DECSE

The Diesel Emission Control – Sulfur Effects (DECSE) Program Summary - December 1999

What's New: Phase 1 Interim Data Reports Issued

- The first interim report, covering diesel particulate filters, lean-NO_x catalysts, and diesel oxidation catalysts, was published in September.
- The second interim report, covering NO_x adsorber catalysts, was published in October.
- The third interim report, for particulate matter, was published in November.

Program Manager's Report

DECSE has just issued the third interim data report for Phase 1. This program summary gives an overview of the major conclusions for each technology type from the three reports. A fourth report will be issued by February 2000 on DPFs. Phase 1 was developed with the following objectives:

(A) Evaluate the effects of varying the level of sulfur content in the fuel on the emissions reduction performance of four emissions 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 emissions control technologies are being tested in Phase I of the program: (1) NO_x (nitrogen oxide) adsorber catalysts; (2) diesel particulate filters (DPF); (3) lean-NO_x catalysts; and (4) diesel oxidation catalysts (DOCs).

The devices being tested include commercially available technologies as well as state-of-the-art technologies that are under development. The sulfur contents in the test fuels are 3, 16 (NO_x adsorber catalysts only), 30, 150 and 350 parts per million (ppm).

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The Technologies:

NO_x adsorber catalysts – catalysts that function by first storing (adsorbing) NO_x and then reducing the stored NO_x under fuel-rich conditions.

Diesel particulate filters – filters designed to remove particulate matter (PM) from the exhaust by collection on a filter element.

Lean-NO_x catalysts – catalysts capable of chemically reducing nitrogen oxides (NO_x) to nitrogen (N_2) in the presence of oxygen.

Diesel oxidation catalysts (DOCs) – catalysts designed to reduce hydrocarbon (HC), carbon monoxide (CO) and the soluble organic compounds associated with PM emissions.

NO_x Adsorbers

The NO_x adsorber functions by first storing NO_x as a stable metal nitrate and then reducing the stored NO_x to N_2 over catalyst materials. Fresh NO_x adsorbers are capable of providing high NO_x conversion levels (e.g., more than 80 percent) across a broad range of operating temperatures when coupled with an optimized calibrated fuel-rich engine, while maintaining a fuel economy penalty of less than 4 percent.

The adsorber has a strong affinity for sulfur; SO_2 in the exhaust undergoes reactions forming sulfates on the catalyst adsorbent. In time, sulfur in the exhaust materials will block the NO_x adsorption sites and reduce its NO_x conversion effectiveness. The effect of fuel sulfur content on NO_x adsorber conversion efficiency was examined in the Phase I testing. The effect of fuel sulfur on relative NO_x conversion efficiencies at 400° and 450°C was measured after 150 hours of testing. Compared to 3-ppm sulfur fuel at 150 hours, both 16- and 30-ppm sulfur fuels resulted in significant performance declines. Although testing with 3-ppm sulfur fuel showed an initial decline in adsorber catalyst conversion efficiency, the performance subsequently appeared to stabilize, out to the 250-hour period. Further aging would be required to determine adverse affects of 3-ppm sulfur fuel beyond this point.

While the NO_x conversion effectiveness may be hindered by sulfur, the tests found that there were no significant sulfur effects on the NO_x adsorber catalysts' ability to reduce engine-out total particulate matter (TPM) and soluble organic fraction (SOF), with up to 250 hours of operation. With fuel sulfur levels up to 30-ppm, adsorber catalysts apparently do not cause elevated sulfate releases into the atmosphere.

The initial calibration of the engine management system did not achieve the desired level of NO_x conversion performance across the range of operating temperatures. Maximum efficiency was achieved at 450° C and was lower than the desired level, both below and above this temperature. The revised calibration, established after aging tests were completed, produced improved conversion efficiency. This calibration will be explored starting in January 2000.

DECSE is supported by the U.S. Department of Energy's Office of Heavy Vehicle Technologies, two national laboratories, the Engine Manufacturers Association, and the Manufacturers of Emission Controls Association.

