

Reversibility of Gasoline Sulfur Effects on the Exhaust Emissions of Late Model Vehicles

Keith Vertin and Aaron Reek
SGS Environmental Testing Corp.

ABSTRACT

The U.S. EPA has proposed a Tier 3 rule to lower average NMOG+NOx emissions from new light duty vehicles by approximately 80% from 2017 to 2025. Early in this time period, gasoline-fueled vehicles are expected to use technologies similar to California SULEV-II/PZEV certified models currently in limited production. These late model vehicles feature engine control systems that promote rapid catalyst light-off and are designed for ultra-high catalyst conversion efficiency.

To enable the use of advanced catalyst coatings and materials, the EPA is also proposing to limit the sulfur content of gasoline to an annual average of 10 ppm while optionally maintaining the current maximum cap of 80 ppm. Fuel sulfur is known to poison precious metal-based catalysts, and the impact on emissions is well understood for older technology vehicles. However, there is a lack of test data on the sensitivity and reversibility of late model vehicle emissions to sulfur.

This study evaluated six late model vehicles to determine if the exhaust emissions effects caused by exposure to 80 ppm high sulfur fuel were reversible, after the vehicles were refueled with 10 ppm sulfur fuel. Catalysts and sensors were aged to full useful life in the laboratory and then installed on the vehicles for testing. A statistical analysis concluded that there was no difference in the mean emissions of NMOG, NOx, CO, Soot and PN measured before and after the high sulfur fuel exposure. The emissions effects caused by high sulfur fuel exposure were reversible for all vehicles with 95% confidence.

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INTRODUCTION

Sulfur is known to poison precious metal-based three-way catalyst emission control systems. A number of studies were conducted by industry and government agencies in the U.S., Europe and Japan in the late 1980s and 1990s to evaluate the sensitivity of gasoline vehicle exhaust emissions to changes in fuel sulfur content and to investigate the reversibility of the sulfur poisoning effect. In 1991 the Auto/Oil Air Quality Improvement Research Program demonstrated the sulfur poisoning effect was reversible [1]. That is, following exposure to high sulfur gasoline the catalyst performance recovered when switching back to lower sulfur gasoline. In the European EPEFE program [2], researchers tested fuels containing 18 and 382 ppm sulfur, and reported that benefits of lower sulfur fuel were strongly dependent on the precious metal formulation used in the catalyst coatings. The Coordinating Research Council evaluated the effect of driving cycle on catalyst reversibility using fuels with 30 and 630 ppm sulfur [3]. The study included a comprehensive statistical analysis that concluded the poisoning effect was completely or partially reversible.

This previous research has shown that sulfur reversibility is influenced by a number of vehicle operating characteristics such as air-fuel ratio control, catalyst temperatures, emission control system design, configuration, and catalyst formulation. The effect of sulfur on today's ultra-low emissions vehicles is not well understood, especially for vehicles aged to full useful life. One study [4] measured the impact of test fuels containing 3 and 33 ppm sulfur on NOx emissions for a single vehicle - a 2009 model year Chevrolet Malibu certified to SULEV-II/PZEV standards. NOx results were reported for the underbody catalyst only. In addition to measuring sulfur sensitivity, the authors also found that use of a high exhaust flow/high engine load driving cycle such as the US06 reversed the sulfur poisoning associated with operation on 33 ppm sulfur fuel.

The present study has expanded upon these previous sulfur reversibility tests, by using fuels and vehicle models that were relevant to the current regulatory situation:

- Six late model vehicles were tested to evaluate a range of technology in the marketplace. Three of the vehicles were equipped with GDI engines. Five of the vehicles were certified to the California SULEV-II/PZEV emissions

standard.

- New catalytic converters and sensors were aged to the equivalent of 120,000 to 150,000 miles and then installed on the vehicles for emissions testing.
- The test sequence included baseline emissions tests run on 10 ppm sulfur fuel, followed by high sulfur fuel exposure tests using 80 ppm fuel, and then reversibility tests after the vehicle was switched back to 10 ppm fuel. The base fuel was a California LEV III certification gasoline containing 10%vol ethanol.
- Gaseous emissions, soot, particle number emissions, and catalyst conversion efficiency were compared for each step in the test sequence.

