Catalytic emission control

Emission-control legislation lays down limits governing pollutant emissions from motor vehicles. On-engine measures on their own are not enough to comply with these limits. In gasoline engines, catalytic exhaust-gas aftertreatment for the purpose of converting the pollutants has now taken center stage. To this end, the exhaust gas passes through one or more catalytic converters located in the exhaust-system branch before being discharged to atmosphere. The pollutants contained in the exhaust gas are converted on the surface of the catalytic converter(s) by chemical reactions into non-toxic substances.

Overview

Catalytic exhaust-gas aftertreatment with the aid of a three-way catalytic converter is currently the most effective form of emission control for gasoline engines. The three-way catalytic converter is an integral component of the exhaust-emission control systems of both manifold-injection engines and gasoline direct-injection engines (Fig. 1).

In the case of homogeneous mixture distribution with a stoichiometric air/fuel ratio ($\lambda = 1$), a three-way catalytic converter at normal operating temperature is able to convert the following pollutants virtually completely: carbon monoxide (CO), hydrocarbons (HCs) and nitrous oxides (NO_X). However, adhering exacting to a figure of $\lambda = 1$ requires mixture formation by means of electronically controlled gasoline injection; today, this system has completely replaced the carburetor, which was used primarily up until the introduction of the three-way catalytic converter. Precise lambda closed-loop control monitors the composition of the air/fuel mixture and regulates it at a value of $\lambda = 1$. Although these ideal conditions cannot always be maintained in all operating states, pollutant emissions can on average be reduced by more than 98 %.

Because the three-way catalytic converter is unable to convert the nitrous oxides in lean mode ($\lambda > 1$), an additional NO_X accumulator-type catalytic converter is used in engines with a lean operating mode. Another means of reducing NO_X at $\lambda > 1$ is Selective Catalytic Reduction (SCR). This process is already being used in diesel commercial vehicles, and development plans are currently underway to introduce it in diesel passenger

1 Exhaust-gas branch with lambda sensors and a three-way catalyst installed in the immediate vicinity of the engine

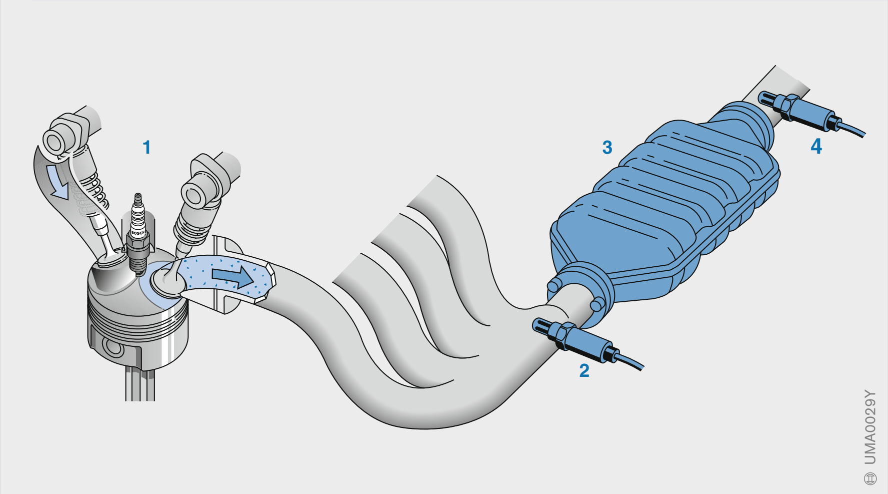

Fig. 1
1 Engine
2 Lambda sensor upstream of catalyst (two-step sensor or wide-band sensor depending on system)
3 Three-way catalyst
4 Two-step lambda sensor downstream of catalyst (only on systems with two-sensor lambda control)

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cars. At this moment, however, it is not possible to foresee whether SCR will also be able to be used in gasoline engines.

The oxidation catalytic converter, which is used in diesel engines to oxidize HCs and CO, is not used separately in gasoline engines, since the three-way catalytic converter performs its function.

Development objectives

In view of the constantly tightening emission limits, reducing pollutant emissions remains an important objective in engine design and development. Whereas a catalytic converter which has reached normal operating temperature achieves very high conversion rates bordering on 100 %, considerably larger amounts of pollutants are emitted in the cold-start and warm-up phases: The actual amounts of pollutants emitted during the starting process and the subsequent post-start phase can make up to 90 % of the total emissions both in the European and American test cycles (NEDC or FTP 75). In order to reduce emissions, it is therefore essential both to ensure that the catalytic converter heats up quickly and to generate the fewest possible untreated emissions in the starting phase and while the catalyst is heating up. Early operational readiness on the part of the lambda oxygen sensor is also an important factor.

Catalytic-converter concepts

Catalytic converters can be divided into the following categories:

- Continuously operating catalysts, and
- Intermittently operating catalysts

Continuously operating catalytic converters convert pollutants uninterrupted and without actively intervening in the engine operating conditions. The following systems are classed as continuously operating: the three-way catalytic converter, the oxidation catalytic converter and the SCR catalytic converter (Selective Catalytic Reduction; currently used in diesel engines only).

Intermittently operating catalytic converters operate in different phases, which are initiated in each case by an active change in the boundary conditions by the catalytic-converter system. The NO_X accumulator-type catalytic converter operates intermittently: In the event of excess oxygen in the exhaust gas, NO_X is accumulated and the system is switched to rich mode (oxygen deficiency) for the subsequent regeneration phase.

Three-way catalytic converter

Method of operation

The three-way catalytic converter converts the following pollutant components into non-toxic components during the combustion of the air/fuel mixture: hydrocarbons (HCs), carbon monoxide (CO) and nitrous oxides (NO_X). The end products which result are water vapor (H_2O), carbon dioxide (CO_2) and nitrogen (N_2).

Conversion of pollutants

The conversion of pollutants can be divided into oxidation and reduction reactions. For example, oxidation of carbon monoxide and hydrocarbons takes place according to the following equations:

$$2\,CO + O_2 \rightarrow 2\,CO_2 \qquad \text{(eq. 1)}$$

$$2\,C_2H_6 + 7\,O_2 \rightarrow 4\,CO_2 + 6\,H_2O \qquad \text{(eq. 2)}$$

Reduction of nitrous oxides takes place according to the following exemplary equations:

$$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2 \qquad \text{(eq. 3)}$$

$$2\,NO_2 + 2\,CO \rightarrow N_2 + 2\,CO_2 + O_2 \qquad \text{(eq. 4)}$$

The oxygen needed to oxidize HCs and CO is drawn either directly from the exhaust gas or from the nitrous oxides present in the exhaust gas, depending on the composition of the air/fuel mixture.

