Why The 10 PPM Sulfur Limit for Gasoline is Necessary for Tier 3

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The Detrimental Impact of Sulfur on Precious Metal Catalysts is Understood

Sulfur is a well-known catalyst poison. There is a large body of work demonstrating sulfur inhibition of the emissions control performance of platinum group metals (PGM) three-way exhaust catalyst systems. Sulfur from gasoline is oxidized during spark-ignition engine combustion primarily to SO2 and, to a much lesser extent, SO3. Sulfur oxides selectively chemically bind (chemisorb) with, and in some cases react with, active sites and coating materials within the catalyst, thus inhibiting the intended catalytic reactions. Sulfur oxides inhibit pollutant catalysis chiefly by selective poisoning of active PGM, ceria sites, and alumina washcoatings. The amount of sulfur retained by the catalyst is primarily a function of its operating temperature, the active materials and coatings used within the catalyst, the concentration of sulfur oxides in the incoming exhaust gases, and air-to-fuel ratio feedback and control by the engine management system.

Selective sulfur poisoning of platinum (Pt) and rhodium (Rh) is primarily from surface layer chemisorption. Sulfur poisoning of palladium (Pd) and ceria appears to be via chemisorption combined with formation of more stable metallic sulfur compounds, e.g. PdS and Ce2O2S, present in both surface and bulk form (i.e., below the surface layer). Ceria, zirconia and other oxygen storage components (OSC) play an important role that is crucial to NOX reduction over Rh as the engine air-to-fuel ratio oscillates about the stoichiometric closed loop control point. Water-gas-shift reactions are important for NOX reduction over catalysts combining Pd and ceria. This reaction can be blocked by sulfur poisoning and may be responsible for observations of reduced NOX activity over Pd/ceria catalysts even with exposure to fairly low levels of sulfur. Pd is also of increased importance for meeting Tier 3 standards due to its unique application in the close-coupled catalysts location required for vehicles certifying to very stringent emission standards. Pd is required in closed-coupled catalysts due to its resistance to high temperature thermal sintering. Sulfur removal from Pd requires rich operation at higher temperatures than required for sulfur removal from other PGM catalysts.

In addition to its interaction with catalyst materials, sulfur can also react with the washcoating itself to form alumina sulfate, which in turn can block coating pores and reduce gaseous diffusion to active materials below the coating surface. This may be a significant mechanism for the observed storage of sulfur compounds at light and moderate load operation with subsequent, rapid release as sulfate particulate matter when high-load, high-temperature conditions are encountered.

Operating the catalyst at a sufficiently high temperature under net reducing conditions (e.g., air-to-fuel equivalence that is net fuel-rich of stoichiometry) can effectively release the sulfur oxides from the catalyst components. However, regular operation at these temperatures and at rich air-to-fuel ratios is not desirable, for several reasons including:

- The temperatures necessary to release sulfur oxides are high enough to lead to thermal degradation of the catalyst over time via thermal sintering of active materials. Sintering reduces the surface area available to participate in reactions.

- Additionally, it is not always possible to maintain these catalyst temperatures (because of cold weather, idle conditions, light load operation) and the rich air-to-fuel ratios necessary can result in increased PM, NMOG and CO emissions.

Thus, reducing fuel sulfur levels has been the primary regulatory mechanism to minimize sulfur contamination of the catalyst and ensure optimum emissions performance over the useful life of a vehicle.

The impact of gasoline sulfur has become even more important as vehicle emission standards have become more stringent. Studies indicate an increase in catalyst sensitivity to sulfur (in terms of percent conversion efficiency) when standards increase in stringency and emissions levels decrease. Emission standards under the programs that preceded the Tier 2 program (Tier 0, Tier 1 and National LEV, or NLEV) were high enough that the impact of sulfur was considered negligible. The Tier 2 program recognized the importance of sulfur and reduced the sulfur levels in the fuel from 300 ppm to 30 ppm in conjunction with the new emission standards.

Studies Carried Out Since Tier 2 Was Promulgated Indicate that Even 30 PPM Sulfur Damages PGM Catalysts

At the time that Tier 2 was adopted, very little work had been done to evaluate the effect of fuel sulfur reductions below 30 PPM– especially on in-use vehicles that may have some degree of catalyst deterioration due to real-world operation.

