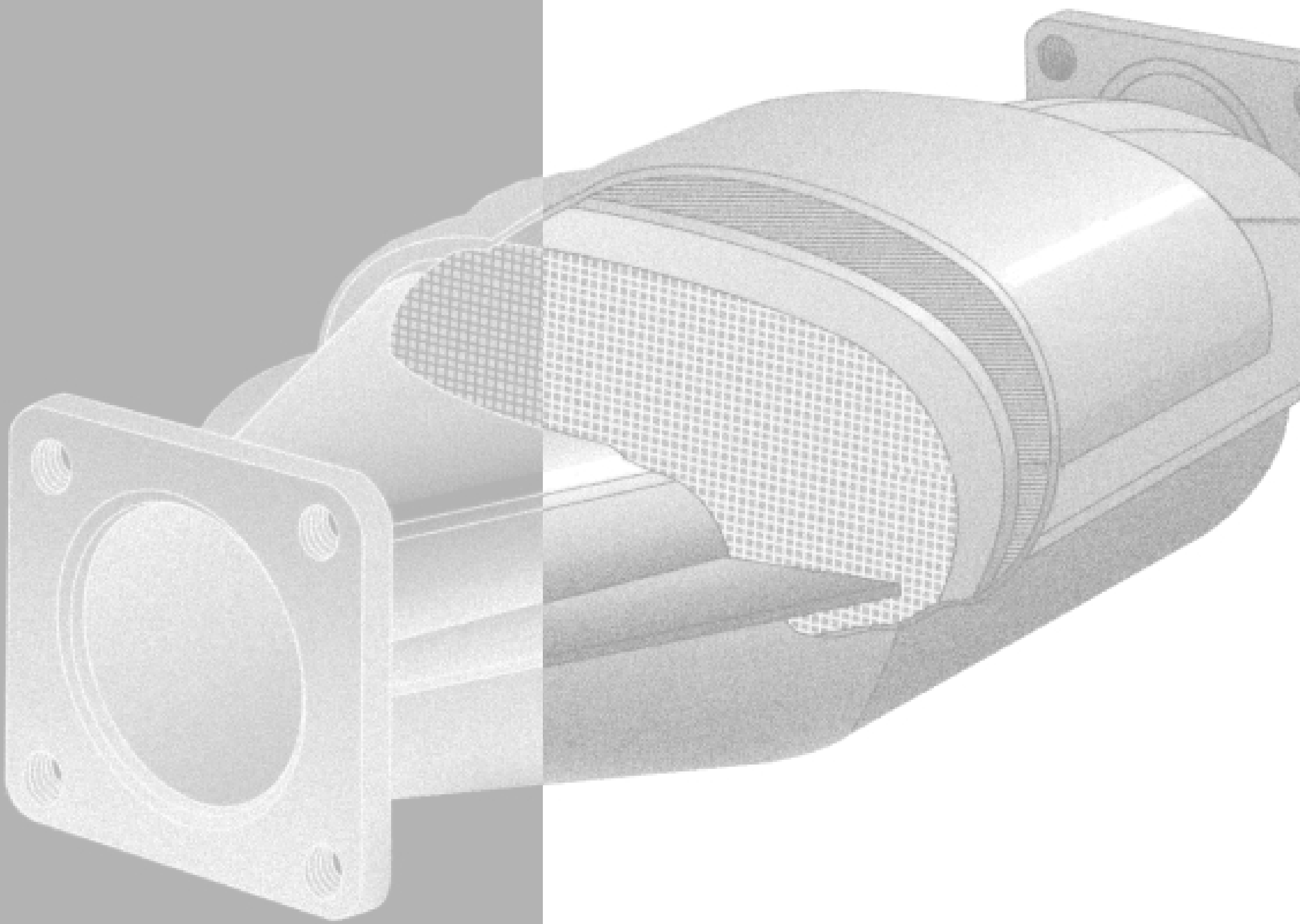
ACEA

# ACEA data of the sulphur effect on advanced emission control technologies



REPORT JULY 2000

# ACEA DATA OF THE SULPHUR EFFECT ON ADVANCED EMISSION CONTROL TECHNOLOGIES

July 2000


## Abstract

The European vehicle manufacturers have collected their most recent in-house data demonstrating the effect of sulphur on advanced emission control technologies. The purpose is to respond to the "mini-review" launched by the European Commission. The objective of the review is to provide evidence for a proposal to amend, if appropriate, the current legislation concerning the sulphur content of gasoline and diesel fuels.

The collected data is mainly related to the advantage of a sulphur content below 50 ppm and in particular to the benefit of sulphur-free fuels.



## Acknowledgement

ACEA gratefully acknowledges the contribution of the individual companies to this report, and in particular acknowledges Volkswagen for its considerable efforts in preparing this report.


ACEA

*ACEA is the association of European automobile manufacturers. Its members include the following passenger car manufacturers: BMW, DaimlerChrysler, FIAT, Ford, GM, Porsche, PSA Peugeot Citroen, Renault, Volkswagen, Volvo.*




Brussels 2000

ACEA

# EXECUTIVE SUMMARY

## ACEA Data of the Sulphur Effect on Advanced Emission Control Technologies

### Background

In the EU the specifications of gasoline and diesel fuels are described in Directive 98/70/EC, which from the 1st January 2005 fixes at 50 ppm the maximum content of sulphur in both gasoline and diesel fuels. On this date also, all new types of vehicles must comply with the EURO 4 emissions limits, and the following year this applies to all new vehicles. The technological development of automotive engines and emission abatement technologies required to meet these emissions limits have indicated the need to further reduce the sulphur in fuels. Therefore, in May 2000 the Commission launched a “Call for Evidence” regarding the appropriate level for the sulphur content of gasoline and diesel fuel used in the Community.

### Scope and Objective of the paper

In order to provide a contribution from the European car and truck manufacturers to the consultation of the Commission on the need to reduce the sulphur content of fuels below 50 ppm, ACEA has asked its members to provide their most recent results on the effect of sulphur on advanced emission control technologies.

The process within ACEA has been based on contributions from the ACEA members. There has not been any collaboration on the type of technologies, nor on the design of the experiments to investigate the sulphur effects.

Consequently, a certain degree of heterogeneity in the collected data can be seen due to the different approaches of the individual manufacturers. Most of the collected data are part of broader projects and have been already published or presented in technical conferences.

The contribution of ACEA members to this paper does not prevent individual manufacturers from providing their additional individual responses to the Commission’s consultation.

## Summary of the results

Data was received from Audi, BMW, DaimlerChrysler, FIAT, Ford, GM Europe, Iveco, MAN, PSA Peugeot Citroen, Renault, Volkswagen and Volvo Trucks.

Although it is not possible to identify exactly the after-treatment technologies that will be adopted to attain future emission objectives, the most promising seem to be the following:

**Passenger cars and light duty vehicles**

| | |
|---|---|
| Gasoline stoichiometric | Three-way catalysts (TWC) |
| Gasoline lean burn | $NO_x$ storage catalysts |
| Diesel | Diesel $NO_x$ storage catalysts or SCR systems and Continuously Regenerative Traps (CRT) or Diesel Particulate Filters (DPF) |

**Heavy duty diesel** Selective Catalyst Reduction (SCR) systems
Continuously Regenerative Traps (CRT)

All of these technologies will benefit from sulphur-free fuels.

Two of them, diesel $NO_x$ storage catalysts and Continuously Regenerative Traps (CRT), can function properly only when operated with sulphur-free diesel. These two technologies are essential to comply with the EURO 4 exhaust emission standards for both diesel passenger cars and commercial vehicles.

Due to the sulphur sensitivity of gasoline $NO_x$ storage catalysts, the full potential of gasoline lean burn engines, in terms of fuel efficiency, cannot be exploited unless operated with sulphur-free gasoline (less than 10 ppm sulphur content).

Preliminary results evaluate the fuel consumption reduction attainable by reducing sulphur in gasoline from 50 ppm to 10 ppm to be in the range of 3% to 5%, due to the consequently available advanced catalyst materials.

## Conclusion

Sulphur-free fuels will permit the application of the emission abatement technologies needed to comply with future exhaust emission standards, in particular for lean burn engines.

To summarise, without a reduction of sulphur content from 50 to less than 10 ppm in diesel and gasoline the following problems will arise:

1. Gasoline engines:
   Potential reduction of fuel consumption of direct injection engines will not be achieved.
2. Diesel engines
   Emission aftertreatment technologies required to attain EURO 4 emission limits will not be available for all the vehicle ranges
   Fuel consumption will be increased
   Secondary sulphates can be formed as ultrafine particles

For commercial vehicles, sulphur-free fuel is needed in order to meet the EURO 4 and the EURO 5 emission standards. Fuel consumption is also an important competition issue for these vehicles and hence diesel engines are essential.

# Contents

# 1 INTRODUCTION

The present document collects the data made available by the European automotive manufacturers on the effect of sulphur on vehicle emissions and aftertreatment technologies. It is a response to the “Call for Evidence” launched by DG-Environment in May 2000.

The manufacturers affirm that lean burn engines are the most promising technologies that will facilitate attainment of the $CO_2$ reduction commitment of ACEA and that lean burn engines, both gasoline and diesel, need new aftertreatment technologies to meet the future exhaust emission requirements.

This is also valid for heavy duty engines, in fact for commercial vehicles the minimisation of fuel consumption is an absolute priority for customers and hence this factor combined with the exhaust emission limit values established for the years 2005 and 2008 demand the introduction of advanced PM and $NO_x$ aftertreatment technologies that are compatible with low fuel consumption technologies.

The collected data relate to the aftertreatment technologies listed below. These have been identified as the technologies with the most potential to satisfy $CO_2$ commitments and near future exhaust emission legislation.

**Gasoline** technology

- Three-way catalysts (TWC)
- $NO_x$ storage catalysts

**Diesel** technology

- Oxidation catalyst
- $DeNO_x$ passive catalysts
- Diesel $NO_x$ storage catalysts
- Selective Catalyst Reduction (SCR) systems
- Diesel Particulate Filters (DPF)
- Continuously Regenerative Traps (CRT)

# 2 GASOLINE TECHNOLOGIES

## 2.1 THREE-WAY CATALYSTS (TWC)

### Description

Three-way catalysts are designed to reduce CO, HC and $NO_x$ emissions from gasoline engines that run under stoichiometric conditions.

### Sulphur effect

A vast literature exists on the enhancing effect of sulphur reduction on the conversion efficiency of TWCs. Several projects (especially from the US) have quantified the effect of sulphur on the exhaust emissions.

The latest generation of TWC is designed to increase the thermal stability needed for close coupled catalysts. Catalysts made with palladium are thermally more stable than those with platinum (i.e. Palladium/Rhodium and Trimetallic catalyst). However palladium is very sensitive to sulphur.

