

**Response by AECC to European Commission Consultation on
the need to reduce the Sulphur Content of Petrol & Diesel Fuels
below 50 parts per million****July 2000****Table of Contents**

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1. Introduction

1.1. AECC

AECC, the Association for Emissions Control by Catalyst, is an international scientific association of European companies engaged in the development, production and testing of catalyst and filter based technologies for vehicle emissions control. This includes the development, testing and manufacture of autocatalysts, ceramic and metallic substrates and speciality materials incorporated into the catalytic converter and filter and catalyst based technologies to control diesel engine emissions (especially particulates and nitrogen oxides). Members' technology is incorporated in the exhaust emission control systems on all new cars and an increasing number of commercial vehicles, buses and motorcycles in Europe.

The principal objectives of the Association are:

- To foster and promote the use of state-of-the-art technologies for the control of noxious emissions from mobile sources
- To collect and disseminate information concerning laws and regulations, safety and environmental concerns, studies relating to vehicle exhaust emissions and methods for their control
- To promote the harmonisation of technical standards, test procedures and safety regulations
- To sponsor scientific research programmes related to the objectives of the Association and disseminate the results at conferences and in scientific publications.

Members of the Association are:

ASEC GmbH, Germany	Engelhard Technologies GmbH, Germany
Corning GmbH, Germany	Johnson Matthey PLC, UK
Degussa Metals Catalysts Cerdec AG, Germany	NGK Europe GmbH, Germany
Emitec Gesellschaft für Emissionstechnologie mbH, Germany	Rhodia Terres Rares SA, France
	Siemens AG, KPW PK, Germany

AECC is qualified to contribute to the following issues on which views are sought

The magnitude of the additional environmental benefit gained from using petrol and diesel with a sulphur content of less than 50 parts per million. More specifically, what are the incremental benefits of using fuels with a sulphur content of (a) 5-10 parts per million and (b) 30 parts per million relative to fuels containing 50 parts per million of sulphur?

Should the uptake of new emissions abatement technology or fuel-efficient technology be encouraged in the automotive fleet? If so what type of low-sulphur fuel marketing regime would be justified? For example, (i) a proportion of the market sold on a voluntary basis, (ii) a proportion of the market sold on a mandatory basis or (iii) the totality of the market that complies with a sulphur content fixed at a value less than 50 parts per million? This should be considered in the context of the advancement of traditional petrol and diesel engine emission abatement technology and looking forward towards the introduction of new vehicle propulsion or power plant technology.

What will be the overall effect on greenhouse gas emissions of moving to petrol and diesel with a sulphur content less than 50 parts per million? This should take account of changes in emissions in the refining and distribution systems and in the vehicle fleet through the pursuance of CO₂ efficient technologies, the so-called "well to wheels" life-cycle effect.

1.2. Lean Combustion

With the development of lean burning direct injection petrol engines and increased use of diesel engines, lean combustion is the big challenge for automotive catalysis. Lean combustion is essential to limit carbon dioxide emissions and to reduce fuel consumption. New diesel technologies with greater use of electronic management and direct injection with unit injectors or common rail injection can achieve further fuel consumption improvements. The conventional three-way catalyst technology used on petrol engines needs a richer environment with lower air-fuel ratios to reduce NO_x so a radical new approach is required.

1.3. The Importance of Fuel and Lubricant Quality

Fuel and Lubricant Quality affects the performance of emission control systems by:

- Preventing the use of a technology unless fuel quality is improved (the improved fuel is “**enabling**” the use of that technology)
- “**Enhancing**” the performance of emission control systems (both existing fleet and new registrations).

Examples of **enabling** fuels are the introduction of:

- Unleaded petrol to allow autocatalysts to be used and
- Ultra low sulphur fuels required for continuously regenerating diesel particulate filters (CR-DPFs) and NO_x adsorbers to be used.

Examples of **enhancing** fuels are:

- Further reductions in lead levels, including the influence of the ban on the sale of leaded petrol in EU and elsewhere, that improve the performance and life of autocatalysts and
- The introduction of ultra low sulphur petrol and diesel fuels as reducing sulphur levels (all the way down to zero) delivers improved performance of catalysts.

Sulphur in petrol and diesel fuel has a major negative impact on catalyst performance.

The effect of sulphur on catalyst performance becomes more critical as lower tailpipe emissions are targeted and the loss of catalyst efficiency caused by sulphur in the fuel has a larger impact at the very low emission levels required in future.

Sulphur strongly competes against pollutants for “space” on the catalyst surface and this limits the efficiency of catalyst systems to convert pollutants at any sulphur concentration. The effect of sulphur as a competitor on the catalyst surface may be reversible but it can cause irreversible changes to the washcoat and some of the base metal components. The conversion of sulphur to a sulphate aerosol can cause net increases in particulate emission.

One tankful of high sulphur fuel will immediately degrade catalyst performance but this will normally be restored on reverting to a low sulphur fuel. The levels of sulphur in fuel are an important factor in the performance of NO_x catalysts and adsorbers. The lower the sulphur levels in fuels the better the catalyst performance that can be obtained.

2. Description of exhaust emission control technologies

2.1. The Catalytic Converter

The term covers the stainless steel box mounted in the exhaust system (Figure 1). Inside is the autocatalyst, a ceramic or metallic substrate with an active coating incorporating alumina, ceria and other oxides and combinations of the precious metals - platinum, palladium and rhodium. The substrate can be protected from vibration and shock by a resilient ceramic or metallic “mat”.

Autocatalysts can be oxidation or three-way types. Oxidation catalysts convert carbon monoxide (CO) and hydrocarbons (HC) to carbon dioxide (CO₂) and water and decrease the mass of diesel particulate emissions but have little effect on nitrogen oxides (NO_x). Three-way catalysts operate in a closed loop system including a lambda, or oxygen, sensor to regulate the air-fuel ratio. The catalyst can then simultaneously oxidise CO and HC to CO₂ and water while reducing NO_x to nitrogen.

