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ABSTRACT

This review summarizes the latest developments in diesel emissions regarding regulations, engines, NOx (nitrogen oxides) control, particulate matter (PM) reductions, and hydrocarbon (HC) and CO oxidation.

Regulations are advancing with proposals for PN (particle number) regulations that require diesel particulate filters (DPFs) for Euro VI in 2013-14, and SULEV (super ultra low emission vehicle) fleet average light-duty (LD) emissions likely to be proposed in California for ~2017. CO_2 regulations will also impact diesel engines and emissions, probably long into the future.

Engine technology is addressing these needs. Heavy-duty (HD) research engines show 90% lower NOx at the same PM or fuel consumption levels as a reference 2007 production engine. Work is starting on HD gasoline engines with promising results. In light duty (LD), engine downsizing is progressing and deNOx is emerging as a fuel savings strategy.

Much has recently been reported on optimized selective catalytic reduction (SCR) systems. The SCR catalyst can be placed before, after, or on the DPF. Work is progressing on non-urea ammonia systems, mixed zeolite catalysts, and on fundamental understanding on issues like ammonia storage, sulfur impacts, and reaction mechanisms. Developments on HC-based deNOx, like lean NOx traps (LNTs), result in a better understanding of durability, reduction in desulfation temperatures, and the use of LNT+SCR systems, wherein the LNT is calibrated to generate ammonia for use in a downstream SCR.

PM control is very effective. US2007 HD engines are very clean, with the DPF systems delivering PM, HC, and CO emissions at levels lower than 10% of the regulation. DPF regeneration advances are reported in strategy, modeling PM loading, and catalyst utilization. The effect of catalyst coatings on PN emissions, and behavior of captured ash is becoming better understood. NO_2 based regeneration of soot is very critical for proper functioning of partial filters. Biodiesel effects on DPF functions are becoming clearer.

Finally, diesel oxidation catalysts (DOCs) are being developed for use with premixed combustion engine strategies that function better at low temperatures, low oxygen levels, and at high HC+CO levels. The problem of platinum (Pt) migration to SCR catalysts from DOCs exposed to high temperatures for long times (850°C, 16 hours) is alleviated somewhat by using palladium (Pd) to replace some of the platinum.

INTRODUCTION

Diesel emissions and control are still very much in the forefront. Interest in the diesel powertrain for LD applications is continuing, and may be increasing as a result of tightening vehicular CO_2 regulations. Also, California is planning a nominal 70% tightening of standards, so efforts are accelerating to continue emissions parity with gasoline vehicles. Although the HD truck market is generally depressed due to economic conditions, Japan and the US implemented the last step in tailpipe regulations in the latter half of 2009 and in 2010. The Euro VI HD regulations (2013-14) will help drive the next generation of technology. The non-road market is in durability testing in preparation for 2011-12 emissions tightening, and technologies are moving into development for the 2014 step. Large locomotive and marine engines are also coming under emissions pressure (but will not specifically be covered here).

This review will delve into the more significant developments and insights that were recently brought to the forefront in the previous year. It will begin where the previous review (1) left off, and will cover the key regulatory developments, engine technologies, and technologies for the control of NOx, particulates, and HC/CO. Although it is now considered an emission, this review will not delve much into CO_2. Given its breadth and significance on technology trends, a separate review covers fuel consumption and CO_2 reductions (2). Also, probably due to the economic situation in the industry over the last two years, it is noted that technical paper offerings in 2009 seemed much more focused on two large conferences than in previous years, the 2009 SAE World Congress and the 2009 Directions in Engine Efficiency and Emissions Research (DEER) Conference. But nonetheless, the developments, quantity, and quality of the work were very good. Finally, as in previous reviews, this one is not intended to be all-encompassing and comprehensive. Representative papers and presentations are chosen here that provide examples of developments and direction.

REGULATORY DEVELOPMENTS

Significant diesel emissions regulations are focused on two different developments - Wrap up of the Euro VI particle number comitology, and work on the California Low Emissions Vehicle 3 (LEV3) light-duty standards.

HEAVY DUTY

On July 18, 2009 the European Union (EU) published the final Euro VI regulation, setting the limit values of 400 mg/kW-hr NOx, 10 mg/kW-hr PM, and 10 ppm ammonia on the European Transient and European Steady-State Cycles (3). Still to be defined through comitology by the Commission are the particle number standards (PN), calculation method for ammonia (generally an average level calculated by an integration method), on-board diagnostic (OBD) details, and limit values on the World-Harmonized Transient and Steady State Cycles (WHTC, WHSC), among other issues. The final comitology is due April 1, 2010. So far, the Commission has proposed the NOx limit be increased to 460 mg/kW-hr, with no increase in PM when using the world cycles. In November 2009, the US EPA (Environmental Protection Agency) agreed to allow US HD certifications on the WHTC, wherein the hot soak period between the cold and hot portions is increased from 5 minutes in Europe to 10 minutes (the US test is 20 minutes), and the cold start weighting is increased from 10% to 14.3% (same as in the US test). Both these changes increase the need for better deNOx performance at the lower temperatures.

Figure 1 shows the collected data on PN emissions on the WHTC from 20 engines equipped with a variety of technologies as measured in the Commission program (4). Based on these tests and numerous workshops, for the

purposes of furthering the discussion, the European Commission proposed 6×10^{11} particles/kW-hr on the WHTC, and 8×10^{11} particles/kW-hr on the WHSC (5). It is perceived that all major stakeholders are satisfied with the proposed limit values, subject to the specific test protocols still to be determined. Unlike the light-duty Euro 5/6 requirements, it is proposed that these limits include weighted figures for periodic DPF regeneration. As in the light-duty PN standard, filter pre-conditioning was shown to be very important, especially on the WHSC.
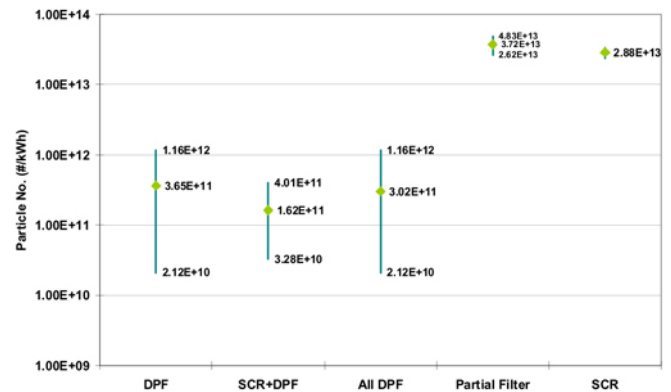

Figure 1. Particle number emissions for various Euro VI engine configurations as measured on the WHTC (4).

