

# Diesel Emissions Control— Sulfur Effects Project (DECSE)

Summary of Reports



Produced for the U.S. Department of Energy (DOE)  
by the National Renewable Energy Laboratory (NREL),  
a DOE national laboratory



**DECSE Final Reports.** The following three final reports contain the results of the four technologies tested in the Diesel Emissions Control—Sulfur Effects (DECSE) project.

- Lean-NO<sub>x</sub> Catalyst and Diesel Oxidation Catalyst (DOC). DECSE Final Report: Diesel Oxidation Catalysts and Lean-NO<sub>x</sub> Catalysts—June 2001.
- NO<sub>x</sub> Adsorber Catalysts DECSE Phase II Summary Report: NO<sub>x</sub> Adsorber Catalysts—October 2000 (final report).
- Diesel Particulate Filters (DPFs). DECSE Program Phase I Interim Data Report No. 4: Diesel Particulate Filters—January 2000 (final report for the two DPFs).

**Final DECSE Program Summary**, June 2001 (a four-page summary of final results).

**Interim DECSE Reports.** These reports presented preliminary test results before the projects were completed.

- DECSE Program Phase I Interim Data Report No. 1—August 1999 (includes descriptions of the four technologies, initial test information, and preliminary conclusions).
- DECSE Program Phase I Interim Data Report No. 2: NO<sub>x</sub> Adsorber Catalysts—October 1999 (includes interim results and initial conclusions for the NO<sub>x</sub> adsorber catalyst only).
- DECSE Program Phase I Interim Data Report No. 3: Diesel Fuel Sulfur Effects on Particulate Matter Emissions—November 1999 (contains preliminary findings on the impacts of fuel sulfur on engine-out and post-catalyst emissions).

Complete texts of DECSE final reports and preliminary studies are available on the World Wide Web at <http://www.ott.doe.gov/decse>

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## Acronyms

<b>APBF-DEC</b>	Advanced Petroleum-Based Fuels—Diesel Emissions Control (project)
<b>ASTM</b>	American Society for Testing and Materials
<b>BSFC</b>	brake-specific fuel consumption
<b>CDPF</b>	catalyzed diesel particulate filter
<b>CIDI</b>	compression ignition, direct injection
<b>CO</b>	carbon monoxide
<b>CO<sub>2</sub></b>	carbon dioxide
<b>CR-DPF</b>	continuously regenerating diesel particulate filter
<b>DECSE</b>	Diesel Emissions Control—Sulfur Effects (project)
<b>DOC</b>	diesel oxidation catalyst
<b>DOE</b>	U.S. Department of Energy
<b>DPF</b>	diesel particulate filter
<b>EPA</b>	U.S. Environmental Protection Agency
<b>ETS</b>	Engineering Test Services
<b>EO</b>	engine-out
<b>FEV</b>	FEV Engine Technology
<b>FTP</b>	Federal Test Procedure
<b>g/bhp-hr</b>	grams/brake horsepower-hour
<b>HC</b>	hydrocarbon(s)
<b>HSDI</b>	high-speed, direct-injection (engine)
<b>HT</b>	high-temperature
<b>LNO<sub>x</sub></b>	lean-NO <sub>x</sub> (catalyst)
<b>LT</b>	low-temperature
<b>N<sub>2</sub></b>	nitrogen
<b>NO</b>	nitric oxide
<b>NO<sub>2</sub></b>	nitrogen dioxide
<b>NO<sub>3</sub></b>	nitrate
<b>NO<sub>x</sub></b>	nitrogen oxides
<b>OICA</b>	Organisation Internationale des Constructeurs d'Automobiles
<b>PM</b>	particulate matter
<b>ppm</b>	parts per million
<b>SCR</b>	selective catalytic reduction technology
<b>SO<sub>2</sub></b>	sulfur dioxide
<b>SO<sub>4</sub></b>	sulfate
<b>SOF</b>	soluble organic fraction
<b>SUV</b>	sport utility vehicle
<b>WVU</b>	West Virginia University

## Background

This summary describes a government and industry cost-shared project to determine the impact of fuel sulfur levels on emission control systems that could be used to lower emissions of nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM) from compression ignition, direct injection (CIDI) diesel-cycle vehicles. The sulfur in diesel fuel adversely affects the operation of diesel exhaust emission control systems. Tests were conducted and data were collected and analyzed for various combinations of fuel sulfur levels, engines, and exhaust emission control systems.

Diesel engines are used to power most heavy vehicles, as well as some light trucks, minivans, and automobiles. Engine exhaust emission standards will be more stringent for all vehicles, including light trucks and sport utility vehicles (SUVs) as new federal regulations are implemented. The U.S. Environmental Protection Agency (EPA) has announced emission standards for heavy-duty trucks that manufacturers will have to meet starting in 2007. These standards require that NO<sub>x</sub> emissions be reduced by 75%–90% and PM emissions by 80%–90%, compared with current standards. EPA

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The DECSE fuels were blended at the Chevron Phillips Chemical Company, LP, in Borger, TX.

also announced lower emission standards for passenger vehicles, requiring that their emissions be 77%–95% cleaner than current emissions and that sulfur in gasoline be reduced by as much as 90% from today's level. These new standards are to be phased in beginning in 2004.

EPA has also ruled that the maximum sulfur content in highway diesel fuel be reduced to 15 parts per million (ppm), a reduction of 97% from the current maximum allowable level of 500-ppm, beginning in mid-2006. The tests described in this summary were conducted by the Diesel Emissions Control—Sulfur Effects (DECSE) project, guided by a steering committee that included representatives of the U.S. Department of Energy, two national laboratories, and manufacturers of diesel engines and emission control systems.

Collecting and analyzing data on the effects of sulfur on various exhaust emission systems were the key steps in a larger cooperative research project. Results from the DECSE tests are being used in continuing work to determine the types of diesel fuel, vehicle engines, and exhaust emission control systems that, working together, will enable diesel-powered vehicles to meet stricter new regulations. The successor project is called the Advanced Petroleum-Based Fuels—Diesel Emissions Control project (APBF-DEC).

### SOURCES OF DECSE FUNDING AND IN-KIND SUPPORT

U.S. Department of Energy, Office of Heavy Vehicle Technologies, Office of Advanced Automotive Technologies and DOE laboratories (National Renewable Energy Laboratory and Oak Ridge National Laboratory)

Engine Manufacturers Association (representing original equipment manufacturers)

Manufacturers of Emission Controls Association

## Introduction

The tests conducted by DECSE were designed to provide data on the effects of various levels of sulfur in diesel fuels on emission control systems. Fuel composition affects engine efficiency, chemical composition of the exhaust, and the amount of a given pollutant or proportions of types of pollutants. Previous studies suggested that the fuel's sulfur level can directly affect the effectiveness of exhaust emission control devices.

