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Advanced Combustion Engine Research and Development

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FY 2010 PROGRESS REPORT FOR ADVANCED COMBUSTION ENGINE RESEARCH AND DEVELOPMENT

Energy Efficiency and Renewable Energy
Vehicle Technologies Program

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Table of Contents

I. INTRODUCTION

I.1 Subprogram Overview and Status

DEVELOPING ADVANCED COMBUSTION ENGINE TECHNOLOGIES

On behalf of the Department of Energy's Vehicle Technologies Program (VTP), we are pleased to introduce the Fiscal Year (FY) 2010 Annual Progress Report for the Advanced Combustion Engine Research and Development (R&D) subprogram. The mission of the VTP is to develop more energy-efficient and environmentally friendly highway transportation technologies that will meet or exceed performance expectations, enable the United States to use significantly less petroleum, and reduce greenhouse gas and other regulated emissions. The Advanced Combustion Engine R&D subprogram supports this mission by removing the critical technical barriers to commercialization of advanced internal combustion engines (ICEs) for passenger and commercial vehicles that meet future Federal emissions regulations. Dramatically improving the efficiency of ICEs and enabling their introduction in conventional as well as hybrid electric vehicles is one of the most promising and cost-effective approaches to increasing vehicle fuel economy over the next 30 years. Improvements in engine efficiency alone have the potential to increase passenger vehicle fuel economy by 25 to 40 percent, and commercial vehicle fuel economy by 30 percent with a concomitant reduction in greenhouse gas emissions, more specifically, carbon dioxide emissions. These improvements are expected to be even greater when coupled with advanced hybrid electric powertrains.

The following are representative goals of the Advanced Combustion Engine R&D subprogram that can contribute to meeting national energy security, environmental, and economic objectives:

- Passenger Vehicles: Increase the efficiency of ICEs resulting in vehicle fuel economy improvements of 25 percent for gasoline vehicles and 40 percent for diesel vehicles by 2015 compared to current gasoline vehicles. The emphasis has shifted to improving the vehicle fuel economy over a real-world driving cycle after the peak engine thermal efficiency goal of 45 percent was met.
- Commercial Vehicles: Increase the efficiency of ICEs from 42 percent (2010 baseline) to 50 percent (20 percent improvement) by 2015, and further improve engine efficiency to 55 percent by 2018 with demonstrations on commercial vehicle platforms.
- Solid State Energy Conversion: Increase the fuel economy of passenger vehicles by at least 5 percent with thermoelectric generators that convert waste heat to electricity by 2015.

The passenger and commercial vehicle goals will be met while utilizing advanced fuel formulations that can incorporate a non-petroleum-based blending agent to reduce petroleum dependence and enhance combustion efficiency.

To meet these goals, two new initiatives were launched in 2010, SuperTruck and the Advanced Technology Powertrains for Light-Duty Vehicles (ATP-LD). These initiatives include nine projects totaling more than $187 million to improve fuel efficiency for heavy-duty trucks and passenger vehicles. The funding includes more than $100 million from the American Recovery and Reinvestment Act, and with a private cost share of 50 percent, will support nearly $375 million in total research, development and demonstration projects across the country.

Three projects were select for SuperTruck which will focus on cost-effective measures to improve the efficiency of Class 8 long-haul freight trucks by 50 percent, 20 percent of which will come from improvements to engine efficiency. The remaining six projects totaling more than $71 million will support efforts to increase the fuel economy for passenger vehicle engines and powertrain systems. The goal is to develop engine technologies that will improve the fuel economy of passenger vehicles by 25-40 percent by 2015 using an engine-only approach.

This introduction serves to outline the nature, current focus, recent progress, and future directions of the Advanced Combustion Engine R&D subprogram. The research activities of this subprogram are planned in conjunction with the FreedomCAR and Fuel Partnership and the 21st Century Truck Partnership and are carried out in collaboration with industry, national laboratories, and universities. Because of the importance of clean fuels in achieving high efficiency and low emissions, R&D activities are closely coordinated with the relevant activities of the Fuels Technologies subprogram, also within VTP.

CURRENT TECHNICAL FOCUS AREAS AND OBJECTIVES

The Advanced Combustion Engine R&D subprogram focuses on developing technologies for all highway transportation ICEs. Fuel efficiency improvement is the overarching focus of this activity, but resolving the interdependent emissions challenges is a critical integrated requirement. The reduction of engine-out emissions is key to managing the extra cost of exhaust aftertreatment devices that can be a barrier to market acceptance. (Penetration of even current-technology diesel engines into the light-duty truck market would reduce fuel use by 25-30% per gasoline vehicle replaced.) Accordingly, research has been emphasizing advanced combustion modes including homogeneous charge compression ignition (HCCI), pre-mixed charge compression ignition (PCCI), lean-burn gasoline, and other modes of low-temperature combustion (LTC) which will increase efficiency beyond current state-of-the-art engines and reduce engine-out emissions of nitrogen oxides (NOx) and particulate matter (PM) to near-zero levels. In parallel, research on those emission control systems is underway to increase their efficiency and durability for overall emissions compliance at an acceptable cost. Projects to stretch engine efficiency via innovative combustion methods and thermal energy recovery (such as compound cycles) are in progress as well. In response to the challenges of realizing and implementing higher efficiency engines, the Advanced Combustion Engine R&D subprogram is working toward achieving the following objectives:

- Further the fundamental understanding of advanced combustion processes which simultaneously exhibit low emissions and high efficiency. This will be used in the development of cleaner, more efficient engines which will operate predominately in low-temperature or HCCI combustion modes. These technology advances are expected to reduce the size and complexity of emission control hardware and minimize potential fuel efficiency penalties. A fuel-neutral approach is also being taken, with research addressing gasoline- and diesel-based advanced engines, including renewable fuels. The effects of fuel properties on combustion are addressed in the Fuels Technologies subprogram. Hydrogen engine R&D is underway as well.
- Improve the effectiveness, efficiency, and durability of engine emission control devices to enable increased penetration of advanced combustion engines in the light-duty market and maintain and/or expand application to heavy-duty vehicles.
- Extend robust engine operation and efficiency through the development and implementation of high-speed predictive models for improvements in combustion control and thermal management.
- Further the development of approaches to producing useful work from engine waste heat such as through incorporation of bottoming cycles, and application of advanced thermoelectric technologies for direct conversion of engine waste heat to useful energy (electricity), that will significantly increase vehicle fuel economy.
- Advance engine technologies such as turbo-machinery, flexible valve systems, advanced combustion systems, and fuel system components to achieve a reduction in parasitic losses and other losses to the environment to maximize engine efficiency.
- Develop key enabling technologies for advanced engines such as sensors and control systems, diagnostics for engine development, and components for thermal energy recovery.
- Improve the integration of advanced engine/emissions technologies with hybrid-electric systems for improved efficiency with lowest possible emissions.
- In cooperation with the Fuels Technologies subprogram, accelerate industry development of a next generation of E85 flexible-fuel engines that exploit ethanol properties for higher efficiency.
- Identify that any potential health hazards associated with the use of new vehicle technologies being developed by VTP will not have adverse impacts on human health through exposure to toxic particles, gases, and other compounds generated by these new technologies.

- Develop thermoelectrics to directly convert waste heat from engines and other sources to electrical energy to improve overall thermal efficiency and reduce emissions.
- Develop thermoelectrics and other solid state systems that provide cooling/heating for vehicle interiors.

The Advanced Combustion Engine R&D subprogram maintains close communication with industry through a number of working groups and teams, and utilizes these networks for setting goals, adjusting priorities of research, and tracking progress. Examples of the cooperative groups are the Advanced Combustion and Emission Control Tech Team of the FreedomCAR and Fuel Partnership and the Engine Systems Team of the 21st Century Truck. Focused efforts are carried out in the Advanced Combustion Memorandum of Understanding (including auto manufacturers, engine companies, fuel suppliers, national laboratories, and others) and the CLEERS (Cross-Cut Lean Exhaust Emission Reduction Simulation) activity for the Advanced Engine Cross-Cut Team.

TECHNOLOGY STATUS AND KEY BARRIERS

Significant advances in combustion, emission controls, fuel injection, turbo-machinery, and other advanced engine technologies continue to increase the thermal efficiency of ICEs with simultaneous reductions in emissions. With these advances, gasoline and diesel engines continue to be the attractive engine options for conventional and hybrid-electric vehicles. These engines offer outstanding drivability, fuel economy, and reliability with low combustion noise and extremely clean exhaust.

The majority of the U.S. light-duty vehicle fleet are powered by spark-ignition (SI) gasoline engines. Substantial progress in gasoline engine efficiency in recent years has been the result of advances in engine technologies including direct fuel injection, flexible valve systems, improved combustion chamber design, and reduced mechanical friction. While all gasoline engines sold in the U.S. operate with stoichiometric combustion, other areas in the world are seeing the introduction of lean-burn gasoline engines.

Recent laboratory research into highly-diluted, stoichiometric gasoline-based engines has produced efficiencies approaching diesels. The challenges to moving from laboratory bench-scale single-cylinder research engine to multi-cylinder platforms will need to be addressed. Being able to achieve high boost levels, achieve and control very highly cooled exhaust gas recirculation (EGR), and maintain the research-scale efficiency are major hurdles. Although these engines are characterized by higher efficiencies at part load, they require more costly lean-NOx emission controls that are currently not adequate for U.S. emissions regulations. In addition, the direct injection technology utilized for most advanced gasoline engines produces particulate emissions that although smaller in mass than the diesel engine still represent significant emissions in terms of particulate number counts. Advances in lean-gasoline emission controls are critical for meeting U.S. regulations and ultimately the introduction of this efficiency technology in the U.S. market.

Attaining the high efficiency potential of lean-burn gasoline technology will require better understanding of the dynamics of fuel-air mixture preparation and other enabling technologies. Consistently creating combustible mixtures near the spark plug and away from walls in an overall lean environment is a challenge requiring improved understanding of fuel-air mixture preparation and modeling tools that embody the information. A comprehensive understanding of intake air flows and fuel sprays, as well as their interaction with chamber/piston geometry over a wide operating range is needed. Generating appropriate turbulence for enhancement of flame speed is a further complexity requiring attention. The wide range of potential intake systems, piston geometries, and injector designs makes the optimization of lean-burn systems dependent on the development of improved simulation tools. Furthermore, reliable ignition and combustion of lean (dilute) fuel-air mixtures remains a challenge. Lean and possibly boosted conditions require a more robust, high-energy ignition system that, along with proper mixture control, is needed to reduce combustion variability. Several new ignition systems have been proposed (high-energy plugs, plasma, corona, laser, etc.) and need to be investigated.

Diesel engines are also well-suited for light-duty vehicle applications, delivering fuel economy considerably higher than comparable SI engines. Key developments in combustion and emission controls, plus low-sulfur fuel have enabled manufacturers to achieve the necessary emissions levels and introduce additional diesel-powered models to the U.S. market. DOE research contributed to all of these areas. Primarily due to the cost of the added components and diesel fuel price, diesels in passenger cars have limited market penetration in the U.S. Hence reducing the cost of emission compliance continues to be addressed.

The heavy-duty diesel is the primary engine for commercial vehicles because of its high efficiency and outstanding durability. However, the implementation of increasingly stringent heavy-duty engine emission standards over the last decade held efficiency gains to a modest level. Current heavy-duty diesel engines have efficiencies in the 42-43% range. With stability in NOx and PM regulations in 2010, further gains in efficiency are now seen as achievable. Continued aggressive R&D to improve boosting, thermal management, and the reduction and/or recovery of rejected thermal energy are expected to enable efficiencies to reach 55%. Heavy-duty vehicles using diesel engines have significant potential to employ advanced combustion regimes and a wide range of waste heat recovery technologies that will improve engine efficiency and reduce fuel consumption.

Emissions of NOx (and PM) are a significant challenge for all lean-burn technologies including conventional and advanced diesel combustion strategies, both light-and heavy-duty, as well as lean-burn gasoline. Numerous technologies are being investigated to reduce vehicle NOx emissions while minimizing the fuel penalty associated with operating these devices. These technologies include post-combustion emissions control devices as well as advanced combustion strategies which make use of high levels of dilution to reduce in-cylinder NOx formation.

In early 2007, the U.S. Environmental Protection Agency (EPA) finalized the guidance document for using selective catalytic reduction (SCR) which makes use of urea for regeneration (urea-SCR) technology for NOx control in light-duty and heavy-duty diesel vehicles and engines. This guidance allows for the introduction of SCR technology in Tier 2 light-duty vehicles, heavy-duty engines, and in other future diesel engine applications in the U.S. Strategies to supply the urea-water solution (given the name “diesel exhaust fluid”) for vehicles have been developed and are being implemented. Using urea-SCR, light-duty manufacturers have been able to meet Tier 2, Bin 5 which is the “gold standard” at which diesel vehicle sales do not have to be offset by sales of lower emission vehicles. Most heavy-duty diesel vehicle manufacturers are adopting urea-SCR since it has a broader temperature range of effectiveness than competing means of NOx reduction and allows the engine/emission control system to achieve higher fuel efficiency. Although urea-SCR is a relatively mature catalyst technology, more support research is needed to aid formulation optimization and minimize degradation effects such as hydrocarbon fouling.

Another technology being used to control NOx levels in diesel engines and potentially lean-burn gasoline engines is lean-NOx traps (LNTs), which are also referred to as NOx adsorbers. An example application is that Volkswagen has certified its 2011 diesel Jetta to Tier 2, Bin 5 and California Low Emissions Vehicle (LEV)-II using an LNT in conjunction with EGR, a diesel oxidation catalyst (DOC) and diesel particulate filter (DPF). Although LNTs have been commercialized for light-duty diesels, further advancement of the technology is needed to expand market penetration of light-duty diesels and to enable use of LNTs in lean gasoline engine passenger car vehicles. A primary limitation to further adoption of current light-duty diesels is cost. Complex engine and EGR systems and the larger catalyst volumes associated with LNTs and DPFs result in higher overall costs in comparison to conventional gasoline vehicle systems. Cost is particularly sensitive for LNTs which require substantial quantities of platinum group metals, and the cost of these materials is high and volatile due to limited sources that are primarily mined in foreign countries. Improvements in the temperature range of operation for LNTs are also desired to reduce cost and enable success in the lean gasoline engine application. Both LNTs and DPFs result in extra fuel use, or a “fuel penalty”, as they require fueling changes in the engine for regeneration processes. Aggressive research has substantially decreased the combined fuel penalty for both devices to approximately four percent of total fuel flow; further reduction would be beneficial. While LNTs have a larger impact on fuel consumption than urea-SCR, light-duty vehicle manufacturers appear to prefer LNTs since overall fuel efficiency is less of a concern and urea replenishment is more of a challenge for light-duty customers as compared to heavy-duty vehicle users. Another improvement being pursued for LNT technology is to pair them with SCR catalysts. The advantage is that the SCR catalyst uses the NH_3 produced by the LNT so no urea is needed.

Formulation and system geometries are being researched to reduce the overall precious metal content of LNT+SCR systems which reduces cost and makes the systems more feasible for light-duty vehicles.

A highly attractive solution to reducing vehicle emissions is to alter the combustion process such that engine-out emissions are at levels which remove or reduce the requirements for auxiliary devices while maintaining or improving engine efficiency. This is the concept behind advanced combustion processes such as HCCI, PCCI and other modes of LTC, which exhibit high efficiency with significant reductions in NOx and PM emissions. Note that emissions of hydrocarbons (HCs) and carbon monoxide (CO) are often higher and require additional controls which are often a challenge with the low exhaust temperature characteristic of these combustion modes. Significant progress continues for these advanced combustion systems, and the operational range continues to be expanded to better cover the speed/load combinations consistent with light-duty and heavy-duty drive cycles. In recent years, DOE adopted the term "high-efficiency clean combustion" (HECC) as an all encompassing term which includes a range of combustion modes which are focused on improvements in efficiency with lowest possible emissions. The major R&D challenges include fuel mixing, intake air conditioning, combustion timing control, and expansion of the operational range. To meet these challenges, there has been significant R&D on allowing independent control of the intake/exhaust valves relative to piston motion and on improvements in air-handling and engine controls. Many of these technologies are transitioning to the vehicle market.

High dilution operation through advanced EGR is a key element of HECC and can be a major contributor to meet the 2010 EPA heavy-duty engine emission standards and is also applicable to light-duty diesel and gasoline engines. There are numerous advantages of advanced EGR compared to urea-SCR and LNT packages including lower vehicle weight, less maintenance, and lower operating cost. The disadvantages relative to post-combustion emission controls include increased heat rejection load on the engine and the potential for increased fuel consumption due to more frequent DPF active regeneration. In 2009 the Advanced Engine Cross-Cut Team formed a working group to study the widespread issues of fouling and corrosion in the EGR systems. The DOE Propulsion Materials subprogram is a co-sponsor.

Complex and precise engine and emission controls require sophisticated feedback systems employing new types of sensors. A major advancement in this area for light-duty engines has been the introduction of in-cylinder pressure sensors integrated into the glow plug. Start-of-combustion sensors (other than the aforementioned pressure sensor) have been identified as a need, and several development projects have been completed. Sensors are also beneficial for the emission control system. NOx and PM sensors are under development and require additional advances to be cost-effective, accurate, and reliable. Upcoming regulations with increased requirements for on-board diagnostics will also challenge manufacturers trying to bring advanced fuel efficient solutions to market. The role of sensors and catalyst diagnostic approaches will be a key element of emission control research in the next few years.

Advanced combustion engines must be compatible with, if not optimized, for renewable fuels. The Energy Independence and Security Act of 2007 mandates 36 billion gallons of renewable fuels by 2022, which would be mostly ethanol for SI engines, biodiesel for diesels, and second-generation renewable fuels for both. Research has confirmed the basic compatibility of these fuels with various interpretations of HECC. The impact of these fuels on emission controls is also under study, principally in the Fuels Technologies area. Recent tests have shown that biodiesel lowers the regeneration temperature of particulate traps and increases the rate of regeneration with the potential for avoiding or reducing the need for active regeneration and its associated fuel economy penalty.

Waste heat recovery is being implemented in heavy-duty diesel vehicles and explored for light-duty diesel and gasoline applications. New engines being introduced by Daimler Trucks include turbo-compounding technology that uses a turbine to extract waste energy and add to engine power output. The addition of turbo-compounding and other engine changes result in a claimed 5% improvement in vehicle fuel economy. Experiments have shown that waste heat recovery has the potential to improve vehicle fuel economy by as much as 10%.

Another form of waste heat recovery is a thermoelectric generator. Vehicular thermoelectric generators directly convert engine waste heat to electricity and are on a path to commercialization.

BMW intends to introduce thermoelectric generators in their 5 and 7 Series cars later this decade in both Europe and North America. Use of thermoelectric devices for vehicle occupant comfort heating or cooling is also being pursued as a more fuel efficient alternative to the conventional mobile air conditioning systems that use refrigerants.

FUTURE DIRECTIONS

Internal combustion engines have a maximum theoretical fuel conversion efficiency that is similar to that of fuel cells and considerably higher than the mid-40% peak values seen today. The primary limiting factors to approaching these theoretical limits of conversion efficiency start with the high irreversibility in traditional premixed or diffusion flames, but more practically the limits are imposed by heat losses during combustion/expansion, structural limits that constrain peak pressures, untapped exhaust energy, and mechanical friction. Emphasis must be placed on enabling the engine to operate near peak efficiency over a real-world driving cycle to improve vehicle fuel economy. For SI engines this means reducing the throttling losses with technologies such as lean-burn, high dilution, and variable geometry. Exhaust losses are being addressed by analysis and development of compound compression and expansion cycles achieved by valve timing, use of turbine expanders, regenerative heat recovery, and application of thermoelectric generators. Employing such cycles and devices has been shown to have the potential to increase heavy-duty engine efficiency to as high as 55%, and light-duty vehicle fuel economy by 25% to 40%. In 2010, VTP announced new awards for engine efficiency R&D within the vehicle context.

Analyses of how "advanced combustion regimes" might impact the irreversibility losses have indicated a few directions to moderate reductions of this loss mechanism, but converting the preserved availability to work will require compound cycles or similar measures of exhaust energy utilization. The engine hardware changes needed to execute these advanced combustion regimes include variable fuel injection geometries, turbo- and super-charging to produce very high manifold pressures, compound compression and expansion cycles, variable compression ratio, and improved sensors and control methods. Larger reductions in combustion irreversibility will require a substantial departure from today's processes but are being examined as a long-range strategy.

Most of the basic barriers to high engine efficiency hold true for both gasoline- and diesel-based engines. Recognizing the dominance of gasoline-type SI engines in the U.S., VTP intends to increase emphasis on their improvement. Gasoline-based engines, including E85 flexible-fuel, can be made at least 20-25% more efficient through direct injection, boosting/downsizing, and lean-burn. Real-world fuel savings might be even higher by focusing attention on the road-load operating points.

Hydrogen engine efficiencies of roughly 45% have been demonstrated based on single-cylinder engine data. The underlying reasons for these impressive levels suggest a case study for applicability to other fuels. Work will continue on increasing the efficiency of hydrogen-fueled engines while maintaining low NOx.

Meeting anticipated future emission standards will be challenging for high efficiency diesel and lean-burn gasoline engines. To address this issue, research on innovative emission control strategies will be pursued through national laboratory and university projects designed to reduce cost and increase performance and durability of NOx reduction and PM oxidation systems. Project areas include development of low-cost base metal catalysts (to replace expensive platinum group metals), lighter and more compact multifunctional components, new control strategies to lessen impact on fuel consumption, and improved sensors and on-board diagnostics for meeting upcoming regulations. Furthermore, simulations of the catalyst technologies are being developed to enable industry to perform more cost-effective system integration during vehicle development. As advanced combustion approaches evolve and engine-out emissions become cleaner, the requirements of emission controls are expected to change as well.

The majority of lean-NOx emission controls development has been focused on diesel engines. With the potential introduction of high efficiency lean-gasoline engines, these technologies will require further research and development as well as emission controls for managing HC/CO emissions.

Engine-out PM emissions from lean-gasoline engines, although lower in mass than the diesel engine, are also a concern and may require new processes due to differences in particle size and morphology.

Enabling technologies being developed by the Combustion and Emission Control R&D activity will address fuel systems, engine control systems, and engine technologies. Fuel systems R&D focuses on injector controls and fuel spray development. Engine control systems R&D focuses on developing engine controls that are precise and flexible for enabling improved efficiency and emission reduction in advanced combustion engines. These control system technologies will facilitate adjustments to parameters such as intake air temperature, fuel injection timing, injection rate, variable valve timing, and EGR to allow advanced combustion engines to operate over a wider range of engine speed/load conditions. Engine technologies development will be undertaken to achieve the best combination that enables advanced combustion engines to meet maximum fuel economy and performance requirements. These include variable compression ratio, variable valve timing, variable boost, advanced sensors and ignition systems, and exhaust emission control devices (to control hydrocarbon emissions at idle-type conditions) in an integrated system. Upcoming EPA onboard diagnostic requirements will be addressed through research on advanced sensors, improved understanding of emission control aging, and development of models that are integral to the diagnostic method.

The Combustion and Emission Control R&D activity will continue to perform the critical role of elevating potential health issues related to advanced combustion engine technologies to the attention of industry partners and DOE/VTP management. It will ensure that vehicle technologies being developed will not have adverse impacts on human health through exposure to toxic particles, gases, and other compounds generated by these new technologies.

The Solid State Energy Conversion activity will continue on developing advanced thermoelectric generators for converting waste heat from engines directly into useful electrical energy to improve overall vehicle energy efficiency and reduce emissions. Effective use of waste heat from combustion engines would significantly increase vehicle fuel economy. In current gasoline production passenger vehicles, roughly over 70% of the fuel energy is lost as waste heat from an engine operating at full power. About 35 to 40 percent is lost in the exhaust gases and another 30 to 35 percent is lost to the engine coolant. There is an opportunity to recover some of the engine's waste heat using thermoelectric materials that will convert it directly to electricity for operating vehicle auxiliaries and accessories. Improving the energy conversion efficiency of thermoelectric materials directly supports the overall goals of improving the fuel economy of passenger and commercial vehicles. Achieving the vehicle-based performance goals requires reduction in the cost of thermoelectrics, scaling them up into practical devices, and making them durable enough for vehicle applications. The concept of a zonal, dispersed thermoelectric cooling system will continue to be pursued to provide occupant comfort cooling using about 630 W compared with the 3,500 to 4,000 W used by conventional mobile air conditioning systems. Air conditioning power reductions of greater than 7% are possible.

The remainder of this report highlights progress achieved during FY 2010 under the Advanced Combustion Engine R&D subprogram. The following 66 abstracts of industry, university, and national laboratory projects provide an overview of the exciting work being conducted to tackle tough technical challenges associated with R&D of higher efficiency, advanced ICEs for light-duty, medium-duty, and heavy-duty vehicles. We are encouraged by the technical progress realized under this dynamic subprogram in FY 2010, but we also remain cognizant of the significant technical hurdles that lay ahead, especially those to further improve efficiency while meeting the EPA Tier 2 emission standards and heavy-duty engine standards for the full useful life of the vehicles.

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I.2 Project Highlights

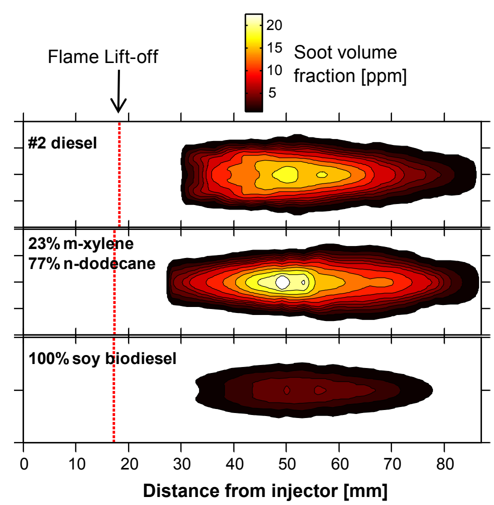
The following projects highlight progress made in the Advanced Combustion Engine R&D subprogram during FY 2010.

ADVANCED COMBUSTION AND EMISSION CONTROL RESEARCH FOR HIGH-EFFICIENCY ENGINES

A. Combustion and Related In-Cylinder Processes

The objective of these projects is to identify how to achieve more efficient combustion with reduced emissions from advanced technology engines.

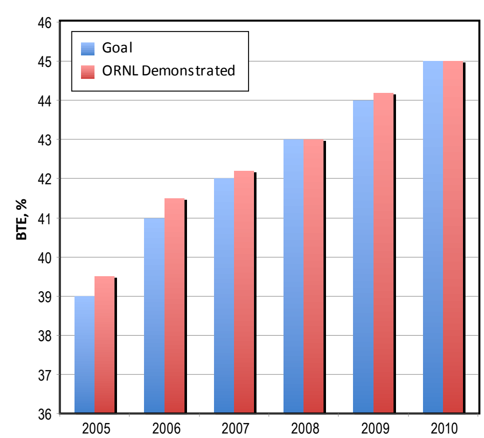
- Argonne National Laboratory (ANL) made a significant discovery showing two mechanisms for spray dilution at the end of injection. They confirmed that fuel cut-off leads to very rapid leaning, as predicted by Musculus of Sandia National Laboratories (SNL), but also that spray broadening enhances this effect. SNL researchers have shown that this effect can contribute to unburned hydrocarbons, and the ANL data helps to explain the mechanisms that cause it. New studies of multiple injection show that the fuel distributions from two consecutive sprays (such as main-post) are very similar, even when the second spray immediately follows the first. This shows that the flow field generated by the first spray has little impact on the second, and is an important feature to capture in computational spray and engine modeling. (Powell, ANL)
- SNL is developing of the physical understanding to guide and the modeling tools to refine the design of optimal, clean, high-efficiency combustion systems. They completed the following during FY 2010: (1) evaluated the impact of biodiesel blending on in-cylinder unburned hydrocarbons (UHC) and CO spatial distributions and on engine-out emissions for low-temperature operating regimes; (2) demonstrated UHC/CO emission advantages for biodiesel blends, despite their lower volatility; (3) isolated the influence of fuel volatility and ignition quality on UHC and CO emissions by examining an orthogonal fuel property matrix and established secondary importance of fuel volatility; (4) imaged increased post-injection wall-wetting when biodiesel blends are employed, and established ineffectiveness of exhaust blow-down flows in impeding jet penetration; (5) applied liquid imaging diagnostics to various low-temperature operating conditions and demonstrated excellent qualitative agreement with simulated spray penetration and droplet distributions; and (6) examined the impact of initial and boundary conditions on predictions of fuel-air mixing leading to unrealistic predicted UHC and CO emissions. (Miles, SNL)
- In-cylinder laser diagnostics developed by SNL showed that LTC conditions have a distinct period of large polycyclic aromatic hydrocarbon (PAH) formation with much slower soot formation. It was shown that late post-injections can generate hydroxyl to oxidize main-injection soot, but spray targeting is important. Optical engine hardware modifications for dual-fueling are underway. Based on previous work, SNL showed how post-injections can help to oxidize UHCs from over-lean near-injector regions. (Musculus, SNL)
- SNL is conducting research to address soot formation and oxidation in diesel, biodiesel, and surrogate diesel fuel sprays. They generated a detailed spray dataset working collaboratively with a dozen institutions from around the world and made the results available on the Engine Combustion Network internet data archive for advanced computational fluid dynamics (CFD) model development.



