Diesel Emission Control – Sulfur Effects (DECSE) Program

Phase I Interim Data Report No. 1
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The U.S. Department of Energy
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The test program and subsequent data analysis represents a collaborative effort of a technical work group consisting of representatives from the U.S. Department of Energy, National Laboratories, Engine Manufacturers Association, and 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 of this effort. 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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List of Acronyms

BPT – balance point temperature
BSCO – brake-specific carbon monoxide
BSFC – brake-specific fuel consumption
BSHC – brake-specific hydrocarbons
$BSNO_x$ – brake-specific oxides of nitrogen
BSPM – brake-specific particulate matter
CDPF – catalyzed diesel particulate filter
CO – carbon monoxide
CPSI – cells per square inch
CR-DPF – continuously regenerating diesel particulate filter
CVS – constant volume sampling
DECSE – Diesel Emission Control—Sulfur Effects
DOC(s) – diesel oxidation catalyst(s)
DOE – U.S. Department of Energy
DPF – diesel particulate filter
ECU(s) – electronic control unit(s)
EGR – exhaust gas recirculation
EMA – Engine Manufacturers Association
EO – engine-out
ETS – Engineering Test Services
FEP – fuel economy penalty
FEV – FEV Engine Technology
FLRS – full-load, rated speed
FTP – Federal Test Procedure
HC – hydrocarbon(s)
HFRR – high frequency reciprocating rig
HSDI – high-speed, direct injection
MECA – Manufacturers of Emission Controls Association
MY – model year
NM – noble metal
NO_x – oxides of nitrogen
NREL – National Renewable Energy Laboratory
OEM – original equipment manufacturer
OICA – Organisation Internationale des Constructeurs d'Automobiles
ORNL – Oak Ridge National Laboratory
PM – particulate matter
ppm – parts per million
R&D – research and development
SOF – soluble organic fraction
SwRI – Southwest Research Institute
TBN – total base number
THC – total hydrocarbon
TWC – three-way catalyst
WVU – West Virginia University

Executive Summary

The Diesel Emission Control–Sulfur Effects (DECSE) program is a joint government/industry program to determine the impact of diesel fuel sulfur levels on emission control systems whose use could lower emissions of nitrogen oxides (NO_x) and particulate matter (PM) from on-highway trucks in the 2002-2004 model years. The program is designed to enhance the collective knowledge base on engines, diesel fuels, and emission control technologies in a systems approach to (1) guide industry in developing lower emitting applications of their products, and (2) provide a portion of the technical basis for government decisions on regulating the content of sulfur in diesel fuel.

Phase 1 of the program was developed with the following objectives in mind:

(A) Evaluate the effects of varying the level of sulfur content in the fuel on the emission reduction performance of four emission control technologies; and

(B) Measure and compare the effects of up to 250 hours of aging on selected devices for multiple levels of fuel sulfur content.

Four emission control technologies are being tested in Phase 1 of the program: (1) NO_x adsorbers; (2) diesel particulate filters (DPF); (3) lean-NO_x catalysts; and (4) diesel oxidation catalysts (DOC). 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 are 3, 16 (NO_x adsorber 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 they 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 stream are exhaust flow rate, stream temperature, and concentrations of NO_x, hydrocarbons (HC), carbon monoxide (CO), and PM.

Participants in the program include representatives from the U.S. Department of Energy's Office of Heavy Vehicle Technologies within the Office of Transportation Technologies (OTT), the National Renewable Energy laboratory (NREL), Oak Ridge National Laboratory (ORNL), the Engine Manufacturers Association (EMA), and the Manufacturers of Emission Controls Association (MECA).

ES.1 NO_x Adsorber

A description of the NO_x adsorber technology and a test matrix are found in Section 2.1. The data generated from this program are currently being analyzed. It is anticipated that the results for the NO_x adsorber technology will be reported in a second Interim Report by October 1, 1999.

ES.2 Continuously Regenerating Diesel Particulate Filters and Catalyzed Diesel Particulate Filters

Two diesel particulate filter (DPF) technologies were chosen for testing in the DECSE program: (1) the continuously regenerating diesel particulate filter (CR-DPF); and (2) the catalyzed diesel particulate filter (CDPF). The DPFs are designed to remove PM from the exhaust by collection on a filter element, which, in these cases, are ceramic wall-flow elements. The critical issue for these technologies is the cleaning or regeneration of the DPF by oxidation of the collected PM to prevent the device from plugging. The CR-DPF accomplishes regeneration by continuously generating NO_2 with the help of a diesel oxidation catalyst (DOC) upstream of the filter. The CDPF accomplishes DPF regeneration by using a catalyst coating on the filter element to promote oxidation of the collected PM.

The two major components of the test program are (1) emissions tests (PM and selected gases), and (2) experiments to measure the effect of fuel sulfur level on the regeneration temperature of the DPFs. Emissions tests were performed using the OICA 13-mode test procedure and tests at peak-torque and "road-load" steady-state conditions of a Caterpillar 3126 engine. Regeneration temperatures were determined at selected engine speeds by measuring the change in pressure across the DPFs while operating the engine at different temperature and torque settings. This interim report presents results from testing with the first two fuels, 3 ppm and 30 ppm.

The results obtained thus far demonstrate the concern about the effects of sulfur on the performance of DPF technologies. PM reduction efficiency over the OICA test cycle was measured at 95% for each of the two devices when tested with the 3-ppm sulfur fuel. However, with 30-ppm sulfur fuel, this weighted OICA efficiency dropped to 72% and 74% for the CR-DPF and CDPF, respectively. This decrease in PM reduction efficiency is illustrated in Figure ES.3. Although not yet confirmed by chemical analysis of the collected PM, this loss in PM control is likely caused by increased sulfate formation with the 30-ppm fuel. A complete PM breakdown analyses for all collected filters will be reported for each of the four fuels in the final DECSE report to confirm this result.

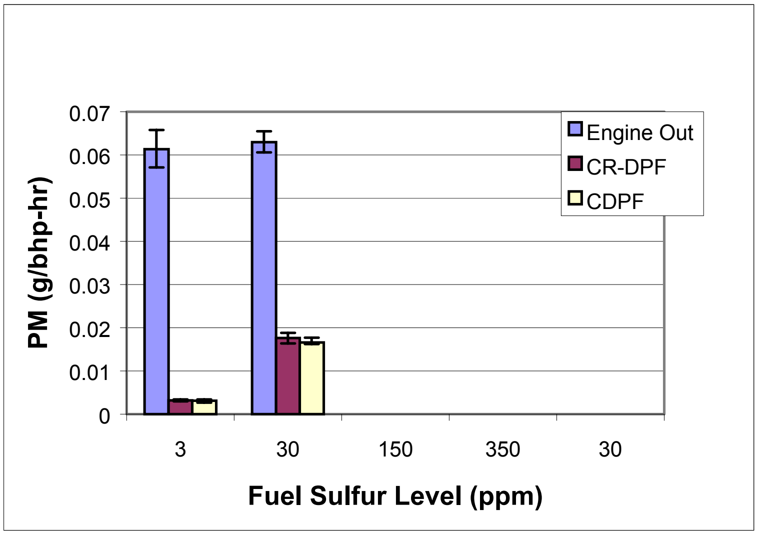


Figure ES.3. Interim results on the effects of fuel sulfur on PM reduction efficiency

Although designed as PM reduction devices, the DPFs reduced total hydrocarbon (THC) by 58% to 91% and carbon monoxide (CO) by 90% to 99%. These reductions were not affected to any significant degree by fuel sulfur level.

Another critical concern on the impact of sulfur on the operation of these DPF devices is its possible effect on the filter regeneration capability. Results to date show that the regeneration temperatures are slightly higher when testing with the 30-ppm fuel compared to results generated with the 3-ppm sulfur fuel. Given the uncertainties in the data, however, it is too early to reach definitive conclusions from testing the first two fuels (3 ppm and 30 ppm). Additional testing is planned with 150-ppm and 350-ppm fuels.

In addition to emissions and regeneration temperature tests using fuels containing 150- and 350-ppm sulfur, a second round of emissions tests with 30-ppm fuel is planned to determine the impact of aging on DPF performance.

ES.3 Lean-NO_x Catalyst

Two types of lean-NO_x catalysts were chosen for the study. The high-temperature lean-NO_x catalyst contained a base metal/zeolite formulation supported on a single, 400 cells-per-square-inch (cpsi), cordierite substrate. The low-temperature catalyst contained a precious metal formulation supported on two 400-cpsi cordierite substrates. Both catalysts require a reductant (supplemental hydrocarbons) in the exhaust stream to reduce the NO_x emissions. The diesel test fuel was supplied as the reductant, and the secondary (reductant) fueling rate was optimized for NO_x reduction while HC and PM slippage were controlled. The high-temperature catalyst was evaluated on a Cummins ISM370 engine and the low-temperature catalyst will be evaluated on a Navistar T444E engine, which were chosen to provide a range of exhaust temperatures.

The main concern with sulfur in diesel fuel is that the sulfates produced during combustion can be adsorbed on the active catalyst surface and block the access of NO_x and HC, resulting in a decrease in the NO_x reduction efficiency and an increase in fuel consumption and HC slip.

For each fuel type (3-, 30-, 150-, and 350-ppm sulfur) fresh catalysts were degreened for ten hours (with 3-ppm sulfur fuel), then will be aged for up to 250 hours. The catalyst aged with 350-ppm fuel will be retested with 30-ppm fuel to determine its ability to recover from use with high-sulfur fuel. Emission evaluations are being performed after 0, 50, 150, and 250 hours of aging with each fuel. This interim report presents only the initial (i.e., zero-hour) emissions results from the high-temperature catalysts with each fuel.

The emission evaluation test selected for the high-temperature lean-NO_x catalyst is comprised of four steady-state modes selected from the OICA 13-mode steady-state test cycle. The overall fuel economy penalty (FEP) due to introduction of fuel reductant (secondary fuel consumption) averaged across modes, was about 4%.

The effects of catalyst inlet temperatures and diesel fuel sulfur level on NO_x reduction efficiencies are shown in Figure ES.4. Secondary fuel consumption rates are also shown. Within the operating temperature range of 360°C to 600°C, the NO_x conversion varies from 0% to 30%. The fuel sulfur trends indicate that the NO_x reduction is lower with the higher fuel sulfur levels but the changes were not statistically significant. Data on sulfur aging effects (50, 150 and 250 hours) are not yet available.

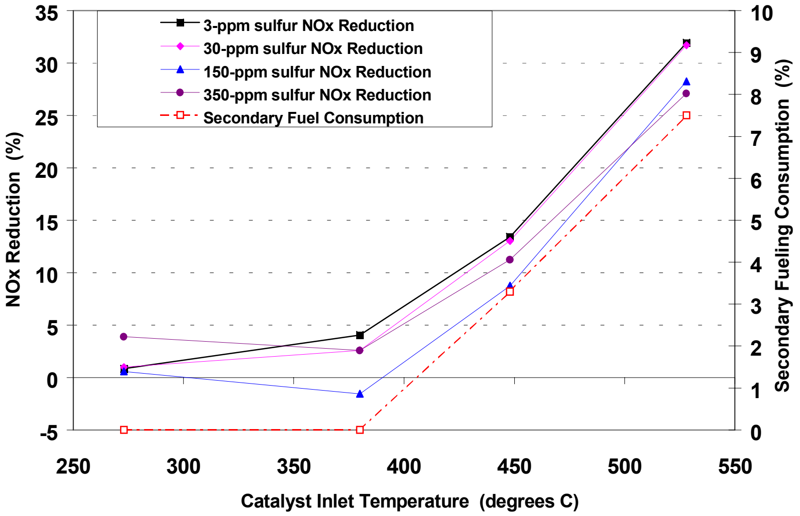


Figure ES.4. Effects of catalyst inlet temperature and fuel sulfur level on NO_x reduction efficiency of the fresh high-temperature lean-NO_x catalyst

Additional conclusions are as follows:

- Diesel sulfur level may have an effect on PM emissions from the high-temperature lean-NO_x catalyst. With 3-ppm sulfur fuel, PM reduction efficiency (based on the 4-mode composite test) was statistically significant at 16%. However, with high sulfur fuels, there was an increase in PM (compared to engine-out emissions), or the reduction efficiency was not statistically significant. This suggests the formation of PM by the lean-NO_x catalytic converter with high sulfur fuels.

- With 150- and 350-ppm sulfur fuels, the engine out sulfate emissions increased by a factor of 2 to 5 compared to the levels observed with 3-ppm sulfur fuel. With the high-temperature lean-NO_x catalyst, the post-catalyst sulfate emissions increased by a factor of 10 to 20. Higher sulfate emissions increase the overall PM emissions.

- The high-temperature lean-NO_x catalyst had difficulty effectively cleaning up the THC emissions resulting from secondary fuel injection (for the NO_x reductant). The post-catalyst emissions (4-mode composite) of HC increased by a factor of 2 to 3 over engine-out emissions, and CO increased by a factor of 6 to 7. The catalyst apparently has poor oxidation power for HC. The CO emissions present downstream of the lean-NO_x catalyst indicate that the partial oxidation of HC was one of the main catalytic reactions. In practical applications, a DOC might be required for this type of high-temperature lean-NO_x catalyst.

- A proper secondary fueling strategy will be required for diesel application of this type of high-temperature lean-NO_x catalyst.

ES.4 Diesel Oxidation Catalyst

Diesel oxidation catalysts are a technology designed to reduce HC, CO and the soluble organic compounds associated with PM emissions found in diesel engine exhaust. These compounds are reduced by oxidation of these compounds over a precious metal catalyst. Selection of catalyst formulation is based primarily upon the exhaust stream temperature range, with the objective of maximizing the effective conversion range of the device. Catalysts highly loaded with precious metal are active at lower exhaust temperatures, and their higher activity provides increased reduction efficiencies over a wider range of engine operation.

A major concern with higher precious metal loadings is the catalyst's proclivity to converting SO_2 in the exhaust gas to sulfate. The performance characterizations of fresh (not aged) DOCs were run on a Cummins ISM370 engine using a 3-ppm sulfur base fuel and fuels with 30-, 150-, and 350-ppm sulfur. CO, HC, and PM emissions were analyzed before and after the DOC over the heavy-duty Federal Test Procedure (FTP), the same 4-mode special test cycle as the lean NO_x test program, and mode 2 (high exhaust temperature) of the OICA 13-mode test cycle.

Fuel sulfur level had a modest effect on HC reduction efficiency (approximately 4 to 8 percentage points lower with high sulfur fuel) and no effect on CO reduction efficiency. However, catalyst-out PM emissions during the high-torque (high-exhaust temperature) steady-state tests (OICA mode 2) showed a strong fuel sulfur influence (shown in Figure ES.5). With 3-ppm sulfur fuel, the PM reduction efficiency was statistically significant at 26%. However, with higher levels of fuel sulfur there are significant increases (negative reduction efficiencies) in post-catalyst PM emissions. Chemical analysis of this PM is consistent with SO_2 in the engine exhaust being oxidized by the DOC and condensing as sulfate-laden PM that is collected on the filter.

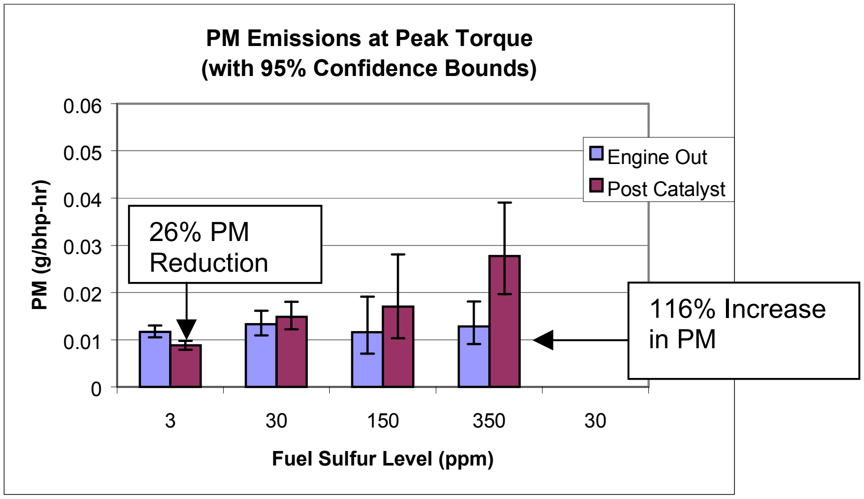


Figure ES.5. DOC PM reduction efficiencies at peak torque as a function of fuel sulfur level (Cummins ISM370)

Section 1

Introduction

This interim data report summarizes results as of August, 1999, from the joint government/industry test program on "diesel emission control–sulfur effects" (DECSE). Questions concerning the DECSE test program may be addressed to either the DECSE Deputy Program Manager, Wendy Clark (303-275-4468, wendy_clark@nrel.gov) or the DECSE Communication Chair, Helen Latham (614-424-4062, lathamh@battelle.org). You may also visit the Web site at http://www.ott.doe.gov/decse.

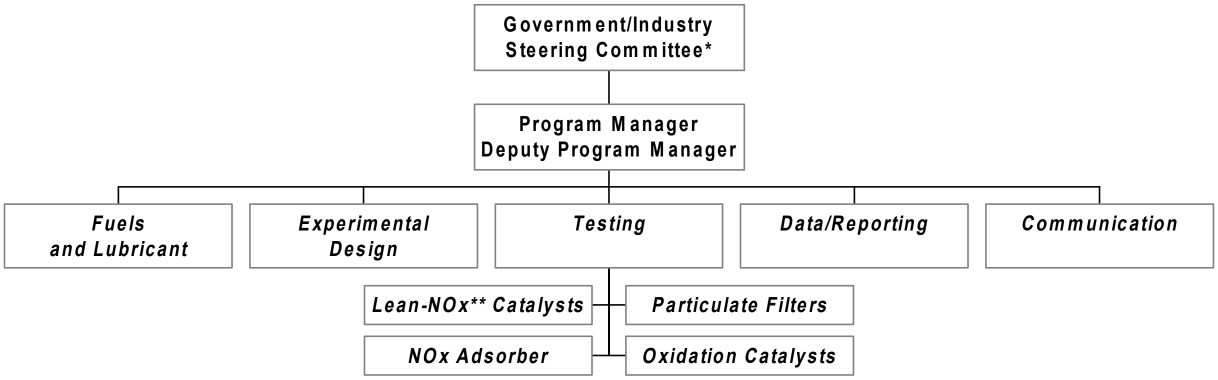
1.1 DECSE Objective

The objective of the DECSE test program is:

> To determine the impact of diesel fuel sulfur levels on emission control systems that could be implemented to lower emissions of nitrogen oxides and particulate matter from on-highway trucks in the 2002−2004 time frame.

The program, spanning calendar year 1999, is being conducted by the U.S. Department of Energy's (DOE) Office of Heavy Vehicle Technologies within DOE's Office of Transportation Technologies; 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).

The DECSE program is overseen by a government/industry steering committee. Technical committees are designed to monitor and report on testing of four emission control technologies. Figure 1.1-1 shows the organization of the project.



*Steering Committee: EMA, MECA, DOE, ORNL, NREL
**NO_x = oxides of nitrogen

Figure 1.1-1. DECSE program management

1.2 Experimental Design Considerations

The DECSE program is designed to result in information on the effects of diesel fuel sulfur levels on the operation of four diesel emission control technologies with different engine applications. A guiding principle in designing the DECSE tests was to use "current" engine, fuel (all properties except sulfur level), and lubricant technologies. The emissions control technologies are: (1) continuously regenerating diesel particulate filter (CR-DPF) and catalyzed diesel particulate filter (CDPF), (2) high-temperature and low-temperature lean-NO_x catalysts, (3) high precious metal and low precious metal diesel oxidation catalysts (DOC), and (4) NO_x adsorber. The devices tested include commercially available technologies as well as state-of-the-art technologies that are under development. The engines in the DECSE program serve principally to provide a source of diesel exhaust to challenge the emissions control devices, as shown in Table 1.2-1.

