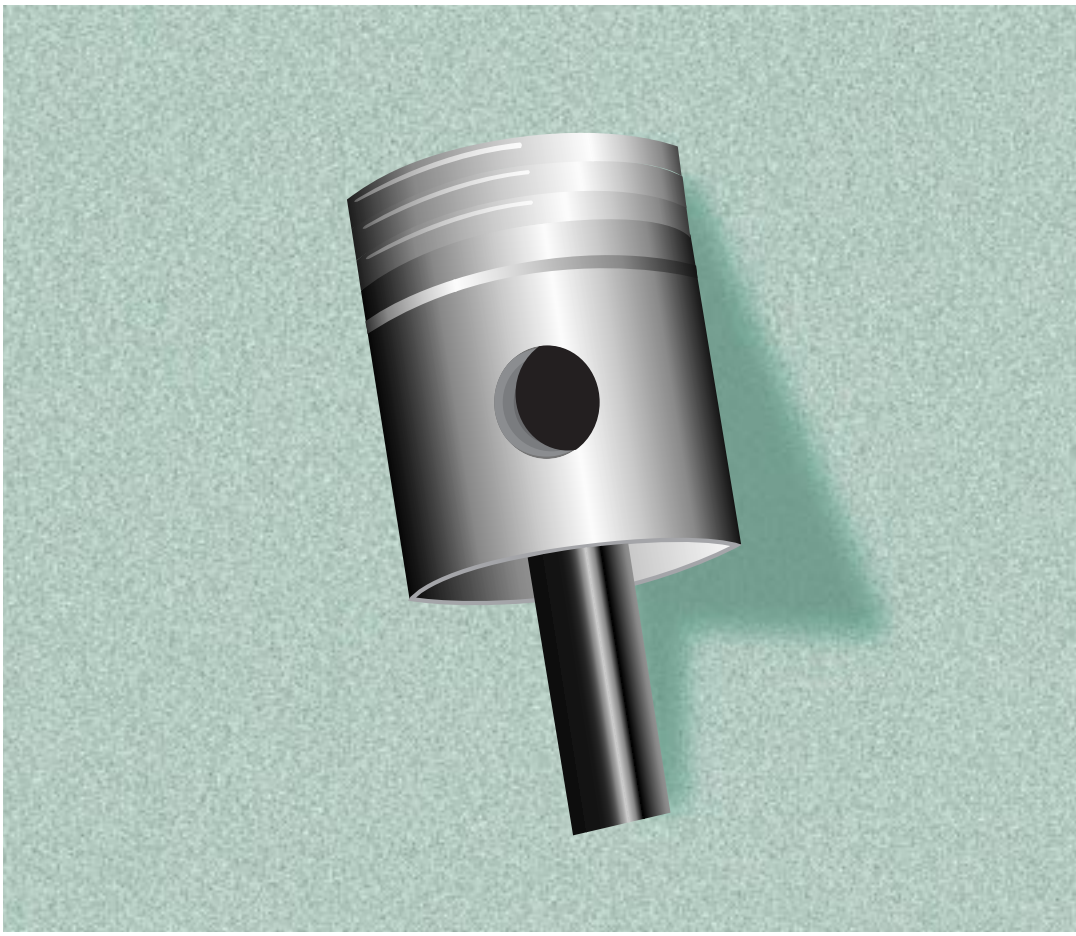
COMBUSTION AND EMISSION CONTROL FOR ADVANCED CIDI ENGINES

2001
ANNUAL
PROGRESS
REPORT



U.S. Department of Energy

Energy Efficiency and Renewable Energy

Office of Transportation Technologies

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Office of Transportation Technologies
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FY 2001

Progress Report for Combustion and Emission Control for Advanced CIDI Engines

Energy Efficiency and Renewable Energy
Office of Transportation Technologies

Approved by Steven Chalk

November 2001

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I. INTRODUCTION

Developing Advanced Combustion and Emission Control Technologies

Gurpreet Singh,
Program Manager

On behalf of the Department of Energy's Office of Transportation Technologies (OTT), we are pleased to introduce the Fiscal Year (FY) 2001 Annual Progress Report for the Advanced Combustion and Emission Control Research and Development (R&D) Program. The Program is focused primarily on the compression ignition, direct injection (CIDI) engine, an advanced version of the commonly known diesel engine, which is used in both light- and heavy-duty vehicles. Both the Office of Advanced Automotive Technologies (OAAT) and the Office of Heavy Vehicle Technologies (OHVT) conduct CIDI engine R&D and have coordinated their research planning and evaluation processes to minimize overlap and maximize the use of available R&D funding. This year's accomplishment report represents the output of this combined effort.

This introduction serves to outline the nature, current progress, and future directions of the Combustion and Emission Control R&D Program for advanced CIDI engines. Together with DOE National Laboratories and in partnership with private industry and universities across the United States, OTT engages in high risk research and development that provides enabling technology for fuel efficient and environmentally-friendly light- and heavy-duty vehicles. The work conducted under this Program relies on the DOE Advanced Petroleum-Based Fuels (APBF) Program to provide on-going reformulated diesel fuel developments, to enable meeting our out-year objectives. (The APBF Program is described in a separate report.)

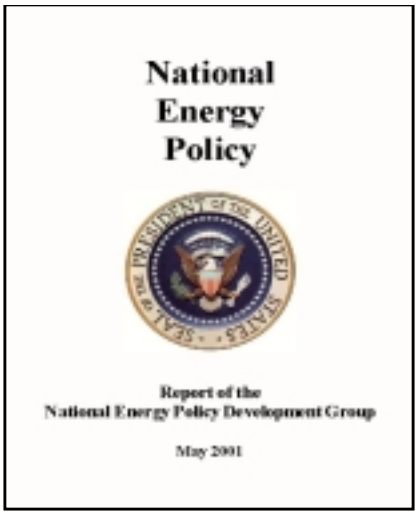
Kenneth Howden,
Program Manager

Combustion and Emission Control R&D activities are sharply focused on improving emission control technologies to maintain the high fuel efficiency of CIDI engines while meeting future emission standards. Up until implementation of the EPA Tier 2 regulations and the recently promulgated heavy-duty engine emission standards for 2007, CIDI engines could meet emissions regulations through enhanced combustion alone. The consensus now is that CIDI engines for both light- and heavy-duty vehicles will need exhaust emission control devices in order to meet both the NO_x and PM emissions regulations. This situation is analogous to the early 1970s, when gasoline vehicles transitioned to catalytic emission control devices. Both NO_x and PM emission control devices will have to achieve conversion efficiencies of 80 to 95 percent to meet the emission standards for both light-duty vehicles and heavy-duty engines.

Kevin Stork,
Program Manager

In his second week in office, President Bush established the National Energy Policy Development (NEPD) Group. The NEPD Group released the National Energy Policy (NEP) report in May 2001 which includes key recommendations for a National Energy Policy. The NEP took a critical look at our current energy supplies and demands, and made several recommendations for moving forward to correct imbalances. One of the major imbalances is supply and demand for petroleum fuels. Our highway transportation system is entirely dependent on petroleum fuels (with the exception of about 3 percent oxygenates added to gasoline). While vehicles today are more efficient than 25 years ago, the average fuel economy of new vehicles has not changed over the past 10 years, in part due to the growth of low fuel economy light trucks (pickups, vans, and sport utility vehicles). The NEP recommended that consideration be given to increasing the fuel economy of new

vehicles without negatively impacting the U.S. automotive industry. Combustion and Emission Control R&D activities go to the heart of increasing the fuel economy of light trucks and cars in the U.S., in a cooperative manner with the U.S. automotive industry to assure that the necessary technology is ready and available for them to implement.



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

Since its inception, the Combustion and Emission Control R&D Program for advanced CIDI engines has supported the government/industry Partnership for a New Generation of Vehicles (PNGV) through its technology research projects. The partnership goals are being re-evaluated to identify changes that will maximize the potential national petroleum-savings benefit of the emerging technologies. When these goal changes have been defined, OTT will adjust the focus of its technology research programs accordingly. Today's CIDI engines achieve impressive thermal efficiency; however, in order to meet future emissions standards, advancements in clean combustion, emission control technology and diesel fuels are necessary. The DOE/OHVT Light Truck goal is to increase the fuel efficiency of light trucks by 35 percent by 2004, while meeting emission standards that apply to both cars and light trucks. Because the emission challenges facing CIDI engines are very similar for both light- and heavy-duty vehicle applications, OAAT and OHVT have co-funded many of the projects whose reports are contained herein.

The Advanced Combustion and Emission Control R&D Program explores the fundamentals of combustion, how emissions are formed, and advanced methods for reducing those emissions to acceptable levels. Testing and modeling are also important elements of the program and enable us to evaluate potential technology and validate technology selection and direction. By working at the forefront of these new technologies in cost-sharing arrangements with industry, we hope to enhance the knowledge base that can be used by automotive partners and suppliers (engine manufacturers, catalyst companies, etc.) to develop highly efficient CIDI engines with emissions that meet future standards.

Challenges

OTT programs have been successful in meeting many of the original milestones established by PNGV. The PNGV emissions goals established were 0.2 grams per mile for NO_x and a "stretch" target of 0.01 grams per mile for PM. Subsequent to this, EPA finalized the Tier 2 emission regulations which lowered the average NO_x emissions that would be allowed from light-duty vehicles. In a separate action, EPA proposed to significantly lower the sulfur content of on-road diesel fuel. In light of these developments, the DOE R&D emission goals were re-evaluated to reduce emissions beyond the minimum required by EPA regulation. The DOE 2007 R&D emission goals target even lower emissions, while simultaneously improving engine efficiency and reducing emission control costs. Meeting the Tier 2 standards requires NO_x and PM emissions to be reduced by about 90 percent. In 2001, EPA finalized emissions regulations for heavy-duty CIDI engines to 0.2 grams per bhp-hour for NO_x and 0.01 grams per bhp-hour for PM, reductions of 90 percent from the previous standards. These new regulations will be phased in over the 2007-2009 model years. In a complementary action, EPA finalized regulations to reduce the sulfur in on-road diesel fuel to 15 ppm or less, by June 2006. Reducing the sulfur in on-road diesel fuel enables the application of NO_x and PM emission control devices which would not be viable otherwise. While this action makes emission control devices feasible, much work remains to make them affordable, reliable, and durable, with acceptable energy consumption. Meeting the DOE goals will facilitate the design of high fuel economy vehicles using CIDI engines to penetrate the market with resultant petroleum fuel reduction and emissions benefits.

Advanced Combustion and Emission Control R&D Program Participants

Originally, it was believed that lean-NO_x catalysts would have sufficient effectiveness to meet the NO_x goal, and oxidation catalysts would meet the PM goal. However, it has now become evident that the capabilities of lean-NO_x and oxidation catalysts are too limited to reach the new goals. Three different NO_x emission control technologies are currently being developed in parallel: adsorber catalysts, non-thermal plasma catalysts, and selective catalytic reduction (SCR) devices. None of them currently have sufficient conversion efficiency and lifetime durability to be viable for transportation vehicles. To meet the PM goals, it is almost certain that catalyzed and continuously regenerating diesel particulate filters (DPFs) will be needed instead of just oxidation catalysts. While such devices look promising, several hurdles remain to be overcome, including durability, effective operation during transients and at low exhaust temperatures, recovery from periodic exposure to high-sulfur fuels, minimization of the fuel economy penalty caused by regeneration energy requirements and increase in engine back pressure, development of viable sulfur traps, development of affordable reductant storage, distribution, and dispensing infrastructure, and effective desulfurization schemes that will keep emission control devices operating near their peak effectiveness.

Durango Test Vehicle with Prototype DDC V6 CIDI Engine - Platform for SCR/DPF Emission Control System Development

Accomplishments

In FY 2001, significant progress was made on emission control subsystems that would allow CIDI-engine-powered passenger cars and light-duty trucks to meet Tier 2 emission standards. Catalyst technology continues to evolve, allowing higher NO_x reduction rates over wider exhaust temperature ranges. New control strategies and sensor technologies are leading to more precise distribution and transient control of exhaust gas recirculation (EGR) to reduce NO_x emissions. More detailed characterization of combustion processes is further reducing engine-out emissions and forming the foundation for the development of advanced combustion technologies such as homogeneous charge compression ignition. Regenerative particulate matter (PM) filtration devices are in advanced development, with several fleet tests in progress. The accompanying table shows current progress relative to the Program 2004 and 2007 Technical Targets for light-duty vehicles. While good progress is being made on NO_x and PM devices that can achieve the technical targets, NO_x devices using 15 ppm sulfur fuel need better durability. Actions will be taken during the coming year to assess the magnitude of the durability hurdle and identify approaches to extending emission control device life.

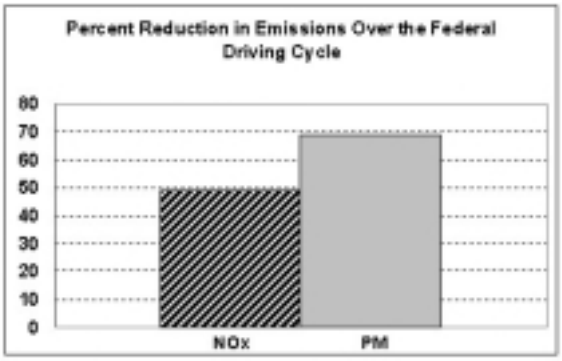
Current Status and Technical Targets for CIDI Engine Technology Development[a]

Characteristics	Units	Calendar year		
		2001 Status	2004	2007
Emission control cost[b]	$/kW	TBD	4	3
Exhaust emission control device volume	L/L[c]	4	2	1.5
NO_x emissions	(g/mile)	0.15	0.07	0.03
PM emissions	(g/mile)	0.015	0.01	0.01
Durability	hrs	<500	5000[d]	5000[d]
Fuel economy penalty due to emission control devices[e]	(%)	10-15	<8	<5

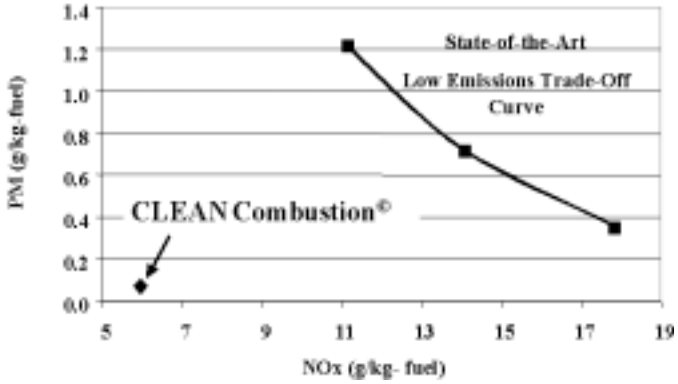
[a]Targets are for a PNGV-type passenger car using advanced petroleum-based fuels with 15 ppm sulfur content; all targets must be achieved simultaneously
[b]High-volume production: 500,000 units per year (a study on emission control device costs will be completed by September 30, 2002)
[c]Liter per liter of engine displacement
[d]Representative of full-useful-life durability for light-duty vehicles.
[e]Energy used in the form of reductants derived from the fuel, electricity for heating and operation of the devices, and any other energy demand of the devices including factors that reduce engine efficiency, such as increased exhaust back-pressure.

DDC Demonstrates Significant NO_x and PM Emissions Reductions Using SCR and a Catalytic Soot Filter

Detroit Diesel Corporation (DDC) has completed the first year of a 36-month program to develop CIDI engine emission control technologies that meet future emission regulations. Their work to date has resulted in substantial reductions in engine-out emissions (CLEAN Combustion') which paves the way for implementation of exhaust emission control devices. For controlling NO_x, DDC has chosen to use selective catalytic reduction (SCR) with urea as a reductant. For controlling PM, they have chosen to use a catalytic soot filter. This combination of reduced engine-out emissions and emission control devices has demonstrated 49% reduction in NO_x and 69% reduction in PM from a light-duty passenger car test vehicle (Dodge Neon) with a prototype CIDI engine. At critical steady-state test points, reductions of 94% NO_x and 80% PM have been observed. DDC plans to enhance its simulation models and optimize the engine and emission control system to obtain further reductions in emissions during the coming year. Important additional information that



Emission Reductions from a CIDI Light-Duty Vehicle (2250 lb.) with Prototype DDC Emission Control System (Unoptimized)

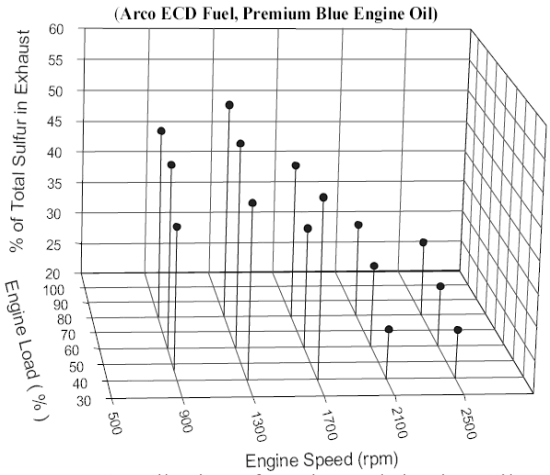


DDC Advancements in Engine-Out Emissions

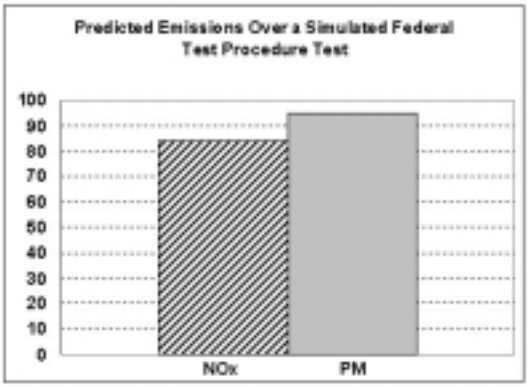
will be generated in the coming year are estimates of emission control device durability and the effect these devices will have on fuel economy.

Cummins Demonstrates Significant NO_x and PM Emissions Reductions Using an NO_x Adsorber and Microwave-Heated Catalytic Soot Filter

Cummins is conducting a similar program as DDC, though using different approaches to NO_x and PM control. They have completed a vehicle/engine/emission control system performance model that was used to select a NO_x adsorber for part of their subsystem development. They are working with Engelhard to specify and develop a suitable NO_x adsorber for this application. The Cummins model predicts that the NO_x adsorber will have to achieve an average effectiveness of 87 percent or better to meet the 2004 R&D objective for NO_x. To date, they have achieved 84% reduction of NO_x and 95% reduction of PM over a simulated FTP driving cycle. Work is proceeding on a hydrocarbon reductant system to regenerate the NO_x catalyst. A by-pass regeneration



Contribution of Engine Lubricating Oil to Sulfur Content in the Exhaust



Predicted Emission Reductions from a CIDI Engine with Prototype Cummins Emission Control System (Unoptimized system with limited durability)

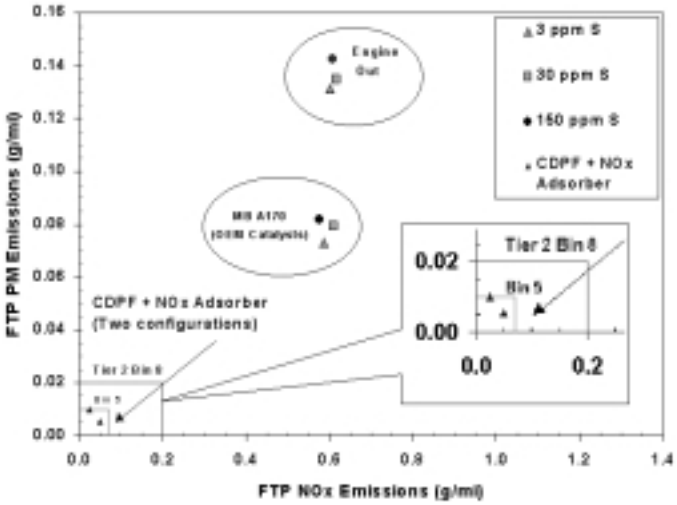
Ford P2000 CIDI Vehicle to be Tested Using the Cummins Emission Control System

strategy is being explored which should reduce the fuel economy penalty due to the reductant used to be under 5 percent. They have also found that with 15 ppm sulfur fuel and a standard diesel engine lubricating oil, up to 50% of the sulfur in the exhaust comes from consumed lubricating oil. In the coming year, Cummins will design and test a sulfur trap with a target life of 20,000 miles, identify the optimum reductant that can be derived from diesel fuel, develop a reductant injection system, and further optimize the emission control system to lower emissions with minimum use of reductant.

Oak Ridge National Laboratory Demonstrates that a Small CIDI Vehicle can Meet Tier 2 Bin 5 Emissions though Durability is a Long Way from Being Acceptable

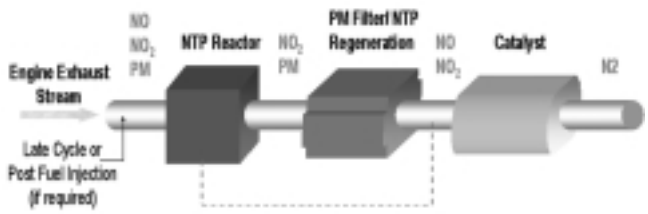
Oak Ridge National Laboratory demonstrated, in a laboratory experiment, that the combination of a NO_x adsorber and a catalyzed diesel particulate filter can achieve simultaneous reductions of NO_x and PM emissions from a CIDI vehicle of over 90% compared with engine-out results over the FTP, US06, and highway fuel economy test cycles. The vehicle used was a 1999 Mercedes A170 model with a CIDI engine using ultra-low sulfur fuel (3 ppm), with prototype NO_x adsorber and diesel particle filter emission control devices. In addition to reductions of PM and NO_x emissions, carbon monoxide and unburned hydrocarbon emissions were lower than the engine-out baseline. The resulting grams per mile emissions levels from these new (degreened) catalysts are consistent with levels established by EPA in the Tier 2 emissions standards, though the Tier 2 levels require this certification at over 120,000 - 150,000 miles of vehicle operation. In addition, these results were achieved using bottled gases as a reductant, which are known to be more effective than reductants produced from the fuel onboard the vehicle. This illustrates the potential of these exhaust emission controls to meet future emissions regulations. However, limited durability testing predicts these devices would fail emissions compliance after only about 20,000 miles when using 15 ppm sulfur fuel. Making this system commercially viable will require developing a means of protecting the adsorber from sulfur (sulfur traps), development of more sulfur-resistant catalysts, development of de-sulfurization techniques, or some combination of these approaches.

The Mercedes A170 Test Vehicle



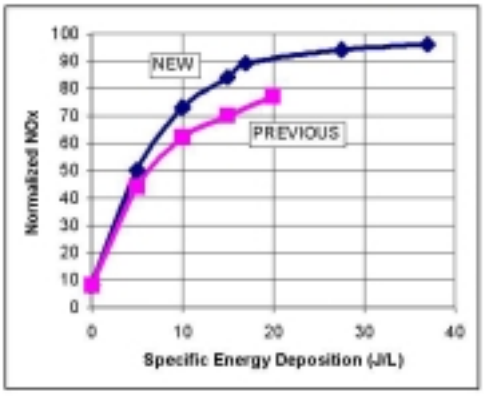
Test Results Showing Tier 2 Standards Can Be Met with New Catalysts and 3 ppm Sulfur Content Fuel

Pacific Northwest National Laboratory Makes Non-Thermal Plasma Emission Control System Advances



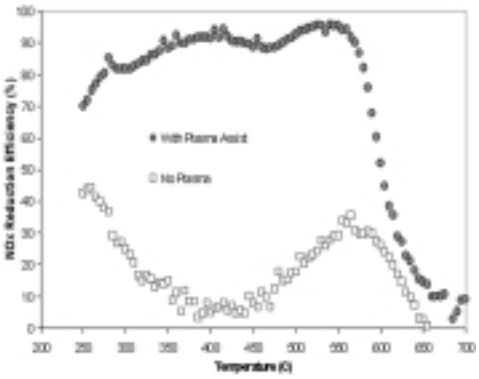
Schematic of Non-Thermal Plasma System

Non-thermal plasma emission control systems have the potential to reduce NO_x and PM simultaneously with relatively low energy requirements. The Pacific Northwest National Laboratory (PNNL) has been working on non-thermal plasma emission control systems under a CRADA whose participants include Ford Motor Company, General Motors, and DaimlerChrysler Corporation. PNNL is also researching non-thermal plasma systems in a CRADA including Delphi Automotive Systems.



Improvement in NO_x Reduction Efficiency

As part of this effort, a catalyst material was formulated and produced that achieves >90% peak NO_x reduction in a simulated diesel exhaust stream, when used in conjunction with an non-thermal plasma reactor. A better understanding of the chemistry that occurs in various steps of an integrated non-thermal plasma assisted PM and NO_x reduction system was developed, and it was discovered that the non-thermal plasma reactor and subsequent plasma chemistry has the ability to directly oxidize a portion of the PM in an engine exhaust stream.



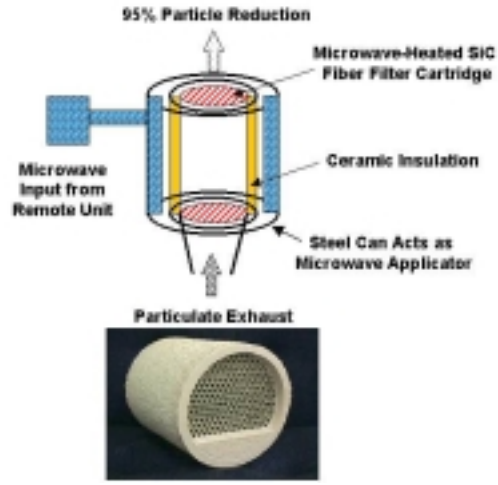
NO_x Reduction Efficiency with and without Plasma

PNNL invented a new conceptual plasma/catalyst system that has a high potential of achieving the NO_x reduction targets with significantly reduced input power requirements. Another important highlight from this year's work is the identification of partially oxidized hydrocarbons produced in the plasma region of a plasma/catalyst device. From prior work, it was widely believed that the most important role for the plasma reactor part of the device is to oxidize NO to NO_2. This year it was demonstrated that partial hydrocarbon oxidation by the plasma is at least as important as NO oxidation if not more so. Testing also demonstrated a sizable reduction in PM, proportional to the input energy of the plasma reactor. In the coming year, studies will focus on the identification of the fate of the PM. In particular, an important question is whether this observed PM reduction is due to electrostatic precipitation or if, indeed, the PM is more fully oxidized (ideally to CO_2).

Industrial Ceramic Solutions Achieves 97 Percent Removal Efficiency from their Microwave-Heated PM Filter

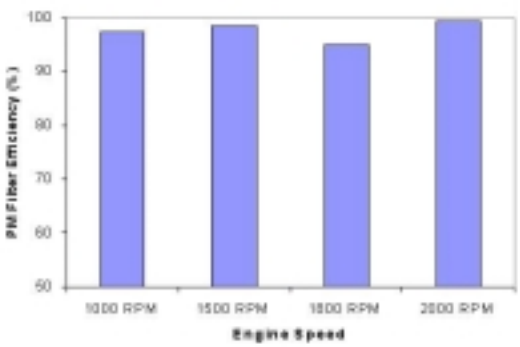
While PM emission control technology is somewhat more developed than NO_x control technology, regeneration of trapped particulate matter presents a problem in that most light-duty CIDI engines do not achieve high enough exhaust temperatures to initiate regeneration except at high engine speeds and loads. Industrial Ceramic Solutions has designed a particulate filter that is regenerated using microwaves that eliminates this problem. It may also be a solution to the cold-start issue that is responsible for a significant quantity of both diesel and gasoline engine emissions. The microwave filter technology is unique due to the discovery and use of a special silicon carbide fiber that efficiently converts microwave energy to heat energy.

These fibers can achieve temperatures of 1,200ºC in 9 seconds in a standard household microwave oven. A process has been developed to incorporate this phenomenon into a filter cartridge and microwave regeneration system for use in diesel engine exhaust streams. The microwave field finite-element program analysis improved the heating efficiency of the filter cartridge from 10% of the filter volume in FY2000 to over 60% in FY2001. The mechanical strength of the ceramic fiber media, at the conclusion of the three-month experimental matrix optimization program, increased from 1.0 psi to 6.0 psi. Calculations have shown that 3.0 psi would be adequate for a typical diesel exhaust stream. Analysis of the materials matrix data shows that further improvements to 10 psi are attainable. Stationary diesel 1.9-liter engine test cell data of the FY 2001 microwave filter system improvements demonstrated an average particulate filtering efficiency of 97%, over a spectrum of normal engine operating conditions. Preliminary road testing of the filter on the Ford 7.3-liter truck proved that the filter could survive the full loading of 1,000 cubic feet per minute of exhaust flow without mechanical failure.



Microwave-Heated PM Filter

In FY2002, the durability of this PM filter will be tested under controlled vehicle operation on a test track. At periodic intervals, chassis dynamometer tests will be conducted to measure the fuel economy impact of this PM filter due to increase in engine back-pressure and the electrical energy needed for regeneration.



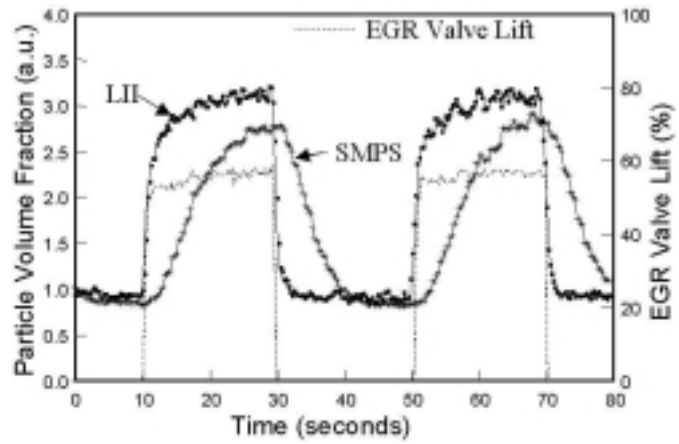
PM Filtering Efficiency at Steady-State Engine Operation

Sandia National Laboratories Develops new CIDI Engine PM Measurement Technique Using Laser-Induced Incandescence

While measuring PM mass can be done quite accurately over driving cycles, analytic tools to measure PM number and identify emission rates during engine transients are not well developed and hinder the ability to develop strategies to minimize PM formation during combustion, and to design efficient particle filters. Sandia National Laboratories is investigating simultaneous measurements of laser-induced incandescence (LII) and laser elastic scattering (LES) to obtain the following PM aggregate parameters:

- particle volume fraction
- diameter of primary particles
- number density of primary particles
- geometric mean of the number of primary particles per aggregate
- geometric standard deviation of the number of primary particles per aggregate
- mass fractal dimension
- radius of gyration of the aggregated primary particles

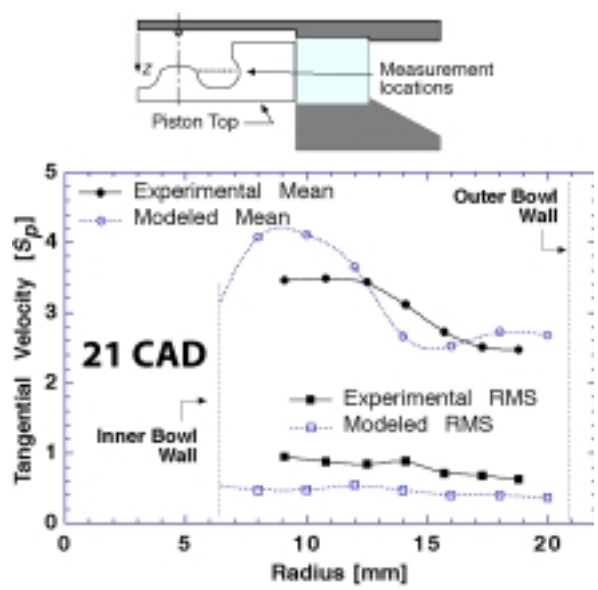
LII is a well-established technique for the measurement of PM volume fraction and primary particle size; it has been applied to both stationary burner flames and diesel engine combustion. Simultaneous measurement of LES from the particles at several discrete angles relative to the incident laser beam can be used to obtain additional information regarding the characteristics of PM aggregates using the RDG-PFA approximation.. The advantages of integrated LII-LES measurements over conventional PM measurement techniques is that it can be applied in any environment (e.g., hot or cold, undiluted or diluted, etc.), it responds in real time and is very sensitive to low PM concentrations (lower limit is estimated to be one part per trillion). Compared to a scanning mobility particle sizer (SMPS), LII has the capability to follow rapid engine transients. Off-the-shelf components are readily available to build an LII-LES measurement system. Sandia National Laboratories is providing assistance to Artium Technologies Inc., who is taking the lead to commercialize this technology. Use of LII PM measurement instruments will allow CIDI engine manu-facturers to better understand under what conditions PM is produced, and to design ways of minimizing PM.



Comparison of LII and SMPS Response to Step Change in EGR Showing the Better Response and Accuracy of LII

Sandia National Laboratories Develops CIDI Engine Swirl Modeling Tools

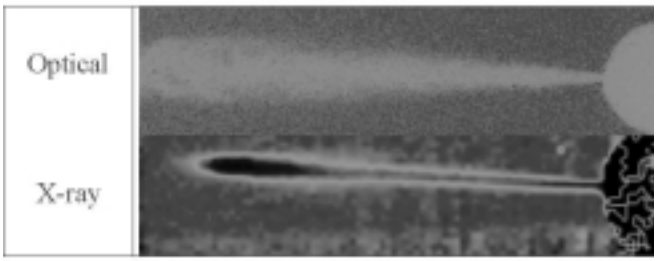
Introduction of flow swirl in CIDI combustion systems is an established technique for reducing engine-out PM emissions and enabling reduced NO_x emissions by permitting injection timing retardation and increasing the combustion system EGR tolerance. In spite of their widespread use, the physics of these swirl-supported combustion systems is still poorly understood, and their optimization consists largely of guesswork and trial-and-error modifications. Sandia National Laboratories has developed the sophisticated modeling tools and is providing the physical understanding required by engine manufacturers to achieve the lowest possible CIDI engine-out emissions. Measurements of the in-cylinder velocity field have satisfied the objectives of: 1) characterizing the velocity field to support interpretation of future experiments, 2) allowing validation of model predictions under fired engine operation, and 3) identifying important aspects of the flow physics that are of technological significance and that are not captured by the model. Future work will continue to further clarify the sources of the disparities seen between the measurements and predictions, evaluation of the performance of improved flow turbulence models, direct measurement of particulate mass, and evaluation of the model predictions as nozzle geometry, swirl, and injection rate shape are varied.



Agreement Between Modeled and Measured Swirl in a CIDI Engine

Argonne National Laboratory Refines Their Fuel Spray X-Ray Imaging Technology

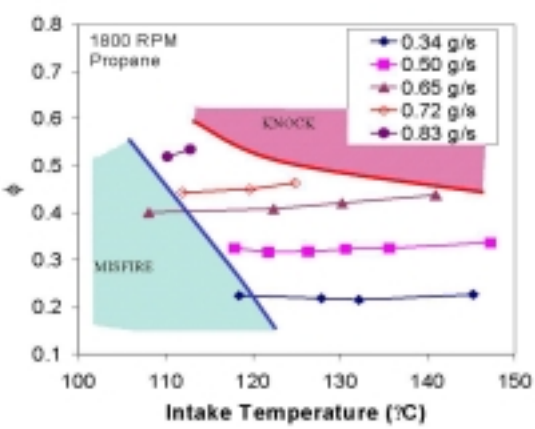
High-pressure, high-speed sprays are an essential technology in many industrial and consumer applications, and especially for CIDI fuel injection systems. The lack of quantitative, time-resolved analysis on the structure and dynamics of sprays limits the accuracy of spray modeling and creates obstacles to improving spray technology. Specifically, higher injection pressures (>1500 bar) and smaller orifice diameters (<200 mm) for small-bore CIDI engines have brought even greater impetus to the understanding of fuel spray behavior. With partial funding by Bosch Corporation, Argonne National Laboratory (ANL) has demonstrated that the dense part of the fuel spray can be quantitatively probed by a non-intrusive method utilizing monochromatic x-radiography techniques. By using fast a 2-D x-ray detector and appropriate x-ray optics, ANL has proven that the x-ray measurement can be performed efficiently and the technique is practical for industrial applications in nozzle diagnosis and spray modeling. In addition, complicated hydrodynamic phenomena, such as generation of shock waves by high-speed fuel sprays, have been quantitatively detected and visualized in a most direct manner. This has allowed the analysis of important thermodynamic properties, such as the density of the gas media inside and near the shock front. By being able to measure these parameters, fuel injection system manufacturers will be able to design injectors that result in lower emissions of PM and NO_x from CIDI engines.



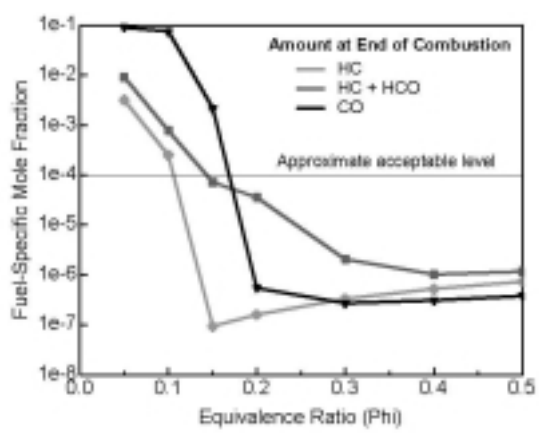
Comparison of Optical and X-Ray Fuel Injection Spray Visualization

Lawrence Livermore National Laboratory and Sandia National Laboratories Explore an "Alternative" Combustion System

Homogeneous Charge Compression Ignition (HCCI) combustion has the potential to be as efficient as CIDI engines while producing ultra-low NO_x and PM emissions. An unique advantage of HCCI engines is that they can operate on gasoline, diesel fuel, and most alternative fuels. While HCCI has been demonstrated and known for quite some time, only the recent advent of electronic sensors and controls has made HCCI engines a potential practical reality. Both Lawrence Livermore National Laboratory (LLNL) and Sandia National Laboratories (SNL) have been working on HCCI combustion. LLNL has developed models to predict HCCI combustion parameters and emissions and have converted an existing CIDI engine to HCCI combustion using



LLNL Results Showing the Acceptable Range of HCCI Combustion Using Propane



SNL HCCI Combustion Results Showing High HC and CO Emissions at Light Loads

propane as fuel. Engine control methods being explored include thermal strategies, use of additives (DME, diesel, etc.), inlet heating, EGR, and exhaust throttling. SNL is developing fundamental understanding of HCCI combustion phenomena through application of advanced laser diagnostics and chemical-kinetic rate computations. A wide range of operating conditions and various fuel injection, fuel/air/residual mixing, and control strategies that have the potential to overcome the technical barriers to HCCI will be investigated. SNL has found that at very light loads and idle, HCCI combustion reactions no longer go to completion, resulting in high HC and CO emissions. SNL has shown through analysis that EGR can smooth out combustion, allowing higher-load operation. Although EGR has been shown to be beneficial, it will not be sufficient by itself to allow high-load HCCI operation over the entire range of engine operation, one of major hurdles to practical HCCI engines.

Future Directions

Last year, as part of the Ultra-Clean Transportation Fuels Initiative, DOE solicited proposals for the development of clean transportation fuels and the integration of these fuels into existing infrastructure, and development of new and innovative emission control systems for advanced CIDI engines. From this solicitation, two new cost-shared projects were initiated:

- General Motors (a CIDI engine manufacturer and developer of emission control systems) heads a team to discover new NO_x reduction catalysts for CIDI engine emission control devices. Other members of the team include Engelhard (a catalytic emission control device developer), ExxonMobil (a fuel supplier), MSI (an informatics supplier) and Los Alamos National Laboratory (instrument development expertise). The extremely large number of potential catalyst combinations makes it likely that better catalysts exist for NO_x emission control devices. Combitorial chemistry techniques developed in the pharmaceutical industry will be used to quickly screen several thousand promising catalyst combinations. The most effective of these will then be subjected to testing using actual engine exhaust. The results of this work should result in more efficient, smaller, and cost-effective NO_x emission control devices. This project has a 3-year duration and the results will be available for development of new emission control catalyst technologies by any potential customer.
- Ford Motor Company will develop and test a prototype light-duty truck using a V-6 CIDI engine with selective catalytic reduction (with urea reductant) for NO_x control and a catalyzed soot filter for PM control. Assisting Ford in this project will be ExxonMobil (fuel supplier and catalyst technology development), other catalyst suppliers to Ford, and FEV (an outside research facility). The major objective is to develop and demonstrate an emission control system that will meet Tier 2 emission standards (0.07 g/mi NO_x and 0.01 g/mi PM) with greater than 5,000 hours durability. A unique aspect of this project is that Exxon/Mobil will supply and demonstrate an integrated urea delivery system that is transparent to the user. A practical and reliable urea distribution, storage, and dispensing system is needed to make urea selective catalytic reduction a viable NO_x emission control option for both light- and heavy-duty vehicles. Demonstrating lifetime low emissions is a prerequisite to development of light-duty trucks and SUVs with CIDI engines that can achieve up to 40 percent improvement in fuel economy with superior torque and trailer towing capabilities relative to similar vehicles with gasoline engines.

<u>Development of New Sensors</u>: On January 25 and 26, 2000, OAAT sponsored a workshop on sensor needs for automotive fuel cell systems; compression-ignition, direct-injection (CIDI) engines; and spark-ignition, direct-injection (SIDI) engines. The purpose of the workshop was to draw upon the expertise of the fuel cell development community, the direct injection engine community, and sensor researchers and manufacturers to define the needs and technical targets for sensors, and to aid DOE in identifying and prioritizing R&D activities in those areas. Sensors are important to being able to control emission control devices and extract the optimum efficiency from them. Based on feedback from the Sensor Workshop conducted during the last year, work on sensors has been expanded. In the coming year, four new projects will be initiated:

- CeramPhysics, Inc. will develop a low-cost, high-performance combined oxygen and NO_x sensor that can be used to control CIDI engines and emission control systems in a cost-sharing agreement with DOE. Prototype sensors will be developed and bench-tested prior to full-scale testing in an engine by Visteon Corp. This project builds upon the recent oxygen sensor developed by CeramPhysics under a prior project funded by DOE.
- Delphi through prime contractor Electricore will develop a robust NO_x sensor for use in CIDI engines under a cost-sharing agreement with DOE. The sensor will be designed to provide performance reliability for the life of the vehicle (>5000 operating hours), and be commercially viable with high-volume, low-cost production.
- Honeywell Laboratories and the University of Minnesota will design and build several prototype particulate matter (PM) sensors in a cost-sharing agreement with DOE. The sensor prototypes will be installed and tested in a CIDI engine test facility at the University of Minnesota's Center for Diesel Research. Gas concentration and particle size and concentration information will be recorded for calibration and verification of sensor test results. Honeywell's commercial Sensing and Controls Division (Micro Switch) will assist in the development of suitable sensor packages and supporting electronics for the PM sensors.
- Delphi through prime contractor Electricore will design and produce a low-cost, wide-range oxygen sensor for use in CIDI engines to control the fuel injection and emission control systems. A prototype oxygen sensor, designed to meet the requirements of an automotive environment, will be demonstrated at the laboratory bench level. Engine qualification tests will be conducted on the sensor to prove functionality and durability, and the cost of the sensor in high-volume production will be estimated. This project is cost-shared with DOE.

<u>Test and Demonstration of Engine/Fuel/Emission Control Systems</u>: Meeting future emission standards requires a coordinated effort to reduce emissions from the engine and incorporation of emission control devices that complement the engine and loads put on the engine by the vehicle. The fuel used is important because it determines in large part the deterioration rate of the emission control devices, and might serve as the source of reductants for NO_x emission control devices. In the coming year, three projects will test different approaches to emission reduction - all three incorporate prototype CIDI engines for use in light-duty vehicles:

- DDC will scale-up their emission control system (selective catalytic reduction with urea reductant for NO_x control and a catalyzed soot filter for PM control) to work with their 4-liter prototype CIDI engine. They will continue their efforts to lower engine-out emissions, explore exhaust temperature management, and continue catalyst development and testing that matches the emissions and exhaust temperatures of their prototype engine. The fuel economy penalty and durability of their emission control system will be quantified through engine and vehicle testing.
- Cummins will continue their efforts to develop an emission control system that uses an NO_x adsorber and catalyzed soot filter for PM control. They have found that the sulfur from 15 ppm sulfur content fuel combined with sulfur from consumed lubricating oil is sufficient to quickly degrade NO_x adsorbers, which are highly sensitive to sulfur. To make this approach viable, they will be designing a sulfur trap with a target life of 20,000 miles. They will also identify the optimum reductant that can be derived directly from diesel fuel and design a reductant injection system that minimizes the impact on fuel economy.
- Apyron Technologies, Inc., Clark Atlanta University, and International Truck and Engine Corporation will develop a commercial exhaust gas sulfur trap for CIDI engine applications in a new cost-shared project. The project will be divided into three separate phases: Phase I will involve synthesis and laboratory testing of the technology; Phase II will focus on adaptation of the technology to a diesel engine and in-line testing with the engine; and Phase III will prepare the technology for production and commercialization.

Homogeneous Charge Compression Ignition: HCCI combustion holds tremendous potential not just because it results in extremely low emissions of NO_x and PM, but because it can also use gasoline as a fuel. Substituting HCCI engines for current spark ignition engines could result in large improvements in the fuel efficiency of light-duty vehicles. HCCI engines are also very well suited to hybrid powertrains which are just now being introduced into highway transportation vehicles. The primary hurdle to development of practical HCCI engines is identifying ways to control the initiation and duration of combustion. Recognizing the potential of HCCI engines, the DOE has awarded two new cost-shared three-year contracts in HCCI combustion to consortiums of Universities that will be initiated in the coming year:

- The University of Michigan along with the Massachusetts Institute of Technology, the University of California at Berkeley, Stanford University, and Texas A&M University will combine their modeling and laboratory testing capabilities to identify HCCI operating ranges and limits using gasoline as fuel, and to assist development and optimization of control strategies. Both single- and multi-cylinder engines will be used to investigate issues of fuel injection strategy, mixture homogeneity, valve timing, internal and external EGR, intake mixture temperature, fuel properties, cooling strategies, and engine transients. Enabling technologies such as variable valve timing, variable compression ratio, and implementation of new engine sensors will be explored.
- The University of Wisconsin along with the Pennsylvania State University, Princeton University, Stanford University, and University of Illinois will develop methods to optimize and control HCCI engines using gasoline as the fuel. This team of universities will use state-of-the-art computer modeling, coupled with innovative engine experiments to devise strategies for optimizing and controlling HCCI engines. Detailed chemical kinetic models will be developed and used to guide HCCI mixture preparation and strength. Four fully instrumented engines will be used by the team that cover a wide range of displacements and include features such as variable valve actuation, electronically controlled direct fuel injection systems, and laser diagnostics.

Honors and Special Recognitions

- Jin Wang, Ramesh Poola, Chris Powell, and Yong Yue of Argonne National Laboratory received the ANL Director's Award in June 2001 for their work on using x-rays to image and measure fuel injector spray patterns. They were also finalists in the Discover Awards (issued by Discover Magazine) for this work.
- M. Lou Balmer-Miller (former PNNL staff member), Stephen Barlow, Suresh Baskaran, Darrell Herling, Russell Tonkyn, and Alexander Panov of Pacific Northwest National Laboratory, plus John Hoard of Ford Motor Company and Galen Fisher of Delphi Research Labs, were awarded an R&D 100 award from R&D Magazine for their work on non-thermal plasma emission control systems.
- The team that prepared the Homogeneous Charge Compression Ignition (HCCI) Technology Report to Congress was recognized with a special achievement award at the CIDI Engine Combustion, Emission Control, and Fuels Review held at Oak Ridge National Laboratory June 11-13, 2001. The team included representatives from Sandia National Laboratories, Lawrence Livermore National Laboratory, Ford, General Motors, DaimlerChrysler, Cummins, DDC, Southwest Research Institute, and QSS Group, Inc. The report is available on the web at www-db.research.anl.gov/db1/cartech/document/DDD/98.pdf.

Patents

- "A Method and System for Reduction of NO_x in Automotive Vehicle Exhaust Systems", John Hoard (Ford), Mari Lou Balmer-Millar, Russell G. Tonkyn, Alexandre Malkine, and Alexander Panov (PNNL). Filed by the Low Emissions Partnership (LEP), Docket No. 1017-047.
- "Cascading Reactors for Increased NOx Reduction", Russell G. Tonkyn, Stephan E. Barlow, Mari Lou Balmer-Millar, and Gary D. Maupin (PNNL). Filed by Pacific Northwest National Laboratory (PNNL), File No. 12934-E.

- "Catalysts for Lean Burn Engine Exhaust Abatement", by K. C. Ott, N. C. Clark, and M. T. Paffett (LANL), serial number SN 09/699,162 filed October 27, 2000.
- Material and System for Catalytic Reduction of Nitrogen Oxide in an Exhaust Stream of a Combustion Process , T. J. Gardner, S. J. Lockwood, S. E. Lott, and L. I. McLaughlin (SNL) U.S. Patent 6,165,934, December 26, 2000.

Invention Disclosures

- "Dual Catalyst System for NOx Reduction Following a Non-Thermal Plasma", Mari Lou Balmer-Millar and Alexander G. Panov (PNNL). Invention Disclosure, PNNL File No. 13155-E.
- "Partial Oxidation of Hydrocarbons by Dielectric Barrier Discharge", Russell G. Tonkyn and Stephan E. Barlow (PNNL). Invention Disclosure, PNNL File No. 13270-E.
- "Efficient Strategies for NOx Adsorber Regeneration", by Charles S Sluder and Brian H West (ORNL). ORNL invention disclosure number 1300000896 filed December 21, 2000.
- "Fuel Additives for Sequestration of Sulfur", Charles S Sluder and Brian H West (ORNL). ORNL invention disclosure number 1300000938 filed March 27, 2001.
- "Engine Exhaust Sulfur Dioxide Analyzer", Michael D. Kass, William P. Partridge Jr., Charles S. Sluder, John M. Storey, Robert M. Wagner and Brian H. West (ORNL). ORNL invention disclosure number 1300000939 filed March 27, 2001.

The remainder of this report highlights progress achieved during FY 2001 under the Advanced Combustion and Emission Control R&D Program. The following 31 abstracts of industry and National Lab projects provide an overview of the exciting work being conducted to tackle tough technical challenges associated with CIDI engines, including fuel injection, exhaust gas recirculation, fuel mixing, combustion processes, and catalytic devices for controlling emissions. We are encouraged by the technical progress realized under this dynamic program in FY 2001 which showed the potential of various emission control technologies to reduce NO_x and PM. However, it also pointed out the barriers still to be crossed, the most prominent of which are achieving acceptable device deterioration rates and energy use (i.e., fuel economy penalty). In FY 2002, we look forward to working with our industrial and scientific partners, to not only advance emission control technology, but to achieve acceptable emission control device durability and minimize the impact on fuel economy.

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II. EMISSION CONTROL SUBSYSTEM TECHNOLOGY DEVELOPMENT

A. Demonstration of Integrated NO_x and PM Emissions for Advanced CIDI Engines

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Main Subcontractors:Engelhard Corporation, Michigan Technological University

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

Barriers

A. NO_x Emissions

B. PM Emissions

Tasks

4c. Selective Catalytic Reduction Catalysts

5a. Catalyzed Diesel Particulate Filter

6. Prototype System Evaluations

Objectives

- Demonstrate technology for PNGV/Personal Transportation (PT) engine families of 0.5 L/cylinder to ~0.7L/cylinder CIDI engines, which will achieve tailpipe emission levels for Federal Tier 2 emission targets.
- Meet specific targets for engine-out emissions, efficiency, power density, noise, durability, production cost, emission control system volume and weight.

Approach

- Use new emerging combustion technologies combined with the most advanced emission control devices to demonstrate an integrated engine, vehicle, and emission control system that meets performance and emission targets.
- Develop emission control and engine systems emissions models for prediction and control of emissions.
- Select and evaluate a "best" (engine and emission control device) system using an integrated experimental and analytical tool set.
- Conduct system performance, emissions and durability evaluation testing.

Accomplishments

- Developed a first generation catalyzed soot filter (CSF) plus selective catalytic reduction (SCR) integrated system, coupled the integrated system with a 0.5 L/cylinder engine and implemented them into a vehicle [PNGV (mule) Neon].
- Demonstrated 94% NO_x and 80% PM reductions over several selected critical steady-state modal points for a 0.5 L/cylinder engine and an emission control system.
- Demonstrated 49% NO_x and 69% PM reductions over the Hot-505 portion of the Federal Test Procedure (FTP; chassis dynamometer test).
- Discovered and refined breakthrough combustion technologies (CLEAN Combustion') providing much lower engine-out NO_x emissions at selected operating conditions.
- Conducted aging tests for different catalysts, and characterized the catalyst performance and emissions over time.
- Developed the first generation of integrated NO_x and PM emission control systems suitable for light-duty (LD) truck applications.
- Developed major portions of the virtual lab (simulation) toolbox.
- Validated and calibrated many of the virtual lab models.

Future Directions

- Refine CLEAN Combustion' technology via systematic subsystem enhancements and methodical integration.
- Explore robust exhaust temperature management.
- Continue catalyst development and testing.
- Implement an integrated emission control system for an SUV/LD truck to address the technology scaling.
- Conduct integrated virtual plus hardware cycles of testing aiming at identifying synergistically new local optima, and a global optimum, for the integrated engine-emission-control-powertrain-vehicle system.

Introduction

DDC is conducting the Low Emissions Aftertreatment and Diesel Emissions Reduction (LEADER) program under a DOE project entitled: "Research and Development for Compression-Ignition Direct-Injection Engines (CIDI) and Aftertreatment Subsystem." LEADER is a 36-month program to develop CIDI engine emission control technologies and demonstrate scalability for various vehicle inertia weight classes. The overall objective of this program is to achieve aggressive vehicle emission targets for 2004 and beyond. DDC has had significant experience in light-duty diesel engine development and has developed unique engines with

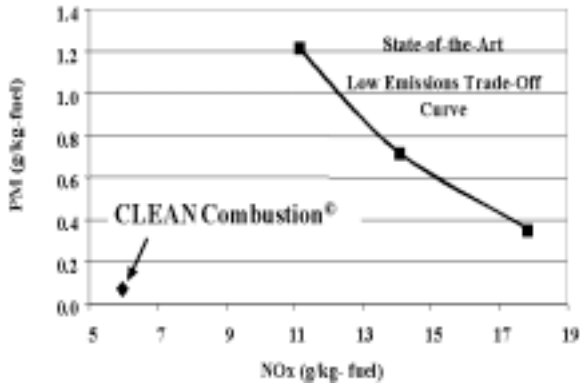

Figure 1. Emerging Combustion Strategy for Light to Medium Load

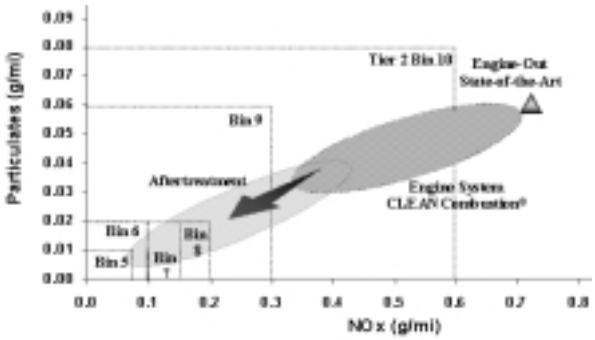

Figure 2. New Integrated Emissions Reduction Road Map

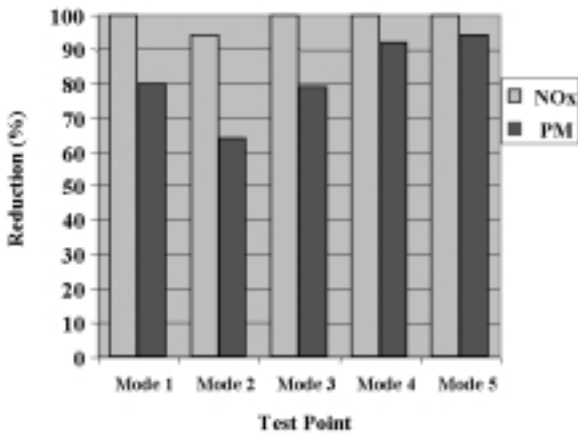

Figure 3. Emissions Reductions over Five Steady-State Modes

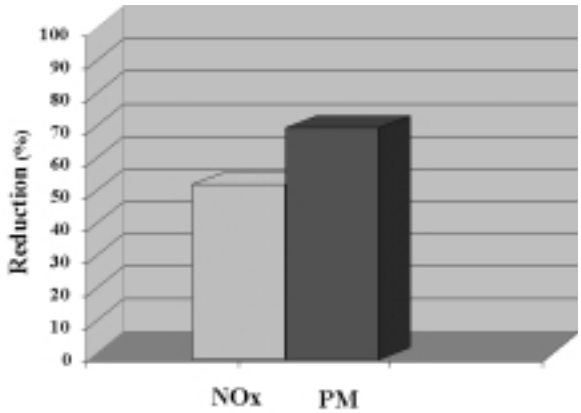

Figure 4. Emissions Reductions of PNGV Mule Vehicle over Hot-505

displacements varying from 0.5 L to 0.67 L per cylinder for different applications.

Approach

Breakthrough CLEAN Combustion' strategies have been emerging, resulting in substantial advantages over conventional engine NO_x-PM trade-off characteristics (Hakim and Bolton, 2001). Figure 1 illustrates that the newly developed combustion technology offers substantial NO_x-PM trade-off compared to the current state-of-the-art low emission characteristic curve. In addition, increases in exhaust temperature will offer an ideal environment for emission control devices. As a consequence, a new integrated emission reduction roadmap is emerging and is shown in Figure 2.

In order to realize the newly developed roadmap, the strategy is to pursue integrated engine, emission control, and vehicle development using our coupled experimental and analytical tool set. DDC and its subcontractors are developing a suite of advanced integrated catalyst and engine emission control models. The objective is to predict emissions for a broad range of engine-out conditions and catalyst design specifications. Validated models will provide further design recommendations and testing directions.

Results

A first generation integrated engine (0.5 L/ cylinder, 3 cylinder CIDI) plus emission control system was developed using bench and engine dynamometer testing. Figure 3 shows the emission reductions over selected steady-state modal points. NO_x was reduced over 94% and PM by over 80%. The ammonia slip was minimized to zero at most modal points.

The DDC team also implemented this first generation system into a PNGV-type (mule) Chrysler Neon vehicle. Displayed in Figure 4 is the Neon mule test data over the Hot-505 portion of the FTP transient chassis dynamometer test. The results demonstrated through this first generation integrated system are extremely encouraging.

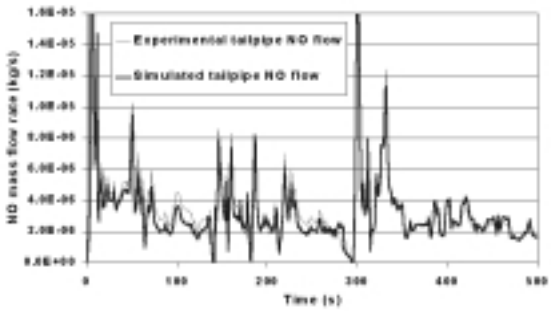

Figure 5. Comparisons of Simulation and Hardware Data for a SCR over a Transient Vehicle Cycle

The development of emission control systems for LD truck applications is also moving forward. The first generation of the emission control hardware and controls is being integrated with the DDC 4-liter DELTA engine.

Significant progress has been made in virtual lab development. The emission control virtual lab technical path and the three layer interactions defined in last year's annual report (Zhang, 2000) are being well executed. DDC and its assembled team have developed major portions of virtual lab 1D, 2D and 3D catalyst models. Integration of these in a seamless fashion is in progress, albeit a daunting task. In the mean time, the models are being selectively tested. As an example, Figure 5 shows a reasonably good comparison of experimental data and simulation for a vehicle equipped with an SCR catalyst over a transient test.

A 2-dimensional single-channel numerical model describing the filtration, flow field, heat transfer and regeneration characteristics of PM traps is being developed by Michigan Technological University (MTU). This model is also being integrated within the DDC simulation library, thus providing a full package to investigate the performance and PM emissions for a given engine and emission control system in the virtual lab. In addition to prediction of pressure drop, the current model can also predict the instantaneous temperature contour inside the filter during a regeneration transient exemplified in Figure 6. The PM model is being validated with transient engine data.

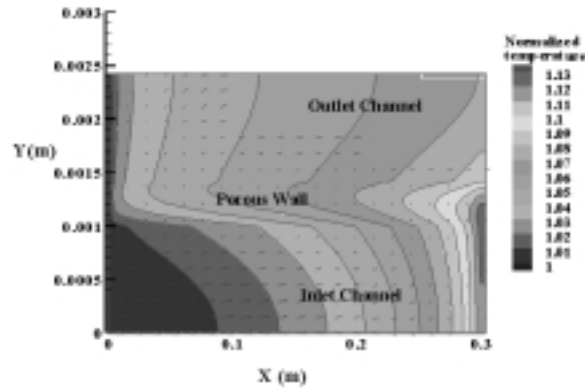

Figure 6. Temperature Contour of a Diesel Particulate Trap

Conclusions

The first generation of integrated engine and emission control (CSF plus SCR) system was developed and implemented into a PNGV mule vehicle. Emissions reductions are encouraging, showing over 49% NO_x and over 69% PM reduction in vehicle transient cycles, and over 94% NO_x and over 80% PM reductions over critical modal points in steady-state engine testing. This can be attributed to the combination of new emerging CLEAN Combustion' technology and advanced emission control systems. Progress in virtual lab development is moving forward, providing further design recommendation and testing directions. This shortens the design and development cycles to achieve near-optimum technology that will meet the Tier 2 emissions targets.

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2. Zhang, H., "Application of Advanced Emission Control Sub-System to State-of-the-Art Diesel Engine," FY2000, Progress Reports for Combustion and Emission Control for Advanced CIDI Engines, U.S. Department of Energy, November, 2000.

