Catalytic Converter

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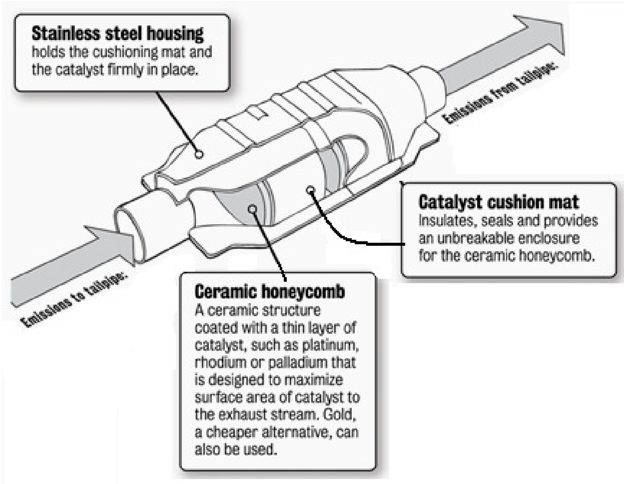
A catalytic converter is a device used to reduce the toxicity of emissions from an internal combustion engine. First widely introduced on series-production automobiles in the U.S. market for the 1975 model year to comply with tightening EPA regulations on auto exhaust, catalytic converters are still most commonly used in motor vehicle exhaust systems.

The catalytic converter was invented by Eugene Houdry, a French mechanical engineer and expert in catalytic oil refining who lived in the United States. About 1950, when the results of early studies of smog in Los Angeles were published, Houdry became concerned about the role of automobile exhaust in air pollution and founded a special company, **Oxy-Catalyst**, to develop catalytic converters for gasoline engines - an idea ahead of its time for which he was awarded a patent (US2742437).

Widespread adoption had to wait until the extremely effective anti-knock agent tetra-ethyl lead was eliminated from most gasoline over environmental concerns, as the agent would "poison" the converter by forming a coating on the catalyst's surface, effectively disabling it. The catalytic converter was further developed by John J. Mooney and Carl D. Keith at the **Engelhard Corporation**, creating the first production catalytic converter in 1973.

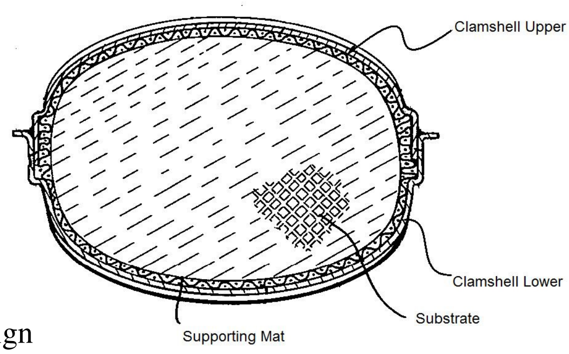
Anatomy of Catalytic Converter



The catalytic converter assembly consists most of these components, inlet/outlet pipes/flanges, steel housing, insulation material, seals, inlet/outlet cones, substrate(s), coating and sensor boss.

