

Diesel Emission Control Review

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August 10, 2005

Full version for website
Presentaton will be condensed

Summary

- Filters are making significant progress with sophisticated regeneration schemes and continuous improvement in back pressure and durability.
- NOx solutions look good.
 - HD NTE dictates 80% NOx efficiency at 500C
 - Zeolite SCR is used in Japan
 - HT LNTs emerging
- Integrated solutions are hitting Bin 5 and US2010

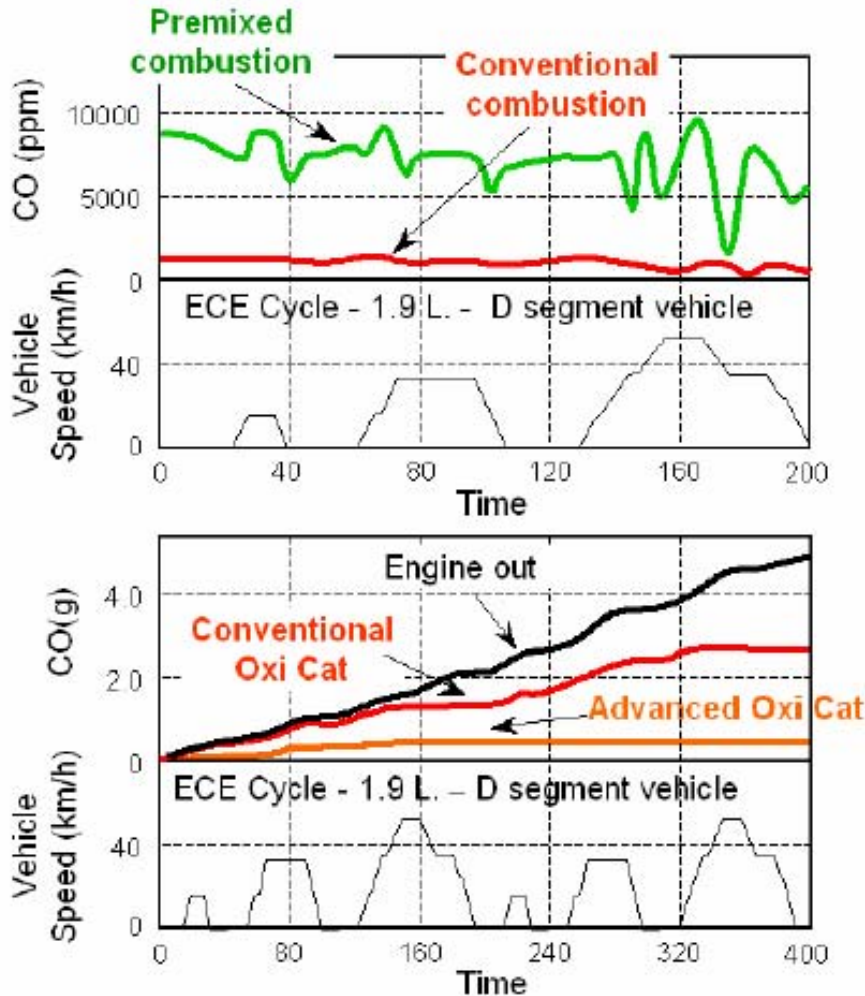
Quick word about mixed mode engines

- Mixed-mode: high HC and CO, and low NOx and PM at low load; inverse at high load; nominal 50% load threshold
- For mixed-mode engines, all emission control requirements change
 - LT HC+CO control will be critical.
 - With mixed mode combustion, filter regeneration can largely be passive.
 - If regeneration is needed at low load, HCs and CO are available
 - With mixed mode, HT NOx performance will be emphasized.
 - Integrated PM and NOx control enhanced with mixed mode combustion.

HC and CO Control at Low Temperature

- Not too critical for traditional combustion, but very critical for HCCI operation under low load
- 125 C idle and 175 C at 25% load
- Several options are available
- Pd-based catalysts are offering better PGM management options

New DOCs are beginning to address CO issue with pre-mixed combustion



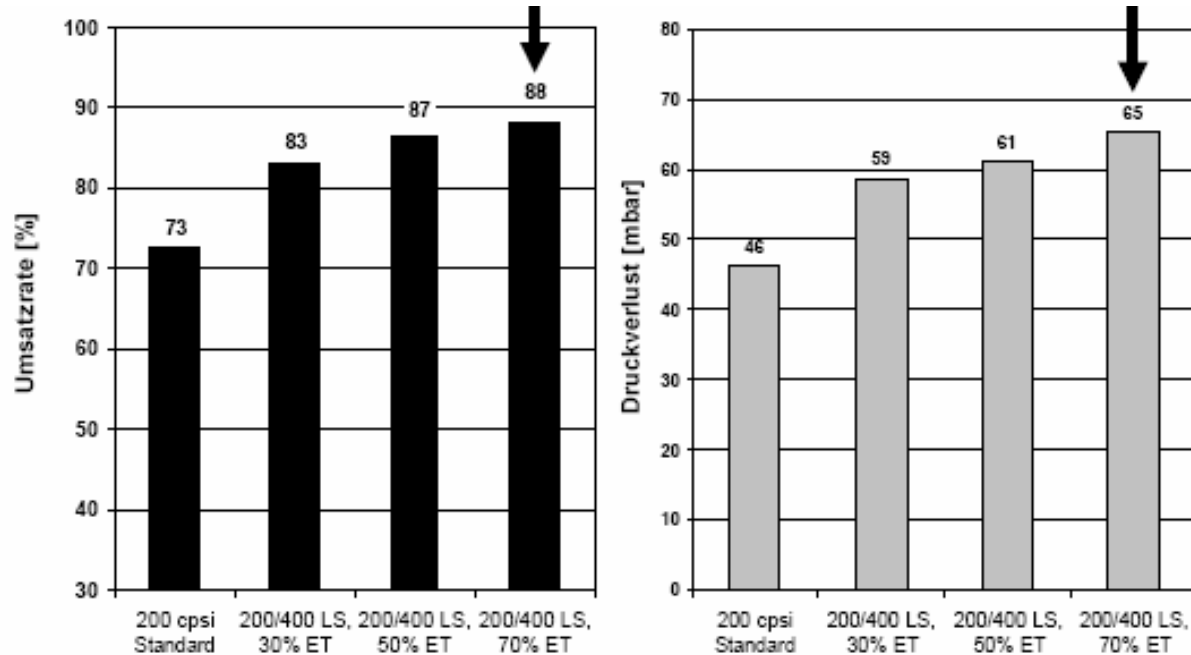
Increase of engine-out CO and HC due to Premixed combustion and/or low-NO_x calibration



Options:

- ✓ Increase noble metal loading
- ✓ Increase size of close coupled Oxidation Catalyst
- ✓ New coating options (Pd) with fuel sulfur content below 10 ppm

Back pressure and efficiency trade-offs for novel DOC substrates are described



Relative efficiency of the best design is 20% better than std. 200-csi, but with 35% higher back pressure.

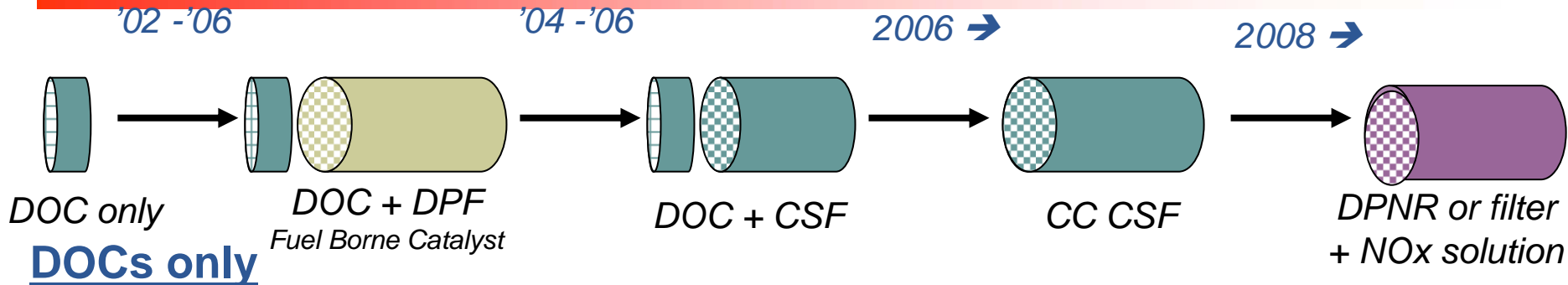
Emitec Vienna Motorsymposium, 4/05

For comparison, standard 400-csi 4 mil web has 10% better relative efficiency, but with similar back pressure as 200-csi (Corning SAE 2004-01-1419).

PM Control

- DPF regeneration strategies are getting increasingly sophisticated (details in DEER LDD DPF regeneration paper).
- Filter systems fundamental understanding is improving
- Some issues still need to be addressed
 - aged soot might present a problem
 - DPFs might have under-utilized catalyst in small pores
 - DPF pore size distribution might be further optimized

OEM Emission System Strategies



- Minimum current diesel system: DOCs for odor control
- Vehicles are able to meet EU IV legislation through engine management.

DOCs + uncatalyzed filters (DPF)

- First system (1999); Incremental improvements in the FBC formulation and delivery and increased DPF ash storage capacity are keeping this competitive.

DOCs + catalyzed filters

- Catalyst on filter improves regeneration while DOC reduces HC, CO and NOx.
- Expands range of passive regeneration, reduces complexity.

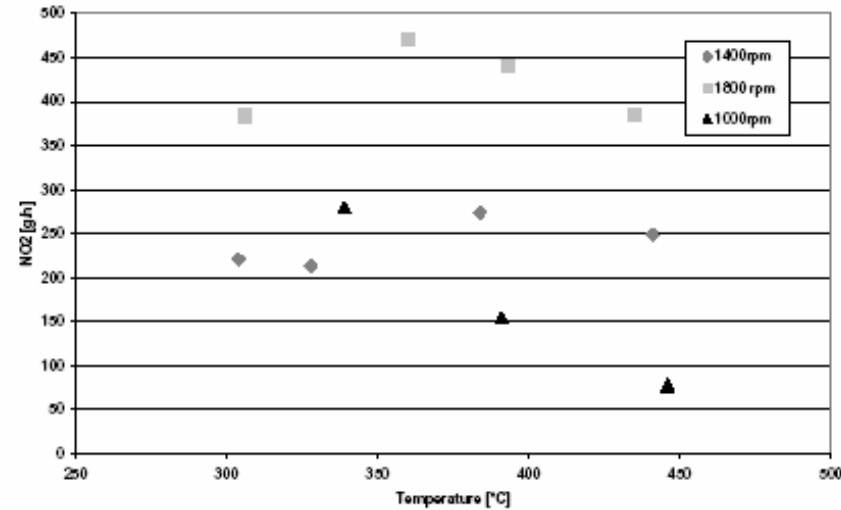
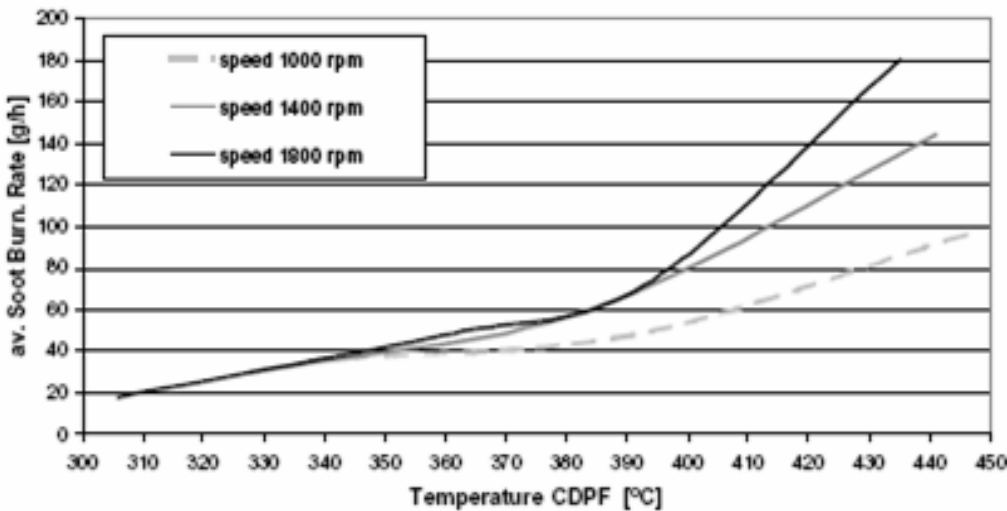
Catalyzed filters only

- Target system for many OEMs: Further complexity reduction and cost.

