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ENERGY CONVERSION TEAM

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Energy Efficiency and
Renewable Energy

Office of Transportation
Technologies

Office of Advanced
Automotive Technologies

ADVANCED PETROLEUM-BASED AND ALTERNATIVE FUELS

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

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Progress Report for Advanced Automotive Fuels

**Energy Efficiency and Renewable Energy
Office of Transportation Technologies
Office of Advanced Automotive Technologies
Energy Conversion Team**

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I. INTRODUCTION

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



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On behalf of the Department of Energy's Office of Advanced Automotive Technologies (OAAT), we are pleased to introduce the Fiscal Year (FY) 1999 Annual Progress Report for the Light-Duty Fuels Utilization Research and Development (R&D) Program. Together with DOE National Laboratories and in partnership with private industry and universities across the United States, OAAT engages in high risk R&D that provides enabling technology for fuel efficient and environment-friendly light-duty vehicles.

The Light-Duty Fuels Utilization R&D Program supports the Partnership for a New Generation of Vehicles (PNGV), an industry-government partnership that aims to develop by 2004 a mid-sized passenger vehicle capable of achieving 80 miles per gallon while adhering to future emissions standards and maintaining

such attributes as affordability, performance, safety, and comfort. In order for PNGV-selected powertrains and energy conversion technologies to maximize their potential in energy efficiency while maintaining low emissions, advanced fuels are needed and serve as key technology enablers. In FY 1999, the Light-Duty Fuels Utilization R&D Program comprised two elements: the Advanced Petroleum-Based (APB) Fuels Program which focused on developing and testing advanced fuels for use with compression-ignition direct-injection (CIDI) engines and fuel cells and the Alternative Fuels Program which focused on natural gas and natural gas derived fuels.



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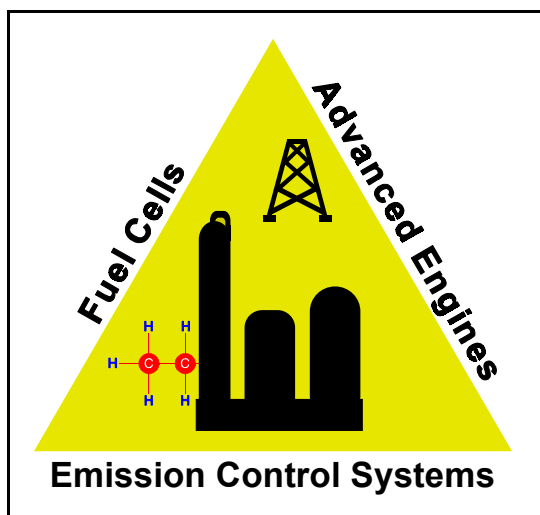
This report highlights progress achieved during FY 1999 under the Light-duty Fuels Utilization R&D Program. It comprises 17 summaries of industry and National Laboratory projects and provides an overview of the exciting work being conducted to tackle tough technical challenges associated with developing clean burning fuels and alternative fuel storage and infrastructure. A brief snapshot of FY 1999 accomplishments and new program directions for FY 2000 is captured in the following. We are encouraged by the technical progress realized under this dynamic program in FY 1999 and look forward to making further advancements in FY 2000.

NEW DIRECTIONS: Advanced Fuels are a Critical Enabler for Cars and Light Trucks to Meet Future Emissions Standards

Over the last two years, the Light-Duty Fuels Utilization R&D Program has shifted its primary emphasis from alternative fuels to advanced petroleum-based fuels. This shift resulted from a growing concern within PNGV over the ability of current CIDI engines to meet future emission requirements

without having advanced fuels to complement the advanced engines and emission control devices being developed. DOE is pursuing CIDI engines because of their high thermal efficiency which is a key component to meeting PNGV fuel economy goals and reducing the fuel consumption of light trucks. Advanced petroleum-based diesel fuels are needed to meet the proposed stringent Tier 2 emission standards through cleaner combustion and enabling more efficient and durable exhaust emission control devices. Advanced petroleum-based diesel fuels have become the third element of the CIDI engine technology development approach that already includes advanced combustion and emission control technologies.

The Advanced Petroleum-Based Fuels Program endeavors to establish and maintain a current knowledge base of the performance, emissions, production, and economics of advanced transportation fuels for highway vehicles and propulsion systems and to determine how fuels can facilitate meeting current and future emissions standards while enabling more efficient engines and propulsion systems. The work in advanced petroleum-based fuels is focused on developing joint programs with the energy and automotive industries to evaluate advanced fuels for PNGV targeted vehicles and for use in both light- and heavy-duty truck engines that will also be required to meet more stringent emission standards.



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

natural gas, such as reducing the costs of natural gas tanks on board the vehicle, reducing the costs and improving the reliability of CNG refueling equipment, and improving natural gas powered vehicle range. The work related to overcoming challenges with natural gas technology is being transferred from the light-duty program and consolidated under the DOE's Office of Heavy Vehicle Technology. The future achievements in natural gas technology realized under the consolidated program will be transferred to light-duty applications, as appropriate.

While CIDI engines are viewed as a nearer-term opportunity to meet the 80 mpg objective set by PNGV, fuel cells are seen as a promising longer-term technology that will be capable of achieving excellent fuel economy with near zero-emissions. One of the key challenges of producing a fuel cell vehicle is developing an appropriate fuel for vehicular applications. Fuel cells can potentially use a wide range of fuels such as hydrogen, methanol, ethanol, and natural gas, and gasoline. The fuels effort to support the Fuel Cell Program is mainly focused on determining the effects of fuel contaminants on the fuel cell system performance and developing advanced fuels and catalyst technologies that will enable highly efficient vehicle operation without compromising their inherently low emissions.

The thrust of the Alternative Fuels Program is directed at tackling the key technical challenges associated with

SIGNIFICANT FY 1999 ACCOMPLISHMENTS

In FY 1999, dramatic particulate matter (PM) reductions were observed by adding 15 percent dimethoxymethane (DMM) to a low-sulfur diesel fuel, without any increase in oxides of nitrogen

(NO_x) emissions. These results were obtained using a state-of-the-art CIDI engine and suggested the potential of fuel formulation to assist in meeting existing and future emissions standards. These promising results spawned several other research projects that are being conducted with industry support. In the fuel cell area, work was completed characterizing the effect of various hydrocarbons on reformer performance, and the development of sulfur removal technology. Numerous natural gas projects were completed to lower the cost of storage, make refueling facilities less expensive and more durable, and devise very efficient and low emission combustion technology. The following lists highlights in each of these areas.

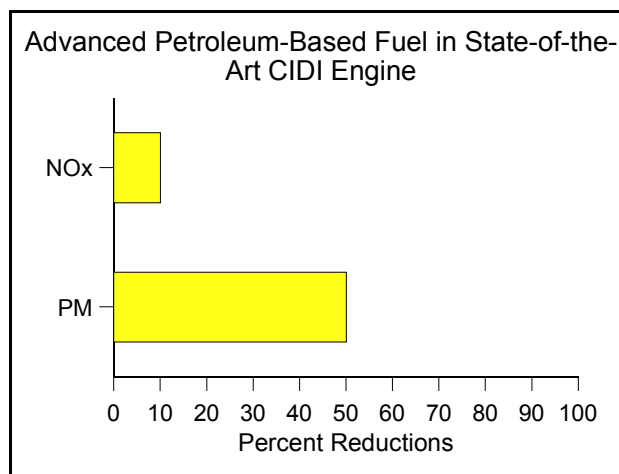
Advanced Petroleum-Based Fuels for CIDI Engines

- Southwest Research Institute (SwRI) performed emissions testing of several advanced diesel fuels using a state-of-the-art CIDI engine. They found that fuel formulation could reduce PM emissions by up to 50 percent, and NO_x emissions by up to 10 percent, without any changes to the engine. By optimizing fuel formulations and corresponding engine calibration, it is believed larger emission reductions are likely.

- The success of the initial SwRI tests spawned three new joint industry-government test projects about fuels for CIDI engines. These projects are:

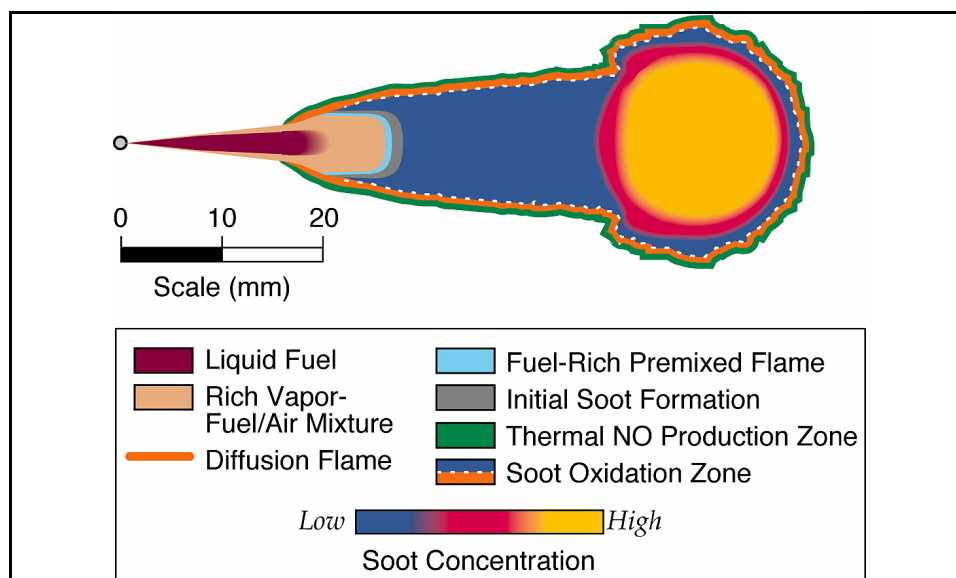
- Oxygenates for Diesel Screening Project
- Chemical Characterization of Toxicologically Relevant Compounds from Diesel Emissions
- Impact of Lube Oil on Advanced Diesel Engine Emissions

Automotive and energy companies are assisting in the planning and conduct of these projects. SwRI will conduct the testing for each of these projects using state-of-the-art CIDI engines. Results are expected in FY 2000.



Significant Reductions in NO_x and PM have been Observed - Larger Reductions are Believed to be Possible

- Projects to understand the fundamental reasons why, and the mechanisms through which oxygenates reduce particulate emissions were initiated at Sandia National Laboratory (SNL) and Lawrence Livermore National Laboratory (LLNL). SNL is using laser diagnostics to try to understand how oxygenates alter the combustion process in CIDI engines. LLNL is approaching the problem by studying how oxygenates affect the chemical kinetics of combustion. The initial results from these fundamental efforts should be available in FY 2000.
- While fuel reformulation has been shown to be able to dramatically decrease emissions from CIDI engines, not all such changes are cost effective, and not all refineries are capable of making such changes. The Oak Ridge National Laboratory (ORNL) is using their refinery modeling expertise to evaluate the impact various fuel reformulations would have on the cost of diesel fuel for CIDI

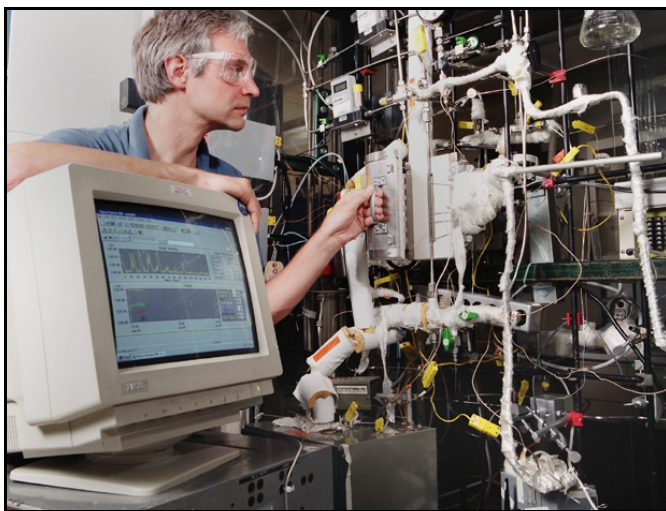


Sandia National Laboratory is using Laser Diagnostics to Study Particulate Matter Production in CIDI Engine Combustion

engines. This work has identified the capability of the current U.S. refinery system to produce very low sulfur diesel fuel (10 to 15 ppm) to satisfy 5 to 10 percent of the on-road diesel fuel market, with only modest changes to the distribution infrastructure. This is sufficient to satisfy the demand caused by new CIDI vehicles for the first several years of their introduction.

Advanced Petroleum-Based Fuels for Fuel Cell Engines

- While renewable hydrogen is acknowledged to be a very good long-term fuel cell fuel, there are several advantages to using fuels that are compatible with the existing petroleum fuel infrastructure. The Argonne National Laboratory (ANL) is exploring how different hydrocarbons affect reformer performance, with the overall objective of identifying an optimized hydrocarbon fuel that could be made by U.S. refineries and which could use the current petroleum fuel distribution system. The progress this project has made this year includes:
 - Built a microreactor for testing fuel constituents and obtaining kinetic information on fuel reforming.
 - Built a dedicated microreactor for long-term testing (up to 1,000 hours).
 - Identified major gasoline components for testing and initiated testing.

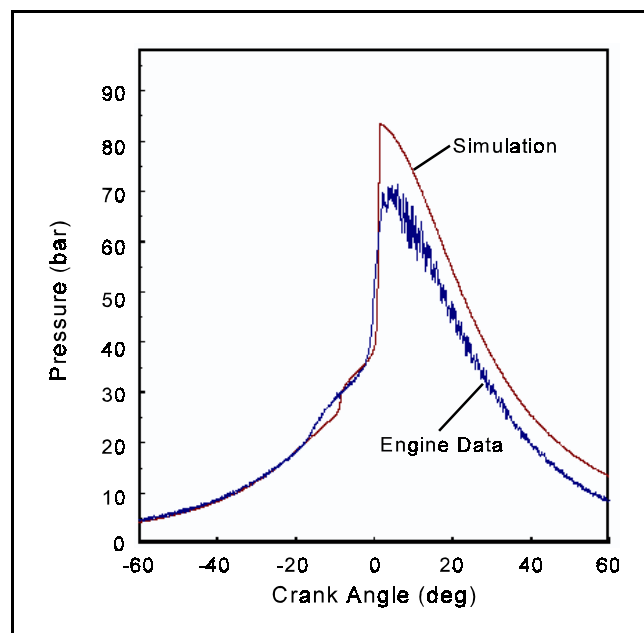


Argonne National Laboratory Microreactor for Testing Fuels

- Have accumulated over 100 hours of test time running with iso-octane in the long-term test reactor.
- Initiated testing on Fisher-Tropsch liquids.
- The Los Alamos National Laboratory (LANL) is exploring ways to improve fuel cell reformer durability and lifetime, reduced volume, improved performance, and other improvements required to meet fuel processor goals. LANL is focusing on improved catalyst formulations to achieve these reformer improvements. The accomplishments they have made in the past year include:
 - Analysis, fabrication and testing of a new instrument including unique catalyst test sample holder features.
 - Evaluation of kinetic vs. equilibrium data for candidate catalysts for POX, shift and PROX sections.
 - Identification of a new PROX catalyst formulation with limited tendency to promote methanation.
- One of the largest hurdles to using hydrocarbons for fuel cell vehicles is that the sulfur contained in gasoline today will poison the reformer and fuel cell catalysts. The Argonne National Laboratory (ANL) is exploring ways to remove this sulfur and define the tolerance of both reformers and fuel cells to fuel sulfur content. A zinc-oxide absorption bed has been fabricated and is being tested to remove sulfur from the fuel to protect reformers and fuel cells. Testing is ongoing into FY 2000.

Alternative Fuels Program

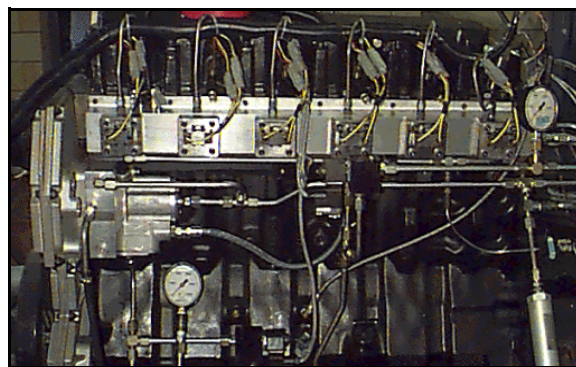
- Natural gas has very low particulate matter and NO_x emissions when it is combusted using the typical spark-ignited engine combustion system. However, in order to achieve significant increases in natural gas engine efficiency, compression ignition similar to diesel combustion is needed. The Lawrence Livermore National Laboratory (LLNL) has demonstrated Homogeneous Charge Compression Ignition (HCCI) of natural gas in a modified diesel engine. The test data suggest that using HCCI could result in vehicles having 30 to 50 percent increase in fuel economy compared with similar size and weight vehicles powered by gasoline engines. Emissions of NO_x are projected to be extremely low (less than 5 percent of the proposed Tier 2 standard for light-duty vehicles in 2009).
- One of the largest challenges facing use of compressed natural gas (CNG) onboard the vehicle is that the high-pressure tanks needed to store it are expensive. About 40 percent of CNG tank costs today are for



Lawrence Livermore National Laboratory HCCI Combustion Model Results

the materials. The Oak Ridge National Laboratory (ORNL) has identified a low-cost carbon fiber that is approximately half the cost of current carbon fibers used for CNG tanks.

- A concern about composite CNG tanks is failure when under high pressure. Analysis of previous failures indicates that they can be avoided through testing. The best test methodology would be one that tests the tanks each time the vehicle is used or at regular intervals during vehicle use. ORNL has devised a monitoring system for composite CNG cylinders that allows periodic testing that identifies imminent failure. The system uses fiber optics embedded within the walls of composite CNG cylinders.
- Compared to gasoline service stations, CNG refueling facilities are five to ten times more expensive. The largest single equipment cost of CNG refueling facilities is the compressor. Most CNG compressors are multi-stage reciprocating units. The Argonne National Laboratory (ANL), in conjunction with IMPCO (a commercial compressor company), is evaluating a new design of CNG compressor using a single screw compressor instead of pistons in cylinders. This compressor has the potential to be less costly and more durable than present compressors. ANL will evaluate the new compressor design at their CNG refueling facility.
- Dimethyl ether (DME) is a fuel made from natural gas that is a good diesel fuel that has very low emissions of particulate matter and NO_x. DME is a liquid only if kept under pressure. To be used in CIDI engines, a new pump is needed. AVL Powertrain Technologies, Inc., designed, built, and tested a fuel injection pump for DME.



The AVL DME Fuel Pump Installed on a 6-Cylinder Diesel Engine

FUTURE INITIATIVES

Our new program initiatives for FY 2000 build upon the progress made in FY 1999 and will focus on those areas that industry agrees are the most promising.

Advanced Petroleum-Based Fuels for CIDI Engines

- Engine and vehicle testing will be conducted at SwRI and ORNL to provide pertinent data in support of EPA's potential ruling on diesel fuel quality. The testing will focus on the effect sulfur content and various fuel properties have on emissions from CIDI engines both with and without exhaust emission control devices.
- SwRI will continue their exploration of advanced fuels for CIDI engines by optimizing engine operating parameters by fuel to identify the maximum potential for emission reduction.
- Cost-effective oxygenates for blending with diesel fuel will be identified to reduce emissions of particulate matter and testing will be initiated.

FY 1999 Progress Report for Advanced Automotive Fuels

- The toxic emissions from diesel fuel will be characterized, and ways of reducing those emissions will be identified.
- The contribution of consumed lubricating oil to particulate matter emission will be quantified along with the effects of lubricating oil composition.
- The cost of producing advanced diesel fuels including use of oxygenates will be estimated.
- Novel ways of producing liquid fuels from natural gas will be identified and demonstrated.
- A Multi-Year Program Plan (MYPP) to research advanced petroleum-based fuels for CIDI engines is being prepared to coordinate and guide the numerous research projects being supported by OAAT. The MYPP is being jointly developed for OAAT and the Office of Heavy Vehicle Technologies since many of the projects to be conducted are independent of engine size and emission control technology and serve the objectives of both offices. The MYPP to be published in FY2000, will incorporate input from the auto manufacturers, the heavy-duty diesel engine manufacturers, manufacturers of emission control devices, and the petroleum industry.

Advanced Petroleum-Based Fuels for Fuel Cell Engines

- Investigation of the effects of various impurities and gasoline constituents on reformer performance will continue and Fischer-Tropsch hydrocarbons from natural gas will be included.
- Recommendations of the hydrocarbons best suited for use in fuel cells will be made. The performance of sulfur removal by zinc-oxide absorption beds will be improved and their tolerance to high-temperature transients will be increased.
- New technologies for removing sulfur from hydrocarbons will be identified and tested.
- A Multi-Year Program Plan (MYPP) is being prepared to define and coordinate fuels research for fuel cells. This MYPP incorporates input from both the auto industry and potential fuel suppliers for fuel cell vehicles, and will be published in FY 2000.