There is a large difference in the emissions using a gasoline with a sulphur content of 100 ppm and 1 ppm. Figure 1 shows the results from a test programme carried out by Alliance and AIAM in the USA with a fleet of 50 passenger cars and commercial vehicles. The maximum potential for emission reduction is achieved by using 1 ppm sulphur content. $NO_x$ emissions are reduced by 13% when gasoline with 1 ppm is used instead of 30 ppm sulphur.

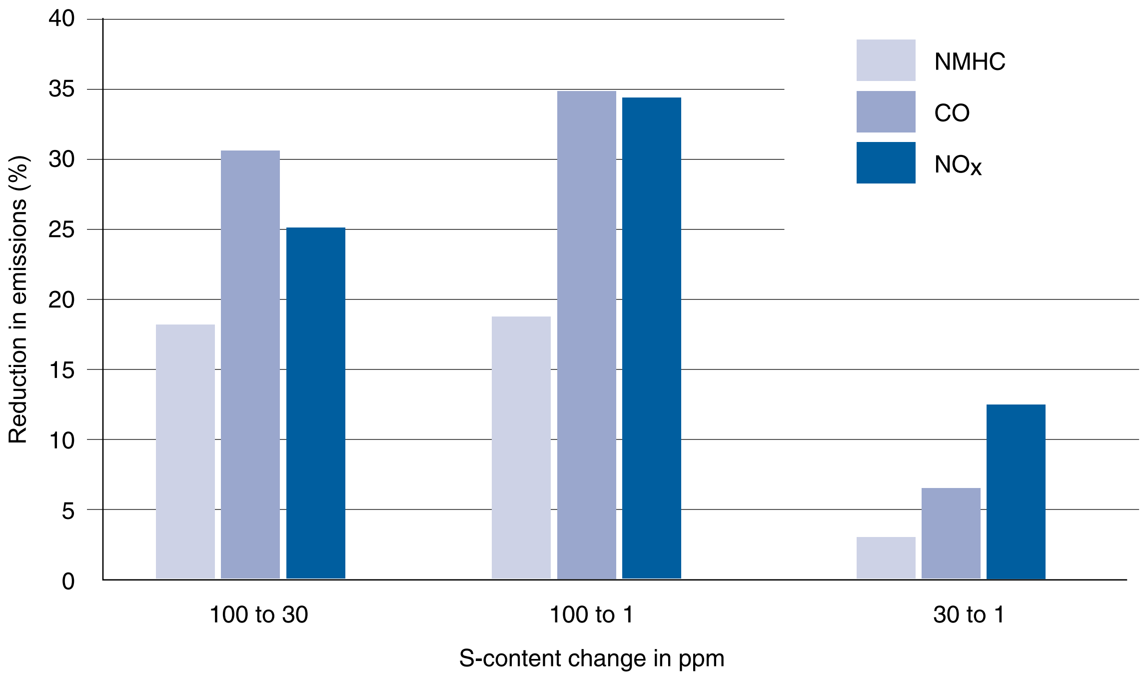



*Figure 1: Sulphur effect on emissions after TWC – US Programmes*

Although the poisoning effect of sulphur of TWCs is considered to be reversible, experimental tests show that the efficiency of the catalyst does not return always to its original state after regenerating for sulphur. Over time this means that the efficiency of the catalyst deteriorates. Figure 2 shows the increasing emissions of a tested vehicle using fuel from 50 ppm up to 600 ppm sulphur. After testing with 600 ppm sulphur, the vehicle was again operated with 50 ppm and the CO emissions did not return to their original level (represented by the dashed line in Figure 2). This shows that the catalyst was irreversibly damaged after one single test with high sulphur fuel.

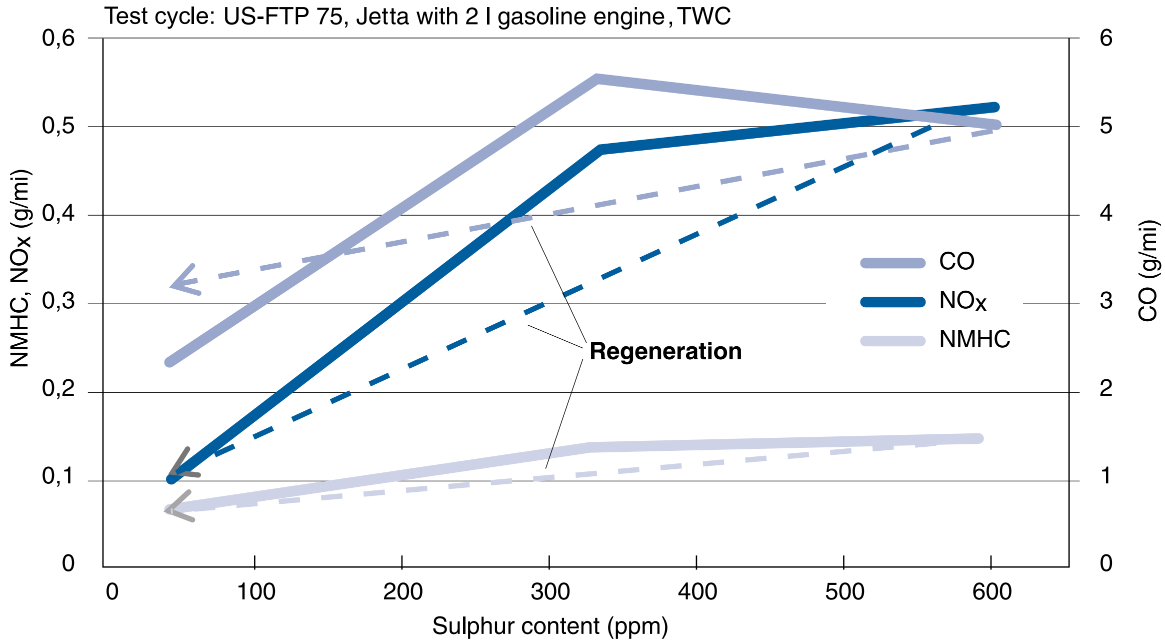



*Figure 2: Influence of sulphur on gasoline emissions – Volkswagen*

Figure 3 demonstrates that, below 450°C the catalyst stores sulphur, whereas above 500°C the catalyst regenerates itself by emitting (as $SO_2$) the previously stored sulphur. The sulphur contained in the gasoline contains penalises the conversion efficiency of the catalyst when working at low temperature.

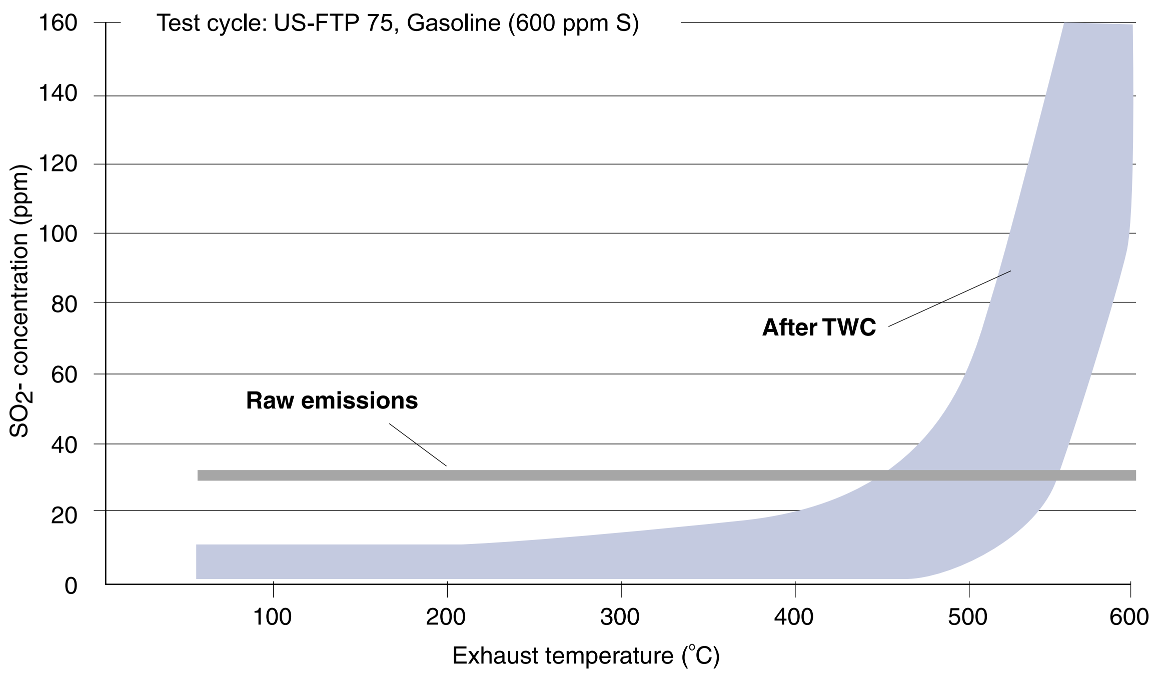



*Figure 3: Sulphur storage and regeneration in a TWC – Volkswagen*

### Prospects

The TWC is the technology used on current gasoline engines. In future it will remain the aftertreatment technology of choice for stoichiometric engines.

The use of stand-alone TWCs will decline when stoichiometric engines are replaced by lean burn engines. However it will still remain in demand as a precatalyst in more advanced systems. Lean burn combustion engines are considered necessary to meet the future targets for $CO_2$ emission reduction.

## 2.2 $NO_X$ STORAGE CATALYSTS

### Description

$NO_x$ storage catalysts or traps typically incorporate basic oxides such as barium oxide into a new catalyst formulation. When the engine runs lean, the NO (nitric oxide) emissions are absorbed by the catalyst to form nitrate. When the Engine Management System evaluates that the catalyst has reached a predetermined $NO_x$ saturation level (below full saturation), it triggers a gasoline-rich excursion that generates carbon monoxide and unburned hydrocarbons. The stored nitrates are decomposed to $NO_2$, which then react with the available reductant (such as CO) over the catalyst to form nitrogen.

