination
  - Smoky Mountain National Park, Biltmore Estate and much more!

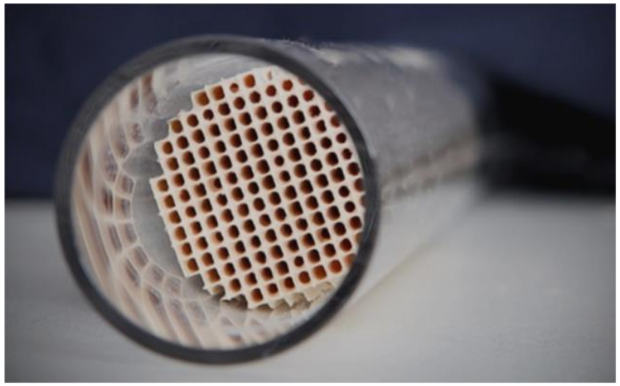
Conference website
http://www.efrc.lsu.edu/ICEC/topics.html

Additional Slides

Full detail on matrix of TWC formulations for NH_3 production studies

- For bench reactor, focusing on modern TWC technology (Umicore recommended formulations)
  - 1.3L TWC is a 2 formulation combination (combo)
    - Total PGM: 0/4.0/0.16 g/L Pt/Pd/Rh (118 g/ft^3 total PGM)
  - Front 0.6L of TWC is Pd-only no Ce
    - High PGM: 0/6.7/0 g/L Pt/Pd/Rh (190 g/ft^3 total PGM)
    - No ceria-based OSC, but oxygen storage measured
      - Expected to proceed via Pd-O formation
  - Rear 0.7L of TWC is Pd/Rh+Ce w/ Ceria
    - Low PGM: 0/1.1/0.3 g/L Pt/Pd/Rh (40 g/ft^3 total PGM)
  - Investigating each portion individually and in combined form
    - Degreened at 16h at 700C in humidified air (2.7% H_2O)

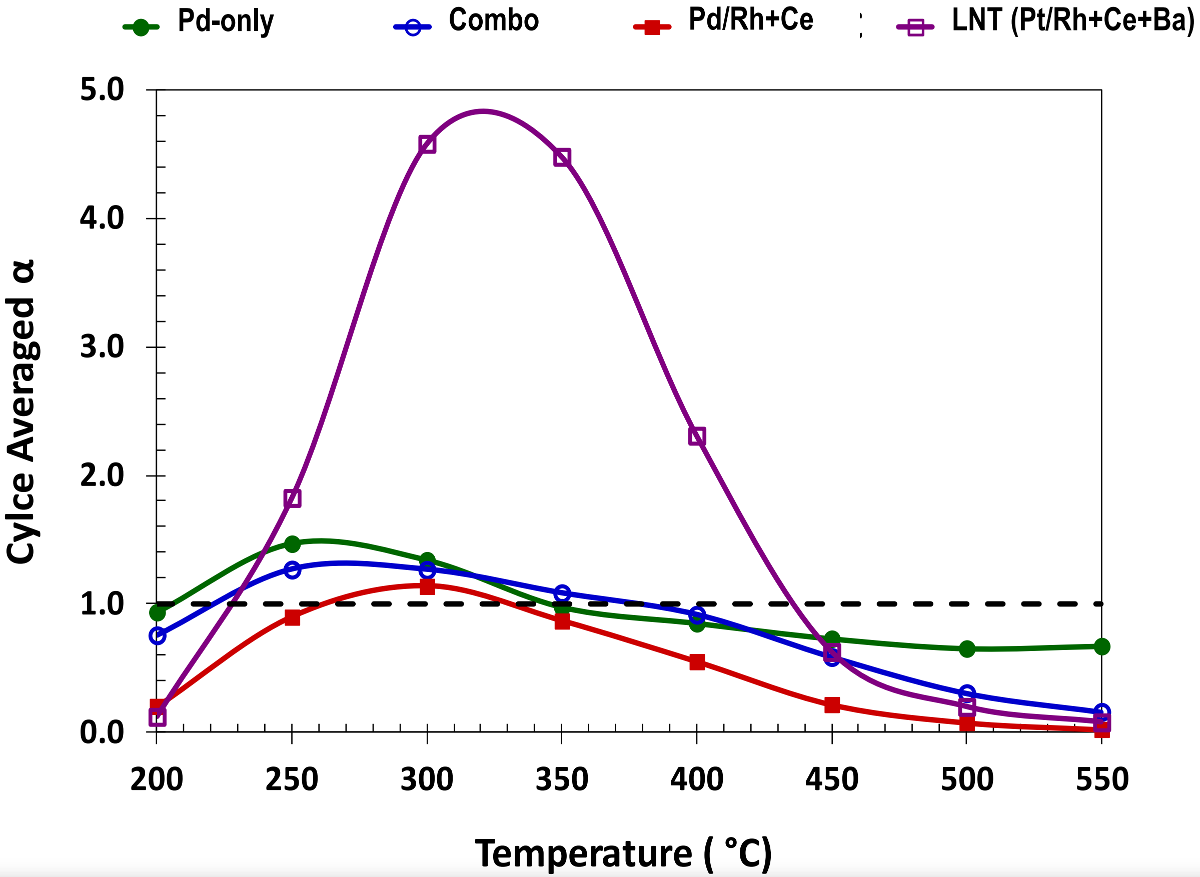


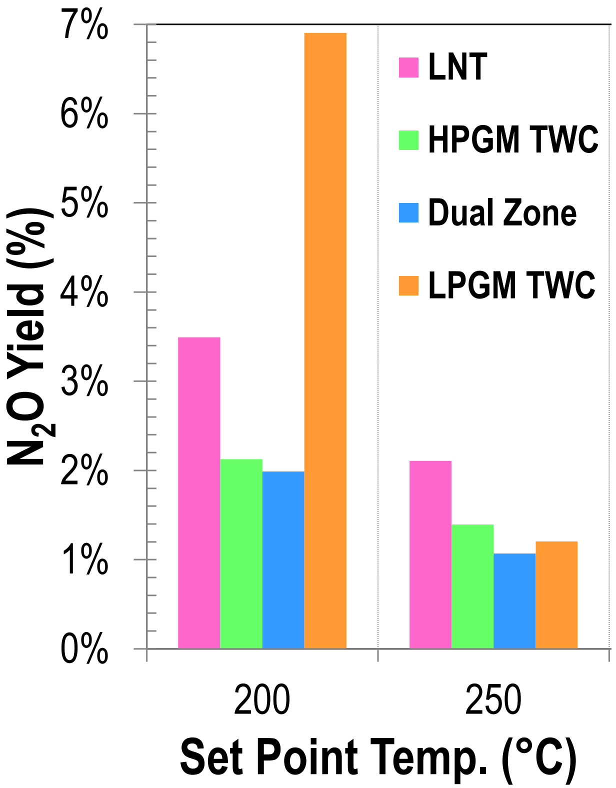


- LNT is commercial formulation from lean gasoline BMW
  - 2.6L Pt/Pd/Rh = 7/3/1, 3.3 g/L-cat (94 g/ft^3); Ba loading: 20 g/L (560 g/ft^3); Ce: 56 g/L (1600 g/ft^3)
  - Degreened at 16h at 700°C in humidified air (2.7% H_2O)