Table 1.2-1. DECSE Engines

Engine	Displacement (L)	Type	Peak kW @ rpm	Peak Torque (Nm @ rpm)
Caterpillar 3126	7.2	I 6	205 (275 hp) @ 2,200	1,086 (800 ft-lb) @ 1,440
Navistar T444E	7.3	V 8	157 (210 hp) @ 2,300	705 (520 ft-lb) @ 1,500
Cummins ISM370	10.8	I 6	276 (370 hp) @ 1,800	1,830 (1,350 ft-lb) @ 1,200
DaimlerChrysler/ DDC Prototype	1.9	I 4	81 (109 hp) @ 4,200	270 (199 ft-lb) @ 2,000

Critical characteristics of the exhaust stream are exhaust flow rate, exhaust stream temperature and concentrations of NO_x, sulfur dioxide (SO_2), and particulate matter (PM). The emissions control devices were properly sized to meet the needs of the given exhaust flow rate range. The temperature of the exhaust gases depends on the duty cycle, and several engines were selected to provide a range of exhaust temperatures that are characteristic of the vehicle applications. For the first three emissions control technologies, the engines are model year 1998 or 1999 engines equipped with electronic control units (ECUs), turbocharging, an after-cooler, and no exhaust gas recirculation (EGR). For the NO_x adsorber technology, the only engine system available to the program and equipped with control technology for controlling lean/rich operation (critical to NO_x adsorber technology) is a prototype light-duty engine with available EGR. The emissions control devices and engines are described in more detail in later sections of this report.

The DECSE program is designed to provide data that will allow DOE and its national laboratories to plan future research and development (R&D) activities on engines, fuels, and emissions control technologies. The U.S. Environmental Protection Agency (EPA) will review the DECSE results as it prepares its Notice of Proposed Rulemaking on the composition of diesel fuel (EPA 1999. *Control of Diesel Fuel Quality,* Advance Notice of Proposed Rulemaking, EPA, *Federal Register*, Vol. 64, No. 92, pp. 26242-26158. [May 13, 1999]). The data will also be used by industry to guide product development. To result in the most timely information, the DECSE test program was set up as a phased program. Phase 1, the subject of this report, aims to obtain information on the effects of sulfur in diesel fuel on the emission control devices in the first 250 hours of operation. Phase 1 results are expected to allow a more detailed Phase 2 study of particular topics related to the effects of sulfur and to extended durability testing.

Table 1.2-2 summarizes the Phase 1 test program in terms of emissions control technologies, engines, fuel sulfur levels, and aging time. In this report, fuel sulfur content values are nominal, not actual. Actual values will be shown in the final report, after all analyses on these fuels are completed. Fuel sulfur levels greater than 3 ppm were produced by doping the base fuel with a mixture of sulfur compounds similar to those indigenous to diesel fuel. Details on fuel selection and composition are given in Appendix A.

A series of evaluation measurements are being made at selected intervals up to 250 hours of aging for certain technologies. A series of replicate tests is designed to provide information on the uncertainty of the measurements. In addition to the aging and evaluation tests, a series of tests is gathering data on the production of PM under engine operating conditions (high-temperature exhaust) most likely to lead to PM generation. The conditions are low engine speed and high torque at mode 2 of the OICA test cycle (European steady-state test cycle). These tests are being conducted for the CR-DPF and CDPF technologies and for the diesel oxidation and lean-NO_x catalysts. For the light-duty diesel truck application, mode 9 (representing a high-temperature point of the US06 test cycle) of the Navistar 9-mode test cycle is being applied to the special PM test for both diesel oxidation and lean-NO_x catalysts. Details are presented in separate sections of this report.

Table 1.2-2. Summary of DECSE Phase 1 Experimental Design

Technology	250 Hours Aging at various fuel-sulfur levels					Evaluation					Engine	Remarks
	3	30	150	350	30*	3	30	150	350	30*		
Diesel Oxidation Catalyst	Special Navistar aging cycle					Navistar 9-mode and simulated FTP-75					T444E (Navistar)	High precious metal loading
	Modified OICA aging cycle					Stabilized OICA and heavy-duty FTP					ISM 370 (Cummins)	Low precious metal loading
Active Lean-NO_x Catalyst	Special Navistar aging cycle					Navistar 9-mode					T444E	Low-temperature catalyst
	Modified OICA aging cycle					Stabilized OICA					ISM 370	High-temperature catalyst
CR-DPF and CDPF	No aging test, used special tests to determine regeneration temperatures and emissions					Steady-state exhaust temperature tests and stabilized OICA					3126 (Caterpillar)	Determine sulfur effect on regeneration temperature
NO_x Adsorber	3	16**	30			3	16**	30			HSDI (DaimlerChrysler/ DDC prototype)	150- and 350-ppm fuel not used based on initial results on lower sulfur levels.
	3-hour aging cycle using 9 temperature points in sequence					NO_x conversion every 50 hours						

*Recovery experiment.

**16-ppm sulfur fuel added to test matrix after 3- and 30-ppm fuel tests were completed.

Sulfur in the exhaust gases originates not only from sulfur in the fuel but also from sulfur compounds in the engine lubricant. Sulfur compounds in the lubricant are designed to provide protection against wear. Sulfur compounds are also found in detergents. In designing the DECSE test program, the fuels and lubricant technical committee researched two options: using a commercial lubricant with sulfur concentrations in the 3,000 to 5,000 ppm level, or using a sulfur-free lubricant.

Calculations provided by the engine manufacturers showed the technical committee that at typical, average oil consumption rates, the contribution to engine-out SO_2 from a 3,500-ppm sulfur-containing lubricant would alone be equivalent to that resulting from operation with a fuel sulfur level of 3 ppm. Further, a cursory search for low-sulfur or zero-sulfur lubricants was not fruitful. Although it is understood that a special lubricant could be formulated with relatively expensive, non-commercial, anti-wear additives and detergents, the committee decided against introducing an additional variable to the experiment. Instead, the committee directed the test laboratories to carefully document oil consumption rates and engine-out SO_2. The commercial lubricant selected, Shell Rotella T® 15W40, has a sulfur content of about 3,500 ppm by weight.

1.3 Schedule for DECSE Results

This interim data report summarizes DECSE results as of August, 1999. As additional data sets become available, they will be released in a series of updates.

Section 2

Description of Technologies and Tests

2.1 NO_x Adsorber

2.1.1 Program Overview

The results of the DECSE test program demonstrate the potential of NO_x adsorber technology across the range of diesel engine operation with a fuel economy penalty less than 4%. That penalty is consistent with: (1) a general upper limit considered viable by engine manufacturers for fleet use, and (2) that used for the lean-NO_x catalysts also being evaluated in the test program. The results show how fresh catalyst performance is affected by sulfur level and how limited aging up to 250 hours affects the performance deterioration rate for three different sulfur levels. Test results include plots of NO_x conversion efficiency for fresh NO_x adsorbers and performance deterioration when operated with 3-, 16-, and 30-ppm fuel sulfur concentrations.

2.1.2 Principle of Operation

A NO_x adsorber catalyst is a flow-through emissions control device that has the potential to significantly lower NO_x, hydrocarbon (HC), and carbon monoxide (CO) emissions from diesel engine exhaust. Because a NO_x adsorber contains high levels of precious metals, it may also be effective in oxidizing the soluble organic fraction of diesel PM.

A NO_x adsorber is a temporary storage device for NO_x. During typical diesel engine operation, NO_x in the lean exhaust gas is stored as a base metal nitrate in the device. Before the NO_x adsorbent becomes fully saturated, engine-operating conditions and fueling rates are adjusted to produce a fuel-rich exhaust. Under these rich conditions, the stored NO_x is released from the adsorbent and simultaneously reduced to N_2 over downstream precious metal sites on the catalyst.

A NO_x adsorber catalyst consists of two principal components: a NO_x adsorbent and a three-way catalyst (TWC). The NO_x adsorbent is typically an alkali or alkaline earth carbonate. These carbonates are capable of chemically interacting with the NO_2 and O_2 in typical diesel engine exhaust to form an alkali or alkaline earth nitrate. Precious metals in the TWC catalyst are responsible for the oxidation of NO to NO_2, which facilitates the adsorption process. Periodically, NO_x stored by the adsorbent is released and reduced to N_2. This process requires a fuel-rich exhaust gas composition and a TWC catalyst. These catalysts are typically based on combinations of platinum (Pt), palladium (Pd), and rhodium (Rh), and they are capable of using the reductants (CO, H_2, and HC) in rich engine exhaust to reduce NO_x selectively to N_2. TWC catalysts have been used for more than 20 years to perform NO_x reduction in the exhaust of stoichiometric gasoline engines.

An engine management system is critical to the operation of a NO_x adsorber system. The engine management system must determine when the NO_x adsorbent is approaching saturation and then trigger the change in engine operation that results in generation of the rich condition required for release and reduction of the stored NO_x. The duration and "richness" (defined by the air-to-fuel ratio) of the rich pulse is also critical. If it is too long and/or too rich, HC and CO can break through the adsorber, which results in poor control of these substances, as well as unnecessary fuel economy penalties.

Combustion in the engine of sulfur compounds in diesel fuel results in the release of SO_2. In a NO_x adsorber, this SO_2 undergoes reactions that are analogous to those of NO_x, and alkali and alkaline earth sulfates are formed. Unlike their corresponding nitrates, these sulfates are extremely stable. It has been shown repeatedly in the literature that the decomposition of these sulfates requires a combination of rich conditions and temperatures exceeding 600°C. As a result, SO_2 in the exhaust is a poison for NO_x adsorption sites without a properly developed regeneration cycle.

The experiments are providing data to address the following study questions:

What is the effect of fuel sulfur level on:

- NO_x reduction efficiency
- Rate of deactivation of catalyst
- Ability of catalyst to recover
- Production of sulfate?

2.1.3 Overview of Test Program

All NO_x adsorber devices were first thermally stabilized with 10 hours of degreening (break-in) in engine exhaust at 400°C. Next, the rich and lean engine operating times were determined, and the NO_x conversion was mapped over the full temperature range (150°C to 550°C, in 50°C increments). Aging of the devices then began. The aging process was interrupted at 50-hour intervals to measure the device performance and to document the extent of deterioration. The experimental matrix is shown in Table 2.1-1.

2.1.4 Experimental

Engine. Given the uniqueness of the required engine operating system, coupled with the time constraints for testing, the DECSE NO_x adsorber technical committee required that the test laboratory have immediate access to a previously developed engine management system that would allow rich/lean operation for a specific engine design. The engine proposed by the single bidder, FEV, is a modern, 1.9-liter, 4-cylinder HSDI engine rated at 81 kW at 4,200 rpm. This engine uses a common-rail injection system. Through a combination of inlet throttling, EGR, and fuel-injection modifications, the engine allows rich/lean operation without affecting driveability. Although the engine management system may not be completely refined, it was required to be reasonably representative of a system with production potential. Before agreeing to its use, the DECSE technical committee reviewed and accepted the performance and emissions data supplied for the proposed engine.

Fuel and Oil. Under contract to NREL, Phillips Chemical supplied fuel to the test laboratory. The test laboratory, FEV, received the fuel in containers identified by sulfur level. The test laboratory blended 50% (by mass) of each of the 3-ppm and 30-ppm fuels to create an additional test fuel, nominally 16-ppm fuel. Shell Rotella T 15W40 engine oil was used. Oil and fuel samples were routinely collected and submitted for analysis.

Catalyst. The NO_x adsorbers supplied to the DECSE program contained a precious metal formulation incorporating Pt, Pd, and Rh, and NO_x adsorbent materials supported on a single 14.4 cm-diameter by 15.2 cm-long, 400-cpsi ceramic substrate for a total volume of 2.5 liters each. Each of the substrates are housed in a stainless steel shell measuring approximately 15.2 cm in diameter by almost 66.04 cm in length, including two 15.2 cm-long by 7.6 cm in diameter inlet and outlet pipes. NO_x adsorber devices, each assembled into a canister, were supplied by an emissions control original equipment manufacturer (OEM). The samples used are identified as 3a, 3b, 16a, 16b, 30a, 30b, S3, and S4, to track at which fuel sulfur levels the tests were performed.

Table 2.1-1. Experimental Design for NO_x Adsorber Catalyst Test Program (1.91 4V DI-Common Rail Diesel Engine with NO_x Adsorber Catalyst)

Aging Hours	**Fuel Sulfur Level** (ppm)		
	3	**16**	**30**
0-12	EO 3a 3b (Map & Aging [1])	EO 16a 16b (Map & Aging)	EO 30a 30b (Map & Aging)
22	EO 3a 3b (Check[2])	EO 16a 16b (Check)	EO 30a 30b (Check)
34	EO 3a 3b (Check)	EO 16a 16b (Check)	EO 30a 30b (Check)
44-56	EO 3a 3b (Aging)	EO 16a 16b (Aging)	EO 30a 30b (Aging)
68	EO 3a 3b (Check)	EO 16a 16b (Check) if required	EO 30a 30b (Check)
82	EO 3a 3b (Check)	EO 16a 16b (Check) if required	EO 30a 30b (Check)
94-106	EO 3a 3b (Aging)	EO 16a 16b (Aging) if required	EO 30a 30b (Aging)
118	EO 3a 3b (Check)	EO 16a 16b (Check) if required	EO 30a 30b (Check)
132	EO 3a 3b (Check)	EO 16a 16b (Check) if required	EO 30a 30b (Check)
144-156	EO 3a 3b (Aging)	EO 16a 16b (Aging) if required	EO 30a 30b (Aging)
168	EO 3a 3b (Check)	EO 16a 16b (Check) if required	Not done
182	EO 3a 3b (Check)	EO 16a 16b (Check) if required	Not done
194-206	EO 3a 3b (Aging)	EO 16a 16b (Aging) if required	Not done
216	EO 3a 3b (Check)	EO 16a 16b (Check) if required	Not done
228	EO 3a 3b (Check)	EO 16a 16b (Check) if required	Not done
238-250	EO 3a 3b (Aging)	Not done	Not done

EO = engine-out test
3a, 3b, 16a, 16b, 30a, 30b= post-catalyst tests

[1] Engine mapping includes gaseous emissions measurements at 150°, 200°, and 550°C, plus PM measurement at 350°C inlet temperature. It is performed just before the zero hour aging test.
[2] Engine check includes gaseous emissions at 350°C inlet temperature (changed to 400°C for 16a/b).

2.1.5 Special Requirements

Engine Management System. The technical committee determined the final acceptability of the rich/lean engine management system by evaluating the NO_x conversion achieved over the catalyst's temperature window during the initial calibration work. Peak conversion was expected to be greater than 80%, and the temperature window was expected to show at least 30% conversion at the extremes of 150°C and 500°C when operated with base fuel (fuel with sulfur concentration of 3 ppm).

Device Regeneration. No attempts were made at this time to desulfurize the catalyst because diesel exhaust gas temperatures do not reach the high level necessary to remove sulfur from the device material during normal operation, and a R&D effort on desulfurization was outside the scope of Phase 1. Desulfurization will be investigated in the next phase of the program.

Systems Flushing Between Tests. To avoid contamination, the engine and test cell fuel systems were flushed when fuels were changed. Fuel filters were changed at the same time. Also, because of possible fuel dilution, engine oil and filters were changed.

2.1.6 Test Procedure

Device Set-Up. FEV configured the engine exhaust flow so that two NO_x adsorber devices could be tested simultaneously, increasing the statistical confidence level in the results.

Conditions were adjusted to maintain equal flow. Maximum back-pressure at the engine was 1.5" of mercury (Hg) unless FEV obtained advanced approval from the DECSE technical committee for a variation.

Test Sequence. Testing followed a five-step sequence:

- Degreening
- Rich and lean timing engine control calibration
- Catalyst sample performance mapping
- Device aging
- Periodic reassessment at a single temperature during aging.

All testing was conducted at 3,000 rpm, providing stable operation at the catalyst's design airflow. Steps in the sequence are described below.

Degreening. Each set of catalysts was first thermally stabilized with a substitute, low-sulfur base fuel (typical of Swedish diesel) to expedite work. Degreening was conducted at 400°C catalyst inlet temperature and 3000 rpm for 10 hours. The engine control system was set to operate lean only (normal diesel operation).

Rich/Lean Time Optimization. The rich/lean engine management system was calibrated with the times for rich and lean operation set to maximize NO_x conversion, except that the fuel consumption penalty did not exceed 4% at any test point. This determination was carried out using the base fuel. The same rich/lean time settings found with the base fuel were used for tests with the other two sulfur levels. Conversion calculations were based on the average of the last 7 of a 15-cycle series.

The 4% fuel consumption penalty was selected as a maximum FEP for commercial operations and because this magnitude of FEP could be commercially viable, and to provide a basis of comparison with the lean-NO_x catalyst technologies also being evaluated in DECSE.

Sample Performance Mapping. Catalyst performance maps were developed for each of the three sulfur levels. The maps show NO_x conversion between 150°C and 550°C in 50°C increments using the 4% fuel penalty settings at 3,000 rpm.

Device Aging. Next, the devices were aged for a nominal 250-hour period, starting with the 3-ppm base fuel. The technical committee selected the 250-hour period after considering previous work that showed major degradation of NO_x adsorber conversion efficiency in less than 100 hours when sulfur levels are greater than 100 ppm. This finding meant that 250 hours was sufficient to define the catalyst's useful life with the higher sulfur level.

The aging cycle was composed of steady-state operation for 20 minutes at each temperature in the following sequence:

150° – 250° – 350° – 450° – 550° – 450° – 350° – 250° – 150°C – repeat

Periodic Reassessment During Aging. NO_x conversion efficiency was reassessed for each set of samples at 50-hour intervals during the aging tests to track the performance of the samples. Reassessment was conducted using the same test procedure as that used for mapping. A device was defined to have failed when the reassessment showed that the NO_x conversion average over the temperature range had dropped by 50% or more from the fresh value.

2.2 Continuously Regenerating Diesel Particulate Filters and Catalyzed Diesel Particulate Filters

This section summarizes the effects of diesel fuel sulfur levels on the operation of diesel particulate filters (DPFs) as represented by the CR-DPF and CDPF classes of diesel exhaust emission control systems.

2.2.1 Principle of Device Operation

The CR-DPF supplied to the DECSE program for sulfur sensitivity evaluation is comprised of two elements. The first element is a washcoated, platinum containing flow-through oxidation monolith. The 400-cpsi cordierite substrate is 26.7 cm (10.5 in.) in diameter by 15.2 cm (6 in.) long, giving a gross volume of approximately 8.5 L, or roughly 520 $in.^3$. The second element, separated from the first by a gap of about 5.1 cm (2 in.), is an uncoated wall-flow filter (100 cpsi/17 mil wall). Overall dimensions of the filter are 26.7 cm (10.5 in.) in diameter by 30.5 cm (12 in.) long, which give a volume of approximately 17 L, or 1040 $in.^3$. The two elements are housed in individual modules which are assembled with band clamps into a single 304 stainless steel modular can. Overall dimensions of the assembled unit, including end cones, are roughly 30.5 cm (12 in.) in diameter by 91.4 cm (36 in.) long.

The CR-DPF and the CDPF were designed to remove PM from the engine exhaust stream. A schematic diagram of the DPF system configurations is provided in Figure 2.2-1. In each device, PM was removed from the exhaust stream by collection on a filter, which in these cases are ceramic wall-flow elements. Unlike other diesel emissions control devices, primary removal of the targeted pollutant (PM) is fixed by the physical characteristics of the filter medium and is relatively unaffected by engine operating conditions. The critical issue, instead, is the cleaning or regeneration of the DPF (by oxidation of the collected PM) to prevent the DPF from plugging.