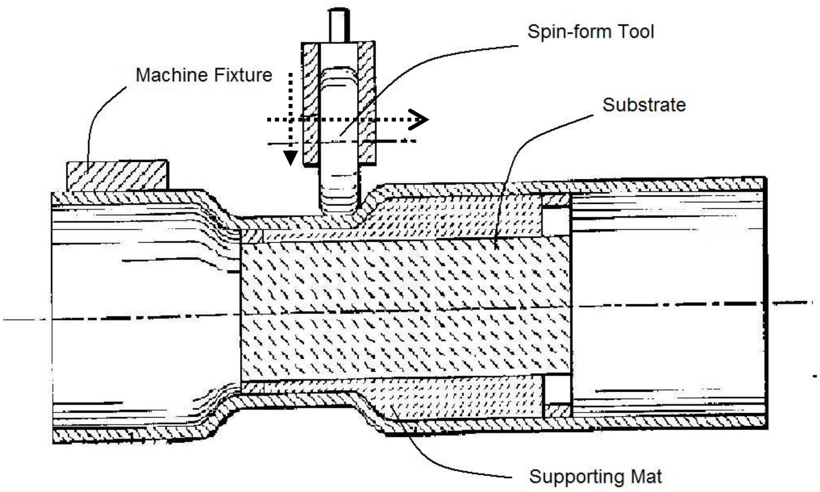
- A steel housing provides protection and structure support for substrate; insulation material (mat or wire mesh) provides heat insulation and support between steel housing and substrate; seals are there to protect mat material from been burned by the exhaust gas.
- The ***substrate*** is often called a "catalyst support". It is a ceramic honeycomb or a stainless steel foil honeycomb in modern catalytic converters. The ceramic substrate was invented by Rodney Bagley, Irwin Lachman and Ronald Lewis at **Corning**, in use to increases the amount of surface area available to support the catalyst.
- The ***washcoat*** is used to make converters more efficient, often as a mixture of silica and alumina. When a washcoat is added to the substrate, it forms a rough, irregular surface, which has a far greater surface area than the flat core surfaces do, which then gives the substrate a larger surface area, providing more sites for active precious metal – the catalytic which is added to the washcoat (in suspension) before being applied to the substrate.
- The ***catalyst*** itself is most often a precious metal. Platinum is the most active catalyst and is widely used. However, because of unwanted additional reactions and/or cost, Palladium and rhodium are two other precious metals that are used. Platinum and rhodium are used as a reduction catalyst, while platinum and palladium are used as an oxidization catalyst. Cerium, iron, manganese and nickel are also used, although each has its own limitations.

There are several well known canning methods that are available in production in automotive industry.



Clamshell Design

- Clamshell or Shoebox – It's just what the word is, the converter can has a upper and a lower two piece structure, they are welded together in the fixture with substrate and the supporting mat mount material sandwiched between them.
- Stuffed – This application is usually a round shape. The catalytic substrate is pre-wrapped with supporting mat material and stuff (pushed with a tool) into the shell (tube), which has smaller diameter than the diameter of supporting mat wrapped substrate.
- Swaged – This application usually is also a round shape. The catalytic substrate is pre-wrapped with supporting mat material and placed (pushed with a tool) into the shell (tube), which has bigger diameter than the diameter of supporting mat wrapped substrate, then the shell diameter is reduced with a tool (swaging machine).
- Tourniquet – Pre-wrapped substrate with supporting mat is wrapped and pulled tied with a steel sheet and is welded together by the sheet material overlapping end along the seam.
- Spin-formed – Pre-measured substrate with supporting mat wrapped and pushed into the outer metal shell (tube), the tube is then fixed on the spinning machine and spinning along the axis of the substrate, and a programmed spin tool thereby forms the metal shell into shape as shown below.



Spin-formed Catalytic Converter

Catalyst Applications

Two-way Converter

Two-way catalytic converter is widely used on diesel engines to reduce hydrocarbon and carbon monoxide emissions, and they were also used on spark ignition (gasoline) engines in USA market automobiles through 1981, when the two-way converter's inability to control NOx led to its supersession by three-way converters.

A two-way catalytic converter has two simultaneous tasks:

- Oxidation of carbon monoxide to carbon dioxide:
  $\mathbf{2CO + O_2 \rightarrow 2CO_2}$
- Oxidation of un-burnt and partially-burnt hydrocarbons to carbon dioxide and water:
  $\mathbf{C_xH_{2x+2} + [(3x+1)/2]\ O_2 \rightarrow xCO_2 + (x+1)\ H_2O}$ (a combustion reaction)

Three-way Converter

Since 1981, three-way catalytic converters have been used in vehicle emission control systems in North America and many other countries on road going vehicles. A three-way catalytic converter has three simultaneous tasks:

