

# Diesel Emission Control in Review

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## ABSTRACT

This summary covers representative developments from 2008 in diesel regulations, engine technology, and NO<sub>x</sub>, particulate matter (PM), and hydrocarbon (HC) control.

Europe is finalizing the Euro VI heavy-duty (HD) regulations for 2013 with the intent of technologically harmonizing with the US. A new particle number standard will be adopted. California is considering tightening the light-duty fleet average to US Tier 2 Bin 2 levels, and CO<sub>2</sub> mandates are emerging in Europe for LD, and in the US for all vehicles.

LD engine technology is focused on downsizing to deliver lower CO<sub>2</sub> emissions, enabled by advances in boost and EGR (exhaust gas recirculation). Emerging concepts are shown for attaining Bin 2 emission levels. HD engines will make deNO<sub>x</sub> systems optional for even the tightest NO<sub>x</sub> standards, but deNO<sub>x</sub> systems enable much lower fuel consumption levels and will likely be used.

NO<sub>x</sub> control is centered on SCR (selective catalytic reduction) for diverse applications. Focus is on cold operation, system optimization, and catalyst durability. LNT (lean NO<sub>x</sub> trap) performance is advancing and precious metal cost content is decreasing. Desulfation is enhanced, and new compositions are emerging based on alumina and ceria. LNCs (lean NO<sub>x</sub> catalysts or HC-SCR) developments are updated.

Diesel particulate filter (DPF) technology is in a state of optimization and cost reduction. New DPF regeneration strategies are described as well as the new learnings on the fundamentals of soot/catalyst interaction and the impact of DPF pore structure.

Finally an update on diesel oxidation catalysts (DOCs) is provided showing potential solutions for advanced combustion strategies.

## INTRODUCTION

The field of diesel engines and emission control technology has been very dynamic since the mid-1990s. Much of the technology evolution is regulatory-driven, and those regulations are now in various stages of implementation. The field is ripe with incremental improvements to address new and old challenges as there are well over 1000 technical papers concerning diesel engines, fuels and emissions, comparable to earlier years.

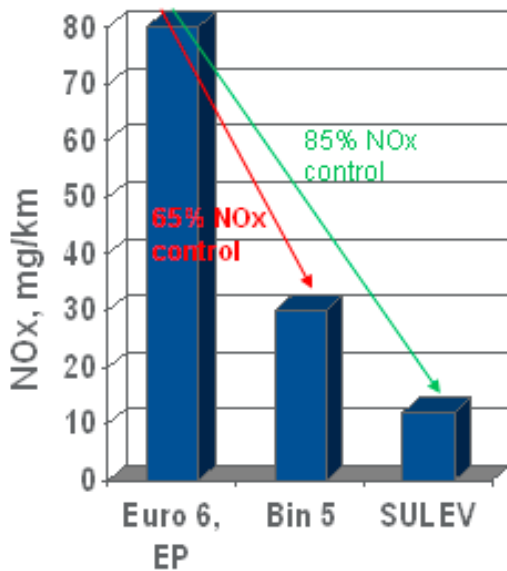
As in the past (1), this review is not intended to be all-encompassing. Rather, the objective is to summarize representative studies that show the key directions in the industry, with an emphasis on reports from 2008. First, the regulatory issues are addressed, followed by a quick overview of engine technologies most pertinent to emissions control. The author will then review NO<sub>x</sub>, PM (particulate matter), and hydrocarbon/CO control developments.

## Regulatory Developments

Regulations are continuing to evolve. California is considering a fleet average emission level equivalent to SULEV (Super Ultra-Low Emission Vehicle), and CO<sub>2</sub> mandates are developing. On the heavy-duty side, Europe is proposing new Euro VI standards.

## LIGHT-DUTY

Light-duty diesel (LDD) criteria emissions regulations are undergoing another round of tightening in California. For LDD, NO<sub>x</sub> is the most demanding pollutant to address, as diesel particulate filters (DPF) are an established technology and are very efficient in eliminating PM. Hydrocarbons (HCs) are generally not an issue with LDD. Although quite preliminary, indications are that the California Air Resources Board (CARB) staff are considering fleet average Super Ultra-Low Emission Vehicle (SULEV) standards, equivalent to US EPA Tier 2 Bin 2, for all LD vehicles. Today, nominally 30% of new cars sold into California are at this level. Figure 1 shows a comparison of this proposal to the Euro 6 regulation (2014) and the US Tier 2 Bin 5 standard on the US Federal Test Procedure (FTP) cycle. While adopting a Euro 6 engine to US Bin 5 standards can be accomplished adding 65% more deNO<sub>x</sub> control, the required 85% control to meet SULEV standards is a stretch for today's deNO<sub>x</sub> technology when cold start emissions are considered. Thus, to meet these proposed regulatory directions, it is likely auto companies would need to develop California-specific engines.

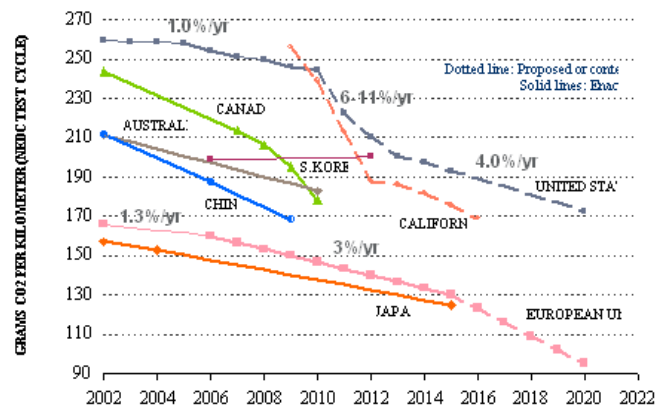


**Figure 1.** Euro 6 (2014) LDD NO<sub>x</sub> regulations compared to US Tier 2 Bin 5 and California SULEV (Bin 2). Test cycle differences are not considered here.