B. Development of Advanced Aftertreatment Subsystem Technologies for CIDI Diesel Engines

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Contractor: Cummins Inc., Columbus, Indiana
Prime Contract No.: DE-FC02-99EE50577; October 15, 1999 — December 15, 2002

Subcontractor: Engelhard Corporation, Iselin, NJ

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

Barriers

A. NO_x Emissions

B. PM Emissions

Tasks

4a. NO_x Adsorber R&D

4f. R&D on Sulfur Trapping Technologies

5a. Catalyzed Diesel Particulate Filter

6. Prototype System Evaluations

Objectives

- Develop the generic aftertreatment emission control technologies applicable for LDV and LDT engines ranging from 55 kW to 200 kW.
- Deliver an optimized aftertreatment subsystem for a 55 kW PNGV application to demonstrate Tier 2 NO_x and PM emissions capability with engine-out emissions of 1.4 g/kW-hr NO_x and 0.15 g/kW-hr PM. Only those technologies which have a reasonable chance of meeting EPA Tier 2, Bin 5 regulations of 0.07 g/mile NO_x and 0.01 g/mile PM will be pursued.

Accomplishments

- The development of an emission control system (ECS) performance model has been completed, and the model is being used in conjunction with critical lab/engine experiments for preliminary emission control subsystem design and analysis.
- The results of preliminary emission control subsystem design and analysis indicated that the best NO_x control approach for LDV and LDT applications is the NO_x adsorber technology. A NO_x reduction efficiency of 87% is required to achieve 0.07 g/mile PNGV vehicle-out NO_x emissions.
- Significant progress has been made on adsorber formulation development, extending operation of the catalysts by about 30 to 50ºC lower temperatures as compared to the previous formulations.

- An 84% NO_x conversion efficiency and 95% PM conversion efficiency have been demonstrated with a breadboard low emission ISB engine and an adsorber/CSF exhaust configuration on a simulated FTP-75 emission cycle.
- Progress has been made on NO_x adsorber bypass regeneration strategies. The results indicate a 40% to 50% reduction in fuel injection penalty as compared to full flow regeneration strategies over a simulated FTP-75 emission cycle. A by-pass regeneration system will be needed to achieve the program target of 5% maximum fuel economy penalty.
- Progress has been made on identifying the best reductant for NO_x adsorber catalysts, measuring ECS emissions, and analyzing catalyst material for ECS development.
- Mapping of exhaust sulfur concentrations with different fuel and oil sulfur levels over a wide range of engine speeds and load conditions has been completed. The results indicate that, in addition to the fuel sulfur content, the sulfur in the oil also plays a major role in adsorber sulfur loading and performance degradation. With a 15 ppm sulfur diesel fuel and a standard heavy-duty lube oil, the sulfur in the oil can account for up to 50% of the total sulfur in the exhaust.
- Test results indicate that the NO_x conversion versus temperature curve for an ISB engine is nearly identical to that of a Diata engine. This suggests that a fundamental and "displacement-size" transparent understanding can be achieved for ECS technology development.

Future Directions / Expected Results

- Continue to develop and optimize selected catalyst formulations for best NO_x conversion efficiency under exhaust temperatures and space velocities consistent with anticipated LDV and LDT applications.
- Continue to develop and design an irreversible sulfur trap to provide sufficient capacity to trap 100% fuel- and oil-derived SO_x for a new target of greater than 20,000 mile operation.
- Identify optimum reductant and develop reductant injection system.
- Define and implement control algorithm including required inputs and outputs.
- Optimize the reductant control for enrichment during steady-state and transient operations for best ECS performance (conversion efficiency, fuel penalty, and HC slip).
- Develop and optimize the NO_x /PM system configuration. Investigation will include different placement and order of NO_x and PM control devices, different injection locations, and full-flow versus by-pass regeneration.
- Obtain preliminary transient FTP-75 results on a P2000 vehicle at Argonne National Laboratory.

Introduction

The key objective of this project is to develop the generic emission control technologies applicable for LDV and LDT engines ranging from 55 kW to 200 kW. This will involve engines with displacements ranging from 1.2 to 6.0 liters. A fundamental and "displacement-size" transparent understanding will be required. Cummins' results indicate that the LDV and LDT exhaust operating characteristics can be simulated with the Cummins ISB mule engines (see Figure 1). Therefore, most of the emission control

Figure 1. Cummins ISB Engine

Figure 2. Ford DIATA Engine

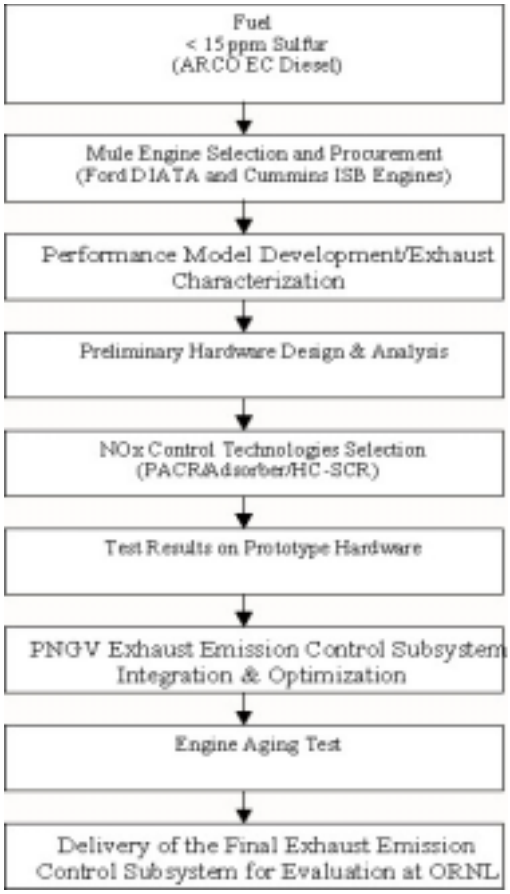

Figure 3. Flowchart of Project Activities

subsystem screening and fundamental understanding will be conducted on the ISB mule engines. In addition, parallel performance validation and final aftertreatment subsystem optimization will be conducted on a DIATA engine developed under the Ford Hybrid Propulsion System Development Program (see Figure 2). The program's primary focus will be on emission control subsystem NO_x and PM conversion efficiency with a minimum impact on fuel consumption penalty, although the higher conversion efficiency required may result in an increase in the cost, size, and weight of the emission control subsystem. Figure 3 is a detailed flow chart of the activities described above.

Approach

Under the phase I program, various NO_x control technologies including non-thermal plasma, NO_x adsorber, and active lean-NO_x, in conjunction with active reductant injection were investigated to select the best NO_x control technology for emission control subsystem integration and development. The areas of development include catalyst formulation for high NO_x conversion over a wider catalyst/exhaust gas temperature range, catalyst structure for increased exhaust gas residence time on active catalyst sites, and an understanding of the various factors that cause deactivation of the catalyst. Fuel reformulation concepts and diesel fuel based onboard hydrocarbon cracking strategies will be investigated to increase the activity of the hydrocarbons introduced into the catalyst systems. Even with the availability of 15 ppm sulfur fuels, the development of a sulfur management scheme is critical to prevent catalyst poisoning and deactivation. The application of a sulfur trap that can be regenerated offline or periodically replaced will be explored.

PM emissions will be addressed by developing a catalyzed soot filter or a combination of catalyzed soot filters with supplemental microwave heating. Soot filter catalysts have been successfully formulated for heavy-duty applications with passive regeneration. However, with the lower exhaust temperatures encountered in PNGV application, an active regeneration scheme with supplemental heating will be investigated.

Finally, the improved emission control components will be integrated and configured optimally in a system developed for a PNGV application. This system will then be calibrated and tested in a controlled environment on a PNGV-sized engine.

Results

In Phase I of this project the three NO_x reduction technologies including plasma assisted catalytic NO_x reduction, active lean-NO_x catalysis, and adsorber catalyst technology using intermittent rich conditions for NO_x reduction were investigated in parallel in an attempt to select the best NO_x control approach for emission control subsystem integration and development. The investigation included critical lab/engine experiments, preliminary design and analysis, and ranking and selection of NO_x control technologies against reliability, up-front cost, fuel economy, service interval/serviceability, and size/weight. Results indicate that the best NO_x control approach for LDV and LDT applications is NO_x adsorber technology. The key advantages of NO_x adsorber technology are its potential for high NO_x conversion (>87%) and its wide temperature range of peak operation (250ºC to 400ºC), although not low enough for light duty applications. Another benefit is that it can use diesel fuel as a reductant, which has advantages of easier enforcement/anti-tampering control and no infrastructure issues (as with urea distribution).

As shown in Figure 4, the NO_x adsorber catalysts have achieved high NO_x reduction levels using very low sulfur (< 3 ppm) diesel fuels under steady-state conditions. However, sulfur poisoning, high fuel penalty during full flow regeneration, and effective regeneration during transient operation at low temperatures remain issues and need to be addressed. The impact of fuel sulfur levels on NO_x conversion efficiency is given in Figure 5. The results indicate that even with the availability of 15 ppm sulfur diesel fuels, an effective exhaust sulfur management scheme is required to keep emission control devices operating near their peak effectiveness. To better understand the effect of adsorber sulfur loading and performance degradation, a mapping of exhaust sulfur concentration over a wide range of engine speeds and load conditions was made. The results, as shown in Figure 6, indicate that, in addition to the fuel sulfur, the sulfur in the lube oil also plays a major role in adsorber sulfur loading and performance degradation. An attempt was made to develop a sulfur trap having sufficient capacity to protect the NO_x adsorber catalyst from sulfur poisoning that would last at least 20,000 miles

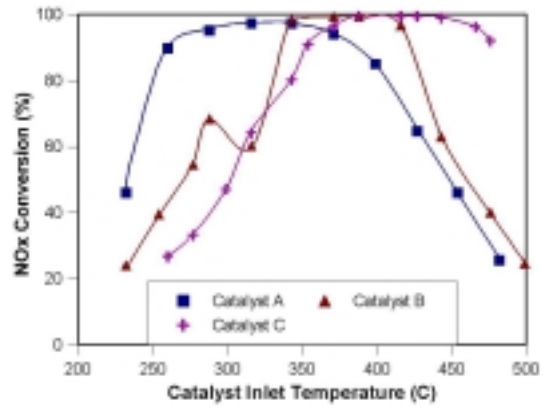

Figure 4. NO_x Conversion Efficiencies for Three Different Adsorber Catalysts

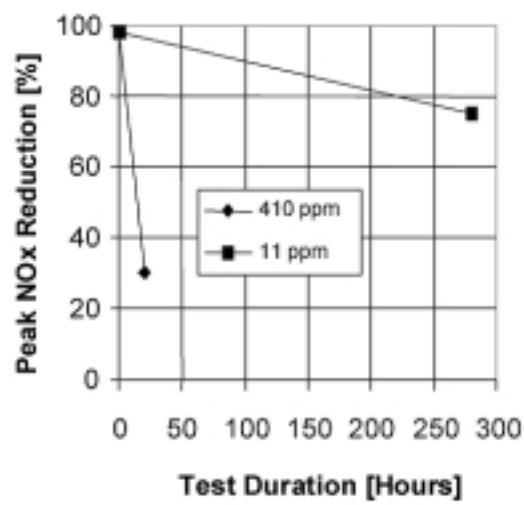

Figure 5. Impact of Fuel Sulfur Levels on Adsorber Performance

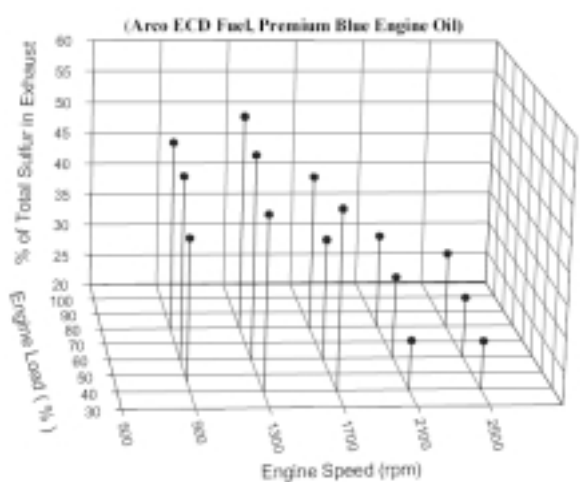

Figure 6. Contribution of Lube Oil Sulfur to Exhaust Sulfur Concentration

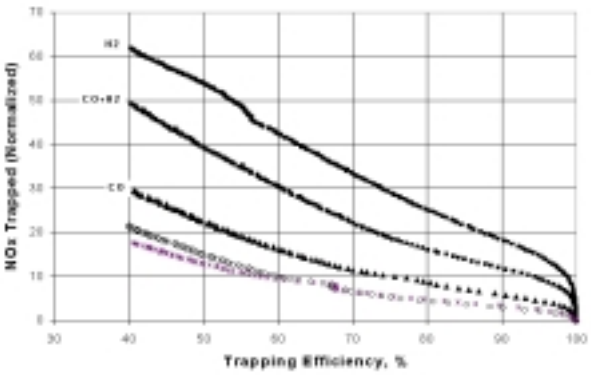

Figure 7. Adsorber Performance for Different Reductants @ 225°C

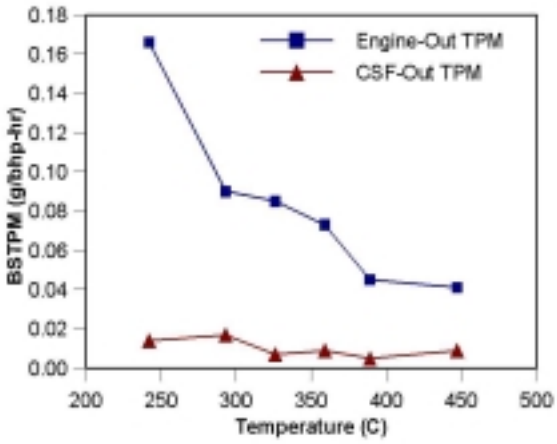

Figure 8. PM Emission Control from Catalyzed Soot Filter

between change intervals. A SO_x trap with a 20 gm SO_2/L capacity, and an estimated 12,000 mile lifetime before change-out has been demonstrated. Alternate substrates with high pore volume are being investigated to provide the increased capacity.

Significant progress has also been made on adsorber formulation development. The engine test results indicate that the advances in adsorber formulation have extended the operating temperature range of catalysts to about 30 to 50°C lower than previous formulations had achieved. However, due to diesel fuel oxidation limitations, the low temperature light-off of an adsorber is not expected below 200°C. Two alternatives have been analyzed to improve low temperature conversion of NO_x adsorbers: (1) using a reformer to generate reductants which can operate at lower temperatures, and (2) raising exhaust temperatures so that diesel fuel may be used directly as the reductant. The reformer produces hydrogen and carbon monoxide, which are active reductants even at 180°C, while diesel fuel is active only above 200°C. The reactor test results indicate that H_2 is the best reductant, followed by a mixture of H_2 and CO, followed by CO (see Figure 7). So for low temperature operation of NO_x adsorbers, either a reformer can be used or the exhaust temperature may be raised by 20°C. A reformer catalyst has been procured and is being prepared for critical performance testing. Calculations show that all the optimum catalytic partial oxidation (CPO) operating conditions without coking cannot be met under certain engine operating conditions. This test will help understand the impact of coking on hydrogen production.

Control of PM emissions was demonstrated using a catalyzed soot filter (CSF). Figure 8 illustrates the capability of the CSF to reduce PM as a function of catalyst temperature. This device has the added advantages of providing reduction in HC and CO emissions. Catalyzed soot filters have been successfully formulated for heavy-duty applications with passive regeneration. However, with the lower exhaust temperatures encountered in PNGV application, a further reduction in soot regeneration temperature or an active regeneration scheme such as supplemental heating or engine exhaust temperature management may be necessary. To further reduce the soot filter regeneration temperature, an advanced catalyzed soot filter is being tested with a precat upstream to evaluate the advantage of NO to NO_2 function in terms of balance point temperature (BPT). BPT results for advanced CSF and advanced CSF w/precat are shown in Figure 9. The precat with advanced CSF gave a 40 to 50°C reduction in the balance point temperature and better regeneration performance.

Testing using microwave regeneration for active soot filter regeneration is also underway. Current results indicate that similar to passive regeneration, active regeneration is most efficient when the filter is regenerated at lower soot loading levels. At high soot loading levels, the soot filter may experience an uncontrolled regeneration, which may result in failure of the filter. Using microwaves for regeneration results in relatively fast soot burning, approximately 10 minutes to regenerate to a clean filter condition as compared to 30 minutes for passive regeneration with a 50g/ft^3 Pt catalyzed soot

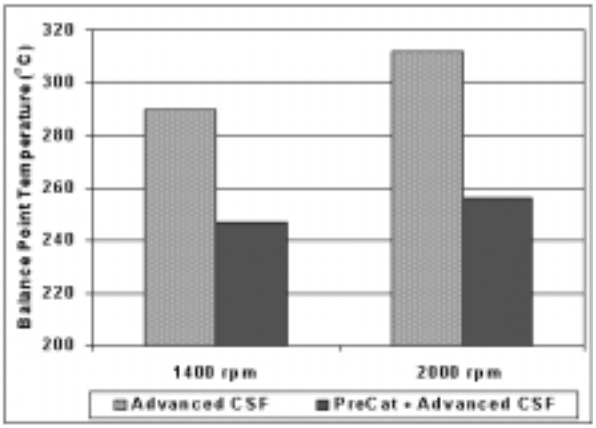

Figure 9. Impact of PreCat on CSF Balance Point Temperatures

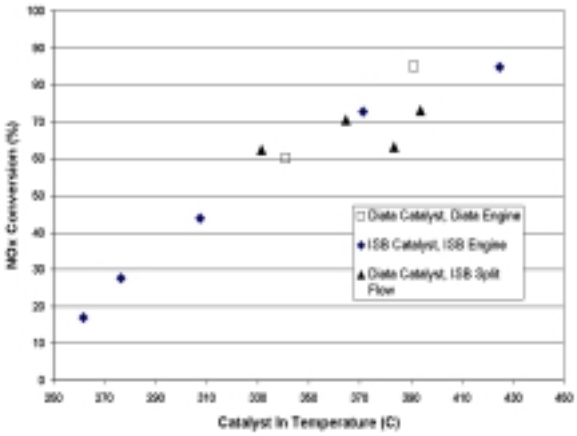

Figure 10. NO_x Adsorber Performance Comparison, ISB vs. DIATA

filter. Additional testing will be conducted evaluating soot loading level, microwave power, and engine conditions.

As part of LDV ECS subsystem development, a split flow arrangement was set up in the test cell to divert part of an ISB's exhaust to a Diata aftertreatment system. The diverted flow was adjusted by valves upstream of the ECS to obtain roughly 20% of total engine exhaust flow (1.2 L engine displacement for Diata versus 6.0 L displacement for ISB). NO_x conversion efficiency obtained from this setup agreed well with previous tests using Diata exhaust flow under engine steady-state operating conditions, as shown in Figure 10. This suggests that a fundamental and "displacement-size" transparent understanding can be made on ECS technology development.

Conclusions

Results of extensive emission control subsystem design and analysis to date indicate that the best NO_x control approach for LDV and LDT applications is NO_x adsorber technology. A NO_x reduction efficiency of 87% is required to achieve 0.07 g/mile NO_x PNGV vehicle-out emissions. Both active lean-NO_x and plasma-assisted catalytic reduction (PACR) technologies are currently not capable of achieving the high conversion efficiency required for DOE emission control subsystem program objectives. Conversion efficiencies of 84% for NO_x and 95% for PM have been demonstrated with a breadboard low emission Cummins ISB engine and an adsorber/CSF exhaust treatment configuration on a simulated FTP-75 emission cycle.

With the lower exhaust temperatures encountered in LDV and LDT applications, the improvement in NO_x conversion efficiency over a wider exhaust temperature range has also been identified as a critical development task. Significant progress has been made on adsorber formulation development, extending the operating temperature range of the catalysts 30 to 50°C lower than that achieved with previous formulations.

Progress has also been made on NO_x adsorber regeneration strategies, reducing the fuel injection penalty by 40 to 50% compared to earlier tests. As part of an early demonstration/validation of NO_x adsorber technology progress, a mobile ECS has been prepared for preliminary chassis dynamometer testing on a diesel hybrid electric PNGV vehicle at Argonne National Lab this year.

Throughout the ECS project the emphasis has been on a fundamental understanding of emission control technologies. Demonstrations have been focused on repeatable performance and development efforts have been directed towards technologies which have a reasonable chance of meeting EPA regulations. Much has been accomplished to date, but much work remains to be done on reliability and durability of these technologies before they will be ready for use on vehicles.

FY 2001 Publications/Presentations

1. Frank F. Mao, "Parametric Investigation of SO_2 Adsorption Kinetics on a Sulfur Trap for Diesel Exhaust Aftertreatment," Diesel Engine Emission Reduction Workshop, Portsmouth, VA, August 2001
2. Neal Currier, Matthew J. De Witt, Alex Yezerets, John Buglass, Geert Bakker, Joe Powell, Steve Cowan, Paul Weider, and C Z Wan, "Employing Reactor Studies for the Research and System Development of Lean NO_x Traps," Diesel Engine Emission Reduction Workshop, Portsmouth, VA, August 2001
3. Robert C. Yu, Scott Cole, and Ken Howden, "Development of Advanced Aftertreatment Subsystem Technologies for CIDI Diesel Engines," Diesel Engine Emission Reduction Workshop, Portsmouth, VA, August 2001

C. Investigation of Sulfur Trap Performance

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Industry Participants: Goal Line Environmental Technologies; Cummins Engine Co.

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

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

Barriers

A. NO_x Emissions

B. PM Emissions

Tasks

4f. R&D on Sulfur Trapping Technologies

Objectives

- Investigate the performance and durability of sulfur trap catalysts and the chemical processes involved.

Approach

- Determine sources and sinks for exhaust sulfur species using gas and particle phase analytical chemistry.
- Utilize advanced measurement capabilities to elucidate NO_x-adsorber/sulfur trap performance with improved resolution and/or sensitivity.

Accomplishments

- Applied Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS) to a full-scale NO_x-adsorber/sulfur trap device and acquired data relevant to device improvement and optimization and model validation and development.
  - Determined the loading behavior for nitrogen and sulfur species and the process rate-limiting steps, diffusion or kinetics.

- Quantified the effects of sulfur poisoning and desulfurization on NO_x-adsorption/desorption/ reduction and reductant-reforming processes.
- Validated the diesel reductant reforming process by demonstrating the detection of olefin and oxygenate HC fragments.

- Discovered significant presence of partial oxidation products of fuel sulfur in the exhaust gas.

Future Direction

- Apply the SpaciMS to formulations with just sulfur-trap function on them.
- Continue to investigate/identify sulfur species in exhaust.

Introduction

NO_x adsorber catalysts provide a promising approach for emissions reduction in the fuel-lean environment of diesel-engine exhaust. However, fuel sulfur remains the biggest barrier to their implementation. Even with fuel sulfur as low as 15 ppm, sulfur poisoning and subsequent desulfurization schemes will be necessary. Sulfur trap catalysts offer the possibility of preventing or attenuating NO_x adsorber poisoning by trapping the SO_2 in the exhaust. Issues with their effectiveness and durability remain, however.

In the article entitled "NO_x Control and Measurement Technology for Heavy-Duty Diesel Engines" contained within this report, Bill Partridge details the use of a high-speed instrument capable of temporally resolving the transient emissions associated with NO_x adsorbers. He describes a Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS) that has been developed in a CRADA project to provide high-speed, minimally invasive, intra-catalyst-channel measurements of a broad range of species. This technology has been applied to a combined sulfur-trap/NO_x adsorber catalyst in order to probe the performance before and after sulfur poisoning, and after desulfurization.

Experimental Description

In the last year, modifications to the SpaciMS were implemented to allow high-speed data acquisition, measurement synchronization to external events (e.g., reductant injection) and real-time switching between any one of twelve sample capillaries. A multi-port valve greatly improves experimental efficiency by allowing for switching between capillaries positioned at various locations within a catalyst monolith to investigate radial and/or axial species and distributions of emissions during transient operation.

A combined sulfur-trap/NO_x adsorber catalyst was investigated at Goal Line Environmental Technologies (GLET) in Knoxville, TN. Figure 1 is a photograph of the system with the SpaciMS in the foreground, and Figure 2 describes the experimental setup and adsorption/regeneration schedule followed in the experiment. Note that two capillaries were deployed in each of the four bricks for a total of eight. The extended adsorption/regeneration schedule allowed for the study of adsorption dynamics and regeneration transients.

For these experiments, a turbocharged, direct-injected medium-duty diesel engine coupled to an electrical generator provided the exhaust. Baseline conditions using ultralow sulfur fuel (<3 ppm) were run at 255°C, 320°C, and 390°C. Then the unit was poisoned for 6 hours with D2 (450 ppm sulfur), with performance checks after 2, 4, and 6 hours. Finally, the unit was desulfurized at 500-550°C for 45 minutes and performance measured again. Total NO_x, O_2, CO_2 and HC species were measured at each capillary position for an entire 5 minute desorption/ regeneration cycle.

Results

NO_x concentration at each of the 8 points in the unit is shown in Figures 3a, 3b and 3c for the baseline condition, after six hours of sulfur poisoning, and after desulfurization, respectively. This unique data characterizes the local NO_x storage capacity within the catalyst as well as loading rate.

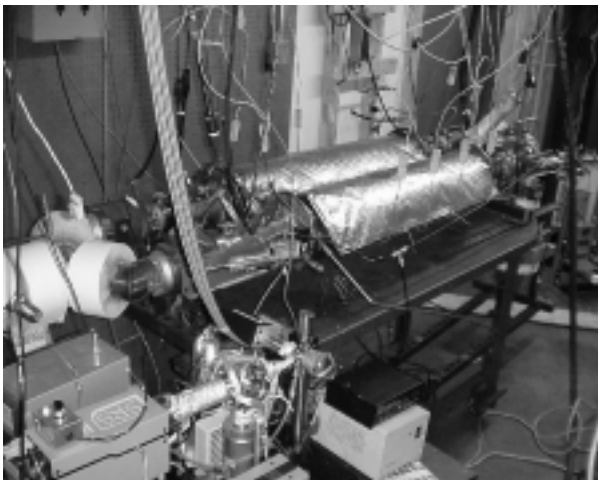

Figure 1. Photograph of the Test Catalyst with SpaciMS Instrument in the Foreground

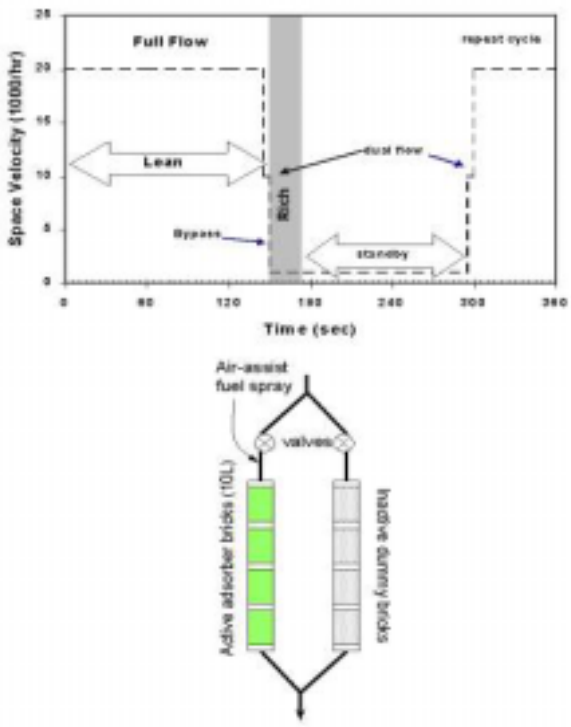

Figure 2. Schematic of the Catalyst Configuration and Adsorption/Regeneration Schedule

In the baseline case (Figure 3a), the loading profiles are spaced monotonically with increasing distance. After 6 hours of sulfur poisoning (Figure 3b), the loading profiles are compressed to the front of the cycle indicating loss of storage capacity in the first three catalysts. We found that the first, second and third bricks became poisoned after 2, 4, and 6 hours, respectively, in a plug flow manner which indicates the sulfur-induced capacity loss is diffusion limited.

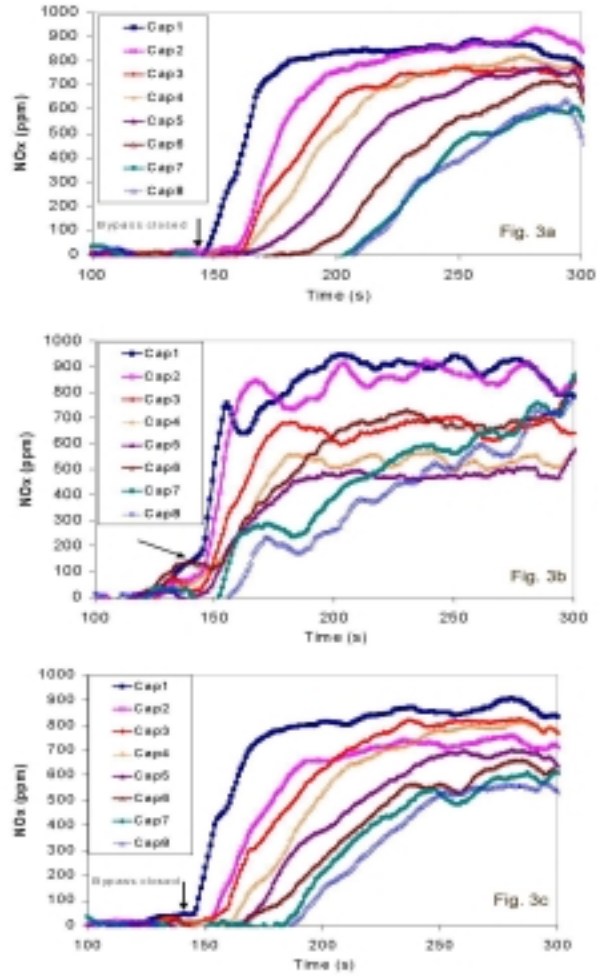

Figure 3. NO_x adsorption behavior as a function of time for (a) fresh unit, (b) sulfur-poisoned unit, (c) unit after desulfurization. Capillaries are placed in the front 1/3 and 2/3 of each of the four bricks, so capillary 1 is in the upstream brick and capillary 8 is in the downstream brick.

Following desulfurization (Figure 3c), significant capacity is recovered in the the front three catalysts as indicated by the monotonic spacing of the loading profiles. However, NO_x emissions are observed in the fourth catalyst at 40 s compared to 60 s prior to sulfur poisoning, indicating some irreversible loss of NO_x-storage capacity. The effects of sulfur poisoning and desulfurization on NO_x-storage capacity can also be characterized via breakthrough curves (Figure 4). These curves are based on the full data of Figure 3 and represent the time required to achieve a specified (~10% engine out) local NO_x slip. The degraded slope in Figure 4 associated with sulfur

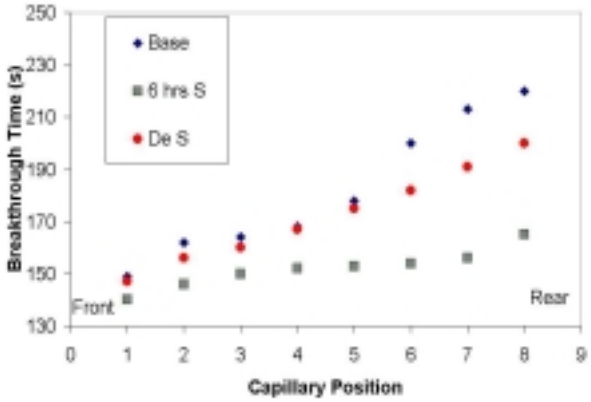

Figure 4. Time to breakthrough of NO_x as a function of axial position. The time to breakthrough is defined as the time it takes the local NO_x concentration to reach 10% of the engine-out value. Note that desulfurization restores the performance of the catalyst with the exception of the last three positions.

poisoning, compared to the baseline condition, indicates decreased capacity and is consistent with the compressed loading curves in Figure 3b. Following desulfurization, the breakthrough curve slope increases but not to the magnitude of the baseline case, which indicates the effectiveness of desulfurization for recovering some NO_x-storage capacity but quantifies the irreversible loss of capacity associated with the poisoning/ desulfurization process.

The SpaciMS was also applied to investigate fuel reforming associated with diesel fuel reductant injection during the regeneration phase of the SCONOx™ (trademark name for the Goal Line Environmental Technologies NO_x adsorber catalyst technology)cycle. Figures 5a, 5b, and 5c indicate the dynamics of relevant HC fragments two inches into the first brick (capillary 1) for the baseline, sulfur poisoned, and post-desulfurization cases, respectively. The specific HC fragments investigated were identified from full mass scans as demonstrating dynamic activity during the regeneration phase. Surprisingly, no fuel HC pulse is measured for any of the catalyst conditions, indicating complete reforming of the diesel fuel to other products (identified as olefinic and oxygenate products) in the first two inches of the front catalyst. The fuel reformer products peak at distinct times. With sulfur poisoning (Figure 5b), the oxygenate

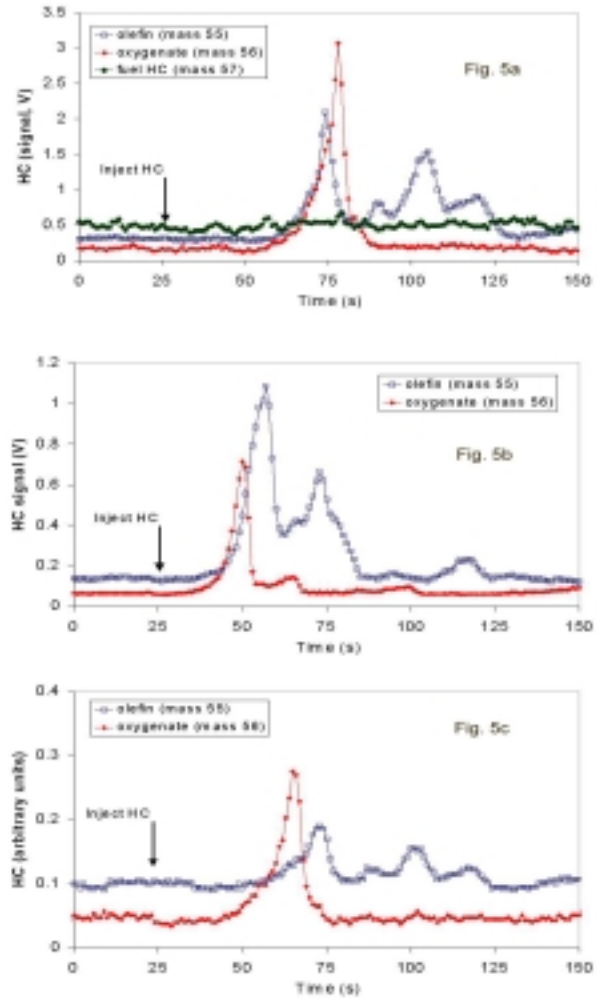

Figure 5. HC species information as a function of time for (a) fresh unit, (b) sulfur-poisoned unit, (c) after desulfurization. The different mass values, m/z=55, 56, 57, correspond to the major mass fragment from olefinic, oxygenate, and paraffinic species, respectively.

species are suppressed relative to the olefinic species. This suppression indicates that in addition to poisoning the adsorber sites (Figure 3b), sulfur poisoning influences the reductant reforming function. Following desulfurization (Figure 5c), the baseline characteristics are recovered, although with lower concentration when compared to Figure 5a. The loss of activity is likely associated with sintering of the metal sites during high-temperature desulfurization.

The unique and previously unavailable data provided by the SpaciMS is critical to developing

catalyst models; understanding the details of NO_x loading, fuel reforming, sulfur poisoning and desulfurization; identifying rate limiting steps; and optimizing catalyst parameters such as reductant quantity required, catalyst aspect ratio, and washcoat formulation.

Future Plans

Further work will include the use of the SpaciMS to investigate a catalyst with only the sulfur trap washcoat on it. We believe that the SO_2 can be monitored in the catalyst which will help determine the dynamic behavior of the exhaust sulfur species. Work will continue to identify all of the sulfur species in the exhaust and their potential influence on NO_x aftertreatment.

Summary

NO_x adsorbers load NO_x in a kinetics-limited or non-plug flow manner. Sulfur poisoning proceeds in a diffusion-limited or plug-flow manner, and it destroys NO_x-storage capacity from the front to back of the catalyst unit. In addition to the detrimental effect it has on NO_x storage, sulfur poisoning affects the reforming function. High-temperature desulfurization restores significant, but not baseline, NO_x-storage capacity. Desulfurization also restores the reductant-reforming function to baseline conditions in terms of products, but with degraded efficiency.

References

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2. W.P. Partridge, J.M.E. Storey, S.A. Lewis, R.W. Smithwick, G.L. DeVault, M.J. Cunningham, N.W. Currier and T.M. Yonushonis, "Resolving NO_x-Adsorber Emissions Transients," presented at and published in the proceeding so the DEER Workshop, San Diego, CA, August 2000.
3. John Storey, Bill Partridge, Sam Lewis, Jim Parks, Aaron Watson, Neal Currier and Jason Chen, "Resolving NO_x-Adsorber Emission Transients and Sulfur Poisoning using Mass Spectrometry," presented at and published in the proceeding so the FY2001 DOE National Laboratory Merit Review and Peer Evaluation, Knoxville, TN, June 2001.

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

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

Barriers

A. NO_x Emissions

B. PM Emissions

Tasks

4a. NO_x Adsorber R&D

5a. Catalyzed Diesel Particulate Filter

6. Prototype System Evaluations

Objectives

- Demonstrate the potential effectiveness of near-term NO_x and PM emissions control technologies using a light-duty CIDI vehicle during transient certification-type tests.
- Improve control of synthesis-gas regeneration technique for further laboratory studies of the effects of exhaust conditions during regeneration on the effectiveness of NO_x adsorber / diesel particle filter emissions control systems.

Approach

- Conduct chassis-dynamometer evaluations of a 1999 Mercedes A170 CIDI vehicle using an ultra-low sulfur fuel. Perform these evaluations using both a prototype NO_x adsorber and a prototype diesel particle filter installed on the vehicle. Utilize the FTP and US06 driving schedules for testing.

Accomplishments

- Collaborated with the Manufacturers of Emission Controls Association (MECA) to acquire additional prototype emissions control devices for use in this project.
- Demonstrated in a laboratory experiment that the combination of a NO_x adsorber and a catalyzed diesel particulate filter can achieve simultaneous reductions of NO_x and PM emissions from a diesel vehicle of over 90% compared with engine-out emissions over the FTP, US06, and highway fuel economy (HFET) test cycles.

- Demonstrated that integration of a catalyzed diesel particle filter with a NO_x adsorber and its regeneration system can allow simultaneous regeneration of both devices through the active measures taken to regenerate the NO_x adsorber.
- Completed laboratory regeneration system upgrades to allow for more repeatable regeneration control, permitting further study of effects of regeneration exhaust conditions on emissions control system performance.

Future Directions

- Investigate the effects of exhaust temperature, exhaust chemistry, and regeneration strategy on the performance of these devices when used together in an emissions control system.

Introduction

Lean-burn direct-injection engines (both compression-ignition and spark-ignition) offer the possibility of very significant fuel-efficiency gains. Unfortunately, both of these engine technologies present NO_x and PM emissions challenges that must be overcome if they are to meet future emissions regulations. To this end, research has been conducted to develop new emissions control technologies that can reduce both PM and NO_x emissions from lean-burn engines. However, these technologies can require large capital expenditures by the nation's industries and some questions remain as to whether these technologies, if implemented, can enable lean-burn engines to meet the stringent EPA Tier 2 emissions standards. These questions are particularly applicable to compression-ignition, direct-injection (CIDI) engines. The Diesel Vehicle Emissions Control Sulfur Effects (DVECSE) project aimed to demonstrate the potential reductions that new emissions control technologies may provide and to investigate the short-term impact of fuel sulfur on these potential reductions.

Approach and Results

A 1999 Mercedes A170 CIDI (Figure 1) was used as the testbed for this project. The Mercedes was selected because it is equipped with an advanced, common-rail direct-injection, turbocharged diesel engine with exhaust gas recirculation. The engine is 1.7 liters in displacement, making it of the approximate size targeted by the PNGV program. The emissions from the A170 equipped with its factory catalytic converters and without any emissions control devices (engine-out emissions) were first measured as baselines for comparison. A regeneration system was developed to allow regeneration of the NO_x adsorber during these transient tests without the need for engine modifications. This regeneration system utilized bottled gases (CO, C_2H_4, and H_2) together with the engine exhaust stream to mimic exhaust conditions that can be generated using late-cycle, in-cylinder injection of diesel fuel. Late-cycle injection is a likely means for generating the exhaust conditions necessary for actively-controlled emissions control technologies. It was not possible to utilize late-cycle injection for this project given time and resource constraints. In previous work reported last year, the Mercedes vehicle was equipped (one-at-a-time) with a catalyzed diesel particulate filter (CDPF) and a NO_x adsorber that were provided by the MECA. These results demonstrated single-pollutant emissions reductions in the high 90% range using ultra-low sulfur fuel.

Figure 1. 1999 Mercedes A170 CIDI Research Vehicle

Following individual evaluations of the CDPF and NO_x adsorber, the two devices were paired to make up an emissions control system that could achieve simultaneous reduction of all 4 criteria pollutants (hydrocarbons, CO, PM, and NO_x). A fuel with nominally 3 ppm sulfur by weight was used.

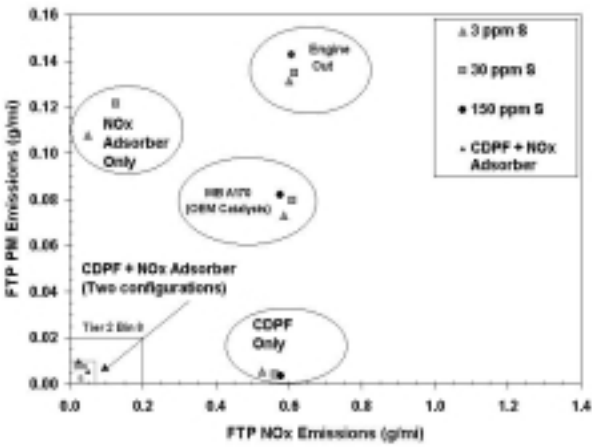

Figure 2. NO_x and PM Reductions Demonstrated in this Project

The regeneration protocol that had previously been used for the NO_x adsorber evaluations was used for the emissions control system evaluations without modification. A light-off catalyst was coupled directly to the turbocharger outlet, with a CDPF located approximately 1 meter downstream. The NO_x adsorber was coupled directly to the outlet of the CDPF. Triplicate FTP, US06, and HFET cycles were then conducted. The results showed that this combination of a CDPF and NO_x adsorber could achieve simultaneous reductions of PM and NO_x emissions of over 90%, while maintaining carbon monoxide and unburned hydrocarbon levels lower than the engine-out baseline. The resulting grams per mile emissions levels from these degreened, but otherwise relatively fresh catalysts, are consistent with levels established by EPA in the Tier 2 emissions standards, though the Tier 2 levels require this certification at 120,000 - 150,000 miles of aging.

Following the work summarized above, the order of the emissions control devices was changed so that the NO_x adsorber was upstream of the CDPF and a brief set of experiments was conducted. In this configuration, the NO_x adsorber performance was not very different than in previous experiments, but the particulate emissions dropped significantly. Although this brief study did not provide a complete explanation of this phenomenon, it provides a further emphasis on the importance of proper integration of these technologies into a vehicle for maximization of the emissions benefits that they offer.

Conclusions

The CDPF and the NO_x adsorber show great promise for enabling light-duty CIDI vehicles to meet future emissions targets (Figure 2). However, considerable development is still needed. Engine controls adequate to efficiently provide the exhaust conditions necessary for regeneration of a NO_x adsorber and CDPF are not yet available, and no long-term durability studies have yet been conducted. Furthermore, it is clear from other studies that the NO_x adsorber technology will require a means of sulfur protection (sulfur traps, de-sulfurization, etc) in addition to lower sulfur fuels.

Publications and Presentations

1. C. Scott Sluder and Brian H. West. "Catalyzed Diesel Particulate Filter Performance in a Light-Duty Vehicle." SAE Paper #2000-01-2848. Society of Automotive Engineers, 2000.
2. Brian H. West and C. Scott Sluder. "NO_x Adsorber Performance in a Light-Duty Diesel Vehicle." SAE Paper #2000-01-2912. Society of Automotive Engineers, 2000.
3. C. Scott Sluder and Brian H. West. "Performance of a NO_x Adsorber and Catalyzed Particle Filter System on a Light-Duty Diesel Vehicle." SAE Paper #2001-01-1933. Society of Automotive Engineers, 2001.
4. R. N. McGill, B. H. West, and C. S. Sluder. "Demonstrating Ultra-Low Diesel Vehicle Emissions." Proceedings of the Diesel Engine Emissions Reduction Workshop, 2000.

E. Stretch Technologies for Near-Zero Emissions: EGR with SCR/CRT Aftertreatment

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

Industry Participants: Cummins Engine Company, Inc., Columbus, IN; Johnson Matthey, Inc., Wayne, PA.

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

Barriers

A. NO_x Emissions

B. PM Emissions

Tasks

6. Prototype System Evaluations

Objectives

- To demonstrate that a modern heavy-duty compression ignition powertrain with aggressive exhaust emission control can achieve very low (near-zero) emissions, thus illustrating progress of "stretch" emission control technology toward meeting the 2007 EPA emissions standards.
- To contribute to the understanding and development of integrated emissions controls (NO_x and PM), including advanced engine technology, fuels and multiple emission control systems.

Approach

- Identify the most promising technologies for very low emissions.
- Choose technologies that are very "aggressive" and coordinate well with other on-going efforts.
- Obtain components to build an experimental powertrain with integrated emissions controls.
- Perform experiments to examine system performance and to demonstrate low emissions.

Accomplishments

- Obtained and installed an engine: Cummins ISB 5.9-L, in-line 6-cylinder engine, inter-cooled with special EGR and fueling system for low emissions.

- Obtained and installed emission control systems: Johnson Matthey continuously regenerated trap (CRT), and selective catalytic reduction (SCR) catalyst with urea spray system.
- Performed a series of experiments to detail performance of the integrated system, using a low-sulfur fuel.
- Quantified the low-emissions capability of the tested powertrain (0.34-0.53 g/hp-h NO_x, 0.01-0.02 g/hp-h PM).

Future Directions

- Focus efforts on continued optimization of integrated system
  - Calibrate/control engine to raise exhaust temperature
  - Reduce idle contribution to NO_x
  - Improve NO/NO_2 ratio
- Work with catalyst suppliers for better low-temperature performance
- Investigate full transient performance
- Evaluate PM constituents and unregulated emissions in more detail

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Introduction

A research, development and demonstration effort known as the near-Zero Regulated Emissions (ZRE) powertrain feasibility study is ongoing at ORNL to explore how clean a diesel powertrain can be. The objective is to demonstrate that a modern, low-emission engine utilizing high quality diesel fuel or alternative fuel, combined with "aggressive" exhaust emission control technology can serve as a near-zero emissions powertrain. One major goal of this effort is to go well beyond characterizing the individual components or sub-systems such as the engine, EGR system, PM filter, SCR catalyst, etc., by exploring the interactions between the components and learning how to control and optimize the entire powertrain.

Approach

To obtain very low engine-out emissions, it was determined that an advanced diesel engine designed for low emissions with features such as electronically controlled fuel systems and cooled EGR would be most appropriate. A special ultra-low sulfur (3 ppm sulfur) fuel was used to enhance engine-out emission control and to aid emission control system function.

A review of diesel particulate filter technologies and NO_x removal technologies explored the following:

PM reduction technologies

1) special CI fuels, advanced fuel injection and combustion,
2) catalytic traps,
3) NO_2 oxidant - trap systems,
4) trap + catalytic fuel additive,

NO_x removal technologies

1) various EGR schemes,
2) urea-to-ammonia based SCR systems,
3) regenerating traps with HC reductant (many developers).

Multiple promising approaches are being pursued to develop potential products for future diesel engine transportation applications. More than one regenerating particulate trap technology is seen to work relatively well and to be at the verge of commercialization. The emission control technologies for removing NO_x appear further from commercialization for vehicle application, but are apparently quite effective under more controlled testing conditions.

Coordinating engine and exhaust emission control device technologies to minimize emissions is a main focus of this work. The new EPA emission standards for 2007 (0.2 g/hp-h NO_x and 0.01 g/hp-h PM) for on-road heavy-duty engines were adopted to be the emissions goal of this effort. Future demonstration of emissions levels less than the 2007 standards with a minimum of N_2O and NH_3 emissions is now a target. Exposing the technical barriers to reaching this target is also an important goal.

Initial System Configuration

The first such system to be studied (Figure 1) features a 1999 Cummins ISB 5.9-L engine (6 cylinder, 24 valve) with advanced cooled-EGR and electronic fuel injection systems. The emission control system includes a continuously regenerating particulate trap in combination with a urea-based selective catalytic reduction system (for NO_x removal). An ultra-low sulfur fuel has been used in testing to date. Consideration will be given to using a low sulfur lubricating oil and other engines and emission control components (such as a NO_x absorber system) as the work progresses.

Preliminary Results

Characterization of the engine-out emissions and the capabilities of the emission control components has been examined using the AVL 8-mode test. This test consists of 8 steady-state operating points. The measured emission results are weighted in a specific fashion to estimate the results of the Heavy-Duty Transient Federal Test Procedure (HDFTP). Engine-out results were close to 2.5 g/hp-h NO_x and 0.08 g/hp-h PM. Tailpipe-out results of 0.4 g/hp-h NO_x and < 0.01 g/hp-h PM have been obtained using the ultra-low sulfur fuel. The progress toward the 2007+ heavy duty standard is shown in Figure 2. It should be noted that the AVL 8-mode results presented here are believed to give somewhat optimistic (low) values for tailpipe-out NO_x emissions (the SCR catalyst temperatures are generally more optimal for the AVL test modes than would actually be realized in the HDFTP).

A small but measurable quantity of PM traceable to injected urea was observed, particularly when the exhaust temperature was near 250°C. Evidence to date points to some urea depositing on the PM collection filters and also to higher molecular weight constituents formed from the decomposition products of urea. Further investigation of this phenomena is planned.

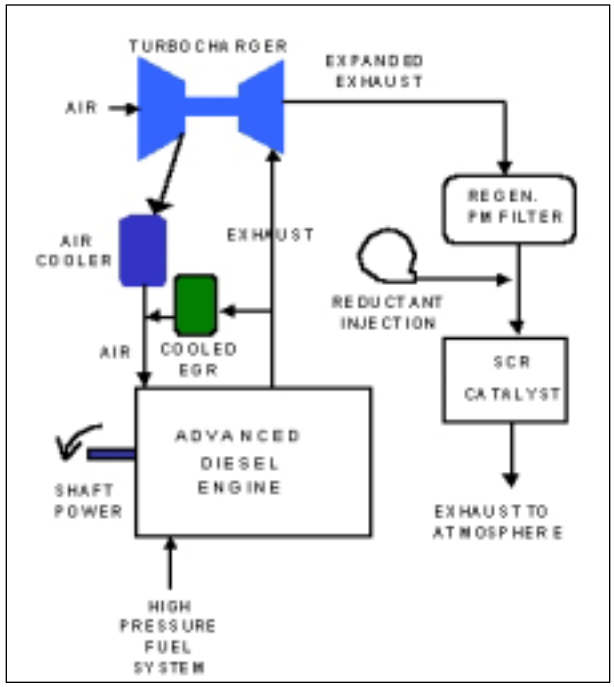

Figure 1. Schematic Representation of the Current Experimental near-Zero Emissions Drivetrain

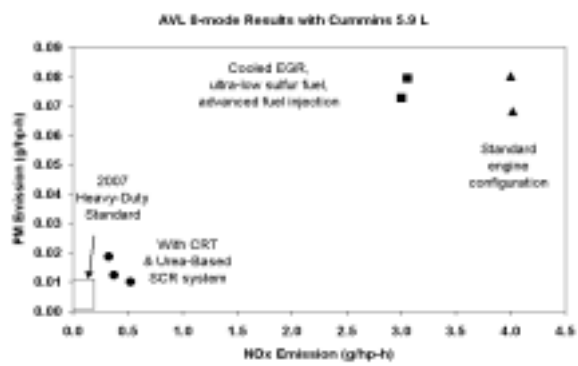

Figure 2. Significant Reductions in NO_x & PM Accomplished with Coordinated Engine Control and Exhaust Emission Control

Conclusions

Experiments completed to date show clearly that the current low emission integrated powertrain comes close to meeting the 2007+ emission standard for PM but is unable to meet this standard for NO_x. A major barrier is the inability to control NO_x to low levels

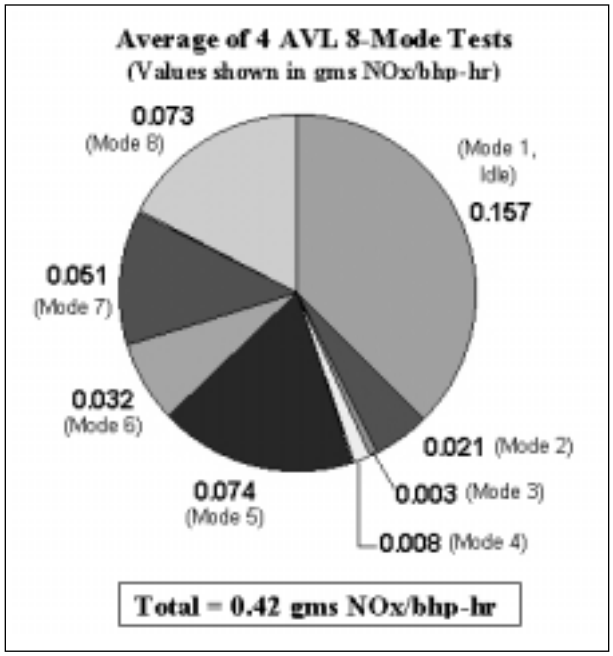

Figure 3. Idle NO_x alone is greater than 75% of the 2007+ HD standard.

when the engine exhaust and SCR catalyst temperatures are in the 100-280°C range. This is illustrated by Figure 3, which shows that the NO_x emission from idle (mode 1 in the figure) alone is more than 75% of the 2007+ regulation (0.2 g/hp-h NO_x). The SCR catalyst was also at relatively low temperatures during test modes 2 and 5. Development of new SCR catalysts with improved NO_x conversion capabilities for the 100-280°C temperature range is seen as a key to meeting the 0.2 g/hp-h NO_x regulation. Such improvements combined with engine technology and controls which increase low-load exhaust temperature while keeping engine-out NO_x low appear as possible solutions.

Control of emissions under certain transient conditions (due to lack of adequate closed loop control at this time) while avoiding significant NH_3 break-through will be quite challenging. Future experimentation using transient test capabilities at the National Transportation Research Center (NTRC) are planned to build on the AVL 8-Mode results.

FY 2001 Publications / Presentations

John F. Thomas, "Evaluation of Urea-Based SCR Technology" FY2001 DOE OTT National Laboratory CIDI Merit and Peer Evaluation, June 11-13, 2001, Oak Ridge National Lab., Oak Ridge, TN.

III. NO_x CATALYSTS AND SENSORS

A. Catalytic Reduction of NO_x Emissions for Lean-Burn Engine Technology

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

Barriers

A. NO_x Emissions

C. Cost

Tasks

4c. Selective Catalytic Reduction Catalysts

Objectives

- Develop new catalyst technology to enable CIDI engines to meet EPA Tier II emission standards with minimal impact on fuel economy.

Approach

- Discover and develop new catalyst materials for reducing NO_x emissions in lean-burn exhaust environments by more than 90% in the 200 to 400°C temperature range using ammonia as a reductant. Materials for study include:
  - Hydrous Metal Oxide (HMO) or other oxide-supported catalysts
  - Microporous materials-supported catalysts, including zeolites
- Evaluate new catalyst materials in both bulk powder and monolith forms. Include short-term durability testing under hydrothermal conditions and in the presence of SO_2.
- Scale up synthesis and processing of promising catalyst formulations to enable fabrication of prototype catalytic converters for CIDI engine dynamometer testing.
- Transfer most promising catalyst formulations and processes to Low Emission Technologies Research and Development Partnership (LEP) CRADA partners.

Accomplishments

- Extended all current National Laboratory/LEP CRADAs into the FY01-03 time frame.
- LEP has defined a simulated medium-duty CIDI engine exhaust gas composition and test conditions for ammonia selective catalytic reduction (SCR), in addition to developing a staged catalyst acceptance criteria.
- Benchmark ammonia SCR catalysts have been obtained from suppliers.
- LANL filed final patent application for Ferrierite (FER)-supported metal catalysts and their use for lean NO_x catalysis.
- LANL and SNL transitioned reactor systems to facilitate catalyst testing for SCR of NO_x *via* NH_3. This included the installation of new photoacoustic and/or Fourier Transform-Infrared (FTIR) detection equipment.
- LANL further characterized hysteresis effects for zeolite catalysts using hydrocarbon reductants. Results indicated a potential 'fatal' flaw for zeolite catalysts for this reaction.
- LANL gave two technical papers on competitive adsorption and reaction studies and the catalytic hysteresis of zeolite-based lean NO_x catalysts. SNL presented an additional three papers on hydrocarbon or ammonia SCR catalysts.

- LANL prepared 30 new microporous catalyst compositions and tested 80 catalyst compositions during the past year; more than 900 catalysts are now in the LANL lean NO_x catalyst library.
- ORNL completed extensive microstructural characterization of SNL hydrocarbon SCR and ammonia SCR catalysts in powder or monolith core form.
- U.S. Patent issued on SNL Pt-CuO/HTO:Si catalyst materials with lower light-off temperature and wider temperature window for lean-burn NO_x reduction *via* hydrocarbons.
- SNL has synthesized ~100 new catalyst formulations for testing *via* ammonia SCR, and ~200 test runs have been completed in the reactor unit. Preliminary efforts at monolith core fabrication with experimental catalyst formulations have been successful. Short term durability and SO_2 aging experiments have also been initiated in conjunction with the staged catalyst acceptance criteria designed by the LEP.
- SNL initiated process variable studies with experimental and benchmark ammonia SCR catalysts. Major effects were identified for the $NO:NO_2$ ratio, $NH_3:NO_x$ ratio, O_2 concentration, and the presence of hydrocarbons in the exhaust gas feed.

Future Directions

- Synthesize, characterize, and test new catalyst compositions as ammonia SCR catalysts.
- Determine if competitive adsorption issues will impact applicability of catalysts, and other porous catalysts, as ammonia SCR catalysts.
- Continue SCR process variable studies as needed to aid catalyst development, process definition, and overall emissions control system integration.
- Continue to examine the effects of low concentrations of hydrocarbons on ammonia SCR catalysts. Determine the possible effects of particulate matter (PM) or SO_3 on the NO_x reduction performance of ammonia SCR catalysts.
- Continue short-term hydrothermal stability and SO_2 durability testing using LEP-defined acceptance criteria.
- Understand ammonia storage issues on catalyst/washcoats and the performance of these materials in transient environments, including effects on ammonia feed and slip.
- Continue microstructural analysis of new LANL and SNL catalysts at ORNL.

Introduction

This multi-partner effort has been continued under OAAT sponsorship and involves separate CRADAs between three national laboratories (Los Alamos National Laboratory [LANL], Oak Ridge National Laboratory [ORNL], and Sandia National Laboratories [SNL]) and the Low Emission Technologies Research and Development Partnership (LEP, composed of DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation). Each of these CRADAs was recently extended through 2003. The project addresses reduction of CIDI engine NO_x emissions using exhaust emission control devices — identified as one of the key enabling technologies for CIDI engine success. The overall CRADA efforts are focused on the development and evaluation of new catalyst materials for reducing NO_x emissions, specifically targeting the selection of appropriate catalyst materials to meet the exhaust emission control needs of light- and medium-duty diesel engines.

This year we completed our program transition toward the selective catalytic reduction (SCR) of NO_x by urea (or ammonia) as a more efficient NO_x reduction option for lean-burn exhaust emission control. Infrastructure issues notwithstanding, this

process has the greatest potential to successfully attain the >90% NO_x reduction required for light-duty CIDI engines to meet the new EPA Tier II emission standards scheduled to be phased in starting in 2004.

LEP Efforts

Our automaker partners have been instrumental in developing standards for simulated exhaust gas compositions to be used in laboratory bench units for standard tests, short term durability tests, and SO_2/SO_3 aging experiments. These exhaust gas compositions were designed to simulate medium-duty CIDI engine exhaust, assuming that an oxidation catalyst is placed upstream of the SCR catalyst. The main purposes of the upstream oxidation catalyst are to remove hydrocarbons from the exhaust and to convert nominally one half of the NO in the native exhaust to NO_2. Both of these features benefit SCR catalyst performance, as will be described later. The various exhaust gas compositions defined by the LEP are shown below in Table 1. Note that NH_3 and SO_2 are never combined in the simulated exhaust gas composition in order to avoid significant plugging problems associated with $(NH_4)_2SO_4$ formation. These problems are not currently being addressed in our project, although we plan to investigate potential solutions in the future.

In addition to this work, a staged catalyst acceptance protocol has been proposed by our automaker partners to aid catalyst screening and development efforts at the national laboratories (see Table 2). The purpose of the staged catalyst acceptance protocol shown below is to ensure that aggressive catalyst development and characterization is pursued only for promising catalyst formulations. Conversely, such efforts should not be wasted on catalyst formulations that fail to meet the acceptance criteria.

The overall project goal for NO_x conversion (to N_2) is >90% over a temperature range from 200 to 400°C. The first primary decision point in the acceptance protocol is to determine if a particular fresh (degreened) catalyst in bulk powder form meets this goal. If this criterion is met, then it is necessary to determine the contribution of NO_x adsorption relative to steady-state catalytic activity.

	Standard Feed*	SO_2 Aging
Temperature (°C)	400-110	400-110
NO (ppm)	175	175
NO_2 (ppm)	175	175
NH_3 (ppm)	350	0
O_2 (%)	14	14
CO_2 (%)	5.0	5.0
H_2O (%)	4.6	4.6
SO_2 (ppm)	0	20
Space Velocity (cc/cc·h^{-1})	30,000	30,000

* Used for both standard catalyst testing and for short term durability experiments.

Table 1. LEP-Defined Exhaust Gas Compositions Simulating Medium-Duty CIDI Exhaust (Assuming the Presence of an Oxidation Catalyst Placed Upstream of the SCR Catalyst).

