The Impact of Gasoline Fuel Sulfur on Catalytic Emission Control Systems

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EXECUTIVE SUMMARY

Catalytic emission control systems, used on passenger cars since 1975, have played a key role in substantially reducing exhaust pollutants from motor vehicles. Exhaust emission control is influenced not only by the emission control system, but by engine design and fuel quality as well. Since 1975, catalyst technology and engine designs have continued to advance dramatically. Changes in fuel quality, most notably eliminating lead in gasoline, have also contributed to achieving very low vehicular emissions. The level of sulfur in gasoline, however, has remained at a relative constant level since the 1970s in the U.S. with the average being about 50 to 300 parts per million (ppm), with a range between 30 to 1000 ppm. In this respect, gasoline sulfur content has not kept pace with engine and catalyst developments.

Sulfur in gasoline inhibits the emission control performance of catalyst technology. A variety of factors influence the degree of this impact and the extent to which it is reversible. These factors include the sulfur level in the gasoline, the catalyst composition, the catalyst design, the catalyst location, the type and control of fuel metering, the engine calibration, and the manner in which the vehicle is operated.

Recent studies have shown that the effect of sulfur inhibition has a greater impact on the emission control systems of vehicles designed to meet LEV and ULEV-type standards and that the effects of sulfur may not be completely reversible on these vehicles. While catalyst manufacturers are continuing design efforts to reduce the effects of sulfur on catalyst technology, the growing body of technical information strongly indicates that reducing the sulfur level in gasoline would have a significant benefit to the emission control performance of past, current and future emission control systems.

Therefore, MECA supports changing the fuel sulfur specifications at the very least to a maximum cap of 80 ppm and an average of 30 ppm. The change should be brought about as quickly as possible, although adequate lead-time should be provided to implement these changes and the limits should include compliance flexibility strategies similar to those used in the past to facilitate cost effective compliance. Finally, MECA recommends that an evaluation be initiated to determine the additional benefits of reducing sulfur below an 80 ppm cap, and a 30 ppm average, particularly in light of the need for emerging technologies such as lean NOx catalysts to operate on very low sulfur fuels.

I. BACKGROUND

Catalytic emission control systems have been used on US passenger cars since the 1975 model year - first oxidation catalysts (OC) and then, since the early 1980s, three-way conversion (TWC) catalysts. For a short period, a combination TWC + OC system was also used. For over 12 years, the closed loop TWC system has dominated as the most efficient automobile exhaust emission control system. This system consists of an oxygen sensor, a three-way catalytic converter, an electronic control unit, and a controllable fuel metering unit. The system provides very good fuel economy and engine performance, as well as the very efficient control of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NOx) exhaust emissions. It is used on virtually all passenger cars and light-duty trucks sold in the U.S. and Canada.

Exhaust emission control is influenced by engine design and fuel quality. The engine, the emission control system, and the fuel are “partners” in engine exhaust control. Engines and the emission control systems have continued to develop and some improvements in gasoline fuel quality have occurred.

Engine Improvements

Engine out emissions for passenger cars, through engine design improvements, have been reduced from approximately 4.1 HC, 34 CO and 4.0 NOx g/mile to levels of 2.0-2.5 HC, 10 CO and 2.5-3.0 NOx g/mile. These improvements have also increased durability, improved power, and fuel economy as well. With a lower engine exhaust baseline, the emission control system can attain lower tailpipe emissions. The fuel metering part of the TWC closed loop system has improved. Air/fuel mixture preparation and control have advanced from single point central injection, to multipoint injection at each cylinder, and then to sequential multipoint fuel injection. Each fuel injection design improvement resulted in a corresponding improvement in TWC performance. The gain from an overall 65-70% rate of catalyst efficiency to over 90% efficiency was a result of improved A/F mixture control through better fuel injection.

Catalyst Technology Advances

The catalyst industry has improved three-way catalyst performance to 97% efficiency by utilizing improved formulations and layered structures. The new catalyst designs are more durable and thermally resistant - lasting for well over 100,000 miles. Also, catalysts have survived temperatures of 1100°C in accelerated aging tests. Development work continues to further improve catalyst technology.

Gasoline Quality

Lead has been removed from gasoline and other improvements to gasoline have occurred in selected areas as a result of the reformulated gasoline requirement contained in the Clean Air Act Amendments of 1990. The gasoline fuel sulfur specification that exists today, however, has not changed since 1970. Reducing the level of sulfur in gasoline is important because gasoline sulfur, upon combustion, results in SO_2 in the exhaust gas and SO_2 is a known inhibitor of three-way catalyst performance. In fact, SO_2 is known to inhibit most gaseous heterogeneous catalytic reactions. Lower gasoline fuel sulfur would be beneficial for engine emission control. Lower sulfur gasoline is critical to achieving the very low emission levels required for future emission standards, and to continue to meet those standards in use. Low sulfur fuel will result in improved performance of three-way catalysts already installed on 125 million on-road US vehicles as it has been shown that low sulfur gasoline improves three-way catalyst performance on these vehicles as well.

Emission Certification Fuel vs. Commercially Available Fuel

It is well known that vehicle in-use emissions do not correspond to those achieved in the certification process used to prove that the vehicles meet the emission standards. This is a result of a disparity between the Indolene gasoline used for the US Federal Test Procedure (FTP) to certify vehicles and that of commercial gasoline. Indolene fuel used in certification typically has a sulfur content below 50 parts per million (ppm). On the other hand, commercial gasoline sulfur content ranges between 30 and 1000 ppm throughout the US with an average of about 300±50 ppm. Indolene gasoline results in reproducible tailpipe emissions from a test vehicle. Commercial gasoline results in a wide range of emissions. The emissions differences are attributable largely to the disparity in gasoline sulfur content.

The average sulfur content of regular unleaded gasoline over the last 20 years in the U.S. has been about 300 ±50 ppm. The range of fuel sulfur has changed little over this period as well. Federal Phase II reformulated gasoline likely will result in lower sulfur levels in gasoline, but the rule will apply only in selected urban areas in the United States. Clean fuels such as natural gas, LPG, and alcohol fuels have very low sulfur levels. As a result of the National Fuel Policy Act of 1992 and other initiatives, clean fuels should become increasingly available over the next decade. However, gasoline will remain the major fuel product.

