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 70% tightening of fleet average light-duty (LD) criteria emissions likely to be proposed in California for ∼2016-22. CO\textsubscript{2} regulations in both the heavy - and light-duty sectors will also tighten and impact diesel engines and emissions, probably long into the future.

Engine technology is addressing these needs. Light-duty diesel engines are making incremental gains with combustion enhancements that allow downsizing for CO\textsubscript{2} savings. Heavy-duty (HD) engine show trade-offs between hardware recipes, exhaust deNOx control, and fuel consumption.

Much has recently been reported on optimized selective catalytic reduction (SCR) systems, with many reports on improving low temperature performance with proper reductant management and new catalyst formulations. Developments on HC-based deNOx are focused on lean NOx traps (LNTs) and the LNT+SCR systems, wherein the LNT is calibrated to generate ammonia for use in a downstream SCR.

PM control with DPFs (diesel particulate filters) are very effective. DPF regeneration advances are reported in strategy, catalyst utilization, and substrate design. Biodiesel effects on DPF functions are becoming clearer.

Finally, diesel oxidation catalysts (DOCs) are investigated in the context of impacting NO\textsubscript{2} coming from a downstream catalyzed DPF for use in an SCR system. Hydrocarbon removal from the DOC is quite important in this regard.

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\textsubscript{2} regulations. Also, California is planning a nominal 70% tightening of criteria pollutant standards, so efforts are accelerating to continue emissions parity with gasoline vehicles. In the HD truck market, criteria pollutant regulations will not tighten until 2013 in Europe, but the US is proposing the first CO\textsubscript{2} regulations for 2014. The combination of criteria pollutant and efficiency mandates will push diesel technologies in both sectors. The non-road market is implementing technologies to meet new 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 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 CO\textsubscript{2}, NOx, particulates, and HC/CO. It is noted that technical paper offerings in 2010 again seemed focused on two large conferences as in previous years, the 2010 SAE World Congress and the 2010 Directions in Engine Efficiency and Emissions Research (DEER) Conference, but there were more excellent papers presented at the smaller conferences this year, probably due to the improved economic situation in the industry. The developments, quantity, and quality of the work continue to be very good. Finally, as in previous
reviews, this review is not intended to be all-encompassing and comprehensive. Representative papers and presentations are chosen here that provide examples of key developments and direction.

REGULATIONS

Diesel regulatory initiatives are focused on a new set of light-duty (LD) regulations in California referred to as LEVIII (Low Emission Vehicle III), and the first-ever proposed CO₂ regulations on heavy-duty (HD) highway vehicles by the US EPA (Environmental Protection Agency).

LIGHT DUTY

The California Air Resources Board (CARB) is planning to propose new light-duty tailpipe regulations soon that will present a new challenge for light-duty diesels. The formal proposal is expected in February and finalization is expected in April of this year. The US EPA is working with CARB on the regulations, with the aim of developing a national regulation (Tier 3).

As indicated in two workshops [2, 3], they will move to a fleet average requirement of NMOC+NOx (non-methane organic gases + nitrogen oxides) roughly equal to SULEV (Super Ultra-Low Emission Vehicle) or US Tier 2 Bin 2 levels of 30 mg/mi. This is about a 70% tightening from today's FTP cycle (Federal Test Procedure) limit value. Up for discussion are a significant tightening of the US06 standards (up to 90%), using a NMOC+NOx standard, significant tightening of PM (80-90%), and extending the phase-in time for the last portions of the fleet to comply.

Specifically, CARB is considering adding three new certification levels to help the automakers meet the SULEV fleet average requirement - two new levels between ULEV (Ultra-Low Emission Vehicle) and SULEV, named ULEV70 and ULEV50 for 70 and 50 mg/mile NMOC+NOx; and SULEV20 to indicate 20 mg/mile NMOC+NOx. All applicable light-duty certification levels being discussed are shown in Figure 1. The two new ULEV levels bridge the relatively large gap between current ULEV and SULEV level allowing more fine-tuning of certification levels, and the SULEV20 level allows a non-zero emission offset. (Note: One ULEV50 vehicle nominally requires two SULEV20 vehicles to offset it.) CARB is also discussing dropping the PM (particulate mass) levels from a cap of 10 mg/mile today to 6 mg/mile in 2016, 3 mg/mile in 2022, and 1 mg/mile in 2025. As an alternative, CARB would allow a PN (particle number) certification of $6 \times 10^{12}$/mile for 2016, $3 \times 10^{12}$/mile in 2022, and $1 \times 10^{12}$/mile in 2025 using the European test protocol. Also worth noting is that the durability requirements are increased from 120,000 miles to 150,000 miles and the 50,000 mile emissions requirements are eliminated.

CARB will also be proposing new light-duty CO₂ standards for 2017-2025 as part of the LEVIII package. They are evaluating tightening between 3 and 6% per year [4]. In September 2010, the US EPA published a Joint Notice of Intent (with CARB and the National Highway Traffic Safety Administration, NHTSA) to propose light-duty greenhouse gas emissions standards within the same range and timeframe by September 30, 2011 and finalize them by July 31, 2012 [5]. A 6%/yr tightening will drop CO₂ levels by 40% relative to 2016, and bring fleet average emissions to about 148 g/mile (89 g/km) in 2025 as measured on the FTP cycle (US Federal Test Procedure). This value is nominally 100 g/km when adjusted to the New European Drive Cycle using the methodology of An [6], and compares to a level of 95 g/km in 2020 in Europe.