2.2. Diesel Oxidation Catalysts (DOCs)

The catalyst oxidises carbon monoxide, gaseous hydrocarbons, and liquid hydrocarbons including those adsorbed on the carbon particles. The liquid HCs are known as the soluble organic fraction (SOF) and make up part of the total particulate matter (PM).

2.3. Diesel Particulate Filters (DPFs)

DPF systems consist of a filter material positioned in the exhaust designed to collect solid and liquid particulate matter (PM) emissions while allowing the exhaust gases to pass through the system. One type of filter material is shown in Figure 2.

Figure 1 Catalytic Converter



Figure 2 Diesel Particulate Filter



A number of filter materials are used, including ceramic monoliths, woven silica fibre coils, ceramic foam, wire mesh and sintered metal. Collection efficiencies of these various filters range from 50 percent to over 90 percent, but the design of most filters today is to achieve 90 percent or greater level of particulate control in terms of mass but over 99% when expressed as numbers of ultra fine particles. A study has found that advanced filter technology almost completely eliminated the fine, carbon particulate in the size range of less than 100 nanometers (nm) diameter with efficiency of >99%¹. This is very important since health experts believe that it is the fine particulate that is carried deep into the lungs and which is thought to be the most dangerous size of PM.

Since the wall flow filter would readily become plugged with particulate material in a short time, it is necessary to "regenerate" the filtration properties of the filter by burning off the collected particulate matter on a regular basis. To achieve regeneration of the collected PM by oxidation or combustion with a DPF without any additional activation mechanism, the collected particulate matter in the filter must attain a minimum temperature in the range of 600 to 650°C in order to auto-ignite and sustain combustion. However, the engine-out exhaust temperature of a heavy-duty diesel engine does not typically achieve these levels and, therefore, is not sufficient to initiate and sustain the regeneration of the filters. The most successful methods to achieve regeneration include:

- Electrical heating of the DPF either on or off the vehicle
- Incorporating a catalytic coating on the DPF to lower the temperature at which particulate matter burns

- Using very small quantities of fuel-borne catalyst, such as cerium oxide. The catalyst, when collected on the DPF as an intimate mixture with the particulate, allows the particulate to burn at normal exhaust temperatures to form carbon dioxide and water, while the solid residues of the catalyst are retained on the DPF
- Incorporating an oxidation catalyst upstream of the DPF that, as well as operating as a conventional oxidation catalyst, also increases the ratio of NO₂ to NO in the exhaust. Trapped particulate matter burns off at normal exhaust temperatures using the powerful oxidative properties of NO₂.

Successful commercial application of DPF technology has been pioneered in Europe where over 10 000 systems have been installed on trucks and buses. The systems are achieving particulate emission reductions of up to 90 percent or more while demonstrating excellent durability. Catalytic DPFs have long been used on mining equipment to significantly reduce PM and HC emissions and have shown excellent durability when operated with the appropriate fuel and serviced properly. Worldwide, over 10 000 DPFs have been installed on off-road diesel engines.

Operating experience in Sweden illustrates that DPF technology is a proven PM control system for diesel engines when low sulphur (<10 ppm) is used and recent work published by Ecotest² finds the cancer risk is lower for this system than with using natural gas.

2.4. DeNOx catalysts and NOx traps

These systems hold out the prospect of substantially reduced emissions of oxides of nitrogen. NO_x conversion rates depend on exhaust temperature and availability of reducing agents. There are four systems under evaluation by industry:

1. **Passive DeNOx Catalysts** using reducing agents available in the exhaust stream
2. **Active DeNOx Catalysts** using added hydrocarbons as reducing agents
3. **Selective Catalytic Reduction** using a selective reductant, such as ammonia from urea
4. **NOx traps or adsorbers** used in conjunction with a three-way catalyst.

Each of these systems offers different possibilities in the level of NOx control possible and the complexity of the system. Fuel parameters such as sulphur content can affect catalyst performance.

DeNOx (or Lean NOx) Catalysts use advanced structural properties in the catalytic coating to create a rich "microclimate" where hydrocarbons from the exhaust can reduce the nitrogen oxides to nitrogen, while the overall exhaust remains lean. Further developments focus on increasing the operating temperature range and conversion efficiency.

NOx Adsorbers (or Lean NOx Traps) are a promising development as results show that NOx adsorber systems are less constrained by operational temperatures than DeNOx catalysts. NOx traps adsorb and store NOx under lean conditions. A typical approach is to speed up the conversion of nitric oxide (NO) to nitrogen dioxide (NO₂) using an oxidation or three-way catalyst mounted close to the engine so that NO₂ can be rapidly stored as nitrate. The function of the NOx storage element can be fulfilled by materials that are able to form sufficiently stable nitrates within the temperature range determined by lean operating points of a direct injection petrol engine. Thus especially alkaline, alkaline earths and to a certain extent also rare-earth compounds can be used.

When this storage media nears capacity it must be regenerated. This is accomplished in a NOx regeneration step. Unfortunately, alkaline and alkaline earth compounds are not only characterised by their extraordinary thermal stability of the corresponding nitrates but also by their strong affinity for sulphation. As a consequence alkaline and earth alkalines are almost irreversibly poisoned by the sulphur contained in the fuel during the NOx storage operation mode, leading to a decrease in NOx-sorption efficiency during operation.

The stored NO_x is released by creating a rich atmosphere with injection of a small amount of fuel. The rich running portion is of short duration and can be accomplished in a number of ways, but usually includes some combination of intake air throttling, exhaust gas recirculation, late ignition timing and post combustion fuel injection.

Under oxygen rich conditions, the thermal dissociation of the alkaline and alkaline earth sulfates would require temperatures above 1000 °C. Such temperatures cannot be achieved under realistic driving conditions. However, it has been demonstrated in various publications ^{3, 4, 5} that it is in principle possible to decompose the corresponding alkaline earth sulphates under reducing exhaust gas conditions at elevated temperatures. In this way the NO_x storage capacity can be restored.