Quantitative Soot Volume Fraction by Planar Laser-Induced Incandescence and Laser Extinction (Pickett, SNL)

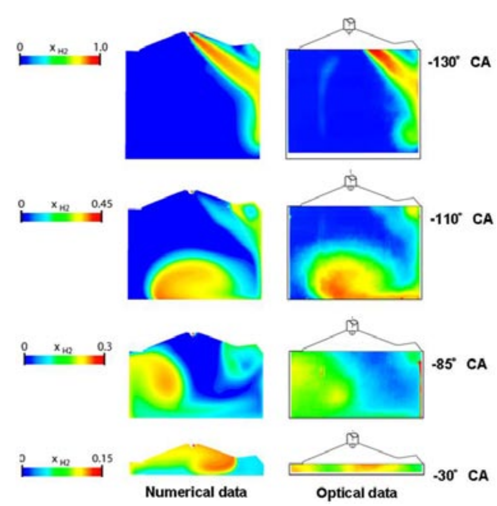
The first quantitative soot volume fraction measurements were made within reacting biodiesel sprays and the first soot size and morphology measurements within reacting sprays were made by transmission electron microscopy-grid thermophoretic sampling. The extent of liquid penetration at late-cycle, post-injection conditions was characterized, allowing assessment of oil dilution likelihood with DPF regeneration. (Pickett, SNL)

- Oak Ridge National Laboratory (ORNL) is investigating potential near-term technologies for expanding the usable speed-load range and to evaluate the potential benefits and limitations of engine technologies for achieving HECC in a light-duty diesel engine. They upgraded their GM 1.9-L engine installation to include a low-pressure EGR loop reflective of recent production engines. Reactivity-controlled compression ignition (RCCI) was achieved at 4.2 bar brake mean effective pressure (BMEP) on a multi-cylinder engine using gasoline and diesel dual fueling. The emissions of RCCI combustion were characterized for comparison with conventional and HECC combustion. (Briggs, ORNL)
- SNL developed simulations of their optical hydrogen-fueled internal combustion engine using validation through comparison of measured and modeled results, chemiluminescence imaging, particle image velocimetry, and planar laser induced fluorescence. They improved performance and usability of the RAPTOR massively-parallel large eddy simulation (LES) solver for internal combustion engine related calculations as part of the DOE Innovative and Novel Computational Impact on Theory and Experiment program. They also developed a hierarchy of benchmark simulations aimed at understanding high Reynolds number, high-pressure, direct-injection processes for LTC and diesel engine applications. (Oefelein, SNL)
- Lawrence Livermore National Laboratory (LLNL) is working on the development and application of computationally efficient and accurate simulation tools for prediction of engine combustion. They see opportunities for reducing simulation time and cost by a factor of 1,000 through innovative numerical solution approaches. Multi-zone chemical kinetics have been demonstrated to be a flexible and accurate tool for simulation of high-efficiency clean combustion modes such as HCCI and PCCI. (Flowers, LLNL)
- SNL is providing the fundamental understanding (science-base) required to overcome the technical barriers to the development of practical HCCI and HCCI-like engines by industry. They showed that hot residuals have almost no effect on thermal stratification (TS) in a low-residual HCCI engine: (1) determined the differences in TS between motored and fired operation, (2) compared one- and two-line temperature-imaging diagnostics and achieved images with precision <5 K, and (3) showed the correlation between hot zones, initial combustion, and crank angle (CA)10 timing (crank angle at 10% of fuel burned). They also investigated the use of intake boost for extending the high-load limit of HCCI: (1) determined the high-load limit over a range of engine speeds, (2) determined why high CA50 retard (to prevent knock) is possible with boost, and (3) initiated an investigation of efficiency improvements for boosted HCCI, achieving about a 9% improvement in fuel economy for intake pressures from 2-2.8 bar. (Dec, SNL)
- SNL is studying negative valve overlap (NVO) using laser diagnostics as a way of controlling HCCI combustion. They performed experiments to test for ignition-enhancement effects of NVO reformed products via single-species seeding experiments, achieved order-of-magnitude improvement of tunable diode laser CO diagnostic by switching to 2,319-nm excitation and implementing wavelength modulation signal processing, applied the tunable diode laser diagnostic to measure CO time-resolved concentrations during fired NVO engine operation, and advanced the capabilities of Sandia's collaborative CFD engine model to include simulation of fired NVO engine operation. (Steeper, SNL)



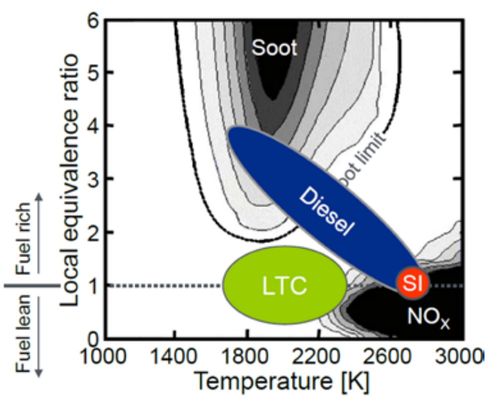
Path to Demonstrating FY 2010 FreedomCAR Engine and Efficiency Milestones (Briggs, ORNL)

- ORNL demonstrated the FY 2010 DOE Vehicle Technologies milestone of 45% peak brake thermal efficiency (BTE) on a light-duty diesel engine. This was accomplished through a combination of shaft power and electrical power generated from an organic Rankine cycle using the exhaust heat of the engine. Through GT-POWER simulations, they demonstrated an average power recovery of 300-400 W from an organic Rankine cycle over a simulated drive cycle. This corresponds to a 5% improvement in vehicle fuel economy. (Briggs, ORNL)
- Los Alamos National Laboratory (LANL) is facilitating engine modeling by improving accuracy of the modeling, and improving the robustness of software. They are continuing to improve the physical modeling methods and developing and implementing new mathematical algorithms, those which represent the physics within an engine. Hp-adaptive characteristic-based split and Petrov-Galerkin finite element methods for all flow regimes were developed, from incompressible to high-speed compressible. KIVA-4 capability has been extended to predict heat conduction and heat flux and a parallel version will be released after more testing and feedback from initial distributions of the beta version. (Carrington, LANL)
- LLNL is developing chemical kinetic models for conventional and next-generation transportation fuels need to be developed so that engine simulation tools can predict fuel effects. During the FY, LLNL: (1) developed first-ever primary reference fuel mechanism for gasoline and diesel fuels; (2) developed of high- and low-temperature mechanisms for series of iso-alkanes that covers the entire distillation range of diesel fuel; (3) successfully simulated intermediate temperature heat release, which plays an important role in maintaining HCCI operation as the boost pressure is increased; (4) developed improved mechanisms for fuel components in gasoline fuels: toluene, pentenes, and hexenes; and, (5) developed a functional-group kinetics modeling approach for n-alkanes that greatly reduces the size of the mechanism for use in multidimensional engine simulations. (Pitz, LLNL)
- SNL is designing a free-piston engine suitable for hybrid vehicle applications. The project has progressed by conducting idealized combustion experiments, designing and procuring the linear alternators required for control and power conversion, and conducting computational fluid dynamics design of the inlet/exhaust processes. The design has evolved into a dynamically balanced configuration suitable for seamless incorporation into an automotive application or distributed power generator. The ultimate goal is to combine the developed components into a research prototype for demonstration of performance. (Van Blarigan, SNL)
- ANL upgraded their single-cylinder research engine used to study the potential of hydrogen direct injection with the intent to increase engine efficiencies. Indicated thermal efficiency levels increased by 6% (from 37% to 43%) over a wide load range through optimization of engine geometry. Peak brake thermal efficiency of 43.6% demonstrated at 3,000 RPM and 14.3 bar IMEP at engine-out emissions levels below 100 ppm using turbocharging. Fast-acting piezo injectors were integrated into the experimental setup to allow expansion of test regime and optimize mixture stratification. A three-dimensional (3D) CFD simulation was developed and validated against optical results from SNL and subsequently used for injection strategy optimization. (Wallner, ANL)
- SNL is investigating advanced hydrogen-fueled internal combustion. Their development efforts are focused on achieving an advanced hydrogen engine with peak break thermal efficiency greater than 45%, near-zero emissions, and a power density that exceeds gasoline engines. This fiscal year, the main focus has been on the characterization of the in-cylinder flow field and the use



Validation of 3D-CFD Hydrogen Combustion Simulation Results with Optical Data (Wallner, ANL) of high-speed Schlieren imaging to study the hydrogen injection and flame propagation. Selected accomplishments include: (1) expanded the air/fuel mixing database by adding fuel concentration data from multi hole nozzles to satisfy the critical needs of our simulation collaborators, (2) implemented a high speed Schlieren imaging system to visualize the hydrogen injection event and the flame propagation in the direct injection hydrogen internal combustion engine, and (3) established accuracy of KIVA and FLUENT simulations (performed at LLNL and ANL, respectively) in predicting pre ignition mixture formation for a single hole nozzle. (Salazar, SNL)

- ORNL is analyzing and defining specific advanced pathways to improve the energy conversion efficiency of internal combustion engines from nominally 40% to as high as 60%, with emphasis on opportunities afforded by new approaches to combustion. They conducted detailed thermodynamic analysis on the fuel conversion efficiency impacts of several unconventional approaches to combustion, including chemical looping combustion, isothermal preheated gas phase combustion, and isothermal preheated gas phase combustion with thermochemical recuperation, and completed in-depth thermodynamic analyses of the impact of fuel type on ideal theoretical engine efficiency. (Daw, ORNL)
- Ford is focusing on complete and optimal system solutions to address boost system challenges, such as efficiency degradation and compressor surge, etc., in diesel combustion/emission control system development, and to enable commercialization of advanced diesel combustion technologies, such as HCCI/LTC. They eliminated the variable diffuser vane compressor based on flow bench testing due to larger than expected operational range constraints; the variable inlet guide vane technology was considered non-compatible with their optimized impeller geometry and did not demonstrate further benefit; and the dual-sequential compressor volute was found to have merit in efficiency and operational range enhancement based on numerical study. However, this technology has difficulty to be implemented in small turbochargers due to package space constraints. (Sun, Ford)
- ANL is quantifying the influence of low-cetane fuel ignition properties to achieve clean, high-efficiency combustion, optimize the advanced controls available to create a combustion system that retains diesel-like efficiency while reducing NOx and other criteria pollutants compared to conventional diesel, and demonstrate the use of combustion imaging techniques to aid in determining the operational boundaries of gasoline compression ignition operation. Several types of low cetane fuels were operated successfully using this strategy; iso-paraffinic kerosene, 75 Research octane number (RON) gasoline, and 65 RON gasoline. Their GM 1.9 L turbodiesel engine, operating on 85 RON gasoline, was successful in producing high power density (3,000 RPM, 16 bar BMEP), high efficiency (40% BTE at 2,750 RPM, 12 bar BMEP) and low NOx (less than 1 g/kW-hr at 2,750 RPM, 12 bar BMEP). (Ciatti, ANL)



Soot and NOx as Function of Phi and Combustion Temperature (Ciatti, ANL)

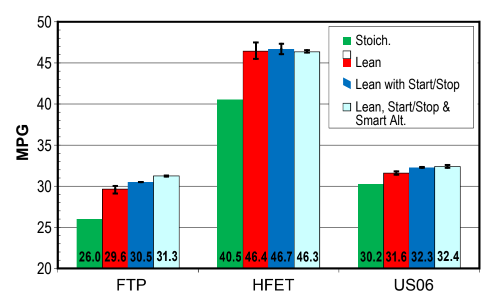
- Volvo Powertrain North America is developing a very high fuel economy, heavy-duty, truck engine utilizing biofuels and hybrid vehicle technologies. The project included fundamental combustion investigations such as the effect of diesel injection pressure and rate shaping to be implemented in an engine designed to operate within a narrow speed range, allowing further optimization of fuel efficiency and emission control. In addition to the development of the reciprocator itself, exhaust waste heat recovery (WHR) is being utilized to further improve net engine output efficiency. Two different WHR concepts are being investigated – capturing exhaust energy through a turbine located in the hot exhaust stream (turbocompound) and the use of a Rankine bottoming cycle, based on exhaust energy, to power a turbine. Both WHR systems can produce energy in either mechanical form or, using a conversion device, in electrical form for storage. Hybrid components and features are included in the powertrain concept allowing for engine shutdown at idle and the recovery of inertial energy of the vehicle during deceleration. Finally, a fully automated power shift transmission is being developed so that the engine can be more effectively operated under optimal conditions and, also, to reduce the losses in the driveline between the engine output and the production of tractive force at the tire-road interface. (Tai, Volvo Powertrain North America)

- ORNL is expanding robust HCCI operation with advanced valve and fuel control technologies. Parametric studies to determine the operable regions of HCCI combustion, as well as the sensitivity to available engine controls were completed. The results show that spark timing has only a minimal impact on engine load and emissions, and its effect is mainly to increased engine stability. Fuel injection timing exhibits a stronger control authority over HCCI combustion, and each engine operating condition has an optimal fuel injection timing for best efficiency. Importantly, many of the engine operating conditions can be reproduced with several different NVO durations, with each having its own optimal fuel injection timing. (Szybist, ORNL)
- Cummins is improving light-duty vehicle (5,000 lb. test weight) fuel efficiency over the Federal Test Procedure (FTP) city drive cycle by 10.5% over today's state-of-the-art diesel engine, and developing and designing an advanced combustion system that synergistically meets Tier 2 Bin 5 NOx and PM emissions standards while demonstrating the efficiency improvements. They achieved 0.08 g/mi NOx on the FTP75 emissions certification cycle without NOx aftertreatment while improving the fuel efficiency by 4.5% relative to the 10.5% target and determined that they can achieve 0.07 g/mi NOx on the FTP75 emissions certification cycle with selective catalytic reaction (SCR) NOx aftertreatment while improving the fuel efficiency by 9.1% relative to the 10.5% target. (Stanton, Cummins)

B. Energy-Efficient Emission Controls

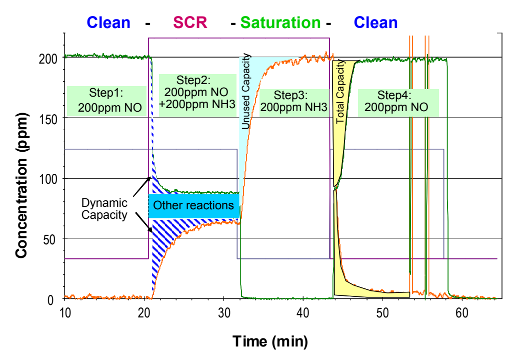
The following project highlights summarize the advancements made in emission control technologies to both reduce emissions and reduce the energy needed for emission control system operation.

- PNNL investigated the HC inhibition of a Fe-zeolite SCR catalyst through steady-state reactor tests and spectroscopic analysis in collaboration with ORNL. They developed a HC storage model and a single-site inhibition kinetic model to quantitatively describe the effects on various SCR reaction steps, such as NH_3 storage and NO oxidation. This project resulted in the first peer-reviewed published study describing the NOx reduction performance of Cu-SSZ-13. PNNL also demonstrated that the sintering of Pt can be minimized through anchoring at penta-coordinated Al sites on the γ-alumina surface that we previously had identified using ultra-high field nuclear magnetic resonance spectroscopy coupled with high resolution transmission electron microscopy. (Lee, PNNL)
- PNNL is developing a fundamental understanding of candidate next-generation LNT materials for NOx after-treatment for light-duty lean-burn (including diesel) engines. Results obtained this year demonstrate that direct NO decomposition is not applicable for the real system. When K is used as storage element, the maximum temperature is shifted to 400°C or higher, depending on the support. PNNL studies demonstrated that a $MgAl_2O_4$ support material provided especially promising NOx uptake performance. (Peden, PNNL)
- ORNL is investigating ways to optimize the emission control and fuel efficiency of diesel engines using advanced combustion strategies including LTC, HECC, and RCCI. The burden of the emissions control system to control NOx and PM emissions is significantly reduced with advanced combustion, but higher CO and HC emission control is needed. New sensors and control systems are being studied. A radio frequency (RF)-based sensor technology was studied on a light-duty diesel engine with an exhaust system containing a DOC and DPF. When compared with the common differential pressure sensor approach, the RF sensor showed more stable and accurate measurement of PM loading during experiments where engine loads



Fuel economy for three different drive cycles for combinations of the fuel saving technologies employed by the BMW 120i vehicle (as compared to stoichiometric-only operation). (Parks, ORNL) and speeds varied. The RF sensor's more accurate measurement of DPF loading will enable fuel consumption reduction from DPF regeneration processes as well as improved diagnostics for on-board diagnostics requirements. (Parks, ORNL)

- SNL modified their previously developed NOx storage and reduction mechanism in order to account for N_2O formation during low-temperature cycles and to allow for complete catalyst regeneration during short (60 s/5 s) cycles under realistic concentrations of reductant. Computational tools were developed to simulate a complex sulfation/desulfation protocol described in the literature, along with a multipart objective function used in fitting the simulation results to key aspects of the experimental behavior. A highly streamlined (nine-reaction) elementary mechanism was also developed for sulfation/desulfation that was nevertheless capable of reproducing the experimental data quite well. In addition, the thermodynamic relations necessary to extract temperature-dependent enthalpies and entropies for the surface species involved in the various mechanisms were formulated, and the results were tabulated in Chemkin format. (Larson, SNL)
- ORNL is developing engine/aftertreatment system configurations and control strategies that meet stringent emissions regulations while improving overall vehicle efficiency in a Cooperative Research and Development Agreement (CRADA) with Navistar, Inc. During FY 2010, they obtained miniature DPFs with several different formulations from suppliers, loaded the filters in engine exhaust, and conducted temperature programmed oxidation experiments in a flow reactor. They observed complex variations in soot oxidation rate and pressure drop evolution for cases with O_2 and NOx in the feed gas, which could be explained by spatial variations in the regeneration process. (Pihl, ORNL)
- ORNL is investigating methods for improving performance and/or durability of LNTs and improving the fundamental understanding of deactivation mechanisms that result during the regeneration of LNTs. In the past year, they found that: (1) ceria is a very effective adsorbant of sulfur. Its inclusion in catalyst formulations suggests that it could offer an initial level of protection from the Ba-phase; (2) using ceria-zirconia as a support for the Ba-storage phase has a large effect on sulfate stability as peak sulfur release decreases by ca. 100°C; and (3) advanced characterization techniques have been developed to monitor the impact of thermal cycling on both Pt size and storage phase morphology under realistic conditions: the results illustrate the importance of using these real-world conditions to correlate materials effects on operating conditions. (Toops, ORNL)
- ORNL is improving diesel engine-catalyst system efficiency through better combustion uniformity, engine calibrations and catalyst control. During the past year, ORNL: (1) quantified induced cylinder-specific exhaust variations on heavy-duty diesel engine via in situ high-speed exhaust concentration measurements; (2) characterized distributed SCR catalyst reactions and effects of thermal aging; providing the basis for developing SCR design and control strategies to achieve improved efficiency and real-time on-board catalyst-state assessment; (3) experimentally verified validity of LNT conceptual model showing basis for increasing effluent NH_3 with progressive sulfation; (4) developed new insights into chromatography effects and non-invasive nature of spatially resolved capillary-inlet mass spectrometer (SpaciMS) capillary sampling via external partnerships; and (5) improved insights into LNT chemistry via modeling work with external partnerships. (Partridge, ORNL)



Cummins 4-Step Protocol for SCR Catalyst Performance Assessment (Partridge, ORNL)

- ORNL continued to co-lead the CLEERS Planning Committee and facilitation of the SCR, LNT, and DPF Focus group telecoms with strong domestic and international participation. ORNL also continued to co-lead the LNT Focus Group and refinement of the standard LNT materials protocol and provide advice to adjust current DOE national lab projects associated with CLEERS to bring them into closer alignment with the 2007 and 2008 CLEERS industry partner priority surveys. Organized the 13th CLEERS workshop at University of Michigan, Dearborn on April 20-22, 2010, and maintained the CLEERS Web site (www.cleers.org) including functionalities, security, and data to facilitate Web meetings and serve focus group interactions. ORNL also increased utilization of models and kinetic parameters produced by CLEERS projects in full system simulations of alternative advanced powertrain options. (Daw, ORNL)

- ORNL is collaborating with SNL and PNNL to produce kinetic information for LNT and urea-SCR aftertreatment devices, both as individual and system integrated components as part of the CLEERS project. They continued a systematic study of LNT regeneration chemistry with an emphasis on resolving spatiotemporal distribution of reaction: impact of reductant type and temperature; NH_3 and N_2O selectivity; and axial redistribution of NOx storage. They experimentally confirmed a conceptual model of how sulfation affects NH_3 generation and conversion in collaboration with the Cummins CRADA project and implemented a global LNT cycling model which incorporates the intermediate roles of NH_3. They collaborated with the Prague Institute of Chemical Technology in global LNT modeling, refined a detailed LNT cycling model in collaboration with SNL, and developed a new transient NH_3 SCR flow reactor evaluation protocol. The SCR protocol on CLEERS reference Fe zeolite and a new commercial Cu-zeolite SCR catalyst was testing using the exhaust from a 2010 diesel truck. (Daw, ORNL)
- ANL is characterizing the oxidation behavior of diesel PM emissions in terms of heat release and oxidation rate. The amount of heat release in diesel PM oxidation and the concentrations of soluble organic compounds were measured. Differences in soot oxidation behaviors were also observed for two different samples: a soluble organic compound-containing PM sample and a dry soot sample. (Lee, ANL)
- PNNL is developing a fundamental understanding of the integration of SCR and DPF technologies for on-road heavy-duty application. The interaction of steady-state and transient DPF-SCR couples will be probed in order to better understand the optimization of combining the two units with a view to proper function and greater integration. The system limitations and define basic design requirements for efficient on-board packaging and integration with the engine will be determined, in order to minimize fuel utilization or impact on vehicle efficiency. The scientific understanding that will lead to the design and optimization of 4-way devices will be determined, which will address soot, HCs, CO, and NOx in a single unit. (Rappe, PNNL)
- PNNL and their CRADA partner GM are investigating fresh, laboratory- and engine-aged DOC and SCR catalysts. These studies are intended to obtain a better understanding of various aging factors that impact the long-term performance of catalysts used in the urea-SCR technology, and improve the correlation between laboratory and engine aging in order to reduce emission control system development time and cost. Results demonstrate that the growth and alloying of PGM in DOCs are the primary materials changes and, thus, likely causes of deactivation. For the case of the urea-SCR catalyst, both the collapse of the zeolite structure and the growth of particles of the active metal are observed for a heavily-aged sample and certainly important causes of activity loss. (Peden, PNNL)

C. Health Impacts

The Health Impacts activity studies potential health issues related to new powertrain technologies, fuels, and lubricants to ensure that they will not have adverse impacts on human health. The following are highlights of the work conducted in FY 2010.

- ORNL is striving to understand the potential impact of developing fuel, combustion, and aftertreatment technologies on air quality and, thereby, human health. They completed characterization of PM emissions from both stoichiometric and lean-burn direct-injection spark ignition (DISI) vehicles operating on gasoline and ethanol blends (E0, E10 and E20). Measurements of aldehyde, ketone, and ethanol for both light-duty DISI vehicles, and comparison of PM emissions from light-duty diesel engine in conventional, PCCI and dual-fuel RCCI operation were completed. (Storey, ORNL)

- NREL continued progress on the Collaborative Lubricating Oil Study on Emissions project. The objective of this project is to quantify the relative contributions of fuels and engine lubricating oil on PM) and semi-volatile organic compound emissions from in-use motor vehicles fueled with gasoline, E10, diesel, biodiesel, and natural gas while operating with fresh and used crankcase lubricants. All heavy-duty vehicle emissions testing was completed in June 2010, and all vehicle emissions testing for the project has been completed. (Lawson, NREL)
- The Health Effects Institute is conducting the Advanced Collaborative Emissions Study to characterize the emissions and assess the safety of advanced heavy-duty diesel engine and aftertreatment systems and fuels designed to meet the 2007 and 2010 emissions standards for PM and NOx. In FY 2010, emissions of engine B' were characterized and the exposure atmosphere at the Lovelace Respiratory Research Institute in Phase 3 was successfully completed, which allowed the main health effects testing during Phase 3B to go forward. During spring and summer of 2010, the short-term mouse and rat exposures were successfully completed. (Greenbaum, Health Effects Institute)

SOLID STATE ENERGY CONVERSION

Several projects are being pursued to capture waste heat from advanced combustion engines in both light- and heavy-duty vehicles using thermoelectrics (TEs). Following are highlights of the development of these technologies during FY 2010.

- BSST, LLC is developing a high-efficiency TE waste energy recovery system for passenger vehicle applications. A prototype high-temperature (600°C inlet gas temperature), cylindrical thermoelectric generator (TEG) was designed, built and tested. The Phase 5 cylindrical TEG subsystem packaging design has been completed including inlet/outlet sections with a coaxial bypass valve in preparation for BMW X6 and Ford Fusion vehicle exhaust system installation. The MATLAB®/Simulink® model was updated to predict performance in the cylindrical TEG form factor. The upgraded model was used to identify sources of performance deficiencies in the bench prototype cylindrical generator. The model was also used to identify design upgrades that provide countermeasures to the deficiencies. (LaGrandeur, BSST)
- Michigan State University is using a TEG to provide a 10% improvement in fuel economy by converting waste heat to electricity used by an over-the-road truck. During the past year, they developed a functionally graded material methodology (and other design improvements) resulting in an 80% reduction of leg failures during operation, developed couple bypass technology, capable of recovering up to 80% of electrical power otherwise lost on account of couple failure, and improved N-type skutterudite, increasing the figure of merit by 25% to 1.2. (Schock, Michigan State University)
- General Motors is identifying distributed cooling and heating strategies that can efficiently augment or replace a vehicle's central heating, ventilation and cooling (HVAC) system by delivering localized cooling/heating of key human body segments that strongly influence an occupant's perceived thermal comfort. Preliminary test results indicate that localized cooling/heating effectively influences an occupant's perceived thermal comfort and that certain combinations of these strategies work well together to positively affect human comfort. Clear preferences regarding the operating parameters of the local cooling/heating HVAC components have emerged from the collected human subject test data. These preferences will guide further refinement of the operating

Thermal Mannequin Inside the Mock-Up Vehicle in the University of California, Berkeley Environmental Test Chamber (Gundlach, General Motors) parameters and the selection of a final set of strategies to be implemented in prototype hardware. (Gundlach, General Motors)

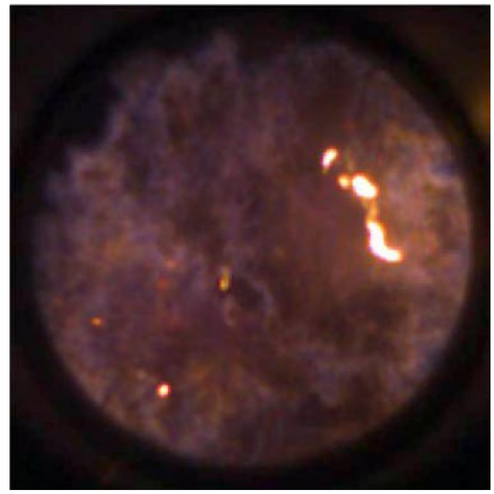
- Ford is identifying technical and business approaches to accelerate deployment of automotive TE HVAC technology. They completed development of metrics to be used for measuring and demonstrating technical performance against objectives in order to measure coefficient of performance and HVAC system efficiency, established thermal comfort and vehicle performance criteria and targets through analytical computer aided engineering and baseline vehicle testing in a climate wind tunnel under representative operating conditions, evaluated and built several TE heat pump designs to study manufacturing and performance trade-offs, and discovered that Sn is a resonant level in Bi_2Te_3 and made progress in showing performance enhancements in commercial p-type alloys. (Maranville, Ford)
- General Motors is developing advanced thermoelectric technology for automotive waste heat recovery. They have made substantial progress on developing, validating, and testing a TE generator for waste heat recovery from a vehicle exhaust system. This includes advances in the design, engineering, and integration of a prototype device, improvements in TE material performance, and advances in TE module design and fabrication processes. (Meisner, General Motors)

UNIVERSITY RESEARCH

- The University of Michigan (UM) is exploring new high-pressure lean-burn combustion that can enable future gasoline engines with 20-40% improved fuel economy and determining the fuel economy benefits of engines and engine cycles designed to utilize advanced combustion modes. During the year, UM demonstrated spark-assisted compression ignition (SACI) in the UM fully-flexible valve actuation engine, enabling load extension up to 7.5 bar net mean effective pressure under naturally aspirated operation by decreasing the peak heat release rates. A comprehensive analytical exploration of laminar flame propagation was carried out for spark-assist conditions at high dilution level and high unburned temperature. A flame speed correlation was developed for use in modeling turbulent SACI flame propagation. Experimental testing of a microwave-assisted spark plug at the University of California, Berkeley has demonstrated stability improvements in HCCI combustion in a CFR engine under lean conditions with potential application to spark-assisted compression ignition. The computational singular perturbation technique has been used to classify ignition regimes encountered in turbulent stratified conditions, according to the relative importance of spontaneous and deflagrative ignition. (Assanis, UM)
- The University of Wisconsin is developing high efficiency internal combustion engines with goals of improved fuel economy by 20-40% in light-duty and 55% BTE in heavy-duty engines. Greater than 55% thermal efficiency achieved using dual fuel reactivity-controlled compression ignition combustion in heavy-duty engines over wide load range with Environmental Protection Agency 2010 NOx and soot levels met in-cylinder (i.e., without need for after-treatment). Guidelines were established for engine control methodologies under light- and high-load operating conditions with consideration of fuel property and mixture preparation effects. Combustion and realistic fuel vaporization submodels were developed and validated for biofuels and gasoline/diesel surrogates to be used for further optimization and combustion system concept evaluation. A methodology was formulated for efficient engine system transient control strategies appropriate for engine speed/load mode transitions. (Reitz, University of Wisconsin)
- Michigan State University (MSU) is demonstrating an SI and HCCI dual-mode combustion engine for a blend of gasoline and E85 (85% ethanol and 15% gasoline) for the best fuel economy. The target SI and HCCI dual-mode combustion engine design was finalized and the real-time control oriented SI, HCCI, and SI-HCCI hybrid combustion engine model was developed and calibrated using the GT-POWER simulation results. The SI combustion optical engine has been designed and fabricated, and the baseline SI combustion tests are underway. The HCCI combustion optical engine design with two-step valve lift and electrical cam variable valve timing is underway. The hybrid combustion simulations show that steady-state operational parameters are not optimized

for mode transient control and model-based control is necessary for a smooth combustion mode transition. (Zhu, Michigan State University)

- The University of Houston is identify the NOx reduction mechanisms operative in LNTs and in situ SCR) catalysts, and to use this knowledge to design optimized LNT-SCR systems in terms of catalyst architecture and operating strategies. Steady-state and transient NOx storage and reduction experiments have been carried out to determine mechanistic pathways and to quantify kinetics of the NO/CO/H_2O on Pt/BaO/Al_2O_3 reaction system. The results clearly show the production of NH_3 does not require H_2 as a reductant, with NH_3 forming by the hydrolysis of an adsorbed nitrogen-carbon-oxygen intermediate and by the generation of H_2 via the water-gas shift reaction. A combination of bench-scale reactor experiments of LNT, SCR, and LNT/SCR systems, which includes the use of SpaciMS, is providing a database for subsequent refinement of reactor models containing kinetic models with varying degrees of complexity. (Harold, University of Houston)



SI Combustion Image from Optical Engine Tests (Zhu, Michigan State University)

- The University of Connecticut is developing 3-D composite nanostructures for lean-NOx emission control devices. ZnO, Ga_2O_3, Zn_2SnO_4 and TiO_2 nanowire/nanodendrite arrays on various substrate such as silicon, glass and ceramic honeycomb substrate were successfully synthesized and characterized. 3-D composite nanostructures (such as ZnO/(La,Sr)MnO_3(LSMO), ZnO/(La,Sr)CoO_3(LSCO) and TiO_2/LSMO) by pulsed laser deposition, were successfully fabricated and characterized using sputtering and wet chemical methods. High activity of $LaMnO_3$ systems was identified for O involving reactions arising from its ability to support partially O covered surfaces by calculation. (Gao, University of Connecticut)
- Michigan Technological University developing experimentally validated DOC, DPF and SCR models with real-time internal state estimation strategies that support future onboard diagnostics, advanced control system, and system optimization objectives for DOC-DPF-SCR aftertreatment systems that minimize the energy penalty of meeting emission regulations. They developed a new procedure to measure a DPF's passive oxidation rate as a function of NO_2 concentration, temperature and PM filter loading, NO_2/PM ratio and exhaust flow rate. They also developed improved SCR models for the Fe-zeolite ORNL reactor data and created a reduced order model of DOC suitable for internal state estimation and a high-fidelity simulation of the DPF. (Johnson, Michigan Technological University)

I.3 Honors and Special Recognitions/Patents

HONORS AND SPECIAL RECOGNITIONS

1. Research on Ag_2O/Zn_2SnO_4 hybrid nanowires and their unique reversible catalytic multi-gas sensing is highlighted as the front cover story on *Journal of Materials Chemistry, Volume 20, issue 25,* June 2010. (Gao, University of Connecticut)

2. Richard Steeper (SNL) was appointed Co-Chair of SAE Powertrain, Fuels, and Lubes Activity.

3. Paul Miles of SNL:

- Delivered the keynote lecture: "Sources of UHC and CO in Low Temperature Diesel Combustion Systems," Thermo- and Fluid-Dynamic Processes in Diesel Engines, Sept. 14–17, 2010.
- Delivered the invited talk: "On the Sources of UHC and CO in Low Temperature Combustion Systems," 11th International Conference on Present and Future Engines for Automobiles, May 30 – June 3, 2010.
- Received the SAE Meyers Award for: "Detailed Unburned Hydrocarbon Investigations in a Highly-Dilute Diesel Low Temperature Combustion Regime," Koci CP, Ra Y, Krieger R, Andrie M, Foster DE, Siewert RM, Durrett RP, Ekoto I, Miles PC. SAE technical paper 2009-01-0928, SAE Int. J. Engines 2:858-879, 2009.
- Lecture series presenter: "Physical Fluid Dynamics and RANS-based Modeling Issues in Reciprocating Engines," Lund University, Feb. 1–5, 2010.
- Elected Co-chair Society of Automotive Engineers Powertrain, Fuels, and Lubricants activities.

4. Lyle Pickett (SNL) was awarded the SAE Excellence in Oral Presentation Award (Caroline Genzale, 2010 World Congress, Paper 2010-01-0610).

5. Charles Westbrook (LLNL) received an Honorary Doctorate Degree from the University of Nancy, France, 2010.

6. Charles Westbrook (LLNL) was elected President of the Combustion Institute.

7. William J. Pitz (LLNL) was awarded the best paper of the year in 2009 from the Combustion Society of Japan.

8. John Dec of SNL:

- Received SAE Excellence in Oral Presentation Award for paper 2010-01-1086, April 2010.
- Invited Panelist & Speaker, SAE International Congress, panel on High Efficiency IC Engines, April 2010.
- Received the ASME 2010 Internal Combustion Engine Award, September 2010.

9. Bill Partridge of ORNL: The CRADA-developed Fuel-in-Oil technology received the 2009 Southeast Regional Award for Excellence in Technology Transfer presented annually by the Federal Laboratory Consortium for Technology Transfer. The award recognizes laboratory employees who have accomplished outstanding work in the process of transferring a technology developed by a federal laboratory to the commercial marketplace.

10. Daniel Flowers (LLNL) gave invited talks at Lund University, Chalmers University, and Volvo Powertrain, all in Sweden, on advanced engine combustion modeling, June 2010.

11. Nick Killingsworth (LLNL) was invited to and sponsored by Tianjin University in China for a visiting postdoctoral research position, conducting advanced PCCI engine control research, August 2009 – November 2009.

12. Daniel Flowers (LLNL) served as external examiner for Ph.D. thesis on HCCI combustion at University of Cape Town, South Africa, May 2010.

13. Salvador Aceves (LLNL) served as an opponent at a Ph.D. exam at University of Castilla la Mancha, Spain, February 2010.

14. 2010 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting R&D Award, presented to John LaGrandeur, BSST.

15. International Conference on Thermoelectrics, July, 2010, Shanghai Chine, Best Technical paper award to Dr. Douglas Crane, BSST.

16. Jae-Soon Choi (ORNL) gave an invited keynote lecture at the 2nd International Symposium on Air Pollution Abatement Catalysis, Cracow, Poland, September 8–11, 2010.

17. Jae-Soon Choi (ORNL) gave an invited lecture at the KIChE Discussions on Catalysis Research, Busan, Korea, June 23–25, 2010.

18. Dennis Siebers (SNL) delivered an invited talk on the "Engine Combustion Network" at the 11th International Conference on Present and Future Engines for Automobiles, May 30 – June 3, 2010.

19. Robert Wagner (ORNL) delivered an invited talk on "Reactivity Controlled Compression Ignition Combustion in a Multi-Cylinder Engine" at the 11th International Conference on Present and Future Engines for Automobiles, May 30 – June 3, 2010.

INVENTION AND PATENT DISCLOSURES

1. "Filled Skutterudites for Advanced Thermoelectric Applications," Yang, J.; Meisner, G.P.; U.S. Patent 7648552 Issued January 19, 2010.

2. "Optimal power determination for a Thermoelectric Generator by setpoint dithering," Reynolds, M.G.; Cowgill, J.D.; P011627, Record of Invention submitted January 29, 2010.

3. "Algorithms for Bypass Valve and Coolant Flow Controls for Optimum Temperatures in Waste Heat Recovery Systems," Meisner, G.P.; P012265, Record of Invention submitted April 8, 2010.

4. "Method of Controlling Temperature of a Thermoelectric Generator in an Exhaust System." Prior, G.P.; Reynolds, M.G.; Cowgill, J.D.; P011519, U.S. Patent Application filed April 2, 2010.

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8. "Thermoelectric Generators for Waste Heat Recovery from Engine Exhaust," Meisner, G.P.; Yang, J.; P012262, U.S. Patent Application filed September 2010.