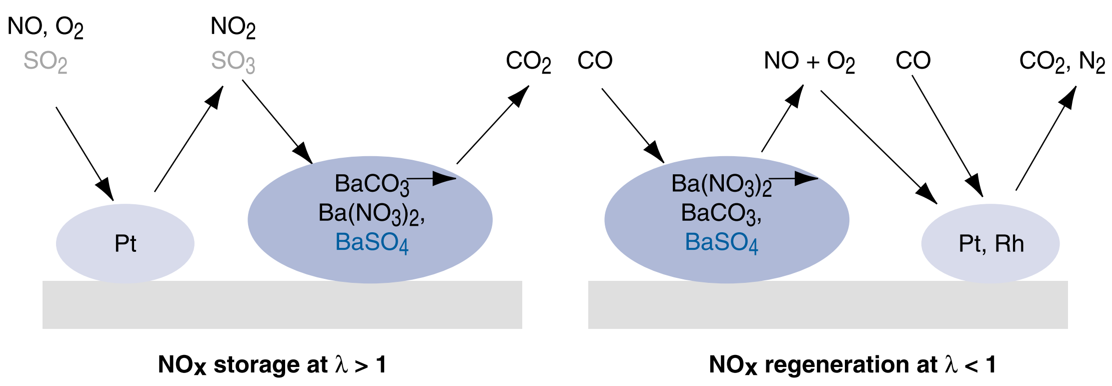



*Figure 4: $NO_x$ and sulphate storage and regeneration of $NO_x$ storage catalysts – Volkswagen*

### Sulphur effect

The sulphur oxides, formed during combustion of fuel containing sulphur, are chemically similar to $NO_x$. They react and are absorbed by the basic oxide to form sulphate and thus competes with the nitric oxides for storage space (Figure 4). The sulphate blocks the $NO_x$ storage, resulting in a loss of efficiency of the catalyst (Figures 5a and 5b). Desulphurisation of the $NO_x$ storage catalyst can only occur at temperatures higher than those required for $NO_x$ conversion (about 650$^o$C), at the expense of some fuel consumption (catalyst heating and fuel enrichment is required during desulphurisation).

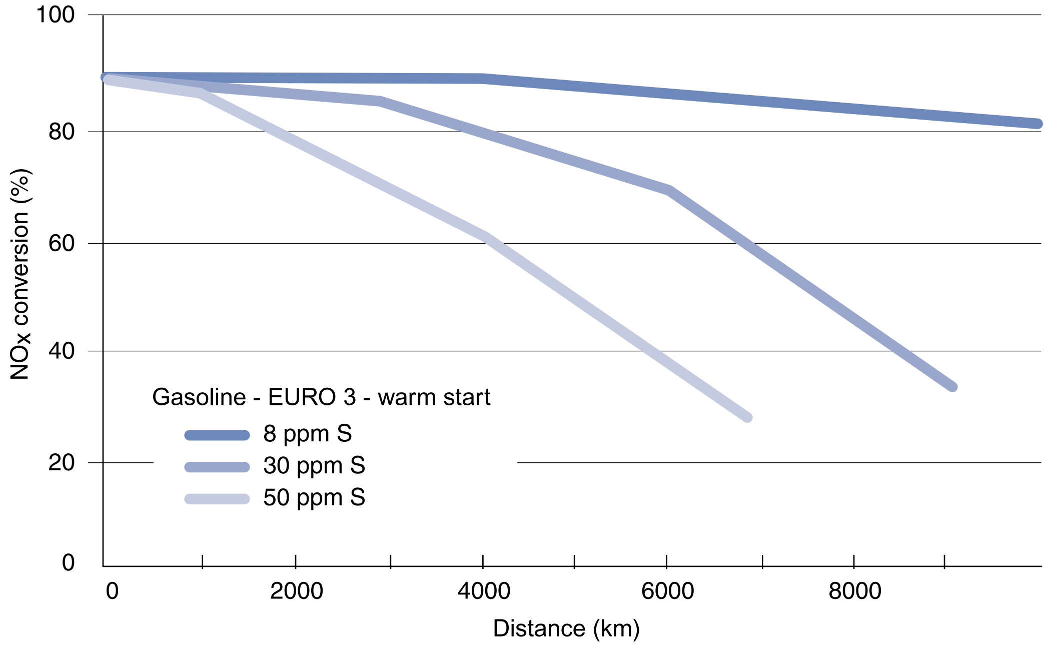



*Figure 5a: The effect of gasoline fuel sulphur content on $NO_x$ storage catalyst conversion efficiencies in an FSI (or GDI) engine – Volkswagen*

After only a few hours the fuel sulphur deteriorates the catalyst to such an extent that the conversion efficiency becomes inadequate. However with sulphur-free gasoline the efficiency remains stable for a longer period or distance as seen in Figures 5a and 5b. In Figure 5a it can be observed that there is even a conversion efficiency deterioration between 30 and 8 ppm gasoline sulphur content.

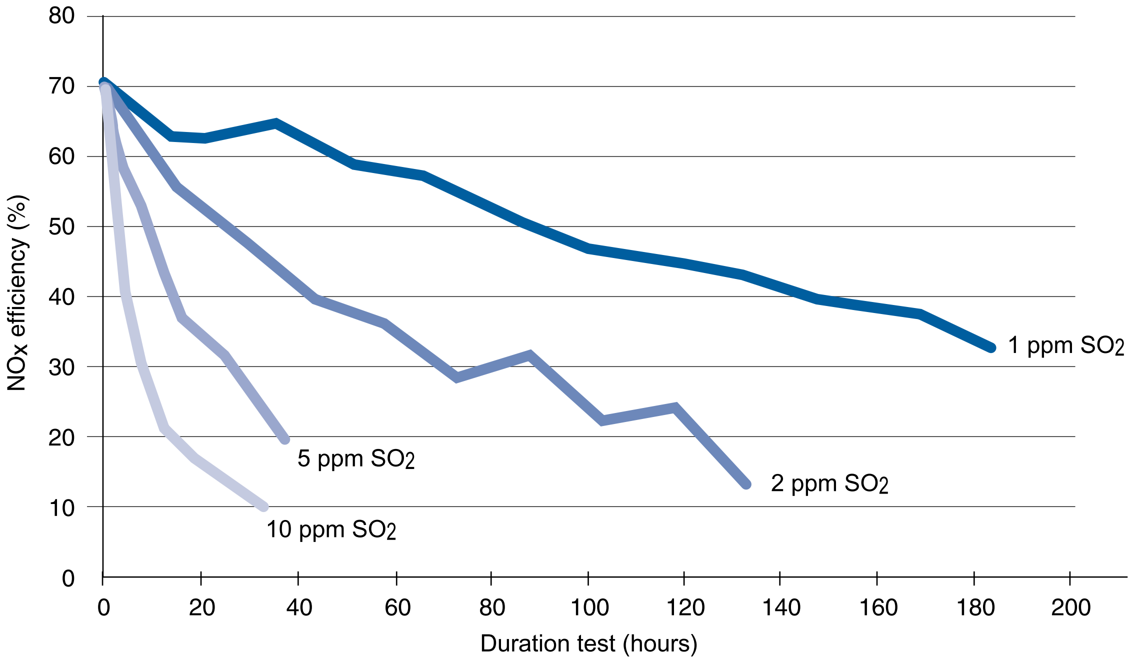



*Figure5b: Impact of sulphur dioxide concentration (1 ppm $SO_2$ = 25 ppm S in fuel) on $NO_x$ storage catalyst, space velocity= $4500h^{-1}$ – Renault*

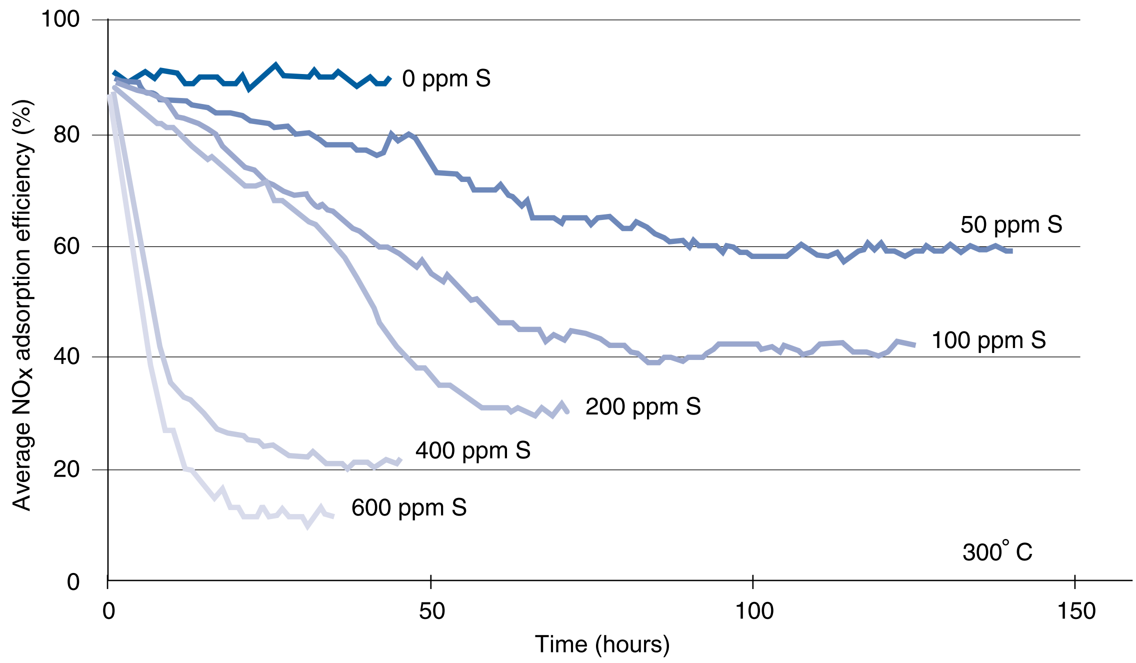



*Figure 6: $NO_x$ storage catalyst conversion efficiency as a function of sulphur content of fuel – Ford*

Sulphur also reduces the durability and mileage of $NO_x$ storage catalysts (Figures 7 & 8). Figure 7 shows that there is a steady increase in the fuel consumption required for desulphurisation as the gasoline sulphur increases. The distance between desulphurisations also drastically differs between gasoline containing 8 ppm and 50 ppm sulphur. Although the data from BMW and DaimlerChrysler show a discrepancy in the distance between desulphurisations for fuel with 50 ppm, it can be seen that the distance to desulphurisation in both cases has disimproved a great deal compared with the distance when run with less than 10 ppm fuel. The difference in values could be caused by dissimilarity in the mode of operation of the two engines where the share of lean burn operation and the regeneration strategies differ. Figure 8 also demonstrates the worsening durability of a $NO_x$ storage trap as the sulphur content of the gasoline increases.

