Catalyst-Based Diesel Particulate Filters and NOx Adsorbers: A Summary of the Technologies and the Effects of Fuel Sulfur

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EXECUTIVE SUMMARY

On May 17, 2000, the U.S. Environmental Protection Agency (EPA) proposed the new highway heavy-duty diesel engine (HDDE) '2007-Rule' with new emission standards and a diesel fuel sulfur limit. Beginning in 2007, reductions in particulate matter (PM) and nitrogen oxides (NOx) emissions will be 90% and 95% respectively from 2004 MY requirements. The proposed fuel sulfur limit of <15-ppm sulfur is a 97% reduction. The standards proposed are a PM emission limit of 0.01 g/bhp-hr and a NOx emission limit of 0.2 g/bhp-hr. These emission limits, measured under both the transient and steady-state test cycles with not to exceed (NTE) requirements over an engine's operating map, will present significant engineering challenges. In order to achieve these proposed reductions in harmful emissions from the diesel engine, an engineered systems approach will be needed to integrate and combine advanced engine designs, advanced exhaust control technologies, and improved diesel fuel quality. MECA believes that with the lead time provided in the proposal and with the extensive development efforts being made by industry in the areas of engine design and exhaust emission control technology that the challenges will indeed be met as long as very low sulfur fuel is available.

In EPA's proposal, the Agency identifies two emission control technologies – 1) diesel particulate filters employing catalyst technology or catalyst-based diesel particulate filters (CB-DPFs). (Specifically, EPA identified two candidate CB-DPF technologies -- filters which rely on an upstream oxidation catalyst and filters which employ a catalyst applied directly on the filter element for their regeneration function) and 2) NOx adsorbers – as technologies that can provide engine manufacturers the means to meet the proposed requirements. EPA has also requested comments on:

1. The current development/commercial status of these technologies.
2. The effect of fuel sulfur on these technologies in light of the proposed requirements.

This report has been prepared to respond to EPA's request for information on these technologies.

Catalyst based-diesel particulate filter technology (CB-DPF) is commercially available today including the two technologies identified by EPA in its proposal and systems which employ a fuel-borne catalyst (FBC). In fact, two European automobile manufacturers have announced their plans to introduce diesel-powered passenger cars equipped with diesel particulate filters as early as this year – Renault and Peugeot-Citroen. CB-DPF technology is a proven technology as the result of over 40,000 systems being installed and operating successfully on various diesel engine applications throughout the world. The diesel fuel sulfur content is usually either <10-ppm or <50-ppm and some even operate with higher sulfur fuel. Although at the higher fuel sulfur levels, the technology has been applied in limited number of engine applications. These limited applications are characterized by vehicle operation which results in elevated exhaust gas temperatures. At sufficiently high exhaust gas temperatures, the adverse effects of fuel sulfur on the regeneration function of the filter system becomes less critical. However, the '2007-Rule' requires that all engines meet a 0.01 g/bhp-hr PM emission standard under the new comprehensive test cycle with a 'not to exceed' limit for other engine operating modes. This standard and test cycle combination, including the NTE limit, cannot be met with CB-DPF technologies identified by EPA and diesel fuel sulfur content above the 15-ppm fuel sulfur limit proposed. To further explain, the CB-DPF technologies identified by EPA utilize an active catalyst incorporated within the filter or an oxidation catalyst upstream of the filter as the key element in destroying collected (filter cake) solid particles as well as destruction of gaseous pollutants hydrocarbons (HC) and carbon monoxide (CO). The active catalyst needed to achieve the emission limits also is active for the oxidation of sulfur oxides to a species that causes sulfuric acid mist PM to form in the exhaust stream. It becomes increasingly much more difficult with the higher sulfur fuel to limit this mechanism of sulfur dioxide oxidation to a PM sulfate. As sulfur levels rise above a 15-ppm sulfur cap, it will become increasingly difficult and then quickly impossible to achieve the NTE limit requirements for the entire engine speed and load map. The recently completed DESCE program confirmed the direct impact between sulfur levels and sulfate PM formation [1].

In addition to increasing sulfate formation, the level of sulfur in diesel fuel negatively affects the temperature level at which regeneration of the filter occurs. Regeneration is defined as the function of oxidation or combustion of the collected particulate either in a continuous and/or periodic manner. Regeneration assures that the CB-DPF is clean and functional for the entire engine life. The major essential requirement for regeneration is sufficient exhaust temperature to initiate the regeneration process either continuously and/or periodically. One indication of the regeneration function of a CB-DPF system is the system's characteristic balance point temperature (BPT). Under specific operating conditions, the BPT is the temperature at which the rate of PM removal via oxidation or combustion from a filter is equal to the rate at which the particulate is collected. BPT tests were used by DECSE to determine the effect of sulfur on this measure of the regeneration function. Comparative test results with several levels of sulfur showed the negative effect fuel sulfur had on the BPT of each of the two CB-DPF systems tested. It was found that increasing the level of sulfur from 3-ppm to 30-ppm resulted in an increased balance temperatures from 23 ^oC to over 30 ^oC [1]. The magnitude of these increases is very significant.

With sulfur levels above a 15-ppm cap, manufacturers of these CB-DPF filter technologies have expressed serious reservations with meeting the stringent PM standard over the 435,000 useful life requirement without experiencing some durability issues in some conditions – in particular, where engines are operated in cold climates and at high altitude. The diesel exhaust temperature measured in normal climates and those measured in cold climates differ by 20 to 30^o C. This will exacerbate the effect of higher sulfur fuels. As noted above, higher sulfur (30-ppm) fuel increases the BPT. We believe that engineering and optimizing the engine/filter system for all applications and ambient temperature conditions will require the lower activation temperature provided by the low sulfur fuel (<15-ppm sulfur).

Development and optimization work with NOx adsorber technology is progressing at a rapid rate, and as noted, MECA member companies are very optimistic that with the proposed low sulfur diesel fuel, this technology will ready for production in the 2006 timeframe for diesel engines. Indeed, the prospect that EPA will require the very low sulfur diesel fuel in the 2006 timeframe has stimulated an increased commitment on the part of emission control manufacturers to bring this technology forward in diesel engine applications. The design objective for NOx adsorber technology combined with advanced engine designs is to exceed a 90 percent control level from 2004 emission requirements. These levels of control have been demonstrated for certain engine operating conditions [2].

Extensive R&D work centers on optimizing the NOx desorption function and conversion to N_2, formulating and applying the more sulfur resistant active catalyst layer to improve sulfur removal and minimize sulfur regeneration frequency, as well as examining the use of sulfur traps upstream of the catalyst. Our members are making the substantial investments in R&D because they believe these issues can be substantially improved. To make this technology a commercial reality, low sulfur fuel is a requirement.

MECA encourages EPA to finalize the '2007-Rule' at a near zero sulfur limit in the range of a 5-ppm cap to permit the most effective utilization of CB-DPF and NOx adsorber technologies. However, with a 15-ppm cap that will result in an average diesel pool sulfur level of <10-ppm, we believe that catalyst-based diesel particulate filters (CB-DPFs) and NOx adsorbers will be designed to help engine manufacturers meet the proposed 0.2 g/bhp-hr NOx and 0.01 g/bhp-hr PM standards.