I.4 Future Project Directions

ADVANCED COMBUSTION AND EMISSION CONTROL RESEARCH FOR HIGH-EFFICIENCY ENGINES

A. Combustion and Related In-Cylinder Processes

The focus in FY 2011 for combustion and related in-cylinder processes will continue to be on advancing the fundamental understanding of combustion processes in support of achieving efficiency and emissions goals. This will be accomplished through modeling of combustion, in-cylinder observation using optical and other imaging techniques, and parametric studies of engine operating conditions.

- ANL is currently fabricating equipment that will allow them to study sprays under conditions defined by SNL's Engine Combustion Network. This collaboration shares identical hardware among leading spray research laboratories around the world, and defines a specific set of conditions for study. They will also begin a new collaboration with Westport Innovations to assist them in the design of their injectors for gaseous fuels. Westport is a leader in injectors for hydrogen and natural gas engines, and is interested in improving the reliability of some of its prototype injectors. ANL will use its X-ray techniques to image the motion of the internal components of the injector in situ, providing Westport with a unique diagnostic of its injector designs. ANL and Delphi Diesel Systems agreed to jointly study fuel injection under a CRADA partnership. Over the next three years, Delphi will deliver modern fuel system hardware to ANL to be studied using several X-ray diagnostics. These measurements will focus on the study of how different nozzle geometries affect the fuel distribution in the combustion chamber. This will provide a U.S. fuel systems company with access to the most advanced spray and injector diagnostics. ANL will also increase the relevance of our measurements by studying sprays under conditions even closer to those of modern diesel engines. Such improvements include faster data acquisition, processing, and analysis, improved X-ray detector systems, increased X-ray intensity, finer spatial resolution, and greater automation. (Powell, ANL)
- SNL is developing the physical understanding to guide and the modeling tools to refine the design of optimal, clean, high-efficiency combustion systems. In the coming year they will: (1) examine the impact of variable injection pressure, swirl ratio, and nozzle hole size on the fuel-air mixing process and subsequent UHC and CO spatial distributions; (2) extend UHC imaging studies to the horizontal plane to capture lack of symmetry in squish volume UHC sources associated with piston top valve pockets and head features; (3) obtain horizontal plane flow field data to support the interpretation of UHC images, to examine asymmetries in the squish flow patterns, and to characterize the attenuation of angular momentum in the squish volume; and (4) examine suitability of compressible-renormalization group k-ε and other turbulence models for engine flow simulations, in collaboration with high-fidelity LES modeling efforts. (Miles, SNL)
- SNL will explore UHC reduction by post-injections in greater depth by quantifying UHC improvements across parameter space to identify critical requirements for operating condition and post injection and using laser diagnostics (fuel-tracer, formaldehyde, and OH planar laser induced fluorescence) to understand UHC oxidation mechanisms of post-injections. They will build an understanding of in-cylinder LTC soot and PAH by using multiple laser wavelengths and high-temporal-resolution imaging/spectroscopy to track PAH growth and conversion to soot. SNL will also probe in-cylinder mixing and combustion processes and improve modeling for high-efficiency dual-fuel operation by: (1) using laser/optical diagnostics to discern flame propagation from distributed autoignition and define conditions that govern transitions from one combustion regime to the other, and (2) incorporating insight and validation data from optical experiments to improve model fidelity. (Musculus, SNL)
- SNL will continue conducting research to address soot formation and oxidation in diesel, biodiesel, and surrogate diesel fuel sprays. In the coming year, they will: perform direct measurements of mixing (equivalence ratio), investigate jet-jet interaction effects on flame lift-off, characterize side-

hole sprays compared to axial-hole sprays, and develop spray and combustion datasets for gasoline direct injection-type injectors. (Pickett, SNL)

- ORNL will continue investigating potential near-term technologies for expanding the usable speed-load range and to evaluate the potential benefits and limitations of these technologies for achieving HECC in a light-duty diesel engine. They plan to expand the load and speed range of RCCI on a multicylinder engine, evaluate performance of RCCI on simple load and speed transients, and conduct experiments to achieve partially premixed combustion on a multicylinder engine using gasoline fueling. (Briggs, ORNL)
- SNL will continue to develop a hierarchy of benchmark simulations aimed at understanding high Reynolds number, high-pressure, direct-injection processes for LTC and diesel engine applications using SNL Engine Combustion Network data. They will perform a series of LES calculations of their optical HCCI engine with emphasis on understanding in-cylinder thermal stratification and combustion processes over full engine cycles. SNL will bridge the gap between basic and applied research by participation in the Innovative and Novel Computational Impact on Theory and Experiment program doing detailed validation and analysis of turbulent reacting flow phenomena. (Oefelein, SNL)
- LLNL will continue working on the development and application of computationally efficient and accurate simulation tools for prediction of engine combustion. In the coming year they plan to: continue to validate and develop chemistry simulation capabilities that will enable the prediction of performance and emissions in the development of new vehicle powertrain technologies, improve computational solvers for chemical kinetic simulations through new numerical strategies, continue development of the next generation multi-zone chemical kinetics model for application to modern parallel computational fluid dynamics codes, and develop computational tools suitable for kinetic chemistry on general purpose graphical processing unit platforms to enable high-fidelity simulations on low-cost engineering workstations. (Flowers, LLNL)
- SNL will continue providing the fundamental understanding (science-base) required to overcome the technical barriers to the development of practical HCCI and HCCI-like engines by industry. In the coming year, they will: (1) complete the side-view imaging study of the evolution of TS from near-wall regions to the bulk-gas for a typical operating condition, (2) extend the side-view TS study to determine the effects of changes in coolant temperature, intake temperature, and engine speed on the development and distribution-pattern of TS, (3) expand the collaboration with J. Oefelein et al. to improve the LES-modeling grid for a better match with experimental data with the goal to understand flows creating TS and how to enhance TS, (4) high-efficiency, boosted HCCI: explore additional methods for increasing thermal efficiency and/or maximum load, including fuel effects, Miller cycle, and operating conditions, and (5) continue collaborations with General Motors on HCCI modeling, and with LLNL on improving chemical-kinetic mechanisms and on CFD/kinetic modeling. (Dec, SNL)
- SNL will continue studying NVO using laser diagnostics as a way of controlling HCCI combustion. They will apply TDL absorption and laser-induced fluorescence optical diagnostics to characterize reforming reactions during the NVO period, apply optical diagnostics to quantify piston wetting during NVO fuel injection to understand its effect on NVO- and main-combustion reactions, continue validation of the CFD model of our optical engine using optical and conventional measurements over a range of NVO operating conditions, and expand our tunable-diode-laser absorption diagnostic to permit in-cylinder measurement of other species such as H_2O, CO_2, and C_2H_2. (Steeper, SNL)
- In the coming year ORNL will: (1) assess efficiency benefits of partially premixed charge compression ignition combustion in a light-duty engine; (2) evaluate the potential performance and efficiency benefit of a combined supercharger/turbocharger on a light-duty diesel engine; and (3) analyze the comparative efficiency of multiple clean combustion approaches, including second-law analysis to identify loss mechanisms. (Briggs, ORNL)
- LANL will continue developing the hp-adaptive finite element method for multispecies flows in all flow regimes, begin implementing this method to perform modeling of internal combustion

engines, other engines, and general combustion, and develop comprehensive comparative results to benchmark problems and to commercial software as part of the verification and validation of the algorithms. They will also continue developing the Conjugate Heat Transfer Model, adding this model to the parallel version of KIVA, develop overset grid method for moving and immersed actuated parts such as valves for robust grid movement, and continue developing cut-cell grid generation. (Carrington, LANL)

- LLNL is developing chemical kinetic models for conventional and next-generation transportation fuels need to be developed so that engine simulation tools can predict fuel effects. During the coming FY, LLNL intends to: (1) develop chemical kinetic model for a high molecular-weight aromatic to represent the aromatics chemical class in diesel fuel; (2) develop low- and high-temperature mechanisms for a new series of iso-alkanes to represent the iso-alkane chemical class in diesel fuel; (3) test surrogate mixture models for gasoline by comparison to HCCI engine and rapid compression machine experiments; (4) validate the chemical kinetic mechanism of 2-methyl heptane, a model iso-alkane; and, (5) develop a functional group method for iso-alkanes in diesel fuel so that the chemical kinetic mechanism can be greatly reduced in size for multidimensional engine simulations. (Pitz, LLNL)
- SNL will continue designing a free-piston engine suitable for hybrid vehicle applications. Future planned activities include: (1) complete assembly of research prototype engine, helium starting system and bounce chamber air control motoring system as well as associated support and data acquisition hardware; (2) quantify piston friction drag with engine fully assembled and lubricated but without magnets installed; (3) perform single-shot tests without fuel to characterize synchronicity of the compressed helium starting system; (4) initially run the engine under bounce chamber air control motoring mode only to test the stabilizing capability of the linear alternator coupling; and (5) perform combustion experiments and measure indicated thermal efficiency at various compression ratios and equivalence ratios with both conventional and alternative fuels: hydrogen, natural gas, ethanol, biofuels, propane, gasoline, other renewables. (Van Blarigan, SNL)
- ANL will assess optimized injection strategies and injector nozzle designs of their direct injection hydrogen engine through integration of experimental work with predictive 3D-CFD simulation. Drive-cycle NOx emissions will be estimated based on steady-state single-cylinder engine test results and determine requirements for in-cylinder emissions reduction. They plan to demonstrate 45% peak brake thermal efficiency while meeting Tier II Bin 5 NOx emissions. (Wallner, ANL)
- SNL will continue investigating advanced hydrogen-fueled internal combustion. Their development efforts are focused on achieving an advanced hydrogen engine with peak break thermal efficiency greater than 45%, near-zero emissions, and a power density that exceeds gasoline engines. In the coming year they plan to: (1) complete the in-cylinder flow field data with velocity measurements under the intake valves and in the pent roof, (2) correlate the flame propagation characteristics with single cycle heat release and performance parameters, (3) compare jet propagation using planar laser induced fluorescence and Schlieren imaging for single and multi hole nozzles, and (4) upload air/fuel mixing data from multi-hole injectors to Sandia's Engine Combustion Network for easy access by modelers and finish the documentation of how to interpret and use the downloadable data posted on the Engine Combustion Network Web site. (Salazar, SNL)
- ORNL is analyzing and defining specific advanced pathways to improve the energy conversion efficiency of internal combustion engines from nominally 40% to as high as 60%, with emphasis on opportunities afforded by new approaches to combustion. In the coming year they plan to: (1) experimentally demonstrate low-irreversibility combustion in the Regenerative Air Preheating with Thermochemical Recuperation bench-top apparatus; (2) investigate feasibility of performing in-cylinder thermochemical recuperation with a VVA engine; and (3) develop and implement detailed models for in-cylinder flow, heat transfer, and reforming in the VVA engine during exhaust heat recuperation. (Daw, ORNL)
- Ford is focusing on complete and optimal system solutions to address boost system challenges, such as efficiency degradation and compressor surge, etc., in diesel combustion/emission control system development, and to enable commercialization of advanced diesel combustion technologies, such

as HCCI/LTC. In the coming year, Ford plans to fabricate the redesigned compressor and turbine wheel for small turbochargers, develop an actuation system, and conduct flow bench test validation and engine dynamometer tests. (Sun, Ford)

- ANL will continue to quantify the influence of low-cetane fuel ignition properties to achieve clean, high-efficiency combustion. They will evaluate the influence of lower compression ratio on successful ignition of gasoline in this engine (14:1, 15:1 and 16:1) compared to the stock 17.5:1 compression ratio, conduct experiments that will allow for transient operation of this combustion system to determine the suitability for application in an automobile, and ptimize the operating parameters to provide for smooth transient operation while retaining the high efficiency and ultra-low emissions signature. (Ciatti, ANL)
- Volvo Powertrain North America is developing a very high fuel economy, heavy-duty, narrow-speed truck engine utilizing biofuels and hybrid vehicle technologies. In the coming year, they will continue development of engine/transmission hardware/software design specifications and preparation for prototype procurement, development of engine/transmission hardware/software, testing and verification of components, and system assembly and demonstrator vehicle verification using biofuels and blends. (Tai, Volvo Powertrain North America)
- ORNL is expanding robust HCCI operation with advanced valve and fuel control technologies. They will develop a robust GT-POWER model, to be calibrated using the Phase 1 experimental data from the ORNL hydraulic valve actuation engine, identify modeling needs and perform the second phase of experiments with the ORNL hydraulic valve actuation engine, investigate the effect of multiple fuel injection strategies, develop cam profile for multi-cylinder HCCI, and demonstrate HCCI control on a multi-cylinder engine. (Szybist, ORNL)
- Cummins is improving light-duty vehicle (5,000 lb. test weight) fuel efficiency over the Federal Test Procedure (FTP) city drive cycle by 10.5% over today's state-of-the-art diesel engine, and developing and designing an advanced combustion system that synergistically meets Tier 2 Bin 5 NOx and PM emissions standards while demonstrating the efficiency improvements. In the coming year they plan to perform multi-cylinder engine testing using the Phase 2 hardware (revised 2-stage sequential turbo, piezo fuel system, high capacity EGR, controls, and aftertreatment) and develop a detailed engine calibration using the Phase 2 technology to meet FTP75 and SFTP2 emissions certification. (Stanton, Cummins)

B. Energy-Efficient Emission Controls

In FY 2011, work will continue on LNTs and urea-SCR to reduce NOx emissions. The focus of activities will be on making these devices more efficient, more durable, and less costly. For PM control, the focus will be on more efficient methods of filter regeneration to reduce impact on engine fuel consumption.

- ORNL will continue working to understand the potential impact of developing fuel, combustion, and aftertreatment technologies on air quality and, thereby, human health. In the coming year, they will determine lubricant contribution to PM emissions in DISI applications, characterize DISI PM emissions from start-stop operations typical of hybrid vehicle operations, and examine effect of combustion phasing on PM emissions from a DISI engine operating on gasoline and ethanol blends. (Storey, ORNL)
- PNNL will: (1) update their SCR model for the state-of-the-art Cu-SCR catalyst, and develop models to describe the performance degradation due to HC inhibition and catalyst aging; (2) evaluate the accuracy of the unit collector model with respect to nano-sized particulates, and improve the accuracy of micro-scale model for prediction of soot-catalyst contact and soot penetration into the filter substrate; (3) conduct detailed characterization of the active sites of the Cu-SCR catalyst with emphasis on the catalyst deactivation; (4) complete studies of CO_2 and H_2O effects on BaO morphology changes and NOx storage properties, and continue fundamental studies of novel high-temperature LNT formulations; (5) examine the interaction between catalysts in the integrated LNT-SCR or SCR-DPF system, including the passive regeneration of soot by

base metal catalyst on advanced filter substrate; and (6) develop advanced imaging techniques for substrate microstructure and soot loading analysis, such as neutron imaging and micro-computed tomography imaging. (Lee, PNNL)

- PNNL is developing a fundamental understanding of candidate next-generation LNT materials for NOx after-treatment for light-duty lean-burn (including diesel) engines. In the coming year they plan to continue to develop a deeper understanding of the mechanisms of NOx storage and reduction activity, and performance degradation of materials that have been reported to show good NOx storage reduction performance at temperatures considerably higher than BaO/alumina-based materials. (Peden, PNNL)
- ORNL is investigating ways to optimize the emission control and fuel efficiency of diesel engines using advanced combustion strategies including LTC, HECC, and RCCI. In the coming year, ORNL will extend the engine load and speed conditions for DOC control of emissions from RCCI combustion, and perform analysis of DOC control of emissions from low-temperature conditions for HECC combustion. (Parks, ORNL)
- SNL will continue their development of chemical kinetics models for LNTs by accounting for the role of hydrocarbons and partial oxidation products as alternate reductant species during normal catalyst regeneration, as suitable experimental data becomes available, enhancing the transient plug flow reactor code with a complete energy balance equation, and use this to simulate the temperature excursions in conventional short storage/regeneration cycles, as these cannot be neglected or easily measured, and investigating the applicability of the techniques developed in this project to the modeling of selective catalytic reduction (SCR). (Larson, SNL)
- ORNL will continue developing engine/aftertreatment system configurations and control strategies that meet stringent emissions regulations while improving overall vehicle efficiency in a CRADA with Navistar, Inc. They plan to perform pulsed oxidation experiments to measure kinetic parameters for soot oxidation by both O_2 and NOx, use kinetic data to improve Navistar DPF regeneration models, and investigate O_2 chemisorption method for in situ soot surface area characterization. (Pihl, ORNL)
- ORNL will continue investigating methods for improving performance and/or durability of lean-NOx (LNTs) and improving the fundamental understanding of deactivation mechanisms that result during the regeneration of LNTs. The following will be done in the coming year: (1) investigate durability of Ca + Ba lattice to understand if the observed performance improvements withstand aging; (2) expand characterization of Ca + Ba to include diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and microscopy; and (3) establish capability to measure the surface and gas-phase species simultaneously using newly developed DRIFTS reactor and SpaciMS. (Toops, ORNL)
- ORNL will continue improving diesel engine-catalyst system efficiency through better combustion uniformity, engine calibrations and catalyst control. In the coming year they will quantify engine combustion non-uniformities and develop mitigation strategies and enable development of self-diagnosing smart catalyst systems through: detailed characterization of the spatiotemporal relationship between natural and indicator chemical functions and catalyst properties throughout the catalyst operation and ageing; and develop methods for in situ, on-engine-system assessment of catalyst state. (Partridge, ORNL)
- ORNL will continue to co-lead CLEERS planning committee, the LNT Focus Group and support the DPF and SCR Focus Groups as needed. They will also provide standard reference LNT materials, data, and kinetic modeling results for focus group evaluation, and will organize and conduct the 2011 CLEERS workshop in the spring of 2011. (Daw, ORNL)
- ORNL is collaborating with SNL and PNNL to produce kinetic information for LNT and urea-SCR aftertreatment devices, both as individual and system integrated components as part of the CLEERS project. In the coming year they plan to: (1) resolve the impact of reductant composition on the effective fuel penalty and emissions performance for LNT catalysts; (2) confirm the roles of NH_3 storage and NOx redistribution on LNT catalyst performance; (3) benchmark CLEERS LNT and SCR reference catalysts against state-of-the-art commercial formulations; (4) quantify impacts

of hydrocarbons and thermal aging on SCR catalyst kinetic parameters; (5) identify key surface species and associated catalyst sites in SCR zeolite catalysts through DRIFTS measurements; and (6) utilize above results to improve models for simulating LNT and SCR NOx reduction performance under both laboratory and vehicle drive cycle conditions. (Daw, ORNL)

- ANL is characterizing the oxidation behavior of diesel PM emissions in terms of heat release and oxidation rate. They plan to define equations for the oxidation rates of diesel particulates, characterize oxidation behaviors of diesel soot with different exhaust emission components, improve pressure drop in filtration, and perform regeneration experiments and find quantitative data. (Lee, ANL)
- PNNL will continue developing a fundamental understanding of the integration of SCR and DPF technologies for on-road heavy-duty application. A detailed literature review, combined with a close examination of the various DPF substrates has provided substantial direction for current and future activities in the effort. Additionally, as a result of high-quality technique development, soot investigations can now move forward with a high level of confidence and reliable predictability in both the expected mass of accumulated soot as well as the ability to gauge the passive regeneration capacity of the system. PNNL also successfully developed, tested, and washcoated an SCR active catalyst phase that exhibited sufficient activity to warrant its use in the integration effort. (Rappe, PNNL)
- PNNL and their CRADA partner GM will continue investigating fresh, laboratory- and engine-aged DOC and SCR catalysts. In the coming year they plan to apply project established techniques to vehicle-aged samples (135,000 miles), and evaluate the most effective characterization tools in order to provide additional crucial information about materials changes in the support materials as well as active catalytic phases. (Peden, PNNL)

C. Health Impacts

The focus of the activities in Health Impacts is to identify and quantify the health hazards associated with exhaust from advanced combustion engines and put them in proper context with other air quality hazards, and to assess the relative hazards of emissions from different fuel, engine, and emission reduction technologies.

- ORNL is striving to understand the potential impact of developing fuel, combustion, and aftertreatment technologies on air quality and, thereby, human health. In 2011, ORNL will determine lubricant contribution to PM emissions in DISI applications, characterize DISI PM emissions from start-stop operations typical of hybrid vehicle operations, and examine effect of combustion phasing on PM emissions from a DISI engine operating on gasoline and ethanol blends. (Storey, ORNL)
- NREL will enter the data analysis phase of the CLOSE project. The data collected throughout the study will be chemically analyzed with detailed speciation to quantify the relative importance of the fuel and lubricant to PM and semi-volatile organic compound emissions from the test vehicles under the variety of testing conditions specified in the study design. (Lawson, NREL)
- The Health Effects Institute is conducting the Advanced Collaborative Emissions Study to characterize the emissions and assess the safety of advanced heavy-duty diesel engine and aftertreatment systems and fuels designed to meet the 2007 and 2010 emissions standards for PM and NOx. Toxicological analyses are well underway with the first results expected in early 2011. (Greenbaum, Health Effects Institute)

SOLID STATE ENERGY CONVERSION

Research will continue in FY 2011 on TEs for converting waste heat from advanced combustion engines directly to electricity. Research will focus on development of practical systems that are suitable for future production.

- BSST, LLC will continue developing a high-efficiency TE waste energy recovery system for passenger vehicle applications. In 2010, the TEG underperformed due to inadequate assembly tooling and processes and subsequent testing on an engine dynamometer was not performed. The factors contributing to TEG underperformance were quantified, and countermeasures were designed and are in the process of being implemented. The evaluation of the full-scale TEG with countermeasures is scheduled for 2011 in bench testing at BSST followed by vehicle installation and evaluation by BMW and Ford. (LaGrandeur, BSST)
- Michigan State University is using a TEG to provide a 10% improvement in fuel economy by converting waste heat to electricity used by an over-the-road (OTR) truck. In the coming year, they will: (1) build a TEG using an advanced skutterudite material with aerogel insulated modules: output >100 Watts, voltage >14 V, modules will feature couple bypass technology, (2) scale up 100 Watt TEG to make a 1 kW generator for an OTR truck, (3) develop stable hot-side interfaces which for skutterudite systems, (4) analyze electrical and thermal resistive losses to translate couple level performance into module level performance, and (5) work to improve reproducibility and uniformity of fabricated legs by looking at different fabrication techniques. (Schock, Michigan State University)
- GM is identifying distributed cooling and heating strategies that can efficiently augment or replace a vehicle's central HVAC system by delivering localized cooling/heating of key human body segments that strongly influence an occupant's perceived thermal comfort. Activities in the coming year include identifying the set of distributed cooling and heating strategies that will be developed into prototype HVAC components for localized cooling/heating, developing initial prototype local HVAC components that utilize TE technology to deliver energy savings, continuing to develop computer-aided engineering tools that support the inclusion of local cooling/heating HVAC components in future energy-efficient vehicle designs, and continuing to investigate new and improved TE materials for automotive waste heat recovery. (Gundlach, GM)
- Ford will continue identifying technical and business approaches to accelerate deployment of automotive TE HVAC technology. They will analyze performance HVAC system architectures to be evaluated using the empirical and analytical tools developed in the previous phase, validate performance of a subscale prototype liquid-to-air TE HVAC subsystem using transient modeling to provide directional performance of devices that will be integrated into the full vehicle demonstration, and test TE device performance in a calorimeter to determine coefficient of performance in heating and cooling. (Maranville, Ford)
- GM will continue exploring new TE materials and optimizing the existing materials at General Motors Global R&D. This work includes collaboration with the University of Nevada, Las Vegas, on fundamental theoretical research involving new computational approaches for determining lattice thermal conductivity, phonon densities of states, nano-cluster doping, and electronic band structure of doped skutterudites. Their aim is to investigate and understand the very low thermal conductivities and the power factor enhancements seen experimentally for some TE materials. (Meisner, GM)

UNIVERSITY RESEARCH

In FY 2011, our university partners will continue their fundamental research into combustion and the chemistry of emission control devices.

- UM will continue exploring new high-pressure lean-burn combustion that can enable future gasoline engines with 20-40% improved fuel economy and determining the fuel economy benefits of engines and engine cycles designed to utilize advanced combustion modes. In the coming year, they plan to: (1) expand thermodynamic and system analyses of new mixed combustion modes, and use new modeling tools to assess the potential benefit of lean/dilute burn, high pressure engine operation, (2) explore fuel and thermal stratification and its interaction with fuel properties and heat transfer for improving and controlling combustion, (3) conduct detailed study of multi-mode ignition and combustion and compare with recently developed models, and (4) explore opportunities for improved engine efficiency through chemistry and properties of novel fuels. (Assanis, UM)

- The University of Wisconsin will continue developing high efficiency internal combustion engines with goals of improved fuel economy by 20-40% in light-duty (LD) and 55% brake thermal efficiency in heavy-duty (HD) engines. Methods to further increase fuel efficiency while maintaining low emissions will continue to be explored, LTC strategies on HD and LD engines will be further demonstrated, optimized injection strategies, matched with piston geometry and fuels, will be developed, and transient control strategies for mixed mode combustion will be demonstrated and tested. (Reitz, University of Wisconsin)
- MSU will continue demonstrating a SI and HCCI dual-mode combustion engine for a blend of gasoline and E85 (85% ethanol and 15% gasoline) for the best fuel economy. They will analyze SI-HCCI hybrid combustion characteristics through optical engine cold flow and combustion studies, develop closed-loop combustion control strategy based upon the control oriented engine model calibrated by GT-POWER and experimental data, and evaluate the developed control strategy for smooth mode transition between SI and HCCI combustions in the hardware-in-the-loop simulation environment. (Zhu, MSU)
- The University of Houston will continue to identify the NOx reduction mechanisms operative in LNTs and in situ SCR catalysts, and to use this knowledge to design optimized LNT-SCR systems in terms of catalyst architecture and operating strategies. They will converge on the mechanism for the non-NH_3 mechanism for SCR catalysts dominated primarily by the breakthrough of hydrocarbons and conditions for which breakthrough occurs. For LNTs, they will complete DRIFTS measurements during typical regeneration conditions on the BASF catalyst. Experimental work will commence in evaluating the LNT/SCR reactor system. They will examine different segmented designs and the double-layer catalyst in terms of NOx conversion and the effect of various operating conditions such as temperature, reductant type, lean-rich timing, etc. (Harold, University of Houston)
- The University of Connecticut will continue developing 3D composite nanostructures for lean-NOx emission control devices. They will conduct systematical optimization of 3D composite nanowire/nanorod arrays based on metal oxides (ZnO, Ga_2O_3, Zn_2SnO_4 and TiO_2) and perovskite (LSMO, LSCO). Precious metal nanoparticles (Pt, Au, Pd) will be loaded before and after barium oxide and perovskite nanofilm loading on metal oxide 3D composite nanowire/nanorod arrays. The catalysis evaluation system set-up will be optimized and the catalytic performance of 3D composite nanowire/nanorod arrays on NOx storage and reduction performance will be evaluated. (Gao, University of Connecticut)
- Michigan Technological University will continue to develop experimentally validated DOC, DPF and SCR models with real-time internal state estimation strategies that support future onboard diagnostics, advanced control system, and system optimization objectives for DOC-DPF-SCR aftertreatment systems that minimize the energy penalty of meeting emission regulations. They plan to calibrate reduced order models with experimental data and quantify the effect of model reduction compared to high-fidelity models, develop state estimation strategies, and understand the effects of different sensor combinations/types, and conduct fundamental studies in DPF PM oxidation kinetics and SCR NO_X reduction kinetics. (Johnson, Michigan Technological University)

II. ADVANCED COMBUSTION AND EMISSION CONTROL RESEARCH FOR HIGH-EFFICIENCY ENGINES

II.A.1 Fuel Injection and Spray Research Using X-Ray Diagnostics

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Objectives

- Study the mechanisms of spray atomization by making detailed, quantitative measurements in the near-nozzle region of sprays from light-duty diesel injectors.
- Perform these measurements under conditions as close as possible to those of modern engines.
- Utilize the results of our unique measurements in order to advance the state of the art in spray modeling.
- Provide industrial partners in the spray and engine community with access to a unique and powerful spray diagnostic.

Fiscal Year (FY) 2010 Accomplishments

- In FY 2010 we made a significant discovery showing two mechanisms for spray dilution at the end of injection. We confirmed that fuel cut-off leads to very rapid leaning, as predicted by Musculus, but also that spray broadening enhances this effect. Sandia researchers have shown that this effect can contribute to unburned hydrocarbons, and our data helps to explain the mechanisms that cause it.
- A new experimental station at the Advanced Photon Source dedicated to transportation research was completed in FY 2009. In FY 2010 we commissioned new beam focusing optics that enabled increased X-ray flux and finer spatial resolution, significantly improving our measurement capability.
- In FY 2009, Prof. Christopher Rutland of the University of Wisconsin's Engine Research Center (ERC) sent one of his doctorate students, Nidheesh Bharadwaj, to work at Argonne for two months. In FY 2010, the data from the experiments performed at Argonne were used to validate ERC's new implementation of large eddy simulation (LES) in its KIVA computational spray model. This is a significant new development, as it has the potential to improve the industry's leading computational models.
- New studies of multiple injection show that the fuel distributions from two consecutive sprays (such as main-post) are very similar, even when the second spray immediately follows the first. This shows that the flow field generated by the first spray has little impact on the second, and is an important feature to capture in computational spray and engine modeling.

Future Directions

- We are currently fabricating equipment that will allow us to study sprays under conditions defined by Sandia's Engine Combustion Network. This collaboration shares identical hardware among leading spray research laboratories around the world, and defines a specific set of conditions for study. We will study the "Spray A" conditions using X-ray diagnostics and share our results with spray modeling groups worldwide.
- In FY 2010 we began a new collaboration with Westport Innovations to assist them in the design of their injectors for gaseous fuels. Westport is a leader in injectors for hydrogen and natural gas engines, and is interested in improving the reliability of some of its prototype injectors. In FY 2011 Argonne will use its X-ray techniques to image the motion of the internal components of the injector in situ, providing Westport with a unique diagnostic of its injector designs.
- In FY 2010 Argonne and Delphi Diesel Systems agreed to jointly study fuel injection under a Cooperative Research and Development Agreement (CRADA) partnership. Over the next three years, Delphi will deliver modern fuel system hardware to Argonne to be studied using several X-ray diagnostics. These measurements will focus on the study of how different nozzle geometries affect the fuel distribution in the combustion chamber. This will provide a U.S. fuel systems company with access to the most advanced spray and injector diagnostics. The CRADA is expected to be signed in early 2011.
- We will increase the relevance of our measurements by studying sprays under conditions even closer to those of modern diesel engines. We have made steady progress over the course of the project, continually increasing the ambient pressure and enabling the use of production nozzles. We have now completed fabrication of a fuel system that is identical to the one in the General Motors 1.9 liter

engine running in Argonne's Engine and Emissions Research group. This will enable us to study sprays under conditions that mimic those in the engine, and use the results to understand the impact that sprays have on engine emissions, efficiency, and performance.

- Improve the measurement technique: while we produce useful results today, improvements to the measurement technique will increase its applicability and accessibility in the future. Such improvements include faster data acquisition, processing, and analysis, improved X-ray detector systems, increased X-ray intensity, finer spatial resolution, and greater automation.
- Increase the impact of our work by fostering collaboration with outside groups. Our collaborations with modeling groups allow our work to increase the fundamental understanding of the mechanics of the spray event, while our collaborations with industry enable us to develop a technique that is useful as a diagnostic for injection system manufacturers. Both of these expand the impact of our research, and help to meet the program objectives of decreased emissions and increased efficiency.

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Introduction

Fuel injection systems are one of the most important components in the design of combustion engines with high efficiency and low emissions. A detailed understanding of the fuel injection process and the mechanisms of spray atomization can lead to better engine design. This has spurred considerable activity in the development of optical techniques (primarily using lasers) for measurements of fuel sprays. Some of these optical techniques have become commercially available and can be readily applied to the testing and development of modern injection systems. Despite significant advances in spray diagnostics over the last 30 years, scattering of light from the large number of droplets surrounding the spray prevents penetration of visible light and limits such measurements to the periphery of the spray. This is especially true in the spray formation region near the injector, which is considered to be the most important region for developing a comprehensive understanding of spray behavior. Existing models of spray structure have only been compared with data acquired in the region relatively far from the nozzle. It is unknown how well these models apply in the crucial near-nozzle region. The limitations of visible light in the near-nozzle region of the spray have led us to develop X-ray diagnostics for the study of fuel sprays. X-rays are highly penetrative, and measurements are not complicated by the effects of scattering. The technique is non-intrusive, quantitative, highly time-resolved, and allows us to make detailed measurements of the spray, even in the densely-packed region very near the nozzle.

Approach

This project studies the sprays from commercially available fuel injectors. Our approach is to make detailed measurements of the sprays from these injectors using X-ray absorption. This will allow us to map the fuel distribution in these sprays, extending the existing knowledge into the near-nozzle region. The X-ray measurements are performed at the Advanced Photon Source at Argonne National Laboratory. A schematic of the experimental setup is shown in Figure 1; detailed descriptions of the experimental methods are given in [1] and [2]. The technique is straightforward; it is similar to absorption methods commonly used in optical analysis. However, X-ray radiography has a significant advantage over optical techniques in the measurement of sprays: because the measurement is not complicated by the effects of scattering, there is a simple relation between the measured X-ray intensity and the mass of fuel in the path of the X-ray beam. For a monochromatic (narrow wavelength bandwidth) X-ray beam, this relationship is given by

$$I/I0 = \exp(-\mu_M M)$$

where I and I_0 are the transmitted and incident intensities, respectively; μ_M is the mass absorption constant; and M is the mass/area of fuel. The constant μ_M is measured in a standard cell, and the incident and transmitted intensities are measured as a function of time by the X-ray detector. This allows direct determination of the mass of fuel at any position in the spray as a function of time. It is the goal of our work to use X-ray radiography to measure sprays from commercial fuel injectors at different injection pressures, different ambient pressures, and using different nozzle geometries. This will enable us to quantify how each of these variables affects the structure of the spray. We will collaborate with industrial partners including engine and fuel injection system manufacturers so that they will have access to these diagnostics for improvement

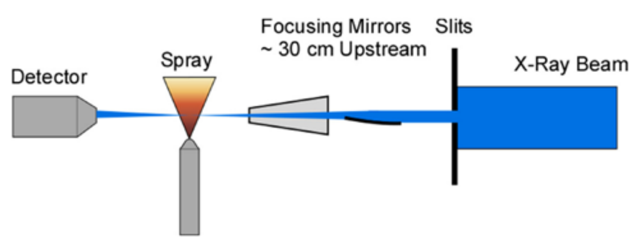

FIGURE 1. Schematic of the experimental setup. The new focusing optics at our dedicated beamline allow us to resolve much finer spray structures.

of their products. We will also collaborate with spray modelers to incorporate this previously unknown information about the spray formation region into new models. This will lead to an increased understanding of the mechanisms of spray atomization and will facilitate the development of fuel injection systems designed to improve efficiency and reduce pollutants.

