Vehicular Emissions in Review

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ABSTRACT

This review paper summarizes major developments in vehicular emissions regulations and technologies (light-duty, heavy-duty, gasoline, diesel) in 2012. First, the paper covers the key regulatory developments in the field, including finalized criteria pollutant tightening in California; and in Europe, the development of real-world driving emissions (RDE) standards. The US finalized LD (light-duty) greenhouse gas (GHG) regulation for 2017-25. The paper then gives a brief, high-level overview of key developments in LD and HD engine technology, covering both gasoline and diesel. Marked improvements in engine efficiency are summarized for gasoline and diesel engines to meet both the emerging NOx and GHG regulations. HD engines are just starting to demonstrate 50% brake thermal efficiency. NOx control technologies are then summarized, including SCR (selective catalytic reduction) with ammonia, and hydrocarbon-based approaches. Emphasis is on low-temperature deNOx, durability, and cost reduction. PM (particulate matter) reduction technologies are evolving around SCR integration and the behavior of soot and ash deposits. Next, DOC (diesel oxidation catalyst) developments are summarized. They mainly involve better understanding of aging and substitution of base metals oxides for precious metal. The paper then discusses some key developments in gasoline emission controls, focusing on new coated GPF (gasoline particulate filter) understanding. Advanced three-way catalysts improve with layered coating technology, and with improved understanding on engine calibration.

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INTRODUCTION

The pressures on the automotive and heavy-duty vehicle industries are like none other in their histories. The pressures are coming from the public and regulatory agencies to decrease criteria pollutants in both the developed and especially in developing countries. Also, fuel efficiency is being aggressively regulated to reduce CO_2 emissions and decrease dependencies on petroleum fuels. And, although markets are growing rapidly in the developing countries, market and economic pressures are forcing vehicle manufacturers in the established markets to strive for the best competitive advantage. On top of this, traditional engines are beginning to be replaced by the grid-powered electric drive train. To address these forces, engine manufacturers are relying very heavily on technology developments.

This review focuses on key developments related to emissions and technologies for both diesel and gasoline engines in the automotive and heavy-duty markets. As in previous years this review paper begins where the previous review [1] of major developments in vehicular emissions and control from 2011 left off. The paper will not specifically address very large bore engines, such as locomotive and ocean marine. However, many of the emission control technologies are transferable.

The review begins with an overview of the major regulatory developments covering criteria pollutants and CO_2. Next, the paper delves into technologies, first very generally covering light-duty gasoline and diesel engines, and then heavy-duty diesel engines. In this section, only high-level broad developments are covered with the intent of summarizing the directions and emissions challenges for the exhaust technologies. Next, the paper covers lean NOx control, diesel PM control, diesel oxidation catalysts, and closes with representative papers on gasoline emission control.

This review is not intended to be all-encompassing and comprehensive. Representative papers and presentations were chosen that provide examples of new, key developments and direction.

REGULATIONS

Most of the regulatory initiatives in 2012 were completions of proposals from 2011, which are detailed elsewhere [1]. The major vehicular regulatory initiatives of 2012 that will be summarized here include

• Finalized LEVIII LD (light duty) regulation from the California Air Resources Board (CARB)

• Developments on real world driving emissions (RDE) in Europe.

• Finalized US LD greenhouse gas reduction regulation from the US Environmental Protection Agency (EPA) and CARB.

• HD regulatory developments - California OBD (onboard diagnostics) and future NOx.

• Non-Road Update

• Developments in China and India

LD Criteria Pollutants

In January 2012 CARB unanimously approved the staff proposals for their Advanced Clean Cars Program [2]. These proposals include future criteria exhaust and evaporative emission standards for light-duty and medium-duty vehicles (LEV III emission standards), post-2016 light-duty greenhouse gas (GHG) emission standards, revisions to ARB's Zero Emission Vehicle (ZEV) requirements, and requirements associated with their Clean Fuels Outlet Program. In addition to these vehicle emission standards, CARB also proposed changes for light-duty and medium-duty OBD II (On-Board Diagnostic) requirements.

The most significant highlights on LD criteria tailpipe emissions include a 75% reduction in fleet average non-methane organic gases (NMOG) and NOx, phased in from 2015 to 2025, at which time NMOG+NOx will be 30 mg/mile for both cars and light-duty trucks. The PM (particulate mass) standard is tightening 90% from 10 mg/mile down to 1 mg/mile by 2025, with an interim value of 6 mg/mile in 2017, and a phase in to 3 mg/mile occurring from 2017 to 2021. CARB will hold a technology review in 2015 to determine the feasibility of measuring to 1 mg/mile, and of moving the full implementation date to 2022. CARB mentioned in oral comments they will consider a PN (particle number) standard if the proposed PM standard is not measurable.

To ensure more representative in-use emissions, the Supplemental Federal Test Procedure (SFTP) limit values are nominally reduced 75% to 50 mg/mile NMOG+NOx on the US06 high-load cycle. The SFTP options include using a test-cycle composite emission calculation, and light-duty diesel provision (60 mg/mile NMOG+NOx in exchange for a 200,000 mile warranty on the diesel particulate filter).

Medium-duty diesel vehicles, up to 14,000 pound (6360 kg) gross vehicle weight, must now certify on the chassis dynamometer and have a new set of NMOG+NOx fleet average standards. This represents about a 50-60% tightening from current certifications [3].

One of the most significant challenges of the regulation is the durability requirements are now 150,000 miles, up from 120,000 miles in LEVII.

The US EPA recently sent the LEVIII-harmonized Tier 3 proposal to the Office of Management and Budget for review.

This is the first step in the formal process to expand LEVIII to the full US. Details are sketchy, but the plans are to finalize the regulation by year-end 2013 to allow it to include MY2017 vehicles. As shown in Figure 1, aside from the timing difference between Tier 3 and LEVIII (2015 in LEVIII), other potential differences in the proposal are E15 certification fuel for gasoline (CARB is E10), 120,000 mile durability, and a 3 mg/mile PM standard [4].

Figure 1. Comparison of California LEVIII regulations and a possible US EPA Tier 3 harmonized proposal, as estimated by ref. 4.

In Europe, an equally significant development is occurring on RDE (real-world driving emissions). The Parliament has requested of the Commission to develop a procedure to bring in-use emissions more in line with type approval levels [5]. One example of the discrepancy was shown in a study done by the Joint Research Center (JRC) in which in-use NOx emissions from light-duty diesels in Europe are 3 to 4X more than the certification test limit values [6]. Although in-use gasoline engine NOx is well within the certification limit, gasoline PN was shown also to have issues [7]. Of the late model vehicles test, both the port-fuel injected (PFI) and gasoline direct injected (GDI) met the PM certification levels. Although the PFI vehicles were close to the certification PN level (6×10^{11}/km), elevated particle emissions were observed under unregulated conditions (low temperature, aggressive acceleration), due to excess over-enrichment. GDIs were found to be high PN-emitters under all driving conditions. Low temperature tests resulted in large PN increases (up to 210%) over the cold start NEDC especially for stoichiometric GDIs.

To address the regulatory challenge, the JRC is undertaking a study to evaluate the efficacy of using random dynamometer testing or PEMS (portable emissions monitoring systems) testing on the road to enforce RDE. Regulators tend to favor the PEMS approach, but there is a technology gap on robustly measuring PN on a vehicle, so it was decided to develop both methods, and phase-in to the PEMS method when suitable technology is available. Test

2016-2025: Typical Cost of CO2 Reductions from 2010 Baseline (~3.0 liter DOHC, 4-valve)
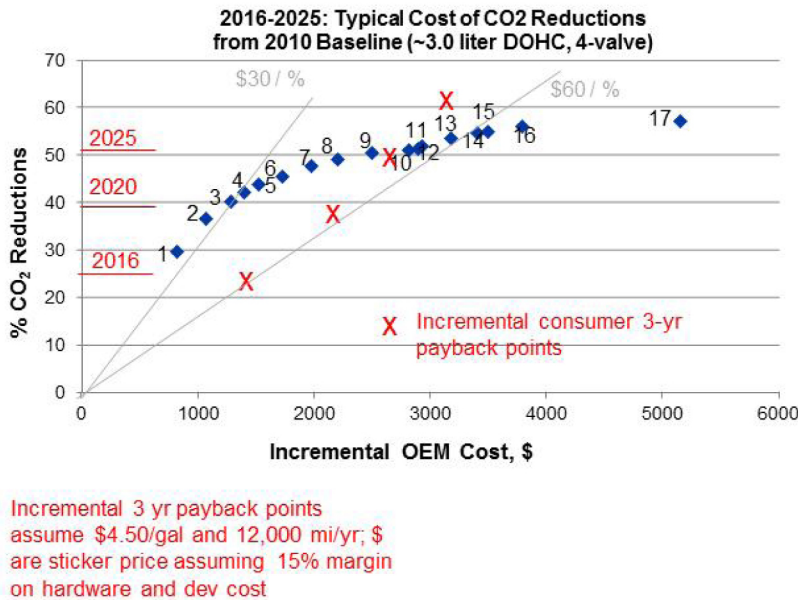
1. Aggr frict red, aggr shift, low drag brake, impr eff accessories, elect PS, aero, LRR tires, high eff gearbox, dual cam phase, 5% WR, 6-sp wet DCT
2. 1 + TC GDI 18 bar BMEP
3. 2 + more aero, accessories eff., LRR tires
4. 3 + 8-sp wet DCT
5. 4 + 10% weight reduction
6. 5 + TC GDI 24 bar BMEP
7. 6 + cEGR
8. 7 + 15% weight reduction
9. 8 + 20% weight reduction
10. 9 + start-stop
11. 10 + secondary axle disconnect (SAX)
12. 11 + MHEV,10% wt red, -EGR, -SAX
13. 12 + cEGR
14. 13 + 15% weight reduction
15. 14 + SAX
16. 15 + 20% weight reduction
17. 16 + discreet var valve lift + ATKCS (?)

