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2014-01-1491 Published 04/01/2014 Copyright © 2014 SAE International doi:10.4271/2014-01-1491 saeeng.saejournals.org

# Vehicular Emissions in Review

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#### ABSTRACT

The review paper summarizes major developments in vehicular emissions regulations and technologies in 2013. First, the paper covers the key regulatory developments in the field, including proposed light-duty (LD) criteria pollutant tightening in the US; and in Europe, the continuing developments towards real-world driving emissions (RDE) standards. Significant shifts are occurring in China and India in addressing their severe air quality problems. The paper then gives a brief, high-level overview of key developments in fuels. Projections are that we are in the early stages of oil supply stability. which could stabilize fuel prices. LD and HD (heavy-duty) engine technology continues showing marked improvements in engine efficiency. Key developments are summarized for gasoline and diesel engines to meet both the emerging NOx and GHG regulations. HD engines are or will soon be demonstrating 50% brake thermal efficiency using common approaches. NOx control technologies are then summarized, including SCR (selective catalytic reduction) systems and SCR filter developments. Emphasis is on low-temperature deNOx and integration of components and control. Diesel PM (particulate matter) reduction technologies are evolving around the behavior of ash deposits and SCR integration. Filters for direct injection gasoline applications are developing very rapidly, and in some cases the back pressure, light-off characteristics, and emissions reductions are very similar to standard three way catalysts (TWCs). Oxidation catalysts mainly involve developments towards stubborn problems, like low-temperature performance with exhaust with high hydrocarbon and CO, and methane oxidation. Finally, the paper discusses some key developments in gasoline gaseous emission control, focusing on matching engine calibration with emissions system characteristics; and on lean burn gasoline emissions control.

CITATION: Johnson, T., "Vehicular Emissions in Review," SAE Int. J. Engines 7(3):2014, doi:10.4271/2014-01-1491.

# INTRODUCTION

The vehicle industry is faced with very challenging and diverse emissions requirements. In addition to the new cutting-edge criteria pollutant regulations being phased-in starting in 2015 in California, large developing countries like China and Brazil are moving forward with their own regulations. The range of allowable emissions in major markets will be more than an order of magnitude. Adding to the challenge are the various fuel consumption or greenhouse gas regulations, fuel quality differences, and very-different market requirements. The technology to help meet these diverse emissions requirements is developing very quickly, and a review of these new developments might be useful to those with an interest.

This paper focuses on key developments in 2013 related to emissions and technologies for both diesel and gasoline engines in the automotive and heavy-duty markets. As in reviews from previous years [<sup>1</sup>], this paper begins with an overview of the major regulatory developments covering criteria pollutants and  $CO_2$ . As the fuels market is changing more now than in decades, and fuels can have major impacts on engine and emissions control, a high-level review of fuel trends is added. This sets the stage for a review of engine technologies, starting with light-duty gasoline and diesel engines, and then heavy-duty diesel engines. In this section, only broad developments are covered with the intent of summarizing the directions and emissions challenges for exhaust technologies. Next, the paper covers lean NOx control, oxidation catalysts, diesel and gasoline PM filters, and closes with representative papers on gasoline emission control.

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

# REGULATIONS

There were not many major regulatory initiatives in 2013, but mainly continuous progress on several large programs. Those covered here are:

- US EPA (Environmental Protection Agency) light-duty Tier 3 emissions.
- European light-duty Real-Driving Emissions (RDE)
- · Developments in China

 Other - India Roadmap, California HD Low-NOx program, Europe Non-Road, International Maritime Organization ship NOx delay

# US Light-Duty Tier 3 Proposal

The proposed US Tier 3 regulations [2] closely follow the California LEV III tailpipe regulations that were finalized in January 2012 [3]. Following are the general features of the proposal:

- Starts in model year 2017-18 for cars <6000 pound (one year later for larger cars) and is fully phased-in by 2025.
- Eventual harmonization of passenger car and light-duty truck standards to 30 mg/mile combined non-methane organic gases (NMOG) plus NOx, nominally 80% tighter than Tier 2 Bin 5 (fleet average).
- 5 certification levels: 20 to 160 mg/mile NMOG+NOx.
- 3 mg/mile FTP PM (particulate matter) standard; 10 and 20 mg/mi on the US06 drive cycle for smaller and larger cars, respectively
- 150,000 mile emissions durability by 2020; 120,000 mile durability option for smaller classes, but with a 15% tighter emission standard
- Fuel enrichment is limited to the leanest mixture that achieves the best torque (no enrichment for cooling the exhaust)
- MDV (medium duty vehicles; 8500-14,000 lbs.) must chassis certify. Fleet average 147 & 278 mg/mile NMOG+NOx (higher value for >10,000 lbs. gross vehicle weight); 7 certification levels: 200 to 400 mg/mile NMOG+NOx; 8-10 mg/mile PM on the FTP (Federal Test Procedure) cycle; 7-10 mg/mile Supplemental FTP
- E15 (15% ethanol in gasoline) certification fuel, 10 ppm maximum sulfur; 87 octane, RVP (Reed Vapor Pressure) 10 psi

Major differences between the Tier 3 proposal and LEVIII are: LEVIII PM standard drops to 1 mg/mile in 2025, subject to review in 2015; LEVIII starts with model year 2015; and LEVIII uses E10 certification fuel with 20 ppm maximum sulfur.

Currently, the Office of Management and Budget (OMB in the White House) is evaluating the regulation and needs to approve the final version before it is done.

# Europe RDE Regulatory Developments

In Europe, the European Commission has been moving forward with developing the Real-Driving Emissions (RDE) supplement to the automobile type approval certification procedure. The primary purposes of the regulation are to better match the NOx emissions from diesels, and PN (particle number) emissions from direct-injection gasoline cars to those measured in certification testing. These two emissions have been problematic. For example, despite European diesel NOx emissions being cut 60%, real emissions have not changed much in 15 years [4]. Depending on driving conditions, NOx emissions can be multiples higher than measured on the test cycle - averaging about 3X in rural and urban conditions, and 2X on the motorway for six Euro 5 diesels [5]. Similarly, in one study, a Euro 6 gasoline direct injection (GDI) car had about 2X higher PN emissions on the autobahn versus on the NEDC [6]. In another study [7] two Euro 6 GDI cars had nearly 10X higher PN emissions versus the NEDC at 130 kph (km per hour).

As such, the Commission is proposing [4] to implement RDE comitology measurements using portable emissions monitoring systems (PEMS) for gaseous pollutants, without mandatory emission limits but with recording of the results in the Certificate of Conformity, by December 2014. It is similar for PN but they propose implementation as soon as possible but no later than September 2017. Mandatory not-to-exceed (NTE) emission limits for both gaseous and PN emissions would be established by mid-2015, and then be introduced from 1 September 2017/18 for all new type approvals/new vehicles.

The lead RDE approach by the Commission for the GDI PN is to use PEMS in on-road driving of cars. PEMS for PN measurements have made much recent progress. Figure 1 shows the correlation to be quite good between PN PEMS and the PMP (particle measurement protocol) over a range of PN emissions [8]. Others have shown excellent correlation between PEMS and laboratory equipment for measuring PN in a variety of exhaust streams [9]. As a back-up plan in case PN PEMS is not satisfactory, the Commission is also developing a random drive cycle methodology that can be conducted in a dynamometer laboratory.



Figure 1. Correlation between PN PEMS measurements on a vehicle and dynamometer testing using laboratory instruments and the PMP protocol [8].

The RDE developments are expected to drive advanced NOx emissions controls for light-duty diesels and gasoline particulate filters (GPFs) for GDI engines. A Euro 6 car with SCR (selective catalytic reduction) had about half of the NOx emissions in urban, rural, and motorway testing than similar Euro 4 and Euro 5 cars [10]. However, the NO<sub>2</sub> emissions were the second highest of all seven cars tested, and the RDE NOx

emissions were still 2 to 4X higher than on the NEDC. In other testing [7], four SCR cars had on average about 30% lower NOx emissions in high-load driving versus eight cars with a lean NOx trap (LNT). One D-segment Euro 6 car without NOx aftertreatment had NOx emissions on the WLTC (World-harmonized Light-duty Test Cycle) that were 3X those of a SCR car or an LNT car. For cars with SCR, urea consumption is expected to go up about 50% from current Euro 6 levels to meet future RDE requirements. Instead of increasing tank size to ~40 liters, the fill interval will decrease from 30,000 km to 8-10,000 km and tank size will drop from 20-30 liters down to 8-15 liters [11, 12].

The need for GPFs to meet RDE PN standards will depend on vehicle segment, timing, and RDE limit value. One study [13] measured random-cycle RDE PN emissions that were 2X higher than allowed on the NEDC in 2017 (limit of 6 × 1011 particles per km) using a C-segment vehicle that had NEDC PN emissions half the 2017 requirement. Depending on test procedures, the RDE PN emissions might be 4X the NEDC limit value.

#### China

World-wide news on poor air quality in Chinese cities was quite common in 2013. Citizens are watching ambient PM2.5 (mass concentration of particles  $<2.5 \mu m$ ) concentrations as they watch the weather. As such, experts are seeing more movement now on air quality initiatives in China than in the past [14]. For example, senior leaders at the highest levels are concerned. Local officials now have ambitious ambient air quality goals, and much air quality data are public. Further, the public is more aware of the adverse health impacts of air pollution. Importantly, the scientific and technical experts are now much more engaged at all policy levels. And, the international community is involved in unprecedented ways. Not only are leading countries offering support, but the World Bank is increasingly active, and the United Nations Environment Program (UNEP) is giving priority to China. Climate change is also coming more to the forefront, and this is leading to awareness on the need for a more coordinated air quality policy.

These high-level movements are resulting in actions on vehicular emissions:

- The State Council (top of the government) stepped in and laid out a clean fuels roadmap for the country. Now in place is a plan that will require gasoline and diesel fuels with a maximum of 50 ppm sulfur by the end of 2014, and 10 ppm sulfur by the end of 2017. In line with this, the government announced China 5 (similar to Euro 5) light-duty tailpipe regulations effective January 1, 2018. Major regions and cities have an even more aggressive schedule, requiring 10 ppm sulfur fuels by 2015. Beijing is already has 10 ppm sulfur fuel for both gasoline and diesel.
- 2. The detailed specification for China 5 gasoline has recently been issued for January 1, 2018, resolving the final

technical hurdle to mandatory implementation of this fuel. Of significant note, maximum allowable manganese octane enhancer is dropped from 8 to 2 mg/liter. Light-duty China 5 standards will be adopted with the same timing, and they are very similar to Euro 5.

