HC-SCR for Diesel NOx Reduction on Supported Metal Catalysts

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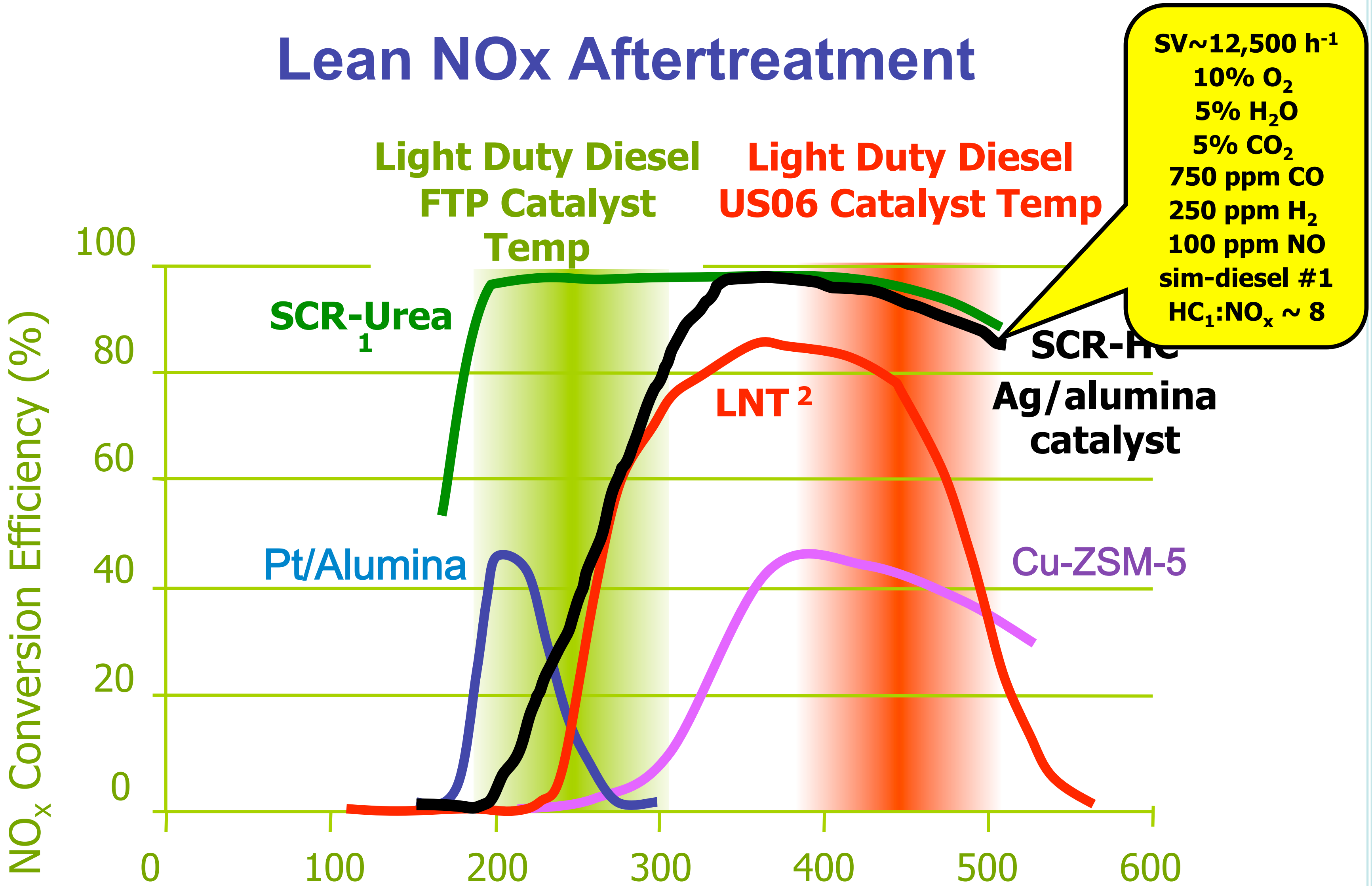
Background:

Hydrocarbon assisted NOx SCR for automotive catalysis

- Copper zeolites late 80's early 90's
  - Held, et al, SAE 900496, 1990
  - Iwamoto, et al, Proc. Catalytic Technology for the Removal of NO, Tokyo, 1990
- Supported catalysts (PGMs and base metals) early 90's
  - Hamada, et al., Applied Catalysis, 1991
  - Bethke, Alt and Kung, Catalysis Letters, 1994
- Ag/alumina
  - Burch and Millington, Catalysis Today, 1996.
  - Shimizu et al., Applied Catalysis B: Environmental, 2000.
- DOE NOx Discovery Project
  - Initiated in August of 2002, completed end of 2007
  - Over 16,000 materials synthesized and evaluated
  - **Ag/alumina selected as optimum material**