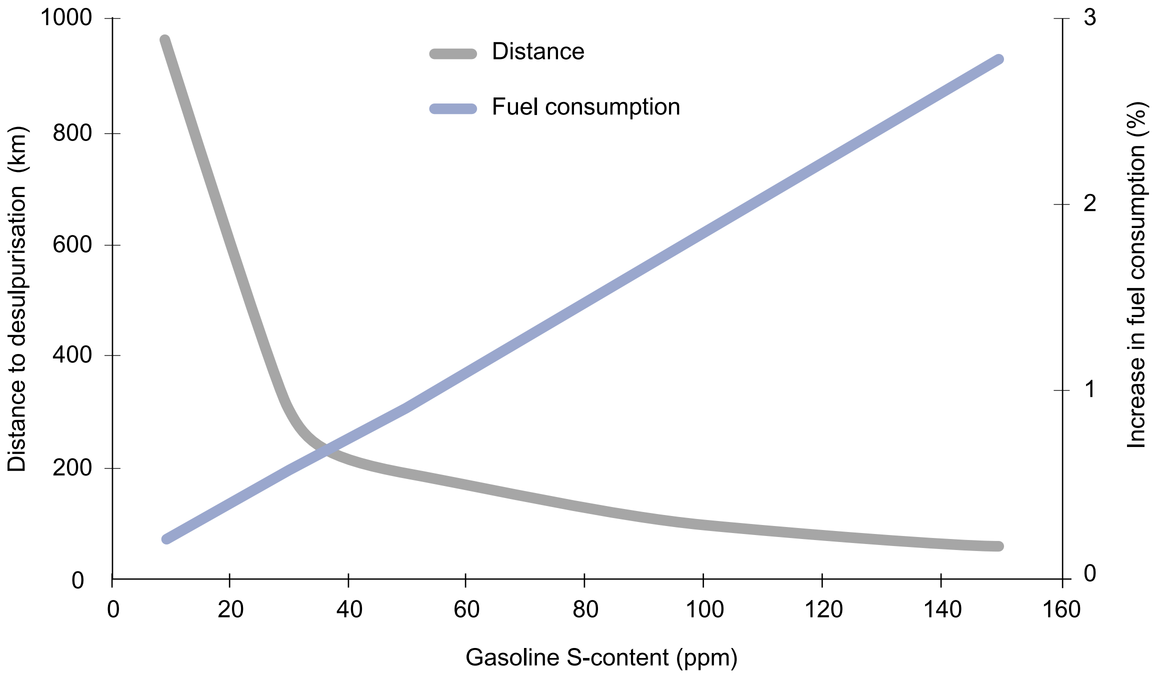



*Figure 7: The effect of fuel sulphur on distance between desulphurisations and hence the effect on fuel consumption – BMW*

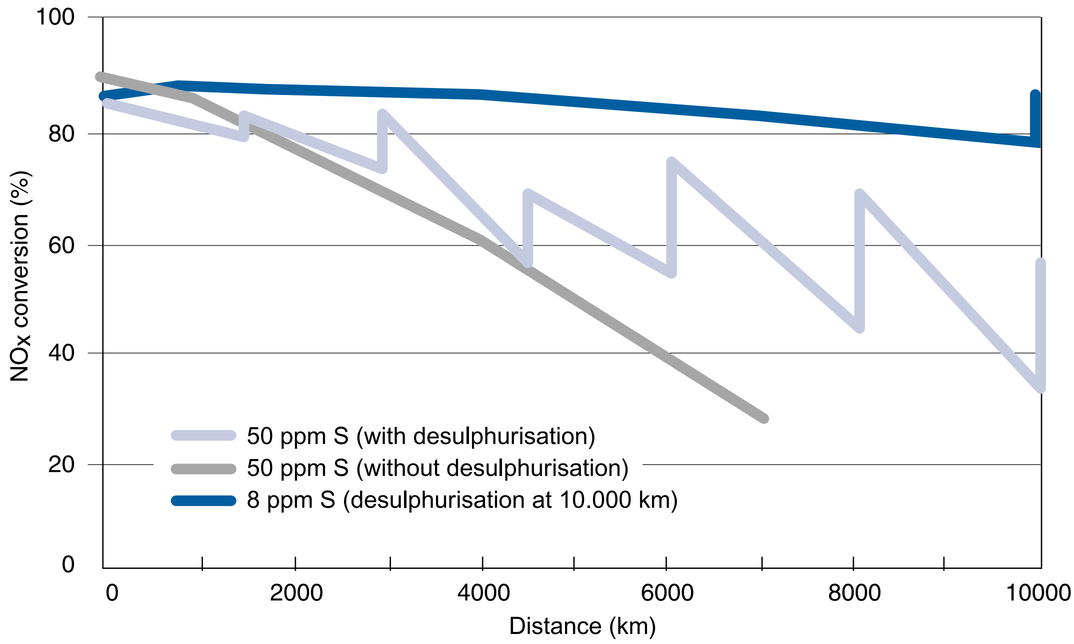



*Figure 8: Endurance test for $NO_x$ storage catalyst as a function of sulphur fuel content – DaimlerChrysler*

Figure 9 shows a further example of the mileage achieved between desulphurisations as a function of the level of sulphur in the gasoline. When the efficiency of the catalyst drops from 95% to 90%, tailpipe $NO_x$ emissions double and desulphurisation occurs. With a fuel containing 0.1 ppm sulphur this occurs after 5000 miles. A fuel containing 160 ppm sulphur, which is approximately the current level in gasoline, only permits a vehicle to travel 115 miles before the catalyst efficiency has dropped by 5%.

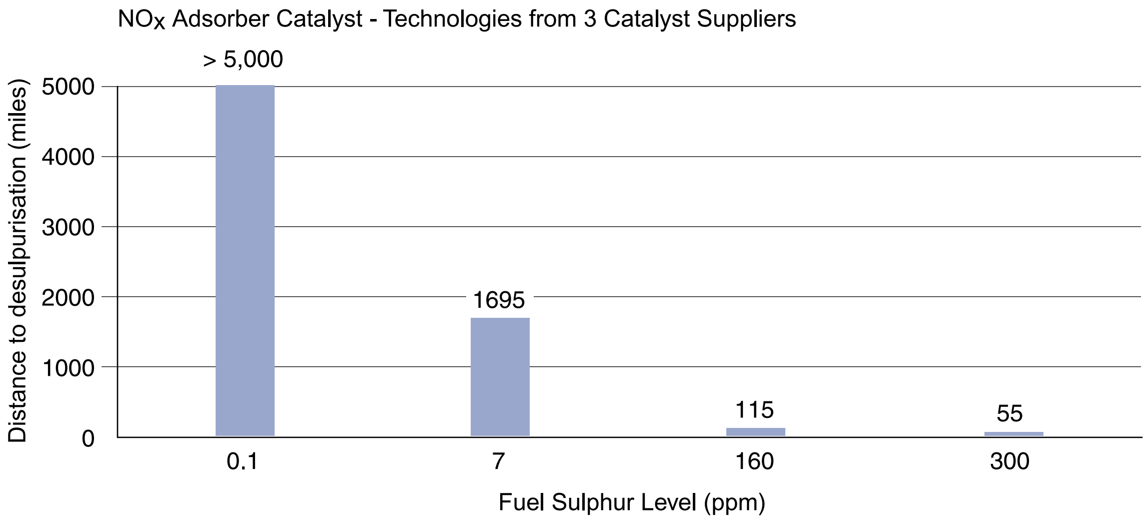



*Figure 9: Distance between desulphurisations that occur at 5% decrease in catalyst efficiency – GM*

Since the presence of sulphur causes more frequent catalyst regeneration, fuel consumption increases accordingly. Sulphur also precludes the use of more efficient catalyst materials, that do not require such frequent regeneration for $NO_x$ but are highly sulphur sensitive.

The availability of sulphur-free gasoline will make possible the development of the next generation of $NO_x$ storage catalysts, which will allow a further improvement in fuel efficiency (3-5% in total compared with current $NO_x$ adsorbers operated with 50 ppm sulphur fuel).

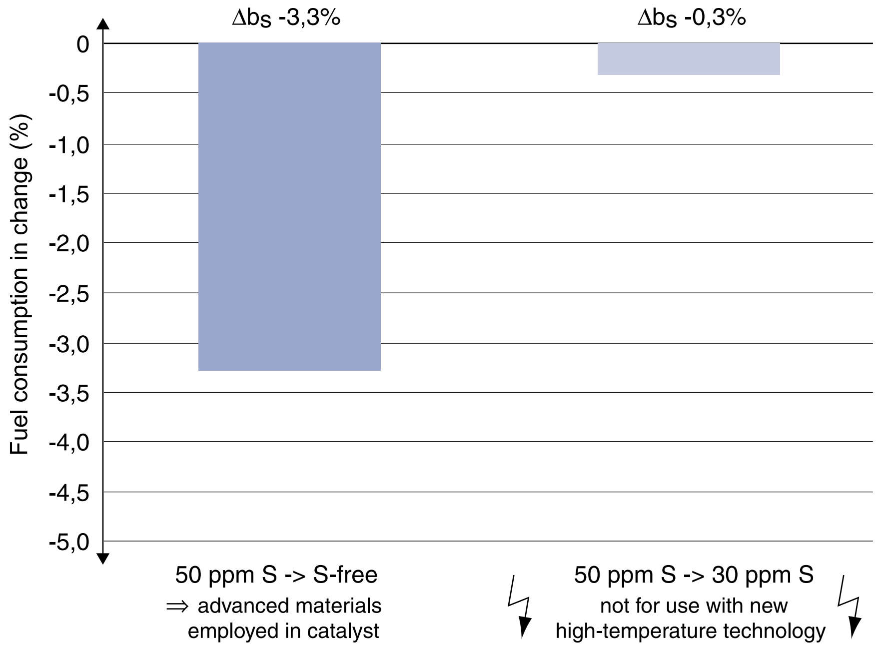



*Figure 10: The improvement in specific fuel consumption (l/100km basis) over a range of fuel sulphur levels – Volkswagen*

## Prospects

$NO_x$ storage catalysts are the most efficient existing lean burn $NO_x$ aftertreatment technology (more than 80% efficiency). They are already on the market in Japan where sulphur-free gasoline is available. In Europe this technology is considered the most promising for gasoline direct injection lean burn engines. Preliminary applications are expected in the next 12 months. Their full potential will not be realised with gasoline containing 50 ppm sulphur, this will only be possible with sulphur-free gasoline.

# 3 DIESEL TECHNOLOGY

## 3.1 OXIDATION CATALYSTS

### Description

Platinum or Palladium based catalysts oxidise CO, HC and PM (SOF) under lean conditions. The carbon fraction of the PM remains unaffected.

### Sulphur effect

Sulphur affects the conversion efficiency of the oxidation catalyst in the same way as it does the TWC. It also causes a delay in the catalyst light-off. In Figure 11 it is seen that when the catalyst is operated with EURO 3 diesel containing 350 ppm sulphur, the temperature for lightoff is 240°C, whereas with Swedish diesel, that contains less than 10 ppm sulphur, the lightoff temperature approaches that of a fresh catalyst at approximately 170°C.

