

# **Diesel Emission Control in Review**

Timothy V. Johnson Corning Incorporated

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400 Commonwealth Drive, Warrendale, PA 15096-0001 U.S.A. Tel: (724) 776-4841 Fax: (724) 776-0790 Web: www.sae.org

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# ABSTRACT

This summary covers the developments from 2007 in diesel regulations, engine technology, and NOx and PM control.

Regulatory developments are now focused on Europe, where heavy-duty regulations have been proposed for 2013. The regulations are similar in technology needs to US2010. Also, the European Commission proposed the first  $CO_2$  emission limits of 130 g/km, which are nearly at parity to the Japanese fuel economy standards.

Engines are making 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 centered on SCR (selective catalytic reduction) for diverse applications. Focus is on cold operation and system optimization. LNT (lean NOx traps) durability is quantified, and performance enhanced with a sulfur trap. LNCs 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 issues with advanced combustion strategies, important interactions on NO<sub>2</sub> formation, and new formulations for enhanced durability.

#### INTRODUCTION

The field of diesel engines and emission 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. Perhaps we are not seeing the dramatic step changes in developments as in the earlier years, but nonetheless, the field is ripe with incremental improvements to address new and old challenges. There are still well over 1000 technical papers concerning diesel engines, fuels and emissions, comparable to earlier years. Consolidating, absorbing, and summarizing all this information is a huge task, but others have recently brought the interested reader up to date (1).

As in the past (2), this review is not intended to be allencompassing. Rather, the objective is to summarize representative studies that show the key directions in the industry, with an emphasis on reports from 2007. First, the regulatory issues are addressed, followed by a quick overview of engine technologies as a means of estimating the exhaust emission control requirements. Then the author will then review NOx, PM (particulate matter), and hydrocarbon/CO control developments.

# REGULATIONS

It is important to put emission control technologies in the perspective of regulations, which are the primary driver for advancements.

Most of the development of new regulations in 2007 occurred in Europe, with the finalization of the light-duty Euro 5 and 6 emissions standards, and a proposal from the Commission for Euro VI heavy-duty standards. In addition to criteria pollutant standards, the first standards on  $CO_2$  were proposed in Europe late in the year, and are expected shortly in the US from the EPA (Environmental Protection Agency).

The US finalized their light duty, on-road, and non-road regulations several years ago, but the final locomotive and marine rule is expected shortly. California is exploring LEV3 (Low Emission Vehicle), but no formal proposals have been put forth. Japan finalized regulations on light and heavy duty vehicles a few years ago for 2009+, and has harmonized with the US and Europe on non-road applications. Other countries have adopted either the European or US protocols with time lags reflective of the relative state of their transportation sectors.

Given this, the author will focus primarily on the more pertinent developments in Europe that will impact the field of diesel emissions.

#### LIGHT-DUTY DIESEL

Europe finalized their light-duty criteria pollutant regulations for at least the next ~10 years (3). On greenhouse gases, the European Commission proposed mandatory standards in December 2007 yet to be considered by the Parliament and the Council of Ministers. California finalized similar regulations in 2005, but implementation is uncertain pending appeal in the courts after the US EPA denied the necessary waiver in the last quarter of 2007.

The regulations of significance on diesel passenger cars are as follows:

	Euro 5	Euro 6
Phase-in Dates	Sept 1, 2009 to Jan 1, 2011	Sept 1, 2014 to Sept 1, 2015
NOx	180 mg/km	80 mg/km
PM	5 mg/km	4.5 mg/km

The first date of implemention is for new vehicle types, and the second date is for all vehicles. In addition to these, there is a "Euro 5.5" (informal designation) PM standard of 4.5 mg/km and a P# (particle number) standard of 6X10<sup>11</sup>/km that are determined using the UN/ECE PMP (Particulate Measurement Program) protocols. These are effective January 1, 2011 through January 1, 2012 for new types and all diesel vehicles, respectively.

The Japanese 2009 NOx and PM standards are numerically identical to the Euro 5 standards but are measured on a different test cycle. The US Tier 2 Bin 5 NOx standards, effective for MY2007 (model year), are nominally 30 mg/km at 80,000 km and 42 mg/km at 190,000 km. PM standards are nominally 13 mg/km for both durability requirements. (Euro 5 and 6 durability requirements are 160,000 km.)

It is expected that the Euro 5 NOx regulations will largely be met without NOx aftertreatment (4), but significant controls will be needed to sell these vehicles in all 50 states of the US. It is more likely that Euro 6 vehicles will be developed in 2009/10 leveraging early incentive programs. Some NOx aftertreatment will be required in that timeframe on the larger vehicles. To seel these vehicles in all 50 states in the US, either lean NOx traps (LNT) or selective catalytic reduction (SCR), will be applied to the lighter vehicles to achieve the additional control. Indeed. 65% NOx some European manufacturers have announced Bin 5 diesels for the US

in this timeframe using these two NOx control technologies.

