Diesel Emission Control in Review

Timothy V. Johnson
Corning Incorporated

ABSTRACT

This summary covers representative developments from 2008 in diesel regulations, engine technology, and NOx, 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_2 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_2 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 deNOx systems optional for even the tightest NOx standards, but deNOx systems enable much lower fuel consumption levels and will likely be used.

NOx control is centered on SCR (selective catalytic reduction) for diverse applications. Focus is on cold operation, system optimization, and catalyst durability. LNT (lean NOx 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 NOx 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 NOx, 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_2 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, NOx 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 deNOx control, the required 85% control to meet SULEV standards is a stretch for today's deNOx 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.
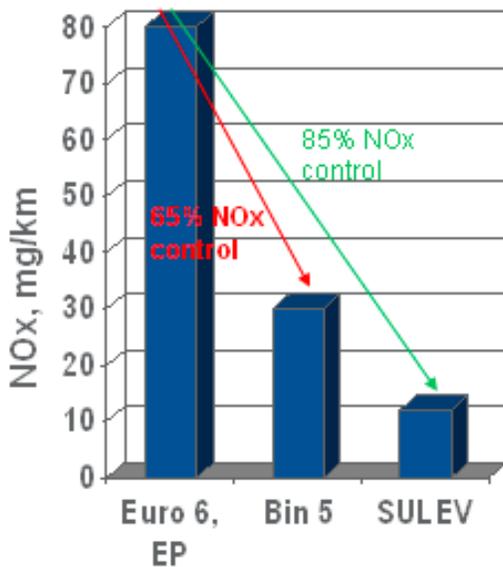

Figure 1. Euro 6 (2014) LDD NOx regulations compared to US Tier 2 Bin 5 and California SULEV (Bin 2). Test cycle differences are not considered here.

Perhaps the more far-reaching regulatory development on LD relates to CO_2 emissions mandates. California was the first to require CO_2 (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_2 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_2 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_2 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_2 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 (NOx, 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.
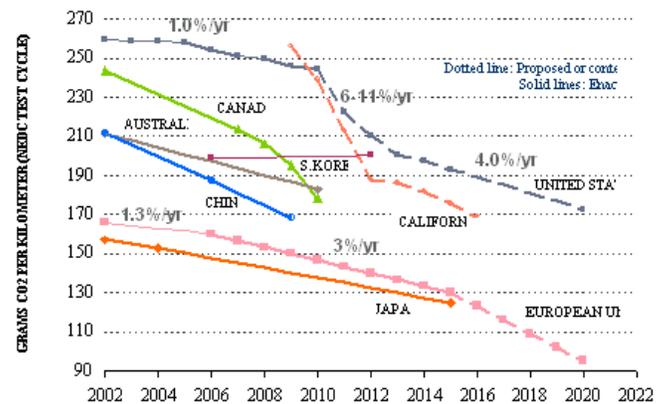

Figure 2. Comparison of worldwide fuel economy, fuel consumption, or proposed CO_2 standards, all normalized to the NEDC and adjusted for fuel mix (2).

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) NOx 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.
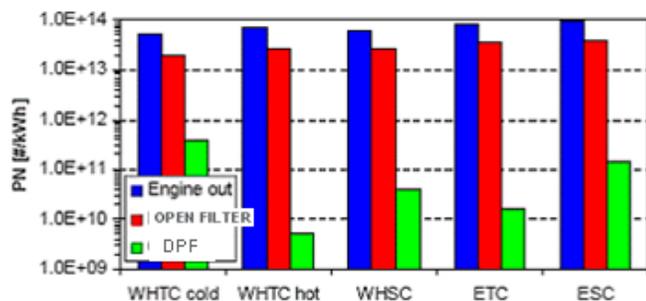

Figure 3. HDD PN emissions using different test cycles and technologies (3).