Alternative Fuels Program

- Test and validate the DME fuel pump and fuel system on a CIDI engine.
- All future natural gas R&D activities will be coordinated from the Office of Heavy Vehicle Technology.
- HCCI combustion will be demonstrated using a current production CIDI engine (the Volkswagen 1.9 liter TDI engine).
- A low-cost natural gas liquefier will be built and its performance measured.

HONORS AND SPECIAL RECOGNITIONS

Charles Westbrook of Lawrence Livermore National Laboratory has been invited to speak at the following prestigious meetings, based on his chemical kinetic modeling work:

- 8th International Conference on Numerical Combustion, Society for Industrial and Applied Mathematics, Amelia Island, Florida, March 2000, on the subject of numerical combustion.
- 28th International Symposium on Combustion, Edinburgh, Scotland, July 2000, on the subject of hydrocarbon ignition in diesel and spark-ignition engines.

Idaho National Engineering and Environmental Laboratory applied for the following two patents based on their work on low-cost LNG refueling systems:

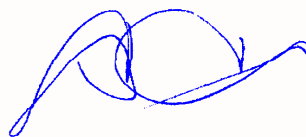
- Application No. 09/212,490: "Apparatus and Method for the Liquefaction and Separation of Gases with Varying Levels of Purity"; and
- Application No. 60/118,563: "Ultrasonic Flow Metering System".

SUMMARY

Advanced petroleum-based fuels and alternative fuels enable the use of high efficiency powerplants such as CIDI engines and fuel cells to create fuel efficient light-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 and alternative fuels complements the efforts to build advanced engines and fuel cells while recognizing that the engine/fuel/emission control system must work together to achieve the maximum benefits possible. As the new fiscal year begins, we look forward to 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. ADVANCED PETROLEUM-BASED FUELS FOR CIDI ENGINES

II.A. CIDI Engine Testing with Advanced Petroleum-Based Fuels

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Objective

- Quantify exhaust emission benefits of selected advanced petroleum-based fuels in an advanced automotive diesel engine

Approach

- Six test fuels were chosen based on their potential for low emissions and economically viable commercial production
- Engine parameters were not optimized for the individual fuels
- Engine-out emissions (no after-treatment) and performance were determined over 13 steady state test modes and compared to the baseline diesel fuel

Accomplishments

- All six test fuels resulted in a reduction of particulate matter (PM) in comparison to the EPA Certification baseline fuel
- A fuel blend containing 15% DMM (dimethoxymethane) lowered the PM emissions by 50%
- The particulate emission reductions were achieved without increases in oxides of nitrogen emissions (NO_x)

Future Directions

- Optimize the DaimlerChrysler OM611 engine operating parameters to the individual test fuels to obtain further improvements in emissions and performance
- Evaluation of exhaust emission control devices on the optimized engine

Introduction

Many studies have demonstrated the exhaust

emissions reduction potential of reformulated and alternative diesel fuels. Variations in fuel properties have been shown to affect light-duty

Table 1. Test Fuels

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

vehicle emissions, with the most prominent effects from variations of density, cetane number, sulfur content, and aromatics level.

In this study, exhaust emissions mapping was conducted for six advanced petroleum-based diesel fuels utilizing a state-of-the-art DaimlerChrysler CIDI engine (Model OM611). The OM611 engine is a 2.2L displacement, direct-injected, four valves per cylinder design, and is equipped with a high pressure, common-rail, fuel-injection system. The engine closely matches the specifications of the Partnership for a New Generation of Vehicles (PNGV) target CIDI engine, though with larger displacement. Triplicate steady-state test sequences were performed for each fuel, as well as a 2-D EPA Certification fuel that served as the baseline. Four of the test points were recommended by industry representatives of PNGV, with the remaining test points chosen to include the operating range of the engine. No adjustments were made to the engine to compensate for any performance differences resulting from fuel property variations.

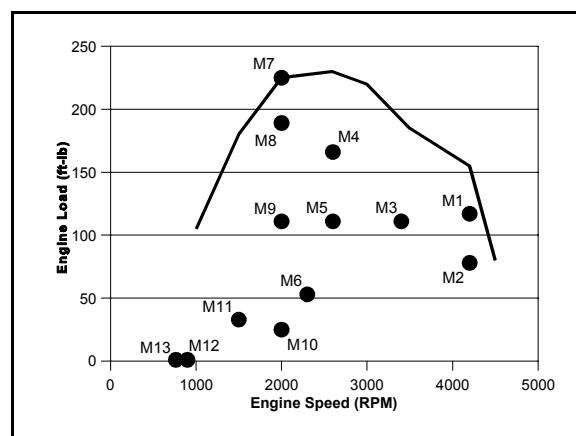


Figure 1. Engine Test Points

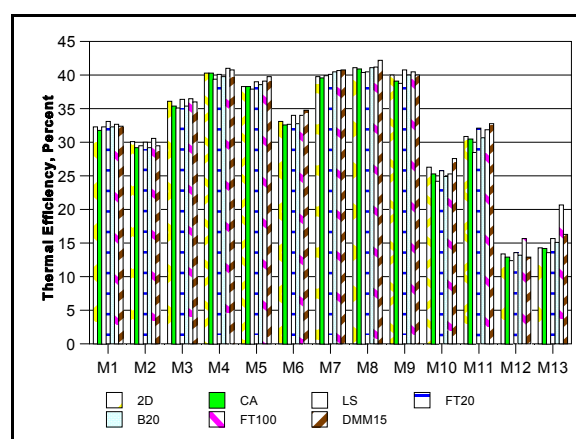


Figure 2. Engine Thermal Efficiency by Fuel and Operating Mode

Approach

The test program was conducted for seven diesel fuels (listed in Table 1), with the 2-D EPA Certification fuel serving as the baseline. The test sequence consisted of 13 steady state speed/load points that covered the operating range of the engine. (The test points are shown in Figure 1.) Exhaust emissions including PM were determined using standard EPA certification methods.

The 2-D EPA Certification fuel was the baseline against which the emissions of the other six fuels were compared. The test fuels were chosen on the expectation of PM emissions benefits. Of the six fuels, three were

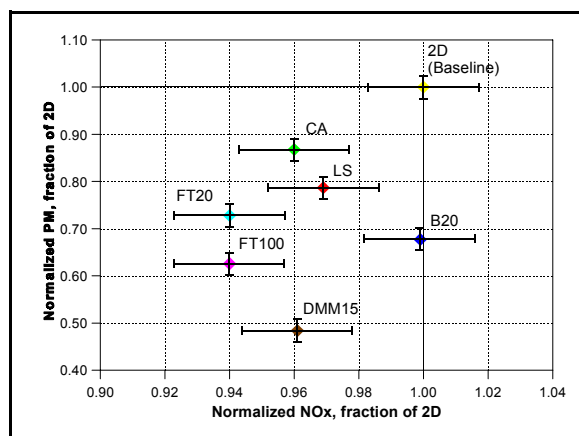


Figure 3. Average NO_x versus PM for the 13 Test Points

straight fuels (neat) and three were blends. The neat fuels included the following: a “pseudo” California (CA) reformulated diesel; a low-sulfur, low-aromatics diesel; and a Fisher-Tropsch synthetic fuel. The remaining test fuels were blends with the low sulfur fuel. The blends included biodiesel, the Fisher-Tropsch synthetic and dimethoxymethane (DMM or methylal). DMM is readily synthesized from methanol, and is completely miscible in petroleum-based fuels.

Results

The test fuels did not degrade the high efficiency of this engine at any of the operating modes tested. Figure 2 shows the effect on efficiency of each test fuel. These results demonstrate that advanced petroleum-based fuels can achieve emissions reductions without engine efficiency trade-offs.

The dramatic reductions in particulate emissions obtained with the test fuels are shown in Figure 3. Here the reduction of PM, without the usual increase of NO_x is evident. All the fuels had lower PM emissions, at the same or lower NO_x levels compared to the standard certification fuel. The 15% DMM blend resulted in a 50% reduction of PM and

4% lower NO_x as compared to the baseline fuel. The second lowest emissions were obtained with the Fischer-Tropsch fuel. The biodiesel blend reduced the PM emission 30%. In general, lower aromatics and higher oxygen content of the fuel resulted in reduced PM emissions. The test fuels are shown as a fraction of the baseline fuel results. The error bars represent the 95% confidence interval for the average.

Conclusions

Advanced petroleum-based fuels have the potential to achieve large engine-out PM emission reductions without compromises in engine efficiency or increases in NO_x emissions. Additional reductions in emissions may be possible if engine operating parameters are optimized for advanced petroleum-based fuels.

Publications/Presentations

“Emissions Comparison of Alternate Fuels in an Advanced Automotive Diesel Engine”, Interim Report No. 338, U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI), November 1998.

“Emissions Comparison of Alternative Fuels in an Advanced Automotive Diesel Engine,” presented at SAE International Spring Fuel and Lubricants Meeting, Dearborn, MI, 4 May 1998.

“CIDI Engine Testing with Advanced Fuels”, Diesel Combustion and Aftertreatment R and D Laboratory Merit Review and Peer Evaluation, Argonne National Laboratory, 23 June 1999.

“Emissions of Diesel Fuel Alternatives in a PNGV-Like Diesel Engine”, EFI Technology Conference, Tucson, AZ, 20 January 1999.

List of Acronyms

CIDI compression ignition direct injection
EPA Environmental Protection Agency

NO_x oxides of nitrogen
PM particulate matter
PNGV Partnership for a New Generation of Vehicles

II.B. Oxygenates for Diesel Fuel

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Objectives

- Address and investigate the impact and limitations of oxygenates on the diesel combustion process.
- Determine the effect of oxygen chemical form on exhaust particulate matter (PM) formation.
- Identify oxygenate compounds for additional exhaust emission testing based on technical properties and potential economic costs.

Approach

- Oxygenate literature will be reviewed to identify potential candidates.
- A hypothesis relating oxygenate properties with particulate formation will be developed.
- Candidate oxygenates will be obtained and analyzed for combustion, lubricity, flammability and other fuel properties.
- The economics of producing the most technically promising oxygenates for fuel use will be investigated.
- Based on economic and technical criteria, candidate oxygenate compounds will be selected for evaluation in the DaimlerBenz OM611 engine for performance and exhaust emissions.

Accomplishments

- Project plans completed and fully coordinated with DOE and Industry.
- Literature search on oxygenate compounds initiated.

Future Directions

- This project is just beginning in late FY 99.

- The effects of exhaust after-treatment devices on PM and NO_x when using oxygenate fuel blend may be investigated.

Introduction

A number of exhaust emissions studies have shown that using neat or pure oxygenates as diesel fuel will substantially reduce or nearly eliminate PM (particulate matter) emissions in the diesel engine exhaust. A number of other studies report that blending oxygenates into diesel fuel will also significantly reduce PM emissions in the diesel exhaust (Figure 1 and Figure 2). The results from these studies suggest that the benefit of blending oxygenates goes far beyond that explained by simple dilution. This leveraging reduction in PM emissions is generally not seen by simply blending in "clean" hydrocarbon compounds. Therefore, it appears that the oxygen in the oxygenated compound provides additional benefits in suppressing the formation of soot or PM during combustion. The impact and the limitations of oxygenates on the diesel combustion process have not been well defined. Questions on their effectiveness by type of oxygenate and the maximum achievable PM reduction with oxygenate blends have not been fully explored in the literature.

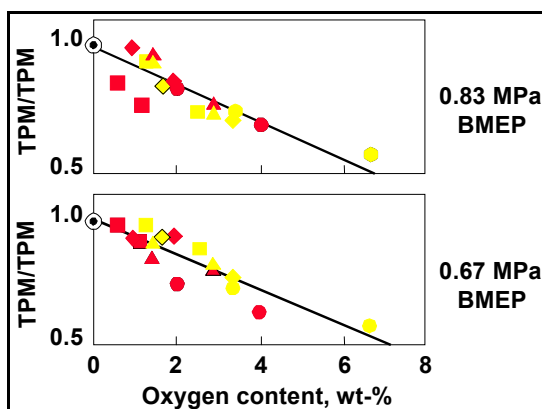


Figure 1. Total Particulate Mass Reduction with Oxygen Relative to Diesel Fuel Without Oxygen, Miyamoto et.al.

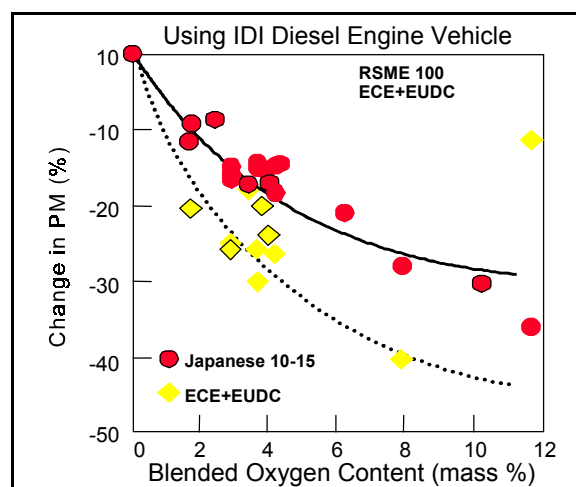


Figure 2. Oxygen Impact on Particulate Emissions, Tsurutani et.al.

Objective

The project will estimate the potential of oxygenates for emission control and determine their impacts on cost, infrastructure compatibility, and safety.

Approach

SwRI will participate in an extensive industry-based review of published information and in-house but non-proprietary data. Data will be collected on the chemical structure, physical properties, and the test methods and results. SwRI, as part of the team comprised of representatives from oil and engine industries, will organize the data for comparison and interpretation and for the development of correlations between the readily measurable properties, such as oxygenate type and concentration, and the emissions results, where sufficient data exist to permit the analyses.

SwRI, in conjunction with the industry-based

review team and representatives from the National Labs, will review publications dealing with the chemical mechanisms of soot formation in flames with respect to the reported effects of oxygenates on flame chemistry. These are expected to vary by compound and the types of oxygen structural groups each compound contains. The objective is to develop a predictive understanding of the ways oxygenates affect those aspects of flame chemistry relating to particulate formation, and to postulate testable hypotheses relating oxygenate properties to particulate emissions.

Based on the results of the literature review, and on the hypotheses formulated, a statistically designed study will be developed to evaluate the possible variables identified, and to quantify the relative importance of fuel oxygenate properties such as oxygen concentration, molecular structure, and physical properties.

Based on the initial results, develop a hierarchy of fuel properties which should be available for the oxygenates and fuel blends of interest. The hierarchy will serve as a guide to the property testing, so that critical, "show-stopper" properties will be measured first, then those which are of less importance, or for which deficiencies could be compensated for in some manner, will be tested later.

Oxygenate compounds will be investigated for their effects on diesel fuel properties such as combustion, fuel handling, fuel stability, flammability and lubricity.

The economics of potential fuel oxygenates will be investigated. To obtain this information, SwRI will subcontract with industrial organizations experienced in chemical processing economics, and the

economic modeling of refineries and chemical plants. Consulting services will be sought from industrial sources to work with the subcontractor(s). The economics of producing the most technically promising oxygenates and incorporating them into the diesel fuel blend will be investigated. At this time, most oxygenates are not produced in the quantities needed for the fuel industry, nor are they being manufactured to "fuel specifications"—which in most cases will be less stringent, particularly in terms of purity, than the specifications for current uses. In some cases, economy might be achieved from making the oxygenate within, or adjacent to, the refinery using an existing refinery stream as one of the feeds. The main goal will be to determine the approaches for making effective, oxygenated diesel fuels, and introduce them into the diesel fuel blend at least cost. A secondary goal will be to determine the main factors that influence the economics of oxygenated fuel production and obtain data that could be used in future phases for process optimization and economic modeling.

A minimum of four (4) oxygenate compounds will be selected which have the highest potential for both technical and economic success as fuel components for reducing particulate matter in diesel exhaust. These choices will be confirmed, or further refined, in a series of engine tests using the DaimlerBenz OM611 engine. Exhaust emission and engine performance effects will be determined for the selected oxygenate compounds blended in low sulfur, low aromatic base fuel.

Conclusions

Upon completion of this project a report will be prepared that describes the details and results of this investigation.

II.C. Impact of Lube Oil on Advanced Diesel Engine Emissions

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Objectives

- Determine the contribution of lube oil to particulate and to nitrogen oxides measured in the exhaust gas stream of an advanced diesel engine.

Approach

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

Accomplishments

- Project plan fully coordinated with DOE and Industry.
- Received the OM611 test engine supplied by Daimler-Benz.
- All test fuels and test lubricants supplied by Industry have been received.

Future Directions

- This project is just beginning in late FY 99.
- Project results will determine if a more detailed study of engine oil contribution to particulate emissions should be conducted.
- Effect of lube oil on emission control system effectiveness may be conducted.

Introduction

The purpose of this study is to determine the contribution of crankcase lube oil to particulate and to nitrogen oxides as measured in the exhaust gas stream of advanced diesel engines. It will be determined whether commercially available synthetic engine oil can significantly reduce the mass of the volatile organic fraction (VOF) of the particulate. In addition, measurements will be made to determine whether changes in engine oil result in a change in nitrogen oxides or other gaseous regulated emissions.

Approach

Regulated gaseous and particulate emissions will be collected from the exhaust gas stream of an unmodified DaimlerChrysler OM611 2.2-liter diesel engine (Figure 1). The gaseous emissions are investigated by the means of gaseous emission analyzer and the particulate emissions are characterized by taking two particulate filters from a particulate dilution tunnel. One of the particulate filters will be analyzed by the direct filter injection gas chromatography (DFI/GC) method to determine the proportion of fuel and oil to the VOF of the particulate. The other filter will be analyzed for the concentration of additive metals, from which an estimate of the engine oil consumption will be calculated.

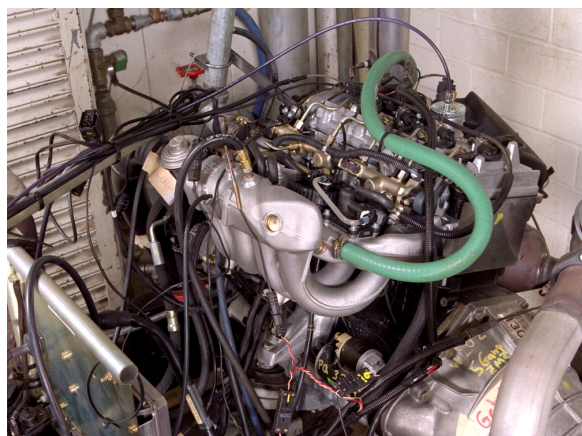


Figure 1. DaimlerChrysler OM611 Engine

These measurements will be made with three different oils: one conventional petroleum-based product and two synthetic-based products. In addition, two fuels will be used. One "CARB" like fuel and one low sulfur and low aromatic fuel with 15 volume percent dimethoxymethane (DMM) added. Measurements will be made over 5 steady-state test points and over the heavy-duty diesel transient procedure. The points chosen for this test program have been selected as a minimum set of operating points that span the engine operating range. Since transient engine operations have shown to be significant contributors to both oil consumption and particulate emissions, the heavy-duty diesel engine transient test procedure will be included.

Conclusions

The results from this project will be a determination of the lubricant-derived fraction of the particulate VOF, for three different oils at six selected operating conditions spanning the engine-operating map. These data will be used to assess significance of lubricating oil to particulate emissions in this type of advanced light-duty automotive diesel engine, and whether synthetic based lubricants can reduce this contribution. In addition, the measurements obtained with the DMM-containing fuel are expected to provide additional information on whether the lubricant becomes a larger contributor to total particulate as fuel-derived particulate emissions are reduced.

Recommendations will include a discussion of whether a more detailed assessment of lubricant contribution to particulate mass using more definitive techniques would be of value.

List of Acronyms

DFI/GC direct filter injection chromatography
VOF volatile organic fraction

PM particulate matter

II.D. Chemical Characterization of Toxicologically Relevant Compounds from Diesel Emissions

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Objectives

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

Approach

- A DaimlerChrysler OM611 diesel engine will be used to determine the effect of diesel fuel type on toxicologically relevant compounds from engine out exhaust emissions.
- Engine will be controlled by SwRI Rapid Prototyping Electronic Control System (RPECS).
- Matrix to include 4 fuels (including one oxygenate blend) operated over 5 speed/load points.
- Each speed load point has two optimized conditions, one for minimum exhaust particulate matter, and a second for maximum fuel economy.
- Four gaseous “toxic” exhaust emissions will be measured.
- Eleven gaseous PAH compounds will be measured.
- Seventeen PAH compounds will be determined for the soluble organic fraction of the exhaust particulate matter.

Accomplishments

- Project plan fully coordinated with DOE and Industry.
- Test engine received from DaimlerChrysler
- All test fuels and lubricants have been received from industry sources.

Future Directions

- This project is just beginning in late FY 99.
- In a follow-on phase, similar investigations will be conducted using an engine with an exhaust emission control system.