- Oxidation of carbon monoxide to carbon dioxide:
  $2CO + O_2 \rightarrow 2CO_2$
- Oxidation of un-burnt hydrocarbons (HC) to carbon dioxide and water:
  $C_xH_{2x+2} + [(3x+1)/2]O_2 \rightarrow xCO_2 + (x+1)H_2O$
- Reduction of nitrogen oxides to nitrogen and oxygen:
  $2NO_x \rightarrow xO_2 + N_2$

These three reactions occur most efficiently when the catalytic converter receives the exhaust gas from an engine running slightly above the stoichiometric point. Below shows the necessary mixing rate of the most common fuels.

Fuel	By mass	By volume	Percent fuel by mass
Gasoline	14.7 : 1	—	6.8%
Natural gas	17.2 : 1	9.7 : 1	5.8%
Diesel	14.6 : 1	0.094 : 1	6.8%

Generally, engines fitted with 3-way catalytic converters are equipped with a computerized closed-loop feedback fuel injection system, which is employing one or more oxygen sensors. Though early in the deployment of 3-way converters, carburetors equipped for feedback mixture control were used. While a 3-way catalyst was used in an open-loop system, NOx reduction efficiency was low. Within a narrow fuel/air ratio band surrounding stoichiometry, conversion of all three pollutants is nearly complete. However, outside of that band, conversion efficiency falls off very rapidly.

When there is more oxygen than required, then the system is said to be running ***lean***, and the system is in oxidizing condition. In that case, the converter's two oxidizing reactions (oxidation of CO and hydrocarbons) are in favor, at the expense of the reducing reaction. When there is excessive fuel, then the engine is running ***rich***. The reduction of NOx is in favor, at the expense of CO and HC oxidation. In today's world, almost everyone likes to run the engine in lean at about 20:1 or higher because of the fuel economy consideration.

Three-way catalytic converters can store oxygen from the exhaust gas stream, usually when the air fuel ratio goes lean. When insufficient oxygen is available from the exhaust stream the stored oxygen is released and consumed. This happens either when oxygen derived from NOx reduction is unavailable or certain maneuvers such as hard acceleration enrich the mixture beyond the ability of the converter to compensate.

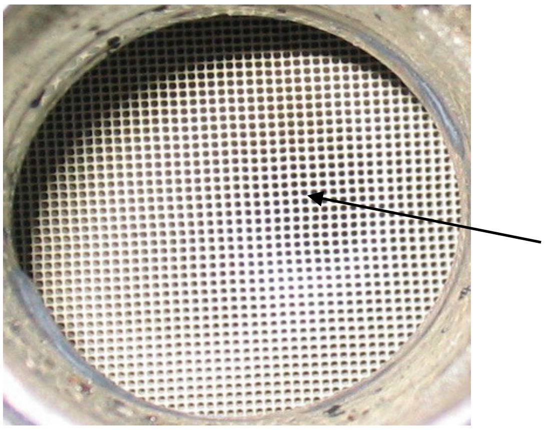
Unwanted reactions can occur in the three-way catalyst, such as the formation of odiferous hydrogen sulfide and ammonia. Formation of each can be limited by modifications to the washcoat and precious metals used. It is very difficult to eliminate all these byproducts entirely.
For example, when control of hydrogen sulfide emissions is desired, nickel or manganese is added to the washcoat. Both substances act to block the adsorption of sulfur by the washcoat. Hydrogen sulfide is formed when the washcoat has adsorbed sulfur during a low temperature part of the operating cycle, which is then released during the high temperature part of the cycle and the sulfur combines with HC.

Gasoline Engine Application

On a global basis, most passenger cars are equipped with stoichiometric Otto engines. Although the exhaust gas after-treatment for such type of engines is well-known, the three-way converter (TWC) has been the primary emission control technology on light-duty gasoline vehicles since the early 1980s. The use of TWCs, in conjunction with the oxygen sensor-based, closed-loop fuel delivery system, allows for simultaneous conversion of the three criteria pollutants, HC, CO, and NOx, produced during the combustion of fuel in a spark-ignited engine.