Addition of NOx storage can significantly increase NH_3 formation, but have to be aware of N_2O

- Cycle Averaged Alpha is 3+ times higher than best TWC formulation
  - Alpha: NH_3 produced / NOx in effluent
- However…Pt content in existing TWC results in high N_2O at low temperatures

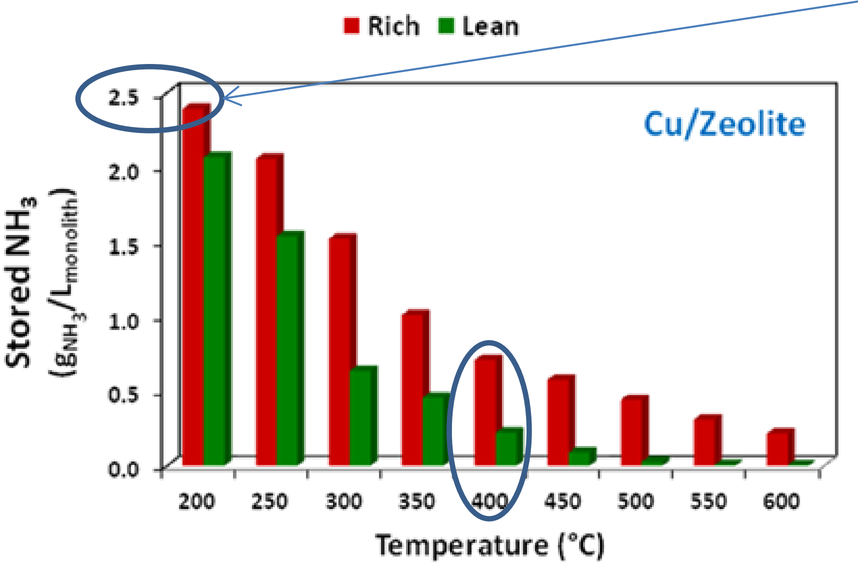


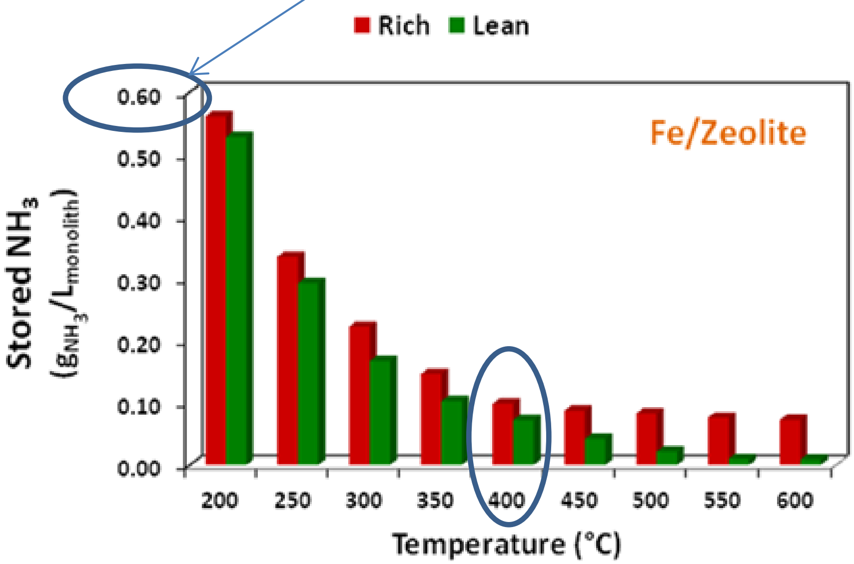


Cu-zeolite stores more than Fe-zeolite, but more sensitive to lean/rich environment

- Cu-zeolite has significantly more stoich/rich storage capacity
  - 2.4 versus 0.56 g NH_3/L-cat at 200°C
  - 0.6 versus 0.1 g NH_3/L-cat 400°C
- Lean utilization is a higher percentage of overall capacity with Fe-zeolite, especially at higher temperatures
  - ~25% utilization on Cu-zeolite
  - ~75% utilization on Fe-zeolite

Different scales





Fe SCR: Impact of SCR temperature

- High temperatures destabilize NH_3, reducing already limited storage capacity and shortening cycle times

