CORNING

Diesel Emission Control Review

Tim Johnson
DEER 2010
Detroit

Summary

- HD regulations being wrapped up, next regs being contemplated
- Further tightening of criteria regs expected. California is completing LEV3 proposal stage. EPA considering Tier 3.
- CO_2 mandates are proposed for HD
  - Onset of another major regulatory-driven technology evolution
- Engine technologies are addressing engine-out NOx and FC
  - control, LT thermal management, advanced combustion approaches
- SCR is addressing “secondary” issues:
  - LT issues: ammonia sources and urea inj; NH3 storage formation, mechanisms.
  - Catalyst HT durability
  - More understanding on SCR+DPF
- New LNT compositions and designs are shown.
  - Better performance, lower cost
  - LNT+SCR systems advancing
- DPF regen, substrate properties, material, and catalysts advancing.
- DOC catalysts performance characterized
  - NO2
  - LDD CO emissions can be difficult

CORNING

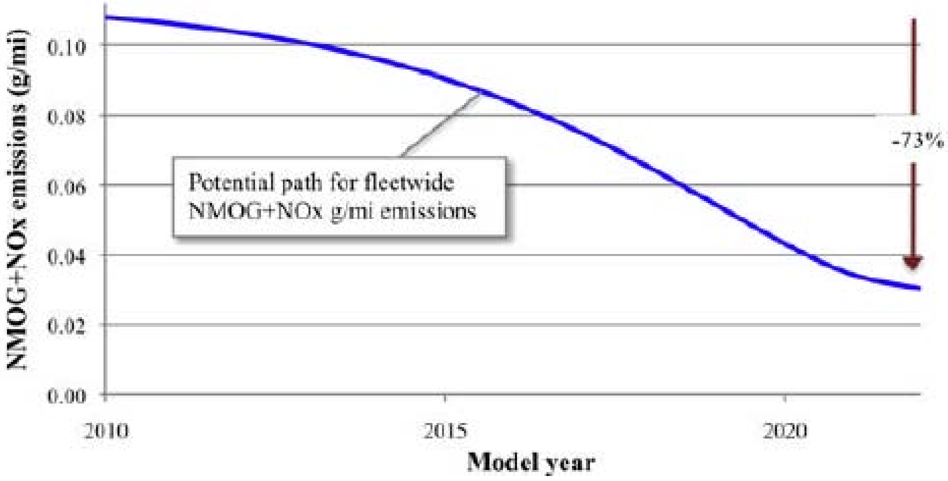
Regulatory Issues

Emerging HD regulatory issues

- Euro VI PN comitology being finalized.
  - 6×10^{11} #/kW-hr on the WHTC
    - Quite tight for clean filters, but pre-conditioning for up to 125 hrs is allowed
- Japan HD will harmonize with Europe in 2016-17
- Off-cycle emissions issues emerging
  - European report shows high urban emissions for SCR trucks
- Next stages of European non-road regs being contemplated
  - Workshops and committees formed

CARB-Proposed LEVIII Standards for 2014-2022

SULEV Fleet Average NMOG+NOx.



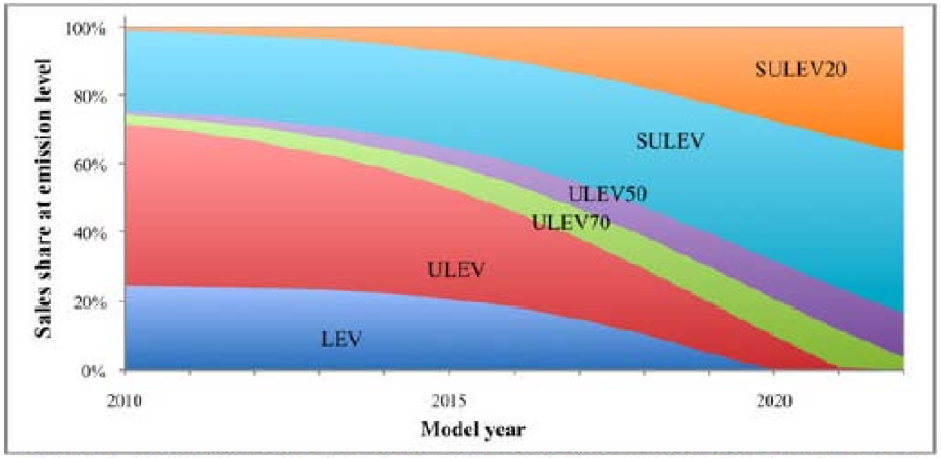


Figure 3. Illustration of sales share of by emission certification level to meet proposed NMOG+NO$_x$ standard

Possible scenario for fleet average NMOG+NOx standards.

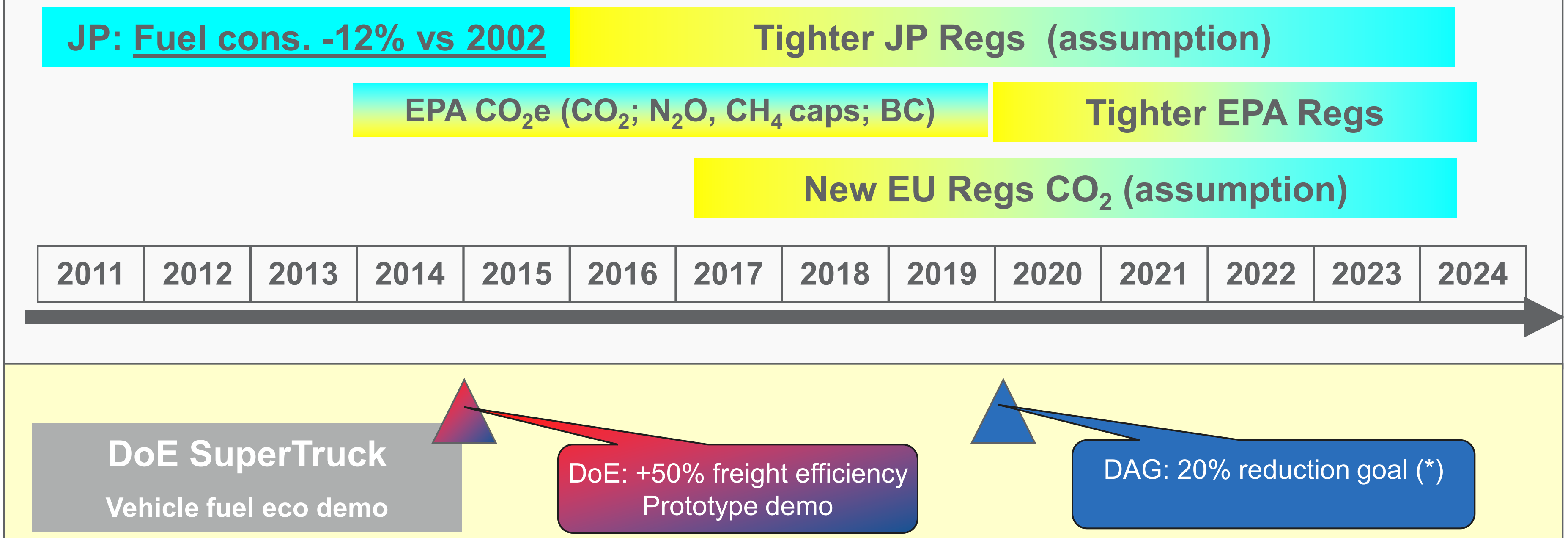
A possible scenario to meet yearly fleet average emissions targets.

PM reduced 70% to 3 mg/mi. Lower values are difficult to measure, and CARB wants a different PN reg that isn't ready yet

EPA will likely follow CARB with a Tier 3 LD regulation.

HD CO_2/Fuel Consumption Reduction: Different approaches

JP: Fuel consumption, EU: CO_2 focus(?), EPA: CO2 focus



JP: <u>Fuel cons. -12% vs 2002</u>

Tighter JP Regs (assumption)

EPA CO_2e (CO_2; N_2O, CH_4 caps; BC)

Tighter EPA Regs

New EU Regs CO_2 (assumption)

2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024

DoE SuperTruck

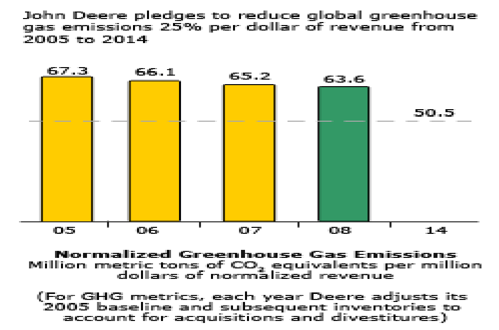
Vehicle fuel eco demo

DoE: +50% freight efficiency
Prototype demo

DAG: 20% reduction goal (*)

DAG's "Shaping Future Transportation" (*)

"Road to Emission Free Mobility (LD & HD)"(*)



John Deere pledges to reduce global greenhouse gas emissions 25% per dollar of revenue from 2005 to 2014

Normalized Greenhouse Gas Emissions
Million metric tons of CO_2 equivalents per million dollars of normalized revenue

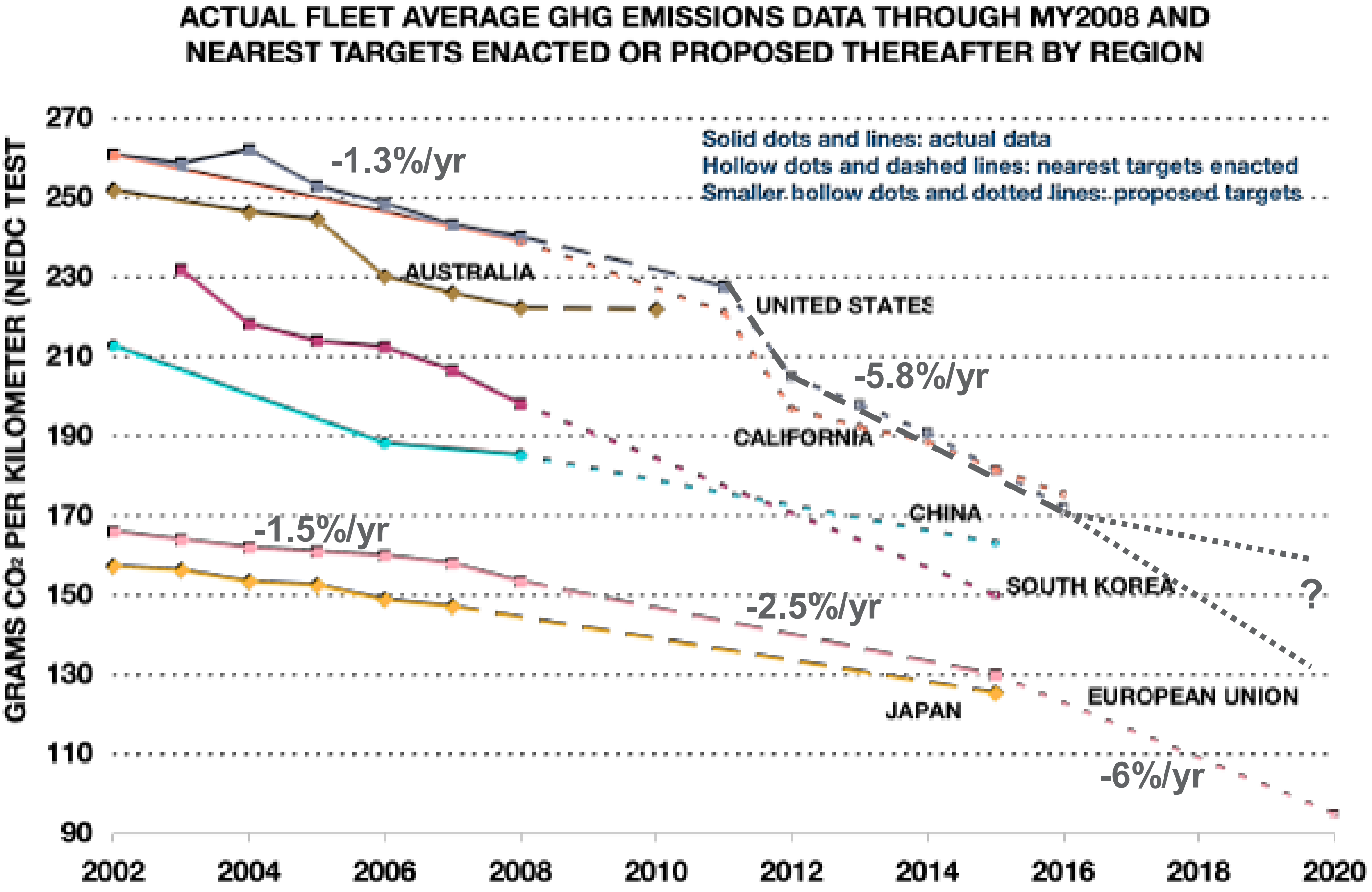
(For GHG metrics, each year Deere adjusts its 2005 baseline and subsequent inventories to account for acquisitions and divestitures)

CO_2/Fuel Eco - Government / OE Initiatives

(*): <u>www.Daimler.com</u>, MTZ 1-'09, <u>http://www.cat.com/sd2009</u>, http://www.deere.com/en_US/globalcitizenship/stewardship/metrics.html

Emerging CO_2 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 FLEET AVERAGE GHG EMISSIONS DATA THROUGH MY2008 AND NEAREST TARGETS ENACTED OR PROPOSED THEREAFTER BY REGION

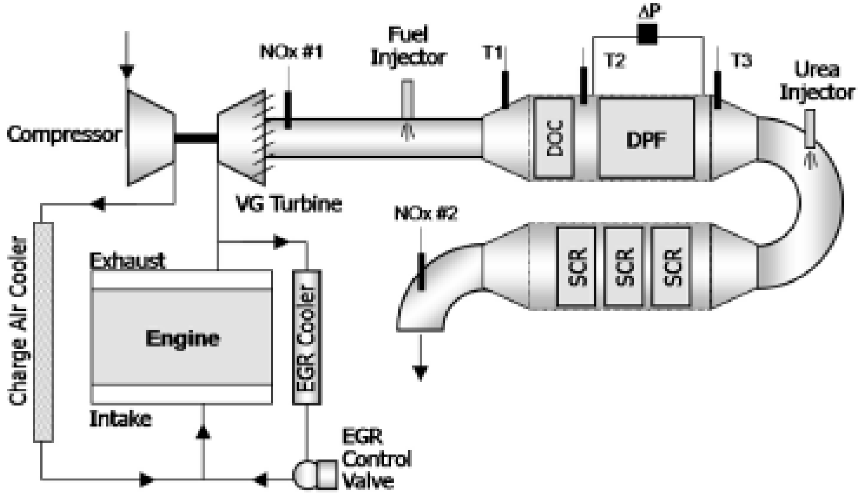
Solid dots and lines: actual data
Hollow dots and dashed lines: nearest targets enacted
Smaller hollow dots and dotted lines: proposed targets

TheICCT.org, updated 11/09

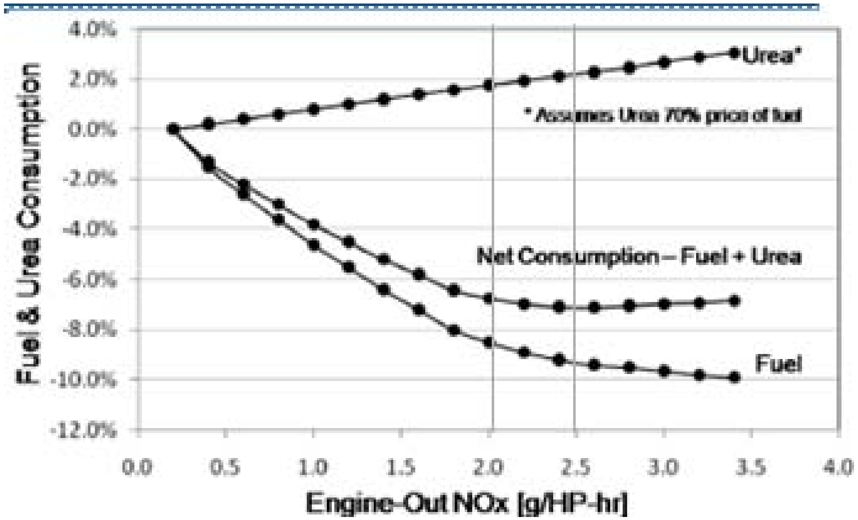
CORNING

Engine Technologies

Hardware and general strategy for meeting US2010 are described.



