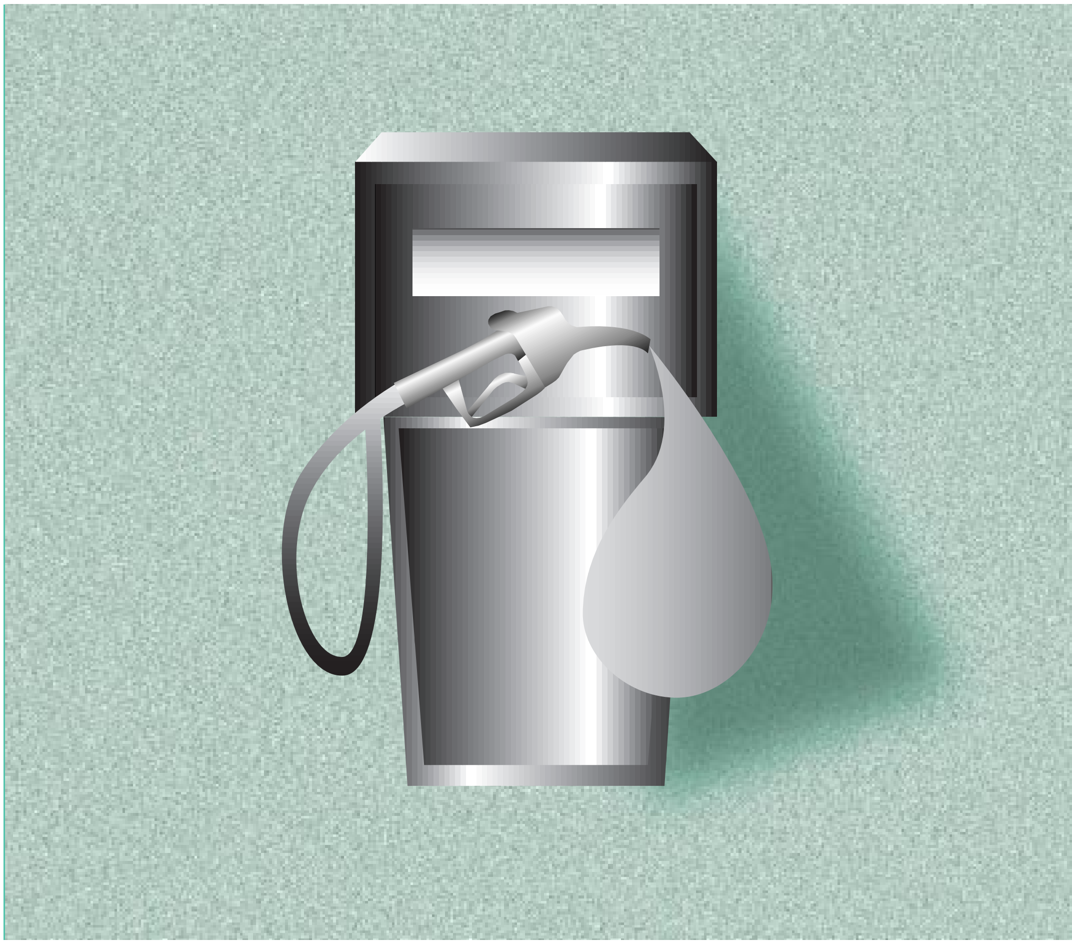
FUELS FOR ADVANCED CIDI ENGINES AND FUEL CELLS

2001 ANNUAL PROGRESS REPORT



U.S. Department of Energy

Energy Efficiency and Renewable Energy

Office of Transportation Technologies

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.

U.S. Department of Energy
Office of Transportation Technologies
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Washington, DC 20585-0121

FY 2001

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 2001

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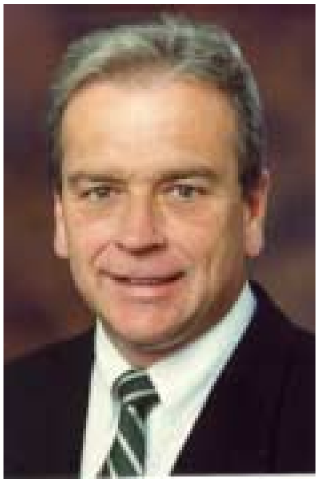
Enabling Advanced Vehicle Technologies through Development and Utilization of Advanced Petroleum-Based Fuels

John Garbak, Program Manager, Fuels for Automotive Advanced CIDI Engines

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



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

Kevin Stork, Program Manager, Heavy Duty Alternative Fuels

On behalf of the Department of Energy's Office of Transportation Technologies (OTT), we are pleased to introduce the Fiscal Year (FY) 2001 Annual Progress Report for the Fuels for Advanced CIDI Engines and Fuel Cells Activity which is part of the Fuels Utilization 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. This Activity is currently focused on: 1) 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, and 2) on ways of supplying hydrogen for fuel cell 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 Activity. Fuels R&D is also coordinated with the Combustion and Emission Control R&D for Advanced CIDI Engines Program and Transportation Fuel Cell R&D Activities (which have their own separate reports), which rely on this Activity for fuels that will enable them to meet their out-year objectives.

Since its inception, the Fuels for Advanced CIDI Engines and Fuel Cells Activity has supported the government/industry Partnership for a New Generation of Vehicles (PNGV) through its technology research projects. The partnership goals are being re-evaluated to identify changes that will maximize the potential national petroleum-savings benefit of the emerging technologies. When these goal changes have been defined, OTT will adjust the focus of its technology research programs accordingly. The

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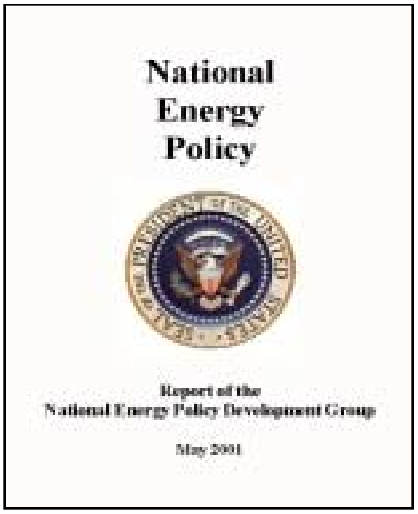
[1] Multiyear Program Plan, Advanced Petroleum-Based Fuels (APBF) RD&T for Compression-Ignition, Direct Injection Engines and Emission Control Systems, DOE Office of Advanced Automotive Technologies and Office of Heavy Vehicle Technologies, November 1, 2000.



The National Energy Policy Report is available from www.whitehouse.gov/energy

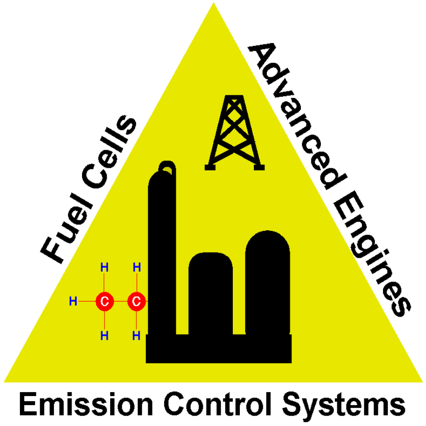
work in advanced petroleum-based fuels is conducted through joint programs with the energy and automotive industries. Advanced petroleum-based fuels will also be necessary for the 21st Century Truck Initiative that proposes to triple medium-duty truck fuel economy and double heavy-duty truck fuel economy on a ton-mile per gallon basis to meet its goals. In FY 2001, the APBF Activity was focused on developing and testing selected advanced fuels in combination with near-term emission control technologies in CIDI engines and transportation fuel cell power systems.

In his second week in office, President Bush established the National Energy Policy Development (NEPD) Group. The NEPD Group released the National Energy Policy (NEP) report in May 2001 which includes key recommendations for a National Energy Policy. The NEP took a critical look at our current energy supplies and demands, and made several recommendations for moving forward to correct imbalances. One of the major imbalances is supply and demand for petroleum fuels. Our highway transportation system is entirely dependent on petroleum fuels (with the exception of about 3 percent oxygenates added to gasoline). While vehicles today are more efficient than 25 years ago, the average fuel economy of new vehicles has not changed over the past 10 years, in part due to the growth of low fuel economy light trucks (pickups, vans, and sport utility vehicles). The NEP recommended that consideration be given to increasing the fuel economy of new vehicles without negatively impacting the U.S. automotive industry. Advanced Petroleum-Based Fuels R&D activities go to the heart of increasing the fuel economy of light trucks and cars in the U.S., in a cooperative manner with the U.S. automotive industry to assure that the necessary technology is ready and available for them to implement.

This report highlights progress achieved during FY 2001 and comprises 25 summaries of industry and National Laboratory projects that were conducted. It provides an overview of the exciting work being 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 Transportation Fuel Cell R&D Activities. 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; the effects of hydrocarbon fuel characteristics on fuel cell reformers; and the health and safety, materials compatibility, and economics of advanced petroleum-based fuels. A brief snapshot of FY 2001 accomplishments and new directions for FY 2002 is captured on the following pages. We are encouraged by the technical progress realized in FY 2001 and look forward to making further advancements in FY 2002.

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.

The APBF Activity is determining the effects of fuel composition on the efficiency and emissions performance of emerging, advanced compression ignition, direct injection (CIDI) engines. Through this research, the APBF Activity will identify the most suitable fuels for these engines. Sulfur content is a very important issue for the APBF Activity. The most desirable emission control devices for nitrogen oxides (NO_x) are deactivated by sulfur in currently available fuels. Results from the APBF Activity were a primary source of information used by the U.S. Environmental Protection Agency (EPA) to establish new diesel fuel sulfur content standards (i.e., 15 ppm maximum) beginning in 2006. Testing to date indicates that current generation NO_x emission control devices are not durable enough to withstand the combined sulfur from consumed lubricating oil plus 15 ppm sulfur content fuel. Future work will focus on quantifying the effect of fuel sulfur content on the durability of NO_x emission control devices, the need for sulfur traps, the development of desulfurization strategies using engine controls, and reductant technologies such as late cycle injection.



During the past year, the EPA finalized new emission regulations for heavy-duty diesel engines (0.2 g/bhp-hr NO_x and 0.01 g/bhp-hr PM). This virtually ensures that heavy-duty CIDI engines will need similar emission control devices as needed by light-duty CIDI vehicles to meet the Tier 2 standards. 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 lives.

Automobile
Ford
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DaimlerChrysler
Toyota

Engines
EMA
Caterpillar
Detroit Diesel
Cummins
John Deere
Mack Trucks
International Truck & Engine

Government
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Technology
Battelle

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MECA
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3M
Engelhard
Siemens
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Clean Diesel Tech.
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Rhodia
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PennzoilQuaker State
Lubrizol
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Chevron Products
Ergon
Valvoline
Motiva
Infineum

Participants in the APBF-DEC Project

A major component of the APBF Activity is the Advanced Petroleum-Based Fuels - Diesel Emission Control project (APBF-DEC). The APBF-DEC is an industry/government project to identify and evaluate: (1) the optimal combinations of low-sulfur diesel fuels, lubricants, diesel engines, and emission control systems to achieve ultra-low NO_x and PM emissions for the 2001 to 2010 time period; and (2), properties of fuels and vehicle systems that could lead to even lower emissions beyond 2010. The activities being conducted under the APBF-DEC include both light-duty and heavy-duty CIDI engines. A systems approach is being used, i.e., simultaneously investigating fuels, lubricants, engines, and emissions control systems. A government/industry steering committee and working groups are guiding the APBF-DEC project.

Another important component of the APBF Activity is the co-operative projects being conducted with the Ad-Hoc Auto/Energy Working Group[1]. Phase I of the Ad-Hoc program looked at engine-out emissions of a diesel fuel with dimethoxy methane, an oxygenated diesel fuel additive. The results from this study showed that this oxygenated fuel additive significantly lowered PM and PAH emissions compared to the base diesel fuel, and its emissions were essentially equivalent to a Fisher-Tropsch fuel. In Phase II, a

Hydrogen Fueling Facility at the California Fuel Cell Partnership

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1. The Auto/Energy Ad-Hoc Working Group consists of the three U.S. automakers, several energy providers (BP, ExxonMobil, Shell, Marathon Ashland, Phillips, and Citgo/PDVSA), and DOE. Their primary purpose is to explore the effects of fuel formulation on emissions.

new set of fuels will be evaluated, including different oxygenates blended in refinery produced low-sulfur fuels. The goal of Phase II is to determine the impact these fuels have on the physical and chemical characterization of PM after an oxidation catalyst and a diesel particulate filter.

Clean hydrocarbon fuels and competitively-priced hydrogen are needed to make fuel cell vehicles a practical reality

While CIDI engines are viewed as a nearer-term opportunity to create fuel efficient cars and light trucks, fuel cells are seen as a promising longer-term technology that will be capable of achieving unprecedented 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 stored directly onboard, or produced onboard from methanol, ethanol, natural gas, or gasoline. The fuels effort to support the Transportation Fuel Cell R&D Activity is currently focused on determining the effects of petroleum fuels on the fuel cell system performance and identifying advanced petroleum-based fuel constituents that will not compromise the fuel cell's inherently high efficiency. Hydrogen stored directly onboard is acknowledged to be the best in terms of energy efficiency and durability though its energy storage density is currently too low to achieve acceptable vehicle operating range. Additional challenges to direct hydrogen for fuel cell vehicles include developing a production and distribution infrastructure and being able to deliver hydrogen safely at a competitive price, all of which are being evaluated as part of the Activity.

SIGNIFICANT FY 2001 ACCOMPLISHMENTS

In FY 2001, much effort continued on the determination of the effects of fuel sulfur content on CIDI NO_x and PM emission control devices. From this work, preliminary findings indicate that NO_x emission control devices currently do not have sufficient durability to last the full useful life of the vehicle due to sulfur contamination from the combined contributions of 15 ppm sulfur fuel and consumed lubricating oil. Future work will focus on quantifying the effect of sulfur (from the fuel and lubricating oil) on emission control device durability, and the need for sulfur traps and development of desulfurization strategies to attain full useful life operation.

Last year, it was shown that oxygenated diesel fuels have the potential to lower engine-out NO_x and PM emissions and to complement the operation of exhaust emission control devices. An initial set of 71 oxygenates was reduced to two, based on physical and chemical properties, compatibility with diesel fuel and diesel vehicles, and economic viability. This year, Lawrence Livermore National Laboratory completed an extensive environmental assessment of the two best oxygenates and initiated analysis of their combustion kinetics to identify why they reduce PM emissions, and Sandia

<u>Notable FY2001 Accomplishments</u>

- Showed that oxygenates can improve EGR tolerance of CIDI engines resulting in significant NO_x and PM emission reductions with potential to meet "fuel reformulation" targets, see Appendix B).
- Developed new measurement technique to determine the origin of PM from CIDI engines, from both the fuel and lubricating oil.
- Completed environmental assessments of dibutyl maleate and tripropylene glycol monomethyl ether.
- Demonstrated that ultra-low sulfur diesel fuel and catalyzed PM traps can reduce HC, CO, and PM by 91 to 99% (preliminary results from an on-going heavy-duty vehicle demonstration).
- Developed a model to compare costs of fuel cell vehicle fuels.
- Completed a technical and economic analysis of the barriers to fuels for fuel cell vehicles.
- Identified the components of gasoline best suited for on-board reforming in fuel cells vehicles.

National Laboratories included them in their combustion studies using laser imaging techniques.

In the fuel cell area, work continues 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 2001, DOE continued its work with the California Fuel Cell Partnership and contributed analyses and information about the energy, emissions, and greenhouse gases generated by various fuels from "well-to-pump." The overall objective of the Partnership is to demonstrate the practicality of fuel cell vehicles, initially operating with hydrogen as fuel. Over the past year, they have held numerous promotional events that educate the public about the benefits of fuel cell vehicles.

The following brief summaries list the highlights of research and testing conducted in the APBF Activity during FY 2001.

APBF-DEC Initiates Six New Projects

Six new APBF-DEC projects commenced in FY 2001 studying the following: (1) effects of lubricant composition on emissions, (2) effects of fuel composition on selective catalytic reduction (SCR)/diesel particle filter (DPF) systems, (3) assessment of infrastructure issues for SCR, and (4) three projects on the effects of fuel composition on NO_x adsorber/DPF systems (passenger car, pickup truck, heavy-duty engine). These projects build on the earlier APBF-DEC results which showed that low sulfur fuels are needed to make NO_x adsorber catalysts viable and to limit sulfate PM from oxidation catalysts and catalyzed particulate filters. Reports from the earlier completed APBF-DEC projects are available from http://www.ott.doe.gov/decse/. The following are highlights from the new APBF-DEC projects initiated this year which are focused on longer term impacts of fuels and lubricants on diesel emission control devices.

Effects of Lubricant Composition on Emissions

As engine-out emissions are decreased and durability requirements are increased (in 2004, heavy-duty engine emission control system durability requirements will be increased to 435,000 miles), the effect of consumed lubricating oil becomes more important. Consumed lubricating oil can contribute sulfur and ash to the exhaust gases, speeding degradation of emission control devices. This project is underway using a 1999 International T444E-HT engine with EGR. The engine has been setup in the laboratory, engine speed/load operating points have been chosen, EGR rates have been established, and the emissions measurement system has been verified to work properly. After the oil consumption rate of the engine and test repeatability have been determined, the main test protocol will be initiated.

Effects of Fuel Composition on SCR/DPF Systems

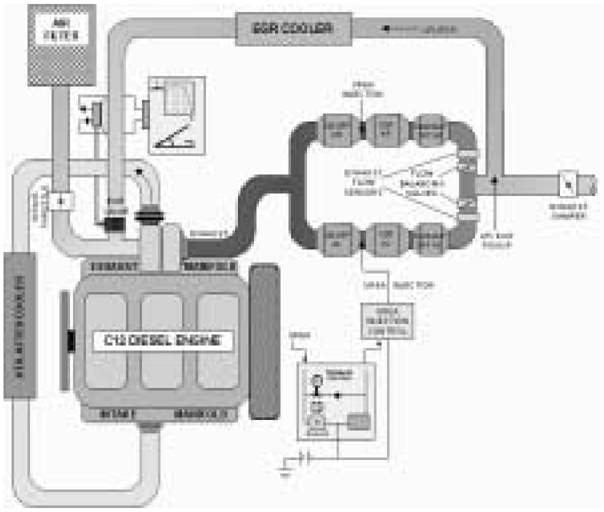
Selective Catalytic Reduction (SCR) using urea as a reductant is gaining support as a NO_x reduction technology for CIDI engines. This project (with technical support provided by Oak Ridge National Laboratory and with Southwest Research Institute as a subcontractor) will evaluate the urea-SCR and its sensitivity to fuel variables. The objectives of the project are to:

- Demonstrate the low-emissions performance of advanced diesel engines plus urea-SCR and diesel particulate filters (DPF)

- Determine the regulated and unregulated emissions with and without emissions controls
- Examine the durability of emission control systems
- Determine toxic and unregulated emission levels
- Evaluate the sensitivities of the emission control devices to fuel variables

In-kind contributions of important elements of the experimental setup have been received from the following organizations:

- Caterpillar - two C12 engines
- STT (Sweden) - Low-pressure loop EGR system
- Robert Bosch - Urea injection system
- Manufacturers of Emissions Control Association (MECA) - SCR catalysts and DPF systems

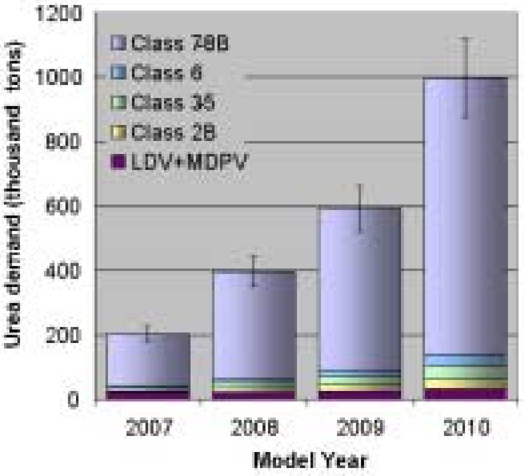


Schematic Layout of Engine and Emission Control System

Two different SCR systems, combined with DPF systems, will be provided by MECA in order to gain experience with different technologies. A fuel matrix of three fuels (minimum) will be evaluated, emphasizing the influence of fuel sulfur level on the performance of the systems.

Assessment of Infrastructure Issues for SCR

Urea is a very effective reductant for SCR systems and a leading contender for use in commercial systems. Urea is widely used as fertilizer and in industrial products, but use in vehicles with CIDI engines would represent an entirely new market. A.D. Little is conducting an assessment to determine what barriers producing and distributing urea might present to using SCR systems. They found that no new or specialized technology needs to be developed to distribute urea to the transportation market, but additional storage would be required at dispensing stations, and specialized dispensing technology may be needed. They also determined that sufficient urea production capacity exists worldwide to meet the demand, even assuming all CIDI vehicles use urea-SCR, and the retail price is likely to be in the range of \$0.70 to \$1.00 per gallon depending on whether the urea is domestically produced or imported.



Potential Urea Demand from New On-Road CIDI Vehicles

Effects of Fuel Composition on NO_x Adsorber/DPF Systems (Three Separate Projects)

NO_x adsorber catalysts and DPFs offer the potential for drastic emission reduction in a broad class of diesel engines, spanning a range of displacement and market segments. As such, three projects have been initiated to research and develop systems that cover the potential range of applications. In FY2001, subcontracts were placed with the following test laboratories to support this research effort:

- Passenger Car Engine/Vehicle: FEV Engine Technologies (Auburn Hills, MI)
- Light Truck Engine/Vehicle: Southwest Research Institute (San Antonio, TX)

Audi A4 Avant Test Vehicle with 1.9 Liter Turbocharged CIDI Engine

- Heavy-Duty Line Haul Engine: Ricardo, Inc. (Burr Ridge, IL)

The passenger car and light truck projects will employ both engine testing and vehicle testing, while the heavy-duty line haul project will focus only on engine testing.

The Passenger Car Engine/Vehicle project has been initiated and the following accomplishments have been reported so far:

- Preparation of baseline engine data for use in the development of the two test emissions control systems
- Initial operating strategy development

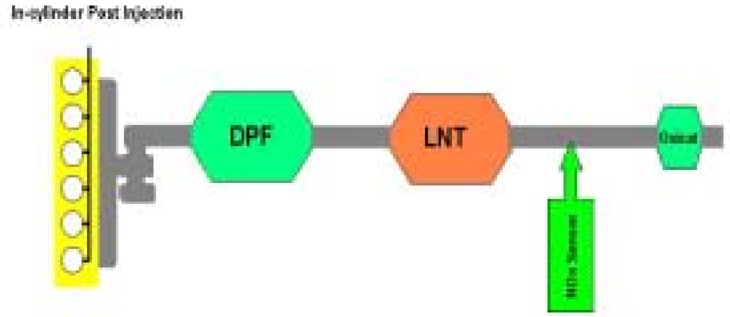
The test vehicle chosen is an Audi A4 Avant with a 1.9 liter turbocharged CIDI engine (currently not offered for sale in the U.S. though Volkswagon uses this engine in their U.S. diesel models).

The Light Truck Engine/Vehicle project has been initiated, the first task has been completed, and the accomplishments thus far include:

- Initiated work with the designated catalyst supplier in the design and development of the emissions control systems
- Initial development of operation strategies

The test vehicle chosen for this project is a GMC 2500 pickup with the Duramax 6.6 liter CIDI engine.

The Heavy-Duty Line Haul Engine project is just getting off the ground, but substantial progress has been achieved. An assessment of single and dual "leg" emission control systems has resulted in selection of the single leg system for reasons of system cost and size constraints for installation on the vehicle. The engine and emission control system is being installed in a test cell for emissions testing.



The Single Leg System Chosen Consisting of a DPF and NO_x Adsorber

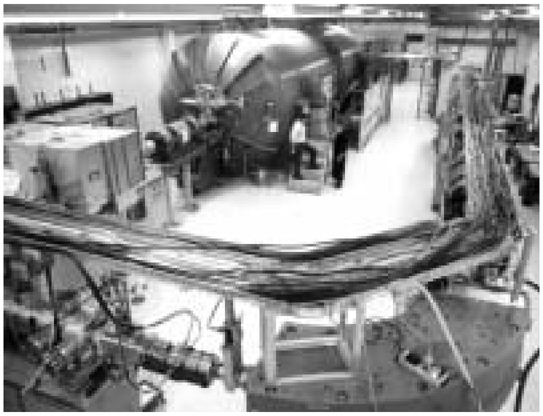
The GM 6600 Duramax V8 Test Engine

SwRI Demonstrates the Advantages of Oxygenated Fuels for NO_x and PM Reductions

Southwest Research Institute (SwRI) has shown that oxygenated fuels, with no other changes, can reduce PM emissions by up to 50%, with NO_x emissions reductions of about 10%. During FY01, SwRI demonstrated that oxygenated fuels allow larger usable EGR levels than non-oxygenated fuels, which can result in engine-out NO_x emissions reductions of up to 45%. This shows the value fuels can have in allowing engine manufacturers the flexibility to trade off NO_x and PM emissions depending on the exhaust gas emission control devices chosen to be used. As a follow-up to these findings, SwRI will test four oxygenated fuel blends and one water emulsion to evaluate their potential for reducing NO_x and PM (see Future Initiatives Section).

LLNL Develops New Technique to Determine the Origin of PM Emissions from CIDI Engines

Lawrence Livermore National Laboratory has developed a technique to accurately determine the origin of PM emissions from CIDI engines using accelerator mass spectrometry (AMS). AMS is an isotope-ratio measurement technique developed in the late 1970s for tracing long-lived radioisotopes (e.g., carbon-14 half life = 5760 yr). The technique counts individual nuclei rather than waiting for their radioactive decay, allowing measurement of more than 100 low-level carbon-14 samples per day. This represents a significant improvement over the more commonly used Direct Filter Ignition/Gas Chromatography (DFI-GC) technique.

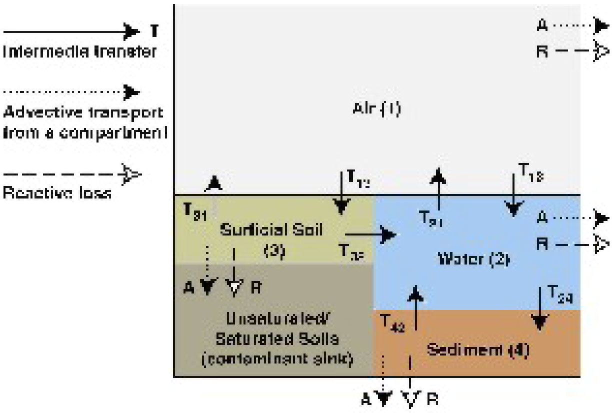


The Accelerator Mass Spectrometer at Lawrence Livermore National Laboratory

The combustion paradigm assumes that large molecules break down into small components and then build up again during soot formation. AMS allows specific fuel components to be labeled, including oxygenates, trace the carbon atoms, and test this combustion modeling paradigm. It can also be applied to the lubricating oil to measure the contribution of consumed lubricating oil to PM emissions. The technique works with both the volatile and non-volatile portions of the PM. It can even be used to monitor the effectiveness of emission control devices to remove specific fuel components. In the coming year, AMS will be used to study the effect of oxygenates on PM formation in CIDI engines.

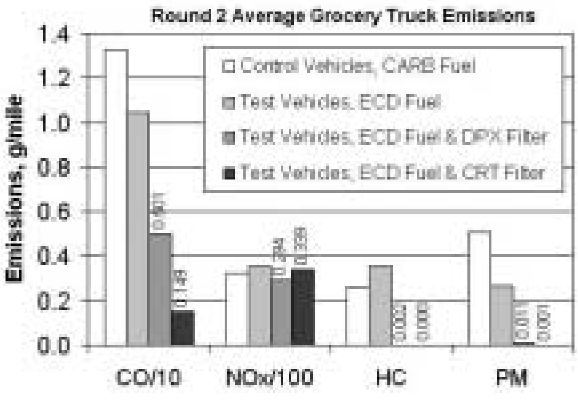
LLNL Completes Environmental Analysis of Promising Diesel Fuel Oxygenates

Research has shown that the addition of oxygen-bearing compounds (oxygenates) to diesel fuel reduces particulate emissions significantly. However, candidate oxygenates also need to be evaluated based on their overall environmental impact and not only their effect on vehicle emissions. Lawrence Livermore National Laboratory has developed a suite of diagnostic models and experimental tests to address this need. This methodology has been applied to two candidate oxygenates: dibutyl maleate (DBM) and tripropylene glycol monomethyl ether (TGME). Preliminary biodegradation tests confirm that DBM is readily degraded. TGME also seems to biodegrade, but more slowly than DBM or benzene. The biodegradation tests were performed using activated sludge, which is a fairly aggressive media. In other natural environments, the rate of biodegradation could be much slower. This fact combined with its high water solubility are indications that TGME would be more mobile in the subsurface than DBM. Additional studies are needed to determine whether TGME would constitute a threat to groundwater when stored in subsurface fuel tanks. In previous work on dimethoxymethane (DMM), indications were that it was likely to be recalcitrant and mobile in ground water, behaving similarly to MTBE in the environment. The results of the biodegradation experiment confirmed the model prediction. These



Conceptual Diagram of the Intermedia Transfer Processes Used to Assess the Environmental Impact of Diesel Fuel Oxygenates results suggest that DBM would be a better choice than TGME as a diesel fuel oxygenate from an environmental standpoint, but further analysis is needed.

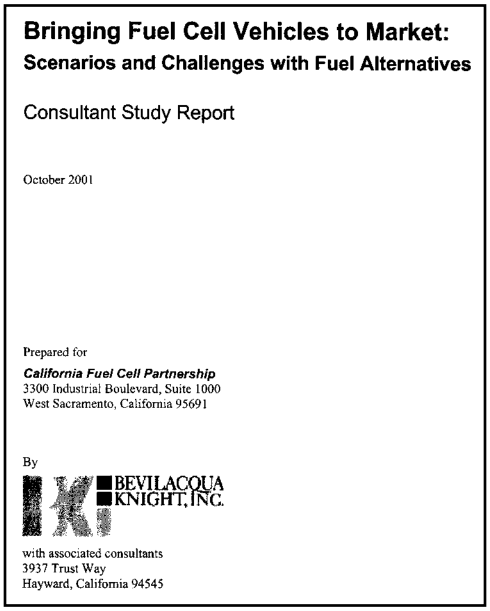
Fleet Tests of EC-Diesel Continue to Show Large Emission Reductions



Average Grocery Truck Emissions over the City-Suburban Heavy Vehicle Route, February-March 2001

ARCO, a BP Company, has developed a new diesel fuel called Emission Control Diesel (ECD). ECD is a heavily hydrocracked fuel produced from typical crude oil. ECD has a maximum sulfur content of 15 ppm, about 10% aromatics by volume, and a nominal cetane number of 60. More recently, BP has introduced ECD-1 into the southern California market. ECD-1 also has 15 ppm maximum sulfur content, but has 22% aromatics and a nominal cetane number of 50. ECD-1 contains both hydrocracked and hydrotreated stocks. A one-year technology validation project was conducted using ECD. Vehicles retrofitted with catalyzed particle filters and fueled with ECD emitted 91% to 99% less particulate matter compared to the California diesel-fueled vehicles having no exhaust filter equipment and fueled with CARB-specification diesel fuel. Hydrocarbon and carbon monoxide emissions were also significantly reduced. The same grocery trucks were retested after twelve months of operation and more than 100,000 miles accumulation per truck. The particle filters were not serviced prior to the second round emissions tests and average particulate matter emissions from the retrofitted trucks were again found to be 89% to 99% less than the California diesel-fueled vehicles having no exhaust filter equipment fueled with CARB-specification diesel fuel. Through the first five months of operation, there was no detectable difference in fuel economy between trucks with and without particle filters, based on an analysis using fleet operation records. In the coming year, ECD-1 will be used and emissions tests will be conducted to measure the difference.

The CaFCP Releases Report on the Challenges of Implementing Fuel Cell Vehicles



Bringing Fuel Cell Vehicles to Market:
Scenarios and Challenges with Fuel Alternatives

Consultant Study Report

October 2001

Prepared for
California Fuel Cell Partnership
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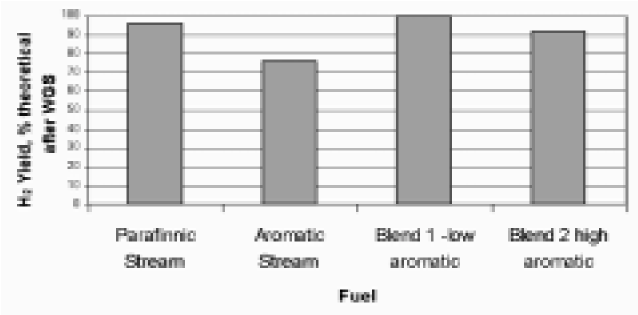
The California Fuel Cell Partnership (CaFCP) is a path-breaking collaboration of auto companies, energy providers, fuel cell companies, and government agencies that will demonstrate fuel cell electric vehicles on the road in California. The Partnership is taking steps to broaden public awareness of fuel cell vehicles by displaying vehicles at various public venues, hosting classroom visits to its headquarters facility, and speaking about fuel cells to organized community groups and industry conferences. Through participation in public events, the CaFCP over the past year has reached thousands of people. The vehicles have served as the pace cars for two marathons - the California International Marathon in Sacramento and the Los Angeles marathon; multiple vehicles and displays were featured at the Orange County Fair; and as part of their ongoing test-drives, vehicles are parked in prominent public gathering places around Sacramento, engendering public attention and excitement. The Partnership's Internet website (www.fuelcellpartnership.org) provides more educational information. The CaFCP also commissioned a report that examines the challenges to using various fuels in fuel cell vehicles and identifies initiatives that can promote success. The study will help start the CaFCP members to begin addressing the challenges associated with developing fuels and infrastructure for fuel cell vehicles. The report is available at www.fuelcellpartnership.org/event_roundtable.html. The CaFCP is testing and demonstrating fuel cell electric vehicles in California through 2003 under day-to-day driving conditions; demonstrating alternative fuel infrastructure technology; exploring 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; and working to increase public awareness of fuel cell vehicle technology and the benefits it can offer.

Fuel Cell Vehicles and the Hydrogen Refueling Facility

In FY 2001 DOE led a study of hydrogen vehicle facilities, using the CaFCP West Sacramento Facility as a model, to determine the impact of hydrogen infrastructure codes and standards on facility costs. Following that initial study, the CaFCP Steering Team has authorized a more in-depth study to be conducted by an external contractor examining the costs for accommodating hydrogen-fueled vehicles in residential garages, commercial parking garages, and service/maintenance facilities, including the cost of retrofitting existing facilities designed for conventional gasoline-fueled vehicles.

ANL Identifies Favorable Gasoline Hydrocarbons for Fuel Cell Vehicles

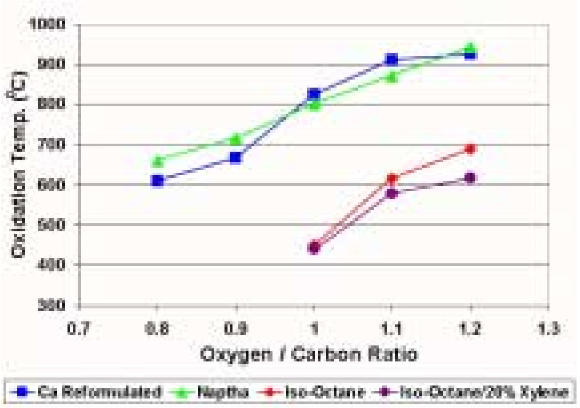


Hydrogen Yield from Several Different Fuels

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, Argonne National Laboratory (ANL) has begun a project to test various components of gasoline and blends of gasoline streams under autothermal reforming conditions. The current work has focused on the effects of blends of components and on the effects of sulfur impurities. Blends are being investigated to determine if the presence of some components can affect the reforming of others. Sulfur is of particular concern due to its propensity to poison catalysts. In the coming year, ANL will continue investigating effects of additives (detergents, antioxidants) and impurities, continue investigating reforming of blended fuels, determine composition/performance relationships from results, investigate differences in fuel reforming with different catalysts, and make recommendations for fuel cell fuels.

LANL Explores the Effects of Fuels and Impurities on Reformers

Los Alamos National Laboratory is exploring the effects of fuels, fuel constituents and fuel impurities on the performance of on-board hydrogen generation devices (reformers) and consequently on the overall performance of a PEM fuel cell system using a reformed hydrocarbon fuel. Different fuels were tested to observe their relative reforming characteristics under various operating conditions. Both catalytic and homogeneous fuel processor partial oxidation stages were used in the tests of pure fuel components and mixtures such as iso-octane and iso-octane/xylene, and real fuels such as a hydro-treated naphtha and reformulated gasoline. Carbon formation was monitored during operation by in-situ laser measurements of the effluent reformate and visual observations of the reactor.



Homogeneous Partial Oxidation Outlet Temperature for Several Fuels and Varying Oxygen to Carbon Ratios

Homogeneous oxidation was found to occur easier with ‘real’ fuels than with the pure components of iso-octane and iso-octane/xylene. The addition of aromatics slows the overall reaction rate for catalytic oxidation. Diesel fuel components (such as dodecane) require higher residence times for similar conversions. The fuel composition (especially sulfur and aromatic content) affects the relative amount of noble metal required for the fuel reformer. Modeling has shown that fuel characteristics can cause variation in the temperature for equilibrium onset of carbon formation by up to 150°C with varying O/C ratios.

FUTURE INITIATIVES

Our new Activity initiatives for FY 2002 build upon the progress made in FY 2001 and will focus on those areas that industry agrees are major technical barriers.

Advanced Petroleum-Based Fuels for CIDI Engines

- In a new project just recently awarded, Honeywell will develop and demonstrate an "on-vehicle" desulfurization fuel filter suitable for both light- and heavy-duty CIDI vehicles. The project consists of four phases: concept design development; prototype filter design; life cycle and regeneration options for spent filters; and life testing and component integration.
- In the coming year, the six recently initiated Advanced Petroleum-Based Fuels - Diesel Emissions Control projects (described earlier) are anticipated to complete the activities described in the following:

  Effects of Lubricant Composition on Emissions: A more thorough evaluation of emissions utilizing all three PM sampling trains will be conducted with two oils of widely different composition. Following this initial evaluation, the main test effort to characterize the impact of lubricant-derived species on the performance and durability of advanced diesel emission control systems will commence.