Lean NOx Aftertreatment

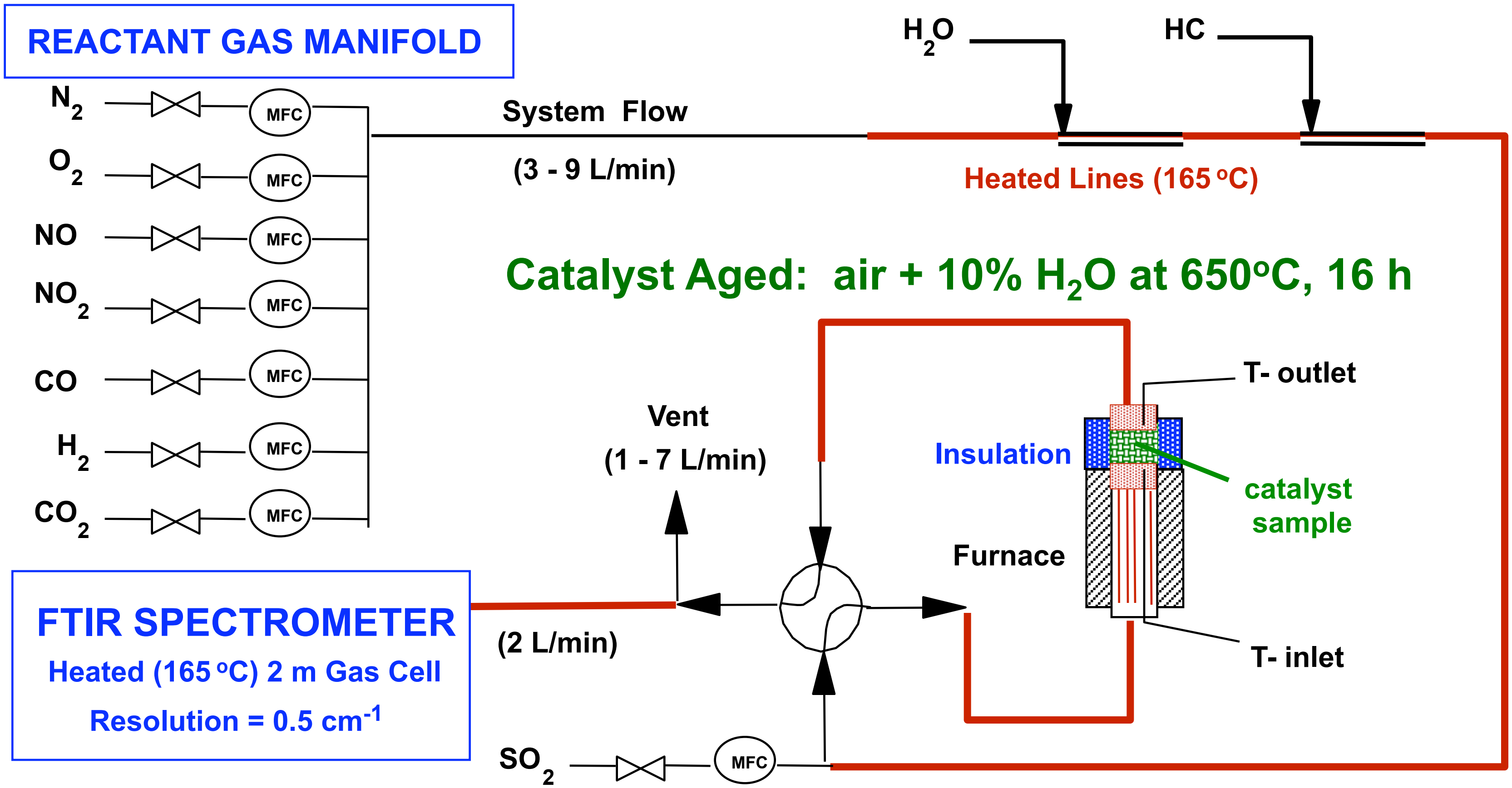


[1] Aged 120 k mi
[2] Aged 120 k mi

HC-SCR Optimization Parameters

- Catalyst formulation (Ag/alumina, optimum loading dependent on the reductant, US Patent Application Number Number 11/533,593)
- Reductants investigated (sim-Diesel, sim-gasoline, ethanol)
- HC/NOx ratio (about 8 for pure HC systems)
- H_2 concentration level (over 100 ppm enhances NOx conversion)
- NOx level & NO_2/NO ratio (lower NOx more effectively reduced, low dependence on ratio)
- Temperature & space velocity
- O_2 concentration level (needs to be above 4%)
- Catalyst deactivation (coking, S poisoning, thermal aging, phosphorous poisoning all investigated)
- Control strategies (US Patent Application Number Number 11/533,434)
- **Dual bed systems (US Patent Application Numbers 61/148,899 and 12/363,054)**

Experimental Apparatus

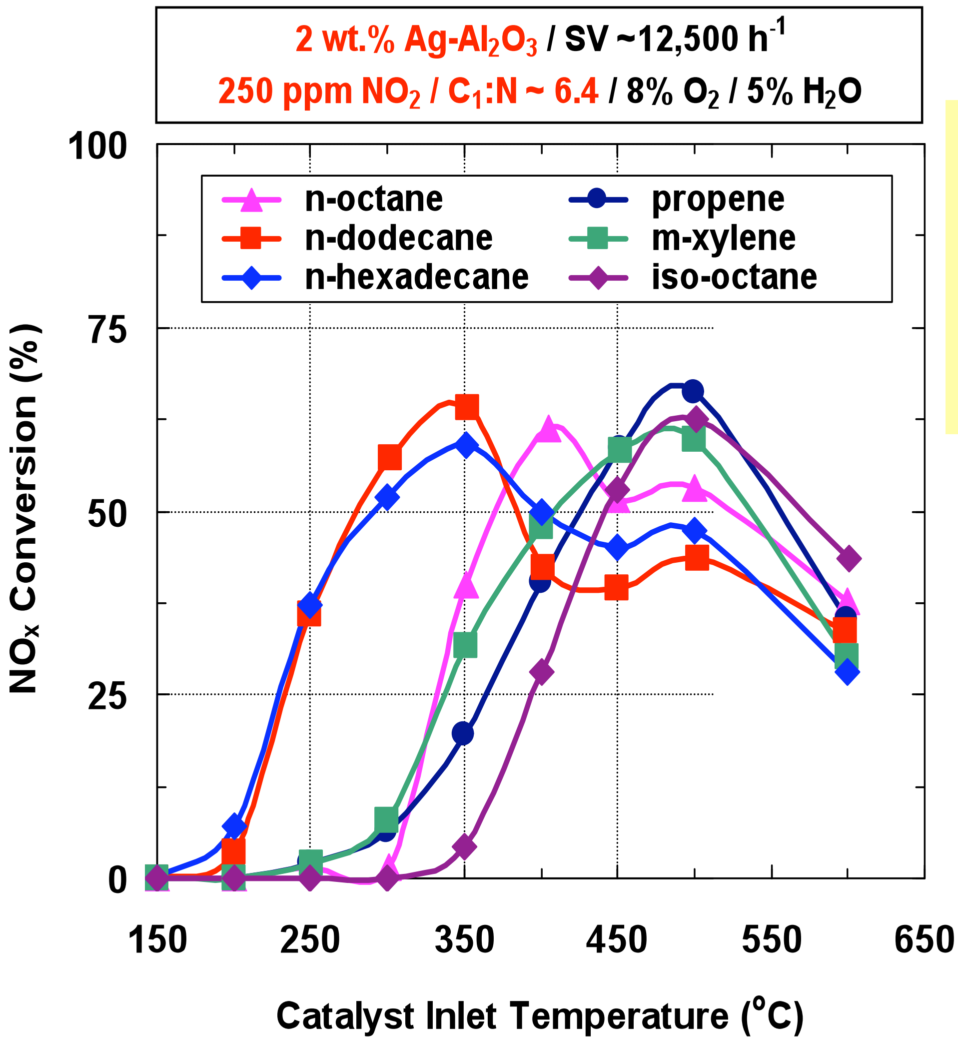


STANDARD CONDITIONS: 10% O_2 / 5% H_2O / 5% CO_2 / 750 ppm CO / 250 ppm H_2

NO_x and simulated diesel fuel (long-chain alkane + aromatic)

