

Emissions and After-Treatment.

Dr Owen Williams – University of Wales TSD:



To control exhaust emissions, which are responsible for two-thirds of the total engine pollutants, two types of systems are used: the air-injection system and the exhaust gas recirculation (EGR) system.

In EGR a certain portion of exhaust gases are directed back to the cylinder head, where they are combined with the fuel-air mixture and enter the combustion chamber. The recirculated exhaust gases serve to lower the temperature of combustion, a condition that favours lower production of nitrogen oxides as combustion products (though at some loss of engine efficiency).

In a typical air-injection system, an engine-driven pump injects air into the exhaust manifold, where the air combines with unburned hydrocarbons and carbon monoxide at a high temperature and, in effect, continues the combustion process. In this way a large percentage of the pollutants that were formerly discharged through the exhaust system are burned (though with no additional generation of power).

Another area for additional combustion is the catalytic converter, consisting of an insulated chamber containing ceramic pellets or a ceramic honeycomb structure coated with a thin layer of metals such as platinum and palladium.

As the exhaust gases are passed through the packed beads or the honeycomb, the metals act as catalysts to reduce the hydrocarbons, carbon monoxide, and nitrogen oxides in the exhaust to convert to water vapour, carbon dioxide, and nitrogen. These systems are not completely effective: during warm-up the temperatures are so low that emissions cannot be catalysed. Preheating the catalytic converter is a possible solution to this problem; the high-voltage batteries in hybrid cars, for example, can provide enough power to heat up the converter very quickly.

In the past, gasoline fumes evaporating from the fuel tank and carburettor were vented directly into the atmosphere. Today those emissions are greatly reduced by sealed fuel-tank caps and the so-called evaporative control system, the heart of which is a canister of activated charcoal capable of holding up to 35 percent of its own weight in fuel vapour. In operation, fuel-tank vapours flow from the sealed fuel tank to a vapour separator, which returns raw fuel to the tank and channels fuel vapour through a purge valve to the canister. The canister acts as a storehouse; when the engine is running, the vapours are drawn by the resultant vacuum from the canister, through a filter, and into the combustion chamber, where they are burned.

Improvements in combustion efficiency are affected by computerized control over the whole process of combustion. This control ensures the most efficient operation of the systems described above. In addition, computer-controlled fuel-injection systems ensure more precise air-fuel mixtures, creating greater efficiency in combustion and lower generation of pollutants.

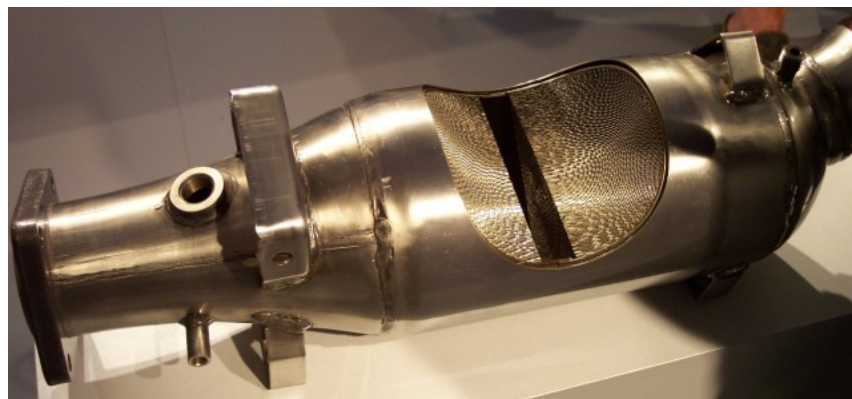
The catalytic converter is a component of emission control systems used to reduce the discharge of noxious and polluting gases from the internal-combustion engine. The catalytic converter consists of an insulated chamber containing a honeycomb structure or pellets coated with catalyst through which the exhaust gases are passed. Hydrocarbons and carbon monoxide in the exhaust are oxidized to water vapour and carbon dioxide, and nitrogen oxides are reduced to nitrogen and oxygen.

The catalytic converter's construction is as follows:

For automotive catalytic converters, the core is usually a ceramic monolith that has a honeycomb structure (commonly square, not hexagonal). (Prior to the mid 1980s, the catalyst material was deposited on a packed bed of pellets.) Metallic foil monoliths made of Kanthal (FeCrAl) are used in applications where particularly high heat resistance is required. The substrate is structured to produce a large surface area.

