

# Diesel Emission Control – Sulfur Effects (DECSE) Program

Final Report: Diesel Oxidation  
Catalysts and Lean-NO<sub>x</sub> Catalysts  
June 2001

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The test program and subsequent data analysis represent a collaborative effort of a technical work group consisting of representatives from the U.S. Department of Energy, its national laboratories, the Engine Manufacturers Association, and the Manufacturers of Emission Controls Association. The work group prepared this report using methods believed to be consistent with accepted practice. All results and observations are based on information available using technologies that were state-of-the-art at the time. To the extent that additional information becomes available, or factors upon which analyses are based change, the findings could subsequently be affected.

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## Acronyms

BSFC	brake specific fuel consumption
CE	conversion efficiency
cfm	cubic feet per minute
CFR	Code of Federal Regulations
CFV	critical-flow-venturi
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
cpsi	cells per square inch
CVS	constant-volume-sampling
DECSE	Diesel Emission Control-Sulfur Effects
DOC	diesel oxidation catalyst
DOE	U.S. Department of Energy
DPF	diesel particulate filter
EGR	exhaust gas recirculation
EMA	Engine Manufacturers Association
EO	engine-out
EPA	U.S. Environmental Protection Agency
ESC	European Stationary Cycle
FEP	fuel economy penalty
FEV	FEV Engine Technology
FTP	federal test procedure
FTP-75	Federal Test Procedure (light duty cycle)
H <sub>2</sub>	hydrogen
HC	hydrocarbon(s)
He	helium
HFID	heated flame ionization detector
HSDI	high-speed, direct injection
HT	high-temperature
LFE	laminar-flow-element
LT	low-temperature
MECA	Manufacturers of Emission Controls Association
N <sub>2</sub>	nitrogen
N <sub>2</sub> O	nitrous oxide
Nav	4-mode steady-state test for low temperature catalysts
NDIR	non-dispersive infrared analyzer
NO	nitric oxide
NO <sub>2</sub>	nitrogen dioxide
NO <sub>3</sub>	nitrate
NO <sub>x</sub>	nitrogen oxides
NREL	National Renewable Energy Laboratory
NVH	noise, vibration, and harshness
O <sub>3</sub>	ozone
OEM	original equipment manufacturer
ORNL	Oak Ridge National Laboratory

OTT	Office of Transportation Technologies
PC	personal computer
Pd	palladium
PM	particulate matter
ppm	parts per million
Pt	platinum
R&D	research and development
Rh	rhodium
RH	relative humidity
RTD	resistance temperature detector
SO <sub>2</sub>	sulfur dioxide
SO <sub>3</sub>	sulfite
SO <sub>4</sub>	sulfate
SOF	soluble organic fraction
THC	total hydrocarbons
TWC	three-way catalyst
WVU	West Virginia University

## Executive Summary

### ES.1 Introduction

The Diesel Emission Control – Sulfur Effects (DECSE) Program is a joint government/industry program which aims to determine the impact of diesel fuel sulfur levels on emission control systems whose use could lower emissions of nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM) from on-highway trucks from the 2002-2004 model years. The program is designed to enhance the collective knowledge base about engines, diesel fuels, and emission control technologies in a systems approach to guide industry in developing lower emitting applications of their products and provide part of the technical basis for government decisions on regulating the sulfur content in diesel fuel.

The program was developed with the following objectives in mind:

- (A) Evaluate the effects of varying the level of sulfur in the fuel on the emission reduction performance of four emission control technologies.
- (B) Measure and compare the effects of up to 250 hours of aging on selected devices for multiple levels of fuel sulfur.

Four emission control technologies have been tested in this program: (1) NO<sub>x</sub> adsorber catalysts; (2) diesel particulate filters (DPFs); (3) lean-NO<sub>x</sub> catalysts; and (4) diesel oxidation catalysts (DOCs). The devices tested included commercially available technologies as well as state-of-the-art technologies that are under development. The sulfur contents in the test fuels were 3, 16 (NO<sub>x</sub> adsorber catalysts only), 30, 150, and 350 parts per million (ppm). The 3-ppm sulfur content fuel represents a diesel fuel that is essentially “sulfur free.” The engines in the DECSE Program represent currently available models and were selected to provide a representative source of diesel exhaust and various exhaust temperature profiles to challenge the emission control devices. Important characteristics of the exhaust are flow rate, temperature, and concentrations of NO<sub>x</sub>, hydrocarbons (HC), carbon monoxide (CO), and PM.

The program, spanning calendar years 1999 and 2000, was conducted by the U.S. Department of Energy’s (DOE) Office of Heavy Vehicle Technologies within DOE’s Office of Transportation Technologies (OTT); the National Renewable Energy Laboratory (NREL); Oak Ridge National Laboratory (ORNL); manufacturers of heavy-duty engines under the Engine Manufacturers Association (EMA); and manufacturers of emission control systems under the Manufacturers of Emission Controls Association (MECA).

This is the final report for the Diesel Oxidation Catalyst and Lean-NO<sub>x</sub> catalyst test programs. Interim results from this study were previously reported in the first DECSE Interim Report, published September 1999, and Interim Data Report No. 3, “Diesel Fuel Sulfur Effects on Particulate Matter Emissions,” published November 1999. These and the other DECSE reports are available on the DECSE section of the DOE OTT Web site at <http://www.ott.doe.gov/decse>. This report covers the effect of fuel diesel sulfur level on the performance and short-term durability of DOCs and lean-NO<sub>x</sub> catalysts.

## ES.2 Program Overview

The DOC/lean-NO<sub>x</sub> test program was led by a technical committee consisting of representatives from engine manufactures, catalyst suppliers, and DOE's national laboratories. West Virginia University (WVU) was contracted to conduct emissions testing for the program. A Navistar International T444E (7.3L) engine and a Cummins ISM370 (11 L) engine were used in this study. The T444E engine is typically used in applications that result in relatively low-temperature exhaust while the higher displacement ISM370 generally operates with higher temperature exhaust conditions. The exhaust temperature profile dictates the choice of catalyst loading. Lower temperature operation (150°C-350°C) typically favors precious metal based catalysts. At higher exhaust temperatures (350°C-600°C), base metal catalysts are generally favored. Both formulation approaches were tested here. The precious metal-coated "low-temperature" (LT) DOC and lean-NO<sub>x</sub> catalysts were aged and evaluated using the T444E, while the base metal "high-temperature" (HT) catalysts were tested on the ISM370.

Testing was performed to assess fresh catalyst performance and performance after aging of each technology using fuels containing various levels of sulfur (3-, 30-, 150-, and 350-ppm S). The DOCs were evaluated under steady-state and transient conditions, while the lean-NO<sub>x</sub> catalysts were only tested at steady-state. Engine manufacturers must now not only certify emissions with a transient cycle which is lightly loaded, they must also certify at individual steady-state modes including peak torque. A steady-state high-exhaust temperature mode was included in this test program specifically to characterize the potential vulnerability of manufacturers with respect to compliance with future emissions standards when devices such as DOCs or lean- NO<sub>x</sub> catalysts are used. Gaseous and PM emissions were sampled in the exhaust before and after the catalysts to determine reduction efficiencies. Complete PM breakdown analyses were also conducted.

The lean-NO<sub>x</sub> catalysts use an active reduction strategy utilizing supplemental hydrocarbons injected into the exhaust stream. In this testing, diesel fuel was used as the hydrocarbon reductant. The injection rate was optimized for peak NO<sub>x</sub> reduction without exceeding 4% of the total fuel consumption. This strategy was only used at operating conditions at which a benefit was observed.

## ES.3 Diesel Oxidation Catalyst Conclusions

The two DOC technologies chosen for this project were performance tested before, during, and following a 250-hour aging cycle using fuels containing four different sulfur levels. The catalysts were evaluated for HC, CO, and PM reduction efficiency during four steady-state operating modes and the heavy-duty federal test procedure (FTP). The tendency of the catalysts to recover any loss of performance after operation with high sulfur fuels was also evaluated. The following are significant conclusions from the DOC study:

- Catalyst response over the transient evaluation cycles differed from the steady-state tests. In the transient tests (FTP-75 mimicry) with the Navistar engine (Figure ES-1), the DOC reduced SOF of the PM by 70-85%, yielding a 35-45% reduction in PM. The reductions in SOF and PM were statistically significant. Fuel sulfur content did not affect SOF emissions or the SOF suppression efficiency of the DOC. Although there is some statistical evidence that SO<sub>4</sub> emissions increased with higher sulfur fuel, the resulting impact on PM (either EO or post catalyst) was negligible and not statistically significant.

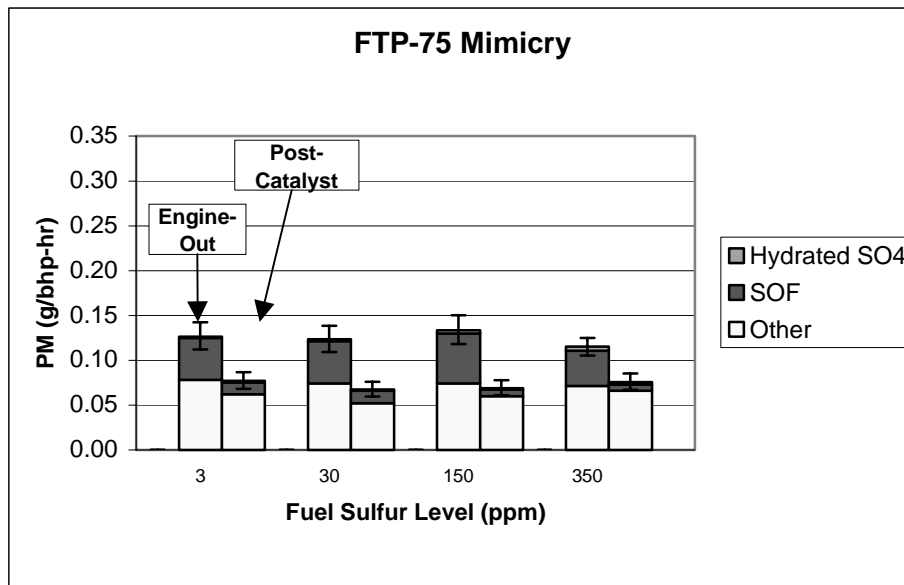


Figure ES-1. EO and post DOC emissions of PM and components under LT (Navistar) applications using the FTP-75 mimicry transient cycle (with 95% confidence intervals on estimated PM)

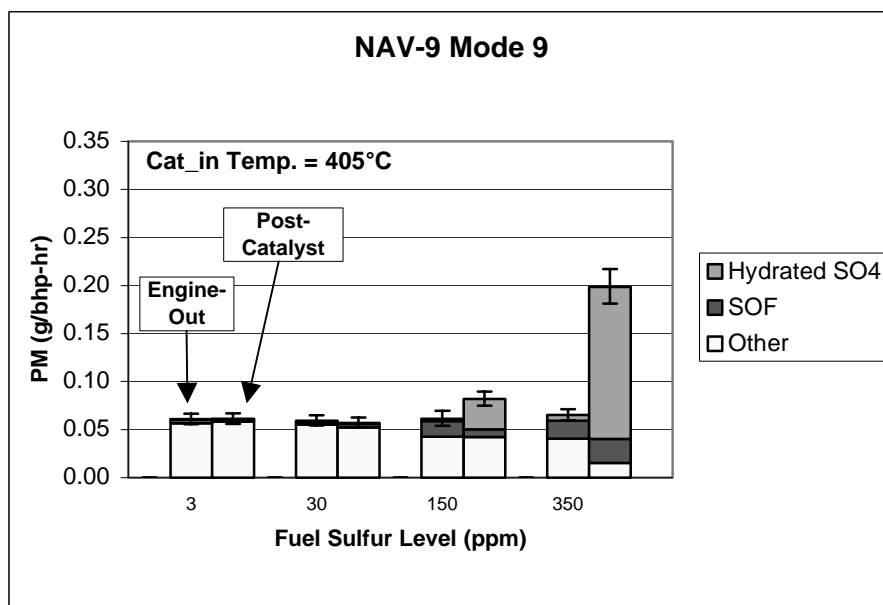
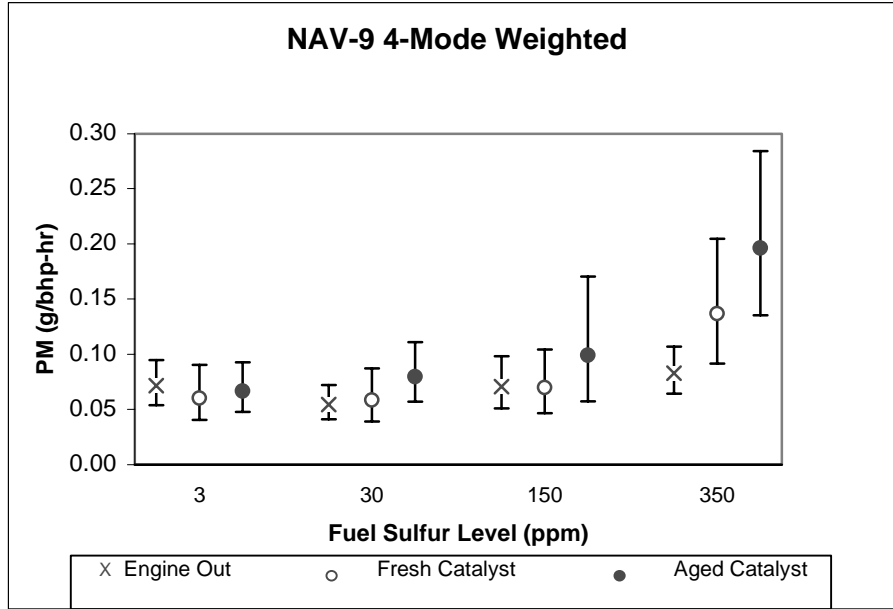


Figure ES-2. EO and post-DOC emissions of total PM and components under LT (Navistar) applications using a Nav-9 mode 9 test (with 95% confidence intervals on estimated PM)



- At the high exhaust temperature steady-state modes (at or near peak torque), there is a statistically significant increase in post-DOC PM over and above the PM measured engine-out. The increase is due almost exclusively to the increase in SO<sub>4</sub> fraction. The effect is seen only with the 150- and 350-ppm sulfur fuels (Figure ES-2).
- Under the transient test conditions, the LT DOCs used on the T444E engine were more effective at PM reduction than the HT DOCs used on the ISM370. The performance difference can be attributed to the higher Pt loading on the LT catalysts which are more active at the characteristically low exhaust temperatures of the transient test cycles.
- HC reduction efficiency of the LT DOC was 90-100% under steady-state and transient conditions. No sulfur effect was observed in either EO or post-catalyst HC emissions from the T444E.
- A statistically significant increase in FTP HC emissions (both EO and post-catalyst) was observed with the ISM370 and high sulfur fuels (150- and 350-ppm S). HC reduction efficiency during the FTP declined from near 100% with 3-ppm sulfur fuel to approximately 91% with 350-ppm sulfur fuel.
- CO reduction efficiency was higher with the LT DOCs than with the HT DOCs. The LT DOCs were 90-99% effective at steady-state CO reduction and 88-92% effective during the transient tests. The HT DOCs were 78-84% effective at steady-state CO reduction but only 41-45% effective during the transients. There is no statistical evidence that sulfur effects CO emissions or the CO reduction efficiency of the DOC under any operating mode.
- In the steady-state tests, post-DOC PM emissions from the LT catalyst aged with 350-ppm fuel exceeded those measured when the catalyst was fresh (0.20 vs. 0.14 g/bhp hr). A much smaller aging effect on total PM was observed with the lower sulfur fuels. (Figure ES-3)
- After aging, the HT catalysts more efficiently reduced the soluble organic fraction and resulted in increased PM reduction efficiency when compared to the fresh catalyst efficiency. This improvement in performance was observed with catalysts aged with 30-, 150-, and 350-ppm sulfur fuel, though the level of sulfur in the fuel did not effect the magnitude of the improvement.
- The CO reduction efficiency of the HT catalysts dropped 10 percentage points after aging. This effect was independent of fuel sulfur content.

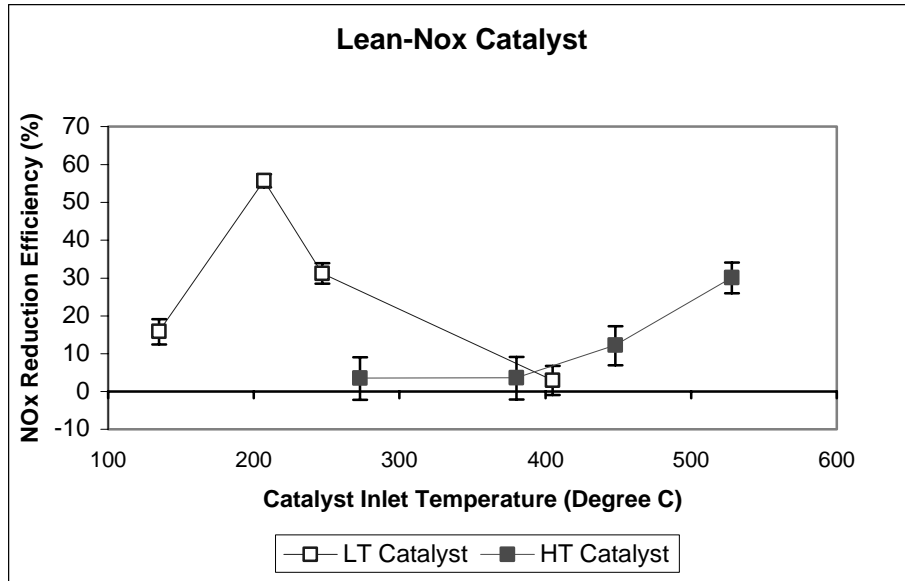


**Figure ES-3. EO and fresh and aged DOC emissions of PM under LT (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)**

#### ES.4 Lean-NO<sub>x</sub> Catalyst Conclusions

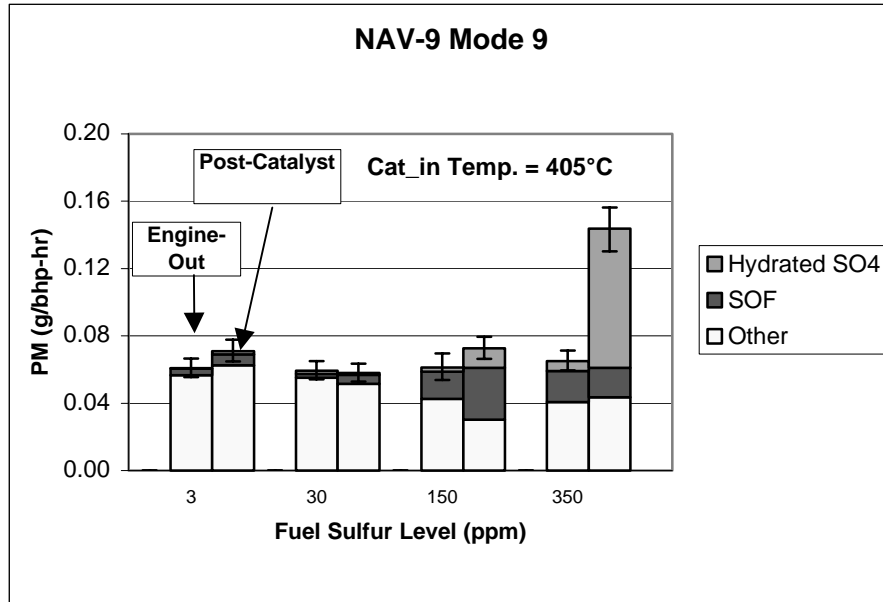
The two lean-NO<sub>x</sub> catalyst technologies chosen for this project were performance tested before, during, and following a 250-hour aging cycle using fuels containing four different sulfur levels. The catalysts were evaluated for NO<sub>x</sub> reduction efficiency, selected gaseous emissions, and particulate matter emissions during selected steady-state operating modes. The tendency of the catalysts to recover any loss of performance after operation with high sulfur fuels was also evaluated. The following are significant conclusions from the lean-NO<sub>x</sub> catalyst study:

- With fresh lean-NO<sub>x</sub> catalysts and with less than 4% fuel penalty, overall NO<sub>x</sub> reduction efficiencies were less than 20% for all catalysts during the defined steady state test cycles. However, over 50% and 30% NO<sub>x</sub> reduction peak efficiencies were observed at specific operating temperatures for both LT and HT catalysts respectively (Figure ES-4). Statistically, the effect of fuel-sulfur-level on NO<sub>x</sub> reduction efficiency was not significant.



**Figure ES-4. NO<sub>x</sub> reduction efficiency of LT (Navistar) and HT (Cummins) lean-NO<sub>x</sub> catalysts at selected catalyst inlet temperatures (with 95% confidence intervals)**

- With fresh LT lean-NO<sub>x</sub> catalysts and higher fuel sulfur levels (150- and 350-ppm sulfur), the increase in catalyst-out sulfate emissions was significant at the high temperature steady state test mode. (Figure ES-5)
- The HT lean-NO<sub>x</sub> catalyst was vulnerable to HC slip with all of the fuels tested. The LT lean-NO<sub>x</sub> catalyst was more effective at controlling HC and CO slip, but only with low sulfur (3- and 30-ppm S) fuels.
- Catalyst aging (up to 250 hours), independent of fuel sulfur level, had no apparent effect on the NO<sub>x</sub> reduction efficiency of the LT and HT lean-NO<sub>x</sub> catalysts.
- For the LT lean-NO<sub>x</sub> catalyst, catalyst aging significantly increased the catalyst-out PM emissions with higher sulfur fuels (150- to 350-ppm S). This was mainly due to high sulfate emissions after 50 hours of catalyst aging. Thermal aging seems to be the primary reason for the PM increase with the lower sulfur fuels. With 350-ppm sulfur fuel, the effects of thermal aging and sulfur aging seemed essentially additive. Unlike the LT lean-NO<sub>x</sub> catalyst, the aging process had only a slight effect on catalyst-out PM emissions with the HT lean-NO<sub>x</sub> catalyst.



**Figure ES-5. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of PM and components under LT (Navistar) applications using a Nav-9 mode 9 test (with 95% confidence intervals on estimated PM)**

- Thermal aging was also the main contributor to the increase of HC slippage with the LT lean-NO<sub>x</sub> catalyst. Thermal aging could make the catalyst more vulnerable to sulfur inhibition, resulting in the higher HC slippage with high sulfur fuels. Likewise, HC slip from the HT lean-NO<sub>x</sub> catalysts increased after aging.
- For the LT lean-NO<sub>x</sub> catalyst, the adverse aging effect on both PM emissions and HC slippage can be essentially reversed within 50 hours of operation with 30-ppm sulfur fuel (Figure ES-6). This finding suggests that the catalyst had not undergone permanent deactivation. For the HT lean-NO<sub>x</sub> catalyst, the recovery test with 30-ppm sulfur fuel actually increased the HC slippage. It is consistent with the trend that the higher the fuel sulfur level, the lower the aging effect on the increase of HC slip.

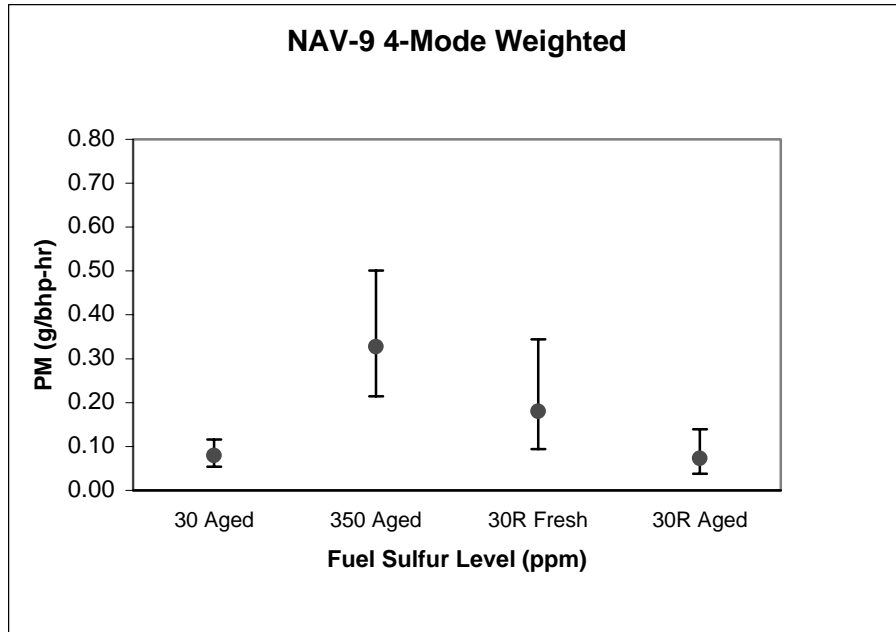


Figure ES-6. PM emissions, with 95% confidence intervals, from LT lean-NO<sub>x</sub> catalysts aged for 250 hours and tested with 30- and 350-ppm sulfur fuels – and 0- and 50-hour 30-ppm recovery tests performed on the catalyst aged for 250 hours with 350-ppm sulfur fuel.

# 1 Introduction

## 1.1 DECSE Program Overview

The Diesel Emission Control – Sulfur Effects (DECSE) Program is a joint government/industry program which aims to determine the impact of diesel fuel sulfur levels on emission control systems whose use could lower emissions of nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM) from on-highway trucks from the 2002-2004 model years. The program was designed to enhance the collective knowledge base about engines, diesel fuels, and emission control technologies in a systems approach to guide industry in developing lower emitting applications of their products and provide part of the technical basis for government decisions on regulating the sulfur content in diesel fuel.

The program was developed with the following objectives in mind:

- (A) Evaluate the effects of varying the level of sulfur in the fuel on the emission reduction performance of four emission control technologies
- (B) Measure and compare the effects of up to 250 hours of aging on selected devices for multiple levels of fuel sulfur

Four emission control technologies have been tested in this program: (1) NO<sub>x</sub> adsorber catalysts; (2) diesel particulate filters (DPFs); (3) lean-NO<sub>x</sub> catalysts; and (4) diesel oxidation catalysts (DOCs). The devices being tested include commercially available technologies as well as state-of-the-art technologies that are under development. The sulfur contents in the test fuels were 3, 16 (NO<sub>x</sub> adsorber catalysts only), 30, 150, and 350 parts per million (ppm). The 3-ppm sulfur content fuel represents a diesel fuel that is essentially “sulfur free.” The engines in the DECSE Program represent currently available models, and were selected to provide a representative source of diesel exhaust and various exhaust temperature profiles to challenge the emission control devices. Important characteristics of the exhaust are flow rate, temperature, and concentrations of NO<sub>x</sub>, hydrocarbons (HC), carbon monoxide (CO), and PM.

The program, spanning calendar years 1999 and 2000, was conducted by the U.S. Department of Energy’s (DOE) Office of Heavy Vehicle Technologies within DOE’s Office of Transportation Technologies (OTT); the National Renewable Energy Laboratory (NREL); Oak Ridge National Laboratory (ORNL); manufacturers of heavy-duty engines under the Engine Manufacturers Association (EMA); and manufacturers of emission control systems under the Manufacturers of Emission Controls Association (MECA).

This is the final report for the Diesel Oxidation Catalyst and Lean-NO<sub>x</sub> catalyst test programs. Interim results from this study were previously reported in the first DECSE Interim Report, published September 1999, and Interim Data Report No. 3, “Diesel Fuel Sulfur Effects on Particulate Matter Emissions,” published November 1999. These and the other DECSE reports are available on the DECSE section of the DOE OTT Web site at <http://www.ott.doe.gov/decse>. This report covers the effect of diesel sulfur level on the performance and short-term durability of diesel oxidation catalysts and lean-NO<sub>x</sub> catalysts.

## 1.2 Diesel Oxidation Catalyst Overview

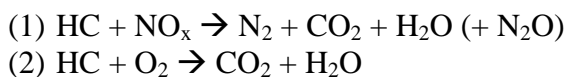
DOCs reduce HC, CO, and PM emissions in engine exhaust by oxidation over precious metal catalysts. PM is lowered by oxidizing the soluble organic fraction (SOF) of diesel PM. Catalyst selection is based on the exhaust temperature requirement. Catalysts highly loaded with precious metal are active at lower temperatures and can provide increased reductions. However, at higher exhaust temperatures, the higher the loading, the more vulnerable the catalyst is to sulfate (SO<sub>4</sub>) production (as a result of the oxidation of sulfur dioxide [SO<sub>2</sub>] to sulfur trioxide [SO<sub>3</sub>]). Therefore, lower precious metal loadings may be desirable.

This part of the DECSE Program examines the impact of diesel fuel sulfur on the performance and short-term durability of DOCs. The following study questions framed the experimental design:

- What is the impact of diesel fuel sulfur level on PM generation from DOC-equipped engines?
- How does fuel sulfur affect DOC functionality in short-term aging evaluations? How does this differ from thermal stressing?
- Can benefits (should they exist) of ultra-low sulfur fuel be recovered after engine/catalyst operation on higher sulfur fuels?

## 1.3 Lean-NO<sub>x</sub> Catalyst Overview

Lean-NO<sub>x</sub> catalyst technology can be used to reduce diesel NO<sub>x</sub> emissions with the assistance of a supplemental HC reducing agent (such as diesel fuel) under lean (oxygen-rich) exhaust conditions. Lean-NO<sub>x</sub> catalysts can be divided into two groups: low-temperature (LT) (170°-300°C) and high-temperature (HT) (350°-600°C). LT catalysts are primarily composed of precious metals such as platinum (Pt); HT catalysts are mainly composed of base metal components such as metal/zeolite (Cu-ZSM) catalysts. For a lean-NO<sub>x</sub> catalyst, two major competing reactions dictate its function:



Depending on the catalyst composition, a catalyst can favor either LT or HT NO<sub>x</sub> reduction. For the LT catalyst, nitrous oxide (N<sub>2</sub>O) may be a by-product. In addition to the temperature effect, other parameters affect catalyst performance: HC and NO<sub>x</sub> concentration (and HC/NO<sub>x</sub> ratio), space velocity, precious-metal (or base-metal) loading, fuel sulfur level, HC speciation, and flow distribution. If diesel fuel is used as the reductant, the types of sulfur components and the level of fuel vaporization also affect the catalyst performance.

Lean-NO<sub>x</sub> catalyst technology has been developed over several years. However, there has been no systematic investigation of the effect of fuel sulfur level on the performance of lean-NO<sub>x</sub> catalysts. For the lean-NO<sub>x</sub> catalyst, this program was designed to provide data to address the following study questions:

What is the effect of diesel sulfur level on:

- Lean-NO<sub>x</sub> catalyst performance in terms of NO<sub>x</sub> reduction efficiency
- Sulfate (PM) formation by the catalyst
- Catalyst deactivation rate
- Catalyst recoverability from SO<sub>2</sub> (or SO<sub>3</sub>) poisoning?

To effectively carry out the lean-NO<sub>x</sub> catalyst evaluation, the DECSE Program was divided into three studies:

- 1) **High-Temperature Lean-NO<sub>x</sub> Catalyst-Fresh Performance.** Evaluates the fresh performance of the HT lean-NO<sub>x</sub> catalyst with different fuel sulfur levels (3-, 30-, 150-, and 350-ppm). The effect of fuel sulfur on catalyst impairment, SO<sub>4</sub> (sulfate) formation, and hydrocarbon (HC) slippage is examined.
- 2) **Low-Temperature Lean-NO<sub>x</sub> Catalyst-Fresh Performance.** Evaluates the fresh performance of the LT lean-NO<sub>x</sub> catalyst with different fuel sulfur levels (3-, 30-, 150-, and 350-ppm). The effect of fuel sulfur on catalyst impairment, SO<sub>4</sub> formation, and HC slippage is examined.
- 3) **Lean-NO<sub>x</sub> Catalyst Aging and Evaluation.** Evaluates the effect of fuel sulfur levels (3-, 30-, 150-, and 350-ppm) on catalyst deactivation. HT and LT lean-NO<sub>x</sub> catalysts are evaluated after being aged for 50, 150, and 250 hours. Sulfur poisoning and thermal deactivation effects are examined. Catalyst recoverability was also investigated with 30-ppm sulfur fuel.

#### 1.4 Overview of West Virginia University Engine Test Laboratory

The engines were tested on the 500-hp DC dynamometer at West Virginia University (WVU) while aging was performed with two Go-Power water brake dynamometers. Emissions were measured using a full-scale dilution tunnel system meeting the Code of Federal Regulations (CFR 40) requirements to certify engines.

Engine exhaust was ducted to a full-scale dilution tunnel (18 inches in diameter and 20 feet long) based on the critical flow venturi (CFV) constant-volume sampling (CVS) concept. Three feet from the tunnel entrance was an 8-inch diameter orifice, which ensured that the dilute exhaust was thoroughly mixed by the time it reached the sampling zone located 10 diameters downstream of the orifice. The quantity of diluted exhaust was measured precisely by a set of CFVs placed upstream of a blower that pulled the dilute exhaust at a constant mass flow rate once the venturi was under sonic or choked conditions. The tunnel provided nominal flow rates of 1000, 1400, 2000, and 2400 scfm to accommodate the respective engine and dilution ratios. Venturi temperature was measured with a 3-wire resistance temperature detector (RTD) and pressure was measured by an absolute pressure transducer. Heated sampling probes and lines directed diluted exhaust to the gas analysis instruments. The intake air for the engines was pre-conditioned. Microprocessor-controlled heated probes and sampling lines were used to draw the gaseous samples into the gas analysis bench.

The exhaust stream was continuously sampled and analyzed by non-dispersive infrared analyzers (NDIR) for CO and carbon dioxide (CO<sub>2</sub>); wet chemiluminescent analyzer for NO<sub>x</sub>; and heated flame ionization detector (HFID) for total hydrocarbons (THC). The gas analysis bench was equipped with exhaust sample conditioning and analysis systems according to U.S.



Environmental Protection Agency (EPA) CFR 40 requirements. Data from the exhaust analyzers, sampling trains, secondary dilution tunnel, and engine were acquired and archived at 5 Hz.

Total particulate matter was sampled on 70-mm fluorocarbon-coated glass fiber filters for subsequent gravimetric analysis. Filters were conditioned in a Thermotron environmental chamber (maintained at 70°F and 50% relative humidity [RH] ). After the filters were conditioned, they were weighed in an environmentally controlled room with a CAHN C-32 microbalance. A schematic of the sampling and analysis train in WVU's heavy-duty engine testing facility is shown in Figure 1-1.