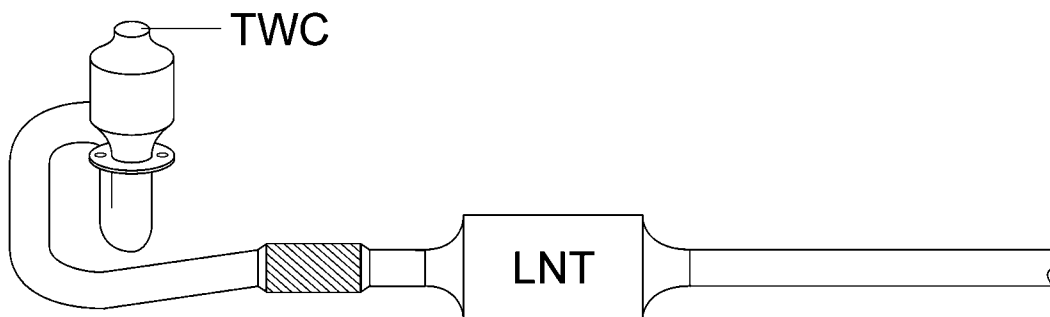
The released NO_x is quickly reduced to N₂ by reaction with CO (the same reaction that occurs in the three-way catalyst proven for spark-ignited engines) on a rhodium catalyst site or another precious metal that is also incorporated into this unique single catalyst layer (see Figures 4 and 5).

One of the demands for a desulphation strategy must be to avoid any H₂S emissions above the odour threshold during desulphation. Therefore, a special desulphation strategy was worked out in order to eliminate any H₂S formation during the desulphation event ^{6, 7}.

The heating of the catalyst that is necessary – for example by late ignition timing – does, however, result in a considerable increase in fuel consumption, which is dependent upon the sulphur content. Therefore, reducing the sulphur concentration in the fuel must be regarded as the most effective way of using the full potential of modern direct injection petrol engines with respect to fuel economy and CO₂ reduction.

Figure 3 shows a typical installation of a Lean NO_x Trap (LNT).

Figure 3 Lean NO_x Trap with Three-way Catalyst



Reduction in engine-out NO_x emissions of as high as 90 percent has been demonstrated. The system is in production with direct injection petrol engines and it appears possible to develop the system into a functional and durable NO_x control system for diesel exhaust. However, NO_x adsorbers are particularly sensitive to sulphur and require low sulphur fuel.

Figure 4

Reaction Steps for Lean NO_x Conversion

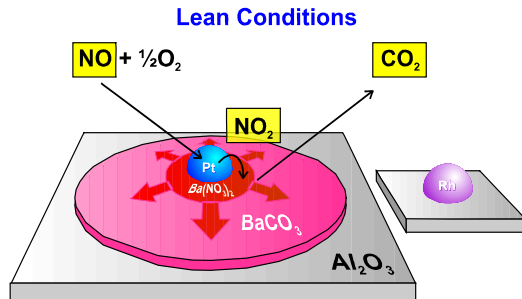
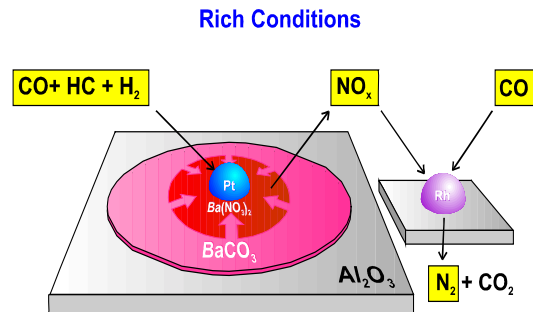


Figure 5

Reaction Steps for Lean NO_x Conversion



2.5. Selective Catalytic Reduction (SCR)

SCR is the widespread technology to reduce nitrogen oxide emissions from coal, oil and gas fired power stations, marine vessels and stationary diesel engines in smaller power generation stations as well as generating set applications. SCR technology has been used successfully for more than two decades.

SCR technology for heavy-duty diesel vehicles has been developed to the commercialisation stage and will be available as an option in the series production of several European truck-manufacturing companies in 2001.

SCR technology is designed to permit the NO_x reduction reaction to take place in an oxidising atmosphere. It is called 'selective' because the catalytic reduction of the NO_x with ammonia (NH₃) as a reductant occurs preferentially to the oxidation of NH₃ with oxygen. Several types of catalysts are used, the choice of which is determined by the temperature of the exhaust environment. SCR technology has been employed in stationary source applications for over 15 years with anhydrous or aqueous ammonia and aqueous urea commonly used as the reducing agent. Recently, SCR has also been evaluated on mobile source applications such as trucks, locomotives and marine engines. For mobile source applications, the reductant source is usually urea (CO(NH₂)₂), which can be rapidly hydrolysed to produce ammonia in the exhaust stream. SCR technology can achieve NO_x reductions in excess of 90 percent.

3. Overview on the effects of Sulphur on the Performance of Emission Control Systems

Sulphur is not a catalyst poison like lead, which completely and permanently destroys catalyst activity. However sulphur is an inhibitor, which strongly competes with the exhaust pollutants for space on the active catalyst surface. The issue of sulphur compounds inhibition on emission control systems performance is quite complex. Upon combustion, fuel sulphur is oxidised to sulphur oxides, primarily sulphur dioxide (SO₂) with small amounts of sulphur trioxide (SO₃). SO₂ and SO₃ are known to inhibit the catalytic function of automobile exhaust catalysts. Sulphur inhibition varies in degree according to the fuel sulphur level, the catalyst formulation, catalytic function, combustion products from various air/fuel mixtures, and exhaust temperature range. Factors that influence the impact of sulphur on catalyst technology are listed in Table 1.