The State of California recognized the benefit of reducing sulfur in gasoline on the emission control of existing vehicles and the need for low sulfur fuel to optimize the performance of new vehicles designed to meet the stringent LEV Program Standards. As a result, California, in establishing its Phase 2 reformulated gasoline requirements, set an averaging unit of 30 ppm and a cap of 80 ppm sulfur in gasoline. For similar reasons, the European Union (EU) Conciliation Committee recently agreed to establishing a two phase reduction in gasoline sulfur to <150 ppm in 2000 and <50 ppm in 2005. A final decision by the European Union Countries is expected in the near future, and the possibility exists that the required sulfur cap levels will be even lower than those endorsed by the ministers.

II. EFFECT OF FUEL SULFUR ON EMISSION CONTROL PERFORMANCE

A. Sulfur Inhibits the Performance of Emission Control Systems

Sulfur is not a catalyst poison like lead which completely and permanently destroys catalyst activity. Rather sulfur is an inhibitor which strongly competes with the exhaust pollutants for “space” on the active catalyst surface. The issue of sulfur compounds inhibition on emission control systems performance is quite complex. Upon combustion, fuel sulfur is oxidized to sulfur oxides, primarily sulfur dioxide (SO_2) with small amounts of sulfur trioxide (SO_3). SO_2 and SO_3 are known to inhibit the catalytic function of automobile exhaust catalysts. Sulfur inhibition varies in degree according to the gasoline sulfur level, the catalyst formulation, catalytic function, combustion products from various air/fuel mixtures, and exhaust temperature range. Factors which influence the impact of sulfur on catalyst technology are listed in Table 1.

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

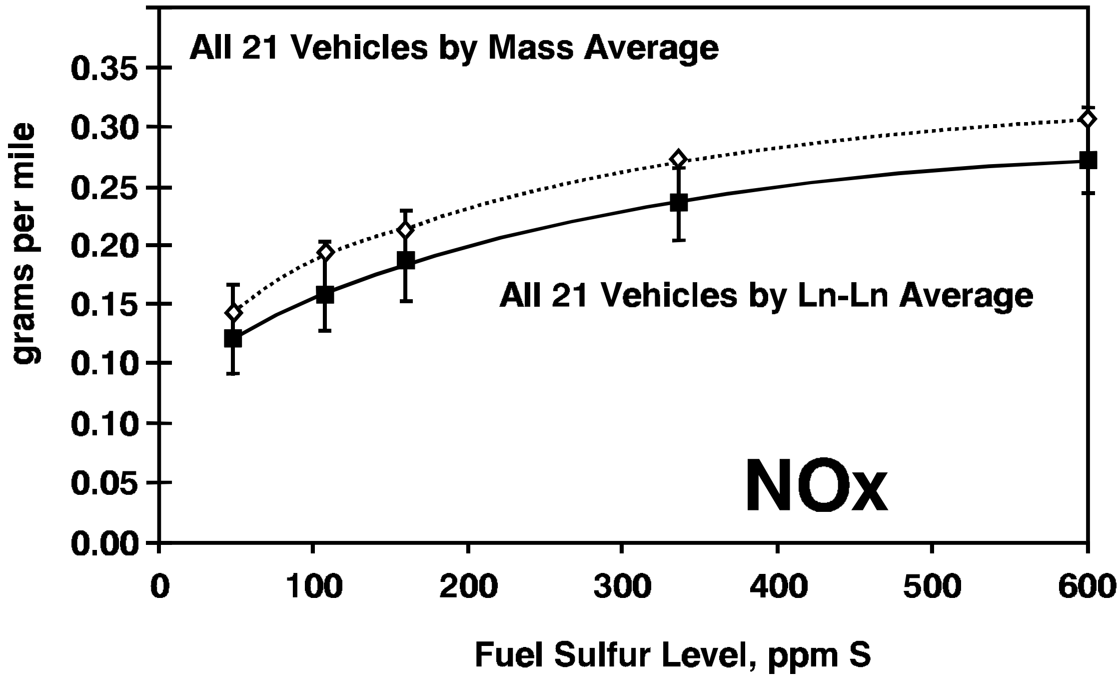
1. Catalyst Composition
   - Precious metals used – palladium (Pd), Pd and rhodium (Rh), platinum (Pt) and Rh, or Pt/Pd/Rh.
   - Precious metal concentrations.
   - Base metal concentrations.
   - Catalyst volume
   - Oxygen storage (i.e., cerium oxide or other compounds)
2. Catalyst design
3. Catalyst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

Catalyst sulfur inhibition is caused by chemisorption of a sulfur species on an active catalyst site (1,2,3,4,5,6,7). The presence of sulfur as an oxide or sulfide (e.g. hydrogen sulfide (H_2S) which can also be present in the exhaust) invariably has a negative, and typically immediate, effect on the performance of heterogeneous catalysts. The sulfur 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 SO_2 and with H_2S. Another undesirable effect of sulfur in gasoline is that the catalyst oxidizes SO_2 to SO_3 which forms sulfates easily with base metal oxides or forms sulfuric acid in reaction with water. Precious metals have an advantage over base metal oxides as they are much more resistant to SO_2 and SO_3. Base metal catalysts more easily form sulfates which are also more difficult to regenerate (3).

It has been reported that sulfur inhibition is worse with vehicle systems calibrated to meet the California LEV standards (8,9). This is a very important future issue for 49-state vehicles calibrated to the National Low Emission Vehicle standards which are expected to take effect in 2001. Gorse (8) reports data showing that sulfur inhibition increases the emission levels of a LEV vehicle to that of a Tier 0 vehicle. Benson (9) reports data showing 60% increase in HC, 65% increase in CO, and 180% increase in NOx when going from 40 to 1000 ppm sulfur fuel.