LIGHT DUTY

The California Air Resources Board (CARB) is planning to propose new light-duty tailpipe regulations soon. It is widely assumed that they will move to a fleet average requirement roughly equal to SULEV or US Tier 2 Bin 2 levels of 10 mg/mi non-methane organic gases (NMOG) and 20 mg/mi NOx. This is about a 70% tightening from today's FTP cycle (Federal Test Procedure) limit value. On the table for discussion are a significant tightening of the US06 standards (up to 90%), using a NMOG+NOx standard, significant tightening of PM (80-90%), and extending the phase-in time for the last portions of the fleet to comply.

The US EPA will work with CARB on the regulations, but is noncommittal at this time on a national regulation. They did release a new mobile emissions model (6) called MOVES 2010 (Motor Vehicle Emissions Simulator). Instead of being based on certification data on standard test cycles, the new model uses modal tests and estimates actual driving patterns. Heavy-duty and light-duty NOx and PM2.5 emissions went up relative to the earlier model meaning that mobile emissions are a larger part of the pollution inventory than previously thought.

Summarized in more detail elsewhere (2), both Europe and the US introduced an effective 20-25% tightening of CO_2 emission standards for full implementation in 2015 in Europe

and 2016 in the US (proposed). The European standards are based on vehicle mass, and the US standards are based on the area between the tires. As such, each manufacturer will have different fleet-average standards. More direct injection gasoline, turbocharging, engine downsizing and stop-start systems are expected. This could be the start of a significant trend of continuous tightening, as the United Nations Intergovernmental Panel on Climate Change (UN IPCC) is recommending 80% cuts in all greenhouse gases (GHG) from 1990 levels by 2050. In that regard, diesel hybrid electric vehicles (HEVs) offer the greatest emissions reductions at the best value over the foreseeable future (2).

BLACK CARBON

Climate change impacts and criteria pollutant emissions have a juncture at black carbon or soot. With the global warming potential factor of black carbon at about 2000X versus CO_2 on a mass basis (7), about 20-25% of the carbon footprint from an unfiltered diesel vehicle is from black carbon. Remediation of diesel soot today is primarily done to minimize the adverse health effects, but the climate forcing impact could further increase interest. Figure 2 shows how worldwide on-road vehicle black carbon emissions vary over time (8). About 60% of the emissions are from diesel trucks. The base case assumes PM regulations that are currently planned. Emissions increase after about 2025 as the developing countries grow. The bars represent emissions if, by 2015, Euro VI HD and Euro 6 LD regulations are implemented in China, India, and Brazil; Euro IV HD and Euro 4 LD standards are implemented in Africa and the Middle East; and Euro 3 motorcycle regulations are implemented in Africa, the Middle East, and Latin America. By 2050, these advanced regulator initiatives remove 19 million tonnes of black carbon, or the equivalent of 38 billion tonnes of CO_2. This is ~20% of the total CO_2 reductions the UN proposes between now and 2050.
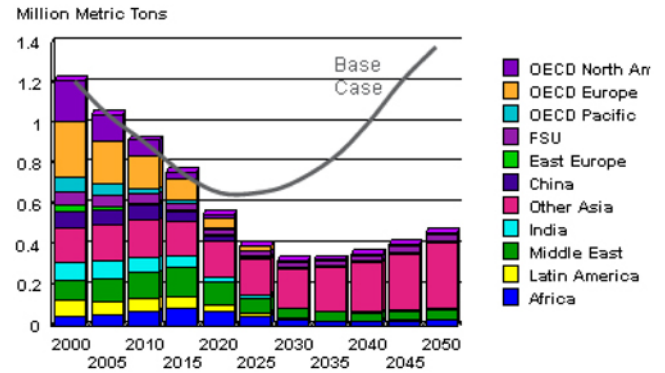

Figure 2. Black carbon reductions from current regulations (line) compared to those if developing countries adopt tighter PM standards by 2015. About 60% are for the HD sector. The difference represents about 20% of the total CO_2 reductions proposed by 2050 (8).

ENGINE DEVELOPMENTS

Engine technology is evolving very rapidly. Most of the developments in the market to date were implemented to address ever tightening criteria pollutant emission standards. However, moving into the future the emphasis will shift to meeting CO_2 or fuel consumption regulations (2). This section will cover the heavy-and light-duty engine developments from a criteria pollutant emissions perspective.

HEAVY DUTY

There is still much room for improvement in emissions from heavy-duty engines. Stanton gave an update on progress using incremental technologies applied to research engines that can result in nominally 90% reductions in engine-out NOx at the same fuel consumption or same PM levels as a 2007 production engine (9). Figure 3 shows the results. Technologies employed included combustion optimization utilizing high pressure and multiple fuel injections, bowl design, variable swirl, variable valve actuation; advanced exhaust gas recirculation (EGR) with low pressure drop, high flow, and advanced cooling; air management with 2-stage boost, electrically assisted turbocharger; and advanced controls for mixed mode combustion, and closed-loop control. Note that deNOx systems are optional on these engines to attain the US2010 NOx standards (0.2 g/bhp-hr), but employing an 85 to 88% efficient deNOx system can result in a 5 to 11% fuel savings. If exhaust emission control achieves 97% deNOx efficiency instead of 85% to attain US2010 NOx standards, an additional 10% fuel consumption reduction might be achieved, exclusive of additional urea consumption.
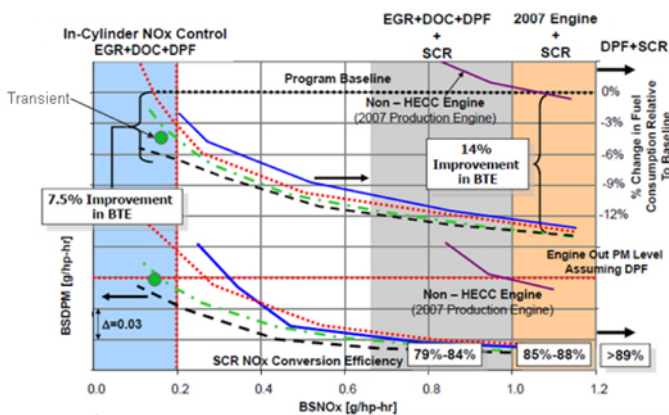
Figure 3. Fuel consumption savings (top curves) and PM reductions (bottom curves) for research engines utilizing generally incremental technologies (9).

There are two general engine pathways to meeting the emerging tailpipe regulations, low EGR and high EGR (exhaust gas recirculation) utilization resulting in significantly different exhaust deNOx strategies. Achieving high levels of EGR can be problematic due to unfavorable pressure differentials between the exhaust and intake manifolds that drive EGR. Specifically, at the later portions of the intake stroke, intake pressures can be higher than EGR loop pressures. A fast intake manifold valve that operates with crank angle resolution was developed to decrease intake pressures in this part of the cycle to drive more EGR (10). Using the system, Euro VI NOx regulations can be attained with no additional NOx emission control and at favorable operating costs compared to selective catalytic reduction (SCR) approaches when considering fuel and urea consumption.

