2012-01-0368
Published 04/16/2012
Copyright © 2012 SAE International
doi:10.4271/2012-01-0368
saeeng.saejournals.org

Vehicular Emissions in Review

Timothy V. Johnson
Corning Inc.

ABSTRACT

This review paper summarizes major developments in vehicular emissions regulations and technologies (light-duty, heavy-duty, gasoline, diesel) in 2011. First, the paper covers the key regulatory developments in the field, including proposed criteria pollutant tightening in California; and in Europe, the newly proposed PN (particle number) regulation for direct injection gasoline engines, test cycle development, and in-use testing discussions. The proposed US LD (light-duty) greenhouse gas (GHG) regulation for 2017-25 is reviewed, as well as the finalized, first-ever, US HD (heavy duty) GHG rule for 2014-17. The paper then gives a brief, high-level overview of key emissions developments in LD and HD engine technology, covering both gasoline and diesel. Emissions challenges include lean NOx remediation for diesel and lean-burn gasoline to meet both the emerging NOx and GHG regulations. NOx control technologies are then summarized, including SCR (selective catalytic reduction) with ammonia, and hydrocarbon-based approaches. Nitrous oxide (N_2O) emissions are also addressed. These technologies are achieving >95% deNOx efficiency averaged over the certification test cycles. PM (particulate matter) reduction technologies are evolving around new DPF (diesel particulate filter) materials for reduced back pressure and SCR integration. Next, DOC (diesel oxidation catalyst) developments are summarized. They mainly involve NO oxidation to NO_2 as a function of catalyst formulation and hydrocarbon oxidation parameters. Finally, the paper discusses some key developments gasoline emission controls. Advanced three-way catalysts improve with zone coating technology, and with precious metal thrifting. Sulfur impacts are significant on the new formulations. Finally, the emerging technology of GPFs (gasoline particulate filters) is summarized.

CITATION: Johnson, T., "Vehicular Emissions in Review," *SAE Int. J. Engines* 5(2):2012, doi:10.4271/2012-01-0368.

INTRODUCTION

The automotive and heavy-duty vehicle industries are going through a revolution like none other in their histories. 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 improvements are 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. Not only are engines significantly downsized in plug-in hybrids, like in the Chevrolet Volt, but they are replaced entirely in pure battery electric vehicles, like the Nissan Leaf. To address these forces, engine manufacturers are relying very heavily on technology developments.

It is interesting to note that the automotive industry has traditionally been quite conservative in implementing technologies. Figure 1 shows that for five common engine technologies from 1975 to 2010, it took about 20 years from the start of production of a viable technology to reach a market penetration of 75-80% (1). Hybrid electric vehicles appear to be on the same or slower path, with the first US market introduction being in 1999 and market penetration of all HEVs being less than 2.5% twelve years later. Some notable exceptions to this trend are regulatory-driven emissions control technologies. For example, diesel particulate filters (DPFs) were introduced by Peugeot in 1999, and less than twelve years later, are on all light-duty diesel engines in the US, Europe, and Japan. One could also place heavy-duty (HD) SCR (selective catalytic reduction) catalysts systems (introduced in 2003) and HD DPFs (introduced in 2006) in the same category. Given the tightening CO_2 regulations, which primarily drive engine technologies, engine advancements could come much faster than in the past.

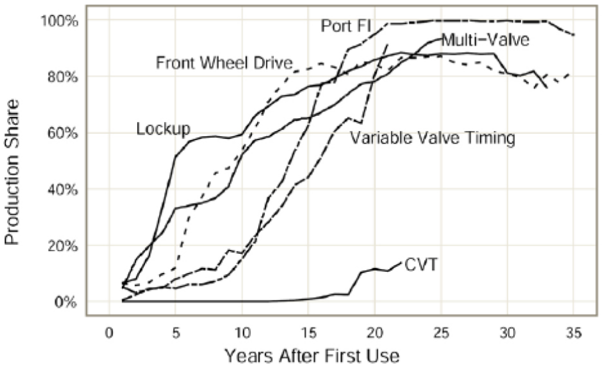


Figure 1. Technology penetration rates for five representative engine technologies. It takes 15 to 20 years from the first major market introduction of a new technology to penetrate to 75 to 80% of the market. (1)

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 of key developments in diesel emissions and control from 2010 (2) left off. Given the significant developments in gasoline engines and emissions control, this year an attempt is made to briefly summarize emissions developments in this field. Also, like in previous years, 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 then 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.

Finally, as in previous reviews, this review is not intended to be all-encompassing and comprehensive. Representative papers and presentations were chosen here that provide examples of new, key developments and direction.

REGULATIONS

Although many of the initiatives described here are formal proposals, they are all developed with close cooperation with the key stakeholders. As such, the final regulations will be very similar. The major vehicular regulatory initiatives of 2011 that will be summarized here include

- Proposed LEVIII LD regulation from the California Air Resources Board (CARB)
- Proposed US LD greenhouse gas reduction regulation from the US Environmental Protection Agency (EPA)
- Proposed Euro 6 gasoline PN (particle number) limits
- Developments on the LD test cycle in Europe and in-use emissions directions.
- Finalized US HD greenhouse gas regulation.

LIGHT DUTY REGULATIONS

Criteria Pollutants

California

CARB has been working with stakeholders on the LEVIII proposal since about 2008. In December 2011 they put forth a formal Advanced Clean Vehicle Program proposal, which covers LEVIII and greenhouse gas (GHG) regulations (3), and ZEV (zero emissions vehicle) requirements (4), to be finalized late-January 2012.

The LEVIII portion covers criteria exhaust emission standards for light-duty and medium-duty vehicles starting with model year 2015. Key provisions include:

- Reduce new vehicle fleet average emissions approximately 75% to super-ultra-low-emission vehicle (SULEV) levels (30 mg/mile NMOG+NOx). Non-methane organic gas refers to hydrocarbon levels adjusted for atmospheric reactivity.
- Phase-in begins in 2015 and ends in 2025. Figure 2 shows the straight-line reductions expected for cars and light-duty trucks (LDT1<3751 lbs., LDT2<8501 lbs.).
- Add new emission certification categories, designated SULEV20, ULEV50 (ultra-low emission vehicle), and ULEV70 (the 20, 50, and 70 designations refer to the NMOG +NOx emissions (mg/mile) measured using the Federal Test Procedure, FTP, test cycle.
- Increase full useful life durability requirements from 120,000 miles to 150,000 miles.
- Tighten particulate matter (PM) standards for light-duty vehicles from 10 mg/mile on the FTP today to 3 mg/mile phasing-in 2017-21 (20% of vehicles per year), and 1 mg/mile phasing-in 2025-28.
- Tighten supplemental FTP (SFTP) standards for light-duty vehicles and establish new limits for MDVs (>8500 lbs.), including a PM standard. US06 emissions (the high-speed cycle) tighten to 50 mg/mile NMOG+NOx, a 64% reduction for cars and LDT1, and 80% for the LDT2 class. A composite value, made up of the US06, SC03 (air conditioning cycle), and FTP results in similar reductions. PM levels are 10 mg/mi for PC and LDT<6000 lbs fully loaded on the US06.
- Require all medium duty vehicles (MDVs) between 8,501-10,000 lbs. to certify on a chassis dynamometer.
- Shift to an E10 (10% ethanol) certification gasoline.

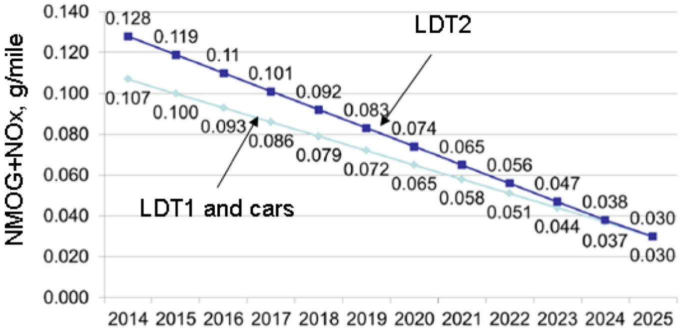


Figure 2. Proposed California LEVIII fleet average combined non-methane organic gas and NOx standards (NMOG+NOx) for cars and light-duty trucks (LDT1 up to 3750 lbs.; LDT2 3751-8500 lbs.). (3)

The regulation will drive emission control and engine technologies in all LD classes. For example, for every ULEV50 or ULEV70 vehicle sold, two or four SULEV20 cars will be needed to meet the fleet average SULEV30 requirement. This could drive current LEV (160 mg/mile NMOG+NOx) and ULEV (125 mg/mile) vehicles to reduce emissions up to 70% (LEV to SULEV); and could reduce emissions from current ULEV and SULEV vehicles up to 85% (ULEV to SULEV20) to get enough low-emission offsets for ULEV50+ vehicles.

Europe

Much activity is also happening in Europe on criteria pollutants. Most significantly, the European Commission proposed particle number regulations for Euro 6 direct injection gasoline engines (5). For new vehicle types made after 1 September 2014 and all vehicle models made after 1 September 2015, the PN emissions on the NEDC (New European Drive Cycle) can not exceed 6×10^{11}#/km, the same limit value established a few years ago as for diesel. However, for up to three years after these dates a particle number emission limit of 60×10^{11}#/km may be applied to Euro 6 direct injection gasoline vehicles upon request of the manufacturer. The intent is to allow manufacturers an additional three years to develop alternatives to meeting the regulations besides gasoline particulate filters (GPFs), acknowledged to perform well and be cost effective.

Also of importance, the United Nations Economic Commission for Europe - The Working Party on Pollution and Energy (UNECEGRPE) is developing the World-Harmonized Light-Duty Test Cycle (WLTC) for application at first for CO_2 regulations, but also for criteria pollutants (6). The developments are still dynamic, but Figure 3 illustrates the general concept (7). Urban, extra-urban, highway, and autobahn cycles are shown in series and each sub-cycle would be tested. Individual countries would arithmetically adjust the weighting of these cycles to best-match their regional driving behavior.

Europe is also looking at using these cycles or portable emissions monitoring systems (PEMS) to reduce in-use emissions relative to vehicle certification value. If the dynamometer testing is considered using these cycles, the lead proposal is to randomize them, conceivably allowing, for example four autobahn cycles to be used. Alternatively, the PEMS method would test vehicles in actual use. Depending on the details, still in development, the in-use emissions program could drive the design of emissions systems and dictate approaches.

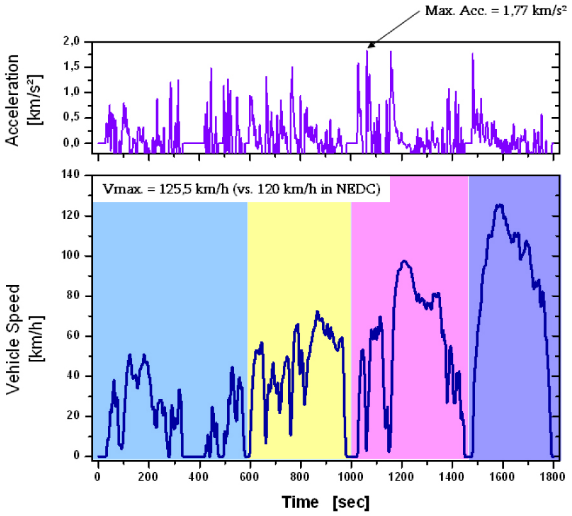


Figure 3. One version of the proposed World-Harmonize Light-Duty Test Cycle (WLTC). Countries would weight each portion of the cycle to match the regional drive behavior.

On-Board Diagnotics (OBD)

In the US, OBD requirements are led by California. As part of the LEVIII proposal (3), CARB is proposing minor changes to the 2013 LD OBD regulations related to DOC (diesel oxidation catalyst) NO_2 generation and catalyzed DPF NMHC performance. Of most significance, acknowledging that PM sensors are not yet widely available in sufficient volumes, CARB relaxed the 2013 LD PM OBD threshold value (17.5 mg/mile or 1.75X the standard) for at least one year. However, manufacturers still need to be able to detect specific DPF failure modes like partial cracks and melting. Generally the same alterations are made to the US HD OBD requirements.

Similarly in Europe, the European Commission is proposing relaxing the PM OBD threshold value for gasoline and diesel vehicles to 25 mg/km for Euro 6 (September 2014 and September 2015), tightening to 12 mg/km three years later (5). The previous threshold limit was 9 mg/km (2X the limit value). Euro 6 NOx thresholds of 150 and 180 g/km for gasoline and diesel vehicles respectively, tighten to 105 and 140 g/km three years later. NMHC proposal thresholds remain at 170 mg/km for gasoline and 290 mg/km for diesel for Euro 6 and beyond.