  Effects of Fuel Composition on SCR/DPF Systems: Durability testing of the two SCR/DPF systems will be in progress. Durability testing of 6,000 hours will be initiated.

  Assessment of Infrastructure Issues for SCR: An environmental impact assessment of urea spills along the distribution pathway will be conducted, and life-cycle greenhouse gas emissions will be estimated for urea production and distribution. A final report will be issued.

  Effects of Fuel Composition on NO_x Adsorber/DPF Systems

  > Passenger Car Engine/Vehicle Project: Hardware procurement and operational strategy development will be completed. All baseline emissions testing and calibration and optimization strategies will be completed or near completion.

  - > Light Truck Engine/Vehicle Project: The emission control system architecture and design, including performance characteristics and requirements for operation of the catalyst/trap (e.g., operating temperature, intended feed gas composition, size, and location), will be completed.
  - > Heavy-Duty Line Haul Engine Project: The test setup will be completed and the optimum control strategy will be determined. Fuel sulfur content effects studies will be completed.
- Field testing of ECD-1, a low-sulfur diesel fuel, will be conducted in California in heavy-duty trucks. Exhaust speciation data and particle size distribution data are being analyzed and will be reported.
- Southwest Research Institute will measure the contribution of synthetic and mineral-based lubricating oil to PM emissions in combination with advanced fuels. A vehicle with a state-of-the-art CIDI engine will be used along with a base fuel representative of those expected in 2007.
- Sandia National Laboratories will continue their testing of oxygenated fuels to determine the effect of fuel-bound oxygen on PM and NO_x emissions. In the coming year, they will test 26 weight-percent di-ethyl adipate because it contains no carbon-to-carbon bonds.
- Southwest Research Institute will evaluate different oxygenates blended in refinery produced low-sulfur fuels to determine their impact on the physical and chemical characterization of PM after an oxidation catalyst and a diesel particulate filter.
- Oak Ridge National Laboratory will demonstrate the potential of urea SCR and diesel particulate filters to reduce NO_x and PM emissions. The engine they will use for their testing is a 4.0 liter DDC DELTA CIDI prototype. The engine is installed for testing and baseline emissions have been measured.
- Southwest Research Institute will test six advanced fuels (oxygenated and water emulsion fuels) in a vehicle with a state-of-the-art CIDI engine and using a baseline fuel representative of diesel fuel properties expected in 2007.

Advanced Fuels for Fuel Cells

- The California Fuel Cell Partnership will continue to demonstrate fuel cell vehicles in California, identify additional sites for refueling facilities, explore additional fuels to use in demonstrations, and assess commercialization activities.
- Arthur D. Little, Inc. will focus their efforts on an integrated analysis of energy, emissions, and economics of various fuel chains and fuel cell platforms.
- Argonne National Laboratory will continue their efforts to identify the practical obstacles to fuel cell vehicles using hydrocarbon fuels. The projects will include:
  - > Investigation of the effects of gasoline detergents, anti-oxidants, and impurities on reformer catalysts.
  - > Finalization of the specifications of a standard fuel cell gasoline that can be used to quantify the performance of different fuel processors.
  - > Improvement of the stability of structured forms of ZnO to remove H_2S from reformate streams. Conduct feasibility studies of non-adsorption technologies to remove H_2S, and evaluate the sulfur tolerance of new water-gas shift and PrOx catalysts.
- Los Alamos National Laboratory will continue their efforts to identify the adverse effects of hydrocarbon fuels on fuel cell reformers. They will:
  - > Measure carbon formation of different fuel constituents.
  - > Measure the effect of bound nitrogen and sulfur on carbon formation.
- During FY 2001, a major solicitation was jointly issued by the Offices of Transportation Technologies and Power Technologies calling for proposals for new research and development projects for fuels for fuel

cells. The following projects selected for negotiation and cooperative agreements will be initiated early in FY2002:

- *Development of a Turnkey Commercial Hydrogen Fueling Station* with Air Products and Chemicals, Inc. as the prime contractor.
- *Autothermal Cyclic Reformer Based Fueling System* to be conducted by GE Energy and Environmental Research Corporation.
- *Development of High-Efficiency Reformer-Based Hydrogen Fueling Station* to be managed by the Gas Technology Institute.
- *Evaluation of Candidate Fuels for Vehicle Fuel Cell Power Systems* to be conducted by Arthur D. Little, Inc.

SUMMARY

Advanced petroleum-based fuels enable the use of high efficiency prime movers such as CIDI engines and fuel cells to create clean and 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, and 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 TESTING ON ENGINE PERFORMANCE

A. Oil Consumption Contribution to CIDI Engine PM Emissions During Transient Operation

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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

Objective

- Quantify the effect of crankcase lubricant type on exhaust emissions measured during transient tests of a vehicle powered by a state-of-the-art CIDI engine.

Approach

- A European Mercedes C 220 D vehicle with a CIDI engine will be tested for transient exhaust emissions over the light-duty Federal Test Procedure (FTP) and US06 test cycles.
- Synthetic and mineral-based crankcase lubricants will be tested in combination with advanced fuels to determine the effect of lubricant composition on particulate matter (PM) and other exhaust emissions.

Accomplishments

- Testing has been delayed pending the availability of a specially-produced base fuel that is representative of projected 2007 U.S. diesel fuel.
- The test lubricants have all been obtained and conditioned to reduce volatile light ends.

Introduction

The Phase 1 project "Impact of Consumed Lube Oil on Advanced CIDI Engine Emissions" revealed a significant oil impact on PM for low-power steady-state conditions and a rather insignificant oil impact over the high-power, heavy-duty engine FTP transient test cycle. However, the oil impact was not investigated for any light-duty transient test cycle.

In the previous project, it was determined by the Direct Filter Ignition/Gas Chromatography (DFI-GC) technique (Figure 1) that the oil volatile organic fraction (VOF) can be reduced from 27% of PM for a petroleum-based SAE 5W30 oil to 8% of PM for a synthetic-based SAE 15W50. This illustrated that a PM reduction of approximately 19% is obtainable by changing the lubricant. This reduction was observed under steady-state, light-duty conditions when using CARB diesel fuel. The fundamental question is whether the oil impact on PM for the light-duty transient cycle will be similar to the oil impact on PM for the low-power steady-state conditions investigated as part of the Phase 1 study.

Approach

A European Mercedes C 220 D vehicle will be tested for transient exhaust emissions following the light-duty FTP and US06 test cycles. Synthetic and mineral-based lubricants will be tested in combination with advanced fuels to determine the effect of lubricant composition on PM emissions.

The European Mercedes-Benz C220 D is equipped with the DaimlerChrysler OM611 CIDI engine. This advanced four-valve-per-cylinder engine is turbocharged and intercooled, and it includes a high-pressure common rail fuel injection system with pilot injection, exhaust gas re-circulation, and intake port cut-off. The vehicle is equipped with both a close-coupled oxidation catalyst and "lean NO_x" catalyst.

All evaluations will be conducted in triplicate over the chassis dynamometer portion of the FTP cycle and the US06 aggressive driving cycles.

A low-sulfur baseline fuel that is representative of expected U.S. diesel fuel in 2007 will be used for the initial evaluation of lubricant contribution to PM emission. The following lubricants will be included in the test matrix: synthetic SAE 5W30, mineral SAE 5W30, synthetic SAE 15W50, and synthetic SAE 0W30. In addition, FTP and US06 tests will be conducted using the lubricants and a blend of 2007 fuel with an oxygenate (tripropylene glycol monomethyl ether).

Exhaust constituents will be analyzed as specified in Table 1.

Figure 2 shows a gas chromatogram of the VOF of PM. The VOF is fractionated into unburned oil and other volatile material.

Figure 1. Direct Filter Injection Gas Chromatograph

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

Table 1. Methods for Analyzing Exhaust Constituents

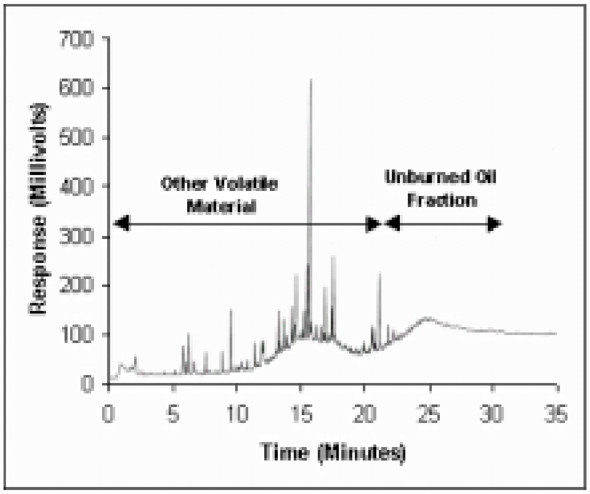

Figure 2. Chromatogram of Volatile Organic Fraction of PM

Appropriate statistical techniques will be used to determine differences between the PM and other exhaust emissions for each lubricant and each lubricant/fuel combination.

Results

Testing has been delayed pending the availability of the 2007 base fuel. This is a specially produced diesel fuel that is projected to be representative of 2007 U.S. diesel fuel.

FY2001 Publications/Presentations

1. SAE Paper 2001-01-1901 "Impact of Lubricating Oil on Regulated Emissions of a Light-Duty Mercedes-Benz OM611 CIDI-Engine," presented at the SAE International Spring Fuels and Lubricants Meeting, Orlando, FL.

B. Effects of Blending Ethanol with Diesel Fuel on Exhaust Emissions from a Heavy-Duty Diesel Engine

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Emissions characterizations of ethanol-diesel fuel blends have been conducted at ORNL for two years at the encouragement of the DOE-OHVT Fuels Team Leader, Steve Goguen. This particular effort was sponsored by ORNL's Energy Efficiency and Renewable Energy (EERE) Program Office, State Partnership Program (SPP). Projects under the SPP are endorsed by one or more state energy agencies and involve significant matching resources from project partners (e.g., private industry, universities, state and local government agencies, and nonprofit organizations). Partners targeted by this program are State Energy Offices and the Association of State Energy Research and Technology Transfer Institutions. The ORNL SPP Manager is Marilyn Brown.

The work was heavily leveraged by the DOE-OHVT Engine/Emission Control Team, which bore the costs of engine cell set-up in preparation for other research projects.

Contractor: UT-Battelle, LLC (Oak Ridge National Laboratory), Oak Ridge, TN
Prime DOE Contract No: DE-AC05-00OR22725
Period of Performance: Feb. 1, 2000 - March 31, 2005

Industrial Partner: David Loos, Illinois Department of Commerce and Community Affairs
(217) 785-3969, e-mail: DLOOS@commerce.state.il.us

Industrial Partner: Glenn Kenreck, Betz-Dearborn Inc.
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Industrial Partner: Mike Lockart, Gromark Industries
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Industrial Partner: Vinod Duggal, Cummins Engine Company, Inc.
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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

Objective

- To investigate potential emissions reduction benefits from blending ethanol (as a microemulsion) with diesel fuel for heavy-duty diesel engines.
- Evaluate viability of ethanol to displace diesel fuel consumption while rendering air quality benefits by lowering particulate matter (PM) and NO_x emissions.

Approach

- Blends of 10% and 15% by volume ethanol in diesel fuel were tested in a Cummins ISB 5.9 L diesel engine subjected to AVL 8-mode test cycles.
- The AVL 8-mode (steady-state) test was employed to compare emissions from the different fuels. This test provides a reasonable estimate of emission results of the Heavy-Duty Transient Federal Test Procedure, and also provides comparisons for a variety of engine conditions.
- Comparisons of emission levels and trends were made against a reference diesel fuel as well as prior efforts.

Accomplishments

- Addition of ethanol was observed to have no noticeable effect upon NO_x emissions and produced undesirable but expected increases in CO and total HC.
- Addition of ethanol (10 and 15 vol% blends) was observed to decrease PM by 20-30% respectively.
- Engine performance was derated by about 8% due to the lower energy content of the ethanol.

Future Directions

- Investigate blend performance and emissions impacts (specifically PM) in older engines more characteristic of the on-road population. Such blends can mitigate emissions from diesels lacking emission control systems.
- Investigate use of such blends to exploit higher CO and HC emissions in enhancing advanced emission control systems (e.g. NO_x adsorbers) that need reducing agents for regeneration.
- Optimize a diesel engine for ethanol blends and evaluate performance and emissions.
- Characterize PM chemistry, size distribution, and microstructure.
- Evaluate influence of different blending agents separately from the effects of ethanol.

Introduction

Over the past 20 years, ethanol has been evaluated as an additive for diesel fuel to both lessen the demand for imported petroleum and to promote the use of a domestic renewable energy resource to power diesel engines. Recent studies have shown that ethanol added to diesel fuel results in a beneficial reduction in particulate matter (PM) emissions. The effects upon carbon monoxide (CO), total hydrocarbons (HC) and oxides of nitrogen (NO_x) are less clear and generally weak. Although it is generally considered that emission control systems will be required to meet future emissions targets, older vehicles may not be required to retrofit them. Indeed, fuel additives or blending components that reduce NO_x and/or PM emissions from unmodified engines offer a feasible means of improving the pollution from this class of heavy vehicles. Additionally, such reduction of NO_x and PM may also improve durability and performance of emission control systems. The purpose of the investigation was to explore the potential for reducing emissions from a heavy-duty diesel engine fueled with these ethanol blends. Fuel mixtures of ethanol and diesel are frequently referred to as E-diesel.

Approach

A study was conducted by the Oak Ridge National Laboratory (ORNL) to evaluate emissions resulting from E-diesel fuels tested in a heavy-duty compression-ignition engine. The test fuels evaluated in this study included two diesel-ethanol blends consisting of 10 and 15 vol% ethanol. A Phillips 66 certification diesel fuel containing 500 ppm sulfur was used as the base fuel for the E-diesel blends (plus a 2% blending agent) as well as being the baseline fuel for this study. A Cummins 5.9 liter ISB turbocharged direct-injection diesel engine, coupled to a 300 hp General Electric DC motoring dynamometer, was used for the evaluation. The test protocol for running the engine followed the AVL 8-mode test sequence that is meant to estimate and forecast the results for the more complex Heavy-Duty Transient Federal Test Procedure (HDFTP). Gaseous emissions and PM were measured for each mode and a weighted average was used to determine emission results. No exhaust emission control devices were utilized during testing, nor was the engine equipped with exhaust gas recirculation; the turbocharger was fixed-geometry with a waste gate.

Gaseous emissions were sampled from the raw exhaust stream and directed to both an Fourier Transform Infrared (FTIR) spectrometer and a standard diesel emissions bench for measurement. The standard bench provided measurements of NO_x, total hydrocarbons (THC), CO, CO_2, and O_2. The FTIR spectrometer provided extended information about the speciation of the hydrocarbon emissions. Fuel consumption was measured using a Max Machinery fuel flow measurement system. A stream of exhaust was sent to a mini-dilution tunnel for measurement of PM and ethanol content. PM mass was measured using conventional filters, while ethanol was measured using a photoacoustic spectrometer. In addition, numerous temperature and pressure measurements were made during the evaluation.

For each fuel tested, the maximum load was measured for each engine speed used for the AVL 8-mode test cycle. This information was used to define the load parameters for the AVL 8-mode simulation of the HDFTP. This test consists of 8 steady-state data points that are weighted in a specific fashion to produce an estimate of the emissions results for the HDFTP. The AVL 8-mode test was run twice for each fuel blend. During the dilution tunnel PM sampling, the dilution ratio was varied to maintain a dilution temperature between 110°C and 125°C.

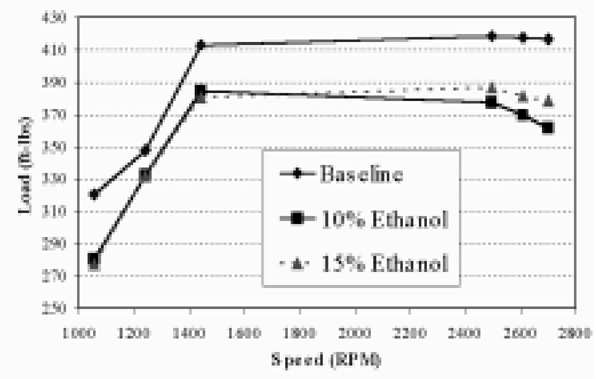

Figure 1. Full Load Results for the Cummins ISB Engine for Each Fuel at Speeds Used for the AVL 8-Mode Test

Results

The maximum brake torque was measured for each engine speed used during the AVL 8-mode test. The results are shown in Figure 1. The ethanol blends, as expected (due to less volumetric energy content), produced less torque at a given condition than did the base fuel. The reduction in torque was roughly 8% for both ethanol blends; this corresponds to the 6-8% difference in the amount of energy contained in a gallon of E-diesel compared to the baseline fuel. It is unclear why the 15% blend reached slightly higher loads at higher speeds than the 10% blend. The opposite trend would be expected.

The AVL 8-mode regulated emissions results for the base fuel and the two E-diesel blends are shown in Figures 2 through 5. The emissions output for each emission species is expressed in g/hp-h.

As shown in Figure 2, the levels of NO_x were not affected (in a statistically significant way) by the addition of ethanol to the base diesel fuel. Several prior studies had shown lower NO_x levels for certain operating conditions with added ethanol; however, the NO_x levels were consistent for the overall AVL 8-mode test as well as each of the 8 individual modes tested in this study.

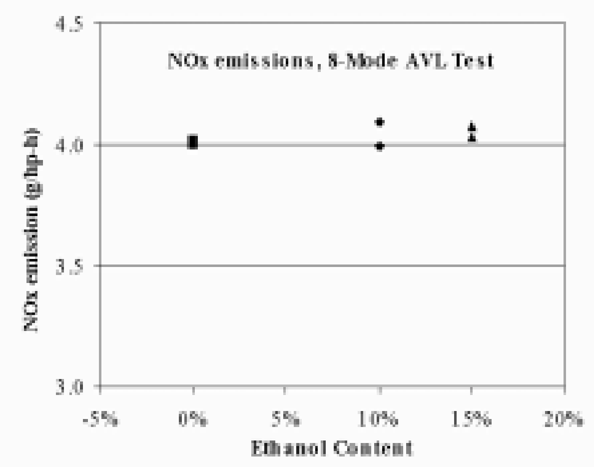

Figure 2. NO_x Emissions from AVL 8-Mode Tests for Ethanol/Diesel Fuel Blends

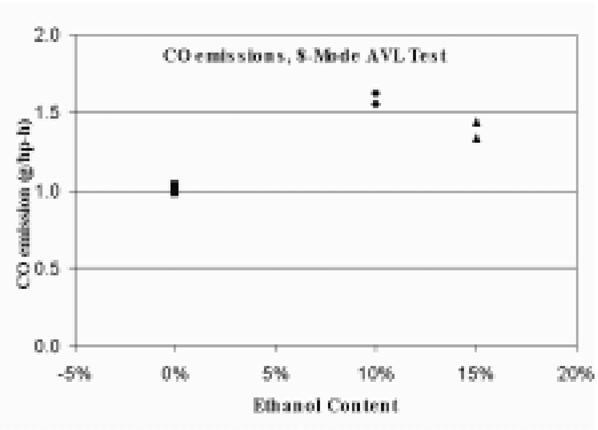

Figure 3. CO Emissions from AVL 8-Mode Tests for Ethanol/Diesel Fuel Blends

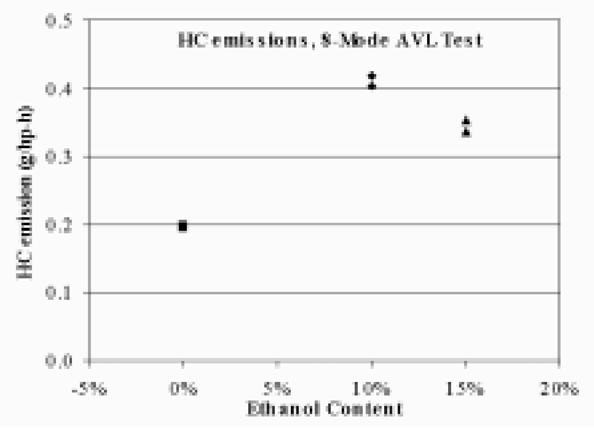

Figure 4. HC Emissions from AVL 8-Mode Tests for Ethanol/Diesel Fuel Blends

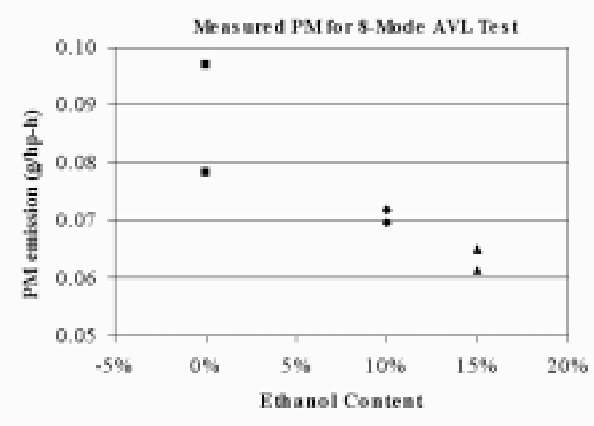

Figure 5. PM Emissions from AVL 8-Mode Tests for Ethanol/Diesel Fuel Blends

Ethanol blends demonstrated significantly higher levels of CO and THC emissions (Figures 3 and 4) than the baseline fuel. (Increases of CO and THC emissions have been reported for other studies of oxygenated fuels and were anticipated in this investigation.) The 10% blend increased CO and THC emissions by nearly 60% and 100% respectively over the baseline, while the 15% blend raised the level of these emissions by 40% and 75%, respectively. We have no clear explanation why these emissions were highest for the 10% ethanol blend, but perhaps a maximum for these pollutants exists for a specific ethanol/diesel ratio. Furthermore, the effect of the blending agent on CO and THC is unknown. Although the emission levels of these two species increased for the ethanol fuels, they are well below current standards and are easily mitigated using commercially-available oxidation catalysts.

The PM emissions were observed to decrease with added ethanol as shown in Figure 5. For the 10% and 15% ethanol blends, the PM was reduced by 20% and 30% from the baseline fuel, respectively. Similar trends have been reported in other studies.

The AVL 8-mode emissions data from an FTIR spectrometer and a Photoacoustic Spectrometer show that the acetaldehyde and formaldehyde emissions remain at less than 10 ppm at all operating modes for each fuel tested. The ethanol emissions were also found to be less than 35 ppm for the operating modes tested.

Although the results do not show reductions for NO_x, CO, and THC, they do indicate that PM emissions might be reduced substantially over the HDFTP for ethanol-added diesel fuels.

Conclusions

The emission results show that ethanol-diesel fuel used in a Cummins 5.9 liter ISB diesel engine causes:

1. a significant drop in PM,
2. a significant increase in the emissions of CO and THC, but still within current emission standards.
3. a negligible effect on NO_x emissions, and
4. no apparent increase in oxygenate emissions.

These results suggest that ethanol-diesel fuel blends may have some use as a low emission fuel for older model vehicles that are not required to meet current EPA emission standards. The use of these fuel types might offer a means of reducing levels of PM currently produced by older diesel engines still operating on the roads. Obviously, much more extensive testing of such fuels types in a variety of diesel engines would be needed to accurately assess performance with ethanol blends. Additionally, the higher THC and CO levels observed suggest that ethanol blends could possibly offer constituents in the exhaust favorable to NO_x adsorber regeneration.

FY 2001 Publications / Presentations

1. SAE Paper No. 2001-01-2018, *Emissions From a 5.9 Liter Diesel Engine Fueled With Ethanol Diesel Blends*, Michael D. Kass, John F. Thomas, John M. Storey, Norberto Domingo and James Wade, Oak Ridge National Laboratory; and Glenn Kenreck, Betz-Dearborn, Inc.

III. FUEL & LUBRICANT EFFECTS ON EMISSION CONTROL PERFORMANCE

A. Durability of NO_x Adsorbers Using Ultra-Low Sulfur Diesel Fuels

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Subcontractors: FEV Engine Technology, Inc., Auburn Hills, MI; Southwest Research Institute, San Antonio, TX; Ricardo, Inc., Burr Ridge, IL

Other Participants: Technical team with representation from Manufacturers of Emission Controls Association (MECA), Engine Manufacturers Association (EMA), American Petroleum Institute (API), American Chemistry Council, U.S. Environmental Protection Agency (US EPA), Oak Ridge National Laboratory (ORNL), California Air Resources Board (CARB), and South Coast Air Quality Management District (SCAQMD).

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
D. Sulfur Impacts

Tasks

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

Objectives

- To use a systems approach to demonstrate the viability of achieving future emissions requirements with emissions control systems that include NO_x adsorber catalysts and diesel particulate filters (DPF), for both light- and heavy-duty diesel engines while maintaining high fuel economy.

- To determine whether NO_x adsorbers will have sufficient conversion efficiency and durability using ultra-low sulfur diesel fuel to meet future emission regulations. The fuel sulfur level will be representative of those expected after June 2006 when the sulfur content of on-road diesel fuel falls to 15 ppm or less.

Approach

The test activities include integrating the selected engines and emission control systems and developing and optimizing engine management systems for effective operation with low sulfur and other fuels. Three projects have been selected, each of which will:

- Complete the system setup, integration and optimization, which includes measuring baseline engine-out emissions and developing regeneration and desulfurization strategies for the emission control devices.
- Evaluate system performance for regulated and unregulated emissions over appropriate federal test procedure (FTP) and off-cycle emissions points using 3-, 8-, 15- and 30-ppm sulfur fuels while keeping all other fuel parameters constant. The most detailed evaluations will be completed using 8- and 15-ppm fuels. Though diesel fuel will be regulated to 15 ppm sulfur or less after June 2006, 30 ppm sulfur fuel was chosen for inclusion in testing to simulate periodic misfueling with higher sulfur fuel (e.g., off-road diesel or batches of out-of-spec on-road diesel). Testing using 30 ppm sulfur fuel will measure the impact of short-term exposure of higher than regulated sulfur contents, and the ability of NO_x adsorbers to recover their conversion efficiency (high fuel sulfur content quickly degrades conversion efficiency).
- Evaluate system performance with selected fuels to enable investigation of the impact of varying other fuel properties. The fuels to be investigated will be determined by the Advanced Petroleum-Based Fuels — Diesel Emission Control (APBF-DEC) Fuels and Lubricants Provision work group.

Accomplishments

- Issued a request for proposals seeking to conduct up to two projects involving light-duty engines/vehicles (one addressing passenger car applications and the other SUV applications) and up to two projects involving heavy-duty engines.
- The evaluation team, including representatives from the industries participating in the APBF-DEC program, selected a light-duty passenger car, a light-duty SUV and a heavy-duty engine project for award.
- Awarded subcontracts, and projects were begun with the following companies during the 4th quarter of FY01:
  - FEV Engine Technology, Inc.: light-duty, 1.9L engine and passenger car
  - Southwest Research Institute: light-duty, 6.6L engine and light-duty truck
  - Ricardo, Inc.: heavy-duty, 15L engine

Future Directions

- Complete the engine and/or vehicle system integration and baseline systems evaluations.
- Develop regeneration and desulfurization strategies for each system.

Introduction

This study is part of a multi-year effort to demonstrate the potential of NO_x adsorber catalysts in combination with diesel particulate filters (DPF), advanced fuels, engines, and engine controls to achieve stringent emission levels while maintaining high fuel economy. The project is one of several being conducted under the APBF-DEC project. The effort is being conducted with the cooperation of the engine and vehicle manufacturers, emission control device manufacturers, energy and additive companies, and federal and state agencies and laboratories. The U.S. Department of Energy's Office of Advanced Automotive Technologies and Office of Heavy Vehicle Technologies are funding the federal government portion of this program.

The Diesel Emission Control-Sulfur Effects (DECSE) project, a predecessor to this effort, has shown the effects of fuel-borne sulfur on the performance of individual emission control devices, including NO_x adsorbers, diesel particulate filters (DPFs), diesel oxidation catalysts, and lean NO_x catalysts [1-6]. Under the current APBF-DEC effort, this project has been designed to demonstrate the viability of NO_x adsorber catalysts and DPFs when combined with advanced fuels and engines. Fuel properties (including additives) may also affect the performance of advanced emission controls.

This project aims to demonstrate the viability of NO_x adsorber and DPF technologies in combination with advanced fuels, advanced engines, and engine controls to achieve stringent emission levels while maintaining high fuel economy. To meet stringent Tier 2 light-duty emissions standards, tailpipe emissions for NO_x must be below 0.2 g/mi. while PM emission levels must be below 0.02 g/mi. The goals of this project are to meet Tier 2 — Bin 5 with limits of 0.07 g/mi NO_x and 0.01 g/mi PM. The 2007 heavy-duty NO_x standard is 0.2 g/bhp-hr with a PM emission standard of 0.01 g/bhp-hr. These emissions levels must be achievable not only on the appropriate transient test cycles but in other modes of operation as well. Additionally, hydrocarbon and carbon monoxide emission standards must be met. Minimizing fuel economy impacts while meeting emission requirements is also an important aspect of the project. The base fuel for the system development stage of the project will be the 3-ppm sulfur DECSE base fuel [1]. Additionally, the 8-, 15- and 30-ppm sulfur fuels will be evaluated, as will other fuels or fuel additives, which will be included in later phases of the project.

Approach

The integrated system will use advanced engines, NO_x adsorbers, DPFs, and fuel technologies. In order to demonstrate the viability of the system, the engine and exhaust emission control technologies will be combined and optimized over the appropriate FTP cycles and other points on the engine map using 3-, 8-, 15-, and 30-ppm sulfur level fuels. The optimization will be used to insure that the appropriate engine operating conditions can be met for proper NO_x adsorber and DPF regeneration as well as adsorber desulfurization while achieving the light- and heavy-duty engine emission targets. Off-cycle and unregulated emissions will also be measured.

Performance testing will determine the combination of engine, fuel, lubricant, and emission control systems (NO_x adsorber and DPF) required to meet future light-duty and heavy-duty emission standards. The aim of the testing is ultimately to establish the properties of advanced fuels that enable these systems to meet emission standards without adversely affecting engine performance. Investigation of system durability is also of interest, and will be pursued in a later project.

Each project is divided into three primary tasks. The first task involves two parts. Part one will setup the engine and/or vehicle test cell(s) and will measure regulated and unregulated engine-out baseline emissions and fuel consumption over the appropriate cycles with 3-, 8-, 15-, and 30-ppm sulfur fuels. Part two will develop the regeneration (both DPF and adsorber) and desulfurization strategies to be triggered while running over the appropriate FTP cycle (these strategies may require engine operation outside of the FTP cycles). The regeneration strategy must allow the NO_x adsorber and DPF to be regenerated at steady-state conditions as well as during transients over the appropriate FTP cycles. The strategies will be refined and tuned for each fuel and new (identical) emission control system (ECS), as well as for each engine application. Two different emission control systems will be evaluated in each project. Members of MECA are committed to providing state-of-the-art NO_x adsorbers, DPFs, other catalysts or emission control system elements, and technical support to the projects.

The second task is the system performance evaluation. This task involves evaluating the performance of the integrated, tuned system for regulated and unregulated emissions over the appropriate FTP and off-cycle emissions points. Setup and benchmarking of each new ECS will be conducted with 3-ppm fuel. Fresh emission control systems will be aged for at least 300 hours in 50-hour increments using 8- and 15-ppm fuels. At each 50-hour increment, a full evaluation of emissions will be conducted. The heavy-duty project will include operation at modal (steady-state) points and the heavy-duty FTP. Light-duty projects include engine and vehicle testing to measure emissions on the FTP, the US06 cycle, and the highway fuel economy test (HFET). If emission control performance has degraded below the defined target level, the regeneration strategy will be refined, as appropriate, to restore performance, followed by another performance evaluation. Limited testing is also planned using 30-ppm fuel.

The third task is extended emissions control system durability performance evaluation testing. Based on the results from the 300 hours of testing under task two, extended testing of the "best" performing emissions control systems and fuel sulfur level combination will be placed under additional testing of up to 1000 hours. This testing is intended to evaluate the long term performance and durability of at least one of the emissions control systems.

In the final task, testing as outlined in the first two tasks will be conducted to examine the effects of other fuel properties besides sulfur content. The specific fuels and properties to be used in this portion of the project will be determined by APBF-DEC's Fuels and Lubricants Provision work group. The testing will investigate the fuel effects on the previously developed regeneration (filter and adsorber) and the desulfurization strategies. The emission control performance and fuel economy impact on the system will be investigated, but the testing will not include extensive aging cycles.

Results/Conclusions

The three projects that are currently underway are analyzing the effects of fuel composition on a light-duty passenger car engine and vehicle, a light-duty SUV/light truck engine and vehicle, and a line-haul class heavy-duty engine. The projects, varying in length from 24 to 30 months, started in the last quarter of FY01. Because testing has not started, data and results are not yet available. The three subcontractors are assembling engines and appropriate subsystems and instrumentation, and preparing test cells. The bulk of the next fiscal year will be spent in setup, system integration, and developing regeneration and desulfurization strategies.

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Program — Phase II Summary Report: NO_x Adsorber Catalysts," August 2000

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B. Lubricant Property Impact on CIDI Emission Control System Durability

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Subcontractor: Automotive Testing Laboratories, Inc., East Liberty, OH (Phase 1)

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
- D. Sulfur Impacts

Tasks

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

Objectives

- Determine the impact of lubricant properties and composition on engine-out emissions
- Determine if lubricant formulation affects the performance and durability of diesel engine emission control systems (ECS)
- Develop guidelines specifying lubricant properties that will be required for use in future low-emissions diesel engines

Approach

- Phase 1: Determine the impact of lubricant formulation (additives and basestock) on the emissions of a compression ignition direct-injection (CIDI) engine. Conventional and developmental additive technologies blended with four different basestocks will be tested in a medium-duty diesel engine.
- Phase 2: Determine the impact of lubricant related emission components on performance and durability of diesel emission control devices using laboratory-scale analysis tools.
- Phase 3: Begin confirmatory testing in cooperation with Advanced Petroleum-Based Fuels - Diesel Emission Control (APBF-DEC) systems projects to study lubricant effects on NO_x adsorber catalysts and selective catalytic reduction (SCR) catalysts in combination with diesel particle filters.

Accomplishments

- An International T444E (7.3L, V8) has been installed in an emission test cell at Automotive Testing Laboratories, Inc. The MY 1999 engine has been equipped with exhaust gas recirculation (EGR) and closed crankcase ventilation (CCV) hardware similar to future base engine designs.
- Test lubricants ranging in sulfur content from 0 to 6500-ppm and ash between 0% and 1.85% have been prepared in a low sulfur API Group II basestock.

Future Directions

- Gaseous and particulate matter (PM) emissions will be measured during a five mode steady-state operating cycle. PM components including sulfate, nitrate, soluble organic fraction, metals, and polycyclic aromatic hydrocarbons (PAHs) will be fully characterized.
- Test lubricants will be blended using other basestocks, including basestocks containing higher sulfur content and synthetics.
- A bench scale apparatus will be developed to test how lubricant related emissions components impact the performance of diesel emissions control catalysts.

Introduction

The Diesel Emission Control—Sulfur Effects (DECSE) program quantified the impact of diesel fuel sulfur on the performance and short-term durability of diesel emission control devices. The sensitivity of some of these devices highlighted the need to study diesel lubricating oil, which is another source of sulfur and other potential poisons.

To address this need, a research program to study lubricant formulation (basestocks and additives) effects on diesel emission control systems is underway. The research is being conducted as part of DOE's APBF-DEC project and leverages participation from the Engine Manufacturers Association (EMA), the Manufacturers of Emissions Controls Association (MECA), the American Petroleum Institute (API), the National Petrochemical & Refiners Association (NPRA), and the American Chemistry Council.

It is anticipated that the results of this study will be critical in defining the needs of future lubricant formulations for both light-duty and heavy-duty diesel engines. Should a need for substantial lubricant reformulations be identified, industry would require significant development time to research "catalyst compatible" formulations that are cost-competitive and that continue to deliver the superior engine protection and long life demanded by engine customers. In addition, engine manufacturers recognize that the lubricant reformulations may drive the need for more robust engine hardware that is tolerant of modified oil chemistry, an endeavor requiring significant development time as well.

Approach

This project is being conducted in three consecutive phases. The first phase will identify and characterize lubricant derived emission constituents. This testing is utilizing a medium-duty CIDI engine that has been equipped with EGR and CCV (Figure 1). A matrix of conventional and experimental lubricant additive packages blended with various petroleum-based and synthetic basestocks is being tested. Twelve additive packages have been selected to provide a range of components including ash content, sulfur, zinc, and phosphorus. The four basestocks being tested span the available production approaches and include products of varying sulfur content, volatility, and degree of saturation. All finished lubricants are SAE 15W-40 viscosity grade.

All testing will be conducted at the five steady-state operating modes illustrated in Figure 2. These modes span the range of operation of the engine from idle to maximum torque and maximum horsepower. Two intermediate points are included that are representative of vehicle operation. Emissions that will be sampled during the five-mode, steady-state

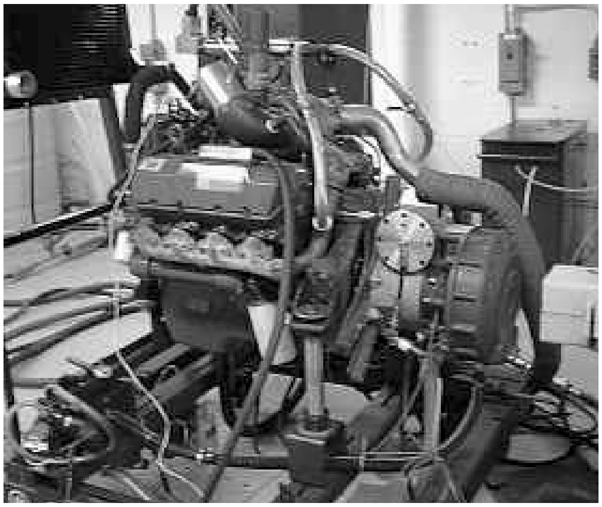

Figure 1. International T444E Engine Installation

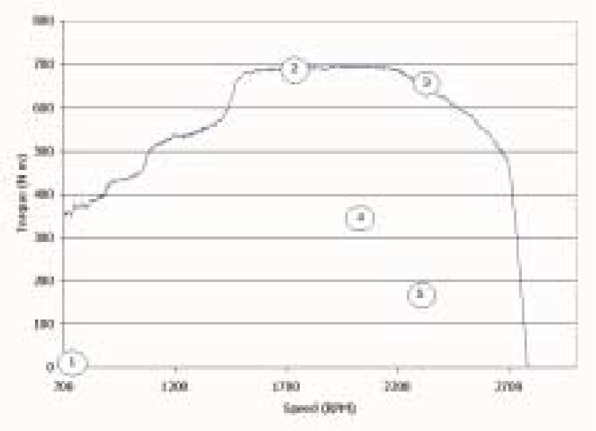

Figure 2. Steady-State Operating Modes for Emission Testing

operating cycle include gaseous hydrocarbons, carbon monoxide, sulfur dioxide, nitrogen oxides, and PM. The PM will be further analyzed for sulfate and nitrate fractions, soluble organic fraction, metals, and PAH content.