At $\lambda = 1$, a state of balance arises between the oxidation and reduction reactions. The residual-oxygen content in the exhaust gas at $\lambda = 1$ (approximately 0.5 %) and the oxygen bound in the nitrous oxide enable HCs and CO to oxidize completely; the nitrous oxides are simultaneously reduced. Thus, HCs and CO acts as reducing agents for the nitrous oxides. The catalytic converter can compensate for minor mixture fluctuations itself.
It has the ability to accumulate and release oxygen. Its substrate layer contains ceroxide, which can make oxygen available via the following balance reaction:

$$2\ Ce_2O_3 + O_2 \longleftrightarrow 4\ CeO_2 \qquad \text{(eq. 5)}$$

In the event of constant excess oxygen ($\lambda > 1$), HCs and CO are oxidized by the oxygen present in the exhaust gas. They are therefore not available for the reduction of the nitrous oxides. The raw NO_X emissions are therefore released untreated. In the event of a constant oxygen deficiency ($\lambda < 1$), the nitrous-oxide reduction reactions takes place with HCs and CO as the reducing agents. Excess hydrocarbons and carbon monoxide which cannot be converted for lack of oxygen are released untreated.

Conversion rate

The quantity of released pollutants is derived from the concentration of the pollutants in the untreated exhaust gas (Fig. 2a) and from the conversion rate, i.e., from the proportion that can be converted in the catalytic converter. Both variables are dependent on the set excess-air factor λ.

The highest possible conversion rate for all three pollutant components requires a mixture composition in the stoichiometric ratio of $\lambda = 1.0$. The window (lambda control range) in which the air/fuel ratio λ must be situated is therefore very small. Mixture formation must therefore be followed up in a lambda closed-loop control circuit.

The conversion rates for HCs and CO rise continuously as the excess-air factor increases, i.e., the emissions decrease (Fig. 2b). At $\lambda = 1$, there is only a very low level of pollutant components in the untreated exhaust gas. With high excess-air factors ($\lambda > 1$), the concentration of these pollutant components remains at this low level.

Conversion of the nitrous oxides (NO_X) is good in the rich range ($\lambda < 1$). Even a small increase in the oxygen content in the exhaust gas from $\lambda = 1$ impedes the reduction of nitrous oxides and causes a sharp increase in their concentration.

2 Pollutants in the exhaust gas

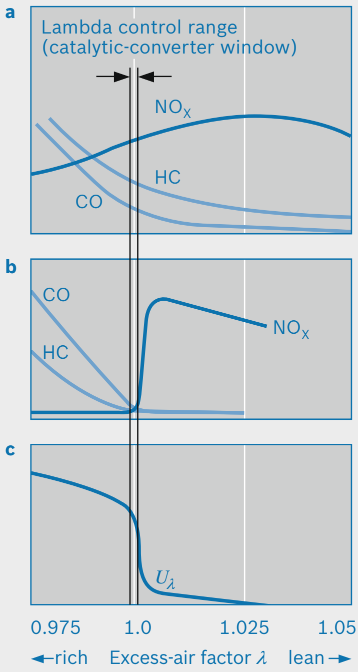

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Fig. 2
- a Before catalytic aftertreatment (untreated exhaust gas)
- b After catalytic aftertreatment
- c Voltage curve of two-step lambda sensor

Design

The catalytic converter (Fig. 3) essentially comprises a sheet-steel housing (6), a substrate (5), a substrate coating (washcoat), and the active catalytic noble-metal coating (4).

Substrates

Two substrate systems have come to the forefront:

Ceramic monoliths
These ceramic monoliths are ceramic bodies containing thousands of narrow passages through which the exhaust gas flows. The ceramic is a high-temperature-resistant magnesium-aluminum silicate. The monolith, which is highly sensitive to mechanical tension, is fastened inside a sheet-steel housing by means of mineral swell matting (2) which expands the first time it is heated up and firmly fixes the monolith in position.
At the same time, the matting also ensures a 100 % gas seal. Ceramic monoliths are at present the most commonly used catalyst substrates.

Metallic monoliths
The metallic monolith is an alternative to the ceramic monolith. It is made of finely corrugated, thin metal foil approximately 0.03...0.05 mm thick which is wound and soldered in a high-temperature process. Thanks to the thin walls, it is possible to incorporate a greater number of passages per surface. This reduces the resistance experienced by the exhaust gas and brings advantages in the optimization of high-performance engines.

Coating

Ceramic and metallic monoliths require a substrate coating (washcoat) of aluminum oxide (Al_2O_3). This coating increases the effective surface of the catalytic converter by a factor of 7000. 1 *l* catalyst volume therefore has an area equating to a soccer field.

The effective catalytic coating contains the noble metals platinum and/or palladium and rhodium. Platinum and palladium accelerate the oxidation of hydrocarbons and of carbon monoxide. Rhodium accelerates the reduction of nitrous oxides (NO_X).

The amount of noble metal contained in a catalytic converter is roughly 1...5 g. This figure depends among other things on the engine displacement and on the exhaust-emission standard to be complied with.

3 Three-way catalytic converter with lambda sensor

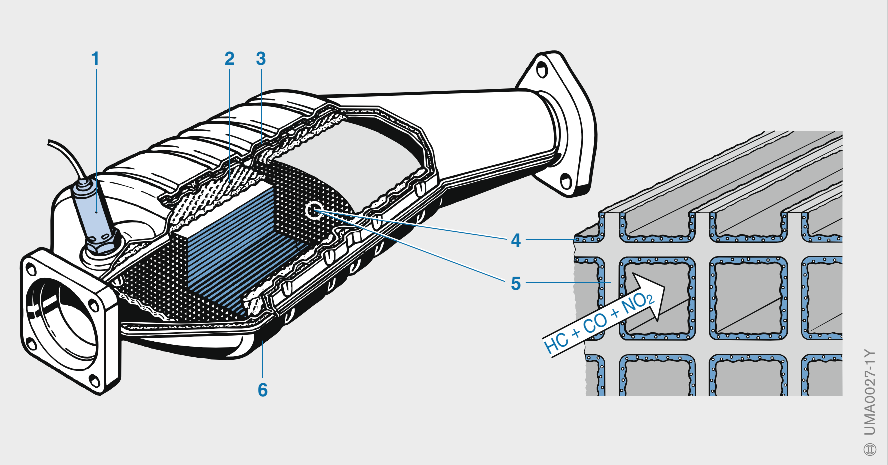


Fig. 3
1 Lambda sensor
2 Swell matting
3 Thermally insulated double shell
4 Washcoat (Al_2O_3 substrate coating) with noble-metal coating
5 Substrate (monolith)
6 Housing