Greenhouse Gas Regulations

California's GHG program is harmonized with the US EPA-NHTSA (National Highway Transportation and Safety Administration) 2017-25 proposal that was released on November 16, 2011 (8).

General provisions are summarized as follows:

- A 163 g/mile (102 g/km) CO_2 industry fleet average emission limit in 2025 is proposed; nominally equivalent to a 54.5 mpg (miles per gallon; 24 km/liter, 4.2 liters/100 km). Reductions would be 5%/year for passenger cars in 2017-25 (ending at 144 g/mi or 90 g/km CO_2; or 62 mpg, 27 km/l, 3.7 l/100 km). For light-duty trucks, 3.5%/year reductions would come in 2017-2021 (going to 40.9 mpg, 17.7 l/km, 5.7 l/100 km), followed by 5%/year reductions in 2022-2025 (ending at 203 g/mile or 125 g/km CO_2; 49.6 mpg, 21.4 l/km, 4.7 l/100 km). There will be a progress review in 2018.

- Like in Europe, all manufacturers will have different fleet average CO_2 requirements, dependent on the size of their cars. However, in Europe the CO_2 requirements are based on vehicle weight; in the US proposal it is based on vehicle footprint (area between the tires).

- Averaging, banking, and trading of credits, established in the MY 2012-2016 program, may be carried forward, or banked, for five years, or carried back three years to cover a deficit in a previous year. Credits will also be allowed for efficiency and leakage improvements in air conditioning systems, and for various “off-cycle” credits (like stop-start systems and high-efficiency lighting). With all credits, in real world driving (five-test-cycle evaluation vs. two-cycle, above), cars are estimated to achieve 40 to 45 mpg (17 to 19 km/l; 5.8 to 5.1 l/100 km).

- The 10 mg/mile (6.2 mg/km) N_2O and 30 mg/mile (19 mg/km) CH_4 caps in the 2012-2016 rule are continued, but the proposal allows for use of CO_2 credits to comply.

- Quite importantly, electrical-grid-powered vehicles are offered significant incentives. For 2017-2021 all plug-in and fuel cell vehicles, grid CO_2 is counted as 0 g/mile. From 2022-25, the cumulative number of vehicles that a company can use here is limited to 200,000 or 600,000, depending on plug-in sales in 2019-2021. Further, a multiplier is offered for all 2017-2021 plug-ins, allowing these vehicles to count as more than one vehicle for the purposes of compliance. For battery electric vehicles/fuel cell vehicles the multiplier starts at 2.0 in 2017 and is reduced to 1.5 by 2021; plug-in hybrid multiplier starts at 1.6 in 2017 and is reduced to 1.3 by 2021.

- Other provisions include a 10-20 g/mile CO_2 credit for hybridizing full-size pickups in significant volumes; and using the “SAE utility factor” for accounting for CO_2 emissions from CNG (compressed natural gas) or dual-fueled vehicles. This accounting does not extend to flex-fueled vehicles (i.e., E85 fuel), for which manufacturers will need to demonstrate real-world use.

Figure 4 shows how the US proposal generally compares to others around the world (9). The European 2020 regulation of 95 g/km CO_2 is the most demanding, as it comes five years ahead of the US regulation. However, the US levels are similar, considering fleet mix. (Directionally, Europe is headed towards 75 g/km in 2025.) Other regions of the world are also tightening to similar levels, namely China and Japan.

The EPA technology assessment indicates there is a wide range of technologies available for manufacturers to consider in reducing GHG emissions and improving fuel economy:

- Advances in gasoline engines and transmissions will account for most of the reductions.

- Vehicle weight reduction, lower tire rolling resistance, improvements in vehicle aerodynamics, diesel engines, and more efficient vehicle accessories.

- Increased electrification of the fleet through stop-start, hybrid, plug-in hybrid electric, and electric vehicles. However, attainment of the proposed 2025 GHG regulations generally does not require plug-in vehicles.

- Air conditioner improvements could provide 10-20% GHG reductions.

The ZEV (zero emission vehicle) part of the California Advanced Clean Vehicle Program (4) proposes, beginning in 2017, to increase ZEV requirements (generally regarded as battery electric vehicles and hydrogen fuel cell vehicles) and plug-in hybrids to about 15.4% of new sales by 2025, for all but the smallest auto manufacturers.

HEAVY DUTY REGULATIONS

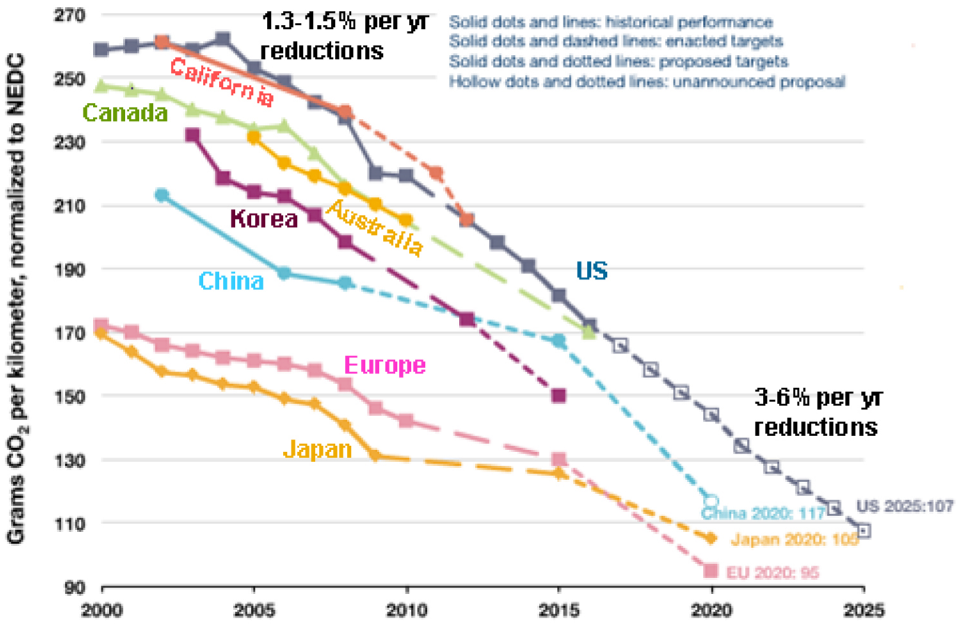
Criteria Pollutants

The most significant development on HD on-road regulations is the year-end announcement that China IV regulations will be delayed until July 2013 (10). The original data was January 1, 2011. The delay will better allow the introduction of 350 ppm sulfur fuel throughout the country.

Also significant is that Japan is targeting to harmonize with Euro VI regulations in 2016, but with a 400 mg/kW-hr NOx limit on the World-Harmonized Transient Cycle (WHTC), versus a 460 mg/kW-hr level for Euro VI (11). It is not known whether Japan will adopt the Euro VI PN standard.

As in the previous round of regulations, Europe is leading the way on Non-Road Mobile Machinery (NRMM) standards. The European Parliament instructed the European Commission to finalize the next round, Stage V, of NRMM by 2014 (12). Goals should be to:

- Harmonize requirements of Euro VI standards for heavy-duty vehicles



[1] China's target reflects gasoline fleet scenario. If including other fuel types, the target will be lower.
[2] US and Canada light-duty vehicles include light-commercial vehicles.

Figure 4. Comparison of finalized and proposed fuel economy or CO_2 regulations around the world, normalized to CO_2 emissions on the New European Drive Cycle (9).

- Adopt a particulate number limit that applies for all compression ignition engine categories
- Retrofit of after-treatment systems on the existing fleet of non- road mobile machinery for a comprehensive approach to AQ
- Periodic in-use testing of non-road mobile machinery and vehicles

Also noteworthy, Beijing will be introducing Stage IIIB equivalent NRMM standards in 2014.

Greenhouse Gases

On August 9, 2011, the US EPA and NHTSA jointly issued their final regulations for establishing fuel efficiency and greenhouse gas emission standards for medium- and heavy-duty trucks (13). The regulation, which begins in 2015 and is fully phased-in by 2018, is the first of its kind in the world, and has some new features that are different from other HD truck regulations (14):

- Breaks diverse truck sector into 3 distinct categories - Line haul tractors, heavy-duty pickups and vans, and vocational trucks.
- Sets separate standards for engines and vehicles to ensure improvements for both
- Sets separate standards for fuel consumption, CO_2, N_2O (0.10 g/bhp-hr), CH_4 (0.10 g/bhp-hr), and hydrofluorocarbons (HFCs).
- Provides incentives for advanced technologies (e.g. EVs, Hybrids, waste heat recovery) - can be counted as 1.5 vehicles
- Manufacturer flexibilities, including averaging, banking and trading
- New compliance methods for heavy-duty hybrids and innovative technologies not contemplated in existing engine and vehicle test procedures

The CO_2 standards for compression ignition engines tested using the US HD engine-dynamometer test procedures are shown in Table 1 (14). In the table, tractor engines (long-haul freight) are measured on the SET cycle (steady-state engine test), and the other vocational engine classes are measured on the US HD FTP cycle (Federal Test Procedure; transient cycle). Not shown are the large pick-ups and vans, which are measured on the highway fuel economy test cycle (chassis test). Relative to the 2010 industry baseline, by 2017 the regulation results in CO_2 reductions from the engine of: 6% for class 7 and 8 tractors, 5% (gasoline) and 8% (diesel) for class 4-8 vocational engines, and 5% (gasoline) to 9% (diesel) for light-heavy duty trucks. Manufacturers can chose an alternative phase-in schedule more aligned to the OBD implementation schedule for 2013 and 2016. Instead of phasing in yearly, in this option the CO_2 standards start about 3% tighter, but are held constant and end somewhat higher than under the main plan in both phase-in periods.

Table 1. CO_2 standards (g/bhp-hr) for various HD compression ignition engine classes that are certified on the engine dynamometer. (14)

Model Years	Light HD	Medium HD, Vocational	Heavy HD, Vocational	Medium HD, Tractor	Heavy HD, Tractor
2014-2016	600	600	567	502	475
2017+	576	576	555	487	460

In addition to the engine standards, the total vehicle also needs to incorporate CO_2 reduction technologies, like reduced aerodynamic drag and rolling resistance. These reductions are on the order of 17% for tractors, 1% for vocational trucks, and 8% for the light heavy-duty trucks.

REGULATORY SUMMARY

The California LEVIII regulations will drive another round of emissions control technologies on the engines and in the tailpipe. The fleet average emissions structure, as well as the sum of NMOG+NOx provides flexibility without sacrificing air quality. Europe is headed towards assuring that real-driving emissions are reduced as much as the certification testing predicts. The US LD GHG proposal also provides flexibility but likewise calls for significant reductions. The combination of criteria pollutant tightening and mandated CO_2 reductions present surmountable but challenging requirements on the auto industry. Long term mandates are defined to provide the industry time to meet the challenge. On the heavy-duty side, GHG emissions reductions are just beginning, and cover both engine and vehicle reductions. For NRMM (non-road mobile machinery) applications, as with the previous round of tightening, Europe is setting up for the next round of criteria pollutant tightening, generally harmonizing with Euro VI.

ENGINE TECHNOLOGIES

Historically, engine technologies were largely influenced by and developed for meeting criteria emissions regulations. However, this is now shifting due to the tighter greenhouse gas regulations in both the light- and heavy-duty sectors. The challenge is significant, and converse to the past wherein exhaust emission control technologies could reduce much of the burden, engine technologies will need to take up most of the challenge of CO_2 reductions.

LIGHT DUTY

Gasoline

Gasoline engines are developing very rapidly to meet the tight European 2020 CO_2 regulations. Various roadmaps are showing 20 to 30% reductions in CO_2 for stoichiometric gasoline engine engines in this timeframe (e.g. 15, 16, 17). Figure 5 shows one such approach, providing 23% reductions, more than half of which comes from significant downsizing enabled by advanced turbocharging, variable valve technology, and cooled exhaust manifolds (16). The balance comes from continuously variable valve lift and variable compression ratio (8% reductions), and optimized thermal management and friction reduction (3%). These technologies are generally additive, but may have small synergies. These are common technologies in most advanced gasoline engine roadmaps.

Engine downsizing calls for higher peak brake mean effective cylinder pressures (BMEPs) to deliver the same power as engines with larger cylinders. For reference, traditional gasoline engines have BMEPs in the 9 to 15 bar range. Fraidl and Kapus (18) show that downsized production engines today are available up to 25 bar BMEP, with prototype engines approaching 30 bar. They estimate ideal maximum BMEP of 30 to 35 bar, with the peak occurring at the lower speed range to enable long gearing. High BMEP engines require high octane fuel to minimize auto-ignition, and even then, a significant issue called low-speed pre-ignition is emerging. It is the subject of several technical symposia. High BMEP engines may require a different trend in fuel. The key could be a larger difference between the RON and MON (research octane number, motor octane number) with an emphasis on reduced MON, rather than the average of the two, as is currently used to qualify fuel octane (19).