Looking at the longer term, there was a marked shift in HD engine technology regarding pre-mixed combustion. Previous efforts on HCCI-type (homogeneous charge compression ignition) combustion hit an obstacle on controlling heat release at mid-load conditions and higher. The problem relates to a large charge igniting within a short timeframe under compression ignition. New approaches take advantage of premixed gasoline charges to produce low emissions and delay ignition; high levels of EGR to slow and further delay combustion; but may use some stratification to ignite the mix under compression (11, 12, for example), hence the name, partially-premixed combustion (PPC).

Three representative approaches are summarized here. Dec, et al., attained stable and low-emission combustion using a fully premixed regular gasoline charge, 60% EGR and 3.2 bar boost (13) at stoichiometry. Indicated thermal efficiency (gross ITE, no friction or pumping losses taken into account) was high for gasoline, 47% at 16.5 bar IMEP (indicated mean effective pressure) and NOx emissions were below US2010 levels. High levels of boost enabled high levels of EGR,

which resulted in a better-controlled release of heat for the fully premixed charge, despite a high and efficient compression ration (CR=14). Reitz, et al., also tested a premixed gasoline charge with high levels of EGR, but ignited the charge with 20% diesel fuel (14). Their 2-liter single-cylinder engine achieved 53% ITE at 11 bar IMEP, with emissions at 20 mg/kW-hr NOx and 8 mg/kW-hr PM. Like Dec, Johansson used only gasoline, but split the injection to give a significant early premixed charge, and a second late injection to stratify some charge for ignition (15). With this strategy, a 12 liter 6-cylinder HD engine achieved a brake thermal efficiency (BTE; all engine losses) of 48% at 18 bar IMEP and 1300 RPM, Figure 4. This represents a 10-15% fuel consumption savings and a greater than 20% CO_2 reduction versus today's diesel engines. However, NOx and PM emissions were much higher than reported by Dec or Reitz.
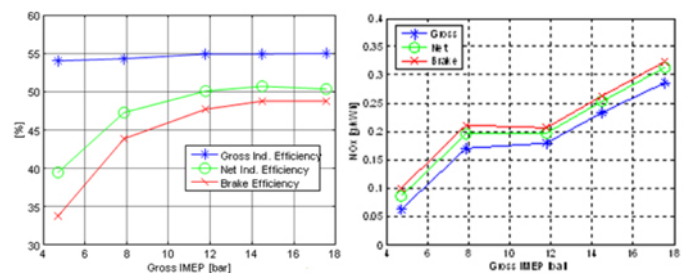

Figure 4. Gasoline PPC using a 6-cylinder, 12-liter engine. High BTE (48%, left panel) at relatively high loads (18 bar IMEP) with moderate NOx emissions (right) were achieved using commercial gasoline (15).

Strategies are beginning to emerge for attaining the final non-road Tier 4 tailpipe regulations. Two strategies were described by Kraljevic and Vlaskos (16). The high-EGR approach (25-35%) requires 2400 bar common rail fuel injection, and 80-85% deNOx efficiency in the exhaust, plus a diesel particulate filter. Engine specific power can range from 26 to 30 kW/liter, depending on turbocharging hardware. The low-EGR approach (15 to 20%) requires a 2000 bar fuel injection system, 90+% deNOx, and 50% PM removal. Engine specific power range is higher, from 30 to 32 kW/liter. Going one step further, the possibility of attaining the final Tier 4 regulation without EGR has also been proposed (17), utilizing SCR to accomplish all required NOx reductions.

LIGHT DUTY

Technology pressure on the light-duty diesel manufacturers is coming from emerging SULEV regulations in California, advances in gasoline engines, and increased offerings of hybrid electric vehicles (HEVs). On the other side, diesel platforms are very attractive for meeting the emerging CO_2 regulations, in which diesels have a 20% advantage over their

gasoline counterparts. The technology pressure is being met with increasingly sophisticated combustion designs and control on diesel engines.

To maintain this advantage, most of the efforts in diesel engine technology are focused on reducing fuel consumption rather than criteria pollutant reductions (2). Rueger gave examples of gasoline and diesel engine trends to reduce CO_2 emissions (18). Most of the reductions in both types of engines came from downsizing, enabled by advances in turbocharging and fuel injection. On the diesel side, deNOx additions and calibrations gave diesel a net 4% added edge, resulting in a widening of the margin.

NOx emissions can go up 20% to 100% with engine downsizing if appropriate measures are not taken. Koerfer, et al. (19), described an integrated engine design approach utilizing advanced swirl concepts, EGR control, high-pressure and flexible injection, and sophisticated combustion chamber design. As a result, CO_2 emissions can drop 17%, NOx emissions 50%, and PM emissions by 10% when downsizing a 2.0 liter Euro 4 baseline engine to 1.6 liters. Leonhard, taking a different approach, described (20) the interplay between and impact of boost, fuel injector design, and injection strategy on fuel consumption and emissions. Fuel consumption is positively affected by the combination of 2-stage turbocharging and a close pilot injection; by the combination of low-flow nozzles and higher injection pressure; and by injection strategy (like a close coupled pilot) with better results coming using a direct needle versus a piezo injector. NOx emissions are not very dependent on the close pilot, but are very strongly impacted by high boost, nozzle flow rate, and injection pressure.

Given California directions towards a SULEV fleet average emission requirement, diesel engineers are moving in that direction on research engines. Cooper (21) extended previous work on a Tier 2 Bin 5 diesel, towards one that can efficiently attain SULEV (Tier 2 Bin 2) levels. They chose an LNT as their exhaust deNOx technology. At these low emission levels, cold-start hydrocarbons become a problems as well as the slip from LNT regeneration. Cold start is aided with pre-turbo oxidation catalysts, but the LNT strategy needs to be developed.