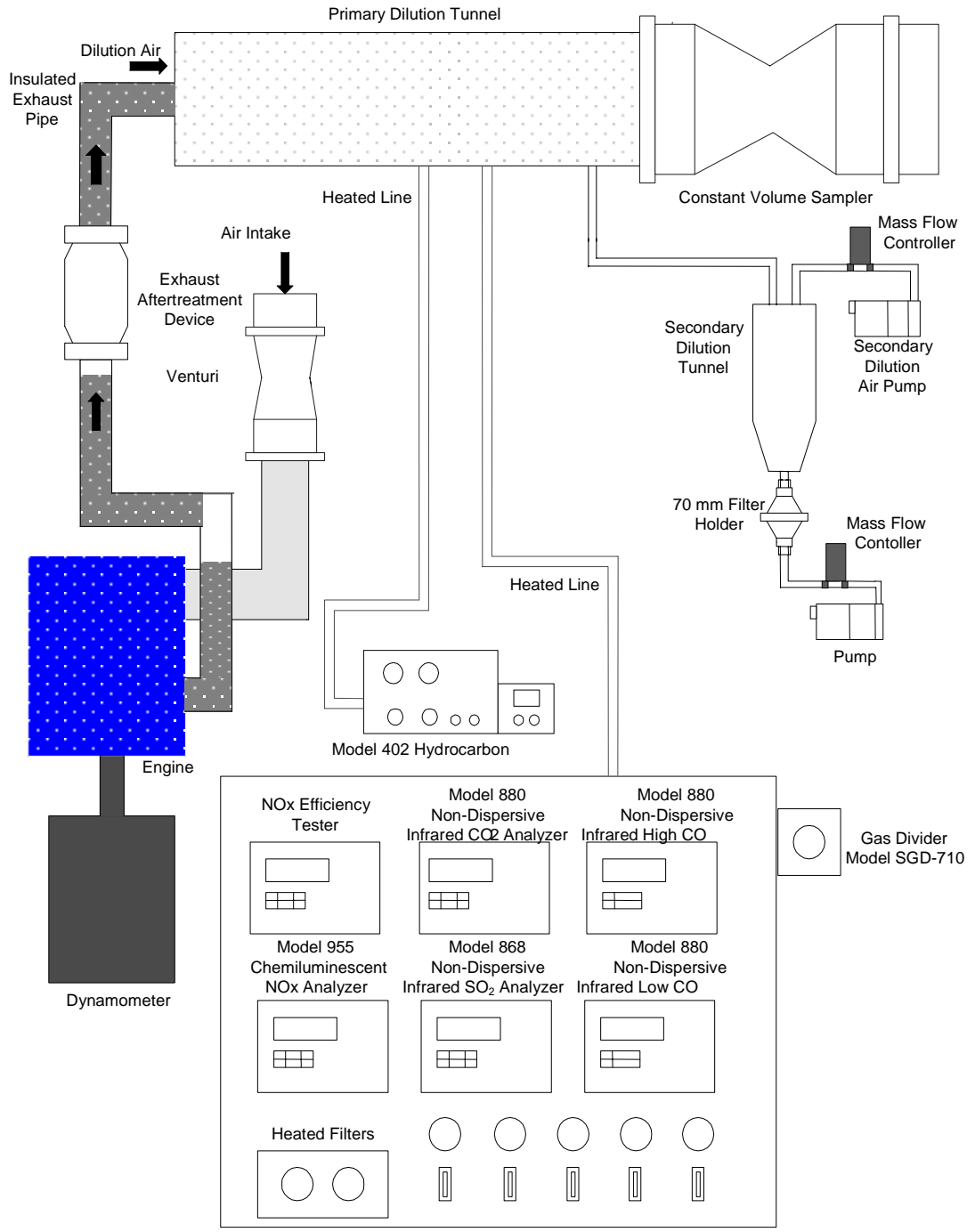


Figure 1-1. Schematic of sampling and analysis train in WVU's heavy-duty engine testing facility

## 2 Technical Approach

### 2.1 Experimental Design

The experimental design for this research project was developed to address the following general study questions related to the performance of DOCs and lean-NO<sub>x</sub> catalysts for low exhaust temperature (e.g., Navistar T444E) and high exhaust temperature (e.g., Cummins ISM370) diesel applications:

1. How do the catalysts affect emissions of NO<sub>x</sub>, HC, CO, particulate matter (PM), and PM components (SOF and SO<sub>4</sub>)?
2. How does the sulfur level in the diesel fuel affect emissions from fresh catalysts relative to engine-out (EO) emissions?
3. How does catalyst thermal aging (without sulfur) affect catalyst performance?
4. What is the effect of fuel sulfur during aging on catalyst performance?
5. How does catalyst performance vary as a function of engine operating conditions, especially exhaust temperature?
6. How does this relationship change as a function of age and fuel sulfur level?
7. If aging with high sulfur fuel affects catalyst performance, can the catalyst recover from the effects? By how much? How quickly?

The design specified the emissions tests to be performed at various times as the catalysts were aged for 250 hours with fuels containing sulfur at levels ranging from 3 to 350 ppm. Catalyst aging time and fuel sulfur level are the primary experimental factors related to study questions 1 through 4. To address study questions 5 and 6, emissions tests consisted of four steady-state modes from the Nav-9 or OICA-13 test procedures for the low temperature (Navistar) and high temperature (Cummins) engines, respectively. Fresh catalysts were also tested under high temperature steady-state modes (Nav-9 mode 9 and OICA-13 mode 2). In addition, the oxidation catalysts were also tested using transient test procedures (an FTP-75 mimicry and the FTP hot cycle). Particulate and gaseous emissions were obtained from samples collected across the 4-mode test procedures (composite samples), the special high exhaust temperature steady-state test mode, and the transient tests. Gaseous emissions were also measured during each mode of the 4-mode steady-state test procedures.

Four catalysts were tested for each combination of catalyst type (DOC and lean-NO<sub>x</sub> catalyst) and application (low and high temperature). As shown in Table 2-1, each of the catalysts (denoted by C1 to C4) were aged for 250 hours and tested with a single fuel. However, to distinguish between the effects of thermal aging and sulfur poisoning, catalyst C1, which was initially aged with 3-ppm sulfur fuel (referred to as thermal aging), was retested with 30-, 150-, and 350-ppm sulfur fuels. These tests were used to answer study questions 3 and 4 and determine whether effects of aging and fuel sulfur are additive.

**Table 2-1. Experimental design for the DECSE DOC/lean-NO<sub>x</sub> test program**

Aging Hours	Fuel Sulfur Level (ppm)				
	3	30	350	30	150
0	EO <sup>(1)</sup> , C1 <sup>(2)</sup>	EO, C2	EO, C4	EO, C4 <sup>(3)</sup>	EO, C3
50	C1	C2	C4	C4	C3
150	C1	C2	C4	C4	C3
250	EO, C1	EO, C2, C1 <sup>(4)</sup>	EO, C4, C1	EO, C4, C1	EO, C3, C1

- (1) Engine-out emissions tests
- (2) Post-catalyst emissions tests performed with catalysts C1-C4 (Identical design for high- and low-temperature DOC and Lean-NO<sub>x</sub> catalyst systems)
- (3) 30-ppm recovery tests performed on catalyst C4 following 250 hours of aging with 350-ppm sulfur fuel.
- (4) Catalyst C1 was retested with 30-, 150-, and 350-ppm sulfur fuel after (thermal) aging for 250 hours with 3-ppm sulfur fuel

To address study question 7 (recovery from aging with high sulfur fuel), catalyst C4, which was initially aged for 250 hours with 350-ppm sulfur fuel, was to be retested with 30-ppm sulfur fuel. The catalyst would then be tested while undergoing additional aging (up to 250 hours) with 30-ppm sulfur fuel. Assuming there were significant differences in emissions from catalysts C2 and C4 at 250 hours of aging with 30-ppm and 350-ppm fuel, respectively, these special “recovery” tests would determine the extent to which the catalyst can recover from the effects of aging with high sulfur fuel.

In order to characterize measurement variability and improve the precision of estimates, the experimental design called for duplicate 4-mode steady-state tests at 0 and 250 hours of aging and duplicate transient tests at all aging points. Engine-out tests were planned at the beginning and end of each aging cycle; however, due to the length of the testing period (17 months), the test laboratory was encouraged to conduct additional engine-out tests as a quality control procedure and to provide additional data for characterizing other sources of experimental error.

The order of testing generally followed according to the order of columns in Table 2-1. However, all fresh catalyst (zero hour) tests were performed first in order to address the first two study questions early in the program.

## **2.2 Selection of Diesel Fuels and Catalysts**

### **2.2.1 DECSE Diesel Fuel**

Details of the selection and composition of test fuels and lubricant used in this program appear in Appendices A and B.

### **2.2.2 Diesel Engine Selection**

Two engine models were used in this study: the 1999 Cummins ISM370 and the 1999 Navistar T444E.

The Cummins ISM370 was selected to represent a modern heavy-duty diesel engine typically used for on-highway operation. The engine is 1999 model year and is designed to meet EPA

1999 emission standards for on-highway engines. The ISM370 was used to age and evaluate the HT catalysts.

The Navistar T444E was selected to represent a modern medium-duty diesel engine used in light trucks. The engine is 1999 model year and is designed to meet EPA 1998 emission standards for light-duty vehicles. The T444E was used to age and evaluate the LT catalysts.

The specifications for each test engine are listed in Table 2-2.

**Table 2-2. Test engine specifications**

Engine	Displacement	Configuration	Peak Power	Peak Torque
Cummins ISM370	10.8L	Inline 6-cyl.	276 kW (370 hp)	1966 Nm (1450 lb-ft)
Navistar T444E	7.3L	V8	157 kW (210 hp)	705 Nm (520 lb-ft)

### 2.2.3 Catalyst Selection

All catalyst technologies provided by MECA represent state-of-the-art technology with conventional catalyst wash-coating and structure. For each device (DOC and lean-NO<sub>x</sub> catalyst), the catalyst samples were formulated for the two applications (ISM and T444E) in terms of space velocity and precious-metal loading. Because exhaust temperature profiles dictate the precious-metal loading, platinum (Pt) levels were limited for the catalysts used with the ISM. The smaller displacement T444E operates at lower temperatures, allowing higher Pt loading. Tables 2-3 and 2-4 detail the specifications for the lean-NO<sub>x</sub> and DOC catalysts used in this study.

**Table 2-3. Lean-NO<sub>x</sub> catalyst specification**

Catalyst Type	Formulation	Substrate Size OD x Length (cm)	# of Substrates	Volume (liters)	Cell Density (cpsi)	Converter Size OD x Length (cm)
High-temperature	Base metal/ zeolite	26.7 x 15.2	1	21.6	400	27.3 x 51.4
Low-temperature	Precious metal	17.8 x 12.7	2	16.0	400	19.1 x 55.9

**Table 2-4. DOC specification**

Catalyst Type	Pt Loading (g Pt / ft <sup>3</sup> )	Substrate Size OD x Length (cm)	Volume (liters)	# of Substrates	Cell Density (cpsi)	Converter Size OD x Length (cm)
High-Temp	2	19.1 x 15.9	4.50	1	400	20.3 x 66.0
Low-Temp	>50	17.8 x 11.8	2.92	1	400	19.1 x 40.6

*Note: Catalysts were sized to handle half the engine's exhaust flow.*

## 2.3 Experimental Procedures

### 2.3.1 WVU Split Exhaust System Design, Installation, and Testing

To thermally age the DOC and lean-NO<sub>x</sub> catalysts simultaneously and economically, each catalyst was sized to accommodate half the engine exhaust flow. Because each catalyst was sized for half the engine exhaust flow, the exhaust had to be split during catalyst-out emissions measurements. The split exhaust system used to evaluate the catalysts is schematically illustrated in Figure 2-1. During emissions measurement, half the engine exhaust was directed through the active catalyst being tested and into a full flow dilution tunnel. The remaining exhaust was directed through an identical “dummy” catalyst (no active washcoat) and vented from the testing facility. The dummy catalyst provided a similar flow restriction to the active catalyst to facilitate balancing the exhaust flow in the two branches of the exhaust system. Before the test cycle, the throttling valves were adjusted at a prescribed steady-state operating point so the flows in the two branches of the exhaust system were balanced while the specified engine back pressure was maintained. Catalyst-out emissions measured in the partial exhaust stream were corrected back to full flow values based on measured CO<sub>2</sub> concentration. For example:

$$(NO_x)_{CORR} = (NO_x)_{SPLIT} \left[ \frac{(CO_2)_{FULL}}{(CO_2)_{SPLIT}} \right]$$

Where (CO<sub>2</sub>)<sub>FULL</sub> was determined by directing the whole engine exhaust to the tunnel during a separate test.

Full-flow engine-out (EO) NO<sub>x</sub> emissions are compared to split-flow corrected emissions in Figure 2-2. The success of the correction is clear.

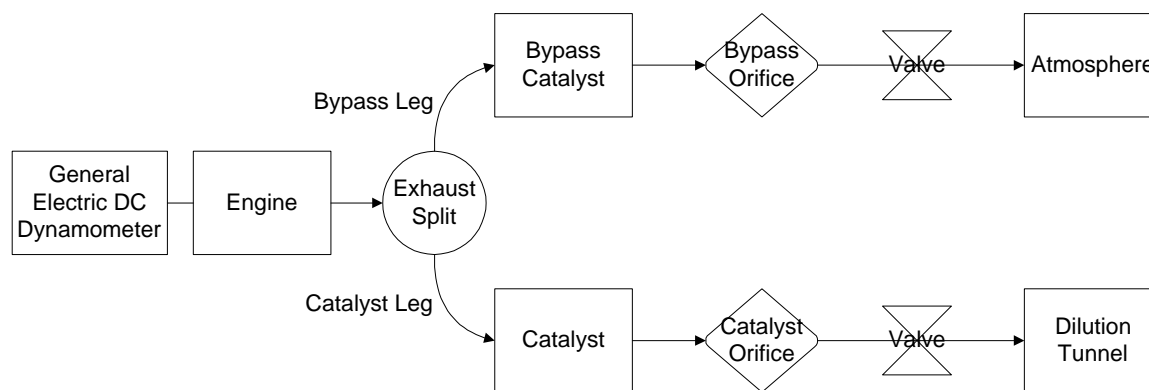


Figure 2-1. Schematic of split exhaust system

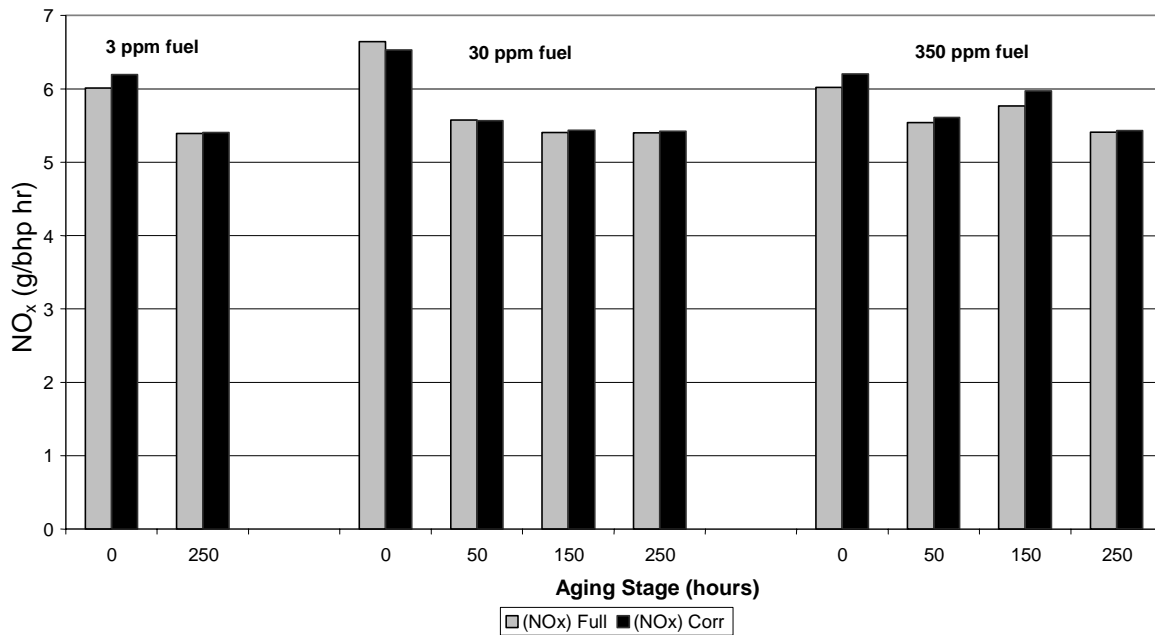


Figure 2-2. Comparison of split flow corrected and full flow EO emissions

### 2.3.2 Secondary Fuel Injection Selection, Installation, and Testing

Lean-NO<sub>x</sub> catalysts reduce diesel NO<sub>x</sub> emissions with the assistance of a supplemental HC reducing agent (such as diesel fuel). Catalyst performance is strongly affected by the ratio of HC to NO<sub>x</sub> in the engine exhaust and thus by the amount of secondary HC reductant introduced into the exhaust stream. In the DECSE study, diesel fuel having the same sulfur content as the fuel consumed by the engine was used as secondary reductant. The fuel was introduced into the exhaust approximately 20 inches upstream of the catalyst inlet to ensure the reductant was reasonably distributed across the cross-section of the substrate. A Fluid Metering Inc., RHV00SKY positive displacement pump controlled by a digital computer metered the reductant. The reductant was introduced into the inlet of the catalyst via a solid cone air-atomizing nozzle. The secondary reductant injection system is shown in Figure 2-3.



**Figure 2-3. Reductant injection system for lean-NO<sub>x</sub> catalysts**

Because of the complexity of controlling reductant injection during transient operation, evaluation of the lean-NO<sub>x</sub> catalyst performance was confined to steady-state conditions. The lean-NO<sub>x</sub> catalysts were aged and evaluated using cycles consisting of four steady-state modes that are discussed later. The reductant injection rates for the HT and LT lean-NO<sub>x</sub> catalyst technologies were optimized to maximize NO<sub>x</sub> reduction efficiency while controlling HC slippage before the catalyst aging experiments started. HC slippage is defined as the percentage increase in HC emissions as a result of reductant passing through the lean-NO<sub>x</sub> catalyst without being reacted.

$$HC \text{ Slippage} = \frac{HC_{\text{passed through}} (g / BhpHr)}{HC_{\text{injected}} (g / BhpHr)}$$

The fuel economy penalty (FEP) associated with lean-NO<sub>x</sub> catalysts is also a concern because the added fuel consumption could result in a significant increase in operating costs.

### **2.3.3 Optimization of Secondary Fueling with Lean-NO<sub>x</sub> Catalysts**

To achieve the optimum NO<sub>x</sub> reduction, reductant injection rates were varied during each steady-state mode, while EO and catalyst-out emissions of NO<sub>x</sub> and HC were recorded. NO<sub>x</sub> reduction efficiency and HC slippage are plotted as functions of HC/NO<sub>x</sub> ratio for the low-temperature lean-NO<sub>x</sub> catalyst in Figure 2-4 and for the high-temperature catalyst in Figure 2-5. The associated fuel penalty calculated as a percentage of brake specific fuel consumption (BSFC) is also shown. Installing the catalyst alone produces some NO<sub>x</sub> reduction as indicated by the first data point on each plot because some reductions occur naturally in the exhaust. The optimum reductant injection rate for each mode was chosen as the point at which additional reductant did not significantly improve NO<sub>x</sub> reduction or produced an excessive increase in HC slippage. The selected reductant injection rate is indicated for each mode. These rates are summarized in Table 2-6 along with the resulting catalyst-out NO<sub>x</sub> and HC emissions for the low- and high-temperature catalyst, respectively.



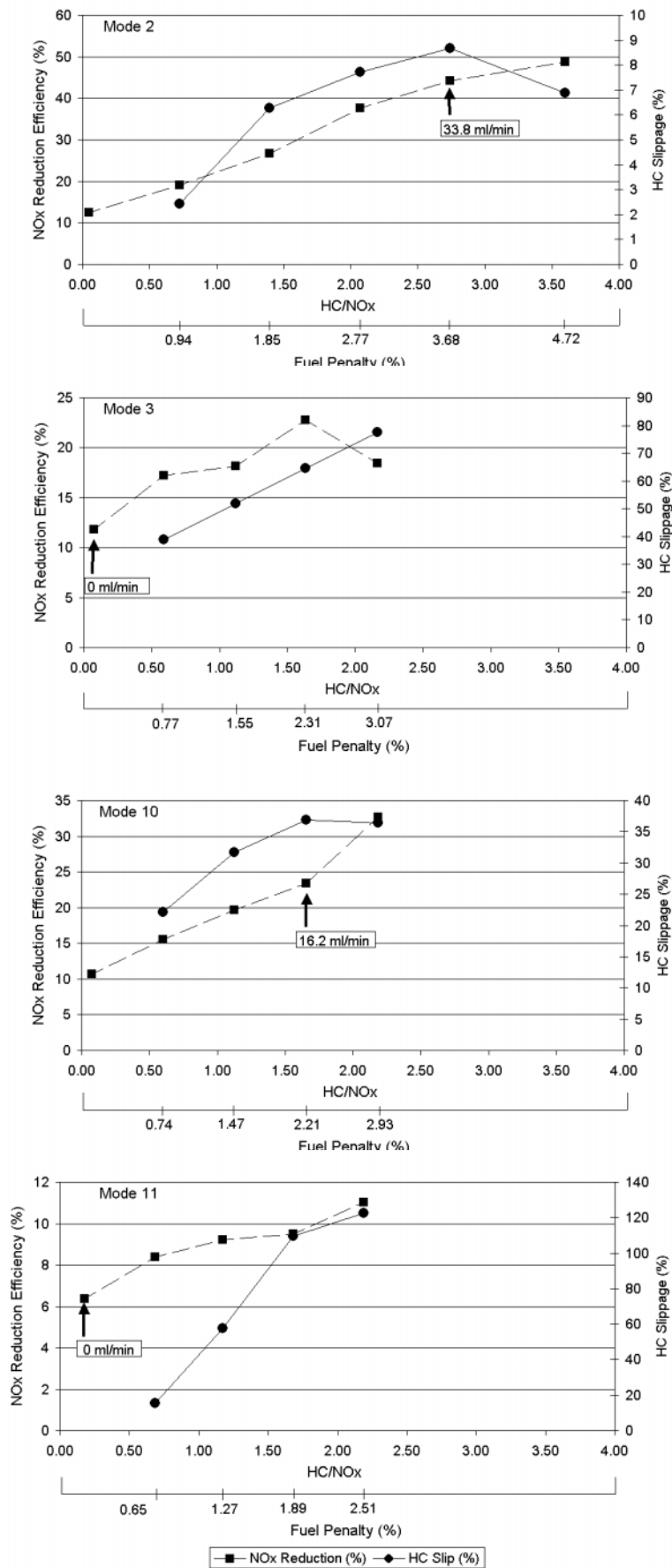


Figure 2-4. Optimization of LT lean-NO<sub>x</sub> catalyst reductant injection rates

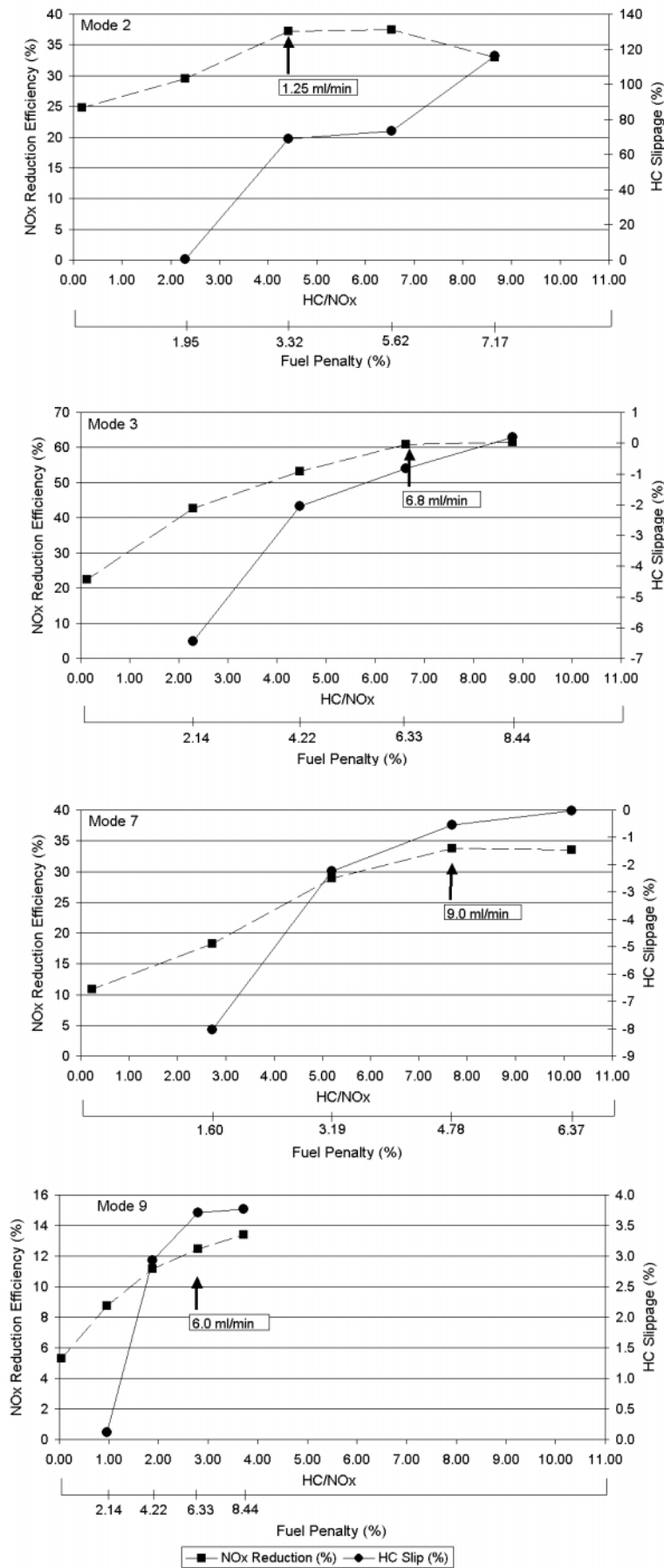


Figure 2-5. Optimization of HT lean-NO<sub>x</sub> catalyst reductant injection rates

**Table 2-5. LT lean-NO<sub>x</sub> catalyst reductant injection rates**

ESC Mode	Reductant Injection		EO (g/Bhp-hr)			Catalyst-Out (g/Bhp-hr)			Reduction Efficiency	HC Slippage
	HC/NO <sub>x</sub>	%BSFC	HC	NO <sub>x</sub>	HC+NO <sub>x</sub>	HC	NO <sub>x</sub>	HC+NO <sub>x</sub>		
2	1.19	1.95	0.343	6.399	6.742	0.352	4.508	4.860	29.55	2.62
3	3.63	6.33	0.222	5.985	6.207	0.126	2.340	2.466	60.90	-43.24
7	3.88	4.78	0.310	4.354	4.664	0.257	2.884	3.141	33.76	-17.10
9	1.01	1.02	0.410	3.222	3.263	0.093	2.863	2.956	11.14	126.83

**Table 2-6. HT lean-NO<sub>x</sub> catalyst reductant injection rates**

Nav-9 Mode	Reductant Injection		Engine Out			Catalyst Out			Reduction Efficiency	HC Slippage
	HC/NO <sub>x</sub>	%BSFC	HC	NO <sub>x</sub>	HC+NO <sub>x</sub>	HC	NO <sub>x</sub>	HC+NO <sub>x</sub>		
11	0.02	0.0	0.425	7.995	8.42	0.041	7.486	7.527	6.37	
3	0.02	0.0	0.172	7.759	7.931	0.002	6.845	6.847	11.78	
10	0.67	1.47	0.159	7.204	7.363	0.881	5.787	6.668	19.67	454.09
2	1.65	3.68	0.102	7.054	7.156	0.597	3.933	4.530	44.24	485.29

**2.3.4 Simulated FTP-75 Cycle Development**

The FTP-75 cycle is generally performed on a chassis dynamometer. The cycle requires the vehicle to be driven according to a prescribed speed-versus-time schedule (Figure 2-2) while the dynamometer simulates vehicle inertia, wind drag, and rolling resistance. Engineers at WVU developed the FTP-75 cycle mimicry for engine dynamometer applications. The engine speed and torque profiles were determined by modeling the drive train and aerodynamics of a Ford F-250 pickup truck (Table 2-7). The vehicle speed schedule was translated into flywheel speed by applying the tire diameter, final drive ratio, and transmission ratios. Gear changes were modeled after the on-road driving experience. The road load was calculated according to the road load equation shown in Table 2-8. The load and speed traces for the engine dynamometer version of the FTP-75 test cycle are shown in Figure 2-6 and 2-7, respectively. The FTP-75 cycle consists of three sections: a cold phase, a transient phase, and a hot-start phase preceded by a 10-minute soak period. The phases are weighted 22%, 50%, and 28%, respectively, to yield a composite result.

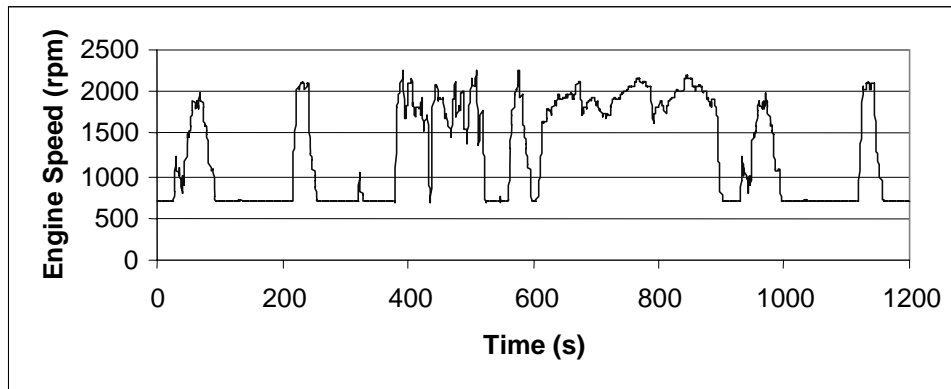
**Table 2-7. Catalyst aging cycles for DOC and lean-NO<sub>x</sub> catalysts**

Engine Speed (rpm)	Navistar Aging Set-Points					Cummins Aging Set-Points					
	Engine Load (ft-lb)	Duration (min)	Lean-NO <sub>x</sub> Injection			Engine Speed (rpm)	Engine Load (ft-lb)	Duration (min)	Lean-NO <sub>x</sub> Injection		
			Exh. Temp (°C)	% BSFC	HC/NO <sub>x</sub>				Exh. Temp (°C)	% BSFC	HC/NO <sub>x</sub>
1000	81	12	135	1.96	1.19	1260	1243	24	273	3.68	1.65
1250	122	12	207	6.33	3.63	1572	600	6	380	0	0
2000	122	12	247	4.78	3.88	1885	997	24	449	1.47	0.67
2200	406	24	405	1.02	1.09	1885	252	6	528	0	0

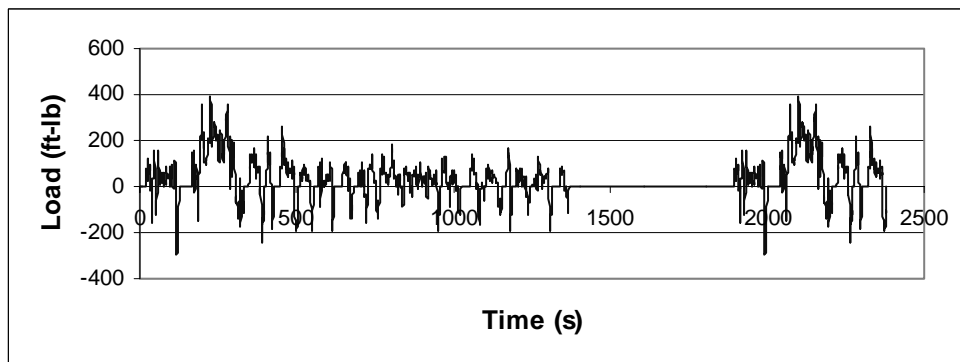
**Table 2-8. 1999 Ford F-250 Super-Duty pickup truck specifications used to generate the FTP-75 cycle**

Gear	Reduction	Parameter	Value	Unit
1	5.79	Mass	3632	kg
2	3.31	Frontal Area	5	m <sup>2</sup>
3	2.1	Drag Coefficient	0.88	
4	1.31	Air Density	1.177	kgm <sup>-3</sup>
5	1	Rolling Resistance	0.0098	
6	0.72	Tire Diameter	0.8125	m
Differential	3.73			

Road Load Equation:  $Power = 0.5 \rho C_d A v^3 + \mu m g v + m v a$



**Figure 2-6. FTP-75 speed versus time**



**Figure 2-7. FTP-75 load versus time**

### **2.3.5 Particulate Matter Sampling System and Analysis Procedure**

Particulate filters used in the testing were 70-mm Pallflex fiberfilm membrane particulate filters made by Gelman Sciences. Before use, ORNL researchers conditioned and pre-weighed fresh 70-mm filters, then shipped them to WVU, where they were conditioned and pre-weighed according to CFR 40 Part 86, subpart N. After the PM samples were collected, the filters were reconditioned and post-weighed with a CAHN C-32 microbalance to determine total particulate mass emissions. The filters were then returned to ORNL for PM breakdown analysis to determine SOF, SO<sub>4</sub>, and nitrate (NO<sub>3</sub>) fractions. A single particulate sample was collected during each steady-state cycle. The European Stationary Cycle (ESC) test procedures require that the PM sample be collected at the end of each mode.

**SOF Determination.** The exposed particulate sampling filters were conditioned for >18 hours at constant relative humidity (RH) and temperature at ORNL and weighed. The filters were then extracted with supercritical CO<sub>2</sub> under proprietary time and temperature conditions. The extracted filters were then reconditioned for >18 hours at constant RH and weighed. The SOF is the simple difference between the pre-extraction weight and the post-extraction weight.

**Sulfate and Nitrate Determination.** After weighing, the filters were rolled into a cylinder, put in 15 ml centrifuge tubes with 10 ml triple distilled water and agitated for one minute. The centrifuge tubes were then put in a rack in a 90°C water bath for 30 minutes. After removal from the bath, the tubes were agitated for one minute, and the supernatant filtered into a sample vial. The samples were then analyzed immediately or refrigerated for analysis in less than 24 hours.

The filtered extracts were analyzed for SO<sub>4</sub><sup>-2</sup> and NO<sub>3</sub><sup>-</sup> by ion chromatography (IC) using standard IC methods for anions. Peak identification is based on retention times compared to standard sulfate solutions. An autosampler was used for convenience and vials containing check standards were inserted among the sample vials. A standard curve is developed from the results for standards at 0.25, 0.50, 1.0, 5.0, and 10 ug/ml. Typical standard curves have a correlation coefficient, r<sup>2</sup>, of 0.999 or better. The sample concentrations were then calculated from the regression equation for the standards. If a sample was more concentrated than the standard curve, dilutions were used to bring the sample within the limits. More than one dilution level was used for the same sample to check for accuracy of dilution. The concentrations were multiplied by the total volume (10 ml) of extract to obtain the total mass of dry SO<sub>4</sub><sup>-2</sup> on a sample filter. The dry SO<sub>4</sub><sup>-2</sup> number is reported. Actual sulfate contribution to the PM mass weight is higher because of water associated with the ion. For comparison of PM sulfate between fuels, however, the dry SO<sub>4</sub><sup>-2</sup> number is adequate.

Blank filters were treated in the same way as exposed filters, and a filter blank was included in each batch of analyses. Blank levels of ions were extremely low, ranging from 2-8 ug/filter for SO<sub>4</sub><sup>-2</sup> and 0-4 ug/filter for NO<sub>3</sub><sup>-</sup>. Blank filter SOF was typically <10 ug. The SO<sub>4</sub><sup>-2</sup> and NO<sub>3</sub><sup>-</sup> masses on samples are corrected for the blank values before calculation of brake specific emission of sulfate and nitrate.

### **2.3.6 Gaseous Emissions Sampling and Analysis System**

Engine exhaust was directed into a full-scale dilution tunnel, CFV-CVS system. THC emissions were measured by an HFID (Rosemount Analytical, Inc., Model 402) and are reported as propane equivalent. NO<sub>x</sub> emissions were measured with a chemiluminescent detector

(Rosemount Analytical, Inc., Model 955) and are reported as nitric oxide (NO) equivalent. CO and CO<sub>2</sub> concentrations were measured with NDIRs (Rosemount Model 880A and Beckman Industrial Model 868, respectively).

### **2.3.7 Catalyst Aging Procedure**

The LT DOC and lean-NO<sub>x</sub> catalysts were aged on a Navistar T444E engine; the HT catalysts were aged on a Cummins ISM370 engine. Separate catalyst aging cells were configured for the Navistar and the Cummins aging engines.

To thermally age the DOC and lean-NO<sub>x</sub> catalysts simultaneously and economically, each catalyst was sized to accommodate half the engine exhaust flow. The catalysts were then simultaneously aged by splitting the engine exhaust into two streams, so half the total exhaust flowed through the DOC and half flowed through the lean-NO<sub>x</sub> catalyst.

Each aging cell consisted of a split exhaust configuration, with the DOC catalyst mounted in the upper branch and the lean-NO<sub>x</sub> catalyst in the lower branch of the exhaust system. The lean-NO<sub>x</sub> exhaust branch was configured for injection of secondary HC reductant. Throttling valves provided flow adjustment for balancing exhaust flow between the two branches. Flow metering orifices were installed into each branch of the split exhaust systems to measure the exhaust flows for balancing purposes. These orifices were calibrated on a dry flow bench using a Meriam Instrument laminar flow element (LFE). Flow through the orifice was inferred from the calibration curve obtained from the LFE. The layout of the LT aging cell is shown in Figure 2-8. Figure 2-9 shows the HT DOC and lean-NO<sub>x</sub> catalysts mounted in the split exhaust system during catalyst aging.