On the HD CO_2 regulatory front, it appears imminent that CO_2 regulations will also apply to HD. CARB held a HD CO_2 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_2 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_2 from diesel vehicles are of increasing interest. Although no tailpipe regulations on NO_2 have been implemented or even proposed, several regions in Europe will have difficulty meeting their 2010 NO_2 immission (ambient air levels) requirements. In the US, California now requires that NO_2 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_2 emissions will be reduced nominally 15% in premium vehicle applications (6). Other opportunities for CO_2 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).
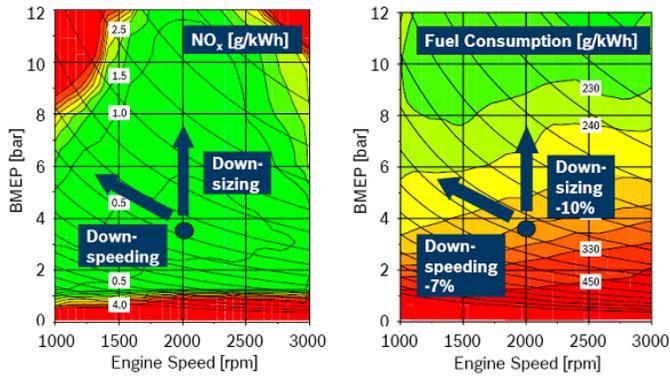

Figure 4. Downsizing and down-speeding engines can result in nominally 10 and 7% decreases in fuel consumption (right), but with ~50% increases in NOx (left). Reference 6.
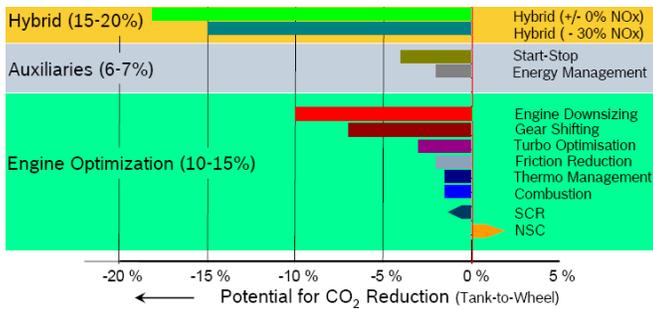

Figure 5. Relative to a Euro 4 diesel with DPF, 20 to 40% CO_2 reductions are possible with light-duty diesels. The engine can contribute 10 to 15% more reductions (6).

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.
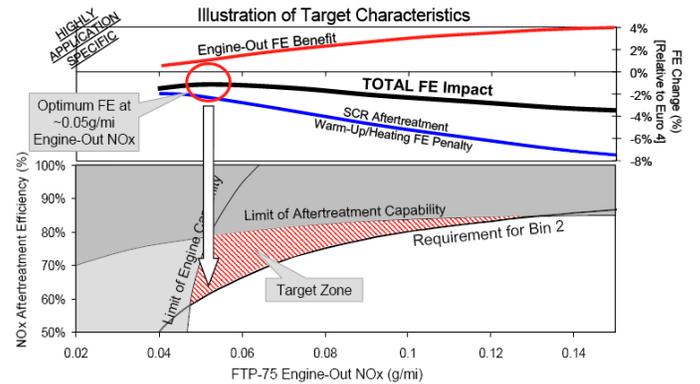

Figure 6. Summary of the challenge of SULEV for LDD (11). The red zone represents the engine and aftertreatment options and is bordered by the engine-out emissions (Bin 5) of a demonstration vehicle and the estimated limit of deNOx aftertreatment of ~80%. The best fuel economy is derived when using the 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 NOx for a range of increasing technologies. These technologies reduce BSFC by about 4 to 6% at the lower NOx 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 NOx levels of 0.2 g/bhp-hr without NOx aftertreatment and at the same or lower fuel consumption of US2007 engines. However, notice that running any one of these engine configurations to higher NOx levels results in significant fuel savings wherein an 82 to 86% efficient SCR deNOx system can return 6 to 7% fuel savings. As such, although deNOx would be optional for these engines, it would be highly desirable.
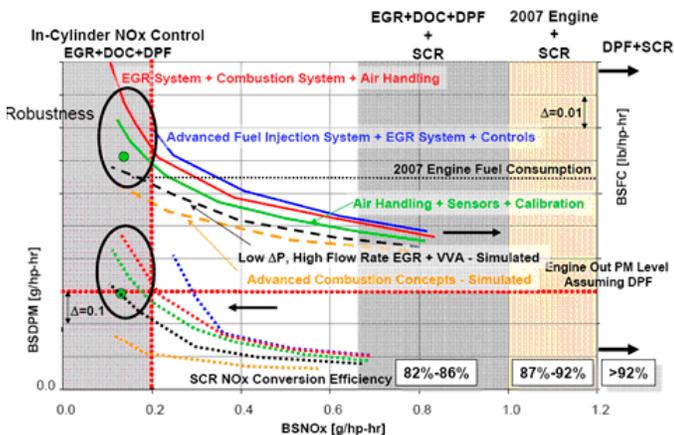