Operating conditions

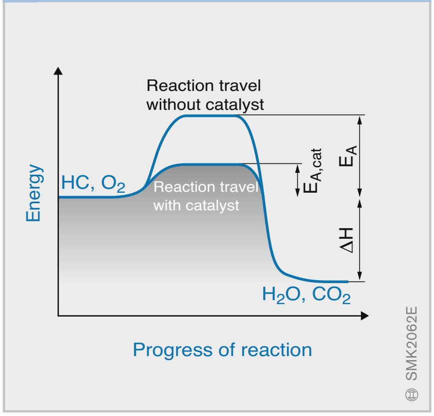
Operating temperature

To enable the oxidation and reduction reactions for converting the pollutants to pass off, the reacting agents must be supplied with a specific amount of activation energy. This energy is provided by the heat from the heated-up catalytic converter.

The catalytic converter reduces the activation energy (Fig. 4) such that the light-off temperature (i.e., the temperature at which 50 % of the pollutants is converted) drops. The activation energy – and thus the light-off temperature – are greatly dependent on the respective reacting agents. Considering a three-way catalytic converter, no worthwhile conversion of pollutants takes place until the operating temperature exceeds 300 °C. Operation within a temperature range of 400...800 °C is ideal for high conversion levels and a long service life.

In the range of 800...1000 °C, thermal aging of the catalytic converter is significantly improved by sintering the noble metals and the Al_2O_3 substrate coat. This leads to a reduction of the active surface. The operating time in this temperature range also has a significant influence here. At temperatures in excess of 1000 °C, thermal aging of the catalytic converter increases sharply, causing the catalyst to be largely ineffective.

4 Activation energy



In the event of engine malfunction (e.g., ignition miss), the temperature in the catalytic converter can rise to up to 1400 °C if unburnt fuel ignites in the exhaust-system branch. Since such temperatures melt the substrate and completely destroy the catalyst, it is imperative that the ignition system be highly reliable so as to prevent this from occurring. Modern engine-management systems are able to detect ignition and combustion miss, and in such cases interrupt the fuel injection to the cylinder concerned so that unburnt mixture cannot enter the exhaust-system branch.

Catalytic-converter poisoning

In order to be able to use a three-way catalytic converter, it is essential for the engine to be run on unleaded fuel. Otherwise, lead compounds would be deposited in the active catalyst coating or clog the pores and thereby reduce their number.

Residues from the engine oil can also “poison” the catalyst, i.e., damage it so far that it becomes ineffective.

NO_X accumulator-type catalytic converter

Function

During lean-burn operation, it is impossible for the three-way catalytic converter to convert the nitrous oxides (NO_X) which have been generated during combustion. CO and HCs are oxidized by the high residual-oxygen content in the exhaust gas and are therefore no longer available as reducing agents for the nitrous oxides. The NO_X accumulator-type catalytic converter (NSC, NO_X Storage Catalyst) converts the nitrous oxides in a different way.

Design and special coating

The NO_X accumulator-type catalytic converter is similar in design to the conventional three-way converter. In addition to the platinum, palladium and rhodium coatings, the NO_X converter is provided with special additives which are capable of accumulating nitrous oxides. Typical accumulator materials contain, for example, the oxides of potassium, calcium, strontium, zirconium, lanthanum, or barium.

Method of operation

At $\lambda = 1$, due to the noble-metal coating, the NO$_X$ converter operates the same as a three-way converter. It also converts the non-reduced nitrous oxides in lean exhaust gases. However, conversion is not a continuous process as it is with the hydrocarbons and the carbon monoxide, but instead takes place in three distinct phases:

1. NO$_X$ accumulation (storage)
2. NO$_X$ removal
3. Conversion

NO$_X$ accumulation (storage)

In lean-burn engine operation ($\lambda > 1$), the nitrous oxides (NO_X) are catalytically oxidized on the surface of the platinum coating to form nitrogen dioxide (NO_2). Then the NO_2 reacts with the special oxides on the catalyst surface and with oxygen (O_2) to form nitrates. Thus, for instance, NO_2 combines chemically with barium oxide (BaO) to form the chemical compound barium nitrate $Ba(NO_3)_2$:

$$2\,BaO + 4\,NO_2 + O_2 \quad \rightarrow 2\,Ba(NO_3)_2$$

This enables the NO$_X$ converter to accumulate the nitrous oxides which have been generated during engine operation with excess air.

There are two methods in use to determine when the NO$_X$ converter is saturated and the accumulation phase has finished:

- The model-supported process calculates the quantity of stored NO$_X$ taking into account the catalyst temperature
- An NO$_X$ sensor (Fig. 5, Pos. 6) downstream of the NO$_X$ converter measures the NO$_X$ concentration in the exhaust gas

NO$_X$ removal and conversion

As the amount of stored nitrous oxides (charge) increases, so the ability to continue to bind nitrous oxides decreases. This means that regeneration must take place as soon as a given level is exceeded, i.e., the accumulated nitrous oxides must be removed and converted. To this end, the engine is switched briefly to rich homogeneous mode ($\lambda < 0.8$). The processes for removing the NO$_X$ and converting it into nitrogen and carbon dioxide take place separately from each other. H_2, HCs, and CO are used as reducing agents. Reduction is slowest with HCs and most rapid with H_2. Removal takes place as follows,

5 Exhaust-gas branch with three-way catalyst as primary catalyst, and downstream NO$_X$ accumulator-type catalyst and lambda sensors