Follow-up work will be conducted to determine if, and to what extent, these lubricant-related emissions species affect the performance and durability of emission control devices designed to reduce NO_x and particulate matter (PM) emissions from diesel engines. Screening tests will be performed on a bench scale apparatus and will be followed up with full-scale confirmatory testing on full engine systems equipped with advanced emissions control technologies.

Results

Phase 1 emissions testing began in July 2001, and it will be completed during the first quarter of CY 2002.

C. Demonstration of Potential for Selective Catalytic Reduction and Diesel Particulate Filters

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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 & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Demonstrate the low-emissions performance of advanced diesel engines plus urea selective catalytic reduction (SCR) and diesel particulate filters (DPF)
- Determine the regulated and unregulated emissions with and without emission controls
- Examine the durability of the emission control systems
- Determine toxic and unregulated emission levels
- Evaluate the sensitivities of the emission controls to fuel variables

Approach

- Set up a heavy-duty engine in an emissions test cell to optimize emission reduction performance of two different emission control systems utilizing urea SCR.
- Apply a low-pressure-loop EGR system to reduce engine-out NO_x to ~ 2.0 - 2.5 g/hp-hr.
- Add emission control system(s) including diesel particulate filters and SCR systems with urea injection to reduce engine-out emissions of both NO_x and PM. (Two different emission control systems - DPF and SCR catalysts - will be evaluated.)
- Integrate controls and optimize performance of systems to reach the lowest possible emissions of NO_x and PM for both systems.
- Perform 6,000 hour durability tests simultaneously with the two different systems, checking emissions - regulated and unregulated - at 2,000 hour intervals.

Accomplishments

- In-kind contributions of important elements of the experimental setup have been received:
  - Caterpillar - C12 engine(s)
  - STT Emtec (Sweden) - Low-pressure loop EGR system
  - Robert Bosch - Urea injection system
  - Manufacturers of Emission Control Association (MECA) - SCR catalysts and DPF systems
- Set up of engine has begun in the emissions lab where the emission control systems will be optimized for emission reductions before moving to the durability phase of the project

Future Directions

- The project has begun at SwRI. The work plan calls for 22 months of effort - 10 months of performance optimization of two different SCR systems followed by 12 months of durability testing of both systems, running 6,000 hours total with emissions re-checks at 2,000-hour intervals.

Introduction

SwRI was chosen to be the contractor for this project as a result of a competitive procurement issued by ORNL. Working with the Advanced Petroleum-Based Fuels — Diesel Emission Control (APBF-DEC) teams and industry groups, we have arranged for significant in-kind support from the Engine Manufacturers Association (EMA), MECA, and individual companies. Caterpillar will supply the engines; MECA will supply the integrated emission control systems (DPF combined with SCR catalysts); STT will provide low-pressure-loop EGR systems; and Robert Bosch will provide the urea injection systems with controls.

Two different SCR systems, combined with DPF systems, will be provided by MECA in order to gain experience with different technologies. A fuel matrix of three fuels (minimum) will be evaluated, emphasizing the influence of fuel sulfur level on the performance of the systems.

Accomplishments

The subcontract was awarded to SwRI, and the contract was officially started in early May, 2001. SwRI has dedicated a heavy-duty emissions test cell to the project for its duration. Two durability test cells will be utilized during the second phase of the project with two identical engines running with the two different emission control packages. The engine and associated systems are being set up in the emissions lab at SwRI. Fuel has been received for the start of the project, and a urea supplier has been identified. Other elements - the EGR system, the urea injection system, and the emission control systems from MECA - are in the process of being provided.

Technical Approach in SwRI Subcontract

SwRI will spend the first 10 months integrating the systems on the engine and optimizing performance for lowest emissions. This will occur in series for the two different emission control systems. The general approach is to start with characterizing the engine-out emissions, which for NO_x is expected to be about 4 g/hp-hr. Adding the EGR system and optimizing its performance is expected to reduce the engine-out NO_x to about 2 g/hp-hr. Then, the addition of the SCR and DPF emission control system and optimization of its performance at 90% conversion efficiency should reduce the NO_x to the future standard of 0.2 g/hp-hr.

Two engines will be set up in separate durability test cells for the 12-month durability test. This will be a 6,000-hour test running the OICA cycle continuously during the period. At 2,000-hour intervals, the emission control systems will be removed from the durability engines, returned to the emissions test cell, mated with the original engine and retested for emissions performance.

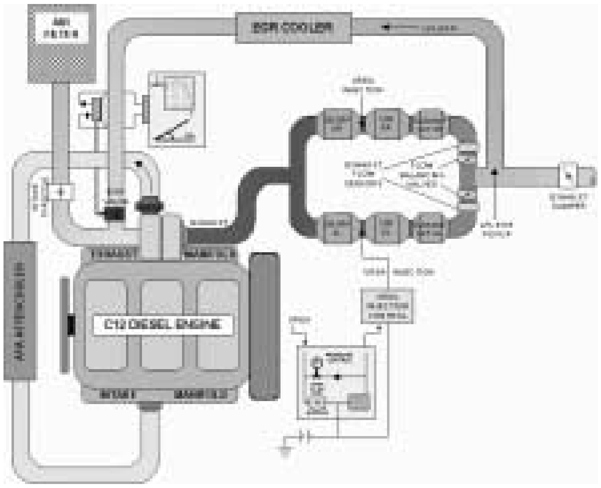

Figure 1. Diesel Engine and Emission Control System Configuration

Concern for preventing excessive back pressure and other practical considerations dictated that the exhaust emission control system be divided into two identical legs. So, for a given SCR/DPF combination, the exhaust will be split into two pathways, each comprised of first the DPF, followed by urea injection, the SCR catalyst, a final oxidation catalyst (for oxidizing any ammonia slip), and finally a flow balancing valve. This is illustrated in Figure 1. This complicates the control systems because it will require two urea injection systems plus the controls for balancing the exhaust flow. However, this was considered a better option than either accepting a higher back pressure or trying to acquire catalysts of a size that would not impose higher back pressures.

Currently, efforts are under way to set up the experiments at SwRI.

IV. VEHICLE TEST AND EVALUATION

A. The Emissions Impacts of Various Fuels on a CIDI Vehicle

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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

B. Fuel Property Effects on Exhaust Emission Control System Technology

E. Toxic Emissions

Tasks

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

Objective

- Quantify the exhaust emission effects of advanced petroleum fuel oxygenate blends in a vehicle powered by a state-of-the-art CIDI engine (DaimlerChrysler OM611).

Approach

- Six fuels will be evaluated for tailpipe exhaust emissions from a European Mercedes Benz "C" (220) series vehicle with the OM611 CIDI engine following the chassis dynamometer portion of the Federal Test Procedure (FTP) and the US06 aggressive driving cycle.

Accomplishments

- The matrix of test fuels includes advanced oxygenate blends, an advanced ethanol-containing fuel, and a fuel blend containing water.
- Testing has been delayed pending the availability of a specially produced base fuel that is representative of projected 2007 U.S. diesel fuel.

Future Directions

- Evaluate the effects of fuel blends containing oxygenated materials in an advanced CIDI powered vehicle that has advanced emission control devices such as NO_x adsorption and diesel particulate filter technologies.

Introduction

Potential exhaust emission reductions have been demonstrated in many previous studies for advanced and reformulated diesel fuels. In previous investigations, exhaust emissions were determined in a Mercedes Benz "C" Series European vehicle for a series of advanced petroleum-based fuels (see Table 1). The vehicle is powered by the OM611 engine, which has a displacement of 2.2 L, and has the following properties: 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. According to the vehicle manufacturer, the emission control system of this 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 the Mercedes Benz C 220 test vehicle.

In the previous investigations, all fuels tested in the C 220 vehicle had exhaust emissions exceeding the EPA Tier 2 standards. (Note that this vehicle was built to meet European emission regulations, which are less stringent than the upcoming Tier 2 standards.) With respect to test cycle severity, the US06 aggressive driving cycle was the most severe, followed by the Federal Test Procedure (FTP) and then the European cycles. Overall, the results showed a benefit in PM reduction for the oxygenated fuel in the FTP and European cycles. While a benefit was also observed for the oxygenated fuel over the US06 aggressive driving cycle, the reduction was not significant compared to the baseline diesel fuel PM emissions. The fuel blend containing 15% dimethoxymethane (DMM) consistently produced the lowest PM emissions; however, a slight increase in NO_x was observed. DMM15 fuel consistently had the lowest levels of volatile organic fraction (VOF). Fuel economy for the DMM15 fuel ranged from 8% to 11% less than the baseline fuel (2D).

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 Used in Previous Studies

Figure 1. Mercedes Benz C 220 CIDI Diesel Test Vehicle

Approach

This project will include exhaust emission evaluations of a Mercedes-Benz C 220 diesel vehicle equipped with the CIDI OM611 engine. This vehicle is equipped with "lean NO_x" catalyst technology (described previously), which relies on low-sulfur fuel to be effective. The vehicle will be tested using the following six fuels:

- 2007 Fuel (projected 2007 U.S. diesel fuel)
- 2007 Fuel + tripropylene glycol monomethyl ether (TPGME) @ 7% oxygen content
- 2007 Fuel + TPGME @ 3.5% oxygen content
- 2007 Fuel + di-butyl maleate @ 7% oxygen content
- Pure Energy blend (ethanol plus additives) in 2007 Fuel
- Puri-NO_x blend (water emulsion) using 2007 Fuel

All six fuels will be evaluated over the chassis dynamometer portion of the FTP and the US06 aggressive driving cycle. All test cycles will be conducted in triplicate.

Testing will utilize a Horiba 48-inch single-roll chassis dynamometer. This dynamometer electrically simulates inertia weights up to 12,000 pounds over the FTP (up to 7,000 pounds for vehicles capable of following the US06 driving trace) and provides programmable road load simulation of up to 125 hp continuously at 65 mph (300-hp momentary duty at 65 mph). SwRI will use a Mears Model to calculate a road load curve for the vehicle. This model requires coastdown data from drive and non-drive axles. A total of three coastdowns will be conducted on each axle, and the average results will be used as input for the Mears Model. The resulting calculated road load curve coefficients will be entered as the target "a", "b", and "c" values for use during the Horiba *Road Load Derivation* routine. With this routine, coastdowns are conducted with the vehicle on the chassis dynamometer to determine appropriate chassis dynamometer load coefficient settings. Vehicle equivalent test weight will be the measured curb weight of the vehicle with a 40 percent fuel fill in the main tank plus 300 pounds to account for a driver and luggage.

Dilute exhaust emission sampling will utilize a positive displacement-type constant volume sampler (CVS). An 18-inch diameter by 16-ft. long stainless steel dilution tunnel will be used in conjunction with the CVS to maintain an average tunnel sampling zone temperature of 110°F, with the maximum temperature not to exceed 125°F during the standard Federal Test Procedure. Nominal CVS flow rate will be 600 cfm. A constant-speed cooling fan of 5,000 cfm capacity will be used in front of the vehicle during operation.

Regulated exhaust emissions (total hydrocarbons, carbon monoxide, oxides of nitrogen, and particulate matter) and carbon dioxide will be sampled and measured in a manner consistent with EPA protocols for light-duty emission testing as given in the Code of Federal Regulations. Proportional dilute exhaust gas samples will be collected in Tedlar bags for analysis of carbon monoxide and carbon dioxide. Total hydrocarbons and oxides of nitrogen will be measured continuously from the dilution tunnel. Concurrently, a proportional sample of the dilute exhaust will be drawn through Pallflex T60A20 fluorocarbon-coated glass fiber filters for determination of particulate matter. Filter samples will be analyzed by direct filter injection gas chromatography (DFI/GC) to determine the particulate VOF and lubricating oil contribution to VOF. Exhaust constituents will be 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

Appropriate statistical techniques will be used to determine differences between the six fuels. Analysis of variance (ANOVA) will determine whether the average response of the six fuels is statistically different. All comparison tests will be made at the 5% level of significance.

Results

Testing has been delayed pending the availability of the 2007 base fuel. This is a specially produced diesel fuel that is projected to be representative of 2007 U.S. diesel fuel.

B. EC-Diesel Technology Validation Program

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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

E. Toxic Emissions

F. Ultra-fine Particles

Tasks

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

Objectives

- Compare exhaust emissions from vehicles fueled with EC-Diesel and California diesel fuels. EC-Diesel, also known as ECD, 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 ECD 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 guide the program.
- Select vehicle fleets in Southern California to participate.
- 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 ARCO (a BP Company), DDC (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 following fleets have been retrofitted with catalyzed particle filters and are participating in the program: San Diego School District School Buses, ARCO Tanker Trucks, Ralphs Grocery Trucks, LA City Refuse Haulers, Los Angeles County MTA Transit Buses, Hertz Equipment Rental Trucks, and shuttle vehicles.
- First round vehicle test results were published in three SAE technical papers. Second round emissions tests have been completed and will be published at the 2002 SAE World Congress. The start-up experience for the Ralphs Grocery truck fleet was published to document retrofit considerations and report on operating cost, maintenance and fuel economy through the first five months of vehicle operation.

Future Directions

- The program has been expanded to test ECD-1, a new fuel that BP is introducing into the California market.
- Three vehicles were selected to chemically characterize the exhaust emission species. These vehicles were fueled with California diesel, EC-Diesel and ECD-1. The vehicles were tested with and without the particle filters. Exhaust speciation data and particle size distribution data are being analyzed and will be published in 2002.
- Further testing is needed to examine the capabilities and limitations of passive particle filters in colder climates and in older vehicles.

Introduction

ARCO, a BP Company, has developed a new diesel fuel called Emission Control Diesel (ECD). ECD is a heavily hydrocracked fuel produced from typical crude oil. ECD has a maximum sulfur content of 15 ppm, about 10% aromatics by volume, and a nominal cetane number of 60. More recently, BP has introduced ECD-1 into the southern California market. ECD-1 also has 15 ppm maximum sulfur content, but has 22% aromatics and a nominal cetane number of 50. ECD-1 contains both hydrocracked and hydrotreated stocks.

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 element. 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 conducted to evaluate ECD 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 truck and bus fleets.

Approach

Seven 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 designated DPX™), or the Johnson-Matthey continuously regenerating technology (hereafter designated CRT™). Both DPX and CRT units are passive devices that were installed in place of the existing muffler system, without any modification to the engines. The retrofitted vehicles are fueled exclusively with ECD 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 (NO_x), total hydrocarbons (HC) and particulate matter (PM) were measured over the City-Suburban Heavy Vehicle Route (CSHVR) and a number of other driving schedules.

Results

Vehicles retrofitted with catalyzed particle filters and fueled with ECD 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.

The same grocery trucks were retested after twelve months of operation and more than 100,000 miles accumulation per truck. The particle filters were not serviced prior to the second round emissions tests (Figure 3). Average particulate matter emissions from the retrofitted trucks were again found to be 89% to 99% less than the

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

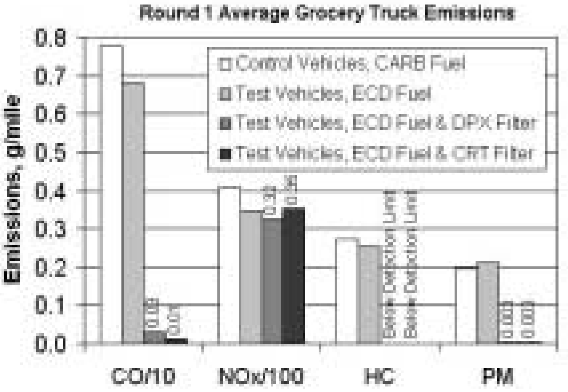

Figure 2. Average Grocery Truck Emissions over the City-Suburban Heavy Vehicle Route, February-March 2000

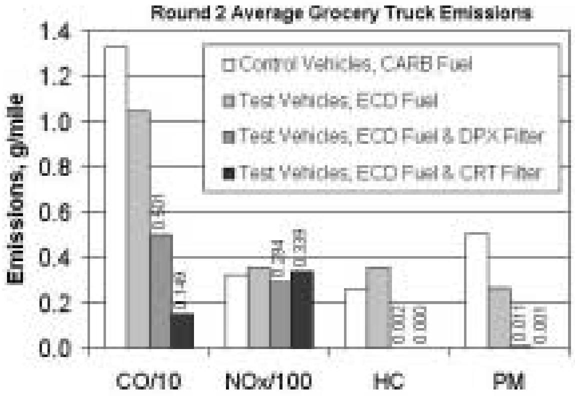

Figure 3. Average Grocery Truck Emissions over the City-Suburban Heavy Vehicle Route, February-March 2001

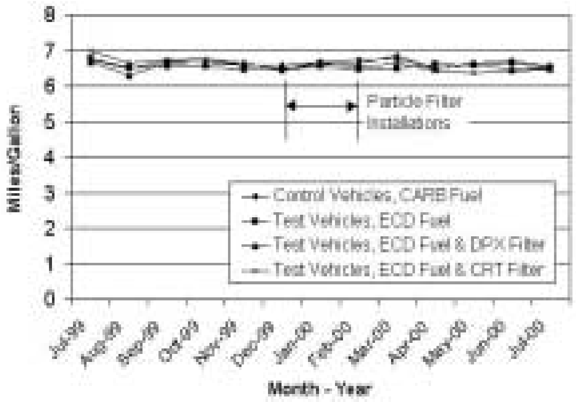

Figure 4. Monthly Average Fuel Economy for Grocery Trucks with and without Diesel Particle Filters

California diesel-fueled vehicles having no exhaust filter equipment.

Through the first five months of operation, there was no detectable difference in fuel economy between grocery trucks with and without particle filters, based on an analysis using fleet operation records (Figure 4).

Conclusions

Several types of heavy vehicles have been successfully retrofitted with catalyzed particle filters. Second round emissions tests indicate that the particle filters have operated reliably over a twelve month period and continue to dramatically reduce particulate matter, hydrocarbon, and carbon monoxide emissions without adversely affecting fuel economy.

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Presentations

1. Vertin, K., "Class 8 Trucks Operating on Ultra-Low Sulfur Diesel with Particulate Filter Systems: A Fleet Start-Up Experience," presented at the SAE International Fall Fuels and Lubricants Meeting, October 16-19, 2001.
2. Clark, N.N., "Class 8 Trucks Operating on Ultra-Low Sulfur Diesel with Particulate Filter Systems: Regulated Emissions," presented at the SAE International Fall Fuels and Lubricants Meeting, October 16-19, 2001.
3. LeTavec, C., "EC-Diesel Technology Validation Program," presented at the 2000 SAE Truck and Bus Conference, December, 2000.
4. Chatterjee, S., "Emission Reductions and Operational Experiences with Heavy Duty Diesel Fleet Vehicles Retrofitted with Continuously Regenerated Diesel Particulate Filters in Southern California," presented at the 2001 SAE World Congress, March 5-8, 2001.

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V. SUPPORTING RESEARCH

A. Effects of Oxygenated Diesel Fuels on In-Cylinder Combustion and Soot-Formation Processes

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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
F. Ultra-fine Particles

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions

Objectives

- Enhance understanding of how diesel oxygenates affect in-cylinder combustion and emissions-formation processes. Specifically:
  - Determine whether oxygen content alone governs the soot-reduction potential of an oxygenated fuel blend, as has been suggested in several recent studies.
  - If it is found that oxygen content is not the only important factor, identify and quantify the extent to which other parameters (*e.g.*, oxygenate molecular structure, fuel thermophysical properties, flame lift-off length, *etc.*) influence the sooting tendencies of a fuel.
- Collaborate with research groups in academia, industry, and national laboratories to maximize the value of research capabilities unique to Sandia.
- 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 1: Implement and verify proper operation of a production Caterpillar hydraulically-actuated, electronically controlled unit injector (HEUI) fuel-injection system in the optical 4-stroke DI diesel engine.
- Phase 2: Prepare a suite of laser/imaging and traditional diagnostics to study the in-cylinder combustion processes of oxygenated fuels in the optical engine.
- Phase 3: Identify four fuel formulations that represent limiting cases that can be used to help determine mechanisms by which fuel property variations can lower emissions and enhance efficiency.
- Phase 4: Conduct experiments that apply the suite of diagnostics developed in Phase 2 to each of the fuels selected in Phase 3.
- Phase 5: Analyze results and report findings to collaborators in industry, academia, and the national laboratories. Publish in the open literature to broadly disseminate results and conclusions.

Accomplishments

- Completed Phase 1. Injector and laboratory infrastructure modifications were made to enable the use of a production Caterpillar HEUI fuel-injection system. Performance of the new system was verified to be representative of production hardware.
- Completed Phase 2. The diagnostics selected are:
  - Imaging of direct luminosity (DL) for general characterization of ignition locations and evolution of regions of high soot concentration and temperature
  - Imaging of Mie-scattered light to visualize spray development and to verify proper injector performance with each experimental fuel
  - Measurement of injected fuel quantity to determine engine efficiency
  - Measurement and thermodynamic analysis of cylinder pressure data to determine heat release rate profiles and combustion phasing
- Completed Phase 3. The fuels selected are:
  - A non-oxygenated, 45-cetane hydrocarbon fuel used as a baseline for comparison with oxygenated fuel results
  - A 50 wt%-oxygen, low-cetane fuel that requires use of a glow plug (GP) for repeatable ignition
  - A 26 wt%-oxygen, typical-cetane fuel containing an ether oxygenate
  - A 26 wt%-oxygen, typical-cetane fuel whose ignition delay has been matched to that of the ether-containing fuel but that contains a di-ester oxygenate[1]
- Completed Phase 4. Baseline engine characterization using the non-oxygenated hydrocarbon fuel was completed. Experiments investigating the GP-assisted ignition and combustion of the highly-oxygenated, low-cetane fuel were completed. Experiments with the two 26 wt%-oxygen fuels also were completed.
- Phase 5 is near completion. Results from Phase 1 have been published in a Sandia Report [2]. Results from Phase 4, using the first two fuels from Phase 3 and the diagnostics from Phase 2, have been

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[1] Both the ether oxygenate and the di-ester oxygenate selected for these tests were identified during the CIDI Oxygenates Screening Project [1].

published in a Society of Automotive Engineers paper [3]. Analysis of results from Phase 4 using the two 26 wt%-oxygen fuels from Phase 3 is in progress. Some key results:

- GP-assisted combustion of the 50 wt%-oxygen, low-cetane fuel reduces in-cylinder soot by at least two orders of magnitude relative to standard diesel fuel while maintaining engine efficiency and reducing engine noise.
- GP-assisted ignition and combustion is strikingly different from standard diesel combustion and may have a pronounced effect on emissions.
- Overall oxygen content is not the only important parameter governing the soot-reduction potential of an oxygenated fuel blend. Differences in oxygenate molecular structure and/or in-cylinder processes can change in-cylinder soot by a factor of two or more even when all other engine parameters are held constant.

Future Research Directions

- Add a blend containing a third oxygenate, di-ethyl adipate, to the 26 wt%-oxygen fuels selected in Phase 3, and conduct experiments using diagnostics from Phase 2. This oxygenate is of interest because it is a di-ester similar to the di-ester tested above, but different in that it contains no carbon-carbon double bonds. Study of such a molecule will further aid in the assessment of the role of molecular structure in soot production.
- Conduct experiments to measure flame lift-off lengths for the three 26 wt%-oxygen fuels. These results will help determine whether differences in in-cylinder soot are due primarily to differences in fuel-air premixing.
- Conduct Laser Induced Incandescence (LII) experiments to study the spatial development of in-cylinder soot for the three 26 wt%-oxygen fuels. These results will provide additional insight into the mechanisms by which different oxygenates affect the production and oxidation of soot.

Introduction

Blending oxygen-containing compounds ("oxygenates") with diesel fuel can lead to reduced soot and NO_x emissions, as well as reduced fuel consumption. The detailed mechanisms that cause such reductions are not well understood. For instance, the literature contains conflicting results as to whether overall oxygen content is the only important parameter in determining the soot-reduction potential of a given fuel, or if oxygenate molecular structure or other variables also play significant roles. The goal of this research is to enhance the understanding of how diesel oxygenates affect in-cylinder combustion and emissions-formation processes. Such an improved understanding will help engine designers, fuel suppliers, and policy makers use diesel fuel formulation to greatest advantage to reduce emissions and cost while enhancing efficiency and energy security.

Engine and Fuels

The Sandia alternative fuels optical engine laboratory shown in Figure 1 features a single-cylinder version of a modern, 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 schematic of the optical engine is shown in Figure 2. The large window in the piston enables combustion processes to be imaged, and a glow plug (GP) enables the study of certain low-cetane alternative fuels. Specifications of the optical engine are provided in Table 1. Fuel compositional information is provided in Table 2. A 1200-rpm, moderate-load operating condition was studied, and injection timing was optimized independently for each fuel such that the engine always operated at peak efficiency.

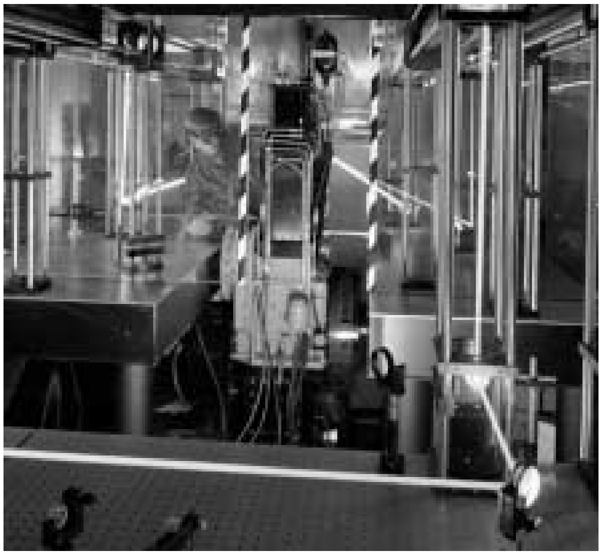

Figure 1. Sandia Alternative Fuels Optical Engine Laboratory in Operation

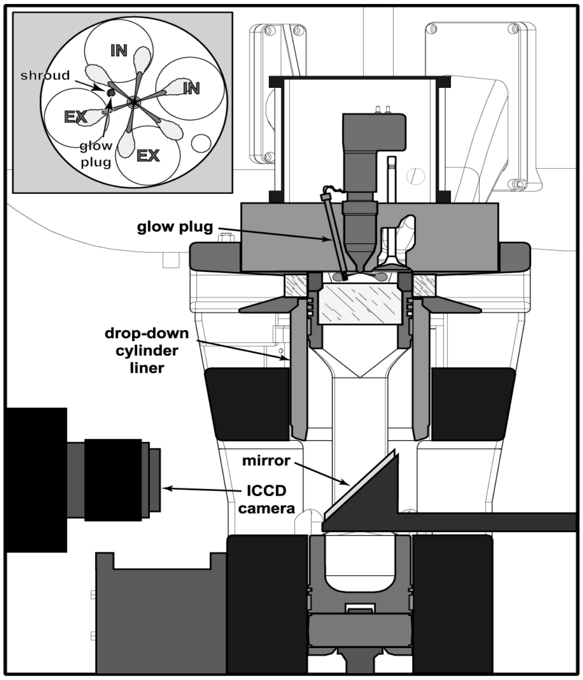

Figure 2. Schematic diagram of the Sandia/Caterpillar optical engine. Inset: View of combustion chamber showing orientation of fuel sprays with respect to glow plug during experiments with M100 fuel.

Production engine type	6-cyl. Caterpillar 3176/C-10
Research engine type	1-cyl. version of 3176/C-10
Cycle	4-stroke CIDI
Valves per cylinder	4
Ignition assist	In-cylinder glow plug
Bore	125 mm
Stroke	140 mm
Peak cylinder pressure	14.0 MPa
Intake valve open	318° ATDC compression
Intake valve close	146° BTDC compression
Exhaust valve open	107° ATDC compression
Exhaust valve close	343° BTDC compression
Connecting rod length	225 mm
Connecting rod offset	None
Bowl diameter	90 mm
Bowl depth	16.4 mm
Swirl ratio	0.59
Displacement per cyl.	1.72 liters
Compression ratio	11.3:1
Simulated compr. ratio*	16.0:1

* TDC conditions in the production engine are matched in the optical engine by preheating and boosting the pressure of the intake air.

Table 1. Specifications of the Sandia/Caterpillar Optical Engine

Fuel	Composition (by volume)	Oxygen Content (by weight)
CN45	64.7% $C_{16}H_{34}$ as HMN[a] 35.3% $C_{16}H_{34}$ as NHD[b]	0%
M100	100.0% methanol 95 ppm DCI-11[c]	50%
GE80	80.0% TPGME[d] 20.0% $C_{16}H_{34}$ as HMN[a]	26%
BM88	88.0% DBM[e] 7.0% $C_{16}H_{34}$ as NHD[b] 5.0% EHN[f]	26%

[a] 2,2,4,4,6,8,8-heptamethylnonane
[b] *n*-hexadecane
[c] corrosion-inhibiting additive from Octel-Starreon Co.
[d] tri(propylene glycol) methyl ether
[e] di-butyl maleate
[f] 2-ethylhexyl nitrate

Table 2. Compositions of Test Fuels

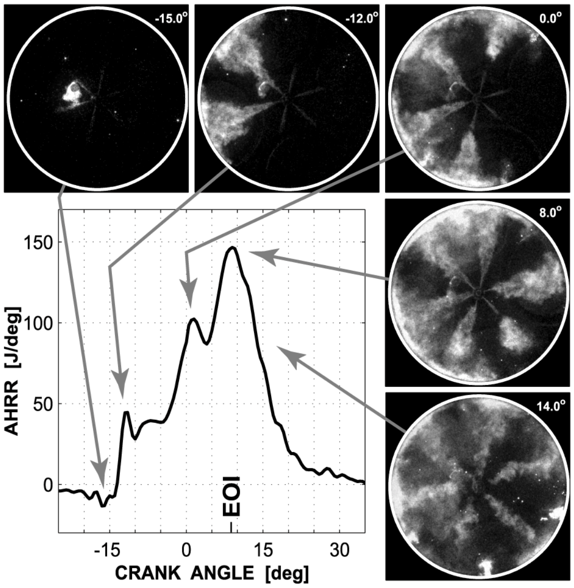

Figure 3. Pair-wise Jet Ignition Events Observed in Direct Luminosity Images of M100 Combustion Correspond to Peaks in Apparent Heat Release Rate

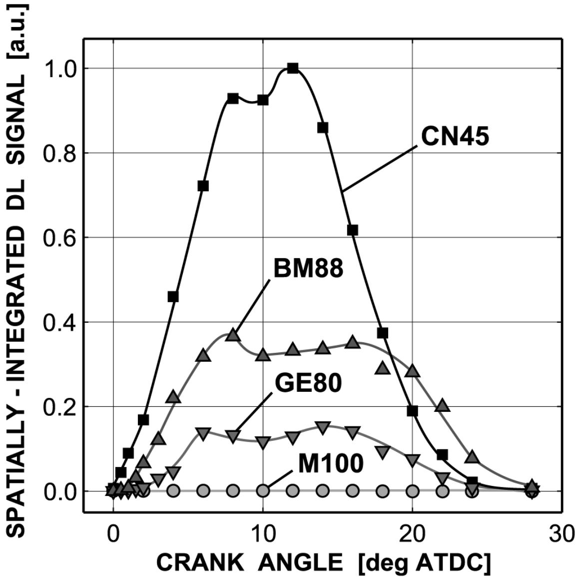

Figure 4. Variation of spatially-integrated direct luminosity for the four test fuels. Peak signal is used as a measure of peak in-cylinder soot.

Diagnostics

In-cylinder images of direct luminosity (DL) and spray development were acquired and coupled with measurements of cylinder pressure and injected fuel quantity. The DL image sequences show the evolution of regions of high soot concentration and temperature throughout the combustion event. The spray-development images provide verification that the experimental fuels do not degrade fuel-injection system performance over time. The cylinder pressure and injected quantity measurements provide information about heat-release rates and engine efficiency, respectively.

Results

The goal of the first set of experiments was to study the GP-assisted ignition and combustion of a low-cetane, highly-oxygenated fuel [3]. The fuel selected for these experiments, M100, had an oxygen content of 50 wt% and a cetane number < 5 such that GP-assisted ignition was essential for stable engine operation. The M100 data show significant departures from the traditional diesel combustion features exhibited by the CN45 hydrocarbon reference fuel. Whereas CN45 readily autoignites at the engine operating conditions studied, M100 does not. The GP-assisted ignition of M100 was found to be strongly dependent on GP temperature and proximity to a fuel jet. The DL images show that M100 ignition occurs at the GP, followed by combustion propagation first to the two jets straddling the GP, then to the adjacent two jets, and finally to the last two jets emanating from the 6-hole, centrally-located injector nozzle. Figure 3 shows this process and indicates how the three spikes in the M100 apparent heat release rate (AHRR) profile are observed to correspond to these pair-wise jet ignition events. Spatially integrating the DL signal within a given image yields a measure of the amount of hot, in-cylinder soot at that crank angle. Calculation of this parameter in each image of the sequence yields a curve showing the variation with crank angle for each fuel. Such data for CN45 and M100, shown in Figure 4, suggest that in-cylinder soot concentrations during M100 combustion are at least 2 orders of magnitude lower than those during CN45 combustion. Peak heat release rates during M100 combustion are only half of those achieved during the premixed burn phase of CN45 combustion, resulting in noticeably quieter engine operation. This observation highlights one advantage of using a GP to assist ignition of a low-cetane fuel, because cetane number decreases typically result in increased, rather than reduced, combustion noise.

The goal of the second set of experiments was to study two oxygenated fuel blends whose only difference is the type of oxygenate used, in order to determine if the type of oxygenate affects the soot-reduction performance of the fuel. Nominal oxygen content was matched at 26 wt% for the two blends selected, GE80 and BM88 (see Table 2). The ignition improvers 2-ethylhexyl nitrate (EHN) and cetane were used to offset the poor ignition quality of DBM (whose cetane number is only approximately 30), shortening the ignition delay of BM88 so that it matches that of GE80. Since injection timing was not changed, this ensured that combustion phasing was matched for the two oxygenated fuels. All engine operating conditions (*e.g.*, TDC temperature and density, speed, load, etc.) were held constant across the experiments as well. The DL images presented in Figure 5 show no dramatic evidence of differences in ignition or combustion processes between the two fuels. Whereas general combustion features are similar, differences between the two blends become apparent when the peak spatially-integrated DL signals are compared. Figure 4 shows that the peak spatially-integrated DL signal for BM88 is more than twice as large as that for GE80. This result suggests that overall oxygen content may not be the only important factor governing the soot-reduction potential of these oxygenated fuels. The difference in peak spatially-integrated DL between the two fuels may be due to molecular structure effects, differences in the degree of fuel-air premixing (lift-off length), and/or limitations of the diagnostic technique. These issues will be addressed in a series of follow-on experiments.

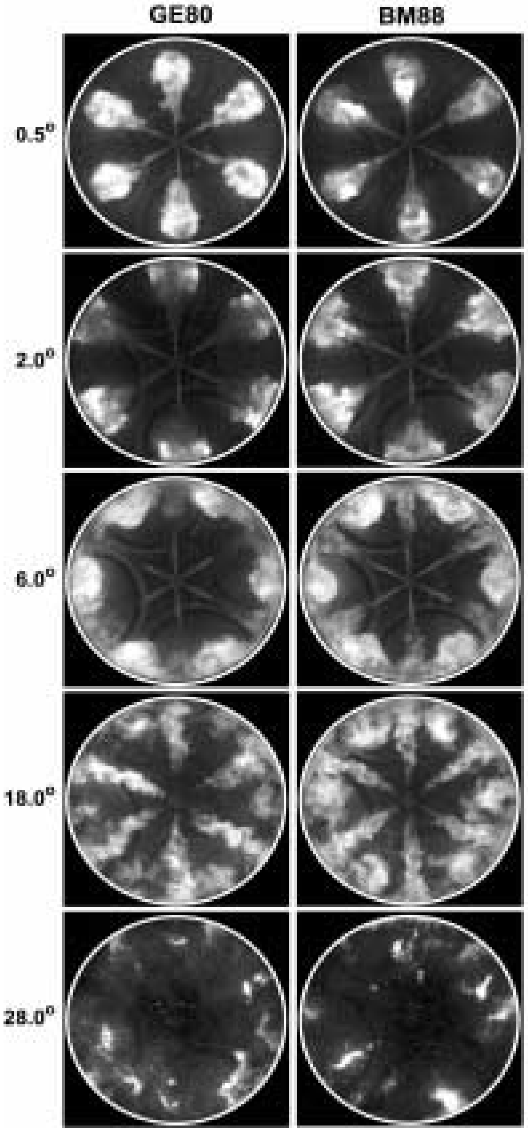

Figure 5. Direct luminosity image sequences for GE80 and BM88 fuels. Significant differences in ignition and combustion processes are not evident. Comparison of apparent brightness between images cannot be used to estimate differences in spatially-integrated direct luminosity because camera gain was adjusted for each image to ensure proper exposure.

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B. 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

- Use a suite of diagnostic models to assess the environmental performance of oxygenated compounds that are candidates for use in advanced petroleum-based fuels to reduce particulate emissions from CIDI engines.
- Design and implement experiments to evaluate the biodegradation potential of selected fuel oxygenates. Compare experimental results against predictions to help establish the level of accuracy and the limitations of biodegradation models.
- Evaluate the nature and magnitude of potential human exposures to oxygenates released to the environment.

Approach

- Review data on the physicochemical properties of two new oxygenate candidates, dibutyl maleate (DBM) and tripropylene glycol monomethyl ether (TGME), and determine their potential for degradation in the environment.
- Determine relevant environmental transport properties.
- Implement and run diagnostic models to determine the fate of DBM, TGME, dimethoxymethane (DMM), and reference fuel compounds for various environmental release scenarios.
- Perform biodegradation experiments, and include benzene and methyl tert-butyl ether (MTBE) as benchmark compounds for data interpretation.

Accomplishments

- Selected, implemented, and improved environmental models suitable for conducting screening-level analyses of fuel oxygenates.
- Simulated the transport and fate of DMM, DBM, TGME, and other fuel compounds in environmental media.

