Emission Control Technologies for Diesel-Powered Vehicles

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Executive Summary

Diesel engines are important power systems for on-road and off-road vehicles. Most heavy-duty trucks and buses are powered by a diesel engine due to the long record of reliability, high fuel-efficiency, and high torque output. Diesel engines are easy to repair, inexpensive to operate, and extremely durable. It is not uncommon for a diesel engine to last 15-20 years and achieve a one million-mile life. From the standpoint of greenhouse gas emissions, diesel engines can compete with other advanced technologies, like hybrid electric vehicles, due to diesel's inherent fuel economy relative to conventional spark-ignited, gasoline engines. Diesel-powered vehicles have demonstrated a 30-40 percent fuel economy advantage over their gasoline counterparts. This translates to about a 20 percent reduction in CO_2 emissions.

While diesel engines have many advantages, they have the disadvantage of emitting significant amounts of particulate matter (PM) and oxides of nitrogen (NOx) into the atmosphere. Diesel engines also emit toxic air pollutants. Health experts have concluded that pollutants emitted by diesel engines adversely affect human health and contribute to acid rain, ground-level ozone, and reduced visibility. Studies have shown that exposure to diesel exhaust causes lung damage and respiratory problems and there is increasing evidence that diesel emissions may cause cancer in humans.

Companies that manufacture emission controls have responded to the challenge of reducing air pollution from diesel engines. Through their efforts, cost-effective technologies have been developed to reduce harmful emissions. In the mining, materials handling and trucking industries, in urban bus fleets, ports, construction, and freight, diesel emission control technologies have demonstrated their ability to significantly reduce unwanted emissions at reasonable costs without jeopardizing vehicle performance. Manufacturers of Emission Controls Association (MECA) member companies, together with engine manufacturers, have worked together to meet the 2007 requirements proposed by EPA on May 17, 2000 in the new highway heavy-duty diesel engine (HDDE) "2007/2010 Rule." These advanced heavy-duty powertrains were introduced in January 2007, with further improvements expected in 2010. Clean diesel technologies are also entering the North American light-duty vehicle fleet, with many vehicle manufacturers targeting diesel passenger car and light-duty truck launches in the 2008-2010 time frame. MECA member companies are also preparing for the next big challenge of emission reductions from off-road engines to meet upcoming federal Tier IV regulations.

Interest in diesel emissions control has grown considerably in recent years as agencies such as the U.S. EPA and California's Air Resources Board (ARB) put forth new regulations and funding to clean up existing and new vehicles. MECA has received many inquiries regarding the installation of emission controls on diesel engines. Inquiries have included requests for technical information, information on past experiences, the types of control technologies available, the suitability of a given technology to a particular application, and the emission reductions that can be achieved. This document has been prepared to supplement information already made available by

MECA on emission control technologies and provides an overview of the types of technologies being developed for new diesel cars and trucks, including their operating and performance characteristics.

Available Control Technologies

Today, viable emission control technologies exist to reduce diesel exhaust emissions from both new engines and vehicles, as well as in-use engines through the use of retrofit kits. The major technologies are listed below. Technologies designed to control particulate matter (PM) include:

- Diesel oxidation catalysts (DOCs)
- Diesel particulate filters (DPFs)
- Closed crankcase ventilation (CCV)

Technologies designed to control oxides of nitrogen (NOx) include:

- Exhaust gas recirculation (EGR)
- Selective catalytic reduction (SCR)
- Lean NOx catalysts (LNCs)
- Lean NOx traps (LNTs)

The descendents of early two-way catalysts for gasoline engines that were used to oxidize hydrocarbons and CO are oxidation catalysts. Diesel oxidation catalysts have been installed on engines for well over 20 years in millions of retrofit applications and tens of millions new vehicles worldwide. Although originally developed to reduce gaseous emissions such as HC and CO, oxidation catalysts have demonstrated 20-50 percent reductions in total particulate matter on a mass basis.

Diesel particulate filters, including flow-through and wall-flow designs, have achieved a significant experience base, with more than 200,000 DPFs installed as retrofits and over 4 million installed as original equipment on passenger cars in Europe. Wall-flow filters are being installed on all new heavy-duty trucks in the U.S. starting in 2007. While flow-through filters are capable of achieving PM reduction of about 30 to 75 percent, high efficiency wall-flow designs can capture well over 90 percent of the particulate. Both types of filters are capable of trapping the sub-micron, ultrafine particles capable of penetrating deep into the lungs. Recently, the Association for Emissions Control by Catalysts (AECC) conducted test programs for particle size and number on light-duty and heavy-duty vehicles using the procedures outlined in the European Particle Measurement Program (PMP). The results of the testing demonstrated the efficiency of wall-flow filters to reduce engine out particle number by three orders of magnitude at a filtration efficiency of 99.9 percent.

Due to its smog and ozone forming ability, NOx has become a target for new and used vehicle regulations. Exhaust gas recirculation (EGR) has been developed to achieve the lowest possible engine out emissions. EGR is capable of achieving up to 50 percent reduction in NOx emissions. Lean NOx catalysts (LNCs) are able to reduce NOx by 10-40 percent using hydrocarbons present in the exhaust, or supplemented via injection into the exhaust stream, as the reductant. LNC technology is attractive because it can be easily applied without the need for core engine modifications or additional reductant infrastructure. Lean NOx traps (LNTs) are capable of achieving upwards of 80 percent NOx reduction. This technology traps NOx as an alkaline earth nitrate compound supported on the substrate and uses on-board fuel injected into the exhaust stream to periodically regenerate the trap and emit nitrogen.

Selective catalytic reduction (SCR), using urea as a reducing agent, has also been installed on diesel-powered vehicles. SCR is capable of reducing NOx emissions from 75 to 90 percent while simultaneously reducing HC emissions up to 80 percent and PM emissions by 20 to 30 percent. SCR systems are available on most Euro IV and V compliant heavy-duty trucks in Europe. SCR technology has been selected by several engine manufacturers for meeting the upcoming U.S. 2010 on-road regulations. Numerous demonstration projects intended to commercialize SCR systems for vehicles in the U.S. are underway at this time.

Any emission control solution used by an engine manufacturer for meeting either the U.S. 2007 or 2010 heavy-duty highway regulations or the U.S. Tier 2 or California LEV II light-duty vehicle emission regulations will be based on a combination of technologies discussed in this paper. Furthermore, a number of other engine-based strategies, not covered in detail here, are also likely to be employed to combine fuel economy, emissions, and space constraints into a systems approach to develop a complete emission strategy for diesel-powered vehicles.

Although diesel emissions from mobile sources have raised health and welfare concerns, a number of effective control strategies exist or are being developed that can greatly reduce the emissions from diesel-powered vehicles. All of the aforementioned technologies have been successfully demonstrated on both on-road and non-road vehicles. These technologies can greatly reduce particulate matter, oxides of nitrogen, and other harmful pollutants from diesel exhaust. Although similar technologies exist for reducing emissions from in-use engines (see the MECA white paper entitled "Retrofitting Emission Controls on Diesel-Powered Vehicles (April 2006)"), this white paper will focus on technologies and approaches currently installed on or being developed for new diesel-powered vehicles to meet existing and/or upcoming emissions regulations.

1.0 Introduction

Diesel engines provide important fuel economy and durability advantages for large heavy-duty trucks, buses, nonroad equipment and passenger cars. They are often the power plant of choice for heavy-duty applications. While they have many advantages, they also have the disadvantage of emitting significant amounts of particulate matter (PM) and oxides of nitrogen (NOx) and, to a lesser amount, hydrocarbon (HC), carbon monoxide (CO), and toxic air pollutants.

Particles emitted from diesel engines are small – in most cases less than 2.5 microns in diameter. The particles are complex, consisting of a carbon core, adsorbed hydrocarbons from engine oil and diesel fuel, adsorbed sulfates, water, and inorganic materials such as those produced by engine wear. Because of their extremely small size and composition, the particles emitted by diesel engines have raised many health concerns. Health experts have expressed concern that diesel PM may contribute to or aggravate chronic lung diseases such as asthma, bronchitis, and emphysema.

There is growing evidence that exposure to diesel PM may increase the risk of cancer in humans. As early as 1988, the International Agency for Research on Cancer (IARC) concluded that diesel particulate is probably carcinogenic to humans. The term "carcinogen" is used by the IARC to denote an agent that is capable of increasing the incidence of malignant tumors. In August 1998, California Air Resources Board identified PM emissions from diesel-fueled engines as a toxic air contaminant and adopted its ground breaking Diesel Risk Reduction Plan in September of 2000 with the goal of reducing diesel PM levels by 85 percent in 2020. In 2000, the U.S. EPA declared diesel PM to be a "likely human carcinogen." A recent report, "Diesel and Health in America: The Lingering Threat," issued in February 2005 by the Clean Air Task Force (CATF), reviews the health impacts of diesel particulate emissions in the U.S. This report states that fine particulate pollution from diesel engines shortens the lives of nearly 21,000 people in the U.S. every year, with health-related damage from diesel PM estimated to total $139 billion in 2010.

NOx emissions from diesel engines also pose a number of health concerns. Once in the atmosphere, oxides of nitrogen react with volatile organic compounds (VOCs) in the presence of sunlight to form ozone. Ozone is a reactive and corrosive gas that contributes to many respiratory problems. Ozone is particularly harmful to children and the elderly. The CATF published a report in 1999 on ozone related respiratory incidents in 37 Eastern states and the district of Columbia for the ozone period of April to October in 1997. The report estimated that there were over 50,000 hospital admissions and approximately 160,000 emergency room visits related to high ozone levels. NOx emissions themselves can damage respiratory systems and lower resistance to respiratory infection. As with ozone, children and the elderly are particularly susceptible to NOx emissions. The American Lung Association estimates that 55 percent of the U.S. population lives in counties which have unhealthy levels of either ozone or particulate pollution.

Despite health and environmental concerns, the diesel engine remains a popular means of powering trucks, buses, and other heavy equipment. Most buses and heavy-duty trucks are powered by diesel engines for good reasons. Diesel engines are reliable, fuel-efficient, easy to repair, and inexpensive to operate. One of the most impressive attributes of the diesel engine is its durability. In heavy-duty trucks, some engines have achieved operating lives of 1,000,000 miles or more. In Europe, more than 50 percent of the new cars sold each year are powered by a diesel engine. This is in part due to the superior fuel economy of the diesel, which delivers in excess of 30 percent higher miles per gallon than its gasoline counterpart. Engine manufacturers have made significant advances in the performance characteristics of today's diesel power plants. Unlike the diesel engines of just 10-15 years ago, which were considered noisy and sluggish, modern diesel engines deliver excellent low-end torque for superior acceleration. This combined with advanced transmissions eliminates the response lag of older diesel engines.

In response to public health concerns, a number of countries worldwide have established significantly lower exhaust emission limits for new diesel engines that are being phased in over the 2005-2015 timeframe. The U.S. EPA has mandated new regulations for on highway diesel trucks and passenger cars to reduce diesel emissions starting with the 2007 model year, with even further reductions in 2010. The emission control technologies discussed in this document represent state-of-the-art approaches that new vehicle manufacturers are using to meet existing and future emission regulations.

Figure 1 shows the current and future emission regulations around the world for heavy-duty diesel engines. The clear trend is toward reductions in PM and NOx usually in a two-stage approach. The first stage requires PM controls, such as diesel particulate filters. The second stage generally follows several years later with NOx controls. The tightest NOx levels remain as set by the U.S. EPA under their on-highway 2010 truck regulations. At the time of this report, the Euro VI heavy-duty vehicle limits are still under discussion and Japan has begun discussions of post-2010 emission standards for diesel vehicles. Whatever the final outcome in Europe and Japan, the trend is clearly toward technology-forcing regulations around the world requiring a systems approach that combines advanced combustion technology with additional exhaust controls for both PM and NOx.

Diesel engine calibration can be adjusted within the temperature-atmosphere combustion map into regions of higher PM or NOx emissions. A combustion environment that gives higher PM emissions will naturally result in lower NOx and vise-versa. Manufacturers can take advantage of this engine calibration control to specify a type of exhaust emission control that is best suited to meet regulations around the world. Therefore the technologies employed may vary depending on the demands of the emission standards in different countries.

