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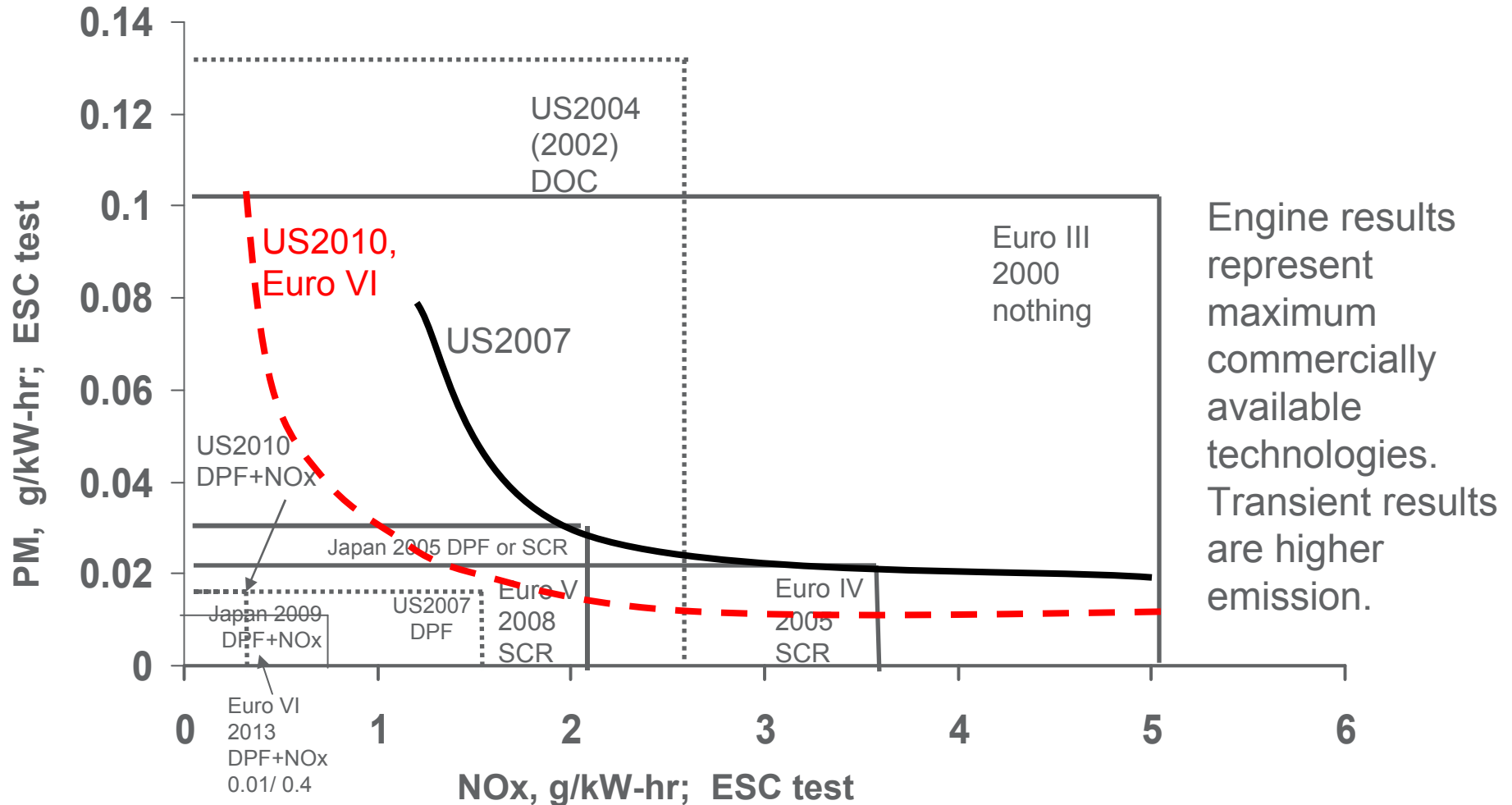
Review of Emerging Diesel Emissions and Control

Tim Johnson
DEER Conference
Dearborn, MI
August 4, 2009

Summary

- Criteria pollutant regulatory efforts are focused on Euro VI HD PN limits, and California LEV3 for LD.
- CO₂ mandates are spreading. Major paradigm shift underway. HDD black soot reductions can meet ~20% of 2050 CO₂ reductions.
- HD engine technologies are enabling US2010 to be attained w/o deNOx treatment.
- LD technologies focused on downsizing for ~90-100 g/km CO₂. NOx up ~20%. DHEV attractive for very significant reductions.
- Fundamental SCR understanding is advancing. Combination DPF+SCR systems insights expanding.
- LNT desulfation understanding shows sulfate differences. Combination LNT+SCR and LNC+SCR systems described.
- DPF catalysts show direct oxidation of soot at 250C. New learnings on deNOx catalyst loadings on DPF pressure drop are counter-intuitive. Interesting ash studies emerging showing membrane phenomenon.
- Pt migration from DOC (or DPF) to SCR is reduced. DOCs are emerging for LTC applications.

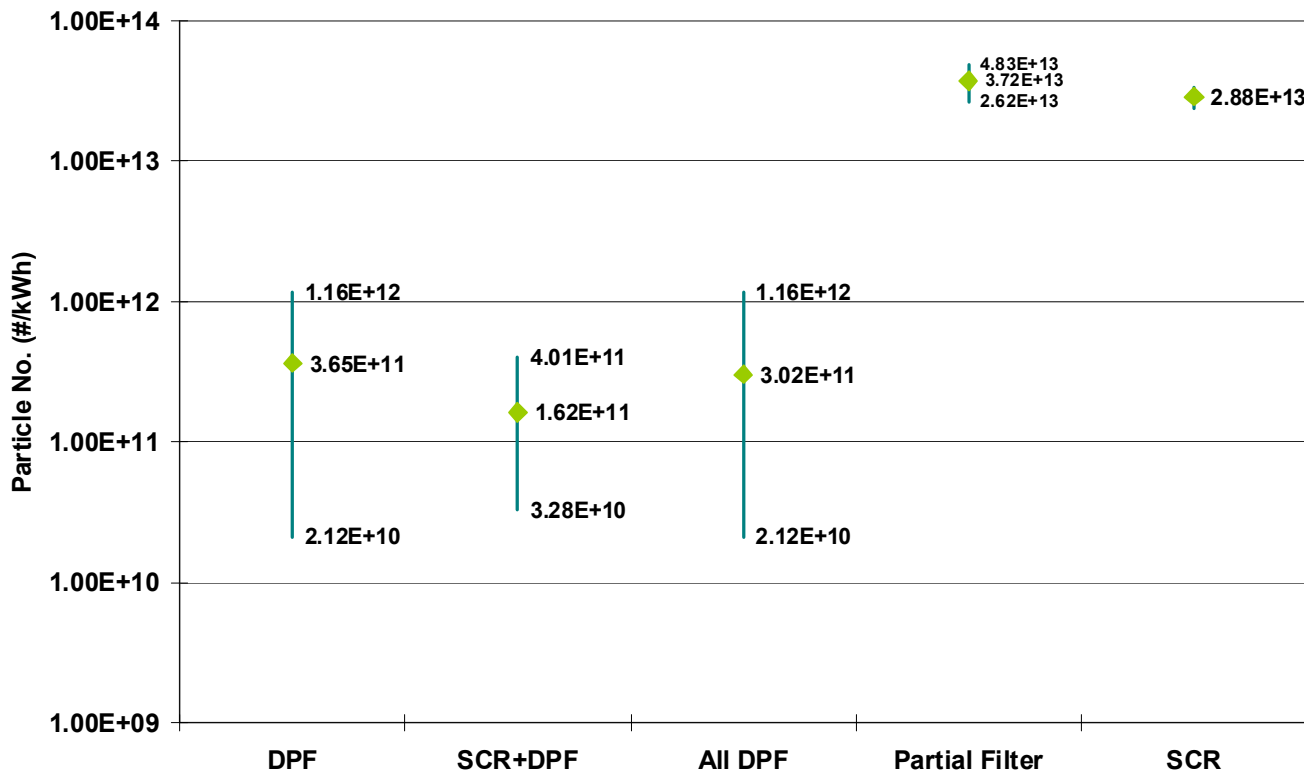
HD regulatory and engine technology framework



Euro VI regulation is nearly complete. Focus is on PN regulation.

PN emissions on WHTC.

5 DPF engines, 7 DPF engines, 6 DPF+SCR, 4 partial DPF, 3 SCR



- Commission floating 5 to 6 X 10¹¹ PN/kW-hr as basis.
- Discussion on how to treat DPF regeneration: 1.2 to 5.1X higher PN with regens every 25 to 5 cycles.

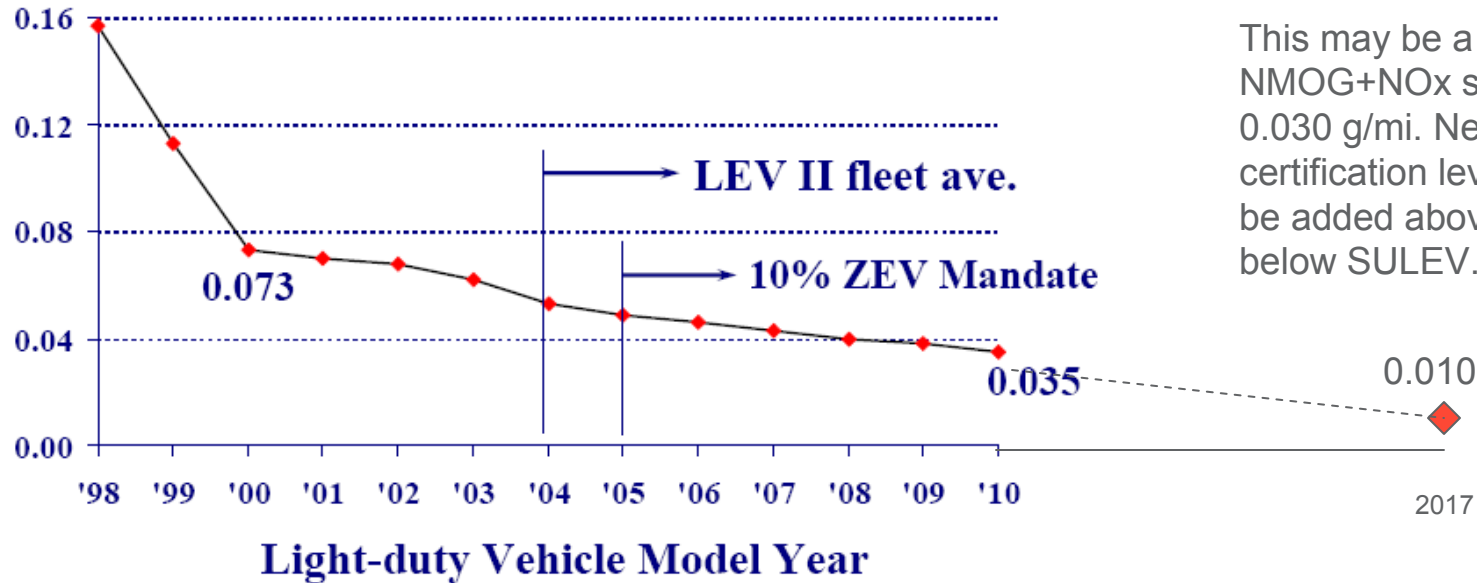
Europe will be reviewing the NRMM 2014 regulation next year

- Required as part of the original regulation
 - Review technology options and the regulation by 2011
- Regulation can tighten or loosen
- We may see a PN regulation to harmonize with the LD and HD on-road regs

CARB is considering LEV3.

Fleet average SULEV on the table for 2017+

FTP NMOG Emissions, g/mi



Enhance flexibility:

This may be a NMOG+NOx standard of 0.030 g/mi. New certification levels may be added above and below SULEV.

Implications:

- Onset of another round of toxic emissions reductions. HD could follow

EPA is implementing new emissions inventory model – MOVES. Results in higher emissions than previous model.

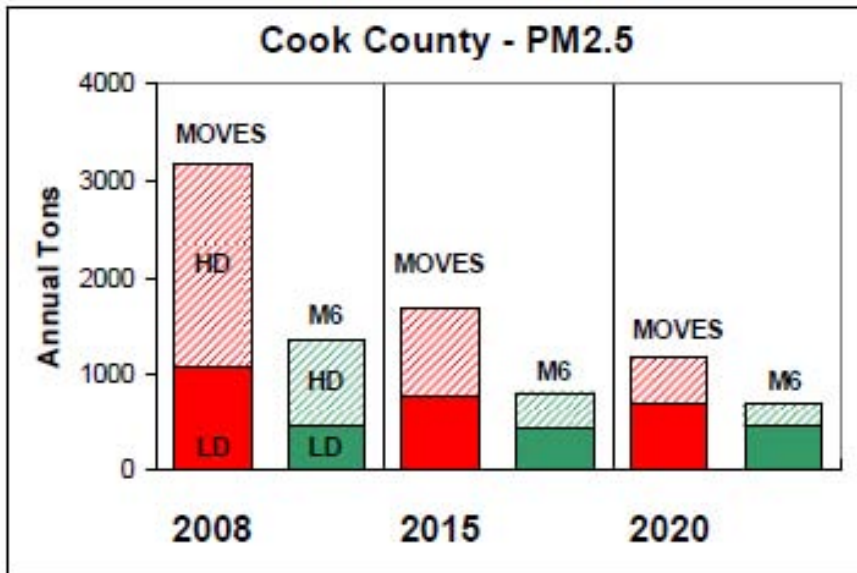
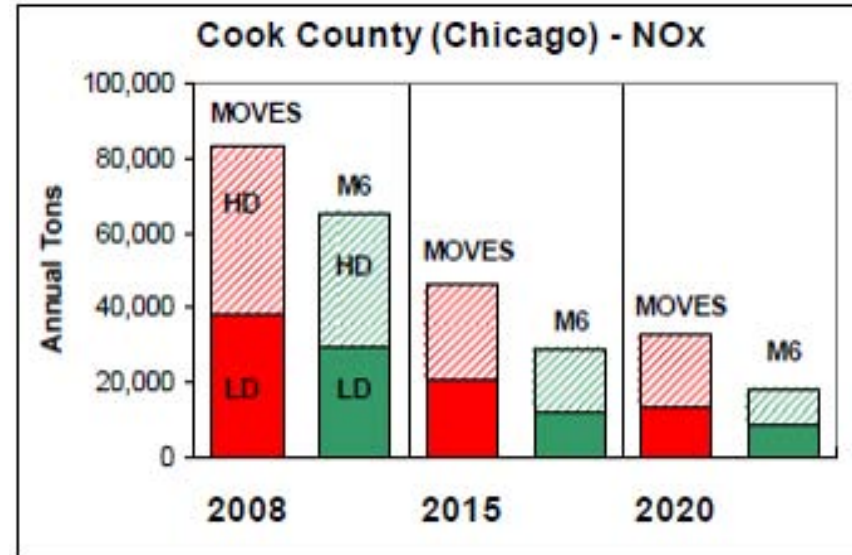
MOBILE6 was “driving cycle” based

- Emissions by speed characterized by set cycles
- Lacked flexibility to analyze different driving patterns

MOVES is “modal” based

- Emissions averaged by operating mode “bin”
- Operating mode bins defined by Vehicle Specific Power (VSP) and instantaneous vehicle speed
- Allows estimation of emissions from any driving pattern
 - Driving patterns can be defined as the distribution of time spent in each operating mode bin (“operating mode distribution”)