Introduction

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

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 program 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 will be made initially on engine out emissions and, in a second phase of this program, on emissions from a current after-treatment device. In future tests, other potentially hazardous compounds may have to be measured depending on the technology used in after-treatment devices.

Approach

A standard set of polycyclic aromatic hydrocarbons (PAH) in organic solvent

extracts of diesel particles and from the gas phase of diesel emissions will be measured in this program. In addition, four toxic air pollutants (as noted above) will also be quantified. The OM611 diesel engine (Figure 1) will be run at five different engine loads and optimized at each condition for minimum brake specific fuel consumption (BSFC; maximum fuel economy) and for minimum particulate emissions. Four fuels will be used for this study - a baseline reference fuel and three additional test fuels. Particulate filter samples will be collected at each optimized parameter (e.g. fuel economy and particulate matter) for each load condition.

It is possible that one of the fuels (15% dimethoxymethane in low sulfur diesel fuel) will emit larger amounts of formaldehyde than emitted using the baseline fuel. Therefore, the four toxic air pollutants from mobile sources

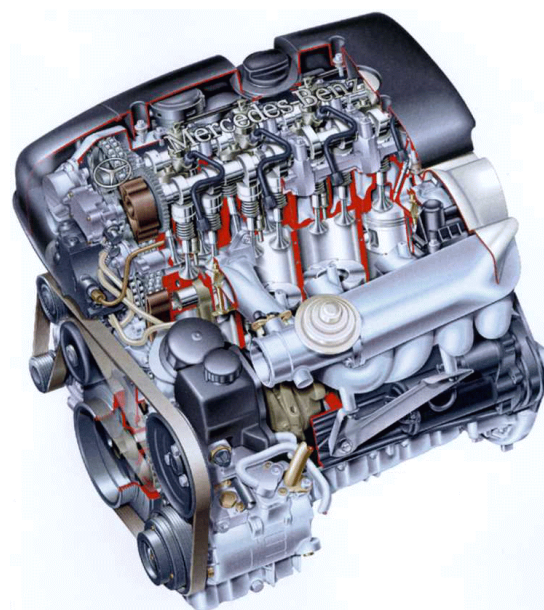


Figure 1. DaimlerChrysler OM611 Engine

cited in the Clean Air Act (formaldehyde, acetaldehyde, benzene, and 1,3-butadiene) will be measured in triplicate at each of the points discussed above.

Conclusions

Upon completion of this study a draft report will be prepared that describes in detail the results of the study. This study will provide information on the PAH content of diesel particles and emissions of four toxic air pollutants from diesel engines. These results will compare the PAH and toxic air pollutant levels of the three modified diesel fuels with

the baseline fuel to see what effect changing the fuels has on the total emissions of these toxicologically important compounds. In a second phase of this project the effect of the after-treatment device on emissions of these compounds will be measured.

List of Acronyms

PAH Polycyclic Aromatic Hydrocarbon
RPECS SwRI Rapid Prototyping Electronic Control System
DMM dimethoxymethane
BSFC Brake Specific Fuel Consumption

II.E. Combustion Characteristics of Oxygenated Diesel Fuels

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Objectives

- Develop the scientific and technological understanding needed to optimize in-cylinder combustion processes while taking full advantage of the soot reduction potential of oxygenated fuels. Research will focus on two specific goals: determining the effects of oxygenates on in-cylinder processes relative to conventional fuels in an automotive-type high-speed, small-bore, direct-injection diesel; and determining the importance of total oxygen concentration versus oxygenate molecular structure on soot reduction.

Approach

- Utilize advanced optical diagnostics coupled with a unique optically-accessible diesel combustion research facilities to conduct these investigations. The two facilities to be used are: the high-speed, small-bore, direct-injection diesel engine (HSDI); and the diesel combustion simulation facility (DCSF).

Accomplishments

- Initiated experiments in the HSDI engine to determine the effects of 15% ethanol in diesel fuel on the combustion performance and the timing and location of ignition and combustion.
- Initiated the design of the injection cooling system needed to conduct experiments with high volatility oxygenated fuels under well controlled fuel temperature conditions in the DCSF.

Future Directions

- Research in FY00 will focus on objectives above and also include 15% DMM as a test fuel. No plans exist for extending the project beyond FY00.

Introduction

Engine exhaust emissions studies have shown that adding oxygenated compounds to diesel fuel will reduce particulate emissions from direct-injection (DI) diesel engines. For example, Southwest Research Institute (SwRI) has shown that addition of 15% dimethoxymethane (DMM) reduces particulate emissions by 40% to 50%. In addition, research by others indicates that when the percent oxygen (by mass) in the fuel reaches approximately 30%, the Bosch smoke number approaches zero. However, the fundamental

chemical and physical mechanisms by which the particulate emission reductions occur are not well understood. Sandia National Laboratories (SNL) will conduct research aimed at developing a fundamental understanding of the effects of oxygenates blended into diesel fuel on soot formation in diesel sprays. The research will be integrated with investigations of oxygenate effects on engine out emissions performed by industry and SwRI, and with the detailed chemical kinetic modeling investigations of the effects of oxygenates on soot formation performed by Lawrence Livermore Laboratory (LLNL). The information developed will help provide the technology and fundamental science base needed by engine designers to optimize in-cylinder combustion processes and engine performance, while taking full advantage of the soot reduction capabilities of oxygenated diesel fuel blends.

Research

The potential mechanisms by which oxygenates affect the production and evolution of soot in diesel sprays include changes in the soot formation chemistry and changes in the overall fuel injection, ignition and combustion processes. Advanced optical diagnostics and optically accessible diesel combustion research facilities will be used to investigate aspects of these mechanisms. The goal will be to determine the relative magnitude of the effect

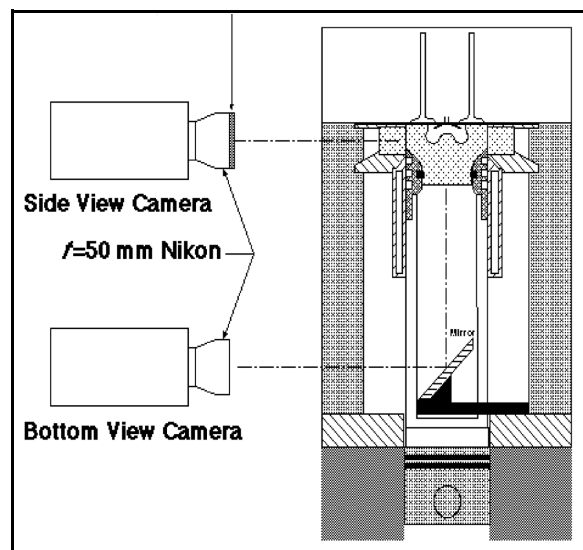


Figure 1. Schematic of the High-Speed, Small-Bore, Direct-Injection (HSDI) Diesel Engine Optical Access

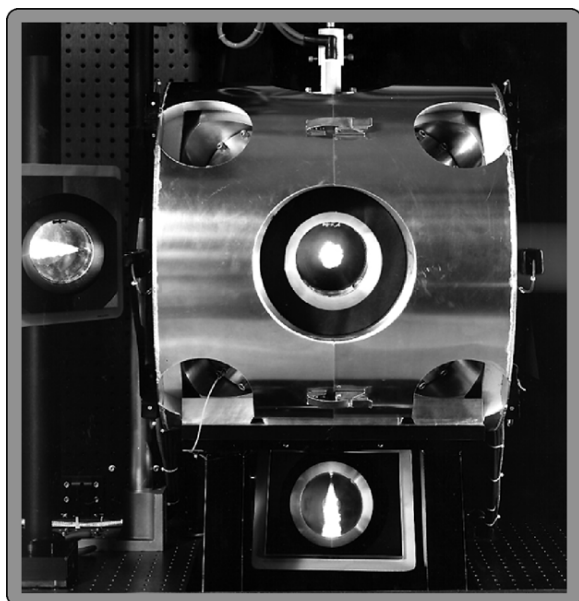


Figure 2. Photograph of the Combustion Vessel in Operation

of the various mechanisms on soot production. Oxygenate chemical structure, concentration in the base fuel, and chemical and physical property effects on soot production in diesel sprays will be explored in this investigation. Two diesel engine research facilities will be used for the investigations, the high speed, direct-injection, optical diesel engine (HSDI) facility (see Figure 1) and the diesel combustion simulation facility (DCSF) (see Figure 2). The HSDI engine is an optically accessible diesel engine based on the high-speed, small-bore diesel being developed for automotive use. The DCSF is a constant volume combustion chamber in which an extremely wide range of diesel engine top-dead-center thermodynamic conditions can be simulated.

The auto-ignition and soot formation processes will be investigated in the HSDI optical engine. Auto-ignition will be investigated by imaging the natural chemiluminescence associated with the onset of combustion. These images will be supplemented by the analysis of in-cylinder pressure measurements from which the ignition delay and rate of

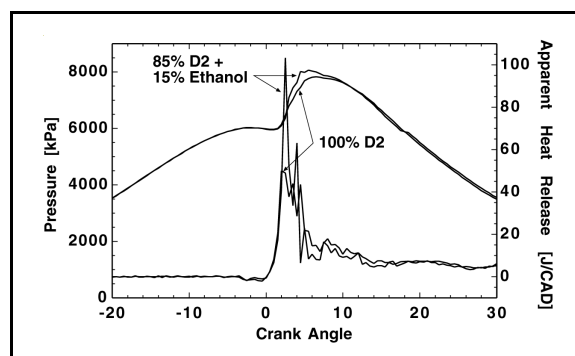


Figure 3. Comparison of pressure and apparent heat release histories for a standard diesel fuel (D2) and a 15% ethanol/D2 blend

apparent heat release will be determined. By comparison with similar measurements obtained with No. 2 diesel fuel, the effect of oxygenates on ignition delay and location will be investigated. Furthermore, any changes that occur in the phasing and relative magnitude of different portions of the heat release curve will be apparent.

Similarly, the in-cylinder soot formation process will be compared to No. 2 diesel fuel through comparison of images of natural soot luminosity. The images will allow the effect of oxygenates on the location and timing of particulate formation to be examined, and the subsequent spatial distribution of these particulates within the cylinder to be determined. Additionally, qualitative information on the quantity of soot formed will be available based on image intensity. The fuels to be tested in the HSDI engine will be blends of 15% ethanol and 15% DMM in low-sulfur diesel fuel. The tests will be conducted at a moderate speed/load condition representative of typical, high-frequency engine operation. Figure 3 shows some of the initial pressure and heat histories for a standard diesel fuel (D2) and a 15% ethanol/D2 blend. Additional high priority fuel blends will be investigated as required.

The research in the DCSF will focus on determining the fundamental effects of

oxygenate molecular structure (e.g., C/O ratio, bond types) and the total oxygen concentration in the fuel on the soot evolution in a diesel spray. This research directly compliments other DOE research in the DCSF focused on determining the effects of injector and in-cylinder engine conditions on the soot evolution in diesel sprays. Together the results will provide significant insight on the relative importance of the various physical and chemical mechanisms by which oxygenates affect soot formation in diesel sprays.

The research in the DCSF will be conducted with single component fuels and fuel blends that allow the molecular structure and the total fuel oxygen concentration to varied in as controlled a manner as possible. Diagnostics such as laser induced incandescence, natural flame emission, line-of-sight absorption, and elastic scatter light will be used to examine the differences in the soot formation regions of diesel sprays with each fuel.

Conclusions

The objective of this project is to advance the scientific and technological understanding needed to optimize in-cylinder combustion processes while taking full advantage of the soot reduction potential of oxygenated fuels. The research will focus on determining (a) the effects of oxygenates on in-cylinder processes in an automotive-type direct-injection diesel relative to conventional fuels, and (b) the importance of oxygen concentration versus molecular structure on reducing soot formation.

The project began in the middle of FY99 and will extend through the end of FY00. Initial investigations of the effects of 15 % ethanol in diesel fuel on combustion and soot formation have begun in the HSDI diesel engine. Work is also proceeding on developing a capability to significantly cool and accurately control the injected fuel temperature in the DCSF, a requirement for conducting experiments with many of the high volatility oxygenate fuels.

II.F. Chemical Kinetic Modeling of Oxygenated Diesel Fuels

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Objectives

- Use kinetic modeling to study performance of alternative oxygenated and other fuels for diesel combustion.
- Study chemistry of soot formation in diesel engines.
- Study chemistry of ignition in diesel engines.

Approach

- Use detailed chemical kinetic reaction mechanisms for conventional diesel fuels and selected oxygenated species to model important features of diesel combustion.
- Analyze selected oxygenated fuels and fuel additives with kinetic models to screen for enhanced diesel performance.

Accomplishments

- Identified role of oxygenated species in suppressing soot production.
- Developed detailed chemical kinetic reaction mechanism to describe production of precursors for soot particles.
- Developed detailed chemical kinetic reaction mechanisms for combustion of dimethyl ether (DME) and dimethoxy methane (DMM), and tested those reaction mechanisms with available experimental data.
- Contributed to enhanced understanding of the mechanism of diesel combustion.

Future Directions

- Examine biodiesel, Fischer-Tropsch, and other selected oxygenated and alternative fuel kinetics under diesel conditions.
- Develop better kinetic models for soot production.
- Develop simplified models for ignition and soot production to incorporate into multidimensional diesel simulation models.

Introduction

There are two major pollutants of primary concern to diesel engine manufacturers, consisting of soot and oxides of nitrogen (NO_x). Generally speaking, variations in engine operating parameters motivated to decrease NO_x emission lead to increased soot production, while modifications to decrease soot production usually lead to increased NO_x production. The same type of tradeoffs are observed for spark-ignited engines, where unburned hydrocarbon emissions vary inversely with NO_x production. A major challenge of diesel engine research is to find a way to minimize both classes of emissions, although conventional wisdom suggests that both cannot simultaneously be reduced.

Recent experimental studies of diesel

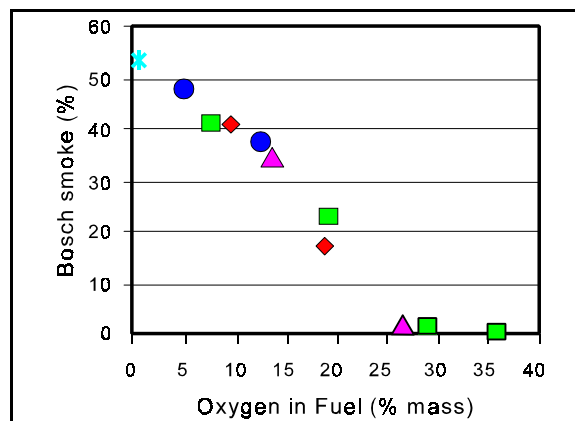


Figure 1. Variations in Experimentally Observed Smoke vs. Fuel Oxygen Content

combustion have demonstrated that there are fuels which do not produce soot under diesel engine combustion conditions. These fuels are all characterized by the fact that oxygen atoms are included in the fuel molecule itself. For example, fuels such as dimethyl ether (DME,

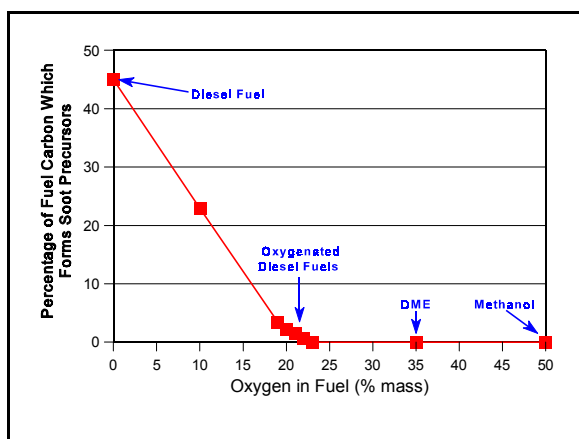


Figure 2. Kinetic Model Prediction of Soot Precursor Formation under Rich Diesel Conditions

CH_3OCH_3), dimethoxy methane (DMM, $\text{CH}_3\text{OCH}_2\text{OCH}_3$) or even methanol (CH_3OH) produce little or no soot when used as diesel fuels. Even more important, when these fuels are mixed with conventional diesel fuels, they reduce the soot production in diesel engines.

The experimental evidence for these trends is summarized in Figure 1, where the sooting tendency is described by the Bosch smoke number, which is seen to decrease steadily as the percent oxygen in the fuel is increased. As the percent oxygen in the fuel reaches approximately 25-30%, virtually no soot is produced.

Chemical Kinetic Modeling

We used chemical kinetic modeling techniques to examine the chemistry of soot formation in diesel engines. Recent experimental studies at Sandia National Laboratories have shown that diesel combustion generally consists of an initial fuel-rich ignition of fuel and a small amount of air, and the products of this rich ignition then proceed to produce soot which is later burned out. Our computer model has analyzed this rich premixed burn to identify those chemical species produced in the rich burn that lead to eventual soot production.

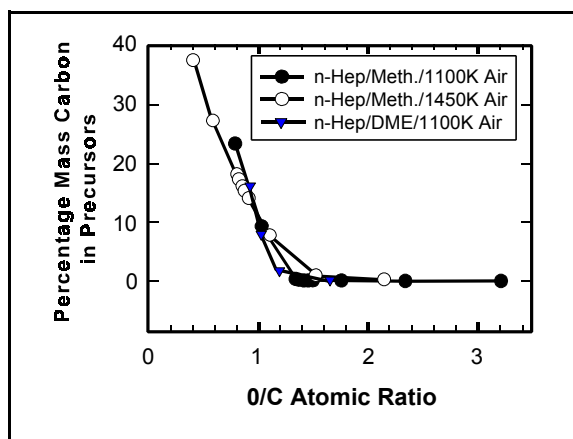


Figure 3. Computed reduction in soot precursor concentrations with oxygen content in the fuel

The fuel n-heptane was used by the kinetic model as being representative of the ignition of conventional diesel fuels; the model then considered ignition of n-heptane with increasingly greater fractions of methanol added to increase the percentage of oxygen in the fuel. The results of these model calculations are summarized in Figure 2. The total concentrations of acetylene (C_2H_2), ethylene (C_2H_4) and propargyl (C_3H_3), all identified in our parallel kinetic studies of soot formation as powerful soot precursors, are plotted against the percentage of oxygen in the fuel mixture. The experimental trends are very closely reproduced by the model simulations, indicating that the model correctly describes the basic features of soot precursor formation.

Finally, the model was used to compare the soot reduction capabilities of other oxygenated additives, including dimethyl ether (DME), and the results in Figure 3 show that the soot precursor reduction capabilities of both additives, methanol and dimethyl ether, depend only on the oxygen content in the additive. Our kinetic modeling shows that the oxygenated additive puts a significantly increased level of atomic oxygen into the rich premixed burn, and these oxygen atoms consume considerable amounts of those chemical species such as acetylene, ethylene

and propargyl that lead to soot production.

Conclusions

Kinetic modeling has been used to study soot production in diesel engines to understand why oxygenated additive species can reduce soot emissions. The model shows very clearly that oxygen in the fuel helps to consume those chemical species that lead to soot production. The implications of this new insight will be examined in the coming year, and the chemical model will be used to motivate new experiments to exploit this enhanced chemical understanding.

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II.G. Refinery Modeling of Advanced Fuels for CIDI Engines

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Objectives

- Characterize relationships between fuel properties and emissions for diesel technologies that could be available in the near-term to meet Tier 2 emissions standards.
- Make preliminary estimation of impacts of alternative diesel fuel specifications on U.S. refineries.
- Develop composited refinery model.
- Use refinery model for estimation of impacts of alternative diesel fuel specifications on U.S. refineries.

Approach

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

Accomplishments

- Compositing begun for ORNL-RYM.
- Data obtained on fuel effects on diesel engine emissions.
- Preliminary estimates made for capability of refineries to shift diesel fuel blendstocks to achieve a range of sulfur values.

Future Directions

- Analyze RFD production sensitivities to future market changes, such as increased jet fuel demand.

Introduction

In the 1998 Diesel Engine Emissions Reduction Workshop, refining challenges were discussed for a scenario with RFD required for all diesel vehicles (McNutt and Hadder 1998). The analysis concluded that refinery investment could be a third of refinery market value, and gas-to-liquid plant investment

could be twice as much as refinery investment, depending on RFD specifications.

While the 1998 study was premised on long-term requirements for RFD, this follow-up analysis estimates current U.S. refining system capability to produce smaller amounts of less severely reformulated diesel fuel without investment. The analysis focuses on the sulfur

property of diesel fuel for the light duty vehicle market (5 to 10 percent of on-road diesel fuel in the near-term) and the infrastructure changes required to deliver that fuel to light duty vehicles.

Approach

The analysis is based on simple spreadsheet calculations, and findings are preliminary and directional. Sophisticated refinery modeling is required to estimate blendstock allocations to satisfy all specifications, and to account for production changes due, for example, to anticipated jet fuel demand growth. The composited ORNL-RYM, under development, will be used for future RFD studies.