$SV_{catalyst}$ ~12,500-75,000 h^{-1} / $T_{HC\text{-}SCR}$ = 150 → 550°C

Effects of Various HC Species on NOx Reduction

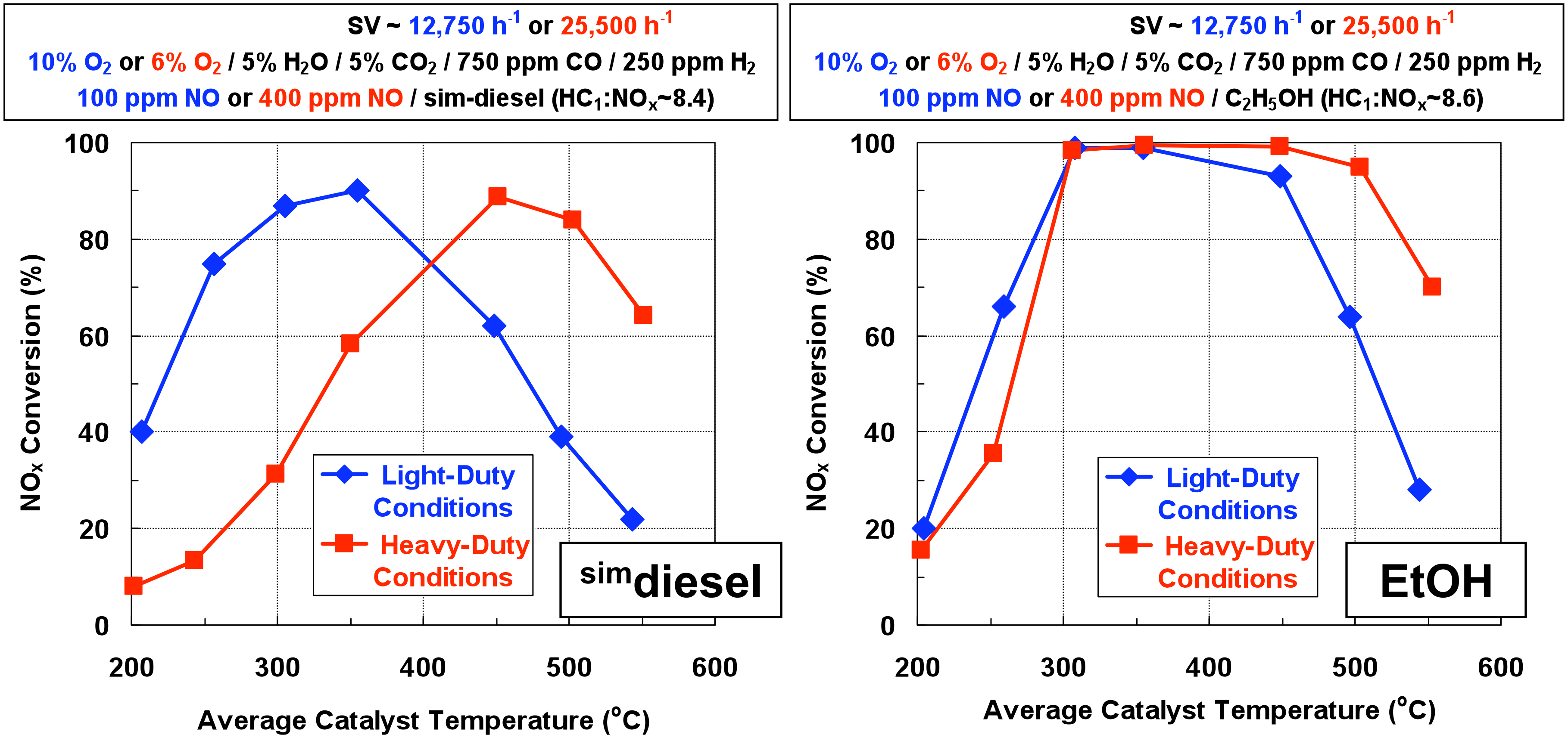


NOx reduction activity trends:

- $C_{12} \approx C_{16} > C_8$ for n-alkanes
- straight-chain > branched-chain HCs
- alcohols/aldehydes > n-alkanes
- m-xylene less active than n-C_{12} or n-C_{16}
- propene not active until T > 350°C

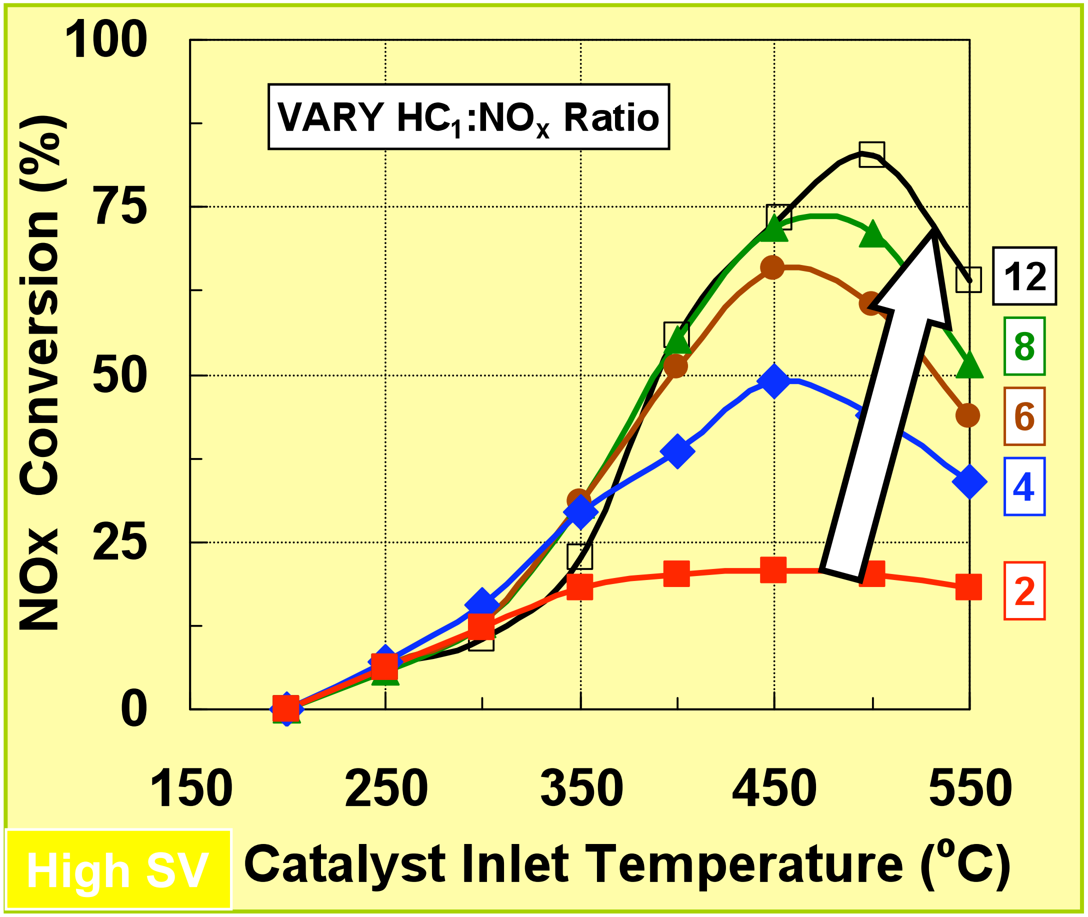
Diesel fuel component HCs are more effective reductants for lean NOx reduction than propane/propene (used in earlier HC/SCR catalyst studies) or gasoline fuel component HCs.