The engine is equipped with VGT to allow optimum EGR control, and 2200 bar CR injection.



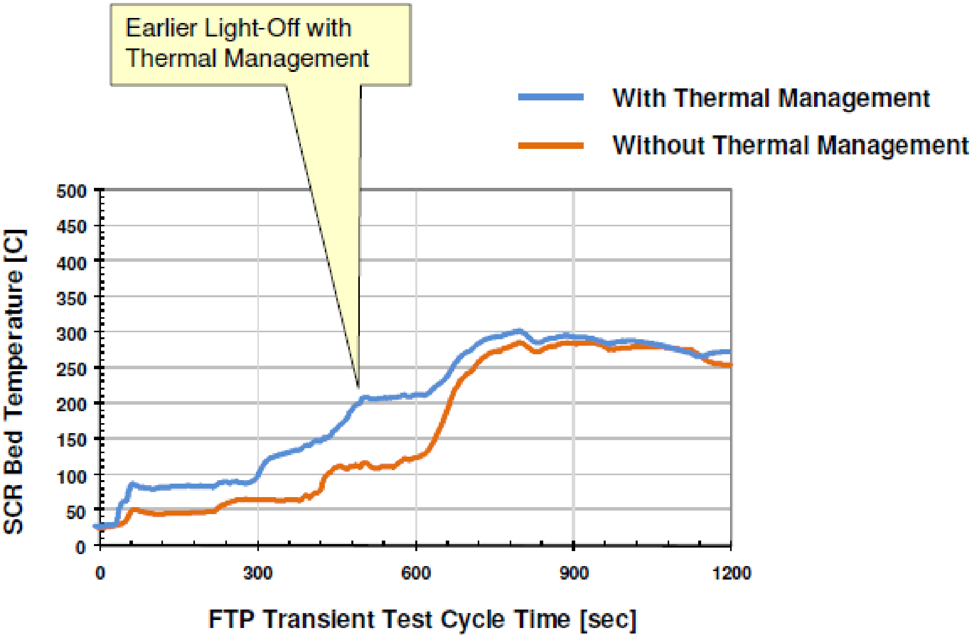
Operating strategy minimizes fuel and urea consumption, with engine-out NOx from 2.0 to 2.5 g/bhp-hr being optimum.

Cummins, AVL PM Forum, 3/10

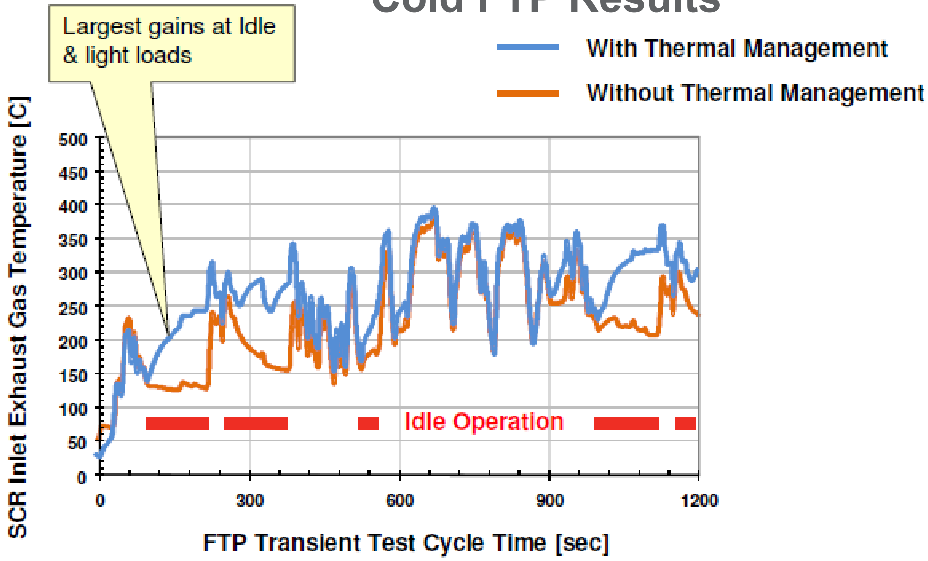
Thermal management is used to reduce cold or low-load NOx. Minimal fuel penalty possible.

Thermal Management

- Control of fuel injection and air handling parameters
- Utilizes the flexibility of the XPI common rail and variable geometry turbocharger
- Allows faster warm-up and SCR light-off
- Minimizes cooling effects of idle and light load operations


Earlier Light-Off with Thermal Management

Cold FTP Results


Largest gains at Idle & light loads

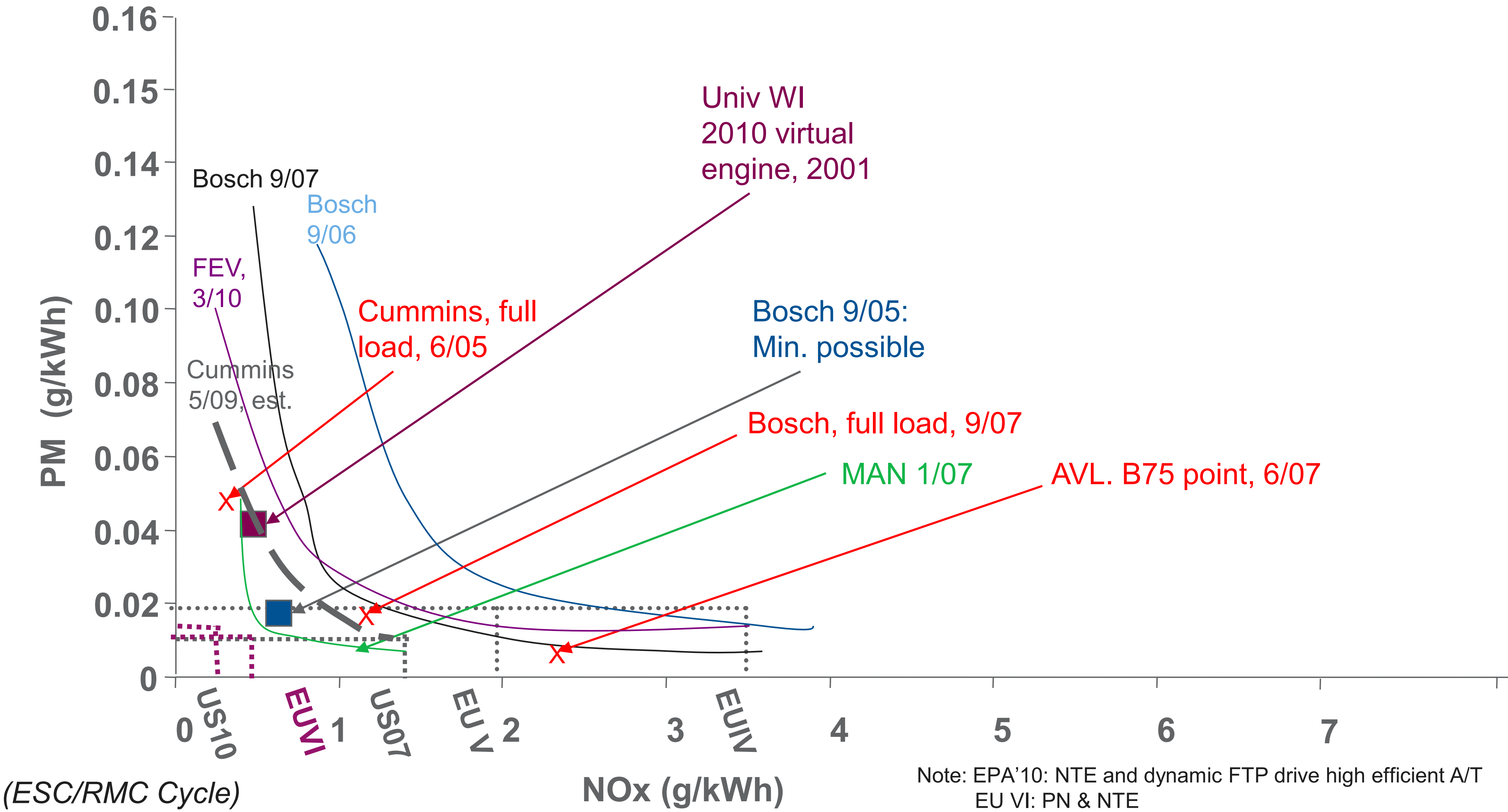
T up from 150 to 250C in 2 minutes under idle conditions.

FTP Phase	Without Thermal Mgt	With Thermal Mgt
Cold Cycle	0.364 g/HP-hr	0.301 g/HP-hr
Hot Cycle	0.357 g/HP-hr	0.031 g/HP-hr
Composite	**0.358 g/HP-hr**	**0.069 g/HP-hr**

Cummins, MinNOx Conf, 6-10

Historical research engines help predict future production engine capability.

Significant engine NOx threshold at ~0.2-0.3 g/kW-hr NOx. Very low PM at higher NOx regimes.

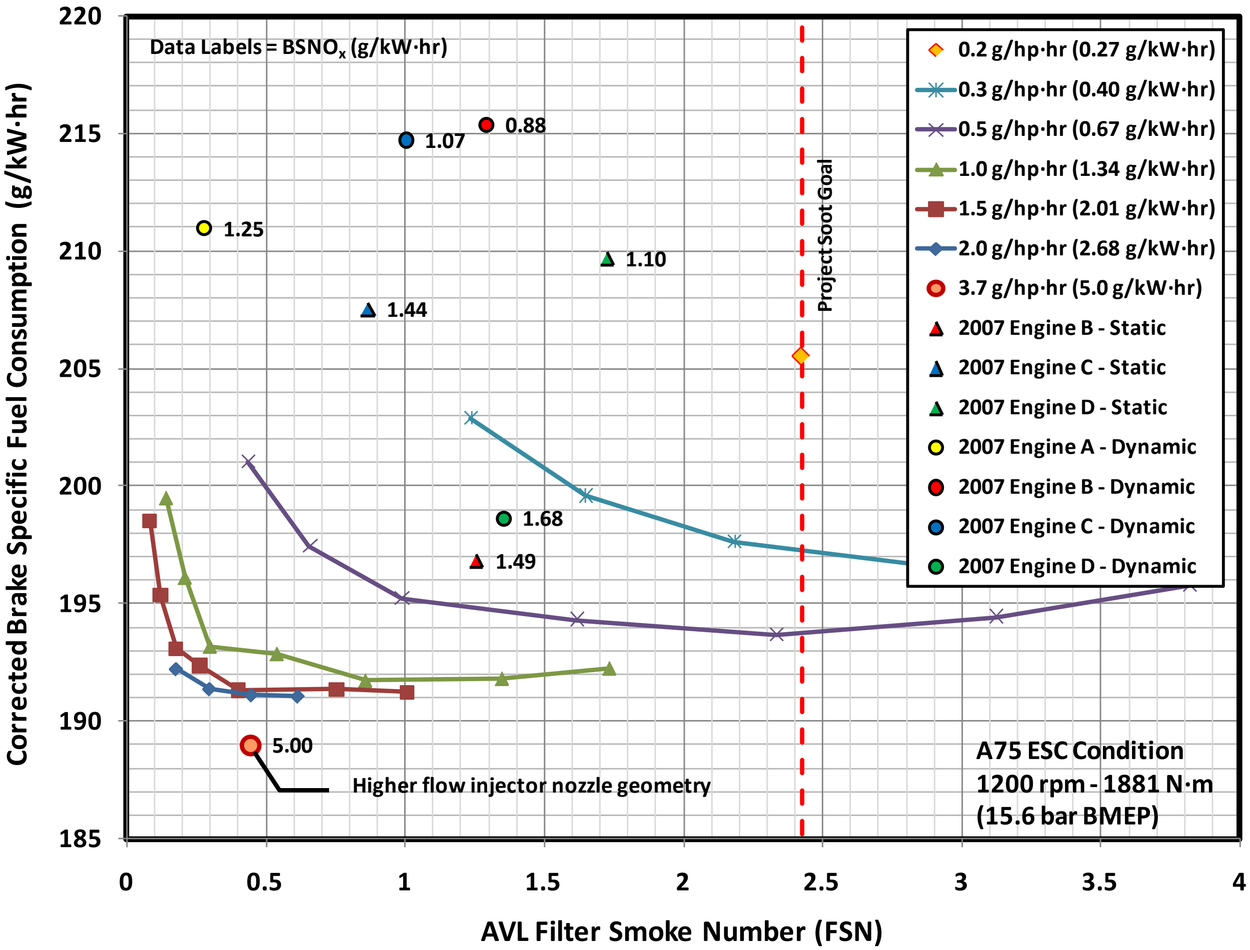


Note: EPA'10: NTE and dynamic FTP drive high efficient A/T
EU VI: PN & NTE

Massive EGR Engine – No NO_X Aftertreatment

Performance Comparison at Higher NOx levels

- Results compared with four 2007 heavy duty diesel engines
- Engine operation has been optimized for low engine speeds
- At similar NO_x levels the Massive EGR provides dramatically improved performance
  - Massive EGR engine was not optimized to operate at higher NOx levels, so further improvements are still possible

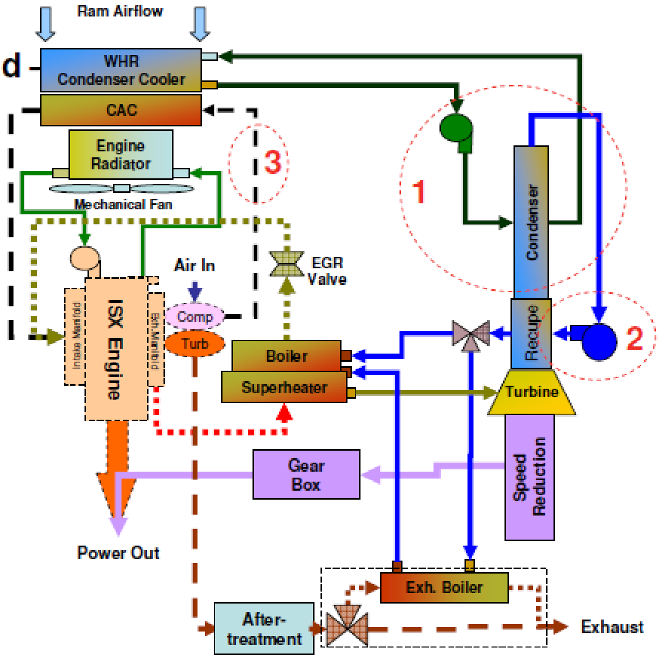


SwRI, Clean Diesel 5 Consortium 8/10

Second generation waste heat recovery system shown.