Stage of Testing Matrix	Primary Decision Point	Additional Test(s)	
Fresh (Degreened) Catalyst	Standard Activity Test	NO_x Activity w/o NH_3 (Deconvolute Adsorption Issues)	
Short-Term Durability (Hydro-thermal Aging) in Full Exhaust Gas Mix (No SO_2)	600°C for 16 h	700°C for 16 h	800°C for 16 h
SO_2/SO_3 Aging in Full Exhaust Gas Mix (No NH_3)	350°C for 24 h	350°C for additional 24 h	350°C for additional 24 h

Table 2. Staged Catalyst Acceptance Protocol Defined by the LEP

Short-term durability testing is then performed; separate catalyst samples are aged hydrothermally ina full exhaust gas mix stream (except no SO_2 is used, see Table 1) for 16 h at 600, 700, and 800°C. Catalyst test data following the 600°C/16h hydrothermal aging are used as the second primary decision point; if the catalyst still continues to reach >90% NO_x conversion from 200 to 400°C, it is identified as worthy of additional development and testing efforts. Hydrothermal testing at 700 and 800°C allows for the extraction of an activation energy for catalyst deactivation.

The next step is SO_2 and SO_3 (generated *in situ* using an upstream oxidation catalyst) aging. SO_2/ SO_3 aging is performed at a nominal exhaust temperature of 350°C. A concentration of 20 ppm SO_2 or SO_3, at least an order of magnitude higher than those expected from fuels meeting future EPA sulfur standards, is used in the feed in an attempt to accelerate the aging of the catalyst. Activity tests are performed after 24, 48, and 72 hours (allowing the extraction of deactivation kinetics as a function of time). The test data following the 24-hour aging is used as the final primary decision point for the stage acceptance protocol. If at this point the catalyst continues to meet the >90% NO_x conversion from 200 to 400°C goal, the catalyst formulation will then be fabricated in monolith core form. Additional testing will be done to determine whether the monolith forms continue to meet >90% NO_x conversion from 200 to 400°C goal over the staged acceptance protocol.

Los Alamos National Laboratory Efforts

Over the last several years, LANL's work has focused on the development of new and stable microporous and zeolite-based catalysts for NO_x reduction in lean-burn exhaust environments. This work has involved the screening of approximately 750-800 catalysts, mainly derived from zeolites or related crystalline, microporous supports. This work is complementary to the SNL work on distinct families of high surface area oxide-supported catalysts. Through the extensive LANL catalyst screening, a family of catalysts that have technologically interesting activity over a broad temperature range was discovered. A patent application has been filed on the preparation and use of these catalysts. As a result of the intense scrutiny we have given these catalysts, we have uncovered previously unrecognized water adsorption issues that may represent a barrier to the applicability of these materials for transient, mobile applications. As a result of these findings, the LEP CRADA team has agreed that a more fundamental understanding of these adsorption issues is required before moving ahead with additional catalyst screening of urea (or ammonia) SCR catalysts. It is critical to understand whether adsorption issues are a hurdle for zeolite-based catalysts using ammonia as the reductant, prior to setting out on an extensive catalyst screening effort for urea SCR. The LEP CRADA team felt that if we could identify such 'show stoppers' early on in the catalyst screening process, we could rapidly shift to other promising candidates and streamline the search for catalyst leads that could go on to the development stage more rapidly.

In response to the decision rendered by the team, LANL has temporarily postponed its intensive catalyst screening effort while it focuses more on the fundamental aspect of low temperature water adsorption on zeolite catalysts. LANL has obtained further evidence that low temperature water adsorption may represent a significant technological hurdle for microporous catalysts when hydrocarbons are used as a reductant. These observations represent a major contribution to the field. The insight it provides about our future materials selection process represents a competitive advantage to our CRADA project.

In FY 2000 the ferrierite (FER) based catalysts developed at LANL for hydrocarbon SCR were found to have good hydrothermal stability and good short term stability in the presence of SO_2. Additional experiments at Ford and at LANL uncovered the unusual effect that the catalytic activity was markedly different when increasing the temperature versus decreasing the temperature of the catalyst in the presence of 5% steam using hydrocarbon reductants. Figure 1 (upper graph) shows that fairly stable activity is observed over 2 hour hold periods during a ramp-down experiment. This stability indicates that the disappearance of NO_x is due to the catalytic conversion to N_2 and not due to NO_x storage on the catalyst. In the ramp-up experiment, significant transient behavior is observed upon heating from 200-300°C and from 300-400°C. The large transient in NO conversion upon going from 300-400°C is associated with the known desorption of water from the pores of the zeolite, and is thus related to transient NO_x storage on the catalyst that then saturates in 20-30 min before returning to steady-state catalytic conversion of NO_x. The steady-state conversion values plotted in Figure 1 (lower graph) indicate the difference in activity, or hysteresis, observed between the ramp-up and ramp-down steady-state catalytic conversion. Based on these results, the studies of hysteresis in the catalytic activity and competitive adsorption of various

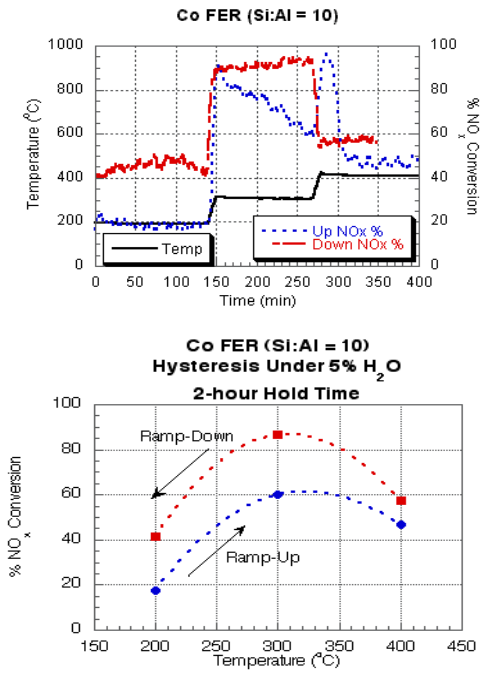

Figure 1. Hydrocarbon SCR NO_x Conversion Data for a Co FER Catalyst Tested Using Ramp-up and Ramp-down Isothermal Profiles in the Presence of 5% H_2O

exhaust gas components have been our focus during the past year and are described in detail below.

Competitive adsorption refers to two or more exhaust gas components competing for the same adsorption sites. If the competition is severe, and a component is excluded from adsorption because of the presence of another, this subsequent, sequential reaction steps can be affected. It is generally thought that in the mechanism of NO_x reduction with hydrocarbons, NO_x must be adsorbed and subsequently reacted with a hydrocarbon or hydrocarbon fragment to form a reactive intermediate that reacts with additional NO_x to form N_2. If water outcompetes NO_x for adsorption to the catalytically active site, and NO_x conversion depends on NO_x being adsorbed on that site, then the rate of NO_x conversion may be slowed dramatically when water is in the channels of the zeolite. Such a scenario is shown schematically in Figure 2.

Because we know that the adsorption and desorption of water occur at different rates at the same temperature in zeolites and other microporous materials (see Figures 3 and 4), we felt that this

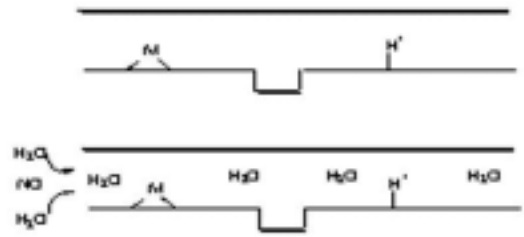

Figure 2. A portrayal of a microporous catalyst (upper drawing) where the catalytically active sites such as metal ions (M), defects, or acid sites (H^+) are situated inside of a micropore of molecular dimension (5.5 angstroms). Below it is a depiction of a situation of competitive adsorption, where water molecules effectively outcompete molecules of NO_x for adsorption sites in the pores of the catalyst.

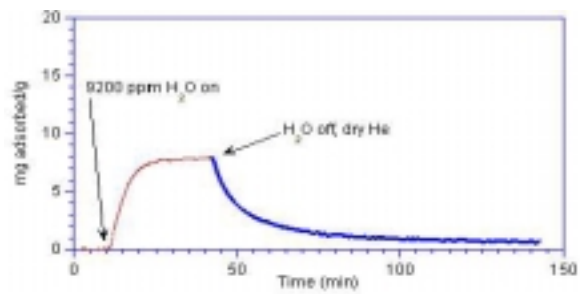

Figure 3. Adsorption of Water and Desorption on a Co FER Lean NO_x Catalyst at 200°C.

hysteresis in water adsorption was related to the observed catalytic hysteresis. When the catalyst is cooled from a temperature higher than the desorption temperature of water, the channel system of the zeolite is relatively free of water, and the rate of NO_x reduction is high. When the catalyst is taken to a low enough temperature to saturate the pores with water, around 200°C, then NO_x is excluded from the pores, and the rate of N_2 formation is slowed. Upon heating the catalyst above 200°C, the water is not removed completely until temperatures in excess of 400°C are achieved, and so the rate of NO_x reduction remains low. Heating the catalyst to temperatures in excess of 400°C then removes the water, and upon cooling, the activity remains high. Consequently, the hysteresis loop, such as shown in Figure 1, is generated. The time required to close the hysteresis loop, i.e. the time required to attain true steady-state, is on the order of hours. This reactivity pattern and response time is obviously problematic for

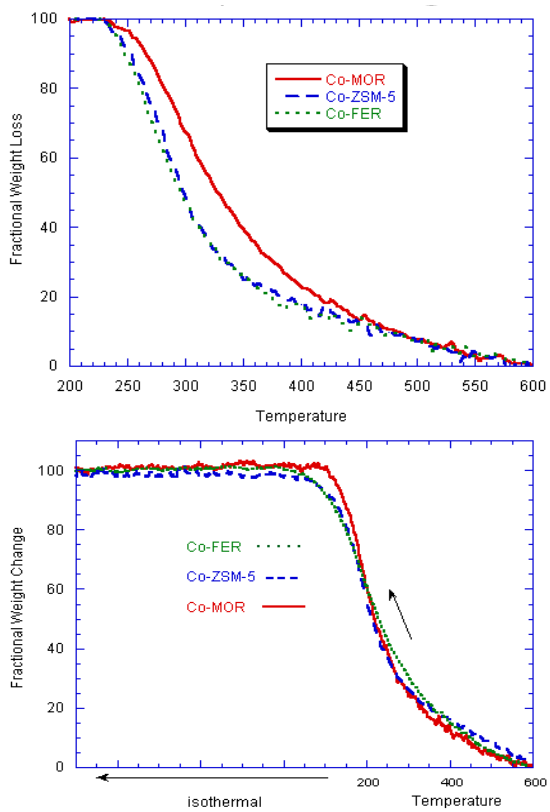

Figure 4. Water Desorption (top) and Adsorption (bottom) as a Function of Temperature at 37% Relative Humidity (21.7°C) for Three Co-Exchanged Zeolites (FER, ZSM-5, and Mordenite)

applications in which the temperature, and hence the amount of water in the pore system, vary widely and rapidly. This hysteresis represents a major hurdle for the application of microporous materials for lean NO_x catalysis with hydrocarbons as reductants.

In order to address whether similar competitive adsorption issues might hinder the utility of microporous catalysts for ammonia SCR, we have studied the competitive adsorption of water and ammonia and have preliminary studies on the influence of water on the reaction rate of ammonia with NO_x at low temperature. We chose a Co FER catalyst that we had previously characterized in terms of its water adsorption properties to test for competitive adsorption with ammonia. The plot of ammonia adsorption on an initially dry catalyst is shown on the top graph in Figure 5. It can be seen that NH_3 adsorption is slower than water adsorption (compare to Figure 3). Only a small quantity of

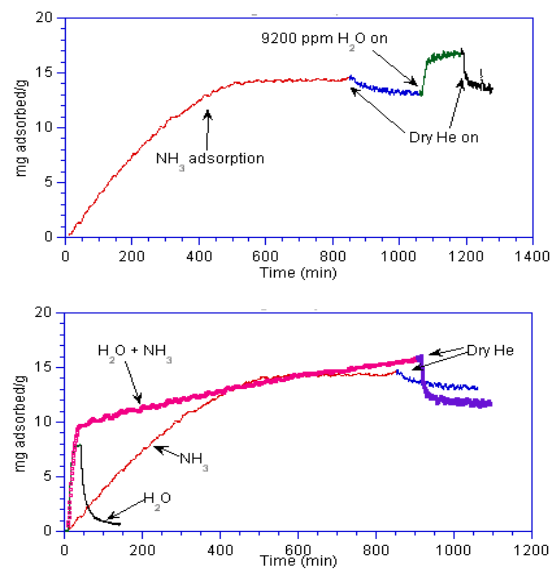

Figure 5. (Top). Adsorption of NH_3 followed by adsorption of H_2O on Co FER catalyst at 200°C. (Bottom). Competitive coadsorption of ammonia and water compared to NH_3 alone and water alone.

weakly adsorbed ammonia is removed *via* dry He purging, and then adsorption and desorption (*via* He purging) of water results in the loss of little, if any, of the ammonia. Therefore, water does not displace ammonia under these conditions. Competitive coadsorption of water and ammonia is shown on the bottom graph of Figure 5. Water is adsorbed more rapidly than the ammonia, but ammonia eventually displaces the water. These results indicate that the competitive adsorption of water and ammonia should not be a problem when using such catalysts for NH_3 SCR.

Next, we examined whether a fully NH_3 saturated catalyst would react with NO_x in the presence of water. We saturated the catalyst with ammonia, and then started a flow of NO_2 through the catalyst held at 200°C. Figure 6 compares the results in the absence of water (1040 ppm NO_2 concentration) with those in the presence of water vapor (500 ppm NO_2 concentration). In the latter case, the NO_2 was diluted by a factor of ~2x by the introduction of water vapor. The initial increase in weight upon introduction of the NO_2/H_2O blend is due to the adsorption of water vapor. Switching to a dry He purge at the end of the runs desorbs weakly bound NO_2. The data indicate that the rate of NO_2

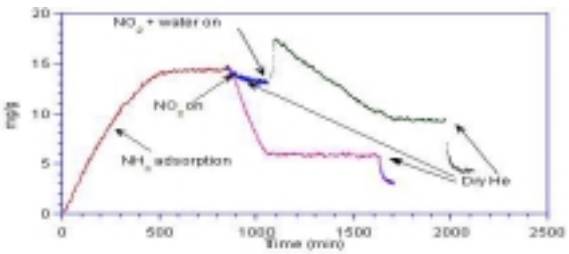

Figure 6. NO_2 Adsorption and Reaction on Co FER Measured With and Without the Presence of H_2O at 200°C.

reduction is similar for both cases when the difference in concentration is accounted for. These results also suggest that in contrast to the hydrocarbon SCR reaction, the NH_3 SCR reactions over microporous catalysts may not be susceptible to low temperature competitive adsorption of water issues that could reduce the rate of N_2 formation.

These results lead us to believe that zeolite and other microporous catalysts are indeed viable candidates as NH_3 SCR catalysts, and therefore we will continue our screening activities on these types of materials and other microporous materials in earnest during the remainder of this fiscal year. The insights these studies have given us will allow the CRADA project to more rapidly assess potential candidates in the future and address competitive adsorption issues early on in the catalyst screening process.

There is still more work to be done in examining competitive adsorption issues on <u>all</u> catalyst types, as the role of adsorption of SO_2 versus catalyst poisoning by sulfur needs better definition and assessment in order to be better addressed by our screening protocols in the future. Also, the adsorption of hydrocarbons on NH_3 SCR catalysts has been said to be deleterious to activity (see SNL Efforts Section). This effect needs to be quantified and accounted for in the LEP CRADA team's catalyst screening activities.

Oak Ridge National Laboratory Efforts

ORNL's continuing role in this project has been to provide characterization of catalyst performance, both in bench scale reactor testing and in an engine laboratory, in addition to microstructure characterization of catalysts using electron microscopy.

Over the past year, significant microstructural characterization efforts have been performed related to SNL catalyst formulations, both for hydrocarbon SCR and for ammonia SCR applications. For hydrocarbon SCR, Pt-CuO/HTO:Si catalysts in monolith core form were evaluated using transmission electron microscopy to determine the location of the Pt and CuO phases. These efforts were tied to other activity and characterization studies used to understand the behavior of these materials, which were recently patented (U.S. Patent No. 6,165,934, December 26, 2000). Z Contrast Scanning Transmission Electron Microscopy (STEM) imaging studies showed evidence of Pt particles dispersed throughout the washcoat (both Al_2O_3 and HTO:Si phases), although a greater density of Pt particles and smaller Pt particles were associated with the HTO:Si phase. Elemental mapping determined that the CuO phase was located throughout the washcoat (both Al_2O_3 and HTO:Si phases) but was significantly enhanced at Pt particles. SO_2 aging experiments at 600°C showed no significant change in the location of the CuO phase relative to the Pt, although small Pt particles were consumed due to sintering/agglomeration phenomena, resulting in a significant increase in Pt particle size. Combined with other characterization efforts, these microstructural studies helped determine the nature of the CuO phase and the location/interaction between the Pt and CuO phases.

Microstructural studies were also performed on ammonia SCR catalyst formulations. Two samples were selected as illustrative of the ORNL microstructural characterization capabilities: WO_3 or V_2O_5 dispersed on a commercial TiO_2 support (Degussa P25 TiO_2). These are very common phases associated with commercial ammonia SCR catalysts for NO_x reduction in stationary source applications. The nature of the dispersion of these phases on the TiO_2 support allows different microscopy techniques to be utilized to benefit characterization efforts. Figure 7 shows the dispersion of small (~1 nm diameter) WO_3 clusters on the TiO_2 support *via* Z Contrast STEM imaging. Vanadia (V_2O_5) disperses on the TiO_2 support in a different manner, as shown

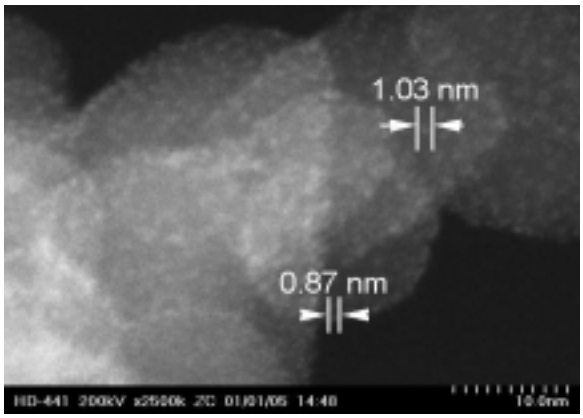

Figure 7. Z Contrast STEM Image of a WO_3 Phase (Brighter Clusters) Dispersed on TiO_2 Support Particles.

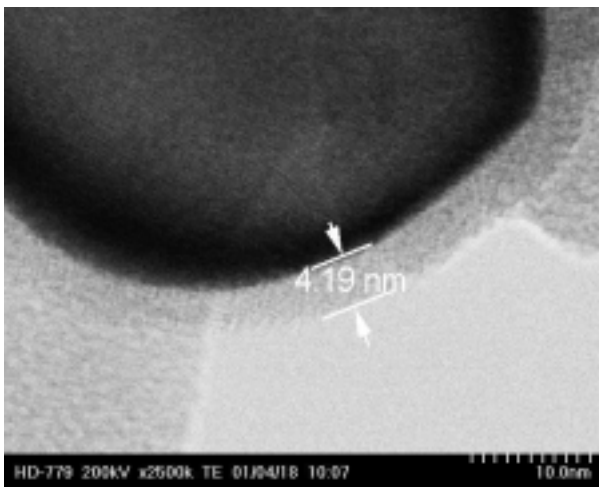

Figure 8. Bright Field STEM Image of a V_2O_5 Phase Dispersed on TiO_2 Support Particles.

by the high resolution bright field STEM image in Figure 8. In this case, the vanadia uniformly wets the TiO_2 support particles, forming a thin (4 nm thick) surface phase. These results demonstrate the power of these electron microscopy techniques to determine the nature and location of various active and promoter phases in catalyst materials. This information can help guide catalyst development efforts designed to optimize catalyst performance.

Sandia National Laboratories Efforts

Over the past year, we rapidly transitioned from catalyst development for SCR of NO_x *via* hydrocarbons to SCR of NO_x *via* ammonia. This transition initially involved modification of our catalyst reactor unit to include separate NO, NO_2, and NH_3 feed lines, as well as the addition of an on-line FTIR unit for reactant and product analysis. Over the last year, approximately 200 catalyst testing runs have been completed in the test unit with ~100 different catalyst formulations. Short-term durability studies were initiated in August, 2000; process variable studies were initiated in November, 2000; and SO_2 aging studies were initiated in January, 2001. The majority of these studies were performed with catalysts in bulk powder form, although we began to synthesize promising catalysts in monolith core form in April, 2001. In addition to these milestones, supplier benchmark catalyst formulations (monolith form) were first received and tested in October, 2000; additional supplier catalyst receipt and testing is on-going.

Table 3 shows the numbers of catalysts that have advanced through different stages of the testing matrix defined in Table 2. These numbers represent the testing of experimental bulk catalyst powders and do not include supplier benchmark catalysts (monolith core form). It is important to note that demands on reactor time, especially those related to the various durability and aging protocols, have required decisions to be made regarding the efficient reactor unit scheduling. Since our research efforts are in a relatively early stage, we have chosen to use more reactor time for fresh catalyst screening experiments. For this reason, not all of the 13 fresh catalysts identified as meeting the catalyst acceptance criteria have completed short term durability testing and SO_2 aging. We plan to complete these studies in the next few months.

Examples of test data for two fresh catalysts passing the initial acceptance criteria are shown in Figure 9. One catalyst is a supported vanadia-based composition, while the other represents a supported base metal composition. Vanadia-based catalysts have long been recognized as active catalysts for the SCR of NO_x *via* NH_3 in stationary source applications. Short-term durability and SO_2 aging tests with these catalysts show that they have excellent resistance to deactivation. However, these commercial vanadia-based catalysts have a severe disadvantage due to the toxicity of vanadium and the volatility of vanadia at elevated temperatures. These problems provide solid motivation for continued catalyst screening efforts to identify other candidate materials for SCR of NO_x *via* NH_3. Figure 9 shows

Stage of Testing Matrix	Total Catalysts Tested	# of Catalysts Meeting Activity Criteria
Fresh (Degreened) Catalyst	88	13
Short Term Durability*	4	3
SO_2 Aging*	1	1

* Using primary decision points as defined in Table 2.

Table 3. Summary of SNL Catalyst Development Efforts to Date With Respect to Staged Catalyst Acceptance Criteria Defined by the LEP (See Table 2)

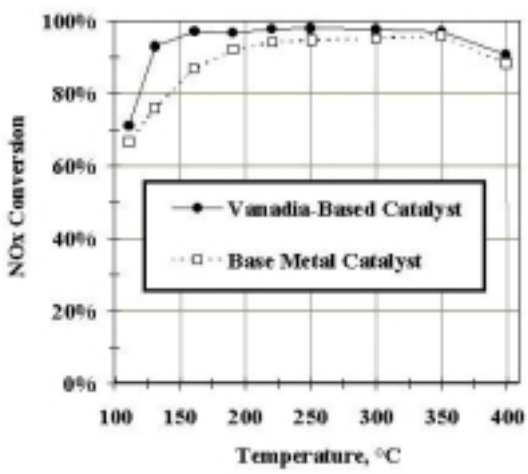

Figure 9. NO_x Conversion Profiles for Fresh Vanadia-Based and Base Metal Catalysts Dispersed on Hydrous Metal Oxide (HMO) Supports

an example of an alternate composition that may be appropriate for meeting mobile source application requirements. No significant NO_x adsorption effects are present for these catalyst materials; reported NO_x conversions are steady-state values.

We have begun an evaluation of supplier benchmark catalysts in monolith core form, along with preliminary efforts to prepare our experimental catalysts in monolith core form. Examples of fresh catalyst activity test results are shown below in Figure 10. All of the catalysts shown below in Figure 10 show good to excellent SCR activity between 200 and 400°C. Performance below 200°C drops off significantly relative to bulk powder catalysts (see Figure 9); this common problem is related to the dilution effect of supporting a thin layer of washcoat on a cordierite monolith structure. Higher SCR activity in the 150-200°C range is desireable, especially for light-duty CIDI exhaust applications. These results are encouraging for

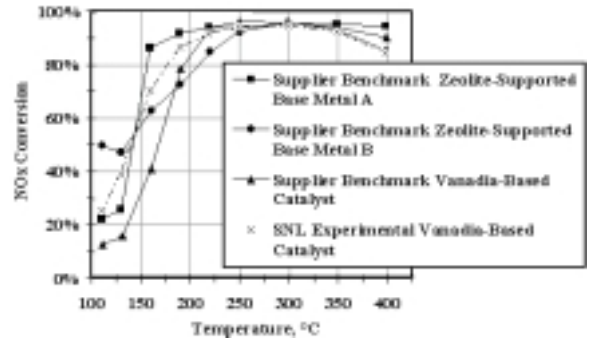

Figure 10. NO_x Conversion Profiles for Fresh Supplier Benchmark Catalysts, as well as an Experimental SNL Vanadia-Based Catalyst, in Monolith Core Form

several reasons. First, similar to the results shown in Figure 9, several non-vanadia catalyst compositions are shown to be relatively active in monolith form for SCR of NO_x *via* NH_3. Second, preliminary efforts at producing a monolith form catalyst at SNL have proven to be very promising relative to commercial benchmark materials.

A final component of our studies this past year has examined the effect of a range of process variables on the performance of SCR catalysts. These results will enable us to understand the feed and process conditions required to optimize catalyst performance. Table 4 shows the simulated exhaust gas composition investigated, which includes the range of variation for several components of the feed. Also included in the far right hand column is a summary of the effect of the specific process variable on the NO_x reduction activity over the range of variation. Most of these tests were performed using an experimental vanadia-based catalyst (bulk powder form), but several key process variables ($NO:NO_2$ ratio and SO_2) were also investigated using supplier benchmark catalysts in monolith core form.

Figure 11 shows the NO_x conversion profiles obtained for various mixtures of NO and NO_2 over an SNL experimental vanadia-based catalyst (bulk powder form). The $NO:NO_2$ ratio is the most dominant process variable affecting catalyst performance. It should be pointed out that nearly all previous work in the literature regarding SCR of NO_x *via* NH_3 has involved only NO since it is the predominant NO_x species present in high temperature

	Standard Feed	Range of Variation	Effect
Temperature (°C)	400-110	400-110	NA
NO (ppm)	175	175	Major
NO_2 (ppm)	175	175	Major
NH_3 (ppm)	350	280-350	Major
O_2 (%)	14	14	Major*
HC (C1):NO_x	0	0-4	Major
CO_2 (%)	5.0	5.0	NA
H_2O (%)	4.6	0-4.6	Minor
SO_2 (ppm)	0	0-20	TBD
Space Velocity (cc/cc·h^{-1})	30,000	30,000-45,000	Minor

Table 4. Process Variable Ranges and Their Qualitative Effect on SCR Catalyst Performance

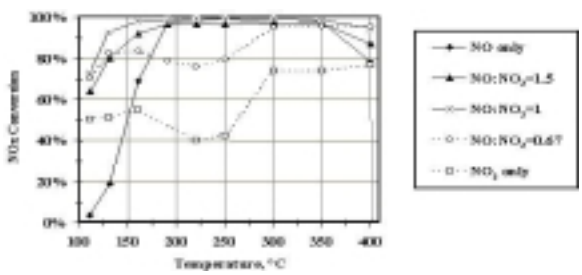

Figure 11. NO_x conversion profiles obtained for an SNL experimental vanadia-based catalyst using different NO:NO_2 ratios in the simulated exhaust gas composition. In all cases the total NO_x (NO + NO_2) was 350 ppm.

combustion environments [1-3]. As shown in Figure 11, reasonable NO_x reduction performance (~50% NO_x conversion at 150°C) is obtained for pure NO feeds. A pure NO_2 feed results in poor NO_x conversion performance, especially at low to intermediate temperatures (< 300°C). Mixtures of NO and NO_2 generally show improved performance relative to the single component feeds; significant improvement is observed at both low (< 200°C) and high (400°C) temperatures used in the catalyst test procedure. This result is important because it shows that significant synergism between NO and NO_2 species can improve SCR catalyst performance. These results are <u>not</u> specific to vanadia-based catalysts; very similar results were obtained using supplier benchmark catalysts containing various base metal active phases as well [4]. Because CIDI engine-out exhaust is NO-rich, increasing the NO_2 content of the exhaust stream would require the use of an oxidation catalyst upstream of the SCR catalyst.

These results are in agreement with recent work published by Koebel et al. [5] that has shown that equimolar concentrations of NO and NO_2 can be beneficial to SCR catalyst performance, particularly at low temperature. There are two reasons proposed for this benefit. First, a fast SCR reaction may take place in which NO_2, rather than O_2, serves as the oxidizing agent that regenerates the active metal site. This reaction is considered fast relative to the traditional SCR reaction involving NH_3, NO, and O_2. Second, at low temperatures, nitrous acid, produced as a by-product of the oxidative regeneration step using NO_2, can react with NH_3 to form an adsorbed ammonium nitrite species, which rapidly decomposes to N_2 and H_2O at low temperatures.

Several other process variables identified in Table 4 had major effects on catalyst performance. As expected, the NO_x conversion scales almost directly with the NH_3:NO_x ratio. Care must be taken to provide enough NH_3 to maximize NO_x conversion without undesireable NH_3 slip or additional NO_x generation at high temperature due to NH_3 combustion. NH_3 adsorption and desorption phenomena associated with the catalyst composition (including the entire washcoat formulation) must be understood to predict the behavior of these materials in transient environments associated with vehicle applications.

The O_2 content of the exhaust stream can have a major effect on the performance of the SCR catalyst, depending on the NO:NO_2 ratio. In equimolar mixtures of NO and NO_2, removal of O_2 from the exhaust stream has little effect on SCR catalyst performance since NO_2 is used to reoxidize redox sites in the active catalyst phase. However, in pure NO feeds, removal of O_2 from the feed dramatically retards the SCR catalyst performance since no oxidant is available for regenerating these redox sites. These results are relevant to real exhaust applications, where air:fuel ratio variations might be utilized for various needs such as increased power or perhaps regenerative procedures that require reducing environments for other emissions control components (e.g., PM traps or NO_x adsorber/ catalysts).

A final major effect was identified in the case of the presence of hydrocarbons in the SCR catalyst reaction environment. A total HC (as C1):NO_x ratio of 4:1 (3:1 mixture of n-octane:propylene) was used for these tests. The presence of hydrocarbons was found to severely retard the NO_x reduction activity of the SCR catalyst. Also, the detrimental effect of the hydrocarbons was not found to be immediately reversible. These results are consistent with recent publications in the literature [6], and point to a second benefit of having an oxidation catalyst upstream of the SCR catalyst, i.e., removal of residual hydrocarbons to protect the SCR catalyst from deactivation.

Next year we will continue our catalyst screening efforts to identify non-vanadia SCR catalyst compositions that meet NO_x reduction activity requirements. Included within these efforts will be catalyst development efforts to improve promising formulations with respect to durability and SO_2/SO_3 aging requirements and efforts to prepare promising catalyst formulations in monolith core form. Benchmark catalyst formulations will continue to be obtained from catalyst suppliers and evaluated relative to experimental formulations.

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Overall Presentations/Publications/Patents

1. D. L. Mowery, T. J. Gardner, L. I. McLaughlin, and R. S. Sandoval, "Challenges in Lean-Burn Automotive Exhaust Catalysis," Presented at the 2000 National Laboratory Catalysis Research Conference, Argonne, IL, October 12, 2000.
2. K. C. Ott, N. C. Clark, and M. T. Paffett, "Catalyst and Process for Preparation of Catalysts for Lean Burn Engine Exhaust Abatement," U. S. Patent Application (from Provisional), October 25, 2000.
3. T. J. Gardner, S. J. Lockwood, S. E. Lott, and L. I. McLaughlin, "Material and System for Catalytic Reduction of Nitrogen Oxide in an Exhaust Stream of a Combustion Process," U.S. Patent No. 6,165,934, December 26, 2000.
4. K. C. Ott, N. C. Clark, J. A. Rau, "Highly Active Lean NO_x Catalysts: Hysteresis in the Presence of Water," Presented at Spring American Chemical Society Meeting, Environmental Catalysis Symposium, San Diego CA, April, 2001.
5. T. J. Gardner, L. I. McLaughlin, D. L. Mowery, R. S. Sandoval, and D. A. Blom, "Supported Pt-CuO Catalysts for Lean-Burn Automotive Exhaust Treatment Applications," Presented at the 17th North American Catalysis Society Meeting, Toronto, June 6, 2001.
6. T. J. Gardner, L. I. McLaughlin, D. L. Mowery, and R. S. Sandoval, "Reduction of NO_x Emissions for Lean-Burn Engine Technology," Presentation at the 2001 OTT CIDI, Emission Control, and Fuels Review, Knoxville, TN, June 11, 2001.
7. K. C. Ott, N. C. Clark, J. A. Rau, "Reduction of NO_x Emissions for Lean-Burn Engine Technology," Presentation at the DOE CIDI Engine Combustion, Emission Control, and

Fuels R&D Review, Knoxville TN, June 11, 2001.

8. T. J. Gardner, "Technology Development - Selective Catalytic Reduction (SCR) Systems," Presentation at the Symposium of the Wisconsin Engine Research Center (Exhaust Aftertreatment: Facts and Fiction), Madison, WI, June 12, 2001.

9. K. C. Ott, N. C. Clark, J. A. Rau, "Hysteresis in Activity of Microporous Lean NO_x Catalysts in the Presence of Water Vapor," accepted for presentation at EuropaCatV, Symposium on Environmental Catalysis, Limerick Ireland, September 2001.

B. Development of a Fuel Processing Reactor for Onboard Reductant Generation

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

Barriers

A. NO_x Emissions

Tasks

4a. NO_x Adsorber R&D

4d. Advanced NO_x Reducing Systems

4e. R&D on NO_x Reducing Technologies

Objectives

- Develop a fuel processing reactor for onboard generation of reductants for NO_x exhaust treatment systems
  - Quantify fuel processor operation and outlet compositions of reductants
  - Show proof of concept that onboard production of reductants is a viable approach for NO_x reduction
  - Optimize fuel processor outlet composition for NO_x reductant formation

Approach

- Examine fuel processing options for reductant formation
  - Identify operating conditions conducive for onboard reductant formation
  - Design reformer for applicable fuel chemistry and reductant quantity for testing
  - Examine individual fuel components, mainly diesel fuel components in fuel reformers
  - Test fuel components with operating conditions favorable for onboard reforming
  - Examine carbon formation in fuel reformer
- Model fuel reforming chemistry
  - Model carbon formation
  - Model equilibrium gas compositions
  - Model thermodynamic properties

Accomplishments

- Identified various operating conditions that affect reductant formation
  - Power (quantity of reductant)
  - Oxidant (oxygen concentration in engine exhaust)
  - System integration for fuel processor formation of NO_x reductants
- Designed and tested diesel and gasoline reformers under conditions expected for NO_x reduction
- Tested pure diesel components and kerosene
- Examined fuels effects with:
  - Catalytic oxidation
  - Monitoring of oxidation conversion
  - Gasoline and diesel fuel components (dodecane, hexadecane)
  - Kerosene
- Modelled fuel and fuel component chemistry
  - Carbon formation conditions
  - Equilibrium gas compositions

Future Directions

- Evaluate thermal losses of small fuel reformers
- Obtain proof of reformate reduction of NO_x with Lean NO_x catalysts
- Obtain proof of reformate regeneration of NO_x adsorbers
  - Measure carbon formation *in situ* with an adiabatic reactor and laser scattering
  - Map carbon formation onset for component/component blends as a function of operating conditions
- Define catalyst requirements for durability

Introduction

The technology being developed uses partial oxidation and steam reforming of onboard fuel (either gasoline or diesel) to produce chemical reductants such as H_2, CO and small unsaturated hydrocarbons such as ethylene (C_2H_4) and propene (C_3H_6) which are known to catalyze the reduction of NO_2 and are known to regenerate NO_x adsorbers. The onboard production of these reductants and subsequent addition to the exhaust would enable NO_x reduction by either lean NO_x reductant catalysts or regeneration reductants for NO_x adsorbers (see Figure 1). This valuable emissions control technology would be consumer friendly, as maintenance is not required, and off-board refueling of a reductant such as ammonia is also not required.

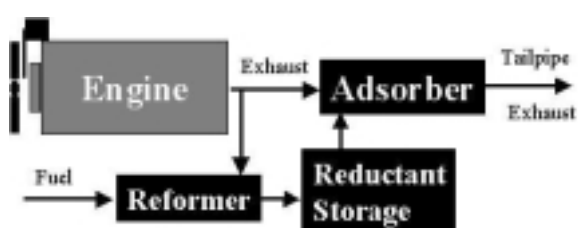

Figure 1. Sample Schematic of NO_x Regeneration by the Onboard Formation of Reductants.

The requirements for reductant formation have been examined, including operating conditions for onboard fuel reforming. Fuel reformers have been

designed and constructed for the production of NO_x reductants. Initial testing to generate NO_x reductants from diesel fuel has been made. Diesel fuel components have been tested, with gas analysis techniques employed to determine the reformate composition. The reformate composition has been used to estimate the potential fuel penalty for such a NO_x reduction system.

Approach

Fuel partial oxidation and reforming is technology being explored for onboard production of hydrogen for applications such as fuel cells. For the chemical conversion of fuel hydrocarbons, air is combusted with fuel, typically over a catalyst to produce hydrogen and carbon monoxide. Equation 1 shows the partial oxidation of a generic hydrocarbon for an air stoichiometry exactly correct (O/C = 1) for the production of hydrogen and carbon monoxide.

$$C_nH_{(2n+2)} + (n/2)O_2 \rightarrow nCO + (n+1)H_2 \qquad (1)$$

If the oxygen-fuel ratio is more fuel rich (O/C < 1), unconverted hydrocarbons will be present in the reformate stream. These hydrocarbons include small unsaturated hydrocarbons such as ethylene and propylene.

$$C_nH_{(2n+2)} + (m/2)O_2 \rightarrow mCO + C_{(n-m)}H_{2(n-m)} + H_2 \quad (2)$$

We have developed partial oxidation (POx) reactors with the supporting test equipment to test the feasibility of generating reductants from fuel onboard a vehicle for the reduction of NO_x emissions. The reactor reacts fuel with air (or simulated engine exhaust) in a fuel-rich mixture to generate a gas stream containing H_2, CO, CO_2, N_2, and small hydrocarbons. One of our research reactors has optical access windows for analysis of the effluent stream by a laser to observe conditions under which carbon formation occurs. Carbon formation is an important consideration of operation, as it will inhibit durability of the system. This work varies operating conditions to map the outlet gas composition as a function of operating conditions and allows for subsequent optimization of the production of the desired reductants. Carbon formation is monitored as a function of fuel component and operating condition. The oxidant feed is simulated for operation from ambient air and

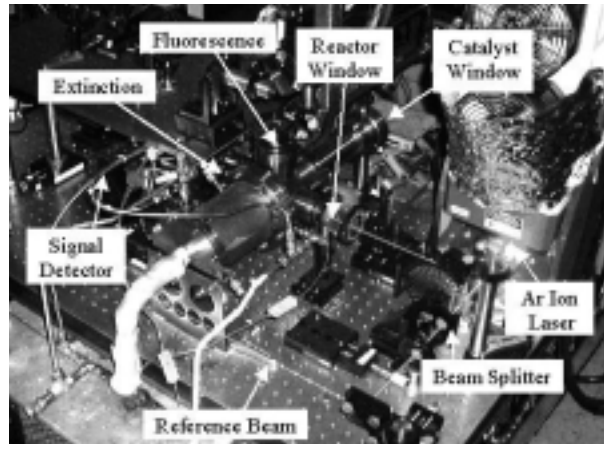

Figure 2. Catalytic Partial Oxidation with Facilities for Laser Extinction and Scattering Measurements with Catalyst Observation

from engine exhaust. Initial operating conditions of the reactor were determined by modeling equilibrium gas compositions for the expected range of S/C and O/C.

The relative distribution of the catalytic conversion has been observed with various fuel components with different catalyst substrates (monoliths and reticulated foams). Mapping of the onset of carbon formation for different fuel components as a function of operating conditions has been initiated with these techniques. The reactor with catalyst observation windows, laser extinction, and scattering facilities is shown in Figure 2.

For onboard formation of NO_x reductants, it is expected that special operating conditions are required, such as low oxygen and steam content in the oxidant, low pressure — slightly above ambient, and low fuel throughput — approximately 1 kW LHV fuel. A reactor has been designed and constructed to operate under these conditions and is shown in Figure 3.

Expected outlet concentrations of the fuel reformer, as well as the relative fuel component effects on the fuel reformer outlet have been modeled. In particular, modeling of equilibrium carbon formation has been used to predict the operating conditions for the onset of carbon formation for various fuel blends.

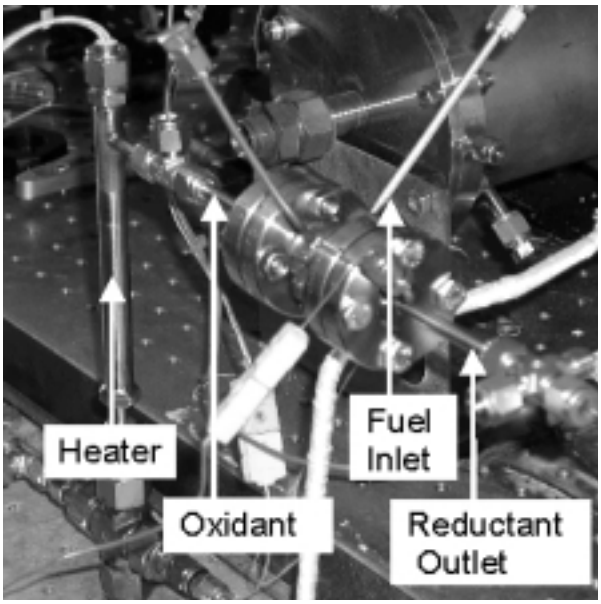

Figure 3. Fuel Reformer for Reductant Formation at Low Pressure and Low Fuel Throughputs

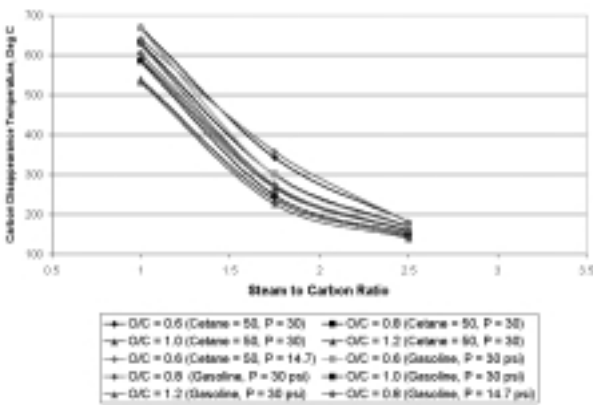

Figure 4. Equilibrium Modeling of Carbon Formation for Various Fuels and Conditions

Results

The reforming of diesel fuel components indicates that higher residence times are required for similar conversion compared to that of gasoline components. In addition, sulfur poisoning has been shown to greatly inhibit non-noble metal catalysts such as nickel. Diesel fuel components have more stringent requirements to prevent equilibrium carbon formation conditions. Figure 4 shows the results of modeling the onset of carbon formation for different fuels and operating conditions to compare with the experimental measurements. Diesel fuel components showing higher temperatures are required to prevent carbon formation, with relative S/C ratio having a dramatic impact on the carbon formation temperature.

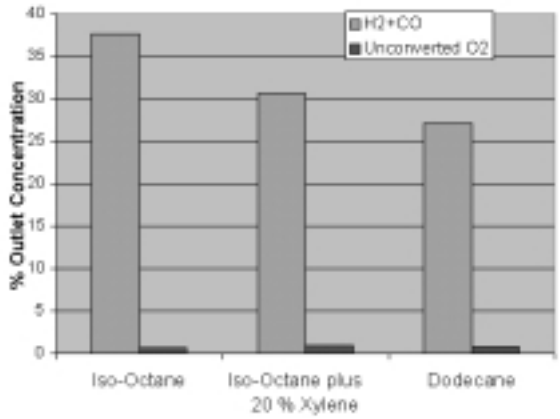

Figure 5. Outlet Concentration Comparison for Iso-Octane, Iso-Octane/Xylene and Dodecane for the Same Oxygen Conversion

% Species Concentration	GC	Gas Analyzers
H2	12.2	
N2	64.3	
O2	0.83	0.6
CO	15.5	16.4
CH4	1.29	
CO2	4.78	4.5
C2H4	0.98	
C2H6	0.056	
C3H6	0.048	
C3H8	0.0048	
>C4	0.051	

Table 1. Outlet concentrations of fuel reforming for dodecane as fuel. Operating conditions were: Residence Time = 43 msec, O/C = 1.2, S/C = 1.9, P = 15 psig, T_{in} = 470 °C and T_{out} = 830 °C.

Partial oxidation outlet concentrations of H_2 + CO are shown for similar fuel conversions for different fuels in a reactor in Figure 5. These results show that as the hydrocarbon chain length is increased, higher O/C ratios are required to get similar fuel conversion in the reactor. Some typical outlet concentrations are shown in Table 1 for the reforming of dodecane.

Based upon the preliminary findings from dodecane reforming, and a reductant stoichiometry of 2.0 with 250 ppm NO engine, a fuel penalty of

	Adiabatic	Reformer
O_2	Temp. Rise	Exhaust Temp.
%	°C	°C
21	789	989
17	690	890
15	639	839
12.5	570	770

Table 2. Adiabatic and Expected Outlet Temperatures from a Reformer with Oxidant Feeds at Low Concentrations Simulating Engine Exhaust

between 1.0 and 2.0 % is calculated to reduce the NO_x. These calculations are based on stoichiometric reduction of NO_x, such as propene reducing NO_x as in eqn. 3, or by H_2 and CO regeneration of a NO_x adsorber chemically. However, these calculations are preliminary, and it remains to be demonstrated that reformate either makes a suitable NO_x reductant or adsorbent regenerator.

$$9NO + C_3H_6 \rightarrow 9/2N_2 + 3CO_2 + 3H_2O \quad (3)$$

For operation onboard a vehicle, the most likely source of oxidant will be the engine exhaust. Typical lean-burn and diesel engines operate lean and, thus, have significant amounts of oxygen present. However, the oxygen is depleted compared with air; thus the adiabatic temperature rise of a reformer will be lower than with operation with comparable air. Adiabatic and expected outlet temperatures (for engine exhaust at 200°C) from a reformer with oxidant feeds at low concentrations to simulate engine exhaust are shown in Table 2. To achieve temperatures required for the prevention of carbon with low oxygen concentration engine exhaust, higher O/C ratios will be required than what are normally used for partial oxidation.

Conclusions

Various fuel components and fuels have been tested with various O/C and S/C ratios in catalytic fuel reformer reactors. The outlet gas composition has been measured to help determine optimum operating conditions for these reactors. Diesel fuel components (such as dodecane) have been found to require higher residence times for similar conversions than comparable gasoline components.

Modeling has shown that fuel effects on the temperature for equilibrium onset of carbon formation can vary up to150°C with varying O/C ratios, and the reformer temperature most likely will need to be kept above 700°C for low S/C reactor feeds. Stoichiometric calculations indicate that the fuel penalty for fuel reformate reduction of NO_x could be between 1 and 2 % of fuel.

C. NO_x Control and Measurement Technology for Heavy-Duty Diesel Engines

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

Barriers

A. NO_x Emissions

C. Cost

Tasks

4. NO_x Control Device R&D

4d. Advanced NO_x Reducing Systems

Objectives

- Advance the development of NO_x aftertreatment systems for diesel engines by quantifying their detailed chemical processes to identify barriers and improvement strategies.

Approach

- Develop advanced measurement capabilities to elucidate relevant aspects of NO_x emission control device performance with improved resolution and/or sensitivity.
- Apply the Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS) to investigation of gas-phase species dynamics, including NO_x slip and desorption and reductant reforming, using bench-scale and full-scale devices.
- Apply Diffuse Reflectance mid-Infrared Fourier Transform (DRIFT) and Raman spectroscopy to characterize surface chemistry including surface nitrogen, sulfur, carbonate and hydroxyl effects on storage, poisoning, passivation and enhancement dynamics.

Accomplishments

- Applied SpaciMS to two full-scale, candidate-production NO_x-adsorber devices and acquired data relevant to device improvement and optimization and model validation and development.
  - Identified regions of fuel reforming, NO_x storage, and inactivity within the devices.
  - Quantified NO_x-adsorption profiles throughout the devices with and without sulfur poisoning.
- Applied both DRIFT and Raman spectroscopies to observe nitrate and sulfate adsorption/desorption on a model NO_x adsorber catalyst.

Future Direction

- Apply the SpaciMS to better understand advanced NO_x emission control devices and sulfur-trap formulations and processes.
- Apply DRIFT and Raman to quantify the performance of species for regenerating NO_x adsorbers and the effects of H_2O, CO_2 and other ancillary species on NO_x adsorber performance.

Introduction

NO_x-adsorber catalysts provide a promising approach for emissions reduction in the fuel-lean environment of diesel engine exhaust. NO_x-adsorber systems have a finite capacity to store NO_x emissions by forming surface nitrogen species at active catalyst sites. These systems are periodically regenerated to restore capacity by injecting pulses of reductant, which causes the stored NO_x to be desorbed and reduced, ideally to H_2O, CO_2, and N_2. Diesel fuel is a convenient reductant, but it requires reforming to produce secondary species such as H_2 and CO that are believed to be more efficient reductants. In-cylinder injection of diesel fuel via a late injection and in-pipe injection are the most common ways of introducing a reductant.

High-speed instruments capable of temporally resolving the transient emissions associated with the dynamic NO_x adsorber process are required to develop and optimize these promising emission control strategies. Minimally or non-invasive diagnostics might allow for intra-channel probing of the catalyst chemistry to quantify the axial distribution of participating species, NO_x loading, reductant reforming, sulfur poisoning and desulfation. Such information is critical to understanding the detailed catalyst chemistry, identifying rate-limiting steps, specifying device size and aspect ratio, and optimizing washcoat formulation to improve storage, reforming, regeneration, and sulfur tolerance performance.

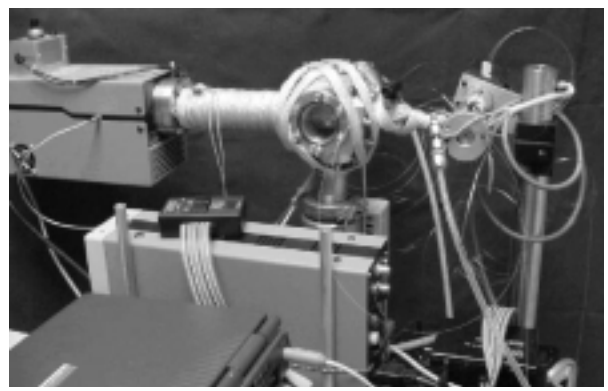

Figure 1. Photograph of the SpaciMS Showing the Capillary/Multi-port-valve Inlet System, Ionization Chamber, Quadrupole, Electronics Unit and Electron-multiplier-output Amplifier

Surface diagnostic techniques such as Raman and DRIFT spectroscopy can be used to elucidate catalyst mechanisms. Using these techniques *in situ*, it is possible to observe the appearance and disappearance of surface species during the adsorption/regeneration processes. Reaction intermediates and unwanted reaction by-products can also be observed.

Approach

Figure 1 shows a SpaciMS that has been developed to provide high-speed, minimally

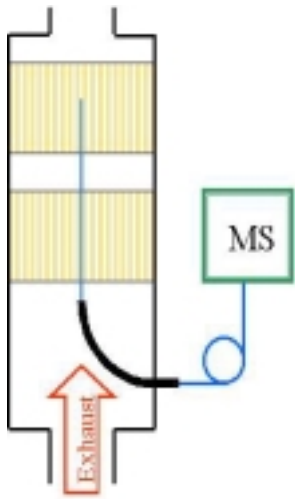

Figure 2. Schematic of Geometry Used for SpaciMS Measurement of Intra-Channel Spatio-Temporal Catalyst Chemistry Distributions

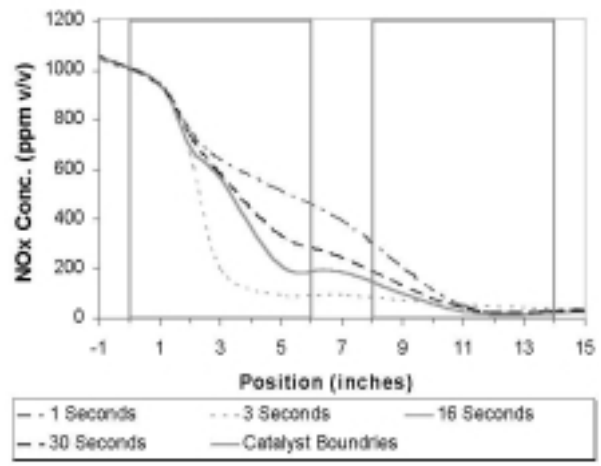

Figure 3. Spatio-temporal NO_x distribution in the probed monolith channel throughout the adsorption-regeneration cycle. The thickness and spacing of the two monoliths are indicated.

invasive, intra-catalyst-channel measurements of a broad range of transient species relevant to the NO_x adsorber process. The instrument uses one or more capillaries to extract and transport small quantities of undiluted exhaust to a mass spectrometer, where single-species measurements are made at rates up to 1MHz. The capillaries are specified to minimize temporal broadening of transient species during capillary transport. The SpaciMS head uses electron-impact ionization, quadrupole mass filtering and Faraday cup or continuous-dynode electron-multiplier detection. The SpaciMS is routinely applied for measurement of total NO_x, O_2, CO_2 and HC fragments indicative of base fuel and reformed olefin and oxygenate products. High-speed single-species (i.e., single-ion) scans are temporally aligned via a trigger (e.g., reductant injection time) to reveal the detailed phase of the various species transients within the NO_x-adsorber cycle. The instrument is transportable and has been deployed to several industrial research labs for secure evaluation of advanced emission-control systems including NO_x adsorbers and EGR.

We have investigated the viability of the SpaciMS for real-time measurement of transient emissions from a NO_x-adsorber catalyst operating with a Cummins 5.9L ISB diesel engine using diesel fuel injected into the exhaust stream as the catalyst-regenerating reductant. That work demonstrated the superior temporal resolution of the SpaciMS for resolving species transients relevant to the NO_x-adsorber process. For instance, the SpaciMS is capable of resolving and characterizing the instantaneous depletion of O_2, which is necessary to specify reductant injection quantities. Moreover, the temporal resolution of the SpaciMS was sufficient to resolve chemical rate limitations in the desorption-reduction process. Specifically, the process is reduction limited in the front of the fuel-rich regeneration pulse, resulting in an initial spike in the NO_x emissions. Approximately 200 to 400 ms into the regeneration pulse, the initial NO_x spike decreases as reduction overtakes the desorption process.

The minimally invasive nature of the SpaciMS sampling probe allows for intra-catalyst-channel measurement of chemical spatio-temporal distributions. Figure 2 shows the geometry used to investigate catalyst chemistry distributions in a candidate production NO_x adsorber operating with a Cummins ISB diesel engine. Two 6-inch thick catalyst bricks were configured in series with a 2-inch spacing. A single capillary was translated through a central channel to spatially resolve the axial distribution of transient species. The SpaciMS was used to monitor HC, O_2, CO_2 and NO_x transients at several axial locations. System operation involved regeneration every 30 seconds via an approximately 0.5-s wide fuel-rich pulse. The full results provide resolution of the spatial/temporal species distributions throughout the channel and

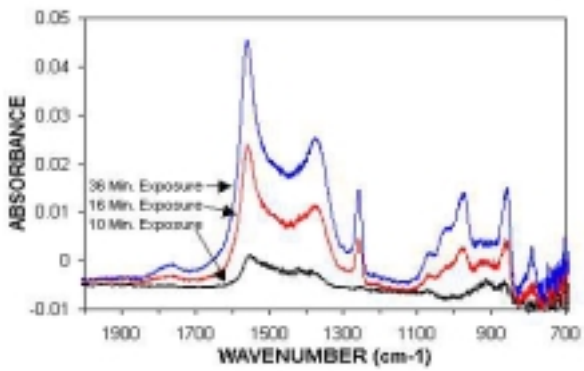

Figure 4. DRIFT spectra of surface species associated with NO_x storage over barium oxide. Stored NO_x is partitioned between monodentate nitrate and monodentate and bidentate nitrite.

regeneration cycle. This represents the first known demonstration of *in-situ* intra-channel catalyst speciation.

Results

Some SpaciMS results of NO_x distribution in the adsorber catalyst are provided in Figure 3, which was generated by sampling the NO_x signal at each location 1 s, 3 s, 16 s and 30 s after the leading edge of the fuel-rich pulse. The flow is from left to right in Figure 3, and the width and spacing of the front and back bricks are indicated. The four curves demonstrate the NO_x loading and desorption-reduction distributions within the catalyst. The NO_x profile in the first inch of the front brick (position 0 to 1 inch) suggests this to be a reforming region where appropriate species for driving the desorption and reduction processes are generated. Three seconds after the regeneration pulse, the adsorber capacity has been restored. The development of the axial-loading profile is evident from the 16-s and 30-s curves. The difference in the 1-s and 30-s curves is indicative of the desorption-reduction profile and quantifies the relative magnitudes of the desorption and reduction functions throughout the device. Figure 3 demonstrates that at the specific engine conditions used here, the back 2 inches of the brick are not necessary. Similar figures have been generated for other species.

The unique and previously unavailable data provided by the SpaciMS are critical to developing catalyst models; understanding the details of NO_x loading, fuel reforming, sulfur poisoning and desulfation; identifying rate-limiting steps; and optimizing catalyst parameters such as reductant quantity required, catalyst aspect ratio and washcoat formulation.

DRIFT spectroscopy provides *in situ* detection and measurement of the identity and relative concentration of various surface species associated with catalysis. Figure 4 shows the DRIFT spectra of NO_x species adsorbed on a neat formulation of BaO powder during exposure to NO_2 and O_2. The powder was reduced and stabilized in a heated cell, then reacted with continuous flow of approximately 1000 ppm NO_2 and 20% O_2 in N_2 at a powder temperature of 200°C. The spectra were obtained at different exposure times (10, 16 and 36 minutes) on the same sample. Both nitrate and nitrite surface species were formed on the BaO, but the formation of $Ba(NO_3)_2$ did not occur. Monodentate nitrate species have absorption bands that appear around 1495, 1290 and 980 cm^{-1}. Monodentate nitrite species were observed at 1460, 1070 and 810 cm^{-1}. The bidentate and bridged nitrite species appear as the bands at 1370 and 860 cm^{-1}. The surface nitrate and nitrite species are stable in their relative concentrations for long time periods after the flow of NO_2 and O_2 is substituted with N_2. Hydrogen regeneration of the BaO at higher temperatures (>350°C) resulted in desorption of the surface NO_x species to below the DRIFT detection limit and regenerated the catalyst to its initial formulation. Similar spectra are used to quantify the effects of sulfur poisoning, desulfation and various model reductants.

Future Plans

In FY2002 the SpaciMS will be applied to investigate NO_x adsorbers, sulfur traps and EGR distribution. DRIFT and Raman will be applied to monitor surface-catalyst chemistry for quantifying the performance of reformed-reductant species for regenerating NO_x adsorbers and the effects of ancillary species on NO_x-adsorber performance.

References

1. W.P. Partridge, J.M.E. Storey, S.A. Lewis, R.W. Smithwick, G.L. DeVault, M.J. Cunningham, N.W. Currier and T.M. Yonushonis, "Time-Resolved Measurements of Emission Transients

by Mass Spectrometry," SAE Paper 2000-01-2552, (2000).

Publications and Presentations

1. W.P. Partridge, J.M.E. Storey, S.A. Lewis, R.W. Smithwick, G.L. DeVault, M.J. Cunningham, N.W. Currier and T.M. Yonushonis, "Resolving NO_x-Adsorber Emissions Transients," presented at and published in the proceeding so the DEER Workshop, San Diego, CA, August 2000.
2. John Storey, Bill Partridge, Sam Lewis, Jim Parks, Aaron Watson, Neal Currier and Jason Chen, "Resolving NO_x-Adsorber Emission Transients and Sulfur Poisoning using Mass Spectrometry," presented at and published in the proceeding to the FY2001 DOE National Laboratory Merit Review and Peer Evaluation, Knoxville, TN, June 2001.

D. Evaluation of NO_x Sensors for Heavy Duty Vehicle Applications

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

CRADA Partner: Ford Motor Company (Dearborn, MI) and Visteon Automotive Systems
Ford Investigators: Rick Soltis (primary contract) and Ken Nietering
Visteon Investigators: Ralph Ross and Joe Giachino

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

Barriers

A. NO_x Emissions

C. Cost

Tasks

2a. Advanced Sensors and Controls

Objective

- The overall goal of this study is to characterize the performance of emission sensors and identify potential areas of improvement.

Approach

- Develop a bench device to evaluate sensor performance under controlled conditions.
- Evaluate the flow characteristics of the test rig to determine baseline system performance.
- Perform sensor evaluation by monitoring controller output.
- Extract the pumping currents from the NGK NO_x sensor.
- Utilize discoveries to seek improvement of sensor response.

Accomplishments

- Developed a bench-scale rig to evaluate sensor response and performance.
- Allows low gas flow rates.
- Allows control of gas temperature.
- Determined the response and certified the gas flow behavior in the bench rig.

- Determined the response (time constant) for a commercially available NGK NO_x sensor.
- Successfully measured the oxygen and NO_x pumping currents.

Future Directions (Beyond FY 2001)

- Measurement and analysis of pumping currents under transient conditions.

Introduction

Urea selective catalytic reduction (SCR) and NO_x adsorber systems are being investigated as devices to reduce NO_x emissions from diesel engines. Optimization of these devices on an automotive platform will likely require feedback control. The availability of emission sensors is limited; in fact, the only currently available NO_x sensors are those manufactured by NGK. Before any NO_x sensor can be integrated into an emission control system, its performance must be accurately assessed to determine its range of operation and response.

The overall objective of this study is to characterize the performance of emission sensors and identify potential areas of improvement. To accomplish this, it is necessary to develop a test apparatus and methodology for controlled evaluations. The second part of the objective is to search out areas of improvement. For the NGK NO_x sensor, the pumping current signature can be evaluated under transient conditions and analyzed to determine if a predictive algorithm could be applied to improve sensor response.

The NGK NO_x sensor design consists of two cells with diffusion barriers. Exhaust enters the first cell, where it is thermally decomposed into NO and elemental oxygen. The oxygen present in the exhaust is pumped out of the first cell to levels approaching 10 ppm. The current generated by pumping out the oxygen from Cell 1 is transformed into a voltage by the controller to become the O_2 signal output for the device. The NO present in Cell 1 moves through a diffusion barrier to Cell 2. In Cell 2, the NO is decomposed into elemental nitrogen and oxygen on a rhodium electrode. The current generated by pumping O_2 out of Cell 2 is used to provide the NO_x output signal of the device.

