Engine and Reactor Evaluations of HC-SCR for Diesel NOx Reduction

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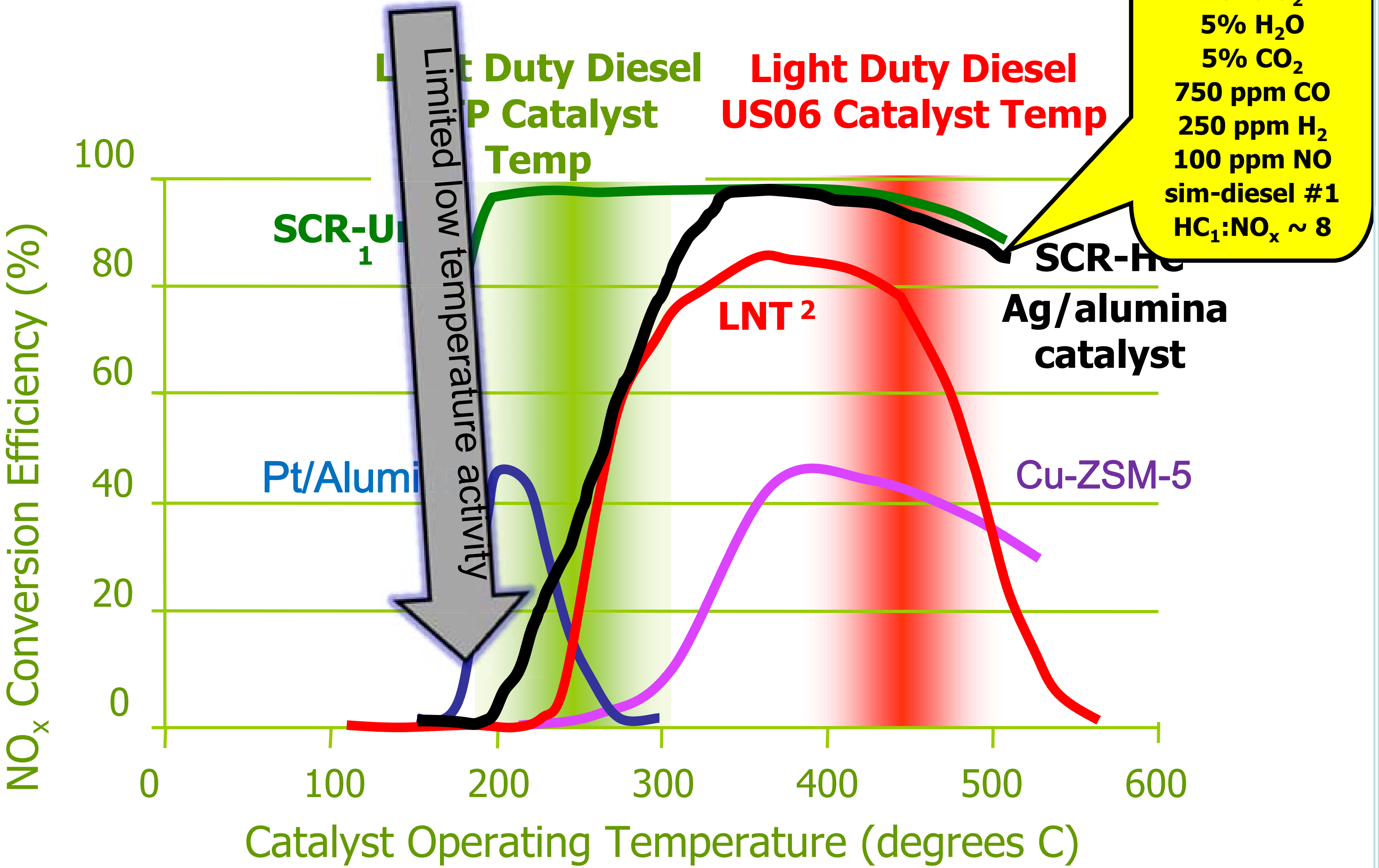
Background:

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



SV~12,500 h^{-1}
10% O_2
5% H_2O
5% CO_2
750 ppm CO
250 ppm H_2
100 ppm NO
sim-diesel #1
$HC_1:NO_x$ ~ 8