HEAVY DUTY

Aside from the continued wrap-up of the Euro VI heavy duty regulations comitology reported last year [1], there was little change on heavy duty criteria pollutants in 2010. India started implementing Bharat Stage IV standards (similar to Euro IV) in eleven major cities in 2010. However, sales have largely gone to Bharat III vehicles, except in Delhi where laws prohibit the practice of registering vehicles outside of the city [2]. China recently delayed the implementation of Euro IV for heavy-duty diesels one year until January 1, 2012; heavy-duty gasoline must still comply to Euro IV norms on January 1, 2011. (Euro 4 light-duty diesel regulations are delayed until July 1, 2013.) Discussions are beginning in Japan to adopt a regulation in 2016 similar to Euro VI.

The most significant regulatory initiative for 2010 came from the US EPA in the form of a proposed greenhouse gas emission standard for heavy duty engines and vehicles [8]. The proposal requires by 2017 about 20% reductions from tractors used to pull trailers, 7 to 10% reductions from vocational vehicles, and 17% from large pick-up trucks and vans (by 2017 or 2018). Except for vocational vehicles, most of these reductions come from vehicle modifications (aerodynamics, idling reduction, low rolling resistance tires),
but 3 to 5% CO\textsubscript{2} reductions are required from the engine relative to 2010 industry average levels by 2014, and another 2 to 4% by 2017. (In special cases, a manufacturer can use their own 2010 engines as the baseline, but only in 2014.) The regulation covers all engines installed in Class 2b (large pick-ups, utility and step vans) through Class 8b vehicles. Figure 2 shows the proposed CO\textsubscript{2} reductions for all classes of engines. Figure 3 shows the CO\textsubscript{2} and fuel consumption standards for engines installed on tractors (for pulling trailers). These engines are tested using the steady state test (SET), and vocational engines are tested on the transient HD FTP cycle (Federal Test Procedure). In the proposal, N\textsubscript{2}O and methane emissions are each capped at 0.050 g/bhp-h. This level of N\textsubscript{2}O is roughly 3% of the carbon footprint of the engine and is about 2X the 2010 capability level.

The only HD fuel consumption regulation in place now is in Japan (9). It calls for nominally 12% increases in fuel economy (km/liter) from a 2002 baseline by 2015.

### ENGINE TECHNOLOGIES

Engine technology is evolving very rapidly, but incrementally. 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\textsubscript{2} or fuel consumption regulations.

### 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 gasoline hybrid electric vehicles (HEVs). However, diesel platforms are still very attractive for meeting the emerging CO\textsubscript{2} regulations, in which diesels have a 20% advantage over their gasoline counterparts. Furthermore, given the high incremental cost of batteries for the incremental CO\textsubscript{2} benefits gained from battery electric vehicles (10), it is reasonable that the diesel engine will continue to receive interest before we see a widespread shift away from the internal combustion engine. The technology pressure is being met with increasingly sophisticated combustion designs and control on diesel engines.

To illustrate the cost-effectiveness of the diesel in meeting CO\textsubscript{2} regulations, Koerfer, et al. (11) compare the costs of bringing a gasoline and a diesel medium-sized Euro 5 car to compliance with the 2020 European CO\textsubscript{2} requirements. They consider 10 different technologies judged to be the most cost effective way for each platform to comply. In the end, the gasoline car fell 13 g CO\textsubscript{2}/km short, despite the €670 added cost, resulting in a €1270 penalty. It would need to be hybridized to eliminate the penalty. On the other hand, at an added cost of €380, the diesel vehicle had a 5 g CO\textsubscript{2}/km surplus.

To maintain this advantage, most of the efforts in diesel engine technology are focused on downsizing without sacrificing performance, as offered by improved combustion control. A good example is described by Tatur [12, who shows a range of technology options for meeting US EPA Tier 2 Bin 5 standards depending on vehicle size and class. Main differences are in fuel injection, boost, and NO\textsubscript{x} aftertreatment. Larger cars will need >2000 bar piezo-electric injectors, 2-stage turbocharging, and selective catalytic reduction (SCR) NO\textsubscript{x} control. Smaller cars can get by with 1450-1800 bar injectors, variable nozzle turbochargers, and lean NO\textsubscript{x} traps (LNTs). Medium sized cars need a mix of these technologies. On the cutting edge, Tatur [12] updates earlier work on advancing LD diesels [13] by adding higher peak cylinder pressure (200 bar), a belt drive stop-start system, advanced cooling control, better air handling (2-stage turbocharging and EGR control), improved combustion
control strategies, and a variable swirl concept using a variable valve train. The result is lower process and cooling losses, delivering the same fuel consumption but with 10% of the NOx as the previous design calibrated to low fuel consumption, as shown Figure 4.

Figure 4. Advances in LD engine design result in 10% of the NOx at roughly the same fuel consumption as an earlier advanced engine calibrated to low fuel consumption. [12]

Tomoda, et al., [14] show a decreasing trend on diesel engine compression ratio (CR) to reduce frictional losses and NOx, but it plateaus at about 15.5:1. Lower compression ratios compromise thermodynamic efficiency but they show an optimum efficiency at 14:1. The problem is poor cold start, especially in cold ambient conditions or at high altitude. The charge does not get hot enough to burn the hydrocarbons or give smooth operation. Tomoda, et al., address these issues by redesigning the bowl, adding more holes to the injector to get more air entrainment, and increasing the number of pilot injections from three to four. With these measures, after about 100 seconds of operation at −25°C, hydrocarbon emissions from a low CR engine are half those of an engine with CR=15.7.