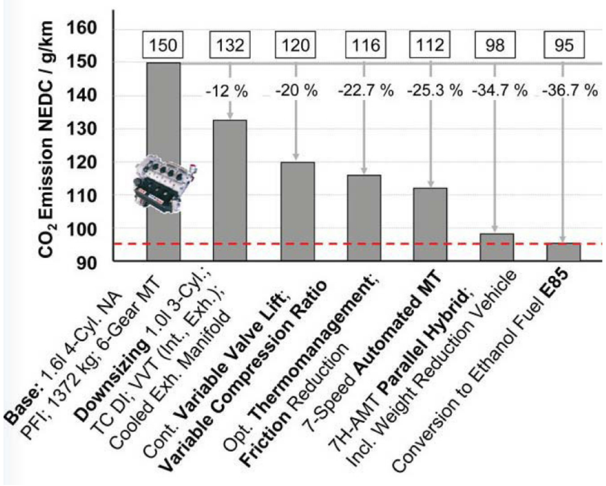


Figure 5. Gasoline engine technologies to achieve European 2020 CO_2 regulations of 95 g/km. (16).

Regarding unique emissions control requirements, direct injection gasoline engines also have high PN emissions and need specific technologies to meet the emerging Euro 6 PN regulations. PN emissions generally come from cold start and from accelerations, but can be emitted throughout the test cycle (18). Remediation approaches generally revolve around keeping the flame out of the rich, high-temperature PM-formation zone using improved air-fuel mixing, reduced wall impingement of the fuel, increased fuel injection pressures

(20), and cooled EGR (exhaust gas recirculation), reference 21.

Lean-burn direct-injection gasoline engines are also of interest, and will require lean deNOx technologies and possibly GPFs to meet emerging emissions regulations. Nakata (22) reported that Toyota is pursuing direct injection gasoline with 30% cooled-EGR for the fourth generation Prius engine, and is looking at going lean with the engine in the fifth generation. Both concepts use the Atkinson cycle, which enable a reduced compression stroke and a long expansion stroke to improve efficiency. with a stroke:bore ratio of 1.5.to improve mixing. The latter version approaches 44% brake thermal efficiency (BTE), higher than today's diesel engines. Figure 6 shows the general efficiency improvements from different technologies in the concept.

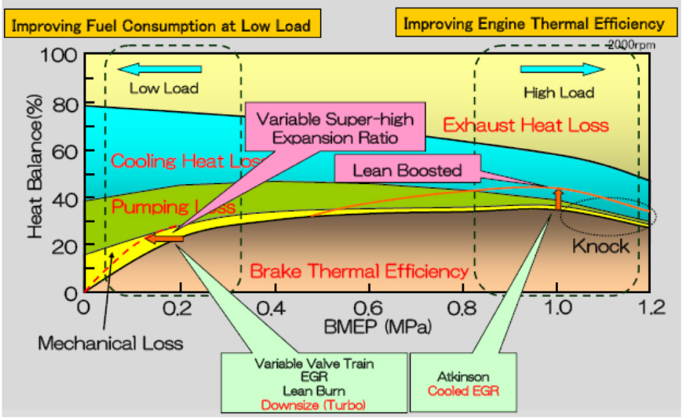


Figure 6. Efficiency improvements for a lean-burn direct injection engine operating with the Atkinson cycle with a very long expansion stroke and cooled-EGR. (22)

Similarly, and pushing the technology, Boggs and King introduced a 50%-downsized lean-burn direct-injection gasoline engine with cooled-EGR, advanced stop-start, advanced friction reduction, an electric supercharger and a peak BMEP of 35 bar (23). The lean regime covers loads less than 15 bar BMEP and speeds from 2200 to 5000 RPM. It achieves 40% reduced CO_2 emissions versus a current production vehicle with port-fueled injection, without compromising performance.

With the large, recent increases in recoverable natural gas (NG) reserves in the US, China, and Europe, use of it as a low-CO_2 nonpetroleum, domestic transportation fuel is increasing in interest. In particular, dual-fueled vehicles (i.e., NG-gasoline) can offer many of the advantages of a plug-in hybrid, such as low cost fuel (40% the cost of gasoline), fueling at home with a home compressor, and gasoline for range, with similar well-to-wheel CO_2 as plug-ins, but at a fraction of the incremental cost of the plug-in. Obiols, et al., (24) took the advantages of a dual-fueled vehicle further by looking at synergies in combustion. They retrofitted a direct-injection gasoline engine with multi-port NG injectors in a way to burn both in the same combustion event (concomitant combustion). Figure 6 shows that at full load, effective gasoline fuel consumption is reduced 14% using a 60% NG / 40% gasoline mixture versus using gasoline only. Further, maximum BMEP increases 20%, NOx drops 48%, and total hydrocarbons decreases 64%.

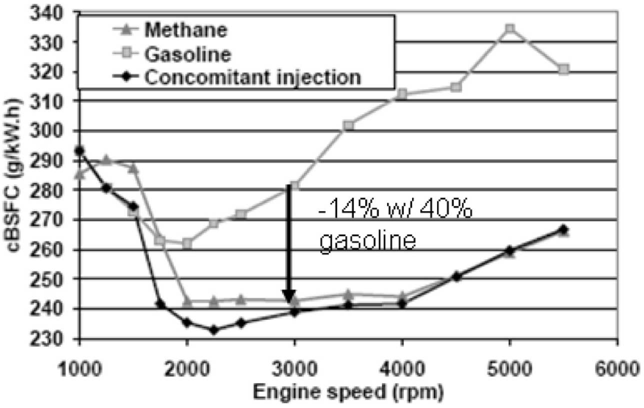


Figure 7. Full load, synergistic combustion effects on fuel consumption for concomitant injection, wherein 60% natural gas and 40% gasoline are burned in the same combustion event. (24)

Numerous emerging low-criteria emissions high-efficiency gasoline engine technologies are in the research labs. Chadwell, et al., evaluated the sensitivity of BTE to turbocharger efficiency for several of these (25). The results are shown in Figure 8. Partially-premixed compression ignition (PCCI) has the highest BTE, but also is quite sensitive to turbocharger efficiency. Homogeneous-charged compression ignition (HCCI) gasoline engines also have low emissions and the next highest BTE at 45% and low turbocharger sensitivity, but the mode is limited to relatively low loads (10 bar BMEP). HEDGE (high-efficiency, dilute gasoline engines; spark ignition) and RCCI (reaction controlled compression ignition) engines, both which have low emissions and use high levels of cooled-EGR and boost, show similar BTE (5% higher fuel consumption) to diesel, but have slightly higher sensitivity to boost efficiency.

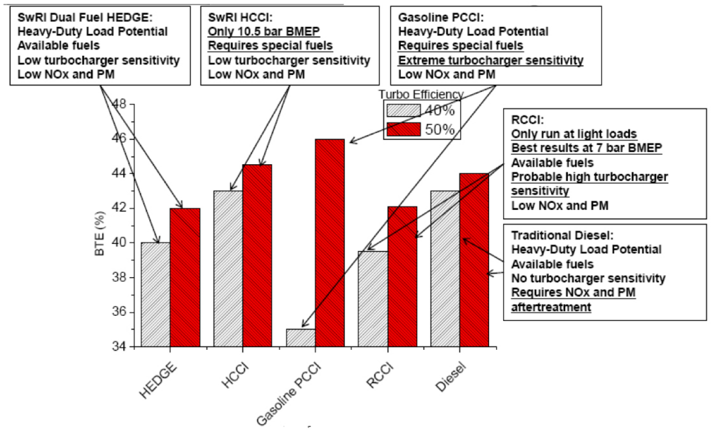


Figure 8. BTE comparisons for various engine technologies and sensitivity to turbocharger efficiency. (25)

Emerging gasoline engines are approaching or exceeding the efficiency of today's diesel engines, but costs are also increasing. Criteria emissions are quite low, but to get the highest efficiencies as the emerging CO_2 regulations demand, lean NOx and possibly particulate control will be needed.

Diesel

Light-duty diesel engines are also improving, to keep the efficiency advantage over gasoline. Pischinger (16) described future technologies for diesel to compare to gasoline engines (Figure 5), and also achieve 35% CO_2 reductions. Major improvements include 25% downsizing (7% reductions), stop-start system (6%), low-pressure EGR (3%), down-speeding (3%).

In the US, to meet the tight LEVIII emissions reduced cold start emissions are the key, requiring significant thermal management methods. Popuri, et al., (26) use an intake throttle, bypass valves for the EGR, turbine, and low-pressure VGT (variable gate turbocharger), idle speed modulation, late cycle fuel injections, cylinder deactivation (fueling cut-off), and an exhaust-manifold integrated diesel oxidation catalyst to allow urea injection 125 seconds earlier than for a baseline engine. Despite that the engine-out NOx increased 20%, and fuel consumption increased 5 to 7% when the methods are used, FTP Bag 1 deNOx was 70% and overall fuel efficiency increased 25%. A 4.5 liter engine in a 5000 pound (2270 kg) vehicle achieved Tier 2 Bin 5 standards at 25.5 MPG (9.1 liter/100 km).

Diesel engine costs have been a problem in competing with modern gasoline engines. Regner, et al., (27) are updating the opposed-piston diesel engine, solving the historic problems using new materials and modern analytical techniques. Because it has no head or valve train, compared to a standard diesel engine it has 40% fewer parts, is 30% lighter, and costs about 10% less. Fuel consumption is 15-20% lower than a state-of-the-art 6.7 liter diesel engine, but lube oil consumption and NOx emissions are about double.

Future LD Prognosis

From a baseline defined as the average 2009 US multi-port injection gasoline vehicle (28.5 MPG), intermediate term gasoline engine technologies to meet the US 2016 CO_2 regulations will drop fuel consumption by about 15 to 20% and cost about $25 per percent CO_2 reduced (17). Payback periods for these technologies are less than 2.5 years at current fuel prices ($3.50/gallon). Greene and Baker (28) show that customers intuitively are risk adverse (exaggerate costs and minimize benefits) and roughly target a three-year payback period (or less). So for these numbers, the economics are attractive. (Greene and Baker used slightly different costs and fuel costs, and conclude the 2016 versions have slightly negative consumer perceived value, attractive despite a positive $406 net present value). Moving forward from a 2016 base, such as to HEVs or LD diesels, the new incremental costs to achieve another 20% CO_2 reduction are nominally $70-120 per percent CO_2 reduced. Assuming $4.50/gallon, the payback period increases to about 7.5 years. This step is not attractive according to Greene and Baker's analyses. Continuing the incremental analysis to diesel HEVs to achieve about 50 MPG provides a payback period of about 12 years at $5.00/gallon.

HEAVY DUTY

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

Roberts (29) described some HD technologies for both high- and low-engine out NOx approaches. A summary is shown in Figure 9. As with previous such descriptions of advance engine technology packages(30), fuel consumption decreases with NOx increases even out at >5 g NOx/kW-hr. In Figure 9, keeping in mind that urea consumption is shown to linearly increase with engine-out NOx to maintain tailpipe emissions (US2010 levels of 0.26 g/kW-hr NOx in this case) Roberts shows minimum fluid operating costs (top line) at 8-11 g/kW-hr NOx. He assumes here that the urea (Diesel Emission Fluid, DEF) is 65% the cost of fuel. Emission control technologies (like SCR) would be needed to achieve at least 97-98% efficiency to achieve this minimum fluid-consumption-cost calibration range. In this regard, a proviso is warranted to Roberts' analysis. The minimum operating cost point will shift to lower NOx levels because the urea consumption curve will bend upwards at the higher NOx levels because excess urea will be needed to achieve the higher deNOx efficiencies.

Table 2. Summary of approaches to achieving DOE goal of 50% BTE HD engines. (33, 36, 37, 38)

Cummins	Advanced combustion, improved aftertreatment, WHR to achieve 48% BTE. Improved gas flow, improved WHR, turbocompounding, reduced parasitics, and powertrain optimization to get 2% more BTE.
Daimler	Combustion chamber optimization, advance aftertreatment, reduced parasitics, better control strategy (mapless), GPS integration for predictive control, WHR, turbocompounding; downsizing being considered.
Navistar	Advanced combustion (VVA, 2-stage boost, 2-stage EGR cooling, 3000 bar common rail possible), turbocompounding, WHR, reduced parasitics
Volvo	Advanced combustion, improved aftertreatment, improved air handling, friction reduction, WHR.