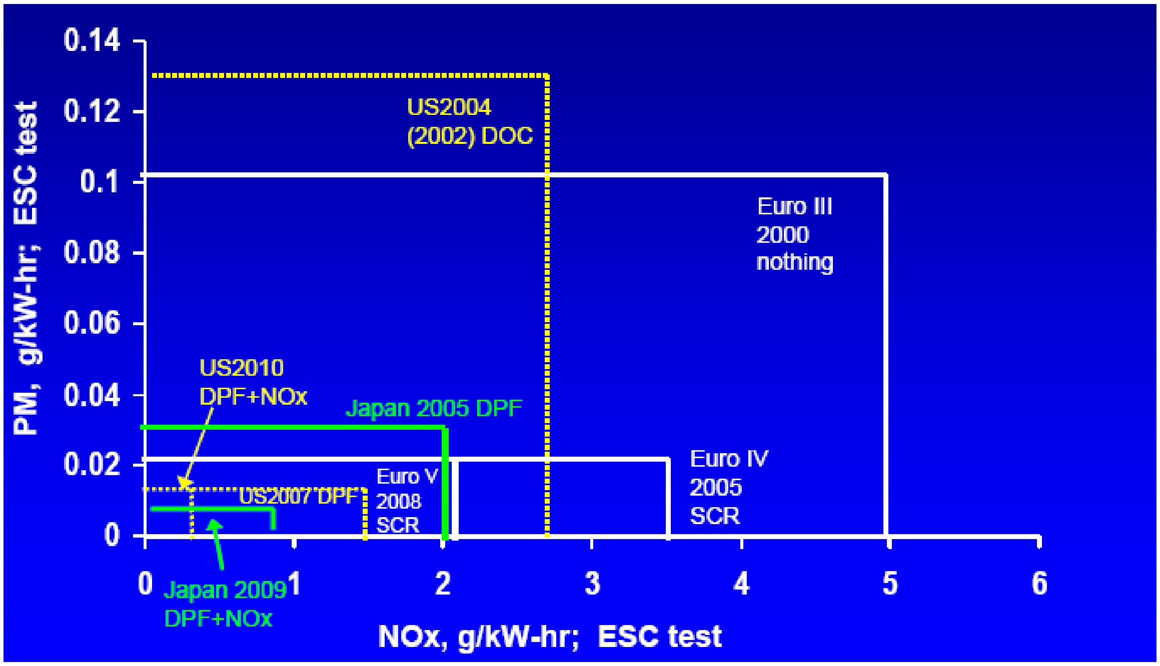


Figure 1. Current and future heavy duty diesel regulations around the world.

2.0 Approaches for Reducing Diesel Emissions

The technological feasibility of meeting the strict U.S. Tier 2 diesel passenger vehicle and 2007/2010 on-highway diesel truck emission standards was predicated on having a low sulfur diesel fuel that was readily available. (The detrimental impact of diesel sulfur on individual emission control technologies will be discussed in each technology section.) The U.S. EPA required the wide-scale availability of ultra-low sulfur diesel (ULSD) having <15 ppm sulfur in October 2006 in advance of the 2007 heavy-duty diesel on-road truck regulation. As detailed in the EPA rulemaking documents for the 2007/2010 heavy-duty on-road regulations, compliance with these regulations would require a systems engineering approach that combines the use of ULSD with advanced engines and advanced exhaust emission control technologies.

2.1 Engine Controls

Engine manufacturers started as early as the late eighties to develop cleaner diesel engines by employing a number of strategies. These approaches include advanced common rail fuel injection, electronic engine controls, combustion chamber modifications, air boosting, improved air/fuel mixing, and reduced oil consumption. Achieving ultra-low exhaust emission targets requires a systems approach. Engine manufacturers are focusing on ways to control engine operation to reduce engine-out emissions as low as possible and reduce the burden on the exhaust emission control systems.

Approaches aimed at reducing cold-start emissions involve retarding the ignition timing to allow some hydrocarbons to pass through in the exhaust and light off the catalyst sooner. This approach can also be effective in generating sufficient exothermic heat over a catalyst to regenerate soot from a particulate filter as will be discussed in subsequent sections.

Variable valve timing (VVT) is being used to introduce some fraction of exhaust gas into the combustion process and reduce HC and NOx emissions. Exhaust gas recirculation (EGR) is used to dilute intake air with some fraction of exhaust gas to lower the combustion temperatures resulting in lower engine-out NOx emissions. This can come at the price of increasing particulate matter in the exhaust.

Direct injection of fuel into the cylinders rather than port injection has allowed for better control of the air fuel ratio during combustion and resulted in better fuel utilization. Improved turbulence and mixing in the intake port of some low emission engines have resulted in fuel savings. Advanced diesel engines have benefited significantly from common rail fuel injection which allows for electronically controlled injection at very high pressures. Through the use of pilot and retarded injection strategies or in combination with injection rate shaping, clean diesels have achieved significant reduction in NOx over conventional diesel injection such as pipe-line or unit injection. Common rail and electronic injection control is very effective in carefully controlling post injection of fuel making it suitable for use with emission control devices such as particulate filters, NOx adsorbers and lean NOx catalysts requiring brief periods of fuel rich exhaust to facilitate regeneration of the catalyst or filter.

Understanding and controlling the combustion process is the first step in reducing engine-out emissions and minimizing the burden on the emission control systems. This allows catalyst developers to design smaller, less costly exhaust controls. Engine design is an important part of controlling and facilitating the combustion process.

In diesel engines, controlling combustion is the key approach to reducing engine out particulate emissions by optimizing the mixing between the fuel and air in the combustion chamber. Some common ways to increase mixing is through combustion chamber modifications to facilitate turbulent flow as well as fuel injector and injection port design to modify the spray pattern. Variable geometry turbocharging (VGT), which delivers variable quantities of pressurized air based on driving conditions, has been effective in reducing PM emissions by maintaining lean combustion in the engine. Reducing the compression ratios has been shown effective in lowering combustion temperatures and, in turn, NOx emissions.

Some engine manufacturers have been able to achieve improvements to combustion during cold-start by making modifications to the design of intake air control valves resulting in a 40-50 percent reduction in HC emissions.

State-of-the-art developments in combustion engineering has led to significant reductions in engine-out emissions on experimental engines. These processes are known by many names and acronyms but they all fall into the general classification of low temperature combustion or pre-mixed homogeneous combustion processes, such as homogeneous charge compression ignition (HCCI), among others.

The conventional wisdom in diesel combustion has been that any change in engine operating parameters to reduce NOx emissions results in an increase in particle emissions. In general, higher combustion temperatures promote complete oxidation of the fuel, thus less soot, but also cause more formation of NOx. Unlike traditional spark-ignited (SI) or compression-ignited (CI) engines, which have specified ignition points, HCCI combustion takes place spontaneously and homogeneously with many nucleated ignition points and therefore without flame propagation. This eliminates heterogeneous air/fuel mixture regions which result in soot particles. Low temperature combustion can be facilitated by the use of ultrafine injector orifice diameters in conjunction with lower excess oxygen content in the fuel mixture to achieve a more homogeneous distribution of the charge, thus reducing both NOx and PM.

These combustion processes occur only within a limited range of the operating cycle, making control difficult under high speed/load and transient operation. For this reason, advanced multi-mode diesel engines combine HCCI operation at lower speeds to minimize PM and NOx while reverting to conventional stratified charge combustion at high speed/load operation to ensure stable operation.

2.2 Exhaust Controls

This section provides a brief description of the available diesel exhaust control technologies, including descriptions of their operating characteristics, control capabilities, and operating experience. More detail on each control technology is provided in subsequent sections.

The majority of hydrocarbon and carbon monoxide emissions from diesel engines that have exhaust catalysts occur during cold-start before the catalyst can achieve optimum operating temperatures. Engine and exhaust system manufacturers have been working together with catalyst companies to develop ways to heat up the catalyst as quickly as possible. The greatest benefit came from the introduction of close-coupled catalysts (CCCs). This positioned the diesel oxidation catalyst (DOC) close to the exhaust manifold to allow rapid heating and therefore rapid oxidation of CO and hydrocarbons. The exothermic heat generated in the DOC by these oxidation reactions facilitates the rapid heat up of the downstream catalysts, such as diesel particulate filters, lean NOx catalysts, and SCR catalysts.

A supporting technology that links engine controls and exhaust controls and has been used effectively by both engine and exhaust technology developers is thermal management. The beneficial impact on reducing cold-start emissions via thermal management has resulted from numerous improvements to the exhaust system components upstream of the DOC in order to retain as much heat as possible in the exhaust gases. Manufacturers have developed ways to insulate the exhaust manifold and exhaust pipe. Attaching the DOC to a double-walled, stainless steel exhaust pipe containing an air gap within the tube walls is probably the most common thermal management strategy used today. This approach has been taken further by incorporating new inlet cone designs and modifications to the shape of the space in front of the close-coupled substrate. Thermal management between catalyst components in the diesel exhaust stream is also important to effectively regenerate the diesel particulate filter by retaining heat from the oxidation catalyst or auxiliary heat source when passive or active regeneration strategies are employed. Retaining enough heat downstream to regenerate a lean NOx trap also requires thermal management and carefully engineered exhaust components.

A brief description of the major technologies employed in the reduction of pollutants from diesel exhaust is included below along with a range of conversion efficiencies that may be achieved. More detailed descriptions of their performance characteristics will be covered in subsequent sections of this paper.

Diesel oxidation catalysts (DOCs) installed on a vehicle's exhaust system can reduce total PM typically by as much as 25 to over 50 percent by mass, under some conditions depending on the composition of the PM being emitted. Diesel oxidation catalysts can also reduce smoke emissions from older vehicles and virtually eliminate the obnoxious odors associated with diesel exhaust. Oxidation catalysts can reduce more than 90 percent of the CO and HC emissions and more than 70 percent of the toxic hydrocarbon emissions in diesel exhaust.

Diesel particulate filters (DPFs) are installed on all new diesel-powered vehicles to meet the U.S. Tier 2 light-duty and 2007 heavy-duty on highway emission limits for PM. DPFs can achieve up to, and in some cases, greater than a 90 percent reduction in PM. High efficiency filters are extremely effective in controlling the carbon fraction of the particulate, the portion of the particulate that some health experts believe may be the PM component of greatest concern. Particulate filters can be designed to also reduce toxic hydrocarbons emissions by over 90 percent. Catalytic exhaust control and particulate filter technologies have been shown to decrease the levels of polyaromatic hydrocarbons, nitro-polyaromatic hydrocarbons, and the mutagenic activity of diesel PM.

Exhaust gas recirculation (EGR) is being used on new light- and heavy-duty diesel vehicles as the primary method of reducing engine-out NOx. EGR is capable of achieving a 50 percent reduction in NOx emissions or more; however, it can result in an increase in engine-out PM emissions.

NOx catalysts have demonstrated NOx reductions of 10 to 40 percent whereas NOx adsorbing catalysts (also known as NOx traps) are capable of 70 percent or more NOx reduction. These NOx catalysts also provide oxidation capabilities that result in significant reductions in exhaust hydrocarbons, CO and the soluble fraction of PM.

Selective catalytic reduction (SCR) using urea as a reducing agent has been shown to be the most effective control technology for reducing NOx emissions, exhibiting conversions of up to 90 percent while simultaneously reducing HC emissions by 50 to 90 percent and PM emissions by 30 to 50 percent.

Closed crankcase ventilation technology is being installed on all new 2007 heavy-duty trucks equipped with turbocharged diesel engines to eliminate crankcase emissions. Crankcase emissions vented to the engine compartment have been found to enter cabin air and can be a significant source of driver and passenger PM exposure. These systems capture particulate generated in the crankcase and return them to the lubricating system of the engine.

3.0 Flow-Through Diesel Oxidation Catalysts

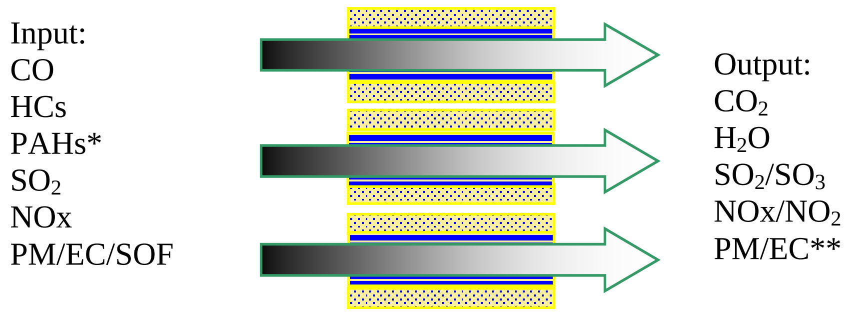
The diesel oxidation catalyst (DOC) is one of the oldest forms of controlling exhaust pollutants such as CO, HC and PM. Originating from the early two-way automotive catalysts, DOCs are designed to oxidize unburned components of fuel in the exhaust to innocuous products like CO_2 and H_2O. The reactants may include exhaust hydrocarbons of all types, CO, or the soluble organic fraction (SOF) of the diesel particulate matter. The SOF consists of unburned hydrocarbons from fuel and lube oil that have condensed on the solid carbon particles.

DOCs are most often based on a flow-through honeycomb substrate (either metallic or ceramic), coated with an oxidizing catalyst such as platinum and/or palladium. Using oxidation catalysts on diesel-powered vehicles is not a new concept. Oxidation catalysts have been installed on over 250,000 off-road vehicles around the world for over 30 years. Tens of millions of oxidation catalysts have been installed on new diesel passenger cars in Europe and on new heavy-duty highway trucks in the U.S since the mid-1990s. These systems have operated trouble free for hundreds of thousands of miles. Oxidation catalysts can be used not only with conventional diesel fuel, but have also been shown effective with biodiesel and emulsified diesel fuels, ethanol/diesel blends and other alternative diesel fuels.

3.1 Diesel Oxidation Catalyst

In most applications, a diesel oxidation catalyst consists of a stainless steel canister that contains a honeycomb structure called a substrate or catalyst support. The substrate may be either made from a ceramic material or metal foil. There are no moving parts, just large amounts of interior surface area. The interior surfaces are coated with catalytic metals such as platinum and/or palladium.