Improvements gain 1.4% FC impact, on top of 6.2% for generation 1.

1. **Replaced water-cooled condenser for air-cooled** – gained 0.2%
2. **Replaced 2-stage, centrifugal pumps with single-stage positive-displacement pump** – gained 0.6%
3. **Added Charge Air heat recovery** – gained 0.6%
4. **5% reduction in power transfer parasitics with MORC**



Second generation Organic Rankine Cycle (ORC) improvements include the condenser, pumps, added heat source, lower parasitic losses, and new working fluid.

Future Directions

- System Architecture and Controls
- Turbine Expander
- Expander to Engine Geartrain
- Heat Exchangers – on and off engine
- Feedpump and instrumentation
- Fluid Development (low GWP alternatives)
- Vehicle Packaging
- Cost Focus

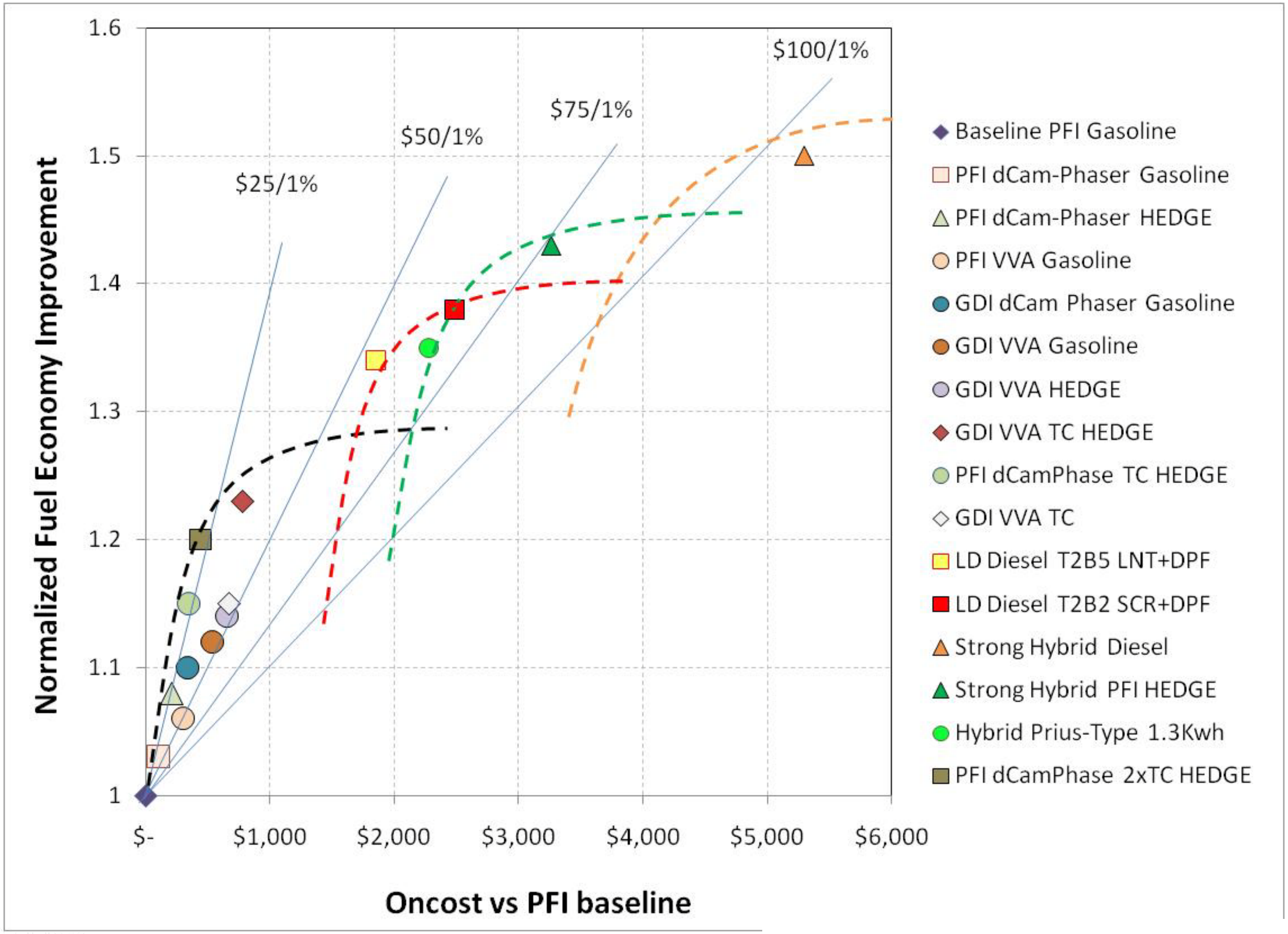
Cummins, Emissions 2010 Conf, 6/10

WHR BTE Benefit
- Charge Air Heat Recovery +1.0%
- Exhaust Heat Recovery +3.0%
- EGR Heat Recovery +2.0%
- Vehicle/ Condenser Capacity +1%
- Component Efficiencies +1%
- Working Fluid +1%

Potential benefit of 9% energy from WHR. 6.2% realized in generation 1.

20% improvements in CO2 cost about $25-$50/%. 30-45% improvements will be $50-$100/%.

Gasoline technologies might peak out at 25-30% improvement, diesel at 40%.



The coming CO_2 regulations will be more difficult to attain than the criteria pollutant regulations.

Engine research should focus on CO_2 reductions. Aftertreatment solutions available for any challenge.

- Three-way catalysts: 1995 vs. 2010
  - Cost -50 to -70%
  - Emissions -98%
- SCR: 2004 vs. 2010
  - Cost -20%
  - Emissions -75%
- LNT: 2005 vs. 2010
  - Cost –70%
  - Emissions -75%
  - Fuel consumption -30%
- DPF: 2003 vs. 2010
  - Cost -50%

Most significant challenge: LT lean deNOX

•LT NH3 injection and thermal management

•LNT + reformer

• Cu-zeolite SCR with NH_3

• pre-turbo components

Evolution trends: Performance improvement at similar cost (like electronics), then more cost reduction while enhancing performance.

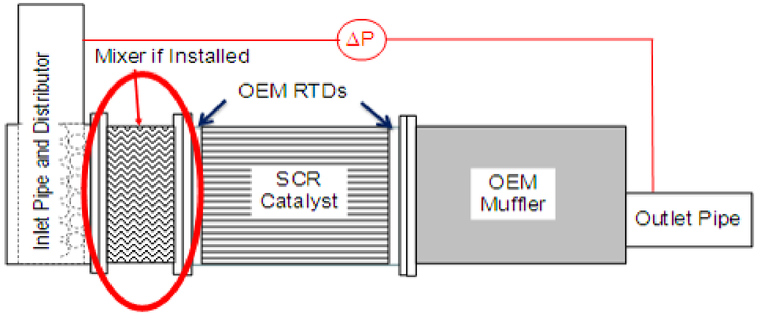
* These are rough estimates of cutting edge improvements to illustrate trends. More rigor is needed to firm these values

CORNING

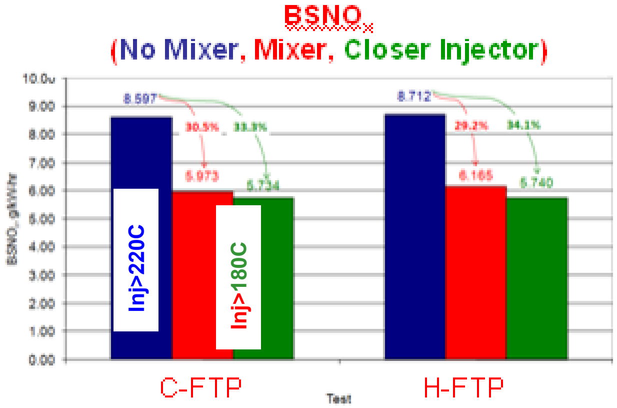
SCR

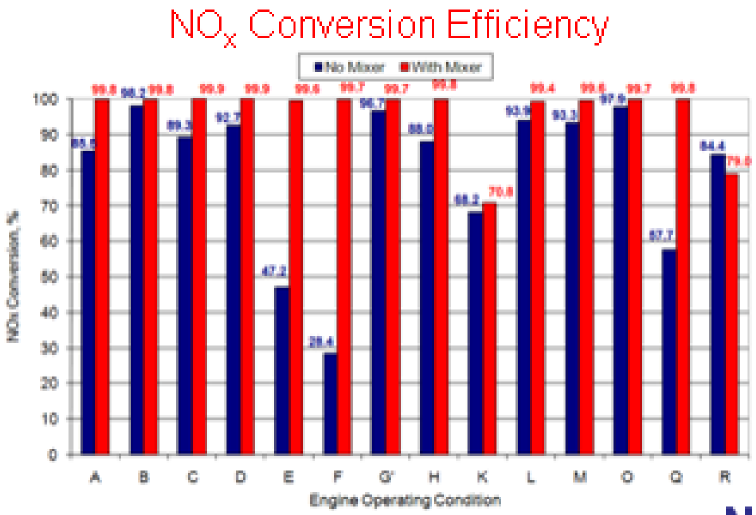
SwRI, SAE 2010-01-1185

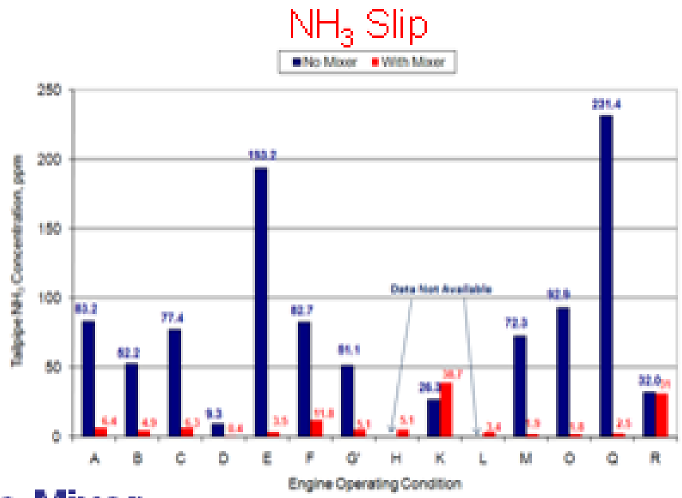
New mixer allows urea injection at T>180C



Mixer has low pressure drop and high surface area. 4.8% max pressure drop in ESC


BSNO$_x$
(No Mixer, Mixer, Closer Injector)

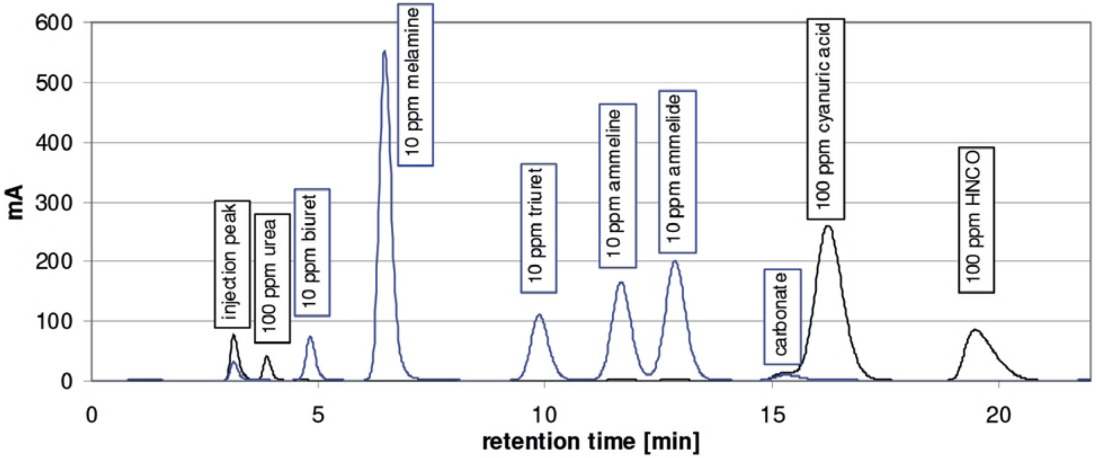

NO$_x$ Conversion Efficiency


NH$_3$ Slip

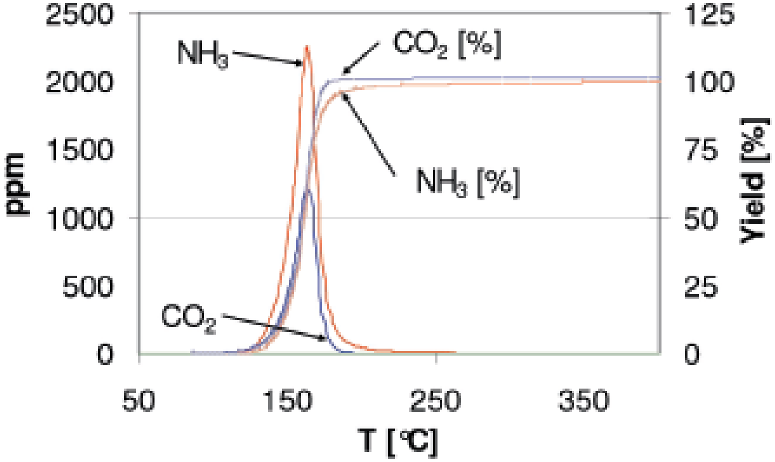
- **No Mixer**
- **Mixer**

The new mixer with revised calibration shows higher efficiency than without at all points. Point E is 181C; F is 225C.