PM and NOx solution

- Mixed-mode combustion synergies enable this cost saving integration

Soot oxidation rate by NO_2 is studied. The balance between NO_x production, NO_2 conversion, flow rate and soot oxidation rate shows soot oxidation kinetics are controlling the rate.

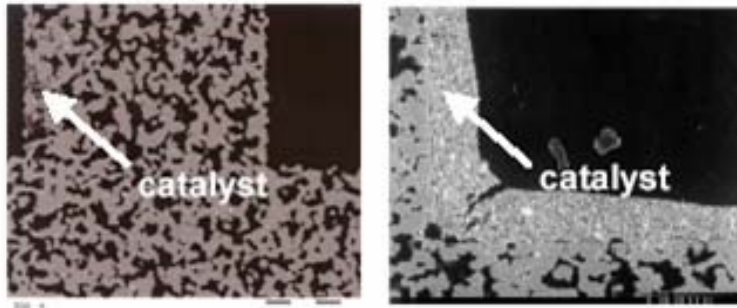


Average soot burning rate (preloaded fillers) on CSF for normal engine exhaust. $T < 380$ C, rate controlled by soot oxidation kinetics. $T > 380$ C soot oxidation by O_2 begins.

High RPM with 350C exhaust gives highest NO_2 production.

When engine NO_x is dropped 70%, soot oxidation rate goes down. However, there is still some NO_2 or active O_2 activity for DPF management.

New DPF catalyst coating process put DOC function on DPF and aids regeneration



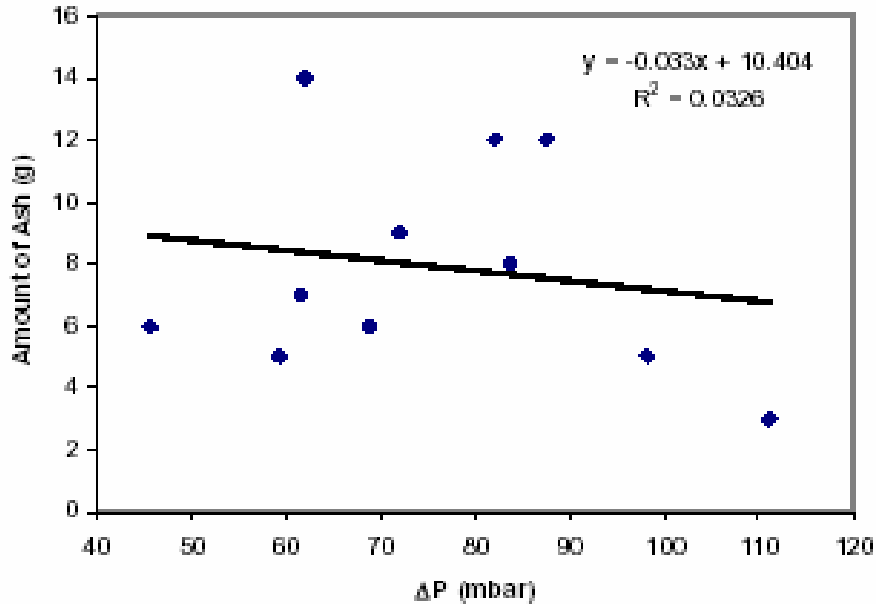
New coating technology puts catalyst into the wall rather than on it. Δp goes up only 5 to 30% vs. 2-3X for standard coating.

- Ash simulation tests show little impact on HC and CO conversion.
- 10 g/liter soot drops CO efficiency from 88 to 80%. Minimal impact on HC.

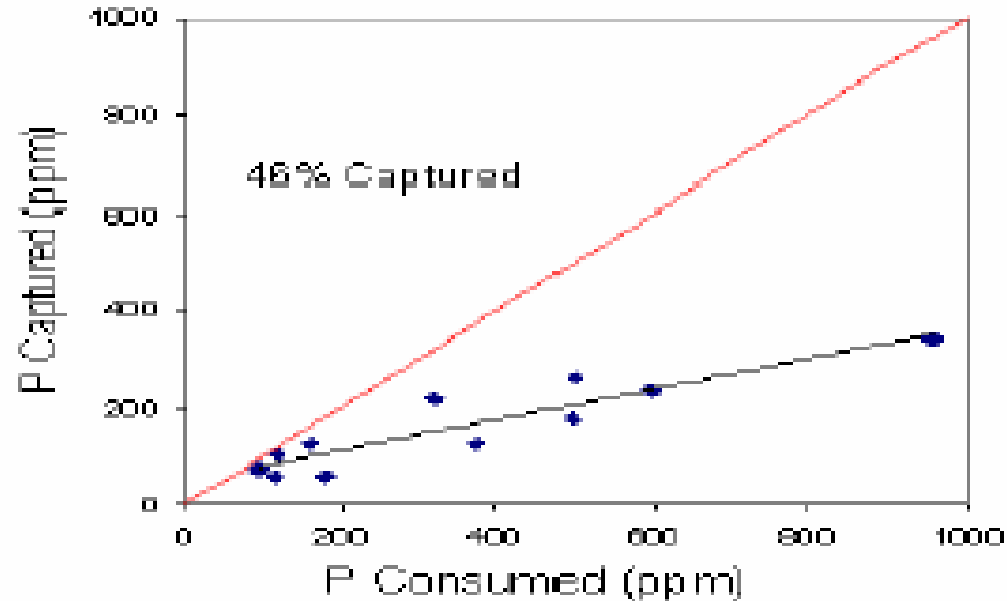
System	Combusted soot amount @ 450°C [g]	Combusted soot amount @ 600°C [g]
System 1: stand-alone CDPF	10,2	17,0
System 2a: DOC / CDPF	1,7	13,5
System 2b: DOC / DPF / FBC	5,5	20,8

At 450C, CDPF 6X more soot than DOC+CDPF system.

Less than 50% of lube oil ash is collected on DPFs, despite >99% removal efficiency of solid particles.



Pressure drop is not a good indicator of ash loading.

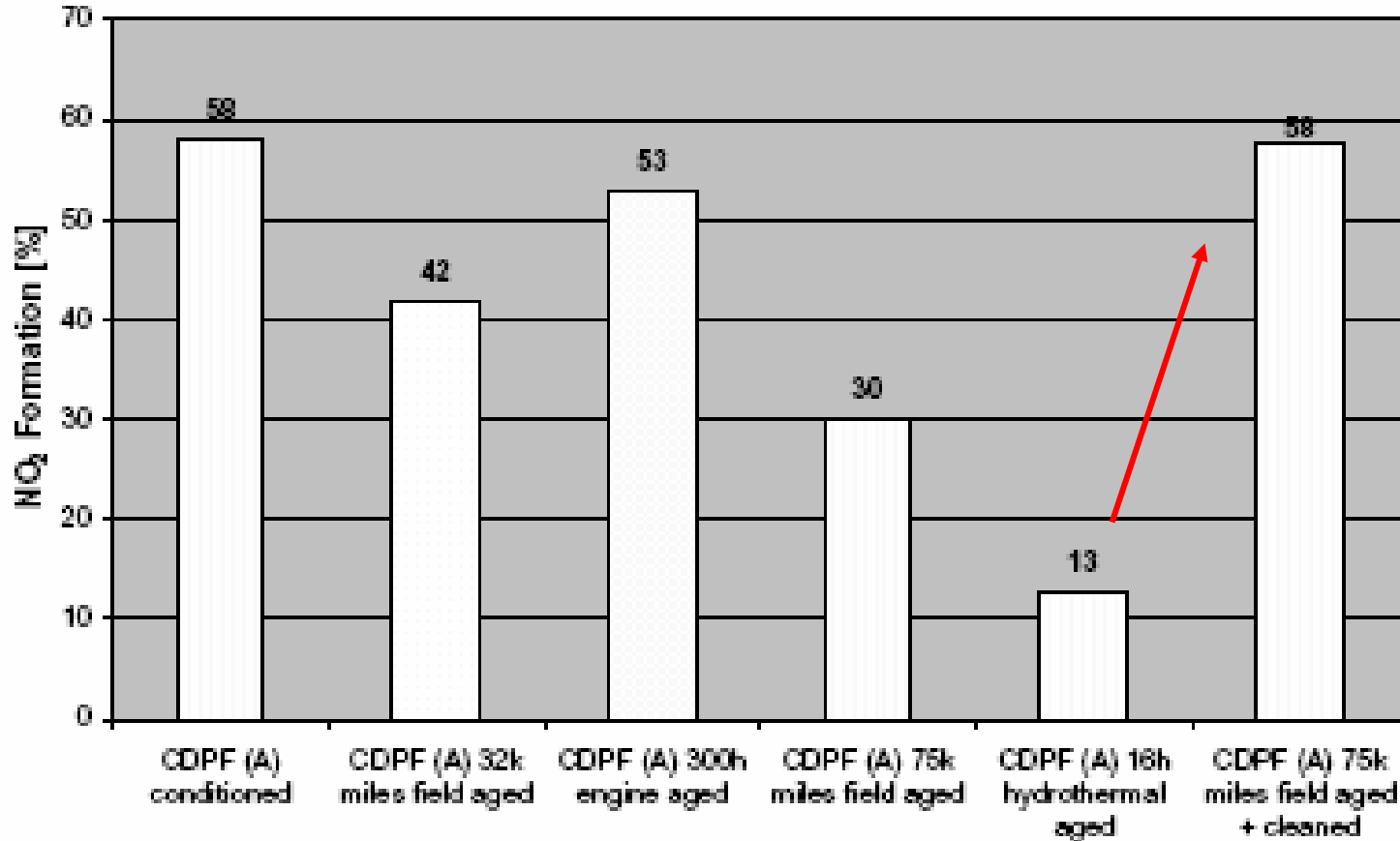


Only 46% of phosphorous from consumed lube oil was captured on the DPF. 37% Ca, 31% Mg, and only 5% of B were captured.

