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ENGINE, EMISSIONS AND VEHICLE RESEARCH DIVISION
FAX: (210) 522-4742

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December 29, 2016

Mr. Greg Kerr
Propane Education and Research Council
1140 Connecticut Ave, NW
Suite 1075
Washington, DC 20036

SUBJECT: Final Letter Report No. 2 for "Effect of Sulfur Level on TWC Performance and Durability".

REFERENCE: SwRI Sub-Preproposal EVR-7624, SwRI Project No. 03.21905.

1.0 INTRODUCTION

The Propane Education and Research Council (PERC) requested SwRI to measure the effect of sulfur levels in propane fuel on the performance and durability of Three-Way Catalysts (TWC). This report discusses the work performed during the second part of the project as described in SwRI Sub-Preproposal EVR-7624. The first part of the project work was reported previously in SwRI Final Report 03-21905 dated June 03, 2016.

2.0 CATALYSTS

A fresh OEM catalyst core sample was extracted from a 2016 6.8 L gasoline catalyst supplied by Roush. The converter consisted of two elements, as shown in Figure 1.



FIGURE 1. OEM THREE WAY TEST CATALYST

The darker coloration at the inlet brick outlet-end suggested that this catalyst is zone coated. Samples were cut from the front and back of the inlet catalyst and from the outlet catalyst, and submitted for elemental composition analysis using the Proton-Induced X-Ray Emission (PIXE) technique. The results are shown in Figure 2. The catalyst is a palladium rhodium formulation. It is likely that both substrates were coated with the same formulation, and then the rear half of the inlet brick was further coated with additional palladium. To replicate this TWC system, half-inch long cores were cut from the front and rear of the inlet catalyst and a one-inch long core was cut from the outlet catalyst. These cores were assembled in series in the Universal Synthetic Gas Reactor™ to form a one-inch diameter by two-inch long core with identical catalyst loading ratios of the full catalyst system.