Table 1 FACTORS WHICH INFLUENCE SULPHUR INHIBITION OF CATALYTIC EMISSION CONTROL SYSTEMS

1. Catalyst Composition
 - Precious metals used – palladium (Pd), Pd and rhodium (Rh), platinum (Pt) and Rh, or Pt/Pd/Rh
 - Precious metal concentrations
 - Base metal concentrations
 - Oxygen storage (i.e. cerium oxide or other compounds)
2. Catalyst volume
3. Catalyst design
4. Catalyst location
5. Emission control system – type and control of fuel metering
6. Engine calibration
7. Vehicle use
8. Fuel
9. Regeneration/recovery conditions

Catalyst sulphur inhibition is caused by chemisorption of a sulphur species on an active catalyst site ^{8,9,10,11,12,13,14}. The presence of sulphur as an oxide or sulphide (e.g. hydrogen sulphide (H₂S) which can also be present in the exhaust) invariably has a negative, and typically immediate, effect on the performance of catalysts. The sulphur species adsorbs on the catalyst site which is then not available for the preferred catalytic reactions resulting in less overall activity than the original value - this is the case with SO₂ and with H₂S. Another undesirable effect of sulphur in petrol is that the catalyst oxidises SO₂ to SO₃, which forms sulphates easily with base metal oxides or forms sulphuric acid by reaction with water. Precious metals have an advantage over base metal oxides as they are much more resistant to SO₂ and SO₃. Base metal catalysts more easily form sulphates that are also more difficult to regenerate ¹⁵.

Table 2 summarises the ways sulphur can affect catalysts and emissions.

Table 2 EFFECTS OF SULPHUR IN FUELS AND LUBRICANTS

Sulphur

1. Inhibits catalyst performance by strong adsorption on surface and competes for space on the catalyst surface with pollutants
2. Limits the amount of NO₂ formed on an oxidising catalyst – a problem for some particulate DPFs and NOx adsorbers that rely on NO₂ for their regeneration
3. Reacts with chemical NOx traps more strongly than NOx – this decreases NOx storage capacity and requires more vigorous and frequent regeneration; increasing fuel consumption
4. Creates sulphate particles, that are measured by current sampling & measurement techniques, with any emission control system that includes a precious metal catalyst with an oxidising function
5. Contributes to coating the catalyst surface.

4. Effect of Sulphur on Emission Control Technology on existing fleets

4.1. Diesel Oxidation Catalysts (DOCs)

An oxidation catalyst will reduce the soluble organic fraction (SOF) of the particulate by up to 90% ¹⁶. Destruction of the SOF is important because this portion of the particulate contains numerous chemicals of concern to health experts. Control of the SOF enables the oxidation catalyst to reduce total particulate emissions by 25 to 50 percent, depending on the constituents

that make up the total particulate. This technology also reduces diesel smoke and eliminates the pungent diesel exhaust odour. DOC technology has been successfully used on all diesel cars sold in Europe since 1996. DOCs may also be used in conjunction with a NO_x adsorber, a DeNO_x catalyst, or SCR to “clean-up” any by-pass of injected hydrocarbons or ammonia.

4.2. Three-way Catalysts (TWCs)

AECC conducted an extensive literature survey in 1997^{17, 18, 19, 20, 21} of published information on the effects of fuel sulphur on the performance of three-way catalyst equipped vehicles. There was a lot of information on the effect of fuel sulphur on the performance of three-way catalysts that is summarised on the Table 3.

Table 3 SUMMARY OF REFERENCES TO SULPHUR EFFECT ON THREE-WAY CATALYSTS

Reference	Conversion Efficiency Increase %					Sulphur Change ppm	Catalyst Information
	HC	NMHC	CO	NO _x	Benzene/ AirToxics		
Ford US	8-9		27	27		600>35	3xTWC
Ford US	8		12	12		600>35	New Technology
US Auto-Oil	18		19	8		450>50	1990 Technology
US CRC	7-76					1000>0	1.5xThreshold
Program	63-94					1000>0	100k miles aged
Ford US	25-67		24-87	5-85		900>30	New Technology
US Auto-Oil:							
SAE 932323	16		13	9		466>49	10x1989TWC cars
SAE 942727	18	18	18	8	21/10	450>50	10x1989TWC cars
SAE 942727	6	6	10	0	12/8	50>10	10x1989TWC cars
EPEFE:							
SAE 961071	ca 10		ca 10	ca 10		382>18	Not disclosed

Most of the studies compare the tailpipe emissions using fuels with different sulphur levels and all conclude that the lower the sulphur level the lower the emissions on fresh or aged catalysts. There is however some evidence of a non-reversible interaction between the washcoat components and sulphur.

The CRC²² and AAMA/AIAM²³ studies carried out in 1997 in the USA both showed a reduction in emissions as fuel sulphur in petrol was reduced, with an enhanced effect below 100 ppm. The lowest sulphur level investigated was 30 ppm.

Some published work²⁴ from Johnson Matthey/BP/Statoil concluded that there was little effect on durability of three-way catalysts up to 80,000 km between fuels with 50 and 450 ppm sulphur. The paper however showed that sulphur caused faster ageing of the lambda sensor, which drifted rich giving lower NO_x and higher CO emissions, and had an instantaneous effect on catalyst performance. A Toyota paper²⁵ concluded that there were significant increases of CO and HC during mileage accumulation on fuel containing 500 ppm sulphur compared to fuel containing 30 ppm sulphur.

The bottom line is that higher sulphur levels in fuel have an effect on durability if the criteria are the amount of untreated pollution emitted over the life of the vehicle. This will only be apparent if the test to check the catalyst/emissions performance is conducted with the same fuel used during the durability test and not, for example, a standard reference fuel. Since the deterioration of catalyst emissions performance is gradual a vehicle aged and tested on a higher sulphur fuel will “fail” to achieve a given emission standard earlier than one on low sulphur fuel.

4.2.1. Summary of Recent Important Papers

Baronik *et al* (Volkswagen)²⁶ investigated the effect of sulphur levels in petrol of 1, 40, 150 and 330 ppm on conversion efficiency of three-way catalysts. They looked at regulated emissions and greenhouse gases such as methane (CH₄) and nitrous oxide (N₂O). N₂O emissions increased from 0.01 gram/mile on 1 ppm sulphur fuel to 0.034-0.086 gram/mile on 330 ppm fuel. The effect on NO_x and methane conversion is shown in Figures 6 and 7. Methane is a refractory molecule and difficult to combust and conversion is consequently greatly reduced by increased sulphur content in petrol.