This type of device is called an oxidation catalyst because it converts exhaust gas pollutants into harmless gases by means of chemical oxidation. In the case of diesel exhaust, the catalyst oxidizes CO, HCs, and the soluble organic fraction of particulate matter into carbon dioxide and water. DOCs also play an important role in continually removing soot from the DPF. This occurs by oxidizing some of the NO to NO_2 which serves to oxidize the soot or by generating heat through the oxidation of CO and HC to raise the DPF temperature above the soot oxidation temperature.



* Polyaromatic hydrocarbons or other toxic hydrocarbon species
** Elemental carbon

Figure 2. Diagram of a Diesel Oxidation Catalyst.

Figure 2 shows a representation of three channels of a straight through, flow path honeycomb. The engine out exhaust gases enter the channels from the left and as they pass over the catalyst coating they are oxidized to the reaction products on the right. The particulate matter entering the DOC consists of elemental carbon (EC) and gaseous, semi-volatile SOF. Exiting the catalyst, most of the volatile SOF has been oxidized, as well as, potentially some of the elemental carbon depending on the temperature. The level of total particulate reduction is influenced in part by the percentage of SOF in the particulate. For example, a Society of Automotive Engineers (SAE) Technical Paper (SAE No. 900600) reported that oxidation catalysts could reduce the SOF of the particulate by 90 percent under certain operating conditions, and could reduce total particulate emissions by up to 40 to 50 percent. PM reductions of 20 to 35 percent are typical for newer model year engines. Destruction of the SOF is important since this portion of the particulate emissions contains numerous chemical pollutants that are of particular concern to health experts.

3.2 Filter Regeneration Catalysts

In 2007, all U.S. heavy-duty diesel vehicles must have a diesel particulate filter (DPF) in the exhaust system to reduce PM to below 0.01 g/bhp-hr. The DPF will be described in greater detail later in this report. An essential part of the proper functioning of any DPF system relies on a prescribed regeneration to occasionally burn soot collected in the filter and reduce the backpressure of the exhaust stream. Many exhaust control systems rely on a DOC or regeneration catalyst upstream of the DPF to assist with regeneration. This strategy can be applied to either coated or uncoated DPFs and essentially performs two functions. The first is to oxidize unburned HC and CO in the exhaust and utilize the exothermic heat of combustion to raise the temperature of the exhaust gas entering the DPF to temperatures sufficient to combust the captured carbonaceous soot. This can be done by enriching the fuel/air ratio going to the cylinders or injecting a small amount of fuel into the exhaust ahead of the DOC. A second DOC regeneration function is to oxidize some of the NOx in the exhaust to nitrogen dioxide

(NO_2) which oxidizes carbon at a lower temperature than oxygen. The presence of higher concentrations of NO_2 thus facilitates filter regeneration at lower exhaust temperatures.

3.3 Impact of Sulfur on Oxidation Catalysts

The sulfur content of diesel fuel has a significant effect on the operation of catalyst technology. Catalysts used to oxidize the SOF of the particulate can also oxidize sulfur dioxide to form sulfate particulate (sulfates are a mixture of sulfuric acid and water), which adds to the mass of the particulate. This reaction is not only dependent on the level of sulfur in the fuel, but also the temperature of the exhaust gases. Diesel oxidation catalysts are the most sulfur resistant catalyst technologies being applied to diesel exhaust and were the only type of catalyst that could be used prior to the introduction of ULSD. In most cases DOCs can operate effectively on fuel with up to 500 ppm S, however the activity and function of the catalyst components can be impacted negatively, resulting in a reduction of catalyst efficiency.

Catalyst formulations have been developed which selectively oxidize the SOF while minimizing oxidation of the sulfur dioxide. However, the lower the sulfur content in the fuel, the greater the opportunity to maximize the effectiveness of oxidation catalyst technology for both better total control of PM and greater control of toxic HCs. Lower sulfur fuel (500 ppm sulfur; 0.05 percent wt), which was introduced in 1993 throughout the U.S., facilitated the application of DOC catalyst technology to diesel-powered vehicles. Now, the availability of ultra low-sulfur diesel (ULSD) fuel (15 ppm sulfur; 0.0015 percent wt) in the U.S. and Canada allows for further enhancements of catalyst performance. Ultra-low sulfur diesel fuel was rolled out across the U.S. and Canada in 2006 as part of EPA's and Environment Canada's 2007-2010 highway diesel engine emissions program (see www.epa.gov/otaq/diesel.htm). ULSD is the required fuel for all 2007 and newer diesel engines.

Starting in 2007, EPA requires a 500 ppm limit for sulfur on diesel fuel produced for nonroad engines, locomotives, and marine applications. The rule also sets a subsequent limit of 15 ppm sulfur (ultra-low sulfur diesel) for nonroad fuel by 2010 and by 2012 for locomotive and marine applications. The availability of these fuels will allow nonroad engines to fully take advantage of catalyst technology for complying with future EPA Tier 4 emission regulations for non-road, marine and locomotive diesel engines. California already requires use of ULSD for all diesel engines except for certain types of ocean-going ships.

4.0 Diesel Particulate Filters

4.1 Operating Characteristics and Control Capabilities

As the name implies, diesel particulate filters remove particulate matter from diesel exhaust by filtering exhaust from the engine. They can be installed on vehicles or stationary diesel engines. Since a filter can fill up over time, engineers that design filter systems must provide a means of burning off or removing accumulated particulate matter. The only practical method of disposing of accumulated particulate matter is to burn or oxidize it within the filter when exhaust temperatures are adequate. By burning off trapped material, the filter is cleaned or "regenerated." Filters that use available exhaust heat for regeneration are termed "passively regenerated" filters. Filters that regenerate in this fashion cannot be used in all situations. Filters that use some kind of energy input, like injection of diesel fuel into an upstream DOC, are termed "actively regenerated" filters. In general, new vehicle applications of DPFs employ a combination of passive and active regeneration strategies to ensure that filter regeneration occurs under all vehicle operating conditions. Active regeneration strategies employ various engine controls to achieve filter regeneration conditions on demand.

Diesel particulate filters can be combined with exhaust gas recirculation (EGR), NOx adsorber catalysts or selective catalytic reduction (SCR) to achieve significant NOx and PM reductions.

4.1a Closed Crankcase Ventilation

In most pre-2007 turbocharged, aftercooled diesel engines, the crankcase is vented to the atmosphere often using a downward directed draft tube. While a rudimentary filter was often installed on the crankcase vent, substantial amount of particulate matter was released to the atmosphere. The particles are predominantly a liquid aerosol generated by the rapidly moving parts in the crankcase. When vented into the engine compartment, they are not only emitted, uncontrolled into the atmosphere, they can easily make their way into the passenger compartment of the vehicle. This PM goes undetected in any kind of engine-out PM measurement. Emissions through the crankcase vent may exceed 0.7 g/bhp-hr during idle conditions on recent model year engines.

All 2007 and newer engines require the control of crankcase emissions and in many cases engine manufacturers are employing closed crankcase systems with filters as shown in Figure 3. This system consists of a multi-stage filter designed to collect, coalesce, and return the emitted lube oil to the engine's sump. Filtered gases are returned to the intake system, balancing the differential pressures involved. Typical systems consist of a filter housing, a pressure regulator, a pressure relief valve and an oil check valve. These systems greatly reduce crankcase emissions. Closed crankcase filter systems can be combined with DOCs or DPFs to reduce PM emissions associated with both the ventilation of the crankcase and the tailpipe.

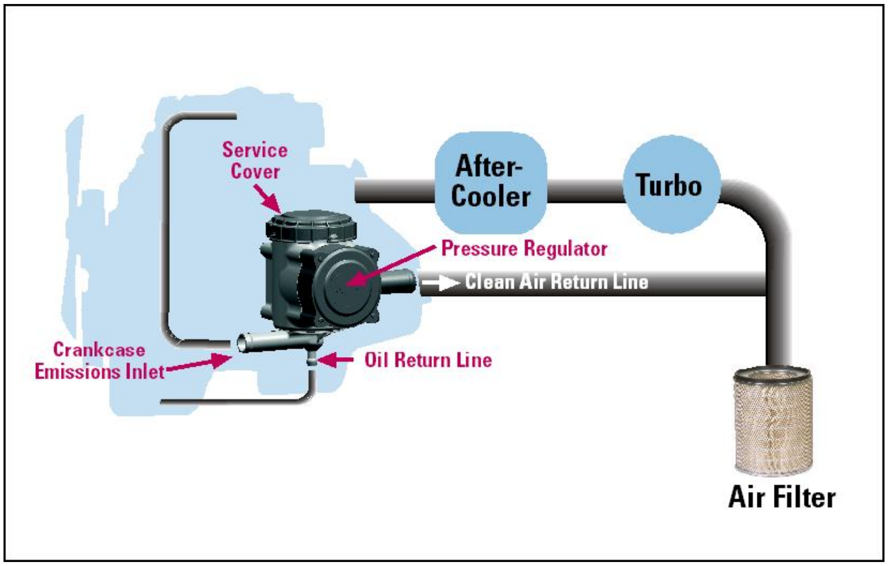


Figure 3. Closed Crankcase Emission Control System.

4.1b Flow-Through or Partial Diesel Particulate Filters

Flow-through filter technology is a relatively new method for reducing diesel PM emissions. Flow-through filters employ catalyzed metal wire mesh structures or tortuous flow, metal foil-based substrates with sintered metal sheets to reduce diesel PM (Figure 4). Partial Filters have been in production for more than 3 years with well over 200,000 pieces installed mostly in heavy-duty and light-duty vehicles in Europe. Because of their maintenance free operation, with no active regeneration or ash removal necessary, they are also verified as a level 2 (>50-84%) PM reduction device under California's retrofit program. Flow-through filters are capable of achieving PM reduction of about 30 to 75 percent, depending on the engine operating characteristics.

Flow through filter technologies can be coated with catalyst materials to assist in oxidizing the soot or used in conjunction with an upstream diesel oxidation catalyst to oxidize diesel soot as the exhaust flows through these more turbulent flow devices. These metal devices may see advantages in applications requiring special shapes or having space limitations due to their relatively smaller package size. Flow-through filters generally do not accumulate inorganic ash constituents present in diesel exhaust. The ash passes through the device, reducing the need for filter cleaning in most applications.

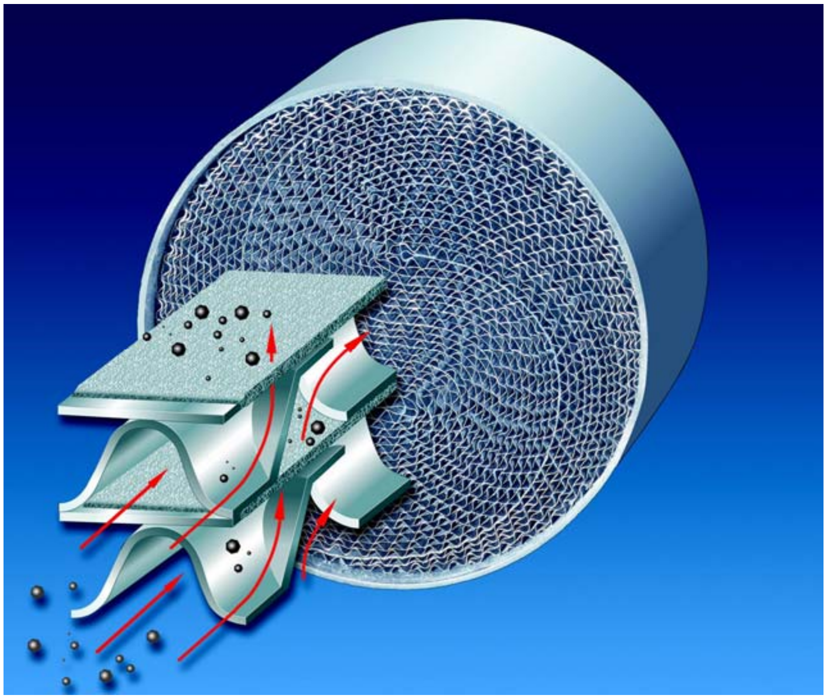


Figure 4. Metallic flow-through filter made up of corrugated metal foil and layers of porous metal fleece.

4.1c High Efficiency Filters

In Europe, vehicles equipped with high efficiency diesel particulate filters are being offered commercially. Filters were introduced on new diesel passenger cars in Europe in mid-2000, with more than four million filter-equipped cars sold since that first introduction. Very few performance or maintenance issues have been reported in Europe with passenger car DPFs. Peugeot (PSA) was the first manufacturer to introduce DPF system for European diesel cars in 2000. Other European automobile manufacturers, such as Audi, Fiat, Ford, VW, BMW, Renault and Mercedes, are now offering DPF systems based on the PSA system and the use of fuel-borne catalysts, or catalyzed filter systems that do not employ a fuel-borne catalyst.

Beginning with the 2007 model year, all heavy-duty highway diesel engines sold in the U.S. are being equipped with high efficiency diesel particulate filters as part of EPA's 2007-2010 highway diesel engine emission program. All new light-duty diesel passenger vehicles and trucks will be required to employ high efficiency DPFs to meet the U.S. Tier 2 or California LEV II 0.01 g/mile emissions limit for PM. High efficiency diesel particulate filters are also standard equipment on new highway diesel engines sold in Japan.