MSAT Study

In 2005 EPA and several automakers jointly conducted a program that examined the effects of sulfur and other gasoline properties, benzene, and volatility on emissions from a fleet of nine Tier 2 compliant vehicles, the "MSAT (Mobile Source Air Toxics) Study". Reductions for FTP-weighted emissions for the sulfur changes in this program were 33 percent for NOX, 11 percent for THC, 17 percent for CO, and 32 percent for methane. The study suggested the effect of sulfur loading was reversible for Tier 2 vehicles, and that there were likely to be significant emission reductions possible with further reductions in gasoline sulfur level.

EPA Tier 2 In-Use Gasoline Sulfur Effects Study[1]

Goals of this study included assessment of reversible sulfur loading in catalysts of Tier 2 compliant light duty gasoline vehicles in the in-use fleet, as well as characterization of the effects of fuel sulfur level on emissions as a function of accumulated mileage. The study sample consisted of 81 cars and light trucks recruited from owners in southeast Michigan, covering model years 2007-9 with approximately 20,000-40,000 odometer miles. The makes and models targeted for recruitment were chosen to be representative of high sales vehicles covering a range of types and sizes. Test fuels were two non-ethanol gasolines, one at a sulfur level of 5 ppm and the other at 28 ppm. A nominal concentration of approximately 30 ppm was targeted for the high level to be representative of retail fuel available to the public in the vehicle recruiting area. All emissions data were collected using the FTP cycle at a nominal temperature of 75°F.

A statistical analysis of the data with the two fuels showed highly significant reductions in several pollutants including NOX and hydrocarbons, suggesting that reversible sulfur loading exists in the in-use Tier 2 fleet and has a measurable effect on aftertreatment performance.

Next, a subset of approximately one in five vehicles (one of each make/model) was kept for an extended test schedule consisting of additional emission test replicates alternated with mileage accumulation. This dataset was used to assess the behavior of emissions as sulfur reloaded toward and beyond the baseline level observed in the vehicles as-received. The fuel was then changed to the low-sulfur test fuel and the procedure repeated, starting with a clean-out procedure followed by alternating emission tests and mileage accumulation. This dataset was used to assess differences in the rate at which sulfur reloading occurred as a function of fuel sulfur level.

[1] U.S. EPA, "The Effects of Gasoline Sulfur Level on Emissions from Tier 2 Vehicles in the In-Use Fleet, Draft," EPA-420-D-13-003, April 2013 (Draft EPA In-Use Study)

Mixed model analysis of all emissions data as a function of fuel sulfur level and miles driven after cleanout found highly significant model fits for several pollutants. These results show cold-start and hot-running NOX emissions were reduced by 11 percent and 59 percent, respectively, comparing low vs. high-sulfur test fuels.

Major findings from this study include:

- Reversible sulfur loading is occurring in the in-use fleet of Tier 2 vehicles and has a measureable effect on emissions of NOX, hydrocarbons, and other pollutants of interest.
- The effectiveness of high speed/load procedures in restoring catalyst efficiency is a function of fuel sulfur level.
- Reducing fuel sulfur levels from 28 to 5 ppm is likely to achieve significant reductions in emissions of NOX, hydrocarbons, and other pollutants of interest in the in-use fleet.

Fuel Sulfur Impacts on Vehicles at the Proposed Tier 3 Levels

The Tier 3 Program would reduce fleet average NMOG+NOX emissions by over 80 percent. The feasibility of the proposed 30 mg/mi NMOG+NOX fleet average standard depends on a degree of emissions control from exhaust catalyst systems that will require gasoline at 10 ppm sulfur or lower. The most likely control strategies will involve using exhaust catalyst technologies and powertrain calibration to reduce NOX emissions to near-zero levels. This would allow sufficient NMOG compliance margin to meet the combined NMOG+NOX emissions standards for the full useful life.

Achieving the proposed Tier 3 emission standards would require very careful control of the exhaust chemistry and exhaust temperatures to ensure high catalyst efficiency. The impact of sulfur on oxygen storage components (OSC) in the catalyst makes this a challenge even at relatively low (10 ppm) gasoline sulfur levels.

Certification Experience

Light-duty vehicles certified to CARB SULEV and Federal Tier 2 Bin 2 exhaust emission standards accounted for approximately 3.5% and 1%, respectively of vehicle sales for MY2009. Non-hybrid vehicles certified in California as SULEV are typically not certified to Federal Tier 2 Bin 2 emissions standards. While this appears puzzling at first since the SULEV and Tier 2 Bin 2 standards are numerically equivalent, EPA notes in its Tier

3 proposal that confidential business information shared by the auto companies indicate that the primary reason is an inability to demonstrate compliance with SULEV/Bin 2 emission standards after vehicles have operated in-use on gasoline with greater than 10 ppm sulfur and with exposure to gasoline up to the Tier 2 80-ppm gasoline sulfur cap.