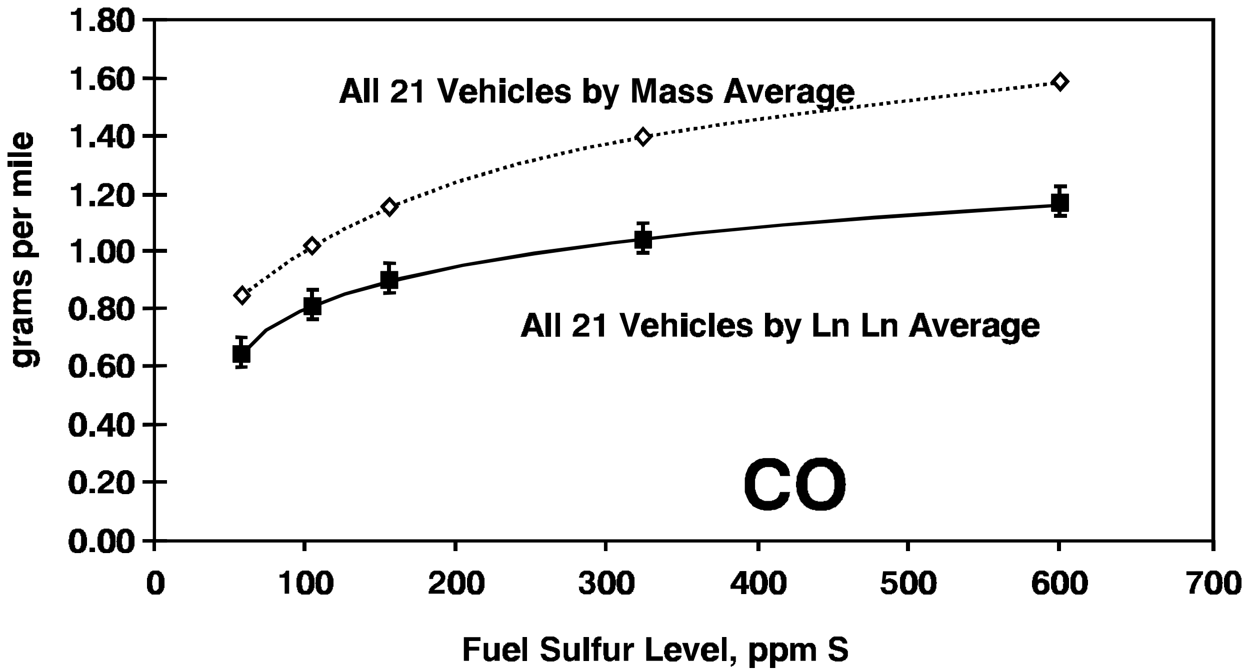
The American Automobile Manufacturers Association (AAMA) and the Association of International Automobile Manufacturers (AIAM) (15) as well as the Coordinating Research Council (CRC) (16) recently conducted independent studies examining the effect of fuel sulfur on LEV-type vehicles. In the first study, twenty-one vehicles from ten automobile manufacturers were each tested with fuels containing various levels of sulfur from 40 to 600 ppm. The catalysts were aged to simulate 50,000 or 100,000 miles of on-road driving. The combined results of all vehicles are shown in Figures 1, 2, and 3 for NOx, CO, and NMHC respectively. The results of the AAMA/AIAM Fuel Sulfur Study (15) showed that LEV-type systems experience greater increases in emissions due to sulfur for HC, NOx, and CO than do Tier 0 or Tier 1 vehicles. In the second study by CRC, twelve vehicles from six automobile manufacturers were each similarly tested with fuels containing various levels of sulfur in the same range as the AAMA/AIAM study and with a catalyst with 10,000 mile vehicle accumulation and again with 100,000 mile aged catalysts. The results of the CRC study for NOx are shown in Figure 4. Both studies show similar sulfur effect results with significant increases in all emissions as the sulfur level was increased. Conversely, stepwise lowering of the gasoline fuel sulfur resulted in reduced emissions. These results support the conclusion that all in-use vehicles will experience improved emission control with lower sulfur gasoline. These studies also are consistent with the results of previous studies and provide a further, sound justification for lowering gasoline fuel sulfur specification.