Figure 7. Impact of some advanced engine technologies on emissions and fuel consumption. Note that technologies make possible US2010 engine-out NOx levels while maintaining US2007 fuel consumption (12). Each PM division is 1.3 mg/kW-hr, and each BSFC division is ~6 g/kW-hr.

NOx 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 deNOx efficiency by up to 10% (15). Urea injection at temperatures less than 190ºC 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 300ºC, but they get very stubborn upon aging and might require exposure to 600ºC 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 800ºC temperatures. Figure 8 shows relative deNOx efficiencies for vanadia, and Cu- and Fe-based zeolite catalysts (17) without NO_2 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 600ºC, whereas zeolites are affected very little with long exposures (64 hours) at upwards of 800ºC (20), as shown in Figure 9.
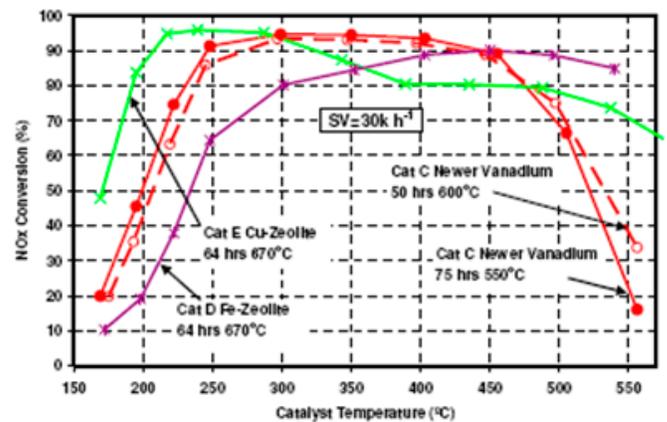

Figure 8. Relative deNOx efficiency for vanadia and zeolite SCR catalysts for NO as the NOx species. Cu-zeolites have the best low temperature performance, and Fe-zeolites are best at higher-temperatures (17).

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 650ºC 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 1000ºC may occur (22). Cu-zeolite formulations exist that have low HC-adsorption without sacrificing deNOx performance. On platinum poisoning, Jen, et al. (23) show slight deterioration of SCR performance if an upstream diesel oxidation catalyst (DOC) is operated at 670ºC, but significant performance declines at DOC temperatures >750ºC, which might occur, for example, during DPF regeneration. Using an ethylene hydrogenation technique, the investigators proved platinum from the DOC sublimes and accumulates (<5 ppm) on the SCR catalyst, resulting in ammonia oxidation.
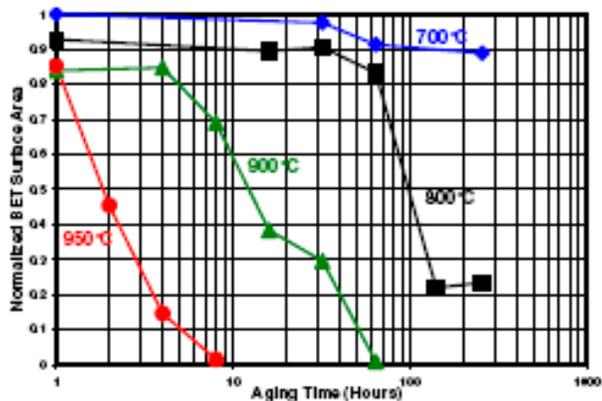

Figure 9. Relationship between SCR catalyst surface area (governs deNOx efficiency) and thermal durability for a Cu-zeolite. This catalyst can withstand period exposures up to 900ºC, and longer term exposure (64 hours) to 800ºC (20).