The washcoat: A washcoat is a carrier for the catalytic materials and is used to disperse the materials over a large surface area. Aluminium oxide, titanium dioxide, silicon dioxide, or a mixture of silica and alumina can be used. The catalytic materials are suspended in the washcoat prior to applying to the core. Washcoat materials are selected to form a rough, irregular surface, which greatly increases the surface area compared to the smooth surface of the bare substrate. This in turn maximizes the catalytically active surface available to react with the engine exhaust. The coat must retain its surface area and prevent sintering of the catalytic metal particles even at high temperatures (1000 °C).

Ceria or ceria-zirconia: These oxides are mainly added as oxygen storage promoters.



The catalyst itself is most often a mix of precious metals. Platinum is the most active catalyst and is widely used but is not suitable for all applications because of unwanted additional reactions and high cost. Palladium and rhodium are two other precious metals used. Rhodium is used as a reduction catalyst, palladium is used as an oxidation catalyst, and platinum is used both for reduction and oxidation. Cerium, iron, manganese, and nickel are also used, although each has limitations. Nickel is not legal for use in the European Union because of its reaction with carbon monoxide into toxic nickel tetracarbonyl. Copper can be used everywhere except Japan.

Upon failure, a catalytic converter can be recycled into scrap. The precious metals inside the converter, including platinum, palladium, and rhodium, are extracted.



Catalytic converters require a temperature of $>400\text{ }^{\circ}\text{C}$ to efficiently convert harmful exhaust gases into inert gases, such as carbon dioxide and water vapor. Therefore, the first catalytic converters were placed close to the engine, to ensure fast heating. However, such placement can cause several problems.

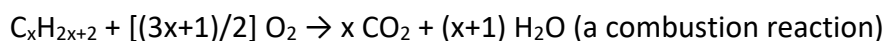
As an alternative, catalytic converters were moved to a third of the way back from the engine and were then placed underneath the vehicle.

Two-way

A 2-way (or "oxidation", sometimes called an "oxi-cat") catalytic converter has two simultaneous tasks:

Oxidation of carbon monoxide to carbon dioxide: $2\text{ CO} + \text{O}_2 \rightarrow 2\text{ CO}_2$

Oxidation of hydrocarbons (unburnt and partially burned fuel) to carbon dioxide and water:



This type of catalytic converter is widely used on diesel engines to reduce hydrocarbon and carbon monoxide emissions. They were also used on gasoline engines in American- and Canadian market automobiles until 1981. Because of their inability to control oxides of nitrogen, they were superseded by three-way converters.

Three-way

Three-way catalytic converters (TWC) have the additional advantage of controlling the emission of nitric oxide (NO) and nitrogen dioxide (NO₂) (both together abbreviated with NO_x and not to be confused with **nitrous oxide (N₂O)**), which are precursors to acid rain and smog.

So, what is Nitrous Oxide N₂O?

Nitrous oxide, commonly known as laughing gas or nitrous, is a chemical compound, an oxide of nitrogen with the formula N₂O. At room temperature, it is a colourless non-flammable gas, with a slight metallic scent and taste. At elevated temperatures, nitrous oxide is a powerful oxidizer similar to molecular oxygen. It is soluble in water.



Nitrous oxide has significant medical uses, especially in surgery and dentistry, for its anaesthetic and pain reducing effects. Its colloquial name "laughing gas", coined by Humphry Davy, is due to the euphoric effects upon inhaling it, a property that has led to its recreational use as a dissociative anaesthetic. It is on the World Health Organization's List of Essential Medicines, the safest and most effective medicines needed in a health system. It is also used as an oxidiser in rocket propellants, and in motor racing to increase the power output of engines.

Nitrous oxide occurs in small amounts in the atmosphere but has been found to be a major scavenger of stratospheric ozone, with an impact comparable to that of CFCs. It is estimated that 30% of the N₂O in the atmosphere is the result of human activity, chiefly agriculture. Being the third most important long-lived greenhouse gas, nitrous oxide substantially contributes to global warming.