- 20-30% ash comes from non-lube oil sources

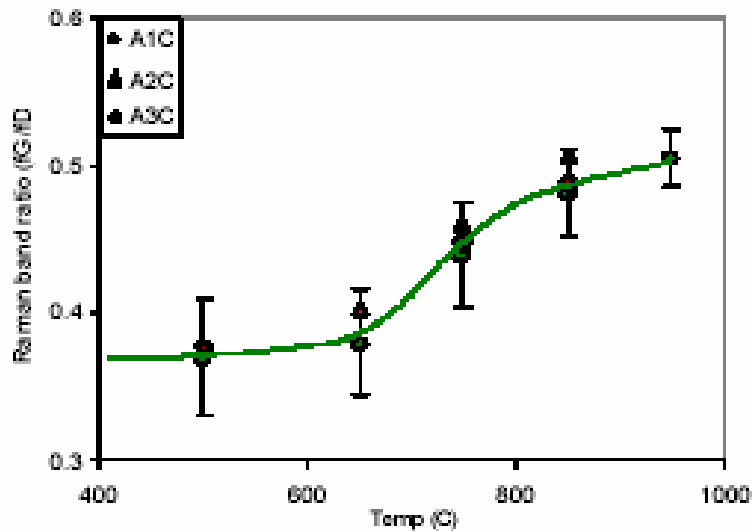
CSF aging studies show strong impact of ash accumulation

Umicore SAE 2005-01-0663



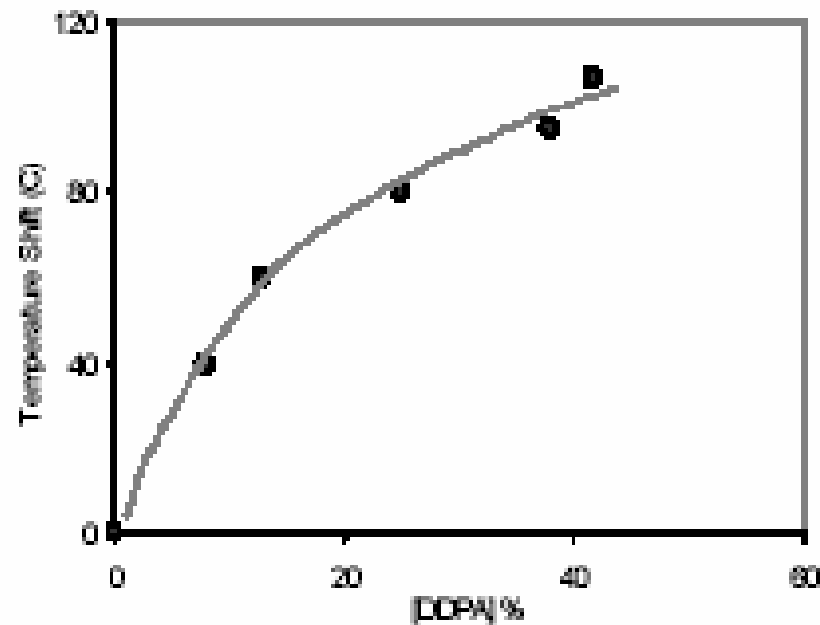
% of theoretical NO₂ 150-400 C. Ash cleaning has big impact on NO₂ formation (~2x). Cleaning might have to be done more frequently than ΔP dictates to keep DPF healthy

Precaution: Aged soot may not easily oxidize and may unknowingly build-up in DPF



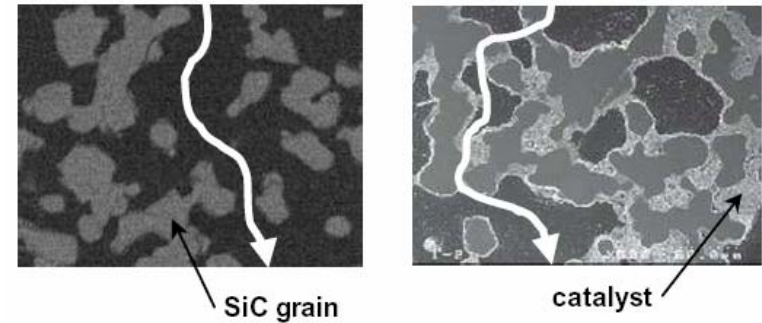
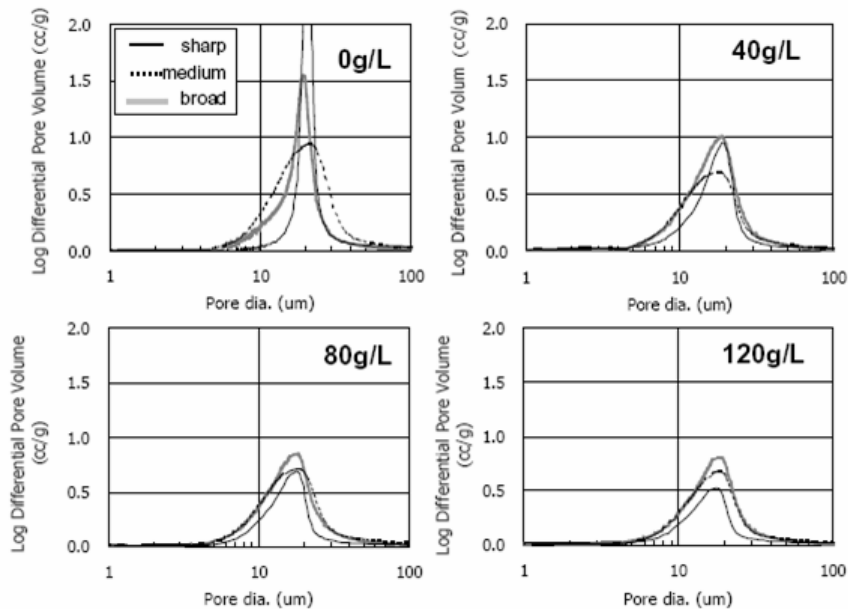
Raman spectroscopy shows changes in diesel soot structure with aging temperature.

- Increase in Raman spectra G/D is correlated to reduced oxidation rate (up to 90% slower). NCMR, DEER 8/04
- **To prevent build-up, occasional complete regenerations are needed.**



Differential oxidation temperature increases with dialkyldithio-phosphoric acid (DDPA) additions. Effect is due to acid base interactions and deactivation of soot active sites.

Pore size distribution of CSF changes little with washcoat loading level. Causes inefficiencies.

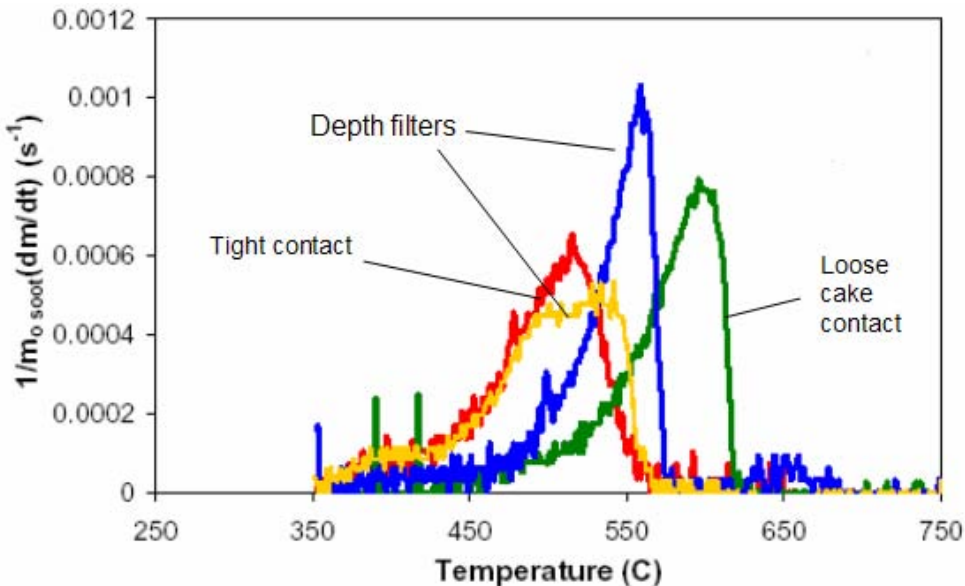


Catalyst preferentially goes into the small pores. Uncatalyzed, left. Catalyzed, right.

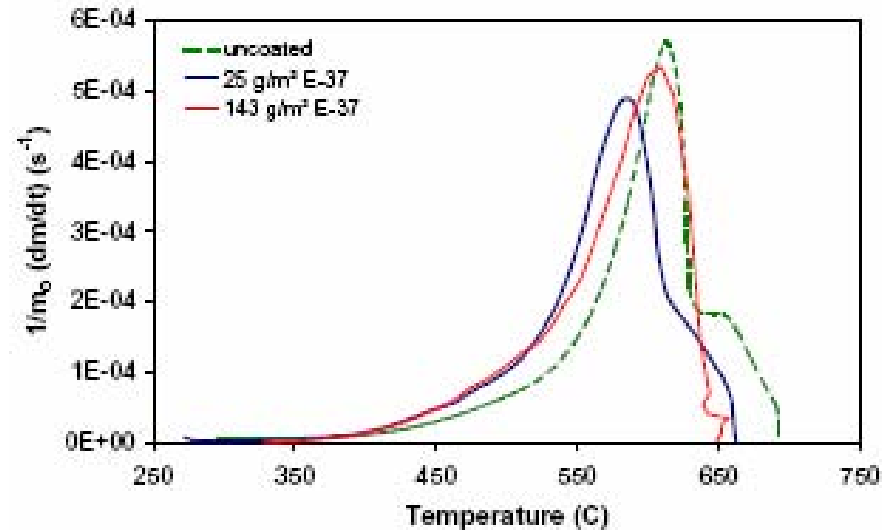
The pore size distribution of various uncatalyzed filters (0 g/l) is very different, but is overwhelmed by the washcoat.

Ibiden SAE 2005-01-0578

Deep bed DPFs have better soot/catalyst contact and thus regenerate better.



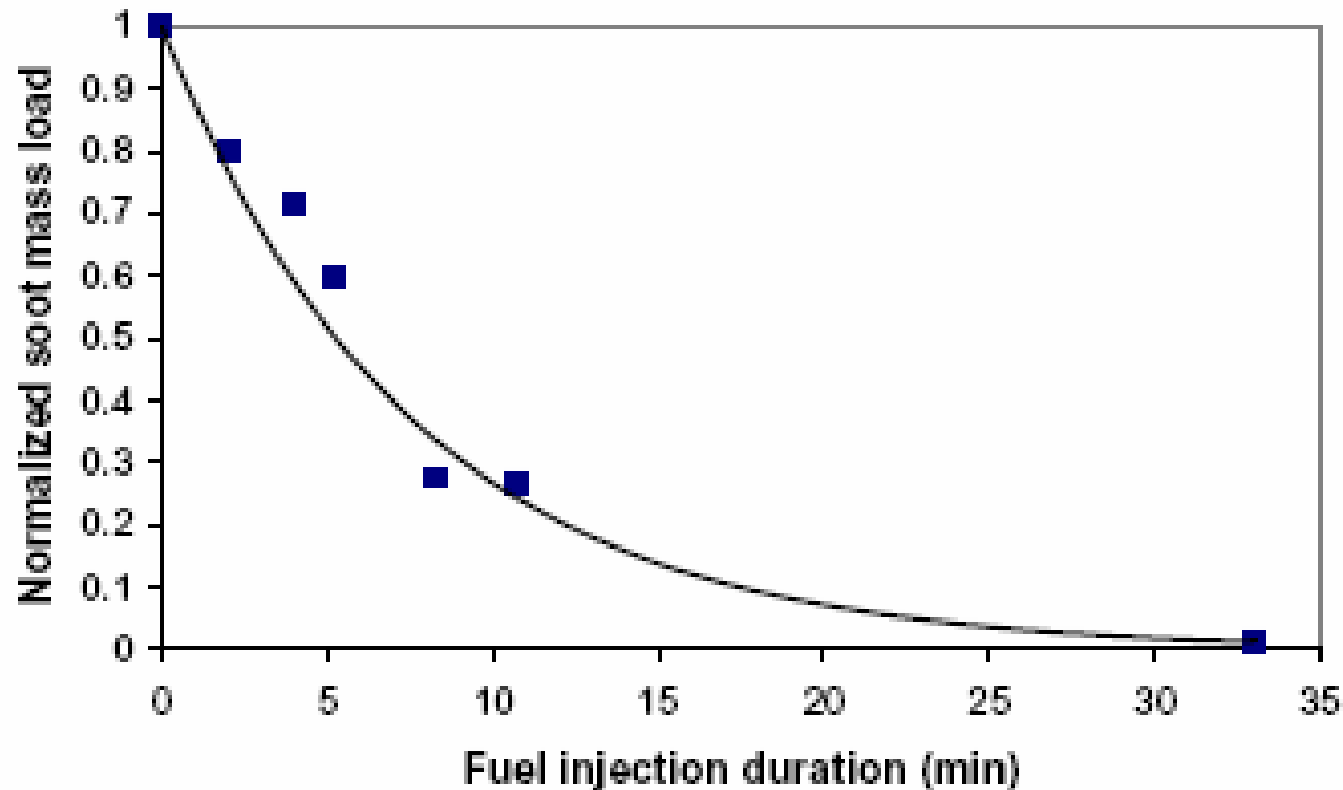
Contact of soot and catalyst is important, as is filtration mechanism. Deep bed filtration gives better soot/catalyst contact.