NO$_X$ CONTROL

As Figure 3 illustrates, within a given diesel engine hardware package fuel consumption goes down as NOx emissions are allowed to increase. In other words, as illustrated with a couple of examples above, deNOx efficiency can translate into fuel consumption savings for both heavy-duty and light-duty applications. Figure 5 illustrates the principle in a light-duty application (20). In this case, increasing levels of engine technology added to a Euro 5 base engine can drop fuel consumption nominally 6% at the same level of NOx (0.15 g/

km, for example). However, an advanced engine package can bring the Euro 5 engine to Euro 6 NOx levels at the same fuel consumption, but added to this, 45 to 50% NOx control can deliver a 6% fuel consumption advantage. Severin showed a similar impact, but the fuel saving is reduced for smaller cars because the flat part of the fuel consumption curve is shifted to the left levels versus for a larger car (22).
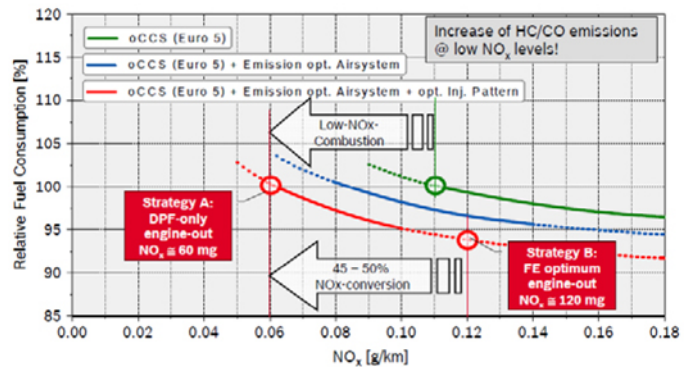

Figure 5. Modest tailpipe NOx control can drop fuel consumption 6% (20).

SELECTIVE CATALYTIC REDUCTION

Selective catalytic reduction (SCR) still remains the leading deNOx approach for diesel engines. DeNOx efficiencies can be 90% or higher with proper control and design.

System level work is continuing on delivering ammonia to the SCR without using liquid urea. Spurred by a truck and engine manufacturer investment (23), a leading non-urea technology is advancing that uses metal ammines to store gaseous ammonia, thus resulting in a large increase in specific ammonia storage capacity ($\sim$2.5X that of urea on a volumetric basis). The ammonia is released with heat, wherein power consumption is significantly reduced using cooling water (24). A 250 watt power draw during cold start allows low-temperature delivery of ammonia at SCR catalyst temperatures down to 100°C. With similar objectives of replacing liquid urea, Tatur, et al. (25) described a truck test using ammonium carbamate [$(NH_2\text{-}CO_2)\text{-}(NH_4)$], which has a specific ammonia storage capacity 3-4X more than urea. The solid is converted to ammonia by heating with a heat transfer fluid (such as oil). Once heated, the system delivers ammonia as needed for high efficiency.

Looking at another key part of the SCR system, Holderbaum, et al.(26) evaluated the placement of the SCR relative to the DPF. Considering the added fuel needed to heat the SCR system for cold start, and to regenerate the DPF with different frequencies due to changes in passive NO_2 regeneration, the authors conclude that for an 1800 kg car with a 2-liter engine, if cold starts occur more frequently than once every 60 km it is better to place the SCR in front of the DPF. Figure 6 shows

some results. Note that the 60 km threshold is greater than the distance used in certification cycles, wherein placing the SCR behind the DPF incurs a 2% fuel penalty versus a front placement. The forward SCR placement aids certification for both CO_2 and NOx emissions.
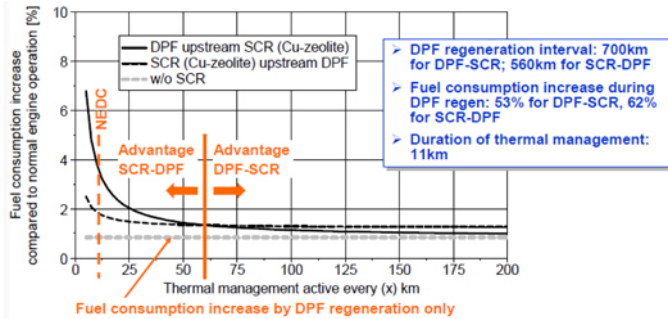

Figure 6. Considering fuel consumption for heating and regenerating the system, placing the SCR in front of the DPF is beneficial if there is less than 60 km between cold starts (26).

In a similar context, much work is being done on placing the SCR catalyst on the DPF. Generally, SCR efficiency is only slightly affected by soot build-up on the DPF (1). Cavataio, et al. (27) nicely characterized a number of operating characteristics of SCR catalysts in general, such as ammonia storage, NO_2, oxygen, and space velocity effects, and found most were consistent with SCR catalysts in general. They noted two potential performance issues, however, when SCR catalysts are placed on DPFs. The first is an unexplained drop in deNOx efficiency when increasing space velocity from 30,000 to 40,000 hr^{-1}. The second is a drop in efficiency in the critical temperature range of 250 to 400°C. They hypothesized that PM was partial oxidized by the Cu-zeolites to produce CO and carburized by-products (coke) in this temperature range, which adversely impacts the SCR catalyst. A follow-up report quantified this phenomenon (28). Indeed, coke derived from diesel vapor negatively impacted one Cu-zeolite SCR catalyst, but not another. The impacted catalyst has a higher soot burning temperature (450°C) than the unaffected catalyst (350°C), indicating the depressed NOx efficiency is tied to oxidation capability of the catalyst. Also indicative, is that the coke that impacts the NOx reduction does not impact back pressure, perhaps implying a closer spatial relationship between the coke and the catalyst than between the coke and the porosity.

Expanding upon the oxidation of soot by SCR catalysts, specifically regarding the competition for NO_2 between the fast SCR reaction and soot oxidation, Ireskaya, et al., (29) showed their catalyst (undefined, but not Cu-zeolite) deNOx function was not impaired by soot consuming NO_2. Conversely, the soot oxidation reaction was not impaired by the consumption of NO_2 by the fast SCR reaction, but these

results are not as clear because the catalyst exhibited soot oxidation properties in the absence of NO_2 at the temperatures of the deNOx tests.

Looking at the catalyst system itself, Theis investigated zone coatings of Cu- and Fe-zeolites to try to take advantage of the better low-temperature deNOx properties of Cu-zeolite, and the improved high temperature properties of Fe-zeolite (30). The deNOx range of the SCR catalyst combination was expanded accordingly. The oxidation of ammonia by Cu-zeolites necessitates that the Cu-zeolite be placed in the back to maintain the advantages of the Fe-zeolite. As such, it was found that the 2/3 Fe- and 1/3 Cu-zeolite combination works best. Further, to maintain maximum efficiency the Fe-zeolite volume was doubled when Cu-zeolite was placed behind it, because any ammonia slip from the Fe-zeolite was partially oxidized to NOx by the downstream Cu-zeolite. Also, for light-duty applications in which NOx light-off is important, adding a small Cu-zeolite catalyst in the front improves the low-temperature performance, albeit at a somewhat reduced HT effectiveness.