INTRODUCTION

Catalytic exhaust control technology will play an important role in future efforts to reduce emissions from diesel engines. The technical challenges are: (1) control of NOx emissions in the lean exhaust environment of a diesel engine where the excess oxygen makes the reduction of NOx to N_2 very difficult and (2) to simultaneously control particulate and hydrocarbon, including toxic hydrocarbon, emissions. CB-DPF technologies have proven successful for applications over a broad range of vehicle applications, driving conditions, and climatic conditions. NOx adsorbers have demonstrated very good NOx control performance – efforts to improve the durability are underway and cooperative programs with engine manufacturers are taking place. The systems integration of both CB-DPF and NOx adsorbers necessary to achieve simultaneous reductions of NOx, particulate, and hydrocarbons in combination with various advanced engine design features will be taking place over the next six years. MECA believes there is sufficient lead-time to accomplish all tasks necessary to meet the proposed requirements of the ‘2007 Rule’.

The adverse effects of sulfur in diesel fuel on catalyst-based exhaust control technologies have been known for years. Current sulfur levels in diesel fuel are a barrier to the commercial introduction of the NOx adsorber. Also, current sulfur levels in on-road diesel fuel inhibits the particulate control efficiencies of CB-DPF technologies identified by EPA in its proposal thus preventing the further optimization of these technologies for maximum effectiveness for PM and hydrocarbon control. Furthermore, current sulfur levels of on-road diesel fuel severely jeopardize the long-term reliability and durability of these filter technologies.

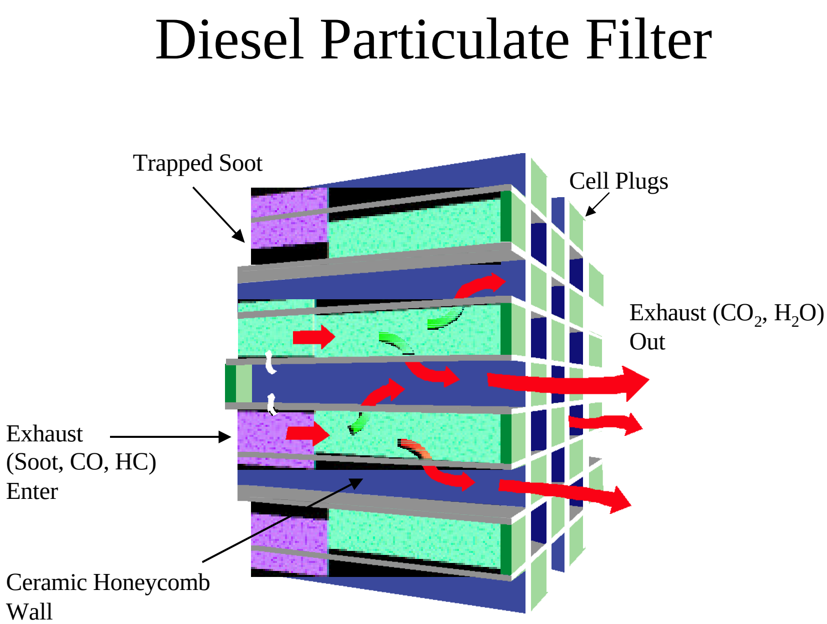
There are two primary goals in meeting the challenges that exist to significantly reduce emissions from diesel engines. These goals are to:

- achieve, within an engineered system, simultaneous reductions in NOx, PM and HC emissions,
- optimize the entire system for engine performance and minimum fuel consumption.

CATALYST-BASED DIESEL PARTICULATE FILTERS

Background and Technology Discussion – CB-DPF systems consist of a filter material positioned in the exhaust designed to collect solid and liquid particulate emissions while allowing the exhaust gases to pass through the system. One type of filter material is shown in Figure 1.

Figure 1



A number of filter materials exist or have been evaluated, including ceramic monoliths, woven silica fiber coils, ceramic foam, wire mesh and sintered metal filters – many other forms are being examined as candidates as well. Collection efficiencies of these various filters range from 50 percent to over 90 percent, but the design of most filters today is to achieve an 80 percent or greater level of particulate control in terms of mass/bhp-hr. A recent study 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% [3]. This latter finding is very important since health experts believe that it is the fine particulate that is carried deep into the lungs of humans and is thought to be the most dangerous size of the PM.

Since the volume of particulate matter generated by a diesel engine is sufficient to fill up and plug a reasonably sized filter over time, some means of disposing of the collected particulate must be provided. This is accomplished by oxidizing (combusting) the particulate to CO_2 and thus regenerating, or cleansing, the filter.

To achieve regeneration of the collected particulate by oxidation or combustion with a diesel particulate filter without any additional activation mechanism, the collected particulate matter in the filter must attain a minimum temperature in the range of 600 to 650 ^{o}C in order to auto-ignite and sustain combustion. However, the engine-out exhaust temperature of a HDDE does not typically achieve these levels and, therefore, is not sufficient to initiate and sustain regeneration of the filters. Therefore, on a HDDE, a filter alone would continue to collect particulate and plug rendering the engine inoperative in a relatively short period of time. To address this issue, catalyst-based diesel particulate filters (CB-DPFs) among other technologies were developed. They act, through catalytic means, to lower the temperature required to auto-ignite the collected particulate (or regenerate) and, therefore, insure that the system operates successfully to cleanse the system of the collected particulate and ensure a ready state for collection of particulate for the life of the engine. One method to achieve spontaneous regeneration of the collected particulate is to apply a catalyst directly on the filter material. This technology is commonly referred to as a "catalyzed" particulate filter. Another means of insuring filter regeneration is to use a catalyst in front of the filter to oxidize NO to NO_2 (a strong oxidant) which then contacts the collected particulate and causes oxidation of the carbon particles. A third technology, relies on the use of a fuel-borne catalyst.

Successful commercial application of CB-DPF technology has occurred in Europe where over 20,000 systems have been installed on trucks, buses, and other vehicles. The systems are achieving particulate emission reductions of up to 90 percent or more while demonstrating excellent durability. Catalytic particulate filters 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 20,000 CB-DPF filters have been installed on off-road diesel engines. Table 1 is a partial list of worldwide CB-DPF applications.

Operating experience in Sweden illustrates that CB-DPF technology is a proven PM control system for diesel engines when low sulfur (<10-ppm) is used. Table 1 outlines the particulate removal efficiencies of seven CB-DPFs used on different applications after having had accumulated significant mileage [4].

As indicated in the table, a variety of applications were investigated in this study including various vehicle applications, different engine sizes and power ratings, and urban and intercity operation or duty-cycles. Very high PM reduction efficiencies were obtained with all the filters, even after high mileage accumulation in actual use. The durability of these systems is directly attributable to the availability of the diesel fuel containing <10-ppm of sulfur as will be discussed later.

Impact of Diesel Fuel Sulfur on Catalyst-Based Diesel Particulate Filters **-** CB-DPFs are effective for removing large fractions of particulate matter – both SOF and solid carbon -- as well as other particles, CO and HC emissions.