In US, the European Union and Japan, the ever ending demand of emission limit control requires even more sophisticated technical solutions. Three-way catalysts are one essential part of this system design. These technologies must guarantee a conversion level in the 95% range and even higher for major pollutants like carbon monoxide, nitrogen oxides and hydrocarbons — over the lifetime of the vehicle.

In gasoline catalytic converter application, the active catalytic materials are present as a thin coating of precious metal (Pt, Pd, & Rh), and oxide-based inorganic promoters and support materials on the internal walls of the honeycomb substrate. The substrate typically provides a large number of parallel flow channels to allow for sufficient contacting area between the exhaust gas and the active catalytic materials without creating excess pressure losses.



Honeycomb substrate in gasoline catalytic converter application

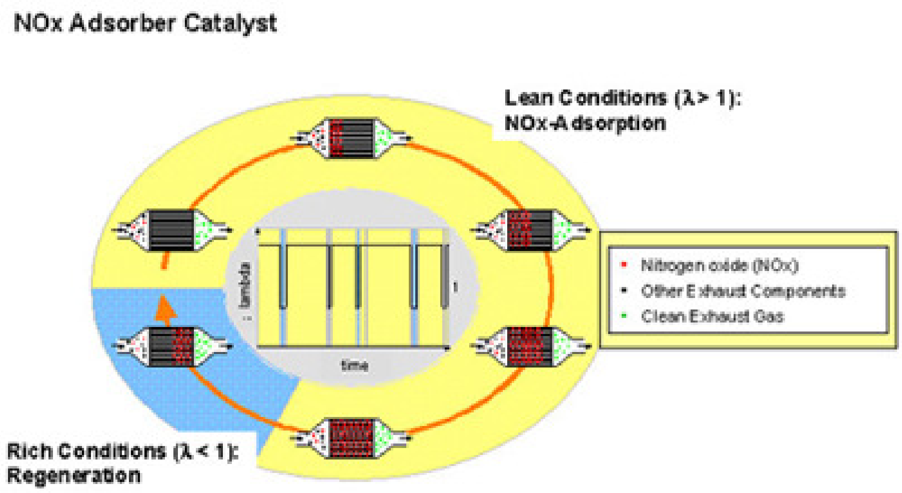
Although the primary components and function of a TWC has remained relatively constant during its more than twenty years of use on light-duty gasoline vehicles, each of the primary converter components (catalytic coating, substrate, mounting materials) has gone through a continuous evolution and redesign process in order to improve the overall performance of the converter while maintaining a competitive cost effectiveness of the complete assembly.

Lean Operating Gasoline Application

Another way to reduce emissions in passenger cars is to reduce fuel consumption. For this reason, ***lean operating Otto engines*** have entered the market offering fuel saving potentials of 15 to 20%. When engine is running in lean condition, the reduction of NOx emission becomes one of major challenge for exhaust gas after-treatment device.

The chemical reduction of nitrogen oxides in an atmosphere that contains large amounts of oxygen is very difficult. To overcome this challenge, the **NOx absorber** catalyst technologies have been developed in close cooperation with the automotive industry. In addition to advanced functions that are implemented in three-way catalyst technologies, these NOx absorber catalysts contain special nitrogen dioxide (NO_2) storage functions, which allow the adsorption (storage) of NO_2 under lean engine operation conditions.

The completely filled absorber can be regenerated in a short period of rich engine operation conditions – hard acceleration or other rich fuel mixture situation, allowing the engine then to return to the fuel-saving lean operation mode.