The objective of the study was to determine if the vehicle exhaust emissions from tests run using 10 ppm sulfur gasoline were reversible following the exposure to 80 ppm sulfur fuel.

APPROACH

Vehicles

Test vehicles were selected to represent the latest in powertrain and emissions controls technology, and were tested as a surrogate for EPA Tier 3 vehicles which were not yet commercially available. Late model vehicles were selected to include a range of exhaust emission control system design configurations available on high selling models. The vehicles fell into three emissions certification categories:

- One SULEV-II / PZEV vehicle, specifically the 2009 Chevrolet Malibu equipped with a 2.4L engine was selected to allow comparison with testing performed in a previous study [4]
- Four vehicles certified to meet either the California SULEV-II / PZEV exhaust emissions standards or the Federal Tier 2, Bin 2 exhaust emission standards
- One vehicle to represent a typical in-use Federal Tier 2 Bin 5 model

The vehicle models selected for the study are listed in [Table 1](#). Several of the vehicle models had the engine and evaporative emissions family certified to both California and Federal emissions standards. Three vehicle models were equipped with SFI engines. Vehicles #03, #04, and #05 were equipped with wall-guided GDI engines. All vehicles in the study had stoichiometric combustion following warm-up, and employed three-way catalysts.

All vehicles were equipped with a close-coupled and underbody catalyst combination, except the Civic which had a single close-coupled catalyst only. From information in the public domain, three of the vehicles employed strategies for accelerating catalyst light-off during start-up: the Malibu used secondary air injection combined with rich operation, the

Sonata used late fuel injection, and the Audi A3 used stratified lean operation on start-up followed by air injection for NMOG reduction.

Table 1. Test Vehicles and Emissions Controls Equipment

Vehicle No.	Year, Make and Model	Engine and Family Code	Emissions Certification, Equipment on Emissions Label, Number of Catalysts
#01	2009 Chevrolet Malibu	2.4L I4 9GMXV02.4026	California SULEV-II PZEV and Federal Tier 2 Bin 5 SFI, HO2S, TWC, AIR 1 CC Catalyst, 1 UB Catalyst
#02	2012 Honda Civic EX	1.8L I4 CHNXV01.8VC2	California SULEV-II PZEV and Federal Tier 2 Bin 2 TWC, AF SENSOR, HO2S, EGR, SFI 1 CC Catalyst
#03	2012 Hyundai Sonata	2.4L I4 CHYXV02.4YPC	California SULEV-II PZEV DFI, HO2S(2), WU-TWC, TWC 1 CC Catalyst, 1 UB Catalyst
#04	2012 Ford Focus	2.0L I4 CFMXV02.0VZ2	California SULEV-II PZEV and Federal Tier 2 Bin 3 TWC, HO2S, DGI, HAFS 1 CC Catalyst, 1 UB Catalyst
#05	2012 Audi A3	2.0L I4 Turbo* CADXV02.03PA	California SULEV-II PZEV and Federal Tier 2 Bin 3 DFI, TWC(2), HO2S(3), AIR, CAC, TC 1 CC Catalyst, 1 UB Catalyst
#06	2012 Toyota Camry	3.5L V6 CTYXV03.5BEC	Federal Tier 2 Bin 5 SFI, 2A/FS, 2WU-TWC, 2HO2S, TWC 2 CC Catalysts, 1 UB Catalyst

* Mid-grade gasoline required, premium recommended

The Audi A3 was equipped with a turbocharged GDI engine. This model was selected to expand the diversity of powertrain technology to be tested. The effects of turbocharging and associated high exhaust flow rates on catalyst performance were of interest. The manufacturer required mid-grade gasoline for this model. The inclusion of the Audi therefore required a premium test fuel be used in the study.

All vehicles were recruited with 5,000 and 11,000 miles on the odometer (8050 to 17700 km). The vehicle inspection criteria and additional details are further documented in another report [5].