## The Technologies

The following four emission control technologies tested included commercially available technologies as well as those under development.

**Diesel particulate filters (DPFs)**—Filters designed to remove PM from the engine exhaust by collection on a filter element. Laboratory: Engineering Test Services (ETS). Test program and report completed in January 2000. Test engine: Caterpillar 3126. Examples of study questions include:

- How does the DPF affect emissions of PM and selected gases?
- How does fuel sulfur affect emissions (engine-out [EO] and post-filter)?
- Does the DPF performance degrade over time?

**Lean-NO<sub>x</sub> catalysts (LNO<sub>x</sub>)**—Catalysts capable of converting NO<sub>x</sub> to nitrogen (N<sub>2</sub>) in the presence of oxygen. Test program and report completed in June 2001. Laboratory: West Virginia University (WVU). Test engines: Cummins ISM370, Navistar T444E. Examples of study questions include:

- How does the catalyst affect the emissions of NO<sub>x</sub>, sulfate (SO<sub>4</sub>), and PM?
- How does the fuel sulfur level affect the post-catalyst emissions?
- What is the effect of sulfur during aging on the catalyst's performance?

**Table 1. DECSE Test Engines**

Engine	Displacement in Liters	Type	Peak Power 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	70 (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

**Diesel oxidation catalysts (DOCs)**—Catalysts designed to reduce hydrocarbon (HC), carbon monoxide (CO), and the soluble organic compounds associated with PM emissions. Test program and report completed in June 2001. Test engines: Cummins ISM370, Navistar T444E. Laboratory: WVU. Examples of study questions include:

- How does the catalyst affect emissions of NO<sub>x</sub>, CO, and PM?
- How does the fuel sulfur level affect the post-catalyst emissions?
- What is the effect of sulfur during aging on the catalyst's performance?

**NO<sub>x</sub> adsorber catalysts**—Catalysts that function by first storing (adsorbing) NO<sub>x</sub> and then reducing the stored NO<sub>x</sub> under fuel-rich conditions. Phase I (sulfur effects) completed in October 1999. Phase II (regeneration/desulfurization) completed in October 2000. Test engine: 1.9-liter high-speed, direct-injection (HSDI) prototype. Laboratory: FEV Engine Technology (FEV). Tasks included:

- Develop and improve calibration to achieve maximum NO<sub>x</sub> reduction.
- Map performance.
- Develop a desulfurization process.
- Demonstrate desulfurization.
- Evaluate performance during repeated aging and desulfurization cycles.

## The Engines

The diesel engines used for the DECSE study met specific selection criteria. They were intended to be commercially available and representative of the marketplace, or the current state of the art. They had to represent light-, medium-, or heavy-duty applications, operating within the range of exhaust temperatures and emissions levels typical of roadway duty cycles (generally of 1998 or 1999 model year). Three met the criteria; the engine used in the NO<sub>x</sub> adsorber test was a prototype. (See Table 1.) The engines and related emission control hardware selected were:

**Navistar T444E engine**/low-temperature lean-NO<sub>x</sub> catalysts and DOC

**Caterpillar 3126 engines**/DPFs

**DaimlerChrysler/DDC 1.9L HSDI engine**/NO<sub>x</sub> adsorber catalyst

**Cummins ISM370**/high-temperature lean-NO<sub>x</sub> catalysts and DOC.

## The Fuels

Chevron Phillips Chemical Company, LP, provided the base fuel, which was similar to commercially available fuel, except for sulfur content, and with limited representation of specific compounds within a class, such as aromatics and polyaromatics.

Fuels for the tests were then formulated by:

- Blending the base fuel to contain 3-ppm of sulfur.
- Adding incremental amounts of a representative mix of sulfur compounds (doping) to create more fuel formulations with sulfur content levels at 16- and 78-ppm (NO<sub>x</sub> adsorber catalyst project only), 30-, 150-, and 350-ppm (the then-current average sulfur content in on highway diesel fuels). Table 2 lists the major properties of the fuels.

## The Tests

Three independent testing laboratories—WVU, FEV, and ETS—gathered data on the engines and emission control technologies as follows:

- Engine speed and load, fuel rate, oil temperature and pressure, compressor/turbine pressure and temperature, exhaust temperatures, and oil consumption.



**Emissions benches like this one at WVU were used to collect data during the tests.**

**Table 2. Major Fuel Properties—DECSE Base Fuel**

Fuel Property	ASTM <sup>a</sup>	DECSE Goal	DECSE Measured
Density, kg/m <sup>3</sup>	D4052	820–850	826.1
Viscosity @ 40C, mm <sup>2</sup> /s	D445	>2.0	2.4
Distillation IBP, C	D86	171–182	185
10% recovery, C	D86	210–226	207
50% recovery, C	D86	254–271	259
90% recovery, C	D86	310–321	314
FBP, C	D86	326–360	350
Sulfur, ppm	D5453	<10	3.1
Aromatics, vol. %	D1319	25–32	27.0
Olefins, vol. %	D1319	1–3	2.3
Saturates, vol. %	D1319	55–70	70.7
Aromatics, wt. %	D5186		28.5
Polyaromatics, wt. %	D5186	3–10	9.6
Non-aromatics, wt. %	D5186		71.2
Cetane number	D613	42–48	45
Cetane index	D976		53.6
HFRR lubricity, um	D6079		635/355 <sup>b</sup>

<sup>a</sup> American Society for Testing and Materials

<sup>b</sup> Values without/with 55-ppm Octel 35a and 211-ppm OLI-9000 additives

- Control technology inlet and outlet temperature and pressure, space velocity and exhaust components such as NO<sub>x</sub>, HC, CO, CO<sub>2</sub>, PM and sulfur dioxide (SO<sub>2</sub>). (See Table 3.)

Tests were conducted on the emission control technologies to measure and compare the effects of as many as 250 hours of aging on engines using diesel fuel containing varying levels of sulfur (see Table 4). In addition, for the NO<sub>x</sub> adsorber catalyst project, tests were conducted to improve the NO<sub>x</sub> regeneration calibration to achieve a greater than 80% NO<sub>x</sub> conversion between operating temperatures of 250°C and 500°C and to develop a desulfurization process to restore NO<sub>x</sub> conversion efficiency lost to sulfur contamination. Table 4 summarizes the DECSE test components.

In general, the DECSE data show the effects that fuel-borne sulfur has on the performance of emission control systems. The reports providing the results of these tests can be found at <http://www.ott.doe.gov/decse>. This document is an executive summary of the results of the DECSE tests.