Production volumes of distillate blendstocks, reported in an industry survey¹, have been totaled by sulfur content. The survey reports process utilization, and production volumes have also been totaled for maximum practical utilization of hydrotreating and hydrogen

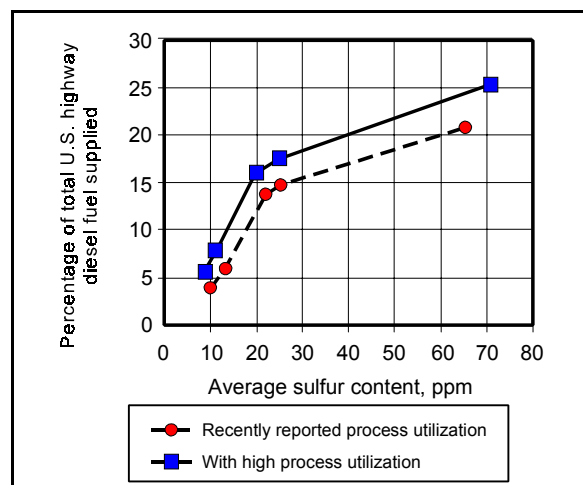


Figure 1. U.S. Low Sulfur Diesel Blendstock Production

¹ American Petroleum Institute and National Petroleum Refiners Association. 1997. *1996 American Petroleum Institute/National Petroleum Refiners Association Survey of Refining Operations and Product Quality*, API Publishing Services, 1220 L. Street, N.W., Washington DC, July.

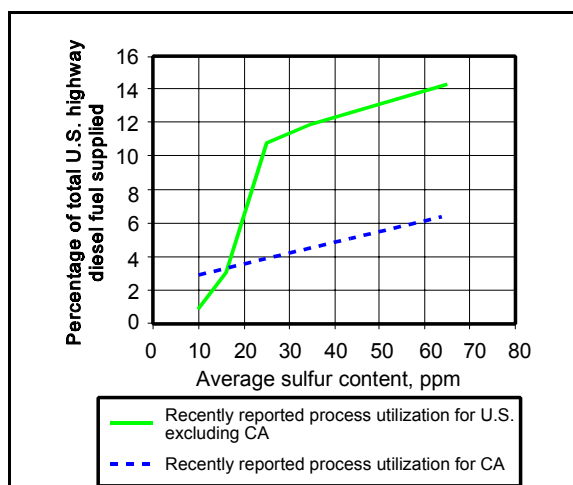


Figure 2. Low Sulfur Diesel Blendstock Production

production capacity. The totals show that, with reported process utilization and blending practice (Figure 1 dash line): 5 percent of the on-road diesel fuel market could be supplied with light duty diesel fuel (LDDF) at 10-15 parts per million (ppm) sulfur; 10 percent of the market could be supplied with LDDF at 15-20 ppm sulfur; 20 percent of the market could be supplied with LDDF at 60 ppm sulfur. The current U.S. highway diesel fuel sulfur specification would be satisfied for fuel remaining after segregation of low sulfur blendstocks. Low sulfur blends may need additional processing to satisfy all specifications.

With practical maximum process utilization (Figure 1 solid line): 5 percent of the on-road diesel fuel market could be supplied with LDDF at 10 ppm sulfur; 10 percent of the market could be supplied with LDDF at 10-15 ppm sulfur; 20 percent of the market could be supplied with LDDF at 40 ppm sulfur.

California is the predominant source of low sulfur distillate blendstocks. California currently produces 10 ppm sulfur diesel fuel equal to 3 percent of total U.S. highway diesel fuel (see Figure 2). In contrast, refineries in the rest of the U.S. produce 10 ppm sulfur diesel fuel equal to just 1 percent of total U.S.

Table 1. Capacity Ratios for Surveyed Refineries

	California	Rest of U.S.
Hydrocracking: crude	0.30	0.08
Hydrogen generation: crude (KSCF/D): (B/SD)	0.6	0.1

highway diesel fuel. A California-type refining system could supply U.S. demand for LDDF at 10 ppm sulfur. Refining systems for production of low sulfur blendstocks for LDDF could have substantial capacity for hydrocracking or aggressive hydrotreating (99 percent sulfur reduction). California blendstocks with ≤ 10 ppm sulfur have been hydrocracked. As shown in Table 1, the California refinery system has much greater relative hydrocracking and hydrogen capacity, compared to other U.S. refineries.

Conclusions

If the LDDF sulfur specification is 10-15 ppm, the current U.S. refinery system could produce low sulfur blendstocks to satisfy near-term light duty vehicle diesel fuel markets (5 to 10 percent of the on-road diesel fuel market) with only modest changes in the wholesale product

distribution infrastructure. Combinations of hydrocracking and aggressive hydrotreating would be required to satisfy the long-term market requirement for LDDF (20 percent of the market).

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List of Acronyms

B/SD	barrels per stream day
KSCF/D	thousand standard cubic feet per day
LDDF	light duty diesel fuel
ORNL-RYM	Oak Ridge National Laboratory Refinery Yield Model
ppm	parts per million
RFD	reformulated diesel fuel

II.H. Cooperative Research in C1 Chemistry

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Subcontractors

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University of Pittsburgh, Pittsburgh, PA

University of Utah, Salt Lake City, UT

Auburn University, Auburn, AL

Objectives

- Develop technology for the conversion of methanol and syngas into oxygenated transportation fuels and fuel additives.
- Develop improved technology for the production of syngas from natural gas by reforming with carbon dioxide.
- Develop new catalysts and processes for the production of hydrogen from syngas, natural gas and methanol.

Accomplishments

- Dimethyl carbonate, a potential diesel fuel/additive has been synthesized using two types of catalysts.
- A continuous unit to produce oxygenated Fischer-Tropsch (FT) products has been constructed.
- Nanoscale, binary catalysts to be used in reforming and water-gas shift reactions have been synthesized and characterized by a variety of analytical techniques.
- Kinetic studies have been conducted of the catalytic reaction of methanol and olefins to produce higher ethers.
- Several in situ analytical instruments for on line investigation of C1 products and catalytic reactions have been designed and are being tested.
- An Industrial Advisory Board for the program has been established.

Introduction

The Consortium for Fossil Fuel Liquefaction Science (CFFLS) is a research consortium with participants from five universities: the University of Kentucky, West Virginia University, the University of Utah, the University of Pittsburgh and Auburn University. For over a decade, the CFFLS has been conducting research on the development of alternative sources for transportation fuel. The current focus of the CFFLS program is C1 chemistry, which refers to the conversion of simple carbon-containing materials that contain one carbon atom per molecule into

valuable products. The feedstocks for C1 chemistry include natural gas, carbon dioxide, carbon monoxide, methanol and synthesis gas (a mixture of carbon monoxide and hydrogen). Synthesis gas, or syngas, can be produced by the reaction of natural gas (methane) with steam or carbon dioxide and by gasification of coal, petroleum coke, or biomass. Syngas is the feedstock for all methanol and Fischer-Tropsch plants and is the source of essentially all hydrogen (Wender 1996).

C1 chemistry is expected to become a major source of transportation fuel in the relatively near future. The CFFLS has formulated a

research program that emphasizes the synthesis of transportation fuel products from syngas and methanol, and the development of novel processes for the conversion of natural gas into syngas and hydrogen. Although the program has only been in place for a short time, a number of interesting results have been obtained and these are briefly summarized in this report.

Oxygenated Transportation Products

A major emphasis of the CFFLS C1 program is to develop catalytic processes for the production of oxygenated transportation fuel products from syngas or methanol. These oxygenated products can either be used directly as diesel fuel or as additives to diesel fuel or gasoline, raising cetane number while lowering particulate emissions. Accomplishments in this area are summarized below.

1. A continuous unit to produce oxygenated Fischer-Tropsch (FT) products has been constructed. A literature search to identify promising catalysts for synthesis of FT products containing large amounts of oxygenated material has been completed.
2. Dimethyl carbonate, which is promising as a diesel fuel or diesel fuel additive, has been synthesized using Cu/Pd chloride and acetate catalysts. At 180°C, the most successful catalyst was a mixture of CuCl₂ and PdCl₂. The acetate catalysts produced ~30-50% less DMC than the chloride catalysts (Figure 1), but also produced less of a dimethoxymethane by-product.
3. Reaction systems have been modified to facilitate the synthesis of higher alcohols from methanol and syngas. Mo/K/C catalysts will be used, initially.
4. Procedures have been developed to investigate the reactions of olefins and

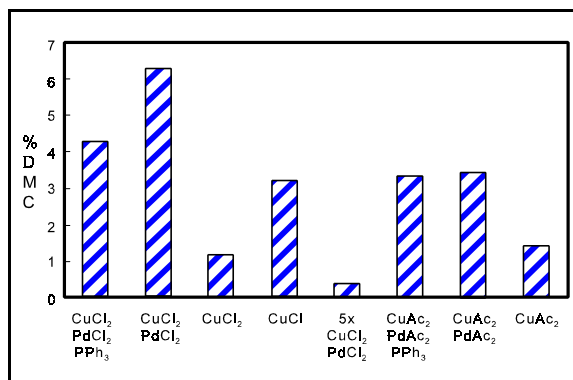


Figure 1. Comparison of Cu and Pd chloride and acetate catalysts for production of dimethyl carbonate

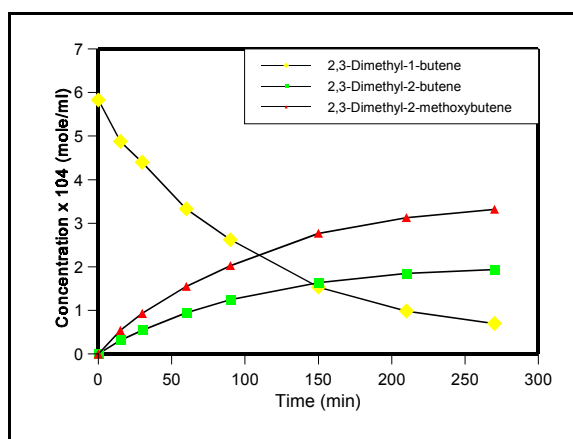


Figure 2. Reaction of methanol and 2,3-dimethyl-1-butene as a function of time. Temperature: 70°C; catalyst: Amberlyst 15, 1.5 wt. %

methanol to produce higher ethers. The reaction kinetics for the production of C7 ethers using an Amberlyst 15 catalyst have been measured as a function of time and catalyst loading. Typical results are shown in Figure 2.

Development of Novel Catalysts for Reforming and Hydrogen Production

Nanoscale, binary catalysts show promise for natural gas reforming and the water-gas shift and related reactions. Initially, this investigation has focused on the synthesis and

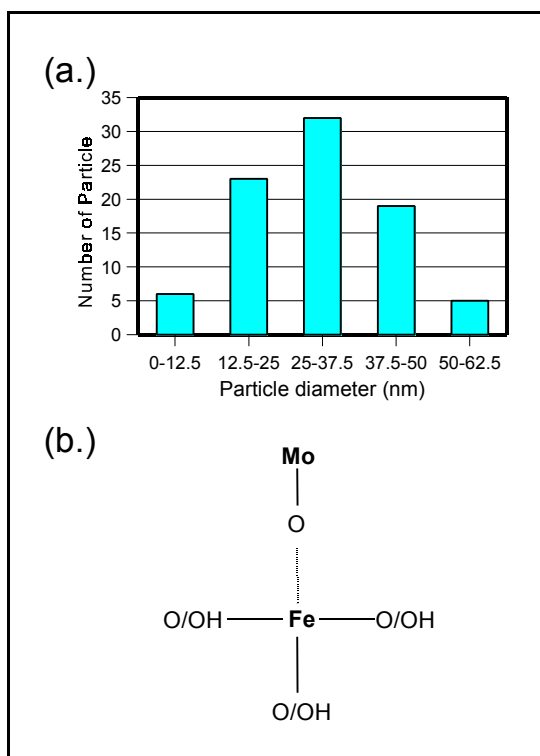


Figure 3. (a) TEM particle size distribution for FHYD/Mo catalyst. (b) Surface structure indicated by SQUID magnetometry and XAFS spectroscopy

structural characterization of a number of Fe-M catalysts, where M is a secondary transition metal and the relative concentrations are Fe/M @ 95/5. Such catalytic materials can be produced with a ferrihydrite (FHYD) structure by co-precipitation techniques. (Zhao et.al. 1994) In this project, FHYD catalysts containing approximately 5% of a variety of metals (Mo, W, Ni, Ru, Ir, Cr) have been prepared. The metals chosen are expected to be active for the reactions of interest: reforming and decomposition of methane, redox cycling of metal catalysts, methanol decomposition and the water-gas shift reaction.

Characterization data obtained to determine the structure of these catalysts has included x-ray diffraction (XRD), SQUID magnetometry (SM), transmission electron microscopy (TEM), and x-ray absorption fine

structure (XAFS) spectroscopy. These TEM and XRD data establish that the particle size distribution is in the nanometer range (Figure 3a), while the XAFS and SM data indicate that the secondary elements are concentrated at the surfaces of the particles (Figure 3b).

Consequently, such catalysts can present an extremely high surface area of an active metal, M, for C1 reactions.

In Situ Analytical Technique Development

The CFFLS analytical team has worked together extensively on a variety of problems. The current research emphasizes in situ analysis of catalyst structure and product distribution during C1 reactions. Progress in this area to date is as follows:

- A specially constructed, portable GC/MS system has been modified to enable direct coupling to a high temperature, medium-pressure, autoclave-type reactor for fast, repetitive, on-line monitoring of catalytic C1 reactions.
- A pulse quench reactor has been designed that will have the features of a micro reactor, including controlled flow or injection of reagents and temperature and pressure control. Quenching from up to 450°C to room temperature in <1 sec will trap phases in the catalyst bed for investigation by ¹³C NMR.
- A novel in situ XAFS spectroscopy cell has been designed. It will consist of a tubular reactor with an x-ray transparent beryllium window enclosing the catalyst bed, temperature and pressure control (up to 800°C and several hundred psig), mass flow controllers for reactant gases and liquids, and the portable GC/MS system mentioned above. A proposal to test and use this system at the Stanford Synchrotron Radiation Laboratory has been written and submitted.

Hydroisomerization Research

An environmentally clean catalyst for the hydroisomerization of a straight-chain alkane (e.g., n-hexadecane) has been used to obtain high conversions and selectivity to isomerized hexadecane. The latter are useful for low pour point diesel fuel as well as jet fuel and lubricating oil. Work on the hydroisomerization of C20-C40 alkanes, which are typical of FT products, has been initiated.

High value products from carbon dioxide

Thermodynamic equilibrium calculations for reactions of carbon dioxide (a global warming gas) with selected organic chemicals that contain a weak carbon-hydrogen bond have been initiated. It appears that metal oxide catalysts will be needed for this reaction. The goal is the reduction in the amount of carbon dioxide emitted to the air while simultaneously transforming a low value substance such as ethylbenzene to styrene, which is a high volume, high value chemical.

Industrial Advisory Board

A five member Industrial Advisory Board (IAB) is being formed to provide guidance to the CFELS C1 research program. The IAB will consist of one representative each from the following organizations: DaimlerChrysler

Corporation, Eastman Chemical Company, the Department of Defense (Wright Patterson AFB), Lyondell, and Chevron Corporation. A one day meeting to review of the program with the IAB is tentatively planned for November.

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List of Acronyms

CFELS	Consortium for Fossil Fuel Liquefaction Science
DMC	Dimethyl Carbonate
FHYD	Ferrihydrite
FT	Fischer-Tropsch
IAB	Industrial Advisory Board
SM	SQUID Magnetometry
TEM	Transmission Electron Microscopy
XAFS	X-ray Absorption Fine Structure
XRD	X-Ray Diffraction

III. ADVANCED FUELS FOR FUEL CELLS

III.A. Effects of Fuel Constituents on Catalytic Fuel Processor Performance

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Objectives

- Identify the major constituents, additives, and impurities in petroleum based fuels for fuel processor catalysts for automotive fuel cell application
- Identify the effects of these constituents on reformer performance
- Determine the effects of alternative fuels (methanol, ethanol, DME, Fischer-Tropsch liquids) on reformer performance

Office of Advanced Automotive Technologies R&D Plan, Fuel Cells: Task 3, Barriers B, E, F

Approach

- Analyze gasoline samples to identify fuel constituents, impurities and additives
- Investigate autothermal reforming of major constituents individually in microreactor
- Rate performance based on byproduct formation, catalyst deactivation, and dependence of hydrogen yield and conversion efficiency on temperature and residence time
- Test selected minor constituents, additives, and impurities by mixing with iso-octane

Accomplishments

- Built a microreactor for testing fuel constituents and obtaining kinetic information on fuel reforming
- Built a dedicated microreactor for long-term testing (up to 1000h)
- Identified major gasoline components for testing
- Initiated testing on major gasoline constituents
- Have accumulated over 100h of test time running with isooctane in long-term test reactor
- Initiated testing on Fisher-Tropsch liquids

Future Directions

- Continue investigation of reforming of gasoline constituents
- Investigate effects of detergents and impurities

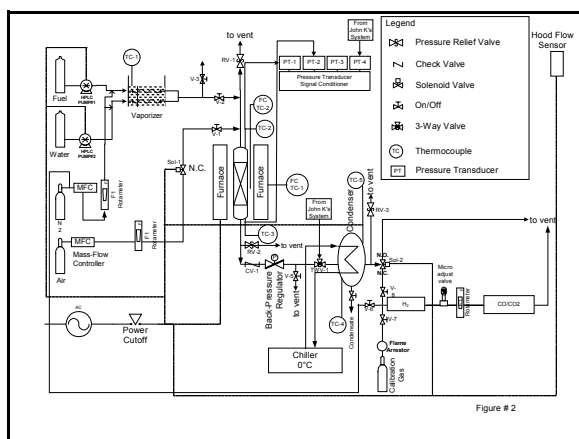


Figure 2. Schematic Diagram of Long-Term Test Reactor

Of the additives, detergents appear to have the most potential for causing problems for the reformer. MMT is not considered to be a problem since its use is limited and it is expected that its use will be totally phased out in the near future. The oxygenates are not expected to cause any difficulties for reforming since they are already partially oxidized. Ethanol has been tested in autothermal reformers previously and reforms well. MTBE is expected to perform well, however; due to the large concentration of MTBE in gasoline it will be tested in the current program. The refinery additives are present in very low concentrations, and do not contain functionality that is expected to poison the catalysts. Detergents are present at much higher levels than the refinery additives, have high molecular weights that may be difficult to breakdown, and contain amine groups that have the potential to poison the catalyst.

Impurities present in gasoline can also cause problems for the catalysts. The impurities include catalyst poisons such as heavy metals and sulfur. Metals such as lead are known poisons for petroleum reforming catalysts. The metals content is generally low, with individual metal content at sub ppm levels. At these levels they are not expected to be problematic. We are most concerned with sulfur. The average sulfur content of US

gasoline is 347 ppm, with 25% of the gasoline containing over 500 ppm sulfur, according to API reports. Of the gasolines shown in Figure 1, the California Certified Phase II gasoline contained 38 ppm sulfur, while the others contained 291 and 400 ppm sulfur. The sulfur is usually present in the form of benzothiophenes, thiophene and some sulfides, with the benzothiophenes generally accounting for the majority of the sulfur. Sulfur is a known catalyst poison, and poisons petroleum-reforming catalysts at levels above about 2 ppm.

We will determine the effects of gasoline constituents on reformer performance by analyzing the reforming of the major components (isooctane, isopentane, trimethylbenzene, toluene, MTBE) individually. The performance of the catalyst will be determined by the kinetics of conversion, presence of any undesirable side products, and any deactivation of the catalyst as seen by a drop in the desired products with time. The effects of minor constituents (naphthenes, olefins), detergents, and impurities (sulfur) will be determined by mixing these components with isooctane, then comparing the reforming of the mixture to that for pure isooctane.

Two microreactors have been designed and built. A long-term test reactor which will allow us to perform tests up to 1000h in duration and a short-term test reactor for fuel comparisons which will allow us to obtain mechanistic information. The long-term test reactor is designed for unattended operation. Safety interlocks are designed into the system to shut down the reactor for off-normal events such as temperature excursions or loss of hood flow. A solid-state hydrogen detector and an infrared carbon monoxide-carbon dioxide detector perform continual monitoring of the gas products. A schematic of the long-term test reactor is shown in Figure 2. The thinner

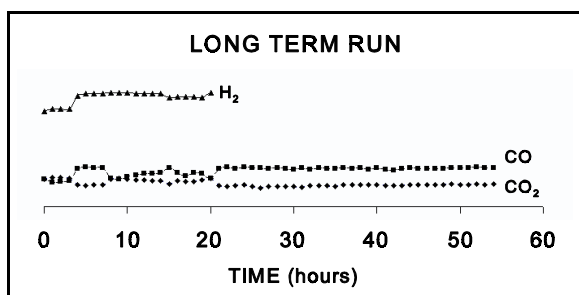


Figure 3. Long-Term Reactor Shows Steady Output

lines represent systems connected by the safety interlocks.