Umicore was among the first catalyst manufacturer to supply the NOx absorber catalyst technology for gasoline vehicles. Some of today's applications already meet the 2015 emission requirements. (www.umicore.com)

Zone – Coated Catalyst Technology

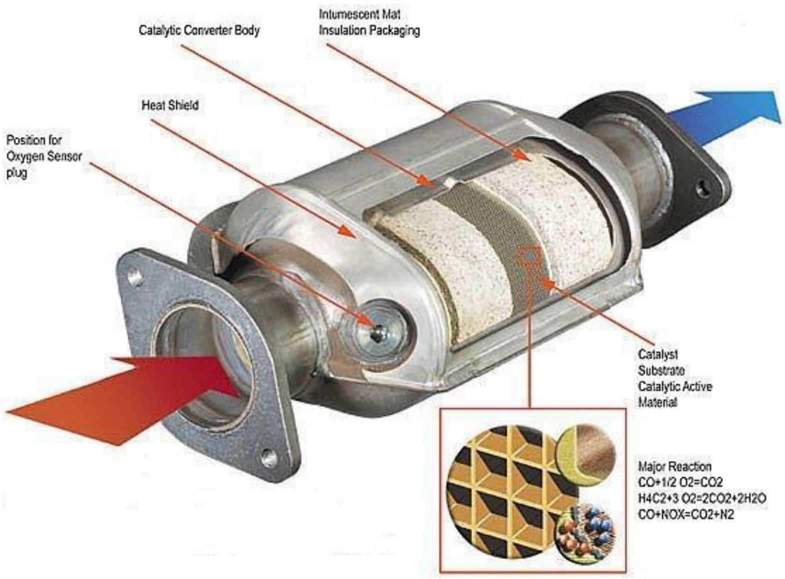
The ever increasing demand for improved catalyst activity and life span has led to more complex catalyst designs comprising multiple catalyst layers on the catalyst supporting substrate structures, each of the layers - containing selected support materials and catalytic components as well as so called promoters, stabilizers and oxygen storage compounds.

In some applications of the gasoline emission control catalyst substrates, the washcoat even carries same or different precious metals with the same or different concentration. The substrate is divided into two even three special zones of washcoat in longitudinal direction in order to serve the function of prolonging catalyst life span from thermal damage, and different exhaust gas cleaning purposes, meanwhile preventing the substrate from been poisoning.

Intensive studies had been done to define the detail dimensions of each zone and the concentrations of the precious metals, especially with light-off can in the gasoline applications. Also, a specified catalyst coating processes had been studied and defined, and meanwhile, a specific group of organic compounds is also selected as wetting agent, in order to achieve the necessary concentration profile of the catalyst precious metals. The optimum profile will depend on the particular application, and it can be determined by the expert through experimentation.

Diesel Oxidation Catalyst (DOC)

For compression-ignition (i.e., diesel) engines, the commonly used catalytic converter is the diesel oxidation catalyst (DOC). In most applications, a diesel oxidation catalyst consists of a stainless steel canister that contains a honeycomb structure called a substrate or catalyst support. There are no moving parts, just large amounts of interior surface area. The interior surfaces are coated with precious metals such as platinum or palladium as oxidation catalytic material. It is called an oxidation catalyst because the device converts exhaust gas pollutants into harmless gases by means of chemical oxidation.