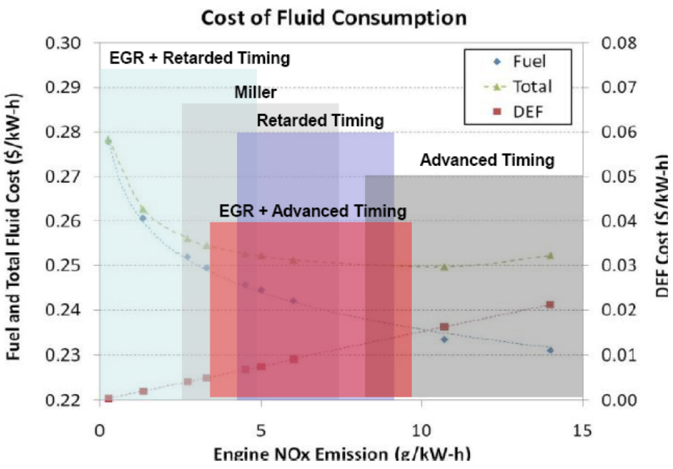


Figure 9. General advance HD engine technologies and the resultant urea (DEF) and fuel cost curves, assuming DEF costs $2.56 per gallon ($0.69/liter) and diesel fuel cost $3.89/gallon ($1.05/liter). Fluid costs are minimized at 8-11 g/kW-hr NOx. (29)

Zybell (31) also described some HD technology packages for meeting low emissions and fuel consumption, but mainly in the context of fuel injection technology. His slopes of fuel consumption versus NOx are not as steep as shown in Figure 9, so his minimum cost range is in the 3-5 g/kW-hr NOx range. However, when fuel injection pressure is increased from 1800 bar to 2400 bar, the fluid consumption drops about 0.6% and the minimum calibration shifts to 2.5 to 4.0 g/kWhr NOx. Continuing the trend, if injection pressure is increased to 3000 bar, fluid consumption drops another 0.1% and the minimum point shifts to 2.0 to 3.0 g/kW-hr NOx.

Kobayashi, et al., (32) gave a detailed account of their attempt to drop engine-out NOx to 0.2 g/kW-hr on a 10.5 liter engine with the following features:2000 bar common rail fuel injection system, low-pressure (LP) and high-pressure EGR, variable valve actuation, 300 bar peak cylinder pressure, variable swirl, and advanced combustion chamber design. With a DPF, the engine achieved 0.8 g/kW-hr NOx on the JE05 Japanese HD transient cycle. This would allow use of an LNT. For example, at 1200 RPM and 8 bar BMEP, substituting about 40-70% LP- for HP-EGR results in similar NOx levels, despite 5 to 10% higher total EGR rates, but with greatly reduced PM and fuel consumption. Also striving for high-efficiency and low-NOx, Ojeda (33) reported that a prototype 13-liter engine with 2-stage EGR cooling, 2-stage turbocharging, a 2200 bar injection system, and optimized combustion system achieved 45% BTE at road loads with a 0.5 g/bhp-hr NOx (0.65 g/kW-hr) NOx level. This is higher-efficiency than some 2010 engines running with SCR at much higher NOx levels.

Improved thermal management is increasing in importance, especially as it pertains to reducing urban NOx from engines with SCR. The issue was brought to the forefront in 2009 by a report (34) showing that if exhaust temperatures are too low urea can't be injected and NOx emissions can be quite high. The first evidence that this issue is being addressed on Euro VI engines was reported by Vermeulen, et al., (35). The 13 liter prototype Scania engine had cooled-EGR to reduce low-load NOx and intake throttling for thermal management. NOx In-Service Conformity was well below the 1.5X limit after allowable calibration adjustments, and NOx emissions generally vary from 0.35 to 0.76 g/kWh for most trips and trips parts. The SCR system was operative after 500 seconds of operation after a 3°C cold start.

Finally, US HD engine manufacturers described (33, 36, 37, 38) their future approaches to meeting the US Department of Energy (DOE) goal of demonstrating 50% BTE (break thermal efficiency) on a HD engine. Table 2 shows a summary of the approaches. All four 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). Improved SCR performance is also mentioned commonly (for higher NOx calibrations).

HD Engine Summary

The low criteria pollutant and emerging CO_2 regulations are placing a significant challenge on HD engine makers. Market forces have always made low fuel consumption a competitive advantage, so these engines are already quite efficient. However, it appears there is still much more that can be done and still deliver customer value. High-NOx calibrations are a leading way of decreasing fuel consumption, but this will require 97+% deNOx capability going into the future. At such high engine-out NOx (>8 g/kW-hr), even a 1% drop in deNOx efficiency can increase NOx emissions by 33%. These deNOx strategies will require excellent control and durability, as well as good oxidation of excess ammonia to prevent forming NOx. Alternatively, the low-NOx high-EGR strategies might deliver more customer acceptance by removing the burden of urea filling and the associated systems cost. These strategies will require robust DPFs and good active regeneration strategies to manage the high soot levels coming from the engine and to minimize the DPF fuel penalty.

LEAN NOX CONTROL TECHNOLOGIES

In the previous sections it was shown that lean NOx control (lean deNOx) technologies will be integral to meeting the emerging criteria pollutant regulations for both gasoline and diesel engines. Minimum removal efficiencies on the order of 85% will be needed, but levels up to 97-98% are desired to allow HD engines to operate in high-NOx low-fuel consumption regimes.

Two broad approaches to lean deNOx control are SCR (selective catalytic reduction) using ammonia, and hydrocarbon-based approaches (HC-deNOx) primarily using lean NOx traps, but also lean NOx catalysts (or HC-SCR).

SCR

SCR technology is entering its third or fourth generation since commercial introduction in Europe in 2003. Then, systems were removing upwards of 75% NOx over the European HD Transient Cycle to meet Euro IV regulations. To meet the emerging Euro VI regulations in 2013, cycle-average deNOx efficiencies approaching 95% may be realized. Work is continuing in the US to go even higher in efficiency to meet the current and emerging LD NOx regulations.

Although the urea infrastructure is well-developed in Europe, Japan, and the US, finding alternative sources for ammonia is still of significant interest to enable SCR catalysts to function better at low exhaust temperatures, decrease the size and cost of the system, and to enable use of the system at very low ambient temperatures. Johannessen (39) updated the developments on a gaseous ammonia system using chloride-based adsorbents. Both HD and LD systems were described, showing 100X dosing ranges within 5% accuracy and <1.5% deviation in set-point under a range of exhaust conditions. Start-up units are used that initially draw 550 W in HD, and 250 W in LD applications, but go down to the 100 W range during normal operation. Safety and durability issues appear addressed, and system optimization through testing and simulation is continuing. Jackson (40) described an alternative approach that utilizes ammonium carbamate (chemical formula NH2COONH4). It is available as pellets that release ammonia upon heating with auxiliary hot water. Ammonia salts dissolve in the water and depress the freezing point to −30°C. Development issues include faster start-up and better, more-efficient heating. Thomas and Highfield (41) described some early performance data with an ammonium formate and urea system containing 54% water, versus 67.5% for standard urea solutions. Advantages include reduced freezing point (−30°C), better high-temperature storage stability, lower hydrolysis temperature, no polymerization like with urea (fewer or no deposits), and they demonstrated full "drop-in" capability in a urea system on a new diesel pick-up truck with and SCR system.

To achieve high deNOx efficiency in light-duty applications, good mixing and fast heat-up are important. In this regard, Alano, et al. (42), describe a compact mixer that needs only 75 mm of urea mixing length, compared to 350 mm in some commercial LD SCR systems, enabling the SCR catalyst to be placed closer to the engine. The mixer achieves a urea mixing index of 0.95 (all cross-section NH_3 measurements are within 5% of one another) over a range of gas flows, with a maximum increase in back pressure of 0.4 kPa (4 mbar) during accelerations relative to a conventional system. In the closer position, in tests the SCR catalyst was up to 25C° hotter and achieved 67% deNOx efficiency on the NEDC versus 37% for a catalyst place further back. The mixer could be useful if SCR catalyst is placed on a diesel particulate filter (DPF) for faster light-off or better DPF regeneration versus two separate systems (DPF-SCR or SCR-DPF).

SCR catalyst formulations and design are improving both low- and high-temperature performance, as well as sensitivity to hydrocarbon and sulfur poisoning. Han, et al. (43) showed that low-temperature performance and reduced hydrocarbon effects can be achieved if a ceria oxygen storage catalyst is layered on top of an iron zeolite catalyst. Figure 10 shows the NOx conversion curve relative to the base catalyst. The catalyst helps urea decomposition, thus improving the low-temperature deNOx capability from 32 to 58% at 200°C a LD steady-state test. After eight hours of exposure to high hydrocarbon levels from a burner, the layered catalyst maintained a deNOx efficiency of 80% at 240°C while the original version was only at 60% under the same conditions due to hydrocarbon poisoning.

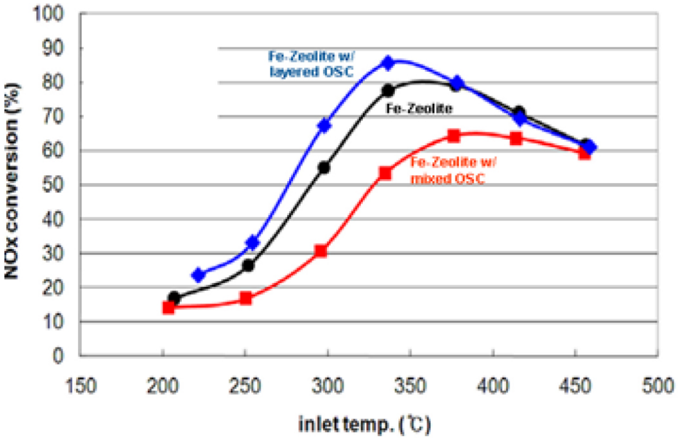


Figure 10. Fe-zeolites layered with a ceria oxygen storage catalyst (OSC) has better urea decomposition performance and is resistant to HC poisoning. (43)

On sulfur poisoning, Tang, et al., (44) using SO2 levels equal to those obtained with ultra-low sulfur diesel fuel (<15 ppm sulfur), the copper zeolite catalyst started losing deNOx efficiency after about 400 hours of operation at temperatures of 200-300°C. Through 1300 hours of operation, the catalyst had deteriorated continuously from 98% deNOx efficiency to 60% efficiency. Also, the NO_2:NOx ratio from the filter deteriorated from 0.60 to 0.30 during the first 600 hours, but then remained the same. They found that most of the sulfur was in the top layer of washcoat in the first third of the catalyst. Most of the poisoning was attributed to ammonium sulfate, which comes off at 400-500°C, and to a much lesser extent, copper sulfate, which comes off at 500-850°C. When heated to 500°C, the SCR catalyst performance recovered, and this was done every 700 hours of operation at the lower temperatures.

Reichert (45) and Narula, et al. (46) showed some new advancements in the zeolite SCR catalyst activity. Reichert showed a new zeolite material that exhibits the same LT performance of copper-zeolites and the same HT performance of iron zeolites. Narula showed that it is possible to modify zeolite structures systematically to influence the electron density at metal centers and to provide ammonia bonding sites in the vicinity of the metal centers. They replaced alumina in the structure with several tri-valent cations. In another contribution (47) they showed that chemical mixtures of copper and iron zeolites can improve LT performance over than copper alone, and when lanthanum is added to the binary formulation performance is improved further.

For US light-duty diesels, removing cold start NOx emissions are key to meeting the tailpipe emissions regulations. A new combination NOx adsorber and SCR catalyst configuration was shown by Henry, et al., (48). Figure 11 shows some performance characteristics. 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 releases 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.

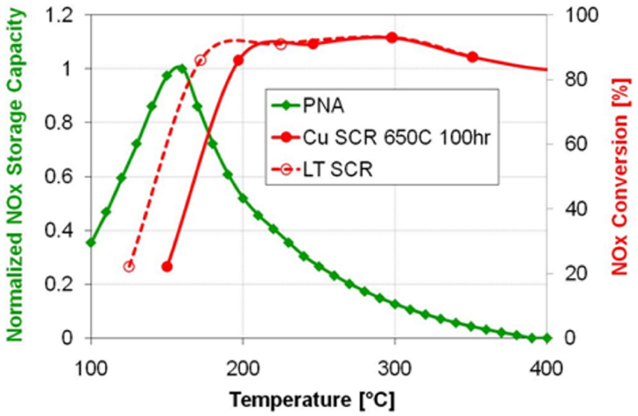


Figure 11. An upstream passive NOx adsorber (PNA) captures NOx generated at T<150°C. A LT urea SCR catalyst can then convert this NOx upon release at T>150°C. (48)

Work is continuing on another type of combination SCR system - the SCR+DPF, wherein SCR catalyst is coated onto the DPF. This allows SCR catalyst to be placed on the vehicle without using an added component, and can get the SCR catalyst closer to the engine for faster light-off. Numerous reports dating to 2008 show total NOx removal efficiency is thus improved, with little compromise in DPF regeneration. Tan, et al., (49) showed a new issue when soot is accumulated on the DPF+SCR: Ammonia storage capacity decreases for fresh samples at all temperatures and soot loadings tested (200-350°C, 1.0 to 2.5 g/liter), but is not affected by soot loading for aged samples (except at 200°C). Loss of ammonia storage capacity impacts SCR performance at 200°C, but not at 300°C at a soot load of 2 g/liter. The researchers also showed that DPF regeneration calibration needs to be adjusted to longer times or higher temperatures to get the same cleaning performance as the base DPF system.