- 3. Beijing is continuing its lead to implement emissions standards. Only China V (like Euro V) trucks and buses with DPFs can be sold in Beijing after January 1, 2015. On light-duty, Beijing is considering a move to California or US EPA standards instead of the Euro 6 requirements in 2016, because Euro 6 does not tighten gasoline gaseous emissions enough from Euro 5 levels. (Europe is much tighter on particulates.) This could place China on a potential pathway toward the significantly more stringent gaseous standards of the US.
- 4. China is now committed to a very aggressive scrappage program intended to remove all pre-2000 model year cars and all pre-2005 diesel vehicles from China's road by 2017 (2015 in the key regions). This will be very difficult, but the national and local governments are pursuing various tools of implementation. If China succeeds, it could be a model for other countries that have problems with older vehicles.

#### **Other Regulatory Developments**

In India, a committee of senior stakeholders is recommending a fuel and vehicular emissions plan for the next 10 years or more. Thirteen major cities currently have Bharat Standards IV (BS IV), similar to Euro IV heavy-duty and Euro 4 light-duty standards, with the rest of the country at BS III. The recommendations are due in early 2014, but in a recent interview [15], the committee's chairman said it is set to recommend BS IV+ light- and heavy-duty standards country wide by 2017 with 40 ppm sulfur fuels (50 ppm sulfur currently required in current 13 cities); and BS V standards by 2022 with 10 ppm sulfur fuel.

In other emerging regulatory developments, the European Commission is developing the Stage V Non-Road Mobile Machinery (NRMM) regulations [16]. It will likely not be implemented before 2020. The Commission appears to be favoring expanding the regulation to smaller (<19 kW) and larger (>560kW) engines, dropping the PM standard by 40% to 15 mg/kW-hr, adding a PN limit, harmonizing comitology with the highway sector, and perhaps dropping NOx further. In a stakeholder survey, the adopting the PN standard and expanding the range of engines were strongly supported.

A key part of the Commission's NRMM initiatives is to improve in-use conformity. In this regard the framework to help screen in-use engines for further testing is described [17]. Figure 2 shows the principle. The work-based moving window approach will be used to determine emissions, similar to Euro VI for trucks. Windows with less than 20% average work are excluded. Figure 2 shows an example of a work-based window with the operating portions outlined that will be included in emissions measurements. Numbered portions are excluded or included because:

- 1. Exclude periods <10% power and longer than 2 min.
- 2. Excluded events shorter than 2 min are merged with surrounding idles >2 min.
- Exclude first period of stability after >2 min idle until 250°C is reached.
- 4. Include last 2 min of a working period.



# Figure 2. Examples of exclusions and inclusions for work-based window averaging of emissions from in-use non-road equipment. See the text for numbered descriptions [<u>17</u>].

On emerging regulations, California nominally needs another 80% NOx reductions to meet 2023 ambient air quality ozone standards in some regions. They are looking to the HD truck sector for more reductions from the US 2010 emissions levels. In that regard, California is sponsoring a technology program to demonstrate 0.020 g/bhp-hr (0.026 g/kW-hr) NOx on the HD FTP (Federal Test Procedure; US HD transient test). The Manufacturers of Emissions Control Association (MECA) will be contributing emissions systems. Southwest Research Institute (SwRI) will be conducting the tests on two engines - a 13 liter diesel and an 11 liter natural gas. For the diesel engine, nominally 99.3% blended cold- and hot- start NOx reductions will be needed on aged parts. Testing is scheduled to be completed by the end of 2015.

Finally, the International Maritime Organization (IMO) is proposing to delay the implementation of Tier 3 NOx standards from 2016 to 2022 for ships operating in the US Emissions Control Areas [<u>18</u>]. The regulations would have dropped the NOx levels for ships made after January 2016 about 75% down to 2.0 to 3.4 g/kW-hr. The ruling will be reviewed for finalization in a March 2014 meeting. Options for meeting the standards are SCR (selective catalytic reduction), EGR (exhaust gas recirculation), and partial or full switching to natural gas [<u>19</u>]. Several hundred ships use SCR today, but only one manufacturer uses EGR.

# **Regulatory Summary**

California finalized the LEVIII LD emissions standards in January 2012, and the US EPA is now finalizing their approach, calling for nominally a 75% reduction in NMOG+NOx, down to 30 mg/mile combined. Europe is also tightening down on LD diesel NOx and GDI PN, but using the RDE (Real Driving Emissions) model of putting vehicles on the road and measuring emissions as part of the certification procedure. China and India both have severe air quality problems in which vehicular emissions are significant part. China is implementing and appears to be very serious. India is putting together a fuel and vehicle technology roadmap through about 2025. Europe is moving to tighten non-road emissions, wherein expansion of the regulation into smaller and larger engines, and harmonization with HD truck test methods and regulations are the direction. Finally, California is investigating the feasibility of tightening HD truck NOx regulations down to 0.020 g/bhp-hr, and a test program is in place to look at it.

# FUELS

There are several recent developments that are highlighted here:

- Long term trends in oil production could affect fuel pricing for the next 15 to 20 years
- · Transportation fuel demand will shift from gasoline to diesel
- Natural gas production is significantly increasing, driving interest in natural gas vehicles
- · Fuel quality can significantly impact emissions

# **Oil Production and Transportation Fuel Trends**

New oil extraction technology is impacting the oil markets in the next decade or two. Deep water exploration has opened up large reserves, particularly off Brazil; and hydraulic fracturing technology (called "fracking") is starting to produce light crudes from oil shale.

The International Energy Agency (IEA), which advises governments around the world on energy policy, predicts [20] that of the new net growth in oil supply of about 8 million barrels per day through 2025 (8-9% growth), 80% will equally come from Brazil, shale oil, and bitumen (Canada oil sands). This growth generally comes from the Americas [21], and conventional oil production is predicted to decline [22]. The Americas will surpass the Middle East in oil production in a few years [21].

Not only will this new supply of oil result in better matching of supply and demand, but it will help to stabilize the oil markets. <u>Figure 3</u> shows the IEA's projections [23] of oil production and oil price through 2035 in three different scenarios. In the

Current Policies Scenario, which is a snapshot of today's policies, oil price increases about 20% through 2035. In the New Policies Scenario, which is based on new policies that are coming but not yet implemented, the price stabilizes and increases little from today. In the most aggressive 450 Scenario, wherein policies are enacted to maintain atmospheric  $CO_2$  concentrations at 450ppm, prices decline 20%.

The stabilizing of oil supply and therefore prices could have a big impact on future direction of engine efficiency and GHG (greenhouse gas) reductions, as this could take out a strong market driver for reducing fuel consumption in the absence changes in fuel tax policy.



Figure 3. IEA projection of oil production and prices for three different scenarios (see text). Oil prices could stabilize in the next two decade [23].

#### Shifts in Transportation Fuel Type

In general, the light-duty transportation fuel is gasoline and the heavy-duty fuel is distillate (like diesel). Although the number of automotive VMT (vehicle miles travelled) in the world will increase, OECD (Organization of Economic Cooperation and Development; generally North America, Europe, and developed Asian countries) gasoline demand is now dropping and total worldwide light-duty fuel demand is projected to drop or flatten after about 2020 [22]. This is mainly due to fuel consumption improvements in cars and to a lesser degree, ethanol substitution for gasoline. At the same time, distillate demand is increasing because it is used to move freight, and this is strongly tied to economic growth. The net result is a change in the distillate to gasoline demand ratio from about 1.5 today to 2.0 in the 2025 to 2030 timeframe, after which it accelerates rapidly to 3.8 in 2050 [24]. This could stress refineries, along with an over-capacity build expected in the developing countries [20]. The net impact is a trend towards diesel fuel prices increasing relative to gasoline prices. This could shift freight and other high-distillate-consuming applications (like mining) away from diesel into natural gas and biodiesel, Figure 4 [22]. Indeed, much development work is going into shifting ships, locomotive, and mining applications to liquid natural gas [<u>25</u>, <u>26</u>, <u>27</u>].



Figure 4. Light-duty fuel demand in the OECD is decreasing but increasing in the non-OECD countries. The net demand could decrease after 2020. Natural gas usage in transportation could quadruple by 2024. [22]

There is much discussion now on natural gas trucks in North America due to an abundance of natural gas afforded by new extraction methods. A large proportion of new refuse haulers are now fueled on compressed natural gas (CNG) due to quieter operation and the possibility of relatively cheap methane from landfills; and some publicly-financed transit buses have been using CNG for a number of years. A spark ignition (SI) CNG class-8 vocational trucks can cost about \$60,000 more (\$50,000 for the truck, plus tax) than a comparable diesel truck, but might save \$1300 per month in fuel at recent fuel price differentials (\$1.35/gallon of diesel equivalent, \$0.36/liter) on 100,000 miles (160,000 km) per year [28]. Tailpipe greenhouse gas emissions (GHG) for such an engine can be nominally 15% lower than diesel, considering 28% less CO<sub>2</sub> per unit of energy than diesel [29], but operating at 10-15% lower energy efficiency [30]. When considering a 0.5% methane leakage rate during production [31], the well-to-wheel GHG emissions are similar to diesel. For lean-burn compression ignition LNG trucks, the leading approach for line-haul trucks, energy efficiency is similar to diesel [30], and well-to-wheel GHG emissions can be 17-25% lower [32]. However, in both CNG and LNG cases, the GHG advantages can be reduced (or become a liability) depending on drive cycle and LNG tank venting [33], or on LNG sources [<u>32</u>].