The CR-DPF accomplishes this filter regeneration by continuously generating NO_2 from engine-emitted NO over a diesel oxidation catalyst placed upstream of the DPF. NO_2 has been established as a more effective low-temperature oxidizing agent for diesel PM than oxygen. Sulfur in the exhaust (originating from the fuel and the lubricant), however, can be oxidized over the CR-DPF, forming sulfates, which are measured as PM. Sulfur oxides also compete for the critical NO and NO_2 reaction, making the regeneration characteristics less effective.

The CDPF accomplishes the DPF regeneration by using a catalyst coating on the DPF element to promote oxidation of the collected PM using available oxygen in the diesel exhaust. Sulfur in the exhaust can be oxidized over the CDPF to form sulfates. Exhaust-gas temperature and fuel-sulfur level are critical factors that affect the performance of both types of DPFs (CR-DPF and CDPF).

The CDPF supplied to the DECSE program used 26.7 cm-diameter by 30.5 cm-long, 100-cpsi, 0.43 mm, or "17-mil" wall ceramic wall-flow substrates containing a high loading of precious metal (Pt).

2.2.2 Overview of Test Program

Two major components make up the DPF test program: (1) emissions tests to evaluate the direct impact of fuel sulfur on selected emission parameters, and (2) experiments to measure the effect of fuel sulfur on the regeneration temperature of the DPF devices. As shown in Table 2.2-1, both testing components were/will be carried out on two types of DPFs using fuels with sulfur levels ranging from 3 to 350 ppm. Emission measurements were obtained in triplicate tests using the OICA 13-mode test procedure and duplicate tests at peak torque and "road-load" steady-state test conditions. The primary means of determining the effect of fuel sulfur on the regeneration capacity of the DPFs was the 5-mode balance point temperature test. During this test, the engine is operated at five different temperature/torque settings while the speed is held constant. Temperature tests, which involve operating the engine at fixed temperatures while varying engine speed and torque settings, were also conducted. A review of the initial results with 3-ppm sulfur fuel revealed that the 5-mode balance point temperature tests provide a more accurate estimate of the regeneration (balance point) temperature than do the constant temperature tests. Therefore, triplicate 5-mode tests were planned for each engine speed. The temperature tests were used primarily for confirmatory analysis.

The experiments are providing data to address the following study questions:

- How does each DPF affect emissions of PM (including SO_4, soluble organic fraction [SOF], and NO_3), HC, CO, NO_x, and CO_2, as well as fuel consumption?
- How does fuel sulfur affect engine-out emissions and post-DPF emissions?
- Does DPF performance degrade over time?
- To what degree does sulfur in the fuel affect the balance point (regeneration) temperature (BPT) of the DPF (at various engine speeds)?
- Does the DPF performance vary as a function of engine operating conditions (exhaust-gas flow rate and temperature)?
- How does the relationship between emissions and operating conditions change as a function of fuel sulfur level?

This interim report presents results related to the first three study questions.

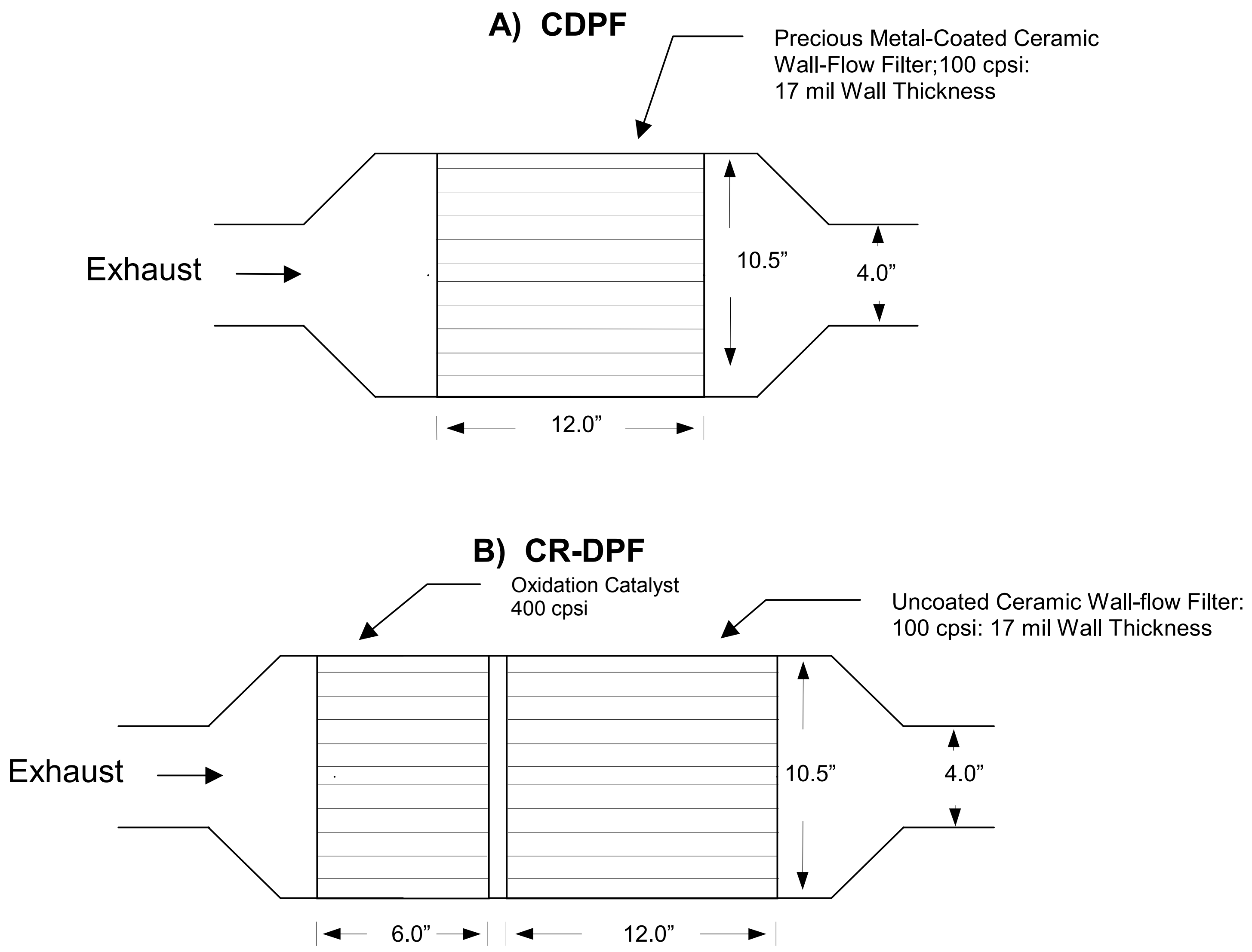


Figure 2.2-1. Schematic diagram of DPF system configurations

Table 2.2-1. Experimental Design for the DECSE DPF Test Program

Test	**Fuel Sulfur Level** (ppm)				
	3	**30**	**150**	**350**	**30**
Baseline Engine Performance	EO (x1)				
Baseline Filter Pressure Drop	CDPF, CR-DPF (x1)				
OICA Emissions	EO (x3) CDPF, CR-DPF (x3)	EO (x3) CDPF, CR-DPF (x3)	EO (x3) CDPF, CR-DPF (x3)	EO (x3) CDPF, CR-DPF (x3)	EO (x3) CDPF, CR-DPF (x3)
Peak Torque Emissions	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)
Road-Load Emissions	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)	EO (x2) CDPF, CR-DPF (x2)
BPT Test	5 temperatures, 3 speeds (x3)	5 temperatures, 3 speeds (x3)	5 temperatures, 3 speeds (x3)	5 temperatures, 3 speeds (x3)	
Temperature Test	T1, T2, T3, T4	T1* and T2*	T1* and T2*	T1* and T2*	
Re-Test OICA Emissions		CDPF, CR-DPF (x3)			

Emissions parameters: PM, SO_4, SOF, NO_3, lubricant, HC, CO, NO_x, and CO_2 in g/bhp-hr and brake-specific fuel consumption (BSFC) in lb/bhp-hr.
EO = engine-out emissions
CDPF and CR-DPF are post-DPF samples.
Post-DPF PM collected on one filter across duplicate or triplicate runs.
Temperature tests were performed for 10 hours with alternating speeds (1,440; 1,700; 2,000 rpm) and matching torques to achieve fixed starting inlet temperatures, Ti (i= 1-4)
(CR-DPF temperatures Ti = 225, 275, 325, 375)
(CDPF temperatures Ti = 275, 325, 375, 425)
T1* = 275°C and T2* = 375°C
Number of replicate tests indicated in parentheses.

2.2.3 Experimental

A Caterpillar 3126 engine rated at 205 kW (275 horsepower) and equipped with electronic controls was used for the tests. The 3126 engines are typically used for applications that result in relatively low temperature engine exhaust (e.g., below 300°C). For such applications, regeneration of the DPF at low temperatures is critical to proper operation of the emissions control system and hence the engine operation (maintaining a low back pressure by not allowing collected PM to build up continuously on the filter). Because fuel sulfur is expected to affect the filter regeneration temperature, these low temperature applications are an excellent test of the effects of fuel-sulfur.

The CR-DPF and CDPF represent two general approaches to passive regeneration of DPFs. Passive regeneration is preferred, as opposed to active regeneration, because passive regeneration offers significant fuel consumption savings and is less complex. Caterpillar and the emissions control manufacturers provided technical support to ensure that these hardware systems were matched for the testing.

Four fuels of different sulfur levels were/will be tested. The sulfur levels were 3, 30, 150, and 350 ppm.

2.2.4 Test Procedures

The laboratory used for this testing is Engineering Test Services (ETS) in Charleston, South Carolina.

Engine and DPF Break-In. To break in the engine and the DPF, the engine was operated at FLRS for 30 minutes, and then for 30 minutes at rated speed and a torque setting as required to give an exhaust temperature of 225°C. The cycle continued for 20 hours. The pressure drop across the DPF was monitored throughout the break-in period.

Baseline Engine Performance Tests. After the engine was broken in, it was operated at full-load, rated speed (FLRS), and the baseline pressure drop across the DPF was determined. The baseline performance curve without the DPF consisted of operating the engine at maximum load and varying the speed from rated to 1,000 rpm in 100-rpm increments. This test ensured that the engine met the manufacturer's specifications. An 8-rpm-per-second, full-load performance curve was run to determine the 13-mode OICA test cycle measurement points.

Emission Tests. The OICA test was conducted by stabilizing the engine system for five minutes at each OICA mode prior to sampling. A single filter was used to collect PM over the entire OICA test cycle.

All emission tests included measurement of HC, CO, NO_x, CO_2, and PM (including soluble organic fraction [SOF]), and sulfate. Because of the high trapping efficiency of the DPF devices, the PM loading on the filter was typically only about 0.2 mg over an OICA cycle. To improve measurement accuracy, PM was collected on the same filter over three consecutive OICA cycles.

Steady-state emissions measurements were also taken at modes 2 and 4 of the OICA cycle. Mode 2 (1047 Nm @ 1,440 rpm) is the peak torque condition at which the engine-exhaust temperature reaches the maximum value. Maximum sulfate conversion occurs at this engine operating condition. Mode 4 (733 Nm @ 1,783 rpm) corresponds to the road-load condition of a typical on-highway heavy-duty diesel truck engine. Because a truck spends much of its operating time under the road-load condition, the emissions at this condition would indicate the emissions level from this type of operation.

BPT Test. The 5-mode balance point temperature test was the primary method for characterizing the effect of fuel sulfur level on the regeneration (soot combustion) temperature of the filter. To prepare the DPF device for the test, the device was completely regenerated by operating the engine at peak torque condition for 30 minutes. The device was then reloaded with PM by operating the engine at 214 Nm and 2,000 rpm for about five hours until the pressure drop across the DPF reached a reference value. For the 5-mode test, the engine was operated at a fixed speed as torque is increased to achieve the specified filter inlet temperatures. The total duration for the final test protocol was 110 minutes, with temperature steps of 40, 25, 15, 15, and 15 minutes. The change in pressure across the filter was continuously recorded.

Temperature Test. In the exhaust temperature tests, the engine was operated at 1,440; 1,700; and 2,000 rpm from lower to higher engine speeds for 20 minutes at each speed during a 10-hour cycle. The engine load for each speed was determined before each test to obtain the desired exhaust temperature at each speed condition. The temperature and pressure drop across the DPF device were monitored continuously for up to 10 hours for each fuel. At each temperature and fuel sulfur level, the pressure drop trace (as a function of time) was expected to either: (1) continuously increase (PM deposits on the filter faster than it can be oxidized), (2) remain relatively stable (PM depositing on the filter equals the amount being oxidized), or (3) continuously decrease (PM depositing on the filter at a rate slower than it is being oxidized). This test is intended to provide another means to determine BPT when the engine speed is varying.

In between each exhaust temperature test, the engine was operated at FLRS for 2 hours (stabilization) to ensure that the DPF was "clean" and that its pressure drop returned to near baseline conditions.

2.2.5 Analysis of Emissions Data

As shown in Table 3.2-1, triplicate OICA 13-mode emissions tests and duplicate steady-state emissions tests (at peak-torque and road-load modes) were conducted separately on engine-out (without CR-DPF or CDPF devices) and post-filter (with CR-DPF or CDPF) exhaust streams. After the initial series of tests with 3-ppm fuel sulfur, the technical committee decided that PM loadings on the filters used in the post-DPF emissions tests were insufficient for PM analysis. For that reason, the same filter was used on each of the two or three replicate tests. The continuous emissions parameters included HC, CO, NO_x, and CO_2, in g/bhp-hr and BSFC in lb/bhp-hr. Filter analysis included PM, SO_4, SOF, NO_3, and lube-related SOF (lube SOF) in g/bhp-hr. Results of this analysis were used to determine the sulfate conversion rate. However, filter analysis results were not available in time for inclusion in this interim report.

The effect of the DPF device on emissions (study question 1) was determined in terms of emissions reduction efficiency:

For each fuel type (3- and 30-ppm sulfur), the statistical significance of the ratio's difference from 0% (indicating no DPF effect) was determined using a standard two-sample t-test on the log-transformed data. As is often the case with emissions data, the log transformation yields measurement errors that are normally distributed with common standard deviation. This common standard deviation was estimated by pooling the individual standard deviations of emissions measurements from the OICA, peak torque, and road-load tests at engine-out and post-filter tests.

The effects of fuel sulfur on the engine-out and post-DPF emissions (study question 2) were also evaluated. The percent change in engine-out emissions is the measure of sulfur's effect on engine-out emissions. The effect of sulfur on DPF efficiency was calculated as the difference in reduction efficiency. The statistical significance of these effects (i.e., whether or not the measures were different from 0%) was determined using two-sample t-tests on the log-transformed data.

Degradation of the DPF performance over time (study question 4) will be addressed by comparing reduction efficiencies with 30-ppm fuel at two different times and tracking the degradation of the regenerated DPF delta-p over time. The second emissions tests with 30-ppm fuel will be conducted after the 150- and 350-ppm fuel sulfur tests are performed.

The relationship between engine operating conditions (speed, torque, and temperature) and engine-out emissions or filter breakthrough (study questions 5 and 6) will be addressed in the final report, following detailed analysis of the OICA 13-mode data.

2.2.6 Analysis of Balance Point Temperature Data

The 5-mode BPT test is used to measure the effect of fuel sulfur on the regeneration (particulate combustion) temperature of the DPF (study question 3). The BPT is defined as the DPF inlet temperature at which the pressure drop across the filter begins to decrease (i.e., the slope of change in pressure [delta–p] across the DPF becomes negative). Each BPT test produces a single estimate of BPT. The tests conducted are listed below.

- 4 fuel sulfur levels (3, 30, 150, and 350 ppm)
- 2 DPF types (CR-DPF, CDPF)
- 3 engine speeds (1,440, 1,700, and 2,000 rpm)
- 3 replicates

Each of the 72 (4x2x3x3) tests include measurements at five DPF inlet temperatures. An example of BPT test results is provided in Figure 2.2-2.

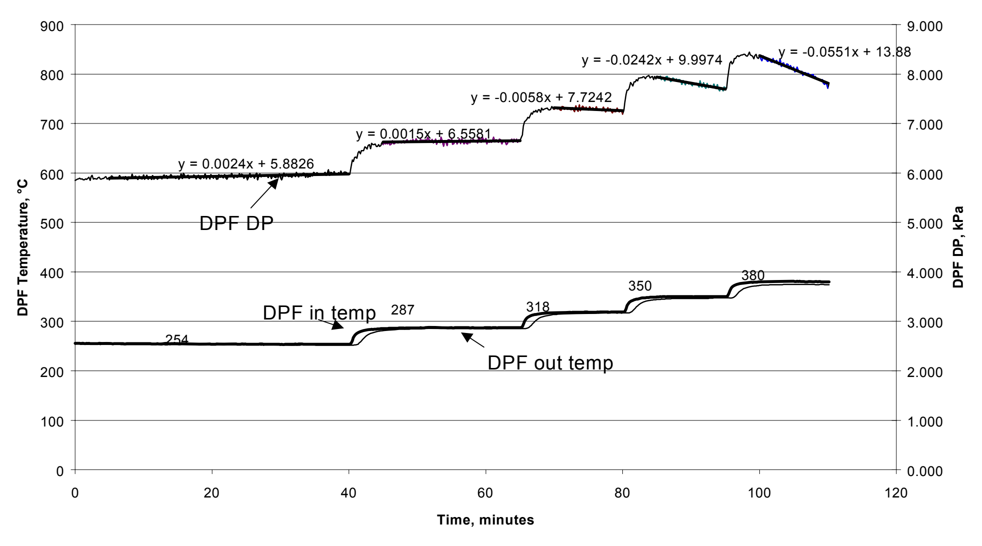


Figure 2.2-2. Example test results from the 5-mode BPT test

The first step in the data analysis involves calculating the least-squares slope of the delta-p versus time (kPa/min) curve, following stabilization at each inlet temperature. Data are first reduced by selecting a linear portion of the delta-p versus time curve. Generally, this will be the 10-minute period beginning 5 minutes after the change in engine temperature. A lack-of-fit procedure is used to determine if a straight-line fit is appropriate. If not, a subset of data is selected according to a defined procedure.