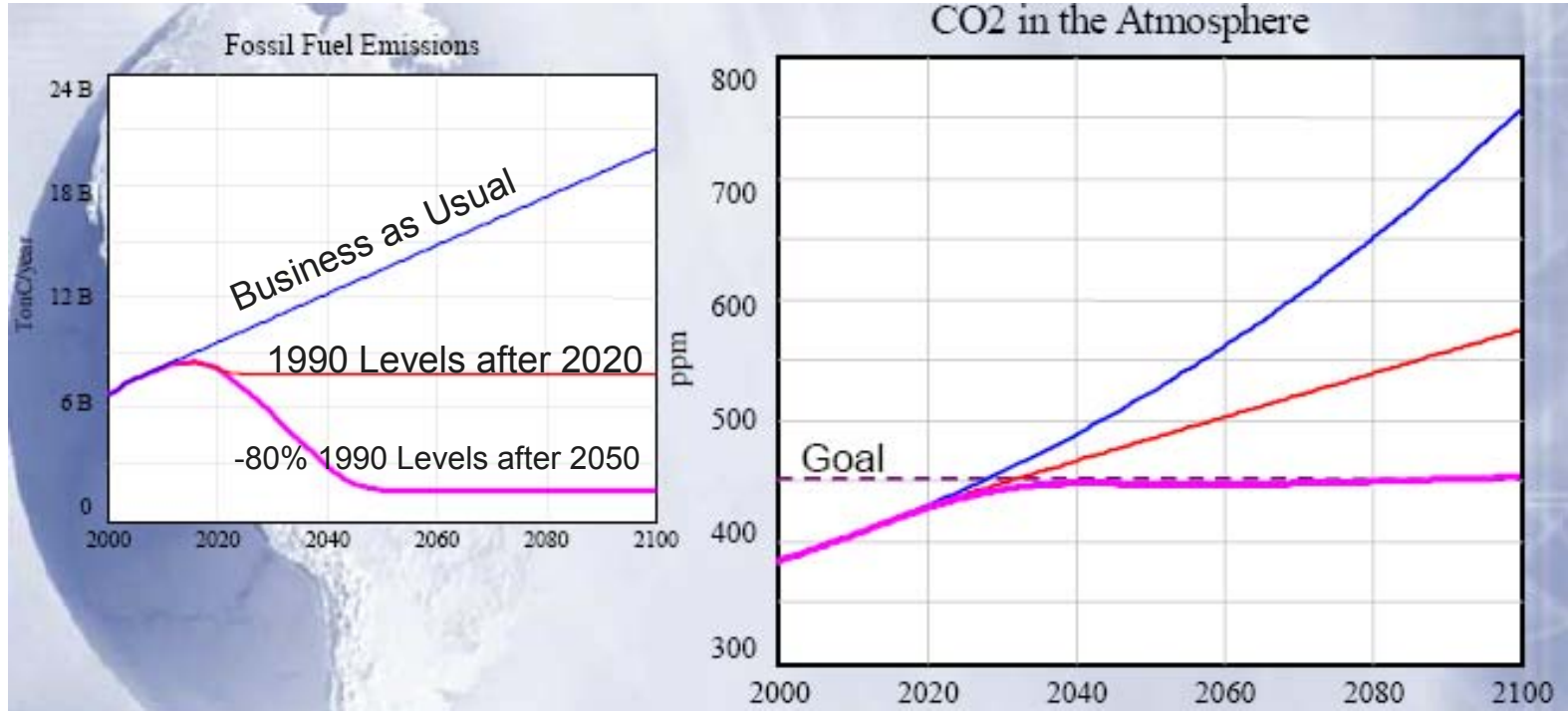
US EPA, MSTRS meeting 5/09



What It Means

- Higher NOx and PM emissions mean mobile sources have bigger role in attainment
- Percent reduction from base year is key to attainment analysis
 - PM2.5 shows higher overall emissions and higher % reductions
 - Effect on attainment demonstrations could be positive
 - NOx shows higher overall emissions but lower % reduction
 - Harder to show attainment
 - Future NOx control measures will have a bigger impact
- States may need to redo some motor vehicle emissions budgets to meet conformity requirements with MOVES

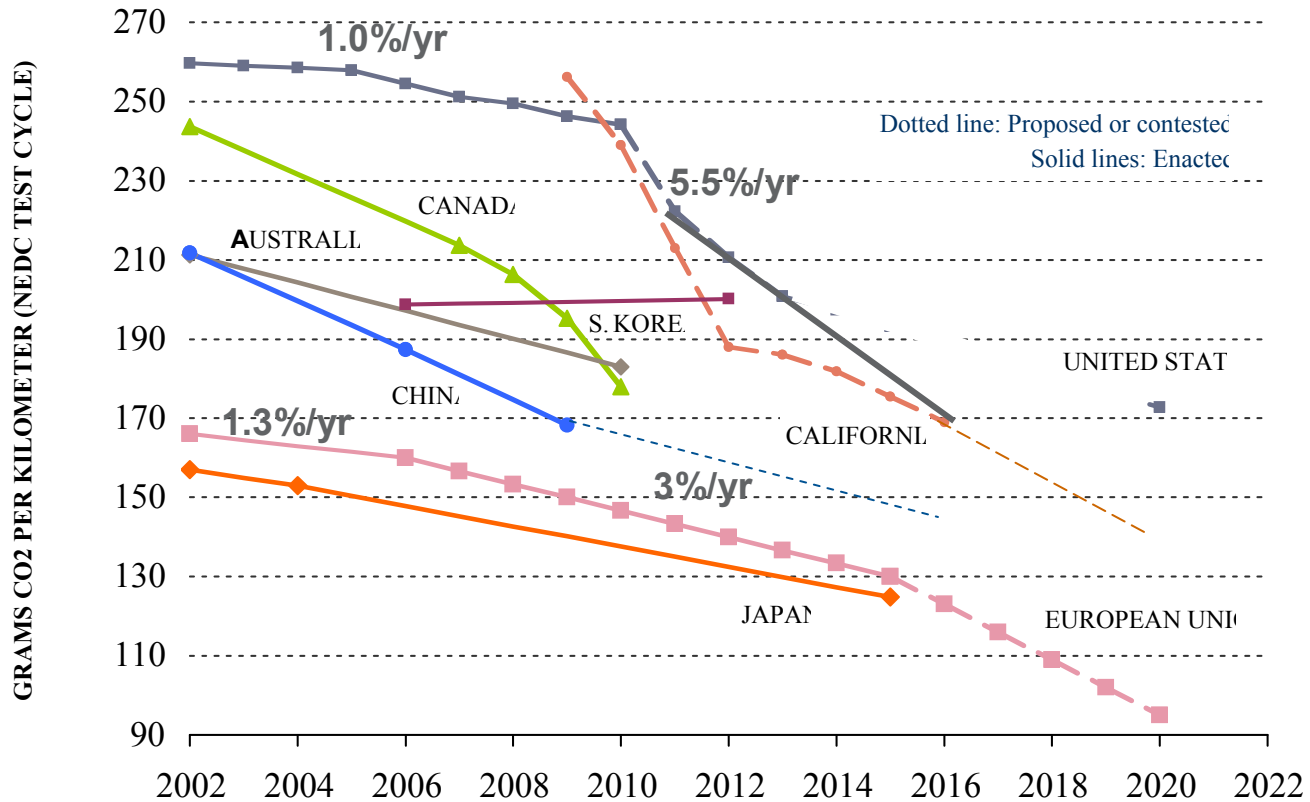
UN IPCC: To stabilize atmospheric CO₂ at 450 ppm, we need 80% reductions in CO₂ (vs. 1990) by 2050



Emerging CO₂ regulations are aggressive and will result in a paradigm shift.

Fuel consumption technologies will no longer be based on the value proposition to the customer. They will be chosen based on mandate economics.

Actual and Projected GHG Emissions for New Passenger Vehicles by Country/Region, 2002-2022



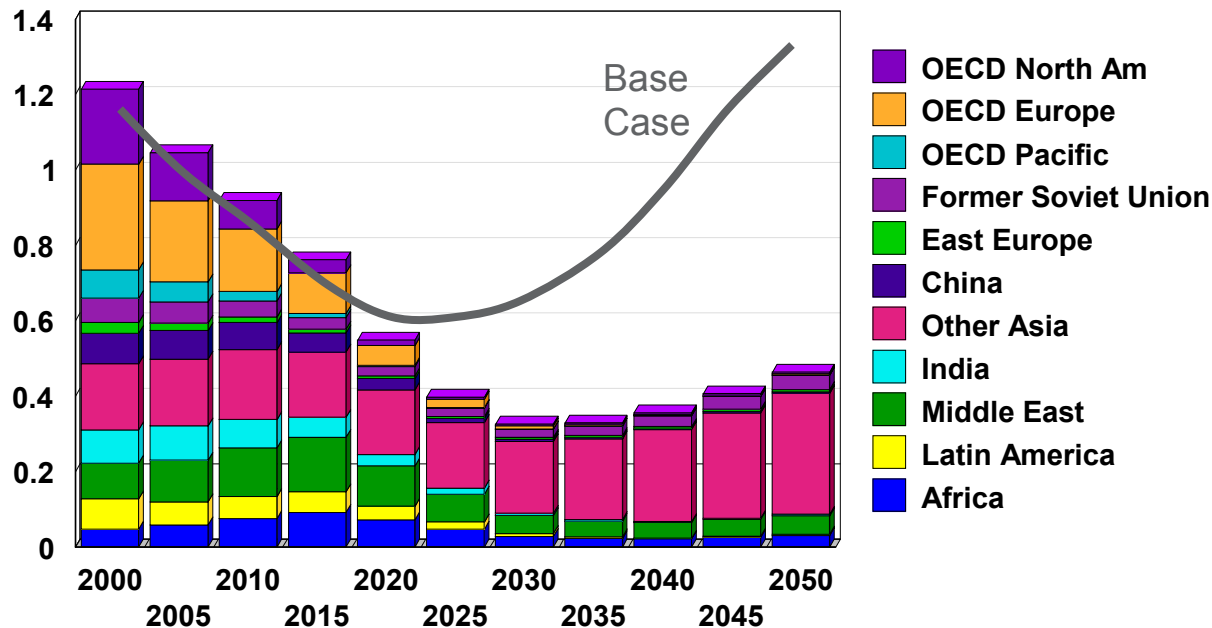
Source: Passenger Vehicle Greenhouse Gas and Fuel Economy Standards: A Global Update, ICCT. January 2009 update.

Black Carbon Opportunity

Driving U.S. and EU Standards is a Meaningful International Solution

On-Road Black Carbon Emissions: The Case for Tighter Regulations

Million Metric Tons



- Substantial black carbon reduction being driven by 2007/10 HDD rule and Euro VI, but rest of world is lagging
- “Wedge analysis” (Socolow, Pacala) quantifies needed global wedge at 25 billion tonnes CO_{2eq} each by 2050 (8 Socolow wedges required)
- Accelerating adoption of Euro standards for light duty and heavy duty could generate 38 billion tonnes of additional CO_{2eq} reduction worldwide by 2050, a total of 1.5 wedges or 22% of all required stabilizing reductions

Note: Assumes adoption by 2015 of Euro 6 and VI in China, India, and Brazil; Euro 4 and IV in Africa and the Middle East; and Euro 3 in Latin America

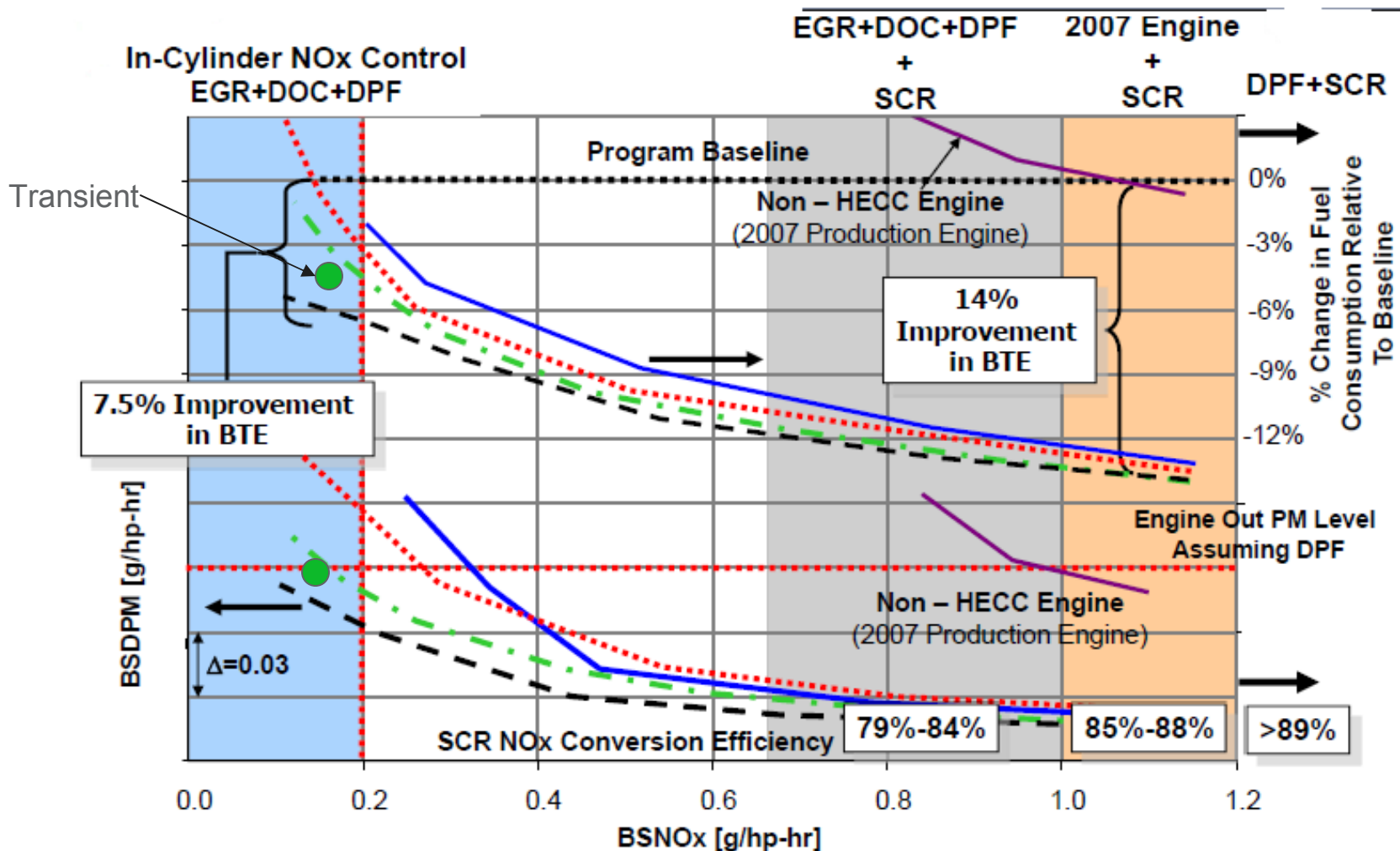
Source: Michael Walsh, Board Chairman, International Council of Clean Transportation

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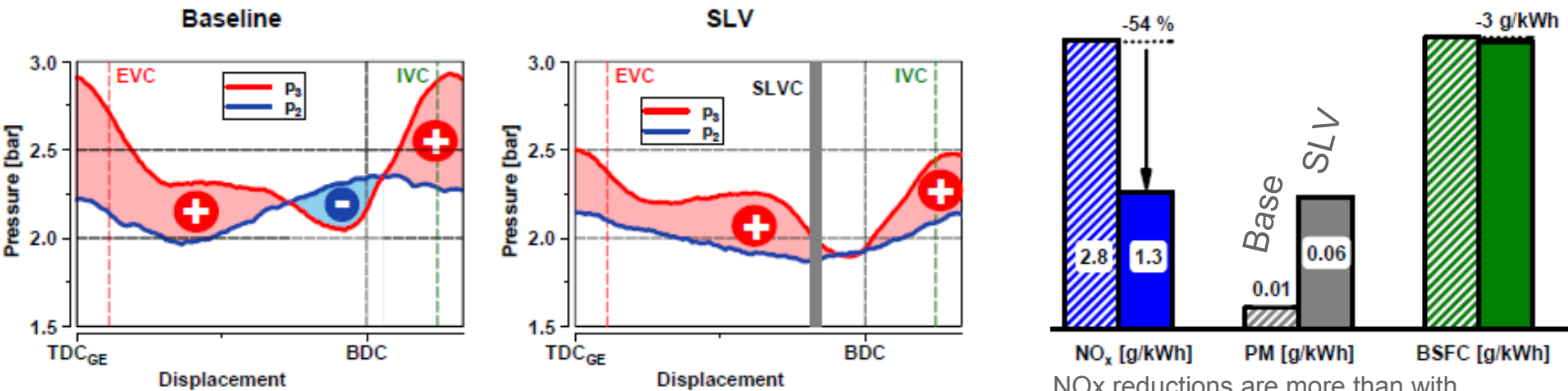
Engines

BSFC and emissions are shown for emerging HD engine technology.