Although the SULEV and Tier 2 Bin 2 standards are numerically equivalent, the increased sulfur exposure of in-use vehicles certified under the Federal Tier 2 program results in certification of California SULEV vehicles to emissions standards under the Federal Tier 2 program that are typically 1-2 certification bins higher (e.g., SULEV certified as Tier 2 Bin 3 or Bin 4) in order to ensure in-use compliance with emissions standards out to the full useful life of the vehicle when operating on higher-sulfur gasoline.

Other Data

Emissions of vehicles certified to the SULEV standard of the California LEV II program, or the numerically equivalent Tier 2 Bin 2 standards, provide some insight into the impact of fuel sulfur on vehicles at the very low proposed Tier 3 emissions levels. EPA notes in its proposal that vehicle testing by **Toyota** of LEV I, LEV II ULEV and prototype SULEV vehicles showed larger percentage increases in NOX and HC emissions for SULEV vehicles as gasoline sulfur increased from 8 ppm to 30 ppm, as compared to other LEV vehicles they tested. In addition, testing of a SULEV-certified PZEV vehicle by **Umicore** showed a pronounced, progressive trend of increasing NOX emissions (referred to as "NOX creep") when switching from a 3 ppm sulfur gasoline to repeated, back-to-back FTP tests using 33 ppm sulfur gasoline.[2] The PZEV Chevrolet Malibu, after being aged to an equivalent of 150,000 miles, demonstrated emissions at a level equivalent to the compliance margin for the Tier 3 Bin 30 NMOG+NOX standard when operated on 3 ppm sulfur fuel and for at least one FTP test after switching to 33 ppm certification fuel. Following operation over 2 FTP cycles on 33 ppm sulfur fuel, NOX emissions alone were more than double the proposed Tier 3 30 mg/mi NMOG+NOX standard. This represents a NOX percentage increase that is approximately 2-3 times of what has been reported for similar changes in fuel sulfur level for Tier 2 and older vehicles over a similar difference in fuel sulfur.

Special Challenges with Heavier Vehicles

[2] Ball, D., Clark, D., Moser, D., Umicore Autocat USA Inc., "Effects of Fuel Sulfur on FTP NOx Emissions from a PZEV 4 Cylinder Application," SAE 2011-01-0300.

EPA notes that it expects that additional catalyst technologies, for example increasing catalyst surface area (volume or substrate cell density) and/or increased PGM loading, would need to be applied to larger vehicles in order to achieve the catalyst efficiencies necessary to comply with the proposed Tier 3 standards. Therefore, any sulfur impact on catalyst efficiency would have a larger impact on vehicles and trucks that rely more on very high catalyst efficiencies in order to achieve very low emissions. Manufacturers therefore face the most significant challenges in reducing cold-start NMOG emissions for these vehicles. Because of the need to reach near-zero NOX levels, any significant degradation in NOX emissions control over the useful life of the vehicle would likely prevent some if not most larger vehicles from reaching a combined NMOG+NOX emissions level low enough to comply with the 30 mg/mi fleet-average standard .

Certifying to a useful life of 150,000 miles vs. the current 120,000 miles would further add to manufacturers' compliance challenge for Tier 3 large light trucks.

Conclusion: Gasoline Sulfur Control Is Required to Meet Tier 3 Emissions Standards

The impact of gasoline sulfur poisoning on exhaust catalyst performance and the relative stringency of the Tier 3 standards, particularly for larger vehicles and trucks, when considered together make a compelling argument for the virtual elimination of sulfur from gasoline. The 10-ppm standard for sulfur in gasoline represents the lowest practical limit from a standpoint of fuel handling and transport especially in light of the large distance of pipeline fuel transfer in the US. A gasoline sulfur standard of 10 ppm also represents the highest level of gasoline fuel sulfur that will allow compliance with a national fleet average of 30 mg/mi NMOG+NOX.

Catalyst Design Changes For Tier 3 Vehicles

Changes to Reduce Catalyst Light-Off Time

A number of different catalyst design changes can be implemented to reduce the time for the catalyst to light-off. Changes include modifying the substrate design, replacing a large volume catalyst with a cascade of two or more catalysts, and optimizing the loading and composition of the platinum group metals (PGM).

Progress continues to be made in the development of the catalyst substrates which provide the physical support for the catalyst components which typically include a high surface area alumina carrier, ceria used for storing oxygen, PGM catalysts, and other components. A key design parameter for substrates is the cell density. Today catalyst substrates can be fabricated with cell densities up to 900 and 1,200 cells per square inch (cpsi) with wall thicknesses approaching 0.05 mm.

