# Exhaust emissions

**The past few years have witnessed a drastic reduction in pollutant emissions from motor vehicles through the application of technical measures. In the case of passenger cars with gasoline engines, a significant role has been played by vehicles equipped with three-way catalytic converters.**

Figure 1 illustrates the decrease in annual emissions from passenger cars. Only $CO_2$ experienced no significant decrease, and this is explained by the fact that $CO_2$ emissions are proportional to fuel consumption. It is therefore only possible to lower these emissions by reducing fuel consumption or by using lower-carbon fuels, such as natural gas.

The percentage contribution by motor vehicles to the total emissions generated by industry, traffic, households and power stations varies for the different substances and is as follows [1])

- 52 % for nitrous oxides
- 48 % for carbon monoxide
- 19 % for carbon dioxide
- 18 % for non-methane volatile hydrocarbons

## Combustion of the air/fuel mixture

If a pure fuel were to be fully combusted under ideal conditions with sufficient oxygen, only water vapor ($H_2O$) and carbon dioxide ($CO_2$) would be created according to the following chemical reaction:

$$n_1C_XH_Y + m_1O_2 \rightarrow n_2H_2O + m_2CO_2$$

Because of the non-ideal combustion conditions in the combustion chamber (e.g., unvaporized fuel droplets) and the other constituents of fuel (e.g., sulfur), sometimes toxic by-products are also produced in addition to water and carbon dioxide in the combustion process.

The production of by-products is being increasingly reduced by procedures for optimizing combustion and improving fuel quality. The amount of $CO_2$ produced, however, is entirely dependent on the carbon content of fuel even under ideal conditions and can therefore not be influenced by combustion management.

1 Consumption and emissions from passenger cars (gasoline and diesel)

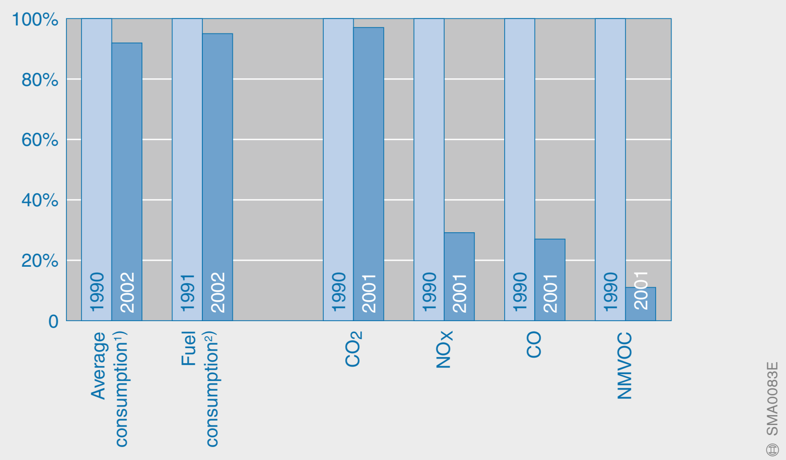

**Fig. 1**

$CO_2$: Carbon dioxide
$NO_X$: Nitrous oxides
CO: Carbon monoxide
NMVOC: Non-methane volatile hydrocarbons

[1] Average fuel consumption, passenger car (liter/distance)
[2] Absolute fuel consumption in passenger-car traffic

Source: German Federal Environment Agency

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1) Provisional figures for 2001

Source: German Federal Environment Agency

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## Main constituents of exhaust gas

### Water ($H_2O$)

The hydrogen chemically bound within the fuel burns with the oxygen in the air to form water vapor, most of which condenses as it cools. This is the source of the exhaust plume visible on cold days. Water makes up about 13 % of the exhaust gas.

### Carbon dioxide ($CO_2$)

During combustion, the carbon chemically bound within the fuel produces carbon dioxide ($CO_2$), which makes up approximately 14 % of the exhaust gas.