Finally on SCR durability, metallic copper can come out of Cu-zeolites exposed to hot (650ºC) 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 deNOx 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_2/NOx ratio, especially at the lower temperatures (<250ºC). Murata, et al. (26) show that SCR efficiency at temperatures <265ºC 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 deNOx efficiency from nominally 50% to 75% in the Japanese HD transient cycle with an average temperature of only 160ºC. Regarding NOx specie management, the fastest SCR reaction uses both NO and NO_2, with a 1:1 ratio being optimum. This is especially critical for good performance at T<200ºC. 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_2 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_2O 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 NOx with SCR (29).

Emerging SCR systems now incorporate the catalyst onto the DPF (21, 30, 31, 32). Performance is generally slightly lower (5-10% deNOx 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_2. Figure 10 shows some preliminary results, wherein soot did accumulate under conditions wherein passive regeneration is expected.
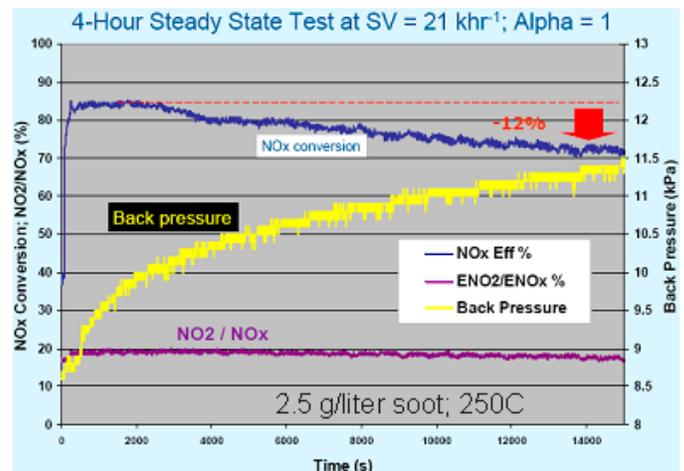

Figure 10. Early results using a DPF that is coated with SCR catalyst (31). Soot builds up and interferes with the SCR reaction, but others show no soot impact (30).

HC-BASED DENOX

In some cases, SCR is not the preferred deNOx 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 NOx 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 NOx, allowing LNTs to focus on NOx entering at temperatures greater than about 350ºC, 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 600ºC range (from 700-750ºC) without compromising high-temperature performance (38).
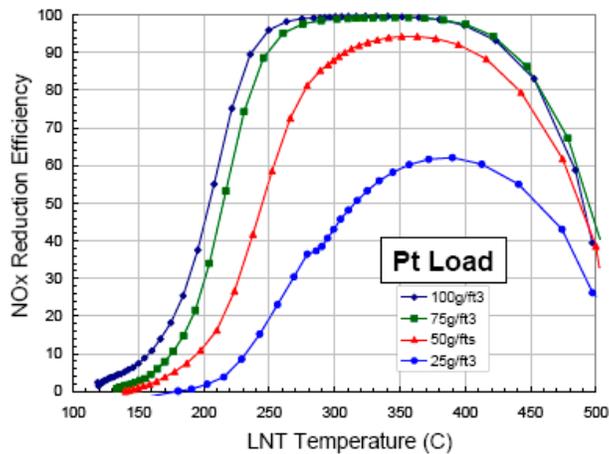