In vehicle racing, nitrous oxide (*often referred to as just "nitrous"*) allows the engine to burn more fuel by providing more oxygen than air alone, resulting in a more powerful combustion.

The gas is not flammable at a low pressure/temperature, but it delivers more oxygen than atmospheric air by breaking down at elevated temperatures. Therefore, it often is mixed with another fuel that is easier to deflagrate (burn). Nitrous oxide is a strong oxidising agent, roughly equivalent to hydrogen peroxide, and much stronger than oxygen gas.

Nitrous oxide is stored as a compressed liquid; the evaporation and expansion of liquid nitrous oxide in the intake manifold causes a large drop in intake charge temperature, resulting in a denser charge, further allowing more air/fuel mixture to enter the cylinder. Sometimes nitrous oxide is injected into (or prior to) the intake manifold, whereas other systems directly inject, right before the cylinder (direct port injection) to increase power.



One of the major problems of using nitrous oxide in a reciprocating engine is that it can produce enough power to damage or destroy the engine. Very large power increases are possible, and if the mechanical structure of the engine is not properly reinforced, the engine may be severely damaged, or destroyed, during this kind of operation.

It is very important with nitrous oxide augmentation of petrol engines to maintain proper operating temperatures and fuel levels to prevent "pre-ignition", or "detonation".

Most problems that are associated with nitrous oxide do not come from mechanical failure due to the power increases. Since nitrous oxide allows a much denser charge into the cylinder, it dramatically increases cylinder pressures. The increased pressure and temperature can cause problems such as melting the piston or valves. It also may crack or warp the piston or head and cause pre-ignition due to uneven heating.

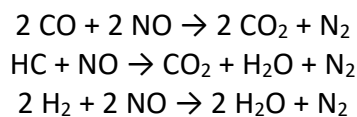
Automotive-grade liquid nitrous oxide differs slightly from medical-grade nitrous oxide. A small amount of sulphur dioxide (SO_2) is added to prevent substance abuse. Multiple washes through a base (such as sodium hydroxide) can remove this, decreasing the corrosive properties observed when SO_2 is further oxidised during combustion into sulfuric acid, making emissions cleaner.

Ok, Back to Catalysts...

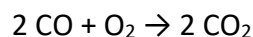
Since 1981, "three-way" (oxidation-reduction) catalytic converters have been used in vehicle emission control systems, with many countries adopting stringent vehicle emission regulations that in effect require three-way converters on gasoline-powered vehicles. The reduction and oxidation catalysts are typically contained in a common housing; however, in some instances, they may be housed separately.

A three-way catalytic converter has three simultaneous tasks:

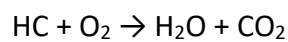
1. Reduction of nitrogen oxides to nitrogen (N_2)
HC = Hydrocarbon



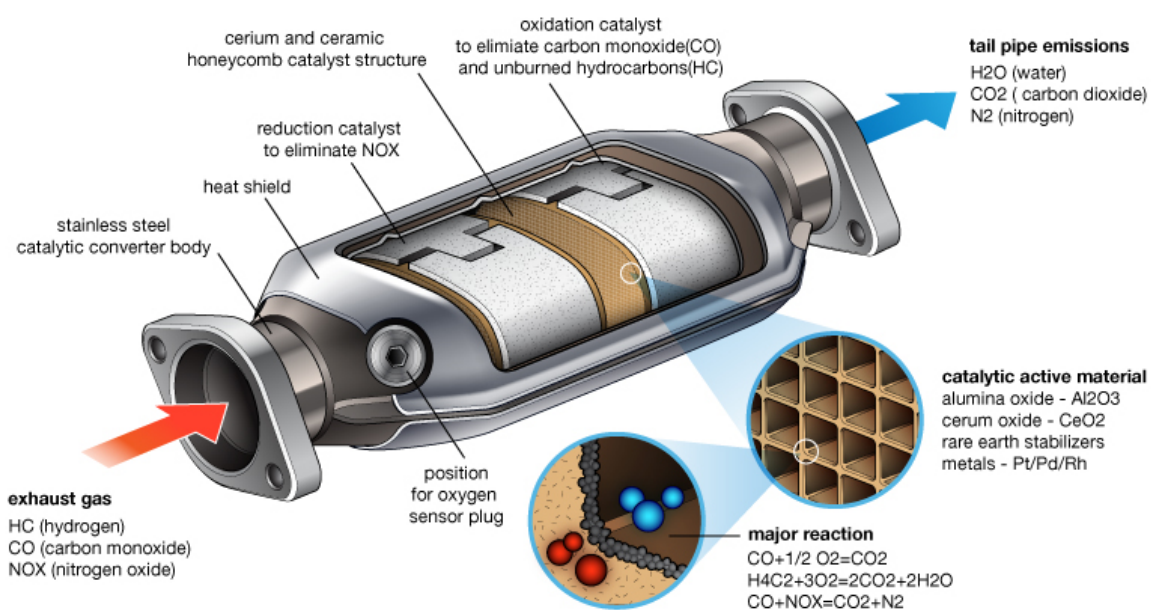
2. Oxidation of carbon monoxide to carbon dioxide



