Report – Review of The Effects of Fuel Sulfur Level on Emissions
from the In-Use Tier 2 Vehicles - DRAFT REPORT

Ronald Heck 2/3/2012

General discussion:

It is very important that the authors discuss right up front that they have taken an approach where the vehicles are considered as "black boxes". This is a totally different approach than that adopted by the Umicore paper (Ball D., Clark D., Moser D. (2011). *Effects of Fuel Sulfur on FTP NOx Emissions from a PZEV 4 Cylinder Application.* SAE 2011 World Congress Paper 2011-01-0300. SAE International: Warrendale, PA.) In the "black box " approach there is no consideration of the engine control strategies (rich or lean bias, cold start strategy, etc.), sensor responses (from aging), vehicle operation (e.g. fuel cut), catalyst technologies, catalyst configurations(close coupled, underfloor, cell density, volume, etc.) See James M. Lyons, David Lax, and Steve Welstand, Investigation of Sulfur Sensitivity and Reversibility in Late-Model Vehicles, SAE 1999-01-3676 for work that takes a more phenomenological approach to sulfur effects. By the way I could not find this reference in the report. In the "black box" approach very little information is given besides the vehicle type, mileage, age, etc. Because of this lack of information it will be difficult for anyone to repeat the authors' experiments and challenge there results. In addition it will be difficult for the authors to explain data anomalies because there are no specifics to tease out a possible explanation. Also since there are so many uncontrolled variables, the statistical analysis may be limited since it is only statistics! This is not meant to say the work has no merit only to provide caution in the final conclusions and merits of too much statistics!

One concern I have is if some of the vehicles have a fuel cut strategies. If so, this could confound the results since in the US06 the catalyst with a fuel cut strategy will see lean excursions while a catalyst without will be stoichiometric during the cycle. Again since no information is given in the report on engine operation it is impossible to go back and uncouple this effect.

Sulfur poisoning is a complex phenomenon for catalysts and the catalyst manufacturers have found recipes to compensate for high and low sulfur levels (see Harold N. Rabinowitz, Samuel J. Tauster, Ronald M. Heck, The effects of sulfur & ceria on the activity of automotive Pd/Rh catalysts, Applied Catalysis A: General 212 (2001) 215–222). If the catalyst companies can design for Tier 2 vehicles at 30 ppm S, then this study may be in question or to put in another way, maybe some of the vehicles you studied already have these types of technologies and that is why you found some responses that didn't show an effect of S level!

The removal of sulfur from the catalyst needs a consistent statement throughout the paper. You show Figure 2-1 from Ford but the text is not consistent in describing this removal which is due to temperature, air to fuel ratio, and sulfur level. Also the degree of removal is different for Pt, Pd and Rh and the oxygen storage materials (Ce, Zr, La, etc.). So this discussion needs a little more technology.

In the report, there are a number of places where symbols are not explained in tables and in text. Also, I did not see an explanation about how one does a hot/cold start FTP. Please make sure this is explained in the text of the report.

At end of papers, please a list of references. I had to go through the entire paper many times to see if a reference was cited. This was painful!

Specific textual comments:

I am including the entire report as a Word document with 27 comments embedded in the text.

Specific Textual Comments Ron Heck		
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2	Fuel sulfur content has long been understood to affect the performance of emission after treatment catalysts in light duty vehicles, where the sulfur and/or its oxides adsorb to the active precious metal sites, reducing the catalyst's efficiency in destroying harmful pollutants.	Fuel sulfur content has long been understood to affect the performance of emission after treatment catalysts in light duty vehicles, where the sulfur and/or its oxides adsorb to the active precious metal sites and oxygen storage materials, reducing the catalyst's efficiency in destroying harmful pollutants.
2	The quantity of sulfur present on the catalyst at any given time is a function of its temperature and the fuel sulfur level . . .	The quantity of sulfur present on the catalyst at any given time is a function of its temperature, air to fuel ratio, and the fuel sulfur level . . .
2	. . . with elevated catalyst temperature and lower fuel sulfur concentration both reducing sulfur loading.	. . . with elevated catalyst temperature , rich of stoichiometric operation, and lower fuel sulfur concentration both reducing sulfur loading.
3	Test fuels were two non-ethanol gasolines with properties typical of certification fuel, one at a sulfur level of 5 ppm and the other at 28 ppm.	Is there any reason to expect different results with ethanol gasolines?
4	[Table ES-1] The clean-out effect is not significant at $\alpha = 0.10$ when no reduction estimate is provided.	Need to explain what p-value is in the text? Also what is in (?????)?
4	This indicates that the catalyst is not fully desulfurized, even after a clean out procedure, as long as there is sulfur in the fuel.	Not sure you can make this conclusion. It may be that the sulfur in fuel equilibrates instantaneously and it is a concentration effect not a desulfurization. To prove this you would have to vary the desulfurization time and see where it reaches steady state.
5	[Table ES-2]	Again what is p value and what is in (….)?