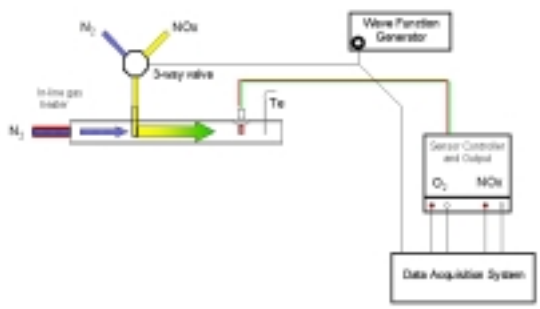

Figure 1. Schematic of Sensor Evaluation System

Approach

A bench-scale rig was developed in order to measure the transient response of selected NO_x (or oxygen) emission sensors. The performance of the rig was modeled assuming well-stirred tank conditions and verified using a fast NO analyzer. Steady-state measurements of NO and NO_2 were initially performed to confirm the baseline performance of the sensors. Transient measurements were made using of NO and O_2 test gases in order to determine sensor response. In order to elucidate the sensor behavior more fully, the O_2 and NO_x pumping currents were measured under both steady-state and transient conditions. Analysis of the pumping currents during transient testing may provide insights into computational techniques to improve sensor response.

Results

A bench-scale rig was developed at ORNL and is depicted in the schematic shown in Figure 1. The test chamber is an open-ended 1.5-inch diameter stainless steel tube. Nitrogen gas is flowed through the chamber from one end. Approximately 7.5 inches from the nitrogen source an injector tube is located with orifices facing downstream of the flow. The injector is connected to a 3-way valve that can switch between nitrogen or another selected test gas, thus maintaining constant flow though the test

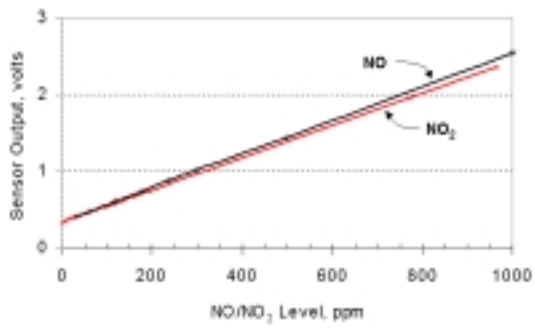

Figure 2. Steady-State Response of the NGK NO_x Sensor to NO and NO_2

Time Constant	Gas Temperature		
	27°C	188°C	350/400°C
RC	1.67s	1.18s	0.87s
t (10-90)	3.60s	2.60s	1.92s
t (33-66)	1.13s	0.80s	0.61s

Table 1. Sensor Response as a Function of Gas Temperature

chamber. The sensor is located approximately 10 inches from the injector to ensure complete radial mixing. Sensor response and valve operation are fed into a data acquisition system and the signals recorded simultaneously at a rate of 500 Hz. The performance of the rig was determined using a Cambustion NO analyzer capable of sampling at 250 Hz. This result served as the baseline reference for further transient evaluations.

Two NGK NO_x sensors were sent to ORNL for evaluation by Ford Motor Company. The sensors were placed in the bench rig and evaluated under steady-state and transient conditions. The steady-state results are shown in Figure 2; they confirmed the baseline performance for this device. Transient tests were performed on the sensor at several different gas temperatures. The sensor response as a function of temperature is shown in Table 1. The t (33-66) time constant decreased with increasing gas temperature and was constant (around 610 ms) for temperatures greater than or equal to 350°C.

The pumping currents of the sensor were measured under steady-state conditions by splicing a pico-ammeter into the sensor wiring. The steady-state values for the oxygen and NO_x pumping currents are shown in Figures 3 and 4, respectively.

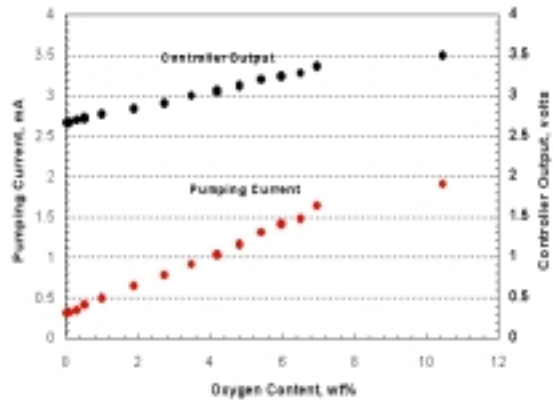

Figure 3. Steady-State Measurements of Oxygen Pumping Current Versus Oxygen Concentration

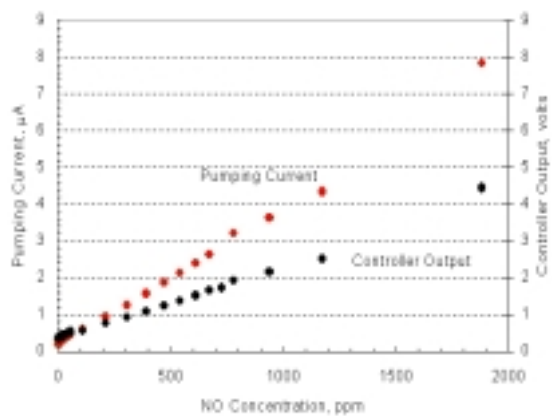

Figure 4. Steady-State Measurements of NO_x Pumping Current Versus NO Concentration

The pumping current for the oxygen increased linearly with increasing oxygen concentration and ranged from 0.2 to 3 mA. The NO_x current also increased linearly with NO concentration, but the current was very low, ranging from 200 nA to around 8 µA. These low currents indicate that the sensor may be susceptible to electromagnetic interference and, therefore, may have limited use.

Conclusions

A bench-scale rig was developed at ORNL to evaluate NO_x sensor performance. The response of the rig was determined and the gas flow behavior was characterized. A commercially available NO_x sensor was placed in the rig and evaluated under steady-state and transient modes of operation. The time constants for the sensor were found to decrease

with increasing temperature up to 350°C. This will be an important consideration when integrating these devices into emission control systems, since the range of exhaust gas temperature in a diesel engine exhaust can vary between 150°C and 500°C.

The pumping currents of the NGK sensor were measured under steady-state conditions. The currents were found to be extremely low and therefore susceptible to electromagnetic interference. Transient analysis of these currents may indicate that computational techniques could be used to improve the sensor response.

E. Plasma Catalysis for NO_x Reduction from Light-Duty Diesel Vehicles

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

Barriers

A. NO_x Emissions

B. PM Emissions

C. Cost

Tasks

4b. Non-thermal Plasma R&D

5e. R&D on PM Reducing Technologies

Objective

- Develop a novel plasma/catalyst NO_x reduction and particulate matter (PM) aftertreatment system that will achieve 90% NO_x reduction using less than 5% of the engine power on a compression ignition direct injection (CIDI) engine.

Approach

- Synthesize and characterize new catalysts. A highly active and stable plasma catalyst material is critical to meeting the program goals.
- Measure plasma/catalyst activity in simulated and real exhaust.
- Through more fundamental mechanistic studies, identify the important reaction intermediates and the rate-limiting reactions in a plasma/catalyst system. Use this information to guide the catalyst synthesis efforts.
- Design and construct prototype plasma/catalyst reactor systems.
- Evaluate prototype reactor systems for emission (NO_x and PM) reduction performance, energy efficiency, and durability.
- Utilize ORNL ceramic processing capabilities to simplify the design of the plasma reactor portion of the emission control device.

Accomplishments

- **90% NO_x reduction demonstrated in two ways** — both reactor concept and insight from fundamental mechanistic studies led to these important results.
- Catalyst improvements have been made in a number of areas:
  - composition of baseline material;
  - catalyst (zeolite) structure; and
  - addition of dopants for enhanced 'temperature window', added 'functionality' of the catalyst, and improved material properties (e.g., catalyst stability).
- Results from our initial particulate removal studies show considerable promise.
- Nitrogen and carbon balances are now routinely obtained in laboratory measurements.
- Prototype ceramic parts have been manufactured at ORNL that offer the potential to greatly simplify the design of proposed plasma reactor device components.
- Planning and preparation for another round of full-scale engine tests has been initiated with the goal of verifying the current status of the technology without the major ambiguities of previous tests.
- General Motors researchers are now operating two reactor systems similar to those at Ford and PNNL. There is some overlap to insure consistency, but mostly complimentary experiments are coordinated to avoid duplication.
- This program was awarded the 2001 DOE CIDI Combustion and Emission Control Program Special Recognition Award.
- Twelve papers have been published, 5 with PNNL as lead authors. Three papers have been presented at both the DEER and Fall SAE conferences. One patent has been issued, 1 is still being prosecuted, and 3 new invention disclosures have been completed (patents being written now). The plasma/catalyst concept is clearly becoming more visible and acceptable due, in large part, to this program's results:
  - Several large vehicle industry programs are now ongoing in Asia (particularly in Japan and Korea; e.g., Toyota, Honda, Mitsubishi and Hyundai), and citing this program's work as the reason they started their research and development efforts;

- Recent accomplishments of this program have been highlighted in a number of 'popular' science journals and industry-specific magazines;
- Four invited talks have been delivered at international scientific meetings.

Future Directions

- Continue and expand fundamental mechanistic studies that focus on the surface chemistry of acetaldehyde and NO_2 on the active plasma catalyst materials.
- Focus studies of the plasma device on identifying conditions for optimized production of the important reductant materials (aldehydes) identified in the mechanistic studies.
- Continue development of catalyst materials with higher activity and improved durability utilizing a 'structured' search guided, in part, by the results from our mechanistic studies.
- Identify fate and form of PM following 'treatment' by the plasma reactor. This will follow up our recent results showing considerable reduction of PM by a plasma device.
- Iterate on production methods and form of plasma reactor ceramic parts produced by ORNL with testing performed at PNNL on PNNL plasma reactor designs.
- Verify current status of this novel technology by regular full-scale engine tests. The next scheduled tests will occur in October or November of this year (2001).

Introduction

In this program, we have been developing a novel plasma/catalyst technology for the remediation of NO_x under lean (excess oxygen) conditions, specifically for compression ignition direct injection (CIDI) diesel engines that have significant fuel economy benefits over conventional stoichiometric gasoline engines. Our previous work has shown that a non-thermal plasma in combination with an appropriate catalyst can provide NO_x emission reduction efficiency of 60-80% using a simulated diesel exhaust [1]. Based on these levels of NO_x reduction obtained in the lab, a simple model was developed in this program last year that allows for the estimation of the fuel economy penalty that would be incurred by operating a plasma/catalyst system [2]. Results obtained from this model suggest that a 5% fuel economy penalty is achievable with the then current state-of-the-art catalyst materials and plasma reactor designs.

Figure 1 is a conceptual schematic of a plasma/catalyst device. Also shown in the figure (to be discussed below), is our current best understanding of the role of the various components of the overall device for reducing NO_x from the exhaust of a CIDI engine. In this last year, we have continued to focus

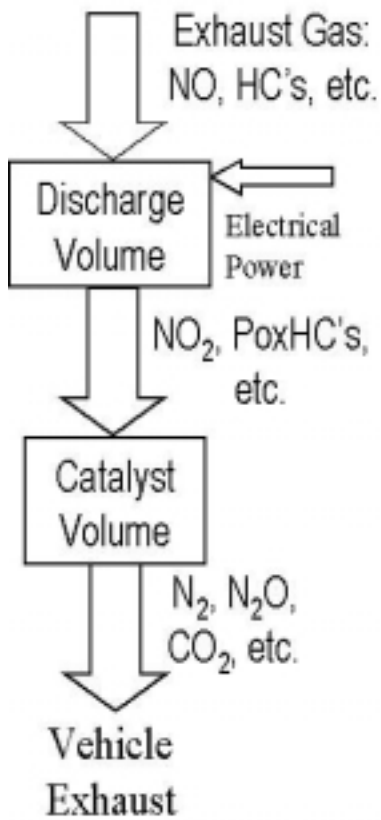

Figure 1. Schematic of a Two-step Discharge/Catalyst Reactor Used for Reducing NO_x and PM from the Exhaust of CIDI Engines

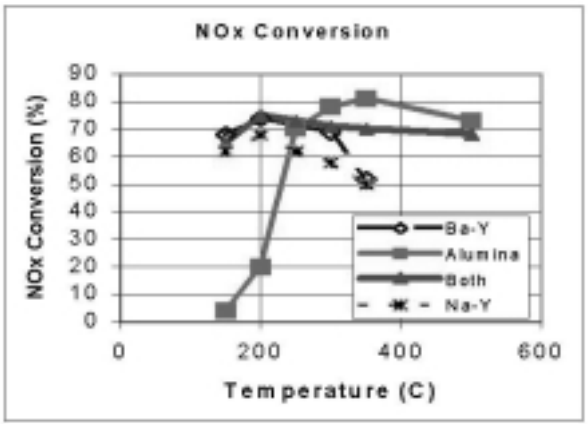

Figure 2. Plasma-assisted NO_x conversion levels over a variety of catalyst materials as a function of exhaust gas temperature. "Both" is 60% BaY, 40% alumina. Reactions were run at a gas flow rate that yields a 12,000 hr^{-1} SV, and with a plasma-reactor energy of 30 J/L. The Gas Feed = 8% O_2, 2% H_2O, 7% CO_2, 200 ppm NO, 40 ppm CO, 715 ppm (C_3) C_3H_6, balance N_2.

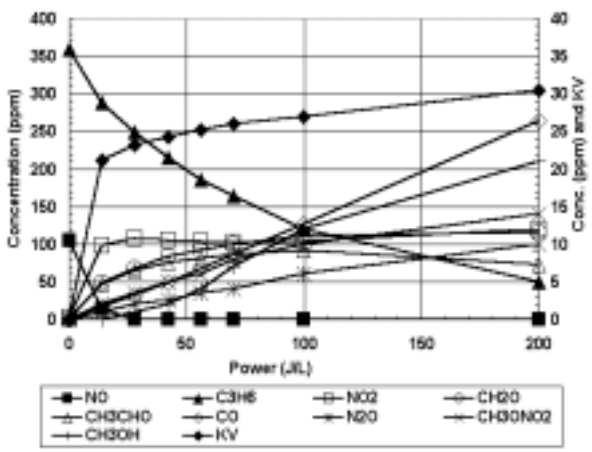

Figure 3. Distribution of products exiting a non-thermal plasma operated with variable power at 500 Hz, a gas temperature ~ 200°C and SV ~ 20,100 h^{-1}. The Gas Feed = 14% O_2, 2.5% H_2O, 25 ppm SO_2, 105 ppm NO, 360 ppm C_3H_6 (C:N ~ 10:1).

on (1) improving the catalyst and plasma reactor efficiencies for NO_x reduction, (2) studies to reveal important details of the reaction mechanism(s) that can then guide our catalyst and reactor development efforts (focus 1), and (3) evaluating the performance of prototype systems on real engine exhaust. In addition, we have initiated more careful studies this last year on the effects of the plasma on PM in real diesel engine exhaust.

Results

Because this program's patent application for the proprietary catalyst materials has now been published (PCT# WO 00/18494), we can identify the materials that we've previously described as "Catalyst A" and "Catalyst B". Figure 2 shows the NO_x conversion over a variety of catalyst systems that we have reported previously. In our prior publications [1], the Na-Y zeolite catalyst has been referred to as "Catalyst A" while, correspondingly, "Catalyst B" represented a Ba-Y zeolite catalyst. As can be seen in the figure, the identification of Ba-Y represented a significant improvement over the prior best material, Na-Y. Also shown in the figure is the measured performance of a specific alumina material both alone, and together with the Ba-Y catalyst. As reported in last year's report, the combination of these two materials, tested as two sequential catalyst beds, provides a significant enhancement of the "temperature window" for high NO_x conversions.

A particularly important highlight from this year's work is the identification of what we believe to be the important partially oxidized hydrocarbon (PoxHC — see Figure 1) produced in the plasma region of a plasma/catalyst device. From prior work, it was widely believed that the most important role for the plasma reactor part of the device is to oxidize NO to NO_2. In fact, we demonstrated this year that partial hydrocarbon oxidation by the plasma is at least as important as NO oxidation if not more so. To identify candidate partially oxidized reductant species, we looked at the hydrocarbon species generated by a plasma reactor on simulated diesel exhaust. Figure 3 shows results obtained at General Motors where it can clearly be seen that aldehydes (formaldehyde and acetaldehyde) are primary PoxHC products formed in the plasma [3]. These results were consistent with modeling studies carried out at the University of Illinois in collaboration with John Hoard at Ford. We then used this information to study the thermal catalytic reaction (no plasma!) of NO and NO_2 with added aldehyde as the reductant. Figure 4 shows that NO_x conversions of 90% or greater were obtained in these experiments [4]. These laboratory results are especially significant because they demonstrate that a plasma/

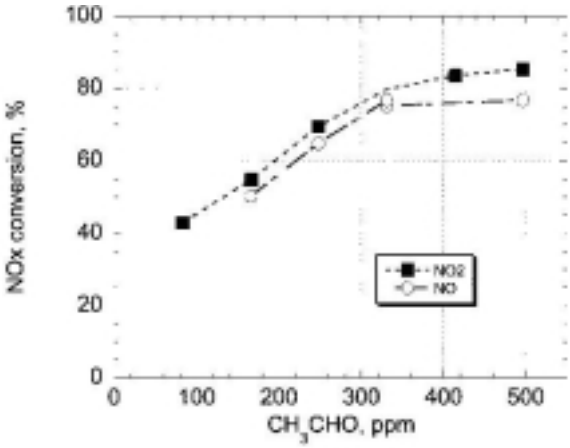

Figure 4. The Effect of Acetaldehyde Concentration on the Thermal Conversion of NO_x over a BaY Zeolite Catalyst (T=250°C, SV=12,000h^{-1}, 200 ppm NOx, 8% O_2, 2% H_2O, balance N_2).

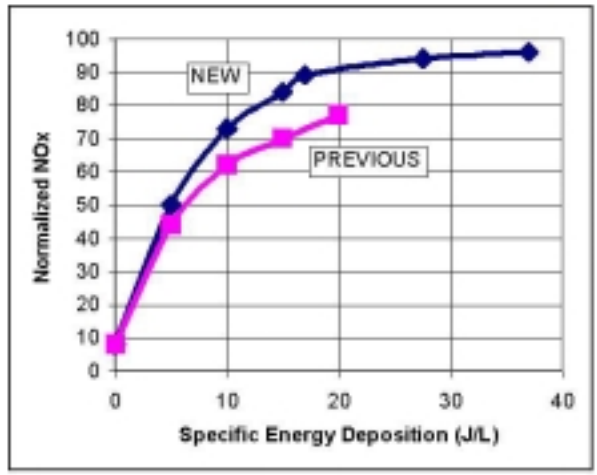

Figure 5. The NO_x Conversion Performance (Percent Conversion) of a New System Design Relative to the Prototype System Used in Previously Described Studies

catalyst device is capable, in principle, of meeting the program targets. Furthermore, they provide important information for how to further optimize the catalyst and plasma reactor components of the device. Using similar experiments, we also studied the ability of longer-chain aldehydes because they are likely to form from the hydrocarbon components in a real diesel exhaust.

Besides the above studies, our catalyst development efforts in FY2001 have focused on: 1) the 'optimum' cation substitution (type and amount) into zeolite-Y; 2) whether the zeolite structure is necessary for creating the 'active catalytic sites' and, if yes, what is the 'optimum' structure; 3) whether the addition of other metal-dopants, reported to be good partial hydrocarbon oxidation catalysts, could increase the yield of desirable aldehyde species; 4) whether both of the high and low temperature activities (see Figure 2) can be 'engineered' into a single catalyst; 5) whether ammonia SCR catalysts (e.g., vanadia/titania and tungstate/titania) are good materials for NO_x reduction following a non-thermal plasma; and finally, 6) whether optimum 'acid site' type and concentration can be engineered into the catalyst.

Our plasma reactor development work this year has consisted of three main activities. 1) As part of 'work-in-kind', DaimlerChrysler will be evaluating a commercial 'plasma reactor' design. The plan is to test a 'Maxwell' ozonizer in engine tests scheduled for October at FEV in Auburn Hills, MI. We expect to have new results from this work to report next year. 2) In collaboration with PNNL (S. Barlow), Steve Nunn at ORNL has been refining the design and fabrication of ceramic parts to reduce part number and complexity. Prototype parts manufactured at ORNL are currently being tested at PNNL in a PNNL-designed plasma-reactor. 3) Most significantly, PNNL has invented a new conceptual plasma/catalyst system that offers the promise of achieving the 90% NO_x reduction targets with significantly reduced input power requirements [5]. Figure 5 provides data obtained this year that demonstrates the validity of the new concept. Importantly, this experimental data is fully consistent with modeling of the reactor.

Besides NO_x reduction, meeting newly legislated particulate matter (PM) standards for the exhaust of CIDI engine-powered vehicles represents a significant challenge. Based on some prior literature, as well as a number of intriguing preliminary experiments carried out previously in this program, we have initiated new experiments designed to determine the fate of PM from the exhaust of a CIDI engine after passing through the oxidizing region of a non-thermal plasma reactor. In this year, we have set up instrumentation to carefully measure the number and size distribution of PM emitted from a Yanmar L70AE, 300cc, 4-cycle diesel generator. The first results are shown in Figure 6 where a sizable

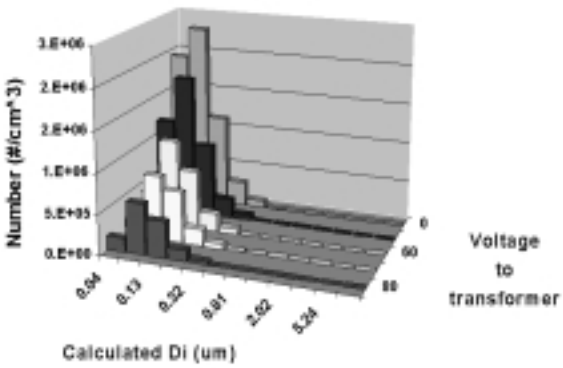

Figure 6. Measured reduction of the number of particulate matter in specific size ranges as a function of increasing energy input to the plasma reactor. These measurements were made after passing the exhaust of a 300cc, 4 cycle diesel generator (Yanmar L70AE), at a 40% load, through a laboratory prototype non-thermal plasma reactor.

reduction in PM, proportional to the input energy of the plasma reactor, is clearly demonstrated. In this next year, we will focus our studies on the identification of the fate of the PM. In particular, an important question is whether this observed PM reduction is due to electrostatic precipitation or if, indeed, the PM is more fully oxidized (ideally to CO_2).

Engine testing of prototype plasma/catalyst devices is an important element of our program to provide a 'calibration' of where the technology is relative to the alternatives and with respect tomeeting the overall goals of the program. In last year's report, we described the first of these engine tests (at ORNL) that demonstrated as much as 50% reduction with an estimated total fuel economy penalty of 6%. Despite these very promising results, there were a large number of experimental ambiguities that suggested even better performance. For this reason, we have designed a vastly improved and flexible test unit that will be used for this fall's scheduled engine dynamometer tests in Detroit. The overall goals of the tests are as follows. 1) Thoroughly test a commercial 'ozonizer' as a possible simple plasma reactor design (these experiments will be conducted by DaimlerChrysler personnel as part of their "work-in-kind"). 2) Determine where we really are on an actual system using our "best available technology". Notably, we plan to remove most, if not all of the ambiguities from prior ORNL tests. These ambiguities include the poorly understood effect of PM on the system performance (e.g., NO_x conversion), the use of probably low quality catalyst coatings on monolith substrates in the catalyst reactor region of the device, and a likely overly simple plasma reactor design used in these first full-scale engine tests.

Conclusions

PNNL and its LEP CRADA partners from Ford, General Motors and DaimlerChrysler have been developing a plasma-assisted catalyst system that is showing great promise for treating emissions of NO_x and PM from the exhaust of CIDI engine-powered vehicles. High NO_x conversions have been demonstrated over a wide temperature range on simulated diesel exhaust. The most significant laboratory results obtained in the last year provide good evidence that the overall program targets of 90% NO_x reduction with less than a 5% fuel-economy penalty are within reach. Careful planning for full-scale engine tests, scheduled for this fall in Detroit, has also occurred this year.

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2. J. Hoard, P. Laing, M.L. Balmer, and R. Tonkyn, "Comparison of Plasma-Catalyst and Lean NO_x Catalyst for Diesel NO_x Reduction", SAE 2000-01-2895.
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5. R.G. Tonkyn and S.E. Barlow, (portions of the title are proprietary until patent is filed) "...Processing of NO_x in Synthetic Diesel Exhaust", SAE 2001 (in press).

List of Publications

1. J. Hoard, P. Laing, M.L. Balmer, and R. Tonkyn, "Fuel Economy Impact of Plasma-Catalyst Versus Active Lean-NO_x Aftertreatment", Proceedings of the Diesel Engine Emissions Reduction Workshop, 2000.
2. R.G. Tonkyn, S. Barlow, S. Yoon, A. Panov, A. Ebeling, and M.L. Balmer, "Lean NO_x Reduction by Plasma Assisted Catalysis", Proceedings of the Diesel Engine Emissions Reduction Workshop, 2000.
3. A.G. Panov, R. Tonkyn, S. Yoon, A. Kolwaite, S. Barlow, and M.L. Balmer, "NO_x Reduction Behavior of Alumina and Zeolite Catalysts in Combination with Non-Thermal Plasma", Proceedings of the Diesel Engine Emissions Reduction Workshop, 2000.
4. J. Hoard, P. Laing, M.L. Balmer, and R. Tonkyn, "Comparison of Plasma-Catalyst and Lean NO_x Catalyst for Diesel NO_x Reduction", SAE 2000-01-2895.
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6. J. Hoard, E. Kalashnikov, S. Kaberline, R.L. Bretz, and L. Haack, "Composition of Clusters Formed by Plasma Discharge in Simulated Engine Exhaust", SAE 2000-01-2967.
7. A.G. Panov, R. Tonkyn, S. Yoon, A. Kolwaite, S. Barlow, and M.L. Balmer, "Effect of Simulated Diesel Exhaust Gas Composition and Temperature on NO_x Reduction Behavior of Alumina and Zeolite Catalysts in Combination With Non-Thermal Plasma", SAE 2000-01-2965.
8. J. Hoard, "Plasma-Catalysis for Diesel Exhaust Treatment: Current State of the Art", SAE 2001-01-0185.
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2. J. Hoard, and M.L. Balmer, "Plasma-Catalyst for Diesel Emission Reduction", invited presentation for the International Chemical Congress of the Pacific Basin Societies, Honolulu, HI, December, 2000.
3. J. Hoard, "Plasma-Catalysis for Diesel Exhaust Treatment: Current State of the Art", invited presentation at the SAE World Congress, Detroit, MI, February, 2001.
4. J. Hoard, R. Tonkyn, A. Panov, and M.L. Balmer, "Plasma-Catalysis for Diesel NO_x Emissions: Technology Overview", invited presentation for the 2nd Asia-Pacific International Symposium on the Basis and Application of Plasma Technology, Kaohsiung, Taiwan, April, 2001.
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9. J. Hoard, A. Panov, R. Tonkyn, M.L. Balmer, and S. Schmieg, "Products and Intermediates in Plasma-Catalyst Treatment of Simulated Diesel Exhaust", presentation at the SAE Fall Fuels and Lubes Meeting, San Antonio, TX, September, 2001.
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12. S.E. Barlow, R.G. Tonkyn, J. Hoard and W. Follmer, (portions of the title are proprietary until patent is filed) "...Discharge/Catalyst Reactors", presentation at the SAE Fall Fuels and Lubes Meeting, San Antonio, TX, September, 2001.
13. R.G. Tonkyn, and S.E. Barlow, (portions of the title are proprietary until patent is filed) "... Discharge/Catalyst Processing of NO_x in Synthetic Diesel Exhaust", presentation at the SAE Fall Fuels and Lubes Meeting, San Antonio, TX, September, 2001.

Special Recognitions and Awards/Patents Issued

1. 2001 DOE CIDI Combustion and Emission Control Program Special Recognition Award
2. Patent issued: J.W. Hoard, "Power Supply for Dielectric Barrier Discharge Plasma", U.S. Patent #6,156,162, December 5, 2000.

F. Non-Thermal Plasma System Development: Integrated PM and NO_x Reduction

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

Barriers

A. NO_x Emissions

B. PM Emissions

C. Cost

Tasks

4b. Non-thermal Plasma R&D

5e. R&D on PM Reducing Technologies

Objectives

- Develop an integrated non-thermal plasma (NTP) assisted catalyst and particulate filter system for PM and NO_x reduction in heavy-duty diesel vehicles.
- Reduce vehicle emissions by an average of 90% for PM and 80% for NO_x over a typical emissions driving cycle test.
- Design a system that is tolerant to sulfur and other diesel fuel impurities.
- Achieve the above objectives with less than a 3% fuel penalty impact on vehicle operation.

Approach

- Develop an integrated NTP system for simultaneous PM and NO_x reduction.
- Use NTP to convert NO to NO_2 and directly oxidize PM to CO_x.
- Model plasma physics and chemistry of a NTP reactor and design an energy efficient reactor based on modeling and experimental results.
- Use selective catalytic reduction of NO_x to N_2 in conjunction with a NTP reactor for NO_x reduction, which will require the development of a highly active catalyst material.
- Remove PM by mechanical filtering with a diesel particulate trap, and regenerate trap by soot oxidation, with NO_2 supplied by NTP reactor.

- Design, optimize, and construct a prototype system to maximize emissions reduction performance while minimizing hydrocarbon and power consumption requirements.

Accomplishments

- Developed numerical models to help guide NTP reactor design.
- Initiated development of an energy efficient NTP reactor design that can be used in an integrated system for PM and NO_x reduction.
- Demonstrated the use of a catalyst material that achieves >90% peak NO_x reduction when used in conjunction with an NTP reactor (simulated exhaust).
- Established that the NTP reactor can directly oxidize a portion of the PM (~30%) to CO_x.
- Initiated experimental efforts to develop and understand mechanisms of diesel particulate filter (DPF) continuous regeneration by NTP.
- Developed an understanding of the chemistry that occurs in various steps of an integrated NTP assisted PM and NO_x reduction system.

Future Directions

- Perform full-scale durability testing of NTP reactor design.
- Increased NO_x catalyst performance at lower temperatures for cold-start operation, and evaluate transient response.
- Evaluate diesel fuel injection for potential hydrocarbon addition if required for adequate operation.
- Test with real diesel engine exhaust.
- Characterize direct soot oxidation in NTP reactor.
- Continue investigation of diesel particulate trap regeneration by NO_2, with NTP assist.

Introduction

The objective of this Cooperative Research and Development Agreement (CRADA) project is to develop an integrated NTP assisted catalyst and particulate filter system for PM and NO_x reduction in heavy-duty diesel vehicles, with an average of 90% PM and 80% NO_x reduction over the heavy-duty engine emissions test cycle. The CRADA partners are the DOE Office of Heavy Vehicle Technologies (DOE-OHVT), Pacific Northwest National Laboratory (PNNL), and Delphi Automotive Systems.

Approach

The approach taken for this project will primarily address three key technical areas associated with the development of an NTP assisted-catalysis system for the reduction of PM and NO_x emissions from heavy-duty diesel engines: 1) NTP reactor development, 2) selective NO_x reduction catalyst material development, and 3) particulate trap regeneration based on NTP technology. The conceptual integrated system that is capable of reducing both PM as well as NO_x emissions from a lean-burn diesel engine is shown in Figure 1.

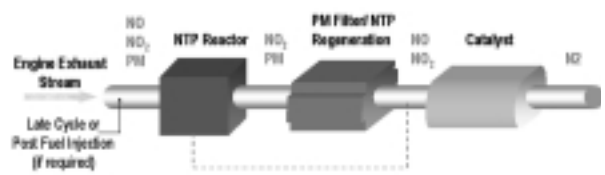

Figure 1. Conceptual schematic of an NTP assisted-catalyst exhaust aftertreatment system. The state of NO_x and PM emissions are shown for each stage of the system.

The project tasks were performed jointly by PNNL and Delphi team members, with the NTP reactor modeling, catalyst material development, and

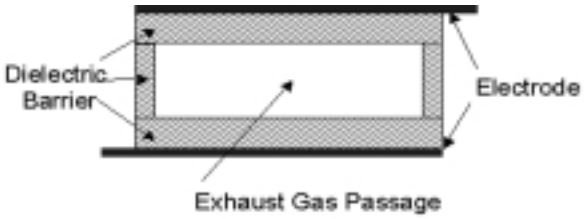

Figure 2. Single Cell Parallel Plate NTP Reactor

system chemistry mechanistic understanding being the primary focus for the PNNL group. The focus for the Delphi group was the application of a DPF and filter regeneration, on-vehicle system evaluations, and power supply/control system development.

Results

NTP Reactor Development

Based on modeling activities and experimental trials, a parallel plate, dielectric barrier discharge (DBD) reactor design was selected as the best and most robust geometry to use for an NTP system. This design is comprised of flat electrodes placed on opposing sides of the exhaust gas passage, as shown in Figure 2, with alumina dielectric barriers used to suppress arcing between the electrodes. Figure 2 shows a single cell unit, but multiple cells can be combined to increase reactor size and capacity based on the engine application.

An integrated NTP model was developed that correlates reactor geometry to performance and chemistry, in order to guide reactor design. In addition, finite element analysis (FEA) of heat transfer and high temperature durability testing have shown that this design is robust. The numerical modeling activities have provided great insight into the proper reactor design. Most NTP reactor designs (barrier discharge type) are similar in performance, if constructed properly. Figure 3 shows the results from a modeling simulation to determine the effect of gap spacing on the performance of the NTP reactor. The modeling results indicate that minimizing the reactor gap distance increases the electric field saturation strength and the fraction of current carried by electrons. However, the better electrical conditions must be balanced between physical conditions, such as the amount of backpressure developed from the device. Therefore, a practical minimum reactor gap distance for the

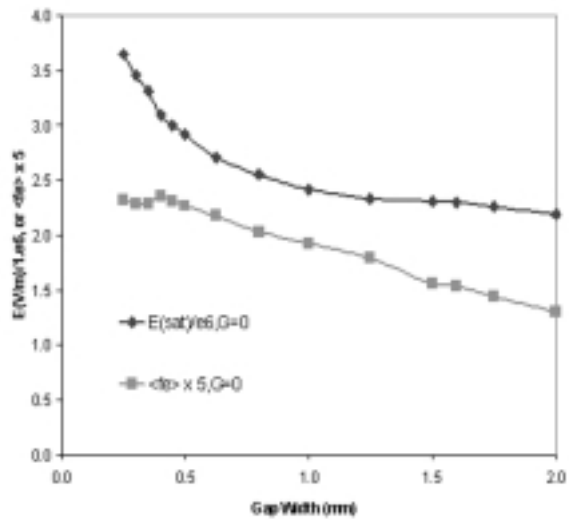

Figure 3. Modeling Results of the Saturation E-field Strength and the Fraction of Current Carried by Electrons, as a Function of Gap Distance

parallel plate design was established to be approximately 1 mm. This gap distance maximizes the electric field strength, while ensuring minimal backpressure through the NTP reactor, with adequate exhaust flow rates.

The exhaust gas species also play a significant role in the energy requirements and NO oxidation efficiency, particularly at high exhaust-gas temperatures. Numerical modeling of the plasma physics, coupled with the gas-phase chemistry for NO to NO_2 conversion, was performed, which provided a better mechanistic understanding of the chemistry that occurs in the plasma. It was found that the production and availability of RO_2 and HO_2 species is important for efficient NO to NO_2 conversion. The reaction rates between NO and HO_2 or RO_2 species are extremely fast, and by maximizing the hydrocarbon, water, and oxygen content in the exhaust stream, the production of these species is increased. Adequate NO to NO_2 conversion is achievable, even at higher exhaust gas temperatures, with minimal NO_2 to NO back reaction, if HC and H_2O levels are high enough. The experimental data shown in Figure 4 validate this notion and show that the NO to NO_2 conversion efficiency increases with increasing H_2O and HC content. Therefore, it is desirable to maximize the HC and H_2O content of the exhaust gas stream, where appropriate.

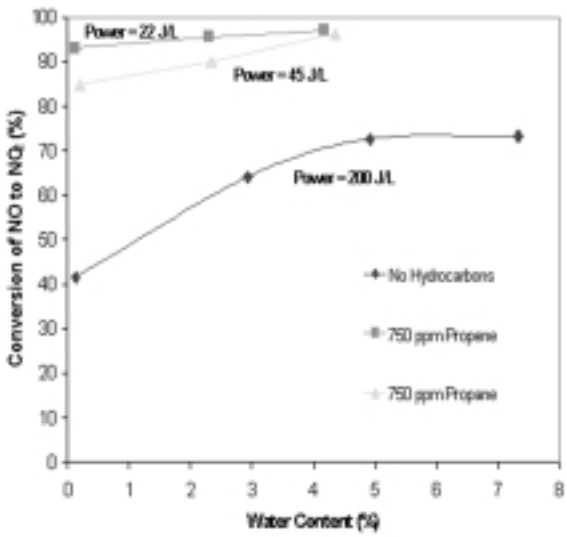

Figure 4. Experimental Results Showing the Importance of Hydrocarbons and Water on the NTP Reactor Performance

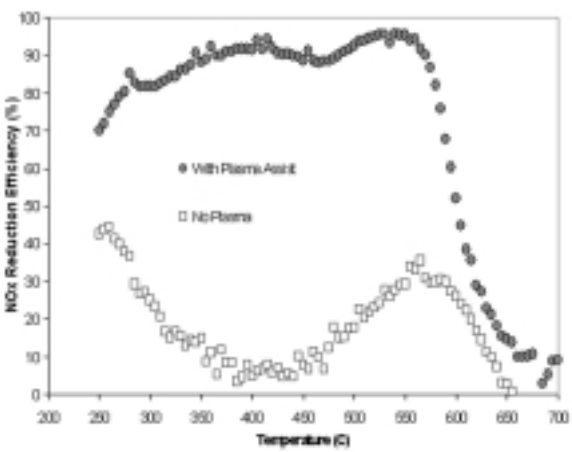

Figure 5. Experimental results of NO_x conversion efficiency from NTP assisted NA1 catalyst, with a simulated exhaust stream. The simulated exhaust gas was comprised of 250 ppm NO, 500 ppm C_3H_6, 10% O_2, 3% H_2O, and 7% CO_2. The NTP reactor temperature was held constant at 250°C, and the energy input was 22 J/L for 95% NO to NO_2 conversion.

Catalyst Material Development

Initial catalyst material development has been focused on metal oxide structures, such as high surface area alumina based materials. The materials investigated were comprised of commercial high surface area alumina products and laboratory-prepared proprietary formulations and synthesis

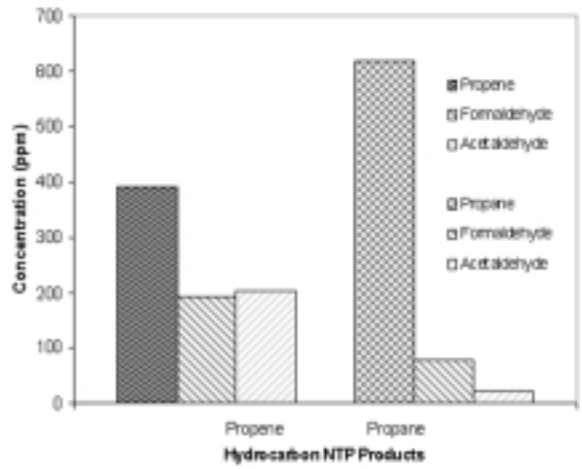

Figure 6. Experimental Results from the Conversion of Propene and Propane to Aldehydes in a Simulated Exhaust Stream

processes. In general, the commercial materials fell significantly short of achieving the high NO_x conversion efficiency required to meet the project goals. The laboratory synthesized materials achieved high peak NO_2 reduction efficiencies (greater than 90%) when run with a simulated exhaust stream. However, one specific catalyst material, identified as NA1, achieved a high level of NO_x reduction over a relatively wide operating temperature window of 250°C to 600°C, when combined with a NTP device. The peak NO_x reduction efficiency was >90%, as shown in Figure 5, but the NO_x conversion efficiency was <40% when NO_2 was injected directly into the catalyst instead of into the gas stream being processed by the plasma. This suggests that the plasma produces other active species that play a role in the catalytic reduction of NO_2 over these catalyst materials.

It was found that aldehyde species are the important reductants that react with NO_2 to convert it to N_2. Experiments were conducted, without the use of an NTP reactor, where supplemental additions of aldehydes, primarily formaldehyde, were injected into the catalyst bed. An increase in catalyst activity was realized, similar to that of the case where an NTP reactor was used. Figure 6 shows how much formaldehyde and acetaldehyde is generated in the plasma from the input of 750 ppm propene and propane. The data also indicate that the generation of aldehydes in plasma is dependent on the type of

hydrocarbons introduced to the plasma, with alkenes producing more aldehydes.

PM Reduction and DPF Regeneration

Since the NTP reactor requires electrical power to produce the plasma discharge, it is desirable to maximize the benefits from the reactor, and therefore use the electrical energy provided by the vehicle's charging system as effectively as possible. In addition to oxidizing NO to NO_2 and converting a portion of the available exhaust HCs to aldehydes, the NTP can also oxidize a portion of the PM to CO_x. It was found that approximately 32% of the total particle count is reduced by passing the exhaust stream through the NTP reactor at power levels equivalent to that required for complete NO to NO_2 conversion. Figure 7 shows the reduction of PM count from a 1.9L direct injected diesel vehicle as a function of NTP reactor power.

Complementary experiments to determine the mass reduction of PM through the NTP reactor revealed approximately a 30% reduction in PM mass, compared to a "reactor off" operating condition.

Even though the NTP reactor can directly convert a portion of the PM to CO_x, a 30% reduction is not enough to meet future emissions regulations. Therefore, the use of a DPF was added to the system for the mechanical removal of PM from an exhaust gas stream. A DPF is very effective at removing PM from the exhaust stream of vehicles. However, once the filter is saturated with PM, it must be regenerated and the soot removed in order to ensure proper engine and DPF operation.

Research was initiated to investigate the use of NO_2 as an oxidant to oxidize soot particles collected on the filter to CO_2 and regenerate the surface of a DPF. Since NO_2 is a strong oxidizer, the conversion of PM at lower temperatures is possible. However, in order for this process to be effective, a high reaction rate is necessary for continuous filter regeneration and to maintain a low pressure-drop across the system. In addition, the system must be capable of regeneration over a wide temperature range (including <400°C), and it must minimize the vulnerability to SO_2 and non-combustible contaminants.

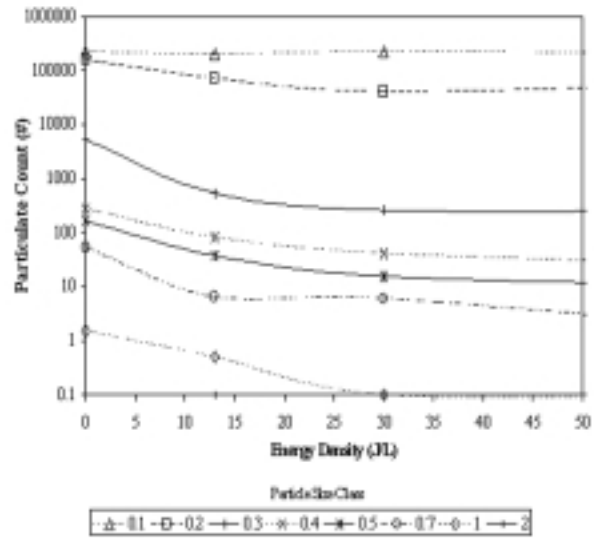

Figure 7. Experimental Results Showing the Reduction in Particulate Counts for Different Particle Size Classes

Experiments were performed to validate the use of NO_2 as an oxidizer of soot collected in a DPF. The experiments were set up so a DPF device was located in the exhaust stream of a running diesel engine, operated on an engine dynamometer system. The engine was initially run with a new DPF for a predetermined amount of time, in order to collect an initial amount of soot in the filter, and then NO_2 from an external source was introduced up-stream of the DPF. Similar experiments were performed with an NTP reactor located up-stream from the DPF, for the purposes of providing the necessary NO_2 for soot oxidation and "forcing" the regeneration to occur at lower temperatures.

The data plotted in Figures 8 and 9 are representative of the results from the DPF regeneration experiments. Filter regeneration was possible in the "injected" NO_2 case, but only at temperatures at or above 400°C. In contrast, filter regeneration occurred in the NTP "forced" condition at temperatures as low as 340°C. In addition, the minimum NO_2 concentration required for "forced" regeneration was ~100 ppm, compared to the 200 ppm of injected NO_2 necessary for continuous regeneration.

The rate of regeneration was measured by monitoring the pressure drop across the DPF, which is directly related to the amount of soot inventory in the filter, and by monitoring the mass of PM on the

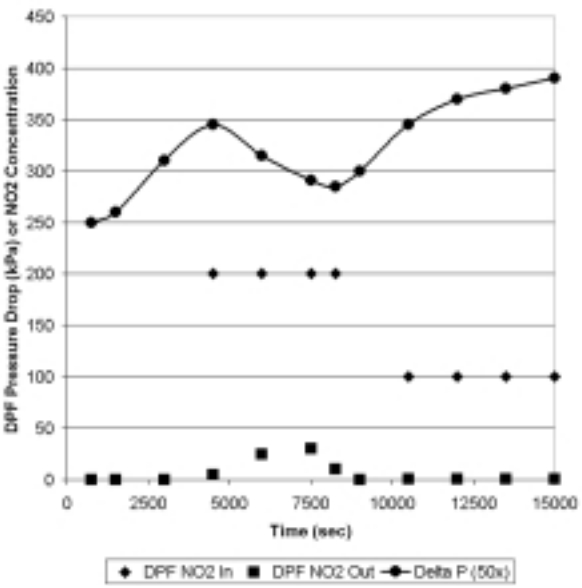

Figure 8. Experimental results showing DPF regeneration with injected NO_2 and filter bed at 400°C. Initial soot loading in DPF when NO_2 was injected was 10.4 grams.

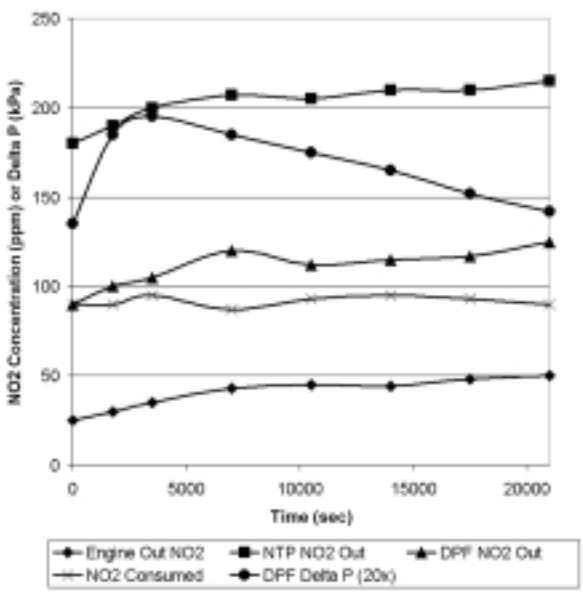

Figure 9. Experimental results showing DPF regeneration using a NTP reactor up-stream from the DPF and plasma assist to generate the NO_2. Exhaust gas temperature at DPF was at 340°C, initial soot loading was 9.9 grams, and final soot loading after 350 minutes of regeneration was 3.0 grams.

filter before and after the experiments. The rate of DPF regeneration and pressure drop change during the forced regeneration condition was -1.5 grams/hour and -0.5 kPa/hour, respectively. The lower temperature and increased rate of regeneration with the NTP reactor suggests other soot reaction mechanisms besides oxidation by NO_2. It is thought that the additional O-radicals and ozone produced in the plasma reactor may be contributing to more soot oxidation at a lower temperature.

Conclusions

Over the course of the last year, the PNNL-Delphi CRADA project has developed numerical models to help guide the NTP reactor design and has initiated the development of an energy efficient NTP reactor design that can be used in an integrated system for PM and NO_x reduction. Small-scale prototype NTP reactors were fabricated and evaluated for their ability to oxidize NO and PM emissions. In addition, a catalyst material was formulated and produced that achieves >90% peak NO_x reduction in a simulated diesel exhaust stream when used in conjunction with an NTP reactor.

A better understanding of the chemistry that occurs in various steps of an integrated NTP assisted PM and NO_x reduction system was developed, and it was discovered that the NTP reactor and subsequent plasma chemistry has the ability to directly oxidize a portion of the PM in an engine exhaust stream. Furthermore, experimental efforts were initiated to understand the chemical mechanisms of DPF continuous regeneration by NTP, through the use of NO_2 as an oxidizing agent in a DPF.

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2. D.R. Herling, M.R. Smith, M. Hemingway, D. Goulette, T. Silvis, "Evaluation of Corona Reactors of Several Geometries for a Plasma Assisted Nitrogen Oxide Emission Reduction Device," Non-Thermal Plasma — SP1566, SAE, Warrendale, PA, pp. 49-58, 2000.

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G. Plasma-Assisted Catalysis for Heavy-Duty Diesel Engines

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Pacific Northwest National Laboratory is operated for the US Department of Energy by Battelle under Contract DE-AC06-76RLO 1830

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

Barriers

A. NO_x Emissions

B. PM Emissions

C. Cost

Tasks

4b. Non-thermal Plasma R&D

5e. R&D on PM Reducing Technologies

Objective

- Develop an exhaust emission control system that will achieve 90% NO_x reduction using 3-5% of the engine power on a heavy-duty diesel engine.

Approach

- An emission control system involving a non-thermal plasma in conjunction with a catalyst is being developed to reduce NO_x emissions. In this endeavor, a partnership between Pacific Northwest National Laboratory (PNNL) and Caterpillar Inc. has been established under a Cooperative Research and Development Agreement (CRADA). PNNL is responsible for plasma system design, bench testing, and catalyst development and characterization. Caterpillar is responsible for catalyst development and characterization, bench testing, and engine cell testing.

Accomplishments

- An extensive set of tests on the effects of sulfur were completed. Catalysts tested include various γ-aluminas, In-doped γ-aluminas, and Ag-doped γ-aluminas.
- Catalyst materials capable of withstanding high operating temperatures have been synthesized and tested up to 600°C. Catalytic activity above 95% for NO_x reduction has been observed for simulated diesel exhaust.
- A variety of selective catalytic reduction (SCR) agents have been tested in combination with plasma and catalysts. Results show that primary alcohols are very active for reduction.
- A steady-state engine test has been completed on a slipstream from a Caterpillar 3126B engine. Results show NO_x removal efficiencies from 40 — 95% depending on engine load and speed conditions, the temperature of the catalysts, the formulation of the catalyst, and the reducing agent.

Future Directions

- Investigate alternative plasma reactor configurations to obtain a high throughput architecture.
- Continue to investigate alternative reducing agents and catalyst mixtures to obtain activity over broad temperature ranges.
- Continue to develop a mechanistic understanding of NO_x reduction in a plasma-catalytic system.
- Examine strategies for reforming fuel into more desirable reducing agents for NO_x control.
- Optimize catalyst formulations into support architectures that are suitable for on-vehicle use (monoliths or ceramic foams).

Introduction

Non-thermal plasma-assisted catalysis (PAC) is an effective method for reducing NO_x emissions in diesel exhaust; however, further advances in plasma system efficiency and catalyst development are needed for vehicle applications. Research in FY01 has focused on finishing an extensive set of experiments on sulfur effects, examining a set of alternate reducing agents for PAC, and completing our first engine test on a slipstream from a Caterpillar 3126B engine.

Results

Currently, over 90 catalysts have been synthesized and tested for NO_x reduction activity. Another 9 commercially available materials have also been examined. The current plasma test stand can operate up to 600ºC with simulated exhaust streams. Simulated exhaust is composed of N_2, O_2, H_2O, NO, NO_2, CO, CO_2, and SO_2. Thus far, conversions exceeding 95% have been obtained for our bench configuration. The most successful formulations are γ-alumina materials with precious metal dopants such as indium and silver. Indium-doped catalysts suffer from poisoning due to sulfur where NO_x reduction drops from above 85% down to 75%. Silver-doped materials do not exhibit problems with sulfur because silver sulfate is also active for NO_x reduction. A silver-doped γ-alumina developed under this program has shown greater than 95% reduction in NO_x on a powder test bench.

Another important aspect of our work in FY01 was the examination of a variety of reducing agents. Propylene has traditionally been used, but a liquid hydrocarbon is desirable for on-vehicle use, particularly if it can be produced from the fuel via on-board reforming. Figure 1 shows results from experiments on γ-alumina where five hydrocarbons with significantly different functionality were used as SCR agents. Methanol was the most active reducing agent over γ-alumina by a large margin. In fact, the remaining NO_x was below the detection limit of our equipment (< 5 ppm) at 500ºC. Notice also that most of the activity is thermal, in that plasma is not required at high temperature when methanol is used. There is also thermal activity for NO_x reduction at 350ºC, but plasma is required to reach the maximum conversion level of 81%.

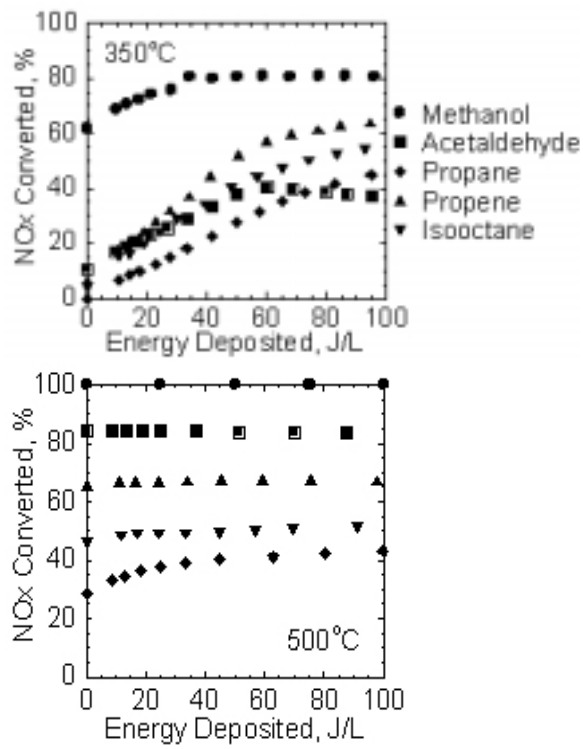

Figure 1. The Activity of γ-Alumina with Various Reducing Agents at 350ºC and 500ºC

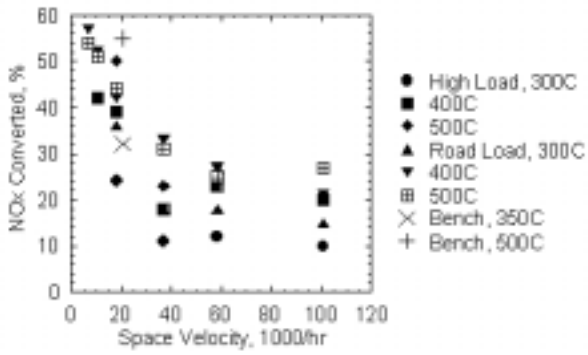

Figure 2. Engine Test Results for γ-Alumina Compared to Bench Data

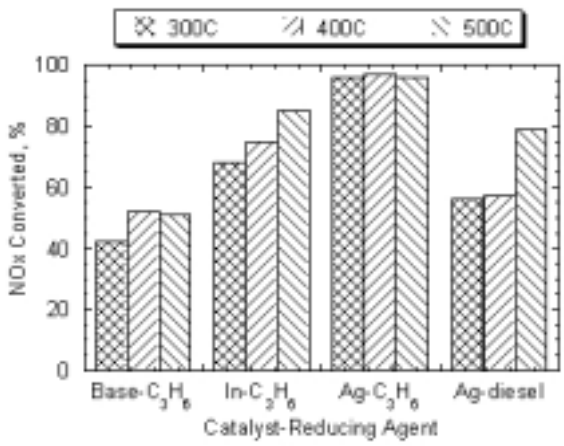

Figure 3. Engine Test Results for Other Catalyst-Reducing Agent Combinations

Another significant milestone was the completion of a steady-state engine test on a slipstream from a Caterpillar 3126B engine. We examined road load and high load engine exhaust with several catalyst-reducing agent combinations. We also tested 2 catalyst volumes to probe the effect of space velocity on activity. Figure 2 shows the results from the CRADA-developed γ-alumina catalyst with propylene as the reducing agent. Notice that activity drops dramatically with increased space velocity. Results are similar to results obtained on our bench system at PNNL. There is roughly a 10% reduction in activity on the engine slipstream compared to lab results on simulated exhaust. It is also evident that high load conditions are more difficult for the system to treat. This is due to the higher NO_x to hydrocarbon ratio when operating in that mode.

Figure 3 shows data for all catalyst-reducing agent combinations examined, operating at a space velocity of 10,000/hr. Propylene with Ag-doped γ-alumina showed the highest activity, which exceeded 95% over the entire temperature range examined. Also notable is the performance of Ag-doped γ-alumina with diesel fuel as the reducing agent, which resulted in NO_x reduction up to 75%.

Conclusion

A sulfur effects study has been completed which shows silver-doped γ-alumina to be a superior catalyst. NO_x reduction efficiencies above 95% have been obtained using catalysts developed under the CRADA. Primary alcohols appear to be the most suitable reducing agents for the γ-alumina PAC system. Steady-state engine tests show up to 95% conversion using monolithic catalysts at lower space velocity. Additional work is needed to enhance performance at higher space velocity.

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Patents

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IV. PARTICULATE CONTROL TECHNOLOGIES

A. Microwave-Regenerated Diesel Exhaust Particulate Filter Durability Testing

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Contractor: Industrial Ceramic Solutions, Oak Ridge, Tennessee
Prime Contract No.: 4000000723

Subcontractors: Microwave Materials Technologies, Inc., Knoxville, Tennessee; Transportation Research Center,East Liberty, Ohio

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

Barriers

B. PM Emissions

C. Cost

Tasks

5c. Microwave Regenerating Diesel Particulate Filter

Objectives

- Improve the heating uniformity and efficiency of the microwave field.
- Demonstrate 95% efficiency in the removal of exhaust particulate matter.
- Increase the strength and performance of the ceramic fiber filter media.
- Conduct on-road vehicle durability testing of the microwave filter system.

Approach

- Utilize computer finite-element modeling to improve the design of the microwave system.
- Perform a matrix of ceramic papermaking and binder addition tests to improve the strength and permeability of the ceramic fiber filter media.
- Validate the materials and microwave improvements in a 1.9-liter stationary diesel engine test cell.
- Install and road test the improved microwave filter system on 1.9-liter and 7.3-liter diesel vehicles.

Accomplishments

- Microwave field uniformity in the filter cartridge was improved from heating 10% of the filter to heating approximately 60% of the filter cartridge volume, which provides efficient regeneration.
- Ceramic fiber filter media burst strength was improved from one to six pounds per square inch, a 500% improvement in mechanical durability, exceeding the calculated strength requirement for diesel exhaust.
- A diesel exhaust particulate matter removal efficiency of greater than 95% was demonstrated on the stationary 1.9-liter engine test cell over the operating range of the engine.
- The microwave filter has been installed on a Ford F-250 7.3-liter diesel pickup, with an exhaust backpressure and temperature data acquisition system, for a 6,000-mile road test.
- The microwave filter system is fabricated and being installed on a 1.9-liter diesel Volkswagen Jetta for a 7,000 mile controlled test track evaluation, with periodic FTP cycle emission testing.

Future Directions

- Integrate the microwave filter PM control unit with NO_x, hydrocarbon, and CO emission devices to develop a total system approach to meet EPA Tier II emission regulations .
- Continue on-road durability testing to improve the filter system, precisely defining the operating cost and FTP cycle emissions performance.
- Enlist exhaust system, engine, and vehicle manufacturers in a product development effort to transfer the microwave filter system to future commercial applications.

Introduction

Current diesel engine particulate filter technologies depend on a catalyst to assist in the regeneration of the filter. Catalyst technology requires an exhaust temperature of approximately 350°C to be effective. Small diesel engines rarely achieve this exhaust temperature, except at high loads indicative of high speed vehicle operation. The microwave-regenerated particulate filter can achieve the required particulate removal efficiencies and regenerate at low exhaust temperatures. It is a potential answer to the low-temperature urban driving cycle where the catalyst technologies are ineffective. It may also be a solution to the cold-start issue that is responsible for a significant portion of both diesel and gasoline engine emissions. Other methods of heating the filter, such as electrical and fuel burners have been tried since the early 1980s, with limited success. The microwave filter technology is unique due to the discovery and use of a special silicon carbide fiber that efficiently converts microwave energy to heat energy. These fibers can achieve remarkably high temperatures of 1,200°C in 9 seconds in a standard household microwave oven. A process has been developed to incorporate this phenomenon into a filter cartridge and microwave regeneration system for use in diesel engine exhaust streams, as shown in Figure 1. This technology has

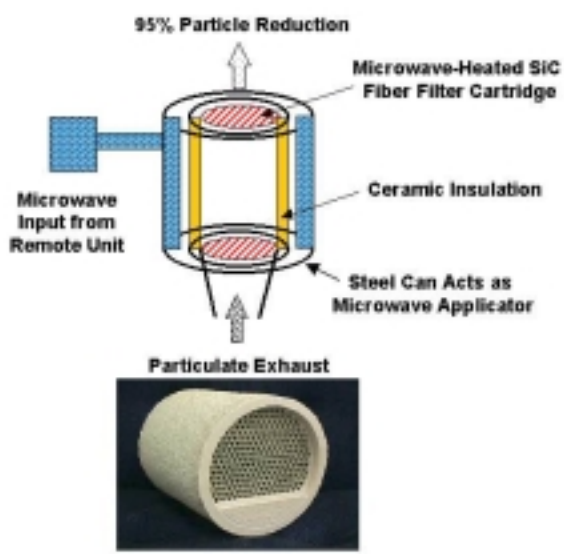

Figure 1. Microwave-Regenerated Diesel Exhaust Filter System

Figure 2. Ford F-250 7.3-Liter On-road Test Vehicle

Figure 3. Test Apparatus on the Exhaust of the Ford Truck

Figure 4. Volkswagen Jetta On-road Controlled Test Track Vehicle

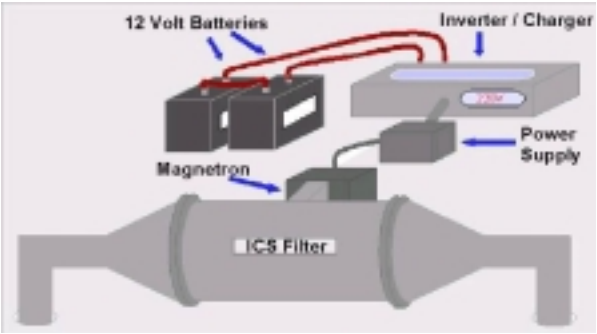

Figure 5. Schematic Diagram of the Volkswagen Microwave Filter System

been demonstrated in stationary diesel engine test cells at the Ford Motor Company, Oak Ridge National Laboratory and the University of Tennessee. The industry partners directed the FY 2001 efforts toward durability testing of the microwave filter system. On-road diesel vehicle testing has been selected as the most effective approach to verification of durability.