NO_x Conversion comparison between ^{sim}Diesel and Ethanol



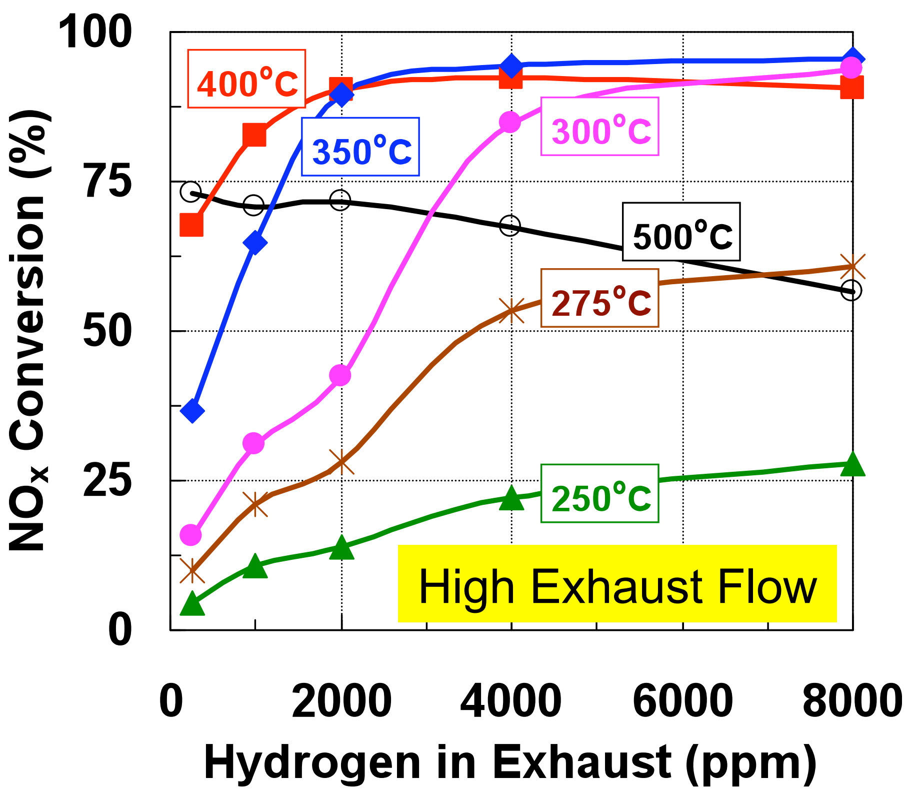
- Much wider temperature window with EtOH as reductant under both low and high SV conditions

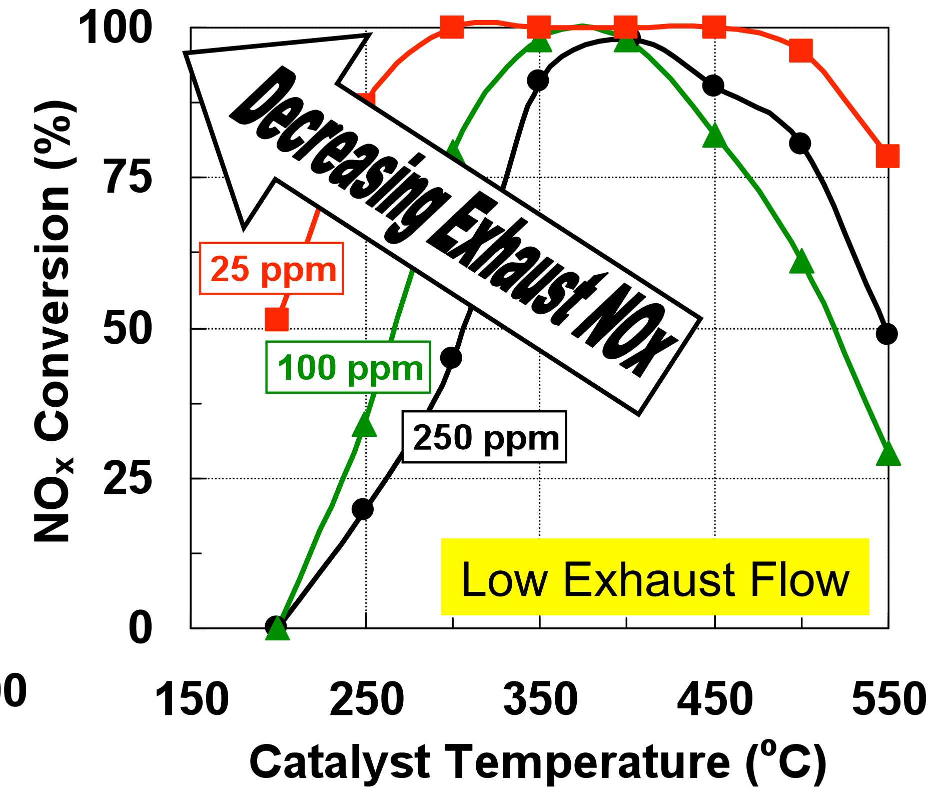
Increased HC Injection Amount Only Improves High T Performance



- Low T engine performance inhibited by HC injection initiation at 300 °C
- High HC:NOx ratios typically have higher HC slip

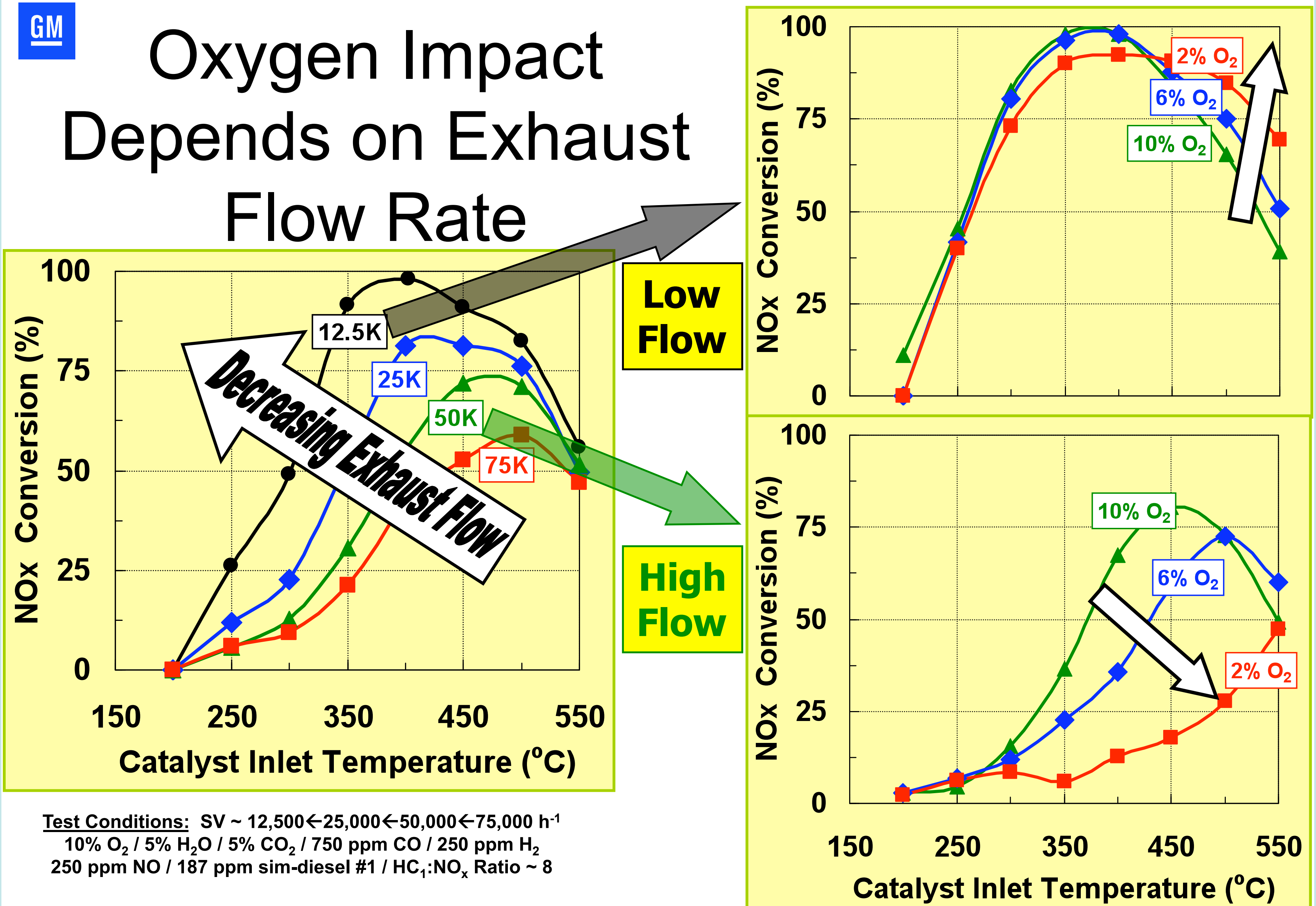
Supplemental H_2 and Lower Exhaust NO_x Enhances NO_x Conversion Efficiency