**Table 3. Summary of DECSE’s Experimental Designs**

Technology	250 Hours Aging at various fuel-sulfur levels				Evaluation				Engine	Remarks
	3	30	150	350	3	30	150	350		
DOC	Special Navistar aging cycle				Navistar 9-mode and simulated FTP-75				T444E (Navistar)	High precious metal loading
	Modified OICA <sup>a</sup> aging cycle				Stabilized OICA and heavy-duty FTP				ISM 370 (Cummins)	Low precious metal loading
Active LNO <sub>x</sub>	Special Navistar aging cycle				Navistar 9-mode				T444E	LT catalyst
	Modified OICA aging cycle				Stabilized OICA				ISM 370	HT catalyst
CR-DPF and CDPF <sup>b</sup>	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 <sub>x</sub> Adsorber	3	16	30	78	3	16	30			
	3-hour and 10-hour aging cycle using 9 temperature points in sequence				Phase 1: NO <sub>x</sub> conversion every 50 hours Phase 2: before and after desulfurization				HSDI (DaimlerChrysler/DDC prototype)	150- and 350-ppm fuel not used based on initial results on lower sulfur levels

<sup>a</sup> A test cycle developed during European work; OICA is the International Organization of Motor Vehicle Manufacturers (Organisation Internationale des Constructeurs d’Automobiles)

<sup>b</sup> Continuously regenerating diesel particulate filters (CR-DPFs) and catalyzed diesel particulate filters (CDPFs).

**Table 4. Summary of DECSE Test Components**

Engine	Test Method	Catalyst Age (hours)	Fuel Sulfur ppm	Emissions Measured <sup>a</sup>	
				Gases and Fuel Economy	Particulate Matter
Cummins ISM370	OICA modes 2, 3, 10, 11	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNO <sub>x</sub>	
	OICA 4-mode wtd.	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNO <sub>x</sub>	EO, DOC, LNO <sub>x</sub>
	OICA mode 2 (w/filter)	0	3, 30, 150, 350	EO, DOC, LNO <sub>x</sub>	EO, DOC, LNO <sub>x</sub>
	FTP hot	0, 50, 150, 250	3, 30, 150, 350	EO, DOC	EO, DOC
Navistar T444E	Nav-9 modes 2, 3, 7, 9	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNO <sub>x</sub>	
	Nav-9 (4-mode) wtd.	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNO <sub>x</sub>	EO, DOC, LNO <sub>x</sub>
	Nav-9 mode 9 (w/filter)	0	3, 30, 150, 350	EO, DOC, LNO <sub>x</sub>	EO, DOC, LNO <sub>x</sub>
	FTP 75	0, 50, 150, 250	3, 30, 150, 350	EO, DOC	EO, DOC
Caterpillar 3126	OICA modes 1-13	Note <sup>d</sup>	3, 30, 150, 350	EO, CDPF, CRDPF	
		Note <sup>d</sup>	30	EO, CDPF, CRDPF	
	OICA 13-mode wtd.	Note <sup>d</sup>	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
		Note <sup>d</sup>	30	EO, CDPF, CRDPF	EO, CDPF, CRDPF
	OICA mode 2 (w/filter)	Note <sup>d</sup>	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
	OICA mode 4 (w/filter)	Note <sup>d</sup>	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
1.9L HSDI prototype	Performance mapping @ 3000 rpm over range of temperatures	As long as 250	3, 16, 30, 78	EO, NO <sub>x</sub> Adsorber Catalyst	EO, NO <sub>x</sub> Adsorber Catalyst

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<sup>a</sup> Entries identify source from which emissions data were obtained for each combination of catalyst/filter age and fuel sulfur level.

EO = engine-out; DOC = diesel oxidation catalyst; LNO<sub>x</sub> = lean-NO<sub>x</sub> catalyst; CDPF = catalyzed diesel particulate filter; CR-DPF = continuously regenerating diesel particulate filter

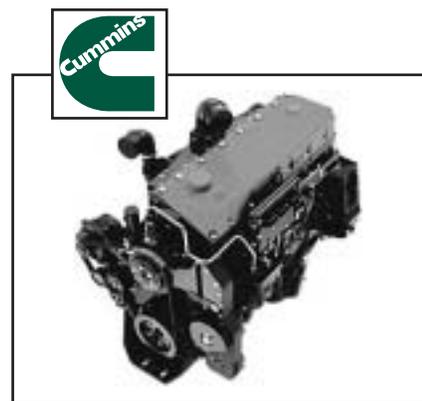
<sup>b</sup> HC, NO<sub>x</sub>, CO, CO<sub>2</sub>, BSFC (a measure of engine efficiency).

<sup>c</sup> Total PM, SOF, SO<sub>4</sub>, NO<sub>3</sub>.

<sup>d</sup> The same CDPF and CR-DPF filters were used throughout the test program. The 30-ppm sulfur fuel was tested after approximately 100 hours and 425 hours of use to evaluate aging effects.



**The Navistar T444E test engine.**



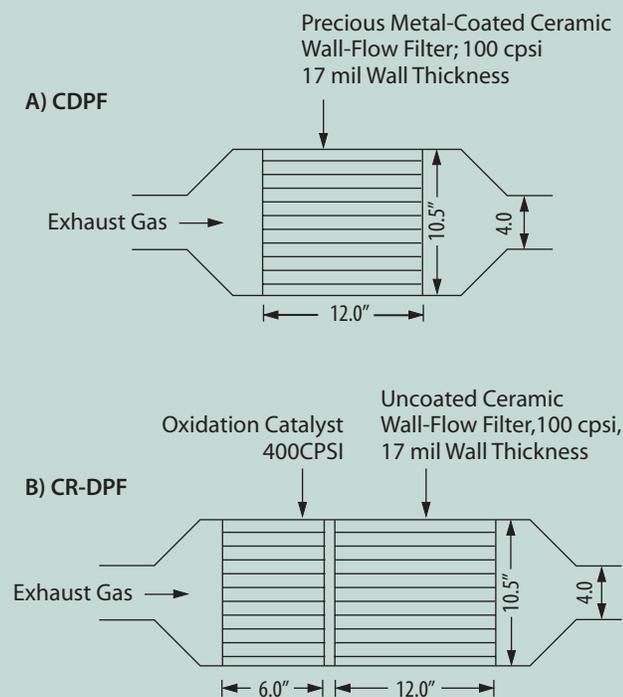
**The Cummins ISM370 test engine.**

## Diesel Particulate Filters

### Test Design

DPFs remove PM from engine exhaust by collecting it on a filter—in this test, a ceramic element. Sulfur in the exhaust can be oxidized over these filters, forming sulfates that are measured as PM. The exhaust gas temperature and fuel sulfur level are critical factors that affect the performance of DPFs. Two types of DPFs—a continuously regenerating DPF (CR-DPF) and a catalyzed DPF (CDPF)—were evaluated. The critical role of these technologies is to clean (or regenerate) the DPF by oxidizing the collected PM to prevent the device from becoming plugged. The CR-DPF regenerates the DPF by continuously generating nitrogen dioxide (NO<sub>2</sub>), with the help of a DOC upstream of the filter. The CDPF regenerates the DPF by using a catalyst coating on the filter element to promote oxidation of the collected PM.