- Conducted biodegradation experiments on DMM, DBM, TGME, and other fuel compounds to serve as a reference (i.e., benzene and MTBE).
- Evaluated potential human exposures to water contaminated with DBM, TGME, MTBE, and benzene.

Future Directions

- Continue to build and improve our library of diagnostic models to assess the environmental impact of oxygenated and other fuel components.
- Develop modeling and experimental methods for studying the fate of fuel compounds and additives in complex mixtures.
- Carry out selected experiments to verify predictions and fill key data gaps for oxygenates and other fuel compounds of interest.

Introduction

Research has shown that the addition of oxygenated compounds to diesel fuels reduces particulate emissions. There are potentially many oxygenates that could be used, but some may have undesirable environmental effects. This project aims to establish a methodology to study the potential environmental impacts of oxygenated fuel compounds. Data developed by the project will assist DOE/OTT and industrial partners in evaluating the potential environmental performance of proposed fuel additives such as TGME and DBM. These compounds were chosen through a selection process based on a series of tests performed by the Southwest Research Institute on 71 oxygenates.

Results

Our analysis of the physicochemical properties indicates that TGME and DBM will not partition significantly into air because of their low vapor pressures, about 5 orders of magnitude less than those of DMM, MTBE and benzene. In addition, DBM has a very low solubility and a high octanol-water partition coefficient (K_{ow}), and therefore will tend to adsorb to the organic phase of soils. On the other hand, TGME is very soluble and will tend to migrate with water. A biodegradation model based on chemical-structure relationships predicts that DBM will biodegrade readily, but TGME will not.

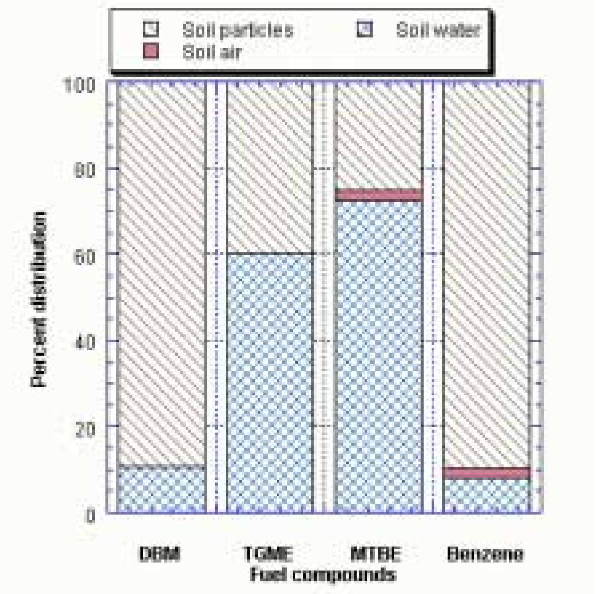

Figure 1. Distribution of Fuel Compounds in the Phases of a Reference Sandy Soil (bulk density = 1.59 g/cm^3; porosity = 0.4 (total), 0.18 (water), 0.22 (gas); organic fraction = 0.0075)

We used an equilibrium model to determine the partitioning of DBM and TGME between the air, water, and solid phases of a reference soil (see Figure 1, MTBE and benzene also included). Neither DBM nor TGME distributes in any significant amount to the air phase. DBM partitions primarily to the solid phase because of its high affinity for organic matter, and TGME partitions preferentially to the water phase because of its high solubility.

Transport in unsaturated soil was simulated using an analytical advection-dispersion model. The initial contamination source was assumed to be uniformly distributed between 1.00 and 1.30 meters beneath the surface of a reference sandy soil. Figure 2 shows the concentration profiles after a year for

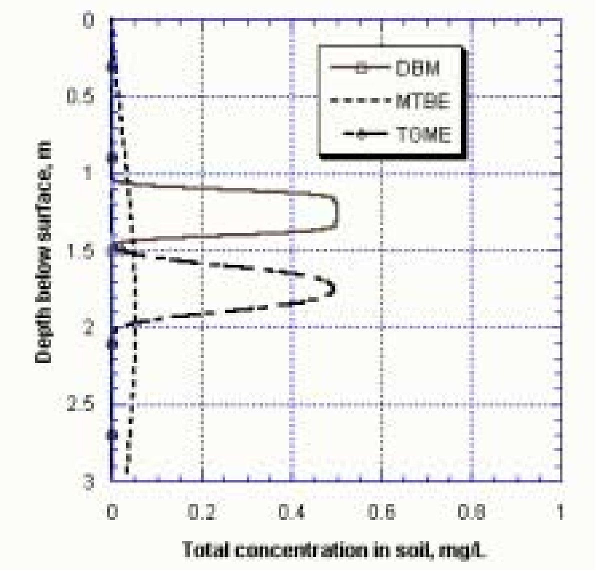

Figure 2. Concentration Profiles of DBM, TGME, and MTBE in Soil after 1 Year of Transport from a Buried Source Uniformly Distributed between 1.00 and 1.30 m at Time = 0

DBM, TGME, and MTBE. Diffusion of MTBE in the gas phase redistributes it through the soil column. TGME moves with infiltrating water, but DBM has barely moved due to its affinity for the solid phase.

Initial results of the biodegradation experiment given as CO_2 concentration in the headspace of sealed microcosm flasks as a function of time are presented in Figure 3. There is no significant difference in the CO_2 concentration between the control, DMM, and MTBE, in a 28-day incubation period. On the other hand, benzene shows a very steep rise in the CO_2 concentration within the first 5 days. DBM shows a clear increase above the background level by day 8 and from then on the CO_2 concentration rises a little and remains more or less constant. TGME shows rising values above background from day 15 on.

We estimated water-based exposures to humans using a nominal concentration of 1 ppm for DBM, TGME, MTBE, and benzene (see Figure 4). Among these compounds, DBM would have the largest skin uptake due to its relatively high K_{ow}, although most of its net uptake would occur via ingestion. TGME exposure would occur exclusively through ingestion. Conversely, the dominant pathway for benzene and MTBE is inhalation. DBM and TGME have very low Henry's Law constants and thus the inhalation pathway is insignificant.

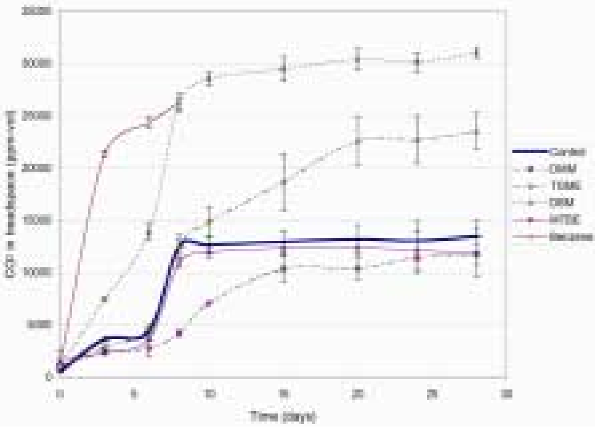

Figure 3. CO_2 Concentration in the Headspace of Microcosm Flasks Containing: DMM, TGME, DBM, MTBE, and Benzene, as a Function of Time

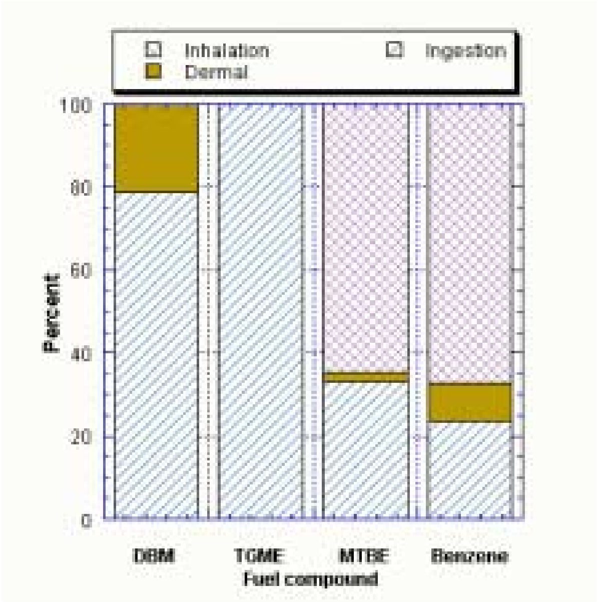

Figure 4. Comparison of Water-based Exposures to DBM, TGME, MTBE, and Benzene in Drinking Water via Inhalation, Dermal Uptake, and Ingestion

Conclusions

Preliminary biodegradation tests confirm that DBM is readily degraded. TGME also seems to biodegrade, but more slowly than DBM or benzene. The biodegradation tests were performed using activated sludge, which is a fairly aggressive media. In other natural environments, the rate of biodegradation could be much slower. TGME's slower biodegradation combined with its high solubility are indications that TGME would be more mobile in the subsurface than DBM. Additional studies are needed to determine whether TGME would constitute a threat to groundwater when stored in subsurface fuel tanks. In our previous work on DMM, we indicated that it was likely to be recalcitrant and mobile in ground water, behaving similarly to MTBE in the environment. The results of the biodegradation experiment confirmed our model prediction.

Presentations and Publications

1. D. Layton, A.A. Marchetti, and M. Knize, "Environmental Performance of Fuels for Advanced Engines: Oxygenate Assessment", presented at the annual review of the Office of Advanced Automotive Technologies, US DOE, June 11-13, 2001.
2. A.A. Marchetti, and D. Layton, "Environmental Performance of Dimethoxymethane (DMM)", (for submission to *Chemosphere*).

C. Chemical Characterization of Toxicologically Relevant Compounds From Diesel Emissions: A Project of the Fuels/Particulate Matter Initiative

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Industry Partners: Ford Motor Company and Marathon Ashland Petroleum LLC

This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

E. Toxic Emissions

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions

Objectives

Phase I (Completed)

- 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, and other gaseous exhaust "toxics" collected from a diesel engine using various fuel compositions.

Phase II (In Progress)

- Investigate the role of fuels on tailpipe exhaust emissions of potentially toxicologically relevant compounds, utilizing a diesel oxidation catalyst and a catalyzed particulate filter.
- Investigate the role of high moleculer weight oxygenate on diesel exhaust toxicity.
- Determine the 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 Daimler-Benz OM611 diesel 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).
- Four gaseous EPA Clean Air Act "toxic" exhaust emissions were measured.
- Eleven gaseous PAH compounds were measured.
- Seventeen PAH compounds were determined for the soluble organic fraction of the exhaust particulate matter.

Phase I

- The matrix included 5 fuels (including one oxygenate blend) operated over 5 speed/load points.
- Each speed/load point operated to hold the Location of Peak Pressure (LPP) of combustion at 7° after top dead center (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 was the stock controller; the other was to include pilot fuel injection while maintaining the Location of Peak Pressure at 7°ATDC.

Phase II

- The matrix will include 6 fuels, including two oxygenate blends with tripropylene glycol monomethyl ether (TPGME), operated over 4 speed/load points.
- The engine will be operated utilizing pilot fuel injection at a low-NO_x engine-out calibration specific for each fuel and speed/load point.
- Measurements are to be taken at engine-out, downstream of the diesel oxidation catalyst, and downstream of the catalyzed particulate filter.

Accomplishments

Phase I

- The project plan was finalized with coordinated input from DOE and industry representatives. The industry representatives specified the cylinder balance approach and EGR levels for each speed/load condition.
- All fuels were tested in triplicate for five modes, pilot injection off, LPP operation. Pilot fuel injection evaluation for all fuels completed in triplicate for two modes and two pilot fuel injection strategies.
- Statistically significant fuel effects on exhaust emissions were identified.
- Oxygenate containing fuel and Fischer-Tropsch fuel produced the lowest overall toxic gas and PAH exhaust emissions.

Phase II

- The project plan has been finalized with coordinated input from DOE and industry representatives. The industry representatives defined the NO_x emission index targets.
- Consulted with industry representatives to define the methodology to achieve the low engine-out NO_x emission index target.
- An engine-out NO_x emission index reduction of 30% is achievable using stock engine modal calibrations.

Future Directions

- Determine fuel effects on emission characterization utilizing a NO_x trap.
- Determine fuel effects on emission characterization for NO_x and particulate trap regeneration.

Introduction - Phase 1

This project 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. It also addresses the chemical characterization of emission compounds with known or suspected toxicological properties (e.g. carcinogens).

Phase 1 Objective

The goal of this project is to better understand the role of fuels on the emissions of a subset of potentially toxicologically relevant compounds. Objectives of this project are: 1) to measure the polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of particles collected from diesel 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 are being made on engine-out emissions.

Phase 1 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 addition, four toxic air pollutants were quantified. The DaimlerChrysler OM611 diesel 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	4.2	15
M 5	2600	8.8	5

Table 1. OM611 Engine Operating Conditions

	CA	ALS	FT-100	ADMM15	DF-2
H, wt%	13.4	14.4	15.1	13.7	13.0
C, wt%	86.4	85.6	84.8	81.6	86.7
O, wt%	0.2	0.0	0.1	4.7	0.3
Cetane Number	45	63	84	59	44
Sulfur, ppm	176	1	0	<2	337
Aromatics, wt%	18.9	9.0	0.2	8.2	30.3

Table 2. Toxicity Test Fuels for OM611 Engine

The four mobile source toxic air pollutants 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. They are California Reference Diesel Fuel (CA), Low Sulfur Diesel Fuel (ALS), Fischer-Tropsch Diesel (FT-100), Oxygenate Blend of 15% Dimethoxymethane in ALS (ADMM15), and EPA 2D Certification Fuel (DF-2).

The particulate matter was sampled from a 203 mm 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 90mm filters. Benzene and 1,3-butadiene were collected in a sample bag from the dilution tunnel sample zone. Formaldehyde and acetaldehyde were trapped on a dinitrophenylhydrazine (DNPH) adsorbent cartridge from the dilution tunnel sample zone.

Phase 1 Discussion

Fuel comparisons utilizing the Auto/Energy Panel Mode Weighting Factors shown in Table 3 were made for brake-specific exhaust emissions with the engine operated under LPP control.

Several statistically significant trends were apparent from an analysis of variation (ANOVA) of the weighted average brake specific emissions data. For HC, CO, PM, and soluble organic fraction (SOF), the lowest emitting fuels were ADMM15 and

Mode	**Mode Weights, seconds**
Mode 11	600
Mode 10	375
Mode 6	200
Mode 5	25
Total	1200

Table 3. Auto/Energy Weighting Factors for Engine-Out Emissions

FT-100, with the higher emitting fuels being DF-2, then CA. 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.

While the mass emissions of PM and SOF reflect the same relative order of fuels, the relative order of the percent of extractable mass from particles generated from the different fuels is not the same. The percent of extractable mass from particles emitted using the different fuels shows a different rank order (Table 4). In this case, ADMM-15 is the fuel that generates PM with the highest percentage of organic soluble material while Fischer-Tropsch fuels have the lowest percentage emissions of organic soluble compounds. This may be important for a complete vehicle system that is equipped with an oxidation catalyst emission control device. A vehicle equipped with an oxidation catalyst, using an ADMM-15 fuel, could conceivably emit very low PM because the catalyst would oxidize most of the organic material bound to the particle, thereby reducing the mass of particles emitted from the vehicle.

The emissions of the four toxic air pollutants specifically cited in the Clean Air Act (benzene, 1,3-butadiene, formaldehyde, acetaldehyde; Table 5) show very similar trends. The use of either the Fisher-Tropsch fuel or the ADMM-15 fuel resulted in the lowest emissions for benzene and 1,3-butadiene. The worst fuels for emitting benzene and 1,3-butadiene were consistently the CA or the DF-2 fuel. All of the fuels were statistically indistinguishable from each other for the emissions of formaldehyde and acetaldehyde. For the four EPA air toxic compounds, ADMM15 and FT-100 were statistically similar emitting fuels.

For both the gas phase and soluble phase PAH compounds, the fuels ranked in the general order from highest emitter DF-2, CA, ALS, with ADMM15 and FT-100 being in the same statistically equivalent lowest grouping. The PAH response appears to be a function of fuel aromatic content. Table 5 summarizes the general rank order for the weighted average mass emissions during LPP engine operation.

Fuel	Percent of Extractable Mass (%)	Mass of PM (g/kW-h)	Mass of SOF (g/kW-h)
ADMM-15	86	0.1431	0.1237
CA	84	0.2627	0.2207
DF-2	79	0.2888	0.2279
ALS	71	0.2249	0.1608
FT-100	54	0.1337	0.0723

Table 4. Percent of PM Extracted by Organic Solvents

Rank	**Highest** →				**Lowest**
PM	DF-2	CA	ALS	ADMM15	FT-100
SOF	DF-2	CA	ALS	ADMM15	FT-100
NO_x	DF-2	ADMM15	FT-100	CA	ALS
Benzene	CA	DF-2	ALS	FT-100	ADMM15
1,3 - Butadiene	CA	DF-2	ALS	ADMM15	FT-100
Formalde-hyde	DF-2	ALS	CA	ADMM15	FT-100
Acetalde-hyde	DF-2	ALS	CA	ADMM15	FT-100
Gas Phase PAH	DF-2	CA	ALS	ADMM15	FT-100
Soluble Phase PAH	DF-2	CA	ALS	ADMM15	FT-100

Table 5. Fuel Rank Order from ANOVA for Weighted Average Emissions for LPP Operation

The effect of pilot fuel injection on exhaust emissions, compared to the LPP operation can be characterized 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
- Both soluble and gas phase PAH increase with pilot fuel injection

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 FT100 lowest, ADMM15 middle, and DF-2 highest
- Gaseous air toxic rank is FT-100 and ADMM15 lowest, with DF-2 highest
- Both soluble and gas phase PAH rank is FT100 and ADMM15 statistically similar as lowest, with DF-2 the highest emitting fuel

Phase I Conclusions

Statistically significant (95% confidence) fuel effects on weighted average exhaust emissions were identified for both regulated and unregulated species.

The oxygenated low sulfur diesel fuel was statistically the same as Fischer-Tropsch fuel for toxic air pollutants, gaseous and soluble PAH, and PM emissions.

The ADMM15 fuel has a larger fraction of SOF than the FT-100 fuel, which has the statistically smallest SOF of all test fuels.

The effect of pilot fuel injection on exhaust emissions, compared to the LPP operation with pilot off can be summarized as follows:

- PM emissions increase, NO_x emissions decrease with pilot fuel injection
- The ratio of SOF/PM changed with pilot fuel injection condition
- Toxic air pollutant levels and both soluble and gas phase PAH increase with pilot fuel injection.
- Toxic air pollutants and soluble and gas phase PAH rank FT100 and ADMM15 statistically lowest.
- The magnitude of the emission response changes but does not significantly alter the fuel rank order.

Phase I Recommendations

The demonstrated effect of the oxygenate compound blended into low sulfur diesel fuel on lowering both regulated and unregulated emissions warrants further investigation. Although the oxygenate utilized in this study, dimethoxy methane, has shown positive emissions benefits, it is a poor choice for commercialization due to volatility characteristics. A parallel oxygenates program has identified two suitable oxygen-bearing compounds which warrant investigation as to oxygenate composition effects on toxic or PAH emissions.

There is evidence which suggests oxygen-bearing diesel fuels would tolerate further EGR before a smoke limit is reached, and thus would be beneficial for lowering engine-out NO_x. The impact on toxic emissions with increased EGR with oxygen-bearing fuels warrants investigation.

Another effect of oxygen is the tendency to increase the SOF content of the total particulate matter, which may be beneficial for PM control with an oxidation catalyst. The oxidation of SOF in a catalyst may crack higher molecular weight PAH compounds into smaller ringed components and increase levels of gaseous PAH or toxic emissions. It is recommended to evaluate the effect of an oxidation catalyst on toxic and PAH emissions.

To meet Tier 2 emission levels, engine-out NO_x emissions will need to be reduced, which will result in an increase in PM emissions. Thus the use of a Diesel Particulate Filter (DPF) to meet Tier 2 PM emission levels may be required. However, the DPF will act as a trap that will periodically need regeneration to lower engine backpressure. The DPF may act as a PAH sponge, trapping toxic compounds. The potential change in gaseous PAH levels due to the accumulation of PM on a DPF warrants investigation.

Phase II Objective & Background

The PM Analysis Phase II project is part of an overall study that examines the effect of oxygenated compounds in diesel fuel on the emission of particulate matter, emission of oxides of nitrogen, and fuel economy when emission control devices are used. The project will focus on the chemical characterization of emission compounds with known or suspected toxicological properties. Exhaust emissions of these compounds will be measured before and after emission control devices to better understand the effects of emission control devices and alternative fuels.

The control of NO_x emissions is probably the greatest technical challenge in meeting future emission regulations for diesel engines. In this project, lowering engine-out emissions of NO_x by increasing EGR and retarding timing will likely cause an increase in PM emissions. In Phase I of this program, it was shown that the use of an oxygenated diesel fuel additive will lower PM emissions. Use of an oxygenated diesel fuel additive thereby can minimize the increase in PM emissions that accompany the techniques used to decrease NO_x emissions.

The overall objective of this project is to better understand the role of fuels and emission control devices on the exhaust emissions of a subset of potentially toxicologically relevant compounds with an engine operated to minimize NO_x emissions. The three objectives of this program are to measure the following pollutants collected from diesel engines under a matrix of engine and fuel conditions:

1. polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of particulate matter
2. gas phase polycyclic aromatic hydrocarbons
3. gaseous toxic compounds (formaldehyde, acetaldehyde, benzene and 1,3-butadiene)

These measurements will be made on engine-out exhaust emissions and, downstream of an oxidation catalyst, and downstream of a diesel particulate filter.

Phase II Discussion

PM Analysis II Emission Control System Selection

A document was prepared for submittal to Manufacturers of Emissions Control Association (MECA) that will serve as the basis for obtaining the required oxidation catalyst and catalyzed diesel particulate filter (CDPF). The document was thoroughly reviewed by the Ad-Hoc CIDI group before release. MECA has surveyed its membership and has received interest in participation. Upon completion of survey responses, MECA will select a supplier.

Low-NO_x Operating Point Definition

The overall program goal is to define reasonable (not fully optimized) low-NO_x operating conditions. Substantial reductions in the NO_x Emissions Index (NO_xEI, g/lb fuel) are achieved by moving from the conditions of the Phase I project to the stock OEM calibrations for the engine. Additional NO_xEI reductions are obtained by varying the EGR rate and injection timing. The objective of this effort is to determine the operating points (e.g., injection timing and percent EGR) to be used for each of the four modes in the PM Analysis Project-Phase II. These points may vary by fuel. For each mode, an attempt to determine the limit between stable and unstable engine operation for low-NO_x operating conditions will be made. New fuel injectors and a fuel injection pump were installed in the OM611 test engine.

An initial methodology for determining the operating condition parameters was conducted with ECD-1 (BP-ARCO ultra-low sulfur diesel fuel) fuel at the Mode 11 (1500-rpm/2.62-bar bmep) operating condition. The approach was to start at the Engine Control Module (ECM) point and add EGR and retard timing, and evaluate NO_x reduction versus change in fuel consumption. Initial data suggest EGR is more cost effective for NO_x reduction in terms of fuel consumption, but leads to high smoke levels. Subsequently, data sets have been generated for Mode 10 (2000-rpm/2.0-bar bmep), Mode 6 (2300-rpm/4.2 bar-bmep), and Mode 12 (900-rpm/1.0bar bmep). Preliminary data were generated for Mode 5. Auto company participants were asked to obtain review/input from their driveability/calibration staff on the EGR and timing sweeps.

The following summary gives the type of vehicle operation each engine mode represents:

Mode 12: Idle with accessory load

Mode 11: Low speed cruise

Mode 10: Low speed cruise with slight acceleration

Mode 6: Moderate acceleration

Mode 5: Hard acceleration

The general rules for selecting operating conditions were revised and are shown in Table 6.

MODE	6	10	11	12
EGR	>OEM (15.8%)	>OEM (32.9%)	>OEM (35.3%)	>OEM (58.4%)
BSFC	3% max. increase	3% max. increase	3% max. increase	3% max. increase
BOOST	50% max. decrease	50% max. decrease	>0	N/A
SMOKE	100% max. increase	100% max. increase	100% max. increase	100% max. increase
HC	No rule	No rule	No rule	100% max. increase

Table 6. Rules for Defining Low-NO_x Operating Conditions

The operating condition which gave the largest NO_x decrease while meeting the tabulated rules was selected as the specific operating condition.

Based on the selection criteria shown in Table 6, the Ad-Hoc CIDI group selected the following operating conditions for the ECD-1 fuel. NO_x index reductions are on the order of 30% for each operating condition selected:

Mode 6

The crank angle for 50% burn was used to indicate engine retard.

Stock conditions are 15.8% EGR/ 15.9 Location of CA50, dATDC

The group selected the following operating point:

EGR=22.5 ± 2%

Location of CA50=16.4 ±1, dATDC

Mode 10

Stock conditions are 32.9% EGR/ 16.1 dATDC location of peak pressure-main combustion (LPPm).

The group selected the following operating point:

EGR=38.9 ± 2%

LPPm=18.4 ±1, dATDC

Mode 11

Stock conditions are 35.3% EGR/ 12.5 dATDC for LPPm

The group selected the following operating point:

EGR=40 ± 2%

LPPm=16 ± 1, dATDC

Mode 12

Stock conditions are 58.4% EGR/ 11.7 dATDC for LPPm

The group selected the following operating point:

EGR=60 ± 2%

LPPm=13.3 ± 1, dATDC

Project Status

1. Final agreement pending on selection of emission control devices.
2. Process to define changes in operating conditions for each mode with respect to each of the other test fuels is in progress.

Publications/Presentations

1. D.M. Yost and E.A. Frame, "Particulate Matter Analysis from an Advanced Diesel Engine; Phase I & II", CIDI Engine Combustion, Emission Control, and Fuels R&D, Merit Review and Peer Evaluation, Oak Ridge National Laboratory, 6-8 June 2001.
2. Ball, et. al., "Dimethoxy Methane in Diesel Fuel: Part 1. The Effect of Fuels and Engine Operating Modes on Emissions of Toxic Air Pollutants and Gas/Solid Phase PAH," SAE 2001-01-3627.
3. Ball, et. al., "Dimethoxy Methane in Diesel Fuel: Part 2. The Effect of Fuels on Emissions of Toxic Air Pollutants and Gas/Solid Phase PAH Using a Composite Of Engine Operating Modes," SAE 2001-01-3628.
4. Ball, et. al., "Dimethoxy Methane in Diesel Fuel: Part 3. The Effect of Pilot Injection, Fuels and Engine Operating Modes on Emissions of Toxic Air Pollutants and Gas/Solid Phase PAH," SAE 2001-01-3630.

D. DECSE Complementary Study of Fuel Sulfur Effects on Unregulated Emissions from Diesel Particulate Filters

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Industry Participants: Detroit Diesel Corp., Manufacturers of Emissions Control Association (MECA)

Contractor: UT-Battelle, LLC (Oak Ridge National Laboratory), Oak Ridge, TN
Contract Number DE-AC05-000R22725 from February 1, 2000 - March 31, 2005

This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

E. Toxic Emissions

F. Ultra-fine Particles

Tasks

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

Objectives

- Investigate the effect of fuel sulfur on the ability of diesel particulate filters (DPFs) to eliminate air toxics.
- Investigate the effect of fuel sulfur on the formation of nanoparticles by DPFs.

Approach

- Use the same fuel and DPF devices used in the Diesel Emissions Control - Sulfur Effects (DECSE) project.
- Measure volatile and semivolatile organics, aldehydes and ketones, and PM soluble organic fraction (SOF) and sulfate (SO_4).
- Use different levels of exhaust dilution and a scanning mobility particle sizer (SMPS) to determine the particle size distribution of the PM from the DPFs.
- Establish the effect, if any, of fuel sulfur on the destruction or formation of air toxics and the formation of nanoparticles by DPFs.

Accomplishments

- Applied a full range of hydrocarbons (HCs) to the exhaust entering DPFs to investigate their destruction efficiency and found that:
    - Aldehydes in and out of the device were variable at low engine speeds and loads.
    - Light HC were oxidized burned even at low temperatures .
    - Fuel sulfur at 40 ppm concentration had only a small effect on HC conversion.
- Conducted particle sizing measurements.

Future Direction

- This project is complete.

Introduction

The recently completed Diesel Emissions Control - Sulfur Effects (DECSE) joint Industry-DOE project provided a comprehensive examination of fuel sulfur effects on the performance of four types of emission control devices for diesel engines [1]. Missing from the DECSE program were the complementary evaluations of the effect of fuel sulfur on the devices testing particle size distribution and on the emissions of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCS) and air toxics. The Advanced Propulsion Technology Center (APTC) at the Oak Ridge National Laboratory (ORNL) recognized the opportunity to leverage some important additional research with that of the existing DECSE program, and thus provide valuable supplemental information on fuel sulfur effects.

The DPFs are likely to have a very positive effect on non-regulated emissions, such as air toxics, benzene, and formaldehyde - an effect which may well be tempered by the presence of sulfur in the fuel. A very recent study showed that a catalyzed diesel particulate filter (CDPF) has a positive effect on poly-aromatic hydrocarbron (PAH) destruction [2]. Furthermore, the ability of the device to remove/affect the soluble organic fraction (SOF) of the PM may be dependent upon sulfur level.

Previous research has demonstrated an influence of emission controls and, perhaps more importantly, test dilution conditions on PM size. For instance, it was found that under EPA-approved dilution conditions, production of ultrafine PM (size<100 nm) can increase with use of particulate traps and oxidation catalysts [3]. Comparing 3000 ppm sulfur fuel with 500 ppm sulfur fuel, Johnson demonstrated that the sulfur contribution to the ultrafine PM was very important [4], thus providing further argument to reducing the level of sulfur in fuel. ORNL evaluated a CDPF with No. 2 diesel reference fuel and also found that the ultrafine fraction of the PM was increased 100-fold [5]. In addition, it was found that this distribution was sensitive to dilution ratio - increasing dilution ratio resulted in smaller and smaller particles.

Experimental Approach

A 1998 heavy-duty (HD) engine with transit bus emission calibration (0.05 g PM/hp-hr) was used for this study. DPFs identical to the ones used in the DECSE project were procured and included a continuously regenerable diesel particulate filter (CR-DPF) and a catalyzed diesel particulate filter (CDPF). DECSE 3 ppm sulfur fuel was used throughout and splash-blended with DECSE 150 ppm sulfur fuel to make 40 ppm sulfur fuel. Dilution for the bag and filter samples was done using a mini dilution tunnel. Dilution for the particle-sizing experiments was accomplished with an ejector pump micro-dilutor, based on a design by Kittelson *et al* [3]. All transfer lines were heat traced, and the dilution ratio was maintained above 20:1 using filtered air. A TSI Scanning Mobility Particle Sizer (SMPS) was used to obtain PM size distributions.

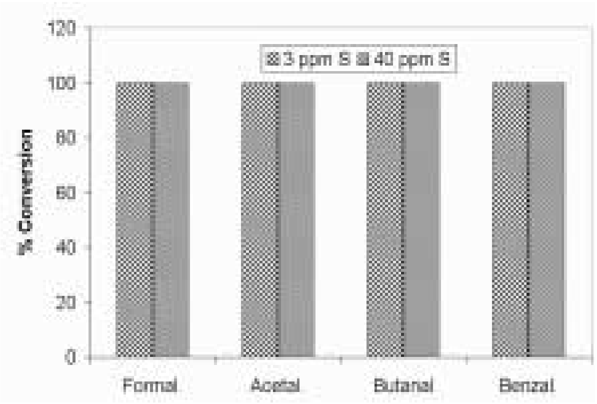

Figure 1. CR-DPF Aldehyde Conversion at Low-Load, 225°C

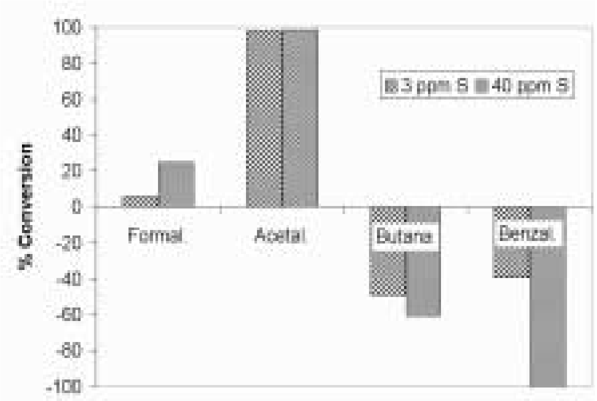

Figure 2. The CR-DPF Forms Some Aldehydes at Idle

Bag HCs were analyzed by gas chromatography with flame ionization detection (GC-FID). Dinitrophenylhydrazine (DNPH) cartridges were used to collect aldehydes from the dilute exhaust and were analyzed by high-pressure liquid chromatography (HPLC).

Results

The results in general showed excellent removal of all HCs, including aldehydes, by the DPFs. Even at temperatures well below the balance point (the temperature at which the DPF is burning PM as fast as it accumulates), there was excellent HC conversion. At idle, however, there was evidence of partial oxidation processes, wherein the DPF actually emitted more of certain aldehydes than went into the device. Particle sizing results showed excellent removal of PM by the DPFs, to near background levels. Fuel sulfur, however, contributed to a 1000-fold increase in the number concentration of particles under 10 nm under certain conditions.

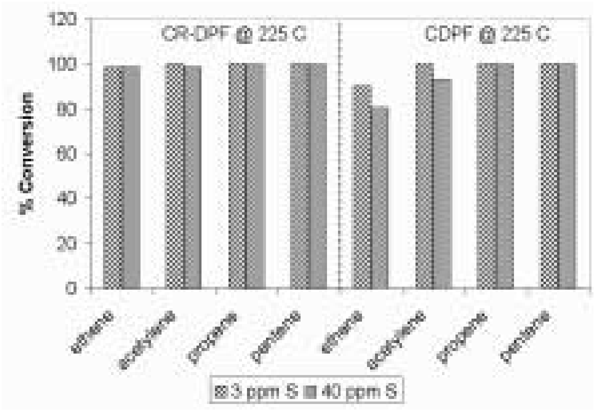

Figure 3. Conversion of Light HCs

HC Results

Light and heavy HCs as well as aldehdyes were measured. As an example, Figure 1 shows aldehyde conversion results for a CR-DPF at a moderate exhaust temperature (225°C), which is well below the balance point of this device. Note the excellent conversion of all species, including formaldehyde, which is somewhat resistant to oxidation at low temperatures. The conversion of aldehydes at higher temperatures was 100%. Fuel sulfur had little or no effect on the device's ability to destroy these compounds. Figure 2 shows the same chart at idle conditons. In this case, there is poor conversion of formaldehyde, and, in the case of benzaldehyde and butanal, actual aldehyde formation, which results in "negative" formation. Note also that fuel sulfur has a positive effect on the removal of formaldehyde. This may be due to the reaction of the formaldehyde with SO_x to form methanesulfonic acid, which was not measured. The low temperatures at idle, the relatively higher engine-out HCs, and the reactive surfaces of the catalyzed DPFs represent ideal conditions for doing partial oxidation reactions and other chemistry. This result points out the need to consider the impact of extended idling periods on emissions when implementing emission control device alternatives.

Work on light HCs is summarized in Figures 3 and 4. Figure 3 shows the elimination of most light HC emissions by both the CDPF and CR-DPF at moderate load conditions and a temperature below the balance point. Of course, at higher temperatures there is complete conversion of HC emissions. Figure 4 shows engine idle data for the CR-DPF. At

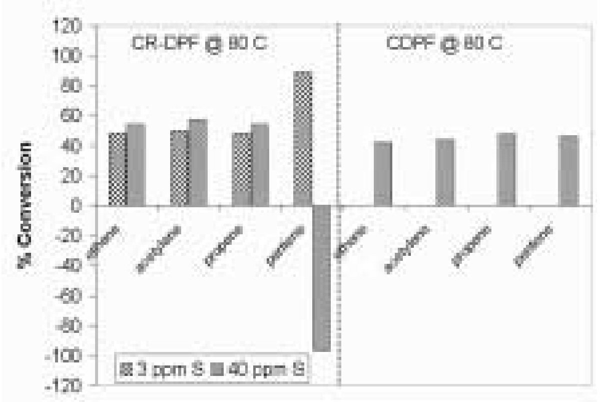

Figure 4. The CR-DPF removes most light HCs at idle, but forms 1-pentene with the higher sulfur fuel.

idle conditions, there was moderate conversion of the light HCs. The main difference between the 3 ppm sulfur fuel results and the 40 ppm sulfur fuel results is the apparent formation of 1-pentene during idle conditions. The extra sulfur in the exhaust may provide the acidic condition on the catalyst necessary for cracking of fuel HCs to occur. The aldehyde formation (Figure 2) was enhanced when 40 ppm sulfur fuel was used.

Particle Sizing Results

As many others have shown, the DPFs are very effective at removing PM mass. This is evident in the particle sizing results, where the large soot fraction that is present in engine-out exhaust disappears in the catalyst-out exhaust . The larger fraction contains most of the mass of the PM. In contrast, the particle emissions from the DPFs compare favorably to ambient particle concentrations in the Smoky Mountain National Park. Figure 5 compares the PM size distribution from a CDPF exhaust with 3 ppm and 40 ppm sulfur fuels to the PM size distribution of ambient air in a National Park. Particle sizing on the exhaust showed the biggest effect of fuel sulfur level. Even at dilution ratios of approximately 20, which is higher than standard full flow dilution tunnels, the higher sulfur content fuel led to the formation of nucleation mode particles on the order of 3-10 nm at concentrations 100-1000X what was present in the low sulfur fuel sample.

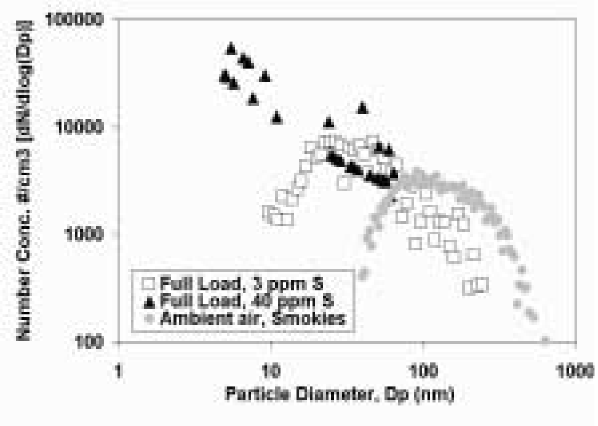

Figure 5. Comparison of number-based particle size distributions from the diluted exhaust of a CDPF using 3 ppm and 40 ppm sulfur fuel. (Engine at full load, rated speed, dilution ratio of 20)

Conclusions

Fuel sulfur appeared to have little effect on the ability of the CR-DPF and CDPF to remove HCs at moderate load, and no effect on HC conversion at high load. With the CR-DPF, under idle conditions, the formation of some aldehydes and a fuel cracking product, 1-pentene, was enhanced by the presence of fuel sulfur. Fuel sulfur, however, has a large impact on ultrafine particle formation by the DPFs. A 2 to 3 order-of-magnitude rise in number concentration was observed for the CDPF operating at high exhaust flow and temperature with 40 ppm sulfur fuel.