 $\underline{CO}_2$ 

The European Commission made a formal proposal to the European Parliament and Council in December 2007 (5). It calls for an emissions limit averaging 130 g/km of  $CO_2$  in 2012 as measured on the NEDC (New European Drive Cycle) test cycle. An additional 10 g/km reduction is to come from implementation of biofuels. The emissions limits vary according to vehicle weight, and manufacturers can pool vehicles with each other to meet the fleet average. This value compares with the Parliament's October 2007 recommendation of a fleet average of 125 g/km in 2015, with limits being based on vehicle foot print. The Parliament also recommended directional targets of 95 g/km in 2020 and 70 g/km in 2025.

Figure 1 shows how the Commission's  $CO_2$  proposal compares with  $CO_2$ -equivalent fuel economy mandates in other countries, adjusted for the NEDC test cycle (6). This author added the point for the US showing the comparison with the recently passed CAFE standards (Corporate Average Fuel Economy) of 35 mpg (miles per gallon) in 2020. The European proposal is near parity with Japan, and the tightest in the world.



**Figure 1.** Cycle-adjusted equivalent  $CO_2$  regulations derived from fuel economy standards in place throughout the world (6).

According to the Commission, the fuel economy of European cars has improved by 12.4% from 1995 to 2004. This averages 1.2% per year, and was achieved by the industry under a voluntary  $CO_2$  reduction commitment, while still meeting market demands (increased weight, power, and performance). This was achieved largely by increasing diesel penetration from nominally 20% to about 50% in this timeframe. Moving forward, the industry will need nominally 4%/year improvements to hit the Commissions proposed target. This will be especially demanding given that significantly increased diesel penetration is not likely.

#### HEAVY-DUTY DIESEL

The on-road heavy-duty diesel (HDD) standards are shown in Figure 2, as are estimates of engine emissions performance. These are unchanged from the author's estimates of last year (2).



**Figure 2**. General comparison of on-road HDD standards in the US, Japan, and Europe. Estimated engine-out emissions for 2007 and 2010 (range) are shown. Steady-state cycle.

Japan and the US have finalized their regulations for the next five to ten years, but Europe is just beginning the process. In that regard, based on industry stakeholder surveys, the European Commission recently proposed (7) NOx standards of 400 mg/kW-hr and PM standards of 10 mg/kW-hr as measured on the current European steady state (ESC) and transient (ETC) cycles. Major stakeholders representing the truck manufacturing industry (The European Automobile Manufacturers Association, ACEA), the emissions controls industry (The Association for Emissions Control by Catalyst, AECC), and the environmental community (The International Council for Clean Transportation, ICCT) supported these levels prior to the Commission's proposal.

As in the final Euro 6 light-duty regulations, the Commission also proposed that particle numbers be limited, with the limit value to be determined later via the UN/ECE PMP process.

In 2006 the European Commission adopted the new World Harmonized Transient Cycle (WHTC) as well as the steady state counterpart. The WHTC is cooler than the European Transient Cycle, with common engines not achieving 200°C until after 500 seconds starting with a cold engine (8). The cold start weighting factor is still to be finalized. In going from the ETC to the WHTC with a 10% cold start weighting factor, ACEA is recommending a +0.3 g/kW-hr NOx adjustment factor (9), as the four engines in their test program using EGR+SCR+DPF (Exhaust Gas Recirculation, Selective Catalytic Reduction, and Diesel Particulate Filters) had WHTC-ETC differences ranging from 0.20 to 0.45 g/kW-hr NOx. The difference in NOx on one engine in an AECC test program (10) using similar technology was about 0.1 g/kW-hr.

#### **ENGINE TECHNOLOGIES**

#### 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, better EGR (exhaust gas recirculation) control, advanced and two-stage turbocharging, variable valve actuation, closed loop combustion control, and advanced model-based control.

Figure 3 depicts the PM/NOx trade-off curve for a lightduty diesel technology package to meet the US Tier 2 Bin 5 standards (11). A similar package was shown for Euro 6, but with a different engine calibration: 165 mg NOx /km (0.26 g/mi) vs. ~ 70 mg/km (0.12 g/mi) in the US. In both systems the deNOx efficiency is nominally 75%, but more NOx has to be removed in Europe (~85 mg/km) than in the US (40 mg/km) presumably resulting in a higher urea consumption for SCR, or a higher fuel penalty for an LNT (lean NOx trap) in Europe which is likely more than offset by the fuel consumption advantage of running at the higher NOx level.



**Figure 3.** Emissions results for a US Tier 2 Bin 5 technology package. The same generally technologies are also applied to meet Euro 6 standards, but with a different NOx/PM calibration (11).

In that regard, Akmadza (12) presented the graph shown in Figure 4, illustrating the fuel consumption NOx tradeoff curve for two advanced engine technologies. Going from a Euro 5 calibration (0.18 g/km NOx) to a Euro 6 calibration (0.080 g/km NOx) results in a nominal 7% fuel penalty. However, in another slide the author shows a "Step 3" engine technology using premixed combustion and long-loop EGR with an optional deNOx solution for "extreme" cases. The choice between additional engine technologies and NOx aftertreatment will need to balance costs and fuel economy benefits.