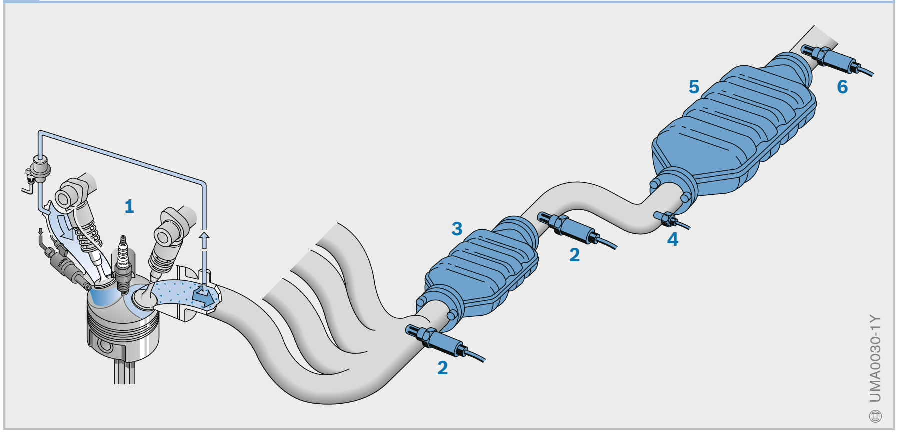


Fig. 5

1	Engine with EGR system
2	Lambda sensor
3	Three-way catalyst (primary catalyst)
4	Temperature sensor
5	NO$_X$ accumulator-type catalyst (main catalyst)
6	Two-step lambda sensor, optionally available with integral NO$_X$ sensor

with CO being used as the reducing agent in the following description: The carbon monoxide reduces the nitrate (e.g., barium nitrate $Ba(NO_3)_2$) to an oxide (e.g., barium oxide BaO). Carbon dioxide and nitrogen monoxide are produced in the process:

$$Ba(NO_3)_2 + 3\,CO \quad \rightarrow 3\,CO_2 + BaO + 2\,NO$$

Subsequently, using carbon monoxide, the rhodium coating reduces the nitrous oxides to nitrogen and carbon dioxide:

$$2\,NO + 2\,CO \qquad \rightarrow N_2 + 2\,CO_2$$

There are two different methods of detecting when the removal phase is complete.

- The model-supported process calculates the quantity of NO_X still held by the NO_X converter.
- A lambda sensor (6) downstream of the converter measures the oxygen concentration in the exhaust gas and outputs a voltage jump from "lean" to "rich" when removal has finished.

Operating temperature and installation point

The NO_X converter's ability to accumulate/store NO_X is highly dependent on temperature. Accumulation reaches its maximum in the range of 300...400 °C, which means that the favorable temperature range is much lower than that of the three-way catalytic converter. For this reason and because of the lower maximum permissible operating temperature of the NO_X converter, two separate catalytic converters must be installed for catalytic emission control:
an upstream three-way catalyst as the primary converter (Fig. 5, Pos. 3) and a downstream NO_X accumulator-type catalyst (5) as the main converter (underfloor converter).

Sulfur loading

The sulfur contained in gasoline presents the accumulator-type catalytic converter with a problem. The sulfur contained in lean exhaust gas reacts with the barium oxide (accumulator material) to form barium sulfate. The result is that, over time, the amount of accumulator material available for NO_X accumulation diminishes. Barium sulfate is extremely resistant to high temperatures, and for this reason is only degraded to a slight degree during NO_X regeneration.

When sour fuels (i.e., containing sulfur) are used, the catalytic converter must be constantly desulfurized. For this purpose, the converter is heated by specific heating measures to 600...650 °C and then exposed for a few minutes to alternately rich ($\lambda = 0.95$) and lean ($\lambda = 1.05$) exhaust gas. The barium sulfate reduces to barium oxide as a result.

Catalytic-converter configurations

Boundary conditions

The design of the exhaust system is defined by various boundary conditions: heat-up performance during cold starting, temperature loading at full load, space situation in the vehicle, and engine torque and power development.

The required operating temperature of the three-way catalytic converter limits the installation options. Upstream converters quickly reach operating temperature in the post-start phase, but can be exposed to extremely high thermal load at high engine load and speed. Downstream converters
are less exposed to these temperature loads. But they do require more time in the heating-up phase to reach operating temperature, if this is not accelerated by an optimized strategy for heating the converter (e.g., secondary-air injection).

Strict emission-control regulations call for special concepts for heating the catalytic converter when the engine is started. The lower the heat flow which can be generated to heat the catalytic converter, and the lower the emission limits, the closer the converter should be installed to the engine – provided no additional measures for improving heating-up performance are taken. Air-gap-insulated manifolds are often used; these demonstrate lower heat losses up to the converter and thus have available a greater quantity of heat for heating the converter.

Primary and main catalytic converters

A widely used configuration of the three-way catalytic converter is the split arrangement with an upstream primary catalyst and an underfloor catalyst (main catalytic converter). Upstream catalytic converters (i.e., near the engine) require their coating to be optimized to provide for high-temperature stability. Underfloor converters, on the other hand, require optimization in the so-called "low light-off" direction (low start-up temperature) and good NO_X conversion characteristics. For faster heating and pollutant conversion, the primary catalyst is usually smaller and has a higher cell density and a greater noble-metal load.

Owing to their lower maximum permissible operating temperature, NO_X accumulator-type catalysts are always installed in the underfloor area.

As an alternative to the classic arrangement of splitting into two separate housings and installation positions, there are also two-stage catalytic-converter configurations (cascade catalytic converters), in which two catalyst substrates are accommodated in a common housing one after the other. The two substrates are separated from each other for thermal-isolation purposes by a small air gap. In a cascade catalytic converter, the thermal load of the second catalyst is, because of the spatial proximity, comparable with the first catalyst. Nevertheless, this arrangement permits independent optimization of the two catalysts with regard to noble-metal load, cell density and wall thickness. The first catalyst general has a larger noble-metal load and a higher cell density for good light-off performance during cold starting. A lambda sensor can be installed between the two substrates for controlling and monitoring exhaust-gas treatment.

Even concepts with only one overall catalytic converter are used. It is possible with modern coating methods to create different noble-metal loads in the front and rear sections of the catalyst. This configuration has a smaller scope for design possibilities but is attractive in cost terms. Provided there is enough space available, the catalyst is located as close to the engine as possible. However, it can also be situated further away from the engine (i.e., downstream positioning) if an effective catalyst-heating process is used.

Multiflow configurations

The exhaust-system branches of the individual cylinders are brought together ahead of the catalyst at least partially by the exhaust manifold. Four-cylinder engines frequently use exhaust manifolds which bring together all four cylinders after a short distance.
This makes it possible to use an upstream catalyst, which can be favorably positioned for heating performance (Fig. 6a).

For optimized-power engine configurations, 4-into-2 exhaust manifolds are the preferred choice in four-cylinder engines; in this arrangement, only two exhaust-gas branches are brought together in each case. Positioning one catalyst after the second junction into a single overall exhaust-gas branch is not good for the heating performance.
For this reason, the ideal solution is to install two upstream (primary) catalysts already after the first junction and if necessary a further (main) catalyst after the second join (Fig. 6b).