Carbon dioxide is a colorless, odorless, non-toxic gas and occurs naturally in the atmosphere. It is not classed as a pollutant with regard to motor-vehicle exhaust emissions. However, it is one of the substances responsible for the greenhouse effect and the global climate change that this causes. Since industrialization, the $CO_2$ content in the atmosphere has risen by roughly 30 % to today's figure of 367 ppm. Reducing $CO_2$ emissions by reducing fuel consumption is therefore seen more and more as a matter of urgency.

### Nitrogen ($N_2$)

Nitrogen makes up 78 % of air and is therefore its primary constituent. It plays virtually no part in the combustion process and at roughly 71 % makes up the majority of the exhaust gas.

**2** Composition of exhaust gas (untreated emission) from gasoline engines during operation at $\lambda = 1$

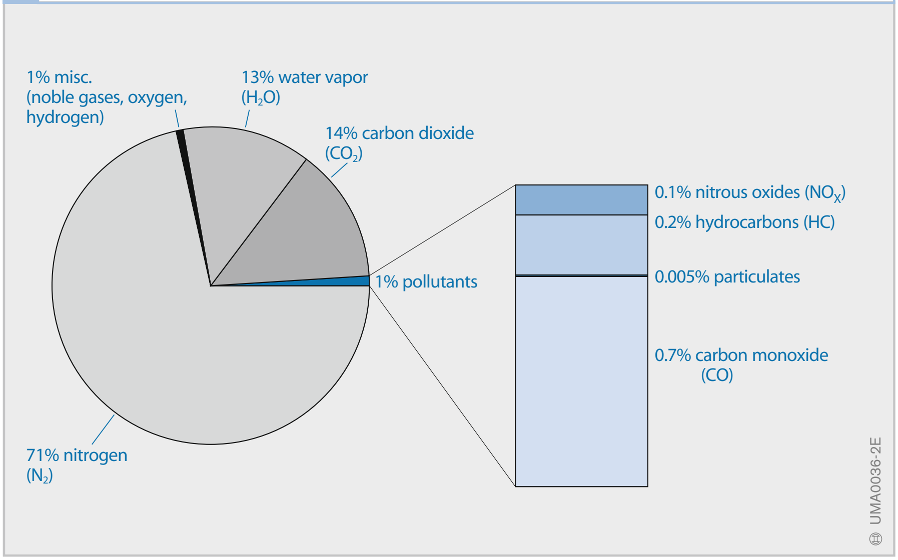


**Fig. 2**
Data in percent by volume

Actual concentrations of exhaust-gas constituents, especially pollutants, can vary in response to engine operating conditions, environmental factors (e.g., atmospheric humidity) and other parameters

## Pollutants

During combustion, the air-fuel mixture generates a number of by-products. With the engine warmed to its normal operating temperature and running with a stoichiometric mixture composition ($\lambda = 1$), the proportion of these by-products in the engine's untreated emissions (exhaust gas after combustion, but before treatment) is about 1 % of the total exhaust-gas quantity.
The most significant of these combustion by-products are

- Carbon monoxide (CO)
- Hydrocarbons (HC), and
- Nitrous oxides ($NO_X$)

With the engine at normal operating temperature, catalytic converters can convert these pollutants at a rate of more than 99 % into harmless substances.

### Carbon monoxide (CO)

Carbon monoxide results from incomplete combustion of rich air/fuel mixtures due to an air deficiency. Although carbon monoxide is also produced during operation with excess air, the concentrations are minimal, and stem from rich zones in the unhomogeneous air/fuel mixture. Fuel droplets that fail to vaporize form pockets of rich mixture that do not combust completely.

Carbon monoxide is a colorless and odorless gas. In humans, it inhibits the ability of the blood to absorb oxygen, thus leading to poisoning.

### Hydrocarbons (HC)

Hydrocarbons are the chemical compounds of carbon (C) and hydrogen (H). HC emissions are caused by incomplete combustion of the air/fuel mixture where there is an oxygen deficiency. The combustion process also produces new hydrocarbon compounds not initially present in the original fuel (e.g., through the separation of extended molecular chains).