The lower catalyst loading on cake filters has better soot oxidation activity. High catalyst loading prevents some depth filtration

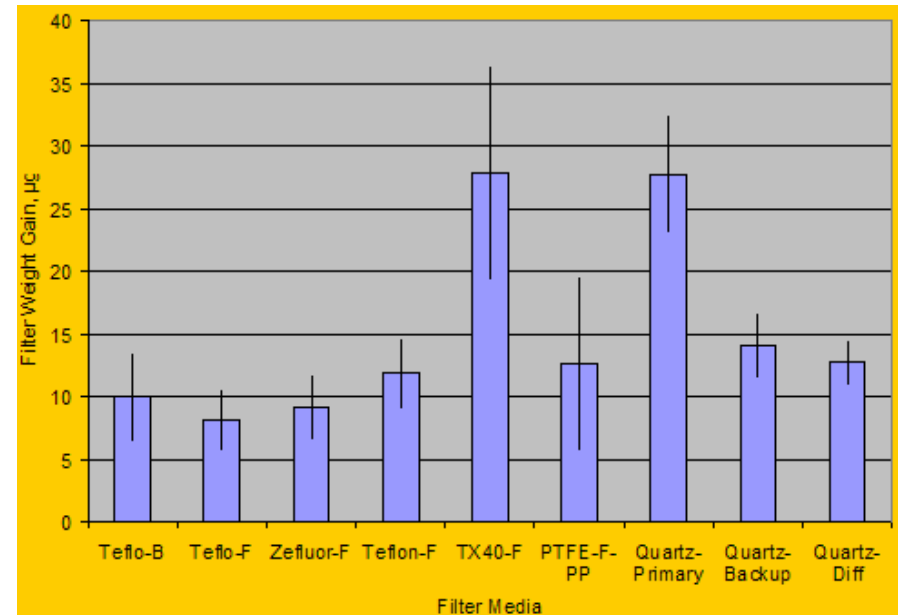
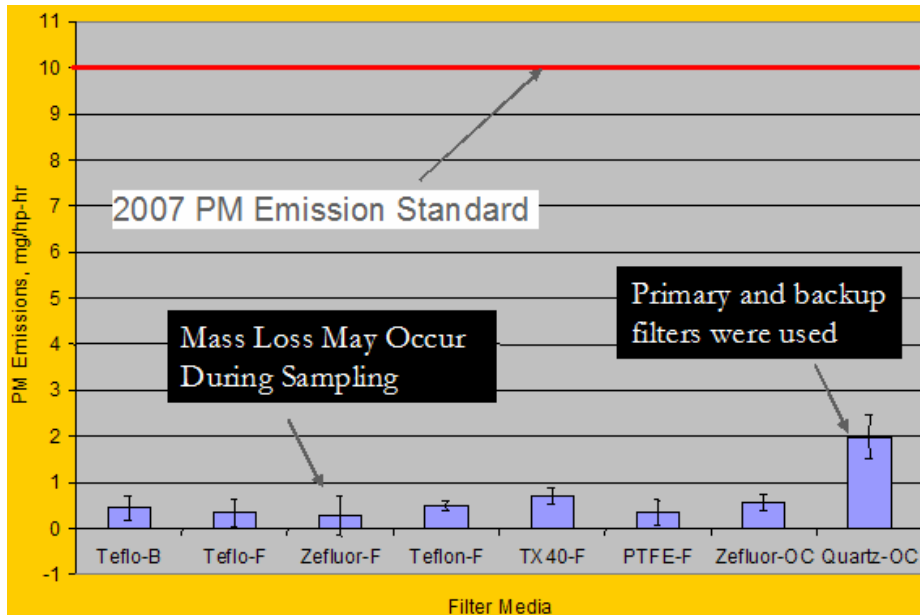
Depth filters have pore sizes >40 microns.

Due to the exponential nature of regeneration degree with fuel consumption partial regenerations can save fuel.



3-5 g/liter soot load operating range will result in only 0.23% fuel penalty; 8 g/liter loading down to clean gives 0.52% penalty

PM emissions using DPF are so low that analytical filter media effects become pronounced

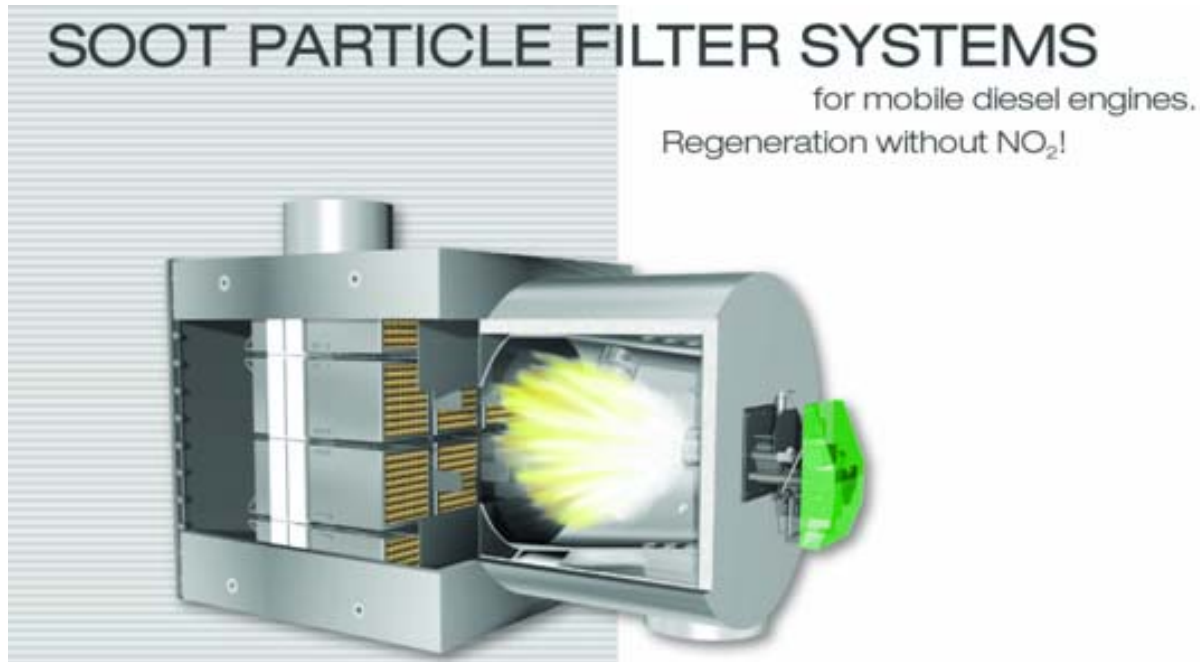


HD FTP PM results show emissions at <10% of the standard using a variety of analytical filter media.

At full load and rated speed, M emissions using approved analytical filter media can vary 2.5X.

Other results show dilution ratio has even a greater impact on emission measurement.

All 800 diesel locomotives will be fit with DPFs within a year



- Burner regeneration at 5/g/liter soot
- Extruded DPF SVR = 5 to maintain <30 mbar ΔP
- Easily adapted to SCR

Other results shown earlier

- Fuel vaporizers improve regeneration fuel efficiency
- Closed-coupled CSF increases optimum regeneration frequency
- New HT filter made from aluminum titanate is going commercial

NOx Control

- Low temperature NOx control is the interest today. This will shift to HT NOx control in 2010.
- SCR leads the NOx aftertreatment field, at least for Class 8 vehicles.
- Lean NOx Traps are developing rapidly and are attractive in lighter applications
- LNC-based concepts look promising