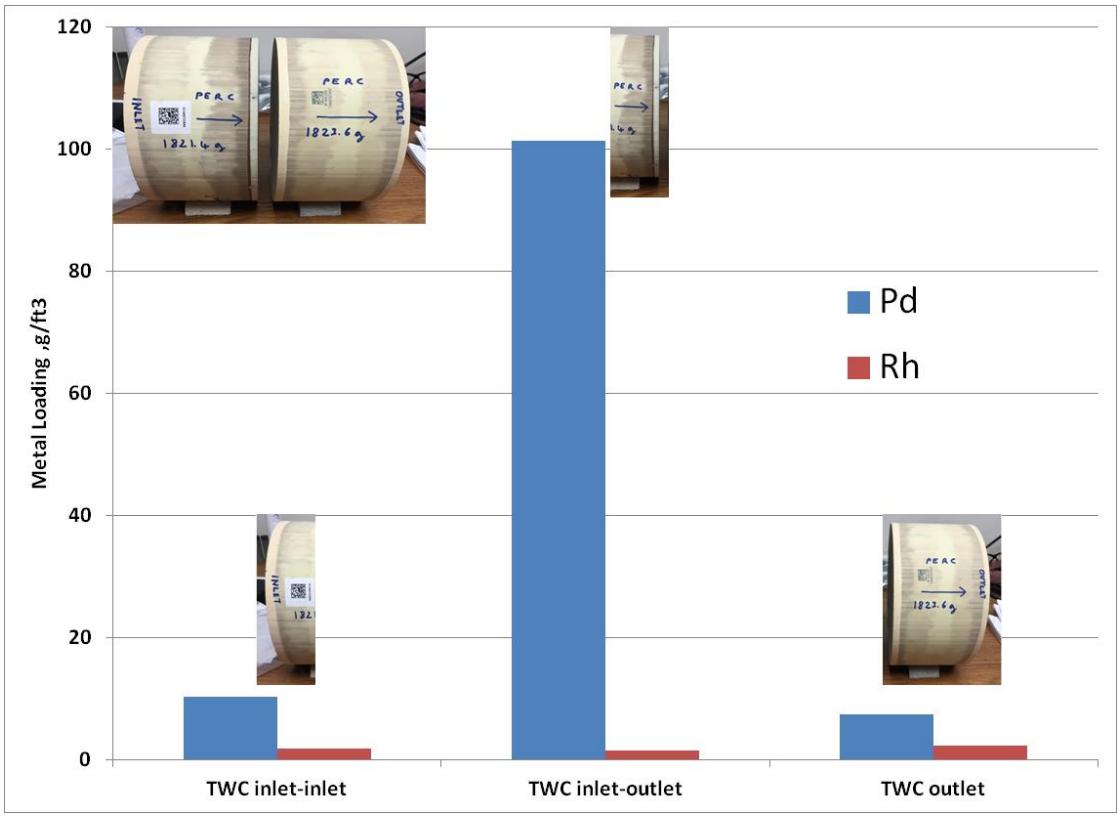


FIGURE 2. ACTIVE METALS IN THREE WAY CATALYST

A second catalyst formulation was also evaluated that was anticipated to exhibit better sulfur tolerance due to the presence of platinum along with palladium and rhodium. It was obtained from a commercial 2013 Cummins ISX12 G natural gas application. Table 1 gives the active metal compositions of the two catalysts. The second catalyst is referred to as the NG catalyst from here on in this report.

TABLE 1. ACTIVE CATALYST METAL LOADINGS

CATALYST	Pt, g/ft³	Pd, g/ft³	Rh, g/ft³	TPM, g/ft³
Roush	0	10/100/7	2/2/2.6	33
2013 Cummins ISX12 G	1.3	57	1.1	59

3.0 TEST PLAN

Fourier transfer infrared (FTIR) spectroscopy was used to measure engine-out emissions from a Ford 6.8 L V-10 during a heavy-duty FTP cold start test. The gas concentrations were identified based on the average emissions measured between 30 and 125 seconds of the cold start FTP cycle and corresponding bottled gasses were purchased to support catalyst core testing. A stoichiometric light-off test was performed on the catalysts in the fresh condition. The catalysts were then aged by sulfur exposure to the equivalent of 33,600 miles, and retested. The Roush catalyst was then desulfated and tested again.

4.0 EXPERIMENTAL CONDITIONS

SwRI used its Universal Synthetic Gas Reactor (USGR®) system, shown in Figure 3. Each core was installed into the USGR and exposed to a perturbated gas mixture that represented the cold start exhaust of the Ford 6.8 L V-10 engine. The gas mixes are listed in Table 2.

4.1 Standard Light-Off Test

A standard light-off test was performed from 150 – 500 °C at a ramp rate of 5 °C/min., and four sulfur concentrations that represented fuel sulfur levels of 11, 22, 45 and 90 mg/kg (0.625, 1.25, 2.5 and 5 ppmV at an AFR of 15:1). Comparison of the results indicated the degree of short term deactivation caused by fuel sulfur level. Sulfur-exposed catalysts were tested at 45 and 90 mg/kg fuel sulfur equivalent for the OEM catalyst, and 22 and 45 mg/kg fuel sulfur equivalent for the NG catalyst.

4.2 Sulfur Exposure Aging

The cores were aged by sulfur exposure. The aging temperature was maintained at 400 °C to efficiently oxidize and store the sulfur within the catalyst matrix. A steady state condition was used with a gas mixture that was slightly lean of stoichiometry to promote sulfur storage. The inlet SO_2 level was set to achieve total sulfur exposure equivalent to 33,600 miles in 16 hours. For an 90 mg/kg sulfur fuel, and fuel consumption rate of 6 MPGe, the total sulfur exposure over the two 7.5 inch diameter by 4 inch long catalysts would be 1,897 L of SO_2. Over the test core this is 8.40 L of SO_2. At a sulfur exposure concentration of 104 ppmV in the gas mixture, this equated to 16 hours = 33,600 miles. After aging, a light-off test was conducted.