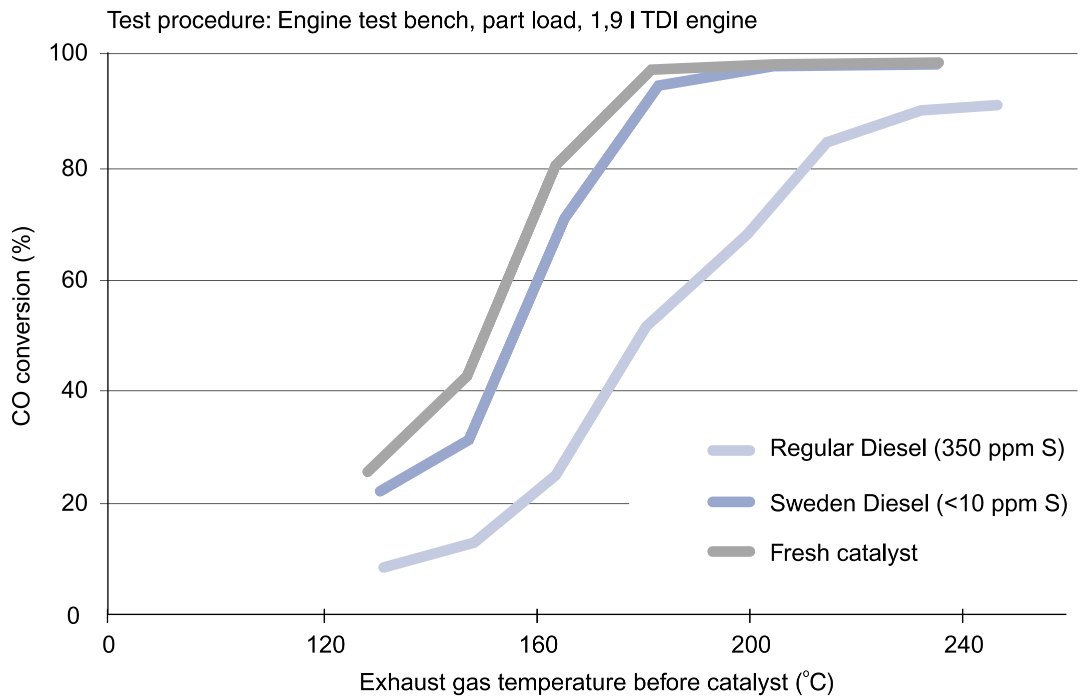



*Figure 11: The effect of diesel sulphur levels on oxidation catalyst efficiency – Volkswagen*

Sulphur is also responsible for secondary PM formation at high temperatures due to $SO_2$ oxidation and sulphate storage. Data from an FEV study shown in Figure 12 illustrates the effect that even a difference between 30 and 10 ppm sulphur diesel content can have on secondary particulate formation. Primary particulate matter emissions remain relatively constant regardless whether 10 or 30 ppm sulphur diesel is used. However the black smoke, or secondary particulates, emitted at low loads, varies between 10 and 30 ppm sulphur content. At 25% load, diesel containing 10 ppm emits 25% less secondary particulates than diesel with 30 ppm sulphur.

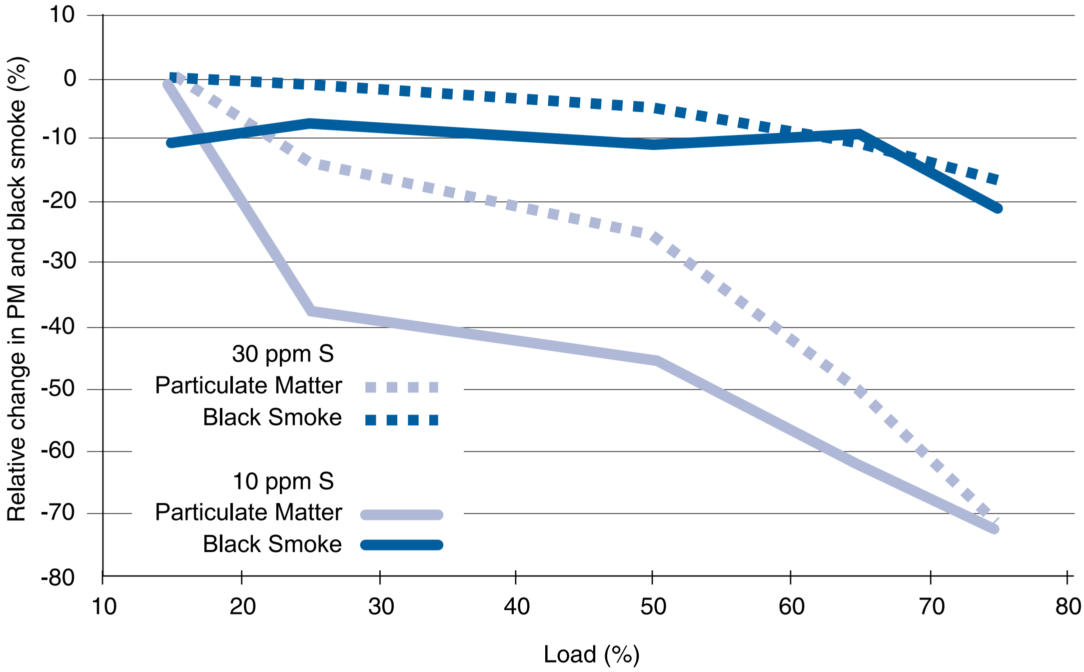



*Figure 12: The influence of the fuel sulphur content on PM and black smoke – FEV study 1999*

## Prospects

This technology is currently used in diesel passenger cars and light duty commercial vehicles. The use of stand alone oxidation catalysts is expected to decline when the EURO 4 exhaust emission regulations enter into force. To comply with EURO 4 regulations, oxidation catalysts will have to be replaced or combined with more advanced aftertreatment systems (i.e. $NO_x$ aftertreatment).

The availability of sulphur-free fuel will make possible the development of the next generation of diesel $NO_x$ storage catalysts, that will be combined with oxidation catalysts, which will allow a further improvement in fuel efficiency. The presence of sulphur in diesel inhibits the development of the formation of particulates.

## 3.2 $NO_X$ REDUCTION SYSTEMS

### 3.2.1 $DeNO_X$ PASSIVE CATALYSTS

#### Description

$NO_x$ control is achieved using the exhaust hydrocarbons as a reducing agent. The $DeNO_x$ passive catalysts are characterised by low $NO_x$ conversion efficiency (20 – 30%) and narrow operating windows for temperature. Hence, the average benefit over the full European cycle is typically 10% $NO_x$ reduction or less. An activity temperature range results from the specific chemical formulation of the catalyst.

#### Sulphur effect

$DeNO_x$ passive catalysts show high sulphur sensitivity in terms of $NO_x$ conversion efficiency. The presence of sulphur shifts the operational temperature range to higher temperatures, as seen in Figure 13. When the catalyst is operated with sulphur-free fuel, the optimal operating temperature is lower and therefore is better suited to modern exhaust temperatures. The data provided by FIAT show that not only is the operational temperature affected by sulphur, but that even a switch from 0 ppm to 10 ppm sulphur content lowers the conversion efficiency by a further 10% approximately. The use of diesel containing 200 ppm reduces the efficiency drastically to half the efficiency of that with 0 ppm sulphur content.

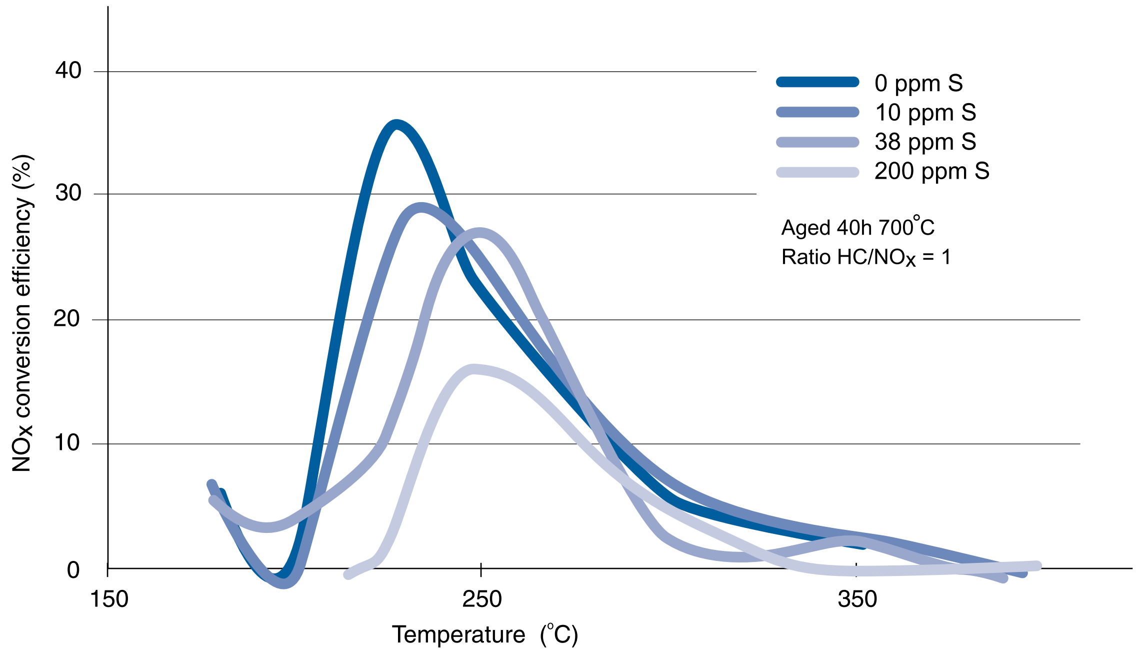



*Figure 13: The influence of sulphur on $NO_x$ passive catalyst efficiency – FIAT*

#### Prospects

The relatively low $NO_x$ conversion efficiency of $DeNO_x$ passive catalysts gives limited prospects for its use in the long term. They can be considered as a possible interim solution for some applications (passenger cars and light duty commercial vehicles).

### 3.2.2 DIESEL $NO_X$ STORAGE CATALYSTS

#### Description

Diesel $NO_x$ storage catalysts operate similar to those used in gasoline vehicles. Under normal (lean) operation, the catalyst system has an oxidation and storage function. Thus the NO is oxidised to $NO_2$ and, at typical exhaust temperatures, this reacts with the basic oxide components to form solid nitrate which can be stored. This reaction is reversed either through an increase in the exhaust temperature or through a change in air-fuel ratio (AFR). In the gasoline case, the engine can be run rich for the necessary short period of time, during which the nitrate is released as $NO_2$ and is reduced by the CO and HC to be emitted as $N_2$. In the diesel engine case, this strategy requires great care in order not to generate high levels of smoke or HC.

#### Sulphur effect

As in gasoline applications, fuel sulphur can follow a very similar reaction path to nitrogen, and becomes stored on the trap as a sulphate, as shown in Figure 4. This is more difficult to remove than the nitrate (requiring higher temperatures), and tends to stay in place during the normal regeneration process. Thus over a period of time the sulphate fills the majority of the capacity of the trap, and the $NO_x$ storage declines significantly, reducing the efficiency of the catalyst (Figures 14, 15, & 16). All three figures illustrate the deterioration in efficiency and durability with increasing diesel sulphur content. The deterioration is evident even between 50 ppm and 10 ppm sulphur content.