Urea decomposition products are measured using a new thermal/gas analysis procedure. TiO2 is an effective urea decomposition catalyst.



Urea decomposition products released into a flowing model gas stream. Heat rate 10Cº/min, 40-550ºC.

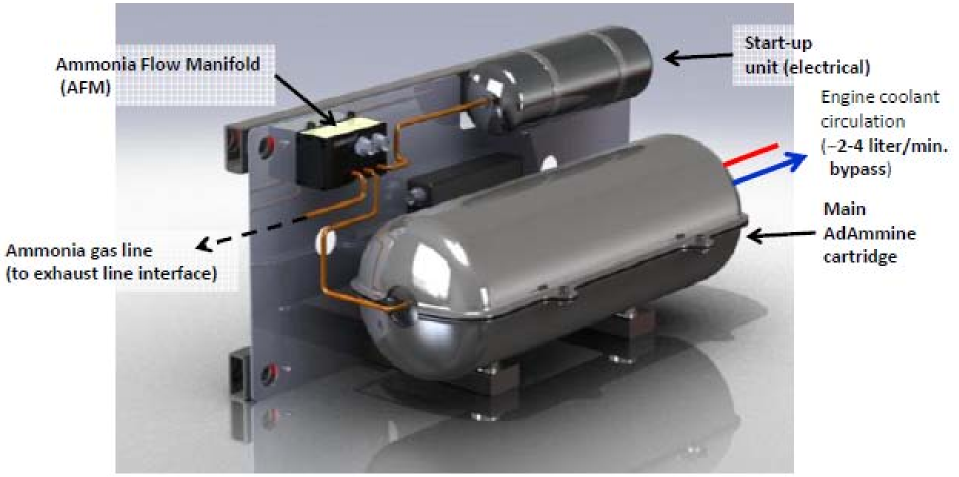


Urea decomposition on a TiO2 catalyst. No by-products were formed. Urea decomposition is not purely a thermal process.

- Biuret decomposition NH3 peak is at 160C.
- Cyanuric acid and melamine NH3 peaks are at 250C.

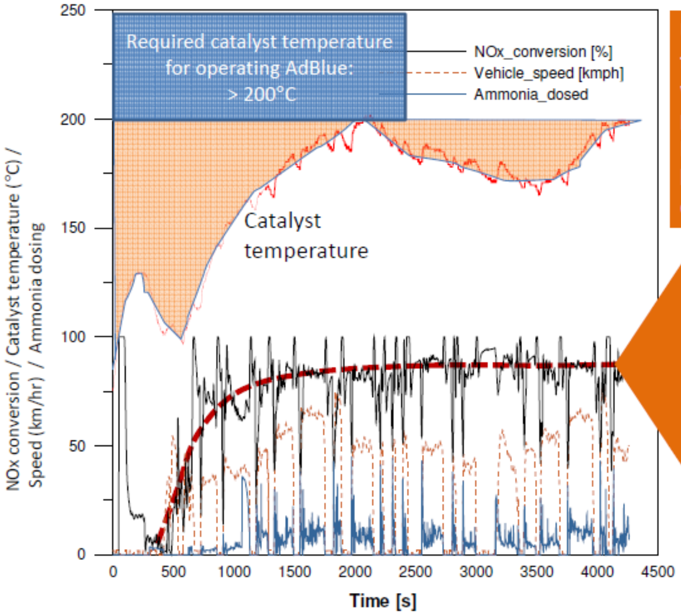
PSI, AVL PM Forum, 3/10

Update on ammonia adsorption SCR. First commercial contract. Production trial in 2011.



ASDS-2/HD: Engine coolant system for MD/HD

- Main cartridge(s) is approx. 16 liters
- Modular system concept
- Max. peak flow of ammonia: 11 g NH_3/minute.
- Max. steady state flow: 9 g NH_3/minute
- AdAmmine cartridge with ~7kg available NH_3.
- Modular system configuration possible

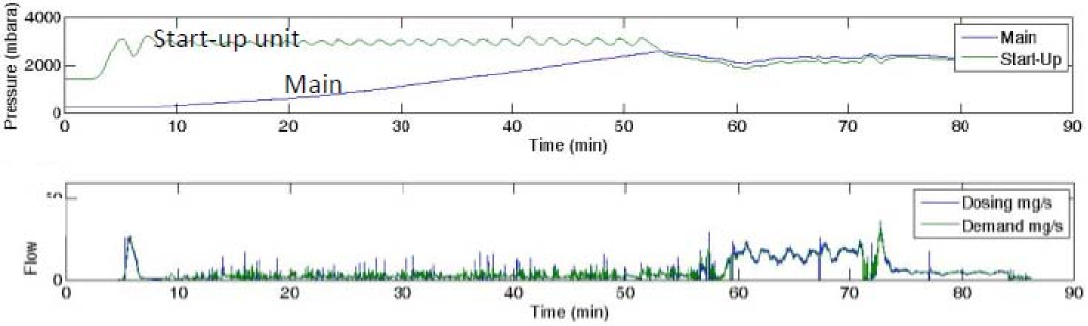


Urban driving pattern for more than one hour with reliable NO_X performance. Performance enabled by gaseous ammonia dosing.

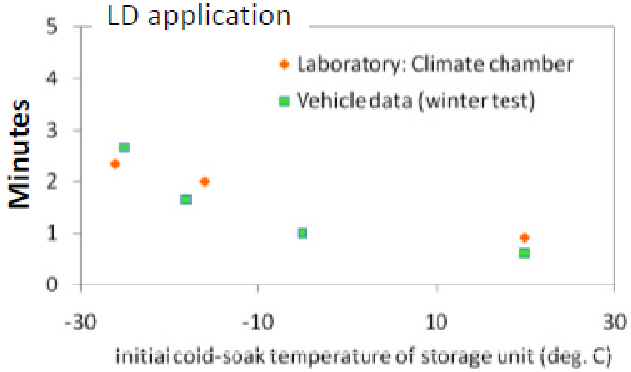
High NO_X conversion possible with continuous cold exhaust temperature using AdAmmine-SCR

Amminex, CTI SCR Conf, 7-10

HD cold start conditions: -10 °C



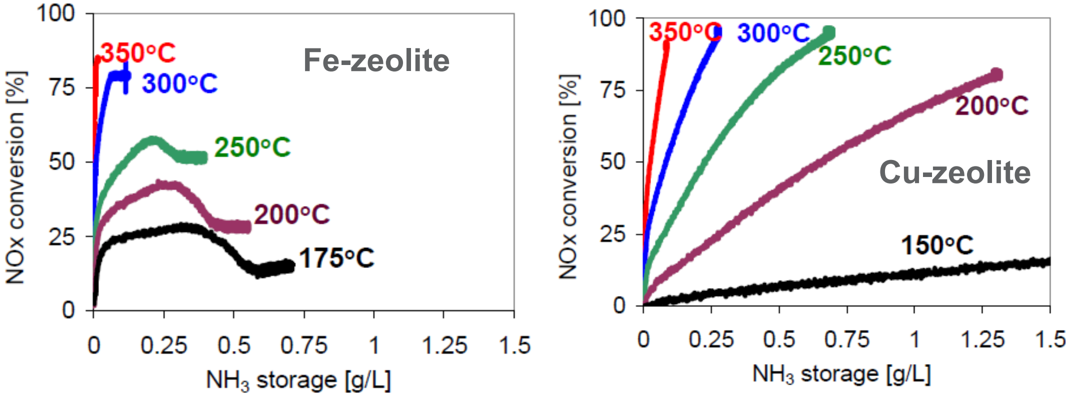
Unit heat-up time



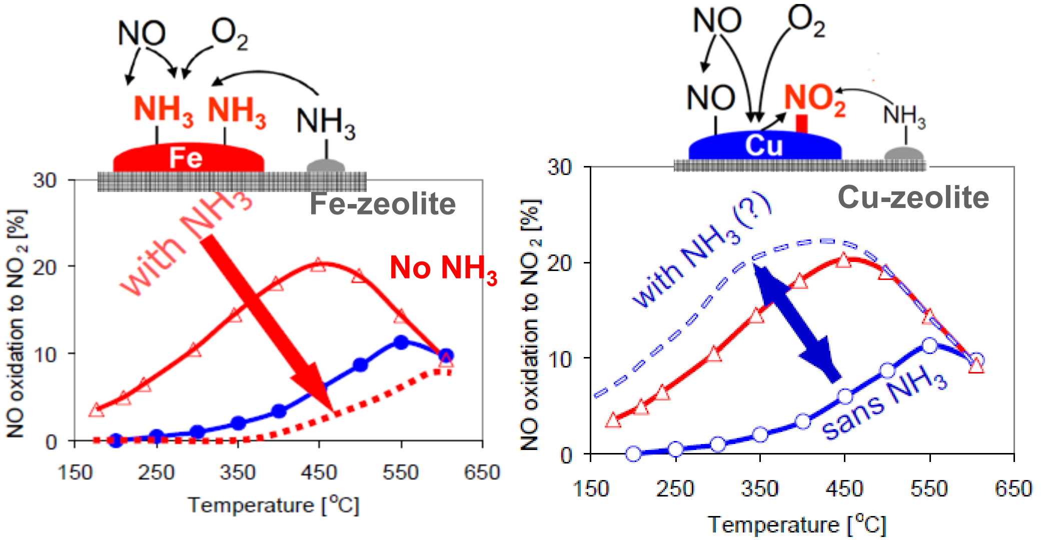
Cummins, SAE 2010-01-1182

Better transient efficiency of Fe-zeolites is explained.

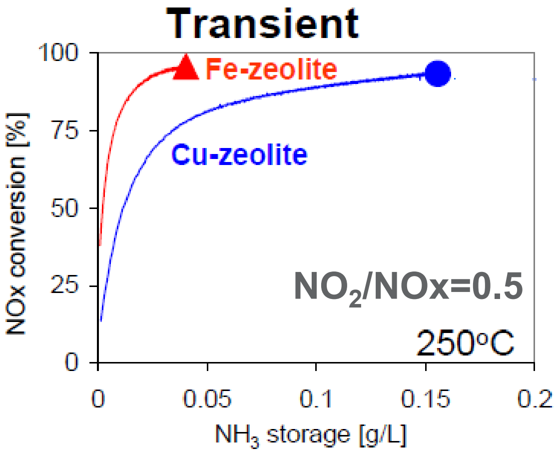
Lower NH3 adsorption and impact on in situ NO oxidation.

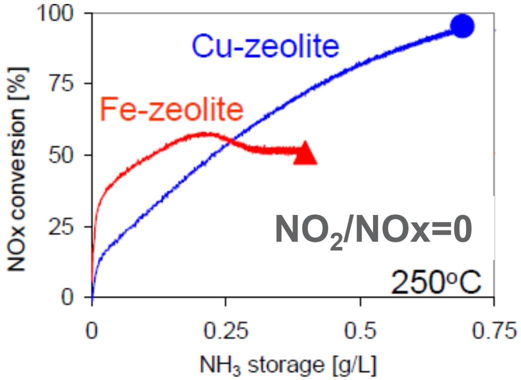


NOx conversion on Fe-zeolites is much more impacted by NH_3 than on Cu-zeolites. NH_3 adsorbs on acidic Fe deNOx sites, not on basic deNOx Cu sites.



Adsorbed NH_3 inhibits NO oxidation on Fe-zeolites. NO_2 adsorption (poisoning) may inhibit NO oxidation on Cu-zeolites. NH_3 may clean Cu sites of NO_2

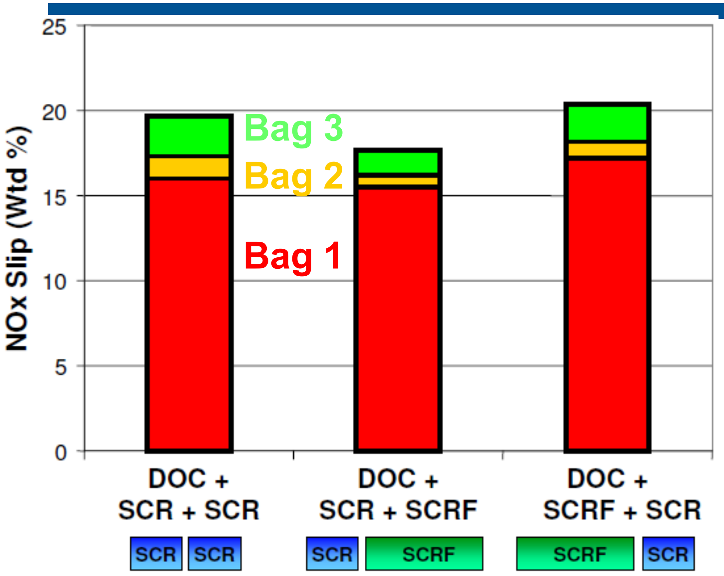




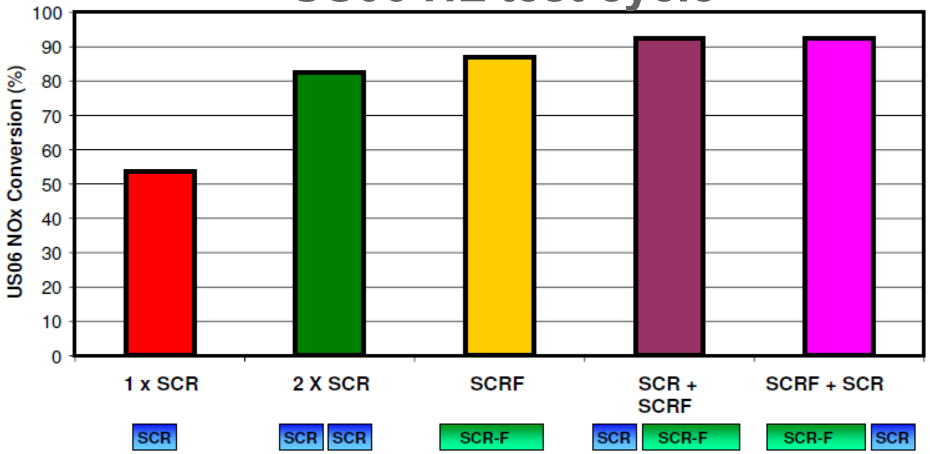
In transients Fe-zeolite converges to NH_3 adsorption equilibrium faster than Cu-zeolite. NH_3 reduces NOx instead of adsorbing (top). Fe-zeolites can oxidize NO more effectively in transients (bottom).

SCR+DPF adds options to improve deNOx performance.