Fuels

The base fuel for the study was California LEV III certification gasoline [6]. This fuel specification has 8 to 11 ppm sulfur, and nominal ethanol content of 10%vol. The certification fuel has a specification for regular and premium octane. The antiknock index, (R+M)/2, was 87 to 88.4 for regular unleaded and 91 minimum for premium unleaded.

At the start of the project, the California LEV III certification fuel was not commercially available. The base fuels were therefore made-to-order fuel batches formulated specifically for this project. The base fuels were ordered with 10 ppm nominal sulfur content and a TOP TIER® detergent additive. Base fuel properties are summarized in [Table 2](#).

Table 2. Base Fuel Properties

Property, ASTM Method	Units	REGULAR CALEV3_10	PREMIUM PRLEV3_10	CA LEVIII Specification
Distillation, D86				
IBP	C	42	43	
10%	C	58	58	54-66
50%	C	101	100	96-102
90%	C	158	158	154-160
EP	C	178	181	199 max
Sulfur, D5453	ppm	9	9	8-11
RVP, D5191	psi	7.2	7.2	6.9-7.2
Ethanol, D4815	%vol	9.8	10.2	9.8-10.2
Lead, D3237	g/gal	None	None	0.1 max
Density@60F, D4052	g/cm ³	0.7496	0.7465	
Carbon, D5291	%mass	82.88	82.39	
Hydrogen, D5291	%mass	13.65	13.82	
Oxygen, D4815	%mass	3.6	3.76	3.3-3.7
Aromatics, D1319	%vol	20.9	21.9	19.5-22.5
Saturates, D1319	%vol			
Olefins, D1319	%vol	4.9	4.4	4-6
Antiknock Index (R+M)/2, D2699	Rating	87.9	92.9	87-88.4 (reg), 91 min (prem)

An 80 ppm sulfur fuel was also prepared for use in the reversibility test sequence. A mixture of sulfur compounds was added to the base fuels to prepare the test fuels with 80 ppm sulfur concentration. The sulfur mixture consisted of 4 wt% dimethyldisulfide, 23 wt% thiophene, and 73 wt% benzothiophene, representing the types and distribution of sulfur compounds present naturally in gasoline [7].

Sulfur content was monitored throughout the study and was found to be within ± 2 ppm of the nominal value for all samples collected [5].

Catalyst and Sensor Aging

New catalytic converters and exhaust system sensors were procured for all vehicles and aged on an engine test stand to the equivalent of 120,000 to 150,000 miles (full useful life). All exhaust parts used for aging were stock and procured from authorized dealerships.

Protocols to accelerate the aging of automotive catalysts on the engine test stand have been in use for many years and

have evolved over time [8, 9, 10]. The Rapid Aging Test, or RAT-A, utilizes a multi-mode sequence to produce elevated exhaust temperatures to thermally age the catalyst. The CARB-modified RAT-A four-mode cycle was chosen as a contemporary method for aging all vehicle systems in this study [10]. The aging cycle parameters used were:

- Mode 1 = 40 seconds engine out condition @ stoichiometric fuel-air ratio
Inlet temperature @ 825°C ($\pm 20^\circ\text{C}$)
80 scfm exhaust flow per converter
- Mode 2 = 6 seconds @ fuel-rich operation
3.0% CO ($\pm 0.3\%$)
- Mode 3 = 10 seconds @ fuel-rich operation (same as Mode 2) with secondary air injection
3.0% O₂ ($\pm 0.3\%$).
- Mode 4 = 4 seconds engine out condition @ stoichiometric fuel-air ratio
Secondary air injection (same as Mode 3)
- 225 hours cycle time run, equivalent to 120,000 to 150,000 miles (193,000 to 241,000 km)

The engine test stand utilized an 8.1L Chevrolet V8 engine with exhaust manifolds joined to a custom quad leg exhaust system. The engine exhaust was split into four legs to allow the aging of catalysts from multiple vehicles simultaneously. The catalysts from all six vehicles were aged in two dynamometer runs. Where possible, manufacturer hardware including interconnecting pipes, flex pieces and flanges were used in the test set-up. The characteristic length between the close-coupled catalyst and underbody catalyst was maintained. The test set-up included air-fuel ratio measurement and thermocouples for exhaust gas and catalyst bed temperature measurement.