Next, a regression model is fit to establish the relationship between delta-p slope and trap inlet temperature. The general form of the regression model is

$$\mathrm{DPS}(t) = \begin{cases} p & \text{if } t < t_0 \\ a + bt + ct^2 & \text{if } t \geq t_0 \end{cases}$$

where DPS(t) = delta-p slope (kPa/min) at DPF inlet temperature t. The function is assumed to be smooth and continuous (as shown in Figure 2.2-3). BPT_0 is defined as the DPF inlet temperature at which the slope of delta-p equals 0. Assuming p > 0,

$$\mathrm{BPT}_0 = \frac{-b + \sqrt{b^2 - 4ac}}{2c}.$$

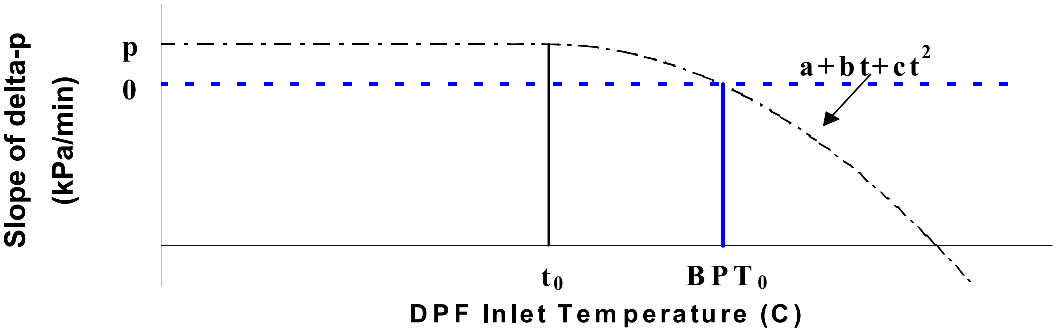


Figure 2.2-3. Calculation of BPT

To account for possible run-to-run variability, a separate regression equation was fit for each run. Also, a single equation is fit to the (pooled) data from all three runs combined. This dual approach is useful for interpreting results when there are run-to-run differences. For each regression model, the BPT_0 is calculated. If there are run-to-run differences in the test procedures, the appropriate estimate of BPT_0 is the average of the values obtained from different runs. This is illustrated in Figure 2.2-4. An approximate 95% confidence interval for the mean BPT_0 across runs is then calculated with the assumptions that these are three independent measurements of BPT_0 and that the errors are normally distributed. The BPT_0 is also calculated from data pooled across the three test runs, and the 95% confidence interval for BPT_0 is determined by calculating the intercepts of the confidence bounds for the regression model. In some cases this approach produces only a confidence bound. For example, as shown in Figure 2.2-5, the estimate of BPT_0 is approximately 315°C with a 95% upper confidence bound at approximately 345°C.

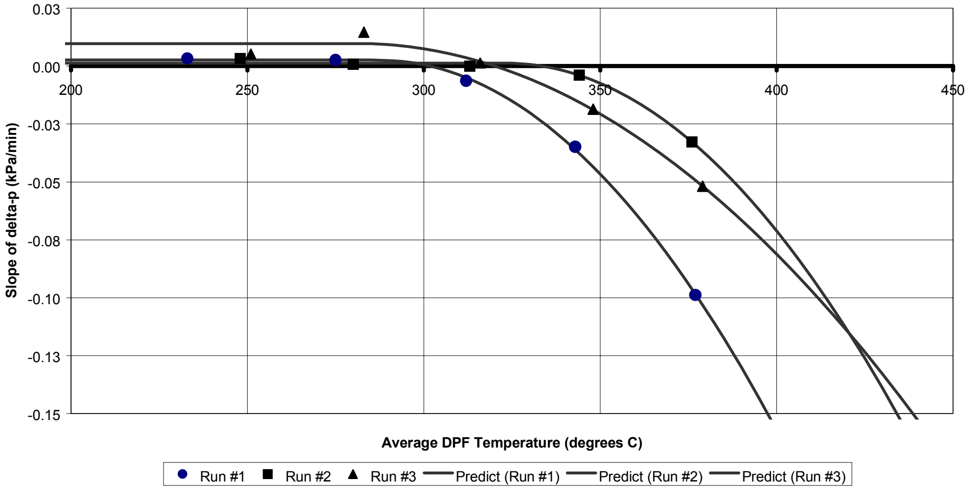


Figure 2.2-4. Estimated delta-p slope versus DPF inlet temperature – by test run

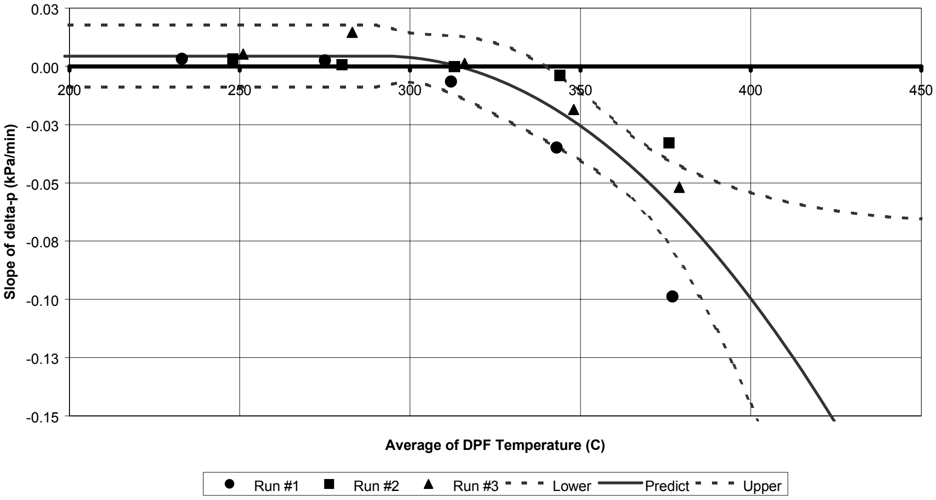


Figure 2.2-5. Estimated delta-p slope versus DPF inlet temperature with 95% confidence limits – pooled model (all runs combined)

BPTs for each fuel sulfur level are compared for three engine speeds: 1,440; 1,700; and 2,000 rpm. Approximate 95% confidence intervals for the difference in BPTs are calculated for both methods of analysis (average BPT and pooled BPT). If a 95% confidence interval does not contain the value zero, one can conclude with 95% confidence that the BPTs are different among fuel levels. It is possible, however, that the two methods of analysis will produce different conclusions. Given the uncertainties in the modeling assumptions, it is appropriate to accept the more conservative result (i.e., the one with the larger confidence interval). This will usually be the result based on the average of three test runs.

2.3 Lean-NO_x Catalysts

2.3.1 Program Overview

Lean-NO_x catalyst technology includes one type of catalyst that can be used to reduce diesel NO_x emissions with the assistance of a supplemental HC reducing agent (such as diesel fuel) under the lean (oxygen-rich) exhaust condition. Lean-NO_x catalysts can be divided into two different groups: low-temperature (170°–300°C) and high-temperature (350°–600°C). Low-temperature catalysts are primarily composed of precious metals, such as platinum (Pt); high-temperature catalysts are mainly composed of base metal components, such as metal/zeolite (Cu-ZSM) catalysts. For lean-NO_x catalysts, two major competing reactions are as follows:

(1) $HC + NO_x \rightarrow N_2 + CO_2 + H_2O\ (+ N_2O)$
(2) $HC + O_2 \rightarrow CO_2 + H_2O$

Depending on the catalyst composition, a catalyst can either favor low-temperature or high-temperature NO_x reduction as mentioned above. For the low-temperature catalyst, N_2O may be a by-product. In addition to the temperature effect, other parameters also affect catalyst performance: HC and NO_x concentration (and HC/NO_x 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 type of sulfur components and the level of fuel vaporization also affect the catalyst performance.

Lean-NO_x 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_x catalysts. The lean-NO_x catalyst experiments are providing data to address the following study questions:

What is the effect of diesel sulfur level on:
- Lean-NO_x catalyst performance in terms of NO_x reduction efficiency
- Sulfate (PM) formation by the catalyst
- Catalyst deactivation rate
- Catalyst recoverability from SO_2 (or SO_3) poisoning?

To effectively carry out the lean-NOx catalyst evaluation, Phase 1 of the DECSE program was divided into three progressive parts:

1) **High-Temperature Lean-NO_x Catalyst—Fresh Performance.** This part will establish the fresh performance of the high-temperature lean-NO_x catalyst with different fuel sulfur levels (3, 30, 150, and 350 ppm). The effect of fuel sulfur on both catalyst impairment and sulfate (PM)

formation will be examined. A Cummins ISM engine (11L, 99 MY) is being employed for this study.

2) **Low-Temperature Lean-NO$_x$ Catalyst—Fresh Performance.** This part will establish the fresh performance of the low-temperature lean-NO$_x$ catalyst with different fuel sulfur levels (3, 30, 150, and 350 ppm). The effect of fuel sulfur on both catalyst impairment and sulfate (PM) formation will be examined. A Navistar T444E engine (7.3L, 99 MY) is being employed for this study.

3) **Lean-NO$_x$ Catalyst Aging and Evaluation**. This part will study the effect of fuel sulfur levels (3, 30, 150, and 350 ppm) on catalyst deactivation. Both high-temperature and low-temperature lean-NO$_x$ catalysts will be evaluated after being aged for 50, 150, and 250 hours.

In this interim report, the high-temperature lean-NO$_x$ catalyst performance (part 1) is summarized and discussed.

2.3.2 Experimental

Testing is being conducted at West Virginia University (WVU). Two Navistar T444E (7.3L, V8, 99 MY) engines and two Cummins ISM 370 (11L, 99 MY) engines are being used for this test program. One engine of each type is being used for the catalyst aging process, and the other two are being used for the catalyst evaluation. The T444E engine is generating exhaust for evaluating the low-temperature lean-NO$_x$ catalyst. Likewise, the ISM 370 engine is generating exhaust for evaluating the high-temperature lean-NO$_x$ catalyst. Both Navistar and Cummins provided the electronic control box, engine calibration software, and test cell accessories. The engines were broken in for 50 hours, according to the recommendations of the engine manufacturers.

With regard to the reductant fuel injection (fuel injected into the exhaust to provide a reductant), two sets of fuel-injection systems (with a fluid-metering pump and an air-atomized injection nozzle) were assembled: one for the aging engine, and one for the evaluation engine. The fuel-injection nozzle is located 20 to 24 inches from the catalyst inlet. The reductant fueling rate (for a given mode) was optimized for NO$_x$ reduction while HC and PM slippage were controlled.

Catalyst manufacturers provided the low-temperature lean-NO$_x$ catalytic converters (precious-metal catalyst) and high-temperature lean-NO$_x$ catalytic converters (base-metal catalyst). The criteria used for catalyst selection were:

- Typical chemical composition and conventional catalyst wash-coating and structure
- The state-of-the-art lean-NO$_x$ technology.

According to information provided by MECA, specifications for the lean-NO$_x$ catalysts are presented in Table 2.3-1.

Table 2.3-1. Lean-NO_x Catalyst Specification

Catalyst Type	**Form-ulation**	**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	8.5	400	27.3 x 51.4
Low-temperature	Precious metal	17.8 x 12.7	2	6.4	400	19.1 x 55.9

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

All the catalysts were degreened by applying a suitable catalyst aging cycle (illustrated in Tables 2.3-2 and 2.3-3) for 10 hours with 3-ppm sulfur fuel. There was no reductant fuel injection during the catalyst degreening process.

Table 2.3-2. Low-Temperature Lean-NO_x Catalyst Aging Cycle (Four Nav-9 Modes, 60 Minutes)

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

Table 2.3-3. High-Temperature Lean-NO_x Catalyst Aging Cycle (Four OICA Modes, 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

WVU has set up split-exhaust systems for both catalyst aging and catalyst evaluation. The purpose of setting up split-exhaust systems is to age both a lean-NO_x converter and a DOC converter simultaneously. As a result, both low-sulfur fuel usage and experiment time can be saved. With the split-exhaust system at the evaluation cell, the partial-exhaust flow rate (passing through a lean-NO_x converter) is monitored by both a CO_2 analyzer and a flow meter (with delta-p and temperature measurements). More detailed information regarding the split-exhaust systems will be discussed in the DECSE final report.

WVU is running both heavy-duty and light-duty FTP transient cycles. NO_x, total hydrocarbons (THC), CO, CO_2, SO_2 and PM emissions are being monitored for a given steady-state or transient test cycle. ORNL is conducting the PM chemical analysis. As a result, the SO_4 emission data are being reported as well.

Diesel fuels with four different sulfur levels (3, 30, 150, and 350 ppm) are being used to evaluate the fresh lean-NO_x catalysts. During the experiments, samples of lubricating oil (Shell Rotella T 15W40) are being taken periodically for chemical analysis.

2.3.3 Test Cycles for Catalyst Evaluation

To evaluate the high-temperature lean-NO_x catalyst, four test modes (2, 10, 3, and 11) were selected from the OICA test cycle to comprise a special 4-mode test cycle. Similarly, four test modes (2, 3, 7, and 9) were chosen from the Nav-9 test cycle for evaluating the low-temperature lean-NO_x catalyst. To maintain consistency, all evaluation modes are the same as the corresponding catalyst aging modes. In order to obtain comparable data with the reductant fuel injection, a pre-stabilization time was assigned to a given test mode before the emissions data were collected. To reduce this pre-stabilization time, the mode-running sequence was designed to run from the lowest temperature mode to the highest temperature mode (11➔3➔10➔2). The total mode time was fixed at 20 minutes for each selected test mode. Sampling time was assigned to each test mode according to the mode-weighting factor. To better estimate the effect of fuel sulfur level on sulfate (PM formation), mode 2 (the highest temperature mode of the OICA test cycle) was selected for testing.

To properly control the THC and CO slippage rate, the secondary fueling rate for a given evaluation mode was optimized. The compromise was made between the NO_x reduction efficiency and the THC and CO slippage rate. A modern DOC can always be applied to clean up the additional THC and CO emissions. As designed, the overall secondary fueling rate is about 4% of the total engine fuel consumption.

Only one single PM filter set (primary and secondary) is being used for the special 4-mode test cycle. According to the definition of the OICA (or Nav-9) test cycle, the weighting factors were applied to determine the sampling time for a given mode. The catalyst evaluation conditions are summarized in Tables 2.3-4 and 2.3-5.

Table 2.3-4. Low-Temperature Lean-NO_x Catalyst Evaluation Modes (Four Nav-9 Modes)

Nav-9 Mode #	**Engine Speed** (rpm)	**Engine Torque** (Nm)	**Catalyst Inlet Temp.** (°C)	**NO_x** (g/bhp-hr)	**Mode Time** (seconds)	**Sampling Time**	**Reductant Fueling** (%)
2	1000	110	135	5.56	1200	*Proprietary*	1.9
3	1250	165	207	5.53	1200	*Proprietary*	6.2
7	2000	165	247	4.63	1200	*Proprietary*	4.7
9	2200	550	405	3.09	1200	*Proprietary*	1.0

Table 2.3-5. High-Temperature Lean-NO_x Catalyst Evaluation Modes (Four OICA Modes)

OICA Mode #	**Engine Speed** (rpm)	**Engine Torque** (Nm)	**Catalyst Inlet Temp.** (°C)	**NO_x** (g/bhp-hr)	**Mode Time** (seconds)	**Sampling Time** (seconds)	**Reductant Fueling** (%)
11	1884	339	273	6.53	1200	100	0
3	1573	815	380	6.37	1200	100	0
10	1884	1353	448	6.12	1200	200	3.3
2	1261	1692	528	6.09	1200	150	7.5

In addition to the special 4-mode test cycles, two high-temperature modes (mode 2 of the OICA test cycle and mode 9 of the Nav-9 test cycle) were specifically selected for examining the effect of fuel sulfur level on sulfate (PM) formation by the catalyst. Individual PM samples are being collected (10 minutes) during the individual mode tests.

2.4 Diesel Oxidation Catalysts

2.4.1 Program Overview

This portion the DECSE program examines the impact of diesel fuel sulfur on the performance and short-term durability of DOCs. When the program is complete, it will have addressed the following study questions:

- 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?

This interim report covers only the first study question.

2.4.2 Principle of DOC Operation

DOCs reduce HC, CO, and PM emissions in engine exhaust by oxidation over precious metal catalysts. PM is lowered by oxidation of the 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 production (as a result of the oxidation of SO_2 to SO_3). Therefore, lower precious metal loadings may be desirable.

2.4.3 Experimental

WVU conducted aging and evaluation of the DOC. Engines used in this program were selected to represent reasonable extremes in operation. The Cummins ISM370 represents a typical heavy-duty line-haul truck engine that meets 1999 certification requirements. The Navistar T444E (7.3L, V8) engine represents lighter-duty (and thus lower-exhaust temperature) operation. Aging sequences were conducted using fuels with each of the following fuel sulfur levels: 3, 30, 150, and 350 ppm. Shell Rotella T 15W40, a widely used commercially available lubricating oil, was used in all phases of the DECSE program.

The test beds were equipped with a dual exhaust arrangement with a flow divider capable of splitting the exhaust flow equally between the two branches. This allows the DOCs and lean-NO_x catalysts to be aged on the same engine (one on each leg). Special non-catalyzed substrates were canned (installed in metal housings) for installation in one leg of the flow to maintain the flow balance while the other technology is being evaluated in the opposite branch. Table 2.4-1 describes each of the DOCs under study.

Table 2.4-1. DOC Specification

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

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

2.4.4. Test Procedures

Evaluations were conducted on the ISM370 engine equipped with fresh (unaged) diesel oxidation catalysts. Both engine-out and catalyst-out evaluations were completed. Performance was evaluated by measuring PM, CO, and HC emissions over the heavy-duty FTP and 4 modes (modes 2, 3, 10, and 11) selected from the OICA mode cycle (illustrated in Figure 2.4-1). A single PM filter was collected across the 4 modes. The modes were identical to those used in the lean-NO_x catalyst aging and evaluation sequences (see Tables 2.3-3 and 2.3-4).

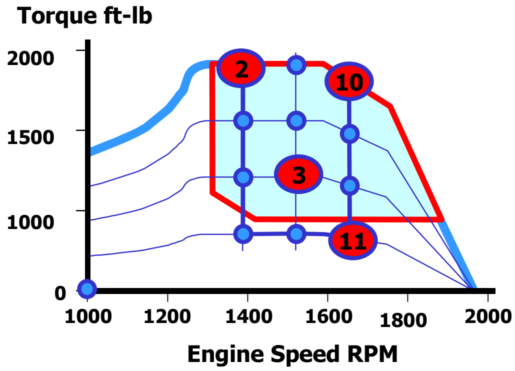


Figure 2.4-1. Test points utilized from the OICA 13-mode test cycle

Previous testing by industry has shown that at high-load, low-speed conditions, the conversion of SO_2 to SO_3 is accentuated, resulting in an increase in PM because of the higher sulfate content. To explore this effect in the DECSE program, a separate evaluation was conducted on mode 2 of the OICA test cycle.

Test engines were broken in per manufacturer specifications. Catalysts were "degreened" for 10 hours of operation on the 4-mode aging sequence. Catalyst performance was evaluated and compared with engine-out (EO) emissions levels with each of the 4 fuels (3-, 30-, 150-, 350-ppm sulfur). Emissions measurement (THC, CO, NO_x, CO_2, SO_2, and PM) tests were conducted. PM was collected on 70-mm-diameter TX40HI20 Pallflex filters. PM was determined gravimetrically at WVU. ORNL conducted subsequent chemical analysis of the collected PM (SOF, sulfate, and nitrate).

Section 3

Interim Results

3.1 NO$_x$ Adsorber

Results from the NO$_x$ adsorber experiments are currently being analyzed. It is anticipated that these results will be reported in a second Interim Report, to be published by October 1, 1999.

3.2 Continuously Regenerating Diesel Particulate Filters and Catalyzed Diesel Particulate Filters

3.2.1 Emissions Results

Table 3.2-1 contains a summary of the emissions results with the 3-ppm and 30-ppm fuel for the DPFs. The results are also presented in graphical form in Figures 3.2-1 through 3.2-3. Each figure plots the average emissions (g/bhp-hr) with 95% confidence limits for selected emission components. Estimated PM reduction efficiencies with 95% confidence limits are also provided. Table 3.2-1 is organized by test variable (emissions, fuel consumption, and engine performance), DPF type (CDPF and CR-DPF), and test type (OICA, peak-torque, and road-load). For each fuel type, average emissions (g/bhp-hr) from engine-out and post-DPF emissions tests are reported, as well as the DPF emissions reduction efficiency as a percentage of engine-out emissions. Results of the statistical test comparing the reduction efficiency with 0% are also reported. For example, average PM emissions through the CDPF were 0.0031 g/bhp-hr, which is 95% less than the average of 0.0613 g/bhp-hr from the engine-out emissions tests. The difference in emissions (or the reduction efficiency's difference from 0%) was significant at the 0.05 level of statistical significance. With the 30-ppm sulfur fuel, the average baseline engine-out PM emission was 0.0630 g/bhp-hr, which was 3% higher than that seen with 3-ppm sulfur fuel. However, this difference was not statistically significant. On the other hand, the PM reduction efficiency dropped from 95% to 74% (a 21 percentage-point decrease) with higher sulfur fuel.