Figure 1



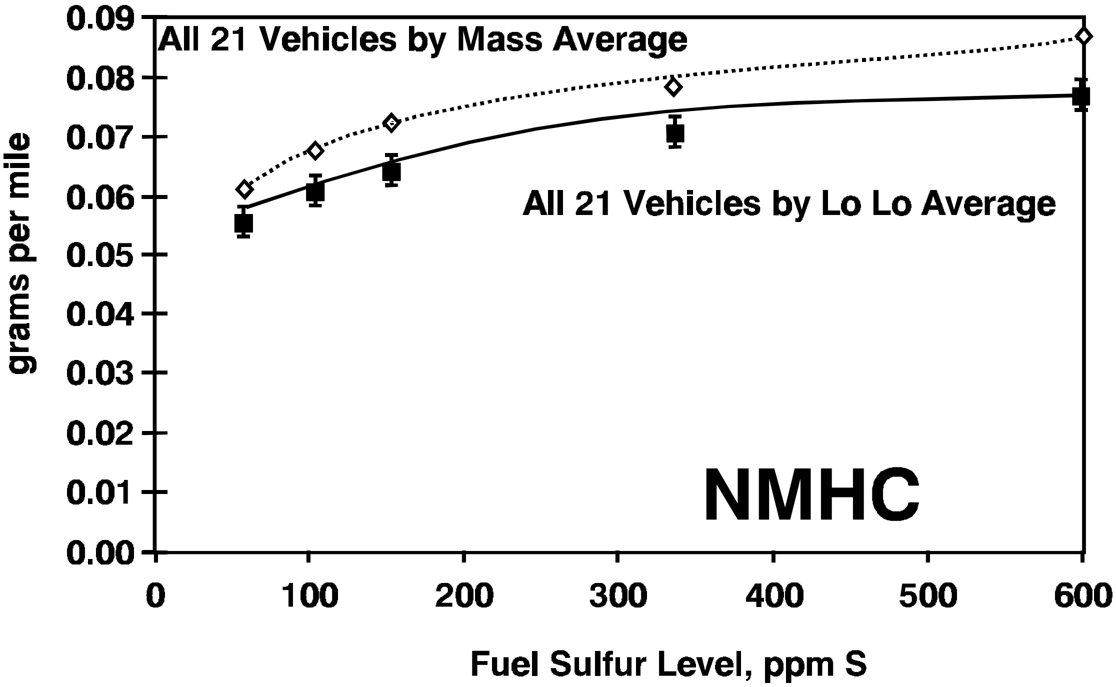
Source: AAMA/AIAM Fuel Sulfur Study

Figure 2



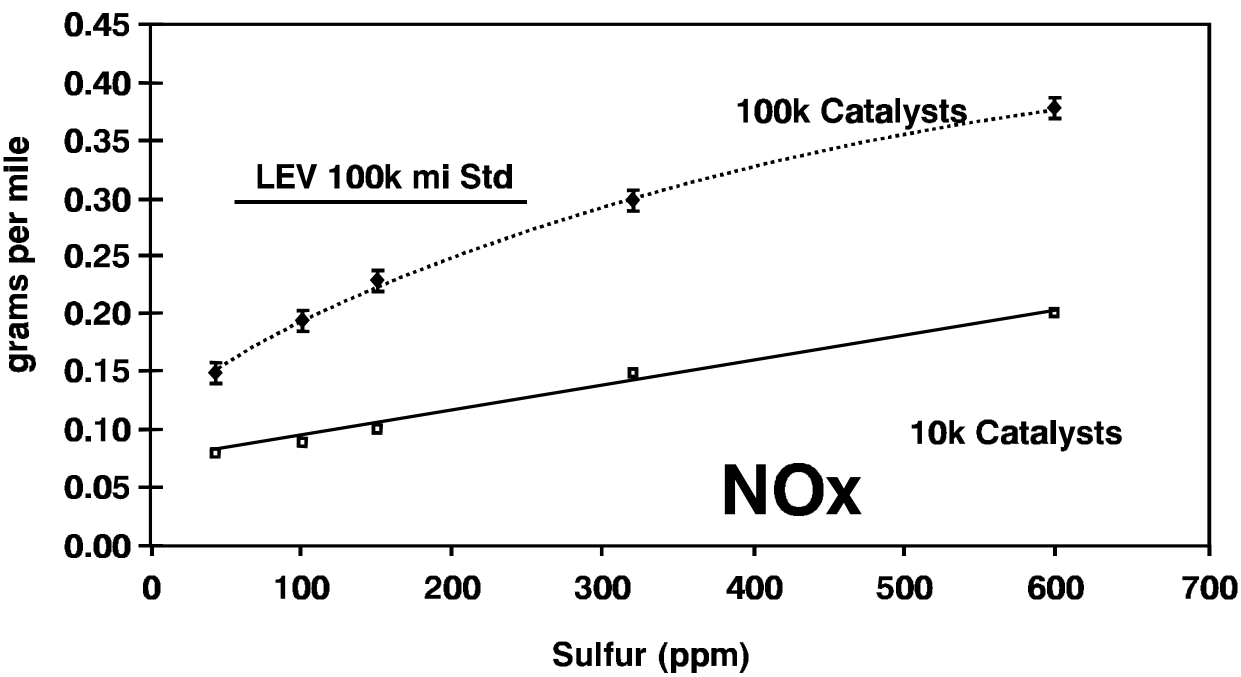
Source: AAMA/AIAM Fuel Sulfur Study

Figure 3



Source: AAMA / AIAM Fuel Sulfur Study

Figure 4



Source: CRC Fuel Sulfur Study

1. Catalyst Composition. The precious metal compositions for three-way conversion catalysts have been Pd-only, Pd/Rh, Pt/Rh, and more recently, Pt/Pd/Rh. Each composition is affected by sulfur differently. Thoss et. al. describe the inhibition of sulfur on three-way catalysts for three of these compositions, and each at several precious metal concentrations (7). This study examines the effects of 100 and 300 ppm sulfur gasoline respectively on the U.S. FTP performance of each catalyst after exposure to high and low exhaust gas temperatures. Sulfur deactivated all three catalysts for HC performance. The Pd-only three-way conversion catalysts gave superior overall HC performance whether exposed to low temperature/high sulfur or high temperature/low sulfur aging (see Figures 5 and 6). However, low temperature/high sulfur aging had a large negative effect on CO and NOx performance of the Pd-only three-way conversion catalysts (see Figures 7 and 8). The conclusions present a rather compelling case supporting low sulfur gasoline fuel as a means of achieving best performance from any three-way conversion catalyst.

Three-way conversion catalyst oxygen storage is provided by cerium oxide. The air/fuel mixture in a closed loop system is constantly changing from slightly rich to slightly lean of stoichiometric and back again at a cycle rate between 0.25 to 1.0 seconds. The A/F mixture is only very briefly at the stoichiometric point. Thus, when the cycle is slightly lean there is excess oxygen which will pass through the catalyst and out the tailpipe. Cerium oxide is incorporated within the catalyst to capture the excess oxygen and store it for use when the A/F mixture is rich and short of oxygen. Cerium oxide possesses two oxidation states which change easily from one to the other in the presence or lack of exhaust oxygen. Thus, oxygen is captured when in excess and given up for oxidative reactions when it is in short supply. The result is a more efficient use of stored oxygen to oxidize CO and HC and more efficient reduction of NO by CO while oxygen storage takes place. The quantity and form of cerium oxide employed determines the oxygen storage capacity. Gasoline fuel sulfur has been found to reduce oxygen storage (8). Oxygen storage is an important factor for OBDII systems which rely on it as a catalyst monitoring technique.