- 2010 baseline 27 mpg (8.8 l/100 km), 3 liter DOHC, 4 valve, 3554 pounds (1615 kg)
- Costs are hardware + development costs

Incremental 3 yr payback points assume $4.50/gal and 12,000 mi/yr; $ are sticker price assuming 15% margin on hardware and dev cost

Figure 2. Cost of CO$_2$ reductions and payback period using US EPA data and one of four incremental technology scenarios.

procedures are expected to be recommended by late-2013 based on the study.

LD Greenhouse Gases

The US EPA and US DOT (Department of Transportation) jointly released the final 2017-2025 light-duty vehicle (LDV) fuel economy and greenhouse gas (GHG) emissions standards in August 2012 (8). They are harmonized with the CARB rules that were finalized in January 2012. CAFE (Corporate Average Fuel Economy) standards are projected to require, on an average industry fleet-wide basis for cars and trucks combined, 40.3-41.0 miles/gallon (~5.8 l/100 km) in model year 2021 and 48.7-49.7 miles/gallon (~4.8 l/100 km) in model year 2025, after all credits are considered. Actual values in real-world driving could be 20% lower. The DOT CAFE values can only be set through 2021, and will need to be formally finalized 2025 in an interim ruling no later than April 2018. The Rule requires fleet average CO$_2$ emissions of 163 g/mile (~98 g/km) in model year 2025, equivalent to 54.5 miles/gallon (4.3 l/100 km) if the vehicles were to meet this CO$_2$ standard only through fuel economy improvements. Some of the key provisions include:

• A generous CO$_2$/CAFE credit averaging, banking, and trading program.

• Credits for some "off-cycle" technologies that are not captured in dynamometer testing, like high-efficiency lights, start/stop, solar roof panels for battery charging, active transmission warm-up, etc.

• An incentive multiplier for electric vehicles, plug-in hybrids, CNG, and fuel cell vehicles.

• Grid-charged vehicles and fuel cell vehicles are assigned zero GHG tailpipe emissions for model years 2017-2021, within production volume caps thereafter. Upstream accounting will be used on volumes exceeding the cap in 2022+.

• For dual-fuel CNG vehicles and plug-in hybrids, EPA will use the SAE "utility factor" method to determine the assumed percentage of operation on CNG or electricity for CO$_2$ emissions compliance.

As part of the rulemaking package, the EPA did vehicle cost and GHG reduction estimates [9, 10]. An analysis of the data in light of the consumer payback period is shown in Figure 2. EPA used four technology pathway scenarios to reach 2025 requirements. All scenarios are close in terms of cost and GHG reductions. Figure 2 depicts the scenario using the mainly incremental technology. The three-year consumer payback calculation is based on a customer replacing a 2010 car with a 2016 car, then replacing the 2016 car with a 2020 car, and finally replacing the 2020 car with a 2025 car (12,000 miles/yr $4.50/gal). The points (X) represent the incremental price to the consumer that provides a three-year payback. The analysis, using the EPA data and the above assumptions on fuel cost and annual miles, shows that in 2016 and 2020 the payback period is much less than three years, and in 2025 it is about three years.

Heavy-Duty Regulations

Very few regulatory developments in HD vehicles occurred in 2012. Perhaps the most significant is that CARB is exploring 75% NOx reductions from trucks, reducing them

to 50 mg/bhp-hr from today's 200 mg/bhp-hr level [11]. The additional reductions are needed for California to meet their ozone requirements about 10 years out.

California also revised and finalized the heavy-duty OBD requirements [12], summarized in Table 1.

Table 1. California finalized HD OBD requirements.

PM

	13MY	14MY	15MY	16MY
Original	3x (one engine) 5x (all others)	← Same	← Same	3x all engines
Revised	Detect a fault at 5x PM standards (all engines)	Phase-in 5x w/o FME* (20% of all engines) ← Same	← Same Phase-in 3x w/o FME (50% of all engines)	20%: 5x Rest: 3x All 3x

NOx

	13MY	14MY	15MY	16MY
Original	+0.2 NOx	← same	← same	← same
Revised	+0.4 NOx	20% at +0.3 Rest at +0.4	50% at +0.3 Rest at +0.4	50% at +0.3 Rest at +0.2

- Natural Gas Trucks: OBD pulled ahead from 2020 to 2018
- HD-HEV – Same engine requirements, but HEV system OBD delayed to 2014

Zwissler [13] compared these requirements with the Euro VI OBD requirements on 16 key DPF (diesel particulate filter) and SCR (selective catalytic reduction) parameters, among a total of 23 total parameters. Of the 23 parameters, 11 had significant discrepancies in requirements. For example, California requires emission threshold monitoring of DPF regeneration and DOC (diesel oxidation catalyst), while Europe requires total system failure monitoring. California requires emission threshold monitoring of urea delivery, while Europe is more stringent and requires performance monitoring.

Non-Road Developments

US Tier 4 final and Europe Stage IV (very similar regulations) will be implemented in 2014. When the regulations were finalized about 10 years ago, it was anticipated both DPFs and deNOx controls would be needed in all but the smallest engine classes. A review of recent equipment manufacturer announcements shows that if a DPF is used to meet the current Tier 4 interim or Stage IIIB standards, they will also be used along with SCR in 2014 for the next step of tightening. If SCR-only is used to meet today's regulation, the 2014 step will use similar architectures.

The European Parliament requested the Commission to begin developing the next round of Non-Road Mobile Machinery regulations (Stage V). The objective is to harmonize with the Euro VI heavy-duty truck regulations regarding PN, in-use monitoring, and comitology. It should also consider retrofit programs. The proposal is due April 2013, the deadline for consideration before the Parliamentary elections. Submission will likely slip to 2014, making it unlikely that a new emissions standard could be implemented before 2018-19.

In late-2011, Beijing announced it is implementing Euro Stage IIIB non-road regulations by January 2014 [14]. The fuel sulfur level is to be 10 ppm.

China and India

With the growth of these two important emerging markets, air quality issues are emerging. For example, more than 50 of India's largest cities exceed the country's own air quality standards, and Beijing's PM levels on several occasions have been more than 10X higher than the World Health Organization (WHO) standards. In response to populace outcries, the governments are taking action.

In December the Chinese State Council announced significant tightening of ambient air quality standards throughout China. The plan requires key regions(including the city clusters) to reduce ambient concentration of SO_2 and PM10 (particulate matter <10 μm) by 10%, NO_2 by 7%, and PM2.5 by 5%. The plan also requires three key regions, namely Beijing-Tianjin-Hebei, Yangtze River Delta, Pearl River Delta to reduce PM2.5 concentration by 6% by 2015, and makes it a binding target for local government in these regions. The focus is on reduced coal burning in populated regions, but it also calls out transportation emissions regulations and clean fuel.

In that regard, recently the government announced the following plans:

• 50 ppm sulfur gasoline will be available nationwide by December 31, 2013. It is only available in major metropolitan areas now (Beijing is supposed to be at 10 ppm). 10 ppm sulfur gasoline needs to be fully phased-in throughout the country by year end 2017.

• 350 ppm sulfur diesel will be available nationwide by July 1, 2013. 50 ppm diesel will go nationwide by year end 2014. 10 ppm will be fully implemented by year end 2017.

• Work to replace all pre-2005 commercial trucks by December 31, 2015 in the three criteria regions (Beijing, Yangtze, Pearl).

• Enhanced inspection and maintenance for emissions by the end of 2013 in priority areas, and by the end of 2014 nationwide. ~$50B (350B RMB) network needs to be built to monitor all air pollution - stationary and vehicles.

• Build up coordinated enforcement and other government programs, and research capability on air pollution. Early focus of investigations will be on construction equipment.

The plans are significant in that they provide realistic phase-in periods with binding endpoints, and place a new emphasis on compliance and enforcement.

India is embarking on the next round vehicular emissions tightening by forming a roadmapping panel to make recommendations on approach through 2025. The panel may find a study [15] by the International Council on Clean Transportation (ICCT) useful. It estimates the cost of converting the refineries in India to make 10 ppm sulfur fuels

amortized at about Rs0.50/liter (₵0.71/liter, ₵3.5/gal). If Euro 6/VI regulations are implemented now, the total benefit:cost ratio is 9:1 in 2030 as shown in Figure 3.
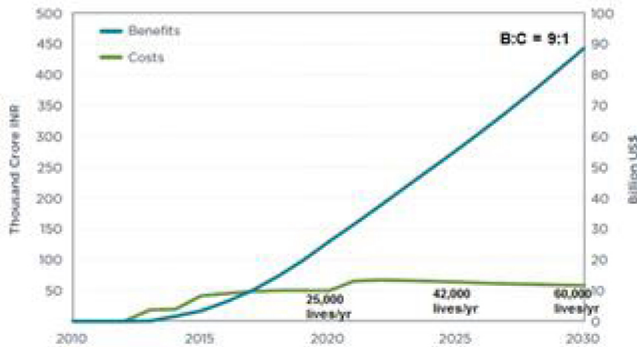

Figure 3. Societal costs and benefits of implementing Euro 6/VI LD and HD standards in India [15].