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

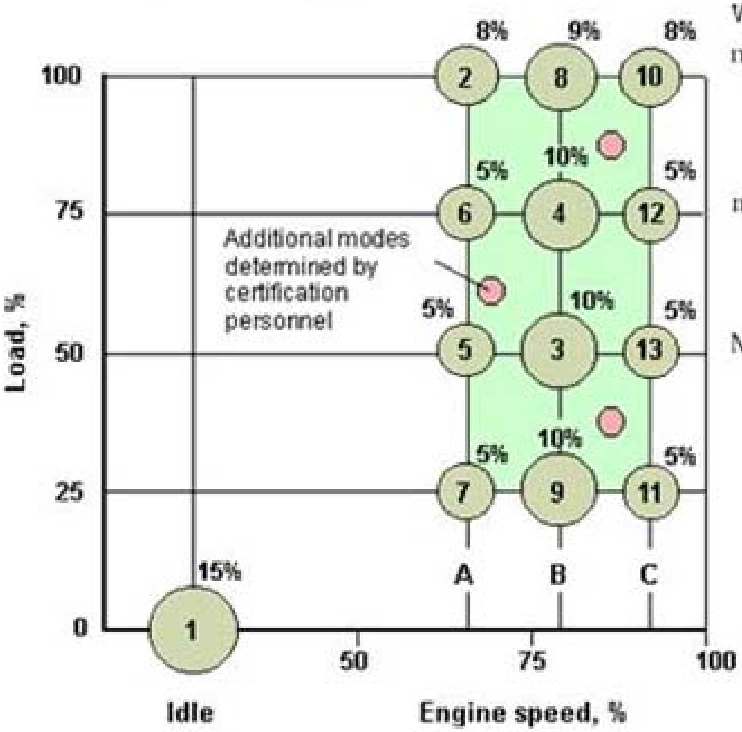
Engine Results

Focus is the heavy duty, US dynamometer certification using the Duramax 6.6 liter diesel

- Catalyst volume:
  - Four, 5.0 liter bricks (20.0L total vol.)
  - emission measurements are after brick 3 and brick 4
- Reductant by in-exhaust injection:
  - diesel fuel
  - ethanol
- Federal test cycles:
  - Heavy duty FTP (HDFTP),
  - Cold-start HDFTP (CHDFTP)
  - Set 13 (Supplemental Emission Test)

Supplemental Emission Test (SET)

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



- 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

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 = $n_{lo} + 0.25 \times (n_{hi} - n_{lo})$
Speed B = $n_{lo} + 0.50 \times (n_{hi} - n_{lo})$
Speed C = $n_{lo} + 0.75 \times (n_{hi} - n_{lo})$

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

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.

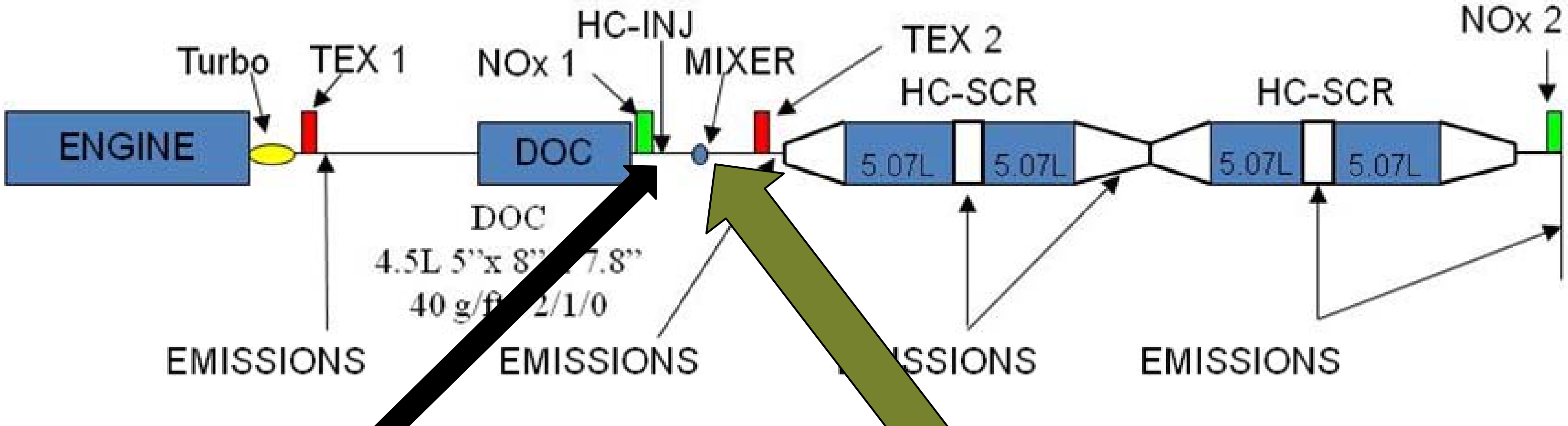
A_{P} = Modal average power, in brake horse-power. Any power measured during the idle mode (mode 1) is not included in this calculation.

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.

