Fuels for Advanced CIDI Engines and Fuel Cells

2000 Annual Progress Report

U.S. Department of Energy

Energy Efficiency and Renewable Energy

Office of Transportation Technologies

2000 Annual Progress Report

Fuels for Advanced CIDI Engines and Fuel Cells

ACKNOWLEDGEMENT

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In addition, we would like to thank all our program participants for their contributions to the programs and all the authors who prepared the project abstracts that comprise this report.

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Office of Transportation Technologies
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FY 2000

Progress Report for Fuels for Advanced CIDI Engines and Fuel Cells

Energy Efficiency and Renewable Energy
Office of Transportation Technologies

Approved by Steven Chalk

November 2000

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I. INTRODUCTION

Enabling Advanced Vehicle Technologies through Development and Utilization of Advanced Petroleum-Based Fuels

John Garbak, Program Manager, Fuels for Advanced CIDI Engines and Fuel Cells

Steve Goguen, Team Leader, Fuels and Lubricants for Heavy-Duty Applications

On behalf of the Department of Energy's Office of Transportation Technologies (OTT), we are pleased to introduce the Fiscal Year (FY) 2000 Annual Progress Report for the Fuels for Advanced CIDI Engines and Fuel Cells Program. Together with DOE National Laboratories and in partnership with private industry and universities across the United States, OTT engages in high risk R&D that provides enabling technology for fuel efficient and environment-friendly vehicles. The Program is currently focused on advanced fuels for the compression-ignition, direct injection (CIDI) engine, an advanced version of the commonly known diesel engine, which is used in both light- and heavy-duty vehicles. Because OTT conducts fuels R&D for CIDI engines in both the Office of Advanced Automotive Technologies (OAAT) and the Office of Heavy Vehicle Technologies (OHVT), they have developed a joint multiyear program plan[1], called the Advanced Petroleum-Based Fuels (APBF) RD&T for CIDI Engines and Emission Control Systems. This year's progress report includes all the projects conducted in support of the APBF Program. Fuels R&D is also coordinated with the Combustion and Emission Control R&D for Advanced CIDI Engines and Transportation Fuel Cell Power Systems Programs (which have their own separate reports), which rely on this Program for fuels that will enable them to meet their out-year objectives.

Pete Devlin, Program Manager, Fuels for Fuel Cells and Advanced CIDI Engines

The Fuels for Advanced CIDI Engines and Fuel Cells Program supports the Partnership for a New Generation of Vehicles (PNGV), an industry-government partnership that aims to develop, by 2004, a mid-sized passenger vehicle capable of achieving 80 miles per gallon while adhering to future emissions standards and maintaining such attributes as affordability, performance, safety, and comfort. In order for PNGV-selected powertrains and energy conversion technologies to maximize their potential in energy efficiency while maintaining low emissions, advanced fuels are needed and serve as key technology enablers. The work in advanced petroleum-based fuels is conducted through joint programs with the energy and automotive industries. Advanced petroleum-based fuels will also be an asset to the 21st Century Truck Initiative that proposes to triple medium-duty truck fuel economy and double heavy-duty truck fuel economy on a ton-mile per gallon basis. In FY 2000, the APBF Program was focused on developing and testing advanced fuels for use in CIDI engines and transportation fuel cell power systems.

This report highlights progress achieved during FY 2000, and comprises 22 summaries of industry and National Laboratory projects that were conducted. It provides an overview of the exciting work being

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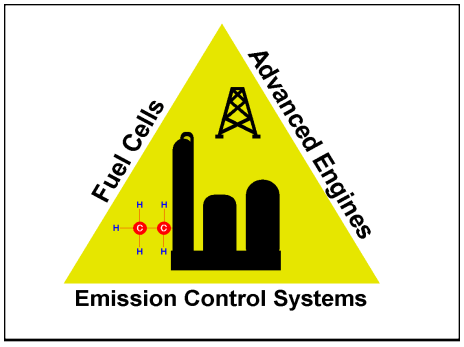
[1] *Multiyear Program Plan, Advanced Petroleum-Based Fuels (APBF) RD&T for Compression-Ignition, Direct Injection Engines and Emission Control Systems*, DOE Office of Advanced Automotive Technologies and Office of Heavy Vehicle Technologies, November 1, 2000.

conducted to tackle the tough technical challenges associated with developing clean burning fuels that will enable meeting the performance goals of the Emission Control R&D for Advanced CIDI Engines and the Transportation Fuel Cell Power Systems Programs. The summaries cover the effects of fuels on CIDI engine emissions and fuel cell power system performance, the effects of lubricants on engine emissions, the effects of fuels and consumed lubricants on exhaust emission control devices, and the health and safety, materials compatibility, and economics of advanced petroleum-based fuels. A brief snapshot of FY 2000 accomplishments and new program directions for FY 2001 is captured in the following pages. We are encouraged by the technical progress realized under this dynamic program in FY 2000 and look forward to making further advancements in FY 2001.

Advanced petroleum-based fuels are a critical enabler to allow the high fuel economy of diesel-powered vehicles to be maintained while meeting future emission standards

Two major regulatory events occurred during the past year: first, the Environmental Protection Agency (EPA) Tier 2 light-duty vehicle emission regulations were finalized which requires low sulfur gasoline (30 ppm average; 80 ppm maximum) and very low emissions for both spark ignition and diesel light-duty vehicles (0.07 g/mile NO_x fleet average, 0.01 g/mile PM for most light-duty vehicles). Second, EPA proposed new emission regulations for heavy-duty diesel engines (0.2 g/bhp-hr NO_x and 0.01 g/bhp-hr PM) that will require exhaust emission control devices and very low sulfur diesel fuel (EPA has proposed 15 ppm maximum). Exhaust emission control devices needed for heavy-duty engines to meet the proposed EPA emission standards will also be needed by light-duty diesel vehicles to meet the Tier 2 regulations. Advanced petroleum-based fuels will ensure that the high fuel economy benefits of advanced CIDI engines are realized while enabling the effectiveness and durability of emission control devices over their full useful life.



Advanced Petroleum-Based Fuels Will Enable Advanced Engines, Emission Control Systems, and Fuel Cells

While CIDI engines are viewed as a nearer-term opportunity to meet the 80 mpg objective set by PNGV, fuel cells are seen as a promising longer-term technology that will be capable of achieving unprecendented fuel economy with zero or near-zero emissions. One of the key challenges of producing a fuel cell vehicle is developing an appropriate fuel for vehicular applications. Fuel cells can potentially use a wide range of fuels such as hydrogen, methanol, ethanol, natural gas, and gasoline. The fuels effort to support the Transportation Fuel Cell Power Systems Program is currently focused on determining the effects of petroleum fuel contaminants on the fuel cell system performance and developing advanced petroleum-based fuels and catalyst technologies that will not compromise the fuel cell's inherently high efficiency.

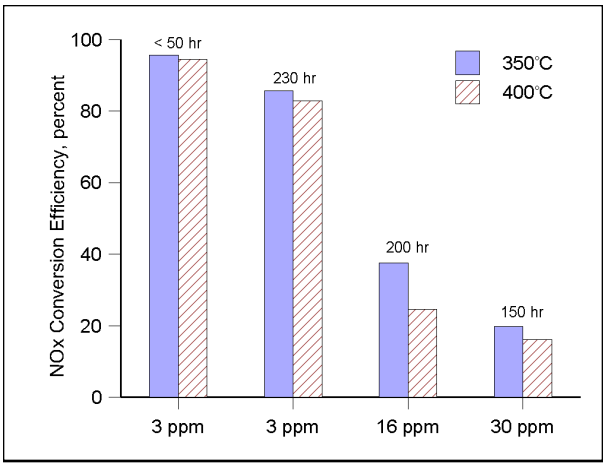
SIGNIFICANT FY 2000 ACCOMPLISHMENTS

In FY 2000, much effort has been devoted to determining the effect of fuel sulfur content on CIDI NO_x and PM emission control devices. While it is still unclear what maximum level of sulfur might be acceptable, the testing conducted in FY 2000 indicated that very low levels of sulfur content are likely to be required for CIDI vehicles and heavy-duty engines to meet the full useful life Tier 2 and proposed heavy-duty engine emission standards. Both NO_x and PM emission control devices will have to achieve conversion efficiencies of 80 to 95 percent so that light-duty vehicles with CIDI engines and heavy-duty CIDI engines will be able to meet the emission standards. In addition, testing of some oxygenated diesel fuels showed potential for lowering both NO_x and PM emissions, and to have some favorable characteristics to complement the operation of exhaust emission control devices. These tests are on-going using state-of-the-art and prototype CIDI engines, and the latest exhaust emission control devices, and a Multiyear Program Plan has been completed to guide this

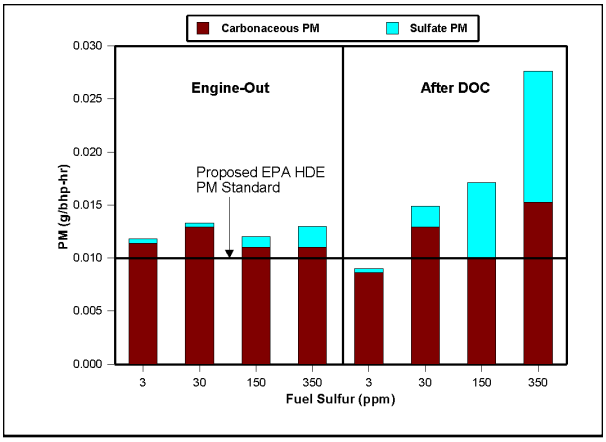
research through 2004. In the fuel cell area, work is progressing on identifying the effects of fuel composition on fuel processor performance, and on means of removing sulfur from the fuel which would otherwise poison the fuel cell. In FY 2000, DOE began its work with the California Fuel Cell Partnership. The overall objective of the Partnership is to demonstrate the practicality of fuel cell vehicles, initially operating with hydrogen as fuel. The following lists the highlights of research and testing conducted in the APBF Program during FY 2000.

Advanced Petroleum-Based Fuels for CIDI Engines

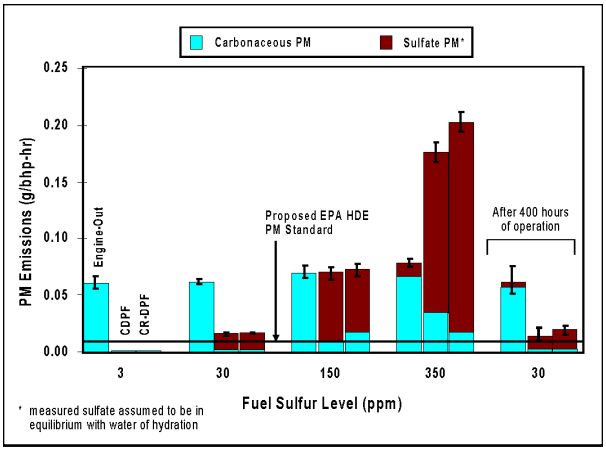
- The National Renewable Energy Laboratory provides coordination and technical support to the Diesel Emission Control-Sulfur Effects (DECSE) program that conducted engine dynamometer tests of the effects of fuel sulfur on several exhaust emission control devices. The DECSE program was funded jointly by industry through the Engine Manufacturers Association and the Manufacturers of Emission Controls Association. Oak Ridge National Laboratory was also part of the team and FEV was contracted to perform the engine dynamometer testing. The NO_x emission reduction devices tested included lean-NO_x catalysts and NO_x adsorber catalysts. The PM emission reduction devices tested included oxidation catalysts, continuously regenerating particulate filters (CR-DPF), and catalyzed diesel particulate filters (CDPF). The fuel used was similar to conventional diesel fuel except for sulfur content. Sulfur contents tested included 3, 16, 30, 150, and 350 ppm. Some of the major findings of this work include:
  - Lean-NO_x catalysts do not have sufficient conversion efficiency at this time.
  - NO_x adsorber catalysts show promise when used with 3 ppm sulfur fuel, but their efficiency degrades rapidly with 16 and 30 ppm sulfur level fuels (see figure).
  - Diesel oxidation catalysts (DOC) have moderate capability to reduce PM emissions, but create significant sulfate PM at fuel sulfur levels above 30 ppm (see figure).
  - Both CR-DPFs and CDPFs have very high PM removal efficiency (95%) when using 3 ppm sulfur fuel. The PM removal efficiency (i.e. filter



Effect of Fuel Sulfur Level on an Engine Dynamometer Test of an NO_x Adsorber (DC/DDC 1.9L Prototype Engine, steady state testing)



Effect of Fuel Sulfur Level on DOC PM Emissions in Steady-State Heavy-Duty Engine Dynamometer Tests (Cummins ISM370 Engine)



Effect of Fuel Sulfur Level on PM Emissions of a CDPF and CR-DPF in Steady-State Heavy-Duty Engine Dynamometer Tests (Caterpillar 3126 Engine)

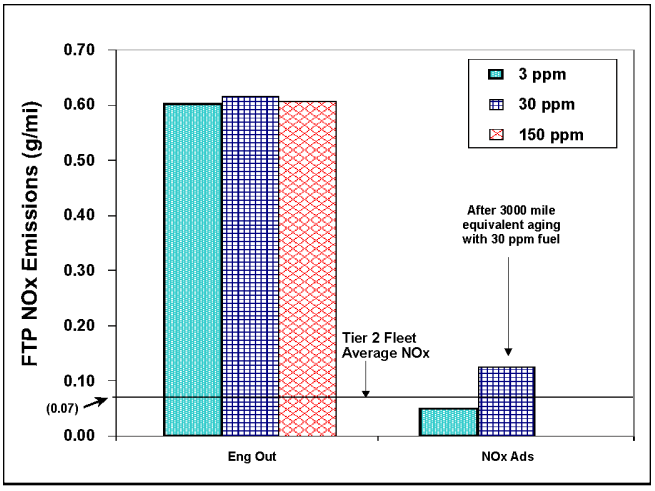
emissions compared to engine-out emissions) degrades significantly when using 30 ppm sulfur fuel (72-74%) and drops nearly to zero efficiency when using 150 ppm sulfur fuel (see figure).

- In the DOC and PM filter tests, the sulfur present in the fuel is converted to sulfate PM at the rate of 40% to 50%, and regeneration temperatures increase with increase in fuel sulfur level.

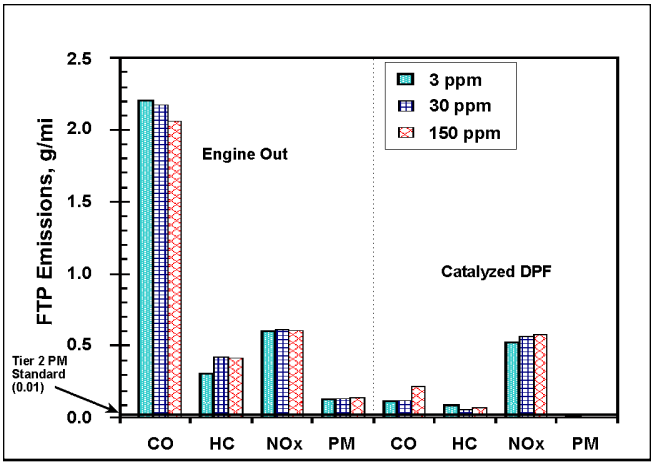
- A second phase of the exhaust emission control device testing described above (DECSE-II) focused on improving the regeneration strategy of the NO_x adsorber and development and demonstration of a process to remove accumulated sulfur from the adsorber following extended operation. It was shown that, with the proper engine calibration, the NO_x conversion efficiency of the NO_x adsorber could be improved to over 90 percent in the temperature range of 300ºC to 450ºC, which suggests that NO_x adsorbers (with further successful development) could allow light-duty vehicles to meet the Tier 2 fleet average of 0.07 g/mile NO_x. It was shown that the fuel required for regeneration was estimated to cause a 4 percent decline in fuel economy. It was also shown that sulfur accumulated on the NO_x adsorber could be removed by subjecting the adsorber to 700ºC temperatures achieved using post injection, a warm-up catalyst upstream of the adsorber, throttling, and EGR. While such strategies hold promise to achieve the Tier 2 NO_x fleet average, several hurdles remain, including the fuel economy penalty incurred and the thermal stability of the catalyst to repeated desulfurizations.

- The Oak Ridge National Laboratory explored the potential of near-term NO_x and PM exhaust emission control devices on a small state-of-the-art CIDI passenger car (Mercedes A170) using fuel with 3, 30, and 150 ppm sulfur content. A NO_x adsorber catalyst and a catalyzed diesel particulate filter were tested independently on the vehicle over the Federal Test Procedure (FTP) (see figures). These tests demonstrate the capability to meet the Tier 2 fleet average NO_x emission standard of 0.07 g/mile using the 3 ppm

ORNL Researchers Conducting Chassis Dynamometer Tests on the Mercedes A170



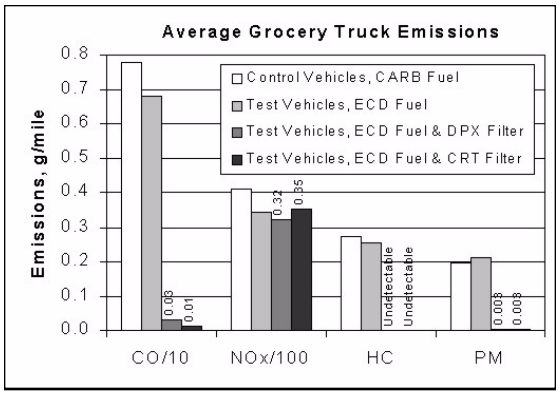
Mercedes A170 NO_x FTP Emissions Using an NO_x Adsorber and Various Fuel Sulfur Contents



Mercedes A170 FTP Emissions Using a CDPF and Various Sulfur Content Fuels with No Advanced NO_x Control Device

sulfur content fuel when the catalyst was relatively new. However, limited durability testing suggests that this device would not meet full useful life standards even when using 3 ppm sulfur content fuel. The catalyzed diesel particulate filter was much less affected by fuel sulfur content and PM emissions were always below 0.01 g/mile. Though these results are very promising, some hurdles remain before such systems could be considered feasible for use: reducing the amount of reductant needed to regenerate the NO_x adsorber, designing the reductant preparation and delivery system, and reducing the regeneration temperature of the catalyzed diesel particulate filter.

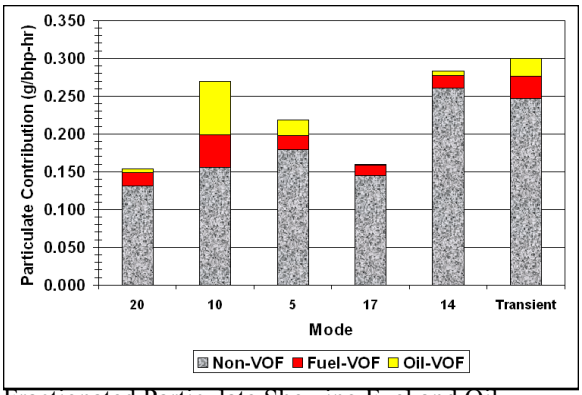
- The National Renewable Energy Laboratory managed a field test of conventional diesel vehicles using a low-sulfur, low-aromatic diesel fuel and retrofitted with catalyzed particulate filters. The fuel is made by BP Amoco and is called EC-Diesel. EC-Diesel has a maximum sulfur content of 15 ppm, less than 10% aromatics by volume, and a nominal cetane rating of 60. BP Amoco has intentions to make EC-Diesel available in Southern California. Eight vehicle fleets participated, all having vehicles with modern, electronically-controlled diesel engines. Two catalyzed particulate filters were supplied by Engelhard and Johnson-Matthey and one of them was retrofitted to each of the vehicles. The vehicles were tested for emissions using the University of West Virginia mobile chassis dynamometer. The combination of ultra low sulfur and low aromatic fuel with the retrofitted catalyzed particulate filters resulted in extremely low PM and hydrocarbon emissions, sometimes indistinguishable from background values (see figure). Emissions of NO_x were not affected. Testing will be conducted at regular intervals to determine how emissions might deteriorate over time.



Average Grocery Truck Emissions over the City-Suburban Heavy Vehicle Route

- Sandia National Laboratory (SNL) and Lawrence Livermore National Laboratory (LLNL) continued projects to understand the fundamental mechanisms of particulate and NO_x formation during combustion. SNL is using in-cylinder imaging of the combustion of fuels with varying levels of particulate production to identify where and how particulates are formed. LLNL is applying the chemical kinetics of combustion to identify the reactions that produce particulates and NO_x, and how the addition of oxygenates affects the formation of both.

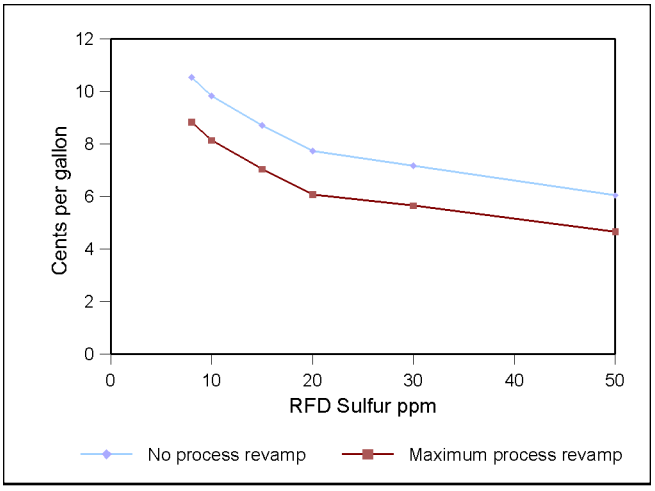
- As emissions of PM from CIDI engines are reduced, the contribution of PM from consumed lubricating oil becomes more important (compared to PM from fuel). Testing conducted by Southwest Research Institute (SwRI) showed that PM is reduced by 19% when using 5W30 mineral oil instead of a 15W50 synthetic oil (Mode 10 steady-state operation representative of typical light-duty vehicle engine load, see Figure) when using CARB diesel fuel. SwRI also found that 27 percent of the PM at Mode 10 was caused by oil consumption (using 5W30 mineral oil) when using CARB diesel fuel. Synthetic oils and high boiling point oils reduce the contribution to PM emissions. High friction oils also reduce PM emissions, but at the expense of higher NO_x emissions. This work suggests that particulate emissions can be significantly reduced through oil formulation, without impact on other emissions.



Fractionated Particulate Showing Fuel and Oil Contributions to PM (CARB Fuel; 5W30 Baseline Mineral Oil)

- In FY 1999, blends of oxygenates in diesel fuel showed potential for very large decreases in PM emissions (50%) with small decreases in NO_x emissions. However, some of these oxygenate blends were not practical for use in the current distribution system, or presented potential safety or materials compatibility problems. Southwest Research Institute managed a project with oversight and direction from auto and energy companies to identify oxygenates that can be used in diesel fuel which may not cause infrastructure or compatibility problems, and might be economical for use as a blending component. Seventy-one oxygenates were screened and six were chosen for more in-depth evaluation. Of these six, two have been selected for comprehensive engine testing in FY 2001.

- Through modeling of the typical U.S. refinery, Oak Ridge National Laboratory estimated that reducing the sulfur in on-road diesel fuel to 15 ppm, as proposed by EPA, would add 7 to 8 cents per gallon to the average cost of production. The marginal cost of sulfur removal increases rapidly for fuel sulfur contents of 25 ppm and lower (see Figure).

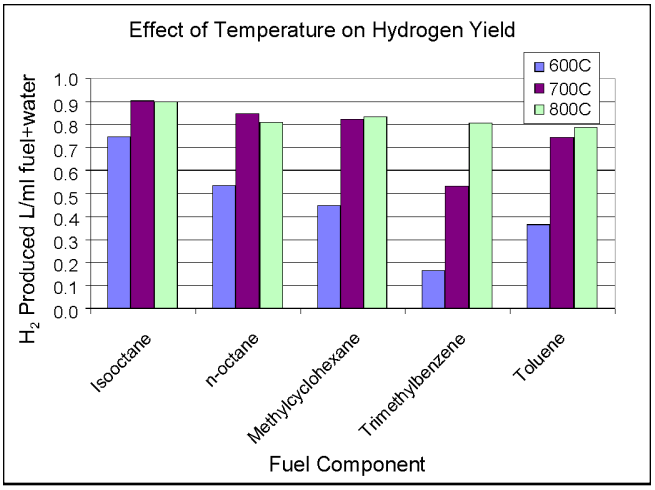


Estimated Production Cost Increase for Reformulated Diesel (RFD)

- Three projects were undertaken during FY 2000 to evaluate the health and safety impacts of CIDI fuels and emissions. The Lawrence Livermore National Laboratory developed a systematic methodology to assess the environmental impact of oxygenated fuel components for potential use in advanced petroleum-based diesel fuels. The methodology includes transport and degradation models to evaluate the relative hazards caused by spills, and prediction of human exposure via ingestion, inhalation, and dermal uptake. In a project being conducted by Southwest Research Institute, the effects of fuels on the engine-out emissions of potentially toxicologically relevant compounds are also being determined. In a project being conducted by the Oak Ridge National Laboratory, transmission electron microscopy and real-time aerosol mass spectroscopy are being used to compare the structure and composition of PM from both gasoline and diesel vehicles. Using these instruments, the chemical composition of both the surface of the PM and the core of the PM will be identified.

Advanced Fuels for Fuel Cells

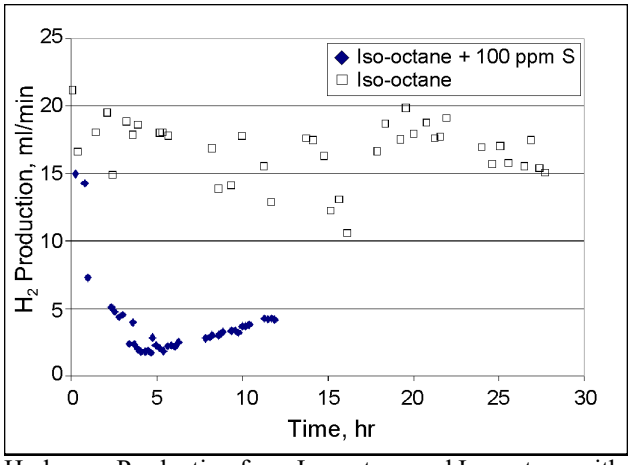
- Hydrogen is acknowledged to be the long-term fuel cell fuel, and fuels that are compatible with the existing petroleum fuel infrastructure are the likely transition step toward that goal. The Argonne National Laboratory (ANL) is exploring how different hydrocarbons affect reformer performance, with the overall objective of identifying which gasoline constituents cause degradation of fuel cell systems (see Figure). Through this project, ANL will work with energy companies to identify how the constituents that cause problems can be minimized, while maintaining compatibility with the present petroleum fuel distribution system. The progress this project has made this year includes:



Effect of Temperature on Hydrogen Yield from Autothermal Reforming of Gasoline Constituents

- completion of short-term testing of six gasoline components;
- completion of long-term tests on iso-octane and two benchmark fuels; and
- initiation of tests on the effect of fuel sulfur content.

- The Los Alamos National Laboratory (LANL) is exploring ways to improve fuel cell reformer durability and lifetime, reduced volume, improved performance, and other improvements required to meet fuel processor goals. LANL is focusing on improved catalyst formulations to achieve these reformer improvements. The accomplishments they have made in the past year include:
  - automation of the test facility to complete multiple tests quickly and efficiently;
  - initiated testing of a fuel-flexible fuel processor and verified operation using natural gas;
  - initiated testing of liquid fuels; and
  - showed that 100 ppm sulfur in the fuel, using a specific fuel processor and catalyst, reduced hydrogen production by 75 percent (see Figure).



Hydrogen Production from Iso-octane and Iso-octane with 100 ppm Sulfur

- One of the largest hurdles to using hydrocarbons for fuel cell vehicles is that the sulfur contained in gasoline today will poison the reformer and fuel cell catalysts. The Argonne National Laboratory (ANL) is exploring ways to remove this sulfur and define the tolerance of both reformers and fuel cells to fuel sulfur content. A zinc-oxide absorption bed has been fabricated and it has demonstrated the capability to decrease H_2S concentration in a reformate stream from10-30 ppm down to less than 1 ppm.
- The California Fuel Cell Partnership will demonstrate fuel cell technology by operating and testing fuel cell vehicles in California. The first vehicles demonstrated will use hydrogen as fuel. In a later phase of the demonstration, fuel cell vehicles may also use methanol and gasoline as fuel. To date, fleets have been identified to use the initial fuel cell vehicles and a hydrogen refueling facility has been designed.

California Governor Gray Davis Announces the California Fuel Cell Partnership at the State Capitol on April 20, 1999

FUTURE INITIATIVES

Our new program initiatives for FY 2001 build upon the progress made in FY 2000 and will focus on those areas that industry agrees are major technical barriers.

Ultra-Clean Transportation Fuels Initiative

- In FY 2001, the Ultra-Clean Transportation Fuels Initiative, which is a new initiative jointly funded by the Office of Energy Efficiency and Renewable Energy and the Office of Fossil Energy, will begin to research

and develop advanced fuels, refinery processes, and vehicle emission control technologies. The advanced fuels technology will produce ultra-clean burning, high performance fuels from a diversity of resources in addition to conventional petroleum. These fuels will be used to support the research and development of innovative vehicle emission control systems with ultra-low NO_x and particulate matter emissions.

Advanced Petroleum-Based Fuels for CIDI Engines

- Quantify the effect of fuel sulfur content on exhaust emission control device durability in terms of deterioration rate, ability to "rebound" from exposure to high sulfur fuels, and the impact on fuel economy penalty for regeneration and desulfurization.
- Conduct vehicle tests of integrated NO_x and PM emission control devices using fuels with several sulfur levels to predict the capability of these systems to meet Tier 2 and proposed heavy-duty engine emission standards.
- Begin testing various selective catalytic reduction (SCR) systems to determine their conversion efficiency and effectiveness at various sulfur contents.
- Study the potential to reduce the fuel economy penalty of regenerating and desulfurizing NO_x adsorbers.
- Complete comprehensive testing of the two most promising oxygenates chosen of the seventy-one which were screened.
- Develop and test models for PM and NO_x formation during combustion and extend these models to incorporate oxygenated fuel components.
- Perform additional testing of the vehicles in the demonstration of EC-Diesel.
- Define environmental parameters for development of screening models for oxygenated diesel fuel components.
- Measure the effect of exhaust emission control devices using several clean diesel fuels on emissions of toxics.
- Analyze the effects of phased market introduction on the price and availability of ultra low sulfur diesel fuel.

Advanced Fuels for Fuel Cells

- Study the effects of fuel constituents (focusing on olefins, napthalenes, and substituted aromatics that may be problematic), additives, and impurities on fuel processor operation.
  - Measure fuel processor transient operation including startup and shutdown and variations in flow rates.
  - Monitor carbon formation *in situ* by use of adiabatic reactor and laser scattering.
  - Map carbon formation of individual fuel constituents with operating conditions.
- Investigate the effect of sulfur on various fuel processor catalysts.
- Evaluate the capability of new structured forms of ZnO to remove H_2S from reformate streams.
- Initiate operation of fuel cell vehicles in California and identify additional refueling sites; identify additional fuels to test; assess commercialization issues; and implement public outreach and education plans.

HONORS AND SPECIAL RECOGNITIONS

- The California Fuel Cell Partnership received the "Blue Sky Innovation Award™" from CALSTART for taking early steps to create a fuel cell market by demonstrating fuel cell vehicles in California.
- The team that prepared the Multiyear Program Plan for Advanced Petroleum-Based Fuels was recognized with a special achievement award at the CIDI Engine Combustion, Emission Control, and Fuels Review held at Argonne National Laboratory May 22-24, 2000. The team included representatives from the National Renewable Energy Laboratory, Argonne National Laboratory, Oak Ridge National Laboratory, Southwest Research Institute, Energetics, and QSS Group, Inc.

SUMMARY

Advanced petroleum-based fuels enable the use of high efficiency powerplants such as CIDI engines and fuel cells to create fuel efficient light-duty and heavy-duty vehicles with the attributes that consumers demand. Fuel efficient vehicles with very low emissions are essential to meet the challenges of climate change, energy security, and improved air quality. The work being conducted on advanced petroleum-based fuels complements the efforts to build advanced engines and fuel cells while recognizing that the engine/fuel/emission control system must work together to achieve the maximum benefits possible. As the new fiscal year begins, we look forward to on-going and new cooperative efforts with the auto and energy industries to develop new and innovative technologies that will be used to make advanced transportation vehicles that are fuel efficient, clean, and safe.

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II. FUEL & LUBRICANT EFFECTS ON CIDI ENGINE EMISSIONS

A. Phase II Testing of Advanced Petroleum-Based Fuels in a State-of-the Art CIDI Engine

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

2. Fuel and Lubricant Properties - Engine-Out Emissions

Objective

- Quantify exhaust emission benefits of selected advanced petroleum-based fuels in an advanced automotive diesel engine, with the engine optimized to take advantage of the individual combustion characteristics of each individual fuel.

Approach

- Three fuels shown to significantly reduce engine out emissions in the DaimlerChrysler OM611 CIDI engine during the first phase of this program, along with fuels suggested by the Ad-Hoc fuels working group, were evaluated for emissions benefits with selected engine control system optimization for each fuel.
- Engine-out emissions (no exhaust emission control devices) and performance were determined at a series of steady-state test modes.
- A partial factorial design of experiment approach was to develop a quadratic response surface model for PM, NO_x and fuel consumption at each speed/load point as a function of the four engine operating parameters. The resulting surface would then be used to find optimum engine control conditions to achieve desired emission goals.

Accomplishments

- The engine's OEM electronic controller was replaced with a SwRI Rapid Prototyping Electronic Control System (RPECS). The engine calibration tables and control signals were duplicated with the RPECS hardware/software, then modified as necessary.
- A partial factorial experimental design was developed to provide a quadratic response surface model for PM, NO_x and fuel consumption at each speed/load point as a function of the four engine operating parameters.

- The resulting response surface model, when completed, did not adequately model the engine-out emissions. However, examination of the collected data clearly showed that reductions in both NO_x and PM from the OEM conditions were achievable.
- Starting from the Ad-Hoc fuels working group test points, which specify the timing of peak cylinder pressure and EGR, a series of measurements of NO_x and Bosch smoke measures were made with increasing levels of EGR. Bosch smoke has been correlated with particulate, and is a quicker measurement to make.
- Preliminary results, comparing emissions with alternative low-sulfur fuel (ALS) and with a fuel blend of 15% dimethoxymethane in ALS (ADMM15), show a clear difference in NO_x and Bosch smoke level. At any smoke level, ADMM15 produces lower NO_x emissions, but requires a higher level of EGR. This result is consistent with previous observations of the lower PM production at constant EGR levels.

Future Directions

- Correlations between Bosch smoke number and particulate are being developed for the fuels being evaluated. These will be used to assess the observed emission responses.

Introduction

This work is a follow-on to the Phase I fuel evaluations utilizing the DaimlerChrysler OM611 CIDI engine. The Phase I testing was designed to evaluate the potential benefits of several alternative diesel fuels without making any adjustments to the engine control system. The objective of this second phase of work is to optimize the OM611 engine for a subset of the seven fuels that were tested in Phase I, as well as fuels recommended by the Auto/Energy Ad-Hoc committee.

Because the fuels under consideration have differing physical and chemical properties, a portion of any change in exhaust emissions measured in Phase I may be due to the response of the engine's fuel injection system to differences in the fuel's physical properties. This phase will recalibrate the engine operating parameters that influence engine emissions and fuel economy. These operating parameters include boost level, exhaust gas recirculation (EGR), fuel injection timing, and pressure in the common rail injection system.

Approach

Three fuels shown to significantly reduce engine-out emissions in the DaimlerChrysler OM611 CIDI engine during the first phase of this program, along with fuels suggested by the Ad-Hoc fuels working group, were evaluated for emissions benefits with selected engine control system optimization for each fuel.

A partial factorial design of experiment approach was to develop a quadratic response surface model for PM, NO_x and fuel consumption at each speed/load point as a function of the four engine operating parameters. The resulting surface would then be used to find optimum engine control conditions to achieve desired emission goals. Engine-out emissions (no emission control devices) and performance were to be determined at a series of steady-state test modes.

In order to deviate from the factory engine operating settings, the engine's OEM electronic controller was replaced with a SwRI Rapid Prototyping Electronic Control System (RPECS). The engine calibration tables and control signals were duplicated with the RPECS hardware/software, then modified as necessary. A high and a low value of each of the four engine operating parameters were determined by individually varying each parameter until one of the following occurred: a 20% NO_x increase was noted, a 20% increase in Bosch smoke was noted, the engine operated roughly, or exhaust temperature exceeded 1450°F.