#### Fuel Quality and Emissions

Fuel quality can have a huge impact on emissions, so it is important for policymakers to match the fuel to the emissions regulations. In that regard, the vehicle and engine trade associations of the US, Europe, and Japan published their latest recommendations on gasoline and diesel fuel quality for different tailpipe emission regulatory limits [34]. A new category was added for markets with highly advanced requirements for emission control and fuel efficiency. For gasoline the minimum research octane number (RON) is raised to 95 to enable some engine technologies that can increase fuel efficiency. For diesel fuel, this category establishes a high quality hydrocarbon-only specification that takes advantage of the characteristics of certain advanced biofuels, including hydrotreated vegetable oil (HVO) and Biomass-to-Liquid (BTL), provided all other specifications are respected and the resulting blend meets defined legislated limits.

Similarly, Walsh summarized the impact of various gasoline and diesel properties on emissions [<u>35</u>]. <u>Table 1</u> shows the impact of gasoline properties on emissions. The main diesel fuel parameters that affect emissions are sulfur, cetane, poly-aromatic hydrocarbons, density, and volatility.

Despite specific fuel quality requirements in developing countries, the actual fuel quality in the market can be much worse. For example, in one developing country the sulfur specification was tightened to 150 ppm, but five years after the requirement was implemented, six fuel samples contained 400 to 800 ppm sulfur [13]. Given such a frequency, engine manufacturers need to design for this worst case to provide customer satisfaction.

#### **Fuels Summary**

Incremental oil production over the next 10 to 15 years will shift from the Middle East to the Americas. Soon, the Americas will surpass the Middle East in oil production. Further, natural gas production is ramping up quickly, relieving oil demand. All this portends stable fuel prices. However, there are trends towards shifts in fuel type, namely more diesel demand than gasoline demand. Also, with increased demands on efficiency and emissions, fuel quality becomes even more important, and harmonization and enforcement of fuel standards will increase in importance.

Table 1. Impact of various gasoline fuel properties and emissions at different levels of vehicle technology. [35]

Gasoline	No Catalyst	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5/6 <sup>3</sup>	Comments
Lead 个	РЬ, НС↑	CO, HC, NO <sub>x</sub> all increase dramatically as catalyst destroyed					Lead is banned in China gasoline since 2000
Sulfur 个 (50 to 450 ppm)	SO₂↑	CO, HC, NO <sub>x</sub> all increase ~15-20% SO <sub>2</sub> and SO <sub>3</sub> increase					Onboard Diagnostic light may come on incorrectly
Olefins 个	Increased 1,3 butadiene, increased HC reactivity, NO <sub>x</sub> , small increases in HC for Euro 3 and cleaner						Potential deposit buildup
Aromatics 个	Increased benzene in exhaust						Deposits on intake valves
	Potential increases in HC, NO <sub>x</sub>	HC个, N CO个	HC $\uparrow$ , NO <sub>x</sub> $\downarrow$ , HC, NO <sub>x</sub> , CO $\uparrow$ and combustion chamber tend to increase				
Benzene 个	Increased benzene						
Ethanol ↑ up to 3.5% O <sub>2</sub>	Lower CO, HC, slight NO <sub>x</sub> increase(when above 2% oxygen content), Higher aldehydes	Minimal effect with new vehicles equipped with oxygen sensors, adaptive learning systems					Increased evaporative emissions unless RVP adjusted, potential effects on fuel system components, potential deposit issues, small fuel economy penalty
MTBE 个 up to 2.7% O <sub>2</sub>	Lower CO, HC, higher aldehydes	Minimal effect with new vehicles equipped with oxygen sensors, adaptive learning systems					Concerns over water contamination
Distillation Characteristics T50, T90个	Probably HC个	нс↑					
ММТ ↑	Increased Manganese Emissions			Possible Catalyst Plugging	Likely Ca Plugging	atalyst	O <sub>2</sub> sensor and OBD may be damaged, MIL light may come on incorrectly
RVP 个	Increased evaporative HC Emissions						Most critical parameter for Asian countries because of high ambient Temperatures
Deposit control additives ↑		Potential HC, NO <sub>x</sub> emissions benefits					Help to reduce deposits on fuel injectors, carburetors, intake valves, combustion chamber

# ENGINE DEVELOPMENTS

Engines are going through a remarkable renaissance that is primarily being driven by market pressures and GHG emissions regulations. Very attractive concepts are being described that will drop fuel consumption as much as 40% in LD gasoline applications (versus multiport-injected engines) and upwards of 20% in HD truck applications. In many cases the criteria emissions also drop, but they can increase (e.g., NOx in HD), or be reduced in a couple categories (NOx, PM) and increased in others (HC, CO).

Following are some examples of the progress being made in both light-duty and heavy-duty applications.

#### Light-Duty Engines

Most market projections show the internal combustion engine (ICE) will dominate the LD vehicle market (>90%) through at least 2025. Both the US EPA 2025 greenhouse gas rule and the European Union counterpart for 2020 can be met without electric vehicles. Indeed, given that engine-based  $CO_2$  reductions are less than half the cost (\$/percent) of plug-ins [1], it is logical that, absent significant government incentives or mandates, the ICE will be developed to its maximum (reasonable) efficiency before a significant penetration of plug-ins are used to meet the regulatory or market efficiency requirements.

#### **Gasoline Engines**

Gasoline engine developments have lagged behind their diesel counterparts mainly because significant engine modifications were not needed to meet criteria emissions regulations. This was accomplished very efficiently with the three-way catalytic converter (TWC). The European  $CO_2$  regulations have changed this historic trend.



Figure 5. Best-in-class  $CO_2$  emissions of 2012 European gasoline (G4) and diesel (D4) cars relative to the European 2020  $CO_2$  regulations. The percentages refer to the approximate reductions needed for gasoline cars. [36]

<u>Figure 5</u> shows the best-in-class European  $CO_2$  emissions for 2012 gasoline and diesel cars relative to the 2020 regulation [<u>36</u>]. Subcompact cars (60 kW engines) will likely adapt efficiency measures already on the larger vehicles, like friction reduction, variable valve timing, direct injection, high

compression ratio, automatic transmissions, downsizing, turbocharging, variable valve lift, and/or cooled EGR (exhaust gas recirculation). Compact cars (90 kW) will be similar, but with more downsizing and perhaps lean-burn. Larger cars will need much more effort, and are likely candidates for mild- or full-hybridization.

Although lean-burn direct injection engines were commercialized by Mitsubishi more than 15 year ago, and more recently both BMW and Mercedes had lean-burn engines on the market, now only Mercedes has a commercial lean-burn engine. They reported that at low speeds the fuel consumption is reduced up to 20% in urban driving and 10% in extra-urban driving relative to homogeneous combustion [37]. In highway driving the fuel consumption is similar to a diesel engine but the CO<sub>2</sub> emission is 13% less. The emission control system utilizes a close-coupled three-way catalyst (TWC), and underbody NOx storage catalyst (NSC), and a combination of the two in between. Relative to advanced and downsized stoichiometric direct injection engines, Bosch estimates lean-burn engine CO<sub>2</sub> emissions can be reduced in NEDC testing by 5 to 8% [36]. Even at these levels, lean-burn engines can deliver relatively cost-effective CO2 reductions compared to alternatives like full hybridization, so it seems likely interest will grow.

Moving to prototype engines, the "dedicated EGR" approach is making progress [38, 39]. In this concept the exhaust from one cylinder is completely fed back into the intake, thus allowing that cylinder to operate rich to generate hydrogen. This enhances the combustion of the remaining cylinders to tolerate a high EGR rate, enhancing efficiency. Peugeot intends to commercialize the technology in 2018 for a 10% fuel savings [40]. Retrofit onto a multi-port injection (MPI) 2.4 liter baseline engine, fuel savings 12-15% are reported [39]. Torque is increased 20%, and knock is reduced, allowing 17 bar BMEP (brake mean effective pressure) and/or lower octane fuel than might be required for such loads. The effect comes from improved thermodynamics resulting from increased high levels of EGR (25% for a 4-cylinder engine), high CO and hydrogen content (6% and 2% respectively at an equivalency ratio of 1.2 for the dedicated cylinder), and higher compression ratio [40]. Future work is targeting 20% fuel savings on a direct-injection gasoline engine.

#### **Diesel Engines**

Diesel engines are still improving, with perhaps another 10% fuel consumption reduction from today's best engines [41]. The challenge will be to deliver both lower fuel consumption and meet tighter US emissions regulations.

To achieve this, the engine needs to be optimized to minimize emissions. Ruth, et al., [42] optimized combustion with high swirl, dual-loop EGR, and an optimized turbocharger to achieve the target 40 mg/mi PM (24 mg/km) and 400 mg/mi NOx (240 mg/km) on the LA4 cycle and 200 mg/mile NOx (120 g/km) on the HWFET (US Highway Federal Emissions Test) cycle [<u>43</u>] for a 2300 kg pick-up truck. The fuel consumption is 25 miles/gallon (9.2 liters/100 km) or 417 g  $CO_2$ /mile (250 g/ km). To meet the LEVIII emissions standards an estimated 90-93% NOx + NMOG (non-methane organic gas) reduction will be needed from the exhaust aftertreatment system.

Diesel hybrid electric vehicles show promise for delivering very low  $CO_2$  values at lower cost than plug-ins. Freitag [44] showed two different operating principles for a full-hybrid diesel architecture. About 18%  $CO_2$  reductions relative to the standard diesel engine were measured on the NEDC when the battery was managed incrementally during the test and kept close to the full state of charge. An improved 20%  $CO_2$  reduction was measured when the battery was more-completely drained during urban driving, and then fully charged in the higher-speed driving at the end of the test.

The 2-stroke opposed piston design concept shows potential for even more reductions in fuel consumption and emissions [45]. In simulations of a multi-cylinder engine using data from a single-cylinder engine, 44% BTE (brake thermal efficiency) is estimated over the speed range of 1600-2100 RPM. In a simulated comparison to Ruth, et al. [42], the concept engine is estimated to achieve 20% lower fuel consumption, but with similar HC+NOx emissions. Interestingly, due to the opposed-piston design, vibration calculations show residual moments that are four orders of magnitude lower than for a similarly powered 60° 3.5 liter V6.

