DECSE

The Diesel Emission Control – Sulfur Effects (DECSE)
Third Program Summary – June 2001

In this final issue:

- Summaries of the final reports: NO_x adsorber catalysts, October 2000; diesel particulate filters, January 2000; lean-NO_x catalysts and diesel oxidation catalysts, July 2001.
- Introduction to follow-on study: Advanced Petroleum-Based Fuels – Diesel Emissions Control Program (APBF-DEC).

Deputy Program Manager's Report

This is the third (and final) DECSE Program Summary, providing excerpted results and brief background information for each of the four emission control technologies tested.

The four technologies are described in the box (above, right). Complete information is provided in the three final reports that are now available at http://www.ott.doe.gov/decse.

The major objective of the DECSE test program was to determine the impact of fuel sulfur levels on emissions control systems, which could be used to lower emissions of NO_x and PM from diesel engine vehicles in the years 2002 to 2004. The sulfur in diesel fuel is known to adversely affect the operation of diesel exhaust emissions control systems.

Tests were conducted and data were collected and analyzed for various combinations of fuel sulfur levels, engines, and exhaust emissions control systems.

The targeted fuel sulfur levels were 3 parts per million (ppm), 16-ppm (NO_x adsorber catalyst only), 30-, 150-, and 350-ppm. During each test, the diesel engine

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The Four 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 Adsorber Catalyst

A NO_x adsorber catalyst is a flow-through emissions control device that temporarily stores NO_2 emissions during diesel engine operation. Before the NO_x adsorbent becomes 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 reduced to N_2 over precious metal adsorber catalysts.

<u>Summary of Results</u>

The improved lean/rich engine calibration achieved during this test resulted in NO_x conversion efficiencies exceeding 90% over a catalyst inlet operating temperature window of 300° to 400° C.

The desulfurization procedure showed that six catalysts exposed to fuel sulfur levels of 3-, 16-, and 30-ppm for up to 250 hours could be recovered to greater than 85% NO_x conversion efficiency over a catalyst inlet operating temperature window of 300° to 450° C after a single desulfurization event.

This desulfurization procedure has the potential to meet in-service engine operating conditions and acceptable driveability conditions.

Although aging with 78-ppm sulfur fuel reduced the NO_x conversion efficiency more than aging with 3-ppm sulfur fuel because of sulfur contamination, the desulfurization events restored the conversion efficiency to nearly the same level. However, repeatedly exposing the catalyst to the desulfurization procedure caused a continued decline in the catalyst's desulfurized performance. The rate of sulfur contamination during aging with 78-ppm sulfur fuel increased with repeated aging/desulfurization cycles.

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Deputy Program Manager's Report
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operated for 250 hours or more to detect any decline in performance.

The emissions control technologies tested included commercially available technologies as well as those under development.

The engines used were currently available models, selected to provide a representative source of diesel exhaust and various temperature profiles to challenge the emissions control devices.

Summaries of the test processes and results of the DECSE testing program for the four technologies are provided in the adjoining columns, beginning on page 1.

In general, the DECSE data show the effects that fuel-borne sulfur has on the performance of emissions control systems and the effects that fuel properties (including additives) have on systems performance.

DECSE results and test experiences have been useful in the successor Advanced Petroleum-Based Fuels—Diesel Emissions Control (APBF-DEC) program, launched in February 2000.

Additional information about the APBF-DEC program is provided on page 4 and is posted at the following web site: http://www.ott.doe.gov/apbf.

NO_x Adsorber Catalyst *(from previous page)*

Test Process

The NO_x adsorber test was designed to address the following questions:

- What NO_x 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_x adsorber and does it vary with fuel sulfur level?

The NO_x adsorber test was conducted in three steps. First, the calibration of the engine management system was improved, which resulted in a NO_x conversion efficiency of at least 80% across engine operating temperatures of 250° to 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_x 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 for as long as 250 hours with varying sulfur-level fuels.

The final step included (1) a series of aging, performance mapping, desulfurization, and performance mapping cycles and (2) multiple consecutive desulfurizations to determine the effect of the high temperature exposure on the catalyst's durability.