2010 NOx levels attained EO, but deNOx delivers value.

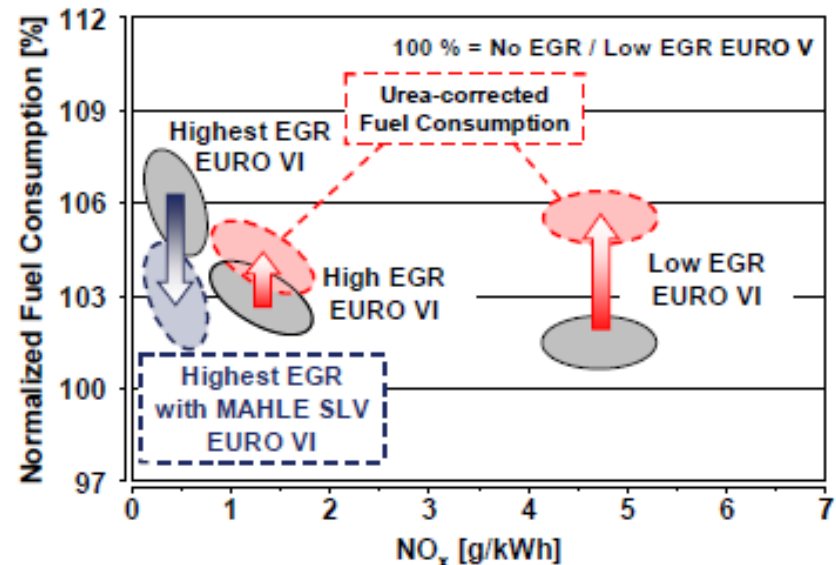
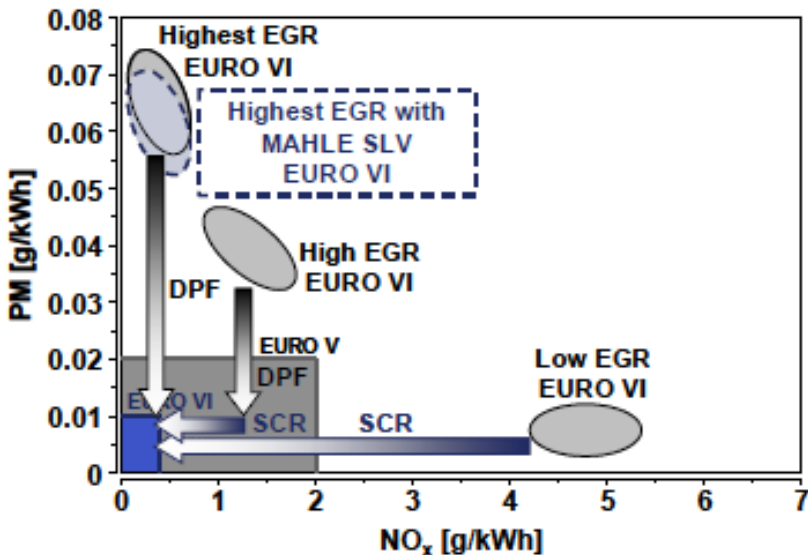


A new fast intake throttle valve (combustion cycle time resolution) results in more EGR with improved BSFC.



NO_x reductions are more than with traditional EGR systems while keeping low BSFC due to low charge exchange losses.

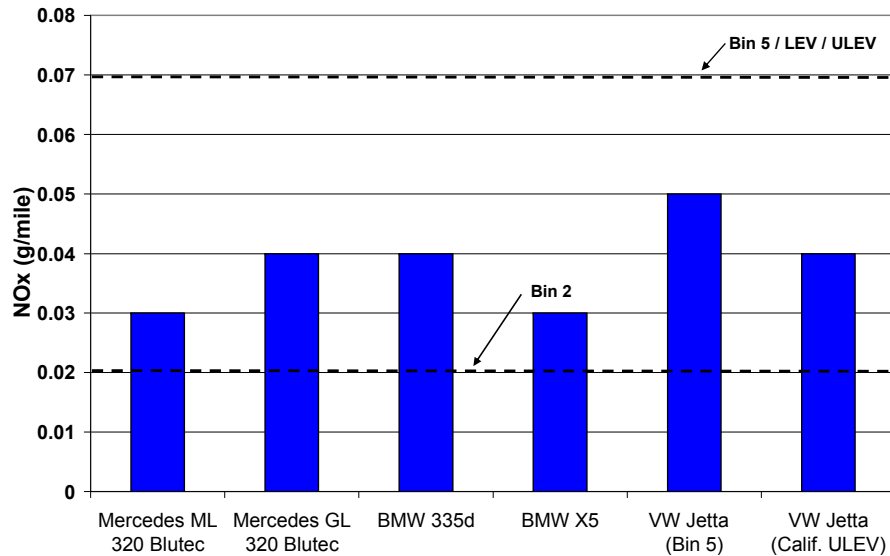
A continuous rotating throttle flap (SLV) decreases charge air pressure to temporarily enable more EGR. P2 is intake air; P3 is exhaust



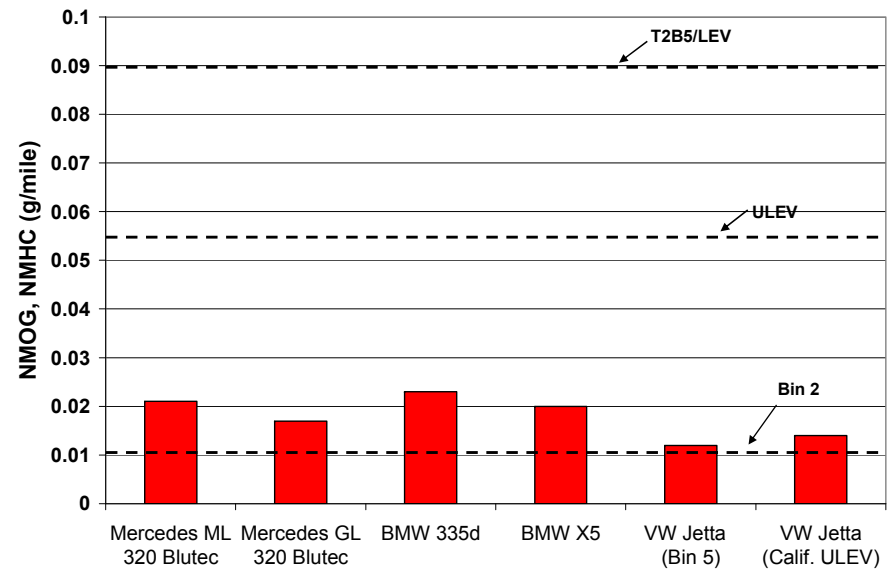
US LDD offerings are at 18 to 30 mg/km NOx and 7 to 13 mg/km NMHC.

Additional -70% NOx and -50% NMHC needed for LEV3.

FTP-75 NOx at Full Usefull Life



FTP-75 NMOG and NMHC at Full Usefull Life

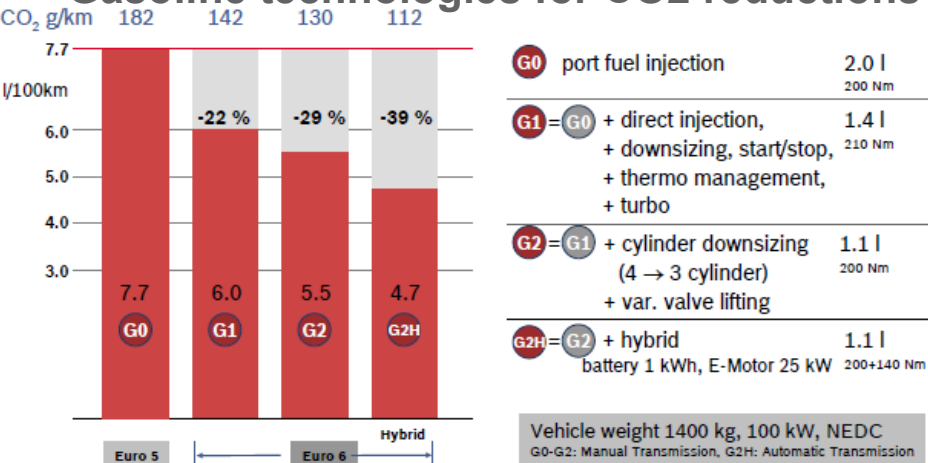


US06 compliance will be more significant challenge.

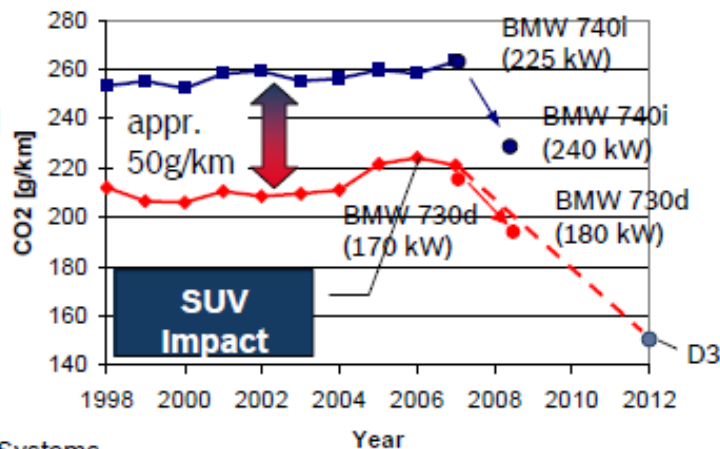
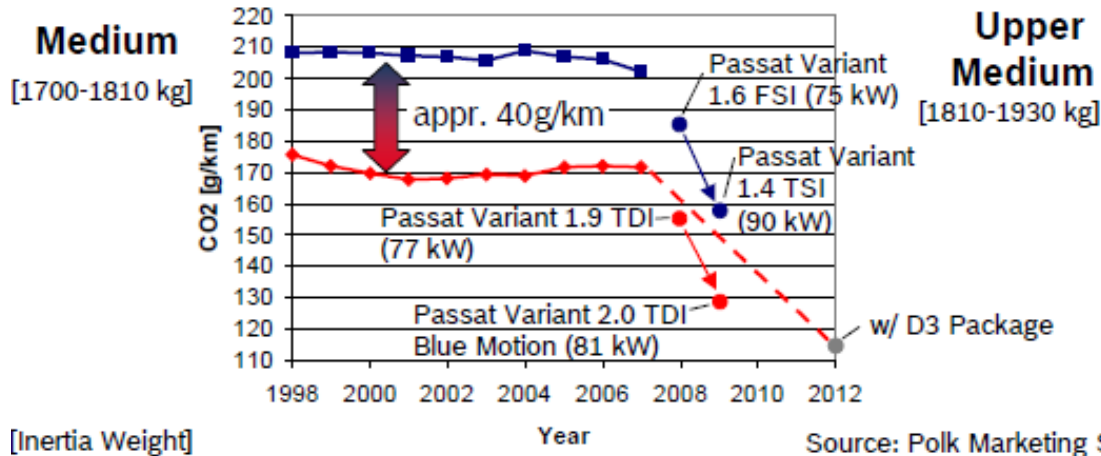
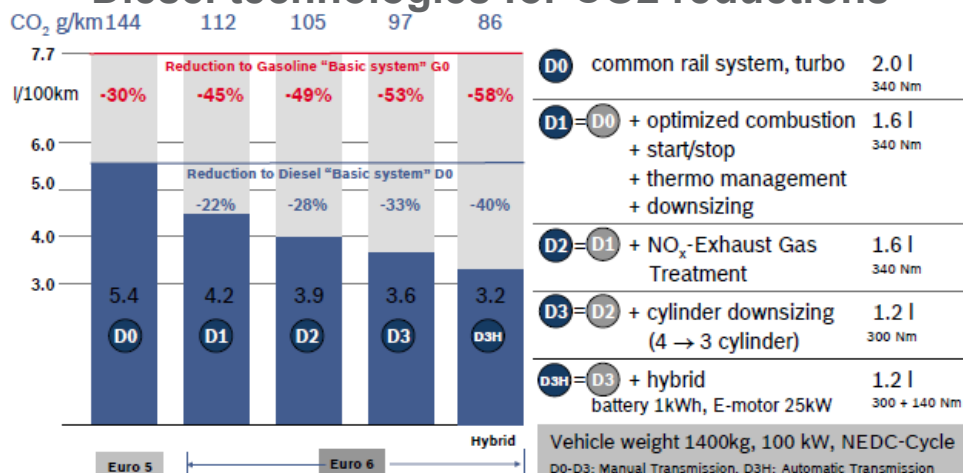
Future technologies will drop gasoline engine CO₂ by 39%, diesel by 40%.