  NOx conversion ⬇

  NH_3 slip ⬆

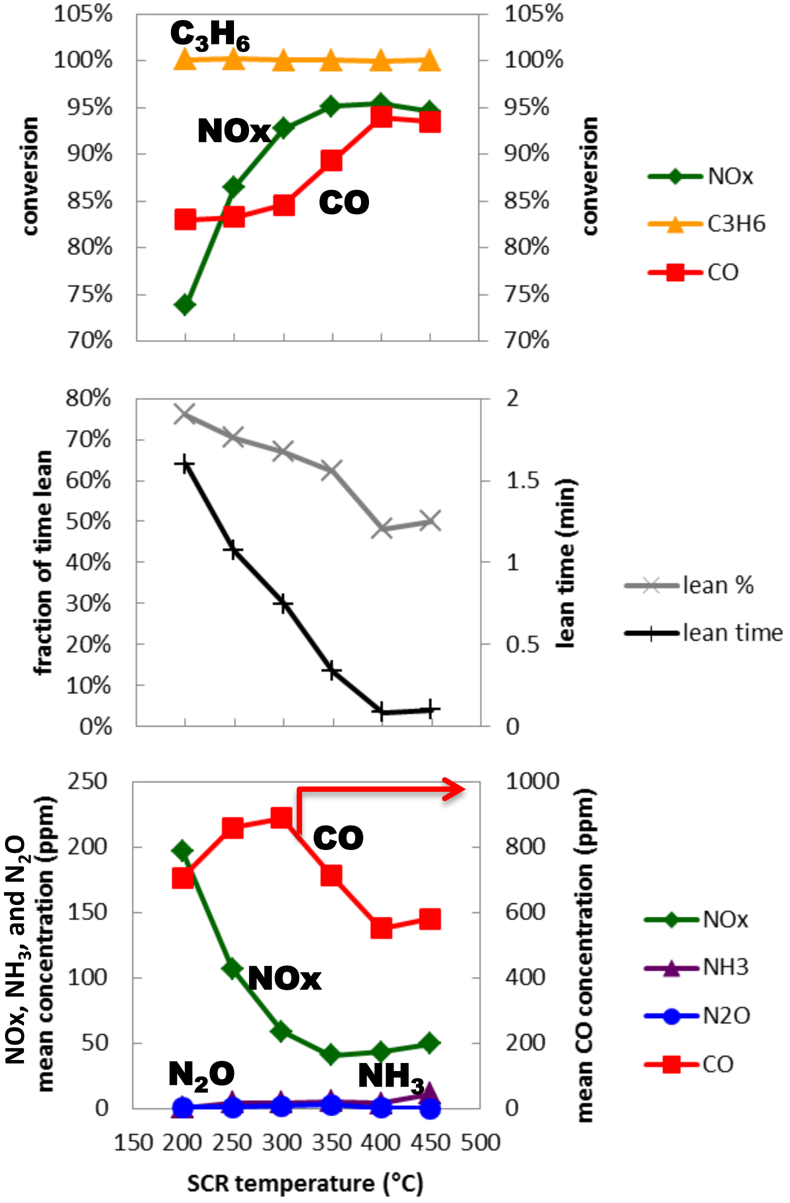
  lean time fraction ⬇

  CO conversion ⬆

- Moderately low temperatures (<350 °C) limit reaction rates

  NOx conversion ⬇

- **Fe SCR operating window limited**
  - Not clear how to combine with Cu-SCR currently



TWC Midbed Temp.: 150-200°C higher

TWC: 450 °C

Rich AFR: 14.0

Rich time: varies

Cu vs. Fe SCR: Impact of formulation

- Fe zeolite has much lower NH_3 storage capacity than Cu, limiting lean operating time and high temperature NOx conversion

lean time ⬇

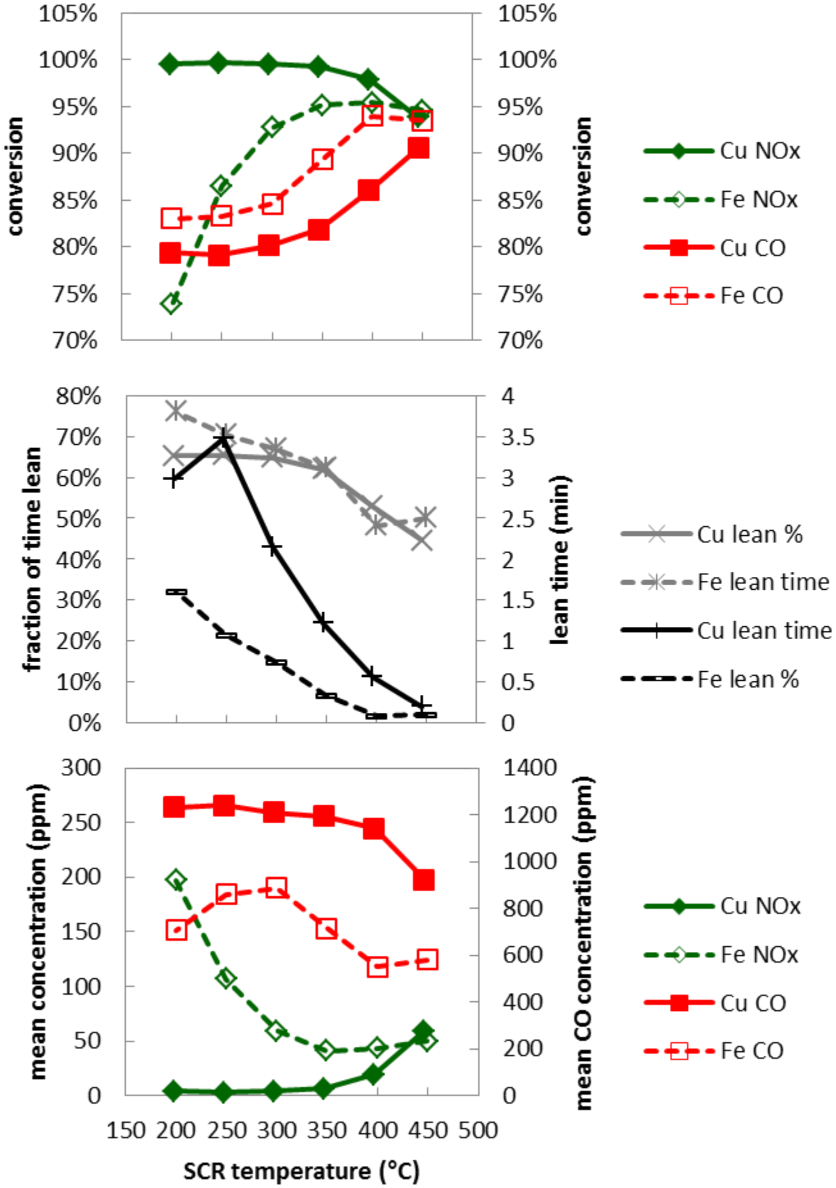
- Fe zeolite is less active in SCR reactions, resulting in much lower NOx conversions, particularly at low temperatures

NOx conversion ⬇

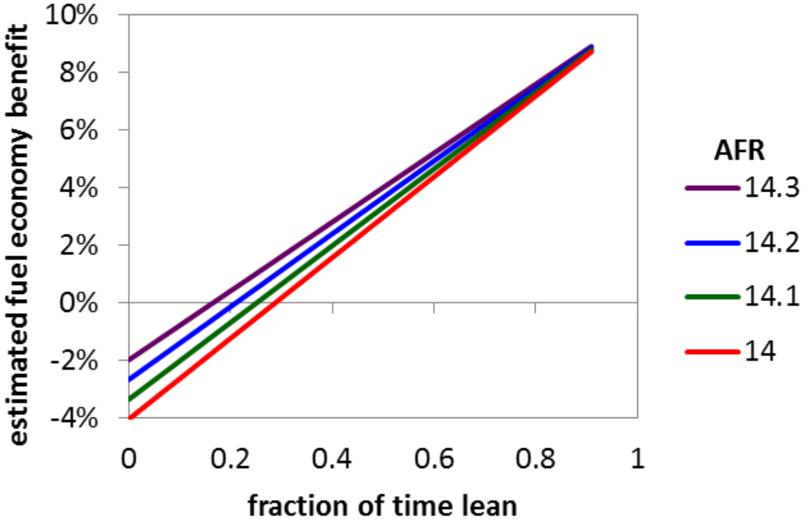
- Fe zeolite does have higher CO conversion