Increased volume is as effective as for flow-through catalysts. Adding catalyst to the DPF can drop emissions 60-65% at low deNOx points.

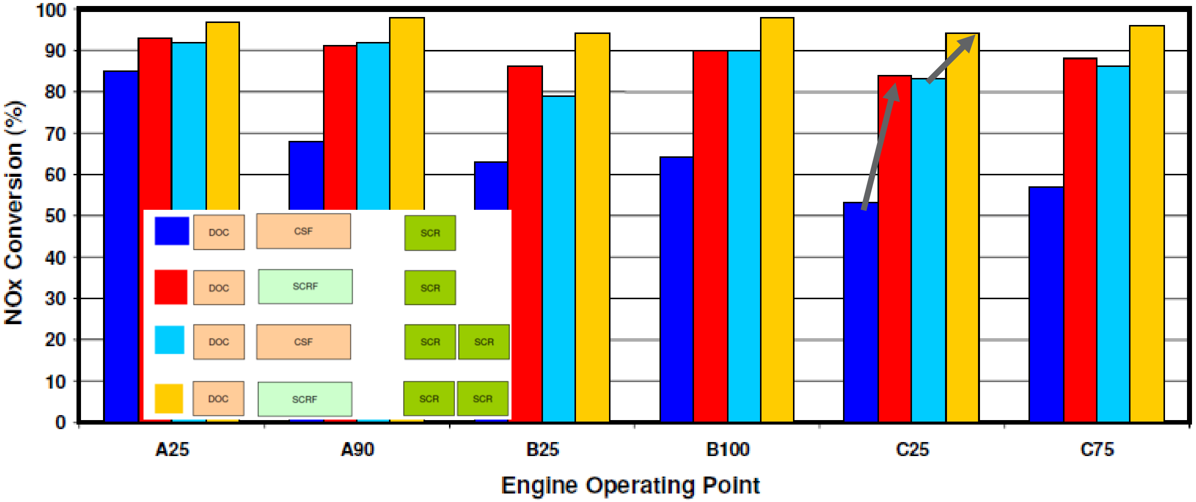


US06 HL test cycle



It matters little if the SCR volume is obtained using flow-through substrates or SCR+DPF (SCR-F)

FTP cold start aided with SCR-F behind SCR

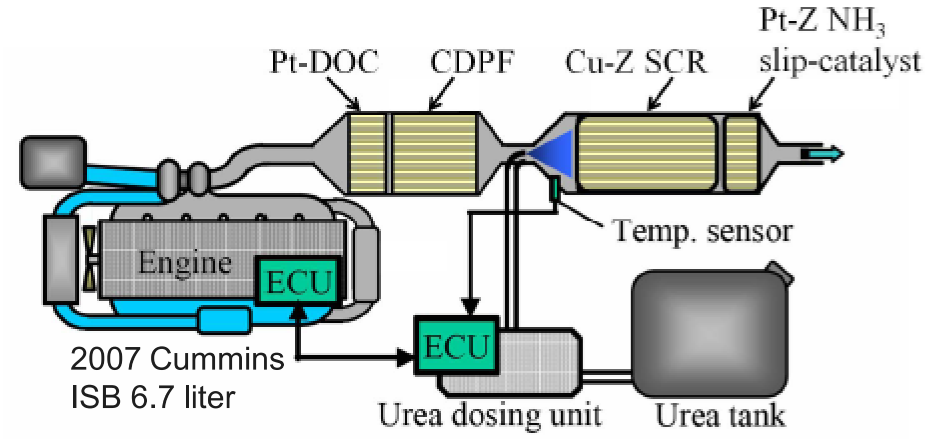


SCR on the DPF cuts emissions about 60-65% at the C25 load point.

JM, SAE Gothenburg HDECC, 9-10

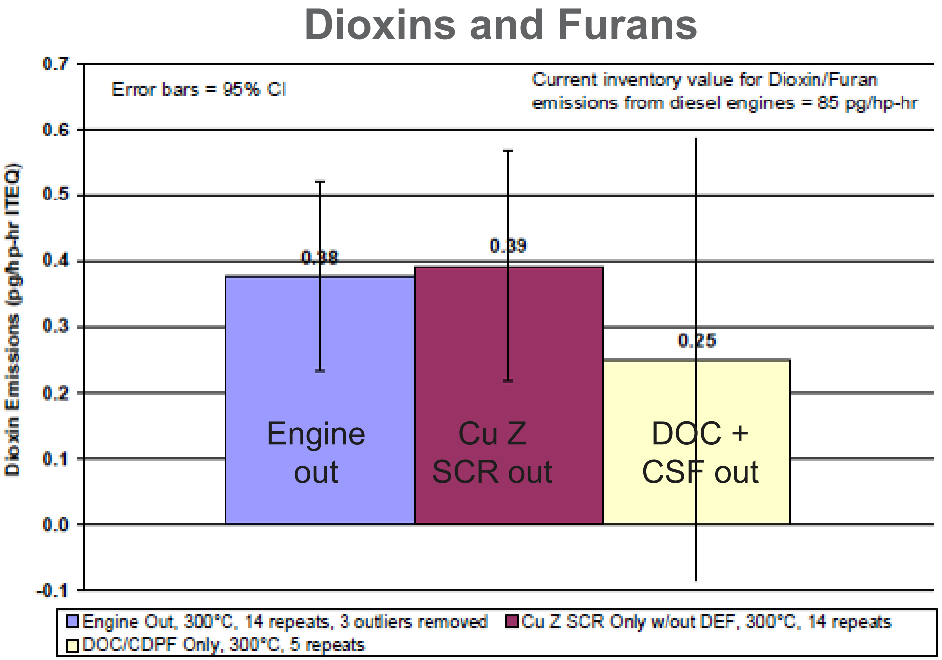
EPA reported on the first phase of the dioxin study.

No issue for “worst case” condition: no PGM, no urea, Cu-zeolite. Next: full system



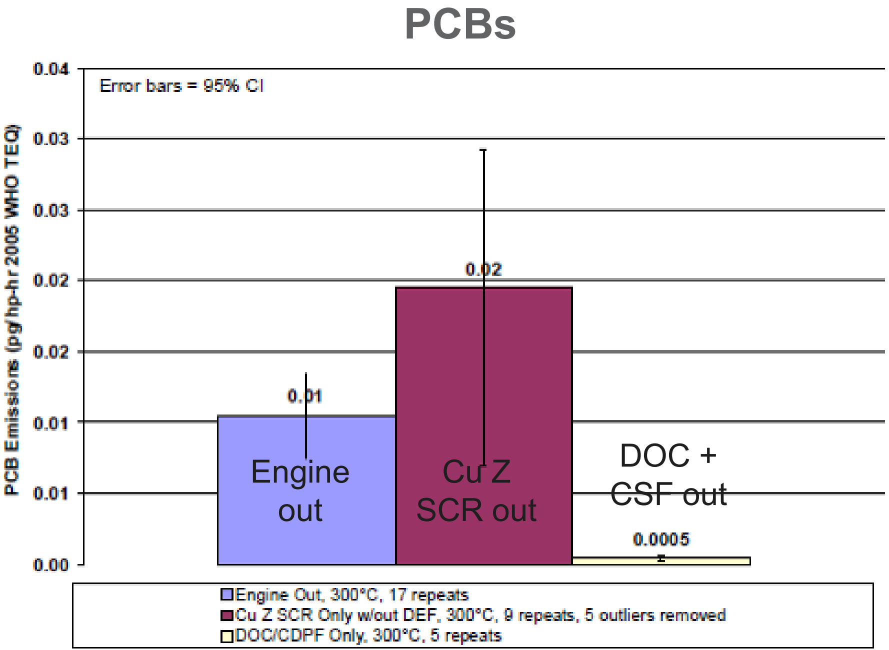
2007 Cummins
ISB 6.7 liter

- PCDD/Fs – Current inventory = 85 pg/hp-hr
  - Engine Out - 14 valid tests
    - Results ranged from 0.15 to 0.88 pg/hp-hr
    - Outliers: 51.98, 8.99, & 3.68 pg/hp-hr (samples dominated by furans)
  - CuZ Only – 14 valid tests
    - Results ranged from 0.10 to 0.94 pg/hp-hr
  - DPF Only – 5 valid tests
    - Results ranged from 0.06 to 0.7 pg/hp-hr
- PCBs
  - Engine Out - 17 valid tests
    - Results ranged from 0.004 to 0.024 pg/hp-hr
  - CuZ Only – 9 valid tests
    - Results ranged from 0.007 to 0.047 pg/hp-hr
    - Outliers: 6.004, 3.796, 3.419, 1.489, and 0.858 pg/hp-hr (all PCBs elevated)
  - DPF Only – 5 valid tests
    - Results ranged from 0.0003 to 0.0007 pg/hp-hr
- PAH results indicate a 99.6 to 99.9% reduction from engine out values when utilizing a DOC/CDPF.
  - The DPF essentially eliminated all PAH emissions within our ability to measure them.
- Field Blank values
  - PCDD/Fs average 0.01 pg/hp-hr
  - PCBs average 0.0024 pg/hp-hr


Dioxins and Furans

Error bars = 95% CI

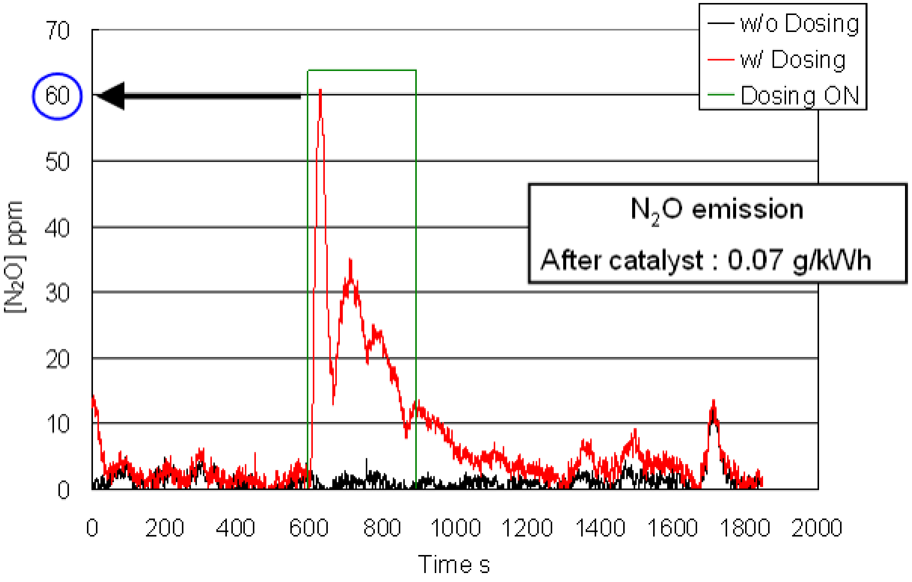
Current inventory value for Dioxin/Furan emissions from diesel engines = 85 pg/hp-hr


PCBs

Error bars = 95% CI

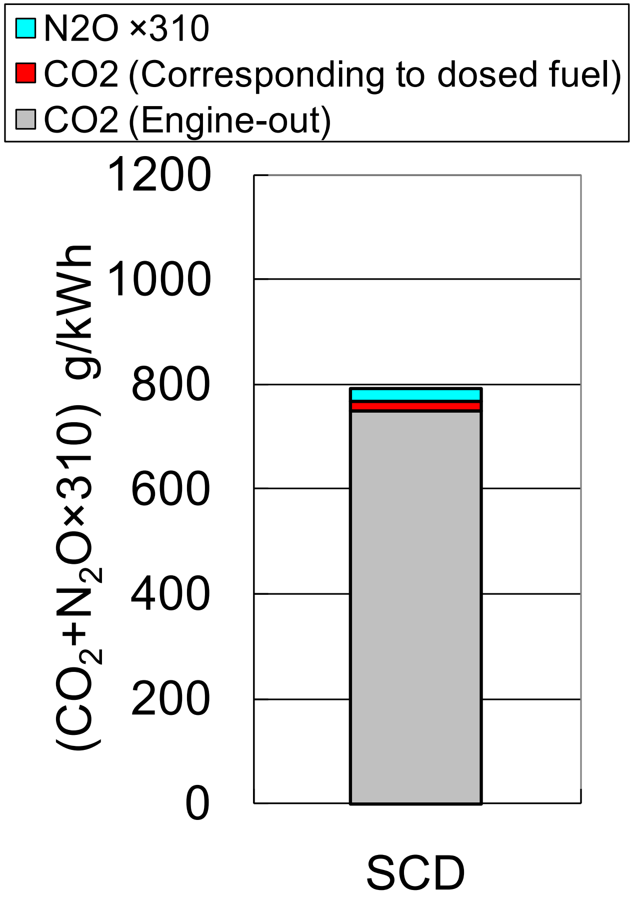
HC-deNOx

LNT can emit N_2O. 3% of total carbon footprint.



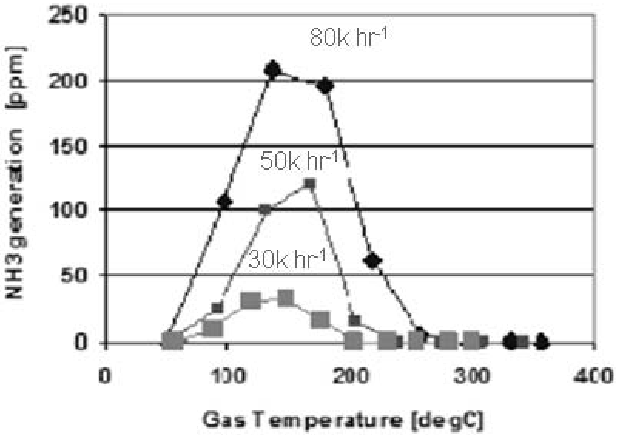
LNT can emit N2O during rich cycle on J05 transient test

New ACE, SAE 2010-01-1066

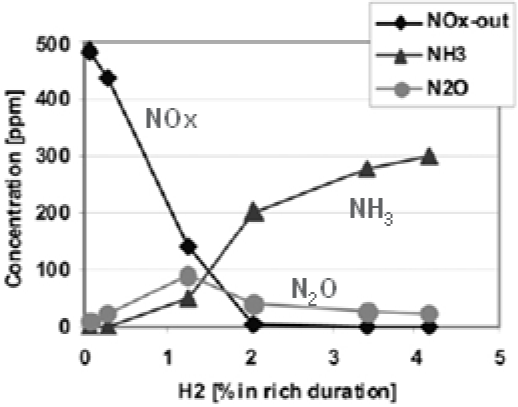


Dosed fuel is 2.4% of total. N_2O is 3% of carbon footprint.