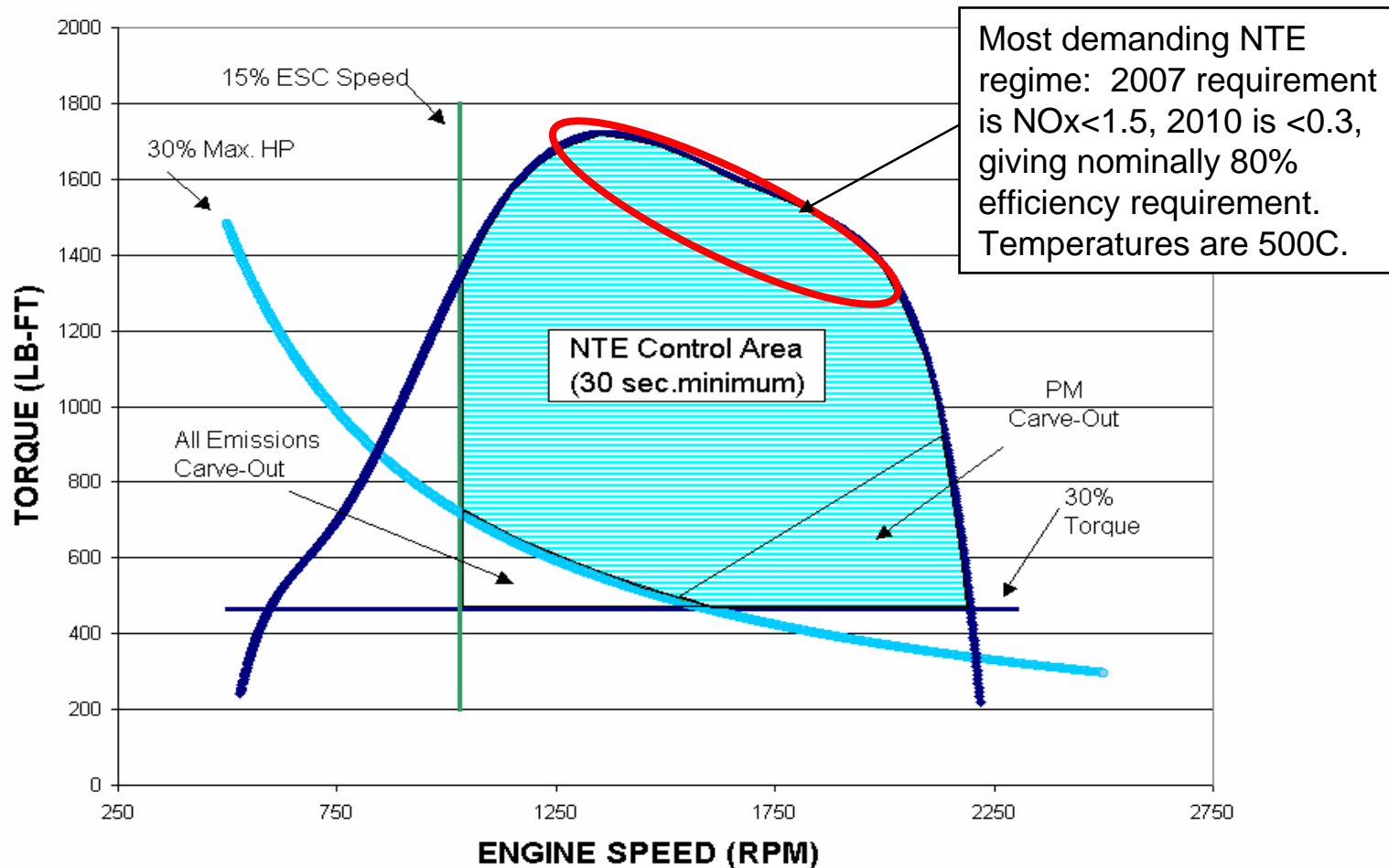


CORNING

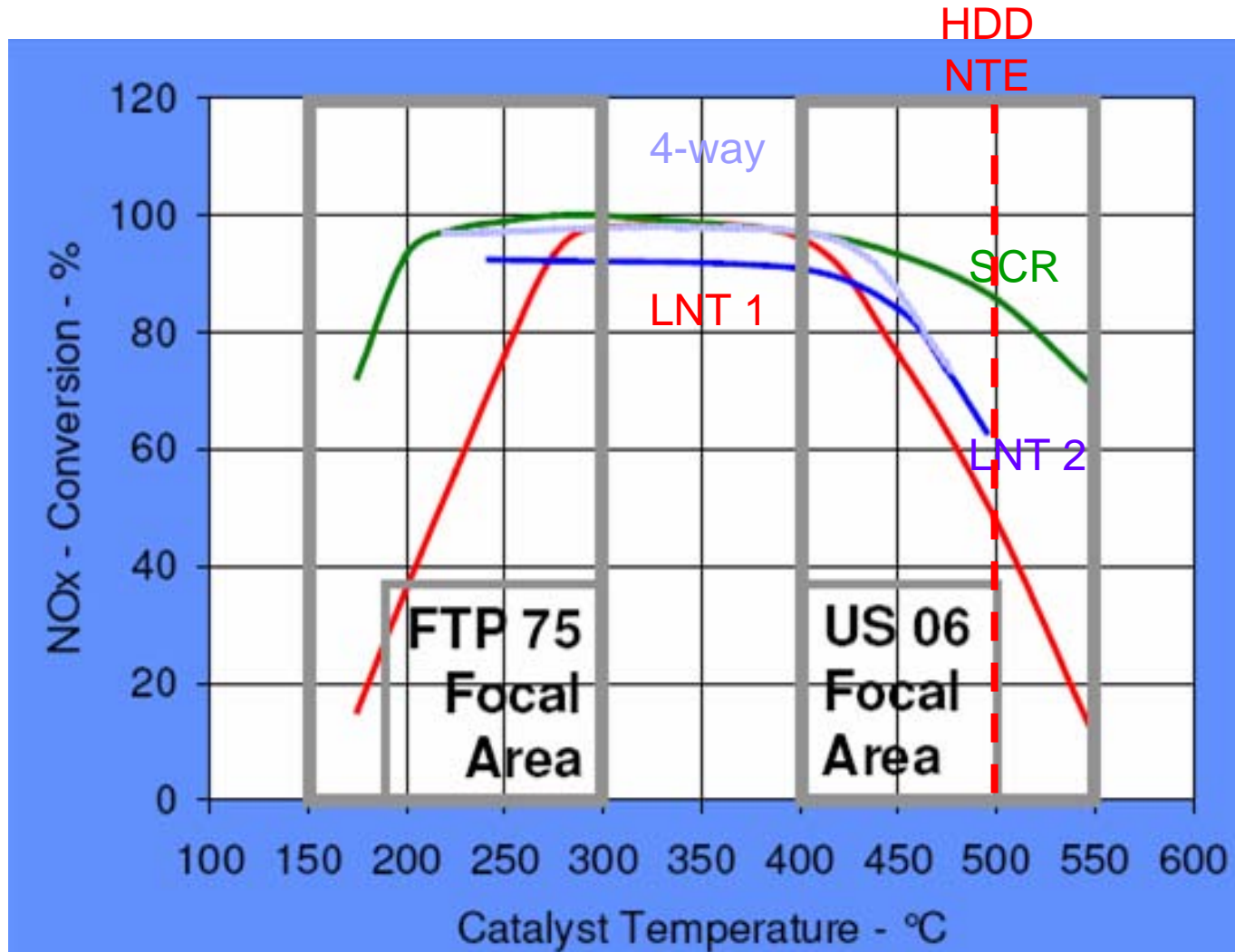
Discovering Beyond Imagination

HD: NTE dictates about 80% NO_x control at T=500C

Not To Exceed Test



Different NOx approaches are compared. SCR has best LT and HT performance.

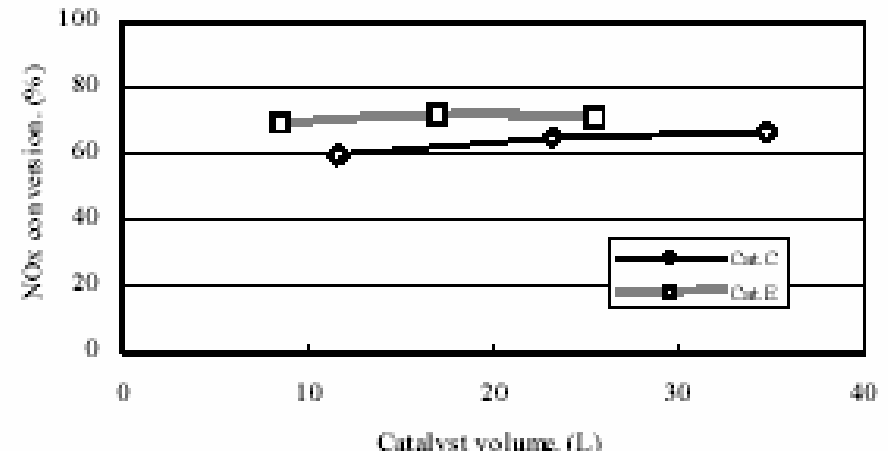
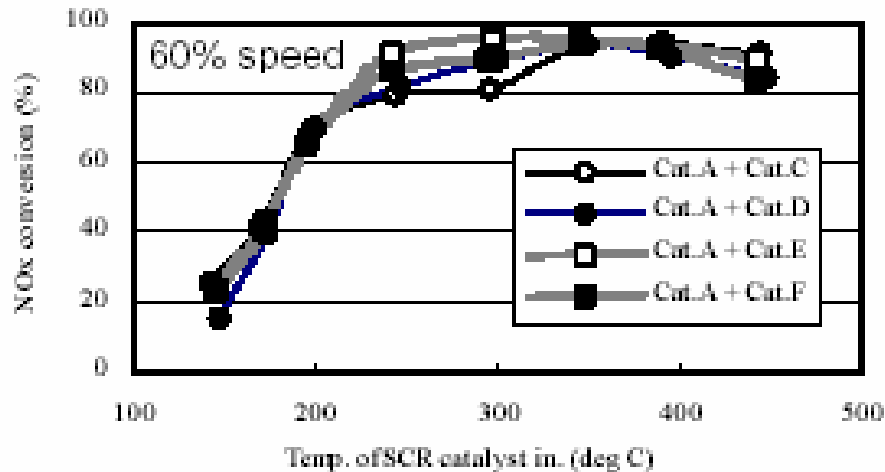


SCR

- Numerous LT efficiency options exist today
- Zeolites are offering a new catalyst option
- Solid urea might address urea infrastructure issues

Nissan Diesel used a comprehensive approach to implement HD SCR

Nissan Diesel SAE 2005-01-1860

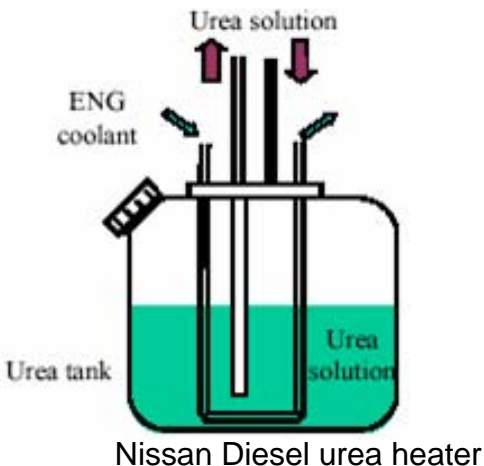
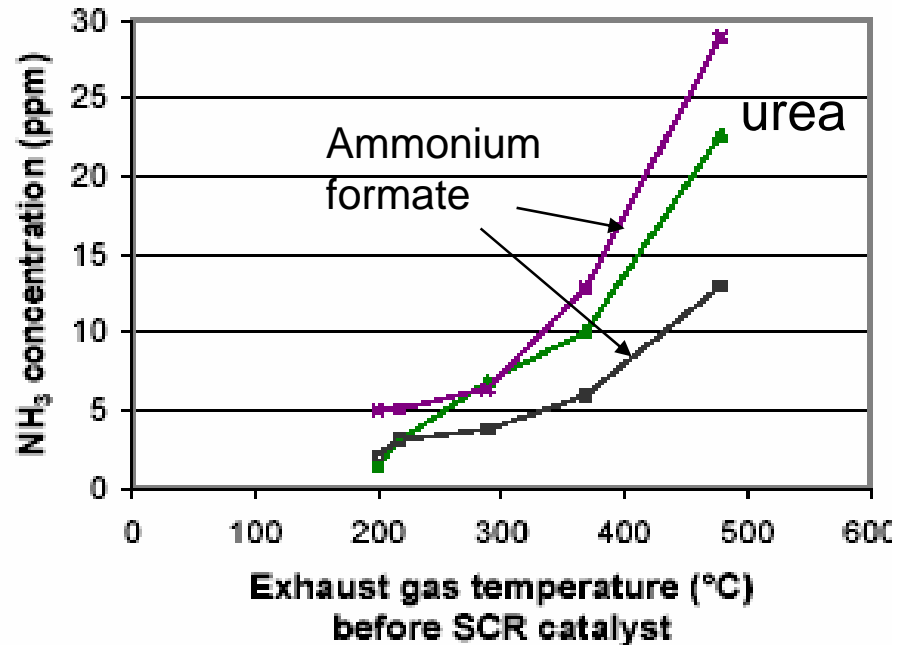
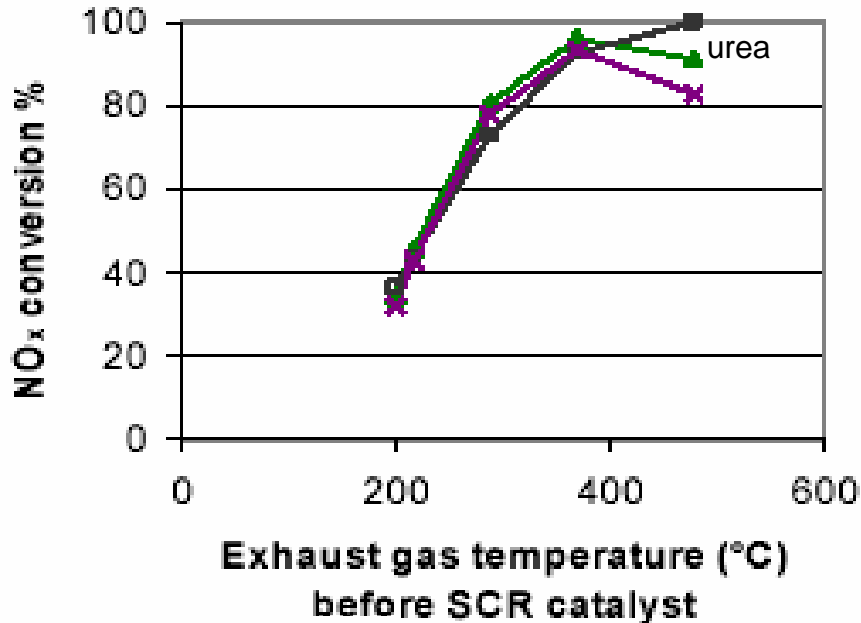


Zeolite catalysts are preferred due to higher efficiency over the temperature range, and due to smaller size.