Table 1
Durability of a CB-DPF in Field Applications when Used with <10ppm S Fuel

Vehicle Application	Engine Displacement (l) and Power (hp)		Accumulated Distance (mi)	PM Reduction Efficiency (%)	
				Euro ESC[1]	US FTP[2]
Intercity Train	14	430	372,902	89	99
Airport Bus	10	292	357,531	80	n.a.
Express Bus	10	368	304,598	94	94
Mail truck	7	236	294,469	78	93
City Bus	11	260	142,205	93	98
Refuse Truck	7	235	128,342	93	n.a.
Refuse Truck	7	235	65,743	92	n.a.
		Averages:	194,456	88	96

n.a.: not available
1. European Steady Cycle.
2. The U.S. Federal Test Procedure.

Diesel fuel sulfur significantly affects the reliability, durability, and emissions performance effectiveness of CB-DPF technologies identified by EPA in its proposal as a result of:

- sulfur inhibition of catalytic activity,
- sulfur competing with other exhaust constituents in desired chemical reactions, and
- creation of PM through catalytic sulfate formation.

Although CB-DPF technology has been successfully used on applications where the diesel fuel sulfur level has been >15-ppm, several factors were considered. First, CB-DPF technology was applied in those limited situations only after a careful assessment of the engine operating conditions, including the exhaust temperature profile, and ambient conditions and it was determined that in those specific applications the filter system could function with sulfur in the fuel above 15-ppm. It is quite a different matter to conclude, therefore, that CB-DPF can be applied to all the highway diesel heavy-duty engines covered by EPA's proposed rule with vastly different engine performance parameters, usage patterns, and ambient conditions. Second, in those applications where CB-DPFs have been used with >15 ppm sulfur, the design control target was not anywhere close to a 0.01 g/bhp-hr standard measured over the enhanced FTP or to maintain performance for 435,000 miles.

Impact of Fuel Sulfur on the EPA Identified CB-DPF Technologies' Reliability and Durability -- The impact of sulfur on the reliability and durability of the CB-DPF technologies identified by EPA is two-fold: the presence of elevated sulfur increases the activation temperature for the regeneration function and longer-term exposure can degrade catalyst performance due to catalyst sulfur inhibition thereby decreasing exotherms which would otherwise benefit the regeneration function. The inhibition also degrades gaseous emissions control performance.

As previously mentioned, diesel engines are used in a variety of applications and are subject to a wide range of operating conditions including:

- long-haul trucks, intercity buses, urban buses, refuse vehicles, urban delivery vehicles, light-duty trucks, air port shuttles;
- urban, suburban, and rural driving cycles;
- high altitude operation; and
- cold and warm weather conditions.

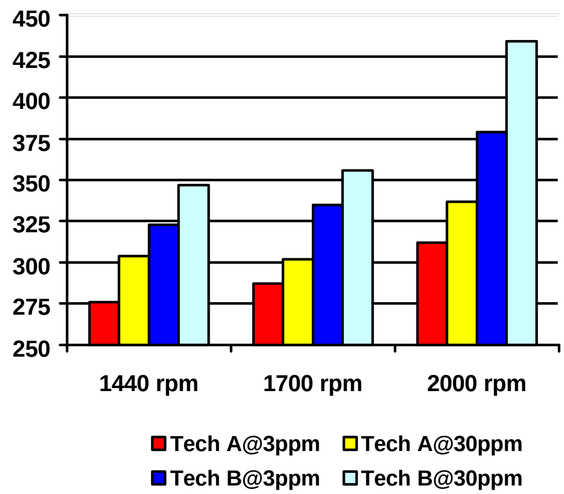
Given the wide range of operating conditions, the most favorable regeneration function conditions are needed to insure the successful application of CB-DPF technologies identified by EPA to the various vehicle applications and driving conditions that will be encountered. This requires low levels of sulfur in diesel fuel as discussed below.

It is important to insure that regeneration of a CB-DPF is functional for all engine-operating conditions. Regeneration can be continuous and/or periodic – the important feature is that the collected particulate is oxidized and the condition of the CB-DPF is returned to the ready state over-and-over for the entire life of the engine. The major parameter is exhaust gas temperature. While idling, the exhaust temperature is low and regeneration will not occur. However, a properly designed CB-DPF would endure the idle condition for days without approaching a 'full' condition.

One measure of the regeneration function of a filter system is the 'balance point temperature' (BPT). This is the exhaust gas temperature at which the rate of particulate deposition is equal to the rate of removal through oxidation. The BPT varies depending on engine operation and other parameters. The balance point temperatures of a filter system are an indication of the regeneration function of a filter system. The BPT can be used for comparing a catalyst variable when the test conditions and engine operating conditions are the same. For a specific CB-DPF system, the BPT is one measure of the effect of one parameter on the regeneration function. Such is the case for measuring the effect of diesel fuel sulfur on the effectiveness of a single system. The lowest balance point temperature is most desirable.

The effects of fuel sulfur level on the balance point temperatures for two different CB-DPF technologies were investigated as part of a joint government/industry program [1]. The results of the investigations for 3-ppm and 30-ppm diesel fuel sulfur levels are shown in Figure 2. Comparisons of the data shown and any conclusions to be drawn should only be made within a specific technology provided that the engine operating conditions, engine back pressure, and space velocity were consistent for each sulfur test point.

Figure 2
CB-DPF Balance Point Temperatures as A Function of Fuel Sulfur
(^{o}C)



As indicated in Figure 2, the balance point temperatures of the systems increased from 15 ^{o}C to 55 ^{o}C when tested with 30-ppm sulfur fuel as compared to 3-ppm sulfur fuel depending on engine speed. On average, the balance point temperatures were increased by 28 ^{o}C. This would imply an average increase of approximately 7 ^{o}C, 14 ^{o}C, 19 ^{o}C and 23 ^{o}C for fuels containing 8-ppm, 15-ppm, 20-ppm and 25-ppm sulfur respectively, assuming a linear relationship between balance point temperature increase and fuel sulfur concentration.

Engines operating in cold climates are characterized by lower exhaust temperatures than when operating in warmer climates. The difference can be as much as 50^{o}C. Because the engine/CB-DPF system has to be engineered and optimized for all applications and ambient temperature conditions, it is essential that low sulfur fuel (<15-ppm) be required to provide the lowest activation temperature for the regeneration function to insure reliability and durability.

To illustrate this point, the experience gained in Europe where over 20,000 systems have been installed on vehicles demonstrates the key role of low sulfur fuel to insure proper filter performance [4]. In Sweden where <10-ppm sulfur fuel is used, there have been no reported filter failures, whereas, in Finland where the fuel is capped at 50-ppm sulfur, 10 percent of the filters have failed in the winter months. The filter system manufacturer has concluded that the field failures occurred because of the higher fuel sulfur levels and the resultant increases in the balance point temperature combined with decreased exhaust gas temperatures due to the cold climatic conditions reduced the regeneration function of the systems to the point where regeneration did not occur. This type of situation could also happen in the northern states of the U.S. and Canada, if fuel sulfur were capped at 50-ppm.