ENGINE DEVELOPMENTS

Light-Duty Engines

Light-duty engines developments have been focused for a few years on decreasing CO_2 emissions. The progress is quite impressive and costs are coming down.

Table 2. Estimated costs and CO_2 reductions for a collection of engine technologies as determined in teardown analyses. [16, 17]

Technology	Hardware Cost	% CO_2 Reduction	$ per %CO_2
5-speed transmission → 6-speed	($108)	0.7%	----
6-speed trans → 6 speed dual clutch	($154)	3.7%	----
V6 N.A., MPI, 3l → I4 2l, TC, GDI, 18 bar BMEP	$113	12%	$9.40
Dual VVT (I4) → hydraulic VVT/L (Fiat)	$149	7%	$21
Cylinder deactivation	$176	6.5%	$27
10% weight reduction	$198	7%	$28
I4, N.A., MPI, 2.4l → I4 1.6l TC GDI 24 bar	$562	20%	$28
Level 1 friction reduction	$80	2.7%	$30
V8, 5.4l SOHC → V6, 3.5l, 2xTC, DOHC, 24 bar	$825	20%	$41
Level 1 friction → Level 2 friction	$97	2.1%	$46
DS, TC, GDI, 24 bar → DS, TC, GDI w/ cEGR	$210	3.6%	$58
MPI, I4, N.A. → LDD, T2B2	$1857	22%	$84
10% wt red pkg → 20% wt red pkg	$688	7%	$98
MPI, N.A., I4 → BEV100 (w/10% wt red)	$15, 459	100%	$155
MPI, N.A. → PHEV40 (w/o charger, 20% wt red)	$12,883	63%	$204
MPI, N.A., 3l → 2.5 l, power split HEV, NiMH	$3589	15.4%	$233
MPI, N.A. → PHEV20 (w/o charger, 20% wt red)	$9724	40%	$243
Mid-SUV I4 → BAS mild HEV, I4	$1726	6.8%	$254

To support the LD GHG rulemaking, the US EPA did a very comprehensive tear-down analysis of late fuel efficiency technologies [16], and projected costs in a volume production mode. The CO_2 reductions were reported separately [17], and the results are combined and summarized in Table 2. Referring to Figure 2, a rough metric of consumer attractiveness might be on the order of $60/percent CO_2

reduction. Many technologies are cheaper, but several are more than 2.5X times this amount. The focus here will be on those engine technologies that seem most attractive and, as a result, mostly incremental.

Gasoline

Gasoline engine technology is advancing surprisingly fast. Three years ago, a review in 2010 showed gasoline engine technologies delivering 15 to 20% CO_2 reductions at an incremental cost of about $500-$750 relative to a 6-cylinder, multiport-fuel injected engine [18]. A year ago, published gasoline engine pathways to the EU 2020 CO_2 goal of 95 g/km required mild hybridization [1], and engine-only reductions were approaching 20-25% at a cost of ~$800 [19]. Common themes are direct injection with turbo-charging, cooled EGR (exhaust gas recirculation), variable valve timing, thermal management, stop-start systems, and significant downsizing.

In 2012, a demonstration vehicle with a downsized GDI engine and mild-hybrid system (using an ultra-capacitor) delivered 45% CO_2 reductions at an estimated cost (mine) of $750 [20], relative to a similar baseline as the earlier studies. Figure 4 shows the concept. Energy from an electric turbo-compounder (and braking) is stored in an ultra-capacitor. The stored energy is used by a supercharger and starter generator. (Mild hybridization is used, but the costs are much lower than others, see Table 2 last line, and the energy is mainly used for combustion optimization.) About 10% of the improvements came from reduced friction, improved transmission, and improved control.
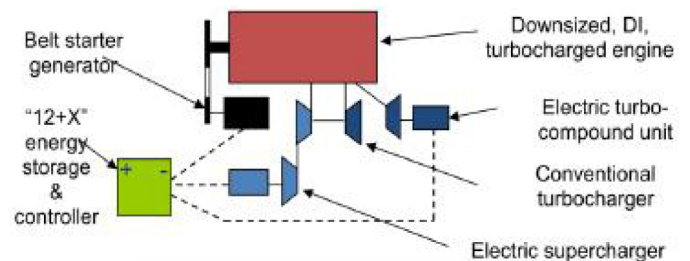

Figure 4. Schematic of a highly efficient gasoline engine concept that delivers 45% CO_2 reductions for the MPI naturally aspirated engine baseline. [18]

Perhaps the most common approach to gasoline CO_2 reductions is the use of direct fuel injection (GDI). The most significant emission trade-off is a tendency to form fine particles. Engines can be designed to meet the 2017 Euro 6c PN emissions regulations of 6×10^{11}/km in certification testing, and even in real-world driving conditions. Winkler [21] described the use of split injections and timing, injection pressure, and internal EGR for dropping cold start and warm emissions by 80 to 90% and hot emissions by 60%. However, fuel penalties ranged from 0 to 5%. Similarly, Walther [22]

dropped PN emissions 97%, mostly with advanced injector design, but with a 1-2% fuel penalty.

Fraidl [23] showed that minor perturbations can cause the PN emissions to increase, perhaps 10X. Engine deposits are especially troublesome and suspect. Figure 5 illustrates the issue, wherein a fuel injector with a deposit had more than 2.5X more PN emission than an injector after cleaning. Examples were made of allowable pump fuels in Europe (1.7X increase), slightly misaligned injectors (1.8 to 5X), and 30 minute idling time (10X).
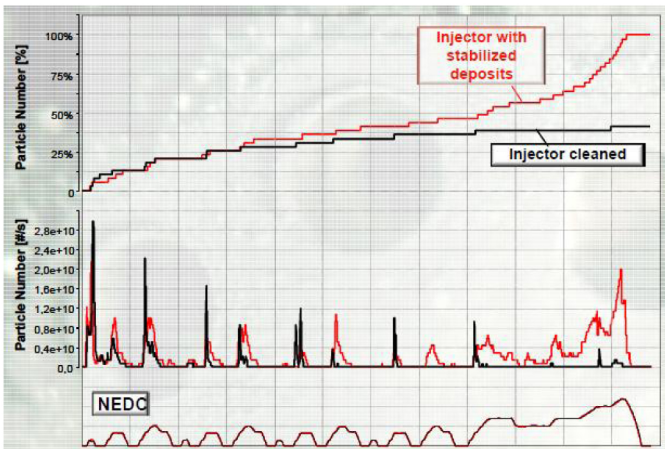

Figure 5. PN emissions are strongly affected by deposits inside the cylinder. Other effects are injector misalignment, pump fuel variations, and idling time. [23]

Cooled EGR is a technology that has been discussed for several years as a CO_2 reduction technology. Alger reported [24] on an extension of this to a technology called "dedicated EGR", wherein all the exhaust from one cylinder goes back into the engine with the air (25% constant EGR with a 4-cylinder engine). This allows that cylinder to run rich, with the remaining cylinders adjusting to maintain stoichiometry for the catalytic converter. This, in turn, generates hydrogen which helps combustion, minimizes knock tendency, and reduces emissions. Fuel consumption drophped 12 to 15%, and the brake thermal efficiency (BTE) is about 42%, similar to today's LD diesel engines. The technology is going commercial in 2018 [25].

Diesel

Diesel engines are also improving, albeit, perhaps not at the same pace as gasoline engines. Tomazic and Nanjundaswamy provided an overview of diesel engine directions [26]. Relative to Euro 4 engines, current leading engines are delivering 17% lower fuel consumption with 67% lower NOx (Euro 6 engine-out, 1700 kg car), with better performance. Emerging engines will have higher specific power (105 kW/liter vs. 80-90 kW/liter), using higher peak cylinder pressure (220 bar vs. 180 bar), higher injection pressure (2500 bar vs. 2000 bar), lower friction, and better

auxiliary systems design. The vehicles will have −95% NOx emissions vs. Euro 6 with advanced emission control design.

Similarly, McCartney, et al. [27] describe developments on downsizing a Euro 5 vehicle in the E-category 3 liter V6 engine with a 2.2 liter engine. They report ~17% reductions with combustion upgrades and a stop-start system, but also use oil and water thermal management to achieve an additional 8% measured fuel consumption reduction. They are expecting another 10-12% reduction from better air management, calibration, parasitic reduction, and fuel injection, bringing total expected reductions to 30% vs. the Euro 5 baseline.

Ruth [28] took a somewhat different approach to diesel engine improvements as part of a US Department of Energy program to replace a 5.6 liter V8 gasoline engine with a 2.8 liter diesel engine in a pick-up truck demonstration. They spent more than 15,000 hours analyzing and optimizing the structural design of the engine. This, plus calibration and combustion design [29], led to an engine that is 63 kg lighter than the gasoline engine (same mass specific power), delivers the same torque, and has 25% less fuel consumption. The team is also achieving LEVIII emissions.