Figure 11. LNT performance dependency on platinum loading. At temperatures <350ºC, platinum loadings of ~75 g/ft^3 desirable. However, at higher temperatures reducing loading by 33% has minimal impact (35). As such, applying low-NOx combustion strategies up to exhaust temperatures of 350ºC can save deNOx 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 500-650ºC) and have good performance in the 150 to 300ºC 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 300ºC 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 550ºC to provide a safe, steady regeneration. As soot is burned, the exhaust temperature is increased in stages to 650ºC 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).
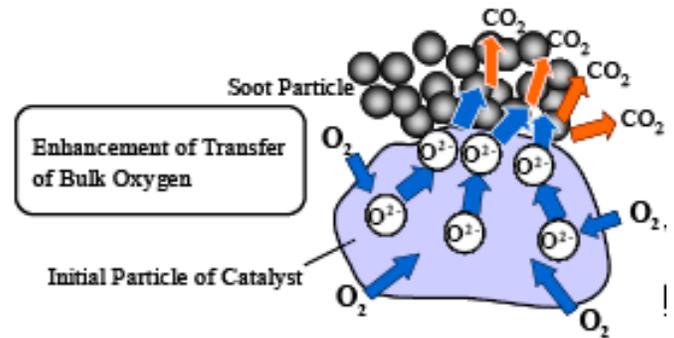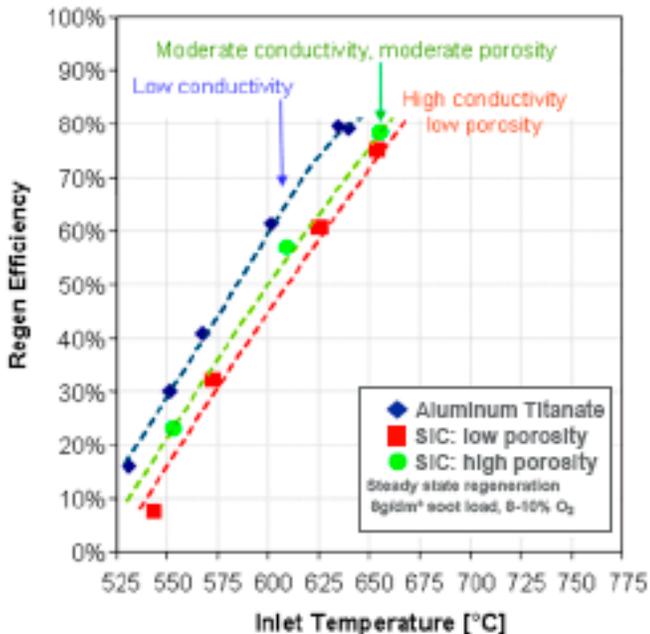

Figure 12. Aluminum titanate DPFs regenerate more efficiently at any given temperature due to their lower thermal conductivity. (47).

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 75Cº, 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 260ºC with very little if any precious metal (54). In this interesting study, Southward, et al. show that NO_2 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 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_2 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_2 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_2 to keep the filter clean will oxidize the sulfur to form significant amounts sulfuric acid PM (62).
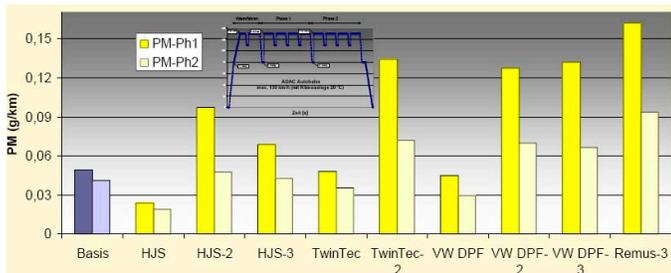
Figure 14. Post POC PM levels are generally higher than engine-out levels (left set of bars) due to "blow-off" during transient testing (cycle in inset). Reference 60.

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_2 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 100Cº and propylene light-off 40Cº, down to 180ºC. In this regard, the US Department of Energy started a project to drop DOC light-off temperatures to the 150ºC 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_2 production. New Pt/Pd DOC formulations produce 60% more NO_2 at 250ºC (67).

CONCLUSIONS

This summary covers key and representative developments in diesel emissions regulations, engine developments, and NOx, PM (particulate matter) and hydrocarbon (HC) remediation.

California is discussing another round of criteria pollutant tightening on light duty. CO_2 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.

NOx 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 NOx traps (LNTs) are effective up to about 70-80% deNOx 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_2 for DPF regeneration at lower temperatures.