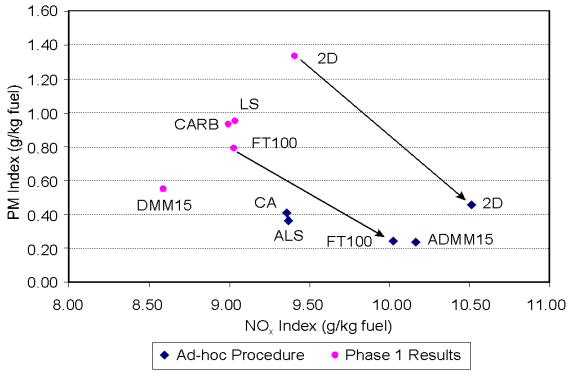

Figure 1. Control Strategy Impacts on NO_x and PM Emissions

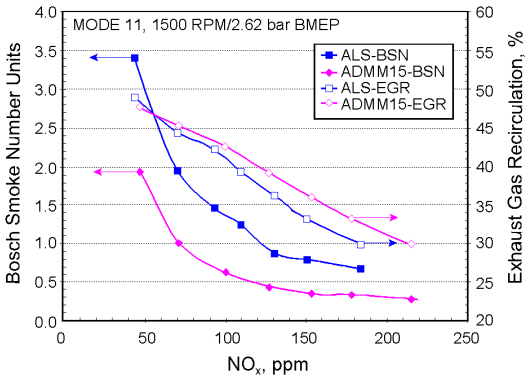

Figure 2. EGR Effect on NO_x and Bosch Smoke

Results

The resulting response surface model, when completed, did not adequately model the engine-out emissions. Analysis of the statistical results suggest that the operating extremes generated by combining already broadly varied control settings resulted in engine responses that varied more "steeply" than the selected model would represent with adequate accuracy. However, examination of the collected data clearly showed that reductions in both NO_x and PM from the OEM conditions were achievable.

Evaluation of the fuels was then conducted at the conditions developed by the Ad-Hoc fuels study group. The fuel injection rail pressure [injection rate] and turbocharger boost pressures were set at OEM conditions, EGR was set at a fixed rate dependent on speed and torque, pilot injection was disabled, and the beginning of injection timing was adjusted to locate peak combustion pressure at 7 degrees after top center. The data presented in Figure 1 were averaged over Modes 5, 6, 10, and 11 from both studies, since this Phase II work was conducted with a reduced number of operating modes. Because of fuel batch changes, only two fuels were actually identical between the two studies: the 2D certification fuel and the FT100 Fischer-Tropsch product. The arrows illustrate the impact of the engine control change on the emissions of these two fuels. This engine control strategy decreased particulate but increased NO_x emissions. Starting from these operating conditions, the EGR rate was increased with ALS and ADMM15 at two operating modes: 6 and 11. A series of measurements of NO_x and Bosch smoke were made with increasing levels of EGR. Bosch smoke has been correlated with particulate, and can be measured more quickly.

Preliminary results, comparing emissions between ALS and ADMM15, show a clear difference in NO_x and Bosch smoke level (Figure 2). At any smoke level, ADMM15 produces lower NO_x emissions but requires a higher level of EGR. This result is consistent with previous observations of the lower PM production at constant EGR levels and suggests that NO_x reductions of 30 percent or more are possible at equal PM levels with ADMM15.

Correlations between Bosch smoke number and particulate are being developed for the fuels being evaluated. These will be used for assessment of the observed emission responses.

Conclusions

These results illustrate both the impact of engine control strategy on engine-out emissions, and the substantial impacts that changes in fuel formulation can have on engine-out particulate emissions. These preliminary results with ALS and ADMM15 indicate that because oxygenated fuels produce lower particulate levels, there is flexibility to operate the engine at higher EGR levels to reduce the engine out NO_x emissions. However, since these initial data do not agree with data from the Ad-Hoc fuels working group, additional substantiation is needed.

List of References

1. Sirman, M.B, Owens, E.C., and Whitney, K.A., "Emissions Comparison of Alternative Fuels in an Advanced Automotive Diesel Engine," Interim Report TFLRF No. 338, November 1998.

List of Acronyms

2D	EPA Certification Fuel
ADMM15	15% by volume dimethoxymethane blended in alternative low sulfur fuel
ALS	Alternative Low-Sulfur
BSN	Bosch Smoke Number
CA	California Reference Diesel Fuel (Supplier A)
CARB	California Reference Diesel Fuel (Supplier B)
CIDI	Compression Ignition/Direct Injection
DMM15	15% by volume dimethoxymethane blended in low-sulfur fuel
EGR	Exhaust Gas Recirculation
FT100	Fischer-Tropsch Fuel
LS	Low-Sulfur Fuel
NO_x	Nitrogen Oxide
OEM	Original Equipment Manufacturer
PM	Particulate Matter
PNGV	Partnership for a New Generation of Vehicles
RPECS	Rapid Prototyping Electronic Control System
SwRI	Southwest Research Institute

B. Oxygenates for Advanced Petroleum-Based Diesel Fuels

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

2. Fuel and Lubricant Properties - Engine-Out Emissions

Objectives

- Assess the benefits and limitations of oxygenated diesel fuels on engine performance and emissions.
- Identify oxygenates for exhaust emissions and performance testing based on physicochemical properties, toxicity, biodegradability, and projected cost of production.
- Select at least two oxygenated compounds for advanced engine testing.

Approach

- Review the oxygenate literature to identify potential candidates.
- Select oxygenate candidates on the basis of:
  - Oxygen content, flash point, solubility in low aromatic diesel fuel, and stability.
  - Fuel properties such as viscosity, cetane number, and lubricity.
  - Elastomer compatibility.
  - Results of a single mode emissions and performance test in a DaimlerChrysler OM611 CIDI engine.
  - Potential toxicity, biodegradability, and air quality.
  - Economics of producing the most technically promising oxygenates for diesel fuel.
- Based on the above criteria, two oxygenate candidates will be selected for multi-mode testing of engine performance and exhaust emissions in the 2.2L DaimlerChrysler OM611 CIDI engine.

Accomplishments

- A literature search on the effect of oxygenate compounds on particulate emissions from diesel engines was performed.

- Seventy-one oxygenate candidates were screened on the basis of oxygen content, flash point, solubility in low aromatic diesel fuel, and stability. Six viable candidates emerged from the screening.
- Nine test fuels including an alternative low-sulfur diesel (ALS) reference fuel and eight oxygenate-ALS blends were tested for exhaust emissions and performance in a 2.2L DaimlerChrysler OM611 CIDI engine. The tests were performed in triplicate at a single operating mode and the emissions measurements included Bosch smoke number, total PM, total volatile fraction, TVF, NO_x, CO, CO_2, O_2, and total hydrocarbons.
- The test fuels were each prepared with 7 wt.% oxygen by adding the appropriate amount of oxygenate to ALS.
- Test fuel properties, including density, viscosity, surface tension, cetane number, boiling point distribution, and lubricity were measured by ASTM methods. Composition was determined using the carbon, hydrogen and oxygen contents of the ALS base fuel and oxygenate.
- The compatibility of the oxygenated test fuels with elastomers was tested. Five O-rings, consisting of two Viton and three Nitrile type elastomers, were immersed in the ALS base fuel and eight oxygenated test fuels for 336 hours at 41°C. Relative to the ALS base fuel, the oxygenated fuels caused significant degradation, especially in the Viton type elastomers.
- The following two oxygenates were recommended for additional research; tri-propylene glycol monomethyl ether and di-butyl maleate.

Future Directions

- Determine the effect of oxygenates in diesel fuel on exhaust emissions when tested under the light-duty transient FTP cycle.
- Examine the effects of exhaust emission control devices on PM and NO_x when using oxygenated diesel fuel. Since catalytic reactors are much more effective in reducing TVF than dry PM, oxygenated fuels are expected to reduce PM emissions even further because they tend to have a higher TVF than the PM from pure hydrocarbon fuels.
- Determine the effect of oxygenated fuels on particle size distribution.
- Evaluate the effect of oxygenates on potentially toxic polynuclear aromatics (PNAs) in particulate matter.
- Define the effect of oxygenate chemical structure on PM emissions.

Introduction

As the demand for energy rises, oil consumption will eventually outpace discovery. Unless infrastructures for alternative energy sources are developed in a timely manner, serious fuel shortages could result. To forestall a potential crisis and allow more time for a smoother transition to alternative energy sources, it is necessary to develop more efficient vehicles. The diesel engine is of particular interest because it is significantly more efficient than its spark ignited counterpart. However, more widespread use of diesel power sources is restricted by unacceptable exhaust emissions. Diesel engine manufacturers have made considerable progress in reducing harmful exhaust emissions. Combustion efficiency has been greatly improved through ultra-high pressure fuel injection and better fluid flow. Electronic control has been used to optimize engine performance and lower exhaust emissions. However, the diesel engine has yet to meet the future emissions standards required by the EPA in the next decade.

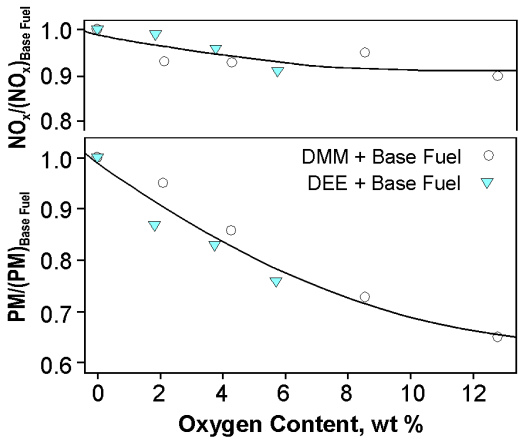

Figure 1. Effect of Oxygen Content on the Relative PM and NO_x Emissions from DMM and DEE Diesel Fuel Blends, Cheng and Dibble, SAE Paper 1999-01-3606

A major problem is that particulate (smoke) emissions are still too high. Since further modifications to the engine design and operation alone will not reduce PM emissions to the required level, cleaner burning fuels and emission control devices are necessary. Future diesel fuels may have greatly reduced sulfur levels. Fuel sulfur has to be reduced because it degrades catalytic activity in emission control devices. Sulfur can be removed by hydrotreating, which also increases the hydrogen to carbon ratio, lowers aromatics, and raises cetane number. Low sulfur fuels also yield lower PM emissions because of the increased hydrogen to carbon ratio and the absence of sulfates, which would otherwise combine with soot to increase particulate mass.

Future reformulation of diesel fuel may involve addition of oxygenates. Several exhaust emissions studies have shown that using pure oxygenates such as methanol and dimethyl ether as diesel fuels essentially eliminate PM emissions. A number of other studies report that blending oxygenates into diesel fuel will also significantly reduce PM emissions in diesel exhaust. Figure 1 shows the effects of dimethoxymethane (DMM) and diethyl ether (DEE) blended with a CARB certified DF-2 on the PM and NO_x emissions from a Cummins 5.9 liter turbodiesel. The results of Cheng and Dibble represent an average of nine operating modes. Figure 1 shows that the emissions benefit of blending oxygenates with diesel fuel goes beyond that explained by simple dilution. This disproportionate reduction in PM emissions is not observed when blending in a similar amount of low-PM hydrocarbon compounds. Several studies with results similar to that in Figure 1 show that it is primarily the added oxygen that suppresses the formation of soot or PM during combustion. However, there are claims in the literature that some oxygenates of different molecular structure are more effective in reducing PM emissions than others.

The impact and the limitations of oxygenates on the diesel combustion process have not been well defined. Questions on the importance of molecular structure and the maximum achievable PM reduction with oxygenate blends is difficult to quantify because the emissions data in the literature are from several engine types and different operating conditions. The purpose of the present study is to evaluate several oxygenates on an equal basis, i.e., establish criteria for the selection of oxygenates and then test them in the same engine under the same operating conditions.

Approach & Progress

Southwest Research Institute (SwRI) participated in an extensive industry-based review of published information and in-house but non-proprietary data. As part of the Oxygenate Analysis Project team which was comprised of representatives from the Ad-Hoc Fuels group (DOE, auto companies, and oil companies), SwRI organized the data for comparison and interpretation and for the development of correlations between the properties of oxygenated diesel fuel and PM emissions.

The literature search was comprised of two parts: 1) to investigate the effect of oxygenates on PM emissions from engines; and 2) to gather data on the physicochemical properties of oxygenates. The engine studies showed that reductions in PM emissions correlated with oxygen content in the fuel. The studies indicated that an oxygen content of at least 7% in the fuel would be required to produce a 50% reduction in PM. The literature was not clear on the effects of molecular structure on PM emissions.

Several oxygenate candidates were revealed in the literature search for the present study. The list of oxygenates finally grew to 71 as the members of the

Oxygenate-ALS Diesel Blend	Oxygenate Vol. %	NACE Corrosion	Cetane Number	Density, g/cm^3	Viscosity, cSt	Surface Tension	Lubricity, microns
ALS-Base Reference Fuel	0	Passed	65.5	0.8169	2.94	30.3	483
Methylal (DMM)	16.06	NA	62.9	0.8217	1.67	28.4	503
Oxygenate-ALS Blends to be Tested in 2.2 L OM611 Engine							
Di-butyl maleate--ALS	21.64	Pass-B	57.7	0.8537	2.78	31.1	268
Tributyrin--ALS	18.35	Pass-B	52.6	0.8550	3.06	30.6	375
Di-ethyl adipate--ALS	18.76	Passed	56.0	0.8506	2.55	30.9	443
2-ethoxy ethyl acetate--ALS	16.72	Pass-A	61.3	0.8397	2.10	31.0	490
2-ethoxy ethyl ether--ALS	21.85	Passed	86.4	0.8342	2.09	31.0	670
Tripropylene glycol monomethyl ether--ALS	19.80	Pass-B	65.0	0.8416	2.73	30.5	505
Dipropylene glycol monomethyl ether--ALS	19.42	Pass-B	61.4	0.8403	2.54	30.4	545
1-methoxy-2-propanol--ALS	17.92	Passed	57.2	0.8321	2.19	30.8	495
Other Candidates							
2-Butoxy ethanol--ALS	24.05	Pass-B	59.6	0.8354	2.50	30.4	395
2,4,7,9-tetra-oxa-decane (TOD)--ALS	13.82	Pass-A	64.5	0.8402	2.24	30.5	623

NA = No Analysis

ALS = Alternative Low Sulfur Diesel Fuel

NACE Corrosion Test is the ASTM D 665 test.

Passed = No visible corrosion on the steel spindle

Pass-A = Light corrosion (fewer than 6 rust spots)

Pass-B = Medium corrosion (less than 50% coverage of spindle with rust spots)

Table 1. Properties of Oxygenate-ALS Diesel Fuels Blended to 7 Percent Oxygen

Oxygenate Analysis Project members proposed new compounds.

The initial criteria used to screen the viable oxygenate candidates were: 1) the amount of oxygenate added to diesel fuel to give 7 wt.% oxygen should not exceed 20 vol.%; 2) the flash point should not be less than 52°C; 3) oxygenate should be soluble in low aromatic diesel fuel at temperatures down to 6°C and should tolerate at least 1000 ppm of water; and 4) oxygenate must not decompose into corrosive products. The data for criteria 1 and 2 were obtained from the literature, while 3 and 4 were measured at SwRI. Solubility tests were performed by vigorously mixing 25 mL of oxygenate with 50 mL of diesel fuel and the allowing the mixture to stand. Fischer Tropsch diesel (FT) and Swedish Low-Sulfur diesel (SLS) were used as reference fuels. FT diesel was mostly composed of paraffins while SLS diesel contained a sizeable fraction of napthenes. Neither reference fuel contained more than 2 percent aromatics. Since aromatics in diesel fuel tend to increase the solubility of oxygenates, the FT and SLS diesels represented a worst case for solubility. Oxygenate solubility was measured in terms of the phase separation that occurred. If there was no separation at room temperature, the test was performed at 6°C. If the mixture passed the low temperature test, 1000 ppm of water was added and the test was repeated.

Stability was measured using the NACE D 665 corrosion test. Oxygenates were blended with SLS diesel in amounts required to achieve an oxygen content of 7 weight percent in the blend. The D 665 test measures the degree of corrosion that develops on a steel spindle immersed in a mixture of 30 mL of water and 300 mL of the oxygenate-SLS diesel blend. The mixture is stirred and held at 60°C for four hours after which the spindle is removed and

Proposed Ranking & Label	Oxygenate-ALS Blend	Relative Emissions				Added Cost, cents/gal	Predicted Biodegradability Relative to Benzene	Elastomer Compatibility Ranking	T90, °C	Oxygen Vol %	Flash Point, °C
		Total PM	Dry PM	NO_x	Toxicity						
9-A	ALSD Base Fuel for reference	100	100	100	LR	0	NA	1	346	0	88
8-D	Dipropylene glycol monomethyl ether	75	62	96	LR	30	NR	NR	342	19	77
7-C	1-methoxy-2-propanol	70	43	112	LR	27	NR	6	343	18	35
6-E	2-ethoxy ethyl acetate	75	67	95	SC	26	1.25	7	344	17	62
5-G	Diethyl adipate	74	62	111	SC	76	1.35	8	340	19	91
4-F	2-ethoxy ethyl ether	75	68	106	LR	43	0.73	3	342	22	78
3-H	Tributyrin	78	56	111	LR	29	1.36	4	342	18	91
2-I	Dibutyl maleate	74	56	119	SC	33	1.33	5	340	22	93
1-B	Tripropylene glycol monomethyl ether	70	52	113	LR	30	0.21	2	342	20	90

LR = lower risk based on limited data; SC = some concern; NA= no analysis; NR = no result; U = unknown

Table 2. Fuel Property Analysis and Engine Emissions Measurements

inspected for corrosion. If there are fewer than six rust spots, the fuel is given an A-rating. If less than 50 percent of the spindle surface has rust spots, a B-rating is given, and if more than 50 percent is rusted, a C-rating is given. Normally, A, B, and C ratings are failures, but since only a few of the oxygenate-DF2 blends passed the test with no rust spots, the test had to be scored more leniently. Ratings of A and B passed, whereas C failed.

Of the 71 oxygenate candidates screened, 28 had flash points too low. Oxygen contents were too low in three of the remaining 43, and 23 of the remaining 40 were insoluble in low-aromatic sulfur-free diesel fuel. One oxygenate had an unbearable odor, and of the sixteen remaining, seven failed the D 665 corrosion test, leaving nine eligible for engine testing.

The eight oxygenate compounds eligible for engine testing were blended with alternative low sulfur diesel fuel, ALS, in the amounts required to achieve an oxygen content of 7 wt.%. The density, viscosity, surface tension, flash point, heat of combustion, boiling point distribution, cetane number, and lubricity of each oxygenate-ALS blend were measured.

Table 1 shows the properties of the oxygenate-ALS blends considered for engine testing. Nine test fuels were selected for exhaust emissions and performance testing at one operating mode in the 2.2L DaimlerChrysler OM611 CIDI engine. They include the ALS base fuel and the eight oxygenate-ALS blends shown in Table 1.

The last three oxygenate-ALS blends selected for engine testing in Table 1 comprise a homologous series of mono-, di-, and tri-propylene glycol mono-methyl ethers. The propylene glycol mono-methyl ethers were included in the test matrix to determine the effect of oxygenate volatility on PM emissions. Oxygenates selected for the engine test contained ether, ester, and alcohol groups.

Emissions tests were performed in triplicate at Mode 6 (2,300 rpm and 4.2 bar BMEP). EGR was set at 15 percent and the location of peak pressure was adjusted to 7° ATDC. The Bosch smoke number, total PM, total volatile fraction (TVF), NO_x, CO, THC, CO_2, and O_2 were measured. Dry PM, which is assumed to form during the combustion process, was calculated by subtracting the TVF from the total PM.

Table 2 summarizes the results of the present study, and Figure 2 shows the effect of oxygenated fuels on TVF, dry PM, and total PM. The fuel labels in Figure 2 are defined in Table 2. The PM emissions from the oxygenate fuels were substantially lower than the reference Fuel A. It is seen that the total PM emissions from the oxygenate-ALS blends are

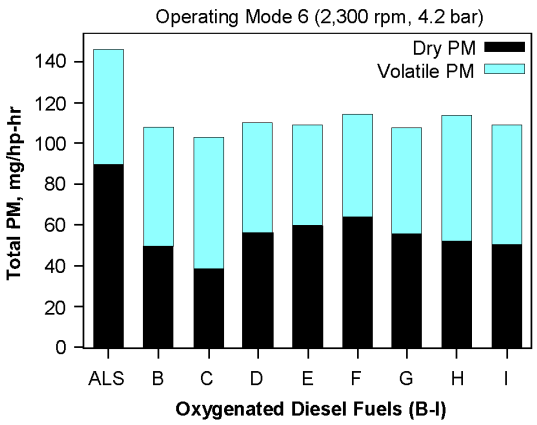

Figure 2. Effect of Oxygenates on the Dry and Volatile Matter Fractions of the Total PM (Oxygenates are identified in Table 2)

essentially equal, while there are distinct differences in the TVF and dry PM emissions. It is also seen that the TVF of the oxygenated fuels is larger than that of the neat ALS reference fuel. The variations in the dry PM suggest that oxygenate composition and structure have some effect on PM emissions. Additional research is needed to define the effect of oxygenate structure on PM emissions. It is also interesting to note that the relatively high TVF of the oxygenated fuels may enhance the completeness of oxidation in catalytic emission control devices.

Other factors important in choosing appropriate oxygenate compounds for use in diesel fuel include the economics of production, toxicity, and biodegradability. Cost was estimated assuming that oxygenates would be made on a scale appropriate for the fuels industry. The estimates (added fuel cost) given in Table 2 were based on the cost and availability of raw materials and production efficiency. Toxicity was given special emphasis in the study. The results given in Table 2 are based on literature data. The relative times for biodegradability given in Table 2 were estimated using a model developed at Lawrence Livermore Laboratories.

According to the data in Table 2, the test fuels are ranked from 1 to 9, with 1 being the highest rating. The two oxygenates given the highest rating are tripropylene glycol monomethyl ether and dibutyl maleate.

Conclusions

Emissions and performance tests have been completed on eight oxygenated diesel fuels at one operating mode in a 2.2L DaimlerChrysler CIDI engine. The data have been analyzed and the following two oxygenates were recommended for additional research: tripropylene glycol monomethyl ether and dibutyl maleate. The final report is in progress.

List of Presentations

1. Naegeli, D.W.m, Moulton, D.S., Childress, K.H., and Yost, D.M., "Oxygenate Analysis Project", presented at the Transportation Panel Meeting, held May 11, 2000 in Troy, Michigan.
2. Naegeli, D.W., Moulton, D.S., Childress, K.H., and Yost, D.M., "Oxygenate Analysis Project," Presented at the CIDI Engine Combustion, Emissions Control, and Fuels R&D Laboratory Merit Review & Peer Evaluation, held May 22-24, 2000 at Argonne National Laboratories.

List of Acronyms

ALS	Alternative Low-Sulfur Diesel Fuel
ASTM	American Society for Testing and Materials
ATDC	After top dead center
BMEP	Brake mean effective pressure
CIDI	Compression-Ignition Direct Injection
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DEE	Diethyl ether
DMM	Dimethoxymethane
FTP	Federal Test Procedure
NO_x	Oxides of Nitrogen
O_2	Oxygen
PM	Particulate Matter
PNA	Polynuclear aromatic
SLS	Swedish low-sulfur diesel fuel
SwRI	Southwest Research Institute
THC	Total Hydrocarbons
TVF	Total Volatile Fraction

C. Production of Transportation Fuel from C1 Chemistry

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Subcontractors: Auburn University, Auburn, AL; University of Pittsburgh, Pittsburgh, PA; University of Utah, Salt Lake City, UT; West Virginia University, Morgantown, WV

This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

G. Advanced Fuel Production and Cost

Tasks

5. Refinery and Fuel Processing Economics

Objectives

- Develop technology for conversion of C1 source materials (natural gas, synthesis gas, carbon dioxide and monoxide, and methanol) into clean, high efficiency transportation fuel, especially diesel fuel.
- Develop improved processes to convert natural gas into syngas.
- Develop new processes for producing hydrogen from natural gas and other hydrocarbons.

Approach

- Faculty and students from five universities (Kentucky, West Virginia, Utah, Pittsburgh, and Auburn) are collaborating on a basic research program to develop novel C1 chemistry processes for the production of clean, high-quality transportation fuel. An Industrial Advisory Board (IAB) with members from Chevron, Eastman Chemical, Teir Associates, DaimlerChrysler, Energy International, and the Department of Defense has been formed to provide practical guidance to the program.

Accomplishments

- Fischer-Tropsch fuels containing oxygen have been synthesized.
- Higher ethers (C_6-C_8) have been synthesized from olefins, methanol and ethanol.
- Dimethyl and diethyl carbonates have been produced from the reaction of methanol and carbon monoxide.

- A small diesel engine has been set up to test the effects of these fuels, either alone or as additives, on particulate matter emissions and cetane level.
- Nanoscale, binary, Fe-based catalysts have been shown to have significant catalytic activity for the decomposition of methane to produce pure hydrogen.
- Work on CO_2 reforming of methane to synthesis gas has been initiated.
- In situ analytical capability has been developed to allow determination of catalyst structures and product suites during C1 reactions.

Future Directions

- All current research projects will continue with continuing evolvement based on guidance from the IAB and DOE.

Introduction

Since 1986, the Consortium for Fossil Fuel Liquefaction Science (CFFLS) has been engaged in research on the development of alternative sources for transportation fuel. Currently, the CFFLS research program is focused on C1 chemistry, which refers to the conversion of feed stocks that have one carbon atom per molecule (natural gas, synthesis gas, carbon dioxide and monoxide, and methanol) into clean, high efficiency transportation fuel. Synthesis gas, or syngas, is a mixture of CO and H_2 that can be produced by reforming of natural gas or gasification of coal, biomass, petroleum coke, and waste materials. Syngas is the principal source material for the production of hydrogen, methanol, Fischer-Tropsch products and many chemicals. Because of the abundance of remote natural gas, the advent of integrated gasification combined cycle (IGCC) power generation, and environmental advantages, syngas availability and industrial interest in C1 chemistry are expected to grow rapidly. The CFFLS will therefore perform a valuable national service by providing science and engineering graduates trained in this important area.

A major goal of the CFFLS C1 program is to develop technology for producing high quality oxygenated transportation fuels and fuel additives from methanol and syngas. There is abundant evidence that oxygenates both increase fuel efficiency (cetane and octane levels) and decrease particulate emissions. The development of novel methods for producing H_2, perhaps the ultimate transportation fuel of the future, is also an important part of the program. Research is also underway on development of new catalysts for conversion of natural gas into syngas by reforming with carbon dioxide. This report briefly summarizes some of the research highlights of the first year of the program.

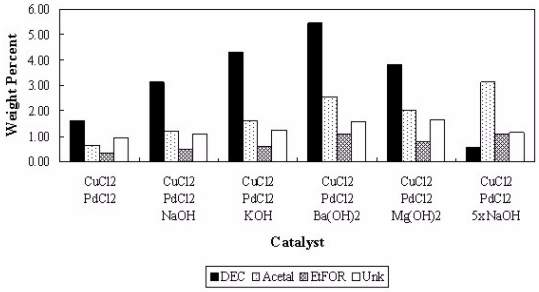

Figure 1. Effect of pretreatment of the catalysts with various metal hydroxides on the yields of DEC, acetaldehyde, ethyl formate, and unidentified species

Catalytic synthesis of organic carbonates

The catalytic synthesis of diethyl carbonate (DEC) and dimethyl carbonate (DMC)(1) is being investigated. Both compounds may be used as additives to diesel fuel to reduce particulate emissions and increase cetane levels. Members of our Industrial Advisory Board have pointed out that DEC is a more promising additive because it has lower volatility and water solubility than DMC. Consequently, only the results of the DEC study are discussed here.

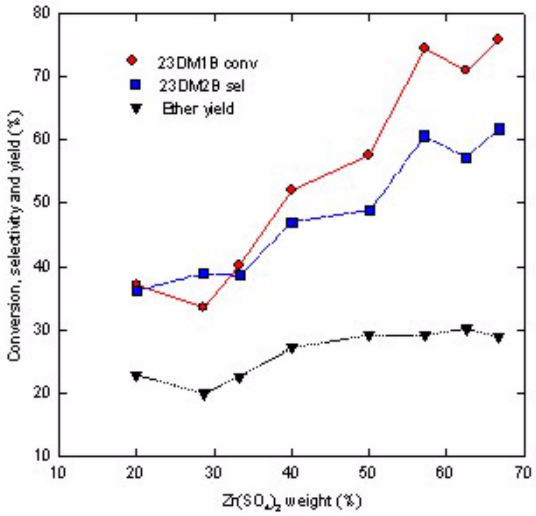

Figure 2. Effect of $Zr(SO_4)_2$ content in $SZ/SiO_2(H_2SO_4)$ system on catalytic activity

The equation describing the desired reaction is:

$$2\,CH_3CH_2OH + CO + \frac{1}{2}O_2 \xrightarrow{Cu^{2+}} O = C(OCH_2CH_3)_2 + H_2O$$

The best yields of DEC have been obtained with a $CuCl_2/PdCl_2$ on activated carbon catalyst. The yield and selectivity is significantly improved by metal hydroxide pretreatment of the catalyst, with the best results provided by $Ba(OH)_2$ (Figure 1).

Synthesis of higher ethers

With the banning of MTBE in California, there is considerable interest in finding suitable oxygenate substitutes. This project is focused on kinetics, reaction conditions and new catalysts for the production of higher ethers that are much less volatile and water-soluble. We have investigated synthesis of a C_7 ether, 2,3 dimethyl-2-methoxybutane (DM2MB), from dimethyl butenes and methanol, and of other higher ethers from this olefin and butanol, propanol and ethanol as well as binary mixtures of these alcohols. Reactions were performed using the commercial catalyst, Amberlyst-15, and several new laboratory-prepared catalysts.

Details of these studies are reported in two forthcoming publications.(2,3) Results obtained with a new catalyst, $Zr(SO_4)_2$ on sulfuric acid-treated SiO_2, are shown in Figure 2. The loading of $Zr(SO_4)_2$

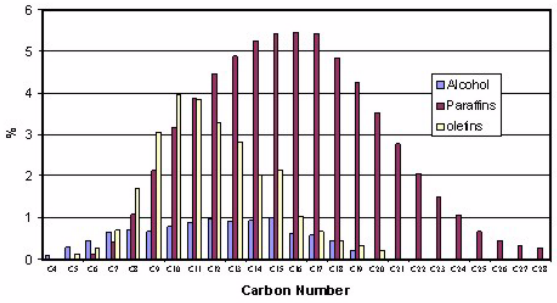

Figure 3. Product distribution of the F-T oil fraction

in $SZ/SiO_2(H_2SO_4)$ greatly influences the catalytic activity and selectivity. Both 2,3-dimethyl-1-butene (23DM1B) and 2,3-dimethyl-2-butene (23DM2B) conversion and ether selectivity generally increase as the $Zr(SO_4)_2$ loading increases. Ether yield saturates at ~30% when the wt% $Zr(SO_4)_2$ exceeds 50%. A catalyst calcination temperature of 600°C has been found to produce the highest ether yield.

Oxygenated Fischer-Tropsch Derived Diesel Fuel

This project aims to convert synthesis gas to F-T products from which environmentally clean diesel fuels containing 4-10 wt% oxygen in the hydrocarbon chain can be produced. The resulting F-T diesel fuel should have a high cetane number and be effective in reducing particulate matter emissions. An automated high pressure, fixed bed, continuous F-T unit has been constructed and is now operational. Temperatures, flow rates and sampling times are controlled and recorded by computer. The products are analyzed using three GC columns and a GC/MS. A Visual Basic program was written to integrate the data and calculate the conversions and product distributions.

A Ru-promoted Co/Al_2O_3 catalyst was prepared by incipient wetness impregnation procedures. The resulting catalyst consisted of 20% Co and 0.5 wt% Ru on γ-Al_2O_3. Oxygenates (primarily alcohols) were obtained when the F-T reaction was conducted at lower temperatures (190-200°C). Product distributions of the collected oil fraction of the F-T product are shown in Figure 3. The amounts of oxygenates, olefins and paraffins are 10.2%, 26.5% and 63.3% respectively.

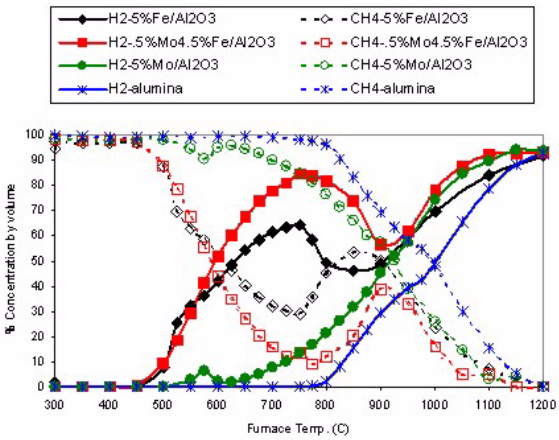

Figure 4. Catalytic CH_4 cracking-effect of catalyst-5% Fe/Al_2O_3, 0.5% Mo/4.5% $FeAl_2O_3$ and 5% Mo/Al_2O_3-reduced in hydrogen at 1000°C for 2 hours

Methane Reforming with Carbon Dioxide

The reforming of natural gas with carbon dioxide for the production of synthesis gas is appealing because: (1) it produces synthesis gas with higher purity and lower H_2/CO ratio than either partial oxidation or steam reforming, which is desirable for the production of transportation fuels; (2) two greenhouse gases are utilized; and (3) CO_2 is frequently a significant component of natural gas and is produced in many industrial processes. Initial studies have focused on calibration and testing of the reforming unit, which features four independently controlled gas feed lines and on-line analysis of the products using a Hewlett-Packard 5890 gas chromatograph. Tests run using a commercial Ni/Al_2O_3 catalyst have shown the expected dependence of the % CH_4 and % CO_2 conversions on reaction temperature. Future studies will focus on transition metal carbide catalysts.

Catalytic methane decomposition

The goal of this project is to develop catalysts and reaction conditions for catalytic, non-oxidative decomposition of hydrocarbons. The advantage of this approach is that it produces hydrogen that is free of CO, which poisons the catalysts used in fuel cells.

It has been demonstrated that nanoscale, binary ferrihydrite catalysts are readily formed by co-precipitation techniques.(4,5) In the current research, nanoscale iron-based catalysts are being precipitated on alumina supports and subjected to various pre-treatments to put them into metallic, carbide, or oxide form prior to reaction. Some typical results for methane decomposition are shown in Figure 4 for several catalysts that were pre-treated by reduction at 1000°C. It is seen that both the 5% Fe/Al_2O_3 and the 0.5%Mo-4.5%Fe/Al_2O_3 catalysts reduce the methane decomposition temperatures by over 300°C, while the 5%Mo/Al_2O_3 catalyst gives results that are similar to the alumina support alone. Further experiments using a variety of pre-treatments and numerous other secondary elements (Pd, Ir, W, V, etc.) are in progress. Liquid hydrocarbons will also be investigated in future work.

Hydroisomerization of Normal Hexadecane with $Pt/WO_3/ZrO_2$ Catalysts

The acid-catalyzed isomerization of alkanes is used to produce clean, high octane gasoline, high cetane diesel fuel, low pour point jet fuel and lubricant base stocks. This work has established that platinum-promoted tungstate-modified zirconia ($Pt/WO_3/ZrO_2$) catalysts are very effective for the hydroisomerization of long-chain linear alkanes under relatively mild conditions, using n-hexadecane (C_{16}) as a model compound. Research has now shifted to the hydroisomerization and hydrocracking of longer paraffinic chains; C_{24}, C_{28} and C_{32}, as well as to the conversion of Fischer-Tropsch waxes to high cetane diesel and jet fuels.

Carbon Dioxide as an Oxidizing (Dehydrogenating) Agent

Utilization of CO_2 in the dehydrogenation of hydrocarbons could be used to produce chemicals efficiently and, at the same time, convert this greenhouse gas to valuable CO gas. Styrene, a high volume, high value chemical, is produced by dehydrogenation of ethylbenzene in the presence of steam and a catalyst.

Dehydrogenation of ethylbenzene could involve the following reactions:

CO could be produced either by reaction (1) or by a combination of reactions (2) and (3). We have

CO_2 + ethylbenzene ⟶ CO + styrene + H_2O (1)

Ethylbenzene ⟶ styrene + H_2 (2)

$H_2 + CO_2$ ⟶ CO + H_2O (3)

identified several catalysts that are effective for these reactions, including Fe/Al_2O_3, $Pt/WO_3/ZrO_2$, and Fe/activated carbon.

Analytical Research

A pulse-quench reactor has been constructed that can quench catalyst beds during C1 reactions from 450°C to room temperature in less than 1 second, in order to investigate reactive species on the catalyst surface by solid-state NMR.

A portable AVS-GC/MS (AVS - ambient vapor sampling) system has been developed for real-time monitoring of the volatile reaction products from C1 reactions.

An in situ cell for x-ray absorption fine structure (XAFS) spectroscopy analysis of catalyst structure during C1 reactions at temperatures up to 700°C has been designed. It will be tested at the National Synchrotron Light Source (NSLS) later this year.

A small diesel engine is being set up that will be equipped with a battery of engine performance and emissions monitoring devices. Among the latter are: NO_x, CO, SO_x, VOC/SVOC (on-line GC/MS), and particulate matter characterization and collection. This engine will enable us to perform realistic tests on the small quantities of diesel fuel produced in our bench scale laboratory experiments.