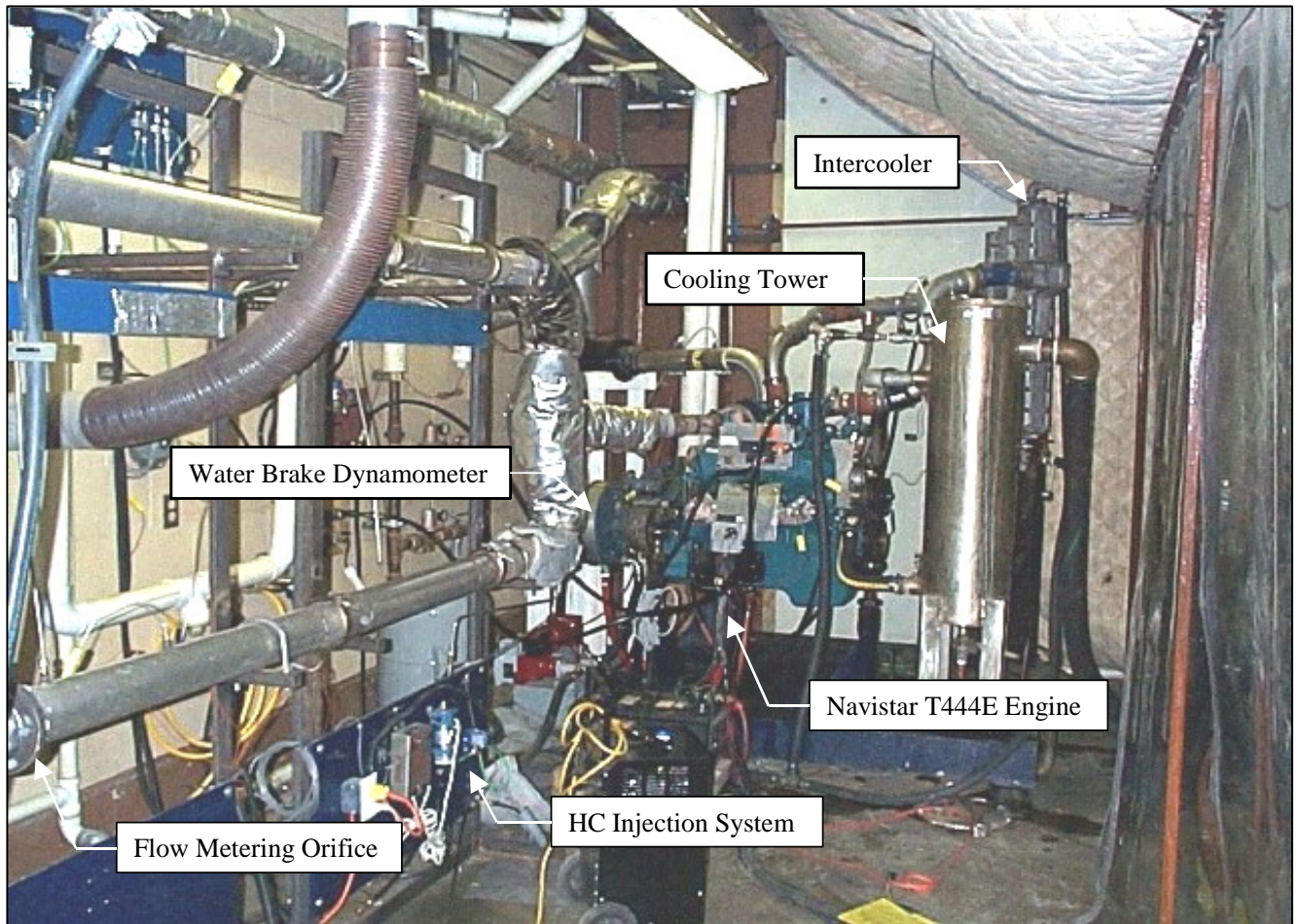
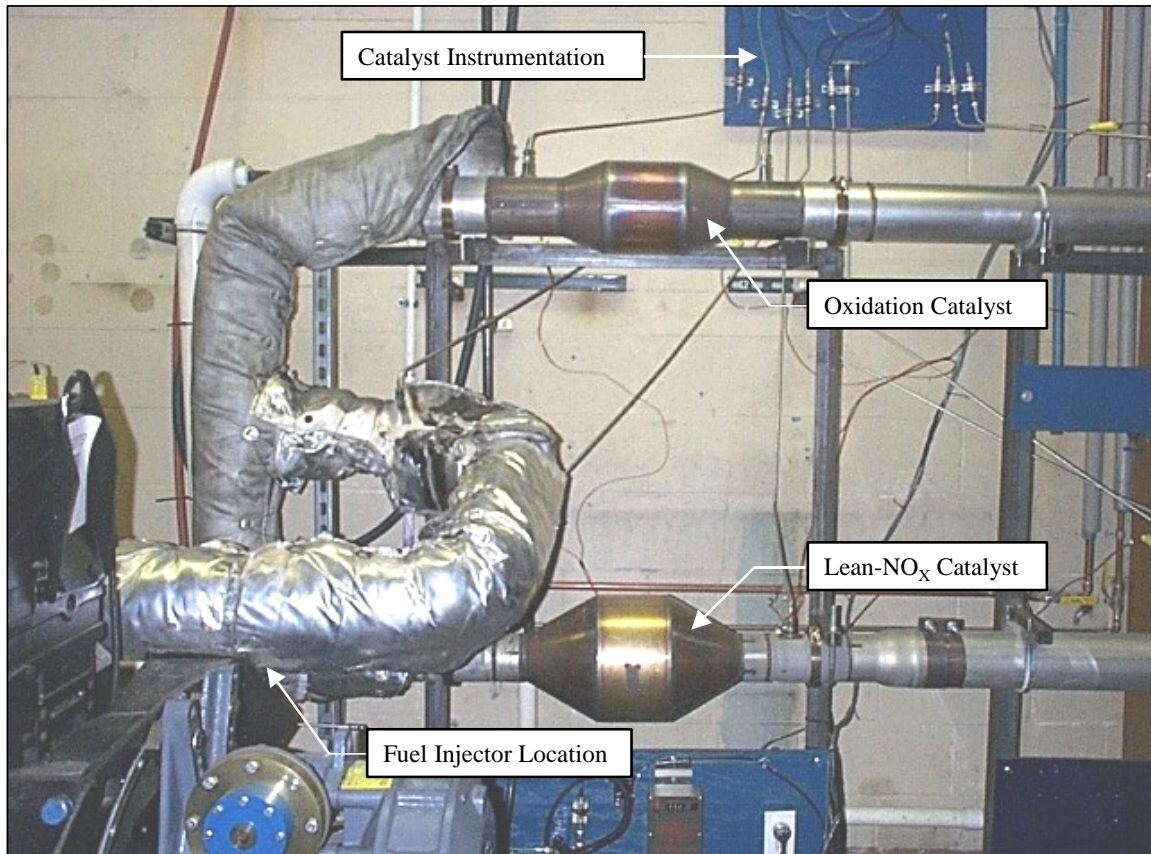


Figure 2-8. LT catalyst aging cell with Navistar T444E engine



**Figure 2-9. HT catalysts mounted in split exhaust for aging**

Go-Power DT-2000 water brake dynamometers were used to provide load to the engine. A personal computer (PC) with project-specific software controlled the engine's throttle and the torque applied by the dynamometer. This PC also monitored and recorded important experimental parameters such as speed, load, coolant temperature, oil pressure and temperature, intake air temperature, and exhaust temperature. Catalyst-related parameters included exhaust flow rate in each branch of the exhaust system, catalyst inlet and exit temperatures, pressure drop across each catalyst, and secondary HC injection pressure.

The catalysts were aged over engine operating cycles composed of four steady-state modes, which were repeated continuously for the specified aging period. The HT catalyst aging cycle was composed of modes 2, 3, 10, and 11 of the ESC. These modes are shown in relation to the Cummins ISM370 engine power torque map in Figure 2-10 and listed in Table 2-7. The LT catalyst aging cycle was composed of modes 2, 3, 7, and 9 of the Navistar 9-mode cycle developed by Ford Motor Company. The LT aging modes are shown relative to the Navistar power torque map in Figure 2-11 and are listed in Table 2-7. The modes were selected to represent a range of engine operation and exhaust temperature.



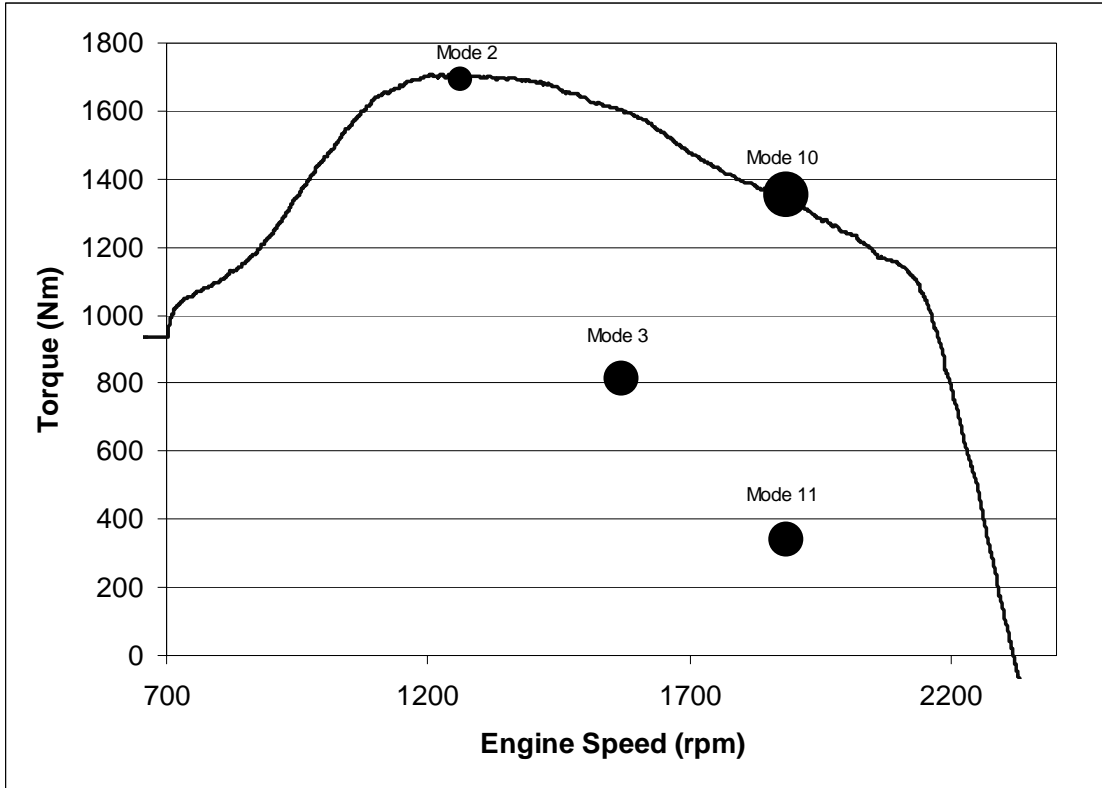


Figure 2-10. Cummins ISM 370ESP engine map

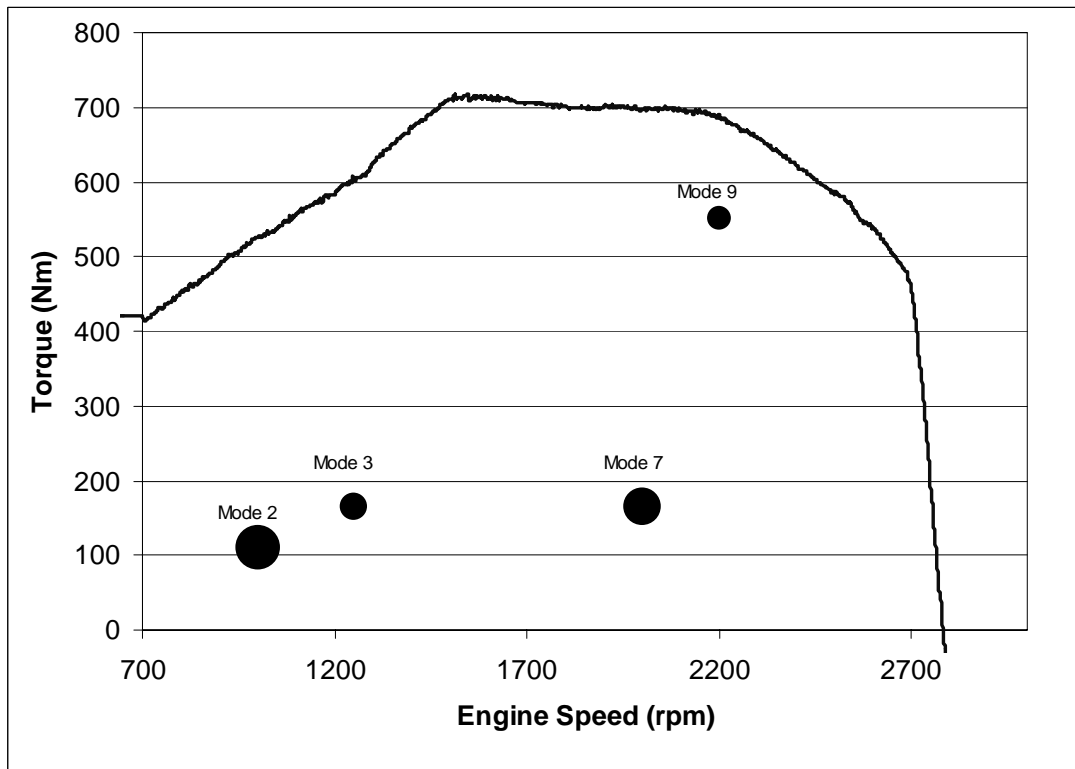


Figure 2-11. Navistar T444E engine map

Each catalyst was aged in 50- and 100-hour intervals separated by emission evaluations. Exhaust flow in the two branches of the split exhaust system was balanced and the exhaust back pressure was adjusted to manufacturer specifications with the engine operating under rated power. The engine was then operated on the specified catalyst aging cycle for a period of 50 or 100 hours as required by the experimental matrix. During the catalyst aging process, the oil level in the engine was maintained through regular checks and oil consumption was recorded. The crankcase oil was sampled at 50-hour intervals and was analyzed by Cummins, Inc. The engines and dynamometers were also maintained as needed.

## 2.4 Catalyst Evaluation Procedures

Catalyst performance was evaluated after 0, 50, 150, and 250 hours of catalyst aging in a transient engine dynamometer testing facility. Emissions of interest included EO and catalyst-out  $\text{NO}_x$ , HC, CO,  $\text{CO}_2$ , PM and PM bound SOF,  $\text{SO}_4$ , and  $\text{NO}_3$ .

### 2.4.1 Heavy-Duty FTP Cycle on the Cummins ISM Engine

The heavy-duty certification FTP cycle, presented in CFR Title 40, was used as the transient emissions testing cycle for the Cummins ISM 370 engine. This cycle was originally created using a Monte Carlo simulation based on statistics derived from measurements of engine torque and speed during on-road truck and bus operation. The schedule is available as dimensionless torque and speed versus time in CFR Title 40, and is converted to actual target torque and speed based on the engine idle speed, engine-rated speed, and a full-power torque map. Figure 2-13 shows the actual target torque for the Cummins engine; Figure 2-6 shows the target speed.

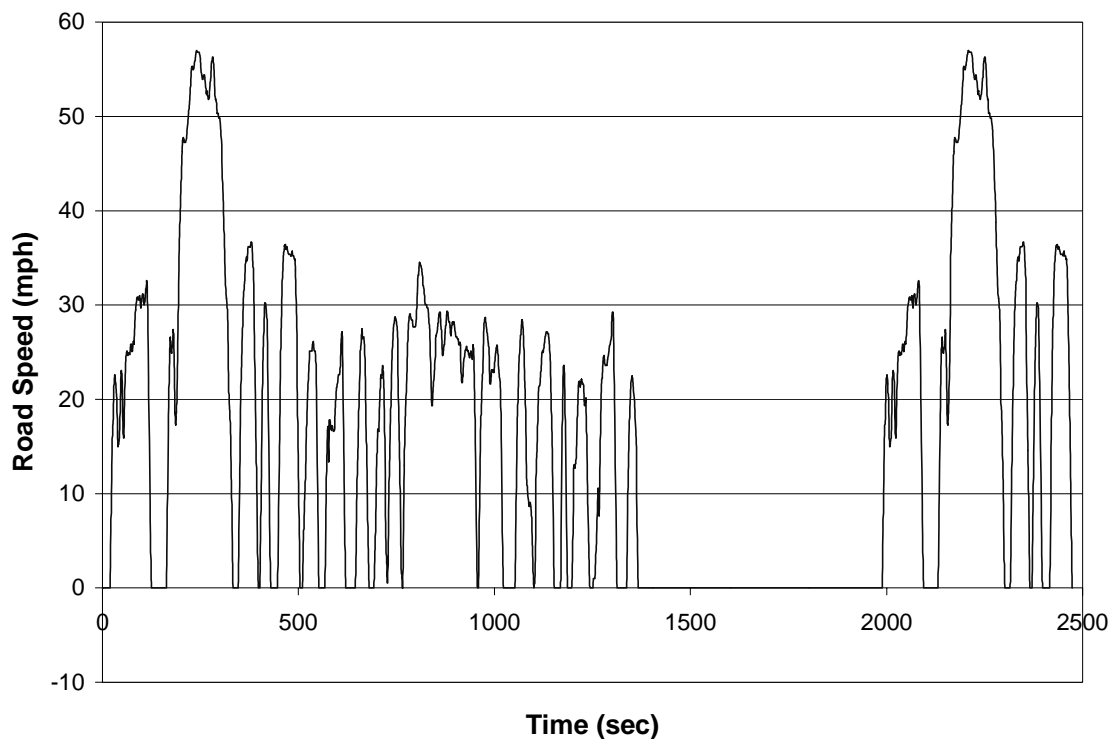


Figure 2-12. Federal Urban Dynamometer Driving Schedule (FTP-75) for Light-Duty Trucks and Vehicles

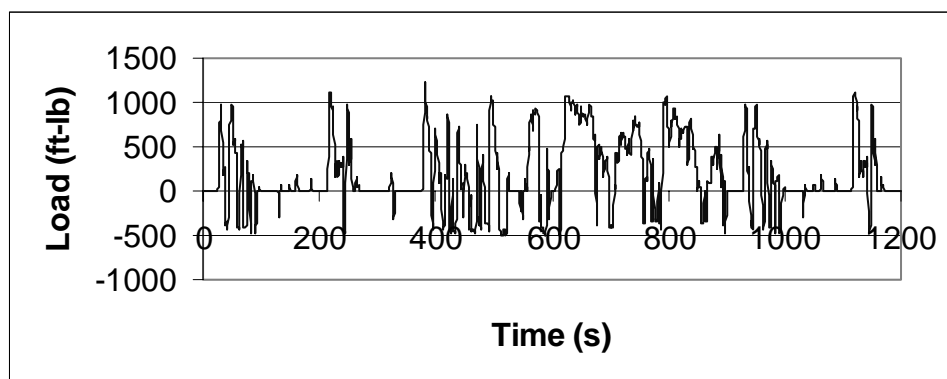


Figure 2-13. FTP load versus time

### 2.4.2 Four-Mode Steady-State Cycle on the Cummins ISM Engine

Modes 2, 3, 10, and 11 of the ESC were selected for the HT catalyst evaluation cycle. In the interest of consistency, the same modes used for catalyst aging were also used for evaluation. Officially, the ESC requires each mode to be 2 minutes in length. However, the DECSE technical committee recommended that the catalyst temperature and catalyst-out emissions be allowed to stabilize before the measurements were recorded. To reduce the time required for the catalyst temperature to stabilize, the modes were executed in the order of increasing exhaust temperature (11, 3, 10, 2). Each mode was 20 minutes; data were collected during the final minutes of the mode. Gaseous and particulate sampling times were selected to reflect the specified modal weighting factors and to ensure that ample particulate mass was collected on the 70-mm filters. Modal weighting factors and sampling times are listed in Table 2-9. When the lean-NO<sub>x</sub> catalyst was tested, secondary reductant injection was initiated 5 minutes into each mode.

Table 2-9. Steady-state evaluation cycles

Navistar 4-Mode Steady State				Cummins 4-Mode Steady State			
NAV-9 Mode Number	Description	Weighting Factor	Sampling Time (s)	ESC Mode Number	Description	Weighting Factor	Sampling Time(s)
Idle	Idle	-	-	Idle	Idle		
2	Low rpm, low torque, low temperature	36	360	11	Low temperature operation	26	170
3	Low rpm, high torque, low temperature	19	190	3	Road load	26	280
7	High rpm, low torque, low temperature	28	280	10	Rated condition	32	190
9	High rpm, high torque, high temperature	17	170	2	High torque, high temperature	16	360
Cool Down	Motoring	-	-	Cool Down	Motoring		

### 2.4.3 Light-Duty FTP-75

Light-duty vehicle emissions are usually measured using a vehicle driving cycle, consisting of a speed-versus-time trace. The vehicle is operated on a chassis dynamometer during the measurement process. For light-duty engine emissions certification, the “FTP-75” speed-time test schedule, described in CFR Title 40, is used. For the DECSE Program, the Navistar engine was deemed to have light-duty applications, but the research could not be performed on a chassis dynamometer. An engine cycle was therefore created to mimic the activity of the engine as if it were installed in a typical vehicle following the FTP-75 chassis test. For this purpose, the engine was considered to be installed in a Ford F-250 pickup truck. The resulting engine cycle consisted of a list of speed and torque versus time. These were applied to the engine in a similar fashion to the heavy-duty FTP engine certification test. Figure 2-7 shows the target torque versus time of the FTP-75 engine test and Figure 2-14 shows the target speed. For this Navistar T444E engine, the FTP-75 elicited 75 hp of integrated work over the cycle. A picture of the Navistar T444E test engine mounted on the transient test bed is shown in Figure 2-15.

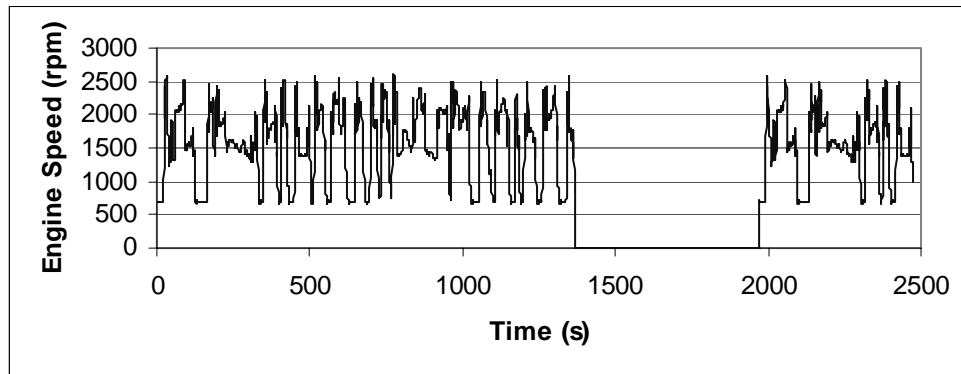
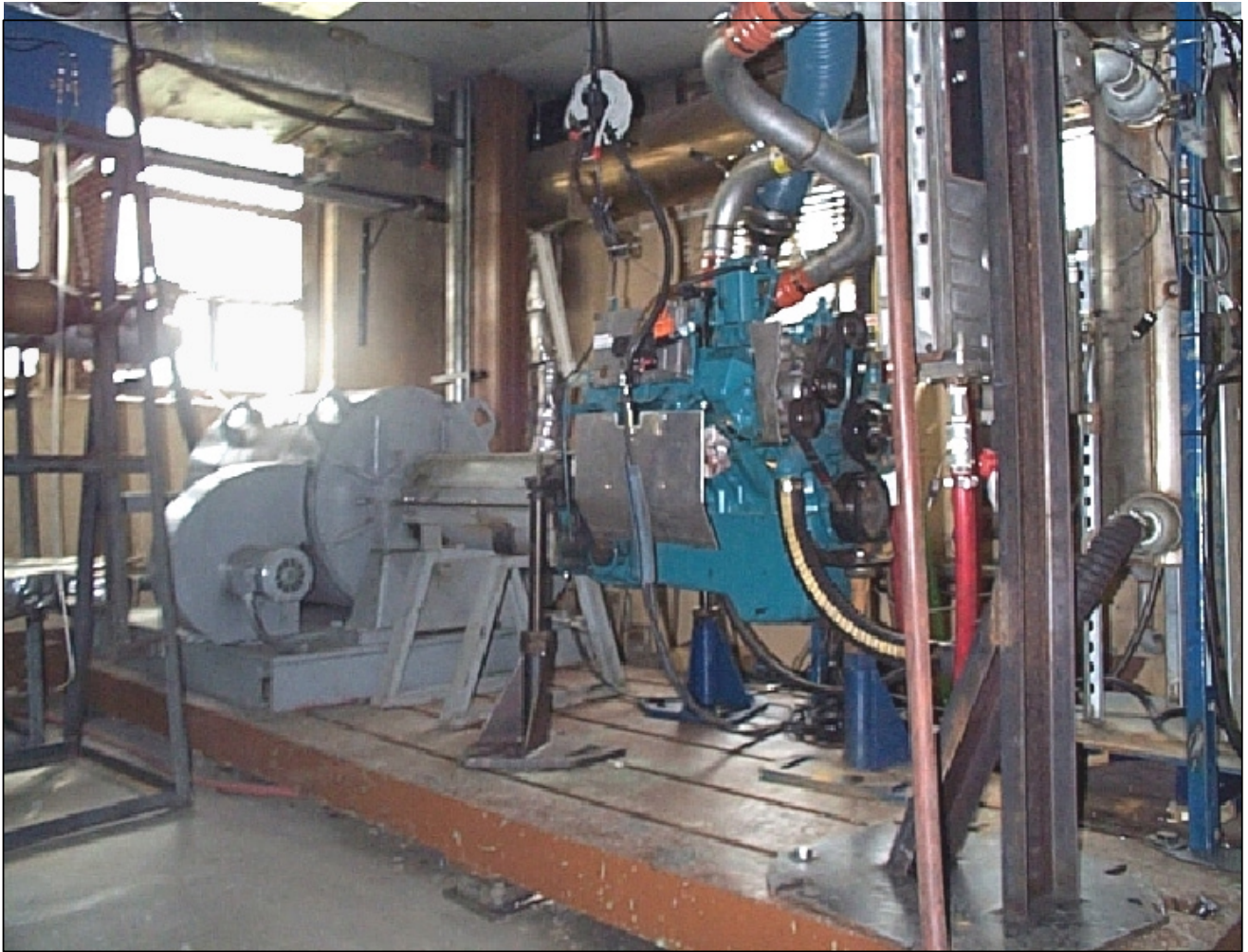


Figure 2-14. FTP-75 speed versus time



**Figure 2-15. Navistar T444E engine mounted in the transient engine test cell**

#### **2.4.4 Four-Mode Steady-State Cycle on the Navistar T444E Engine**

The LT catalysts were evaluated using modes 2, 3, 7, and 9 of the Navistar 9-mode cycle, which also corresponded to the aging modes. The modes were also performed in the order of increasing exhaust temperature, which was coincidentally 2, 3, 7, and 9. The same sampling procedures described for the Cummins steady-state cycle were used for the Navistar testing. Weighting factors and sampling times can be found in Table 2-11.

#### **2.4.5 Evaluation Test Sequence**

Catalyst performance was evaluated after 0, 50, 150, and 250 hours of exposure to exhaust during engine operation on the respective fuel sulfur level. A typical catalyst evaluation series consisted of the following series of test cycles.

1. Full-flow EO transient test (FTP or FTP-75).
2. Full-flow EO steady-state test (ESC or NAV).
3. Split-flow EO transient test (FTP or FTP-75).
4. Split-flow EO steady-state test (ESC or NAV).

5. DOC catalyst-out transient test (FTP or FTP75).
6. DOC catalyst-out steady-state test (ESC or NAV).
7. Lean-NO<sub>x</sub> catalyst-out steady-state test (ESC or NAV).

Full-flow EO cycles were performed to determine CO<sub>2</sub> concentration in the engine's exhaust steam. These data were used to correct the split-flow to full-flow levels. Split-flow EO tests were performed to confirm that the split-flow corrected emissions agreed with the full-flow results. Full-flow and split-flow EO data were used to calculate catalyst reduction efficiencies. The DOC was then installed into the split exhaust system and catalyst-out cycles were performed. The secondary reductant injection system was disabled during DOC evaluations. Finally, the lean-NO<sub>x</sub> catalyst was installed into the exhaust system and the steady-state catalyst-out evaluations were performed. All cycles were performed on a warm engine.

## **2.5 Data Management and Statistical Analysis**

Throughout the program, the gaseous emissions and total PM data generated at WVU and the PM breakdown analysis data (SOF, SO<sub>4</sub>, and NO<sub>3</sub>) prepared by ORNL, were periodically transferred to the data team at Battelle where a centralized database was maintained. A restricted-access Web site was established to provide the technical committee with data collection status reports, data summaries in the form of descriptive tables and figures, and interim findings from ongoing statistical analyses.

Tables 2-10 and 2-11 show the actual number of gaseous and particulate emissions measurements performed with the low-temperature and high-temperature tests, respectively. The catalysts tested included the low-temperature DOC and lean-NO<sub>x</sub> catalysts (denoted by B1-B4 and L1-L4, respectively) and high-temperature DOC and lean-NO<sub>x</sub> catalysts (denoted by A1-A4 and H1-H4 respectively). The difference between the numbers shown in these tables and Table 2-1 reflect lost measurements, additional tests performed as quality checks, and decisions made by the technical committee following review of preliminary results. For example, the committee decided not to continue the recovery experiments because the early results suggested that recovery was not an issue or had occurred within the first 50 hours of aging with 30-ppm sulfur fuel. The committee also chose to forego the 150-hour tests with 150-ppm sulfur fuel when it was clear that they would not provide new information. Finally, the 350-ppm sulfur aging experiments with the Navistar engine were extended to 400 hours due to data collection issues at 250 hours.

Section 2.5.1 discusses selected data management and processing procedures implemented by the data team, and Section 2.5.2 describes the statistical analysis methods.

**Table 2-10. Numbers of gaseous/particulate emissions measurements performed with the low temperature (Navistar) engine**

Test Type	Fuel Sulfur (ppm)		Catalysts Tested	Age (Hours)	Source of Emissions		
	Test Engine	Aging Engine			Engine-Out	Post-DOC (B1-B4)	Post-Lean-NO <sub>x</sub> (L1-L4)
Nav-9, 4-mode	3	3	B1/L1	0	2/2	2/2	2/1
				50	0/0	1/1	1/0
				150	2/2	1/1	1/1
				250	2/2	2/2	2/2
	30	30	B2/L2	0	2/2	2/2	2/2
				50	0/0	1/1	1/1
				150	2/2	1/1	1/1
				250	2/2	2/2	2/2
	150	150	B3/L3	0	3/3	2/1	2/2
				50	2/2	1/1	1/1
				250	2/2	2/2	2/2
	350	350	B4/L4	0	3/3	2/2	2/2
				50	4/2	2/2	2/2
				150	2/0	1/0	1/0
				400	2/1	2/2	2/2
	30	3	B1/L1	250	0/0	1/1	1/1
	150	3	B1/L1	250	0/0	1/1	1/1
	350	3	B1/L1	400	0/0	1/1	1/1
	30R <sup>(1)</sup>	30	B4/L4	0/400 <sup>(2)</sup>	2/1	1/1	2/2
				50/450	2/2	1/1	1/1
FTP 75	3	3	B1	0	2/2	2/2	
				50	0/0	2/2	
				150	3/3	2/2	
				250	3/3	2/2	
	30	30	B2	0	2/2	2/2	
				50	0/0	2/1	
				150	2/2	2/1	
				250	3/3	2/2	
	150	150	B3	0	3/2	2/2	
				50	2/2	2/2	
				250	2/2	2/2	
	350	350	B4	0	4/4	2/2	
				50	2/1	2/2	
				150	3/0	2/0	
				400	1/0	3/3	
	30	3	B1	250	0/0	2/2	
	150	3	B1	250	0/0	2/2	
	350	3	B1	400	0/0	1/1	
	30R	30	B4	0/400	2/1	2/2	
				50/450	2/2	2/2	
Nav-9, Mode 9	3		B1/L1	0	2/2	2/2	2/2
	30		B2/L2	0	2/2	2/2	2/2
	150		B3/L3	0	2/1	2/2	2/2
	350		B4/L4	0	2/2	2/2	2/2

(1) Recovery tests performed following aging with 350-ppm sulfur fuel

(2) Number of “recovery hours”/total hours

**Table 2-11. Numbers of gaseous/particulate emissions measurements performed with the high temperature (Cummins) engine**

Test Type	Fuel Sulfur (ppm)		Catalysts Tested	Age (Hours)	Source of Emissions		
	Test Engine	Aging Engine			Engine-Out	Post-DOC (A1-A4)	Post-Lean-NO <sub>x</sub> (H1-H4)
OICA-13, 4-mode	3	3	A1/H1	0	2/1	2/2	2/2
				50	1/0	2/1	1/0
				150	2/0	1/1	1/1
				250	2/2	2/2	2/1
	30	30	A2/H2	0	2/1	1/1	1/1
				50	2/0	1/1	1/1
				150	2/1	1/1	1/1
				250	2/2	2/2	1/1
	150	150	A3/H3	0	2/2	2/2	2/2
				50	2/2	1/1	1/0
				150	2/2	1/1	1/1
				250	2/2	2/2	2/2
	350	350	A4/H4	0	2/0	1/1	2/2
				50	2/1	1/1	1/1
				150	2/2	1/1	1/1
				250	1/0	2/2	2/2
	30	3	A1/H1	250	0/0	1/1	1/1
	150	3	A1/H1	250	0/0	1/1	1/1
	350	3	A1/H1	250	0/0	1/1	1/1
	30R <sup>(1)</sup>	30	A4/H4	0/250 <sup>(2)</sup>	0/0	1/1	2/2
				50/300	2/1	1/1	1/1
FTP Hot	3	3	A1	0	3/2	2/2	
				50	1/0	2/2	
				150	3/2	2/2	
				250	2/2	2/2	
	30	30	A2	0	2/1	2/2	
				50	4/3	2/2	
				150	2/1	2/2	
				250	3/3	2/2	
	150	150	A3	0	1/1	2/2	
				50	2/2	2/2	
				150	2/2	2/2	
				250	2/2	2/2	
	350	350	A4	0	2/1	2/2	
				50	2/1	2/2	
				150	2/2	2/2	
				250	2/1	2/2	
	30	3	A1	250	0/0	2/2	
	150	3	A1	250	0/0	2/2	
	350	3	A1	250	0/0	2/1	
	30R	30	A4	0/250	0/0	2/2	
				50/300	2/1	2/1	
OICA-13, Mode 2	3		A1/H1	0	1/1	1/1	1/1
	30		A2/H2	0	1/1	1/1	1/1
	150		A3/H3	0	1/1	1/1	1/1
	350		A4/H4	0	1/1	1/1	1/1

(1) Recovery tests performed following aging with 350-ppm sulfur fuel

(2) Number of "recovery hours"/total hours



### **2.5.1 Data Management and Processing Procedures**

Test data from the engine testing laboratory (WVU) included second-by-second emissions measurements of NO<sub>x</sub>, THC, CO, and CO<sub>2</sub>, as well as measures of various engine performance parameters. The laboratory also prepared summary reports containing average brake-specific gaseous emissions (g/bhp-hr) for each mode of the 4-mode steady-state tests (OICA-13 and Nav-9) and weighted average emissions across the composite 4-mode steady-state and FTP transient tests. Total PM emissions for the composite steady-state and transient tests were also reported.

PM breakdown analysis, performed at ORNL, produced estimates of SOF, SO<sub>4</sub>, and NO<sub>3</sub> on a mg/filter basis. In addition to the primary and secondary main filters, primary and secondary “tunnel” filters and analytical blanks were analyzed throughout the program. SOF and SO<sub>4</sub> loadings from the tunnel filters and analytical blanks were statistically analyzed to determine if there were systematic trends over time or patterns with respect to main filter results. No such trends or patterns were observed.