Gasoline HEV: 112 g/km; DHEV 86 g/km; Larger LDD to 115 to 145 g/km

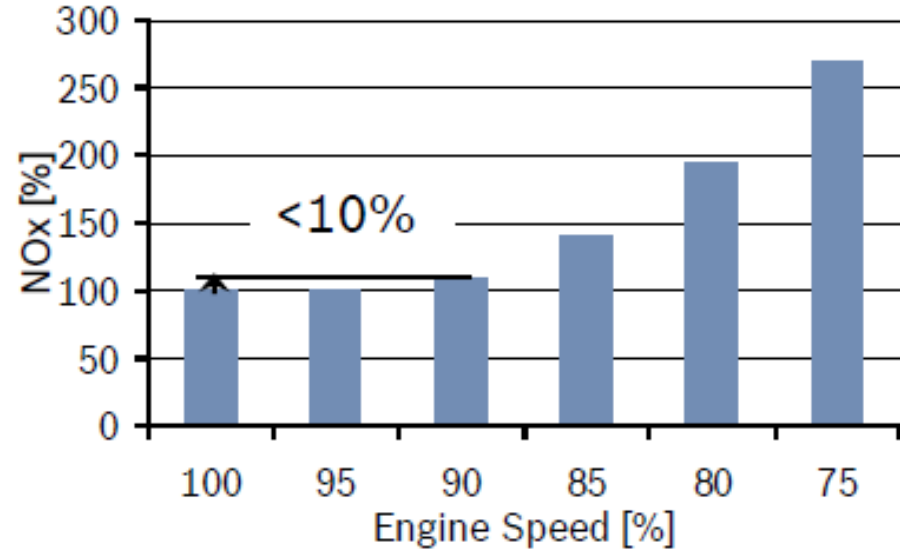
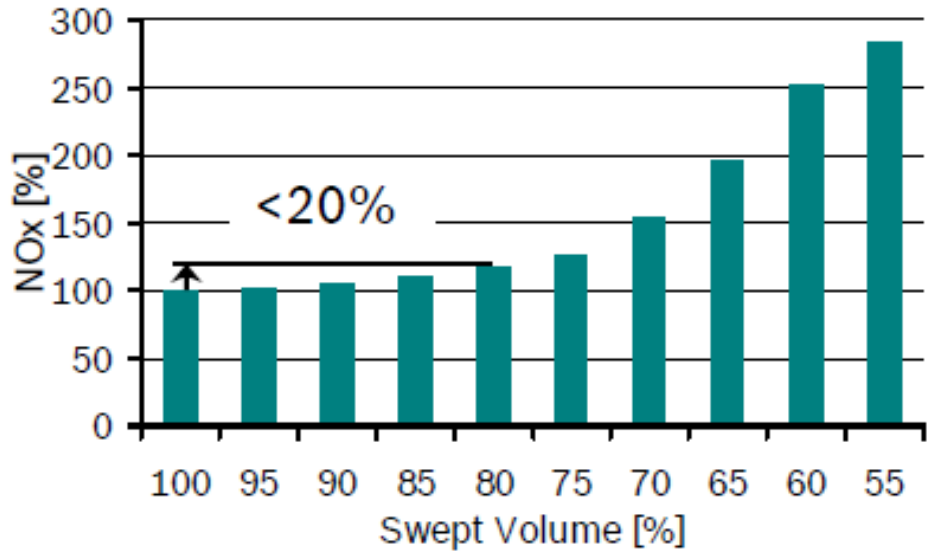
Gasoline technologies for CO₂ reductions



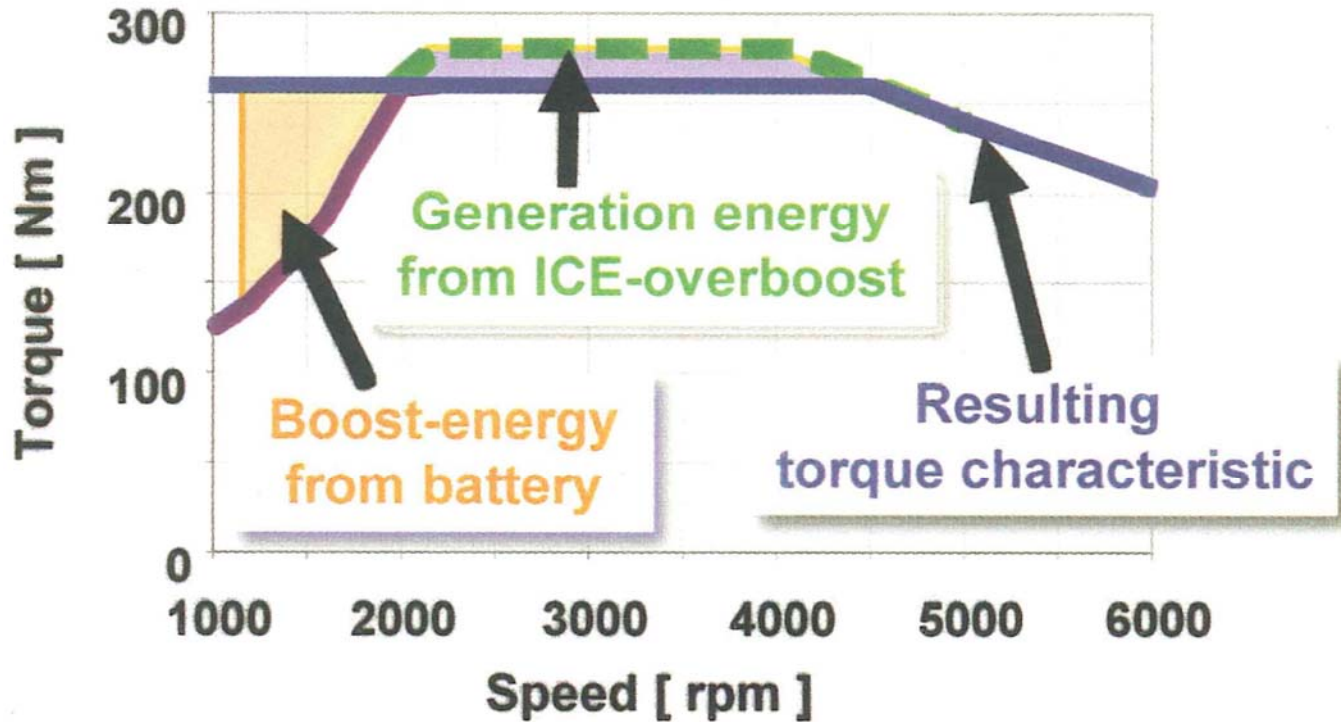
Diesel technologies for CO₂ reductions



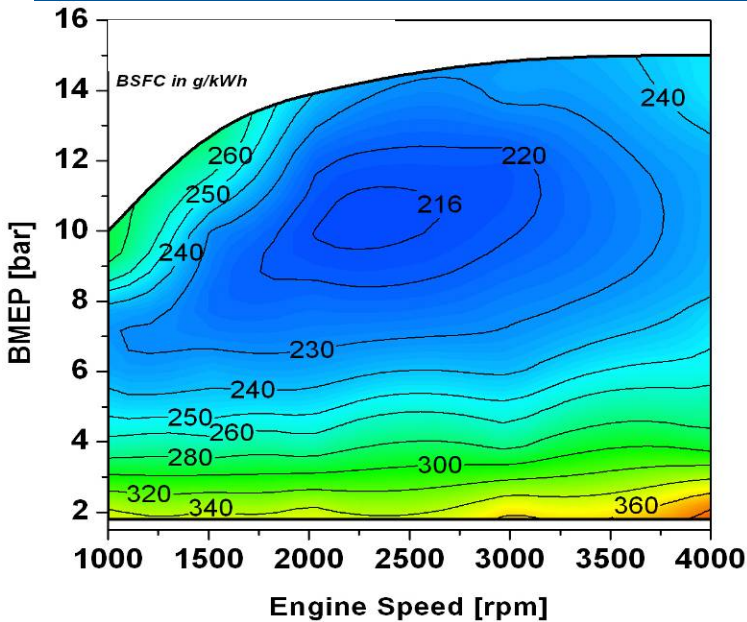
Downsizing and downspeeding will increase engine out NOx about 10-20%. HC goes down.



Mild HEV technologies offer new flexibilities on managing ICEs.

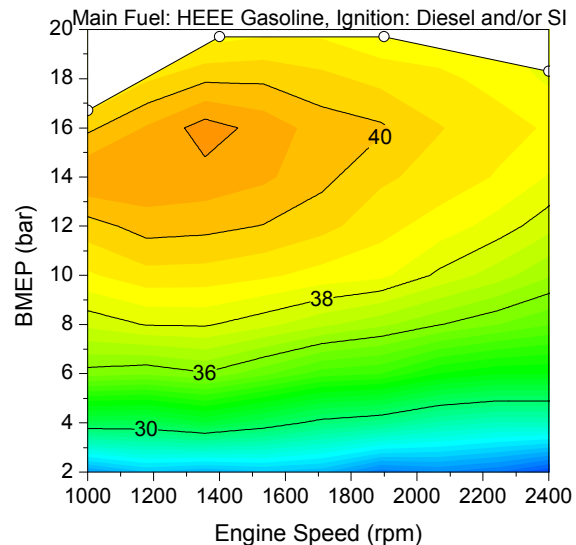
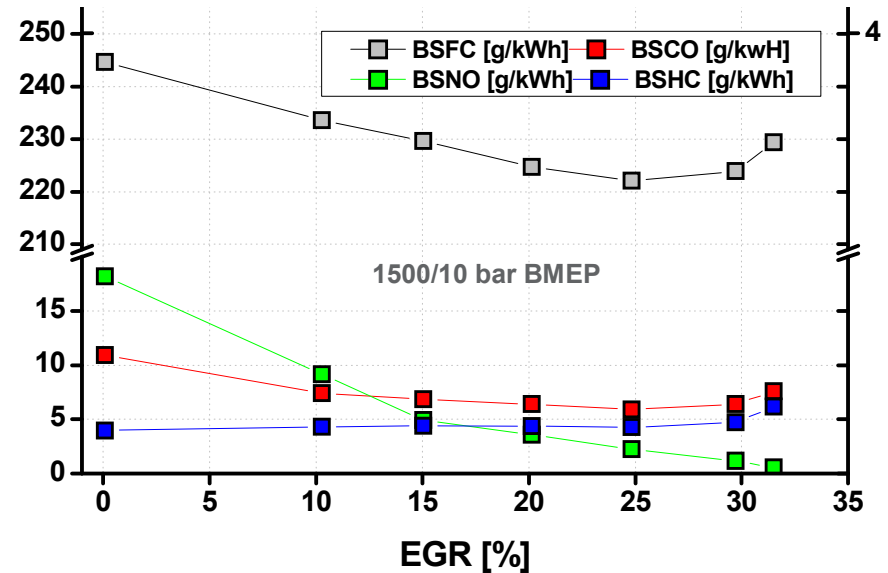


High-Efficiency Dilute Gasoline Engines (HEDGE) are advancing. Turbo, cEGR, MPI, $\lambda=1$, strong ignition



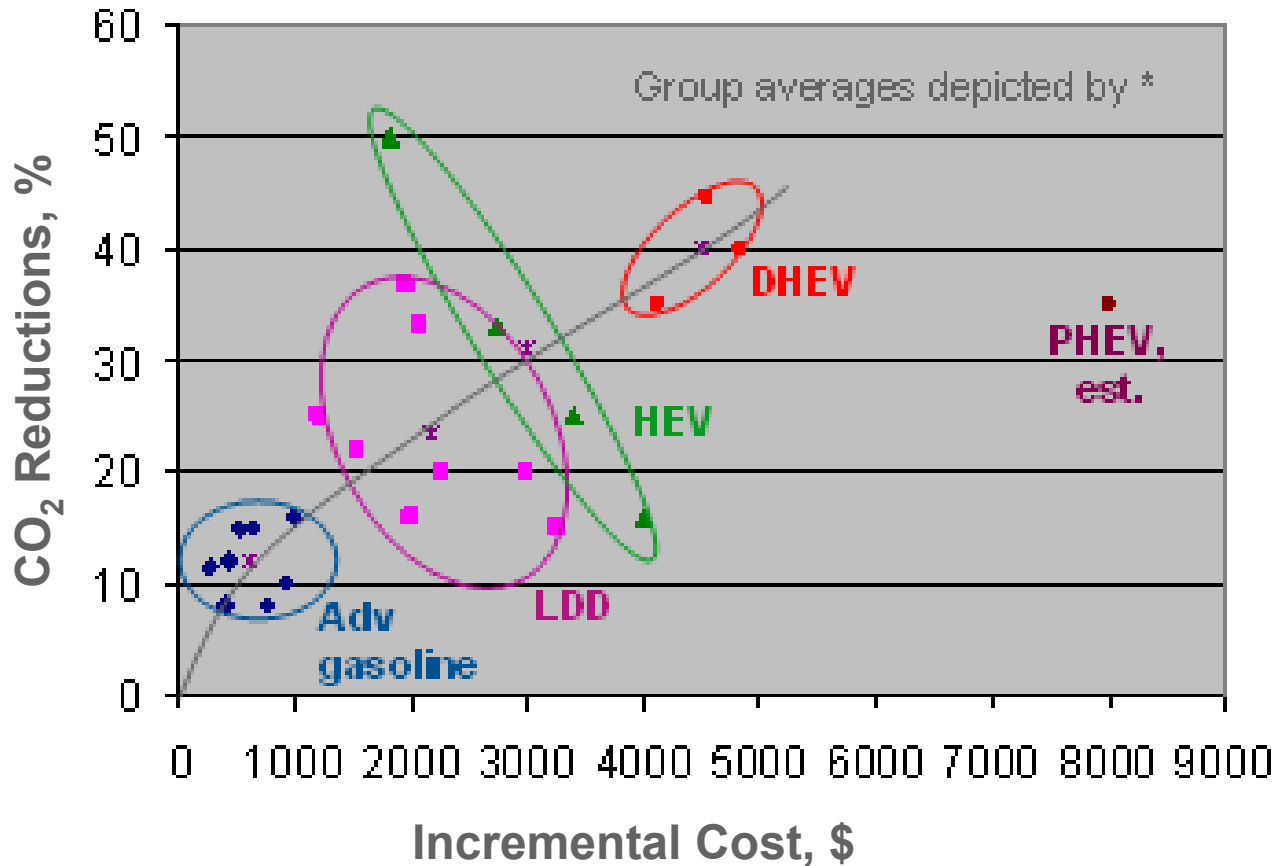
Spark ignition 2.4 liter MPI $\lambda=1$; Best in class commercial GDI BSFC is 234 g/kW-hr at 10 bar (12 bar peak).

SwRI consortium, June 2009



4 liter - 4 cyl MD engine w/ diesel micro-pilot ignition approaches diesel BTE

Significant CO₂ reductions can be attained, but at generally proportional cost. DHEV delivers lowest CO₂



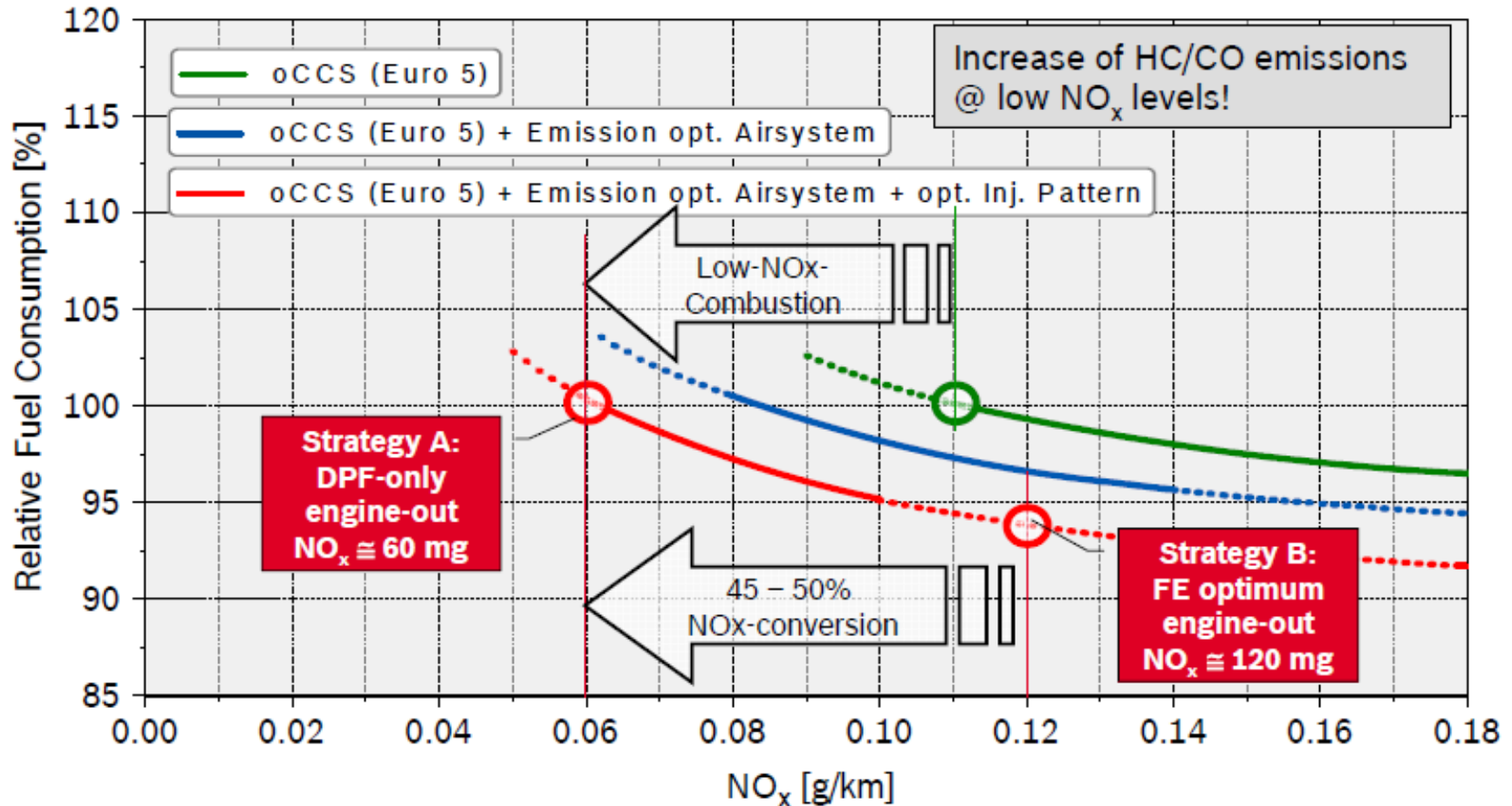
All data are approximately normalized to a Bin 5 mid-size passenger car