Results

In 2009, Musculus of Sandia National Laboratories proposed a model that predicted rapid dilution of fuel at the end of injection [3]. In FY 2010, we began to study the behavior of diesel sprays at the end of injection. By using X-rays, rather than visible light, a high-accuracy measurement of the end-of-injection structure was obtained. The measurements confirmed parts of the Sandia analytical model of end-of-injection structure. A rapid dilution of the spray occurs near the nozzle, with a slower dilution farther downstream. The X-ray measurements also showed behaviors that have been invisible to previous measurements. For example, a three-dimensional reconstruction of the spray showed that the spray width increases significantly at the end of injection. This widening was not accounted for in the Sandia end-of-injection model, and causes a significant enhancement to the spray dilution at the end of injection (Figure 2). By providing a better understanding the spray structure at the end-of-injection, this research will help engine researchers better understand the source of hydrocarbon and carbon monoxide emissions in low-temperature combustion regimes and how to better tailor these regimes to lower engine-out emissions.

In FY 2009, a new experimental station at the Advanced Photon Source dedicated to transportation research was completed. This facility was built with

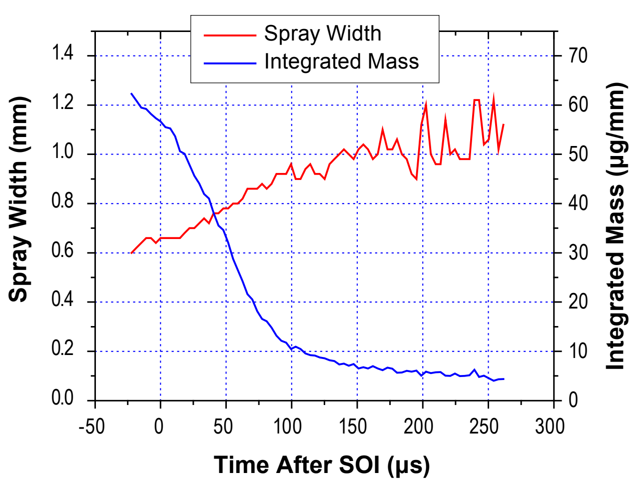

FIGURE 2. The spray width and fuel mass near the end of injection. The spray widens considerably at the end of injection, enhancing the fuel dilution.

both Basic Energy Sciences and Energy Efficiency and Renewable Energy funds, and signifies the important collaboration between basic and applied research. In FY 2010 a new pair of focusing mirrors was installed in the new facility, and significantly improved the X-ray focusing while increasing the X-ray flux. This significantly enhanced our ability to measure very small structures in the spray, allowing us to see finer details of spray structure. This improves both the quality of the data that we can provide to our collaborators, and the speed with which it can be acquired.

In FY 2009, Prof. Christopher Rutland of the University of Wisconsin-Madison's ERC sent one of his doctorate students, Nidheesh Bharadwaj, to work at Argonne for two months. During this time, Mr. Bharadwaj took part in several spray measurements, including measurements that were part of a collaboration among Argonne, Sandia, and ERC. In 2010, Bharadwaj and Rutland used the X-ray data to validate their new implementation of LES turbulence modeling in ERC's KIVA engine modeling code, with the goal of improving its ability to predict spray behavior. They found that the new model has a good ability to reproduce the measured fuel distributions, and more accurately predicts spray behavior [4]. This is a significant new development with the potential to improve the industry's leading computational engine modeling software.

Argonne developed a technique for directly measuring the valve opening inside an operating fuel injector in 2004. In FY 2010, we began a systematic study of the valve motion during multiple injection events, such as pilot, main, and post injections. In addition, the impact of multiple injections on the fuel distribution was measured to see whether a post injection behaves differently than a main injection. Even for very short dwell times between main and post injection, it was discovered that the near-nozzle fuel distributions are very similar between the two events, including fuel density, spray cone angle, and penetration (Figure 3) [5]. These experiments are particularly important since multiple injection strategies are commonly employed in modern diesel engines, and the data form a very stringent test for computational fluid dynamics models attempting to predict fuel mixing and engine performance.

Conclusions

- The X-ray measurements can be used to help understand the mixing of fuel and air in the engine, and its impact on engine emissions and performance. Such measurements are not possible using other imaging techniques, and represent a powerful data set for validating computational models of fuel flow.

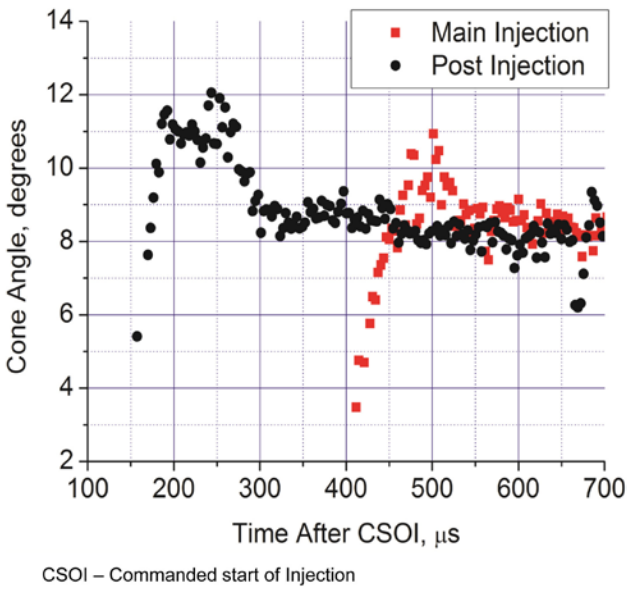

FIGURE 3. Spray cone angle versus time for both main and post injection. Even though the dwell between the two sprays was very short, the presence of the main appears to have little impact on the post injection.

- The time-dependent mass measurements provide unique information to spray modelers, and allow them to test their models in the spray formation region, something that was impossible previously. This data is crucial for the development of accurate spray models and for the detailed understanding of spray behavior. The quantitative measurements that we have provided may help to elucidate the mechanisms of spray atomization. This could ultimately lead to the design of cleaner, more efficient engines.
- The impact of our work on the engine community is shown by the expanding list of collaborators and by the significant in-kind contributions to our work that are being made by fuel system and engine manufacturers.

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II.A.2 Low-Temperature Automotive Diesel Combustion

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Objectives

- Provide the physical understanding of the in-cylinder combustion processes needed to minimize the fuel consumption and the carbon footprint of automotive diesel engines while maintaining compliance with emissions standards.
- Develop efficient, accurate computational models that enable numerical optimization and design of fuel-efficient, clean engines.
- Provide accurate data obtained under well-controlled and characterized conditions to validate new models and to guide optimization efforts.

Fiscal Year (FY) 2010 Accomplishments

- Evaluated the impact of biodiesel blending on in-cylinder unburned hydrocarbons (UHC) and carbon monoxide (CO) spatial distributions and on engine-out emissions for low-temperature operating regimes. Demonstrated UHC/CO emission advantages for biodiesel blends, despite their lower volatility.
- Isolated the influence of fuel volatility and ignition quality on UHC and CO emissions by examining an orthogonal fuel property matrix. Established secondary importance of fuel volatility.
- Imaged increased post-injection wall-wetting when biodiesel blends are employed, and established ineffectiveness of exhaust blow-down flows in impeding jet penetration.
- Applied liquid imaging diagnostics to various low-temperature operating conditions and demonstrated excellent qualitative agreement with simulated spray penetration and droplet distributions.
- Examined the impact of initial and boundary conditions on predictions of fuel-air mixing leading to unrealistic predicted UHC and CO emissions.

Future Directions

- Examine the impact of variable injection pressure, swirl ratio, and nozzle hole size on the fuel-air mixing process and subsequent UHC and CO spatial distributions.
- Extend UHC imaging studies to the horizontal plane to capture lack of symmetry in squish volume UHC sources associated with piston top valve pockets and head features.
- Obtain horizontal plane flow field data to support the interpretation of UHC images, to examine asymmetries in the squish flow patterns, and to characterize the attenuation of angular momentum in the squish volume.
- Examine suitability of compressible-renormalization group k-ε and other turbulence models for engine flow simulations, in collaboration with high-fidelity large eddy simulation modeling efforts.

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Introduction

Direct-injection diesel engines have the highest fuel conversion efficiency of any reciprocating internal combustion engine technology. However, conventional diesel combustion produces elevated emissions of both soot and oxides of nitrogen (NO_x). To address this shortcoming, low-temperature combustion techniques that prevent the formation of these pollutants within the engine are being developed. These techniques generally rely on high levels of charge dilution with recirculated exhaust gases to keep in-cylinder temperatures low. High dilution levels, with attendant low charge oxygen concentrations, make it difficult to mix the fuel with sufficient oxygen to achieve complete combustion. Moreover, the low combustion temperatures also slow the kinetic rates of oxidation. Both factors can promote incomplete combustion–characterized by high UHC and CO emissions–and result in a significant fuel economy penalty. A major focus of this work is to understand the main causes of combustion inefficiency through examination of the in-cylinder sources of UHC and CO emissions. This year, we have particularly concentrated on understanding how biodiesel blends, as well as other alternative fuels, can impact combustion efficiency and emissions under low-temperature operating conditions.

Identifying emission sources is insufficient, however. An ability to accurately predict emissions and how they vary with different engine design parameters is required to enable the design of clean, more efficient engines. Consequently, we also carefully compare the experimentally measured CO and UHC fields with the results of numerical simulations. Through this comparison, we refine computer modeling and simulation practice and improve predictions of efficiency and emissions.

Approach

The research approach involves carefully coordinated experimental, modeling, and simulation efforts. Detailed measurements of in-cylinder flows, fuel and pollutant spatial distributions, and other thermo-chemical properties are made in an optical engine facility with geometric and thermodynamic characteristics that allow it to closely match the combustion and engine-out emissions behavior of a traditional, all-metal test engine. These measurements are closely coordinated and compared with the predictions of numerical simulations.

The experimental and numerical efforts are mutually complementary. Detailed measurements of the in-cylinder variables permit the evaluation and refinement of the computer models, while the model results can be used to obtain a more detailed understanding of the in-cylinder flow and combustion physics–a process that is difficult if only limited measurements are employed. Jointly, these efforts address the principal goals of this project: development of the physical understanding to guide and the modeling tools to refine the design of optimal, clean, high-efficiency combustion systems.

Results

Using biodiesel fuel blends can change engine-out UHC and CO emissions through a variety of mechanisms. Biodiesel, especially palm oil-based fuel, typically has better ignition quality than U.S. diesel fuel. This provides a shorter ignition delay and can reduce emissions associated with the formation of overly lean mixtures. However, biodiesel components have a boiling range near the high-temperature end of the diesel fuel distillation curve. Under early-injection, low-temperature operating conditions, this can lead to increased liquid penetration, increased wetting of combustion chamber surfaces, and slower vaporization of fuel films formed on these surfaces. Wall-wetting and formation of liquid films are often considered to result in increased UHC (and CO) emissions [1].

To investigate the relative importance of these opposing mechanisms, we have imaged the in-cylinder spatial distributions of UHC and CO using laser-induced fluorescence (LIF) techniques, and correlated these distributions with engine emissions for several different fuel blends with palm methyl esters (PME) and soy methyl esters (SME). The relevant distillation and ignition properties of these blends are provided in Figure 1, and UHC and CO emissions measured during an ignition timing sweep are shown in Figure 2.

	Diesel [% vol]	PME [% vol]	SME [% vol]	LHV [MJ/kg]	Cetane
Cert. Diesel	100	0	0	42.9	47.1
PME-20	80	20	0	41.5	50.3
PME-50	50	50	0	39.5	55.1
SME-20	80	0	20	41.6	47.0
SME-50	50	0	50	39.9	46.9
SME-100	0	0	100	36.9	44.5

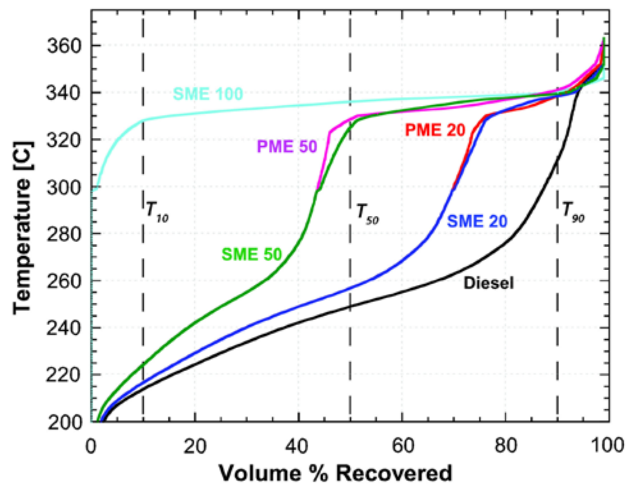
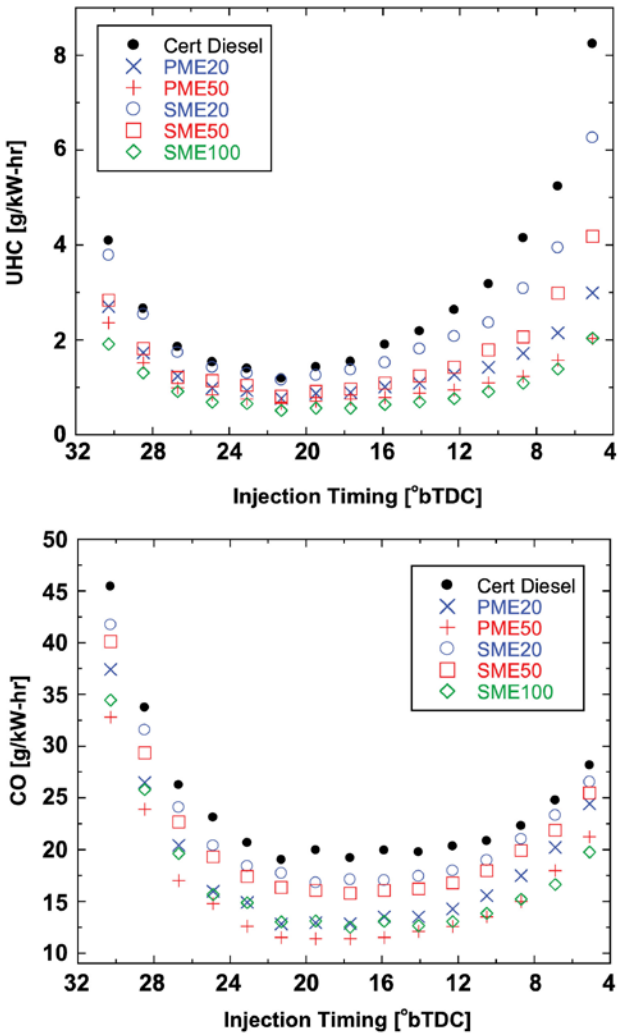


FIGURE 1. Composition, heating value, and estimated cetane number and distillation curves for each of the fuel blends tested

Each of the fuels show the same variation in UHC and CO emissions with ignition timing, providing the lowest emissions near an injection timing of -20° after top dead center (aTDC). As with more conventional diesel combustion regimes, increased biodiesel content results in lower UHC and CO emissions. A greater reduction is seen for the PME blends than for the SME blends. The UHC emissions show a much more pronounced sensitivity to injection timing than the CO emissions, especially at retarded injection timing. In general, UHC and CO emissions are found to correlate strongly with the combustion phasing, which–at constant injection timing–is predominantly impacted by the ignition quality of the fuel. Despite the similarity of the estimated blend cetane numbers listed in Figure 1, the SME blends are found to ignite more readily than the neat diesel fuel. A significant conclusion which can be drawn from Figure 2 is that high ignition quality biodiesel blends can enable low-temperature operation with lower UHC and CO emissions than neat diesel fuels, though some penalty in NO_x and soot (for the PME blends) may result [2].

The imaging experiments confirm the conclusions drawn from the emissions measurements. Figure 3 shows that at fixed injection timing, increased fuel ignition quality causes a reduction in the diffuse bulk gas fluorescence from UHC and CO–both in the central regions of the cylinder and in the squish volume. Load



bTDC - before top dead center

FIGURE 2. The variation of UHC and CO emissions at a light-load, low-speed (3 bar gross indicated mean effective pressure [gIMEP], 1,500 rpm) operating condition over a range of injection timings. The emissions are presented on an energy-specific basis to account for the change in fuel heating value.

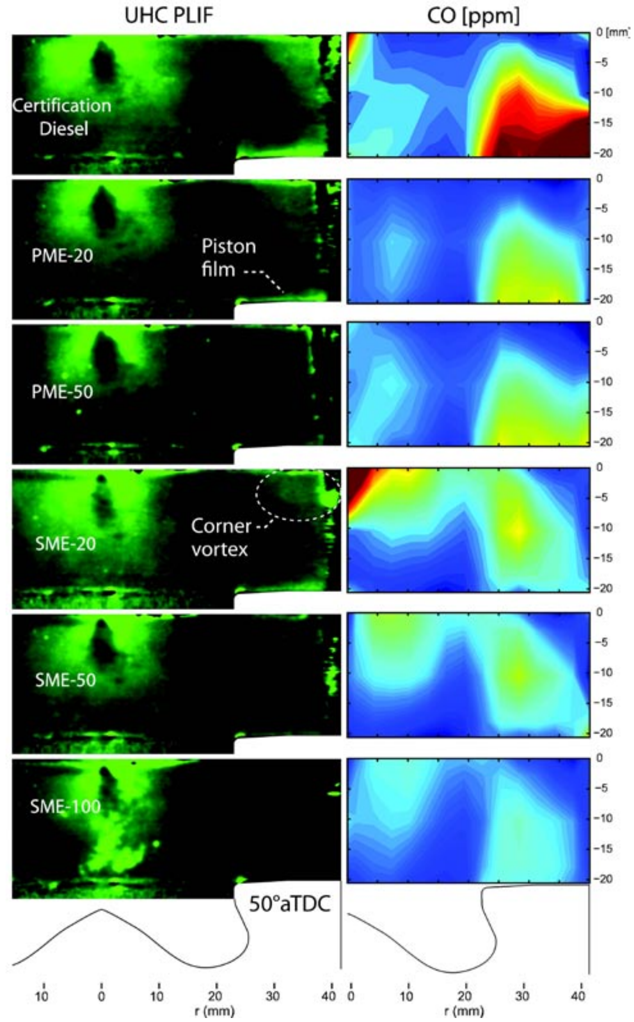


FIGURE 3. Cycle-averaged spatial distributions of UHC (left) and CO (right) obtained with laser-induced fluorescence techniques for the fuel blends tested. Details of the diagnostic techniques can be found in [2]. The operating conditions match those of Figure 2.

sweeps demonstrate that this diffuse fluorescence arises from overly lean mixture, which is reduced as the ignition delay is shortened. Surprisingly, the images also suggest that UHC in the corner vortex formed by the ring-land crevice flow and in fuel films on the piston surface is also lessened for the biodiesel blends, despite the expected increase in liquid penetration associated with the high boiling point components. Overall, however, the effect of fuel distillation properties on UHC and CO emissions is expected to be small. Further experiments conducted on an orthogonal matrix of fuel distillation and ignition properties (see Figure 4) demonstrated that the impact of fuel distillation properties on UHC and CO emissions is minor. For changes in the 90% volume recovered temperature (T_{90}) of roughly 60°C (the difference between center and right-hand columns of Figure 4), changes in UHC and CO emissions were minimal. Even with changes in T_{90} of nearly 250°C, UHC emissions increased by only 50% and CO by less than 15%.

A second focus of this research is the improvement of our predictive modeling capability, with the objective of further facilitating simulation-based engine optimization and calibration. To this end, we have invested significant effort to clarify the causes of the discrepancy between the measured in-cylinder sources of UHC and CO and those predicted by multi-dimensional simulations. This discrepancy, which was first reported in our FY 2009 annual progress report, is shown in Figure 5. The UHC distribution shown in Figure 5 was obtained with a different diagnostic than was used to obtain the results shown in Figure 3; the latter technique is not capable of detecting the dominant UHC species in the partial oxidation products of moderately fuel-rich

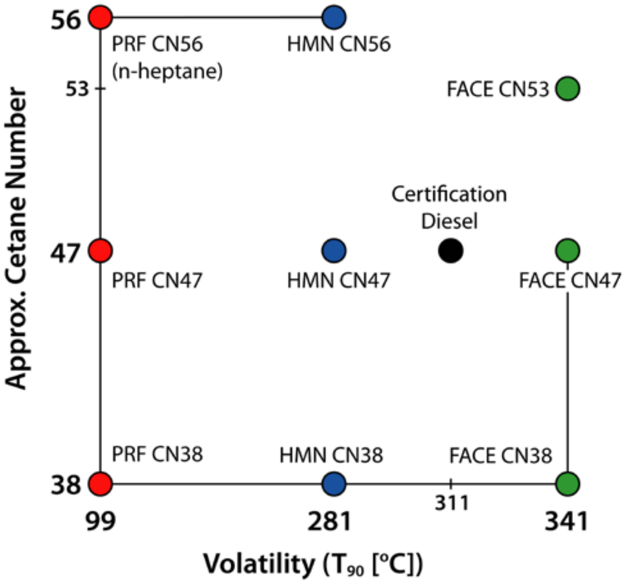


FIGURE 4. The orthogonal matrix of fuels properties, in which ignition quality (cetane number) and distillation properties (volatility) were varied independently.

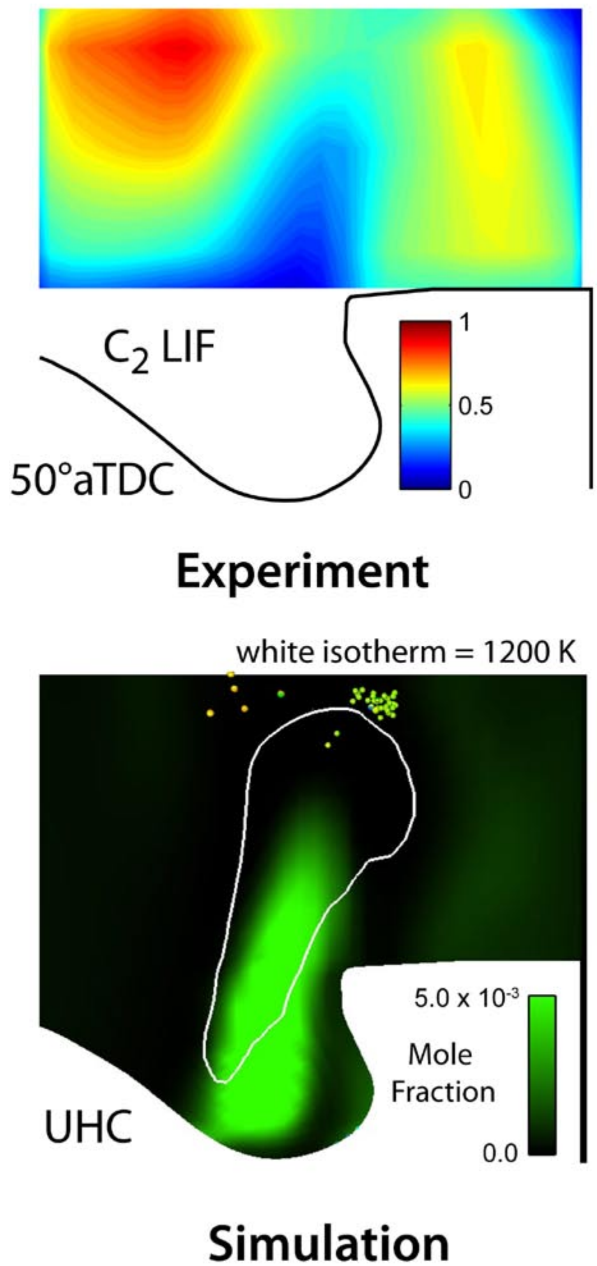


FIGURE 5. A comparison of the measured and simulated spatial distributions of UHC at 3 bar gIMEP and 1,500 rpm. The simulations capture the diffuse bulk gas UHC in the squish volume and in the central portion of the cylinder, but predict a dominant plume leaving the bowl that is not observed experimentally.

mixtures. The simulation results clearly predict that the dominant source of UHC is associated with a plume of rich mixture leaving the bowl. This plume is not seen in the experimental distribution shown in Figure 5, nor in the measured distributions of UHC or CO shown in Figure 3.

Improvements to the reduced chemical kinetic mechanism governing hydrocarbon oxidation made in FY 2009 significantly reduced the magnitude of the UHC predicted to be embedded in the rich-mixture plume leaving the bowl. However, the discrepancy was not eliminated. During FY 2010, we have examined additional potential causes of this discrepancy associated with possible errors in the boundary and initial conditions provided to the simulations. Errors in intake temperature, O_2 concentration, bowl volume, and injection rate have been ruled out as possible causes, as has insufficient grid resolution. The most probable remaining cause is inaccurate modeling of the fuel-air mixing process. Current work is focused on further clarifying this issue through measurement and simulation of UHC and CO distributions obtained with varying injection pressure, swirl ratio, and injector hole size.

Conclusions

- UHC and CO emissions from light-duty diesel engines operating in low-temperature combustion regimes can be significantly improved when high ignition quality biodiesel blends are used. Imaging of the in-cylinder spatial distributions of these species demonstrates that the improvement is due to the reduced formation of overly lean fuel-air mixtures.
- The decreased volatility (higher distillation temperatures) of biodiesel blends does not result in a significant UHC or CO emissions penalty. Examination of emissions measured from an

orthogonal matrix of fuels with varying ignition and distillation properties has demonstrated that the impact of fuel volatility is minor.

- The discrepancy between measured and simulated emissions cannot be explained by errors in the initial and boundary conditions provided to the simulations. Work is underway to characterize the accuracy with which fuel-air mixing processes are simulated.

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21. "Detailed Unburned Hydrocarbon Investigations in a Highly-Dilute Diesel Low Temperature Combustion Regime," Koci CP, Ra Y, Krieger R, Andrie M, Foster DE, Siewert RM, Durrett RP, Ekoto I, Miles PC. *SAE Int. J. Engines 2:858-879, 2009.*

Special Recognitions & Awards/Patents Issued

1. Keynote Lecture: "Sources of UHC and CO in Low Temperature Diesel Combustion Systems," Miles PC. Thermo- and Fluid-Dynamic Processes in Diesel Engines, Sept. 14–17, 2010.

2. Invited Talk: "On the Sources of UHC and CO in Low Temperature Combustion Systems," Miles PC. *11th International Conference on Present and Future Engines for Automobiles*, May 30 – June 3, 2010.

3. SAE Meyers Award: "Detailed Unburned Hydrocarbon Investigations in a Highly-Dilute Diesel Low Temperature Combustion Regime," Koci CP, Ra Y, Krieger R, Andrie M, Foster DE, Siewert RM, Durrett RP, Ekoto I, Miles PC. *SAE technical paper 2009-01-0928*, *SAE Int. J. Engines 2:858-879, 2009.*

4. Lecture Series: "Physical Fluid Dynamics and RANS-based Modeling Issues in Reciprocating Engines," PC Miles. *Lund University,* Feb.1–5, 2010.

5. Co-Chair: Society of Automotive Engineers Powertrain, Fuels, and Lubricants activities.

II.A.3 Heavy-Duty Low-Temperature and Diesel Combustion & Heavy-Duty Combustion Modeling

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Objectives

The overall Vehicle Technologies Program goal for this project is to develop a fundamental understanding of advanced low-temperature combustion (LTC) technologies. The project includes diesel combustion research at Sandia National Laboratories (SNL) and combustion modeling at the University of Wisconsin (UW). The specific goals for Fiscal Year (FY) 2010 include:

- Understand the spatial and temporal evolution of soot formation in low-temperature diesel combustion (SNL).
- Identify the in-cylinder post-injection processes that oxidize squish-volume soot from the main injection (SNL).
- Improve modeling of both flame propagation and distributed autoignition in LTC diesel engines (UW+SNL).
- Quantify the potential for post-injections to reduce unburned hydrocarbon emissions (UW+SNL).

FY 2010 Accomplishments

- In-cylinder laser diagnostics showed that LTC conditions have a distinct period of large polycyclic aromatic hydrocarbon (PAH) formation with much slower soot formation.
- Showed that late post-injections can generate hydroxyl (OH) to oxidize main-injection soot, but spray targeting is important.
- Optical engine hardware modifications for dual-fueling are underway and a student experiment/modeling visit will commence in FY 2011.
- Building on previous work, showed how post-injections can help to oxidize unburned hydrocarbons (UHCs) from over-lean near-injector regions.

Future Directions

- Explore UHC reduction by post-injections in greater depth:
  - Quantify UHC improvements across parameter space to identify critical requirements for operating condition and post-injection.
  - Use laser diagnostics (fuel-tracer, formaldehyde, and OH planar laser induced fluorescence, PLIF) to understand UHC oxidation mechanisms of post-injections.
- Build understanding of in-cylinder LTC soot and PAH:
  - Use multiple laser wavelengths and high-temporal-resolution imaging/spectroscopy to track PAH growth and conversion to soot.
- Probe in-cylinder mixing and combustion processes and improve modeling for high-efficiency dual-fuel operation:
  - Use laser/optical diagnostics to discern flame propagation from distributed autoignition and define conditions that govern transitions from one combustion regime to the other.
  - Incorporate insight and validation data from optical experiments to improve model fidelity.

✧ ✧ ✧ ✧ ✧

Introduction

Particulate matter (PM) emissions contain both carbonaceous soot and PAH species. Many PAHs are known to be carcinogenic and are to some extent adsorbed on the carbonaceous soot, adding to the soluble fraction of PM [1,2]. The soluble fraction can become more prominent in exhaust from modern diesel engines that use exhaust gas recirculation (EGR) to operate at LTC conditions to limit emissions of nitrogen oxides (NOx) [3]. Some adsorbed PAH in PM emissions is directly from molecules in the fuel, but most PAH is due to incomplete combustion.

The emission and absorption spectra of PAH molecules depend on their size and structure [4,5]. Accordingly, the size of a PAH molecule can be determined to some degree by the red-shift of its absorption (or emission) spectrum. Developing and applying diagnostic techniques to probe and understand the in-cylinder evolution of PAH and soot is important for the advancement of LTC strategies.

The potential for post-injections to reduce UHC emissions for low-load LTC strategies is also important. Previous work from this project in FY 2008 showed that the region near the injector rapidly over-mixes during the ignition dwell after the end of injection, so that mixtures become too fuel-lean to achieve complete combustion [6]. Figure 1 shows a summary of some imaging observations from various laser diagnostics, along with a diagram of the conceptual model extension for low-load LTC conditions, which was developed in FY 2009 [7]. The fuel tracer measurements (lower left corner) show that by 5° after the end of injection, mixtures near the injector have equivalence ratios of 0.5 or less, which chemical kinetics simulations show are too fuel-lean to achieve complete combustion. Indeed, the images in Figure 1 show that formaldehyde (red) remains late in the cycle near the injector, and OH (green) only appears farther downstream, indicating that regions near the injector do not achieve complete combustion, and would contribute to UHC emissions. Since the UHC problem is due to over-leaning after the end of injection, it is conceivable that a properly timed post injection could enrich the near-injector mixtures so that ignition reactions could commence.

Approach

This project uses an optically-accessible, heavy-duty, direct-injection diesel engine (Figure 2). Windows provide imaging access to either (i) the squish region above the piston bowl-wall, through a window in the cylinder head in place of one of the exhaust valves, or (ii) the piston bowl, through a flat piston-crown window. For the PAH study, we use the first option, to view soot and PAH in the downstream part of one of the in-cylinder diesel jets that passes into a cut-out in the piston bowl (see Figure 2). For the post-injection study, we used the second option, to view the upstream parts of the jets, near the injector.