Concerning ammonia oxidation on Cu-zeolites, Figure 7 shows that the reaction can begin at 250°C (27). The reaction is 90% selective to nitrogen at temperatures less than 500°C on the specific catalyst. One new and interesting aspect of this work is that two types of stored ammonia are defined, wherein one type, TSC (Threshold Storage Capacity), is defined by the threshold at which the ammonia storage efficiency drops below 97% (10 ppm slip) given a 350 ppm inlet concentration. The TSC ammonia is the more tightly bound type, and represents about half of the ammonia. In steady-state NOx reduction experiments, the initial reaction rates were lower than the steady state rate due to the delayed release of the TSC ammonia.
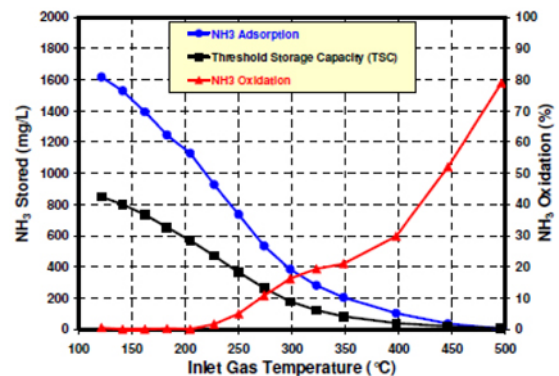

Figure 7. Ammonia oxidation to nitrogen (greater than 90% selectivity) on Cu-zeolites. TSC is tightly bound stored ammonia and represents half of the total (27).

Many have reported on the susceptibility of Cu-zeolites to sulfur exposure (1). Cheng, et al., (31) showed this is due to SO_3 reaction and not SO_2, so poisoning is more of an issue if

there is an oxidation function before the SCR. When Cu-zeolite is exposed to 40 ppm sulfur oxide for 1.5 hours (simulates a tank fuel of 350 ppm sulfur), deNOx efficiency drops 0-10% if the sulfur is in the form of SO_2, but drops 80-90% if the species is SO_3. Indications are that the sulfur forms highly dispersed $CuSO_4$. The sulfur begins releasing at ∼350°C if there is no sulfur present in the inlet gas.

Finally, in some interesting fundamental work, Tronconi, et al. (32) showed that hydrogen nitrate and nitrite stability differences on Cu- versus Fe-zeolites correlate well with commonly observed reaction phenomenon. For example, these nitrates are less stable on Fe-zeolites (50C° lower decomposition temperature), they react easier at lower temperatures with NO_2 than on Cu-zeolites. This explains why NO_2/NOx control is much more critical to enhance LT performance of Fe-zeolites. Nitrate stability also explains why Fe-zeolites tend to form more N_2O from NO_2. Enhanced nitrite stability on Cu-zeolites was used to explain the propensity for ammonium nitrate to decompose to N_2O more so on Cu-zeolites than on Fe-zeolites. The researchers hypothesized all these differences might be due to the lower acidity of Cu-zeolites. This work signals that altering the surface stability nitrates or nitrites could lead to better SCR catalysts.

HYDROCARBON-BASED DENOX

Lean NOx traps (LNTs) are the key deNOx technology that uses diesel fuel as the reductant instead of ammonia, as with SCR. LNTs are the preferred approach for smaller cars due to reduced cost, wherein increased precious metal costs are more than offset by eliminating the urea system, and lack of space for urea mixing in the exhaust and delivery systems on the vehicle.

One issue with LNTs is hydrocarbon (HC) slip during rich regeneration. Two methods for reducing HC slip are proposed: Using zeolites to adsorb the HCs and hold them until the lean cycle, and using oxygen storage catalysts (OSC) to use oxygen stored during the lean cycle for HC oxidation during the rich spikes (33). Of the two proposals, the zone-coated zeolite route provides the best remediation of HC slip at temperatures up to 300°C, and achieved 60 to 70% HC conversion from 150 to 350°C. The precious metal loading on the zeolite was more than accounted for by reduced loading on the LNT, saving precious metal.

LNT durability has improved significantly over the years, mainly due to better materials and to the need for lower desulfation temperatures. Toops, et al. (34) developed a rapid thermal aging test protocol, and then determined (35) the thermal aging mechanisms of the three unit operations in an LNT: NO oxidation, NO_2 adsorption, and NO_2 reduction. NO

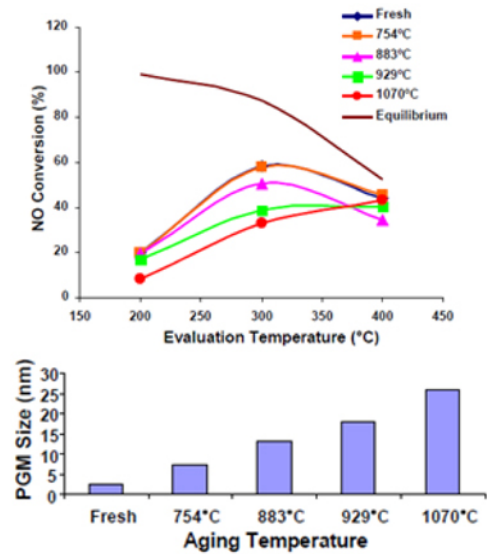oxidation is hampered by loss of precious metal surface area, Figure 8.

Figure 8. Platinum grain growth is the main aging mechanism affecting the oxidation of NO to NO_2 on an LNT (35). Aging at 754°C did not affect NO oxidation performance for up to 20 hours of thermal cycling.

The adsorption of NO_2 is largely affected by the loss of alumina surface area, especially at the lower adsorption temperatures. As baria is relatively unaffected at the higher temperatures and alumina loses surface area at ∼900°C, this overall effect is not as significant to the LNT function as the loss of precious metal oxidation kinetics. Aging actually helps the reduction unit process because the larger baria grains release the nitrate slower, reducing NOx slip.

Regarding reducing desulfation temperatures as a means of improving LNT durability, Chen, et al. (36) added POx catalyst (partial oxidation catalyst) to partially reduce hydrocarbons to hydrogen and CO. The result, as shown in Figure 9, is a 150C° drop in desulfation temperature with double the amount of sulfur coming off. In addition to this benefit, LT performance slightly improves, and expensive rhodium could be replaced with cheaper palladium, reducing precious metal costs.