Aliphatic hydrocarbons (alkanes, alkenes, alkines, and their cyclic derivatives) are virtually odorless. Cyclic aromatic hydrocarbons (such as benzene, toluene, and polycyclic hydrocarbons) emit a discernible odor.

Some hydrocarbons are considered to be carcinogenic in the event of long-term exposure. Partially oxidized hydrocarbons (e.g., aldehydes, ketones) emit an unpleasant odor. The chemical products that result when these substances are exposed to sunlight are also considered to act as carcinogens in the event of extended exposure to specified concentrations.

### Nitrous oxides ($NO_X$)

Nitrous oxide is the generic term for compounds of nitrogen and oxygen. Nitrous oxides are produced during all combustion processes with air as a result of secondary reactions with the nitrogen contained in the air. The main forms found in the exhaust gases from internal-combustion engines are nitrogen oxide (NO) and nitrogen dioxide ($NO_2$), with dinitrogen monoxide ($N_2O$) also present in small concentrations.

Nitrogen oxide (NO) is colorless and odorless and is slowly converted in air into nitrogen dioxide ($NO_2$). Pure $NO_2$ is a toxic, reddish-brown gas with pungent odor. $NO_2$ can induce irritation of the mucous membranes when present in the concentrations found in heavily polluted air.

Nitrous oxides play their part in damaging woods and forests (acid rain) and creating smog.

### Sulfur dioxide ($SO_2$)

Sulfur compounds in exhaust gases – primarily sulfur dioxide – are produced by the sulfur content in fuels. $SO_2$ emissions are caused only to a small extent by motor vehicles and are not restricted by emission-control legislation.

Nevertheless, the production of sulfur compounds must be avoided to the greatest possible extent, since $SO_2$ sticks to catalytic converters (Three-Way Catalysts, TWC, $NO_X$

accumulator-type catalysts) and poisons them, i.e., reduces their reaction capability.

Like nitrous oxides, $SO_2$ contributes to the creation of acid rain, because it can be converted in the atmosphere or after settling into sulfuric or nitric acid.

## Particulates

Solids are created in the form of particulates as a result of incomplete combustion. While exhaust composition varies as a function of combustion process and engine operating condition, these particulates basically consist of chains of carbon particles (soot) with an extremely extended specific surface ratio. Uncombusted and partly combusted hydrocarbons form deposits on the soot, where they are joined by aldehydes, with their overpowering odor. Aerosol components (minutely dispersed solids or fluids in gases) and sulfates bond to the soot. The sulfates result from the sulfur content in the fuel.

The problem of solids (particulates) in exhaust gas is primarily associated with diesel engines. Levels of particulate emissions from gasoline engines are negligible.

### Greenhouse effect

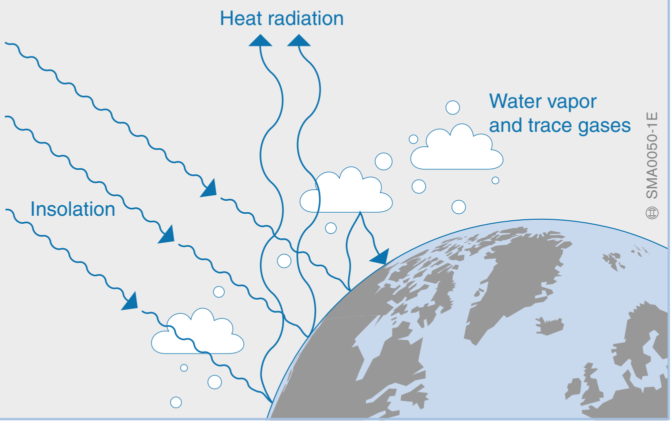
Short-wave solar radiation penetrates the Earth's atmosphere and continues to the ground, where it is absorbed. This process promotes warming in the ground, which then radiates long-wave heat, or infrared energy. A portion of this radiation is reflected by the atmosphere, causing the Earth to warm.

Without this natural greenhouse effect the Earth would be an inhospitable planet with an average temperature of – 18 °C. Greenhouse gases within the atmosphere (water vapor, carbon dioxide, methane, ozone, dinitrogen oxide, aerosols and particulate mist) raise average temperatures to approximately + 15 °C. Water vapor, in particular, retains substantial amounts of heat.