The reactor is now operating with isooctane to establish a baseline and determine whether the catalyst remains active for 1000h. We have currently accumulated over 100 h of testing with isooctane with no observable degradation in performance. Figure 3 illustrates the steady output and indicates no degradation in performance. The hydrogen detector failed after 20 h and is being repaired.

The short-term reactor is shown in Figure 4. The reactor has several sampling ports to sample the catalyst bed at different positions and residence times. The gas products are continually monitored by a quadrupole mass spectrometer. In addition, batch samples can be obtained for analysis by GC-mass spectrometry or the gas effluent can be directed to the solid state hydrogen detector and infrared CO-CO₂ detectors for the long term test reactor.

Experiments with the major gasoline constituents have been initiated. Isooctane (C8 isoparaffin) and trimethyl benzene (C9 aromatic) are currently being studied. Initial results suggest that coking may be a problem with trimethylbenzene under the conditions investigated.

We will continue to investigate the effects of major gasoline constituents on the

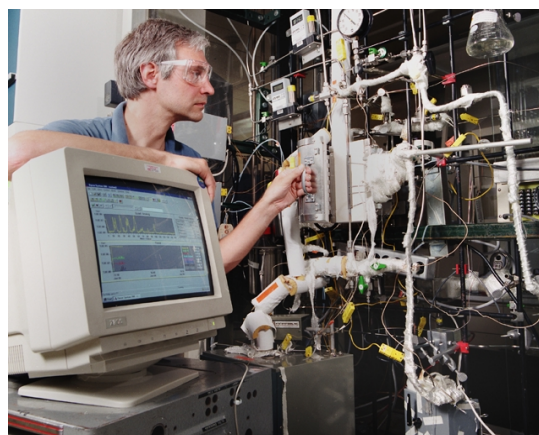


Figure 4. Short-Term Test Reactor for Fuel Comparisons

performance of the autothermal reforming catalyst. Future plans include obtaining mechanistic data for autothermal reforming of isooctane, isopentane, trimethylbenzene, toluene, and MTBE. We plan to begin investigations of the minor constituents and impurities in the coming fiscal year, focusing on mixtures of isooctane with detergent additives and sulfur impurities found in gasoline.

While this work has focused on the suitability of gasoline for fuel reforming, the results will be valuable in determining the suitability of other fuels as well. The mechanistic information should allow us to predict how different chemical species will behave, and help direct the designing of a fuel specific for fuel cells in the future. We have contributed to discussions on the choice of fuels for fuel cells and investigating alternative fuels as well. Towards this goal we have initiated an investigation of synthetic Fisher-Tropsch fuels.

List of Acronyms

DME	Dimethyl Ether
GC	Gas Chromatograph
MMT	Methylcyclopentadienyl Manganese Tricarbonyl
MTBE	Methyl Tertiary Butyl Ether

III.B. Sulfur Removal from Reformed Fuels

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Objectives

- Define maximum H₂S concentration for fuel processor and fuel cell catalysts.
- Identify candidate technologies for sulfur removal from reformat.
- Determine the appropriate operating parameters (e.g., H₂S equilibrium, sulfur loading, temperature, space velocity) to design the sulfur removal process.
- Evaluate the performance of the sulfur removal process in an integrated fuel processor system.

Office of Advanced Automotive Technologies R&D Plan, Fuel Cells: Task 3, Barriers B, E, F

Approach

- Thermodynamic calculations to estimate H₂S tolerance of fuel processor and anode catalysts (bulk sulfide formation) and to predict H₂S equilibrium partial pressure for candidate sulfur removal technologies.
- Modeling to identify key parameters governing performance and to predict lifetime and transient response associated with the sulfur removal process.
- Experimental work to verify design parameters and to evaluate process performance in an integrated system.
- Identify/resolve issues.

Accomplishments

- Constructed a microreactor test system designed to minimize H₂S loss to the plumbing.
- Identified operating parameters for a ZnO adsorption bed. Testing of the bed in the integrated reformer has begun.

Future Directions

- Better define the H₂S tolerance for the fuel processor and fuel cell system.
 - Continue experimental work to determine if ZnO will meet both the target H₂S concentration and the size/weight requirements for the automotive application.
 - Evaluate new/alternative technologies for H₂S removal.
-

Introduction

This report describes our technical progress in developing an efficient sulfur removal process to decrease the hydrogen sulfide (H_2S) content of reformat produced from sulfur-containing fuels, such as commercial-grade gasolines, to a concentration of 1 ppm or less. Recently, it has been reported (see reference 1) that H_2S irreversibly poisons the Pt in the anode electrode at a concentration of 1 ppm.

Sulfur is present in gasoline as organic sulfur, primarily as thiophene derivatives. The sulfur content of gasoline varies, depending on both the grade of gasoline and the region of the United States where it is sold. The average sulfur content for all grades of gasoline currently sold domestically is 347 ppm; however, certain grades can contain as much as 1000 ppm. During fuel reforming, this sulfur is converted to H_2S under the reducing conditions that exist in the reformer. The concentration of H_2S in the reformat (ppmv - volume basis) is approximately one-tenth the concentration of sulfur in the fuel (ppm - weight basis). Thus, the H_2S concentration will be 30-35 ppmv in reformat produced from gasoline with a sulfur content of 347 ppm.

Sulfur removal may also be needed to prevent sulfur poisoning in certain fuel processing catalysts. Hydrogen sulfide is known to poison many industrial catalysts, often at a concentration of 1 ppm or less. Commercial CuZnO water-gas shift catalysts being considered for use in fuel processing systems by some developers have a H_2S tolerance of 50 ppb.

Identifying Candidate Technologies for Sulfur Removal

The first phase of this project was to identify candidate technologies capable of reducing the H_2S concentration in reformat to less than 1 ppm under fuel processing conditions.

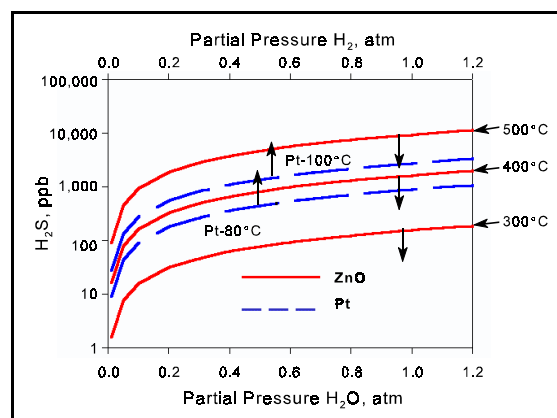
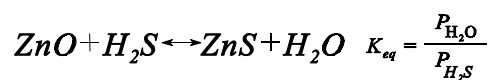


Figure 1. H_2S equilibrium partial pressure for ZnO/ZnS as a function of H_2O partial pressure and for Pt/PtS as a function of H_2 partial pressure

Adsorption with chemical reaction, the first technology we have investigated, involves the reaction of the H_2S with a solid (generally a metal oxide) that “traps” the sulfur by converting it into a stable metal sulfide. Integration of an adsorption bed into the fuel processor system should require no significant changes in the design or operation of the system, especially if no attempt is made to regenerate the absorbent on-board the vehicle.

Considerable research has been conducted to identify metal oxide adsorbents for removing H_2S from hot coal gases. After reviewing the literature, we have chosen ZnO as our initial candidate adsorbent. Commercial adsorbent-grade ZnO is available from various manufacturers.

The equilibrium between ZnO and H_2S is a function of the temperature and the ratio of the partial pressure of H_2O to H_2S :



(Equation 1)

Figure 1 compares the H_2S equilibrium partial pressure for ZnO/ZnS to the H_2S equilibrium partial pressure for Pt/PtS under typical fuel

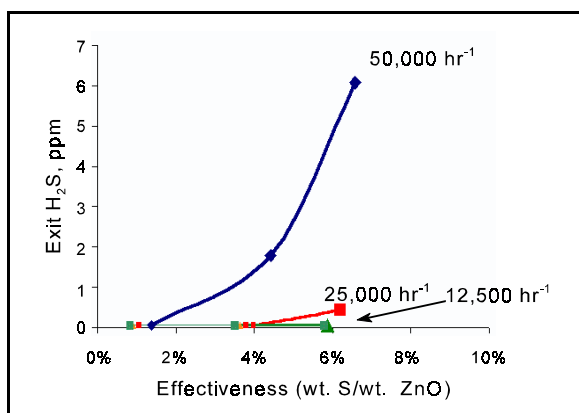


Figure 2. Effect of space velocity on effectiveness of ZnO to remove H₂S from reformat at a temperature of 300°C

processing and fuel cell operating conditions, respectively. The ZnO bed must operate at a temperature below 400°C in order to inhibit the conversion of Pt to PtS at an anode operating temperature of 80°C. The H₂S equilibrium partial pressure for Pt/PtS does not define the maximum H₂S concentration that the Pt-anode electrode can tolerate. The H₂S concentration limit can only be determined by experimental work; however, the Pt/PtS equilibrium does provide a “rough order of magnitude estimate” of the acceptable H₂S concentration.

Designing a ZnO Bed for Sulfur Removal

The rate of mass transfer of H₂S through the ZnO pellet and, to a lesser extent, the kinetic reaction rate determine the weight of ZnO required.

Operating parameters that influence the rate of mass transfer and chemical reaction include (1) the space velocity of the reformat through the bed, (2) the operating temperature of the bed, (3) the sulfur content of the fuel, and (4) the sulfur loading of the bed. Since the fuel processor will operate under varying loads (in terms of fuel cell power output), these parameters will vary depending on the processing load and the sulfur content of the fuel. In general, the sulfur removal efficiency of

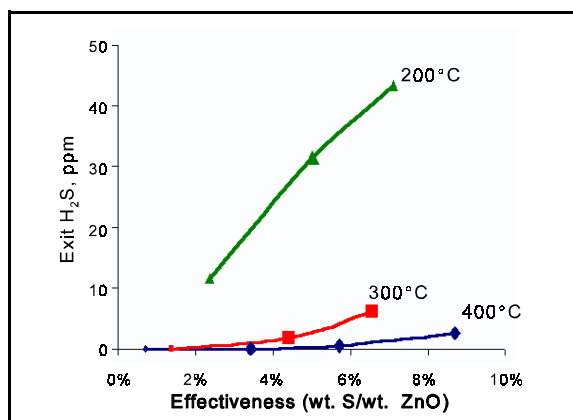


Figure 3. Effect of operating temperature on effectiveness of ZnO to remove H₂S from reformat at a space velocity of 25,000 hr⁻¹

ZnO decreases if either the space velocity increases (Figure 2), the bed operating temperature decreases (Figure 3), or the inlet H₂S concentration increases (not shown) for a given ZnO sulfur loading.

Other factors that influence the rates of both mass transfer and chemical reaction involve changes in the physical properties of the ZnO pellets with increasing sulfur loading. These factors depend more on the past operating history of the fuel processor than on current conditions.

To size the ZnO bed for fuel processing using commercial grade ZnO adsorbents, the manufacturer recommends a space velocity range of 700-3000 (v/v) hr⁻¹ and a bed operating temperature of 340-400°C for maximum bed efficiency. Table 1 shows the estimated ZnO bed sizes and performance for two design cases: an average power of 10 kW_e and a maximum peak power of 50 kW_e. For the 50-kW_e design case, the ZnO bed size is too large, given the target volume for the entire fuel processing system. For the 10-kW_e design case, at a space velocity of 3000 hr⁻¹, both the weight of ZnO required and expected lifetime of the bed may be acceptable. Transient operation of this bed at much

Table 1. Estimated ZnO bed sizes required to reduce H₂S concentration to less than 1 PPM as a function of space velocity at design power levels of 10 and 50 kWe

Space Velocity (hr ⁻¹)	10 kWe-Average			50 kWe-Peak			Sulfur Loading (w/w%)
	Volume (L)	Weight (kg)	Life Time (gals) ¹	Volume (L)	Weight (kg)	Life Time (gals) ¹	
1,500	11.7	14.6	4,000	58.7	73.3	20,000	25
3,000	5.9	7.4	1,500	29.3	36.6	7,200	18
15,000	1.2	1.5	65	5.9	7.3	318	4

¹ - Based on 347 ppm S/gallon of gasoline- Conditions: Bed Temperature=400°C; H₂O Inlet=10-15 mole %; H₂S Exit=<1 ppm

greater power, ranging up to 50 kWe, would decrease the expected bed lifetime; however, to what extent the lifetime is decreased is not known. A mathematical model is being developed to predict the effect of transient operation on the lifetime performance of the 10-kWe bed.

A microreactor system has been constructed to conduct scoping experiments to evaluate various candidate technologies for sulfur removal, to define the appropriate operating conditions, and to measure the physical and kinetic parameters necessary to design and predict the long-term performance of selected sulfur removal technologies. Some key features of this reactor system are (1) the use of silica-coated steel tubing and fittings to minimize loss of H₂S in the plumbing and (2) on-line gas analysis capable of detecting H₂S at concentration levels below 1 ppm. Currently experiments are in progress to measure the rate of H₂S removal by ZnO under transient conditions (e.g., varying space velocity, inlet H₂S concentration, and temperature). The data from these experiments will be used to validate the mathematical model.

Future Work

Future work is directed at improving the

performance of ZnO by increasing its effectiveness at higher space velocities (~10,000 hr⁻¹). The objective of this work is to minimize the reduction in bed lifetime due to transient operation at power outputs well above the bed design power rating. In addition, work is continuing on identifying alternative technologies to metal oxide adsorption for H₂S removal that will improve the rate of removal or significantly reduce the weight/size of the process unit.

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List of Acronyms

H₂S Hydrogen Sulfide
 ppm Parts per Million (weight)
 ppmv Parts per Million (volume)
 Pt Platinum
 PtS Platinum Sulfide
 ZnO Zinc Oxide

III.C. Fuel Composition Effects on Fuel Processing Dynamics for Fuel Cell Applications

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Objectives

- Improve understanding of fuel processor catalyst performance including catalyst degradation mechanisms from various fuels or fuel constituents through combination of modeling and experiments to include:
 - Dynamics of chemical processes occurring during oxidation, hydrocarbon reformation, shift and methanation using catalysts with carefully controlled fluid dynamic test conditions.
 - Evaluation of new and previously-used catalysts to determine variation in rates and reaction mechanisms during life, to evaluate durability.
 - Evaluation of short-residence-time reaction events, supporting unique fuel processor designs and concepts.

Office of Advanced Automotive Technologies R&D Plan, Fuel Cells: Task 3, Barriers B, E, F

Approach

- Investigate the effects of varying fuel constituents and contaminants within candidate fuels.
- Understand and document catalyst performance through a range of relevant experimental conditions chosen to replicate anticipated fuel-processing regimes.
- Replicate experiments using new and partially spent catalyst samples, for example catalysts previously used for POX and PROX experiments.

Accomplishments

- Analysis, fabrication and testing of a new instrument including unique catalyst test sample holder features.
- Evaluation of kinetic vs. equilibrium data for candidate catalysts for POX, shift and PROX sections.
- Identification of a new PROX catalyst formulation with limited tendency to promote methanation.

Future Directions

- Complete automation of test fixture, including automation of reactant mixture flow control and of sample injection.

- Evaluate unique catalyst samples with appropriate geometry to replicate short-residence-time processes and with tagged constituents for study of exchange reactions.
- Evaluate fuel processing samples obtained from 50-kW hardware to learn mechanistic details causing altered kinetics and lifetime.

Introduction

This report covers technical progress during FY99 on fuel processing catalyst characterization. These development efforts support DOE activities in the development of compact, transient capable reformers for on-board hydrogen generation starting from candidate fuels of methanol, ethanol, propane and reformulated gasoline. The long-term objective includes increased system durability and lifetime, in addition to smaller volume, improved performance, and other specifications required to meet fuel processor goals.

The technical barriers of CO poisoning, compact fuel processor size, transient capability, and compact, efficient thermal management all are functions of catalyst performance. Significantly, work at LANL now tests large-scale fuel processors for performance and durability, as influenced by fuels and fuel constituents. It is one objective

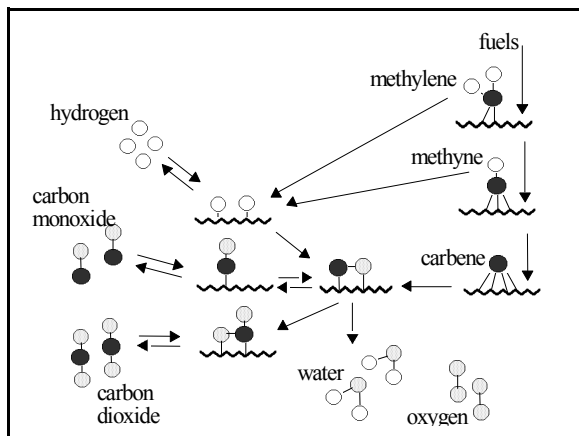


Figure 1. Fuel processing chemistry involves hydrogen abstraction from fuels, resulting in a carbene-adduct, which reacts with oxygen to form carbon oxides

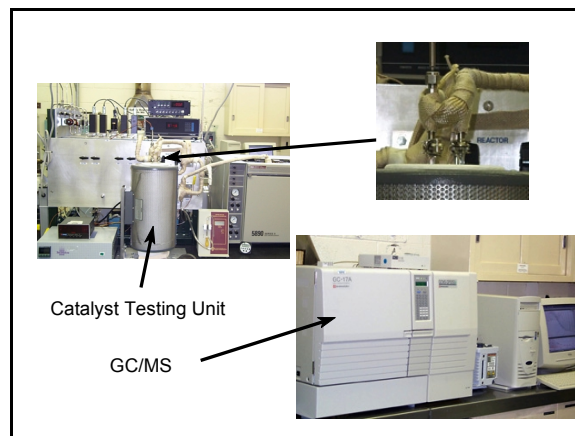


Figure 2. Instrumentation used for these catalyst dynamic studies

of this study to develop new diagnostic tools that permit molecular description of changes in catalyst performance on the hydrogen generation (reforming), shift and PROX stages.

Fuel Processing Dynamics

The chemical processing of fuels is the result of a complicated set of gas phase and surface reactions. Useful routes, suggested in Figure 1 involve sequential methylene oxidation with chain scission resulting in the desired products of hydrogen and carbon oxides. Conditions which result in concentration of methylene-like intermediates may also lead to formation of soot and other undesired pathways. Prompt methylene removal conditions rely on oxygen exchange reactions, between oxygen sources adsorbed on catalyst surfaces and carbon species. We suspect that useful catalysts are those which promote the oxygen exchange step, resulting in rapid hydrogen-generation rates. Moreover we suspect that catalysts which have been degraded by a variety of mechanisms will tend to show decreased

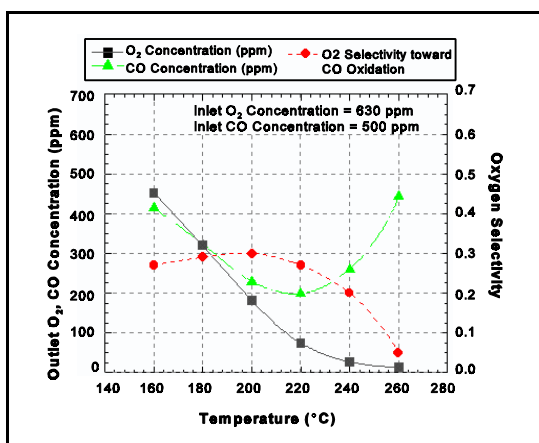


Figure 3. CO oxidation on Pt-alumina catalyst showing results with an inlet concentration of 500 ppm CO

facility in this regard. The initial experiments described here are selected to evaluate the “oxygen-exchange” component of the reaction mechanisms. The fact that these reactions are also those that occur in the shift zones and PROX zones is apparent. Experiments are done at different temperatures and with different catalysts to evaluate performance. These investigations support the entire ongoing LANL fuel processing endeavors.

Considerable effort was spent to design, fabricate and evaluate the sample holder. The holder is made to accommodate precise catalyst sections formed either as pieces of catalyzed monoliths/foams, screens or thin layers of powders. The holder assures well mixed, temperature controlled laminar flow which is exposed to the catalyst.

Reactant gaseous sample mixtures, chosen to replicate the reacting gaseous stream at specific sampling locations, are formed by on-line blending of steam, hydrogen, carbon dioxide, carbon monoxide, nitrogen, etc., and then the requisite mixture is heated prior to entering the catalyst holder. Experiments involve conversion of a specific sampling mixture or conversion of a specific component following pulsed injection prior to the sample holder.