Sasaki and Sono, et al., (13) describe an advanced combustion engine with three modes of operation, generally characterized by injection timing and EGR levels, Figure 5. To balance between unstable combustion and soot formation regimes, very careful control of injection timing and EGR is needed. At low loads, high EGR and early injection timing is used (upper left of diagram) for low NOx and PM, but higher CO and HC (hydrocarbon). In intermediate loads, "mixture formation phasing" is used, wherein some fuel is injected into the squish zone (outside the bowl) and the rest is injected into the bowl as the piston rises. The result is that the mixture is locally leaner than if all the fuel was injected into the bowl. At higher loads, later injection and lower EGR are used for traditional diesel combustion.



**Figure 4.** Fuel consumption vs. NOx trade-off curves for three different engine technologies. Approximately 7% fuel penalty is implied when going from a Euro 5 (0.180 g/km) to a Euro 6 (0.080 g/km NOx) level (12).



**Figure 5.** A three-mode advanced combustion engine is depicted on the fuel injection vs. EGR map. The strategy is to balance between high soot formation and unstable combustion at all loads (13).

Kuhn (14) gave a pathway to hitting SULEV (Super Ultra Low Emission Vehicle California certification or Tier 2 Bin 2 US Federal level). The fully pre-mixed combustion regime was extended to about 8 bar BMEP (brake mean effective pressure) or about 45% peak load. Advanced EGR handling was described to drop the specific NOx in this regime to <0.3 g/kW-hr. Regarding fuel consumption, simulation shows that when going from a Euro 4 to a Tier 2 Bin 5 engine configuration, net fuel consumption decreases ~3.5% to accompany the 87% engine-out NOx reduction. Kuhn estimates that a modest LNT would be needed to hit SULEV, but the simulation results show a stiff 15% fuel penalty from the Bin configuration.

Ryan (15) also briefly described results from steady-state engine testing and transient testing simulation showing a pathway to SULEV with a modest LNT and Bin 5 engineout NOx.

To wrap-up, Euro 5 regulations will require diesel particulate filters (DPFs) but no NOx aftertreatment. To meet Euro 6 early tax incentives in 2009 and beyond, NOx aftertreatment will be needed on the heavier vehicles, although deNOx aftertreatment can deliver fuel consumption benefits. US Tier 2 Bin 5 standards will be met with advanced deNOx technologies. Advanced combustion strategies, in which engine-out NOx levels over large parts of the certification cycle are very low, would require some NOx aftertreatment in the higher load regimes.

#### HEAVY-DUTY

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 Euro V (2008) regulations are largely addressed using more conventional engine technologies and SCR. (Some Japan 2005 applications also use SCR.)

For reference, the reader is pointed to Charlton (16) for an excellent comprehensive overview of US2007 technologies. He describes how EGR flow doubled while EGR cooler effectiveness improved from US2004 levels. Injection pressure increased 40% approaching 2000 bar at higher speeds. NOx dropped 50% and fuel consumption is down 2%, with modest PM reduction on top of it.

Moving on to Japan 2009, US2010, and Euro VI, we will also see incremental advancements from the earlier regulatory technology requirements. For Japan 2009 (0.7 g/kW-hr NOx), Shimoda (17) lists 2000 to 2400 bar injection pressures, up to 30% cooled EGR using both short and long loops, pre-mixed combustion up to 3 bar BMEP, new combustion chamber design, and nominally 50% deNOx from aftertreatment. Requirements for US2010 are similar, but 2-stage boost is added and 85% deNOx is needed (18). Peak cylinder pressures range from 220 to 250 bar. Technologies for Euro VI are similar (19), but pre-mixed combustion regimes are not described, deNOx levels of 80% are required, and cooled EGR levels of 20% are proposed. On the cutting edge of emissions results, Emmerling (20) showed the NOx/PM trade-off curve reproduced in Figure 6. Technologies were not described. The relatively sharp corner at low NOx and PM levels, shown here at nominally 0.5 g/kW-hr NOx, in combination with rapid increases in PM at lower NOx levels and the flat character at higher NOx levels is an interesting characteristic. If the shape duplicates itself on the BSFC/NOx (brake specific fuel consumption) trade-off curve, as is common with most technology packages, little is gained by running at higher NOx levels. More moderate levels of deNOx would be needed.



**Figure 6.** Cutting edge NOx/PM trade-off curve for a HD engine with advanced technologies (20).

Regarding improving the fuel efficiency of HD engines, Schmidt (21) summarized the theoretical opportunities for gains. Improving combustion efficiency from 57 to 60% and reducing wall heat loss emerge for the greatest improvements.

Stanton (22) took the analyses one step further and summarized engine results and gave insights into the technologies. Using increased injection pressure (unspecified), multiple injections, improved EGR, improved combustion controls, pre-mixed combustion, and electric turbocharging, Stanton shows BTE (brake thermal efficiency) improving from 42.5% for US2007 engines to 45% in the lab today, to 47% projected for 2008. Along with the efficiency improvements, NOx levels from nominally 0.22 to 0.46 g/kW-hr were shown (presumably cycle averaged), while still achieving 6 and 8% relative thermal efficiency gains.