Perhaps the more far-reaching regulatory development on LD relates to CO<sub>2</sub> emissions mandates. California was the first to require CO<sub>2</sub> (equivalent) mandates, but the US EPA declined a waiver needed for implementation. (This decision is being re-evaluated by the new EPA Administrator.) Similarly, in December 2008 the European Parliament approved CO<sub>2</sub> mandates for 2016 of 130 g/km on the New European Drive Cycle (NEDC), and 95 g/km in 2020. The Council of Ministers, although in agreement, still needs to formally approve these standards. Similarly, the US EPA closed a formal comment period on an Advanced Notice of Proposed

Rulemaking (ANPRM) that signaled CO<sub>2</sub> mandates may be forthcoming at the US national level.

Figure 2 shows a comparison of how these mandates compare with fuel economy or consumption requirements across the world, normalized to CO<sub>2</sub> emissions on the New European Drive Cycle (NEDC) (2). For the purposes here, the rate of change of reductions is most interesting. In both the US and Europe if all technology improvements went into fuel consumption improvement, vehicle CO<sub>2</sub> reductions progressed nominally 1.0 to 1.5% per year. Decisions to use technologies were based on the value proposition on returning fuel savings to the end customer. Going into the future, regulators are requiring 3 to 11% per year improvements, meaning a much faster pace of reductions than the market demanded in the past will be required. Technology additions will be treated similar to criteria emission (NO<sub>x</sub>, PM, etc.) reduction technologies, that is, best performance relative to one another rather than being based on a customer value proposition. This is a major paradigm shift.



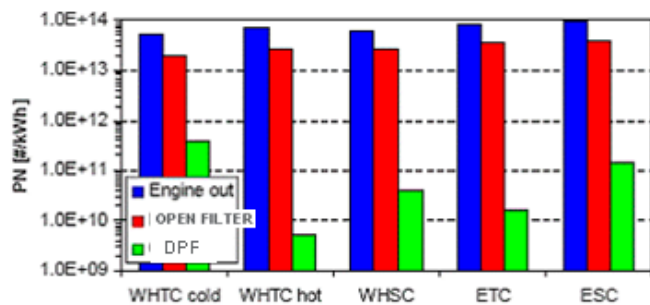
**Figure 2.** Comparison of worldwide fuel economy, fuel consumption, or proposed CO<sub>2</sub> standards, all normalized to the NEDC and adjusted for fuel mix (2).

## HEAVY-DUTY

On the emerging heavy-duty regulatory front, Europe is finalizing its Euro VI regulations for the 2013 timeframe. In December 2008 the European Parliament passed onto the Council of Ministers a final proposal that should technologically harmonize the European regulations with those of the US and Japan. Key provisions are:

- European Transient Cycle (ETC) NO<sub>x</sub> emissions of 400 mg/kW-hr vs. 260 mg/kW-hr in the US2010 regulation.
- PM emissions of 10 mg/kW-hr vs. 13 mg/kW-hr in the US2010 regulation.
- A Particle Number (PN) regulation that is based on DPF capability.
- Ammonia slip limits of 10 ppm.

A PN regulation was developed for the Euro 5b LDD regulation (2011), and its principles are now expanding into heavy duty. The European Union regulators' stated desire is to have DPFs on all these engines. The limit value is still to be determined by the European Commission, and is to be based on DPF capability. Figure 3 shows how the PN values vary with test cycle and technology using the European test protocols (3). A limit value of  $\sim 10^{11}$  #/kW-hr seems reasonable, given DPF blended (10% cold and 90% hot) World Harmonized Test Cycle (WHTC) performance of  $\sim 3.5 \times 10^{10}$  #/kW-hr (99.95% efficiency). Further, it seems reasonable that future engines could have engine-out emissions approaching  $10^{13}$  #/kW-hr levels. As open filters show potential for 90% PN removal (4), tailpipe levels with such devices can approach  $10^{12}$  #/kW-hr levels. To ensure DPFs as desired by the regulators, limit values less than  $10^{12}$  #/kW-hr levels are thus needed, in this author's opinion.



**Figure 3.** HDD PN emissions using different test cycles and technologies (3).

On the HD CO<sub>2</sub> regulatory front, it appears imminent that CO<sub>2</sub> regulations will also apply to HD. CARB held a HD CO<sub>2</sub> workshop in December 2008 exploring the possibility of using low rolling resistant tires and aerodynamic cowling beginning in 2010 for large fleets. Also, the EPA ANPRM referenced above solicited comments on HD and non-road vehicle CO<sub>2</sub> reductions.

Finally, US EPA and CARB On-Board Diagnostic (OBD) requirements were finalized. In place now is the rudimentary monitoring just to make sure the DPF is present and other systems are functioning. In 2010, the OEMs have to implement more demanding OBD on one engine family in each year from 2010-12, and across the board in 2013. NOx OBD is needed on all engine platforms beginning in 2010, as there are adequate sensors available today. In 2010, the DOC, deNOx, and DPF will have emission threshold warnings which tighten in 2013, shown Table 1. In other words, if emissions exceed these values, the malfunction indicator light (MIL) goes on. The pertinent NOx standard is with credits. Additionally, DPF regenerations and partial regenerations need to be monitored (no MIL warning). CARB DPF frequent regeneration monitoring is to 2X the NMHC (non-methane hydrocarbon) standard or the NOx standard + 0.2g/bhp-hr starting in MY 2013. EPA light-

duty OBD limits are 1.5X the standard for NMHC and NOx, and to alert of a catastrophic DPF failure.

CARB LD OBD limits are 3X for NMHC, 2.5X for NOx, and 4X for PM in 2010, and 1.75X for all emissions in 2013.