3. Oxidation of unburnt hydrocarbons (HC) to carbon dioxide and water, in addition to the above NO reaction



In general, engines fitted with 3-way catalytic converters are equipped with a computerized closed-loop feedback fuel injection system using one or more oxygen sensors, though early in the deployment of three-way converters, carburetors equipped with feedback mixture control were used.



Three-way converters are effective when the engine is operated within a narrow band of air-fuel ratios near the stoichiometric point, such that the exhaust gas composition oscillates between rich (excess fuel) and lean (excess oxygen). Conversion efficiency falls very rapidly when the engine is operated outside of this band.

Under lean engine operation, the exhaust contains excess oxygen, and the reduction of NO_x is not favoured. Under rich conditions, the excess fuel consumes all of the available oxygen prior to the catalyst, leaving only oxygen stored in the catalyst available for the oxidation function.

Closed-loop engine control systems are necessary for effective operation of three-way catalytic converters because of the continuous balancing required for effective NO_x reduction and HC oxidation. The control system must prevent the NO_x reduction catalyst from becoming fully oxidized yet replenish the oxygen storage material so that its function as an oxidation catalyst is maintained.

Three-way catalytic converters can store oxygen from the exhaust gas stream, usually when the air-fuel ratio goes lean. When sufficient oxygen is not available from the exhaust stream, the stored oxygen is released and consumed

(Cerium(IV) oxide, also known as cerium dioxide, is an oxide of the rare-earth metal cerium. It is a pale yellow-white powder with the chemical formula CeO_2 . It is an important commercial product and an intermediate in the purification of the element from the ores. The distinctive property of this material is its reversible conversion to a nonstoichiometric oxide).

A lack of sufficient oxygen occurs either when oxygen derived from NO_x reduction is unavailable or when certain manoeuvres such as hard acceleration enrich the mixture beyond the ability of the converter to supply oxygen.

Unwanted reactions

Unwanted reactions can occur in the three-way catalyst, such as the formation of odoriferous hydrogen sulphide and ammonia. Formation of each can be limited by modifications to the washcoat and precious metals used. It is difficult to eliminate these by-products entirely. Sulphur-free or low-sulphur fuels eliminate or reduce hydrogen sulphide.

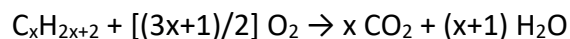
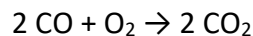
For example, when control of hydrogen-sulphide emissions is desired, nickel or manganese is added to the washcoat. Both substances act to block the absorption of sulphur by the washcoat. Hydrogen sulphide forms when the washcoat has absorbed sulphur during a low-temperature part of the operating cycle, which is then released during the high-temperature part of the cycle and the sulphur combines with the hydrocarbons.

Diesel Emission Control.

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For compression-ignition (i.e., diesel) engines, the most commonly used catalytic converter is the diesel oxidation catalyst (DOC). DOCs contain palladium, platinum, and aluminium oxide, all of which catalytically oxidize the hydrocarbons and carbon monoxide with oxygen to form carbon dioxide and water.



These converters often operate at 90 percent efficiency, virtually eliminating diesel odour and helping reduce visible particulates (soot). These catalysts do not reduce NO_x because any reductant present would react first with the high concentration of O₂ in diesel exhaust gas.