Figure 6 NO_x Conversion and S content

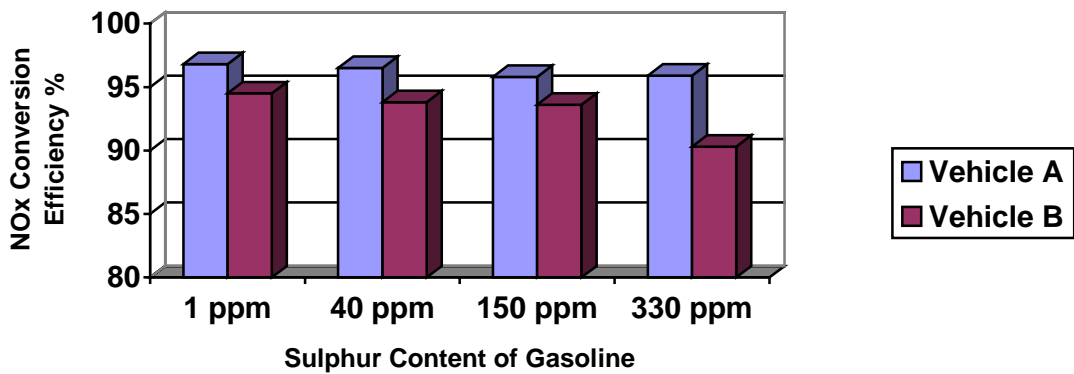
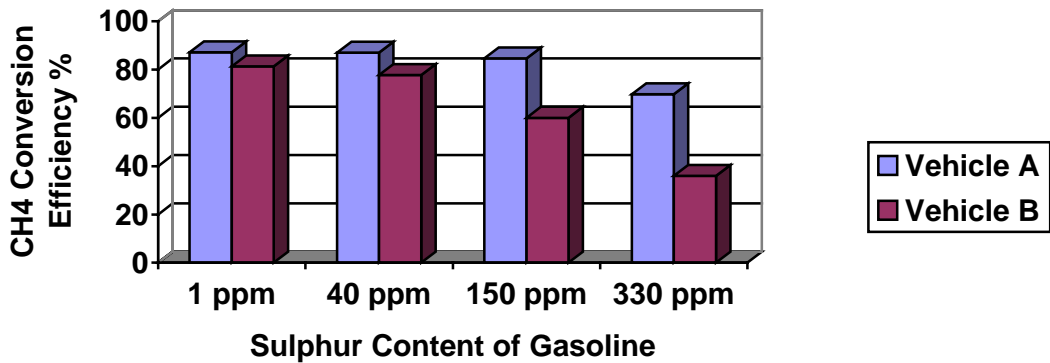


Figure 7 Methane Conversion and S Content



5. Effect of Sulphur on Emission Control Technology on future fleets

5.1. Vehicles equipped with diesel engines and Particulate Matter DPFs (Catalyst-based Diesel Particulate Filter (CDPF)/ Continuously Regenerating Diesel Particulate Filter (CR-DPF)/ Fuel-borne Catalyst (FBC) Diesel Particulate Filter and combined systems), DeNOx catalysts (active/passive), NOx adsorber/catalyst and SCR

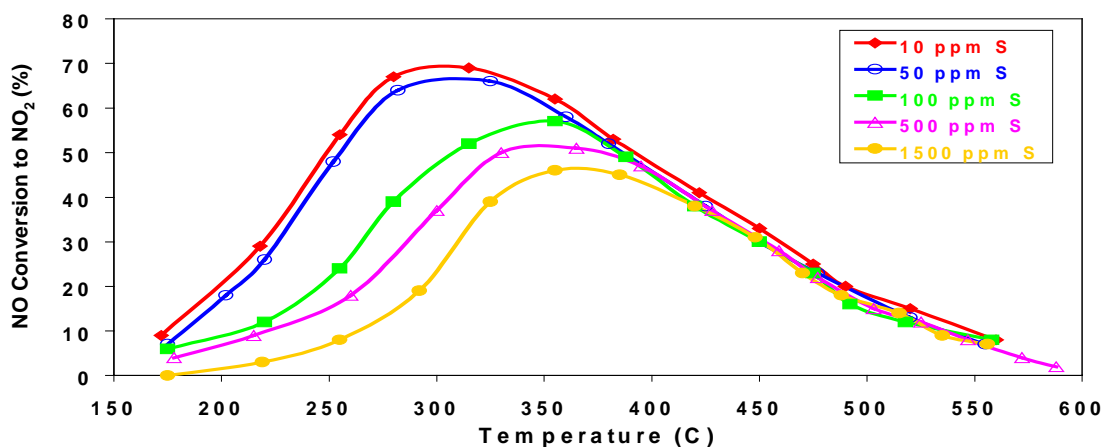
5.1.1. Fuel Sulphur Effects on Catalyst-based Diesel Particulate Filter (CDPF)

The effects of the sulphur in the fuel on the efficiency of the CDPF are quite similar to those with a diesel oxidation catalyst (DOC). There is a clear dependence between efficiency and sulphur level in the fuel. Compared to other particulate filter systems the effects of sulphur on performance is limited because the active coating is physically close to the filtered particulate matter and the regeneration process is not dependent mainly on NO₂ formation. Base metal oxides in the coating are an important factor for this function. They are quite tolerant to different sulphur levels. The sulphur tolerance of the system in case of misfuelling has been proven. The design allows optimising the coating for higher sulphur levels but with reduced efficiency to destroy pollutants. A fuel with a maximum of 10ppm sulphur allows for a significant increase in the activity in the low temperature range. This make the soot filter viable even for very low speed inner city buses at low ambient temperatures.