	2010		2013	
	EPA	CARB	EPA	CARB
NOx	Std+0.6	Std + 0.3	Std+0.3	Std + 0.2
PM	0.05	0.07	0.05	0.03 (2016)
NMHC	2.5X	2.5X	2.0X	2.0X

**Table 1.** Recently finalized HDD OBD standards. The values are relative to the tailpipe standards, except if a number is given. Units are g/bhp-hr.

In 2013 it is estimated that in addition to NOx sensors, PM sensors will also be needed.

Finally, the emissions of NO<sub>2</sub> from diesel vehicles are of increasing interest. Although no tailpipe regulations on NO<sub>2</sub> have been implemented or even proposed, several regions in Europe will have difficulty meeting their 2010 NO<sub>2</sub> immission (ambient air levels) requirements. In the US, California now requires that NO<sub>2</sub> comprises no more than 20% of the NOx in the tailpipe for retrofit systems.

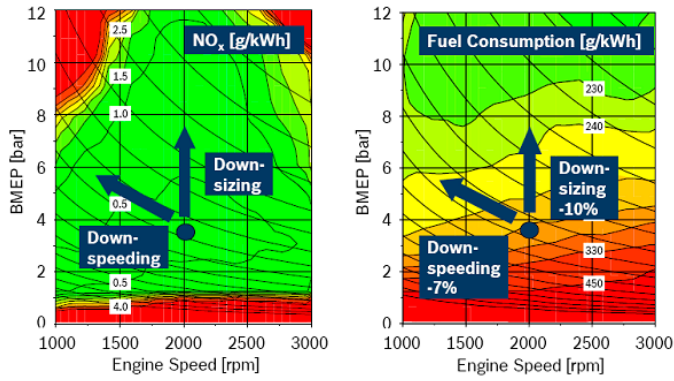
## Engine Developments

### LIGHT DUTY

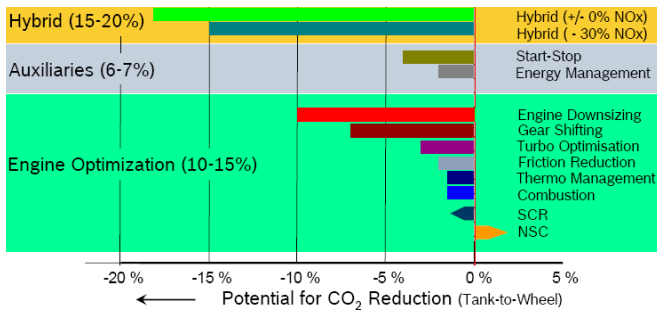
Regulatory, market, and fuel economy requirements are making great demands on the diesel engine. Further, advanced gasoline concepts and hybrid electric vehicles are exerting competitive technology pressures. Diesel engine developers are responding by using advanced fuel injection technologies, EGR (exhaust gas recirculation) control, advanced and two-stage turbocharging, variable valve actuation, closed loop combustion control, and advanced model-based control. Downsized prototype diesel engines (5) are now approaching 110 kW/liter specific power and 31 bar Indicated Mean Effective Pressure (IMEP). However, as shown in Figure 4, NOx emissions can increase 50% for such engines over advanced engines (80 kW/liter), but CO<sub>2</sub> emissions will be reduced nominally 15% in premium vehicle applications (6). Other opportunities for CO<sub>2</sub> savings are shown in Figure 5 (6).

Regarding advances in EGR and boost, Czarnowski, et al. (7) show that low pressure loop EGR and series turbocharging are valuable tools for achieving low engine-out NOx while still returning up to a 3% fuel savings. BMW is using variable twin series turbochargers on their US Bin 5 diesels (8), and stated that low pressure loop EGR can drop NOx 30% more and save fuel. Dual loop EGR with a single turbocharger is on the 2 liter engine of the award-winning (California Green Vehicle of the Year) Bin 5 Volkswagen Jetta (9), and can deliver 30% EGR at full load. By adding a second set of series turbochargers a

3 liter sport utility vehicle is close to attaining Euro 6 NOx standards, engine-out (10).



**Figure 4.** Downsizing and down-speeding engines can result in nominally 10 and 7% decreases in fuel consumption (right), but with ~50% increases in NOx (left). Reference 6.



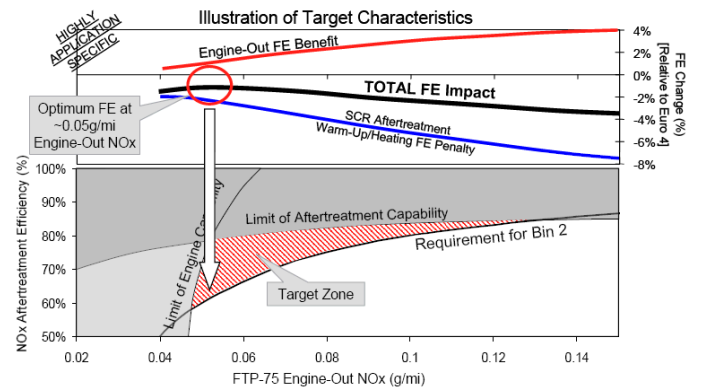
**Figure 5.** Relative to a Euro 4 diesel with DPF, 20 to 40% CO<sub>2</sub> reductions are possible with light-duty diesels. The engine can contribute 10 to 15% more reductions (6).

On the cutting edge for attaining SULEV, Cooper (11) updated a previous Tier 2 Bin 5 (engine-out) demonstration vehicle with further controls and NOx aftertreatment. Figure 6 shows the outline. The lower part of the chart shows a red region of operation, which is bordered on the top by a maximum deNOx aftertreatment efficiencies of ~80% and to the left by the best engine-out NOx levels. Notice the best fuel economies are derived by applying the cleanest engine technologies.