Two types of tests—emission tests (PM and selected gases) and experiments to measure the effect of fuel sulfur level on the regeneration temperature of the DPFs—were conducted using the OICA’s 13-mode test procedure. Fuels used had sulfur levels ranging from 3- to 350-ppm. A Caterpillar 3126



Two types of DPFs were tested in this project.

engine (which has a relatively low temperature exhaust) was tested using the OICA 13-mode test procedure and tests at peak-torque and “road-load” steady-state conditions. 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.

### Key Results

- Increasing the fuel sulfur level from 3- to 350-ppm produced an essentially linear 29% increase in the EO PM emissions. No significant changes in the EO gas phase emissions or baseline fuel consumption were observed as a result of increasing the fuel sulfur level.
- Fuel sulfur had significant effects on post-DPF total PM emissions. Both DPFs effectively reduced PM emissions (95% over the OICA cycle), when used with 3-ppm sulfur fuel. With 30-ppm sulfur fuel, the PM reduction efficiencies dropped to 73%. When tested with the 150-ppm sulfur fuel, PM reduction efficiency was nearly zero. With the 350-ppm sulfur fuel, PM *increased* by more than 100% (see Figure 1).
- Fuel sulfur levels lower than 150-ppm were required to achieve any reduction in total PM. Similarly, a sulfur level of 3-ppm was required to achieve the total PM emissions target of the 0.01 grams per brake horsepower-hour (g/bhp-hr) standard for the 2007 federal regulation.
- Approximately 40%–60% of fuel sulfur was converted to SO<sub>4</sub> PM as measured over the 13-mode cycle for both DPFs.

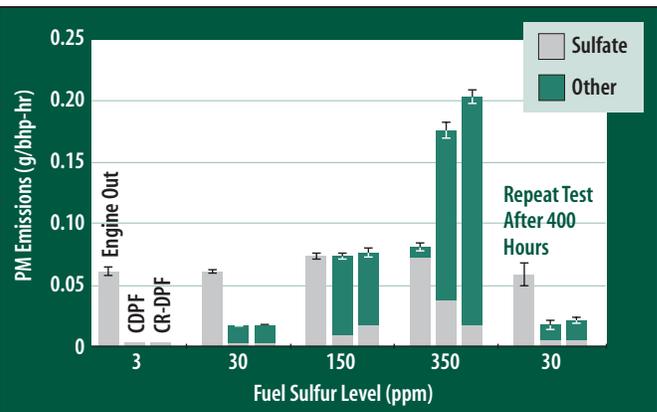


Figure 1. Engine-out and post-DPF emissions of total PM and components as a function of fuel sulfur level for the OICA cycle (with 95% confidence intervals on estimated PM)

- The exhaust temperature required to regenerate the DPF devices increased by about 25°C when changing from 3- to 30-ppm sulfur fuel. The regeneration temperature remained stable at 150- and 350-ppm fuel sulfur level for the CDPF.
- Within the range of fuel sulfur levels required to achieve any PM reduction (less than 150-ppm), the temperature required for filter regeneration was consistently higher for the CDPF than for the CR-DPF. The average difference when operating with the 3-ppm sulfur fuel was 54°C. When operating with 30-ppm sulfur fuel, the regeneration

temperature of the CDPF averaged 66°C higher than the regeneration temperature for the CR-DPF.

- Fuel consumption increases of up to 2% above the baseline were measured when operating with the DPFs. This increase, which resulted from the additional exhaust back-pressure created by the DPFs, was generally larger with the CR-DPF than with the CDPF.
- The performance of the DPFs when exposed to 400 hours of testing with the higher sulfur levels did not degrade (see Figure 1 on previous page).

## Lean-NO<sub>x</sub> Catalysts

### Test Design

Lean-NO<sub>x</sub> catalysts can reduce diesel NO<sub>x</sub> emissions with the assistance of a supplementary reductant (such as diesel fuel) under a lean (oxygen-rich) exhaust. The main concern about sulfur in diesel fuel is that the sulfates produced during combustion can be adsorbed on the active catalyst surface and block the adsorption of NO<sub>x</sub> and HC. This results in a decrease in the catalyst's efficiency in reducing NO<sub>x</sub> and an increase in fuel consumption and HC slip. (This refers to the amount of HC that is more than what is needed to reduce the NO<sub>x</sub>. The unconsumed HC is then exhausted into the air.)

The two lean-NO<sub>x</sub> catalysts used were performance tested only at steady-state test cycles and before, during, and after a 250-hour aging cycle using four fuel sulfur levels. Two types of lean-NO<sub>x</sub> catalysts—a high-temperature lean-NO<sub>x</sub> catalyst and a low-temperature catalyst were chosen for the study. Both catalysts require a reductant (supplemental HC) in the exhaust stream to reduce the NO<sub>x</sub> emissions.

The diesel test fuel was used as the reductant. The injection rate was optimized for peak NO<sub>x</sub> reduction without exceeding 4% of the total fuel consumption. The high-temperature (360°–600°C) catalyst was evaluated on a Cummins ISM370 engine and the low-temperature (170°–300°C) catalyst was evaluated on a Navistar T444E engine, which was chosen to provide a range of exhaust temperatures. Four steady-state modes were selected from the OICA 13-mode steady-state test cycle for the high-temperature catalyst tests. The low-temperature catalysts were evaluated using selected modes from the Navistar 9-mode cycle.



The Navistar T444E engine was installed on a GE-2000 DC dynamometer at WVU's test facility.

Gaseous and PM emissions were sampled in the exhaust before and after the catalysts to determine reduction efficiencies. PM breakdown analyses were also conducted.