Increasing the surface area of the catalyst improves the performance of the catalyst. Higher substrate cell densities increases the surface area for a given catalyst volume thereby improving the catalyst efficiency and durability.

The limitation of the higher cell density substrates include increased exhaust system pressures at high load conditions. The cell density and substrate frontal area are significant factors that need to be considered to optimize the catalyst performance while limiting flow loss at high load operation.

During the cold start phase of the FTP the engine speeds and load are low during the first 50 seconds of the test. One method for reducing the catalyst light-off time is to replace a larger volume catalyst with two catalysts which total the same volume as the single catalyst. The reduced volume close-coupled catalyst reduces the heat needed for this front catalyst to reach the light-off temperature. The front catalyst of the two catalyst system will reach operating temperature before the larger volume single catalyst, reducing the light-off time of the system.

All other parameters held constant, increasing the PGM loading of the catalyst also improves the efficiency of the catalyst. The ratio of PGM metals is important as platinum, palladium, and rhodium have different levels of effectiveness promoting oxidation and reduction reactions. Therefore, as the loading levels and composition of the PGM changes, the light-off performance for both NMOG and NOX need to be evaluated. Based on confidential conversations with manufacturers EPA concluded that there appears to be an upper limit to the PGM loading, beyond which further increases do not improve light-off or catalyst efficiency.

Improving catalyst NOX efficiency during warmed-up operation

Significant quantities of NOX emissions are produced by vehicles during warmed-up vehicle operation on the FTP for Tier 2 Bin 5 certified vehicles. The stabilized NOX emission levels will need to be reduced to achieve the proposed Tier 3 NMOG+NOX emission standard. This can be achieved by improving the catalyst efficiency during warmed-up operation. As previously described the performance of the catalyst can be improved by modifications to the catalyst substrate, increasing cell density, increasing PGM loadings and reducing the sulfur level of gasoline. Three-way catalyst efficiency is also affected by frequency and amplitude of the air/fuel ratio. For some vehicles warmed-up catalyst NOX efficiency can be improved by optimizing the air/fuel ratio control and limiting the amplitude of the air fuel ratio excursions. It is anticipated that a combination of changes will be made by manufacturers including further improvements to air/fuel ratio calibration and catalyst changes including cell density and PGM loadings.

EPA anticipates that manufacturers will use these catalyst and calibration technologies to improve the warmed up NOX emissions performance of vehicles in all classes, passenger cars, LDTs, MDPVs, and HDTs.

New Information Has Emerged During the Public Comment Period

Ford Motor Company Tier 3 Sulfur Test Program

A testing program was designed by Ford to assess the exhaust emission difference for a vehicle operating with 10 ppm sulfur gasoline compared to the same vehicle operating with the same gasoline formulation but containing 30 ppm sulfur.

The vehicle selected was a Ford Explorer 2.0L GTDI calibrated to meet BIN50 or ULEV50 tailpipe emissions. The vehicle included an exhaust emission aftertreatment system that is representative of technologies under study by Ford to meet Tier 3 emissions standards (close-coupled, catalyst volume of 110 in3, 150 g/ft3 loading of precious metal). Additionally, the catalysts were dynamometer aged to simulate 150,000 miles.

The gasoline formulation used for this testing program was aligned with the specifications approved for LEV 3 (having 10 vol% ethanol, 8-11 ppm sulfur, 87-88.4 AKI). The LEV 3 certification fuel was chosen since the Tier 3 certification fuel is yet to be finalized. Given that the Tier 3 program is structured to harmonize with LEV 3, the Ford team agreed that the LEV 3 certification fuel would be the most suitable fuel.

In order to minimize the variability in as many fuel parameters as possible and to eliminate any potential secondary effects on the emissions measurements, the higher sulfur gasoline blend was produced from the same batch of LEV III certification fuel by blending a sulfur additive into a portion of the LEV III fuel. The sulfur additive (Tert-butyl sulfide or Di-tert-butyl-disulfide) was selected to be the same additive used by EPA in their Tier 2 sulfur testing program and used in the SGS sulfur study that API included as part of their Tier 3 comments. (See discussion of this study below.)

Typical certification procedures and practices were followed to conduct emission testing. Catalyst temperatures were recorded during a sampling of both city and highway driving on local area roads.

The data shows that NMHC+NOx emissions increased by 16 mg/mile for the 26.5 ppm sulfur fuel compared to the emissions measured when using the 10 ppm sulfur gasoline. Statistical analyses using the T-test on the emissions data sets resulted in a P-value of 0.0216, which indicates that the difference between the two sulfur levels tested is statistically significant.