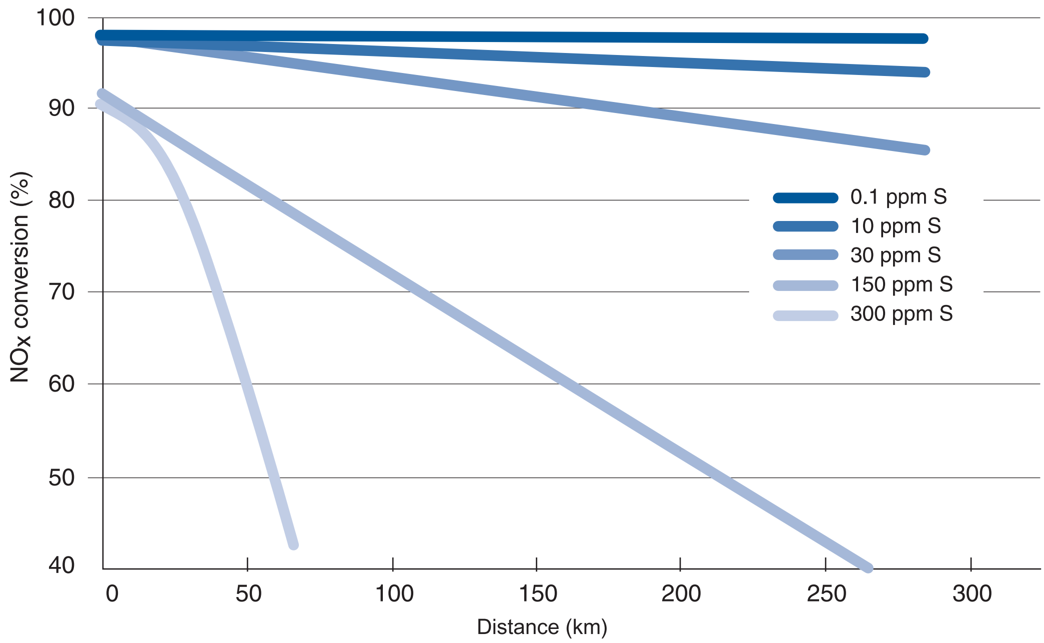



*Figure 14: $NO_x$ storage catalyst conversion efficiency as a function of sulphur content of diesel fuel – General Motors*

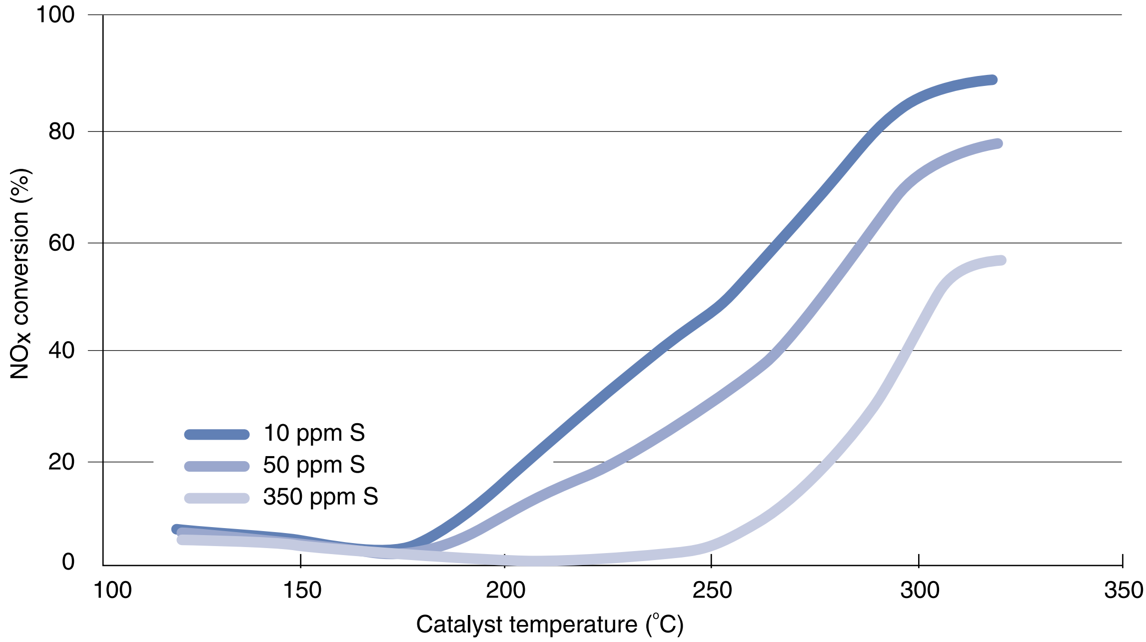



*Figure 15: $NO_x$ storage catalyst lightoff temperature and conversion rate as a function of diesel sulphur content – Audi*

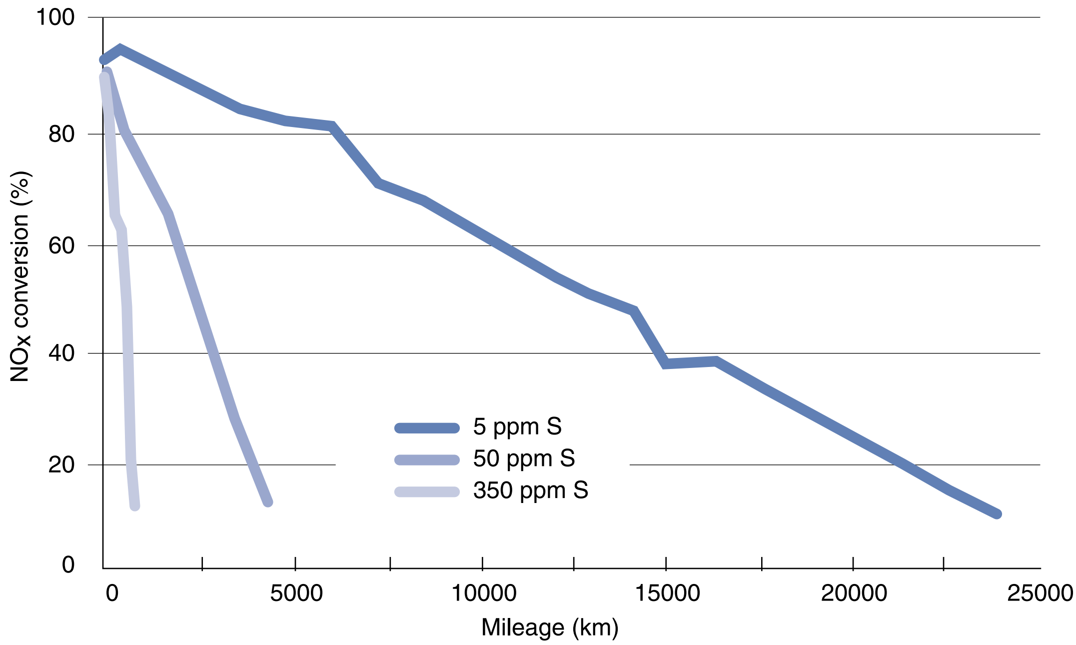



*Figure 16: Influence of diesel sulphur content on $NO_x$ conversion alteration – Renault*

The removal of the stored sulphate on $NO_x$ storage catalysts is a greater problem for diesel engines than for gasoline engines due to the lower and less controllable diesel exhaust gas temperatures. In particular, turbocharged diesel engines will not be able to meet the desulphurisation temperature requirements under urban driving conditions. Under these conditions, the engine is operated richer than normal operation leading to worsening of the fuel economy (Figure 17). However when the desulphurisation process cannot be initiated under the prevailing conditions, diesel vehicles do not have the option to operate as rich as in $\lambda$=1 mode in the manner of gasoline engines. This means that the key requirement for diesel $NO_x$ trap application is the reliability of the desulphurisation process. This prevents the introduction of this technology on the markets, where fuel sulphur content is too high.

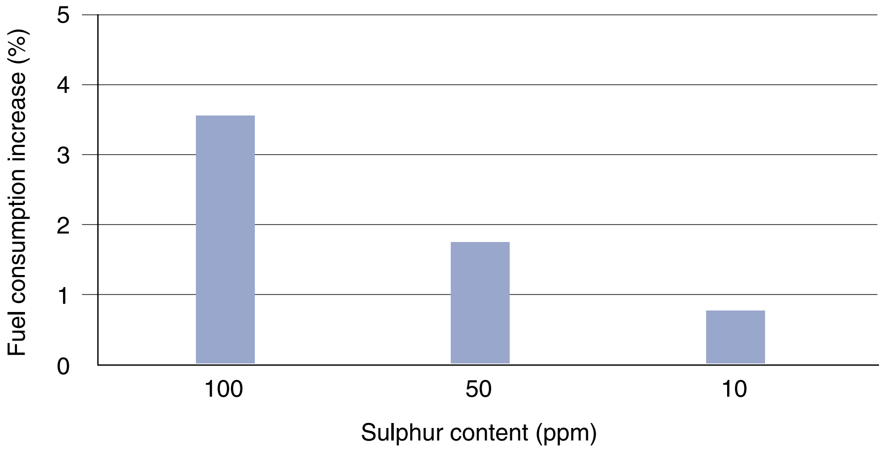



*Figure 17: Fuel consumption as a function of diesel sulphur content for a $NO_x$ storage catalyst – Volkswagen*

### Prospects

The diesel $NO_x$ storage catalyst is the only technology, apart from SCR systems, that shows high $NO_x$ conversion efficiency under lean burn conditions. Since the SCR is more suitable for trucks, diesel $NO_x$ storage catalysts is the crucial technology that will enable diesel passenger cars and light duty commercial vehicles to meet EURO 4 exhaust emission standards.

## 3.2.3 SELECTIVE CATALYTIC REDUCTION (SCR) SYSTEMS

### Description

This technology is based on the injection of a reducing agent (i.e. urea) into the exhaust gas before the catalyst. The urea provides the necessary ammonia which is the reductant.

The reducing agent reacts with $NO_x$ to form $N_2$, $H_2O$, $CO_2$.

The injection rate must be carefully controlled to avoid low $NO_x$ conversion or ammonia slip. Normally, the SCR system is coupled with an oxidation postcatalyst to avoid ammonia slip.

### Sulphur effect

Sulphur-free fuels are required to avoid reversible ammonium bi-sulphate formation. SCR systems are also operated with an oxidation precatalyst to oxidise the HC, CO and SOF of PM. The efficiency worsens with increasing diesel sulphur content. Figure 18 illustrates the high sensitivity of SCR systems with precatalysts to sulphur. The emissions vary from 0.027 g/kWh to 0.012g/kWh between operation with diesel containing 50 ppm and 15 ppm.