Approach

FY 2000 testing revealed that improvements in uniform microwave heating of the filter cartridge were necessary. Finite-element computer programs were used to model the microwave heating of the silicon carbide filter cartridge. The results of the computer modeling were used to refine the filter cartridge and microwave component configurations. A microwave engineering effort was conducted to reduce the size of the microwave source components. Calculations of the mechanical stresses on the filter cartridge by the diesel exhaust showed that the current 1.0 psi burst strength of the ceramic fiber filter media needed to be increased to at least 3.0 psi to survive the full-load operating conditions of a diesel engine. A three-month materials science experimental matrix program was conducted to increase the mechanical strength of the ceramic fiber filter media. This program addressed such variables as ceramic papermaking, binder addition techniques and furnace processing. The microwave and materials improvements were incorporated into an experimental prototype. This prototype system was tested on a 1.9-liter stationary diesel engine test cell at the Oak Ridge National Laboratory. With satisfactory results from these tests, the on-road diesel vehicle microwave filter system components were designed. Two vehicles were selected for on-road testing of the microwave filter system. Instrumentation was designed, fabricated and tested to continuously monitor the backpressure resulting from carbon particulate accumulation on the filter, the exhaust flow and the temperature of the exhaust, during vehicle operation. The instrumented filter exhaust systems were installed on a Ford F-250 7.3-liter diesel pickup (Figures 2 and 3) and a Volkswagen Jetta 1.9-liter diesel car provided by the U.S. DOE (Figures 4 and 5). The Ford truck is being tested under routine highway driving conditions for approximately 6,000 miles. The filter will be

removed and microwave-cleaned in the laboratory to understand the effects of microwave heating on the particulate loaded cartridge. The Volkswagen Jetta is being equipped with an on-board microwave regeneration system. This vehicle will be driven for 7,000 miles under controlled test track conditions by the Transportation Research Center near Columbus, OH. It will be subjected to FTP cycle chassis dynamometer emissions testing at periodic intervals. The data from both on-road tests will be used to improve the performance of the microwave-regenerated particulate filter, verify system durability, and precisely quantify the fuel penalty resulting from filter operation.

Results

The microwave field finite-element program analysis improved the heating efficiency of the filter cartridge from 10% of the filter volume in FY-2000 to over 60% in FY 2001. The mechanical strength of the ceramic fiber media, at the conclusion of the three-month experimental matrix optimization program, increased from 1.0 psi to 6.0 psi. Calculations have shown that 3.0 psi would be adequate for a typical diesel exhaust stream. Analysis of the materials matrix data shows that further improvements to 10 psi are attainable. The diesel engine manufacturers have insisted that 95% particulate matter destruction is necessary to comply with the U.S. EPA Tier II requirements. Stationary diesel 1.9-liter engine test cell data, using the FY 2001 microwave filter system improvements, demonstrated an average particulate removal efficiency of 97%, over a spectrum of normal engine operating conditions (Figure 6). Preliminary road testing of the filter on the Ford 7.3-liter truck proved that the filter could survive the full loading of 1,000 cubic feet per minute of exhaust flow without mechanical failure.

Conclusions

The microwave-regenerated filter was introduced to the DOE program in FY 1999. The technology has met or surpassed its milestone goals each year. The principal remaining question is the durability of the microwave filter system in on-road testing. The conclusion of the FY 2001 on-road diesel vehicle demonstrations will provide the answer to that question. Positive results will lead to

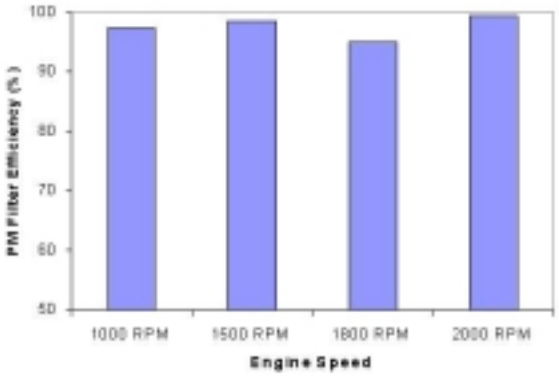

Figure 6. FY-2001 Particulate Removal Efficiency Data

product development partnerships with exhaust system suppliers, engine builders or vehicle manufacturers. These strategic partnerships are expected to move this technology to integration into a total commercial diesel exhaust emissions control system.

FY 2001 Publications/Presentations

1. J. Green, R. Nixdorf, J. Story, and R. Wagner, "*Microwave-Regenerated Diesel Exhaust Particulate Filter*", SAE Paper 2001-01-0903, Society of Automotive Engineers, Warrendale, PA.
2. R. Nixdorf, "Microwave-Regenerated Diesel Particulate Filter" presented at the Society of Automotive Engineers World Congress, March 5-8, Detroit, MI, 2001.
3. R. Nixdorf, "Microwave-Cleaned Ceramic Filter Using Silicon Carbide Fibers" presented at the American Filtration Society National Technical Conference, May 1-4, Tampa, FL, 2001.
4. J. Wainwright, R. Nixdorf, "Microwave-Regenerated Diesel Particulate Filter" presented at The University of Wisconsin Exhaust Aftertreatment Symposium, June 12-13, Madison, WI, 2001.

B. The Impact of Oxidation Catalysts on Diesel Engine Emissions

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Subcontractors: Coordinating Research Council, Inc., Alpharetta, GA; Southwest Research Institute, San Antonio

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

Barriers

B. PM Emissions

Tasks

5. Particulate Matter Control Device R&D
6. Prototype System Evaluations

Objectives

- Assess the impact of diesel oxidation catalysts (DOCs) in altering the particulate and gaseous emissions characteristics of a state-of-the-art light-duty diesel engine
- Test multiple DOCs to characterize engine-out and tailpipe diesel emission characteristics
- Evaluate an engine/oxidation catalyst technology combination that with appropriate particulate trap technology will meet Tier 2 emission standards, but only explore the effect of the DOC

Approach

- Task 1 - Catalyst Procurement. Catalyst suppliers will provide DOCs for evaluation. These catalysts will be close-coupled to the engine and at least three advanced catalysts will be obtained for the study.
- Task 2 - Catalyst Degreening and Stabilization. Each catalyst will be installed on a vehicle and then operated for 4,000 miles to achieve stable performance.
- Task 3 - Equipment Setup and Measurement Repeatability Verification. Theoretical analysis will be conducted to determine particle losses that may occur in the particulate sampling system for particle sizes ranging from 10 nanometers to 1 micron. Experimental loss analysis will also be performed in the micro-dilution tunnel using solid particle standards. Repeatability of all particulate and gaseous measurements will be determined in this task.
- Task 4 - Catalyst Evaluation with Low Sulfur Fuel. The contractor will evaluate three diesel oxidation catalysts using a light-duty 1999 Mercedes Benz C220 CDI vehicle equipped with a 2.2L OM611 CIDI engine. The contractor will operate the vehicle using a fuel expected to be representative of the 2007 federal specification. The fuel will be procured with a sulfur content of approximately 10 ppm. Test cycles will include three steady-state conditions, the FTP, and the US06 to achieve exhaust temperatures in the range of 150 ºC to 450 ºC.

- Task 5 - Chemical and Physical Characterization of Exhaust Emissions. Regulated gaseous emissions will be sampled and measured according to appropriate EPA protocols as identified in the CFR. In addition to dilute exhaust samples, second-by-second raw exhaust concentrations will be recorded upstream of the close-coupled catalyst to assure consistent operation of the vehicle. Concurrent with the collection of gaseous emissions, a variety of particulate samples will be collected for physical and chemical characterization. Total particulate mass, volatile organic fraction of particulate, sulfate fraction of particulate, trace metals and inorganic ash, elemental and organic carbon particulate content, poly-aromatic hydrocarbons (PAHs), nitro-PAHs, oxy-PAHs, PM2.5 mass fraction, PM10 mass fraction, and PM size distribution will each be measured for characterization of exhaust particulate matter upstream and downstream from the diesel oxidation catalyst. Speciation of gaseous emissions will also be determined including C1 to C4 species, C5-C12 species, benzene and toluene, and aldehydes and ketones upstream and downstream of the catalyst. SO_2 to SO_3 conversion over the catalyst will also be determined.
- Task 6 - Statistical Analysis. The experimental design for the project will be established to determine significant differences between engine-out and catalyst-out emission levels and characteristics for each test cycle using the test fuel.

Accomplishments

- Project coordinated with industry through the Coordinating Research Council (CRC)
- Final test fuel to target 2007 federal specification
- Experimental design has defined the number of replicates required for each test condition
- The Manufacturers of Emission Controls Association (MECA) agreed to provide test catalysts
- Test vehicle (Mercedes Benz C220 vehicle equipped with a 2.2L OM611 CIDI engine) procured for the project

Future Directions

- Conduct experimental testing in 2001
- Prepare final report in 2002

Introduction

CIDI engines are highly efficient and have been identified as a key technology to development of cars and light trucks with high fuel economy. They have advanced technology and typically include four valves per cylinder, common rail injection, and turbocharging. However, CIDI engines have a disadvantage of higher particulate emissions compared to gasoline engines. In addition, these particulates may contain unburned fuel species or products of combustion, which are undergoing scrutiny as potential air toxics. CIDI exhaust also contains gaseous hydrocarbon species that may be air toxics.

To reduce particulate emissions from diesel engines, emission control equipment manufacturers are developing several technologies, including particulate filters, catalytic traps, and oxidation catalysts. In addition, technologies employing plasma and microwave techniques are being explored. These technologies have the potential to not only reduce the particulate mass loading, but also to alter the other characteristics of the diesel exhaust. For example, an oxidation catalyst may be effective in oxidizing or reducing some of the gaseous organics in the exhaust or the liquid organic species deposited on the particulate. Therefore, these particulate control devices may beneficially alter the overall emissions characteristics of a CIDI vehicle.

Approach

This project is being conducted with collaborative funding and technical support from the Advanced Vehicle Fuel and Lubricant (AVFL) Committee of CRC. The project is designated as AVFL-3 at CRC -- see www.crcao.com. MECA is providing in-kind technical services and catalyst materials to support the work. NREL is coordinating specification and acquisition of the test fuel and selection of the catalysts in concert with other related DOE research projects. The experimental program will be conducted through a contract with SwRI in their Department of Emissions Research.

The detailed approach for accomplishing the project objectives is described in the corresponding section above. The emission sampling system used by SwRI is depicted in Figure 1. The test vehicle is illustrated in Figure 2.

Conclusions

At the time of this report the test program is about to start and no conclusions have been generated.

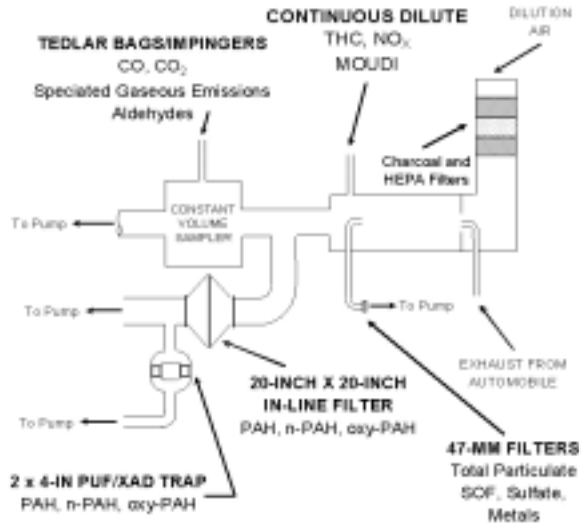

Figure 1. Sampling System for DOC Emissions Characterization

Figure 2. Mercedes Benz C220 Vehicle Equipped with a 2.2L OM611 CIDI Engine

C. Diesel Particle Scatterometer

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Contractor: Lawrence Berkeley National Laboratory
Contract No.: DE-AC03-76SF00098

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

Barriers

B. PM Emissions

Tasks

2. Sensors and Controls

Objectives

- Develop and use the Diesel Particle Scatterometer (DPS) for *real-time* diesel particle size and property measurements
- Study how particle characteristics change with operating conditions, dilution, engine type, fuel composition, and emission control system
- Extend DPS capabilities in time, sensitivity, and application
- Interpret optical properties of particles
- Commercialize instrument

Approach

- Measure angle-dependent polarized laser light scattering from diesel exhaust particles, including the scattering intensity (millisecond response) and two polarization transformations
- Model soot scattering as: spheres - Mie scattering theory to fit data; agglomerates - check validity using coupled dipole model of particle clusters
- Determine size distribution and the refractive and absorptive properties (n, k) of soot by comparing measured data with scattering modeled by the DPS

Accomplishments

- Received the Energy100 award in 2000 for DPS development, distinguishing this project as one of the 100 best scientific and technological accomplishments of the DOE in this century
- Developed strategy to improve instrument speed 50 to 100 fold

- Installed and tested non-spherical sensor (S22)
- Demonstrated enhanced size sensitivity with ultraviolet (UV) laser
- Explored effects of non-dense soot clusters on the DPS scattering model
- Contacted instrument companies to begin commercialization of the DPS

Future Directions

- Use the DPS to investigate effects on exhaust particles from engine type, operating conditions, dilution, and fuel
- Study performance of emission control devices and exhaust dilution effects
- Implement hardware and software improvements for high-speed operation
- Evaluate need for ultraviolet measurements
- Pursue tech transfer of the DPS to an instrument company

Introduction

The control of particulate emissions is critical to the wide spread acceptance of CIDI engines in the United States. To quantify the characteristics of diesel exhaust particulate matter requires new instrumentation that can provide *real-time* information on diesel particulates including their size distribution, composition and morphology. Existing instruments typically require collection or operate too slowly to monitor particle characteristics during transients. We are developing a new instrument, the Diesel Particle Scatterometer (DPS) for *real-time* diesel particle size and property measurements. We have designed, built and compared the DPS with other instruments and techniques for measuring diesel particulates. Presently we are operating two instruments, one at LBNL and one at ORNL.

Approach

The DPS is an optical instrument that measures the intensity and polarization of light scattered from a diesel exhaust stream. Three quantities (one dc and two ac signals) are measured by 13 detectors arrayed at angles around the exhaust stream. The signals are obtained by the synchronous detection of the polarized light that is modulated at a 50 kHz rate by the polarization modulator. The three angle-dependent signals are plotted on the computer monitor and are fit by Mie scattering calculations using a Levenburg-Marquardt optimization program. The results are plotted as a size distribution and the refractive and absorptive optical properties of the particles. The absorptive component of the index of refraction gives a measure of the graphitic carbon content of the exhaust particles. An important advantage of the instrument is its rapid response time; it has been tested at greater than 1 Hz data acquisition rate. This speed allows for the measurement of engine transients and even cylinder-to-cylinder variations.

Results

In the past two years we designed and built two DPS's for real-time diesel particle measurements and operated them at LBNL and ORNL. The instruments have been used to study the effects of operating conditions, dilution, fuel composition, EGR rates, and emission control system on particle characteristics. This year we have concentrated on extending the instrument capabilities and data interpretation.

CIDI engine designers have expressed the need for obtaining particle size and optical properties at high data rates to resolve transient diesel engine behavior. To investigate speeding up the instrument data rates we analyzed the high-speed DPS signals illustrated in Figure 1. Figure 2 illustrates the standard deviation in the data as a function of integration time. It can be seen that the standard deviation is only slightly more for very short

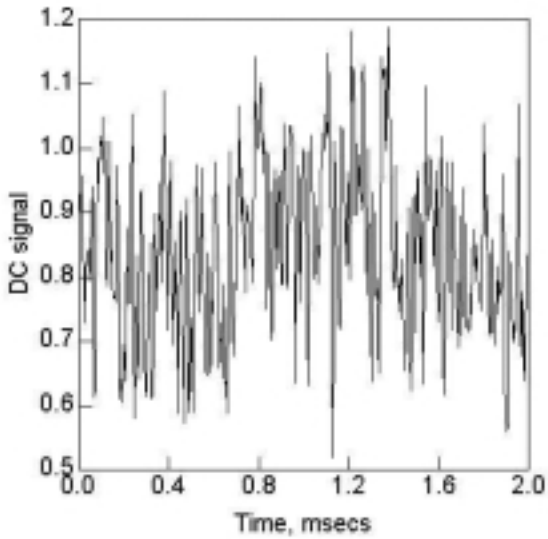

Figure 1: Time history of light intensity measured by one PMT. (Average of 100 points with a 0.4 millisecond time window).

integration times. This analysis indicates that data rates up to 60 Hz are possible with modifications to the DPS. Compared to the designed operating speed of about one Hz, these rates represent a very significant improvement. The hardware and software modifications to accomplish this task are underway.

The second area we studied involved investigating the robustness of DPS particle modeling if the particles were non-dense clusters of primary particles or not spherically symmetric. Literature values for soot refractive indices are not appropriate if the particles are not fully dense but instead are loose soot clusters. We studied the effect on the optical properties of soot particles by 'eroding' a sphere or ellipsoid by random removal of sub-elements to simulate particle clusters. The coupled dipole model was then used to predict the scattering from the clusters, and the results were averaged over all angles. Then the DPS Mie modeling program was used to calculate the effective optical constants of the particles. We determined several cogent facts from this study: the particle sizes predicted using the DPS software continued to give the correct particle size until more than 70% of the mass of the particle was removed, and the refractive and absorptive indices scaled linearly with the mass of the cluster. The

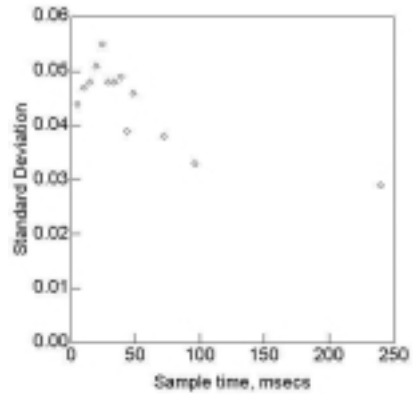

Figure 2: S_{12}-linear polarization analyzed with increasing time windows. Standard deviation of S_{12} values only falls from 0.044 to 0.030 for 50x increase in data record length.

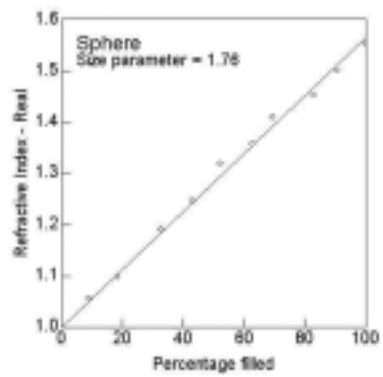

Figure 3a: The refractive index of the porous sphere obtained by a Mie-fit of coupled dipole simulations. At 100% refractive index is 1.55 + 0.53i - characteristic of graphitic soot. Real part of the refractive index falls linearly with density of soot particle.

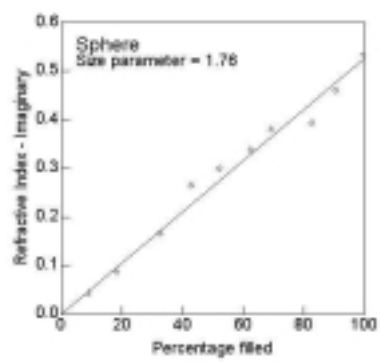

Figure 3b: Mie fits to coupled dipole simulations. The imaginary part of the refractive index is related to the light absorption and the carbon content of the particle falls linearly with the density of the soot particle.

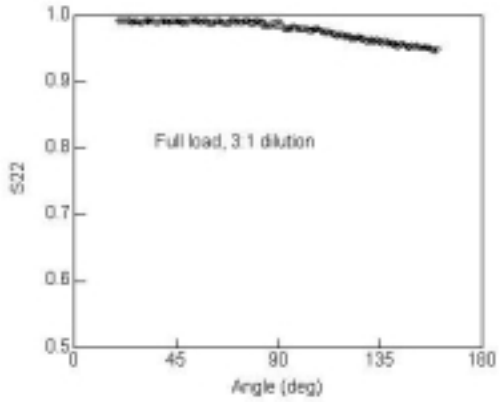

Figure 4: S22 for single cylinder engine. S22(θ)>0.9. Mie fit spherical assumption is valid.

results are shown in Figures 3a and 3b for a particle diameter of 130 nm with refractive index of 1.55 + 0.53i which is characteristic of graphitic soot. This confirms our supposition that the amount of elemental carbon can be predicted from the values of the absorptive part of the refractive index.

The issue of the response of the DPS to non-spherical diesel particles was also clarified this year. Numerical studies of non-spherical particles confirmed that if the normalized value of the S22 matrix element was above 0.9 at all angles, the assumption of spherical particles would be valid. Figure 4 illustrates that the value of S22 measured from diesel soot from our motor generator unit stays well above 0.9, indicating that the assumption of spherical symmetry is justified in modern diesel engines.

Conclusions

Substantial progress was made this year in both the hardware and the software of the DPS. In particular, we were able to show that we can increase the data acquisition speed of the DPS by about 50 times. We have verified that the indices of refraction of the diesel particles returned by the DPS are consistent with a model of a particle as a cluster of primary particles. Consequently, the diameter of the particles can be correctly predicted even when they are very porous, and the reported indices of refraction scale linearly with the density of the particles. With this and other advances in FY2001, the DPS is approaching the stage of development suitable for commercialization. Contacts with instrument companies will be renewed and it is anticiated that a suitable manufacturer will come forward to provide a commercial version of the DPS.

References/Publications

1. P. Hull, I.G. Shepherd and A.J. Hunt, "Modeling Light Scattering from Diesel Soot Particles," submitted to Applied Optics.
2. A.J. Hunt, I.G. Shepherd and J. Storey, "Diesel Particle Scatterometer," 2000 Annual Report Office of Advanced Automobile Technologies, Washington, DC.
3. A.J. Hunt, M.S. Quinby-Hunt, I.G. Shepherd, "Polarized Light Scattering for Diesel Exhaust Particulate Characterization," Proc. of the Diesel Engine Emissions Reduction Workshop, DOE/EE-0191 1999.
4. A.J. Hunt, M.S. Quinby-Hunt, I.G. Shepherd, "Diesel Exhaust Particle Characterization by Polarized Light Scattering," SAE Transactions 982629, LBNL-43695.
5. A.J. Hunt, I.G. Shepherd, M.S. Quinby-Hunt and J.M. Storey, "Size and Morphology Studies of Diesel Exhaust Particles using Polarized Light Scattering," 5th International Congress on Optical Particle Sizing, Minneapolis, MN Aug 10-13, 1998

D. Optical Diagnostic Development for Exhaust Particulate Matter Measurements

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

Barriers

B. PM Emissions

Tasks

2. Sensors and Controls

Objectives

- Develop real-time, engine-out particulate matter (PM) diagnostics for measuring size, number density and volume fraction.
- Transfer resulting technology to industry.

Approach

- Simultaneous measurements of laser-induced incandescence (LII) and laser elastic scattering (LES) will be used to obtain the following PM aggregate parameters using the Rayleigh-Debye-Gans polydisperse fractal aggregate (RDG-PFA) approximation:
  - particle volume fraction
  - diameter of primary particles
  - number density of primary particles
  - geometric mean of the number of primary particles per aggregate
  - geometric standard deviation of the number of primary particles per aggregate
  - mass fractal dimension
  - radius of gyration of the aggregated primary particles
- Laser-induced vaporization with Laser elastic scattering (LIVES) will be used to measure the soluble organic fraction (SOF) of the PM.
- A scanning mobility particle sizer (SMPS) will be used as the reference standard for particle size distributions.
- Off-the-shelf components are used to build a measurement system that can be easily duplicated by industry partners.
- Artium Technologies Inc., Los Altos Hills, CA will commercialize the resulting technology.

Accomplishments

- Real-time LII measurements of PM volume fraction have been obtained for engine startup/shutdown, EGR and throttle transients, and compared with scanning mobility particle sizer (SMPS) measurements.
- A collaborative investigation of the effects of EGR on PM was conducted with the Combustion Research Group at the National Research Council (NRC) of Canada.
- A Particulate Matter Collaboratory web page has been established as a part of the DOE Diesel Collaboratory Project. Initial members include Sandia and NRC.
- A phone-modem network connection has been established between Sandia's TDI diesel engine laboratory and Artium Technologies, Inc. for the development of a commercial LII instrument.

Future Directions

- Continue the collaboration with Artium toward commercialization of an LII system for PM measurements.
- Develop LIVES as a technique for distinguishing SOF from solid-phase carbon.
- Develop experimental and modeling capability for RDG-PFA approximation for aggregate characterization.
- Apply the LII-LES and LIVES techniques to diesel exhaust.

Introduction

LII is a well-established technique for the measurement of PM volume fraction and primary particle size; it has been applied to both stationary burner flames and diesel engine combustion. Light from a high-energy pulsed laser is used to quickly heat the PM to its vaporization point, resulting in gray-body radiation that is proportional to the PM volume fraction; the cooling rate of the PM following laser heating is a measure of primary particle size. Simultaneous measurement of LES from the particles at several discrete angles relative to the incident laser beam can be used to obtain additional information regarding the characteristics of PM aggregates using the RDG-PFA approximation.

The advantages of LII-LES over conventional PM measurement techniques are that it can be applied in any environment (e.g., hot or cold, undiluted or diluted, etc.), it responds in real time, and it is very sensitive to low PM concentrations (lower limit is estimated to be one part per trillion).

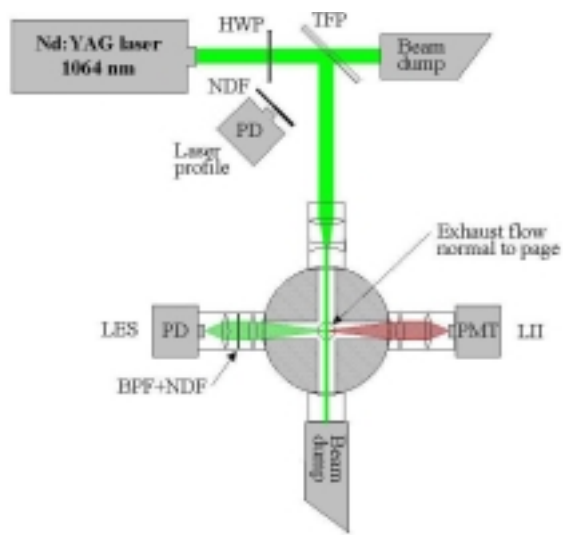

Figure 1. Schematic of the LII-LES Experimental Setup

Approach

A schematic of the LII-LES experimental setup is shown in Figure 1. The first harmonic output of a Nd:YAG laser at 1064 nm is used for excitation. The laser fluence is controlled using a half wave plate (HWP) and thin film polarizer (TFP). Three measurements are simultaneously obtained with fast photodetectors: 1) Incident temporal profile of the

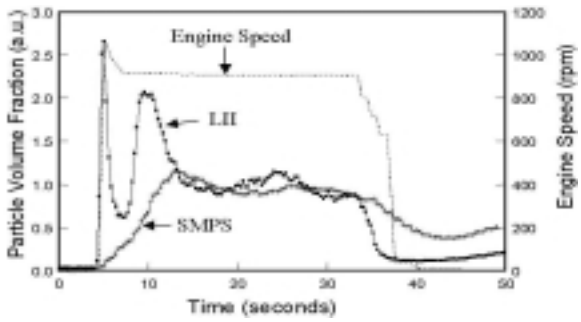

Figure 2. LII and Composite-SMPS Particle Volume-Fraction Measurements during Start/Stop Transient

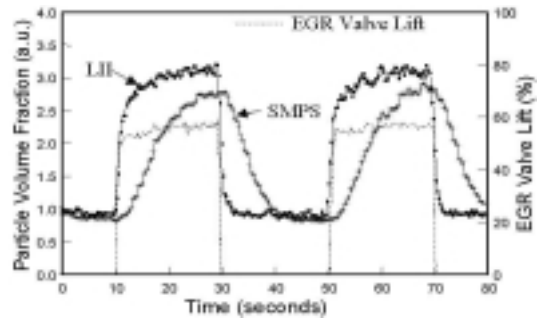

Figure 3. LII and Composite-SMPS Particle Volume-Fraction Measurements during EGR Transients

laser pulse, detected from diffuse scattering through a neutral density filter (NDF); 2) LII signal, detected with a photomultiplier tube with spectral response from 300-650 nm; 3) LES, detected through an NDF and an interference bandpass filter (BPF) centered at 1064 nm.

Results

To demonstrate the excellent temporal response of the LII technique, transient tests were performed for a cranking-start/idle/shutdown sequence and on/off cycling of EGR. Simultaneous measurements were also obtained with an SMPS operated in "fixed-size" mode for selected sizes of 30, 60, 90, 120, and 150 nm; these five measurements are ensemble-averaged to approximate the volume fraction. Shown in Figure 2 are the results for the startup/idle/shutdown sequence. We have scaled the LII and SMPS data so that the plateau regions of the two measurements have comparable magnitude. We believe this represents a fair comparison of the two techniques, and clearly shows the better temporal resolution of LII. This figure also reveals a large difference between the two measurements after engine shutdown. The most likely explanation for this behavior is condensation of volatile material because of colder gas temperatures - this affects only the SMPS measurements. The slight rise in the LII volume fraction in this region is most likely due to agglomeration of particles.

For the EGR transient, we ran the engine at 1200 rpm and alternated every 20 seconds between no EGR and approximately 80% EGR valve lift, as shown in Figure 3. The very rapid increase in the LII signal with EGR again illustrates its excellent temporal response, and suggests that the ensuing slower increase toward a constant level is most likely indicative of the actual EGR concentration in the cylinders. In contrast, the SMPS measurements are again seen to be slower to respond; the 10 seconds required to recover from shutting off the EGR would appear to be representative of the temporal response of the SMPS system.

Conclusions

Laser-induced incandescence has been shown to be a promising diagnostic for exhaust PM measurements. Its capability to follow rapid engine transients was demonstrated for several operating conditions. Compared to an SMPS operating in fixed-size mode, LII exhibits far better temporal response. In general, the performance characteristics of LII can be summarized as follows:

Advantages -

1. Signal amplitude is directly proportional to the carbon volume fraction, and the primary particle size can be determined from the signal decay rate.

2. Self-calibrating via the procedure developed by Snelling et al. (U.S. Patent 6,154,227).

3. High sensitivity, estimated to be on the order of a few parts/trillion.

4. Fast response, with submicrosecond measurement period.

5. Dilution and cooling of exhaust gas is not required.

6. Can be applied in situ or with continuous sampling.
7. Measures only the solid carbon content of PM.
8. When combined with LES, the aggregate size, area, and fractal dimension can be determined.

Disadvantages -

1. Window fouling must be avoided.
2. Directly measures only the solid carbon content of PM.
3. Real-time resolution is limited by laser repetition rate.
4. High energy, invisible laser beam is a safety hazard.

List of Publications

1. Witze, P. O., Hochgreb, S., Kayes, D., Michelsen, H. A., and Shaddix, C. R., "Time-Resolved Laser-Induced Incandescence and Laser Elastic Scattering Measurements in a Propane Diffusion Flame," A*pplied Optics* 40:2443-2452, 2001.
2. Witze, P. O., "Diagnostics for the Measurement of Particulate Matter Emissions from Reciprocating Engines," Proceedings of The Fifth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines (COMODIA 2001), Nagoya, Japan, July 1-4, 2001.
3. Witze, P. O., "Qualitative Laser-Induced Incandescence Measurements of Soot Emissions During Transient Operation of a Port Fuel-Injected Engine," Proceedings of The Fifth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines (COMODIA 2001), Nagoya, Japan, July 1-4, 2001.
4. Witze, P. O., "Qualitative Laser-Induced Incandescence Measurements of Soot Emissions During Transient Operation of a TDI Diesel Engine," SAE Paper to be published at the Fall Fuels & Lubricants Meeting, September, 2001.

List of Presentations

1. Witze, P. O., "Laser-Induced Incandescence and Laser Elastic-Scattering for Reciprocating Engine Particulate-Matter Measurements," DOE Diesel CRADA Meeting, Livermore, January 2001.
2. Witze, P. O., "Time-Resolved Laser-Induced Incandescence and Laser Elastic Scattering Measurements in a Propane Diffusion Flame," Joint Sections Meeting, The Combustion Institute, Oakland, March 2001.
3. Witze, P. O., "Qualitative Laser-Induced Incandescence Measurements of Soot Emissions During Transient Operation of a Port Fuel-Injected Engine," Joint Sections Meeting, The Combustion Institute, Oakland, March 2001.
4. Witze, P. O., "Laser-Induced Incandescence and Laser Elastic-Scattering for Particulate-Matter Measurements," OTT CIDI Annual Review, Oak Ridge, June 2001.
5. Witze, P. O., "Diagnostics for the Measurement of Particulate Matter Emissions from Reciprocating Engines," The Fifth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines (COMODIA 2001), Nagoya, Japan, July 2001.
6. Witze, P. O., "Qualitative Laser-Induced Incandescence Measurements of Soot Emissions During Transient Operation of a Port Fuel-Injected Engine," The Fifth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines (COMODIA 2001), Nagoya, Japan, July 2001.
7. Witze, P. O., "Qualitative Laser-Induced Incandescence Measurements of Soot Emissions During Transient Operation of a TDI Diesel Engine," SAE Fall Fuels & Lubricants Meeting, San Antonio, September 2001.

V. EXHAUST GAS RECIRCULATION FUNDAMENTALS

A. Extending the Exhaust Gas Recirculation Limits in CIDI Engines

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ORNL Technical Advisor: Brian West
(865) 946-1231, fax: (865) 946-1248, e-mail: westbh@ornl.gov

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

CRADA Partner: Ford Motor Company, Dearborn, MI
CRADA No. ORNL 95-0337

Ford Investigators: John Hoard, Lee Feldkamp, Tony Davis
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This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

A. NO_x Emissions

C. Cost

Tasks

2. Sensors and Controls

4d. Advanced NO_x Reducing Systems

Objectives

- Reduce engine-out NO_x emissions by approximately 50% with a minimal penalty for HC and PM emissions.
- Lower the performance requirements for post-combustion emission controls.

Approach

- Identify correlations between EGR operating and system parameters and combustion emissions.
- Evaluate correlations between existing engine sensors and pressure/emissions signals to develop a virtual HC/PM/NO_x sensor concept to detect combustion quality.

- Develop a low-order dynamic model that captures the relationship between EGR, combustion, and emissions.
- Exploit information from the virtual sensor and model to develop a dynamic EGR control concept (diagnostics and control logic that anticipates / detects emissions spikes and adjusts feedback to counteract).
- Develop a rapid sensing and feedback combustion diagnostic to optimize EGR utilization.

Accomplishments

- Performed in-depth analysis of data from FY 2000 EGR experiments on the 1.2-L, 4-cylinder Ford DIATA (Direct Injection, Aluminum, Through-bolt Assembly) diesel engine, and the 1.9-L, 4-cylinder Volkswagon TDI engine at ORNL.
- Identified on-line diagnostic that could be used to make cycle-resolved combustion quality measurements and provide active feedback.
- Identified three types of combustion variations that must be accounted for in diagnostic and control actions.
- Obtained GT Power combustion model and physically-based Ford Wiebe model.
- Commissioned Rapid Prototype Engine Control System (RPECS) from SwRI and re-engineered software and algorithms to allow full-pass control over all engine parameters of a Mercedes 1.7-L, turbocharged, 4-cylinder CIDI engine.

Future Directions (Beyond FY 2001)

- Investigate various fuel injection control strategies for potential feedback.
- Implement feedback control strategies to improve EGR utilization in a Mercedes 1.7-L, turbocharged, 4-cylinder CIDI engine.
- Develop correlation between emissions and existing engine sensors.

Introduction

This activity builds on previous collaborations between ORNL and Ford under a Cooperative Research And Development Agreement (CRADA #ORNL 95-0337). Under the original CRADA, the principal objective was to understand the fundamental causes of combustion instability in spark-ignition engines operating with lean fueling. The results of this earlier activity demonstrated that such combustion instabilities are dominated by the effects of residual gas remaining in each cylinder from one cycle to the next. A very simple, low-order model was developed that explained the observed combustion instability as a noisy, nonlinear, dynamic process. The model concept led to development of a real-time control strategy that could be employed to significantly reduce cyclic variations in production spark-ignition engines using existing sensors and engine control systems.

With funding from OAAT, the effort has progressed from examining combustion instabilities in spark-ignition engines to examining relationships between EGR, combustion, and emissions in CIDI engines. Information from CIDI engine experiments, data analysis, and modeling are being employed to develop an on-line combustion diagnostic (virtual sensor) to make cycle-resolved combustion quality assessments for active feedback control. Analysis and modeling of experimental data from a 1.9-L, 4-cylinder Volkswagen (VW) engine and a 1.2-L, 4-cylinder DIATA (Direct Injection, Aluminum, Through-bolt Assembly) engine have led to the development of an on-line combustion diagnostic for active feedback control near the practical EGR operating limit. Efforts for the remainder of the fiscal year will focus on conducting additional experiments with a Mercedes 1.7-L engine (see Figure 1), examining the robustness of the virtual

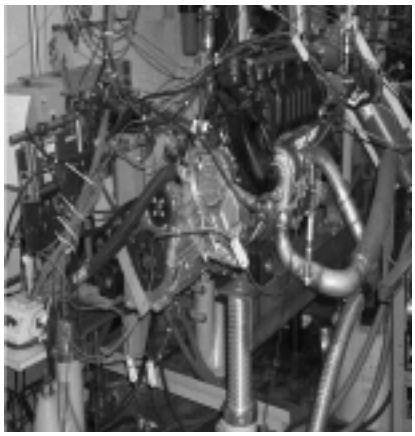

Figure 1. Mercedes 1.7-L, turbocharged, 4-cylinder, common rail engine.

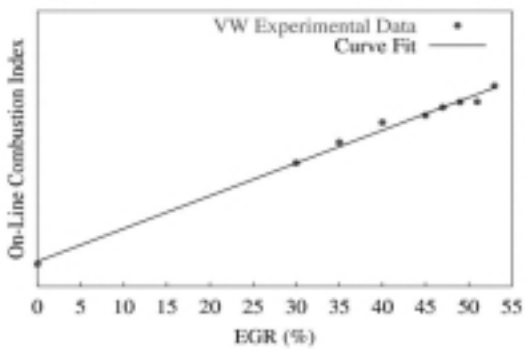

Figure 2. VW data analysis reveals a linear correlation between late-stage combustion and EGR. This information can be used to construct an on-line engine diagnostic or "virtual sensor".

sensor, evaluating the ability of the virtual sensor to detect cylinder-to-cylinder emissions variations, and using the virtual sensor to correlate cycle-to-cycle variations with emissions.

Approach

It is well documented that actual EGR utilization is typically less than optimal because of spikes in unburned hydrocarbons (HC) and particulate matter (PM) emissions during transients. The latter are often associated with cycle-to-cycle and cylinder-to-cylinder variations resulting as EGR rates are increased towards the critical threshold. ORNL is employing a combustion index that characterizes combustion quality on a cycle-by-cycle basis to provide active, real-time feedback for predictive control. Since the combustion index is derived from in-cylinder pressure measurements that detect

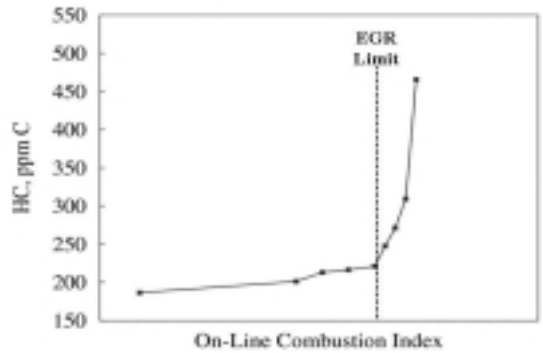

Figure 3. The mean value of the on-line combustion index can be used to develop correlations between combustion quality and emissions.

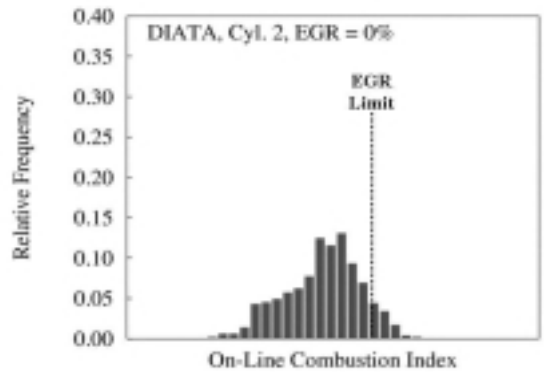

Figure 4. Probability histogram of cycle resolved values of the on-line combustion statistic for cylinder two of the DIATA at 0% EGR. Note that most of the data are to the left of the dotted EGR limit line, indicating an acceptable level of PM and HC emissions.

correlations between late-stage combustion and emissions, it can be used to detect unacceptable levels of HC and PM emissions at high EGR levels (see Figures 2 and 3). This information can then be used as an on-line diagnostic for EGR utilization (see Figures 4 and 5). More specifically, it can serve as a platform for detection of incipient emissions spikes and initiate the counteracting feedback (e.g., fuel injection modulation).

Results

In this year's effort, data from FY 2000 EGR experiments on the 1.2-L, 4-cylinder Ford DIATA diesel engine and FY 1999 EGR experiments on the 1.9-L, 4-cylinder VW TDI engine at ORNL were subjected to more rigorous combustion analysis. The

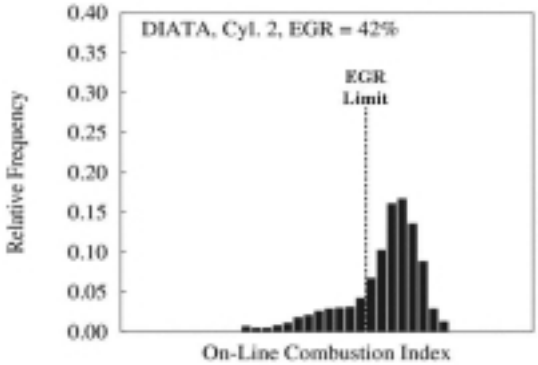

Figure 5. Probability histogram of cycle resolved values of the on-line combustion statistic for cylinder two of the DIATA at 42% EGR. Note that most of the data are to the right of the dotted EGR limit line, indicating an unacceptable level of PM and HC emissions.

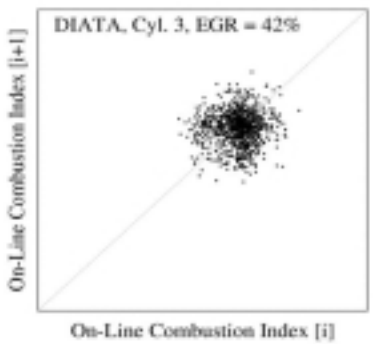

Figure 6. Return map of the on-line combustion index depicting cycle-to-cycle interactions for cylinder three of the DIATA at 42% EGR. The small amount of cyclic variability in the data suggests that this cylinder is producing an acceptable level of PM and HC emissions, even though the engine is operating at its EGR limit.

more rigorous data analysis led to the discovery of an on-line combustion index that can be employed to detect cycle-to-cycle variations in combustion quality. The in-depth analysis of the cyclic data led to identification of three principal forms of variation in combustion quality: cylinder-to-cylinder imbalances (Figures 6 and 7), drift under otherwise steady-state conditions (Figures 8 and 9), and cycle-to-cycle variations (Figures 10 and 11). Figures 6 and 7 use return maps of the on-line combustion index to depict cylinder-to-cylinder differences created by EGR mal-distribution which persist over long time scales. Also note the high level of

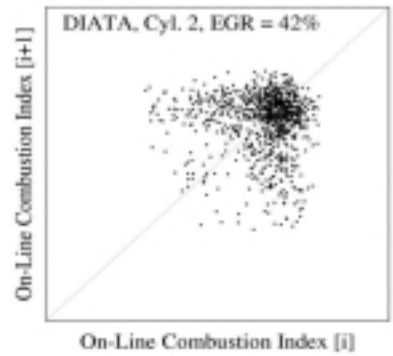

Figure 7. Return map of the on-line combustion index depicting cycle-to-cycle interactions for cylinder two of the DIATA at 42% EGR. The large amount of cyclic variability in the data suggests that this cylinder is producing a disproportionate level of PM and HC emissions, compared to cylinder three.

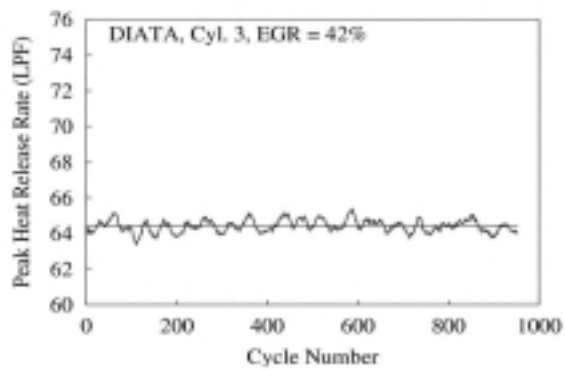

Figure 8. Low-pass filtered peak heat release rate data for cylinder three of the DIATA at 42% EGR. The data are fairly symmetric about the mean, suggesting that there are small variations in combustion quality and the PM and HC emissions.

variability in the return map of Figure 7, which suggests that cylinder two is contributing a disproportionate share of the unburned HC and PM emissions at this condition. In observing low-pass filtered peak heat release rate data over 1,000 consecutive cycles shown in Figures 8 and 9, variations among cylinders were also detected, with one cylinder behaving steadily and the other cylinder exhibiting a slow drift that persists over hundreds of cycles. This slow drift was more pronounced near the critical EGR limit for emissions. Additionally, in examining the influence of EGR on cycle-to-cycle combustion, some cylinders experience significant prior-cycle interactions. Figures 10 and 11 depict an

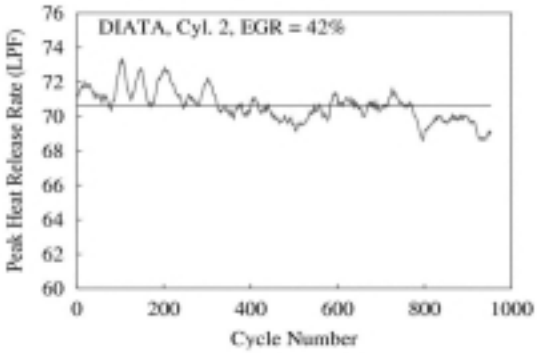

Figure 9. Low-pass filtered peak heat release rate data for cylinder two of the DIATA at 42% EGR. The data are not symmetric about the mean and exhibit a downward trend, suggesting that there are large variations in combustion quality and large spikes in the PM and HC emissions.

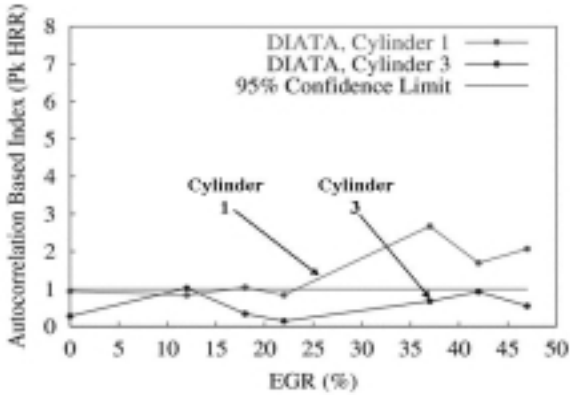

Figure 10. Illustration of cycle-to-cycle interactions for cylinders one and three of the DIATA as a function of EGR rate. Values above one indicate strong cycle-to-cycle interactions and unacceptable PM and HC emissions. Note that cylinder one exhibits strong cycle-to-cycle interactions near the EGR limit, while cylinder three does not.

autocorrelation-based index of peak heat release data as a function of EGR for the DIATA and VW experiments respectively. Near the EGR limit of both engines, significant cycle-to-cycle interactions develop, as the data from the index take on values greater than one. This information may be useful for making predictive cycle-by-cycle control actions.

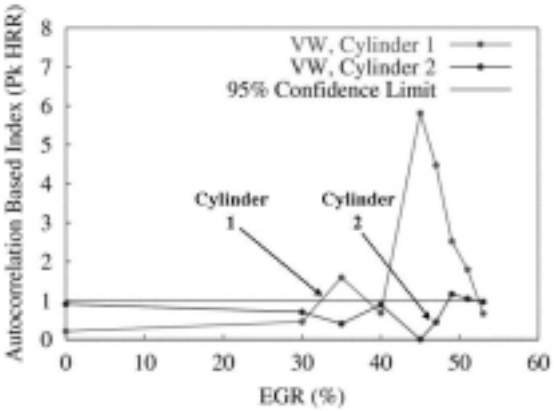

Figure 11. Illustration of cycle-to-cycle interactions for cylinders one and two of the VW as a function of EGR rate. Values above one indicate strong cycle-to-cycle interactions and unacceptable PM and HC emissions. Note that cylinder one exhibits strong cycle-to-cycle interactions near the EGR limit, while cylinder two does not.

Conclusions

The on-line combustion index offers insight into the variations in combustion quality near the EGR limit. This information can be exploited to develop a virtual sensor and a control logic that detects emissions spikes and makes counteractive feedback adjustments to extend the practical EGR limit in CIDI engines. During the investigation, three types of combustion variations were identified. These combustion variations must be accounted for in any diagnostic or control strategy.

Additional experiments with a Mercedes 1.7-L, turbocharged, 4-cylinder CIDI engine with full-pass control are planned. In advance of these plans, ORNL commissioned a Rapid Prototype Engine Control System (RPECS) from SwRI and began modifying its software and algorithms to emulate the Mercedes engine. To continue development of the virtual sensor concept, a series of experiments are designed to test robustness and evaluate the capability to detect cylinder-to-cylinder emissions variations. Under otherwise steady-state conditions, non-stationary heat release (or "drift") and combustion variability are observed at high EGR levels, with drift varying from cylinder to cylinder. Hence, the virtual sensor lends itself to investigation and identification of the source of this slow drift in

one or more cylinders. In addition, the expected development path includes looking at various fuel injection strategies for potential feedback control.

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3. Finney C.E.A., Green J.B. Jr., Daw C.S. (1998). "Symbolic time-series analysis of engine combustion measurements", SAE Paper No. 980624.
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7. Wagner R.M., Green J.B. Jr., Storey J.M., Daw C.S. (2000). "Extending exhaust gas recirculation limits in diesel engines", 2000 Annual Conference and Exposition of the Air & Waste Management Association (Salt Lake City, Utah USA; 2000 June 18 - 22), Paper 643.

FY 2001 Publications / Presentations

1. Wagner R.M., Daw C.S., Green J.B. Jr. (2001). "Characterizing lean spark ignition combustion instability in terms of a low-order map", Second Joint Meeting of the U.S. Sections of the Combustion Institute (Oakland, California USA; 2001 March 25-28).
2. Davis L.I. Jr., Feldkamp L.A., Hoard J.W., Yuan F., Connolly F.T., Daw C.S., Green J.B. Jr. (2001). "Controlling cyclic combustion variations in lean-fueled spark-ignition engines", SAE Paper No. 2001-01-0257.

Special Recognitions & Awards/Patents Issued

1. Davis L.I. Jr., Daw C.S., Feldkamp L.A., Hoard J.W., Yuan F., Connolly F.T. (1999). United States Patent Number 5,921,221, 1999.

B. Measuring the Cylinder-to-Cylinder Distribution of Recirculated Exhaust Gas during Transient Operation of a High-Speed, CIDI Diesel Engine

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Contractor: Sandia National Laboratories, Livermore, CA

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

Barriers

A. NO_x Emissions

Tasks

2a. Advanced Sensors and Controls

4d. Advanced NO_x Reducing Systems

Objectives

- Develop a non-intrusive, optical diagnostic to measure the cylinder-to-cylinder exhaust gas recirculation (EGR) distribution in production diesel engines during both steady-state and transient operation.
- Make the technology available to industry by performing measurements on development and/or prototype engines in industrial test cells.

Approach

- Apply the diagnostic to a production engine minimizing perturbations to basic engine geometry.
- Use infrared (IR) absorption spectroscopy to measure the CO_2 concentration in the flow within the intake manifold and/or entering the intake port of each cylinder.
- Set up data acquisition to allow measurements during both steady and transient operation.
- Acquire the data in a manner that is both crank-angle and cycle-sequence resolved.

Accomplishments

- An optical diagnostic based on CO_2-absorption spectroscopy has been developed to measure the cylinder-to-cylinder distribution of EGR.
- Refined steady-state and transient measurements in a Volkswagen 1.9L TDI engine have successfully demonstrated the credibility and capability of the diagnostic.
- Collaborations with three industry partners were developed to enable the measurement of EGR-distribution on development/prototype engines running in the partners' test cells.

- An optical probe was designed that allows the absorption measurements to be made with only single-point access to the intake system. In addition, the probe provides significant increase in the sensitivity and signal-to-noise characteristics of the data.

Future Directions

- In the next, and final phase of this project, we will use our optical diagnostic to perform EGR-distribution measurements on development and prototype engines in the test cells of our three industrial partners.

Introduction

The new generation of small-bore, high-speed, direct-injection diesel engines being developed for automotive applications is expected to use large amounts of EGR to control the emission of NO_x. Large quantities of EGR could result in mixing problems in the intake manifold and, ultimately, a poor cylinder-to-cylinder distribution of EGR. The problem is most likely exacerbated during transients in the operation of the engine. In order to make an accurate assessment of the cylinder-to-cylinder distribution of EGR during an engine transient, we have devised a non-intrusive, optical diagnostic technique which will allow the measurement of the cylinder-to-cylinder EGR distribution during engine transients.

Approach

The diagnostic we have developed is based on laser absorption spectroscopy of the CO_2 molecule, a primary component of the recirculated exhaust. An infrared diode laser provides light that is tuned to, and scanned through, an absorption transition of CO_2. The extremely narrow output bandwidth of this laser allows us to directly measure the absorption-line profile which is a function of the particular species, the concentration of that species, and the gas temperature and pressure. The measured absorption-line profiles are fit to a theoretical profile of the absorption spectrum to determine the average concentration of CO_2 in the optical path of the laser.

For measurements in the development/prototype V-8 and V-6 engines involved in our industrial collaborations, we designed a single-point-access probe. Using this probe, we are able to create an optical line-of-sight, requiring only a single opening, at the locations within the intake system where we want the measurements to be made. The laser light is transmitted through optical fibers to the probe, where it is directed to the optical path created within the probe - passing through the gas in the intake system where the concentration of EGR is being measured. The light exiting the optical path is then collected in another fiber, which transmits it to a detector.

Figures 1a & b. The 'single-point-access' absorption probe is designed to create an optical line-of-sight path in an enclosed flow field using only a single opening in the enclosure for optical access, while maintaining the gas-tight integrity of the enclosure.

The single-point-access probe is shown in Figure 1. The light exiting the laser-coupling fiber, which is connected to the probe, is collimated into a beam in the upper housing of the probe. The beam then passes through a gas-seal window into the lower housing of the probe which is located within the

Figure 2. The 'single-point-access' absorption probe is shown installed in an intake-flow channel.

manifold and through which the intake gas is flowing. The beam passes through the intake flow to a mirror (supported at the base of the lower housing) and back through the flow to the window. Back in the upper housing, it is launched into the detector-coupling fiber and transmitted to the detector. This double-pass characteristic of the single-point-access probe gives us a much longer optical path through the flow which, in turn, leads to an improved sensitivity and signal-to-noise ratio.

Status

All of our effort during the first part of FY01 has been devoted to the design and development of the optical access strategy and hardware that will allow the EGR diagnostic to be used on a "V"-style engine. This turned out to be a significant task, since it was necessary to achieve optical access in a situation where there are many engine components that limit the access to the intake manifold, in addition to the severe thermal and vibrational environments which are quite detrimental to the optical components we employ in our measurements. This effort has resulted in a solution that will overcome the problems described above and allow us to perform our measurements in the International, Ford and Cummins "V"-style engines.

The collaborative work at International Truck and Engine Corporation will involve EGR measurements made in the intake manifold of a V-8 Diesel engine. We will perform our experiments under both steady-state and transient conditions. The measurements will focus on the bank-to-bank EGR distribution, as well as the progress of the mixing of the EGR with the fresh charge of air as the intake flow proceeds along each bank of cylinders. Figure 2 illustrates the installation of the probe into the intake flow. Note from Figure 2 that only the upper housing of the probe, with the fibers connected, is visible; the lower housing is located in the flow passage with its opening aligned with the direction of the intake flow.

The collaborative work with Ford will be similar to the work carried out at International Engine Corporation, since the International V-8 manifold is very similar to the Ford V-6 manifold, allowing us to use the same probe for the measurements. The big difference between the engines is the space occupied by engine components located in the area above the intake manifold. On the V-6 engine, this equipment seriously hinders our ability to install the probe in the manifold and to attach the optical fibers to it. Ford is providing a solution to this problem by repositioning the offending engine components so we can access the intake manifold with our fibers and optical probe. Ford intends to accomplish this modification by raising these components a small distance above the manifold and extending the plumbing connections as necessary. This configuration should allow us easy access to the intake manifold.

Our collaboration with Cummins Engine Company will involve a V-8 engine that uses an intake manifold that is significantly different from those of International and Ford. This engine is configured in a manner that allows us easy access to the intake manifold, but the configuration of the manifold creates problems installing the same optical probe that we are using at International and Ford. We have solved this problem by designing an adapter that can be installed in the Cummins manifold that will allow us to install and utilize the probe without modifying it. This probe adapter is shown in Figure

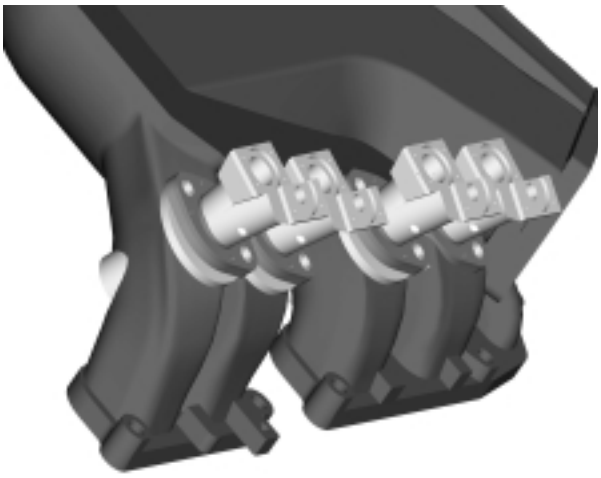

Figure 3. One bank of runners on the intake manifold of the Cummins V-8 engine. The probe adapter along with an installed probe is illustrated for each measurement location on this bank.

3; the measurement locations on one bank of runners of the intake-manifold are illustrated in the figure by the position of the adapters with the optical probe installed.

Summary

During the first phase of this project, we developed and demonstrated an optical diagnostic with a low detection limit and high precision that is capable of accurately measuring the cylinder-to-cylinder EGR distribution in a production engine, under both steady and transient operating conditions. The data acquired can be both crankangle-resolved and cycle-resolved during a sequence of cycles that define a transient in the engine operation. We are currently preparing to begin collaborative, experimental measurements on development/ prototype engines in test cells at International Truck and Engine Corporation, Ford Motor Company and Cummins Engine Company. For this work we have designed and fabricated a 'single-point-access' probe that is needed for measurements on the "V"-style engines that our collaboration partners are developing. Furthermore, we have set up a strategy to use the same probe on all the engines that we will study experimentally. This collaborative work will begin early in July and be completed by the end of the fiscal year.

Publications

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C. Corrosion Risk Assessment in a Diesel Engine Utilizing Exhaust Gas Recirculation

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

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

Barriers

A. NO_x Emissions

C. Cost

Tasks

2. Sensors and Controls
6. Prototype System Evaluations

Objective

- Assess the corrosion risk in a diesel engine utilizing exhaust gas recirculation (EGR) by constructing a boundary map of the corrosive effects of EGR as a function of engine operating mode, fuel sulfur level, and ambient conditions.

Approach

- Obtain and equip a heavy-duty diesel engine with an EGR system.
- Modify the EGR loop for in-situ coupon corrosion monitoring and sampling.
- Obtain corrosion probe for comparison.
- Monitor corrosion during engine operation.
- Evaluate the corrosion risk under potential conditions (EGR rate, fuel sulfur, ambient temperature and humidity, and engine operating mode).

Accomplishments

- Obtained and installed an EGR system on a Cummins 5.9 liter ISB diesel engine. The system also included a modified turbocharger, fuel pump, and fuel injectors.

- Conducted a preliminary study to determine the corrosion rate by measuring the mass loss on mild steel coupons placed at two locations in the EGR system.
- Quantified the mass loss due to corrosion.
- Identified the corrosion product iron sulfate.

Future Directions

- Procure sensitive corrosion probe.
- Monitor corrosion during engine operation including transients.
- Evaluate the corrosion risk under potential conditions (EGR rate, fuel sulfur, ambient temperature and humidity, and engine operating mode).

Introduction

In order to meet future NO_x emissions requirements, heavy-duty diesel engines are looking to utilize exhaust gas recirculation (EGR) technology as a means of lowering NO_x emissions. It has been shown that cooling the EGR will improve fuel economy and further lower emissions of NO_x. Recirculated exhaust gas is used in automotive engines as a diluent in the fuel-air mixture to reduce the peak combustion temperatures and thus reduce NO_x emissions. However, EGR can lead to accelerated corrosion and wear in the intake manifold and fouling in the EGR cooler. Within the intake manifold, ambient conditions (such as temperature and humidity) and coolant conditions are believed to play a critical role in the formation of highly corrosive acidic compounds, especially sulfuric acid. At a recent Heavy Vehicles Propulsion Materials Workshop hosted by the Oak Ridge National Laboratory, representatives of the diesel engine manufacturers articulated that corrosion/wear risk associated with EGR is a priority issue.