A very different approach beside downsizing and adding technology to meet CO2 requirements is to de-rate the diesel to take out cost, but still keeping it attractive relative to gasoline or downsizing options. Weissbaeck, et. al, [15] argue that downsized engines with high specific power add expense and perhaps require three engines to meet diverse vehicle needs (1.0, 1.5, 2.0 liter). On the other hand, starting with a standard base engine with lower specific power (reduced friction) and taking out cost and weight through optimization, like using an integrated exhaust manifold, and adding or subtracting components, like fuel injectors, can meet mass market vehicle needs with one platform. The high displacement allows low-load operation in certification cycles, eliminating the need for NOx aftertreatment. Performance is reduced compared to the downsized engine, but still attractive, and CO2 levels of <100 g/km might be attained. (In the simulated vehicle comparison, the downsized diesel with SCR attained 91 g/km CO2.)

Diesel engines are moving into hybridization, and seeing unique synergies related to emissions that may give them a relative advantage over similar steps with gasoline engines. Cisternino evaluated a second generation mild hybrid architecture on a 1.9 liter Euro 4 engine in dynamometer testing [16]. The hybrid system (15 kW motor, 0.63 kWh battery) utilized stop-start for idle reduction and assist on starts and accelerations, and enabled energy recuperation going downhill or on decelerations. Fuel consumption is dropped 10%. CO is cut 80% and hydrocarbon (HC) drops 20% due to hotter DOC (diesel oxidation catalyst) temperatures as a result of less idling. NOx is reduced 15% due to milder transients. The emissions reductions are unique synergies to diesel, which can result in further fuel reductions upon recalibration. When tested on a vehicle, time to accelerate from 24 to 100 km/sec drops 15% and noise and vibration decrease substantially. Similarly, upon hybridizing (25 kW motor, 1.5 kWh battery) a 1.6 liter engine, Krueger, et al. [17] realized synergies unique to the diesel engine. The low-load hybrid assist meshes well with the high-load diesel efficiencies to provide near uniform fuel consumption in urban and highway driving, giving about 20% less fuel consumption than the conventional diesel on certification test cycles. Further, CO and HC are cut 75% as a result of lower engine-out emissions and faster DOC light-off.

HEAVY DUTY

The first heavy-duty systems incorporating both diesel particulate filters (DPFs) and selective catalytic reduction (SCR) were introduced into the market in Japan in late 2009 and in the US in late 2010. Generally, the US trucks have 3 to 5% lower fuel consumption than their 2009 counterparts (no SCR), but consume upwards of about 2% urea relative to the fuel. The required NOx levels are less than 0.2 g/bhp-h (0.27 g/kWh) as measured in certification test cycles compared to their 2009 counterparts at about 1.1 g/bhp-h (1.5 g/kWh).

A nice summary of the US 2010 large HD engine features was provided by Charlton who described the Cummins 11.9 liter engine [18]. As shown in Figure 5, assuming the price of urea is 70% that of the fuel, the engine is calibrated to optimum fuel and urea consumption at about 2.5 g/bhp-h (3.3 g/kWh) NOx, or more than 2X the 2009 level. Note that the combined fuel and urea consumption is relatively flat at NOx levels greater than about 2.3 g/bhp-h (3.1 g/kWh). As urea has a fraction of the CO2 emission of diesel fuel, under a tight CO2 regulation it seems plausible to operate at higher NOx levels without adversely affecting operating cost, yet achieve lower CO2 emissions. This requires an SCR system that can
remove 95% of the NOx to meet current regulations. Charlton shows an average of 94.2% deNOx efficiency over a field run of 24 hours for a line haul truck using the engine.

In that regard, high-efficiency SCR will require less engine technology. Parche, et al., [19] and Sassen [20] make estimates of required engine hardware and operating parameters needed to meet a range of NOx levels. A summary is shown in Table 1. Regarding fuel consumption, Parche, et al., show the higher NOx calibrations using 1800 bar injection pressure have 1% lower fuel consumption than the lowest NOx calibration using 3000 bar pressure. Fuel consumption at the higher NOx calibrations is much less dependent on fuel injection pressure than at the lower NOx calibrations. Not discussed is the impact of other advanced engine designs on fuel consumption when calibrated for high NOx emissions. Stanton [21] shows continuously decreasing fuel consumption with increasing NOx emissions (up to 11 g/kWh) as more advanced engine hardware and calibration is employed. Given this, it is reasonable that tight CO₂ regulations will require both advanced engine technologies as well as highly efficient deNOx exhaust emission control.

An emerging issue for HD trucks with SCR is their capability to reduce NOx emissions under low-load driving when urea injection is not feasible. Ligterink, et al., [22] report that Euro V with SCR have NOx emissions 2 to 4X higher (per kg of CO₂) than trucks that primarily use engine methods, like EGR, for NOx control when driven at speeds less than about 60 km per hour (kph). At 80 kph both truck type have similar NOx emissions. Engine thermal management is one approach to managing this problem. Dollmeyer and Grana [23] use control of fuel inject and air handling parameters to increase exhaust gas temperatures more than 100°C during the idle and low-load portions of the cold FTP certification test, and reach urea injection temperatures of 200°C about 200 seconds faster than without the strategies. If air flow is reduced at any given load, exhaust temperatures will increase with little or no fuel penalty [24].