CO conversion ⬆

TWC=450°C
Rich AFR=14.0
Rich time varies

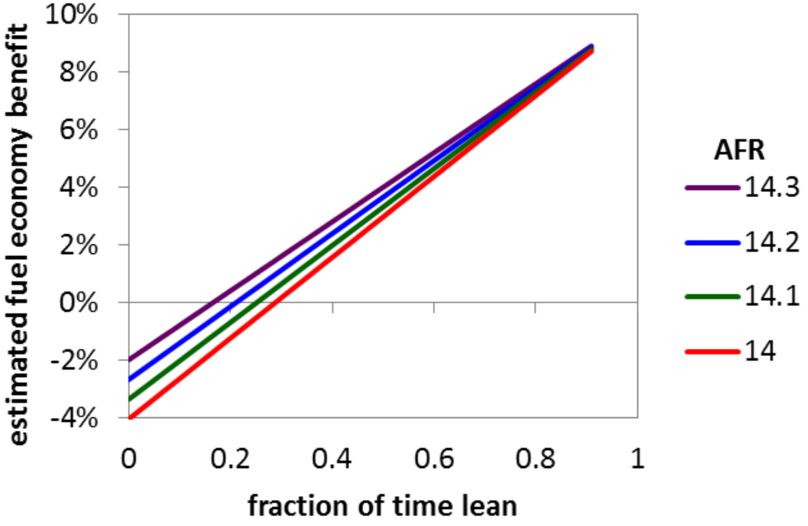


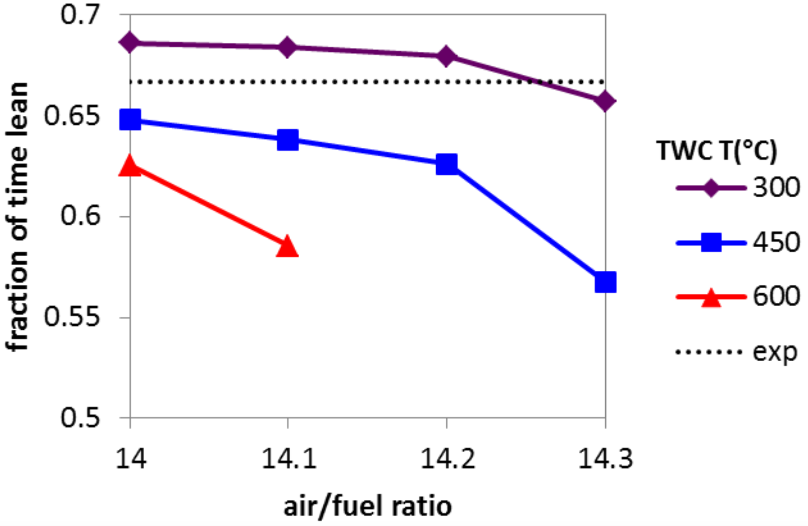
Fuel economy impacts of NOx emissions compliance with passive SCR



- Rich excursions to generate NH_3 increase fuel consumption due to:
  - temporary loss of lean operation fuel economy boost (assumed 10%)
  - injection of excess fuel
- Overall impact on fuel economy depends on:
  - how long the engine can run lean
  - how rich it must go to generate NH_3

Fuel economy impacts of NOx emissions compliance with passive SCR

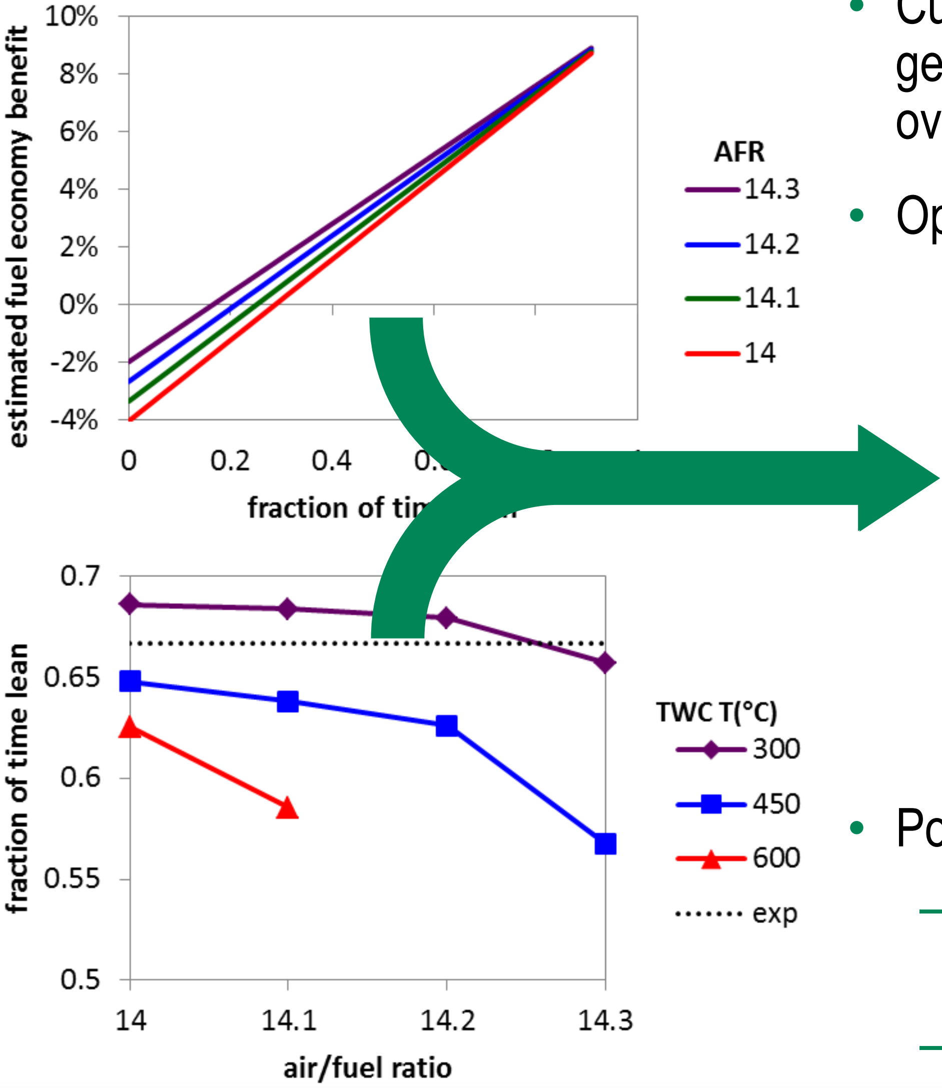


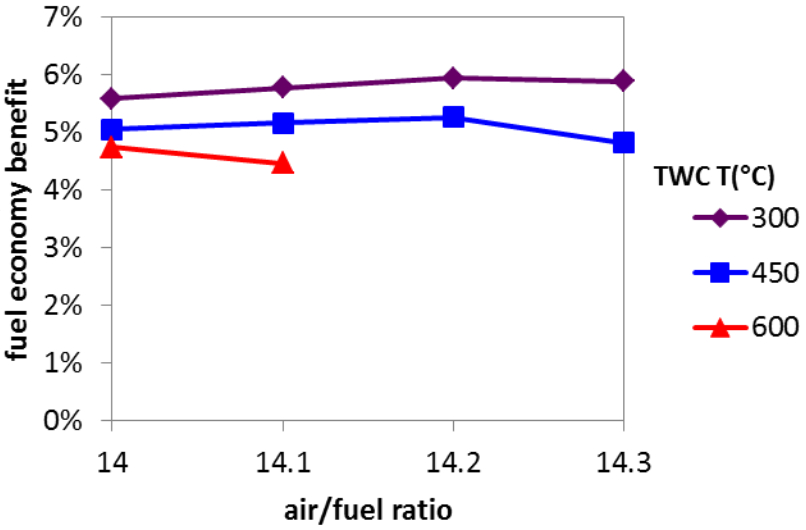


- Fraction of time lean depends on:
  - NH_3 yield during rich operation
    - decreases with TWC T and AFR
  - relative NOx flux (concentration and flow rate) during rich vs. lean
    - rich NOx = 2 x lean NOx here
- Exploiting flow changes during transient driving could increase lean operation time
- Higher than expected lean time at 300°C due to NOx storage over TWC during lean operation
  - possible formulation strategy
- For all conditions shown NOx conversion is > 99%