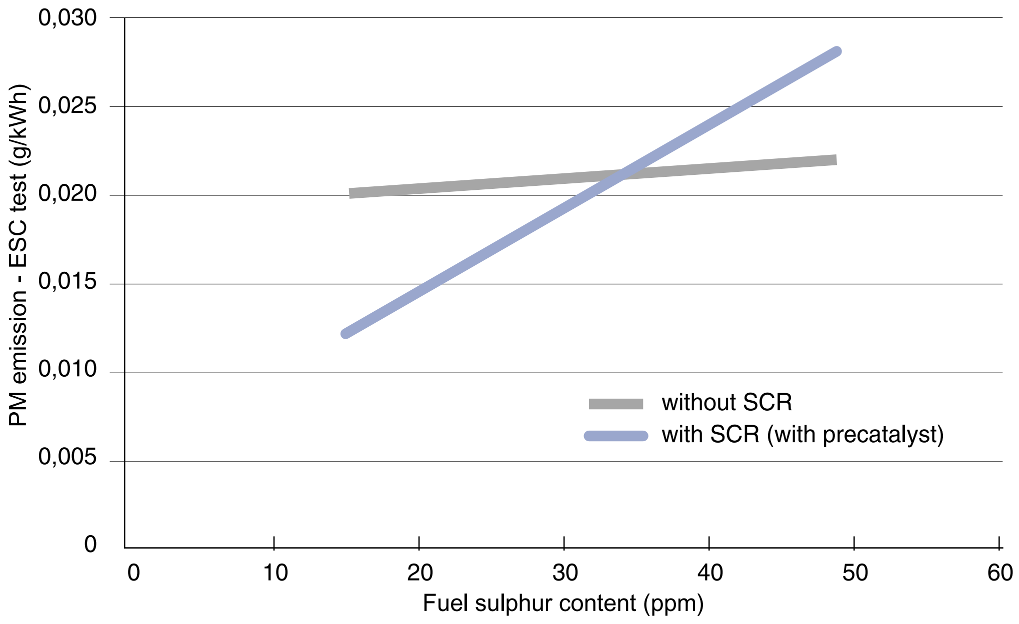



*Figure 18: Effect on PM emissions of diesel sulphur content using SCR aftertreatment – IVECO*

## Prospects

SCR technology is considered probable for heavy duty vehicles. The infrastructure for the distribution of the reducing agent, the cost for the agent and on-vehicle storage with accurate metered injection are other problems to be solved for an effective application as well as the sulphur level of diesel.

## 3.3 PARTICULATE CONTROL SYSTEMS

### 3.3.1 DIESEL PARTICULATE FILTER (DPF) OR PM TRAP

#### Description

The system consists of a trap which filters the full flow of the exhaust gas. There are several types of traps (Cordierit monolith, SiC monolith, sintered metal woven ceramic fiber). All of them have a very high filtration efficiency but generate exhaust back pressure, which increases with particulate loading. Therefore, a periodical regeneration is necessary.

Among the different DPF regeneration systems, the use of catalytic additives with diesel fuels is one promising possibility.

#### Sulphur effect

There have been three situations identified by PSA Peugeot Citroën where sulphur is observed to have a detrimental effect on particle filters. These are the following:

1. Sulphate is formed in the oxidation catalyst which is located upstream of the DPF. This increases the back pressure across the DPF and regeneration is more frequently required. This penalises the fuel consumption.
2. When regeneration occurs, sulphate stored in the filter is decomposed and partially converted to sulphur dioxide or $SO_2$. If a catalytic device is placed downstream of the filter, which is likely in future advanced aftertreatment systems, the $SO_2$ is oxidised to $SO_3$. This highly hygroscopic molecule can react with water to form white smoke. This phenomenon is considered as unacceptable and only occurs when fuels with more than 30 ppm sulphur content are used.
3. $SO_2$ in combustion gases is converted to sulphates by the oxidation catalyst upstream of the DPF, as mentioned in the first point. In steady state conditions at speeds higher than 100-120 kph, the $SO_3$ remains as a gas. This allows it to pass through the DPF and condense downstream forming secondary particles that can be weighed and measured. Fuel containing less than 50 ppm sulphur prevents this occurring.

#### Prospects

This is a possible solution for PM removal in large passenger cars. The cost, system, tank for the additives and fuel consumption penalisation will need to be optimised for better prospects in the long term.

### 3.3.2 PASSIVE SELF-REGENERATING DIESEL PARTICULATE FILTERS - CONTINUOUSLY REGENERATIVE TRAP (CRT™)

#### Description

The CRT is the most used passive self-regenerating diesel particulate filters for retrofit use. There are other catalytic soot filters on the market, but with less field experience than the CRT. CRT continuously converts diesel soot particles (elemental carbon) to $CO_2$. The temperature of the carbon combustion is lowered by the use of $NO_2$ as the oxidizing agent. Since the proportion of NO2 in the raw exhaust gas is relatively low, an active oxidation catalyst (platinum) is used upstream of the trap to convert a significant proportion of the NO to $NO_2$. The high activity of the oxidation catalyst gives very low CO and HC emissions.

## Sulphur effects

There are two different problems with sulphur and CRT.

The sulphur in diesel fuel decreases the NO to $NO_2$ conversion. Therefore, high levels of sulphur in diesel raise the regeneration temperature required in the CRT for particle combustion and hence penalise the trap regeneration (soot combustion). Operation with too high sulphur level fuel can cause the filter to be loaded with so much soot that an uncontrolled soot burning occurs, which can damage the filter material due to overheating.

Because of the strongly oxidizing platinum catalyst in the CRT system, the sulphur forms sulphuric acid, which is hygroscopical. Most of the PM weight on the test filter paper comes from water, bounded to the sulphuric acid. Thus the current measuring method of PM does not give the real amount of diesel soot particles. Sulphur does not affect the soot filtration efficiency, so there is no black smoke from the exhaust pipe if high sulphur is used. (The high PM measured is from sulphate and water.)

Johnson Matthey, the producer of the catalyst for the CRT system, originally declared that the system was compatible with 50 ppm sulphur in the fuel. Recently Johnson Matthey have stated that the latest generation of CRT systems use fuel with 20 ppm sulphur as a maximum. Vehicle manufacturers' data show the tremendous need for sulphur-free fuels for this technology.

Figures 19 and 20 illustrate the sensitivity of total particulate emissions measured after a CRT system to the level of sulphur in diesel. These figures show that the particulate emissions differ greatly between operation with diesel containing 50 ppm and less than 10 ppm. The data from Johnson Matthey, confirmed by similar data from IVECO, show a doubling of emissions between 3 ppm and 45 ppm. Volvo Trucks found the effect to be dependent on driving conditions but that a significant difference in emissions was apparent when fuel was changed from 44 ppm to 1 ppm sulphur content.

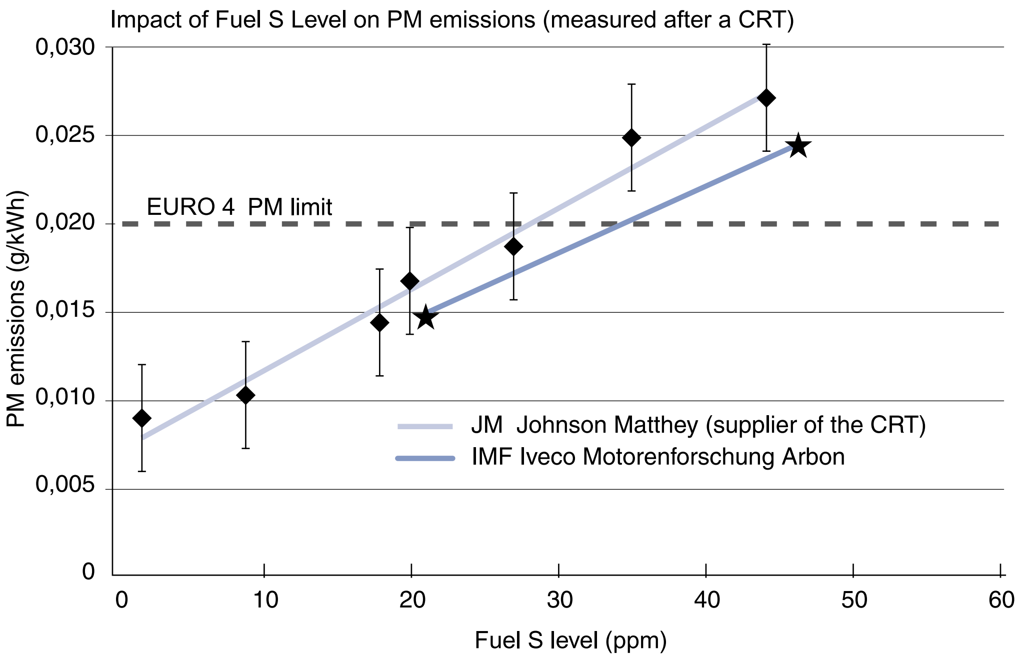



*Figure 19: Effect of sulphur content on emissions after CRT – IVECO*

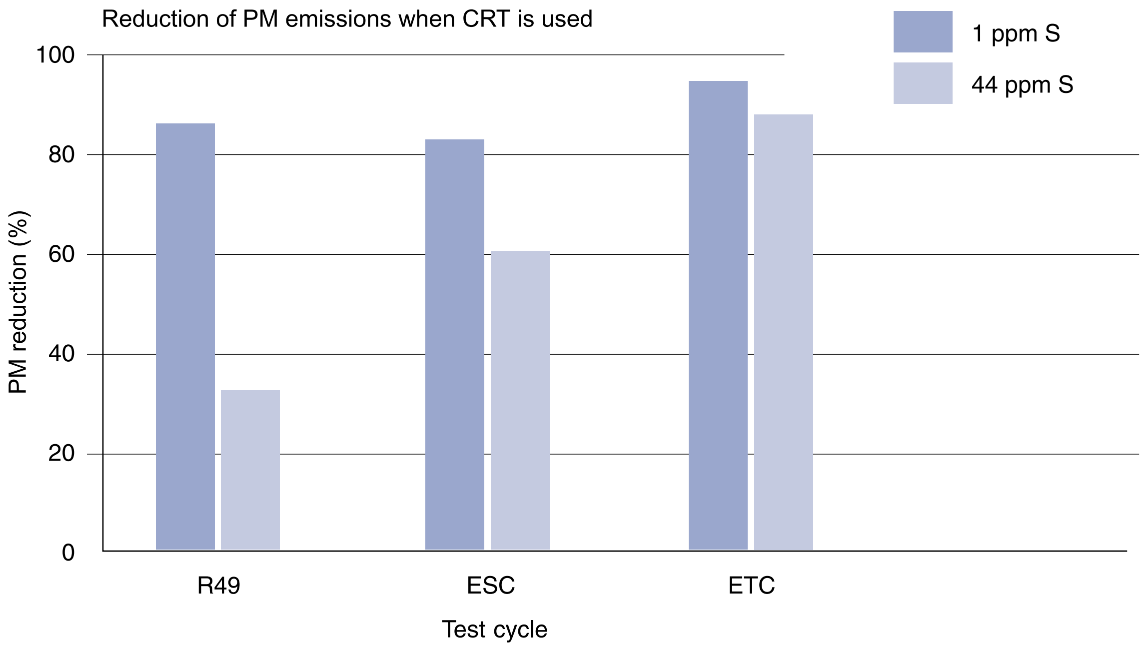



*Figure 20: Sensitivity to sulphur of PM emissions after CRT system – Volvo Trucks*

The balancepoint temperature of the catalyst required for continuous regeneration of the catalyst is also affected, as seen in Figure 21. The balancepoint temperature is the temperature at which the accumulated soot on the filter can be oxidised at the same rate it is accumulated**.** The presence of sulphur in fuel raises this temperature. The data from Volkswagen in Figure 21 demonstrates a difference in balancepoint temperature of 40°C between diesel with 350 ppm and 10 ppm sulphur. This is a result of the lower conversion rate of the NO oxidation process to the $NO_2$ that is necessary for continuous regeneration. This can be critical in low load situations where it is difficult to raise the temperature to above 200°C in advanced combustion systems. In order to raise the exhaust temperature to higher temperatures more fuel is consumed. Even at 50 ppm sulphur content an increase in fuel consumption of around 2%, compared with operation with sulphur-free diesel, has been observed by Volkswagen.