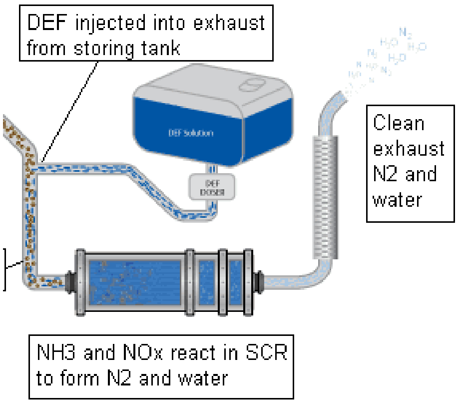


Diesel Oxidation Catalyst

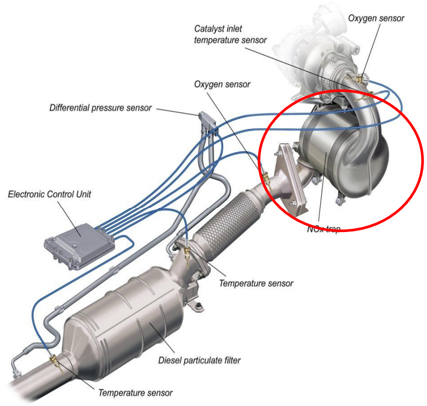
In the case of diesel engine exhaust, the catalyst oxidizes CO, HC, and the liquid hydrocarbons adsorbed on carbon particles. In the field of mobile source emission control, liquid hydrocarbons adsorbed on the carbon particles in engine exhaust are referred to as the ***soluble organic fraction*** (SOF) -- the soluble part of the particulate matter in the exhaust. Diesel oxidation catalysts are efficient at converting the soluble organic fraction of diesel particulate matter into carbon dioxide and water, typically can achieve 25% to 40% over all particulate reduction by simply burning the SOF component of particulate matter.

About 30 percent of the total particulate matter (PM) mass of diesel exhaust is attributed to liquid hydrocarbon. Under certain operating conditions, DOCs have achieved SOF removal efficiencies of 80 to 90 percent. Actual emission reductions vary however, as a result of engine type, size, age, duty cycle, condition, maintenance procedures, baseline emissions, test procedure, product manufacturer and the fuel sulfur level. However, as all chemical reactions always occur in the simplest possible way - the existing O2 in the exhaust gas stream would react first, the NOx will be remained in the exhaust gas stream.

To reduce NOx on a compression ignition engine, the chemical composition of the exhaust must first be changed. Two main techniques are used: ***selective catalytic reduction*** (SCR) and ***NOx traps*** (or NOx Absorbers).



Typical SCR System



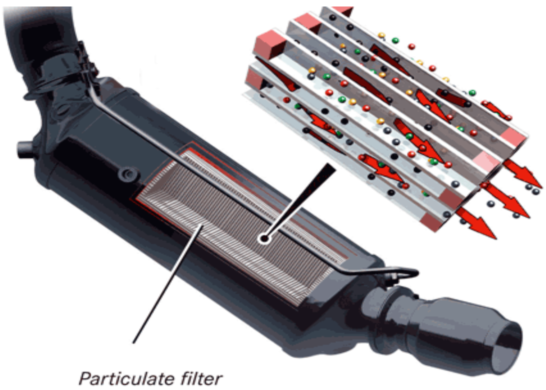
Typical NOx Trap System (Renault)

Catalytic converters cannot clean up elemental carbon, although they remove up to 90% of the soluble organic fraction (SOF), so the rest of the particulates are cleaned up by a soot trap or diesel particulate filter (DPF). In the United States, all on-road heavy-duty vehicles powered by diesel and built after 1 January 2007 must be equipped with a catalytic converter and a diesel particulate filter. DOC and DPF are sometimes packaged together in one can in order to save space and cost in automotive and HD truck industry.

Diesel Particulate Filters (DPF)

Diesel particulate filters remove particulate matter found in diesel exhaust by filtering exhaust from the engine. In order to meet the stringent particulate emissions that are required for diesel light duty vehicles starting with the 2007 model year, the highest efficiency particulate filter is required. The filters are commonly made from ceramic materials such as cordierite, aluminum titanate, mullite or silicon carbide.

Mercedes E-Class DPF



The basis for the design of wall flow filters is a honeycomb structure with alternate channels plugged at opposite ends. As the gasses passes into the open end of a channel, the plug at the opposite end forces the gasses through the porous wall of the honeycomb channel and out through the neighboring channel. The ultrafine porous structure of the channel walls results in greater than 90% percent collection efficiencies of these filters. Wall flow filters capture particulate matter by interception and impaction of the solid particles across the porous wall. The exhaust gas is allowed to pass through in order to maintain low pressure drop.