Reduction in NO_x emissions from compression-ignition engines has previously been addressed by the addition of exhaust gas to incoming air charge, known as exhaust gas recirculation (EGR). In 2010, most light-duty diesel manufacturers added catalytic systems to their vehicles to meet new emissions requirements.

There are two techniques that have been developed for the catalytic reduction of NO_x emissions under lean exhaust conditions:

1. Selective Catalytic Reduction (SCR)
2. The lean NO_x trap or NO_x absorber.

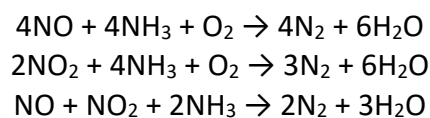
Instead of precious-metal containing NO_x absorbers, most manufacturers selected base-metal SCR systems that use a reagent such as ammonia to reduce the NO_x into nitrogen. Ammonia is supplied to the catalyst system by the injection of urea into the exhaust, which then undergoes thermal decomposition and hydrolysis into ammonia. The urea solution is also referred to as Diesel Exhaust Fluid (DEF).

The use of SCR is now vital in meeting the EURO6 diesel emissions standards for heavy trucks, and also for cars and light commercial vehicles. In many cases, emissions of NO_x and PM (Particulate Matter) have been reduced by upwards of 90% when compared with vehicles of the early 1990s; thanks in no small part to SCR technology.

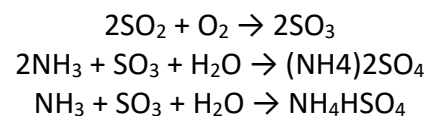
The NO_x reduction reaction takes place as the gases pass through the catalyst chamber. Before entering the catalyst chamber the ammonia, or other reductant such as urea (Urea, also known as carbamide, is an organic compound with chemical formula CO(NH₂)₂.) (This amide has two –NH₂ groups joined by a carbonyl (C=O) functional group.)



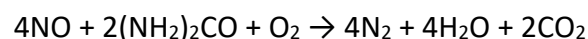
This is injected and mixed with the gases. The chemical equation for a stoichiometric reaction using either anhydrous or aqueous ammonia for a selective catalytic reduction process is:



With several secondary reactions:



The reaction for urea instead of either anhydrous or aqueous ammonia is:



The ideal reaction has an optimal temperature range between 630K and 720K but can operate from 500K to 720K with longer residence times. The minimum effective temperature depends on the various fuels, gas constituents, and catalyst geometry. Other possible reductants include cyanuric acid and ammonium sulphate.



Diesel exhaust contains relatively high levels of particulate matter (PM). Catalytic converters do not remove PM so particulates are cleaned up by a soot trap or diesel particulate filter (DPF). All on-road light, medium and heavy-duty vehicles powered by diesel and built after January 1, 2007, must meet diesel particulate emission limits, meaning that they effectively have to be equipped with a 2-way catalytic converter and a diesel particulate filter.

Note that this applies only to the diesel engine used in the vehicle. As long as the engine was manufactured before January 1, 2007, the vehicle is not required to have the DPF system. This led to an inventory runup by engine manufacturers in late 2006 so they could continue selling pre-DPF vehicles well into 2007.



Diesel engines produce a variety of particles during combustion of the fuel/air mix due to incomplete combustion. The composition of the particles varies widely dependent upon engine type, age, and the emissions specification that the engine was designed to meet. Two-stroke diesel engines produce more particulate per unit of power than do four-stroke diesel engines, as they burn the fuel-air mix less completely.

Diesel particulate matter resulting from the incomplete combustion of diesel fuel produces soot (black carbon) particles. These particles include tiny nanoparticles, smaller than a one micron.

New particulate filters can capture from 30% to greater than 95% of the harmful soot. With an optimal diesel particulate filter (DPF), soot emissions may be decreased to 0.001 g/km or less.

The quality of the fuel also influences the formation of these particles. For example, a high sulphur content diesel produces more particles. Lower sulphur fuel produces fewer particles and allows use of particulate filters. The injection pressure of diesel also influences the formation of fine particles.



Variants of DPFs

Unlike a catalytic converter which is a flow-through device, a DPF retains bigger exhaust gas particles by forcing the gas to flow through the filter; however, the DPF does not retain small particles and maintenance-free DPFs break larger particles into smaller ones.