An alcohol-free gasoline with 91 antiknock index was used for the catalyst aging tests. Several batches of fuel were used during the aging period, with fuel sulfur content varying from 18.5 to 43 ppm.

Precise control of air-fuel ratio and secondary air injection was critical to ensure proper catalyst aging. Exposure to excessive exhaust temperatures may potentially cause non-reversible thermal deactivation of the catalyst coating, and such damage would not be representative of real world use. A complete record of the air-fuel ratio, catalyst inlet and bed temperatures was recorded to allow analysis of the thermal exposure [5]. Histogram temperature data are presented for Vehicle #01 in [Figure 1](#). Temperature was hottest near the front face of the close-coupled catalyst, due to an exothermic reaction of the exhaust gas. A peak catalyst temperature measurement of 1015°C was reached during the aging cycle.

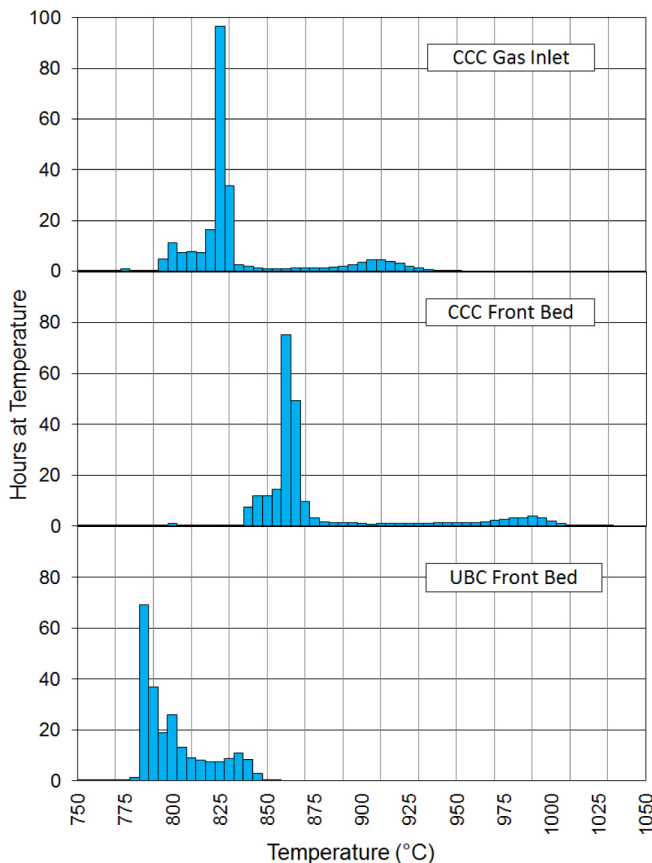


Figure 1. Exhaust Gas Inlet, Close-Coupled Catalyst and Underbody Catalyst Temperature Histograms for Vehicle #01 over the 225 Hour Aging Period

Median and peak catalyst exposure temperatures for each vehicle are summarized in Table 3. Vehicle #03 had the highest catalyst exposure temperature of 1035°C. Vehicle #02 had significantly lower exothermic reaction at the CCC front bed location. The close-coupled catalyst temperature results for Vehicle #06 pertain to the left bank of the V6 engine.

Table 3. Median and Peak Catalyst Exposure Temperatures over the 225 Hour Aging Period

Vehicle	Make	Close-Coupled Catalyst Front Bed Temperature (°C)		Underbody Catalyst Front Bed Temperature (°C)	
		Median	Peak	Median	Peak
#01	Malibu	859	1015	791	850
#02	Civic	853	955	NA	NA
#03	Sonata	891	1035	809	895
#04	Focus	868	1025	809	895
#05	A3	891	1015	823	895
#06	Camry	865	1005	788	870

Emissions Test Procedure

The aged catalysts and sensors were installed on the late model vehicles for emissions testing on a chassis dynamometer. Each vehicle was tested using a base fuel with 10 ppm sulfur concentration, exposed to 80ppm fuel and tested, and then retested upon refueling with 10ppm fuel.