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E. Cooperative Research in C1 Chemistry

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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.
- Develop novel 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, Energy International, Teir Associates, and the Department of Defense has been formed to provide practical guidance to the program.

Accomplishments

- The addition of acetylenic compounds in Fischer-Tropsch (FT) synthesis is found to produce significant amounts of oxygenated products in FT diesel fuels. Such oxygenated products should decrease particulate matter (PM) emissions.
- Nanoscale, binary, Fe-based catalysts supported on alumina have been shown to have significant activity for the decomposition of methane into pure hydrogen and potentially valuable multi-walled carbon nanotubes.

- Catalytic synthesis processes have been developed for synthesis of diethyl carbonate, higher ethers, and higher alcohols from C1 source materials. Testing of the effect of adding these oxygenates to diesel fuel on PM emissions has begun using a well-equipped small diesel engine test facility.
- Supercritical fluid (SCF) FT synthesis has been conducted under SCF hexane using both Fe and Co catalysts. There is a marked effect on the hydrocarbon product distribution, with a shift to higher carbon number products.

Future Directions

- Future research projects will emphasize improvements in FT synthesis, hydrogen production from various hydrocarbons, evaluation of carbon nanotube byproducts, and C1 synthesis of fuel additives and high value chemicals.

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. For the past two years, the CFFLS research program has 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. 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 as a source of transportation fuel are growing rapidly. The CFFLS is therefore performing a valuable national service not only by generating novel C1 technology for the synthesis of premium transportation fuels, but also by providing science and engineering graduates trained in this important area.

The current report briefly summarizes some of the research highlights of the second year of the program.

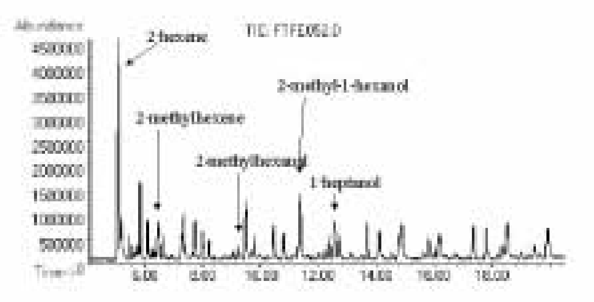

Figure 1. GC/MS Analysis of FT Products with 2-Hexyne Addition

Effect of Probe Molecules on Oxygenated Products in Fischer-Tropsch Synthesis

It is reported that particulate matter (PM) emission reductions of 4-10% can be achieved forevery 1% of oxygen blended into diesel fuel. In this project, the production of oxygenated diesel fuels by modifying Fischer-Tropsch (FT) catalysts and reaction conditions is being investigated. The addition of acetylenic molecules, specifically 1- and 2-hexyne, into the FT synthesis with iron and cobalt catalysts to produce oxygenated products is reported here.

1-Hexyne is readily incorporated into the FT reaction to produce heptanol, heptanal and C8+ straight chain alcohols. In the case of 2-hexyne addition, a large amount of branched C7+ oxygenates is produced. At lower temperatures, these hexynes initiate chain-growth in the FT reaction and produce mainly C7+ products. Typical gas chromatography/mass spectroscopy (GC/MS) analyses of the FT products of such reactions are shown in Figure 1. The mode of incorporation of acetylenic molecules into FT reactions is under investigation.

Hydrogen Production by Catalytic Decomposition of Methane

Traditionally, hydrogen has been produced by reforming or partial oxidation of methane to produce synthesis gas, followed by the water-gas shift reaction to convert CO to CO_2 and produce more hydrogen, followed in turn by a purification or separation procedure. This research is investigating the direct catalytic decomposition of undiluted methane into pure hydrogen and carbon using nanoscale, binary, Fe-M catalysts (M = Pd, Mo, and Ni) supported on alumina [(4.5% Fe — 0.5%M)/Al_2O_3]. All of the supported Fe-M catalysts reduced methane decomposition temperature by 400-500°C relative to non-catalytic thermal decomposition and exhibited significantly higher activity than Fe or any of the secondary metals (Pd, Mo, and Ni) supported on alumina alone. At reaction temperatures of approximately 700-800°C and space velocities of 0.1 per hour, the product stream was comprised of over 85 volume % of hydrogen, with the balance being unconverted methane. No C2 or higher hydrocarbons were observed in the product gas.

High resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterization established that almost all carbon produced at 700-800°C is in the form of potentially useful multi-walled nanotubes (Figure 2). At somewhat higher temperatures (> 850°C), hydrogen production is decreased and carbon is deposited on the catalysts in the form of amorphous carbon, carbon flakes, and carbon fibers.

Supercritical Fluids as a Reaction Medium for Fischer-Tropsch Synthesis

Supercritical fluids offer several advantages over traditional solvents as reaction media for catalytic reactions. Advantages of SCF-phase Fischer-Tropsch synthesis (SCF-FT) include high diffusivity and improved heat transfer (relative to a liquid) and high solubility (relative to a gas). In this investigation, FT synthesis has been conducted under SCF hexane conditions in a continuous, high-pressure reactor employing traditional Fe and Co catalysts (e.g., 15%Co-0.5%Pd/Al_2O_3). Steady-state operation was quickly achieved under SCF conditions and the product distributions obtained were constant over extended periods of operation (over 40 hours). The SCF-FT process has a marked effect on the hydrocarbon product distribution with a shift to higher carbon number products due to enhanced heat and mass transfer from the catalyst surface. Relatively flat product distributions with similar mass percentages of the C11-C17 products were obtained (Figure 3). In addition, an obvious difference is observed for the 1-olefin content obtained in the SCF-FT synthesis, which is always higher than that from gas or liquid phase FT synthesis. This phenomenon suggests that the SCF-FT reaction rate is not diffusion controlled, whereas the secondary olefin hydrogenation and isomerization reactions are diffusion limited. The SCF-FT process results in higher diffusivity and

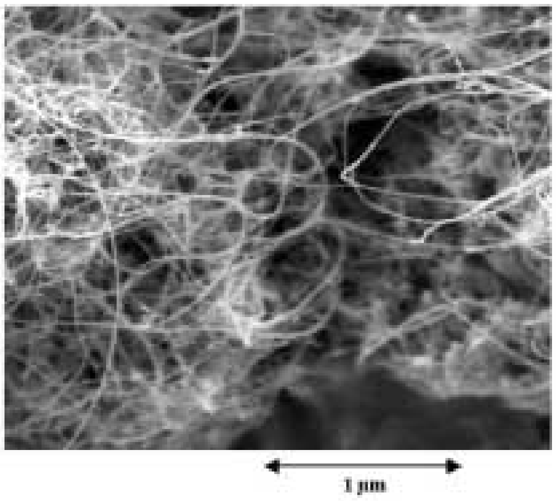

Figure 2. Carbon Nanotubes Produced by Decomposition of Methane over a (4.5%Fe-0.5%Mo)/Al_2O_3 Catalyst

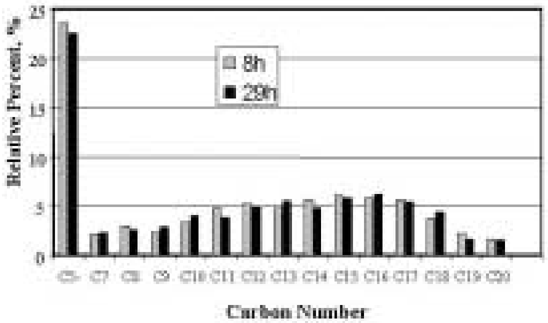

Figure 3. Product Distribution from Fischer-Tropsch Synthesis under SCF Hexane Conditions

more rapid removal of high molecular weight 1-olefins from the catalyst surface thereby suppressing secondary hydrogenation and isomerization reactions.

Catalytic Synthesis and Testing of Oxygenated Compounds for Use as Fuel Additives

Effective catalysts have been developed for the synthesis of several oxygenated compounds that may be useful as fuel additives. These include higher alcohols, higher ethers, and organic carbonates.

- Carbon-supported molybdenum-based catalysts, promoted with Ni and K, were found to be good catalysts for synthesis of higher alcohols from syngas. Reactivity studies were carried out at 250-350°C. The liquid product contained appreciable quantities of C_{1-5} alcohols in an aqueous phase with no hydrocarbon phase.
- A C_7 ether, 2,3 dimethyl-2-methoxybutane (DM2MB), was synthesized from dimethyl butene and methanol. Several other higher ethers were synthesized 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 laboratory-prepared catalysts ($Zr(SO_4)_2$ on sulfuric acid-treated SiO_2).
- Synthesis of diethyl carbonate (DEC) from ethanol, CO, and O_2, was accomplished using a Cu/Pd/activated carbon catalyst pretreated with potassium hydroxide, KOH. X-ray diffraction characterization of the catalysts has established that the most active state of the catalyst is paratacamite, $Cu_2Cl(OH)_3$.

Diesel Engine Test Facility

A small diesel engine test facility utilizing a two-cylinder Kubota model Z482B has been established. The facility includes a TSI Scanning Mobility Particle Sizer (SMPS) that measures particle size distributions from 7 nm to 300 nm, and a Lasair 310 optical particle counter (OPC) that measures particle counts in seven size ranges from 0.3 µm to 10 µm. The laboratory also has a high volume particulate matter (PM) sampler for collecting large quantities of PM with diameter less than 10 µm. For gas-phase emissions, the laboratory has the capabilities to measure CO, CO_2, NO_x, and total hydrocarbons. In addition, the laboratory can measure real-time PAH and elemental carbon on particles. Initial tests conducted using the DEC additive in a conventional diesel fuel exhibited a significant reduction in PM emissions.

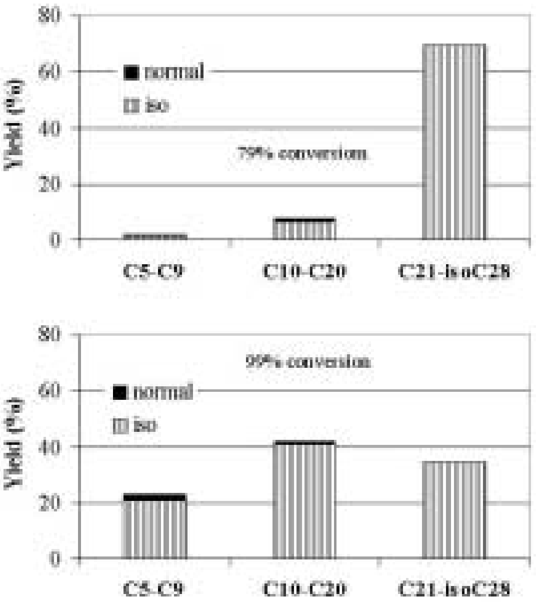

Figure 4. Effect of Conversion on Product Distribution for Reacted C_{28} at 220°C and 500 psig

Hydrocracking and Isomerization of Alkane Chains Representative of FT Products

Laboratory work was carried out successfully in a small continuous trickle-bed reactor using a $Pt/ZrO_2/WO_3$ catalyst. A 90 wt% iso-C_{16} selectivity and a 71wt% iso-C_{16} yield were achieved at 79 wt% conversion of hexadecane. The objective in the last half-year has been to extend research to the conversion of paraffins longer than hexadecane, such as those produced in the FT process, to a variety of clean transportation fuels. This was carried out using the stable and selective $Pt/ZrO_2/WO_3$ catalyst to hydroisomerize and hydrocrack pure compounds, namely n-C_{16}, n-$C_{20,}$ n-C_{24} n-C_{28} and their mixtures, representative of alkane chains found in FT products.

Figure 4 shows yield-product distribution graphs at two different conversions for octacosane (C_{28}) at

220°C. The lube-base oil yield is highest at 79% conversion (Figure 4, top) and consists of only branched isomers, mostly iso-C_{28}. The yield of lube-base oil decreases gradually with increasing conversion as the yield of diesel fuel and gasoline increases. The major product is diesel fuel at 99% conversion (Figure 4, bottom), only a 20% change in conversion. If the reaction is carried to 100% conversion, the major product becomes highly branched gasoline. Switching between these three fuels occurs at high conversion values. It appears possible to obtain the desired fuel range by adjusting the conversion at a selected temperature but maintaining relatively high conversion.

Conclusions

Collaborating faculty and students at the five CFFLS universities (Kentucky, West Virginia, Pittsburgh, Utah, and Auburn) have continued to make excellent progress on research to develop innovative C1 chemistry processes to produce clean, high efficiency transportation fuel. In the second year of the program, emphasis was placed on various aspects of Fischer-Tropsch synthesis and on hydrogen.

VI. MODELING/DATA ANALYSIS/ASSESSMENTS

A. The Impact of Oxygenated Blending Compounds on PM and NO_x Formation of Diesel Fuel Blends

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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
E. Toxic Emissions
F. Ultra-fine Particles

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions

Objectives

- Develop detailed chemical kinetics reaction models for hydrocarbon species existing in diesel fuel
- Develop detailed chemical kinetics reaction models for oxygenated hydrocarbon fuel additives
- Use kinetic models to study the fundamental chemistry of PM production and NO_x production in diesel combustion
- Characterize the role of oxygenated additives in reduction of PM emissions from diesel engines
- Collaborate with other contractors to simulate chemistry of diesel combustion

Approach

- Identify components of diesel fuels and potential diesel additives and their molecular structures
- Develop kinetic reaction mechanisms for diesel fuels and additives
- Compute ignition temperature of fuel mixture or model flame structure for fuel/air and fuel/air/additive mixtures
- Compare predicted levels of PM and NO_x with and without additive and use a detailed chemical model to determine the mechanisms for the emissions changes

Accomplishments

- Studied ignition under diesel conditions and identified key chemical reactions responsible for ignition
- Used ignition insights to explain role of diesel ignition enhancers
- Predicted reductions in PM emissions for mixtures of diesel fuel with addition of methanol, ethanol, dimethyl ether and dimethoxy methane
- Developed model for simulated biodiesel fuel and predicted reduction in PM emissions for biodiesel additives
- Based on kinetic model predictions, developed correlation between amount of oxygen in diesel/additive fuel mixture and PM reduction that agrees with experimental results in diesel engines
- Determined fundamental limits to possible NO_x reductions from diesel engines, based on combustion lean flammability limit at minimum diesel engine compression pressure levels

Future Directions

- Extend model capabilities to additional fuel constituent compounds, especially aromatics
- Extend model capabilities to additional oxygenated blending compounds
- Increase collaborations with programs outside LLNL dealing with diesel fuel issues

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Introduction

The application of a combination of laser diagnostics and computational chemistry modeling has profoundly changed our current understanding of the details of diesel combustion [1]. This understanding offers new opportunities to reduce diesel emissions of oxides of nitrogen (NO_x) and soot or particulate mass (PM) to comply with federal Clean Air Act regulations. However, diesel combustion remains extremely complex. For example, diesel fuel is a mixture of many classes of hydrocarbon molecules, each of which can affect PM and NO_x production in different ways, so it is essential to have the capability to model the combustion of each class of fuel components. While past kinetic modeling studies have provided a great deal of valuable information on these processes, the kinetic models being used have not included two important classes of hydrocarbons, cycloalkane and aromatic compounds. The present work includes extension of the modeling to include these additional classes of fuel components. In addition, we have used the kinetic model to examine the fundamental chemical kinetics of ignition, determining the key chemical reactions and showing how ignition leads directly to PM production under conditions typical of diesel engine combustion.

Recent experimental studies have indicated that the use of selected oxygenated diesel fuel additives can reduce these emissions, especially PM emissions [2]. However, these have been purely experimental correlations, without any fundamental understanding of why such additives are so effective. In particular, the experiments alone do not provide any basis for prediction of other possible oxygenated additives which might be even more effective in reducing PM emissions. The present project is intended to provide a fundamental explanation for the experimental observations and guidance for screening other potential oxygenated compounds as diesel fuel additives. Further kinetic modeling is used in a similar manner to address NO_x production in diesel combustion and possible methods of NO_x reduction.

Approach

The analysis employs chemical kinetic modeling of diesel combustion processes, including ignition, formation of PM precursors, kinetic interactions between the fuel and any additive molecules, and eventual production of NO_x. The inclusion of the very detailed chemical kinetic reaction pathways makes the computed results very general, and the technical conclusions derived can be extended conveniently to other related problems.

Kinetic reaction models have been developed at LLNL for many realistic hydrocarbon fuels and fuel mixtures, most recently for n-heptane [3], a single-component fuel that represents many of the combustion characteristics of diesel fuel. The diesel modeling work has computed diesel ignition and combustion using the heptane model and additional models for many oxygenated additives of interest to industry and DOE, including methanol, ethanol, dimethyl ether, dimethoxy methane, and, in the past year, biodiesel fuels.

Similar kinetic model calculations, using a variety of fuels, were carried out at operating conditions characteristic of diesel combustion, particularly at elevated pressures, to try to understand the fundamentals of NO_x production in diesel engines. Model results have provided considerable insights into this problem.

Results

Using operational insights derived from recent diesel engine experiments by Dec [4], it is assumed that PM production in diesel combustion occurs from reactions of chemical species created during fuel-rich ignition near the fuel injection location. Because there is insufficient oxygen in this region to burn the fuel completely, the hydrocarbon species remaining there react instead to produce PM. Our kinetics calculations show that when the fuel itself contains some oxygen, that oxygen helps convert more of the ignition products into chemical species that do not contribute to PM production.

The reduction in the levels of PM produced during diesel combustion can be dramatic. Figure 1 shows the computed reductions in concentrations of diesel soot precursors as the amounts of oxygen in the fuel/additive mixture is steadily increased. Somewhat surprisingly, sooting tendency is reduced at approximately the same rate by all of the oxygenated blending agents. In each case, it appears that the soot production is completely suppressed when the oxygen level in the mixed fuel reaches about 35% by mass. The rate of soot reduction, the prediction that soot production disappears at 30-35% oxygen, and the relative independence of this behavior on the specific oxygenate being added, all agree very well with experimental results from diesel engine experiments [5,6].

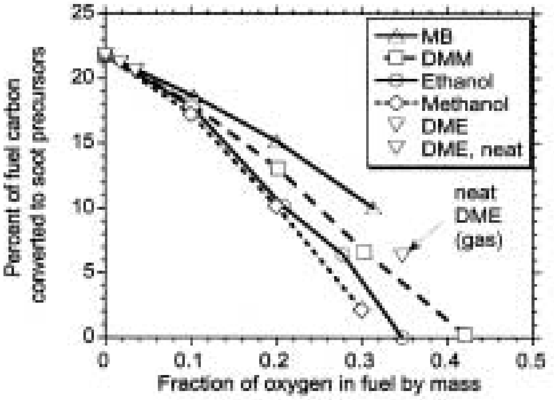

Figure 1. Reduction of PM precursors with fraction of oxygen in fuel. Oxygenated additives include methyl butanoate (MB, a biodiesel fuel), dimethoxy methane (DMM), ethanol, methanol and dimethyl ether (DME).

It is important to realize, however, that 35% oxygen in the fuel mixture corresponds to a fuel which is dominated by the oxygenated additive, so most practical operations in real diesel engines would take place at oxygen levels of less than 10%. Still, the computed results not only provide the chemical understanding of the mechanism of soot reduction, but also suggests strongly that the critical parameter for soot reduction is the total amount of oxygen and not the particular type of molecule which contains the oxygen. This type of result can guide studies looking for better, more efficient and perhaps more engine-friendly additives that will still be effective at providing soot reduction.

The model also shows that much of the kinetic activity in toluene combustion occurs on the methyl side chain, which is converted to $-CH_2$ (benzyl radical) and then to $-CH_2O$, as seen in the Figure 2. The same work [7] showed that when toluene is present as 30% of the total diesel fuel, its main contribution to soot precursor production is a significant increase in benzene concentrations in the products of the fuel-rich ignition event.

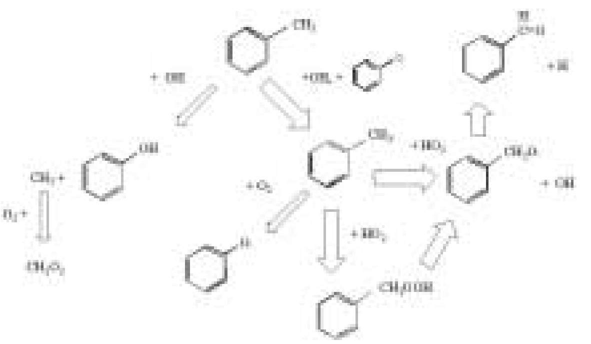

Figure 2. Reaction pathways for toluene consumption. Toluene is shown in the top center of the figure, showing reactions with OH to produce either phenol or the benzyl radical. The benzyl radical then reacts via other paths to produce benzylaldehyde. A key feature of this process is that most of the reaction occurs on the side chain rather than through reactions of the ring structure itself.

The inclusion of a typical aromatic species will also make other diesel combustion modeling projects more useful and more likely to reflect the true character of diesel fuel. We are currently working to add a similar submodel for methyl cyclohexane as a typical cycloalkane fuel component.

In other work carried out this year, kinetic modeling was used to simulate flame propagation near the lean limit of combustion at pressures in the ranges found in diesel combustion, which are commonly as high as 100 bar. This work [8] showed that these high pressures modify the rates of specific elementary chemical reactions that are important for flame propagation, especially reactions between atomic hydrogen and molecular oxygen:

$$H + O_2 = O + OH \quad (1) \text{ and}$$

$$H + O_2 = HO_2 \quad (2)$$

This competition, which favors the less reactive path (2) at elevated pressures, gradually suppresses flame propagation to the extent that the lean limit for flame propagation at 100 bar pressure is reached at an equivalence ratio of about 0.65, compared to the lean limit at atmospheric pressure of about 0.5. More importantly, the adiabatic flame temperature (or the product flame temperature) at the lean limit at 100 bar is about 1950K, compared to the flame temperature at atmospheric pressure of about 1400K.

Production of NO_x is extremely sensitive to flame temperature and begins to become rapid at temperatures of about 1900K and above. The computed kinetic modeling results therefore indicate that the high pressures characteristic of diesel engine combustion makes it inevitable that NO_x will be produced in significant amounts in diesel engines, regardless of strategies employed to limit that production. The same is true of spark-ignition engines and shows that some degree of exhaust gas catalytic treatment will always be required for diesel and spark-ignition engines to reduce NO_x levels to those required by regulations. This is not true in engines using Homogeneous Charge Compression Ignition (HCCI) due to the very low equivalence ratio of such engines and the lack of any requirement to propagate a flame.

Finally, we have used kinetic modeling [9] of diesel ignition to demonstrate that the elementary reaction step that is responsible for the actual ignition is the unimolecular decomposition of hydrogen peroxide,

$$H_2O_2 = OH + OH(3)$$

which floods the reactive fuel/air mixture with highly reactive OH radicals, each of which consumes a fuel molecule and permits the reaction to proceed very rapidly. This decomposition occurs when the temperature provides enough thermal energy to break the O - O bond, which takes place at about 1000K, consistent with experimental observations in the engine. The insights provided by this analysis explain the effectiveness of such diesel ignition enhancing additives as ethyl hexyl nitrate, which provide early heat release and make the reactive mixture reach this ignition temperature earlier in the engine cycle.

Conclusions

Kinetic modeling has been used to extract a considerable amount of valuable insight into the controlling features of diesel engines and the processes leading to PM and NO_x production. This information has contributed to experimental advances in engine technology. In addition, this modeling approach has discovered areas, especially those dealing with NO_x production, where it is very unlikely that any combustion modification will entirely eliminate emissions and where exhaust gas catalytic treatment will always be required.

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B. A Multi-Property Vector Approach to Assessment of Diesel Fuels and Emissions Impacts

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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
4. Develop Empirical Relationships

Objectives

- Characterize relationships between fuel properties and emissions for diesel technologies to meet near-term (for example, Texas Low Emission Diesel Fuel) and Tier 2 emissions standards.
- Use advanced statistical methods and refinery modeling to study reformulated diesel fuel production impacts on the transportation fuel supply system.

Approach

- Analyze role of diesel fuel composition changes on emissions from advanced diesel engines.
- Provide guidance on diesel engine emissions test designs.
- Provide insights on cost-effective refinery production of reformulated diesel fuels.

Accomplishments

- Reports on statistical analysis of diesel fuel quality and emissions (McAdams, Crawford, and Hadder, 2000a and 2000b).
- Report on engine test program design concepts and recommendations (McAdams, 2001).

Future Directions

- Develop emissions models for optimizing refinery production of reformulated diesel fuels.

Introduction

Multiple regression analysis is widely used for expressing the dependence of a response variable on several predictor variables. In spite of its evident success in many applications, multiple regression analysis can face serious difficulties when the predictor variables are to any appreciable extent covariant. Efforts to evaluate the separate effects of fuel variables on the emissions from heavy-duty diesel engines are often frustrated by the close association of fuel properties.

Most heavy-duty diesel engine research has been conducted with test fuels "concocted" in the laboratory to vary selected fuel properties in isolation. While it might eliminate the confounding effect caused by naturally covarying fuel properties, this approach departs markedly from the real world, where reformulation of fuels to reduce emissions will naturally and inevitably lead to changes in a series of interrelated properties. To address these concerns, we have implemented an alternative approach to modeling the effects of fuel characteristics on emissions.

Approach

The alternative approach is based on the use of Principal Components Analysis to describe fuels in terms of vector quantities called *eigenfuels*. Each eigenfuel represents a unique and mathematically independent characteristic of diesel fuel, and the most important eigenfuels can be related to refinery processing and blending. When applied as predictors for emissions in regression analysis, eigenfuels have many advantages, including:

- *Simplification of the analysis*, because the mathematical independence of eigenfuels eliminates correlations among the variables and the complications introduced by multi-collinearity.
- *Economy of representation*, because a smaller number of such vector variables may effectively replace a larger number of original variables.
- *Greater understanding of the patterns of variation that are important to emissions,* and how these patterns relate to refinery processing and blending.
- *New insight into the optimal economic formulation of fuels to reduce emissions*, and improved experiment design for the estimation of fuels effects.

Knowing the extent of interdependence among fuel variables, we should not be surprised by the difficulty of selecting an "optimal" set of variables for a regression model. We may believe that natural cetane or density has an important influence on emissions, but either may be nearly replaced by a combination of other variables. Stepwise regression, a commonly used multiple regression analysis technique, searches through a sequence of differing model formulations to find one that is "optimum." With diesel fuel test data, there can be many different sets of variables that perform nearly as well as the one set ultimately chosen.

Figure 1 brings this point into focus. There are 4,095 different regressions models that can be formed from twelve fuel properties, and these models form the universe among which stepwise regression searches.

It will take all twelve properties to place a model at the very end of the curve. Forty-five different models populate the last 0.02 in R^2, and these models typically involve 7-9 fuel property variables. The coefficients of the fuel property variables can be significantly different among these models, leading to uncertainty about their relative importance in testing and in the cost-effective blending of refinery stocks. However, models based on a small number of eigenfuels perform well, with five eigenfuels explaining nearly 97 percent of the fuels-related variance in NO_x. The eigenfuel coefficients are unambiguous and theoretically correct for test designs and for cost-effective blending of refinery stocks.

Conclusions

A database of heavy-duty diesel engine testing was compiled from the literature and used to demonstrate the eigenfuel methodology, recognizing that the existing data are inadequate to answer fully the many questions related to the effect of fuels on

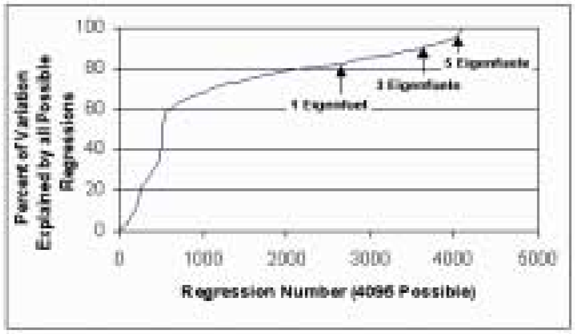

Figure 1. NO_x Variation Explained by All Possible Regressions

emissions. Within this limitation, we find that the eigenfuel approach leads to new perspectives on diesel fuel-emissions relationships:

- *Fuel properties are only surrogate variables for underlying causal factors*. Much of the emissions reduction seen in past testing comes from reducing highly aromatic cracked stocks in diesel fuel. Because these stocks are low in cetane number and high in density, researchers have tended to attribute the emissions reductions to the increase in cetane number or reduction in density associated with their removal, rather than to the compositional change itself.
- *How one varies a fuel property can be the most important factor in determining the emissions response*. A given fuel property can be changed in many ways, and a unit change in that property can produce markedly different effects on emissions depending on how that change is introduced.
- *Past studies may understate the impacts of fuels on emissions*. If density is varied in several ways - one of which has a strong effect on emissions and the others not all - a study will tend to see only the average, diluted effect.

The eigenfuel approach provides new ways to design test fuels that are far more likely to be representative of future fuels that will be produced in refineries, compared to fuels blended in an effort to vary selected properties independently. These test fuels will express the natural correlations among fuels properties. While these correlations would be confounding factors in conventional analysis, they can be exploited in eigenfuel analysis.

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C. System Emissions 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
D. Sulfur Impacts
E. Toxic Emissions
F. Ultra-fine Particles

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions
3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions
4. Develop Empirical Relationships

Objectives

- Establish system emissions reduction (SER) analysis framework.
- Develop and use systems level analysis tools that incorporate empirical emission relationships and first principle models 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 (MYPP).

Approach

- Define the SER framework to augment the Advanced Vehicle Simulator (ADVISOR) with new component modules (e.g., emission control devices) and laboratory data.
- Develop empirical data relationships on sulfur effects for pathway analysis, initially making use of data and analysis from the Diesel Emissions Control — Sulfur Effects (DECSE) project.
- Provide a sample pathway analysis for one type of vehicle and configuration from each of the three platforms.

- Recommend future analyses and continue to expand input databases, identify gaps in the data required for valid predictions and use this information as a guide to develop future R&D programs.

Accomplishments

- Developed and refined SER analysis framework and data collection protocols.
- Performed vehicle sample pathway analysis for two platforms results from light truck platform provided in Figure 1.
- Developed engine modeling enhancements within the analysis framework using 1-D engine modeling software (25% complete).
- Integrated diesel oxidation catalyst model with ADVISOR as an initial test of emission control system submodel integration.

Future Directions

- Expand understanding of fuel formulation effects on emissions.
- Identify and collect relevant data already existing from research partners.
- Refine SER analysis approach by continuing to analyze data and develop maps and modules for ADVISOR.
- Analyze pathways for reducing emissions from enhanced samples for three platforms and investigate specific applications of analysis tools such as the effect of compression ratio, EGR, and emission control devices on efficiency.
- Develop a process to validate the model at a systems level.

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 future emission standards, while continuing to improve engine efficiency and durability.

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

Approach

NREL is using fuel property and emission data from APBF-DEC and associated empirical data relationships, in conjunction with first-principle models to evaluate the most promising pathways for reducing emissions using the SER approach. The system concept consists of an analysis tool that accounts for the interaction of fuel, combustion strategy, and emission control devices. This approach is being built around NREL's ADVISOR (advanced vehicle simulator) model. ADVISOR requires a detailed map of gaseous emissions, PM emissions (real-time), fuel consumption, exhaust temperature and EGR temperatures, at many engine speeds and loads. Such maps can be acquired as actual datasets from engine testing or generated using one-dimensional engine models with a more limited (i.e. 8-mode) dataset and various engine parameters as input. This work will involve continually developing these engine performance maps using data acquired from other APBF projects, as well as incorporating conversion efficiency data (as a function of exhaust temperature and flow parameters) for various emission control devices. Empirical relationships of emissions and specific, targeted fuel properties such as sulfur content, cetane number, and aromatic content will be used to estimate the impacts of fuel properties. These components will be used to evaluate the best pathways for achieving the technical targets of the overall APBF-DEC Program.

The SER approach is designed around the following:

- Use ADVISOR as an analysis platform to link system components (i.e. empirical emission relationships, first principle models, and parameterized models). Identify the best pathways for achieving the technical targets on a vehicle level as defined by the APBF Program.
- Collect data sets from engine laboratories and develop empirical relationships linking emissions to fuel properties.
- Develop 1-D engine models for vehicle platforms for which complete datasets are not available. Expand the CIDI engine map library in ADVISOR and provide enhanced exhaust gas characteristics to be used as inputs to emission control device submodels.
- Expand the emissions control and emission control device modeling capabilities in ADVISOR in order to enhance emissions predictions.

Results

Information is needed to investigate SER pathways. Table 1 identifies the three systems of interest and the types of information that will enable pathway analysis to be completed. Technical targets for NO_x and particulate matter (PM) are identified, and projects representing sources for emissions data are included.

	NO_x Reduction	**PM Reduction**
Advanced Automobile - 1.7 to 2.2 liter HSDI with Common Rail Injection	Target: 0.07 g/mile Research: NO_x adsorber, engine optimization, and EGR strategies	Target: 0.01 g/mile Research: Engine optimization, fuel formulation, and DPF
Light-Duty Truck - Navistar 7.3 liter T44/ Powerstroke	Target: 0.07 g/mile Research: NO_x adsorber, engine optimization, and EGR strategies	Target: 0.01 g/mile Research: Engine optimization, fuel formulation, oxidation catalyst and DPF
Heavy-Duty Truck Engine - 11 to 12 liter CIDI	Target: 0.2 g/bhp-hr Research: lean-NO_x catalyst, NO_x adsorber, and EGR strategies	Target: 0.01 g/bhp-hr Research: Engine optimization, fuel formulation, oxidation catalyst and DPF

Table 1. Targets and Representative Research Areas for Data

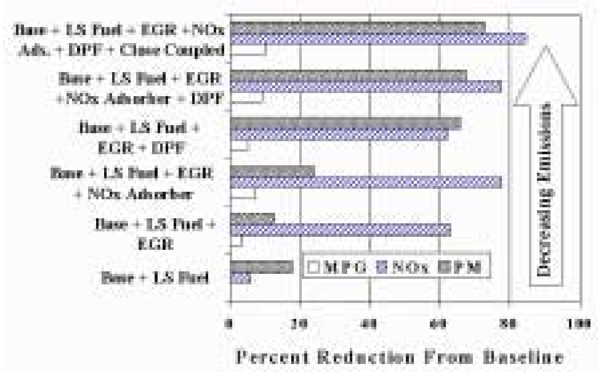

Figure 1. Sample Pathway Analysis Results for Light-Duty Truck Platform

Two primary activities contributed to the results in FY01. The first is the development of the SER analysis framework and testing of analysis pathways. The second is the development of emission control device submodels and the initiation of 1-D engine modeling development. Sample pathway analyses for two platforms have been completed. Figure 1 shows the results of an emissions reduction pathway for the light-duty truck platform using low sulfur fuel in conjunction with exhaust gas recirculation (EGR), a diesel particulate filter, and a NO_x adsorber catalyst. This figure illustrates how the progressive addition of emissions control approaches can reduce PM and NO_x emissions. The figure also shows the estimated fuel consumption impacts that will parallel these emissions reductions.

Conclusions

Progress has been made on developing components necessary to enable a system level analysis of the emissions pathways for advanced engines and vehicles. Relationships between fuel and emissions data obtained from testing engines, vehicles, and advanced emission control devices are being developed in submodels that form the building blocks of the SER framework. This framework will provide the capability to predict potential emissions and efficiency improvements for automobiles, light-trucks, and heavy-duty engines.

Future efforts will focus on: 1) expanding the number of parameterized emission control device submodels, 2) enhancing the empirical data relationships previously developed, and 3) applying the analysis tool. Significant effort will be focused on continuing to develop an array of engine performance/emissions maps and 1-D engine models to enhance the SER analysis capabilities. Additional effort will be devoted to developing fuel property versus emissions correlations using NREL's existing database, enhancing NREL's database, and incorporating other fuel property emissions databases such as the one being developed by EPA. The project will continue to focus on evaluating three technology platforms (automobile, light-duty truck, and heavy-duty engine) and will emphasize the inclusion of a heavy-duty engine model into ADVISOR. The project will also evaluate applications related to these platforms as required by DOE and the needs of the APBF-DEC program. The SER analysis will provide DOE with analysis of the potential effectiveness of different combinations of fuel, CIDI engine control strategies, and emission control devices on achieving emission reduction targets and engine and vehicle performance goals.

D. Fuel Property 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
D. Sulfur Impacts
E. Toxic Emissions
F. Ultra-fine Particles

Tasks

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

Objectives

- Establish and populate a web-based, searchable fuel property database for the Advanced Petroleum-Based Fuels (APBF) program, which links to available emissions data.
- Utilize the database to develop empirical relationships between emissions and fuel properties.

Approach

- Define the fuel properties, engine and vehicle characteristics, and emissions to be included in the database.
- Build the database, web pages and appropriate web interfaces for the searchable database.
- Utilize regression analysis to reveal empirical relationships between targeted fuel properties (such as sulfur content) and emissions from advanced emission control systems.

Accomplishments

- Completed a searchable fuel property database and made it available on the World Wide Web at http://www.ott.doe.gov/fuelprops/.
- Linked the fuel property database to the existing heavy vehicle emissions database.

- Implemented an improved user interface to facilitate connection of fuel property and emissions databases.
- Initiated implementation of a similar database, also linked to the fuel property database, for engine emissions results from the APBF program.
- Developed regression equations allowing the prediction of particulate matter (PM) emissions from engines equipped with diesel particulate filters (DPF) and NO_x adsorber/catalyst systems.

Future Directions

- Continue to populate fuels and emissions databases as data become available.
- Complete expansion of the emissions database to include light-duty emissions data and engine emissions data, particularly from the APBF program.
- Examine other empirical correlations including impact of fuel properties on exhaust treatment systems and engine-out emissions.