5.1.2. Fuel Sulphur Effects on Continuously Regenerating Diesel Particulate Filter (CR-DPF)

While CR-DPFs have been released for selected retrofit applications with 50 ppm fuel within the context of current legislation, in common with other catalyst based emission control systems they perform with increasing efficiency as the fuel sulphur content is lowered. Early experience with the CR-DPF has been with less than 10 ppm sulphur fuel in Scandinavia. Figure 8²⁷ shows that high levels of conversion of NO to NO₂, necessary for good DPF regeneration, are obtained with 10 and 50 ppm sulphur levels.

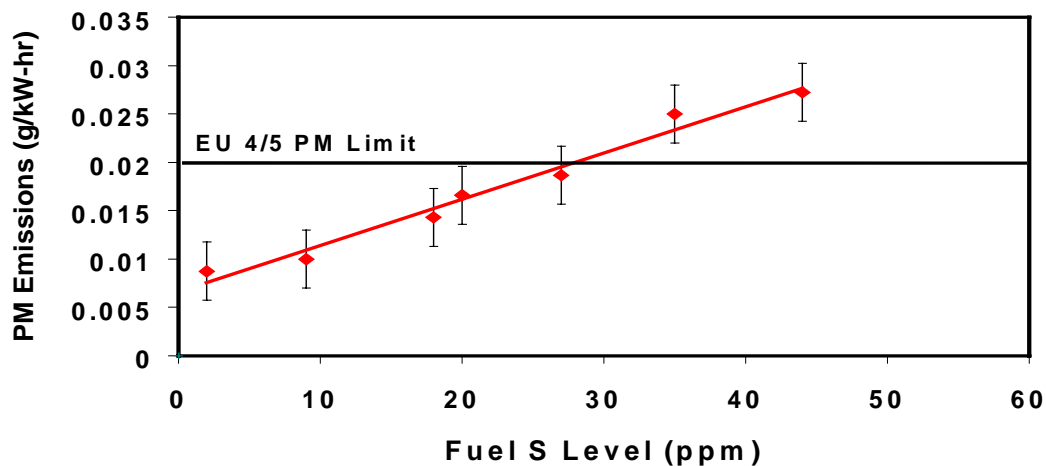
Figure 8 Effect of Temperature and Fuel S Level on CR-DFP Performance



The 2005 heavy-duty particulate standards of 0.02/0.03 g/kWh will require careful control of the fuel sulphur levels. For a CR-DPF requiring low temperature PM removal using the NO₂-PM reaction, NO₂ production is essential but catalysts that oxidise NO into NO₂ also oxidise SO₂ into SO₃. This SO₃ is trapped on the filter paper during PM measurement and contributes to PM mass. To investigate the magnitude of this effect a Swedish MK1 base fuel (3ppm sulphur) was doped to

a number of sulphur levels between 3 and 50ppm using thiophene and evaluated on an engine. Figure 9²¹ shows that fuel sulphur levels of 30 ppm are enough to bring particulate levels up to the Euro 4/5 PM limit values even if the CR-DPF removes all the carbon- and hydrocarbon-based particulate.

Figure 9 Effect of Fuel S Level on Measured PM Emissions



5.1.3. Impact of 10 ppm sulphur versus 50 ppm sulphur on Fuel-borne Catalyst (FBC) with DPF

Sulphur reduction in diesel fuel is certainly desirable to avoid the emission of sulphur oxides into the atmosphere, but the ability of cerium oxide as a fuel-borne catalyst to facilitate the regeneration of the filter is not affected by the current level of sulphur, with which it is possible to lower the soot burning temperature to 350-450°C.

In addition the low catalytic activity of cerium oxide towards SO₂ oxidation avoids the formation of sulphates at high temperatures.

FBC is often unfairly targeted as being responsible for filter clogging. No doubt, FBC residues are retained in the filter, but clogging incidents are typically caused by lubricating oil ashes. Even without a FBC, filters can become clogged after 100 000 km and even less if oil consumption is high. This is due to the combination of the calcium (a residue from motor oil) with SO₃ from sulphur in the fuel. Ashless oil and low sulphur fuel will limit this clogging but will not avoid the need of regular maintenance. The filter can be easily washed and dried to recover its original porosity.

A sulphur content of 10 ppm instead of 50 ppm will have a negligible impact on the catalytic activity of the FBC for the regeneration of the DPF, but it will have a positive impact on fuel consumption by decreasing the build-up of calcium sulphate ash.

5.1.4. Summary of Recent Important Papers

Zelenka (AVL List)²⁸ found that a Euro IV engine with EGR and a catalyst/DPF operating on 10 ppm sulphur fuel emitted no measurable particulate matter in the size ranges 35-150 nm and 200-800 nm. However below 20 nm there is up to a one order of magnitude increase in the number of particulates due to sulphate formation. As demonstrated in other papers much of the sulphur in fuel is converted to ultra fine particulate matter.

Clark *et al*²⁹ reviewed the results from Phase 1 of the US Diesel Emission Control – Sulfur Effects Program (DECSE). This paper included a review of results from tests on Diesel Oxidation Catalysts and Diesel Particulate Filters (CR-DPF and CDPF). Key results include:

- Diesel oxidation catalysts can increase PM emissions above engine-out emissions due to conversion of fuel sulphur
- PM reductions with DPFs of 95% are achieved with 3 ppm sulphur fuel; however with 30 ppm fuel this falls to 72% (CR-DPF) or 74% (CDPF) and to near zero with 150 ppm fuel
- Conversion efficiency of fuel sulphur to sulphate is 40-50%
- Regeneration temperatures are around 25 °C higher with 30 ppm than with 3 ppm sulphur fuel.

Salvet *et al* (PSA Peugeot Citroën) ³⁰ have described the particulate reduction system installed on the new Peugeot 607 HDi diesel car. While the system has been designed to operate on current diesel fuels, in tests on fuels containing 500, 300, 50 and <10 ppm sulphur it gives the lowest particulate emission results on <10 ppm sulphur fuel.