There are a variety of diesel particulate filter technologies on the market. Each is designed around similar requirements:

Fine filtration
Minimum pressure drop
Low cost
Mass production suitability
Product durability

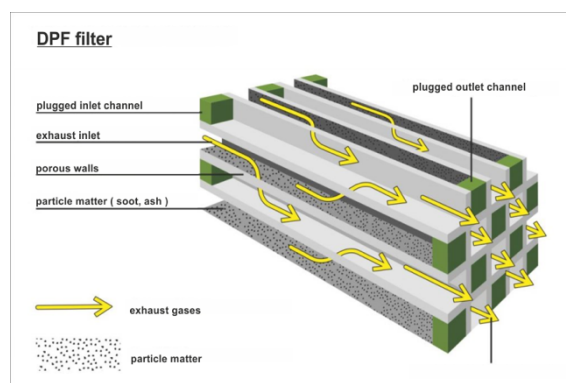
Cordierite wall flow filters

The most common filter is made of cordierite (a ceramic material that is also used as catalytic converter supports (cores)). Cordierite filters provide excellent filtration efficiency, are relatively inexpensive, and have thermal properties that make packaging them for installation in the vehicle simple. The major drawback is that cordierite has a relatively low melting point (about 1200°C) and cordierite substrates have been known to melt during filter regeneration. This is mostly an issue if the filter has become loaded more heavily than usual and is more of an issue with passive systems than with active systems, unless there is a system break down.

Cordierite filter cores look like catalytic converter cores that have had alternate channels plugged - the plugs force the exhaust gas flow through the wall and the particulate collects on the inlet face.

Silicon carbide wall flow filters

The second most popular filter material is silicon carbide, or SiC. It has a higher (2700 °C) melting point than cordierite, however, it is not as stable thermally, making packaging an issue. Small SiC cores are made of single pieces, while larger cores are made in segments, which are separated by a special cement so that heat expansion of the core will be taken up by the cement, and not the package. SiC cores are usually more expensive than cordierite cores, however they are manufactured in similar sizes, and one can often be used to replace the other. Silicon carbide filter cores also look like catalytic converter cores that have had alternate channels plugged - again the plugs force the exhaust gas flow through the wall and the particulate collects on the inlet face.



The characteristics of the wall flow diesel Particulate filter substrate are as follows: broad band filtration (the diameters of the filtered particles are 0.2–150 μm); high filtration efficiency (can be up to 95%); high refractory; high mechanical properties. high boiling point.



Ceramic fibre filters

Fibrous ceramic filters are made from several different types of ceramic fibres that are mixed together to form a porous media. This media can be formed into almost any shape and can be customized to suit various applications. The porosity can be controlled in order to produce high flow, lower efficiency or high efficiency lower volume filtration. Fibrous filters have an advantage over wall flow design of producing lower back pressure. Ceramic wall-flow filters remove carbon particulates almost completely, including fine particulates less than 100 nm diameter with an efficiency of greater than 95% in mass and greater than 99% in number of particles over a wide range of engine operating conditions. Since the continuous flow of soot into the filter would eventually block it, it is necessary to 'regenerate' the filtration properties of the filter by burning-off the collected particulate on a regular basis. Soot particulates burn-off forms water and CO_2 in small quantity amounting to less than 0.05% of the CO_2 emitted by the engine.

Metal fibre flow-through filters

Some cores are made from metal fibres, and generally the fibres are "woven" into a monolith. Such cores have the advantage that an electrical current can be passed through the monolith to heat the core for regeneration purposes, allowing the filter to regenerate at low exhaust temperatures and/or low exhaust flow rates. Metal fibre cores tend to be more expensive than cordierite or silicon carbide cores, and generally not interchangeable with them because of the electrical requirement.

Paper Filters

Disposable paper cores are used in certain specialty applications, without a regeneration strategy. Coal mines are common users; the exhaust gas is usually first passed through a water trap to cool it, and then through the filter. Paper filters are also used when a diesel machine must be used indoors for short periods of time, such as on a forklift being used to install equipment inside a store.

Filter Maintenance

Filters require more maintenance than catalytic converters. Ash, a by-product of oil consumption from normal engine operation, builds up in the filter as it cannot be converted into a gas and pass through the walls of the filter. This increases the pressure before the filter. Warnings are given to the driver before filter restriction causes an issue with driveability or damage to the engine or filter develop. Regular filter maintenance is a necessity.