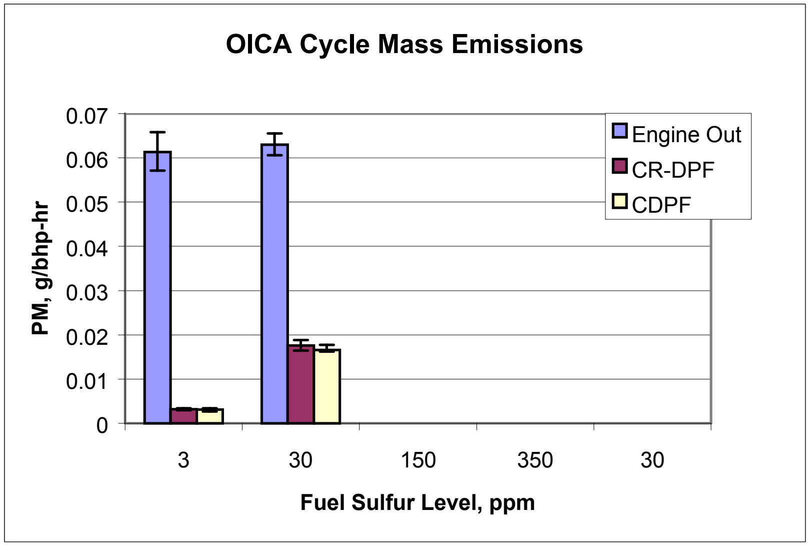
In general, PM reduction efficiencies based on OICA, peak-torque, and road-load emission tests using 3-ppm sulfur fuel ranged from 91% to 97%. However, with 30-ppm fuel, PM reduction efficiencies (RE) were reduced to levels of 72% to 81%. The differences (RE30-RE3) were all statistically significant. For peak-torque emissions, a portion of this sulfur effect is caused by the 13 percentage-point increase in engine-out peak-torque emissions with 30-ppm sulfur fuel. This increase was statistically significant. The OICA and road-load tests with 30-ppm sulfur fuel were about the same as when testing with 3-ppm sulfur fuel. Thus, it appears that fuel sulfur directly affects the PM reduction performance of the DPF.

It has been observed in past engine tests (without catalysts) that typically 1% to 3% of the fuel sulfur is converted to sulfate through the diesel combustion process. However, in the presence of a precious metal catalyst, the conversion of sulfur is increased. The data obtained in this study, although not yet confirmed by particulate fraction analysis, appear to demonstrate this. For example, when comparing total PM emissions during operation with 3-ppm and 30-ppm sulfur fuels at the peak torque test condition, engine-out PM emissions increased from 0.0432 to 0.0489 g/bhp-hr, an increase of 13%. Results from the DPF devices when tested at these same conditions showed

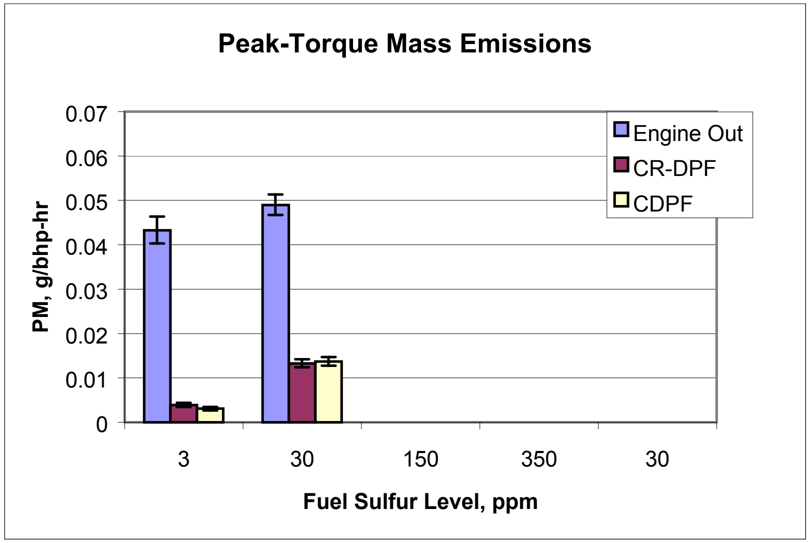
Table 3.2-1. Interim Emission Results for DPFs

Variable	Filter Type	Test Type	Fuel Sulfur Level						Sulfur EO Effect (%)	RE30-RE3 (%)
			3 ppm			30 ppm				
			Baseline Engine Out Test	Post DPF Test	Reduction Efficiency (%)	Baseline Engine Out Test	Post DPF Test	Reduction Efficiency (%)		
PM (g/bhp-hr)	CDPF	OICA	0.0613	0.0031	95**	0.0630	0.0166	74**	3	-21**
		Peak Torque	0.0432	0.0031	93**	0.0489	0.0137	72**	13**	-21**
		Road Load	0.0410	0.0026	94**	0.0414	0.0082	80**	1	-14**
	CR-DPF	OICA	0.0613	0.0032	95**	0.0630	0.0176	72**	3	-23**
		Peak Torque	0.0432	0.0039	91**	0.0489	0.0133	73**	13**	-18**
		Road Load	0.0410	0.0012	97**	0.0414	0.0088	81**	1	-17**
HC (g/bhp-hr)	CDPF	OICA	0.0542	0.0228	58	0.0560	0.0182	68**	3	10
		Peak Torque	0.0220	0.0064	71**	0.0194	0.0041	79**	-12	8
		Road Load	0.0344	0.0093	73**	0.0352	0.0067	81**	2	8
	CR-DPF	OICA	0.0542	0.0136	75**	0.0560	0.0052	91**	3	16*
		Peak Torque	0.0220	0.0040	82**	0.0194	0.0030	85**	-12	3
		Road Load	0.0344	0.0040	88**	0.0352	0.0031	91**	2	3
CO (g/bhp-hr)	CDPF	OICA	0.98	0.06	94**	0.96	0.02	98**	-2	4*
		Peak Torque	1.36	0.02	99**	1.36	0.01	99**	0	1
		Road Load	0.66	0.02	98**	0.68	0.03	96**	3	-1
	CR-DPF	OICA	0.98	0.10	90**	0.96	0.06	94**	-2	4
		Peak Torque	1.36	0.05	97**	1.36	0.04	97**	0	0
		Road Load	0.66	0.02	97**	0.68	0.03	96**	3	-1
NO_x (g/bhp-hr)	CDPF	OICA	4.94	4.92	0*	4.98	4.80	4*	1	3**
		Peak Torque	4.45	4.42	1*	4.45	4.32	3*	0	2**
		Road Load	4.26	4.22	1*	4.36	4.25	3*	2**	2**
	CR-DPF	OICA	4.94	4.96	0	4.98	4.84	3*	1	3**
		Peak Torque	4.45	4.41	1*	4.45	4.28	4*	0	3**
		Road Load	4.26	4.29	-1*	4.36	4.15	5*	2**	6**
BSFC (lbs/bhp-hr)	CDPF	OICA	0.355	0.359	-1**	0.359	0.360	0	1**	1**
		Peak Torque	0.341	0.344	-1**	0.342	0.346	-1**	0*	-0*
		Road Load	0.344	0.347	-1**	0.346	0.347	0	1**	1**
	CR-DPF	OICA	0.355	0.362	-2**	0.359	0.363	-1**	1**	1**
		Peak Torque	0.341	0.347	-2**	0.342	0.346	-1**	0*	1**
		Road Load	0.344	0.350	-2**	0.346	0.352	-2**	1**	0

*Different from 0% at 0.10 level of statistical significance.
**Different from 0% at 0.05 level of statistical significance.



	Peak Torque	Road Load
CR-DPF		
Engine RPM	1,440	1,783
Torque, ft-lb	772	541
Filter inlet T, °C	585	457
CDPF		
Engine RPM	1,440	1,783
Torque, ft-lb	780	541
Filter inlet T, °C	547	433



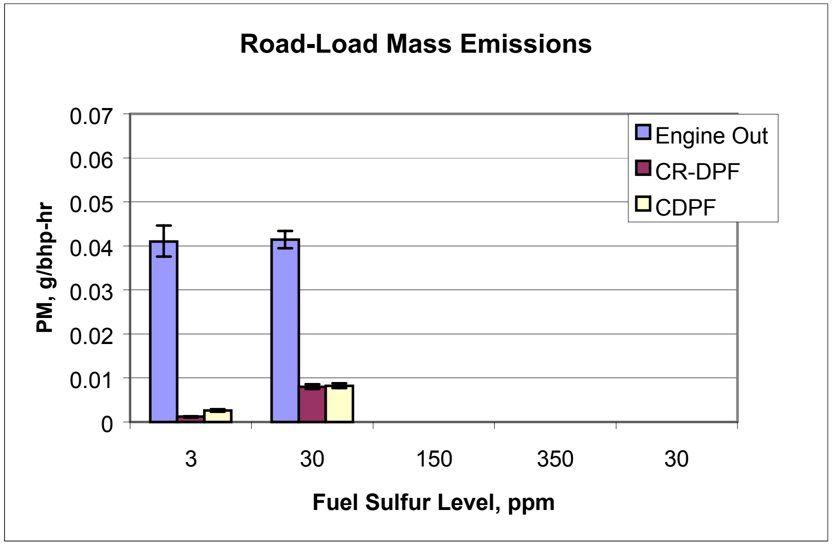
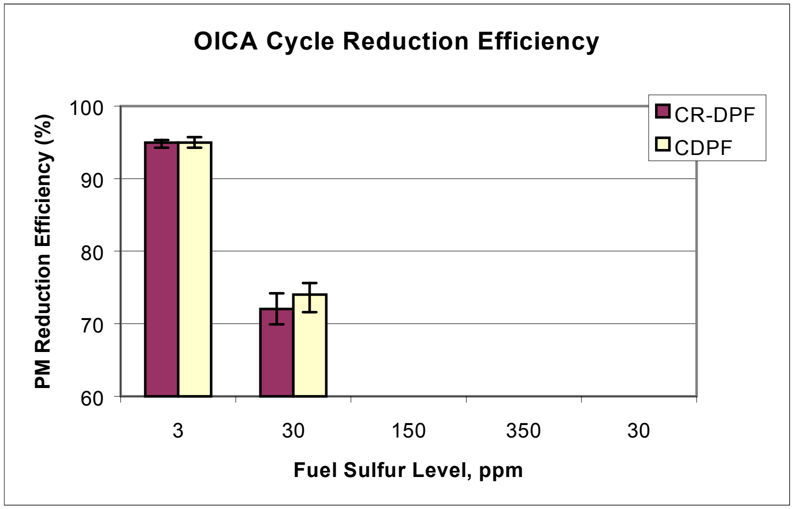


Figure 3.2-1. Effect of fuel sulfur level on PM emissions



	Peak Torque	Road Load
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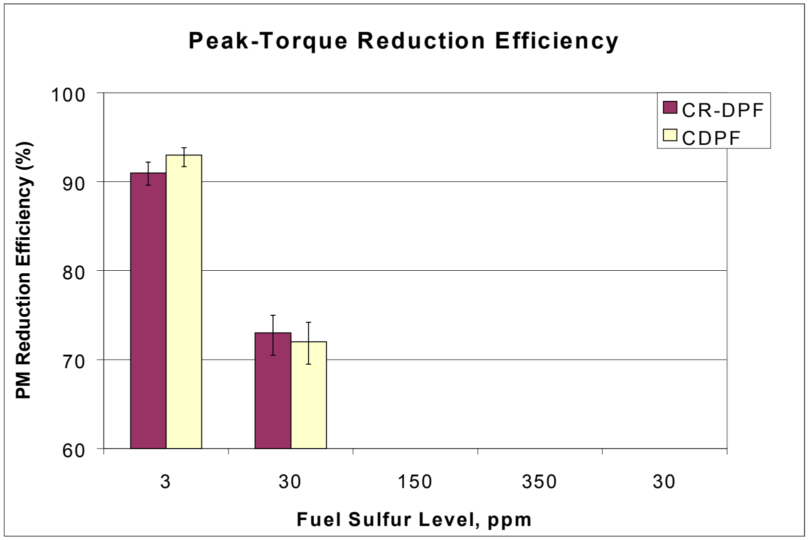


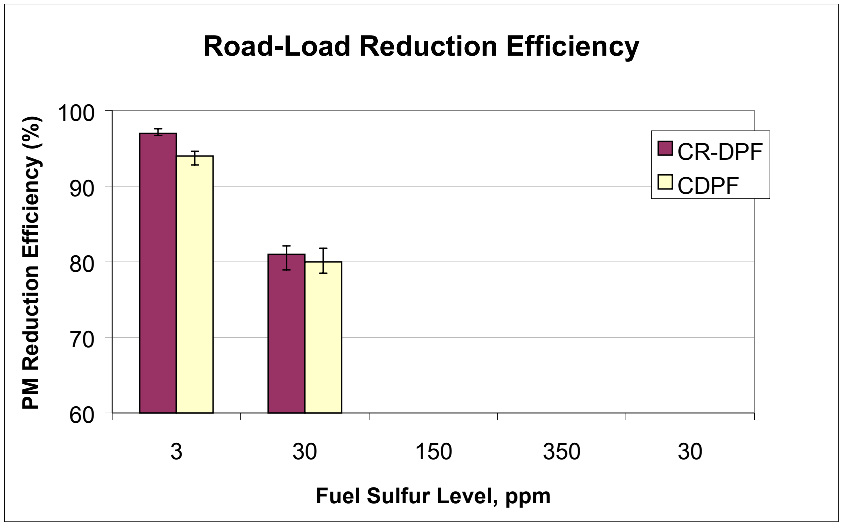


Figure 3.2-2. Effect on fuel sulfur level on PM reduction efficiency

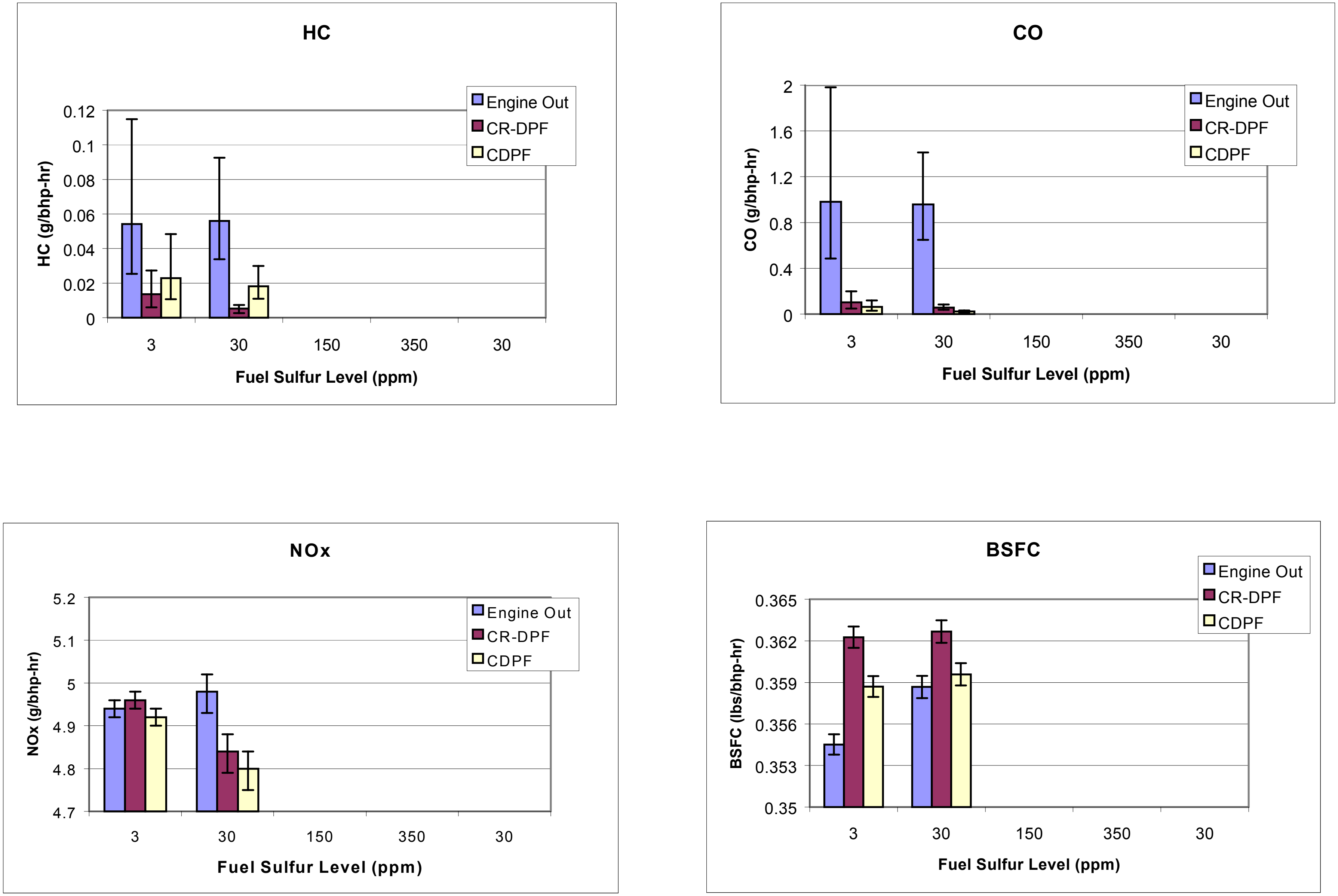


Figure 3.2-3. Effect of fuel sulfur level on OICA cycle emissions (HC, CO, NO$_x$, and BSFC)

significantly larger increases. Total PM emissions from the CR-DPF, for example, increased from 0.0039 to 0.0133 g/bhp-hr, an increase of 241%.

Here are some observations related to gaseous emissions and fuel consumption with 3-ppm and 30-ppm sulfur fuel:

- Both DPFs reduce emissions of HC and CO, but by different amounts. For example, the CDPF HC reduction efficiency is 58% to 73%, while the CR-DPF device has HC reduction efficiency of 75% to 90%. There is no consistent statistical evidence that the reduction efficiencies are affected by the difference in sulfur levels.

- The NO_x reduction with the control devices varied from 1% to 5%, probably due to the increase in back-pressure that the control devices apply to the engine.

- There was no evidence of differences in engine performance across the tests with the exception that fuel consumption increased by 1-2% when using the CR-DPF and CDPF. This is caused by the increased exhaust back-pressure created by the CR-DPF and CDPF.

The final report will contain similar analyses of emissions data with 150-ppm and 350-ppm sulfur fuel. It will also address the relationships between engine operating conditions, fuel sulfur level, and age of the filter.

3.2.2 Results from Balance Point Temperature Tests

This interim report presents the results of BPT tests with CDPF and CR-DPF devices operating at three engine speeds (1,440; 1700; and 2,000 rpm) with 3-ppm and 30-ppm sulfur fuel. Initially, three tests were performed for each combination of DPF type, engine speed, and fuel type. Following completion of the three test runs with the CR-DPF and the first test run with CDPF using 3-ppm sulfur fuel, the test protocol was modified to improve the repeatability of test results. The most significant change was to specify that the test temperatures be nearly the same for all tests. All the 30-ppm tests were performed under the new protocol.