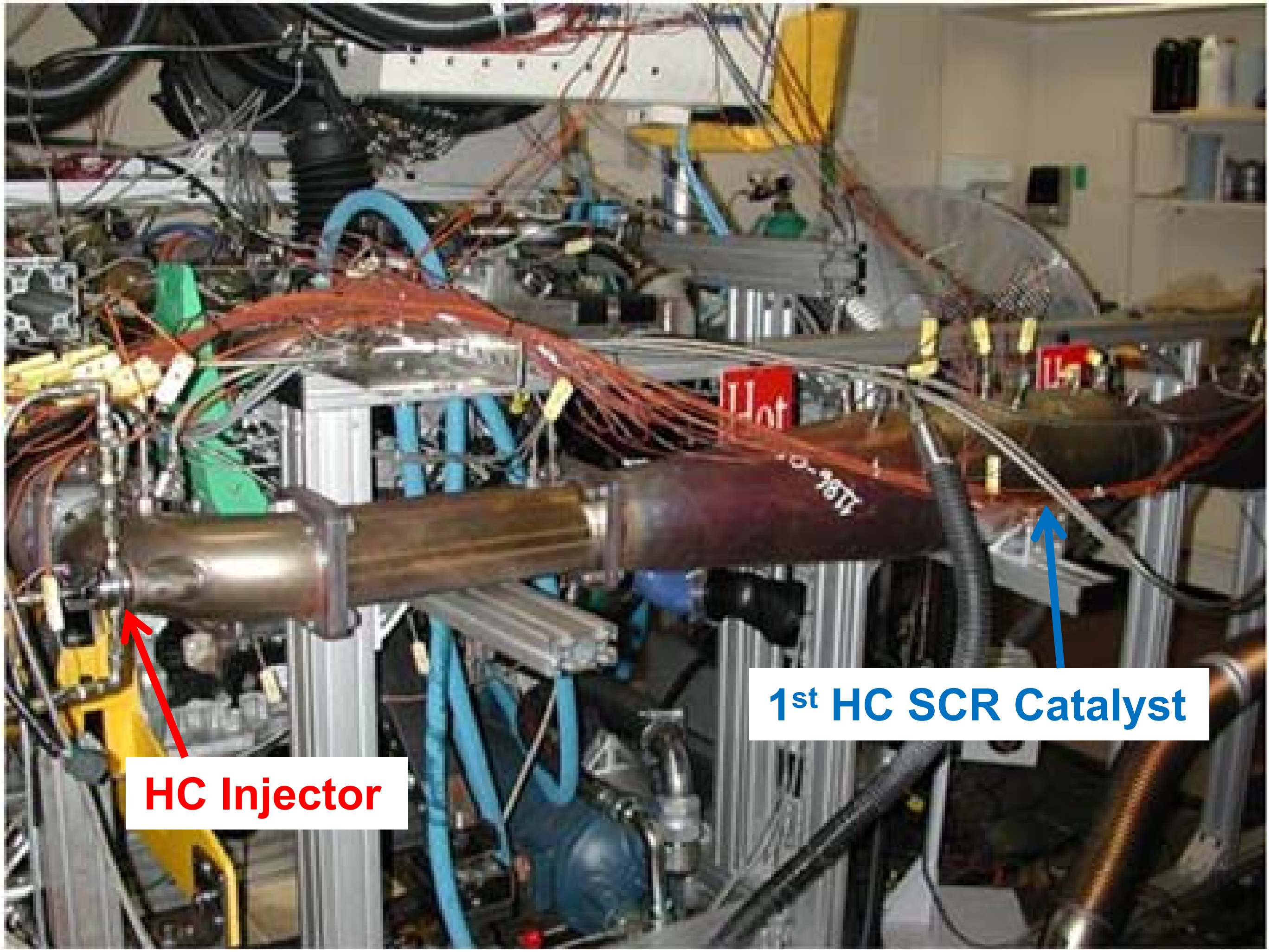
n = 13, corresponding to the 13 modes of the steady-state test cycle, as defined in paragraph (b)(1) of this section.