A similar situation arises in engines with more than four cylinders, especially in engines with more than one cylinder bank (V-engine). Primary and main catalysts can be used on each bank in accordance with the above descriptions. Two different arrangements may be used: The exhaust system is completely designed as a dual-flow arrangement (Fig. 6c), or a Y-shaped junction merging into an overall exhaust-gas branch is used. In the latter case, a joint main catalyst serving both cylinder banks can be used in a configuration with primary and main catalysts (Fig. 6d).

6 Catalytic-converter configurations

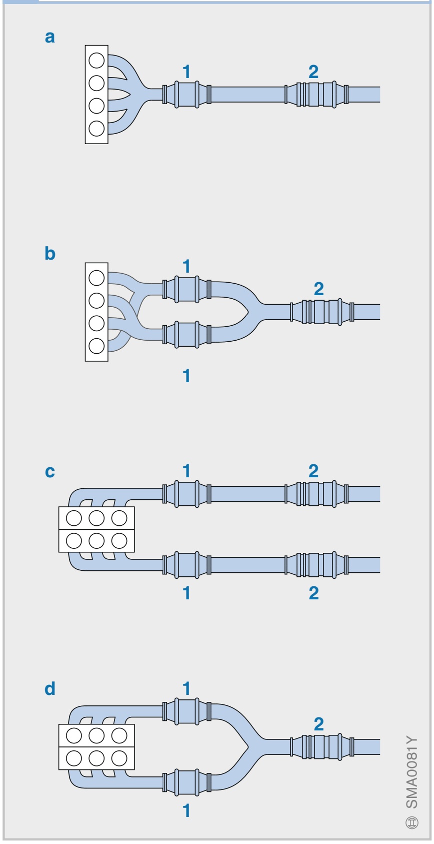


Fig. 6
a Four-into-one exhaust manifold
b Four-into-two exhaust manifold
c Twin-branch exhaust system
d Y-shaped exhaust system

1 Primary catalyst
2 Main catalyst

Catalytic-converter heating

The three-way catalytic converter must reach a minimum temperature of roughly 300 °C (light-off) before pollutants can be converted; this temperature threshold can be even higher on older catalysts. With the engine and exhaust system initially cold, the catalytic converter must be heated up as quickly as possible to operating temperature. This requires a short-term supply of heat, which can be provided by a variety concepts.

Purely on-engine measures

To ensure effective catalyst heating with on-engine measures, it is necessary to increase both the exhaust-gas temperature and the exhaust-gas mass flow. This is achieved using a variety of measures, which reduce engine efficiency and therefore create an increased exhaust-gas heat flow.

The heat-flow demand on the engine is dependent on the catalyst position and the layout of the exhaust system, because the exhaust gas cools on its way to the catalyst when the exhaust system is cold.

Ignition timing

The main measure for increasing the exhaust-gas heat flow is ignition-timing retardation. Combustion is initiated as late as possible and takes place during the expansion phase. The exhaust gas has a relatively high temperature at the end of the expansion phase.

Retarded combustion has an unfavorable effect on engine efficiency.

Idle speed

A supporting measure is to raise the idle speed and thereby increase the exhaust-gas mass flow. The increased engine speed permits a greater ignition-timing retardation; however, in order to ensure reliable ignition, the ignition angles are limited to roughly 10° to 15° after TDC. The heat output limited in this way is not always enough to achieve the current emission limits.

Exhaust-camshaft adjustment

A further contribution to increasing the heat flow can be achieved if necessary with exhaust-camshaft adjustment. The process of the exhaust valves opening as early as possible interrupts the retarded combustion early and the mechanical work generated is thus reduced further. The corresponding quantity of energy is available as a quantity of heat in the exhaust gas.

Stratified-charge/catalyst heating and homogeneous split

In the case of gasoline direct injection, there are further processes which can quickly heat the catalyst to operating temperature without the need for additional components.
In the "stratified-charge/catalyst heating" operating mode, during stratified-charge operation with high levels of excess air a further injection of fuel takes place at the end of combustion. This fuel burns partly in the exhaust manifold first and delivers an additional injection of heat to the catalyst. The "homogeneous-split" measure involves initially creating a homogeneous, lean basic mixture. A subsequent stratified-charge injection facilitates retarded moments of ignition and results in high exhaust-gas heat flows. These measures render the process of secondary-air injection unnecessary in engines with gasoline direct injection.

Secondary-air injection

Thermal afterburning of unburnt fuel constituents increases the temperature in the exhaust system. A rich ($\lambda = 0.9$) extending up to a very rich ($\lambda = 0.6$) basic mixture is set for this purpose. A secondary-air pump supplies oxygen to the exhaust system to produce a leaner exhaust-gas composition.

Where the basic mixture is very rich ($\lambda = 0.6$), the unburnt fuel constituents oxidize above a specific temperature threshold. To achieve this temperature, it is necessary on the one hand to raise the temperature level with retarded ignition angles and on the other hand to introduce the secondary air as closely as possible to the exhaust valves. The exothermic reaction in the exhaust system increases the heat flow to the catalyst and therefore shortens the heating period. Furthermore, by comparison with purely on-engine measures, HC and CO emissions are reduced before entering the catalyst.

Where the basic mixture is less rich ($\lambda = 0.9$), there is no significant reaction ahead of the catalyst. The unburnt fuel constituents oxidize in the catalyst and heat it up from the inside. For this purpose, however, the end face of the catalyst must first be brought up to a level above the light-off temperature by means of conventional measures (such as ignition-timing retardation).

7 Influence of secondary-air injection

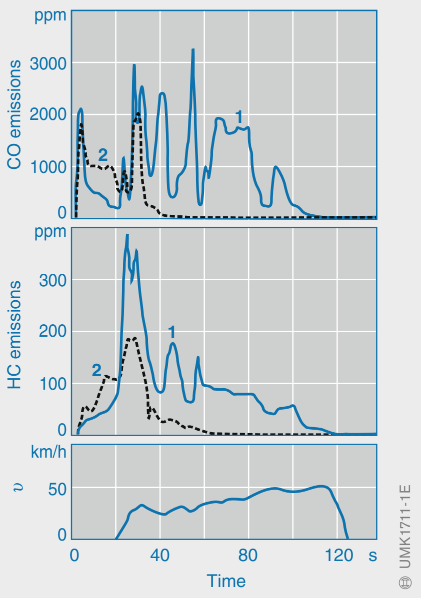


Fig. 7
1 Without secondary-air injection
2 With secondary-air injection

v Vehicle speed

In reality, it is always a combination of these two extreme cases that occurs. Figure 7 shows by way of example the curves for HC and CO emissions downstream of the catalyst in the first few seconds of an emission test (FTP 75), with and without secondary-air injection.