The conversion of SOF and SO<sub>4</sub> filter concentrations to brake-specific emissions was performed according to the following formula (as shown for SOF):

$$\text{SOF(g/bhp-hr)} = [\text{PM(g/bhp-hr)/PM(mg/filter)}] * [\text{SOF(mg/filters)} - 2 * \text{SOF}_{\text{blank}}(\text{mg/filter})],$$

where SOF(mg/filters) is the sum of SOF weights on the primary and secondary filters, and SOF<sub>blank</sub>(mg/filter) is the average weight of SOF on all analytical blanks. The average blank approach was used because there was no systematic trend in blank filter measurements.

Because most emissions data reduction routines require calculations involving calibration equations or differences in gross filter weights, gaseous and particulate emissions measurements were sometimes reported as negative values. These values were replaced with zero before any further calculations or statistical analysis were performed.

A variety of data quality assurance procedures were implemented to ensure data completeness and accuracy. After comparing the data received with the data collection plan, the data were stored in an Access database, which was controlled by a database administrator. Changes, updates, and corrections were carefully monitored and controlled. To identify gross outliers (unusual and unexplained emissions results) and unexplained variations or trends associated with laboratory procedures, various types of graphical summaries were prepared and shared with the laboratories and the technical committee. The graphical summaries included plots of emissions versus fuel sulfur level, aging hours, and time. These preliminary plots were also used to identify appropriate statistical models for analyzing the data.

Two types of data issues were identified: individual outliers and temporal effects. Lists of outliers were sent to the two laboratories with instructions to check for clerical errors, equipment failures, or other external factors that could explain the deviation in results. Clerical errors were corrected and outliers that could be explained by equipment failures or external factors were flagged and not included in the final data analysis. If no explanation was available, the data were retained for the first phase of statistical analysis. This phase involved fitting regression models to the updated data. A second outlier analysis was performed using the standardized residuals from

the regression analysis. Standardized residuals are commonly used to identify individual data points that are statistically inconsistent with the underlying structure of the data set. Several outliers were identified by this approach; however, only three measurements were eliminated from the final statistical analysis. This is discussed further in the next section.

Temporal effects were also apparent when plotting emissions measurements versus analysis date. Fortunately, additional engine-out tests were included, which made it easy to identify potential factors affecting the measurement process during the 17 months of data collection. After considering the dates on which various “events” took place (engine changes, dynamometer calibrations, equipment failures, and extended downtime), the team concluded that there were several time periods during which the measurement process appeared to be in a state of statistical control (i.e., no unexplained variations). Although adjustment factors were identified for some emissions measurements, applying these adjustments tended to create trends and temporal effects in other emissions measurements. Therefore, the recommended solution was to include a temporal effects term in the statistical regression model that was used to analyze the data. The advantage of this approach is that it does not introduce new biases by attempting to correct the data. The disadvantage is that it uses valuable data to estimate the correction factor and, thereby, reduces the power of the statistical tests involving the factors of interest (i.e., fuel sulfur level, catalyst, and catalyst age). The statistical model for estimating these correction factors is discussed in the next section.

### **2.5.2 Statistical Modeling and Analysis**

Statistical analyses were performed to test specific hypotheses concerning the performance of fresh and aged diesel oxidation and lean-NO<sub>x</sub> catalysts with diesel fuels containing various levels of sulfur. In particular, the analyses were designed to address the seven study questions presented in Section 2.1.

The analyses were divided into three parts: fresh catalyst analysis, aging effects analysis, and recovery and thermal aging analysis. Fresh catalyst analysis was conducted using only the emissions data collected at age zero, while the aging effects and recovery analyses used all emissions data obtained over 250 or 400 hours of aging.

The statistical analysis approach used generalized linear models that simultaneously consider the effects of fuel sulfur level, source of emissions (engine-out or post catalyst), catalyst aging, and various sources of systematic and random experimental errors. The analysis was carried out using PROC GLM and PROC MIXED procedures in the Statistical Analysis System (SAS®) software package. Detailed descriptions of the analyses are provided below.

Prior to applying the linear models, the emissions data were transformed to a log scale because it was determined that the emissions data follow a lognormal distribution. Before applying the log transformation, emissions reported as zero were replaced with one half the detection limit, if reported. Otherwise, the zero value was replaced with one half of the minimum positive value of the reported emissions. Emissions data from different engines were analyzed separately. In a preliminary analysis, standardized residuals were calculated to identify statistical outliers relative to the fitted models. Three data points were identified as “significant” outliers that clearly did not fit the pattern of similar data. The following values were therefore excluded from the statistical analysis.

1. CO emissions at 350-ppm and 0-hour under NAV-9 4-Mode test condition from the lean-NO<sub>x</sub> catalyst (value = 0 g/bhp-hr)
2. HC emissions at 3-ppm and 150-hours under OICA-13 4-Mode test condition from the DOC (value = 0 g/bhp-hr)
3. NO<sub>x</sub> emissions at 350-ppm and 150-hour under NAV-9 4-Mode test condition from the lean-NO<sub>x</sub> catalyst (value = 4.463 g/bhp-hr)

### Fresh Catalyst Analysis

We began this analysis using the following fixed effect model to characterize the effects of fuel sulfur on emissions at age zero:

$$\log(\text{Emissions}) = \mu + S + \text{Cat} + S*\text{Cat} \quad (1)$$

where

$\mu$  = overall mean

S = the (fixed) effect of fuel sulfur (3-ppm, 30-ppm, 150-ppm, and 350-ppm)

Cat = the (fixed) effect of catalyst (Engine-out, post-DOC and post-lean-NO<sub>x</sub>)

S\*Cat = the interaction of fuel sulfur and catalyst

To simplify the presentation, the coefficients of the effects and error terms are not presented.

Whenever possible, estimates of error standard deviations were obtained by pooling the data across various combinations of fuel sulfur level and catalyst type (engine-out, post-DOC, and post-lean-NO<sub>x</sub>) for each test type (4-mode or FTP). This approach, using Equation (1), was used for total PM, SOF and SO<sub>4</sub> emissions. However, because of the differences in the variability of engine-out and post-catalyst emissions of HC, CO and NO<sub>x</sub>, it was necessary to analyze EO, post-DOC and post-lean-NO<sub>x</sub> data separately using the following fixed effect model.

$$\log(\text{Emissions}) = \mu + S \quad (2)$$

For the lean-NO<sub>x</sub> catalyst, we also investigated the effects of fuel sulfur on emissions by individual test condition. The following fixed effect model, as well as a reduced model assuming no sulfur effect, were fit to post-lean-NO<sub>x</sub> gaseous emission data:

$$\log(\text{Emissions}) = \mu + S + \text{Mode} + S*\text{Mode} \quad (3)$$

where

$\mu$  = overall mean

S = the (fixed) effect of fuel sulfur (3-ppm, 30-ppm, 150-ppm, and 350-ppm)

Mode = the (fixed) effect of test condition (OICA-13 4 modes or NAV-9 4 modes)

S\*Mode = the interaction of fuel sulfur (3-ppm, 30-ppm, 150-ppm, and 350-ppm) and test condition (OICA-13 4 modes or NAV-9 4 modes)

Appropriate analysis of variance procedures were used to establish the statistical significance of the parameters in models. If there was no evidence of statistical significance, the parameters were eliminated and a reduced model was fit to the data.

Confidence intervals were used to characterize the statistical uncertainty of emissions estimates and to determine if there were significant effects of specific fuel sulfur levels on engine-out (or post-catalyst) emissions. This approach was also used to compare reduction efficiencies across fuel sulfur levels. Reduction efficiency was defined as:

$$RE = \left( 1 - \frac{Post - Catalyst}{Engine - Out} \right) \times 100 \quad (4)$$

### Analysis of Aging Effects

For this analysis, engine-out and post-catalyst emissions data were analyzed separately for the diesel oxidation and lean-NO<sub>x</sub> catalysts. Preliminary analyses indicated that, with few exceptions, there were no significant trends in emissions between 50 and 250 (or 400) hours of catalyst aging. Thus, we combined data from aged catalysts into a single age category. As discussed in the previous section, the statistical model was used to adjust for systematic temporal effects associated with the experimental process. The following fixed effect model was fit to the data for investigating sulfur and age effects:

$$\log(\text{Emissions}) = \mu + TP_2 + TP_3 + TP_4 + TP_5 + S + PC + PC*Age + S*PC + S*PC*Age \quad (5)$$

where

$\mu$  = overall mean

$TP_i$  = temporal effect for emissions collected during Test Period #  $i$ ,  $i = 2$  to  $5$

$S$  = the (fixed) effect of fuel sulfur (3-ppm, 30-ppm, 150-ppm, and 350-ppm)

$PC$  = the (fixed) effect of catalyst ( $PC=0$  if engine-out and  $PC=1$  if post-catalyst)

$PC*Age$  = the interaction of catalyst and catalyst age ( $Age=0$  if 0 hour and 1 if  $>0$  hour)

$S*PC$  = the interaction of fuel sulfur and catalyst

$S*PC*Age$  = the interaction of fuel sulfur, catalyst and catalyst age

This model simultaneously considers the main effects and interactions of fuel sulfur, catalyst, and age of the catalyst (fresh vs. aged). For PM, SOF, SO<sub>4</sub>, and NO<sub>x</sub> emissions, the model errors were assumed to be normally and independently distributed random variables with mean zero and a common variance  $\sigma^2$ . However, for HC and CO emissions, the separate variance components,  $\sigma_{EO}^2$  and  $\sigma_{PC}^2$ , were applied for engine-out and post-catalyst emissions.

As was done for the fresh catalyst analysis, appropriate analysis of variance procedures were used to establish the statistical significance of the parameter estimates and confidence intervals were constructed to characterize the statistical uncertainty of emissions estimates.

### Impact of Statistical Modeling Assumptions

The linear regression models used in these analyses are based upon assumptions that the model errors are distributed independently according to normal distributions. Preliminary analysis demonstrated that the emissions data tend to follow a lognormal distribution; therefore, a log transformation was applied to the data before fitting the models. In general, moderate departures from normality are of little concern in the fixed effects ANOVA since ANOVA is fairly robust to the normal assumptions. On the other hand, the assumption of independent errors is important to evaluate, especially when it's not possible to randomize the order of testing. In particular, one

concern was that events, such as equipment failures and recalibrations, could create correlation among data collected in the same time period. However, having identified the potential events and having accounted for their impact in the regression model, as shown in Equation (5), most of these dependencies are eliminated.

### 3 DOC Experimental Results and Discussion

#### 3.1 Fresh Catalyst Results

Fresh diesel oxidation catalysts (0-hour, after degreening) were evaluated using each of the four test fuels before the aging sequences began. The protocol included a weighted composite steady-state evaluation (4-modes each from OICA-13 and NAV-9), a transient evaluation (FTP hot-cycle and FTP75 mimicry), and a high exhaust temperature steady-state mode (OICA-13 mode 2 and NAV-9 mode 9). Additional details of this evaluation scheme can be found in Section 2. The results of these 0-hour evaluations (EO and catalyst-out) are summarized here.

##### 3.1.1 Particulate Matter

Figure 3-1 shows EO and post catalyst emissions of PM from the Navistar using mode 9 of the NAV-9 and illustrates the composition of the collected PM. The height of each bar represents the estimated PM emissions, which were measured at 50% relative humidity. Because SO<sub>4</sub> emissions are measured under dry conditions, the contribution of SO<sub>4</sub> to total PM is calculated by multiplying the SO<sub>4</sub> mass by a factor of 2.33, representing hydrated SO<sub>4</sub> with seven molecules of water per molecule of sulfuric acid (Reference 1995 SAE Handbook). The contributions of “other” PM components (e.g., ash) are calculated by taking differences. Also shown are the 95% confidence intervals on the total PM emissions.

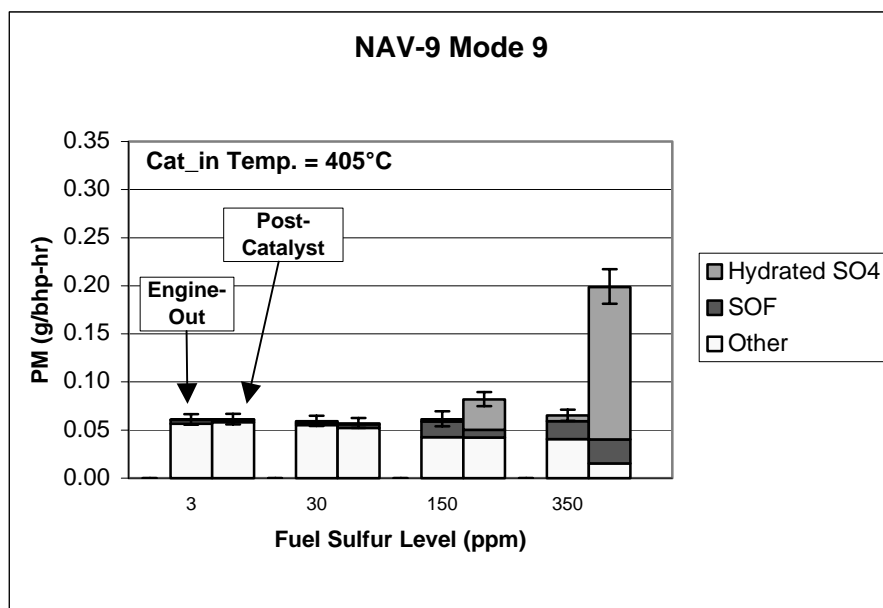
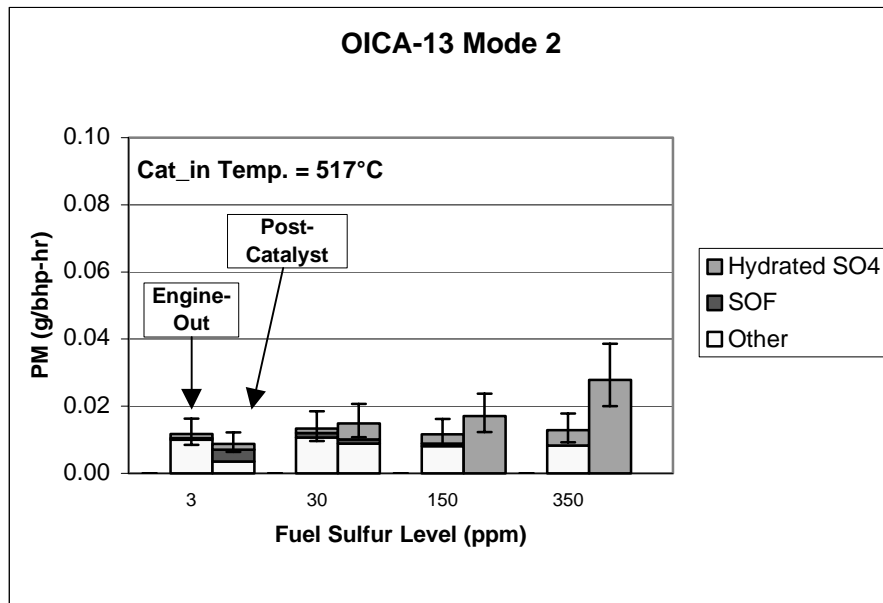


Figure 3-1. EO and post-DOC emissions of total PM and components under LT (Navistar) applications using a Nav-9 mode 9 test (with 95% confidence intervals on estimated PM)

There is a statistically significant increase in PM with high sulfur fuel due almost exclusively to the increase in the SO<sub>4</sub> fraction of the total PM. At this high exhaust temperature (405°C at catalyst inlet), the DOC accelerates the conversion of SO<sub>2</sub> to SO<sub>3</sub>, thereby increasing the SO<sub>4</sub> fraction of the PM. As expected, the effect is seen only with the higher sulfur (150- and 350-ppm S) fuels.

With the 350-ppm S fuel, post catalyst PM emissions from the Navistar engine are approximately 200% higher than those measured without an active catalyst during Mode 9. The exhaust temperature during this mode is 405°C. The SO<sub>4</sub> increased from 0.0026 g/bhp-hr EO to 0.0680 g/bhp-hr after the catalyst. The increase is proportionately similar with the 150-ppm S fuel.

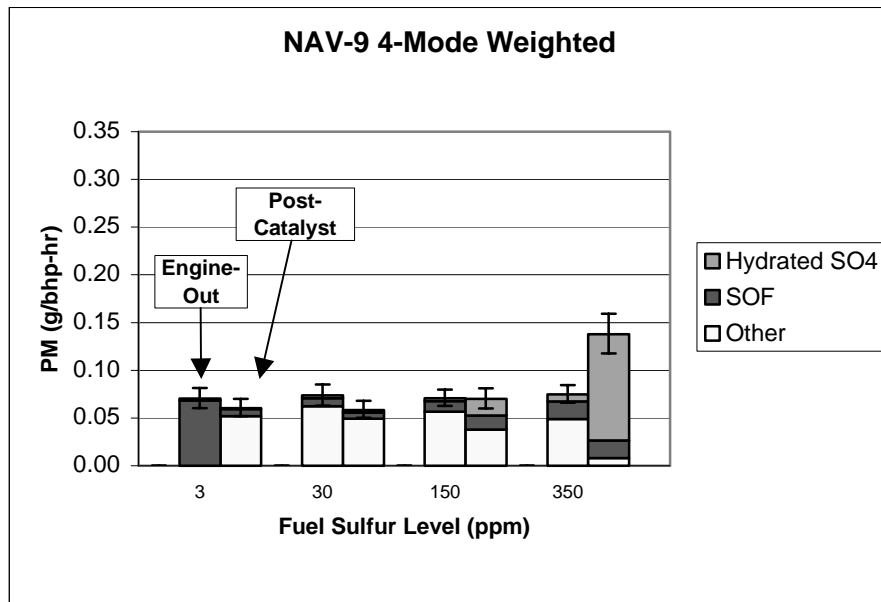
Figure 3-2 plots PM emissions from the fresh catalyst evaluations with the Cummins engine, measured at peak torque. With the 350-ppm S fuel, post-catalyst PM emissions from the Cummins engine are approximately 100% higher than those measured without an active catalyst during OICA Mode 2. The exhaust temperature during this mode is 517°C. The SO<sub>4</sub> increased from 0.002 g/bhp-hr to 0.013 g/bhp-hr.



**Figure 3-2. EO and post DOC emissions of PM and components under high temperature (Cummins) applications using an OICA-13 mode 2 test (with 95% confidence intervals on estimated PM)**

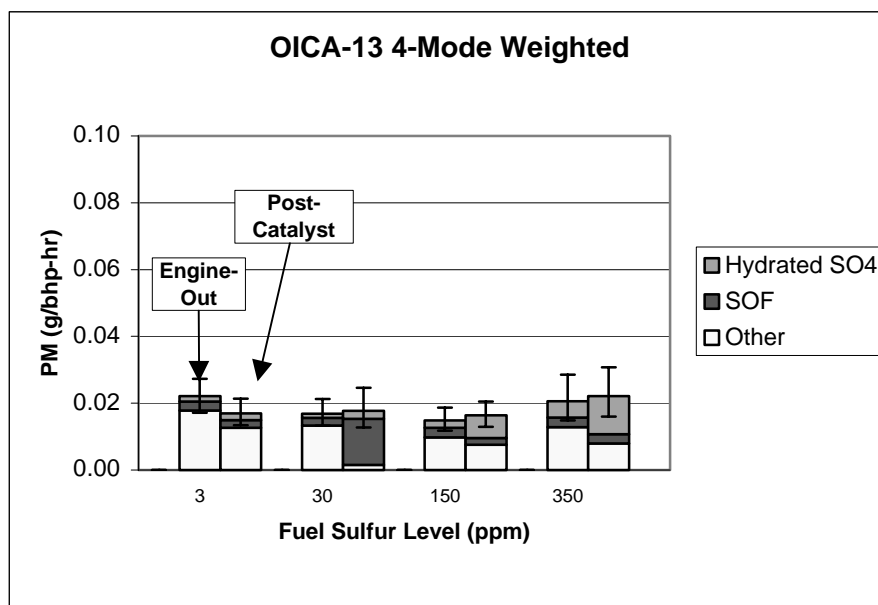
The relative magnitude of the Navistar and Cummins results can be attributed to the difference in precious-metal loading on the respective catalysts. The LT catalysts used with the Navistar engine contained over 50 g/cm<sup>3</sup> Pt; the HT catalysts used with the Cummins engine contained only 2 g/cm<sup>3</sup>. The choice of Pt loading is often a compromise between desired LT performance and the proclivity to increase SO<sub>4</sub> formation at higher temperatures. To this end, lower sulfur fuels enable the use of higher Pt loadings and therefore more robust catalyst performance.

Though the impact was less significant, the results of the modal composite evaluations of the fresh catalysts were similar to those measured during the HT mode. Figure 3-3, which contains the results from the NAV-9 weighted 4-mode evaluation, illustrates an 84% increase in post-catalyst PM emissions and a 14-fold increase in SO<sub>4</sub> with 350-ppm S fuel. The data from the Cummins engine (Figure 3-4) show similar trends; however, the estimated effects are much smaller and the differences between EO and post-catalyst are not statistically significant.



**Figure 3-3. EO and post DOC emissions of PM and components under LT (Navistar) applications using a 4-mode composite test from Nav-9 cycle (with 95% confidence intervals on estimated PM)**





**Figure 3-4. EO and post DOC emissions of PM and components under HT (Cummins) applications using a 4-mode composite test from OICA-13 cycle (with 95% confidence intervals on estimated PM)**

The 4-mode weighted composite steady-state protocol included the high-temperature mode (OICA-1302 or NAV-9 mode 9), in addition to three lower temperature modes. The data collected during this high-temperature mode suggest that it was the highest contributor to the SO<sub>4</sub> collected over the four operating modes.

Catalyst response over the transient evaluation cycles differed from the steady-state tests. In the transient tests (FTP-75 mimicry) with the Navistar engine (Figure 3-5), the DOC reduced SOF of the PM by 70-85%, yielding a 35-45% reduction in PM. The reductions in SOF and PM were statistically significant. Fuel sulfur content did not affect SOF emissions or the SOF suppression efficiency of the DOC. Although there is some statistical evidence that SO<sub>4</sub> emissions increased with higher sulfur fuel, the resulting impact on PM (either EO or post catalyst) was negligible and not statistically significant.

With the Cummins engine, the DOC had similar but less significant effects on SOF and PM reduction efficiency over the FTP hot-cycle (Figure 3-6). SOF suppression efficiency was 4-81% but resulted in a less than 10% reduction in PM. The PM reduction was not statistically significant, and there was no evidence of a sulfur effect at this operating condition.

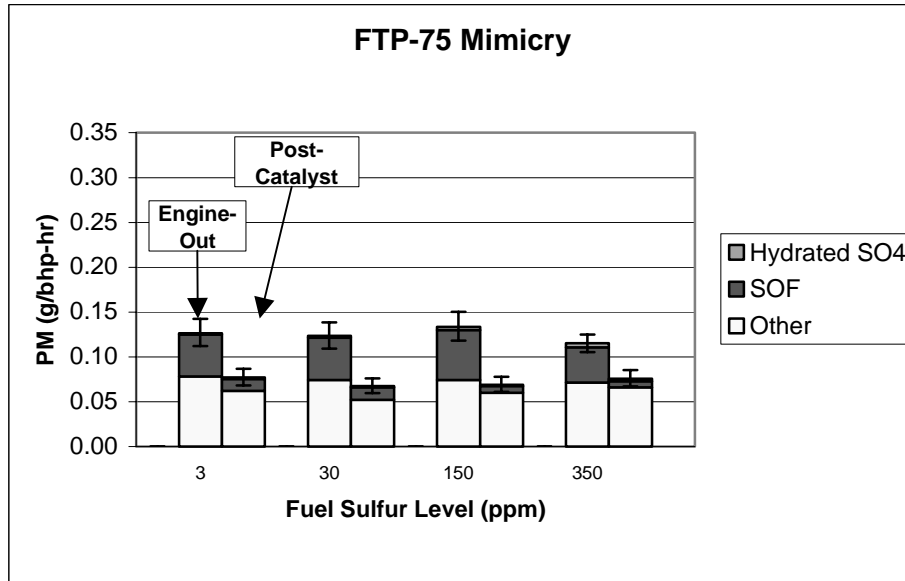


Figure 3-5. EO and post DOC emissions of PM and components under LT (Navistar) applications using the FTP-75 mimicry transient cycle (with 95% confidence intervals on estimated PM)

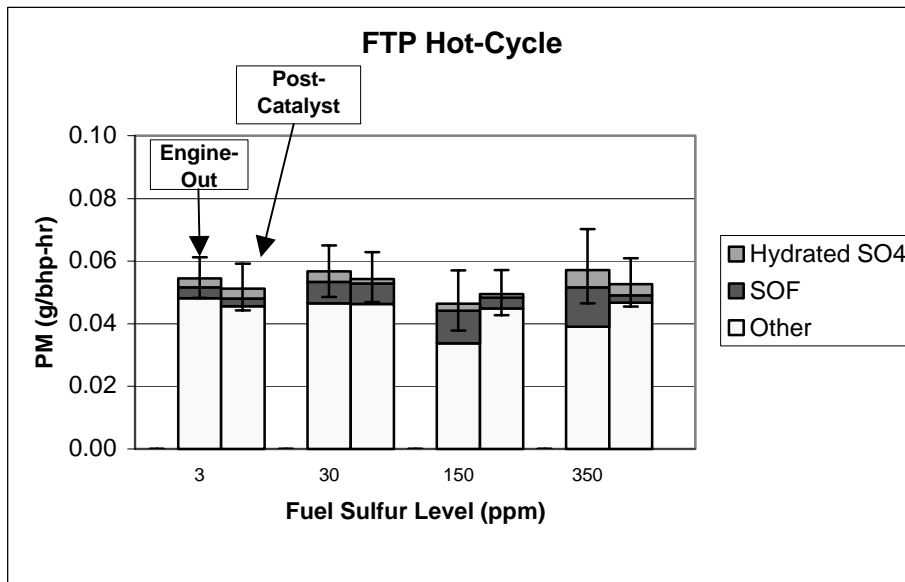


Figure 3-6. EO and post DOC emissions of PM and components under HT (Cummins) applications using the FTP-hot transient cycle (with 95% confidence intervals on estimated PM)

As evidenced by these results, the higher Pt loading enhances PM reduction (via SOF suppression) over the transient test cycles. These cycles are lightly loaded and result in relatively low average exhaust temperatures where Pt is most active. For the Navistar T444E, catalyst inlet temperature was 105°C-229°C (average = 172°C) during the FTP-75 mimicry. For the Cummins ISM370, catalyst inlet temperature was 124°C-352°C (average = 239°C) during the FTP hot-cycle.

### 3.1.2 Gaseous Emissions and Fuel Consumption

The diesel oxidation catalysts used in this study were highly effective at reducing gaseous pollutants. Tables 3-1 and 3-2 summarize the HC and CO emissions, respectively. For example, Table 3-1 shows the estimated EO and post-catalyst HC emissions and the estimated reduction efficiency, with 95% confidence bounds, for each combination of engine, test mode, and fuel sulfur level. Because there are no significant effects of fuel sulfur level, data from all fuels were combined to produce overall estimates of EO and post-catalyst emissions and reduction efficiency.

**Table 3-1. EO and post DOC emissions of HC and emissions reduction efficiency for each combination of engine, test mode, and fuel sulfur level (with 95% confidence intervals)**

Engine	Test Mode	Fuel Sulfur (ppm)	HC		
			Engine-Out (g/bhp-hr) (95% Confidence Interval)	Post-DOC (g/bhp-hr) (95% Confidence Interval)	Reduction Efficiency (%) (95% Confidence Interval)
Navistar	NAV-9 4-Mode Weighted	3	0.1 (0.08, 0.126)	0 (0, 0)	100 (99, 100)
		30	0.061 (0.048, 0.076)	0 (0, 0)	99 (99, 99)
		150	0.109 (0.091, 0.131)	0 (0, 0)	100 (99, 100)
		350	0.112 (0.093, 0.134)	0 (0, 0)	100 (99, 100)
		All	0.096 (0.079, 0.116)	0 (0, 0)	99 (99, 100)
	FTP-75 Mimicry	3	0.59 (0.447, 0.78)	0.002 (0, 0.052)	100 (91, 100)
		30	0.313 (0.237, 0.413)	0.016 (0.001, 0.438)	95 (-39, 100)
		150	0.605 (0.482, 0.76)	0.053 (0.002, 1.474)	91 (-142, 100)
		350	0.613 (0.503, 0.746)	0.003 (0, 0.078)	100 (87, 100)
		All	0.537 (0.438, 0.657)	0.008 (0.002, 0.041)	98 (92, 100)
Cummins	OICA-13 4-Mode Weighted	3	0.162 (0.146, 0.18)	0.01 (0.004, 0.024)	94 (85, 98)
		30	0.171 (0.154, 0.19)	0.006 (0.002, 0.023)	96 (87, 99)
		150	0.172 (0.155, 0.192)	0.017 (0.007, 0.044)	90 (76, 96)
		350	0.178 (0.16, 0.199)	0.015 (0.004, 0.057)	92 (69, 98)
		All	0.171 (0.163, 0.179)	0.012 (0.007, 0.019)	93 (89, 96)
	FTP Hot-Cycle	3	0.266 (0.25, 0.282)	0.001 (0, 0.003)	100 (99, 100)
		30	0.262 (0.244, 0.281)	0.002 (0.001, 0.005)	99 (98, 100)
		150	0.314 (0.283, 0.348)	0.025 (0.01, 0.067)	92 (79, 97)
		350	0.33 (0.307, 0.355)	0.028 (0.011, 0.075)	91 (77, 97)
		All	0.285 (0.26, 0.313)	0.006 (0.002, 0.024)	98 (91, 99)

Note: RE =  $(1 - 10^{\{\text{LOG}(\text{DOC}) - \text{LOG}(\text{EO})\}}) * 100$

**Table 3-2. EO and post DOC emissions of CO and emissions reduction efficiency for each combination of engine, test mode, and fuel sulfur level (with 95% confidence intervals)**

Engine	Test Mode	Fuel Sulfur (ppm)	CO Emissions		
			Engine-Out (g/bhp-hr)	Post DOC (g/bhp-hr)	Reduction Efficiency (95% Confidence Interval)
Navistar	NAV-9	3	0.834 (0.788, 0.882)	0.083 (0.006, 1.126)	90 (-35, 99)
		30	0.764 (0.722, 0.809)	0.043 (0.003, 0.58)	94 (24, 100)
		150	0.83 (0.792, 0.869)	0.043 (0.003, 0.577)	95 (30, 100)
		350	0.789 (0.754, 0.826)	0.004 (0, 0.06)	99 (92, 100)
		All	0.805 (0.779, 0.831)	0.029 (0.008, 0.105)	96 (87, 99)
	FTP75	3	2.266 (2.158, 2.38)	0.187 (0.074, 0.474)	92 (79, 97)
		30	1.878 (1.788, 1.972)	0.201 (0.079, 0.509)	89 (73, 96)
		150	2.058 (1.977, 2.142)	0.255 (0.1, 0.645)	88 (69, 95)
		350	2.078 (2.008, 2.151)	0.175 (0.069, 0.445)	92 (79, 97)
		All	2.067 (1.98, 2.159)	0.202 (0.146, 0.28)	90 (86, 93)
Cummins	OICA Weighted	3	0.254 (0.231, 0.28)	0.055 (0.04, 0.075)	78 (72, 83)
		30	0.237 (0.215, 0.261)	0.038 (0.024, 0.059)	84 (76, 89)
		150	0.258 (0.234, 0.284)	0.043 (0.032, 0.059)	83 (78, 87)
		350	0.27 (0.245, 0.298)	0.055 (0.035, 0.086)	80 (70, 86)
		All	0.255 (0.242, 0.268)	0.048 (0.04, 0.057)	81 (77, 84)
	FTP Hot	3	0.91 (0.835, 0.993)	0.497 (0.461, 0.537)	45 (40, 50)
		30	1.038 (0.934, 1.155)	0.613 (0.568, 0.662)	41 (34, 47)
		150	0.968 (0.833, 1.125)	0.534 (0.495, 0.577)	45 (36, 52)
		350	1.016 (0.914, 1.13)	0.567 (0.526, 0.613)	44 (38, 50)
		All	0.974 (0.917, 1.036)	0.552 (0.513, 0.593)	43 (38, 48)

Note: RE = (1-10<sup>[(LOG(DOC)-LOG(EO))]</sup>)\*100

With the Navistar engine, the DOC was 90-100% effective in both steady-state and transient HC emissions reduction. No sulfur effect was observed in either EO or post-catalyst HC emissions from this engine.

With the Cummins engine, there is a statistically significant increase in FTP HC emissions (both EO and post catalyst) with the high sulfur fuels (150- and 350-ppm). HC reduction efficiency over the FTP-hot cycle also declines from nearly 100% with 3-ppm sulfur fuel to approximately 91% with 350-ppm sulfur fuel.

CO reduction efficiency varied by test cycle and by engine. In general, the LT DOCs were more effective at CO reduction. They were 90-99% effective over the NAV-9 weighted 4-mode cycle and 88-92% over the FTP-75 mimicry. The HT catalysts on the Cummins engine were less effective, especially during the transient tests. CO reduction efficiency was 78-84% during the OICA-13 weighted 4-mode cycle but only 41-45% over the FTP hot-cycle. There is no statistical evidence that sulfur affects CO emissions or the CO reduction efficiency of the DOC under any operating mode evaluated here.

### 3.2 Aging Effects

Following the initial evaluation, each fresh catalyst was aged on-engine for 250 hours, with periodic catalyst evaluations conducted at 50, 150, and 250 hours to gauge any deviations from their performance. The aging sequences were conducted with each of the four test fuels. The experimental design allowed thermal degradation and sulfur effects to be decoupled. Details of the catalyst aging procedure were covered in 2.3.7. The results of the aged catalyst evaluations are presented here.

Several statistical regression models were fit to the data to determine how aging affects catalyst performance. In some cases (combinations of engine, test mode, and fuel), aging affected emissions. However, there was no evidence of change in catalyst emissions beyond the effect that was observed at 50 hours. For this reason, all data collected during catalyst evaluations at 50, 150, and 250 hours were combined for comparison with the performance with fresh catalysts.

### 3.2.1 Particulate Matter

Figures 3-7 and 3-8 and Table 3-3 compare fresh and aged catalyst emissions with their corresponding EO results for the LT catalysts on the Navistar engine. The figures show the estimated engine-out, fresh catalyst, and aged catalyst PM emissions, with 95% confidence intervals, for tests conducted with 3-, 30-, 150-, and 350-ppm sulfur fuel. Table 3-3 displays estimated EO and post catalyst (fresh and aged) PM, SO<sub>4</sub>, and SOF emissions and reduction efficiencies for each combination of test cycle and fuel tested.