Carbon dioxide has risen substantially since the dawn of the industrial age more than 100 years ago an. The primary cause of this increase has been the burning of coal and petroleum products. In this process, the carbon bound in the fuels is released in the form of carbon dioxide.

The processes that influence the greenhouse effect within the Earth's atmosphere are extremely complex. While some scientists maintain that anthropogenic emissions (i.e., caused by humans) are the primary cause of climate change, this theory is challenged by other experts, who believe that the warming of the Earth's atmosphere is being caused by increased solar activity.

There is, however, a large degree of unanimity in calling for reductions in energy use to lower carbon-dioxide emissions and combat the greenhouse effect.



## Factors affecting untreated emissions

The primary by-products when the air/fuel mixture is combusted are the pollutants $NO_X$, CO and HC. The quantities of these pollutants present in untreated exhaust gases (post-combustion gases prior to exhaust treatment) display major variations in response to different kinds of engine operation. The excess-air factor $\lambda$ and the moment of ignition have a crucial influence on the formation of pollutants.

The catalytic-converter system converts pollutants to the greatest possible extent so that the emissions discharged by the vehicle to atmosphere are far lower than the untreated emissions. In order to minimize the discharged pollutants for tenable exhaust-gas treatment, it is essential however to keep untreated emissions as low as possible.

### Influencing factors

#### Air/fuel ratio

Another primary factor defining the engine's toxic emissions is the air/fuel ratio (excess-air factor $\lambda$). To obtain maximum emissions reductions from three-way catalytic converters, manifold-injection engines run on a stoichiometric air/fuel mixture ($\lambda = 1$) in most operating ranges.

Engines with gasoline direct injection engines can be operated in stratified-charge or homogeneous mode, with selection varying according to the engine operating point. In homogeneous mode, the system injects fuel during the intake stroke to produce conditions comparable to those encountered with manifold injection. The system reverts to this mode of operation in response to demand for high torque and at high engine speeds. In this operating mode, the set excess-air factor is usually equal to or in the immediate vicinity of $\lambda = 1$.

The fuel is not distributed evenly throughout the entire combustion chamber during stratified-charge operation. The desired effect is achieved by waiting until the compression stroke to inject the fuel. The mixture cloud formed at the center of the combustion chamber should be as homogeneous as possible, with an excess-air factor of $\lambda = 1$. Virtually pure air or an extremely lean mixture is present in the extremities of the combustion chamber. This results in an overall ratio of $\lambda > 1$ (lean) for the entire combustion chamber.

#### Mixture formation

In the interests of optimal combustion efficiency, the fuel destined for combustion should be thoroughly dispersed to form the most homogeneous mixture possible with the air. In manifold-injection engines, this refers to the overall combustion chamber, while in engines with gasoline direct injection this refers only to the stratified-charge cloud in the center of the combustion chamber.

Consistent distribution of uniform mixture to all cylinders is important for low pollutant emissions. Fuel-injection systems that employ their intake manifolds exclusively to transport air ensure consistent mixture distribution by discharging fuel into the intake port directly in front of the intake valve (manifold injection) or directly into the combustion chamber (gasoline direct injection). This type of consistency is less certain with systems relying on carburetors and single-point injection, as fuel tends to condense on the walls of the individual intake runners.

#### Engine speed

Higher engine speeds lead to greater friction losses within the engine as well as increased power consumption by auxiliary systems (e.g., water pump). Under these conditions, the power output per consumed unit of energy decreases. The engine's operating efficiency falls as engine speed rises.

Generating a given level of power at high engine speed equates with a higher level of fuel consumption than producing the same output at a lower engine speed. This leads to higher levels of pollutant emissions.