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5	This analysis found highly significant reductions for several pollutants, as shown in Table ES-3; reductions for Bag 2 NOx were particularly high, estimated at 59 percent between 28ppm and 5ppm overall	This analysis found highly significant reductions for several pollutants, as shown in Table ES-3; reductions for Bag 2 NOx were particularly high, estimated at 59 percent between 28ppm and 5ppm overall.
5	Other results, such as Bag 1 hydrocarbons, did show a significant miles-by-sulfur interaction.	Does this mean that the effect never equilibrates? Are you comfortable in saying this?
7	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 and the concentration of sulfur oxides in the incoming exhaust gases.	Again air to fuel ratio is important as you mention in the next sentence for reducing conditions.
8	However, the temperatures necessary to release sulfur oxides can also lead to thermal degradation of the catalyst over time.	No where do you mention that normal operation of the vehicle, the catalyst is constantly being exposed to rich/lean condition from the control system using an oxygen sensor. So the catalyst is being regenerated in-situ form the perturbation around stoichiometric.
11	The level of reversible in-use sulfur storage and release (or loading) within an exhaust catalyst system can be assessed by measuring emissions from the vehicle as received, performing a high speed, high load clean-out cycle, then measuring emissions again.	In describing the cleanout it is important to mention the temperature range and the air to fuel ratio. Also depending on the vehicle calibration the degree of richness and time at such could be different from vehicle to vehicle. How is this taken into account for the degree of cleanout?
11	A vehicle with relatively high exhaust temperature at the catalyst location, and/or significant excess loading of certain platinum group metals (PGM) and other active materials in the catalyst may be relatively insensitive to sulfur loading regardless of driver behavior.	Up to now you have not mentioned the effect of S on the oxygen storage components which will affect NOx and lightoff in cold start. Is there a reason this is not mentioned?
12	This loading continues over time with vehicle operation and can be observed as an increase in emissions (sometimes referred to in the auto industry as “NOx creep”).	Is this due to PGM and/or oxygen storage component deactivation??/
13	Table 4-1 Test Vehicles Recruited	If you look at the Umicore study you will see details about the e3mission

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		control system (close coupled, underfloor, etc.) You give no such detail in this study. Also, they also show a plot of engine lambda during the FTP. This is important background information to possibly explain outliers or unusual results. This study loses significant meaning without this information. You are treating the cars as black boxes and I think this is a mistake! Also, the oxygen sensor response is very important as well as it age. This is never mentioned in this entire study.
17	[Figure 6-1]	Do you explain what a hot/cold start FTP is anywhere in the report??
25	[Table 7-1]	What does the value in (…) mean?? Please explain.
35	[Table 7-4] The clean-out effect is not significant at $\alpha = 0.10$ when no reduction estimate is provided.	Explain what is in (….)?
38	Furthermore, the reduction in emissions from cleanout shown in Table 7-4 would likely be larger if the low sulfur test fuel at 5 ppm had been used for the cleanout procedure and the tests immediately following the as-received baseline emissions.	This looks like a conjecture. Present evidence?
39	[Table 7-6]	Explain what is in (……)?
40	For example, vehicle IDs 0011, 0022, and 0178 clearly show large effect of fuel sulfur level on emissions while the effect is only marginal for vehicle IDs 0123 and 0264.	Differences can be A/F ratio, close coupled catalyst, oxygen storage components, temperature history. This is why more information on vehicle characteristics is important to explain unusual results.
46	The BIC value for the first-order autoregressive structure was 764.90.	Did you explain BIC?? If not then do so.
47	[Table 7-8]	What if Pr? Explain.
55	[Figure 7-10]	Is there an explanation as to why these lines diverge and are not parallel?? Need some discussion here from the model.
56	[Table 7-11]	What is in (….)?

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57	[Table 7-13]	Is "Probt" probability??
59-60	Comparing emissions immediately following the clean-out procedure on 5 vs. 28 ppm fuel, FTP composite NO_x emissions were 18% lower, NMHC 9% lower, and CO 8% lower.	To make this conclusion you need to age with 28, clean out with 28 and test with 5 and compare age with 5, cleanout with 5 and test with 5. I went back in text and really didn't see this discussed in analysis. If I missed it OK otherwise need some discussion in analysis.