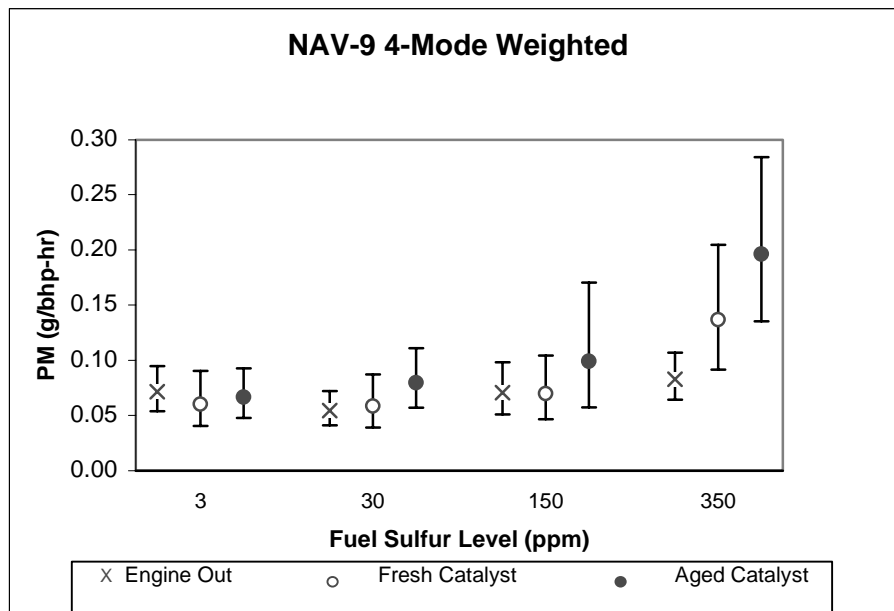


Figure 3-7. EO and fresh and aged DOC emissions of PM under LT (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)

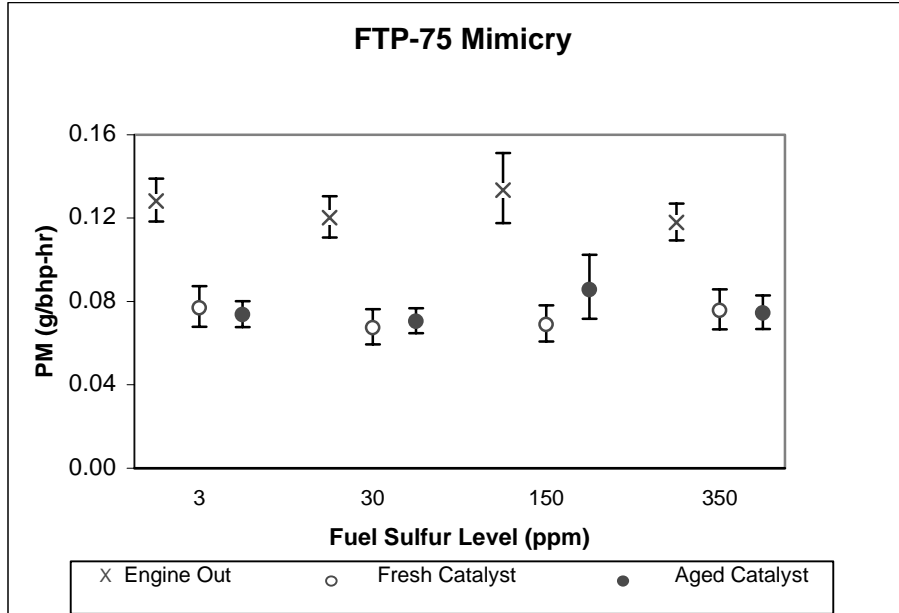


Figure 3-8. EO and fresh and aged DOC emissions of PM under LT (Navistar) applications using the FTP-75 mimicry test cycle (with 95% confidence intervals)

Table 3-3. EO and post-DOC (fresh and aged) PM, SO<sub>4</sub>, and SOF emissions and reduction efficiencies under LT (Navistar) applications for each combination of test mode and fuel sulfur level.

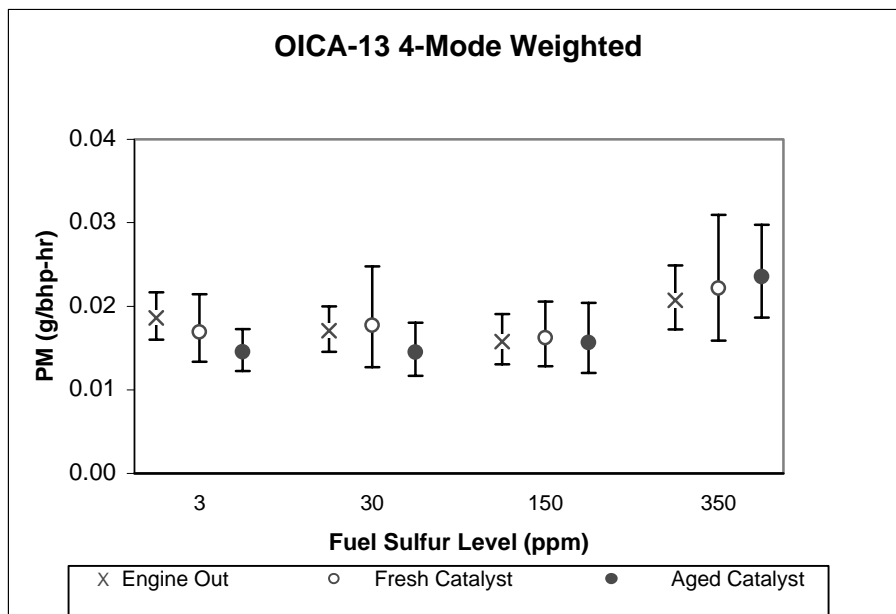
Test Mode	Fuel Sulfur (ppm)	Fresh/ Aged	PM			SO <sub>4</sub>			SOF		
			Engine-Out (g/bhp-hr)	Post-DOC (g/bhp-hr)	Reduction Efficiency (%)	Engine-Out (g/bhp-hr)	Post-DOC (g/bhp-hr)	Reduction Efficiency (%)	Engine-Out (g/bhp-hr)	Post-DOC (g/bhp-hr)	Reduction Efficiency (%)
NAV-9 4 Mode Weighted	3	F	0.0715	0.0604	16	0.0002	0.0005	-164	0.0132	0.0065	51
		A		0.0666	7		0.0017	-879*		0.0020	85*
	30	F	0.0544	0.0584	-7	0.0009	0.0012	-30	0.0066	0.0050	25
		A		0.0797	-46*		0.0104	-1034*		0.0015	77
	150	F	0.0707	0.0699	1	0.0013	0.0074	-472	0.0100	0.0147	-47
		A		0.0990	-40		0.0187	-1348*		0.0043	57
	350	F	0.0829	0.1369	-65*	0.0039	0.0417	-958*	0.0145	0.0178	-23
		A		0.1963	-137*		0.0874	-2114*		0.0141	3
FTP-75 Mimicry	3	F	0.1282	0.0770	40*	0.0007	0.0007	-3	0.0391	0.0124	68*
		A		0.0736	43*		0.0006	16		0.0068	83*
	30	F	0.1202	0.0673	44*	0.0011	0.0006	49*	0.0365	0.0129	65*
		A		0.0705	41*		0.0003	74*		0.0053	85*
	150	F	0.1334	0.0689	48*	0.0015	0.0006	58*	0.0556	0.0074	87*
		A		0.0857	36*		0.0007	52*		0.0121	78*
	350	F	0.1178	0.0756	36*	0.0021	0.0012	43	0.0407	0.0068	83*
		A		0.0744	37*		0.0019	10		0.0056	86*

\*Different from 0% at 0.05 level of statistical significance.  
 Note: RE = (1-10<sup>LOG(DOC)-LOG(EO)</sup>)\*100

In the steady-state tests, post-catalyst PM emissions from the catalyst aged with 350-ppm fuel exceeded those measured when the catalyst was fresh (0.20 vs. 0.14 g/bhp hr). A much smaller aging effect on total PM was observed with the lower sulfur fuels. However, post-catalyst emissions of sulfate were significantly higher than EO emissions with all fuels when catalysts were aged. During transient evaluations, aged catalyst PM emissions did not differ from those measured when the catalysts were fresh. The SOF reduction efficiency observed with the fresh catalysts were maintained following the aging period.

The results from the Cummins engine are presented in Figures 3-9 and 3-10 and Table 3-4. With the Cummins engine there appears to be an increase in EO and post-catalyst PM emissions under steady-state evaluation when using the 350-ppm sulfur fuel. Although the results are similar to the Navistar engine results, the estimated effects with the Cummins engine are not statistically significant. An aging effect is more apparent under the transient evaluation conditions. PM reduction efficiency with the aged catalysts is greater than observed with the fresh catalysts. This improvement in performance was observed with catalysts aged with 30-, 150-, and 350-ppm sulfur fuel though the level of sulfur in the fuel does not appear to affect the improvement. The performance enhancement with aging is a result of improved SOF suppression efficiency, which ranged from 25-67% with fresh catalysts and improved to 39-91% after aging.

The results of these aging experiments illustrate sharp differences in the response of these two types of catalyst formulation. The LT (high precious metal) catalysts used with the Navistar engine lost effectiveness after the 250-hour aging sequence, especially under steady-state conditions. To some extent, the HT (low precious metal) catalysts used with the Cummins engine improved in performance following aging. This disparity in aged performance may illustrate a difference in break-in response of these two DOC formulations.



**Figure 3-9. EO and fresh and aged DOC emissions of PM under HT (Cummins) applications using the OICA-13 weighted 4-mode test cycle (with 95% confidence intervals)**

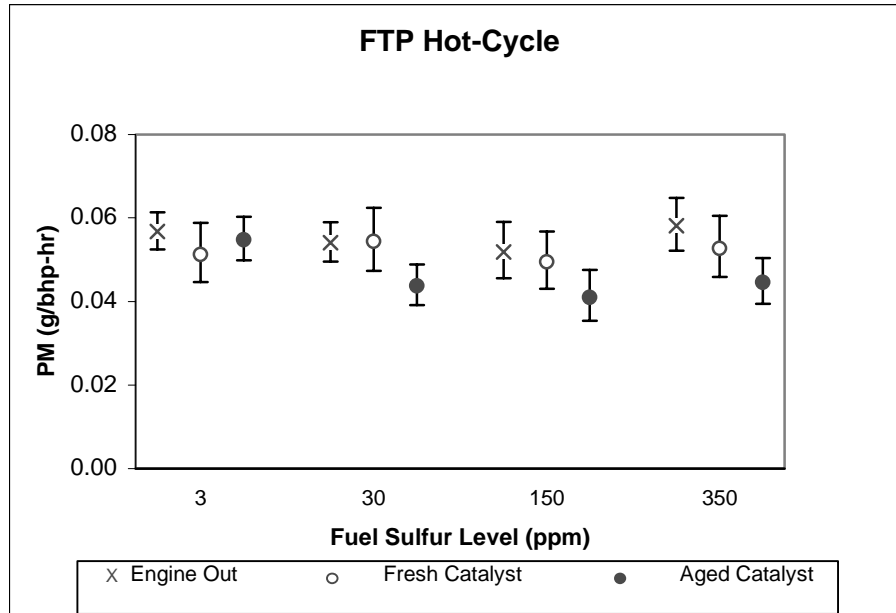


Figure 3-10. EO and fresh and aged DOC emissions of PM under HT (Cummins) applications using the FTP hot test cycle (with 95% confidence intervals)

Table 3-4. EO and Post-DOC (fresh and aged) PM, SO<sub>4</sub>, and SOF emissions and reduction efficiencies under HT (Cummins) applications for each combination of test mode and fuel sulfur level

Test Mode	Fuel Sulfur (ppm)	Fresh/ Aged	PM			SO <sub>4</sub>			SOF		
			Engine-Out (g/bhp-hr)	Post-DOC (g/bhp-hr)	Reduction Efficiency (%)	Engine-Out (g/bhp-hr)	Post-DOC (g/bhp-hr)	Reduction Efficiency (%)	Engine-Out (g/bhp-hr)	Post-DOC (g/bhp-hr)	Reduction Efficiency (%)
OICA-13 4-Mode Weighted	3	F	0.0186	0.0169	9	0.0003	0.0008	-230	0.0034	0.0023	33
		A		0.0145	22*		0.0002	40		0.0012	64
	30	F	0.0171	0.0177	-4	0.0007	0.0010	-51	0.0021	0.0138	-542
		A		0.0145	15		0.0012	-75		0.0007	65
	150	F	0.0158	0.0162	-3	0.0015	0.0028	-87	0.0027	0.0020	24
		A		0.0157	1		0.0023	-55		0.0051	-93
	350	F	0.0207	0.0222	-7	0.0046	0.0049	-6	0.0025	0.0028	-13
		A		0.0235	-14		0.0101	-119		0.0012	52
FTP Hot-Cycle	3	F	0.0567	0.0512	10	0.0007	0.0013	-78	0.0040	0.0024	39
		A		0.0548	3		0.0012	-57		0.0024	39
	30	F	0.0540	0.0543	-1	0.0007	0.0005	22	0.0071	0.0053	25
		A		0.0437	19*		0.0009	-33		0.0008	88*
	150	F	0.0519	0.0494	5	0.0034	0.0005	86*	0.0071	0.0036	50
		A		0.0410	21*		0.0006	83*		0.0022	69
	350	F	0.0581	0.0527	9	0.0033	0.0015	56	0.0071	0.0023	67
		A		0.0446	23*		0.0023	32		0.0006	91*

\*Different from 0% at 0.05 level of statistical significance.  
 Note: RE = {1-10<sup>^[LOG(DOC)-LOG(EO)]</sup>}\*100



### 3.2.2 Gaseous Emissions

Figures 3-11 and 3-12 summarize results of fresh and aged catalyst hydrocarbon reduction efficiency for the Navistar engine. Under steady-state evaluation, the aged catalysts appear less efficient in HC control, although the effect is not significant. Under transient conditions, the fresh catalyst performance was maintained after aging with all of the fuels except the one containing 350-ppm sulfur. This catalyst declined in performance from 100% to 87% HC reduction efficiency after aging.

Hydrocarbon reduction efficiency of the HT catalysts exhibited similar performance decline upon aging (Figures 3-13 and 3-14). The average steady-state performance decline was 6 percentage points, independent of fuel sulfur level. The average transient performance decline after aging was 7 percentage points, also independent of fuel sulfur level. Carbon monoxide reduction efficiencies for the fresh and aged catalysts on the Navistar engine are plotted in Figures 3-15 and 3-16. Catalyst aging did not have a significant effect on post-DOC CO emissions from the Navistar engine over either evaluation cycle. However, the HT catalysts used with the Cummins engine did suffer performance deterioration with respect to CO reduction efficiency (Figures 3-17 and 3-18). Although the effect was independent of sulfur level, CO reduction performance dropped 10 percentage points on average over both the steady-state and transient cycles.

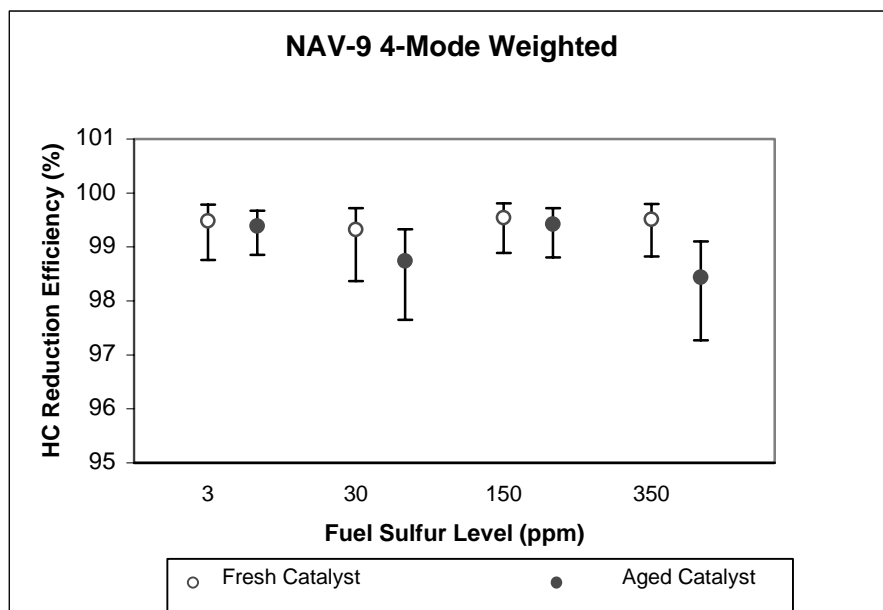
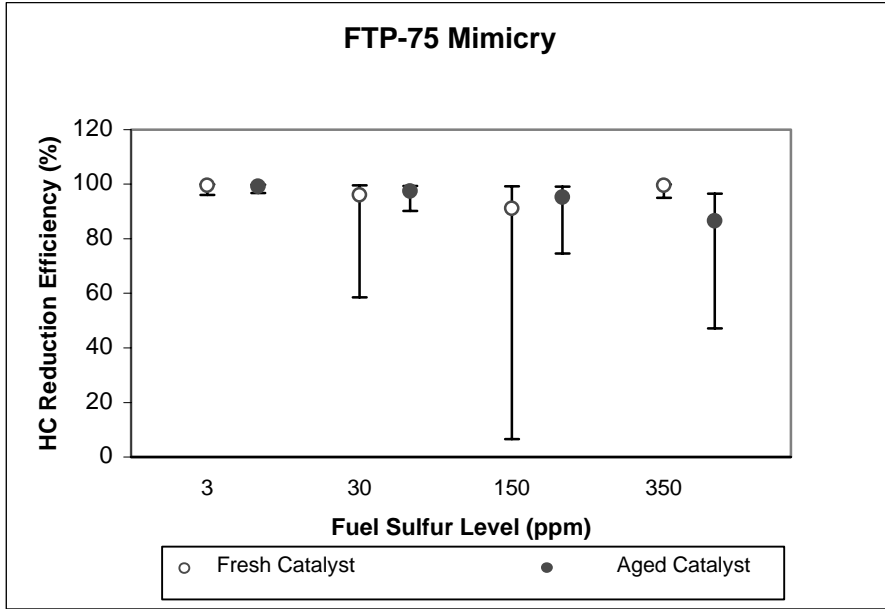
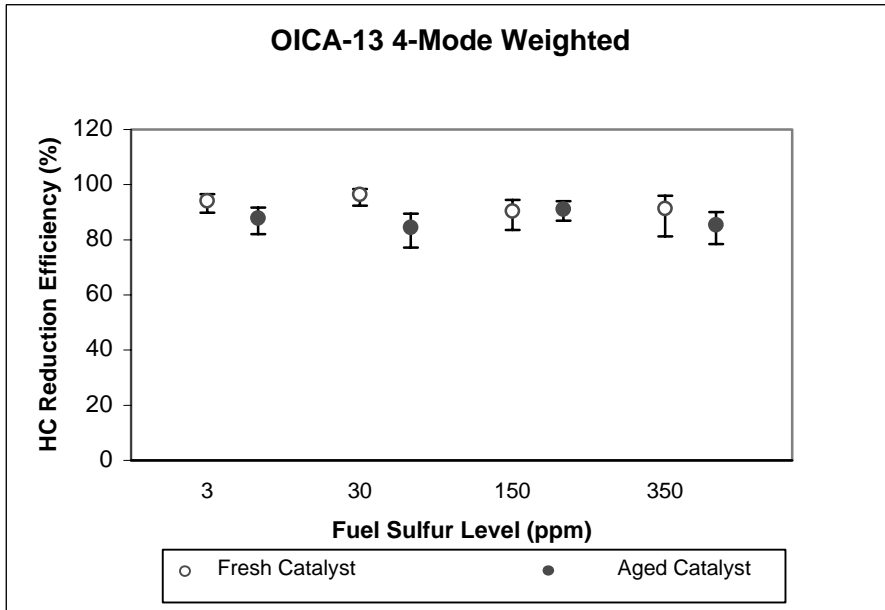


Figure 3-11. HC reduction efficiencies with fresh and aged DOC under LT (Navistar) applications using the Nav-9 weighted 4-mode cycle (with 95% confidence intervals)



**Figure 3-12. HC reduction efficiencies with fresh and aged DOC under LT (Navistar) applications using the FTP-75 mimicry test cycle (with 95% confidence intervals)**



**Figure 3-13. HC reduction efficiencies with fresh and aged DOC under HT (Cummins) applications using the OICA-13 weighted 4-mode cycle (with 95% confidence intervals)**

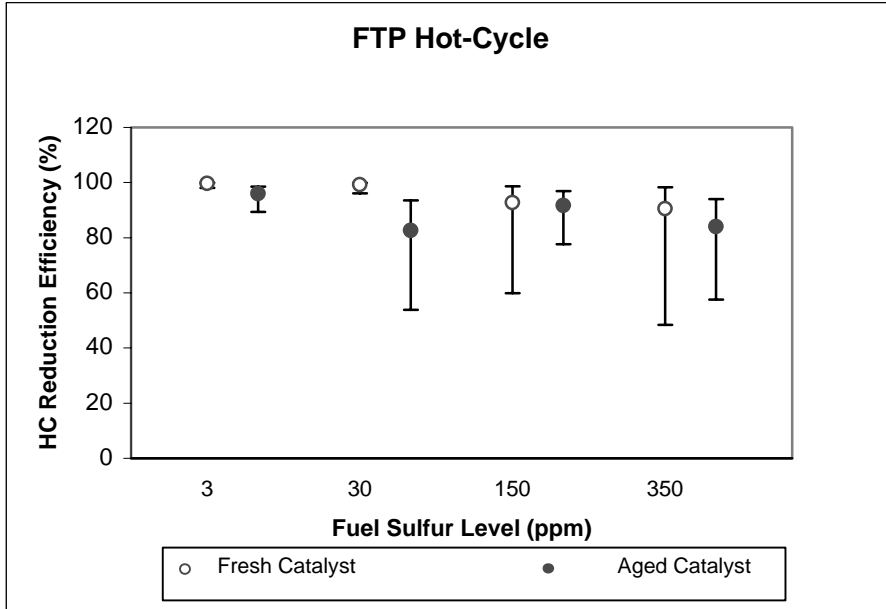


Figure 3-14. HC reduction efficiencies with fresh and aged DOC under HT (Cummins) applications using the FTP hot test cycle (with 95% confidence intervals)

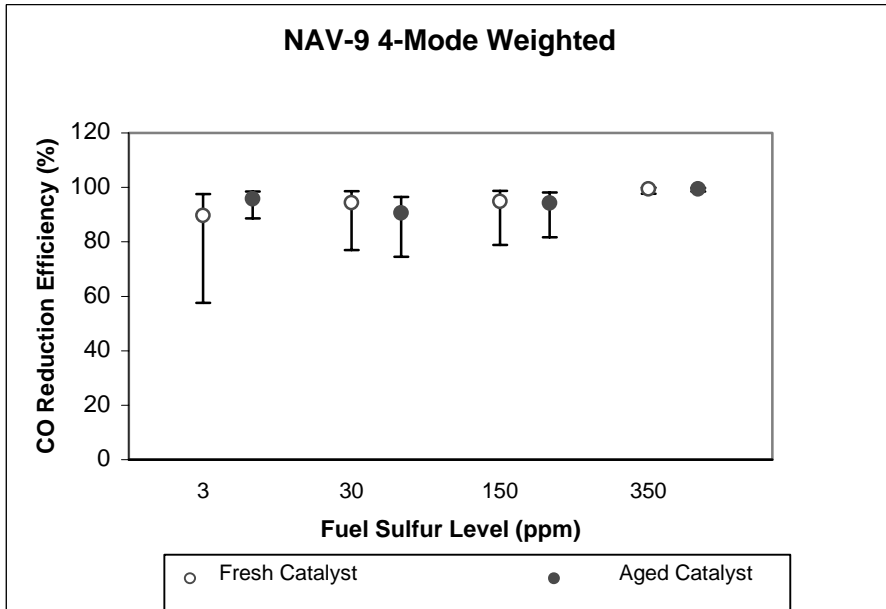
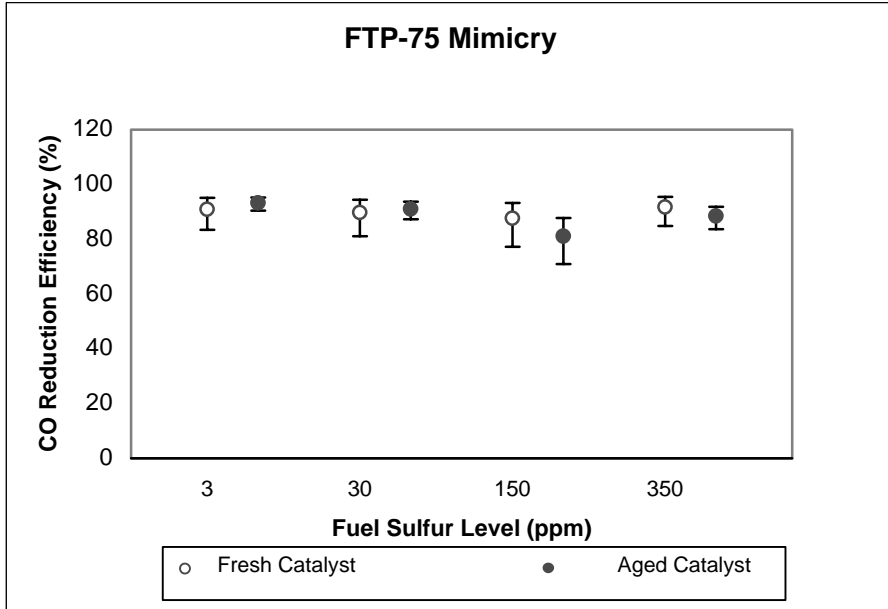
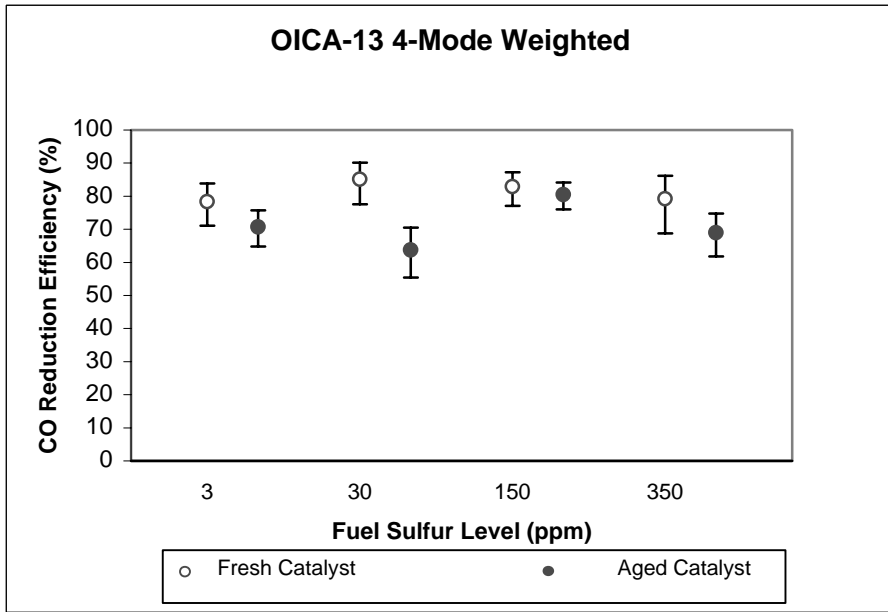


Figure 3-15. CO reduction efficiencies with fresh and aged DOC under LT (Navistar) applications using the Nav-9 weighted 4-mode cycle (with 95% confidence intervals)



**Figure 3-16. CO reduction efficiencies with fresh and aged DOC under LT (Navistar) applications using the FTP-75 mimicry test cycle (with 95% confidence intervals)**



**Figure 3-17. CO reduction efficiencies with fresh and aged DOC under HT (Cummins) applications using the OICA-13 weighted 4-mode cycle (with 95% confidence intervals)**

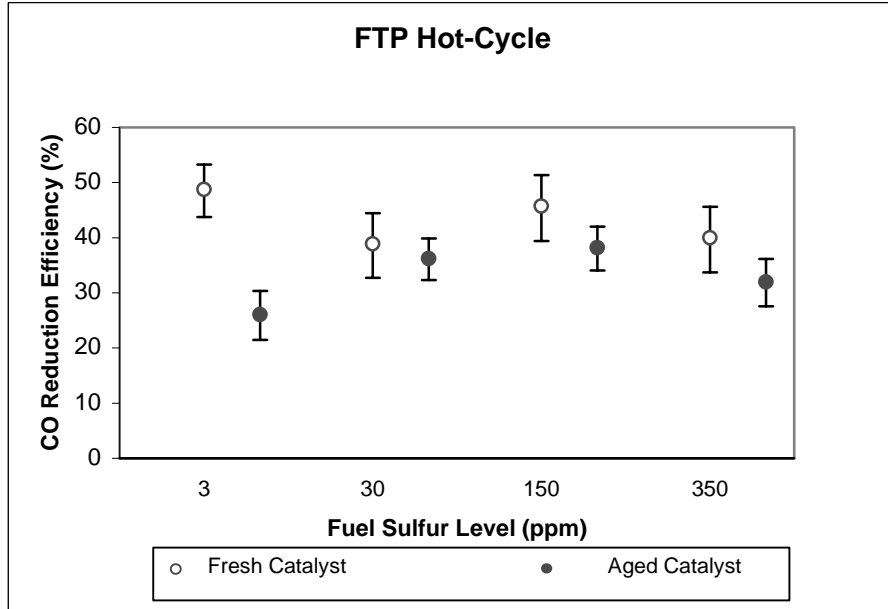


Figure 3-18. CO reduction efficiencies with fresh and aged DOC under HT (Cummins) applications using the FTP hot test cycle (with 95% confidence intervals)

### **3.3 Recovery and Thermal Aging**

Special experiments were conducted to compare the post-catalyst emissions effects of fuel sulfur level with the effects of thermal aging of catalysts. Additional experiments were performed to evaluate the catalyst's ability to recover from extended exposures to high sulfur fuel. The thermal aging experiments consisted of running 4-mode emissions tests with 30-, 150-, and 350-ppm sulfur fuel using the catalysts aged for 250 hours with 3-ppm sulfur fuel. By comparing these results with the emissions from the catalysts aged with corresponding high sulfur fuels, it is possible to determine whether the thermal aging and fuel sulfur effects are additive or, alternatively, there is a cumulative poisoning effect when catalysts are aged with sulfur-containing fuel. The recovery experiments consisted of performing additional tests on the catalyst aged for 250 hours with 350-ppm sulfur fuel. The additional tests were performed with 30-ppm sulfur fuel after zero and 50 hours of additional aging with 30-ppm sulfur fuel. Results are compared with the 250-hour results from the 30-ppm and 350-ppm sulfur aging experiments to determine whether recovery occurred.

As described earlier, very little sulfur related performance deterioration was observed with the DOC. For this reason, the recovery experiments have been omitted.

## 4 Lean-NO<sub>x</sub> Experiment Results and Discussion

The DECSE lean-NO<sub>x</sub> program was aimed at evaluating the effect of fuel sulfur level on performance of both low-temperature and high-temperature lean-NO<sub>x</sub> catalysts. The DECSE diesel fuels, with four different sulfur levels (3-, 30-, 150-, and 350-ppm), were used in this experiment. The Navistar T444E engine was used for aging and evaluating the low-temperature lean-NO<sub>x</sub> catalyst. Likewise, the Cummins ISM370 engine was employed for aging and evaluating the high-temperature lean-NO<sub>x</sub> catalyst. The Nav-9 4-mode cycle and the OICA-13 4-mode cycle were initially defined based on operating temperature windows for both low- and high-temperature lean-NO<sub>x</sub> catalysts. Through a preliminary optimization process, the secondary fueling rates were defined for all steady state test modes. To reduce emissions and temperature stabilization time of a given mode for a test cycle, the mode running sequence was designed to run from the lowest temperature mode to the highest temperature mode, and the given mode time was kept at 20 minutes.

### 4.1 Evaluation of Fresh Lean-NO<sub>x</sub> Catalysts

Prior to testing, all lean-NO<sub>x</sub> catalysts were degreased for 10 hours with the specified aging cycles (refer to Table 4-5 & 4-6). Then, all catalysts were evaluated as fresh catalysts with the DECSE diesel fuels (3-, 30-, 150-, and 350-ppm S). The low-temperature (LT) lean-NO<sub>x</sub> catalysts were evaluated with the Nav-9 4-mode cycle, and the high-temperature (HT) lean-NO<sub>x</sub> catalysts were evaluated with OICA-13 4-mode cycle.

#### 4.1.1 NO<sub>x</sub> Reduction Efficiency

Tables 4-1 and 4-2 summarize estimated engine-out and post-catalyst NO<sub>x</sub> emissions and reduction efficiencies, with 95% confidence intervals, for all test modes conducted with 3-, 30-, 150-, and 350-ppm sulfur fuel. Results demonstrate that NO<sub>x</sub> reduction efficiencies vary considerably across the four test modes. When averaged across the four modes, NO<sub>x</sub> reduction efficiency is approximately 15% for both the LT and HT applications. Under LT applications, there is some statistical evidence that post-catalyst NO<sub>x</sub> emissions are slightly higher with 3-ppm sulfur fuel than with higher sulfur fuels (11% NO<sub>x</sub> with 3-ppm sulfur fuel versus 14 to 19% with higher sulfur fuel). Otherwise, there are no significant effects of fuel sulfur level on NO<sub>x</sub> emissions or reduction efficiencies. Tables 4-1 and 4-2 also provide the estimated NO<sub>x</sub> emissions and reduction efficiencies averaged across all fuel sulfur levels.