#### NON-ROAD

Dreisbach (23) very nicely summarizes the technologies needed for non-road engines to attain the interim Tier 4 (2011) and final Tier 4 (2014) emission levels. The results are summarized in Figure 8. In the reference he describes the technology packages for 56-130 kW and >130 kW engines to hit the interim Tier 4 (2011) and final Tier 4 (2014) standards. The details are beyond the scope of this review. In short, EGR and filters are capable of hitting

the interim levels for all engines, but need higher injection pressures (200 bar more), 2-stage turbocharging (for the higher specific power engines) and better cooling systems than SCR-only options. He chooses SCR because high deNOx capability (>80%) is desired and the high exhaust temperatures (>250°C) in the Non-Road Transient Cycle (NRTC) fit SCR nicely. Moving into the final Tier 4 engines, EGR, advanced cooling, and SCR are needed in all cases, except the 56 to 75 kW class where-in SCR is not needed. In almost all cases, PM regulations can be reached with partial filters, but DPFs are recommended to meet certain market or political needs. Others (24, 25) are showing only DPFs as the non-road PM-reduction technology solution. In that regard, this author notes that Switzerland is proposing a particle number emission cap for new construction equipment with engines >18 kW of 1X10<sup>12</sup> particles per kW-hr measured on the NRTC.



**Figure 7.** Progress to date on achieving high BTE engines (22).



**Figure 8.** Non-Road technology roadmap for addressing future emissions regulations (23).

# NOx CONTROL

Given the tight NOx emission regulations in the US and Japan, and the fuel economy impacts NOx aftertreatment can have, NOx control technologies will play a key role going into the future. Following is an assessment of the state-of-the-art on selective catalytic reduction (SCR), lean NOx traps (LNT), and lean NOx catalysts.

#### SELECTIVE CATALYTIC REDUCTION

Although SCR has been applied to commercial vehicles for upwards of four years, the technology is relatively dynamic with improvements being made on low temperature performance, urea delivery systems, system design, and alternatives to liquid urea.

There is significant motivation to improve low temperature SCR performance: SCR is emerging in the light-duty sector where reduced cold start emissions are critical, further NOx reductions in the HD sector are needed, and greater NOx reductions are desired in urban driving or other low load conditions.

Urea decomposition is one barrier to good low temperature SCR performance. Although this is not a significant issue with vanadia catalysts, wherein urea decomposes faster to ammonia than the catalyst can utilize it at all temperatures, it can limit the performance of zeolite catalysts according to Kroecher (26). He shows that NO<sub>2</sub>, which is desired at the 50% level of NOx, adversely affects the decomposition of urea, in that the decomposition efficiency of a Fe-ZSM5 catalyst dropped from 70 to 40% at 150°C in the presence of NO<sub>2</sub>. Kroecher does show some new urea decomposition catalysts that can help significantly, Figure 9.



**Figure 9.** Efficiency of emerging urea decomposition catalysts (26).

In another paper, Kroecher proposes the reduction mechanisms for the SCR reactions over zeolite catalysts (27). He shows that with NOx present only as NO, the oxidation to  $NO_2$  to promote the "fast SCR reaction" is the rate limiting step. Once  $NO_2$  is present or formed, an important intermediary in the reactor steps is  $NH_4NO_3$  (ammonium nitrate). Ammonium nitrate begins forming with decreasing temperature at about 200°C, and significantly hampers the reduction reaction after about 15 minutes at 190°C and 5 minutes at 180°C. Catalyst performance is restored upon heating to T>200°C.

In the same paper, Kroecher shows that  $NO_2$  can partially reduce to  $N_2O$  over Cu- and Fe-zeolites, beginning in the 150 to 250°C temperature range. This is problematic as  $N_2O$  is a potent greenhouse gas. In his experiments, fresh Cu-zeolites had peak  $N_2O$  formation, 110 ppm, at 250°C, while aged Fe-zeolites peaked at 45 ppm at 300°C. Fresh Fe-zeolites did not form  $N_2O$ . The results illustrate the difficulty in balancing  $NO_2$  concentration to optimize low temperature SCR performance, catalyst choice, wherein Cu-zeolites have better NOx conversion at low temperature, and secondary emissions. He shows a new Fe-zeolite catalyst formulation that decreases or eliminates  $N_2O$  formation.

Urea evaporation and decomposition can be strongly dependent on getting good mixing. There are several papers on modeling to improve urea injection and mixing using a variety of devices (28, 29, 30). About 10-20% deNOx efficiency improvements can come from good injection practice, with nominally 5-10% coming from using a variety of mixers.

Because of the low-temperature limitations of SCR, getting high deNOx efficiency in the light-duty test cycles is problematic. In one system (11), for US Tier 2 Bin 5 certification on the US FTP with the SCR system located behind the close-coupled DPF, some deNOx started after about 180 seconds at exhaust temperatures approaching 150°C. For Euro 6 applications, deNOx did not begin until ~800 seconds into the cycle at temperatures of about 170°C.

Ammonia storage models can help with early deNOx. Grumbrecht (31) retrofited a Euro 4 sport utility vehicle with SCR behind the DPF to achieve Euro 6 NOx levels. "Preconditioning" the catalyst with ammonia storage increased deNOx efficiency by ~20% on the NEDC. To achieve the Euro 6 NOx standard, catalyst heating resulted in a 4% fuel penalty, but recalibrating the engine at high load got this back.