Results using three catalyst samples are described in this report. These are 1.) 0.5 wt % Pt on Al₂O₃, 2.) 0.5 wt % Ru/Al₂O₃ and 3.) 5.0 wt % Ru on C. 40-mg samples diluted with 160-mg alumina were utilized, except the Ru/C sample was 10-mg catalyst. These catalysts are those used previously during PROX development, and therefore quantities of new and previously utilized samples are available. For the experiments described here the test gas mixture was 36% H₂, 29% N₂, 17% CO₂ and 17% H₂O, a mixture selected to replicate a reformat stream generated from

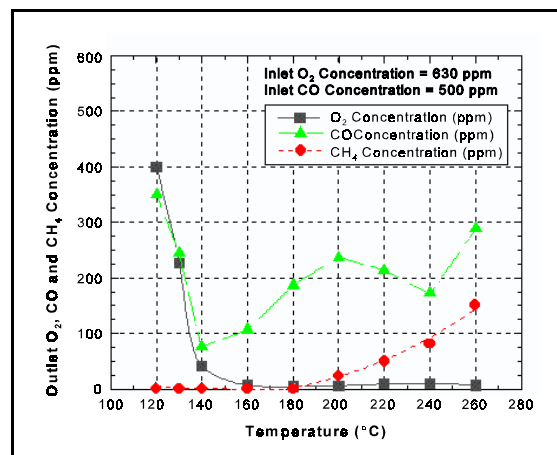


Figure 4. CO oxidation of Ru/alumina catalyst, showing results with inlet concentration of 500 ppm and oxygen stoichiometry of 2.5

gasoline. Variation of the sample flow rate allowed change in the residence time during these catalyst tests.

The reactions of interest in these experiments are CO oxidation, H₂ oxidation, the shift reaction, and methanation. Both CO oxidation and methanation, $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$, are useful for CO elimination during processes such as PROX, selected to clean up the hydrogen fuel mixture by removal of carbon monoxide. The data shown in Figure 3 summarize results obtained using a 500 ppm CO inlet concentration mixed into the test mixture including oxygen at a stoichiometric

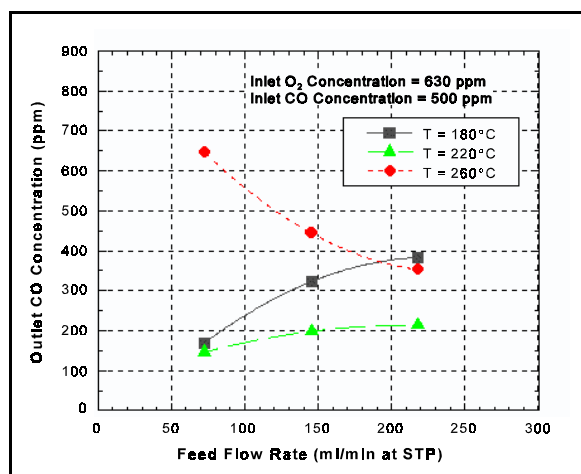


Figure 5. Effects of residence time on CO conversion on Pt/Al₂O₃ surfaces

ratio of 2.5, or oxygen at 625 ppm. (A stoichiometric ratio of 1.0 adds just sufficient oxygen to convert all the CO to O₂-which would require 250 ppm of O₂ in this case.) The curve shows data through the temperature range of 160°C to 260°C. Samples were diluted with inert alumina to decrease the volumetric heat generation rate, resulting in conditions where only small temperature increases occur across the catalyst sample. At lower temperatures oxygen converts CO successfully. At higher temperatures considerable selectivity is lost and the reverse shift reaction generates CO as well, an adverse result. These experimental conditions are selected to evaluate catalyst performance, not to remove CO sufficiently to achieve good fuel cell performance, as is done in the PROX section.

A different result is apparent when conducting the same test operation on Ru/Al₂O₃ surfaces. Those data are shown in Figure 4, repeating the reaction condition of 500 ppm CO with a 2.5 oxygen stoichiometry. The ruthenium catalyst reacts at lower temperature and at that temperature consumes oxygen more efficiently than does platinum. Hydrogen and carbon dioxide both remove oxygen from catalyst sites to form water and carbon dioxide. The lowest measured CO concentration occurs

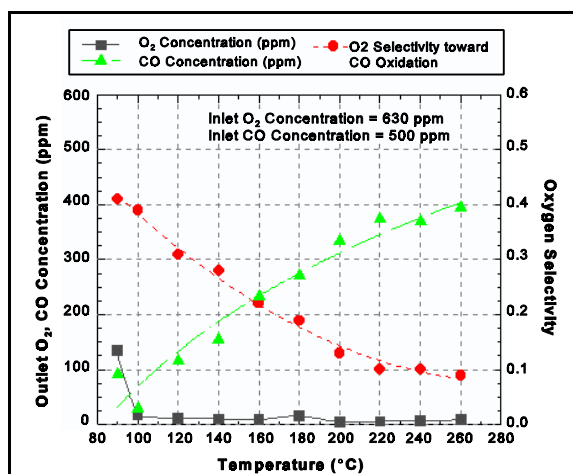


Figure 6. CO control on Ru/C catalyst surfaces

when CO oxidation is fast compared to hydrogen oxidation. As temperatures increase, > 160°C, both the reverse shift process and methanation interact to yield a complex CO pattern. At elevated temperatures methane is generated resulting, for instance, in a 150 ppm methane concentration at 260°C. This methane is in addition to any which "slips" from the fuel processor section.

Compact fuel processors involve short-residence-times designs, reactors with geometry selected for kinetic reaction control. (The PROX work done at LANL is an example of such a design approach.) Therefore this test fixture is also designed to evaluate the effects of flow rates on conversion. The first experiments to illustrate those effects are shown here as a variation in sample flow rate (see Figure 5). As the flow rate increases, a sample molecule experiences catalyst surfaces for a shorter time, so the residence time can be varied in this way. Interesting and significant effects are apparent. These data permit identification of processing conditions for a variety of catalyst systems. Design parameters include the oxygen stoichiometry, strategies for oxygen addition, catalyst type and surface area, entrance temperature, residence time and thermal management.

This report also illustrates effects of varying the nature of the support material. Figure 6 shows data again for a catalyst composed of Ru but supported on graphite, contrasted to a metal oxide support. The results show even more rapid oxygen depletion at low temperature, $< 100^{\circ}\text{C}$. At such low temperatures catalyst selectivity toward carbon monoxide oxidation is high, but selectivity is lost with increasing temperature. This catalyst system is remarkable in that no evidence of methanation is observed—even at a temperature of 260°C , methane is not detected, a concentration level below 10 ppm.

These data on various catalysts are not intended to endorse any one specific catalyst for any section of the on-board reforming hardware. Rather they show new facility

within DOE's OAAT program to understand catalyst reactivity. Moreover these new experiments allow facility for rapid evaluation of catalyst reactivity for any of the significant steps in the fuel-processing event.

FY2000 Technical Plans

We will extend capability for characterization of reactivity, looking both at new catalyst types, new reactor designs, and at catalysts which have been used with specific fuels and fuel constituents. Of interest is to understand the consequence of carbon deposition processes on catalyst surfaces, such as could result of PROX catalysts following unplanned soot-forming conditions in up-stream processing units.

IV. NATURAL GAS

IV.A. Lower Cost Composite Materials for CNG Storage

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Objectives

- Identify technologies and develop methods that will reduce the cost and increase safety in composite over-wrapped compressed natural gas (CNG) fuel tanks for light duty vehicles.

Office of Advanced Automotive Technologies R&D Plan, Fuels, Compressed Natural Gas: Task 1; Barrier A

Approach

- Assess current state-of-the-art and identify potential improvements
- Evaluate these improvements in terms of structural performance and manufacturability

Accomplishments

- Identified the major cost element of manufacturing composite CNG fuel tanks was the raw material cost of the carbon fiber. Cost analysis showed that this was 40% of the total tank cost.
- Identified large tow-size (50,000 filaments) carbon fiber as a potential improvement. The cost of large tow-size carbon fiber is approximately ½ the cost of conventional tow-size carbon fiber.
- Developed manufacturing processes and test procedures for large tow-size carbon fiber.
- The as-manufactured performance of large tow-size carbon fiber is currently being evaluated to ensure safe design margins.

Future Directions [All transportation-related natural gas R&D is being consolidated under the Office of Heavy Vehicles]

- Complete performance evaluation of large tow-size carbon fiber composites for stress rupture of sub-scale pressure vessels.
- Provide results from completed durability test matrix on large tow-size carbon fiber composites to GRI contractees.

Introduction

Compressed natural gas (CNG) is an alternative fuel that is stored under high pressure (3600 psi) on the vehicle. The use of natural gas as an alternative fuel in automotive applications is not widespread primarily because of the high cost and durability of carbon fiber composite storage tanks and the widespread availability of refueling stations. Carbon fiber composites are relatively expensive because of the raw material cost of the carbon fiber, which accounts for approximately 40% of the total tank cost. By introducing large tow-size carbon fiber in the tank design there is the potential for a tremendous cost savings. The cost of large tow-size carbon fiber is approximately one-half the cost of conventional tow-size carbon fiber. However, not all of this savings is realized in the final overall tank cost because of the lower fiber strength and lower strength translation that has been demonstrated in large tow-size carbon fiber composite structures.

Tank Manufacturing

Composite CNG tanks are typically fabricated using the wet-filament winding process. This is a process where the fiber tow is passed through a resin bath to impregnate the tow and then wrapped around a mandrel prior to curing in an oven at elevated temperature. The Akzo Fortafil 3(C) large tow-size carbon fiber was selected for evaluation based on the vendor-reported impregnated strand tensile strength and the fiber's processing characteristics. It was determined from process trials that modifications to the manufacturing method were required when using the Akzo large tow-size carbon fiber. A typical process trial fabrication set-up is shown in Figure 1. The modifications consisted of increasing the fiber tension, pulley diameters, and bandwidth, and modifying the type of compaction used. The bandwidth is the amount of tow advance per one revolution of

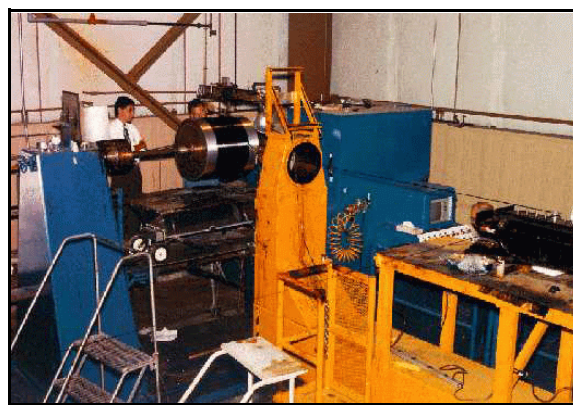


Figure 1. Process Trial for Wet-filament Winding of Large Tow-size Carbon Fiber Composite

the mandrel. Composition data for fiber, resin, and void content from nine process trials were inconclusive and it was determined that additional process trials were needed to achieve the high fiber content and low void content that are achievable with the standard tow-size carbon fiber. Cylinder fabrications for machining the ring specimens were completed using the processing parameters of 25 to 30-lbs. of fiber tension, 20 lbs. of compaction, and a 0.442-inch bandwidth.

Performance Evaluation

Performance of the Akzo large tow-size carbon fiber was evaluated to determine any design impacts that would prohibit their introduction into the fabrication process of CNG storage tanks. The evaluation was based on completing a durability test matrix. The tests consisted of impregnated strand, composite ring, and sub-scale pressure vessel tests for static strength, fatigue, and stress rupture. The static strength data were needed to ensure that the design safety factor of 2.25 on burst pressure was met, whereas the fatigue and stress rupture data were used to estimate reliability over the lifetime of the tank for refueling cycles and time under constant internal pressure loads.

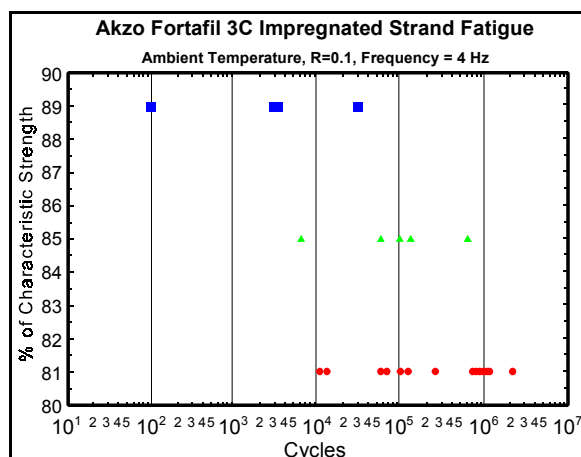


Figure 2. Large Tow-Size Carbon Fiber Strand Fatigue Data

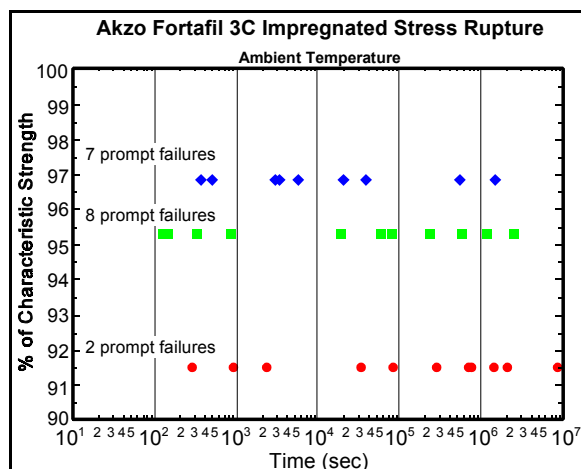


Figure 3. Large Tow-Size Carbon Fiber Strand Stress Rupture Data

New test methodologies were developed for testing large tow-size impregnated strands and composite rings under tension-tension fatigue loading. The highest impregnated strand tensile strength was measured when specimens were fabricated using a 0.114-inch orifice and then potting the ends of the strand with a high elongation epoxy. This technique was also successful for conducting the strand tension-tension fatigue tests. Fatigue data for large tow-size carbon fiber are plotted in Figure 2 as a percent of characteristic strength versus cycles to failure. The characteristic strength was determined from the static tensile

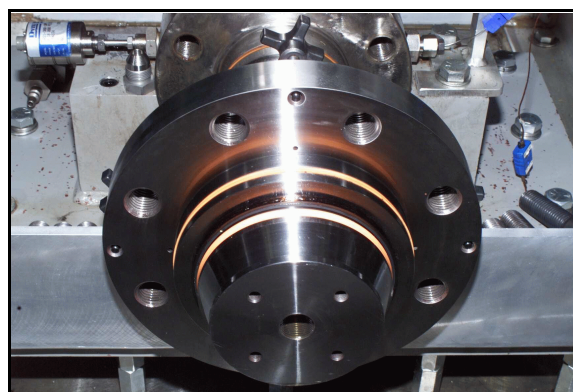


Figure 4. Hydro-Burst Test Fixture for Conducting Composite Ring Fatigue Tests

tests and a Weibull analysis of the data. The stress rupture data are presented in Figure 3 where the percent of characteristic strength is plotted as a function of time to failure.

In the characterization of filament-wound composite materials, rings are typically fabricated as test specimens for measuring the in-plane tensile strength in the hoop direction. Composite ring hoop strengths are commonly determined by using a method (split-d or NOL) that produces significant bending stresses in the specimen. In tension-tension fatigue these bending stresses become even more critical. To eliminate the bending stresses, a hydro-burst test fixture was designed for conducting the static and fatigue tests on the Akzo large tow-size carbon fiber composite rings. This fixture, as shown in Figure 4, loads the ring by internal pressure using hydraulic fluid. Work is in progress for completing the ring tests by the end of FY 99.

Publications

Publications based on this work are planned as follows:

- Final report in December 1999.
- Technical paper at the SAE/DOE Future Car Congress in April 2000.

List of Acronyms

CNG Compressed Natural Gas

GRI Gas Research Institute

NOL Naval Ordnance Laboratory

SAE Society of Automotive Engineers

IV.B. Onboard CNG Storage Tank Diagnostic System

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Objectives

- Apply existing sensor technology for achieving cost-effective, in-service non-destructive evaluation (NDE) that is a reliable indicator of developing hazardous conditions in CNG composite fuel tanks

Office of Advanced Automotive Technologies R&D Plan, Fuels, Compressed Natural Gas: Task 4; Barriers A & C

Approach

- Complete a review and evaluation of previous related work, including historical failures and inspection techniques for composite pressure vessels
- Identify the critical damage type and candidate sensor technologies
- Conduct laboratory demonstration tests

Accomplishments

- Completed literature survey and identified impact as the critical damage type
- Identified embedded fiber optic sensors and modal analysis techniques as candidate technologies for in-service non-destructive evaluation (NDE) of CNG composite fuel tanks
- Completed laboratory demonstration tests on a composite panel and a composite CNG fuel tank that was supplied by Lincoln Composites
- Successfully demonstrated two non-destructive diagnostic techniques that, with further development, have the potential for "smart" onboard inspection of NGV composite tanks

Future Directions

[All transportation-related natural gas R&D is being consolidated under the Office of Heavy Vehicles]

- Develop manufacturing processes for embedding fiber optic sensors.
- Determine damage criteria for an "unsafe" tank condition

- Manufacture prototype composite tanks and conduct field demonstrations

Introduction

Carbon fiber composites are prone to impact damage that over the life of the CNG storage tank may lead to an unsafe condition for the vehicle operator. Normal degradation over time of a composite CNG tank, as it relates to structural integrity, durability, and expected service life, is accounted for by the design qualification standards. However, unexpected and/or unforeseen damage can occur that may render the tank unsafe for future refilling. To date, no reliable, cost-effective technique has been demonstrated for in-service NDE that could warn of a developing hazardous condition (this is commonly called "smart" tank technology). Two techniques that potentially may be a reliable indication are embedded fiber optic sensors and modal analysis.

Fiber Optic Sensors

Several embedded fiber optic sensing techniques have been developed for composite structures, where optical fibers act as transducers sensing changes in light amplitude, frequency, and time-delay. These changes can be accurately correlated to

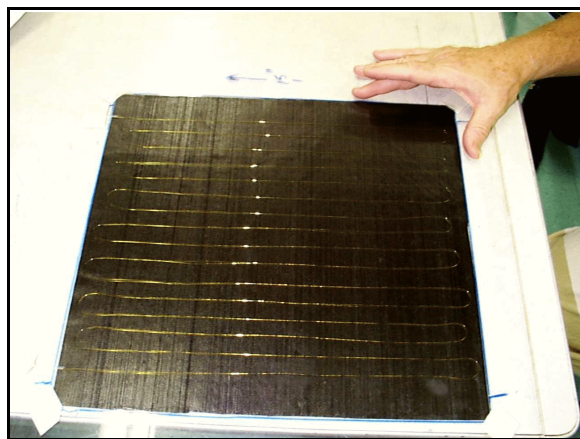


Figure 1. Pattern of Fiber Optic Embedded in Composite Panel

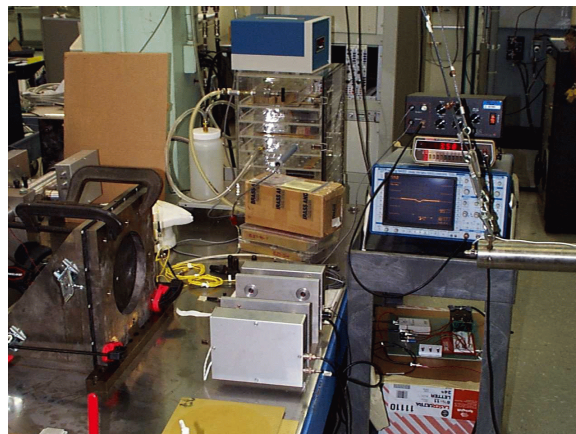


Figure 2. Ram Impact Experimental Set-up

physical phenomena such as strain, pressure, and temperature, depending on the configuration and sensing technique employed.

The feasibility of using embedded fiber optics in composites as a NDE method for detecting impact damage in high-pressure natural gas fuel composite cylinders was demonstrated by a series of laboratory experiments. Two different structures, a nominal 35 cm by 35 cm, 24 layer, composite panel and a NGV Fuel Container supplied by Lincoln Composites, a division of Advance Technical Products, Inc., were used to evaluate the various fiber optic techniques being considered.

An optical fiber was embedded in a serpentine pattern within the composite panel (see Figure 1) and the strain in the panel was evaluated using a simple low-cost light output and detection circuit as well as an optical time domain reflectometer (OTDR). Also, embedded with the composite panel was a fiber-optic Fabry-Perot strain gage system. The panel was tested in a cantilever beam set up both before and after subjecting the panel to impact damage. Conducting a ram impact experiment produced the impact damage. The

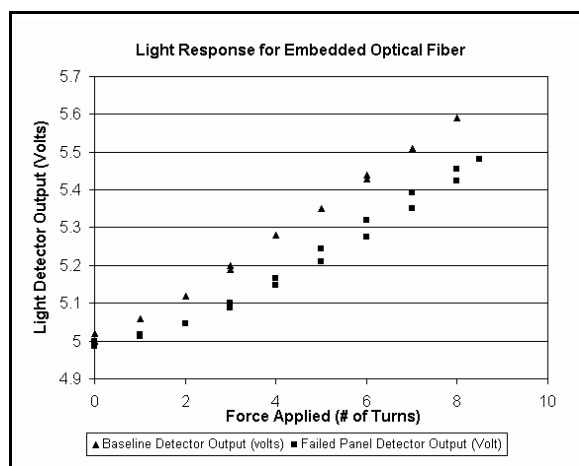


Figure 3. Detector Response Measured for Baseline and Failed Composite Panel

experimental set-up, as shown in Figure 2, consisted of a vertical-mounting fixture to secure the composite panel, and a ram device to impart an impact force on the composite panel. The ram device was designed such that it could be raised to some vertical height above the contact point on the panel then allowed to swing in a pendulum motion to contact the panel.