**Table 4-1. Engine-out and post lean-NO<sub>x</sub> catalyst emissions of NO<sub>x</sub> and NO<sub>x</sub> reduction efficiency under low temperature (Navistar) applications for each combination of test mode and fuel sulfur level (with 95% confidence intervals)**

Test Mode	Fuel Sulfur (ppm)	NO <sub>x</sub>		
		Engine-Out (g/bhp-hr) (95% Confidence Interval)	Post-LNO <sub>x</sub> (g/bhp-hr) (95% Confidence Interval)	Reduction Efficiency (%) (95% Confidence Interval)
NAV-9 Mode 2	3	5.758 (5.427, 6.109)	5.129 (4.959, 5.305)	11 (5, 17)
	30	5.799 (5.466, 6.152)	4.841 (4.681, 5.007)	17 (11, 22)
	150	6.263 (5.968, 6.573)	5.04 (4.872, 5.213)	20 (15, 24)
	350	5.955 (5.613, 6.318)	5.106 (4.936, 5.281)	14 (8, 20)
	All	5.976 (5.807, 6.149)	5.028 (4.887, 5.173)	16 (12, 19)
NAV-9 Mode 3	3	5.333 (5.027, 5.658)	2.574 (2.489, 2.662)	52 (48, 55)
	30	5.383 (5.074, 5.711)	2.324 (2.247, 2.404)	57 (54, 60)
	150	5.657 (5.39, 5.937)	2.414 (2.334, 2.497)	57 (55, 60)
	350	5.284 (4.98, 5.606)	2.32 (2.243, 2.4)	56 (53, 59)
	All	5.439 (5.285, 5.597)	2.406 (2.338, 2.475)	56 (54, 57)
NAV-9 Mode 7	3	4.186 (3.946, 4.441)	3.078 (2.976, 3.184)	26 (21, 31)
	30	4.232 (3.989, 4.489)	2.882 (2.787, 2.981)	32 (27, 36)
	150	4.281 (4.079, 4.493)	2.875 (2.78, 2.974)	33 (29, 37)
	350	4.09 (3.855, 4.34)	2.74 (2.649, 2.834)	33 (28, 37)
	All	4.206 (4.087, 4.328)	2.891 (2.81, 2.975)	31 (28, 34)
NAV-9 Mode 9	3	3.046 (2.872, 3.232)	3.088 (2.986, 3.194)	-1 (-8, 5)
	30	3.091 (2.914, 3.28)	3.005 (2.906, 3.109)	3 (-4, 9)
	150	3.173 (3.023, 3.33)	2.921 (2.824, 3.021)	8 (3, 13)
	350	3.013 (2.84, 3.197)	2.984 (2.885, 3.087)	1 (-6, 7)
	All	3.091 (3.003, 3.181)	2.999 (2.915, 3.086)	3 (-1, 7)
NAV-9 4-Mode Weighted	3	3.485 (3.384, 3.589)	3.103 (3.038, 3.169)	11 (8, 14)
	30	3.529 (3.428, 3.634)	2.982 (2.92, 3.046)	16 (13, 18)
	150	3.641 (3.555, 3.729)	2.932 (2.871, 2.995)	19 (17, 22)
	350	3.453 (3.371, 3.536)	2.958 (2.897, 3.022)	14 (12, 17)
	All	3.53 (3.463, 3.598)	2.993 (2.932, 3.055)	15 (13, 17)



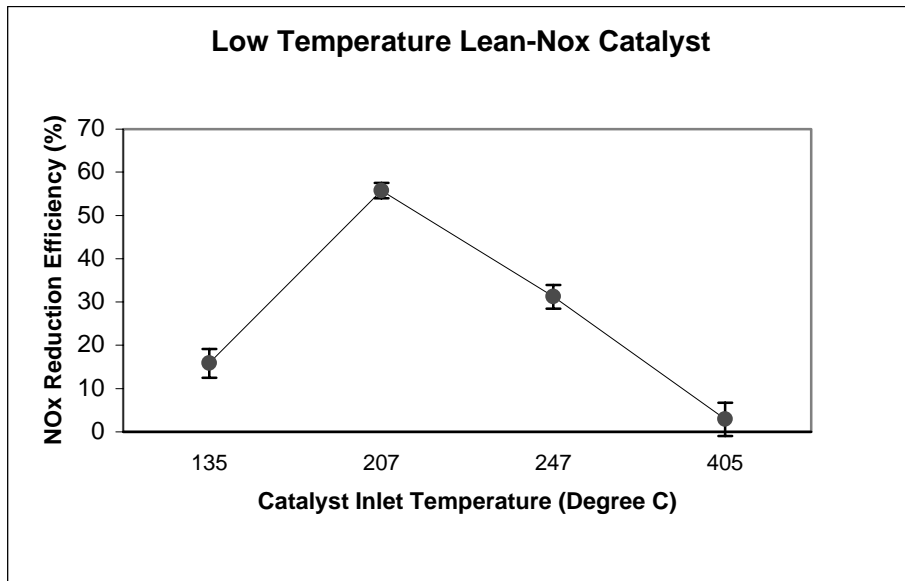
**Table 4-2. Engine-out and post lean-NO<sub>x</sub> catalyst emissions of NO<sub>x</sub> and NO<sub>x</sub> reduction efficiency under high temperature (Cummins) applications for each combination of test mode and fuel sulfur level (with 95% confidence intervals)**

Test Mode	Fuel Sulfur (ppm)	NO <sub>x</sub>		
		Engine-Out (g/bhp-hr) (95% Confidence Interval)	Post-LNO <sub>x</sub> (g/bhp-hr) (95% Confidence Interval)	Reduction Efficiency (%) (95% Confidence Interval)
OICA-13 Mode 11	3	6.712 (6.178, 7.292)	6.73 (6.305, 7.185)	0 (-11, 9)
	30	7.255 (6.678, 7.882)	6.801 (6.201, 7.46)	6 (-6, 17)
	150	6.663 (6.133, 7.239)	6.398 (5.993, 6.83)	4 (-6, 13)
	350	6.688 (6.155, 7.266)	6.514 (6.102, 6.954)	3 (-8, 12)
	All	6.825 (6.519, 7.146)	6.582 (6.335, 6.839)	4 (-2, 9)
OICA-13 Mode 3	3	6.477 (5.961, 7.037)	6.357 (5.955, 6.786)	2 (-9, 11)
	30	6.986 (6.43, 7.591)	6.599 (6.016, 7.238)	6 (-6, 16)
	150	6.305 (5.804, 6.851)	6.04 (5.657, 6.447)	4 (-6, 13)
	350	6.43 (5.918, 6.986)	6.386 (5.982, 6.817)	1 (-10, 10)
	All	6.544 (6.251, 6.852)	6.306 (6.07, 6.552)	4 (-2, 9)
OICA-13 Mode 10	3	6.175 (5.683, 6.709)	5.561 (5.209, 5.936)	10 (0, 19)
	30	6.938 (6.385, 7.538)	5.897 (5.376, 6.468)	15 (4, 24)
	150	6.199 (5.706, 6.735)	5.385 (5.044, 5.749)	13 (4, 21)
	350	6.391 (5.882, 6.944)	5.832 (5.463, 6.226)	9 (-1, 18)
	All	6.419 (6.131, 6.72)	5.632 (5.421, 5.852)	12 (7, 17)
OICA-13 Mode 2	3	6.125 (5.637, 6.654)	4.364 (4.088, 4.658)	29 (21, 36)
	30	6.992 (6.436, 7.597)	4.748 (4.329, 5.208)	32 (24, 40)
	150	6.146 (5.657, 6.677)	4.183 (3.918, 4.465)	32 (25, 38)
	350	6.249 (5.752, 6.79)	4.665 (4.37, 4.98)	25 (17, 33)
	All	6.368 (6.083, 6.667)	4.448 (4.281, 4.621)	30 (26, 34)
OICA-13 4- Mode Weighted	3	6.261 (5.609, 6.989)	5.425 (4.918, 5.985)	13 (2, 23)
	30	6.986 (6.259, 7.799)	5.74 (4.996, 6.595)	18 (5, 29)
	150	6.234 (5.584, 6.958)	5.205 (4.718, 5.742)	16 (6, 26)
	350	6.371 (5.708, 7.112)	5.625 (5.099, 6.205)	12 (1, 22)
	All	6.456 (6.114, 6.817)	5.461 (5.217, 5.716)	15 (10, 21)

Note: RE = {1-10^[LOG(LNO<sub>x</sub>)-LOG(EO)]}\*100

Figures 4-1 and 4-2 display the operating temperature windows for LT and HT lean-NO<sub>x</sub> catalysts, respectively. Each figure presents the NO<sub>x</sub> reduction efficiency, averaged across fuel sulfur levels, at selected catalyst inlet temperatures, along with 95% confidence intervals. These results were obtained with optimized secondary fuel strategies, which required a fuel penalty of less than 4%. For the LT lean-NO<sub>x</sub> catalyst (Figure 4-1), the operating window ranged between 135 and 335°C (>15% NO<sub>x</sub> reduction) with a peak NO<sub>x</sub> reduction (>50%) at 207°C. The HT lean-NO<sub>x</sub> catalyst (Figure 4-2) activates above 380°C and reaches 30% NO<sub>x</sub> reduction at 528°C. The operating temperature windows and peak NO<sub>x</sub> reductions are consistent with initial predictions for lean-NO<sub>x</sub> catalyst technologies.

After applying the weighting factors for both Nav-9 4-mode cycle and OICA-13 4-mode cycle, weighted-average NO<sub>x</sub> reduction efficiency is plotted against fuel sulfur level in Figure 4-3 for LT catalysts and Figure 4-4 for HT catalysts. Except for the slightly lower NO<sub>x</sub> reduction with 3-ppm sulfur fuel under LT applications, the sulfur effect on NO<sub>x</sub> reduction efficiency is not significant and the overall NO<sub>x</sub> reduction is below 20% under the weighted 4-mode test cycles.



**Figure 4-1. NO<sub>x</sub> reduction efficiency of fresh lean-NO<sub>x</sub> catalyst under LT (Navistar) applications at selected catalyst inlet temperatures (with 95% confidence intervals)**

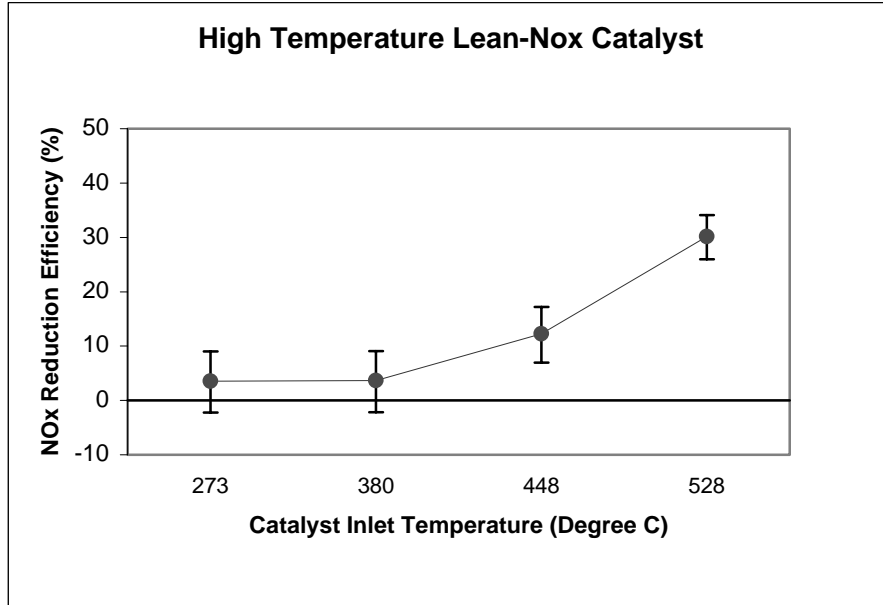


Figure 4-2. NO<sub>x</sub> reduction efficiency of fresh lean-NO<sub>x</sub> catalyst under HT (Cummins) applications at selected catalyst inlet temperatures (with 95% confidence intervals)

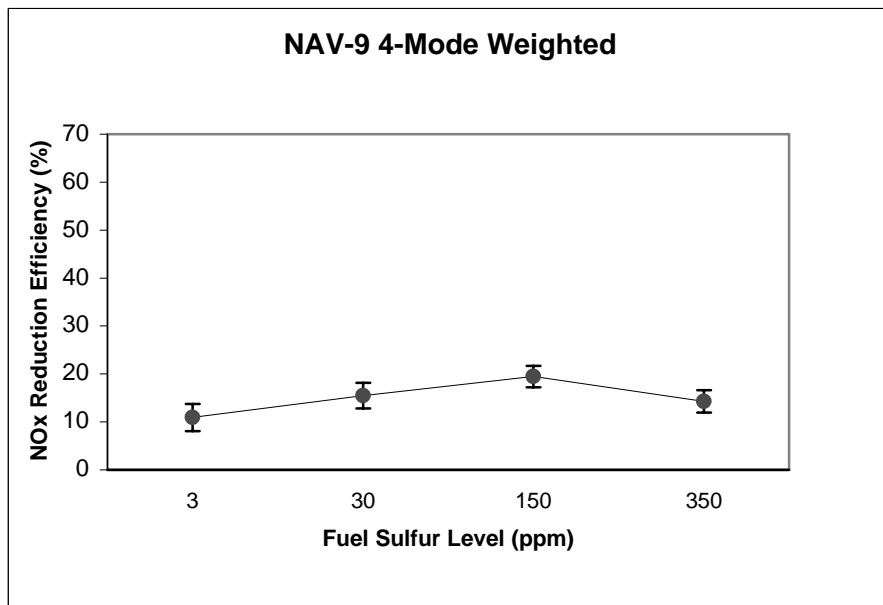
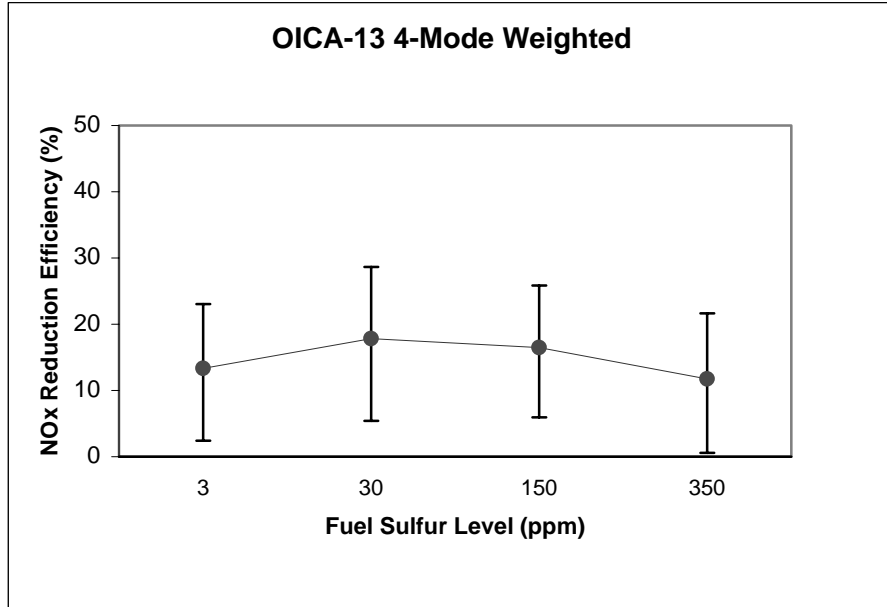


Figure 4-3. NO<sub>x</sub> reduction efficiency of fresh lean-NO<sub>x</sub> catalyst under LT (Navistar) applications using Nav-9 weighted 4-mode test cycle versus fuel sulfur levels (with 95% confidence intervals)



**Figure 4-4. NO<sub>x</sub> reduction efficiency of fresh lean-NO<sub>x</sub> catalyst under HT (Cummins) applications using OICA-13 weighted 4-mode test cycle versus fuel sulfur levels (with 95% confidence intervals)**

### 4.1.2 Particulate Matter Emissions

If temperature conditions are favorable, a lean-NO<sub>x</sub> catalyst has potential to oxidize SO<sub>2</sub> to SO<sub>3</sub> and make sulfate with moisture in diesel exhaust. The sulfate associated with water molecules contributes to the PM emissions. To examine sulfate formation and PM emission with a lean-NO<sub>x</sub> catalyst, both engine-out and catalyst-out PM samples were taken at selected steady-state test modes as well as at the 4-mode composite test cycles consisting of selected steady-state test modes.

In addition to measuring total PM, the collected PM samples were analyzed for three components: Hydrated Sulfate, SOF (soluble organic fraction) and Other (residual carbon and other material). Engine-out and post catalyst PM emissions at four fuel sulfur levels are depicted in Figures 4-5 and 4-6 for the LT catalysts and Figures 4-7 and 4-8 for the HT catalysts. The height of each bar represents the estimated total PM emissions, which was measured at 50% relative humidity. Because SO<sub>4</sub> emissions are measured under dry conditions, the contribution of SO<sub>4</sub> to total PM is calculated by multiplying the sulfate mass by a factor of 2.33, representing hydrated SO<sub>4</sub> with seven molecules of water per molecule of sulfuric acid (Reference 1995 SAE Handbook). The contributions of “other” PM components (e.g., ash) are calculated by taking differences. Also shown are 95% confidence intervals on the total PM emissions.

With regard to the LT lean-NO<sub>x</sub> catalyst (Figure 4-5), increases in EO and post-catalyst SO<sub>4</sub> emissions are not statistically significant under Nav-9 4-mode weighted evaluation, although trends are apparent. However, as shown in Figure 4-6, the high load mode (Mode 9: ~405°C) produces a statistically significant increase in PM emissions with 350-ppm S fuel, due to a 13-fold increase in SO<sub>4</sub> (from 0.0026 g/bhp-hr EO to 0.0354 g/bhp-hr post catalyst). This indicates that the given LT lean-NO<sub>x</sub> catalyst is very active in generating SO<sub>4</sub> at high exhaust temperatures. Considering a potential light-duty diesel application, it could make SO<sub>4</sub> over the US06 transient cycle.

Likewise, for HT lean-NO<sub>x</sub> catalysts (Figure 4-7), there are apparent but not statistically significant increasing trends in EO and post-catalyst SO<sub>4</sub> emissions over the OICA-13 4-mode composite test cycle. At a HT mode (Figure 4-8) near peak torque (Mode 2: ~528°C), the findings are similar to those at mode 9 of the NAV-9 evaluation; but the increase in PM emissions is not statistically significant. The estimated post-catalyst PM emissions with 350-ppm sulfur fuel are approximately 30% higher than EO emissions, mostly due to a 157% increase in sulfate (from 0.002 to 0.0051 g/bhp-hr). The mechanism of SO<sub>4</sub> formation with a HT lean-NO<sub>x</sub> catalyst needs to be further investigated. However, such an effort is outside the scope of this project.

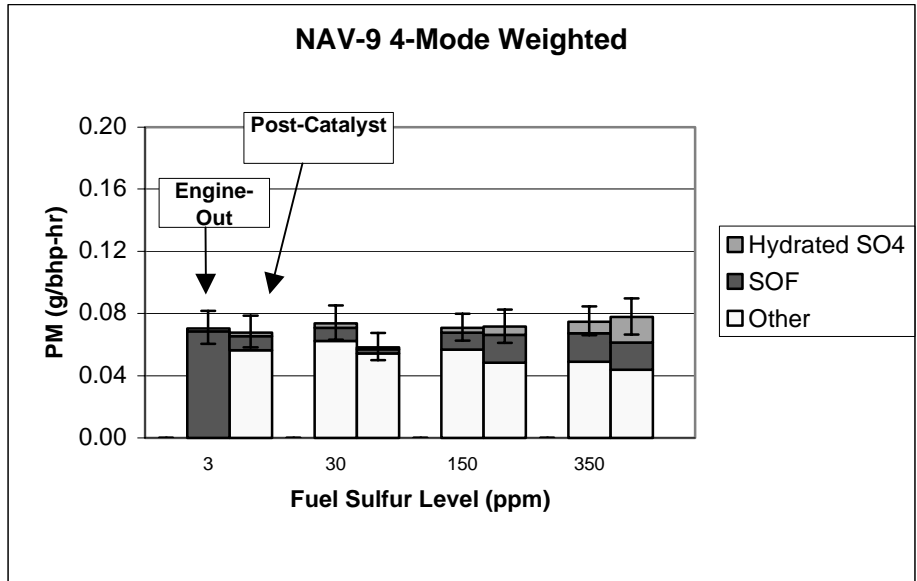


Figure 4-5. EO and post lean-NO<sub>x</sub> catalyst emissions of PM and components under LT (Navistar) applications using a 4-mode composite test from Nav-9 cycle (with 95% confidence intervals on estimated PM)

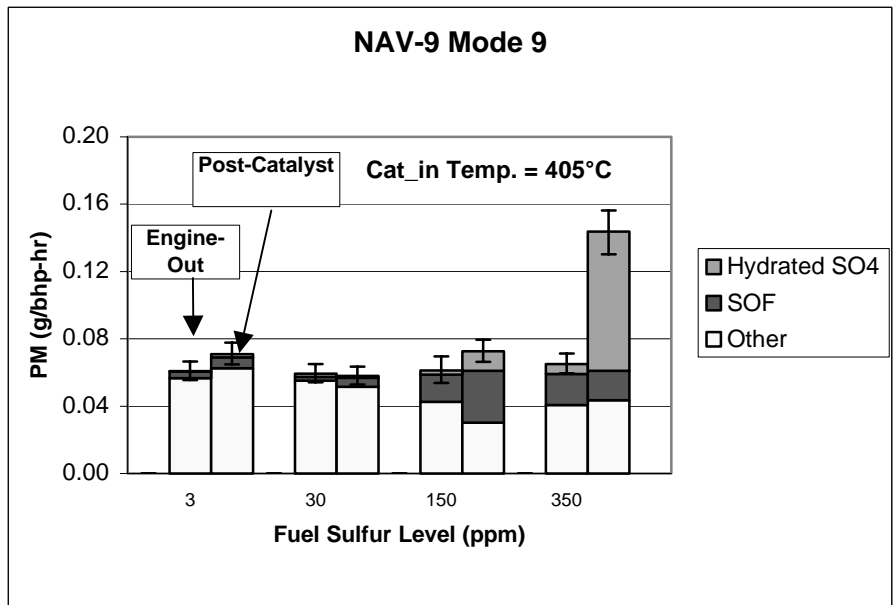


Figure 4-6. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of PM and components under LT (Navistar) applications using a Nav-9 mode 9 test (with 95% confidence intervals on estimated PM)

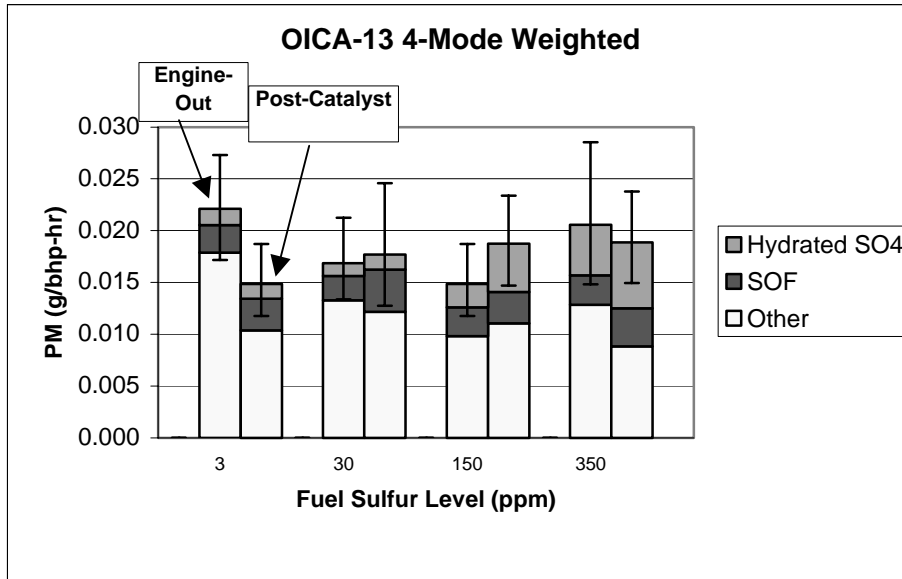


Figure 4-7. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of PM and components under HT (Cummins) applications using a 4-mode composite test from OICA-13 cycle (with 95% confidence intervals on estimated PM)

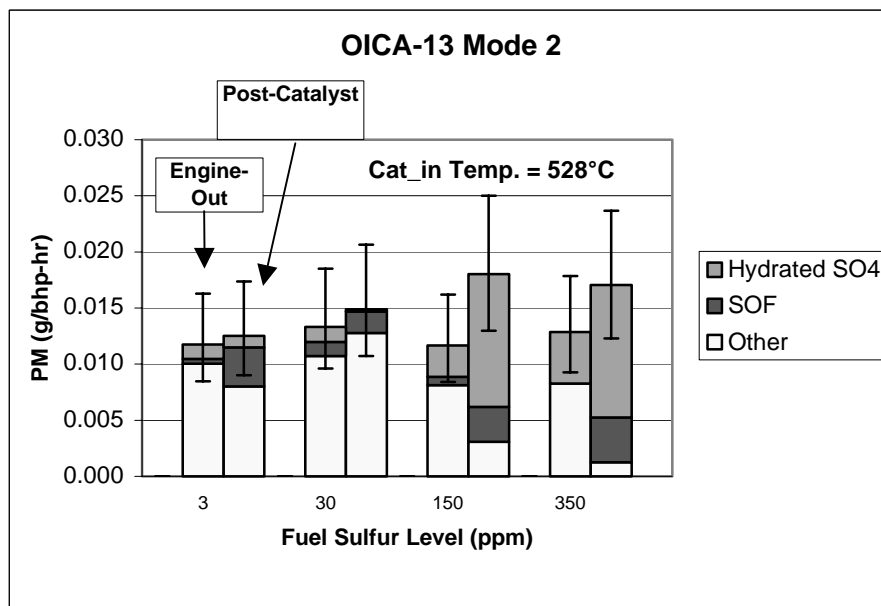


Figure 4-8. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of PM and components under HT (Cummins) applications using an OICA-13 mode 2 test (with 95% confidence intervals on estimated PM)

### 4.1.3 Other Gaseous Emissions

The effects of HT and LT lean-NO<sub>x</sub> catalysts on other gaseous emissions and FEP were also investigated. Results for HC and CO are presented here.

#### 4.1.3.1 Hydrocarbon Emissions

Generally speaking, HC emissions are relatively low with diesel engines. However, with active lean-NO<sub>x</sub> catalysts, additional HC, usually in the form of diesel fuel, are added into the exhaust to act as a reductant to facilitate NO<sub>x</sub> conversion. In this case, the HC slippage has to be monitored and controlled effectively both for emissions control and for FEP reduction. In principle, the fuel sulfur level could have an effect on HC break-through or slippage.

Figures 4-9 and 4-10 show EO and post-catalyst emissions of HC at selected catalyst inlet temperatures by fuel sulfur level for LT and HT catalysts, respectively. Operating temperatures and fuel sulfur affect HC slippage with the given LT lean-NO<sub>x</sub> catalyst (Figure 4-9). When 150- and 350-ppm S fuels were used, very high HC slippage was observed at mode 2 (207°C) of the Nav-9 cycle. Mode 2 also produced the highest NO<sub>x</sub> reduction (>50%). Furthermore, at this operating temperature, higher sulfur fuels produced the greatest HC slippage through the LT lean-NO<sub>x</sub> catalyst.

For the HT lean-NO<sub>x</sub> catalyst (Figure 4-10), supplemental fuel was **not** provided at Mode 11 (273°C) and Mode 3 (380°C) of the OICA-13 cycle due to low NO<sub>x</sub> reduction efficiencies. In other words, the catalyst was running passively at these two modes and oxidizing residual HC in the diesel exhaust. However, when secondary fuel is injected in the exhaust, the HT lean-NO<sub>x</sub> catalyst has poor HC oxidation capability. Both at Mode 10 (448°C) and Mode 2 (528°C) of the OICA-13 cycle, an increased amount of HC slippage was detected. There are no consistent patterns concerning the effect of fuel sulfur level on catalyst-out HC emission or HC slippage through the HT catalyst. For reference, Table 4-3 lists the estimated EO and post-catalyst HC emissions (with 95% confidence intervals) by fuel sulfur level under LT and HT applications using the weighted 4-mode test cycles.



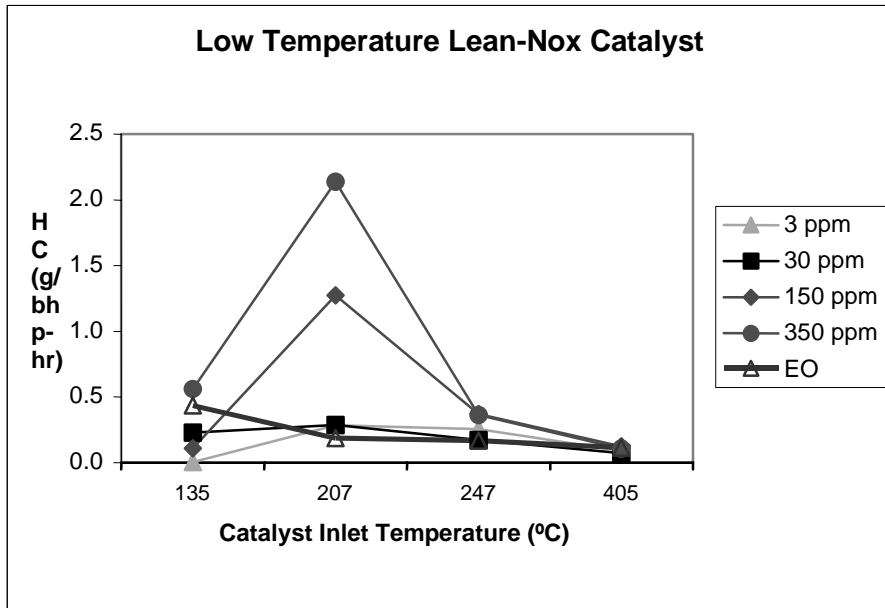


Figure 4-9. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of HC under LT (Navistar) applications at selected catalyst inlet temperatures – by fuel sulfur level

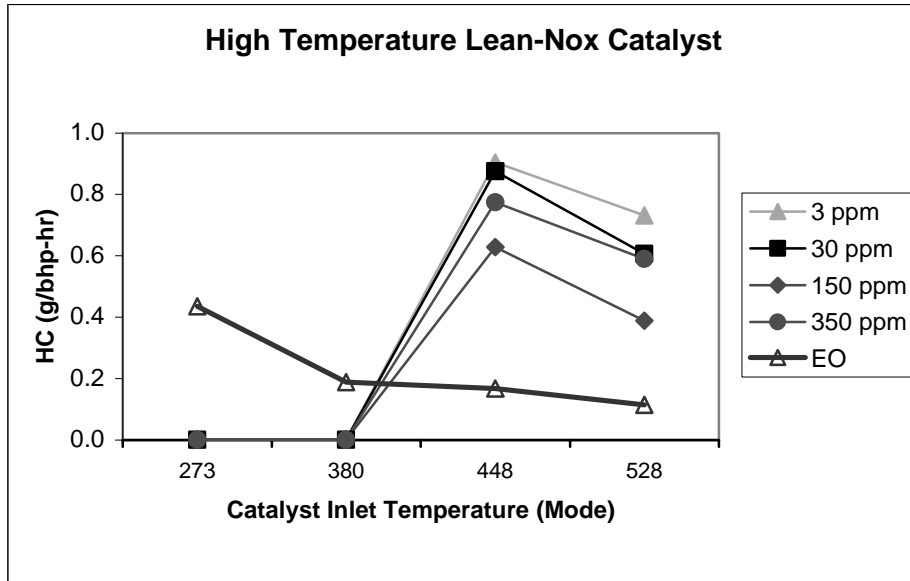


Figure 4-10. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of HC under HT (Cummins) applications at selected catalyst inlet temperatures – by fuel sulfur level

**Table 4-3. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of HC under LT (Navistar) and HT (Cummins) applications versus fuel sulfur level (with 95% confidence intervals)**

Test Mode	Fuel Sulfur (ppm)	HC (g/bhp-hr)	
		Engine-Out (95% Confidence Interval)	Post-LNOx (95% Confidence Interval)
NAV-9 4- Mode Weighted	3	0.1002 (0.08, 0.1256)	0.1259 (0.0933, 0.1701)
	30	0.0608 (0.0485, 0.0761)	0.1097 (0.0812, 0.1481)
	150	0.109 (0.0907, 0.1311)	0.2644 (0.1958, 0.357)
	350	0.1115 (0.0928, 0.1341)	0.352 (0.2607, 0.4753)
OICA-13 4- Mode Weighted	3	0.162 (0.1455, 0.1803)	0.5708 (0.5112, 0.6374)
	30	0.1711 (0.1537, 0.1905)	0.507 (0.4338, 0.5926)
	150	0.1724 (0.1549, 0.1919)	0.3573 (0.32, 0.399)
	350	0.1785 (0.1603, 0.1986)	0.4755 (0.4258, 0.5309)
	All	0.1709 (0.1632, 0.179)	

#### 4.1.3.2 Carbon Monoxide Emissions

For the same reason discussed in Section 4.1.3.1, the CO slippage was investigated for LT and HT lean-NO<sub>x</sub> catalysts. CO reduction efficiency for LT catalysts and CO emissions for HT catalysts, with 95% confidence intervals, at selected catalyst inlet temperatures are displayed in Figures 4-11 and 4-12, respectively. Even with secondary fueling, excellent CO oxidation efficiencies (>85%) were observed with the LT lean-NO<sub>x</sub> catalyst across four modes (Figure 4-11). Fuel sulfur level does not have a significant effect on CO emissions or CO oxidation efficiency. By contrast, the HT lean-NO<sub>x</sub> catalyst cannot oxidize CO. With the secondary fueling during modes 10 (448°C) and 2 (528°C) of the OICA-13 cycle, the CO slippage was high. Although there are statistically significant differences in amount of CO slippage with the given HT catalyst at different fuel sulfur levels, no consistent patterns support a conclusion that fuel sulfur affects CO emissions. Figure 4-12 shows that CO emissions at 528°C are highest with 3- and 350-ppm sulfur fuel. For reference, Table 4-4 contains the detailed CO emissions results using weighted 4-mode test cycles.

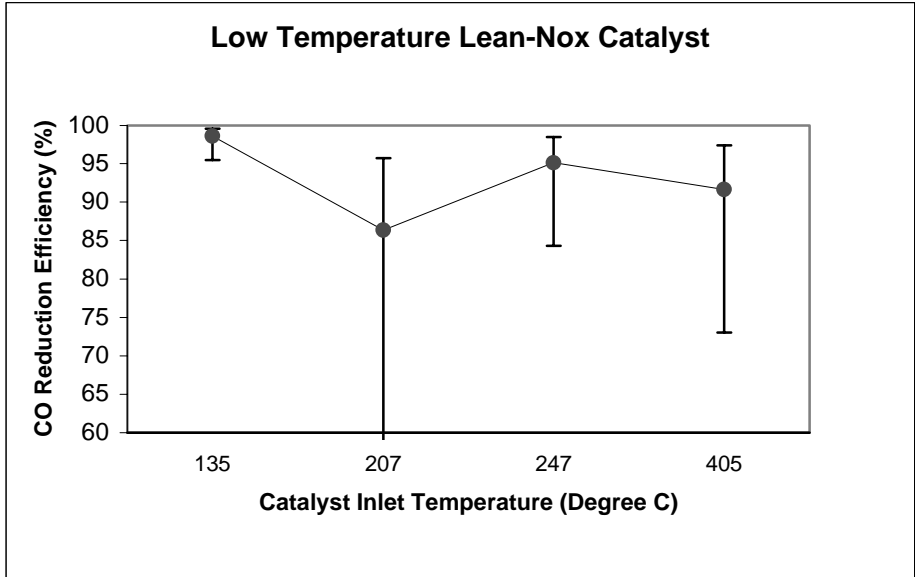


Figure 4-11. CO emission reduction efficiency of a fresh lean-NO<sub>x</sub> catalyst under LT (Navistar) applications at selected catalyst inlet temperatures (with 95% confidence intervals)

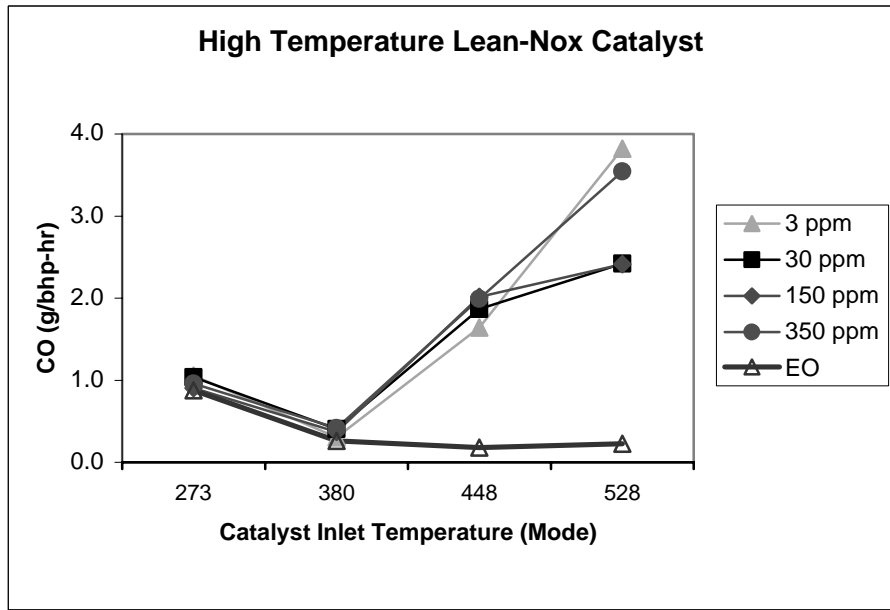


Figure 4-12. EO and post lean-NO<sub>x</sub> catalyst (fresh) emissions of CO under HT (Cummins) applications at selected catalyst inlet temperatures – by fuel sulfur level

**Table 4-4. EO and post lean-NO<sub>x</sub> catalyst (fresh) CO emissions and reduction efficiencies versus fuel sulfur level (with 95% confidence intervals)**

Test Mode	Fuel Sulfur (ppm)	CO		
		Engine-Out (g/bhp-hr) (95% Confidence Interval)	Post-LNO <sub>x</sub> (g/bhp-hr) (95% Confidence Interval)	Reduction Efficiency (%) (95% Confidence Interval)
NAV-9 4-Mode Weighted	3	0.8338 (0.7881, 0.8821)	0.0653 (0.0431, 0.0989)	92 (88, 95)
	30	0.7643 (0.7224, 0.8085)	0.0656 (0.0433, 0.0994)	91 (87, 94)
	150	0.8296 (0.7923, 0.8686)	0.0509 (0.0336, 0.0771)	94 (91, 96)
	350	0.7892 (0.7537, 0.8263)	0.098 (0.0545, 0.1762)	88 (78, 93)
	All	0.8048 (0.7794, 0.831)	0.0645 (0.051, 0.0817)	92 (90, 94)

Note:  $RE = \{1 - 10^{\{ \text{LOG}(LNO_x) - \text{LOG}(EO) \}}\} * 100$

## 4.2 Aging Effects on Lean-NO<sub>x</sub> Catalysts

As expressed earlier, the lean-NO<sub>x</sub> catalysts were aged for a total of 250 hours using Navistar T444E (7.3L) and Cummins ISM (11L) engines for the HT and LT catalyst systems, respectively. Catalyst aging cycles covered all selected evaluation modes and the secondary fueling rates for the steady-state modes were the same as those used in the catalyst evaluation experiments. More detailed catalyst aging information is described in Tables 4-5 and 4-6.