The test sequence for each vehicle is shown in Table 4. The test procedures included common chassis dynamometer emissions test cycles, with abbreviations provided in the Appendix. Special care was taken to ensure fuel changes were complete and the vehicle was conditioned on each fuel before emissions testing began. Each vehicle was driven 125 miles during the initial baseline tests using 10 ppm sulfur gasoline, followed by approximately 372 miles of operation on the 80 ppm sulfur gasoline, and 72 miles after refueling with 10 ppm sulfur fuel.

Table 4. Vehicle Test Sequence for Sulfur Reversibility Study

Test Segment	Procedure	Miles	Cumulative Miles Driven for Segment
Catalyst Sulfur Purge, 10ppm Sulfur Fuel	Double Fuel Drain and 70% Refill EPEFE + 2 LA4	42.2	125.4
Baseline Emissions 10ppm Sulfur Fuel	12 to 24 Hour Soak FTP75 Emissions Test 2 LA4 + 1 US06 Preparation Cycle	11.1 22.9	
	12 to 24 Hour Soak FTP75 Emissions Test 1 US06 Preparation Cycle	11.1 8.0	
	12 to 24 Hour Soak FTP75 Emissions Test 1 US06 Preparation Cycle	11.1 8.0	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
Exposure to 80ppm Sulfur Fuel	Double Fuel Drain and 100% Refill 300 Miles on Dyno, SRC 70% Fuel Refill 2 LA4 + 1 US06 Preparation Cycle	300.0 22.9	372.1
	12 to 24 Hour Soak FTP75 Emissions Test 1 US06 Preparation Cycle	11.1 8.0	
	12 to 24 Hour Soak FTP75 Emissions Test 1 US06 Preparation Cycle	11.1 8.0	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
Establish Degree of Reversibility, 10ppm Sulfur Fuel	Double Fuel Drain and 70% Refill 2 LA4 + 1 US06 Preparation Cycle	22.9	72.1
	12 to 24 Hour Soak FTP75 Emissions Test 1 US06 Preparation Cycle	11.1 8.0	
	12 to 24 Hour Soak FTP75 Emissions Test 1 US06 Preparation Cycle	11.1 8.0	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	
	12 to 24 Hour Soak FTP75 Emissions Test	11.1	

The test sequence began with an EPEFE cycle [11] consisting of ten WOT events to elevate exhaust and catalyst temperatures for sulfur purge. Previous studies have shown the EPEFE cycle is an effective means for catalyst sulfur purge. The EPEFE + 2 LA4 cycles served to condition all vehicles uniformly using 10 ppm low sulfur, prior to the baseline emissions tests.

The purpose of the four baseline tests was to establish vehicle exhaust emissions using the 10 ppm low sulfur fuel, following the catalyst sulfur purge and prior to the 80 ppm sulfur fuel exposure. The baseline emissions were the basis for comparison, used to quantify fuel sulfur sensitivity and reversibility effects for the tests that followed.

A US06 prep cycle was performed in lieu of an LA4 prep cycle, prior to each soak period and FTP75 emissions test. The LA4 and FTP75 cycles used for emissions certification purposes reach a top vehicle speed of only 56.7 mph, and exhaust temperatures are low in comparison to other chassis dynamometer cycles. Therefore, repeated dynamometer testing using the LA4 and FTP75 cycles was not necessarily representative of real-world driving. The US06 cycle was developed to address the shortcomings with the FTP75 test cycle, to better represent higher speed and higher acceleration driving behavior. Data from the U.S. Federal Highway Administration show that nearly 46% of the average daily vehicle miles of travel at posted speeds of 60 mph or higher occurs on urban roads [12]. To better represent real-world driving behavior, the reversibility test sequence used in this study included alternating US06 and FTP75 cycles, to encompass both higher speed and lower speed vehicle operation. Other researchers have used a similar test combination to study sulfur reversibility [3, 4].