### Heavy-Duty Engine Developments

Heavy-duty diesel engine advancements are primarily aimed at improved fuel economy, reliability, cost, and durability. As such, advancements tend to be conservative and incremental. The US 2004 regulations were generally addressed using advanced EGR and turbocharging concepts. US 2007 and Japan 2005 technologies added diesel particulate filters, while Euro IV (2005) and now Euro V (2008) regulations are largely addressed using more conventional engine technologies and SCR.

Moving on to Japan 2009 and US 2010, we will also see incremental advancements from the earlier regulatory technologies. However, as with light-duty engines, we could see some advanced combustion strategies emerge to handle low-load NOx emissions issues. Because most of the fuel in heavy-duty applications is spent under higher load regimes, engine researchers are focusing more on traditional diesel combustion hardware and strategies, and they are making significant progress.



**Figure 6.** Summary of the challenge of SULEV for LDD (11). The red zone represents the engine and aftertreatment options and is bordered by the engine-out emissions (Bin 5) of a demonstration vehicle and the estimated limit of deNOx aftertreatment of ~80%. The best fuel economy is derived when using the cleanest engines.

Table 2 shows a summary from the literature of >300 kW HD engine technologies that might be used to attain the next wave of tailpipe regulations. These advanced engines might have 2-stage turbocharging, and will have significant EGR, >200 bar peak cylinder pressures and >2000 bar common rail fuel injection pressures.

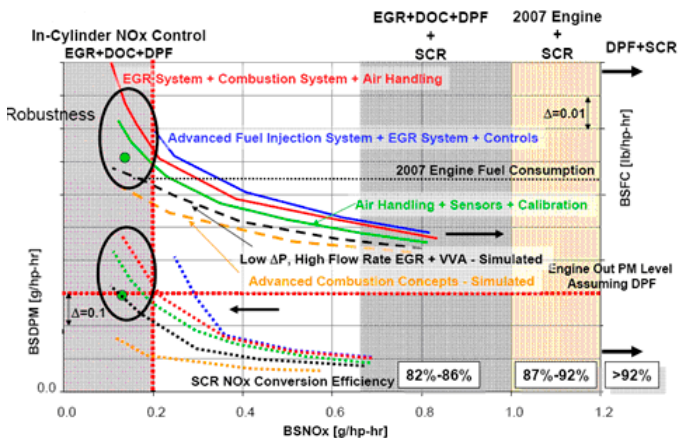
	US2007	US2010	Euro VI	Tier 4A Non-Road w/ DPF
Turbocharging	1- and 2-stage; up to 4.5 bar	2-stage;	2-stage	1- and 2-stage
Full load EGR	25%	up to 35%	25%	~15%
Peak cylinder pressure	190-210 bar	220-250 bar	220 bar	180-210 bar
Fuel injection	2200 bar UI	2500 bar CR	>2200 bar CR	2000 bar CR

**Table 2.** Summary of expected HD engine technologies for the >300 kW class of engines to attain future tailpipe regulations.

Moving into the future, Stanton provides a roadmap for improving brake thermal efficiency from about 43% today to 52% by 2015 (12). Figure 7 shows some of the results. The top part of the figure shows how brake specific fuel consumption (BSFC) depends on engine



calibration for NO<sub>x</sub> for a range of increasing technologies. These technologies reduce BSFC by about 4 to 6% at the lower NO<sub>x</sub> levels. The bottom part of the figure shows PM is also reduced upwards of 25% with increasing technology. More interestingly, the figure shows the potential for an engine to attain the US2010 NO<sub>x</sub> levels of 0.2 g/bhp-hr without NO<sub>x</sub> aftertreatment and at the same or lower fuel consumption of US2007 engines. However, notice that running any one of these engine configurations to higher NO<sub>x</sub> levels results in significant fuel savings wherein an 82 to 86% efficient SCR deNO<sub>x</sub> system can return 6 to 7% fuel savings. As such, although deNO<sub>x</sub> would be optional for these engines, it would be highly desirable.



**Figure 7.** Impact of some advanced engine technologies on emissions and fuel consumption. Note that technologies make possible US2010 engine-out NO<sub>x</sub> levels while maintaining US2007 fuel consumption (12). Each PM division is 1.3 mg/kW-hr, and each BSFC division is ~6 g/kW-hr.

## NO<sub>x</sub> Control Technologies

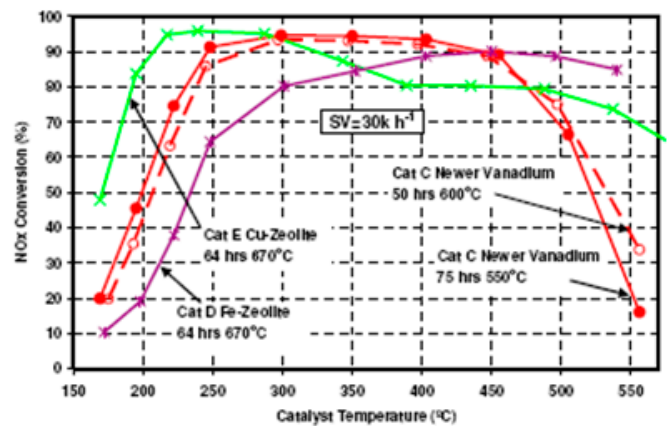
### SELECTIVE CATALYTIC REDUCTION

Much was shown in the literature in 2008 about SCR systems. They can be quite complex. For example, the tank typically has level, temperature, and urea quality sensors, and has to be engineered to withstand freezing and thawing of the urea (13). This requires expansion zones and designs to relieve expansion stresses upon freezing. Further, the outlet line has to be engineered to allow access to the first liquid upon thawing, but also to urea under a variety of vehicle positions. When there is frozen urea sloshing around in the tank, sensors and lines need to be protected from mechanical damage.