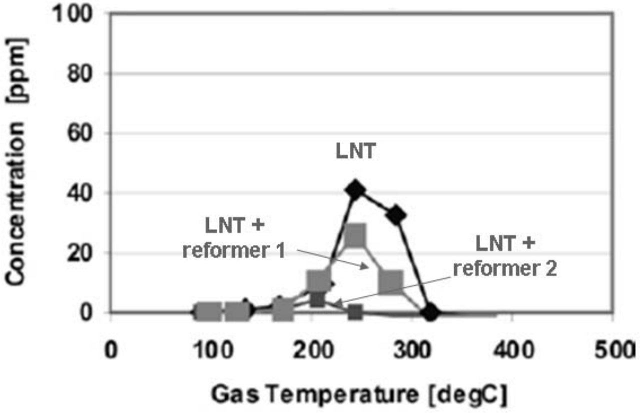
Parameters affecting NH_3 production in an LNT are investigated. Flow rate and hydrogen are major factors.



NH3 production in the LNT increases with flow rate for parts of equal length. However, decreasing length at the same flow to achieve high SV did not increase NH3 (not shown). 80K SV with shorter parts performed similarly to the 50K curve here.



Hydrogen has a big impact on NH3. Here 2% is stoichiometry for the amount of NOx.



WGS catalysts did not improve ammonia formation. However, system NOx conversion was improved, especially at LT .

3 g/liter PGM

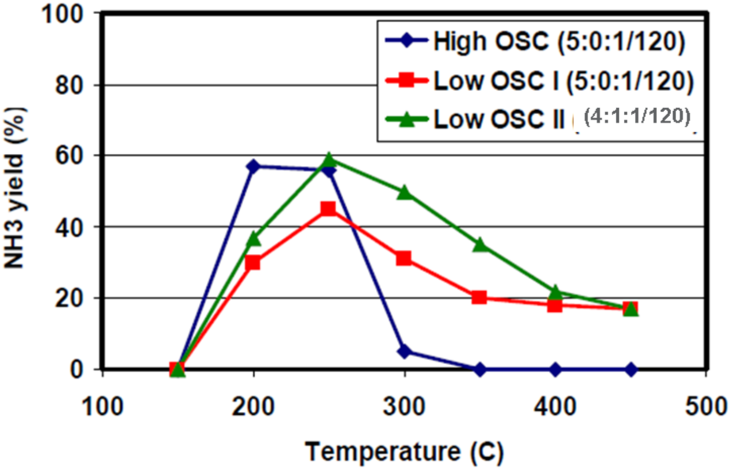
Other impacts:

- Shorter LNT substrates did not appreciably impact system deNOx performance
- Longer rich times increase NH3 and decrease N2O.
- NO/NOx ratio has little impact.
- Residual oxygen in the rich gas can have a large negative impact on ammonia production

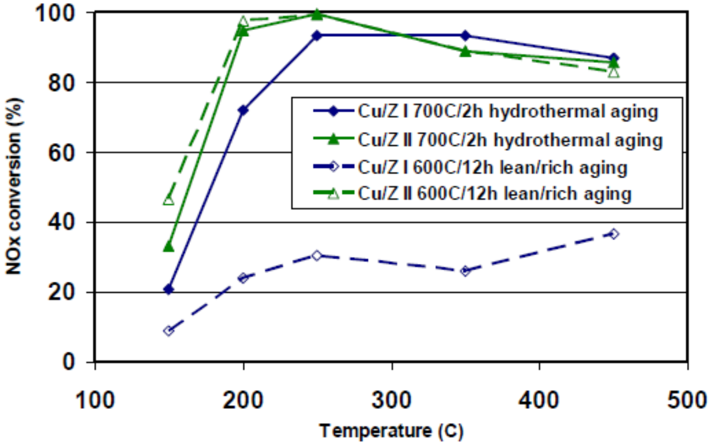
MIT, SAE 2010-01-1071

Performance of an NAC+SCR system is improved.

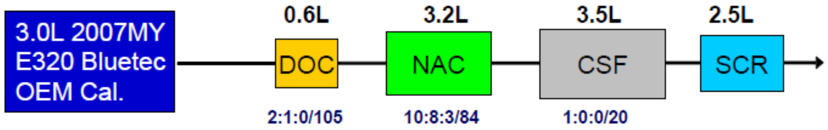
NAC NH3 formation enhanced with Pd and low-OSC. SCR durability improved.

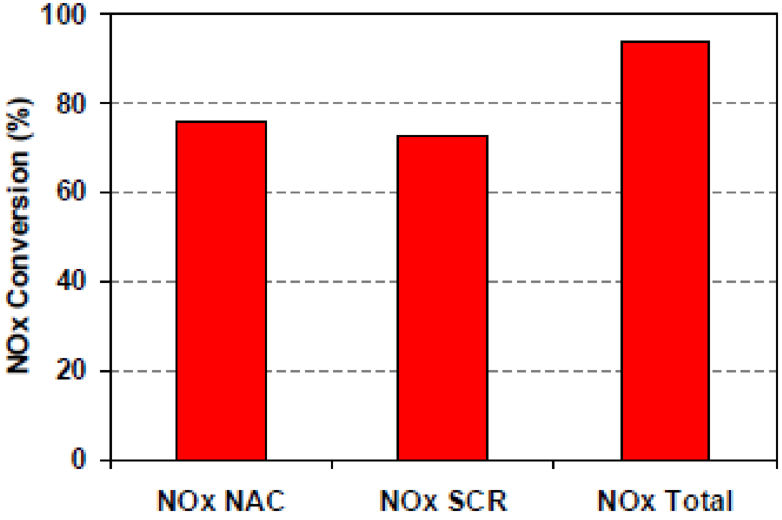


Reducing the OSC and replacing 20% of the Pt with Pd improves the NAC ammonia generation.



Improvements are made to the lean-rich HC cycle durability of the Cu-zeolite catalyst.





The improved combination system delivers 93% using the OEM calibration. The SCR increased overall performance of the low-PGM NAC by 17%.

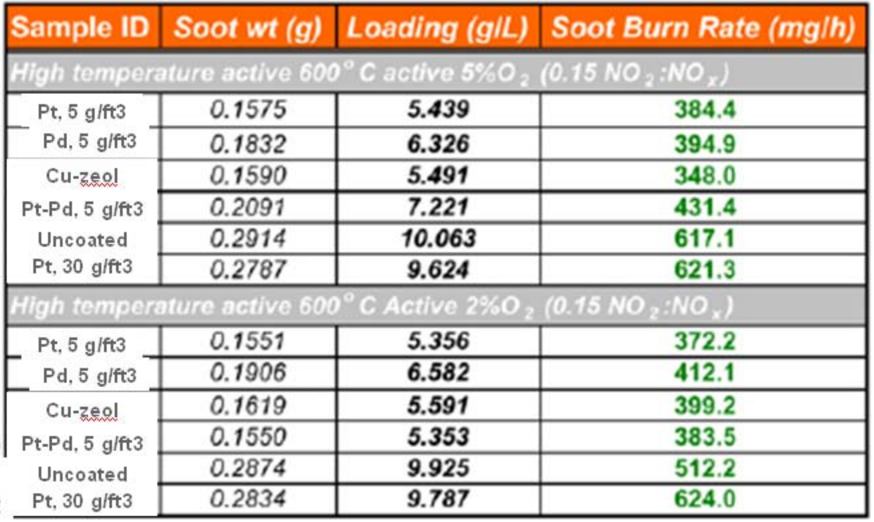
JM, SAE 2010-01-0302

CORNING

DPF

Ford demonstrates characteristics of active and passive DPF regen. Active: No O2 impact (>2%), soot load important, little PGM influence; Passive: NO2 2.5X than w/o, Pt is key, zeolite had no impact.

Active Regenerations



	Sample ID	Soot wt (g)	Loading (g/L)	Soot Burn Rate (mg/h)
	High temperature active 600° C active 5%O_2 (0.15 NO_2:NO_x)			
1	Pt, 5 g/ft3	0.1575	5.439	384.4
2	Pd, 5 g/ft3	0.1832	6.326	394.9
3	Cu-zeol	0.1590	5.491	348.0
4	Pt-Pd, 5 g/ft3	0.2091	7.221	431.4
5	Uncoated	0.2914	10.063	617.1
6	Pt, 30 g/ft3	0.2787	9.624	621.3
	High temperature active 600° C Active 2%O_2 (0.15 NO_2:NO_x)			
7	Pt, 5 g/ft3	0.1551	5.356	372.2
8	Pd, 5 g/ft3	0.1906	6.582	412.1
9	Cu-zeol	0.1619	5.591	399.2
10	Pt-Pd, 5 g/ft3	0.1550	5.353	383.5
11	Uncoated	0.2874	9.925	512.2
12	Pt, 30 g/ft3	0.2834	9.787	624.0

a. Little impact between 2 and 5% O2 (1-4 vs. 7-10). 1% needs 50C higher inlet.

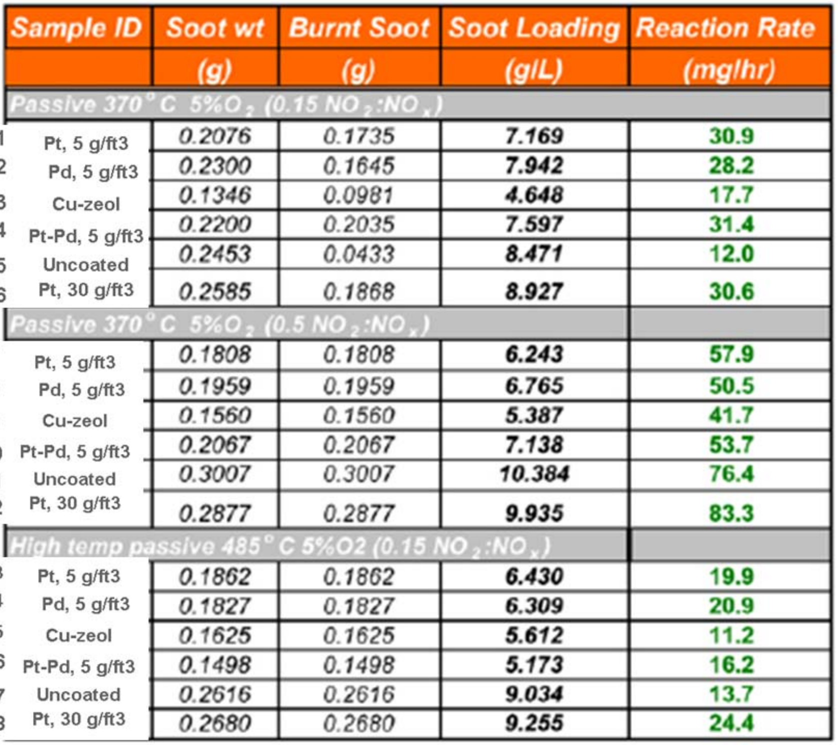
b. Soot mass more dominant (5&6 and 11&12 vs. others) Auxiliary results not shown.

c. Pt and Pd are similar (1 vs. 2, 7 vs. 8) and convert to CO2. Cu-Z similar to uncoated (CO:CO2=60:40). PGM had no impact on rate.

Other:

- Active regen costs 0.5 MPG
- Passive extends regen freq from 400 to 467 miles, saves 0.1 MPG
- HNCO needs to be counted for regen of uncoated filters

Passive Regenerations



	Sample ID	Soot wt (g)	Burnt Soot (g)	Soot Loading (g/L)	Reaction Rate (mg/hr)
	Passive 370° C 5%O_2 (0.15 NO_2:NO_x)				
1	Pt, 5 g/ft3	0.2076	0.1735	7.169	30.9
2	Pd, 5 g/ft3	0.2300	0.1645	7.942	28.2
3	Cu-zeol	0.1346	0.0981	4.648	17.7
4	Pt-Pd, 5 g/ft3	0.2200	0.2035	7.597	31.4
5	Uncoated	0.2453	0.0433	8.471	12.0
6	Pt, 30 g/ft3	0.2585	0.1868	8.927	30.6
	Passive 370° C 5%O_2 (0.5 NO_2:NO_x)				
7	Pt, 5 g/ft3	0.1808	0.1808	6.243	57.9
8	Pd, 5 g/ft3	0.1959	0.1959	6.765	50.5
9	Cu-zeol	0.1560	0.1560	5.387	41.7
10	Pt-Pd, 5 g/ft3	0.2067	0.2067	7.138	53.7
11	Uncoated	0.3007	0.3007	10.384	76.4
12	Pt, 30 g/ft3	0.2877	0.2877	9.935	83.3
	High temp passive 485° C 5%O2 (0.15 NO_2:NO_x)				
13	Pt, 5 g/ft3	0.1862	0.1862	6.430	19.9
14	Pd, 5 g/ft3	0.1827	0.1827	6.309	20.9
15	Cu-zeol	0.1625	0.1625	5.612	11.2
16	Pt-Pd, 5 g/ft3	0.1498	0.1498	5.173	16.2
17	Uncoated	0.2616	0.2616	9.034	13.7
18	Pt, 30 g/ft3	0.2680	0.2680	9.255	24.4

a. 50% NO2 gives 2.5X faster rate (1-6 vs. 7-12)

b. NO2 is more effective at 370C than at 485C (7-12 vs 13-18

c. Pt samples at 370C and 50% NO2 are 15% faster (7, 10, 12 vs. 8, 9, 11); at 485C: 25% faster

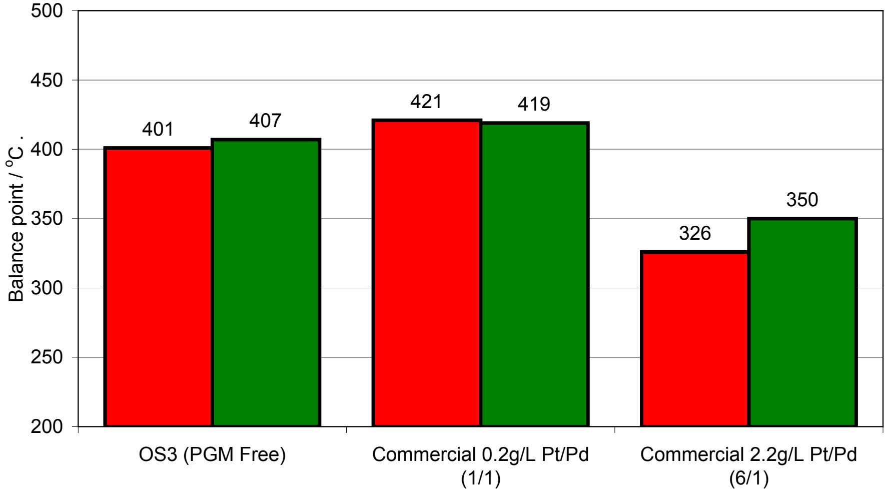
d. Cu-Z similar to uncoated.