Tables 3.2-2 and 3.2-3 contain the estimated BPTs and confidence intervals for each test run with the CDPF and CR-DPF technologies, respectively. For example, the estimated BPTs for CDPF at 1,440 rpm with 30-ppm fuel vary between 340°C to 354°C, with an average of 347°C. The estimated BPT based on the combined data set is 349°C. Ninety-five percent confidence intervals are provided for each estimate as well as for the difference in estimates across fuel types. Using the "averaging" method, we cannot conclude that the difference (347°C versus 323°C) is statistically significant (because the confidence interval contains the value zero). On the other hand, using the "pooling" method, it appears that the difference is significant. In this case, the more conservative "averaging" method should be used because there is evidence of run-to-run variability.

Figures 3.2-4 and 3.2-5 show the raw data and the "pooled" estimated BPT for each fuel level. In general we see that BPTs are slightly higher with the 30-ppm fuel compared to the 3-ppm fuel. However, most of the differences are not statistically significant. Given some of the uncertainties in the data, it is too early to reach definitive conclusions about the effects of fuel sulfur on the regeneration performance of these DPFs. Additional tests are planned with 150-ppm and 350-ppm fuels.

Table 3.2-2 CDPF Balance Point Temperature Estimates with 95% Confidence Limits

Engine Speed (rpm)	Run No.	Fuel Type				
		3 ppm		30 ppm		Difference
		n	BPT in °C	n	BPT in °C	
1440	**1**			5	340 (336, 344)	
	2	5	335 (<350)	5	349 (344, 354)	
	3	5	311 (<326)	5	354 (347, 360)	
	Average		323 (171, 476)		347 (330, 365)	24 (-80, 128)
	Pooled	10	323 (<344)	15	349 (340, 357)	25 (2, 58)
1700	**1**			5	335 (327, 342)	
	2	5	326 (305, 341)	5	377 (<394)	
	3	5	343 (322, 357)	5	356 (350, 361)	
	Average		335 (225, 444)		356 (304, 408)	21 (-26, 69)
	Pooled	10	337 (324, 348)	15	344 (<367)	7 (-19, 33)
2000	**1**			5	381 (362, 428)	
	2	5	377 (367, 394)	5	391 (365, 551)	
	3	5	381 (367, 408)	5	397 (382, 425)	
	4			7	437 (425, 447)	
	Average		379 (357, 401)		401 (362, 441)	23 (-16, 62)
	Pooled	10	380 (>351)	22	437 (428, 446)	58 (27, 89)

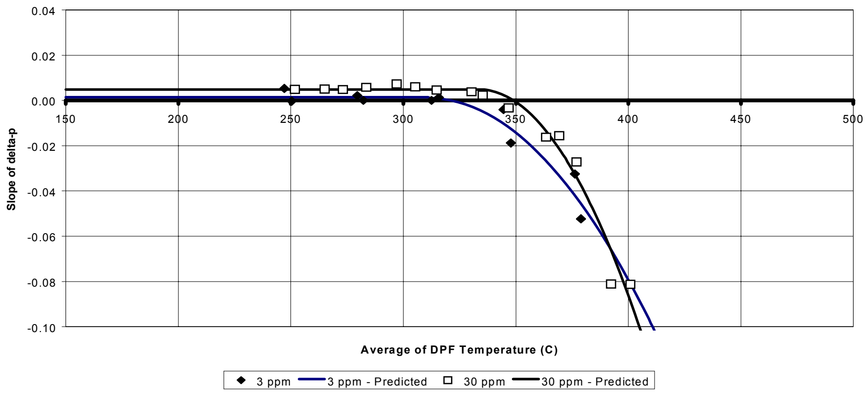
Note: Slopes of the delta-p (versus time) generated from 3ppm run 1 data were excluded from the analysis.

Table 3.2-3. CR-DPF Balance Point Temperature Estimates with 95% Confidence Limits

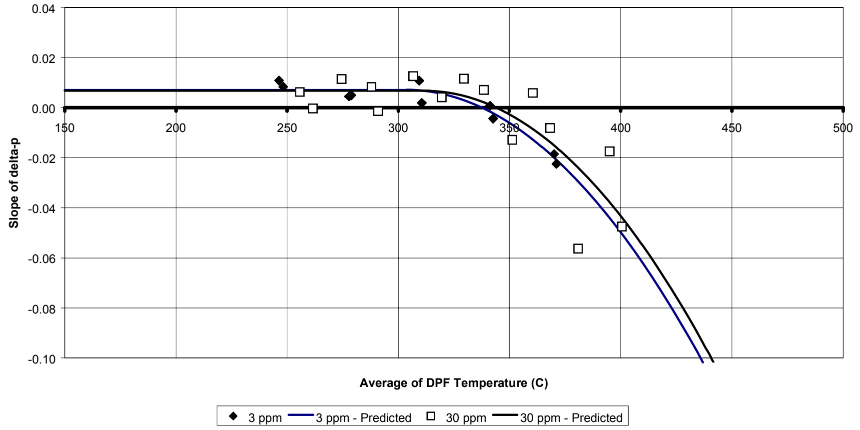
Engine Speed (rpm)	Run No.	Fuel Type				
		3 ppm		30 ppm		Difference
		n	BPT in °C	n	BPT in °C	
1440	**1**	5	256 (<266)	5	312 (303, 319)	
	2	5	296 (<312)	5	312 (<325)	
	3			5	290 (<323)	
	Average		276 (22, 530)		304 (273, 335)	29 (-138, 196)
	Pooled	10	262 (<293)	15	302 (<313)	41 (8, 74)
1700	**1**	5	320 (<347)	5	302 (<310)	
	2	5	268 (264, 272)	5	NA	
	3	5	271 (<288)	5	NA	
	Average		287 (214, 359)		302 (-)	15 (-57, 88)
	Pooled	15	256 (<295)	15	NA	NA
2000	**1**	4	324 (323, 325)	5	339 (<356)	
	2	5	306 (298, 314)	5	324 (319, 328)	
	3	5	305 (296, 313)	5	349 (<361)	
	Average		312 (286, 338)		337 (306, 368)	25 (-1, 52)
	Pooled	14	313 (308, 318)	15	336 (321, 347)	23 (9, 37)

** Data from test at 425°C at 2000 rpm for Run 1 was excluded from the analysis.
NA = BPT estimate not available

CDPF - 1440 RPM



CDPF - 1700 RPM



CDPF - 2000 RPM

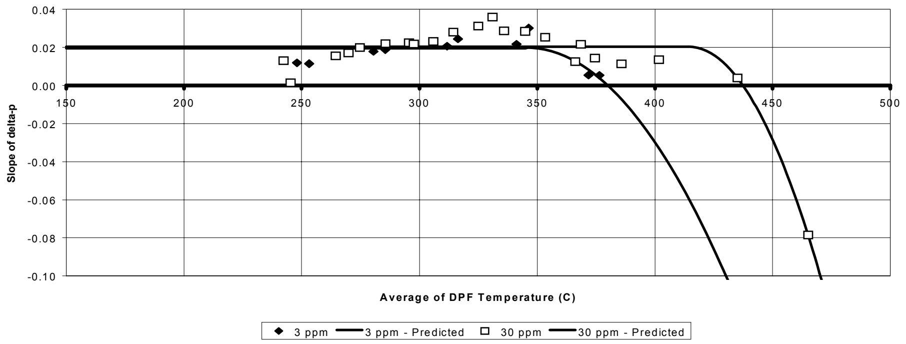
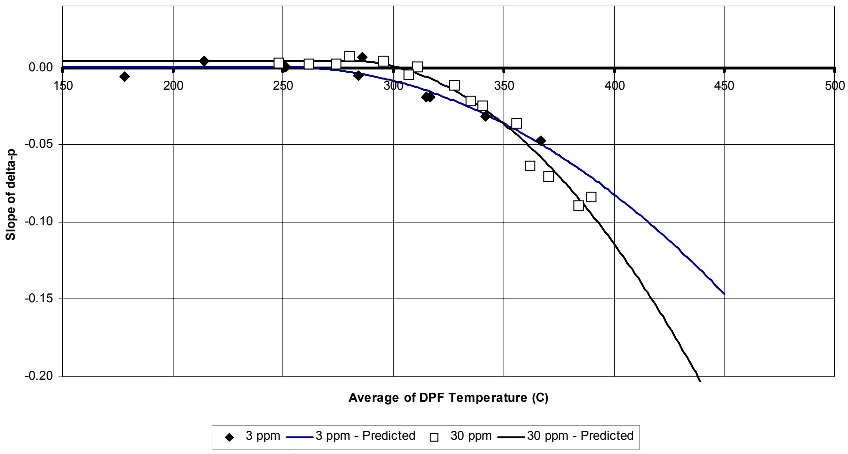
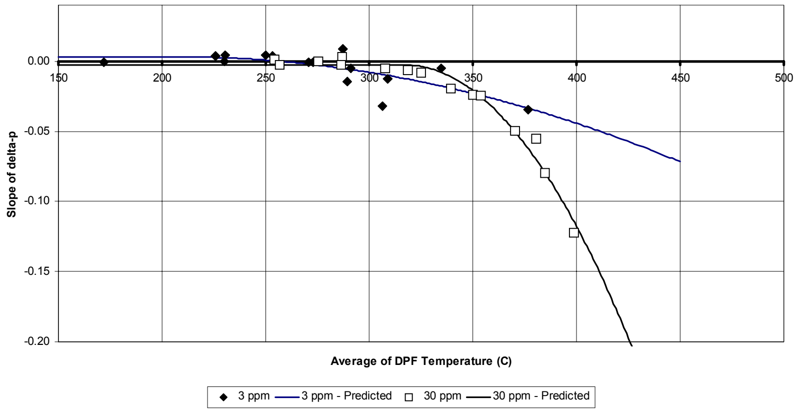


Figure 3.2-4. BPT test results for CDPF at three engine speeds (test results from run #1 with 3-ppm sulfur fuel are not included)

CR-DPF - 1440 RPM



CR-DPF - 1700 RPM



CR-DPF - 2000 RPM

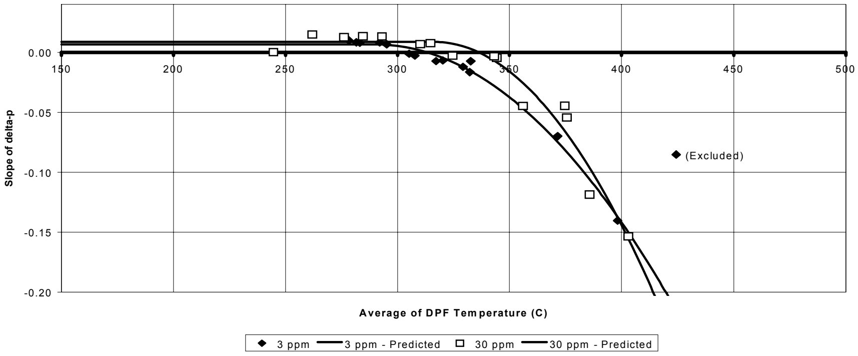


Figure 3.2-5. BPT test results with CR-DPF at three engine speeds

Two important decisions were made concerning the inclusion and exclusion of data. First, the initial tests on CDPF with 3-ppm fuel were eliminated, because all the remaining test runs were performed under the new protocol. It was not possible to do this for CR-DPF without losing all the 3-ppm tests results. Another decision excluded one data point from a 3-ppm test at 2,000 rpm with the CR-DPF device. The delta-p slope at the highest temperature (425°C) increased significantly. Although no cause was found for this result, the point was eliminated because the temperature was beyond the range of temperatures for other tests and it had a large influence on the fitted model. This is shown in Figure 3.2-5.

In some cases (specifically CR-DPF at 1,700 rpm with 30-ppm fuel), it was not possible to calculate a BPT because the slope of delta-p is estimated to be less than zero at nearly all engine speeds tested. For this interim report, the data are eliminated. However, the final report will contain a more comprehensive analysis of these data.

These interim results indicate that fuel sulfur may tend to increase the BPT of the DPF. However, firm conclusions can not be reached at this time. The final report, which will contain results from the 150-ppm and 350-ppm BPT tests, as well as results from the confirmatory tests using the "temperature" test protocol, will yield more definitive conclusions.

3.3 Lean-NO_x Catalysts

This interim report is aimed at evaluating the high-temperature lean-NO_x catalyst baseline. The purpose of conducting the catalyst baseline test is to evaluate the effect of fuel sulfur levels on fresh catalyst performance.

The results of the high-temperature lean-NO_x catalyst baseline tests are summarized in Table 3.3-1. If a given test was repeated, the emissions and BSFC values presented in the table are average values of the two tests. Except for SO_2 data, all critical gaseous emissions reduction data have a 95% confidence level according to a statistical analysis.

Generally, lean-NO_x catalysts are temperature sensitive. The operating temperature of the high-temperature lean-NO_x catalyst ranged between 360°C and 600°C as expected. With regard to the four selected OICA modes (11, 3, 10 and 2), mode 11 is out of the temperature window of the high-temperature lean-NO_x catalyst; mode 3 is at the low edge of the window; and modes 10 and 2 are within the window (as shown in Table 2.3-5). At mode 3, the development work showed that the small amount of secondary fuel injection had little effect on NO_x reduction, but created THC and CO slippage. Therefore, both modes 11 and 3 (273° and 380°C in Figure 3.3-1) were kept as passive modes without injecting any secondary fuel. Considering the secondary fuel injection at modes 10 and 2, a compromise was made between NO_x reduction efficiency and by-products emissions. The optimal secondary fueling rates were 3.3% and 7.5%, respectively. Figure 3.3-1 shows the effect of diesel sulfur level on NO_x reduction efficiency.

Table 3.3-1. Fresh Performance of the High-Temperature Lean-NO_x Catalyst

Definition	Mode	NO_x (g/bhp-hr)				PM (g/bhp-hr)				HC (g/bhp-hr)			
	Fuel Sulfur Level (ppm)	**3**	**30**	**150**	**350**	**3**	**30**	**150**	**350**	**3**	**30**	**150**	**350**
Converter-Out	4-Mode Weighted	5.21	5.51	4.93	5.37	0.0570	0.0701	0.0717	0.0740	0.55	0.49	0.34	0.46
Engine-Out	4-Mode Weighted	6.19	6.53	5.57	6.20	0.0681	0.0677	0.0568	0.0780	0.16	0.18	0.16	0.17
Efficiency, %	4-Mode Weighted	15.95	15.58	11.50	13.30	16.32	-3.44	-26.20	5.20	-246	-173	-112	-169
Converter-Out	11	6.47	6.58	6.12	6.26	.	.	.	.	0.00	0.00	0.00	0.00
Engine-Out	11	6.53	6.65	6.16	6.51	.	.	.	.	0.42	0.47	0.41	0.47
Efficiency, %	11	0.83	0.99	0.59	3.89	.	.	.	.	100	100	100	100
Converter-Out	3	6.11	6.36	5.75	6.11	.	.	.	.	0.00	0.00	0.00	0.00
Engine-Out	3	6.37	6.53	5.66	6.28	.	.	.	.	0.18	0.21	0.17	0.20
Efficiency, %	3	4.05	2.59	-1.55	2.57	.	.	.	.	100	100	100	100
Converter-Out	10	5.29	5.63	5.05	5.55	.	.	.	.	0.90	0.88	0.63	0.77
Engine-Out	10	6.12	6.48	5.54	6.25	.	.	.	.	0.16	0.18	0.17	0.17
Efficiency, %	10	13.42	13.03	8.74	11.24	.	.	.	.	-469	-397	-274	-353
Converter-Out	2	4.15	4.49	3.91	4.40	.	.	.	.	0.73	0.61	0.39	0.59
Engine-Out	2	6.09	6.58	5.45	6.03	.	.	.	.	0.11	0.12	0.12	0.11
Efficiency, %	2	31.91	31.69	28.26	27.09	.	.	.	.	-565	-409	-233	-436
Converter-Out	OICA-2	4.32	4.63	4.03	4.17	0.0125	0.0148	0.0180	0.0170	0.81	0.77	0.48	0.59
Engine-Out	OICA-2	6.12	6.49	5.56	5.96	0.0117	0.0133	0.0116	0.0128	0.10	0.11	0.11	0.11
Efficiency, %	OICA-2	29.36	28.67	27.65	30.02	-6.40	-11.66	-54.21	-32.61	-691	-605	-348	-451

Definition	Mode	CO (g/bhp-hr)				CO_2 (g/bhp-hr)				BSFC (lb/bhp-hr)			
	Fuel Sulfur Level (ppm)	**3**	**30**	**150**	**350**	**3**	**30**	**150**	**350**	**3**	**30**	**150**	**350**
Converter-Out	4-Mode Weighted	1.93	1.60	1.64	1.99	489	479	451	479	0.345	0.337	0.318	0.339
Engine-Out	4-Mode Weighted	0.23	0.21	0.25	0.27	489	479	451	479	0.342	0.335	0.316	0.336
Efficiency, %	4-Mode Weighted	-725	-652	-569	-641	0.00	0.00	0.00	0.00	-0.79	-0.61	-0.65	-0.83
Converter- Out	11	1.06	1.04	0.91	0.96	590	575	551	571	0.412	0.401	0.385	0.398
Engine-Out	11	0.82	0.81	0.93	0.95	590	575	551	571	0.412	0.402	0.386	0.400
Efficiency, %	11	-28.2	-28.7	2.5	-1.4	0.00	0.00	0.00	0.00	0.00	0.25	0.26	0.50
Converter- Out	3	0.30	0.41	0.37	0.42	489	478	446	477	0.340	0.333	0.311	0.333
Engine-Out	3	0.24	0.21	0.26	0.29	489	478	446	477	0.341	0.333	0.311	0.333
Efficiency, %	3	-27.7	-90.2	-40.3	-45.5	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.00
Converter- Out	10	1.64	1.87	2.02	2.00	484	473	442	475	0.340	0.333	0.311	0.335
Engine-Out	10	0.18	0.16	0.17	0.19	484	473	442	475	0.337	0.330	0.308	0.331
Efficiency, %	10	-837	-1074	-1080	-950	0.00	0.00	0.00	0.00	-0.89	-0.91	-0.97	-1.06
Converter- Out	2	3.82	2.42	2.42	3.54	484	475	453	476	0.343	0.334	0.319	0.337
Engine-Out	2	0.23	0.21	0.24	0.26	484	475	453	476	0.337	0.331	0.316	0.332
Efficiency, %	2	-1541	-1075	-928	-1242	0.00	0.00	0.00	0.00	-1.63	-0.91	-0.95	-1.51
Converter- Out	OICA-2	4.05	2.69	2.88	3.60	484	475	453	476	0.343	0.335	0.320	0.337
Engine-Out	OICA-2	0.23	0.24	0.23	0.25	484	475	453	476	0.337	0.331	0.316	0.332
Efficiency, %	OICA-2	-1675	-1005	-1162	-1365	0.00	0.00	0.00	0.00	-1.78	-1.21	-1.27	-1.51

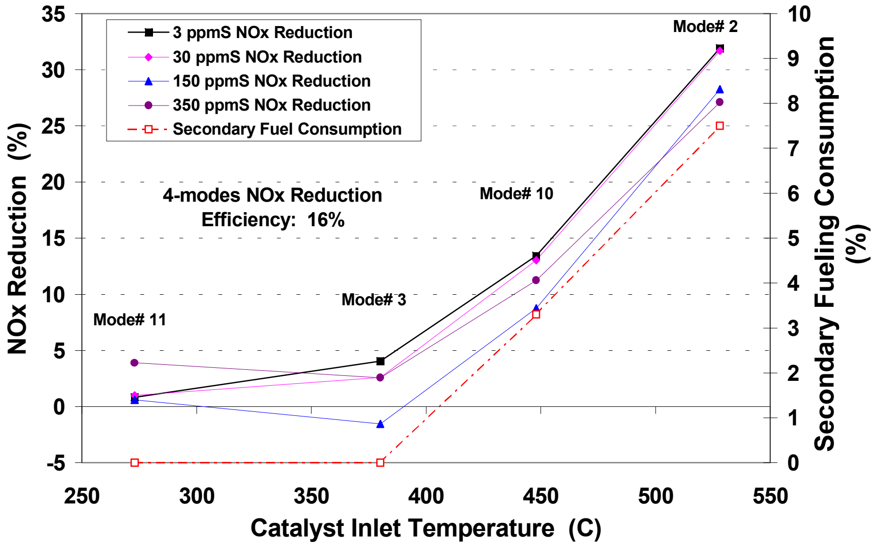


Figure 3.3-1. Effect of diesel sulfur level on the fresh high-temperature lean-NO_x catalyst performance (Cummins ISM engine)

As indicated, the catalyst inlet temperature plays a key role in lean-NO_x catalyst performance. As far as the fuel sulfur effect is concerned, the 30-ppm sulfur fuel showed little effect on the NO_x reduction efficiency. Relative to the system performance when operating on 3-ppm sulfur, when increasing the diesel sulfur level to 150 ppm, the NO_x reduction efficiency dropped considerably for several modes. Further increasing the diesel sulfur level to 350 ppm, the catalyst performed better than with the 150-ppm sulfur fuel. The reason for this is unclear. Bear in mind that this study was based on the fresh catalyst performance (baseline). The effect of diesel sulfur level on catalyst deactivation will be examined later in the program.