Diesel Aftertreatment testing architecture using 6.6 Duramax engine

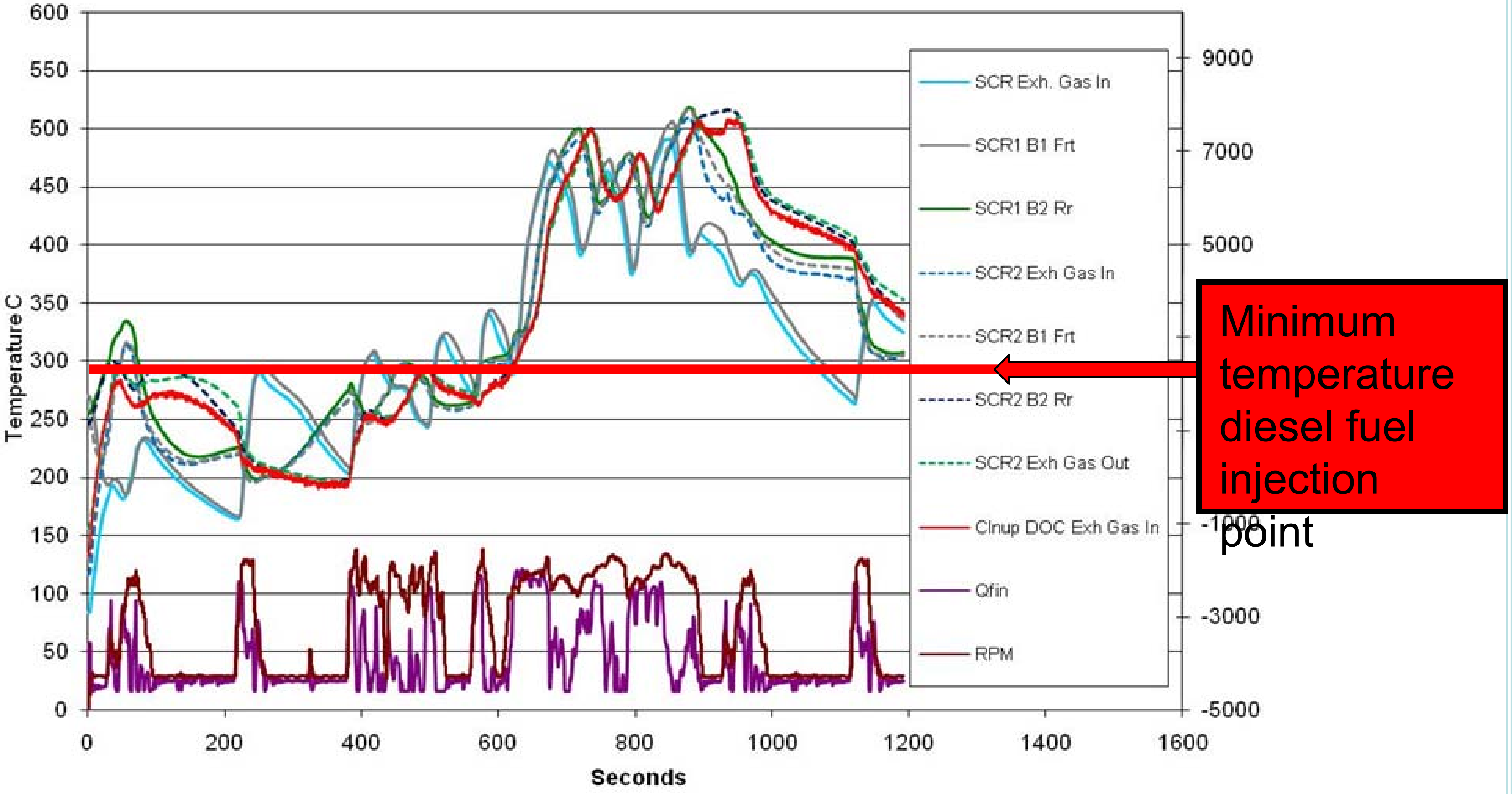


- Diesel fuel
- Ethanol

Picture of Dyno Aftertreatment System, Injector and First Can.