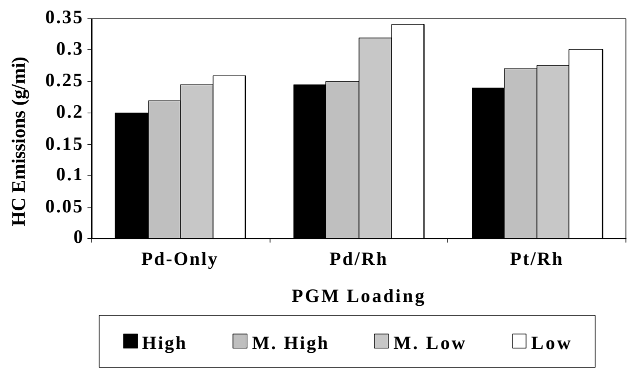
2. TWC Catalyst Design Factors. Three-way catalyst designs are complex. Three-way catalysts are designed to provide separate functions - NOx reduction, and HC and CO oxidation. A Pd-only three-way catalyst designed for close coupled operation needs to have high temperature resistance, quick light-off performance, and maximum oxygen storage capacity. Pt/Rh and Pd/Rh three-way catalysts have to avoid unwanted alloy formation. Each has to be designed in combination with base metal promoters in such a way as to optimize all functions. The design has to be durable over the complete temperature range with a minimum of base metal and precious metal sintering and little loss of support surface area.

Minimizing sulfur inhibition further complicates the catalyst design. Some attempts to improve sulfur intolerance have been reported. Pd/alumina (Al_2O_3) catalysts are reported to be particularly sulfur intolerant. Anderson and Riecke (10) reported that the addition of ceria and lanthana and other promoters to Pd only TWC catalysts can be used to improve resistance to the effects of sulfur to some degree. For example, a laboratory experiment of three Pd-only TWC catalysts is shown in Figure 9. The experiment studied the effects of fuel

