Diesel engines: the road to zero harmful emissions

WearCheck technical manager, Steven Lara-Lee Lumley, unpacks diesel engine emissions and outlines the legislation and technologies being put in place to mitigate against harm.

Barely a week goes by where climate change, global warming and the quality of air and airborne pollutants are not in the news, and quite often vehicle emissions are the primary focus of the headline.

Every day, millions of diesel-powered ships, trains and trucks busily move consumer goods and raw materials from ports, distribution centres and rail yards to stores and industrial facilities throughout the world. Diesel engines are also widely employed in pipeline pumps, electric and water plants, industrial machinery, mining equipment, factories and oil fields.

Unmatched in their reliability, durability and fuel efficiency, diesel engines play a fundamental role but, through their exhaust emissions, they are also associated with a number of environmental and health-related issues.

To successfully navigate the road to zero harmful emissions, we must understand the emissions we are trying to limit, the standards that govern them, the technologies we can employ and the role of the fuels and lubricants we select.

The diesel exhaust gas emissions we are trying to limit

The four main pollutant emissions generated by diesel engines are carbon monoxide (CO), hydrocarbons (HC), particulate matter (PM) and nitrogen oxides (NOx). NOx is a general term referring mainly to nitric oxide (NO) and Nitrogen Dioxide (NO_2) gases.

The gas portion of diesel exhaust is mostly CO_2, CO, NOx, sulphur dioxides (SO_2), and HCs, including polycyclic aromatic hydrocarbons (PAHs). CO and HCs are generated in the exhaust as the result of incomplete combustion of fuel, but exhaust hydrocarbons can also come from the lubricant.

SO_2 is generated from the sulphur present in diesel fuel, so the concentration of SO_2 in the exhaust gas depends on the sulphur content of the fuel. Oxidation of SO_3 produces sulphur trioxide (SO_2), which is the precursor of sulphuric acid which, in turn, is responsible for the sulphate particulate emissions and acid rain.

Out of the various compounds produced, NOx gas and PM are typically portrayed as the two 'bad boys' of diesel exhaust and have proven to be the most challenging of regulated pollutants when it comes to diesel engine design that is compliant with emission standards.

NOx gases are generated from nitrogen and oxygen under the high pressures and temperature conditions in engine cylinders. Diesel engines run both hotter and at higher pressures than their petrol counterparts and subsequently produce more NOx gases.

Diesel emissions of NOx contribute to the formation of ground level ozone, which irritates the respiratory system, causing coughing, choking, and reduced lung capacity. Ground level ozone pollution, formed when nitrogen oxides and hydrocarbon emissions combine in the presence of sunlight, presents a hazard for both healthy adults and individuals suffering from respiratory problems.

PM or soot is created during the incomplete combustion of diesel fuel. Its composition often comprises hundreds of chemical elements, including sulphates, ammonium, nitrates, elemental carbon, condensed organic compounds and heavy metals such as arsenic, selenium, cadmium and zinc. Though just a fraction of the width of a human hair, particulate matter varies in size from coarse particulates (less than 10 µm in diameter) to fine particulates (less than 2.5 µm) to ultrafine particulates (less than 0.1 µm).

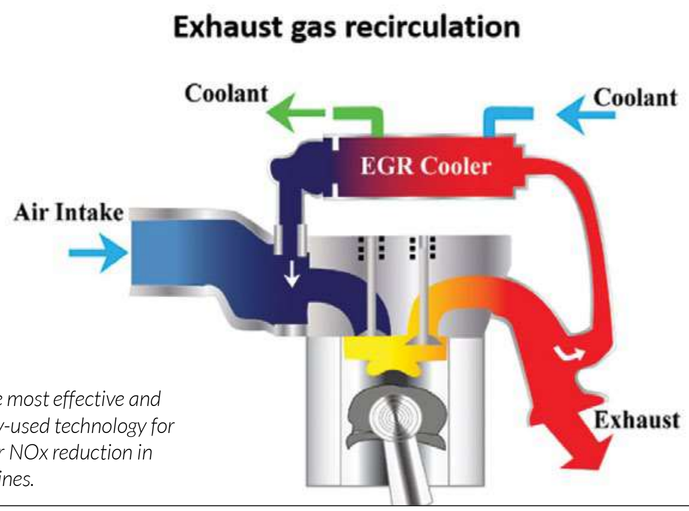
Ultrafine particulates, which are small enough to penetrate the cells of the lungs, make up 80-95% of diesel soot pollution. When one inhales these microscopic particulates, they can become embedded in your lungs and impair the breathing function. As a result of this, diesel PM was officially classified as carcinogenic by the WHO in 2012.