The objective of this project is to determine the boundary conditions of enhanced corrosion in an engine utilizing EGR. A particular concern is the formation of sulfuric acid caused by the reaction of water with recirculated sulfur compounds. The formation of sulfuric acid is essentially a three-step process. First, SO_2 is formed (during combustion) when sulfur present in the diesel fuel oxidizes. The SO_2 subsequently oxidizes to SO_3, the formation of which occurs more slowly than SO_2 formation. In the third step SO_3 reacts with moisture in the exhaust to form sulfuric acid, H_2SO_4. These stages can be represented by the following general reactions:

Stage 1: $S + O_2 \rightarrow SO_2$

Stage 2: $2SO_2 + O_2 \rightarrow 2SO_3$

Stage 3: $SO_3 + H_2O \rightarrow H_2SO_4$

Cooling of recirculated exhaust gas can allow sulfuric acid to condensate within the EGR loop and in the intake manifold, resulting in enhanced corrosion at these locations. A corrosion boundary map will be determined by controlling the ambient conditions at selected modes of engine operation. The corrosion risk will be assessed via electrical resistance corrosion probes (near real time) and coupon testing. By understanding the corrosion potential associated with EGR, boundary conditions on engine operation can be established to avoid enhanced corrosion.

Approach

Since very few, if any, heavy-duty diesel engines are currently equipped with EGR, it will be necessary to procure an appropriate diesel engine (5.9 liter Cummins ISB) to which a prototype EGR system developed by Cummins could be added. Included in this kit is a prototype electronic control module (ECM) containing a valve lift schedule developed by Cummins engineers to drive the EGR valve along with a valve control override for manual operation. The EGR system will be modified so that the corrosion potential can be measured downstream of the EGR cooler. Additionally, the intake manifold

will be modified to allow similar measurements to be made at that location as well. These sampling locations were selected based on diesel industry input and were chosen for two reasons: 1) the corrosion potential is considered relatively high at these two sites, and 2) the corrosion probe will be relatively unaffected by extreme temperature variations. A commercially available corrosion probe will be used to monitor corrosion activity over a period of engine operation (including transients). In addition, coupons will be placed in the test regions to elucidate corrosion chemistry and to provide benchmark comparison to probe data. The engine will be connected to a dynamometer in order to control engine speed and load.

Results

The diesel engine used for preliminary corrosion evaluations was a 5.9 Liter Cummins ISB. This engine is rated at 215 hp at 2300 rpm. Cummins Engine Company delivered a prototype EGR system for this engine that included a prototype ECM which automatically operated the EGR valve to minimize NO_x and particulate matter emissions (PM) over a range of operation. In order to achieve this optimization, the engine had to be derated to 175 hp. This was achieved by replacing the fuel injectors, fuel pump, and turbocharger with derated versions. The engine was coupled to a GE direct current motoring dynamometer to control load and speed.

Coupons were machined from mild carbon, cleaned, and weighed to 0.1 mg accuracy. A background scan of the surfaces was taken using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The specimens were mounted at the chiller exit in the EGR loop and in the intake entrance as shown in Figure 1. The engine was fueled with current specification diesel fuel (~350 ppm sulfur) and ran for four hours at a high rate of EGR. The temperature of the gas exiting the chiller was maintained at around 60°C to ensure condensation of sulfuric acid.

After four hours of exposure the coupons were removed and reweighed, and the surfaces were scanned using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The surface of an exposed coupon is shown in Figure 2. The surfaces of the specimens were relatively free of particulate

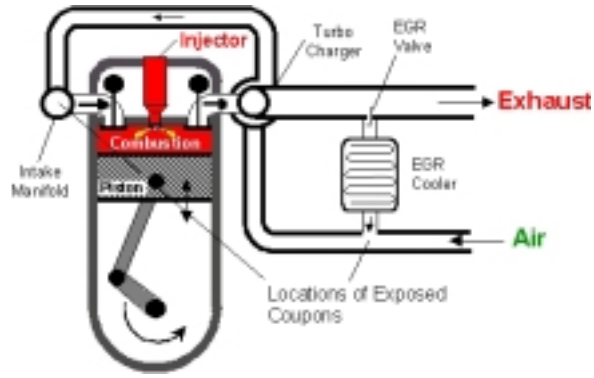

Figure 1. Schematic representation of the EGR system used in this study. The locations of the corrosion coupons are depicted in the circled regions.

Figure 2. Mild Steel Coupon Exposed for Four Hours near the Chiller Exit

matter but did appear to be slightly corroded. The corrosion rates were found to be low (around 10 to 20 mg/h at both the chiller exit and at the intake). This indicates that coupon measurements may not be the most efficient method of measuring corrosion rate during engine testing. DRIFT spectroscopic analysis (a typical scan is shown in Figure 3) revealed that the corrosion product iron sulfate was formed on the surfaces. The DRIFT spectroscopic analysis also observed that the surface chemistry of the specimen exposed in the intake differed from the specimen exposed near the chiller exit.

Conclusions

Preliminary studies have shown that the corrosion rates of exposed mild steel specimens are too low for this technique to be utilized in a reasonable

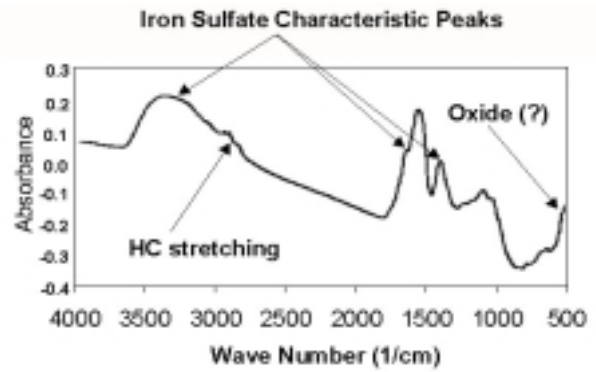

Figure 3. DRIFT Spectra of Exposed Coupon Surface Showing Peaks Corresponding to the Formation of Iron Sulfate

timeframe. A more sensitive corrosion probe is being procured which should allow near real-time measurements at exceptionally low corrosion rates. Another advantage is that the probe will enable measurements to be made during transient testing. The coupons did reveal that sulfuric acid had attacked the specimen surfaces, resulting in the formation of iron sulfate. Surface analysis also showed that the surface chemistry was different for the chiller exit and intake regions.

VI. CIDI COMBUSTION AND MODEL DEVELOPMENT

A. Swirl-Supported Diesel Combustion

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

Barriers

B. PM Emissions

C. Cost

Tasks

1a. Advanced Fuel Systems

3a. Identification of Advanced Combustion Systems

Objectives

- Provide the physical understanding of the in-cylinder combustion processes needed to meet future diesel engine emissions standards while retaining the inherent efficiency and low CO_2 emissions of the direct-injection diesel engine.
- Improve the multi-dimensional models employed in engine design and optimization and validate the model predictions against in-cylinder measurements and tailpipe emissions.

Approach

- Measurements of flow and thermophysical properties are obtained in an optically-accessible engine using laser-based measurement techniques.
- Engine performance, fuel economy, and emissions are measured in a traditional, non-optical test engine with the identical geometry.
- Optical and traditional test engine measurements are compared against model predictions, and the model is refined accordingly.

Accomplishments

- Acquired detailed velocity field measurements at an idle condition. These detailed measurements are the first ever to be obtained in a firing diesel engine.
- Measured engine-out emissions, fuel economy, and performance for varying levels of EGR, injection pressure, and nozzle hole geometry.

- Performed detailed velocity field comparison between the measured and modeled results. Demonstrated ability of the model to accurately predict large-scale flow structures, and identified model short-comings in predicting turbulent fluctuations. Identified previously unknown late-cycle production of turbulence and probable generation mechanism.
- Compared measured and predicted engine-out emissions with varying levels of EGR and injection pressure. Established ability of the model to predict major and minor trends in the emissions data.

Future Directions

- Further investigate the physical mechanisms responsible for in-cylinder turbulence generation, and establish the importance of these mechanisms at various loads and speeds. Implement and evaluate various alternative turbulence models.
- Extend engine-out emissions and performance measurements to include additional flow swirl levels and the use of pilot/split injection strategies. Investigate the ability of the model to follow changes in nozzle geometry, swirl, and injection shape.

Introduction

Direct-injection diesel engines have the highest fuel conversion efficiency of any reciprocating internal combustion engine technology, with concomitant low emissions of CO_2. This efficiency comes at the cost, however, of NO_x and particulate matter (PM) emissions which are high in relation to proposed future emission standards. Introduction of flow swirl in direct-injection diesel combustion systems is an established technique for reducing engine-out PM emissions and enabling reduced NO_x emissions by permitting injection timing retardation and increasing the combustion system EGR tolerance. In spite of their widespread use, the physics of these swirl-supported combustion systems is still poorly understood, and their optimization consists largely of guesswork and trial-and-error modifications. This work focuses on providing the physical understanding and the sophisticated modeling tools required to achieve the lowest possible engine-out emissions from swirl-supported diesel combustion systems, through an integrated approach combining measurement and modeling of the combustion and emissions formation processes.

Approach

A three-pronged approach is taken toward obtaining the required physical understanding and validated modeling capabilities: (1) detailed measurements of the flow and combustion processes are made in an optically-accessible laboratory test engine; (2) emissions, performance and fuel consumption measurements are made in a traditional single-cylinder test engine; and (3) computer simulations are performed and compared to the data obtained in both the optical and traditional test engines. Natural synergies emerge among these three areas. For example, the comparison of the computed and the experimental results serves to establish the validity of the various sub-models in the codes, to verify the ability of the codes to accurately predict global parameters such as emissions, and to assist in the interpretation of the experimental data. Similarly, traditional test engine measurements serve to identify interesting operating parameter trade-offs that bear further investigation either numerically or experimentally in the optical engine.

The optically-accessible diesel engine facility is depicted in Figure 1. This facility employs a slotted, extended piston assembly with a quartz combustion chamber that permits the progress of combustion to be visualized from below. In addition, the upper region of the cylinder liner is equipped with quartz windows that allow a lateral view of the combustion process to be obtained. This lateral view capability, in a configuration that maintains the faithful combustion chamber geometry, is a unique aspect of this facility. The engine bowl geometry, bore, stroke, and fuel injection equipment are typical of state-of-the-art direct-injection diesel engines for passenger

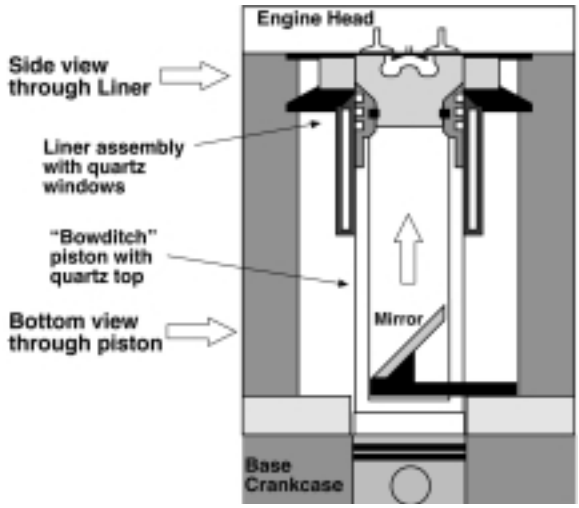

Figure 1. Schematic View of the Optical Engine Facility

car applications. Variable cylinder swirl levels can be achieved through throttling of one of the intake ports.

Results

Research performed in FY2001 in the optical engine focused on measurement of the in-cylinder velocity field using laser Doppler velocimetry. These measurements satisfy three separate objectives. First, the velocity field must be characterized to allow proper interpretation and to facilitate the understanding of the results of later experiments. Second, model predictions of the velocity field in diesel engines have not been adequately validated even under non-firing engine operation. There have been no previous attempts to evaluate the predictive abilities of the model for fired operation. Third, examination and interpretation of the measurements identifies certain aspects of the physics of swirling flows which are not captured by conventional models and thus cannot be discovered and studied computationally.

The first measurement objective is illustrated in Figure 2, where the measured radial profiles of the tangential mean and root mean square (RMS) velocity are shown. These profiles have been measured in order to provide supporting data for pilot injection studies. The pilot injection, occurring roughly 25 to 30 crank angle degrees (CAD) before the main injection, mixes with in-cylinder air and burns. The resulting pool of combustion products is convected by the mean flow and is subjected to

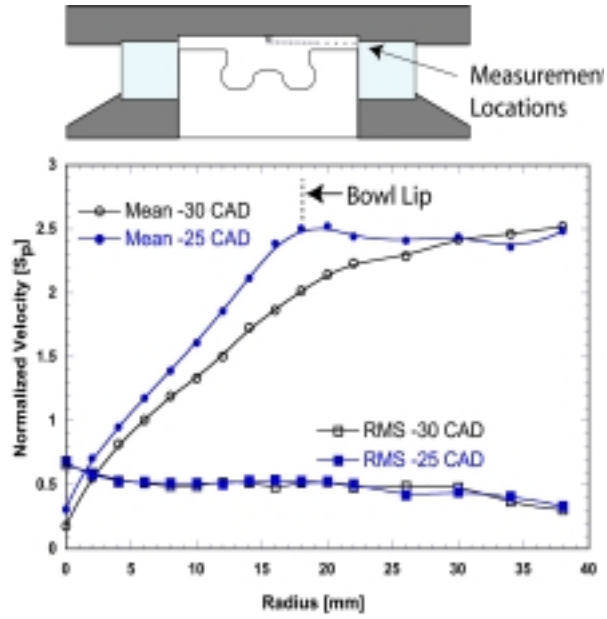

Figure 2. Mean and RMS Velocity Profiles at the Time of Pilot Injection, 25-30 CAD BTDC

turbulent diffusion during the time preceding the start of the main injection. Interpretation of planar images of gas temperature and combustion radical concentration, and ultimately an understanding of how the pilot injection influences the main injection ignition process, depends critically on a thorough characterization of the turbulent velocity field.

An illustration of the second objective is shown in Figure 3, where the measurements and the predictions of the axial profiles of the tangential and radial velocity profiles are compared during the latter stages of combustion. Close agreement in the mean velocity profiles is clearly observed; both the measurements and the model predictions demonstrate the existence of a large-scale rotating structure in the axial plane, which is more clearly seen in the full-field model predictions shown in Figure 4. This rotating structure is combustion induced; the non-fired measurements (indicated by the lighter arrows in the radial velocity profile of Figure 3) indicate only the existence of a reverse-squish-like fluid motion.

In contrast to the mean velocity profiles, the profiles of the RMS fluctuations show poor agreement with the model predictions. The experimental values exceed the measured values

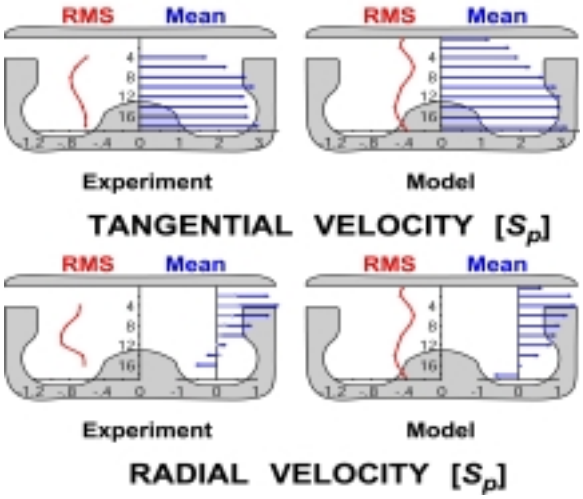

Figure 3. Comparison of measured and predicted axial profiles of the tangential and radial velocity components after combustion, at 21 CAD. The predicted RMS fluctuations are derived from the turbulent kinetic energy assuming isotropic turbulence. All velocities are presented normalized by the mean piston speed, S_p.

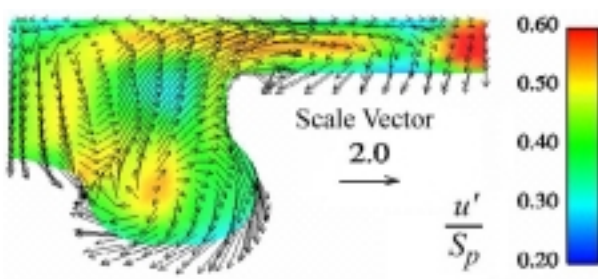

Figure 4. Full-field vector map illustrating the computed mean velocity field. The false-color background represents the predicted RMS fluctuating velocity.

over the full height of the combustion chamber, and particularly poor agreement is seen in the upper-central bowl regions. Because the mixing promoted by the turbulent fluctuations is extremely important to the PM oxidation process, the observed disparity is of profound technological importance.

The third measurement objective, identifying important aspects of the flow physics, is illustrated by analyzing the possible sources of the increased late-cycle RMS fluctuations seen in Figure 3. The analysis indicates that the source is likely due to the unusual, free-vortex-like radial profile of tangential velocity which develops within the piston bowl, as

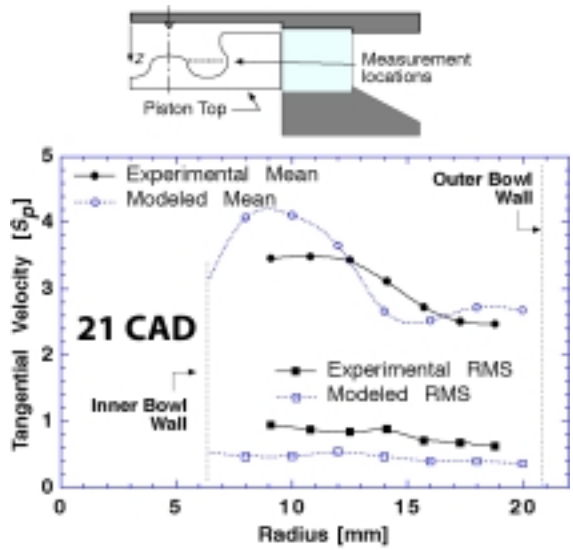

Figure 5. Comparison of the measured and predicted radial profiles of the mean and RMS tangential velocities within the bowl at 21 CAD. The mean velocity profile, which features large tangential velocities at the inner radii, is a likely source of enhanced late-cycle turbulence.

seen in Figure 5. Such a profile can lead to enhanced turbulence production, beyond the usual shear production, due to the centrifugal forces acting on a fluid element in a rotating flow. Standard models of engine turbulence do not capture this additional turbulence production, though the model also predicts the free-vortex-like mean flow structure.

In a parallel research effort, model predictions for varying EGR rates and injection pressure were compared to engine-out emissions measurements that were obtained at WSU. The results of this comparison are shown in Figure 6. The comparison is currently semi-quantitative, as the measured soot (PM) is characterized in terms of Bosch smoke units rather than mass units. The trends of decreasing NO_x and increasing soot as EGR is increased are clearly seen by the model. Moreover, some lesser, secondary trends are also well predicted. For example, the decreasing sensitivity of NO_x emissions to increased injection pressure is also captured, as is the diminishing returns of increased injection pressure beyond approximately 800 bar, especially at high EGR rates.

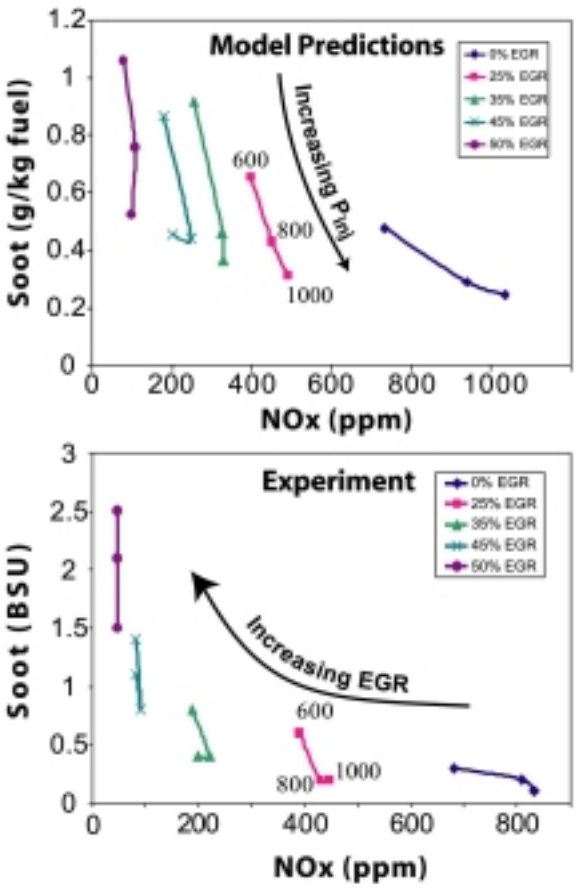

Figure 6. The Variation of Measured and Modeled Engine-out Emissions as EGR Rate and Injection Pressure Are Varied

Conclusions

Measurements of the in-cylinder velocity field have satisfied the objectives of: 1) characterizing the velocity field to support interpretation of future experiments, 2) allowing validation of model predictions under fired engine operation, and 3) identifying important aspects of the flow physics that are technologically significant and that are not captured by the model. Future work will continue to clarify the sources of the disparities seen between the measurements and predictions and will evaluate the performance of improved flow turbulence models.

Comparison of measured and predicted engine emissions and performance measurements has demonstrated the ability of the model to predict the trends in NO_x and PM emissions as the EGR rate and injection pressure are varied. Future work will involve direct measurement of particulate mass and evaluation of the model predictions as nozzle geometry, swirl, and injection rate shape are varied.

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B. Effects of Injector and In-cylinder Conditions on Soot Formation in Diesel Sprays

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

Barriers

B. PM Emissions

C. Cost

Tasks

1a. Advanced Fuel Systems

3a. Identification of Advanced Combustion Systems

Objectives

- Investigate the effects of engine and injector parameters on soot formation in direct-injection (DI) diesel sprays:
  - Determine the effects of engine and injector conditions on DI diesel spray lift-off length.
  - Determine if there is a link between the fuel-air premixing that occurs upstream of the lift-off length and soot formation in a DI diesel spray.
  - Develop planar laser induced incandescence and line-of-sight extinction techniques for measuring soot concentrations in a diesel fuel jet.
  - Provide a database on lift-off length and soot in diesel sprays for validating the multidimensional, computational models being developed for diesel engine design and optimization.

Approach

- Utilize advanced optical diagnostics coupled with a unique optically-accessible diesel combustion simulation facility to conduct the investigations.
  - Simultaneously measure flame lift-off length using hydroxyl radical (OH) chemiluminescence (a marker of high temperature combustion) and the total soot incandescence for DI diesel sprays.
  - Use planar laser induced incandescence and line-of-sight extinction techniques to measure soot distributions in diesel sprays.
  - Conduct experiments over a wide range of conditions, including those in current, as well as proposed advanced diesel engines.

Accomplishments

- Completed a comprehensive database on the effects of in-cylinder and injector conditions on the lift-off length on diesel sprays.
- Showed that there is a strong link between soot formation in diesel spray and the fuel-air premixing that occurs upstream of the lift-off length. Understanding this link will be instrumental in interpreting soot measurements currently being made.
- Setup planar laser induced incandescence and line-of-sight extinction techniques for measuring soot volume fraction in DI diesel sprays.
- Initiated detailed measurements of soot volume fractions in DI diesel sprays to investigate the effects of injector and in-cylinder conditions on soot.
- Showed how changes in engine and injector parameters made to meet emissions regulations have changed the diesel combustion process. Results are providing insight on how future changes in these parameters will affect the diesel combustion and emission processes.

Future Directions

- Complete detailed measurements of the effects of in-cylinder engine and injector conditions (including EGR) on soot formation in the near injector region of a diesel spray.
- Investigate wall impingement effects on the evolution of soot in diesel sprays.
- Investigate injection rate modulation effects on diesel combustion and emission processes.
- Investigate orifice geometry effects on diesel combustion and emission processes.

Introduction

Improving our understanding of in-cylinder combustion and emission formation processes in diesel engines is critical to developing advanced diesel engines with lower engine-out emissions. There is growing evidence to suggest that soot formation in diesel sprays is affected by flame lift-off, making the lift-off length on a diesel spray of significant practical importance to diesel engines. (The lift-off length is the distance from the injector tip to the initial flame location on a DI diesel spray.) Fuel and air are allowed to be premixed to some degree in the region of the spray upstream of the lift-off length. The fuel premixed with air upstream of the lift-off location reacts in a fuel rich combustion zone just downstream of the lift-off length. The product gases of this rich reaction zone are ideal for forming soot. Measurements have shown that small soot particles begin forming in these product gases, then grow as the gases are transported downstream.

The goal of this research is to investigate the soot formation process in DI diesel sprays downstream of the lift-off length and determine how various engine and injector parameters affect this process. The first phase of this research was to determine the effects of injector and engine conditions on the lift-off length of a DI diesel spray. This phase of the investigation was completed this year. The lift-off length data will be essential for understanding and interpreting the detailed soot concentration measurements that are currently being made downstream of the lift-off length as part of the next phase of the soot formation research. Previously, there was virtually no understanding of the role that flame lift-off plays in DI diesel combustion and emissions formation processes.

Approach

The research was performed in the Diesel Combustion Simulation Facility (DCSF) using an electronically controlled, common-rail diesel fuel injector. The range of conditions that can be covered in this facility is unique in the world. They include conditions in current and proposed advanced diesel engines. Figure 1 shows a picture of the DCSF.

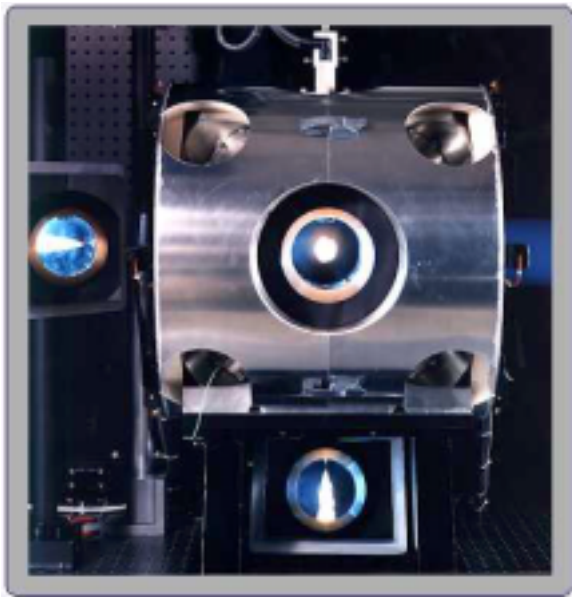

Figure 1. Photograph of the Combustion Vessel in Operation (view from the crankcase; fuel spray images shown at left and bottom)

Parameters varied in the investigation included: injection pressure, orifice diameter, and ambient gas temperature, density and oxygen concentration. A reduction in the ambient gas oxygen concentration is a primary effect of EGR in an engine. The fuel used for all experiments was a #2 diesel fuel.

An OH chemiluminescence imaging technique was developed for measuring the flame lift-off length on DI diesel sprays [Higgins and Siebers, 2001]. Total soot incandescence measurements were made with a photodiode to examine the link between lift-off and soot formation. Detailed soot volume fraction measurements, recently initiated, are being made with laser induced incandescence and line-of-sight extinction techniques.

Results

The initial phase of the research was to develop an understanding of the role that lift-off length plays in soot formation [Siebers and Higgins, 2001]. The lift-off length data acquired with the OH chemiluminescence imaging technique developed for measuring lift-off provided the first comprehensive database on lift-off length on diesel sprays [Siebers and Higgins, 2000, 2001]. Figure 2 shows an example set of lift-off length data acquired for an injection pressure drop across the injector orifice of

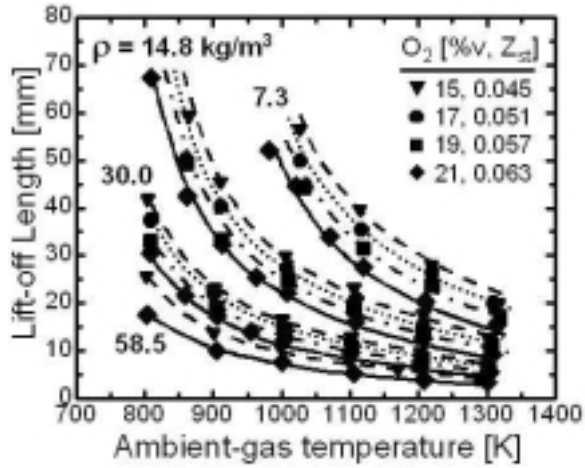

Figure 2. Lift-off Length Versus Ambient Gas Temperature for Four Ambient Gas Densities and Four Ambient Gas Oxygen Concentrations

140 MPa and an orifice diameter of 180 μm. Data are shown for ambient temperatures from 800 K to 1300 K, ambient densities from 7.3 kg/m^3 to 58.5 kg/m^3, and ambient oxygen concentrations from 15% to 21%. An oxygen concentration of 15% represents 40% EGR at a high load condition.

The general trends noted in Figure 2 are a decrease in lift-off length with either increasing ambient temperature or density, and an increase in lift-off length with decreasing oxygen concentration. The trend with respect to temperature is caused by an increase in flame speed with temperature that allows the flame on a spray to stabilize closer to the injector. The trend with respect to density is caused by the effects of density on both the overall spray development and the flame speed. The effect of oxygen concentration is caused by a decrease in flame speed with decreasing oxygen concentration, which results in the flame stabilizing further from the injector.

Increasing injection pressure was found to increase the lift-off length. The injection pressure effect was caused by increasing injection velocities that pushed the flame further from the orifice. When plotted in terms of injection velocity, the lift-off length was found to increase linearly with increasing injection velocity. The linear dependence on injection velocity is the same dependence noted for atmospheric pressure gas jets.

With respect to orifice diameter, lift-off length was found to decrease with decreasing orifice diameter. This trend differs from that noted for atmospheric pressure gas jets. The lift-off length on an atmospheric pressure gas jet has been found to be independent of orifice diameter. The difference is believed to be caused by fuel vaporization processes in diesel sprays.

Estimates of the amount of fuel-air premixing upstream of the lift-off length (*i.e.*, prior to any combustion) were made based on the scaling of diesel sprays developed through past research in the DCSF [Siebers, 1998 and 1999; Naber and Siebers, 1996]. The estimates are given in terms of the percent of stoichiometric air [Siebers and Higgins, 2000, 2001]. The percent of stoichiometric air is a measure of the amount of air entrained into the spray upstream of the lift-off length relative to the amount of fuel injected. The results show that temperature, orifice diameter, and injection pressure have strong effects on the percent of stoichiometric air entrained upstream of the lift-off length. However, ambient gas density and ambient gas oxygen concentration were found to have little effect on the amount of air (*i.e.*, oxygen) entrained relative to the amount of fuel injected. The results imply that temperature changes associated with changes in EGR, compression ratio, intake pressure boosting, intercooling will have strong effects on the amount of fuel air premixing upstream of the lift-off length, while changes in ambient gas density will not. The results also indicate that oxygen concentration changes with EGR changes will not affect the amount of oxygen entrained upstream of the lift-off length relative to the amount of fuel injected, although the fuel-air mixture at the lift-off length will be more dilute as a result of EGR.

The soot incandescence measurements made to explore the link between soot formation and fuel-air premixing upstream of the lift-off length are shown in Figure 3. The soot incandescence measurements provide a relative measure of the total amount of soot formed. In Figure 3, the total soot incandescence data is normalized by the fuel flow rate and plotted versus the percent of stoichiometric air estimated from each simultaneously measured lift-off length. Data are shown for ambient gas densities from 7.3 to 58.5 kg/m^3, ambient gas temperatures from 800 to

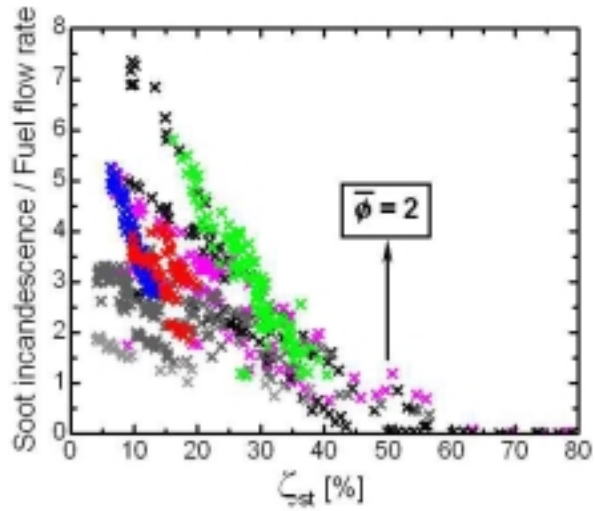

Figure 3. The relative total soot incandescence (normalized by the fuel flow rate) versus the percent of stoichiometric air entrained upstream of the lift-off length. (Each data point represents an individual injection.)

1300 K, injection pressures from 40 to 190 MPa, and orifice diameters from 100 to 363 μm. The data shows a dominant trend that as the air entrainment upstream of the lift-off length increases, the soot incandescence (*i.e.*, the amount of soot formed) decreases and approaches zero when the percent of stoichiometric air entrainment reaches approximately 50%. The disappearance of soot incandescence when the percent of stoichiometric air entrainment equals 50% (which corresponds to an average equivalence ratio of two) agrees with studies of soot formation under premixed conditions, showing that typical hydrocarbon fuels do not produce soot for equivalence ratios less than two. The overall trend in Figure 3 shows a strong link between fuel-air premixing upstream of the lift-off length and soot formation in diesel sprays.

Conclusions

The lift-off length measurements completed over the past year provide the first comprehensive data base on the lift-off phenomena related to DI diesel fuel sprays. The results show that air entrainment upstream of the lift-off length will vary with conditions, and thus alter all remaining combustion and emission formation processes downstream of the flame lift-off location. Soot formation was shown to be strongly linked to the amount of fuel-air

premixing that occurs upstream of the lift-off length (see Figure 3). Understanding the relationship between fuel-air mixing upstream of the lift-off length and soot formation is proving critical for interpreting the detailed measurements of the effects on injection pressure, orifice diameter, ambient gas conditions (temperature and density), and EGR on soot formation in diesel sprays currently being made with laser induced incandescence and line-of-sight extinction techniques.

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1. D. Siebers and B. Higgens, "Flame Lift-Off on Direct-Injection Diesel Sprays Under Quiescent Conditions," Paper No. 2000-01-0530, SAE International Congress, Detroit, MI, March, 2001.
2. B. Higgens and D. Siebers, "Measurement of the Flame Lift-Off Location on DI Diesel Sprays Using OH Chemiluminescence," Paper No. 2001-01-0918, SAE International Congress, Detroit, MI, March, 2001.
3. D. Siebers and B. Higgens, "Effects of Injector Conditions on the Flame Lift-Off Length of DI Diesel Sprays," accepted for Thiesel 2000, Conference on Thermofluidynamic Processes in Diesel Engines, Valencia, Spain, September, 2000.
4. D. Siebers, "Scaling Liquid-Phase Fuel Penetration in Diesel Sprays Based on Mixing-Limited Vaporization," Paper No. 1999-01-0528, SAE International Congress, Detroit, MI, February, 1999.
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Publications

1. L. Pickett and D. L. Siebers, "Orifice Diameter Effects on Diesel Fuel Jet Flame Structure," Submitted to the Internal Combustion Engine Division of the ASME 2001 Fall Technical Conference, Chicago, IL, September, 2001.
2. P. J. O'Rourke, D. L. Siebers and S. Subramaniam, "Some Implications of a Mixing-Controlled Vaporization Model for Multidimensional Modeling of Diesel Sprays," *Submitted to* Atomization and Sprays, March, 2001.
3. D. L. Siebers and B. Higgens, "Flame Lift-Off on Direct-Injection Diesel Sprays Under Quiescent Conditions," Paper No. 2000-01-0530, SAE International Congress, Detroit, MI, March, 2001.
4. B. Higgens and D. L. Siebers, "Measurement of the Flame Lift-Off Location on DI Diesel Sprays Using OH Chemiluminescence," Paper No. 2001-01-0918, SAE International Congress, Detroit, MI, March, 2001.
5. D. L. Siebers and B. Higgens, "Effects of Injector Conditions on the Flame Lift-Off Length of DI Diesel Sprays," Accepted for publication in Thiesel 2000, Springer-Verlag, Heidelberg, Germany, April, 2001.
6. L. Pickett and D. L. Siebers, "Effect of Orifice Diameter on the Structure of Diesel Spray Flames," *2nd Joint Meeting of the U.S. Sections of the Combustion Institute*, Oakland, CA, March, 2001.

Presentations

1. D. Siebers, "Progress on DI Diesel Spray Soot Investigations," Diesel Combustion/Alternative Fuels CRADA Meeting, University of Wisconsin, Madison, WI, June, 2001.
2. D. Siebers, "Diesel Combustion Cross-Cut Research," CIDI Combustion, Emission Control & Fuels R&D Laboratory Merit Review & Peer Evaluation, Oak Ridge National Laboratory, Oak Ridge, TN, June, 2001.
3. L. Pickett and D. Siebers, "Effect of Orifice Diameter on the Structure of Diesel Spray Flames," *2nd Joint Meeting of the U.S. Sections of the Combustion Institute*, Oakland, CA, March, 2001.
4. D. Siebers, "Effects of Engine and Injector Conditions on Soot Formation in Diesel Sprays," OAAT Mid-Year Review, Sandia National Laboratories, Livermore, CA, March, 2001.

5. D. Siebers, "Flame Lift-Off on Direct-Injection Diesel Sprays Under Quiescent Conditions," Paper No. 2000-01-0530, SAE International Congress, Detroit, MI, March, 2001.
6. D. Siebers, "Progress on DI Diesel Spray Flame Lift-Off / Soot Investigations," Diesel Combustion/Alternative Fuels CRADA Meeting, Sandia National Labs, Livermore, CA, January, 2001.
7. D. Siebers, "Flame Lift-Off (*i.e.*, Fuel-Air Premixing) in DI Diesel Sprays," Diesel Combustion/Alternative Fuels CRADA Meeting, USCAR, Detroit, MI, October, 2000.
8. D. Siebers, "Effects of Injector Conditions on the Flame Lift-Off Length of DI Diesel Sprays," Thiesel 2000, Conference on Thermofluidynamic Processes in Diesel Engines, Valencia, Spain, September, 2000.
9. D. Siebers, "Flame Lift-Off in DI Diesel Sprays: Impact on Soot Formation", Diesel Engine Emissions Reduction Workshop, San Diego, CA, August, 2000.

C. Heavy-Duty Diesel Engine Combustion: In-Cylinder Soot Deposition and Flame Lift-Off

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Contractor: Sandia National Laboratories, Livermore, CA
Prime DOE Contract Number: DE-AC04-94AL85000

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

Barriers

B. PM Emissions

C. Cost

Tasks

1. Fuel Systems R&D

3a. Identification of Advanced Combustion Systems

Objectives

- The overall objective of this project is to advance the understanding of diesel engine combustion and emissions formation through the application of advanced laser-based diagnostics in an optically-accessible diesel engine capable of realistic operating conditions.
- Specific objectives for FY 2001 include:
  - Quantification of soot deposition rates on the piston bowl wall and comparison with engine-out emissions to establish the importance of soot wall deposition and subsequent blow-off as a pathway for engine-out soot emissions.
  - Initial observations of diffusion flame lift-off, which influences air entrainment and subsequent soot formation during the mixing-controlled burn of diesel combustion.

Approach

- Investigation of piston-bowl wall deposition rates:
  - Develop a laser-based line-of-sight (LOS) absorption measurement technique for soot wall deposition layer thickness and soot volume fraction within the combusting jet.

- Compare the LOS technique measurements with Bosch-smoke type exhaust soot measurements for 1) standard diesel fuel with variations in speed, load, injection timing and simulated EGR, and for 2) a range of oxygenated fuels at the base operating condition.

- Initial observations of diffusion flame lift-off:
  - Use a hydroxyl radical (OH) chemiluminescence imaging technique to examine the diffusion flame lift-off over a range of engine operating conditions with standard diesel fuel (D2).
  - Develop an image processing scheme to extract flame lift-off lengths from images for characterization of flame lift-off in this engine and for comparison with observations in simulated diesel combustion environments.

Accomplishments

- Conducted a detailed investigation of the significance of soot wall deposition/blow-off mechanism of exhaust soot emission.
  - Developed a laser-based absorption technique for measurement of soot wall deposition rate and soot volume fraction within the combusting plume.
  - Established that the soot deposition/blow-off pathway is not a significant contributor to the well-known soot-NO_x emissions tradeoff that is commonly exploited to achieve emissions targets.
  - Demonstrated that soot volume fraction measurements correlate well with soot wall deposition rates, leading to a new quantitative laser-based absorption diagnostic technique that may be used even when the sooty region of the jet is optically thick, for which other absorption-based measurements are precluded.
- Initiated an investigation of diffusion flame lift-off in a realistic engine environment:
  - Initial flame lift-off data suggest that differences in flame lift-off may be responsible for changes in soot deposition rates for different fuels.
  - Due to potential fluid mechanical and thermal effects, flame lift-off measurements in this engine are shorter and display significantly more structure than observations of flame lift-off in simulated combustion environments. Accordingly, additional work is required so that knowledge gained from the well-defined simulated combustion experiments may be properly applied to realistic engine conditions.

Future Directions

- Examine structure of diffusion flame using side-on hydroxyl radical (OH) Planar Laser-Induced Fluorescence (PLIF) near the lift-off length with real diesel fuels to examine the influence of flame structure on mixing and soot formation.
- Combine the wall deposition measurement technique with flame lift-off measurements for several fuels to examine interactions of air mixing and fuel oxygen content on soot formation.
- Integrate data from optical diagnostics and chemical kinetic modeling to continue to expand our current understanding of diesel combustion and pollutant formation for real diesel fuels.

Introduction

Over the past decade, laser diagnostics have improved our understanding of many aspects of diesel combustion. However, the importance of in-cylinder soot deposition and subsequent blow-off as a pathway to exhaust soot emissions has not been thoroughly investigated. It has been suggested that soot layers, deposited on in-cylinder surfaces during combustion, build in thickness until they separate

from the surfaces and are ejected from the cylinder, thus contributing to exhaust soot emissions [1,2]. The conclusions of these studies were disparate, and neither the mechanisms nor the importance of the wall deposition/blow-off pathway for engine-out emissions were established. Recently, we have established a mechanism for soot wall deposition: interactions between the diffusion flame and the piston bowl wall lead to extinction of the diffusion flame at the wall, allowing soot to come in close contact with the wall so that a mechanism such as thermophoresis can carry the soot through the boundary layer to become a deposit [3]. However, questions regarding the rate of deposition/blow-off and its relative importance for exhaust emissions remained unanswered. The rate of soot deposition on in-cylinder surfaces will depend on the soot concentration in the core of the combusting plume, which is affected by the amount of fresh air entrained into the fuel jet upstream of the leading edge of the diffusion flame, termed the "lift-off length." Recent evidence confirms that the lift-off length plays an important role for soot formation in simulated diesel combustion [4], but characterization and quantification of lift-off in real diesel engines is required to properly apply these new insights regarding pollutant formation to engine conditions.

The objective of the current work is to quantify the soot deposition rates on the piston bowl wall and compare them with engine-out emissions to establish the importance of soot wall deposition/blow-off as a pathway for engine-out soot emissions. An investigation of diffusion flame lift-off was also initiated. This investigation, and all of the work on this project, is conducted in cooperation with our CRADA partners (Cummins, Caterpillar, and Detroit Diesel), and the results are presented at the cross-cut diesel CRADA meetings.

Approach

In the current study, an LOS continuous wave (CW) laser-absorption technique was used to monitor the accumulation of soot on the surface of the piston bowl rim and to measure the soot volume fraction in the plume of a combusting fuel jet. This diagnostic was applied to a realistic diesel environment in the Sandia/Cummins optically accessible heavy-duty diesel engine. A schematic of the optical setup used for the attenuation measurements is shown in Figure

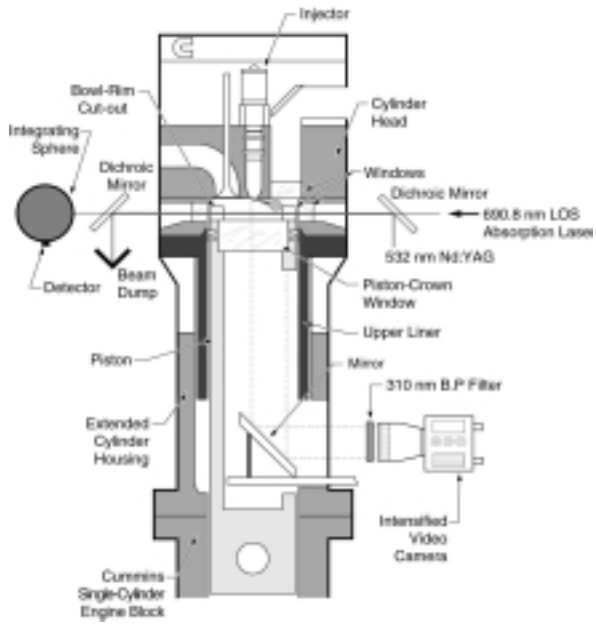

Figure 1. Schematic of the Optical Engine Showing the Paths for the LOS and Nd:YAG Laser Beams Used in the Absorption Measurements, and Camera View for OH Chemiluminescence Imaging

1. A portion of the piston bowl rim was replaced with a quartz window, upon which soot was deposited during combustion. A diode-laser beam was passed through both the cylinder-wall window and the bowl-rim window and soot deposit before intersecting one of the combusting plumes. A cutout in the piston bowl rim on the opposite side combined with a special injector nozzle with a "missing" fuel jet allowed the LOS laser to pass through the remainder of the combustion chamber without further attenuation, for transmission measurements. The transmitted LOS beam was collected with a large integrating sphere, effectively eliminating the effects of beam steering. Using dichroic optics, a high power Nd:YAG laser was aligned co-axially with the LOS beam and was pulsed at an appropriate time to ablatively remove minor soot deposits from the cylinder windows only. Crank-angle resolved transmittance data were obtained for number 2 diesel fuel (D2) across a range of engine speeds, loads, injection timings, and simulated EGR rates. At a base operating condition, measurements were also made for three low-sooting oxygenated fuel blends, consisting of 70%, 80%, and 90% tetraethoxypropane (TEOP) in heptamethylnonane (HMN). Exhaust soot emissions at each condition

were measured using a Bosch-smoke type technique [5].

Diffusion flame lift-off was extracted from images of natural OH chemiluminescence from the diffusion flame, acquired through the piston crown window as shown in Figure 1, using appropriate spectral filters. Due to inherent and unavoidable scattering interference present in the OH chemiluminescence images from the engine, a straightforward image processing scheme was developed to spatially filter and smooth the images so that flame lift-off length statistics could be objectively extracted from instantaneous images using a simple thresholding scheme.

Results

Shown in Figure 2 are the wall deposition and engine-out soot emission rates for D2 over a range of speeds, loads, injection timings, and simulated EGR rates. Changes in the rate of deposition at different operating conditions did not correlate well with changes in exhaust soot emissions. This suggests that the soot deposition/blow-off pathway is not a major contributor to the increased soot emissions typically observed as engine operating conditions are adjusted to reduce NO_x emissions.

As shown in Figure 3, the relative attenuation due to soot deposition correlated very well with attenuation due to soot within the reacting plume for all four fuels at the base operating condition. Accordingly, laser-absorption measurement of the soot wall deposition rate appears to be a useful diagnostic for determining the soot volume fraction within a combusting fuel jet, even for conditions where the sooty region of the jet is optically thick. This is significant because the soot plumes are optically thick for most operating conditions when D2 is used, thus precluding direct laser-absorption measurements of the soot levels within the plume. Additionally, the rate of soot deposition (and soot volume fraction) correlated well with the changes in the O/C ratio of the oxygenated fuels. However, D2 had a much higher deposition rate than expected from a linear extrapolation of the oxygenated-fuel data to a zero oxygen-content blend of these alkane-based fuels. Possible explanations for the increased soot levels with D2 include its aromatic content or

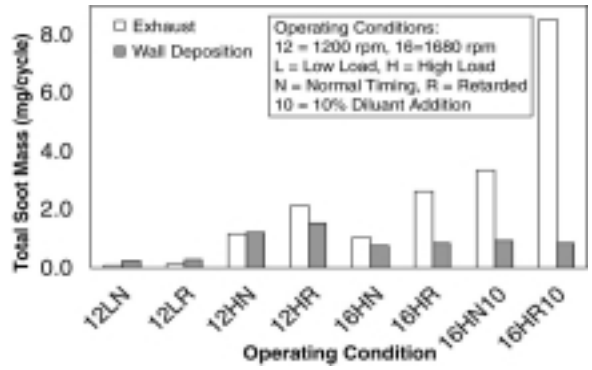

Figure 2. Wall Deposition and Exhaust Soot Emission Rates for D2 Across a Range of Engine Speeds, Loads, Injection Timings, and Simulated EGR Rates (operating condition nomenclature is explained in the inset)

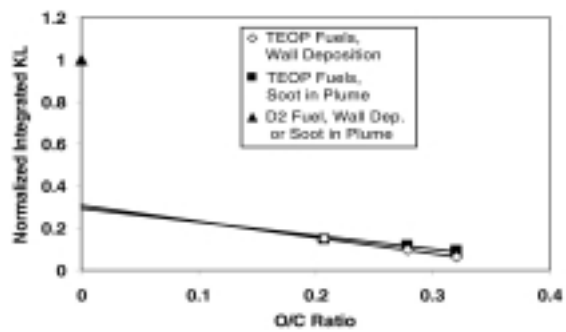

Figure 3. Optical Thickness of the Soot Wall Deposition Layer and the Soot Within the Reacting Plume for Three Low-Sooting TEOP Fuel Blends and for D2

reduced air entrainment into the mixture within the plume as a result of differences in flame lift-off.

An OH chemiluminescence imaging technique was used to measure flame lift-off at a number of operating conditions with D2. Shown in Figure 4 is an instantaneous OH chemiluminescence image illustrating the scattering interference from liquid fuel droplets and in-cylinder surfaces. Clear interactions between weak in-cylinder swirl flows and the structure of the diffusion flame near lift-off are also evident, with flame lift-off on the "downswirl" side of the plume extending much farther upstream than on the "upswirl" side. Using the image processing scheme described above, flame lift-off statistics were extracted from hundreds of images. Average values of flame lift-off are shown in Figure 5 for three different operating conditions.

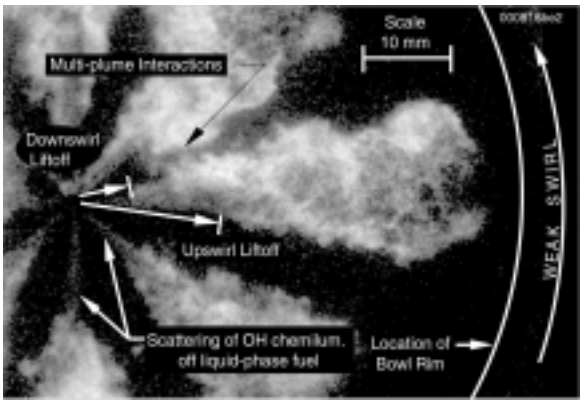

Figure 4. Instantaneous image of OH chemiluminescence for D2. The image is offset from the injector axis to improve the spatial resolution for the fuel spray of interest (3 o'clock jet).

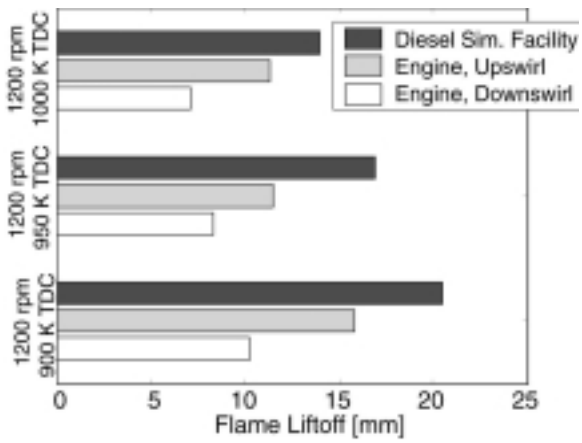

Figure 5. Average Flame Lift-off for Simulated Diesel Combustion and Upswirl / Downswirl Flame Lift-off Measured in the Engine for D2

The flame lift-off is shorter than that observed previously using an OH PLIF technique with oxygenated fuels [6], supporting the possibility that flame lift-off is responsible for observed differences in soot wall deposition rates between D2 and oxygenated fuels. The flame lift-off with D2 was also much shorter than that observed for diesel plumes in similar simulated engine conditions [4], which could be attributed to multi-plume interactions, in-cylinder surface effects, hot gas entrainment and differences in jet entrainment rates between experiments.

Conclusions

A detailed investigation of the soot wall deposition rates in a heavy-duty diesel engine has been conducted using a laser-based light absorption technique. The data show that changes in the rate of soot wall deposition do not correlate with changes in exhaust soot emissions as engine operating conditions are changed. This is significant because it shows that the soot deposition/blow-off pathway is not a significant contributor to the well-known soot-NO_x emissions tradeoff that is commonly exploited to achieve emissions targets. Flame lift-off data in this engine shows that differences in flame lift-off could be responsible for changes in soot deposition rates for different fuels and allows knowledge gained from detailed observations of flame lift-off in simulated combustion environments to be properly applied to engine conditions.

The results of this investigation improve our understanding of the mechanisms of in-cylinder soot formation and exhaust soot emission. As engine manufacturers strive to produce engines with extremely low emissions, all potential mechanisms must be understood. This understanding allows the manufacturers to develop accurate engineering models and to better focus their development efforts on appropriate areas. It also provides information necessary for the development of more accurate predictive numerical-models of diesel combustion.

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2. Suhre, B. R. and Foster, D. E., "In-Cylinder Soot Deposition Rates Due to Thermophoresis in a Direct Injection Diesel Engine," SAE Technical Paper no. 921629, 1992.
3. Dec, J. E. and Tree, D. R., "Diffusion-Flame / Wall Interactions in a Heavy-Duty DI Diesel Engine," SAE Technical Paper no. 2001-01-1295.
4. Higgins, B. and Siebers, D., "Measurement of the Flame Lift-Off Location on DI Diesel Sprays

Using OH Chemiluminescence," SAE Technical Paper no. 2001-01-0918, 2001.

5. Tree, D. R. and Dec, J. E., "Extinction Measurements of In-Cylinder Soot Deposition in a Heavy-Duty DI Diesel Engine," SAE Technical Paper no. 2001-01-1296, 2001.
6. Dec, J. E. and Coy, E. B., "OH Radical Imaging in a D.I. Diesel Engine and the Structure of the Early Diffusion Flame," *SAE Transactions*, Vol. 105, Sec. 3, pp. 1127-1148, paper no. 960831, 1996.

FY 2001 Publications/Presentations

1. Dec, J. E. and Tree, D. R., "Diffusion-Flame/ Wall Interactions in a Heavy-Duty DI Diesel Engine," SAE paper no. 2001-01-1295, 2001.
2. Tree, D. R. and Dec, J. E., "Extinction Measurements of In-Cylinder Soot Deposition in a Heavy-Duty DI Diesel Engine," SAE paper no. 2001-01-1296, 2001.
3. Tree, D. R. and Dec, J. E., "Line-of-Sight Extinction Measurements of Oxygenated Fuel Blends and Diesel Fuel in a Heavy-Duty, Direct-Injection Diesel Engine," 2nd Joint Meeting of the United States Sections of the Combustion Institute, Oakland, CA, March 26-28, 2001.
4. Dec, J. E. and Kelly-Zion, P., "An Understanding of DI Diesel Combustion and Soot Burnout Based on Laser-Sheet Imaging," Invited seminar for European Clean Diesel Meeting, June 16, 2000.
5. Dec, J. E., "Diesel Combustion Project Report," Cross-Cut Diesel CRADA Meeting, October, 2001.
6. Musculus, M. P., "Future Research Directions in the Sandia Heavy-Duty Diesel Engine Laboratory," Cross-Cut Diesel CRADA Meeting, January 2001.
7. Dec, J. E., "Overview of Heavy-Duty Diesel Combustion Research at Sandia," Two-Hour Invited Seminar at the International Truck and Engine Company, Mar. 9, 2001.
8. Dec, J. E., "An Understanding of DI Diesel Combustion and Soot Burnout based on Laser-Sheet Imaging," Invited presentation at the ASME National Heat Transfer Conference, Anaheim, CA, June 10, 2001.
9. Dec, J. E. and Musculus, M. P., "Heavy-Duty Diesel Engine Combustion: In-Cylinder Soot Deposition and Diffusion Flame Lift-Off," DOE CIDI Combustion, Emission Control, and Fuels Peer Review, June 11-13, 2001.
10. Musculus, M. P. "Observations and Implications of Flame Liftoff in the Sandia/Cummins Optical Diesel Engine," Cross-Cut Diesel CRADA Meeting, June 27-28, 2001.

Awards and Recognition

1. SAE Arch T. Colwell Merit Award for an outstanding contribution to the SAE literature for SAE paper no. 1999-01-0509, "Diesel Combustion: An Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation."
2. SAE Oral Presentation Award for SAE paper no. 2000-01-0238, "The Effects of Injection Timing and Diluent Addition on Late-Combustion Soot Burnout in a DI Diesel Engine based on Simultaneous Laser-Sheet Imaging."
3. Energy 100 Award for one of the top 100 discoveries and innovations from the DOE that have resulted in improvements for American consumers (1977-2000).
4. Work featured in a new edition of Internal Combustion Engines by C. Ferguson and A. Kirkpatrick.
5. Work featured in a new comprehensive book entitled Engine Combustion Instrumentation and Diagnostics, by H. Zhao and N. Ladommatos.

D. CHAD Modeling Activities

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Subcontractor
ICEM-CFD Engineering, Livonia, MI

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

Barriers

A. NO_x Emissions

B. PM Emissions

Tasks

3. Fundamental Combustion R&D

3a. Identification of Advanced Combustion Systems

Objectives

- Develop advanced, parallel Computational Fluid Dynamics (CFD) code named CHAD (Computational Hydrodynamics for Advanced Design) for simulations of in-cylinder flows in CIDI engines
- Perform full-cycle, coupled port, in-cylinder flow simulations in realistic CIDI engine geometries
- Compare simulation results with experimental measurements

Approach

- Address deficiencies of current engine CFD models using CHAD's new numerical capabilities
  - Develop automated meshing strategies for full-cycle simulations using CHAD's hybrid-unstructured computational meshes
  - Bring unprecedented computer power to CIDI simulations using CHAD's scalable performance on parallel and massively-parallel computer platforms
  - Perform highly resolved diesel spray simulations using CHAD's explicit/implicit advection method and enhancements to CHAD's spray model

Accomplishments

- Developed and evaluated an engine meshing strategy based on use of LAGriT (Los Alamos Grid Tool Kit) for mesh maintenance and repair of distorted meshes. In its present form, LAGriT was judged unsuitable for engine simulations.
- Subcontracted with ICEM-CFD Engineering to develop an engine meshing interface, called CHAD-ICE, between CHAD and ICEM's unstructured-mesh generation software.

- Evaluated the performance of several iterative methods for solving CHAD's implicit finite difference approximations.
- Extended and applied a simple mixing-controlled model for diesel sprays first developed at Sandia National Laboratories.

Future Directions

- Evaluate the CHAD-ICE interface in simulations of realistic engine geometries. If CHAD-ICE performs well, subcontract with ICEM-CFD to develop a parallel version of CHAD-ICE.
- Following development of a parallel version of CHAD-ICE, perform full-cycle simulations in Caterpillar engine geometries
- Continue the effort to speed up the CHAD code's single processor performance
- Continue improvements to CHAD's spray model.

Introduction

The fluid dynamics Group T-3 at Los Alamos National Laboratory is developing the CHAD code for diesel engine applications. CHAD is a next-generation hydrodynamics code beyond the KIVA code and differs from KIVA in three fundamental respects. First, CHAD utilizes hybrid-unstructured grids in which computational elements may be hexahedra, tetrahedra, prisms, pyramids, or one of a variety of other three-dimensional solid figures. Second, CHAD's difference approximations are more accurate and robust than KIVA's. In particular, CHAD utilizes a variable explicit/implicit advection scheme[1] that is more accurate and efficient than KIVA's. The largest difference between CHAD and KIVA, however, is that CHAD is written to run on parallel and massively parallel computers. Thus, CHAD can potentially bring far greater computer power to bear on the computer-intensive problems of simulating in-cylinder flows in diesel engines.

Approach

Our approach is to utilize CHAD's enhanced capabilities to remove the roadblocks to performing more accurate diesel engine simulations. A major roadblock lies in the area of grid generation, and this is where we have devoted most of our effort this past year. We are exploiting CHAD's hybrid-unstructured meshing capability to enable faster, automated meshing with more geometric flexibility and better quality meshes. Two meshing efforts have been pursued, one at Los Alamos and one through a subcontract with ICEM-CFD Engineering.

A second roadblock is computational speed. CHAD has demonstrated scalable performance if one uses a minimum number of mesh nodes (500 or more) per processing element, and CHAD has performed parallel calculations on machines with up to 2000 processors. Its single processor speed, however, is between a factor of five to twenty slower than KIVA's, partly due to CHAD's more accurate numerical methods and partly due to slower iterative convergence of CHAD's current implicit equation solver. To enable CHAD's use by the engine modeling community, in which massively parallel computers are by and large not currently available, we must improve CHAD's computational speed. We are investigating improved implicit equation solvers as a means to speed up the code. Use of alternative iterative solution procedures has not resulted in code speed-up to date, but other promising speed-up strategies remain to be tried.

A third roadblock is in the area of diesel spray modeling. During the past year, in collaboration with researchers at Sandia National Laboratory — Livermore, we have extended a mixing-controlled model for diesel sprays and explored the implications of this model for multidimensional diesel spray simulations[2]. The results imply that a two-phase continuum model should be used in the near-nozzle region because of the high liquid volume fractions in this region. We are currently implementing a two-phase continuum model in CHAD.