Another LEVIII approach was reported by Balland, et al, [30]. The most significant challenge for SCR and other deNOx systems is in reducing high-load NOx. They show that a standard diesel oxidation catalyst (DOC) can efficiently remove NOx if run rich or at stoichiometry. Given this, they use tight control of EGR, the turbocharger, and other engine parameters to run the engine accordingly during accelerations. This "air-based control" approach, similar to that of gasoline engines, puts much of the high-flux deNOx burden on the DOC. The strategy is part of cold-start thermal management, as exhaust temperatures increase in this mode of operation.

Finally, Mazda is signaling a 2014 introduction of a full size car with a 2.2 liter advanced diesel engine that achieves US EPA Tier 2 Bin 5 NOx levels (7 mg/mile, 4.2 mg/km) without NOx aftertreatment [31, 32]. Such a design would nominally need 75% NOx and hydrocarbon reductions to achieve the LEVIII fleet average emissions requirements. The technology [33] delivers 20% lower fuel consumption versus their current diesel version, and is based on a 14:1 compression ratio. The cold start is managed with strong glow plugs, variable valves to enhance exhaust scavenging, two-stage turbocharging, and an egg-shaped combustion chamber design and calibration to minimize diffusion flame combustion.

Contrary to HD applications, wherein deNOx improvements are now being pushed further to their limits to reduce fuel consumption, modern light-duty diesel engines do not have as strong a relationship between NOx and fuel consumption in their typical low load operation range. In the US, most of the available deNOx efficiency will be needed to meet the LEVIII LD NOx regulations. In Europe, engine technologies could meet the NOx regulations without aftertreatment in all but the heaviest vehicles, but emission

control systems that deliver deNOx efficiencies of 50-70% are generally being implemented to optimize cost, criteria emissions, and fuel economy tradeoffs. Cold start, low-load operation, and high-flux load points are major challenges.

Heavy-Duty Engines

Heavy-duty engine technology is in development to meet the next round of OBD (on-board diagnostics) tightening in the US and Europe, and to meet the new CO_2 regulations in 2014. Concurrent with this, the Euro VI regulations come into play in 2013-14.

Stanton [34] shows in Figure 6 that EGR is an efficient approach to delivering low NOx and can have fuel consumption benefits at engine-out NOx levels of <2.5 to 5 g/kW-hr NOx) in low-load operating regimes. However, at higher NOx levels, EGR results in a fuel penalty. Given this, EGR can be eliminated if SCR can attain a 98% cycle-average deNOx efficiency. Running at higher engine-out NOx can also return substantial fuel consumption benefits. In the high-NOx regimes, about 1% fuel can be saved for every 1.2-1.5% urea solution consumed (relative to fuel) to drop the NOx. This is beneficial for both CO_2 reductions and fluid cost savings (urea plus fuel).

US HD engine manufacturers described their approaches to meeting the US Department of Energy (DOE) goal of demonstrating 50% BTE (break thermal efficiency) on a HD class 8 engine [1]. All four US HD truck engine manufacturers get much of their efficiency improvements from combustion (chamber design, control, mixing, etc.), reduction of friction and parasitic losses, and Rankine cycle waste heat recovery (WHR). Figure 7 shows an example of improvements [35]. Improved SCR performance is also a commonly mentioned approach.
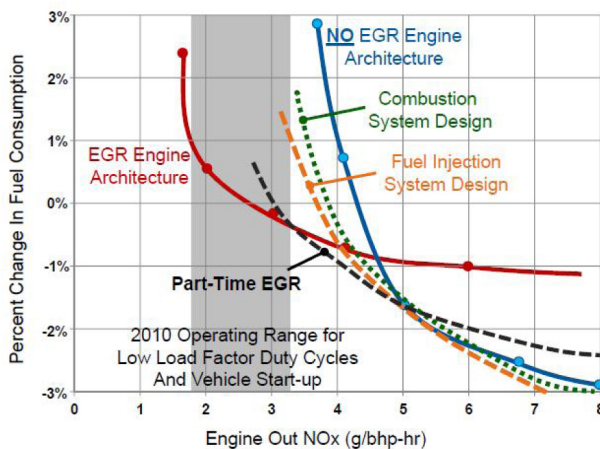

Figure 6. EGR has deNOx and fuel consumption advantages at low engine-out NOx levels (<4 g/bhp-hr or 5.2 g/kW-hr). At higher NOx calibrations there is a fuel penalty versus high-efficiency SCR approaches. [34]
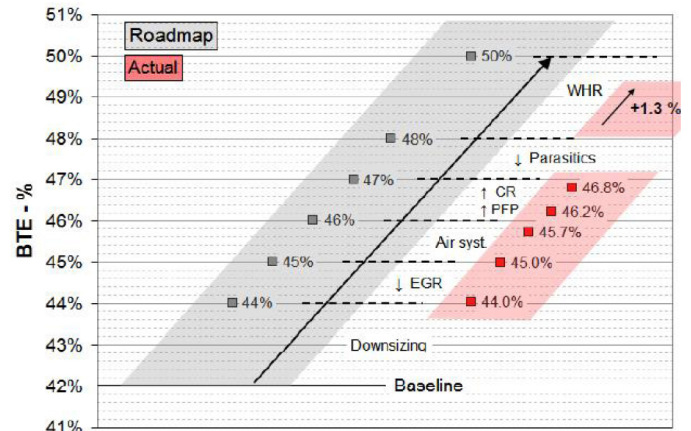

Figure 7. Pathway from a 42% BTE engine to a 50% BTE HD engine. Several approaches are combined, with the most impact expected from downsizing (increasing BTE from 42 to 44%, as planned) and waste-heat recovery (WHR,), currently achieving 1.3% absolute BTE improvement vs a 2% target. [35]

Finally, in the medium-duty engine field (HD certified), the 2-stroke - opposed piston engine has many fundamental thermodynamic advantages [36], including reduced heat transfer due to less cylinder area/volume ratio, increased ratio of specific heats due to leaner operating conditions from the two-stroke cycle, and decreased combustion duration at the fixed maximum pressure rise rate because of the lower energy release density. From a mechanical perspective it has fewer moving parts, with no head or valve train, and shows potential to have reduced weight and cost. As such, interest is increasing and money is being directed towards developing the engine [37], and there is OEM interest as well. Simulation models using data from a single cylinder engine [38] are showing potential to achieve 46% BTE at the A100 load point (low speed, high load). NOx emissions range from 1.6 to 4.5 g/kW-hr at turbine-out exhaust temperatures of 277 to 404°C, making them manageable with SCR. PM emissions are low, ranging from 6 to 32 mg/kW-hr. Lube oil consumption is now a greatly diminished development issue, running about 0.11% of fuel.

NOx control technologies will be integral to meeting the emerging HD criteria pollutant regulations and reducing fuel consumption for diesel engines. Minimum removal efficiencies on the order of 85% will be needed, but levels up to 98% are desired to allow engines to operate in high-NOx low-fuel consumption regimes.

NOₓ CONTROL

Stanton [34] provided the targets for HD NOx control: 98% deNOx efficiency will allow EGR to be taken off the engines and result in significant fuel savings. In LD systems, maximum deNOx efficiencies are needed to meet the emerging LEVIII regulations, but can also take out costs in the engine. Further, deNOx systems can help control the

growing NO_2 issue in Europe, where NO_2 emissions in "real-world" representative drive cycles have increased 3X in Euro 5 cars versus Euro 2 cars [39].

The lead NOx control technology for most passenger cars and for all HD and non-road applications is SCR. Urea infrastructure is well-developed in Europe, Japan, and the US, and is being developed in Brazil, China, and India. For smaller passenger cars in Europe, where the NOx regulations are not as tight as in the US, lean NOx traps are used. The precious metal costs are lower than the cost of an on-board urea delivery system, and the space required for the system is also prohibitive.

Selective Catalytic Reduction (SCR)

Although SCR systems are in their third commercial generation, and are approaching 95-96% deNOx efficiency, improving these systems to 98% efficiency will require significant efforts in catalyst development, durability, ammonia adsorption control, and system design.

Copper zeolite SCR catalysts are generally the preferred high-performance catalyst due to their impressive performance at low temperatures (even with sub-optimal NO_2 levels), high efficiency at high space velocities, and impressive high-temperature durability. As such, much work has gone into further improving their performance, some results of which are provided by Walker in Figure 8 [40]. The early improvements were over the whole temperature range, but more recent improvements have been at lower temperatures; NOx conversion efficiency at 175 and 200°C increased about 15% absolute from "Generation 3" to the latest version, Generation 5. It should be noted that high-temperature durability also increased significantly over this timeframe.
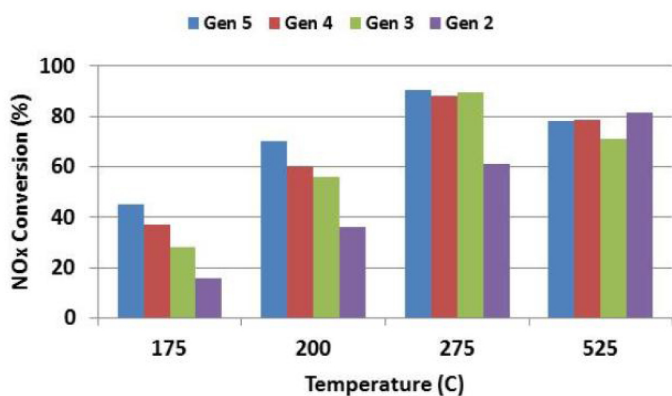

Figure 8. Generational improvements in Cu-zeolite SCR catalysts. Samples aged for 100 hours at 650°C and tested at a space velocity of 100,000/hr. [40]

Vanadia catalysts are primarily of interest in the developing countries and in some non-road applications. The catalyst is resistant to sulfur and HC poisoning, and new versions are less sensitive to low NO_2 in the exhaust [40]. The catalyst type cannot tolerate the high-temperature

exposure of an active DPF regeneration, but new versions can sustain long exposures to 580°C.