The standards that govern diesel emissions

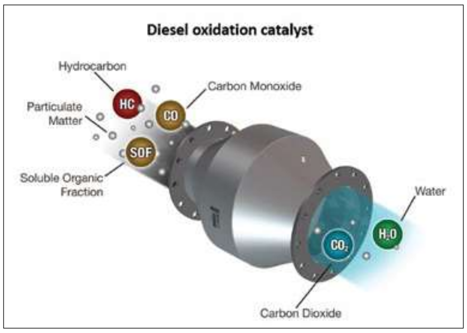
Emission standards set quantitative limits on the permissible amount of specific air pollutants that may be released from specific sources over specific timeframes. They are generally designed to achieve air quality standards and to protect human life. Different regions and countries have different standards for engine emissions. In order to conform to these emission standards, engines need to produce cleaner exhaust emissions by producing less harmful by-products.

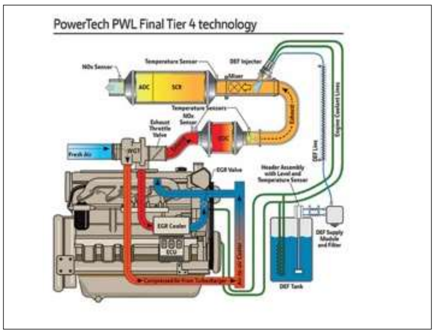
There are four main sets of emissions standards: United States (TIER), Japanese (CEC Central Environment Council), India (BHARAT) and European (EURO) with various markets outside of these regions mostly using these as their base. The European standards are the most widely-followed vehicle emission guidelines in the world, and as such South Africa has elected to follow this standard - although in a somewhat lagged fashion.

Although emissions regulations date back to 1970, the first EU-wide standard – known as Euro I – wasn't introduced until 1992. Since



EGR is the most effective and commonly-used technology for in-cylinder NOx reduction in diesel engines.





Left: Diesel oxidation catalysts (DOCs) are highly effective devices that reduce CO and gas and liquid-phase HC emissions by 80% or more. Middle: Diesel particulate filters (DPFs) are designed to trap and retain solid particles until they can be completely oxidised or burned. Right: A schematic of a diesel engine emissions system that meets the Euro Tier IV emissions standard, which specifies: NOx control through a vanadium-based, open-loop selective catalytic reduction (SCR) system or exhaust gas recirculation (EGR); PM control through the use of a diesel oxidation catalyst (DOC) or an aftertreatment system comprising a DOC and an SCR.

then, there has been a series of Euro emissions standards, leading to the current Euro VI version introduced in September 2015.

The aim of Euro emissions standards is to reduce the levels of harmful exhaust emissions, primarily NOx, CO, HC, PM emissions and, in the case of Euro VI-compliant engines, ammonia (NH_3).

Emission mitigation technologies we can employ

Diesel emission control systems can be broadly broken down into two categories: (1) in-cylinder strategies and (2) aftertreatment systems. The selection and configuration of which technologies are used depends on the engine manufacturer and machine application.

In-cylinder technologies

As emissions standards tightened, more advanced in-cylinder control strategies were applied, that included energy-efficient cylinder heads and valve train systems, closer piston-to-bore clearances and modified ring positioning to assist in lower emissions output. In the last two decades, the design of diesel engines has progressed rapidly, most significantly in the areas of fuel injection systems, electronic controls and air handling through the use of variable-geometry turbochargers.

Many of the latest generation engines have common-rail or unit-injector designs, a common feature that produces far higher injection pressure than the old mechanical systems, coupled with precise electronic control of injection timing. Other in-cylinder techniques also include the adoption of the Miller cycle, diesel water injection and homogenous charge compression ignition (HCCI). These various techniques help achieve a more complete combustion and reduce particulate formation and fuel consumption.

Air handling strategies have focused on the use of variable geometry turbochargers to provide the right amount of air under specific engine operational conditions. Tuning these parameters minimises production of both PM and NOx.

Another popular in-cylinder technology for NOx control is an exhaust gas recirculation (EGR) system, which recirculates a portion of cooled exhaust gas back to the engine's cylinder, reducing peak combustion temperatures and temperature-dependent NOx formation. EGR is the most effective and commonly-used technology for in-cylinder NOx reduction in diesel engines.

Since EGR reduces the available oxygen in the cylinder, incomplete combustion and the production of PM increases when EGR is applied, so NOx and PM must be traded against each other in diesel engine design.

Aftertreatment systems

An aftertreatment system treats post-combustion exhaust gases prior to tailpipe emission. In other words, it is a device that cleans exhaust gases to ensure the engines meet emission regulations.

Within the aftertreatment category there are a further two classes – filters and catalysts.