The US EPA capped nitrous oxide (N_2O) emissions in the HD greenhouse gas rule, and is proposing a cap in the LD greenhouse gas rule. Kamasamudram, et al., (50), show that N_2O is very stable, and forms by three mechanisms in an SCR catalyst:

1. LT (T<250°C) decomposition of ammonium nitrate by the reaction $NH_4NO_3 \rightarrow N_2O + 2\ H_2O$.

2. HT oxidation of ammonia by copper zeolites by the reaction: $2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$.

3. Reaction of excess NO_2 (>50% of NOx) to form ammonium nitrate by the reaction: $2NH_3 + 2NO_2 \rightarrow NH_4NO_3\downarrow + N_2 + H_2O$. Ammonium nitrate then decomposes as above.

SCR catalyst improvements can decrease N_2O formation by the first two mechanisms, and better DOC design and control can prevent the third mechanism. Kamasamundram shows that it is possible to reduce N_2O to nitrogen, but these reactions occur at much higher temperatures than those at which they're formed.

For high efficiency SCR deNOx, excess urea injection is needed, perhaps up to 20% more. Ammonia slip catalysts are needed to prevent ammonia release, but these catalysts can also form N_2O. Matsui, et al., (51) show in Figure 12 that the up to 80% of the ammonia going into the slip catalyst can convert to N_2O if there is also a relatively high amount of NO (2X vs. NH_3); the reaction is $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$. A high NO:$NH_3$ ratio coming out of the SCR catalyst can occur, for example, if there is poor urea mixing prior to entering the SCR catalyst and urea is injected at less than stoichiometric requirements. Kamasamundram, et al (50) show that slip catalysts with lower precious metal content minimize N_2O formation.

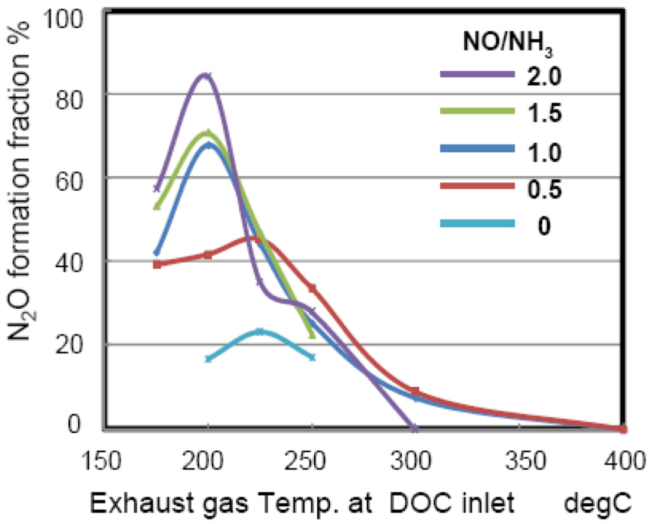


Figure 12. Nitrous oxide formation in ammonia slip catalysts is promoted by high NO:NH_3 ratios coming out of the SCR catalyst. (51)

HC-BASED NOX CONTROL

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%, 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. 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 (selective catalytic reduction) catalyst.

Theis, et al., reported (52) on an interesting study whereby they alternated LNT and SCR slices in one can to check the effect of NOx, ammonia, and hydrocarbon distribution on deNOx performance. The system performance improved as the number of alternating slices of the LNT and SCR increased, keeping the total volume constant. The deNOx efficiency for the eight segment system (four pairs of LNT and SCR catalysts) was 81% in a reference test at 275°C, vs. 78% for four segments, and 60% for two segments. The reference single LNT with no SCR catalyst had only 30% deNOx efficiency. The authors also show reduced N_2O, NH_3, hydrocarbon, and CO emissions with the segmented systems. Various dynamics are operative, but the segmented systems tend to better-match the NO and ammonia concentrations in the SCR, and alternating SCR slices better-adsorb hydrocarbons for enhanced utility.

Xu, et al., reported vehicle and laboratory testing on a 2nd generation LNT+SCR system (53). The DOC+LNT+SCR +DPF system was installed on a prototype F-150 pick-up truck (2610 kg, 4.4 liter V8, turbo-diesel). The aged system (64 hr, 750°C) reduced NOx by 96% to 13.5 mg/mi, and hydrocarbon emissions were 14 mg/mi (−99%), bringing the vehicle to within the emerging California LEVIII limit values (30 mg/mi hydrocarbon + NOx) on the standard certification test cycle. The laboratory work focused on hydrocarbon reductions from the system. The SCR component reduced hydrocarbons about 75%, mainly by adsorption under rich conditions and oxidation under lean conditions. Cavataio et al., (54) compared this capability to that of a urea SCR system for meeting the US EPA Tier 2 Bin 2 (or CARB LEVIII fleet average) standards. Although the LNT+SCR system is 18% smaller, it had met the target emissions while the SCR system fell short. Further, the LNT+SCR system is estimated to be slightly cheaper, but has most of the cost tied up in precious metal (with its inherent price volatility). On the downside, the fuel penalty was high at 10%, versus 2% for the SCR system. Also, sulfur management of the LNT +SCR system was not considered.

In what might be a newly discovered reaction phenomenon, the temperature range of the LNT was extended from 350°C to well over 600°C by managing it differently. Some results are shown in Figure 13. Bisaiji and co-workers at Toyota (55) oscillate the air-fuel ratio between 16 and 24 depending on conditions, but all within the lean regime using an auxiliary exhaust injector. They propose a mechanism involving partially oxidized hydrocarbon intermediaries (observed) reacting with chemisorbed nitrate species, in a type of HC-SCR reaction. The frequency of fuel injection is in the 0.5 Hz range and the deNOx efficiency increases with amplitude of the oscillation, up to about three air:fuel ratio points. Fuel penalties are on the order of 1.5 to 3.0% at medium to high load, and running at about 80% deNOx efficiency (56). The method is sensitive to sulfur poisoning, but can take loadings 3.0X higher than a standard LNT before dropping off below 80% deNOx efficiency. At inlet NOx levels of 100 ppm and temperatures of 370-420°C the method delivers >80% deNOx efficiency at a space velocity (SV) of 125,000/hr with a 2% fuel penalty. The new method is best operated at >50% load (lower loads at higher RPM), and complements standard LNT operation at the lower loads.

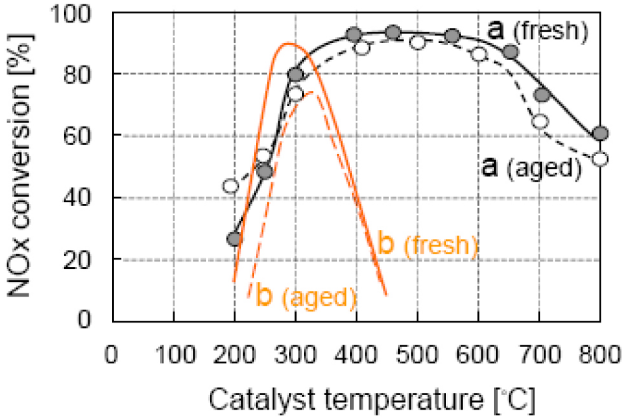


Figure 13. NOx reduction curves for a standard LNT operation (b) and for the same LNT run using the new method (a) of lean air:fuel oscillations at ~0.5 Hz. (55, 56)

HC-SCR

To manage LT NOx, Hirabayashi, et al., use new HC-SCR (hydrocarbon-SCR) approach using a Pt catalyst on a front DOC, and Pd/Pt catalysts on the DPF and rear DOC, in addition to an undisclosed HC-adsorbant material (57). Fuel is dosed ahead of the front DOC to provide NOx reductant. The combination system has a peak deNOx efficiency at 200°C of about 70%, but it rapidly decreases to 20% at 275°C. The system achieves 37% deNOx efficiency on the JE05 heavy-duty transient certification test cycle. Engine methods are used at the higher temperatures to reduce NOx.

Finally, to wrap up the representative studies on deNOx, Jackson (40) updated the industry on using an LNC (silver-alumina) with E85 reductant (15% gasoline, 85% ethanol). Converse to urea, E85 does not freeze and does not leave deposits when injected at low temperatures. The system performs well (>90% efficiency at 350-450°C, SV=38,000/hr) after 500 hours of aging at 650°C, and 100 hours at 800°C. The catalyst was coated onto a DPF and demonstrated 60% deNOx efficiency at 350°C with a C:N level of 3:1. When E100 is used, reductant consumption is 25 to 35% less than for urea SCR at similar levels of performance: >90% deNOx efficiency in the 275 to 375°C range (SV=38,000/hr).

LEAN NOX CONTROL SUMMARY

Lean deNOx control is the leading area of interest in the field of vehicular emissions for good reason - NOx and GHG regulations are tightening, and deNOx translates to "deCO$_2$" using diesel or lean gasoline strategies. Work is continuing on alternative reductant forms involving gaseous and solid reagents, as well as fuels. Urea-SCR is accomplishing deNOx efficiencies of 95% with reasonable systems and temperature ranges. SCR catalysts are evolving with improvements at both the low- and high-temperature regimes. HCSCR approaches are also improving. New system designs for LNT +SCR (in-situ ammonia) improve performance further, and the potential to meet the tightest NOx regulations is demonstrated. When run in novel ways, the applicable temperature range of a standard LNT can be significantly expanded (to 650°C), with modest deNOx efficiencies (80%) at high space velocities (125,000/hr), and modest fuel penalties (<3%). Traditional HC-SCR (LNC) methods are getting renewed attention in commercial applications and with E85 reductant.

DIESEL PARTICULATE FILTERS (DPF)

Although DPFs have been in commercial production for OEM application for more than 10 years, there is still much optimization activity in the field. Work is continuing on DPF regeneration, but several papers were presented on next-generation DPF substrates. More than 10 years ago, in the first wide-scale application of DPFs for particulate control on light-duty diesels, Peugeot chose a ceria-based fuel borne catalyst (FBC) to facilitate the regeneration of the DPF. A new generation of FBC is based on iron, and further improves DPF regeneration characteristics with or without PGM on the DPF (58). Compared to the original of 30 ppm Ce and 10 ppm Ce/Fe in the previous version, the new formulation uses only 5 ppm Fe with similar performance, resulting in half the ash load on the DPF. The authors estimate that for a car with a fuel consumption of 7 liters/100 km (33 miles/gallon), the DPF ash cleaning interval is 300,000 to 400,000 km, depending on filter design. The new FBC drops the DPF regenerating start temperature of a stock PGM-catalyzed DPF (CSF) from 410°C to 360°C, and increases the total soot burn from 12% in the baseline ramp-up test (to 500°C) to 75% with the FBC-CSF combination. The improved regeneration efficiency and decreased temperature will reduce thermal exposure of the SCR catalyst in Euro 6 systems, as well as reduce DPF regeneration fuel penalty when the SCR system is located upstream of the DPF.

More work on DPF membranes were reported to enhance filtration and reduce back pressure (59). In vehicle testing, pressure drop was reduced 30-40% depending on speed and soot load, relative to the same filter without a membrane. This membrane benefit was also demonstrated on SCR-coated DPFs in engine dynamometer testing. Alternatively, in engine tests the investigators demonstrated that the membrane can be used to increase the soot mass limit of a cordierite DPF about 2 g/liter without a back pressure penalty by applying it to a lower-porosity substrate.

Boger, et al., took a different approach to reducing back pressure in DPFs (60). They tightened the pore size distribution and decreased porosity in the next-generation aluminum titanate filter to provide either a 2-3 g/liter increase in soot mass limit, or a 20-25% back pressure reduction, depending on cell geometry. Catalyzed samples of the low-pressure-drop version has 20-30% lower back pressure with no soot on the filter and 15-20% lower back pressure with 6 g/liter soot loading, Figure 14. The soot mass limit was similar to that of an SiC (silicon carbide) filter with the same cell geometry, but the SiC version has 50% higher back pressure. As a result of lower thermal conductivity, the regeneration efficiency of the new filter in a standard drop-to-idle test at 575°C is 6% higher than the earlier version, and 16% higher than the SiC comparison.