### Key Results

- Fresh lean-NO<sub>x</sub> catalysts achieved NO<sub>x</sub> reduction peak efficiencies of less than 20% with a maximum fuel penalty of 4% for all catalysts during the defined steady-state test cycles. However, reductions of more than 50% and 30% NO<sub>x</sub> were observed at specific operating temperatures for the low-temperature and high-temperature catalysts, respectively (see Figure 2). The effect of the fuel sulfur level on NO<sub>x</sub> reduction efficiency was not statistically significant.
- There was a significant increase in the catalyst-out SO<sub>4</sub> emissions when operating with fresh low-temperature lean-NO<sub>x</sub> catalysts under the high-temperature, steady-state test mode (405°C) at higher fuel sulfur levels (150- and 350-ppm sulfur) (see Figure 3 on the next page).
- The high-temperature lean-NO<sub>x</sub> catalyst was vulnerable to HC slip (more than 50% of injected fuel in certain test modes) with all fuels tested. The low-temperature lean-NO<sub>x</sub> catalyst more effectively controlled HC and CO slip, but only when using low-sulfur fuels (3- and 30-ppm sulfur).
- Catalyst aging (as long as 250 hours) had no apparent effect on the NO<sub>x</sub> reduction efficiency of the low-temperature and high-temperature lean-NO<sub>x</sub> catalysts, independent of fuel sulfur level.

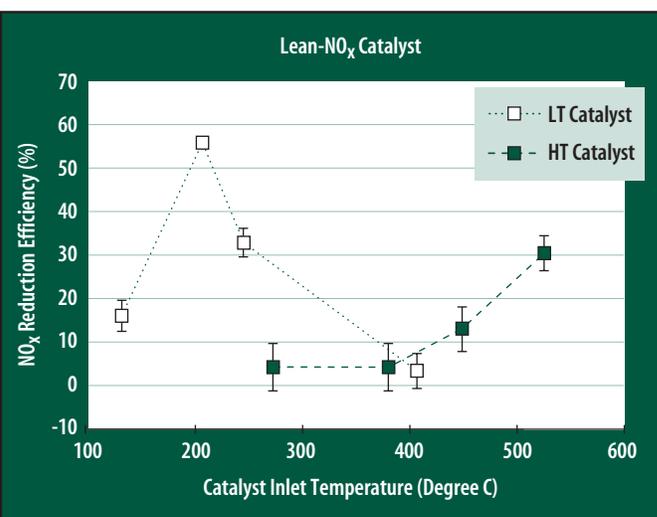
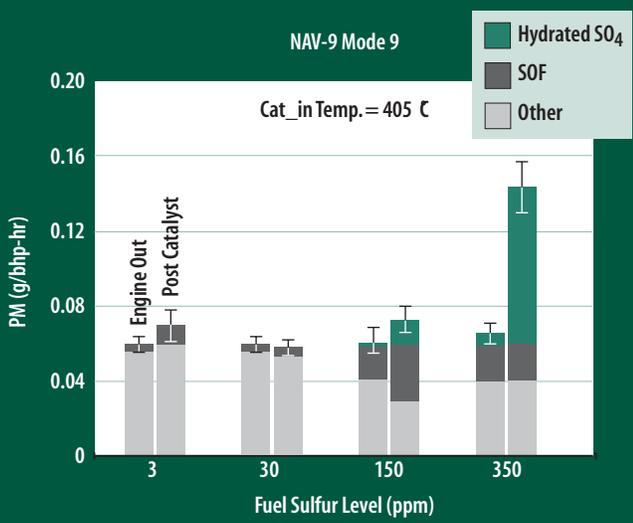
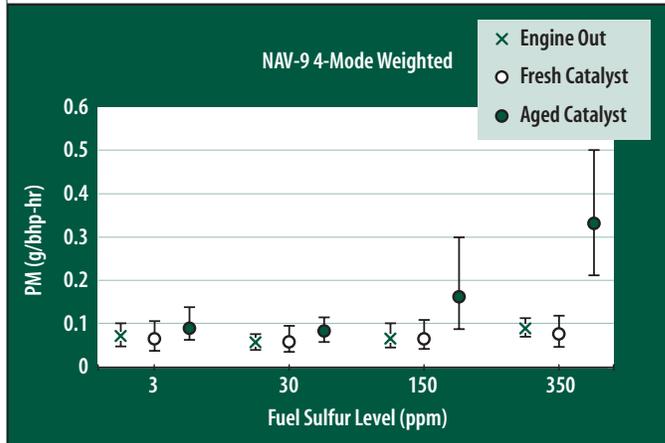


Figure 2. NO<sub>x</sub> reduction efficiency of low-temperature (Navistar) and high-temperature (Cummins) lean-NO<sub>x</sub> catalysts at selected catalyst inlet temperatures (with 95% confidence intervals)



**Figure 3. Engine-out and post-lean-NO<sub>x</sub> catalyst (fresh) emissions of PM and components under low-temperature (Navistar) applications using a Nav-9 mode 9 test (with 95% confidence intervals on estimated PM)**

- PM emissions from aged (50 hours) low-temperature lean-NO<sub>x</sub> catalysts increased significantly, mainly because of higher SO<sub>4</sub> emissions with higher sulfur fuels (150- to 350-ppm) (see Figure 4). Thermal aging seems to be the primary reason for the increase of PM with the lower sulfur levels. With 350-ppm sulfur fuel, the effects of thermal aging seemed essentially additive. Unlike the low-temperature lean-NO<sub>x</sub> catalyst, the aging process had only a slight effect on catalyst-out PM emissions with the high-temperature lean-NO<sub>x</sub> catalyst.



**Figure 4. Engine-out and fresh, aged lean-NO<sub>x</sub> emissions of PM under low-temperature (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)**

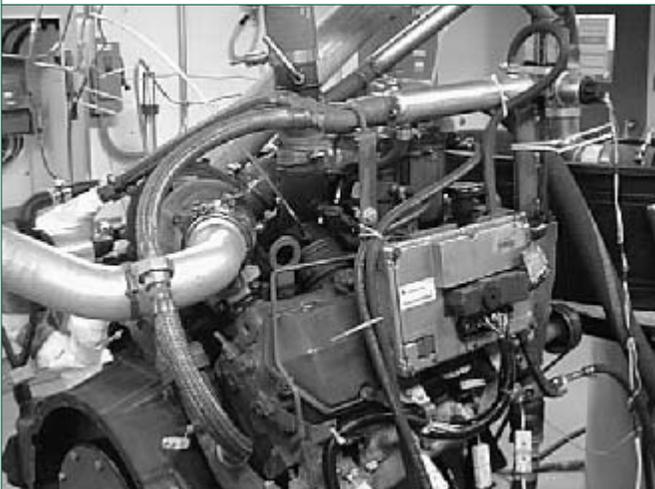
- Thermal aging was also the main contributor to the increase of HC slip with the low-temperature lean-NO<sub>x</sub> catalyst. Thermal aging could be making the catalyst more vulnerable to sulfur inhibition, resulting in the higher HC slippage with high-sulfur fuels. The HC slip from the high-temperature lean-NO<sub>x</sub> catalysts also increased after aging.
- For the low-temperature lean-NO<sub>x</sub> catalyst, the adverse aging effects on PM emissions and HC slip were reversed within 50 hours of operation with 30-ppm sulfur fuel. This suggests that the catalyst had not been permanently deactivated. For the high-temperature lean-NO<sub>x</sub> catalyst, HC slip increased after switching from high-sulfur fuel (350-ppm) to low-sulfur fuel (30-ppm).