Figure 5

Effect of PGM Type and Loading on HC Emissions

Low Temperature/High Sulfur Aging

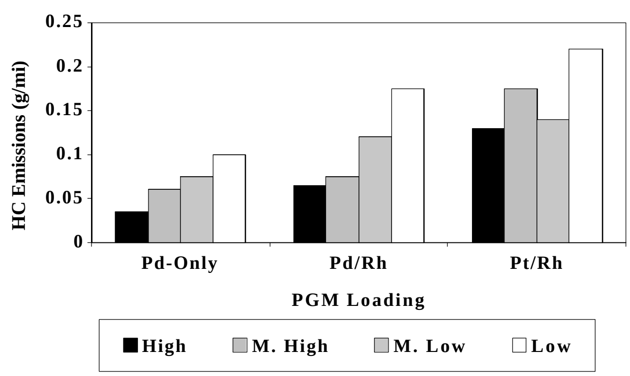


Source: SAE Paper 970737

Figure 6

Effect of PGM Type and Loading on HC Emissions

High Temperature/Low Sulfur Aging

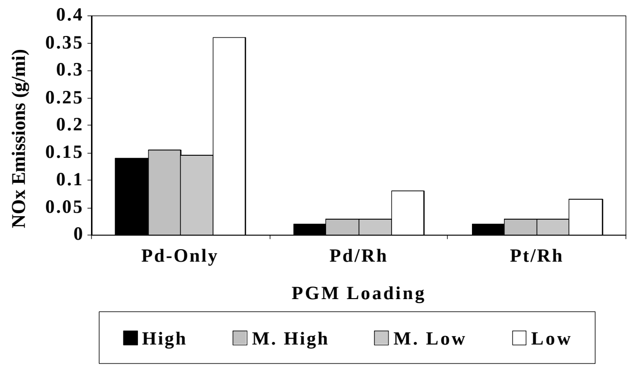


Source: SAE Paper 970737

Figure 7

Effect of PGM Type and Loading on NOx Emissions

Low Temperature/High Sulfur Aging

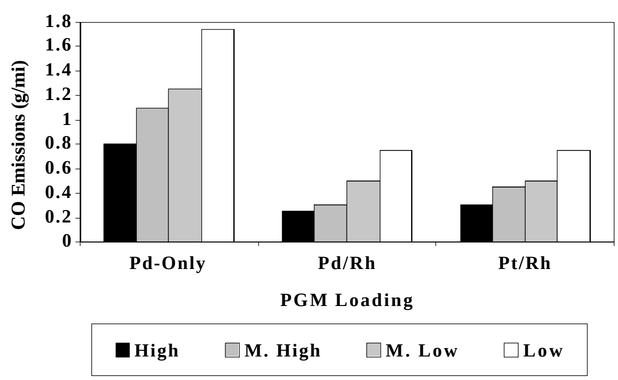


Source: SAE Paper 970737

Figure 8

Effect of PGM Type and Loading on CO Emissions

Low Temperature/High Sulfur Aging



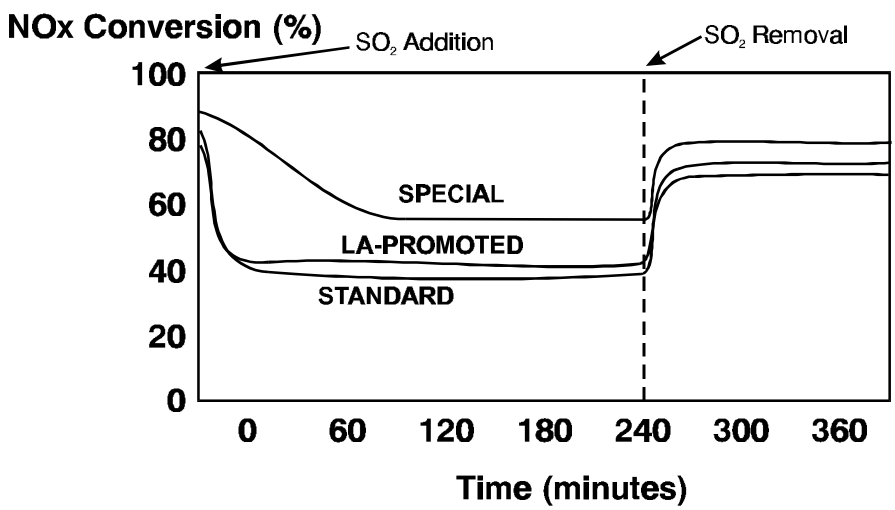
Source: SAE Paper 970737

sulfur on NOx performance of a standard Pd-only catalyst, a lanthanum promoted Pd-only catalyst, and a Pd-only catalyst substituting a special promoter combination that interacted more strongly with sulfur than lanthanum. As shown graphically in Figure 9, sulfur addition had an immediate negative performance effect on both the standard Pd-only and Pd-only Lanthanum promoted catalysts although the latter had better overall performance. The performance effect of sulfur addition on the special promoted catalyst was gradual with time but with continued exposure NOx catalytic activity decreased significantly from the range of 90% to around 60%. The same authors evaluated a standard Pd-only TWC catalyst (Cat A) and a special promoted Pd-only catalyst (Cat B) on a vehicle during the hot conditions of Bag 2 of the U.S. FTP. The test was conducted with low sulfur gasoline (100 ppm S), then with high sulfur gasoline (1000 ppm S) and then again with low sulfur gasoline. The results are shown in Figure 10 (10). Cat B has better NOx performance than Cat A. Both catalysts experienced NOx performance inhibition when exposed to the high sulfur gasoline. Cat B recovered almost all NOx activity when retested with low sulfur gasoline. (Note: The phenomena of performance recovery is further discussed in Section 8).

While progress has been made in reducing somewhat the impacts of sulfur on catalysts, sulfur remains a serious problem to maintenance of catalyst performance.

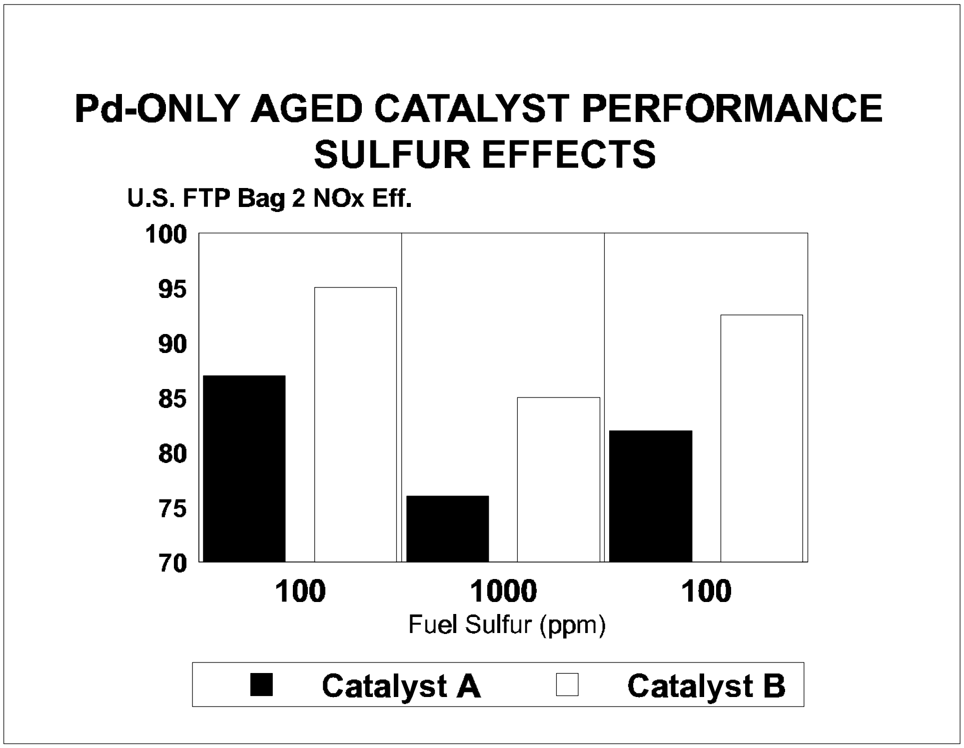
Figure 9

RESPONSE OF PD-ONLY CATALYST ACTIVITY TO ADDTION AND REMOVAL OF SO_2



Source: SAE Paper 970739

Figure 10



Source: SAE Paper 970739

3. Catalyst Location. The position of a catalyst within the exhaust system is an important factor in the degree of sulfur inhibition. Pd-only catalysts have more high temperature resistance and are often located very close to the exhaust manifold in order to function quickly after the engine is started. In this position, the Pd catalyst operates at higher temperatures. Sulfur inhibition is greatest at temperatures below 400-425°C and Pd-only catalysts located in the manifold position experience temperatures from 500 to 1050°C, where inhibition is considerably lower. Pd-only catalysts located in positions where they are exposed to lower temperatures would be more greatly affected by sulfur. A catalyst system with underfloor catalysts (usually about 1 meter downstream of the manifold) experience cooler temperatures and sulfur inhibition is greater. In addition, the underfloor position makes it more difficult to regenerate and recover lost performance due to sulfur.

4. Emission Control System - Type of Fuel Metering. As explained above, the closed loop system provides an air/fuel mixture that constantly swings or "cycles" slightly rich and then slightly lean of the control point (approximately stoichiometric). Recovery from sulfur inhibition (i.e. regeneration) after exposure to high level fuel sulfur and then a return to normal fuel sulfur levels has been shown to occur with cycled stoichiometric exhaust (8). Advanced closed loop systems that decrease the extent and increase the frequency of these swings (i.e., amplitude) achieve higher catalyst performance. In fact, the latest advanced closed loop system demonstrated recently by Honda practically eliminate the rich/lean swing entirely (11). Sulfur inhibition may be more problematic with advanced closed loop fuel metering systems.

5. Engine Calibration. Engine calibration affects sulfur inhibition and the potential for catalyst regeneration. Some engines employ fuel cut-off for deceleration to avoid decel misfire. When fuel cut-off occurs, 100% air is drawn through the engine. Deceleration from high speed therefore passes air through the catalyst at a high catalyst temperature condition. Catalyst regeneration and recovery close to the original catalyst performance level can occur under this engine mode because of the excess oxygen present. If the engine does not have this feature, the high temperature oxidizing condition does not occur and regeneration will not take place.

Another engine calibration is fuel enrichment during full acceleration. Exhaust gas temperatures during acceleration are high. Regeneration of the catalyst can occur during a fuel enriched acceleration. However, fuel enrichment during acceleration also causes higher emissions. The new U.S. FTP includes a cycle that requires emissions testing during full accelerations. In order to meet the new emission limits, fuel enrichment during hard acceleration will be severely restricted as an engine calibration strategy. Thus, catalyst regeneration resulting from operating in a fuel enriched acceleration environment is not likely to occur in future engines designed to comply with the new FTP.