Fuel economy impacts of NOx emissions compliance with passive SCR

- Current implementation of passive SCR generates a net fuel economy benefit of 5-6% over a comparable stoich. engine
- Optimal AFR depends on TWC T





- Possibilities for reducing fuel penalty:
  - higher NOx flux ratios during transient operation on vehicle
  - addition of a NOx storage material

Lean Gasoline Engine Research Platform Operational

- Platform based on BMW 120i lean gasoline engine vehicle commercialized in Europe
- Drivven based system allows OEM map operation as well as full control of engine for custom control (Emphasis is chemistry and AFR control, not driveability)

Timeline (since last AMR)

July 2012: Chassis dyno mapping

Aug. 2012: Analysis of mapping data complete

Sept. 2012: installation of engine on dyno and first controller installation (first burn) and sensor/actuator checks

Oct. 2012: map development and controller programming

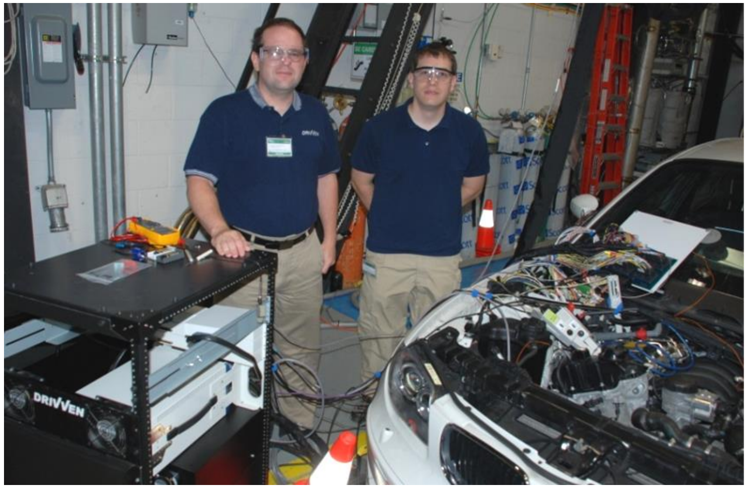
Nov. 2012: controller tuning and implementation

Found difficulty in controlling AFR during lean stratified operation off of OEM map settings (poor cylinder balance and misfires)

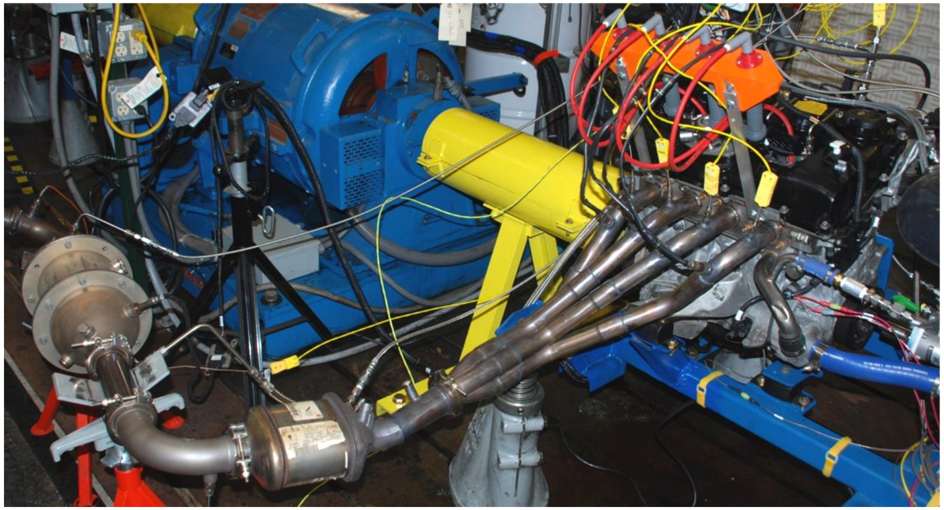
Jan. 2012: re-programming and implementation of UEGO per cylinder AFR control

Feb. 2012: final controller tuning and check of UEGO per cylinder AFR control

Engine Fully Operational!



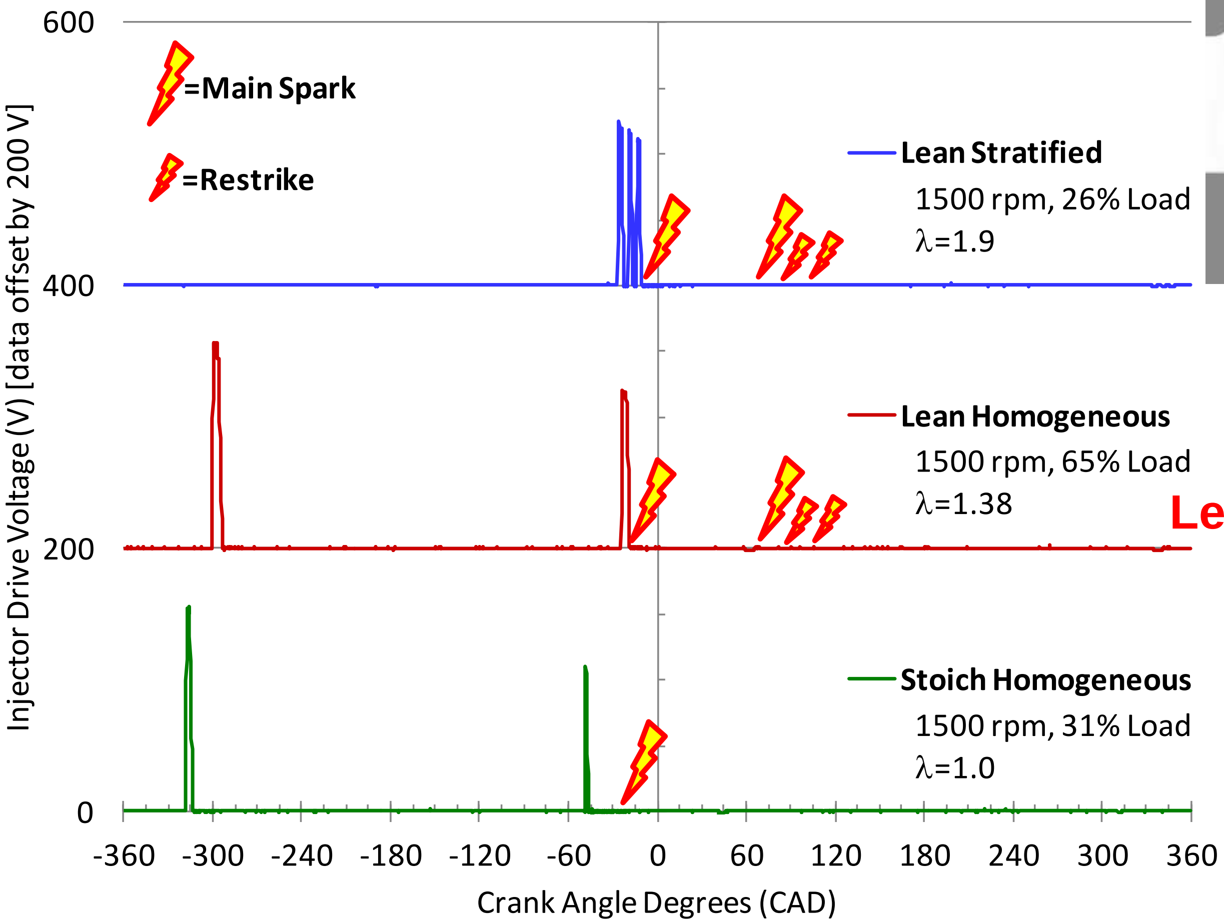
Engine mapping of BMW 120i in ORNL chassis dyno lab with Drivven staff (via subcontract)