To simplify the urea delivery system, an airless injector without a urea return line was introduced (32). Instead of keeping the injector cool using excess urea, which is returned to the tank, the injector is raised off the exhaust pipe and cooled with convection air and fins. Also, upon shut-off, the urea line drains, eliminating freezing and the need for line heaters.

Given the proposed  $CO_2$  mandates expected in Europe, Figure 10 shows how an integrated engine system and SCR can improve fuel economy (33). The Euro 4 base engine is upgraded to Euro 5 (#1 in the figure), with the reference fuel consumption/NOx trade-off curve showing a 3% fuel penalty at Euro 6 NOx levels, #2. With SCR applied to the Euro 5 engine, a 1% fuel penalty is measured to attain Euro 6 NOx levels, #3. Alternatively, more engine alterations can be made to allow engine downsizing and a 7% cut in fuel consumption at Euro 5 NOx levels, #4, and a 6% fuel consumption cut at Euro 6 calibration with SCR, #5. In this example, SCR saves ~ 2% fuel consumption vs. engine calibration alone to reduce NOx. One has to keep in mind that urea comes from natural gas feedstocks and the processing of urea has an innate  $CO_2$  penalty with it. Gram for gram, urea has about 3-4X more "well-to-wheel"  $CO_2$  than diesel fuel. In Euro 5 applications with a 5% urea consumption rate relative to fuel, the urea total  $CO_2$  contribution is about 10-15% (34).

To facilitate OBD (on-board diagnostics) and closed loop SCR control, aside from the established NOx sensors (35), an ammonia sensor was introduced (36). It has  $\pm 5$  ppm ammonia detection accuracy up to about 30 ppm ammonia, and has negligible cross interference from NOx, hydrocarbons, or CO.



**Figure 10.** Illustration of how SCR can be used to deliver fuel consumption reductions vs. engine means alone, for attaining Euro 6 standards (reproduced from reference 33).

Finally, progress is being made on further developing the alternative SCR reductants to liquid urea: solid urea (37) and magnesium dichloride ammonia storage media (38). Both options have 3X more ammonia per liter than liquid urea. System engineering is moving forward on developing solid urea and a consortium project with 13 companies is in place. One major development in the last year is in the method to heat the pellets to the decomposition The urea evaporator is temperature of 200-250°C. attached to the exhaust pipe to supplement the electrical heating. Regarding magnesium dichloride, in a passenger car application, after applying 350W to heat up the material from room temperature (100 seconds), 45 to 120W was needed to deliver enough ammonia in the US06 test cycle. Dynamic response was excellent.

#### LEAN NOx TRAPS

Lean NOx traps offer an attractive NOx solution for lightduty applications and those HD applications in which an extended urea infrastructure might be problematic. In US HD applications the challenge for LNT is acceptable high temperature efficiency to meet the NTE requirements (50-70% control at 500-520°C), and do it over the useful life of the vehicle (185,000 miles for medium HDD and 435,000 miles for heavy HDD). On the light-duty side, efficiencies need to be high enough to hit Tier 2 Bin 5 (70% using traditional diesel combustion; 30-50% in the 50 to 70% load range using mixed mode combustion) over the useful life of the vehicle (120,000 miles).

In addition to favorable economics in the smaller engine class (39), LNTs can also be placed closer to the engine than SCR systems, which require more distance for urea mixing, giving LNTs technical advantage, especially for smaller vehicles. Wiartalla (40) shows that the resulting 60C° temperature advantage can give a 10% deNOx efficiency advantage over an SCR system placed further downstream for a 1450 kg vehicle.

The durability of LNTs subjected to aggressive desulfation cycling was quantified (41). The decrease in deNOx efficiency shown in Figure 11 when going from 800 to 900°C exposure is mainly caused by potassium migration from the LNT catalyst to the cordierite substrate. Precious metal grain size increased only 15% in this temperature interval.



**Figure 11.** The significant loss in deNOx efficiency when going from 800 to 900°C is mainly due to potassium migration out of the LNT catalyst (41).

To keep sulfur off the LNT, Yoshida, et al., described a sulfur trap material (42). The material can store 20-30 g/liter of sulfur and has 80-100% efficiency at a 50,000/hr space velocity. The authors estimate a life of about 40,000 km with ultra-low sulfur diesel fuel. A critical aspect of the capacity is full material utilization. This is difficult because the migration of the sulfate into the material is slow. Migration is enhanced by periodically heating to 550°C and spreading the trap material over a larger surface area using substrates with a higher cell density.

#### LEAN NOX CATALYSTS

Morita, et al. (43) and Wada, et al. (44) expanded upon the double-layer lean NOx catalyst described by Satoh, et al. (45) in 2006. In the concept, lean NOx is adsorbed by a ceria-containing material. During rich regeneration,

ammonia formation is promoted, and it is stored in a catalyst that will have supplemental deNOx capability in lean conditions. Morita showed that rich-phase ammonia formation was enhanced by CO formed in rich combustion rather than by excess fuel from a post injection. A nominal 4% fuel penalty is observed for the new LNC concept. Wada generally reports a fast heatup combustion strategy that can also be used to keep the catalyst hot under cold or low load conditions. Instantaneous fuel consumption goes up about 6% to get the catalyst 43C° hotter. It is effective at about 180 seconds into the FTP. In that regard, Wada also shows a three-way catalyst (TWC) in the system, and describes how it reduces NOx during the rich portions of the LNC operation. In answer to a question after presenting the paper. Wada also mentioned the TWC can aid in cold start, presumably when using the low temperature combustion strategy outlined by Sasaki and Sono (13).