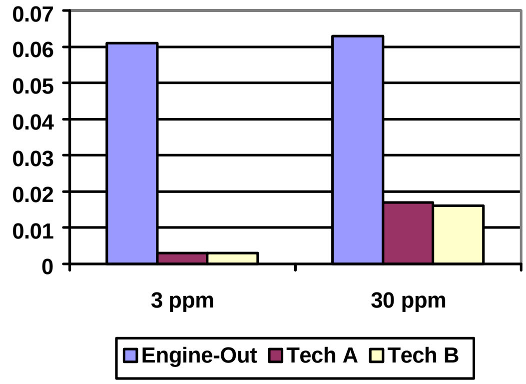
Another situation that requires the most favorable regeneration function conditions, and hence lowest fuel sulfur level, is operation at high altitudes. Operating a diesel engine at high altitudes increases the PM burden on a CB-DPF because of the decreased oxygen content of the engine intake air. This results in a higher PM emission rate and lower oxygen levels in the exhaust. The higher PM emission rate results in a higher PM accumulation rate in the filter. The reduced oxygen level in the exhaust also impedes the rate of regeneration. As noted above, this would be further exacerbated in the winter months. Again, it is important not to lose the lower activation temperature provided by low sulfur fuel (<15-ppm).

Catalyst inhibition due to long term exposure to higher sulfur levels is also of concern. Sulfur causes inhibition of catalyst performance for the oxidation of HC and CO thus decreasing the exotherm generated by these exothermic reactions. Thus the temperature within the CB-DPF is lower than optimum. The low sulfur fuel (<15-ppm) diminishes this negative effect. The experience in Sweden has proven that the systems operate reliably and are durable as noted in Table 2 when <10-ppm sulfur fuel is used.

In order for CB-DPF technologies identified by EPA to be applied nationwide, the systems will be required to operate on a broad range of vehicles, in winter months, in urban centers, at high altitudes, for 435,000 miles, and under many other possible situations. To insure reliable and durable performance, the lowest fuel sulfur level possible will be needed. Even with the low sulfur fuel, thermal management strategies will be needed to insure that the maximum available exhaust gas temperature is provided to the filter system. Considerable challenges exist to engineer and optimize a reliable and durable system even with a 15-ppm S cap. We believe strongly that these challenges will be met with system engineering and integration of the total system by combining advanced engine modifications and thermal management technologies that are currently emerging.

Effect of Fuel Sulfur on the EPA Identified CB-DPF Technologies' Emissions Performance -- Fuel sulfur content is directly related to a decrease in the effectiveness of CB-DPF technologies identified by EPA in controlling PM emissions. This is due to the nature of catalysts employed in CB-DPF technologies. The aggressive catalyst designs incorporated into effective CB-DPF technology to achieve efficient oxidation of HC and CO and the initiation of carbon particulate combustion also will easily oxidize exhaust SO_2 to SO_3 which combines with water in the exhaust system to form sulfuric acid mist – a PM emission. Sulfuric acid PM is created by the catalytic function of CB-DPFs. The impact of this reaction on PM emissions and the effectiveness of CB-DPF technologies are dramatic as was shown in the DECSE study [1]. Figure 3 shows the effectiveness of two CB-DPF technologies when tested with 3-ppm and 30-ppm sulfur fuel over the European OICA test cycle.

Figure 3
Increased PM Emissions due to Sulfation (g/bhp-hr)



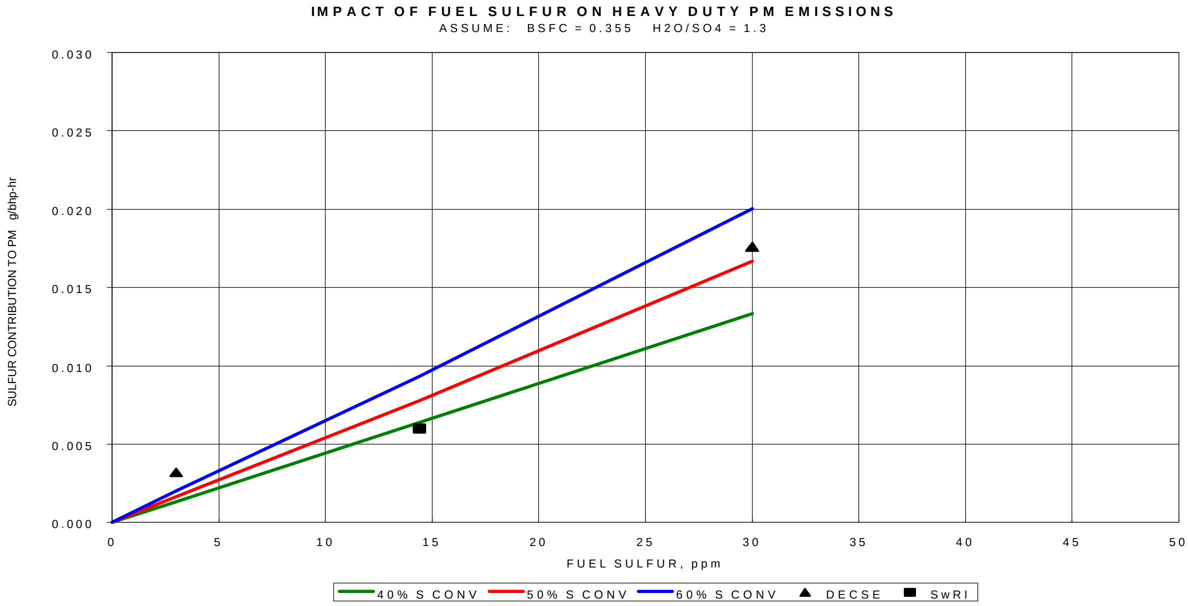
Source: DECSE, 2000

As illustrated, a 0.01 g/bhp-hr PM emission standard cannot be met over this test cycle with fuel containing 30-ppm sulfur. Figure 4 illustrates the calculated PM emissions as a function of fuel sulfur content over the OICA test cycle assuming a 40 percent, 50 percent, and 60 percent conversion of SO_2 to H_2SO_4 by a CB-DPF [5]. The actual measured results generated from the DECSE program and an independent SwRI study are also shown. As can be seen, the results from the DECSE program and the independent SwRI study correlate reasonably well with the calculated 50 percent conversion curve.

It is evident from examination of the 50% conversion curve illustrated in Figure 4 that with the 15-ppm fuel sulfur cap, the 0.01 g/bhp-hr PM emission standard can be achieved. However, the standard would be exceeded at fuel sulfur levels of approximately 18-ppm and higher.

A major benefit of CB-DPF technology is the substantial reductions that are achieved in CO and HC including those HC species that are classified by health officials as toxic air contaminants. A study carried out on a 1998 MY, 400 hp diesel engine found that CB-DPF technologies can reduce CO, HC, and toxic HC emissions by greater than 60 percent, 90 percent, and 80 percent, respectively [6]. Long-term exposure to elevated sulfur levels in diesel fuel will inhibit catalyst performance and, consequently, its ability to reduce these emissions effectively as the systems accumulate mileage.