Diesel Particulate Filters (DPFs)

DPFs are designed to remove PM from the engine exhaust by collecting it on a filter element—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 were evaluated: a catalyzed diesel particulate filter (CDPF) and a continuously regenerating diesel particulate filter (CR-DPF).

Summary of Results

Increasing the fuel sulfur level from 3-ppm to 350-ppm produced an essentially linear 29% increase in the engine-out PM emissions—from 0.0613 to 0.0793 grams per brake horsepower-hour (g/bhp-hr). No significant changes in the engine-out 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 were effective in reducing PM emissions when used with 3-ppm sulfur fuel. With 30-ppm sulfur fuel, the PM reduction efficiencies dropped to 74% and 72% for the CDPF and CR-DPF, respectively.

Fuel sulfur levels below 150-ppm were required to obtain any reduction in total PM. Similarly, a sulfur level of 30-ppm was required to achieve total PM emissions approaching the 0.01 g/bhp-hr standard for the 2007 regulation.

Approximately 40% to 60% of fuel sulfur was converted to sulfate PM as

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Diesel Particulate Filters *(continued from page 2)*

measured over the 13-mode International Organization of Motor Vehicle Manufacturers (OICA) cycle for both DPFs.

The exhaust temperature required for regeneration of the DPF devices increased by roughly 25° C when changing from 3-ppm to 30-ppm sulfur fuel. Within the range of fuel sulfur levels required to achieve useful PM reduction, the temperature required for filter regeneration was consistently higher for the CDPF than for the CR-DPF.

Fuel consumption increases of up to 2% above baseline were measured when operating with the DPF devices, which results from the additional exhaust back-pressure, and were generally larger with the CR-DPF than with the CDPF.

Both DPFs were effective in removing much of the hydrocarbon—the CDPF, a reduction efficiency of about 70% and the CR-DPF about 83%. Both DPFs were also efficient in reducing CO, by 90% to 99% percent across the various fuel sulfur levels and three test modes.

Test Process

The two DPF technologies underwent (1) emission tests to measure reductions in total PM and selected gases and (2) experiments to measure the effect of fuel sulfur levels on the regeneration balance point temperature (BPT). Fuels used had sulfur levels ranging from 3- to 350-ppm. Tests were conducted with increasing fuel sulfur levels to determine how fuel sulfur affects the BPT at various engine speeds. A second set of OICA emissions tests with 30-ppm sulfur was performed last to evaluate the effects of aging.

Lean-NO_x Catalysts

Lean-NOx catalysts can be used to reduce diesel NOx emissions with the assistance of a supplementary reductant (such as diesel fuel) under a lean (oxygen-rich) exhaust condition.

Summary of Results

With fresh lean-NO_x catalysts and less than a 4% fuel penalty, overall NO_x reduction efficiencies were less than 20% for all catalysts during the defined steady state test cycles. However, more than 50% and 30% NO_x reduction peak efficiencies were observed at specific operating temperatures for the low temperature and high temperature catalysts, respectively. Statistically, the effect of the fuel sulfur level on NO_x efficiency was not significant.

With fresh lean-NO_x catalysts and higher fuel sulfur levels (150- and 350-ppm sulfur), the increase in catalyst-out sulfate emissions was significant at high temperature steady-state modes. The high-temperature lean-NO_x catalyst was vulnerable to HC slip with all of the fuels tested. The low temperature lean-NO_x catalyst was more effective at controlling HC and CO slip, but only with low sulfur (3- and 30-ppm sulfur) fuels. Catalyst aging (up to 250 hours), independent of fuel sulfur level, had no apparent effect on the NO_x reduction efficiency of the low and high temperature lean-NO_x catalysts.

For the low temperature lean-NO_x catalyst, the catalyst aging significantly

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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

To access **DECSE** reports, go to: **www.ott.doe.gov/decse**.

What is APBF-DEC?

In January 2000, representatives of governmental agencies, trade associations, and private industry launched the Advanced Petroleum-Based Fuels–Diesel Emissions Control Program (APBF-DEC).