## Diesel Oxidation Catalysts

### Test Design

DOCs reduce HC, CO, and the soluble organic fraction (SOF) of PM by oxidation over a precious metal catalyst. A concern with higher precious metal loadings is the DOC's tendency to convert SO<sub>2</sub> in the exhaust gas to SO<sub>4</sub>. Testing was performed to assess fresh catalyst performance and its performance after aging.

The performance of the base metal, fresh high-temperature DOCs was evaluated on a Cummins ISM370 engine using a 3-ppm sulfur base fuel and fuels with 30-, 150-, and 350-ppm sulfur. The precious metal-coated low-temperature DOC catalysts were aged and evaluated using a Navistar T444E engine operating on the same fuels. CO, HC, and PM emissions were analyzed before and after the high-temperature DOC using the heavy-duty Federal Test Procedure (FTP) transient test cycle. Similarly, the low-temperature DOCs were evaluated using the FTP-75 transient test procedure. Both the high-temperature and low-temperature DOCs were tested using four steady-state modes from the OICA 13-mode test cycle. Gaseous and PM emissions were sampled in the exhaust before and after the catalysts to determine their efficiency in reducing the CO, HC, and PM emissions.



The exhaust gas recirculation system was tested on the Navistar T444E engine at WVU's test facility.

### Key Results

- At the high exhaust temperature (405°C) steady-state modes (at or near peak torque), there was a statistically significant increase in post-DOC PM over and above the

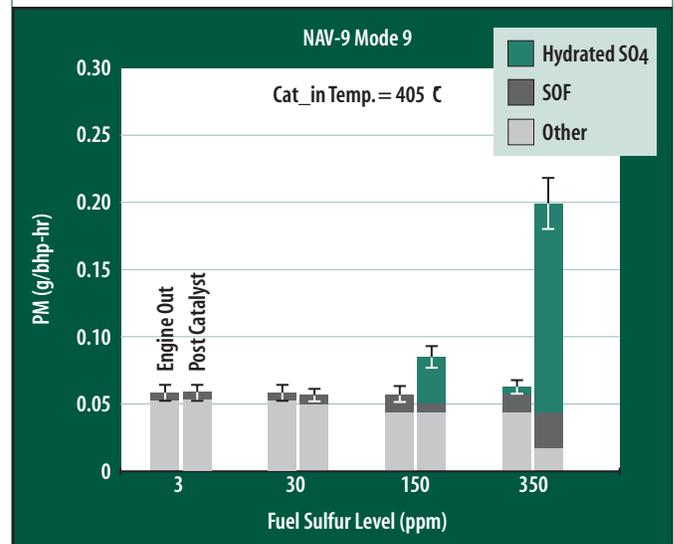


Figure 5. Engine-out and post-DOC (fresh) emissions of total PM and components under low-temperature (Navistar) applications using a Nav-9 mode 9 test (with 95% confidence intervals on estimated PM)

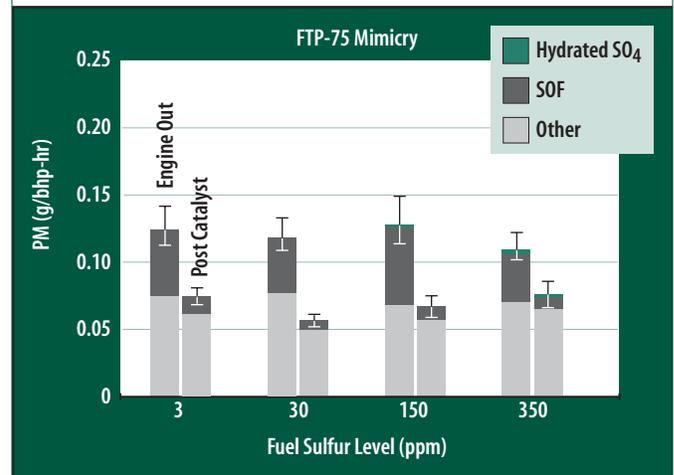


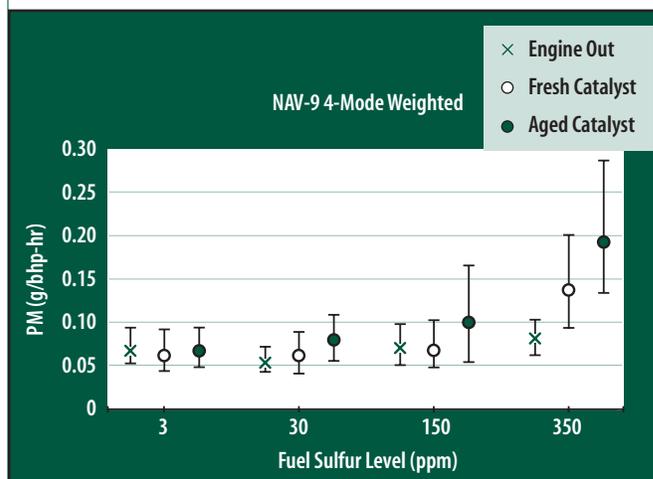
Figure 6. Engine-out and post-DOC emissions of PM and components under low-temperature (Navistar) applications using the FTP-75 mimicry transient cycle (with 95% confidence intervals on estimated PM)

PM measured at EO. The increase is due almost exclusively to the increase in SO<sub>4</sub> fraction. The effect is seen only with the 150- and 350-ppm sulfur fuels (see Figure 5).

- The catalyst response over the transient evaluation cycles differed from the steady-state tests. In the transient tests (FTP-75 mimicry) with the Navistar engine (see Figure 6), the DOC reduced the SOF of the PM by 70%–85% and PM by 35%–45%. The reductions in SOF and PM were statistically significant. Fuel sulfur content did not affect

SOF emissions or the DOC's SOF suppression efficiency. Although there is some statistical evidence that  $\text{SO}_4$  emissions increased with higher sulfur fuel, the resulting impact on PM (either EO or post-catalyst) was negligible and not statistically significant.