Figure 4


IMPACT OF FUEL SULFUR ON HEAVY DUTY PM EMISSIONS
ASSUME: BSFC = 0.355 H2O/SO4 = 1.3
SULFUR CONTRIBUTION TO PM g/bhp-hr
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
5
10
15
20
25
30
35
40
45
50
FUEL SULFUR, ppm
40% S CONV
50% S CONV
60% S CONV
DECSE
SwRI

NOx ADSORBERS

Background and Technology Discussion – NOx destruction requires removal of the oxygen (O) from the NOx molecule leaving nitrogen which combines with another nitrogen molecule to form gaseous N_2. NOx emission control of diesel engine exhaust is inherently difficult because the oxygen-rich exhaust environment of diesel engines makes reduction (removal of oxygen) hard to achieve catalytically. Also this reaction requires a reductant (HC, CO or H_2) and there is a lack of sufficient reductant(s) (primarily in this case hydrocarbon reductants) necessary to reduce the NOx to nitrogen. Direct NOx decomposition is thermodynamically attractive. However, the activation energy is very high for this method. Therefore, the lean NOx control technologies employed in diesel exhaust must rely on catalytic reaction between NOx and a reducing agent. Success with this technology has been slow to develop.

Another NOx control technology, called a NOx adsorber, has made significant progress and is currently being optimized for diesel engine emission control. NOx adsorber technology is currently being applied to gasoline-powered vehicles and the results are impressive. In fact, Volkswagen, Daimler-Chrysler, and Peugeot-Citroen are at different stages of commercially introducing NOx adsorber catalysts on some of their models powered by lean-burn gasoline engines. While the application of NOx adsorber technology to diesel engines offers different challenges than gasoline applications, the experience being gained in gasoline applications is an important compliment to NOx adsorber technology developments on the diesel side. Reductions in engine out NOx emissions of as high as 90 percent has been demonstrated and it appears possible to develop the system into a functional and durable NOx control system for diesel exhaust. The results of the Diesel Vehicle Emission Control – Sulfur Effects (DVECSE) program run at Oak Ridge National Laboratory showed NOx adsorber technology can achieve NOx emission reductions in excess of 90% for a light-duty diesel- powered vehicle [7]. However, NOx adsorbers are particularly sensitive to sulfur and require low sulfur diesel fuel.

NOx adsorber development is a new catalyst advance for removing NOx in a lean (i.e., oxygen rich) exhaust environment for both diesel and gasoline lean-burn direct-injection engines. With this rapidly developing technology, NO is catalytically oxidized to NO_2 and stored in an adjacent chemical trapping site as a nitrate. The stored NOx is removed in a two-step reduction step by temporarily inducing a rich exhaust condition. NOx adsorbers employ precious metal catalyst sites to carry out the first NO to NO_2 conversion step. As stated above, the NO_2 then is adsorbed by an adjacent alkaline earth oxide site where it chemically reacts and is stored as a nitrate. When this storage media nears capacity it must be regenerated. This is accomplished in a brief NOx regeneration step. The stored NOx is easily released by creating a rich atmosphere with injection of a small amount of diesel fuel. The released NOx is quickly reduced to N_2 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 5 and 6).

Figure 5

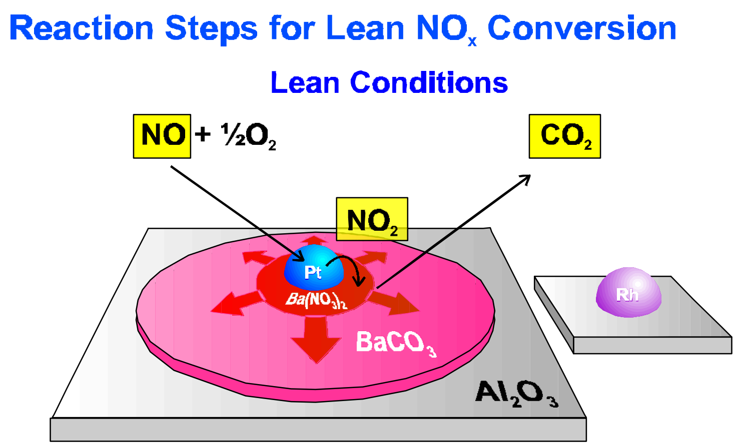


Figure 6

As discussed above, under normal diesel engine operation, the NOx adsorber captures the NOx emissions. In order to reduce the trapped NOx to nitrogen, called the NOx regeneration cycle, the engine must be operated rich periodically for a short period of time (a few seconds). This cycling is also referred to as a lean/rich modulation. The rich running portion is of short duration and can be accomplished in a number of ways. In-cylinder methods to obtain the rich condition usually include some combination of:

- intake air throttling,
- exhaust gas recirculation; and
- post combustion fuel injection.

In-exhaust fuel supplementation often in conjunction with by-pass valves or other controls to minimize the exhaust oxygen content are under consideration as another method to achieve the required rich conditions.

Development and optimization of NOx adsorber systems has been and is currently underway for diesel engines. Adsorber systems 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 diesel fuel sulfur content [8,9].

An important consideration in designing a NOx adsorber emission control system is the effect on fuel economy. For a diesel engine, it has been reported that the overall reaction stoichiometry during the NOx regeneration step requires 0.051 moles of $C_{16}H_{34}$ to convert one mole of NO to N_2 assuming that CO is used as the reductant in the reaction [10]. Assuming an engine characterized by brake-specific fuel consumption of 0.35 lb/bhp-hr and an engine-out NOx emission rate 2.5g/bhp-hr, the fuel economy penalty associated with the NOx regeneration step would be 0.6% under ideal conditions. Oxygen in the exhaust stream would increase the amount of fuel required to complete the NOx regeneration step, but it is unclear at this point in time what the actual fuel economy penalty will be to carry out the NOx regeneration step. However, there is potential to overcome this associated penalty by utilizing system engineering and taking advantage of all components. For instance, an approach to minimize the fuel economy penalty associated with the NOx regeneration step would be calibrate the engine for maximum fuel economy at points on the engine map where the NOx adsorber is performing at its peak conversion efficiency. Although such a calibration results in higher engine-out NOx emissions, with the NOx adsorber functioning at its peak conversion efficiency, NOx emissions could still be kept low.

Recent work under the DECSE program illustrates the importance of an engineered systems approach when designing an emission control system using NOx adsorber technology [2]. Initial testing of the performance of the NOx adsorbers used in the test program is shown in Figure 7. As can be seen, the conversion efficiency of the adsorber across the temperature range tested was marginal. Changing the lean/rich modulation to the cycle shown in Table 2 improved the performance dramatically as also shown in Figure 7 where conversions up to 90 percent were achieved across a broad operating temperature were achieved.