The most common high efficiency filter is based on a porous wall, square cell, honeycomb design where every alternate channel is plugged on each end (Figure 5). These wall-flow filters can be made from a variety of ceramic materials. High efficiency filters made of sintered metal fibers are also available. Wall flow filters exhibit high strength and thermal durability.

Figure 5 simplifies the operation of a wall-flow DPF. Particulate-laden exhaust enters the filter from the left. To make the exhaust flow through the porous cell walls, channels are capped at opposite ends in a checkerboard configuration. As the gas passes through the porous walls of the filter cells (thus the wall-flow filter designation) the particulate matter is deposited on the upstream side of the cell wall. Cleaned exhaust gas exits the filter to the right. Over time the soot deposited on the cell wall will result in a build-up of backpressure and will have to be cleaned by a process known as regeneration which will be discussed in Section 4.2.

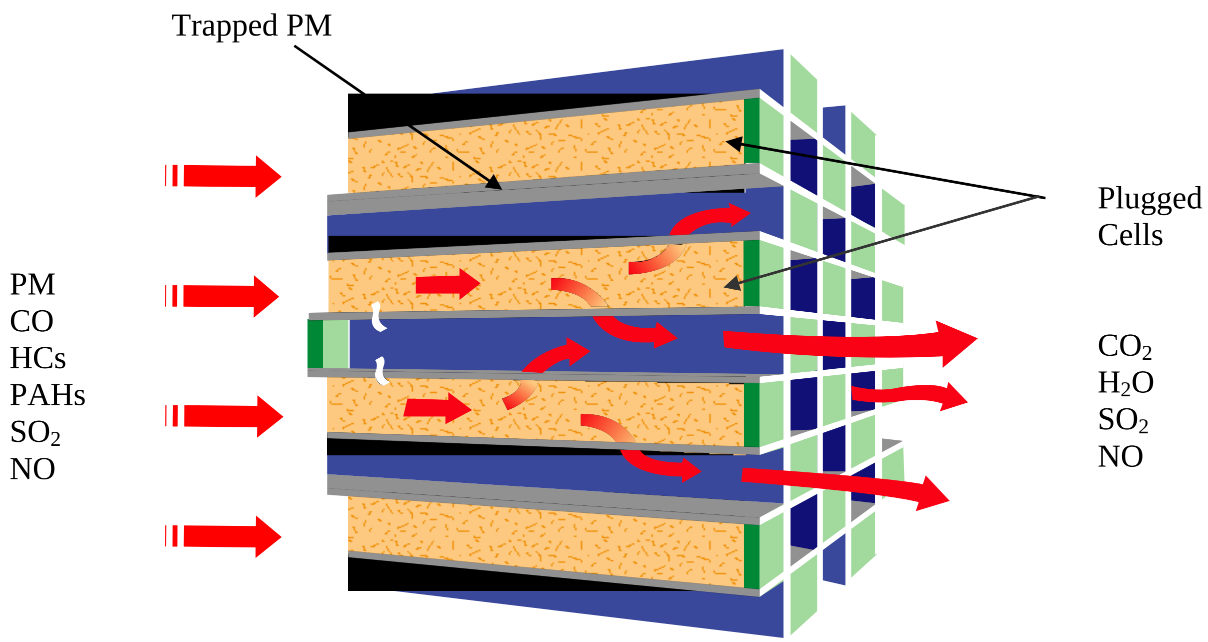


Figure 5. Diagram of a Wall-Flow Diesel Particulate Filter.

Increasing interest has been raised regarding the health impacts of particulate size and number in addition to the total mass. At this time, research has not determined which physical characteristic or chemical component is the most significant. The European Union has actively pursued the measurement and characterization of ultrafine particles and particle number when promulgating new emission regulations. Future European light-duty emission standards will include emission limits for both PM mass and number. The future Euro VI heavy-duty standards being developed are also considering including requirements for both types of PM measurements. The Association for Emissions Control by Catalysts (AECC) conducted a test program for particle size and number on light-duty and heavy-duty vehicles using the procedures outlined in the European Particle Measurement Program (PMP). The heavy-duty testing was conducted using both the European Transient Cycle (ETC), as well as, the World Harmonize Test Cycle (WHTC) and looked at the total number of particles within the range of 25 nm to 2,500 nm

(2.5um). The results for heavy-duty engines under both test cycles are shown in Figure 6 and demonstrated the efficiency of wall-flow filters to reduce engine out particle number by three orders of magnitude at a filtration efficiency of 99.9 percent.

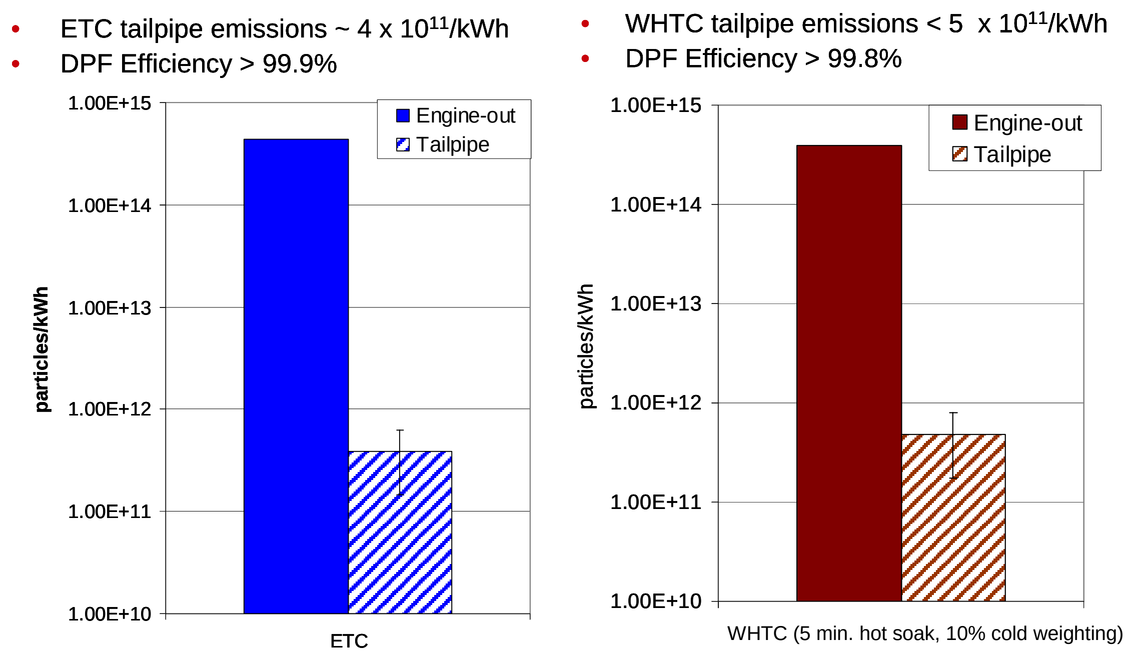


Figure 6. Particle number measurements with and without wall-flow DPF controls on heavy-duty vehicles using the PMP guidelines (AECC Euro VI Heavy-Duty Symposium, October 2007).

The most commonly used ceramic materials for wall-flow DPFs are cordierite and silicon carbide. Cordierite has been used as a substrate material in exhaust catalysts for many years due to its strength, low thermal expansion coefficient (which makes it ideal in high thermal stress environments) and low cost. A high porosity version of cordierite was designed for wall-flow DPF applications. Most large heavy-duty diesel applications use cordierite filters. In contrast, most light-duty diesel passenger cars to date have been equipped with filters made from silicon carbide (SiC). SiC offers much higher temperature tolerance than cordierite for applications where exhaust or regeneration temperatures may require it. The high strength of SiC makes it suitable in high thermal stress exhaust environments. The combination of these properties allows for a higher soot loading limit as the higher thermal conductivity of SiC controls the peak temperature during regeneration. On the other hand, SiC has a higher thermal expansion coefficient than cordierite and requires a segmented architecture within the filter element. Other wall flow ceramic materials being offered commercially include aluminum titanate (Al_2TiO_5) and mullite (Al_2SiO_5) for their high temperature capability and thermal shock properties.

Filter efficiency has rarely been a problem with the filter materials listed above when applied to wall-flow filter designs. Work has continued to: 1) optimize filter efficiency and minimize back pressure, 2) improve the radial flow of oxidation in the filter during regeneration, 3) improve the mechanical strength of filter designs, and 4) increase the ash storage capacity of the filter. Technological developments in DPF design include advancements in cell shape and cell wall porosity optimization aimed at minimizing engine backpressure and extending the interval between filter service. Advances such as higher pore volume, increased pore connectivity along with thinner web designs facilitate catalyst coating while maintaining longer times between soot regeneration events. Figure 7 shows how these relative improvements in filter design benefit overall pressure drop. Shown are results for 200 cpsi/ 19 mil wall thickness and 275 cpsi/ 14 mil thin wall-flow ceramic filters.

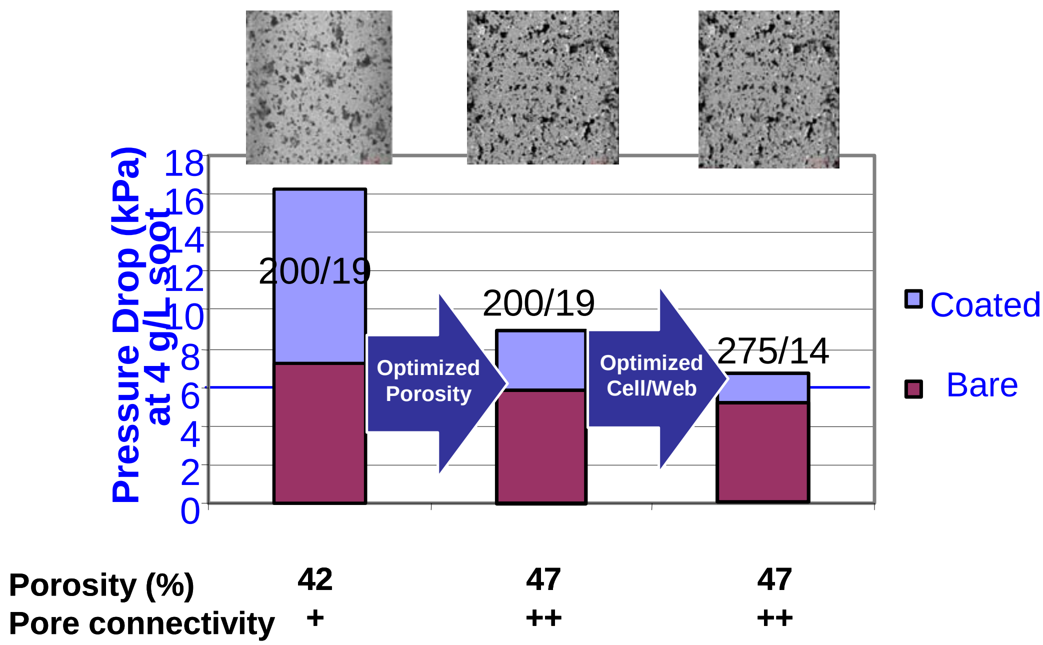


Figure 7. Pressure drop across a wall-flow DPF loaded with 4 g/l of soot as a function of percent wall porosity and relative level of pore connectivity for catalyzed and uncatalyzed filters.

4.2 Filter Regeneration

During normal operation of the diesel particulate filter, soot or particulate matter from the engine exhaust will be collected on the walls of the inlet channels. Since a filter will fill up over time, engineers that design filter systems must provide a means of burning off, or removing, the accumulated particulate matter. A convenient means of removal of accumulated particulate matter is to burn or oxidize it on the filter when exhaust temperatures are adequate. By burning off trapped material, the filter is cleaned or “regenerated.” This is referred to as passive regeneration and will be covered in more detail below. Filters that regenerate in this fashion cannot be used in all situations, primarily due to insufficient exhaust gas temperatures associated with the operation of some types of diesel engines, the level of PM generated by a specific engine, and/or application operating experience. To ensure proper operation, filter systems are designed for the particular engine/vehicle application and account for exhaust temperatures and duty cycles of the specific vehicle type. In low exhaust temperature operation an active regeneration strategy may need to be implemented to raise the exhaust temperature sufficient for oxidizing the soot.

Sulfur in diesel fuel significantly affects the reliability, durability, and emissions performance of catalyst-based DPFs. Sulfur affects filter performance by inhibiting the performance of catalytic materials upstream of or on the filter. Sulfur also competes with chemical reactions intended to reduce pollutant emissions and creates particulate matter through catalytic sulfate formation. Catalyst-based diesel particulate filter technology works best when the fuel sulfur level is less than 15 ppm. In general, the less sulfur in the fuel, the better the technology performs.

4.2a Passive Regeneration

The simplest type of filter is known as a passive design because it requires no driver or engine intervention to combust the soot on the filter. In this case the ceramic or metal filter substrate is coated with a high surface area oxide and precious or base metal catalyst. The catalyst acts to reduce the ignition temperature of the accumulated particulate matter by up to several hundred degrees centigrade. . The reduction in ignition temperature allows the DPF to regenerate passively on some applications, but there will be others for which the exhaust temperature is too low to regenerate the filter. Because passive regeneration requires a minimum exhaust temperature, it is not applicable to all types of engines and vehicles.