Significant progress has been made in relating the magnetic properties of a number of catalysts under investigation to their activities in C1 reactions.(6-8)

Conclusions

Collaborating faculty and students at five universities have made excellent progress on C1 chemistry research projects focused on the development of new synthesis processes for transportation fuel. The products emphasized include oxygenated diesel fuel and fuel additives, and hydrogen. An annual report of research conducted during the first year of the program is available at the CFFLS web page, http://www.cffls.uky.edu.

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List of Acronyms

23DM1B	2,3-dimethyl-1-butene
23DM2B	2,3-dimethyl-2-butene
AVS-GC/MS	Ambient vapor sampling gas chromatograph/mass spectrometer
CFFLS	Consortium for Fossil Fuel Liquefaction Science
DEC	Diethyl Carbonate
DM2MB	2,3-dimethyl-2-methoxybutate
DMC	Dimethyl Carbonate
F-T	Fischer-Tropsch Diesel
IAB	Industrial Advisory Board
IGCC	Integrated Gasification Combined Cycle
MTBE	Methyl Tertiary Butyl Ether
NSLS	National Synchrotron Light Source
XAFS	X-Ray Absorption Fine Structure

D. Modeling of Soot and NO_x Formation from Combustion of Oxygenated Fuels in CIDI Engines

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

4. Develop Empirical Relationships

Objectives

- Use detailed kinetic modeling of hydrocarbon combustion to understand the chemistry of soot and NO_x formation in diesel combustion.
- Examine impacts of oxygenated hydrocarbon additives on diesel soot production, using kinetic models.
- Develop and apply kinetic models for selected biodiesel fuels to determine sooting tendencies.
- Use model results to screen possible oxygenated diesel fuels and select those to be studied experimentally.
- Develop reduced kinetic models for incorporation into 3D CFD models of engine combustion.

Approach

- Develop kinetic models for specific hydrocarbon and oxygenated hydrocarbon fuels.
- Establish baseline model simulations of soot precursor production during diesel ignition and NO_x formation during diffusion flame combustion.
- Repeat baseline combustion model calculations with modified fuels and fuel/additive mixtures to estimate sooting and NO_x trends.
- Propose and test reduced submodels for sooting and NO_x production in CFD models of diesel combustion.

Accomplishments

- Established the connection between fuel-rich premixed ignition products and formation of soot precursors in diesel combustion.
- Developed and validated kinetic models for dimethyl ether, dimethoxy methane, ethanol, methanol, methyl formate, and methyl butanoate.
- Used mixtures of n-heptane as diesel fuel surrogates with selected oxygenated alternative fuel additives to predict reductions in soot precursor production.

- Established minimum NO_x levels for diesel combustion conditions.

Future Directions

- Develop and test reduced models for soot and NO_x production in diesel engine combustion.
- Extend kinetic models to new oxygenated alternative diesel fuels, and test their effectiveness in soot precursor production.
- Use models to identify potentially effective new additives.

Introduction

Experimental studies have indicated that use of oxygenated hydrocarbon fuels in conventional diesel engines can reduce soot production and emissions of oxides of nitrogen (NO_x). However, it is not clear why these reductions occur, or whether or not they are a feature of all oxygenated fuels.

Kinetic modeling capabilities at LLNL have been shown to be able to describe the mechanisms of soot precursor production in conventional diesel combustion, as well as the chemistry of NO_x formation in engine systems. In addition, current kinetic modeling is able to establish reliable models for proposed oxygenated fuels as needed. The goal of the present project is to use this diesel combustion modeling capability to examine the role of oxygenated fuel components in reducing soot production and NO_x emissions from diesel engines.

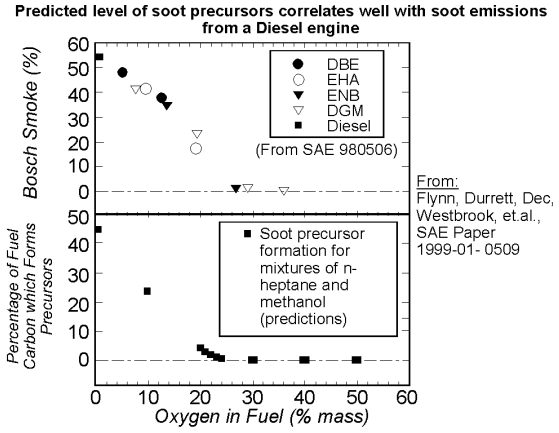

Figure 1. Experimental soot emissions from diesel engines with mixtures of diesel fuel and oxygenated additives. Results taken from Miyamoto et al., SAE-980506.

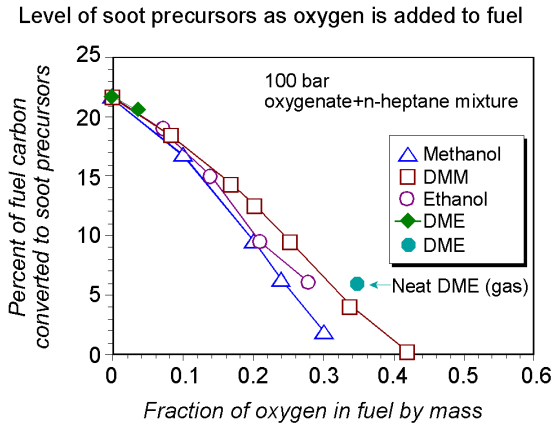

Figure 2. Computed soot precursor concentrations using kinetic models, using n-heptane as the diesel fuel, with a variety of oxygenated additives, as noted.

Approach

Fuel-rich, premixed diesel fuel ignition calculations are carried out to simulate the creation of soot precursors at elevated pressures characteristic of diesel combustion. Soot precursors are identified as hydrocarbon species that are known to be particularly effective at producing aromatic hydrocarbon species growth, processes which encourage soot production, and the concentrations of these species in the rich ignition products are correlated with sooting tendency. A baseline level of these soot precursors are determined using n-heptane as a non-oxygenated fuel that is typical of conventional diesel fuel.

Selected oxygenated species are then substituted for portions of the n-heptane fuel, ranging from very small amounts of the oxygenated additive to completely oxygenated fuels, and for each ignition calculation, the total concentrations of the soot precursor species are determined. The same

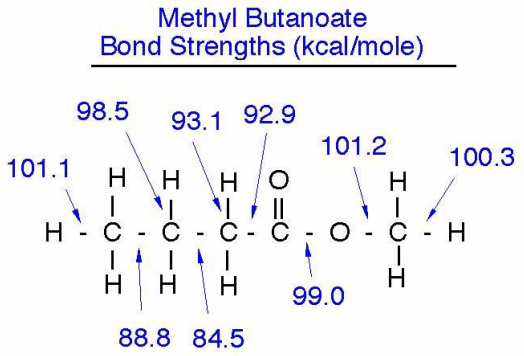

Figure 3. Bond energies in methyl butanoate, a surrogate biodiesel fuel. Values are in kcal/mole.

modeling calculations are repeated for a wide range of different oxygenated species. For many of these oxygenates, new kinetic reaction mechanisms must be developed, using data of many types, such as the different bond energies shown in Figure 1. In this manner, the variation in concentrations of proposed soot precursors with the type of oxygenated additive and with the relative concentration of the oxygenate in the diesel fuel can be determined.

Results

The oxygenated species used in this numerical modeling study included methanol, ethanol, dimethyl ether, methexoy methane, and a sample biodiesel fuel. For every oxygenated fuel component, the soot precursor concentrations decreased steadily as the fraction of the additive was increased in the n-heptane diesel fuel. These results are summarized in Figure 2 as functions of the oxygen fraction in the fuel. The level of the precursors became close to zero at about 30% oxygen in the fuel, in good agreement with the experimental results from the literature. Furthermore, all of the results showed approximately the same dependence on oxygen additive concentrations in the fuel.

Close investigation of the computed results indicated that the most important factor in these kinetic processes was the fact that all oxygen atoms in these fuels were bonded to C atoms. During the combustion, these C - O bonds were not broken by elementary reactions, remaining intact all the way until emerging as reaction products. As a result, those C atoms were not ever converted into the types of hydrocarbon fragments that contribute to soot production reactions, thereby lowering the levels of species which lead to sooting.

The next steps in this program will be the study of further oxygenated additive species identified by the project leadership and industry representatives. The same type of analysis will be carried out. In addition, kinetic models with reduced complexity will be derived to make it possible to include sooting submodels into existing CFD codes.

Conclusions

This modeling work has established the primary factors influencing the role that fuel oxygen plays in reducing soot production in diesel engines. Kinetic models for many oxygenated fuels have been developed, and prototype fuels for other classes of oxygenated additives, particularly biodiesel fuels, have been identified. A computational basis for screening new oxygenated and other proposed diesel fuels has been tested and validated. This approach will be extended in the coming year to other important diesel fuel issues, including fuel sulfur, other oxygenated additives, and the development of reduced kinetic models for use in CFD models.

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List of Acronyms

C	carbon
CFD	computational fluid dynamics
DBE	di-n-butyl ether
DGM	diethylene glycol mono-n-butyl ether
DME	dimethyl ether
DMM	dimethoxymethane
EHA	ethylhexyl acetate
ENB	ethylene glycol mono-n-butyl ether

E. In-Cylinder Imaging of Advanced Diesel Fuel Combustion in a CIDI Engine

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions

Objectives

- Build and verify proper operation of a state-of-the-art, heavy-duty optical engine laboratory dedicated to the study of liquid-phase alternatives to conventional diesel fuel.
- Develop and apply laser-based and other imaging diagnostic techniques in the optical engine. Use results to advance the fundamental understanding of how fuel physical and chemical property variations affect in-cylinder combustion and emissions-formation processes.
- Feed back new knowledge to engine manufacturers, fuel suppliers, and other stakeholders so that engine design and fuel formulation can be used together in an optimal manner to meet future emissions and efficiency goals.

Approach

- Phase I: Construction and final assembly of Sandia/Caterpillar alternative fuels optical engine laboratory.
- Phase II: Initial shakedown/evaluation of engine performance, hardware infrastructure, and data acquisition systems.
- Phase III: Preliminary imaging study of glow plug assisted ignition and combustion of a low-cetane, highly-oxygenated alternative fuel. The fuel, M-85, was composed of 85% methanol and 15% gasoline.
- Phase IV: Detailed imaging study to characterize differences between combustion of M-85 and diesel reference fuel. Evaluation of potential of M-85 to reduce soot emissions.
- Phase V (ongoing): Periodically report results to partners in academia and industry through CIDI Oxygenates Screening Project and Alternative Fuels CRADA #1561.

Accomplishments

- All phases of the research listed above were completed.

- A world-class alternative fuels research facility was brought into operation.
- Direct flame luminosity, chemiluminescence, and Mie-scattering imaging techniques were demonstrated and used to gain insight into in-cylinder combustion processes.
- A new fuel injection strategy using slightly modified production Caterpillar equipment has been identified to enable the laboratory to most quickly recover from setbacks caused by the original injector platform.

Future Directions

- Quantify effects of fuel molecular structure and thermodynamic properties on soot formation using laser-induced incandescence (LII) and/or line-of-sight laser absorption diagnostics. Test fuels include blends of a low-sulfur base fuel with several particularly promising oxygenated molecules identified by the CIDI Oxygenates Screening Project [1].
- Study glow plug assisted combustion of neat methanol. Although methanol is not a practical near-term fuel for CI engines, its high oxygen content (50% oxygen by mass) and lack of carbon-carbon bonds make it an attractive fuel for studying the maximum soot reduction potential of an alternative fuel. These results also will establish a valuable experimental database for comparison to numerical simulations, since the chemical-kinetic oxidation mechanism of methanol is fairly simple and well understood.

Introduction

Existing experimental and modeling results indicate that advanced petroleum-based and alternative fuels can significantly reduce regulated pollutant and greenhouse gas emissions from diesel-cycle engines. Fuels derived from domestic resources have the added benefit of enhancing U.S. energy security. However, many promising new fuels have physical and chemical properties that are vastly different from those of traditional diesel fuel. Gaining insight into how these property differences affect mixing, combustion, and emissions-formation processes inside the engine cylinder is the goal of this research. Such an improved understanding will help engine designers use new fuels to their greatest advantage, and could ultimately enable the identification of an optimal fuel blend for a given set of performance criteria.

Experimental Approach

The new Sandia alternative fuels optical engine laboratory features a single-cylinder version of a modern-technology, Caterpillar 4-stroke DI diesel engine that has been modified by Sandia to provide extensive optical access into the combustion chamber. The optical engine is based on the Caterpillar 3176/C-10 platform used in heavy-duty trucking. A photograph of the new laboratory is presented in Figure 1. A cutaway schematic of the optical engine is shown in Figure 2. The engine features a large window in the piston to image combustion processes, windows in the cylinder and piston bowl walls for laser access, and a glow plug to enable the study of certain low-cetane alternative fuels. Specifications of the optical engine are provided in Table 1. Fuel was injected using a pre-

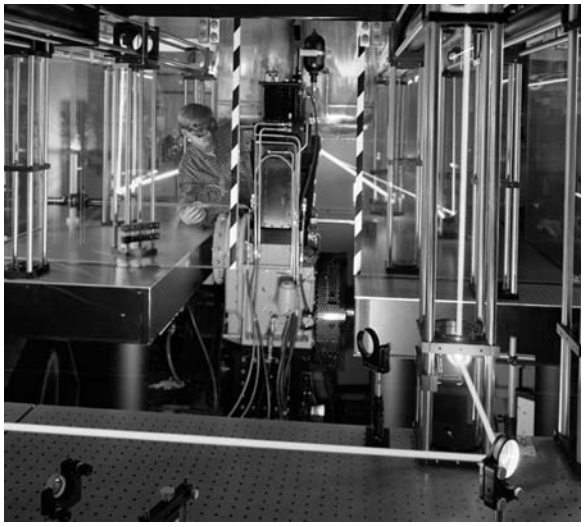

Figure 1. Sandia alternative fuels optical engine laboratory in operation

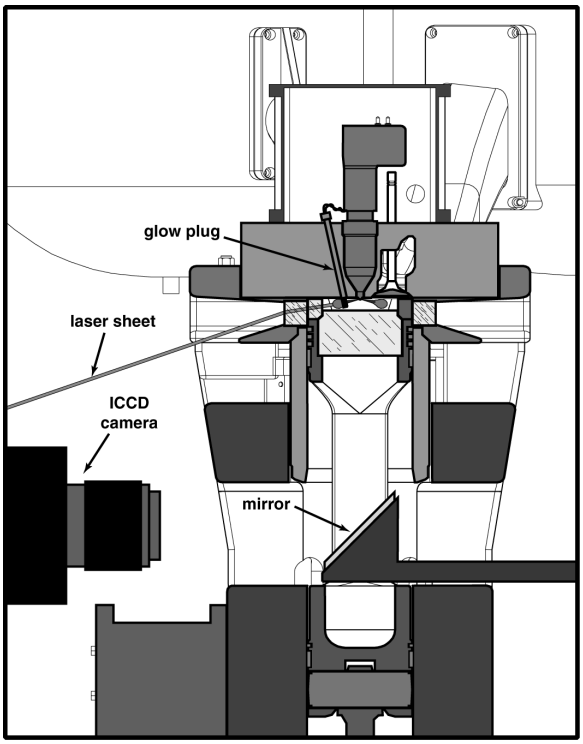

Figure 2. Schematic diagram of the Sandia/Caterpillar optical engine

production prototype hydraulically-actuated, electronically-controlled unit injector (HEUI).

Results

Initial tests with Phillips #2 diesel reference fuel showed that the optical engine's performance is representative of the production engine after which it is modeled. The motored gross IMEP, polytropic compression exponent, and heat release rates were all well within expected ranges. The tests also established that the extensive experimental infrastructure and all data acquisition systems were functioning properly. Traces of cylinder pressure and apparent heat release rate (AHRR) from the optical engine are shown in Figure 3.

The capability of operating with low-cetane alternative fuels was demonstrated by fueling the engine with M-85 and acquiring the sequence of direct flame luminosity (DFL) images, three frames of which are presented in Figure 4. The images, which were taken through the window in the piston with the glow plug on, show that M-85 ignition occurs at the glow plug, ignites the two fuel jets straddling the glow plug, and then the flame

Production Engine Type	6-cylinder 3176 / C-10
Research Engine Type	1-cylinder version of 3176
Cycle	4 Stroke CIDI
No. Valves per Cylinder	4
Ignition Assist	In-Cylinder Glow Plug
Bore	125 mm
Stroke	140 mm
Peak Cylinder Pressure	14.0 MPa
Connecting Rod Length	225 mm
Connecting Rod Offset	None
Bowl Diameter	90 mm
Bowl Height	16.4 mm
Swirl Ratio	Quiescent
Displacement	1.72 liters
Compression Ratio [1]	11.3:1
Simulated Compression Ratio	16.0:1

[1] TDC conditions of the production engine are matched to the optical engine by preheating and boosting the intake air

Table 1. Specifications of the Sandia/Caterpillar optical engine

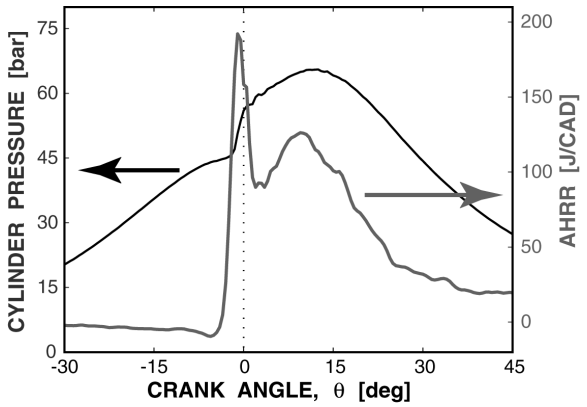

Figure 3. Cylinder pressure and apparent heat release rate (AHRR) for the optical engine when fueled with #2 diesel reference fuel at a moderate load/1200 rpm operating condition.

propagates to adjacent pairs of jets as it traverses the combustion chamber. The lack of luminous combustion on the side opposite the glow plug, coupled with lower-than-expected engine efficiency, suggests that fuel in this region may not completely burn. However, since the bulk of the DFL signal comes from the incandescence of hot soot, combustion in the region may be occurring, but in a

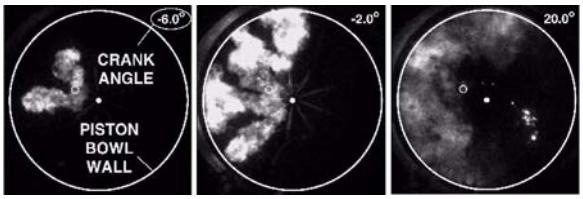

Figure 4. Three frames from a movie of glow plug assisted combustion of M-85 acquired using DFL diagnostics. The central dot shows the injector location, the small circle the glow plug position, and the large circle the piston bowl wall. Conditions at TDC are 900 K and 60 bar. Injection timing is set for maximum indicated torque at 8.0 bar gross IMEP load and 1200 rpm.

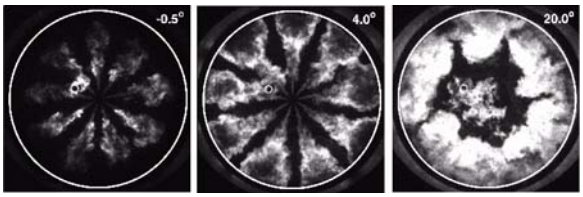

Figure 5. Three frames from a DFL movie of glow plug assisted combustion of CN45 (a diesel reference fuel) for comparison to Figure 4. Ignition, combustion, and soot formation processes are drastically different between the two fuels (see also Figure 6). Engine operating conditions are the same as in Fig. 4.

non-sooting (and therefore non-luminous) premixed mode.

For comparison, Figure 5 shows three frames from a DFL image sequence at the same speed, load, and glow plug conditions as Figure 4, except that the engine was fueled with a 45-cetane diesel reference fuel mixture (CN45). It is clear from the images that the ignition and combustion processes of the CN45 diesel fuel are markedly different from those of M-85. Although the glow plug is energized, the CN45 ignition occurs symmetrically on all jets at once. There is no jet-to-jet flame propagation process as was observed with M-85. In addition, the CN45 images are more than 3 orders of magnitude brighter, as shown in Figure 6. Since the DFL signal is dominated by incandescence of hot soot, and the signal differences between the two fuels cannot be explained by differences in soot temperature, it is clear that the M-85 produces far less soot than the

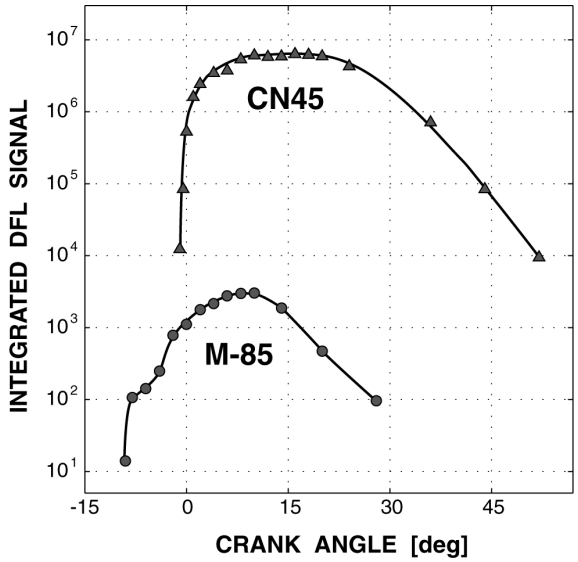

Figure 6. Spatially-integrated DFL image signal as a function of crank angle for M-85 (circles) vs. CN45 (triangles) at the operating conditions of Figures 4 and 5. Since bulk of signal is produced by soot incandescence, more than 3 orders of magnitude difference between the fuels indicates significant soot reduction potential of M-85.

CN45 diesel fuel. Additional experiments were conducted using chemiluminescence and Mie-scattering diagnostics, at other speed/load operating conditions, and with the glow plug on vs. off [2].

Caterpillar provided two experimental, instrumented fuel injectors to Sandia for this project. Figure 7 shows a Mie scattering image of the exceptional spray symmetry produced by the injectors. Unfortunately, prolonged exposure to methanol caused the first injector to fail after the preliminary M-85 imaging study. Major mechanical problems that precluded further data acquisition with the second injector became apparent during the CN45 experiments. A large array of additional experiments (many of which touch on proprietary issues) were necessary to characterize the problems. It was found that the problems were caused by improperly tuned elements within the injector that could not be fixed by Sandia nor by Caterpillar. In hindsight, Caterpillar agrees that these "one-of-a-kind" experimental injectors should not have been provided to Sandia for use in research. Since production Caterpillar injectors do not exhibit such mechanical problems, a plan has been implemented

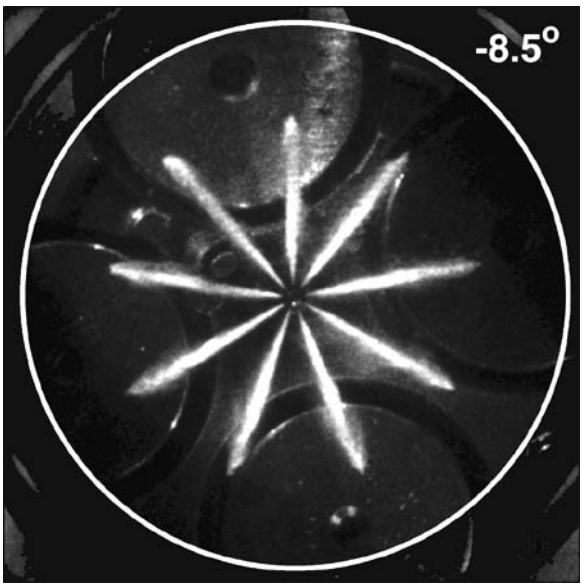

Figure 7. Mie-scattered light from droplets in CN45 fuel spray shows exceptional spray symmetry of Caterpillar injector.

that will enable the use of production injectors in the optical engine.

Conclusions

A new, state-of-the-art optical engine laboratory dedicated to the study of alternative fuels has been brought into operation. Experiments verify that the engine and laboratory are functioning properly. Images of glow plug assisted M-85 and CN45 combustion are presented that show that ignition, combustion, and soot production processes are vastly different between the two fuels. Differences of these types must be understood for new CI fuels to be deployed with maximum emissions and efficiency benefits. The valuable capabilities that have been developed will be used in the next phases of the project to systematically identify fuel property effects on in-cylinder combustion and emissions-formation processes.

List of References

1. Naegeli, D., "Oxygenate Analysis Project," Proc. of CIDI Engine Combustion, Emission Control, and Fuels Program Review, May 22-24, 2000, Argonne National Laboratory, Argonne, IL.
2. Musculus, M.P., and Mueller, C.J., "Initial Results from Experiments on Alternative Fuels in the Sandia/Caterpillar Optical Engine," Sandia Report (in preparation), Sandia National Laboratories, Livermore, CA.

List of Publications

1. Mueller, C.J., "Recent Research Results on In-Cylinder Combustion Processes of Alternative Fuels for Diesel-Cycle Engines," Proc. of CIDI Engine Combustion, Emission Control, and Fuels Program Review, May 22-24, 2000, Argonne National Laboratory, Argonne, IL.
2. Musculus, M.P., and Mueller, C.J., "Initial Results from Experiments on Alternative Fuels in the Sandia/Caterpillar Optical Engine," Sandia Report (in preparation), Sandia National Laboratories, Livermore, CA.

List of Presentations

1. Mueller, C.J., "Alternative Fuels Research at Sandia National Laboratories," invited lecture, Sept. 14, 1999, Caterpillar Technical Center, Peoria, IL.
2. Mueller, C.J., "Glow Plug Assisted CI Combustion of M-85 in the Sandia/Caterpillar Optical Engine," Joint Heavy-Duty/Alternative Fuels Combustion CRADA Review Meeting, Oct. 12, 1999, US Council for Automotive Research, Detroit, MI.
3. Musculus, M.P., "Alternative Fuels Combustion in the Sandia/Caterpillar Optical Engine: Establishing the Baseline," Joint Heavy-Duty/ Alternative Fuels Combustion CRADA Review Meeting, Jan. 20, 2000, Sandia National Laboratories, Livermore, CA.
4. Mueller, C.J., "Biodiesel Research at Sandia National Laboratories: Capabilities and Results," Annual Biodiesel Research Coordination Meeting, Feb. 2, 2000, Phoenix, AZ.
5. Mueller, C.J., "Recent Experiments in the Sandia/Caterpillar Alternative Fuels Optical Engine," Dept. of Energy Mid-Year Program Review, March 16, 2000, Washington, DC (videoconference).
6. Musculus, M.P., "Overview and Results from Sandia Alternative Fuels Combustion Research," invited lecture, May 30, 2000, General Motors Technical Center, Warren, MI.

7. Mueller, C.J., "Status Report: Sandia Alternative Fuels Research Program," Joint Heavy-Duty/ Alternative Fuels Combustion CRADA Review Meeting, May 31, 2000, US Council for Automotive Research, Detroit, MI.

List of Acronyms

AHRR	Apparent Heat Release Rate
CN45	Diesel reference fuel with cetane number = 45.0 by definition. Composition is 35.3 vol.% *n*-hexadecane and 64.7 vol.% heptamethylnonane.
DFL	Direct Flame Luminosity
HEUI	Hydraulically-actuated, Electronically-controlled Unit Injector
IMEP	Indicated Mean Effective Pressure
LII	Laser-Induced Incandescence (of soot)
M-85	Fuel composed of 85% methanol and 15% gasoline.
TDC	Top Dead Center

F. Impact of Consumed Lube Oil on Advanced CIDI Engine Emissions

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

2. Fuel and Lubricant Properties - Engine-Out Emissions

Objective

- Determine the contribution of lube oil to particulate and to nitrogen oxide emissions measured in the exhaust gas stream of a state-of-the-art CIDI engine.

Approach

- A DaimlerChrysler OM611 CIDI engine was used to determine the effect of crankcase lube oil consumption on engine-out exhaust emissions (particulate matter [PM] and gaseous regulated emissions).
- Contribution of crankcase oil consumption to PM was determined by direct filter injection gas chromatography (DFI/GC) and by analysis of PM filter for concentration of lube oil additive metals.
- Three lubricant types were evaluated. One is conventional petroleum based and two are synthetic.
- Two fuels were included - one California type diesel fuel (CARB) and one low-sulfur fuel blend containing 15 volume percent dimethoxymethane (ADMM15).
- Measurements were conducted over 5 steady-state engine operation modes and over the heavy-duty diesel engine transient test procedure.

Accomplishments

- Project completed with delivery of draft report.
- Based on the DFI/GC technique and applying the CARB fuel, the oil-derived fraction of PM can be reduced from 27% for M5W30 oil to 8% for S15W50 oil for the important light-duty steady-state Mode 10. This indicates that a particulate matter reduction of approximately 19% is obtainable for this fuel and mode by changing the lubricant. It should be mentioned that this is a lower estimate for the oil impact on particulate at this operating condition since the oil might impact the fuel-VOF and non-VOF as well.
- Based on the DFI/GC technique, the highest oil impact to particulate measured was 36% (ADMM15 fuel, M5W30 oil, and at steady-state Mode 10).

- Oil impacts nitrogen oxide emissions through its effect on friction characteristics.
- With this set of data, the impact of lubricant on the light-duty vehicle FTP exhaust emissions is inconclusive.

Future Directions

- Investigate the impact of consumed lube oil on vehicle emissions following the light-duty transient test cycle.
- Investigate the impact of ultra-low viscosity oils on exhaust emissions.
- Determine the oil impact on insoluble PM.
- Determine the impact of engine oil on polycyclic aromatic hydrocarbon emissions.

Objective

The purpose of this study was to determine the contribution of crankcase lube oil consumption to particulate and to nitrogen oxide emissions as measured in the exhaust gas stream of a state-of-the-art CIDI engine. It was determined whether commercially available synthetic engine oil can significantly reduce the mass of the volatile organic fraction (VOF) of the particulate. In addition, measurements were made to determine whether changes in engine oil result in a change in nitrogen oxides or other gaseous regulated emissions.

Approach

Regulated gaseous and particulate emissions were collected from the exhaust gas stream of an unmodified DaimlerChrysler OM611 2.2-liter CIDI engine (Figure 1). The gaseous emissions were investigated by the means of a gaseous emission analyzer and the particulate emissions were characterized by taking two particulate filters from a particulate dilution tunnel. One of the particulate filters was analyzed by the direct filter injection gas chromatography (DFI/GC) method to determine the proportion of fuel and oil contribution to the VOF of the particulate. A second filter was analyzed by X-ray fluorescence spectroscopy for oil additive metals in the PM.

These measurements were made with three different oils: one conventional petroleum-based product with an SAE viscosity grade of 5W30, one synthetic oil with an SAE viscosity grade of 5W30

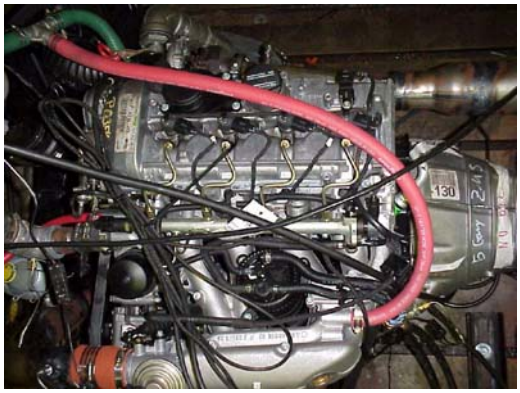

Figure 1. DaimlerChrysler OM611 Engine

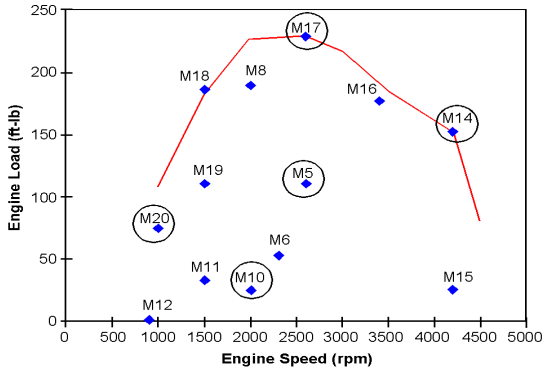

Figure 2. Steady-State Test Modes

and one synthetic oil with an SAE viscosity grade of 15W50. In addition, two fuels were used, one "CARB"-like fuel and one low-sulfur and low-aromatic fuel with 15 volume percent dimethoxymethane (DMM) added. Measurements were made over 5 steady-state test engine operation modes and over the heavy-duty diesel transient procedure. The modes chosen for this test program

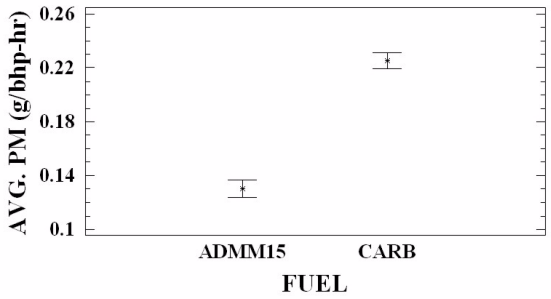

Figure 3. Fuel Effect on Particulate for Average Steady-State Mode, Average across Lubricant Oils

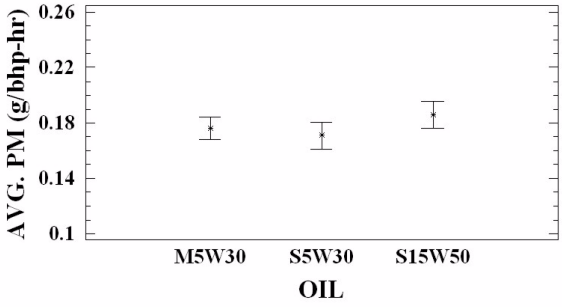

Figure 4. Oil Effect on Particulate for Average Steady-State Mode, Average across Fuels

have been selected as a minimum set of operating modes that span the engine operating range and are presented in Figure 2. Transient engine operations have been shown to be significant contributors to both oil consumption and particulate emissions. While this engine is intended for light-duty vehicles, the light-duty FTP requires a total vehicle, and engine dynamometer simulations of this procedure are not standardized and are very sensitive to the assumed vehicle configuration. In order to examine transient operating effects, the engine dynamometer based heavy-duty FTP procedure was used.

These measurements may underestimate the total contribution of the engine oil to the particulate mass, since the DFI/GC technique only assesses the volatile portion of the particulate. For these conditions, the part of the PM that was non-volatile ranged from a low of 46% (ADMM15, M5W30, M5) to as much as 94% (CARB, S5W30, M14) of the total PM.

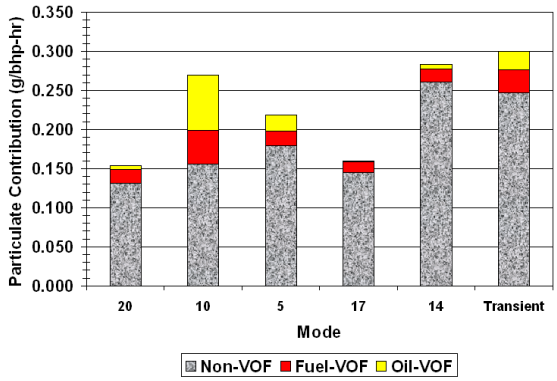

Figure 5. Fractionated Particulate Showing Fuel and Oil Contributions to PM (CARB Fuel; 5W30 Baseline Mineral Oil)

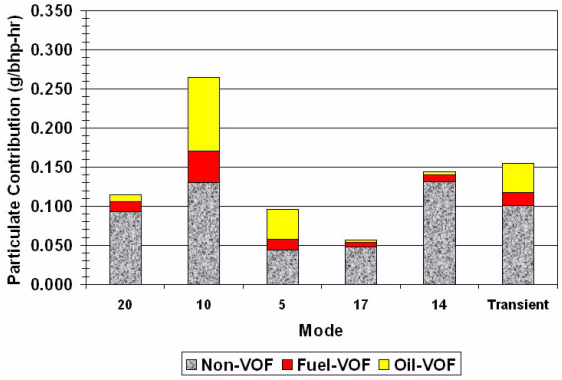

Figure 6. Oil and Fuel Contribution to Particulate Emissions for the Fuel/Oil Combination Yielding the Highest Oil Contribution to PM (ADMM15 Fuel and 5W30 Baseline Mineral Oil)

Results

- The steady-state results were arithmetically averaged to give an average steady-state mode. Confirming previous studies, fuel effect on particulate emissions is significant for the average steady-state condition (Figure 3). Applying ADMM15 fuel, particulate emissions decreased by 40-50% as compared to the baseline CARB fuel.
- When grouping all the data for the fuels, the effect of oil on particulate emissions is insignificant for the average steady-state conditions (Figure 4). However, fractionating the particulate yields another interpretation. For Mode 10, which is typical of light-duty operations, the oil has substantial impact on

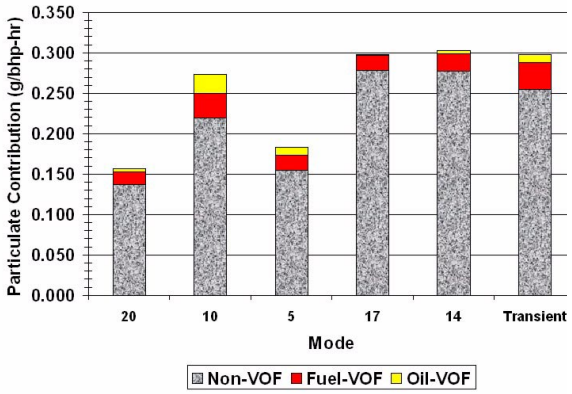

Figure 7. Oil and Fuel Contribution to Particulate Emissions for the Fuel/Oil Combination Yielding the Lowest Oil Contribution to PM (CARB Fuel and 15W50 Synthetic Oil)

particulates as shown in Figures 5, 6, and 7. With the CARB fuel and mineral 5W30 oil, the oil made up at least 27% of the total particulate mass at Mode 10 (Figure 5).