Figure 7
NOx Conversion Potential of NOx Adsorber Technology

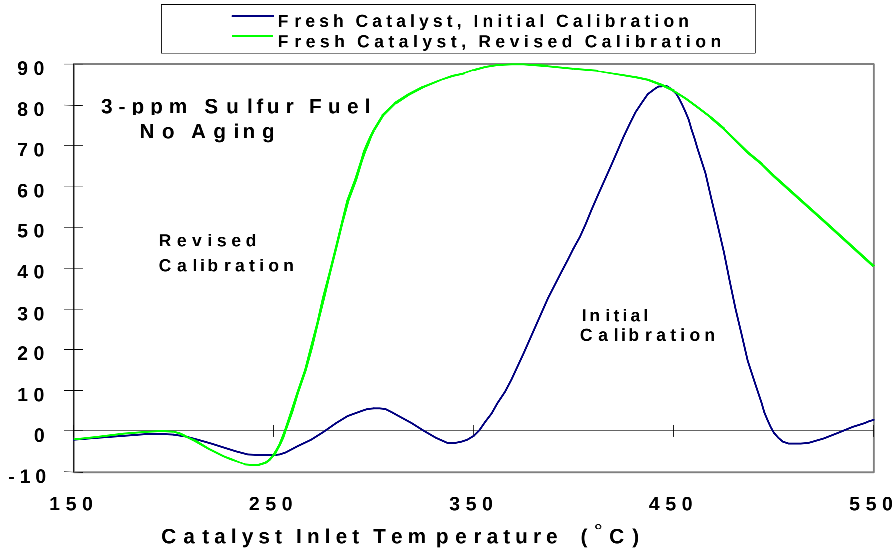


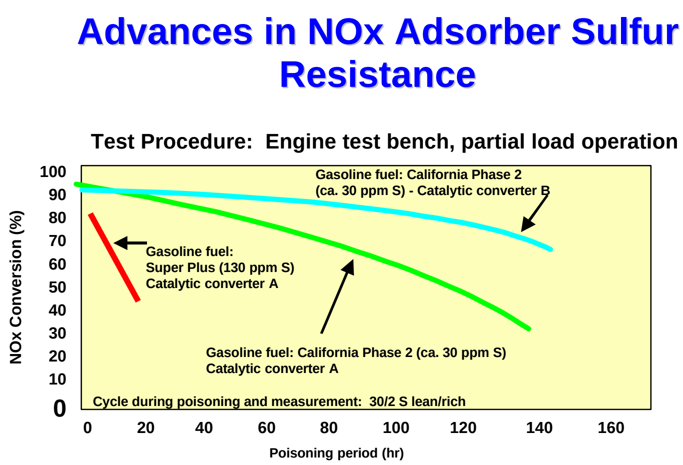
Table 2: Lean/Rich Modulation Employed in the DECSE Program

Temperature Point [°C]	150	200	250	300	350	400	450	500	550
Lean Timing	60	60	60	60	60	60	60	70	80
Rich Timing	2	2.5	3	3.5	4	4	4	4	4

The rich running conditions were achieved using a combination of intake air throttling, exhaust gas recirculation, and post combustion injection for both the initial lean/rich modulation calibration and that shown in Table 2. Close examination of the initial calibration highlighted that the engine calibration used during rich operation did not generate adequate quantities of the appropriate reducing agents in the exhaust to properly desorb and then subsequently reduce the NOx emissions at some of the engine temperature operating points indicating the importance of proper engine calibration for the NOx regeneration step.

The emission control industry continues to invest considerable efforts in further developing NOx adsorber technology. Specifically, formulations and on-vehicle configurations that improve low temperature performance are being investigated, catalyst materials that allow for lower temperature sulfur removal are being sought, advances in thermal durability have been made, and continued efforts are being made to improve sulfur resistance, for instance, as shown in Figure 8 [11].

Figure 8

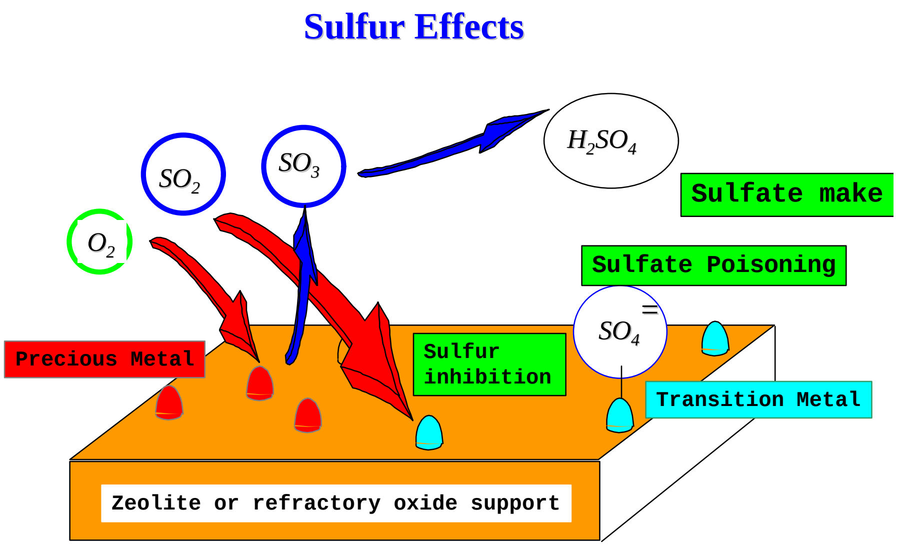


Source: Quissel et al, 1998

NOx adsorber technology offers tremendous potential for providing a high level of NOx reduction across a wide range of operating conditions (temperature and NOx concentration) -- conditions which are consistent with the diversity in engine-out exhaust associated with both light- and heavy-duty diesel applications.

Impact of Diesel Fuel Sulfur on NOx Adsorbers (NOx "Traps") - To operate effectively, NOx adsorber technology must remain stable for extended periods during which the exhaust environment modulates between rich and lean conditions. Given the similarities in the chemical properties of gaseous sulfur and nitrogen oxides, the NOx adsorber is extremely sensitive to sulfur poisoning, and consequently, sulfur poisoning poses the most serious challenge to the durability of the NOx adsorber technology. Specifically, SO_2 derived from the sulfur in the fuel can catalytically react with oxygen and then with the NOx storage components, such as $BaCO_3$, forming stable sulfates ($BaSO_4$) and rendering the NOx adsorbing capabilities of the system ineffective. In addition, SO_2 can be catalytically converted to sulfate in the exhaust stream resulting in higher particulate emissions. These two effects are illustrated in Figure 9.

Figure 9



Impact of Fuel Sulfur on NOx Adsorber Reliability and Durability – The exhaust temperature of diesel engines is typically less than 550 ^{o}C and the operating temperature window for NOx adsorber technology typically ranges from 200 to 550 ^{o}C. These temperatures are insufficient for thermal decomposition of barium sulfate ($BaSO_4$) or its complete reduction during the periodic rich excursions needed for adsorber NOx regeneration. As a result, sulfur accumulates on the NOx adsorber catalyst and eventually the NOx storage (or trapping) is completely lost. Therefore, NOx adsorbers will require desulfurization even when low fuel sulfur levels exist.