To image the evolution of in-cylinder PAH, we take advantage of the red-shift in absorption for large PAH species. Using planar laser-induced fluorescence with excitation at 532 nm, only the larger PAH molecules, with at least five rings, should be excited. Smaller PAH molecules, such as those from the fuel itself, are not excited by 532-nm laser light. LIF excitation at 532 nm will also yield some laser-induced incandescence (LII) of soot in regions where both PAH and soot reside. Indeed, it is well recognized that soot LII signals using 532-nm excitation may be contaminated by PAH fluorescence [8]. To discriminate between these two components of the signal, soot LII is also excited nearly simultaneously using 1064-nm laser radiation. Two intensified charge-coupled device (ICCD) cameras record both laser-induced emissions through the cylinder head window, using a 50% reflecting broadband beamsplitter, as shown in Figure 2. The engine was operated with and without EGR, so that intake oxygen concentrations were either 21% or 9.5%. The start of injection was -5° after top-dead-center (ATDC) and the

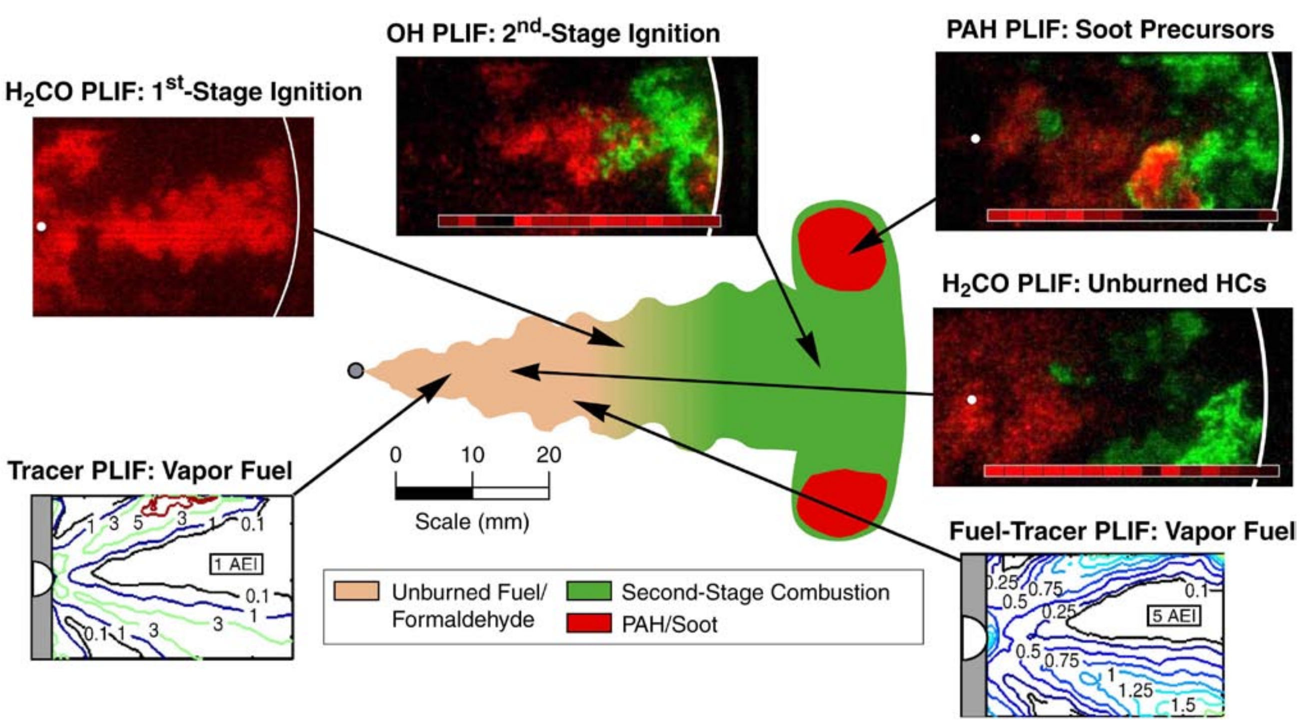

FIGURE 1. Diagram from conceptual model for low-load LTC showing stages of ignition and combustion, with example optical diagnostic images.

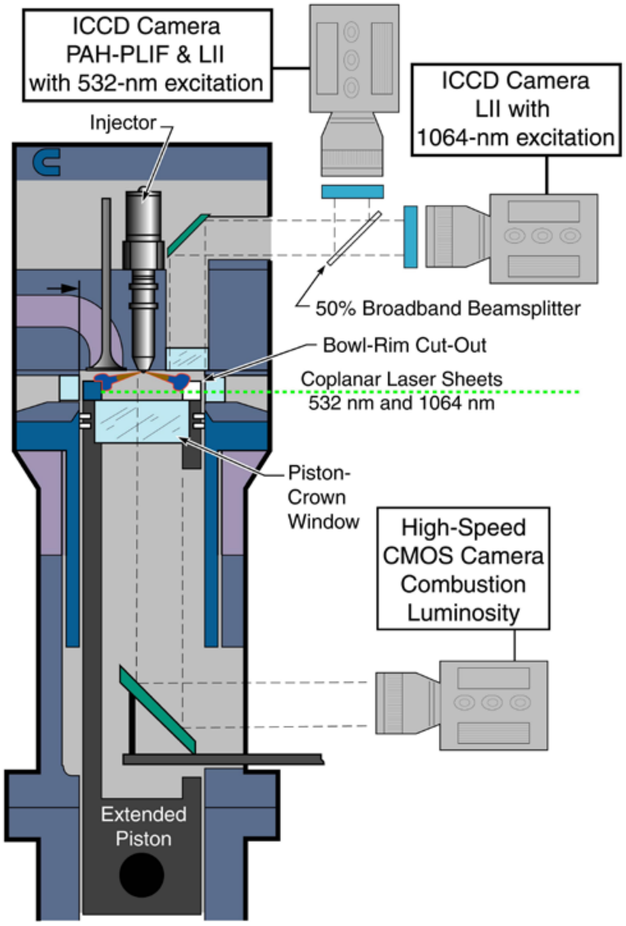

FIGURE 2. Schematic diagram of the optically accessible direct injection diesel engine and optical setup.

load was near 8 bar indicated mean-effective pressure (IMEP).

The ignition and interaction of post injections with the over-mixed fuel in the wake of the main injection was visualized using high-speed imaging of combustion luminosity, which consists of both chemiluminescence emission and soot luminosity. A complementary metal oxide semiconductor (CMOS) camera imaged combustion luminosity at a rate of 7,200 frames per second through the piston-crown window, as shown in Figure 2. The engine was operated at a low-load (3 bar IMEP) EGR-diluted LTC condition with 12.7% intake oxygen, and used a main injection at -5° ATDC and a close-coupled post-injection.

Results

Figure 3 shows images of laser-induced emission from the diesel jet, acquired during the early soot-formation process from 0 to 2° ATDC. One of the eight fuel jets propagates horizontally from left to right in these images, while the laser sheets enters the engine cylinder from right to left (see Figure 1). The fuel injector is 27 mm to the left of the edge of the 50-mm diameter circular field of view through the periscope window, and hence is not visible in the images. The images are a composite of the laser-induced emissions from both 532-nm excitation (false-colored green) and 1064-nm excitation (false-colored red). The green-colored signal from 532-nm excitation contains both PAH-LIF and some soot-LII whereas the red-colored signal from 1064-nm excitation is soot-LII only. Hence, regions exclusively containing PAH with no soot appear as green in the composite images. Regions containing soot have emission upon excitation at both wavelengths, and thereby appear yellow in the images (secondary color for red and green).

Laser-induced signals first appear at 0.5° ATDC (close to the premixed heat release rate peak) with both 532-nm and 1064-nm excitation, indicating the start of soot formation at this timing. The signals from both the excitations largely overlap (yellow color), indicating that soot appears almost simultaneously (within the half-crank-angle resolution of 70 microseconds) with any PAH for this condition. A few small, isolated green-colored PAH-PLIF spots appear in most early images, but most of the signals arise from regions containing soot. As the diesel jet evolves, soot-LII (along with possible PAH-PLIF) continues to occupy most signal area (yellow), with very little exclusive regions of PAH (green). By 2° ATDC, significant attenuation

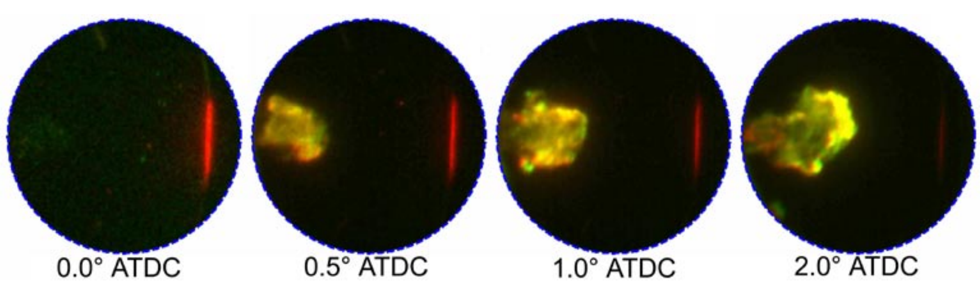

FIGURE 3. Single-shot image sequence acquired for engine operating at 21% intake O_2 fraction, recorded nearly simultaneously with 1,064 (false-colored red) and 532-nm laser excitation (false-colored green). Regions where the signals spatially overlap appear yellow.

of the 532-nm beam relative to the 1,064-nm beam is evidenced by more widespread red coloring in the upstream (left) part of the jet. With no EGR, flame temperatures at this condition are likely high enough to rapidly convert large PAH to soot. This description of rapid soot formation is consistent with the conceptual model of conventional (i.e., no EGR) diesel combustion proposed by Dec [9].

With decreased intake oxygen concentrations typical of EGR-diluted LTC operation, the evolution of in-cylinder PAH and soot is much different from that described in Dec's conceptual model. Figure 4 shows images of laser-induced signals with 532-nm and 1,064-nm laser excitation at a high EGR condition with 9.5% intake oxygen. The initial images from 2° to 5° ATDC show weak PAH fluorescence emission (green) within the jet. Relatively weak soot-LII (red and yellow) is first detectable at 6° ATDC, but only in the outer regions of upstream portions of the jet. Later in the cycle, images increasingly show laser-induced emission filling more of the field of view as the jet penetrates deeper into the cylinder. By the end of the image sequence at 15° ATDC, the 532-nm and 1,064-nm images largely overlap (as indicated by the significant yellow regions), suggesting that most of the signal area is filled with soot with little regions of exclusively PAH-LIF.

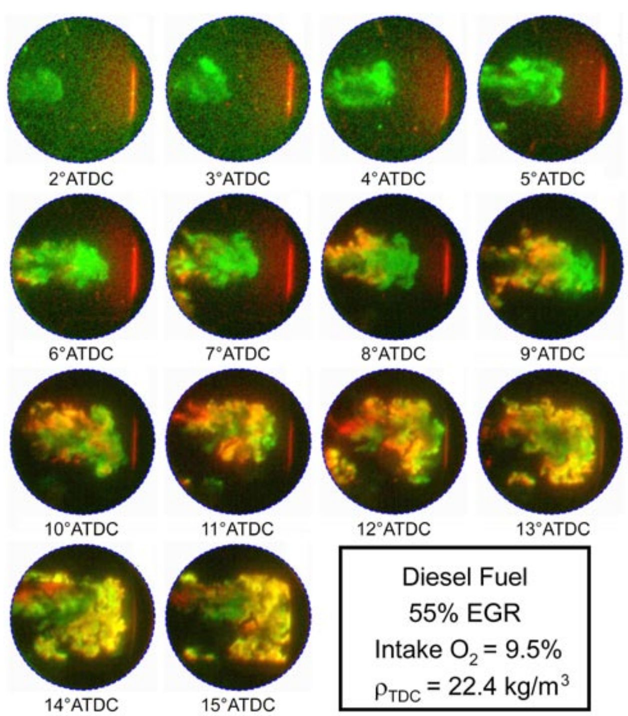

FIGURE 4. Single-shot image sequence acquired for engine operating at 9.5% intake O_2 fraction, recorded nearly simultaneously with 1,064-nm (red) and 532-nm laser excitation (green). Regions where the signals spatially overlap are shown in yellow.

The duration over which the PAH exists locally without soot is greater at high dilution of the intake stream. Although PAH synthesis occurs over most of the jet at these conditions, soot formation typically starts near the periphery of the jet, and primarily in the upstream regions. This is in contrast to the accepted conceptual-picture of conventional diesel combustion proposed by Dec [9], where soot formation occurs uniformly across the jet cross-section and close to the jet-head. At LTC conditions, by contrast, soot formation generally progresses from upstream to downstream, reaching the head of the jet last.

The increase in spatial extent and duration of persistence of PAH at LTC conditions may contribute to the composition of PM in the engine exhaust. It is possible that at LTC conditions, more large PAH species synthesized in-cylinder would not be converted to soot and could survive through the high-temperature portion of the power stroke to appear in the engine exhaust. This speculation is consistent with a recent study [10] that quantified engine exhaust particle-size distribution at LTC conditions. They reported that particulate matter obtained from LTC combustion comprises of increased number of smaller particles and a larger fraction of volatile species like PAH adsorbed on the particles. The change in exhaust composition could also have implications for engine after-treatment systems.

Regarding the use of post-injections to reduce UHC emissions, Figure 5 shows two images of combustion luminosity acquired through the large piston-crown window. The fuel injector is in the center of the images, and the outer circle is the piston bowl-wall. Both images are acquired at 10° ATDC, but the left image is for a condition with a main-injection only (no post injection), while the right image is for a condition with a slightly smaller main injection and a close-coupled post injection added. The combustion luminosity is due to both chemiluminescence emission (medium intensity) and soot luminosity (strong intensity). The

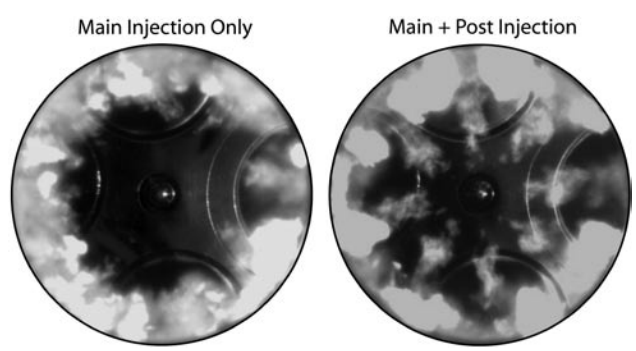

FIGURE 5. High-speed combustion luminosity images acquired through the piston-crown window at 10° ATDC either with a single main injection (left) or with a main and a close-coupled post injection (right).

chemiluminescence emission indicates regions that have achieved second-stage ignition and relatively complete combustion (corresponding to the green OH-PLIF images in Figure 1).

Consistent with the incomplete combustion depicted in the LTC conceptual model of Figure 1, with the main injection only (left image in Figure 1), no chemiluminescence appears in the center of the left image, which is the upstream regions of the jets, near the injector. It is these regions that become over-mixed and contribute to UHC emissions. When a close-coupled post injection is added (right image in Figure 1), the upstream region of the jets near the injector shows significantly increased combustion luminosity, indicating more complete combustion there. Indeed, exhaust measurements show that the UHC emissions are reduced by 20% with the post injection, even though the load is identical for the two conditions. This particular post injection is not optimized, so higher reductions may be possible with optimization, but the UHC emissions were very dependent on the post-injection timing and quantity. Most post-injection conditions tested did not produce any significant reduction in exhaust UHC emissions when adjusted for engine load. Only when the post-injection was small enough so that it did not penetrate too far into the combustion chamber, and properly timed so that ignition occurred in the upstream regions, did the post-injection reduce UHC emissions at a constant load. Further study using planar laser diagnostics would better reveal the mechanism of UHC reduction by post-injections.

Conclusions

The recent research efforts described in this report provide improved understanding of in-cylinder LTC spray, combustion, and pollutant-formation processes required by industry to build cleaner, more efficient, heavy-duty engines. Specific conclusions include:

- Dilution increases the residence time of PAH before soot formation. At all dilution levels, at its onset, PAH rapidly fills most of the downstream cross-section of the jet, with a relatively uniform fluorescence intensity distribution. At zero dilution (21% intake oxygen), the PAH residence time was less than 70 microseconds, while at higher dilution (12.7% or 9.5% intake oxygen), the PAH residence time was hundreds of microseconds to a millisecond or more before the appearance of soot, depending on the spatial location within the jet.
- Dilution shifts soot inception upstream. At low dilution, soot rapidly filled the downstream head of the jet. With increasing dilution, soot inception shifted to the midstream periphery of the jet, and later soot formation gradually progressed downstream.
- A post-injection strategy was identified that effectively reduced engine-out UHC emissions by 20% compared to a single injection at the same load. The post-injection caused the upstream mixtures to achieve second-stage ignition, as evidenced by chemiluminescence emission imaging.

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2. "In-Cylinder Processes of EGR-Diluted Low-Load, Low-Temperature Diesel Combustion," M. Musculus, L. Pickett, P. Miles, J. Dec, T. Lachaux, C. Genzale, K. Kattke, DEER 2009, August 3, 2009.

3. "Entrainment Waves in Diesel Jets," M. Musculus and K. Kattke, SAE International Journal of Engines 2:1170-1193, October 2009.

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II.A.4 Low-Temperature Diesel Combustion Cross-Cut Research

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DOE Technology Development Manager:
Kellen Schefter

Objectives

- Lead a multi-institution, international, research effort on diesel sprays called the Engine Combustion Network (ECN), focusing on specific injector and operating conditions.
- Develop a quantitative dataset of penetration, mixing, combustion, soot volume fraction, and soot particle morphology for neat biodiesel, diesel, and surrogate diesel.
- Quantify the extent of liquid penetration at problematic post-injection conditions, injections which are now used for diesel particulate filter (DPF) regeneration.

Fiscal Year (FY) 2010 Accomplishments

- Generated a detailed spray dataset (Spray A) working collaboratively with a dozen institutions from around the world. Made the results available on the ECN internet data archive for advanced computational fluid dynamics (CFD) model development.
- Made the first quantitative soot volume fraction measurements within reacting biodiesel sprays. Also made the first soot size and morphology measurements within reacting sprays by transmission electron microscopy (TEM)-grid thermophoretic sampling.
- Characterized the extent of liquid penetration at late-cycle, post-injection conditions, allowing assessment of oil dilution likelihood with DPF regeneration.

Future Directions

- Perform direct measurements of mixing (equivalence ratio) at Spray A conditions.
- Investigate jet-jet interaction effects on flame lift-off.
- Characterize side-hole sprays compared to axial-hole sprays.
- Develop spray and combustion datasets for gasoline direct injection-type injectors.

Introduction

Spray experimentation at controlled high-temperature and high-pressure conditions is intended to provide a more fundamental understanding of combustion than can be achieved in engine experiments. This level of understanding is needed to develop the high-fidelity multi-scale CFD models that will be used to optimize future engine designs. This type of experimentation provides opportunities to address important challenges facing the development of high-efficiency, low-emission engines. For example, emissions of soot particulate matter (PM) are a tax on engine efficiency because they prevent operation at the most efficient cycle and additional fuel must be consumed to oxidize the PM stored in the particulate trap. However, predictive engine CFD models for soot formation and oxidation still do not exist, particularly for new fuel streams such as biodiesel. These CFD models can be improved with quantitative measurements at engine conditions.

Approach

We conducted research to address soot formation and oxidation in diesel, biodiesel, and surrogate diesel fuel sprays, as well as other experiments listed in the Accomplishments sub-section. A constant-volume vessel is used for this research because of the ability to carefully control the charge-gas temperature and density within the chamber, as well as the full optical access (100-mm access from multiple angles) for advanced diagnostics. Figure 1 shows the combustion vessel and several optical diagnostic setups. A common-rail diesel injector (single-hole) generates a spray that penetrates and autoignites at representative engine conditions. A more detailed description of the facility may be found in [1].

Quantitative soot volume fraction measurements were made using simultaneous laser extinction and planar laser-induced incandescence (PLII) as shown in Figure 1. We also applied thermophoretic sampling, followed by TEM analysis, to determine the structure, number, and size of soot primary particles and aggregates. Soot sampling and TEM analysis is widely used to observe the visual nature and morphology of soot in laminar flames or in the exhaust of a diesel. But our study provides unique data about the soot

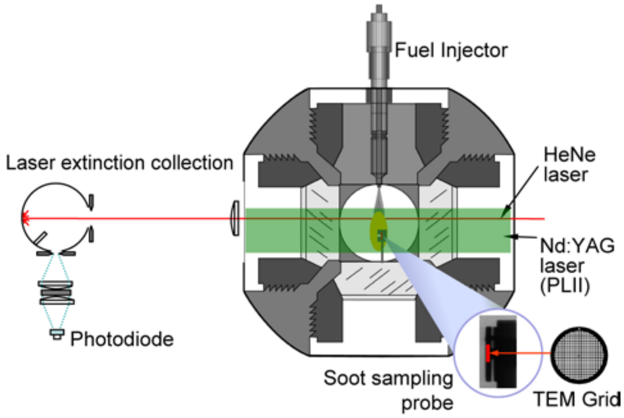

FIGURE 1. Combustion vessel and setup for optical and TEM sampling soot measurements.

morphology and soot volume fraction at the high-pressure conditions of the reacting fuel jet [2].

We also leveraged other high-temperature, high-pressure vessels from institutions around the world for spray combustion research as part of the ECN as shown in Table 1. Targeting the same ambient gas conditions (900 K, 60 bar, 22.8 kg/m^3, 15% oxygen) and using the same injector (common rail, 1,500 bar, KS1.5/86 nozzle, 0.090 mm orifice diameter, n-dodecane, 363 K), we collaborated with institutions such as IFP Energies Nouvelles to develop the Spray A dataset for the ECN [3]. This effort seeks to leverage the research capabilities and advanced diagnostics of all participants in the ECN to create a high-quality dataset to be used for advanced computational model development.

TABLE 1. Participating Experimental Institutions at Spray A Conditions of the Engine Combustion Network

Institution	Facilities	Personnel
Sandia	Preburn CV	L. Pickett
IFP	Preburn CV	G. Bruneaux
CMT	Cold, and Flow PV	J. Manin, R. Payri
Chalmers	Flow PV	M. Linne
GM	Flow PV	S. Parrish
Mich. T.U.	Preburn CV	J. Naber
Argonne	Cold V, X-ray Synchrotron	C. Powell, A. Kastengren
Caterpillar	Flow PV	T. Bazyn, G. Martin
Aachen	Flow PV	H. Pitsch
Meiji U.	Preburn CV	T. Aizawa
Seoul Nat.	Preburn CV	K. Min
Eindhoven	Preburn CV	C. Luijten

GM - General Motors; Mich. T.U. - Michigan Technological University

Results

Concurrent measurements of Spray A boundary conditions and spray penetration and combustion were performed at combustion vessels at Sandia and IFP Energies Nouvelles. To our knowledge, there has never been a direct comparison of spray combustion at two different facilities of this type. The ensemble-average penetration from a set of ten different injections is shown in Figure 2. We include penetration of the liquid phase, as well as reacting vapor penetration with 15% O_2. Considering the complexities of the experiment, the good agreement between the liquid, vapor, and reacting flame penetration at each facility is quite remarkable. Both facilities show that reacting penetration exceeds the non-reacting penetration, and there is similar liquid penetration during the steady period of injection. Differences between facilities fall within a 95% confidence interval for repeatability in the average vapor penetration at each facility.

At similar conditions as Spray A, we performed measurements of the soot volume fraction for various fuels using the optical techniques described in Ref. [2]. Results are shown in Figure 3 for #2 diesel with 27% aromatics, a surrogate fuel consisting of 77% n-dodecane and 23% m-xylene, and a soy biodiesel fuel. The soot measurements were taken long after the start of injection and start of combustion, representing the steady-state soot distribution during mixing-controlled combustion. Because of its importance on soot production, the lift-off length was also measured but there is little difference in lift-off length for these fuels. The surrogate fuel produces soot volume fractions similar to that of regular diesel. But the biodiesel fuel has soot levels that are

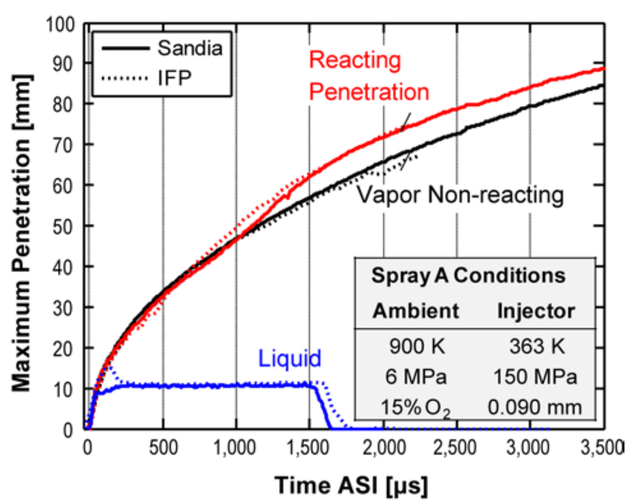

FIGURE 2. Comparison of liquid, vapor, and reacting flame penetration at IFP Energies Nouvelles and Sandia. Liquid length threshold is 3% of maximum. Vapor penetration was determined as in Naber and Siebers, 1996.

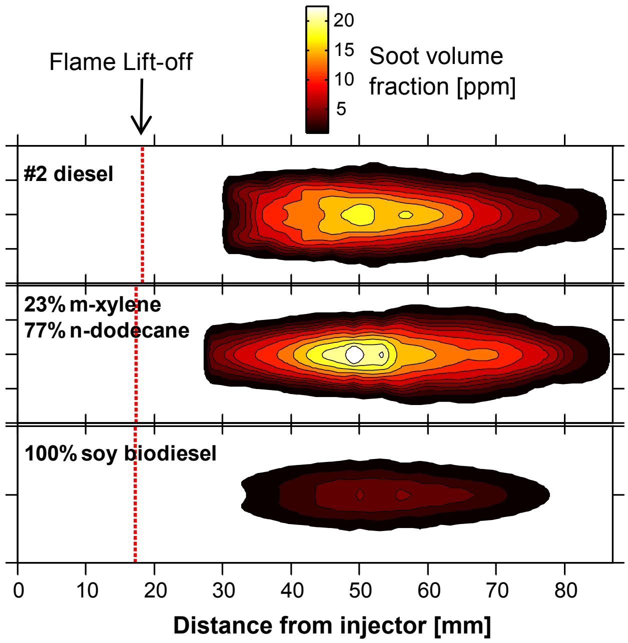

FIGURE 3. Quantitative soot volume fraction by PLII and laser extinction. Ambient conditions: 1,000 K, 22.8 kg/m^3, 15% O_2. Injector conditions: 0.090-mm orifice, 150 MPa fuel pressure, 363 K. Measured lift-off lengths are indicated by the vertical dashed red line.

roughly a factor of five lower, which is consistent with engine-out PM measurements.

The generation of quantitative datasets on soot production such as these is important to soot model development on several levels. First, the choice of a two-component surrogate fuel that matches the soot production in regular diesel permits soot model development using known physical and chemical properties of the surrogate fuel rather than undefined properties for the multi-component diesel fuel. Detailed chemical mechanisms exist for n-dodecane and m-xylene, allowing systematic treatment of the growth from gas-phase soot precursors to soot. Second, soy biodiesel also consists of five known fatty-acid methyl esters, with the composition for our sample given in [4]. Researchers are also working to develop detailed chemical mechanisms for biodiesel, but soot model development for biodiesel is in the very early stages. As biodiesel is now accepted as a blend fuel with diesel, it becomes more important to understand its effect on combustion and soot formation. The soot volume fraction distribution provided in Figure 3 for a reacting biodiesel and diesel surrogate sprays represents the first in situ measurements of soot formation and oxidation for these important fuel components. It allows CFD soot model development based upon reacting sprays at engine conditions, rather than relying upon engine-out PM.

The soot measurements were carried further by direct sampling with a probe as shown in Figure 1. The probe holds a carbon-coated TEM grid (3-mm diameter) at the jet centerline. The probe is placed parallel to the jet axis to skim gas from the jet while attempting to minimize flow disturbance. Through a 1-mm diameter hole, flow containing soot enters the probe and soot particles are deposited on the cooler TEM grid via thermophoresis. This restrictive passage ensures quenching of combustion and also protects the grid from excessive heating. Soot morphology is then analyzed after image acquisition in the TEM [2].

TEM images for samples taken for the diesel surrogate fuel are shown in Figure 4. The bottom-right corner of each image shows the soot sampling probe location in distance from the injector. The probe was fixed at the jet centerline but the axial location was varied to observe differences in soot with respect to the soot formation and oxidation processes corresponding to the soot distribution given in Figure 3. For example, soot begins to form starting at 30 mm from the injector, reaches a peak at 50 mm, and then decreases by oxidation to near zero at 90 mm.

Relatively small particles with low contrast and no well-defined boundary were collected in the soot formation region. For example, at 30 mm from the nozzle, it is apparent that some particles are transparent to the electron beam. At the peak soot location (50 mm), the number of soot aggregates also reaches a maximum and clusters of well-defined, solid primary particles are evident. Then, the aggregates and primary particles shrink during the oxidation.

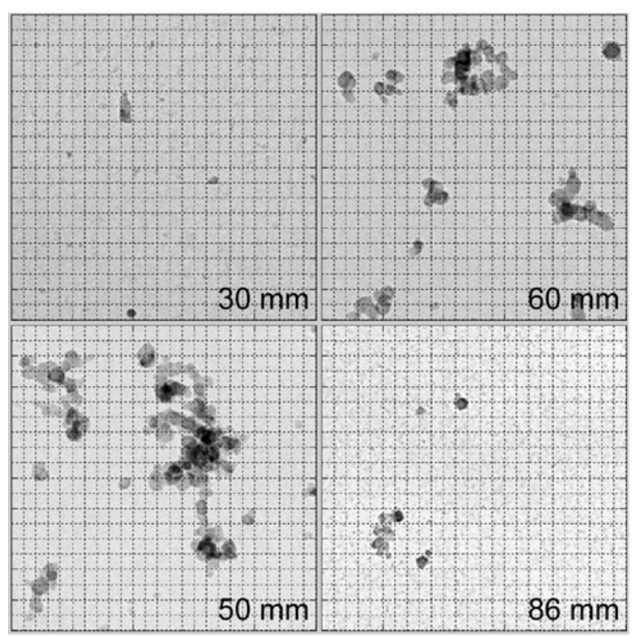

FIGURE 4. TEMs of soot particles sampled at the jet centerline, with the axial distance given in the lower right. Twenty nm dotted squares are overlaid on the image to provide a scale. Diesel surrogate fuel : 77% n-dodecane, 23% m-xylene by volume.

Visualization of the size of the spherical primary particles and aggregates is aided in Figure 4 by the placement of 20 nm dotted squares in the images. Most primary particles appear smaller than 20 nm. To present statistically meaningful data, the size distribution of primary particles was obtained using image analysis software and with manual oversight. For each TEM grid (sample), five different locations were processed by TEM, yielding thousands of primary particles and aggregates.

The effect of transition from the peak soot location to a soot oxidation location is depicted in probability density functions (PDFs) for primary particle size as given in Figure 5. Soot primary particle sizes are distributed from approximately 5 nm to 30 nm at the peak soot location (50 mm) with a number mean of 16 nm. As expected, the primary particle size decreases in the oxidation zone (number mean of 16 nm at 86 mm) and the PDF narrows. While the shift in normalized PDF occurs, the total number of particles decreases significantly in the oxidation zone. The coverage of soot particles on the TEM grid at 86 mm is only 7% of that at 50 mm, consistent with the soot volume fraction changes shown in Figure 3.

Conclusions

Diagnostics at the Spray A conditions show reasonable similarity in different high-temperature, high-pressure facilities at Sandia and IFP despite the challenges of providing matched boundary conditions at these unique facilities. These encouraging findings suggest that parallel research, and leveraging experimental work at different facilities, can accelerate the development of a high-quality dataset and improved understanding of spray combustion. To facilitate this dataset development and exchange, data for Spray A is available on the ECN Web site [1], together with the total uncertainty and experimental variance for each measured quantity.

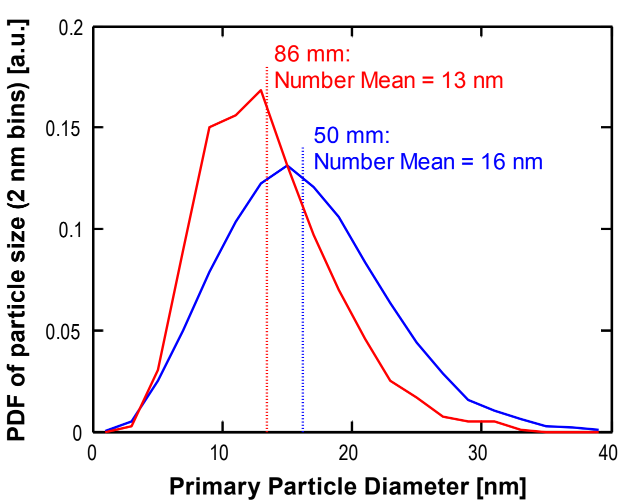

FIGURE 5. PDF by number for the soot primary particle diameter at the peak soot location (50 mm) and the oxidation location (86 mm) for the fuel given in Figure 4.

A quantitative dataset of penetration, mixing, combustion, soot volume fraction, and soot particle morphology has been developed for neat biodiesel, diesel, and surrogate diesel fuels.

Collectively, these data provide unique information needed for the development of high-fidelity CFD models that will be used to optimize future engine designs.

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Special Recognitions & Awards/Patents Issued

1. SAE Excellence in Oral Presentation Award (Caroline Genzale, 2010 World Congress, Paper 2010-01-0610).

II.A.5 High-Efficiency Clean Combustion in Light-Duty Multi-Cylinder Diesel Engines

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Objectives

- Expand operational range of high-efficiency clean combustion (HECC) for conditions consistent with the Urban Dynamometer Driving Schedule (UDDS) as well as future down-sizing and down-speeding conditions.
- Improve the fundamental understanding of HECC from a thermodynamics perspective.
- Characterize the effect of thermal boundary conditions of the engine on HECC stability, efficiency, and emissions.
- Support demonstration of DOE FreedomCAR emissions milestones for light-duty diesel engines.

Fiscal Year (FY) 2010 Accomplishments

- Upgraded General Motors (GM) 1.9-L engine installation to include a low-pressure exhaust gas recirculation (EGR) loop reflective of recent production engines.
- Achieved reactivity-controlled compression ignition (RCCI) at 4.2 bar brake mean effective pressure (BMEP) on a multicylinder engine using gasoline and diesel dual-fueling.
- Characterized emissions of RCCI combustion for comparison with conventional and HECC combustion.