- FEV, AVL Motor Vehicle and Environment Conference, Sept 2006.
- Ricardo, DEER Conference, August 2007.
- VW, DEER Conference, August 2007.
- Ricardo, CTI Emissions Conference, January 2008.
- Bosch, Vienna Motor Symposium, May 2008.
- SwRI, Near-Zero Emission Vehicle Conference, June 2009.
- Bosch, Near-Zero Emission Vehicle Conference, June 2009

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SCR

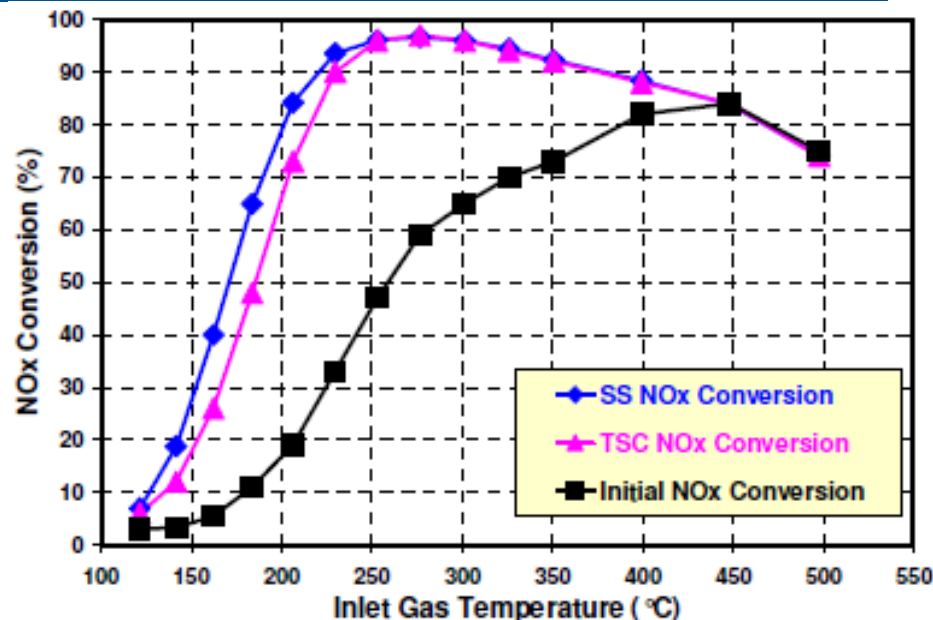
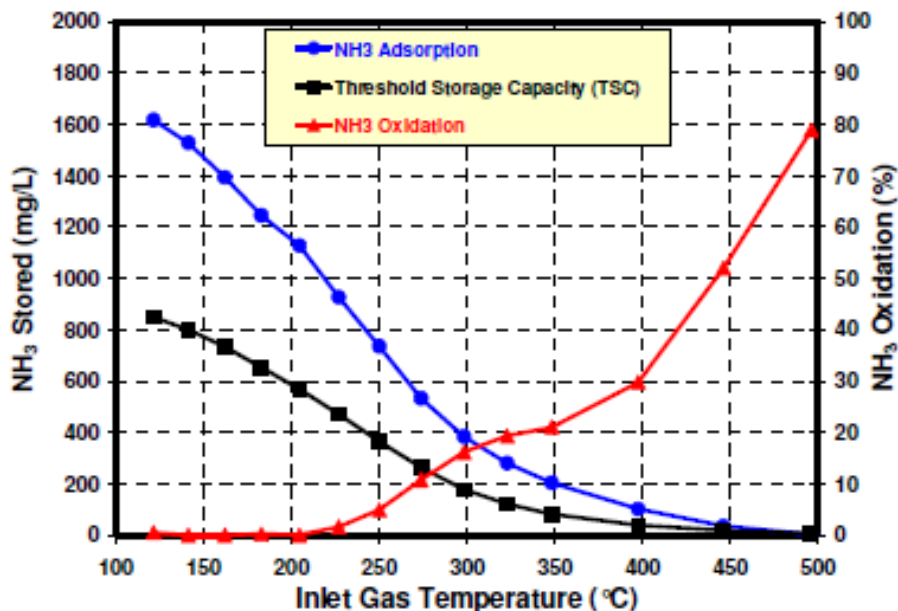
50% deNO_x can return 6% FC reduction for advanced engines.



oCCS: Optimized Conventional Combustion System

More insights provided for ammonia behavior on Cu-zeolites.

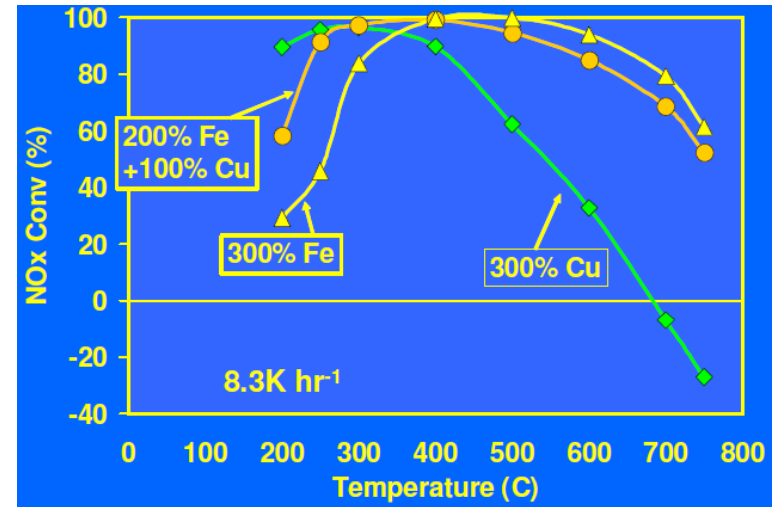
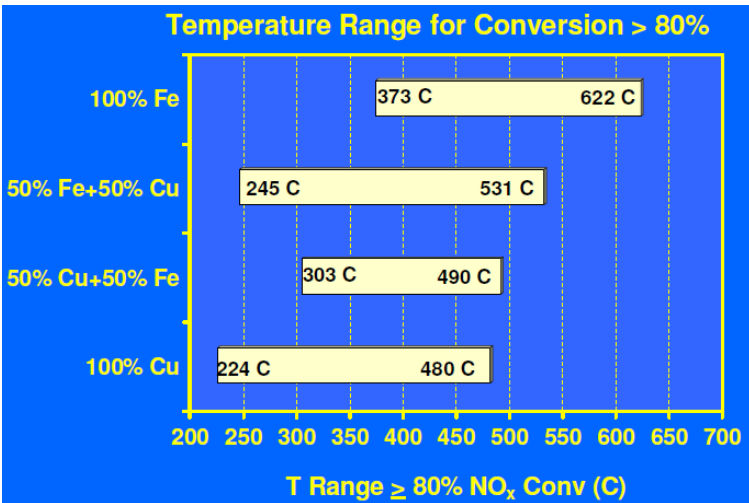
NH₃ oxidation compromises some HT perf.; NH₃ storage critical



NH₃ oxidation by Cu-zeolites begins at ~250C. TSC is thought to be tightly bound NH₃ (>97% capture eff. at 350 ppm NH₃ inlet); >90% oxid to N₂ at T<500C;

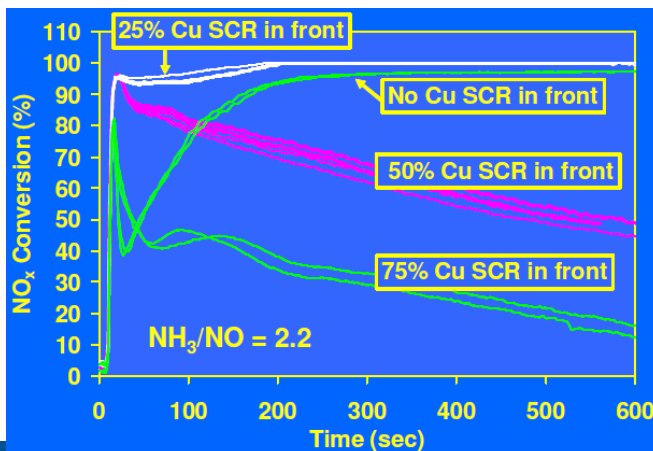
T<400C: NOx conversion strongly depends on stored ammonia.

Detailed study optimizes Fe- to Cu-zeolite sizes and architecture. Cu-zeolite aging, NH₃ oxidation, and light-off balanced.



Fe-zeolite followed by Cu performed best. Rear Cu protected from aging exotherm; Front Fe gets NH₃ at HT.

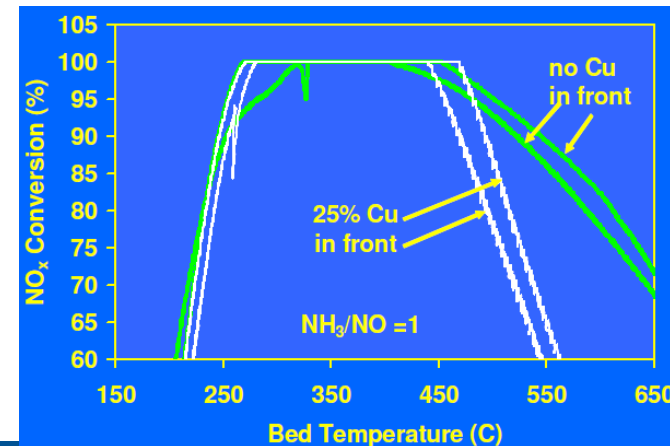
Optimization exp show 2:1 Fe-Cu ratio best at 3X the size of base system.



Ford, SAE 2009-01-0901

Light-off improved with small Cu-zeolite placed up front.

Slice of Cu in front oxidizes NH₃, compromising HT perf.



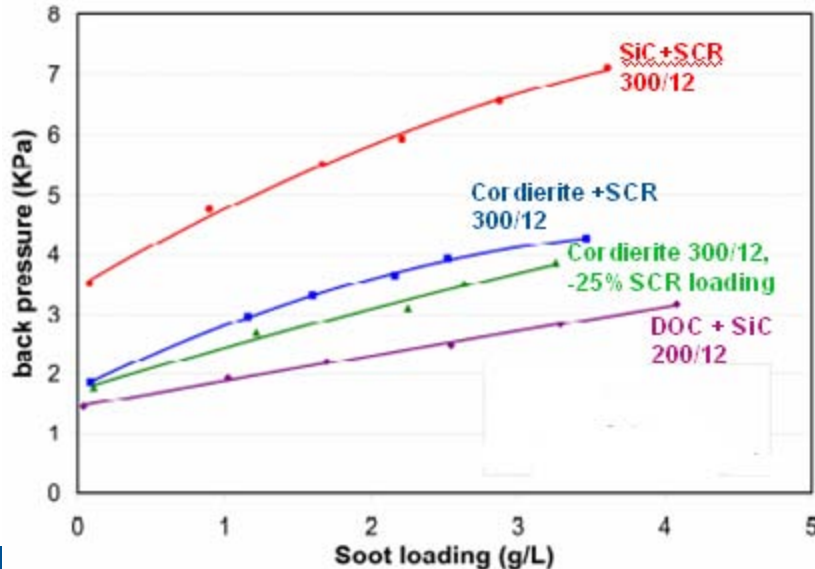
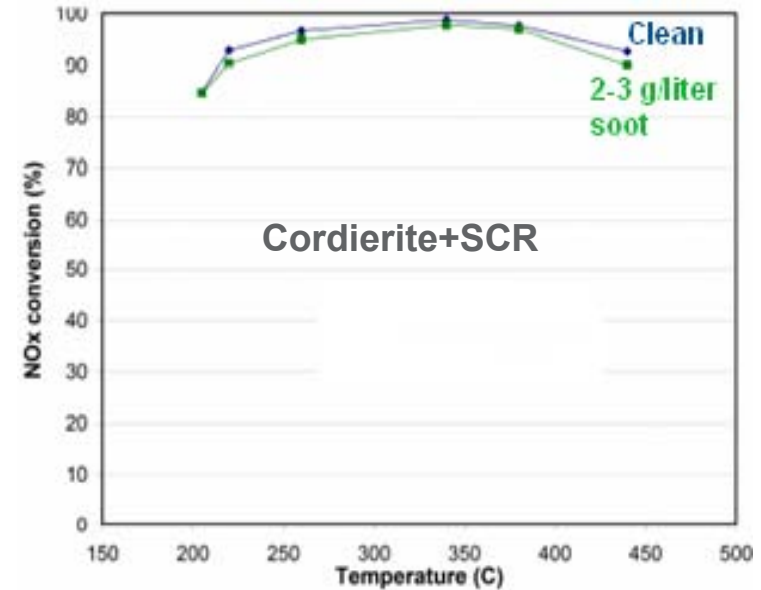
More information emerging on SCR+DPF units.