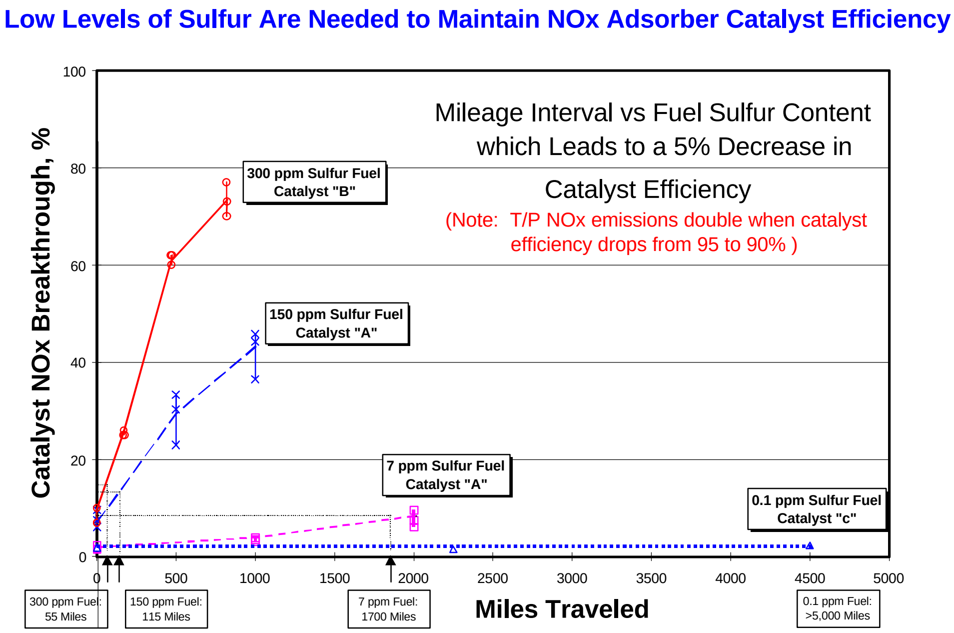
As noted above, the NOx adsorber can only work with low sulfur fuel. Fuel sulfur is converted to SO_2 in the engine. SO_2 is readily oxidized in the NOx adsorber system to SO_3 on the same catalyst site designed to oxidize NO to NO_2. This sulfur species (SO_3) easily reacts with the NOx storage media to form a very stable sulfate form. Thus the NOx storage capacity declines in direct relation to sulfate formation. Stored sulfate is not regenerated during the NOx regeneration step. A special high temperature desulfurization step is needed requiring special engine operating conditions. Eventually even the low sulfur levels of low sulfur fuel and consumed lubricating oil will require that the sulfur be removed (desulfurization) to regain catalyst performance. The sulfur regeneration step is more difficult than the NOx regeneration step. It is accomplished by creating an exhaust gas temperature to the NOx adsorber above 600^{o}C and providing a rich exhaust gas composition. The sulfur regeneration step takes several minutes whereas the NOx regeneration step takes a few seconds. The sulfur regeneration step has negative effects on fuel economy and potentially induces thermal stress on the engine depending on how it is achieved. In work currently being carried out as a continuation of the DECSE program, a catalyst upstream of the NOx adsorber is used to facilitate attainment of the required desulfurization temperature downstream of thermally sensitive engine components like the turbocharger.

Low sulfur fuel is needed for efficient operation of the NOx adsorber system to reduce the frequency of desulfurization events. This will minimize the associated fuel penalty, thermal impacts on the engine and catalyst system, and off-cycle emissions. The NOx regeneration step of the NOx adsorber is a *functional step* of the system. The sulfur regeneration step is a *maintenance step* that needs to be minimized to insure the fuel economy and the reliable and durable operation of diesel engine emission control system. Because of the required duration of the desulfurization event, much higher quantities of diesel fuel are consumed when compared the amount of fuel consumed for NOx regeneration. This can also expose the catalyst and engine components, e.g. the turbocharger, to high temperatures for periods of time which may result in thermal degradation. Therefore, it is imperative that the frequency of desulfurization, which is a function of fuel sulfur level, be minimized to insure fuel economy and reliable and durable operation.

The sulfur poisoning effect of NOx adsorbers has been reported for NOx adsorber technology developed for direct injection gasoline-powered engines, but the effects are equally applicable for this technology on diesel engines. Despite the improvements in sulfur resistance previously mentioned, even very low levels of sulfur in diesel fuel present challenges for NOx adsorber technology. This is illustrated in Figure 10 [5].

As illustrated in Figure 10, with very low levels of sulfur (0.1-ppm), the NOx adsorber eliminates in excess of 95 percent of the NOx emissions for in excess of 4,500 miles. However, exposure to just 7-ppm of sulfur in the fuel causes a reduction in efficiency of 5 percent in less than 2,000 miles. Therefore, even at low sulfur levels desulfurization will be required. However, it is imperative that the frequency, which is a function of fuel sulfur level, be minimized to insure reliable and durable operation of the diesel engine and catalyst system. In another study, the authors made several important conclusions [12]. First, sulfur poisoning of the NOx adsorber catalyst is more severe at lower temperatures (400-500 ^{o}C) than at higher temperatures (700 ^{o}C). Second, reductions in the sulfur concentrations can significantly reduce the rate of sulfur poisoning, and as a result, prolong the operation of the NOx adsorber catalyst. Finally, even after rich desulfurization at elevated temperatures, certain barium sites appeared to be permanently poisoned which jeopardizes long term durability. This also necessitates more frequent desulfurization as the sulfur more quickly poisons the remaining active sites which results in a compound, negative effect.

Figure 10
Mileage Accumulation versus Sulfur Level



In another study carried out by Mercedes-Benz, the impact of fuel sulfur level on NOx adsorber durability during extended vehicle operation was evaluated [10]. This work was carried out on a lean burn gasoline engine, but the conclusions are equally applicable to the diesel application. When operated on fuel containing 50-ppm sulfur, over a period of operation corresponding to 2000 kilometers, average NOx conversion efficiency measured over the European driving cycle (MVEG hot-tests) declined from 90% to 80%. Under the same operating conditions except utilizing a fuel containing 8-ppm sulfur, NOx conversion efficiency was maintained at a level greater than 80% for 10,000 km. This study also suggests that a higher desulfurization frequency would be required for 50-ppm sulfur fuel.

The conditions required for desulfurization of a NOx adsorber are arduous on the diesel engine itself and the NOx adsorber where some degree of thermal sintering can be expected. Minimizing the exposure of the engine and catalyst to these arduous conditions will allow manufacturers to adequately design for the deterioration of the NOx adsorber over time while still meeting a NOx emission limit of 0.2 g/bhp-hp over the full useful life of the diesel engine. The more often desulfurization must occur, the less likely that this emission level can be met for the full useful life of the engine.

These studies outlined above clearly show that high diesel fuel sulfur levels could negatively impact the durability of promising NOx adsorber technology. The lower the fuel sulfur level, the better, and levels at or below 5-ppm would indeed be beneficial. However, manufacturers of NOx adsorbers believe that, although challenges exist to insure long term reliability and durability at levels averaging <10-ppm and never exceeding 15-ppm, the technology can be successfully applied. This will not be without challenges. However, with seven years to further develop the technology and to properly integrate the technology with advanced diesel engine designs, the industry believes that these challenges can be met. At levels in excess of 15-ppm, manufacturers do not believe that these challenges can be met in a manner required to offer reliable and durable performance while maintaining fuel economy and driveability of the diesel engine in the broad range of vehicle applications and driving cycles that will be encountered.