HDFTP Temperature Measurements

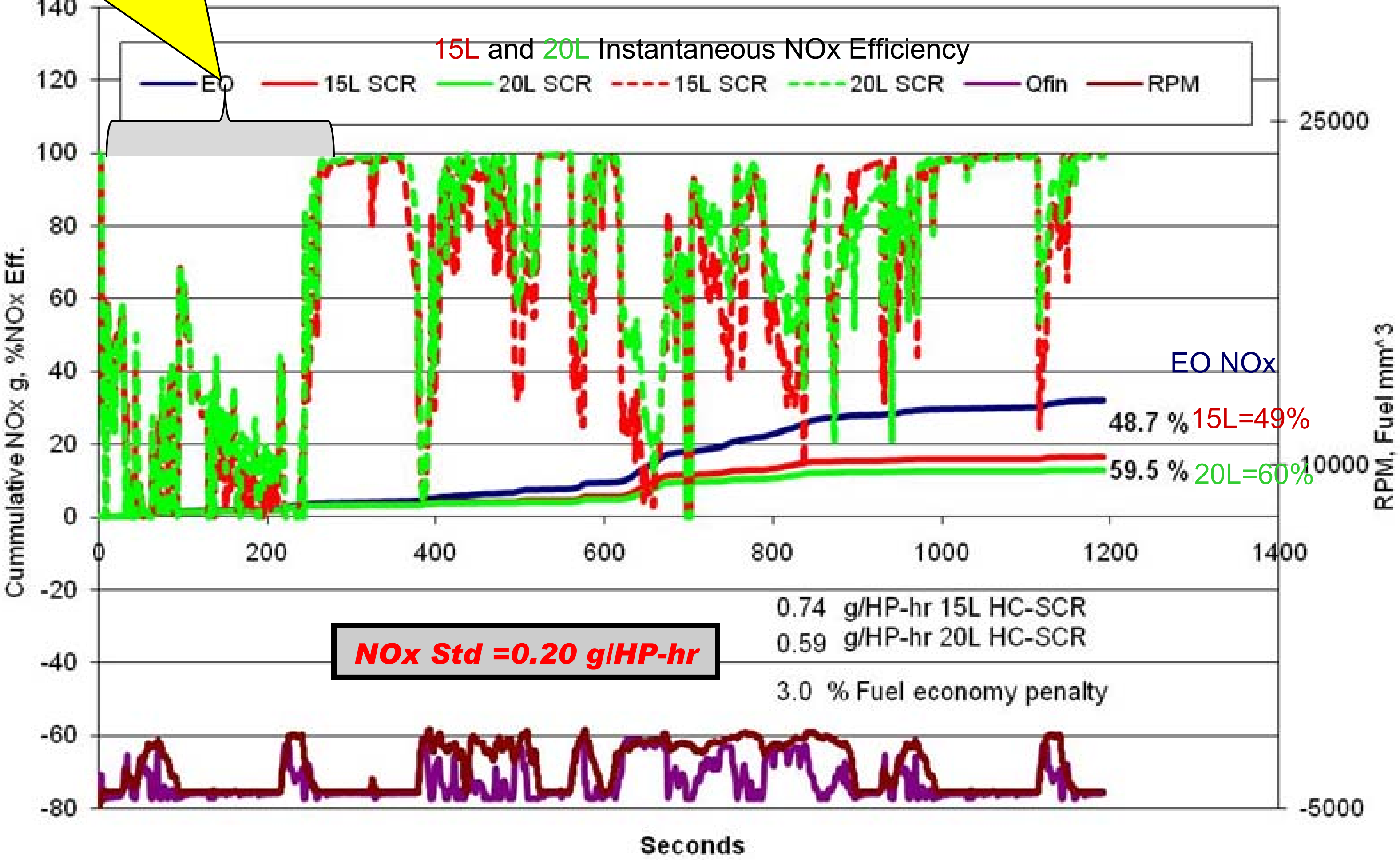


Minimum temperature diesel fuel injection point

- Exhaust temperatures vary from 150 °C to 500 °C
- First 600 seconds show catalyst in temperatures no higher than 250 °C
- **Conclusion: Almost half the HDFTP is completed before the exhaust reaches the optimum NOx conversion temperature**