Although the total amount of sulfur exposure to the catalyst during this sulfur study appears to be relatively small, it is enough to contaminate the catalytic exhaust emission aftertreament system to result in an increase in tailpipe emissions for NMHC+NOx by 45 %.

Ford concludes that this sulfur study again confirms the deleterious effects of sulfur in fuel. Specifically, upon inspection of the emissions data from this Test Program, the following conclusions can be drawn:

- The test vehicle exhaust emission aftertreatment system was exposed to approximately 1.1 grams of sulfur during the mileage accumulation period (~ 15 gallons over 400 miles)
- For a BIN50 certified vehicle under the proposed Tier 3 regulations, the sulfur contamination was:

  1. Sufficient to cause the NMHC+NOx to increase by 45% and
  2. Enough to result in a failed In-Use Verification Protocol (IUVP) test

- A T-test was completed on the emissions data set (comparing 10 ppm sulfur and 26.5 ppm sulfur) with the conclusion that the two populations are significantly different (P = 0.0261) @ 95% confidence level

• This study shows that ~30 ppm sulfur still contaminates today's vehicles and is not compatible with future vehicles required to meet the low emissions regulations related to the proposed Tier 3 rules

Ford Comments on the SGS Environmental Testing Corp. (SGS Study)

Recently, the American Petroleum Institute (API) sponsored a new study of sulfur reversibility conducted by SGS Environmental Testing Corp. (SGS Study) and subsequently submitted the results as part of joint API and AFPM comments regarding the Tier 3 NPRM. This SGS study examined the sulfur reversibility in a set of six late model vehicles in the under-6000 pound vehicle class. Five of the vehicles were certified to California SULEV II/PZEV, and one was certified to Federal Tier 2 Bin 5 standards. The SGS Study included new catalysts that were then aged using 18-43 ppm sulfur fuel for the equivalent of 120,000- 150,000 miles. After the aged catalysts were installed in each respective test vehicle, the study conducted catalyst purging for each vehicle using the EPEFE protocol, involving 10 wide open throttle (WOT) cycles, to establish baseline vehicle exhaust emissions. The vehicles were then operated and tested using the following order of 10, 80 and 10 ppm sulfur fuels. The base fuel used to test emissions after the catalyst purge contained 10 ppm sulfur while the high sulfur test gasoline contained 80 ppm sulfur. The study's results indicated that the increase in exhaust emissions due to 80 ppm sulfur fuel was fully reversible after 70 miles of driving (operating with 10 ppm sulfur fuel) and preparation (purge) cycles linked to LA4 and US06 emission drive cycles.

In summary, the following conclusions were drawn from the SGS study:

• Gaseous exhaust emissions were higher for the vehicles conditioned and tested using 80 ppm sulfur fuel, relative to baseline tests run using 10 ppm sulfur fuel.

• Mean emissions increased for vehicles run on the 80 ppm sulfur (relative to 10ppm sulfur) fuel as follows, with greater than 95% confidence:

o Fleet average NMOG increased by 20% (0.002 g/mile change)

o Fleet average NOx increased by 58% (0.006 g/mile change)

o Fleet average CO increased by 31% (0.078 g/mile change)

Ford notes that even if the sulfur effects were demonstrated to be reversible in the SGS Study, it is the average sulfur level on the catalyst that degrades efficiency and degrades criteria emission conversion performance, and, more importantly, that the act of purging (reversing the sulfur contamination) negatively impacts fuel economy.

When comparing the 2.0L GTDI Ford Explorer data to the results from the SGS study, the following was observed by Ford:

- The 2.0L GTDI Explorer experienced an increase in NOx tailpipe emissions from a loss in catalyst efficiency (~0.5% less efficient). Most likely, the 2.0L GTDI Explorer NOx feedgas was greater than that of the API/SGS Study vehicles – this could be related to the engine displacement to vehicle mass ratio - the 2.0L GTDI Explorer represents an engine displacement to vehicle mass ratio that aligns with what is expected to achieve CO2 compliance in the near future.
- 2.0L GTDI Explorer exhibited higher air mass flow (and encountered boosting during the second hill of the FTP) compared to the 2.0L Focus PZEV
- 2.0L GTDI Explorer with 26.5ppm sulfur content in gasoline resulted in considerably higher emission degradation than the 80 ppm sulfur used in the SGS Study for a comparable engine

Additional Comments of the Alliance of Automobile Manufacturers on Market Gasoline Sulfur