- With the low PM forming ADMM15 fuel, the mineral 5W30 oil contribution to PM increased to at least 36% at Mode 10 (Figure 6).
- The lowest apparent contribution of oil to PM was with CARB fuel and synthetic 15W50 oil, which had at least 8% of the PM derived from the oil at Mode 10 (Figure 7).
- Oil effect on nitrogen oxides is significant for the average steady-state condition (Figure 8). The oil effect is correlated with friction characteristics of the oil, and applying the synthetic 15W50 oil, the nitrogen oxides increase 10-20% as compared to the 5W30 oils.
- Oil effect on carbon dioxide is significant for the average steady-state condition (Figure 9). The oil effect is correlated with friction characteristics of the oil, and applying the synthetic 15W50 oil, the carbon dioxide increases 5-10% as compared to the 5W30 oils.

Conclusions

- Based on the DFI-GC technique and applying the CARB fuel, the oil-VOF fraction can be reduced from 27% for M5W30 oil (Figure 5) to 8% for S15W50 oil (Figure 7) for the important light-duty steady-state Mode 10. This indicates that a particulate matter reduction of approximately

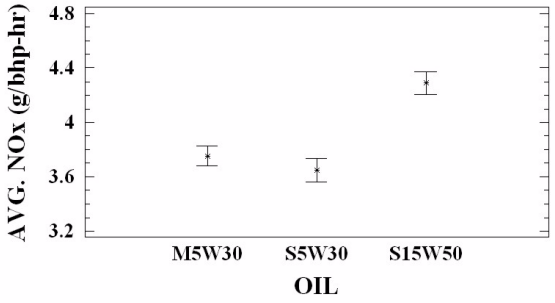

Figure 8. Oil Effect on Nitrogen Oxides for Average Steady-State Mode, Average across Fuels

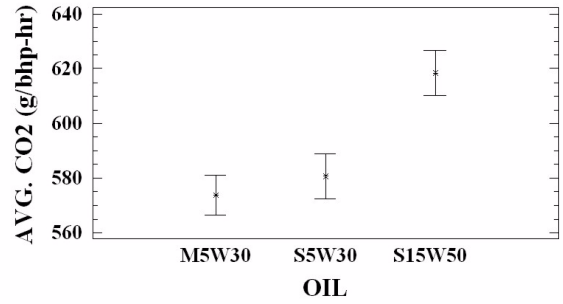

Figure 9. Oil Effect on Carbon Dioxide Emissions for Average Steady-State Mode, Average across Fuels

19% is obtainable for this fuel and mode by changing the lubricant. It should be mentioned that this is a lower estimate for the oil impact on particulate at this operating condition since the oil might impact the fuel-VOF and non-VOF as well.

- As fuel-derived PM is reduced, either through fuel changes (as in this project) or fuel injection system improvements, the lubricant will become an even larger factor in PM emissions.
- Oil impacts nitrogen oxides through its effect on friction characteristics.
- With this set of data, the impact of lubricant on the light-duty FTP exhaust emissions is inconclusive.

Recommendations

- Since the results from this work suggest a high oil contribution to particulate emissions for light-load conditions, it is recommended that the effect of oil consumption on emissions be investigated

in a vehicle using the FTP light-duty transient cycle.

- It is recommended that the effect of engine oil on polycyclic aromatic hydrocarbon emissions and insoluble PM be further investigated.
- The effects of ultra-low viscosity engine oil on exhaust emissions should be examined.

List of Publications

1. Abstract is submitted to the 2001 Spring Fuels & Lubricants Meeting & Exposition to be held in May 2001 in Orlando, FL.

List of Presentations

1. Presentation "Impact of Lube Oil on Advanced CIDI-Engine Emissions" at the DOE CIDI Combustion, Emission Control, and Fuels R&D Peer Review, May 24, in Argonne, Illinois

List of Acronyms

ADMM15	15% DMM and 85% low-sulfur fuel blend
CARB	California reference fuel
DFI/GC	direct filter injection gas chromatography
DMM	dimethoxymethane
ft-lb	foot-pound (torque)
FTP	Federal Test Procedure
M5W30	Petroleum-based SAE 5W30 crankcase oil
NO_x	oxides of nitrogen
PM	particulate matter
RPM	revolutions per minute
S5W30	Synthetic-based SAE 5W30 crankcase oil
S15W50	Synthetic-based SAE 15W50 crankcase oil
SAE	Society of Automotive Engineers
VOF	volatile organic fraction

III. FUEL & LUBRICANT EFFECTS ON EXHAUST EMISSION CONTROL DEVICES

A. Overview of the Diesel Emission Control-Sulfur Effects (DECSE) Program, Phase I

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Project Partners: Glenn Keller (Engine Manufacturers Association), Dale McKinnon (Manufacturers of Emission Controls Association), Michael J. Quinn (Caterpillar, Inc.), Ronald L. Graves (Oak Ridge National Laboratory)

This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

B. Fuel Property Effects on Exhaust Emission Control System Technology

D. Sulfur Impacts

Tasks

2. Fuel and Lubricant Properties - Engine-Out Emissions
3. Fuel and Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Identify the effects of various levels of sulfur in diesel fuel on the operation of four types of exhaust emissions control technologies:
  - Diesel oxidation catalysts.
  - Active lean-NO_x catalysts.
  - Continuously regenerating diesel particulate filters (CR-DPF) and catalyzed diesel particulate filters (CDPF).
  - NO_x adsorber catalysts.
- Measure and compare the effects of up to 250 hours of aging at various fuel sulfur levels.

Approach

- The experimental design for the testing is shown in Table 1.

Accomplishments

- Four interim reports providing Phase 1 DECSE results are available at http://www.ott.doe.gov/decse/.
- Completed work on NO_x adsorber catalyst and diesel particulate filters.
- Completed work on fresh diesel oxidation and lean-NO_x catalyst.
- Aging studies continuing on diesel oxidation and lean-NO_x catalysts

Future Directions

- The DECSE program was the precursor to the Advanced Petroleum-Based Fuels-Diesel Emissions Control (APBF-DEC) Program. This government/industry program aims to identify the optimal combinations of fuels, lubricants, diesel engines, and emission control systems to maintain high fuel economy while meeting projected vehicle emission standards for the 2000 to 2010 time period.

TECH-NOLOGY	250-Hour 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 and simulated FTP-75					T-444E (Navistar)	High precious metal loading
	Modified OICA** aging cycle					Stabilized OICA and heavy-duty FTP					ISM 370 (Cummins)	Low precious metal loading
Active Lean-NOx 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
NOx 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.

Table 1. Summary of Phase 1 Experimental Design

Introduction

The DECSE program was initiated in January 1999 to determine the impact of various levels of diesel fuel sulfur on emission control systems whose use could lower emissions of NO_x and PM from diesel on-highway trucks and light-duty vehicles. Existing and proposed emission standards require both light- and heavy-duty diesel emission control devices to achieve NO_x and PM conversion efficiencies of approximately 90 percent. The U.S. Department of Energy, two national laboratories, the Engine Manufacturers Association, and the Manufacturers of Emission Controls Association

Engine	Test Method	Catalyst Age (hrs)	Fuel Sulfur (ppm)	Emissions Measured [1]	
				Gases and Fuel Economy [2]	Particulate Matter [3]
Cummins ISM370	OICA modes 2, 3, 10, 11	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNOx	
	OICA 4-mode wtd.	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	OICA mode 2 (w/ filter)	0	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	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, LNOx	
	Nav-9 (4-mode) wtd.	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	Nav-9 mode 9 (w/ filter)	0	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	FTP 75	0, 50, 150, 250	3, 30, 150, 350	EO, DOC	EO, DOC
Caterpillar 3126	OICA modes 1-13	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	
		Note [4]	30	EO, CDPF, CRDPF	
	OICA 13-mode wtd.	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
		Note [4]	30	EO, CDPF, CRDPF	EO, CDPF, CRDPF
	OICA mode 2 (w/ filter)	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
	OICA mode 4 (w/ filter)	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
1.9L HSDI prototype	Performance mapping @ 3000 rpm over range of temperatures	< 50	3, 16, 30	EO, NAC	EO, NAC

[1] 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; LNOx = Lean NOx Catalyst; CDPF = Catalyzed Diesel Particulate Filter; CRDPF = Continuously Regenerating Diesel Particulate Filter, NAC = NOx Adsorber Catalyst

[2] HC, NOx, CO, CO2, BSFC

[3] Total PM, SOF, SO4, NO3

[4] The same CDPF and CRDPF 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.

Table 2. Emissions Data Collected

support DECSE. The program is conducted by a government/industry steering committee.

Approach

The effect of various levels of sulfur [3 (essentially sulfur free), 16 (NO_x adsorber catalysts only), 30, 150, and 350 parts per million] on diesel oxidation catalysts (DOCs), lean-NO_x catalysts, diesel particulate filters, and NO_x adsorber catalysts was evaluated in the DECSE program. Engines used in the tests were selected to provide a representative source of diesel exhaust and various exhaust temperature profiles (see Table 2). Table 2 shows the emissions data collected.

Results

Fresh Diesel Oxidation Catalysts

- Sulfate conversion is temperature-dependent and varies with operating condition.
- Sulfur levels have a modest effect on hydrocarbons (HC) and no effect on carbon monoxide (CO) reduction efficiency.
- Particulate matter (PM) reduction efficiency is 26 percent for 3-parts-per-million (ppm) sulfur

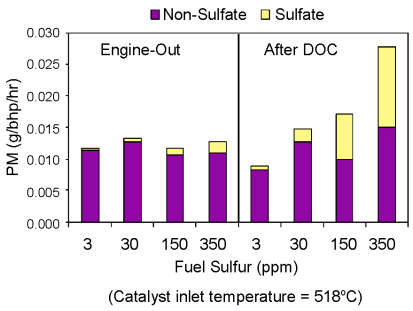

Figure 1. OICA Mode 2 (Peak Torque) PM Emissions-Cummins ISM 370-DOC

levels, but with higher levels of sulfur there are significant increases in PM emissions at high exhaust temperatures.

- PM emissions increase (proportional to the amount of sulfur in the fuel) because of an increase in sulfate fraction (see Figure 1).

Fresh Lean-NO_x Catalysts

- NO_x emissions are reduced up to 30 percent at temperature ranges of 360° to 600°C.

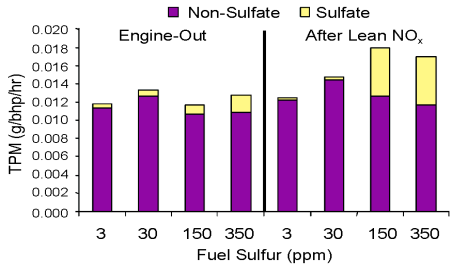

Figure 2. Comparison of SO_3 Emissions between Converter-out and Engine-out with the Fresh High-Temperature Lean NO_x Catalyst (Cummins ISM Engine Mode 2)

- Post-catalyst total hydrocarbon (THC) emissions increase by a factor of 2 to 3 over engine-out emissions, and CO increases by a factor of 6 to 7.
- Sulfate emissions increase by a factor of 10 to 20 for diesel fuels with levels of sulfur greater than 150 ppm.
- At 3-ppm sulfur levels, PM reduction efficiency is 16 percent; however, with high-sulfur fuels (greater than 150 ppm), sulfate emissions increase by a factor of 10 to 20 (see Figure 2).
- At 150- and 350-ppm sulfur levels, sulfate emissions increase by a factor of 2 to 5 compared to 3-ppm sulfur levels.
- HC emissions increase by a factor of 2 to 3 and CO by a factor of 6 to 7.

Continuously Regenerating Diesel Particulate Filters and Catalyzed Diesel Particulate Filters

- PM reduction efficiency is 95 percent when operating with 3-ppm sulfur fuel. However, at 30-ppm sulfur levels, efficiency decreases to 72 percent for CR-DPFs, and 74 percent for CDPFs, and drop to near zero when operating on 150-ppm sulfur fuel (see Figure 3).
- HCs are reduced by 58 to 91 percent, and CO by 90 to 99 percent, but these reductions are not affected by fuel sulfur levels.
- The conversion efficiency of fuel sulfur to sulfate particulate is 40 to 50 percent.
- DPF regeneration temperatures are higher with 30-ppm fuel than with 3-ppm fuel.

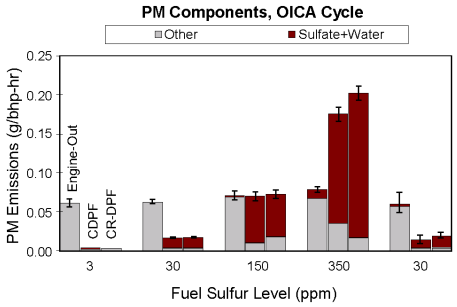

Figure 3. PM Emissions Components as a Function of Fuel Sulfur Level, by Sulfur Portion and All Other PM for the OICA Cycle

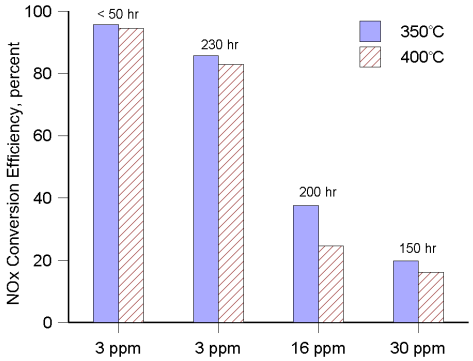

Figure 4. Effect of Fuel Sulfur Level on an Engine Dynamometer Test of an NO_x Adsorber (DC/DDC 1.9 L prototype CIDI engine, steady-state testing)

NO_x Adsorber Catalysts

- At 3-ppm sulfur levels, efficiency initially declines, then stabilizes up until 250 hours of operation.
- For operation less than 50 hours using 3 ppm fuel, NO_x conversion efficiencies greater than 90 percent are achieved. After 230 hours of operation, the conversion efficiency percentage is reduced to the mid 80s (see Figure 4).
- Conversion efficiencies with fuels containing 16 and 30 ppm sulfur decline compared to 3 ppm sulfur levels after 150 hours of operation.

Conclusions

Tests of these NO_x emission control devices suggest that they are feasible given very low sulfur

content fuel. Tests using 3 ppm, 16 ppm, and 30 ppm sulfur fuel suggests that only the 3 ppm sulfur fuel enables the NO_x emission control devices tested to meet emission standards when these devices are new (although after conditioning). Similarly, only the 3 ppm fuel was shown to enable the PM emission control devices tested to meet the emission standards when relatively new (although full useful life certification has not been demonstrated) because higher sulfur fuels cause both catalyzed NO_x and PM devices to produce sulfate PM from sulfur in the fuel.

List of Publications

1. U.S. Department of Energy. "Diesel Emission Control-Sulfur Effects (DECSE) Program Phase 1 Interim Data Report," August 1999.
2. U.S. Department of Energy. "Diesel Emission Control-Sulfur Effects (DECSE) Program Phase 1 Interim Data Report No. 2: NO_x Adsorber Catalysts," October 1999.
3. U.S. Department of Energy. "Diesel Emission Control-Sulfur Effects (DECSE) Program Phase 1 Interim Data Report No. 3: Diesel Fuel Sulfur Effects on Particulate Matter Emissions," November 1999.
4. U.S. Department of Energy. "Diesel Emission Control-Sulfur Effects (DECSE) Program Phase 1 Interim Data Report No. 4," January 2000.

List of Acronyms

BSFC	brake specific fuel consumption
C	Celsius
CDPF	catalyzed diesel particulate filter
CO	carbon monoxide
CO_2	carbon dioxide
CR-DPF	continuously regenerating catalyzed diesel particulate filter
DECSE	Diesel Emission Control-Sulfur Effects (program)
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
HC	hydrocarbon
N_2	nitrogen
NO_x	nitrogen oxides
OICA	International Organization of Motor Vehicle Manufacturers
PM	particulate matter
ppm	parts per million
SOF	soluble organic fraction
SO_2	sulfur dioxide
SO_3	sulfate
THC	total hydrocarbons

B. NO_x Adsorber Testing with Fuels of Varying Sulfur Content

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Subcontractor: FEV Engine Technology, Inc., Auburn Hills, MI

Other Participants: Technical team with representation from Manufacturers of Emission Control Association (MECA), Engine Manufacturers Association (EMA), Oak Ridge National Laboratory (ORNL), Battelle Memorial Institute

This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

B. Fuel Property Effects on Exhaust Emission Control System Technology

C. Emission Control System Degradation

Tasks

2. Fuel and Lubricant Properties - Engine-Out Emissions

3. Fuel and Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- To optimize the oxides of nitrogen (NO_x) regeneration calibration developed in the Diesel Emission Control-Sulfur Effects (DECSE) Phase 1 effort, achieving 80+% NO_x conversion efficiency over the operating temperature range.
- To develop and demonstrate a NO_x adsorber desulfation process to enable NO_x conversion efficiency recovery from sulfur poisoning.

Approach

- A 1.9 L high-speed, direct-injection (HSDI) diesel engine with common rail injection and complete instrumentation package used to:
  - Complete the optimization of the NO_x regeneration calibration, and remap performance of the catalyst pairs tested in Phase 1 using the improved calibration.
  - Develop a desulfation process using a spare aged catalyst.
  - Evaluate the ability of the desulfation strategy to recover NO_x conversion efficiency using the catalyst poisoned in the Phase 1 testing.
  - Further investigate the desulfation process using new catalysts, and a series of aging cycles followed by desulfation events.

Accomplishments

- Developed an improved NO_x regeneration strategy, which achieved greater than 90% NO_x conversion with a fresh catalyst.
- Developed desulfation strategy to recover NO_x conversion efficiency from a sulfur poisoned catalyst.
- Desulfurized catalysts poisoned with 3-parts per million (ppm), 16-ppm and 30-ppm sulfur fuel. NO_x conversion efficiency recovered to more than 80% in each case.
- Achieved similar NO_x conversion recovery in aging/desulfation cycling tests on fresh catalyst pairs aged with two different sulfur level fuels (3-ppm and 75-ppm).

Future Directions

- Evaluations of NO_x adsorber technologies will continue under the Advanced Petroleum-Based Fuels-Diesel Emissions Control (APBF-DEC) Program. Representatives of government agencies, trade associations, and private industry are jointly funding Phase 2 to identify the optimal combinations of fuels, lubricants, diesel engines, and emission control systems to maintain high fuel economy while meeting projected emission standards for the 2000 to 2010 time period. The program will also identify properties of fuels and vehicle systems that could lead to even lower emissions beyond 2010.

Introduction

This project was initiated in FY99 under the DECSE program, a joint government/industry program to determine the impact of diesel fuel sulfur levels on emissions control systems (see report III.A.). NO_x adsorber catalysts were one of four emission control technologies selected for evaluation during Phase 1 of this project.

A NO_x adsorber catalyst is a flow-through emissions control device that has the potential to lower NO_x, hydrocarbons (HC) and carbon monoxide (CO) emissions from diesel engine exhaust. It is a temporary storage device for NO_x. During typical diesel engine operation, the device stores NO_x from the lean exhaust gas as a nitrate on the catalyst surface. Before the device is fully saturated with nitrate, engine operating and fueling conditions are adjusted to produce a fuel-rich exhaust. Under the rich conditions, the nitrate is released and simultaneously reduced to molecular nitrogen by the adsorber catalyst. The duration and air-to-fuel ratio of the rich pulse is critical. If it is too long or too rich, HC and CO can break through the adsorber, resulting in poor control of these pollutants and reduced fuel economy. If it is too short, incomplete regeneration occurs. These devices are susceptible to sulfur poisoning from the sulfur contained in diesel fuel.

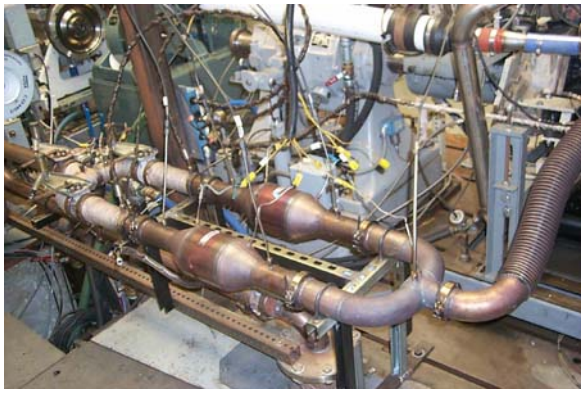

Figure 1. Catalyst Installation in Test Cell

The Phase 1 effort illustrated the effect of sulfur in the fuel on NO_x conversion efficiency, but the initial calibration of the engine management system did not achieve the desired level of NO_x conversion performance over the range of operating temperatures. This follow-on effort was undertaken to optimize the NO_x regeneration strategy (to improve NO_x conversion), and to investigate desulfation of NO_x adsorber catalysts that have been poisoned by sulfur in diesel fuel.

Approach

The 1.9 L HSDI diesel engine equipped with a common rail fuel injection system that was used in DECSE Phase 1 was installed in the test cell at FEV

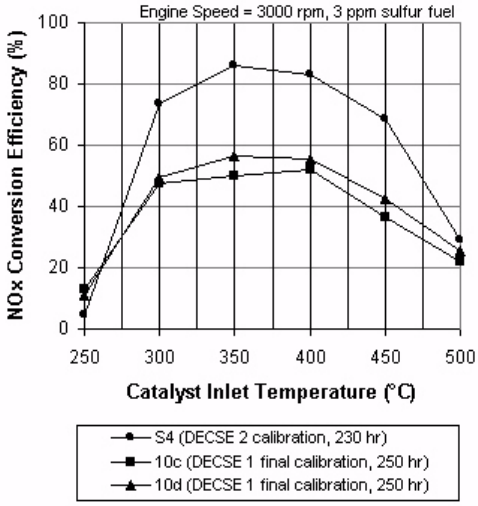

Figure 2. NO_x conversion efficiency from DECSE 1 optimized calibration compared to efficiency of catalyst with similar number of operating hours mapped with the calibration developed in this project

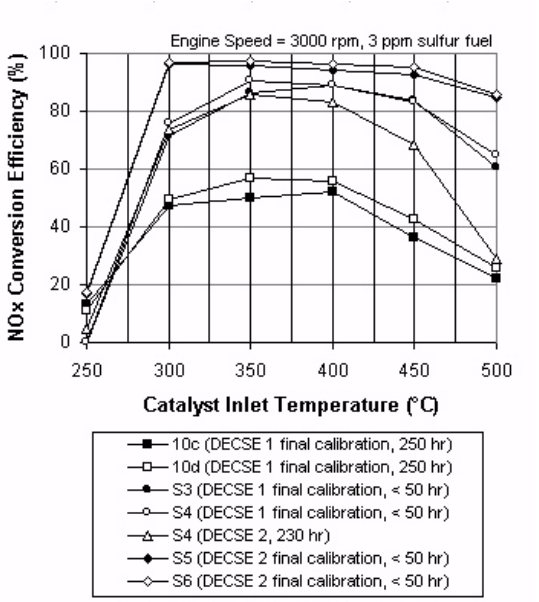

Figure 3. Summary of NO_x conversion efficiencies from different regeneration calibrations

Engine Technologies (see Figure 1). Installation of the same instrumentation package as utilized in the Phase 1 effort was completed. The exhaust system was set up to divide the exhaust supplied to the two catalysts in parallel, with butterfly valves installed to balance the flow through the catalysts.

The initial focus of this project involved modification of the conditions for regeneration to improve and achieve the highest NO_x conversion efficiency possible. FEV first investigated varying engine operating conditions including exhaust gas recirculation (EGR) level, throttling, main injection start, post injection start and the quantity of post injection. The second part of the optimization focused more on the characteristics of the catalyst. Both the lean and rich operating times were varied to maximize NO_x conversion while minimizing additional fuel use.

The next task was to remap the performance of the catalyst pairs previously tested in Phase 1, using the newly optimized NO_x regeneration strategy. All catalyst performance maps were run at an engine speed of 3000 rpm, at catalyst inlet temperatures ranging from 250°C to 500°C with the engine running on 3-ppm sulfur level diesel fuel.

The remainder of this project focused on developing a desulfation procedure to enable the NO_x adsorber catalyst to recover conversion efficiency lost due to sulfur poisoning of catalyst sites. During development of the desulfation process, catalysts were poisoned until their conversion ratio had fallen by 25%. Desulfurization required certain conditions, including a relatively high catalyst inlet temperature and rich engine operation. MECA indicated that the appropriate target temperature was 700°C. An air-to-fuel ratio of 0.9 was expected to achieve desulfation in a reasonable time period. The desulfation procedure was further demonstrated by attempting to release sulfur from the catalyst pairs tested under the DECSE Phase 1 project.

The final task of this project was to investigate the ability of the NO_x adsorber to maintain performance over several aging and desulfation cycles. This testing started with two new pairs of catalyst, which were degreened for 10 hours and aged for 10 hours. Each pair of catalysts was put through a series of aging, performance map, desulfation, and remapping cycles. The only difference in the testing of the two pairs was that aging was completed using 3-ppm sulfur fuel for one and 75-ppm sulfur fuel for the other.

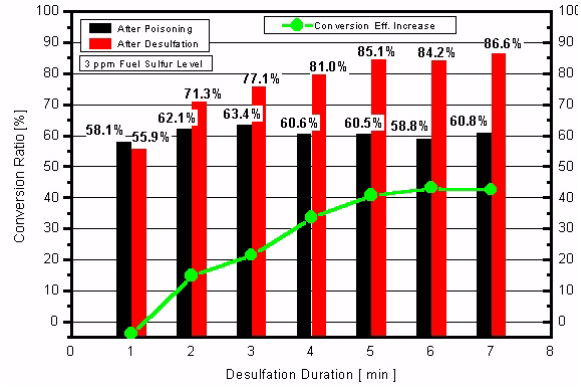

Figure 4. Results from development of desulfation strategy

Results

Efforts to improve the NO_x regeneration strategy over that developed under the DECSE 1 project were fairly successful, especially in the mid-range of the temperature window investigated (300°C to 450°C). Figure 2 displays NO_x conversion efficiency from the DECSE 1 optimized calibration (10c and 10d) compared to calibration developed in this Phase 2 project (S4). These results are for tests at an engine operating speed of 3000 rpm using 3-ppm sulfur fuel. The catalyst compared had a similar amount of accumulated operating hours or aging.

Figure 3 shows NO_x conversion efficiency for calibrations developed under the DECSE 1 and 2 projects, including a fresh catalyst pair (S5 and S6), which was degreened and aged. With the exception of the 250°C point, the fresh catalyst achieved in excess of 80% NO_x conversion efficiency over the range of operating temperatures and in excess of 90% conversion efficiency over the mid-range temperatures. The catalyst manufacturer indicated that this catalyst would not achieve the 80+% conversion target at 250°C. These conversion efficiency levels were achieved while staying within the 4% fuel economy penalty target defined at the start of the project.

The basic requirements to achieve sulfur release from a poisoned NO_x adsorber catalyst include high catalyst inlet temperature and rich engine operation. MECA representatives recommended temperatures in the range of 700°C. In order to reach this temperature range, it was necessary to install a

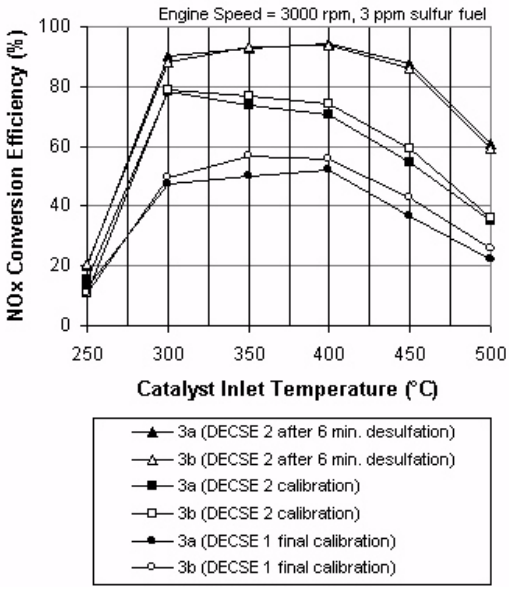

Figure 5. NO_x conversion efficiency of DECSE Phase 1 catalysts aged with 3-ppm sulfur fuel before and after desulfation

warm-up catalyst during the development and operation of the desulfation procedure.

Development of the desulfation process was conducted using the S4 catalyst, with all desulfation events conducted using 3-ppm fuel. The conversion efficiency was checked before and after desulfation at the 400°C operating temperature. The catalyst was poisoned to a target of 60% NO_x conversion efficiency between each desulfation. Poisoning was accomplished with 330-ppm sulfur (wt %) commercial Amoco diesel fuel. The 60% target represented a 25% reduction in efficiency from the original conversion efficiency at the 400°C operating temperature. The length of the desulfation event was varied from one to seven minutes to establish the optimum desulfation duration (results displayed in Figure 4). With increasing desulfation event duration, the percent conversion ratio recovery increased up to a maximum of about 43% at a six-minute duration. This corresponds to an absolute conversion efficiency of just over 84%, which was higher than the initial NO_x conversion efficiency at the 400°C operating point.

The desulfation strategy was then used to release sulfur from the three catalyst pairs tested under the DECSE 1 project. These catalysts had been aged

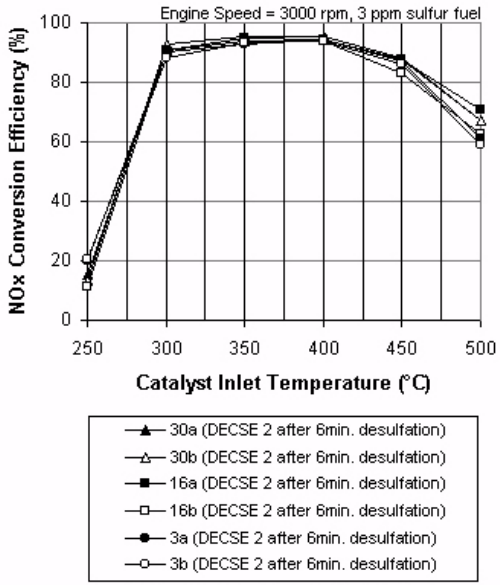

Figure 6. NO_x conversion efficiency of DECSE Phase 1 catalysts following desulfation

using 3-ppm, 16-ppm, and 30-ppm sulfur fuel, and had been aged for 250, 200, and 150 hours, respectively. The performance of each of these catalyst pairs had been remapped using the improved NO_x regeneration strategy developed in this project. The NO_x conversion efficiency was improved over the DECSE 1 calibration results for each of the catalyst pairs.

A six-minute desulfation event was conducted on each of the catalyst pairs. Figure 5 demonstrates the results. The figure presents performance maps for the catalyst pair aged with 3-ppm sulfur fuel. There was a clear improvement in the conversion performance with the revised NO_x regeneration calibration (squares compared to circles). Following the desulfation event, there was significant recovery in the NO_x conversion efficiency. The recoveries in the catalysts aged with 16-ppm and 30-ppm sulfur fuel were even more dramatic, as both had lower pre-desulfation conversion efficiency than the catalysts aged with 3-ppm fuel. Figure 6 shows the post-desulfation results for the catalysts originally aged with 3-ppm (3A & 3B), 16-ppm (16A & 16B) and 30-ppm (30A & 30B) sulfur level fuels. Each of the catalyst pairs returned to similar, high levels of NO_x conversion performance. Although not investigated in this study, it is worthwhile to note that there will also be a fuel economy impact associated with

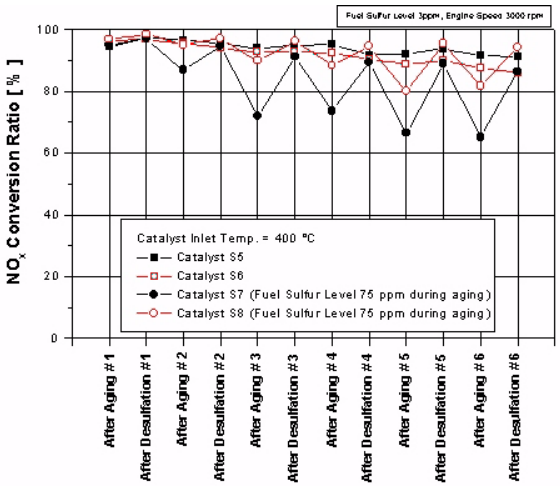

Figure 7. NO_x conversion efficiency of catalyst pairs aged with 3-ppm and 75-ppm sulfur fuel, following each aging and each desulfation cycle at the 400°C operating temperature

desulfurization, which will depend on the frequency of desulfurization events.

The final task was to conduct a series of aging-performance map-desulfation-performance map cycles on two fresh sets of catalysts. Initially each catalyst pair was degreened for ten hours, and aged for ten hours using 3-ppm sulfur fuel. Six testing cycles were conducted on each catalyst pair. Aging of one catalyst pair was done with 3-ppm sulfur fuel; 75-ppm fuel was used for the other pair.

An example of the type of results obtained is provided in Figure 7. This plot shows the post-aging and post-desulfation NO_x conversion efficiency of the two catalyst pairs at the 400°C operating temperature. Following each aging, the NO_x conversion performance of the catalysts aged with 75-ppm sulfur tended to be lower than that of the catalyst exposed to 3-ppm sulfur fuel. However, both pairs of catalysts recovered to similar levels of NO_x conversion efficiency following desulfation. The NO_x conversion efficiency tends to decrease with increased age for both catalyst pairs. It is not clear at this point whether this decrease is a thermal effect that will stabilize, or a poisoning effect that is not completely released.

Conclusions

This project proved successful in meeting its primary objectives of improving the NO_x regeneration strategy (developed under DECSE Phase 1) and of developing a desulfation procedure. An improved NO_x regeneration strategy was demonstrated. In fresh catalysts, NO_x conversion efficiencies in excess of 90% at catalyst inlet temperatures from 300ºC to 450ºC were achieved. The DECSE Phase 1 effort showed that even relatively low sulfur level fuels can have a significant impact on the NO_x conversion efficiency of NO_x adsorber catalysts. In DECSE 2 demonstration tests, the desulfation process returned the NO_x adsorber catalyst to a high level of NO_x conversion efficiency.

List of Publications

1. U.S. Department of Energy. "Diesel Emission Control-Sulfur Effects (DECSE) Program Phase 1 Interim Data Report No. 2: NO_x Adsorber Catalysts," October 1999.

List of Presentations

1. Windsor Workshop, June 2000
2. SAE Clean SUV & Light Truck TOPTEC, June 2000
3. CEC/SAE International Fuels & Lubricants Meeting, June 2000

List of Acronyms

CO	carbon monoxide
DECSE	Diesel Emission Control-Sulfur Effects Program
EGR	exhaust gas recirculation
EMA	Engine Manufacturers Association
HC	hydrocarbons
HSDI	high-speed, direct-injection
MECA	Manufacturers of Emission Controls Association
NO_x	oxides of nitrogen
ORNL	Oak Ridge National Laboratory

C. Evaluation of Advanced Petroleum-Based Fuels in a Mercedes Benz "C" Class CIDI Vehicle

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

2. Fuel and Lubricant Properties - Engine-Out Emissions

Objective

- Quantify the exhaust emission benefits of selected advanced petroleum-based fuels in a vehicle powered by a state-of-the-art CIDI engine (OM611).

Approach

- Seven fuels were chosen that had been evaluated in steady-state emission tests of the OM611 engine in FY 1999.
- Tailpipe exhaust emissions from a European-specification Mercedes Benz "C" (C220) series vehicle were measured for all fuels following the chassis dynamometer portion of the Federal Test Procedure (FTP), and the US06 aggressive driving cycle. Selected fuels were evaluated over the ECE15/EUDC European Driving Cycle.

Accomplishments

- All fuels tested in the vehicle had exhaust emissions that are greater than the EPA Tier 2 standards.
- Test cycle severity with respect to particulate matter (PM) and NO_x was as follows: US06 was the most severe, followed by the FTP, with the ECE+EUDC being the least severe.
- The fuel blend containing 15% dimethoxymethane (DMM) consistently produced the lowest PM, and a slight increase in NO_x levels across all test cycles.
- The DMM15 fuel consistently produced the lowest volatile organic fraction (VOF) of PM.
- Fuel economy for the DMM15 fuel ranged from 8 to 11% less than the 2D baseline fuel.

Future Directions

- Evaluate the effect on vehicle exhaust emissions of selected oxygenate compounds that were identified in DOE Project "The Oxygenates for Advanced Petroleum-Based Diesel Fuel".
- Evaluate vehicle exhaust emissions of other advanced petroleum-based fuels such as ultra-low sulfur diesel and other oxygen containing fuel blends.