HDFTP NOx Emissions Results with Diesel

Low NOx efficiency because diesel fuel not injected below 280C



0.74 g/HP-hr 15L HC-SCR

0.59 g/HP-hr 20L HC-SCR

3.0 % Fuel economy penalty

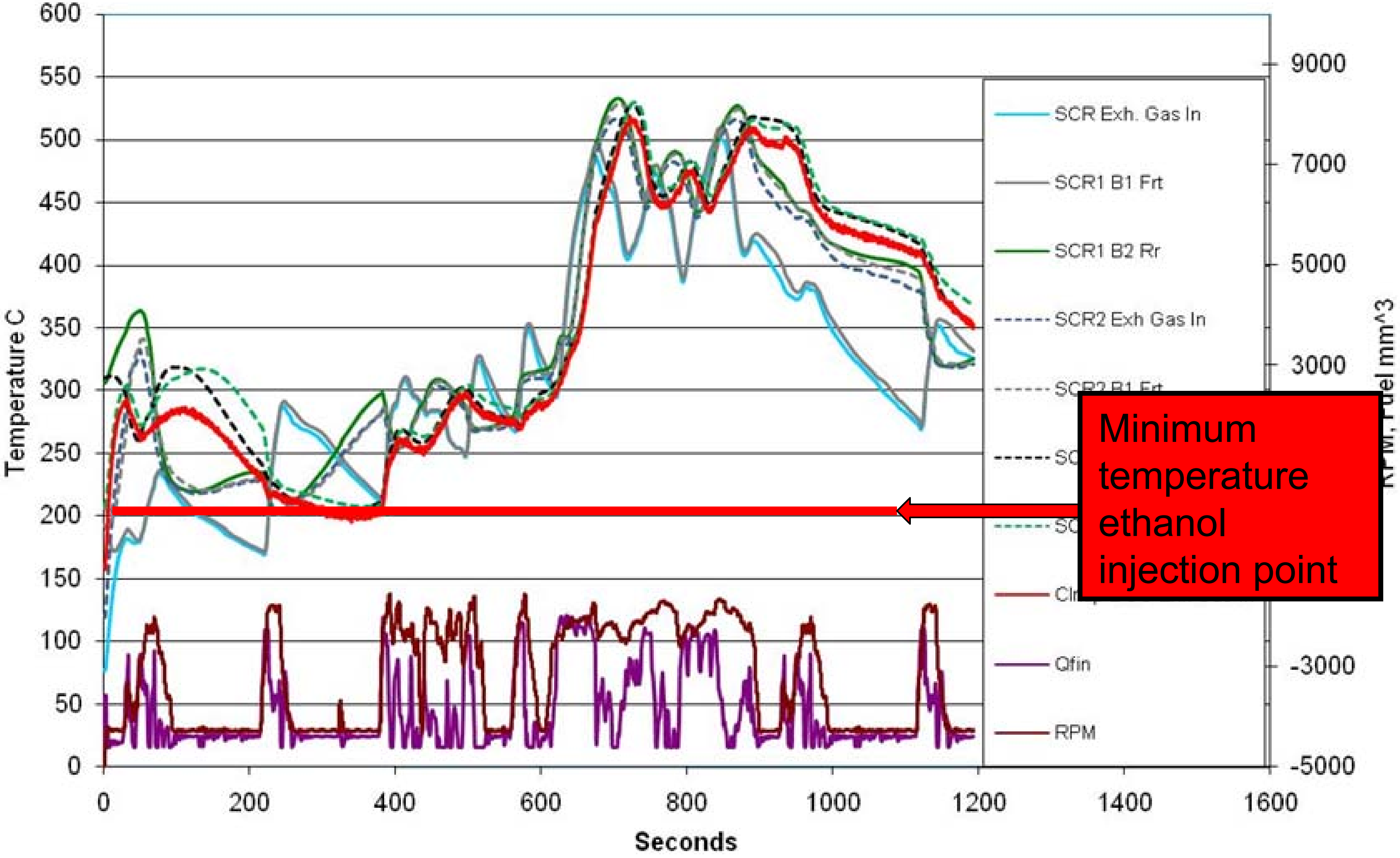
NOx Std =0.20 g/HP-hr

15.6L UREA-SCR 82% NOx efficiency

SET 13 NOx Emissions Results with Diesel

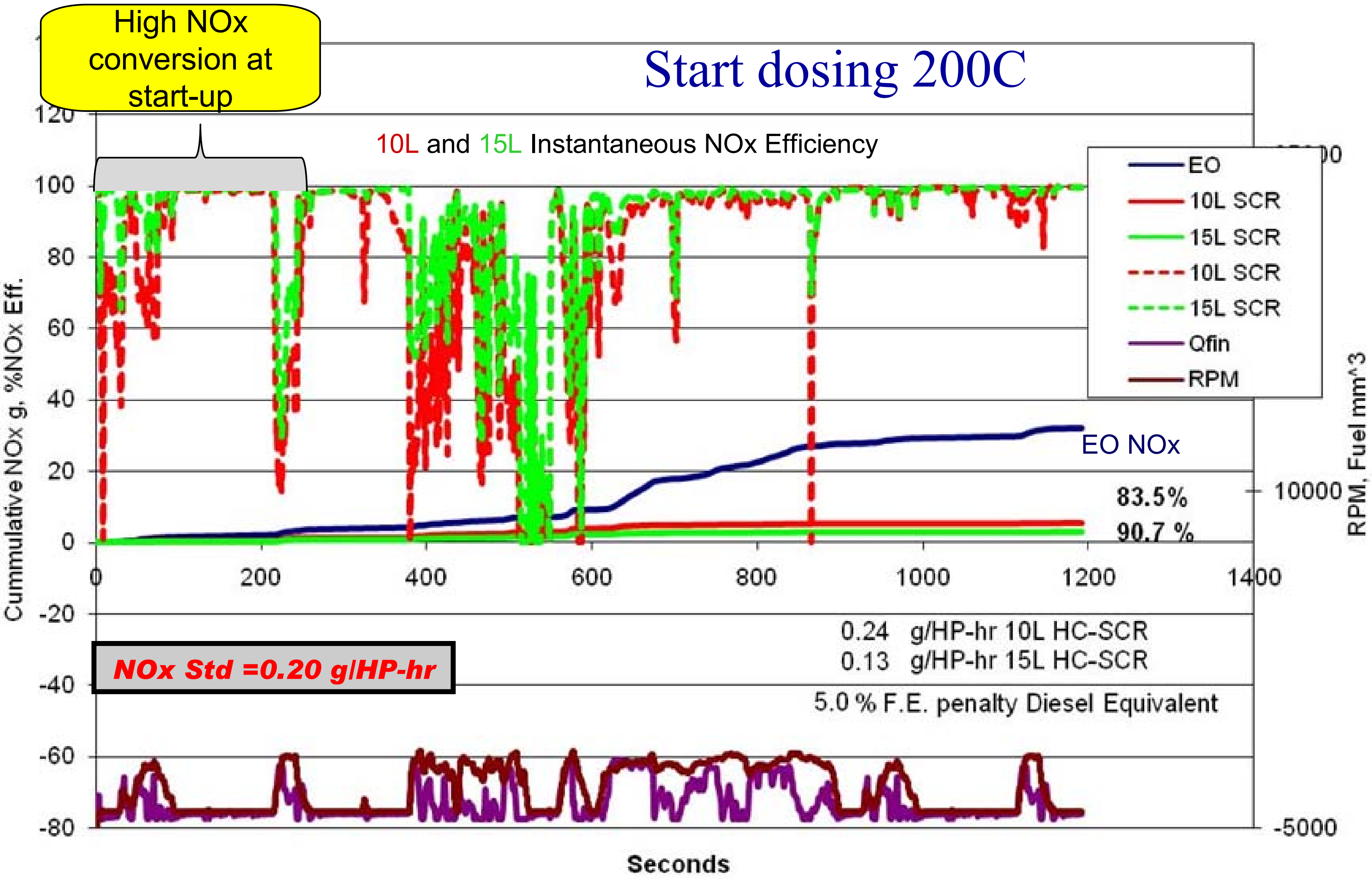
Space velocity, oxygen concentration and gas temperature each contribute to the NOx conversion at a give engine operating point