Tier 3 Vehicles Need 10 ppm Sulfur Gasoline

While fuel is carefully metered and combusted to provide vehicle propulsion, fuel contaminants such as sulfur accumulate on the emissions control hardware. Sulfur poisoning of three way catalysts can be at least partially reversed, with the degree of reversibility depending on many factors. One factor is the amount of sulfur in the fuel itself—catalyst poisoning is much less reversible when the vehicle is using higher sulfur fuels. Vehicle driving mode also is very important because high speed and/or high load operation can help enrich the air-fuel mixture with additional hydrocarbons and raise the exhaust gas temperature, both of which conditions are necessary for any desulfurization to occur. Such so-called aggressive events are not without side effects, however. For example, while helping to return the catalyst to its original or baseline performance, each purge event degrades the catalyst and reduces its effectiveness to some extent, causing subsequent, post-purge baseline emissions to slowly increase with repeated purging cycles (“emissions creep”). Other important impacts include reduced fuel economy, since aggressive driving and enriching the A/F consume more fuel, and increased emissions of greenhouse gases (e.g., methane and nitrous oxide). In any case, relying on aggressive driving to purge the catalyst is not an effective emission control strategy, given that there is no assurance of sufficient, predictable aggressive driving across the population.

Fuel sulfur also contributes to particulate, ammonia (NH3) and nitrous oxide (N2O) emissions. Sulfates themselves are fine particulates, and they also interact with HC and fine ash in the exhaust and in the environment to form larger particles.

Reducing the sulfur in the fuel mitigates these unnecessary emissions, compromises and tradeoffs.

Design Limits and Tradeoffs

One of the most important design factors is the formulation and amount of platinum group metal (PGM) coating, which is applied to a honeycomb substrate containing open cells through which the exhaust gases flow. Today's coatings are highly advanced technology and have many complexities according to the Alliance; determining the formula and amount are not simple endeavors. One cannot simply add more PGM coating to the catalyst to improve its efficacy; indeed, too much coating can sometimes lead to increased back pressure on the engine, which reduces its fuel efficiency.

Increasing the number of catalyst cells per square inch (cpsi) is another factor in catalyst performance, because it increases the surface area and number of active sites. Cell density now ranges to 1200 cpsi or more, up from 400 cpsi just a few years ago. The problem with increasing cell density much further, however, is that the walls of the catalyst substrate, often made of ceramic materials, can become too thin, according to the Alliance. Cell density may already be approaching the point where the substructure is more vulnerable to cracking before the end of the vehicle useful life, due to the thinness of the walls.

Another issue is back pressure. When the catalyst cells become too small, the gas molecules encounter friction. This friction slows the gas flow, increases back pressure, increases temperature and reduces vehicle efficiency.

Yet another key design factor is the catalyst's distance from the engine: the closer the catalyst is to the engine, the quicker it will warm up and begin to reduce cold-start emissions. This strategy began to be used with Tier 2 vehicles, and it is now common practice. Close-coupled catalysts must fit within a more limited space than downstream (under-floor) catalysts, so they have a relatively smaller size. Importantly, they must use heat-tolerant materials that can survive at temperatures that routinely exceed 800°C. Currently, palladium is the only metal that can be used for such high temperature applications, and it is also the PGM that is most sensitive to sulfur poisoning. Substrate materials also must be carefully selected for high temperature durability, so they, too, will last the useful life of the vehicle—150,000 miles in the case of the proposed Tier 3 standard. It should be mentioned that these catalysts are already placed very close to the engine, so moving them even closer is unlikely to be an option.

Sulfur and the Air-Fuel Ratio (A/F)

It has been suggested that automakers can further optimize the air/fuel ratio (A/F) as a way to improve catalyst efficiency and reduce emissions, and since sulfur presumably does not affect the A/F, this approach can help automakers achieve the proposed new standard without the necessity of reducing fuel sulfur. Similarly it has been asserted that modified exhaust piping and secondary air injection, two components affecting A/F, are insensitive to sulfur. The Alliance points out that while it is correct that changes to the A/F will help reduce vehicle emissions it is incorrect to suggest that fuel sulfur will not affect the ultimate outcome. Both temperature and A/F play critical roles in the reaction processes that occur on the surface of the catalyst, including sulfate adsorption and desorption, which in turn, affects catalyst efficiency. Thus, these A/F system changes (e.g., modified exhaust piping and secondary air injection) do not make the system less sensitive to sulfur contamination.