Introduction

Potential exhaust emission reductions have been demonstrated in many previous studies for alternative and reformulated diesel fuels. In the current investigation, exhaust emissions were determined from a Mercedes Benz "C" Series European-specification vehicle for a series of advanced petroleum-based fuels (Table 1) that had been tested previously under steady-state conditions in the OM611 engine. The vehicle is powered by the OM611 engine, which has a displacement of 2.2 L, and has the following characteristics: direct-injection, four valves per cylinder, turbocharged and intercooled, high-pressure common rail fuel injection system with pilot injection, exhaust gas recirculation, and intake port cut-off. This engine closely matches the specifications of the Partnership for a New Generation of Vehicles (PNGV) target CIDI engine except for a slightly larger displacement. According to the vehicle manufacturer, the emission control system of the C 220 Turbodiesel vehicle includes one catalytic converter close to the engine with a volume of 2.1 L, and an additional underbody catalytic converter with a volume of 1.8 L. Both converters have a platinum coating on a zeolith substrate and provide oxidation of HC and CO with a slight reduction in NO_x. The converter closest to the engine has an internal by-pass so that the underbody converter is supplied with hydrocarbons to assist in an additional slight reduction in NO_x. Figure 1 is a photograph of a Mercedes Benz C220 Turbodiesel vehicle undergoing testing.

Fuel Code	Fuel Description
2D	2-D EPA Certification Diesel
CA	California Reference Diesel
LS	Low Sulfur Diesel
FT100	Neat Fischer-Tropsch Diesel
DMM15	15% DMM with 85% LS Diesel
FT20	20% Fischer-Tropsch with 80% LS Diesel
B20	20% Biodiesel with 80% LS Diesel

Table 1. Test Fuels

Figure 1. Mercedes-Benz C220 Undergoing Testing

Approach

All seven test fuels shown in Table 1 were evaluated over the chassis dynamometer portion of the Federal Test Procedure (FTP), and US06 aggressive driving cycle. In addition, selected fuels were evaluated over the ECE15/EUDC European Driving Cycle. The complete test matrix is shown in Table 2.

Exhaust constituents were analyzed as specified below:

Constituent	Analysis Method
Total Hydrocarbon	Heated Flame Ionization Detector
Carbon Monoxide	Non-Dispersive Infrared Analysis
Carbon Dioxide	Non-Dispersive Infrared Analysis
Oxides of Nitrogen	Chemiluminescent Analysis
Particulate Matter	Gravimetric
Volatile Organic Fraction of PM	Direct Filter Injection Gas Chromatography
Oil Fraction of VOF	Direct Filter Injection Gas Chromatography
Sulfate Portion of PM	Ion Chromatography

Results

Exhaust emissions data for all fuels and all test cycles are presented in Figure 2. All testing was conducted in triplicate. Percent changes in exhaust emissions and fuel economy from the baseline 2D fuel are presented in Table 3. The shaded areas in the table are statistically significant results. Compared to 2D fuel, the following statistically significant results are noted: in the FTP, DMM15 fuel produced 40% reduction in PM and a 16% increase in NO_x. In

Fuel	Test Cycle		
	FTP	US06 Aggressive Driving Cycle	European ECE+EUDC
2D	√	√	√
CARB	√	√	X
LS	√	√	√
FT100	√	√	√
FT20/LS	√	√	X
B20/LS	√	√	X
DMM15/ LS	√	√	√

√ = Tests Completed

X = Not Included in Test Matrix

Table 2. Test Matrix

the FTP, all other test fuels had increased PM compared to the 2D fuel. This unexpected increase in PM was attributed to better catalytic converter response to the 2D fuel during the FTP. In the US06 test, there was no significant difference in PM for all fuels tested. DMM15 had a 14% increase in NO_x. In the ECE+EUDC test, DMM15 resulted in a 63% decrease in PM with a 26% increase in NOx compared to 2D fuel. The LS and FT100 fuels also had statistically significant reductions in PM during the European test cycle. Fuel economy for the DMM15 fuel ranged from 8 to 11% less (volumetric) than the 2D baseline fuel over the test cycles.

In addition to the dilute exhaust samples, raw exhaust emissions were recorded on a second-by-second "modal" basis for THC, CO, and NO_x prior to the close-coupled catalyst (engine-out) and following the underbody catalyst (tailpipe-out). Catalyst efficiency was calculated and is presented in Table 4. Catalyst efficiency for total hydrocarbons (THC) varied from 86-95%. The lowest estimated catalyst efficiencies were obtained during the European test cycles that operate at a lower exhaust temperature.

Particulate samples were analyzed to determine the particulate volatile organic fraction (VOF), the contribution of unburned lubricating oil to VOF, and the sulfate fraction of the particulate. These results are presented in Table 5. Sulfate levels were highest over the US06. The DMM15 fuel consistently had the lowest levels of VOF over all test cycles. In general, there were no large differences in the percentage of unburned oil in the VOF among the fuels.

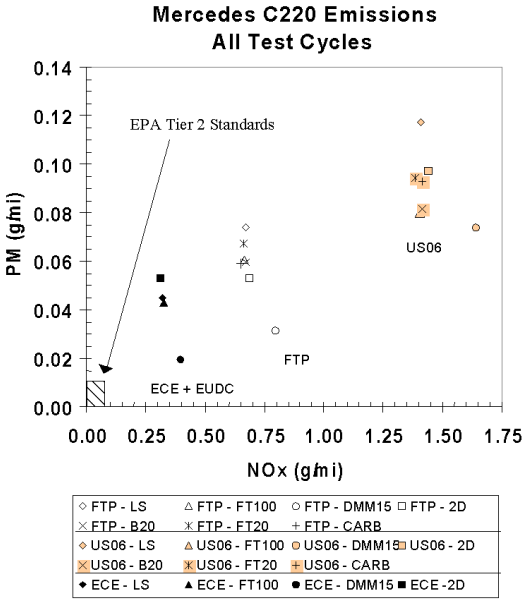

Figure 2. Preliminary Emissions Data for All Fuels and All Test Cycles

Conclusions

All fuels tested in the C220 vehicle had exhaust emissions that were greater than EPA Tier 2 standards. With respect to test cycle severity, the US06 was the most severe, followed by the FTP and then the European cycles. The fuel blend containing 15% DMM consistently produced the lowest PM emissions; however, a slight increase in NO_x was observed. DMM15 fuel consistently had the lowest levels of VOF. Fuel economy for the DMM15 fuel ranged from 8-11% less (volumetric) than the 2D baseline fuel.

List of Presentations

1. Preliminary results were presented during a Poster Session at the DOE peer review on May 23, 2000 at Argonne National Laboratory.

List of Acronyms

CIDI	compression ignition direct injection
CO	carbon monoxide
CO_2	carbon dioxide
DMM	dimethoxymethane
ECE+EUDC	European test cycles
EPA	Environmental Protection Agency

FE	Fuel Economy	PNGV	Partnership for a New Generation of Vehicles
FTP	Federal Test Procedure		
L	liter	THC	Total hydrocarbons
NO_x	oxides of nitrogen	US06	Aggressive Driving Test Cycle
PM	particulate matter	VOF	Volatile Organic Fraction

Cycle	Measurement	LS, %	FT100, %	DMM15, %	CARB, %	B20, %	FT20,%
FTP	HC (g/mi)	-56	-52	-54	-3	-54	-74
	CO (g/mi)	-73	-54	-66	-33	-58	-52
	NO_x (g/mi)	-2	-3	16	-5	-2	-4
	PM (g/mi)	39	14	-40	11	12	27
	FE (mi/gal)	-3	-5	-9	-3	-3	-3
US06	HC (g/mi)	-5	-52	-27	-21	-64	-45
	CO (g/mi)	-2	14	-64	-43	-1	62
	NO_x (g/mi)	-2	-3	14	-2	-2	-5
	PM (g/mi)	26	-14	-20	1	-12	2
	FE (mi/gal)	-4	-6	-8	-1	-3	-3
ECE	HC (g/mi)	-69	-74	-78			
	CO (g/mi)	-61	-74	-64			
	NOx (g/mi)	3	4	26			
	PM (g/mi)	-15	-19	-63			
	FE (mi/gal)	0	-12	-11			

Note: shaded areas denote statistically significant changes from 2D baseline

Table 3. Percent Change from 2D Baseline Fuel

Test Cycle	Fuel	Catalyst Efficiency, percent	
		THC	CO
FTP	2D	95	97
	DMM15	93	98
	FT100	90	98
	LS	94	97
	B20	92	98
	FT20	90	98
	CARB	94	97
US06	2D	94	99
	DMM15	92	99
	FT100	92	99
	LS	94	98
	B20	92	99
	FT20	90	99
	CARB	93	99
ECE	2D	90	81
	DMM15	90	85
	FT100	86	86
	LS	87	86

Table 4. Estimated Catalyst Efficiency

Test Cycle	Fuel	Total PM, mg/mi	Wet Sulfate, mg/mi [a]	VOF, mg/mi	Unburned Oil, % (+/- 10%)
ECE	2D	52.8	0.44	6.55	18
	DMM15	19.9	0.36	3.52	< 9
	FT100	42.6	0.50	6.71	14
	LS	45.0	0.42	4.76	32
FTP	2D	53.0	0.13	7.96	30
	B20	58.6	0.20	6.55	27
	CARB	58.9	0.25	9.19	20
	DMM15	31.7	0.47	6.11	< 9
	FT100	60.2	0.60	8.64	11
	FT20	66.9	0.25	9.67	21
	LS	73.7	0.71	10.34	16
US06	2D	92.7	4.05	5.75	14
	B20	81.7	2.69	4.05	17
	CARB	93.0	6.91	6.02	23
	DMM15	74.0	3.89	3.00	< 9
	FT100	80.0	3.50	5.22	14
	FT20	95.3	2.01	4.70	14
	LS	117.0	2.14	5.46	9

[a] Total includes "dry" sulfate value plus associated water of hydration

Table 5. Breakdown of Particulate Emissions

D. NO_x and PM Emission Control Device Evaluation in a Mercedes-Benz 1.7L CIDI Vehicle

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This Project addresses the following OTT R&D Barriers and Tasks:

Barriers

B. Fuel Property Effects on Exhaust Emission Control System Technology

C. Emission Control System Degradation

Tasks

2. Fuel and Lubricant Properties - Engine-Out Emissions

3. Fuel and Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Demonstrate the potential effectiveness of near-term NO_x and PM emissions control technologies using a light-duty CIDI vehicle during transient certification-type tests.
- Investigate the short-term effects of fuel-sulfur level on the effectiveness of these technologies.

Approach

- Conduct repetitive chassis-dynamometer evaluations of a 1999 Mercedes A170 CDI using fuels with varying sulfur levels. Perform these evaluations with the vehicle equipped with its original catalysts, with no emissions control devices whatsoever, with a catalyzed diesel particulate filter installed, and with a NO_x adsorber installed. Utilize the FTP and US06 driving schedules. Design and implement a regeneration system (using bottled gases) for the NO_x adsorber as necessary to accomplish these evaluations.

Accomplishments

- Demonstrated, in a laboratory experiment, that a catalyzed diesel particulate filter (degreened, low mileage) can provide greater than 95% reduction in particulate emissions compared with the engine-out emissions levels on the FTP and US06 driving schedules.
- Demonstrated, in a laboratory experiment, that a NO_x adsorber (degreened, low mileage) can provide 92% reduction in NO_x emissions compared with engine-out emissions levels on the FTP driving schedule, and 89% reduction on the US06 driving schedule.
- Showed that the equivalent of a 3,000 mile exposure to 30-ppm sulfur fuel degraded NO_x adsorber performance. After sulfur poisoning, NO_x adsorber effectiveness was reduced to only 80% on the FTP, and reduced to only 66% on the US06 cycle.

- Showed that the short-term effects of fuel sulfur on the catalyzed diesel particulate filter and the original-equipment catalysts were not statistically significant.

Future Directions

- Demonstrate simultaneous control of the four regulated pollutants (carbon monoxide, nitrogen oxides, unburned hydrocarbons, and particulate matter) using both the NO_x adsorber and catalyzed diesel particulate filter technologies together with a more refined control system/strategy.
- Investigate the effects of exhaust temperature, exhaust chemistry, and regeneration strategy on the performance of these devices when used together in an emissions control system.

Introduction

Lean-burn direct-injection engines (both compression-ignition and spark-ignition) offer the possibility of very significant fuel efficiency gains. Unfortunately, both of these engine technologies present NO_x and PM emissions challenges that must be overcome if they are to meet future emissions reduction targets (Figure 1). To this end, a great deal of research has been conducted to develop new emissions control technologies that can reduce both PM and NO_x emissions from lean-burn engines. However, these technologies can require large capital expenditures by the nation's industries and some questions remain as to whether these technologies, if implemented, can enable lean-burn engines to reach the EPA Tier 2 emissions standards. These questions are particularly applicable to compression-ignition, direct-injection (CIDI) engines. The Diesel Vehicle Emissions Control Sulfur Effects (DVECSE) project aimed to demonstrate the potential reductions that new emissions control technologies may provide, and to investigate the short-term impact of fuel sulfur on these potential reductions. The project was a laboratory experiment with the goal of providing information; many issues (including reliability) remain to be solved before these technologies can be considered commercially viable.

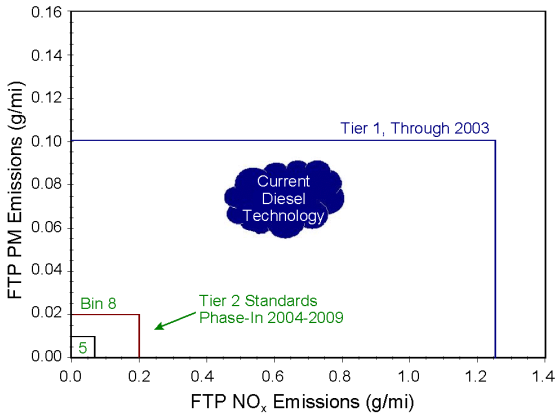

Figure 1. Current (Tier 1) and Future (Tier 2) Emissions Levels

Figure 2. 1999 Mercedes A170 CIDI Research Vehicle

Approach

A 1999 Mercedes A170 CIDI (Figure 2) was used as the testbed for this project. The Mercedes was selected because it is equipped with an advanced, common-rail direct-injection, turbocharged diesel engine with exhaust gas recirculation. The engine is 1.7 liters in displacement, making it of the approximate size targeted by the PNGV program. The emissions from the A170 as equipped with its factory catalytic converters and without any emissions control devices (engine-out emissions) were first measured as baselines for comparison. The Mercedes was then equipped (one-at-a-time) with a catalyzed diesel particulate filter (CDPF) and a NO_x adsorber that were provided by the Manufacturers of Emissions Controls Association (MECA). Repetitive FTP and

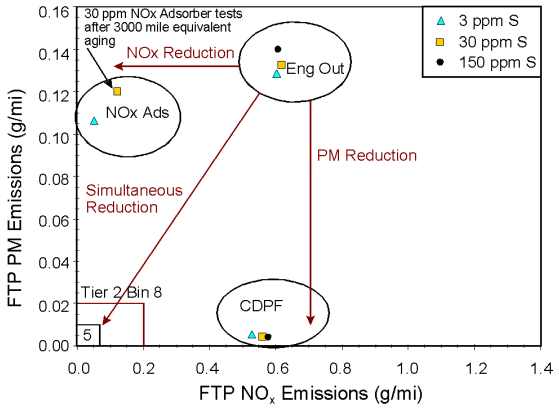

Figure 3. NO_x and PM Reductions Demonstrated in This Project

US06 tests were conducted on each of these devices with fuels of varying sulfur level. A regeneration system was developed to allow regeneration of the NO_x adsorber during these transient tests without the need for engine modifications. This regeneration system utilized bottled gases (CO, C_2H_4, and H_2) together with the engine exhaust stream to mimic exhaust conditions that can be generated using late-cycle in-cylinder injection of diesel fuel. Late-cycle injection is a likely means for generating exhaust conditions necessary for actively-controlled emissions control technologies. It was not possible to utilize late-cycle injection for this project given time and funding constraints.

The factory oxidation catalysts had no significant effect on NO_x, but reduced PM emissions by 30-40%. This reduction was primarily accomplished through oxidation of the soluble organic fraction of the PM, and is not adequate to reach PM reduction targets. The factory catalysts were very effective at reducing CO and hydrocarbon emissions. No statistically significant impact from fuel sulfur on the oxidation catalysts was found.

The CDPF reduced CO and hydrocarbon emissions at approximately the same effectiveness as the factory oxidation catalysts and had no significant effect on NO_x emissions compared with the factory catalysts and engine-out emissions results. However, the CDPF reduced PM emissions by more than 95% compared with engine-out results. Measured PM emissions for the FTP and US06 cycles were less than 0.01 grams per mile (g/mi), even during regeneration. (Regeneration of a CDPF is the desired effect of burning of stored particulate caused by a combination of exhaust heat and catalytic coatings on the CDPF.) Fuel sulfur to sulfate PM conversion was found to be negligible during the FTP and US06 cycles, and was only significant during regeneration when the 150 ppm sulfur fuel was used. Even during this case, the PM emissions remained at or below 0.01 g/mi.

The NO_x adsorber reduced NO_x emissions by 92% (to 0.05 g/mi) on the FTP cycle and by 89% (to 0.14 g/mi) on the US06 cycle. These reductions were achieved at the expense of hydrocarbon and CO emissions. HC and CO increased somewhat from regeneration (purging and chemical reduction of the stored NO_x), but generally remained at or near Tier 2 targets. However, with a more refined regeneration system and strategy, reduction in the hydrocarbon and CO emissions is thought to be possible. A short exposure (equivalent to 3,000 miles using 30 ppm sulfur fuel) to higher sulfur fuel resulted in serious degradation in the performance of the NO_x adsorber. After this exposure, the reduction in NO_x emissions dropped to only 80% on the FTP and 66% on the US06 as compared with the engine-out results.

Conclusions

The CDPF and the NO_x adsorber show great promise for enabling light-duty CIDI vehicles to meet future emissions targets (Figure 3), however considerable development is still needed. Engine controls adequate to provide the exhaust conditions necessary for regeneration of a NO_x adsorber and CDPF are not yet available, and no long-term reliability studies have yet been conducted. Furthermore, it is clear that the NO_x adsorber technology will likely require a means of sulfur protection (sulfur traps, de-sulfurization, etc) in addition to lower sulfur fuels.

List of Publications

1. C. Scott Sluder and Brian H. West. "Catalyzed Diesel Particulate Filter Performance in a Light-Duty Vehicle." Submitted for publication at the Society of Automotive Engineers 2000 Fall Fuels and Lubricants Meeting.

2. Brian H. West and C. Scott Sluder. "NO_x Adsorber Performance in a Light-Duty Diesel Vehicle." Submitted for publication at the Society of Automotive Engineers 2000 Fall Fuels and Lubricants Meeting.

List of Presentations

1. Presentation to the Department of Energy, March 15-16, 2000.
2. Presentation to the Department of Energy, March 28, 2000.
3. Presentation at the Ford Sci-Lab, March 29, 2000.
4. Presentation to the Environmental Protection Agency, March 30, 2000.
5. Presentation to Navistar International, May 12, 2000.
6. Presentation at the Society of Automotive Engineers SUV TOPTEC, June 9, 2000.
7. Presentation to Cummins Engine Company, June 12, 2000.
8. Presentation at the Oak Ridge National Laboratory On-Site Review, June 22, 2000.

List of Acronyms

CDPF	Catalyzed diesel particulate filter
CIDI	Compression ignition direct injection
CO	Carbon monoxide
DVECSE	Diesel Vehicle Emissions Control Sulfur Effects
EPA	Environmental Protection Agency
FTP	Federal Test Procedure
MECA	Manufacturers of Emissions Controls Association
NO_x	Oxides of nitrogen
PM	Particulate matter
US06	Aggressive driving test cycle

E. EC-Diesel Technology Validation Program

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Subcontractors: West Virginia University, Morgantown, WV; Battelle, Columbus, OH

This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

B. Fuel Property Effects on Exhaust Emission Control System Technology

Tasks

3. Fuel and Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Compare exhaust emissions from vehicles fueled with EC-Diesel and California diesel fuels. EC-Diesel is an ultra-low sulfur diesel fuel with 15 ppm maximum sulfur content.
- Evaluate the performance, emissions, and durability of the vehicles retrofitted with catalyzed particle filters and fueled with EC-Diesel over twelve or more months of service.
- Collect fuel consumption, maintenance, reliability, and operating cost data for the participating vehicle fleets and compare to control vehicles fueled with California diesel fuel.

Approach

- Establish a government and industry working group to direct the program.
- Select participating vehicle fleets in Southern California.
- Retrofit a select number of vehicles with catalyzed particle filters and assist with start-up of the test fleets.
- Conduct a first round of vehicle emissions tests in the winter of 2000.
- Conduct a second round of vehicle emissions tests in the winter of 2001 and compare with first round results.
- Objectively analyze vehicle performance and emissions data for both fuels, and draw conclusions.

Accomplishments

- A government-industry working group has been established. Industry participants include BPAmoco/ARCO, Detroit Diesel Corporation, International Truck and Engine Corporation, Cummins Engine Company, Ford Motor Company, Engelhard Corporation, Johnson-Matthey, Corning, NGK-Locke, and Fleetguard Nelson. Participating government agencies include the U.S. Department of Energy, the National Renewable Energy Laboratory, the California Air Resources Board, the California Energy Commission, and the South Coast Air Quality Management District. The working group produced an

Emissions Test Plan for the first round of vehicle tests.

- A total of 184 vehicles have been selected to participate in the program. To date, the following fleets have been retrofitted with catalyzed particle filters: San Diego School District School Buses, ARCO Tanker Trucks, Ralphs Grocery Trucks, LA City Refuse Haulers, Los Angeles County MTA Transit Buses, and Hertz Equipment Rental Trucks.
- First Round vehicle test results were published in EC-Diesel Technology Validation Program Interim Report , SAE Technical Paper 2000-01-1854, authored by Chuck LeTavec, Jim Uihlein, and Jack Segal of ARCO Products Company and Keith Vertin of the National Renewable Energy Laboratory. The interim report was presented at the SAE 2000 Spring Fuels and Lubricants Conference and the SAE 2000 Government and Industry Meeting.

Future Directions

- Data collected from the grocery truck fleet will be analyzed in detail and a series of technical papers will be prepared to document vehicle performance, emissions, and the fleet operating experience.
- A second round of emissions tests will be conducted in the winter of 2001. The second round of testing will examine possible performance or emissions deterioration, and will include characterization of regulated and unregulated exhaust emissions.

Introduction

BP Amoco (formerly ARCO) has recently developed a new diesel fuel called Emission Control Diesel (EC-D). EC-D is produced from typical crude oil using a conventional refining process. EC-D has a maximum sulfur content of 15 ppm, less than 10% aromatics by volume, and a nominal cetane number of 60. BP Amoco has intentions to make ultra-low sulfur diesel fuel widely available in Southern California.

Previous studies in the engine laboratory have shown that catalyzed particle filters operate more efficiently as diesel fuel sulfur content decreases [1,2,3]. Ultra-low sulfur fuels lower the exhaust gas temperature required to burn particulate matter collected on the filter. Ultra-low sulfur fuels expand the exhaust gas temperature window needed for filter regeneration, thereby improving particulate matter conversion efficiency over a wider range of engine operating conditions.

A one-year technology validation program is being run to evaluate EC-D and catalyzed particulate filters using diesel vehicles operating in Southern California. The fuel's performance, impact on engine durability and vehicle performance, and emission characteristics are being evaluated in several fleets in various vocations.

Figure 1. Tanker Truck Testing on the West Virginia University Transportable Chassis Dynamometer and Emissions Laboratory

Approach

Eight vehicle fleets are being evaluated in Southern California. All vehicles are equipped with modern electronically-controlled diesel engines. Each fleet contains unmodified vehicles fueled with a typical California (CARB) diesel fuel, hereafter referred to as control vehicles. For each fleet, a select number of vehicles were retrofitted with either the Engelhard catalytic soot filter (hereafter

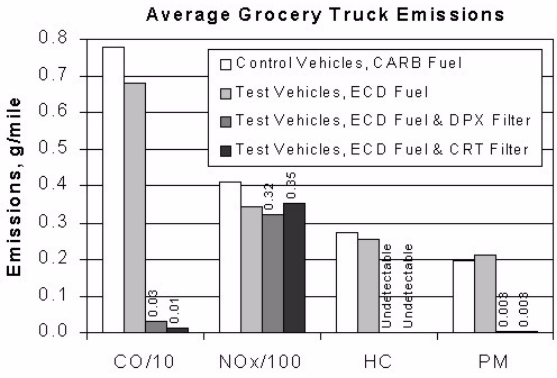

Figure 2. Average Grocery Truck Emissions over the City-Suburban Heavy Vehicle Route

designated DPX™), or the Johnson-Matthey continuously regenerating technology (hereafter designated CRT™). Both DPX and CRT filters are passive devices that were simply installed in place of the existing muffler system, without any modification to the engines. The retrofitted vehicles are fueled exclusively with EC-D fuel using segregated fuel storage tanks.

Each fleet participating in the program contains a number of vehicles that are nominally identical (same model year, engine, chassis configuration, and equipment) except for the exhaust system which may have been retrofitted with DPX or CRT filter.

A subset of vehicles from each fleet was selected for emissions testing. The vehicles were tested using the West Virginia University transportable emissions laboratory. The transportable laboratory consists of a heavy-duty chassis dynamometer and an emissions measurement laboratory (Figure 1). Emissions of carbon monoxide (CO), nitrogen oxides (NOx), total hydrocarbons (HC) and particulate matter (PM) were measured over the City-Suburban Heavy Vehicle Route driving schedule.

Results

Vehicles retrofitted with catalyzed particle filters and fueled with EC-D emitted 91% to 99% less particulate matter compared to the California diesel-fueled vehicles having no exhaust filter equipment. Hydrocarbon and carbon monoxide emissions were also significantly reduced. Average exhaust emissions results for the grocery trucks are compared in Figure 2.

For several vehicles retrofitted with catalyzed particle filters, particulate matter and hydrocarbon emissions were equal to or less than background levels sampled at the test site.

Test vehicles equipped with the catalyzed particle filters and fueled with EC-D fuel have operated reliably during the program start-up period. No significant maintenance issues have been reported for fleets that have been operating for over six months. A more detailed report of fleet operating experience will be published when the program is completed.

Conclusions

Several types of heavy vehicles have been successfully retrofitted with catalyzed particle filters. First round tests revealed that retrofitted vehicles fueled with EC-D reduced particulate matter, carbon monoxide, and hydrocarbon emissions by more than 90% compared to CARB-fueled vehicles without emission control devices.

List of References

1. U.S. Department of Energy, Engine Manufacturers Association, and Manufacturers of Emission Controls Association, "Diesel Emission Control- Sulfur Effects (DECSE) Program, Phase I Interim Data Report No. 4: Diesel Particulate Filters Final Report", http://www.ott.doe.gov/decse, Jan. 2000.
2. Warren, J., Allansson, R., Hawer, P., Wilkins, A., "Effects on After-treatment on Particulate Matter when using the Continuously Regenerative Trap (CRT™)", IMechE Technical Paper S491/006/98, 1998.
3. Cooper, B., Thoss, J., "Role of NO in Diesel Particulate Control", SAE Technical Paper 890404, 1989.

List of Publications

1. LeTavec, C., Uilein, J., Segal, J., and Vertin, K., "EC-Diesel Technology Validation Program Interim Report", SAE Technical Paper 2000-01-1854, 2000.

List of Presentations

1. LeTavec, C., Segal, J., and Uihlein, J., "EC-Diesel Technology Validation Program", presented at the 2000 SAE Fuels and Lubricants Meeting, June 19-22, 2000.
2. Vertin, K., "EC-Diesel Technology Validation Program", presented at the 2000 SAE Government/Industry Meeting, June 21-22, 2000.

List of Acronyms

CARB fuel	Fuel meeting California Air Resources Board quality standards
CO	Carbon monoxide
CRT	Johnson-Matthey trademark for Continuously Regenerating Technology filters
DPX	Engelhard trademark for catalytic soot filters
EC-D	EC-Diesel fuel
HC	Total hydrocarbons
NO_x	Oxides of nitrogen
PM	Particulate matter
ppm	Parts per million
SAE	Society of Automotive Engineers

F. Systems Emission Reduction (SER) Analysis for Automobiles, Light Trucks, and Heavy-duty Engines

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

B. Fuel Property Effects on Exhaust Emission Control System Technology

C. Emission Control System Degradation

Tasks

4. Develop Empirical Relationships

Objectives

- Collect final data sets from the Diesel Emission Control Sulfur Effects (DECSE) project and other DOE projects, and develop empirical relationships linking emissions to fuels properties.
- Develop and use systems level analysis tools that incorporate the empirical emission relationships to identify the best pathways for achieving the technical targets for compression ignition direct injection (CIDI) engines, identified in the Advanced Petroleum-Based Fuels (APBF) Multiyear Program Plan.
- Make data and empirical relationships available to DOE research partners.

Approach

- Define the SER framework to augment ADVISOR with new component modules (e.g., emission control devices) and laboratory data.
- Develop empirical data relationships on sulfur effects, initially making use of data and analyses from the DECSE project.
- Provide a sample pathway analysis for one type of vehicle and configuration, for each of the three platforms.
- Recommend future analyses and continue to expand input databases, to identify gaps in the data required for valid predictions; use as a guide to develop future R&D programs.

Accomplishments

- Data collection to define empirical relationships for the fuel sulfur effect on NO_x Adsorber, Lean NO_x, and Diesel Oxidation catalysts is 95% complete.
- Empirical relationships have been developed for fuel sulfur effects on Diesel Particulate Filters.
- Vehicle types/configuration for sample analysis have been identified.

Future Directions

- Finalize fuel sulfur effects empirical data relationships.
- Identify and collect relevant data already existing from research partners.
- Develop protocols for future engine emissions lab data collection/transmission.
- Establish SER analysis approach by analyzing data and developing maps and modules for ADVISOR.
- Perform sample emission reduction pathway analysis for three platforms.

Introduction

The APBF program seeks to identify and establish the ability of advanced petroleum fuels and non-petroleum fuel blending components to enable light-duty CIDI vehicles and heavy-duty CIDI engines to meet projected emission standards, while continuing to improve engine efficiency and durability.

A component of the APBF program is establishing an SER framework for automotive, light truck and heavy-duty engine applications. This framework is focused on applying a systems approach to analyzing system emissions reduction pathways and fuel options. Establishing the SER modeling approach requires analysis of available data, and development of maps and modules to add to the existing ADVISOR system model.

Activities have been initiated to collect available fuels and emissions data, and to develop the databases from which maps and analysis modules can be generated. Efforts to develop the sample pathway analysis for passenger car, light truck and heavy-duty engine applications are underway.

Approach

The SER model will be implemented in ADVISOR, which involves developing and adding modules and empirical relationships to the existing software package. In the first year of this multi-year effort, development of the capability to analyze fuel effects within a system context began. A fuel property database was established, incorporating fuel property data from a number of projects and sources, and including links to the existing heavy-duty chassis emission database. Data from the effects of fuel sulfur on emissions, investigated in the DECSE project, are being used to develop empirical relationships. Collection of fuel and emissions data is the initial step in working to develop modules and empirical relationships for the SER model. Other tasks underway include:

- Outlining how data from research partners are included, and defining the preferred and minimum protocols for collecting engine laboratory data,
- Outlining how the "research pathway analysis" will be completed,
- Collecting data from participating research partners including other national labs, and
- Completing a sample pathway analysis for two of the applications of interest.

Results

A collection of information is needed to investigate SER pathways. Table 1 identifies the three systems of interest and types of information necessary to enable pathway analysis to be completed. Technical targets for NO_x and particulate

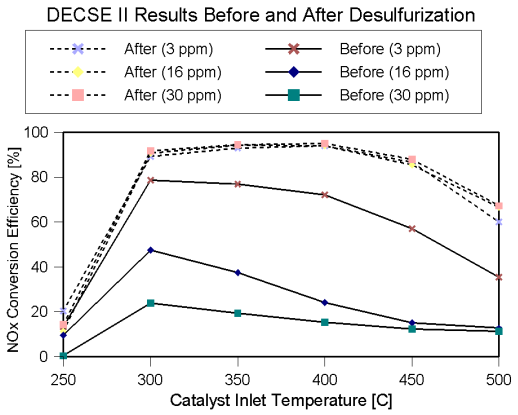

Figure 1. Comparison of NO_x conversion efficiency before and after desulfurization for catalysts aged with 3, 16, and 30 ppm sulfur level fuels for 250, 200, and 150 hours respectively

matter are identified and projects representing sources for emissions data are included.

Fuel property data have been collected from a number of sources including the DECSE project, and the Ad Hoc fuels evaluation project. These data have been incorporated into a database, which has a web-based interface to enable users to do queries of fuel properties.

Empirical data relationships between fuels and emissions have been developed based on evaluations conducted in the DECSE project. Analysis of these data provided insight into the general fuel sulfur level effects on PM and NO_x emissions from several exhaust emission control devices. The diesel particulate filter (DPF) and NO_x adsorber were tested and analyzed for their effectiveness in controlling PM and NO_x respectively. Both technologies were shown to be effective in emissions control, but were also sensitive to fuel sulfur levels. As an example, the NO_x adsorber conversion efficiency as a function of fuel sulfur level and inlet temperature is shown in Figure 1.

Additional empirical data relationships will be developed in the future as data are generated from APBF-DEC projects and other future projects. Table 2 summarizes some of the available DECSE data that are being evaluated for use in developing empirical data relationships. The empirical relationships, as well as the fuel and emission data, are being used to develop modules to be added in the existing ADVISOR model.

Conclusions

Progress has been made on developing components necessary to enable a system level analysis of the emissions pathways for advanced engines and vehicles. A sample pathway analysis for two of the platforms has been completed and it is anticipated that a refined pathway analysis for all platforms will be in place by the end of FY 2001. Fuel and emissions data from testing engines, vehicles and advanced emission control devices are being transformed into modules and submodels that form the building blocks of the SER model. This model will provide the capability to predict potential emissions and efficiency improvements for automobiles, light-trucks and heavy-duty engines.

List of Acronyms

ADVISOR	Advanced Vehicle Simulator
APBF	Advanced Petroleum-Based Fuels
APBF-DEC	Advanced Petroleum-Based Fuels-Diesel Emission Control
CIDI	compression ignition direct injection
DECSE	Diesel Emission Control - Sulfur Effects program
DPF	diesel particulate filter
DVECSE	Diesel Vehicle Emission Control - Sulfur Effects
EGR	exhaust gas recirculation
EUI	electronic unit injector
HEUI	high pressure electronic unit injector
HSDI	high speed direct injection
NO_x	nitrogen oxides
PM	particulate matter
SER	Systems Emissions Reduction

Vehicle Systems	Advanced Automobile (80 mpg)	Light-Duty Truck	Heavy-Duty Truck Engine
Engines	Various-1.7, 1.9, 2.2 liter HSDI's with Common Rail Injection	Navistar 7.3 liter T444/Powerstroke with HEUI	Cummins 11 liter ISM with EUI
NO_x Reduction	Target: 0.05 g/mile Research: DECSE/FEV NO_x Adsorbers, SwRI and Automaker Fuels and Engine Optimization Study, ORNL DVECSE, previously published EGR strategies	Target: 0.05 g/mile Research: DECSE/lean-NO_x catalyst, SwRI and Automaker Fuels and Engine Optimization Study, previously published EGR strategies, data from Ricardo/ International study	Target: 1 g/bhp-hr Research: DECSE/lean-NO_x catalyst, previously published EGR strategies
PM Reduction	Target: 0.01 g/mile Research: SwRI and Automaker Fuels and Engine Optimization Study, ORNL DVECSE, Ad-Hoc (Oxygenates and PM), previously published diesel particulate filter data	Target: 0.01 g/mile Research: DECSE/oxidation catalyst, Ad-Hoc (Oxygenates and PM), previously published diesel particulate filter data	Target: 0.0125 g/bhp-hr Research: DECSE/oxidation catalyst, EC-Diesel and DPF evaluation, Ad-Hoc (Oxygenates and PM), previously published diesel particulate filter data

Table 1. Systems of Interest in Systems Emission Reduction Pathways

Engine	Test Method	Catalyst Age (hrs)	Fuel Sulfur (ppm)	Emissions Measured [1]	
				Gases and Fuel Economy [2]	Particulate Matter [3]
Cummins ISM370	OICA modes 2, 3, 10, 11	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNOx	
	OICA 4-mode wtd.	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	OICA mode 2 (w/ filter)	0	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	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, LNOx	
	Nav-9 (4-mode) wtd.	0, 50, 150, 250	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	Nav-9 mode 9 (w/ filter)	0	3, 30, 150, 350	EO, DOC, LNOx	EO, DOC, LNOx
	FTP 75	0, 50, 150, 250	3, 30, 150, 350	EO, DOC	EO, DOC
Caterpillar 3126	OICA modes 1-13	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	
		Note [4]	30	EO, CDPF, CRDPF	
	OICA 13-mode wtd.	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
		Note [4]	30	EO, CDPF, CRDPF	EO, CDPF, CRDPF
	OICA mode 2 (w/ filter)	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
	OICA mode 4 (w/ filter)	Note [4]	3, 30, 150, 350	EO, CDPF, CRDPF	EO, CDPF, CRDPF
1.9L HSDI prototype	Performance mapping @ 3000 rpm over range of temperatures	< 50	3, 16, 30	EO, NAC	EO, NAC

[1] 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; LNOx = Lean NOx Catalyst; CDPF = Catalyzed Diesel Particulate Filter; CRDPF = Continuously Regenerating Diesel Particulate Filter, NAC = NOx Adsorber Catalyst

[2] HC, NOx, CO, CO2, BSFC

[3] Total PM, SOF, SO4, NO3

[4] The same CDPF and CRDPF 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.