Much of the HD engine work recently reported pertains to non-road engines. Conicella [25] was one of the first to report the capability of meeting Euro 2012 Stage IIIB (or US Tier 4 interim) non-road regulations in the 56 to 130 kW engine class without aftertreatment. The engine family uses 15% cooled EGR at rated power 2000 bar common rail fuel injection with a specific spray configuration, unique piston bowl design, variable geometry turbocharging, and closed-loop combustion control with accurate control of the air:fuel ratio. The engine will need an additional ∼90% deNOx control to attain 2014 standards.

Unger [26] describes non-road engine strategies for 2014 Euro Stage IV (US Tier 4 final) for multiple applications in the 56-500 kW class using a modular engine and aftertreatment approach. Figure 6 shows a summary. It is suggested that high-load applications, like agricultural tractors, use mid-level engine technologies to achieve NOx levels of about 3 to 4 g/kWh (requiring 90% deNOx and PM control) on the Non-Road Transient Cycle (NRTC), depicted as curve B in the figure. This will result in lower fuel consumption and less heat rejection. Light-load applications

Table 1. Estimated hardware and operating parameters to achieve designated engine-out NOx levels, according to Parche, et al. [19] and Sassen [20].

<table>
<thead>
<tr>
<th>Engine-out NOx levels</th>
<th>Euro VI 0.4 g/kW-hr</th>
<th>~US2007 1.6 g/kW-hr</th>
<th>Euro VI ~90% deNOx ~US2010 ~94% deNOx 3.2 g/kW-hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel injection pressure, bar</td>
<td>3000 bar</td>
<td>2200 bar</td>
<td>1800 bar</td>
</tr>
<tr>
<td>Peak cylinder pressure</td>
<td>230 bar</td>
<td>180 bar</td>
<td>150 bar</td>
</tr>
<tr>
<td>EGR at full load</td>
<td>45%</td>
<td>27%</td>
<td>15%</td>
</tr>
<tr>
<td>Charge cooling relative to rated engine power</td>
<td>90%</td>
<td>50%</td>
<td>30%</td>
</tr>
</tbody>
</table>
can use more engine technology to advantage to deliver 1 to 2 g/kWh NOx on the NRTC, requiring 75% deNOx and PM control. Similarly, Jaussi [27], balances fuel and urea consumption, first cost, and engine cooling requirements to lead to an engine design that is calibrated to about 3 to 4 g/kWh NOx. In all three strategies, 95% NOx reduction in the tailpipe enables the 2014 regulations to be attained without PM control. In that regard, Unger shows in other data that 90% of the NOx comes from high-load operation in which SCR delivers 97 to 98% deNOx efficiency.

As engines become more efficient and regulators get more concerned about low-load NOx emissions, better low-temperature SCR system performance will be required. Currently good performance is limited by urea injection issues (evaporation and hydrolysis, evaporation) at temperatures <200°C. Improved mixers allow urea injections at temperatures as low as 180°C and thus drops NOx ~30% over the US cold HD transient cycle relative to no mixer [29]. To accomplish the same objective, urea hydrolysis catalysts are emerging. Kroecher, et al., [30] show that upwards of eight different decomposition products are emitted from urea upon heating, but with a titania decomposition catalyst, as shown in Figure 7, ammonia is produced at temperatures as low as 150-160°C in model gas with no other unexpected decomposition products. A more active approach is to spray the urea onto an electrically heated catalyst, as Brueck, et al. [31] show. Urea injection can begin at 100°C, resulting 60 to 70% higher deNOx efficiency on low-load cycles relative to systems without the heater.

For the 2011-12 non-road regulations, according to public announcements, there will be a mix of emission control strategies employing EGR-only, DPF, or DOCs strategies in the <130 kW class. In the 130-500 kW class SCR or cooled-EGR plus DPF strategies are claimed. For the 2014 regulations, NOx control will be needed, but there is increasing indication that PM control will be optional.

**NOX CONTROL**

The previous section illustrates that, in addition to being widely needed to meet heavy-duty highway NOx regulations, NOx control can deliver CO2 reductions and reduce engine costs and complexity. DeNOx efficiencies on the order of 95+% are highly desirable. In the light-duty sector, 90+% NOx control is used to meet the US regulations. In Europe, up to 80% deNOx control is being planned to meet the Euro 6 NOx regulations, with an emphasis on reducing CO2 [28]. In the light-duty case, low-temperature control is much more critical.

**SELECTIVE CATALYTIC REDUCTION (SCR) TECHNOLOGY**

SCR is the leading NOx emission control technology for both heavy duty and light duty applications. The field is advancing rapidly with new developments reported on catalyst enhancements and system improvements.

Another approach to improving low-temperature performance of SCR systems is to inject gaseous ammonia instead of urea. Johannessen [32] provides an update on the ammonia storage system that uses strontium chloride as the adsorbent. As ammonia is released by heating, injection can occur within one minute at −10°C ambient in LD applications, and within 5 minutes in HD applications. At −25°C, LD injection can occur within 3 minutes. Injection can begin at about 100°C. The tested SCR catalyst reduces emissions by ~50% at these temperatures. Fischer [33] shows that injecting ammonia at 120°C instead of 200°C can drop NOx ~60% on the NEDC test cycle (New European Drive Cycle). The first commercial order has been received and a manufacturing plant trial will occur this year. A propane tank model for ammonia recharging is proposed, wherein expired canisters are replaced with fresh ones at fueling stations or other
distribution outlets, and the canisters are refilled at centralized facilities.