5.2. Vehicles equipped with lean burn petrol or diesel engines with NOx adsorbers concepts

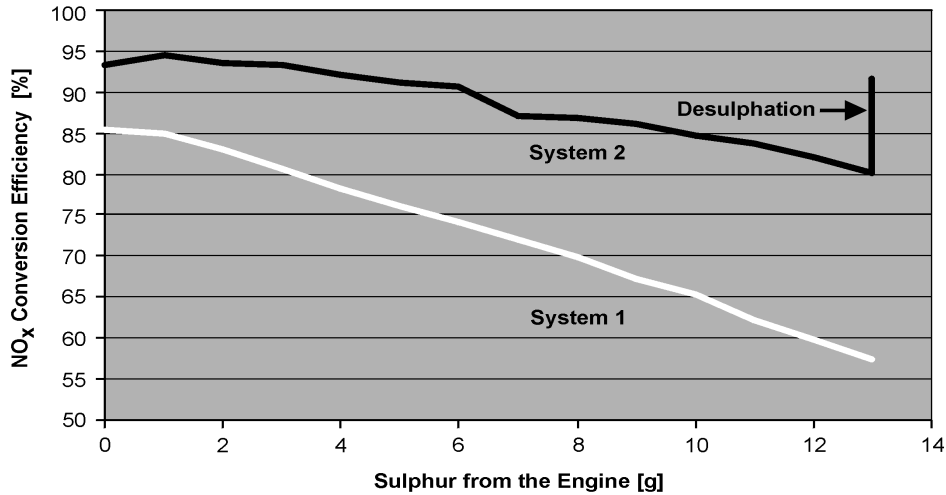
5.2.1. Summary of Recent Important Papers on DeNOx catalysts (active/passive) and NOx adsorber/catalyst

Developments and optimisation of NOx adsorber systems have been and are currently underway for diesel and petrol engines. These technologies have demonstrated NOx conversion efficiencies ranging from 50 to in excess of 90 percent depending on the operating temperatures and system responsiveness, as well as fuel sulphur content ^{31,32}. It is estimated that about a 3% fuel economy penalty will be required to use NOx adsorber technology on diesel engines because of the requirement to inject additional fuel into the system during the NOx regeneration step. However, there is potential to overcome this associated penalty by utilising system engineering and taking advantage of all components. For instance, it is possible that the NOx adsorber can achieve equal or above 90 percent NOx conversion in-use. In that event, the NOx adsorber technology is very attractive because it allows the engine to be calibrated to approach near maximum fuel economy (about 15% better). Although such a calibration results in higher engine-out NOx emissions, with the NOx adsorber controlling over 90 percent of the engine-out NOx emissions, the tail pipe NOx levels of the system can still be extremely low. The gain in fuel economy would compensate or even more than offset the estimated three percent loss in fuel economy mentioned above.

Quissek *et al* (ADA) ³³ showed DaimlerChrysler data showing >80% NOx conversion on a DI petrol engine for 10 000 km on the EU III hot test on 8 ppm sulphur fuel but falling to <30% with 50 ppm sulphur fuel.

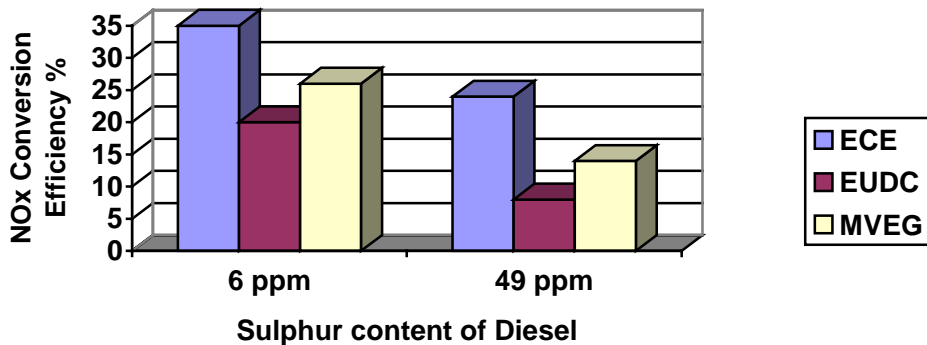
Menne *et al* (Ford/Johnson Matthey) ³⁴ demonstrated the NO_x conversion efficiency of two aged NOx trap systems run on a prototype petrol engine on a test bench with a fuel sulphur content of 200 ppm. (Figure 10) The efficiency of both systems decreases with time as sulphur is accumulated but the later system gives both a higher initial conversion, due to improved thermal durability, and a slower rate of sulphur poisoning. At the end of the test the best system was subjected to a rich exhaust at 650 °C for three minutes to decompose the accumulated sulphates and the initial performance returned. However as explained in section 2.4 above fuel is needed to desulphate the NOx trap, which erodes the fuel economy advantages. This system is not proven on a vehicle under real life testing, the reversibility of sulphur adsorption is problematic (see **Asunama *et al* (Toyota)** ³⁵), a complex control system is required and there are the possibility of emissions of H₂S and SO₂.

Figure 10 Sulphation of NO_x Trap Systems on a Bench Engine, 200 ppm sulphur fuel, evaluated on 60 s lean/ 5 s rich cycle at 350 °C



Lepperhoff *et al* (FEV/AECC) ³⁶ described a vehicle investigation programme that evaluated the influence of diesel fuel sulphur content on the performance of a passive DeNO_x catalyst for NO_x control. The programme was conducted with two specially prepared fuels with different sulphur contents, but where other fuel parameters were unchanged. The NO_x conversion efficiency of the DeNO_x catalyst increased from 14 to 26% over the new European test cycle when the sulphur content of the diesel fuel was reduced from 49 to 6 ppm (see Figure 11).

Figure 11 NO_x Conversion and S Content



Clark *et al* ³⁷ reviewed the results from Phase 1 of the US Diesel Emission Control – Sulfur Effects Program (DECSE). This paper included a review of results from tests on Lean-NO_x Catalysts and NO_x Adsorber/Catalysts. Key results include:

- At 3 ppm sulphur PM is reduced by 16% with a lean NO_x catalyst; with high sulphur fuels PM is increased or reduced insignificantly
- With 150 and 350 ppm sulphur fuels engine-out sulphate emissions increased by 2-5 times that with 3 ppm sulphur fuel. With a lean NO_x catalyst the increase was 10-20 times.