CONTACT

JohnsonTV@Corning.com

REFERENCES

1. Johnson, T.V., "Diesel Emission Control in Review" *SAE Int. J. Fuels Lubr.* **1**(1):68-81, 2008.
2. "Passenger Vehicle Greenhouse Gas and Fuel Economy Standards: A Global Update", The International Council on Clean Transportation, July 2007, www.theicct.org.
3. Provided by Andersson, J., European UN-PMP program.
4. Mueller-Haas, K., et al., "Emission Reduction Systems for Non-Road Applications", CTI Non-Road Forum, Stuttgart, July 1-2, 2008.
5. Koerfer, T., et al., "The Future Power Density of HSDI Diesel Engines with Lowest Engine out Emissions – A Key Element for Upcoming CO2 Demands", FISITA Conference, Munich, September 2008, F2008-06-015.
6. Rueger, J., "Clean Diesel – Real Life Fuel Economy and Environmental Performance", SAE Government and Industry Meeting, Washington, D. C., May 2008.
7. Czarnowski, R. , et al., "Can Future Emissions Limits be Met with a Hybrid EGR System Alone?", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.
8. Mattes, W., "BMW Diesel - Engine Concepts for Efficient Dynamics", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.
9. Dorenkamp, R., "Volkswagen's Exhaust Gas Aftertreatment Concepts to Meet the Lowest Emissions Standards", FAD Conference, Dresden, November 2008.
10. Joergl V., et al., "Can Future Emissions Limits be Met with a Hybrid EGR System Alone?", IAV MinNOx Conference, Berlin, June 2008.
11. Cooper, B., "US Tier 2 Bin 2 Diesel Research Progress", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.
12. Stanton, D., "Advanced Combustion Technology to Enable High Efficiency Clean Combustion", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.
13. Ostertag, M., "Urea Reservoir Systems for Off-Highway and the Heavy Duty Market", CTI deNOx Conference, Detroit, December 2008.
14. Breedlove, R., et al., "S, M, L, XL – Optimized Urea Injection", CTI deNOx Forum, Detroit, December 2008.
15. Gorbach, A., „Urea Preparation in Exhaust Systems of Commercial Vehicles", CTI Emission Control Forum, Nuertingen, January 2009.
16. Way, P., panel discussion Diesel Emission Control: Urea Deposits and Byproducts at SAE Commercial Vehicle Conference, Chicago, October 2008.
17. Girard, J.W., Montreuil, C., Kim, J., Cavataio, G. et al., "Technical Advantages of Vanadium SCR Systems for Diesel NOx Control in Emerging Markets" *SAE Int. J. Fuels Lubr.* **1**(1):488-494, 2008.
18. Girard, J., Cavataio, G., Snow, R. and Lambert, C., "Combined Fe-Cu SCR Systems with Optimized Ammonia to NOx Ratio for Diesel NOx Control" *SAE Int. J. Fuels Lubr.* **1**(1):603-610, 2008.
19. Iretskaya, S., et al., "Two Catalyst Formulations – One Solution for NOx After-Treatment Systems", US Dept. of Energy Diesel Engine Emissions and Energy Reduction Conference (DEER), Detroit, August 2008.
20. Cavataio, G., Jen, H-W., Warner, J.R., and Girard, J.W. et al., "Enhanced Durability of a Cu/Zeolite Based SCR Catalyst", *SAE Int. J. Fuels Lubr.* **1**(1):477-487, 2008.
21. Anderson, Paul, et al.," SCR Catalysts for Low-Emitting Diesels", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.
22. Girard, J., et al., "Influence of Hydrocarbon Storage on the Durability of SCR Catalysts", SAE 2008-01-0767.
23. Jen, H-W, Girard, J.W., Cavataio, G., and Jagner, M.J., "Detection, Origin and Effect of Ultra-Low Platinum Contamination on Diesel-SCR Catalysts", *SAE Int. J. Fuels Lubr.* **1**(1):1553-1559, 2008.
24. Huang, Y., Cheng, Y., and Lambert, C., "Deactivation of Cu/Zeolite SCR Catalyst Due to Reductive Hydrothermal Aging" *SAE Int. J. Fuels Lubr.* **1**(1):466-470, 2008.
25. Verdier, S., et al.," Acidic Zirconia Materials for Durable NH3-SCR deNOx Catalysts", SAE 2008-01-1022.
26. Murata, Y., et al., "Improvement of NOx Reduction Rate of Urea-SCR System by NH3 Adsorption Quantity Control", SAE 2008-01-2498.
27. Murata, Y., et al., Waseda Univ, Proceedings of JSAE, No.20085846 (2008).
28. Voss, K. and Kakwani, R., "Heavy Duty Diesel 4-Way Aftertreatment Systems Development for US 2010 and Beyond", SAE Commercial Vehicle Conference, Chicago, October 2008.
29. Suzuki, H. and Ishii, H., "Analysis of Emission and Formation Characteristics of Nitrous Oxide (N2O) under Urea SCR", JSAE 143-08.
30. Lee, J.H., Paratore, M.J., and Brown, D.B., "Evaluation of Cu-Based SCR/DPF Technology for Diesel Exhaust Emission Control" *SAE Int. J. Fuels Lubr.* **1**(1):96-101, 2008.
31. Oladipo, B., et al., "Simplification of Diesel Emission Control System Packaging Using SCR Coated on DPF", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.