As low temperature ammonia supply progresses, the low temperature behavior of the catalyst becomes more important. Kamasamudram, et al., [34] propose explanations to low-temperature performance differences between Cu- and Fe-zeolites. Ammonia readily adsorbs on the acidic reaction sites of Fe-zeolite, but much less so on the basic Cu-zeolite sites. This can inhibit the low temperature performance of Fe-zeolites. This effect is explained in more detail by Nova, et al., [35]. On the other hand, NO₂ adsorbs on Cu-zeolite reaction sites, inhibiting further NO oxidation. Most interestingly, the behavior results in better low-temperature transient performance for Fe-zeolites, wherein the adsorbed ammonia readily reacts with NOx for Fe-zeolites. Conversely, the Cu-zeolite draws ammonia from physical absorption sites instead, and the early reaction can be further inhibited by the suppressed NO oxidation reaction.

Generally, low-temperature SCR reactions are controlled by the rate of chemical reaction mechanisms rather than mass transfer. In that regard, higher catalyst loadings can enhance low-temperature performance. Ido, et al., [36] show a strong relationship between ammonia adsorption and deNOX efficiency, which is also tied to zeolite catalyst loading. Because most of the stored ammonia resides in the front half of extruded Fe-β3 zeolite honeycombs, they can be reduced in size by half that of typical washcoated catalysts without sacrificing low-temperature performance. At higher temperatures, more urea is needed to maintain performance of the smaller extruded catalyst. In another approach to improving SCR catalyst performance at low temperatures, Forzatti, et al., [37] show that ammonium nitrate injections along with urea can substitute for NO₂ to enhance the low-temperature (200°C) reduction of NO using Fe-zeolite catalysts. The effect was somewhat more pronounced with vanadia catalyst. The reaction mechanisms are described and involve the nitrate oxidizing NO to NO₂.

SCR catalyst formulations are also expanding the operating temperature range and improving durability. Yang and Narula [38] report on preliminary work to synthesize zeolite SCR catalysts using different metal oxide additives. When iron and copper are mixed in the synthesis stage (rather than mechanically), surprisingly the low-temperature performance improves relative to either of the base zeolites. The high-temperature performance is intermediate between the two. However, at 650°C the new zeolite degrades more than the copper zeolite, so the performance is similar after aging. More interestingly, when some rare earths or other transition metals are added, performance is enhanced. Figure 8 shows the basic deNOx efficiency curve when lanthanum is added to the iron and copper formulation. Although their work uses the older ZSM-5 baseline zeolite technology, the results are indicative of what might happen with better-performing base catalysts.

New families of catalysts are also being reported. Rohart, et al., [39] describe an acidic zirconia catalyst that, after aging for 24 hours at 800°C, achieves 75 to 85% deNOx efficiency on a vehicle using an ammonia to NOx ratio of 0.9 (1.0 is stoichiometric) and a swept volume ratio of 1.5. Casapu, et al. [40] developed a new niobium-, cerium oxide SCR catalyst that performs similarly to vanadia catalysts at low temperatures, but more importantly, they oxidize soot at 380°C, showing potential to be a multi-purpose DPF catalyst.

Standard SCR catalysts are also showing improvements, mainly in durability. Vanadia SCR catalysts are used in Europe and emerging markets, but not in the US or Japan due to durability issues related to thermal exposure when DPFs are regenerated. Advances are now reported [41] on vanadia SCR catalysts that have no volatility up to 750°C or higher, versus 550-600°C for some commercial catalysts, giving them similar HT durability to zeolites. DeNOx performance at 250 and 350°C is 5-10 points better after HT aging (>700°C) than for a benchmarked commercial catalyst, but less-severely aged catalysts have lower efficiencies than the base catalyst. Walker [42] reports that new Cu-zeolite formulations now sustain aging to 900°C and form less N₂O.

To get additional deNOx functionality in a limited space, advances are being made on applying SCR catalyst to DPFs. Walker [42] shows that when SCR catalyst is added to the DPF, NOx emissions drop about 60%, and there is little functionality difference whether the catalyst is added on another flow-through substrate or on a DPF. Adelman, et al., [43], et al., show the importance of properly applying the SCR catalyst to the filter. They show examples in which

Figure 8. New zeolite formulations are being synthesized. The tri-metal formulation of iron, copper, and lanthanum has excellent low-temperature performance in preliminary screening experiments. [38]
lower coating levels achieve higher deNOx efficiency and lower back pressure.

To achieve the highest deNOx efficiency, it might be desirable to over-dose about 10% with urea and rely on an ammonia slip catalyst to convert the extra ammonia to nitrogen. However, it is common for these catalysts to convert ammonia to NO and/or N\textsubscript{2}O. Walker \[42\] shows a new slip catalyst with improved selectivity to nitrogen. NOx emissions from excess ammonia are cut in half and N\textsubscript{2}O is cut up to 75% at the critical temperature of 250°C. Selectivity to nitrogen is about 90% at 350°C. Folić, et al., \[44\] cut precious metal loading in half on their improved slip catalyst, relative to an earlier version, and show 97.5% conversion of ammonia with 93% selectivity to nitrogen on the for a HD application (swept volume ratio of 1) on the World Harmonized Transient Cycle (WHTC).