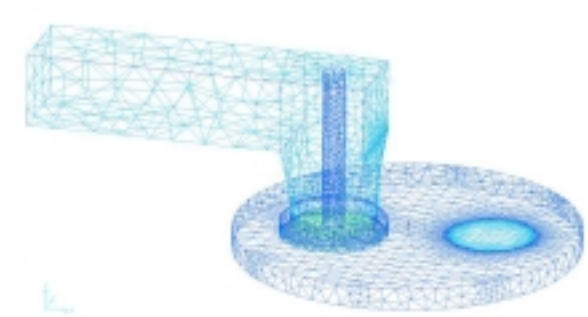

Figure 1a. Mesh Near TDC of Intake Stroke

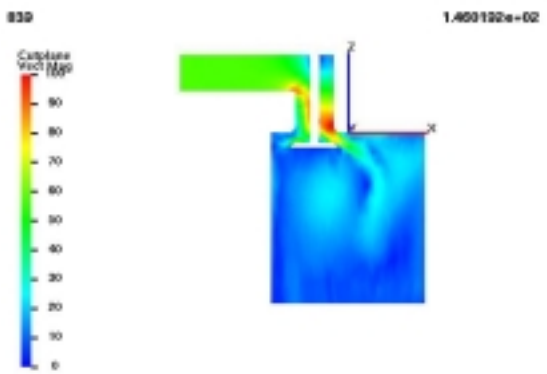

Figure 1b. Velocity Magnitudes on Symmetry Plane during Intake Stroke

Most of our effort this year has been to develop a computational meshing strategy for full-cycle, coupled port, in-cylinder flow simulations, and we confine the discussion in the next section to a summary of our results in this meshing effort.

Results

Meshing for engine calculations is complicated by the fact that the mesh must move to follow valve and piston motion. Periodically, this causes sufficient degradation in mesh quality that the mesh must be repaired, or a new mesh generated.

The Los Alamos meshing effort uses the Los Alamos Grid Tool Kit (LAGriT) for unstructured-mesh maintenance and repair. LAGriT was developed at Los Alamos under a CRADA with the semiconductor industry. An advantage of using LAGriT is that parallel engine calculations using LAGriT and CHAD can now be performed. The CHAD/LAGriT interface was tested in calculations of a generic two-valve engine geometry. Figure 1 shows the mesh near top dead center (TDC) of the intake stroke and a plot of the computed velocity

Figure 2. Geometry (Upper) and Surface Mesh (Lower) for Caterpillar 3208 Engine

magnitudes during the intake stroke of one such calculation. After much testing it was decided that mesh generation with LAGriT required too much user intervention and that all our engine meshing resources be devoted to the collaboration with ICEM-CFD Engineering.

The advantages of the ICEM-CFD meshing effort are that ICEM has considerable previous experience with engine geometries and has links to all CAD packages used by the engine companies. The disadvantage of the ICEM-CFD effort is that parallel calculations cannot currently be performed because ICEM's mesh motion algorithm is not parallelized. Testing of ICEM's meshing is being performed on the Caterpillar 3208 engine geometry shown in Figure 2. The meshing algorithm is now completed, and the CHAD-ICE link to CHAD is now being developed.

The ICEM meshing strategy makes extensive use of CHAD's hybrid-unstructured mesh capability. Figure 3 shows the mesh at one crank angle during

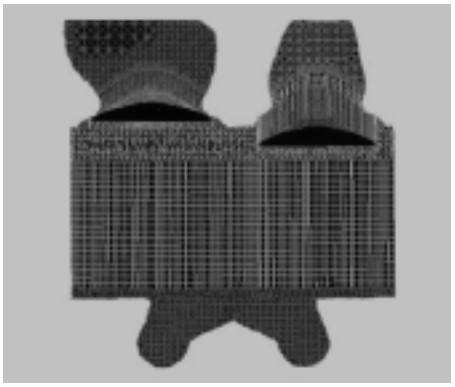

Figure 3. CHAD-ICE Mesh during Exhaust Stroke of Caterpillar 3208 Engine

the exhaust stroke of the Caterpillar engine. Hexahedra are used above the valve, and prisms are used in the cylinder. These are regions that expand and contract due to wall motion, and the hexahedra and prisms can expand and contract with little distortion. Tetrahedra are used under the valve, in small regions above the valve, in the piston bowl, and in the ports. Some pyramids are used to transition between the hexahedra above the valve and the tetrahedra below the valve. Using these element types, a full-cycle "no-hydro" calculation in the 3208 geometry has been performed by ICEM.

Conclusions

During this year our major effort has been to develop a strategy for mesh generation for computer simulations of full-cycle, coupled port, in-cylinder diesel engine flows using the next-generation CHAD code. A strategy utilizing the ICEM-CFD mesh generation software appears to hold the most promise. This meshing strategy, using ICEM's meshing software, has been completed, and the interface CHAD-ICE between CHAD and ICEM is currently being written. Following a period of evaluation of CHAD-ICE, we hope to subcontract with ICEM-CFD to write a parallel version of their mesh motion algorithm so that parallel calculations can be performed.

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2. O'Rourke, P.J., Siebers, D.L., and Subramaniam, S., "Some Implications of a Mixing Controlled Vaporization Model for Multidimensional Modeling of Diesel Sprays," Los Alamos unpublished report LA-UR-01-1716 (submitted to *Atomization and Sprays*).

FY 2001 Publications/Presentations

1. O'Rourke, P.J., Siebers, D.L., and Subramaniam, S., "Some Implications of a Mixing Controlled Vaporization Model for Multidimensional Modeling of Diesel Sprays," Los Alamos unpublished report LA-UR-01-1716 (submitted to *Atomization and Sprays*).
2. Oral presentations of progress at DOE Diesel CRADA meetings at Sandia National Laboratory-Livermore (Jan. 2001) and the University of Wisconsin-Madison (June 2001) and at the Diesel Combustion and Emissions Control R&D Meeting at Oak Ridge National Laboratory (June 2001).

E. Diesel Fuel Spray Measurement Using X-Rays

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

Barriers

B. PM Emissions

Tasks

1. Fuel Systems R&D

Objectives

- Understand the diesel fuel structure and dynamics in the region close to nozzles with small orifice diameter operated at high injection pressure.
- Develop highly quantitative and time resolved methods.
- Establish a knowledge base regarding spray breakup and droplet interactions in such an optically dense region as a prelude to realistic computational modeling.

Approaches

- Stage 1. Use synchrotron-based, monochromatic x-rays for radiographing diesel fuel sprays in a time-resolved and quantitative manner.
- Stage 2. Develop and utilize 2-dimensional (2-D) x-ray detectors for collecting the x-radiographic data more efficiently.
- Stage 3. Analyze the image data for qualitatively evaluating the spray characteristics such as structure (time-resolved fuel mass volume-fraction distribution) and dynamics (speed of spray core, supersonic properties associated with the sprays).
- Stage 4. Understand high-pressure sprays by theoretical modeling and computational approaches based on physical models best describing high-pressure injections.

Accomplishments

- Data collection with 2-D detectors and intense x-rays generated by a wide-bandpass x-ray monochromator has greatly enhanced the efficiency of the method. The new experimental method has reduced the data collection time significantly (from days to a few hours) so that the x-ray diagnosis becomes practical for potential commercial use.
- Several Bosch injectors (regular, non-hydro-ground and hyper-hydro-ground) have been tested with different fluids (diesel, diesel with cerium-containing additives, and diesel with polymers intended for improving atomization) at various injection pressures.

- Shock waves generated by high-pressure diesel fuel sprays have been directly imaged using the x-ray method and analyzed quantitatively for their thermodynamic properties.
- By using this high-energy x-ray phase imaging technique, the interior of the nozzle has been imaged, which has paved the way to study the fuel flow and possibly the cavitation inside a nozzle in a realistic and yet non-intrusive manner.
- Many technical papers and presentations have been published or presented on the subject.

Future Directions

- Continue to develop x-ray detectors and optics suited for 2-D data collection so that the spray test using x-rays can be performed routinely at the 1-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory.
- Conduct the diesel spray measurements under conditions similar to operating engine pressure and temperature. A test chamber with x-ray access that is compatible with high pressure and high temperature is currently being designed and constructed.
- Develop two-phase flow models for realistically simulating the spray core and atomization near the injection nozzles. The insights revealed by the present x-ray measurements have indicated that the current and conventional computational fluid dynamics (CFD) approaches may not be able to simulate the high-pressure spray behaviors adequately.

Introduction

High-pressure, high-speed sprays are an essential technology in many industrial and consumer applications, including fuel injection systems. In most cases, either the fuel spray is optically dense or the liquid droplets generated by the spray scatter light so strongly that the detailed structure of the spray cannot be resolved by conventional optical means. In particular, this problem occurs in the region near the injection nozzle, which is often the region of greatest interest in understanding the structure and the dynamics of the spray. The lack of quantitative, time-resolved analysis on the structure and dynamics of sprays limits the accuracy of spray modeling and creates obstacles to improving spray technology. Specifically, higher injection pressures (>1500 bar) and smaller orifice diameters (<200 μm) for small-bore diesel engines have brought even greater impetus to the understanding of fuel spray behavior. Despite significant advances in laser diagnostics over the last 20 years, the region close to the nozzle has remained impenetrable to experiments designed to acquire quantitative information. Multiple scattering from the large number of droplets prevents the penetration of the light in this near-nozzle region and, thus, limits quantitative evaluation with these techniques. In the previous year, we demonstrated that the dense part of the fuel spray can be quantitatively probed by a non-intrusive method utilizing monochromatic x-radiography techniques. Presently, by using a 2-D x-ray detector and appropriate x-ray optics, we have proved that the x-ray measurement can be performed efficiently, and the technique is practical for industrial applications in nozzle diagnosis and spray modeling. In addition, complicated hydrodynamic phenomena, such as generation of shock waves by high-speed fuel sprays, have been quantitatively detected and visualized directly. This visualization has allowed the analysis of important thermodynamic properties, such as the density of the gas media inside and near the shock wave front.

Approach

The fuel spray was generated using a high-pressure injector typical of CIDI engines. In most cases, the diesel fuel used in the test was doped with a cerium-containing additive in order to increase its x-ray absorption. Injection was performed in a spray chamber filled with inert gas at atmospheric pressure and at room temperature. Sulfur hexafluoride (SF_6), a very heavy gas, was used to create a relatively

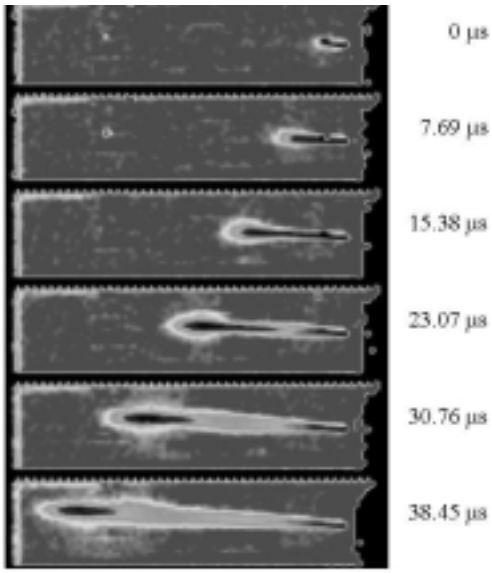

Figure 1. Time resolved x-ray images of fuel sprays measured with the PAD detector. The injection pressure was 135 MPa and the time resolution was set at 5.1 s. The area of the image was measured at 13.8 mm (H) x 3.45 mm (V) as defined by the x-ray beam size.

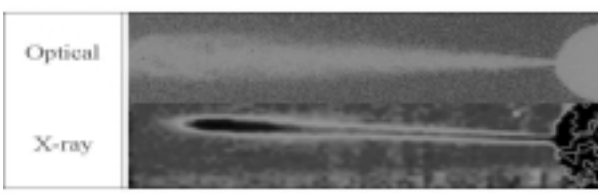

Figure 2. Comparison between the optical and x-ray images collected under similar injection conditions. The optical image was a shadowgraph and taken by a gated charge-coupled device (CCD) camera with illumination from an intense strobe light.

dense ambient environment in the injection chamber. The experiments were performed at either the 1-BM beamline of the Synchrotron Radiation Instrumentation Collaborative Access Team (SRI-CAT) at APS or the D-1 line at the Cornell High Energy Synchrotron Source (CHESS). A 6 keV x-ray beam was focused and then collimated by a pair of X-Y slits to a size of 500 m (horizontal, H) × 50 m (vertical, V) for using a point x-ray detector, avalanche photodiode (APD) or to a size of about 15 mm (H) × 3.5 mm (V) for the use of the 2-D x-ray detector, pixel array detector (PAD). The transient x-ray attenuation signal due to the fuel spray was measured and recorded by detectors. The x-ray absorption technique using a monochromatic beam is distinguished from conventional measurements by the quantitative nature of the measurement. With proper calibration, the x-ray absorption directly yields the absolute fuel mass quantity in the beam and the mass distribution throughout the spray core.

Results

A series of the x-ray images taken with the PAD is shown in Figure 1 with injection time as marked. The images were obtained with an average of 20 injections. The time-resolution was chosen to be 5.13 μs although better time resolution could be easily achieved. The images clearly show a strong mass fluctuation inside the spray core from which the dynamics of the spray can be deduced. To illustrate the effectiveness of the x-ray imaging technique, the spray images taken at similar injection conditions and at roughly the same injection time are compared in Figure 2. These images imply the inadequacy associated with conventional methods of imaging high-pressure sprays with visible light. The majority of the fuel mass is concentrated in a narrow spray core, although not in a pure liquid form, and is completely invisible to visible light. For instance, one of the important parameters, the spray cone angle, defined by the visible light images, becomes essentially meaningless in characterizing the properties of the high-pressure sprays.

Previously, we found that the high-pressure diesel spray can be supersonic in the region near the nozzle. To confirm the supersonic nature of the sprays, the shock waves were visualized in the same spray system by optical Schlieren imaging of visible light. The shock wave front can be clearly observed when the injection pressure reaches 80 MPa, at which the shock waves generated by the fuel spray composed of liquid/gas mixture were imaged. The direct imaging of the shock waves has become possible with highly brilliant synchrotron x-ray sources and the use of a 2-D detector such as PAD. Figure 3 shows an x-radiograph of the fuel spray at a time of 200 μs after the beginning of the injection process. The false-color levels of the images have been set to accentuate small differences in the x-ray intensity arising from the slightly increased x-ray absorption in the compressed SF_6 gas. The shock wave front, or the so-called Mach cone, is clearly

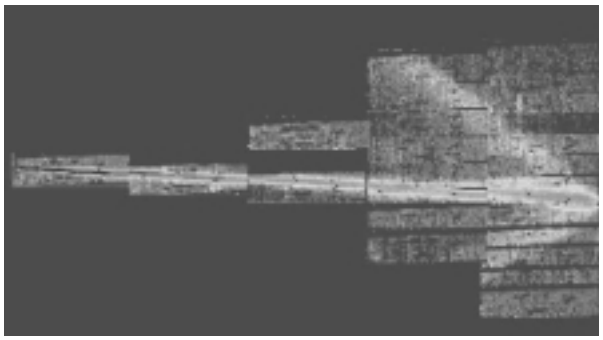

Figure 3. A snapshot of shock waves generated by the high-pressure diesel spray and recorded by x-radiography. The injection pressure was 135 MPa and the instance was ca. 200 μs after the injection. The shock front caused an average compression of ca.10 kPa excess pressure above the ambient pressure in the injection chamber, assuming the temperature in the shock has equilibrated with the ambient. The image size is ca. 60 mm (H) x 25 mm (V). The "tile-look" unit in the image represents the x-ray beam size. The entire image was captured by scanning the injection chamber with respect to the x-ray beam.

observed as emanating from the leading edge of the fuel jet. A quantitative analysis of the Mach cone has been performed to deduce the speed of the spray penetration as well as the thermodynamic parameters in the surrounding gas medium.

Conclusions

In summary, ANL has demonstrated how a fast 2-D x-ray detector makes it possible to x-radiograph high-pressure diesel sprays efficiently. ANL has also demonstrated that the high-pressure fuel sprays are supersonic and that the Mach cone generated by the supersonic sprays in the gaseous medium can be directly imaged by x-radiography. The technique also allows quantitative analysis of the shock wave parameters. This experiment demonstrates a methodology to quantitatively study the fluid dynamics of high speed liquid sprays in situations which do not lend themselves to analysis by optical methods. The dynamics of fuel injection in internal combustion engines is an excellent example of why better experimental methods for studying high speed liquid jets are needed. Relatively little progress has been made in understanding fundamental processes in the so-called two-phase or multi-phase fluid dynamics of the high-speed jets that are central to every fuel injector. In the absence of such understanding, simultaneous optimization of the many variables associated with fuel injectors (e.g., the nozzle shape and finish, fuel pressure, gas pressure, duration of injection, etc.) has been a highly empirical process with significant uncertainty. The x-radiographic method described here provides quantitative experimental methods to validate computational fluid dynamics modeling efforts.

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Awards

1. Pacesetter Award, Argonne National Laboratory, October 2000
2. Director's Award, Argonne National Laboratory, June 2001
3. Finalist Discover Magazine Award, June 2001

F. Pressure Reactive Variable Compression Ratio Piston Development

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Contractor: Ford Motor Company, Dearborn Michigan
DOE Cooperative Agreement No. DE-FC02-99EE50576
Period of Performance: 09/30/1999 through 09/29/2001

Subcontractors: University of Michigan, Ann Arbor, Michigan; Federal-Mogul Corporation, Plymouth, Michigan

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

Barriers

A. NO_x Emissions

C. Cost

Tasks

2. Sensors and Controls

3a. Identification of Advanced Combustion Systems

Objectives

- Develop and demonstrate a pressure reactive piston (PRP) for a spark-ignited (SI) engine
- Develop and demonstrate a pressure reactive piston for a compression-ignited (CI) engine
- Quantify engine efficiency and emission effects due to the pressure reactive piston

Approach

- SI and CI engine simulation analysis
- SI and CI single-cylinder engine baseline testing
- PRP spring design
- PRP dynamic analysis
- PRP design
- PRP component mechanical, thermal, and dynamic stress analysis
- SI and CI PRP prototype manufacture
- SI and CI PRP single-cylinder engine testing

Accomplishments

- SI and CI baseline engine simulation analysis
- SI baseline engine simulation correlation to test data
- SI engine simulation code modified to include the PRP degree of freedom
- SI engine simulation efficiency predictions with the PRP
- Baseline single-cylinder engine dynamometer installation complete
- SI PRP spring design complete
- PRP dynamic analysis initiated
- SI PRP design and analysis complete
- Baseline SI single-cylinder engine testing complete
- Initial SI PRP testing complete
- SI PRP hardware complete
- Initial CI PRP design initiated
- CI baseline engine simulation correlation to test data
- CI engine simulation code modified to include the PRP degree of freedom

Future Directions

- CI PRP design completion
- CI PRP component mechanical, thermal, and dynamic stress analysis
- CI PRP prototype manufacture
- Refine and iterate the dynamic model
- Refine and iterate engine simulation models
- CI baseline single-cylinder engine testing
- SI PRP testing with second iteration spring set
- CI PRP single-cylinder engine testing

Introduction

The pressure reactive piston technology is based on Ford Motor Company U.S. Patent #5,755,192 (Variable Compression Ratio Piston) granted in 1998. The PRP is a two-piece piston, separated by a spring system (see Figure 1). The patent was based on work in the late 1980s to early 1990s, which resulted in hardware being run in one cylinder of a multi-cylinder engine. This work was promising; however, the efficiency and emission effects were not quantified.

Many variable compression ratio piston designs have been patented and developed to some level over the history of the internal combustion engine. These technologies typically control the compression ratio throughout the engine cycle and vary the compression ratio on demand (e.g., through controlling the oil volume in an upper versus lower chamber in the piston). The rate of compression ratio change may not be adequate at times where rapid load changes are demanded on the engine. The unique feature of PRP technology is that the upper piston reacts to cylinder pressure during the power stroke of the engine - during the rest of the engine

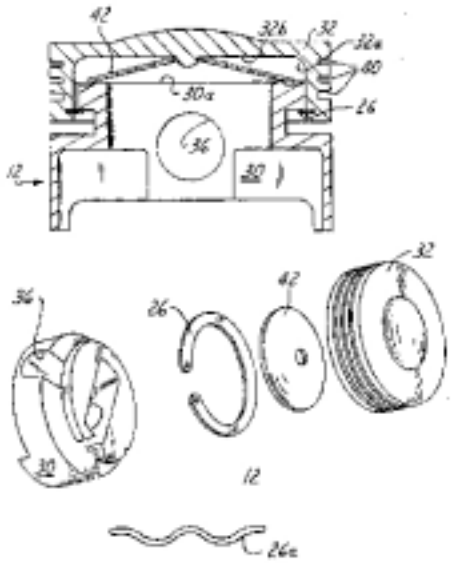


Figure 1. Variable Compression Ratio Piston, Referred to Here as Pressure Reactive Piston

cycle the upper piston remains in the high compression position.

The PRP operation strategy for a SI engine is to set the spring system preload to allow high compression (13:1) operation during partial engine load operation. During high engine load operation the spring system and piston geometry allow the effective compression ratio to drop (upper piston deflects relative to the piston pin) to prevent detonation or spark knock. Detonation is prevented because the peak cylinder pressure is limited by the deflection of the upper piston, which is controlled by the spring system. The expected result is higher engine efficiency at partial load, which is typical operation for automotive engine applications. Reduced high load engine noise is also anticipated.

The PRP operational strategy for a CI engine is to set the spring system preload to allow high compression (19:1) for start-up operation. Firing loads, even light engine load operation deflects the PRP spring system; however, high engine load operation deflects the upper piston further. This upper piston deflection controlled by the spring system limits the peak cylinder pressure, and therefore reduces gas temperature. The expected result is lower engine-out NO_x at the same engine efficiency and power output. Lower engine friction and noise are also expected.

Approach

A careful balance of analysis and experimental techniques are employed, as this leads to the most time and resource effective solutions to engineering problems. Analysis results are correlated with experimental results, and analysis tools are utilized with designed experimental techniques to quickly sort the many possible variables. For engine simulation, University of Michigan Diesel Engine Simulation and Spark Ignition Simulation codes are being utilized. The PRP dynamic modeling is being done with University of Michigan code. Spring design configuration analysis has been accomplished with University of Michigan code, based on SAE Belleville spring references. Federal Mogul is performing finite element analysis on the PRP including thermal, mechanical, and dynamic loads. Functional prototypes will allow major issues to be discovered and accelerate resolution. Single-cylinder engine testing will correlate the engine simulation models as well as demonstrate the capabilities of the PRP. Ricardo SI and CI Hydra engines (as well as associated emission, fuel, and torque instrumentation) will be used for experimental testing at the University of Michigan.

Business strategies were used to improve the possible transition from research to product application. Utilizing a major automotive piston supplier to design, analyze, and prototype the PRP adds credibility and implementation readiness to the project. University graduate students are utilized to improve "out of the box thinking" and help train future automotive engineers. Utilizing single-cylinder SI and CI engines allow efficiency and emissions effects to be isolated and quantified. It is well accepted that single-cylinder engine results and components can be readily applied to multi-cylinder engines.

Results

The Ricardo Hydra spark and compression ignition single-cylinder engines, with double-ended motoring dynamometer, have been installed at the University of Michigan - Lay Automotive Building. The SI engine baseline testing has been completed, summarized and reported. The CI engine is operational and is being used to correlate the engine simulation analysis.

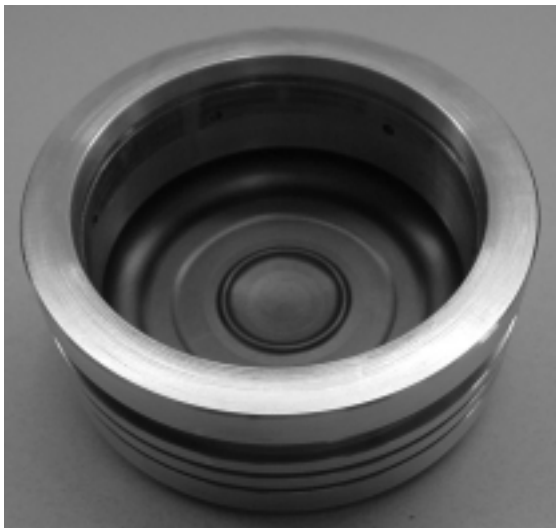


Figure 2. SI PRP Upper Piston, Bottom View

Figure 3. SI PRP Lower Piston, Side View

Federal-Mogul has completed the analysis and design of the SI PRP. Detail drawings have been completed for all PRP components (available upon request). All PRP hardware has been completed, including upper & lower piston, spring set, retaining ring, piston pin, and rod. Federal Mogul manufactured the upper (Figure 2) and lower piston (Figure 3); Associated Spring manufactured the Belleville spring set, spacer ring, and retaining ring (Figure 4). Ford modified the Ricardo Hydra piston pin and rod to be compatible with the PRP (Figure 5).

The individual Belleville springs and spring set from Associated Spring were measured on a load deflection machine. The SI spring set received from

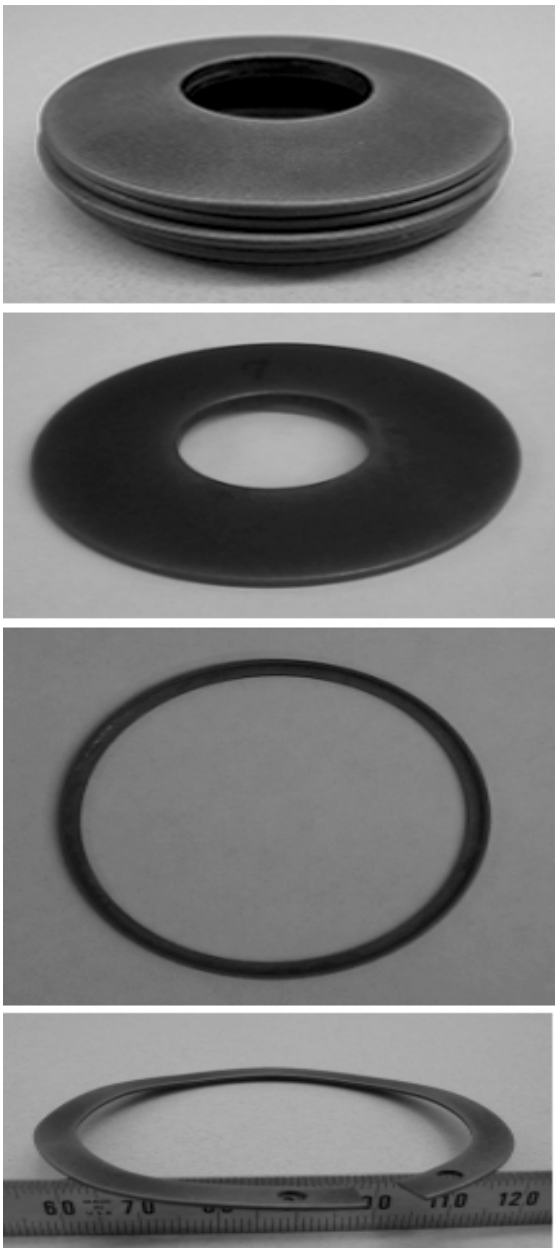


Figure 4. SI PRP Spring Set, Individual Spring, Spacer (for Pre-Load Adjustment), Retaining Clip

Figure 5. SI PRP Connecting Rod and Piston Pin

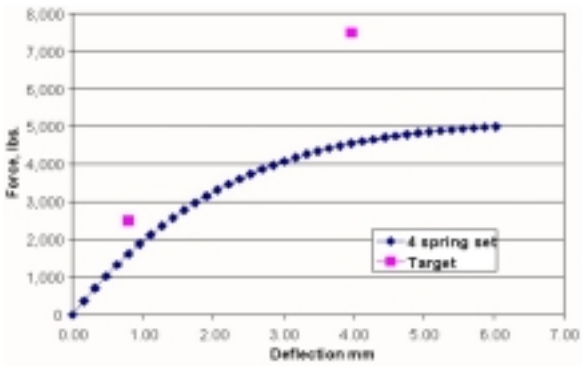


Figure 6. SI PRP Spring Set, Actual Versus Target Load Versus Deflection

Associated Spring was dimensionally correct, but did not match the load deflection intended. The spring set is not as stiff as the target as shown in Figure 6. This discrepancy appears to be a result of a communication error between the University of Michigan (U of M) and Federal Modul. Predicted (based on the U of M code and SAE Belleville spring reference) and measured load deflection characteristics correlated very well. Predicted stress levels were substantially higher than actual (spring radii are not comprehended in the stress prediction equations). Based on these results, finite element analysis of the spring set will be utilized for the CI spring set. We elected to run the SI PRP despite the lower than desired spring pre-load.

SI PRP assembly and disassembly details had not been fully developed in the design stage. Rapid prototype components were made to aid in assembly issues. Actual hardware was utilized to develop the final assembly and disassembly details of the PRP. Minor modifications to the upper piston and retaining ring were made to facilitate assembly and dis-assembly (not currently shown on the part drawings).

The SI PRP was assembled in the engine and first fired on July 14, 2001. The engine was run with the SI PRP for approximately 15 hours, at which time the upper piston separated from the lower piston, causing significant engine damage. During the 15 hours of operation, the PNGV speed load points and most of the 2000 rpm load sweep data were recorded. Full load at 2000 rpm was not reached before failure (max. torque may be lower with the PRP). No audible engine noise could be identified associated

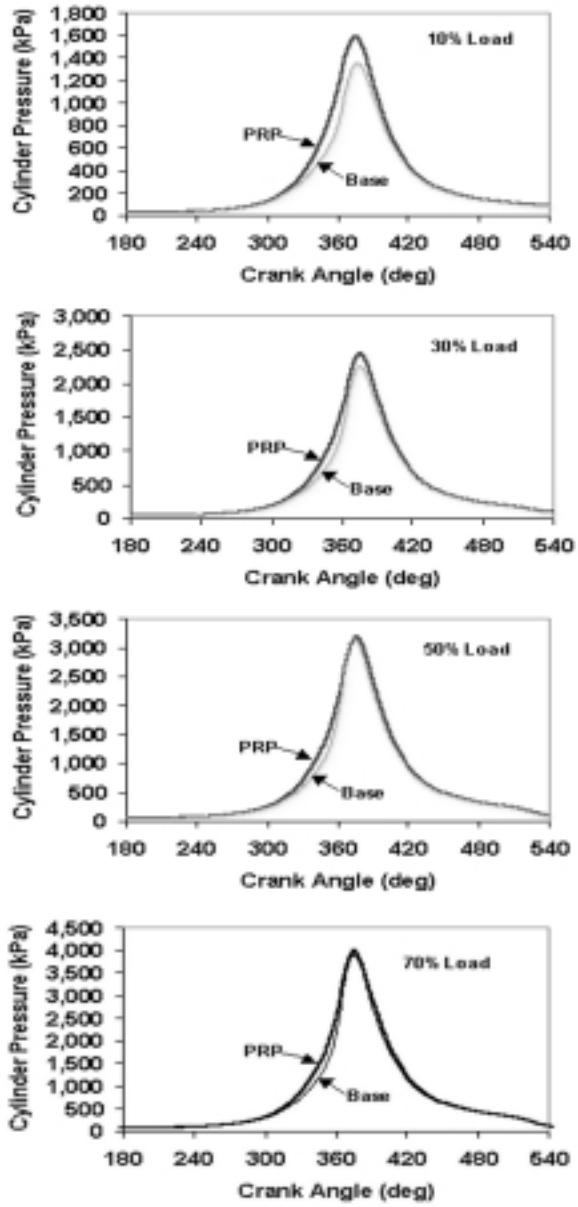


Figure 7. Comparison of Peak Cylinder, Pressure PRP Versus Base Piston

with the PRP, regardless of speed or load (speeds up to 2300 rpm, and loads up to 80% of full load). The lack of audible noise associated with piston deflection indicates that the wavy shape of the retaining ring is effective.

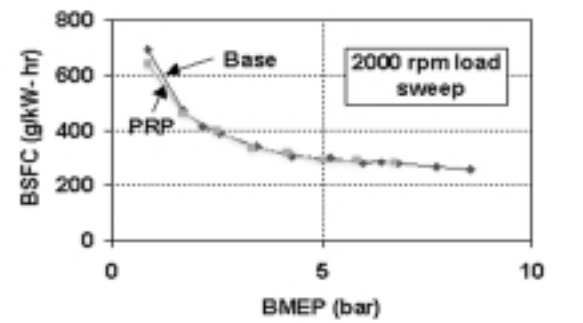
Cylinder pressure was compared from the base piston (9.25:1 CR) versus the SI PRP (13.5:1 CR un-deflected). Cylinder pressure @ 2000 rpm from 10% to 70% of full load is shown in Figure 7. At the 10% of full load condition, it is clear that the peak

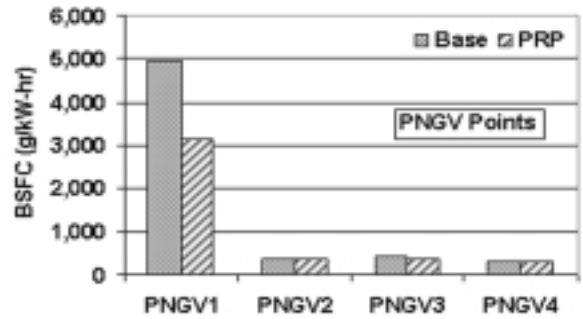
pressure is higher with the PRP. However, at 30% of full load condition, the PRP is slightly higher in pressure than the base piston, and by 50 and 70% of full load, the peak pressures are nearly equivalent. The cylinder pressure comparison is clear evidence that piston deflection is occurring at lower engine loads than desired. The intention was not to have significant upper piston deflection until above 70% engine load.

Brake specific fuel consumption was compared from the base piston and the SI PRP. The 2000 rpm load sweep, as well as the PNGV speed/load points, brake specific fuel consumption (bsfc) results are shown on Figure 8. Improvements in efficiency were observed only at the lightest load points (e.g., 7.8% improvement in bsfc at 10% load). Note that PNGV point #1 is a very light load, and the engine was not stable (high coefficient of variation of brake mean effective pressure [bmep]). These results indicate that a stiffer sring set is required to obtain efficiency improvements at higher engine load conditions (above 10% engine load). However, this also indicates that the PRP is operating as intended and resulting in efficiency improvement.

Nitric oxide emissions were compared from the base piston and the SI PRP. The 2000 rpm load sweep as well as the PNGV speed/load points NO results are shown on Figure 9. There appears to be an NO reduction in the mid-load range. We have not been able to explain this, since we expected an NO increase due to the higher compression ratio at light loads (we expect an NO reduction on the CI PRP). Interestingly, the mbt spark advance (the minimum spark advance for the best torque) was lower with the PRP at the same points where the NO is lower, as shown on Figure 10.

The SI PRP failed after approximately 15 hours of testing. Engine inspection indicated that the upper piston separated from the lower piston. The PRP lower piston broke in many pieces (after separation and before the engine was stopped), as well as the spring set, spacer and retaining ring. The engine exhaust valves bent, and the rod broke through the cylinder liner. Further PRP failure analysis indicated that the springs were cracked, starting at the inner diameter and moving radially inward. The springs were rotating relative to one another, causing scuffing on the faces of the springs and wearing





	BMEP [bar]	Speed [rpm]
PNGV1	0.10	900
PNGV2	2.62	1500
PNGV3	2.00	2000
PNGV4	4.20	2300
PNGV5	8.80	2600

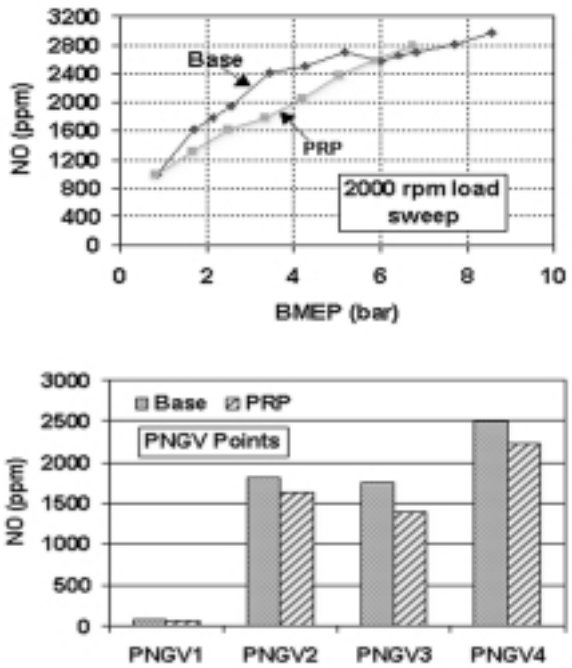
Figure 8. Brake Specific Fuel Consumption Base Piston Versus PRP

through the anodized surfaces of the upper and lower piston. No signs of fatigue were found on the lower piston, so the assumed failure mode is the retaining ring came out of the groove after excessive upper piston motion was experienced (due to the cracked springs).

Compression ignition engine analysis has been initiated and utilized to characterize the spring set requirements. An initial spring set has been developed to provide the desired pre-load and maximum deflection loads. The initial design of the CI PRP is shown in Figure 11.

Conclusions

Initial SI PRP testing indicates brake specific fuel consumption improvement at light load. It also indicates that to obtain bsfc improvement at higher load, a stiffer spring set is required. We have asked for a six-month, no cost extension to the contract,



	BMEP [bar]	Speed [rpm]
PNGV1	0.10	900
PNGV2	2.62	1500
PNGV3	2.00	2000
PNGV4	4.20	2300
PNGV5	8.80	2600

Figure 9. Comparison of NO Emissions PRP Versus Base

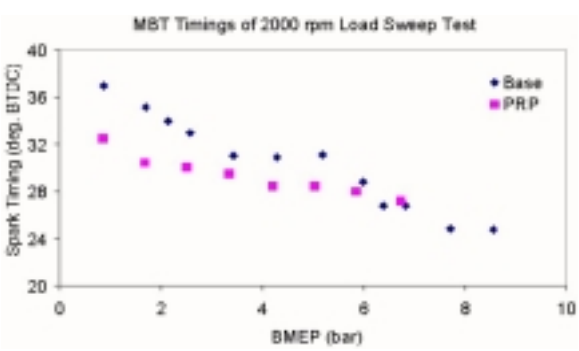


Figure 10. Spark Advance at the 2000 RPM Load Sweep

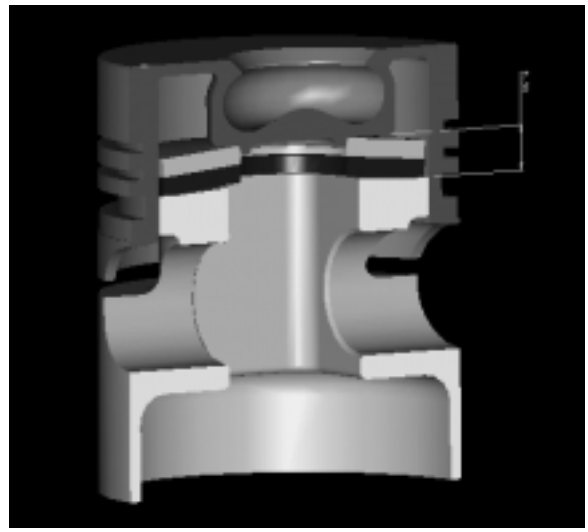


Figure 11. CI PRP Initial Solid Model Design

and it has been approved. With this time, we hope to test a stiffer spring set in the SI PRP (utilizing the existing upper and lower piston). Design changes to the springs and retaining ring are being made to improve durability as well.

CI PRP design is proceeding and appears to be feasible despite the package space lost by the combustion bowl, and the non-symmetric design of the bowl. Experience with the SI PRP has been very valuable in the design and analysis of the CI PRP.

Publications

1. "Simulation and Development of a Pressure Reactive Piston for Spark Ignition and Compression Ignition Engines", University of Michigan Graduate Program Report, Jason Martz, Ryan Nelson, Jeff Sanko
2. "Characterization of a Single Cylinder Port Fuel Injection Spark Ignition Engine", University of Michigan Graduate Program Report, Jason Martz

G. University CIDI Combustion Projects

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These projects address the following OTT R&D Plan barriers and tasks:

Barriers

A. NO_x Emissions

B. PM Emissions

Tasks

3. Fundamental Combustion R&D

Introduction

A significant part of the overall OAAT engine combustion program is a well-coordinated University program. These projects were awarded from a carefully crafted competitive bid process; as a result, they form an integral part of the overall engine combustion program. Sandia National Laboratories provides technical management of these projects to ensure a well-focused overall program. Biannual meetings where recent research results are presented and future directions are discussed between the University projects, the National Laboratory projects, and the Industrial partners insure the program remains well focused and collaborative. Following are individual reports on work performed during phase II of these contracts (June 2000 to May 2001).

Radiation Effects on Combustion and NO_x Emissions in Direct Injection Engines

J. P. Gore (primary contact), S. H. Frankel, and X. L. Zhu
School of Mechanical Engineering, Purdue University
Grant Number DE-FG04-99AL66266

Objectives

The objectives of this project are to examine the effects of thermal radiation, using detailed laminar flame calculations, on detailed chemical reactions, including the emissions of NO_x and soot from CIDI engines; to validate the resulting predictions using available experimental data; and to illustrate a method of incorporating a sub-model for the inclusion of the radiation effect in engine simulations.

Approach

The Sandia National Laboratory code OPPDIF is being used as a platform for the laminar flame studies. During a previous year of the project, atmospheric and high-pressure methane air flames were considered to avoid the complications and uncertainties of higher hydrocarbon chemistry. Finite rate soot chemistry was not considered as a first step and soot volume fractions necessary for radiation calculations were obtained from experimental data. Only the emission of thermal radiation from the flame was considered as a first step. This approximation is valid for optically thin flames in the limit of no external radiation such as from hot walls. The results showed that even small reductions in temperature affect the flame structure sufficiently to cause significant differences in the amount of NO_x and CO emitted to the surroundings. The effects were found to be particularly significant for low stretch rate flames leading to qualitative and quantitative changes in the response of the peak flame temperature, and CO and NO_x emissions to the stretch rate. Preliminary evaluation of the effects of radiation from the soot particles and of absorption of radiation revealed that these processes are significant particularly at high pressures.

During the reporting period, several enhancements were made to the Sandia OPPDIF code as follows:

1. Finite rate soot kinetics processes using the global model of Lindstedt were added, including the effects of soot formation on the concentrations of gaseous species, density of the two-phase mixture, and gas phase energy balance. Thermophoretic transport of soot was considered.
2. The effects of radiation from the gas species as well as from the soot particles were added to the energy equation, and the relative contributions from the two were studied.
3. The effects of self-absorption of radiation energy emitted by one part of the flame by other parts were considered using an integral method with an exact solution for the case of parallel plane gas layers.
4. Comparisons with existing data for atmospheric pressure flames with and without soot were made specifically to evaluate the effects of radiation, including self- absorption on the structure.
5. The effects of higher air temperatures representative of the compressive heating observed in actual engines were examined.
6. Preliminary calculations with heptane as the fuel were conducted using the LLNL mechanism available at the University of Utah website.

Results and Conclusions

The following results can be summarized and conclusions reached from the computations of the reporting period.

1. The consideration of finite rate soot chemistry, including the effects of self-absorption, confirms the significance of thermal radiation in determining the concentrations and emission of soot, CO, and NO_x from methane air diffusion flames in the 1 to 80 atm pressure range with a range of air temperatures accounting for compressive heating.
2. The significant reduction in quantitative and qualitative effects of stretch rates on the diffusion flame structure are also observed in the presence of soot radiation and self-absorption.
3. There are three distinct regions in the flame in which emission of thermal radiation by gaseous species and by soot and net self-absorption of thermal radiation by soot occurs. Therefore, none of these three processes can be ignored because of their importance in different parts of the flame.
4. Neglect of the effects of radiation on chemistry for low stretch rate flames leads to 40 to 200% overestimation of CO, NO_x and soot emissions depending on the air preheat and pressure.
5. The inclusion of real hydrocarbon chemistry represented by heptane fuel increases the computational penalty significantly, resulting in a limited set of converged solutions. However, the preliminary results indicate that the effects of radiation transfer on flames with higher hydrocarbon fuels are even more dramatic than those on methane-air flames.
6. Comparisons with predictions for gas phase data from Sandia (Barlow) show excellent agreement for three partially premixed flames when the effects of both emission and absorption are

included. Comparisons with existing data from the literature were less satisfactory, emphasizing the need for high quality data in evaluation of flame chemistry computations.

7. The comparisons of soot volume fraction predictions with literature data result in contradictory conclusions, with significant over-prediction of one set of data and significant under-prediction of a second set of data. Therefore, systematic new data with the quality represented by the Sandia data cited above are necessary for evaluation of the radiation-chemistry interactions.

Future Directions

The work during the third year of the grant will involve inclusion of more detailed soot kinetics based on the methods of Frenklach and co-workers, including the effects of soot diameters, agglomeration, aging and radiation property changes; completion of calculations with heptane chemistry; and demonstration of the computational methods in an engine simulation code.

Measurements and Modeling of the Fuel/Air Mixing and Combustion in the Cylinder of a Compression-Ignition Direct-Injection (CIDI) Diesel

Chia-Fon Lee
University of Illinois at Urbana-Champaign
Grant DE-FG04-99AL66267

Objective

The objective of the project of the University of Illinois at Urbana-Champaign is to provide detailed information on the mixing and combustion processes in a small bore CIDI engine. Our second-year effort involves performing Exciplex planar laser-induced fluorescence (PLIF) experiments to measure the distributions of liquid and vapor phase fuel in the cylinder and initiating nature flame emission experiments to image the chemiluminescence and flame luminosity in the cylinder. This report covers results obtained from the above two sets of experiments, as well as some studies using Mie Scattering during the second year.

Results

I. Optical Engine

The engine used in all the studies is based on the 1.2 liter, 4-cylinder Ford DIATA CIDI engine. The engine is equipped with a Bosch common rail electronic fuel injection system and is capable of electronic port deactivation for swirl modulation. The engine has external cooling/heating and oiling systems, both with reservoirs and immersion heaters in order to bring the engine up to operating temperatures more quickly. All engine operation and data acquisition were performed with the LabView software of National Instruments. Optical access to the combustion chamber is achieved by using a quartz piston and adding quartz side windows. The quartz piston mimics the shape of the production piston in order to preserve the original configuration of the engine. A mirror is mounted within the Bowditch piston extension, which reflects the desired signal from the combustion chamber to the imaging system. The optical engine design also allows for rapid cleaning of the quartz piston and side windows, since significant fouling is likely to occur from liquid impingement and soot buildup. The conversion and instrumentation of the engine to an optical engine was completed in early December of the year 2000. The laser diagnostics were performed shortly thereafter.

II. Mie Scattering

The main reasons Mie scattering was performed within the engine were to verify the mechanical operation of the optical engine and to verify that the electronics were operating in the manner they were designed. Images of the Mie scattering investigations were completely successful. These Mie scattering images helped verify operation of not only the optical engine, but also the electronic

systems necessary to synchronize the camera and laser operations.

III. Exciplex Planar Laser-Induced Fluorescence (PLIF)

Simultaneous liquid and vapor images were taken within the engine. Because the presence of oxygen severely quenches the exciplex fluorescence, the engine was supplied with nitrogen and was motored for all cases. The engine was operated in a skip fire mode for all exciplex tests - one injection cycle was followed by 10 flushing cycles. Incoming laser energies were constant throughout testing at 10 mJ per pulse at a wavelength of 355 nm. The cameras were gated for 5 μs in all images. Images were taken every π crank angle degree after the first evidence of liquid within the cylinder. Four testing parameters were investigated in this study. The effect of injection timing, injection pressure, swirl number and injection quantity (load) were presented. A single testing point was picked as our baseline case: -5° after top dead center (ATDC) injection timing, 800 bar injection pressure, low swirl (swirl number of 2.5) and a load of 7 mm^3. Variations of the four parameters were made from this baseline case.

Effect of injection pressure: The higher and lower injection pressures investigated were 600 and 1000 bars. The injection delay was observed to be constant across the injection pressures, at roughly 1.50 crank angle degrees. It was found that the rate of liquid penetration for the lowest injection pressure is slower than that of higher injection pressures. Moreover, the jets with the highest injection pressure evaporate the earliest, and the jets with the lowest injection pressures later. This makes physical sense, as higher injection pressures lead to better atomization, which would reduce the vaporization time. Similar to the liquid jets, the vapor penetration rate for the lowest injection pressure is slower than those for the higher injection pressures. Even with no liquid impingement at the lowest injection pressure, there is evidence of vapor impingement, which helps improve mixing.

Effect of injection timing: The earlier and later injection timings investigated were -7 and -3 crank angle degrees ATDC. The development of the liquid jet does not vary significantly for injection timing; the jet penetration is similar for all three timings. It can also be seen that for all injection timings, the liquid impinges upon the bowl lip and/or bowl wall of the piston at the same nominal crank angle degree after start of ignition (ASOI). The liquid jets are seen to evaporate entirely all within π crank angle degrees of each other for the three different injection timings. Throughout the range of image timings, the vapor images are similar for all injection timings.

Effect of swirl number: The higher swirl number investigated was 4.0. The development of the liquid jet is similar for the two swirl numbers; impingement occurs for both cases at the same nominal crank angle ASOI. The liquid jets for the high swirl case were found to evaporate entirely at a slightly earlier crank angle than those in the low swirl case. There is a slight difference in how quickly the vapor becomes distributed throughout the cylinder for the higher swirl number.

Effect of load: The higher load investigated was 10 mm^3. In the case of higher loading, the liquid jets remain within the cylinder for a longer period of time because longer injection durations are necessary to inject more fuel. Surprisingly, there is a slight difference in how quickly the vapor becomes distributed throughout the cylinder; the higher load case distributes the vapor phase throughout the cylinder slightly quicker than the lower load. This could be from more induced turbulence from a longer injection duration. In the late cycle, vapor distributions are similar between the two injection quantities. Overall, the Exciplex PLIF studies provide very useful insight for the fuel/air mixing process in CIDI engines and provide a valuable set of data for the verification of the modeling of sprays in CIDI engines.

IV. Natural Flame Emission

In order to facilitate combustion, the nitrogen intake line was switched to an ambient air supply. Images of the flame luminosity were taken every π crank angle degree after the first evidence of ignition within the cylinder. The engine was operated in a skip fire mode for all combustion tests - one injection cycle was followed by 10 flushing cycles. Injection timings (-7°, -5°, and -3° ATDC) were varied in these preliminary combustion tests. The onset of ignition for all three timings is roughly 10 crank angle

degrees ASOI. The intensity of the luminosity seen in any image is related to the local temperature within the combustion chamber. On average, the earliest injection timing gives the highest perceived intensities, which means that it reaches the highest in-cylinder temperatures. This is consistent with what would be expected for diesel combustion. Within a few crank angle degrees after ignition, the entire field of view can be visualized. This means that there is combustion within the squish region that is visible in the engine. An interesting artifact seen in all three injection timings is the evidence of luminosity in the region of liquid impingement at late times ASOI. This leads us to believe that these are either regions of high soot concentrations that have been heated to high temperatures, or that there are actual liquid fuel film fires on the surface of the bowl. Visual inspection of the piston after combustion revealed high concentrations of soot in these areas. Further investigation will improve understanding of the combustion process in CIDI engines.

Understanding Direct-Injection Engine Combustion with Dynamic Valve Actuation and Residual-Affected Combustion

Prof. Chris Edwards
Department of Engineering, Stanford University
Grant DE-FG04-99AL66268

Studies at Stanford have focused on how Variable Valve Actuation (VVA) can be used to (1) induce homogeneous charge compression ignition (HCCI) over a broad range of operating conditions without the need to throttle and (2) incorporate HCCI into an multi-combustion-mode engine capable of meeting consumer demands for power, PNGV targets for efficiency, and Tier II standards for emissions. Both port-fuel injected strategies (minimal cost) and gasoline direct-injection engine strategies are envisioned, with emphasis on direct-injection engines. Gasoline is the fuel of choice in this application, and achieving HCCI with low compression ratio and high-octane fuels is critical to the effort. Key issues that must be addressed include phasing of the HCCI process with piston motion, the dynamic range over which HCCI operation can be achieved, and development of robust control strategies to manage transitions between optimal combustion regimes as speed/load requirements vary.

Achieving HCCI with low compression ratio (10:1) and high-octane fuels (propane, pump octane = 104) via reinduction has been demonstrated at Stanford. These results were obtained using an electrohydraulic VVA system developed at Stanford as shown in Figure 1. This system allows arbitrary lift profiles to be executed by both the intake and

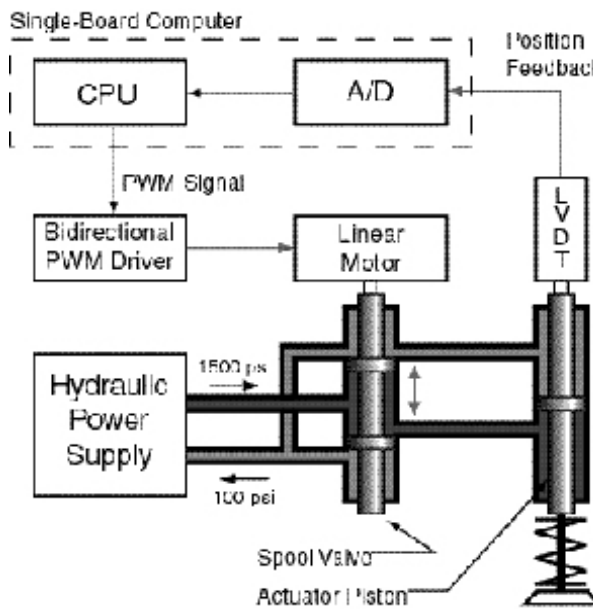

Figure 1. Schematic of the Stanford VVA System Used to Induce HCCI by Exhaust Reinduction

exhaust valves. Using this system, a single engine can operate as a conventional, spark-ignited engine on one operating cycle and execute a completely different mode of combustion on the next cycle. Current capabilities include execution of four of the six major combustion strategies on a cycle-by-cycle basis: homogeneous-charge spark-ignition (SI) combustion, lean-burn SI combustion, residual-

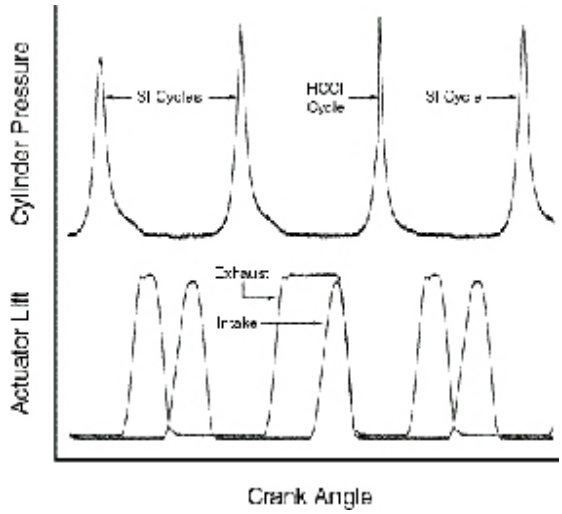

Figure 2. Multi-combustion-mode operation on a cycle-by-cycle basis. The third cycle is HCCI induced by late exhaust valve closing.

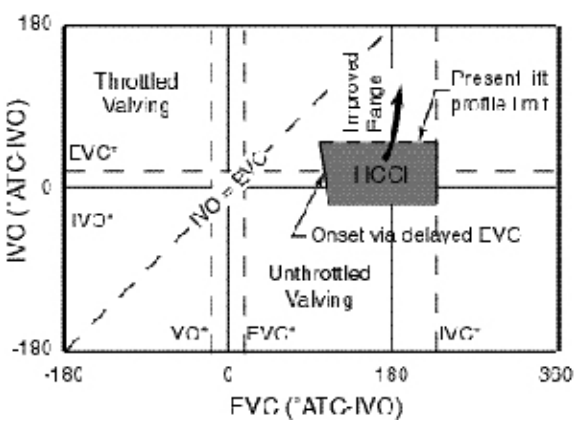

Figure 3. Range of Valve Timings Where HCCI Combustion Can Be Achieved Through Exhaust Reinduction

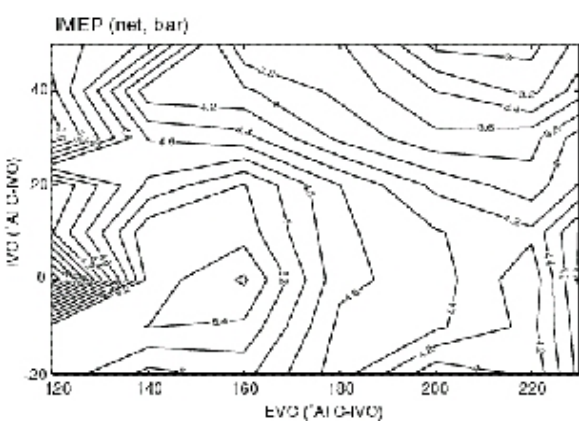

Figure 4. Contours of IMEP over the Range of Valve Timings Where HCCI Combustion Can Be Achieved

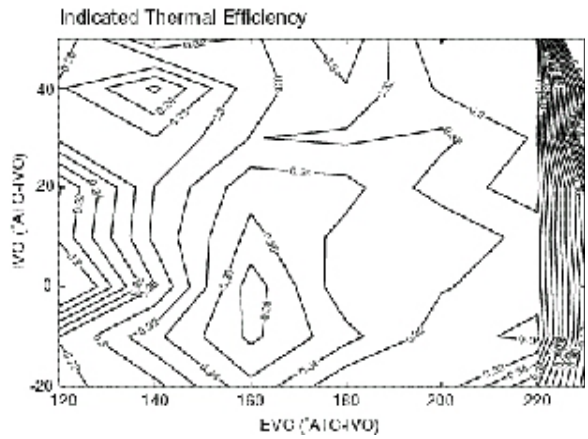

Figure 5. Contours of Thermal Efficiency over the Range of Valve Timings Where HCCI Combustion Can Be Achieved

diluted SI combustion, and HCCI combustion. All of these modes can be operated with or without throttling; when throttling is desired, it is provided by the intake valve. All can also be operated with advanced breathing strategies including optimal phasing at any engine speed, early- and late-intake-valve closing (Miller cycle) and/or modification of the effective expansion ratio through modification of exhaust valve closing.

Figure 2 shows how the system can be used to alternate between combustion modes on a cycle-by-cycle basis. In this example, late exhaust valve closing (holding the valve open during the intake stroke) permits enough hot exhaust to be inducted with the fresh charge to cause compression ignition. Research during the past year has centered on exploring the regimes in which HCCI can be induced by late exhaust valve closing and, in addition, late intake valve opening, as shown in Figure 3.

Values of indicated mean effective pressure (IMEP - a measure of the work produced by combustion) ranging from 30 to 60% of wide-open throttle, SI-engine combustion have been achieved using this strategy, and further improvements in low-end dynamic range are thought to be achievable by further delaying the timing of the intake valve opening (IVO) event.

Figure 4 shows a complete map of indicated mean effective pressure (IMEP) over the range of

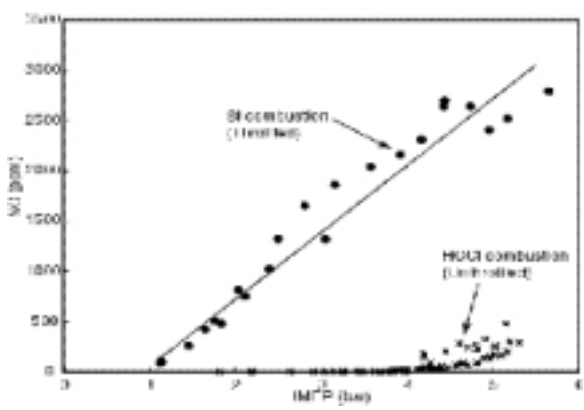

Figure 6. Nitric Oxide Emissions for Reinduction-Induced HCCI in Comparison with SI Combustion

timings where HCCI can be achieved. Figure 5 shows the accompanying thermal efficiency.

These data indicate that use of dynamic valving provides not only reasonable dynamic range (in work output) but also high efficiency. In fact, there exists a ridge along which both high thermal efficiency (34-38%) and wide dynamic range (30-56% load) can be simultaneously achieved.

Current efforts are focused on identifying the emissions advantages that may be accrued using HCCI combustion. In these studies, the same valve delay strategy outlined above is used in a steady-state operating mode. Figure 6 shows the nitric oxide emissions achievable using HCCI in comparison to those of an unthrottled engine. Although HCCI can only be used at 2/3 load and below, within that range, this mode of combustion exhibits NO emissions that are at least one order of magnitude below those of conventional combustion while simultaneously exhibiting higher thermal efficiency. Hydrocarbon and carbon monoxide emission measurements are currently in progress.

In the next phase of the work, advanced valve actuation strategies will be employed to expand the operating range of HCCI, and studies aimed at providing optimal phasing of heat release will be conducted. VVA will also be used in conjunction with direct injection in order to demonstrate integration of HCCI into a multimode combustion engine that includes stratified charge and possibly even conventional diesel combustion.

In addition to measurements in "conventional" (metal wall) engines, an optically-accessible engine tailored for investigating the key parameters of direct-injection HCCI with exhaust reinduction is in construction. The data from this experiment will help researchers to develop a quantitative (computational) capability to predict the performance of these new hybrid engines, and it will enable designers to better understand the processes that lead to optimal system performance.

H. Late-Cycle Air Injection for Reducing Diesel Particulate Emissions

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

Barriers

A. NO_x Emissions

B. PM Emissions

C. Cost

Tasks

3a. Identification of Advanced Combustion Systems

Objectives

- Reduce diesel engine particulate and NO_x emissions through in-cylinder technologies
- Maintain or improve diesel engine fuel efficiency

Approach

- Modeling
  - Use the Computational Fluid Dynamics (CFD) KIVA-III code at the University of Wisconsin's Engine Reasearch Center (ERC) to conduct a parametric study of the effects of late-cycle gas injection on exhaust emissions
  - Use the model to identify the dominant characteristics of gas injection that influence the engine exhaust emissions.
  - Determine the effects of gas composition on the gas injection's effectiveness for reducing emissions.
- Experimental

- Generate experimental data using a Caterpillar 3401 research engine installation at ANL to validate the KIVA results.

Accomplishments

- Modeling
  - Parametric studies showed that the mixing caused by the jet momentum from the introduction of the gas jet is the dominant mechanism that controls the particulate oxidation during the diffusion phase of the combustion cycle. Altering the composition of the air being introduced (oxygen enriched air) provided little additional benefit in reducing particulate matter. Only with low injection pressures were the effects of enriched injected air shown to have additional benefits.
- Experimental
  - Baseline engine data was taken and shown to be comparable with Caterpillar lab data.
  - Engine instrumentation set up for combustion analysis was completed.
  - A modified cylinder head was designed together with Caterpillar. The new head design is being made by Caterpillar, and delivery is expected at the end of FY01.

Future Directions

- Model a modified grid to duplicate the actual gas injection setup planned to run in the engine experimental work.
- Generate experimental engine data to validate the modeling results, including the effect of air composition.
- Experimentally explore optimization of the gas injection with fuel injection characteristics.