**Table 4-5. Low-temperature lean-NO<sub>x</sub> catalyst aging cycle (Nav-9 4-Mode, 60 minutes)**

Nav-9 Mode	Description	Minutes per Cycle	Weighting Factor (percent)
9	High rpm, high torque, high temperature	24	40
7	Higher rpm and low torque, low temperature	12	20
3	Lower rpm and higher torque, lower temperature	12	20
2	Low rpm, torque, temperature	12	20

**Table 4-6. High-temperature lean-NO<sub>x</sub> catalyst aging cycle (OICA-13 4-Mode, 60 minutes)**

OICA Mode	Description	Minutes per Cycle	Weighting Factor (percent)
2	High torque, temperature	24	40
10	Rated condition	24	40
3	Road load	6	10
11	Low temperature operation	6	10

For each fuel sulfur level, a fresh catalyst was used for the aging experiment. In addition to the fresh catalyst evaluation (0 hour), the aging catalysts were evaluated at 50 hours, 150 hours, and 250 hours, respectively. For the same reasons presented in Section 3.2 for the DOC technology,

all data collected during catalyst evaluations at 50, 150, and 250 hours were combined for comparison with the performance of fresh catalysts. That is, there was generally no evidence of changes in catalyst emissions beyond the effect observed at 50 hours.

#### 4.2.1 NO<sub>x</sub> Reduction Efficiency

The first critical finding from the aging experiment is that catalyst aging (within 250 hours) had no obvious effect on NO<sub>x</sub> reduction with LT and HT lean-NO<sub>x</sub> catalysts. Figures 4-13 and 4-14 show fresh and aged catalyst NO<sub>x</sub> reduction efficiency, with 95% confidence intervals, for LT and HT lean-NO<sub>x</sub> catalysts, respectively, using the appropriate weighted 4-mode cycles. There were some apparent statistical anomalies concerning the NO<sub>x</sub> reduction efficiencies for 150-ppm S fuel. However, no consistent patterns across fuel sulfur levels support a conclusion that fuel sulfur affects NO<sub>x</sub> reduction efficiency.

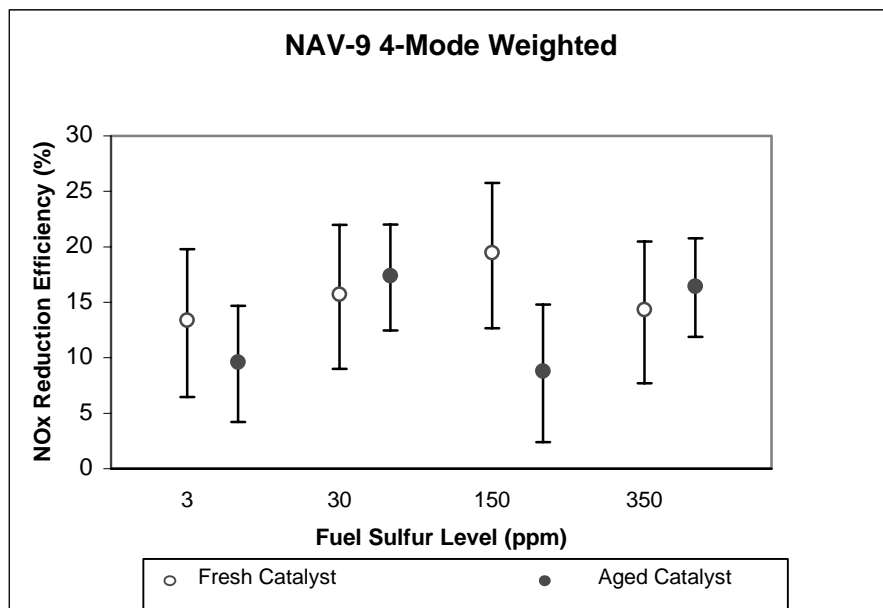
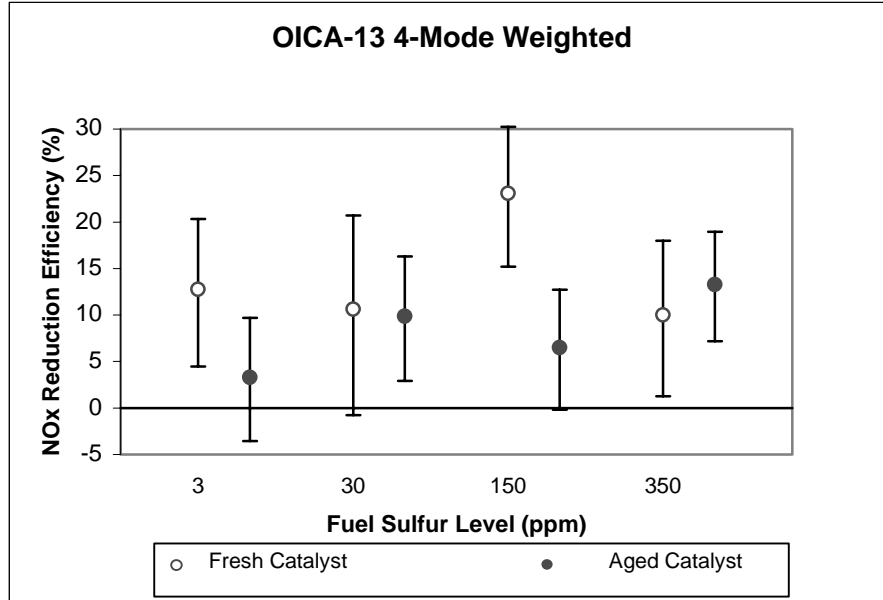


Figure 4-13. NO<sub>x</sub> reduction efficiencies with fresh and aged lean-NO<sub>x</sub> catalyst under LT (Navistar) applications using the Nav-9 weighted 4-mode cycle (with 95% confidence intervals)



**Figure 4-14. NO<sub>x</sub> reduction efficiencies with fresh and aged lean-NO<sub>x</sub> catalyst under HT (Cummins) applications using the OICA-13 weighted 4-mode test cycle (with 95% confidence intervals)**

#### **4.2.2 Particulate Matter Emissions**

Estimated EO, fresh catalyst, and aged catalyst PM emissions for LT and HT lean-NO<sub>x</sub> catalysts using weighted 4-mode cycles are depicted in Figures 4-15 and 4-16, along with 95% confidence intervals on the estimates. Statistical analysis demonstrated that catalyst aging significantly increased catalyst-out PM emissions with high-sulfur fuels (150–350 ppm S) for the LT lean-NO<sub>x</sub> catalyst (Figure 4-15). For example, with 350-ppm S fuel, the catalyst-out PM emissions increased by 300% (from 0.08 to 0.33g/bhp-hr) after aging. On the other hand, the fuel sulfur level had no obvious effect on the catalyst-out PM emissions during the HT catalyst aging (Figure 4-16). However, the aging process did show certain effects on the deterioration of PM emissions (16-46% PM increases) with the HT lean-NO<sub>x</sub> catalyst.

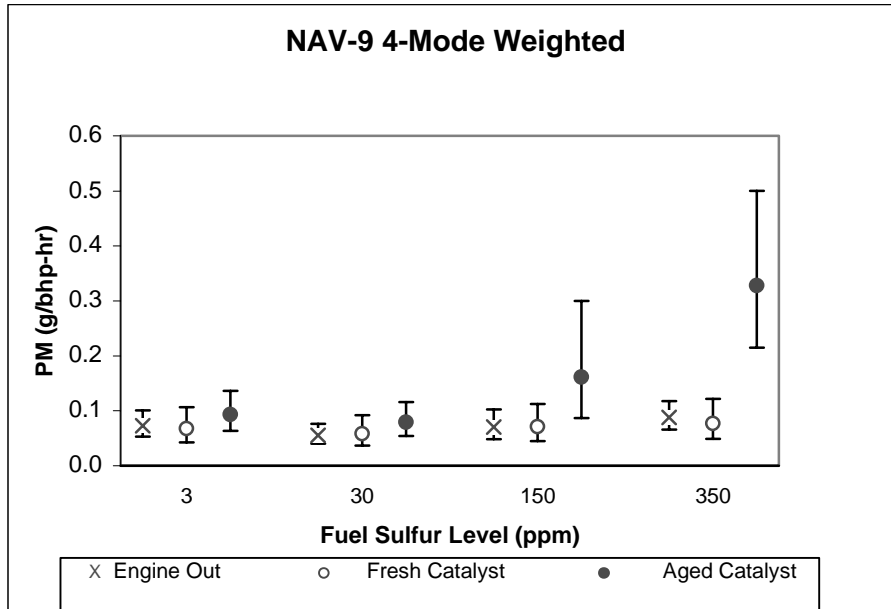


Figure 4-15. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of PM under LT (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)

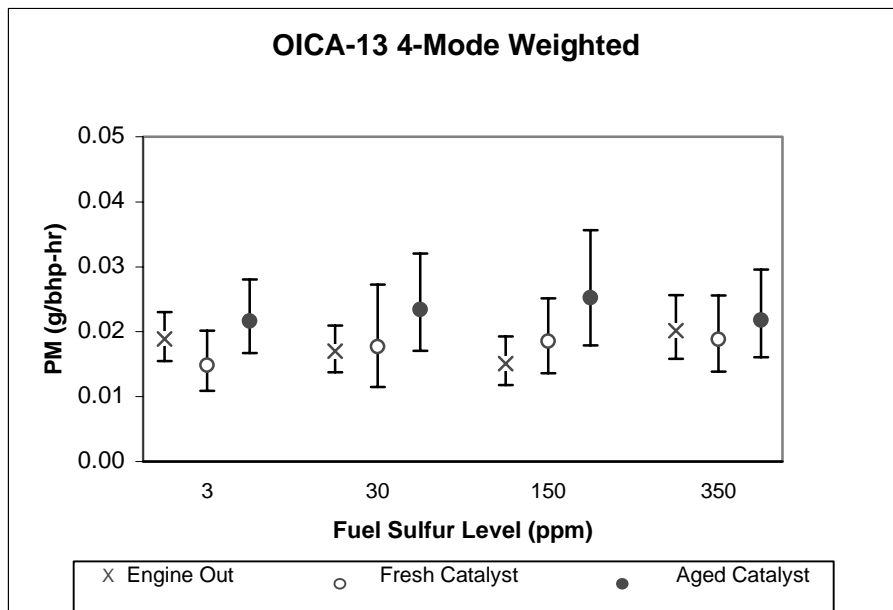
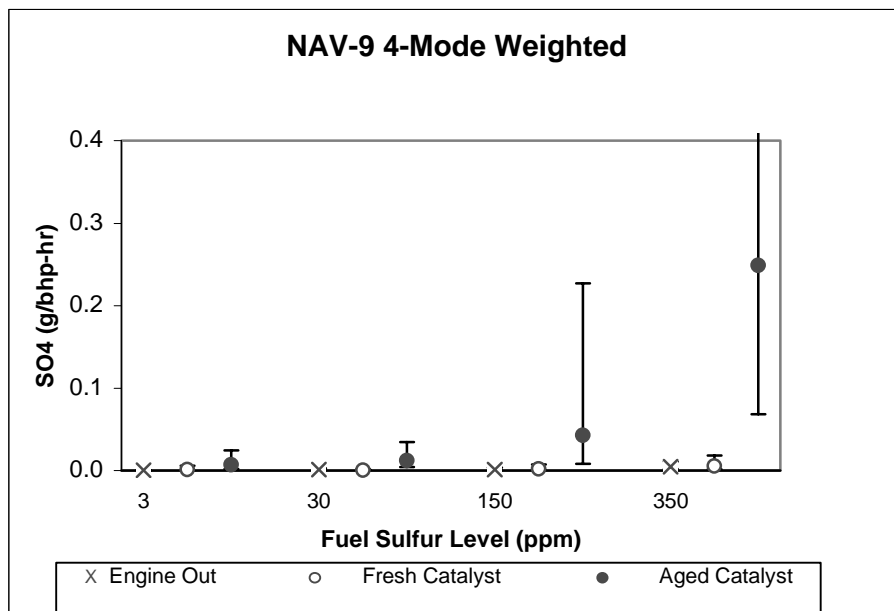


Figure 4-16. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of PM under HT (Cummins) applications using the OICA-13 weighted 4-mode test cycle (with 95% confidence intervals)

Based on the PM breakdown analysis, EO, fresh catalyst, and aged catalyst sulfate emissions for LT and HT lean-NO<sub>x</sub> catalysts using weighted 4-mode cycles are plotted in Figures 4-17 and 4-18. Comparing Figures 4-15 and 4-17, it is evident that high SO<sub>4</sub> emissions were the main contributors to the increase of PM emissions with high sulfur fuels for the LT lean-NO<sub>x</sub> catalyst. This could be attributed to SO<sub>4</sub> accumulation (inside the LT lean-NO<sub>x</sub> catalyst) during the aging cycle. The accumulated sulfate could be partially released during the catalyst evaluation to generate the high SO<sub>4</sub> emissions when high sulfur fuels (150–350 ppm S) were used. This phenomenon could also depend on the wash-coating structure of a given LT lean-NO<sub>x</sub> catalyst. The HT lean-NO<sub>x</sub> catalyst did not show the same pattern of high SO<sub>4</sub> emissions with the high sulfur fuels under a similar aging cycle (Figure 4-18).

In principle, a lean-NO<sub>x</sub> catalyst has a certain ability to oxidize SOF in PM. Therefore, the SOF emissions could indicate catalyst activity. Results of EO, fresh catalyst, and aged catalyst SOF emissions for LT and HT lean-NO<sub>x</sub> catalysts using weighted 4-mode cycles are shown in Figures 4-19 and 4-20. However, the effect of aging on SOF emissions is not obvious with the LT lean-NO<sub>x</sub> catalyst. With the HT lean-NO<sub>x</sub> catalyst, aging shows a deteriorating effect on SOF emissions, except for 350-ppm S fuel. Results are consistent with the observed increase in PM emissions with aged HT lean-NO<sub>x</sub> catalysts, as shown in Figure 4-16.



**Figure 4-17. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of SO<sub>4</sub> under LT (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)**



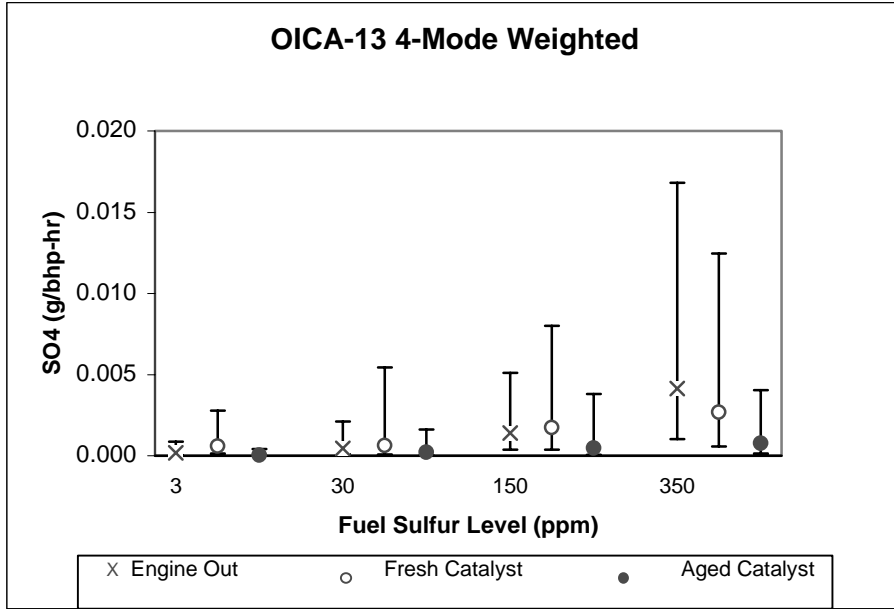


Figure 4-18. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of SO<sub>4</sub> under HT (Cummins) applications using the OICA-13 weighted 4-mode test cycle (with 95% confidence intervals)

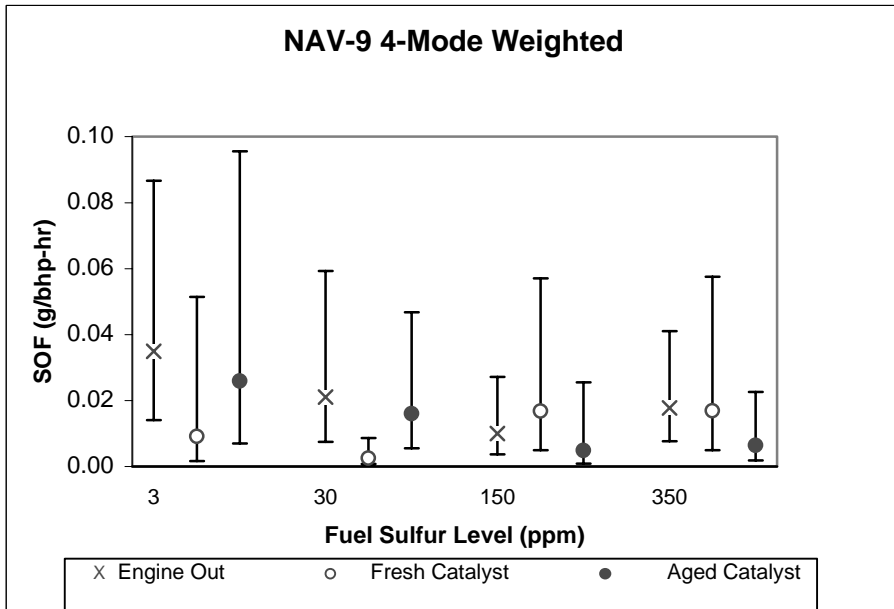
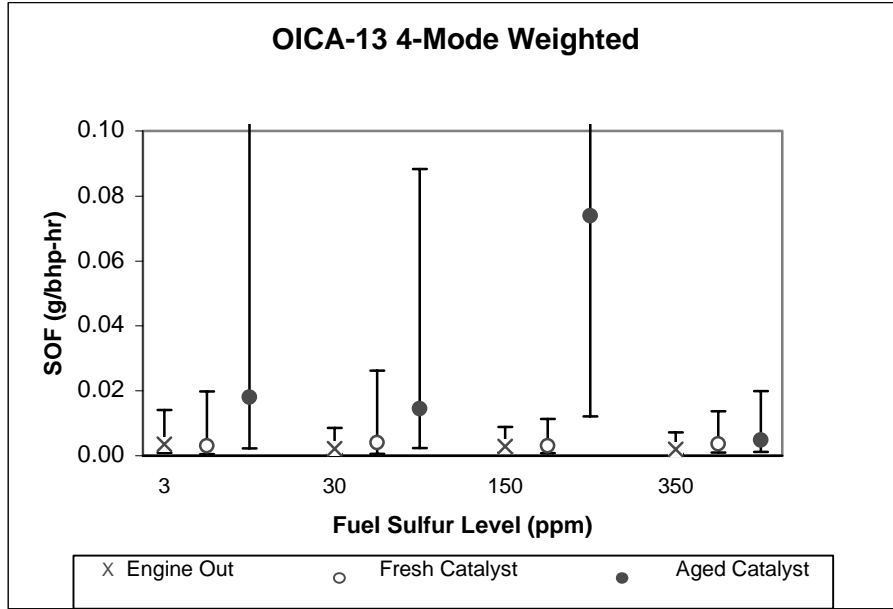


Figure 4-19. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of SOF under LT (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)



**Figure 4-20. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of SOF under HT (Cummins) applications using the OICA-13 weighted 4-mode test cycle (with 95% confidence intervals)**

For reference, Table 4-7 summarizes estimated EO and post-catalyst (fresh and aged) PM, SO<sub>4</sub>, and SOF emissions and reduction efficiencies, with 95% confidence intervals, for each combination of test cycle and fuel tested.

**Table 4-7. EO and post lean-NO<sub>x</sub> catalyst (fresh and aged) PM, SO<sub>4</sub>, and SOF emissions and reduction efficiencies under LT (Navistar) and HT (Cummins) applications using weighted 4-mode test cycles - by fuel sulfur level**

Engine	Test Mode	Fuel Sulfur (ppm)	Fresh/Aged	PM			SO <sub>4</sub>			SOF		
				Engine-Out (g/bhp-hr)	Post LNO <sub>x</sub> (g/bhp-hr)	Reduction Efficiency (%)	Engine-Out (g/bhp-hr)	Post LNO <sub>x</sub> (g/bhp-hr)	Reduction Efficiency (%)	Engine-Out (g/bhp-hr)	Post LNO <sub>x</sub> (g/bhp-hr)	Reduction Efficiency (%)
Navistar	NAV-9 Weighted	3	F	0.0730	0.0676	7	0.0002	0.0010	-383	0.0349	0.0091	74
			A		0.0932	-28		0.0068	-3233*		0.0259	26
		30	F	0.0555	0.0581	-5	0.0011	0.0005	56	0.0211	0.0025	88*
			A		0.0794	-43		0.0120	-1010*		0.0161	24
		150	F	0.0707	0.0711	-1	0.0013	0.0021	-65	0.0100	0.0168	-67
			A		0.1614	-128*		0.0428	-3206*		0.0048	52
		350	F	0.0881	0.0772	12	0.0047	0.0053	-13	0.0178	0.0169	5
			A		0.3278	-272*		0.2488	-5174*		0.0064	64
Cummins	OICA Weighted	3	F	0.0189	0.0148	21	0.0002	0.0006	-235	0.0035	0.0031	12
			A		0.0217	-15		0.0000	77		0.0181	-416
		30	F	0.0170	0.0177	-4	0.0005	0.0006	-35	0.0022	0.0041	-86
			A		0.0234	-38*		0.0002	53		0.0145	-562*
		150	F	0.0151	0.0185	-23	0.0014	0.0017	-24	0.0029	0.0030	-5
			A		0.0253	-68*		0.0005	67		0.0740	-2453*
		350	F	0.0202	0.0188	7	0.0041	0.0027	35	0.0020	0.0037	-84
			A		0.0218	-8		0.0008	82*		0.0048	-141

\*Different from 0% at 0.05 level of statistical significance.

Note: RE = (1-10<sup>LOG(LNO<sub>x</sub>)-LOG(EO))</sup>)\*100

### 4.2.3 Other Gaseous Emissions

During the aging experiment, other gaseous emissions were investigated as well with LT and HT lean-NO<sub>x</sub> catalysts.

#### 4.2.3.1 Hydrocarbon Emissions

Figures 4-21 and 4-22 show estimated EO and post catalyst (fresh and aged) HC emissions, with 95% confidence intervals, for LT and HT lean-NO<sub>x</sub> catalysts using weighted 4-mode cycles. As discussed in Section 4.1.3.1, high sulfur fuels resulted in greater HC slippage with the LT lean-NO<sub>x</sub> catalyst. Figure 4-21 and supporting statistical analysis demonstrate that catalyst aging increases the amount of slippage, especially with high-sulfur fuel. The Nav-9 cycle (4-mode) results indicate that HC emissions increased by more than 100% over 250 hours with both 150- and 350-ppm sulfur fuels. This effect corresponds to the increase of PM and sulfate emissions with high sulfur fuels during the aging process. Even though the aged HT lean-NO<sub>x</sub> catalyst gave significantly higher levels of HC slippage, the effect of aging decreased as the sulfur level of the fuel increased. Figure 4-22 shows this interesting phenomenon with the OICA-13 cycle (4-mode).

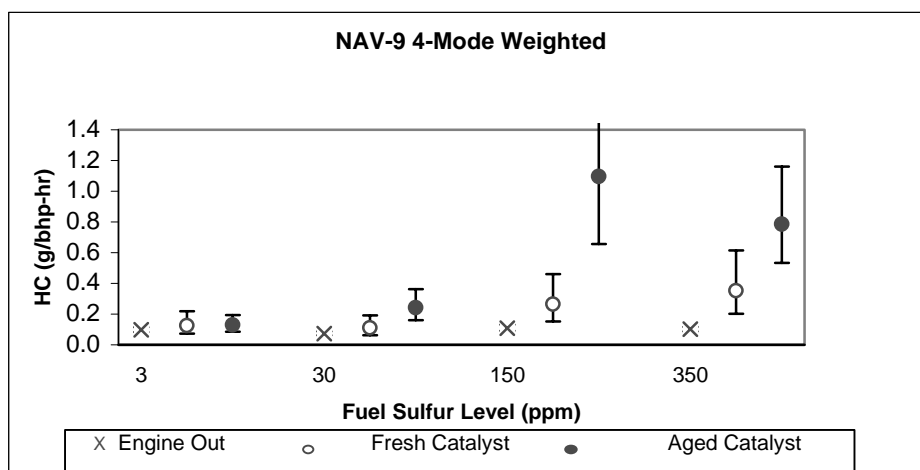
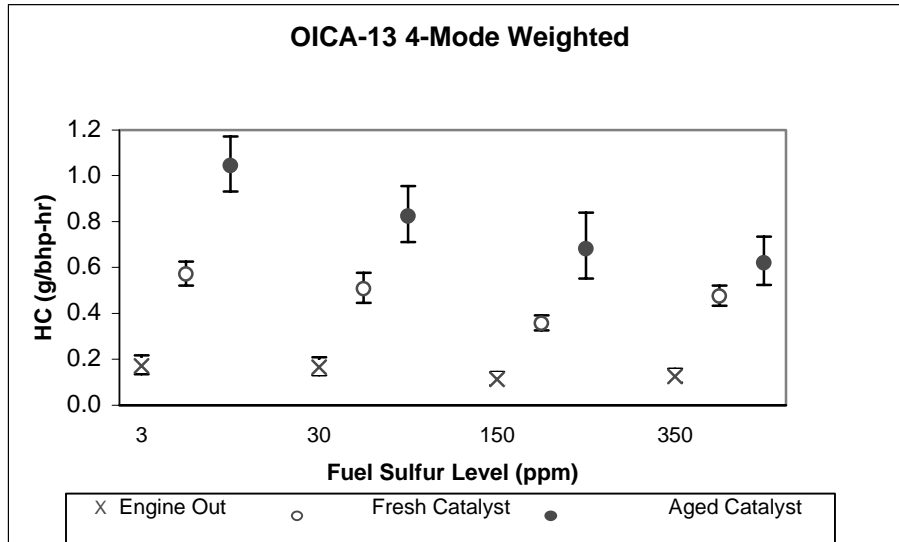


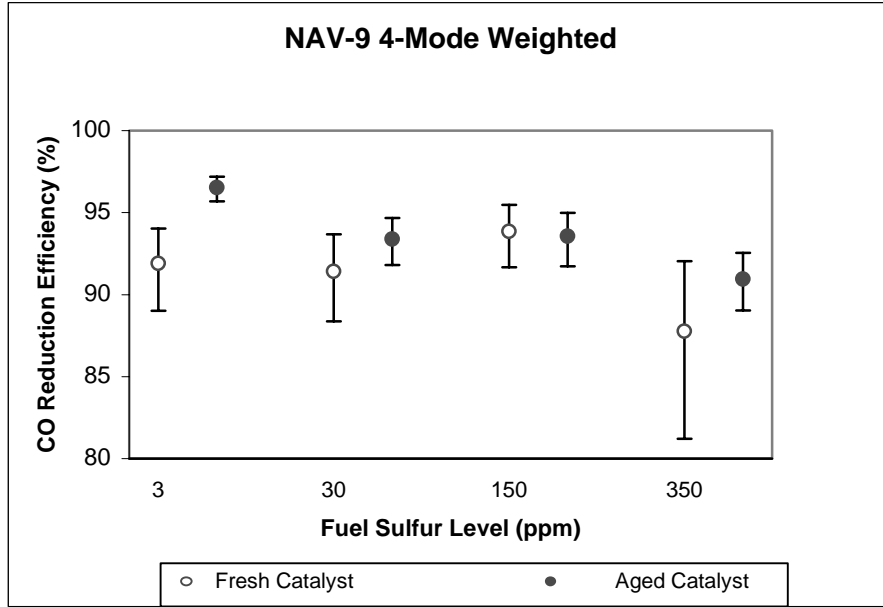
Figure 4-21. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of HC under LT (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)



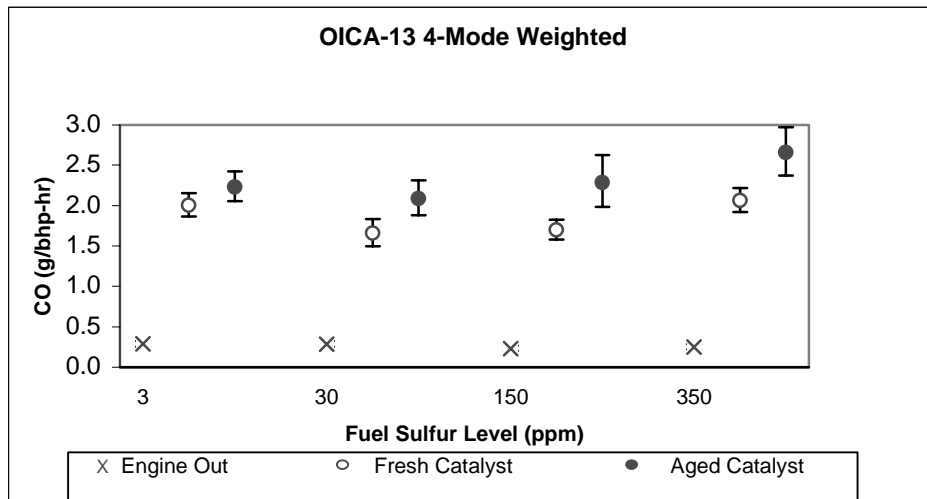
**Figure 4-22. EO and fresh and aged lean-NO<sub>x</sub> catalyst emissions of HC under HT (Cummins) applications using the OICA-13 weighted 4-mode test cycle (with 95% confidence intervals)**

#### 4.2.3.2 Carbon Monoxide Emissions

Figure 4-23 shows the estimated CO reduction efficiencies with fresh and aged LT lean-NO<sub>x</sub> catalysts, with 95% confidence intervals, by fuel sulfur level. Depending on the fuel sulfur level, there were small (0 – 5%) but statistically significant increases in CO reduction efficiency observed with the aged catalyst over the Nav-9 cycle (4-mode). The results for HT lean-NO<sub>x</sub> catalysts are presented in Figure 4-24. Catalyst-out CO emissions increased by 25% between 50 and 250 hours of aging, mostly due to the CO increase at mode 2 of the OICA-13 cycle. There was a larger aging effect with high sulfur fuels (150- and 350-ppm S).



**Figure 4-23. CO reduction efficiencies with fresh and aged lean-NO<sub>x</sub> catalysts under LT (Navistar) applications using the Nav-9 weighted 4-mode cycle (with 95% confidence intervals)**



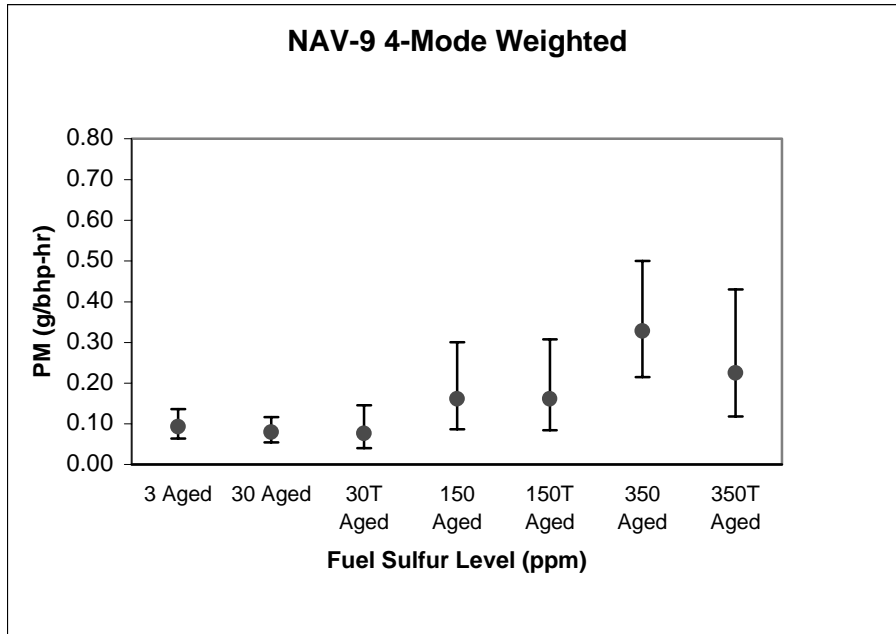
**Figure 4-24. Engine-out and fresh and aged lean-NO<sub>x</sub> catalyst emissions of CO under HT (Cummins) applications using the OICA-13 weighted 4-mode test cycle (with 95% confidence intervals)**

### 4.3 Evaluation of Thermal Effects on Catalyst Performance and Recovery from Aging with High Sulfur Fuel

Special experiments were conducted to compare the post-catalyst emissions effects of fuel sulfur level with the effects of thermal aging of catalysts. Additional experiments were performed to evaluate the catalyst's ability to recover from extended exposures to high sulfur fuel. The thermal aging experiments consisted of running 4-mode emissions tests with 30-, 150-, and 350-ppm sulfur fuel using the catalysts aged for 250 hours with 3-ppm sulfur fuel. By comparing these results with the emissions from the catalysts aged with corresponding high sulfur fuels, it is possible to determine whether the thermal aging and fuel sulfur effects are additive or, alternatively, there is a cumulative poisoning effect when catalysts are aged with sulfur-containing fuel. The recovery experiments consisted of performing additional tests on the catalyst aged for 250 hours with 350-ppm sulfur fuel. The additional tests were performed with 30-ppm sulfur fuel after zero and 50 hours of additional aging with 30-ppm sulfur fuel. Results are compared with the 250-hour results from the 30-ppm and 350-ppm sulfur aging experiments to determine whether recovery occurred.

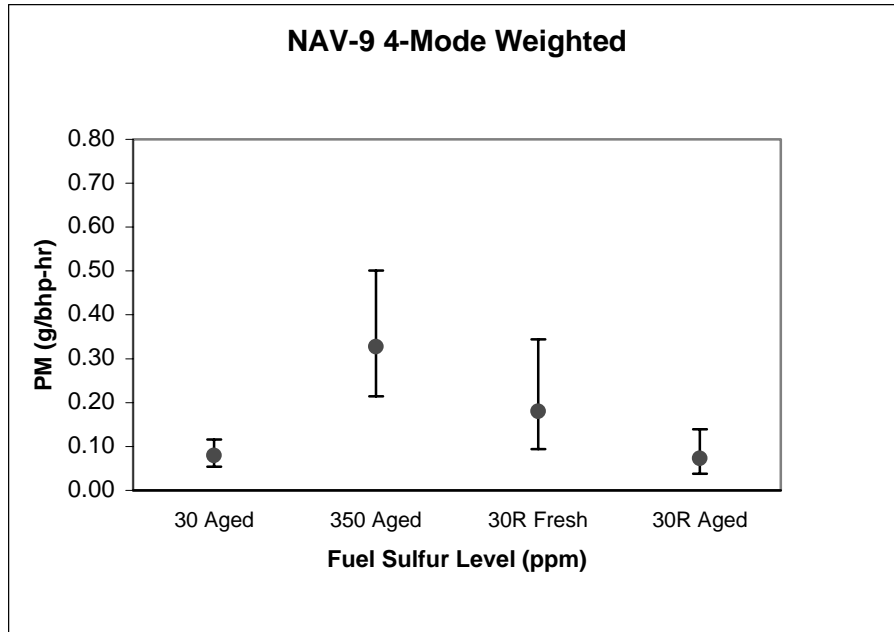
Since catalyst aging with various fuel sulfur levels did not show an obvious effect on  $\text{NO}_x$  reduction efficiencies with both LT and HT lean- $\text{NO}_x$  catalysts, thermal and sulfur effects on PM emissions and HC slippage are the main focus on the following discussions. It is known that the thermal aging effect on a catalyst is difficult to reverse, whereas the sulfur aging effect could be partially or fully reversed.

Figure 4-25 shows the estimated post LT lean- $\text{NO}_x$  PM emissions, with 95% confidence intervals, under various test conditions. Tests labeled 3 Aged, 30T Aged, 150T Aged, and 350T Aged were performed with the indicated fuel sulfur level on the LT catalyst that was thermally aged with 3-ppm sulfur fuel. As demonstrated, with both 30- and 150-ppm sulfur fuel, the PM results were statistically similar when compared to the PM results from both 30- and 150-ppm sulfur aging under the same evaluation conditions, implying that the thermal aging was the main cause for PM increase with less than 150-ppm sulfur fuel. In other words, the thermal aging itself could enhance the catalyst's ability to make sulfate. With 350-ppm sulfur fuel, the results suggest that the effects of thermal aging and sulfur aging are essentially additive. Notice that the confidence intervals overlap for thermally-aged (e.g., 350T Aged) and sulfur-aged (e.g., 350 aged) catalysts, indicating that the differences in estimated emissions are not statistically significant.