The experience with catalyzed filters indicates that there is a virtually complete reduction in odor and in the soluble organic fraction of the particulate, but some catalysts may increase sulfate emissions. Companies utilizing these catalysts to provide regeneration for their filters have modified catalyst formulations to reduce sulfate emissions to acceptable levels. Ultra-low sulfur diesel fuel (15 ppm sulfur maximum) is now available in the U.S. and has greatly facilitated these efforts.

Catalyst-based passive regeneration also relies on an upstream oxidation catalyst to facilitate oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2). Nitrogen dioxide is a much stronger oxidizer than oxygen allowing filter regeneration at lower temperatures. The nitrogen dioxide oxidizes the collected particulate thus substantially reducing the temperature required to regenerate the filter.

4.2b Active Regeneration

Actively regenerated, high-efficiency filter systems can be applied to a much larger range of applications. Because of added complexity needed to expand the range, they are generally more expensive than passive filters. Some of the active technology options are burners (some operate while the engine is running, others while the engine is turned off), injection of diesel fuel into the exhaust stream for oxidation across a DOC upstream of the DPF, or electrical heaters.

The most commonly applied method of active regeneration is to introduce a temporary change in engine mode operation or an oxidation catalyst to facilitate an increase in exhaust temperature.

Engine mode strategies include:

- Air-intake throttling. Throttling the air intake to one or more of the engine cylinders can increase the exhaust temperature and facilitate filter regeneration.

- Post top-dead-center (TDC) fuel injection. Injecting small amounts of fuel in the cylinders of a diesel engine after pistons have reached TDC introduces a small amount of unburned fuel in the engine's exhaust gases. This unburned fuel can then be oxidized over an oxidation catalyst upstream of the filter or oxidized over a catalyzed particulate filter to combust accumulated particulate matter.

- Post injection of diesel fuel in the exhaust upstream of an oxidation catalyst and/or catalyzed particulate filter. This regeneration method serves to generate heat used to combust accumulated particulates by oxidizing fuel across a catalyst present on the filter or on an oxidation catalyst upstream of the filter.

The above techniques can be used in combination with a catalyzed or uncatalyzed DPF.

In special applications where sufficient exhaust temperatures cannot be reached using the above techniques it may be necessary to use external means such as on-board fuel burners or electrical resistive heaters to heat the filter element and oxidize the soot. These can be used with catalyzed or uncatalyzed filter elements. In some cases regeneration can be accomplished while the vehicle is in operation, whereas in other cases the engine must be turned off for regeneration to proceed.

In some situations, installation of a filter system on a vehicle may cause a very slight fuel economy penalty. This fuel penalty is due to the backpressure of the filter system. As noted above, some filter regeneration methods involve the use of fuel burners and to the extent those methods are used, there will be an additional fuel economy penalty. Many filter systems, however, have been optimized to minimize, or nearly eliminate, any noticeable fuel economy penalty. The experience with U.S. 2007 heavy-duty filter technology has been consistent with manufacturer's projections of a 1 percent or less fuel penalty associated with filter operation.

4.2c Fuel-Borne Catalysts

The widest experience with fuel-borne catalysts (FBC) has been demonstrated on European passenger vehicles where FBC in combination with high efficiency wall-flow filters have been used on new diesel cars since 2000. Fuel-borne catalysts are a colloidal dispersion of base metal oxides or organic compounds containing precious or base metal ions such as platinum, cerium or iron and are added to the diesel fuel prior to the combustion process. The catalyst is added in minute, parts per million level, quantities either directly to the fuel tank or mixed with the fuel on-board the vehicle prior to injecting the catalyst-fuel mixture into the cylinder. In the combustion process, the organic fraction of the additive is combusted leaving the inorganic metal or oxide catalyst finely distributed within the soot particles and other combustion products. The homogeneous distribution of the catalyst in the fuel prior to combustion results in a fine, intimate distribution of catalysts particles within the soot. The direct contact between catalyst particles and soot particles reduces the temperature required for ignition of trapped particulate matter that is collected together on the filter media. When used with high efficiency wall-flow filters, the catalyst remains in the filter media and adds to the inorganic ash that accumulates within the filter and must be periodically removed as part of a regularly scheduled filter maintenance program.

4.2d Filter Maintenance

In addition to collecting soot, filters also collect inorganic-based exhaust constituents that are derived from several sources, including the combustion of engine lubricants, products of normal engine wear and/or corrosion, and materials associated with fuel-borne catalysts in DPF applications that use these catalysts to assist in the filter regeneration process. These inorganic oxides do not combust during filter regeneration events. Over extended operation on the vehicle, these ash species slowly accumulate within the filter and gradually increase the pressure drop across the filter. Since excessively high backpressure on the engine will result in a degradation of engine performance, the accumulated ash material within the filter needs to be periodically removed. This ash removal or cleaning operation is a necessary filter maintenance operation. Engine oil consumption characteristics, the total ash content of engine lubricant formulations, vehicle duty cycles, filter designs, and fuel-borne catalyst dosing rates all impact ash accumulation profiles and required filter maintenance cleaning intervals. Because of the toxicity of the material in the DPF, filter cleaning must be done on special machines that will fully capture the material for safe disposal. Many diesel engine service facilities will have the machines.

Filter systems do not appear to cause any additional engine wear or affect vehicle maintenance. Concerning maintenance of the filter system itself, manufacturers are designing systems to minimize maintenance requirements during the useful life of the vehicle. In most U.S. 2007, and later model year, heavy-duty vehicle applications, filter maintenance intervals are expectd to exceed 300,000 miles of service. A new generation of low ash containing lubricants has been introduced for these heavy-duty engine applications to help maximize filter cleaning intervals. Manufacturers provide the enduser with appropriate information on filter maintenance schedules. More information on filter maintenance can be found in MECA's technical document, "Diesel Particulate Filter Maintenance: Current Practices and Experience," available on MECA's website at: www.meca.org.

5.0 NOx Reduction Technologies

The superior fuel economy of diesel engines over gasoline lies in their operation at high air to fuel ratios where there is excess oxygen. The oxygen-rich combustion environment in combination with high combustion temperatures results in the formation of nitrogen oxides (NOx) in the combustion process. Gasoline engines also generate NOx by the same mechanisms; however, their typical stoichiometric air/fuel ratio in combination with three-way catalysts (TWCs) allows for very low tailpipe NOx levels. These approaches are generally not employed on diesel engines in order to maintain the significant fuel economy and low CO_2 benefits of these engines. Therefore, a new set of technologies have been developed by exhaust emission control manufacturers to significantly reduce NOx in oxygen-rich exhaust streams. Below is a brief overview of the types of technologies that are being developed and commercialized to reduce NOx from diesel engines and vehicles.

5.1 Exhaust Gas Recirculation (EGR)

As the name implies, EGR involves recirculating a portion of the engine's exhaust back to the charger inlet (or intake manifold in the case of naturally aspirated engines). In most systems, an intercooler lowers the temperature of the recirculated gases. The cooled recirculated gases, which have a higher heat capacity and lower oxygen content than air, lower the combustion temperature in the engine, thus inhibiting NOx formation. There are two types of EGR:

- *High pressure EGR* captures the exhaust gas prior to the turbocharger and redirects it back into the intake air.
- *Low pressure EGR* collects the clean exhaust after the turbocharger and after a diesel particulate filter and returns it to the intercooler. Diesel particulate filters are always used with a low-pressure EGR system to ensure that large amounts of particulate matter are not recirculated to the engine which would result in accelerated wear in the engine and turbocharger.

In some cases, engine manufacturers have also incorporated catalysts within high pressure EGR loops to reduce PM levels that are recirculated back through the combustion process. EGR systems typically recirculate about 25 to 40 percent of the combustion atmosphere to cool combustion temperatures and are capable of achieving NOx reductions of more than 40 percent. A schematic of a low-pressure EGR+DPF system is shown in Figure 8.

In order to optimize the engine out NOx reduction over the largest portion of the engine map and improve the fuel economy at the same time, manufacturers have developed combined technology air breathing solutions. The benefits of variable turbine geometry (VTG) turbochargers and low pressure EGR have been combined to provide both efficiency and NOx reduction. At low engine speeds and loads, the low pressure EGR system maintains the energy flow to the turbine (and thus power and efficiency), while, at higher speeds and high load portions of the engine map, the high pressure EGR system matches the flow requirements within the optimal turbine geometry to minimize losses. The blended EGR (high and low pressure) in combination with a VTG turbocharger can also match all operating conditions and provide better charge temperature control. The optimized combination of technologies is capable of achieving 30 percent NOx reduction while delivering a 3-4 percent reduction in brake specific fuel consumption (BSFC).

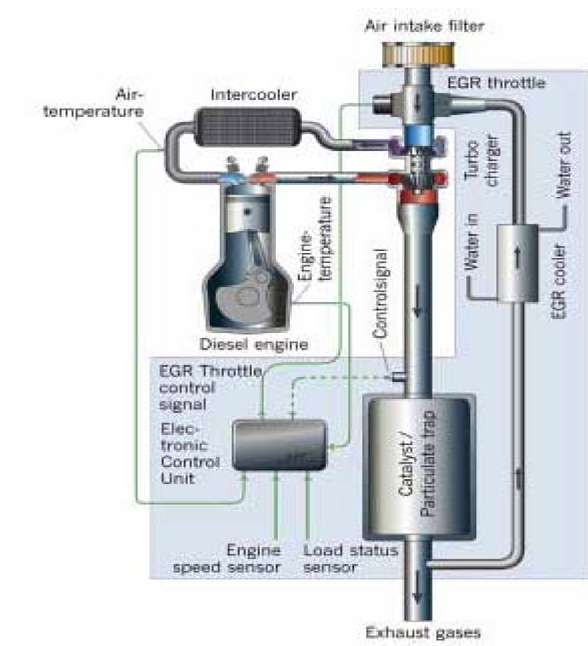


Figure 8. Low Pressure Exhaust Gas Recirculation (EGR) + DPF.

5.2 Lean NOx Catalysts

In the oxygen-rich environment of diesel exhaust, it is difficult to chemically reduce NOx to molecular nitrogen. Direct NOx decomposition is thermodynamically attractive, but the activation energy is very high for this method and no catalysts have been developed for wide-spread use.

Catalysts have been developed that use a reductant like HC, CO, or H_2 to assist in the conversion of NOx to molecular nitrogen in the diesel engine exhaust stream. They are generally called “lean NOx catalysts.” Because sufficient quantities of reductant are not present to facilitate NOx reduction in normal diesel exhaust, most lean NOx catalyst systems inject a small amount of diesel fuel, or other reductant, into the exhaust upstream of the catalyst. The added reductant allows for a significant conversion of NOx to N_2. This process is sometimes referred to as hydrocarbon selective catalytic reduction (HC-SCR). Currently, NOx conversion efficiencies using diesel fuel as the reductant are around 10 to 30 percent over transient test cycles. Other systems operate passively without any added reductant at reduced NOx conversion rates.

Lean NOx catalysts often include a porous material made of zeolite having a microporous, open framework structure providing trapping sites within the open cage network for hydrocarbon molecules along with either a precious metal or base metal catalyst. These microscopic sites facilitate reduction reactions between the trapped hydrocarbon molecules and NOx.

Lean NO_x catalyst systems have been demonstrated and verified for diesel retrofit application and thousands have been commercially applied. However, due to the relatively low NOx conversions (20-30 percent over transient cycles) and corresponding fuel economy penalties associated with the operation of these systems, lean NOx catalysts are generally not being considered for upcoming U.S. 2010 new vehicle regulations for either light-duty or heavy-duty applications where NO_x conversions of at least 60 percent are expected to be required. Nonetheless, researchers are developing methods to improve the conversion efficiencies and hydrothermal durability of lean NOx catalysts to identify formulations that meet the needs of the industry, perhaps in combination with advanced engine technologies like HCCI. One such program has identified several promising catalyst formulations using combinatorial screening techniques with conversion efficiencies as high as 75 percent on the US06 driving cycle (CLEERS Workshop 5/07).

5.3 NOx Adsorber Catalysts

NOx adsorber catalysts, also referred to as lean NOx traps (LNT), provide another catalytic pathway for reducing NOx in an oxygen rich exhaust stream.

5.3a Operating Characteristics and Performance

NOx adsorber technology removes NOx in a lean (i.e. oxygen rich) exhaust environment for both diesel and gasoline lean-burn GDI engines. The mechanism involves (see Figures 9 and 10):

1. Catalytically oxidizing NO to NO_2 over a precious metal catalyst.
2. Storing NO_2 in an adjacent alkaline earth oxide trapping site as a nitrate.
3. The stored NOx is then periodically removed in a two-step regeneration step by temporarily inducing a rich exhaust condition followed by reduction to nitrogen by a conventional three-way catalyst reaction.