HDFTP NOx Emissions Results with EtOH



Minimum temperature ethanol injection point

HDFTP NOx Emissions EtOH


High NOx conversion at start-up

Start dosing 200C

10L and 15L Instantaneous NOx Efficiency

0.24 g/HP-hr 10L HC-SCR
0.13 g/HP-hr 15L HC-SCR

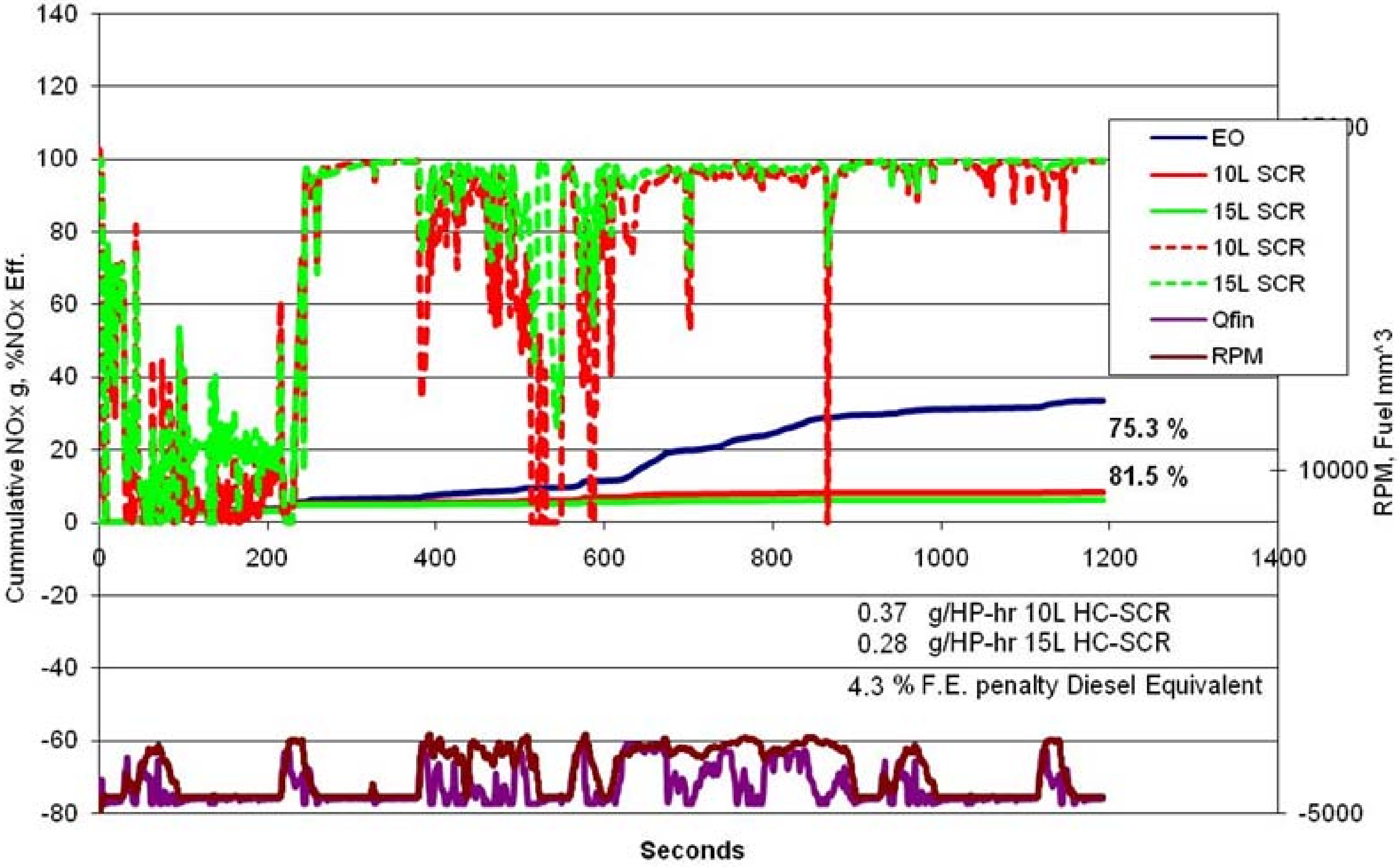
5.0 % F.E. penalty Diesel Equivalent

NOx Std =0.20 g/HP-hr

SET 13 NOx Emissions Results with EtOH

Conversions uniformly higher at each engine operating point

CHDFTP NOx Emissions EtOH



0.37 g/HP-hr 10L HC-SCR
0.28 g/HP-hr 15L HC-SCR

4.3 % F.E. penalty Diesel Equivalent

NOx conversions for cold start HDFTP are reasonable

Engine Dynamometer Test Results

Light-Duty w/ ULSD	Catalyst Volume	NOx Conversion	Fuel Economy Penalty	Weighted Emissions	Emission Standard
FTP75	20L	60%	3.1%	0.640 g/mi	0.070 g/mi
US06	20L	76%	2.6%	0.149 g/mi	0.400 g/mi
HWYFET	20L	92%	2.4%	0.024 g/mi	0.070 g/mi
Heavy-Duty w/ ULSD	**Catalyst Volume**	**NOx Conversion**	**Fuel Economy Penalty**	**Weighted Emissions**	**Emission Standard**
Hot HDFTP	20L	60%	3.0%	0.59 g/BHP-h	0.20 g/BHP-h
SET 13-Mode	20L	65%	2.7%	0.63 g/BHP-h	0.20 g/BHP-h
Heavy-Duty w/ Ethanol	**Catalyst Volume**	**NOx Conversion**	**Fuel Economy Penalty**	**Weighted Emissions**	**Emission Standard**
Hot HDFTP	15L	82%	4.3% (diesel eq.)	0.13 g/BHP-h	0.20 g/BHP-h
SET 13-Mode	15L	91%	4.7% (diesel eq.)	0.16 g/BHP-h	0.20 g/BHP-h
HDFTP (wtd. hot+cold)	15L	86%	4.7% (diesel eq.)	0.20 g/BHP-h	0.20 g/BHP-h