Ford, SAE 2010-01-0533

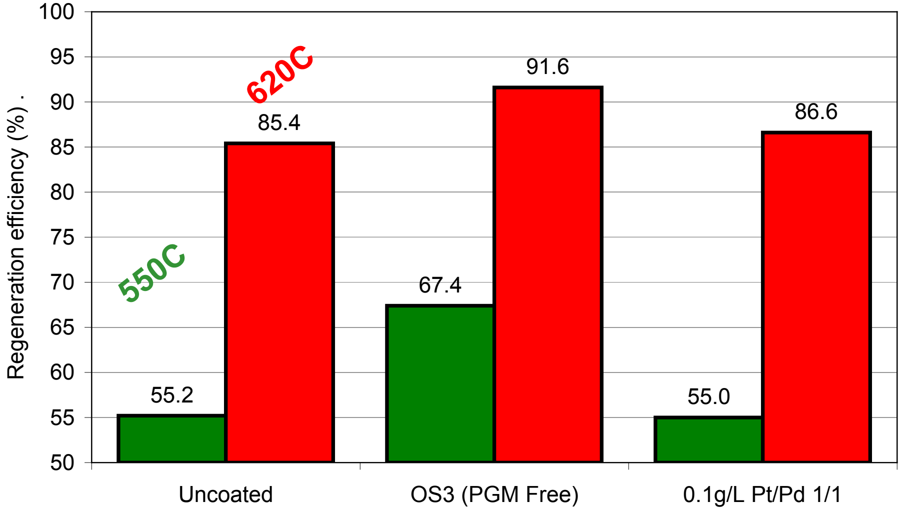
Direct oxidation soot catalyst is advanced.

Low or no PGM. Oxidation at 200C without NO_2

- Basis is direct oxidation of soot by oxygen at the soot-catalyst interface. O^{2-} conducting catalyst; no NO_2
- Catalyst oxidizes soot at temperatures as low at 160C. Oxidation complete at 220C. No or low PGM
- Aided by good soot contact, but propagation occurs via exotherm. Low thermal mass DPF is beneficial.
- Small amount of PGM will drop CO emissions from soot burn



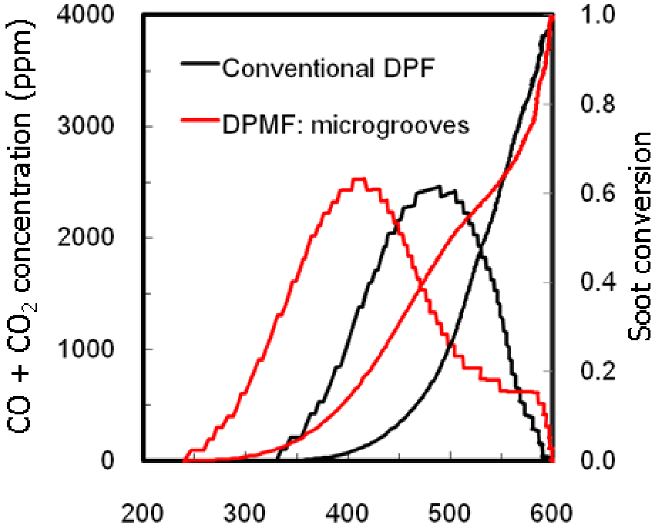
Repeat BPT tests show PGM-free catalyst perf better than light PGM DPF.



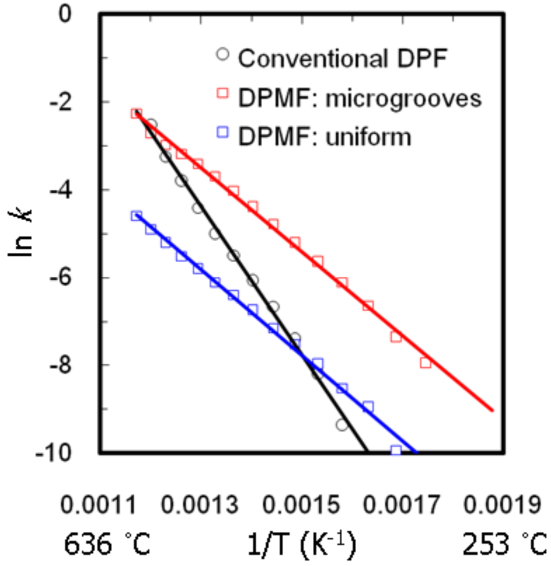
Regeneration efficiency is better than DPF with light PGM loading.

SiC membrane added to DPF drops activation energy and ignition temperature for soot burning.

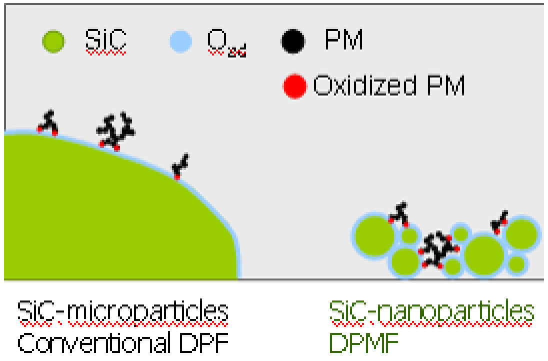
Shift in reaction mechanism is shown.



The DPF with SiC membrane reacts about 100C lower than conventional



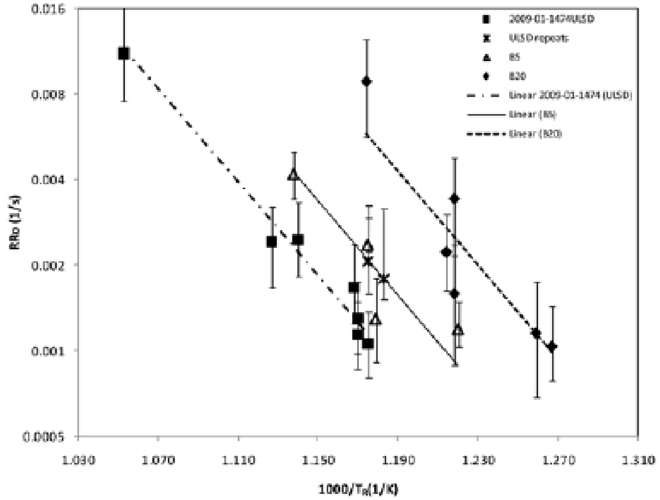
The activation energy of soot burning with the SiC membrane is lower (80 vs. 130 kJ/mole).



SiC has an adsorbed layer of oxygen. The high surface area makes it the predominant oxidation mechanism.

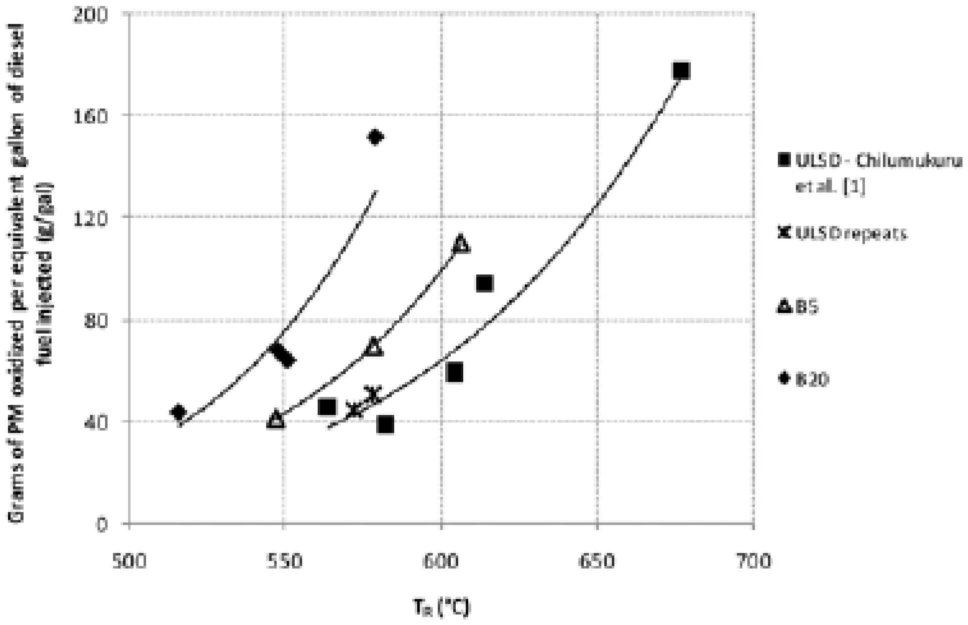
Tokyo Inst Tech, SAE 2010-01-0808

Biodiesel blends burn faster and consume less fuel for regeneration.

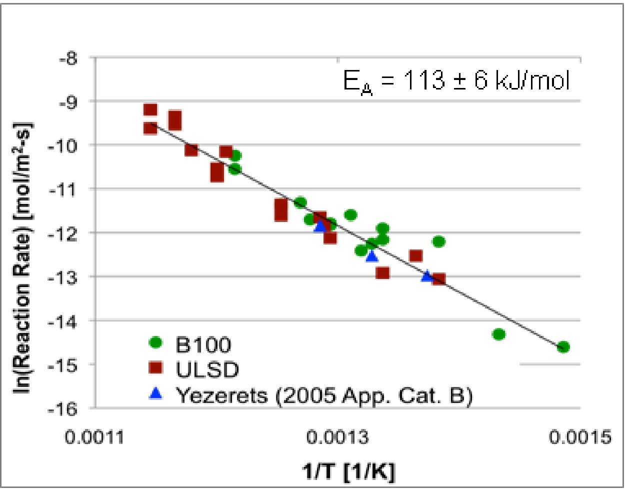


Soot from 20% biodiesel burns 3X faster than regular soot.

MTU, SAE 2010-01-0557

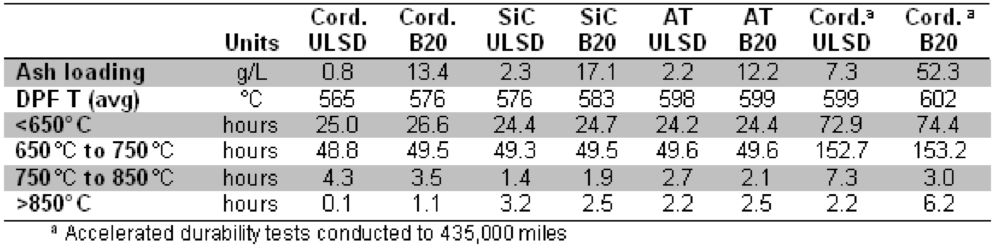


3X more soot is burned per unit of fuel when 20% biodiesel is used.



Biodiesel soot has more initial surface area. When this is normalized, reaction rates converge. (ORNL, CLEERS, 2010)

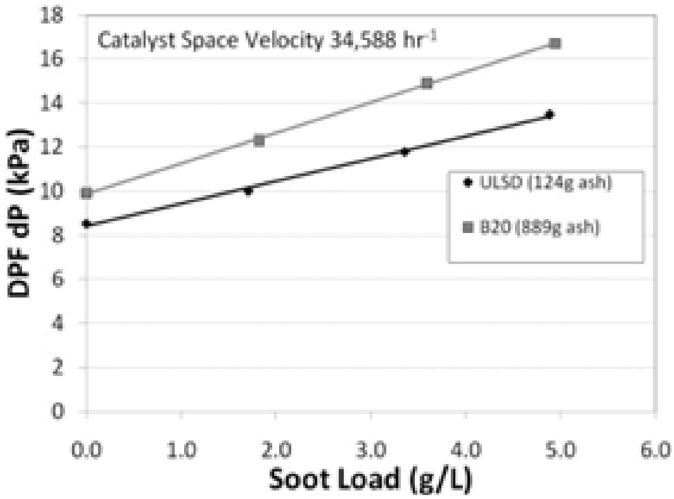
Preliminary results are available on the effect of B20 ash on DPFs and DOCs.



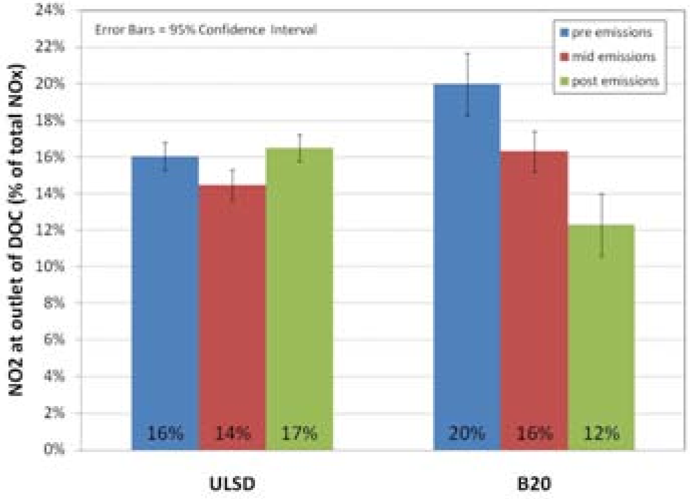
	Units	Cord. ULSD	Cord. B20	SiC ULSD	SiC B20	AT ULSD	AT B20	Cord.[a] ULSD	Cord.[a] B20
Ash loading	g/L	0.8	13.4	2.3	17.1	2.2	12.2	7.3	52.3
DPF T (avg)	°C	565	576	576	583	598	599	599	602
<650° C	hours	25.0	26.6	24.4	24.7	24.2	24.4	72.9	74.4
650 °C to 750 °C	hours	48.8	49.5	49.3	49.5	49.6	49.6	152.7	153.2
750 °C to 850 °C	hours	4.3	3.5	1.4	1.9	2.7	2.1	7.3	3.0
>850° C	hours	0.1	1.1	3.2	2.5	2.2	2.5	2.2	6.2

[a] Accelerated durability tests conducted to 435,000 miles

B20 ash was at the maximum spec for Ca+Mg and alkali in accelerated loading (27X higher levels in fuel). Cordierite exposed to T>750C for >3-4 hrs.