#### Advanced LD Concept Engines

Years of effort went into understanding HCCI (homogeneous charged compression ignition) engines. The main problem is that the charge ignites too rapidly at higher loads. This is now being addressed with strategies like Reactivity Controlled Compression Ignition (RCCI), wherein stratification is introduced into the charge by using two fuels of differing reactivity. The combustion is spread out over more crank angle degrees, yet the advantages of low NOx and low PM from low-temperature combustion are largely maintained.

Some of the challenges with RCCI are reported in a 1.9 liter engine using port-fuel injected gasoline to deliver power and direct-injected diesel fuel to react it [46]. In steady-state testing the engine delivers 5-7% higher BTE than diesel combustion (nominally 15% lower fuel consumption) in the operating range of typical LD test cycles, but HCs and CO are 10X higher and exhaust temperatures 80-120C° lower, presenting a challenge to oxidation catalysts. NOx emissions are up to 20% lower, but typically 5-10% lower, and PM is 30-70% lower. Solid particulate numbers are reduced two orders of magnitude from diesel.

A direct-injection compression ignition gasoline concept engine is moving from single-cylinder to multi-cylinder testing [47]. Indicated fuel steady-state fuel consumption is 184 g/kW-hr at 1500 RPM and 6 bar BMEP, and 175 g/kW-hr at 2000 RPM and 11 bar BMEP using 88 octane E10 (RON; 10% ethanol). Modeling based on steady-state testing shows a 30-35% CO<sub>2</sub> reduction versus the MPI baseline on the US combined CAFE (Corporate Average Fuel Economy) cycles. PN (particle number) emissions are near those of filtered ambient air, and engine-out NOx emissions at the above test points are close to Tier 2 Bin 5 levels. Indicated CO and HC emissions are high at (30 g/kW-hr and 6 g/kW-hr, respectively, at 1500 RPM 6 bar), and exhaust temperatures are only ~280°C, so there are new emission control challenges.

Chang et al. [<u>48</u>] ran a compression-ignition engine on a heavy naphtha fuel (52 RON octane), with the objective of demonstrating a fuel that might alleviate future pressures on refinery mix caused by increasing diesel and decreasing gasoline demand (see the fuel section). Measured  $CO_2$ emissions are at the lower range for current diesel cars (122 g/ km; 1590 kg vehicle), NOx emissions within the Euro 6 limit, PM emissions somewhat lower than diesel but similar using a DPF (diesel particulate filter), without compromising drivability. The fuel can save about 8% well-to-tank greenhouse gas emissions versus diesel.

#### Heavy Duty Engines

Heavy duty diesel engines have improved significantly in the last decade and are still evolving rapidly. Tailpipe PM emissions are down 98%, NOx emissions are down more than 95%, and fuel consumption is down 8% versus 2003 and 3% versus peak efficiency in the pre-EGR (high NOx) era.

There are several engine operating strategies that can be used to heat the emissions control system. Theissl, et al. [49] calibrated a modern engine (10.5 liter, 297 kW, 1800 bar injection, 200 bar peak cylinder pressure) for four conditions: optimum cold start, cold exhaust system, low NOx via EGR, and then high-SCR and temperature for SCR efficiency and low fuel consumption. Strategies most effective for heating the SCR system are to use hot-EGR and intake throttling. If urea costs the same a fuel, it is 0.3% cheaper to run a line haul cycle at 3.5 g/kW-hr NOx than at 5.5 g/kW-hr (2.3% fuel savings, but higher urea rate). However, if urea is half the cost of fuel it is 1% cheaper to run at the higher NOx.

Although advanced heavy-duty diesel engines are very clean and efficient, Stanton [50] lists and describes numerous technologies that can drop fuel consumption another 20% relative to US 2010 line haul and vocational engine baselines. <u>Figure 6</u> shows the summary for the line haul engine. The technologies are categorized as improving mechanical efficiency, open cycle efficiency (gas exchange), closed cycle efficiency (compression, combustion, and expansion), and waste energy recovery. Most of the technologies are additive, and applicable to vocational trucks, which can achieve 22% fuel consumption reductions. <u>Figure 7</u> summarizes the BTE progress to date and projections to 2020 [51].



Figure 6. Examples technologies that can decrease fuel consumption of line haul truck engines. Reductions are relative to a US 2010 baseline. [50]





The above background sets the stage for the US DOE (Department of Energy) SuperTruck program. Four companies (Cummins, Daimler, Navistar, and Volvo) are receiving US government support to demonstrate engine technologies on a dynamometer that can achieve 50% BTE at line haul loads by 2015. Further, participants need to define a roadmap for demonstrating 55% BTE by 2020. Table 2 is a summary of the general approaches the participants are employing to meet these two general objectives [52, 53, 54, 55]. Common themes are related to combustion, air handling, parasitic reductions with mechanical improvements, and waste heat recovery, as Stanton describes [50]. Differences are the degree of waste heat recovery (WHR), turbocompounding, down speeding, and variable valve actuation. Moving forward to 55% BTE targets, all will be optimizing these technologies; and all but Daimler are investigating new fuels as part of the improvement.

Table 2. Summary of DOE SuperTruck Program results and approaches. CR: compression ratio increases, FIE: fuel injection equipment, PCP: peak cylinder pressure, WHR: waste heat recovery, D.sp. (DS): down speeding, EAT: exhaust aftertreatment, DCT: dual clutch transmission

	BTE, May 2013	50% BTE Approach	55% BTE Possibilities
Cummins	51.1%	Combustion - CR, bowl, FIE, calibration Gas Flow - EGR flow, turbo improve Parasitics - seals, pumps, piston, lube WHR - EGR, exhaust, oil, water	Optimization Fuels
Daimler	48.1%	Combustion - PCP, bowl, FIE, calib Turbo – low $\Delta p$ Parasitics - cylinder, lube WHR - EGR	Engine Optimization Turbocompounding WHR
Volvo	48%	Combustion – cyl geom, FIE, D.sp., EAT Air Management Parasitics – cooling and lube cicuits WHR – Gen 1 Rankine + turbocompound Other – DCT, idle reduction, axles (DS)	Combustion Pumping WHR Fuels
Navistar	48.2%	Combustion – PCP, FIE Parasitics – base comp., lube, cooling WHR – electric turbocompounding Variable Valve Actuation	Fuels More turbocomp More VVA

In industry consortium work, Roberts [56] showed that a 2010 commercial engine with turbocompounding has a BSFC (brake specific fuel consumption) of about 185 g/kW-hr in 13-mode steady state testing at 10 g/kW-hr engine out NOx levels. Improvements can drop this to 175 g/kW-hr at >48% BTE. Simulations show the possibility to get down to 170 g/kW-hr with waste heat recovery. For reference, the US 2017 HD GHG rule requirement is at about 195 g/kW-hr. Regarding thermal management, combinations of 50% cylinder cut-off, post-injection of fuel, and early exhaust valve closing all effectively increased post-turbine temperatures to >200°C.

An example of European HD engine efficiency developments and direction was offered by Bergmann [57]. Current engines are attaining 46% BTE, up from 42% in 1999, but it is feasible to be at 50% BTE without WHR, and 55% with it. An integrated energy management system incorporating the engine, cooling system, auxiliaries, gearbox, emission control system, and energy storage is contemplated.

Finally, as mentioned earlier in the Fuels section, large bore engines are shifting to compression-ignition natural gas. These engines either use a small amount (<10%) of diesel to ignite the natural gas charge, or are dual fueled with a range of diesel and natural gas combinations. Generally, these engines will still need diesel particulate filters (DPFs) and NOx treatment. Baufeld, et al., [58] evaluated a dual-fuel approach in a single cylinder large-bore (250 mm) engine. At 70% natural gas substitution, the CO<sub>2</sub> level at 20 bar BMEP is 20% less than with a diesel charge. Smoke is very low, but CO and hydrocarbon emissions are quite high (6 to 13 g/kW-hr each) and increase with later initial injections of diesel. NOx emissions are up to 20% higher than for diesel at a start of injection (SOI) of 12° before top center, but decrease to diesel levels at 10° SOI before top center. There are lambda-SOI operating regimes at 18 bar BMEP wherein NOx emissions are

within IMO Tier 3 (2 g/kW-hr for this engine) and HC emissions are low. Faghani, et al., [<u>59</u>] demonstrated the effect of natural gas post injections using a high-pressure dual fuel injector in a 15 liter truck engine with only one cylinder operating. Post injections of about 15-20% of the fuel can reduce PM and CO by about 80%. Methane emissions are reduced about 25%, NOx changes are almost within the variability of results, and fuel consumption increases about 1%.

#### Advanced HD Engine Concepts

RCCI (Reactivity-Controlled Compression Ignition) combustion started as a heavy-duty engine concept. Progress is impressive. Experiments were conducted on a single-cylinder heavy-duty diesel engine [<u>60</u>]. Gross indicated efficiencies in excess of 59% were measured, with corresponding near-zero levels of NOX and PM. The combustion method provides a potential pathway to meet the DOE Super Truck efficiency goal 55% BTE.

Finally, Musculus, et al., [61] provided a valuable conceptual model for partially premixed low-temperature diesel combustion (LTC), wherein early fuel injections mix better with the air and prevent regions of PM and NOx formation by keeping flame temperatures low and lean. In conventional combustion (injection is near top dead center and hotter) the diesel jet enters a "quasi-steady state" period, wherein fuel is burned during injection. A fuel-rich, soot-filled flame interior is surrounded by a hot diffusion flame that generates NOx. This leaves remnant PM and NOx emissions. In LTC, ignition occurs throughout most of the jet, from lean upstream mixtures to richer downstream mixtures, and ends after the end of injection in the downstream jet. Late in the combustion cycle, most of any soot that is formed will oxidize. Fuel-lean regions contribute to unburned hydrocarbons and CO emissions. The net result is low NOx and PM, but high CO and HC emissions. In the light-duty model, the charge impinges and is mixed by the piston bowl. The jet is split, with rich mixtures mostly in bowl and lean mixtures in the squish zone outside the bowl. These lean portions don't burn completely.