Light-Duty: SAE 2008-01-2487 (M.B. Viola)

Heavy-Duty: submitted SAE 2009 (M.B. Viola)

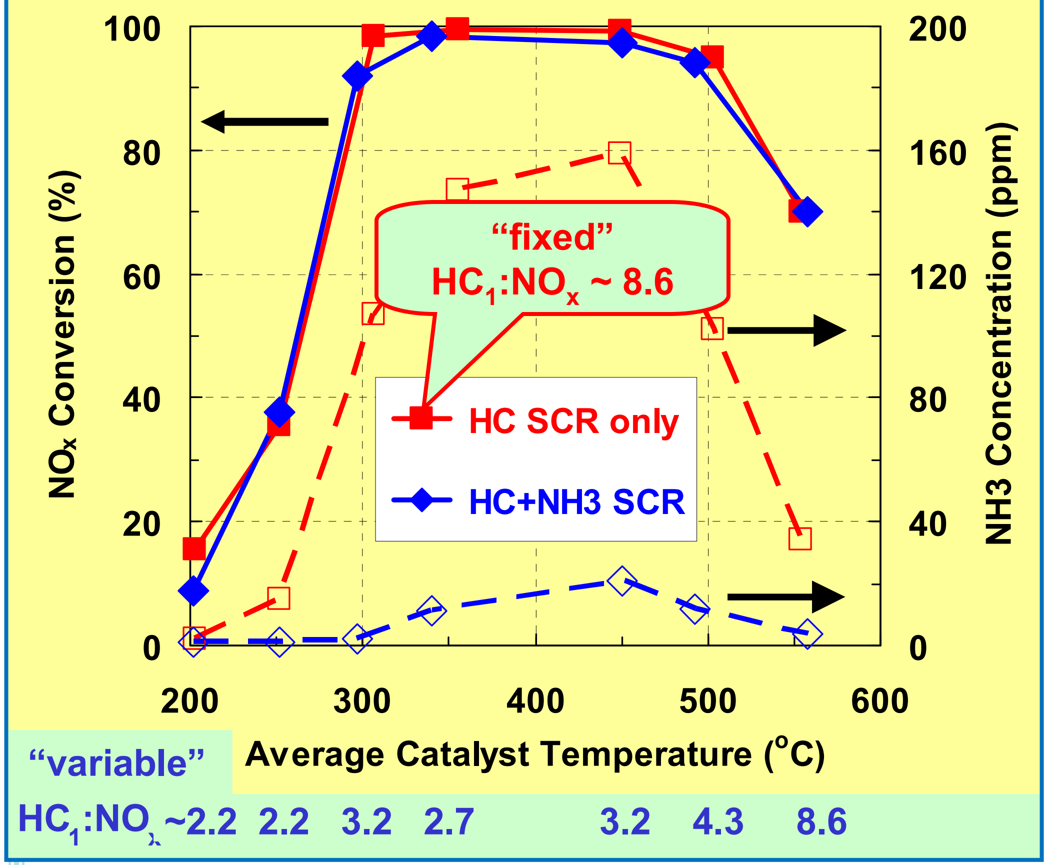
Dual-Catalyst Concept: HC-SCR+NH_3-SCR

HC-SCR NH$_3$-SCR

SOLUTION: $NOx + C_2H_5OH \rightarrow N_2 + NOx + NH_3 \rightarrow N_2$

3.0 wt.% Ag_2O/Al_2O_3 + Cu-zeolite

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)



- Tune ethanol injection amount to "balance" NO_x and NH_3 breakthrough
- High NO_x conversion levels maintained while lowering amount of ethanol injected
- System optimization still required

Engine Results Status

- With diesel as a reductant
  - HDFTP: 60% NOx reduction using 3x engine displacement (ED)
  - SET 13-Mode: 65% NOx reduction using 3x ED
- With EtOH as a reductant
  - HDFTP: 84% (1.5 ED), 91% (2.3 ED) NOx reduction
  - SET 13-Mode obtained 90% (1.5 ED) NOx reduction
  - Cold start HDFTP: 82% (2.3 ED)
- Poisoning and aging evaluations
  - Sulfur does poison, but is regenerable
  - Phosphorous does deposit, but does not appear to degrade performance abnormally
  - Heavy HC's do poison, but are also regenerable

Summary

- Accomplishments
  - High-throughput technology has optimized the HC-SCR catalyst formulation
  - Effectiveness of diesel fuel 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