4.3 Desulfation

Desulfation was performed on the OEM catalyst using the full gas mixture, including 45 mg/kg S equivalent, and a lean:rich cycle of 20s lean and 10s rich. The catalyst was heated to 650 °C inlet temperature and SO_2 evolution monitored using an FTIR. After desulfation, another light-off test was performed.



FIGURE 3. SWRI'S UNIVERSAL SYNTHETIC GAS REACTOR

TABLE 2. TEST GAS MIXTURES

GAS	CONCENTRATION
H_2O	16.4 %
CO_2	10.13 %
CO	[1]2900, 2600, 2100, 1200 ppm
H_2	[1]967, 867, 700, 400 ppm
NO	1013 ppm
CH_4	[1]97, 194, 388, 776 ppm
C_2H_4	63 ppm
C_2H_6	14 ppm
C_2H_2	19 ppm
C_3H_6	18 ppm
C_3H_8	258 ppm
O_2	[1]0.50, 0.51, 0.55, 0.61 %
SO_2	[1]0.625, 1.25, 2.5, 5.0 ppm
[1]CH_4 used as carrier for SO_2	

5.0 RESULTS AND DISCUSSION

The first tests performed were on the fresh OEM catalyst with varying exposure to SO_2. Figure 4 shows the light-off curves at 11 mg/kg fuel sulfur equivalent. Figure 5 shows the T_{50} temperatures (the temperature at which 50 percent conversion is achieved) for CO, NO, propane, ethane, propene, ethene and acetylene as a function of fuel sulfur content. It is apparent that NO, ethane and propane light-off temperatures increased at and above 45 mg/kg fuel S equivalent. Unsaturated hydrocarbon light-off temperatures were unaffected by fuel sulfur level.