Table 2. Example DECSE Data being Incorporated into SER

IV. HEALTH & SAFETY, MATERIALS COMPATIBILITY, ECONOMICS, AND DISSEMINATION

A. Environmental Performance of Oxygenated Fuel Compounds Used in Advanced Petroleum-Based Fuels

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

H. Health, Safety, and Regulatory

Tasks

8. Safety, Health, and Consumer Acceptance Aspects of Liquid Fuels

Objectives

- Develop a systematic methodology to assess the environmental impact of oxygenated fuel compounds for use in advanced petroleum-based fuels in order to reduce particulate emissions from CIDI engines.
- Evaluate the nature and magnitude of potential human exposures to oxygenates released to the environment.
- Apply the environmental assessment techniques to the oxygenate dimethoxy methane (DMM) and compare its predicted environmental performance with other fuel compounds.

Approach

- Identify and implement environmental transport and fate models for use in conducting assessments of the behavior of fuel oxygenates in regional landscapes, soils, ground water, surface water, etc.
- Compile and review data on the physicochemical properties of DMM and determine the potential for its degradation in the environment.
- Calculate relevant environmental transport properties using available software and/or models to fill information gaps and for quality assurance.
- Implement and run screening-level models to determine the fate of DMM and reference fuel compounds for various environmental release scenarios associated with its life cycle.
- Predict human exposures via ingestion, inhalation, and dermal uptake.

Accomplishments

- Selected and implemented environmental models suitable for conducting screening-level analyses of fuel oxygenates.
- Researched, installed, and tested software for property estimation, including biodegradation prediction.
- Simulated the transport and fate of DMM and other reference fuel compounds in environmental media.
- Evaluated potential water-based human exposures to water contaminated with DMM.

Future Directions

- Evaluate property-estimation models and software for selected physicochemical parameters (e.g., Henry's law constant, solubility in water, partition coefficients, etc.) and environmental transformation processes (e.g., hydrolysis, biodegradation, hydroxyl radical oxidation, etc.) with benchmark fuel components, such as benzene, MTBE, and isooctane.
- Define environmental parameters for screening models that reflect a range of site-specific conditions.
- Conduct screening-level assessments of diesel fuel oxygenates.
- Carry out selected experiments to verify predictions and/or fill key data gaps for oxygenates of interest.

Introduction

Research conducted in recent years has demonstrated that the addition of oxygen-bearing compounds to diesel fuels reduces particulate emissions. While there are potentially many compounds that could be used to add oxygen to fuel, some compounds may have undesirable environmental impacts, for example, contamination of ground water from leaking underground fuel tanks. This project, therefore, aims to establish a methodology to assess the potential environmental impacts of oxygenated fuel compounds. Assessments and supporting data developed by the project will assist DOE/OTT and industrial partners to evaluate the nature and magnitude of the environmental impacts of fuel oxygenates.

Approach

The assessment of a given fuel compound begins with the characterization of its key physicochemical properties. Next, we conduct screening-level analyses to predict the likely environmental fate(s) of the compound when released into reference landscapes. Potential inhalation, ingestion, and dermal exposure pathways are addressed as well. Information on the toxicity of the compound is then evaluated. In turn, we identify key data gaps, specify the kinds of studies needed to obtain the necessary data, and evaluate any special methodological issues related to the assessment of the fuel oxygenate. The fuel compound that we have addressed initially using this methodology is DMM. For purpose of comparison, we also show the results of applying these models to other typical fuel components.

Results

Our analysis of the physicochemical properties of DMM indicates that its tendency to partition to water is actually greater than that of MTBE, suggesting that its environmental transport will depend in part on the movement of water in an environmental compartment. In the atmosphere, DMM will be degraded mainly by OH oxidation, with a half-life of about 2 days. By comparison, DMM is not predicted to biodegrade quickly in ground water. Model predictions based on chemical-structure relationships, for example, indicate that DMM will not biotransform readily (see Figure 1). The predictions are in agreement with experimental data that showed DMM to be recalcitrant. This fact and its high solubility in water are preliminary indications that DMM would behave like MTBE in

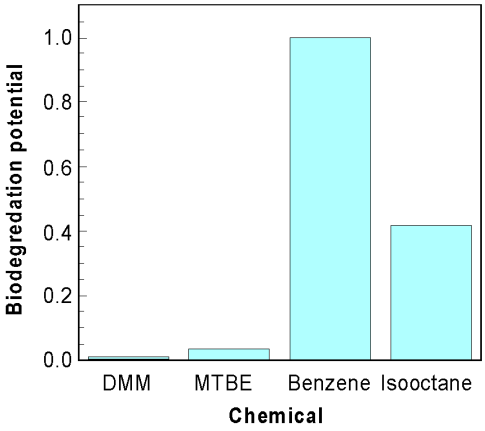

Figure 1. Biodegradation potential for DMM and other fuel compounds. A value above 0.5 indicates rapid biodegradation.

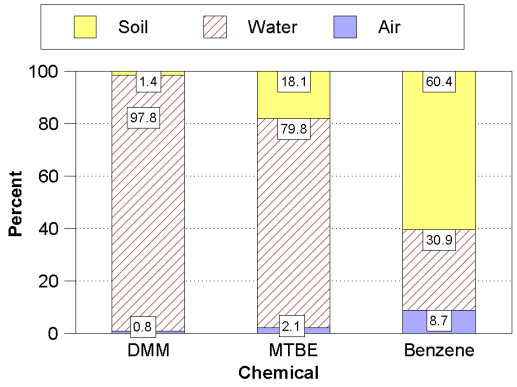

Figure 2. Partitioning of DMM and other fuel compounds in soil.

the environment to the detriment of ground water resources.

We used an equilibrium model to determine the partitioning of DMM between the air, water, and solid phases of a reference soil (see Figure 2, MTBE and benzene also included). DMM favors the soil water phase by 98%. We also simulated the transport of DMM, MTBE and benzene from a uniformly contaminated 30-cm surface-soil layer to a ground water well located 50 m down gradient from the source region by using a vadose-zone transport model linked to a 3D groundwater transport model. As seen in Figure 3, DMM and MTBE concentrations peak at around the same time in the well water. Benzene concentrations in the well water peaks at an earlier time due to its more rapid

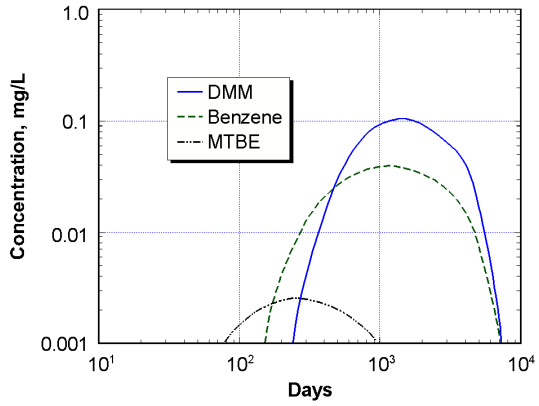

Figure 3. Time-varying concentrations of DMM, MTBE, and benzene predicted in a well downgradient from a contaminated surface soil.

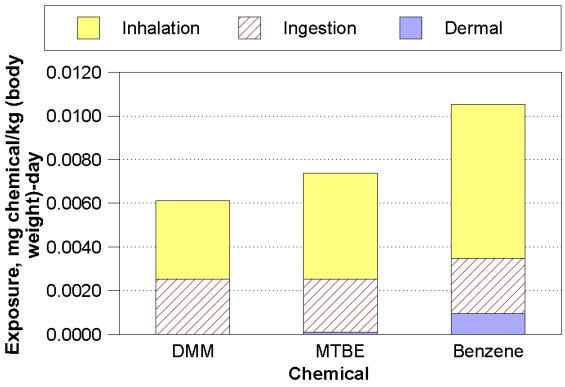

Figure 4. Water-based exposures to DMM, MTBE, and benzene in drinking water.

transport in soil, but its predicted concentration is significantly diminished by biodegradation.

We then estimated human exposure to water containing 1 ppm of DMM, MTBE, and benzene (see Figure 4). The main routes of exposure to DMM are inhalation and ingestion; dermal uptake is negligible due to its relatively low octanol-water partition coefficient. The overall exposure is similar to that of MTBE and about half that of benzene.

Conclusions

Previous work conducted on DMM indicates that its use as a diesel-fuel oxygenate would be limited because its high vapor pressure would require fuel-system modifications. Nevertheless, we have also shown that high vapor pressure is not the only

undesirable property of DMM. It is likely to be recalcitrant and mobile in ground water, behaving similarly to MTBE in the environment. Our evaluation of available property-prediction software indicates that most of the key physicochemical parameters required for transport modeling can be estimated from chemical structure information. However, such estimates are best used for comparative, screening-level analyses of fuel oxygenates. Experiments will be needed to refine property estimates, and importantly, define temperature-dependent relationships.

List of Presentations

1. David W. Layton, William J. Pitz, Jeffrey I. Daniels, Steve Carle, Reed M. Maxwell, and Ken L. Carroll, "Dimethoxy Methane as a Potential Oxygenate for Diesel Fuel: Preliminary Assessment of its Environmental Behavior", presented at the American Chemical Society 219th National Meeting & Exposition, March, 2000.
2. David W. Layton, Alfredo A. Marchetti, and Jeffrey I. Daniels, "Life Cycle Assessments of Fuels for Advanced Engines: Oxygenate Assessment", Office of Transportation Technologies Annual Review, Argonne National Laboratory, May, 2000.

List of Acronyms

3D	Three-dimensional
DMM	Dimethoxy methane
DOE	US Department of Energy
MTBE	Methyl tert-butyl ether
OH	Hydroxyl radical
OTT	Office of Transportation Technologies
ppm	Part per million

B. Chemical Characterization of Toxicologically Relevant Compounds From Diesel Emissions

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

E. Toxic Emissions

F. Ultra-fine Particles

Tasks

8. Safety, Health, and Consumer Acceptance Aspects of Liquid Fuels

Objectives

- Investigate the role of fuels on the engine-out exhaust emissions of potentially toxicologically relevant compounds.
- Determine polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of exhaust particulate matter; gaseous exhaust PAH; other gaseous exhaust "toxics" collected from a diesel engine using various fuel compositions.

Approach

- A DaimlerChrysler OM611 CIDI engine was used to determine the effect of diesel fuel type on toxicologically relevant compounds from engine-out exhaust emissions.
- The engine was controlled by a SwRI Rapid Prototyping Electronic Control System (RPECS).
- The test matrix included 5 fuels (including one oxygenate blend) operated over 5 speed/load points.
- Each speed/load point was devised to hold location of Peak Pressure (LPP) of combustion at 7°ATDC, while maintaining cylinder balance within 5% of the Indicated Mean Effective Pressure (IMEP), with pilot fuel injection disabled.
- Two of the speed/load points were operated at two different pilot fuel injection strategies. One pilot strategy used the stock controller, while the other was to include pilot fuel injection while maintaining the Location of Peak Pressure at a constant.
- Four gaseous "toxic" exhaust emissions were measured.
- Eleven gaseous PAH compounds were measured.
- Seventeen PAH compounds were determined from the soluble organic fraction of the exhaust particulate matter.

Accomplishments

- All fuel tests completed in triplicate for five modes, pilot injection off, LPP operation. Pilot fuel injection effect evaluation for all fuels completed in triplicate for two modes and two pilot fuel injection strategies.
- Statistically significant fuel effects on exhaust emissions identified.
- Oxygenate-containing fuel and Fischer-Tropsch fuel produced the lowest overall toxic gas and PAH exhaust emissions.

Future Directions

- In a follow-on phase, similar investigations will be conducted using an engine with exhaust emission control devices.

Introduction

This program is part of an overall study that examines the effects of alternative diesel fuels including one oxygenated compound (dimethoxymethane) in diesel fuel on the emissions of particulate matter, oxides of nitrogen, and fuel economy. This program addressed the chemical characterization of engine-out emissions of compounds with known or suspected toxicological properties (e.g. carcinogens).

Objective

The goal of this project was to better understand the role of fuels on the emissions of a subset of potentially toxicologically relevant compounds. Objectives of this program were: 1) to measure the polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of particles collected from CIDI engines under a matrix of engine and fuel conditions, 2) to measure the gas-phase polycyclic aromatic hydrocarbons from this engine and, 3) to measure formaldehyde, acetaldehyde, benzene, and 1,3-butadiene using the same conditions that are used to collect particles. These measurements were made on engine-out emissions.

Approach

A standard set of polycyclic aromatic hydrocarbons (PAH) in organic solvent extracts of diesel particles and from the gas phase of diesel emissions were measured in this program. In addition, four toxic air pollutants (as noted above) were quantified. The OM611 CIDI engine was run at five different engine speeds and loads and controlled to hold location of peak pressure of combustion at 7°ATDC. Individual cylinder balance was maintained within 5% of the Indicated Mean Effective Pressure (IMEP), with pilot fuel injection disabled. The engine was also controlled at two speed and load combinations using two different pilot injection control strategies. Particulate filter samples were collected at each load and control condition. The engine operating conditions are shown in Table 1.

Mode	RPM	BMEP, bar	% EGR
M 12	900	0.10	40
M 11	1500	2.62	30
M 10	2000	2.00	30
M 6	2300	4.20	15
M 5	2600	8.80	5

Table 1. OM 611 Engine Operating Conditions

The four toxic air pollutants from mobile sources cited in the Clean Air Act (formaldehyde, acetaldehyde, benzene, and 1,3-butadiene) were measured in triplicate at each of the points discussed above. The five test fuels, along with selected fuel properties are shown in Table 2.

The particulate matter was sampled from a 203mm-dilution tunnel using carbon dioxide tracer for determining dilution ratio. A polyurethane foam and XAD-2 resin trap were utilized for sampling gas phase PAH compounds. Soluble phase PAH compounds were extracted from 90 mm filters.

Fuel (Code)	H, wt %	C, wt %	O, wt %	Cetane Number	Sulfur, ppm	Aromatics, wt %
California Reference Diesel Fuel (CA)	13.4	86.4	0.2	45	176	18.9
Low-Sulfur Diesel Fuel (ALS)	14.4	85.6	0.0	63	1	9.0
Fischer-Tropsch Diesel (FT-100)	15.1	84.8	0.1	84	0	0.2
Oxygenate Blend: 15% Dimethy-oxymethane in ALS (ADMM15)	13.7	81.6	4.7	59	< 2	8.2
EPA 2D Certification Fuel (DF-2)	13.0	86.7	0.3	44	337	30.3

Table 2. Toxicity Test Fuels

Mode	Mode Weights, seconds
Mode 11	600
Mode 10	375
Mode 6	200
Mode 5	25
Total	1,200

Table 3. Weighting Factors for Engine-Out Emissions

Rank	**HC**	**CO**	**PM**	**SOF**	**NO_x**	**CO_2**
Highest	DF-2	DF-2	DF-2	DF-2	DF-2	ADMM15
↓	CA	CA	CA	CA	ADMM15	DF-2
	ALS	ALS	ALS	ALS	FT-100	CA
	ADMM15	ADMM15	ADMM15	ADMM15	CA	ALS
Lowest	FT-100	FT-100	FT-100	FT-100	ALS	FT-100

Table 4. Fuel Rank Order from ANOVA for Weighted Average Regulated Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

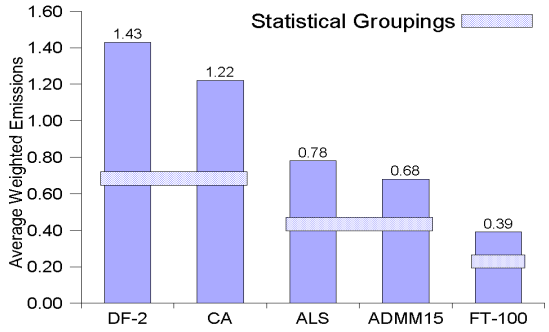

Figure 1. Test Fuel Hydrocarbon Weighted Average Mass Emissions (g/kWh)

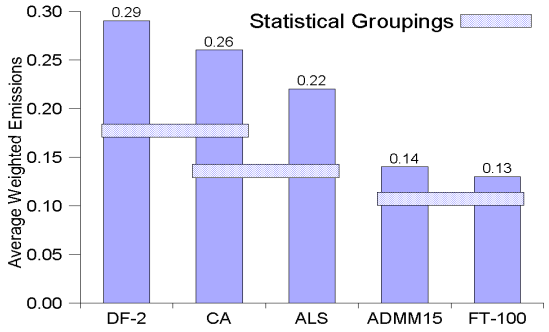

Figure 2. Test Fuel Weighed Average Particulate Matter Mass Emissions (g/kWh)

Benzene and 1,3-Butadiene were collected in a sample bag from the dilution tunnel sample zone. Formaldehyde and Acetaldehyde were trapped on a DNPH adsorbent cartridge from the dilution tunnel sample zone.

Discussion

Fuel comparisons utilizing the Ad-Hoc Fuels Group Mode Weighting Factors shown in Table 3 were made for brake specific exhaust emissions with the engine operated under LPP control with pilot fuel injection turned off.

Rank	Benzene	1,3 Butadiene	Formaldehyde	Acetaldehyde
Highest	CA	CA	DF-2	DF-2
↓	DF-2	DF-2	ALS	ALS
	ALS	ALS	CA	CA
	FT-100	ADMM15	ADMM15	ADMM15
Lowest	ADMM15	FT-100	FT-100	FT-100

Table 5. Fuel Rank Order from ANOVA for Weighted Average Air Toxic Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

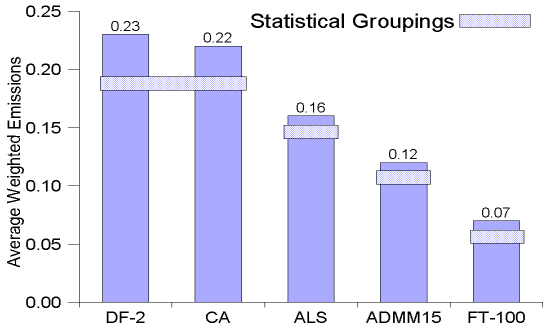

Figure 3. Test Fuel Weighted Average Soluble Organic Fraction Mass Emissions (g/kWh)

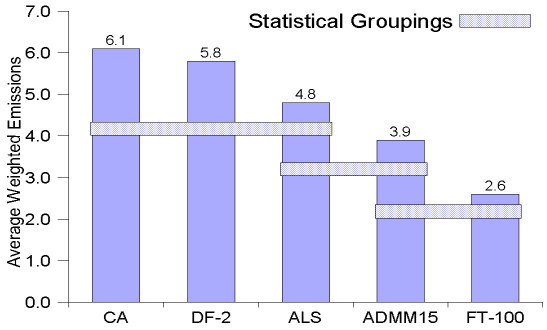

Figure 5. Test Fuel Weighted Average 1,3-Butadiene Emissions (mg/kWh)

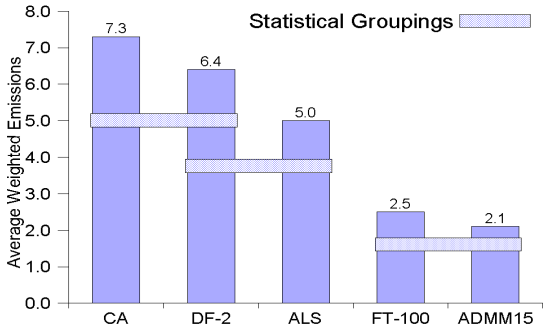

Figure 4. Test Fuel Weighted Average Benzene Emissions (mg/kWh)

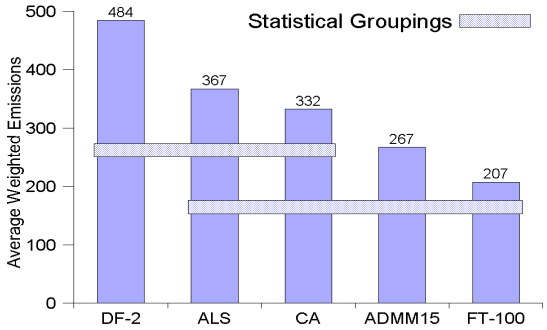

Figure 6. Test Fuel Weighted Average Formaldehyde Emissions (mg/kWh)

Several statistically significant trends, at 95% confidence, were apparent from an ANOVA of the weighted average brake specific emissions data. Table 4 summarizes the qualitative general rank order for the regulated weighted average mass emissions during LPP engine operation with pilot fuel injection turned off. For HC, CO, PM, and SOF the lowest emitting fuels were ADMM15 and FT-100, with the higher emitting fuels being DF-2 then CA. Figure 1 shows the relative levels of test fuel hydrocarbon emissions with statistically similar groupings shown with horizontal bars. The statistical groupings and relative levels of particulate matter emissions are shown in Figure 2 for the test fuels. The relative SOF levels of the particulate matter and their statistical groups are represented in Figure 3. The highest NO_x emitter was DF-2, followed jointly by ADMM15, FT-100, and CA, with ALS being the lowest NO_x emitting fuel.

Table 5 is the qualitative ranking of the test fuels for the four EPA Clean Air Act toxic compounds. Figure 4 shows the ranking and statistically significant similar groupings (horizontal bars) for

Rank	Naphthalene	Acenapthylene	Acenapthene	Fluorine	Phenanthrene
Highest	DF-2	CA	DF-2	DF-2	DF-2
↓	CA	DF-2	CA	CA	CA
	FT-100	FT-100	FT-100	ADMM15	FT-100
	ADMM15	ADMM15	ADMM15	FT-100	ALS
Lowest	ALS	ALS	ALS	ALS	ADMM15

Rank	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthra-cene	Chrysene
Highest	DF-2	DF-2	DF-2	DF-2	DF-2
↓	CA	ALS	ALS	CA	CA
	FT-100	CA	CA	ALS	ALS
	ADMM15	FT-100	FT-100	FT-100	FT-100
Lowest	ALS	ADMM15	ADMM15	ADMM15	ADMM15

Rank	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(e)pyrene
Highest	DF-2	DF-2	DF-2
↓	ALS	CA	CA
	CA	ALS	ALS
	ADMM15	ADMM15	FT-100
Lowest	FT-100	FT-100	ADMM15

Table 6. Fuel Rank Order from ANOVA for Weighted Average Particulate Matter PAH Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

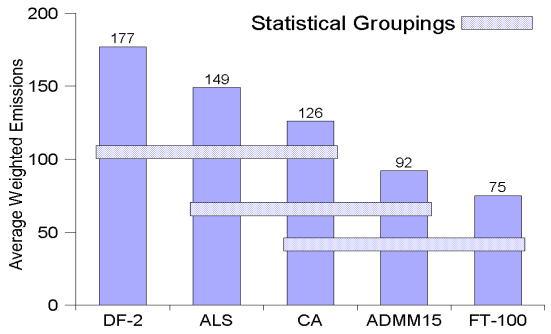

Figure 7. Test Fuel Weighted Average Acetaldehyde Emissions (mg/kWh)

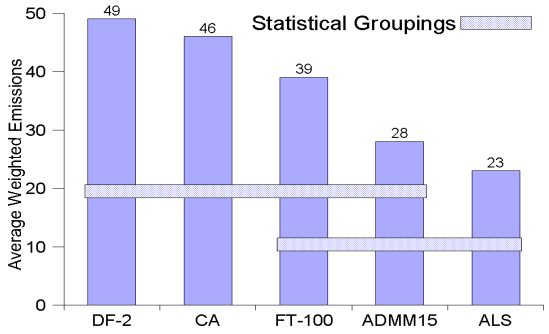

Figure 8. Test Fuel Weighted Average Particulate Phase Naphthalene Emissions (µg/kWh)

benzene emissions. For 1,3-butadiene the lowest emitting fuels were FT-100 and ADMM15, then ALS, with the highest emitting fuels being DF-2 and CA; the statistical groupings are shown in Figure 5. The highest formaldehyde and acetaldehyde emitter was DF-2, followed by ALS, CA, then jointly by ADMM15 and FT-100. Figure 6 shows the relative levels and statistical groupings for formaldehyde. The corresponding groupings for acetaldehyde are shown in Figure 7. For the EPA air toxic compounds, ADMM15 and FT-100 were statistically similar emitting fuels, and always in the lowest grouping for LPP operation with pilot fuel injection turned off.

The fuel rankings for thirteen of the particulate bound soluble phase PAH compounds are shown in Table 6. Due to non-detects, four PAH compounds are being analyzed again with a higher-resolution instrument. The four compounds being reanalyzed

Rank	Naphthalene	2-Methyl-napthalene	1-Methylnaphthalene	2,6-Dimethyl-naphthalene	Acenaphthyl-ene
Highest	CA	DF-2	DF-2	DF-2	DF-2
↓	DF-2	CA	CA	CA	ALS
	ALS	ALS	ALS	ALS	CA
	ADMM15	ADMM15	ADMM15	ADMM15	ADMM15
Lowest	FT-100	FT-100	FT-100	FT-100	FT-100

Rank	Acenapthene	Fluorene	Phenan-threne	Anthracene	Fluoranthene	Pyrene
Highest	DF-2	DF-2	DF-2	DF-2	DF-2	DF-2
↓	CA	CA	CA	CA	CA	CA
	ALS	ALS	ALS	ALS	ALS	ALS
	ADMM15	FT-100	FT-100	ADMM15	ADMM15	FT-100
Lowest	FT-100	ADMM15	ADMM15	FT-100	FT-100	ADMM15

Table 7. Fuel Rank Order from ANOVA for Weighted Average Gas Phase PAH Mass Emissions for LPP Operation with Pilot Fuel Injection Turned Off

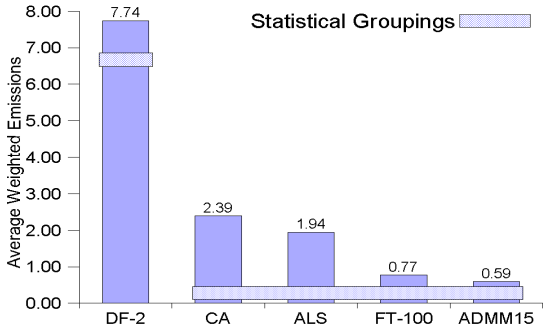

Figure 9. Test Fuel Weighted Average Particulate Phase Chrysene Emissions (µg/kWh)

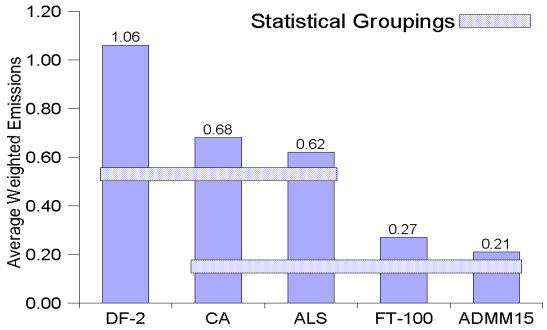

Figure 10. Test Fuel Weighted Average Particulate Phase Benzo(e)pyrene Emissions (µg/kWh)

are benzo(a)pyrene, indeno(123-cd)pyrene, dibenzo(a-h)anthracene, and benzo(ghi)perylene. Figure 8 shows the statistical groupings for the PAH naphthalene bound to the particulate matter. Figure 9 is the statistical groupings for the particulate phase PAH chrysene. The emissions of particulate bound PAH benzo(e)pyrene are shown in Figure 10, along with the statistical groupings. For the majority of PAH compounds, DF-2 fuel was statistically different from the other test fuels. The ADMM15 and FT-100 fuels were in the statistically equivalent (95% confidence) lowest grouping for particulate bound PAH compounds.

The gas phase PAH emissions rank the test fuels qualitatively in the general order shown in Table 7. The gas phase PAH naphthalene mass emissions are shown in Figure 11 along with the statistical groupings. In general, the other gas phase PAH compounds had statistical groupings similar to naphthalene.

Statistical groupings for engine control strategy, which includes pilot fuel injection effects, from an ANOVA for modes 10 and 11 are shown in Figure 12 for particulate matter emissions and in Figure 13 for NO_x emissions. For the least square means of the combined modal and fuel data, each engine control approach was statistically unique for PM and NO_x. The air toxic benzene response in Figure 14 indicates the two pilot conditions are statistically similar, but different from LPP operation with pilot turned off. The LPP with pilot off was statistically the lowest control strategy for the four air toxic emissions. The

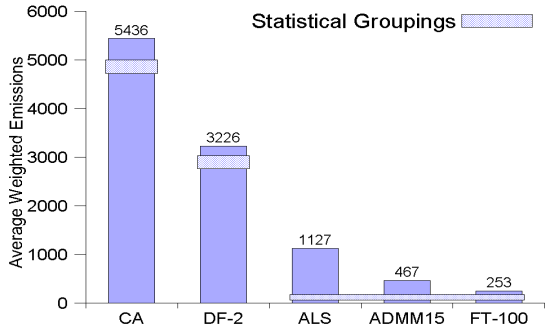

Figure 11. Test Fuel Weighted Average Gaseous Phase Naphthalene Emissions (µg/kWh)

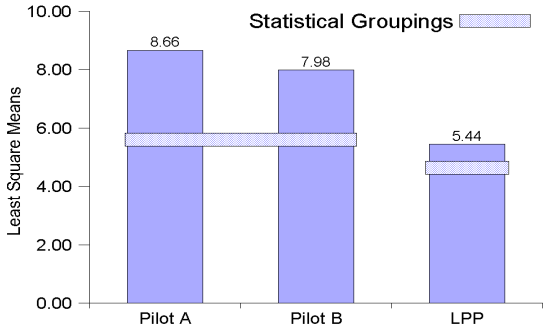

Figure 14. Pilot Fuel Injection Effect on Air Toxic Benzene Emissions (mg/kWh)

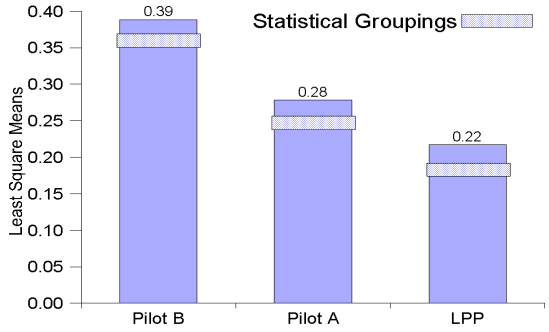

Figure 12. Effect of Pilot Fuel Injection on PM Emissions (g/kWh)

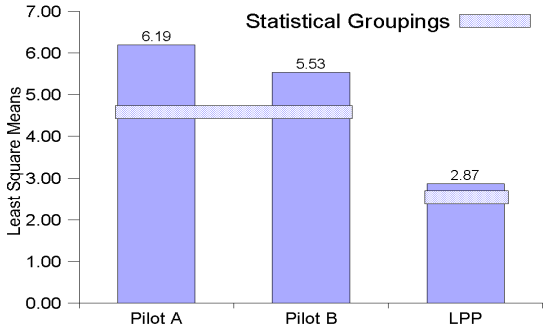

Figure 15. Pilot Fuel Injection Effect on Particulate PAH Chrysene Emissions (µg/kWh)

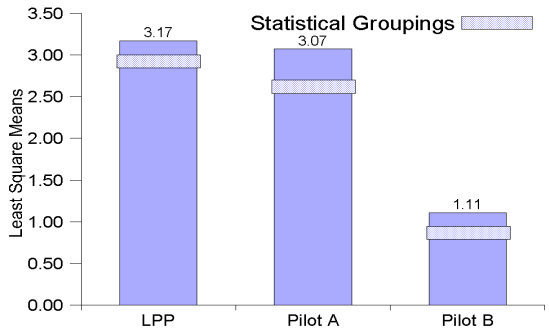

Figure 13. Effect of Pilot Injection on NO_x Emissions (g/kWh)

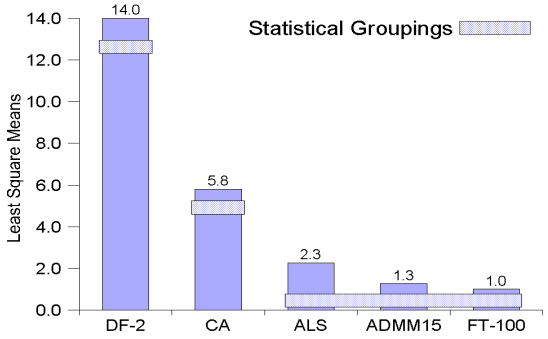

Figure 16. Test Fuel Least Square Means for Pilot Fuel Injection for Particulate PAH Chrysene Emissions (µg/kWh)

particulate bound PAH chrysene emissions in Figure 15 show pilot operation to be different from LPP operation. The same statistical conclusion could be made for the other particulate PAH compounds. The effect of pilot fuel injection on exhaust emissions, compared to the LPP operation with pilot turned off, can be summarized as follows:

- PM emissions increase with pilot fuel injection;
- NO_x emissions decrease with pilot fuel injection;
- Gaseous air toxic levels increase with pilot fuel injection; and

- Both soluble and gas phase PAH increase with pilot fuel injection.

The fuel rank order, along with the statistical groupings for the particulate bound PAH chrysene emissions, is shown in Figure 16. The least square means are calculated by combining the modal and control data. Figure 16 may be compared to Figure 9, which suggests pilot fuel injection increases the PAH chrysene emissions, but the fuel ranking is similar. The other particulate bound and gas phase PAH compounds revealed fuel ranking and relative magnitude results similar to chrysene. The fuel rank order for exhaust emissions with pilot fuel injection operation can be summarized as follows:

- PM rank for ADMM15 and FT-100 lowest, with DF-2 highest;
- NO_x rank is FT-100 lowest, ADMM15 middle, and DF-2 highest;
- Gaseous air toxic rank is FT-100 and ADMM15 lowest, with DF-2 highest; and
- Both soluble and gas phase PAH rank is FT-100 and ADMM15 statistically similar as lowest, with DF-2 the highest emitting fuel.

Conclusions

- ADMM15 or FT-100 had the lowest overall weighted average emission response of the test fuels.
- ADMM15 fuel was statistically the same as FT-100 fuel for toxic, PM, and PAH emissions.
- Pilot fuel injection changes the magnitude of the emission response, but does not significantly alter the fuel rank order.

List of Presentations

1. Yost, D.M. and E.A. Frame, "Particulate Matter Analysis from an Advanced Diesel Engine", CIDI Engine Combustion, Emission Control, and Fuels R & D, Merit Review and Peer Evaluation, Argonne National Laboratory, 22-24 May 2000.

List of Acronyms

ADMM15	15% by Volume DMM blended in ALS Fuel
ALS	Low Sulfur Diesel Fuel
ANOVA	Analysis of Variance
ATDC	After Top Dead Center
BSFC	Brake Specific Fuel Consumption
CA	California Reference Diesel Fuel
DF-2	EPA Certification Diesel Fuel
DMM	dimethoxymethane
DNPH	Dinitrophenylhydrazine
FT-100	Neat Fischer-Tropsch Fuel
IMEP	Indicated Mean Effective Pressure
LPP	Location of Peak Pressure
NO_x	Oxides of Nitrogen
PAH	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter
RPECS	SwRI Rapid Prototyping Electronic Control System
SOF	Soluble Organic Fraction

C. Comparing and Contrasting Particle Emissions from Spark Ignition and Compression Ignition Engines

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

F. Ultra-fine Particles

Tasks

8. Safety, Health, and Consumer Acceptance Aspects of Liquid Fuels

Objectives

- To document and report the characteristics of particulate matter (PM) emissions for several gasoline vehicles in order to help develop a more complete understanding of the need and potential for reducing emissions of particulate matter from vehicles, both spark ignition and diesel. By studying the PM emissions of past, current, and emerging gasoline vehicles with a level of scrutiny being afforded diesel engine exhaust, a more comprehensive and accurate foundation for our environmental and energy strategy can be formed.

Approach

- ORNL is assisting in forming a comprehensive database on PM emissions from both compression ignition (diesel) and spark ignition engines. Augmenting ongoing studies of PM characteristics and health effects, ORNL is engaged in the following efforts:
  - Developing historic trends in gasoline vehicle PM data, noting key impacts of fuel changes, and determining likely achievable PM emission reductions.
  - Application of transmission electron microscopy (TEM) to characterize the morphology of exhaust PM.
  - Development and application of a new mass-spec instrument to determine the composition of individual particles and the compounds adhering to their surface.

Accomplishments

- Tested and documented the PM emissions from a pre-emission-control era gasoline vehicle with leaded and unleaded fuel to serve as a historical benchmark.