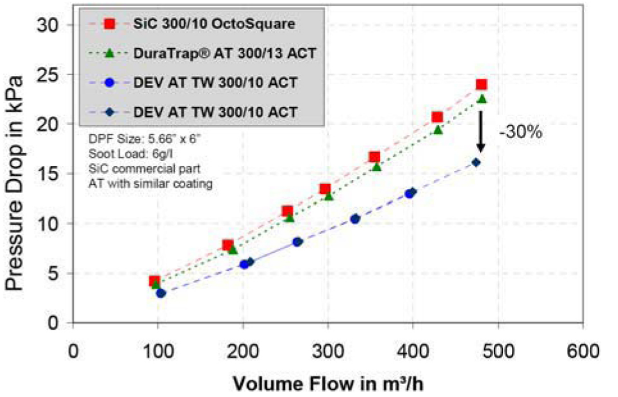


Figure 14. Pressure drop comparisons for the next generation aluminum titanate filter (DEV AT), in the low-pressure-drop thinwall (TW) version. 300/10 refers to 300 cells per square inch with 10 mil wall thickness. (60)

Taking advantage of improvements in SCR technology, future heavy-duty engines will be calibrated to higher NOx and lower PM to save fuel. This will result in favorable conditions for passive oxidation of soot by NO_2 and dramatically decrease the need for active regeneration of the DPF at high soot loads. Less thermal mass will be needed in the DPF to provide a buffer against uncontrolled active regenerations. Boger, et al., reported on the next-generation thinwall cordierite filter to address this trend (61). Relative to the current offering, the pore size distribution was tightened and made nominally smaller, and the porosity was increased to ~55%. Wall thickness was reduced 33% in the 200-csi (cells/square inch) geometry. To enable this, the inherent strength of the cordierite was increased. As with membrane technology, this redesigned porosity allows little, if any, soot penetration into the wall that causes rapid build-up of back pressure. Also, coated and uncoated filters have little back pressure differences. The result is that soot-laden filters have 40-50% lower back pressure than their 2010 predecessors under a variety of conditions. Interestingly, because of the reduced thermal mass, skin temperatures are higher but centerline temperatures are the same during active regeneration, reducing the thermal stress in the part. Although the authors made no mention of soot mass limit impacts, the filter survives worst-case drop-to-idle testing at 3.5 g/liter soot. The lower thermal mass of the DPF allows faster heat-up of a downstream SCR catalyst, resulting in 10% more time for urea injection in the US certification test cycle. This can result in 15% lower cumulative NOx emissions in the cold-start test (62).

To facilitate the addition of deNOx catalyst to the DPF, Warkins et al., (63) increased the porosity in a new aluminum titanate (ATHP) filter. Figure 15 shows that with a heavy catalyst coating and high soot loading, the pressure drop of the new DPF is 25% higher than a lightly-coated low-porosity (LP) thinwall version designed for low-pressure drop (−25% vs. current). However, the AT-HP filter does not require a separate SCR catalyst, so overall system back pressure is reduced upwards of 20%. The new AT-HP filter also has a 2 g/liter higher soot mass limit than the current commercialized AT filter. Cycle-averaged deNOx efficiency with SCR catalyst on the HP filter was 62% (urea injection starts at 400 seconds), vs. 23% (injection at 1100 second) when a separate SCR catalyst is placed behind the uncoated DPF.

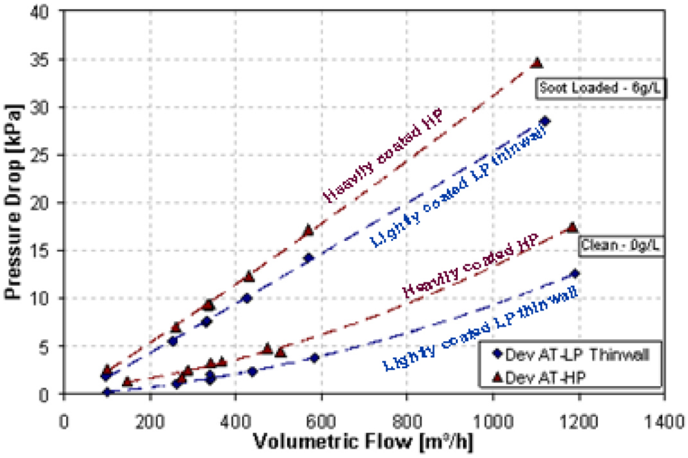


Figure 15. A new AT high-porosity filter (AT-HP) with high catalyst loading has slightly higher back pressure than a lightly coated low-porosity low-back pressure filter. However, the overall system back pressure is reduced 20% if a separate SCR catalyst is eliminated. (63)

The DPF field was also advanced with some insightful fundamental work. Fujii (64) looked at how DPF cell geometry and porosity affect filtration efficiency and back pressure as ash (from lube oil and wear) is collected in the filter. He studied filters with 200- and 300-csi (cells per square inch) and 12 mil (0.3 mm) wall thickness, with 50% porosity and 15 μm average pore size and 65% porosity with 20 μm pore size. Because early ash loadings prevent soot from penetrating into the wall, the lowest back pressure with high filtration efficiency appears with an ash loading of 4-10g/liter. Low-back pressure sensitivity to soot and ash loading depends on DPF designs and materials: Larger open frontal area gives lower sensitivity, as does higher porosity. Interestingly, filters that were continuously regenerated (like with NO_2) achieve high filtration efficiency (>97%) after only 20 g/liter ash is accumulated. Filters managed by periodic regeneration need 140 g/liter ash to achieve the same level of efficiency because the ash generally collects in the back of the filter without forming much of a filtration membrane. Rakovec, et al., (65) used wafers machined out of commercial DPFs to look at how filter wall permeability varies with gas flow rate, PM loading, and PM type. Most of the wall permeability impacts are due to the substrate. Normalized wall permeability starts out similarly for high face velocity, independent of particle number (PN) levels in the exhaust. But later, exhaust with low PN levels produces higher permeability due to more particles going into wall and forming a thinner cake. Low flow, high PN allows low cake density and higher ending permeability, but with a thicker cake. High nucleation-mode particle loading allows particle penetration into the wall and early bridging, resulting in a fast drop in permeability and low final permeability. The results should be useful in refining filter back pressure models that are used to manage filter regeneration.

DPF SUMMARY

Filter technology is advancing to provide systems with incrementally 20-30% lower back pressure, similar or higher soot mass limit to improve DPF management, and better filtration efficiency. DPF designs can help deNOx performance through reduced thermal mass, allowing faster heat-up of the downstream deNOx catalyst or by allowing incorporation of the catalyst on the filter, allowing faster light-off with reduced system back pressure. Fundamental knowledge on ash and soot membranes will allow the trend to continue.

DIESEL OXIDATION CATALYSTS (DOC)

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.

Henry, et al. (66), looked at the interplay of these two functions by using a series of iterative reaction-decoupling experiments to explain interactions between hydrocarbon and NO oxidation. They showed that NO oxidation is inhibited on Pt/Pd due to the reduction reaction with NO_2 by hydrocarbons. Long chain alkanes had a more adverse effect than short chain alkenes due to slower oxidation rate with oxygen. Decreasing space velocity was shown to help NO_2 formation in the presence of hydrocarbons. Pre-storing hydrocarbons on the DOC improved NO oxidation up to 300°C.

Kim, et al. (67), did a systematic study on the effects of varying the Pt:Pd ratio on DOC hydrocarbon and NO oxidation and durability in a variety of conditions. All bimetallic Pt-Pd catalysts show better hydrocarbon light-off activity and thermal stability than the Pt- or Pd-only catalyst. NO oxidation to NO_2 was found to always depend directly on platinum content, with similar durability trends as with hydrocarbons. Figure 16 shows a schematic representation of these findings. They found that hydrocarbon-CO mixtures synergistically have ∼20C° lower light-off temperatures than either one alone.

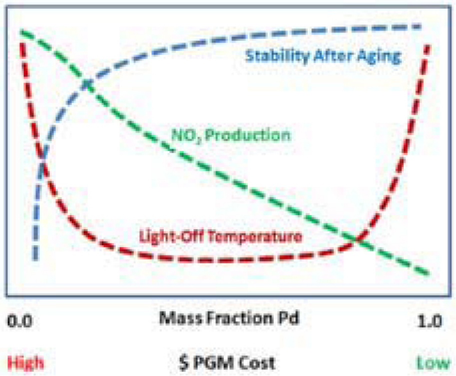


Figure 16. Conceptual impact of increasing Pd content at the expense of Pt in DOCs. Moderate substitutions improve durability and HC oxidation, without significant deterioration of NO oxidation. (67)

Glover and coworkers (68) also did a study on Pt:Pd effects on DOC properties, adding N_2O formation and looking more at fundamentals. CO plays a key role on the overall catalyst performance by its positive effect on propylene oxidation which, in turn, is responsible for NO reduction to N_2O and the onset of NO_2 formation. On the Pt:Pd=4:1 catalyst, propylene partially reduces NO to form N_2O at about 200°C, but this temperature shifts to 250°C when is CO added. The effect of higher Pd concentration on NO conversion is detrimental for NO oxidation to NO_2, but is positive for producing less N_2O, especially at high oxygen concentrations. NOx storage and release may play an important role in NO_2 formation over the lightly-loaded full Pt DOC formulation studied. A 40g/ft3 (1.4 g/liter) bimetal formulation (Pt:Pd=4:1) is comparable on CO and HC light-off to a 113g/ft3 Pt formulation. Closing on N_2O formation, Kamasandrum, et al. (50) show propylene forms much more N_2O than dodecane ($C_{12}H_{26}$).

Potential adverse effects of biodiesel ash on DOCs and other emissions control components was described by a large research group led by the National Renewable Energy Laboratory (69). The group reported that, after a simulated 150,000 miles of durability testing, HC slip increased nominally 20-25% over the range of temperatures in steady-state tests (240-390°C) as a result of alkali exposure from the biodiesel ash. NO_2 formation declined from 35 to 20%. In addition, the thermal shock parameter of the DPF, as indicated by mechanical property measurements, declined 69% after simulated exposure of 435,000 miles, again due to alkali attack of the cordierite substrate. NOx emissions from the SCR increased about 50%, but more work was needed to determine if this was due to alkali attack of the zeolite catalyst. The group concluded that operating with fuel at the maximum alkali ash specification will significantly deteriorate emission control system performance.

GASOLINE EMISSION CONTROL

In the last year or two, the automotive industry has become more interested in gasoline emission control technology, driven by the LEVIII and Euro 6 PN regulations for direct injection engines.

Aoki, et al., reported on complex TWC coating architectures as a way of improving performance and reducing precious metal loadings (70). They showed that HC light-off time is reduced 50% if all the palladium is concentrated in the front 20% of the catalyst substrate. Conversely, because rhodium is poisoned by phosphorous poisoning (from lube oil ash), it should be concentrated in the back 20% of the substrate. They also showed that ceria-zirconia washcoats can be formulated for different properties and distributed on the substrate accordingly. Zirconia-rich recipes (0 to 0.40 ceria:zirconia mole ratio) release oxygen fastest, and therefore should be in the front half of the catalyst, while ceria-rich formulations (0.8 to 1.2) store more oxygen, and are best located in the back half. To wrap up the study, they showed that an alumina addition can prevent zirconia sintering and allow better rhodium dispersion, and niobia can prevent grain growth of rhodium catalyst.

Ball, et al. (71), reported on meeting the LEVIII challenge more efficiently by moving the under body catalyst to directly behind the close-coupled catalyst. Hydrocarbon and NOx emissions are cut 25%. They also looked at optimizing precious metal loadings with the new design. Six recipes reduce precious metal loading by up to 25% from the previous PZEV (partial zero emission vehicle) design, while meeting a 20 mg/mile NMHC+NOx on the FTP (Federal Test Procedure) light-duty transient cycle. This is low enough to meet the lowest certification level in the proposed LEVIII regulation.

In another contribution, Ball, et al. (72), showed why low-sulfur gasoline is an important enabler for modern catalysts to meet the LEVIII regulations. Figure 17 shows the results. If the fuel contains 33 ppm sulfur, the poison builds up on the catalyst in back-toback tests (T1-T3, first set of data). If a hot US06 high-load test cycle is run, some of the sulfur is purged, dropping NOx emissions 30% (second set of bars). Alternatively, and quite pertinent to urban low-load operation, if the fuel sulfur is dropped to 3 ppm the NOx emissions are cut by 40% without the need for a high-load purge.