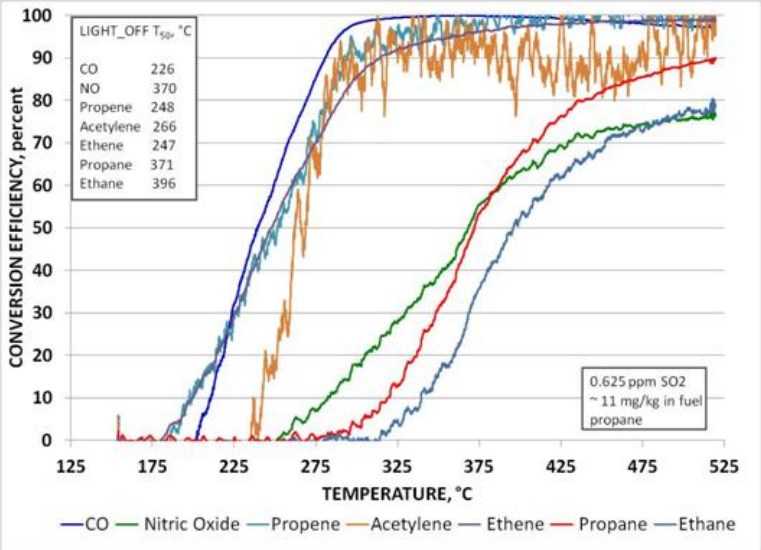


FIGURE 4. OEM CATALYST FRESH LIGHT-OFF TEST AT 11 MG/KG FUEL SULFUR EQUIVALENT

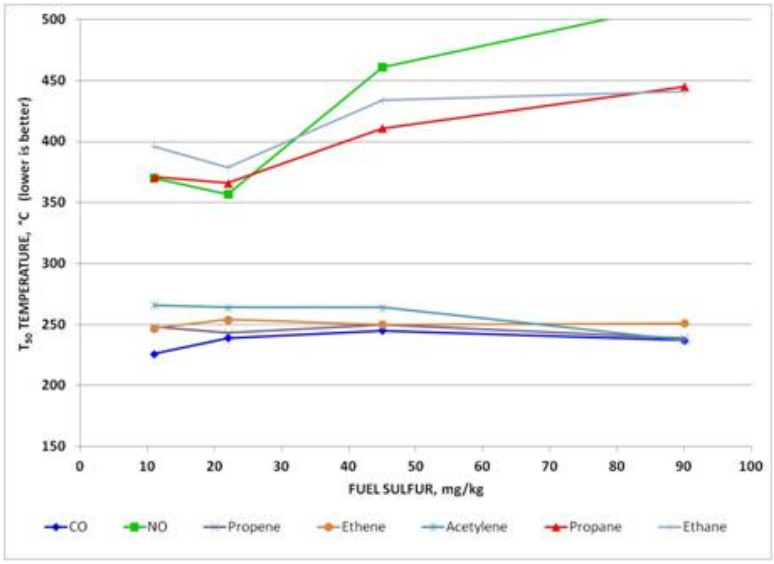


FIGURE 5. OEM FRESH LIGHT-OFF PERFORMANCE VERSUS FUEL SULFUR LEVEL

The next set of tests introduced a rich bias to the perturbation. By rich-biasing the engine out exhaust gases during the cold start, it was anticipated that improvements in NO_X light off could be achieved. Figure 6 shows the results with rich:lean times of 3:1, 2:1 and 3:2 seconds compared to the baseline 1:1 seconds. The NO light-off temperature decreased by 139 °C at the smallest bias of 3:2. It decreased by another 37 °C at the largest bias of 3:1. Therefore, even a small rich bias during the cold start can substantially reduce the NO light off temperature, leading to reduced NO_X emissions during an FTP test. Additionally, the propane light off temperature also decreased by 70 °C.

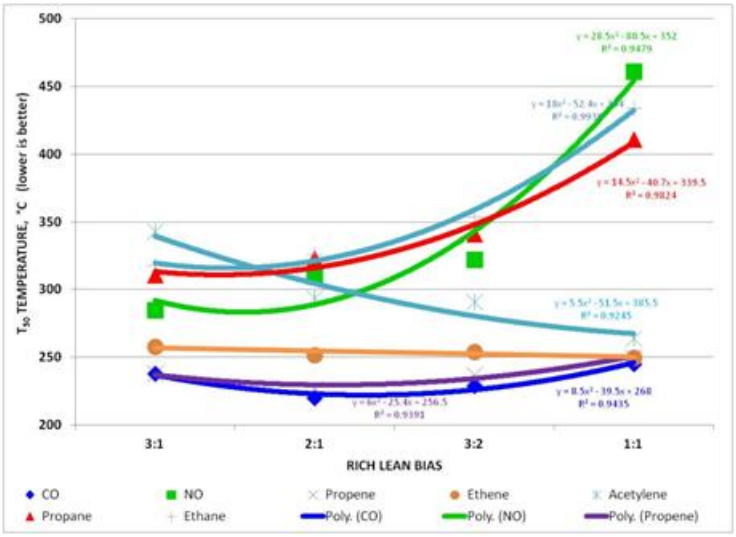


FIGURE 6. OEM FRESH LIGHT-OFF PERFORMANCE VERSUS RICH BIAS

The OEM catalyst was then aged to the equivalent of approximately 33,600 miles by exposing it to 104 ppm of SO_2 at 400 °C for 16 hours. Light off tests were then performed at 45 and 90 mg/kg fuel S equivalent SO_2 levels. The results are shown in Figure 7.