Introduction

Numerous studies have investigated the impact of fuel properties such as density, aromatic content, sulfur content and cetane number on emissions from various diesel engines. There is also a great deal of data on diesel vehicle emissions using various advanced and alternative fuels (such as ultra-low sulfur diesel, CARB diesel, biodiesel, and FT-diesel). Fuel properties directly affect combustion chemistry, diesel spray properties, and performance of mechanical systems such as fuel injectors. Fuel properties can also impact aftertreatment systems, with sulfur content as the most obvious example. As engine systems advance and in many cases become more complex, it becomes critical to understand how engine technology and fuel properties interact to influence performance and emissions.

The Advanced Petroleum-Based Fuels program includes a System Emissions Reduction Analysis effort that 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

Over the past several years the Alternative Fuels Data Center website at NREL has accumulated a large database of heavy-duty vehicle chassis testing emissions data. This database has proven useful for examination of trends in diesel emissions [1], as well as comparison of diesel and alternative fuel emissions. Many of these studies also included a detailed analysis of the test fuel, and this is currently a requirement for all ongoing and future studies. Under this project a database for this fuel property information has been created and populated, and linked to the vehicle emissions database. Additionally a user-friendly interface for database queries has been developed that requires no particular programming skill. Search results can be displayed or exported to text files for examination with other software tools.

Results

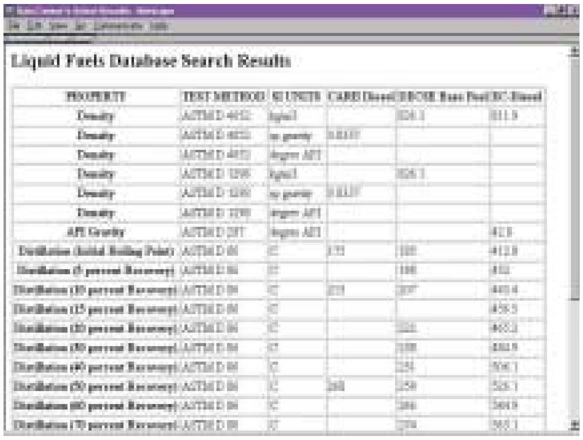
The fuel property database was developed to include physical, chemical, and operability property data, as well as environmental health and safety information. The database is accessible via the World Wide Web at http://www.ott.doe.gov/fuelprops/ (see Figure 1).

The database was set up 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

Figure 1. Fuel Property Database Homepage

Petroleum-Based Fuels Property Database

Figure 2. Fuel Property Database Selection Page



Liquid Fuels Database Search Results

Figure 3. Sample Results from Fuel Property Query

description of the fuel. Figure 3 provides a sample of the results a user would get back from a query, with all selected (or available) data displayed in a table format. 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 in which he or she is interested (see Figure 4) and display vehicle characteristics and emissions data for all vehicles tested with that fuel.

Ongoing developments will allow creation of data files containing selected fuel properties for many fuels and related, selected vehicle and emissions data. For example, one could examine the impact of several diesel fuel properties on emissions for vehicles powered by conventional diesel, biodiesel, and Fischer-Tropsch diesel. A similar capability has been created for engine testing data.

Heavy Vehicle Chassis Emissions Data

Figure 4. Heavy Vehicle Chassis Emissions Data Selection Page

Engine data on how fuel sulfur content impacts performance of DPF and NO_x adsorber/catalyst systems were obtained as a part of the APBF Program. These results were used to develop empirical correlations of emissions with fuel sulfur content. As an example, results for the DPF are described here. The DPF study generated engine-out and post-filter PM emissions data from a Caterpillar 3126 engine using fuel containing sulfur at four levels (3, 30, 150, and 350 ppm) under three test conditions: (1) OICA 13-mode (one integrated sample), (2) "Road-Load" OICA mode 4 (733 Nm @ 1,783 rpm), and (3) "Peak-Torque" OICA mode 2 (1,047 Nm @ 1,440 rpm). Two types of DPF systems were tested: Catalyzed diesel particulate filter (CDPF) and continuously regenerated diesel particulate filter (CR-DPF). The best fit, based on linear correlation coefficients and other goodness-of-fit criteria, was achieved with the following model:

$$\log(PM) = \alpha + \beta * \log(S) + e, \quad (3.1)$$

where:

- log(PM) = log (base 10) of total PM emissions (g/bhp-hr)
- α and β are constants
- log(S) = log (base 10) of fuel sulfur level (ppm)
- e is a random error associated with measurement and testing.

This model was applied separately to engine-out, post-CDPF, and post-CR-DPF total PM emissions. A comparison of data and empirical model predictions for engine-out and post-CDPF PM

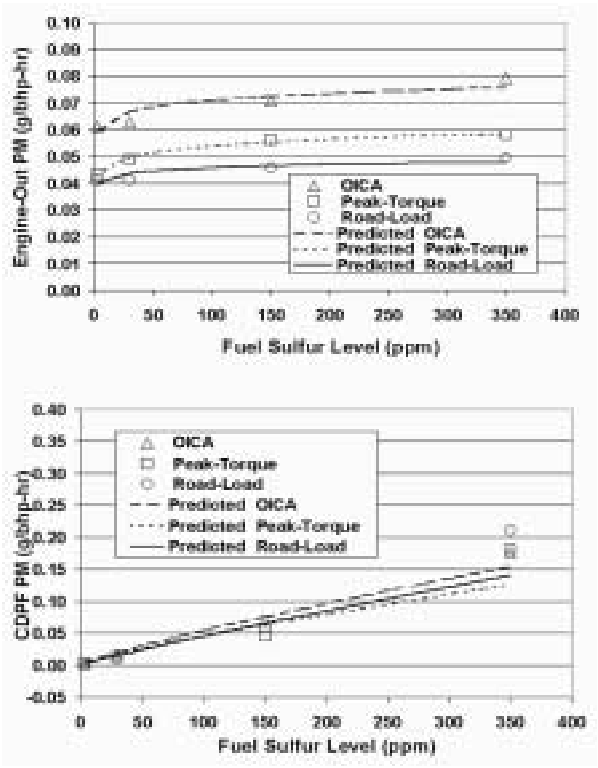


Figure 5. Predicted and average measured engine-out PM emissions (Cat 3126 engine) versus fuel sulfur level (top). Predicted and average measured post-CDPF PM emissions versus fuel sulfur level (bottom).

emissions as a function of fuel sulfur content are shown in Figure 5. The models developed quite accurately fit engine-out emissions. For the post-CDPF results there appears to be certain lack of fit at the 350-ppm sulfur fuel; this is likely due to increased variability that is typically found at higher emissions values. Log-linear models, commonly used in emissions analysis, assume that the magnitude of experimental error is proportional to the average value. Thus, the uncertainty in the predicted emissions tends to be proportional to the prediction. On a log scale the deviations from the regression line appear to be random, and variability is constant across fuel sulfur levels.

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 as the database grows it will be utilized to develop predictive tools for estimating the effects that fuel properties have on emissions and emission control system performance.

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E. Isotopic Tracing of Fuel Components in Particulate Emissions from Diesel Engines Using Accelerator Mass Spectrometry (AMS)

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DOE contract number W-7405-Eng-48

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

- Determine contribution of diesel fuel components and oxygenates to soot formation.
- Separate volatile and non-volatile fractions of soot.
- Test combustion paradigm that all carbon and oxygen in fuel is equal.
- Produce data to validate combustion modeling.

Approach

- Construct filter assembly to collect exhaust soot.
- Analyze carbon isotope content of all fuel components and lubrication oil.
- Collect soot from skip fired 1.7L optical engine. Complete isotopic analyses of soot and determine contributions from available carbon sources.

Accomplishments

- Filter assembly constructed and in use.
- Preliminary tests completed to determine engine operating conditions for loading filters with sufficient soot for isotopic analyses.

- Determined lubrication oil leakage into the cylinder to be a major contributor of carbon emissions from the test engine.

Future Directions

- Determine contributions of major fuel components to soot production and test selected oxygenates.
- Collect gaseous emissions and separate major components.
- Obtain carbon-14 (^{14}C) labeled lube oil and run it in conventional diesel engine. Determine contribution of lube oil to soot and CO_2 emissions.
- Apply tracing techniques to HCCI engines.

Introduction

Accelerator mass spectrometry (AMS) is an isotope-ratio measurement technique developed in the late 1970s for tracing long-lived radioisotopes (e.g., ^{14}C half life = 5760 yr). The technique counts individual nuclei rather than waiting for their radioactive decay, allowing measurement of more than 100 low-level ^{14}C samples per day (Vogel et al, 1995) (see Figure 1).

The contemporary quantity of ^{14}C in living things (1.2 parts in 10^{12} or 110 fmol ^{14}C/ g C) is highly elevated compared to the quantity of ^{14}C in petroleum-derived products. This isotopic elevation is sufficient to trace the fate of bio-derived fuel components in the emissions of an engine without the use of radioactive materials. If synthesis of a fuel component from biologically-derived source material is not feasible, another approach is to purchase ^{14}C-labeled material (e.g., dibutyl maleate (DBM)) and dilute it with petroleum-derived material to yield a contemporary level of ^{14}C. In each case, the virtual absence of ^{14}C in petroleum-based fuels gives a very low ^{14}C background that makes this approach to tracing fuel components practical.

Regulatory pressure to significantly reduce the particulate emissions from diesel engines is driving research into understanding mechanisms of soot formation. If mechanisms are understood, then combustion modeling can be used to evaluate possible changes in fuel formulation and suggest possible fuel components that can improve combustion and reduce PM emissions. The combustion paradigm assumes that large molecules break down into small components and then build up again during soot formation. AMS allows us to label specific fuel components, including oxygenates, trace the carbon atoms, and test this combustion modeling paradigm.

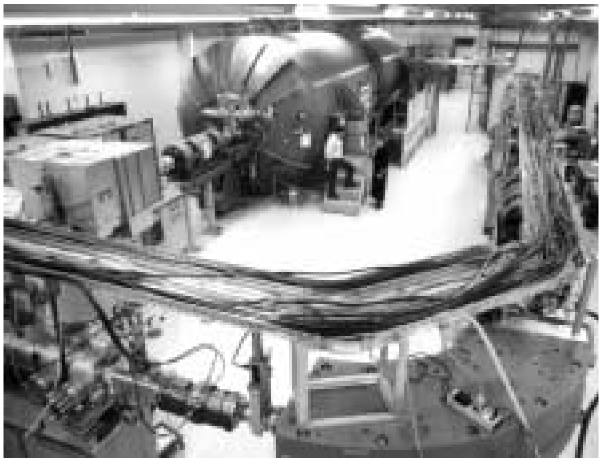

Figure 1. View of LLNL AMS system from above the high energy magnets. The shared facility annually measures 10,000 ^{14}C samples at precisions up to 0.8% and $^{14}C/C$ ratios as low as 1 part in 10^{15}.

Volatile and non-volatile organic fractions (VOF, NVOF) in the PM can be further separated. The VOF of the PM can be oxidized with catalysts in the exhaust stream to further decrease PM. The effectiveness of exhaust stream catalysts to oxidize products from tracer fuel components can be monitored through AMS measurement of carbon in PM.

Approach

The ^{14}C concentration of all fuel components and the lubrication oil were checked by AMS and confirmed to be of petroleum origin ($^{14}C/C$ ratios ~10^{-15}). A test fuel containing 88% DBM, 7% n-

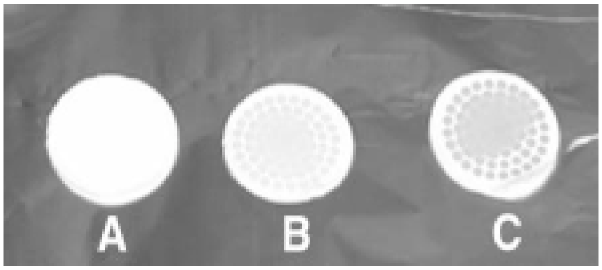

Figure 2. Quartz filters loaded with emissions from optical engine. The filters were loaded with the following engine operating conditions: (A) motored only without firing, 12x48 cycles, 0.2 mg C from lube oil; (B) motored with 48 skip fires, 12x48 cycles, 0.28 mg C from lube oil and soot; (C) motored with 96 skip fires, 2x12x48cycles, 0.61 mg C from lube oil and soot.

hexadecane (NHD) and 5% ethylhexyl nitrate (EHN) was spiked with [maleate-1,4-^{14}C]- DBM to obtain fuel containing 78 fmol ^{14}C/ g C, approximately 70% of the ^{14}C found in living things.

Pre-combusted quartz filters were loaded with PM drawn from the exhaust manifold of a modern-technology, 4-stroke, heavy-duty DI diesel engine that has been modified to provide extensive optical access into the combustion chamber. Injection timing was optimized such that the engine produced maximum gross indicated torque. The engine operated at 1200-rpm and moderate load (8.00 bar gross indicated mean effective pressure (gIMEP)). The optical engine was run in skip fire mode (firing every 12th cycle) and required 48 fires to deposit sufficient soot for isotopic analysis (see Figure 2). Filters were handled with stainless steel forceps and placed on aluminum foil after loading to avoid contamination with other carbon sources.

Some filters were baked at 340°C for 2 hr to remove the VOF fraction of the soot. The remaining carbon on the filters was assumed to be the NVOF. A procedure was developed using NIST SRM 2975 diesel soot to obtain consistent isotope ratios and mass fraction of the NVOF. SRM 2975 has a 7% VOF by this procedure. A similar VOF is expected from the optical engine since the soot is collected close to the exhaust manifold without using a dilution tunnel.

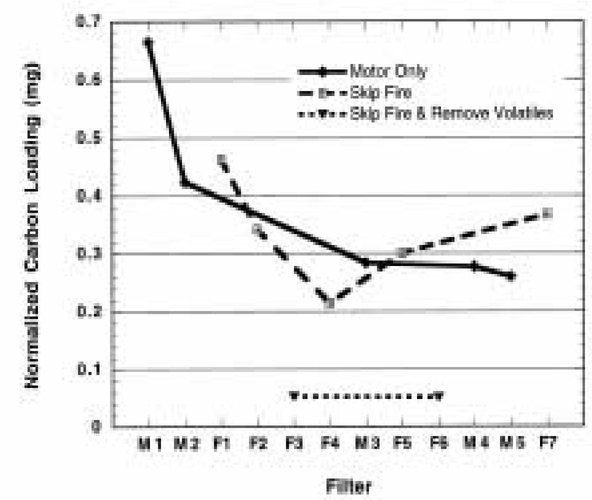

Figure 3. Carbon mass deposited on motored (M) and skip fired (F) filters during a day of operation. The filters are listed on the x-axis in the order in which they were collected. The mass of carbon was normalized to12x48 cycles for samples with different collection times. The NVOF carbon mass appeared to be consistent, suggesting the lube oil departed in the VOF.

Results

All filters were loaded with a significant amount of carbon. Lubrication oil deposition on the filters was found to be a major component of the carbon inventory. The lube oil deposition decreased over the course of a day, but the total carbon remained significant on filters collected with motored cycles only (see Figure 3). The mass of carbon on filters collected with skip fires was no higher than those with motored cycles only. Furthermore, the ^{14}C content of the motored and skip fired samples is almost identical. Although the ^{14}C concentration in the fuel is ~1000x that of the lube oil, the carbon mass on the filters is almost entirely due to lube oil or its combustion products. The thermal treatment to isolate the NVOF removed all the carbon on control filters loaded with 2-7 mg of lube oil. Removing the VOF from the skip fired filters produced a consistent carbon mass (0.05 mg), but the isotope content varied by a factor of six. Only one NVOF sample had elevated ^{14}C content so it is not clear if the labeled DBM in the NVOF or contemporary contamination introduced during processing is responsible for the signal. With the limited data available, it appears as though the ^{14}C atoms in the DBM do not participate in soot formation.

Conclusions

The large contribution of lubricating oil to the exhaust emissions, both as oil from non-fired cycles and as combusted soot, complicates quantitation of fuel components in PM. Results indicate that ^{14}C atoms in the DBM contribute virtually no carbon to soot formation in this engine. It is impossible to separate the contributions of the other fuel components, NHD and EHN, from the lube oil due to their similar isotopic signatures. The lube oil signal needs to be reduced either by limiting leakage down the valves and into the cylinder or by removing non-combusted oil as part of sample pretreatment. The logical next step is to obtain labeled lubrication oil for use in this and a conventional engine and determine its contribution to PM emissions. Determining the contribution of lube oil to emissions is important for assessing viability of exhaust catalyst technology.

Reference

1. Vogel, J. S.; Turtletaub, K. W.; Finkel, R.; Nelson, D. E. (1995) Accelerator Mass Spectrometry - Isotope Quantification at Attomole Sensitivity. *Anal. Chem.* **67**, 353-9A

FY 2001 Presentation

1. Bruce Buchholz, Chuck Mueller, and Glen Martin. "Isotopic Tracing of Fuel Components in Particulate Emissions from Diesel Engines Using Accelerator Mass Spectrometry." DOE 2001 Review of OTT CIDI Engine Combustion, Emission Control, & Fuels R&D National Laboratory Program, Oak Ridge, TN, June 11-13, 2001.

VII. FUELS FOR FUEL CELL VEHICLES

A. Demonstration of Fuel Cell Vehicles and Refueling Technology

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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

E. Health, Safety, and Regulatory Issues
F. Fueling Infrastructure For Non-Petroleum Based Fuels
H. Hydrogen Storage and Dispensing
J. Codes and Safety Standards
K. Full Fuel Cycle Emissions Analysis

Tasks

6. Demonstrate Off-board Hydrogen Fueling Infrastructure Technologies

Objectives

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

Approach

- Adopt an organizational structure consisting of an Executive Committee, a Working Group, and a Communications Team 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;
  - Phase III 2002-2003, demonstrate more cars and buses using hydrogen, methanol, gasoline or other fuels as determined by the Partnership.

Accomplishments

- Headquarters facility built and occupied.

- Additional partners added.
- Vehicle demonstration plans underway.
- Fuel Scenarios study completed.

Future Directions

- Identify additional fueling sites and fuel choices; assess commercialization issues; and determine potential post-partnership activities.

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, General Motors, Honda, Hyundai, Nissan, Toyota and Volkswagen; Ballard Power Systems, International Fuel Cells, and XCELLSiS; BP, ExxonMobil, 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.

Additionally, there are ten Associate Partners who assist with specific areas of expertise to help meet the CaFCP's goals: hydrogen gas suppliers (Air Products and Chemicals, Inc. and Praxair); hydrogen fueling stations (Hydrogen Burner Technology, Pacific Gas & Electric, Proton Energy Systems, Inc., and Stuart Energy Systems); a methanol fuel supplier (Methanex); and transit bus agencies (AC Transit and Santa Clara Valley Transportation Authority which operate in the Greater San Francisco Bay area, and SunLine Transit Agency in the Palm Springs area).

Together, these members are working to investigate and evaluate the commercialization of fuel cell vehicle technology for the 21st century.

The CaFCP is testing and demonstrating fuel cell electric vehicles in California through 2003 under day-to-day driving conditions; demonstrating alternative fuel infrastructure technology; exploring 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; and working to increase public awareness of fuel cell vehicle technology and the benefits it can offer.

Figure 1. The CaFCP Headquarters Facility in West Sacramento, CA

Approach

Highlighting progress for the past year is completion of a headquarters facility in West Sacramento, California, which opened in November 2000 to serve as an operations base for vehicle demonstrations and fueling operations (see Figure 1). The facility houses vehicle maintenance bays and a hydrogen fueling station (see Figure 2). It also serves as an educational center for fuel cell technology, with a public gallery and scheduled facility tours.

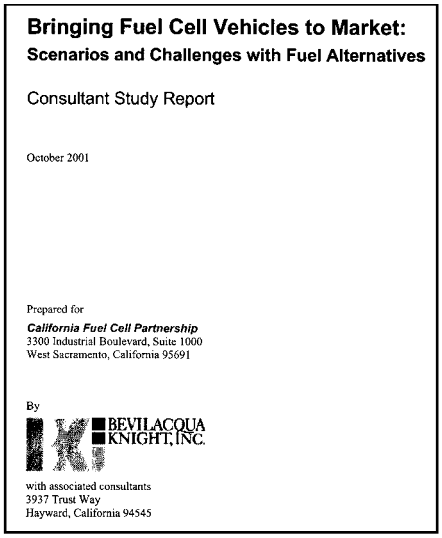
To demonstrate fuel cell technology, ten passenger cars and one bus are currently operating on the city streets and highways of California. Over 70 are expected to be in operation by the end of 2003. This activity not only provides vital technical information, but also serves to raise the profile of fuel cell vehicles by operating in public view and through participation in special public events.

Figure 2. The Hydrogen Fueling Station - West Sacramento, CA

To support the driving demonstration, a fueling infrastructure for fuel cell vehicles is underway, beginning with hydrogen fuel. Methanol is expected to be in use by the end of 2001. The partners are also working together 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 members also commissioned a consultant-developed report that examines the challenges of using various fuels and infrastructure and identifies initiatives that can promote success. (Known as the Fuel Scenarios Study, the report was released to CaFCP members and the public in Fall 2001—see Figure 3.) Although the report has a California focus, similar challenges will exist in markets across the United States and around the world. The study will help the CaFCP members as well as others to become more fully engaged in addressing the challenges associated with the different possible fuel scenarios.

The Partnership is taking steps to broaden public awareness of fuel cell vehicles by displaying vehicles at various public venues (see Figures 4 and 5), hosting classroom visits to its headquarters facility, and speaking about fuel cells to organized community groups and industry conferences. Through participation in public events, the CaFCP over the past year has reached thousands of people. The vehicles have served as the pace cars for two marathons — the California International Marathon in



Bringing Fuel Cell Vehicles to Market:
Scenarios and Challenges with Fuel Alternatives

Consultant Study Report

October 2001

Prepared for
California Fuel Cell Partnership
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Figure 3. The fuels scenarios study, completed in October 2001, is available at www.fuelcellpartnership.org/event_roundtable.html.

Figure 4. Vehicles on Display at the Headquarters Facility

Figure 5. Ford Focus on Display at Earth Day 2001 Event, Los Angeles, CA

Sacramento and the Los Angeles marathon; multiple vehicles and displays were featured at the Orange County Fair; and as part of their ongoing test-drives, vehicles are parked in prominent public gathering places around Sacramento, engendering public attention and excitement. The Partnership's Internet website (www.fuelcellpartnership.org) provides more educational information.

Conclusion

The second year of the project featured several milestones marking the cooperative progress of this diverse, competitive, yet cooperative effort. The construction of a headquarters facility has boosted the effort to provide hands-on, visible evidence of the fuel cell in operation — a necessary step on the road to commercialization.

B. Well-to-Wheel Analysis of Energy and Emission Impacts of Fuel-Cell Vehicle Fuels

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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

K. Full Fuel Cycle Emissions Analysis

Tasks

2. Conduct Technical, Economic, and Environmental Assessments

Objectives

- Develop a comprehensive model to evaluate "well-to-wheel" (WTW) energy and emissions associated with fuel-cell vehicles powered by different fuels.
- Characterize production pathways of various fuel-cell fuels, such as gaseous hydrogen, liquid hydrogen, methanol, gasoline, ethanol, and Fischer-Tropsch (FT) naphtha.
- Analyze key issues in production and distribution of fuel-cell fuels and evaluate their impacts on WTW energy and emissions.

Approach

- Revise Argonne's GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation) model to accommodate fuel-cell fuel options.
- Estimate emissions of greenhouse gases (CO_2, CH_4, and N_2O) and criteria pollutants (VOCs, CO, NO_x, PM_{10}, and SO_x) and energy use for all energy sources, fossil fuels (petroleum, natural gas, and coal), and petroleum used to make fuel-cell fuels.
- Specify production and distribution pathways for individual fuel-cell fuels.
- Search for literature and contact experts to obtain data on new technologies, energy efficiencies, and emissions associated with key WTW activities (e.g., fuel production and fuel-cell vehicle operations).
- Evaluate and process the data obtained for application to the GREET model.
- Conduct GREET simulations to generate WTW energy and emission results for various fuel-cell fuels.

Accomplishments

- Included the following fuel-cell fuels in the GREET model: gaseous hydrogen ($G.H_2$), liquid hydrogen ($L.H_2$), methanol, gasoline, ethanol, naphtha, compressed natural gas (CNG), diesel, liquefied natural gas (LNG), and liquefied petroleum gas (LPG).
- Specified production and distribution pathways for each of the above fuels.
- Completed a new version of the GREET model — GREET 1.6. The beta version was sent to a group of selected GREET users for testing and evaluation.
- Applied GREET 1.6 to a study with General Motors Corporation comparing different vehicle technologies and fuels (see www.transportation.anl.gov).
- Generated WTW energy and emission results for various fuel-cell fuels for the California Fuel-Cell Partnership.

Future Directions

- Revise key assumptions in GREET l.6 to reflect future technologies related to hydrogen production, distribution, and storage.
- Coordinate with managers of other ongoing DOE projects to better predict fuel economy of fuel-cell vehicles powered by different fuels.
- Seek feedback from GREET users to further improve the functionality of the GREET model.
- Continue to evaluate WTW energy and emissions impacts of fuel-cell fuels.

Introduction

Fuel-cell vehicles are being promoted for their energy efficiency and zero or near-zero emissions. Although experts agree that, in the long term, hydrogen will be selected as the best fuel-cell fuel, it may not be available on a large scale in the foreseeable future, mainly because of production and distribution infrastructure constraints. Intensive R&D efforts are being focused on other potential fuel-cell fuels. Because production and distribution of various fuel-cell fuels are subject to different energy efficiencies and emissions, WTW analysis is necessary to obtain impartial evaluations of fuel-cell vehicle/fuel systems.

Since 1995, with funds from DOE's Office of Transportation Technologies (OTT), Argonne has been developing the GREET model to estimate fuel-cycle energy use and emissions associated with new transportation fuels and advanced vehicle technologies. We have released a series of GREET versions with revisions, updates, and upgrades. The newest version — GREET 1.6 — is discussed in Wang (2001).

Approach

For a given vehicle technology/transportation fuel combination, the GREET model separately calculates:

1. Fuel-cycle energy consumption for three energy categories (total energy, fossil fuels, and petroleum)
2. Fuel-cycle emissions of three greenhouse gases (CO_2, CH_4, N_2O)
3. Fuel-cycle emissions of five criteria pollutants (total and urban emissions — VOCs, CO, NO_x, PM_{10}, and SO_x)

Figure 1 shows the stages covered in GREET simulations of fuel cycles. A fuel-cycle analysis (also called a WTW analysis) includes the feedstock, fuel, and vehicle operation stages. The feedstock and fuel stages together are called well-to-pump (WTP) stages, and the vehicle operation stage is called the pump-to-wheel (PTW) stage. In GREET, fuel-cycle energy and emission results are presented separately for each of the two stages.

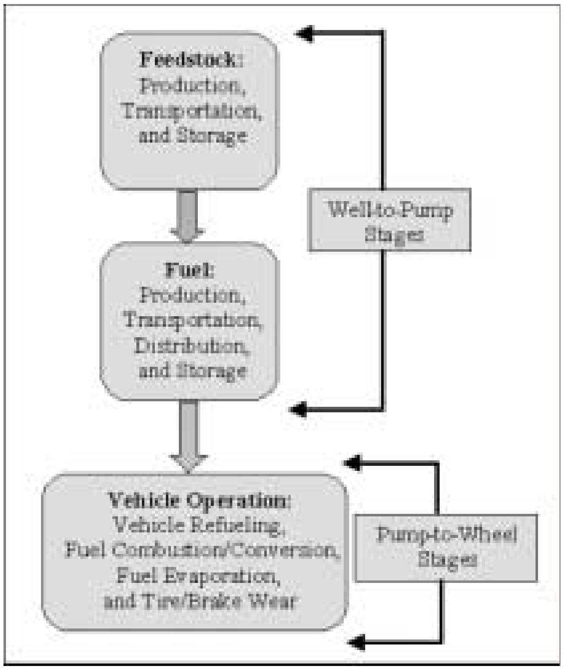

Figure 1. Stages Covered in GREET Fuel-Cycle Analysis

GREET includes a variety of vehicle propulsion technologies and transportation fuels, of which fuel-cell technologies and fuels are a sub-set. Table 1 lists the fuel-cell fuels included in the GREET model. GREET can simulate multiple options for a given pathway. For example, GREET 1.6 includes 48 options for $G.H_2$ and $L.H_2$ pathways.

Results and Conclusions

Argonne applied GREET 1.6 to estimate WTW energy and emission impacts of various fuel-cell fuels. We cannot include all the results here, but Figures 2-4 provide a snapshot of WTW total energy use, fossil energy use, and CO_2-equivalent greenhouse gas (GHG) emission impacts of fuel-cell fuels (see Figure Notes at end of section).

For total energy use (including both nonrenewable and renewable energy sources), use of electrolysis hydrogen and cellulosic ethanol may increase total energy use, relative to baseline gasoline vehicles. However, when one considers fossil energy use (petroleum, natural gas, and coal), cellulosic ethanol is much more superior to any other fuel-cell fuels in reducing fossil fuel use.

Fuel-Cell Fuel	Production Pathways
$G.H_2$ and $L.H_2$	Central plant production from NA and NNA NG Central plant production from NNA flared gas (FG) Refueling station production from NA & NNA NG Refueling station production from NNA FG Solar photovoltaic Electrolysis of water with conventional electricity
Methanol	Production from NA and NNA NG Production from NNA FG
Gasoline	Federal Reformulated Gasoline (RFG) California RFG
Diesel	Low-sulfur diesel
Ethanol	Production from corn Production from woody biomass Production from herbaceous biomass
CNG and LNG	Production from NA and NNA NG Production from NNA FG
LPG	Production from crude oil Production from NG
Naphtha	Production from NA and NNA NG via FT process Production from NNA FG via FT process Production from crude oil

Table 1. Fuel-Cell Fuels and Production Pathways

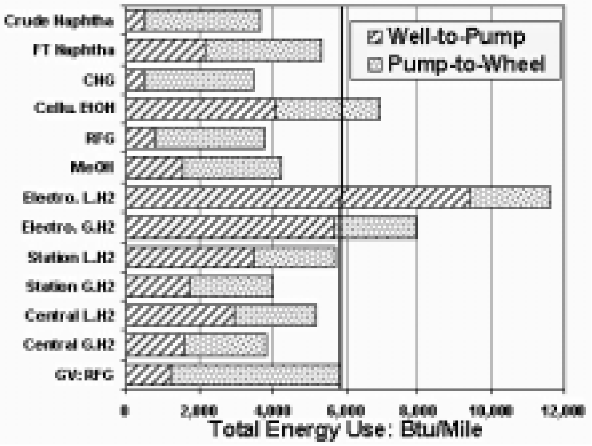

Figure 2. WTW Total Energy Use of Fuel-Cell Vehicles (Btu/mile)

Except for hydrogen via electrolysis, all the fuel-cell fuels achieve GHG emission reduction benefits (although if clean electricity such as hydroelectricity is to be used for hydrogen production, electrolysis hydrogen pathways will certainly achieve large GHG emission reduction benefits). Not surprisingly, renewable ethanol achieves the largest GHG emission benefits.

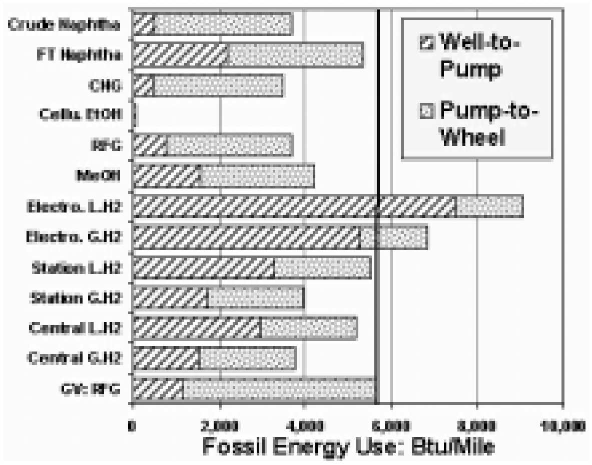

Figure 3. WTW Fossil Energy Use of Fuel-Cell Vehicles (Btu/mile)

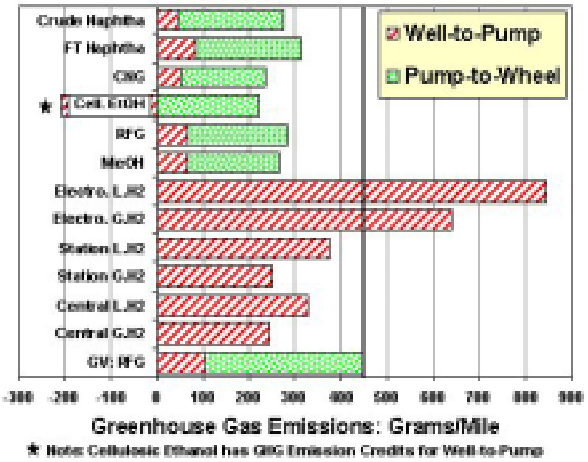

Figure 4. WTW Greenhouse Gas Emissions of Fuel-Cell Vehicles (grams/mile)

The results depend heavily on assumptions regarding fuel production efficiencies and fuel-cell vehicle fuel economy. The GREET model can readily test alternative assumptions and provide WTW energy and emission results.

Figure and Table Notes

NA	North American
NNA	Non-North American
NG	natural gas
FG	flared gas
Central $G.H_2$	gaseous hydrogen produced in centralized plants
Central $L.H_2$	liquid hydrogen produced in centralized plants
Station $G.H_2$	gaseous hydrogen produced in refueling stations with NA NG
Station $L.H_2$	liquid hydrogen produced in refueling stations with NA NG
Electro. $G.H_2$	gaseous hydrogen produced in refueling stations via electrolysis with U.S. average electricity
Electro. $L.H_2$	liquid hydrogen produced in refueling stations via electrolysis with U.S. average electricity
MeOH	methanol produced from NA NG
CNG	compressed NG produced from NA NG
FT naphtha	naphtha produced from NNA NG via the Fischer-Tropsch (FT) process
Crude naphtha	naphtha produced from crude oil in petroleum refineries
WTP	well-to-pump stages
PTW	pump-to-wheel stages

Reference

1. Wang, M., 2001, *Development and Use of GREET 1.6 Fuel-Cycle Model for Transportation Fuels and Vehicle Technologies,* ANL/ESD/TM-163, Center for Transportation Research, Argonne National Laboratory, Argonne, Ill., June.

C. Guidance for Transportation Technologies: Fuel Choice for Fuel Cell Vehicles

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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

C. Emission and Environmental Impacts
D. Advanced Fuel Production, Specifications, and Costs
E. Health, Safety, and Regulatory Issues
F. Fueling Infrastructure For Non-Petroleum Based Fuels
G. Distributed Hydrogen Production
H. Hydrogen Storage and Dispensing
I. Economic Feasibility
J. Codes and Safety Standards
K. Full Fuel Cycle Emissions Analysis

Tasks

2. Conduct Technical, Economic, and Environmental Assessments
7. Conduct Technical, Economic, and Environmental Assessments for Hydrogen Fueling Infrastructure

Objectives

The goal of this project is to help establish refined research and development (R&D) targets for direct-hydrogen fuel cell vehicles (FCVs) based on a comprehensive analysis of direct-hydrogen FCVs and competing vehicle technologies.

- Establish R&D targets for direct-hydrogen FCVs based on well-to-wheel comparison to reformer-based FCVs and other vehicles.
  - Provide an independent analysis that leverages, and can be easily related to, previous DOE and Arthur D. Little analyses.
- Characterize various fuel chain and vehicle options based on well-to-wheel efficiency, greenhouse gas emissions, cost, and safety.
  - Include methanol, ethanol, diesel, and gasoline, but focus on hydrogen fuel chains.
  - Include internal combustion engine and hybrid vehicles, but focus on direct-hydrogen and reformer-based FCVs.

Approach

- Task 1: Develop a well-to-tank fuel chain model.
- Task 2: Determine fuel costs for each fuel chain.

- Task 3: Develop a tank-to-wheel vehicle model.
- Task 4: Determine vehicle costs.
- Task 5: Perform a fuels safety analysis.

Accomplishments

All tasks have been completed, and final results are under review.

This paper reports on the final results for Tasks 1 and 3 (efficiency and emissions analyses), as well as preliminary results for Tasks 2 and 4 (cost analyses). All data shared are still under final review and should therefore be considered preliminary.

Future Directions

As a part of the remainder of Phase II of this project, we will:

- Review preliminary fuel chain and vehicle results internally and with industry experts.
- Develop targets for on-site hydrogen production options and direct-hydrogen fuel cell vehicle systems.

In Phase III of the program, to commence in FY 2002, we will further expand the list of fuels considered, evaluate the impact on the current fuels infrastructure in more detail, and evaluate the risk of the fuel chain options to each of the stakeholders, in particular with respect to the financial exposure and risk for each of the stakeholders in the fuel chain.

Background

The DOE Office of Transportation Technologies has been supporting the development of polymer electrolyte membrane fuel cells (PEMFCs) for transportation applications. It has focused on gasoline-fueled fuel cell vehicles (FCVs), where the fuel (e.g. gasoline) is processed onboard the vehicle to generate hydrogen. An alternative strategy is to generate hydrogen at a fueling station and carry the molecular hydrogen onboard the vehicle for use in the PEMFC. DOE has commissioned this study to assess the opportunities and costs for generating hydrogen at fueling stations and storing it onboard vehicles, comparing the feasibility, efficiency, economy, and safety of this option with on-board reforming of gasoline. This information will develop a firm basis from which to set targets for a direct-hydrogen fuel cell vehicle program.

Approach

Arthur D. Little is developing detailed well-to-wheel performance and cost calculations taking into account technology options, system integration and efficiencies, hybridization, vehicle weight, and drive cycle. To the extent possible, we have taken advantage of Argonne National Lab's Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) model, which provides a relatively well-referenced backbone for the model. This approach ensures efficient utilization of DOE's resources and provides results that are as consistent with previous Argonne results as possible. However, we made several important improvements and extensions to the capabilities of GREET:

- We separated the well-to-tank analysis from the tank-to-wheel analysis to allow for sensible and transparent comparisons with existing fuel chains;
- we updated the assumptions (especially for the fuel chain) with in-house Arthur D. Little information and original analysis where necessary; and
- we incorporated a more detailed and thorough analysis of fuel cell power unit performance over the drivecycle, based on a careful assessment of

fuel cell system turn-down characteristics. The basis for the analysis was the fuel cell performance model developed as a part of the automotive fuel cell costing program.