#### Engines Summary

Both light-duty and heavy-duty engines are making impressive gains. Gasoline engine fuel consumption reductions of up to 30% versus the MPI baseline are in development, and LD diesel might achieve 20% reductions versus the very efficient engines of today. On the HD side, both government and private programs are demonstrating potential for 50% BTE (10-12% fuel consumption reductions), with goals set to achieving 55% BTE (20% reductions from today). Work is advancing on compression ignited natural gas engines, wherein post injections can significantly drop PM and methane emissions. Greenhouse gas reductions will increasingly be needed, and very low criteria pollutant emissions will be the default requirement.

# **DIESEL NOX EMISSION CONTROL**

Because diesel engine fuel consumption generally drops as the NOx emission increases, diesel NOx control is among the leading approaches for reducing fuel consumption. Indeed, all of the DOE SuperTruck participants cite improved exhaust deNOx performance as a critical parameter to achieving 50% BTE. By far, the leading approach for deNOx is the SCR (selective catalytic reduction) system. In light-duty applications, lean NOx traps (or NOx storage catalysts) are the preferred approach in smaller light-duty diesel applications in Europe through Euro 6, while for heavier European applications and US Bin 5 applications, the direction is towards SCR.

#### SCR

Over the years the SCR system improvements have been impressive. The first heavy-duty truck tests were conducted in the mid-1990s and achieved nominally 60% NOx reductions on systems that were perhaps 6X in size relative to the swept volume of the engine. Systems today are less than half the size and are reducing NOx emissions more than an order of magnitude from the early levels.

The system improvements are still advancing, with cycleaveraged HD SCR-system deNOx efficiency being increased from 94% in 2012 to 96% today, and projected to be 98% in 2016 [50]. Many of these improvements are coming from enhanced monitoring and control. A modern emission control system might have 10 or more sensor inputs and outputs. One concept reported last year [62] is to use two SCR catalysts with an ammonia sensor located between them. The concept went commercial in 2013 in a HD application [51], and enabled system deNOx efficiency to increase from 93.5% to 97.4%. In the closed-loop control strategy, ammonia slip from the first SCR catalyst provides feedback into the urea injection controller [63]. This allows the first catalyst to have close to maximum NH<sub>3</sub> storage to facilitate both cold start application [59] and improved SCR kinetics [64]. The ammonia slip response times are much faster, potentially allowing higher NH<sub>3</sub>:NOx injection ratios for higher efficiency, without more ammonia slip.

Improved SCR catalysts are also helping system efficiency. Reith, et al., [65] show data on an improved copper zeolite catalyst with better durability and 14 to 23% higher NOx reduction capability at 200°C than a Euro VI catalyst, as tested on the Non-Road Transient Cycle (NRTC). Cox [66] also showed better low temperature performance for a new copper zeolite, as well as lower N<sub>2</sub>O emissions on aged samples (650°C) over the whole temperature range but especially around 200°C. Geisselmann [67] tested catalysts coated onto 600-csi (cells per square inch) substrates. NOx conversion efficiency improved 2 to 4% versus the 400-csi design at temperatures greater than 400°C. In another approach, increasing the catalyst loading by 35% increases back pressure 15%, but improves low-temperature (200-250°C) deNOx efficiency by 4 to 7% and higher-temperature (350500°C) efficiency by 3 to 13%. Figure 8 summarizes the results with higher washcoat loadings on the World-Harmonized Heavy-Duty Transient Cycle (WHTC). High-porosity substrates can decrease this pressure drop penalty by enabling the catalyst to reside in the wall [68]. In this work, more washcoat improves deNOx efficiency 12% at 200°C, and another 3% is added with 600-csi substrates (15% total improvement); but at the higher temperatures (275 and 550°C) more washcoat improved efficiency only 2 to 5% and the higher cell density added 2% efficiency (at 275°C).



Figure 8. Improvement in NOx conversion efficiency by increasing catalyst washcoat (wc) loading by 35% on the WHTC with NO2/NOx = 0.40 and ammonia:NOx=1.2. [67]

High deNOx efficiency requires good urea mixing, especially at the lower temperatures. This can be particularly challenging when space is limited. Hovda [69] showed that for urea injected at 200 g/hr onto mixer blades, the blade temperature can drop 40C°, resulting in deposit formation. A compact design that has no metal-urea contact zones is shown in which the urea is injected into an axial hole through the center of the DOC (diesel oxidation catalyst) and is mixed with the gas by a swirling action imparted by a baffle at the DOC exit. Urea injection rates can increase versus base designs, allowing higher NOx conversion rates and lower ammonia slip.

Fundamental understanding of SCR catalysts will enable better formulations and designs in the future. Schmeisser and Nova, et al., [70] showed significant low temperature NO to  $NO_2$ oxidation in a copper zeolite SCR, and the that  $NO_2$  can be adsorbed in the cooler (50°C) dry exhaust conditions. This can occur during the first 100 seconds of a cold start when the exhaust water vapor condenses on upstream components. Once the upstream components heat up and water vapor is made available at the SCR catalyst, the resultant water adsorption exotherm causes the NOx to be released.

Hydrocarbon poisoning of SCR catalysts was summarized last year [1] as it relates to deNOx efficiency and durability. More recently, Kumar, et al., [71] looked at the behavior of long- and short-chained hydrocarbons (n-dodecane and propene) on a

small-pored (0.38 nm) copper zeolite in the chabazite family. Even this type of zeolite can store a significant amount of large hydrocarbons (2.8 g/liter at 350°C), but they are stored on the outside of the zeolite chrystallites after breaking down into carbon-rich deposits. The deNOx efficiency is adversely impacted but the ammonia storage and release is not. On the contrary, small hydrocarbon can penetrate into the zeolite pores and adversely impact both NOx conversion efficiency and ammonia storage characteristics. This can be an important distinction, as LTC combustion can produce more smaller hydrocarbon species than conventional diesel combustion [72].

Low temperature NOx emissions pose a challenging problem. Thermal management using throttles and/or fuel injection can be effective, but will increase CO<sub>2</sub> emissions. Large Euro VI trucks (40 tonne) without EGR have the same NOx emissions (g/km) in urban driving as some Euro 6 diesel passenger cars, and are about half that of Euro 4 and 5 cars by using thermal management methods to increase SCR temperatures [73]. As this kind of driving can have much stop-and-go traffic, and the idling exhaust is cool and convectively extracts heats from a catalyst system, Gabrielsson [74] showed that an engine stop-start system can be as effective as thermal management methods for maintaining exhaust temperatures. The US EPA identified idling NOx emissions as an issue they wish to investigate, as they measured 6-16% of the NOx from Class 8 trucks came from idling under "normal" driving condition using four trucks [75]. Two trucks measured 27 and 40% of the total NOx from idling.

Cold start emissions are becoming a greater part of the vehicular NOx inventory. More work is occurring on passive NOx adsorbers (PNAs). Chen, et al., [76] showed some of the properties of a recent PNA formulation. It can capture upwards of 80-90% of the NOx at 80°C, up to a capacity of about 0.3 g/ liter of adsorber. Most of the NOx is "passively" released at temperatures between 200 and 350°C, presumably when a downstream SCR catalyst is operative. Sulfur can displace NOx, but it can be regenerated at 720°C for 15 minutes in a lean atmosphere. Geisselmann [67] showed a PNA with similar NOx adsorption and desorption behavior, wherein they captured 1 g/liter of NOx if the efficiency can be allowed to decrease to 50% at 200°C. Both Chen and Geisselmann contemplate multi-functional components in which the PNA is added to the DOC and/or DPF. Perhaps 1/3 of the cold start NOx can be captured with this approach in HD applications [62]. For LD PNA applications, Koerfer, et al., [77] simulated a PNA+SCR system on an 1800 kg 2-liter LD diesel. They got down to about 60 mg/mile NOx (376 mg/mile engine out) on the FTP using optimized thermal management of the SCR but not the PNA at a fuel penalty of 1.8%. For a 2% fuel penalty they optimized thermal management of both the PNA and SCR, and achieved roughly LEVIII levels of NOx (25 mg/mile).

One cold-start SCR technology that is now commercialized in LD systems is the integrated SCR+DPF (SCR filters). This enables the SCR catalyst to be placed closer to the engine for

faster heat-up, without the burden of having to regenerate a DPF that is downstream of a dedicated SCR system. Further, Geisselmann [67] showed the SCR catalyst is better utilized on the filter than in a flow-through substrate. In Figure 9, Rose and George, et al., [78] show the deNOx efficiency for the SCR filter at steady-state load points is 30% greater at 250°C and 4% greater at 425°C than if an equal volume of SCR catalyst is separate from the filter. In NEDC testing, the SCR filter was 30-50C° hotter over the test. Soot did not impair the NOx performance, and the filter could accept about 1.5 to 2 g/liter more soot for a safe regeneration. Soot-loaded back pressure is equivalent to the system with separate components.



Figure 9. Comparison of steady-state testing of SCR filters (SCRF) and standard SCR catalysts at four different load points (inset). [78]

In a heavy-duty application, an SCR filter plus a small SCR catalyst has 15% lower back pressure than the separate filter-SCR system with 3X the volume of SCR behind the filter [79].

The deNOx efficiency of an aged SCR filter system is only 1-2% lower than that for the dedicated SCR system in European Steady-State Cycle (ESC) testing. SCR filters are even being tested on inland commercial marine vessels in Europe to save space relative to a separate DPF+SCR system [80]. More than 80% NOx conversion efficiency was obtained with no increase in back pressure on a 600 kW patrol boat and a 450 kW barge.

To achieve high NOx conversion efficiencies, over-dosing of urea is often needed. The excess urea is oxidized in an ammonia slip catalyst (ASC), but undesirable by-products like NOx and  $N_2O$  can form. Newman [79] provides an update on the latest layered ASC. Ammonia is stored in the top SCR layer, and any excess ammonia is oxidized by the underlying oxidation catalyst (precious metal) layer. NOx formed by the oxidation catalyst diffuses through the top SCR layer and is reduced. Relative to the earlier generation of layered ASC, the NOx,  $N_2O$ , and  $NH_3$  emissions are dropped about 40-45%.