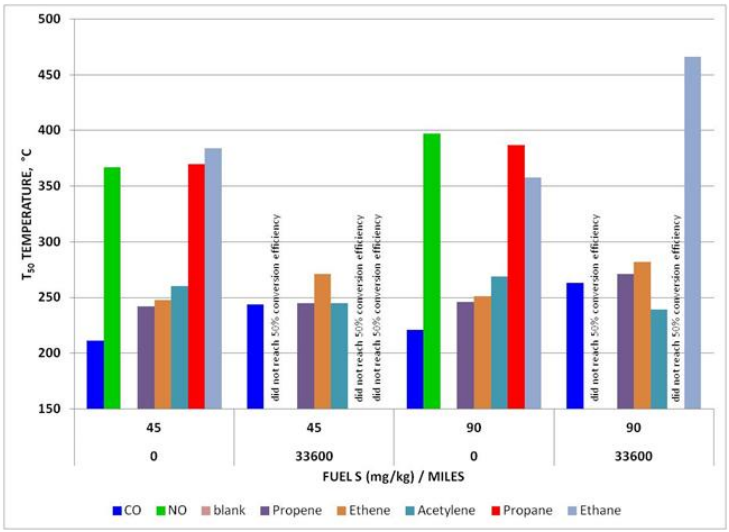


FIGURE 7. OEM AGED LIGHT-OFF PERFORMANCE

Propane and NO failed to achieve 50 percent conversion efficiency after aging, indicating the strong effect of sulfur on the OEM catalyst durability.

The second catalyst formulation, containing platinum and approximately twice the total precious metal loading of the OEM catalyst, was evaluated next. Figure 8 shows the differential light-off temperatures for the OEM and NG catalysts. The NG catalyst exhibited lower light off temperatures at all sulfur levels with particularly good performance at the 45 mg/kg fuel S equivalent level. It is believed that the improvement is more a result of the higher precious metal loading than the presence of platinum, although that cannot be ruled out.

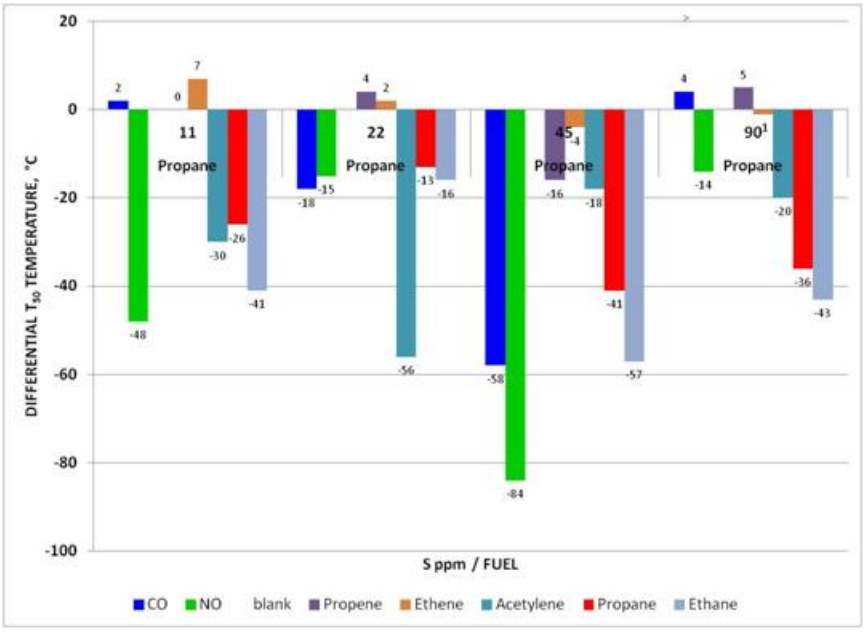


FIGURE 8. COMPARISON OF FRESH OEM AND NG CATALYST PERFORMANCE

The NG catalyst was aged to the equivalent of about 33,600 miles by exposing it to 104 ppm of SO_2 at 400 °C for 16 hours. Light off tests were then performed at 22 and 45 mg/kg fuel S equivalent SO_2 levels. The results are shown in Figure 9. There was no apparent deactivation of the catalyst as a result of sulfur exposure. This excellent result is attributed mostly to the presence of platinum in the formulation.