As discussed above, under normal lean diesel engine operation, the NOx adsorber stores the NOx emissions. In order to reduce the trapped NOx to nitrogen, called the NOx regeneration cycle, the engine must be operated rich periodically for a short period of time (a few seconds). This cycling is also referred to as a lean/rich modulation. The rich running portion can be accomplished in a number of ways including:

- Intake air throttling
- Exhaust gas recirculation
- Post combustion fuel injection in the cylinder
- In-exhaust fuel injection

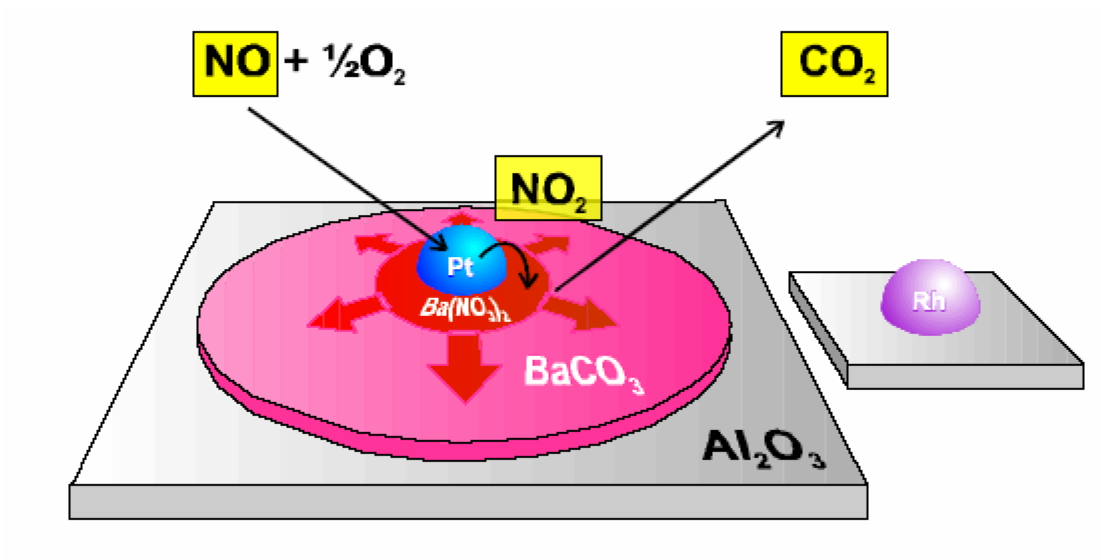


Figure 9. NOx trapping mechanisms under lean operating conditions.

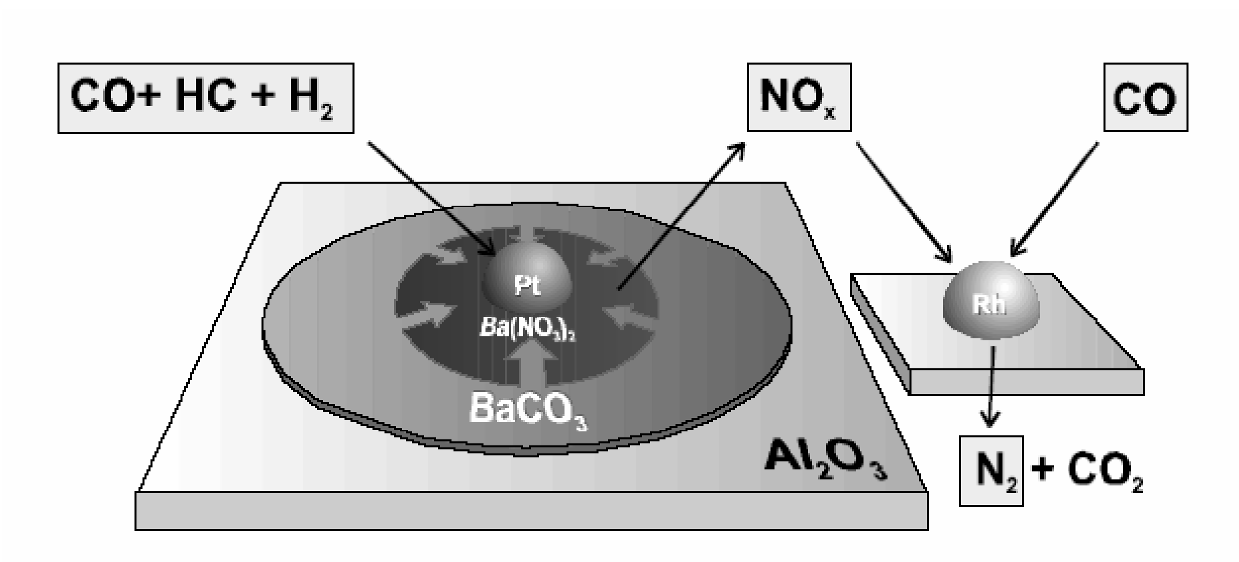


Figure 10. NOx trap regeneration occurs under brief periods of rich operation.

Development and optimization of NOx adsorber systems is continuing for diesel engines. Adsorber systems have demonstrated NOx conversion efficiencies ranging from 50 to in excess of 90 percent depending on the operating temperatures and system responsiveness, as well as diesel fuel sulfur content. An important consideration in designing a NOx adsorber emission control system is the effect on fuel economy. LNTs may experience a fuel economy penalty as a result of the fuel necessary to generate a rich exhaust environment during regeneration of the catalyst. There is potential to overcome this associated penalty by utilizing system engineering and taking advantage of all components. For instance, an approach to minimize the fuel economy penalty associated with the NOx regeneration step may be to calibrate the engine for maximum fuel economy at points on the engine map where the NOx adsorber is performing at its peak conversion efficiency. Although such a calibration results in higher engine-out NOx emissions, with the NOx adsorber functioning at its peak conversion efficiency, NOx emissions could still be kept low.

The importance of an engineered systems approach when designing an emission control system using NOx adsorber technology can not be underestimated. Conversion efficiency of up to 90 percent are achievable over a broad temperature range and the NOx efficiency can be directly impacted by changing the lean/rich modulation of the cycle. LNTs can achieve even higher NOx reduction (>90 percent) when regenerated with on-board generated hydrogen via a fuel reforming reaction over an appropriate catalyst.

The emission control industry continues to invest considerable efforts in further developing and commercializing NOx adsorber technology. Specifically, formulations and on-vehicle configurations that improve low temperature performance and lower temperature sulfur removal. NOx adsorber technology offers tremendous potential for providing a high level of NOx reduction across a wide range of operating conditions (temperature and NOx concentration) which are consistent with the diversity in engine-out exhaust associated with both light- and heavy-duty diesel applications. Figure 11 shows the improvements that are achievable through advances in NOx storage compounds. Advanced storage components have resulted in lower light-off temperatures and wider operating windows for NOx conversion.

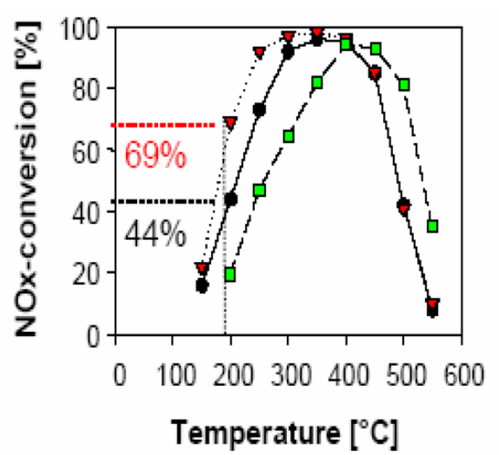


Figure 11. Advanced NOx storage materials can lower conversion temperatures and broaden operating window for NOx adsorber catalysts (square - potassium-based, circle – barium-based, triangle - advanced barium-based technology) (SAE 2006-01-1369).

5.3b Impact of Fuel Sulfur and Durability

The same compounds that are used to store NOx are even more effective at storing sulfur as sulfates, and therefore NOx adsorbers require ultra low sulfur diesel fuel. The durability of LNTs is linked directly to sulfur removal by regeneration and is a major aspect of technology development. Sulfur is removed from the trap by periodic high temperature excursions under reducing conditions, a procedure called "DeSOx". The DeSOx regeneration temperatures are typically around 700^{o}C and require only brief periods of time to be completed. However, the washcoat materials and catalysts used in these technologies begin to deactivate quickly above 800^{o}C and therefore methods are being developed to reduce the desulfation temperature. Figure 12 shows how the NOx conversion window is impacted following numerous sulfation/desulfation cycles. Advanced thermally stable materials have allowed LNTs to achieve durability over their full useful life.

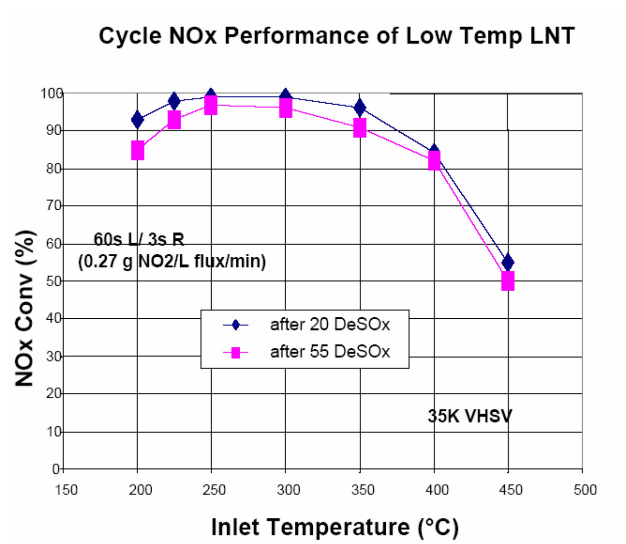


Figure 12. Durability of advanced LNTs can be maintained over many high temperature desulfation cycles.

5.3c Application of NOx Adsorber Technology

NOx adsorber technology has made significant progress and has recently been commercialized on a medium duty pick-up truck meeting EPA's 2010 on-highway emission standards. Several vehicle manufacturers have announced plans to commercialize LNT catalysts on diesel passenger vehicles prior to 2010.

NOx adsorber technology is also being applied to gasoline vehicles powered by gasoline direct injection (GDI) engines and the results are impressive. In fact, a number of vehicle manufacturers have commercially introduced NOx adsorber catalysts on some of their models powered by lean-burn gasoline engines in both Europe and Japan. While the application of NOx adsorber technology to diesel engines offers different challenges than gasoline applications, the experience being gained in gasoline applications is an important compliment to NOx adsorber technology developments on the diesel side. The

U.S. Department of Energy's large Advanced Petroleum Based Fuel-Diesel Emission Control program included vehicle demonstrations of NOx adsorber catalyst technologies that achieved NOx emission reductions in excess of 90 percent for a light-duty and medium-duty diesel-powered vehicles (www.nrel.gov/vehiclesandfuels/apbf/apbf_dec.html).

5.4 Selective Catalytic Reduction (SCR)

SCR has been used to control NOx emissions from stationary sources such as power plants for over 20 years. More recently, it has been applied to select mobile sources including cars, trucks, marine vessels, and locomotives. Applying SCR to diesel-powered vehicles provides simultaneous reductions of NOx, PM, and HC emissions. Many engine manufacturers are now offering SCR systems on new highway heavy-duty engines sold in Europe to comply with the European Union's Euro IV or Euro V heavy-duty engine emission requirements. More than 100,000 new, SCR-equipped trucks are operating in Europe using a urea-based reductant.

SCR systems have also been installed on marine vessels, locomotives and other non-road diesel engines. Significant numbers of marine vessels have been equipped with SCR including auto ferries, transport ships, cruise ships, and military vessels. The marine engines range from approximately 1250 hp to almost 10,000 hp and the installations have been in operation since the early to mid-1990s.

SCR offers a high level of NOx conversion with high durability. Open loop SCR systems can reduce NOx emissions from 75 to 90 percent. Closed loop systems on stationary engines have achieved NOx reductions of greater than 95 percent. Engine manufacturers here in North America are seriously considering combined DPF+SCR system designs for complying with EPA's 2010 heavy-duty highway emission standards. A number of combined DPF+SCR system demonstration projects have been completed or are still underway on highway trucks both here in the U.S. and Europe. DOC+SCR systems are being used commercially in Japan for new diesel trucks by several engine manufacturers to comply with Japan's 2005 emission standards.

Modern SCR system designs combine highly controlled reductant injection hardware, flow mixing devices for effective distribution of the reductant across the available catalyst cross-section, durable SCR catalyst formulations, and ammonia slip clean-up catalysts that are capable of achieving and maintaining high NOx conversion efficiencies with extremely low levels of exhaust outlet ammonia concentrations over thousands of hours of operation.

5.4a Operating Characteristics and Control Capabilities

An SCR system uses a metallic or ceramic wash-coated catalyzed substrate, or a homogeneously extruded catalyst, and a chemical reductant to convert nitrogen oxides to molecular nitrogen and oxygen. In mobile source applications, an aqueous urea solution is the preferred reductant. In open loop systems, the reductant is added at a rate calculated by a NOx estimation algorithm that estimates the amount of NOx present in the exhaust stream. The algorithm relates NOx emissions to engine parameters such as engine revolutions per minute (rpm), exhaust temperature, backpressure and load. As exhaust and reductant pass over the SCR catalyst, chemical reactions occur that reduce NOx emissions. In closed loop systems, a sensor that directly measures the NOx concentration in the exhaust is used to determine how much reductant to inject.