In Figure 3, the results from both the as-built or baseline panel and the same panel after being damaged in the ram impact test are plotted. The data measured by the light output and detection circuit indicated a change in the system response due to the panel damage. A simple light input and detection circuit similar to this could be used to monitor the time history of a composite structure, in this case a NGV composite fuel tank.

The Lincoln Composite NGV all composite fuel tank was over-wrapped with approximately 110 meters of glass-on-glass 100/140 Teflon-coated optical fiber which mimicked the wrap pattern of the carbon composite. Two pressurization tests were completed where the fiber length was measured first at atmospheric pressure and then at incremental pressure increases of 3450

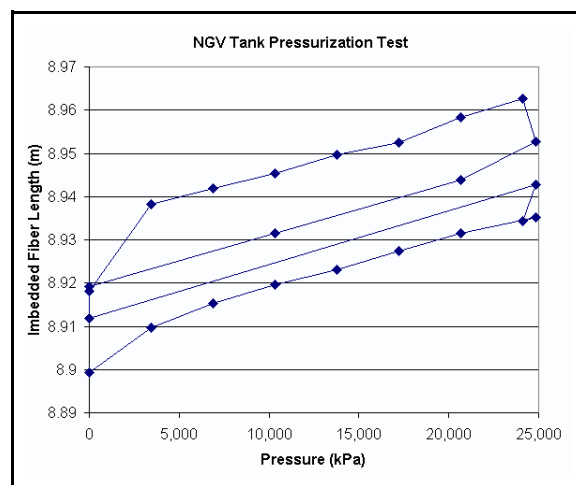


Figure 4. Plot of the Measured Fiber Length During the Tank Pressurization Test

kPa (500 psig) until the maximum operating pressure of 24,820 kPa (3600 psig) was reached. The pressure was then reduced incrementally back to atmospheric pressure. Figure 4 shows a plot of the measured fiber length during each pressure cycle. Note that for each pressure cycle the slope remains essentially constant. Changes in the slope would be the indicator of any change in the condition of the NGV composite tank. Thus, by monitoring the slope of the pressure versus fiber length in association with structural tests on the tank, one can establish limits on the change in the slope allowed for maintaining certification of the vessel under operating conditions. Additional work is needed to quantify the results and correlate various levels of impact damage with changes in measured fiber length. An accept or reject criteria could then be established.

Modal Analysis

In the modal analysis technique, structural modal parameters are used as global indicators of complete structures including composite cylinders. The modal parameters such as natural frequency and damping can characterize the health or structural integrity of a component and may be used to detect defects in the material. Modal parameters may

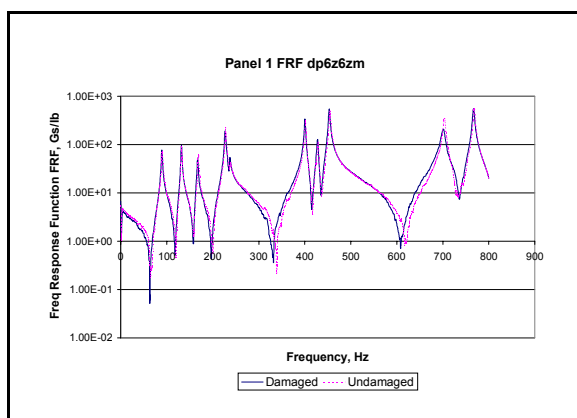


Figure 5. Modal Analysis Results for Composite Panel

not be able to determine the exact location of the defect, but studies have shown that the defect size in composite materials can be correlated with changes in natural frequency and damping. These parameter changes (from baseline) are used to identify defects in the material.

Modal tests and analyses were completed on the same undamaged and impact damaged panel used in the fiber optic sensor study. A plot of the frequency response function is shown in Figure 5 comparing the damage and undamaged responses. The resonant

frequencies and damping were determined and the results indicated that the damaged panel had slightly lower peaks for certain deformation modes and that the resonant frequencies shift downward with damage. Overall, the results showed that the damping parameter could be used to discriminate between damaged and undamaged panels for certain damage levels. However, the frequency shift was not a strong indicator of damage.

Publications

Publications based on this work are planned as follows:

- Technical paper at the SAMPE/ACCE/DOE First Automotive Conference, Detroit, MI, September 27-28, 1999.
- Final Report, September 1999.

List of Acronyms

CNG compressed natural gas
 NDE nondestructive evaluation
 NGV natural gas vehicle
 OTDR optical time domain reflectometer

IV.C. Natural Gas Homogeneous Charge Combustion Ignition Engine R&D

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Objectives

- Obtain controlled low emissions, high efficiency operation of homogeneous charge compression ignition (HCCI) engines.
- Advance our analysis techniques to learn the fundamentals of HCCI combustion and to make accurate predictions of combustion and emissions.

Office of Advanced Automotive Technologies R&D Plan, Fuels, Compressed Natural Gas: Task 5; Barrier C

Approach

- Conduct experiments on a single cylinder Coordinating Fuels Research (CFR) engine and on a 4 cylinder Volkswagen TDI engine to evaluate startability and control strategies.
- Develop and use single zone and multi-zone chemical kinetics models for analysis of HCCI combustion.

Accomplishments

Part 1. Analysis

- Extensively modified the chemical kinetics code HCT (Hydrodynamics, Chemistry and Transport) for application to engines by including models for heat transfer, internal EGR and supercharger/intercooler. The HCT code was developed at LLNL and has been extensively validated. Current runs use a chemistry set with 179 species and 1125 reactions (includes C1 - C4 and NO_x chemistry).
- Chemical kinetics model has been successfully used to predict start of combustion, NO_x emissions, sensitivity of engine operation to fuel composition, and acceptable operating conditions.
- An HCCI engine performance map has also been predicted with the HCT model. The performance map was used along with a vehicle analysis code to calculate fuel economy, emissions and performance, obtaining very promising results of 52 mpg combined cycle fuel economy, 0.0011 g/mile combined cycle NO_x emission (1/64th of Federal Tier 2), and 0 - 60-mph acceleration in 10 seconds.

Part 2. Experimental

- Single cylinder CFR engine has been modified and fully instrumented for HCCI operation. The engine is currently generating data that will be analyzed in the near future.
- The single cylinder engine has been run with a heater in the intake and with variable amounts of DME (dimethyl ether) and natural gas as possible control strategies.
- The four cylinder TDI engine has been delivered to the engine laboratory, and it is currently being modified and instrumented for HCCI operation.

Future Directions [All transportation-related natural gas R&D is being consolidated under the Office of Heavy Vehicles]

- The analytical and experimental work is dedicated to achieve controlled combustion out of an HCCI engine. Possible methods of HCCI engine control that will be analyzed include the use of

additives (DME, diesel, etc.), inlet heating, EGR, and exhaust throttling.

- We will convert Volkswagen TDI engine to HCCI operation. To achieve satisfactory operation, we will apply lessons learned from CFR engine testing and results from analysis to multi-cylinder engine control.
- We will also use our analytical capabilities and experimental facilities to achieve a satisfactory method of starting the engine under any environmental condition that may exist.
- We will expand our analytical capabilities to improve our predictions of HCCI combustion and emissions, and to reduce the computer resources necessary to make a run.

Introduction

This work supports the need to develop a new combustion concept that allows both high efficiency and low emissions for light duty vehicles, trucks and SUVs. The high efficiency of diesel engines is highly desirable; however, diesel engines are well known as significant sources of NO_x and particulate matter emissions. The use of Homogeneous Charge Compression Ignition (HCCI) combustion systems represents a promising approach that needs further research and development. Current plans focus on natural gas as a clean fuel with a developing infrastructure. Gaseous fuels also mix very quickly with air, avoiding the potential of having non-homogeneous mixtures.

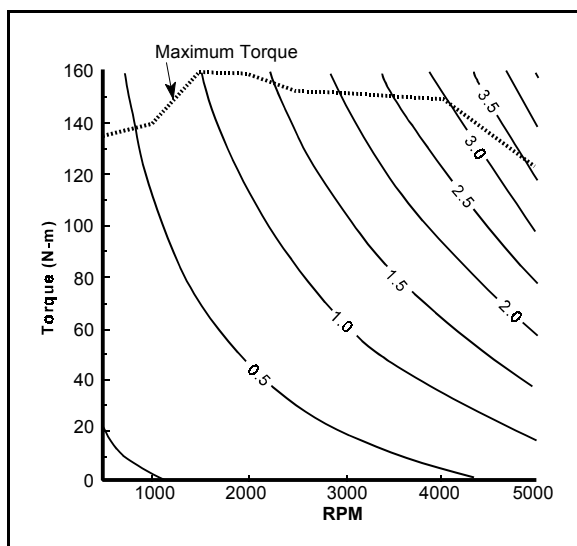


Figure 1. Performance Map for 1.9 L Engine. Contours Are Fuel Flow (gm/s).

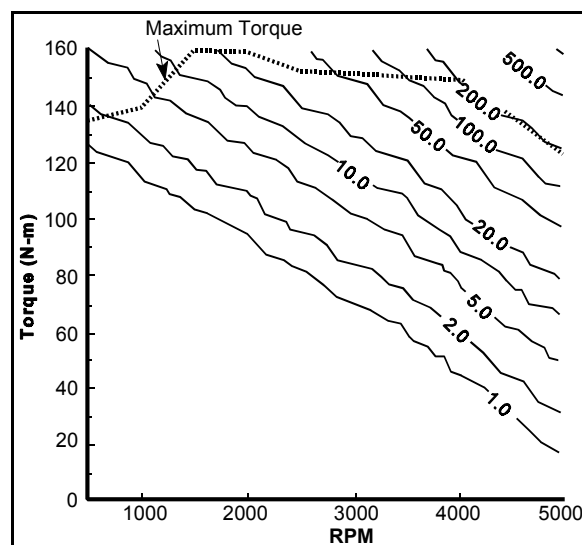


Figure 2. Performance Map for 1.9 L Engine. Contours are NO_x Emissions (ppm).

Analysis

All of the modeling computations in this study are carried out using the HCT model (Hydrodynamics, Chemistry and Transport; Lund, 1978). The computational model treats the combustion chamber as a homogeneous reactor with a variable volume. HCT has been modified to include a heat transfer correlation (Woschni, 1967) and a turbocharger and an internal EGR model. The present analysis considers a single-zone, lumped model that ignores spatial variations in the combustion chamber, treating heat loss as a distributed heat transfer rate.

The single zone model has been applied to investigate the effect of natural gas variability

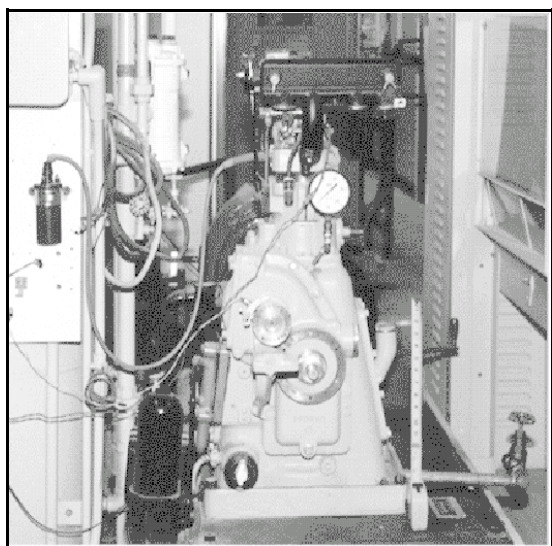


Figure 3. CFR Engine at Experimental Facility

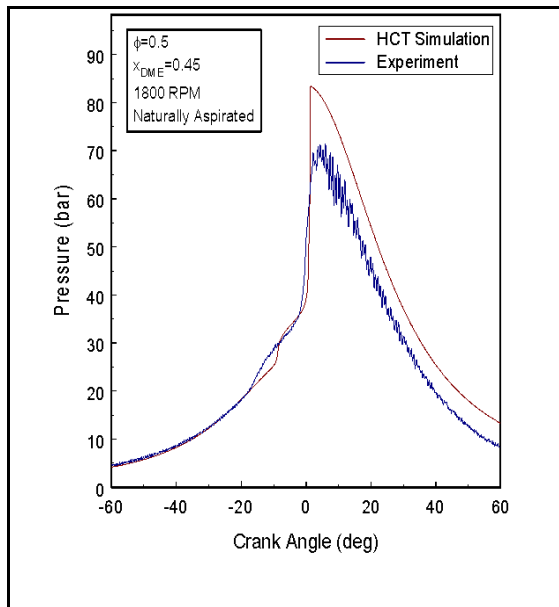


Figure 4. CFR Engine Pressure Trace Compared to Single-Zone HCT Model Results

on HCCI combustion. The results indicate that the higher hydrocarbons in natural gas have the effect of advancing combustion by a few degrees with respect to pure methane. The possibility of using DME as an additive for achieving HCCI combustion has also been evaluated.

The single zone model has also been applied to evaluate an engine performance map. The performance map, developed from single-zone HCT engine model simulations, has been used to predict fuel consumption and NO_x production in a conventional road vehicle. The performance map has been used to simulate a conventional road vehicle being operated in highway and urban driving cycles. The engine has 4 cylinders and 1.9 L displacement. The vehicle has a 1200 kg empty weight.

Figures 1 and 2 show the torque-speed performance map with contours of fuel consumption and NO_x emissions. Torque is limited by the maximum cylinder pressure, which has been specified as 250 bar for single zone HCT results. The results for the combined Federal Urban and Highway Driving Cycle indicate that an HCCI engine can achieve very high fuel economy, nearly 52 mpg gasoline equivalent, with ultra low NO_x emissions, 0.0011 g/mile (1/64 of Tier 2), assuming a PNGV-size vehicle weighing 1336 kg. Engine-out hydrocarbon emissions are high but should be able to be controlled within standards using a simple oxidation catalyst. The estimated fuel economy represents approximately a 25% increase over the same vehicle with a state-of-the-art spark ignition engine. The 0-60 acceleration time (10 s) shows that there is no compromise in performance with an HCCI engine, due to the high torque achievable over the range of operation.

Experimental

Single cylinder engine testing is currently underway. The CFR engine (Figure 3) has been operated in HCCI mode with methane and with methane/dimethyl ether blends. Dimethyl ether is used because it is very prone to autoignition at room temperature and the mixture can be run in HCCI mode without additional intake heating. Figure 4 shows

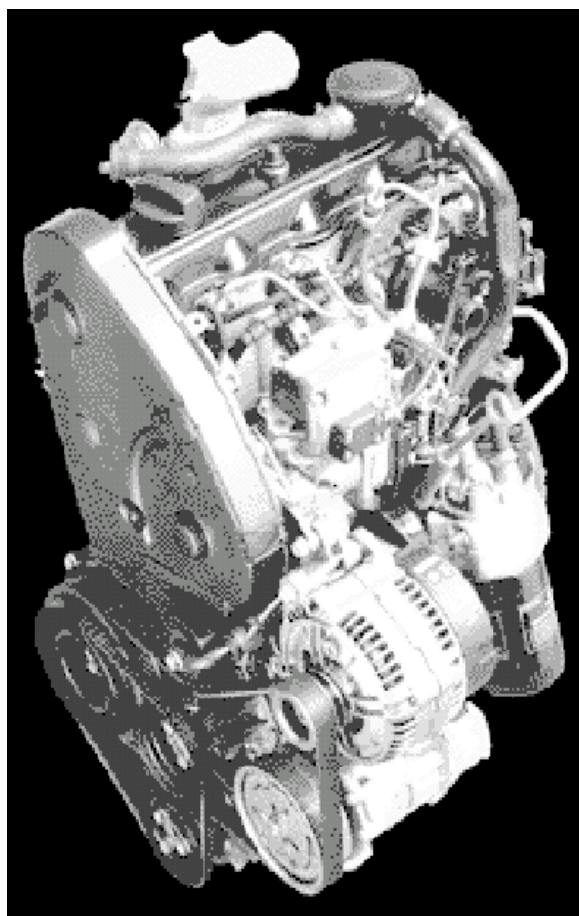


Figure 5. The Volkswagen TDI Engine Being Modified for HCCI Operation

preliminary experimental results for 1800 RPM at 18:1 compression ratio, for a mixture of natural gas and DME. The figure also shows the pressure trace predicted by the single zone HCT model. The single zone model predicts very fast combustion because it neglects the effect of the colder boundary layers, which take a longer time to ignite, therefore stretching the burn duration.

We have received a Volkswagen TDI diesel engine and a synchronous AC alternator from Volkswagen of America. The engine is shown in Figure 5. This engine is currently being instrumented and modified to operate as a multi-cylinder HCCI engine.

Conclusions

During the present year we have achieved significant progress in evaluating HCCI combustion, both by analysis and experiments. In analysis, we have developed a chemical kinetics model that has been applied to predict sensitivity to fuel composition, engine startability and to generate an engine performance map. The experimental work has achieved HCCI operation of a single cylinder CFR engine. Future plans include operation of a multi-cylinder engine and addressing all the control and startability issues associated with HCCI operation.

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List of Acronyms

CFR	Coordinating Fuels Research
DME	Dimethyl Ether
EGR	Exhaust Gas Recirculation
HCCI	Homogeneous Charge Compression Ignition

HCT Hydrodynamics, Chemistry, &
Transport

LLNL Lawrence Livermore National
Laboratory
TDI Turbocharged Direct Injection

IV.D. CNG Refueling Infrastructure R & D

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Objectives

- Cut CNG fueling station capital cost by 50%
- Reduce CNG fueling station operating costs by 33%
- Significantly improve fueling station performance
- Improve CNG vehicle performance

Office of Advanced Automotive Technologies R&D Plan, Fuels: Task 7; Barrier B

Approach

- Evaluate existing CNG fueling technology to identify opportunities for cost and operational improvements.
- Address key issues for CNG infrastructure improvement through a combination of in-house and cost-shared R&D with commercial partners.
- Carry out independent testing and evaluation of advanced components.
- Transfer technology and advanced products to industry for commercialization

Accomplishments

- Evaluation of fueling station costs to identify the most promising opportunities for significant cost reductions.
- Participation in a Natural Gas Vehicle Infrastructure Working Group initiated by DOE and GRI.
- Collection of data on the maintenance requirements (scheduled and unscheduled), energy consumption, and regulatory compliance costs for Argonne's CNG fueling station.
- Investigation of laser hardening of compressor components to reduce wear.
- Acquisition of a commercial compressor for baseline testing as part of a proof-of-concept test of an

advanced, low-cost, single-screw compressor design.

- Design and construction of a versatile test facility needed for the single-screw compressor development program.
- Collection of information on flow-measuring techniques and other auxiliary equipment applicable to CNG fueling stations.

Future Directions [All transportation-related natural gas R&D is being consolidated under the Office of Heavy Vehicles]

- Continued development, testing, and commercialization of a low-cost CNG compressor based on the new approach to a single-screw rotary design.
- Application of surface-hardening and low-friction coating techniques to development of an advanced oil-free compressor and to improve the reliability of current compressor designs.
- Development of improved gas metering technology and techniques for gas-composition sensing.
- Investigation of communication between vehicles and the CNG station in order to better control fueling and provide gas-composition information to improve vehicle performance.
- Promotion of appropriate changes in code requirements for CNG station designs which will reduce costs while maintaining a high level of safety.

Introduction

Compressed natural gas offers a number of benefits as a vehicle fuel, including high octane, low emissions, and displacement of imported petroleum. However, the growth of CNG use has been limited by the lack of an adequate fueling infrastructure. This project was initiated late in FY97 with the objectives of identifying cost and performance issues that need to be resolved in order to spur infrastructure growth, and of establishing a research and development program to address the most pressing of those issues. During FY99, project activities have focused on acquisition of costs for current technology, collection of data from an operating fueling station located at the Argonne site, application of wear reduction techniques to components in existing commercial systems, and development of an advanced compressor concept offering lower cost and higher performance than existing designs.

Cost Study

The costs for CNG stations have often been

characterized as 5 to 10 times those for gasoline stations. The exact ratio depends strongly on the sizes and types of stations that are being compared, the location, and whether one is simply comparing capital costs for "typical" facilities or normalizing costs to equivalent fueling capacity. For example, the installed cost for a typical public access CNG station of 200 scfm capacity could be about \$400K. Such a facility would probably have two fueling hoses and be capable of pumping less than 2 gallons gasoline equivalent per minute (gge/min) on a continuous basis (the use of storage tanks increases the flow capacity for short periods). On the other hand, a gasoline system with three tanks and six dispensers (12 hoses) would cost on the order of \$250K and have a continuous fueling capacity of close to 120 gpm. Irrespective of the basis used for comparison, there is clearly a significant disparity between the costs for CNG and gasoline fueling facilities.