Final BMW 120i engine setup installed in ORNL engine dyno lab

BMW 120i Engine Features Three Main Combustion Modes

- Piezoelectric injectors operate at different voltages as well as different duration
- Multiple sparks enable ignition under lean operation



Lean Stratified (λ~1.6-2.2)

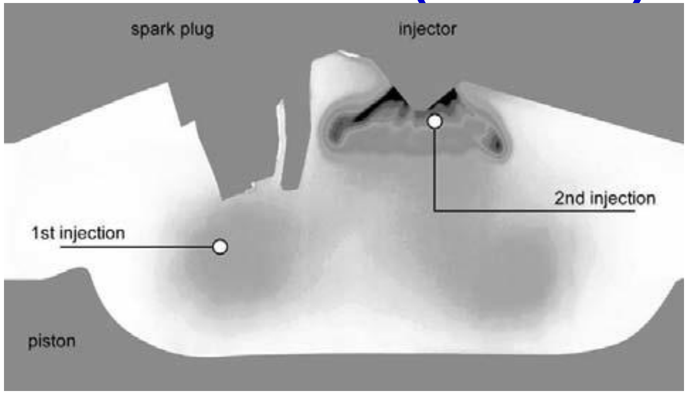


Fig. 5 from SAE 2006-01-1265 (Schwarz, et.al., BMW Group)

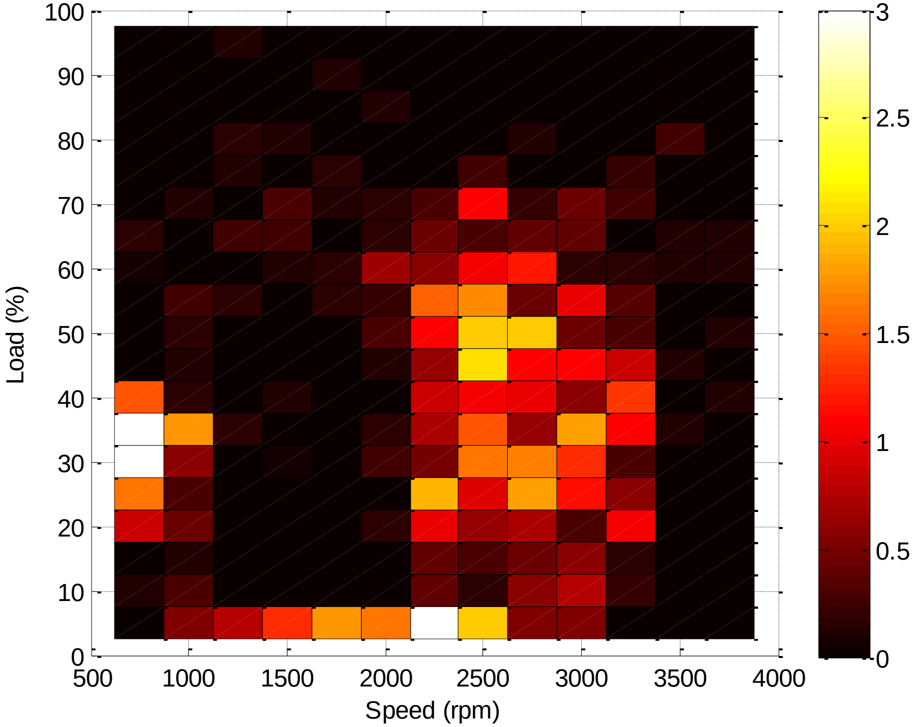
Lean Homogeneous (λ~1.3-1.6)

Stoich Homogeneous (λ=1)

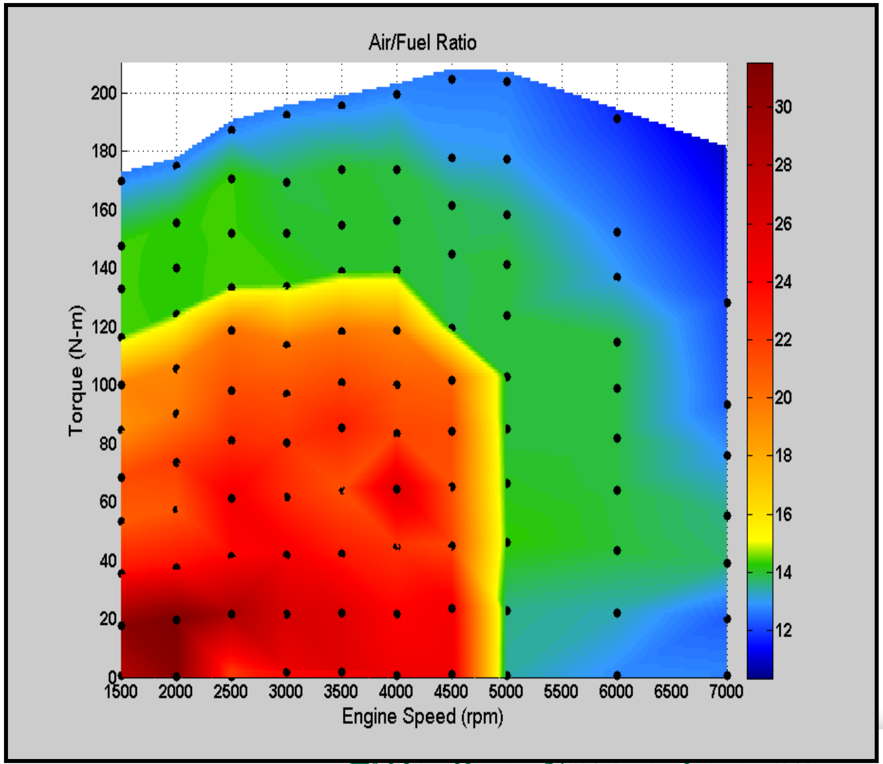
Mode of Operation Depends on Speed and Load