32. Gandhi, H., et al., "Urea SCR Options for a Tier 2 Light-Duty Diesel Truck", FISITA Conference, Munich, September 2008, Paper F2008-06-022.
33. Johnson, T. V., "Diesel Emission Control in Review", US Dept. of Energy Diesel Engine Efficiency and Emissions Reduction (DEER) Conference, Detroit, August 2006.
34. Theis, J., et al., " The Effects of Aging Temperature and PGM Loading on the NOx Storage Capacity of a Lean NOx Trap", SAE 2005-01-1117.
35. Parks, J., et al., "Lean NOx Trap Catalysis: Exhaust Chemistry Related to Advanced Diesel Engines", SAE Light-Duty Diesel Symposium, Ypsilanti, MI, November 2008.
36. Inoue, M., et al., "Development of Advanced NOx Storage and Reduction System for Cleaner Diesel Aftertreatment", IAV MinNOx Conference, Berlin, June 2008.
37. Ohashi, N, et al., "Development of Next-Generation NOx Reduction System for Diesel Exhaust Emission", SAE 2008-01-0065.
38. Goebel, U., et al., "Diesel NOx-Aftertreatment Systems for North America", Vienna Motorsymposium, April 2008.
39. Park, J., et al., "Characterization of Lean NOx Trap Catalysts with In-Cylinder Regeneration Strategies", SAE 2008-01-0448.
40. Onodera, H., Nakamura, M., Takaya, M., and Akama, H., "Development of a Diesel Emission Catalyst System for Meeting US SULEV Standards" *SAE Int. J. Fuels Lubr.* **1**(1):231-238, 2008.
41. Xu, L., et al., "The Feasibility of an Alumina-Based Lean NOx Trap (LNT) for Diesel and HCCI Applications", SAE 2008-01-0451.
42. Rohart, E., et al., "Ceria-Based Materials for DeNOx Catalysts Efficient at Low Temperature and with Improved Sulphur Tolerance", SAE 2008-01-0450.
43. Zimmerman, C., et al., "Sensor for Directly Determining the State of a NOx Storage Catalyst", SAE 2008-01-0447.
44. Blint, R., "HC-SCR Lean NOx Catalysis for Automotive Applications", CTI deNOx Forum, Detroit, December 2008.
45. Schmieg, S.J. and Blint, R.J., "Control Strategy for the Removal of NO_X from Diesel Engine Exhaust using Hydrocarbon Selective Catalytic Reduction" *SAE Int. J. Fuels Lubr.* **1**(1):1540-1552, 2008.
46. Catellano, C. R., et al., "Catalyst to Reduce NOx in an Exhaust Gas Stream and Methods of Preparation", US Patent US2008/0070778, March 20, 2008.
47. Boger, T., Rose, D., and Tilgner I-C., "Regeneration Strategies for an Enhanced Thermal Management of Oxide Diesel Particulate Filters" *SAE Int. J. Fuels Lubr.* **1**(1):162-172, 2008.
48. Suresh, A., Yezerets, A., Currier, N., and Clerc, J., "Diesel Particulate Filter System – Effect of Critical Variables on the Regeneration Strategy Development and Optimization" *SAE Int. J. Fuels Lubr.* **1**(1):173-183, 2008.
49. Harlé, V., et al., "Latest Development and Registration of Fuel Borne Catalyst for DPF Regeneration", SAE 2008-01-0331.
50. Boger, T., Tilgner, I-C., Shen, M., and Jiang, Y., "Oxide Based Particulate Filters for Light-Duty Diesel Applications – Impact of the Filter Length on the Regeneration and Pressure Drop Behavior" *SAE Int. J. Fuels Lubr.* **1**(1):252-264, 2008.