Urea injection quality and mixing are also complex and critically important. Breedlove, et al., (14) show different nozzle designs can provide different drop quality, with a range of characteristics at different stages of the injection. This, in turn can impact system deNO<sub>x</sub> efficiency by up to 10% (15). Urea injection at temperatures less than 190°C is fraught with problems related to incomplete evaporation of the urea and the

build-up of solid deposits in the exhaust system. Cyanuric acid is the main component, and can decompose at 300°C, but they get very stubborn upon aging and might require exposure to 600°C in these cases to remove them (16). Regarding mixing, Gorbach (15) saw system efficiencies vary from 60 to 95% depending on how well ammonia was distributed across the catalyst. Urea mixers come in a variety of types, ranging from wire mesh designs to vanes and honeycombs.

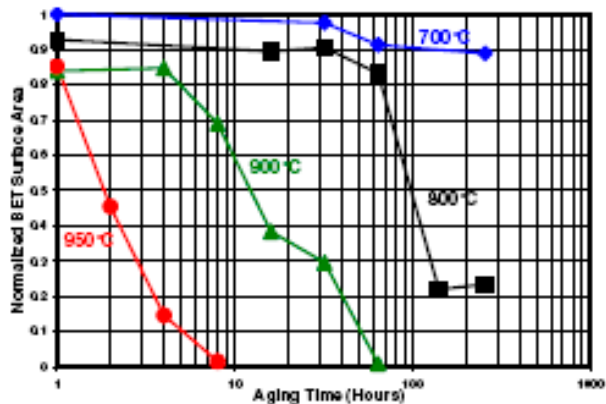
On the catalyst itself, in Europe, China, and India SCR catalysts are based on vanadia. If DPFs are used with SCR systems, such as in Japan and the US, zeolites are preferred due to the better high temperature durability needed when exotherms associated with DPF regeneration can expose SCR catalysts to 800°C temperatures. Figure 8 shows relative deNO<sub>x</sub> efficiencies for vanadia, and Cu- and Fe-based zeolite catalysts (17) without NO<sub>2</sub> management. Cu-zeolites have the best low temperature performance, and Fe-zeolites have the best high-temperature performance. Copper and iron zeolites can be used together for a balanced performance over a broad temperature range (18, 19). Vanadia is cheaper and more sulfur tolerant, but deteriorates at temperatures greater than 600°C, whereas zeolites are affected very little with long exposures (64 hours) at upwards of 800°C (20), as shown in Figure 9.



**Figure 8.** Relative deNO<sub>x</sub> efficiency for vanadia and zeolite SCR catalysts for NO as the NO<sub>x</sub> species. Cu-zeolites have the best low temperature performance, and Fe-zeolites are best at higher-temperatures (17).

Regarding durability and stability of performance, a number of studies show susceptibility to sulfur, hydrocarbon, and platinum poisoning. Like vanadia, Fe-zeolites are quite tolerant to sulfur exposure, but Cu-zeolite performance deteriorates (21). In this case, performance can be restored if a desulfation cycle is run (18, 21), which depends on formulation but can be at temperatures up to 650°C in lean conditions. The catalyst may never recover if sulfur levels are high (2000 ppm) and exposure is long (17). Zeolites are known to adsorb hydrocarbons, and if the hydrocarbons accumulate (such as during DPF regeneration or pre-

mixed combustion modes) and then oxidize, exotherms up to 1000°C may occur (22). Cu-zeolite formulations exist that have low HC-adsorption without sacrificing deNO<sub>x</sub> performance. On platinum poisoning, Jen, et al. (23) show slight deterioration of SCR performance if an upstream diesel oxidation catalyst (DOC) is operated at 670°C, but significant performance declines at DOC temperatures >750°C, which might occur, for example, during DPF regeneration. Using an ethylene hydrogenation technique, the investigators proved platinum from the DOC sublimates and accumulates (<5 ppm) on the SCR catalyst, resulting in ammonia oxidation.



**Figure 9.** Relationship between SCR catalyst surface area (governs deNO<sub>x</sub> efficiency) and thermal durability for a Cu-zeolite. This catalyst can withstand period exposures up to 900°C, and longer term exposure (64 hours) to 800°C (20).

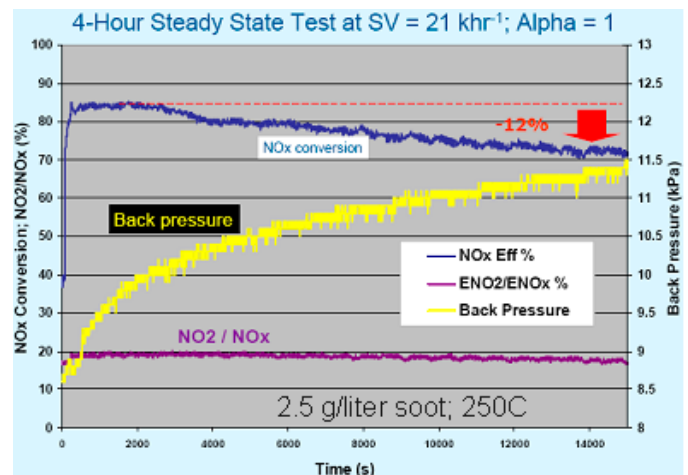
Finally on SCR durability, metallic copper can come out of Cu-zeolites exposed to hot (650°C) and rich (1% oxygen) conditions (24). This has raised the suspicion of the US EPA because under proper conditions copper can catalyze dioxin formation if chlorine is present. They are currently investigating this. New zeolite formulations are being developed for low temperature deNO<sub>x</sub> without copper (19), and new catalyst families based on acidic zirconia are also emerging (25).