→ Lower exhaust NO_x improves performance into the FTP temperature range <u>w/o</u> adding extra H_2

Oxygen Impact Depends on Exhaust Flow Rate



Test Conditions: SV ~ 12,500←25,000←50,000←75,000 h^{-1}
10% O_2 / 5% H_2O / 5% CO_2 / 750 ppm CO / 250 ppm H_2
250 ppm NO / 187 ppm sim-diesel #1 / HC_1:NO_x Ratio ~ 8

HC-SCR Control Strategy

Catalyst Temperature
HIGH > 350°C
LOW < 350°C

Space Velocity
HIGH ≥ 50,000 h^{-1}
LOW ≤ 12,500 h^{-1}

Exhaust NO_x Concentration
HIGH ≥ 250 ppm
LOW ≤ 100 ppm

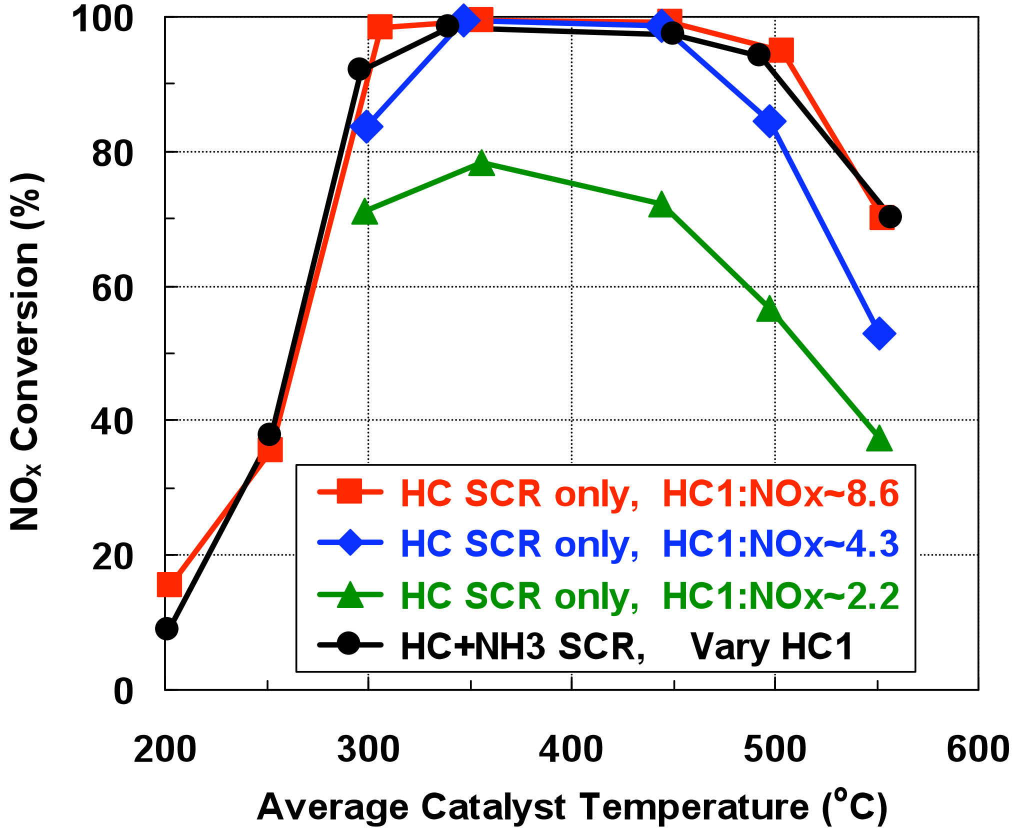
Exhaust Condition	#1	#2	#3	#4
Catalyst Temperature	HIGH	HIGH	LOW	HIGH
Space Velocity (Exhaust Flow Rate)	HIGH	HIGH	HIGH	LOW
Exhaust NO_x Concentration	HIGH	LOW	HIGH	HIGH
Control Strategy O_2 concentration: $HC_1:NO_x$ ratio: H_2 concentration:	> 10% ~ 10 - 15 ~ 2000 ppm	> 10% ~ 15 - 20 ~ 1000 ppm	> 10% ~ 4 - 8 ~ 4000 ppm	< 10% ~ 10 - 15 ~ 250 ppm
Exhaust Condition	**#5**	**#6**	**#7**	**#8**
Catalyst Temperature	LOW	LOW	LOW	HIGH
Space Velocity (Exhaust Flow Rate)	LOW	LOW	HIGH	LOW
Exhaust NO_x Concentration	HIGH	LOW	LOW	LOW
Control Strategy O_2 concentration: $HC_1:NO_x$ ratio: H_2 concentration:	~ 10% ~ 10 - 15 ~ 1000 ppm	~ 10% ~ 15 - 20 ~ 1000 ppm	> 10% ~ 10 - 15 ~ 4000 ppm	< 10% ~ 15 - 20 ~ 250 ppm

US Appln. No. 11/533,434

- S.J. Schmieg, R.J. Blint, L. Deng, M.B. Viola, J.-H. Lee

Dual Bed NO_x Conversion (HC-SCR + NH_3-SCR)

HC-SCR @ SV ~ 25,500 h^{-1} +/- NH_3-SCR @ SV ~ 60,000 h^{-1}
6% O_2 / 5% H_2O / 5% CO_2 / 750 ppm CO / 250 ppm H_2
400 ppm NO / 431 - 1724 ppm C_2H_5OH (HC_1:NO_x~ 2.2 to 8.6)