Hydrocarbon poisoning is an issue for both iron- and copper-zeolites. HCs can adsorb at the lower temperatures, and then ignite at the higher temperatures, causing thermal deterioration of the catalyst. Prikhodko et al. [41] quantified HC adsorption for state-of-the-art Cu-zeolite (chabazite from MY 2011 Ford diesel pick-up) and Fe-zeolite SCR catalysts. They show that, after three hours of exposure at 115°C to engine exhaust, Fe-zeolite adsorb upwards of 5-10X more hydrocarbons than Cu-zeolite, but the Cu-zeolite oxidizes a higher percentage upon release, risking an exotherm. Both types adsorb more HCs in PCCI combustion mode (premixed charge compression ignition) than in conventional diesel combustion mode due to changes in HC speciation. Cu-zeolites are more susceptible. This is more significant for LD applications wherein PCCI mode is used more, and more time is spent at lower temperatures. Luo et al. [42] studied the effects of propylene (C_3H_6) and dodecane (n-$C_{12}H_{26}$) exposure on the SCR performance of two Cu-exchanged zeolite catalysts, one was state-of-the-art with relatively small pores, and the other was a standard Cu/beta zeolite with somewhat larger pores. The small-pored sample was completely unaffected by dodecane at temperatures lower than 300°C, and only slightly inhibited (less than 5% conversion loss) by propylene. With the standard beta catalyst at 150°C, no adverse effect of propylene was noted, due lack of partial oxidation of the propylene to inhibiting intermediates; but at 300°C, both oxidation intermediates and coke formation led to deactivation. Dodecane inhibition was observed over the whole temperature range by strong HC adsorption blocking of pores and active catalyst sites. The small pores in the state-of-the-art sample do not allow the diffusion of large hydrocarbon molecules into the pores to hinder adsorption onto active sites.

Work is continuing on the combination SCR+DPF system, wherein SCR catalyst is coated onto the DPF. This saves space and allows the SCR catalyst to be placed closer to the engine for faster light-off. Numerous reports dating to 2008 show total NOx removal efficiency is thus improved. Schrade, et al. [43] report that soot on the DPF can help deNOx functionality if the NO_2 content is higher than optimal (50% of NOx), but hinders it if the NO_2 lower. The soot will be oxidized by NO_2, resulting in lower levels getting to the underlying SCR catalyst. They also found that NH_3 storage capacity increases with soot loading.

A developing SCR catalyst seems well suited for the SCR +DPF application. Rohe, et al. [44] show that the new acidic-zirconia mixed-oxide catalyst performs better on a flow-through catalyst versus a commercial Euro V HD catalyst. When placed on a filter, the performance is not greatly impacted by relatively high soot loadings (9 g/liter). Interestingly, the new catalyst drops the oxygen-based regeneration temperature by about 40-50C° (to 540°C) compared to a Cu-zeolite catalyst.

Stiebels, et al. [45] showed that during DPF regeneration the SCR catalyst on the DPF can remove 70-90% NOx at inlet temperatures of 560-630°C if NH_3 is injected. They also show the Cu-zeolite has impressive thermal durability, wherein deNOx performance was barely compromised after 100 drop-to-idle DPF regenerations at 800°C, and 30 such events at 1000°C.

Understanding NH_3 adsorption behavior is fundamental to extending SCR efficiency, especially at low temperatures. Partridge, et al. [46] did an interesting fundamental study on the NH_3 storage distribution in an SCR catalyst as a function of temperature, gaseous ammonia concentration, and NOx levels. They found that the dynamic capacity, when NOx is present, deviated from the total capacity in the axial direction, and that the departure correlates to the knee of the Langmuir adsorption isotherm. (In the Langmuir model, adsorption increases with gas concentration, but then tapers off at higher gas concentrations.) From this and other results, the authors deduce that ammonia adsorption kinetics are faster than the SCR reaction.

SCR catalyst systems will age, and this impacts NH_3 capacity. Bartley, et al [47] describes NH_3 storage capacity as a function of SCR catalyst aging time and temperature. The researchers modeled the aging using first-principle Langmuir adsorption isotherms. These data can be used in model-based control algorithms to calculate the current NH_3 storage capacity of an SCR catalyst operating in the field, based on time and temperature history.

To achieve high SCR deNOx efficiency, it is desirable to over-inject urea. The excess NH_3 needs to be oxidized to prevent slip. Ammonia slip catalysts are a source of NOx and N_2O, but they are improving [40]. Modern catalysts have similar performance to the first generation catalysts but with only 20% of the platinum loading. The latest catalyst has much better selectivity to nitrogen (75% at 400°C) with less undesirable by-products, yet with half the precious metal of its predecessor.

For US light-duty diesels, removing cold start NOx emissions is key to meeting the tailpipe emissions regulations. A new combination NOx adsorber and SCR catalyst configuration was shown by Henry et al. [48]. The system consists of an upstream passive NOx adsorber (PNA) that might capture 65% of the NOx at temperatures less than 150°C, and then passively release it at temperatures greater the 150°C. At these temperatures a copper zeolite is just becoming active and can reduce some of this released NOx. The technology enables NOx reductions of about 15 mg/mile (24 mg/km) on the US LD FTP cycle. Walker [40] reported on improvements in the PNA wherein 90% of the NOx is adsorbed at 80°C, and held up to 250-300°C, well within the range of SCR catalyst activity.

Another approach to managing the stored ammonia for improved low-temperature performance is described by Yasui et al. [49] and illustrated in Figure 9. They use two Fe-zeolite SCR catalysts placed downstream from the DPF system. An ammonia sensor is placed between the two SCR catalysts, and ammonia is injected to keep the first catalyst loaded at all times, as conditions allow. This accomplishes two goals. First, the efficiency of the SCR system is improved as there is plentiful ammonia present in the system. More importantly, the strategy helps cold start management. In traditional cold start thermal management, the SCR catalyst is heated as fast as possible to get it active and allow urea injection. Here, the catalyst is always loaded with ammonia, and the catalyst is heated slowly to prevent rapid release of ammonia during this period.
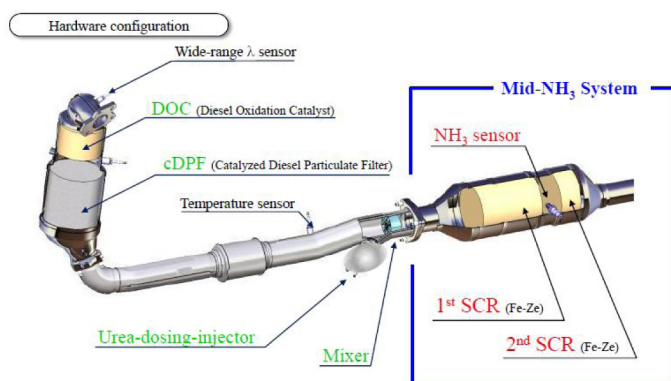

Figure 9. Layout of a new LD SCR system incorporating two SCR catalysts with an ammonia sensor in between. The first catalyst is kept loaded with ammonia, as indicated by the sensor.[47]

Two system designs that show good potential to meet LEVIII fleet average requirements were reported. Cummins used the combination of a PNA (passive NOx adsorber), SCR-F (SCR+DPF), downstream SCR, and gaseous ammonia injection. The heat-up deNOx strategy is shown in Figure 10. The PNA begins removing NOx right away. So that stored NH_3 is available on the SCR-F by the time the PNA releases NOx, gaseous NH_3 injection also begins early. Normal SCR functionality commences when the downstream SCR-F reaches 200°C. Engine-out emissions are about 0.6 g/mile, and the system drops this to 20 mg/mile (96-97% reduction). The addition of gaseous ammonia injection drops NOx about 15 mg/mile, the PNA removes another 15 mg/mile, and adding catalyst to the DPF takes out another 10 mg/mile; the 40 mg/mile total brings the vehicle from Tier 2 Bin 5 to Bin 2 (the LEVIII fleet average requirement).