OBD has three warning: urea level plus alarm, urea quality issue, and system problem.

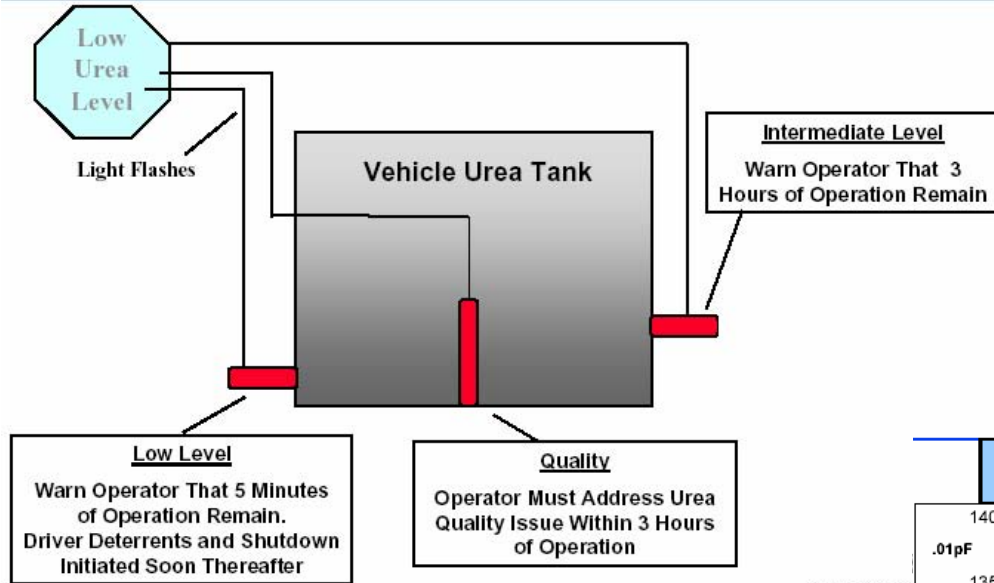
There are a couple approaches to cold climate urea management – heaters and ammonium formate



Ammonium formate solutions have same ammonia content as urea, but significantly lower freezing point

CO emissions increase 50% with formate vs. urea

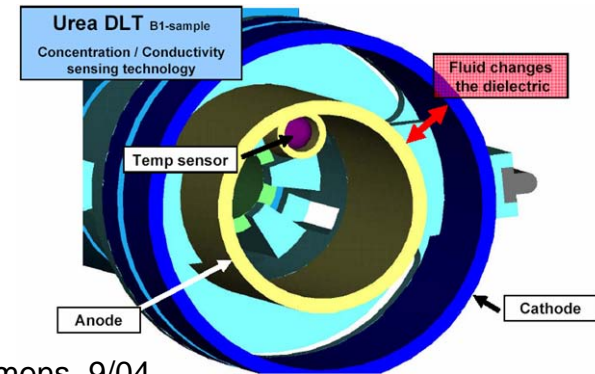
Urea OBD issues, in lieu of a reliable NOx sensor, is moving forward



DaimlerChrysler, DEER 9/04

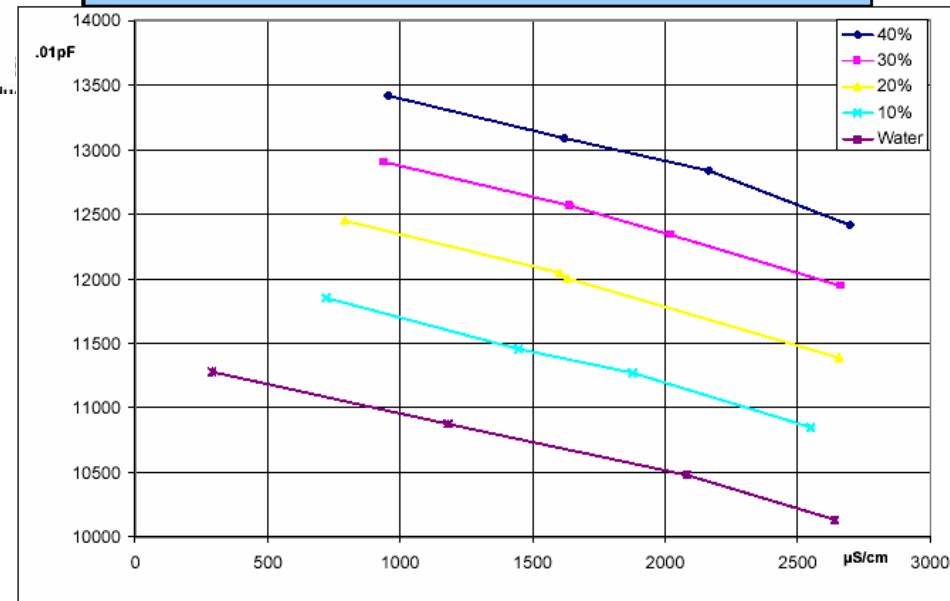
Current Euro IV OBD status:
 Urea tank filled? Consumption correlated to NOx, and 1) Is it urea in the tank? Or: 2) NOx from tailpipe?

Urea quality sensor



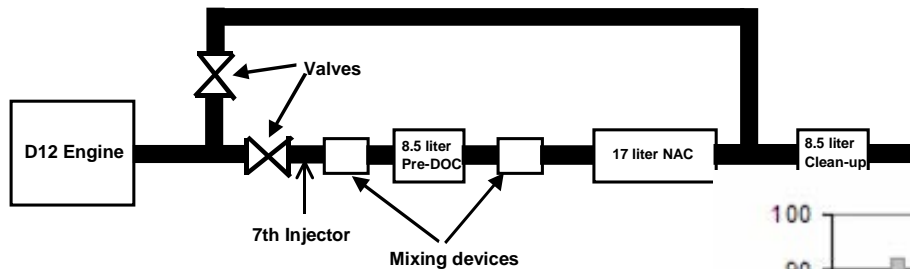
Siemens, 9/04

ϵ_r characteristic vs. Urea concentration at Room temperature

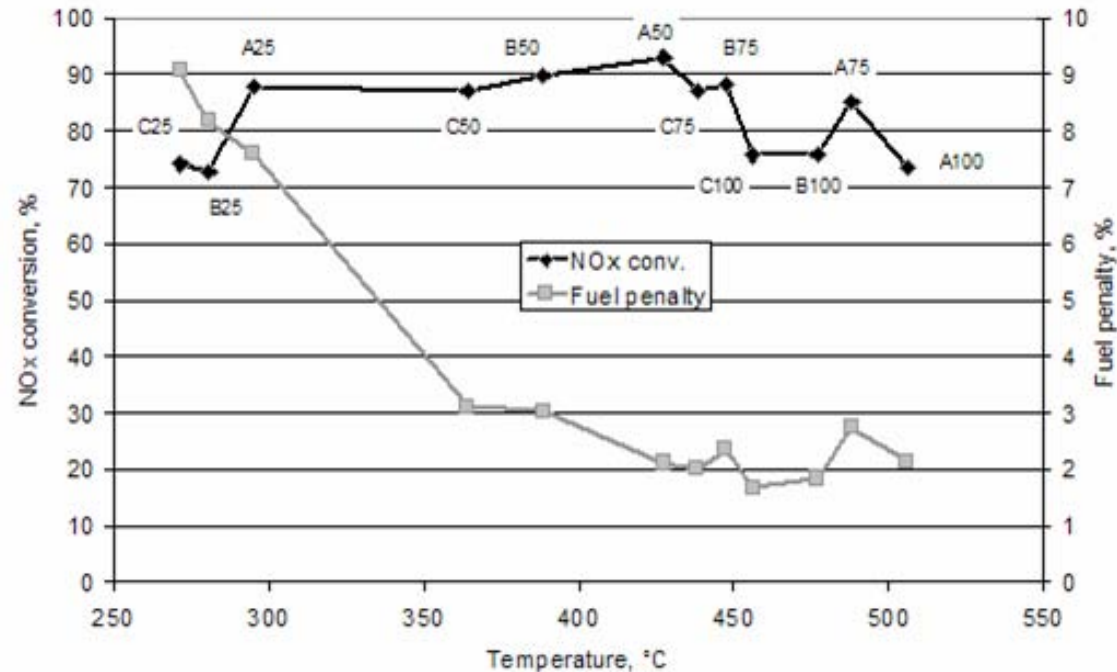


Lean NOx Traps

New HT LNT shows 80% efficiency at 500C in a by-pass system. 2% fuel penalty



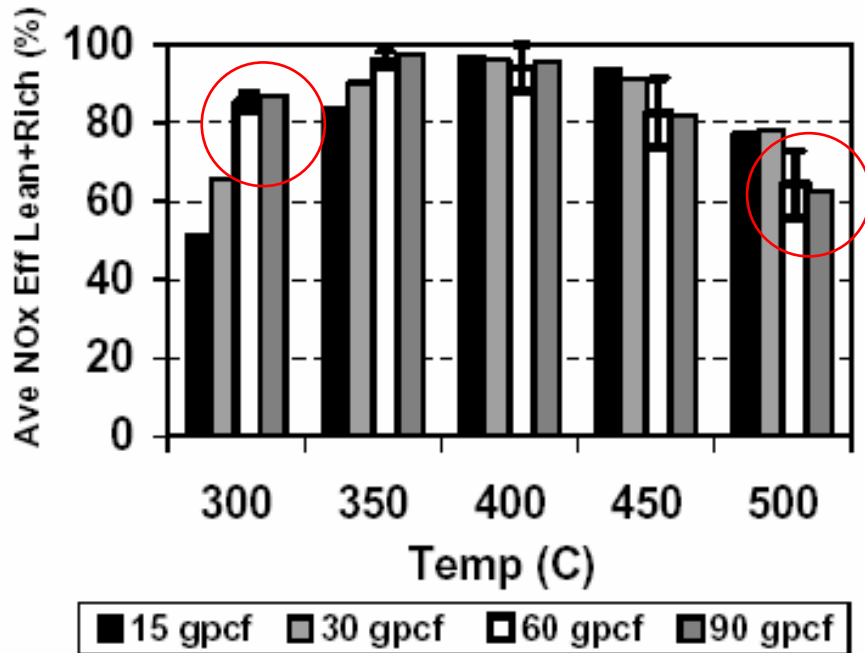
- Desulfation temperatures of 700C
- Little thermal degradation of LNT upon desulfation.



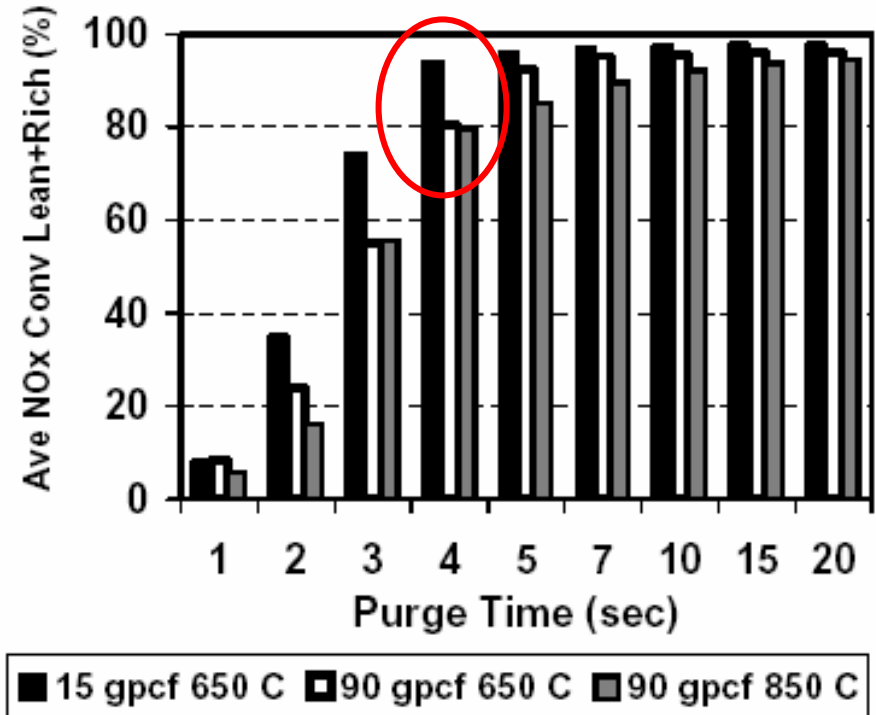
JMI SAE 2005-01-1084

NOx conversion efficiency and fuel penalties with the by-pass system. FP high at low load due to need for heat for LNT.