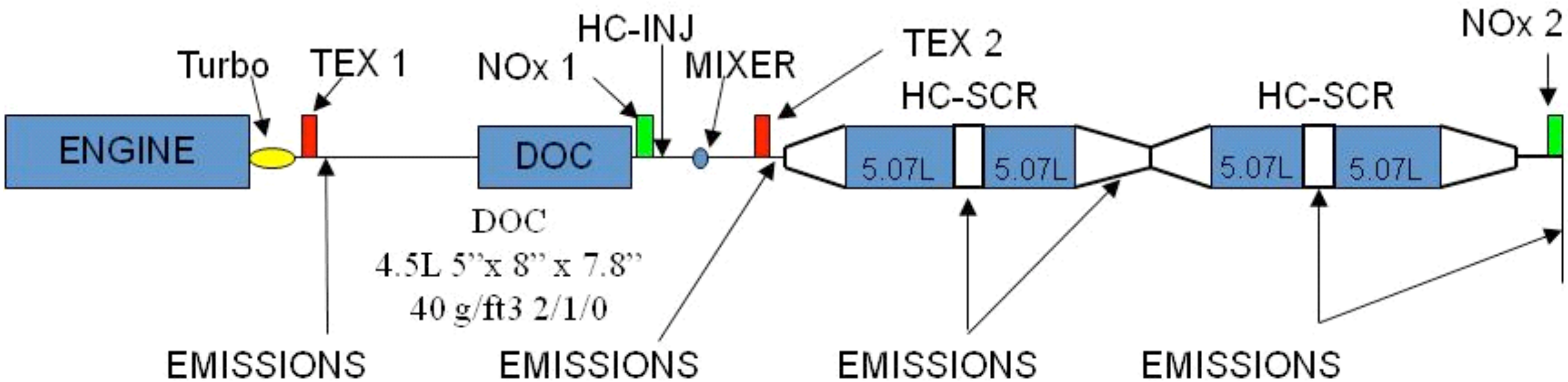
HC_1:NO_x ~2.2 2.2 3.2 2.7 3.2 4.3 8.6

NH3-SCR catalyst:
→ 2010 CIDI Cu-zeolite formulation aged in air + 10% H_2O at 700°C for 50 h

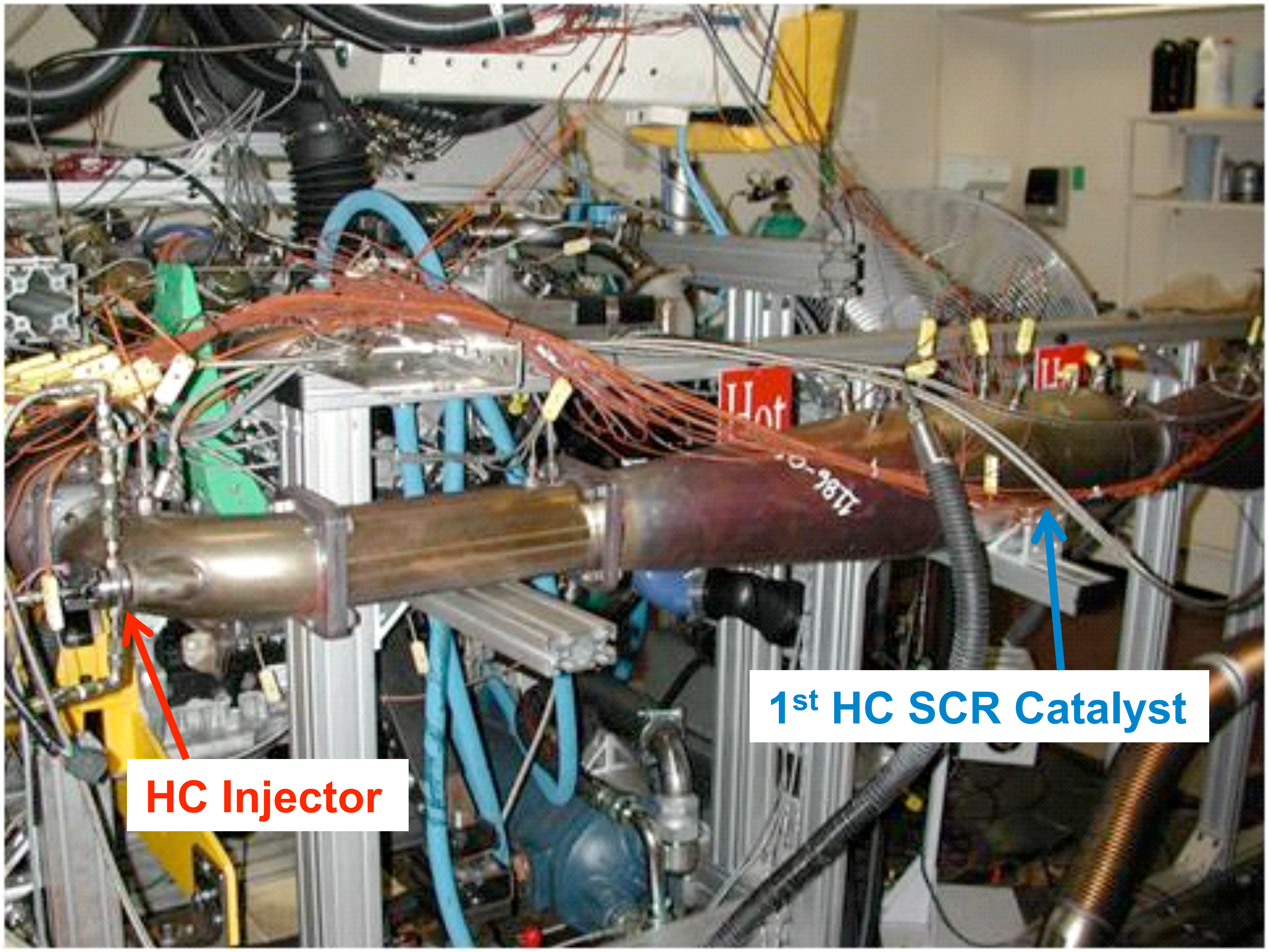
Ethanol as reductant

→ High NO_x conversion levels are maintained while lowering the amount of ethanol injected