Optimized operation of zeolite SCR catalysts depends on control of adsorbed urea and using oxidation catalysts to deliver the proper NO<sub>2</sub>/NO<sub>x</sub> ratio, especially at the lower temperatures (<250°C). Murata, et al. (26) show that SCR efficiency at temperatures <265°C is strongly dependent on the amount of ammonia that is stored in the catalyst. They developed an algorithm that kept stored urea within control limits, resulting in improving deNO<sub>x</sub> efficiency from nominally 50% to 75% in the Japanese HD transient cycle with an average temperature of only 160°C. Regarding NO<sub>x</sub> specie management, the fastest SCR reaction uses both NO and NO<sub>2</sub>, with a 1:1 ratio being optimum. This is especially critical for good performance at T<200°C. However, excess NO is occasionally needed to oxidize ammonium nitrate (27), which can condense and block catalyst sites. Anderson, et al. (21), show that low-

temperature Fe-zeolite performance can surpass that of Cu-zeolites if the NO<sub>2</sub> content is optimized.

Good SCR system performance is strongly dependent on injecting the right amount of urea, wherein the high temperature performance of Cu-zeolites can equal that of Fe-zeolites if excess urea is used (21). Voss shows that Cu-zeolites will oxidize ammonia, but as with vanadia and Fe-zeolites, they can benefit from ammonia slip catalysts (28). However, if not properly designed, N<sub>2</sub>O may be formed by incomplete oxidation of the ammonia on slip catalysts, resulting in a 15 to 20% increase in the greenhouse gas emissions of a truck, far offsetting any fuel economy savings attributed to running high engine-out NO<sub>x</sub> with SCR (29).

Emerging SCR systems now incorporate the catalyst onto the DPF (21, 30, 31, 32). Performance is generally slightly lower (5-10% deNO<sub>x</sub> efficiency) than using a separate catalyst, but good DPF regeneration control is needed to prevent deterioration of the catalyst. Results are mixed on the impact of soot on blocking SCR performance (30, 31), and back pressure is somewhat higher for the system due to high catalyst loading on the DPF (31). A key topic for future work is the impact on passive DPF regeneration from NO<sub>2</sub>. Figure 10 shows some preliminary results, wherein soot did accumulate under conditions wherein passive regeneration is expected.



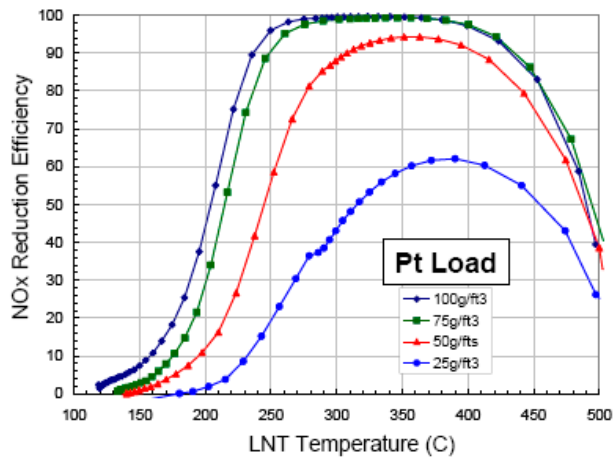
**Figure 10.** Early results using a DPF that is coated with SCR catalyst (31). Soot builds up and interferes with the SCR reaction, but others show no soot impact (30).

## HC-BASED DENOX

In some cases, SCR is not the preferred deNO<sub>x</sub> technology. In some non-road and vocational vehicle applications, urea handling might be problematic. Also, mainly because of the fixed cost of an on-board urea system, small lean NO<sub>x</sub> traps (LNTs) are cheaper for engines less than about 2.0 to 2.5 liters (33). Finally, as mixed-mode engines greatly reduce low-load NO<sub>x</sub>, allowing LNTs to focus on NO<sub>x</sub> entering at temperatures greater than about 350°C, about 50-70% of the precious

metals might be removed (34, 35), which may make them more economically attractive than SCR for cars with up to 5- or 6-liter mixed-mode engines. In this regard, Figure 11 shows how LNT deNOx performance varies with precious metal loading (35).

Improved LNT formulations are coming. Precious metal dispersion is greatly enhanced, resulting in reduced usage and improved performance (36). Components are added to the LNT to inhibit sulfate formation (37), and desulfation temperatures for new formulations are coming down as well, to the 600°C range (from 700-750°C) without compromising high-temperature performance (38).



**Figure 11.** LNT performance dependency on platinum loading. At temperatures <350°C, platinum loadings of ~75 g/ft<sup>3</sup> desirable. However, at higher temperatures reducing loading by 33% has minimal impact (35). As such, applying low-NOx combustion strategies up to exhaust temperatures of 350°C can save deNOx cost.

Regarding regeneration, generating rich conditions in the cylinder via a delayed and extended main injection provides more hydrogen and CO for better regeneration (39) than an extra post injection, but exhaust port injection of fuel when combined with oxygen depletion using engine means was as effective and more robust (37).

Onodera, et al., (40) describe a combination HC-adsorber LNT design, wherein the zeolite HC-adsorber was applied first to the honeycomb substrate and the LNT material was placed on top. The HC adsorber helps reduce cold start HC emissions and adsorbs HC during the lean periods. Upon release during the hotter rich periods, hydrogen and CO are formed to help LNT regeneration. The concept helped achieve SULEV emission levels in the demonstration program.

Two reports on new LNT formulations are noteworthy. Xu, et al. (41) show that alumina-based LNTs desulfate easily (1-2 minutes at 500-650°C) and have good performance in the 150 to 300°C range, making them attractive for use near the back of an aftertreatment

system. Rohart, et al. (42) expand on this, adding ceria and mixed rare earths for enhanced performance while maintaining easier desulfation. They also show an enhanced water-gas shift reaction that might help form ammonia for use in a supplementary SCR catalyst.