DPF filters go through a regeneration process which removes this soot and lowers the filter pressure. There are three types of regeneration: passive, active, and forced. Passive regeneration takes place normally while driving, when engine load and vehicle drive-cycle create temperatures that are high enough to regenerate the soot buildup on the DPF walls. Active regeneration happens while the vehicle is in use, when low engine load and lower exhaust gas temperatures inhibit the naturally occurring passive regeneration. Sensors upstream and downstream of the DPF (or a differential pressure sensor) provide readings that initiate a metered addition of fuel into the exhaust stream. There are two methods to inject fuel, either downstream injection directly into the exhaust stream, downstream of the turbo, or fuel injection into the engine cylinders on the exhaust stroke. This fuel and exhaust gas mixture passes through the Diesel Oxidation Catalyst (DOC) creating temperatures high enough to burn off the accumulated soot. Once the pressure drop across the DPF lowers to a calculated value, the process ends, until the soot accumulation builds up again. This works well for vehicles that drive longer distances with few stops compared to those that perform short trips with many starts and stops. If the filter develops too much pressure, then the last type of regeneration must be used - a forced regeneration. This can be accomplished in two ways. The Vehicle operator can initiate the regeneration via a dashboard mounted switch. Various signal interlocks, such as park brake applied, transmission in neutral, engine coolant temperature, and an absence of engine related fault codes are required (vary by OEM and application) for this process to initiate. When the soot accumulation reaches a level that is potentially damaging to the engine or the exhaust system, the solution involves a garage using a computer program to run a regeneration of the DPF manually.

Regeneration is the process of burning off (oxidizing) the accumulated soot from the filter. This is done either passively (from the engine's exhaust heat in normal operation or by adding a catalyst to the filter) or actively introducing very high heat into the exhaust system. On-board active filter management can use a variety of strategies:

- Engine management to increase exhaust temperature through late fuel injection or injection during the exhaust stroke
- Use of a fuel borne catalyst to reduce soot burn-out temperature
- A fuel burner after the turbo to increase the exhaust temperature
- A catalytic oxidizer to increase the exhaust temperature, with after injection
- Resistive heating coils to increase the exhaust temperature
- Microwave energy to increase the particulate temperature

All on-board active systems use extra fuel, whether through burning to heat the DPF, or providing extra power to the DPF's electrical system, although the use of a fuel borne catalyst reduces the energy required very significantly. Typically, a computer monitors one or more sensors that measure back pressure and/or temperature and based on pre-programmed set points the computer makes decisions on when to activate the regeneration cycle. The additional fuel can be supplied by a metering pump. Running the cycle too often while keeping the back pressure in the exhaust system low will result in high fuel consumption. Not running the regeneration cycle soon enough increases the risk of engine damage and/or uncontrolled regeneration (thermal runaway) and possible DPF failure.

Diesel particulate matter burns when temperatures above 600 degrees Celsius are attained. This temperature can be reduced to somewhere in the range of 350 to 450 degrees Celsius by use of a fuel borne catalyst. The actual temperature of soot burn-out will depend on the chemistry employed.

The start of combustion causes a further increase in temperature. In some cases, in the absence of a fuel borne catalyst, the combustion of the particulate matter can raise temperatures above the structural integrity threshold of the filter material, which can cause catastrophic failure of the substrate. Various strategies have been developed to limit this possibility. Note that unlike a spark-ignited engine, which typically has less than 0.5% oxygen in the exhaust gas stream before the emission control device(s), diesel engines have a very high ratio of oxygen available. While the amount of available oxygen makes fast regeneration of a filter possible, it also contributes to runaway regeneration problems.

Some applications use off-board regeneration. Off-board regeneration requires operator intervention (i.e. the machine is either plugged into a wall/floor mounted regeneration station, or the filter is removed from the machine and placed in the regeneration station).

Lean-burn spark-ignition engines

For lean-burn spark-ignition engines, an oxidation catalyst is used in the same manner as in a diesel engine. Emissions from lean burn spark ignition engines are very similar to emissions from a diesel compression ignition engine.