To round out the SCR section, the EPA described their results on testing for dioxins, furans, and other highly toxic compounds that might be emitted from SCR filter systems [81]. The concern was that when soot is in contact with copper or iron catalysts, dioxin or furan might be formed. Overall, the results show that the dioxin and furan emissions appear to be unaffected by the use of copper and iron zeolites applied to filters. Further, when compared to inventory values, the emission factors suggest a four-order-of-magnitude reduction in these emissions from diesel engines and that modern diesel engines are a minor contributor to the dioxin and furan inventory when compared to stationary sources. The results also show that PAH (poly-aromatic hydrocarbon) emissions are unaffected by the presence of copper and iron zeolites on a DPF, and that the DOC is highly effective at oxidation of PAHs in the exhaust.

#### Lean NOx Traps

Lean NOx traps (LNTs) might be a good choice over SCR for small engine applications, but their NOx reduction efficiencies are much lower than for SCR systems. Current US light-duty diesels with SCR need about 50-60% more NOx+NMOG (non-methane organic gases) reductions to certify at the LEVIII fleet average limit of 30 mg/mile NMOG+NOx. So, recent work is looking at adding an LNT to the SCR system to deliver these required emissions reductions.

Neely [82] investigated replacing the DOC with a lean NOx trap (LNT) on a current 2-liter diesel car (with SCR) to improve cold start NOx. The engine calibration was adjusted for lower HC and higher temperatures, but NOx went up. A new 2 liter low-temperature LNT formulation was chosen, resulting in a 50% reduction in NOx+NMOG versus the base engine-out emissions after the first hill in the FTP. An addition reduction of 10% is obtained by using only the ammonia generated by the LNT and stored on the SCR. Adding the LNT to the original SCR system with the new calibration just missed the average LEVIII limit.

With a large LNT in the above system, one might consider adding some LNT to the DPF, similar to the DPNR (diesel particulate and NOx reduction) catalyst Toyota introduced more than 12 years ago. However, Mataresse, et al., [83] found that the presence of soot decreases the NOx storage capacity of the LNT about 10-30% due to the competition for NO<sub>2</sub> between the soot and the NOx storage sites. Soot also decreases the stability of the stored NOx, and there are indications of oxidation of soot by the stored nitrates. Further, soot combustion caused the Pt-K/Al<sub>2</sub>O<sub>3</sub> catalyst to age, resulting in 40% less NOx storage capacity and lower soot oxidation activity.

#### NOx Summary

Lean NOx systems are continuing to evolve. SCR system architecture is improving with better control and system layout. Catalyst formulations and designs and also adding to the NOx reductions. Much focus is on low-temperature performance. Also, consolidation of components, like SCR and filters, and addition and synergies different components with different capabilities, like passive NOx adsorbers and lean NOx traps added to SCR systems are of significant interest.

# PARTICULATE FILTERS

After the three-way catalyst, the diesel particulate filter (DPF) is the most significant vehicle emissions control device. Now, gasoline particulate filters (GPFs) are in production and being considered as a major pathway for gasoline direct injection engines to meet the European light-duty Euro 6c and RDE (real-driving emissions) particle number (PN) regulations in 2017-18. This section will cover the key developments on both DPFs and GPFs in 2013.

#### **Diesel Particulate Filters**

Given DPFs were first applied to new vehicles more than 13 years ago and because we are in, perhaps, our fourth generation, few new reports on DPFs are summarized here. Most of the significant recent reports on DPFs are related to integrating SCR catalyst into them for both PM and NOx reductions. Some of this is described above at it pertains to NOx reductions, but later in this section the summary will pertain to SCR filter management and particulate performance.

On the DPF front, Khalek, et al. [84] reported emissions results from the Advanced Collaborative Emissions Study (ACES) on three 13-15 liter 2011 US engines with DPF and SCR systems. Testing was done on the US FTP and a custom 16-hour cycle. The overall purpose of the program is to guantify the emissions and their health effects of representative Class 8 engines. Relative to 2007 engines (DPF systems only), the 2011 engines have 72% particle number reductions on the 16-hour cycle. The difference is due to the lack of DPF regenerations afford by the high-NOx low-PM calibrations of the 2011 engines. There were no DPF regenerations on the 2011 engines over three consecutive 16-hour cycles, wherein the 2007 engines regenerated one to three times per cycle. Emissions of CO<sub>2</sub> are 3% lower on the 2011 engines but, due to the higher N<sub>2</sub>O emissions, the global warming potential is similar. NOx emissions are 94% lower even though the regulation calls for a nominal 82% reduction (on the FTP). PM emissions are very low at 0.6 mg/bhp-hr (0.9 mg/kW-hr) and are 67% lower than in 2007; but the composition shifted in that sulfates were greatly reduced but nitrates increased on an absolute basis. It is hypothesized the sulfates are stored (125 hours of testing), and if so, will ultimately be released. Other major categories (elemental and organic carbon, elements) were significantly reduced. Unregulated, but very toxic emissions (polycyclic aromatic compounds, dioxins, furans) were further reduced from the low 2007 levels. The health studies are in progress, but rats exposed to the exhaust for more than 28 months showed no overt clinical signs of disease [<u>85</u>].

DPFs are so effective in reducing particulates that they typically far surpass the regulatory requirements. In addition to the above example, Kassel, et al., [86] analyzed US EPA non-road engine certification data for the Tier 4i 2011 regulation, and found that relative to the 20 mg/kW-hr PM standard, DPF-equipped engines on average emitted about 16 mg/kW-hr (-75%) less PM than the requirement, while non-DPF engines were only 3 mg/kW-hr (-15%) under the standard. They estimate this 13 mg/kW-hr "PM surplus" has full-useful engine life monetized values of \$600 to \$10,000 per engine, depending on application and PM-related health costs.

Metal oxide ash from lube oil and wear is captured in DPFs and will impact DPF performance and lifetime. Bardasz [87] showed that the DPF back pressure can depend a lot on type of lube oil that is used. Lube oil with 1.8% sulfated ash and other ash-forming components can increase DPF back pressure 5X more than a lower-ash lube oil over 80,000 km. The difference in fuel consumption between the two lube oils after 100,000 km of operation was1.4% favoring the low-ash version, or about €360 per year in an average truck application.

Kotrba, et al., [88] evaluated parameters affecting passive regeneration of soot with  $NO_2$ . Applying a PGM washcoat to a DPF can significantly improve PR rate up to a point (specified only as "low" vs. "high"), suggesting that there is a limit to the benefit that can be gained by increasing PGM loading. Installing a DOC upstream of an uncoated DPF increases the passive regeneration rate nearly 5 times, but adding additional catalyst to the filter has minimal impact. Increasing the inlet temperature from 300°C to 400°C increases the soot burn rate by nearly 4 times under steady-state conditions, and this explains why faster transients increases burn rates.

Sappok, et al., [89] used a variety of methods enabling them to propose a conceptual model of how ash collects at the back of the filter inlet cell. Soot particles contain 10-30 nm primary ash particles. When soot is deposited and oxidized, the action consolidates ash particles into larger (~100 nm) secondary particles. Once deposited on the DPF surface these particles cannot be re-entrained in the gas flow, given both their small size and the velocity profile at the DPF surface. However, when subsequent soot layers oxidize, they shrink and curl and bring the loose ash particles with them. This action causes the soot to applomerate into hollow particles 25 microns in diameter (1000X the primary particle), which then become entrained in the gas and migrate to the back of the cell. To enhance DPF performance, the authors suggest that the filter be continuously regenerated to allow ~10 g/liter ash to build a membrane; then regenerate only after thick soot builds to allow transport of subsequent ash agglomerates to the back of the filter. In this way, the ash membrane enhances filtration efficiency without building up a thick layer on the cell wall surface.

Spark-ignition stoichiometric natural gas engines are emerging in vocational applications, and require only a three way catalyst to meet emissions regulations. PM levels are quite low and comparable to filtered diesel engines. However, these are almost all from lube-oil derived ash. Thiruvengadam, et al., [90] measured particulate emissions on the UDDS cycle, on a 45 mile per hour (72 km per hr) cruise, and at idle on two school buses with 8.9 liter stoichiometric natural gas engines with EGR and certified to the US 2010 standards. Metal oxide particles were measured at about 4 mg/mile and were largely attributed to lube oil and wear components. This is roughly 3 mg/kW-hr. For reference, Khalek, et al. [84] measured about 0.008 mg/kW-hr on a representative 16-hr cycle on US2010-cerified diesel engines with DPFs, or three orders of magnitude lower. Further, Thiruvengadam did some preliminary health screening on the natural gas particulates, and found the toxicity to alveolar macrophages (lung cells that collect impurities) to be strongly correlated to Cu, Zn, and P components.

When SCR catalyst is incorporated into the filter, passive regeneration with NO<sub>2</sub> is hampered. Tang, et al., [91] modeled the NO<sub>2</sub> profile in an SCR filter with and without urea injection. Figure 10 shows the results. Without urea injections (Figure 10a), the NO<sub>2</sub> concentration profile is symmetric throughout the soot cake and wall. However, when urea is present (Figure 10b), the SCR reduces it much faster than the soot can consume it, setting up a sink in the wall for NO<sub>2</sub> that draws it away from the soot cake.



Figure 10.  $NO_2$  concentration profiles in the soot cake and filter wall for an SCR filter with (b) and without (a) urea present. The SCR catalyst acts as a sink for NO2 resulting in lower concentrations in the soot cake. [91]

Despite this negative effect of SCR filters on passive soot regeneration with  $NO_2$ , Blakeman [92] showed this can be managed, <u>Figure 11</u>. Although the percent back pressure increase for the SCR filter (SCRF) system is higher than the base DOC+CSF (oxidation catalyzed soot filter) after 15 test

cycles, after 30 and 50 cycles, the three SCR+filter designs have lower back pressure increases than the base design, indicating soot accumulation is controlled.



# Figure 11. Percent increases in non-SCR and SCR-filter (SCRF) designs in back-to-back FTP (Federal Test Procedure) testing. [92]

In designing SCR filter systems, filtration pores might be larger, and attention must be paid to filtration efficiency. For example, Vonarb [93] tested four different SCR filters with and without soot (3-4 g/liter) on the Non-Road Transient and Non-Road Steady-State Cycles (NRTC and NRSC), and all of the configurations passed the Swiss PN requirement ( $1 \times 10^{12}$  particles /kW-hr) on the NRTC with soot, but only one of the four designs passed on the NRSC with and without soot. Vonarb also quantified the regimes of active (with O<sub>2</sub>) and passive (NO<sub>2</sub>) filter regeneration. At 290°C, the NOx:soot should be greater than 1250, and at 335°C is should be greater than 500.