ΔP issues need resolving, deNOx is excellent; little impact on active DPF regen (CO emissions up)

US06 results

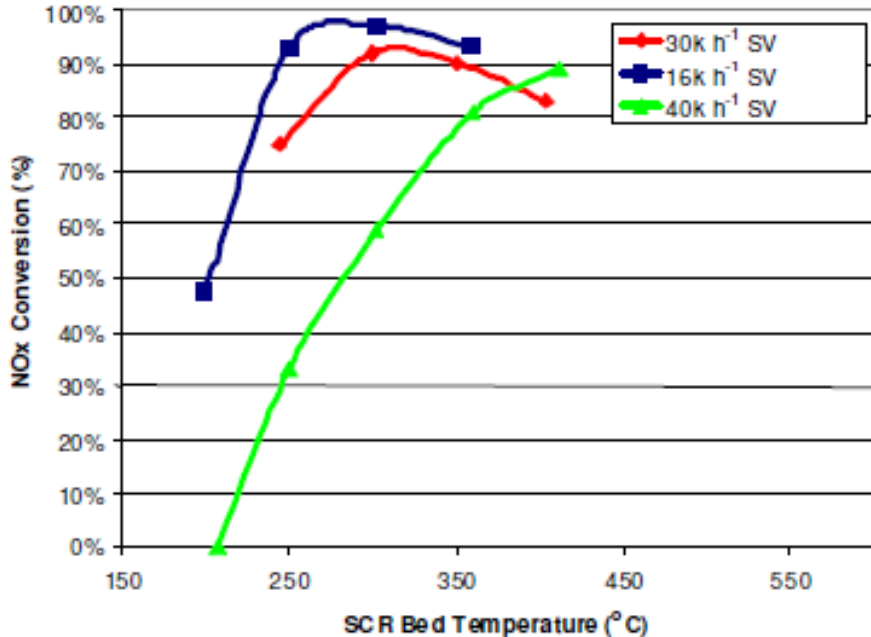
	Total NOx conversion	Total HC conversion	Total CO conversion
SCR coated C650	87%	88.2%	99.1%
SCR coated MSC-14	81.5%	88.9%	98.4%
SCR C650 reduced WCL	81.0%	89.7%	98.9%

LA04 had 90.7, 88.0, and 82% deNOx (Cordierite, SiC, Cordierite -25%);



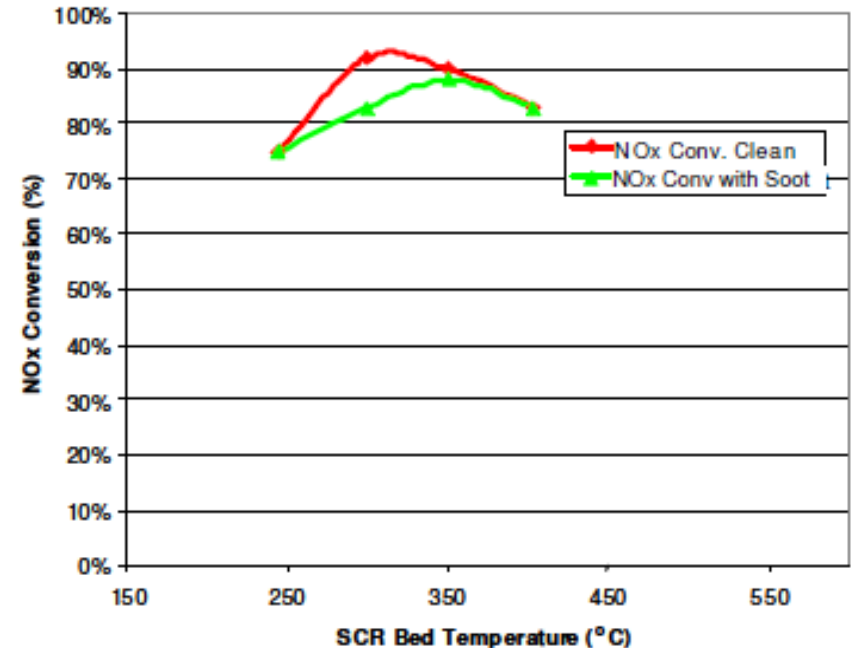
- All DPFs 2X SVR; hydro-aged 64 hrs. at 800C; Cu-zeolites
- All units loaded with NH3 prior to test (max. efficiency boundary condition)
- Regeneration times nearly the same as baseline for all DPFs
- CO emissions during regen increased vs. baseline: 59-68% conversion vs. 100% for base

Results on DPF+SCR show unexplained SV sensitivity and PM interaction.



Engine dyno results show a SV threshold at 30-40,000/hr. Unexplained and not evident in bench reactor.

Authors desire lower ΔP with no deNO_x compromise and suggest pore control to minimize resistance and maximize catalyst-gas contact.

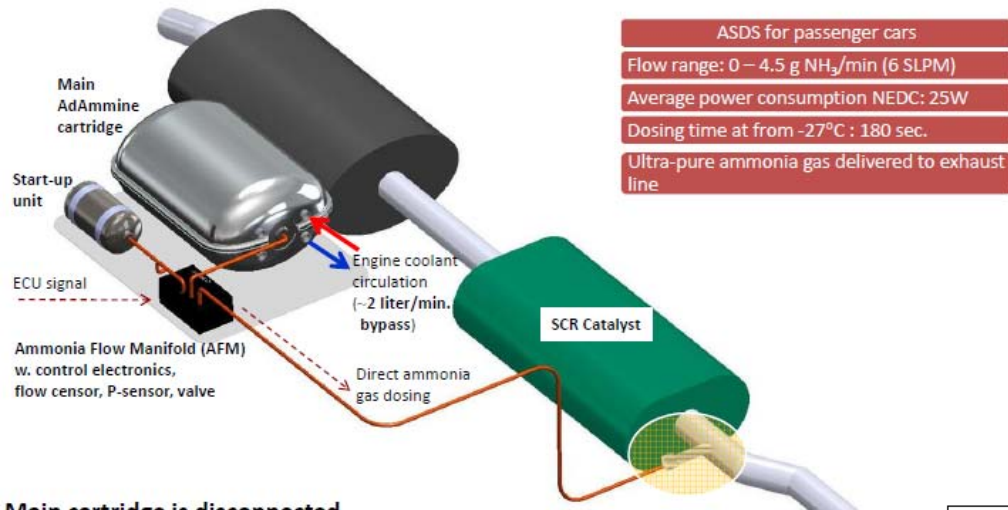


PM can interfere with SCR reaction. Hypothesis: HC coking phenomenon due to poor oxidation. Reproducible results.

Ford, SAE 2009-01-0897

Up-date on NH₃ storage and release system.

Cooling water heating. NH3 injection at 100C.



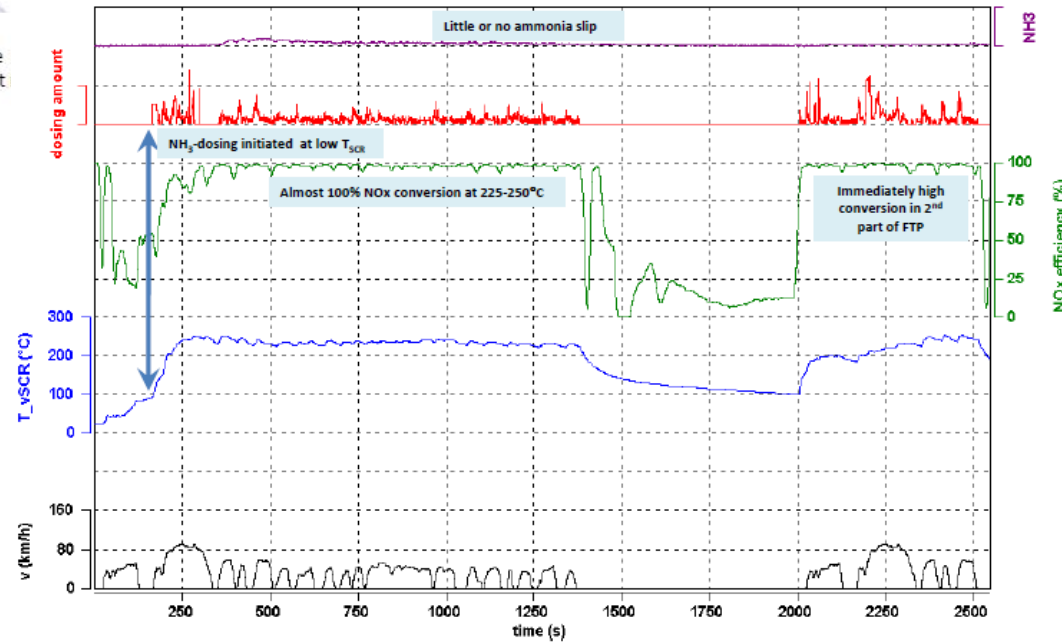
Amminex, VDI Conf 6-09

Main cartridge is disconnected and replaced at oil-service

- No injector needed;
- Steel-tube "penetrating" the pipe
- Simple exhaust geometry & short
- Low pressure drop

Recent advances focused on using cooling water to release ammonia, and improvements in design. Starter unit is permanent, main unit is replenished at lube oil change intervals. Maximum power draw is ~250 watts during heat-up.

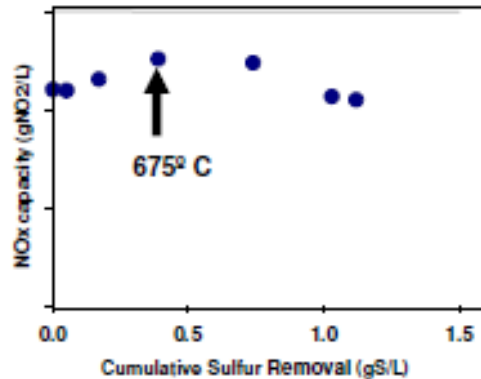
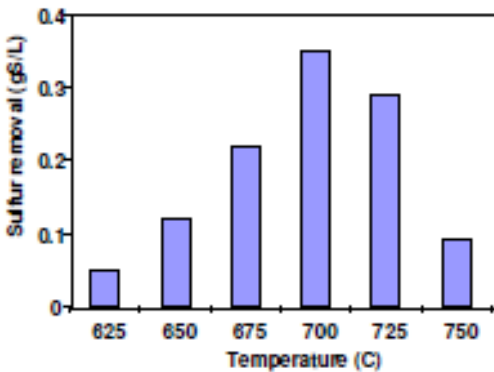
US FTP testing shows NH₃ injection at 100C SCR temperature.



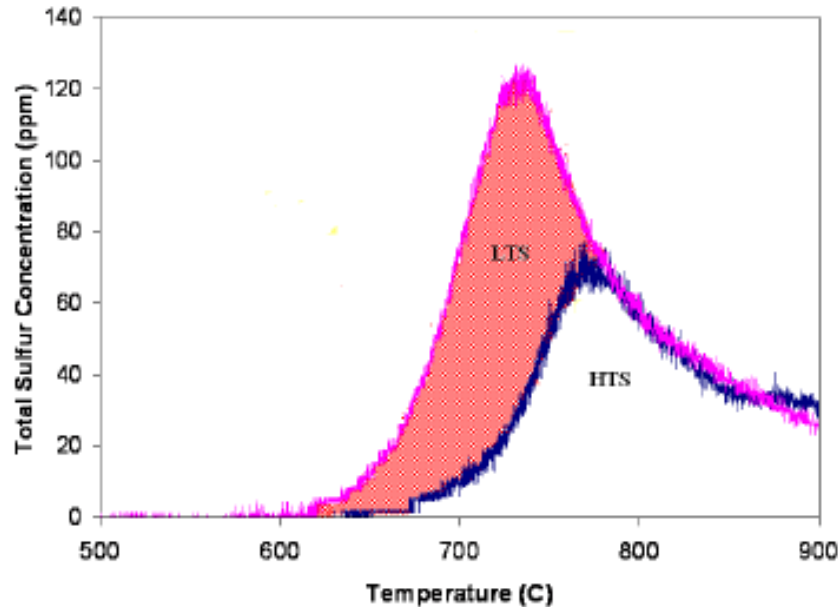
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HC-deNO_x

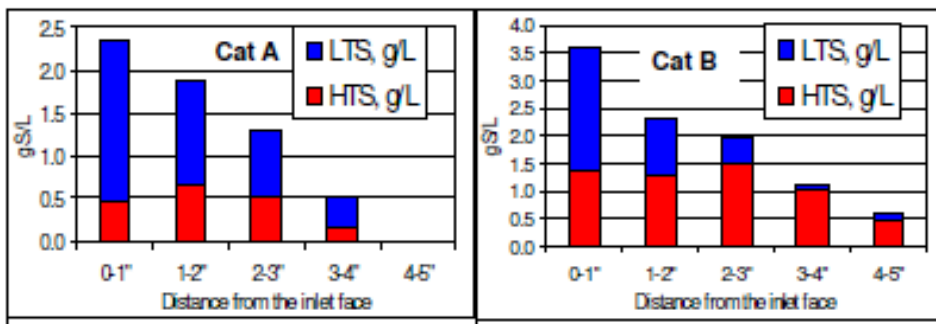
LNT desulfation study identifies LT and HT sulfate.



Desulfation improves with increasing temperature, but NOx capacity decreases for T>675C due to thermal deterioration.



LT and HT sulfate is identified. HT sulfate is likely in the center of the grains.



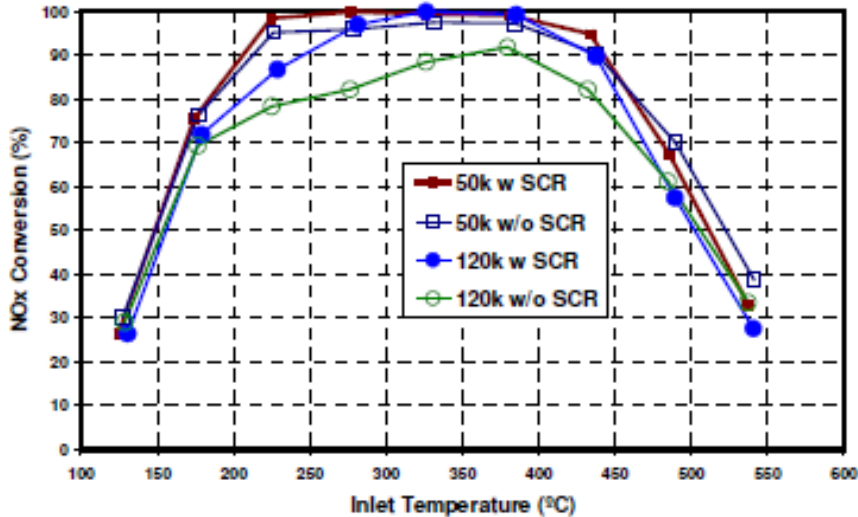
Sulfur loads up the LNT front to back, but different catalysts can give a different distribution of LT and HT sulfate.

Cummins SAE 2009-01-0275

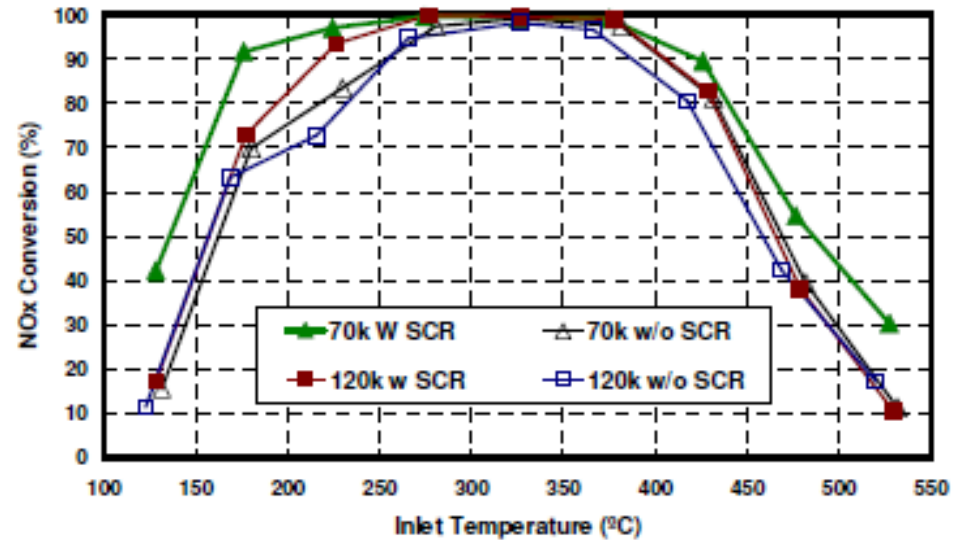
LNT+SCR system allows reduced PGM loadings.

Better performance at <475C for aged systems.