Guo, et al., \[45\] report on Ford's leading deNOx approach to bring larger personal vehicles into US Tier 2 Bin 5 compliance. Fast SCR catalyst light-off is critical, so the Cu-zeolite SCR catalyst is located upstream of the DPF, and urea storage and dosing strategies are very important. The authors showed that with an EGR (exhaust gas recirculation) strategy, the SCR becomes active after about 120 second on the US-FTP75 cycle. In the first minute or so after light-off, a high dosing rate of urea (5X stoichiometry) provides 30% more deNOx than a stoichiometric injection. Ammonia slip can be an issue, so Cu-zeolite SCR catalyst is added to the downstream DPF to capture and utilize it. Regarding urea storage, a 13X range of urea injection concentration provided a 3X range of stored urea at 100°C, but this reduces to a 1.5X stored range at 200°C. Ammonia stored in the entry sections of the SCR catalyst is most critical to performance.

Finally, regulators have a concern about dioxin and furan emissions from Cu-zeolite catalysts. These extremely toxic components can form if chlorine, poly-aromatic hydrocarbons (PAHs), and copper catalyst are present together in exhaust conditions. In an update, the US EPA (Environmental Protection Agency) gave interim results of their test program to investigate this \[46\]. Shown in Figure 9, a Cu-zeolite SCR catalyst with no precious metal in the system or DEF (diesel exhaust fluid or urea) created no dioxins or furans (expressed in the figure as International Toxic Equivalent to dioxin) from very-low engine levels (0.4 pg/bhp-h). Precious metal catalysts, used in practice on the DOC (diesel oxidation catalyst) and DPF, are expected to reduce toxic emissions relative to engine-out levels, and the preliminary results show a trend in that direction. Further work will be done on Fe-zeolites and with higher chlorine levels in the fuel.

**HYDROCARBON-BASED NOX CONTROL**

The lean NOx trap (LNT) is currently the leading deNOx concept for the smaller lean-burn (diesel, direct injection gasoline) passenger cars, and is of interest in applications with limited space or in which urea usage is difficult. The deNOx efficiency is nominally 70%, much lower than that of the next generation SCR system at 90-95%, and the precious metal usage is high (~10-12 g for a 2 liter engine). As a result, efforts are focused on improving efficiency while reducing precious metal usage. Qi, et al., \[47\] describe a new platinum-free LNT catalyst that oxidizes NO to NO\textsubscript{2} (the Pt function) using rare-earth oxides (perovskites). Performance is similar to a Pt-containing LNT at T>300°C, but deNOx efficiencies are about 10% lower at 250°C. However, the cost is half that of the Pt-containing formulation. The new catalyst also tends to form much ammonia, for use in a downstream SCR catalyst.

One of the leading concepts is to use the LNT to generate ammonia during the periodic rich regeneration part of the cycle, and then to store and use this ammonia in a downstream SCR catalyst (1). Recent studies extend the understanding of this system, and improve upon the performance. It is generally better to design the LNT to convert NOx to ammonia for use in the SCR catalyst. Bonzi, et al. \[48\] show that when hydrogen is present during the rich phase of LNT operation, NOx (from the alkali-earth nitrate) is reduced through an ammonia intermediary. If SCR catalyst is intimately mixed within the LNT, the SCR will adsorb the ammonia, making it available for lean NOx removal. Overall deNOx efficiency is better for the mixture.
Kodoma and Wong [49] show that increasing flow rate (space velocity up to 80,000/hr tested) and hydrogen content (up to 4%) in the feed gas can markedly increase ammonia production in an LNT with 3 g/liter precious metal. However, increasing the space velocity by decreasing the length gave no benefits beyond 50,000/hr, converse to the flow studies. Further, the total system performance was minimally affected by decreasing LNT length. Hypotheses concerning ammonia and NOx reduction kinetics, rich-lean mixing interfaces, and oxygen storage dynamics with length were proposed but not investigated. Other factors impacting ammonia generation are residual oxygen in the rich gas (strong negative impact), and longer rich times (positive impact). The NO/NOx content of the feed gas had little impact. Water gas shift reformers result in less ammonia production, but improve system low-temperature denoX performance.

Xu, et al., [50] discovered that other non-ammonia species formed in the LNT can contribute to the downstream SCR performance. The effect is more pronounced with less aggressive LNT rich purges (less rich, shorter duration). In one case with only two purges over a whole certification test cycle, the system removed ~70% of the NOx with the LNT doing most of it (50%), but >80% of the SCR performance was attributed to the non-ammonia species. The leading hypothesis is that organo-nitrogen compounds formed during the rich purge, and are captured and utilized by the downstream SCR catalyst. Forzatti, et al. [51] indeed show that cyanoates and iso-cyanates are reaction intermediaries in the LNT reduction reaction with CO. Xu, et al. also show that a low precious metal LNT+SCR (3 g/liter on the LNT) performs as well as a highly-loaded LNT (not quantified, but 3.8 to 4.5 g/liter is typical) alone or with an SCR. Cu-zeolite performs better than Fe-zeolite. Interestingly, they looked at a variety of LNT and SCR configurations (in series or alternating), and conclude that the series arrangement is best due to faster LNT light-off. On a vehicle, the system achieves ~97% denoX efficiency for a system roughly the same size as an SCR-only system.