Higher PGM loadings on LNTs are not necessarily better



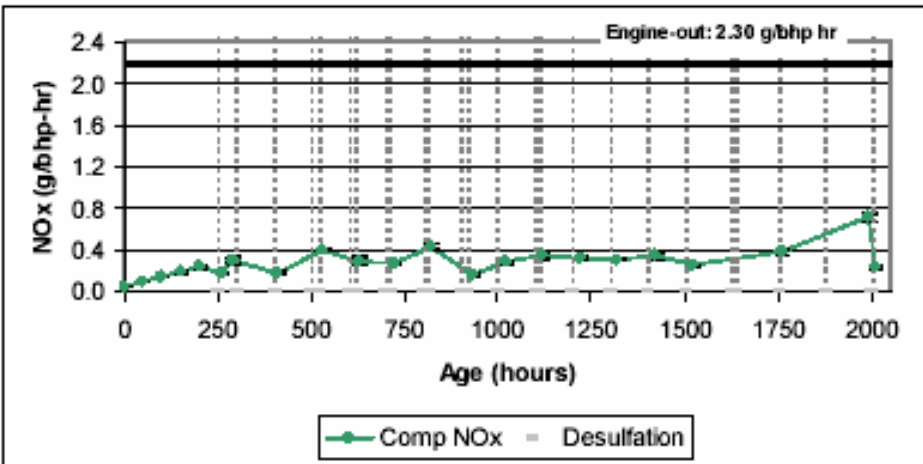
After aging at 650C. At LT, PGM helps NO₂ formation. At HT, 90 gpcf PGM loadings cause nitrate decomposition in lean conditions, dropping capacity. Trend holds to 800C aging. Gasoline application.



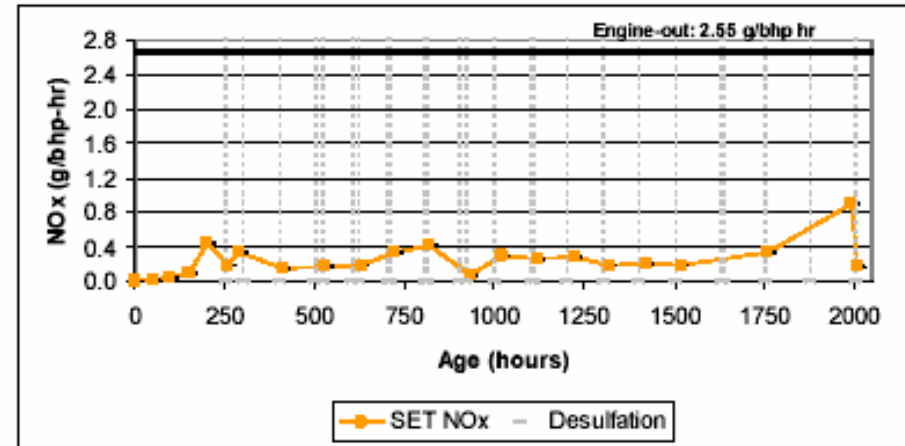
Aging at 650C. Low PGM loading helps NO_x efficiency at 300C at short purge times. High PGM loadings have higher oxygen storage capacity, resulting in more purge being needed.

After 2000 hours of testing, LNT emissions stabilized up to 2000 hours

HD FTP

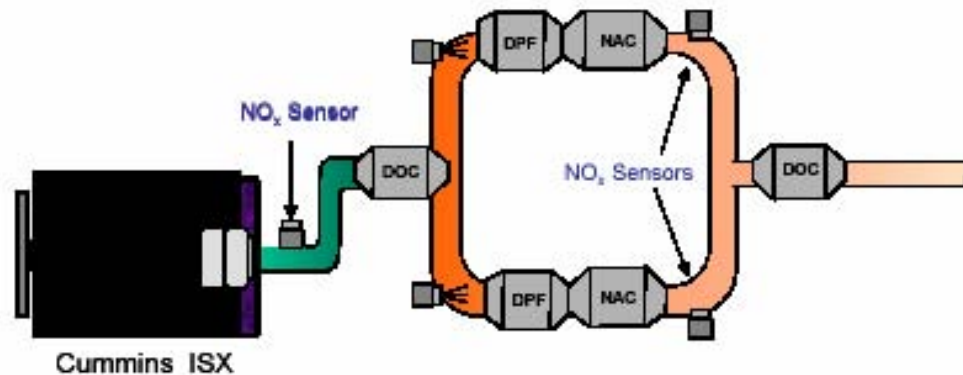


HD S.E.T.



components.

APBF SAE 2005-01-1760



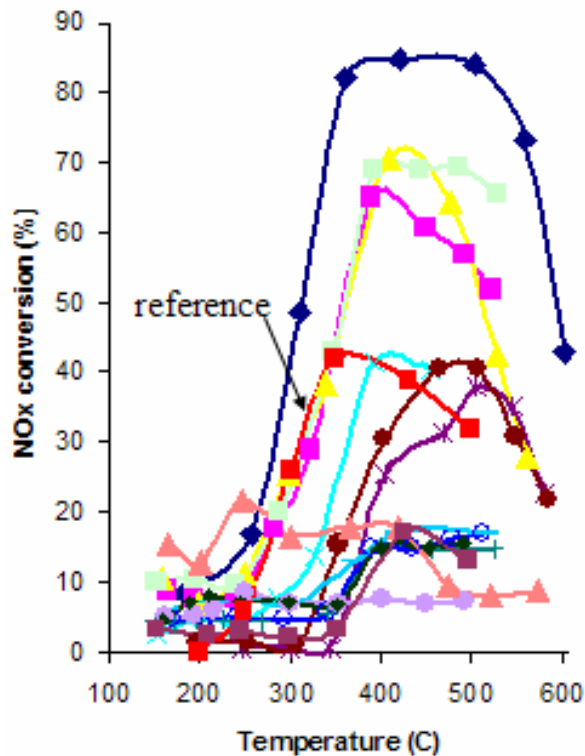
15 liter engine
SVR LNT = 3

LNT management is improving

- Pulsed desulfation (rich lean modulation) minimizes H₂S emission and help thermal management (numerous papers)
- HT in early stages of desulfation helps; low lambda drives later desulfation (Renault SAE 2000-01-1874)
- Desulfation greatly enhanced when both CO and hydrogen are used (Mitsubishi SAE 2004-01-2004-01-0580)
- Dual oxygen sensors can imply state of sulfur loading by looking at HC consumption during NO_x regeneration (Ford SAE 2002-01-0731)
- Adaptive models are used to implement appropriate regeneration (Mitsubishi 2005-01-1090)

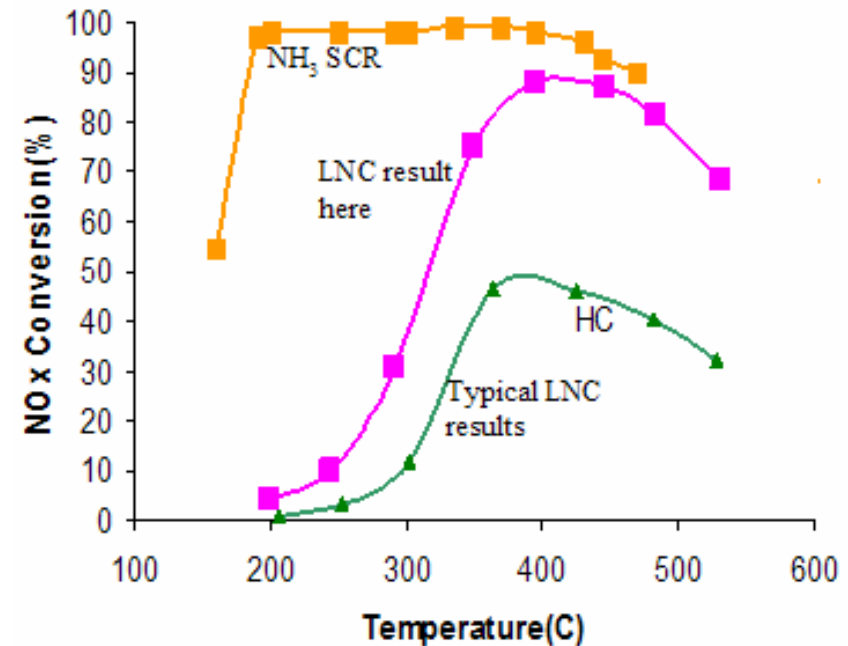
A rapid screen process for LNC compositions is beginning to yield results.

GM, Gordon Conference 8/05



Extrudate results. More than 4500 LNC compositions have been evaluated. Some give superior performance to the standard.

A leading candidate shows resistance to sulfur, good selectivity, and decent performance at modest C/N ratios.



Low temperature results need improving, but high temperature results are favorable and significantly better than standard.

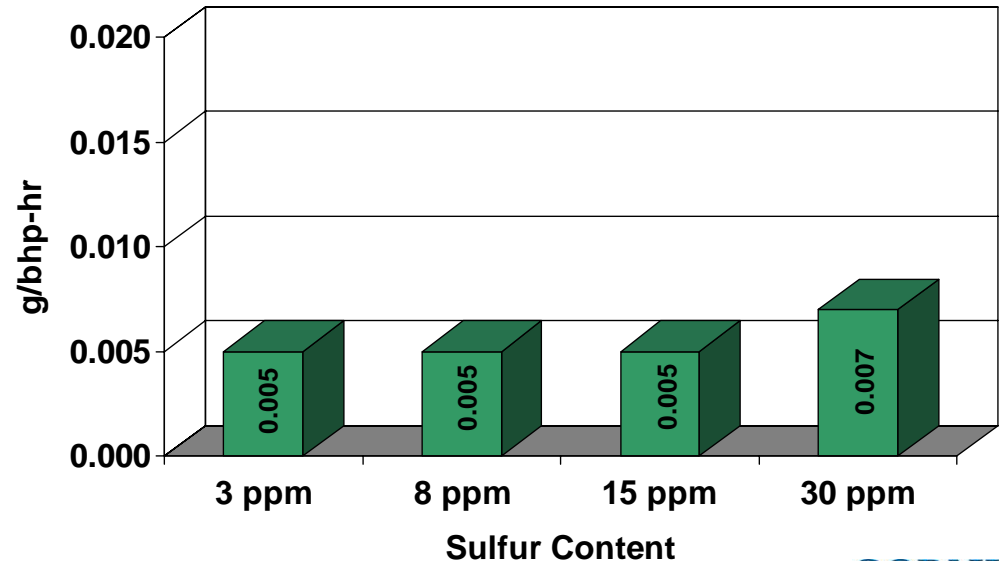
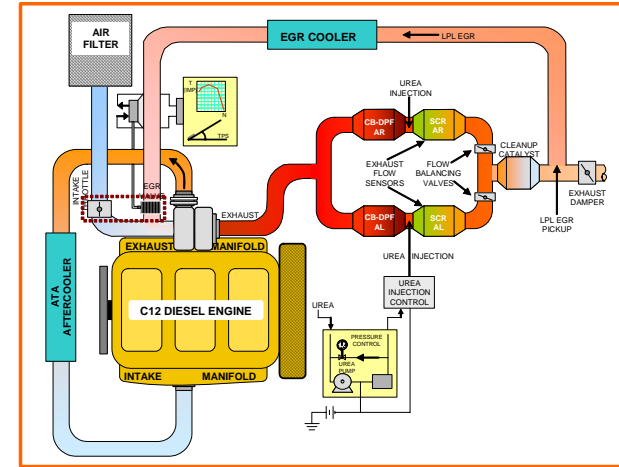
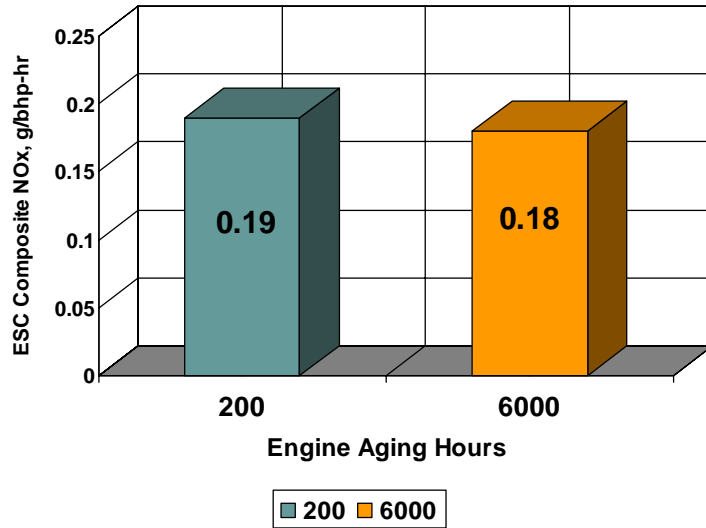
What is the prognosis NOx control?