Finally, the interesting LNC developments reported by Blint (46) in 2005 were updated (47) last year. Recall that combinatorial chemistry was used to scan thousands of potential HC-SCR catalyst formulations. The best possibilities were evaluated using a rapid test protocol, and the best of these were eventually screened to a few potential formulations. Figure 12 shows the latest results. The catalyst achieved 60 and 75% deNOx efficiency on the US FTP and US06 cycles, respectively. The deNOx T50 temperature increased 10C° to 240°C upon exposure to sulfur and with subsequent regeneration. Hydrocarbon dosage in this work was 8X that of the NOx level (HC<sub>1</sub>:NOx=8) Work is continuing on developing the catalyst and improving its durability and sulfur tolerance.



\*Engine evaluation on aged LNT catalyst (4.9 L 5250 lbs weight class) •Reactor conditions (water, CO<sub>2</sub>, 25 ppm NO, 250 ppm H<sub>2</sub>, 10% O<sub>2</sub>, 80 ppm <u>simuliesel</u> or ammonia) •Reactor samples <u>hydrothermally</u> aged for 16 hours at 650 °C



# **PM CONTROL**

DPFs have been applied to production vehicles since 1999, and are now standard equipment on most European diesel cars and all US and Japanese cars. All 2007 HD truck engines in the US and all but the long haul trucks in Japan use them. Moving into the future, the prognosis is that DPFs will be as significant a part of the diesel engine as direct injection and turbocharging is today.

As such, the field is quite active on optimizing regeneration strategies, improving substrates and catalysts, and exploring on-board diagnostics (OBD).

# **REGENERATION STRATEGIES**

Ootake, et al. (48) describe a DPF regeneration strategy based on oxygen control using a lambda sensor. The method allows better-controlled regenerations, resulting in increased specific soot loadings of about 20%. The strategy is adaptive to account for air flow meter and other input variation. This allows better dynamic control in transient conditions.

Parks, et al. (49) evaluated fuel injection strategies to enhance DPF regeneration. They delayed the main injection by 20° and extended (delayed extended main, DEM) it to get more fuel for heating the DPF. They also evaluated a post injection at 80° after top dead center (P80) and an in-pipe injection of fuel. At exhaust temperatures of 150°C, only the DEM strategy heated the system and created an exotherm in the DPF after about 200°C at an instantaneous fuel consumption of +40% over normal. At 300°C, the P80 and in-pipe strategies were better. When the DEM strategy was used in only one cylinder, PM, hydrogen and CO levels dramatically increased with increases in fuel beyond the consumption level. allowed +50% This better temperature control in the DPF, despite the higher PM levels.

# CATALYSTS AND DPF SUBSTRATES

Konstandapolous, et al. (50) looked at the combination of DPF substrate porosity and catalyst configuration in the light of a proposed two layer soot oxidation model. At temperatures of about 450°C or in the initial stages of oxidation at higher temperatures, the layer of soot in direct contact with the catalyst begins oxidizing. As oxidation proceeds, soot contact is lost and the rate decreases until the higher temperatures when direct gas/soot oxidation begins (~600°C). In Figure 13, the authors show that these phenomena can be controlled with the use of advanced DPF substrates and an advanced catalyst coating to improve contact. With proper design, good contact can be achieved throughout the oxidation proceess.



**Figure 13.** DPF porosity and catalyst coating can impact soot oxidation rates. The differences are explained by intimacy of soot/catalyst contact using a 2-layer soot model (50).

Concerning soot/catalyst contact, Suzuki, et al. (51) used isotopic oxygen in the gas to show the soot oxidation mechanisms of oxygen-storage washcoats. Figure 14 illustrates the shifting reaction kinetics for a Pr-Ce washcoat. The reaction of soot with only lattice oxygen (<sup>16</sup>O) begins first (625°K, ~350°C) and peaks at 700°K (~430°C). Reaction with gaseous oxygen then begins at 650°K (~380°C) with a mixture of the isotopes. With this material, the reaction with purely gaseous oxygen (<sup>16</sup>O) also begins at 650°K (~480°C) and also likely occurs through the lattice exchange of oxygen.



**Figure 14.** Using gaseous isotopic oxygen, the soot oxidation mechanism on Ce-Pr based catalyst can be determined (51). It was shown that all the oxygen transfer at these temperatures occurred through the lattice.

In other DPF catalyst developments, a sol gel process was described (52) that results in half the back pressure of a traditional washcoat at similarly high loadings (40 g/liter). More data are reported on the substitution of palladium for platinum (53). Pt/Pd formulations had lower light-off temperatures than Pt-only catalysts (240°C vs. 295°C) in the aged state, generated as much NO<sub>2</sub> for passive soot oxidation, and are resistant to sulfur contamination. A nominal 3:1 ratio of Pt:Pd was shown to be a good level of substitution.