- Lean operation occurs at low loads and speeds
- Hot FTP drive cycle analysis shows a high percentage of operation under low speed, low load
  - Over Hot FTP,34% of time in stoichiometric or rich modes and 66% time in lean mode
- Load/Speed points for engine dynamometer studies will be based on FTP analysis and recommended points by OEM partners

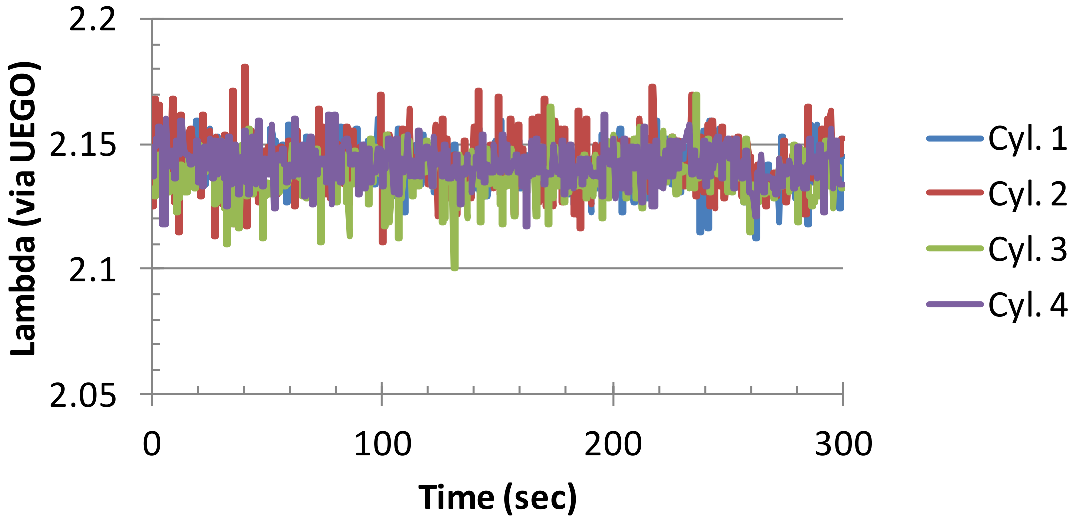
Histogram of operation over FTP drive-cycle
Map shows regions during FTP operation are primarily <3500 rpm and <70% load



AFR as function of load and speed:
Map shows regions of lean operation as well as regions of rich operation for catalyst protection



Example AFR control and LNT cycling

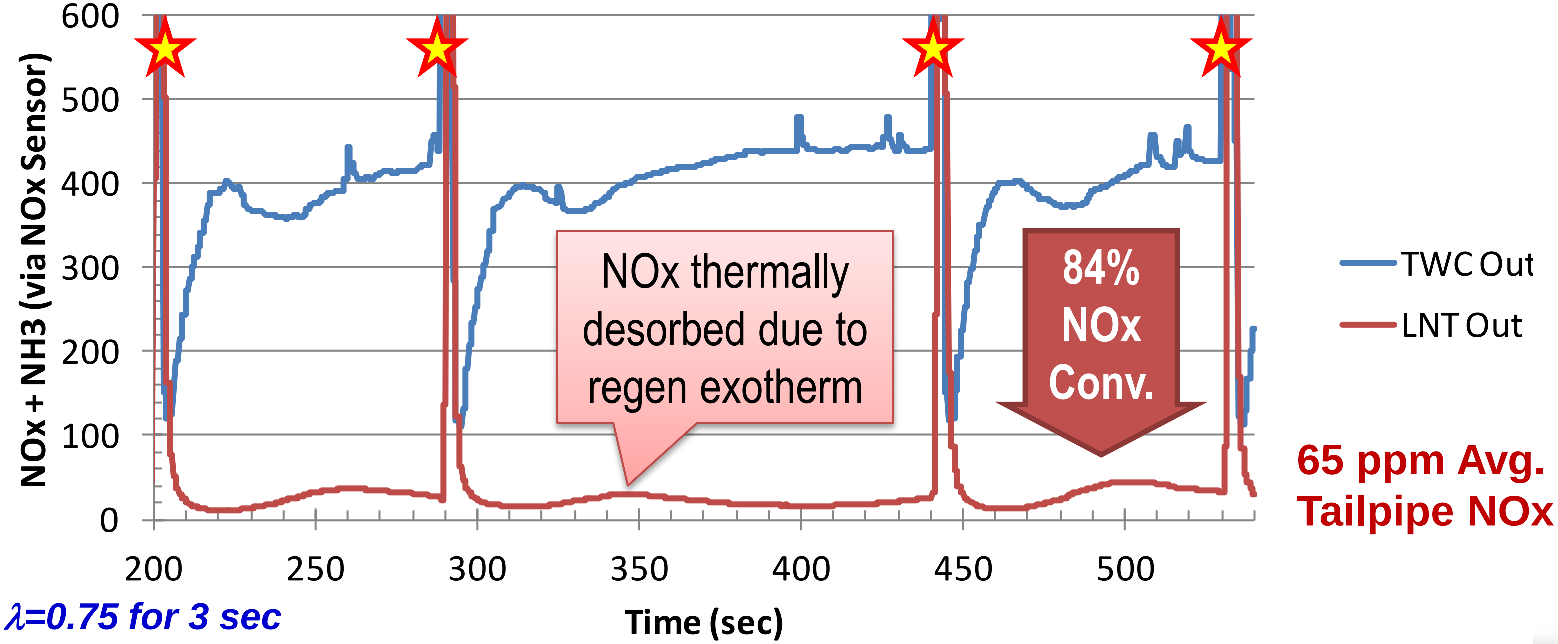


2000 rpm, 25% load, λ=2.14

	Cylinder λ (via UEGO)			
	1	**2**	**3**	**4**
Mean	2.142	2.143	2.137	2.142
Std. Dev.	0.009	0.012	0.010	0.008
COV	0.41%	0.55%	0.45%	0.38%