Program Manager's Report (continued)

The 3-ppm sulfur content fuel represents a diesel fuel that is essentially "sulfur-free."

The engines in the DECSE program are currently available models. They were selected to provide a representative source of diesel exhaust and various exhaust temperature profiles to challenge the emissions 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 particulate matter (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).

The first three interim reports for Phase 1 are now available on the DOE/OTT website at: http://www.ott.doe.gov/decse.

Phase 2 of the DECSE program, which is expected to begin in January, will start with development of desulfurization procedures for NO_x adsorbers and projects on lubricant reformulation and selective catalytic reduction (SCR).

Diesel Particulate Filters (DPFs)

Diesel particulate filters (DPFs) are designed to remove PM from the engine exhaust stream. The results thus far demonstrate the effects of sulfur on the performance of DPF technologies.

In these tests, the DPFs removed PM by collecting it on 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 these DPFs.

The tests found that fuel sulfur has significant effects on PM emissions. PM reduction efficiency over the test cycle was measured at 95 percent for each of the two devices when tested with the 3-ppm sulfur fuel. However, with 30-ppm sulfur fuel, this weighted efficiency decreased. 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. Although designed as PM reduction devices, the DPFs reduced total hydrocarbon (THC) by 58 percent to 91 percent and CO by 90 percent to 99 percent. These reductions were not affected to any significant degree by the fuel sulfur level.

Another concern about the impact of sulfur on the operation of these DPF devices is its possible effect on the filter's 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).

A complete PM breakdown analysis for all collected filters will be reported for each of the four fuels (3, 30, 150, and 350 ppm) in the next DECSE interim report.

Lean-NO_x Catalysts

Lean-NO_x catalysts reduce diesel NO_x emissions with the assistance of secondary fuel injection under a lean (oxygen-rich) exhaust condition.

The effect of diesel sulfur level on NO_x reduction with a fresh high-temperature lean-NOx catalyst was first evaluated in Phase I. In an operating temperature range of 360 – 600°C, the given lean-NOx catalyst was able to achieve up to 30% NOx reduction under given OICA-13 test modes. The fuel sulfur trends indicated that the NOx reduction was lower with the higher diesel sulfur levels but the changes were not statistically significant.

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

Diesel sulfur level had an effect on TPM emission from the high-temperature lean-NO_x catalyst. With 3-ppm sulfur fuel, the reduction of TPM was statistically significant at 16 percent. With high sulfur diesel fuels, the sulfate emissions from the catalysts increased by a factor of 10 to 20. This suggests the formation of sulfate by the given lean-NO_x catalyst with high sulfur fuels. Tests also showed that with the high exhaust temperature (approximately 518ºC), the percentage of sulfate in TPM was higher than from the test cycles for both engine-out and catalyst-out data. Higher sulfate emission will contribute to the overall TPM emission.

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Lean-NO_x Catalysts (continued)

A secondary fueling strategy will be required for diesel application of the given high-temperature lean-NO_x catalyst.

The aging tests (50, 150, and 250 hours) of the high-temperature lean-NOx catalyst are under way with different diesel sulfur levels.

A fresh low-temperature lean-NOx catalyst has been evaluated with different diesel sulfur levels. The aging tests for this catalyst are under way as well.

Diesel Oxidation Catalysts (DOCs)

DOCs reduce HC, CO, and soluble organic compounds by oxidation over a precious metal catalyst. A major concern with higher precious metal loadings is the DOC's proclivity to convert SO_2 in the exhaust gas to sulfate.

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.

The testing found that under certain operating conditions, DOCs can increase PM emissions above engine-out emissions due to an increase in sulfate fraction. The magnitude of this increase is directly proportional to the amount of sulfur in the diesel fuel. This sulfate increase counteracts the SOF reduction benefit of the DOC.

PM emissions during the high-torque (high-exhaust temperature) steady-state tests showed a strong fuel sulfur influence. With 3-ppm sulfur fuel, the PM reduction efficiency was statistically significant at 26 percent.