In evaluating the costs for various types of CNG fueling facilities, it is readily apparent that compressors are the single largest cost item. In most cases, the compressors and



Figure 1. On-Site CNG Fueling Facility

associated equipment account for at least half of the total capital cost. Gas drying, storage, and dispensing make up the balance. Compressors are also a significant maintenance item and consumer of energy. For example, electrically driven compressors use between 1 and 2 kWh per gge of gas compressed. Thus, improvements in compressor technology offer the greatest potential for facility cost reductions and performance improvements.

Argonne Fueling Station Operation

Argonne's CNG fueling station (Figure 1) was designed and operated as a commercial public-access facility before being acquired by the Laboratory. Thus, it incorporates technology in daily use throughout the industry. It has a compressor capacity of about 50 scfm and currently serves a fleet of 24 light trucks (vans and pickups). Experience during the past year with the station has revealed several problem areas that include leaks in the compressor valves (which were most frequent during the severe winter weather), drifting of settings in the valves that control the fill pressure (and prevent overfilling of the vehicle), and early compressor wear leading to excessive blow-by and oil consumption. Energy usage has been somewhat higher than expected, with values ranging from 2 - 2.5 kWh/gge. Future plans call for continued monitoring of station performance and use of the station as a test bed for advanced components.

Compressor Wear Reduction

Commercial CNG compressors are multi-stage reciprocating designs with typical outlet pressures in the 3500 to 4000 psi range. The difficulties encountered in adequately sealing the piston-to-cylinder gap at these high pressures have led to problems with early wear and excessive maintenance for many units. Recently developed techniques such as laser hardening of surfaces and the application of extremely low friction coatings may offer means to reduce wear and extend maintenance intervals. During FY99, Argonne worked in cooperation with a commercial compressor

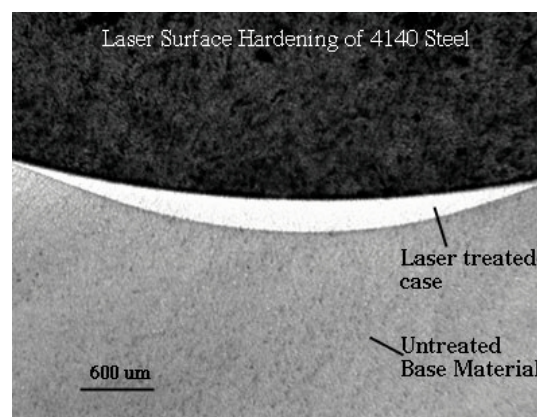


Figure 2. Cylinder Surface With Laser Hardening

company to identify wear issues and potential solutions. Samples of cylinder liners were obtained, characterized for hardness and surface roughness, and treated with a laser to harden and smooth the surface (Figure 2). Based on the results of those preliminary tests, additional samples were obtained to be used in optimizing the process. The objective is to produce a cylinder that will exhibit very low wear while also extending the life of the piston rings.

Advanced Compressor Development

As noted above, compressors represent the most obvious target for development leading

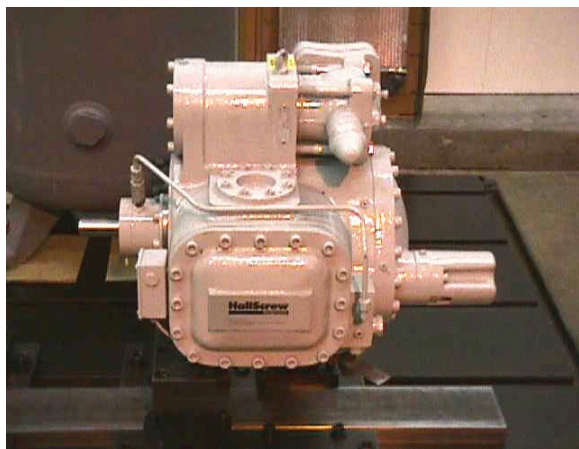


Figure 3. Commercial Single-Screw Compressor for Baseline Studies

to significant cost reductions and performance improvements. The units in service today are derived from air compressor technology and have evolved little since the introduction of natural gas vehicles. Following a survey of available options and proposed developmental concepts, Argonne identified a new approach to single-screw compressor design/manufacture as having significant commercial promise. While similar compressors have been produced in the past for refrigeration, the new approach should greatly reduce manufacturing costs and extend the range of applications. At the end of FY98, Argonne contracted with IMPCO Technologies to conduct a proof-of-concept test of the new approach. During the first three quarters of FY99, IMPCO obtained a commercial compressor of this type (Figure 3) to be used in establishing a performance baseline, designed and constructed a test facility (Figure 4) for characterizing both the commercial and developmental compressors, and made preparations for manufacturing the components needed in the new approach. Following completion of the proof-of-concept tests in early FY00, current plans call for development of a prototype CNG compressor that will ultimately be subjected to extended testing at the Argonne CNG fueling station.



Figure 4. Compressor Test Facility with Commercial Compressor (lower right)

Summary

During FY99, this project has continued to acquire data on the costs and operating issues associated with CNG fueling facilities. Improvements in compressor technology have been sought through investigation of surface treatment techniques for wear reduction, as well as through initial development of an advanced compressor concept that could significantly reduce both capital and operating costs for fueling facilities. Future project plans call for further development and testing of the advanced compressor with Laboratory input on materials and tribology issues that are likely to arise. Other components of the fueling system will also be addressed, with emphasis on improved flow measurement and sensing of gas composition so that fuel characteristics can be communicated to the vehicle for optimizing performance.

Acronyms

CNG	Compressed Natural Gas
DOE	Department of Energy
GRI	Gas Research Institute
scfm	Standard Cubic Feet per Minute
gge	Gasoline Gallon Equivalent
gpm	Gallons per Minute
kWh	Kilowatt Hours

IV.E. Low-Cost Natural Gas Liquefaction Station

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Objectives

- Design, develop, and demonstrate a small-scale methane liquefaction plant for local production of liquefied natural gas (LNG) for use as an alternative vehicle fuel.

Approach

- Local production and consumption of LNG to reduce or eliminate shipping costs.
- Minimize construction costs; target of \$350,000 to \$500,000; use off-the-shelf components where possible
- Minimize operating costs; minimize energy inputs to the process; target output of 10,000 gallons per day
- Collaborate with industry for cost-sharing and transfer of new technologies to the private sector.

Accomplishments

- Explored design strategies that exploit the pressure drop at the junction of a high-pressure commercial natural gas delivery line and the low-pressure branch line, using volume expansions and heat exchangers to provide refrigeration, converting a fraction of the natural gas stream to liquid methane without the use of energy inputs
- Identified two low-cost design strategies that appeared to be promising but proved through computer modeling and analysis to be unsuitable. These design strategies would have relied completely on passive operation (no moving parts) to provide refrigeration
- Developed and modeled a viable design strategy that uses a turbo-expander to optimize the effectiveness and efficiency of the refrigeration process, by extracting work from the pressure drop in the natural gas stream. The model showed 14% of the natural gas flow converted to liquefied methane at -209°F, using no energy inputs for refrigeration or compression, exploiting a pressure drop of 340 psig in a natural gas stream starting at 60°F.
- Negotiated a cooperative research and development agreement (CRADA) with a collaborating partner for further development, with new technologies (patents applied for) to be transferred to the private sector party. Terms of the CRADA have been agreed upon (as of July 1999), and the

CRADA will be signed before the end of the fiscal year.

Future Directions [All transportation-related natural gas R&D is being consolidated under the Office of Heavy Vehicles]

- Optimize the design of the liquefaction plant.
- Work with collaborating partner to build, test, and demonstrate methane liquefaction plants under the terms of the CRADA.

Introduction

The Idaho National Engineering and Environmental Laboratory (INEEL) is collaborating with Pacific Gas and Electric (PG&E), Southern California Gas (So Cal Gas), the Gas Research Institute, and others in a project that will advance the use of liquefied natural gas (LNG) as a vehicle fuel. We plan to develop and demonstrate a small-scale methane liquefaction plant (production of about 10,000 gallons per day) to supply fuel to LNG-powered transit buses and other heavy-duty vehicles specially equipped to run on low-saturation-pressure (very cold) LNG fuel. INEEL is performing the research and development work. The collaborators will deploy the new facilities commercially in demonstration projects in California. INEEL and the collaborators have agreed in principle to the terms of a CRADA, and work will proceed as soon as the CRADA is signed.

Discussion

The plant will produce liquid methane from commercial natural gas. Using a process invented at the INEEL, the plant will exploit the pressure drop between the natural gas high-pressure main delivery line (400 psig) and the low-pressure local branch line (60 psig) to liquefy the methane. The process uses a turbo-expander to optimize the benefit from the pressure drop, and uses two or more heat exchangers to cool the input stream. Figure 1 shows one of the designs we are considering, and includes temperature and pressure data

from the modeling effort. No energy inputs are needed for compression or refrigeration; the only compressor in the plant is the one driven by the turbo-expander. This feature makes the plant inexpensive to operate. The system is mostly passive, with very few moving parts except for the turbo-expander-compressor assembly. This feature makes the plant inexpensive to maintain. The design shown in Figure 1 and other similar designs are protected by U.S. and international patents (patents applied for).

The modeling effort showed that the process will convert about 14% of the natural gas in the input stream to cryogenic liquid methane at a saturation pressure of 60 psi (-209°F). The rest passes through a return line and falls into the low-pressure branch line, for delivery as usual to other natural gas customers. The system includes provision to remove impurities (oil, dust, water, carbon dioxide, etc.) from the input stream and to remove heavy hydrocarbons (butane, propane, ethane) from the LNG output stream. The plant can be placed at any location where a sufficient pressure drop occurs in a commercial natural gas delivery system, considering that the volume of natural gas return flow discharged by the plant can not exceed the commercial consumption downstream in the low-pressure branch line. We expect to achieve even better yields by making minor improvements to the design.

We explored two possible designs that, though they appeared promising, proved to be unsuitable. One design used Joule-Thompson valves in series, each associated with a heat exchanger to exploit the temperature drop that occurs at the valve's volume expansion nozzle. At each step, one of the heavy hydrocarbons would condense, then serve as a refrigerant for a heat exchanger. Computer modeling showed too small a margin for us to have confidence in its success, especially if the fraction of heavy hydrocarbons in the gas stream was small.

The other design proposed the innovative use of vortex tubes installed in series, each separating its respective input stream into a hot flow stream and a cold flow stream, with the intention of producing liquid methane at the third or fourth separation. Testing of vortex tubes and analysis of the results showed that the function of an individual vortex tube relies not so much on the pressure difference as on the pressure ratio, in absolute terms. (A pressure drop from 98 psia to atmosphere at 14 psia has the same pressure ratio as a pressure drop from 700 psia to 100 psia.) This feature makes the installation of vortex tubes in series unworkable for the liquefaction plant. However, we still might find use for vortex tubes not installed in series.

Summary and Conclusions

With the use of a turbo-expander to exploit a 340-psig pressure drop in a natural gas line, it

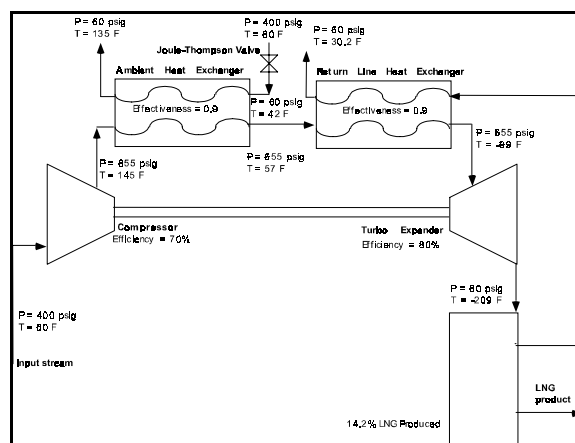


Figure 1. Configuration of the Small-scale Methane Liquefaction Plant

is certainly possible, without external energy inputs, to extract a portion of the flow stream as liquefied methane. A CRADA with private sector parties will provide for refinement of the design, then construction and demonstration of the small-scale methane liquefaction plant. The final design might include Joule-Thomson valves and/or vortex tubes, along with the turbo-expander, to optimize the process.

List of Acronyms

CRADA	Cooperative Research & Development Agreement
INEEL	Idaho National Engineering & Environmental Laboratory
LNG	Liquefied Natural Gas
PG&E	Pacific Gas & Electric
psig	Pounds per Square Inch (Gauge)
psia	Pounds per Square Inch (Absolute)

IV.F. Natural Gas Derived DME Fuel Injection System

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Objectives

- Design, build, test, and validate a DME fuel supply pump for a light-duty CIDI engine and vehicle system that meets PNGV targets

Office of Advanced Automotive Technologies R&D Plan, Fuels, Dimethyl Ether: Task 1; Barrier A

Approach

- Design entire vehicle fuel system, including fuel injection, leakage control and fuel storage and delivery subsystems
- Model, simulate and optimize the variable displacement supply pump and the fuel injection system
- Design and construct a special pump performance and endurance test bench that will allow measurement of pump drive power and that is capable of running the pump under both low (-18°C) and elevated (40°C) ambient conditions
- Build pump, map and run for 200 hours or to failure, whichever occurs first
- Disassemble and inspect the pump after test and publish a final report

Accomplishments

- System concept design completed and submitted
- Pump and fuel injection system successfully modeled, simulated and optimized
- Detail design created for variable displacement pump
- Pump assembled and tested for 6 hours
- Variable displacement concept demonstrated and validated
- Special pump performance and durability test bench designed and constructed
- Pump with design corrections assembled and extensively tested
- Pump durability tested for 122 hours; 98 hours peak torque (max pump loading), 18 hours high idle and 6.5 hours rated load) without major incident

Future Directions

- Phase 2 will test and validate the DME fuel pump and fuel system on a CIDI engine

Introduction

The Partnership for a New Generation Vehicle (PNGV) is considering CIDI (compression ignition, direct injection) engine technology as one option for its 2004 production prototype vehicles. Recent engine research has shown

that CIDI engines fueled with dimethyl ether (DME) can achieve ULEV exhaust emissions while maintaining the thermal efficiency of a conventional diesel. Research has also shown that fuel injection equipment specially designed for DME is necessary to cope with

Table 1. Pump Drive Power Goals

Engine Speed (rpm)	Pump Speed (rpm)	Engine Power (kW)	Pump Power (kW)	Load
4000	2000	55	1.1	Rated
2000	1000	4	0.16	Road

Table 2. Pump Durability Test Schedule

Engine Load	Pump Speed (rpm)	Pump Outlet Press (ksi)	Amb. Temp. (°C)	Test Hours
P.T. ¹	1000	3	25	98
H.I. ²	2100	1	25	18
Rated	2000	3	25	78
P.T.	1000	3	-18	1
H.I.	2100	1	-18	1
Rated	2000	3	-18	1
P.T.	1000	3	40	1
H.I.	2100	1	40	1
Rated	2000	3	40	1

1/Peak Torque

2/High Idle

the unique physical properties of DME, and to ensure lowest exhaust emissions and the highest fuel efficiency.

The overall objective of this project is to design, develop, test and validate a complete DME fuel system for a small CIDI powered passenger car, and to demonstrate in-vehicle fuel economy, performance and exhaust emissions. This will be done in two program phases. In this initial phase, the focus is on the concept development, and the design and validation of a variable displacement fuel supply pump. This variable displacement fuel

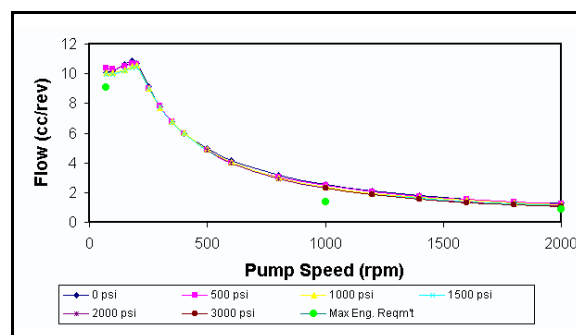


Figure 1. Pump Flow Performance After 78 Hours

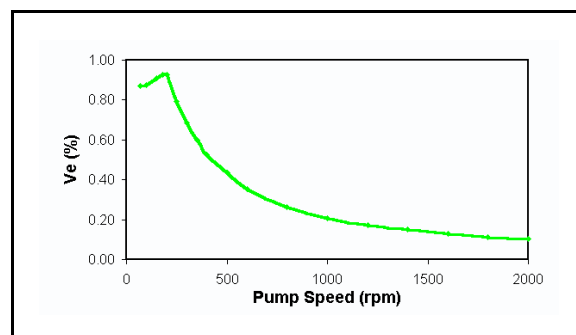


Figure 2. Corrected Volumetric Efficiency at 1000 PSI Outlet Pressure

supply pump is a new technology that is the key to the success of the overall program. A variable displacement supply pump is required to provide low parasitic losses at road loads, which is necessary to meet program fuel economy goals (80 mpg). The power and durability targets for the pump are given in Tables 1 and 2.

Summary of Results and Discussion

A pump flow map, shown in Figure 1, illustrates the variable displacement feature of the pump and compares test results to calculated engine requirements. The pump output closely matches calculated full load engine requirements (66 kW @4000 rpm). Volumetric efficiency (corrected for fuel bulk modulus effects) is plotted in Figure 2. Peak efficiency is 93% at 180 rpm, which shows that internal pump leakage is low (147 cc/min, 0.8 cc/rev). At higher speeds, the apparent

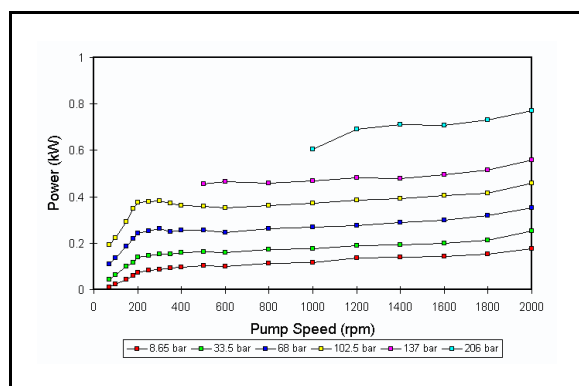


Figure 3. Pump Drive Power

volumetric efficiency falls sharply because of throttling induced, 2-phase flow. We calculate that if the pump were not throttled, pump volumetric efficiency would approach 99% at rated speed and load. This is exceptional considering the kinematic viscosity of DME is only 0.25 cSt.

A pump drive power map for an 83-hour period and a 0.9 mm orifice is shown in Figure 3. Overall, the drive powers are very low and reflect >90% overall pump efficiency across the engine operating range. Measured drive power versus program goals is shown in Table 3.

Conclusions

All program objectives were essentially met, and a final report submitted. Details of the design, testing, and validation can be found in appendices to the Final Report. Durability testing (without tappets) was started in March 1999. The durability test ran for 122 hours: 98 hours peak torque (max pump loading), 18 hours high idle and 6.5 hours rated load) without major incident. At 122.5 hours, pump outlet pressures dropped to zero and could not be restored. Disassembly, inspection and analysis revealed:

- the pump drive shaft failed by rotating bending fatigue, just behind the cam. The fatigue initiated at a crack in the nitride white layer. This crack was probably

Table 3. Pump Drive Power Goals & Results

Pump Speed (rpm)	Engine Load (rail press., bar)	Pump Power Goals (kW)	Meas. Pump Power (kW)	Goals
2000	Full (206)	1.1	0.77	Met
1000	Road (82)	0.16	0.31	Still Above

formed during a previous pump build when the pump was run at approximately twice the design load. A metallurgical and stress analysis is included in Appendix G of the Final Report

- the thrust bearing ball cage (bronze) is worn.
- one mechanical issue was identified during this testing—intensifier tappet sticking. This will be corrected in phase II.

All other pump components were in excellent condition.

References/Publications

Program review with NREL & USCAR on December 17, 1998. Pump performance results, mechanical problems & solutions were presented and discussed in detail. A copy of the presentation is included in Appendix E of the Final Report.

A comprehensive program review meeting was held with NREL and DOE. on March 17, 1999. The presentation from this meeting is included in Appendix F of the Final Report.

FY 1999 Progress Report for Advanced Automotive Fuels

List of Acronyms

CIDI Compression Ignition Direct Injection
DME Dimethyl Ether
NREL National Renewable Energy

Laboratory
PNGV Partnership for a New Generation of
Vehicles
ULEV Ultra Low Emission Vehicle

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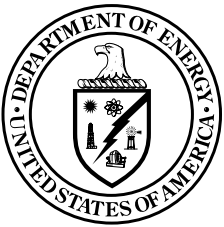
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