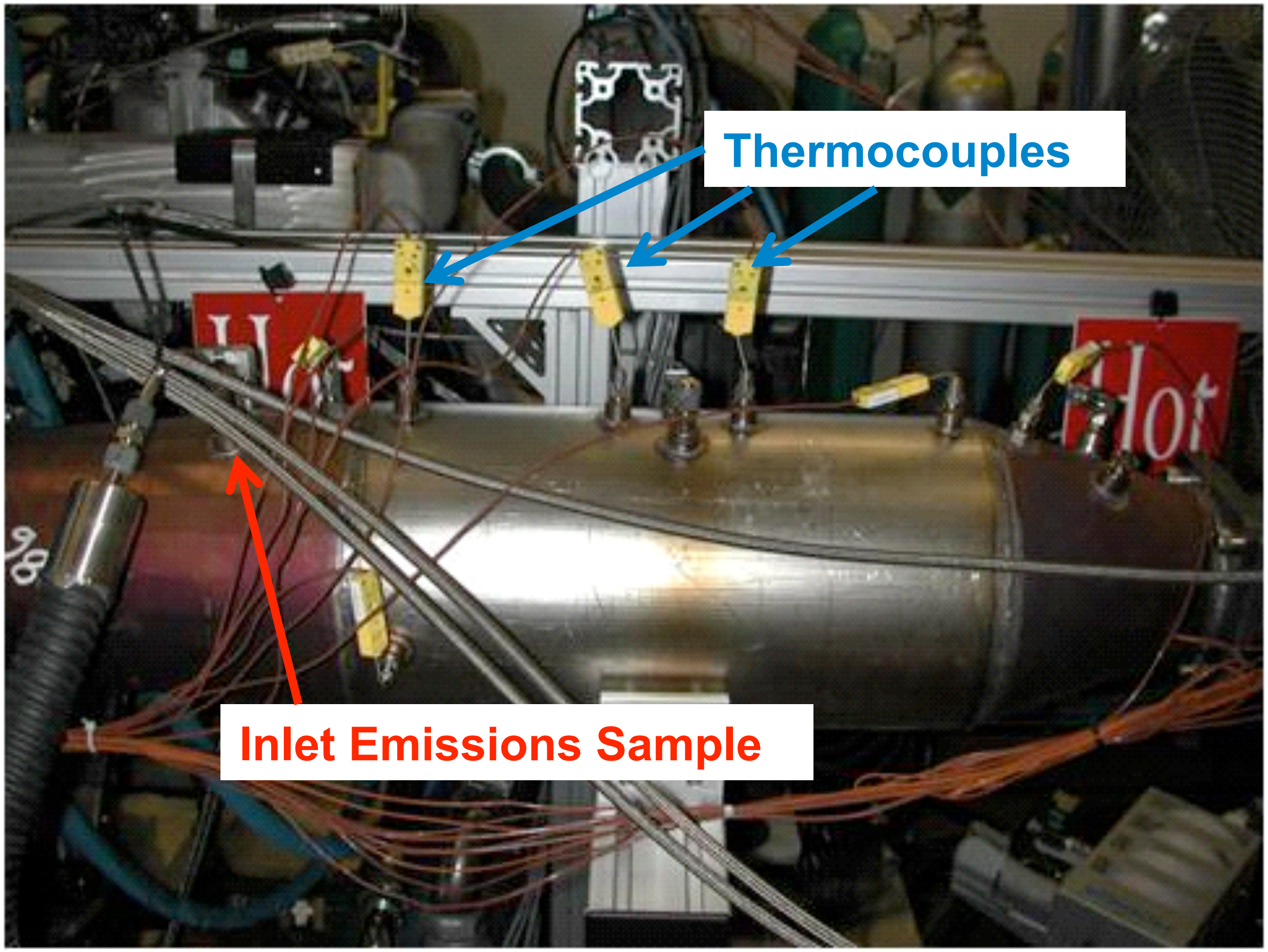
Diesel Aftertreatment testing architecture using 6.6 Duramax engine



Picture of Dyno Aftertreatment System, Injector and First Can.

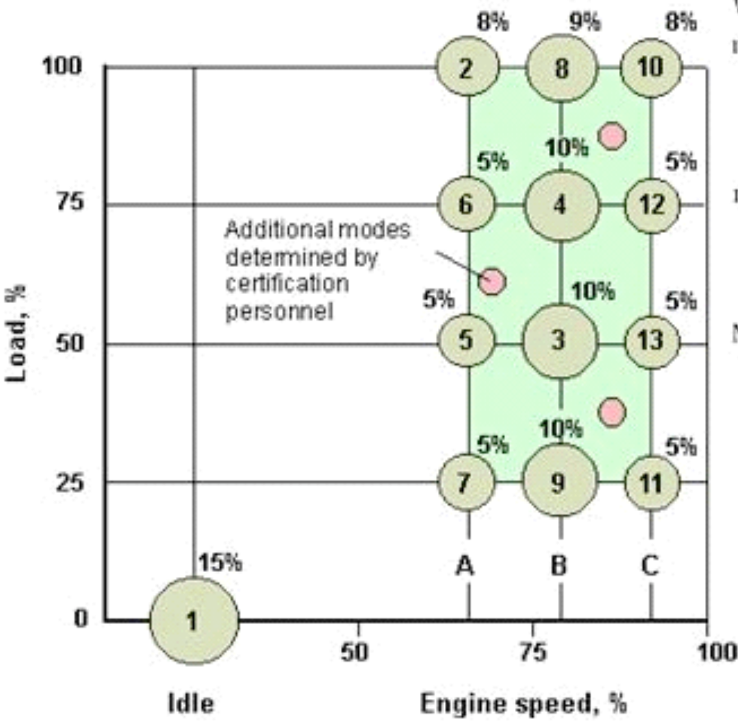


First HC-SCR Can Thermocouple Location and Inlet Emissions Sample



Supplemental Emission Test (SET)

(aka Steady State Test / 13 Mode Test, Euro III - European Stationary Cycle / ESC)



Where:

n_{hi} = High speed as determined by calculating 70% of the maximum power. The highest engine speed where this power value occurs on the power curve is defined as n_{hi}.

n_{lo} = Low speed as determined by calculating 50% of the maximum power. The lowest engine speed where this power value occurs on the power curve is defined as n_{lo}.

Maximum power = the maximum observed power calculated according to the engine mapping procedures defined in § 86.1332.

Speed A = n_{lo} + 0.25 × (n_{hi} − n_{lo})
Speed B = n_{lo} + 0.50 × (n_{hi} − n_{lo})
Speed C = n_{lo} + 0.75 × (n_{hi} − n_{lo})

$$A_{WA} = \frac{\sum_{i=1}^{n} [A_{Mi} \times WF_i]}{\sum_{i=2}^{n} [A_{Pi} \times WF_i]}$$

Where:

A_{WA} = Weighted average emissions for each regulated gaseous pollutant, in grams per brake horse-power hour.

A_M = Modal average mass emissions level, in grams per hour. Mass emissions must be calculated as described in §86.1342.

A_P = Modal average power, in brake horse-power. Any power measured during the idle mode (mode 1) is not included in this calculation.

W_F = Weighting factor corresponding to each mode of the steady-state test cycle, as defined in paragraph (b)(1) of this section.