Theis, et al., [52] investigate the aging properties of the LNT +SCR system. With constant LNT management, the SCR advantage decreases if the LNT is aged for 4.5 hours at 700°C versus the baseline of 600°C aging. The effect is attributed to precious metal aging on the LNT and less efficient ammonia production. Longer rich periods as the system ages can counteract these impacts. During LNT desulfation, the SCR effectively oxidizes H2S and COS to SO2.

Chen, et al., (53) report on further optimization of both the LNT and the SCR. The ammonia generation performance of the LNT is improved by decreasing the oxygen storage capacity (OSC) and replacing 20% of the platinum with palladium. The results are shown in Figure 10. The lower OSC allows more ammonia to be produced at higher temperatures without as much oxidation. As known in the market, the palladium promotes the NOx reduction function. The Cu-zeolite is improved by adjusting the support material. It better-withstands rich-lean cycling, wherein hydrocarbons are adsorbed in the rich period and then oxidize in the lean period, creating damaging exotherms.

Finally, Japanese researchers report on the CO2 and N2O emissions coming from a heavy duty LNT system [54] applied to an advanced engine with low NOx emissions. About 3% of the global warming potential of the exhaust comes from the N2O emitted by the LNT during the rich period. Another 2.4% is attributed to the dosed fuel to make a rich purge gas. The balance, 94.6%, comes from the engine.

**PARTICULATE CONTROL**

Although DPFs have been in commercial production for OEM application for more than 10 years, there is still much optimization activity in the field. Papers on DPF regeneration dominate, with new understanding on current and new regeneration methods.

Warner, et al., investigated current DPF regeneration dynamics [55]. Active regeneration efficiency, wherein exhaust temperature is increased to ~600°C and the soot is burned by oxygen, is not strongly dependent on oxygen content at levels >2%, nor on whether the filter contains precious metal, although the precious metal does oxidize the resultant CO to form CO2. However, the efficiency is strongly dependent on soot loading due to the build up of heat. Passive regeneration, wherein the soot is oxidized by NO2, is much more effective (>3X) at 370°C than at 485°C, as the decomposition of NO2 back to NO at the higher temperatures overwhelms the faster soot oxidation rate at...
these temperatures. A DPF with Cu-zeolite behaves similarly to the uncoated filter, and has minimal impact on DPF regeneration. This indicates that NO\textsubscript{2} prefers to oxidize soot rather than be reduced on the zeolite. HNCO is a byproduct of active regeneration without catalyst, and needs to be taken into account in the mass balance when examining regeneration effectiveness. Active regeneration “costs” about 2-3% fuel consumption, and passive regeneration strategies can drop this penalty by about 20%.

Direct oxidation catalysts have been of interest in the field for more than five years. These catalysts use oxygen conducting materials (such as ceria, zirconia, or manganate) to burn the soot at the soot-catalyst interface, rather than by oxygen in the gas phase. Southward, et al., shows that a complex ceria material can begin oxidizing soot with model gas at 160°C with completion at 220°C using no or very little precious metal \[56\]. The exotherm from CO or hydrocarbon oxidation initiates the reaction. Once started, the exotherm causes soot not in contact with the catalyst to oxidize via the gas phase oxygen. When tested using vehicle exhaust, the balance point temperature (BPT; soot accumulation rate is the same as the oxidation rate) is 20°C lower than with a commercial filter coated with 0.2 g/liter of 1:1 platinum and palladium (BPT=420°C). The regeneration efficiency, shown in Figure 11, is much better than for a lightly catalyzed filter at 550°C, but similar at 620°C. Iretskaya, et al., show a rare-earth base metal oxide catalyst has a BPT of 350°C in the absence of NO\textsubscript{2} \[57\].

![Figure 11. A DPF with direct oxidation catalyst (OS3) regenerates much better at 550°C than either an uncoated filter or one with light catalyst loading. \[56\].](image)

Soot can also be burned by adsorbed oxygen on the surface of a SiC fine-particle membrane. Researchers at the Tokyo Institute of Technology \[58\] show much lower activation energy for a DPF with the SiC membrane compared to one without (80 kJ/mole versus 130 kJ/mole), indicating a shift in reaction mechanism. In the paper they show anecdotal evidence of the surface oxidation phenomenon, but the presentation had new data confirming this mechanism using Thermal Desorption Spectroscopy. In another study, it was shown that membranes cause the soot to deposit as a layer rather than being dispersed through the porous wall of the filter \[59\]. This creates a more localized exotherm that improves regeneration efficiency upwards of 10-15%.

DPF substrates are also improving. For low-soot applications, Heibel \[60\] shows that low-mass DPF prototype cordierite substrates can allow a downstream SCR catalyst to heat-up faster, dropping NOx emissions by 15% in cold start testing. Back pressure is also reduced 35% relative to US2010 DPFs.

For applications with higher soot loadings, Boger, et al., \[61\] developed a new aluminum titanate DPF composition with reduced porosity but better pore design. The higher thermal mass can be used to achieve a soot mass limit (SML) 2-3 g/liter higher than the earlier version without higher back pressure; or, the walls can be made thinner for low back pressure (~20 to ~30%) at the same SML. The new design allows higher peak temperatures and thermal gradients, giving much better robustness. The low pressure-drop version has similar SML to recently commercialized SiC, as shown in Figure 12. The high SML version exceeds that of SiC by 4 g/liter when evaluated in a demanding fuel-borne catalyst application.