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.

The testing also showed that catalyst-out sulfate conversion with a DOC is temperature dependent and varies with operating condition: one percent over the heavy-duty FTP (Federal test procedure); eight percent at peak torque; and 15 percent over a four-mode steady-state composite test.

Other News & Information

Read about the U.S. Environmental Protection Agency's proposed Heavy-Duty Engine Emission Regulations on the web at **http://www.epa.gov/oms/hd-hwy.htm#regs**.

In November 1999, the EPA released its revised *Health Assessment Document for Diesel Emissions, SAB Review Draft.* This draft, which is undergoing a review by the Clean Air Scientific Advisory Committee, is now available on the web at **http://www.epa.gov/ncea/diesel.htm**.
According to the EPA, "The current draft assessment focuses on health hazards . . . and also provides background information about diesel engine emissions and exposure that is useful for putting the health information into context."

Abbreviations

C – Celsius

CO – carbon monoxide

DECSE – Diesel Emission Control-Sulfur Effects (program)

DOC – diesel oxidation catalyst

DOE – U.S. Department of Energy

DPF – diesel particulate filter

EMA – Engine Manufacturers Association

FTP – Federal test procedure

HC – hydrocarbon

MECA – Manufacturers of Emission Controls Association

N_2 – nitrogen

NO_x – nitrogen oxides

NREL – National Renewable Energy Laboratory

OICA – International Organization of Motor Vehicle Manufacturers

ORNL – Oak Ridge National Laboratory

OTT – DOE's Office of Transportation Technologies

PM – particulate matter

ppm – parts per million

SO_2 – sulfur dioxide

SOF – soluble organic fraction

TPM – total particulate matter

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www.ott.doe.gov/decse

What is DECSE?

The Diesel Emission Control–Sulfur Effects (DECSE) program is a joint government/industry program to determine the impact of diesel fuel sulfur levels on emissions 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 emissions 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.

Upcoming Events

- Beginning of Phase 2, January 2000
- Fourth interim Phase 1 report, February 2000
- Final Phase 1 report, May 2000
- SAE conference, June 2000, Paris, France

Summary of Phase 1 Experimental Design

TECH-NOLOGY	**250 hours aging** at various fuel sulfur levels (ppm)	**Evaluation**	**ENGINE**	**REMARKS**
	3 | 30 | 150 | 350 | 30*	3 | 30 | 150 | 350 | 30*		
Diesel Oxidation Catalyst	Special Navistar aging cycle	Navistar 9-mode & simulated FTP-75	T-444E (Navistar)	High precious metal loading
	Modified OICA** aging cycle	Stabilized OICA & heavy-duty FTP	ISM 370 (Cummins)	Low precious metal loading
Active Lean-NO_x Catalyst	Special Navistar aging cycle	Navistar 9 mode	T444E	Low temp. catalyst
	Modified OICA aging cycle	Stabilized OICA	ISM 370	High temp. catalyst
CR-DPF and CDPF***	No aging test, used special tests to determine regeneration temperatures and emissions	Steady-state exhaust temperature tests & stabilized OICA	3126 (Caterpillar)	Determine sulfur effect on regen. temp.
NO_x Adsorber	3 | 16**** | 30	3 | 16**** | 30	HSDI (Daimler-Chrysler 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.
** A test cycle developed during European work; OICA is the International Organization of Motor Vehicle Manufacturers
*** Continuously Regenerating Diesel Particulate Filters (CR-DPF) and Catalyzed Diesel Particulate Filters (CDPF)
**** 16-ppm sulfur fuel added to test matrix after 3- and 30-ppm fuel tests were completed.

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DECSE Contacts:

Deputy Program Manager – Wendy Clark, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393, phone 303-275-4468, fax 303-275-4415, e-mail wendy_clark@nrel.gov

Communications – Helen Latham, Battelle, 505 King Avenue, Columbus, Ohio 43201-2693, phone 614-424-4062, fax 614-424-5601, e-mail lathamh@battelle.org