Particulate Filters Regeneration

Since a filter can fill up over time by developing a layer of retained particles on the inside surface of the porous wall, engineers that design engines and filter systems must provide a means of burning off or removing accumulated particulate matter and thus regenerating the filter. A convenient means of disposing 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" to its original state, this is called "***regeneration***". The frequency of regeneration is determined by the amount of soot build-up resulting in an increase in ***back pressure***. To facilitate decomposition of the soot, a catalyst is used either in the form of a coating on the filter or a catalyst added to the fuel.

Filters that regenerate in this so-called "passive" fashion cannot be used in all situations. The experience with catalyzed filters indicates that there is a virtually complete reduction in odor and in the soluble organic fraction of the particulate. Despite the high efficiency of the catalyst, a layer of ash may build up on the filter requiring replacement or servicing. The ash is made up of inorganic oxides from the fuel or lubricants used in the engine and will not decompose during the regular soot regeneration process. In some applications or operating cycles, the exhaust never achieves a high enough temperature to completely oxidize the soot even in the presence of a catalyst. In these instances, an ***"active" regeneration*** system must be employed.

Active regeneration utilizes a fuel burner or a resistively heated electric element to heat the filter and oxidize the soot. Active regeneration can be employed either in-place on the vehicle or externally.

- In place vehicle regeneration, the DPF will periodically undergo active regeneration. In this process, a small mist of diesel fuel is injected into the exhaust stream at the turbocharger outlet; the mist travels through the exhaust pipe to wet the DPF's pre-catalyst. This causes a chemical reaction which raises DPF temperatures to the level required to convert the soot into CO_2. Active regeneration normally takes about 15 minutes and the operation is not noticeable to the driver. This event is triggered when sensors – in most cases pressure sensors located at the inlet and outlet end of the DPF that alert the vehicle computer (ECU) that the restriction across the particulate trap is increasing and the particulate trap is becoming full.
- During external regeneration, the filter is removed from the vehicle and heated in a controlled chamber to remove the PM.

Monitoring Sensors

Temperature sensors

- Temperature sensors are used for two purposes. The first is as a warning system, typically on 2-Way catalytic converters such as are still sometimes used on LPG forklifts. The function of the sensor is to warn of catalytic converter temperature above the safe limit of 750 °C (1,380 °F). More recent catalytic converter designs are not as susceptible to temperature damage and can withstand sustained temperatures of 900 °C (1,650 °F).
- Temperature sensors are also used to monitor catalyst functioning - usually two sensors will be fitted, with one before the catalyst and one after to monitor the temperature rise over the catalytic converter core. For every 1% of CO in the exhaust gas stream the exhaust gas temperature will rise by 100°C.

Oxygen sensors

The Oxygen sensor is the basis of the closed loop control system on a spark ignited rich burn engine, however it is also used for diagnostics. In vehicles with OBD II, a second oxygen sensor is fitted after the catalytic converter to monitor the O2 levels. The on-board computer makes comparisons between the readings of the two sensors. If both sensors give the same output, the computer recognizes the catalytic converter is not functioning or removed, and will operate a 'check engine' light and retard engine performance.

Simple "oxygen sensor simulators" have been developed to circumvent this by simulating the change across the catalytic converter with plans and pre-assembled devices available on the internet, though these are not legal for on-road use. Similar devices apply an offset to the sensor signals, allowing the engine to run a more fuel economical lean burn that may however damage the engine or the catalytic converter.

NOx sensors

NOx sensors are extremely expensive and are generally only used when a compression ignition engine is fitted with a selective catalytic reduction converter (SCR), or a NOx trap / absorber in a feedback system. When fitted to an SCR system, there may be one or two sensors. When one sensor is fitted it will be pre-catalyst, when two are fitted the second one will be post catalyst. They are utilized for the same reasons and in the same manner as an oxygen sensor - the only difference is the substance being monitored.