Secondary-air injection is performed with an electric secondary-air pump (Fig. 8, Pos. 1), which is switched by means of a relay (3) on account of the high power demand. Since the secondary-air valve (5) prevents backflow of exhaust gases into the pump, it must remain closed when the pump is deactivated. Either it is a passive non-return valve or it is actuated by purely electrical or (as shown here) pneumatic means with an electrically actuated control valve (6). When the control valve is actuated, the secondary-air valve opens in response to the intake-manifold vacuum. The secondary-air system is coordinated by the engine ECU (4).

8 Secondary-air system

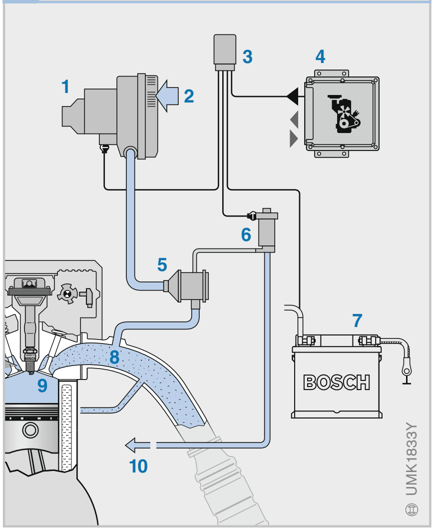


Fig. 8

1 Secondary-air pump
2 Induction air
3 Relay
4 Engine ECU
5 Secondary-air valve
6 Control valve
7 Battery
8 Point of introduction into exhaust pipe
9 Exhaust valve
10 To intake-manifold connection

Concepts for active heating

Measures for active catalytic-converter heating are processes which do not use the internal-combustion engine as the heat source or which do not use the engine as the sole heat source. The advantage of such processes lies in the fact that the heat can be supplied locally and does not have to pass through the exhaust system to the catalyst. Unlike conventional heating strategies with upstream catalysts, these concepts have failed to catch on.

Electrically heated catalytic converter

In the case of an electrically heated catalyst, the exhaust gas first flows through an approximately 20 mm thick catalytic substrate plate which can be heated with an electrical output of roughly 2 kW. A secondary-air system can be used to provide assistance. The additional exothermic effect (heat release) during the conversion of the exhaust-gas/secondary-air mixture in the heated plate accelerates the heating process further.

When compared with the heat currents of up to 20 kW which can be achieved with on-engine measures if necessary in conjunction with secondary-air injection, an electrical output of 2 kW seems relatively low. However, it is the temperature of the catalyst substrate and not the temperature of the exhaust gas which is crucial to catalyst operation. Direct electrical heating of substrate is highly effective and results in very good emission values.

In a conventional passenger car with a 12 V supply voltage, the high currents that occur for heating the catalyst place a significant strain on the car's electrical system. An amplified alternator and if necessary a second battery are therefore required. This system is better suited for use in electric hybrid vehicles, which have more powerful electrical systems anyway.

The electrically heated catalytic converter has previously been used in individual small-scale production projects.

Burner system

Another concept for locally heating the catalytic converter is a fuel-powered burner, the hot combustion exhaust gases of which are fed upstream of the catalyst to the engine exhaust system (Fig. 9). The burner system is supplied with air along the same lines as a secondary-air system and has its own ignition device and fuel-metering facility. In order to achieve low emission targets, good fuel atomization and mixture formation in the burner are crucial to low burner emissions, especially during starting.

Heating-output figures of 15 kW can be achieved with the burner system; however, in contrast to the electrically heated catalyst, the substrate is indirectly heated here.

Mixing the gas flows of the engine and burner (which differ greatly in temperature) can be problematic. However, as well as local heating, the burner system offers a further advantage: Unburnt constituents of the engine exhaust gas oxidize in the hot burner exhaust gas before entering the catalyst, and this results initially in a purely thermal reduction of the pollutants.

The burner system has only previously been used in prototypes and has not been used at all in volume-scale production.

9 Burner system for heating the catalytic converter

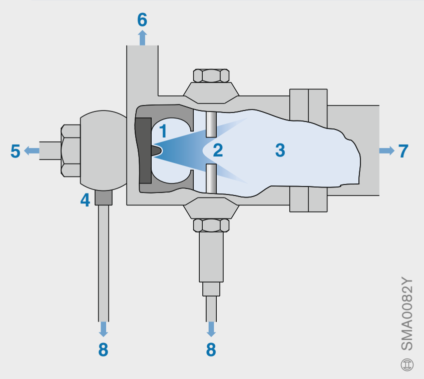


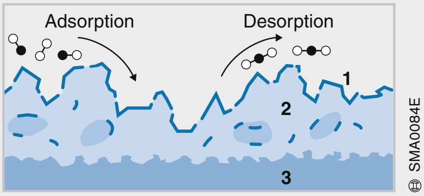
Fig. 9
1 Burner nozzle
2 Ignition electrodes
3 Combustion chamber
4 Fuel shutoff valve
5 Fuel supply via fuel regulator
6 Air supply from secondary-air pump
7 To catalyst
8 To control system

Catalysis

In order for chemical reactions to take place, bonds in the starting substances must be relaxed and then split. This requires a minimum amount of energy (activation energy) which must be supplied to the starting substances, for example in the form of heat. Many thermodynamically possible reactions do not take place at noticeable speed, since the activation energy is very high, and this energy barrier therefore is only overcome by a very small number of molecules.

A catalytic converter accelerates the reaction in two ways. Firstly, it reduces the activation energy of the reaction so that this energy barrier can be overcome by a greater number of molecules. Secondly, the adsorption of the reacting agents on the catalytic converter reduces the distance between them, and the probability that the reacting agents will interact with each other is thereby increased.

There are different mechanisms for the reaction on the catalytic-converter surface; for instance, the oxidation of CO on the platinum catalyst takes place according to the Langmuir-Hinshelwood mechanism, whereby both reacting agents (CO and O_2) are adsorbed on the catalyst surface. The bonds within the O_2 molecule are relaxed and the reactivity of the CO increases. Finally, the O_2 breaks down into atomic oxygen, which can now react with the adsorbed CO. The CO_2 created in this way is then desorbed again into the gaseous phase.