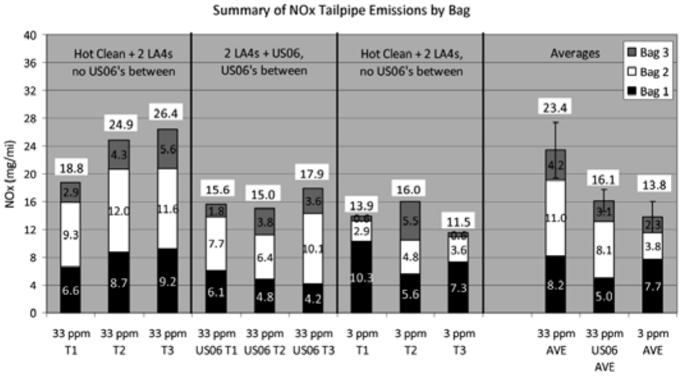


Figure 17. Sulfur adversely impacts NOx emissions from TWC. It builds up in sequential urban testing (LA4 cycle, first set of bars), but is partially purged in high-load cycles (US06, second set of bars). Purges are not needed if the fuel-sulfur level is 3 ppm. (72)

Lean burn direct injection engines are emerging to meet the current and upcoming CO_2 regulations in the major world automotive markets. Lean NOx Traps (LNTs) are used to meet the NOx regulations, but GM showed in two papers an alternative design (73, 74). They describe a TWC+SCR approach, similar to the LNT+SCR approach, wherein ammonia generated from the TWC during rich tipins in normal operation is stored and utilized in a downstream SCR catalyst for use during lean operation. The first paper shows that ammonia production in the TWC is enhanced with palladium-only formulations, while rhodium, although beneficial for CO oxidation and stoichiometric NOx reduction, contributes little to ammonia generation. Oxygen storage catalyst (OSC) detracts from ammonia generation, but is beneficial for CO and HC oxidation. However, CO and HC oxidation can be promoted with higher palladium loadings (200 g/ft3 vs. 60 g/ft3 in the base formulation). The authors conclude that the system might be suitable for European applications, where the NOx regulations are not as tight, but more research is needed on optimizing precious metal and washcoat formulations, and in improving the SCR catalyst durability and performance. In the second paper, the researchers used the TWC+SCR system in a stoichiometric direct injection engine adapted for lean idle and aggressive deceleration fuel cutoff (DFCO), saving 11% on fuel consumption. DFCO sends air through the system, cooling the catalyst and saturating the OSC with oxygen, adversely impacting stoichiometric deNOx functionality. The combination aftertreatment system drops NOx by 95% with this engine strategy compared to a TWC system only.

Finally, Sato, et al. (75), describe some fundamental differences between gasoline particulate filtration and diesel. Gasoline PM emissions are much lower (20%), but much hotter (700°C vs. 400°C, max). And, while the oxygen levels are much lower for gasoline (0-20% vs. 10-20%), the combination of light loading, high temperatures, and periodic high oxygen, for example on fuel cut-off during decelerations, allows the gasoline particulate filter (GPF) to passively regenerate. Filters placed in the cooler under body position versus the close coupled position have 15% higher filtration efficiency (92% vs. 77%), probably due to lower gas velocity due to cooler exhaust; but on the NEDC there was complete GPF regeneration for the close-coupled filter, while the underbody filter only partially regenerated. A GPF with a back pressure of 10 kPa at full load drops engine power output by only 1%, and has a negligible CO_2 impact on the NEDC. These results are similar to those reported by Mikulic, et al. (76). Of course, if the GPF needs to be actively regenerated, the CO_2 emission will go up. This impact is being investigated.

SUMMARY/CONCLUSIONS

REGULATIONS

The California LEVIII regulations will drive another round of emissions control technologies on the engines and in the tailpipe. The fleet average emissions structure, as well as the sum of NMOG+NOx provides flexibility without sacrificing air quality. Europe is headed towards assuring that real-driving emissions are reduced as much as the certification testing predicts. The US LD GHG proposal also provides flexibility but likewise calls for significant reductions. The combination of criteria pollutant tightening and mandated CO_2 reductions present surmountable but challenging requirements on the auto industry. Long term mandates are defined to provide the industry time to meet the challenge. On the heavy-duty side, GHG emissions reductions are just beginning, and cover both engine and vehicle reductions. For NRMM (non-road mobile machinery) applications, as with the previous round of tightening, Europe is setting up for the next round of criteria pollutant tightening, generally harmonizing with Euro VI.

ENGINES

Light-duty gasoline engine technology is headed towards up to 40% CO_2 reductions compared to today's multi-port injection engines. Key technologies are to downsize the engine with direct injection, turbocharging, and variable valve actuation. BMEPs could get as high as 35 bar, presenting auto-ignition and fuel octane issues. Lean burn engines are also indicated. Diesel engines are also advancing, but more incrementally. The CO_2 emissions will likely remain lower than those of future gasoline engines, making them an attractive option.

On the HD side, the low criteria pollutant and emerging CO_2 regulations are placing a significant challenge on engine makers. Market forces have always made low fuel consumption a competitive advantage, so these engines are already quite efficient. However, it appears there is still much more that can be done and still deliver customer value. High-NOx calibrations are a leading way of decreasing fuel consumption, but this will require 97+% deNOx capability going into the future. At such high engine-out NOx (>8 g/kW-hr), even a 1% drop in deNOx efficiency can increase NOx emissions by 33%. These deNOx strategies will require excellent control and durability, as well as good oxidation of excess ammonia to prevent forming NOx. Alternatively, the low-NOx high-EGR strategies might deliver more customer acceptance by removing the burden of urea filling and its system cost. These strategies will require robust DPFs and good active regeneration strategies to manage the high soot levels coming from the engine and to minimize the DPF fuel penalty.

LEAN NOX TREATMENT

Lean deNOx control is the leading area of interest in the field of vehicular emissions for good reason - NOx and GHG regulations are tightening, and deNOx translates to “deCO_2” using diesel or lean gasoline strategies. Work is continuing on alternative reductant forms involving gaseous and solid reagents, as well as fuels. Urea-SCR is accomplishing deNOx efficiencies of 95% with reasonable systems and temperature ranges. SCR catalysts are evolving with improvements at both the low- and high-temperature regimes. HCSCR approaches are also improving. New system designs for LNT +SCR (in-situ ammonia) improve performance further, and the potential to meet the tightest NOx regulations is demonstrated. When run in novel ways, the applicable temperature range of a standard LNT can be significantly expanded (to 650°C), with modest deNOx efficiencies (80%) at high space velocities (125,000/hr), and modest fuel penalties (<3%). Traditional HC-SCR (LNC) methods are getting renewed attention in commercial applications and with E85 reductant.

DIESEL PARTICULATE FILTERS

Filter technology is advancing to provide systems with incrementally 20-30% lower back pressure, similar or higher soot mass limit to improve DPF management, and better filtration efficiency. DPF designs can help deNOx performance through reduced thermal mass, allowing faster heat-up of the downstream deNOx catalyst or by allowing incorporation of the catalyst on the filter, allowing faster light-off with reduced system back pressure. Fundamental knowledge on ash and soot membranes will allow the trend to continue.

DIESEL OXIDATION CATALYSTS

Much of the new reports on DOCs concerned the interplay of precious metal formulations on hydrocarbon oxidation, NO oxidation to NO_2, and the formation of N_2O. Hydrocarbon and CO oxidation is promoted by replacement of platinum with palladium, but NO_2 formation is compromised. NO_2 can not form if hydrocarbons are present, as the HCs will reduce any NO_2 back to NO. HCs are also instrumental in reducing NO to N_2O, particularly at ~200-250°C if CO is not present.

GASOLINE EMISSIONS CONTROL

The three-way catalyst is advancing, with zone coating of palladium, rhodium, and oxygen storage material. Precious metal usage is decreasing, even as performance improves. Some new designs to meet the LEVIII regulations are introduced, and sulfur impacts can be quite significant, even at 33 ppm sulfur in the fuel and particularly in low-load driving conditions. Gasoline particulate filter operating parameters are described, and they appear to be an option to meeting the new PN regulations in Europe.

CONTACT INFORMATION

Tim Johnson can be reached at JohnsonTV@Corning.com

ACKNOWLEDGEMENTS

Justin Sloan of Stoneridge provided a useful summary of the key OBD regulations.

REFERENCES

1. US EPA, "Light-Duty Automotive Technology, Carbon Dioxide Emissions, and Fuel Economy Trends: 1975 Through 2010", EPA 420-R-10-023, November 2010.
2. Johnson, T., "Diesel Emissions in Review," *SAE Int. J. Engines* 4(1): 143-157, 2011, doi:10.4271/2011-01-0304.
3. "Low-Emission Vehicles (LEV) & GHG 2012", http://www.arb.ca.gov/regact/2012/leviiighg2012/leviiighg2012.htm
4. "Zero Emission Vehicles 2012", http://www.arb.ca.gov/regact/2012/zev2012/zev2012.htm.
5. MVEG meeting notes from October 10, 2011, http://circa.europa.eu/Public/irc/enterprise/automotive/library?l=/mveg_vehicle_emissions/110th_october_2011
6. http://globalautoregs.com/ee_rules
7. Honardar, S., Busch, H., Schnorbus, T., Severin, C., et al., "Exhaust Temperature Management for Diesel Engines Assessment of Engine Concepts and Calibration Strategies with Regard to Fuel Penalty," SAE Technical Paper 2011-24-0176, 2011, doi:10.4271/2011-24-0176.
8. "2017 and Later Model Year Light-Duty Vehicle Greenhouse Gas Emissions and Corporate Average Fuel Economy Standards" http://www.gpo.gov/fdsys/pkg/FR-2011-12-01/pdf/2011-30358.pdf; summary and supporting documents at http://www.epa.gov/otaq/climate/regulations.htm#1-1.
9. Graph is updated frequently at www.TheICCT.org. version here is from August 2011.
10. Minister of Environmental Protection Announcement No. 92, 2011, December 29, 2011.
11. November 2011 communication with Prof. Yasuhiro Daisho.
12. Directive 2011/88/Eu of the European Parliament And Of The Council of 16 November 2011, http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:305:0001:0005:EN:PDF
13. "Greenhouse Gas Emissions Standards and Fuel Efficiency Standards for Medium- and Heavy-Duty Engines and Vehicles", 57106 Federal Register / Vol. 76, No. 179 / Thursday, September 15, 2011 / Rules and Regulations. Other documentation and summaries at http://www.epa.gov/otaq/climate/regulations.htm#1-2.
14. Bunker, B., "U.S. HDV GHG and Fuel Efficiency Final Rule", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
15. Leonhard, R., "Clean Diesel Technology - Efficient Emission Reduction", Near-Zero Emission Vehicle Conference, Jeju, Korea, June 2009.
16. Pischinger, S., "Efficient Powertrain Technology for the Future", keynote speech, Joint SAE/SIAT Conference, Pune, India, January 2012.
17. Johnson, T. V., "Vehicle Emissions Review - 2011 (so far), US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
18. Fraidl, G. K., Kapus, P. E., "GDI-tc Solutions for the Worldwide Market", CTI Emissions 2011 Conference, Detroit, May 2012.
19. Kalghatgi, G., "Implications of IC Engine Technology Trends for Future Road Transport Fuels", keynote speech at Joint SAE/Naples SAE ICE2011 Conference, Naples, September 2011.
20. Schumann, F., Buri, S., Kubach, H., Spicher, U., Hall, M. J., "Investigation of Particulate Emissions from a DISI Engine with Injection Pressures up to 1000 bar", Aachen Colloquium, October 2010.
21. Khalek, A., "Particle Emissions from StoichiometricGDI Engines", CTI Emissions 2011 Conference, Detroit, May 2011.
22. Nakata, K., "Future Engine Technologies for Improving the Fuel Economy," Presentation at SAE High-Efficiency Engine Symposium, Detroit, April 2011.
23. Boggs, D., King, J. "Application of Synergistic Technologies to Achieve High Levels of Gasoline Engine Downsizing", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
24. Obiols, J., Soleri, D, Dioc, N., and Moreau, M., "Potential of Concomitant Injection of CNG and Gasoline on a 1.6L Gasoline Direct Injection Turbocharged Engine," SAE Technical Paper 2011-01-1995, 2011, doi:10.4271/2011-01-1995.
25. Chadwell, C., Alger, T. Roberts, C., and Arnold, S., "Boosting Simulation of High Efficiency Alternative Combustion Mode Engines," *SAE Int. J. Engines* 4(1):375-393, 2011. doi:10.4271/2011-01-0358.
26. Popuri, S., Langenderfer, D., Cunningham, M., Vajapeyazula, P., Garimella, P., Joshi, A., Cecil, A, Frazier, T., and Stanton, D., "Demonstration of >10% FTP75 Cycle Efficiency Improvement for a Light-Duty Diesel Engine System at T2B5 Tailpipe Emissions Levels", SAE Light-Duty Diesel Emissions Symposium, Detroit, November 2011.
27. Regner, G., Herold, R., Wahl, M., Dion, E., et al., "The Achates Power Opposed-Piston Two-Stroke Engine: Performance and Emissions Results in a Medium-Duty Application," *SAE Int. J. Engines* 4(3): 2726-2735, 2011, doi:10.4271/2011-01-2735.
28. Greene, D., Baker, H. H.Jr., "Energy Efficiency Potential of Global Transportation to 2050", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
29. Roberts, C., "The Pursuit of High Efficiency Engines-SwRI Programs", Emissions 2011 Conference, Ann Arbor, MI, June 2011.
30. Stanton, D., "Technology Development for High Efficiency Clean Diesel Engines and a Pathway to 50% Thermal Efficiency", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, September 2009, Detroit.
31. Zybell, J. G., "Technology Path to Meet Future Fuel Economy Targets in the CV Segment", Integer Diesel Emissions Conference and DEF Forum, Atlanta, October 2011.
32. Kobayashi, M., Aoyagi, Y., Adachi, T, Murayama, T., Hashimoto, M., Goto, Y., Suzuki, H., "Effective BSFC and NOx Reduction on Super Clean Diesel of Heavy Duty Diesel Engine by High Boosting and High EGR Rate," SAE Technical Paper 2011-01-0369, 2011, doi:10.4271/2011-01-0369.
33. de Ojeda, W., "Development and Demonstration of a Fuel-Efficient HD Engine (Dept of Energy Supertruck Program)", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
34. Ligterink, N., de Lange, R., Vermeulen, R., Dekker, H., "On-Road NOx Emissions of Euro-V Trucks", TNO report MON-RPT-033-DTS-2009-03840, 2 December 2009, Assignor Ministerie van VROM, Den Haag.
35. Vermeulen, R., Vonk, W., and Dekker, H., "Real-World Exhaust Gas Emissions of a Prototype N3 Heavy Duty Vehicle with Euro VI Technology", TNO-RPT-2011-00076, 27 October 2011.
36. Koeberlein, D., "Cummins SuperTruck Program Technology Demonstration of Highly Efficient Clean, Diesel Powered Class 8 Trucks", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
37. Aneja, R., Singh, S., Sisken, K., Rotz, D., and Ziegler, M., "Super Truck - 50% Improvement In Class 8 Freight Efficiency", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
38. Pascal Amar, P., Gibble, J., Brantley, K., "Volvo Super Truck Program", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.
39. Johannessen, T., "Next Generation SCR System for Fuel-Efficient NOx Reduction," Presentation at SAE Light-Duty Diesel Emissions Symposium, Detroit, November 2011.
40. Jackson, T., "Alternatives to Liquid Urea SCR for NOx Abatement HC LNC and SOLID SCR", CTI Emissions Conference, May 2011, Detroit.
41. Thomas, D., and Highfield, T., "Ammonium Formate/Urea Based Diesel Exhaust Fluid for Superior Low Temperature SCR Performance," Presentation at SAE Light-Duty Diesel Emissions Symposium, Detroit, November 2011.