Engine Out NOx=287 ppm

2000 rpm
35% load
λ=1.72



NOx thermally desorbed due to regen exotherm

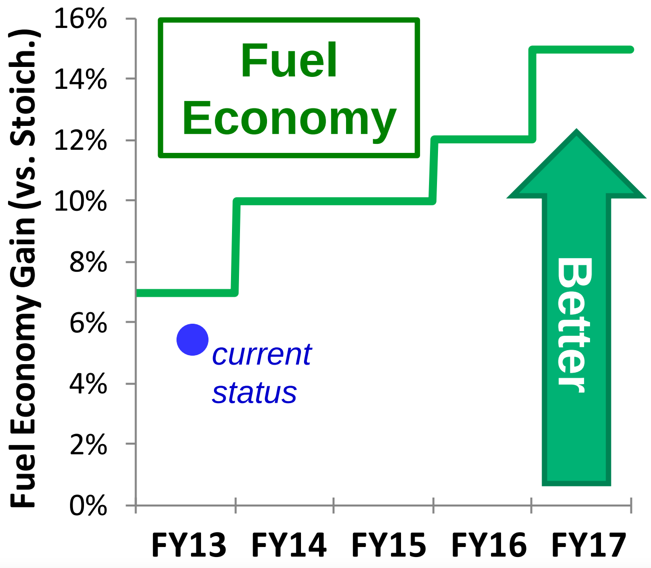
84% NOx Conv.

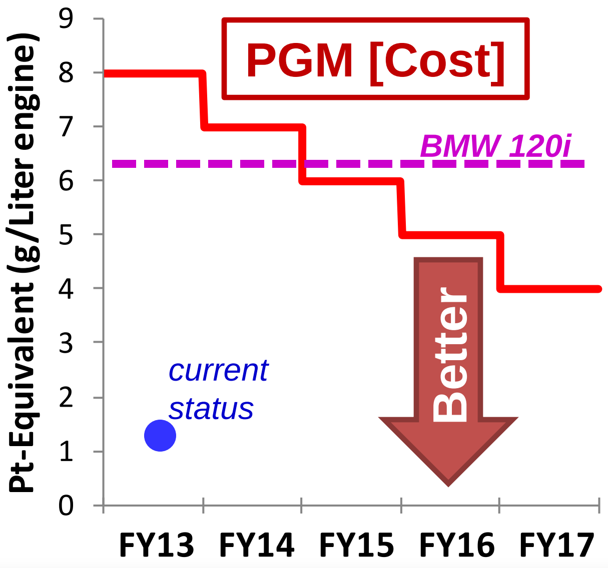
65 ppm Avg. Tailpipe NOx

★ *LNT Regens at λ=0.75 for 3 sec*

Future Work

- Continue bench flow reactor studies of catalyst formulation effects (focus on NOx, NH_3, N_2O)
  - Role of NOx storage component on TWC
  - Combination of PGMs, oxygen storage, and NOx storage components
  - TWC+LNT+SCR geometry (LNT at underfloor position/temperature)
  - Effect of S on NH_3 production by TWC
- Conduct studies of TWC+SCR system on engine
  - Investigate role of rich AFR profile on emissions
  - Characterize fuel penalty for passive SCR at representative speed and load points





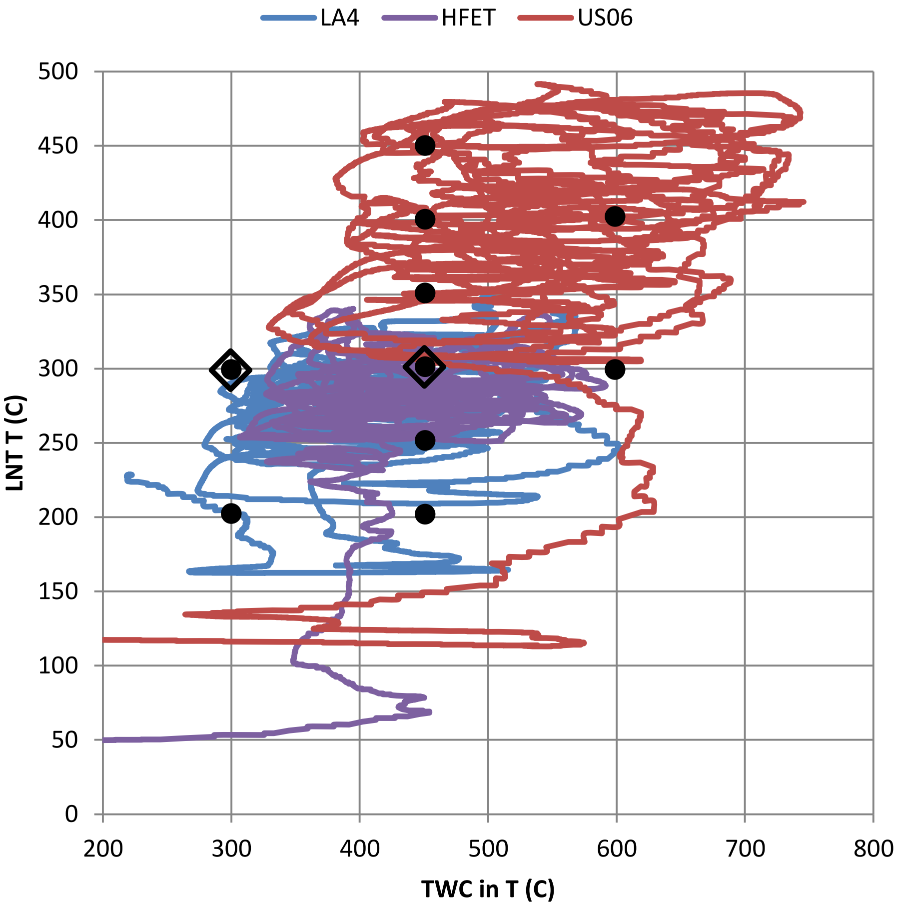
Estimated from bench reactor data with AFR calculation

Note: CO emissions excessive to Tier 2 Bin 2 goal

For reference, BMW 120i TWC+LNT system=6.3 g/L_{engine}

Two-reactor system to study passive NH_3 approach

- TWC and SCR temperatures chosen based on BMW 120i drive cycle data
- High temperature furnace to simulate close-coupled catalyst
  - Start with High PGM Pd-only catalyst
  - TWC inlet Ts: 300, 450, 600°C
- Low temperature furnace to simulate underfloor catalysts
  - Start with Cu-zeolite
  - SCR Ts: 200, 250, 300, 350, 500, 450°C
- Lean/rich switching:
  - Rich to lean switch after fixed times
  - 2 times for each SCR temperature
    - Maximum rich time (MRT)
      - with <10 ppm NH_3 slip
    - half of MRT
  - Lean to rich switch at 20 ppm NOx slip from SCR



● - AFR = 14.0

◇ - AFR = 14.0, 14.1, 14.2 and 14.3