SCR catalysts formulations based on vanadia-titania and base metal-containing zeolites have been commercialized for both stationary and mobile source applications. The maximum NOx conversion window for SCR catalysts is a function of exhaust gas composition, in particular the NO_2 to NO ratio. The three common NOx reduction reactions are:

$$4\,NH_3 + 4\,NO + O_2 \longrightarrow 4\,N_2 + 6\,H_2O \qquad (1)$$
$$2\,NH_3 + NO + NO_2 \longrightarrow 2\,N_2 + 3\,H_2O \qquad (2)$$
$$8\,NH_3 + 6\,NO_2 \longrightarrow 7\,N_2 + 12\,H_2O \qquad (3)$$

Low temperature SCR is promoted by NO_2. Of the three competing reactions over a vanadia catalyst, reaction 3 is the slowest and reaction 2 is the fastest. Titania supported vanadia catalysts have been used for many years and are effective at temperatures less than 500^{o}C. Modern zeolite based SCR catalysts aged at 700^{o}C for 50 hours show little deterioration whereas the vanadia catalyst degrades rapidly at these temperatures (Figure 13).

Base metal zeolite SCR catalysts, in particular, have been selected, and are continuing their development, for applications that require NOx performance and durability under higher exhaust operating temperatures that may be encountered in some mobile source applications. For low temperature NOx conversion efficiency, emission control system design engineers have a number of options available including the composition of the SCR catalyst itself, control of the ratio of NO_2 to NO present at the inlet of the catalyst, and improving the urea decomposition process at low exhaust temperatures.

Figure 14 compares the conversion window for a vanadia SCR catalyst and two zeolite-based SCR catalysts. Catalyst A represents a copper zeolite catalyst having the lowest temperature light-off characteristics of the three shown. The vanadia based catalyst shows better low temperature conversion that the iron zeolite system (Catalyst-B) however the conversion efficiency drops off above 400^{o}C whereas the iron zeolite maintains peak efficiency above 500^{o}C. Both zeolite-based catalysts show better high temperature conversion than the conventional vanadia catalyst.

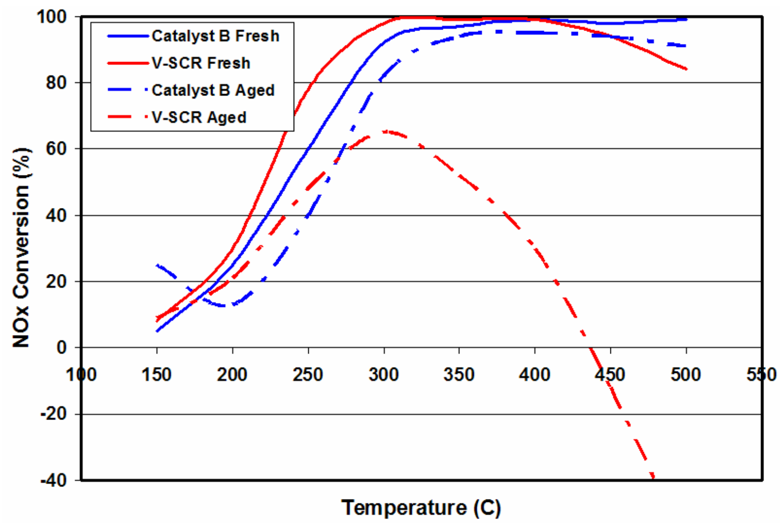


Figure 13. Durability of vanadia catalyst (V-SCR) compared to a base metal zeolite catalyst (B).

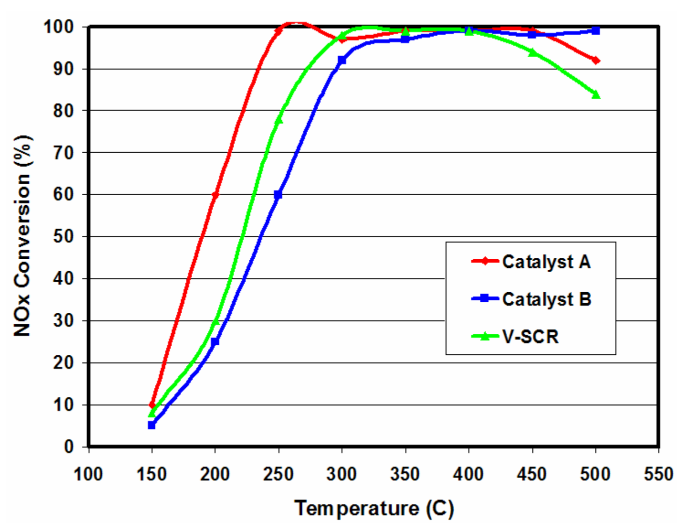


Figure 14. Catalyst A: Cu-Zeolite and Catalyst B: Fe-Zeolite are compared to a vanadia-based SCR catalyst.

SCR catalysts based on vanadia exhibit a strong sensitivity of NOx conversion to the NO_2:NOx ratio of the exhaust gas. Optimum conversion is achieved at a ratio of 1:1 or a 50 percent NO_2 composition. Zeolite based catalysts have shown less sensitivity to NO_2 concentration as shown in Figure 15.

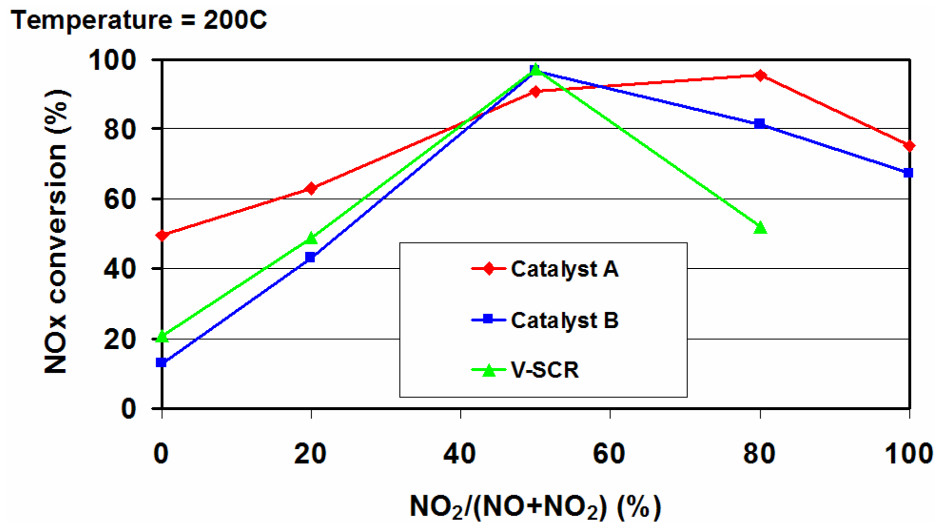


Figure 15. Catalyst A: Cu-zeolite and Catalyst B: Fe-zeolite are compared to a vanadia-based SCR catalyst with respect to NO_2 sensitivity.

In an actual application, the SCR system can be placed either upstream or downstream of the DPF depending on the temperature sensitivity and filter regeneration strategies employed by the manufacturer. Figure 16 shows a typical arrangement where the SCR is downstream of the DOC/DPF. The final catalyst in the exhaust system is an oxidation catalyst designed to remove any ammonia slip that might occur in the SCR.

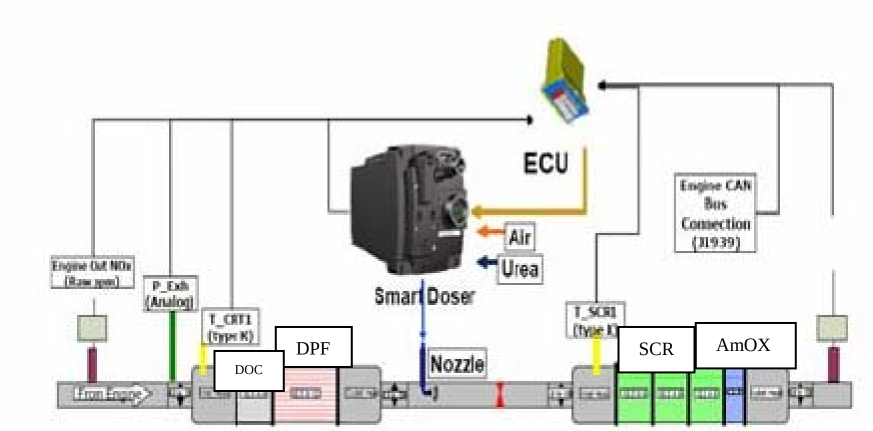


Figure 16. Diagram showing SCR (green) catalyst downstream of DOC (light gray)/DPF (pink) catalyst, urea dosing nozzle. The blue section represents an ammonia clean-up catalyst. Some of the types of monitors and controls feeding back to the control unit are also shown.

A typical layout for an SCR system for heavy-duty highway vehicle is shown in Figure 17. In this system a DPF is followed by an SCR catalyst for combined reductions of both diesel PM and NOx. A urea tank is positioned under the steps and is large enough to last over 10,000 miles of highway operation.

In addition to NOx, SCR systems reduce HC emissions up to 80 percent and PM emissions 20 to 30 percent. They also reduce the characteristic odor produced by a diesel engine and diesel smoke. Like all catalyst-based emission control technologies, SCR performance is enhanced by the use of low sulfur fuel. Combinations of DPFs and SCR generally require the use of ultra-low sulfur diesel to achieve the highest combined reductions of both PM and NOx.

Significant advancements have been made not only to improve the catalyst performance and durability but also in the urea injection hardware to insure an accurate and well distributed supply of reductant. This insures that the entire catalyst volume is being utilized and the ammonia slip is minimized. Manufacturers are developing high precision injectors and mixer systems to disperse the reductant upstream of the catalyst. Urea injector suppliers are moving away from air driven injectors to airless designs to eliminate the need for air pumps specific to the urea supply.

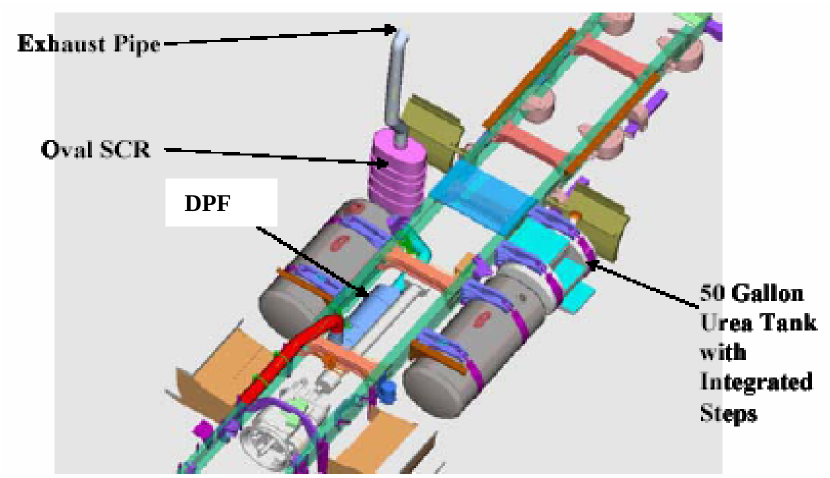


Figure 17. An example of how a DPF/SCR catalyst system may be installed on an on-road Class 8 heavy duty truck chassis.

To ensure that urea-SCR technology for vehicles is never operated without a reductant on board, the U.S. EPA has issued a guidance document to outline the types of fail safe controls manufactures must incorporate into their urea SCR systems to receive vehicle certification (EPA-HQ-OAR-2006-0886; FRL-8242-1). Vehicle manufacturers are considering a series of driver warnings and inducements that will warn operators when the urea level falls below that required to make it to the next refueling stop. Additional requirements put on manufacturers include assurances that the urea used in the vehicle is of high quality and always available while the engine is running.

On-board urea level and quality sensors may be one approach used by vehicle manufacturers to meet the EPA requirements and insure that vehicles are not operated with the NOx control disabled. These sensors can be designed to warn the driver when the urea level is low and to disable vehicle operation if urea quality or concentration is not adequate for proper SCR system operation. A variety of sensors like the one shown in Figure 18 are becoming available on the market to insure that urea is not replaced by any other fluid.

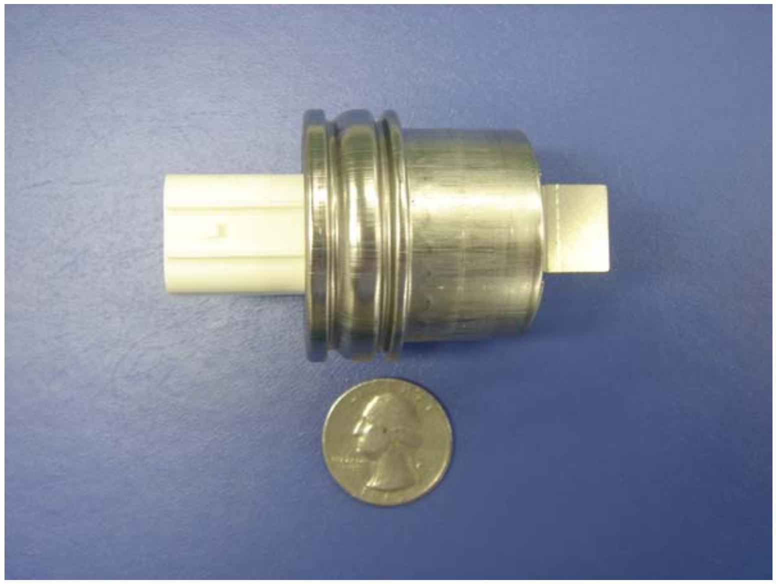


Figure 18. Onboard urea quality sensor.