Additionally, we are determining fuel and vehicle ownership costs based on detailed local hydrogen fueling station cost analysis and bottom-up fuel cell component cost analysis. The vehicle cost estimates are based on, and consistent with, our automotive fuel cell costing study also carried out for DOE OTT. Also, we are identifying major potential safety issues for each of the fuel chains and comparing them to each other. Finally, we are using the analysis results to help formulate well-founded targets for the DOE's direct-hydrogen FCV program.

Each of the options analyzed and shown in this report represents a future established market for fuels and vehicles, not early market penetration of the technologies. This means that for the purpose of the analyses, we assumed that for each fuel chain:

- Assumptions are consistent with established markets:
  - The necessary fuel infrastructure has been established for each option and the infrastructure is operating at normal capacity.
  - Vehicles are produced in high volumes (i.e. 500,000 units per powertrain configuration).
- Assumptions are consistent with the situation in 2010:
  - Scenarios for 2010 technology performance and cost are used.
  - EIA commodity energy price estimates for 2010 were used as the baseline for energy price calculations.

Following is a brief description of the tasks carried out in this study.

Task 1: Develop well-to-tank fuel chain model

Arthur D. Little has adopted Argonne National Lab's GREET framework to obtain efficiency and emissions results (on a g/GJ basis) independent of vehicle choice. The GREET model already includes a number of petroleum-based fuels, ethanol, methanol, and hydrogen, with inputs expressed as lower heating value efficiencies. We reviewed model inputs and compared those with existing internal models and data. Technology selection and other fuel chain assumptions were checked and additional hydrogen fuel chains were analyzed. For each hydrogen fuel chain, we evaluated the efficiency and emissions based on in-house information, literature review, and detailed system modeling. Centralized and local on-site hydrogen production options and high- and low-pressure hydrogen storage options were evaluated.

Task 2: Determine fuel costs for each fuel chain

The sources and methodology used to arrive at the fuel costs varied from fuel chain to fuel chain. For some of the conventional fuel chains, commodity price forecasts could be used, while for other options (including all the distributed hydrogen production options) costs were established based on detailed vendor quotes. All of the information was augmented with in-house ADL information and system modeling when appropriate. The capital cost estimates were based on an assumption of significant market penetration of each of the fuel chains (i.e. not addressing the "first hydrogen station" issue). Fuel prices are being determined based on the capital, operation and maintenance (O&M), and energy costs and appropriate economic assumptions.

Task 3: Develop tank-to-wheel vehicle model

Arthur D. Little is developing detailed tank-to-wheel performance calculations for fuel cell vehicles (FCV) incorporating vehicle weights, specifications (acceleration, top speed, hill climb), degree of hybridization, drivetrain efficiencies, and drive cycle. Technology selection and performance assumptions of the FCV options are being checked with in-house information, literature review, and system modeling, when appropriate. We are basing our FCV powerplant efficiency and power density estimates on our detailed 50 kW automotive fuel cell system model, which we developed for DOE/OTT under a separate program. Vehicle power plant size is scaled to vehicle weight for different drivetrain options. Drivetrain efficiencies at partial load (i.e. performance curves) have been generated based on available data and additional analysis.

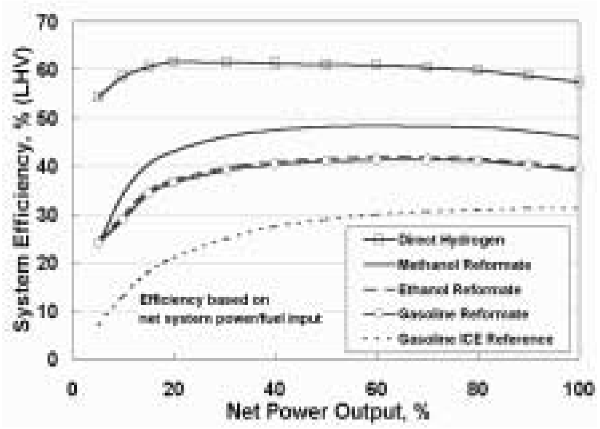

Figure 1: Drive-train Efficiency Assumptions

Task 4: Determine vehicle costs

Vehicle costs are being estimated based on component capital and O&M costs. A detailed cost assessment is being conducted on the fuel cell vehicle components, including the fuel cell stack, fuel processor or hydrogen storage, motor/ transmission, hybrid batteries (if necessary), and balance of plant. Vehicle capital costs are being combined with fuel costs to determine the total consumer cost for fuel cell, electric, hybrids, and conventional vehicle options. We are basing our FCV powerplant cost estimates on our detailed 50 kW automotive fuel cell system model, which we developed for DOE/OTT under a separate program.

Task 5: Perform fuels safety analysis

Arthur D. Little is reviewing the latest information on codes and standards and is identifying the key safety barriers for each fuel chain and end use option. As all of the fuels are already produced for industrial applications, the safety analysis is focusing on local storage, transportation, and vehicle end use. The results of this task include a presentation style report that documents references of fuel safety issues and properties of each fuel that affect safety. In addition to reviewing how fuel properties affect safety, the information is being categorized in terms of safety barriers for fuel dispensing, vehicle operation, and vehicle garage/ maintenance.

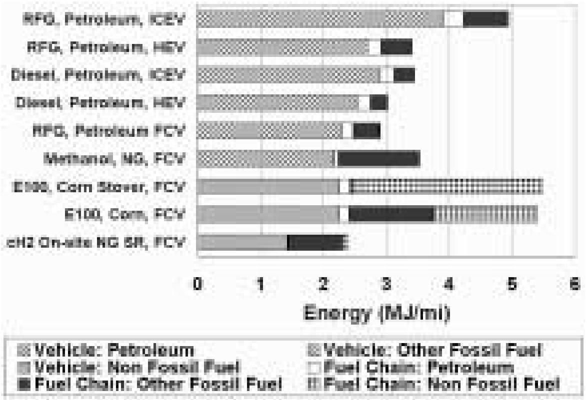

Figure 2: Well-to-Wheel Energy Use for Various Vehicles

Preliminary Results

The drivetrain efficiency assumptions (i.e. performance curves) for FCVs are presented in Figure 1 with a comparison to a conventional internal combustion engine (ICE). Power electronics and motor efficiencies are not presented, but each varies between 85-95%. The performance curves are constructed from the sum of the fuel cell, parasitic power, and reformer (when present) efficiencies at full to partial load. The fuel cell efficiencies are constructed from our kinetic analysis of reformate and direct-hydrogen fuel cells based on current data and projected future performance. The analysis includes the effect of low pressure at partial load and high temperature membrane operation. The single-cell voltage at full power is selected to be 0.8 V for consistency with the cost analysis and previous DOE analyses. The single-cell voltage operating point is higher at partial load. The parasitic power calculations are based on the DOE goals for compressor/expander module performance and our own thermodynamic analysis for direct-hydrogen and reformer-based systems. The reformer efficiencies are based on in-house thermodynamic and kinetic analyses. We assumed future improvements in reformer turn-down and/or operating strategies that will allow a turn-down of 20:1.

Preliminary well-to-wheel energy use (MJ/mi) results for conventional Internal Combustion Engine Vehicles (ICEV), Hybrid Electric Vehicles (HEV), and Fuel Cell Vehicles (FCV) can be found in Figure 2. Additional results for direct-hydrogen FCV

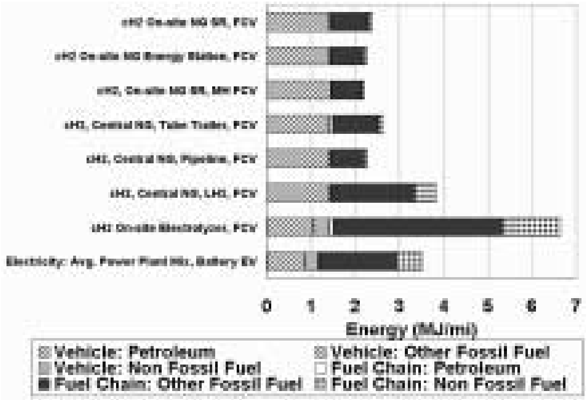

Figure 3: Well-to-Wheel Energy Use for EVs and Direct-Hydrogen FCVs

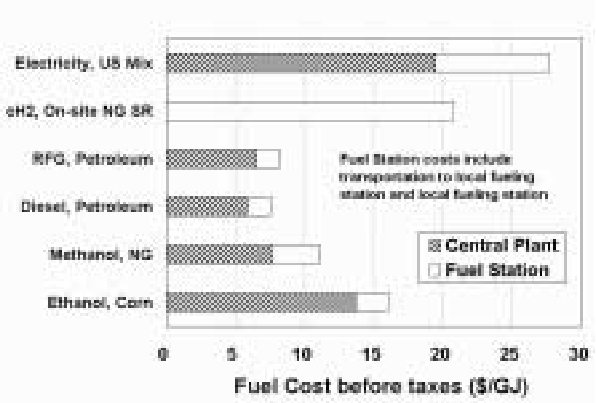

Figure 4: Fuel Cost for Various Fuels

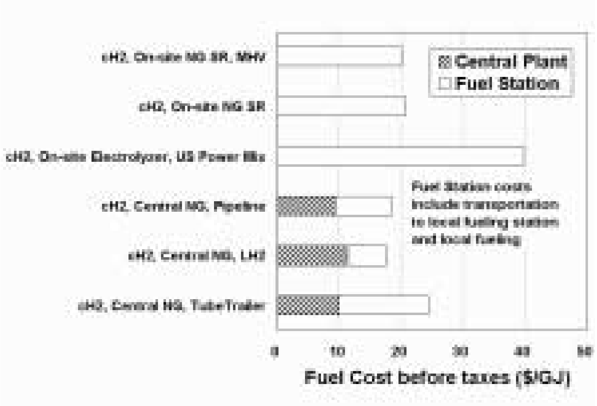

Figure 5: Fuel Cost Hydrogen

options and a Battery-Electric Vehicle (BEV) are presented in Figure 3. FCV results are based on aggressive technology improvements compared with the current technology status. These improvements would occur if existing multi-year R&D programs were successful in achieving their technical targets within reasonable bounds, and if the system integration were optimized to take advantage of the improvements in basic stack and fuel processor technology. The most significant improvement in fundamental technology assumed here was the availability of high temperature membranes.

The gasoline (RFG) and ethanol (E100) FCVs are assumed to be PEMFCs with autothermal reformers (ATR) for hydrogen generation. The methanol FCV uses a low temperature steam reformer (SR) to generate hydrogen, while the hydrogen for the compressed hydrogen (cH_2) FCVs is produced off-board. Energy inputs for corn stover and corn-based E100 production are partially allocated to other coproducts. The corn stover option reflects collecting corn residue or other agricultural residues from existing agricultural operations.

The central production cH_2 options include central steam reformer production from natural gas (NG) with tube trailer, liquid, and pipeline delivery to a hydrogen fueling station. The on-site cH_2 production options include local on-site SR production from NG and on-site electrolyzer production from the U.S. average power plant mix. The energy station option assumes on-site SR production from NG with cogen heat from the reformer exhaust. All cH_2 FCV options assume high pressure on-site storage (3600 psia on-site storage to 5000 psia on-board the vehicle) except the metal hydride (MH) FCV option, which assumes low pressure on-site storage (100 psia on-site and on-board storage). Energy inputs for EV operation are based on the U.S. average power plant mix.

Preliminary fuel cost estimates ($/GJ) for gasoline (RFG), diesel, methanol, ethanol, electricity, and cH_2 can be found in Figure 4. "Central Plant Cost" includes the central production costs and "Fuel Station Cost" includes transportation from the central plant (when applicable), capital, operation and maintenance, and energy costs of the local fueling station. The gasoline and diesel central plant costs are based on the EIA 2010 projection of crude oil price and historical wholesale gasoline to wholesale crude price ratios. The ethanol central plant cost is based on a USDA benchmark survey of wet and dry mill corn ethanol plants and our internal estimates for new dry mill capital costs. The methanol central plant cost is based on internal estimates and previous analysis. All central plant options assume 50 miles transportation distance to the local fueling station.

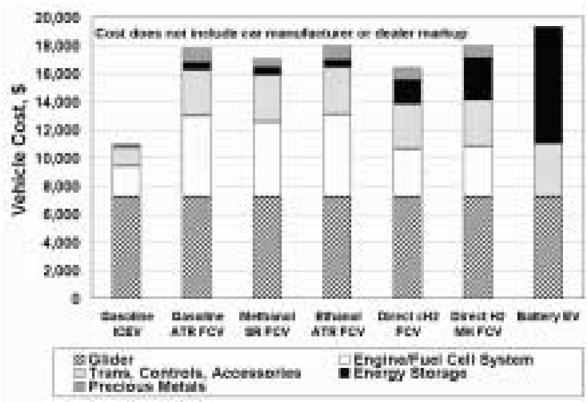

Figure 6: Vehicle Capital Costs for Various Vehicles

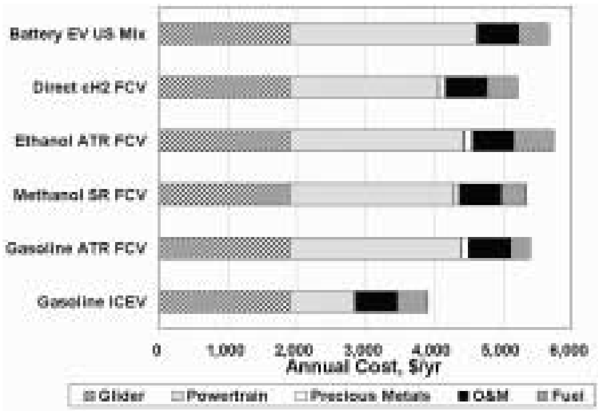

Figure 7: Vehicle Ownership Costs for Various Vehicles

Costs include margins but exclude taxes. Fuel prices for a variety of hydrogen options are shown in Figure 5. Hydrogen fueling station capital costs are based on detailed vendor quotes for equipment, which we have adjusted for higher production volumes. Assumed capital recovery factors for fueling stations and central plants are 11% and 17%, respectively. The EIA Annual Energy Outlook projected 2010 electricity and natural gas prices are used to calculate fuel and power cost inputs to the central plant and local fueling station. The natural gas and electricity costs for the local fueling stations are assumed to be $5/MMBtu and $0.07/kWh, respectively, based on the EIA projection for commercial rates. All fueling stations assume 275,000 scfd hydrogen capacity (~300 vehicles/day) integrated into existing gasoline fueling stations.

Preliminary vehicle factory cost estimates are presented in Figure 6. FCV costs are based on stretch goals for fuel cell system performance and assume high automotive production volume (500,000 units/year) manufacturing. The results presented separate the cost of the precious metals in the fuel cell and reformer (when applicable). These precious metals will likely have 80-90% salvage value at the end of the vehicle life. ICEV costs are based on conventional vehicles. All vehicles assume the same mid-sized vehicle platform with 350 mile range except for the EV, which has only a 120 mile range. Figure 7 shows vehicle ownership costs on a $/year basis. The analysis assumes 14,000 miles/yr of driving, 4% APR interest rate, 5 years finance period, and 39% residual vehicle value at the end of the 5 year finance period for all vehicles. The precious metal content is assumed to have an 85% salvage value. Fuel costs are estimated based on calculated vehicle fuel economies and fuel prices before taxes. The fuel price for hydrogen vehicles assumes $20/GJ. Operation and maintenance (O&M) costs assume 5,000 hour fuel cell stack life. O&M costs have not been analyzed in detail and are assumed to be essentially the same for all vehicles.

Well-to-wheel emissions data is not presented but will be included in the final report. The safety issues analysis is currently under review and results are not presented here.

Conclusions

Although some of the analyses are still under review, some key conclusions can already be drawn:

Drivetrain Efficiency Assumptions (Figure 1):

- Partial load efficiency is a major contributor to overall well-to-tank energy use because the vehicle spends most of its time at partial load.
- Reformer-based drivetrains have much lower efficiency at partial load due to heat losses and other inefficiencies in the reformer.
- High turn-down or other operating strategies that improve the minimum load efficiency are essential to the performance of reformer-based vehicles.

Well-to-Wheel Energy Use Results (Figures 2 and 3):

- Fuel cell powertrains are expected to be able to achieve the lowest well-to-wheels energy consumption, provided efficient fuel chains are used.

- Direct-hydrogen FCVs carrying compressed hydrogen produced from natural gas can offer well-to-wheels energy consumption of approximately half of conventional gasoline-fueled vehicles: an unparalleled well-to-wheels efficiency.
- This high efficiency for direct-hydrogen FCVs is due to high continuous power efficiency and excellent turn-down performance.
- Achieving this high efficiency is possible with hydrogen production from natural gas, provided that:
    - hydrogen production facilities are thermally well-integrated,
    - high vehicle fuel economy can be attained, and
    - transportation distances are modest (50 miles or less) for centralized production.
- If hydrogen for FCVs is produced via electrolysis, or hydrogen is liquefied in the fuel chain, well-to-wheels energy use of those FCVs is expected to be worse than that of vehicles based on other advanced powertrains. The electrolysis option would almost double primary energy use compared with conventional vehicles.
- Gasoline-fueled FCVs (with on-board reformer) are expected to achieve a 40% lower well-to-wheels energy consumption than conventional vehicles.
- The use of methanol in fuel cell vehicles leads to a considerably higher well-to-wheels energy consumption, despite the high vehicle efficiency, due to the significant losses incurred in fuel production. However, the use of methanol simplifies on-board fuel processing.
- The inefficiency of ethanol production leads to well-to-wheels primary energy consumption for ethanol FCVs slightly above that of conventional vehicles. Primary fossil fuel consumption is, of course, strongly reduced.
- Diesel HEVs can also approach a 40% reduction in well-to-wheels energy consumption over conventional vehicles.
- EV "fuel" chains have high energy consumption due to the relative inefficiency of power generation, resulting in a well-to-wheels energy consumption roughly the same as that of conventional vehicles.

Fuel Cost Results (Figures 4 and 5):

- The most economical hydrogen fuel chains are expected to be two to three times more expensive than gasoline, on a $/GJ basis.
    - Hydrogen capital costs are four to seven times more expensive than gasoline capital costs (including local fueling station and central plant capital).
    - Transportation and distribution costs (including on-site compression and storage for distributed production) are far higher than those for gasoline.
- Ethanol production and distribution in high volume is slightly less expensive than hydrogen from natural gas with the assumptions used in this study; however, these results depend strongly on natural gas prices and ethanol production costs.
- Future methanol price projections are close to gasoline prices on a $/GJ basis, assuming large-scale fuel-methanol plants will be built in regions with remote or stranded natural gas.
- Electrolyzer-based production is costly with EIA energy price projections. Scenarios for load shifting and power price reductions were not analyzed here.
- Some alternative fuels, especially hydrogen, will require a significant upfront investment, representing a risk to both vehicle manufacturer and fuel provider stakeholders. Dealing with this risk represents a formidable barrier to the use of hydrogen for FCVs.

Vehicle Cost Results (Figures 6 and 7):

- Even including the technology improvements over current FCV technology, FCVs are expected to add several thousand dollars to conventional ICE powertrain cost.

- Powertrain costs for direct-hydrogen FCVs are lower than those of systems with on-board reformers:
    - Fuel processors add cost directly.
    - Weight of fuel processors increases power requirements to achieve desired performance, thus increasing powerunit capacity.
    - Reformer-based system fuel cell stack cost is higher due to reformate quality effects.
- Direct-hydrogen FCV cost could be further reduced if cost were optimized such that efficiency dropped to provide equal well-to-wheels primary energy consumption to gasoline FCVs.
- Higher vehicle costs for gasoline reformer based FCVs make them more expensive despite fuel cost savings. However, fuel costs have a significant impact on consumer opinion.
- Substantial additional technology breakthroughs will be required to achieve FCV cost competitiveness with ICEVs.
- Fuel economy results and cost results are based on aggressive technology goals for hydrogen storage, fuel cell, and reformer power density, cost, and performance.

D. 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

B. Impact of Specific Fuel Constituents and Impurities on Fuel Processor/Fuel Cell Systems

Tasks

3. Evaluate Effects of Candidate Fuels on Fuel Processor

Objectives

- Identify the effects of major constituents, additives, and impurities of petroleum-based fuels on reformer performance.
- Evaluate the effects of fuel constituents and impurities on catalyst stability.
- Collaborate with major oil companies for development of future fuels for fuel cells.

Approach

- Investigate autothermal reforming of fuels and fuel constituents in microreactor. Rate performance based on byproduct formation, catalyst deactivation, and dependence of hydrogen yield and conversion efficiency on temperature and residence time.
- Begin tests with major constituents of gasoline, then test selected minor constituents, additives, and impurities by mixing with iso-octane.
- Test blends of fuel components to establish a composition/performance relationship matrix.
- 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 major gasoline components
- Made recommendations to DOE on benchmark fuel compositions
- Completed long-term tests on iso-octane and two benchmark fuels, one without sulfur, one with sulfur
- Completed long-term testing of four reforming catalysts with benchmark fuels
- Determined that fuels with high aromatic content can be reformed for long periods (1000 h) with no adverse effects.
- Determined effects of sulfur on reforming catalyst performance are dependent on the catalyst
- Determined that Pt/Ceria catalysts are sulfur tolerant

- Determined that sulfur promotes coking on Co/Ceria catalysts

Future Directions

- Continue investigating effects of additives (detergents, antioxidants) and impurities
- Continue investigating reforming of blended fuels, determine composition/performance relationships from results
- Investigate differences in fuel reforming with different catalysts
- Make recommendations for fuel cell fuels

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 and blends of gasoline streams under autothermal reforming conditions.

Prior work focused on the autothermal reforming of some of the major constituents of gasoline. We investigated the autothermal reforming of iso-octane, n-octane, octane, trimethylbenzene, toluene, methylcyclohexane, and methylcyclopentane. These chemicals represent the branched paraffins, straight chain paraffins, olefins, aromatics, and cyclic paraffins present in gasoline. We observed that trimethylbenzene required more severe reforming conditions than the other components [1]. The current work has focused on the effects of blends of components and on the effects of sulfur impurities. Blends are being investigated to determine if the presence of some components can affect the reforming of others. Sulfur is of concern due to its propensity to poison catalysts.

Approach

Reforming of the fuel blends is 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 fuels. Short term (<20h) tests are performed in a reactor containing ~2g of catalyst. The fuel and water are vaporized, then mixed and sent to the reactor where oxygen is added. Four sampling ports allow for testing at various positions (and space velocities) 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.

Long-term tests (> 1000 h) are performed in a separate reactor equipped with a solid state on-line hydrogen sensor and infrared carbon monoxide and carbon dioxide detectors. Batch sampling can be performed at the exit stream. This system allows us 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

Testing blended fuels/mixtures

We have investigated the effects of reforming several fuel blends and refinery streams as well as mixtures of iso-octane and xylene to try to determine if there are synergistic or inhibitory effects from mixing the different components. As expected, aromatic fuel streams with high (>90%) aromatic content reformed poorly at low temperatures. In addition, blended streams that contained aromatics at about the 20% level provided lower hydrogen yields than paraffinic fuels at 750°C. Results from some of these tests are shown in Figure 1. We also observed that when aromatics were present the kinetics of C4

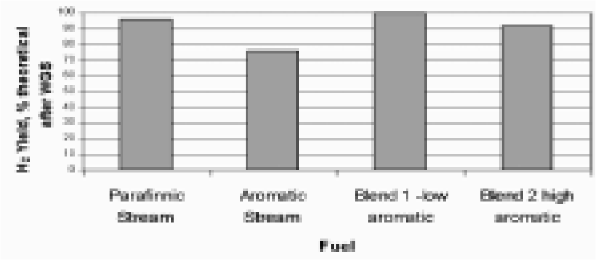

Figure 1. Hydrogen Yield from Different Fuels at 750°C and GHSV of 15000 Showing Lower Hydrogen Yields for Fuels with High Aromatic Content

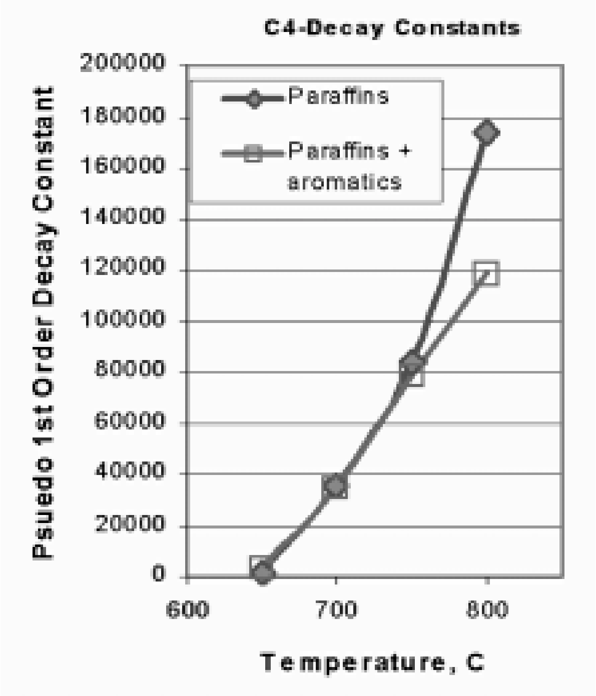

Figure 2. C4 Decay Constants as a Function of Temperature for a Paraffinic Fuel and a Paraffinic Fuel with 20 wt% Aromatics Added

decay was decreased (C4 species are the main thermolysis product from isooctane). This is illustrated in Figure 2, which plots the butane decay constants determined for a paraffinic fuel and a paraffinic fuel with 20 wt% aromatics. This is similar to the inhibiting effects observed in combustion studies [2,3].

Effect of Sulfur

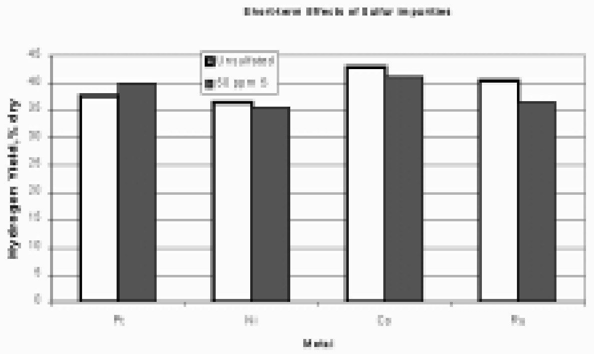

Figure 3. Comparison of Hydrogen Yield from Reforming Iso-octane and Iso-octane + 50 wppm S over Several Different Catalysts (T=800°C, GHSV 15,000 h^{-1})

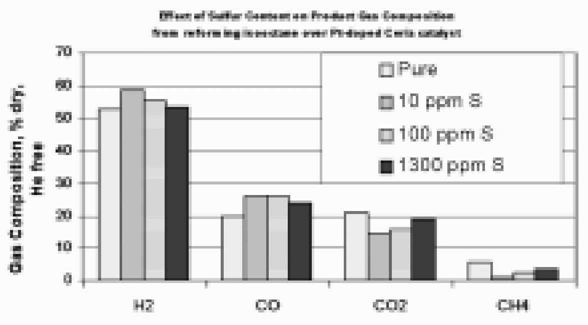

Figure 4. Effect of Sulfur Concentration on Reforming of Iso-octane over Pt-Ceria Catalysts (T=800°C, GHSV 15,000 h^{-1})

The effect of sulfur impurities on iso-octane reforming was determined by reforming iso-octane doped with benzothiophene to provide solutions with 50 wppm sulfur. The effect on hydrogen yield at a gas hourly space velocity (GHSV) of 15,000 and a temperature of 800°C is shown in Figure 3. Hydrogen yields dropped for Ni, Co and Ru doped ceria catalysts, but increased for the Pt doped ceria catalyst. This suggests that sulfur is detrimental to reforming over Ni, Co and Ru catalysts, but that the Pt catalyst appears to benefit slightly from S. To investigate this effect further, isooctane solutions doped with benzothiophene to provide S levels of 0, 10, 100, and 1000 wppm were investigated. The product gas composition for reforming these solutions at 800°C and a GHSV of 15,000 is shown in Figure 4. The hydrogen and CO yields increase when going from pure iso-octane to iso-octane + 10 wppm S, but then decrease as the sulfur content is increased to 100 and 1300 wppm. Conversely, the methane and CO_2 levels decrease when the sulfur level is increased from 0 to 10 wppm, then increase as the sulfur level is increased to 100 and 1300 wppm. These tests indicate that the effect of sulfur impurities on reforming depends on the catalyst, and

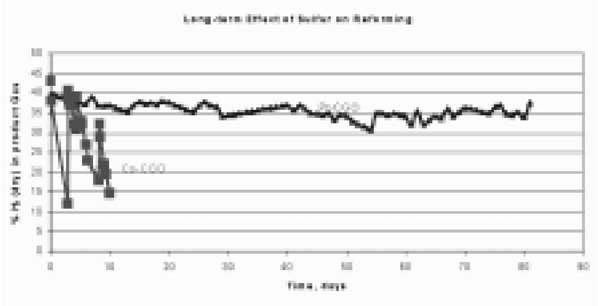

Figure 5. Long-term Effects of Reforming Fuel with 50 wppm S over Pt-Ceria and Co-Ceria Catalysts (GHSV 5,200 h^{-1})

can vary from a negative effect for Ni, Co, and Ru catalysts to a positive effect for the Pt catalyst. With the Pt catalyst, the effect of sulfur impurities is also dependent on the sulfur content of the fuel.

Long-term tests were also performed to determine the long-term effect of sulfur on reforming. The fuel for these tests was the benchmark fuel (74 wt% iso-octane, 20 wt% xylenes, 5 wt% methylcyclohexane, 1 wt% pentene) doped with benzothiophene to provide 50 wppm S. Results for reforming over Pt-doped ceria and Co-doped ceria are shown in Figure 5. The Co catalyst activity decreased rapidly. The catalyst was regenerated and the test resumed, however activity again died off. After several regeneration-reaction cycles the original activity could no longer be achieved and the test was stopped. In contrast, the Pt catalyst activity remained high throughout the test, and degradation over the length of the test was similar to that for sulfur-free fuel.

Post-test examination of the Co catalyst revealed extensive coke formation, with carbon levels of 10-14 wt% on the catalyst. A microscopic examination revealed the formation of carbon throughout the catalyst and the formation of carbon fibers extending into the void regions. However, very little sulfur was found on the catalyst (< 50 wppm S). These tests suggest that sulfur promotes coking on the Co-doped ceria catalysts.

Conclusions

Fuel composition can have a large effect on reforming behavior. Fuels with high aromatic content were more difficult to reform. Aromatics were also found to have an impact on the kinetics for reforming of paraffins. The effects of sulfur impurities were dependent on the catalyst. Sulfur was detrimental for Ni, Co and Ru catalysts. Sulfur was beneficial for reforming with Pt catalysts; however, the effect was dependent on the sulfur concentration.

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E. Testing of Fuels in Fuel Cell Reformers

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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

A. Impact of Fuel Properties on Fuel Processor Performance

Tasks

4. Test Fuels in Fuel Processors and Fuel Cell Stack Systems

Objectives

- Explore effects of fuels, fuel components and fuel impurities on the performance of hydrogen generation technologies
  - Quantify fuel effects on fuel processor performance
  - Quantify fuel and fuel impurity effects on catalyst durability
  - Understand the parameters that affect fuel processor lifetime and durability

Approach

- Examine fuel effects on fuel processing
  - Examine individual fuel components
  - Examine fuel component blends
  - Examine ‘real’ fuels
- FY 2001: Concentrate on the fuel effects on:
  - Carbon formation
  - Gas phase vs. catalytic oxidation
  - Catalyst performance and degradation
- Model fuel reforming chemistry
  - Model carbon formation
  - Model equilibrium gas composition
  - Model thermodynamic properties

Accomplishments

- Tested iso-octane, iso-octane/xylene, naphtha, reformulated gasoline, diesel fuel components
- Examined fuels effects with:
    - Homogeneous partial oxidation
    - Catalytic oxidation
    - Measurement of fuel oxidation kinetics and conversion
    - Diesel fuel components (dodecane, hexadecane)
- Observed carbon formation during experiments
    - Used *in situ* laser diagnostics to monitor carbon formation
    - Visually monitored carbon formation
- Modeled fuel and fuel component chemistry
    - Carbon formation conditions
    - Equilibrium gas compositions
    - Thermodynamic properties of fuel mixtures

Future Directions

- Evaluate effects of fuel constituents on fuel processor operation:
    - Monitor carbon formation
        - Measure carbon formation *in situ* with an adiabatic reactor and laser scattering
        - Map carbon formation onset for component/component blends as a function of operating conditions
        - Delineate carbon formation mechanisms
        - Measure carbon effect on reforming and oxidation kinetics
        - Measure carbon formation during start-up and reactor transients
        - Measure carbon formation kinetics
        - Define catalyst requirements for durability
    - Measure fuel impurity effects
        - Measure effects of bound nitrogen compounds
        - Define partial oxidation/steam reforming nitrogen conversion products
        - Measure sulfur effect on carbon formation
    - Determine fuel additive effects on fuel processing
        - Anti-oxidants
        - Fuel detergents
        - Oxygenated hydrocarbons
- Integrate fuel cell stack testing with fuel processor operation to evaluate system integration effects of fuels

Introduction

This report describes our FY01 technical progress in examining the effects of fuel on hydrogen generation technology. The technology under study is designed to produce hydrogen for polymer electrolyte membrane (PEM) fuel cells for transportation. The goal of this research is to explore the effects of 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 using a reformed hydrocarbon fuel.

Different fuels have been tested to observe their relative reforming characteristics with various operating conditions. Both catalytic and homogeneous fuel processor partial oxidation stages were used in the tests of pure fuel components and mixtures such as iso-octane and iso-octane/xylene, and real fuels such as a hydro-treated naphtha and reformulated gasoline. Carbon formation was monitored during operation by *in situ* laser measurements of the effluent reformate and visual observations of the reactor.

Approach

To examine the fuels' effects on hydrogen production devices, various fuel components and real fuels have been tested in fuel reformers. These fuels have been tested in catalytic partial oxidation and steam reforming reactors, and in non-catalytic (homogeneous) partial oxidation/steam reformers. Homogeneous partial oxidation has a potential advantage for meeting DOE start-up targets, as homogeneous partial oxidation does not require preheating before light-off of the reactor. This reactor was added to existing test facilities in FY2001, and is shown in Figure 1.

In situ laser measurement of the effluent reformate and visual observation of the reactor catalyst during operation have been developed and used in this work to monitor carbon formation during operation. The relative distribution of the catalytic conversion has been observed with various fuel components with different catalyst substrates (monoliths and reticulated foams). Mapping of the onset of carbon formation for different fuel components as a function of operating conditions has been initiated with these techniques. The reactor with catalyst observation windows, laser extinction, and scattering facilities is shown in Figure 2.

Figure 1. Homogeneous Partial Oxidation/Catalytic Steam Reforming System

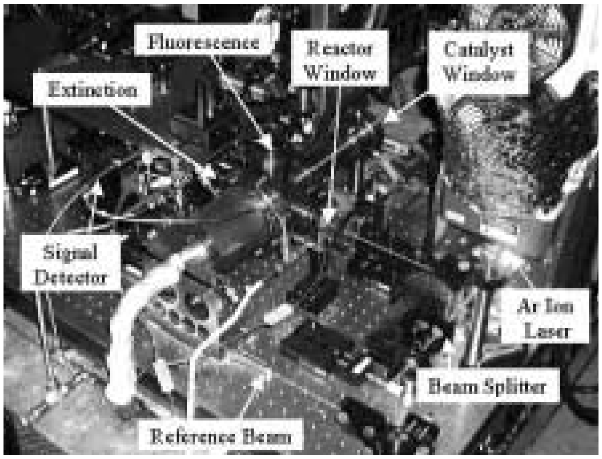

Figure 2. Catalytic Partial Oxidation with Facilities for Laser Extinction and Scattering Measurements with Catalyst Observation

Expected outlet concentrations of the fuel reformer, and the relative fuel component effects on the fuel reformer outlet have been modeled. In particular, modeling of equilibrium carbon formation has been used to predict the operating conditions for the onset of carbon formation for various fuel blends. The thermodynamic properties of fuel components have been calculated and modeled to create blends of pure fuel components that simulate gasoline with a minimal number of chemical components.

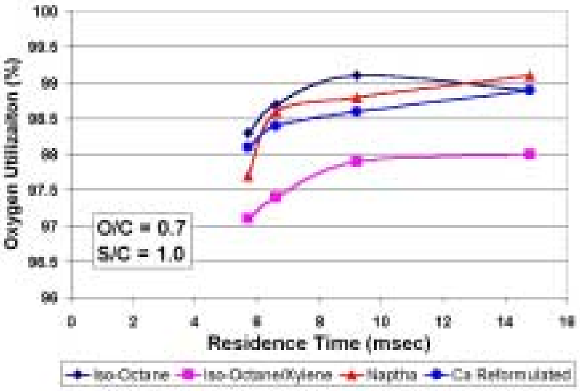

Figure 3. Catalytic Partial Oxidation Fuel Effects at O/C = 0.7 with Varying Residence Times

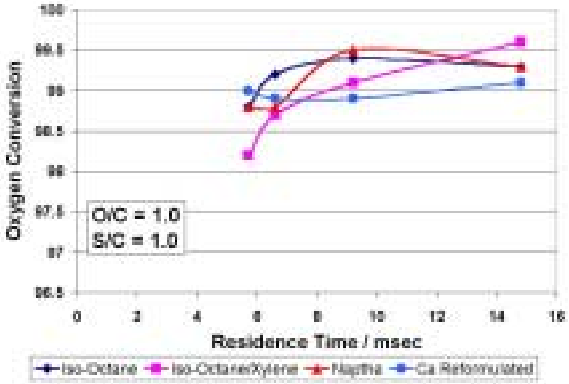

Figure 4. Catalytic Partial Oxidation Fuel Effects at O/C = 1.0 with Varying Residence Times

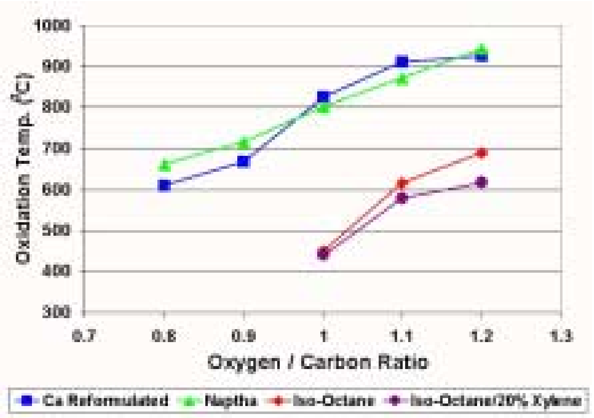

Figure 5. Homogeneous Partial Oxidation Outlet Temperature for Various Fuels with Varying O/C

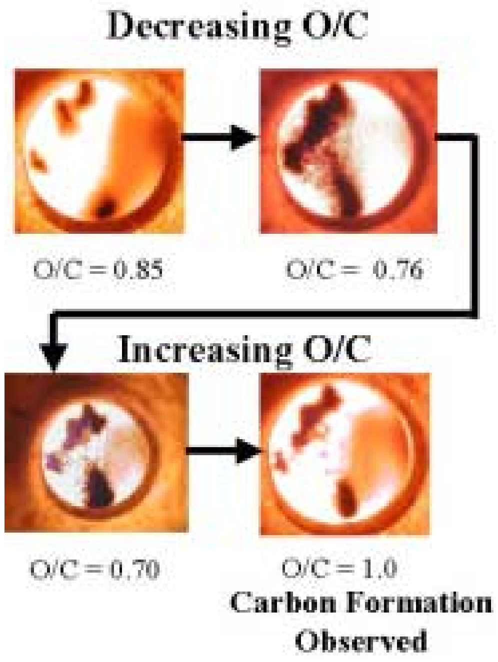

Figure 6. Visual Observation of Partial Oxidation Catalyst Showing the Initiation and Hysteresis of Carbon Formation

Results

Fuel Effects Comparisons of Homogeneous and Catalytic Partial Oxidation

Fuel effects on the relative rates of the catalytic partial oxidation reaction for different fuels have been measured. Figure 3 shows relative oxygen conversion as a function of residence time at an O/C = 0.7 for iso-octane, iso-octane/xylene, reformulated gasoline, and hydro-treated naphtha. As the reactor residence time decreases the relative conversion decreases for all of the different fuels tested; however, the addition of aromatic compounds to iso-octane decreases the relative conversion at all residence times. At a higher relative oxygen content, O/C = 1.0, the fuel component effect on conversion is decreased as evidenced by Figure 4.