- Under the transient test conditions, the low-temperature DOCs on the T444E engine more effectively reduced PM SOF than the high-temperature DOCs used on the ISM370. The performance difference can be attributed to the higher platinum loading on the low-temperature catalysts, which are more active at the characteristically low exhaust temperatures of the transient test cycles.
- The low-temperature DOC's HC reduction efficiency was 90%–100% under steady-state and transient conditions. No sulfur effect was observed in either EO or post-catalyst HC emissions from the T444E.
- A statistically significant increase in the high-temperature DOC's HC emissions (both EO and post-catalyst) was observed during FTP transient tests with high-sulfur fuels (150- and 350-ppm sulfur). HC reduction efficiency during the FTP declined from near 100% with 3-ppm sulfur fuel to approximately 91% with 350-ppm sulfur fuel.
- Low-temperature DOCs were 90%–99% effective in reducing CO concentrations at steady-state and 88%–92% effective during the transient tests. The high-temperature DOCs were 78%–84% effective in CO reduction at steady-state but only 41%–45% effective during the transient tests. There is no statistical evidence that sulfur affects CO emissions or the CO reduction efficiency of the DOC in any operating mode.



**Figure 7. Engine-out and fresh, aged DOC emissions of PM under low-temperature (Navistar) applications using the Nav-9 weighted 4-mode test cycle (with 95% confidence intervals)**

- The steady-state PM emissions from the low-temperature DOC aged with 350-ppm sulfur fuel exceeded those measured when the catalyst was fresh (0.20 versus 0.14 g/bhp-hr). A much smaller aging effect on total PM was observed with the lower sulfur fuels (see Figure 7).
- After aging, the high-temperature catalysts more efficiently reduced the SOF and resulted in greater PM reduction efficiency than the fresh catalyst. This improvement was observed with catalysts aged with 30-, 150-, and 350-ppm sulfur fuel, though the level of sulfur in the fuel did not affect the magnitude of the improvement.
- The CO reduction efficiency of the high-temperature catalysts dropped 10 percentage points after aging. This effect was independent of the level of fuel sulfur.

## NO<sub>x</sub> Adsorber Catalysts

### Test Design

A NO<sub>x</sub> adsorber catalyst is a flow-through emission control device that temporarily stores NO<sub>2</sub> emissions during the operation of a diesel engine. Before the NO<sub>x</sub> adsorbent becomes saturated, engine operating conditions and fueling rates are adjusted to produce a fuel-rich exhaust. Under these conditions, the stored NO<sub>x</sub> is released from the adsorbent and reduced to N<sub>2</sub> over three-way precious metal catalysts.

The NO<sub>x</sub> adsorber test was designed to address the following questions:

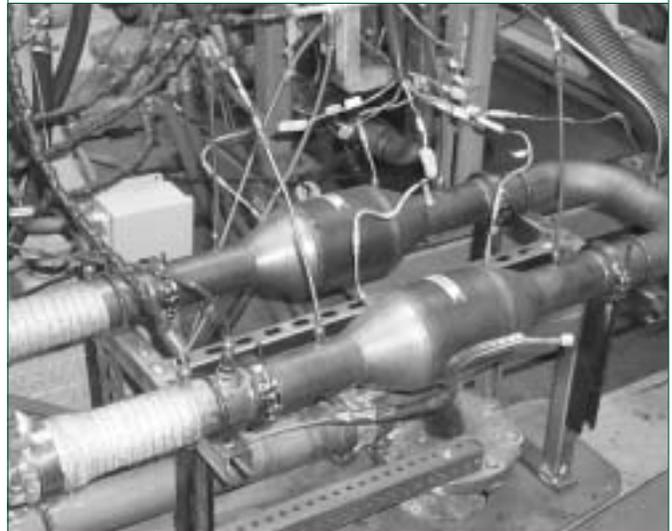
- What NO<sub>x</sub> conversion efficiency is possible with an improved lean/rich regeneration calibration?
- Can a practical on-engine desulfurization cycle be developed?
- What effect does the desulfurization process have on the long-term performance of the NO<sub>x</sub> adsorber, and does it vary with the fuel sulfur level?

The NO<sub>x</sub> adsorber tests were conducted on duplicate systems (see photo) using a three-step process. First, the calibration of the engine management system was improved, which resulted in an NO<sub>x</sub> conversion efficiency of at least 80% across engine operating temperatures of 250°–500°C, using the 3-ppm sulfur base fuel. This was achieved with no more than a 4% average increase in fuel consumption.

Next, the test focused on desulfurizing the NO<sub>x</sub> adsorber catalyst by controlling the air/fuel ratio and catalyst inlet temperatures to achieve the high temperatures required to release the sulfur from the device. The desulfurization process was demonstrated by running it on the catalysts periodically over 250 hours with varying sulfur-level fuels.

The final step included:

- A series of aging, performance mapping, and desulfurization cycles.
- Multiple consecutive desulfurizations to determine the effect of the high temperature exposure on the catalyst's durability.



NO<sub>x</sub> adsorber catalysts were installed in this test cell at FEV in Auburn Hills, MI.

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### Key Results

- The improved lean/rich engine calibration achieved as a part of this test resulted in NO<sub>x</sub> conversion efficiencies exceeding 90% over a catalyst inlet operating temperature window of 300°–450°C (see Figure 8). This was achieved while staying within the 4% fuel economy penalty target defined for the regeneration calibration. This calibration was developed using 3-ppm sulfur level fuel.

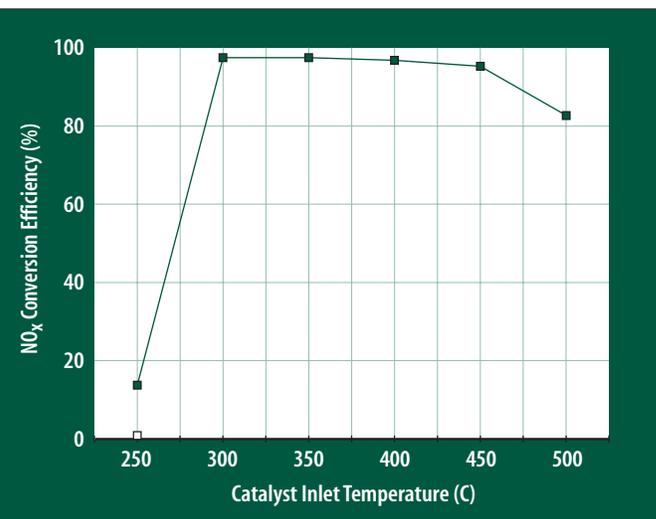
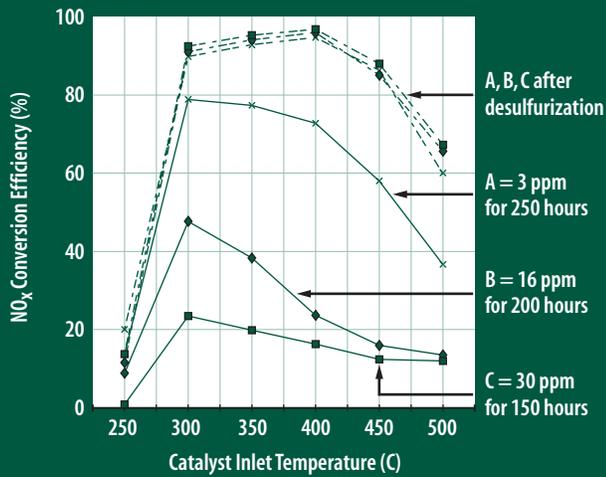
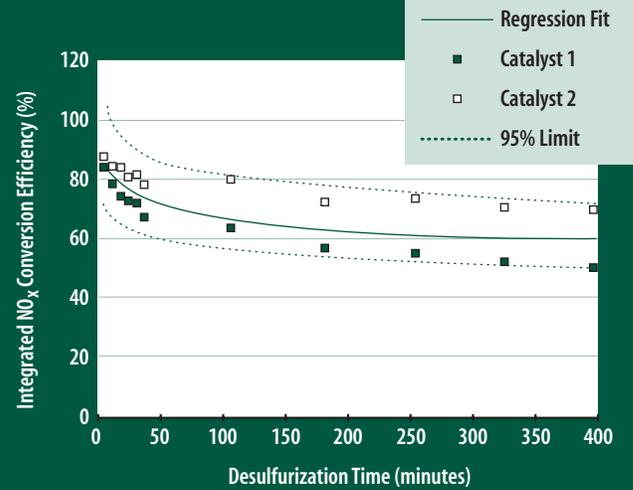