The A/F ratio also affects the amount of NOx produced during combustion. While a lean A/F (i.e., more air, less fuel, as opposed to more rich, with less air and more fuel) helps reduce HC and CO emissions from the engine, it also tends to increase engine-out NOx emissions and shift the point at which TWCs operate most efficiently for all three emissions. These catalysts can increase HC and CO control when operating in a lean environment, but they reach their highest efficiency for NOx reduction only under stoichiometric or more fuel-rich conditions. Thus, managing the optimum emission reductions for all three emissions requires a careful balancing of the air-fuel ratio. Importantly, sulfur has a larger adverse impact on the catalyst under leaner conditions, as detailed below.

Making the A/F more lean is a key strategy for improving fuel economy and reducing GHG/CO2 emissions in most vehicles. Thus, automakers continue to examine the A/F factor very closely, along with all other fuel efficiency and emission control-related strategies.

The alliance noted that research by Ford[3] provides new insight into the complex relationships among air, catalyst efficiency and sulfur. Ford undertook the study to look more closely at the impact of sulfur at stoichiometric and leaner conditions, especially in light of the Umicore study mentioned earlier. The study evaluated several Tier 2/LEV II TWC samples in a laboratory setting designed to replicate the typical inlet catalyst exhaust environment encountered during vehicle operation.

The results show the test TWC achieving a higher percent efficiency for all three criteria emissions when operating with 0 ppm sulfur fuel as compared with 30 ppm fuel. Second, most importantly for this discussion, they show a widening of the CO/NOx window of A/F operation (the area under the CO and NOx curves) as a function of Lambda when moving from 30 ppm sulfur fuel to 0 ppm sulfur fuel. When the engine operated outside of this A/F window, the test catalyst efficiency dropped precipitously. Thus, the 0 ppm fuel enabled a higher catalyst efficiency under a wider operating window compared to the 30 ppm fuel.

The study demonstrated a 44% emissions reduction for both CO and NOx when the sulfur was reduced from 30 to 5 ppm and an even greater reduction from 30 to 0 ppm. This result bolsters one of the Malibu study findings, namely, that using a 3 ppm sulfur fuel reduced tailpipe NOX emissions by 40% compared to 33 ppm.

Emissions Creep over the Vehicle Useful Life

In a testing program completed by the Manufacturers of Emission Controls Association (MECA), the potential for achieving lower HC and NOx exhaust emissions from larger, heavier, light-duty gasoline vehicles using advanced TWC systems showed significant sulfur sensitivity after completing full useful life accelerated aging.[4] The MY 2004 GMC Yukon Denali , which was equipped with an advanced TWC system using only under floor catalysts, showed both NMHC (non-methane hydrocarbon) and NOx emissions

[3] Ford Technical Discussion, Sulfur Effects on Gasoline Exhaust Emissions with Advanced Catalyst Formulations, May 2011

[4] Anthony, J., Kubsh, J., “The Potential for Achieving Low Hydrocarbon and NOx Exhaust Emissions from Large Light-Duty Gasoline Vehicles,” SAE 2007-01-1261 (MECA 2007). The study also tested a 2004 MY Ford F-150, which showed consistent results as the GMC Yukon Denali.

slowly increasing over three successive runs ("emissions creep") of FTP testing on a converter system having 220 hours of accelerated aging. This finding is consistent with the expectation that under floor catalysts will experience sulfur contamination to a greater extent than close coupled catalysts, since they operate at relatively lower exhaust and catalyst temperatures that are less capable of removing sulfates.

Leaner and Cooler Exhaust: Sulfur's Impact on Advanced Fuel Efficient Technologies

To meet the coming matrix of multiple regulations, vehicle manufacturers will need to integrate advanced emission control technologies with advanced fuel efficient powertrain technologies such as downsized turbocharged engines, gasoline direct injection (GDI) engines and greater levels of hybridization. Some very advanced GDI engines can operate in a lean-burn mode, which is significantly more fuel efficient than in non-lean-burn mode. GDI-type engines also offer potential reductions in HC and CO relative to other gasoline engines. While conventional spark-ignition engines are also getting more efficient, these new technologies offer new options and the potential for step improvements in both emissions and fuel efficiency.

Such fuel efficient technologies as turbocharging and GDI tend to produce cooler exhaust temperatures compared to today's vehicles. While these types of technologies are in use today with three-way catalysts for emission control, the TWC performance is affected by the leaner and cooler conditions in which the TWC operates. The Alliance notes that lean port fuel injected (PFI) engines can operate leaner than conventional engines at stoichiometric A/F, homogeneous lean burn engines can operate leaner than lean PFI, and stratified lean burn engines can operate under the leanest conditions, with A/F ratios ranging higher than 25:1 by mass. All these leaner technologies have this in common: due to the cooler and leaner exhaust, their emission control systems are more susceptible to sulfur poisoning and are less easily purged. The leaner the exhaust, the less likely they will be able to comply with the proposed Tier 3 standards unless ultra-low sulfur gasoline is readily available.