- Applied new methods of exhaust particle capture and TEM analysis to compare the morphology of gasoline and diesel engine PM.
- Assembled a new mass spectrometry instrument for analysis of the composition of exhaust particle surface and core. Real-time aerosol mass spectrometer (RTAMS) has been built and is undergoing initial tests.

Future Directions

- Continue to build and report database on gasoline engine PM, including emerging technology direct injected gasoline engines, as well as supplementing data on diesel PM.
- Apply TEM and RTAMS to characterize the composition and morphology of exhaust PM in unprecedented detail.

Introduction

The feasibility of emerging diesel emissions control appears highly dependent on the availability of low-sulfur diesel fuel. An analogous situation faced the automakers around 1970 where the catalytic converter was needed to achieve new emissions regulations, yet was incompatible with the lead-containing gasoline of the era. History has borne out that the availability of unleaded gasoline, eventually also with reduced sulfur, was pivotal in gasoline cars achieving the remarkably low emissions of today. The diesel engine may be at the same crossroads, approximately where the gasoline engine was before catalysts. To be able to present this historic perspective, emissions data from gasoline vehicles, with and without their catalysts, are being compiled.

Approach

Historical Benchmark. The effort has begun with the emissions study of a pre-control era vehicle using both leaded and unleaded fuel. A restored 1967 Chrysler 300 was selected as the pre-control era subject. The PM from the vehicle on unleaded fuel was quite low, although the gaseous emissions were of course alarming by today's standards. Leaded fuel more than doubled the mass of PM (Figure 1). PM size distribution via MOUDI showed the dominance of particles under 50 nm typical of gasoline engines, except in the case of leaded fuel a large population of particles appeared at 100 nm (see Storey et. al.).

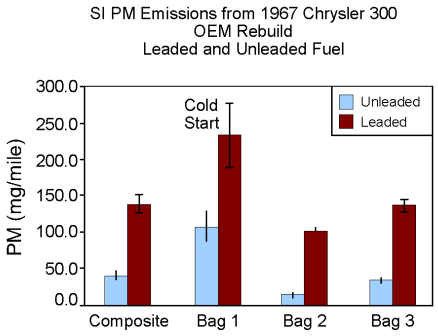

Figure 1. SI PM Emissions from 1967 Chrysler 300

The next phase of the study will address the direct injected gasoline engine, with and without aftertreatment.

Analysis by TEM and RTAMS. The Northern Front Range Air Quality Study concluded that for the Denver metropolitan area during 1996 and 1997, 55% of $PM_{2.5}$ was attributable to motor vehicle exhaust. It is of vital interest to understand the chemistry, morphology, size distribution and microstructure of motor vehicle exhaust. Our goal was to apply the techniques of TEM and energy dispersive X-ray spectroscopy (EDS) to the analysis of the microstructure, morphology and microchemical composition of particulate matter from motor vehicle exhaust. Source sampling from a variety of vehicles was conducted. As part of an ongoing research project into the health effects of motor vehicle particulate matter, Southwest Research Institute (SwRI) is performing chassis dynamometer tests on a fleet of spark ignition vehicles. PM was collected from the following vehicles: 1993 Mercury

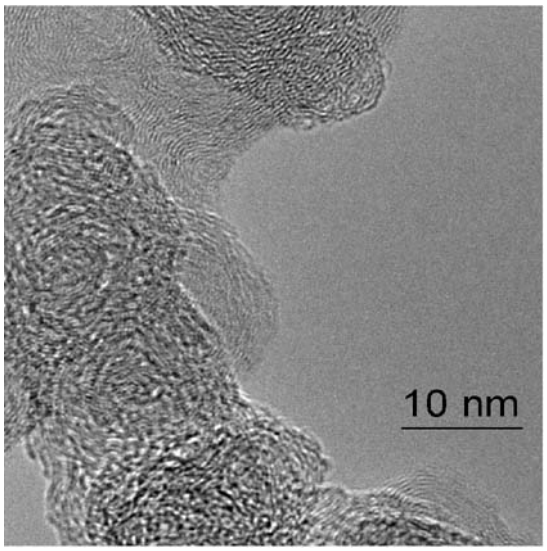

Figure 2. High resolution micrograph showing turbostratic crystal structure in exhaust emission PM

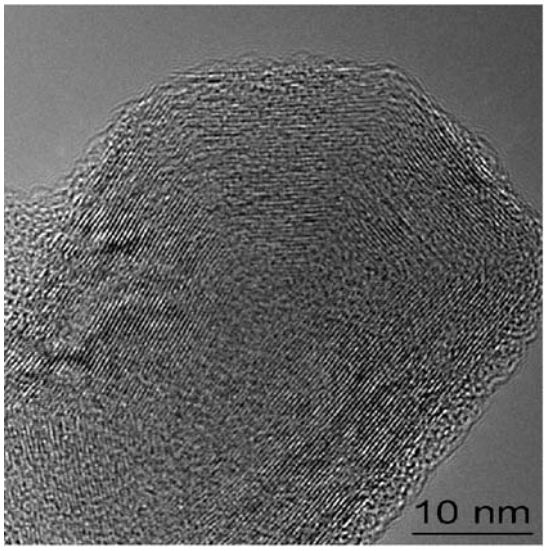

Figure 3. High resolution micrograph of a graphitized particle emitted by a motor vehicle

Sable, 1996 Mazda Millenia, 1998 Honda Accord (ULEV), and a 1976 Ford F-150 which produced visible black smoke. A range of properties was observed among the vehicles under different operating conditions. Figures 2 and 3 are high-resolution micrographs showing structural differences in particulate matter. Figure 2 illustrates the "onion peel" microstructure known as turbostratic. The planes of carbon atoms are only organized in two dimensions and is typical of moderate temperature combustion processes. Figure 3 is an example of a graphitic crystal structure where

Figure 4. Real-time single particle analyzer mass spectrometer in ORNL engine lab

the carbon atoms are well organized in all three dimensions. Graphitic microstructures are indicative of high combustion temperatures. Additional differences in chemical composition have been observed among the various samples of PM. Electron microscope characterization of particulate matter can be a valuable tool in understanding the microchemistry, morphology and microstructure at an atomic level.

Another feature of exhaust PM that must be determined to fully understand the health risks is the chemical composition of both the surface as well as the core of the particle. The surface, typically laden with hydrocarbons, is what actually contacts the tissues inside the respiratory system. A new instrument, the RTAMS has been built for this analysis, and is undergoing initial trials in the ORNL engine lab. The instrument as designed will yield real-time particle mass spectra as a function of particle size from molecular size (<1nm) to well above 100 nm. Dilute exhaust gas is sampled directly into the RTAMS and the particles charged electrostatically. The RTAMS uses the same principles for analyzing large molecules using mass spectroscopy. Particle size can be discriminated by charging the particle at different voltages, or by changing the frequency of the ion trap. Once inside the ion trap, the particle is ionized with an ultra-fast burst of laser energy.

The optimal working range of the spectrometer is expected to be below 20 nm where only a single charge on each particle is necessary for trapping it. We will be able to exceed this limit by repetitive

charging of the particles, so when more mature the instrument's upper size limit should be in the hundreds of nanometer range. Since the instrument is a mass spectrometer, we will also be able to simultaneously measure the neutral gas phase species as well as the particle phase species. Its tandem mass spectrometry (MS/MS) configuration is key to analyzing the organic materials present on the particles. This should yield unprecedented real-time information regarding particle nucleation and growth with minimal effort. Figure 4 shows the instrument as configured for the engine lab. A significant portion of the effort to date has been supported by laboratory exploratory funds. The initial undertaking was encouraged by DOE's Dr. Sidney Diamond.

Conclusions

Development of more complete instrumentation for studying the characteristics of particulate emissions from both spark-ignited and compression-ignited engines has made possible more comprehensive investigation of the similarities and differences between particles emitted from these engines. This level of investigation of particle characteristics is needed to more fully recognize and minimize the impacts of particle emissions on the health of the population. First steps have been taken towards a full characterization of particle emissions by revisiting the emissions from an older vehicle. Continuing work will focus on performing similar analyses on vehicles of current and emerging engine technology.

List of References

1. J.M.E. Storey, C. Scott Sluder, Douglas A. Blom, Oak Ridge National Laboratory, and Erin Higginbotham, Automotive Testing Laboratories, Inc., "Particulate Emissions from a Pre-Emissions-Control Era Spark Ignition Vehicle: A Historical Benchmark.," SAE paper 2000-01-2213, June 2000.
2. "Northern Front Range Air Quality Study", Colorado State University, 1997.

List of Acronyms

EDS	Energydispersive x-ray spectroscopy
PM	Particulate Matter
RTAMS	real time aerosol mass spectrometer
SwRI	Southwest Research Institure
TEM	transmission electron microscopy

D. Lubricity of High Volatility, Low Sulfur CIDI Fuels

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Subcontractor: Southwest Research Institute, San Antonio, TX

This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

I. Infrastructure Impacts

Tasks

7. Vehicle Materials Compatibility

Objectives

- Characterize the lubricity of high volatility and low-sulfur compression ignition, direct injection (CIDI) fuels and explore additives to improve the lubricity of these fuels.
- Complete correlation of the High Pressure High Frequency Reciprocating Rig (HPHFRR) and the standard High Frequency Reciprocating Rig (HFRR).

Approach

- Conduct a series of baseline tests to compare the HPHFRR and the standard HFRR.
- Conduct a series of lubricity tests on selected fuels blended with different additives.

Accomplishments

- HPHFRR and HFRR baseline tests showed better agreement than expected between two identical HFRR rigs (as outlined in Precision and Bias section of HFRR test method, ASTM D-6079).
- The lubricity of each fuel tested was improved by at least one of the additives evaluated, with the treat rates varying among the fuels.

Future Directions

- No future work is planned at this time.

Introduction

The lubricity of a fuel has a direct impact on the wear of engine components such as fuel injection systems. Testing the lubricity of promising fuels, fuel blends, and additives is a necessary part of evaluating the potential of advanced fuels. Advanced fuels will need to meet or exceed accepted lubricity levels for standard diesel fuels measured on an HFRR.

Many of the advanced fuels under consideration for use in advanced engines (such as DME) have high vapor pressures. As a result, these fuels are gaseous under ambient conditions and form a

Parameter	Units	HRFF	HPHFRR
Speed	Hz	20-100	5-200
Load	grams	100-1000	200
Stroke	mm	0.1 to 2	0 to 2
Temperature	°C	ambient to 60	ambient to 300
Pressure	kPa	ambient	ambient to 7
Fuel Volume	ml	2	25

Table 1. Range of test conditions available on HFRR and HPHFRR

lubricating liquid only at elevated pressures. In addition, many fuel systems operate at elevated temperatures and pressures, which may not be adequately duplicated at ambient temperatures of the standard HFRR.

In FY99, a project was initiated with Southwest Research Institute to design and develop a pressurized test rig to enable wear test evaluation of advanced diesel-type fuels. A pressurized fuel lubricity test apparatus, the High Pressure High Frequency Reciprocating Rig, was designed. It reproduces the operating conditions of the standard HFRR, but enables lubricity testing at elevated temperatures and pressures.

In this follow-on project, a series of tests were conducted to compare the results from the new HPHFRR and the standard HFRR. In addition, the HPHFRR was used to evaluate the lubricity of several fuels with and without additives.

Approach

An initial test sequence was performed to verify the agreement between the HPHFRR and the results of standard HFRR tests performed according to ASTM D 6079 at 25°C. The range of test conditions available on the HFRR and HPHFRR is described in Table 1. Tests were performed using a matrix of 44 fuel and additive combinations. Only fuels with negligible vapor pressure at ambient temperature were evaluated, as fuels with high vapor pressure cannot be tested using the standard HFRR. Each of the different fluids was evaluated with both the HFRR and the HPHFRR at 25°C, and a difference was computed.

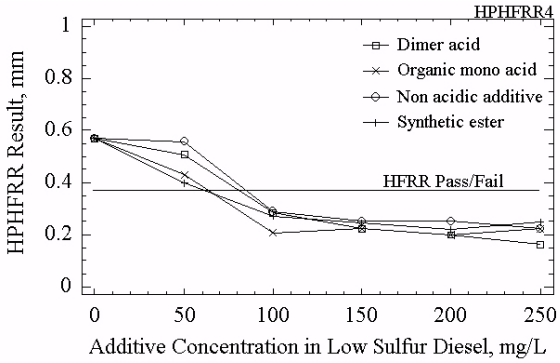

Figure 1. Effect of additive concentration on lubricity of very low sulfur diesel (3-ppm sulfur) as measured by the HPHFRR at 25°C

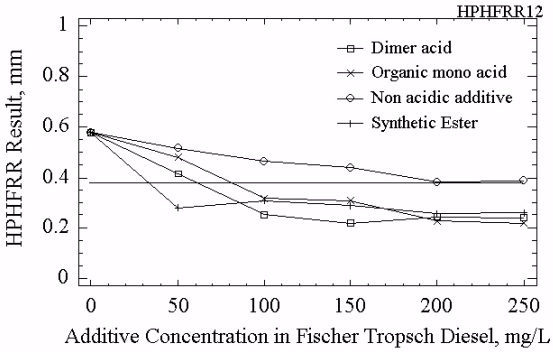

Figure 2. Effect of additive concentration on lubricity of FT diesel as measured by the HPHFRR at 25°C

Following the verification test series, a test series was conducted to evaluate the lubricity of very low-sulfur diesel (LSD), dimethyl ether (DME), and Fischer-Tropsch (FT) with four different additives. Treat rate curves were generated for four different additives.

Results

The initial test sequence was performed to verify the agreement between the HPHFRR and the HFRR. ASTM D 6079 requires that the repeatability of the HFRR for tests performed by a single apparatus on identical test material should exceed 0.062 mm in only one case in 20. The reproducibility between data produced by two different operators in two different laboratories (essentially two different rigs) should not exceed 0.127 mm. In this study, which used two different machines within a single laboratory, the variability of the test results was expected to be between 0.062 and 0.127 mm.

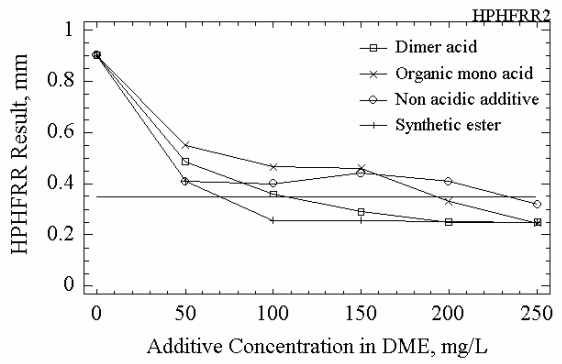

Figure 3. Effect of additive concentration on lubricity of DME as measured by the HPHFRR at 25°C

The differences (HPHFRR results minus HFRR results) in this test series were found to follow a Gaussian distribution. On average, the results produced by the HPHFRR were 0.0049 mm lower than those of the HFRR. A paired t-test was approximately 0.90, indicating no significant difference in the average test results. Overall, the agreement between the HPHFRR and HFRR was as good as or better than the ASTM defined acceptable variability limit between two HFRR machines of 0.127 mm.

The suitability of four additives in improving the lubricity of fuels was evaluated. The fluids evaluated included a very low sulfur diesel (3-parts per million sulfur), a Fischer-Tropsch diesel, and DME, which has high volatility compared to the other fuels. The additives selected included a wide range of chemistries, including organic mono and dimer acid based compounds, as well as modern non-acidic and synthetic ester based chemistries. The results of HPHFRR tests performed as a function of additive concentration are plotted in Figures 1, 2, and 3 for the LSD, FT and DME fuels, respectively. The industry accepted maximum allowable wear scar diameter for HFRR tests at 25°C is 0.380 mm. The line at 0.380 mm on Figure 1, 2, and 3 is the pass/fail line indicating the wear scar limit. Each of the additives was effective at improving lubricity at a concentration of 100 ppm or below when used with the LSD fuel (see Figure 1). Further increases in additive concentration resulted in only marginal improvement in lubricity.

Changes in additive chemistry had varying effects on performance when used in the FT fuel (see Figure 2). A newer non-acidic additive chemistry was less effective at all levels than the other additives evaluated, only achieving acceptable lubricity result at the highest treat rate evaluated. Additive treat rates of 50 to 100 mg/L were required to achieve acceptable lubricity in FT fuel.

The lubricity of neat DME is much worse than that of most other diesel fuels. As a result, high additive concentrations are required to reduce wear to an acceptable level, as shown in Figure 3. Only the synthetic ester additive produced acceptable wear at a concentration of 100 mg/L.

Conclusions

The High Pressure High Frequency Reciprocating Rig was developed to evaluate wear characteristics of volatile fuels. It may also be used to evaluate lubricity of conventional liquid fuels at high temperature. Other than test pressure and temperature, the contact parameters exactly duplicate those of the standard HFRR. The reproducibility between the HPHFRR and HFRR was equivalent to that expected to occur between two conventional HFRR apparatuses.

Unadditized FT and low sulfur diesel fuels have poor lubricity, which may be improved by use of certain lubricity additives. One non-acidic based additive was not effective in the FT fuel. DME has exceptionally poor lubricity, worse than conventional diesel fuels. DME lubricity can be improved by using additives, but the concentrations required can be as much as twice that needed for diesel fuels.

List of References

1. American Society for Testing and Materials, "Annual Book of ASTM Standards 2000, Section Five: Petroleum Products, Lubricants and Fossil Fuels," Volume 05.04, 2000.

List of Publications

1. "Lubricity of Volatile Fuels for Compression Ignition Engines," SAE Paper No. 00FL-422, presented at CEC/SAE Spring International Fuels and Lubricants Meeting, June 2000.

List of Acronyms

ASTM	American Society for Testing and Materials
CIDI	compression ignition, direct injection
DME	dimethyl ether
FT	Fischer-Tropsch
HFRR	High Frequency Reciprocating Rig
HPHFRR	High Pressure High Frequency Reciprocating Rig
LSD	low sulfur diesel
ppm	parts per million

E. Refinery Modeling of the Production of Advanced Petroleum-Based Fuels

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LLC Prime Contract No. DE-AC05-00OR22725

Subcontractors: Energy and Environmental Analysis, Inc. , Arlington, VA; EnSys Energy and Systems, Flemington, NJ; H.T. McAdams, AccaMath Services, Carrollton, IL; R.W. Crawford, RW Crawford Energy Systems, Tucson, AZ

This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

G. Advanced Fuel Production and Cost

Tasks

5. Refinery and Fuel Processing Economics

Objectives

- Characterize relationships between fuel properties and emissions for diesel technologies that could be available to meet Tier 2 emissions standards.
- Develop methodology for relating diesel fuel composition to emissions from advanced diesel engines.
- Make preliminary estimation of impacts of alternative diesel fuel specifications on U.S. refineries.
- Develop composited refinery model.
- Use refinery model for estimation of impacts of alternative diesel fuel specifications on U.S. refineries.

Approach

- Stage 1. Define engine emission control technologies available to meet Tier 2 standards. Analyze relationships of fuel composition, additives, and emissions from advanced engines. Define range of fuel parameter values that could affect ability of engines to meet standards.
- Stage 2. Analyze cases based on diesel fuel specifications from Stage 1. Use spreadsheet-based approach to estimate shifts in diesel fuel blendstocks and refinery operations. Use results from Stage 2 in screening fuels for Stage 4.
- Stage 3. Use eigenfuel concept to analyze diesel data to understand the role of fuel composition changes on emissions from advanced diesel engines
- Stage 4. Modify Oak Ridge National Laboratory Refinery Yield Model (ORNL-RYM) by compositing crude oils, for improved analyst productivity and greater credibility with industry. Add promising technologies to model.
- Stage 5. Use Stage 3 refinery model for scenario studies of fuel quality changes identified in Stages 1 and 2. Estimate costs, shifts in diesel fuel blendstocks, and other refining impacts. Use global model to evaluate impacts of increased reformulated diesel fuel (RFD) demand on U.S. refinery viability.

Accomplishments

- Composited version of ORNL-RYM completed.
- Initial case studies completed for estimating refinery impacts of reformulated diesel fuel.
- Eigenfuel methodology developed for relating diesel fuel emissions to fuel composition.

Future Directions

- Analyze RFD production sensitivities to future market circumstances, including phased introduction.

Introduction

To achieve the potential use of a large number of future diesel engines, diesel's pollution problems must be solved. Diesel fuel quality improvements could enable diesel engines with advanced emission control systems to achieve necessary emissions performance. Because of increased processing difficulty for quality improvements in reformulated diesel fuel (RFD) production, a large demand for RFD will present technical and economic challenges for the U.S. refining industry. It is important to the national economy and security that these challenges do not adversely affect the efficiency and reliability of transportation fuel production and distribution systems. Refinery modeling and advanced statistical methods are being used to study impacts of RFD production.

Approach

EnSys Energy and Systems used the latest uncomposited version of ORNL-RYM to analyze the processing and cost effects of diesel sulfur reduction (EnSys Energy & Systems, Inc. 2000).

Conclusions

This analysis is a preliminary step in the task sequence that leads to use of the composited version of ORNL-RYM in RFD production studies. Key results are summarized in Figures 1 and 2, which show incremental and differential costs of sulfur reduction. The average cost increase for RFD ranges from 5 cents per gallon (cpg) at 50 parts per million (ppm) sulfur to 11 cpg at 8 ppm. The Figures show the sensitivity of cost to revamping opportunities. Focusing on manufacturing cost, this study did not allow for benefits of market and production flexibilities. The study design also

Cases	Key Premises	
Base case	LSG30 (Case 1)	
Key cases	Low-sulfur RFD (Case 2)	
	Regulation of off-road distillates (Case 3)	
	Volume-phased introduction of RFD (Case 4)	
Follow-up and sensitivity cases	Low-sulfur and low aromatics RFD (Case 5)	
	Refinery modeling with preliminary Complex Model for diesel fuel emissions. Use of oxygenates in RFD blending (Case 6)	
	RFD impacts on refineries of different capabilities	Mid-capability (Case 7)
		Challenged (Case 8)
	LSG30, winter (Case 9)	
	Technology sensitivity (Case 10)	
	Impacts of additional constraints on jet fuel quality (Case 11)	

Table 1. Refinery Modeling Study Matrix for RFD

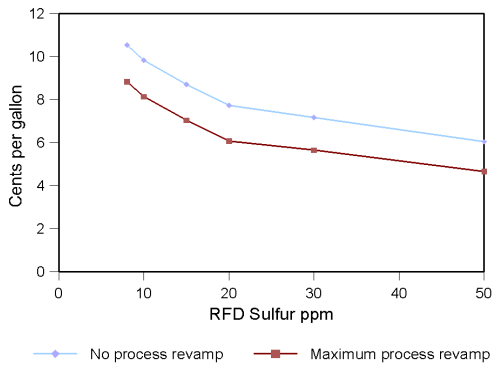

Figure 1. RFD Cost Increase

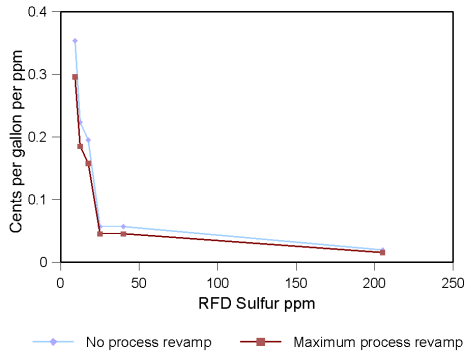

Figure 2. Differential RFD Cost

separated investment decisions for low sulfur gasoline and RFD, eliminating potential cost reduction through integrated investment. Process economics were based on proven and recently commercialized technologies. Future catalyst or process improvements may reduce costs.

The composited version of ORNL-RYM may indicate more or less severe impacts of diesel fuel reformulation. Table 1 summarizes case studies to be performed with the composited model.

The ORNL-RYM analysis used RFD property specifications, rather than emissions performance specifications. Emissions modeling could provide a means for predicting the emissions performance of RFD, given fuel sulfur content, cetane number, and other property values. An emissions model could give refiners significant technical and economic flexibility in RFD production. AccaMath Services and RWCrawford Energy Systems have developed a methodology for estimating an RFD emissions model (McAdams, Crawford and Hadder 2000). Because of fuel property covariance, it is found advantageous to redefine predictor variables as *vectors*, in which original fuel properties are components, rather than as *scalars* each involving only a *single* fuel property. The approach clearly shows that only a few basic patterns of fuel-property variations affect emissions. Given adequate engine-emissions test data, an RFD emissions model will be used in future ORNL-RYM studies.

List of References

1. McAdams, H.T., R.W. Crawford and G.R. Hadder. 2000. "A Vector Approach to Regression Analysis and Its Application to Heavy-Duty Diesel Emissions," Society of Automotive Engineers, Paper 2000-01- 1961, June.

2. EnSys Energy & Systems, Inc. 2000. "Modeling Impacts of Reformulated Diesel Fuel," ORNL

Subcontract 80X-SY527V, Draft, Flemington, NJ, June 6.

List of Acronyms

cpg	cents per gallon
LSG30	low sulfur gasoline with 30 ppm sulfur
ORNL-RYM	Oak Ridge National Laboratory Refinery Yield Model
ppm	parts per million
RFD	reformulated diesel fuel

F. Fuel Property and Emissions Database

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency
B. Fuel Property Effects on Exhaust Emission Control System Technology
C. Emission Control System Degradation
D. Sulfur Impacts
E. Toxic Emissions
F. Ultra-fine Particles
G. Advanced Fuel Production and Cost
H. Health, Safety, and Regulatory
I. Infrastructure Impacts

Tasks

4. Develop Empirical Relationships
9. Test and Validate the Empirical Relationships

Objective

- Establish a web-based, searchable fuel property database for the Advanced Petroleum-Based Fuels Program, which links to available emissions data.

Approach

- Define the fuel properties and related information to be included in the database.
- Build the database, web pages and appropriate web interfaces for the searchable database.

Accomplishments

- Searchable fuel property database completed and available on World Wide Web at http://www.ott.doe.gov/fuelprops/, includes link to available heavy vehicle emissions data.

Future Directions

- Will continue to populate database with new fuels and property data, as they become available from various fuel-related projects. Plan to expand emissions database to include light-duty emissions data, and engine-out emissions data.

Introduction

Numerous studies have investigated the impact of fuel properties, such as density, aromatic content, and cetane number on emissions from various diesel engines. Fuel properties directly affect engine operation, as well as emissions. Engine systems, like fuel injection systems, are impacted as fuel properties change. As engine systems advance and in many cases become more complex, it becomes more critical to understand how fuels are changing and the impact of those changes on engine performance and emissions.

The Advanced Petroleum-Based Fuels Program includes a Systems Emission Reduction analysis effort which will develop predictive tools for estimating the effects that fuel property variations can have on the emission response of engines, and exhaust emission control systems. A detailed fuel property database is a key information component and resource for the development of these predictive empirical models.

Approach

The development of the fuel property database includes the following tasks:

- Review of generally available fuel property data, and evaluation of property data that are needed to develop empirical models.
- Organization and development of database for the fuel property data.
- Gathering available fuel property data, and populating the database.
- Development of the web interface to enable the data to be available to DOE research partners via the Internet.

Figure 1. Fuel Property Database Home Page Logo

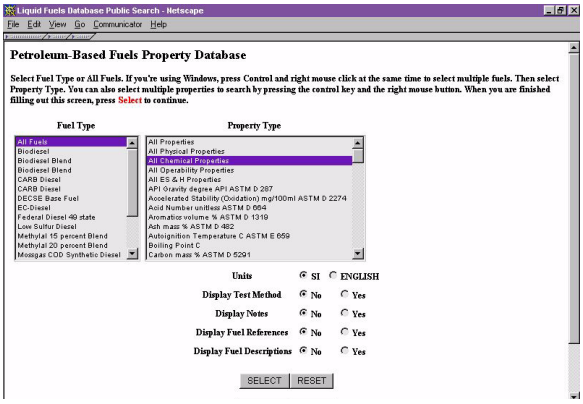
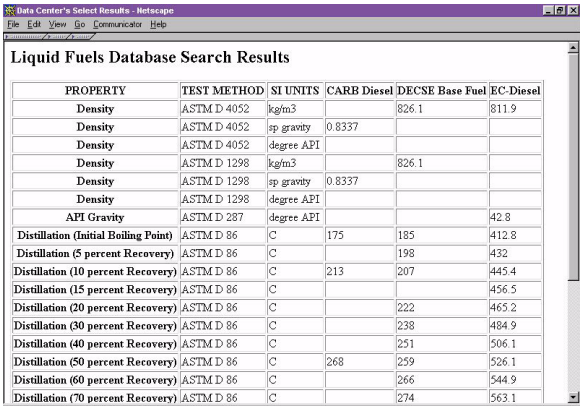


Figure 2. Fuel property database selection page, includes pull-down lists of fuels and properties

Results

The fuel property database was developed to include physical, chemical, and operability property data, and environmental health and safety information. The database is accessible via the World Wide Web at http://www.ott.doe.gov/fuelprops/ (see Figure 1).

The database was setup to allow the user to select individual fuels or properties, or to select all fuel and all property data. The initial page includes lists of fuels and properties that can be selected (see Figure 2). Output can be displayed in either SI or English units. The users can also access information on the test method used to obtain the property data, the reference source for the data, and a brief description of the fuel. Figure 3 provide a sample of the results a user would get back from a query, with all selected (or available) data displayed in a table format.



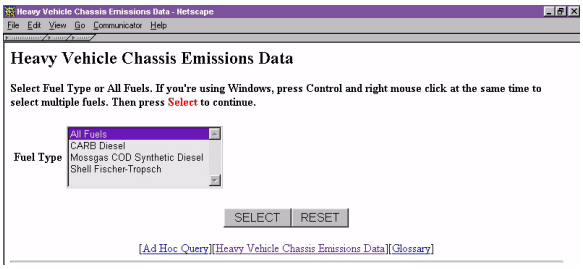
Data Center's Select Results - Netscape

File Edit View Go Communicator Help

Liquid Fuels Database Search Results

PROPERTY	TEST METHOD	SI UNITS	CARB Diesel	DECSE Base Fuel	EC-Diesel
Density	ASTM D 4052	kg/m3		826.1	811.9
Density	ASTM D 4052	sp gravity	0.8337		
Density	ASTM D 4052	degree API			
Density	ASTM D 1298	kg/m3		826.1	
Density	ASTM D 1298	sp gravity	0.8337		
Density	ASTM D 1298	degree API			
API Gravity	ASTM D 287	degree API			42.8
Distillation (Initial Boiling Point)	ASTM D 86	C	175	185	412.8
Distillation (5 percent Recovery)	ASTM D 86	C		198	432
Distillation (10 percent Recovery)	ASTM D 86	C	213	207	445.4
Distillation (15 percent Recovery)	ASTM D 86	C			456.5
Distillation (20 percent Recovery)	ASTM D 86	C		222	465.2
Distillation (30 percent Recovery)	ASTM D 86	C		238	484.9
Distillation (40 percent Recovery)	ASTM D 86	C		251	506.1
Distillation (50 percent Recovery)	ASTM D 86	C	268	259	526.1
Distillation (60 percent Recovery)	ASTM D 86	C		266	544.9
Distillation (70 percent Recovery)	ASTM D 86	C		274	563.1

Figure 3. Sample results from fuel property query



Heavy Vehicle Chassis Emissions Data - Netscape

File Edit View Go Communicator Help

Heavy Vehicle Chassis Emissions Data

Select Fuel Type or All Fuels. If you're using Windows, press Control and right mouse click at the same time to select multiple fuels. Then press Select to continue.

Fuel Type All Fuels / CARB Diesel / Mossgas COD Synthetic Diesel / Shell Fischer-Tropsch

SELECT RESET

[Ad Hoc Query][Heavy Vehicle Chassis Emissions Data][Glossary]

Figure 4. Heavy vehicle chassis emissions data selection page

The database is also linked to the heavy vehicle chassis emissions data available from various DOE projects managed by NREL. The user can select the fuel which he or she is interested in (see Figure 4). The list only includes fuels for which emissions data are currently available. The emissions query works similarly to the fuel property query, with data displayed in a summary table.

Conclusions

The fuel property database has been designed and developed, and it is being populated with fuel property data from various sources and programs. The database is accessible to DOE research partners via the Internet. This database is a warehouse of fuel properties, and it is one of the significant data sets that will be utilized to develop predictive tools for estimating the effects that fuel properties have on emissions and emissions control system performance.

V. ADVANCED FUELS FOR FUEL CELLS

A. Fuel Composition Effects on Fuel Processing Performance

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

E. CO Poisoning

F. Fuel Processor System Integration and Efficiency

G. Fuel Processor Startup/Transient Operation

Tasks

3. Fuel-Flexible Fuel Processor Component and Materials Development

Objectives

- Explore the effects of various fuels, fuel components and fuel impurities on the performance of onboard hydrogen generation technologies
- Measurement of fuel effects on fuel processor performance and durability
  - Fuel composition and component effects
  - Fuel impurity effects
- Measurement of automotive-scale (50 kW) fuel processor performance and durability
- Measurement of fuel effects on catalyst durability

Approach

- Develop automotive-scale fuel processor test capabilities for:
  - Precision measurement of flow, pressure, temperature, and chemical species;
  - Transient control and measurement; and
  - Operation on hydrocarbon fuels with capability to blend test impurities into fuels and fuel mixtures.
- Examine commercial and LANL prepared catalysts.
  - Measure adiabatic reforming performance; and
  - Determine kinetics and performance under iso-thermal conditions.

Accomplishments

- Completed installation of fuel processor test capabilities including:
  - Gas composition and emissions analysis instrumentation.
  - Experiment automation.
  - Initiated testing with an Autothermal Fuel-Flexible Fuel Processor.
  - Designed, constructed and operated adiabatic catalyst test reactor.
  - Operation of isothermal catalyst test reactor.
  - Received modular pressurized flow reactor.
  - Verified operation of Autothermal Fuel-Flexible Fuel Processor on natural gas.
  - Verified test facility operation and capabilities including reactant management, pressure control, and emissions instrumentation.
  - Initiated testing of liquid hydrocarbon fuels.

Future Directions

- Study fuel processor operation on petroleum-based fuels to evaluate effects of fuel constituents
  - Monitor carbon formation *in situ* by use of adiabatic reactor and laser scattering.
  - Map carbon formation of individual fuel constituents with operating conditions.
  - Examine commercial catalysts to observe carbon formation tendencies.
  - Measure fuel processor operation with individual fuel constituents and fuel blends.
  - Measure fuel processor operation with fuel impurities.
  - Measure fuel processor transient operation including startup/shutdown and variations in flow rates.
  - Use modular reactor to examine fuel effects with a homogeneous reactor.
- Integrate fuel cell stack testing with fuel processor operation to evaluate system integration effects of fuels.

Introduction

This report describes our FY00 technical progress in examining fuel effects on hydrogen generation technology research for the specific purpose of hydrogen production for proton-exchange-membrane (PEM) fuel cells. The goal of this research is to explore the effects of various fuels, fuel constituents and fuel impurities on the performance of on-board hydrogen generation devices and consequently on the overall performance of a PEM fuel cell system utilizing a hydrocarbon fuel.

Fuels and fuel impurities have effects on fuel processor operation, efficiency, reformate gas composition, transient performance, lifetime, and durability. These effects are being investigated through experiments with various fuel processor hardware in Los Alamos National Laboratories' fuel processor test facility. The fuel effects ultimately determine the performance and operation of the fuel cell system from their effect on the anode feed stream composition.

In this report, we describe our progress of examining fuel composition effects on fuel processing, including the use of various fuel

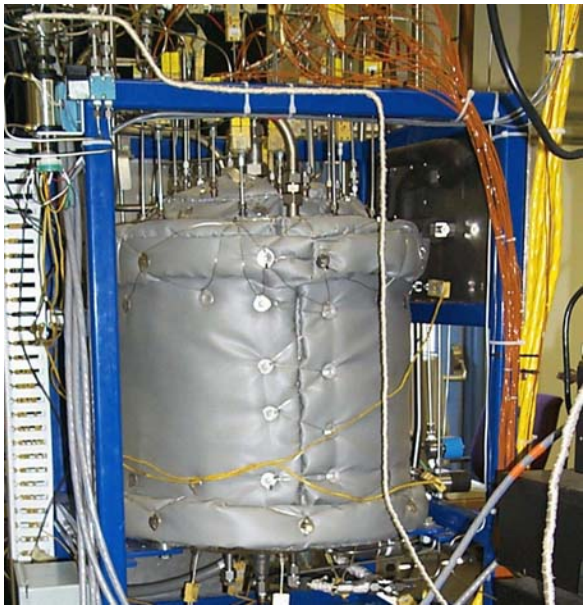

Figure 1. Autothermal Integrated Fuel Flexible Fuel Processor

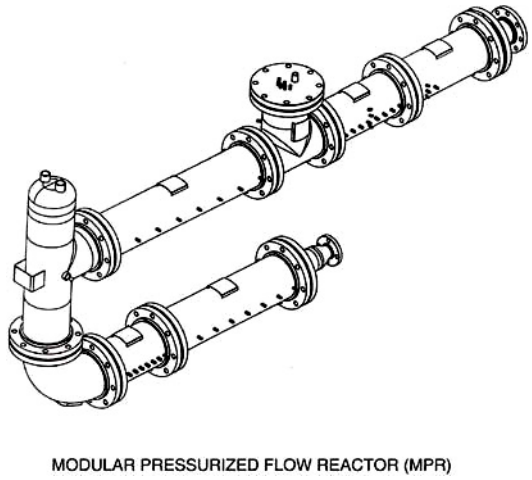

Figure 2. Isometric drawing of the Modular Pressurized Flow Reactor

constituents, fuel impurities, reaction catalysts, fuel processor test reactors and reactor test systems.