The APBF-DEC program is an outgrowth of DECSE and will benefit from DECSE's results and test data.

The goal of the APBF-DEC program is to identify the optimal combinations of fuels, lubricants, diesel engines, and emission control systems to meet projected emission standards for the 2002 to 2010 time period.

The program will also identify properties of fuels and vehicle systems that could lead to even lower emissions beyond 2010.

Information about the APBF-DEC program is available at: www.ott.doe.gov/apbf. The site provides fact sheets and Quarterly Updates as well as technical information.

If you are interested in receiving APBF-DEC information directly, please contact Helen Latham at Battelle, phone 614-424-4062, fax 614-424-5601, e-mail lathamh@battelle.org.

APBF-DEC Contacts:

Program Manager – George Sverdrup, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401-3393, phone 303-275-4433, fax 303-275-4415, e-mail george_sverdrup@nrel.gov

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

Lean-NO_x Catalysts *(continued from page 3)*

increased the catalyst-out PM emissions with high sulfur fuels (150- to 350-ppm sulfur). This was mainly due to high sulfate emissions after 50 hours of catalyst aging. Thermal aging seems to be the primary reason for PM increase with the lower sulfur fuels. With 350-ppm sulfur fuel, effects of thermal aging and sulfur aging were essentially additive. Unlike the low temperature lean-NO_x catalyst, the aging process had only a slight effect on catalyst-out PM emissions with the high temperature lean-NO_x catalyst.

<u>Test Process</u>

The two lean-NO_x catalysts used were performance-tested only at the steady-state and before, during, and after a 250-hour aging cycle using four different fuel sulfur levels. Diesel fuel was used as the hydrocarbon reductant. The injection rate was optimized for peak NO_x reduction without exceeding 4% of the total fuel consumption. Gaseous and PM emissions were sampled in the exhaust before and after the catalysts to determine reduction efficiencies. Complete PM breakdown analyses were also conducted.

Diesel Oxidation Catalysts (DOC)

Diesel oxidation catalysts (DOCs) reduce HC, CO, and the soluble organic fraction of particulate matter by oxidation over a precious metal catalyst. A concern with higher precious metal loadings is the DOC's tendency to convert SO_2 in the exhaust gas to sulfate.

<u>Summary of Results</u>

At the high exhaust temperature steady-state modes (at or near peak torque), there is a statistically significant increase in post-DOC PM over and above the PM measured in the engine-out emissions. The increase is due almost exclusively to the increase in SO_4 fraction. The effect is most pronounced with the 150- and 350-ppm sulfur fuels. Under transient test conditions, the low-temperature DOCs used on the Navistar T444E engine were more effective at PM reduction than the high-temperature DOCs used on the Cummins ISM370 engine. The HC reduction efficiency of the low-temperature DOC was 90% to 100% under steady-state and transient conditions. No sulfur effect was observed in either engine-out or post-catalyst HC emissions from the T444E engine. A statistically significant increase in the HC emissions (both engine-out and post-catalyst) was observed with the ISM370 engine and high sulfur fuels (150- and 350-ppm sulfur). HC reduction efficiency declined from nearly 100% with 3-ppm sulfur to approximately 91% with 350-ppm sulfur fuel. CO reduction efficiency was higher with the low-temperature DOCs than with the high-temperature DOCs. The low-temperature DOCs were 90% to 99% effective in steady-state CO reduction and 88% to 92% effective during the transient tests. The high-temperature DOCs were 78% to 84% effective in steady-state CO reduction but only 41%-45% effective during transient tests.

<u>Test Process</u>

Testing was performed to assess fresh catalyst performance and performance after aging, using fuels containing 3-, 30-, 150-, and 350-ppm sulfur levels. The DOCs were evaluated under steady-state and transient conditions. Gaseous and PM emissions were sampled in the exhaust before and after the catalysts to determine reduction efficiencies. Complete PM breakdown analyses were also conducted. The precious metal-coated low-temperature DOC catalysts were aged and evaluated using a Navistar T444E engine; the base-metal high-temperature catalysts were tested on a Cummins ISM370 engine.