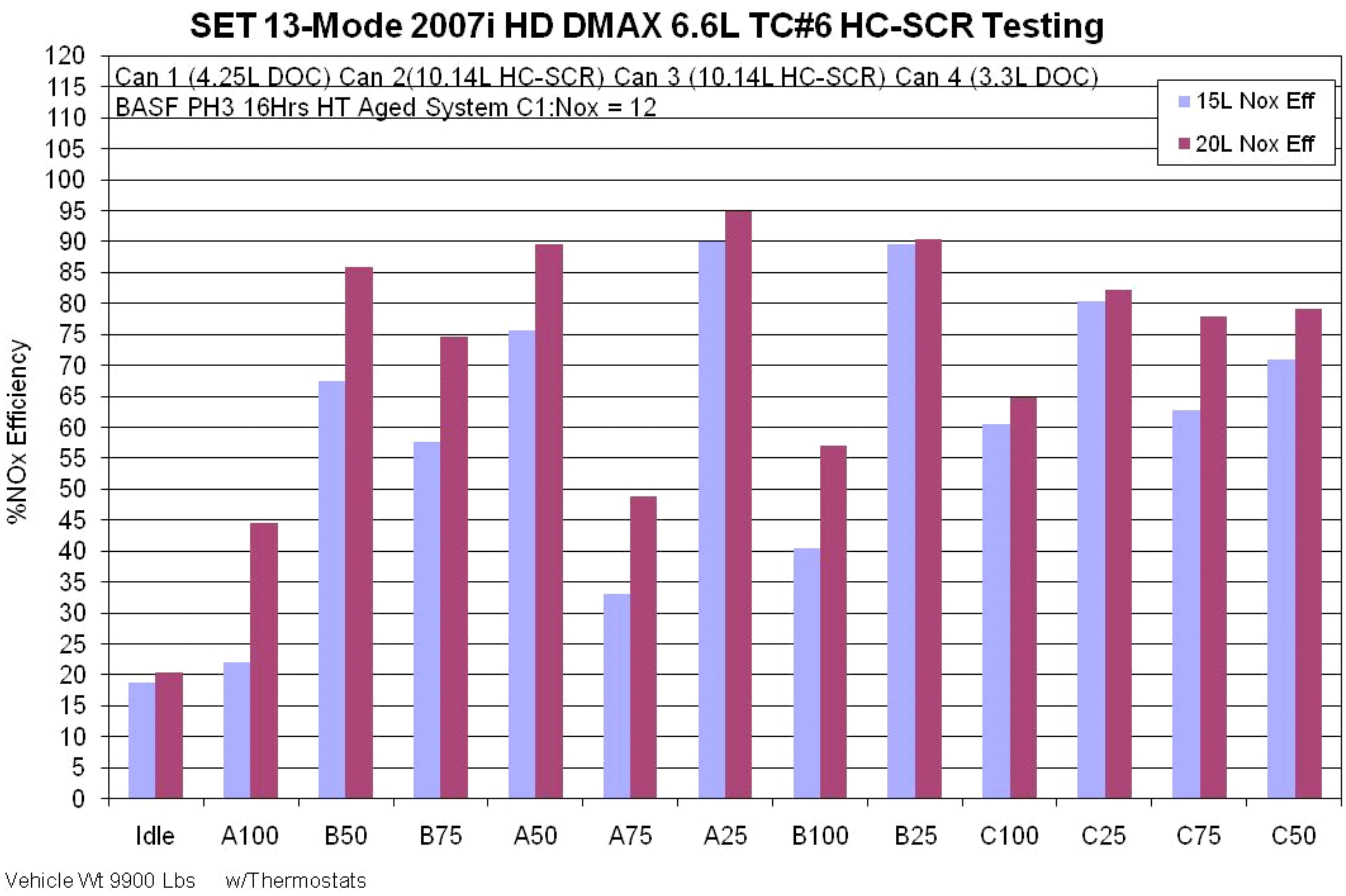
i = The modes of the steady-state test cycle, as defined in paragraph (b)(1) of this section.

n = 13, corresponding to the 13 modes of the steady-state test cycle, as defined in paragraph (b)(1) of this section.

- rpm/load changes complete within first 20 sec of each mode
- 2 minutes at each non-idle mode, 4 minutes at idle
- 1 PM filter for over 13 modes

Diesel Fuel Only Conversions at Steady State Points

SET06142007T3



Ethanol Only Conversions at Steady State Points

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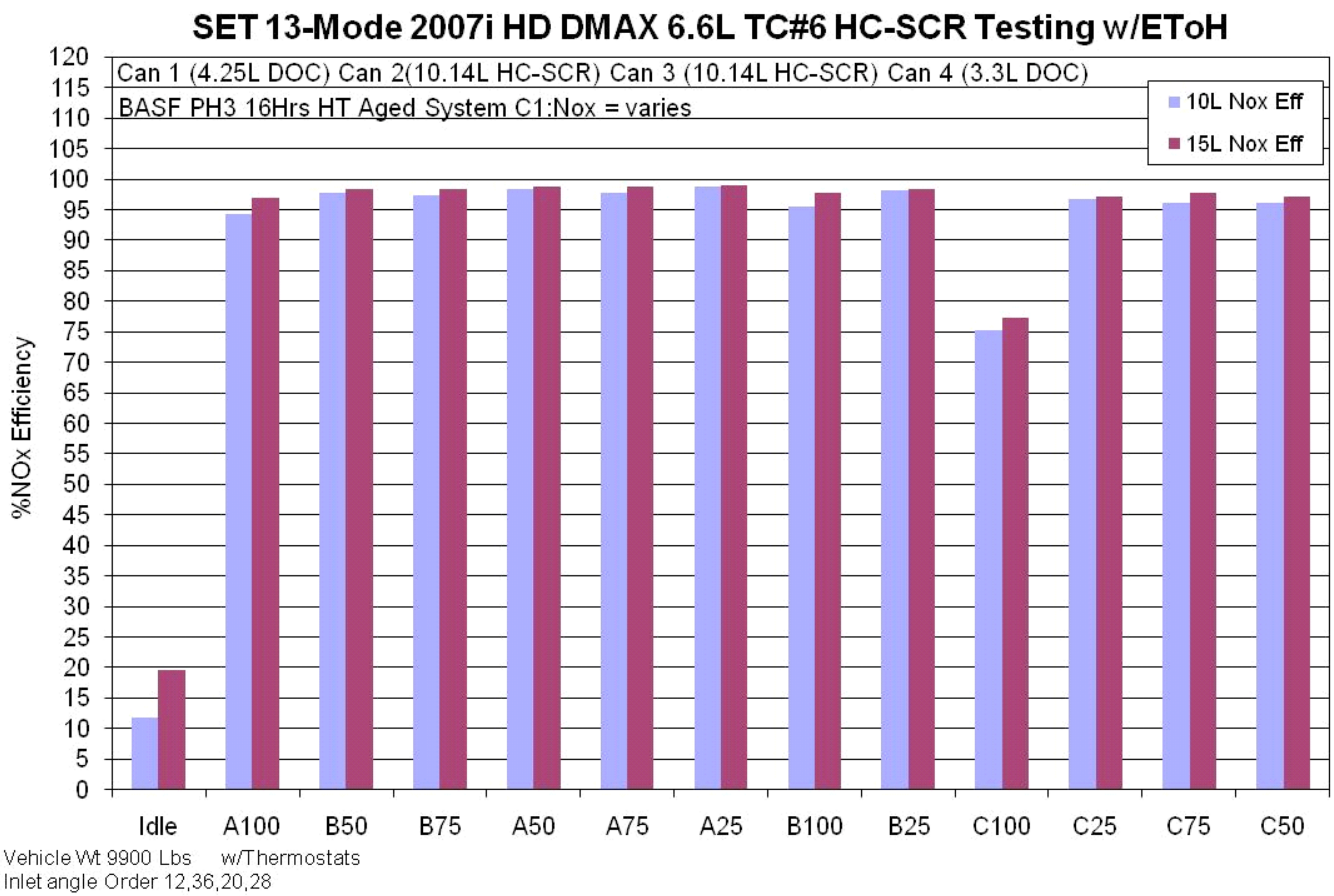

Summary

- Accomplishments
  - High-throughput technology has optimized the HC-SCR catalyst formulation
  - Effectiveness of diesel fuel, gasoline and ethanol demonstrated in both reactor and engine testing
  - HC-SCR control strategy has been developed
  - Dual bed technology demonstrated
  - All degradation mechanisms identified and redaction schemes devised
- Drawbacks
  - High SV significantly reduces the NO_x conversion efficiency
  - Poor diesel fuel vaporization at low T can limit reductant delivery
  - Degradation modes require close engine control
  - Hydrocarbon slip