High PGM LNT



Low PGM LNT



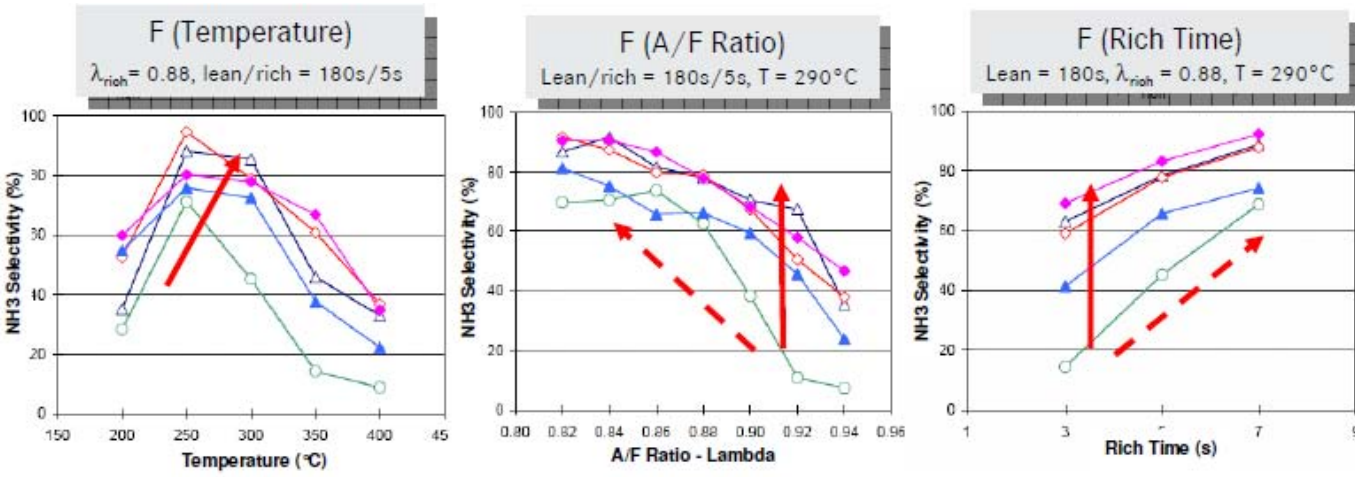
LNT+SCR system with lower PGM loading performs better up to 475C than the higher PGM system at 120k miles.

Other advantages:

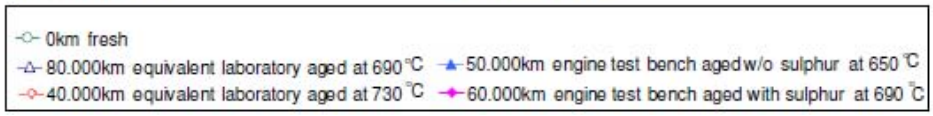
- Much less NH₃ slip
- Lower H₂S emission on desulfation

More details on BlueTec 1 (LNT+SCR) are provided.

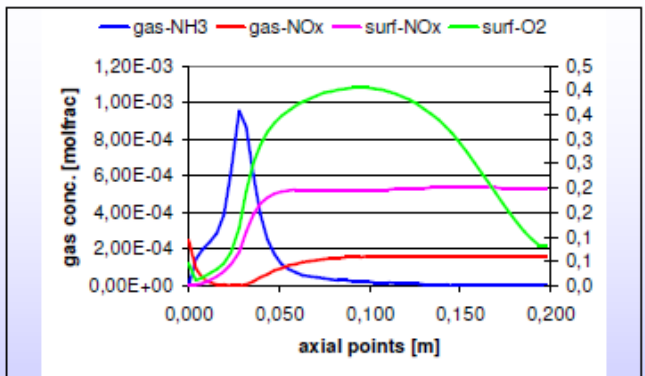
NH₃ selectivity of 70-80%, but it moves through LNT in a wave.



NH₃ formation favored by aging, richer gas, and long rich duration.



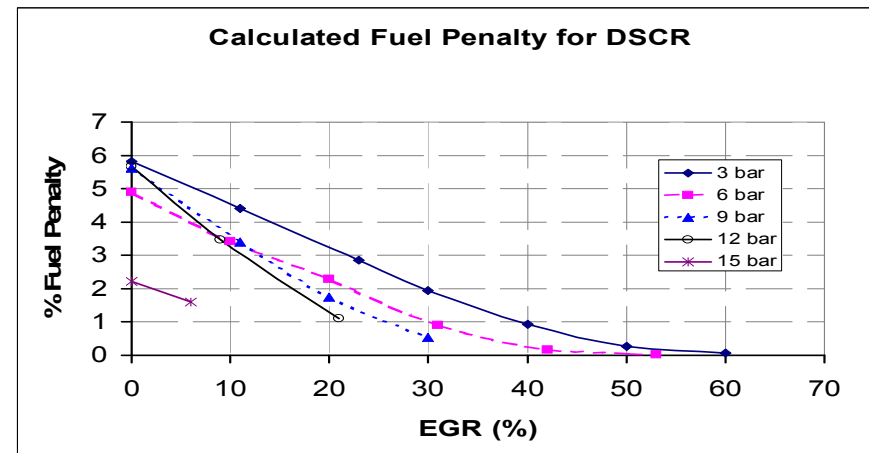
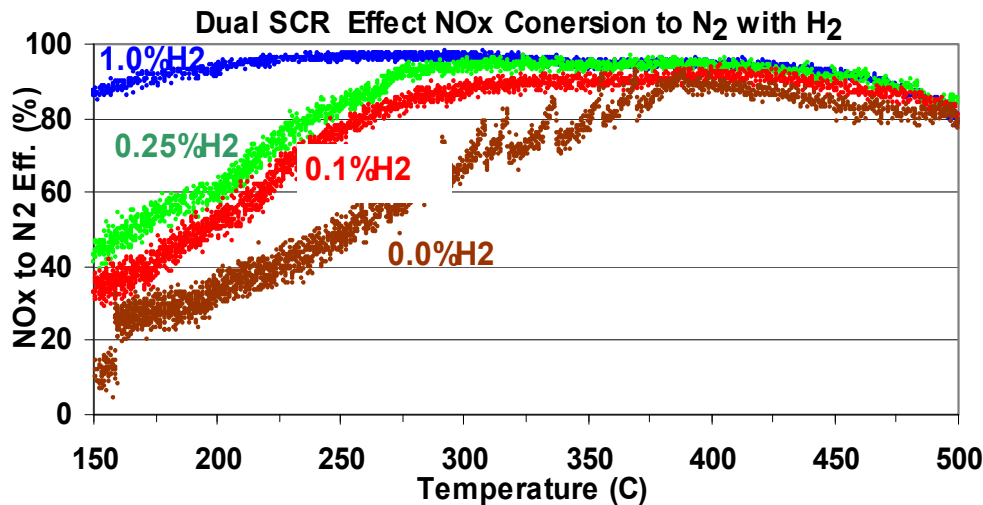
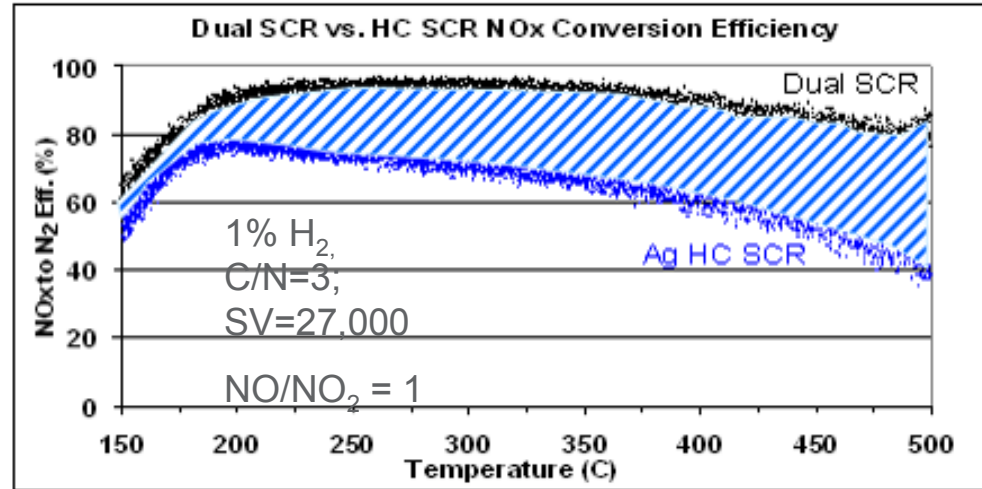
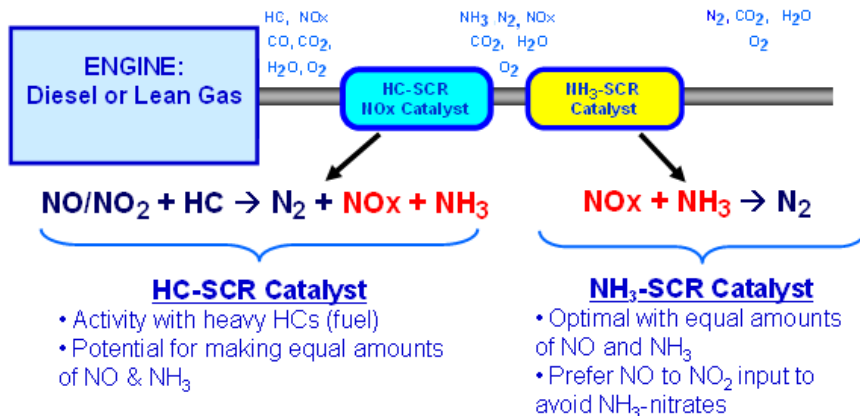
Species evolution after 2s rich



- Better LNT formulations are available today.
- H₂S is converted in the SCR to SO₂

LNC+SCR combo shows potential for low cost deNOx with high efficiency.

- HC-SCR catalyst reduces NOx to both N₂ & NH₃
- NH₃-SCR catalyst further reduces NOx using NH₃

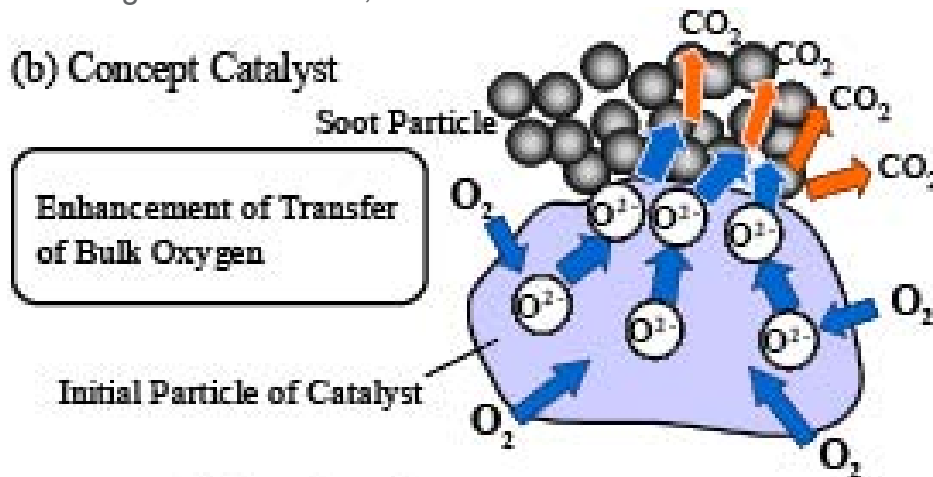


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DPF

Soot oxidation mechanism is shifting from gas-soot to catalyst-soot. First generation in series production.

Figure from Mazda, FISITA 9-08



Soot is not significantly oxidized by gas.
Oxygen is transferred through the oxide lattice to the soot-catalyst interface. No NO_2 is needed. PGM levels are greatly reduced.
Good soot-catalyst contact is needed.

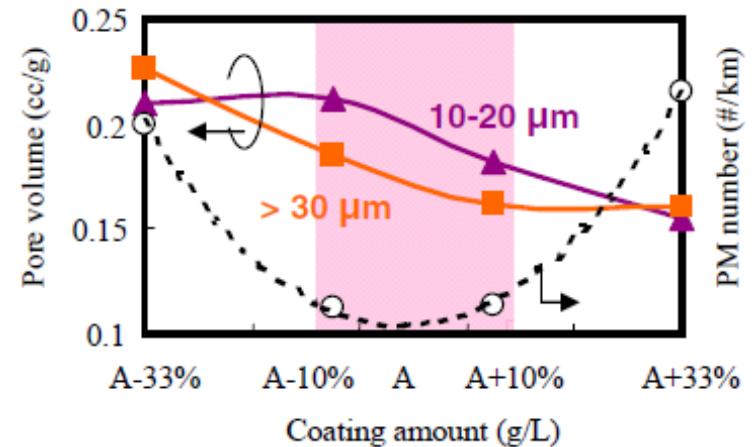
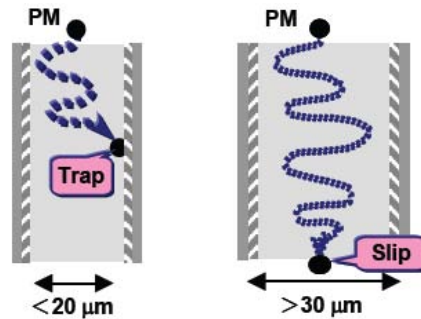
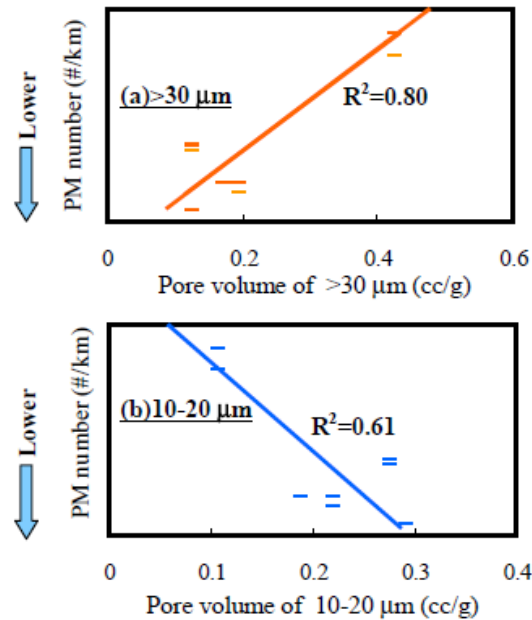
Reported fast soot oxidation temperatures:

475°C; zirconia; Mazda, FISITA 9/08

275°C; ceria mixture; Umicore SAE, 4-08

250°C; MnO_3 mixture; Honda, SAE, 4-09

Heavy DPF coating dynamics and PN filtration efficiency are explained.



PN emissions are high if pores $>30 \mu\text{m}$ are more volume than $10-20 \mu\text{m}$ pores. Capillary forces and coating dynamics postulated.

Strongest PN – pore size correlations are for $10-20 \mu\text{m}$ and $>30 \mu\text{m}$ pores. Explained with Brownian motion theory.

Toyota, SAE 2009-01-0290

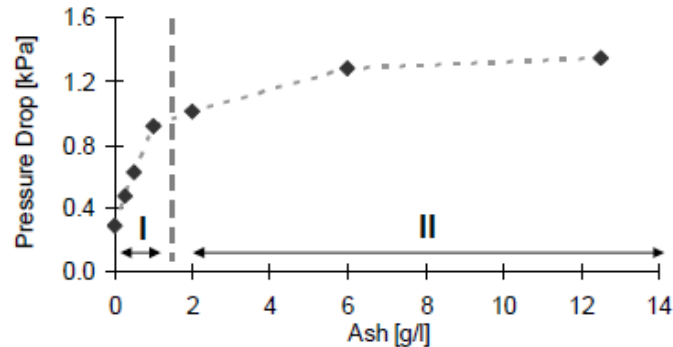
Some ash dynamics on DPFs are shown.

Ash goes into the wall, but membrane forms keeping soot out. ΔP sensitivity to soot greater with high ash loads.