Some newer systems provide a constantly varying mixture that quickly and continually cycles between lean and rich to keep the first catalyst (NOx reduction) from becoming oxygen loaded, and to keep the second catalyst (CO oxidization) sufficiently oxygen-saturated. They also utilize several oxygen sensors to monitor the exhaust, at least one before the catalytic converter for each bank of cylinders, and one after the converter. Some systems contain the reduction and oxidation functions separately rather than in a common housing.

Catalyst Poisoning

Catalyst poisoning occurs when the catalytic converter is exposed to exhaust containing substances that coat the working surfaces, encapsulating the catalyst so that it cannot contact and treat the exhaust. The most notable contaminant is lead, so vehicles equipped with catalytic converters can only be run on unleaded gasoline. Other common catalyst poisons include manganese primarily from the gasoline additive MMT, and silicone which can enter the exhaust stream if the engine has a leak allowing coolant into the combustion chamber. Phosphorus is another catalyst contaminant. Although phosphorus is no longer used in gasoline, it (and zinc, another low-level catalyst contaminant) was until recently widely used in engine oil anti-wear additives such as ZDDP. Beginning in 2006, a rapid phase out of ZDDP in engine oils was begun.

Depending on the contaminant, catalyst poisoning can sometimes be reversed by running the engine under a very heavy load for an extended period of time. The increased exhaust temperature can sometimes liquefy or sublimate the contaminant, removing it from the catalytic surface. However, removal of lead deposits in this manner is usually not possible due to lead's high boiling point.

Any condition that causes abnormally high levels of unburned hydrocarbons — raw or partially-burnt fuel — to reach the converter will tend to significantly elevate its temperature, bringing the risk of a meltdown of the substrate and resultant catalytic deactivation and severe exhaust restriction. Vehicles equipped with OBD-II diagnostic systems are designed to alert the driver of a misfire condition, along with other malfunctions, by all means of the "Check Engine" light on the dashboard.

Removing Catalytic Converter

Some early converter designs created a great deal of restriction to the flow of exhaust, which negatively affected vehicle performance, drivability, and fuel economy, because they were used with carburetors incapable of precise fuel/air mixture control, and they could overheat and set fire to flammable materials under the car.

Removing a modern catalytic converter in new condition will only slightly increase vehicle performance without retuning, but their removal or "gutting" continues. The exhaust section where the converter was may be replaced with a welded-in section of straight pipe, or a flanged section of "test pipe" legal for off-road use that can then be replaced with a similarly fitted converter-choked section for legal on-road use, or emissions testing. In many other jurisdictions including US, it is illegal to remove or disable a catalytic converter for any reason other than its immediate replacement; vehicles without functioning catalytic converters generally fail emission inspections. The aftermarket supplies high-flow converters for vehicles with upgraded engines, or those owners who prefer an exhaust system with larger-than-stock capacity.

Catalytic converters have proven to be reliable and effective in reducing noxious emissions. However, they may have some adverse environmental impacts in use.

Fuel economy - The requirement for a rich burn engine to run at the stoichiometric point means it uses more fuel than a "lean burn" engine running at a mixture of 20:1 or less. This increases the amount of fossil fuel consumed and the carbon dioxide emissions of the vehicle. However, NOx control on lean burn engines is problematic.

Carbon dioxide and global warming - Although catalytic converters are effective at removing hydrocarbons and other harmful emissions, most of exhaust gas leaving the engine through a catalytic converter is carbon dioxide (CO_2), one of the greenhouse gases indicated by the Intergovernmental Panel on Climate Change (IPCC) to be a "most likely" cause of global warming. Additionally, the U.S. Environmental Protection Agency (EPA) has stated catalytic converters are a significant and growing cause of global warming, due to their release of nitrous oxide (N_2O), a greenhouse gas over 300 times more potent than carbon dioxide.

Regional pollution - Catalytic converter production requires palladium and/or platinum; part of the world supply of these precious metals is produced near the Russian city of Norilsk, where the industry among others has caused Norilsk to be added to Time Magazine's list of most polluted places.

Emission Control Alternative