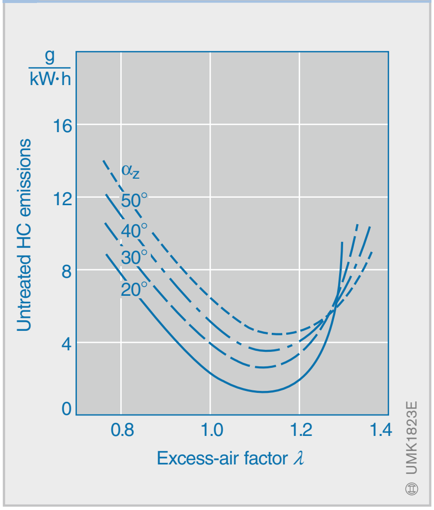
### Engine load

The engine load or the generated engine torque has different effects on the pollutant components carbon monoxide (CO), unburnt hydrocarbons (HC) and nitrous oxides ($NO_X$). The various influences are described in more detail below.

### Moment of ignition

The ignition of the air/fuel mixture, i.e., the period of time between flashover and the formation of a stable flame front, is of decisive significance to the combustion sequence. The character of the ignition process is shaped by the timing of the flashover, the ignition energy, and the composition of the mixture at spark plug. A large quantity of ignition energy translates into stable ignition with positive effects, both on the consistency of the consecutive combustion cycles and the composition of the exhaust gases.

1 Untreated HC emissions as a function of excess-air factor $\lambda$ and ignition angle $\alpha_Z$



## Untreated HC emissions

### The influence of torque

The temperature in the combustion chamber rises as torque increases. The depth of the zone in which the flame is extinguished close to the combustion-chamber wall as a result of low temperatures therefore shrinks as torque rises. Fewer unburnt hydrocarbons are then produced on account of more complete combustion.

In addition, the high exhaust-gas temperatures that accompany higher combustion-chamber temperatures under high-torque operation promote secondary reactions in the unburned hydrocarbons during the expansion and push-out phases to produce $CO_2$ and water. Because high-torque operation equates with higher temperatures in combustion chambers and exhaust gases, it leads to reductions in quantities of unburnt hydrocarbons relative to units of power generated.

### The influence of the air/fuel ratio

The HC emissions from a gasoline engine increase as engine speeds rises, because the time available for preparing and combusting the mixture becomes shorter.

### The influence of the air/fuel ratio

During operation with an air deficiency ($\lambda < 1$), incomplete combustion leads to the formation of unburnt hydrocarbons. Richer mixtures produce progressively greater HC concentrations (Fig. 1). In the rich range, therefore, HC emissions increase as the excess-air factor $\lambda$ decreases.

HC emissions also increase in the lean range ($\lambda > 1$). Minimum HC generation coincides with the range $\lambda = 1.1...1.2$. The rise within the lean range is caused by incomplete combustion at the extremities of the combustion chamber. Extremely lean mixtures, where combustion lag can ultimately lead to ignition miss, aggravate this effect and produce a dramatic rise in HC emissions. This phenomenon is caused by unequal mixture distribution in the combustion chamber and thus poor ignition conditions in lean combustion-chamber zones.

The gasoline-engine's lean-burn limit is primarily dependent on the excess-air factor at the spark plug at the instant of ignition, and by the composite excess-air factor (air/fuel ration considered over the entire combustion chamber). The flow pattern of the charge in the combustion chamber can be manipulated to obtain a more homogeneous mixture to ensure more reliable ignition, while at the same time accelerating propagation of the flame front.

The stratified-charge method used in conjunction with gasoline direct injection presents a contrasting picture. Instead of focusing on obtaining a homogeneous air/fuel mixture throughout the combustion chamber, this concept creates a highly ignitable mixture only in the area immediately adjacent to the tip of the spark plug. This concept thus allows substantially higher composite excess-air factors than would be available using a homogeneous mixture. HC emissions in stratified-charge mode are essentially determined by the mixture formation process.

It is vital in the case of direct injection wherever possible to avoid depositing liquid fuel on the combustion-chamber walls and the piston, as the resulting wall-applied film usually fails to combust completely, leading to high HC emissions.