42. Alano, E., Jean, E., Perrot, Y., Brunel, J.-P., Ferrand, N., Ferhan, M., Chapel, J., and Pajot, K, "Compact SCR for Passenger Cars," SAE Technical Paper 2011-01-1318, 2011, doi:10.4271/2011-01-1318.

43. Han, J., Kim, E., Lee, T., Kim, J., Ahn, N., and Han, H.-S., "Urea-SCR Catalysts with Improved Low Temperature Activity," SAE Technical Paper 2011-01-1315, 2011, doi:10.4271/2011-01-1315.

44. Tang, W., Huang, X., and Kumar, S., "Sulfur Effect and Performance Recovery of a DOC + CSF + Cu-Zeolite SCR System", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.

45. Reichert, M., "Experience with SCR Systems and Expectations on Future Developments", 7th International CTI Conference: SCR-Systems, July 2011, Stuttgart.

46. Narula, C., Yang, X., Bonnesen, P., and Hagaman, E., "High Performance NH3 SCR Zeolite Catalysts for Treatment of NOx in Emissions from Off-Road Diesel Engine," SAE Technical Paper 2011-01-1330, 2011, doi:10.4271/2011-01-1330.

47. Yang, X., Narula, C., "Simple Approach to Tuning Catalytic Activity of MFI-Zeolites for Low Temperature SCR of NOx", poster at US Department of Energy "Directions in Engine Efficiency and Emissions Research (DEER) Conference", September 27-30, 2010, Detroit.

48. Henry, C., Langenderfer, D., Yezerets, A., Ruth, M., Chen, H.-Y., Hess, H., and Naseri, M., "Passive Catalytic Approach to Low Temperature NOx Emission Abatement", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.

49. Tan, J., Solbrig, C., and Schmieg, S. J., "The Development of Advanced 2-Way SCR/DPF Systems to Meet Future Heavy-Duty Diesel Emissions," SAE Technical Paper 2011-01-1140, 2011, doi: 10.4271/2011-01-1140.

50. Kamasamudram, K., Henry, C., and Yezerets, A., "N_2O Emissions From 2010 SCR Systems", US Department of Energy, Directions in Engine Efficiency and Emissions Research (DEER) Conference, October 3-6, 2011, Detroit.

51. Matsui, W., Suzuki, T., Ohta, Y., Daisho, Y., Suzuki, H., and Ishii, H., "A Study on the Improvement of NOx Reduction Efficiency for a Urea SCR System (Sixth Report) - Clarifying N_2O formation mechanism", JSAE paper 20115720, October 2011.

52. Theis, J. R., Dearth, M., and McCabe, R., "LNT+SCR Catalyst Systems Optimized for NOx Conversion on Diesel Applications," SAE Technical Paper 2011-01-0305, 2011, doi:10.4271/2011-01-0305.

53. Xu, L., McCabe, R., Tennison, P., and Jen, H-W., "Laboratory and Vehicle Demonstration of "2nd-Generation" LNT + in-situ SCR Diesel Emission Control Systems," *SAE Int. J. Engines* 4(1):158-174, 2011, doi:10.4271/2011-01-0308.

54. Cavataio, G., Guo, K., Xu, L., Dobson, D., Warner, J., Dearth, M., Theis, J., Ruona, W., McCabe, R., and Lambert, C., "Comparing Urea SCR to in-situ LNT+SCR Aftertreatment Systems for Light Duty Vehicles", SAE Light-Duty Diesel Emissions Symposium, November 2011, Ypsilanti, MI.

55. Bisaiji, Y., Yoshida, K., Inoue, M., Umemoto, K., and Fukuma, T., "Development of Di-Air - A New Diesel deNOx System by Adsorbed Intermediate Reductants," *SAE Int. J. Fuels Lubr.* 5(1):380-388, 2012, doi:10.4271/2012-01-2089.

56. Inoue, M., Fukuma, T., Bisaiji, Y., and Yoshida, K., "Di-Air: The New deNOx System for Future Emission Compliance", Aachen Colloquium, October 2011.

57. Hirabayashi, H., Furukawa, T., Koizumi, W., Koyanagi, W., Saitou, Y., and Tanaka, S., "Development of New Diesel Particulate Active Reduction System for both NOx and PM Reduction," SAE Technical Paper 2011-01-1277, 2011, doi:10.4271/2011-01-1277.

58. Rocher, L., Seguelong, T., Harle, V., Lallemand, M., Pudlarz, M., and Macduff, M., "New Generation Fuel Borne Catalyst for Reliable DPF Operation in Globally Diverse Fuels," SAE Technical Paper 2011-01-0297, 2011, doi:10.4271/2011-01-0297.

59. Iwasaki, S., Mizutani, T., Miyairi, Y., Yuuki, K., and Makino, M., "New Design Concept for Diesel Particulate Filter," *SAE Int. J. Engines* 4(1): 527-536, 2011, doi:10.4271/2011-01-0603.

60. Boger, T., Jamison, J., Warkins, J., Golomb, N., Warren, C., and Heibel, A., "Next Generation Aluminum Titanate Filter for Light Duty Diesel Applications," SAE Technical Paper 2011-01-0816, 2011, doi: 10.4271/2011-01-0816.

61. Boger, T., He, S., Collins, T., Heibel, A., Beall, D., and Remy, C., "A Next Generation Cordierite Diesel Particle Filter with Significantly Reduced Pressure Drop," *SAE Int. J. Engines* 4(1):902-912, 2011, doi: 10.4271/2011-01-0813.

62. Heibel, A., "Advances in HD Substrate Technology", SAE Heavy-Duty Emissions Symposium, Gothenburg, September 2010.

63. Warkins, J., Heibel, A., George, S., Golomb, N., and Warren, C., "Light Duty Filters", Presentation at SAE LD Diesel Emissions Control Sypmosium, November 2011, Ypslilanti, MI.

64. Fujii, S., "DPF Design Optimization from View Point of the Lifetime Performance with Ash Loading", Emissions 2011 Conference, June 2011, Ann Arbor, MI.

65. Rakovec, N., Viswanathan, S., and Foster, D., "Micro-scale Study of DPF Permeability as a Function of PM Loading *SA*," *SAE Int. J. Engines* 4(1):913-921, 2011, doi:10.4271/2011-01-0815.

66. Henry, C., Currier, N., Ottinger, N., Yezerets, A., Castagnola, M., Chen, H.-Y., and Hess, H., "Decoupling the Interactions of Hydrocarbons and Oxides of Nitrogen over Diesel Oxidation Catalysts," SAE Technical Paper 2011-01-1137, 2011, doi:10.4271/2011-01-1137.

67. Kim, C. H., Schmid, M., Schmieg, S. J., Tan, J., and Li, W., "The Effect of Pt-Pd Ratio on Oxidation Catalysts Under Simulated Diesel Exhaust," SAE Technical Paper 2011-01-1134, doi:10.4271/2011-01-1134.

68. Glover, L., Douglas, R., McCullough, G., Keenan, M., Revereault, P., and McAtee, C., "Performance Characterisation of a Range of Diesel Oxidation Catalysts: Effect of Pt:Pd Ratio on Light Off Behaviour and Nitrogen Species Formation," SAE Technical Paper 2011-24-0193, 2011, doi:10.4271/2011-24-0193.

69. Williams, A., McCormick, R., Luecke, J., Brezny, R., Geisselmann, A., Voss, K., Hallstrom, K., Leustek, M., Parsons, J., and Abi-Akar, H., "Impact of Biodiesel Impurities on the Performance and Durability of DOC, DPF and SCR Technologies," *SAE Int. J. Fuels Lubr.* 4(1): 110-124, 2011, doi:10.4271/2011-01-1136.

70. Aoki, Y., Sakagami, S., Kawai, M., Takahashi, N., Tanabe, T., and Sunada, T., "Development of Advanced Zone-Coated Three-Way Catalysts," SAE Technical Paper 2011-01-0296, 2011, doi: 10.4271/2011-01-0296.

71. Ball, D., Zammit, M., Wuttke, J., and Buitrago, C., "Investigation of LEV-III Aftertreatment Designs," *SAE Int. J. Fuels Lubr.* 4(1):1-8, 2011, doi:10.4271/2011-01-0301.

72. Ball, D., Clark, D., and Moser, D., "Effects of Fuel Sulfur on FTP NOx Emissions from a PZEV 4 Cylinder Application," SAE Technical Paper 2011-01-0300, 2011, doi:10.4271/2011-01-0300.

73. Kim, C. H., Perry, K., Viola, M., Li, W., and Narayanaswamy, K., "Three-Way Catalyst Design for Urealess PassiveAmmonia SCR: Lean-Burn SIDI Aftertreatment System," SAE Technical Paper 2011-01-0306, 2011, doi:10.4271/2011-01-0306.

74. Guralp, O., Qi, Q., Li, W., and Najt, P., "Experimental Study of NOx Reduction by Passive Ammonia-SCR for Stoichiometric SIDI Engines," SAE Technical Paper 2011-01-0307, 2011, doi:10.4271/2011-01-0307.

75. Saito, C., Nakatani, T., Miyairi, Y., Yuuki, K., Makino, M., Kurachi, H., Heuss, W., Kuki, T., Furuta, Y., Kattouah, P., and Vogt, C.-D., "New Particulate Filter Concept to Reduce Particle Number Emissions," SAE Technical Paper 2011-01-0814, 2011, doi:10.4271/2011-01-0814.

76. Mikulic, I., Koelman, H., Majkowski, S>, and Vosejpka, P., "A Study about Particle Filter Application on a State-of-the-Art Homogeneous Turbocharged 2.0 L DI Gasoline Engine", Aachen Colloquium, October 2010.