6.0 Vehicle Use. Vehicles operate under a wide range of conditions of speed and load. Vehicles that operate at low speed and low load will have lower exhaust gas temperatures than those that operate at high speed and high load. As noted above, exhaust temperature is an important factor for sulfur inhibition. Sulfur inhibition is strongest at temperatures below 425°C and less strong at temperatures above 425°C. Therefore, vehicles which operate at low speed and load would experience greater inhibition and have fewer opportunities for regeneration. The type of vehicle, i.e. passenger car, sport/utility vehicle, or light/medium duty truck, is also important for the same reasons detailed above.

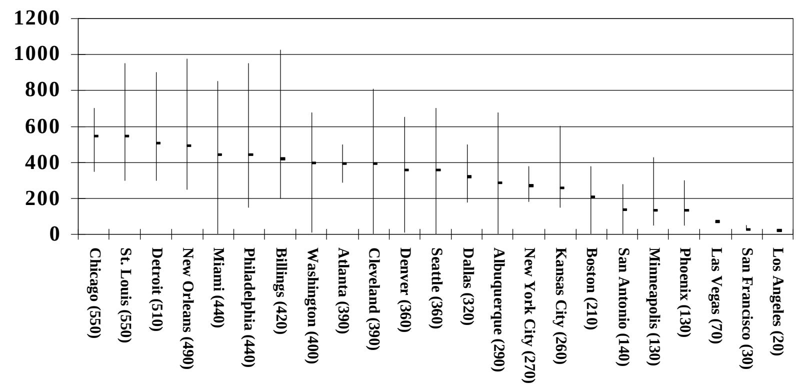
7. Fuel. Fuel sulfur content ranges widely throughout the US and among the various grades of gasoline. As noted, the higher the sulfur level, the greater the impact on the catalyst. Figures 11 and 12 below show the range of sulfur for two grades of gasoline in several regions of the U.S. (12). As stated above, any catalyst will perform differently on each grade of fuel and will vary widely in performance depending on the level of sulfur in the fuel used resulting in large variations in in-use-emissions (7,9,10).

Figure 11

1996 AAMA Summer Fuel Survey Results

Sulfur Level in Regular Unleaded Fuels

Average (in parenthesis) and Range



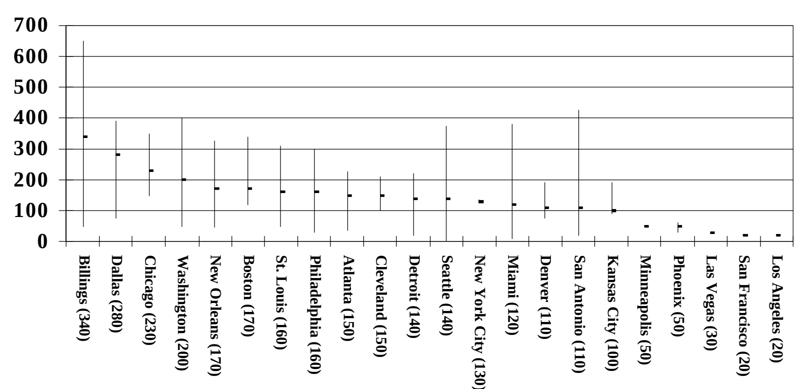
Source: AAMA, 1998

Figure 12

1996 AAMA Summer Fuel Survey Results

Sulfur Level in Premium Unleaded Fuels

Average (in parenthesis) and Range



Source: AAMA, 1998

8. Regeneration. Sulfur inhibition of automobile catalysts can be temporary and recovery to original performance has been achieved by return to low sulfur fuel under the appropriate operating condition. However, recent data from tests on low-emitting vehicles indicated full recovery was not occurring. Ford reported test results on low sulfur fuel (60 ppm S base fuel), followed by exposure to high sulfur fuel (930 ppm S), and then again a return to low sulfur fuel (8). The test were performed on a vehicle meeting the California ULEV standards. In the presentation, Gorse showed that exposure to high sulfur fuel increased HC emissions from 0.04 g/mile to about 0.12 g/mile. A return to low sulfur fuel resulted in improved performance but only to about 0.07 g/mile, but a subsequent rich calibration hot cycle was required to return performance to the original performance level. Experiments conducted by Thoss et. al. did not show significant regeneration upon evaluation with low sulfur gasoline (87 ppm Sulfur) or with treatments at 700°C under slightly lean conditions (7). A companion paper showed almost complete recovery of a new improved Pd-only three-way conversion catalyst when fuel was switched from 1000 ppm to 100 ppm sulfur (10) (See Figure 10). Benson noted that sulfur inhibition was reversible at high exhaust gas temperatures with low sulfur fuel for current technology vehicles, but that sulfur effects are more critical with lower emission vehicles and may not be reversible (9).

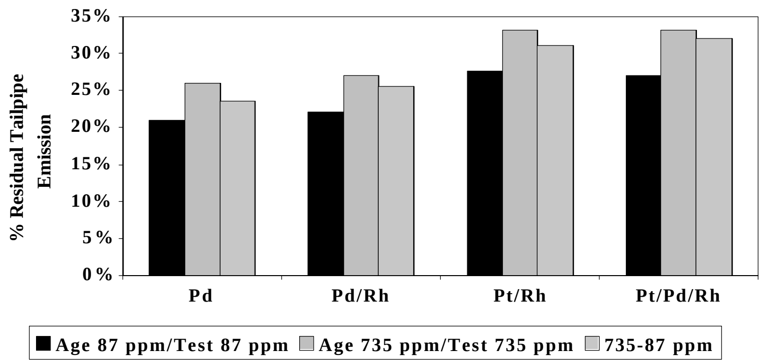
In two recent studies of the effect of gasoline fuel sulfur on LEV and ULEV-type vehicles by AAMA/AIAM (15) and CRC (16), the issue of sulfur removal was addressed. Both studies used a sulfur purge cycle to remove previous accumulated sulfur from catalysts. "The cycle employed a series of five vehicle wide-open-throttle (WOT) acceleration/ cruise/deceleration excursions and a steady state drive to increase the catalyst temperature and provide a rich air-to-fuel operating condition to facilitate the release of the sulfur compounds that accumulate on the catalyst. This cycle was repeated to give a minimum of ten acceleration/cruse/deceleration excursions. In this LEV/ULEV test program, some manufacturers increased the stringency of the sulfur purge cycles to ensure adequate sulfur removal. To ensure adequate catalyst temperature (650°C or higher), the catalyst inlet temperature was monitored with a thermocouple. From these studies it appears that special cycle conditions have to exist in order to regenerate catalyst performance via sulfur purging.