In chemistry, a catalyst is a substance that causes or accelerates a chemical reaction without itself being affected. Catalysts participate in the reactions but are neither reactants nor products of the reaction they catalyse. A catalytic convertor is a device that uses a catalyst to reduce the toxicity of emissions from an internal combustion engine either through the process of oxidation or reduction.

The first diesel emission catalysts, introduced in the 1970s for underground mining applications, were simple oxidation catalysts designed for the conversion of CO and HC, but as the years rolled on and requirements intensified, more specialised catalysts were developed.

Filters do exactly as their name implies, they physically filter out something. To be more specific, these are porous devices for removing impurities or solid particles from a liquid or gas passing through it.

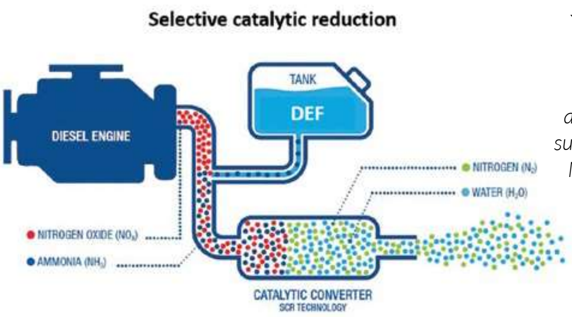
Ultimately, using a combination of physical mechanisms and chemical reactions these systems can, under the right conditions, achieve near complete removal of particulates and harmful gases. Let's take a closer look at some of these technologies and how they work.

A diesel particulate filter (DPF) is a device designed to remove soot from diesel engine exhaust gases. DPFs operate by trapping soot particles from the engine exhaust, preventing them from reaching the environment. Unlike catalytic converters, which are designed to reduce gas-phase emissions flowing through the catalyst, the particulate filter is designed to trap and retain the solid particles until the particles can be oxidised or burned in the DPF itself, through a process called regeneration.

The most common DPFs in widespread use are cellular ceramic honeycomb filters with channels that are plugged at alternating ends. The ends of the filter, plugged in a checkerboard pattern, force the soot-containing exhaust to flow through the porous filter walls. While the exhaust gas can flow through the walls, the soot particles are trapped within the filter pores and in a layer on top of the channel walls. Soot particles are captured and retained in the DPF through a combination of depth filtration inside the filter pores and surface filtration along the channel walls. Given the small pore size and design of the honeycomb filters, DPFs can achieve a particle trapping efficiency of 99% or greater.

The honeycomb design provides a large filtration area while minimising pressure losses, and has become the standard, so-called wall-flow filter for most diesel exhaust filtration applications. Ceramic materials are widely used for particulate filters, given their good thermal durability, with the most common ceramic materials being cordierite, silicon carbide and aluminium titanate.

However, over time the trapped soot accumulated in the filter, if not removed, increases backpressure, which can compromise engine performance, increase fuel consumption and eventually lead to DPF failure. To prevent this, the DPF must periodically be regenerated to remove soot through a process that burns off (oxidises) the soot. There are two broad categories of the regeneration processes, (1) active and (2) passive, although most com-



Selective catalytic converters use a diesel exhaust fluid (DEF) such as aqueous urea to successfully convert NOx gases into N_2 and water.

mercial applications use some combination of the two.

Active regeneration requires the addition of heat to the exhaust to increase the temperature of the soot to the point at which it will oxidise in the presence of excess oxygen. The combustion of soot in oxygen typically requires temperatures in excess of 550 °C. Since these high temperatures generally do not occur in the exhaust/DPF during normal engine operation, active regeneration systems may include the use of a diesel burner to directly heat the exhaust entering the DPF; or the use of a diesel oxidation catalyst (DOC) to oxidise diesel fuel over the catalyst as a means of increasing the DPF temperature.

DOCs also require excess diesel fuel in the exhaust, which may be accomplished through a fuel injector/hydrocarbon doser mounted in the exhaust upstream of the DOC; or through late in-cylinder post injection strategies. Other forms of active regeneration include the use of electrical heating elements, microwaves or plasma burners. The use of a DOC in combination with some form of exhaust fuel dosing is, however, the most common active regeneration strategy currently used for on- and off-highway applications.

Passive regeneration, as the name implies, does not require additional energy to carry out the regeneration process. Instead, this strategy relies on the oxidation of soot in the presence of NO_2, which can occur at much lower temperatures. In order to achieve this, a passive system uses a catalyst, which contains precious metals such as platinum, to convert NO in the exhaust to NO_2, which reduces the ignition temperature of the soot to below 550°C. In some cases, the catalyst coating is applied directly to the DPF; or an upstream oxidation catalyst may also be used. Many commercial systems use a combination of a DOC and Catalysed DPF (C-DPF).