Future Directions

- Expand the load and speed range of RCCI on a multicylinder engine.
- Evaluate performance of RCCI on simple load and speed transients.
- Conduct experiments to achieve partially premixed combustion (PPC) on a multicylinder engine using gasoline fueling.

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Introduction

Advanced combustion modes such as PCCI, RCCI, and PPC have shown promise as potential paths for meeting 2010 and beyond efficiency and emissions goals. ORNL as well as others have shown success in achieving reduced emissions and acceptable efficiency using high charge dilution for a somewhat limited speed-load range. Recent results from the University of Wisconsin and Lund University have shown the ability to achieve low engine-out emissions and high thermal efficiency over a wide range of speeds and loads. ORNL is leveraging many years of HECC experience to explore these various combustion approaches, to evaluate the emissions impacts, and to develop strategies for stable operation on multicylinder engines. The primary objective of this project is to investigate potential near-term technologies for expanding the usable speed-load range and to evaluate the potential benefits and limitations of these technologies for achieving HECC in a light-duty diesel engine.

Approach

The RCCI combustion strategy has shown engine-out emissions approaching the 2010 heavy-duty legislated limits while achieving very high indicated efficiencies. RCCI uses two fuels of different cetane ratings to stratify the fuel reactivity within the cylinder, thus broadening the combustion event. This longer combustion duration enables high-load operation without high-temperature combustion occurring. The results to date have been from modeling and single-cylinder engine experiments, which precludes the measurement of brake thermal efficiencies (BTEs) or the consideration of EGR imbalances, turbomachinery performance, and other real-world constraints on engine operation. By implementing RCCI on a multicylinder engine at ORNL which is equipped with full instrumentation and a flexible microprocessor-based control system it is possible to evaluate these constraints and to measure the brake efficiency of an engine operating with RCCI.

Results

A GM 1.9-L diesel engine installed at ORNL was modified to include a port fuel injection system using conventional gasoline injectors. These injectors were then supplied with unleaded 96 Research octane number gasoline while the existing diesel fuel injectors were supplied with conventional ultra-low sulfur diesel. The modified intake manifold installed on the engine in shown in Figure 1.

An experimental matrix was run to evaluate the impact of the following parameters:

- Gasoline to diesel fuel mass ratio
- Diesel start-of-injection timing
- Intake charge temperature
- Swirl ratio
- Boost level

The engine operating condition was held fixed at 2,300 rpm, 4.2 bar BMEP. This point was selected so that direct comparison with results from the University of Wisconsin's modeling and single-cylinder engine results. This operating condition corresponds to a moderate acceleration in a vehicle and is well within the speed-load range of the UDDS cycle.

In comparison to conventional diesel combustion, RCCI combustion exhibits significantly higher peak cylinder pressures, and pressure rise rates. In effect, RCCI can be described as HCCI with an extended combustion duration. This yields the emissions and efficiency benefits of HCCI while reducing combustion noise and allowing a wider range of operation. Figure 2 displays a comparison of conventional diesel combustion and RCCI combustion at the same operating point.

The optimum operating condition for RCCI was found to be with 77% gasoline, 1.2 bar boost, and moderate swirl. At this condition the BTE was measured at 33.6% compared to 32.1% BTE for conventional combustion. At the same time, oxides of nitrogen (NO_x) emissions were reduced by a factor of 10 and particulate matter (PM) was reduced by a factor of 90. The engine operation was not fully optimized at this operating condition, so there is still more efficiency potential to be gained. Even so, the achievement of engine-out NO_x and PM emissions below the 2010 regulatory standard while improving on the efficiency of conventional combustion shows great promise for RCCI. The complete results are shown in Table 1.

To further understand RCCI combustion the emissions were analyzed in detail. The data generated can be used to shed light on details of combustion and also to evaluate impacts of non-regulated emissions that may have health or other impacts. An aldehyde analysis performed with a Fourier transform infrared spectrometer. The results of this analysis revealed significant increases in emissions of formaldehyde, acetaldehyde, and benzaldehyde compared with conventional combustion. It is expected that this increase is due to the larger proportion of mono-aromatic hydrocarbon species in gasoline than in diesel fuel, and these are leading to higher concentrations of these aldehydes in the exhaust. Figure 3 shows the measured aldehyde results for conventional combustion,

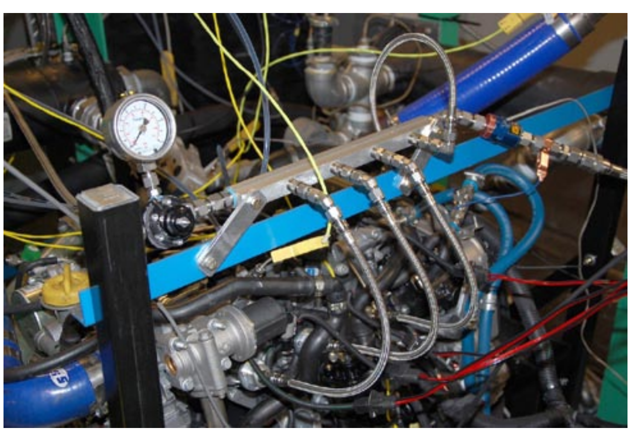

FIGURE 1. Port Fuel Injection System Installed on the Engine

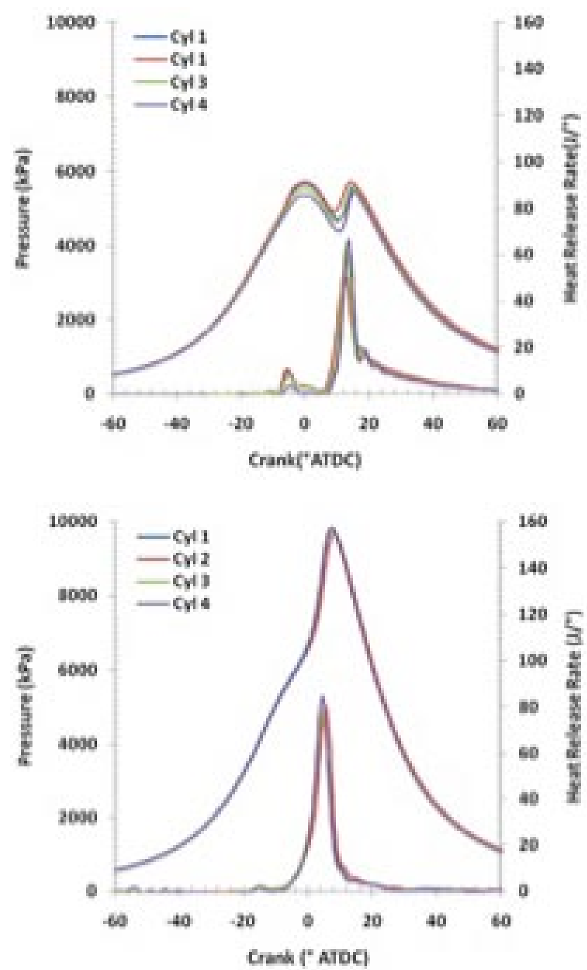

FIGURE 2. Pressure and Heat Release Rate (bottom) Traces for Conventional Diesel Combustion (top) and Dual-Fuel RCCI Mode (bottom)

TABLE 1. Efficiency and Emissions Measures for Conventional Diesel and RCCI Combustion Modes

	Conventional Combustion	RCCI
% Gasoline	0	77
BTE (%)	32.1	33.6
ITE_{net} (%)	39.4	39.5
ITE_{gross} (%)	41.0	43.1
Boost (bar)	1.18	1.20
Swirl angle (°)	35.8	75.9
NO_x (g/kg_{fuel})	3.65	0.34
CO (g/kg_{fuel})	9.97	40.96
HC (g/kg_{fuel})	3.46	34.60
Smoke number	1.78	0.02
Turbo out temperature (°C)	412	260

ITE - indicated thermal efficiency; HC - hydrocarbons

PCCI combustion from previous years' experiments, and RCCI combustion.

The particulate emissions were also carefully studied to determine the impact of RCCI combustion on the particulate characteristics. The size distribution of the particulates was found to have two local maxima, at 11 nm and 37 nm. This suggests that there may be multiple particulate formation pathways in the combustion process, each leading to a different characteristic size of particle. The size distribution of the particles is shown in Figure 4.

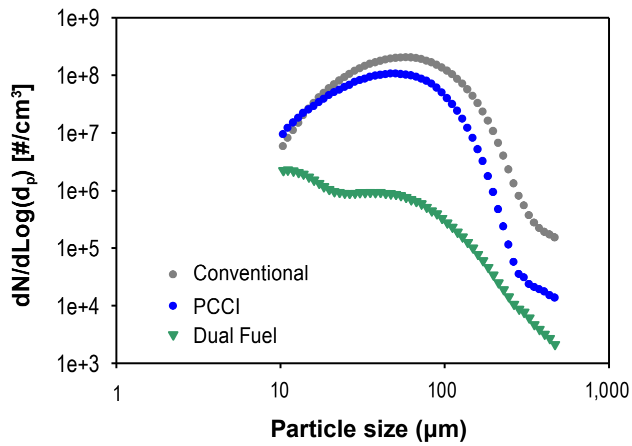

FIGURE 4. Particle Size Distribution for RCCI Combustion

Conclusions

This activity has been successful at providing new insight into the implementation of advanced combustion operation on multi-cylinder engines and is an important component to demonstrating 2010 FreedomCAR efficiency and emissions milestones on light-duty diesel engines. Specific accomplishments are as follows:

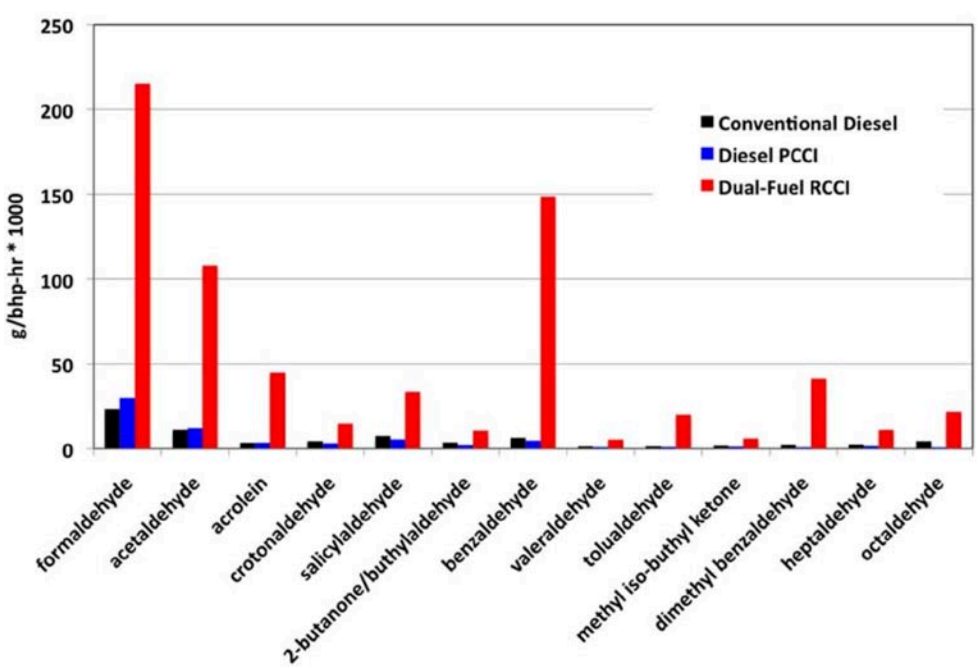

FIGURE 3. Engine-Out Gaseous Aldehyde and Ketone Emissions in Conventional Diesel, Diesel PCCI, and Dual-Fuel RCCI Combustion Modes

- RCCI combustion was achieved on a multicylinder engine with only minor modifications. Partially-optimized combustion yielded a BTE slightly higher than that of conventional combustion while simultaneously generating substantially lower engine-out emissions.
- Detailed analysis of the emissions from RCCI combustion indicate different combustion pathways for generating hydrocarbon and PM emissions than in conventional combustion. This will require matching of the aftertreatment system to the unique characteristics of RCCI.

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II.A.6 Large Eddy Simulation (LES) Applied to Low Temperature and Diesel Engine Combustion Research

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Objectives

- Combine unique state-of-the-art simulation capability based on the large eddy simulation (LES) technique with advanced engine combustion research and development activities.
- Perform companion simulations that directly complement optical engine (and supporting) experiments being conducted at the SNL Combustion Research Facility (CRF) and elsewhere.
- Maximize benefits of high-performance massively-parallel computing for advanced engine combustion research using DOE capability-class computer platforms.

Fiscal Year (FY) 2010 Accomplishments

- Simulations of the optical hydrogen-fueled internal combustion engine in collaboration with Kaiser et al. and systematically worked toward homogeneous charge compression ignition (HCCI) combustion in collaboration with Dec et al.
  - Validation through comparison of measured and modeled results.
  - Chemiluminescence imaging and particle image velocimetry.
  - Planar laser induced fluorescence.
- Improved performance and usability of Oefelein's massively-parallel LES solver ("RAPTOR") for internal combustion engine related calculations as part of the DOE Innovative and Novel Computational Impact on Theory and Experiment (INCITE) Program.
  - New grand-challenge grant for central processing unit (CPU) time on DOE "capability-class" computers was awarded based on project objectives with Oefelein as principal investigator.
  - Multiyear award spanning 2011-2013 in collaboration with the National Center for Computational Sciences, Oak Ridge National Laboratory (ORNL, see www.nccs.gov).
  - Thirty-million CPU hours awarded for 2011 on the CRAY XT system called Jaguar (currently fastest computer in the world).
- Developed hierarchy of benchmark simulations aimed at understanding high Reynolds number, high-pressure, direct-injection processes for low-temperature combustion (LTC) and diesel engine applications.
  - Direct treatment of liquid hydrocarbon injectors in collaboration with Musculus and Pickett (see www.ca.sandia.gov/ECN).
  - Detailed calculations using actual production engine geometries and operating conditions.

Future Directions

- Continue to develop a hierarchy of benchmark simulations aimed at understanding high Reynolds number, high-pressure, direct-injection processes for LTC and diesel engine applications in collaboration with Musculus and Pickett using Engine Combustion Network (ECN) data.
- Perform series of LES calculations of the CRF optical HCCI engine configuration in collaboration with Dec et al. with emphasis on understanding in-cylinder thermal stratification and combustion processes over full engine cycles.
- Continue leveraging between DOE Office of Science and Energy Efficiency and Renewable Energy (i.e., bridge gap between basic and applied research).
  - Detailed validation and analysis of turbulent reacting flow phenomena.
  - Access to high-performance capability-class computers via the INCITE Program.

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Introduction

The combination of high performance computing and the LES technique has significant potential to provide new insights into the dynamics of internal combustion engine flow processes. The objective of this project is to fully integrate the combined merits of high-performance computing and LES in a manner that provides some of the highest-fidelity, most detailed calculations ever performed to investigate turbulent reacting flow processes in internal combustion engines.

Two complementary projects have been established. The first is funded by the DOE Office of Science, Basic Energy Sciences, and focuses on LES of turbulence-chemistry interactions in reacting multiphase flows. The second project (funded by the DOE Vehicle Technologies Program) focuses on the application of LES to LTC and diesel engine combustion research. Objectives and milestones for both projects are aimed at establishing high-fidelity computational benchmarks that match the geometry and operating conditions of key target experiments using a single unified theoretical-numerical framework. The projects are complementary in that the Office of Science, Basic Energy Sciences activity provides the basic science foundation for detailed model development and the Vehicle Technologies Program activity provides the foundation for advanced engine research and technology transfer to industry.

Our unique linkage with the Office of Science has enabled the development of formal collaborations with the National Center for Computational Sciences at ORNL under the DOE INCITE Program. These collaborations have led to unprecedented amounts of CPU allocations on the ORNL CRAY XT system (i.e., Jaguar, see http://www.nccs.gov). The total allocation in 2010 was 30-million CPU hours and was used to continue to validate high-pressure injection models; and subsequently to perform detailed simulations of the optically accessible hydrogen internal combustion engine being studied by Kaiser et al., and the optical HCCI engine being studied by Dec et al. In November of 2010, we were awarded a new multiyear INCITE grant spanning 2011-2013 entitled "High-Fidelity Simulations for Advanced Engine Combustion Research," which will further support this project. The investment in time and resources provides two significant benefits. After systematic validation of key processes using available experimental data, quantitative information can be extracted from the simulations that are not otherwise available. This information will provide: 1) a detailed description of intricately coupled processes not measurable by experimental diagnostics, and 2) the information required to understand and develop improved predictive models for engineering.

Approach

In addition to providing a unique massively-parallel multiscale modeling framework based on LES, we have established direct collaborations with two of the "flagship" experimental efforts at the CRF. A scientific foundation for advanced model development has been established as a direct extension of the International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames (i.e., the "TNF Workshop," www.ca.sandia.gov/TNF). Similarly, under this project we have established collaborative research activities that focus on key optical engine experiments and model validation using the ECN (see www.ca.sandia.gov/ECN). The ECN has analogous objectives to those of the TNF Workshop. Our most recent activities have led to targeted external collaborations with University of Wisconsin (Rutland et al.), Penn State University (Haworth et al.), General Motors (Kuo et al.) and the University of Michigan (Sick et al.), among others. Our approach for all of the tasks are to provide direct one-to-one correspondence between measured and modeled results by performing detailed simulations that incorporate the fully coupled dynamic behavior of a given configuration in the full experimental or device-scale geometry without canonical approximations. We are currently focused on two key areas of research: 1) development and validation of multiphase combustion models with emphasis on direct-injection processes in collaboration with Musculus and Pickett et al., and 2) to establish a parallel task focused on HCCI engines in collaboration with Dec et al. The integrated set of tasks provides an optimal combination of in-cylinder and out-of-engine studies to validate and understand key processes typically present in internal combustion engines.

Results

As one example of work over the past year, we have completed high-fidelity LES calculations of a transient jet that mimics diesel injection dynamics. Results were presented in a Society of Automotive Engineers (SAE) paper [1] as part of the SAE 2010 Congress in Detroit, MI. Based on this work we have been collaborating with the University of Wisconsin-Madison (the group directed by Professor Chris Rutland) with emphasis on enhancing the accuracy of their industry-oriented LES which is performed with much coarser grid spacing.

Our study of transient jets is motivated by recent diesel-injection experiments showing that mixing is significantly altered during the jet deceleration [2,3]. The injection process is highly transient and exhibits a quasi-steady phase (roughly corresponding to the time period during injection) followed by a deceleration phase (roughly corresponding to the time period after the end of injection). For a conventional diesel engine, mixing characteristics during the quasi-steady phase are important because both heat release and pollutant formation largely occur during the quasi-steady phase. However, for LTC engines, the deceleration phase plays a much more important role because both the heat release and pollutant formation primarily occur during this phase. Recent experiments have shown that mixing between fuel and air is significantly enhanced during the deceleration phase. The effect of this enhanced mixing is desirable for soot reduction. On the other hand, it can be undesirable because unburned hydrocarbons emissions are increased as a result of over-mixing. While quasi-steady jets have been well-understood, much less is understood about decelerating jets. Therefore, our primary goal was to better understand the unique mixing characteristics of a decelerating jet in relation to the corresponding quasi-steady jet. Emphasis was placed on entrainment because it is the rate-controlling process for air-fuel mixing in diesel jets. Using high-fidelity LES, we aimed at quantifying the entrainment process and identifying key mechanisms responsible for altering entrainment during the deceleration phase.

In the present work, we used the RAPTOR code developed by Oefelein [4]. This code has been extensively verified and validated over the last several years. Hence, we have gained sufficient confidence with this code to study the present transient gas jet case. Figure 1 shows the mean injection profile of the jet, which matches the experiment of Witze [5] and is similar to a real diesel-injection jet in many aspects. Correlated velocity fluctuations were added to this mean profile to mimic the turbulence developed inside the injector nozzle. In the calculation we used an optimally stretched mesh of three million cells combined with a time-step of 160 ns to guarantee both spatial and temporal accuracy.

We quantified entrainment using entrainment coefficients. An entrainment coefficient is defined as a normalized entrainment rate, which equals the entrained mass per unit axial distance [1]. Figure 2 shows the axial profiles of entrainment coefficient at several instants during deceleration, 4.5 ms, 4.7 ms, and 4.9 ms, respectively. Also shown is the corresponding quasi-steady jet for comparison. Note that plotted on the top are the profiles calculated from the instantaneous LES data. On the bottom are the smoothed profiles, which clearly emphasize the global features. Two observations can be made. First, during deceleration, a region of increased entrainment, which is indicated by higher entrainment coefficients compared with the quasi-steady jet, is observed at the downstream region, e.g., x/D=8~16 for 4.5 ms. Second, this region of increased entrainment propagates downstream as time elapses. This is consistent with the "entrainment wave" predicted by the one-dimensional model [2].

Our data suggest that structural differences between the quasi-steady jet and the decelerating jet are linked to the different entrainment in these two jets. For example, Figure 3 compares the representative contours of the scalar field on a two-dimensional plane between the quasi-steady jet and the decelerating jet. It shows that the decelerating jet involves much more large-scale flow structures along the jet boundary, which are referred to as interface-indentations here. Figure 4 shows the jet boundary and the velocity vectors for the decelerating jet. Strong entrainment fluxes exist inside each indentation region. This explains why the interface-

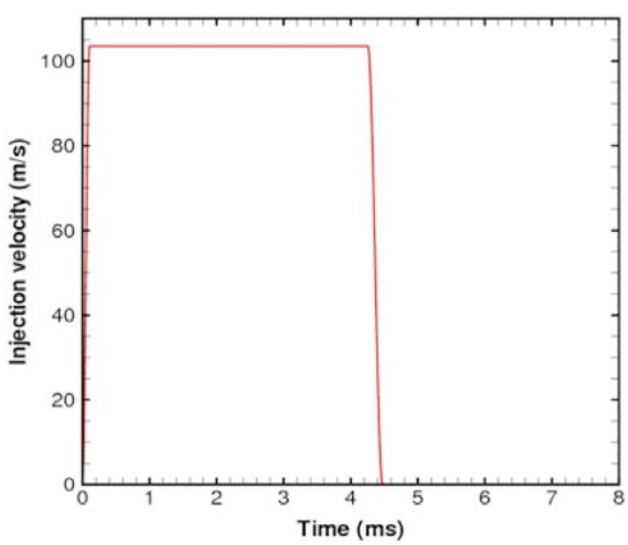

FIGURE 1. Temporal profile of the mean centerline axial velocity at the nozzle exit.

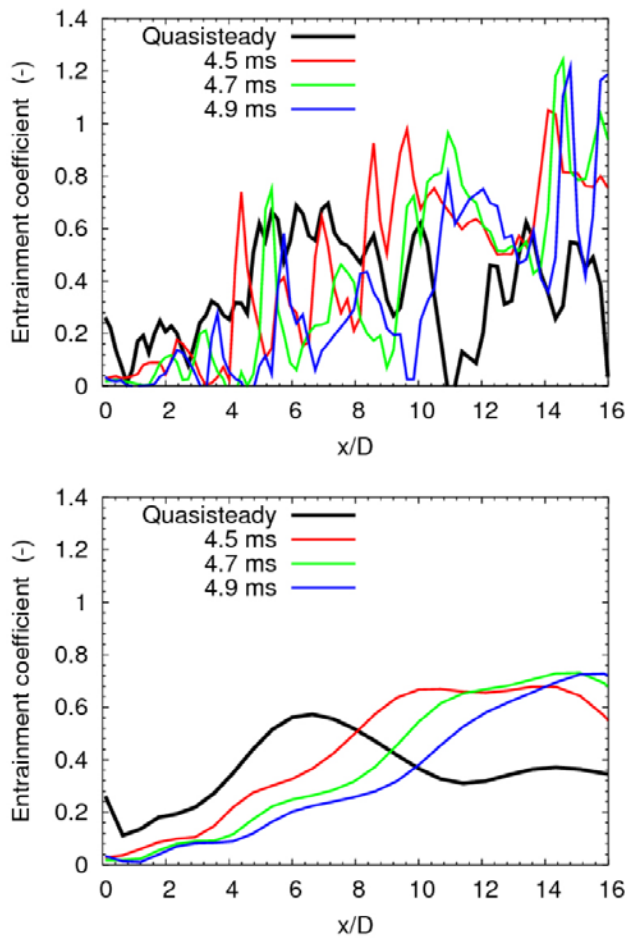

FIGURE 2. Axial profiles of entrainment coefficient of the quasi-steady jet and the transient jet at several times, 4.5 ms, 4.7 ms, and 4.9 ms, during deceleration. The top sub-figure shows the instantaneous profiles and the bottom sub-figure shows the smoothed profiles.

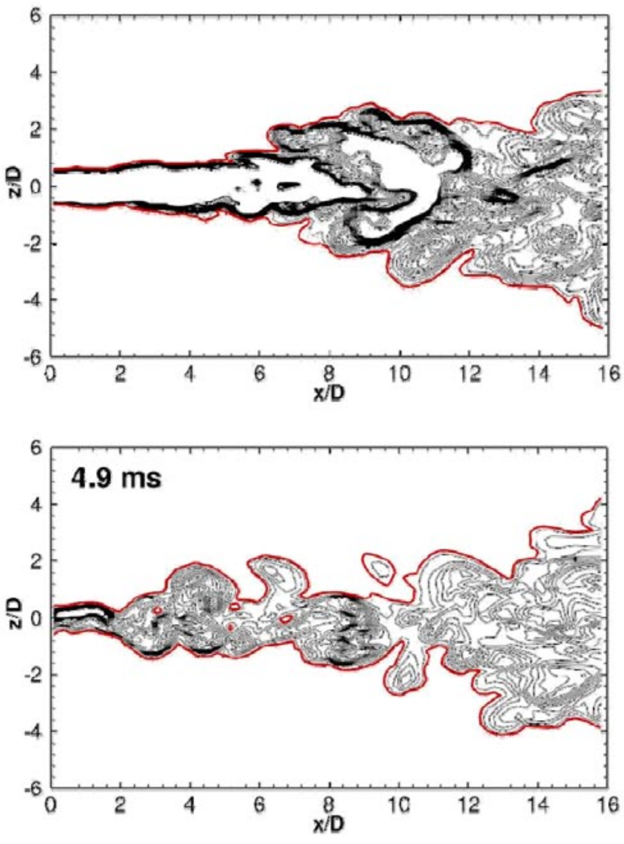

FIGURE 3. Scalar contours and the jet boundary (represented by red curve) on a two-dimensional plane including jet axis for the quasi-steady jet (top) and the decelerating jet at 4.9 ms (bottom).

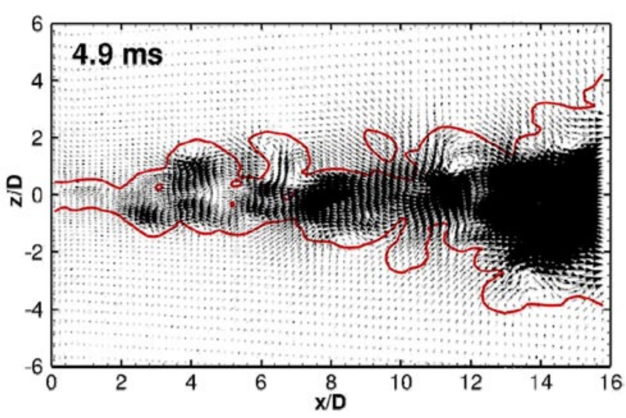

FIGURE 4. Jet boundary represented by red curve and velocity vectors represented by black arrows on a two-dimensional plane including jet axis for the decelerating jet at 4.9 ms.

indentations are linked to entrainment. To further verify this view, we plotted the azimuthally-averaged jet boundary and entrainment coefficient as function of axial coordinate, x/D, in Figure 5. As indicated by the arrows, each indentation accompanies a region of

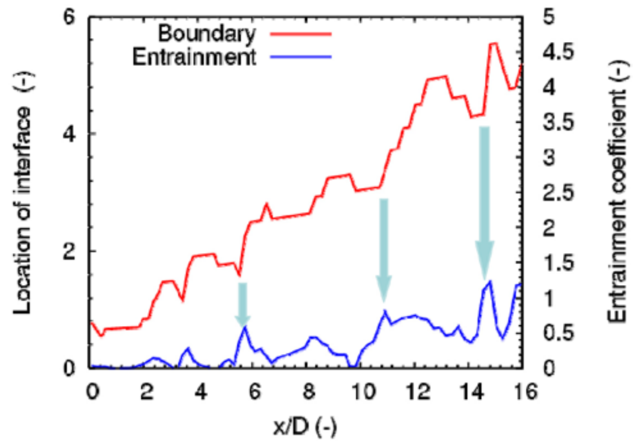

FIGURE 5. Axial profiles of the jet boundary and corresponding entrainment coefficient for the decelerating jet at 4.9 ms.

increased entrainment. These observations suggest the following entrainment phenomenology. An indentation is a manifestation of an engulfment region. Lying inside this engulfment region, large packets of ambient fluid have a higher probability to be drawn across the jet boundary; i.e., to become entrained.

Conclusions

Results from the high-fidelity LES have confirmed that entrainment is enhanced during deceleration compared with the quasi-steady jet. Specifically, a region of increased entrainment forms and propagates downstream during the deceleration phase. The jet during deceleration exhibits much more interface-indentations than the quasi-steady jet. The data suggest that growth of interface-indentations is a key mechanism responsible for enhancing entrainment. By theory, interface-indentations must be caused by large-flow scale flow motions and the large flow-scale flow motions can be enhanced by flow instability. This implies that manipulating injection-jet instability, as part of injection strategies, can control the downstream mixing in diesel engines.

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II.A.7 Computationally Efficient Modeling of High Efficiency Clean Combustion Engines

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Subcontractors:
- University of Wisconsin, Madison, WI
- University of California, Berkeley, CA

Objectives

- Enhance understanding of clean and efficient engine operation through detailed numerical modeling.
- Gain fundamental and practical insight into high efficiency clean combustion (HECC) regimes through numerical simulations and experiments.
- Develop and apply numerical tools to simulate HECC by combining multidimensional fluid mechanics with chemical kinetics.
- Reduce computational expense for HECC simulations.
- Democratize high-resolution engine simulation by bringing computational tools to the desktop computer for use by engine designers and researchers.

Fiscal Year (FY) 2010 Accomplishments

- Improved numerical methodologies demonstrate as much as a factor of 250 reduction in computational time for multi-zone combustion chemistry simulation.
- Multi-zone model used for investigating cycle-to-cycle instability in homogeneous charge compression ignition (HCCI) to spark ignition (SI). Successfully simulated Oak Ridge National Laboratory (ORNL) HCCI-to-SI transition experiments.
- Applied the KIVA-3V engine computational fluid dynamics software coupled with our artificial neural network combustion model to predict direct-injected premixed charge compression ignition (PCCI) experiments from Sandia National Laboratories.
- Successfully predicted negative valve overlap (NVO) PCCI engine operation with multi-cycle KIVA-3V multi-zone simulation code compared to Sandia National Laboratories experiments.
- Demonstrated detailed chemical species thermodynamic property calculations on a general purpose graphical processing unit (GP-GPU), achieving up to 300-fold speedup in property calculations.

Future Directions

- Continue to validate and develop chemistry simulation capabilities that will enable the prediction of performance and emissions in the development of new vehicle powertrain technologies.
- Improve computational solvers for chemical kinetic simulations through new numerical strategies.
- Continue development of the next generation multi-zone chemical kinetics model for application to modern parallel computational fluid dynamics codes.
- Develop computational tools suitable for kinetic chemistry on GP-GPU platforms to enable high-fidelity simulations on low-cost engineering workstations.

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Introduction

This research and development project focuses on the development and application of computationally efficient and accurate simulation tools for prediction of engine combustion. Simulation of combustion aids in development of new high-efficiency and low-emissions engines by allowing for detailed characterization of in-cylinder engine processes that are difficult to measure directly. Simulation also allows for suppositional investigation of new concepts, such as new combustion chamber geometry, allowing valuable and limited experimental resources to be focused on the most promising strategies.

Combustion simulation is computationally demanding because it combines three-dimensional turbulent fluid flow with highly exothermic chemical reactions. As such, simulation of an internal combustion engine cycle with chemistry and fluid flow typically requires access to large-scale computing resources. One major motivation of this research is to use physical and mathematical methods to reduce computational expense of combustion simulation. These computationally efficient tools are applied to understanding the fundamental physical processes occurring in engines utilizing high efficiency clean combustion strategies.

Approach

We use high-fidelity simulations to predict internal combustion engine operation; looking to maximize computational performance by taking advantage of physical discretization strategies, numerical methods, and computer architectures. Thermo-kinetic chemistry and fluid mechanics that occurs in engine combustion (diesel, SI, HCCI, etc.) is challenging to simulate because of the large gradients present and the wide range of time-scales over which processes occur, from nanoseconds to milliseconds. We developed a multi-zone solver that significantly reduces the computational burden of chemistry simulation combined with computational fluid mechanics with little loss in accuracy. The multi-zone model solves chemistry in a non-geometric thermo-chemical phase-space, significantly reducing the number of chemistry calculations needed to calculate an engine cycle relative to the standard geometric discretization.

The multi-zone approach is the first step, but many additional opportunities exist to dramatically reduce combustion simulation cost through numerical solution methods. We have been using applied mathematics techniques to look at the structure of the chemical system that is being solved. For example, Eigenstructure analysis of the differential equations in the chemical system has informed development of "preconditioners" to the system that allow for much more efficient solution of the system of equations. We have a roadmap to apply a variety of strategies to solution of chemical systems that can lead to at least a 1,000 times speedup in computational chemistry. The improved performance of these simulation codes not only enables industrial design utilization, but also allows us to simulate more complex problems. We have used our multi-zone models with improved solvers to investigate multi-cycle simulations of HCCI to SI transition, as well as NVO PCCI combustion.