Finally, in developing countries the preferred method to meet Euro IV HD standards for smaller urban vehicles is using EGR for NOx control and an open filter design to manage PM. In the filter, some of the gas is filtered and some passes through without filtering. The design will not shutdown the engine if the filtered pathway plugs due to lack of regeneration. However, previous designs can create much smoke upon acceleration after the filter fills with soot. He, et al. [94] describe a new "partial filter" designed after a standard ceramic wall-flow DPF, except the inlet plugs are missing. Half the channels are open, and the channels with a plug on the end impart filtration. As all the soot is collected in a plugged cell, there is not soot blow-off. Filtration efficiency is up to 70% (for both PM and PN), and if the filtering channels block, the engine can still run and the filter will ultimately return to normal operation. Aluminum titanate is the material of choice to provide significant robustness. Zhang, et al. [95] did a modeling study on the concept in earlier work.

#### Gasoline Particulate Filters

As discussed in the Regulations section, PN emissions from GDI (Gasoline Direct Injection) engines are problematic and coming under RDE (real-driving emissions) regulations. GPFs are seriously being considered to meet these requirements. So, much activity has been reported on GPFs in the last three years. Earlier reports focused on uncatalyzed filters that were retrofit in the under-body position behind a three-way catalyst (TWC). The next generation were catalyzed to help on gaseous emissions. Last year, more improvements were reported involving optimizing for emissions efficiency, light-off, and back pressure.

For example, Harth, et al., [96] showed that since 2009 back pressure has dropped 30% with little change in filtration efficiency; CO and hydrocarbon emissions have dropped 20-30%; and NOx dropped 35%, at the same precious metal loading. They even propose meeting the Euro 6 LD emissions standards with only a catalyzed GPF, wherein NOx emissions are 14% lower than with a standard TWC, but CO is 10% higher. At constant precious metal loadings, better gas emissions reductions are obtained with higher washcoat loadings.

Blakeman [92] also described a coated GPF that can meet Euro 6 requirements by itself. Two designs are shown - one designed for low emissions and the other for low back pressure. The low emissions design has 10% lower PN and 30% lower NOx emissions, but at a 50% higher back pressure during accelerations.

Ash can be an issue with GPFs, but a TWC in front of the GPF can trap upwards of 80% of it, resulting in 25 to 50% lower gaseous emissions across the GPF than if it was up front collecting all the ash [92]. GPF back pressure is 25% lower if it is placed behind the TWC, due to this ash effect [97]. Schmitz, et al. [98] report some accelerated ash loading results, wherein calcium collects in the back, but zinc and phosphorous are evenly distributed in the axial direction of the GPF.

To round out the GFP section, substrates and catalyst coating methods are advancing to the point where back pressure and light-off of coated GPFs are nearly equivalent or better than production TWC. Rose, et al. [99] showed the heat-up results in Figure 12. The inlet temperatures are nearly identical in the case of the TWC and the catalyzed GPF, but after 20 seconds the GPF outlet temperature increases faster than those of the TWC. By 40 seconds the GPF is 50°C hotter. The effect is attributed to low thermal mass and better heat transfer kinetics in the wall-flow design. In other tests, back pressure for a coated GPF is lower than for a standard TWC in low and intermediate flow conditions (-50% at 200 m<sup>3</sup>/hr) at 750°C, but is higher at high flow conditions (+30% at 700 m<sup>3</sup>/hr). Like Blakeman [91], Rose, et al., reported that fuel cut-offs during decelerations provide enough oxygen to burn any collected soot. Rose, et al., reported more such events during urban driving, but the higher temperatures in highway driving

counter-balanced the fuel cut-off effect. Coated filters cause the soot to burn faster and hotter, but temperature are kept <1100°C up to a high soot load (for gasoline) of 4 g/liter.



Figure 12. Catalyzed GPF (gasoline particulate filter) heats up faster after 20 seconds than the stock TWC (three-way catalyst). [99]

#### Particulate Filter Summary

Particulate filters are certainly a success story for cleaning diesel engines. Careful analyses of PM and associated emissions are becoming more difficult because the levels are so low. In applications with a choice of using filters or not using them to meet PM regulations, the PM and PN emissions are significantly lower when the filter is chosen. Studies on ash are adding insight into how to use the ash to a benefit, or at list minimize the consequences. Adding SCR catalyst to the filter affects filter regeneration, but it is manageable, and back pressure is coming down on these integrated components. Filters are now moving into gasoline applications, and the progress has been very impressive in the last few years. Back pressure is now similar to standard three-way catalyst (TWC) converters, light-off is faster in some cases, and gaseous emissions reductions due to the filter is adding the possibility of entirely replacing the TWC with a GPF to meet Euro 6 emissions requirements.

# **OXIDATION CATALYSTS**

Oxidation catalysts were the first catalysts to go on vehicles in the 1970s (on US cars), and they are now at the heart of the diesel emission control system. In addition to HC and CO reductions, diesel oxidation catalysts (DOCs) play a major role in pre-conditioning the exhaust by forming NO<sub>2</sub> for filter management and enhanced SCR performance. However, the new challenge for DOCs is with the high HC and CO emissions from the emerging LTC (low-temperature combustion) engines.

Natural gas engines are also challenged on methane emissions. Progress on both of these issues are summarized here.

Curran, et al., [100] defined the exhaust challenge for one type of LTC advanced engine, the Reactivity Controlled Compression Ignition engine (RCCI; see Engine Developments section for description). In urban driving, as indicated by the Urban Dynamometer Drive Cycle (UDDS), hydrocarbon emissions are nominally 20 g/kW-hr, versus a US standard of 0.18 g/kW-hr. CO levels are also quite high, at 50 g/kW-hr (standard is about 20 g/kW-hr). The challenge is the temperature - it is less than 240°C throughout most of the cycle, and significant parts at less than 200°C. Prikhodko, et al., [101] highlighted some issues with current DOCs. Shown in Figure 13 are results on a standard diesel oxidation catalyst (3.5 g/liter Pt; swept volume ratio 0.66) on both a conventional diesel engine and an RCCI engine. The HC light-off temperature (temperature at 50% conversion; T<sub>50</sub>) increases from 190°C for diesel to 240°C for RCCI. There was no catalyst activity in RCCI exhaust at temperatures less than 200°C. The hydrocarbon mix is also quite different, with carbonyls, and especially mono-aromatic carbonyls, increasing significantly, probably due to the use of gasoline as the main fuel component.



Figure 13. RCCI exhaust behaves differently in a DOC than conventional diesel exhaust, increasing light-off temperatures by more than 50°C. [101]

Some potential solutions are emerging. Toops, et al. [102] describe a gold catalyst on a ceria/zirconia support that was aged to 700°C and has CO  $T_{50}$  of 50°C with 1% CO in the gas. This compares with the CO  $T_{50}$  of 300°C in RCCI exhaust measured by Prikhodko, et al. [101]. However, Toops, et al., started with the Au-CuO<sub>2</sub> system, and it had a very low CO  $T_{50}$ , but it was too sensitive to NO and HCs. It was not known if this characteristic will translate to the Cu-free gold catalyst. For mixed-mode engines that might run LTC at lower loads and conventional diesel combustion at high loads, Parks [103]

showed a hydrocarbon trap concept that holds onto HCs in the 200-250°C range during RCCI operation, but releases them in diesel mode when the DOC is operative. Hydrocarbons drop by 79% with the concept versus only 40% with a standard DOC arrangement when an engine is run through mode changes (diesel-RCCI-diesel) over a 40 minute period (20 minutes in RCCI mode).

Natural gas engines can emit significant amounts of methane. This historically was not a big issue, as methane does not react in the atmosphere to form ozone, but it is a strong greenhouse gas and coming under scrutiny. Palladium catalysts can convert methane in lean combustion, but the light-off temperatures are still high at 450°C, and they are sensitive to sulfur poisoning, for example from lube oil, odorants in the fuel, or from landfill or biogas (cleaned from >1% sulfur). Guliaeff, et al., [104] developed a method of impregnating zeolites with platinum up to the 3% level (1% was previously a limit) to enable selected oxidation of small hydrocarbons, like methane and propane. The catalyst is quite resistant to sulfur poisoning. The methane T<sub>50</sub> for aged samples (650°C for 24 hrs) is 425°C, compared to the base Pd/Pt catalyst at 450°C. The reference catalyst lost most of its activity in an aggressive sulfur pre-treatment (100 ppm SO<sub>2</sub> at 500°C for 125 hrs) but the new catalyst still maintained a methane T<sub>50</sub> of 450°C. Similarly, Kinnunen, et al., [105] reported on a noble metal natural gas catalysts with improved washcoat formulations (ZrO<sub>2</sub>, TiO<sub>2</sub>, others) that have a methane T50 of 430°C after exposure to 25 ppm SO<sub>2</sub> for 20 hours at 400°C, but can be regenerated with 2% methane enrichment for 20 minutes at 550°C, after which the methane  $T_{50}$  drops to 380°C, similar to the fresh catalyst (360°C).

Kim, et al. [106] went further on methane  $T_{50}$ . They studied the thermal aging effects on methane catalysts, and made significant improvements by improving HC oxidation to help on the exotherm, stabilizing the Pd through better dispersion, and using oxygen storage catalysts and promoters to enhance activity. Individually, the methods drop methane  $T_{50}$  by 11 to 40C°, with the additive effects dropping the methane  $T_{50}$  from 402°C to 317°C. The improved catalyst also exhibits much better durability, maintaining performance beyond 38 hrs when the reference catalyst lost efficiency at 4 hrs.

#### **Oxidation Catalyst Summary**

The new LTC combustion processes will challenge oxidation catalysts. A standard DOC did not perform well with RCCI combustion exhaust wherein hydrocarbon and CO removal efficiencies are too low in urban driving conditions for this engine. Methane catalysts for natural gas engines are making incremental improvements, becoming more sulfur tolerant, and dropping the  $T_{50}$  for methane from 402°C for a standard Pt/Pd catalyst down to 317°C by incorporating a number of methods like new supports and coating methods, and promoters.