Catalytic converters

Diesel oxidation catalyst: CO, as well as gas and liquid-phase HC emissions, result from the incomplete combustion of diesel. Diesel oxidation catalysts (DOCs), are highly effective devices that reduce these emissions by 80% or more from diesel.

In most applications, a DOC consists of a stainless-steel canister that contains a honeycomb structure called a substrate, which is made up of thousands of small channels. Each channel is coated with a highly porous layer containing precious metal catalysts such as platinum or palladium. As exhaust gas travels down the channel, CO and HCs react with oxygen within the porous catalyst layer to form CO_2 and water vapour.

Using a DOC also protects the DPF. Hydrocarbon liquids or vapour can interfere with the DPF's ability to trap and remove particulate matter, so engine manufacturers often route the exhaust through the DOC first, then into the DPF.

Selective catalytic reduction (SCR): NOx gases generated from nitrogen and oxygen under engine combustion conditions can be successfully converted to N_2 and water using SCR technology – one of the most effective technologies available today. SCR systems are classified into two groups, Urea-SCR and Hydrocarbon-SCR, the latter being most commonly known as a lean NOx catalyst (LNC).

Urea-SCR uses a reductant known as a diesel exhaust fluid (DEF), which is injected into the exhaust gas to help reduce NOx emissions over a catalyst, with aqueous urea (CH_4N_2O) being the reductant of choice in SCR systems for mobile diesel engines.

The urea-SCR system uses a metallic (e.g. vanadium-based) or ceramic (e.g. zeolite-based) wash-coated catalysed substrate and the chemical reductant – usually aqueous urea – to convert nitrogen oxides into molecular nitrogen and oxygen in oxygen-rich exhaust streams.

On thermal decomposition in the exhaust, urea decomposes to ammonia (NH_3), which serves as the reductant. As exhaust and reductant pass over the SCR catalyst, chemical reactions occur that reduce NOx emissions to nitrogen and water. Urea-SCR catalysts are often combined with a particulate filter for combined PM and NOx reduction.

The reaction between NOx and NH_3 is never perfect and, even though SCR systems can achieve efficiency rates often higher than 95%, there is sometimes a waste stream of unreacted NH_3 that goes into the atmosphere. This excess NH_3 is known as NH_3 slip.

For this reason, SCR systems may also include an oxidation catalyst, called the ammonia slip catalyst (ASC), downstream of the SCR catalyst, which oxidises ammonia slip to harmless N_2 and water, usually over a platinum/aluminium oxide base. The ASC is increasingly important in SCR systems designed for high NOx conversion efficiency, especially in the higher-rated Euro engines.

Lean NOx catalyst (LNC): Catalytic reduction of NOx with hydrocarbons is an attractive NOx abatement method under lean burn conditions, especially when the diesel exhaust is used as a reducing agent. In this process the system injects a small amount of diesel fuel or other hydrocarbon reductant into the exhaust upstream of the catalyst. The fuel or hydrocarbon reductant serves as a reducing agent for the catalytic conversion of NOx to N_2.

A lean NOx catalyst often includes a highly-ordered porous channel structure made of zeolite, along with either a precious metal or base metal catalyst. The zeolites provide microscopic sites that are fuel/hydrocarbon rich where reduction reactions can take place.

NOx adsorber catalysts (NAC): NOx adsorber catalysts (NACs), also referred to as lean NOx traps (LNTs), provide another catalytic pathway for reducing NOx in an oxygen-rich exhaust stream. They are known as adsorbers or traps because part of their function includes trapping the NOx in the form of a metal nitrate during lean operation of the engine.

Typically, NACs consist of precious metals (e.g. platinum or palladium), a storage element (e.g. barium hydroxide or barium carbonate) and a high surface area support material.

Under lean air to fuel operation, NOx reacts to form NO_2 over the precious metal catalyst, followed by reaction with the barium compound to form barium nitrate.

Following a defined amount of lean operation, the trapping function becomes saturated and must be regenerated. This is commonly done by operating the engine in a fuel-rich mode for a brief period of time to facilitate the conversion of the barium compound back to its original state and giving up NOx in the form of N_2 or NH_3 gas.

The role of fuel and lubricants

Steven Lumley will continue this discussion around reducing air pollution through stricter diesel engine emission standards and techniques in Part 2 of her Technical Bulletin, which we hope to present in summarised form in our next edition.

Part 2 will examine the intricacies of appropriate lubricant viscosity as well as the performance criteria of a range of additives and how they contribute to the war against harmful emissions, or not. ❑