In one investigation, the platinum was completely substituted for palladium with use of a base metal catalyst (54). Interestingly,  $NO_2$  emissions were generally lower than from uncoated DPFs and much lower than from DPFs using platinum at the same catalyst loading (1.5 g/liter). Also, the balance point temperature was ~25C° lower and HC emissions were lower.

Moving on to substrate materials. Figure 14 shows how the initial particle number (P#) filtration efficiency (15 to 500 nm) varies with mean pore size of the DPF substrate (55). All have a similar catalyst coating. Based on these data and other data in the paper, the authors show that initial filtration efficiency drops off dramatically if pores larger than ~20 µm are present. However, as the filter cake builds up, filtration efficiency recovers. This is demonstrated in a sister paper (56), wherein the filters with a pore size of 25 µm reached near parity with 15 µm filters after about 0.5 g/liter soot was captured using a diesel fuel burner ria. In vehicle testing on the NEDC with loaded filters, the larger-pored filters had a filtration efficiency of 94% compared to 98% for the filters with 15 µm pores.

The performance of aluminum titanate filters was described by Ingram-Ogunwami (57). Figure 16 shows higher initial filtration efficiency compared to SiC filters. The SiC filter had a 70% higher back pressure at a soot loading of 6 g/liter. The safe operating regime of the filter was described in terms of maximum temperature and thermal gradients, and coincided with a soot mass limit of 7 to 8 g/liter under the test conditions.



**Figure 15.** Initial P# filtration efficiency drops off significantly as DPF mean pore size approaches 20  $\mu$ m (55).



**Figure 16.** Initial and loaded filtration efficiency of aluminum titanate (AT) filters is compared to that of SiC (57).

In a novel concept, inserting the entry plugs of a DPF 76 mm into the part (rather than on the face), leaving a 203 mm DPF, results in 10% lower back pressure than a standard 76 mm DOC plus 203 mm DPF configuration. As the front part does some filtration, the soot is better distributed for a more controllable regeneration (58).

The P# emissions of the two leading Euro IV and V HD concepts were compared to Euro III engines with and Figure 17 shows that the P# without DPFs (59). emission rates of the Euro IV PM Kat (open filter system) are similar to a Euro V SCR-equipped system without DPFs emitted 99% fewer particles. filters. Similar relationships were shown at lower load points, but at the 100% load point the Euro V engine (SCR) had higher P# emissions than the Euro III (no aftertreatment) or Euro IV engines, which had similar emission levels. The investigators also show that the P# emission rates are higher for the loaded open filters, inverse to that of DPFs, and NO, emissions are much higher than for the Euro V SCR system.



**Figure 17**. Particle number emissions for a Euro V engine with SCR, a Euro IV engine with an open filter system, and a Euro III engine with no aftertreatment and with a DPF (59).

Finally, although a little off the subject of filter catalysts and materials, but still pertinent to P# efficiency, Foster, et al. (60) showed that in two low temperature combustion modes (LTC, 38° BTDC injection timing, 650 and 1160 bar rail pressure 60% EGR), the ultrafine particulate emissions are still quite high. Figure 18 shows some results, wherein emission levels are similar in magnitude to conventional combustion in medium speed and medium load conditions. The results signal that even if low temperature advanced combustion can be used over the whole engine map, DPFs might still be needed to hit emerging P# emissions standards.

#### **ON-BOARD DIAGNOSTICS**

OBD could emerge as a major issue going into 2013 when California fully phases in their requirements. If emissions exceed 1.5X the standard, the OBD system needs to detect this. For light-duty applications, Figure 5 shows engine-out PM levels of 50 mg/mile relative to an OBD threshold of 15 mg/mile. In this case, the OBD system must detect if a DPF has <70% filtration efficiency.



**Figure 18.** Ultrafine emissions when running in Low Temperature Combustion Mode, compared to conventional combustion (60).

There are a couple studies worth highlighting concerning the performance of cracked filters. Zelenka (61) showed that SiC filters with a typical ring-off crack, caused by a hot core and relatively cool outer region, lost only 5% P# filtration efficiency at full load, and was still filtering at 99% efficiency at half load, although without the crack the efficiency was 99.999%. PM emissions went from 1 mg/km to 2.5 mg/km, but this is still well under the 5 mg/km standard.

In an attempt to better quantify the effects of damage, Seiler (62) drilled holes in the filter and measured various parameters. Consistent with Zelenka, filtration efficiency showed only minor decreases for partially damaged filters (25%), except in transient conditions (-50%) but dropped to 30-50% for heavily damaged filters (100%). Backpressure changes showed very little reliable and repeatable differences for partially damaged filters, but heavily damaged filters showed changed behavior. The researchers conclude that a PM sensor will likely be needed for OBD. In that regard, Hauser (63) showed interesting results on a soot sensor. In the sensor, soot transfers charge from one plate to another, the rate of which correlates to soot concentration. Figure 17 shows the results of transient testing using a partially cracked filters, wherein the sensor follows the particulate emission very well.