![Figure 12. A new low porosity aluminum titanate DPF in the thin wall option (low Δp) has a soot limit comparable to commercialized SiC filter but 30% lower back pressure when loaded with 6 g/liter soot. \[51\].](image)

PM on-board diagnostic (OBD) regulations are expected to require a post-DPF soot sensor. Five general types have been in recent reports. The most common type collects soot between two electrodes and measures changes in electrical conductivity \[62\]. It is periodically heated to remove soot, the frequency of which indicates PM level over the period.
Resolution is acceptable, but the early 2009 version could not detect DPF failure within the timeframe of the NEDC test, as the regulation requires [63]. The second type also collects soot, but between two parallel plate electrodes [64]. The change in capacitance indicates the amount of soot that is collected, and hence, the soot PM level in the exhaust. The soot is also periodically burned out. The investigators show acceptable resolution and the ability to detect a failure within the NEDC test. The third type is a real-time sensor and measures soot carrying an electrical charge as it passes between two electrodes [65]. This is the only type that does not accumulate soot and is apparently capable of measuring particle number as well as PM. The fourth type is different from the others, as it is not based on electrical properties of soot [66]. A slip stream contains a small monitoring DPF that begins filling with leaked soot. This results in reduced flow in the slip stream, which is detected with a thermocouple. The device has the required resolution and has potential to take a reading within the NEDC. The fifth device uses radio frequency to measure soot loading on the filter.

In other developments worth noting, soot formed from burning fuel containing 20% biodiesel burns 3X faster than soot from fuel without [67]. The increased reactivity is due to increased particle surface area [68]. Also, acting under Brownian diffusion effects, very small nanoparticles (1 nm) are nearly all trapped in the surface porosity of DPFs, while larger particles (>10 nm) are trapped throughout the filter wall and may breakthrough [69].

**HYDROCARBON AND CARBON MONOXIDE CONTROL**

Diesel oxidation catalysts (DOC) have been applied to engines for more than 20 years, yet we are still improving them and learning fundamentals. They serve two primary purposes to oxidize hydrocarbons (HC) and CO that is innate in the exhaust or added to provide fuel for regenerating a DPF, and to generate NO2, which is used to oxidize soot on a continuous basis or for improving the low temperature performance of SCR catalysts. On the latter point, Spark, et al., [70] investigated NO2 coming from a catalyzed DPF for use in a downstream SCR system. Surprisingly, they found the NO2 coming out of the DOC and going into the DPF is not as important as the HCs coming from the DOC. Essentially, the HCs going into the DPF can interfere with the NO2 formation in the DPF. The Pt/Pd ratio is much more important to NO2 formation than precious metal loading on the DPF.

**SUMMARY/CONCLUSIONS**

If historical trends repeat themselves, there may be another broad round of criteria pollutant regulatory tightening for vehicles, starting with new light-duty tailpipe regulations in California. The California Air Resources Board (CARB) will be proposing LEVIII (Low Emission Vehicle III) light-duty (LD) vehicle regulations in the coming months. The US EPA will likely follow with their version. Tailpipe hydrocarbon and NOx standards are expected to tighten about 70% from today's levels between 2016 and 2022. The regulations will challenge LD diesel, but they have added flexibilities to somewhat ease the burden. PM (particulate mass) levels will likely tighten 90% by 2025. California and the EPA are also considering tightening LD CO2 emission standards from 3 to 6% per year from 2017 through 2025. The first HD CO2 regulations have been proposed by the EPA. The proposal requires by 2017 about 20% reductions from tractors used to pull trailers, 7 to 10% reductions from vocational vehicles, and 17% from large pick-up trucks and vans (by 2017 or 2018). For long haul trucks, about 6% of this is from the engine; 9% reductions are proposed from vocational truck engines.

LD engine technology is making incremental advances, mostly aimed at CO2 reductions offered by enhanced combustion control, and subsequent downsizing. An argument is made that more cost-effective investments can be made to bring diesel to 2020 European CO2 standards rather than gasoline. Studies are reported on cost effectiveness relative to platform management, technologies that allow lower compression ratios (14:1), and on unique synergies that come from hybridizing diesel. HD technology reports show engine hardware versus deNOx efficiency trade-offs to minimize fuel consumption. Increased hardware technology is needed to attain lower NOx levels (Euro VI, 0.4 g/kWh), but does not provide lower fuel consumption versus lesser hardware designs and higher NOx calibrations with deNOx emission systems. Some Tier 4 non-road strategies are shown. Balances are made between hardware, first cost, and heat rejection. High engine technology recipes are better suited for low-load applications in which fuel consumption is not as critical.

Selective catalytic reduction (SCR) technology is focused on improving performance particularly at the lower temperatures. Various strategies are presented for improving low temperature performance, namely better mixers, thermal management, different ammonia sources, and improved catalysts. New types of zeolites are being investigated, and a couple entirely new SCR catalyst types are explored. Standard zeolite and vanadia catalyst durability and performance are improved. Hydrocarbon-based deNOx is focused again this year on the LNT+SCR configurations.

DPF (diesel particulate filter) studies are showing improved understanding of regeneration. Passive and active regeneration parameters and influences are compared. New catalysts and substrates are described. In short, regeneration temperatures are going down, catalysts are getting less
expensive, and system back pressure and fuel efficiency are improving. Five types of PM sensors are being considered for on-board diagnostics.

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REFERENCES