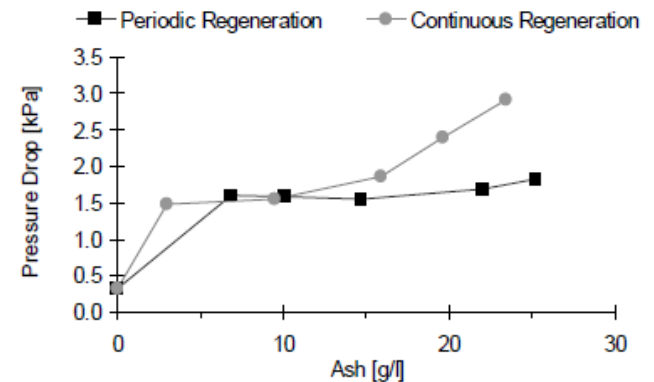
MIT SAE 2009-01-1086

Accelerated ash loading:

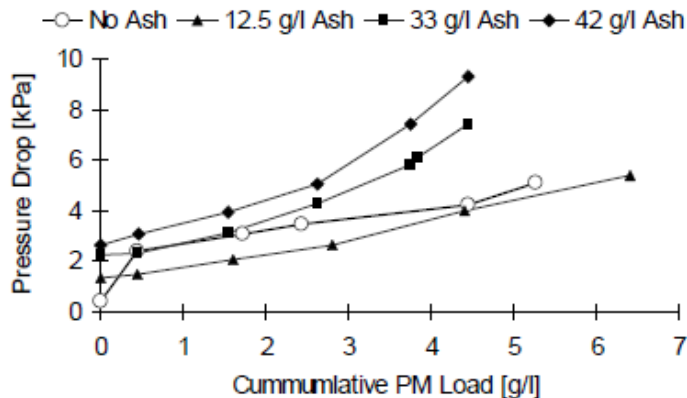
- Lube oil is injected into diesel fuel combustor chamber
- Heat exchangers control exhaust temperature
- Diesel engine exhaust provides soot



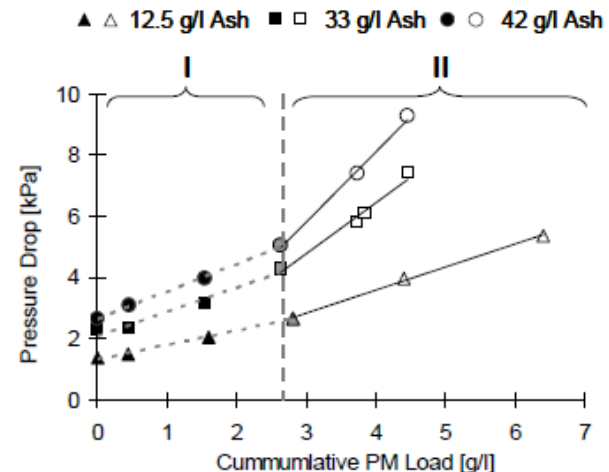
In accelerated ash testing, about 2 g/liter ash penetrates into the wall resulting in rapid ΔP increase (Stage I)



Generally, continuous regeneration lays down a growing membrane whereas periodic regeneration collects ash at the DPF end.

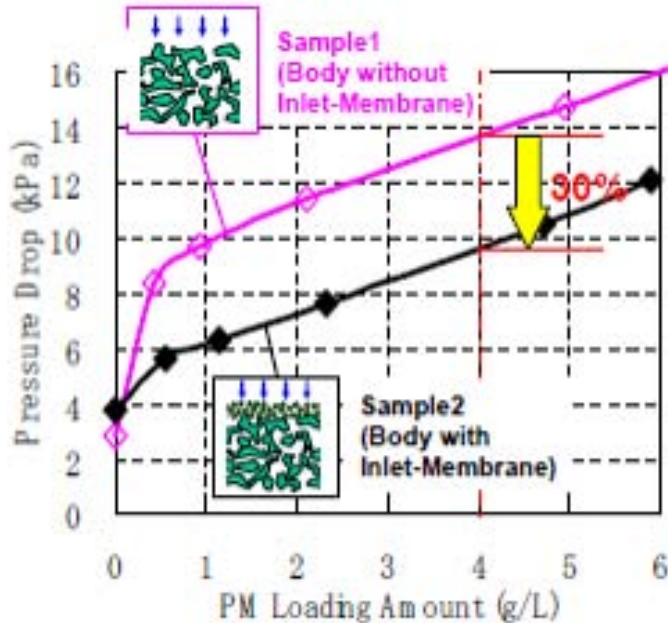


Filters with 33 g/liter ash have same ΔP at >0.4 g/liter soot as ashless DPF. 12.5 g/liter ash is lower. Ash membrane keeps soot out of wall.

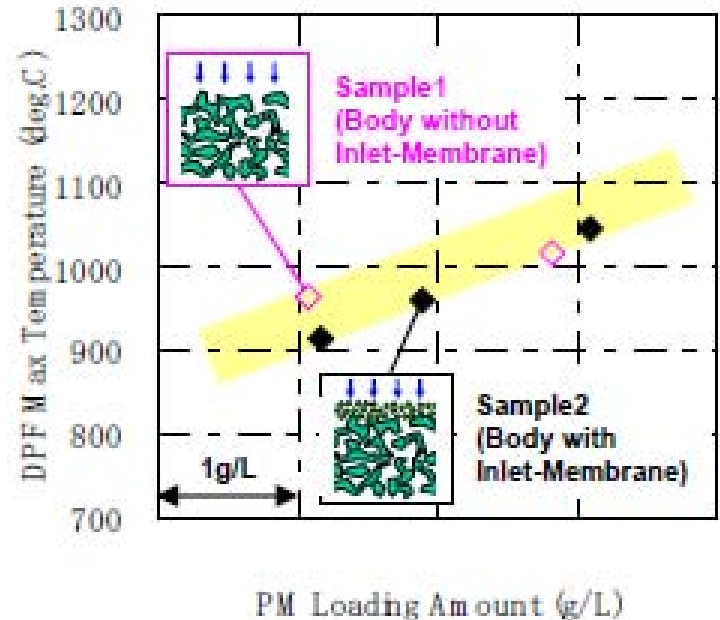


ΔP sensitivity to soot (slope) increases with ash load.

Results on membrane-coated honeycombs are reported.



Because initial soot does not enter wall, soot-loaded back pressure is reduced 30%. Initial back pressure higher.



Regeneration exotherm is similar

Initial, clean DPF PN filtration efficiency up 20% vs. the baseline condition.

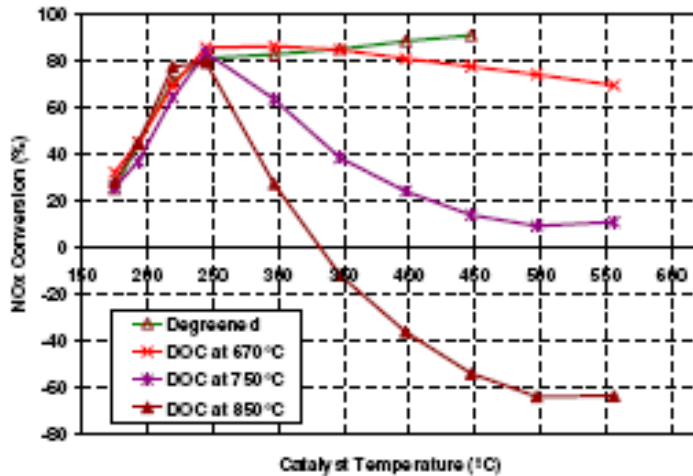
Note: Ash membrane eventually forms to give similar results.

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DOC

Pt from upstream DOCs (or DPFs) can contaminate downstream SCR.

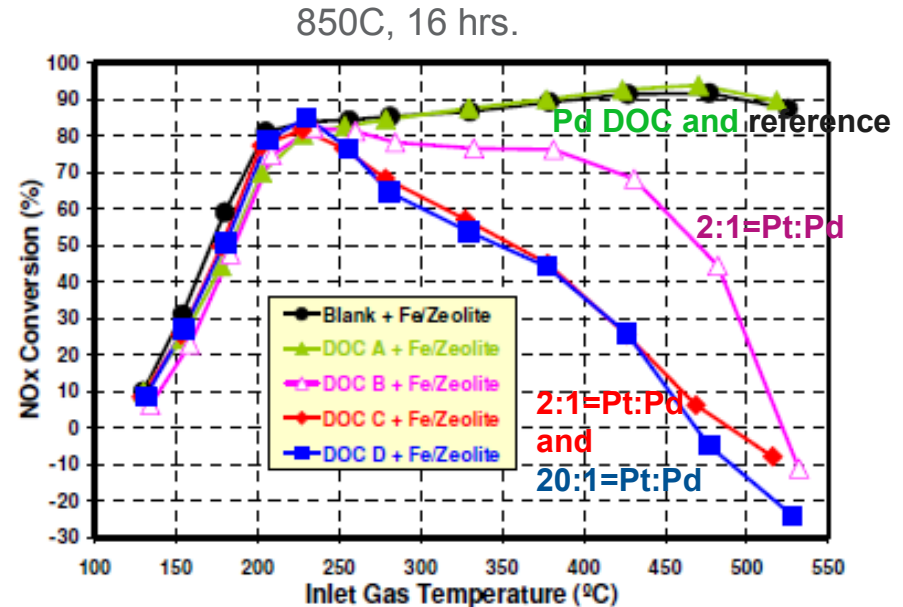
Ford, SAE 2009-01-0627



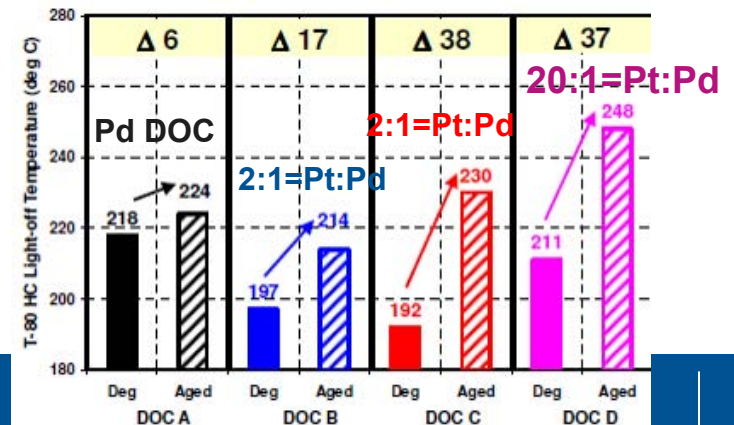
Fe-zeolite deNOx held for 16 hrs downstream of DOC. Loss of efficiency due to Pt poisoning.

- Traditional detectable limit is 5 ppm
- In addition to the ethylene method, an enhanced XRD method was used, and a lab set-up successfully duplicated dyno results.
- N₂O emissions can also be high

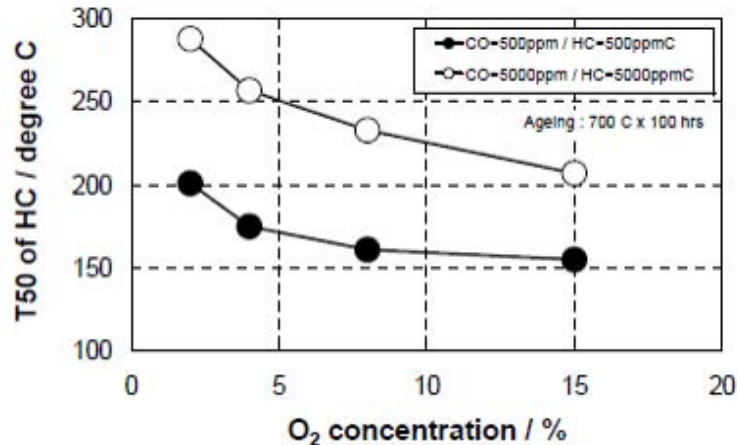
Ford, SAE 2008-01-2488



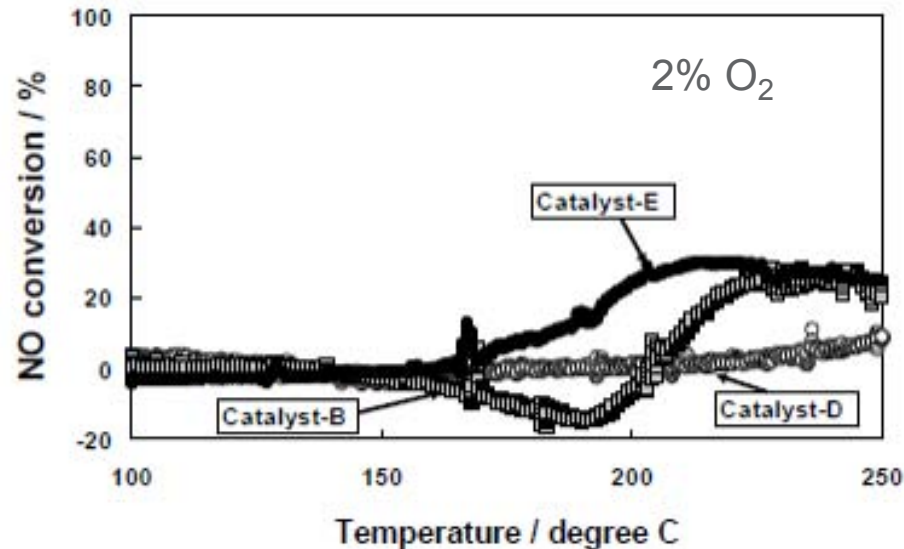
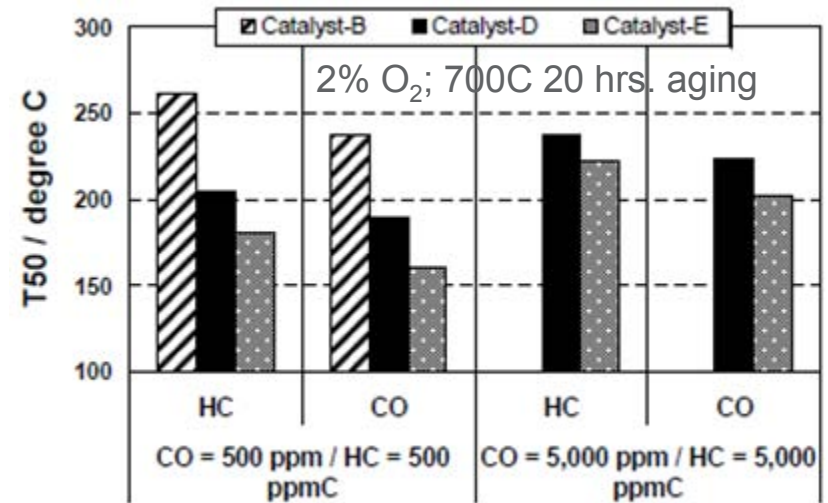
Replacing Pt with Pd decreases Pt migration from DOC to SCR. Formulation within composition can matter.



New DOC formulations drop T50 in presence of low oxygen and high HC+CO. Designed for pre-mixed combustion



Difficult to get commercial DOCs to light-off in 2% O₂ w/ high HC+CO levels



Enhanced catalyst formulations:

- Materials to supply oxygen
- CO adsorption suppressant
- Plurality of active sites for multiple function

Summary

- Criteria pollutant regulatory efforts are focused on Euro VI HD PN limits, and California LEV3 for LD.
- CO₂ mandates are spreading. Major paradigm shift underway. HDD black soot reductions can meet ~20% of 2050 CO₂ reductions.
- HD engine technologies are enabling US2010 to be attained w/o deNOx treatment.
- LD technologies focused on downsizing for ~90-100 g/km CO₂. NOx up ~20%. DHEV attractive for very significant reductions.
- Fundamental SCR understanding is advancing. Combination DPF+SCR systems insights expanding.
- LNT desulfation understanding shows sulfate differences. Combination LNT+SCR and LNC+SCR systems described.
- DPF catalysts show direct oxidation of soot at 250C. New learnings on deNOx catalyst loadings on DPF pressure drop are counter-intuitive. Interesting ash studies emerging showing membrane phenomenon.
- Pt migration from DOC (or DPF) to SCR is reduced. DOCs are emerging for LTC applications.

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