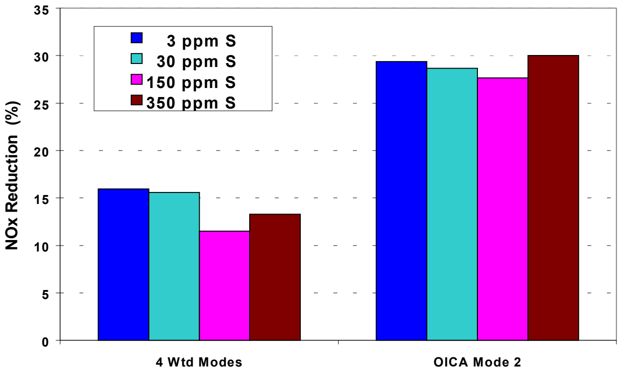


Figure 3.3-2. Effect of diesel sulfur level on NO_x reduction efficiency of the fresh high-temperature lean-NO_x catalyst (Cummins ISM engine, 4-mode composite and OICA mode 2)

The effect of diesel sulfur level on NO_x reduction efficiency is further depicted in Figure 3.3-2. Both 4-mode weighted composite results and mode 2 results are compared. With 150-ppm sulfur fuel, the NO_x reduction efficiency (4-mode composite) dropped by 4.5 percentage points compared with that of the 3-ppm sulfur fuel. At high temperature (528°C) and with high secondary fueling rate (7.5%), the sulfur level appears to have less effect on the NO_x reduction efficiency at mode 2.

One of the main concerns is the effect of diesel sulfur level on PM emissions that results from sulfate formation by a lean-NOx catalyst. Figure 3.3-3 demonstrates that the increase in diesel sulfur level can drastically increase the PM emissions under both the 4-mode test cycle condition and the OICA mode 2 condition. Kinetically, the higher the catalyst temperature, the higher the sulfate-making rate of a catalyst. The lower PM reduction (or higher PM emission) at the OICA mode 2 corresponds with this principle. The emission reduction for the 350-ppm sulfur fuel is greater than that for the 150-ppm fuel. This apparently anomalous result will be investigated as the aging tests are conducted.

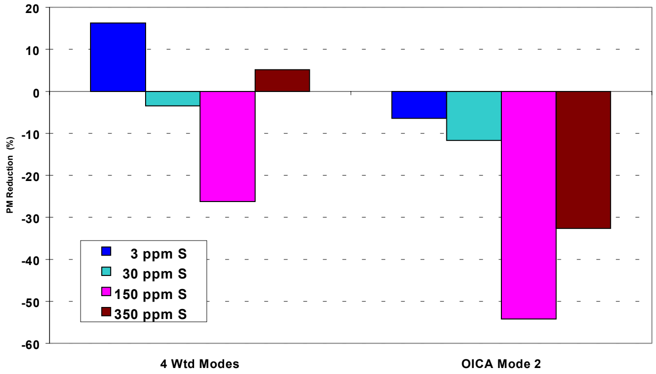


Figure 3.3-3. Effect of diesel sulfur level on PM reduction with the fresh high-temperature lean-NO$_x$ catalyst (Cummins ISM engine, 4-mode composite and OICA mode 2)

When applying a catalytic converter, by-product emissions are a potential issue. Because the secondary fuel must be added (as a reductant) to reduce NO$_x$ under a lean environment, the by-product issue with a lean-NO$_x$ catalyst is more severe. Although the THC and CO emissions were compromised by reducing NO$_x$ reduction efficiency in this study, considerable amounts of THC and CO were still able to break through the high-temperature lean-NO$_x$ converter when injecting secondary fuel (modes 10 and 2, as shown in Table 2.3-5). To summarize, the by-product emissions across the 4-mode test cycle are displayed in Figure 3.3-4. Evidently, the high-temperature lean-NO$_x$ catalyst had difficulty in effectively cleaning up the THC emissions with secondary fueling. More importantly, the catalyst apparently has poor oxidation power for HC. The high CO emissions after the converter indicate that the partial oxidation of HC was one of the main catalytic reactions. For the DECSE program, the lean-NO$_x$ catalyst was not sized to clean up THC and CO emissions. A modern DOC can be used to clean up the THC and CO emissions downstream of a lean-NO$_x$ catalyst in practical applications.

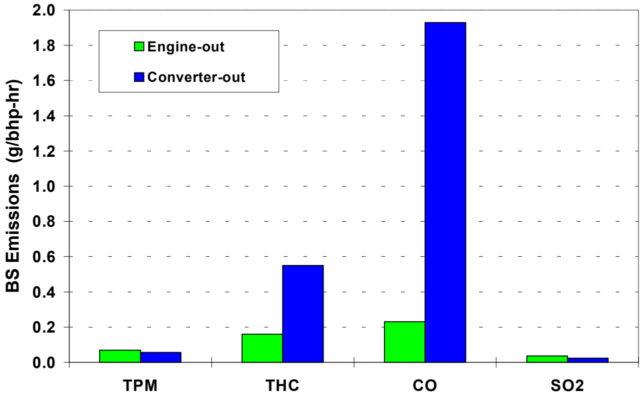


Figure 3.3-4. A comparison of by-product emissions between the converter-out and engine-out with the high-temperature lean-NO_x catalyst (Cummins ISM engine, 3-ppm fuel, 4-mode composite)

The high-temperature lean-NO_x catalyst has the potential to make SO_4 or PM if the diesel sulfur level is high enough to provide a suitable SO_2 concentration. According to the chemical breakdown analysis conducted by ORNL, the SO_4 emission data are presented in Figures 3.3-5 and 3.3-6. Only the primary particulate filters were analyzed for the purposes of this report. As demonstrated, the high-temperature lean-NO_x catalyst sulfate emissions (catalyst-out) were higher than that of the engine baseline (for both the 4-mode composite and OICA mode 2 tests) with the 150- and 350-ppm sulfur fuels. The higher the diesel sulfur level, the higher the SO_4 emission level. This result implies that the high-temperature lean-NO_x promotes SO_4 formation.

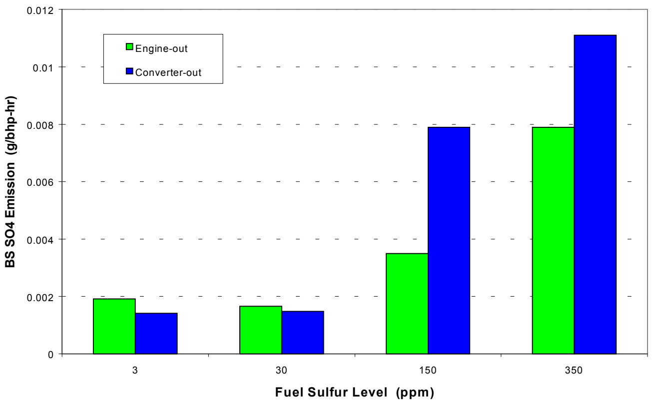


Figure 3.3-5. Comparison of SO_4 emissions between converter-out and engine-out with the fresh high-temperature lean-NO_x catalyst (Cummins ISM engine, 4-mode composite)

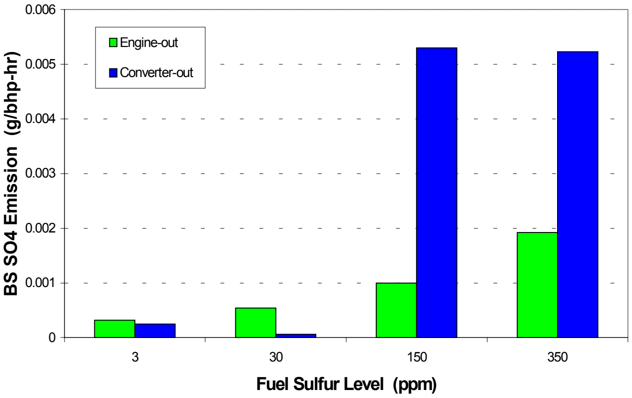


Figure 3.3-6. Comparison of SO_4 emissions between the converter-out and engine-out with the fresh high-temperature lean-NO_x catalyst (Cummins ISM engine, OICA mode 2)

3.4 Diesel Oxidation Catalysts

This interim report covers performance evaluations of the DOC on a Cummins ISM370 engine at four steady-state operating modes and over the heavy duty Federal Test Procedure (FTP). Post-catalyst emission measurements are compared to engine-out measurements (with the same fuel and operating conditions) to determine the HC, CO, and PM reduction efficiencies.

3.4.1 Engine-Out Emissions

Table 3.4-1 summarizes engine-out emissions from the ISM370 with each of the four fuels. The results include the 4-mode composite average, the modal breakdown, separate mode 2 (high torque) data, and FTP results. Because PM from the 4-mode testing was collected on a single filter, a modal breakdown could not be determined.

In general, engine-out HC and CO emissions did not vary with fuel sulfur. The data do not suggest a correlation between PM emissions and fuel sulfur level, as might have been expected. PM emissions with the 150-ppm sulfur fuel over the FTP are unexplainably higher than those demonstrated with 3-, 30-, and 350-ppm sulfur fuel; however, the SOF extracted from this PM was relatively high (0.0124 g/bhp-hr). PM emissions vary insignificantly with fuel sulfur over the 4-mode and peak-torque evaluations.

Table 3.4-1 Engine-Out Emissions—Cummins ISM370

	Total Hydrocarbon (THC) Emissions (g/bhp hr)			
	3 ppm	**30 ppm**	**150 ppm**	**350 ppm**
4 MODE - Weighted	**0.16**	**0.18**	**0.16**	**0.17**
Mode 11	0.42	0.47	0.41	0.47
Mode 3	0.18	0.21	0.17	0.20
Mode 10	0.16	0.18	0.17	0.17
Mode 2	0.11	0.12	0.12	0.11
Mode 2	0.10	0.11	0.11	0.11
FTP	**0.26**	**0.25**	**0.31**	**0.33**
	Carbon Monoxide (CO) Emissions (g/bhp hr)			
	3 ppm	**30 ppm**	**150 ppm**	**350 ppm**
4 MODE - Weighted	**0.23**	**0.21**	**0.25**	**0.27**
Mode 11	0.82	0.81	0.93	0.95
Mode 3	0.24	0.21	0.26	0.29
Mode 10	0.18	0.16	0.17	0.19
Mode 2	0.23	0.21	0.24	0.26
Mode 2	0.23	0.24	0.23	0.25
FTP	**0.93**	**1.03**	**0.97**	**1.08**
	Particulate Matter (PM) Emissions (g/bhp hr)			
	3 ppm	**30 ppm**	**150 ppm**	**350 ppm**
4 MODE - Weighted	**0.0681**	**0.0677**	**0.0568**	**0.0780**
Mode 2	0.0117	0.0133	0.0116	0.0128
FTP	**0.0559**	**0.0646**	**0.0919**	**0.0572**

3.4.2 Baseline Diesel Oxidation Catalyst Evaluations

Total Hydrocarbon and Carbon Monoxide Emissions. Figures 3.4-1 through 3.4-4 illustrate THC and CO emissions over the 4-mode OICA tests and the heavy-duty FTP for each of the four fuel sulfur levels studied. Both engine-out and catalyst-out data are presented. THC reduction efficiency exceeds 90% on the OICA 4-mode test with each of the fuels and does not correlate with fuel sulfur level (Figure 3.4-1). The DOC reduces THC emissions below detectable levels for the 3- and 30-ppm sulfur fuels and reduces THC by more than 90% for the 150- and 350-ppm fuels when tested on the FTP cycle (Figure 3.4-2).

The DOC reduces CO emissions by approximately 80% over the 4-mode OICA cycle, independent of fuel sulfur level (Figure 3.4-3). The DOC is less efficient over the FTP (40% to 48%) but, similarly, the reduction efficiency is not affected by sulfur level.

Based on the operating principle of DOCs, no dependence of performance on fuel sulfur level was expected for the unaged DOCs. The remainder of the testing in the DECSE program will evaluate if sulfur in diesel fuel affects the performance of aged catalysts. The catalysts will be periodically evaluated after 50, 150, and 250 hours on the engine to determine if fuel sulfur accelerates catalyst activity suppression.

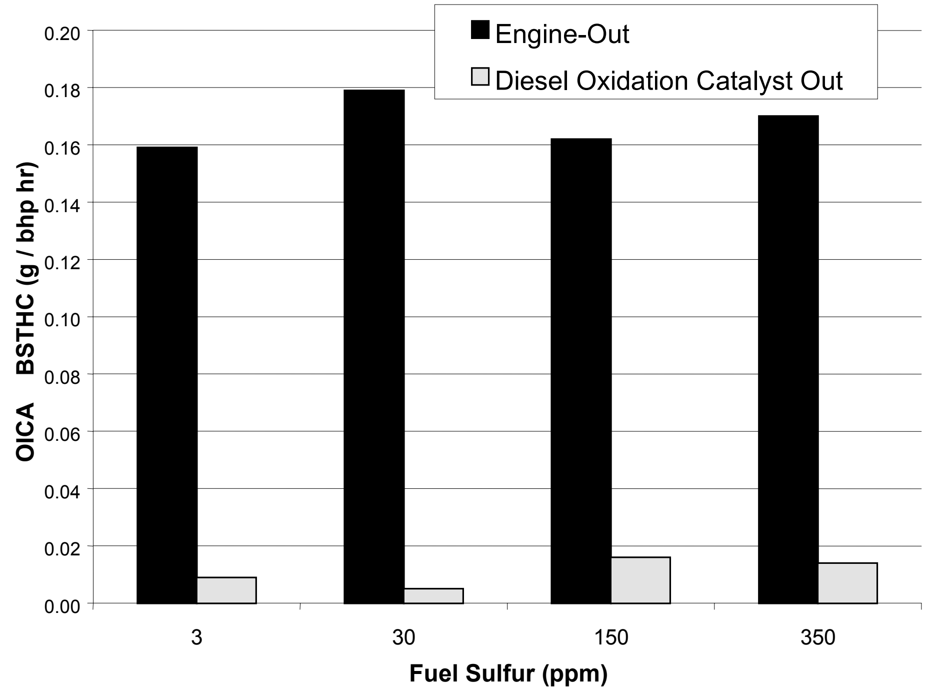


Figure 3.4-1. 4-mode OICA THC emissions—fresh DOC—ISM370

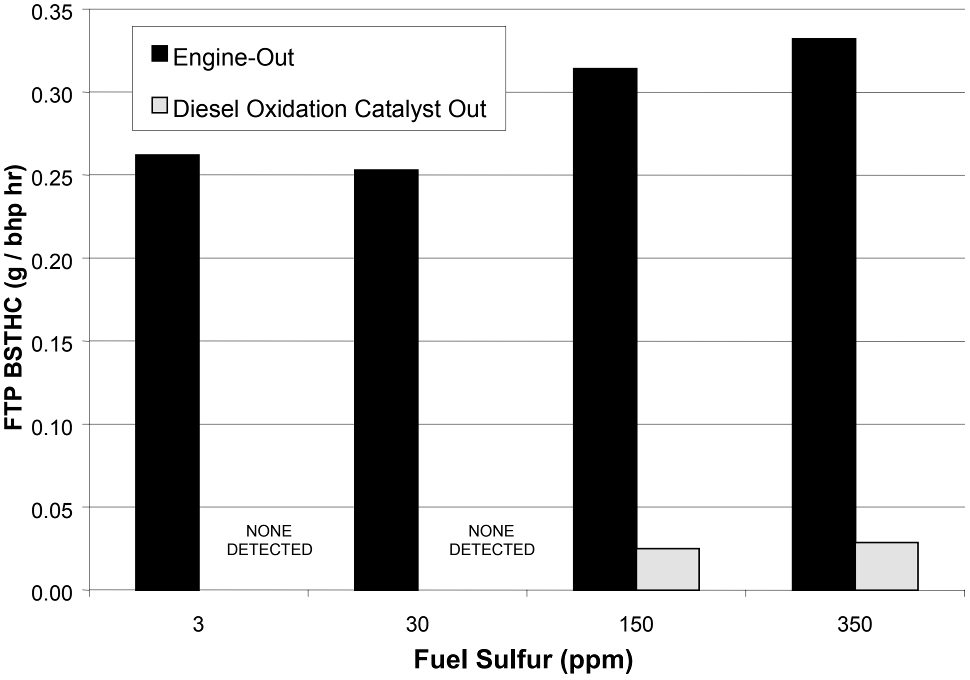


Figure 3.4-2. FTP THC emissions—fresh DOC—ISM370

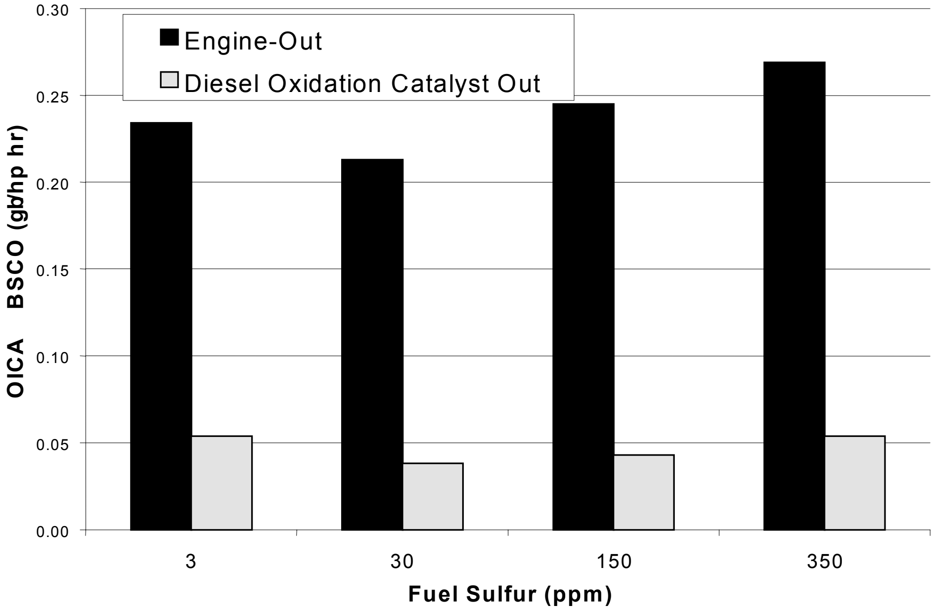


Figure 3.4-3. 4-mode OICA CO emissions—fresh DOC—ISM 370

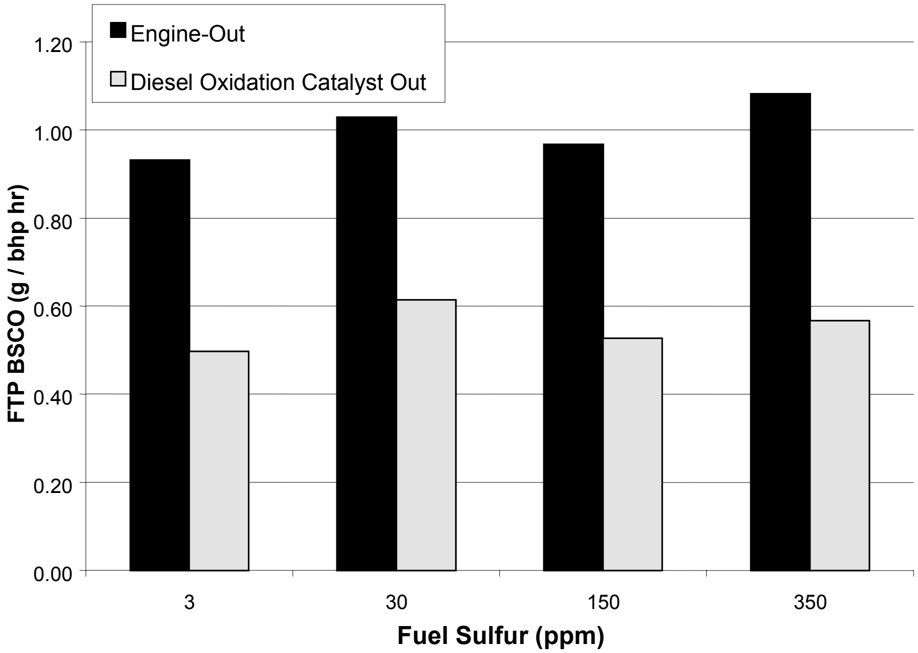


Figure 3.4-4. FTP CO emissions—fresh DOC—ISM370

PM Emissions. Of interest in this phase of the study is the impact of fuel sulfur on PM emissions, and specifically the response of DOC-equipped engines to fuel sulfur. Figures 3.4-5 and 3.4-6 illustrate PM emissions (engine-out/catalyst-out) from the OICA 4-mode and FTP for each of the four fuels studied. PM reduction over the OICA is negligible (<5%) and is not influenced by fuel sulfur level. DOC PM reduction efficiency is higher over the FTP (8%–16%). The 45% reduction observed with the 150-ppm fuel could be attributed to an anomalous engine-out result. This result will be investigated before the final report is issued.