○ Oxygen
● Carbon

1 Catalytic layer
2 Substrate coating
3 Substrate

Lambda control loop

Function

In order that the conversion rates of the three-way catalytic converter are as high as possible for the pollutant components HC, CO and NO_X, the reaction components must be present in the stoichiometric ratio. This requires a mixture composition of $\lambda = 1.0$, i.e., the stoichiometric air/fuel ratio must be adhered to very precisely. Mixture formation must therefore be followed up in a control loop, because sufficient accuracy cannot be achieved solely by controlling the metering of the fuel.

Method of operation

When the lambda control loop is used, deviations from a specific air/fuel ratio can be detected and corrected through the quantity of fuel injected. The residual-oxygen content in the exhaust gas, which is measured with lambda oxygen sensors, serves as the measure for the composition of the air/fuel mixture.

For the purpose of two-step control which can only maintain a value of $\lambda = 1$, a two-step lambda sensor (Fig. 10, Pos. 3a) is incorporated in the exhaust-gas branch upstream of the primary catalyst (4). However, the use of a wide-band lambda sensor also permits continuous lambda closed-loop control to λ values which deviate from the value 1.

Greater accuracy is achieved by a two-sensor control system in which a second lambda sensor (3b) is located downstream of the main catalyst (5).

Two-step control

Two-step lambda control maintains the air/fuel mixture at $\lambda = 1$. A two-step lambda sensor serving as a measuring sensor in the exhaust pipe constantly provides information on whether the mixture is richer or leaner than $\lambda = 1$. A high sensor voltage (e.g., 800 mV) indicates a rich mixture, while a low sensor voltage (e.g., 200 mV) indicates a leaner mixture.

10 Functional diagram of lambda closed-loop control

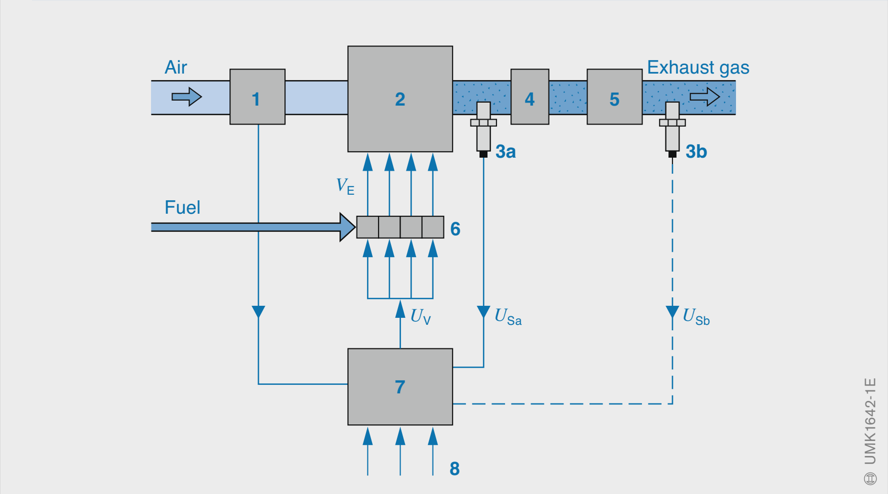


Fig. 10

1	Air-mass sensor
2	Engine
3a	Lambda sensor upstream of primary catalyst (two-step lambda sensor, or wide-band lambda sensor)
3b	Two-step lambda sensor downstream of main catalyst (only if required; gasoline direct injection: with integral NO_X sensor)
4	Primary catalyst (three-way catalyst)
5	Main catalyst (manifold injection: three-way catalyst; gasoline direct injection: NO_X accumulator-type catalyst)
6	Fuel injectors
7	Engine ECU
8	Input signals
U_S	Sensor voltage
U_V	Valve control voltage
V_E	Injected fuel quantity

On each transition from rich to lean and lean to rich, the sensor output signal demonstrates a voltage jump, which is evaluated by a control circuit. The manipulated variable changes its control direction in response to each voltage jump: The lambda controller lengthens or shortens the time that the fuel injector is activated and thereby increases or reduces the injected fuel quantity.

The manipulated variable (lengthening or shortening factor of the injection duration) is made up of a jump and a ramp (Fig. 11). In other words, when there is a jump in the sensor signal, the mixture is first altered immediately by a specific amount (jump) in order to bring about a mixture correction as quickly as possible. Then the manipulated variable follows an adaptation function (ramp) until another sensor-signal voltage jump occurs. The air/fuel mixture thus constantly changes its composition in a very narrow range around $\lambda = 1$.

The typical shift of the oxygen zero crossing (theoretically at $\lambda = 1.0$) and thus of the lambda-sensor jump, conditioned by the variation of the exhaust-gas composition, can be compensated for by shaping the manipulated-variable curve asymmetrically (rich/lean shift). The preferred option here is to maintain the ramp value for the sensor jump for a controlled dwell time t_V after the sensor jump (Fig. 11): During the shift to "rich", the manipulated variable remains for a dwell time t_V in the rich position, even though the sensor signal has already jumped in the "rich" direction. Only after the dwell time has elapsed do the jump and ramp follow the manipulated variable in the "lean" direction. If the sensor signal then jumps in the "lean" direction, the manipulated variable is controlled in the directly opposite direction (with jump and ramp) without remaining in the lean position.

During the shift to "lean", the behavior is reversed: If the sensor signal indicates a lean mixture, the manipulated variable remains for the dwell time t_V in the lean position and is only then controlled in the "rich" direction. On the other hand, countercontrol is effected immediately when the sensor signal jumps from "lean" to "rich".

Continuous-action lambda control

Continuous-action lambda control enables the composition of the air/fuel mixture to be controlled to values which deviate from the stoichiometric ratio. Thus, controlled enrichment ($\lambda < 1$), e.g., to protect components, and controlled leaning ($\lambda > 1$), e.g., for a leaner warm-up during catalyst heating, can be effected.