Introduction

The desire and need to identify novel approaches for reducing diesel engine emissions has been well documented and recognized by DOE. The application of varying air composition techniques has been expanded to explore the area of an auxiliary gas injection. Such an auxiliary gas injection would introduce high-pressure gas (air or possibly oxygen enriched air) late in the diffusion phase of the combustion cycle. The combination of turbulent mixing and increased localized oxygen content surrounding the oxidizing particulate matter in the combustion chamber would be expected to reduce the overall generation of particulate matter (PM) in the engine exhaust. Also, by introducing this late in the combustion cycle, the formation of NO_x should be unaffected.

By combining this late-cycle injection technique with optimization of the fuel injection timing, reduction of both PM and NO_x simultaneously can become a possibility. This would ultimately lead to an improvement in the traditional PM/NO_x tradeoff that exists with the majority of today's current in-cylinder emission reduction technologies.

Results

A matrix was developed to evaluate the effects of late-cycle oxygen injection parameters along with fuel injection parameters of a truck diesel engine. In collaboration with University of Wisconsin-Madison, analytical studies using the KIVA-3 model were conducted to evaluate the effects of late-cycle oxygen-enriched air injection on both particulate and NO_x emissions. The engine used for these studies was a Caterpillar 3401 single-cylinder engine, which was the same as the engine being installed at Argonne for experimental studies. A 60-degree section of the combustion chamber was used as the model grid for this study in order to conserve computer processing time (see Figure 1). A central gas injector location was employed to evaluate different auxiliary gas injection parameters such as pressure, duration, orientation, timing, and oxygen

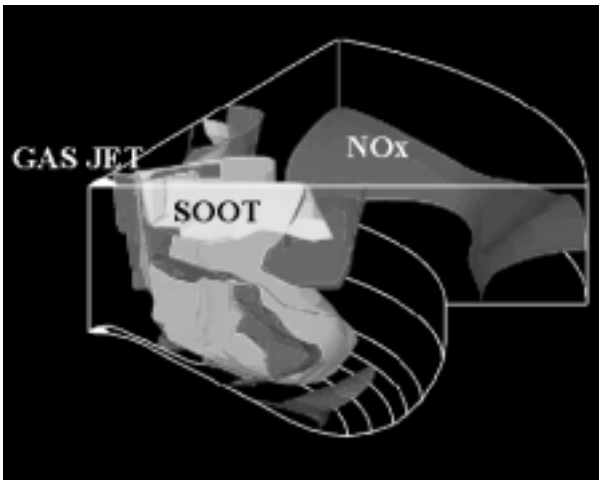

Figure 1. KIVA Model Used for Parametric Study of Gas Characteristics - Central Gas Injection Location

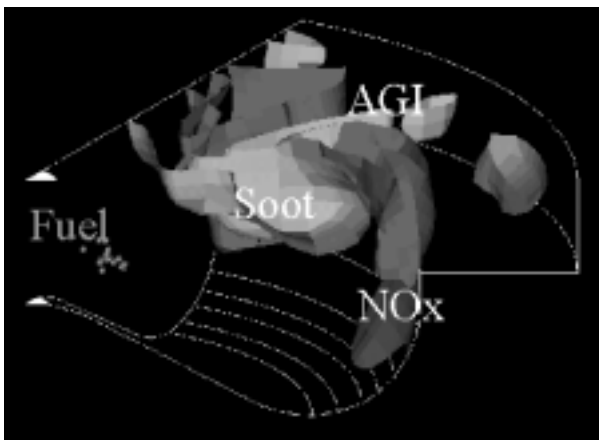

Figure 2. KIVA Model - Edge Gas Injection Location - 60° Grid

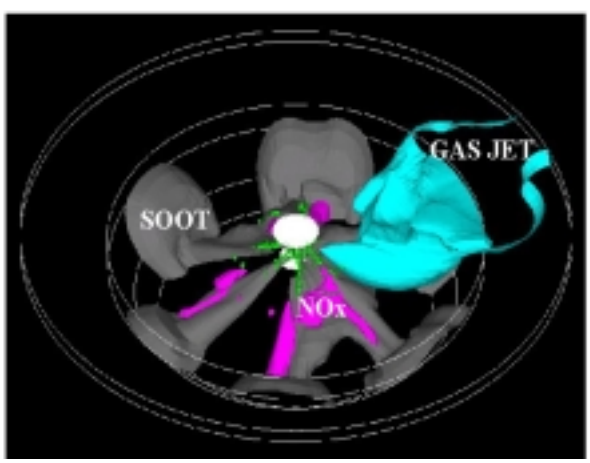

Figure 3. KIVA Model for Late Cycle Gas Injection - Single Side Gas Injection Model - 360° Grid

concentration. More than 80 runs were made to conduct parametric studies (a typical run requires about 36 hrs of CRAY time). Preliminary results from this study indicated that using late-cycle air injection alone could result in more than 50% reduction in soot emissions while minimally affecting NO_x emissions.

By combining an auxiliary air injection system with modification to the fuel injection system, the model showed benefits both in further emissions reduction and in improved engine fuel efficiency. The graph in Figure 4 shows the simultaneous reduction in both NO_x and particulates achieved through this approach at one specific operating condition. In addition, the graph shows an improvement in fuel consumption. Further analysis has shown that the improvement in fuel consumption would be more than adequate to provide the additional energy needed to generate the air injection pressure for the gas injection.

The KIVA model has also been used to determine the effects of relocating the air injector in the combustion chamber. This approach was important in generating model data that could more easily be verified with the engine and in determining the feasibility of locating an air injector in various locations of the engine cylinder head. The use of a centrally located injector required the development of a dual fluid single injector. A more likely approach would be to add an additional air injector into the cylinder head, separate from the fuel injector. These studies indicated that a side or "edge" air injector was also capable of achieving NO_x and particulate emissions reductions, as shown in Figure 2. The quantity of reduction, however, was not as great as with the central injector location, according to the model results. Also modeled was the full 360-degree grid shown in Figure 3.

The experimental phase of the program has only just begun with completion of baseline engine performance data on the recently completed engine test facility. An experimental program to validate the KIVA model results will be completed in the 1st half of FY2002.

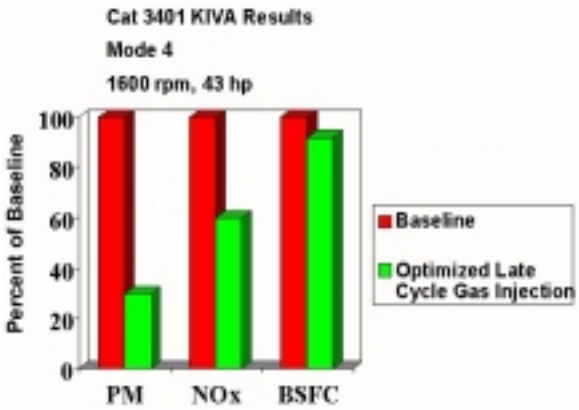

Figure 4. KIVA Model Results - Shows Simultaneous PM and NO_x Reduction

Patents

ANL Patent issued No. 6173567 B1 on 1/15/01, which details the use of late-cycle enriched air injection for reduction of particulate emissions in diesel engines.

Presentations

DOE Program Review Committees

1. DOE OTT's OAAT CIDI Merit Review, 6/22/99, "Diesel Engine Particulates Reduction by Late Cycle Injection of O_2 Enriched Air," by Ramesh Poola, ES; Daniel Mather, University of Wisconsin ERC.
2. DOE OTT's OAAT CIDI Merit Review, 5/24/00, "Diesel Engine Particulates Reduction by Late Cycle Air Injection," by Doug Longman, ES.
3. DOE OTT's OHVT Diesel Engine Emissions Reduction (DEER) Workshop, San Diego, CA, 8/23/00, "Late-Cycle Injection of Air / Oxygen-Enriched Air for Diesel Exhaust Emissions Control," by Daniel Mather, University of Wisconsin ERC (presented on behalf of Argonne).

Other Presentations

1. American Society of Mechanical Engineers Fall 2000 Conference, Peoria, IL, 9/26/00, "A Parametric Study of the Factors that Influence the Impact of Auxiliary Gas Injection in a Diesel Engine," by Daniel Mather, University of Wisconsin ERC.

Figure 5. ANL Experimental Engine Facility Caterpillar 3401 Research Engine

2. GlobeEx 2000 Conference and Tradeshow, Las Vegas, NV, 7/25/00, "Air Composition Management to Reduce Diesel Exhaust Emissions," by Doug Longman.
3. External Peer Review of Variable Air Composition for Enhanced Engine Combustion, Argonne, IL, 11/14/00, "Diesel Engine Particulate Reduction by Late-Cycle Injection of Air / O_2 Enriched Air," by Doug Longman.

Publications

1. Mather, D.K., E.M. Kurtz, D.E. Foster, R.B. Poola, D.E. Longman, A. Chanda, and R.J. Vachon, *A Parametric Study of the Factors that Influence the Impact of Auxiliary Gas Injection in a Diesel Engine,* American Society of Mechanical Engineers Fall 2000 Conference, Peoria, IL, 9/26/00.

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

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

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

E. Toxic Emissions

F. Ultra-fine Particles

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions

Objectives

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

Approach

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

Accomplishments

- Studied ignition under diesel conditions and identified key chemical reactions responsible for ignition
- Used ignition insights to explain role of diesel ignition enhancers

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

Future Directions

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

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Introduction

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

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

Approach

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

Kinetic reaction models have been developed at LLNL for many realistic hydrocarbon fuels and fuel mixtures, most recently for n-heptane [3], a single-component fuel that represents many of the combustion characteristics of diesel fuel. The diesel modeling work has computed diesel ignition and combustion using the heptane model and additional

models for many oxygenated additives of interest to industry and DOE, including methanol, ethanol, dimethyl ether, dimethoxy methane, and, in the past year, biodiesel fuels.

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

Results

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

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

It is important to realize, however, that 35% oxygen in the fuel mixture corresponds to a fuel which is dominated by the oxygenated additive, so most practical operations in real diesel engines

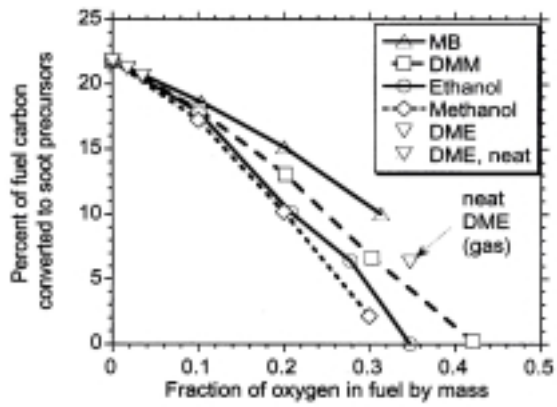

Figure 1. Reduction of PM precursors with fraction of oxygen in fuel. Oxygenated additives include methyl butanoate (MB, a biodiesel fuel), dimethoxy methane (DMM), ethanol, methanol and dimethyl ether (DME).

would take place at oxygen levels of less than 10%. Still, the computed results not only provide the chemical understanding of the mechanism of soot reduction, but also suggests strongly that the critical parameter for soot reduction is the total amount of oxygen and not the particular type of molecule which contains the oxygen. This type of result can guide studies looking for better, more efficient and perhaps more engine-friendly additives that will still be effective at providing soot reduction.

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

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

In other work carried out this year, kinetic modeling was used to simulate flame propagation near the lean limit of combustion at pressures in the ranges found in diesel combustion, which are

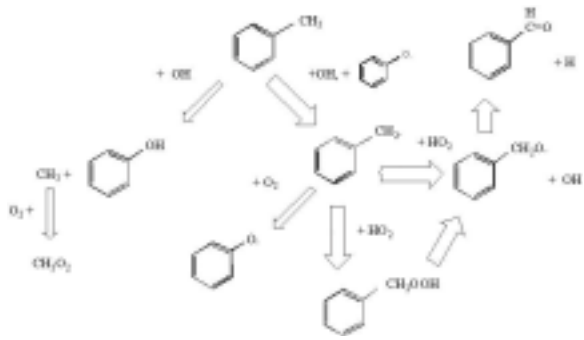

Figure 2. Reaction pathways for toluene consumption. Toluene is shown in the top center of the figure, showing reactions with OH to produce either phenol or the benzyl radical. The benzyl radical then reacts via other paths to produce benzylaldehyde. A key feature of this process is that most of the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

commonly as high as 100 bar. This work [8] showed that these high pressures modify the rates of specific elementary chemical reactions that are important for flame propagation, especially reactions between atomic hydrogen and molecular oxygen:

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

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

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

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

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

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

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

Conclusions

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

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J. Hydrocarbon Speciation for Lean-NO_x Catalyst Analysis

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ORNL CRADA # ORNL-97-0484

Industry Participants: Detroit Diesel Co., Nabil Hakim, Jim Hoelzer

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

Barriers

A. NO_x Emissions

C. Cost

Tasks

3. Fundamental Combustion R&D

4e. R&D on NO_x Reducing Technologies

Objectives

- Determine the chemical composition of the hydrocarbons (HC) in diesel engine exhaust with (and without) in-cylinder HC injection that exist or can be generated.
- Determine the effects of specific HCs upon lean-burn catalyst NO_x reduction.

Approach

- Identify species of hydrocarbons in the exhaust gases from DDC Series 30 and Series 50 diesel engines.
- Develop emissions and performance maps with and without in-cylinder post fuel injection using different diesel blends.
- Benchmark performance of various lean-NO_x catalysts.

Accomplishments

- Observed substantial increase in engine-out CO levels with secondary fuel injection. Engine-out NO_x levels were lower, perhaps enabling use of NO_x adsorber catalyst.
- In-cylinder injection species were affected by injection timing and HC/NO_x ratios. PM emissions (mostly soluble organic fraction [SOF]) increased as secondary injection rates increased.
- In-cylinder HC injection results in formation of alkenes (e.g ethylene), higher alkanes (>heptane), and mono-aromatics (benzene), which are good reductants for NO_x emission control devices.

- In-pipe HC injection provided very low fractions of alkenes but large fractions of higher alkanes and branched alkanes, which are fair reductants for lean-burn catalysts.
- No substantial changes in regulated emissions past the turbocharger were noted for two sample locations. The measured HC components were observed to be dependent on engine load.

Future Directions

- No further experiments or analysis planned.

Introduction

It is widely accepted in the automotive research community that lean-NO_x catalysis offers unmatched "passiveness" as a technology for mitigating regulated emissions from CIDI engines, especially when post-injection of hydrocarbon fuel is introduced to enhance reduction. Similarly, NO_x adsorber technology will require a HC reductant — potentially introduced the same way. Research presented in the literature has borne out that the lean-NO_x reduction process is affected by the composition of the HC reductant. Hence, it is reasoned that manipulation of the hydrocarbon post-injection process can be utilized to tailor the NO_x conversion and HC composition in the exhaust. An important step in this research is identification and quantification of the various hydrocarbon species in the exhaust stream.

Approach

Experimental Apparatus

A DDC Series 30/Navistar 7.3l diesel engine was modified to permit secondary fuel injection (i.e. post injection) using the hydraulically-actuated, electronically controlled unit injection (HEUI) system. The electronics control (a modified drive module provided by Navistar) permitted variations in start point, duration and flow-rate of post injection pulse. Figure 1 shows the engine and exhaust sampling equipment installed at ORNL. Determination of HC speciation (over 50 compounds examined) utilized gas chromatograph/mass spectroscopy (GC/MS), supplemented with Auto/Oil Air Quality Improvement Research Program (AQIRP) gas chromatography/flame ionization detection (GC/FID) and other methods to detect the lightest gases and aldehydes/ketones. (The AQIRP developed analytical methods based on GC/FID for speciating light HCs that were collected in bags from the FTP.)

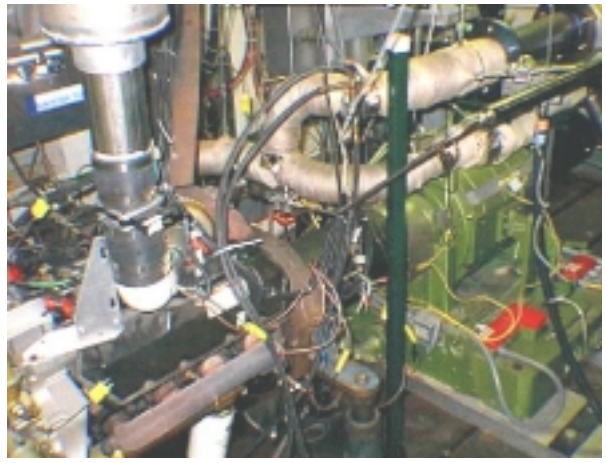

Figure 1. DDC Series 30 Engine Installed at ORNL

Experimental Approach

The experimental approach was to use the range of control over secondary fuel (DF-2) injection to determine the optimum injection timing to obtain a maximum HC/NO_x ratio out of the engine, and to determine the effects of secondary injection upon HC species, NO_x and CO. The engine was mapped with a 42-point matrix of engine conditions at 1900 rpm (peak torque) and 3200 rpm (rated power). A five-point load sweep (100%, 80%, 60%, 40%, 20%) was conducted at each of the two speeds, and at four HC/NO_x ratios for each load point. Two additional points were done at 0% load for each speed, with no additional HCs required to meet the highest HC/NO_x ratio. Data on engine performance, regulated emissions constituents, and hydrocarbon species were collected at each operating point in the matrix. A total of over 50 compounds were measured. Comparisons were made of HC species and other emissions sampled at the turbocharger outlet and at

the catalyst inlet. Similar comparisons were made for the configurations where secondary injection is introduced in-cylinder and in the exhaust pipe.

Results

A parametric variation of secondary injection timing (constant duration of 632 μ-sec) revealed that 220 degrees ATDC gave the highest consistent HC/NO_x ratio (Figure 2), and this value was used in the remainder of the experiments. In general, NO_x levels were somewhat constant during this sweep of injection timing, and CO levels increased slightly when injection was introduced late in the exhaust stroke. The engine was baselined at peak torque speed of 1900 RPM (100% load) both with and without in-cylinder injection occurring at 220 deg ATDC. In the absence of secondary injection, engine-out NO_x levels were highest and CO and HC levels were lowest. The injection pulsewidth was steadily increased to yield data at three additional conditions: HC/NO_x=3,6 and 8 (Figure 3). As greater amounts of fuel were injected, engine-out CO levels increased, signifying oxidation of excess hydrocarbons. NO_x diminished slightly and hydrocarbons increased dramatically as expected.

At the 3000 RPM condition, in-cylinder secondary fuel injection resulted in increased CO levels and decreased NO_x. The cause of the NO_x emissions decrease is still unclear, although several research groups have observed the same phenomenon with late in-cylinder injection. One explanation for the NO_x decrease is selective non-catalytic reduction of the NO_x by the fuel HCs, although specific experiments to validate this theory have not been done.

To investigate the effects upon various HC species arising from changes in secondary injection timing, two timings (120 deg ATDC and 220 deg ATDC) were checked at moderate speed (1900 RPM) and reduced load (60%). Injecting HCs later in the exhaust stroke (220 deg) decreases the amount of olefins or alkenes (propylene) and aromatics (benzene) produced and increases the amount of alkanes or paraffins (decane) (Figure 4). Olefinic compounds are easily oxidized and so tend to have poor oxidation stability.

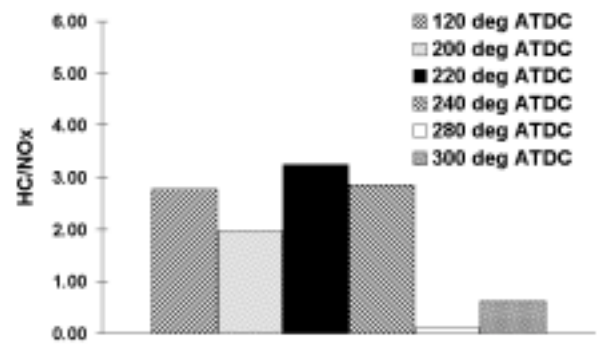

Figure 2. HC/NO_x Ratios for Various Secondary Injection Timings (1900 RPM, 60% load)

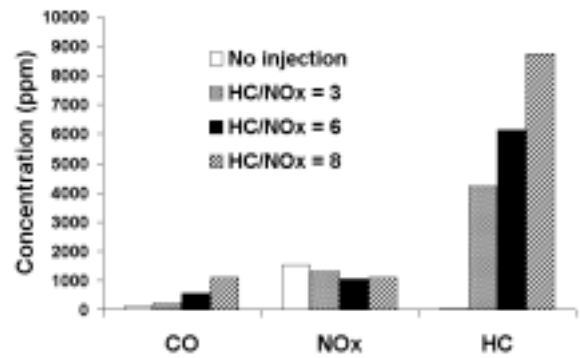

Figure 3. Engine-Out Emissions at Three HC/NO_x Ratios (1900 RPM, 100% load)

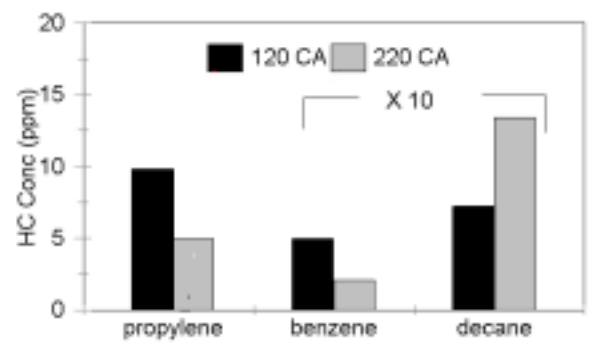

Figure 4. Effect of Secondary Injection Timing on HC Species (1900 RPM, 60% load)

Next, load was increased and HC species from in-exhaust pipe injection were compared against the previous in-cylinder emissions data (Figure 5). These two locations yield significantly different species, with in-cylinder HC injection demonstrating large fractions of alkenes (e.g ethylene), higher alkanes (>heptane), and mono-aromatics (benzene), which are good reductants for NO_x emission control devices. In-pipe HC injection provided very low fractions of alkenes, but large fractions of higher

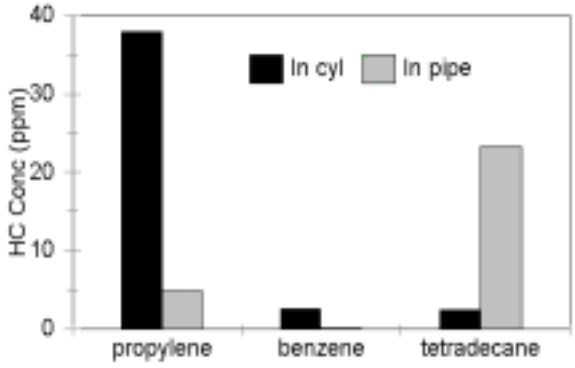

Figure 5. Effect of Secondary Injection Location on HC Species (1900 RPM, 100% load)

alkanes and branched alkanes, which are fair reductants for lean-burn catalysts. A subsequent check of various in-pipe locations showed no appreciable variation in regulated emissions constituents from turbo exit to catalyst inlet. A closer inspection of HC types showed some dependence upon load (and by inference, exhaust temperature), but fuel HCs remained basically independent of sample position. The slightly higher concentrations of HC at the catalyst inlet sampling port may be attributed to less oxidation due to pipe cooling with in-pipe injection.

Secondary injection at increasing pulsewidths generates substantial increases in particulate matter (PM), up to 2.5 gm/hp-hr. Increases in PM were also observed as secondary fuel introduction was moved from in-cylinder to in-pipe. Most of the PM increase was attributed to the increase in soluble organic fraction (SOF).

Conclusions

The importance of these results lies in the relative effectiveness of the various hydrocarbon species for lean-NO_x reduction processes. Alkenes, higher alkanes and mono-aromatics all perform well and appear in significant concentrations in the exhaust according to secondary injection and load. Thus, their role in NO_x mitigation from the tailpipe is validated and further understood, allowing more detailed studies to be mounted in which optimized mixes of these various HC species can be tailored for specific engine configurations and conditions.

VII. HOMOGENEOUS CHARGE COMPRESSION IGNITION

A. Natural Gas HCCI R&D

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Contractor: Lawrence Livermore National Laboratory

Subcontractor: University of California Berkeley, Berkeley, CA

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

Barriers

A. NO_x Emissions

B. PM Emissions

C. Cost

Tasks

1a. Advanced Fuel Systems

3. Fundamental Combustion R&D

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.
- Use our control capabilities to determine and evaluate control and startability strategies.

Approach

- Conduct experiments on a 4-cylinder Volkswagen TDI engine and on a single-cylinder Caterpillar 3401 engine to evaluate startability and control strategies.
- Develop and use single zone and multi-zone chemical kinetics models for analysis of HCCI combustion and for evaluation of possible control strategies.

Accomplishments

Part 1. Analysis

- A single-zone model has been used for evaluation of possible control strategies. In particular, we have considered a system where the equivalence ratio, the EGR and the intake pressure are modulated to obtain satisfactory combustion. The results have been used for generating a full performance map of the engine.
- A multi-zone model has been developed that can take into full consideration the temperature gradients that exist within the cylinder. Our analytical results agree very well with experimental results. This agreement validates the basic assumption that HCCI combustion is dominated by chemical kinetics, with minor (second-order) effects from turbulence, diffusion and mixing. We have validated our methodology with data from Cummins. We have also extended the methodology to analyze long-chain hydrocarbons such as iso-octane.

Part 2. Experimental

- The 4-cylinder Volkswagen TDI has been run under multiple conditions, and we have generated performance maps for this engine, with and without EGR. The results show the allowable boundaries for operation in the HCCI engine.
- A Caterpillar 3401 engine is being converted to HCCI operation. This is a single-cylinder engine with 2.2 liter displacement, and it is representative of heavy truck engines. Experiments have been initiated with the engine operating in HCCI mode.
- Ford has recently donated to us a Zetec 2.0 liter engine that has a cross-flow head with independent cooling passages into each cylinder. This configuration significantly reduces the cylinder-to-cylinder variations, resulting in a broader range of HCCI operation.

Future Directions

- The two fundamental problems of HCCI engines are the difficulties in controlling the engine and achieving high power. In this project, the analytical and experimental work are dedicated to solving these two problems. We have studied HCCI engine control by thermal means. Further control methodologies will be studied. Possible methods of HCCI engine control that will be analyzed include the use of additives (dimethyl ether, diesel, etc.), inlet heating, EGR, and exhaust throttling.
- We will use our analytical techniques to study the details of the combustion process in the Volkswagen TDI engine and to predict the emissions of hydrocarbon and CO emissions.
- We will 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.
- Experiments will be run using the Caterpillar 3401 engine (an ideal test bed for heavy truck engine applications).

Introduction

This work supports the need to develop a new combustion concept that allows both high efficiency and low emissions for trucks and SUVs. The high efficiency of diesel engines is highly desirable for improving the fuel economy of light-duty trucks and SUVs. 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.

Analysis

All of the modeling computations in this study are carried out using the Hydrodynamics, Chemistry and Transport (HCT) model. HCT has been modified to include a heat transfer correlation, a turbocharger, and an internal EGR model. Two different models have been developed: a single-zone model and a multi-zone model.

Part 1. Single-Zone Model

The single-zone model ignores spatial variations in the combustion chamber, treating heat loss as a distributed heat transfer rate over the whole volume. The computational model treats the combustion chamber as a homogeneous reactor with a variable volume. The single-zone model has been used for investigating an equivalence ratio-EGR control system for HCCI engines. For this application, HCT is linked to an optimizer that determines the operating conditions that result in maximum brake thermal efficiency, while meeting the restrictions of low NO_x (less than 100 ppm) and peak cylinder pressure (less than 250 bar). The results show the operating conditions that yield optimum efficiency as a function of torque and engine speed. For zero torque (idle), the optimizer determines operating conditions that result in minimum fuel consumption. The optimizer is also used for determining the possibility of transitioning between HCCI and spark-ignited modes of operation.

Figure 1 shows a schematic of the thermal system used for HCCI engine control, and Figure 2 shows the engine performance map, including lines of constant brake thermal efficiency for the engine

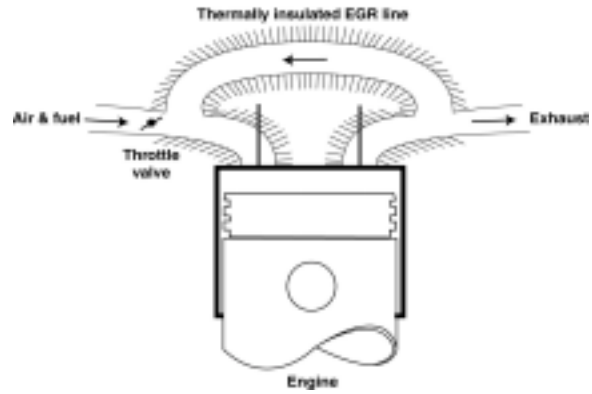

Figure 1. Schematic of the equivalence ratio-EGR control system for the HCCI engine.

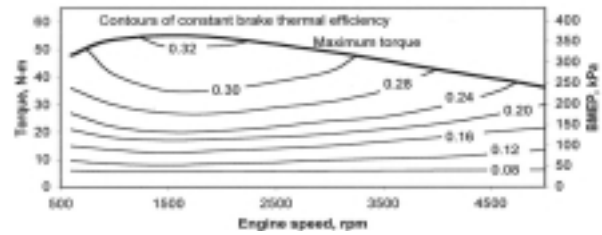

Figure 2. Performance maps for the Volkswagen TDI engine operating in HCCI mode under the equivalence ratio-EGR control strategy.

operating with the optimum equivalence ratio, EGR and intake pressure. The engine performance map shows that the brake thermal efficiency is quite high for the low power output that is being generated. The high efficiency is due to the absence of throttling losses in most of the operating range and due to the fast combustion using HCCI, which approaches the combustion obtained in an ideal Otto cycle.

Part 2. Multi-Zone Model

The multi-zone model can be used to make detailed performance estimates. We have developed a methodology for predicting HCCI combustion and emissions that combines a detailed fluid mechanics code with a detailed chemical kinetics code. Instead of directly linking the two codes, which would require an extremely long computational time, the methodology consists of first running the fluid mechanics code to obtain temperature profiles as a function of time. These temperature profiles are used as input to a multi-zone chemical kinetics code. The advantage of this procedure is that a small number of zones (10) is enough to obtain accurate results. This procedure achieves the benefits of linking the fluid

mechanics and the chemical kinetics codes with a great reduction in the computational effort, to a level that can be handled with current desktop computers. The success of this procedure is in large part a consequence of the fact that for much of the compression stroke the chemistry is inactive and thus has little influence on fluid mechanics and heat transfer. Then, when chemistry is active, combustion is rather sudden, leaving little time for interaction between chemistry and fluid mixing and heat transfer. This sequential methodology is capable of explaining the main characteristics of HCCI combustion that have been observed in experiments.

The validated multi-zone model will be used for detailed analyses of operating points selected as optimum by the single-zone model. The results will determine a very accurate picture of all the important operating parameters of HCCI combustion (peak cylinder pressure, efficiency, NO_x, CO and HC emissions). The results for HC and CO emissions obtained from the multi-zone model will be used to determine the required characteristics of a catalytic converter that will oxidize enough of these pollutants to meet the desired emissions standards. The detailed model will also be used to study the effect of combustion chamber design on HCCI engine efficiency and emissions. The analysis will evaluate the effect of crevices, piston bowls, etc. on engine operation.

The model has recently been validated with experimental data generated by Cummins for propane. The model has also been extended to analyze long chain hydrocarbons (iso-octane, n-heptane). Results for propane and iso-octane have shown a great accuracy in predicting heat release rates, pressure traces and emissions of HC and CO emissions. Figure 3 shows a comparison between experimental and numerical pressure traces for iso-octane.

HCCI Experiments

Our experimental work has had three major thrusts: a 4-cylinder TDI engine, a single-cylinder Caterpillar 3401, and a Ford Zetec 4-cylinder engine, which has been recently donated to our program. Experiments with the CFR engine were successfully concluded last year.

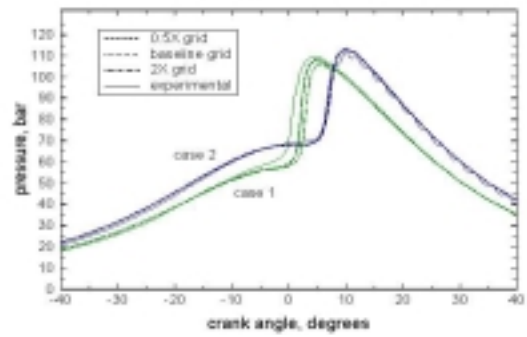

Figure 3. Comparison between experimental pressure traces and calculated pressure traces for the experimental conditions evaluated at Cummins for iso-octane fuel on a 10.5:1 compression ratio engine.

Part 1. 4-Cylinder TDI Engine Experiments

Experiments have been conducted for naturally aspirated operation with propane fuel. The engine performance, combustion process, and emissions are monitored for variations in intake temperature and fuel flow rate. The engine has been operated over a wide range of conditions. The intake temperature ranges from roughly 105°C to 145°C. Five different fuel flow rates have been studied: 0.34 g/s, 0.50 g/s, 0.65 g/s, 0.72 g/s, and 0.83 g/s; all at 1800 rpm, no throttle. Operating an HCCI engine in multi-cylinder mode is more difficult than running a single-cylinder engine in HCCI mode because HCCI combustion is very sensitive to temperature. Small differences in temperature from one cylinder to the next can cause a colder cylinder to misfire or a hotter cylinder to ignite very early.

Figure 4 shows the engine performance map for the TDI engine. Performance is limited on the low temperature end by misfire and on the high temperature end by knock. Figure 5 shows pressure traces for each cylinder at four different intake manifold temperatures at 0.65 g/s fuel flow rate. At the lowest temperature operating point, 108°C intake temperature, operation is inconsistent between the cylinders. At these conditions, intake manifold temerature inhomogeneities or slight variations in cooling water temperature, oil temperature, or compression ratio of each cylinder could result in significant variations in the combustion process. For example, in the VW TDI engine the cooling water runs longitudinally through the engine entering near

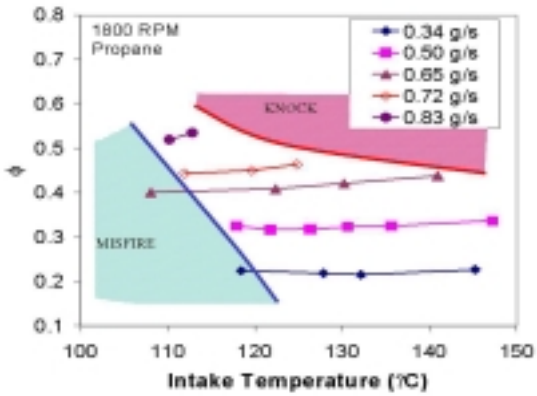

Figure 4. Performance map for the Volkswagen TDI engine in HCCI mode with propane fuel. The performance range is limited by misfire at the low temperature end and by knock at the high temperature end.

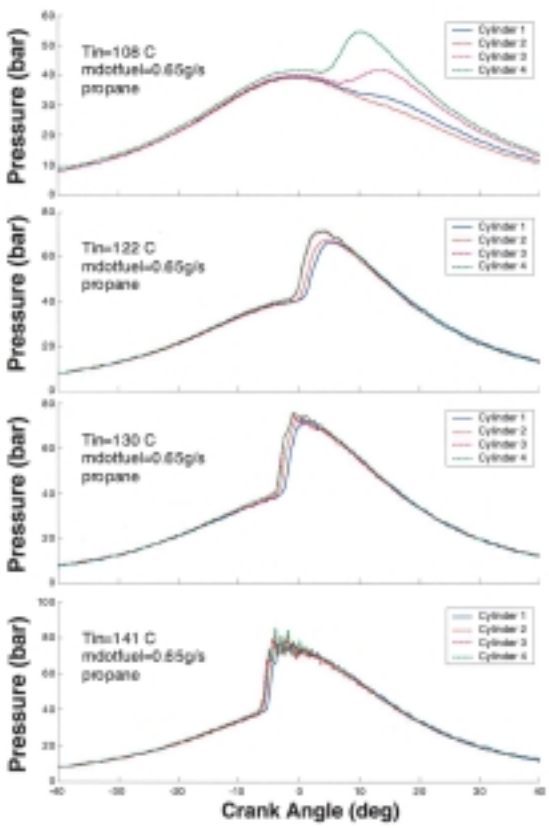

Figure 5. Pressure traces for four different intake manifold temperatures at 0.65 g/s fuel flow rate (average of 332 instantaneous traces), for the Volkswagen TDI engine operating in HCCI mode on propane fuel.

cylinder 1 and exiting at cylinder 4. Consequently, a higher water temperature gradient along the engine may form, resulting in variations in heat transfer throughout the engine. The 108°C operating point may be near the lower limit of operation, and the slight differences in the parameters mentioned above could explain this inconsistent operation.

Figure 5 shows that as the intake temperature is increased the combustion process becomes more consistent among the cylinders. At the highest temperature in the range (141°C) there is little difference between the cylinder pressure traces, but combustion is very advanced, and significant pressure oscillations (knock) are observed. The pressure oscillations set an upper limit to the intake temperature for satisfactory combustion. The results of Figure 5 show that controlling individual cylinders requires a strategy strong enough to overcome a variety of operating factors.

The TDI engine combustion chambers will be modified from the current bowl-in-piston chamber to a pancake combustion chamber by installing flat-top pistons. This change will significantly improve overall combustion performance by reducing heat transfer. Other modifications to the intake and exhaust system will be done to achieve HCCI operation.

Part 2. Caterpillar 3401 Engine

The Caterpillar 3401 is representative of a family of engines that can be applied to heavy-duty trucks. In-cylinder pressure measurements will allow direct comparison with the HCT simulations of the start of combustion, heat release rate, and indicated mean effective pressure (IMEP). Engine-out emissions will also be compared to the simulations.

The converted Caterpillar 3401 engine will be run in HCCI mode over a wide range of operating conditions with multiple fuels (methane, propane, natural gas, etc.) to analyze engine performance and validate our models. The use of a large-displacement, single-cylinder engine makes it easier to obtain the high-quality data necessary for model validation. This engine will be equipped to handle intake heating, EGR, and fuel additives. Experiments will be performed to further study these control options. Because in-cylinder pressure

transducers may be impractical for production engines, investigation into the use of low-cost block mounted sensors for detection of peak pressure rise and peak heat release will be performed. Control strategies can be developed and tested on the single-cylinder engine before being implemented in the more complicated environment of the multi-cylinder TDI engine. Strategies for starting the engine will also be analyzed. Some possibilities are additives (dimethyl ether, diesel, etc.), intake preheating, and variable compression ratio.

Conclusions

During the present year we have made significant progress in evaluating HCCI combustion, both by analysis and experiments. In analysis, we have used our detailed chemical kinetics model to generate an engine performance map and evaluate a thermal control strategy. A multi-zone model has been developed that can predict HCCI combustion parameters with very good accuracy. The multi-zone model is the only existing procedure for calculating HC and CO emissions out of an HCCI engine. In experimental work, we have completed a set of runs with the 4-cylinder TDI engine. We also have a single-cylinder Caterpillar 3401 running on HCCI mode and a Ford Zetec engine that will be converted to HCCI combustion..

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1. "Thermal charge conditioning for optimal HCCI engine operation," Joel Martinez-Frias, Salvador M. Aceves, Daniel Flowers, J. Ray Smith, Robert Dibble, Accepted for publication, Journal of Energy Resources Technologies, 2001.
2. "HCCI In A CFR Engine: Experiments And Detailed Kinetic Modeling," Daniel Flowers, Salvador M. Aceves, Ray Smith, John Torres, James Girard, and Robert Dibble, SAE Paper 2000-01-0328.
3. "A Multi-Zone Model for Prediction of HCCI Combustion and Emissions," Salvador M. Aceves, Daniel L. Flowers, Charles K. Westbrook, J. Ray Smith, William Pitz, Robert Dibble, Magnus Christensen and Bengt Johansson, SAE Paper 2000-01-0327.
4. "Detailed Chemical Kinetic Simulation of Natural Gas HCCI Combustion: Gas Composition Effects and Investigation of Control Strategies," Daniel Flowers, Salvador M. Aceves, Charles Westbrook, J. Ray Smith and Robert Dibble, Journal of Engineering for Gas Turbines and Power, Vol. 123, pp. 433-439, 2001.
5. "Compression Ratio Effect on Methane HCCI Combustion," Salvador M. Aceves, J.R. Smith, Charles Westbrook and William Pitz, ASME Journal of Engineering for Gas Turbines and Power, Vol. 121, pp. 569-574, 1999.
6. "HCCI Combustion: Analysis and Experiments," Salvador M. Aceves, Daniel L. Flowers, Joel Martinez-Frias, J. Ray Smith, Robert Dibble, Michael Au, James Girard, SAE Paper 2001-01-2077.
7. "Operation of a Four-Cylinder 1.9L Propane Fueled Homogeneous Charge Compression Ignition Engine: Basic Operating Characteristics and Cylinder-to-Cylinder Effects," Daniel Flowers, Salvador M. Aceves, Joel Martinez-Frias, J. Ray Smith, Michael Au, James Girard, Robert Dibble, SAE Paper 2001-01-1895
8. "1.9-Liter Four-Cylinder HCCI Engine Operation with Exhaust Gas Recirculation," Michael Y. Au, James W. Girard, Robert Dibble, Daniel Flowers, Salvador M. Aceves, Joel Martinez-Frias, Ray Smith, Christian Seibel, Ulrich Maas, SAE Paper 2001-01-1894.
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B. HCCI Combustion Research Using Liquid-Phase Fuels

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Prime DOE Contract Number: DE-AC04-94AL85000

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

Barriers

A. NOx Emissions

B. PM Emissions

C. Cost

Tasks

1a. Advanced Fuel Systems

3. Fundamental Combustion R&D

Objectives

- Establish an HCCI engine research laboratory to apply advanced diagnostics to investigations of HCCI combustion fundamentals.
  - Results will be passed to U.S. industry to help them overcome the technical barriers to the development of HCCI engines.
  - Building the laboratory is a multi-year task. FY 2001 objectives include:
    - > Design and install lab subsystems common to all-metal and optically accessible engines.
    - > Complete design and assembly of all-metal engine and begin initial experiments.
    - > Design optically accessible engine.
- Conduct chemical-kinetic rate computations of the following aspects of HCCI:
  - Low-load operation: Investigate kinetic effects on the heat release rate and on HC and CO emissions.
  - EGR addition: Determine the potential of exhaust gas recirculation (EGR) to slow the heat release rate.

Approach

- HCCI Engine Laboratory: Build a versatile facility with both all-metal and optically accessible engines to allow investigations of various fueling, mixing, and control strategies.
  - Compression ratio variable from 13:1 to 21:1, and engine speeds to 3600 rpm.
  - Variable swirl to alter mixing and heat transfer rates.
  - Three fueling systems: premixed, port fuel injection (PFI), and direct-injection (DI) gasoline or diesel fuel.
  - Intake charge conditioning for mixture (including EGR), temperature, and pressure control.
  - Optical engine with full optical access of combustion chamber near TDC, optional quartz cylinder, and drop-down cylinder for rapid cleaning.
- Compute the chemical-kinetic rate using iso-octane as a surrogate for gasoline-like fuels to develop a fundamental understanding of:
  - The role of kinetics in slowing the heat release rate at low fuel loads and the potential for bulk-gas contributions to HC and CO emissions.
  - The effects of EGR on the heat release rate, independent from its effects on ignition timing.
    - > Compensate for reduced compression heating to isolate the effect on combustion rate.

Accomplishments

- Laboratory is on track as planned.
  - Subsystems for intake-charge conditioning and oil and water heating and circulation are complete. Fueling systems are on track to be completed before the end of this FY.
  - Metal engine is complete, and motored operation has been tested to 3000 rpm with good compression curves. On track to test fired-operation and begin experiments by end of FY01.
  - Design of optical engine and stress analysis are complete. On track to produce detailed drawings by the end of FY01.
- Conducted two computational studies of HCCI combustion using CHEMKIN with the full kinetic mechanisms for iso-octane (from LLNL).
  - Completed a parametric study over a range of low-load conditions and showed the limits of complete bulk-gas combustion and the associated HC and CO emissions.
  - Showed that EGR reduces peak heat release rates, but that most reduction observed in past experiments was due to a shift in ignition time caused by reduced compression heating.

Future Directions

- Conduct HCCI experiments with fully premixed fueling.
  - Establish a base operating point using iso-octane fuel.
  - Investigate operating range and sensitivity by systematically varying conditions about the base point and comparing results with CHEMKIN calculations.
- Investigate PFI and DI-gasoline fueling as compared to fully premixed.
- Establish exhaust emissions testing (HC, CO, and NO_x).

- Complete setup of optically accessible engine.
- CHEMKIN calculations: Conduct a full parametric study of the effects of EGR/residuals, and make additional computations as needed to support metal-engine experiments.
- Obtain a variable valve timing (VVT) system and begin developing control methodology.

Introduction

Homogeneous charge, compression ignition (HCCI) is an alternative engine combustion process that can provide high diesel-like efficiencies and very low emissions of NO_x and particulates. However, research is required to overcome the technical barriers to producing a practical HCCI engine, such as: control of ignition timing over the load/speed map, slowing the heat-release rate at higher loads, controlling hydrocarbon (HC) and carbon monoxide (CO) emissions, reliable cold starting, and smooth response through rapid transients.

The objective of this project is to develop the fundamental understanding necessary to overcome these barriers. To achieve this objective, an HCCI engine laboratory is being established that will be equipped with two HCCI engines of the same basic design. 1) An all-metal engine will be used to establish operating points, develop combustion-control strategies, and investigate emissions. 2) An optically accessible engine will be used to apply advanced laser diagnostics to the in-cylinder processes. In addition a modest computational modeling effort is underway to guide the engine design, selection of operating conditions, and provide a fundamental understanding of selected HCCI processes.

This research project is being conducted in close cooperation with both the automotive and heavy-duty diesel engine industries, with the results being presented at the regularly scheduled cross-cut diesel CRADA meetings.

Approach

A versatile HCCI engine laboratory is being built that will allow investigations of a wide range of operating conditions and various fuel injection, fuel/air/residual mixing, and control strategies that have the potential to overcome the technical barriers to HCCI. Since no HCCI production engines exist today, two Cummins B-series diesel engines are being converted into the HCCI research engines. This SUV-sized engine (0.98 liters/cylinder) was selected as being capable of providing an operating range relevant to both automotive and heavy-duty manufacturers. The six-cylinder production engines are being converted for balanced single-cylinder HCCI operation and are capable of speeds up to 3600 rpm. The engines are being equipped with a variety of special features for HCCI research and a special intake-charge conditioning system to control intake mixture, temperature, and pressure across a wide range of conditions.

Chemical-kinetic rate computations are also being conducted to investigate two key aspects of HCCI engine combustion: 1) low-load operation, and 2) the effect of EGR on the heat release rate. These studies are being accomplished using the CHEMKIN kinetics-rate code modified to allow time-varying compression with the full chemistry mechanisms for iso-octane (from LLNL). Iso-octane is a reasonable surrogate for gasoline, and it was selected as the fuel for these computations based on our previous detailed investigation which showed that gasoline-like fuels have significant advantages for HCCI [1].

Results

A substantial portion of the laboratory construction has been completed during the past year. Most significantly, the all-metal engine and supporting laboratory subsystems are in place, and shakedown testing of its operation is underway. During the conversion of this engine, several special features were added for HCCI research, including: an open combustion chamber design that minimizes crevices and surface area, interchangeable pistons to allow the compression ratio to be varied from 13:1 to 21:1, modified intake ports and control valves to provide variable swirl ratios from 0.9 to 3.2, and three fueling systems for investigations of various combustion-control strategies. These fueling

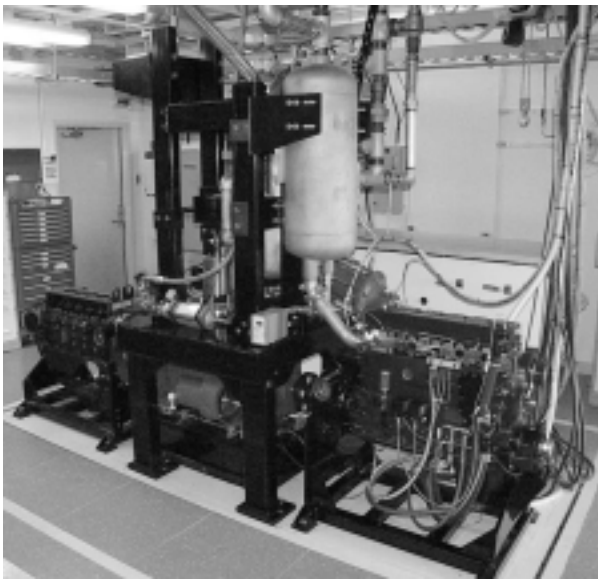

Figure 1. Photograph of the HCCI Engine Laboratory Showing the Fully Assembled All-Metal Engine on the Right

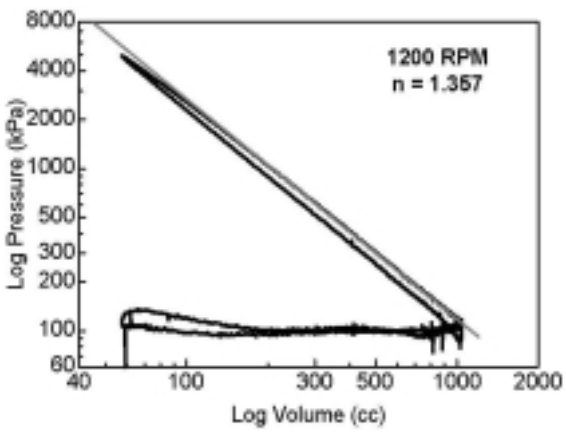

Figure 2. A Log-Volume, Log-Pressure Plot for Motored Operation of the Metal Engine

systems include: a heated vaporizer to provide fully premixed fueling, a port fuel injector, and a direct-injection (DI) gasoline injector (optionally, a high-pressure DI-diesel injector can also be installed). In addition, a complete intake-charge conditioning system has been installed. This system allows the engine to be supplied with precisely metered quantities of air, simulated or real EGR gases, or an inert flow of nitrogen for investigations of non-fired conditions. It also allows the temperature and pressure of the intake mixture to be boosted to 200°C and three atmospheres absolute, respectively, to simulate the use of hot EGR and turbocharging. A

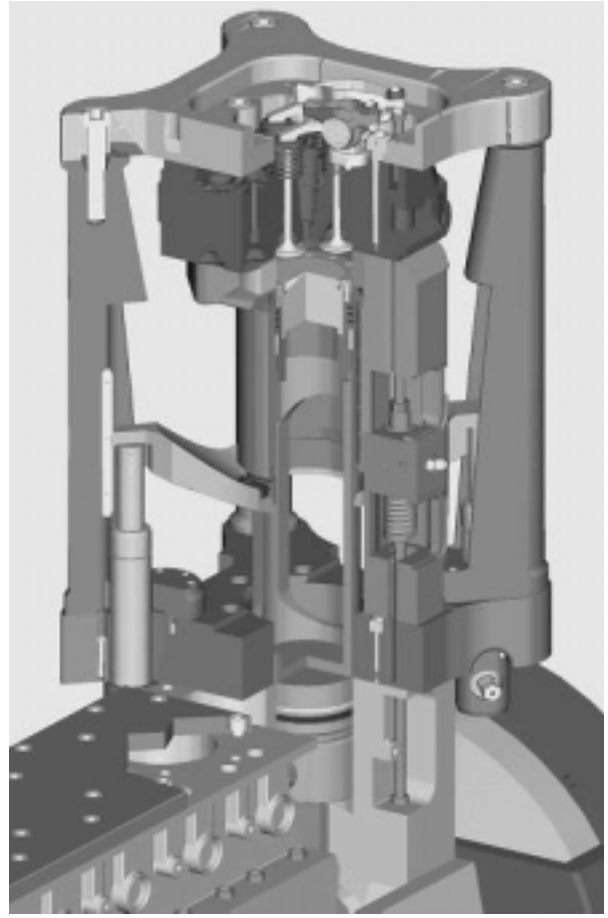

Figure 3. Schematic of the Optically Accessible Engine

computerized control system adjusts and maintains the intake parameters and engine speed.

Figure 1 shows a photograph of the all-metal engine installed on the vibration isolation pad to the right of the double-ended dynamometer (the base engine for the optical engine is installed at the left). The framework over the dynamometer supports the intake and exhaust surge tanks, flame arrestor, premixed fueling system, and associated plumbing. Note that the exhaust surge tank in the center of the photo is connected only to the left-most cylinder of the metal engine. This is the active HCCI cylinder; the pistons in the other five cylinders have no compression and serve only to balance the engine. Behind the metal engine is the enclosure that houses the circulating pumps and heaters for the engine oil and cooling/heating water. Motored operation of the all-metal engine has been tested to 3000 rpm. A typical log-volume, log-pressure plot of motored operation at 1200 rpm (shown in Figure 2) indicates that the engine is operating well. The log-linear fit to

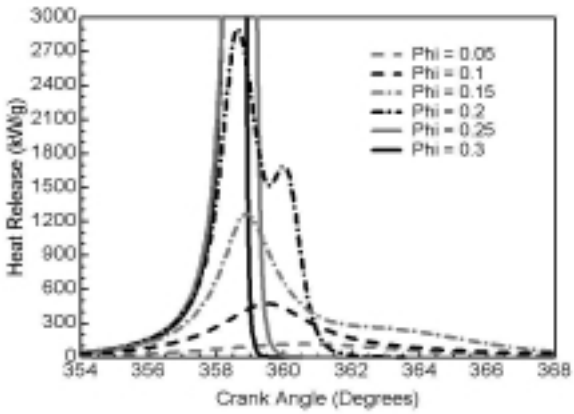

Figure 4. Computed Heat Release Rate Curves for HCCI at Various Low-Load Equivalence Ratios (Phi)

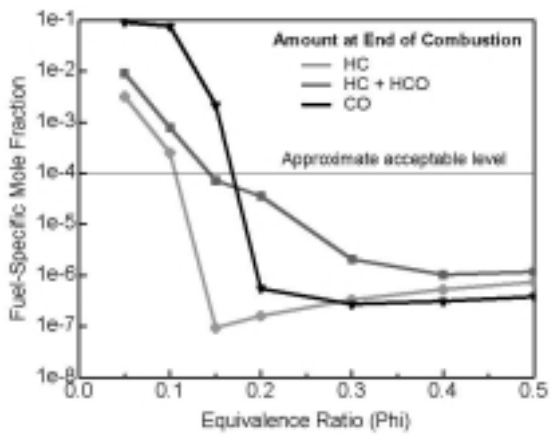

Figure 5. Fuel-Specific Emissions of CO, HC, and HC + HCO (Partially Oxygenated Hydrocarbons) as a Function of Fuel Loading (Equivalence Ratio) for Fully Homogeneous HCCI Operation

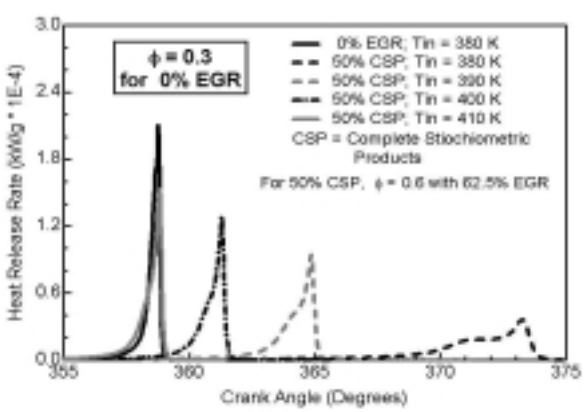

Figure 6. Heat Release Rates Curves for Moderate-Load HCCI Show the Effect of EGR on the Heat Release Rate and Ignition Timing

the extended cylinder for the the compression stroke (gray line) matches the data well and has a reasonable polytropic coefficient (1.357). The design of the optically accessible engine has been completed, and a schematic showing its main features is presented in Figure 3. The design provides full optical access near TDC, an optional quartz upper cylinder for investigations of mixture preparation, and a hydraulically operated drop-down cylinder for rapid cleaning and cylinder interchange.

Chemical kinetic modeling of fully homogeneous HCCI combustion at low loads shows that kinetic rates play a significant role in smoothing the heat release rate for equivalence ratios below about 0.25, as shown in Figure 4. This is beneficial; however, when the fueling rate is further reduced to equivalence ratios of 0.15 and lower (very light load and idle), combustion temperatures become so low that the CO-to-CO_2 reactions no longer go to completion, even in the bulk gases (i.e., gases that are not near walls or crevices). This leads to inefficient combustion and emissions of CO and HC from these bulk gases as shown in Figure 5. This understanding has significant implications for the design of HCCI combustion strategies for light loads.

In addition, a computational investigation has been initiated to determine the effects of EGR on the heat release rate. Previous experimental investigations [2] have suggested that EGR significantly increases the combustion duration; however, ignition timing was not maintained in these experiments. Our previous work [1] has shown that EGR also reduces compression heating due to its lower ratio of specific heats (c_p/c_v) which will retard the ignition timing, causing an increase in the combustion duration independent of any kinetic-rate effect. In order to separate these two effects, intake temperatures were adjusted to compensate for the reduced compression heating with EGR. As shown in Figure 6, EGR addition does increase the combustion duration, but when the intake temperature is increased to maintain ignition timing, the improvement is substantially reduced.

Conclusions

Chemical-kinetic rate computations for fully homogeneous HCCI have shown that at low loads,

the bulk-gas reactions slow considerably, smoothing the heat release rate. However, for very light loads and idle, the combustion reactions no longer go to completion, resulting in high HC and CO emissions. These results suggest that partial charge stratification will be required for light-load HCCI operation.

A computational investigation of the effect of EGR on the heat release rate in HCCI engines has shown that, when ignition timing is maintained, EGR addition causes only a 40-50% increase in the combustion duration. Although this modest increase is beneficial, it will not be sufficient by itself to allow high-load HCCI operation.

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ACRONYMS

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AGI	Auxiliary Gas Injection
Al_2O_3	Aluminum oxide
ANL	Argonne National Laboratory
ASME	American Society of Mechanical Engineers
ATDC	After Top Dead Center
atm	Atmosphere
BaO	Barium oxide
bhp-hr	Brake horsepower-hour
Bmep	Brake mean effective pressure
Bsfc	Brake specific fuel consumption
BTDC	Before Top Dead Center
ºC	Degrees Celsius
C_2H_4	Ethylene
CAD	Crank Angle Degrees
cc	Cubic centimeter
CFD	Computational Fluid Dynamics
CFR	Coordinating Fuels Research
CI	Compression Ignition
CIDI	Compression Ignition Direct Injection
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_x	Carbon oxide containing x oxygen atoms
CSF	Catalyzed Soot Filter
CRADA	Cooperative Research & Development Agreement
CRT	Continuously Regenerated Trap
CuO	Copper oxide
C_x	Hydrocarbon containing x carbon atoms
DDC	Detroit Diesel Corporation
DECSE	Diesel Emissions Control Sulfur Effects
DEER	Diesel Engine Emissions Reduction Workshop
deg	Degrees
DI	Direct Injection
DIATA	Direct Injection, Aluminum, Through-bolt Assembly
DOE	Department of Energy
DPF	Diesel Particulate Filter
EAS	Exhaust Aftertreatment Subsystem
ECS	Emission Control System
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency
ERC	Engine Research Center
FEA	Finite Element Analysis
FTP	Federal Test Procedure
FY	Fiscal Year
g	Gram
g/hp-h	Grams per horsepower-hour
h	Hour
H_2	Diatomic hydrogen
H_2O	Water
HC	Hydrocarbon
HCCI	Homogeneous Charge Compression Ignition
He	Helium
HO_2	Hydroxyl radical
hp	Horsepower
HSDI	High Speed Direct Injection
Hz	Hertz
IMEP	Indicated Mean Effective Pressure
in	Inch
IR	Infrared
ISB	Integrated System B (Cummins diesel engine)
kHz	Kilohertz
kPa	Kilopascal
J/L	Joules per liter
keV	Kilovolt-electric
KPa	Kilopascal
KW	Kilowatt
L	Liter
LANL	Los Alamos National Laboratory
LBNL	Lawrence Berkeley National Laboratory
LD	Light Duty
LDT	Light-Duty Truck
LDV	Light-Duty Vehicle
LHV	Lower Heating Value
LLNL	Lawrence Livermore National Laboratory
m	Meter
mA	Milliampere
µA	Microampere
MECA	Manufacturers of Emissions Controls
mg	Milligram
MHz	Megahertz
mi	Mile
min	Minute
mJ	Millijoule
mm	Millimeter
µm	Micron

MPa	Megapascal
ms	Millisecond
µs	Microsecond
N_2	Diatomic nitrogen
nA	Nanoampere
Na	Sodium
NH_3	Ammonia
nm	Nanometer
N-m	Newton-meters
NO	Nitric oxide
N_2O	Nitrous oxide
NO_2	Nitrogen dioxide
NO_x	Oxides of nitrogen
NREL	National Renewable Energy Laboratory
O_2	Diatomic oxygen
OAAT	Office of Advanced Automotive Technologies
O/C	Atomic oxygen to atomic carbon ratio
OEM	Original Equipment Manufacturer
OH	Hydroxyl radical
OHVT	Office of Heavy Vehicle Technologies
O-Radicals	Oxygen radical species
ORNL	Oak Ridge National Laboratory
OTT	Office of Transportation Technology
P	Pressure
PAH	Poly-Aromatic Hydrocarbon
PM	Particulate Matter
PNGV	Partnership for a New Generation of Vehicles
PNNL	Pacific Northwest National Laboratory
POx	Partial Oxidation
ppm	Parts per million
psi	Pounds per square inch
Pt	Platinum
R&D	Research and Development
RMS	Root mean square
RO_2	Hydrocarbon radicals
RPM	Revolutions Per Minute
s	Second
S	Sulfur
SAE	Society of Automotive Engineers
S/C	Steam to carbon ratio
SCR	Selective Catalytic Reduction
Si	Silicon
SI	Spark Ignition
SNL	Sandia National Laboratories
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
SOF	Soluble Organic Fraction
SO_x	Oxides of sulfur
SUV	Sport Utility Vehicle
SV	Space Velocity
SwRI	Southwest Research Institute
TC	Turbocharged
TDC	Top Dead Center
TDI	Turbocharged Direct Injection
THC	Total hydrocarbons
TiO_2	Titanium dioxide
US06	EPA high speed/load transient driving cycle
V_2O_5	Vanadia
VW	Volkswagen
WO_3	Tungsten trioxide

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