**Figure 4-25. PM emissions, with 95% confidence intervals, from LT lean-NO<sub>x</sub> catalysts aged for 250 hours and tested with various fuel sulfur levels - and corresponding results from thermally aged (3-ppm sulfur fuel) catalysts**

The recovery tests were performed with 30-ppm sulfur fuel on the catalysts aged for 250 hours with the indicated fuel. Figure 4-26 shows the PM results from the recovery tests with the LT lean-NO<sub>x</sub> catalysts. The 30 Aged and 350 Aged results are the same as those shown in Figure 4-25. However, the 30R Fresh and 30R Aged results were obtained from the 350-ppm aged catalyst following zero and 50 hours of additional aging with 30-ppm sulfur fuel. This demonstrates that 30R Fresh results are significantly higher than the corresponding 30 Aged results, indicating that the 350-ppm aged catalyst did not fully recover when retested with 30-ppm fuel. However, after 50 hours of aging (recovery) with 30-ppm sulfur fuel, the results (30R Aged) are consistent with the 30-ppm aged catalyst, indicating full recovery from the sulfur-aging effect.



**Figure 4-26. PM emissions, with 95% confidence intervals, from LT lean-NO<sub>x</sub> catalysts aged for 250 hours and tested with 30- and 350-ppm sulfur fuels – and 0- and 50-hour 30-ppm recovery tests performed on the catalyst aged for 250 hours with 350-ppm sulfur fuel**

When revisiting Figure 4-16 (section 4.2.2), it is evident that the PM increases during the HT lean-NO<sub>x</sub> catalyst aging (with various fuel sulfur levels) were mainly due to the effect of thermal aging. The sulfur aging effect on PM increase was not obvious with the HT catalyst.

Figure 4-27 contains the corresponding thermal-aging results for HC emissions from the LT lean-NO<sub>x</sub> catalyst. Again, with less than 150-ppm sulfur fuel, thermal aging was the major contributor to the increase of HC slippage. The sulfur aging effect is different from the sulfur effect itself. High fuel sulfur levels such as 150- and 350-ppm do inhibit the LT catalyst activity and increase its HC slippage rate even with the fresh LT catalyst (refer to Figure 4-21). The thermal aging seems to make the LT catalyst more sensitive to sulfur inhibition, resulting higher HC slippage with higher sulfur fuel. With 350-ppm sulfur fuel, certain effects of the sulfur aging (not significantly) are seen, in addition to the thermal aging effect. However, after the 50-hour recovery test was performed on the 350-ppm aged catalysts with 30-ppm sulfur fuel, there were no significant differences between the results from the 30-ppm aged tests and the recovery tests (Figure 4-28: 30R Fresh vs. 30R Aged), indicating full recovery of the catalyst from sulfur aging.



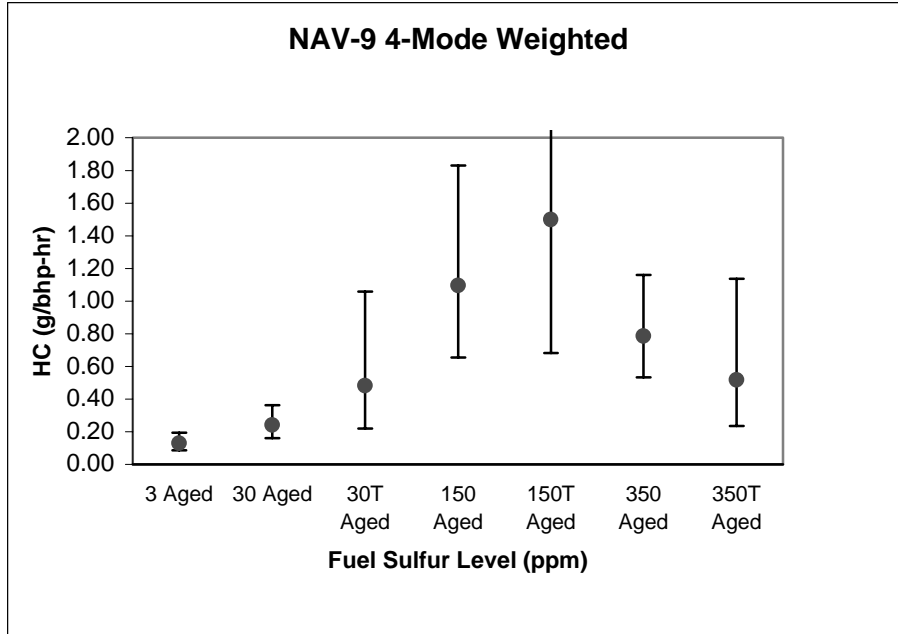


Figure 4-27. HC emissions, with 95% confidence intervals, from LT lean-NO<sub>x</sub> catalysts aged for 250 hours and tested with various fuel sulfur levels - and corresponding results from thermally aged (3-ppm sulfur fuel) catalysts

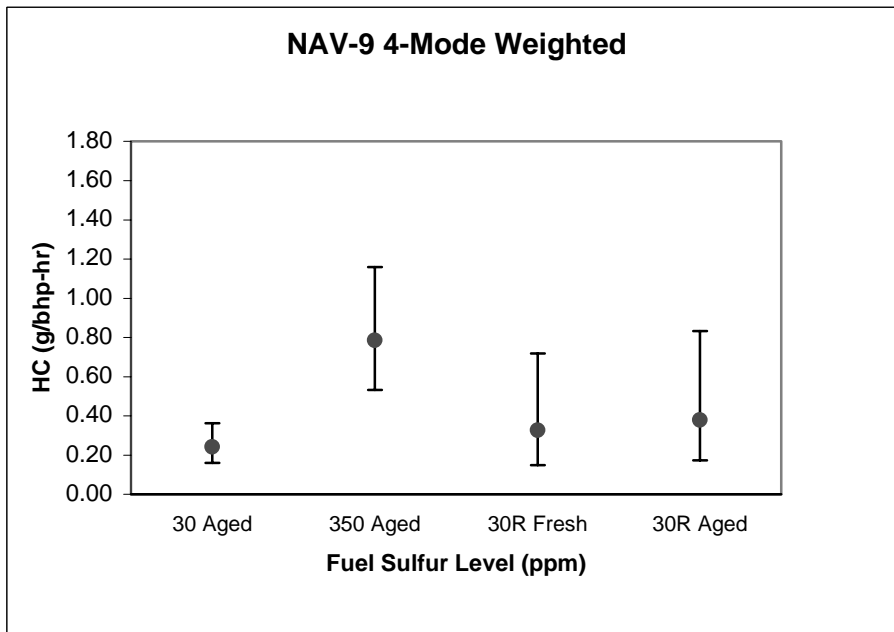
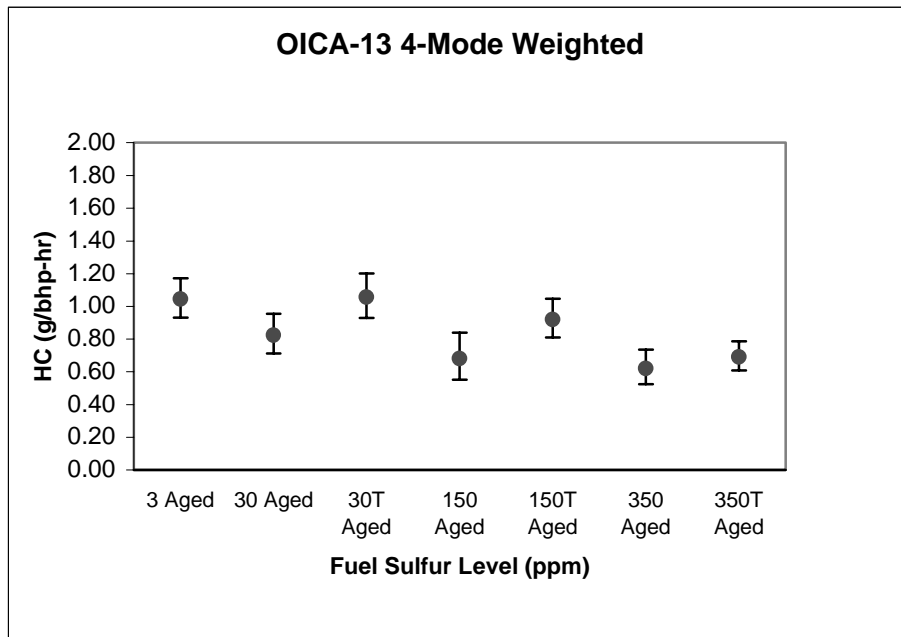
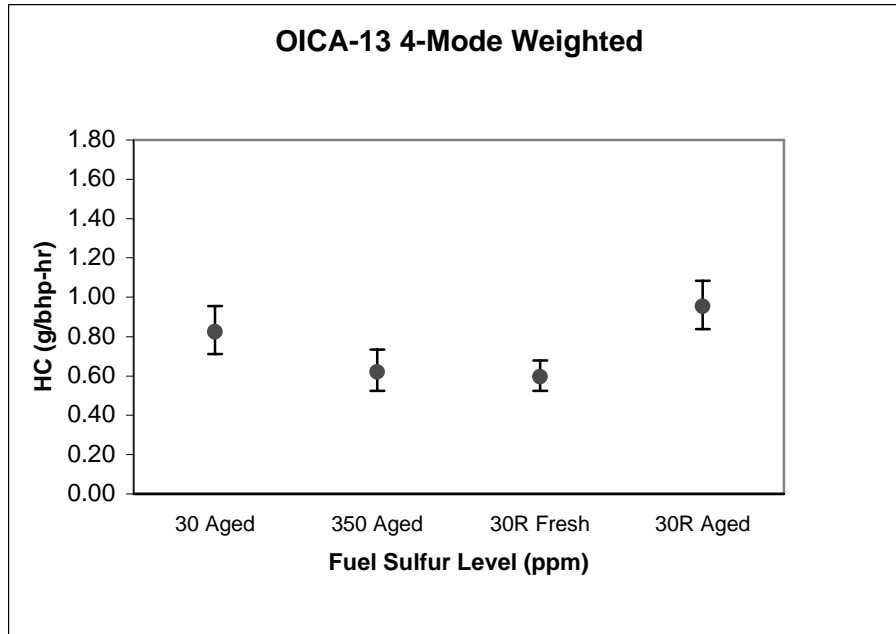


Figure 4-28. HC emissions, with 95% confidence intervals, from LT lean-NO<sub>x</sub> catalysts aged for 250 hours and tested with 30- and 350-ppm sulfur fuels – and 0- and 50-hour 30-ppm recovery tests performed on the catalyst aged for 250 hours with 350-ppm sulfur fuel

Finally, Figures 4-29 and 4-30 contain the thermal aging and recovery results for HC emissions from the HT Lean-NO<sub>x</sub> catalyst. As discussed in Section 4.2.3.1, the effects of aging HT catalysts on HC emissions decrease with high sulfur fuel. Although the differences are not always statistically significant, Figure 4-29 shows that the thermally aged catalysts tend to produce slightly higher HC emissions when compared to the catalysts aged with the same high sulfur fuel. The recovery results (Figure 4-30) also illustrate aspects of this phenomenon. The reason for this phenomenon is unknown. Notice that the HC emissions from the catalyst aged for 50 hours with 30-ppm sulfur fuel (after 250 hours with 350-ppm sulfur fuel) are consistent with the results from the catalyst aged with 30-ppm sulfur fuel, but significantly higher than the levels measured immediately after 250 hours of aging with 350-ppm sulfur fuel.



**Figure 4-29. HC emissions, with 95% confidence intervals, from HT lean-NO<sub>x</sub> catalysts aged for 250 hours and tested with various fuel sulfur levels - and corresponding results from thermally aged (3-ppm sulfur fuel) catalysts**



**Figure 4-30. HC emissions, with 95% confidence intervals, from HT lean-NO<sub>x</sub> catalysts aged for 250 hours and tested with 30- and 350-ppm sulfur fuels – and 0- and 50-hour 30-ppm recovery tests performed on the catalyst aged for 250 hours with 350-ppm sulfur fuel**

#### 4.4 Conclusions of Lean-NO<sub>x</sub> Catalyst Evaluation

- With fresh lean-NO<sub>x</sub> catalysts and with less than 4% fuel penalty, overall NO<sub>x</sub> reduction efficiencies were less than 20% for all catalysts during the defined steady-state test cycles. However, over 50% and 30% NO<sub>x</sub> reduction peak efficiencies were observed for both LT and HT catalysts, respectively. Statistically, the effect of fuel sulfur level on NO<sub>x</sub> reduction efficiency was not significant.
- With fresh lean-NO<sub>x</sub> catalysts and higher fuel sulfur levels (150- and 350-ppm sulfur fuels), the increase in catalyst-out sulfate emissions were significant at high-temperature steady-state modes.
- The HT lean NO<sub>x</sub> catalyst was vulnerable to HC slip with all of the fuels tested. The LT lean-NO<sub>x</sub> catalyst was more effective at controlling HC and CO slip, but only with low sulfur (3- and 30-ppm S) fuels.
- Catalyst aging (up to 250 hours), independent of fuel sulfur level, had no apparent effect on the NO<sub>x</sub> reduction efficiency of the LT and HT lean-NO<sub>x</sub> catalysts.
- For the LT lean-NO<sub>x</sub> catalyst, catalyst aging significantly increased catalyst-out PM emissions with higher sulfur fuels (150- to 350-ppm S), mainly due to high sulfate emissions after 50 hours of catalyst aging. Thermal aging seems to be the primary reason for the PM increase with the lower sulfur fuels. With 350-ppm sulfur fuel, the effects of thermal aging and sulfur aging seemed essentially additive. Unlike the LT lean-NO<sub>x</sub> catalyst, the aging process had only a slight effect on catalyst-out PM emissions with the HT lean-NO<sub>x</sub> catalyst.

- Thermal aging was also the main contributor to the increase of HC slippage with the LT lean-NO<sub>x</sub> catalyst. Thermal aging could make the catalyst more vulnerable to sulfur inhibition, resulting in the higher HC slippage with high sulfur fuels. Likewise, HC slip from the HT lean-NO<sub>x</sub> catalysts increased after aging.
- For the LT lean-NO<sub>x</sub> catalyst, the adverse aging effect on both PM emissions and HC slippage can be essentially reversed within 50 hours of operation with 30-ppm sulfur fuel. This finding suggests that the catalyst had not undergone permanent deactivation. For the HT lean-NO<sub>x</sub> catalyst, the recovery test with 30-ppm sulfur fuel actually increased the HC slippage. It is consistent with the trend that the higher the fuel sulfur level, the lower the aging effect on the increase of HC slip.

## 5 Program Recommendations

### 5.1 Diesel Oxidation Catalyst

New HD diesel emissions standards will require manufacturers to certify to 0.2 g/bhp hr NO<sub>x</sub> and 0.01 g/bhp hr PM by 2007. These standards represent 90% reductions of both pollutants from certification limits previously required. DOCs have no NO<sub>x</sub> control capability and as demonstrated here, they have insufficient PM control effectiveness to meet the target; however, DOCs will likely be a critical component in the emissions control system.

The most promising NO<sub>x</sub> control technologies, NO<sub>x</sub> adsorber catalysts and selective catalytic reduction (SCR) catalysts, may each require a DOC. NO<sub>x</sub> adsorber catalyst systems may utilize a DOC to cleanup HC emissions during rich regeneration. Researchers have proposed use of a DOC in SCR systems either as a pre-catalyst for NO → NO<sub>2</sub> conversion or as a clean-up catalyst to control ammonia slip.

In order to achieve robust DOC performance across a broad exhaust temperature range, a precious metal-containing catalyst will certainly be required in these systems. The testing conducted here clearly demonstrates the vulnerability of platinum-loaded DOCs used with fuels containing even modest levels of sulfur. In tests with 350-ppm sulfur fuel, the sulfate fraction of the PM alone exceeded the 0.01 g/bhp hr PM standard for 2007 by as much as 15 times. For compliance with future standards, ultra-low sulfur fuel will be required in systems utilizing precious metal-containing catalysts.

As evidenced by the short-term durability tests conducted in this experiment, fuel sulfur does not significantly contribute to performance degradation of DOCs. However, the technologies tested here did show some loss of performance in only 250 hours. With emission system durability requirements extending to 435,000 miles in 2004, attention must be given to the deterioration factors of all system components.

### 5.2 Lean-NO<sub>x</sub> Catalyst

With the limited NO<sub>x</sub> reduction efficiency (~20%), the lean-NO<sub>x</sub> technologies will not be capable of addressing the stringent EPA diesel emissions regulation for Model Year 2007 and beyond. However, lean-NO<sub>x</sub> catalysts could still have the opportunity to address EPA Model Year 2004 emissions regulations for both light-duty (LD) and heavy-duty (HD) diesel engines. For LD engines, LT lean-NO<sub>x</sub> catalysts can be used. For HD engines, both LT and HT lean-NO<sub>x</sub> catalysts have to be applied simultaneously to broaden the operating temperature window. This is typically accomplished by putting a HT lean-NO<sub>x</sub> brick in front of a LT lean-NO<sub>x</sub> catalyst brick. Depending on the targeted NO<sub>x</sub> reduction efficiency, either a passive or an active (with secondary fueling) approach can be implemented. A diesel oxidation catalyst (DOC) might be required for HC clean up when the active lean-NO<sub>x</sub> (or De-NO<sub>x</sub>) approach is implemented. In light of potential lean-NO<sub>x</sub> catalyst applications and based on this DECSE lean-NO<sub>x</sub> catalyst evaluation, the following technical issues are recommended:

1. Both LT and HT lean-NO<sub>x</sub> catalysts possess a narrow operating temperature window. If these windows can be somehow broadened, it will certainly enhance their NO<sub>x</sub> reduction efficiency and reduce the overall cost of a lean-NO<sub>x</sub> catalyst system.

2. For high temperature or HD diesel applications, the sulfate making issue with both LT and HT lean-NO<sub>x</sub> catalysts needs to be properly addressed. The EPA Model Year 2004 emissions certification regulation requires the supplemental test cycle (OICA-13) along with not-to-exceed zones for both NO<sub>x</sub> and PM emissions. Federal certification fuel (~350-ppm sulfur) or California certification fuel (~200-ppm) will have to be used for meeting the EPA 2004 emissions regulation.
3. The HC slippage issue, especially with active HT lean-NO<sub>x</sub> catalysts, has to be alleviated. Beginning in 2004, HC emissions will be as critical as NO<sub>x</sub> emissions according to the EPA regulations. Inefficient use of supplemental hydrocarbon impairs catalyst performance and increases the fuel penalty.
4. The effect of thermal and sulfur aging (up to 250 hours in this study) on performance of the LT lean-NO<sub>x</sub> catalyst was noticeable in two areas. Even though the NO<sub>x</sub> reduction efficiency was maintained, the PM emissions and HC slippage rate was substantially increased. This could be a potential problem for LD diesel applications using high sulfur fuels.
5. The hydro-thermal durability of a base metal – zeolite type HT lean-NO<sub>x</sub> catalyst has been a critical issue to blocking its use in the field. With the limited scope of this study, it was not possible to give a thorough investigation on this imperative issue. If necessary and whenever applicable, further study is needed to investigate ways to improve HT lean-NO<sub>x</sub> catalyst durability.

## **Appendix A - DECSE Fuel Selection and Composition**

This appendix discusses information related to the selection and composition of the DECSE test fuels.

### **A.1 Introduction**

The focus of this program is to investigate the effect of fuel sulfur levels on the operation of diesel exhaust emission control devices. The fuels specified for use in this program were processed with this in mind.

To isolate the effects of fuel sulfur content from other fuel properties, fuels of various sulfur levels were obtained by doping an ultra-low sulfur base fuel with a mixture of sulfur-containing compounds. Except for the sulfur content, the properties of this base fuel were selected to be representative of diesel fuels sold and used in the United States. The base fuel contained 3-ppm sulfur and was doped to 30-, 150-, and 350-ppm sulfur.

### **A.2 Base Fuel Properties**

The base fuel is an ultra-low sulfur fuel that is otherwise representative of diesel fuels used in the United States. Table A-1 shows the specifications for this fuel, and the properties of the base fuel as blended. This fuel has a sulfur content of 3 ppm and is therefore designated as the 3-ppm sulfur base fuel. The measured property values are averages of analyses performed by Phillips Chemical, Southwest Research Institute, and Core Laboratories.

### **A.3 Achieving Desired Fuel Sulfur Contents**

Diesel fuels of differing sulfur levels can be obtained by:

- Seeking available diesel fuels that have different sulfur contents
- Blending varying amounts of a low-sulfur diesel fuel and a high-sulfur diesel fuel to produce intermediate sulfur concentrations
- Adding varying amounts of sulfur to a low-sulfur diesel fuel.

All three options were considered. The first two have an advantage in that the sulfur will be in chemical forms that exhibit all the natural diversity of petroleum-based fuels. Another advantage is fully realized impacts from different refining processes for lowering sulfur on the diversity of the petroleum-based fuels.

However, if the sulfur content were varied by changing the fuel, other fuel properties would change as well. Therefore, as the identity of the fuel changed, the unavoidable changes in such fuel properties as density, aromatics content, polyaromatics content, and/or volatility could lead to questions about whether changes in these properties, and not changes in the sulfur content of the fuel, were responsible for any observed changes in emission control device effectiveness.

Keeping in mind the program objective and the issues outlined above, the DECSE technical committee chose the third option (adding varying amounts of sulfur-containing compounds to a low-sulfur fuel). This process is generally referred to as “doping” the fuel, and the sulfur compounds used for this purpose are sometimes termed “dopants.”

**Table A-1. Specifications and measured properties of 3-ppm sulfur base fuel**

<b>Fuel Property</b>	<b>ASTM Test</b>	<b>DECSE Goal</b>	<b>DECSE Measured</b>
Density, kg/m <sup>3</sup>	D1298/D4052	820-850	826.1
Viscosity @ 40°C, mm <sup>2</sup> /s	D445	>2.0	2.42
Distillation IBP, °C	D86	171-182	185
5% recovery, °C	D86		198
10% recovery, °C	D86	210-226	207
20% recovery, °C	D86		222
30% recovery, °C	D86		238
40% recovery, °C	D86		251
50% recovery, °C	D86	254-271	259
60% recovery, °C	D86		266
70% recovery, °C	D86		274
80% recovery, °C	D86		287
90% recovery, °C	D86	310-321	314
95% recovery, °C	D86		338
FBP	D86	326-360	350
Carbon, mass %	D5291		86.3
Hydrogen, mass %	D5291		13.4
Sulfur, ppm	D5453**	<10	3.1
Avg. molecular weight			196.5*
Saturates, vol %	D1319	55-70	70.7
Olefins, vol %	D1319	1-3	2.3
Aromatics, vol %	D1319	25-32	27.0
Aromatics, mass %	D5186		28.5
Polyaromatics, mass %	D5186	3-10	9.6
Non-aromatics, mass %	D5186		71.2
Sediment, water, vol %	D1796	<0.05	< 0.01
Ash, mass %	D482		<0.001*
Ramsbottom carbon	D524		0.01*
Copper corrosion	D130		1A*
Heat Comb, net, MJ/kg	D240		43.1*
Flash point, PMCC, °C	D93	>52	71
Cetane number	D613	42-48	44.8
Cetane index	D976		53.6*
Cloud point, °C	D2500		-21.0
Pour point, °C	D97		-21.0
HFRR** lubricity, μm	D6079		635/355* ****

**Notes:** \* Value based on intermediate scale-up of fuel blend  
 \*\* Phillips used ASTM D4045 for sulfur determination  
 \*\*\* HFRR = high-frequency reciprocating rig  
 \*\*\*\* Values without/with 205 ppm Octel FOA 35a additive



#### **A.4 Selection of Fuel Sulfur Levels**

The sulfur contents selected for the test fuels were 3-, 30-, 150-, and 350-ppm. Sulfur content is defined as the mass fraction of elemental sulfur in the fuel. The 3-ppm fuel is intended to represent a fuel that is essentially sulfur-free. A sulfur dopant mix was used to increase the sulfur content of the 3-ppm base fuel to desired levels. The 30-ppm fuel is intended to represent a fuel that meets a proposed 30-ppm diesel fuel sulfur standard. The 150-ppm fuel is intended to represent a fuel of intermediate sulfur content, and was part of the oil industry's response to EPA's 2007 emissions and diesel fuel sulfur rulemaking. The American Petroleum Institute indicated this sulfur level could be made available in the near-term. The 350-ppm fuel is intended to represent a fuel of sulfur content consistent with the current U.S. average.

#### **A.5 Selection of Sulfur Dopants**

##### ***A.5.1 Technical Background***

Virtually all the mass of the fuel is oxidized in the engine: the carbon in the fuel is oxidized to CO<sub>2</sub>, the hydrogen in the fuel is oxidized to water, and the sulfur in the fuel is primarily oxidized to SO<sub>2</sub>. The composition of the engine exhaust is essentially a function of the mass fraction of each of these fuel elements. According to this view, the amount and chemical identity of sulfur in the engine exhaust is independent of the identity of the sulfur compound(s) used to dope the fuel, and the effect of varying sulfur levels in the fuel could be duplicated by merely adding SO<sub>2</sub> to the exhaust.

However, to increase the realism of the test and to allow for the possibility that some small amount of sulfur-containing compounds may remain unburned, sulfur dopants were used. This ensures that sulfur is contained in the test fuels in a way that is similar to the indigenous sulfur in diesel fuel. In this context, "similar" is defined by the following statements:

1. The chemical forms of the sulfur compounds used to dope the fuel are similar to those that are indigenous to diesel fuel.
2. The volatility of the sulfur compound(s) used to dope the fuel is similar to the volatility of diesel fuel.

##### ***A.5.2 Information on Sulfur Compounds in Diesel Fuels***

Information on the exact chemical identity of naturally occurring sulfur compounds in diesel fuel is sparse. Although there is consensus concerning the general classes of chemical compounds present, no complete information on the speciation of sulfur compounds in diesel fuel could be located. Conversations with industry sources and review of a comprehensive study of sulfur compounds in crude oil performed by the U.S. Bureau of Mines<sup>1</sup> showed that:

- Various substituted dibenzo[b]thiophenes and benzo[b]thiophenes are the most common sulfur-containing constituents of diesel fuel, with the dibenzo[b]thiophenes being more abundant than the benzo[b]thiophenes.
- Other sulfur-containing constituents include disulfides and sulfides. The sulfides include cyclic and alkyl aryl sulfides.

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<sup>1</sup> Sulfur Compounds in Crude Oil, U.S. Bureau of Mines Bulletin 659, (1972).

### A.5.3 Logistical Criteria

Because dopants must be commercially available in the necessary quantities, selection is limited in practice to sulfur compounds offered by commercial chemical vendors in multi-kilogram quantities at reasonable cost.

### A.6 Selection of Dopant Composition

A dopant composition was developed that represents each of these four classes of sulfur compounds: dibenzo[b]thiophenes, benzo[b]thiophenes, disulfides, and sulfides, and whose volatilities were within the diesel fuel range. Table A-2 describes this dopant composition, and properties of the dopants are shown in Table A-3.

Table A-2. Dopant composition

Constituent	Dopant Mass/ Sulfur Mass	Desired Mass Percent Sulfur	Dopant (wt%)
Dibenzo[b]thiophene	5.75	50	59.4
Benzo[b]thiophene	4.18	30	25.9
di-t-butyl disulfide	2.78	10	5.7
ethyl phenyl sulfide	4.31	10	8.9
<b>Totals</b>		<b>100</b>	<b>100.0</b>

Table A-3. Properties of proposed dopants

Constituent	CAS Number	MW	Sulfur Atoms	Sulfur (%)	Constituent Mass/ Sulfur Mass	Boiling Point (°C)	Melting Point (°C)	Density (kg/L)
Dibenzo[b]thiophene	132-65-0	184.26	1	17.40	5.75	332	99	*
Benzo[b]thiophene	95-15-8	134.20	1	23.90	4.18	221	29	1.149
di-t-butyl disulfide	110-06-5	178.36	2	17.98	5.56	200	*	0.923
ethyl phenyl sulfide	622-38-8	138.23	1	23.20	4.31	204	*	1.021

\* Data not available.

#### A.6.1 Sulfur Levels of Doped Fuels

Table A-4 shows the analysis values for the sulfur levels of several samples of the various doped fuels.

**Table A-4. Sulfur levels of doped fuels**

<b>Nominal Sulfur Content (ppm)</b>	<b>Average Sulfur Content As Analyzed (ppm)</b>
30	30.2
150	130
350	308

## **A.7 Active Lean-NO<sub>x</sub> Catalyst Reductant**

### **A.7.1 Background**

The lean-NO<sub>x</sub> catalysts used in this program required the use of a chemical reductant, which is used to facilitate NO<sub>x</sub> reduction.

### **A.7.2 Rationale for Reductant Selection**

Because using a separate, dedicated reductant fuel supply increases logistical complexity (requiring both separate on-board storage and a separate fuel supply infrastructure), it is anticipated that the engine fuel could probably be used for this purpose.

If the dopant mixture used for the engine fuel supply is representative of the sulfur-containing compounds native to diesel fuel, it should also be representative of diesel fuel used as a reductant. Thus, the same doped fuel was used as a reductant, where needed. If other diesel fuels were used as reductants, they could differ in the nature of sulfur-containing species present, and would inevitably differ in other fuel properties. For this reason, if additional experiments were performed to compare the reductant performance of fuels with native sulfur content of doped fuels, it would be difficult to solely attribute any observed difference in emission control device performance to the type of sulfur compounds present in the reductant fuel.

Consistent with this rationale, the test fuels used as reductants are the same as those used as engine fuel.

## **A.8 Fuel Quality Control Procedures**

Quality control procedures were implemented to ensure that both the base and doped fuels met initial specifications and maintained their integrity as they are transported to the point of use.

The procedures included:

- Pre-cleaning of tank trucks, drums, and other containers used to transport fuel.
- Numbering of fuel containers to allow each test to be associated with a specific container of fuel.
- Sampling and analysis of each lot of fuel before shipment to verify that it meets project specifications.
- Drawing samples from each container of fuel. These samples were retained until the project was complete. [Not all samples were analyzed, but they were available, if needed.]

- The samples from the first, middle, and last containers in each separate delivery of fuel were analyzed for sulfur and density. Examining these basic fuel properties helped verify that the correct fuel was used.
- Comparison of pre- and post-shipment fuel analysis results.

## **Appendix B - DECSE Lubricating Oil Selection and Test Procedures**

This appendix covers the selection and use of the engine lubricating oil for the DECSE Program.

### **B.1 Objectives for Selection of Lubricating Oil**

The selection of the DECSE lubricating oil was intended to meet the following objectives:

- Oils meeting the requirements of Advanced Petroleum Institute CH-4 are formulated to provide adequate lubrication, and to have the anti-wear, dispersant, detergent, and other necessary operational qualities required by heavy-duty diesel engines designed to meet modern emissions standards. Therefore, the lubricating oil should be a commercial product meeting CH-4 specifications.
- The viscosity grade should be 15W40 as defined by SAE J300. This is the predominant viscosity recommendation for heavy-duty diesel engines in the United States.
- The lubricating oil should be a product with significant market share and be representative of oils used in the marketplace.
- The sulfur content of the lubricating oil selected should be at the low end of the observed range of commercially available products.
- The lubricating oil should be purchased as a single batch to eliminate the possibility of formulation changes during the course of the study.

### **B.2 Results of Lubricating Oil Selection Process**

Based on this information and analysis, the EMA recommended that Shell Rotella T 15W40 oil would meet commercial specifications, have a significant market share, and have a sulfur content of about 4,000 ppm, which is at the lower end of the range for commercial oils. For these reasons, and because supply of this oil was available in a single batch, the Shell Rotella T 15W40 lubricating oil was selected.

### **B.3 Procedures for Lubricating Oil Use**

Several procedures were developed for the use of engine oil in the DECSE project.

#### ***B.3.1 Aging***

The lubricating oil was aged for at least 10 hours after each oil change to stabilize the oil consumption and to minimize the chance that sulfur release or particulate matter formation related to the use of new oil would affect the variability of experimental results.

#### ***B.3.2 Oil Change Interval***

The oil and oil filter change interval was 250 hours, maximum. However, a double flush of oil was not considered necessary. The amount of oil left in the pump and internal passageways is estimated to be negligible. The engine oil in the evaluation engine was not changed during the course of testing.

### **B.4 Lubricating Oil Sampling and Analysis**

Lubricating oil samples are collected and analyzed periodically according to the following procedures.

### **B.4.1 Sample Collection Procedures**

Oil samples are collected from the engine at “warmed up” conditions while idling. Samples are taken from the oil gallery, but methods of collection depend on the given engine’s configuration. A 240-mL sample is adequate to complete all routine analyses, leaving additional samples available for confirmatory or additional analyses. After sampling, an identical amount of fresh oil is added to the engine to compensate for the drained sample. (The sample line is flushed before collecting the sample, and the oil drained from the line reintroduced to the engine.) Sample bottles are labeled to identify the test laboratory, test hours (hours since last oil change), engine type, fuel sulfur level, date sampled, and the corresponding catalyst.

For each 250-hour aging sequence, oil samples are taken at 0, 50, 100, 150, 200, and 250 hours. The initial oil sample (zero hour) for each sequence was not collected until the engine had warmed up and had adequate time to circulate (about 30 minutes to 1 hour).

### **B.4.2 Oil Analysis Procedures**

Table B-1 outlines the oil analysis procedures used for each oil sample.

**Table B-1. Oil sample analyses**

<b>Property</b>	<b>Test Method</b>	<b>Significance</b>
Kinematic Viscosity (at 40°C)	D 445	Low viscosity identifies fuel or coolant leaks. High viscosity indicates oxidation or soot thickening.
Total Base Number (TBN)	D 4739 or D 2896	A measure of the base reserve available for acid neutralization; depletes as oil ages. Rate of depletion may be dependent on fuel sulfur level
Additive Metals (Ca, Mg, Zn, P)	ICP	Confirms additive concentration (QC). Rise in Ca or Mg level can indicate base oil volatility.
Wear Metals (Fe, Pb, Cu, Cr)	ICP	Characterizes wear rates; can indicate abnormal wear or corrosion of certain components.
Contaminant Metals (Si, Na)	ICP	Indicative of coolant leaks
Soot	IR or TGA	High soot levels can thicken the oil and accelerate wear rates. IR methods are quicker and less expensive and are typically calibrated to correlate with TGA results.
Sulfur*	X-ray Fluorescence D 4927	Lends insight into the fate of crankcase sulfur; will help in the interpretation of the test results.

\*not all samples were analyzed for sulfur content

## **B.5 Consideration of Lubricating Oil Sulfur Content**

Sulfur from the lubricating oil can contribute to overall EO sulfur emissions. There is some sulfur in the lubricating oil base stock. However, much of the sulfur content is associated with detergents and anti-wear additives in the additive packages of commercial CH-4 lubricating oils. Specifically, the anti-wear additives typically contain sulfur and phosphorus in the form of zinc dithiophosphates. Many detergent packages contain alkyl sulfonates as well.

The net effect is that commercial diesel engine lubricating oils contain from 4,000- to 10,000-ppm sulfur. Proven substitutes for the sulfur-bearing additives are not available and, overall, little research has been done to date on the development of a low-sulfur lubricating oil for diesel engines. Therefore, the near-term possibility of procuring a zero-sulfur lubricating oil equivalent to current commercial CH-4 oils was not considered favorable.

The use of synthetic oil was also considered. Although synthetic oils do not use a petroleum-derived base stock and will not have any sulfur from the base stock, they still use sulfur-containing additives. Moreover, because petroleum-derived base stocks are highly refined and hydrotreated, lowering the base stock contribution to the overall sulfur content through the use of synthetic oils would be expected to provide only a minor advantage.

### ***B.5.1 Oil Analysis Results***

An analysis of three samples of fresh, unused Shell Rotella T 15W40 oil showed an average sulfur content of 3,520 ppm. The oil contained 2,600 ppm calcium, 1,300 ppm zinc, 1,200 ppm phosphorus, and 500 ppm boron.