Following the change to 80ppm fuel, each vehicle was conditioned on the chassis dynamometer for 300 miles using the EPA Standard Road Cycle. Three emissions tests were then run to determine the sensitivity of vehicle exhaust emissions to catalyst poisoning that occurred during exposure to the 80 ppm sulfur fuel.

The vehicle fuel tank was then drained and refilled with 10 ppm sulfur fuel, conditioned, and triplicate emissions tests were run. These final tests were performed to determine if the exhaust emissions effects caused by 80ppm sulfur fuel exposure were reversible. That is, the exhaust emissions from this final segment were compared with the baseline emissions, to determine if there were any statistical differences in results before and after the high sulfur fuel exposure.

Laboratory Equipment

Emissions tests were performed in a certification-compliant chassis dynamometer emissions laboratory. All tests were run in the same laboratory featuring a Burke Porter 48" roll dynamometer in a temperature and humidity controlled environment. The laboratory was equipped with a constant

volume sampling system (CVS), and raw modal and dilute bag gas sampling and analysis. The emissions sampling arrangement is shown in Figure 2.

Bag samples were simultaneously collected from the diluted vehicle exhaust and from the ambient, to ensure quantification of the background and accurate calculation of cycle average exhaust mass emissions. Bag gas analysis included measurement of CO, CO₂, NO_x, total HC, and CH₄. Methane measurement was by gas chromatograph FID. Bag measurements were used for the statistical analysis and for all charts presented in this paper unless otherwise indicated.

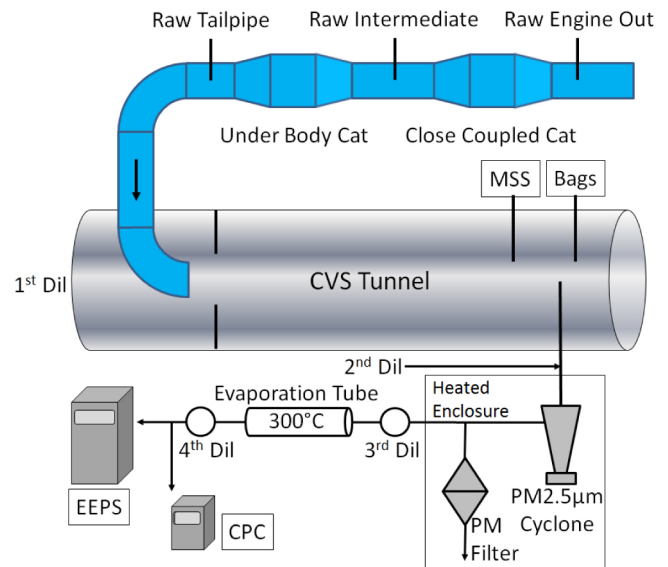


Figure 2. Emissions Sampling Arrangement

Speciation of the exhaust gas for NMOG determination was beyond the scope of this study. NMOG mass emissions were estimated using a formula from an experimental correlation [13]:

$$\text{NMOG}_{\text{EST}} = (\% \text{EtOH} * 0.0071 + 1.0302) * \text{NMHC}$$

where %EtOH was vol% ethanol in fuel. NMOG results presented in this report were estimated using this formula. For gasoline containing 10%vol ethanol, $\text{NMOG}_{\text{EST}} = 1.1012 * \text{measured NMHC}$.

Continuous raw engine-out, intermediate and tailpipe emissions were also measured to provide information on the time to catalyst light-off and catalyst conversion efficiency.

The effect of sulfur on particulate matter and particle number emissions was of interest, especially with the inclusion of GDI-equipped vehicles in the study. The entire exhaust volume was diluted in a full dilution tunnel (Figure 2) for the purposes of particulate matter measurement.

The primary particle mass measurement for the study was made using an AVL483 photoacoustic monitor (MSS). This instrument sampled from the dilution tunnel to minimize