Regarding LNT diagnosis, a new sensor was reported that uses the impedance of the LNT catalyst, imbedded in the sensor, to determine the state of loading of the LNT (43).

Finally, on HC-based deNOx systems, there are recent and interesting developments on HC-SCR catalysts reported by Blint, et al.(44, 45). Instead of using urea (ammonia) as the reductant, they use HCs from the fuel. The catalyst has very low precious metal loadings (0.7 g/liter, reference 46), but needs temperatures greater than about 300°C to perform well. As such, these catalysts might also fit in with a mixed-mode engine in which deNOx is only needed at higher load operation. The investigators reported (44) a control strategy that includes hydrogen (250 to 4000 ppm), oxygen (about 10%), HC:NOx ratio (4 to 20), temperature, and exhaust flow. In dynamometer testing, they reported 60 to 92% deNOx efficiency depending on test cycle.

## PM Control Technologies

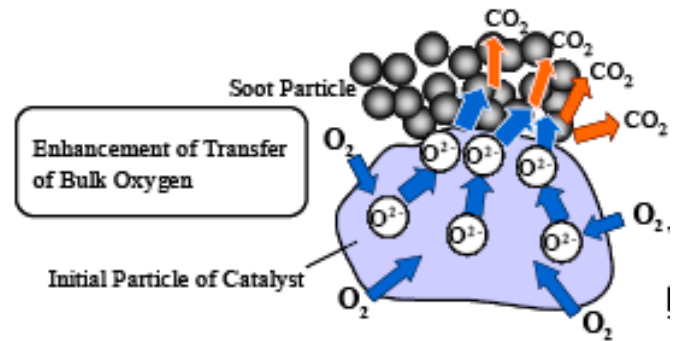
Diesel particulate filters (DPFs) are now as much a part of the diesel engine as fuel injectors. Virtually all new diesel cars in Europe, the US, and Japan have or will shortly have DPFs. They have a high penetration in new Japanese trucks, and all new US HD truck engines had them since January 2007.

To keep lube oil ash from sintering to itself and to protect DPF catalyst, maximum soot burning exotherms need to be controlled. Some parameters to enable this are filter type (material and catalyst), exhaust temperature and flow rate, and soot loading and characteristics. Boger, et al., (47) provide an excellent example of how maximum exothermic temperatures under worst case “drop-to-idle” conditions (DTI; start soot combustion at high temperature and flow, and then drop to idle) can be controlled when using aluminum titanate filters. The regeneration is initiated at about 550°C to provide a safe, steady regeneration. As soot is burned, the exhaust temperature is increased in stages to 650°C to result in faster, complete regeneration. They show that oxide filters regenerate more efficiently at any given temperature versus SiC filters, Figure 12. The authors show this feature can be useful in transient conditions wherein regeneration may be sporadic.

In other reports on DPF regeneration, Suresh, et al., (48) show that DOCs are needed to get hot DPF face temperatures, wherein the first centimeters might not regenerate without a DOC. They also show that decreasing air/fuel ratio and using injection strategy are more effective for heating a DOC than using continuous fuel injection, although this latter method can work for



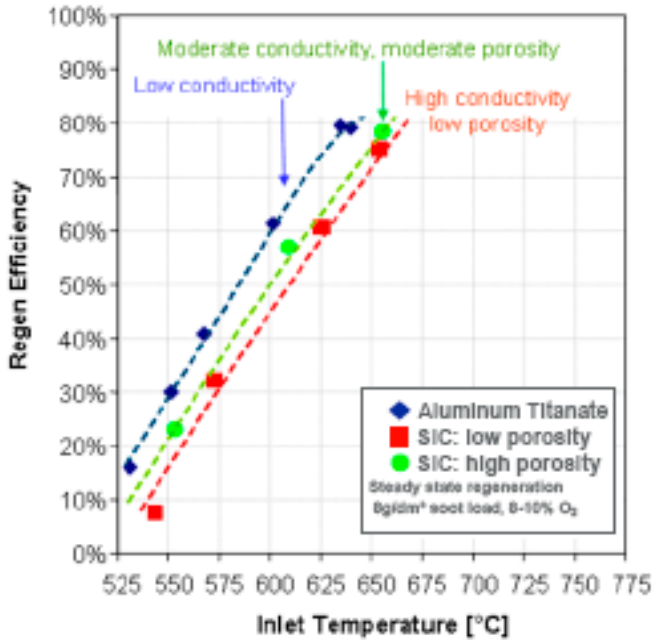
large DOCs or high PGM loadings. Harlé, et al., (49) reported on the third generation fuel borne catalyst. It is based on 3 ppm iron allowing a 1.7 liter tank to last the life of the vehicle (240,000 km), and requiring no DPF ash cleaning. Shorter DPFs regenerate more efficiently and have lower thermal gradients, allowing a higher specific soot capacity for a safe regeneration (50, 51). Finally, the enhanced oxidation of biodiesel soot is shown to be due to remnant adsorbed oxygen on the soot surface (52).



**Figure 13.** New zirconia soot catalyst transfers oxygen from the gas to the soot-catalyst interface for 70% faster soot oxidation rates at lower temperatures (53).

Understanding of DPF fundamentals is moving forward. Wafers of DPF material were loaded under a variety of conditions and the partitioning of soot and SOF (soluble organic fraction) was evaluated (58). SOF collected inside the wall before a cake was formed, and increased with gas velocity. Finer particles (54 nm average) form a filter cake before larger particles (98 nm) due to faster particle diffusion to the ceramic pore. The authors thought the partitioning of SOF has implications to organic carbon particulate oxidation in the filter. Others show that when a porous membrane is added to the inlet wall, soot is kept out of the wall and filtration efficiency and back pressure improve, as well as the correlation between back pressure and soot loading (59).