Effect of Fuel Sulfur on NOx Adsorber Emissions Performance -- The joint government/industry DECSE program [2] which investigated the effects of different diesel fuel sulfur levels on an advanced NOx adsorber formulation concluded:

"Although the initial engine calibration resulted in lower adsorber catalyst conversion efficiency than anticipated, the DECSE NO_x adsorber technical committee decided that data on the effects of sulfur could nonetheless be investigated in the temperature regions where the engine calibration resulted in higher conversion efficiencies. Therefore, testing proceeded with the initial, less than optimal calibration.

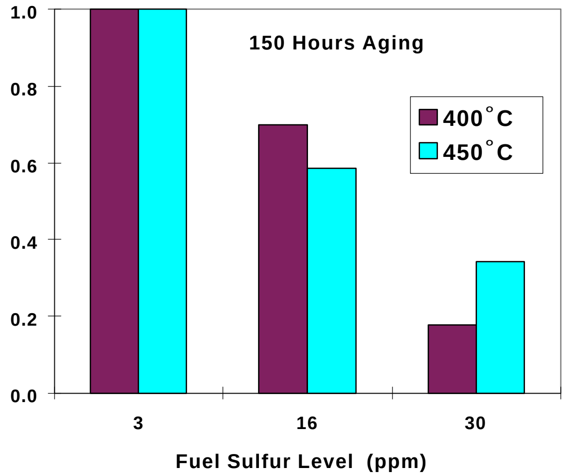
The interim conclusions are:

- *The effect of fuel sulfur content on NO_x adsorber conversion efficiency is shown in Figure 11. The figure illustrates the effect of fuel sulfur on relative NO_x conversion efficiencies at 400° and 450°C after 150 hours of testing. Compared to 3-ppm sulfur fuel at 150 hours, both 16- and 30-ppm sulfur fuels resulted in significant performance declines.*

- *Although testing with 3-ppm sulfur fuel showed an initial decline in adsorber catalyst conversion efficiency, the performance subsequently appeared to stabilize, out to the 250-hour period. Further aging would be required to determine adverse affects of 3-ppm sulfur fuel beyond this point*."

As indicated in Figure 11, increasing the diesel fuel sulfur level from 3-ppm to 16-ppm decreased NOx conversion efficiency from 30 to 40 percent in just 150 hours. Using 30-ppm sulfur caused a decline in conversion efficiency from 70 to 80 percent in this same time period. The magnitude of decline in conversion efficiency found for 16-ppm sulfur would be nearly identical for fuel containing 15-ppm sulfur, dramatically increasing the required frequency of desulfurization as compared to a fuel containing 3-ppm sulfur.

Figure 11
Fuel Sulfur Effects on Relative NOx Conversion Efficiency



SUMMARY AND RECOMMENDATIONS

Significant reductions in PM and NOx emissions from HDDEs will require a "systems approach" utilizing advanced engine designs, advanced and integrated exhaust control technologies, and low sulfur fuel.

Low sulfur diesel fuel is required for the CB-DPF technologies identified by EPA in its proposal and NOx adsorber technologies to be effectively used to achieve EPA's proposed PM and NOx emission requirements of 0.01 g/bhp-hr and 0.2 g/bhp-hr, respectively, for 435,000 miles in the broad application of on-road diesel engines, with the diverse driving cycles that will be encountered, under all climatic conditions, and high altitudes. MECA believes that a diesel fuel sulfur cap no higher than 15-ppm will be required. There will be challenges, but we believe with the lead-time provided, these challenges can and will be met.

CB-DPF technologies are available and in-use in significant numbers today. It has been proven that CB-DPF technology can substantially reduce PM emissions from diesel engines. The CB-DPF technologies identified by EPA require a fuel sulfur cap of 15-ppm to help achieve the proposed 0.1 g/bhp-hr PM standard across the nation under all the operating conditions that will be encountered. It has been demonstrated that NOx adsorber technology can be applied to diesel engines to obtain NOx emission reductions of 90 percent or more and it is expected that an acceptable fuel economy penalty will be associated with the use of the technology. Tests to prove durability of the NOx adsorber system are planned over the next several years. NOx adsorber technology is extremely sensitive to sulfur in fuel. Although sulfur regeneration procedures (desulfurization) have been developed, it is important for the long-term reliability and durability of the technology and for the efficient operation and durability of the diesel engine that these sulfur regeneration procedures be as infrequent as possible. NOx adsorber technology requires the lowest fuel sulfur level possible. MECA still strongly recommends that a 5-ppm cap be considered to provide this new NOx control technology the best conditions under which to operate. But MECA is confident that with the lead time available and continued development that a 15-ppm sulfur cap will enable the use of the technology.

New production facilities or revisions to existing facilities for both technologies will require 6 to 18 months to be operational. This lead-time is not expected to limit formula developments during this period. The CB-DPFs are currently produced in limited volumes. Substrate manufactures and catalyst manufactures are currently considering methods for large scale manufacturing. NOx adsorber technology will not be sufficiently different from current catalyst emission control products with the exception of size and can take advantage of existing production facilities.

MECA encourages EPA to establish a near zero sulfur requirement in the range of a 5-ppm sulfur cap to permit the most effective utilization of CB-DPF and NOx adsorber technologies. However, with a 15-ppm sulfur cap that will result in an average diesel pool sulfur level of <10-ppm, we believe that CB-DPFs and NOx adsorbers can be designed to help engine manufacturers meet the proposed 0.2 g/bhp-hr NOx and 0.01 g/bhp-hr PM standards.

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ACRONYMS and ABBREVIATIONS

A/F	air/fuel
Al_2O_3	aluminum oxide
ARB	California Air Resources Board
$Ba(NO_3)_2$	barium nitrate
$BaCO_3$	barium carbonate
bhp-hr	brake horsepower hour
CIDI	compression ignition direct injection
CO	carbon monoxide
$CO(NH_2)_2$	urea
CO_2	carbon dioxide
CB-DPF	catalyst-based diesel particulate filter
CRT	continuously regenerating trap
Cu	copper
Cu-ZSM-S	copper zeolite
DeNOx	lean NOx
DOC	diesel oxidation catalyst
DOE	U.S. Department of Energy
DPF	diesel particulate filter
EPA	U.S. Environmental Protection Agency
FBC	Fuel-Borne Catalyst
FTP	Federal Test Procedure
H_2	hydrogen
H_2O	water
HC	hydrocarbon
HDE	heavy-duty engine
Ir	iridium
LDV	light-duty vehicle
MECA	Manufacturers of Emission Controls Association
mg	milligram
mg/s	milligram per second
MVEG	motor vehicle emission group
N_2	nitrogen
NH_3	ammonia
nm	nanometer
NO	nitrogen oxide
NO_2	nitrogen dioxide
NOx	oxides of nitrogen
O_2	oxygen
PAH	polyaromatic hydrocarbon
Pd	palladium

PM	particulate matter
PNGV	Partnership for a New Generation of Vehicles
ppm	parts per million
Pt	platinum
Rh	rhodium
S	sulfur
SCR	selective catalytic reduction
SI	spark ignition
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SOF	soluble organic fraction
SUV	sport-utility vehicle
SV	space velocity
TWC	three-way catalyst
V_2O_5/TiO_2	vanadium oxide/titanium oxide
^oC	degrees Celsius