A Honda approach is three-fold [47, 50]. As described in the LD diesel engine section, the first approach is to minimize NOx going to the SCR under HL transient conditions by running the engine at stoichiometry and allowing the DOC to remove much of the NOx. The second leg of the approach is a low-HC, fast light-off process using multiple fuel injections to get the DOC hot. The third part is the ammonia storage method described above, combined with a slower heat-up strategy after the DOC is hot, so as to control release of the stored ammonia for maximum utility in

NOx reduction. The approach results in the following US FTP-75 (Federal Test Procedure) results compared to the 4000 pound (1820 kg) baseline case: High EGR and combustion control drop NOx 50%, stoichiometric DOC operation drops NOx 5 mg/mi, and the SCR gets 93% deNOx efficiency. The previous SCR version of the LDD system achieved 12 mg/mile NMHC (non-methane HC) and 48 mg/mile NOx. The updated system gets 5 and 12 mg/mile, respectively.
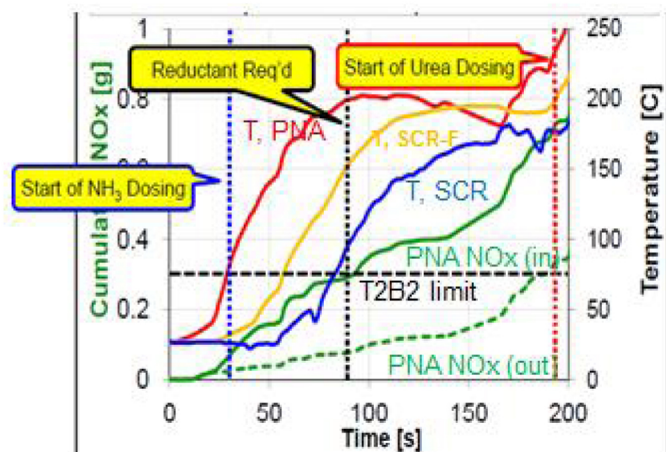

Figure 10. Reductant injection strategy for a LEVIII deNOx system using a passive NOx adsorber, an SCR-F (combo SCR+DPF), downstream SCR, and gaseous NH$_3$ injection. [48]

In miscellaneous developments, a European consortium of four auto companies was formed to explore the adsorbed gaseous ammonia injection system (by Amminex). The consortium did real-world testing and achieved 72-83% deNOx in low-load city driving (average exhaust temperatures of 155°C), depending on NH$_3$ storage calibration [51].

The US EPA completed its testing of zeolite SCR systems for dioxin and PCB (polychlorinated biphenyl) emissions. In all cases (Cu- and Fe-zeolites, on or separate from the DPF, DPF+DOC only, high chlorine levels), toxin levels were much below engine-out levels [52]. The tests were very difficult to run, as the emissions were very low (picograms per liter of fuel), so new test procedures were developed.

Detecting stored ammonia levels is showing potential. Researchers at Bayreuth Engine Research Center and Umicore correlated and measured stored ammonia on a catalyst using a radio frequency method [53]. In addition, they were also able to diagnose the oxygen storage levels of a three-way catalyst and the soot loading on a DPF. (General Electric developed a DPF soot sensor based on a similar principle.)

Lean NOx Traps (LNT)

The lean NOx trap 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 70-80%, much lower than that of the next generation SCR system at 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.

Tomazic and Nanjundaswamy [26] identified the gaps in NOx control using LNTs. Figure 11 shows the sources of NOx emissions for four different vehicles equipped with an LNT. On the order of 55 to 75% of the NOx slip occurs during operating points when the LNT is functional (T>200°C, medium to high space velocities). Cold start or low temperature operation accounts for 15 to 30% of the emissions.
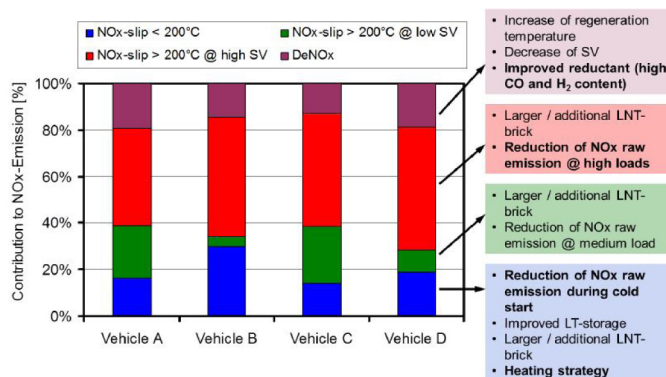

Figure 11. Operational sources of NOx emissions from four vehicles equipped with LNTs. [26]

Much of the issue on NOx slip is related to LNT size and platinum group metal (PGM) loading, so technologies that can reduce PGM loadings through improved utilization are key to LNT improvement. Researchers at Nissan used a selective PGM deposition process to enhance precious metal dispersion [54]. The concept is to use a surfactant to preferentially apply the platinum to the ceria rather than to the alumina in the washcoat. Upon aging, the grain growth of platinum is greatly reduced because the small ceria grains limit the growth. Precious metal usage is cut 50% without compromise in NOx emissions. The researchers also have identified that the NOx desorption rate is considerably slower than adsorption or catalyst reactions at low temperature. NOx desorption rate is increased by enhancing contact of ceria and baria, the NOx trapping material. Work is continuing to verify the effect.

A different and comprehensive approach to improving LNT performance was described by Tsukamoto, et al. (55). They improved the low-temperature NOx storage performance using silver to replace platinum. The silver balances basicity and adds adsorbed oxygen. To improve desulfation, titania was added, which also improved silver dispersion, helping NOx adsorption at 150°C. Desulfation was realized at temperatures less than 600°C. A small amount of palladium (0.1 g/liter) was added to improve NOx

desorption during the rich phase of operation, and decreasing oxygen storage catalyst and improving the rhodium functionality helped react the desorbed NOx at temperatures <250°C.

One of the more promising approaches to improving LNT performance is to couple them with an SCR catalyst that can trap and utilize the ammonia that is generated in the LNT during the rich regeneration phase. Previously described iterations are to use separate catalyst systems in various configurations [1]. Harold, et al. [56] found that, instead of using a separate SCR catalyst, the system performance can also be improved by putting the SCR catalyst on top of the LNT catalyst on the same substrate in a layered architecture. This is similar to the design described by Morita, et al., [57], who use a ceria-based material for its NOx adsorption functionality as the under-layer. Compared to the design with two separate catalysts, the Harold, et al. layered catalyst gives deNOx improvements of 20 to 25% at 200-250°C relative to an LNT alone. Interestingly, when ceria is added to the back portion of the LNT catalyst, performance improves. Here, the temperatures are lower than in the front, so there is more opportunity to form ammonia with the hydrogen formed in the water-gas shift reaction, rather than oxidizing it, as occurs at T>250°C in their experiments.

One of the more interesting LNT developments in recent years is from Toyota, wherein they significantly improve HT performance by oscillating the air:fuel ratio in the lean regime to achieve much better NOx removal (first reported in [58]). Subsequent reports describe more of the underlying fundamentals [59] and system optimization [60]. Fundamentally, as depicted in Figure 12, at high temperatures (>450°C) hydrocarbons reduce NOx more effectively than hydrogen and CO in lean conditions, which preferentially react more with oxygen than with NOx. Conditions that enhance the utility of hydrocarbons are higher auxiliary hydrocarbon injection pressures (3 MPa), but with shorter durations and longer intervals (3 seconds) between injections. Hydrocarbons with eight to ten carbons were shown to be preferred. Better mixing allowed the goals of >75% NOx reduction with <2% fuel penalty to be achieved at critical HT operating points, including peak load at intermediate engine speeds. The system will be used on a diesel passenger car application this year in Japan.

In summary, deNOx systems will play a key role in meeting emerging NOx and GHG regulations. Catalysts are improving, and more is being learned on increasing durability. System optimization is advancing, with more understanding on system integration, as illustrated with SCR +DPF and layered LNT+SCR architectures. Low temperature performance is improving with the use of novel ammonia and NOx storage approaches; and high-temperature performance is improving by building upon earlier catalyst improvements, and new understanding and approaches to running LNTs.
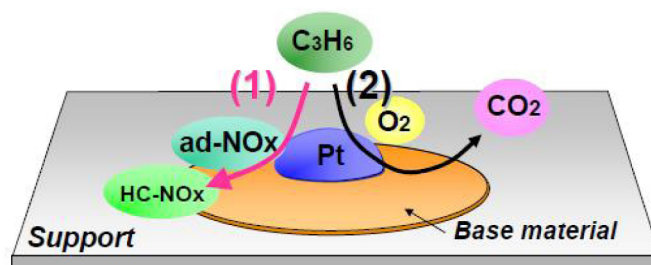

Figure 12. Schematic of the reaction mechanisms providing HT NOx reduction by operating an LNT under relatively high frequency air:fuel ratio oscillations. [60]

DIESEL PM CONTROL

Key recent developments in diesel particulate filters (DPFs) include studies on the how SCR catalyst integration and loading impact filter back pressure and regeneration characteristics; more information on biodiesel impacts on soot; and fundamental studies on the complexities of ash and soot accumulation.

Folic and Johansen [61] looked at the relationship between filter porosity, SCR catalyst deNOx efficiency, and back pressure. With all filters there was an optimum back pressure versus deNOx performance, wherein generally they both increase together but at higher catalyst loadings the deNOx efficiency can decrease with increasing back pressure. Filters with >60-65% porosity have better deNOx performance at a given back pressure than filters with <60% porosity. Further, Folic and Johansen, as well as Walker [40], show that passive DPF regeneration with NO2 is adversely impacted by adding SCR catalyst to the DPF, but still occurs and can be managed. The effect is likely related to competition with the SCR reaction for NO_2 and lack of re-oxidation recycling of the NO molecule that occurs under the soot layer in platinum-catalyzed DPFs.