# GASOLINE GASEOUS EMISSIONS CONTROL

Three-way catalysts (TWC) have been the staple emissions control approach for gasoline engines for more than 30 years. In 2000 the TWC was already approaching 20 years of age Since then the light-off temperature has dropped 35C° and the precious metal cost has dropped more than 60% [107]. The technology is so effective in meeting ever-tightening tailpipe regulations that gasoline engine technologies to meet emissions advanced very little until cold-start control became important in the late 1990's. Some of the latest developments in TWCs will be highlighted here, as well as progress on hydrocarbon traps and advanced lean-burn gasoline emissions reductions.

To set the stage for future emissions approaches, Ball, et al., [108] benchmarked gasoline engine and catalyst emissions technologies on two gasoline cars certified to Tier 2 Bin 5 standards, and two certified to California PZEV (Partial Zero Emissions Vehicle) standards (similar to LEVIII fleet average) in the 1.4 to 2.0 liter engine class. The Bin 5 cars had specific power ratings of 88 and 100 kW/liter, and the PZEV cars were 12% lower at 77 to 83 kW/liter. Common technologies among the four engines are variable valve technologies (to various degrees), and single stage turbocharging with a close-coupled catalyst. Both PZEV cars used wide range lambda sensors and underbody catalysts. The authors looked at idling speed, air-fuel ratio, and ignition timing to quickly heat the catalyst. The PZEV engines idle slower (900 and 1300 RPM versus 1500 RMP), deliver lean mixtures ( $\lambda$ =1.05) to the catalyst (one Bin 5 is rich, the other lean), and both retard spark until 20° after top center (versus 10° for the Bin 5 cars) to delay the fuel burn for hotter exhaust. These measures allow the catalyst on PZEV cars to reach 300°C at the within 10 seconds during idle, while the Bin 5 cars take 20 to 30 seconds, into the first hill, on the US FTP. It was demonstrated that through proper catalyst design and placement of the precious metals, significant reductions in precious metal loading are possible with minimal impact on exhaust emissions. For example, nearly 4 grams of Pd was taken from the underbody catalyst in one design while still meeting the Bin 5 emissions regulations. Also, significant interactions between catalyst technology and lambda control exist, especially with deceleration fuel cut-offs (DFCOs). For example, higher oxygen storage capacity can drop NOx emissions upon acceleration after a DFCO event. New technologies like HC traps can reduce emissions about 15% in the early portions of the US FTP, but upwards of 30% when DFCOs are used. These examples show that gasoline emissions systems need to be designed much more closely with the engine calibration as the greenhouse gas and criteria emissions tighten.

 $N_2O$  is a powerful greenhouse gas and will become increasing more important as part of the emission inventory of gasoline engines as the CO<sub>2</sub> emissions drop further. Ball, et al. [109]

examined the N<sub>2</sub>O emissions from modern SULEV (Super Ultra-Low Emission Vehicle) vehicles. Three way catalysts produce more N<sub>2</sub>O emissions with aging. Three cars aged for 6,400 km, produced < 1 mg/mile N<sub>2</sub>O during the FTP; all of the vehicles with dynamometer aged catalysts produced between 1.2 and 8 mg/mile of N<sub>2</sub>O, which is below the 10 mg/mile regulation. This represents perhaps 0.2-1.5% of the GHG footprint of emerging vehicles (2020 in Europe). More severely aged catalyst may exceed the 10 mg/mile N<sub>2</sub>O US LD GHG limit. There appears to be many system interactions (calibration, fuel injection, catalysts and their combinations etc) other than catalyst temperatures that effect N<sub>2</sub>O emissions. In general, aged catalysts produce N<sub>2</sub>O emissions at between 300°C and 500°C. The period after a hot start can produce much of the N<sub>2</sub>O emissions due to extended periods of time when both the close coupled and underbody catalysts are in this temperature range. Secondary air injection does reduce cold start N<sub>2</sub>O formation, but lowering the ceria in a closecoupled catalyst increases N<sub>2</sub>O formation during the FTP at exhaust temperatures of 550°C.

On lean burn gasoline, there are unique emissions challenges, namely lean NOx. Three way catalysts can't function well in these conditions, and the NOx levels are generally too high for practical urea SCR. Philipp, et al. [110] described the emission control system for the Mercedes-Benz lean burn gasoline engine for Euro 6 and the concept system for the US version. They combine the TWC with the NOx storage catalyst (NSC; or LNT) to make a TWNSC single component in the close coupled position, followed by an underbody NSC. The US SUILEV concept adds a TWC in front of the first TWNSC to deliver quicker light-off. A more significant challenge was in managing the sulfur trapped by the two NSCs. During desulfation to prevent the sulfur coming off the front TWNSC from depositing on the back one, two separate types of NSCs with different sulfur release properties were developed. Figure 14 shows some results. Upon heat-up the system is design using a lower temperature formulation in the back than the front to match the release of sulfur at roughly the same time.



Figure 14. Desulfation behavior of the front and back NOx storage catalysts match the heat-up properties of the system so the sulfur passes through the system. [110]

Another lean-burn gasoline concept is to capture ammonia generated in the TWC during rich operation in a downstream SCR catalyst for use during lean operation. Parks [104] reported preliminary tests wherein the air:fuel ratio is oscillated between rich and lean. For the rich portion, the best compromise between a CO and ammonia is at lambda 0.96. The approach removes >99% of the NOx. Fuel economy is about 5.4% with a steady-state cycle of 80 sec rich, 40 sec lean at 2000 RPM and 2 bar BMEP.

#### Gasoline Gaseous Emissions Summary

To move from LEVII or Tier 2 Bin 5 to LEVIII (-75%NMOG+NOx) gasoline automobiles will need to change. Models that meet the regulations today have reduced idling speeds, 10° more ignition delay, and wide-range lambda sensors, more flexible variable valve technology, and some have secondary air injection to the catalyst. Emissions architecture needs to be optimized with the engine calibration, requiring close cooperation between the two engineering entities. N<sub>2</sub>O appears not to be a major issue for LEVIII, but might represent perhaps 1% of the GHG footprint of the car. Lean burn emissions technologies are advancing, with concepts being developed for transferring the technology from Europe to the US.

#### SUMMARY/CONCLUSIONS

#### Regulations

California finalized the LEVIII LD emissions standards in January 2012, and the US EPA is now finalizing their approach, calling for nominally a 75% reduction in NMOG+NOx, down to 30 mg/mile combined. Europe is also tightening down on LD diesel NOx and GDI PN, but using the RDE (Real Driving Emissions) model of putting vehicles on the road and measuring emissions as part of the certification procedure. China and India both have severe air quality problems in which vehicular emissions are significant part. China is implementing and appears to be very serious. India is putting together a fuel and vehicle technology roadmap through about 2025. Europe is moving to tighten non-road emissions, wherein expansion of the regulation into smaller and larger engines, and harmonization with HD truck test methods and regulations is the direction. Finally, California is investigating the feasibility of tightening HD truck NOx regulations down to 0.020 g/bhp-hr, and a test program is in place to look at it.

#### Fuels

Incremental oil production over the next 10 to 15 years will shift from the Middle East to the Americas. Soon, the Americas will surpass the Middle East in oil production. Further, natural gas production is ramping up quickly, relieving oil demand. All this portends stable fuel prices. However, there are trends towards shifts in fuel type, namely more diesel demand than gasoline demand. Also, with increased demands on efficiency and emissions, fuel quality becomes even more important, and harmonization and enforcement of fuel standards will increase in importance.

#### Engines

Both light-duty and heavy-duty engines are making impressive gains. Gasoline engine fuel consumption reductions of up to 30% versus the MPI baseline are in development, and LD diesel might achieve 20% reductions versus the very efficient engines of today. On the HD side, both government and private programs are demonstrating potential for 50% BTE (10-12% fuel consumption reductions), with goals set to achieving 55% BTE (20% reductions from today). Greenhouse gas reductions will increasingly be needed, and very low criteria pollutant emissions will be the default requirement. Work is advancing on compression ignited natural gas engines, wherein post injections can significantly drop PM and methane emissions.

#### NOx Control

Lean NOx systems are continuing to evolve. SCR system architecture is improving with better control and system layout. Catalyst formulations and designs and also adding to the NOx reductions. Much focus is on low-temperature performance. Also, consolidation of components, like SCR and filters, and addition and synergies different components with different capabilities, like passive NOx adsorbers and lean NOx traps added to SCR systems are of significant interest.

#### Filters

Particulate filters are certainly a success story for cleaning diesel engines. Careful analyses of PM and associated emissions are becoming more difficult because the levels are so low. In applications with a choice of using filters or not using them to meet PM regulations, the PM and PN emissions are significantly lower when the filter is chosen. Studies on ash are adding insight into how to use the ash to a benefit, or at list minimize the consequences. Adding SCR catalyst to the filter affects filter regeneration, but it is manageable, and back pressure is coming down on these integrated components. Filters are now moving into gasoline applications, and the progress has been very impressive in the last few years. Back pressure is now similar to standard three-way catalyst (TWC) converters, light-off is faster in some cases, and gaseous emissions reductions due to the filter is adding the possibility of entirely replacing the TWC with a GPF to meet Euro 6 emissions requirements.

#### **Oxidation Catalysts**

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#### **Concluding Comments**

Vehicular emissions control technologies have help enable highly-efficient and clean vehicles to meet customer requirements. Moving forward, balancing ever-demanding CO<sub>2</sub> standards and criteria emissions with vehicles that customers will buy will be the challenge. The projected stability in the next decade or two in petroleum supply and demand will make this more difficult. The emissions control industry has a stellar record. Future engine developments should focus on CO<sub>2</sub> reductions, and consider the criteria emissions but leave much of this technology evolution to the emissions control field. The collaboration between engine calibration and the emissions control system will become increasingly vital.

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# ACKNOWLEDGEMENTS

The SAE reviewers of this paper deserve special recognition. Their patience and diligence is greatly appreciated, and their expert opinions and perspectives certainly added to the quality of this review paper.

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