### The influence of the moment of ignition

Increasing the ignition advance (high $\alpha_Z$) produces a rise in emissions of unburnt hydrocarbons, as the resulting reduction in exhaust-gas temperature has a negative effect on secondary reactions in the expansion and exhaust phases (Fig. 1). It is only during operation with extremely lean mixtures that this response pattern is inverted. These types of lean mixtures result in such a low flame-front propagation rate that the combustion process will still be in progress when the exhaust valve opens if ignition is late. With late ignition, the engine reaches its lean-burn limit early, at an excess-air factor of $\lambda$.

## Untreated CO emissions

### The influence of torque

As with untreated HC emissions, the higher process temperatures that accompany high torque foster secondary reactions in CO during the expansion phase. The CO oxidizes to form $CO_2$.

### The influence of engine speed

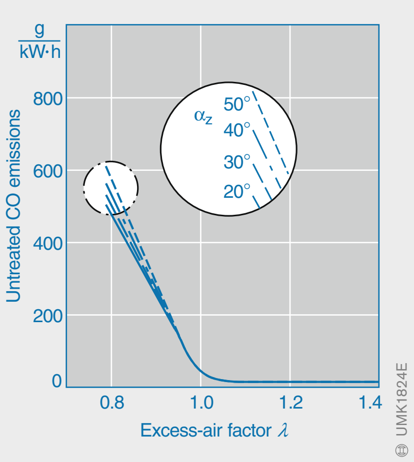
CO emissions also mirror the pattern of HC emissions in their response to variations in engine speed.

### The influence of the air/fuel ratio

In the rich range, CO emissions display a virtually linear correlation with the excess-air factor (Fig. 2). This is the result of the incomplete carbon oxidation during operation with an air deficiency.

In the lean range (excess surplus), CO emissions remain at extremely low levels, and the influence of changes in the excess-air factor is minimal. Under these conditions, the only source of CO generation is incomplete combustion of a poorly homogenized air/fuel mixture.

**2** Untreated CO emissions as a function of excess-air factor $\lambda$ and ignition angle $\alpha_Z$



### The influence of the moment of ignition

The moment of ignition has virtually no influence on CO emissions (Fig. 2), which are almost entirely a function of the excess-air factor $\lambda$.

## Untreated $NO_X$ emissions

### The influence of torque

The higher combustion-chamber temperatures that accompany increased torque generation promote the formation of $NO_X$. As torque output rises, untreated $NO_X$ emissions display a disproportionate increase.

### The influence of engine speed

As the response time available to form $NO_X$ is shorter at higher engine speeds, $NO_X$ emissions decrease as engine speed increases. In addition, the residual-gas content in the combustion chamber must be considered since it causes lower peak temperatures. Because this residual-gas content tends to fall off as engine speed rises, this effect counteracts the response pattern described above.

### The influence of the air/fuel ratio

The maximum level of $NO_X$ emissions lies with slight excess air in the range of $\lambda = 1.05...1.1$. In the lean and rich ranges, $NO_X$ emissions drop, since the peak combustion temperatures decrease.

A characteristic of stratified-charge operation in engines with gasoline direct injection is a high excess-air factor. The $NO_X$ emissions are low when compared with the operating point at $\lambda = 1$, since only some of the gas takes part in the combustion process.

### The influence of the moment of ignition

Throughout the range with excess-air factors of $\lambda$, $NO_X$ emissions rise as ignition advance is increased (Fig. 3). The higher combustion temperatures promoted by earlier ignition timing not only shift the chemical equilibrium toward greater $NO_X$ formation, but – most significantly – they also accelerate the speed at which this formation takes place.

## Soot emissions

Gasoline engines produce only extremely low soot emissions during operation on mixtures in the vicinity of stoichiometric. However, soot can be generated in engines with gasoline direct injection during stratified-charge operation, when its formation can be fostered by localized areas with extremely rich mixtures or even fuel droplets. To ensure that adequate time remains available for efficient mixture formation, operation in stratified-charge mode must therefore be restricted to low and moderate engine speeds.

**3** Untreated $NO_X$ emissions as a function of excess-air factor $\lambda$ and ignition angle $\alpha_Z$