The fuel components and impurities help define the amount of noble metal that is required for the partial oxidation/steam reforming reactor. Sulfur has been observed to poison nickel steam reforming catalysts, whereas sulfur-free fuels may be reformed over nickel.[1] The addition of aromatic compounds decreases the relative conversion, thus increasing the need for additional noble metal loading. The results from the catalytic partial oxidation reactor indicate that for about a 50 kWe equivalent fuel production, about 2 g Pt is required if sulfur-free aliphatic hydrocarbons are used. However, with aromatic fuel addition, this increases by almost a factor of 2.

The partial oxidation conversion for different fuels in a reactor with non-catalytic partial oxidation and catalytic steam reforming sections is shown in Figure 5. The results for homogeneous oxidation are significantly different than those for catalytic oxidation as the homogeneous reactor can operate with 'real' fuels achieving full conversion at lower O/C ratios. With the pure components the homogeneous oxidation could not fully convert the fuel, and the reactor temperature was drastically decreased. For full fuel conversion with the pure components, the required O/C ratio was > 1.0.

Carbon Formation

Figure 6 is a series of digital images of the outlet of the partial oxidation reactor during operation with hydro-treated naphtha fuel. As the O/C carbon ratio is decreased, carbon formation initiates at a relatively cool portion of the catalyst monolith, at an O/C ratio of 0.7. As the O/C ratio is increased, carbon formation continues, even though the operating conditions are repeated where it was not previously observed.

Laser extinction measurements have also been conducted to observe carbon formation. An example of this is shown in Figure 7. As the O/C carbon ratio is decreased, the outlet temperature (T19) decreases, and as the outlet temperature reaches approximately 620°C, an increase in laser absorbance is measured, indicating the onset of carbon formation. Laser scattering measurements are being initiated to provide greater sensitivity in the measurement of carbon formation.

Figure 8 shows the results of modeling the onset of carbon formation for different fuels and operating conditions to compare with the experimental measurements. Diesel fuel components show higher temperatures are required to prevent carbon formation, with relative S/C ratio having a dramatic impact on the carbon formation temperature.

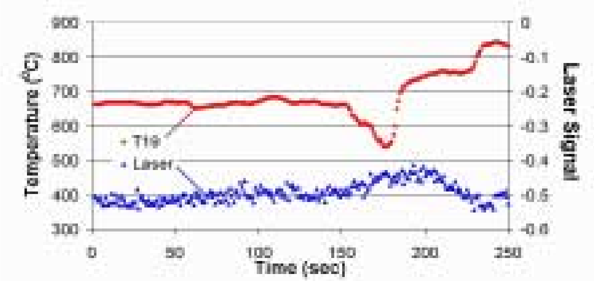

Figure 7. Extinction Laser Signal Showing Carbon Formation as Partial Oxidation O/C Ratio is Decreased (as observed by decreasing temperature)

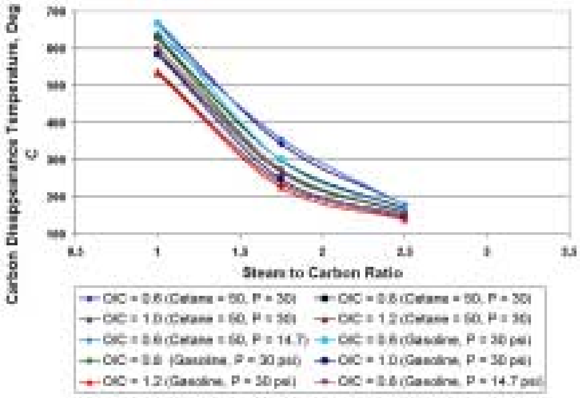

Figure 8. Equilibrium Modeling of Carbon Formation for Various Fuels and Conditions

Conclusions

Various fuel components and fuels have been tested with various O/C and S/C ratios in both catalytic and homogeneous partial oxidation reactors. Homogeneous oxidation occurs easier with 'real' fuels than with the pure components of iso-octane and iso-octane/xylene. The addition of aromatics slows the overall reaction rate for catalytic oxidation. Diesel fuel components (such as dodecane) require higher residence times for similar conversions. The fuel composition, especially sulfur content and aromatic content, affects the relative amount of noble metal required for the fuel reformer. Modeling has shown that fuel effects on the temperature for equilibrium onset of carbon formation can vary up to 150°C with varying O/C ratios. Carbon formation has been observed to occur with hysteresis.

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F. Standard Hydrocarbon Fuel for Fuel Cell Vehicles

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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

D. Advanced Fuel Production, Specifications, and Costs

Tasks

3. Evaluate Effects of Candidate Fuels on Fuel Processor

Objectives

- The objective of this project is to determine the specifications for a fuel cell reference fuel which can be used to quantify the performance of different fuel processors.

Approach

- Specify a mixture (blend) of a small number of individual hydrocarbons and some of the typical gasoline additives.
- Test the benchmark fuel in the Argonne National Laboratory (ANL) auto-thermal reformer (ATR) to characterize its performance.

Accomplishments

- Specifications for a benchmark fuel (Fuel I) have been developed.
- The composition/formulation of Benchmark Fuel I has been provided to several organizations that are developing automotive fuel processors.

Future Directions

- This project has been carried to completion to support the currently planned fuel reformer and fuels characterization R&D at ANL. Other fuel constituents can be added to the fuel specification to support future work as needed.

Introduction

California reformulated gasoline (C-RFG) has been identified as one fuel to be used in fuel cell systems to be developed under DOE sponsorship. However, there are considerable variations in the composition of C-RFG from one batch to the next. Another option is to use the certified gasoline provided by Phillips Petroleum Company for emissions certification of new vehicles in fuel reformer development. A third alternative is to specify a mixture (blend) of a small number of individual hydrocarbons and some of the typical gasoline additives. This blend could then be prepared by any of the fuel processor or fuel cell system developers as and when needed. A preliminary selection of a Benchmark Fuel I has been developed and is being used in Argonne fuel processing R&D. The formulation has also been provided to others developing fuel processors for transportation applications. Specifications for additional benchmark fuels can be developed as needed.

Approach

Our approach involved a literature survey of gasoline formulations, detailed analyses of selected samples of retail gasoline, consultations with major energy suppliers, and modeling and experimental work. Experimental studies were conducted in a microreactor system to validate the predicted operating parameters.

Results

Based on discussions with suppliers, a survey of the literature, and detailed chemical analyses of selected samples of retail gasoline, the most representative components of current gasoline blends were selected in the percentage amounts shown in Table 1 to define the Benchmark Fuel I.

To represent the sulfur anticipated to be present in future grades of reformulated gasoline, benzothiphene may be added to provide 50 ppm (by weight) of sulfur.

An example of the initial reformate produced by the autothermal reforming of Benchmark Fuel I using a commercial formulation of the Argonne-developed catalyst is shown in Figure 1. The test was begun with sulfur-free Benchmark Fuel I. After 115 h, the fuel was switched to sulfur-containing Benchmark Fuel I. The data show the reformability (product gas composition) of the sulfur-free and sulfur-containing fuels to be comparable.

Conclusions

Benchmark Fuel I was developed to be representative of future reformulated gasoline using widely available hydrocarbons. This fuel specification can be reproduced in any laboratory, and the results for reforming this fuel can be compared to determine the difference attributable to the process and not the input fuel. Further development of a standard fuel can be undertaken as needed in the future to accommodate further refinements in fuel cell component development objectives.

Component	Wt% in Benchmark Fuel I
Iso-octane	74
Xylenes	20
Methylcyclohexane	5
n-pentene	1

Table 1. Benchmark Fuel I Composition

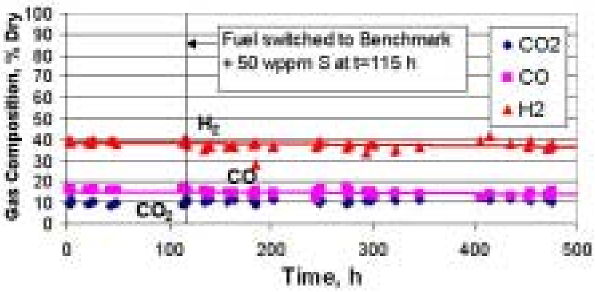

Figure 1. Long-term Test of Commercial Autothermal Reforming Catalyst with Benchmark FuelI without and with 50 wppm S

G. Sulfur Removal from Reformate

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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

B. Impact of Specific Fuel Constituents and Impurities on Fuel Processor/Fuel Cell Systems

Tasks

3. Evaluate Effects of Candidate Fuels on Fuel Processor

Objectives

- Adapt proven technologies for on-board fuel processing capable of reducing the H_2S concentration to <1 ppm in reformate.
- Develop new technologies or improve existing technologies to meet the following DOE targets for H_2S removal: (1) H_2S concentration of <0.1 ppm in reformate, (2) a reactor size of <0.06 L/kWe (<0.06 kg/kWe), and (3) gas hourly space velocity (GHSV) of 50,000 h^{-1}.

Approach

- Perform thermodynamic calculations to predict the H_2S equilibrium partial pressure for candidate adsorbents (metal sulfide-H_2S equilibrium) and identify candidate materials.
- Complete reaction modeling to estimate the operating parameters for a sulfur removal unit based on adsorption.
- Conduct experimental studies in a microreactor system to determine design parameters (e.g., sulfur loading capacity, rate of reaction) as a function of operating parameters (e.g., temperature, GHSV, water content in reformate).

Accomplishments

- ZnO-coated monoliths were fabricated by Sud-Chemie.
- Evaluated the performance of the ZnO-coated monoliths, demonstrating that the H_2S concentration can be reduced to ~1 ppm under fuel processing conditions.
- Concluded that a sulfur removal process based solely on ZnO will not meet the DOE targets for on-board sulfur removal.
- Identified new classes of compounds that may be capable of meeting the DOE target for the H_2S concentration in reformate.

Future Directions

- Improve the mechanical stability of the ZnO microchannel and evaluate its performance.
- Screen CuO/MnO and CuO/MoO sorbents for use in fuel processing.
- Conduct feasibility studies of non-adsorption technologies such as membrane separations and chemical processing for removing sulfur from reformate in the fuel processor.
- Evaluate sulfur tolerance of new water-gas shift and POx catalysts.

Introduction

With the new lower sulfur content of 30 ppm average and 80 ppm maximum (by weight) proposed for gasolines in FY 2006, reformate produced by autothermal reforming of these gasolines will contain 3-8 ppm of H_2S. Even at this low concentration, H_2S is known to poison many of the catalysts being developed for use in the fuel processor for polymer electrolyte membrane fuel cell (PEMFC) systems. For example, an H_2S concentration of <50 ppb is recommended for copper-zinc oxide water-gas shift catalysts. Further, the Pt-anode catalyst in the PEMFC is irreversibly poisoned at an H_2S concentration as low as 200 ppb.[1]

In earlier work, 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 should be capable of reducing the concentration of H_2S to <1 ppm and which do not promote any undesirable side reactions under fuel processing conditions. Zinc oxide was selected as the initial candidate sorbent. We concluded that a thin ZnO layer (~50-100 μm) supported on a structured form, such as a monolith or microchannel, would be better suited for transportation applications than the commercial pellet form of ZnO, resulting in a significant reduction in the weight of the sulfur removal unit while providing better mechanical stability.

Approach

Our approach involves both modeling and experimental work. Thermodynamic equilibrium calculations and non-catalytic gas-solid reaction models, such as the shrinking core model, are used to design the sulfur removal unit and to determine the optimal operating parameters (e.g., temperature, space velocity, bed lifetime) for ZnO. Experimental studies are conducted in a microreactor system to validate the predicted operating parameters.

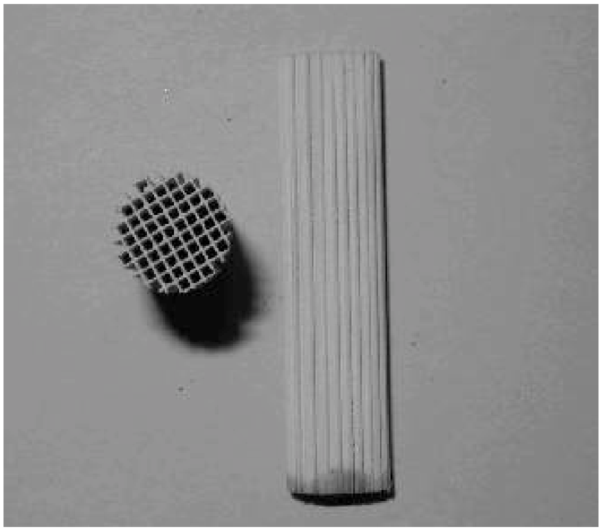

Figure 1. Core Sample of a ZnO-Coated Cordierite Monolith Produced by Sud-Chemie, Inc.

Based on such modeling, a thin ZnO layer (~50-100 μm) supported on a structured form, such as a monolith or a microchannel configuration, is predicted to provide a higher reactive surface area per unit volume and to be more efficient than a pellet form for removing H_2S from reformate in a fuel processor. To test these conclusions, a cordierite monolith was coated with a thin ZnO layer by Sud-Chemie, Inc. The monolith was cored to provide smaller diameter samples for testing in our microreactor system (see Figure 1). The samples were evaluated by exposing them to simulated reformates containing 10-100 ppm H_2S at various temperatures, space velocities, and water vapor content. The removal efficacy was determined by measuring the H_2S concentration in the effluent stream (using gas chromatography) as a function of the H_2S and H_2O concentration in the inlet stream, temperature, and gas hourly space velocity.

Results

Based on thermodynamic calculations, ZnO should be able to reduce the H_2S concentration to ≤1 ppm in reformate containing ≤0.35 atm of H_2O at an operating temperature of ≤400°C (see Figure 2). To meet the more stringent DOE FY 2008 target of 0.1 ppm H_2S, the ZnO sorbent would need to operate at a temperature of ≤300°C.

Experimental testing of the core samples from the ZnO monolith indicated that high operating temperatures are required to overcome the slow reaction rate

$$H_2S + ZnO \leftrightarrow ZnS + H_2O$$

and that equilibrium concentrations of H_2S can not be achieved when operating at ≤400°C, even at a GHSV as low as 1000 h^{-1} (see Figure 3). For simulated reformate containing 19 ppm H_2S and 0.18 atm H_2O, an H_2S concentration of 1-2 ppm was measured in the effluent after contacting the ZnO-coated monolith at 480°C and a GHSV of ≤2000 h^{-1}. When the temperature was decreased to 280°C, the H_2S concentration increased to 4-5 ppm, in contrast to the thermodynamic equilibrium value of ~60 ppb. A comparison of the residual H_2S concentration for a dry and a wet (0.18 atm) reformate, both containing 19 ppm H_2S, shows that the H_2S concentration increases nearly linearly with increasing GHSV above 2000 h^{-1} at 380°C (see Figure 4). This increase in the residual H_2S concentration with increasing GHSV is most likely due to "breakthrough" as a consequence of the laminar flow in the flow channels of the monolith.

Conclusions

ZnO offers certain advantages for sulfur removal in fuel processing: it is stable under reformate conditions, it does not need any activation before use, and it does not catalyze any undesirable secondary reactions. Because of the extremely slow reaction kinetics, however, a ZnO-based sulfur

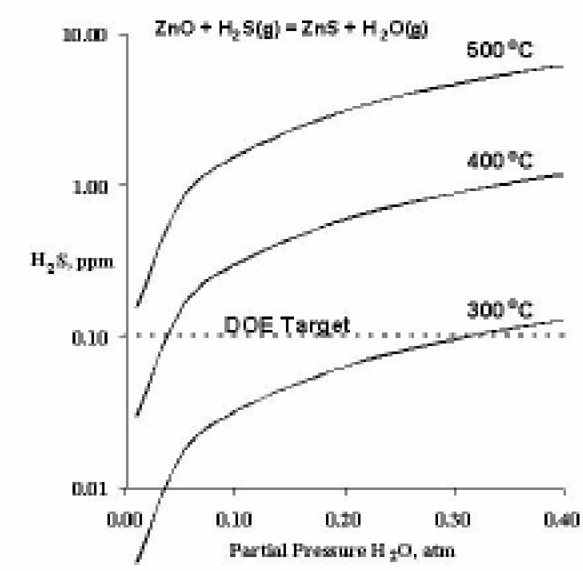

Figure 2. Equilibrium Concentration of H_2S as a Function of the H_2O Partial Pressure in Reformate at Temperatures between 300°C and 500°C

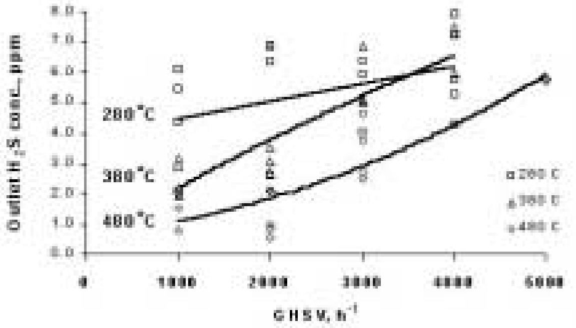

Figure 3. Outlet H_2S Concentration as a Function of GHSV at Various Temperatures for an Inlet H_2S Concentration of 19 ppm and a Water Partial Pressure of 0.18 atm H_2O

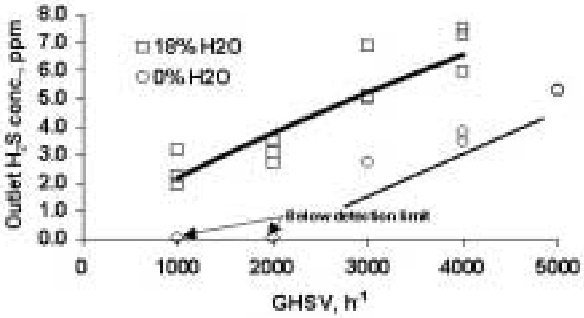

Figure 4. Outlet H_2S Concentration as a Function of GHSV for Two H_2O Partial Pressures (0 atm and 0.18 atm H_2O) at 380°C for an Inlet H_2S Concentration of 19 ppm

removal unit will need to operate at temperatures well above those that are necessary to achieve the target of 0.1 ppm H_2S. Even at the higher temperatures, this structured form of ZnO must be operated at a GHSV considerably lower than the long-term target value of 50,000 h^{-1}.

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VIII. DME FUEL SYSTEM TESTING

A. Exhaust Emissions and Performance of a CIDI Engine Fueled with DME - Phase 3

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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
7. Vehicle Materials Compatibility

Objectives

- Develop a dimethyl ether (DME) fuel injection system for a small CIDI engine
- Demonstrate the exhaust emissions potential of a DME fueled CIDI engine under road loads

Approach

- Phase 1— Design a DME common rail fuel injection system suitable for use on a small CIDI engine, including a variable displacement, high-pressure supply pump to ensure system efficiency (reported previously—not part of this report).
- Phase 2 — Fabricate fuel system; test and develop hardware on a test bench (reported previously—not part of this report).
- Phase 3 — Demonstrate exhaust emissions and performance of the Ford DIATA CIDI engine fueled with DME (using the fuel system developed in previous phases).

Accomplishments

- NO_x emissions were lowered 85-90% (to 0.33 g/kW-hr) compared to the best published diesel results by use of much larger percentages of EGR than is possible with compression-ignition direct injection (CIDI) engines using diesel fuel.
- Smoke was reduced below the level of detection (0.05 Bosch Smoke Number).
- Fuel consumption (energy equivalent) was similar to the diesel baseline

- CO emissions were excessive at very low NO_x levels; an oxidation catalyst is necessary to provide acceptable levels of CO.

Introduction

The potential of dimethyl ether (DME) as an automotive fuel was first reported in 1995[1]. This report showed that very low emissions could be achieved using DME, but that an all-new fuel system would be necessary.

In 1997, AVL Powertrain Technologies began the development of a complete DME fuel system for a small CIDI engine. Ultimately, this program led to the emissions demonstration reported here.

The fuel system that was developed and later demonstrated includes a unique fuel storage tank and delivery system[2], a novel common rail fuel injection system[3], and a highly efficient, variable displacement (inlet throttled) high pressure supply pump[4]. In addition to these hardware developments, significant investigations were made regarding the thermo-chemical properties of DME[5].

Summary of Results

Figure 1 shows the DME fuel injection system installed on the Ford DIATA CIDI engine. This hardware packages well on the engine and is production feasible.

Figure 1. DME Fuel System Installed on Ford DIATA CIDI Engine

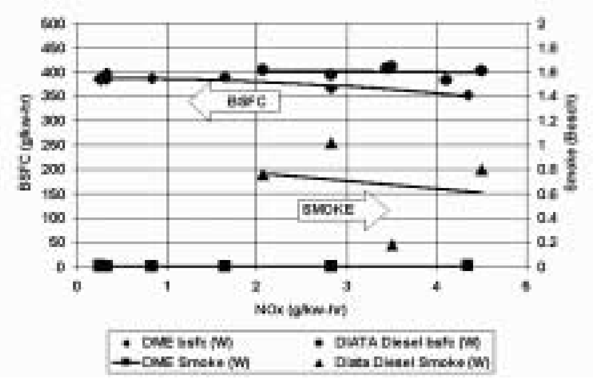

Figure 2. NO_x-BSFC-Smoke Relationship (2000 RPM, 2 Bar BMEP-Optimum Calibration)

Figure 2 compares diesel and DME NO_x emissions, fuel consumption and smoke at 2000 rpm, 2-bar brake mean effective pressure (bmep). As shown, DME achieves an 85% NO_x reduction with similar or lower fuel consumption (energy equivalent). Smoke emissions are reduced below detection limits with the use of DME.

The very low NO_x levels with DME were achieved by using high rates of EGR (~70%). This is not possible using diesel fuel because EGR raises smoke emissions significantly and the allowable smoke limit is reached at 15 to 40% EGR, depending on engine speed and load.

Figure 3 compares NO_x-CO-HC emissions of the diesel baseline and DME at 2000 rpm, 2-bar bmep. CO & HC emissions are similar for both fuels at a given NO_x emission level. When NO_x emissions are lowered to <1 g/kW-hr (1/2 the diesel best), CO

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3. SAE 970220 Development of a Novel Fuel Injection System for DME
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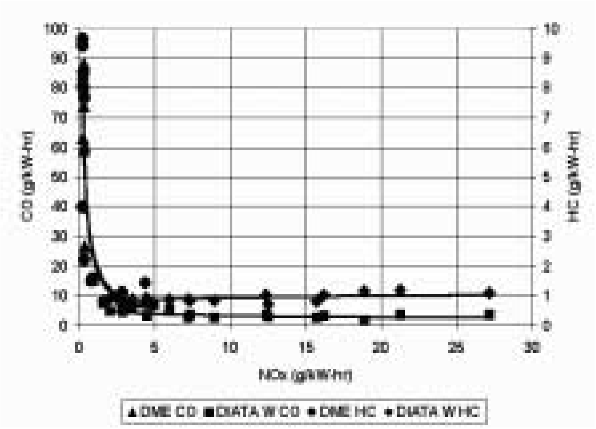

Figure 3. NO_x-CO-HC Characteristics (2000 RPM, 2-bar bmep)

Fuel	**Diesel**	**DME**	**DME**
NO_x (g/kW-hr)	2.06	0.33	0.33
BSFC (g/kW-hr)	404	385	385
CO (g/kW-hr)	4.97	26	2.6
HC (g/kW-hr)	0.89	2.19	0.219
Smoke (Bosch)	0.76	0	0
EGR (%)	40	65-70	65-70
Remarks	Baseline diesel @ smoke limit	DME engine out	Estimated DME + oxidation catalyst

Table 1. 2000 RPM, 2-bar bmep Emissions and Performance Summary

Fuel	**Diesel**	**DME**	**DME**
NO_x (g/kW-hr)	2.12	0.29	0.29
BSFC (g/kW-hr)	332	326	326
CO (g/kW-hr)	8	29.4	2.94
HC (g/kW-hr)	0.60	2.13	0.213
Smoke (Bosch)	0.70	0	0
EGR (%)	32	65-70	65-70
Remarks	Baseline diesel @ smoke limit	DME engine out	Estimated DME + oxidation catalyst

Table 2. 1500 RPM, 2.62-bar bmep Emissions and Performance Summary

emissions increase rapidly. An oxidation catalyst can suppress CO & HC emissions to acceptable levels when NO_x is lowered to ~0.3 g/kW-hr.

Fuel	**Diesel**	**DME**	**DME**
NO_x (g/kW-hr)	4.3	0.42	0.42
BSFC (g/kW-hr)	290	328	328
CO (g/kW-hr)	2.22	18.34	1.83
HC (g/kW-hr)	0.37	2.94	0.29
Smoke (Bosch)	0.79	0	0
EGR (%)	15	65-70	65-70
Remarks	Baseline diesel @ smoke limit	DME engine out	Estimated DME + oxidation catalyst

Table 3. 2300 RPM, 4.2-bar bmep Emissions and Performance Summary

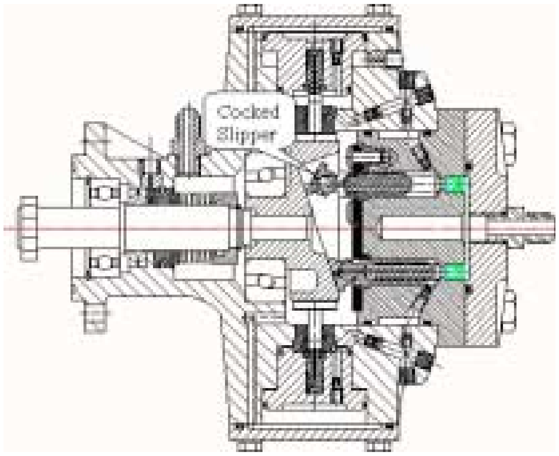

Figure 4. Cross-Section of DME Direct Injection Fuel Pump Illustrating the Plunger Slipper Failure

Tables 1-3 summarize and compare emissions and performance of diesel to those of DME at 3 speeds and loads. DME reduces NO_x emissions 85-90%, eliminates smoke emissions and achieves similar fuel consumption (energy equivalent). Although CO and HC emissions are high at very low levels of NO_x, an efficient oxidation catalyst circumvents this problem.

A fuel pump mechanical failure terminated the test program before all of the desired test data could be run. A plunger slipper separated from the cam face, causing damage to the cam and adjacent plungers (see Figure 4).

Failure analysis showed that the plunger spring force was not sufficient to assure that slippers remain in their proper orientation with the cam under all running conditions. Design changes have been made to increase plunger spring loads and eliminate future similar failures.

Conclusions

- A production feasible DME fuel system has been successfully demonstrated.
- Test results with DME indicate that with additional development, Tier 2 NO_x and particulate emissions might be achieved (though probably only the higher bins) without the use of emission control devices such as particulate traps and NO_x adsorbers.
- DME facilitates much lower NO_x emissions through much higher tolerance of EGR.

APPENDIX A - Acronyms

1-D	One-dimensional
AIChE	American Institute of Chemical Engineers
Al_2O_3	Aluminum oxide
ANL	Argonne National Laboratory
APR	Annual Percentage Rate
atm	Atmospheres
bhp-hr	Brake horsepower-hour
Bmep	Brake mean effective pressure
BSFC	Brake Specific Fuel Consumption
C	Carbon
°C	Degrees Celsius
CARB	California Air Resources Board
CFD	Computational Fluid Dynamics
cfm	Cubic feet per minute
CH_4	Methane
CIDI	Compression Ignition Direct Injection
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide
CRADA	Cooperative Research & Development Agreement
Cu	Copper
CuO	Copper oxide
DECSE	Diesel Emissions Control Sulfur Effects
DI	Direct Injection
DIATA	Direct Injection, Aluminum, Through-bolt Assembly
DOE	Department of Energy
DPF	Diesel Particulate Filter
ECS	Emission Control System
EGR	Exhaust Gas Recirculation
EIA	Energy Information Administration
EPA	Environmental Protection Agency
°F	Degrees Fahrenheit
Fe	Iron
FT	Fischer Tropsch
ft	Foot/feet
FTP	Federal Test Procedure
FY	Fiscal Year
g	Grams
g/GJ	Grams per gigajoule
g/hp-h	Grams per horsepower-hour
GHSV	Gas Hourly Space Velocity
h	Hours
H_2	Diatomic hydrogen
H_2O	Water
HC	Hydrocarbon
HCCI	Homogeneous Charge Compression Ignition
He	Helium
HO_2	Hydroxyl radical
hp	Horsepower
hr	Hour
H_2S	Hydrogen sulfide
ISB	Integrated System B (Cummins diesel engine)
J/deg	Joules per degree
K	Potassium
kg	Kilogram
kW	Kilowatt
kWe	Kilowatt-electric
kWh or kW-hr	Kilowatt-hours
L	Liter
LANL	Los Alamos National Laboratory
LHV	Lower Heating Value
LLNL	Laurence Livermore National Laboratory
MECA	Manufacturers of Emissions Controls Association
mg	Milligram
mi	Mile
MJ/mi	Megajoule per mile
μm	Micron
mm	Millimeter
MMBtu	Million British Thermal Units
MnO	Manganese oxide
Mo	Molybdenum
MoO	Molybdenum oxide
MPa	Megapascals
mph	Miles per hour
Ni	Nickel
Nm	Newton-meters
nm	Nanometers
NO	Nitric oxide
N_2O	Nitrous oxide
NO_x	Oxides of nitrogen
NREL	National Renewable Energy Laboratory
NVOF	Non-Volatile Organic Fraction
O_2	Diatomic oxygen
OAAT	Office of Advanced Automotive Technologies
O/C	Oxygen to carbon ratio
OEM	Original Equipment Manufacturer

OH	Hydroxyl radical
OHVT	Office of Heavy Vehicle Technologies
ORNL	Oak Ridge National Laboratory
OTT	Office of Transportation Technology
PAH	Polycyclic Aromatic Hydrocarbon
Pd	Palladium
PM	Particulate Matter
PEM	Polymer Electrolyte Membrane
POx	Partial oxidation
ppb	Parts per billion
ppm	Parts per million
psia	Pounds per square inch absolute
psig	Pounds per square inch gauge
Pt	Platinum
R&D	Research and Development
RPM	Revolutions Per Minute
Ru	Ruthenium
s	Seconds
S	Sulfur
SAE	Society of Automotive Engineers
S/C	Steam to carbon ratio
scfd	Standard cubic feet per day
SCR	Selective Catalytic Reduction
Si	Silicon
SNL	Sandia National Laboratories
SO_4	Sulfate
SOF	Soluble Organic Fraction
SO_x	Oxides of sulfur
SUV	Sport Utility Vehicle
SwRI	Southwest Research Institute
TDC	Top Dead Center
THC	Total hydrocarbons
US06	EPA high speed/load transient driving cycle
USDA	United States Department of Agriculture
V	Volts
VOC	Volatile organic compound
VOF	Volatile organic fraction
vol%	Percent by volume
WO_3	Tungsten trioxide
wt-% or wt%	Percent by weight
yr	Year
ZnO	Zinc oxide
Zr	Zirconium

APPENDIX B - APBF Technical Targets for CIDI Engines

Table B-1. 2003 Targeted Emissions-Reduction Contributions for the Major Elements of CIDI Engine Power Systems

[For an 80-mpg PNGV-type passenger car (2000 lb)]

	Emissions, g/mile		**Emission reductions, g/mile**		**Percentage reduction**		**Comments**
	NO_x	PM	NO_x	PM	NO_x	PM	
Baseline	0.40	0.04					Scaled from emissions index from current CIDI engines extrapolated to a PNGV-type passenger car
Engine development	0.36	0.04	0.04	0	10	0	Advanced combustion, improved fuel injection, optimum use of EGR
Fuel reformulation[a]	0.36	0.03	0	0.01	0	25	Estimates supported by existing data
Emission control devices	0.07	0.01	0.29	0.02	81[b]	67[b]	Assumes NO_x adsorber and catalyzed soot filter
Targets	0.07	0.01					Targets met

[a] These are emission targets obtained by advanced petroleum-based fuels that must also enable all CIDI engine targets (e.g., durability, emissions, fuel economy penalty) to be met simultaneously.

[b] These are the average percentage reductions needed. It is recognized that the actual percentage reductions will need to be higher to account for deterioration in use and production variability.

Table B-2. Technical Targets for Advanced Petroleum-Based Fuels

Characteristic	**Units**	**2003 Targets**
		80-mpg PNGV-type car
Health effects Unregulated toxics and ultra-fine PM Groundwater contamination potential Health and safety of fuel	(by analysis)	No significant increase in composite risk compared with conventional fuels
Life-cycle greenhouse and criteria emissions	(by analysis)	No increase
Increase in fuel price	% of retail premium diesel	<5
Cost-effective emission reduction (NO_x plus nonmethane hydrocarbons; based on incremental emission control system costs)	$/ton	less than 5000[a]

[a] Value based on EPA estimates in the Tier 2 Regulatory Impact Analysis for a Tier 2 light-duty vehicle relative to a national low-emission vehicle.

APPENDIX C - Fuels for Fuel Cells Technical Targets

Table C-1. Technical Targets for the Fuels for On-Board Fuel Flexible Fuel Processing

Description	Target
• Fuel Retail Price	• <5% increase over premium gasoline at retail
• Fuel Processor/Fuel Cell Stack System Durability	• Over 5,000 hours thermal cycling simulating realistic driving cycles
• Well-to-Wheel Fuel Cycle Energy Efficiency	• Factor of 1.5 improvement relative to conventional SI-IC engine
• Emissions	• 0.02 g/mile NO_x and 0.01 g/mile PM (full useful life FTP emissions)
• Greenhouse Gases	• One-third reduction compared to conventional SI-IC engines in similar type vehicles
• Health and Safety Impacts - Toxics - Groundwater contamination	• Equal to or improvement relative to conventional gasoline (by model analysis)

Table C-2. Preliminary Technical Targets for the Off-Board Hydrogen Infrastructure

		Units	Current	2004 [1]	2008
Reforming	Cost [2]	\$/GJ H_2	7.38 [3]	7.20	7
	GHGs [4]	g/km	0	0	0
	Energy Efficiency	% (HHV)	75-80 [5]	80-82	85
Purification	Cost [2]	\$/GJ H_2	1.50 [6]	1.20	1
	GHGs [4]	g/km	108	100	91
	Energy Efficiency	% (HHV)	75-90 [7]	82-90	90
Compression	Cost [2]	\$/GJ H_2	2.06 [8]	1.50	1 [9]
	GHGs [4]	g/km	10	8.5	7
	Energy Efficiency	% (HHV)	80-90 [10]	82-92	85-93
Storage & Dispensing	Cost [2]	\$/GJ H_2	2.40 [11]	2.20	2
	GHGs [4]	g/km	0	0	0
	Energy Efficiency	% (HHV)	100 [12]	100	100

[1] 2004 target taken to be halfway between current status and 2008 targets. The 2004 targets represent a 1.5X vehicle in terms of fuel efficiency and a 2.1X vehicle in terms of GHGs. The 2008 targets represent a 2.0X vehicle in terms of fuel efficiency and a 2.3X vehicle in terms of GHGs.

[2] Cost based on a hydrogen fueling station serving 300 cars per day (~10,000 std m^3 per day). Assumes 3 employees at \$50,000/year. Annual capital charge, mark-up (profit, marketing, etc.), and maintenance assumed to be 15%, 25%, and 10% of total capital cost, respectively.

[3] Based on ADL bottoms-up cost analysis of a partial oxidation (POX) reformer and BOP at production volumes of 100 units per year. Natural gas and electricity demand based on ADL experience. Assumes a natural gas price of \$3/GJ and electricity price of \$0.05/kWh.

[4] The reformer exhaust goes directly into the purification process, where the GHGs are separated from hydrogen and emitted.

[5] Assuming a steam methane reformer operating at 5-20 atm.

[6] Based on low end of vendor quotes for a small-scale PSA system.

[7] Assuming a small-scale PSA system operating at reformer outlet pressure.

[8] Based on a 4 stage compressor with intercooling and a cooling tower. Maximum outlet pressure assumed to be 400 atm. Compressor assumed to be 20% more expensive than comparable CNG compressors. Assumes an electricity price of $0.05/kWh.

[9] Assuming low-pressure (50 atm) hydrogen storage (such as hydrides). Compressor electricity demand would be about half that at high pressure (400 atm). Assumes compressor capital costs would also be reduced in half due to simplicity of design (less intercooling, no cooling tower, etc.).

[10] Based on a 4 stage intercooled compressor with an exit pressure of 400 atm. Assumes a US average power generation efficiency of 30%, and compressor adiabatic efficiency of 65-75%.

[11] Based on high-pressure (400 atm) gas storage. Estimated from multiple vendors of comparable CNG equipment.

[12] Assuming high-pressure gas storage with no leaks during storage or dispensing.

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