The first light-duty diesel sold in the US to meet recent tailpipe regulations had the BlueTec™ 1 emission control system, utilizing an LNT followed by an SCR catalyst. The unique system used the rich cycle of the LNT to generate ammonia, which was captured and used by the downstream SCR for lean NOx reduction. Krutzsch, et al. (37) reported that ammonia selectivity increases with aging and rich period, and decreases with increasing the air/fuel ratio (λ). Under conditions of λ=0.88 and rich periods of 5 sec (180 sec lean), ammonia selectivity is greater than 70% in the temperature

range of 225 to 350°C for all aging tests temperatures greater that 600°C and 50,000 miles. The SCR adds about 20% deNOx efficiency over an LNT only configuration.
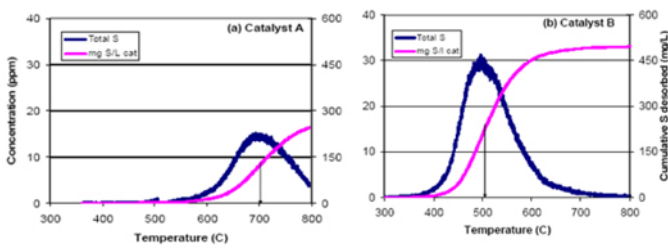

*Figure 9. Desulfation results on an LNT with POx catalyst added (right) compared to one without (*36*). Twice as much sulfur comes off at 150C° lower temperature.*

The LNT+SCR combination can achieve optimum performance if the LNT is designed to produce ammonia. The fundamentals of ammonia formation in LNTs was investigated by Kouakou, et al. (38), who related the ammonia formation to the occurrence of an oxidation exotherm (H_2/O_2, CO/O_2) that may free up precious metal sites to facilitate a route for H_2 and NO dissociation and/or subsequent surface reactions, leading to the ultimate formation of ammonia.

Given that the SCR adds to the total system deNOx efficiency, precious metal loadings on the LNT can be reduced 25% or more (39). The system performs better than an LNT-only configuration with the same precious metal loading, and the reduced precious metal loading even helps generate ammonia, which aids in the performance of the combination system. Xu, et al., (40) updated progress on a second-generation system with 30% reduced precious metal loading (85 g/ft^3) and size (swept volume ratio of deNOx is ~1.9X). The system was applied to a 5750 pound (2614 kg) pick-up truck and achieved 96% deNOx efficiency on an aged system (120,000 mile, thermal age), achieving Tier 2 Bin 3 tailpipe levels on the FTP. Figure 10 shows the results, along with those on a Euro 3 Land Rover. Nominally 85% deNOx efficiency was achieved on the US06 high-load cycle on two other vehicles, albeit with 25% more LNT and less aging. Interestingly, Xu shows that other reductants might be present, as all of the deNOx activity can not be explained by looking only at ammonia. He hypothesized that HC intermediaries come into play. Aside from reduced precious metal costs, HC and CO emissions are reduced (39, 41), and the downstream SCR removes H_2S during desulfation (37, 39).

LNTs are not the only components that can generate ammonia. Silver-based alumina lean NOx catalysts (LNC, or HC-SCR) also can do so. DiMaggio, et al. (42) used the "dual

SCR" approach, wherein ammonia is generated during standard lean operations on the LNC from the continuously injected fuel. The downstream SCR uses the ammonia to add 20% system deNOx efficiency over a broad temperature range. Figure 11 shows some results. Even small amounts of hydrogen in the gas, as low as 0.1%, can have a marked positive impact on LT performance. This impact is the subject of much fundamental investigation. Further, compared to earlier systems wherein HC injections might be at HC/NOx greater than 8, this system can operate efficiently at HC/NOx of about 3. Fuel penalties can thus be ~2% for modern low-NOx engines. The system can operate on a wide range of fuels (43), but may need 1% hydrogen for acceptable performance.
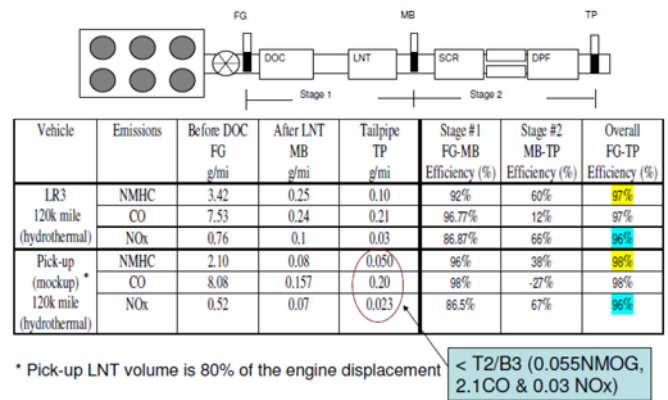

*Figure 10. An LNT+SCR system helped a 2613 kg pick-up achieve Tier 2 Bin 3 FTP emission levels (*40*). The deNOx system was 1.8X the swept volume of the engine.*
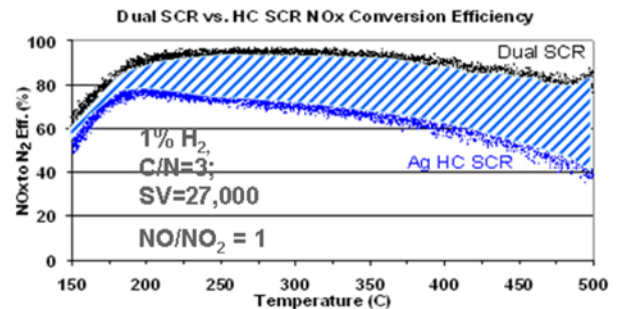

*Figure 11. Laboratory results on a "dual SCR" system utilizing a HC-SCR to reduce NOx and generate ammonia for use in a downstream SCR (*42*).*

PM CONTROL

Diesel particulate filters (DPFs) have been applied to new passenger cars for about 10 years, and to new HD vehicles for about 3 years. Emissions results are impressive and the systems are being optimized for even better performance and reduced cost.

The emissions of a US2007 heavy-duty diesel engine were measured in detail in the first phase of a US government/ industry collaboration to investigate the health effects of exhaust exposure from new large HD engines (44). PM, HC, and CO emissions were less than 10% of the US2007 standard and NOx emissions were 10% below the standard. Particle number (PN) emissions were 99% lower than for a 2004 engine. Measurements were ~4 × 10^{12} particles/bhp-hr on the FTP transient cycle with DPF regenerations. During a regeneration, PN emissions were about 10X those during normal operation. All HC classes were at least 80% lower than for the 2004 engine, but NO_2 emissions were up 2 to 7X. This is due to the promotion of passive NO_2 regeneration. Most US2010 engines will be equipped with deNOx systems, so NO_2 levels are expected to be much lower moving forward.

Much of the work on DPFs is focused on improving regeneration. Chilumukuru, et al., (45) concluded that to minimize DPF regeneration fuel penalty, partial regenerations at high soot loadings are preferred. Figure 12 shows the results leading to the conclusion, wherein more soot is burned per unit of fuel at the higher soot loadings, and up to 70% regeneration, the point of diminishing oxidation and increased fuel consumption. Leaving some soot membrane on the filter improves back pressure by keeping soot from penetrating into walls (no ash membrane). It should be noted, however, that one should be very careful in leaving soot on the DPF for too long, as it can age (graphitize or become poisoned) and become very difficult too oxidize, but may occasionally burn unexpectedly.
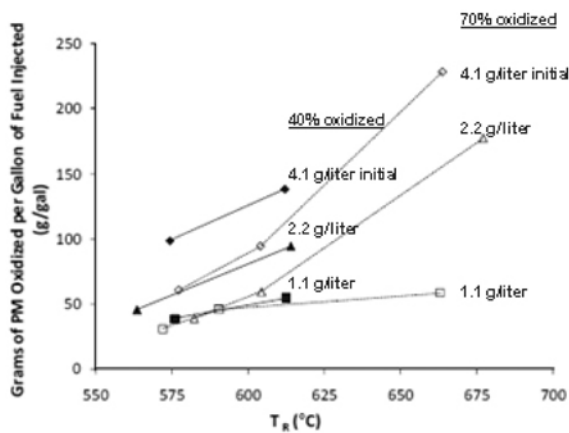

Figure 12. More soot is burned per unit of fuel for high soot loadings and for up to 70% regeneration efficiency (45).