In heavy-duty applications most (or all) of the soot is burned passively using NO_2 generated in a DOC and in the catalyzed filter. Investigators at Michigan Technological University quantified this effect for ultra-low sulfur diesel (ULSD) fuel and biodiesel blends [62]. They loaded the filters to about 2 g/liter soot in a controlled fashion, and then introduced exhaust gas with the desired composition and temperature to measure oxidation of the soot with the NO_2. They found that soot generated by burning biodiesel oxidized slightly slower than that from ULSD fuel, contradicting other studies showing enhanced reactivity for biodiesel soot in thermal regeneration. However, their Arrhenius plot did not take into account less DOC activity, which can occur with biodiesel usage. Interestingly, the investigators quantified the NO re-oxidation recycling phenomenon in the catalyzed filter. Recycling rates were quite low at temperatures less than 300°C, but were very high at 450°C at which each NO molecule recycled three to four times.

Ash and PM interactions can be very complex and affect DPF filtration mechanisms and back pressure. Continuing an earlier investigation of DPF permeability and PM impacts using wafers made from DPF materials [63], University of Wisconsin investigators looked at both ash and PM impacts [64]. Under lower face velocities and in conditions of lower loading (low PM), the ash can penetrate into the pores of the filter and form a low-density ash coating. At high temperatures (filter regeneration) the ash sinters and consolidates into a higher porosity formation than would be the case with ash deposited under high face velocity. Particle breakthrough is related to the PM loadings needed to develop a filter cake, which in turn, is related to the ash loading characteristics and DPF pore structure. This fundamental information could be very useful in developing better DPF soot loading models.

Researchers at the Massachusetts Institute of Technology looked at the recycling of the NO molecule, among other phenomena, in catalyzed filters in a unique way - they used a novel "focused beam ion milling" technique to vaporize away layers of material, ending up with a clean cross-section of the substrate, washcoat, catalyst, ash, and soot (65). They found voids between the soot and the catalyst that are likely formed by the back diffusion of NO_2 generated by the catalyst. In other cases, the catalyst was blinded by ash, and NO oxidation was hampered [66]. Evidence suggested this behavior is dependent on ash composition, and potential ways of minimizing adverse impacts are proposed.

Curiously, images were shown [63, 64, 67] of ash agglomerates measuring 20 μm in diameter (1000X that of the primary ash particle) that largely consisted of large voids. In-situ optical observations [63] show that when soot is deposited on top of an ash membrane, and is then oxidized, ash can be peeled away from the substrate and transported to the back of the filter forming a plug. This is consistent with ash peeling observations of Fujii [68].

Particulate oxidation catalysts (POCs) are a cross between a DPF and a DOC wherein the soot is trapped by turbulence mechanisms, forcing particles to make contact with the filter and become captured. They are a leading approach in developing countries because they don't plug if not properly regenerated. However, these countries might not have low-sulfur fuel. Bielaczyc, et al., (69) looked at the effects of fuel sulfur on the performance of these devices. Although the dry soot coming from the engine was the same in all tests, the total PM (particulate matter) coming from the engine increased due to the increased sulfate. Between 20 and 40 hours of operation the filtration efficiency using the high-sulfur fuel (365 ppm) dropped about 10% across the particle size range, while that of the clean fuel changed very little. This is likely due to the availability of NO_2 to keep the filter clean and operating more efficiently, given that NO_2 generation in the DOC is hampered by sulfur.

DIESEL OXIDATION CATALYSTS

Diesel oxidation catalysts play two primary roles in commercial emission control systems: 1) oxidize hydrocarbons and CO, either to reduce emissions coming from the engine, or to create exothermic heat used to regenerate a DPF; and 2) oxidize NO to NO_2, which is used for continuously oxidizing soot on a DPF, and/or for enhancing the SCR deNOx reactions, particularly at low temperatures.

Aging of DOCs is a critical phenomenon to understand. It can impact hydrocarbon emissions, DPF regeneration, and SCR performance. Investigators at Cummins [70] analyzed several field-aged DOCs retrieved from in-use vehicles, sectioned them, and studied the aging characteristics of the segments. As shown in Figure 13, irreversible aging imparted different types of deterioration. Catalyst cut from the rear of the DOC has a higher NO light-off temperature than those from the front. The opposite is true for hydrocarbon (C_3H_6) oxidation, wherein the rear parts have a lower light-off temperature. The front catalysts are aged primarily due to ash contamination, while the back catalysts are generally thermally aged. The light-off characteristics deteriorate due to both effects as the mileage increases. The authors also report reversible deterioration caused by hydrocarbon and sulfur poisoning, which can be removed with a thermal treatment.
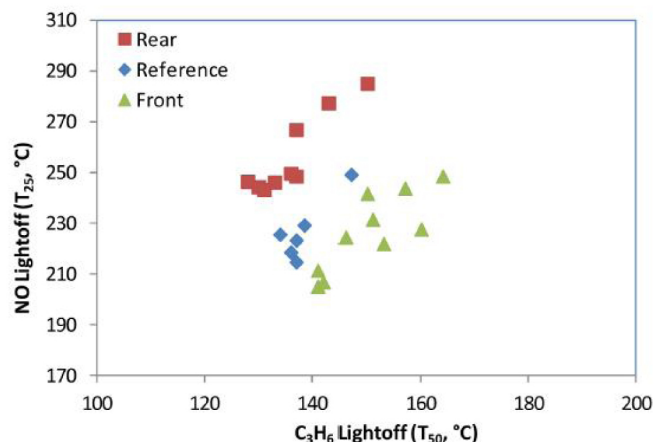

Figure 13. NO and hydrocarbon light-off properties for samples taken from the front and rear of field-aged DOCs. The reference catalyst laboratory aged. [70]

Three new DOC types were reported. Millo and Fezza added a low-temperature NOx adsorber material to the DOC (71). The material stores NOx (presumably as a nitrate) at low-temperatures, and then releases the NOx at higher temperatures when the downstream SCR catalyst is operative. The adsorber aged substantially, but still could give significant NOx reductions over an SCR-only configuration. The second DOC development is reported by Ishizaka, et al. [72]. They developed and tested a PGM-free formulation that oxidized CO and hydrocarbons as good or better than a Pt-based DOC with 3 g/liter loading. In certification test cycle

driving, the aged (30 hours at 700°C) Ag/YMnO3 catalysts had 20% higher CO conversion and 10% higher hydrocarbon conversion than the reference Pt catalyst. The new catalyst had little or no deterioration when exposed to high-sulfur conditions for 90 hours. Similarly, Wang, et al., [73] developed an NO oxidation catalyst that does not use any precious metal. The manganite-based catalyst drops the NO oxidation temperature about 50C° to 250°C versus a platinum reference catalyst (2% Pt on γ-alumina) at the optimum point of 50% conversion.

Finally, methane oxidation at low temperatures is quite difficult, wherein the best conventional catalysts (primarily Pd) light-off at maybe 450°C. This can be important for natural gas engines. Compared to traditional catalysts, in which the palladium is deposited on ceria, by encompassing the palladium inside a ceria "rice ball" the T50 light-off temperature was reduced 130C° to about 300°C [74].

GASOLINE EMISSION CONTROL

Gasoline emission control catalysis has been commercialized for more than 35 years, and the three-way catalyst (TWC) for more than 30 years. Yet, it is still evolving and showing significant improvements. Much of the current gasoline emissions control work is being done on gasoline particulate filters (GPFs), but the three-way catalyst (TWC) is also still evolving.

Gasoline Particulate Filters

To meet the new gasoline particle number regulations of the light-duty Euro 6 regulation in 2017, there is much interest in gasoline particulate filters (GPFs). Early testing was done with uncatalyzed filters, but current evaluations use TWC on the filter. Richter, et al. [75] evaluated two TWC-coated configurations, wherein the total PGM loading in one configuration was the same as the base design but was distributed between the close-coupled TWC and the GPF; the other configuration had an optimized coating. With the same PGM loading, the investigators found the NOx emissions dropped 20% versus the baseline. With an optimized zone coating on the close-coupled catalyst, 6% less PGM was used compared to the baseline, NOx emissions remained at the low level, but CO emissions dropped 30% from the other GPF case. The researchers reported that the TWC on the GPF aided filter regeneration. No fuel penalty was observed when the GPF was applied.

Work by Environmental Canada (the environmental regulating authority in Canada) was reported on the importance of pre-conditioning on filtration efficiency [76]. They measure 80+% filtration efficiency on US FTP-75 cycle with a clean uncoated filter, but upwards of 95+% efficiency after 230 seconds of operation. Conversely, as shown Figure 14, on the much-hotter US06 cycle, the filtration efficiency has no temporal relationship because it would periodically regenerate throughout the cycle. Note the high filtration efficiency in the smaller size fraction (<~20 nm) due to

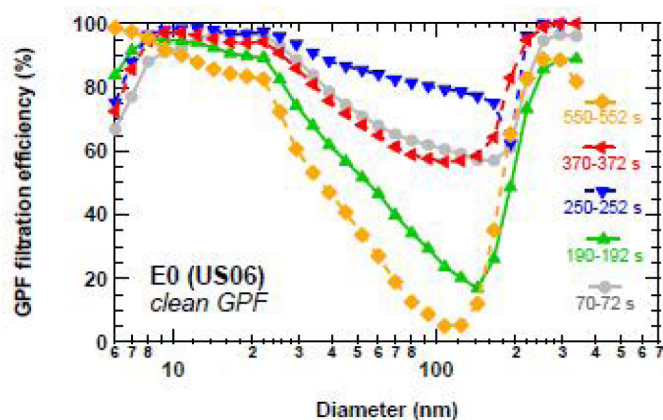Brownian movement of the particle, and in the larger size fraction >250 nm due to interception mechanisms.