Approach: Fuel Processors and Fuel Processor Test Capabilities

The fundamental tools for our research on the effects of fuels and fuel impurities on on-board hydrogen generation technology are the reactor test beds in which the fuel effects are monitored and the gas analysis and catalyst characterization techniques employed in this work. The balance-of-plant framework, the necessary analytical instrumentation

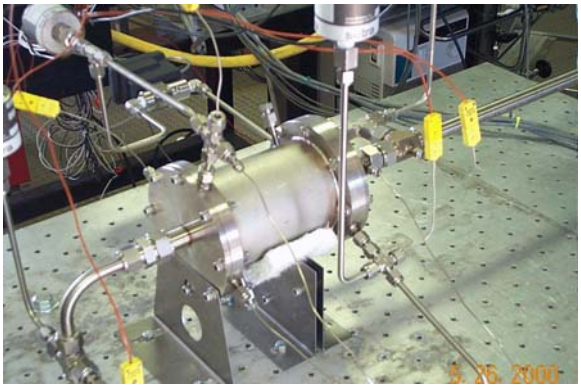

Figure 3. Adiabatic partial oxidation reactor

and the supervisory control to characterize operation and performance of different fuel processors and fuel components allows determination of fuel component effects on fuel processing. Different reactors serve complementary roles in our laboratory, including integrated and modular fuel processing systems, heterogeneous and homogeneous oxidation, and adiabatic and isothermal test beds.

The Fuel-Flexible Fuel Processor (F^3P) is an integrated fuel processor incorporating a partial oxidation reformer (auto-thermal reformer), a high-temperature shift reactor, a zinc oxide sulfur-removal bed, a low-temperature shift reactor, integral steam generator, and combustion-driven fuel vaporizer. This fuel processor is being used for studying the effects of fuels and fuel impurities on a thermally integrated system where the interactions between components are close-coupled. The fuel processor, shown in Figure 1, was received from Hydrogen Burner Technology and was operational as of January 2000. Initial operation of this system was conducted on gaseous fuels, methane and natural gas, after which liquid fuel testing was initiated.

The Modular Pressurized Flow Reactor (MPR) received from Nuvera (Epyx), is a fuel processor incorporating sequential/modular unit operations of the different fuel processing sections. This modular configuration can be seen in the isometric drawing of the reactor shown in Figure 2. This reactor will be installed and made operational in the 4th quarter of FY2000.

An adiabatic reactor for use in evaluating fuel components and the fuel component tendency for carbon formation is shown in Figure 3. This reactor

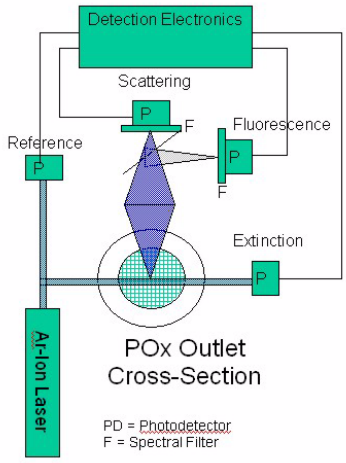

Figure 4. Schematic for the *in situ* measurement of carbon formation

incorporates ease of catalyst replacement, *in situ* carbon formation monitoring, gas and temperature measurements with radial and axial profiles. The reactor was operational in May 2000, the *in situ* carbon formation monitoring will be added in the 4th quarter of FY2000. Figure 4 is a schematic showing laser detection for *in situ* carbon formation. An argon ion laser will be used with extinction monitoring to observe the onset of carbon formation. Scattering will used to observe relative carbon particle size distributions, and spectral detection will allow for fluorescence detection of PAHs (poly-cyclic-aromatic-hydrocarbons).

A micro-scale isothermal catalyst test bed for use in fuel and catalyst measurements under well defined and controlled conditions uses a furnace to keep the reactor under isothermal conditions. This reactor is constructed of a quartz tube with typical catalyst samples of 300 - 500 milligrams.

Results: Fuel Constituent Effects

Initial operation of the autothermal reactor was conducted with gaseous fuels, specifically natural gas and pure methane. The transition between natural gas and pure methane is shown in Figure 5. As the fuel to the fuel processor was changed from natural gas to methane, the reactor control temperature (not shown in Figure 5) decreased. The control software increased the relative O/C ratio, which resulted in a higher auto-thermal outlet temperature. The higher temperature resulted in a

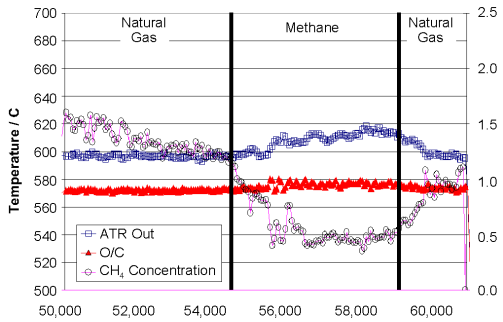

Figure 5. Operation of autothermal reactor showing transition of operation between pure methane and natural gas.

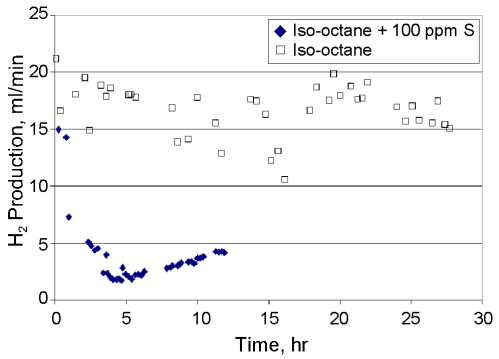

Figure 6. Hydrogen production from iso-octane and iso-octane with 100 ppm sulfur

higher conversion of methane, thus lower methane composition out of the reactor. It appears this is the result of differences in heat of combustion of the fuels. Even though the natural gas composition included 97% methane, calculating the heat of combustion shows significant differences at low O/C. The stoichiometric combustion of methane and natural gas have heat of combustions of 212.8 and 213.9 kJ/mol - less than a 0.5 % difference, however the heat of combustion of the fuels at O/C = 1 is 35.65 and 37.43 which is over 5 % different. The natural gas composition was 97.067% methane, with small amounts of ethane (1.479%), propane (0.203%), butanes (0.0622%), pentanes (0.0197%), C_6 (0.0144%), N_2 (0.172%) and CO_2 (0.978%).

Figure 6 shows hydrogen production from iso-octane and iso-octane doped with 100 ppm sulfur. This test was conducted with a nickel supported on alumina catalyst. The initial hydrogen production, shown in Figure 6 as ml/min, was similar for both

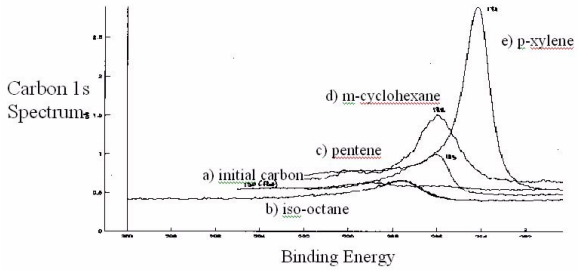

Figure 7. XPS (x-ray photoelectron spectroscopy) of catalysts (a) initial carbon signal, and after partial oxidation with (b) iso-octane, (c) 1-pentene, (d) methylcyclohexane (e) p-xylene

fuel compositions. However, the iso-octane with 100 ppm sulfur within five hours saw reduced hydrogen production, which was the result of much lowered iso-octane conversion. The pure iso-octane fuel has consistent hydrogen production over the test period of 24 hours. The sulfur effect on this catalyst appears to have greatly inhibited both the oxidation and steam reforming kinetics, thus lowering the iso-octane conversion. This effect has been observed to be less severe on nickel catalysts supported on ceria.(1)

Carbon formation has been monitored by the carbon buildup on the catalyst surface over time as a function of different fuel components. Figure 7 shows the XPS (X-ray Photoelectron Spectroscopy) C1s signal for a nickel catalyst sample tested with iso-octane, pentene, methylcyclohexane and xylene. This shows relative carbon formation to be much higher with the aromatic and unsaturated compounds than the aliphatic hydrocarbons.

Conclusions

Test capabilities have been developed which are capable of testing fuel processors with gaseous and liquid fuels. These capabilities provide the balance-of-plant necessary to support operation of fuel processor systems including analytical instrumentation and the supervisory control required to characterize operation and performance of different fuel processors and fuel components.

These capabilities are being used to measure fuel constituent and fuel impurity effects on fuel processor technology. Differences between natural gas and pure methane have been observed which can be explained by the difference in heat of combustion at low O/C ratios. The effect of sulfur on hydrogen production has shown dramatic effects on a Ni/Al_2O_3 catalyst, with hydrogen production (iso-octane conversion) decreasing by over a factor of 3 within only five hours of operation. The tendency for carbon formation has been observed to be a function of the fuel component, with the general trend for carbon formation: xylene > methyl cyclohexane > pentene > iso-octane.

List of References

1. J. Kopasz, "Effects of Fuels/Contaminants on Reforming Catalysts" presented at the Annual National Laboratory R&D Meeting, DOE Fuel Cells for Transportation Program, Richland, WA, June 7, 2000.

List of Presentations

1. "Measurement of the Effects of Fuel Constituents on Fuel Processor Performance," Presentation to the AIChE, Atlanta, GA, March 2000.
2. Presentation at the 2000 Lab Review Meeting, Argonne, IL, May 2000.

List of Acronyms

CNG	Compressed natural gas
F^3P	Fuel-Flexible Fuel Processor
HBT	Hydrogen Burner Technology
kW	Kilowatt
LANL	Los Alamos National Laboratory
MPR	Modular Pressurized Flow Reactor
PAH	Polycyclic Aromatic Hydrocarbons
XPS	X-ray Photoelectron Spectroscopy

B. Effects of Fuel Constituents on Fuel Processor Catalysts

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

E. CO Poisoning

F. Fuel Processor System Integration and Efficiency

G. Fuel Processor Startup/Transient Operation

Tasks

3. Fuel-Flexible Fuel Processor Component and Materials Development

Objectives

- Identify the effects of major constituents, additives, and impurities in petroleum based fuels on reformer performance.
- Determine the effects of alternative fuels (methanol, ethanol, DME, Fischer-Tropsch liquids) on reformer performance.
- Evaluate the effects of fuel constituents and impurities on catalyst stability.

Approach

- Investigate autothermal reforming of major constituents individually in a microreactor.
- Rate performance based on:
  - Byproduct formation,
  - Catalyst deactivation, and
  - Dependence of hydrogen yield and conversion efficiency on temperature and residence time.
- Test selected minor constituents, additives, and impurities by mixing with iso-octane.
- Use long-term tests (1000 h) to determine effects of fuel components on catalyst stability, poisoning and long-term degradation.

Accomplishments

- Completed short-term testing of 6 gasoline components.
- Made recommendations to DOE on benchmark fuel compositions.
- Completed long-term tests on isooctane and two benchmark fuels, one without sulfur, one with sulfur.
- Initiated tests on effects of sulfur impurities.

Future Directions

- Continue investigation of reforming of gasoline constituents - focusing on olefins and minor constituents which may be problematic such as napthalenes and substituted aromatics and begin to look at synergistic effects.
- Investigate effects of additives (detergents, antioxidants) and impurities.
- Investigate differences in sulfur effects with different catalysts.

Introduction

On-board reforming of petroleum based fuels, such as gasoline, may help ease the introduction of fuel cell vehicles to the marketplace. Although gasoline can be reformed, some constituents and impurities may have detrimental effects on the fuel processing catalysts (which may lead to compromised performance and decreased fuel conversion efficiency). In order to identify which constituents are beneficial and which are detrimental to the reformer we have begun a program to test various components of gasoline under autothermal reforming conditions.

The current work focuses on the autothermal reforming of iso-octane, n-octane, trimethylbenzene, toluene, methylcyclohexane, and methylcyclopentane. These chemicals represent the branched paraffins, straight chain paraffins, aromatics, and cyclic paraffins present in gasoline. In addition, we have investigated the effects of sulfur impurities on the reforming of isooctane. These results will be used to help determine the requirements for a fuel cell fuel and determine if a special fuel cell-grade gasoline formulation would improve overall system performance.

Approach

We have chosen representative chemicals from gasoline and are investigating the autothermal reforming of these compounds as a function of temperature and space velocity. Reforming was performed under constant O_2:C and H_2O:C ratios (0.42 and 1.4) on identical catalysts to allow for comparisons between the different chemicals.

Short term (<20h) tests were performed in a reactor designed to allow for sampling at different space velocities. Four sampling ports allow for testing at various positions in the catalyst bed. A small portion (< 1%) of the gas stream is diverted through one of these ports to the residual gas analyzer for analysis. The remainder of the gas stream continues through the reactor bed to the exit stream. Batch sampling can be performed at the reactor exit.

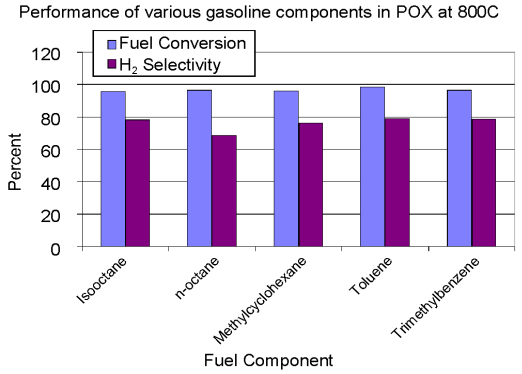

Figure 1. Comparison of Autothermal Reforming Conversion Efficiency and Hydrogen Selectivity for Various Gasoline Constituents

Long-term tests (> 1000 h) were performed to determine the durability of the autothermal reforming catalyst and to determine if there are any long-term problems (poisoning, coking) caused by the fuel components.

Results

Short-term tests

All of the gasoline components investigated to date were converted to a hydrogen rich gas at 800°C and a Gas Hourly Space Velocity (GHSV) of 15,000/h. Conversions were all above 95%. Hydrogen selectivities were generally close to 80% at 800°C (see Figure 1).

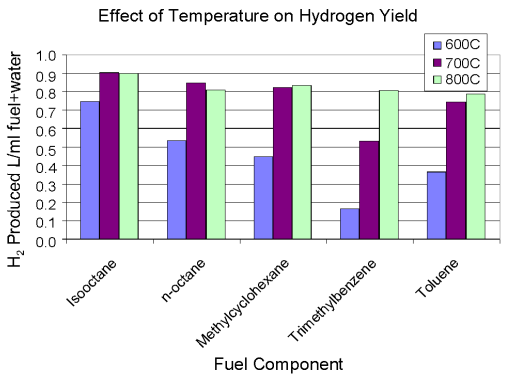

Figure 2. Effect of Temperature on Hydrogen Yield from Autothermal Reforming of Gasoline Constituents

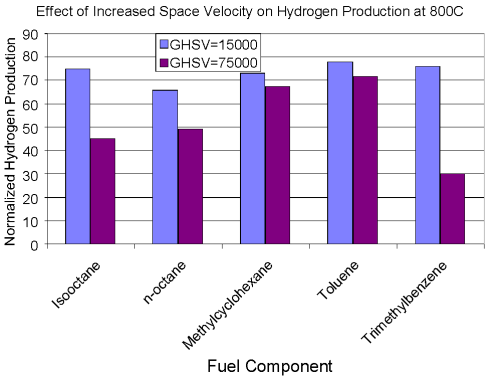

Figure 3. Effect of Increasing GHSV on the Reforming of Various Gasoline Components

The temperature dependence for hydrogen production from several gasoline constituents at a GHSV of 15,000/h is shown in Figure 2. Temperature has the largest effect on trimethylbenzene reforming and the smallest effect on isooctane reforming. The general trend indicates aromatic compounds (trimethylbenzene and toluene) require higher temperatures than napthenes, which require higher temperatures than straight chain and branched paraffins.

We have also investigated the effect of GHSV on autothermal reforming of several gasoline constituents. Results are illustrated in Figure 3. Again, trimethylbenzene reforming is the most sensitive. Hydrogen yield dropped dramatically when the GHSV was increased from 15,000/h to 75,000/h. The next most sensitive components were isooctane and n-octane, while toluene and

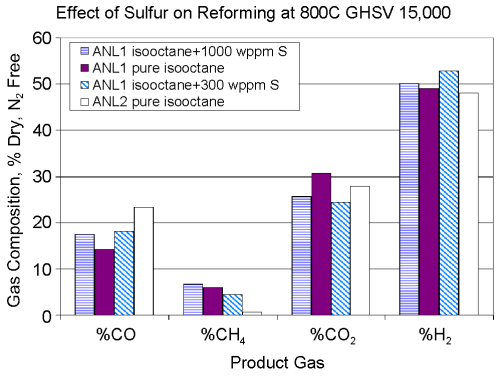

Figure 4. Effect of Sulfur on Isooctane Reforming over Pt Containing Catalysts

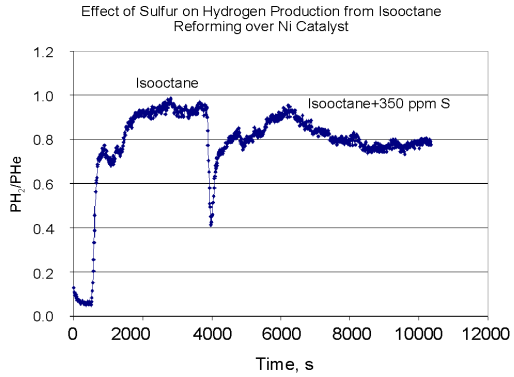

Figure 5. Effect of Sulfur on Isooctane Reforming Over a Ni Containing catalyst

methylcyclohexane were the least sensitive to increases in GHSV.

Effect of Sulfur

Sulfur impurities may pose a large problem for fuel processing. To determine the effects of sulfur impurities on the autothermal reforming catalyst we have reformed isooctane doped with benzothiophene to provide sulfur levels of 300 and 1000 wppm S. A comparison of the hydrogen production from pure isooctane and sulfur doped isooctane reformed over two different Pt containing catalysts is shown in Figure 4. For both catalysts hydrogen production was higher for the isooctane with sulfur added than for pure isooctane.

Nickel was substituted for Pt in the preparation of our ANL catalyst, and the sulfur tolerance of this catalyst was investigated. The results are shown in Figure 5. Reforming was initiated with pure isooctane. At ~ 4000 s the fuel was switched to

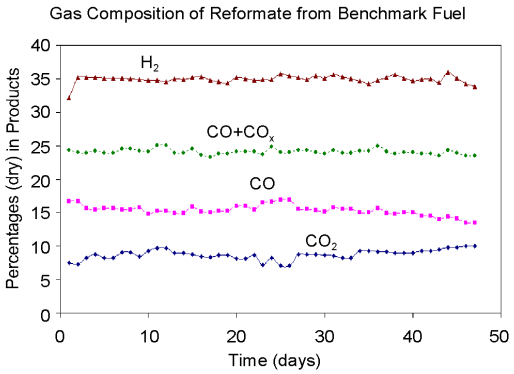

Figure 6. Long-term Test Indicates Little Degradation over 1000 h of Operation with Benchmark Fuel

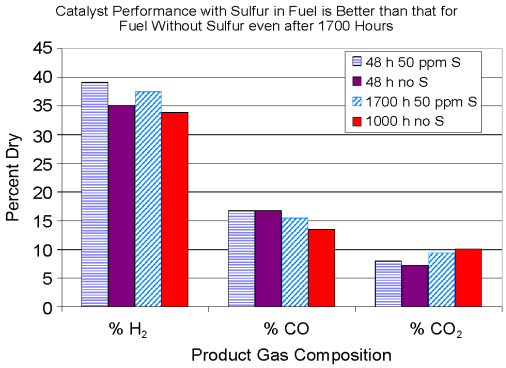

Figure 7. Comparison of Long-Term performance with Benchmark Fuel and Benchmark Fuel+50 wppm S

isooctane doped with benzothiophene to provide 380 wppm S. After the fuel was switched the hydrogen production returned to the level observed with pure isooctane, but then decreased. Eventually the hydrogen production leveled off about 15% lower than that for pure isooctane. The fuel was switched back to pure isooctane and reforming continued for several hours. After this period the hydrogen production had returned to the initial level observed for pure isooctane over the virgin Ni catalyst.

Long-term Tests

Long-term (≥ 1000 h) tests were performed on Pt containing catalysts under autothermal reforming conditions. Tests were performed at temperatures of 700 to 750°C at a GHSV of 4400/h, with start/stop cycles to provide thermal cycling. Product gas composition was followed over the length of the tests to determine if there was any substantial degradation in catalyst performance over time. Results with isooctane indicate the total gas output dropped by 6% after 1000 h of operation while the hydrogen output dropped by approximately 10%. Test results for a benchmark fuel (74 wt% isooctane, 20 wt% dimethylbenzene, 5 wt% methylcyclohexane and 1 wt% 1-pentene) are shown in Figure 6. There was less than a 5% decrease in hydrogen production after 1000 h of operation.

The effects of sulfur on long-term performance were investigated by doping the benchmark fuel with benzothiophene to provide a sulfur content of 50 wppm. Results again indicated an increase in hydrogen production for fuel containing sulfur compared to fuel with no sulfur present, even after 1700 h. A comparison of the catalyst performance with the benchmark fuel plus sulfur to the benchmark fuel without sulfur is shown in Figure 7.

Conclusions

This work indicates that all of the major types of chemicals found in gasoline (straight-chain and branched paraffins, napthenes, and aromatics) can be autothermally reformed to provide a hydrogen rich gas. Of the components tested trimethylbenzene required the most severe reforming conditions, requiring both high temperature (800°C) and low space velocities. This suggests a gasoline without trimethylbenzene would lead to higher overall efficiency and may allow for smaller catalyst beds operating at lower temperatures. The effects of sulfur impurities on the catalyst are dependent on the catalyst. Sulfur appears to improve the hydrogen yield for Pt containing catalysts but appears to reversibly poison Ni containing catalysts. There was no major long-term degradation caused by adding unsaturated components or sulfur to the fuel.

List of Publications

1. Summary of work published in *Advances in Hydrogen Energy*, Kluwert Academic Publishing, 2000.

List of Presentations

1. Presentation at the 1999 ACS National Meeting.
2. Presentation at the 2000 AIChE Annual Meeting.
3. Presentation at the 2000 Fuel Cell Seminar.

List of Acronyms

DME	Dimethyl ether
DOE	U.S. Department of Energy
GHSV	Gas Hourly Space Velocity
Ni	Nickel
Pt	Platinum
S	Sulfur

C. Sulfur Removal from Reformate

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This Project addresses the following OTT R&D Plan Barriers and Tasks:

Barriers

E. CO Poisoning

F. Fuel Processor System Integration and Efficiency

G. Fuel Processor Startup/Transient Operation

Tasks

3. Fuel-Flexible Fuel Processor Component and Materials Development

Objectives

- Define maximum H_2S concentration for fuel processor and fuel cell catalysts.
- Develop a sulfur removal process based on adsorption technology that reduces the H_2S concentration in reformate to <1 ppm under fuel processing conditions.
- Determine the appropriate operating parameters (e.g., H_2S equilibrium, sulfur loading, temperature, space velocity) for candidate adsorbents.
- Evaluate the performance of the candidate adsorbents in both a microreactor test system and an integrated fuel processor system.
- Identify and develop alternative sulfur removal technologies if required to meet sulfur tolerance requirements of new catalysts.

Approach

- Perform thermodynamic calculations to estimate H_2S tolerance of fuel processor and anode catalysts (bulk sulfide formation) and to predict H_2S equilibrium partial pressure for candidate adsorbents.
- Conduct modeling to optimize the geometry of the adsorbent, identification of key parameters governing performance, and prediction of lifetimes and transient responses of candidate adsorbents under fuel processing conditions.
- Fabricate new structured forms of ZnO which optimize reactivity while minimizing the weight of ZnO required.
- Complete experimental work to verify design parameters and to evaluate process performance in both a microreactor test system and an integrated fuel processing system.

Accomplishments

- Fabricated two new structured forms of ZnO, a ZnO-coated cordierite monolith and a self-supporting ZnO layer in a spiral microchannel configuration.
- Demonstrated that the self-supporting ZnO layer is capable of reducing the H_2S concentration in a simulated reformate stream from 10-30 ppm to less than 1 ppm.

Future Directions

- Evaluate the performance of the new structured forms of ZnO in a 1000-h test in a microreactor fuel reformer.
- Define better the H_2S tolerance for the fuel processor and fuel cell catalysts.
- Identify new/alternative technologies for H_2S removal.

Introduction

Even with the lower sulfur content proposed for gasolines in 2004 of 30 ppm average and 80 ppm maximum (by weight), reformate produced from these gasolines by autothermal reforming for use with PEMFC will contain 3-8 ppm of H_2S. H_2S is known to poison many catalysts, often at a concentration of 1 ppm or less. For example, an inlet H_2S concentration of 50 ppb is recommended for copper-zinc oxide water-gas shift catalysts being considered for use in fuel processing systems by some developers. It has been reported (1) that H_2S at a concentration of 1 ppm irreversibly poisons the Pt-anode catalyst in the PEMFC.

In FY1999, we conducted a review of the technical and patent literature to identify candidate technologies for removing H_2S from reformate under fuel processing conditions. We identified adsorption with chemical reaction as the most promising technology. Based on thermodynamic equilibrium calculations, we identified candidate metals and metal oxides that are capable of reducing the concentration of H_2S to <1 ppm, are thermodynamically stable, and does not promote any undesirable chemical reactions under fuel processing conditions. Based on these criteria ZnO was selected as the initial test candidate. A sulfur removal unit, using commercially available ZnO pellets, was sized based on manufacturer-supplied operating parameters.

Figure 1. ZnO-coated cordierite monolith. ZnO weight loading is 40 wt%

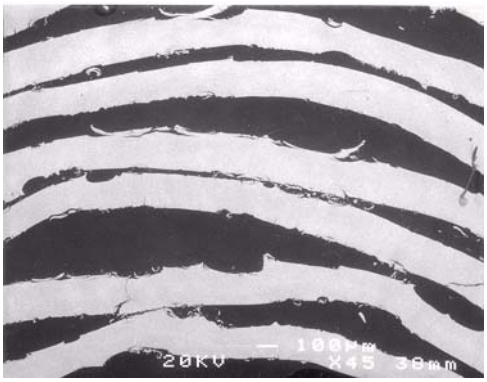

Figure 2. Self-supporting ZnO layer in the form of a spiral microchannel configuration

Approach

Our approach involves both modeling and experimental work. Thermodynamic equilibrium calculations are used to predict the optimal operating

Bed Form	Space Velocity [1] (hr^{-1})	Sulfur Content of Gasoline (ppmw)	Lifetime of Bed [2] (gals of gasoline)	Weight of Bed [3] (kg)
Pellet	2000	30	8×10^4	31.0
Structured	5000	30	6×10^3	5.4

[1] Based on 20 kWe power.

[2] Based on 50% of stoichiometric loading of ZnO bed (~18 g S/g ZnO).

[3] Weight of bed is based on a density of 2 g/cm^3 for both the pellets and the structured form.

Table 1. Comparison of the estimated size and weight of a sulfur removal unit using commercial ZnO pellets and a structured form of ZnO

conditions for candidate sulfur adsorbents, such as ZnO. Once the optimal operating conditions are defined, gas-solid reaction models, such as the shrinking core model, are used to define the optimal geometry of the adsorbent and to predict the performance of the adsorbent under processing conditions. Based on such modeling, a structured form of ZnO, such as a monolith or a microchannel configuration, consisting of a thin ZnO layer (~50-100 μm) is predicted to be more reactive per unit volume and to use the ZnO more effectively than a cylindrical pellet form for removing H_2S from reformate in a fuel processor.

Two new structured forms of ZnO have been fabricated including a ZnO-coated cordierite monolith (see Figure 1) and a self-supporting ZnO layer in a spiral microchannel configuration (see Figure 2). The ZnO-coated monolith was fabricated using a slurry coating process to deposit a ~50 μm thick layer of ZnO onto a cordierite monolith. The self-supporting ZnO microchannel was fabricated using a tape casting and rolling process to produce a ZnO layer with a thickness of ~100 μm.

The H_2S removal efficiency of these new structured forms of ZnO was evaluated in a microreactor test system using a simulated reformate stream consisting of 10-100 ppm H_2S. The removal efficiency was determined by measuring the H_2S concentration in the effluent stream (using gas chromatography) as a function of the H_2S concentration in the inlet stream, temperature, and gas hourly space velocity.

Results

The self-supporting ZnO layer in a spiral microchannel configuration was capable of reducing the H_2S concentration in a simulated reformate stream from 10-30 ppm to less than 1 ppm at 400°C and space velocities up to 8,000 h^{-1}. For comparison, a space velocity of 700-2,000 h^{-1} is recommended for commercial ZnO in pellet form. It is estimated that the higher reactivity per unit volume of a structured form of ZnO will significantly reduce the weight and volume of the sulfur removal unit (by as much as ~80%) compared to a unit that uses the pellet form as illustrated in Table 1.

The performance of the ZnO-coated cordierite monoliths produced in-house did not meet expectations due primarily to non-uniform coating of the monolith channels. Currently, we have contracted a commercial catalyst company with expertise in coating monoliths to produce a ZnO-coated monolith for evaluation.

Long-term performance of these new structured forms of ZnO will be tested in a microreactor fuel reformer for 1000-h and in an integrated fuel processing system being developed at ANL. Developmental work will continue to improve the reactivity and mechanical properties of these new structured forms. Experimental work will focus on better defining the H_2S tolerance of various catalysts, such as reforming, water-gas shift, and selective CO oxidation, being developed for fuel processing.

Conclusions

The ability of the self-supporting ZnO layer verifies that under the test conditions, the ZnO adsorbent bed can be used for the capture of H_2S in gasoline reformate. Removal of H_2S from the fuel gas is essential if the high performance of the fuel cell stack is to be maintained when operating the fuel cell system with sulfur-containing fuels. New

adsorbents, as well as alternative technologies, will be investigated if new catalysts being developed require lower H_2S concentrations than can be achieved with ZnO.

List of References

1. T. Zawodzinski, J. Bauman, T. Rockward, B. Mueller, T. Springer, F. Uribe, J. Valerio, and S. Gottesfeld: "R&D on Optimized Cell Performance for Operation on Reformate and Air," Presented at DOE Fuel Cells for Transportation National Laboratory R&D Meeting, June 23-25, 1999, Argonne, IL.

List of Presentations

1. T. Krause, D. Myers, and C. Pereira, "Reducing the Volume/Weight of the Fuel Post Processor for PEFC Power Systems", to be presented at the Fuel Cell 2000 Conference, October 30-November 2, 2000, Portland, Oregon.
2. T. Krause, J.P. Kopasz, S. Ahmed, and M. Krumpelt, "Gasoline-How its Composition Effects Reforming and the Implication for Developing New Catalysts for On-board Reforming for Fuel Cell Vehicles", to be presented at the Annual Meeting of the American Institute of Chemical Engineers, November 12-17, 2000, Los Angeles, California.

List of Acronyms

ANL	Argonne National Laboratory
PEMFC	polymer electrolyte membrane fuel cell

D. The California Fuel Cell Partnership

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Objectives

- Demonstrate fuel cell technology by operating and testing vehicles on California's roads.
- Demonstrate alternative fuel infrastructure technology.
- Explore the path to commercialization.
- Increase public awareness through a coordinated outreach plan.

Approach

- Adopt an organizational structure consisting of an Executive Committee, Project Group and communications group to provide a decision-making structure for developing a workplan, budget, headquarters facility, and outreach strategy under the following timetable:
  - Phase I - through 1999, project development and planning, adding new partners, and preparing vehicle and refueling facilities;
  - Phase II - 2000-2001, demonstrate cars and buses using hydrogen fuel; and
  - Phase III - 2002-2003, demonstrate more cars and buses using hydrogen, methanol, gasoline or other fuels as determined by the Partnership.

Accomplishments

- Startup budget developed.
- Additional partners added.
- Plans for initial vehicle arrival and location determined.
- Commercialization study commissioned.
- Headquarters facility under construction.
- Hydrogen fueling structure identified and planned.

Future Directions

- Prepare for on-road fuel cell car and bus demonstrations; identify additional fueling sites and fuel choices; assess commercialization issues; and implement public outreach and education plans.

Figure 1. The CaFCP Logo

Figure 2. California Governor Gray Davis Announces the Partnership at the State Capitol on April 20, 1999

Introduction

The California Fuel Cell Partnership (CaFCP) is a path-breaking collaboration of auto companies, energy providers, fuel cell companies and government agencies that will place fuel cell electric vehicles on the road in California. The partners include companies and organizations from around the world: DaimlerChrysler, Ford, Honda, Hyundai, Nissan, and Volkswagen; Ballard Power Systems and International Fuel Cells; BP Amoco, Shell, and Texaco; and the California Air Resources Board, the California Energy Commission, the United States Department of Energy, the United States Department of Transportation and the South Coast Air Quality Management District.

The partners are working together to achieve a common vision - preparing to commercialize the emerging vehicle technology of the 21st Century. The partnership will demonstrate fuel cell electric vehicles in California through 2003 under day-to-day driving conditions. Vehicle maintenance and fueling facilities will be constructed and used throughout the course of the project. The partnership will also explore the path to commercializing fuel cell electric vehicles by examining such issues as fuel infrastructure requirements, vehicle and fuel safety, market incentives, and consumer acceptance. The partnership will increase public awareness of fuel cell vehicle technology and the benefits it can offer through a number of outreach tools, including hands-on vehicle demonstrations and classroom curricula.

Figure 3. Partners "dig in" at the fuel cell facility groundbreaking ceremony on April 18, 2000

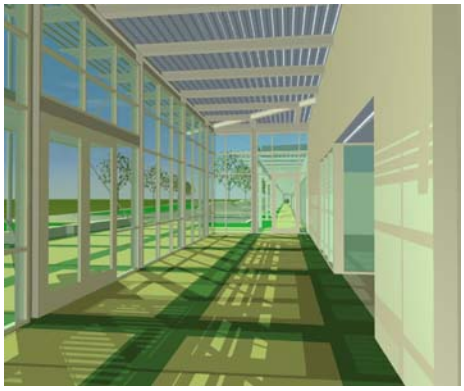

Figure 4. Architectural image of fuel cell facility, due to be completed in fall 2000

Approach

While the CaFCP consists of a variety of industries and government agencies, all members have one thing in common: a desire to demonstrate fuel cell vehicle technology and promote its commercialization. It is an entirely voluntary commitment for all the partners, and one that depends on industry's firm belief that this is a viable technology for the future.

To demonstrate fuel cell technology, over 70 vehicles will be driven on city streets and highways to test and demonstrate how they can meet the real transportation needs of California consumers. A fueling infrastructure for fuel cell vehicles will also be demonstrated, beginning with hydrogen fuel in the first stage of the project. Methanol and a gasoline cleaner than California RFG will be added in the later stages of the program. The partners also hope to promote the development of standards and specifications for fuels and the vehicle-fueling interface. This is a key benefit of bringing together vehicle manufacturers and fuel providers early in the process.

The partners plan to conduct joint commercialization studies that examine the consumer market, identify opportunities and challenges to using various fuels and infrastructure, and identify initiatives that can promote success. They plan to provide input to the development of codes and standards for vehicles, fuels and facilities. They will also promote the development of educational materials, safety procedures and emergency response training materials.

The partnership will take steps to broaden public awareness of fuel cell vehicles and their potential to provide environmental and vehicle performance benefits. This is a critical element of the program, as less than one in four Californians currently knows about fuel cells. The vehicles will be available for demonstrations in a variety of public venues. The Partnership's Internet website (www.drivingthefuture.org) will provide educational information.

The CaFCP is also constructing a facility in West Sacramento to be completed in fall 2000. This facility will house the partnership offices, a public gallery with fuel cell displays, and vehicle bays where the auto partners will house, service and maintain the fuel cell passenger cars. There will also be a hydrogen fuel station on-site.

The state-of-the-art facility will meet all safety and technical requirements. But most importantly, it makes a statement about the nature of the partnership. This one-of-a-kind venture will bring together competitors under one roof as they work toward a common goal, and underscores their true commitment to making the project a success.

Conclusion

The first year of the project has produced remarkable progress given the unique dynamics of this partnership. A cooperative approach, focused on specific goals and the necessity for consensus-based decisions, has set the stage for success in the on-road demonstration phase, generating win-win benefits for the environment and the new economy.

Special Recognitions and Awards

1. Blue Sky Innovation Award™ from CALSTART - the advanced transportation consortium - for taking early steps to create a fuel cell market by demonstrating fuel cell electric vehicles in California

List of Acronyms

CaFCP	California Fuel Cell Partnership
RFG	Reformulated Gasoline

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