Approaches like this require accurate estimates of soot loading. Rose and Boger described two soot estimation methods for doing so (46). They used a modal estimate of soot accumulation and of soot oxidation via passive regeneration, and combined it with a closed-loop model based on pressure drop. The method got them to within ±1.5 g/liter of measured soot.

Regarding catalyst understanding and developments, few updates were made to the direct oxidation of soot at the soot-catalyst interface, converse to previous years wherein there was much activity. However, Isogui (47) presented very low temperatures for soot to be oxidized directly by oxygen: Oxidation started at ~210°C and reaches a peak at ~250°C using a $YMn_{0.95}Ru_{0.05}O_3$ catalyst. Optimized catalyst utilization was modeled and validated by Koltsakis, et al. (48). Several interesting results were proposed. Having a DOC (diesel oxidation catalyst) overwhelm catalyst loading and substrate porosity effects in promoting passive NO_2 regeneration, and about half of the total DPF system catalyst should be on the DOC for optimum performance. Despite very different back pressure as a function of soot load for different filters, all were similar after partial regenerations because of filter cake effects. HC and CO oxidation is more dependent on washcoat dispersion in the DPF than on precious metal content. Depth filtration does not result in better soot burn, and low porosity DPFs have lower back pressure than high porosity filters due to preferred cake filtration.

When high catalyst loadings are added to a DPFs, such as when applying deNOx catalysts, PN emissions can counter-intuitively increase if excessive catalyst is applied (49). The effect is illustrated in Figure 13. PN emissions are correlated to porosity: Emissions go down as 10-20 μm porosity increases, but they go up if pores greater than 30 μm increase in volume fraction. As coating loading increases large pores volume goes down but 10-20 μm pore volume remains flat. The net result is decreased PN emission. However, if coating load increases further, the opposite occurs: Coating decreases 10-20 μm porosity but large pores remain largely unaffected, giving the net result of increased PN emission.
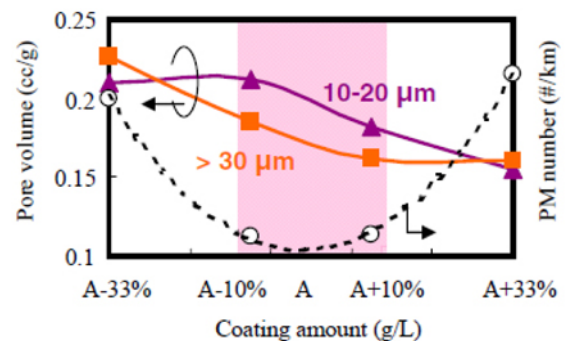

Figure 13. PN emissions (dashed line) reach a minimum with catalyst coating amount, due to the counteracting impact of loading on 10-20 μm and >30 μm pore volume (49).

Furuta et al., ([50](#)) continued their work on developing DPF membranes that are applied on the inlet surface of the DPF wall. The soot-loaded back pressure is lower with the membrane because soot does not enter the wall. Initial filtration efficiency is higher due to the membrane making up for absence of filter cake. The membrane does not impact regeneration characteristics.

However ash naturally forms a membrane with much of the same results ([51](#), [52](#)). An ash membrane is formed before it migrates to the end of the DPF cell to form a plug at the exit side of the DPF ([52](#), [53](#)). Zinc has a lower packing density than calcium or CJ-4 lube oil mixed ash, so it forms a membrane first ([52](#)). Sappok, et al. showed ([51](#)) that back pressure is generally linear with ash and soot accumulation, as shown by region I in Figure 14. But after about 12.5 g/liter of ash accumulates (~50,000 miles) back pressure rapidly increases with increasing soot beyond about 3 g/liter, zone II. This effect is thought to be caused by compression of the soot/ash membrane caused by increasing back pressure ([53](#)).
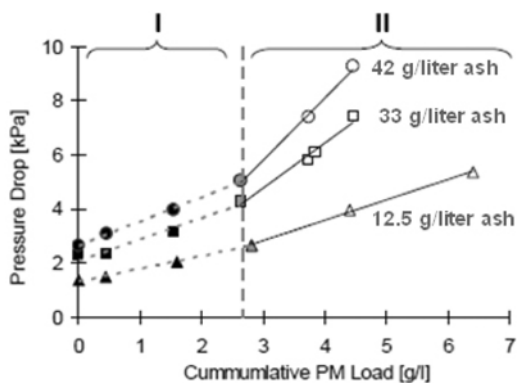

Figure 14. Pressure drop increases faster with increasing soot and ash loading beyond a certain threshold (region II) due to compressing of the membrane from higher back pressure ([53](#)).

Biodiesel can impact soot loading and DPF regeneration properties. Vertin, et al. ([54](#)) conducted a comprehensive investigation of B20 impacts on cordierite DPFs. They blended soy-based methyl ester biodiesel with ultra-low sulfur diesel fuel, and ran dynamometer tests to generate results. PM emissions were reduced 20% with B20 in transient tests, but were similar in steady state tests, indicating PM differences are cycle dependent. Back pressure relationships are the same for B20 as for standard fuels. Regarding regeneration, at 300°C B20 does not burn as effectively in the DOC, requiring more fuel to regenerate the DPF. The excess fuel likely collects on the soot, resulting in a larger exotherm during uncontrolled regenerations. At temperatures greater than 300°C the fuel burns better. There is minor improvement in passive NO_2 regeneration with B20. No deterioration in catalyst performance was observed after ~120 active regenerations.

Finally, partial flow filters are emerging in China and India as the preferred PM solution to meet Euro IV HD tailpipe standards in mainly urban applications. Mayer, et al. ([55](#)) evaluated four types of partial filters that are reported to have ~30-50% filtration efficiency. In a retrofit light-duty diesel application, they found the best filtration efficiency with one type was indeed 63%. However, under critical but realistic conditions filtration of the others measured substantially lower than the expected 30 %, depending on operating conditions and prior history, and could even completely fail. Scatter between repeated cycles was very large and results were not reproducible. Even worse, with all 4 filters, deposited soot, stored in these systems during light-load operation was intermittently blown-off. A mass balance calculation shows under typical operating conditions that there is not enough NO_2 to oxidize the soot, so soot will tend to accumulate, block the filter pathway, and then blow-off. For HD applications, passive soot oxidation by NO_2 is more likely given the higher temperatures, but if the vehicle is operated under regimes wherein this is unlikely, similar results can occur.