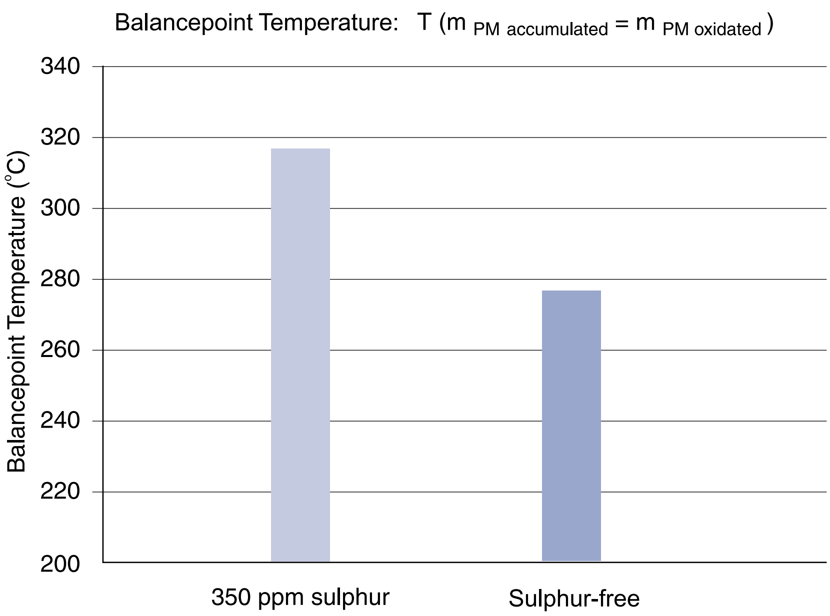



*Figure 21: Effect of fuel sulphur content on lightoff temperature of CRT system – Volkswagen*

## Prospects

This is one of the most interesting PM control technologies for both passenger cars and heavy duty vehicles. It will be required for larger passenger cars to meet EURO 4 exhaust limits.

An example of their application with Volvo Truck exists in Sweden, where sulphur-free diesel has been available for a decade.

# 4 EXISTING TECHNICAL LITERATURE

The data presented in chapters 2 and 3 are only the most recent results provided by ACEA members. As mentioned above, a vast technical literature exists on the effect of sulphur on the exhaust after treatment technologies.

In all recent conferences, new results have become available. This has been the case at the SAE Conference – Detroit, March 2000, CAPOC 5 – Brussels – April 2000, Vienna – May 2000, the World Fuel Conference – Brussels - May 2000 and the CEC-SAE Symposium – Paris – June 2000, just to mention the latest events.

In addition to that, several official reports are available. In particular:

> Among the projects carried out in the US, the DECSE Programme (Diesel Emission Control Sulfur Effects) has to be mentioned. It was launched at the beginning of 1999 with the objective to determine the impact of fuel sulphur levels on emission control systems. The project has already produced four interim reports.
> The Report n° 2 is devoted to $NO_x$ Absorber catalyst and the Report n° 4 to the Diesel Particulate Filter. Both are relevant to the purpose of the present paper.
>
> At the end of 1999, the FEV issued a report titled “Influence of the sulphur content in fuel on the fuel consumption and pollutant emissions of vehicles with gasoline and diesel engines”, which represents a comprehensive overview of the state of the art vehicle emission technologies and the influence of sulphur on them.
>
> In February 2000, Ford presented a “Review of the impact of Fuel Sulphur on Advanced Aftertreatment Systems”. This report collects the latest information of the poisoning effect of fuel sulphur on advanced emission after treatment systems.
>
> In April, the four most important automobile associations (ACEA, Alliance, EMA and JAMA) published a new version of the World-Wide Fuel Charter, introducing the sulphur-free fuels (Category 4). The technical background chapter summarised some of the most important evidences of the sulphur effect. In the annex, some of the most relevant reports are listed.

The list of the documents available at the ACEA Secretariat is reported on page 32.

# 5 CONCLUSIONS

Among the various exhaust after treatment possibilities, some uncertainty remains regarding which technologies will be used in the future to meet the exhaust emission standards and the $CO_2$ reduction target. A precise answer to this question is difficult because different solutions can be used by different automobile manufacturers and because the forecast of future vehicle technologies is a competitive issue.

In general, it seems that the $NO_x$ storage catalyst is the most promising solution for GDI and diesel passenger cars, whereas Selective Reduction Catalyst (SCR) is the most probable technology that will be used to reduce $NO_x$ emissions in heavy duty vehicles.

Regarding diesel particulate emissions, the two aftertreatment technologies under consideration are the Continuously Regenerating Trap (CRT) and the Diesel Particle Filter (DPF) with fuel additives.

The existing technical literature and the most recent results provided by ACEA members indicate that sulphur-free fuels are an enabling requirement for diesel $NO_x$ storage catalysts and CRT systems.

The last generation of Selective Reduction Catalysts (SRC), which is coupled with a high efficiency oxidation catalyst, also shows high sensitivity to the sulphur in diesel fuel.

A substantial improvement in efficiency can be observed for gasoline $NO_x$ storage catalysts with sulphur-free fuels.

Without a sulphur content in fuels of less than 10 ppm, the full fuel economy potential of gasoline direct injection engines will not be realised.

Sulphur-free fuels also enhance the performance of other existing and future exhaust after treatment technologies, such as three-way catalysts (TWCs), oxidation catalysts, DPF.

# List of Figures

# Abbreviations

| | |
|---|---|
| **ACEA** | European automobile manufacturers association |
| **AFR** | Air/Fuel Ratio |
| **AIAM** | Association of International Automobile Manufacturers |
| **Alliance** | Alliance of Automobile Manufacturers |
| **CO** | Carbon monoxide |
| **$CO_2$** | Carbon dioxide |
| **CRT** | Continuously Regenerative Trap |
| **DECSE** | Diesel Emission Control Sulphur Effect |
| **DPF** | Diesel Particulate Filter |
| **EMA** | Engine Manufacturer Association |
| **ESC** | European Steady State Cycle |
| **ETC** | European Transient Cycle |
| **EURO 3** | Emission standards entering into force in year 2000 |
| **EURO 4** | Emission standards entering into force in year 2005 |
| **EURO 5** | Emission standards according to row B2 of Directive 1999/96/EC, effective from 01.10.2008 |
| **GDI** | Gasoline Direct Injection |
| **HC** | Hydrocarbons |
| **JAMA** | Japan Automobile Manufacturers Association |
| **$NH_3$** | Ammonia |
| **NMHC** | Non Methane Hydrocarbons |
| **$NO_x$** | Oxides of Nitrogen |
| **PM** | Particulate Matters |
| **ppm** | Part per million |
| **S** | Sulphur |
| **SCR** | Selective Catalyst Reduction |
| **$SO_2$** | Sulphur dioxide |
| **SOF** | Soluble Organic Fraction |
| **TWC** | Three-way Catalyst |

## List of available reports on sulphur in fuels

1. *Worldwide Fuel Charter – ACEA/Alliance/EMA/JAMA – April 2000*
2. *Review of the Impact of Fuel Sulphur on Advances After treatment Systems – Ford Motor Company – February 2000*
3. *Worldwide Fuel Charter – Final Draft – ACEA/Alliance/EMA/JAMA – January 2000*
4. *Sulphur Content in Fuels: Survey – Opel presentation – January 2000*
5. *Diesel Emission Control – Sulphur Effects (DECSE) Program – Phase I Interim Data Report Nr. 4 - US Dept. of Energy – January 2000*
6. *Diesel Emission Control – Sulphur Effects (DECSE) Program – Phase I Interim Data Report Nr. 3 – US Dept. of Energy – November 1999*
7. *Influence of the sulphur content in fuel on the fuel consumption and pollutant emissions of vehicles with gasoline and diesel engines – FEV – 2 November 1999*
8. *Refining economics of diesel fuel sulphur standards – The Engine Manufacturers Association – 5 October, 1999*
9. *Diesel Emission Control – Sulphur Effects (DECSE) Program – Phase I Interim Data Report Nr. 2 – US Dept. of Energy – October 1999*
10. *Worldwide Fuel Charter – ACEA/Alliance/EMA/JAMA – September 1999*
11. *Comments on the Proposed Tier 2 Motor Vehicle Emissions Standard and Gasoline Sulphur Requirements – AAM – 2 August 1999*
12. *Diesel Emission Control – Sulphur Effects (DECSE) Program – Phase I Interim Data Report Nr. 1 – US Dept. of Energy – August 1999*
13. *Demonstration of advanced emission control technologies enabling diesel-powered heavy-duty engines to achieve low emission levels – MECA – August 1999*
14. *ACEA Position paper "Problems associated with the measurements of low particulate levels" – April 1999*
15. *The Impact of Sulphur in Diesel Fuel on Catalyst Emission Control Technology – MECA – 15 March, 1999*
16. *Developments in Central European Refining – WEFA Conference – 25 & 26 June 1998*
17. *Overview of Central & East European Refining Activities – C.P. Hälsing – Fluor Daniel (the 1998 European Oil Refining Conference & Exhibition – Prague, Czech Republic, June 25 & 26, 1998*
18. *Diesel Sulphur Effects on Control Technologies – EMA/MECA Meeting – 27 May 1998*
19. *Gasoline Sulphur Issues – EPA Staff Paper – 1 May 1998*
20. *Study on the Effects of Fuel Sulphur on Low Emission Vehicle Criteria Pollutants – AAMA/AIAM – December 1997*
21. *ACEA Position on Fuel sulphur – May 1997*
22. *Arthur D. Little report: "Sulphur in transport fuels – Re-analysis of the cost to reduce EU sulphur levels in gasoline and diesel" – February 1997*

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