51. Bumbaroska, M., "Diesel Particulate Filter (DPF) Ring-off Crack Robustness Investigation", SAE Light-Duty Diesel Symposium, Dearborn, November 2008.
52. Strzelec, A., et al., "Studies of Biofuel Impacts on Diesel PM", US Department of Energy CLEERS Workshop, May 2008.
53. Koichiro, H., et al., "Development of High Performance Catalyzed DPF with New Soot Burning Mechanism", FISITA Conference, Berlin, September 2008.
54. Southward, B. W. L. and Basso, S., "An Investigation into the NO_2-Decoupling of Catalyst to Soot Contact and Its Implications for Catalysed DPF Performance" *SAE Int. J. Fuels Lubr.* **1**(1):239-251, 2008.
55. Ogyu, K., et al., "Improving of the Filtration and Regeneration Performance by the SiC-DPF with the Layer Coating of PM Oxidation Catalyst", SAE 2008-01-0621.
56. Lorentzou, S., Pagkoura, C., Zygogianni, A. Kastrinaki, G. et al., "Catalytic Nano-structured Materials for Next Generation Diesel Particulate Filters" *SAE Int. J. Mater. Manuf.* **1**(1):189-198, 2008.
57. Lorentzou, S., "Advanced Catalyst Coatings for Diesel Particulate Filters", SAE 2008-01-0483.
58. Wirojsakunchai, E., et al., "Impact of Filtration Velocities and Particulate Matter Characteristics on Diesel Particulate Filter Wall Loading Performance", The Seventh International Conference on Modeling and Diagnostics for Advanced Engine Systems (COMODIA 2008), July 28-31, 2008, Sapporo, Japan.
59. Mizuno, Y., et al., "Study on Wall Pore Structure for Next Generation Diesel Particulate Filter", SAE 2008-01-0618.
60. Kolke, R., et al., „ADAC Verbraucherschutztest on Nachrueslfiltern fur Pkw", FAD Conference, Dresden, November 2008.
61. Diesel Emission Control – Sulfur Effects Program (DEC-SE), US Department of Energy, Phase 1 Interim Data Report 4: Diesel Particulate Filters – Final Report, January 2000.
62. Cartus, T., et al., "Meeting Chinese Phase IV Emission Levels for Commercial Vehicles by Adapting/Selecting Proper Exhaust Aftertreatment Concepts and Boundary Conditions for the Chinese Market", CICEIA Conference 2007.

63. Dabhoiwala, R., et al., "A Methodology to Estimate the Mass of Particulate Matter Retained in a Catalyzed Particulate Filter as Applied to Active Regeneration and On-Board Diagnostics to Detect Filter Failures", SAE 2008-01-0764.

64. Sandig, R., et al., „Partikelsensoren zur Uberwachung der DPF-Funktion – Ergebnisse der Felderprobung an Off-Road Maschinen", FAD Conference, Dresden, November 2008.

65. Fujdala, K. L., et al., "Rational Design of Oxidation Catalysts for Diesel Emission Control", SAE 2008-01-0070.

66. Rappe, K., et al., "Low-Temperature Hydrocarbon/CO Oxidation Catalysis in Support of HCCI Emission Control", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.

67. Andersen, P., et al., "SCR Catalyst Technology for Low Emission Diesels", US Dept. of Energy Diesel Engine Emissions and Energy Reductions Conference (DEER), Detroit, August 2008.