Figure 8. The NO<sub>x</sub> conversion efficiency of the fresh NO<sub>x</sub> adsorber catalyst under improved lean/rich engine calibration



**Figure 9. Comparison of NO<sub>x</sub> conversion efficiency before and after desulfurization for catalysts aged as long as 250 hours with 3-, 16-, and 30-ppm sulfur level fuels**

- The desulfurization procedure recovers efficiency of at least 85% NO<sub>x</sub> conversion from fuel sulfur levels of 3-, 16-, and 30-ppm for as long as 250 hours over a catalyst inlet operating temperature window of 300°–450°C (see Figure 9).
- This desulfurization procedure has the potential to meet in-service engine operating requirements and acceptable drivability conditions.
- Aging with 78-ppm sulfur fuel reduced NO<sub>x</sub> conversion efficiency more than aging with 3-ppm sulfur fuel as a result of sulfur contamination. However, the desulfurization events restored the conversion efficiency to nearly the same



**Figure 10. Regression model (with 95% confidence interval) of post-desulfurization NO<sub>x</sub> conversion efficiency versus total desulfurization time. Data for catalyst pair aged on 78-ppm sulfur level fuel.**

level of performance. Exposing the catalyst repeatedly to the desulfurization procedure caused a continued decline in the catalyst's desulfurized performance (see Figure 10). Additional work will be necessary to identify the cause of this decline.

- The rate of sulfur contamination during aging with 78-ppm sulfur fuel increased with repeated aging/desulfurization cycles (from 10% per 10 hours to 18% per 10 hours). This was not observed with the 3-ppm fuel, where the rate of decline during aging was fairly constant at approximately 2% per 10 hours.

## Recommendations

By 2007, EPA emission standards for heavy-duty diesel engines will require that NO<sub>x</sub> and PM emissions be reduced by 90% below current limits. Passenger vehicles will need to be 77%–95% cleaner than those now on the road and refiners will need to reduce the sulfur content of diesel fuel by as much as 97%. Beginning in 2004, this tailpipe standard will also limit NO<sub>x</sub> emissions to an average of 0.07 grams per mile for all classes of passenger vehicles, including all light-duty trucks and the largest SUVs.

### Diesel Oxidation Catalyst

DECSE tests demonstrated that the DOC does not control PM emissions well enough to meet the EPA's 2007 standards. However, it could be useful in an emission control system to clean up the HC emissions during rich regeneration. The DOC may be effective when used in combination with selective catalytic reduction (SCR), either as a pre-catalyst for converting NO to NO<sub>2</sub> or as a post-catalyst to control ammonia slip.

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

With its limited reduction efficiency (~20%), this technology cannot meet the EPA's 2007 emission standards. But it could meet the 2004 emission regulations for light- and heavy-duty diesel engines. A DOC could be used to clean up HC slip when this approach is used.

### NO<sub>x</sub> Adsorber Catalyst

This technology is promising for meeting future NO<sub>x</sub> standards. However, more study is needed to investigate the frequency of desulfurization and to more accurately characterize thermal degradation associated with the high-temperature desulfurization cycle. More detailed studies are also needed to address the long-term operation of the NO<sub>x</sub> adsorber catalyst, including the durability of the engine and catalyst, and other exhaust constituents—such as smoke levels during regeneration—and on which trade-offs are required to reduce or keep them low.

### Diesel Particulate Filter

When used with low-sulfur fuel, this technology is capable of meeting future PM standards. Research is needed to demonstrate that DPFs can be beneficial in combination, respectively, with SCR and a NO<sub>x</sub> adsorber. Additional research should be conducted on measurements for PM mass, size, and composition, as well as for air toxics.

## The Next Step

Results and test experiences from the DECSE project are being used by its successor, the APBF-DEC project, to identify the optimal combinations of fuels, lubricants, diesel engines, and emission control systems to meet projected EPA emission standards for 2002 to 2010. APBF-DEC also will identify properties of fuels and vehicle systems that could lead to even lower emissions beyond 2010.

The APBF-DEC project selected two emission control technology systems for further study:

### Selective Catalytic Reduction/ Diesel Particulate Filter

The SCR is an emissions reduction device that, combined with a DPF and advanced fuel formulations, may reduce regulated (especially NO<sub>x</sub>), unregulated, and toxic emissions. Two types of SCR-based catalysts are being evaluated in combination with DPFs and possibly DOCs.

### NO<sub>x</sub> Adsorber Catalyst/ Diesel Particulate Filter

The NO<sub>x</sub> adsorber may significantly reduce NO<sub>x</sub>, HC, and CO emissions from diesel engine exhaust. Combined with a DPF, the NO<sub>x</sub> adsorber can also effectively oxidize the PM and other unregulated emissions from diesel exhaust. Two systems are being evaluated on light-, medium-, and heavy-duty engines and light- and medium-duty vehicles.

For detailed information about the progress of the APBF project, visit <http://www.ott.doe.gov/apbf>. Direct your questions about the DECSE or APBF-DEC to:

**Wendy Clark**

**DECSE Deputy Project Manager**

**National Renewable Energy Laboratory**

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# Summary of DECSE Reports

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