To determine if the OEM performance could be recovered by desulfating, it was exposed to the full gas mixture, including 45 mg/kg fuel S equivalent, at 650 °C using a rich:lean cycle of 20 s rich and 10 s lean. Desulfation continued until no more SO_2 was evolved from the catalyst. The desulfation data are shown in Figure 10. Desulfation only began above 600 °C, with SO_2 emitted during every rich transient. The outlet SO_2 reached equilibrium after about 30 minutes. The inlet SO_2 was then turned off, and the level dropped to about a 5 ppm baseline. It is believed the FTIR SO_2 reading at this level is offset due to interference from the other components in the gas mixture. The performance of the desulfated OEM catalyst relative to its original degreened performance is shown in Figure 11. At 22 mg/kg S fuel sulfur equivalent the NO_X light off recovered and the propane and ethane light offs partially recovered. At 45 mg/kg S fuel sulfur equivalent the NO_X light off was improve over the fresh baseline, and the propane and ethane light offs fully recovered. The improvement in NO_X light off temperature is likely due to a temporary improvement in catalyst performance due to rich preconditioning during the desulfation. It is concluded that the OEM performance can be recovered using a suitable desulfation procedure.

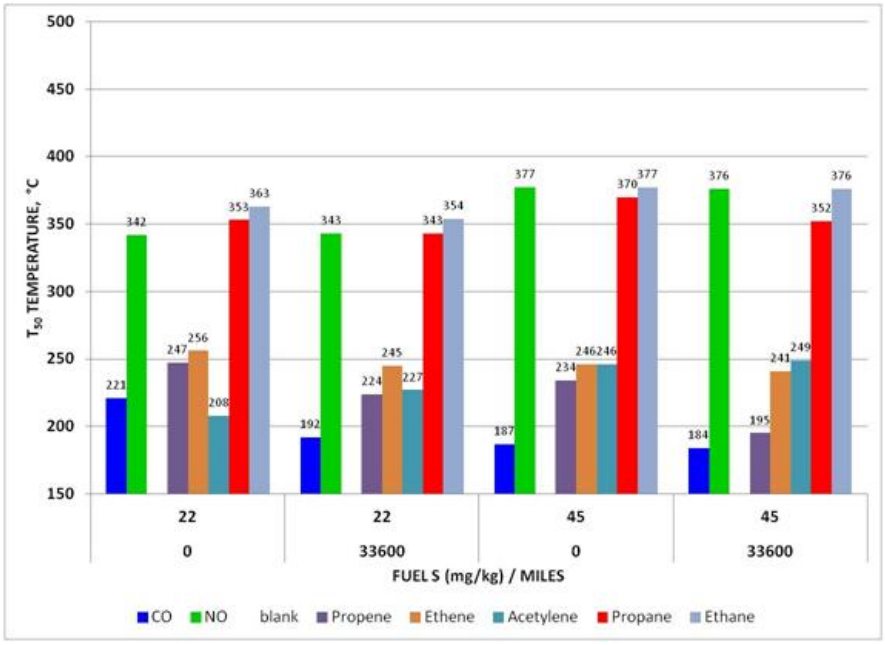


FIGURE 9. COMPARISON OF FRESH AND AGED NG CATALYST PERFORMANCE

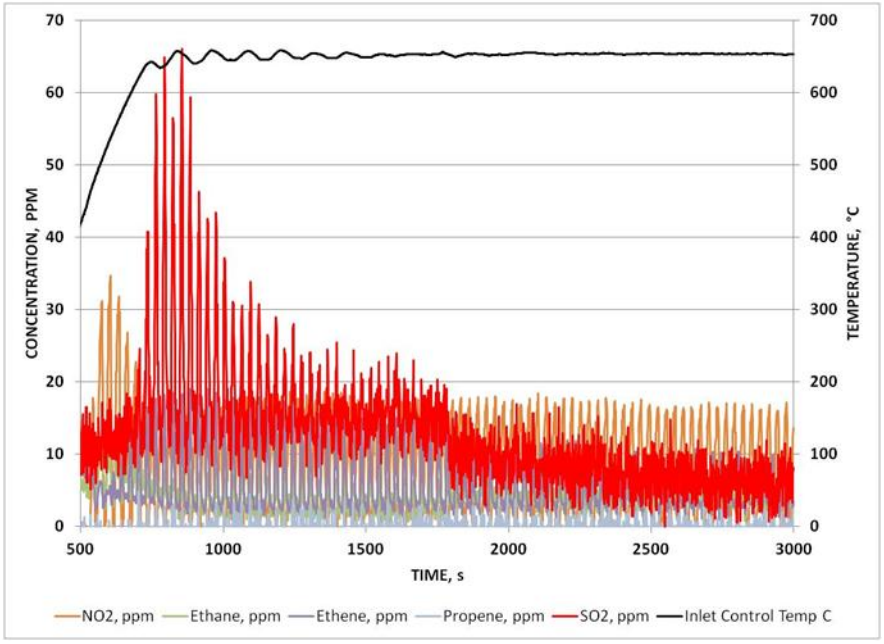


FIGURE 10. DESULFATION OF OEM CATALYST

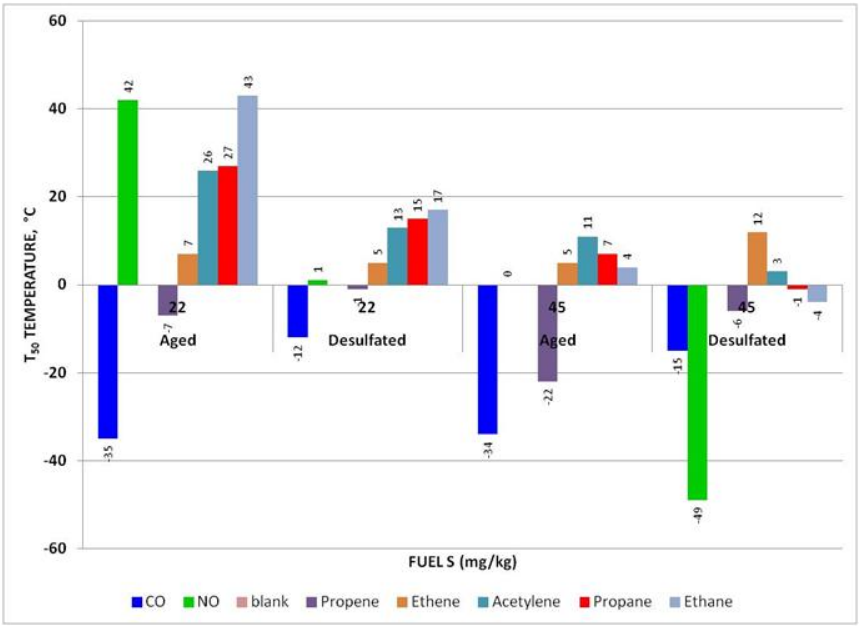


FIGURE 11. COMPARISON OF AGED AND DESULFATED OEM CATALYST PERFORMANCE

6.0 SUMMARY AND CONCLUSIONS

Increasing the precious metal content of the catalyst can result in lower light off temperatures and improved cold start performance. The addition of platinum in the formulation can also significantly improve the sulfur tolerance of the catalyst. A sulfur poisoned catalyst can be recovered using a suitable desulfation procedure.

7.0 CLOSURE

SwRI is pleased to provide this second letter report, and we look forward to working with you again soon. If you have any questions regarding this work, please contact Gordon Bartley by phone at (210) 522-5871, or by e-mail at gordon.bartley@swri.org or Michael Ross.

Prepared by:

Gordon J. Bartley, Ph.D., Principal Scientist
Catalyst & Aftertreatment R&D
Diesel Engine and Emissions R&D Department

Approved by:

Cary A. Henry, Ph.D., Manager
Catalyst & Aftertreatment R&D
Diesel Engine and Emissions R&D Department

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