Results

Chemical kinetics prediction is critical to the development of new high-efficiency clean combustion systems for engines. However, chemical kinetics simulation is computationally intensive, limiting the capability of researchers and designers to utilize these simulations in engine development. The following describes examples of our research and development activities related to improving fundamental understanding of engine combustion and enabling more efficient computation for research and design.

Chemical kinetics simulation involves solving a system of non-linear ordinary differential equations. Solution approaches can be explicit or implicit. Implicit solution of ignition chemical kinetic differential equations allows for faster solutions by allowing much larger timesteps, but requires defining trajectory information for the chemical system, the so-called Jacobian Matrix. For a typical hydrocarbon combustion chemical kinetic mechanism, determining the Jacobian Matrix can be more than 99% of the computational expense of the solution. Thus, reducing computational cost of generating and solving the Jacobian Matrix can greatly accelerate chemical kinetic simulation.

Our strategy is to perform computationally inexpensive mathematical operations upon the chemical system equations to transform them into a system that is less numerically costly to solve. This transformed system is "preconditioned," and can achieve much faster convergence with appropriate numerical solvers.

We are investigating Jacobian preconditioning strategies that can greatly reduce the computational cost of chemical simulations. Figure 1 shows an example of solving a chemical system using an implicit solver with

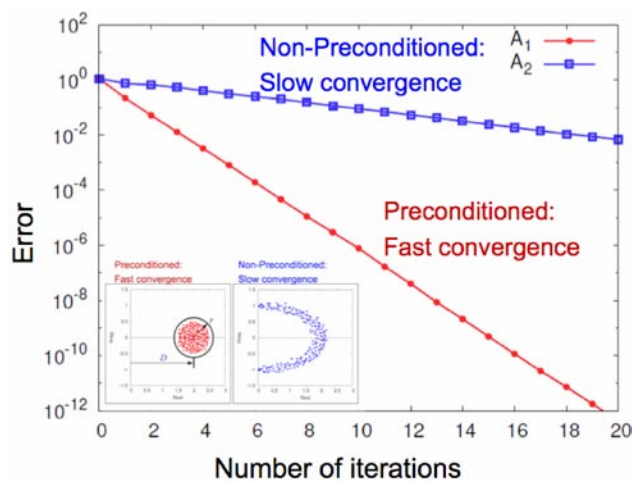


FIGURE 1. Jacobian preconditioning results in much faster solution using solvers appropriate for chemical kinetic systems. The ordinary differential equation system solved with a preconditioned Jacobian (A1) converges much faster that a non-preconditioned Jacobian (A2), demonstrated by the much more rapid decrease in error. Inset shows real and imaginary components of Eigenvalues for the preconditioned and non-preconditioned systems. Tightly clustered Eigenvalues away from the origin yield much faster solution convergence.

and without Jacobian preconditioning. At each timestep the solver residual error is reduced below a threshold value as a criterion for considering the solution converged. In this example, after 20 solver iterations the error in the preconditioned system is 10^{10} lower than the non-preconditioned system. The non-preconditioned system may require hundreds of times as many iterations to reach the convergence criteria. Preconditioning can greatly improve the solvability of the chemical kinetic system differential equations, but the challenge is determining the appropriate preconditioning strategy.

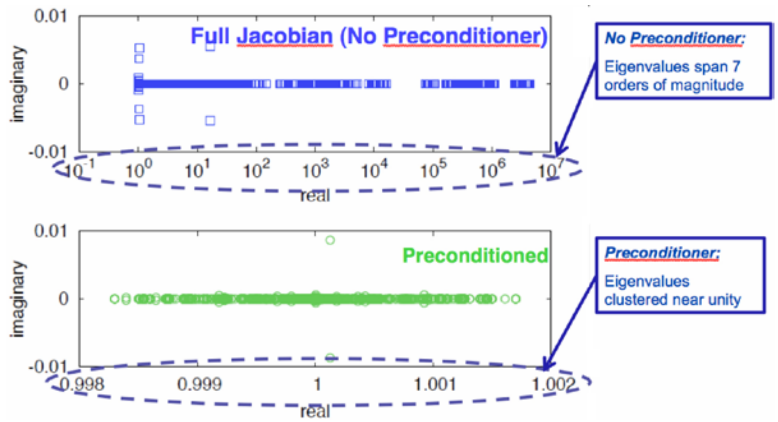


FIGURE 2. Eigenvalue distribution for a preconditioned and non-preconditioned 857 species isooctane mechanism during lean autoignition. The preconditioner reduces the range in Eigenvalues by 10 orders of magnitude, greatly improving solvability of the chemical kinetic system and reducing computational time.

Looking in detail at the mathematical structure of the Jacobian Matrix gives us insight into how to form the preconditioner, as well as how effective a preconditioning strategy works. "Eigenvalues" are mathematical constructs that give fundamental information on the character of a linear algebraic system. In the case of the Jacobian Matrix of a chemical kinetic system, the Eigenvalues give information on the range of timescales over which various reactions are occurring. The inset plots in Figure 1 show the Eigenvalues for the preconditioned and non-preconditioned systems. With advanced iterative solvers, systems suitable for chemical kinetics simulations with Eigenvalues tightly clustered away from the origin will converge much faster than systems with widely spread Eigenvalues. The Eigenvalues for the chemical system are typically not tightly clustered, as many timescales are present. By using numerically inexpensive operations upon the system of chemical equations, we are able to transform the equations into a system with better characteristics for the solver, i.e. a system with highly clustered Eigenvalues.

Figure 2 shows the Eigenvalue space for a preconditioned and non-preconditioned system at a timestep during lean autoignition of isooctane in a constant volume reactor. The isooctane mechanism has 857 species and thus chemical species equations [1]. A heuristic preconditioning strategy based on the Jacobian Matrix Eigenstructure is applied. The preconditioner condenses the range in Eigenvalues by 10 orders of magnitude, greatly improving system conditioning and solvability.

Preconditioning techniques have been applied to the LLNL multi-zone model for simulation of HCCI to SI transition. The simulation time reduction allows for simulation of hundreds of engine cycles in the same time as one cycle simulation solved with standard solution methods. Figure 3 shows the benefit of preconditioning for a multi-zone simulation of an engine cycle with full kinetics. The comparison shows the simulation time for preconditioned and non-preconditioned multi-zone simulation of HCCI operation in the ORNL engine. For a 40-zone simulation with a 63 species chemical kinetic mechanism a factor of 250 reduction in simulation time is observed.

The multi-zone model has been shown to be predictive of transition from spark ignition to HCCI operation. Experiments at ORNL evaluated cycle-to-cycle stability by looking at fraction of heat release from a cycle relative to the previous cycle [2]. Transition is achieved by adjusting valve timing to trap increasing amounts of exhaust gas recirculation (EGR). Figure 4 shows the comparison between experiment and simulation for three different operating points: pure SI, SI-to-HCCI transition, and pure HCCI. Experiments and simulations results compare consecutive cycle heat release for hundreds of cycles. In pure SI (Figure 4, left column) and pure HCCI mode (Figure 4, right column) operation is very stable; little variation from cycle-to-cycle is observed. During transition (middle column) the experiment shows widely scattered cycle-to-cycle instability, and the simulation captures this unstable process.

Multi-zone modeling coupled with computational fluid dynamics has shown effective for prediction of non-homogeneous advanced combustion modes. Figure 5 shows simulation of NVO PCCI combustion compared with experiments from the Sandia National Laboratories automotive PCCI engine [3]. Injection occurs during the NVO period between exhaust valve closing and intake valve opening as well as during the main injection. The experimental engine has metal and optical surfaces, and the simulation includes surface temperature differences for the different materials. Comparison of pressure versus crank angle and pressure versus volume between experiment and simulation show very good agreement.

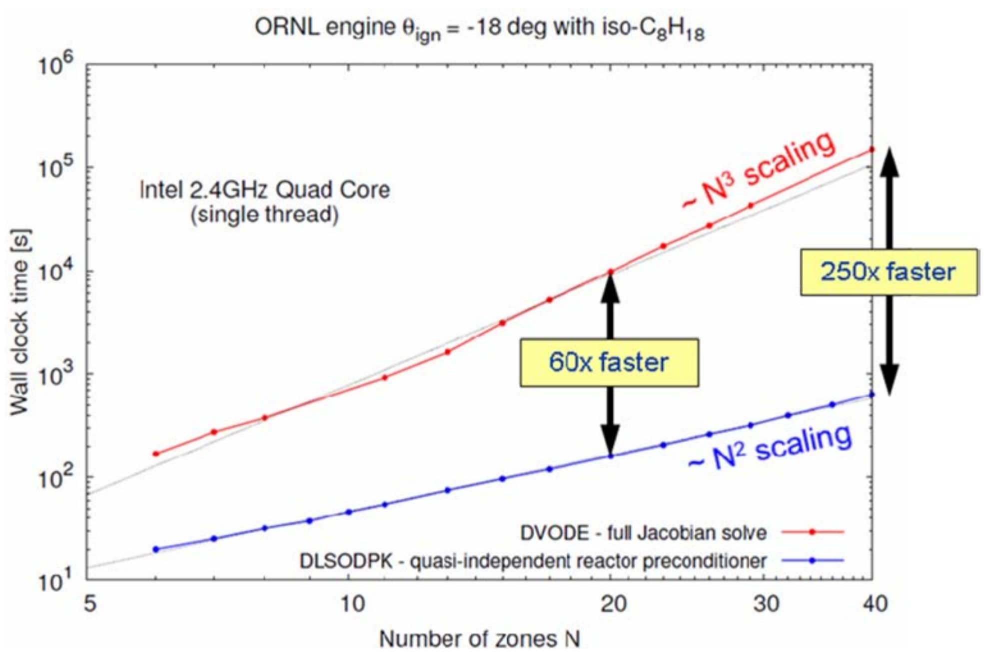
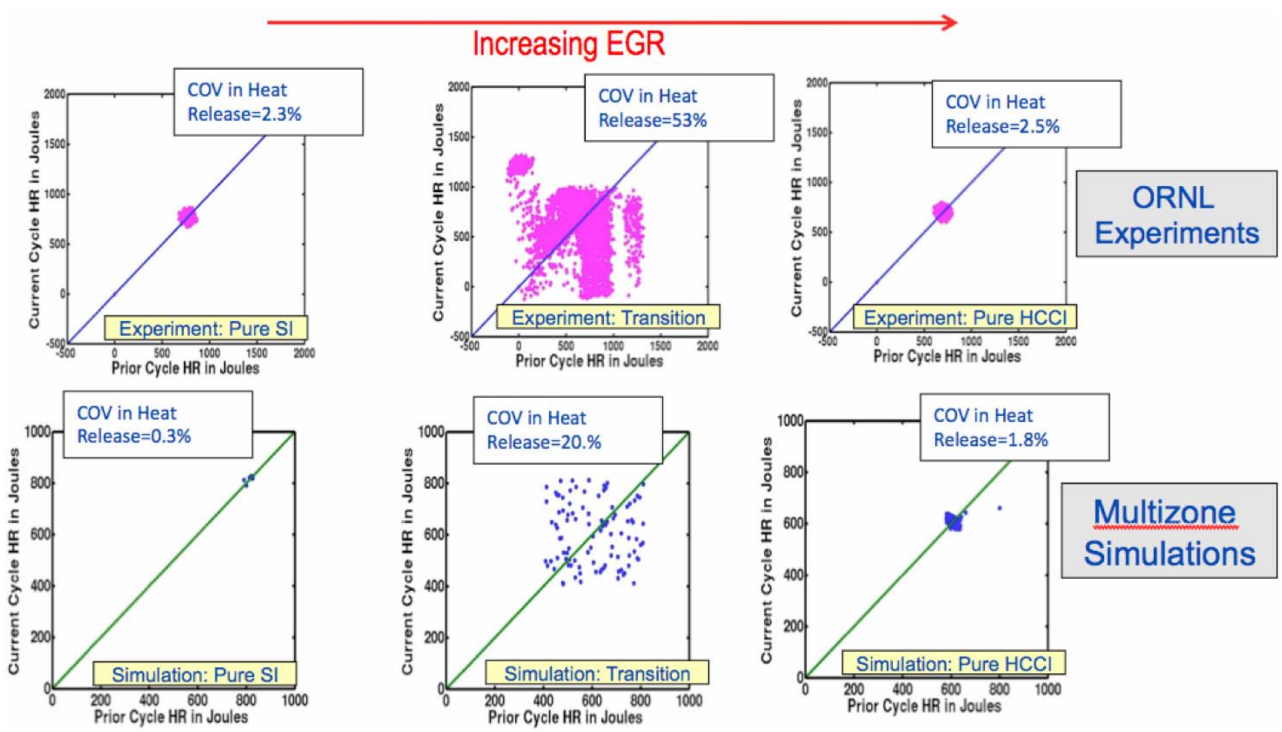


FIGURE 3. Comparison of simulation time for a multi-zone simulation of HCCI in ORNL experiments. The preconditioned system results in a factor of 250 speedup in the simulation relative to the standard solution method. DVODE – LLNL variable order differential equation solver DLSODPK – LLNL ordinary differential equation solver, with preconditioned Krylov iteration



COV - coefficient of variation

FIGURE 4. Top row shows ORNL experiments for transition from spark ignition to HCCI operation by increasing EGR, bottom row shows simulations. Each plot is a “return map” showing the fraction of heat release for one cycle relative to the previous cycle as a measure of cycle to cycle stability.

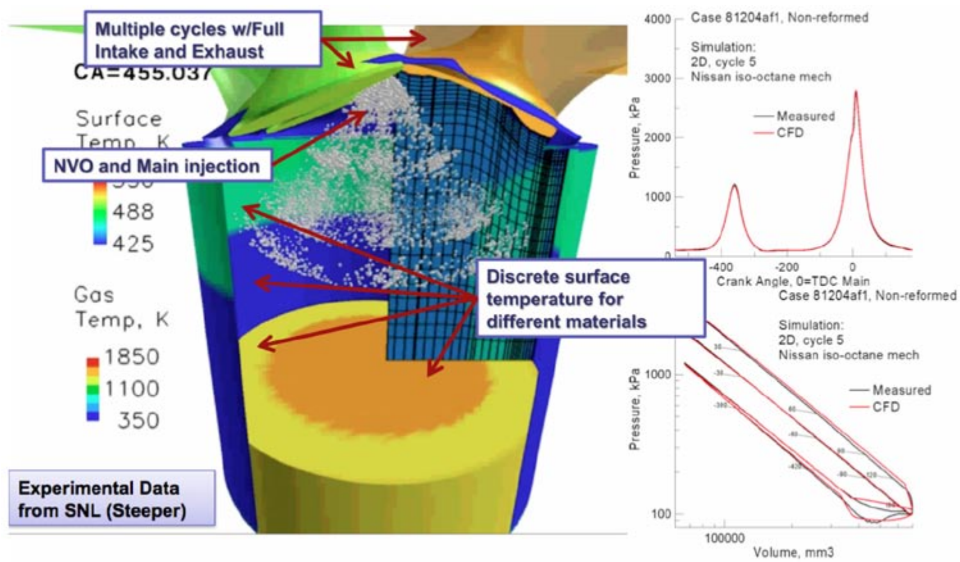


FIGURE 5. Simulation of NVO PCCI combustion compared to Sandia experiments.

Conclusions

- Our research and development project in advanced combustion simulation focuses on gaining fundamental understanding of engine combustion processes through high fidelity multi-dimensional simulations combining computational fluid mechanics and chemical kinetics.
- Chemical kinetics simulation is computationally expensive; we see opportunities for reducing simulation time and cost by a factor of 1,000 through innovative numerical solution approaches.
- Multi-zone chemical kinetics have been demonstrated to be a flexible and accurate tool for simulation of high-efficiency clean combustion modes such as HCCI and PCCI.
- Future work focuses on continuing to improve simulation fidelity through parallel computational fluid dynamics, improved physical models, and higher efficiency numerical methods.

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Special Recognitions & Awards/Patents Issued

1. Daniel Flowers gave invited talks at Lund University, Chalmers University, and Volvo Powertrain, all in Sweden, on advanced engine combustion modeling, June 2010.

2. Nick Killingsworth was invited to and sponsored by Tianjin University in China for a visiting postdoctoral research position, conducting advanced PCCI engine control research, August 2009 – November 2009.

3. Daniel Flowers served as external examiner for Ph.D. thesis on HCCI combustion at University of Cape Town, South Africa, May 2010.

4. Salvador Aceves served as an opponent at a Ph.D. exam at University of Castilla la Mancha, Spain, February 2010.

II.A.8 HCCI and Stratified-Charge CI Engine Combustion Research

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DOE Technology Development Manager:
Kellen Schefter

Objectives

Project Objective:

- Provide the fundamental understanding (science-base) required to overcome the technical barriers to the development of practical homogeneous charge compression ignition (HCCI) and HCCI-like engines by industry.

Fiscal Year (FY) 2010 Objectives:

- Determine the impact of hot residuals on thermal stratification (TS), and investigate the differences in TS between motored and fired operation.
- Initial investigation of the near-wall sources of TS and how it spreads into the bulk gas, using side-view imaging with a vertical laser sheet.
- Evaluate the potential of intake boost to extend the high-load limit of HCCI over a range of engine speeds, and determine how changes in engine speed affect thermal efficiency.
- Initiate a large eddy simulation (LES) modeling project with J. Oefelein (Sandia) to supplement TS-imaging experiments and help develop an improved understanding of the mechanisms producing the TS.
- Support chemical-kinetic, computational fluid dynamics (CFD), and other modeling of HCCI at Lawrence Livermore National Laboratory (LLNL), the University of Michigan, and General Motors.

Accomplishments

- Showed that hot residuals have almost no effect on TS in a low-residual HCCI engine.
- Determined the differences in TS between motored and fired operation:
  - Compared one- and two-line temperature-imaging diagnostics. Achieved images with a precision <5 K.
  - Showed the correlation between hot zones, initial combustion, and the crank angle (CA) for 10% of the fuel burned (CA10).
- Initiated a comparative investigation of TS in near-wall and bulk-gas regions, using a vertical laser sheet and side-view imaging technique developed for this study.
- Investigated the use of intake boost for extending the high-load limit of HCCI:
  - Determined the high-load limit over a range of engine speeds.
  - Determined why high CA50 retard (to prevent knock) is possible with boost.
  - Initiated an investigation of efficiency improvements for boosted HCCI, achieving about a 9% improvement in fuel economy for intake pressures from 2-2.8 bar.
- Collaborated with J. Oefelein et al. to establish an initial LES modeling capability for investigating the formation of TS.
- Expanded our investigation of ethanol-fueled HCCI, in collaboration with M. Sjöberg of the Alternative Fuels Direct-Injection Spark-Ignition (DISI) Engine Laboratory.
- Supported chemical-kinetic and CFD modeling work at LLNL, the University of Michigan, and General Motors by providing data and analysis.

Future Directions

- Complete the side-view imaging study of the evolution of TS from near-wall regions to the bulk-gas for a typical operating condition.
- Extend the side-view TS study to determine the effects of changes in coolant temperature, intake temperature, and engine speed on the development and distribution-pattern of TS.
- Expand the collaboration with J. Oefelein et al. to improve the LES-modeling grid for a better match with experimental data. Goal is to understand flows creating TS and how to enhance TS.
- High-efficiency, boosted HCCI: explore additional methods for increasing thermal efficiency and/or maximum load, including fuel effects, Miller cycle, and operating conditions.
- Continue collaborations with General Motors on HCCI modeling, and with LLNL on improving chemical-kinetic mechanisms and on CFD/kinetic modeling.

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Introduction

HCCI engines have significant efficiency and emissions advantages over conventional spark-ignition and diesel engines, respectively. However, several technical barriers must be addressed before it is practical to implement HCCI combustion in production engines. One of the most important barriers is extending HCCI operation to higher loads, and two areas of study during FY 2010 addressed this barrier. First, to improve our understanding of the causes and development of naturally occurring TS in an HCCI engine, two laser-sheet imaging studies were conducted, and an LES modeling effort was initiated. Understanding TS is important because it is critical for slowing HCCI combustion to allow high loads without knock. Second, our recent work has shown that intake-pressure boosting can extend HCCI operation to achieve loads close to those of turbo-charged diesel engines, and this work was extended during FY 2010 to determine the high-load limits of boosted HCCI over a range of engine speeds. Additionally, a detailed analysis was conducted to determine why a high degree of combustion-phasing retard, which is critical for controlling engine knock, is possible with boosted HCCI using gasoline fueling. Two other studies addressed further increases in the thermal efficiency of boosted HCCI and the potential of ethanol as an HCCI fuel.

Approach

These studies were conducted in our dual-engine HCCI laboratory using a combination of experiments in both the all-metal and optically-accessible HCCI research engines. This facility allows operation over a wide range of conditions, and it provides precise control of operating parameters such as combustion phasing, injection timing, intake temperature and pressure, and mass flow rates of supplied fuel and air. The facility also allows the use of cooled EGR. For the current studies, both engines were equipped with compression-ratio = 14 pistons. Additionally, the laboratory is equipped with a full emissions bench (hydrocarbons [HC], CO, CO_2, O_2, oxides of nitrogen [NO_X], and smoke).

The optically-accessible engine was used for the laser-imaging studies of the thermal stratification using two different optical configurations. First, using a horizontal laser sheet, the temperature and mixture distributions in the central bulk gas were imaged through the piston-crown window. This study was conducted in collaboration with Prof. R. Hanson and J. Snyder of Stanford University, who supplied two excimer lasers for two-line planar laser-induced fluorescence (PLIF) measurements. 3-Pentanone was selected as the fluorescent tracer for this work because it is insensitive to oxygen quenching, allowing measurements for both fired and motored operation. With appropriate in situ calibration, this two-line technique provides simultaneous temperature and mixture images to determine the extent of fresh-charge and residual mixing. Additionally, for well-mixed conditions, bulk-gas temperature maps (T-maps) that had precision uncertainties <5 K were obtained from a single-line analysis of the PLIF images and used to study the development of bulk-gas thermal stratification.

A second optical configuration was used to image the near-wall and bulk-gas portions of the charge simultaneously. For these experiments, the laser sheet was oriented vertically as it passed through windows in the upper part of the cylinder wall. Images were acquired from the side through a third cylinder-wall window. This technique provides a measurement of the thermal distribution across a representative cross section of the combustion chamber in a single image, including the bulk gas and the near-wall regions along the firedeck, piston top, and cylinder walls. Toluene was used as the tracer for these measurements because it allows background fluorescent noise (present with this optical configuration) to be removed with spectral filtering.

Studies of the effects of intake-pressure boost, methods of increasing efficiency, and operation with ethanol were conducted in the all-metal engine. The intake air was supplied by an air compressor and precisely metered by a sonic nozzle. To compensate for the pressure-induced enhancement of autoignition and to provide the required combustion-phasing retard, a combination of reduced intake temperature and cooled EGR was used. For most of these studies, the intake charge was fully premixed using an electrically-heated fuel vaporizer. Research-grade 87-octane gasoline was used for the intake-boost and efficiency studies.

Results

Naturally-occurring TS reduces the HCCI heat release rate (HRR), and therefore the propensity for engine knock, because it causes the charge to autoignite sequentially. Previous motored-engine measurements show that substantial TS arises from wall heat transfer and convection by in-cylinder flows; however, it is also possible for incomplete mixing between the fresh-charge gases and hot residuals to produce TS. To determine the importance of his second pathway, two-line PLIF imaging was applied in a fired engine to obtain simultaneous temperature and mixture-fraction images as discussed above.

Figure 1 shows a temporal sequence of these simultaneous images during the intake stroke with the laser sheet location selected to provide an image that is representative of the bulk gas (i.e. in the mid-plane of the charge, or 20 mm below the cylinder head for later crank angles). The two intake valves are located (in

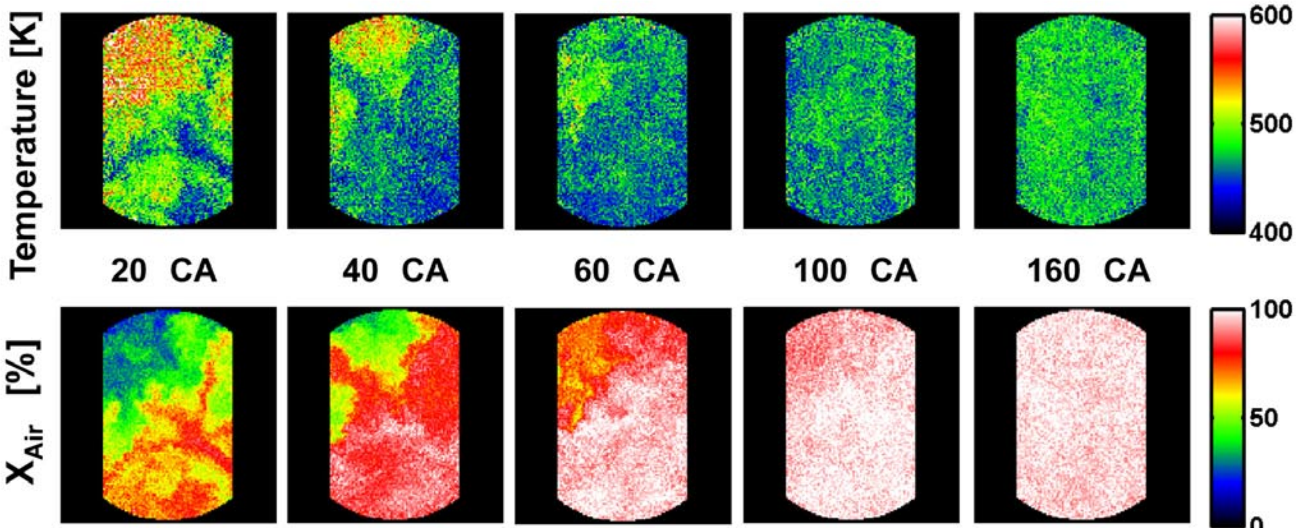

FIGURE 1. Temporal sequence of simultaneous temperature and mixture-fraction images at various times during the intake stroke.

the cylinder head above the image plane) at the bottom and right side of the image, and the exhaust valves are at the top and left. As can be seen in the figure, at 20°CA (0°CA = top dead center [TDC]-intake) a high concentration of air is evident on the intake-valve side of the image, and the corresponding T-map shows a lower temperature in this region. Temperatures are higher in the upper left where concentrations of residuals are higher. However, as the intake stroke progresses, the region of high air concentration and lower temperature extends progressively further across the charge, and by near the end of the intake stroke, 160°CA, the charge mixture is nearly uniform. Thus, these images indicate that incomplete mixing is unlikely to be an important contributor to the TS in HCCI engines operating with conventional valve timing. This finding is also supported by other T-map image data that shows the TS is virtually identical for cycles with cold or hot residuals (i.e. previous cycle motored or fired, respectively).

Thus, the main source of TS in the bulk gases is the convection of cooler near-wall gases into the central part of the charge. To better understand how this process occurs, a study has been initiated in which the laser sheet is oriented vertically and images are acquired from the side as is shown schematically at the top of Figure 2. This optical setup has the advantage of providing images showing both the bulk-gas and near-wall gases simultaneously, as discussed in the Approach section. However, this optical setup also creates several challenges for accurate conversion of the raw PLIF images into T-maps. Preliminary images have been acquired, and efforts are underway to acquire higher-quality PLIF images and to develop the algorithms required for a more accurate conversion to T-maps. The lower part of Figure 2 presents a sample of these preliminary images at a typical operating

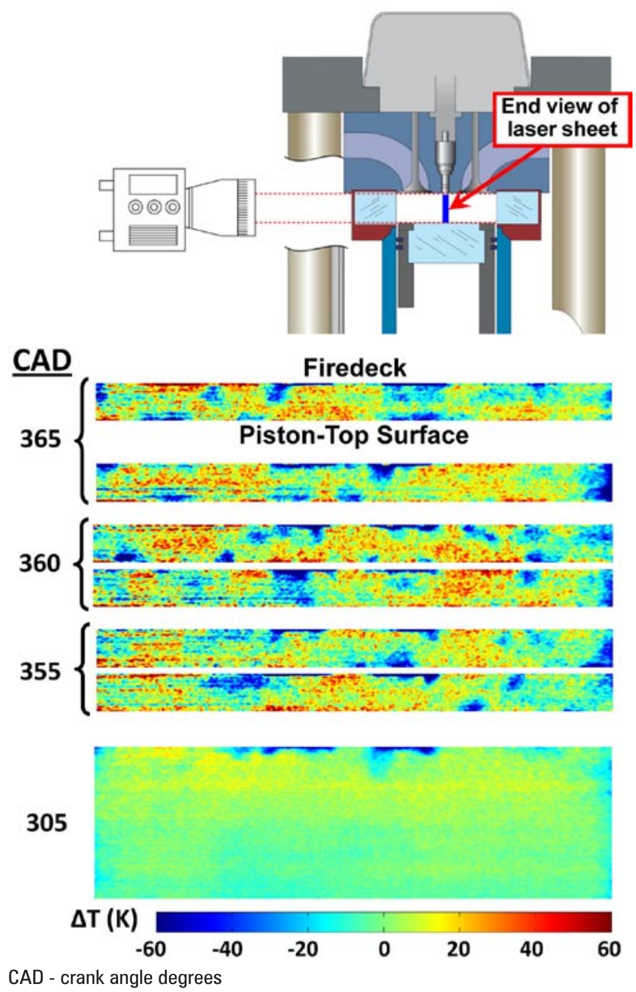

FIGURE 2. Optical setup for side-view imaging (top), and images of the temperature relative to the mean temperature of the image (ΔT) at various crank angles (bottom).

condition. These images show that at 305°CA (360°CA = TDC-compression), the bulk-gas temperature is nearly uniform, and cold pockets are only evident along the firedeck. Near TDC, however, significant TS has developed, and cold pockets occur throughout the bulk gas, even though they are still more prevalent near the walls. It is also noteworthy that the images near TDC still show large conterminous hot regions, indicating that it may be possible to increase the TS by altering the in-cylinder flows to produce more cold pockets, which has the potential for allowing higher loads without knock.

Our recent work has shown that HCCI engines can reach loads as high as 16.3 bar indicated mean effective pressure, gross ($IMEP_g$) without knocking and with ultra-low NO_X emissions at a typical 1,200 rpm operating condition, using conventional gasoline. To accomplish this, a combination of reduced intake temperature and cooled exhaust gas recirculation (EGR) was used to compensate for the pressure-induced enhancement of autoignition and to provide sufficient combustion-phasing retard to control knock [1]. During FY 2010 this work has been extended to determine how the high-load limit changes with engine speed at a representative boost level of 2 bar absolute. As with our previous boost work, the ringing intensity [2] was held ≤5 MW/m^2 so that there was no audible knocking or significant oscillations on the pressure trace. As shown in Figure 3, for this 2 bar intake pressure (P_{in}), the maximum load decreased moderately, from 12 to 10.7 bar $IMEP_g$, as engine speed was increased from 1,000 to 1,800 rpm. Stability remained very good with the coefficient of variation (COV) of the $IMEP_g$ being ≤2% for all data points shown, and NO_X emissions were ultra-low, more than a factor 10 below U.S.-2010 limits. Interestingly, the thermal efficiency for these maximum-load points increased from 43.3% to 45.7% with increasing speed as shown in the bottom plot of Figure 3. This efficiency increase results mainly from the decreasing amount of EGR required to maintain combustion phasing as engine speed increases.

Achieving these high loads under boosted conditions with a ringing intensity ≤5 MW/m^2 and a low COV of $IMEP_g$ requires that combustion phasing (CA50) be retarded as late as 379°CA (19° after TDC) with good stability. To understand why this was possible for boosted operation with gasoline fueling, a further investigation was undertaken. As described in an earlier work [3], the stability of HCCI combustion depends on the rate of temperature rise prior to the hot ignition point. For retarded combustion, this temperature-rise rate is controlled by the magnitude of the early combustion reactions (intermediate temperature heat release, ITHR [4]) and the rate of expansion cooling due to piston motion. Figure 4a shows the mass-averaged in-cylinder temperature for the highest loads achieved for a range of intake pressures. As can be seen, the temperature-rise rate, prior to the knee in the curves that indicates hot ignition, increases with increasing boost pressure, despite a general trend of more combustion-phasing retard. To understand the reason for this, a detailed analysis of the HRR was

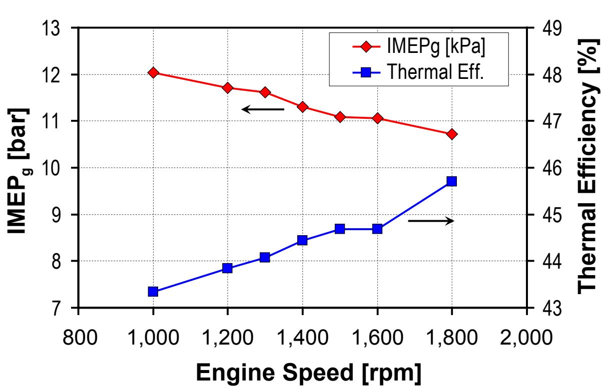

FIGURE 3. The high-load limit for HCCI with P_{in} = 2 bar as a function of engine speed, and the corresponding indicated thermal efficiencies.