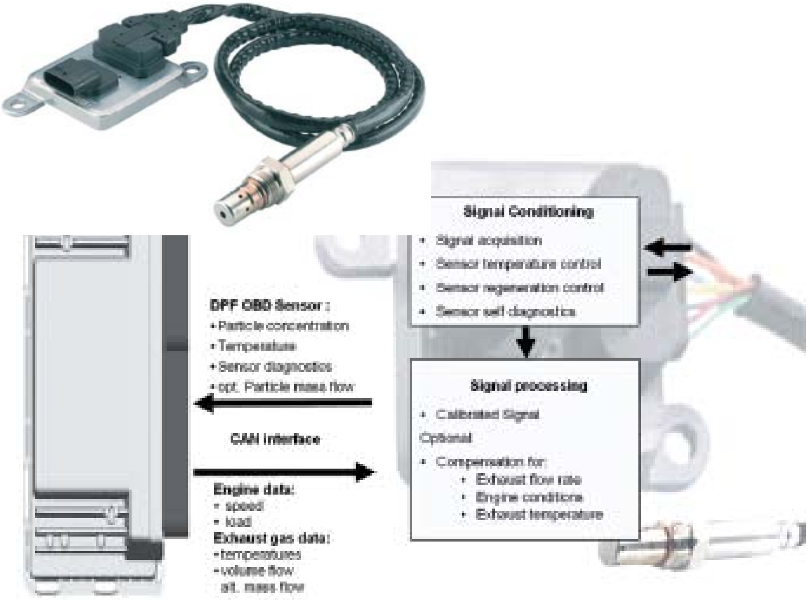
435,000 mile B20 ash loads results in 25% higher back pressure

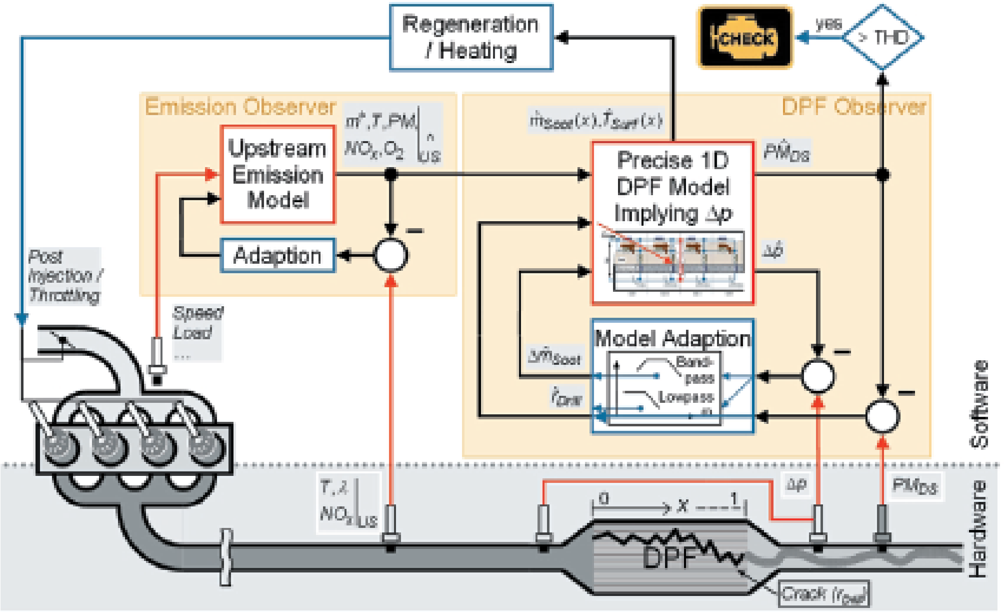


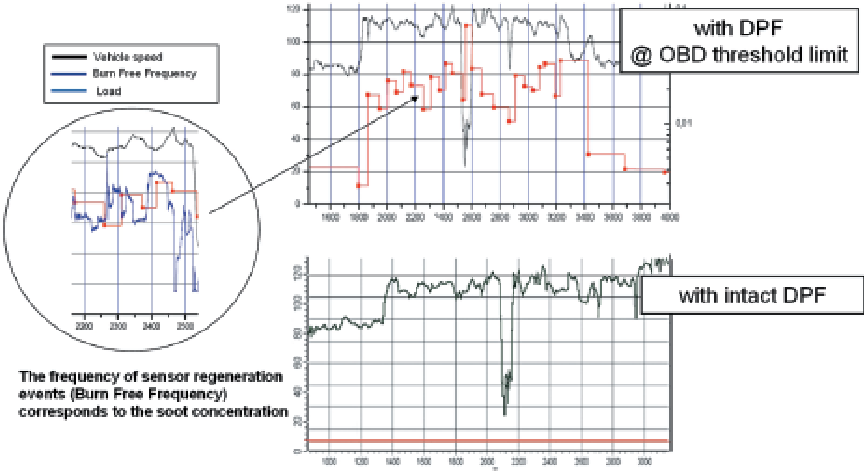
150,000 mile effect of B20 on DOC NO2 formation.

- Filter properties of cordierite at 150,000 mile were the same for B20 and ULSD.
- Alkali was shown to chemically penetrate up to 30% into the cordierite wall.

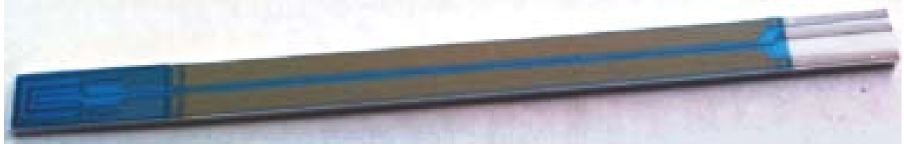
PM sensor for OBD is reported.







Continental, AVL Exhaust Gas and Particulate Forum, 3/10



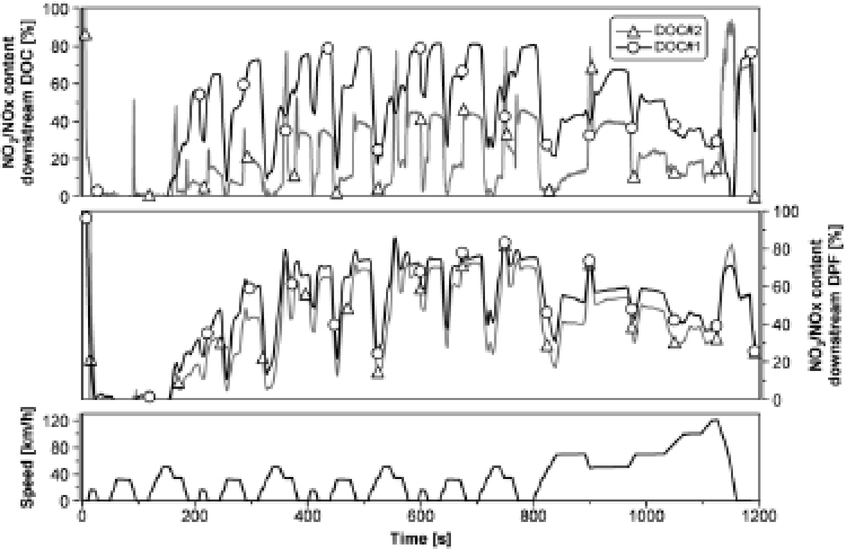
Sensor element collects soot and monitors current, then periodically regenerates to give an average soot level for the period. Signal here is with DPF at OBD threshold compared to good DPF.

CORNING

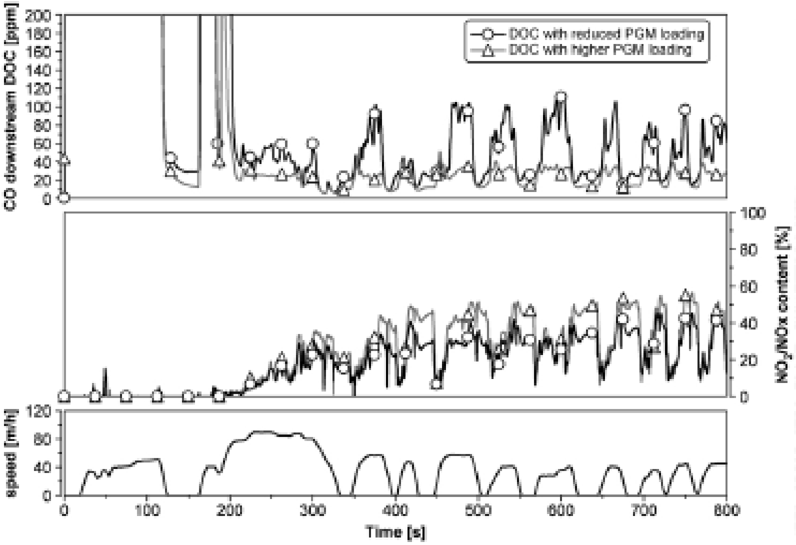
Oxidation Catalysts

NO_2 coming out of DPF is strongly dependent on DOC CO+HC removal efficiency and Pt loading of DPF.

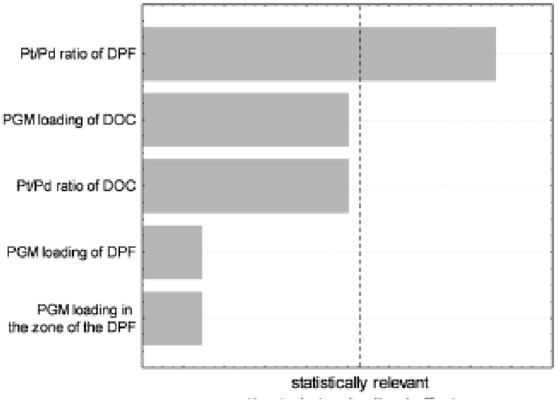
NO2 out of DOC minor impact. Zone coated DPF not effective



NO2 level coming out of CSF is generally independent of NO2 coming out of DOC. Both DOCs remove HC+CO efficiently.



On the other hand, NO2 coming out of CSF is much more dependent on CO+HC coming out of DOC.

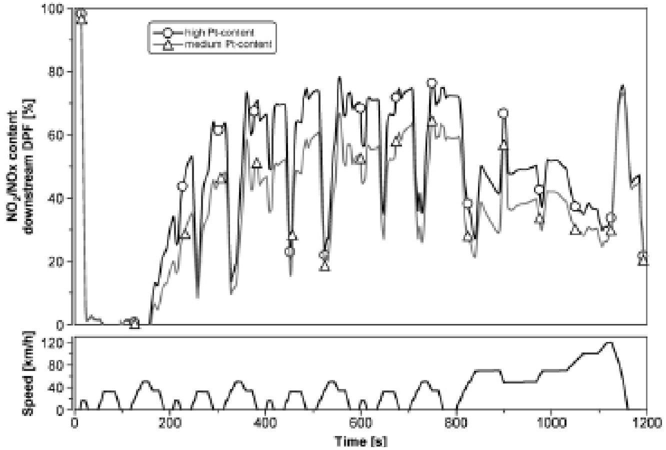


Pt/Pd ratio on DPF far outweighs PGM loading on DPF for NO2 formation.

Other:

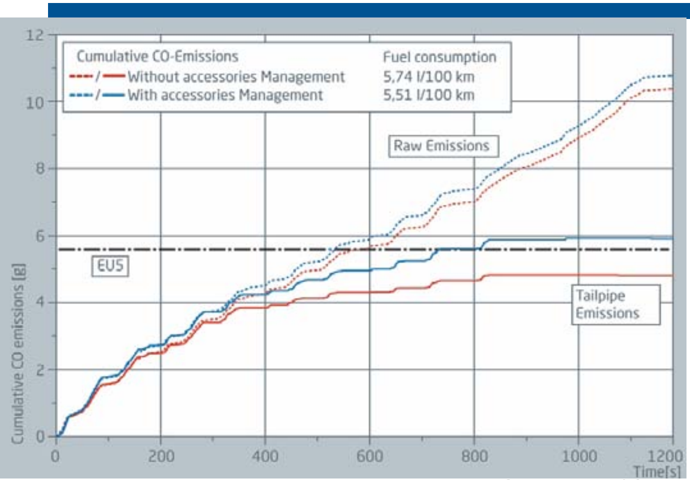
- Zone coated DPF not as good as homogeneous coating. Even though front high loading cuts CO+HC, low rear loading can't form NO2

Umicore, AVL PM Forum 3/10



Impact of high Pt/Pd ratio in DPF. Same total loading

Fuel conservation measures can drop exhaust temperatures 5-10Cº, resulting in CO increases. Intake throttling and EGR cutoff are effective measures to keep DOC hot.

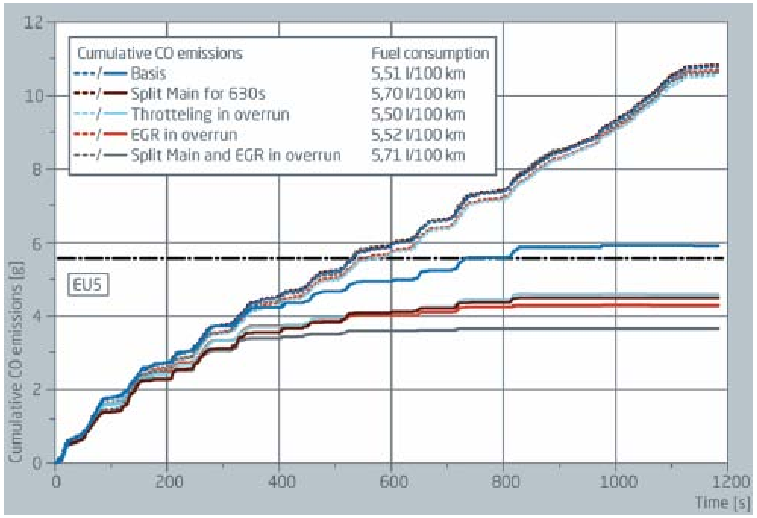


Auxiliary management can drop FC by 3-5%, but exhaust T drops 5-10Cº. CO emissions can increase 20%. 2 liter Euro 5, 1590 kg, 2-stage turbo.

IAV, AVL PM Symposium 3/10.

NVH concerns

1. Reduction of CO raw emissions by:
    - 1.1 Optimization of pilot injection quantities
    - 1.2 Shortening of pilot injection intervals
    - 1.3 Optimization of rail pressure
    - 1.4 Increasing of air mass
2. Increase exhaust-gas temperature to improve CO conversion by:
    - 2.1 Retarding of main injection
    - 2.2 Reduction of rail pressure
    - 2.3 Splitting of main injection into two injection events ("split main")
    - 2.4 Activation of the throttle valve while coasting
    - 2.5 Activation of exhaust-gas recirculation (EGR) while coasting (includ the necessary throttle valve control)



Measures increase exh T by 10-30C. EGR and throttling upon coasting are effective for this veh w/o FC incr.

Summary

- HD regulations being wrapped up, next regs being contemplated
- Further tightening of criteria regs expected. California is beginning LEV3 proposal stage. EPA considering Tier 3.
- CO_2 mandates are proposed for HD
  - Onset of another major regulatory-driven technology evolution
- Engine technologies are addressing engine-out NOx and FC
  - control, LT thermal management, advanced combustion approaches
- SCR is addressing “secondary” issues:
  - LT issues: ammonia sources and urea inj; NH3 storage formation, mechanisms.
  - Catalyst HT
  - More understanding on SCR+DPF
- New LNT compositions and designs are shown.
  - Better performance, lower cost
  - LNT+SCR systems advancing
- DPF regen, substrate properties, material, and catalysts advancing.
- DOC catalysts performance characterized
  - NO2
  - LDD CO emissions can be difficult