HYDROCARBON AND CO CONTROL

Diesel oxidation catalysts (DOCs) have been used in more vehicles than any other emission control device. They are critical to proper functioning of DPF and deNOx systems. Given this, they are by no means mature and are still evolving.

A critical HC and CO issue has largely gone unresolved. Premixed combustion strategies offer advantages in low load operating points due to significantly reduced NOx and PM emissions. However, these advantages come at the price of greatly increased HC and CO emissions, lower exhaust temperature, and lower oxygen content, intuitively presenting a significant challenge to DOCs. Indeed, Sumiya, et al., ([56](#)) showed that the light-off temperature of DOCs increases with decreasing oxygen and increasing HC and CO. They enhanced a catalyst formulation by using materials to supply oxygen, applying a CO adsorption suppressant, and creating a plurality of active sites for multiple functions. As a result the light-off temperature (T50, temperature of 50% conversion) for aged catalysts dropped from 260°C to 180°C for exhaust with 500 ppm HC, 500 ppm CO, and 2% oxygen. The values for 5000 ppm HC and CO levels were 225°C from 280°C previously.

An earlier report ([57](#)) showed that platinum can migrate from DOCs (or presumable DPFs) to SCR catalysts if they are exposed to temperature greater than 670°C for extended periods of time (16 hours). SCR efficiencies can decrease, especially if the DOC is exposed to temperatures greater than 750°C, as even minute quantities of platinum can cause oxidation of ammonia. Cavataio, et al. ([58](#)) showed that if palladium replaces some of the platinum in the DOC, less

migration can occur. Figure 15 shows results after the DOC was exposed for 16 hours at 850°C. Although the 2:1 Pt:Pd mixture shows some deterioration in SCR deNOx efficiency, it is much worse for the Pt-only formulation (efficiency line crosses the x-axis at 325°C, reference 57). Washcoat formulation and or processing can make a difference, and NO, HC, or CO oxidation is unaffected or enhanced with the Pd additions.
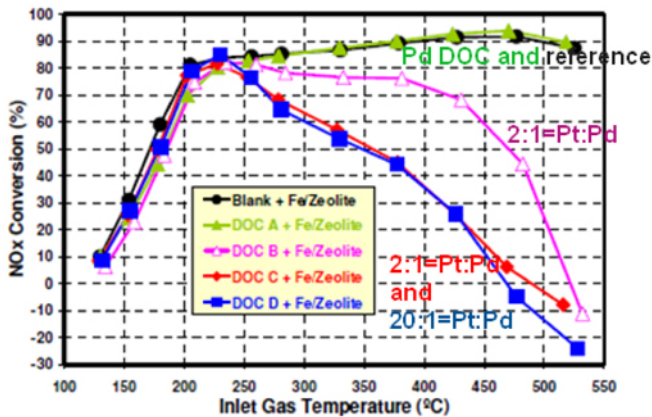

Figure 15. Platinum migration for DOCs exposed to 850°C for 16 hours is improved if Pd replaces some of the Pt. Washcoat formulation and/or process can have an impact (58).

CONCLUSIONS

A broad yet representative review of the latest information on diesel emissions and control is summarized here.

Regulations are advancing with proposals for DPF-forcing PN (particle number) regulations for Euro VI in 2013-14, and SULEV (super ultra low emission vehicle) fleet average LD emissions likely to be proposed in California for ~2017. Over-riding these and promising to dominate the future regulatory landscape will be CO_2 regulations. About 20-25% tightening for cars is finalized for Europe in 2015 and proposed for the US in 2016. HD will likely follow, as well as further LD tightening. Black carbon from road vehicles has significant climate change potential.

Engine technology is addressing these needs. HD research engines using incremental technologies have 15% lower fuel consumption versus a reference 2007 production engine, and 90% lower NOx at the same PM or fuel consumption levels. Gasoline HD engines operating with partial premixed combustion (PPC) offer high efficiency and low NOx and PM emissions in tested high load modes. In LD, engine downsizing will be used, but can result in higher NOx emissions at lower temperatures. DeNOx is emerging as a fuel savings strategy.

Much has recently been reported on optimized SCR systems. The SCR catalyst can be placed before, after, or on the DPF. Fuel consumption is reduced in applications with a high cold start frequency (less than 60 km) if the SCR is in front. When placed on the DPF, coking reactions can impede performance. NO_2 preferentially may go to the SCR rather than the soot in one catalyst system, although this might not have a big impact on soot oxidation. Work is progressing on non-urea ammonia systems, mixed zeolite catalysts, and on fundamental understanding on issues like ammonia storage, sulfur impacts, and the role of nitrate intermediaries on reaction kinetics.

Developments on HC-based deNOx, like lean NOx traps (LNTs) result in a better understanding of durability, reduction in desulfation temperatures, and the use of LNT +SCR systems, wherein the LNT is calibrated to generate ammonia for use in a downstream SCR. These systems can have reduced precious metal loadings, higher efficiency, and lower HC and H_2S emissions. Large vehicle testing for Tier 2 Bin 3 levels looks promising. The concept of a dual SCR system is introduced, wherein a HC-SCR (lean NOx catalyst) generates ammonia for the SCR.

PM control is very effective. US2007 HD engines are very clean, with the DPF systems delivering PM, HC, and CO emissions less than 10% of the regulation. However, NO_2 emissions, which are used to passively regenerate the DPFs, is 2 to 7X higher than for previous engine models. DPF regeneration advances are reported in regeneration strategy, modeling PM loading, and catalyst utilization. PN emissions can go up or down with DPF catalyst loading, and the effect is attributed to 10-20 μm and greater than 30 μm pore volumes. Ash behavior is becoming better understood. It can form a membrane to impart better filtration efficiency and initially lower back pressure. At high loadings it can compress and cause increased back pressure. NO_2 based regeneration of soot is very critical for proper functioning of partial filters, wherein efficiency can drop and/or soot can accumulate and blow-off if this does not occur. Biodiesel does not burn well in DOCs at 300°C or lower, and this can cause high exotherms across the DPF.

Finally, DOCs are being developed for use with premixed combustion engine strategies that function better at low temperatures, low oxygen levels, and at high HC+CO levels. The problem of platinum migration from DOCs exposed to high temperatures for long times (850°C, 16 hours) to SCR catalysts is alleviated somewhat by using palladium to replace some of the platinum.

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DISCLAIMER

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