A recent study by Cooper shows that the effects of sulfur do not appear to be completely reversible when the catalyst is aged on high sulfur fuel and then tested on low sulfur fuel (17). The study evaluated four different catalyst formulations - Pd, Pd/Rh, Pt/Rh, and Pt/Pd/Rh – that were aged using low sulfur fuel (87 ppm) and an identical set of four catalysts that were aged using high sulfur fuel (735 ppm). The catalysts were then emission tested using both 87 ppm and 735 ppm fuels. For each catalyst formulation, emission levels were higher for the catalysts aged on the high sulfur fuel. As shown in Figure 13, testing the catalysts on low sulfur fuel after aging on high sulfur fuel failed to return the catalyst formulations to their original control efficiencies for HC. Next each catalyst aged on high sulfur fuel was treated under three sulfur-purging cycles (5 hours at 700°C, 5 hours at 800°C, and 5 hours at 900°C) using 87 ppm fuel. Emissions were again measured after each treatment to determine the extent of recovery. As shown in Figure 14, treatment at increasing temperatures caused further recovery in some cases, but in no instance did the catalysts aged

Figure 13

Fuel Sulfur Effects on Hydrocarbon Emissions

Emissions Recovery 735-87 ppm Fuel S

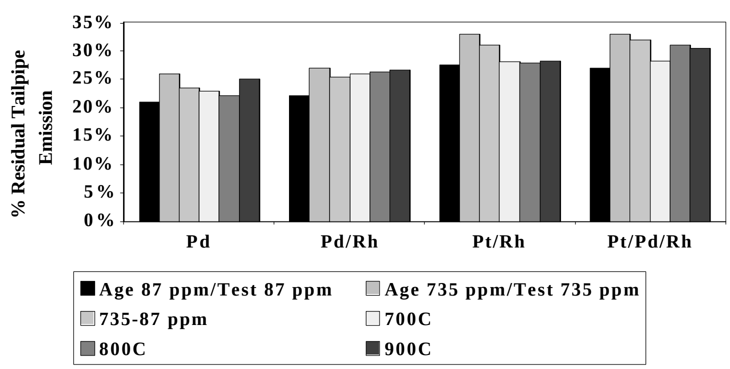


Source: Cooper, 1998

Figure 14

Fuel Sulfur Effects on Hydrocarbon Emissions

Emissions Recovery 735-87 ppm Fuel S



Source: Cooper, 1998

using high sulfur fuel return to the same low emission state for HC as the catalyst aged using low sulfur fuel.

The parameters of the Dynamometer Aging Cycle and the Dynamometer Sulfur Recovery Cycle are shown below:

- Dynamometer Aging Cycle
  - 45 hours – 5 min rich/5 min lean
  - Rich: A/F=12.7 650°C Catalyst Bed Temperature
  - Lean: A/F=16.0 900°C Catalyst Bed Temperature
  - 87 ppm fuel sulfur or 735 ppm fuel sulfur

- Dynamometer Sulfur Recovery Cycle
  - 5 hours "steady state"
  - A/F=Stoich +- 0.5 AFR @ 0.10 Hz (5 sec rich/5 sec lean)
  - 700°C Catalyst Bed Temp. (then 800°C then 900°C)
  - 87 ppm sulfur fuel

B. Low Sulfur Fuel is Required for Future Systems.

Low sulfur fuel is required for future engine emission control. Lean burn engines and GDI (gasoline direct injection) engines are being developed. Both engines give much better fuel economy than the current stoichiometric engine. The major problem with both of these engines is the control of NOx emissions. An innovative NOx catalyst works well in Japan where gasoline fuel sulfur is very low, but U.S. gasoline sulfur levels are too high for this catalyst technology (13).

Developers of lean-burn and GDI engines hope to have functional lean NOx catalysts for these engines. Catalyst companies have directed R&D toward the development of a lean NOx catalyst for several years - however, a practical lean NOx catalyst still awaits demonstration. Three types of reactions have been studied: 1) NOx decomposition, 2) NOx reduction and 3) NOx storage and destruction. NOx decomposition potential is completely poisoned by sulfur (3). NOx reduction with a reductant is inhibited by the presence of sulfur. The NOx storage technology is known as a lean NOx trap. In this case NOx is oxidized to NO_2 and stored as a base metal nitrate and later released and destroyed. However, with this promising lean NOx technology, sulfur rapidly poisons as the SO3 formed by the catalyst reacts with the trap materials to form base metal sulfates preferentially. Researchers need to know the level of sulfur in future fuels. Fuel sulfur near zero would greatly help the development of lean NOx catalysts.

Another consideration for lean NOx catalyst technologies is the catalytic oxidation of SO_2 to SO_3 which is favorable in automotive exhaust conditions and is dependent on the oxygen concentration (14). The SO_3 further reacts with water to produce sulfuric acid mist which will increase particulate emissions significantly.

III. MECA RECOMMENDS REDUCING THE SULFUR LEVEL IN GASOLINE

MECA recommends changing the commercial gasoline fuel specification for sulfur to a level which will beneficially effect the performance of past, current and future emission control. Implementation of the limits should include both adequate lead time and compliance flexibility strategies similar to those used in the past in order to facilitate cost effective compliance with the limits. MECA further recommends that an evaluation be initiated to determine the additional benefits of reducing sulfur below an 80 ppm cap, particularly in light of emerging technologies such as lean NOx catalysts.

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