Since the TWC becomes ineffective as enleanment goes past stoichiometric operation, especially for NOx emissions, TWCs are unsuitable for advanced fuel efficient technologies such as lean PFI and lean-burn GDI. Leaner engines also have the characteristic of generating relatively more engine-out NOx due to the leaner operating conditions. Instead of using TWC, therefore, these technologies must use emission control systems similar to those used in diesel vehicles, such as lean NOx traps (LNT).

LNT devices are especially sensitive to sulfur and are feasible only at ultra-low sulfur levels comparable to those now allowed for diesel fuel, and the lower the better.

Advanced NOx storage catalysts typically incorporate oxides such as barium oxide into the catalyst formulation. As the engine runs lean, the catalyst adsorbs nitric oxide (NO) molecules and converts them to nitrites and nitrates (NOx) while they remain on the catalyst. When the engine control module (ECM) observes that the catalyst has reached a predetermined NOx saturation level, it initiates a gasoline (HC)-rich event that generates CO and unburned HC. The CO acts as a reductant, converts the stored NOx to NO2, NO and finally N2. Sox, however, competes with NOx for the active catalyst storage sites, blocks NOx storage and causes lower NOx conversion efficiency.

Desulfurization can occur only at temperatures higher than required for NOx conversion, resulting in increased fuel consumption due to the catalyst heating and fuel enrichment required to achieve desulfurization. Thus, the more purging is required, the less fuel efficient the technology.

The Future of Lean Burn and Turbocharging Technologies in the US

One of the claims made is that lean burn technology will have limited, and eventually declining, application in the United States, even with a 10 ppm sulfur standard. This claim is based on a study conducted in 2010 by Martec, which interviewed automobile manufacturers and technology suppliers, among other sources of information. Both Europe and Japan have regulations that cap retail gasoline sulfur at 10 ppm, which enabled the introduction of lean burn technology into the Japanese and European markets during the last decade. Martec found the technology's penetration in Europe peaking at 2% in 2010 and predicted it would decline steadily after then. In Japan, it found the technology also peaked at 2% but much earlier, in 2001, before Japan had implemented its 10 ppm sulfur cap for gasoline. Based on a variety of factors, Martec predicted that potential adoption in the U.S. would be limited to large vehicles with large engines, and that the application would decline as other technologies with superior characteristics became available. The implication is that the U.S. should not require 10 ppm sulfur gasoline to enable this sulfur-sensitive technology because manufacturers will have less sulfur-sensitive alternatives become available in the next several years. In their comments, the Alliance took issue with this assertion.

To begin, the Alliance argues that the Martec analysis is already out of date. It was completed before vehicle fuel economy/GHG standards for 2017 and beyond were adopted and this Tier 3 rulemaking was proposed. This suite of vehicle standards is the most stringent in the world, and it will require automakers to consider using all available technologies to meet the standards. When the study was conducted in 2010, before these new requirements were known, Martec pointed to the automotive industry belief that homogenous charge compression ignition (HCCI) engines would become a preferred fuel economy technology beginning in the 2015-2017 time frame and that lean burn GDI would be limited to a very small portion of the US fleet, specifically, those now using V8 engines, which would eventually be phased out. But Martec also admits that several problems with HCCI technology had yet to be overcome. For example, HCCI does not perform well under transient conditions, operation is currently limited to low loads and the combustion chambers are susceptible to carbon buildup. Even now, HCCI has not yet overcome these operational problems, and according to the Alliance the automotive industry now believes lean burn GDI technology is closer to commercialization than HCCI. The bigger point is that, regardless of the apparent attractiveness of an individual technology choice, manufacturers must pick and choose the technology that works best in each application. The choice will be influenced by a variety of factors and what seems to be the best fit in a given case. Manufacturers should not be constrained in their choices due to a solvable problem like inadequate market fuel quality.

Another issue some have raised is that the GHG benefit of lean burn technology may be smaller than previously believed and potentially too small to outweigh the additional cost. Considerable research into different lean burn engine designs and emission control technology combinations is ongoing, however, and automakers and technology suppliers continue to maintain it will significantly reduce fuel consumption, which correlates to CO2 emission reductions. In their latest edition of the Worldwide Fuel Charter, published