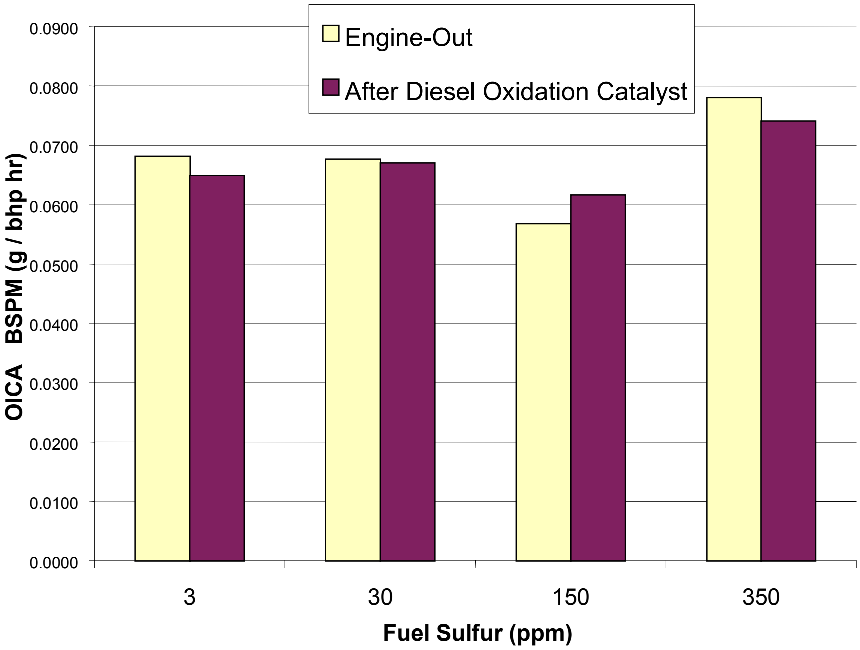


Figure 3.4-5. 4-mode OICA TPM—DOC—ISM370

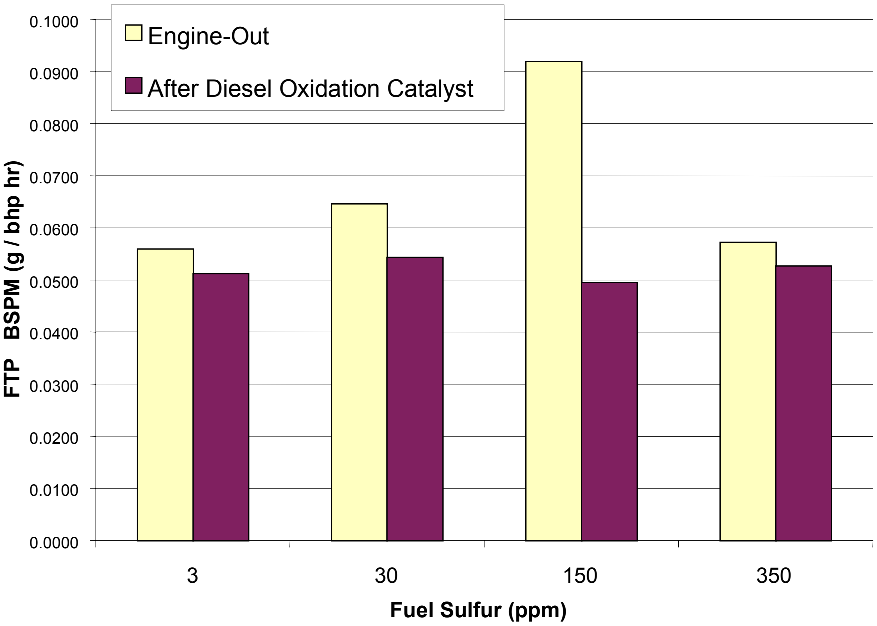


Figure 3.4-6. FTP TPM—DOC—ISM370

A separate evaluation of mode 2 was conducted with PM collected on a separate filter. Mode 2 was selected because this high torque point generates high catalyst temperatures at which conversion of SO_2 to SO_3 is likely to be accelerated. Figure 3.4-7 shows mode 2 TPM as a function of fuel sulfur level. Although engine-out PM emissions for mode 2 vary independently, the catalyst-out emissions increase significantly with fuel sulfur level. As shown in Figure 3.4-8, sulfate PM emissions after the DOC are as high as six times those measured engine-out. The catalyst facilitates the oxidation of SO_2 to SO_3, which condenses as sulfate to form PM. Much of the difference between engine-out and catalyst-out PM emissions (Figure 3.4-7) is likely caused by the increase in sulfate and the associated bound water.

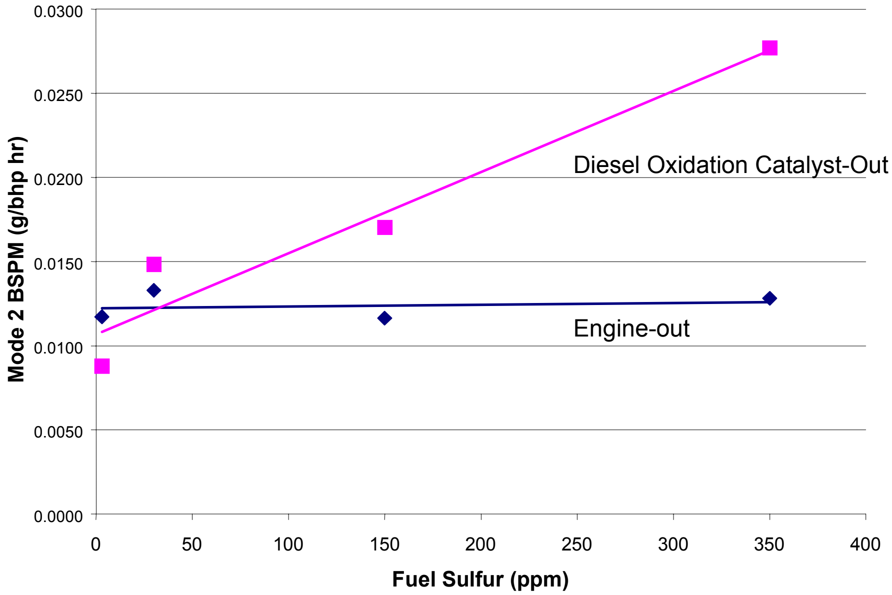


Figure 3.4-7. OICA mode 2 TPM—fresh DOC—ISM370

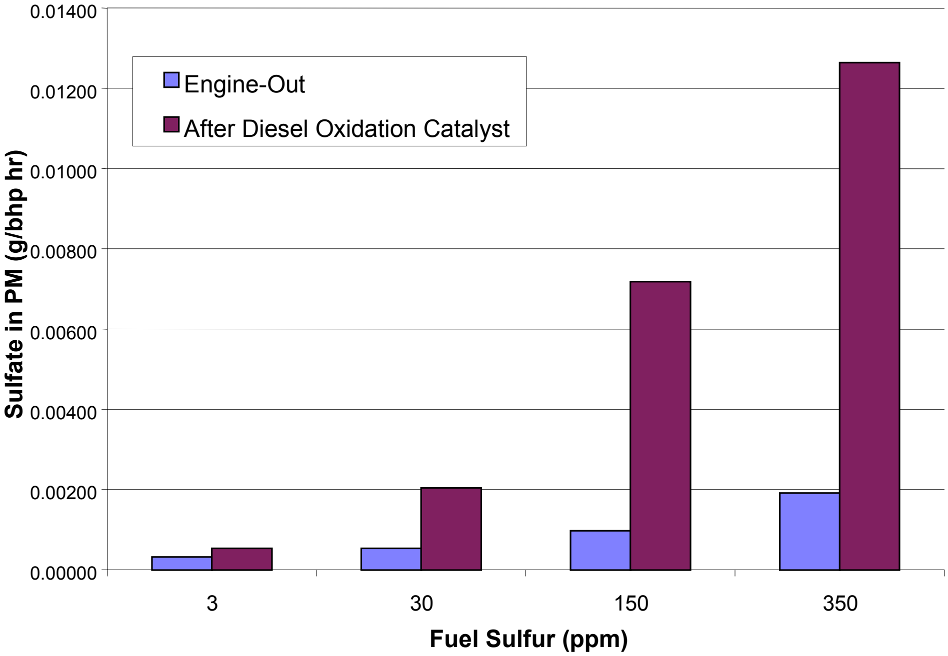


Figure 3.4-8. OICA mode 2 sulfate in PM—fresh DOC—ISM370

Section 4

Interim Conclusions

4.1 NO_x Adsorber

Conclusions cannot be drawn until the data analysis of the NO_x adsorber experiments is completed. It is anticipated that results and conclusions will be reported in a second Interim Report, to be published by October 1, 1999.

4.2 Continuously Regenerating Diesel Particulate Filters and Catalyzed Diesel Particulate Filters

The two DPF technologies chosen for the program, CR-DPF and CDPF, underwent (1) emissions tests for PM and selected gases, and (2) experiments to measure the effect of fuel sulfur level on the regeneration temperature of filter devices. The tests resulted in the following conclusions:

- Fuel sulfur has significant effects on PM emissions. Both DPFs were effective in reducing PM emissions (95% over OICA cycle) when used with 3-ppm sulfur fuel. With 30-ppm sulfur fuel, the PM reduction efficiencies dropped to 72% to 74%.

- Although designed as PM reduction devices, the DPFs reduced THC and CO emissions. These reductions were not affected to any significant degree by fuel sulfur level.

- Results to date show that the DPF regeneration temperatures (at which the collected PM is oxidized to prevent plugging) are slightly higher when testing with the 30-ppm fuel compared to results from testing with the 3-ppm fuel. However, it is too early to reach definitive conclusions. Additional testing is planned with the 150-ppm and 350-ppm fuels.

4.3 Lean-NO_x Catalysts

Lean-NO_x catalysts use a base or precious metal catalyst and a reductant in the exhaust stream to reduce NO_x emissions. Test results support the following conclusions:

- Within the operating temperature range of 360°C to 600°C, the NO_x conversion varies from 0% to 30%. The fuel sulfur trends indicate that the NO_x reduction is lower with the higher fuel sulfur levels, but the changes were not statistically significant. Data on sulfur aging effects (at 250 hours) are not yet available.
- Diesel sulfur level may have an effect on PM emissions from the high-temperature lean-NO_x catalyst. With 3-ppm sulfur fuel, PM reduction efficiency (based on the 4-mode composite test) was statistically significant at 16%. However, with high sulfur fuels, there was an increase in PM (compared to engine-out emissions), or the reduction efficiency was not statistically significant. This suggests the formation of PM by the lean-NO_x catalytic converter with high sulfur fuels.
- With 150- and 350-ppm sulfur fuels, the engine-out sulfate emissions increased by a factor of 2 to5 compared to levels observed with 3-ppm sulfur fuel. With the high-temperature lean-NO_x

catalyst, the post-catalyst sulfate emissions increased by a factor of 10 to 20. Higher sulfate emissions increase the overall PM emissions.

- The high-temperature lean-NO_x catalyst had difficulty effectively cleaning up the THC emissions resulting from secondary fuel injection (for the NO_x reductant). The post-catalyst emissions (4-mode composite) of HC increased by a factor of 2 to 3 over engine-out emissions, and CO increased by a factor of 6 to 7. The catalyst apparently has poor oxidation power for HC. The CO emissions present downstream of the lean-NO_x catalyst indicate that t he partial oxidation of HC was one of the main catalytic reactions. In practical applications, a DOC might be required for this type of high-temperature lean-NO_x catalyst.
- A proper secondary fueling strategy will be required for diesel application of this type of high-temperature lean-NO_x catalyst.

4.4 Diesel Oxidation Catalysts

DOCs are a technology designed to reduce HC, CO, and the soluble organic compounds associated with PM emissions found in diesel engine exhaust. Test results demonstrate the following:

- Fuel sulfur level has a modest effect on HC reduction efficiency (approximately 4 to 8 percentage points lower with high sulfur fuel) and no effect on CO reduction efficiency. However, catalyst-out PM emissions during the high-torque (high-exhaust temperature) steady-state tests (OICA mode 2) showed a strong fuel sulfur influence. With 3-ppm sulfur fuel, the PM reduction efficiency was statistically significant at 26%. However, with higher levels of fuel sulfur, there are significant increases (negative reduction efficiencies) in post-catalyst PM emissions. Chemical analysis of this PM is consistent with SO_2 in the engine exhaust being oxidized by the DOC and condensing as sulfate-laden PM that is collected on the filter.

Appendix A

DECSE Fuel Selection and Composition

This appendix discusses information related to the selection and composition of the fuel for the DECSE program.

A.1 Introduction

A major DECSE program goal is to investigate the specific effects of diesel fuel sulfur levels on the operation of diesel exhaust emission control devices. The fuel selection and specification process was directed toward achieving this overall goal.

To isolate the effects of fuel sulfur content from other fuel properties, differences in fuel sulfur level were obtained by doping an ultra-low sulfur base fuel with 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. Sulfur doping levels of 30, 150, and 350 ppm were selected. Selected tests were also repeated with 16-ppm fuel to provide additional differentiation at low sulfur levels for the NO_x adsorber technology.

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.2-1 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 base fuel. The measured property values were averages of analyses 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 options have the advantage 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.

Table A.2-1. Specifications and Measured Properties of 3-ppm Sulfur Base Fuel

	ASTM	DECSE	DECSE
Fuel Property	**Test**	**Goal**	**Measured**
Density, kg/m3	D1298/D4052	820-850	826.1
Viscosity @ 40°C, mm 2/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

However, if the sulfur content were varied by changing the fuel, other fuel properties would change as well. Thus, 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."

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 higher levels. For some tests, an intermediate 16-ppm sulfur fuel was used to obtain a finer differentiation between the essentially sulfur-free 3-ppm fuel and the 30-ppm fuel. 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. This was a sulfur level that the American Petroleum Institute indicated could be made available in the short-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 carbon dioxide, the hydrogen in the fuel is oxidized to water, and the sulfur in the fuel is primarily oxidized to sulfur dioxide. The composition of the engine-out exhaust is essentially a function only of the mass fraction of each of these fuel elements. According to this view, the amount and chemical identity of sulfur in the engine-out 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 sulfur dioxide to the exhaust itself.

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:

- The chemical forms of the sulfur compounds used to dope the fuel are similar to the chemical forms of sulfur compounds that are indigenous to diesel fuel.
- 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 that are 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[1] 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.

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[1] Sulfur Compounds in Crude Oil, U.S. Bureau of Mines Bulletin 659, (1972).

- Other sulfur-containing constituents include disulfides and sulfides. The sulfides include cyclic and alkyl aryl sulfides.

A.5.3 Logistical Criteria

Because dopants must be commercially available in the necessary quantities, selection is limited in practice to those 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.6-1 describes this dopant composition, and properties of the dopants are shown in Table A.6-2.

Table A.6-1. Dopant Composition

Constituent	Dopant Mass/ Sulfur mass	Desired Mass Percent Sulfur	Percent Dopant by Weight
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
Totals		**100**	**100.0**

Table A.6-2. Properties of Proposed Dopants

Constituent	CAS Number	MW	Sulfur Atoms	Sulfur (%)	Constituent mass/ sulfur mass	Boiling Point (%)	Melting Point (%)	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.6-3 shows the analysis values for the sulfur levels of several samples of the various doped fuels.

Table A.6-3. Sulfur Levels of Doped Fuels

Nominal Sulfur Content (ppm)	**Average Sulfur Content As Analyzed** (ppm)
15	16.6
30	30.2
150	130
350	308

A.7 Selection of Fuel for Use as a Reductant

A.7.1 Background

In this test program, some NO_x control devices required the use of a chemical reductant, which is used to regenerate the NO_x-reducing capability.

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 itself would 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 the above 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 tanks 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 prior to shipment to verify that the fuel being shipped meets project specifications.
- Drawing samples from each container of fuel. These samples will be retained until the project is over. [Not all samples will be analyzed, but they will be available, if needed.]
- The samples from the first, middle, and last containers in each separate delivery of fuel will be analyzed for sulfur and density. Examining these basic fuel properties will help 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 (API) 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, to be representative of those oils used in the marketplace.
- Consistent with the above three objectives, the sulfur content of the lubricating oil selected should be at the low end of the observed range.
- 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 lubrication oil in the DECSE project.

B.3.1 Aging

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

B.3.2 Oil Change Interval

The oil change interval will be 250 hours, maximum. The oil will be changed after each change in fuel-sulfur level. However, a double flush of oil will not be necessary. The amount of oil left in the pump and passageways is estimated to be negligible.

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 prior to 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 is not collected until the engine has warmed up and has had adequate time to circulate (about 30 minutes to 1 hour).

B.4.2 Oil Analysis Procedures

Table B.4-1 outlines the oil analysis procedures used for each oil sample.

Table B.4-1. Oil Sample Analyses

Property	Test Method	Significance
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.

B.5 Consideration of Lubricating Oil Sulfur Content

Sulfur from the lubricating oil can contribute to overall engine-out sulfur emissions. There is some sulfur in the lubricating oil base stock. However, much of this 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 a 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.