11 Manipulated-variable curve with controlled lambda shift

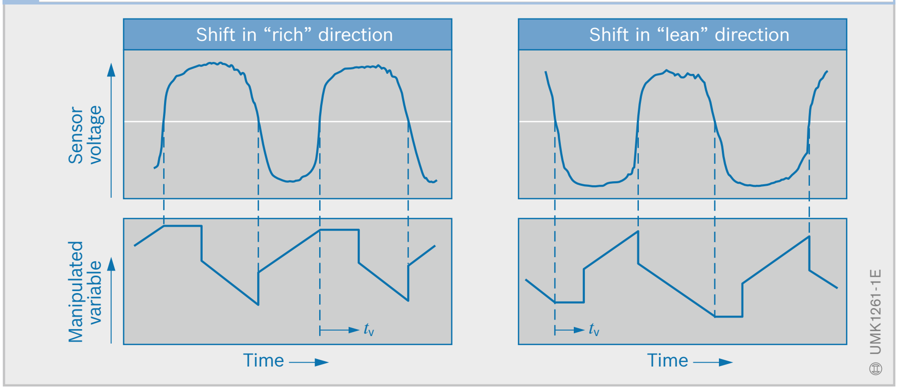


Fig. 11
t_V Dwell time after sensor jump

The wide-band lambda sensor outputs a continuous voltage signal U_{Sa}. This means that not only the lambda range (rich or lean) but also the amount of the deviation from $\lambda = 1$ can be measured and directly evaluated. In this way, lambda control can react more quickly to a mixture deviation. The increased dynamic response results in an improved control response.

It is also possible with the wide-band lambda sensor (in contrast to control with a two-step lambda sensor) to effect control to mixture compositions which deviate from the stoichiometric ratio ($\lambda = 1$). The measurement range stretches to lambda values in the field of $\lambda = 0.7$ up to "pure air"; the range of active lambda control is limited, depending on the application. Continuous-action lambda control is therefore suitable for lean and rich operation.

Two-sensor control

When it is situated upstream of the catalyst, the lambda sensor is heavily stressed by high temperatures and untreated exhaust gas, and this leads to limitations in lambda-control accuracy. Locating a lambda sensor (Fig. 10, Pos. 3b) downstream of the catalyst means that these influences are considerably reduced. However, lambda control on its own with the sensor downstream of the catalyst demonstrates disadvantages in dynamic response on account of the gas travel times, and responds to mixture changes more slowly.

Greater accuracy is achieved with two-sensor control. Here, a slower correction control loop is superimposed on the two-step or continuous-action lambda control described by means of an additional two-step lambda sensor.

Lambda closed-loop control for gasoline direct injection

Lambda closed-loop control for gasoline direct injection does not differ for homogeneous operation ($\lambda = 1$) from the control strategies described above. Systems which additionally support lean engine operation ($\lambda > 1$) require control of the NO_X accumulator-type catalytic converter. The NO_X accumulator-type catalyst has a dual function. During lean-burn operation, NO_X accumulation and HC and CO oxidation must take place. In addition, at $\lambda = 1$, a stable three-way function is needed which provides for a minimum level of oxygen accumulation. The lambda sensor upstream of the catalyst monitors the stoichiometric composition of the mixture.

12 Lambda closed-loop control with control cascade for three-sensor control

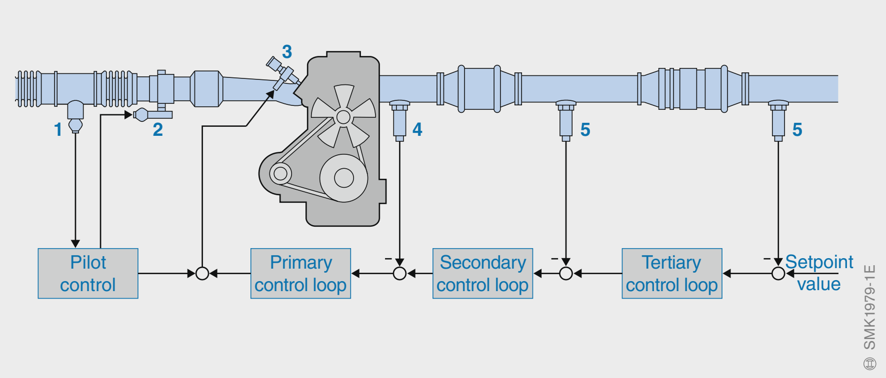


Fig. 12
1 Air-mass sensor (HFM)
2 Throttle valve
3 Fuel injector
4 Wide-band lambda sensor
5 Two-step lambda sensor

In addition to contributing to two-sensor control, the two-step sensor downstream of the NO_X accumulator-type catalyst also monitors the combined O_2 and NO_X accumulation performance (detection of the end of the NO_X removal phase).

Three-sensor control

In the interests of both catalytic-converter diagnosis (separate monitoring of the primary and main catalysts) and exhaust-gas constancy, the use of a third sensor downstream of the main catalyst is recommended in SULEV vehicles (Super Ultra-Low-Emission Vehicle, a category defined in the Californian emission-control legislation) (Fig. 12). The two-sensor control system (single cascade) is expanded to include extremely slow control with the third sensor downstream of the main catalyst and thereby facilitates faster control with the second sensor.

Individual-cylinder control

Above all with upstream primary catalysts, it is not possible to ensure that the exhaust gases from the individual cylinders are sufficiently mixed together before they pass through the catalyst. The fact that exhaust gas passes through the catalyst segments in strands, depending on the deviation from $\lambda = 1$ of the cylinders, results in insufficient conversion. Lambda coordination of the individual cylinders can bring about significant reductions of exhaust emissions; this process involves adjusting the cylinders individually to $\lambda = 1$. Extremely high demands must be place on the dynamic response of the lambda sensor in order to obtain the lambda values for the individual cylinders from a measured lambda signal.

▶ Ozone and smog

Exposure to the sun's radiation splits nitrogen-dioxide molecules (NO_2). The products are nitrogen oxide (NO) and atomic oxygen (O), which combine with the ambient air's molecular oxygen (O_2) to form ozone (O_3). Ozone formation is also promoted by volatile organic compounds such as hydrocarbons. This is why higher ozone levels must be anticipated on hot, windless summer days when high levels of air pollution are present.

In naturally occurring concentrations, ozone is essential for human life. However, in higher concentrations it leads to coughing, irritation of the throat and sinuses, and burning eyes. It adversely affects lung function, reducing performance potential.

There is no direct contact or mutual movement between the undesirable ozone formed at ground level, and the stratospheric ozone that reduces the amount of ultraviolet radiation from the sun.

Smog can be created in winter in response to atmospheric layer inversions and low wind speeds. The temperature inversion in the air layers prevents the heavier, colder air containing the higher pollutant concentrations from rising and dispersing.

Smog leads to irritation of the mucous membranes, eyes, and respiratory system. It can also impair visibility. This last factor explains the origin of the term smog, which is a contraction of the words "smoke" and "fog".