- SCR is closest today to meeting 2010 HD requirements
 - Zeolites looking good as alternative to vanadia
 - HT durability seems solvable
- LNT need to solve HT deficiencies and PGM cost issues
 - Need efficiency out to 550C without binding stubborn sulfate
 - Attractive for LD applications
- LNC shows “renaissance” with hydrogen and new formulations show promise

Given continued rapid developments in LNT and LNC, but short timeframe to 2010 decisions and maturity of SCR, SCR is preferred for any HD applications, but with the expectations that HC-based technologies might be better alternatives in the future. However, once installed and optimized, SCR will be tough to beat.

Integrated systems

A retrofit SCR+DPF system (2007 technology+SCR) hit US2010 after 6000 hours of aging



APBF-DEC Heavy-Duty SCR Project
Slide courtesy of SwRI

EPA's "Clean Diesel Combustion" technology is on a minivan prototype. Bin 5 w/o NOx aftertreatment, 30 mpg vs. 32 mpg (stock) city fuel economy.

Vehicle Performance

Engine Test	Fuel Economy (mpg)	HC (g/mi)	CO (g/mi)	NOx (g/mi)	PM (g/m)
Stock					
FTP city	32	0.05	0.10	0.8	0.028
FTP hwy	49	0.01	0.02	0.7	0.027
US-06	32	0.01	0.03	1.8	0.069
Tier 2, Bin 5 (120k mi)					
US-06 (NOx+HC)		0.09	4.20	0.07	0.010
CDC on Vehicle					
FTP city	30	0.20	0.68	0.08	0.001
FTP hwy	46	0.03	0.02	0.06	0.0004
US-06	30	0.05	0.05	0.14	0.008

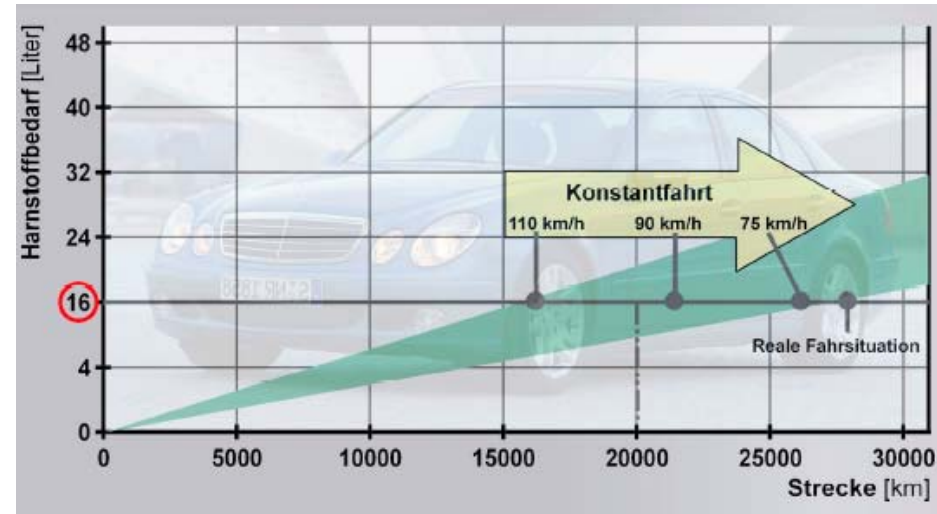
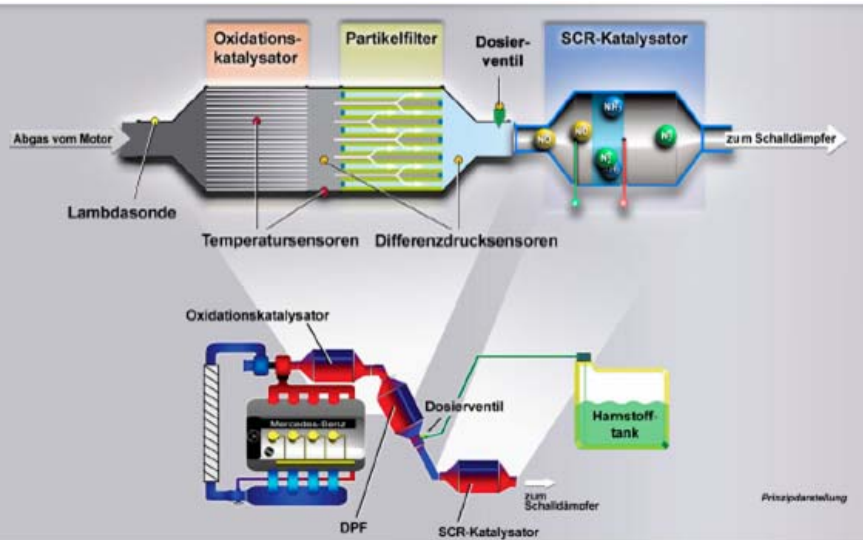
4200 lbs chassis weight, 1.9L diesel engine, 6-spd MT



4200 pound minivan with a 1.9 liter diesel engines hits Tier 2 Bin 5, and achieves 30 mpg (city), without NOx aftertreatment.

- LP EGR after DPF provides large amount of clean EGR for low NOx
- Advanced turbocharging and/or supercharging needed to provide high boost.
- Advanced FIE promotes fast combustion for manageable smoke; stratified charge

DaimlerChrysler generally describes their DPF+SCR system

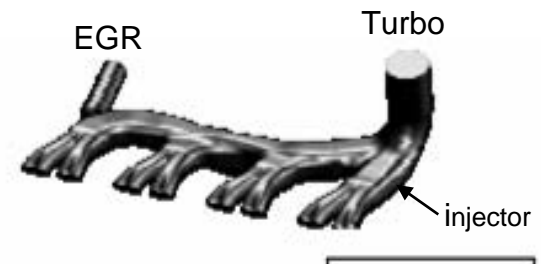
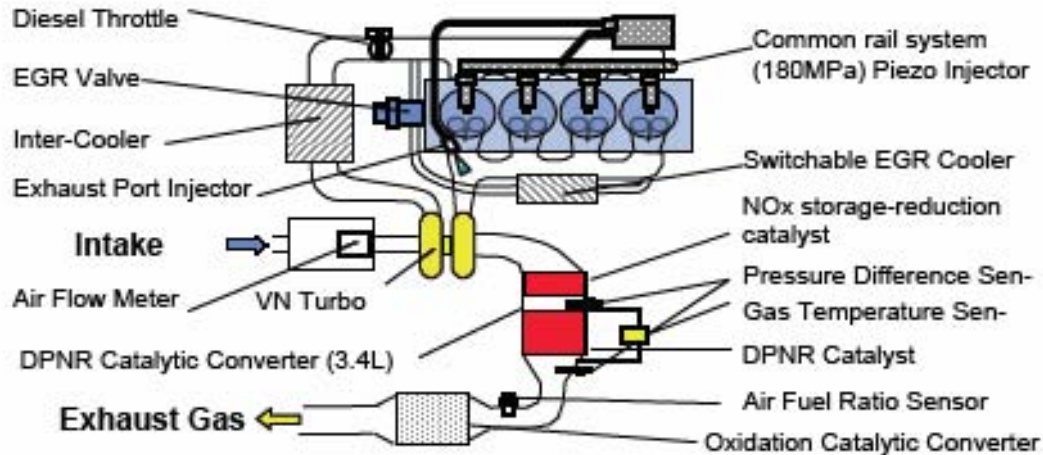


The SCR system follows the DOC+DPF. Urea comes from a remote tank, and is injected right after the DPF.

About a 1% urea consumption is anticipated. A 16 liter tank will be filled at oil drain intervals and can last 16,000 to 27,000 miles.

A fleet is going to US EPA for evaluation. Could be commercialized before MY09.

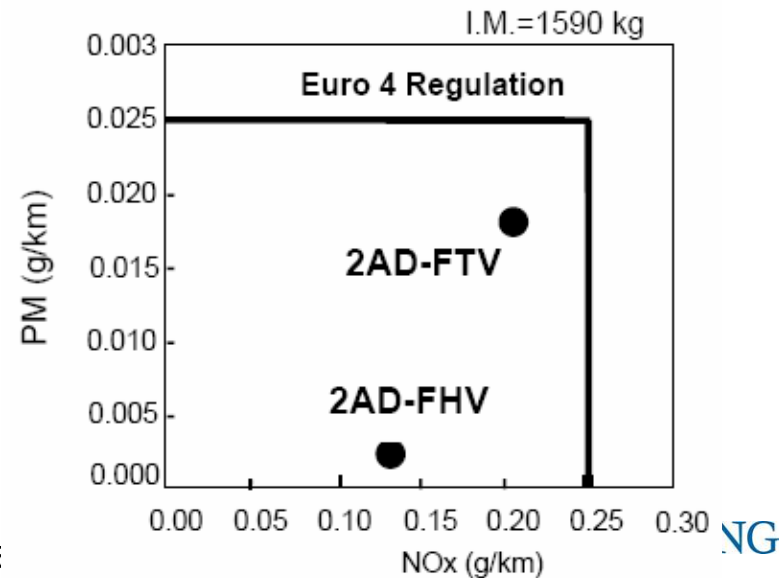
Toyota introduces their redesigned 2.2 liter engine with DPNR



A new exhaust manifold design minimizes the amount of auxiliary fuel that goes to EGR. EGR DOC taken out.

Third generation 2.2 liter engine with DPNR has an increased DPNR SVR from 1.2 to 1.5. Switchable EGR cooler is added.

Euro IV easily attained (3 mg/km PM, 130 mg/km NO_x. With DOC only, and similar engine, 18 mg/km PM, 220 mg/km NO_x.)



Summary

- Filters are making significant progress with sophisticated regeneration schemes and continuous improvement in back pressure and durability.
- NOx solutions look good.
 - HD NTE dictates 80% NOx efficiency at 500C
 - Zeolite SCR is used in Japan
 - HT LNTs emerging
- Integrated solutions are hitting Bin 5 and US2010