Figure 14. Size dependent filtration efficiency of an uncoated GPF on the US06 as a function of time. There is no temporal relationship in the mid-size range due to periodic burning of the filter cake. [76]

Morgan [77] tested several coated GPF configurations and demonstrated ways to balance performance attributes. Zone coating can increase light-off and drop emissions by ~10%. Back pressure and NOx emissions can be balanced: − 33% back pressure, but NOx goes up 40% and PN up 20% (still ~80% efficient) with a back-pressure optimized coating. As with Richter, et al. [75], Morgan showed that a coated GPF regenerates PM much more readily than an uncoated part, and moving catalyst from a flow-through substrate onto a downstream GPF can drop emissions. They attributed this effect to less aging of the downstream catalyst.

Finally, Speiss, et al. [78] tested the durability of a close-coupled catalyst / coated GPF configuration containing the same amount of precious metal as in a stock vehicle with only a close coupled catalyst. Filtration efficiency improved from about 84% on the fresh part to more than 98% after it accumulated 150,000 km. NOx emissions after 150,000 km were the same as after 1000 km for the GPF system, but HC emissions increased 50%, yet still remaining less than half the regulatory standard.

Three-Way Catalysts

Since the mid-90's, when the TWC was perhaps in its third generation, emissions have dropped more than 95% and PGM loading is down perhaps 70% of what it was then. The progress is still continuing.

For example, Honda and Johnson Matthey scientists describe a new layered catalyst for improving performance of both close coupled and underbody catalysts [79]. The improvements cut PGM usage by 75% while meeting the new California LEVIII SULEV30 standard (Low Emission Vehicle III, Super Ultralow Emission Vehicle - 30 mg/mile non-methane HC+NOx). The close-coupled catalyst is layered with higher-activity palladium and lower oxygen

storage catalysts (OSC) on the top, to better withstand phosphorous poisoning and to achieve better HC conversion. The catalyst demonstrates that Pd-only catalysts can have application for the lowest emissions applications. The underbody catalyst utilizes zirconia-based OSC, allowing 50% less rhodium to be used versus the current version of catalyst.

System design and calibration are significant contributors to low gasoline emissions. Ball and Moser [80] benchmarked five of the cleanest gasoline engine vehicles in the market with a variety of hardware calibration strategies, ranging from port-fueled and direct injection, with and without secondary air, with different injection timing, engine speeds, and air:fuel ratios. Light-off strategies use various combinations of high idle speed, aggressive ignition retard, secondary air, and split injections. All designs achieve catalyst light-off during idle before the first hill in the test cycle. Secondary air is not necessarily needed, but helped the catalyst heat to 950°C in the first idle versus 500°C without secondary air. Turbocharged direct injection engines use split injection, secondary air, and late injection to aid cold start. The investigators ran emissions tests to help estimate how much catalyst will be needed for meeting the new California regulations. Figure 15 shows the case for a highly-calibrated, port-fuel injected, naturally-aspirated 2.0 liter engine without secondary air. Approximately 2 liters of catalyst at $81 is needed to achieve the SULEV 30 target, based on Pd at $578/oz and rhodium at $1700/oz. This compares with about 2.5 liters of catalyst at $125 to achieve the same result on a 2.4 liter engine with secondary air.

In an entirely different approach to evaluating cost and emissions, Zammit, et al. [81] changed the distance from the engine of a close-coupled TWC and measured the emissions. They made estimates of the increased PGM loadings to offset the increased distance while keeping the emissions the same: $0.95 to $1.28 per cm, for palladium at $800/oz.

Finally, the emerging GHG emissions regulations could be addressed with lean-burn gasoline engines, but like with diesel, they have a lean-NOx problem. However, compared to modern light duty diesel, NOx levels during gasoline lean operation are considered too high for it to be practical to use urea-based SCR solutions. Researchers at Oak Ridge National Laboratory did a fundamental investigation to a TWC+SCR approach that similar in principle to the LNT+SCR approach, wherein NH_3 is generated in situ by the TWC [82]. TWCs are shown to produce NH_3 over a broad temperature window. Key variables for system performance are PGM content, temperature and control of the air:fuel ratio. Greater than 99% NOx conversion was observed using the approach. Lean-only NOx conversion was >98%. CO slip is a concern and will need to be addressed. A significant fuel economy gain can be realized by using an LNT approach rather than a TWC to generate the NH_3 because the period of time the engine must run rich is reduced.
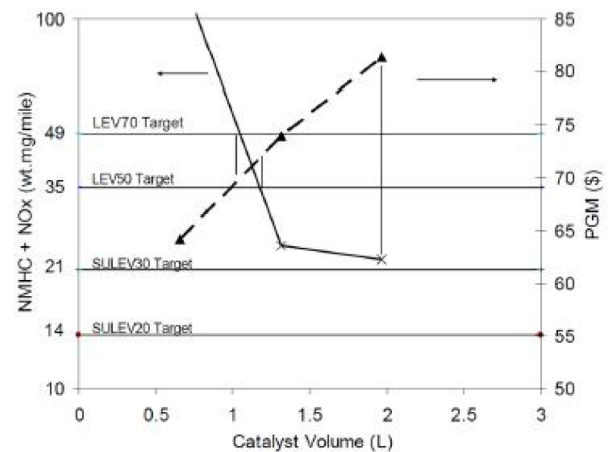

Figure 15. Estimated required amount of catalyst to achieve various emissions levels on a 2.0 liter PFI enigne without secondary air. [80]

SUMMARY/CONCLUSIONS

Regulatory developments

California finalized the LEVIII LD emissions standard, calling for a ~75% reduction in fleet average NMOG+NOx (non-methane organic gas), and a 90% cut in PM, down to 1 mg/mile, by 2025. Europe is developing a far-reaching real-world driving emissions (RDE) standard that will involve random dynamometer and/or PEMS (portable emissions monitoring system) testing. The US EPA finalized the LD GHG regulations for 2016-2025, calling for 50% reductions from today's levels. On the HD side, California is contemplating a 75% NOx reduction (to 0.05 g/bhp-hr) to help it achieve 2023 ozone standards. India and China are starting new emissions and clean fuel initiatives that will help alleviate their severe air pollution problems.

Engine developments

Numerous LD engine technologies are available to help meet the European 2020 and US 2025 GHG standards, and likely provide an attractive payback period for consumers. Downsizing and mild hybridization are leading the way for gasoline engines, utilizing direct injection, turbocharging, ultra-capacitors, superchargers, and variable valve technology. PN number emissions from direct injection engines are quite sensitive to real-life operating variables. Light-duty diesel engines are following the incremental improvements of previous years, with some prototype engines achieving a specific power of 105 kW/liter. Some new emphasis is on cost reduction through new structural design and synergies with high-production gasoline engines. Much work is being done on demonstrating LEVIII fleet-average emissions levels (30 mg/mile NMOG=NOx). On the heavy-duty side, 98% efficient deNOx aftertreatment is called upon to help eliminate cooled EGR. US engine manufacturers

are demonstrating the potential to meet a US Department of Energy goal of 50% BTE (brake thermal efficiency) using downsizing, combustion optimization, waste heat recovery, and improved SCR performance. New LD and HD engine designs include dedicated EGR, stoichiometric diesel high-load transients, and 2-stroke opposed pistons.

NOx control

Much recent emphasis has been on improving the low-temperature performance of SCR catalysts, increasing and understanding durability factors, and novel system designs, including the use of passive NOx adsorbers, dual SCR catalysts with an integrated ammonia sensor, SCR+DPF integration, and gaseous ammonia injection. Lean NOx Traps are using lower precious metal content, and are evolving into layered and zoned designs with SCR catalysts. More understanding is reported on improving the HT performance of LNTs using air:fuel oscillations.

Diesel PM control

More understanding is emerging on how DPF performance can be impacted by applying an SCR coating. Back pressure goes up with SCR catalyst loading, but deNOx efficiency peaks, wherein more catalyst can cause a loss of efficiency. DPF passive regeneration is adversely affected by the addition of SCR catalyst, but it is still manageable. NOx recycling for soot burn on normal catalyzed DPFs was quantified, and can be as much as 4X at 450°C. Several fundamental studies on the complex relationship between ash and soot on DPFs are reported.

Diesel oxidation catalysts

The field-aging of DOCs is quantified. The front portions of the catalyst age due to ash effects, and the back experiences more thermal aging. Base metal formulations are shown to perform equivalently or even better than precious metal versions for NO and hydrocarbon oxidation under certain conditions.

Gasoline emission control

When some three-way catalyst (TWC) is transferred from a close-couple catalyst to a downstream GPF, emissions are shown to decrease. Coated GPFs also regenerate more efficiently at lower temperatures. GPF filtration efficiency is strongly related to the presence of a filter cake, but increases markedly with aging. TWCs are improving with better understanding of layering advantages and engine calibration impacts.

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