Hachisuka *et al* (Toyota Motor Corp.) ³⁸ describe a new NO_x storage-reduction (NSR) system for lean burn petrol engines being introduced into the Japanese market where sulphur

levels in petrol are much lower. The first generation of NSR catalyst introduced by Toyota gave (after 100 hours of aging on fuel containing 500 ppm sulphur) NO_x conversion one-eighth of the level obtained with a fuel sulphur of 30 ppm - but even at this level NO_x conversion efficiency gradually decreases. Improvements of NO_x conversion of 50% in the new catalyst still give limited application in Europe because of fuel sulphur levels. Toyota say “it is critical that sulphur content in fuels be reduced”.

Bailey *et al* (ASEC) ³⁹ showed that NO_x conversion efficiency after aging for 30 hours at 400°C increases from a peak of <55% at 10 ppm SO₂ in the exhaust to over 95% at 5 ppm and less. A more recent paper ⁴⁰ reports on attempts to protect NO_x adsorbers with sulphur traps reports limited success and concludes that improved SO_x and NO_x adsorbants are required in conjunction with lower sulphur content fuels.

Johnson (Corning Inc.) ⁴¹ published a comprehensive review of 1999 SAE papers on “Gasoline Vehicle Emissions”. He cites the conclusion of **Asunama *et al* (Toyota)** ⁴² that increased sulphate grain size results from higher petrol sulphur levels and this makes NO_x trap desulphation more difficult. After aging for 16 000 km at various sulphur levels they showed that at 8 ppm fuel NO_x conversion efficiency could be instantly returned to >90% by regeneration at 620°C whereas at 500 ppm sulphur 30 minutes regeneration restored conversion from <20% to only 50%. At 30 ppm sulphur 30 minutes regeneration restored NO_x conversion from 75% to <90%.

5.3. Vehicles equipped with Selective Catalytic Reduction (SCR) catalysts

5.3.1. Summary of Recent Important Papers on SCR as stand-alone-solution

SCR for heavy-duty vehicles reduces NO_x emissions by approx. 80%, HC emissions by approx. 90% and PM emissions by approx. 40% in ESC and ETC test cycles, using today’s diesel fuel (max. 500 ppm sulphur) ^{43, 44}. On road fleet tests with SCR technology show excellent NO_x reduction performance over more than 500,000 km of truck operation, and the experience is based on over six million km of accumulated commercial fleet operation ^{45, 46, 47}.

The future European NO_x emission standards can be met with SCR technology with today’s diesel fuel, and with the future 50 ppm sulphur diesel fuel further reduced PM emission will be achieved.

5.3.2. Summary of Recent Important Papers on SCR in combination with other emission control technologies

For further reduction of particulate matter emissions the use of an advanced SCR system or SCR in combination with PM DPFs could be suitable. The combination of SCR with a pre-oxidation catalyst, an hydrolysis catalyst and an oxidation catalyst enables higher NO_x-reduction at low-load/low temperature conditions. For combination technologies applying oxidation catalyst, catalysed filters or any catalyst formulations including precious metals the use of diesel fuel with sulphur lower than 10 ppm is mandatory to keep the formation of H₂SO₄ and sulphates low enough ^{48, 49, 50}.

PM DPFs combined with an SCR-System show significant reduction of both, NO_x and particulate matter ^{51, 52, 53}. The sulphur of the fuel is responsible for sulphate deposits on the DPF surface, which causes an increase of exhaust gas backpressure resulting in a need for more frequent regeneration, and therefore an increase of fuel consumption and CO₂ emissions. To avoid this, sulphur-free fuel (<10 ppm) is required.

6. Conclusions

1. Sulphur in fuel and lubricant adversely affects the performance for emissions control (regulated and unregulated) of all current and future emission control technologies. The degree to which they are affected varies from technology to technology.

For the existing fleet of vehicles lowering sulphur levels in petrol to below 10 ppm would give a reduction in emissions from all three-way catalyst equipped vehicles of up to 20%. US data indicates an enhanced effect on emissions at 30 ppm sulphur and it is known that sulphur affects catalyst performance all the way down to 0 ppm.

New technologies to control ultra fine particulate matter perform better on diesel fuel below 10 ppm. However for technologies incorporating precious metal catalysts fuel sulphur levels significantly below 30 ppm will be necessary to avoid the mass of sulphate particulate matter (formed from the fuel sulphur) exceeding the 2005/08 heavy-duty particulate matter limit values.

The promising NO_x adsorber technology that diesel and lean burn engines need requires sulphur levels significantly below 10 ppm. This will avoid compromising the lower fuel consumption and CO₂ emissions by requiring frequent regeneration to remove the sulphur that is “clogging” the NO_x adsorption capacity.

2. The best option to allow the unconstrained development and introduction of new emission control technologies is to set a specification for sulphur levels at below 10 ppm for introduction as soon as possible. This will allow Member States to introduce tax incentives and for market forces to bring the ultra low sulphur fuels to the market to allow the early introduction of the new technologies.
3. Ultra low sulphur fuels are shown to reduce greenhouse gas emissions by:
 - Reducing CO₂ emissions by allowing low fuel consumption vehicles, e.g. diesel and lean burn/petrol fuel injection, to flourish
 - Reducing emissions of greenhouse gases such as methane (CH₄) and nitrous oxide (N₂O) by allowing catalysts to more efficiently remove them.

7. Sources of Information

Manufacturers of Emission Controls Association (US): <http://www.meca.org/>

Publications available on line include:

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Alliance of Automobile Manufacturers, Inc: <http://www.lowsulfurfuel.com/>

Publications available on line include:

“Influence of the sulphur content in fuel on the fuel consumption and pollutant emissions of vehicles with gasoline and diesel engines” (Report for VDA by FEV)

US Office of Transportation Technologies: <http://www.ott.doe.gov/decse/>

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