# HYDROCARBON AND CO CONTROL

Diesel oxidation catalysts (DOCs) can be formulated to perform several key roles in diesel emission control systems. In addition to being designed to specifically reduce hydrocarbon (HC) and CO emissions, they can also be formulated to oxidize NO to  $NO_2$ , which is important in the passive regeneration of soot on filters and improves the performance of SCR systems. They are also the primary way of heating up filters during active regeneration using unburned fuel.



**Figure 19**. Soot charge sensor tracks PM emission very well in transient testing using a partially damaged filter (53).

The US EPA is aware of concerns that DOCs may increase the NO, fraction of total NOx emissions. The NO, produced by a DOC is dependent on the catalyst formulation. CARB (California Air Resources Board) has established a limit on incremental NO<sub>2</sub> from diesel retrofit devices and all DOCs on its list of verified products comply with this limit. Data EPA has reviewed to date indicate that EPA verified DOCs also comply with the CARB limit. Data supplied by DOC manufacturers to both CARB and EPA show that, for some verified DOCs, the NO<sub>2</sub> fraction of total NOx actually decreases slightly. DOCs do not raise total NOx levels. EPA is continuing to analyze NO, data from verified technologies and is looking to implement an NO<sub>2</sub> requirement for verified technologies that would maintain harmonization with California (64).

In advanced combustion mode, the HC and CO emissions can be several times higher than in conventional engines, making DOC performance critical. Knafl, et al. (65) showed that the T50 light-off temperatures for HC and CO can be 50-60C° higher for

advanced combustion modes than for conventional combustion. They showed the HC concentration to be higher in ethene and n-undecane. In a related study from the same group (66), propylene was shown to have a strong negative effect on the oxidation of CO using a typical DOC formulation.

Two studies (67, 68) on the formation of  $NO_2$  in DOCs reached the same conclusion:  $NO_2$  will not form and will be consumed as long as HC and CO are present in the exhaust. Only after the HC and CO light-off, can NO be oxidized to  $NO_2$ . Figure 20 shows the supporting data (66). It follows that aged DOCs can be a net consumer of  $NO_2$  as the light-off temperature of HC and CO increases (67).



**Figure 20.**  $NO_2$  is not formed and is consumed in DOCs if HC and CO is present. Not until HC and CO are oxidized can  $NO_2$  be formed (67).

For burning HC to generate temperature for active DPF regeneration, good high-temperature durability is important. Katare (69) described the development of a ZrSi-based washcoat with significantly improved high temperature durability and sulfur tolerance. Under severe aging conditions at 850°C, the new formulation dropped the light-off temperature of CO about 30C° versus alumina.

#### CONCLUSIONS

The combination of tight criteria pollutant tailpipe regulations combined with proposed limits on CO, emissions will place new demands on diesel engines and systems. However, this review of the state of diesel emissions and control in 2007 shows that the challenges of the emerging regulations can be met with a number of engine and aftertreatment options. Highlighted LD engine technologies show the same technology packages can be used with different calibrations to hit the tight NOx requirements of the US or potentially the CO, targets in Europe. Emerging engine technologies are showing better potential for hitting the SULEV emission levels, a goal that seemed unrealistic only a few years ago. On the HD side, generally the same technologies are being proposed to hit the emerging

US2010, Japan 2009, and Euro VI (proposed) regulations. In addition, to dramatic reductions in NOx, research engines are showing 10% fuel savings using incremental technologies. These engines are hitting 47% BTE, with goals of going to 53% BTE by 2013. Non-road engine technologies are generally following the model set forth in the highway sector. In general, this points to 2-stage turbocharging; increasing EGR, cooling, and control; higher pressure flexible fuel injection; and premixed or low temperature combustion strategies.

In the tailpipe, SCR efficiencies are approaching 90%+, with better mixing and control. Low temperature deNOx is being addressed with increased efficiencv understanding on limitations, such as ammonium nitrate formation at T<200°C, and with urea decomposition catalysts. Advances are also being made on liquid urea substitutes - solid urea, and gaseous ammonia storage in magnesium dichloride. LNT advances include a better understanding of HT aging issues via potassium migration, and the development of a sulfur trap that might last 40,000 km. Lean NOx catalysts made significant strides, with improvements to a double layer concept utilizing ammonia generated in a NOx adsorber material, and a new HC-SCR catalyst that is performing nearly as good in preliminary work as ammonia SCR catalysts.

More is being learned on DPF regeneration pertaining to control, in-cylinder injection strategies, and fundamentals on how soot interacts with catalyst. More information was provided on the newest DPF substrate material, aluminum titanate. Studies are summarized on P#

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emissions from the latest European HD commercial engines, wherein Euro V engines with SCR perform similarly to Euro IV engines with open filters, but not nearly as well as retrofit Euro III engines with DPFs. Although low-temperature combustion strategies can have very low PM levels, P# emissions can be similar to those with conventional combustion systems.

Finally, on DOCs, the high HC emissions from low temperature combustion engines might be difficult to treat perhaps due to the class of hydrocarbons generated. More was learned on the  $NO_2$  generation capabilities of DOC in that  $NO_2$  is not formed at temperatures below the light-off temperature of HC and CO.

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JohnsonTV@Corning.com

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