5.5 Combined LNT/SCR NOx Reduction Technologies

Engine and technology manufacturers are looking at novel approaches to address the need for alternative NOx control systems that do not require separate on-board reductant, like urea. Several hybrid systems were introduced at the 12th Diesel Engine-Efficiency and Emissions Research Conference (DEER) in 2006 and again updated in 2007. These hybrid systems combine the catalyst functionality of lean NOx traps and ammonia SCR catalysts without the need for a second reductant on board the vehicle. These experimental systems typically incorporate a fuel reformer catalyst to generate a hydrogen rich reformate from the onboard fuel which is then used to regenerate the lean NOx trap. The regeneration of the LNT forms ammonia which is then stored within the SCR catalyst. The systems primarily rely on the LNT for the bulk of the NOx reduction during lean operation but the SCR uses the stored ammonia to further reduce NOx, thereby extending the time between LNT regeneration and desulfations to reduce fuel penalties associated with these strategies.

An example of one of the designs being developed is illustrated in Figures 18. This design shows LNT and SCR catalysts in series and utilizes valves to bypass the LNT during regeneration. The reformate used to regenerate the LNT feeds ammonia rich gas to the SCR to achieve NOx reduction of the bypassed exhaust gas during this step.

Another example of an LNT plus SCR hybrid system is shown in Figure 19. This design shows the reformer, LNT and SCR catalyst all in series within the exhaust stream. In contrast to the system shown in Figure 20, this system does not require a bypass valve for LNT regeneration. The reformer processes the entire exhaust stream to generate the reductants used for LNT regeneration and ammonia formation.

Several vehicle manufacturers have announced commercial systems designed to meet EPA's Tier 2 Bin 5 emission standards for 2010 based on a combined NOx catalyst approach. Both systems rely on dual LNT and SCR catalysts where the SCR stores ammonia formed during LNT regeneration. The Mercedes E320 Blutec system uses independent LNT and SCR catalysts whereas Honda has announced a single catalyst with dual layer functionality.

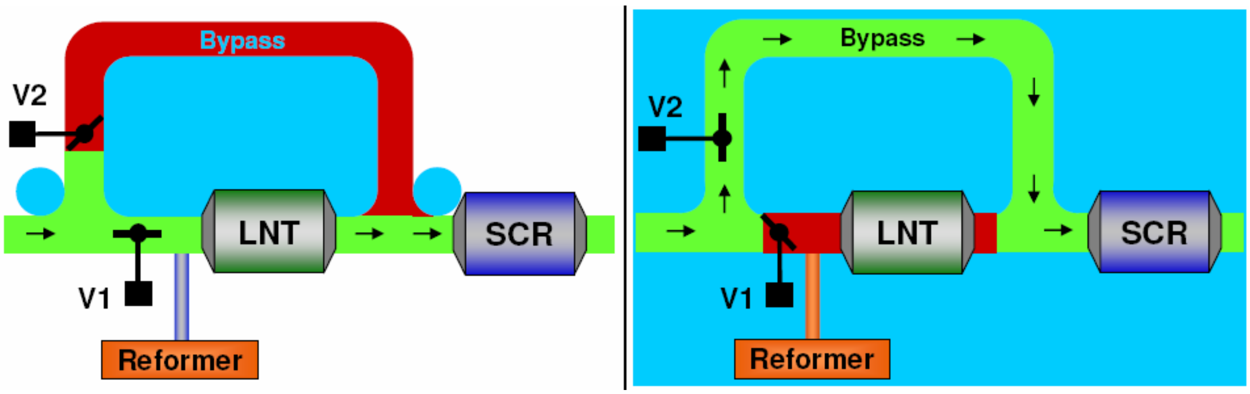


Figure 19. LNT/SCR combined catalyst: parallel design (DEER 2006).

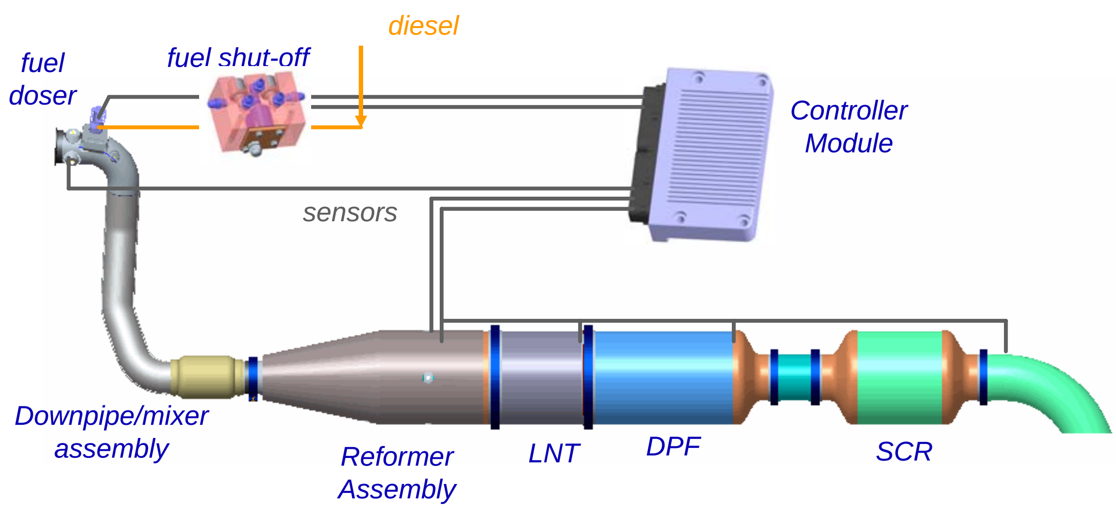


Figure 20. LNT/SCR combined catalyst: series design (DEER 2007).

The layered concept incorporates a first washcoat layer based on a NOx trap catalyst and an outer layer of an SCR catalyst composition. The ammonia that is released during regeneration of the trap is stored within the SCR layer and later utilized for selective catalytic reduction during lean operation.

6.0 On-Board Diagnostic Requirements

ARB has finalized requirements for light-duty and heavy-duty diesel vehicles to implement OBD systems in the 2010 to 2016 time frame. These diagnostic system must monitor the functionality of engine combustion processes as well as the proper functioning of the DOC, DPF and NOx control systems that may be on-board the vehicle. EPA has proposed similar heavy-duty NOx and PM OBD emission thresholds for 2010, however ARB continues to tighten the thresholds out to 2016. In addition to the threshold limits set on the DPF, the system is expected to monitor the frequency of regenerations and illuminate the malfunction indicator light (MIL) if they occur more frequently than recommended by the manufacturer. Monitors should also indicate a fault if the substrate is damaged or missing, the system undergoes an incomplete regeneration, or malfunctions of the active regeneration system occur. For passive DPFs, a NMHC threshold is required comparable to that required for DOCs. Other monitors with emission thresholds include fuel system pressure and injection sensors that may contribute to engine-out emissions. Use of temperature sensors, oxygen sensors, A/F ratio sensors and/or NOx sensors are all technologies that could be used on future vehicles to insure that the exhaust control system is operating per design specifications and to comply with these OBD requirements.

The OBD requirements for diesel vehicles and engines have lead to advances in the development and commercialization of advanced sensor technologies to provide both alarms and closed loop controls. Oxygen sensors are an essential part of the OBD system on gasoline vehicles today to insure that the three-way catalyst is functioning properly. Oxygen sensors in combination with temperature sensors may be used to insure functionality of the DOC by forcing a rich excursion in the typical lean diesel exhaust and monitoring an exotherm or oxygen storage function of the DOC.

Differential pressure monitors are being used to detect failure of the DPF and soot loading models and backpressure monitors are being developed to insure proper regeneration. Ash loading must be incorporated into the models and can alert operators when filter maintenance is required. Several manufacturers are also working to develop soot sensors that would provide a direct measurement of exhaust PM levels that may provide filter diagnostic capabilities.

NOx and ammonia sensors will likely be an integral part of the NOx catalyst OBD system for LNT and SCR based systems. Their function is primarily to monitor the NOx conversion efficiency of the catalyst. NOx sensors represent state of the art technology that can be applied to diesel engines as part of a broader engine control or diagnostic system used to insure proper operation of the NOx emission control system. These sensors can be incorporated independent of the NOx emission control technology used on the vehicle. The sensors can work as part of a feedback loop to the control unit on the emissions system to make real time adjustments and optimize NOx conversion. The principle of operation of one type of NOx sensor is based on proven solid electrolyte technology developed for oxygen sensors. The dual chamber zirconia sensing element and electro-chemical pumps work in conjunction with precious metal catalyst electrodes to control the oxygen concentration within the sensor and convert the NOx to NO and nitrogen. The sensor sends output signals in volts that are directly proportional to NOx concentration. The sensors can be incorporated upstream and downstream of the catalyst, for example, to provide a feedback control loop to the ECU of the emissions system. The ECU can then make adjustments to optimize NOx conversion performance. In the case of SCR technology, feedback can also be provided to the urea dosing system whereas in the case of lean NOx trap technology a feedback loop could signal the need for regeneration of the trap. A NOx sensor looks very much like an oxygen sensor (Figure 21).

Figure 21. NOx sensor and ECU.

Sensor manufacturers are continually improving the durability and accuracy of NOx sensors to meet the tight OBD thresholds required in 2010 and beyond. One of the limitations of the current generation of NOx sensors is that they are equally sensitive to ammonia which may be present in the exhaust downstream of the catalyst. Ammonia sensor manufacturers are developing control strategies to detect ammonia slip past the catalyst and use that as a feedback control to the urea injection system to reduce the amount of urea being injected upstream of the catalyst. The use of NOx sensors may be another tool that vehicle manufacturers may use to insure that urea solution of the right concentration is being used by the operator in order for the SCR system to function properly. The combination of multiple sensors can significantly improve the precision in closed loop control of the NOx catalyst and provide OBD monitoring.

7.0 Conclusion

- Diesel emissions from mobile sources have raised health and welfare concerns, but a number of technologies exist that can greatly reduce emissions from diesel-powered vehicles.

- The widespread availability of ultra low sulfur diesel for on-road vehicles has enabled the application of advanced emission control systems for diesel engines and vehicles. The future expansion of low sulfur fuels for off-road applications will allow the implementation of the same advanced control technologies to the full range of diesel vehicles including locomotive and marine engines.

- Diesel oxidation catalysts, diesel particulate filters, exhaust gas recirculation and crankcase emission controls have been successfully rolled out on new 2007 onroad vehicles. These technologies offer opportunities to greatly reduce emissions of particulate matter and other pollutants like toxic HCs.

- Advanced NOx control technologies are being developed to meet EPA's 2010 on highway emission standards. Technologies such as lean NOx traps and selective catalytic reduction have been demonstrated to be durable and effective methods of achieving low tailpipe NOx levels from diesel and other lean burn engines.

- Some of the technologies that reduce particulate matter and NOx are also applicable to the diesel engines already on the road today, offering a cost-effective way to reduce diesel emissions during their remaining life.

- Advanced sensors are being developed to monitor all components of the exhaust control system. These sensors will allow diesel engines to meet the same OBD and emissions requirements already in place for gasoline spark-ignited engines and vehicles.

Acronyms and Abbreviations

A/F - air/fuel
Al_2O_3 - aluminum oxide
ARB - California Air Resources Board
$Ba(NO_3)_2$ - barium nitrate
$BaCO_3$ - barium carbonate
bhp-hr - brake horsepower hour
CCC - close coupled catalyst
CO - carbon monoxide
CO_2 - carbon dioxide
CDPF - catalyzed diesel particulate filter
Cu - copper
DeNOx - lean NOx
DOC - diesel oxidation catalyst
DPF - diesel particulate filter
EGR - exhaust gas recirculation
EPA - U.S. Environmental Protection Agency
FBC - fuel-borne catalyst
FEL - family emission limit
FTP - federal test procedure
H_2 - hydrogen
H_2O - water
HC - hydrocarbon
HCCI - homogeneous charge compression ignition
HDD - heavy-duty diesel
LDV - light-duty vehicle
LNC - lean NOx catalyst
LNT - lean NOx trap
LTC - low temperature combustion
MECA - Manufacturers of Emission Controls Association
mg - milligram
N_2 - nitrogen
NH_3 - ammonia
NMHC - non-methane hydrocarbon
NO - nitrogen oxide
NO_2 - nitrogen dioxide
NOx - oxides of nitrogen
O_2 - oxygen
PAH - polyaromatic hydrocarbon
Pd - palladium
PM - particulate matter
ppm - parts per million
Pt - platinum
Rh - rhodium

S - sulfur
SCR - selective catalytic reduction
SO_2 - sulfur dioxide
SO_3 - sulfur trioxide
SOF - soluble organic fraction
TWC - three-way catalyst
V_2O_5/TiO_2 - vanadium oxide/titanium oxide
^oC - degrees Celsius