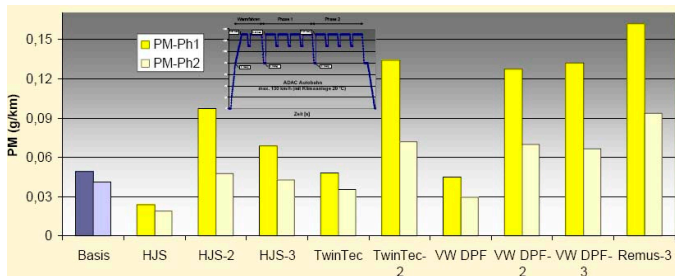
Particulate oxidation catalysts (POCs), sometimes referred to as partial filters or open filters, are being investigated for Euro IV equivalent applications in India and China. Presumed advantages are that the POC does not need to be regenerated to prevent plugging. However, filter regeneration by NO<sub>2</sub> oxidation of soot is needed to maintain filtration efficiency. It is thought that as the filtered pathway fills, more gas goes through unfiltered. Various POCs were evaluated in German LDD retrofits. Filtration efficiency drops from 45% for fresh POCs to nominally 30% after only 1500 km of testing (60). More alarming was that collected soot was released from all filter types as an emission (blow off) under transient driving conditions. This is shown in Figure 14 wherein post filter PM is higher than engine-out levels. If >50 ppm sulfur fuel is used, as is expected in China and India, NO<sub>2</sub> regeneration is significantly compromised (61), and this effect might be more prevalent. Further, the strong oxidation catalyst typically used in these systems to produce NO<sub>2</sub> to keep the filter clean will oxidize the sulfur to form significant amounts sulfuric acid PM (62).



**Figure 12.** Aluminum titanate DPFs regenerate more efficiently at any given temperature due to their lower thermal conductivity. (47).

Filter catalyst technology is also advancing impressively. New formulations based on ceria or zirconia react the soot directly with oxygen at the catalyst-soot interface. As shown in Figure 13, oxygen from the gas dissociates on the catalyst, and diffuses through the lattice to the soot (53). Soot oxidation temperatures are reduced 75°C, and oxidation rates increased 70% in dynamometer testing. The catalyst is now in series production. Enhanced versions based on ceria are showing potential to oxidize at temperatures as low as 260°C with very little if any precious metal (54). In this interesting study, Southward, et al. show that NO<sub>2</sub> oxidation of soot, as is the common passive regeneration mode today, can actually detract from these new soot oxidation catalysts by reducing the soot-catalyst interfacial area. Good soot-catalyst contact is important, so high-surface area DPFs (55) and specialized catalyst washcoats (56, 57), as well as low soot loadings from the engine (as with advanced combustion strategies) will enable these designs.





**Figure 14.** Post POC PM levels are generally higher than engine-out levels (left set of bars) due to “blow-off” during transient testing (cycle in inset). Reference 60.

Regarding OBD of DPF systems, a refined soot model using wall permeability algorithms shows promise for meeting OBD requirements (63). The oxidation behavior of soot was much different for cracked filters than for good filters, and this could be picked up by the model. If models are not accurate enough for OBD, soot sensors may be needed. Sandig, et al., (64) tested two sensor concepts. The concept using charge transfer by soot from one charged plate to another was much more sensitive to post-DPF particulate measurement than the one using PM film electrical property measurement.

## Oxidation Catalysts

Diesel oxidation catalysts (DOCs) serve the role of oxidizing HC and CO emissions, burning fuel to actively regenerate filters, and generating NO<sub>2</sub> for passive DPF regeneration. Low temperature light-off is important in all cases. Fujdala, et al., (65) created CO-exclusion zones on platinum catalysts that leave room for more oxygen adsorption at lower temperatures, hence decreasing CO light-off temperatures 100°C and propylene light-off 40°C, down to 180°C. In this regard, the US Department of Energy started a project to drop DOC light-off temperatures to the 150°C range to facilitate higher HC emissions at lower temperatures from advanced combustion modes (66). Passive soot oxidation can be enhanced at low temperatures by increasing NO<sub>2</sub> production. New Pt/Pd DOC formulations produce 60% more NO<sub>2</sub> at 250°C (67).

## CONCLUSIONS

This summary covers key and representative developments in diesel emissions regulations, engine

developments, and NO<sub>x</sub>, PM (particulate matter) and hydrocarbon (HC) remediation.

California is discussing another round of criteria pollutant tightening on light duty. CO<sub>2</sub> regulations are being discussed in the developed markets. The US mandates on fuel economy and the proposed standards in Europe and California will result in a paradigm shift, wherein technologies previously rejected based on customer value will now be re-evaluated. Heavy duty regulatory developments are now focused on Europe, where Euro VI regulations have been proposed for about 2013. The regulations are intended to be technology harmonizing with the US and Japanese regulations.

Engines are continuing to make very impressive progress, with clean combustion strategies in active development mainly for US light-duty application. Heavy-duty research engines are more focused on traditional approaches, and will provide numerous engine/aftertreatment options for hitting the tight US 2010 regulations.

NO<sub>x</sub> control is focusing on selective catalytic reduction (SCR) for diverse applications. Zeolite catalysts will be the mainstay for Japan, US, and Euro VI applications. Focus is catalyst improvements and system optimization. Lean NO<sub>x</sub> traps (LNTs) are effective up to about 70-80% deNO<sub>x</sub> efficiency, and are being used for light-duty applications with significant improvements coming on precious metal utilization.

Diesel particulate filter (DPF) technology is in a state of optimization and cost reduction. Very sophisticated management strategies are being utilized, which open up options for new filter materials and alternative system architectures. New catalyst formulations that oxidize soot at the catalyst-soot interface are emerging and are enhancing regeneration in the first commercial applications.

Diesel oxidation catalysts (DOCs) are lighting-off and generating more NO<sub>2</sub> for DPF regeneration at lower temperatures.

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