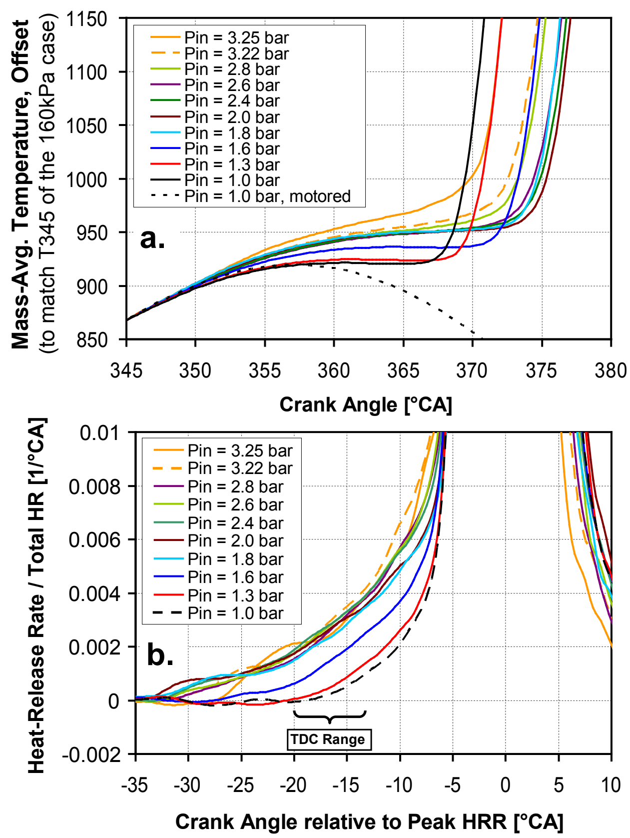

FIGURE 4. Bulk-gas temperatures (a) and normalized HRR (b) for the maximum-load points with boosted HCCI. P_{in} varies from 1.0 to 3.25 bar as noted in the legend. Note that both plots are presented with an amplified scale to show the effect of the early ITHR, which occurs from about 30° to 6° before the peak HRR.

conducted. The key results, plotted in Figure 4b, show a strong trend of an increasing amount of ITHR with boost up to P_{in} = 1.8 bar. This increased ITHR with boost for conventional gasoline, provides good stability with retarded CA50. A full discussion may be found in reference [5]. This behavior with conventional gasoline contrasts sharply with the behavior of ethanol, which our recent studies have shown, has no enhancement in ITHR with boost and therefore, a more limited maximum load [6]. Several other studies of the performance of ethanol as an HCCI fuel were also conducted, as reported in references [6,7].

HCCI engines inherently have high thermal efficiencies, and intake boosting further improves the efficiency. However, even greater efficiencies are desirable to achieve DOE's long-range goals, and for commensurate reductions in fuel consumption and greenhouse gas emissions. Accordingly, an initial investigation was conducted to assess the potential of several methods for improving the thermal efficiency compared to the high-load data points published in reference [5]. The connected data points forming the curve in the bottom part of Figure 5 show thermal efficiencies for the highest loads attained at each intake pressure (P_{in} = 1 to 3.25 bar), from reference [5], plotted against the load ($IMEP_g$). As can be seen, these thermal efficiencies typically range from 43 to 44%. For P_{in} = 2, 2.4, and 2.8 bar, the load was moderately reduced from the maximum value to allow implementation of various adjustments to the operating parameters. The data points at the top of the plot show that for all three intake pressures, efficiencies from 47 to 48% could be attained with only a modest reduction in $IMEP_g$ of about 10 to 15% below the corresponding high-load value.

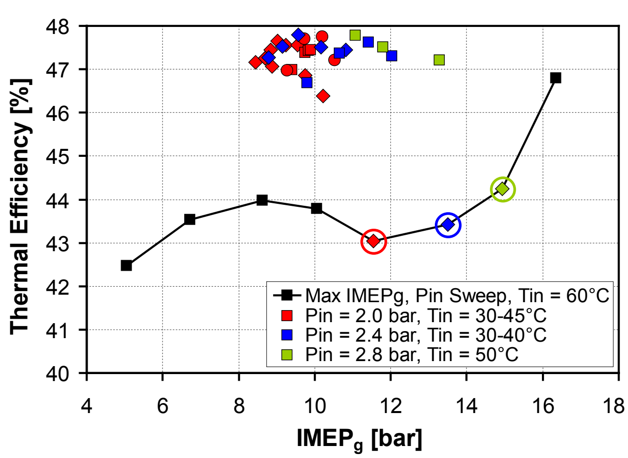

FIGURE 5. Indicated thermal efficiencies for intake-boosted HCCI as a function of load ($IMEP_g$). The points on the curve at the bottom of the plot correspond to the maximum-load points for each P_{in} (the same conditions as for Figure 4). The points near the top of the plot show the high-efficiency results, with the color of the points indicating the intake pressure as indicated in the legend.

This improvement in thermal efficiency would yield a reduction in the indicated specific fuel consumption on the order of 9%. In general, efficiency was found to improve with less EGR, less timing retard, reduced intake temperature, and a lower fuel/charge mass ratio. Based on these findings, further efficiency gains should be possible with a less reactive fuel, which would require less EGR with boosted operation, or with a Miller cycle, which limits the compression heating while still providing a large expansion ratio for good work extraction.

Conclusions

This work produced significant results toward three Advanced Combustion Technologies goals: 1) developing an improved understanding of in-cylinder processes, 2) obtaining high loads with a low-temperature combustion process that has ultra-low NO_X and particulate emissions, and 3) increased thermal efficiency.

- Simultaneous temperature and mixture-fraction images show that mixing between the fresh charge and hot residuals is essentially complete by the end of the intake stroke. Therefore, incomplete mixing is unlikely to be an important contributor to TS in HCCI engines with conventional valve timing (i.e. no enhancement of retained residuals).
- Temperature images show that the development of TS in a fired engine is nearly identical to that of a motored engine, up to onset of ignition:
  - This finding, combined with the mixture-fraction imaging results, shows that the production of TS is dominated by wall heat transfer and convection of cooler near-wall gases into the central part of the charge.
- Simultaneous images of the near-wall and bulk-gas regions, acquired using a newly developed side-view imaging technique, provide insight into the development of TS:
  - By TDC, TS has spread from the near-wall regions into the bulk gas, but it remains more prevalent near the walls.
  - The large size of many hot regions near TDC indicates that significantly more TS is possible, offering a potential method for achieving higher loads without knock.
- Intake-pressure boost enhances the early ITHR of gasoline allowing substantial combustion-phasing retard with good stability. Taking advantage of this mechanism allows boosted HCCI to reach high loads without engine knock.
- Intake boosting is effective for achieving high-load HCCI across a range of engine speeds (demonstrated for 1,000-1,800 rpm).

- An increase in the thermal efficiency of boosted HCCI from 43-44% to 47-48% has been demonstrated for loads in the range of 8 to 13 bar $IMEP_g$. This translates into a decrease in fuel consumption of about 9%.
- For ethanol fueling, the ITHR is not enhanced with intake boost, limiting the allowable CA50 retard compared to gasoline. This limits the maximum load that can be achieved without knocking for boosted operation. However, when ethanol is blended in small amounts with gasoline, this effect may be beneficial for reducing the EGR required with boost, which could result in higher efficiencies.

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10. Dec, J.E., "HCCI Combustion for High Efficiency with low NO_X and PM," SAE International Congress, panel on High Efficiency IC Engines, April 2010.

11. Sjöberg, M, and Dec, J.E., "Effects of EGR and Its Constituents on HCCI Autoignition of Ethanol," 33rd International Symposium on Combustion, Beijing, China, August 2010, accepted for *Proceedings of the CI*.

12. Sjöberg, M. and Dec, J.E., "Smoothing HCCI Heat Release with Vaporization-Cooling-Induced Thermal Stratification using Ethanol," DOE Advanced Engine Combustion Working Group Meeting, August 2010.

Awards & Special Recognition

1. SAE Excellence in Oral Presentation Award for paper 2010-01-1086, April 2010

2. Invited Panelist & Speaker, SAE International Congress, panel on High Efficiency IC Engines, April 2010.

3. ASME 2010 Internal Combustion Engine Award, September 2010

II.A.9 Automotive HCCI Combustion Research

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Objectives

This project comprises optical-engine investigations designed to enhance our understanding of in-cylinder processes in automotive-scale homogeneous charge compression ignition (HCCI) engines. Our objectives include:

- Ongoing engine experiments characterizing the negative valve overlap (NVO) strategy used to control and extend HCCI combustion.
- Development of laser-based diagnostics, and testing of the diagnostics in Sandia HCCI research engines.
- Development and application of collaborative engine simulation and analysis tools for automotive HCCI combustion strategies.

Fiscal Year (FY) 2010 Accomplishments

- Performed experiments to test for ignition-enhancement effects of NVO reformed products via single-species seeding experiments.
- Achieved order-of-magnitude improvement of tunable diode laser (TDL) carbon monoxide (CO) diagnostic by switching to 2,319-nm excitation and implementing wavelength modulation signal processing.
- Applied the TDL diagnostic to measure CO time-resolved concentrations during fired NVO engine operation.
- Advanced the capabilities of our collaborative computational fluid dynamics (CFD) engine model to include simulation of fired NVO engine operation.

Future Directions

- Apply TDL absorption and laser-induced fluorescence (LIF) optical diagnostics to characterize reforming reactions during the NVO period.
- Apply optical diagnostics to quantify piston wetting during NVO fuel injection to understand its effect on NVO- and main-combustion reactions.
- Continue validation of the CFD model of our optical engine using optical and conventional measurements over a range of NVO operating conditions.
- Expand our tunable-diode-laser absorption diagnostic to permit in-cylinder measurement of other species such as H_2O, CO_2, and C_2H_2.

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Introduction

Major challenges to the implementation of HCCI combustion–including phasing control, operating-range extension, and emissions control–require advanced charge-preparation strategies. Alternative strategies such as retarded injection and variable valve timing can be used to modify local charge composition and temperatures, thereby controlling ignition phasing, rate of heat release, combustion efficiency, and engine-out emissions. A current focus of our research is understanding the NVO strategy for automotive HCCI combustion. Partial fueling during the NVO period can affect main combustion both thermally (NVO reactions elevate residual gas temperature) and chemically (NVO reformation reactions produce species that persist until main combustion), and understanding these effects is necessary in order to take full advantage of the strategy. Knowledge gained in this project supports DOE's goal of facilitating the development of energy-efficient, low-emission engine combustion.

Approach

A variety of optical and traditional diagnostics provide details of HCCI in-cylinder processes. In-cylinder spray imaging allows assessment of spray evolution, penetration, and wall-wetting; LIF imaging produces instantaneous composition and temperature distribution maps; laser-absorption produces crank-angle-resolved bulk concentration data; chemiluminescence imaging provides details of ignition and combustion; and engine-out emission measurements quantify combustion performance and calibrate in-cylinder diagnostics. Development of new diagnostics is enhanced through continuing interactions with partners such as Stanford University. Similarly, development of advanced CFD/chemical kinetics models is supported through collaboration with University of Wisconsin (UW) and Lawrence Livermore National Laboratory (LLNL). Regularly scheduled technical exchanges with engine and vehicle manufacturers, national labs, and academia provide feedback and guidance for the research project.

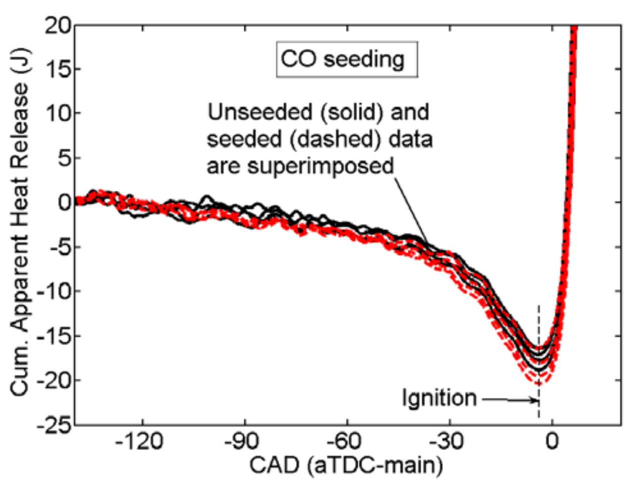
Results

Thermal and Chemical Effects of NVO Fueling

Last year we documented NVO split-fueling conditions (specifically, *late* NVO injection of about 15% of the total iso-octane injected) that produced previously unobserved heat release prior to the start of main combustion. We speculated that this was evidence of reactive species carrying over from NVO fuel reformation and chemically affecting main ignition. To further investigate these chemical effects, this year we began experiments to test candidate species by seeding them singly into intake air while operating the engine at conditions that, absent the seeding, do not produce any observable chemical effects.

An obvious candidate species selected for the seeding experiments is CO since it is a likely abundant product of NVO reactions. Firing the engine with iso-octane at low load (170 kPA) and 50% residual gas fraction, we compared apparent heat release with and without 5,500-ppm CO seeded of the intake stream (becoming 2,750 ppm after mixing with residual gas). Based on CHEMKIN simulations, this level of CO mimics the in-cylinder concentration expected during our typical NVO fueling operation. As shown in Figure 1, heat release prior to main ignition for the seeded and unseeded cases is indistinguishable – we see no evidence of chemical reactions prior to ignition, and no effect on ignition phasing. Thus the experimental results rule out CO as responsible for the chemical effects observed earlier.

A second candidate species selected for the experiments was acetylene (C_2H_2). Since the chemical effects observed previously occurred only for late NVO injection (which causes piston wetting), we reasoned that rich combustion was likely, and C_2H_2, a known ignition promoter, might be produced in these cases. Results of these experiments were positive. As seen in Figure 2, starting at around -60 crank angle degrees (CAD) the seeded curves deviate upward from the unseeded curve. Since there is no reason for a difference in heat loss, the positive deviation is attributed to exothermic reactions. This pattern of pre-ignition heat release is very similar to that observed previously for late NVO fueling, supporting the hypothesis that late NVO injections create a locally rich combustion regime, producing C_2H_2 that survives through the intake stroke and reacts just prior to main ignition.



aTDC - after top dead center

FIGURE 1. Comparison of low-load HCCI-NVO operation with and without CO seeding (several cases of each). Cumulative apparent heat release is shown for the compression stroke, from intake valve closing to start of main combustion. CO is seeded into the intake air at a concentration of 5,500 ppm. The main fuel is iso-octane, injected at the beginning of the intake stroke.

Laser-Absorption CO Diagnostic

As a means of further quantifying effects of NVO fueling, we continued our development of a laser-absorption diagnostic for in-cylinder CO detection. As illustrated in Figure 3, the diagnostic uses a tunable diode laser, a multipass geometry, and a fast infrared detector to provide spatially averaged, time-resolved measurements of CO in the engine. This year we upgraded the TDL from the second-overtone CO absorption band (1560 nm) to the first overtone (2,319 nm) to achieve an order-of-magnitude increase in sensitivity. In addition, we implemented wavelength-modulation signal processing as a means of further improving the signal-to-noise ratio. The wavelength-modulation technique adopted makes use of the rapid tuning capability of the TDL to dither the laser wavelength around the CO absorption line. The resulting beam is launched through the cylinder and the detected output is demodulated at twice the dither

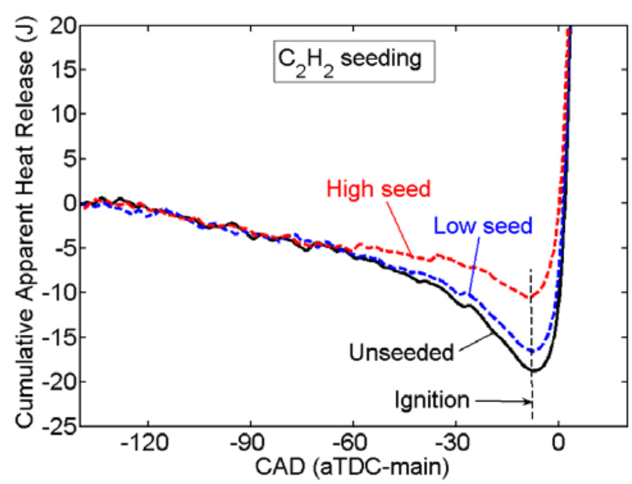


FIGURE 2. Comparison of low-load HCCI-NVO operation with and without C_2H_2 seeding. C_2H_2 is seeded into the intake air at two concentrations: 1,750 (low) and 4,000 ppm (high).

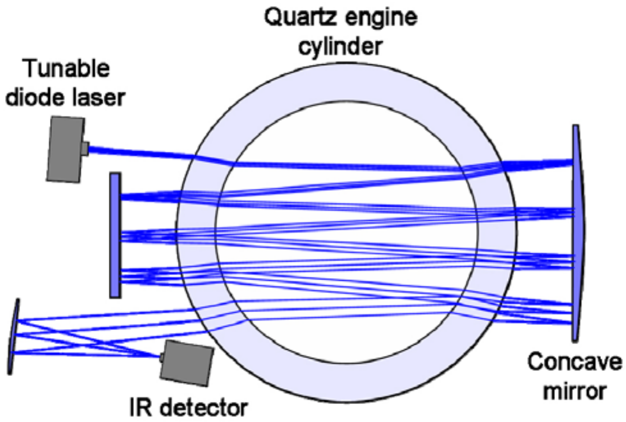
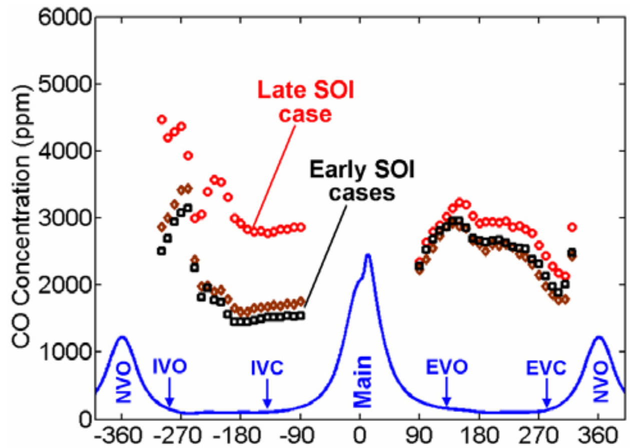


FIGURE 3. Schematic of the TDL absorption diagnostic as implemented in the optical engine.



IVO/IVC/EVO/EVC - intake/exhaust valve opening/closing

FIGURE 4. TDL measurements of CO concentration (discrete data points) during fired operation with split injection. A typical fired pressure trace (solid line) is superimposed to orient the data with respect to events of the HCCI-NVO cycle. Main injection of 8 mg of iso-octane is at -270 CAD; NVO injection of 1.3 mg is at 280 and 330 CAD (early) and 350 CAD (late).

frequency to yield a low-noise signal peak whose height varies with CO concentration.

The diagnostic was used this year for both motored calibration runs and fired data collection. Seeding CO into the intake air during motored operation allowed us to calibrate and validate the instrument over a range of CO concentrations. The motored TDL data agree within a few hundred ppm of two independent measurements (intake flow measurements and exhaust emission measurements). To test the diagnostic during fired operation, we performed an NVO injection-timing sweep similar to our prior experiments that revealed the chemical effects of NVO fueling.

Figure 4 plots TDL data for a range of NVO start-of-injection (SOI) timings. In this figure, each CO data point represents a 10-CAD temporal average, and the obvious gaps in the data are due to the piston obscuring the selected measurement plane and due to tuning of the diagnostic for lower pressure portions of the cycle. The data marked *early SOI cases* are typical of cases with NVO injections between 280 and 330 CAD: all such cases show similar CO concentration histories throughout the cycle. Production of CO during NVO and again during main combustion can be seen as rapidly rising concentrations starting at -300 CAD and again at +90 CAD. Following mixing, we find relatively stable values of CO concentration around intake valve closing (IVC), and again around the bottom of the exhaust stroke (180 CAD). Interestingly, the *late SOI case* plotted in Figure 4 follows the same trends, but shows a dramatic increase in CO levels. The TDL measurements thus corroborate our earlier observations that late NVO fueling represents a unique operating regime.

CFD Model of the Optical Engine

CFD modeling of our automotive HCCI engine progressed this year in collaboration with LLNL and UW. This year we began validation of the model under fired conditions, again selecting the same NVO injection-timing sweep discussed above. The CFD simulations provided an opportunity to consider the details of reformation and combustion during the NVO period. To demonstrate, Figures 5 and 6 compare the apparent NVO heat release obtained from experiments and CFD, respectively. Three split-injection cases with NVO injection timings of 280, 330, and 345 CAD aTDC-main are presented, along with a main-fuel-only case (i.e., no NVO fueling) for reference.

Comparing the CFD predictions in Figure 6 with the experimental results of Figure 5 we see that the model successful predicts the phasing and magnitude of NVO heat release. Peak values are truncated somewhat relative to the experiment, but extended durations help achieve comparable values of total heat release. This good agreement builds confidence that the model's prediction of NVO reactions can provide useful details for understanding the effects of NVO fueling on main-combustion phasing.

Conclusions

- Seeding experiments suggest that acetylene is a possible contributor to late NVO injection effects on main combustion phasing.

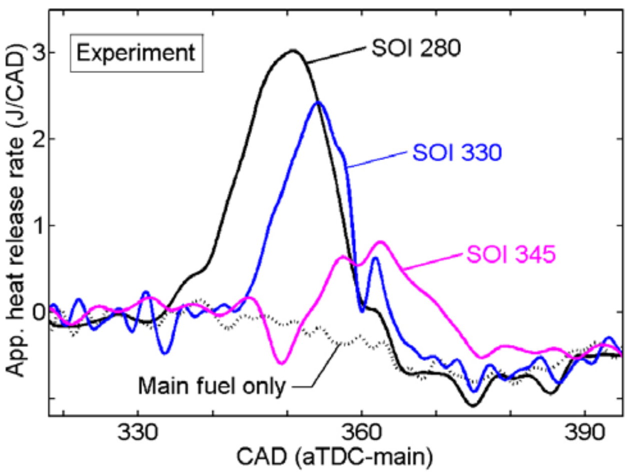


FIGURE 5. Apparent heat release rate during the NVO period derived from experimental data. SOI labels represent the start of NVO injection in CAD aTDC-main. Split-injection operating conditions are similar to those of Figure 4, with about 15% of total fuel injected during NVO.

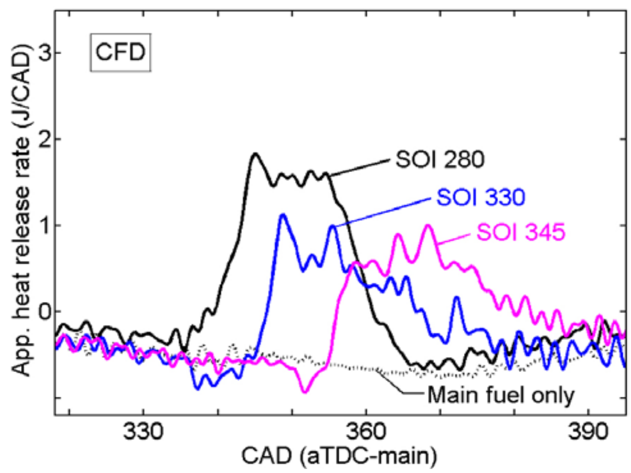


FIGURE 6. Apparent heat release rate during the NVO period from CFD simulations. Conditions are the same as for Figure 5.

- The TDL absorption diagnostic provides in-cylinder CO measurements useful for understanding the effects of the NVO fueling strategy.
- The TDL CO data, along with other in-cylinder measurements, will serve to validate the CFD model, providing an accurate predictive tool for HCCI engines.

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2. Rothamer, D.A., Snyder, J.A., Hanson, R.K., Steeper, R.R., and Fitzgerald, R.P., "Simultaneous Imaging of Exhaust Gas Residuals and Temperature During HCCI Combustion," Proceedings of the Combustion Institute **32**(2):2869-2876, 2009, doi: 10.1016/j.proci.2008.07.018.

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10. Fitzgerald, R.P., "Thermal and Chemical Effects of NVO Fuel Injection on HCCI Combustion," SAE World Congress, Apr. 12, 2010.

11. Steeper, R.R., "Automotive HCCI Engine Research," DOE Vehicle Technologies Annual Merit Review, Washington, D.C., June 8, 2010.

12. Steeper, R. R., "Laser Absorption Measurements of CO in the Automotive HCCI Optical Engine," DOE Advanced Engine Combustion Working Group Meeting, USCAR, Aug. 31, 2010.

Special Recognitions & Awards

1. Appointed Co-Chair of SAE Powertrain, Fuels, and Lubes Activity.

II.A.10 Achieving and Demonstrating Vehicle Technologies Engine Fuel Efficiency Milestones

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Kellen Schefter

Objectives

- Demonstrate Fiscal Year (FY) 2010 DOE Vehicle Technologies milestone of 45% peak brake thermal efficiency (BTE) on a light-duty diesel engine.
- Characterize the efficiency potential of an organic Rankine cycle for converting exhaust thermal energy to electrical power.
- Exercise an organic Rankine cycle (ORC) model within GT-POWER to better understand potential and issues across a simulated light-duty drive cycle.

FY 2010 Accomplishments

- Demonstrated a peak BTE of 45.0% on a light-duty diesel engine through a combination of shaft power and electrical power generated from the exhaust heat of the engine.
- Through GT-POWER simulations, demonstrated an average power recovery of 300-400 W from an ORC over a simulated drive cycle. This corresponds to a 5% improvement in vehicle fuel economy.

Future Directions

- Assess efficiency benefits of partially premixed charge compression ignition combustion in a light-duty engine.
- Evaluate the potential performance and efficiency benefit of a combined supercharger/turbocharger on a light-duty diesel engine.
- Analyze the comparative efficiency of multiple clean combustion approaches, including second-law analysis to identify loss mechanisms.

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Introduction

Modern light-duty diesel engines have peak BTEs in the range 40-42% for high-load operation and lower efficiencies for part-load operation. The FreedomCAR roadmap established efficiency and emissions goals through 2010, with a final peak efficiency target of 45%, while meeting Tier 2 Bin 5 emissions levels. The objective of this project is not to develop all the necessary technology to meet the efficiency and emissions goals but to serve as a focus for the integration of technologies into a multi-cylinder engine platform and to provide a means of identifying pathways for improved engine efficiency.

Approach

This activity makes use of knowledge discovery from internal ORNL activities, other national laboratories, universities, and industry. Internal activities include those focused on advanced combustion operation, aftertreatment, fuels, and unconventional approaches to improve combustion efficiency. This activity also makes use of technical contributions from external sources through regular interactions with the Advanced Engine Combustion working group administered by Sandia National Laboratories, the Cross-Cut Lean Exhaust Emissions Reductions Simulations working group administered by ORNL, and one-on-one interactions with industry teams such as Cummins Engine, Caterpillar, BorgWarner, VanDyne SuperTurbo, etc.

Substantial improvements in engine efficiency will require a reduction in loss mechanisms associated with the combustion process. With less than half of fuel energy converted to useful work in a modern engine, opportunity exists for significant advancements in engine efficiency. A fundamental thermodynamics perspective in combination with simulations and laboratory experiments has been used toward this purpose to provide guidance on developing and evaluating a path for meeting the 2010 milestone as well as longer term insight into the potential of future high efficiency engine systems.

The following methodology is and has been used in this activity:

1. Characterize current state-of-the-art light-duty engine development. Note that this is a moving target as more advanced engines enter the marketplace.

2. Improve fundamental understanding of internal combustion engine efficiency losses and opportunities.
3. Identify and evaluate promising strategies to recover and/or reduce thermodynamic losses to the environment through engine-system simulations and experiments.
4. Perform proof-of-principle demonstrations of selected concepts.

Technologies for improving efficiency and emissions in light-duty engines are being evaluated at ORNL on a General Motors (GM) 1.9-L common rail four-cylinder diesel engine. Earlier experiments were performed on a Mercedes-Benz (MB) 1.7-L common rail four-cylinder diesel engine. The engine platform was upgraded to reflect a change in the state of the art in the marketplace. The GM engine is equipped with a microprocessor-based dSpace control system that permits unconstrained access to engine hardware including the integration of custom control algorithms. This engine also has an engine control unit donated by GM that allows for the monitoring and manipulation of the base engine calibration.

Results

A peak BTE of 45% has been demonstrated on a light-duty diesel engine through a combination of engine shaft power and electrical power generated from the exhaust heat of the engine with an ORC. This accomplishment is the final Vehicle Technologies milestone on the path to 45% peak BTE and Tier 2 Bin 5 emissions. Advanced engine technologies identified and investigated in FY 2010 included thermal energy recovery, advanced lubricants, and fuel properties. In addition, a flexible microprocessor-based control system was used for the re-optimization of engine parameters to make better use of these technologies. Peak BTE milestones and demonstration status are shown in Figure 1 for the past several years.

An ORC was developed and evaluated for the on-engine recovery of thermal exhaust energy. The system is a recuperated Rankine cycle with a three-stage boiler including a preheater, evaporator, and superheater as shown in the schematic in Figure 2. The system was designed to minimize refrigerant and exhaust restrictions to achieve maximum efficiency and minimum engine backpressure. Industrial grade components were used whenever possible as packaging was not a design consideration since the system is only intended for laboratory evaluation. The most critical component to the ORC is the expander. After substantial research and discussions with suppliers and engine companies, an integrated turbine/generator system was chosen for the expander. The expander was developed by Barber-Nichols for use with R245fa working fluid and thermal

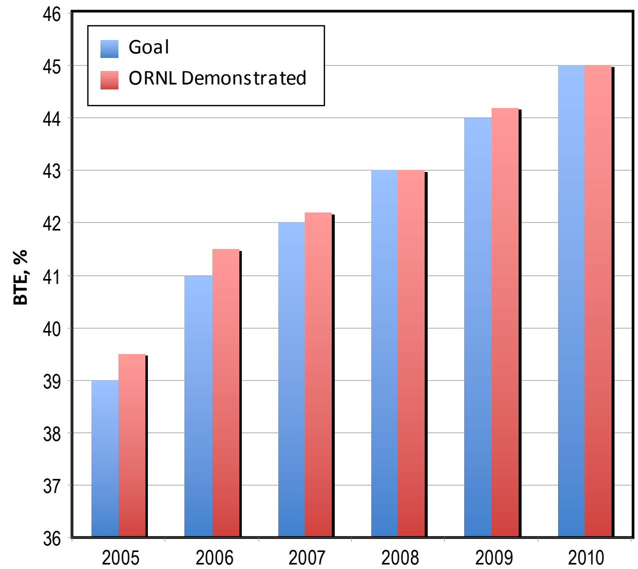

FIGURE 1. Path to Demonstrating FY 2010 FreedomCAR Engine and Efficiency Milestones

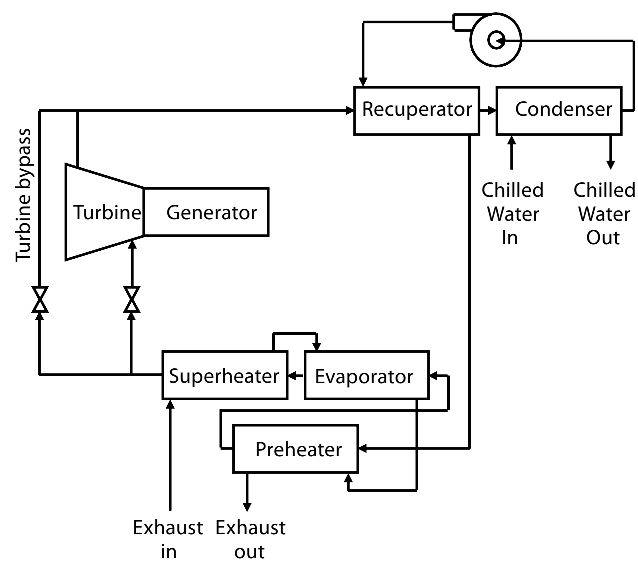

FIGURE 2. Schematic of Recuperated ORC

conditions consistent with the GM 1.9-L peak efficiency point of 2,250 rpm, 18 bar brake mean effective pressure (BMEP). The working fluid was selected based on thermal performance but there are no substantial environmental concerns associated with this fluid. The ORC system is shown in Figure 3.

The ORC system was evaluated on-engine at the engine peak efficiency condition of 2,250 rpm and 18 bar BMEP. At this condition the system was able to generate 3.9 kW of net electrical power from the exhaust heat, which corresponds to a 13% ORC efficiency. The 3.9 kW of net electrical power combined with the 66 kW

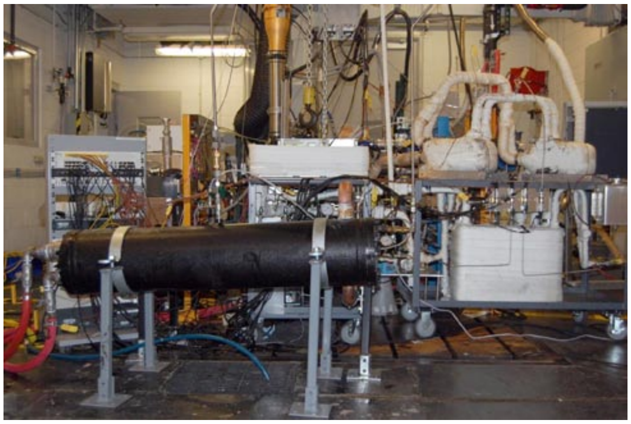

FIGURE 3. ORC and Integrated Turbine/Generator Expander Installed in the Test Cell

engine output (at an engine efficiency of 42.4%) yields a combined BTE of 45.0%. Combined power from the engine shaft and ORC are shown in Figure 4.

A model of the ORC was developed using the GT-SUITE engine simulation codes in order to evaluate part-load and transient performance of the ORC when coupled to the GM 1.9-L engine. The model indicated that the ORC could generate 0.4 kW of net electrical power while the engine was running at 1,500 rpm, 2 bar BMEP, which is a typical road-load operating condition. This electrical output corresponds to an increase in BTE of 2.1% at this condition, from 24.4% to 26.5%. An energy balance of the engine and ORC at this operating point is shown in Figure 5.

The ORC model was also used to investigate the transient performance of a coupled engine and ORC system. The model indicated that the ORC would generate 0.2 kW of net electrical power on average over a warm Urban Dynamometer Driving Schedule test. This has been estimated to be equivalent to a 5% increase in tank mileage over the drive cycle.

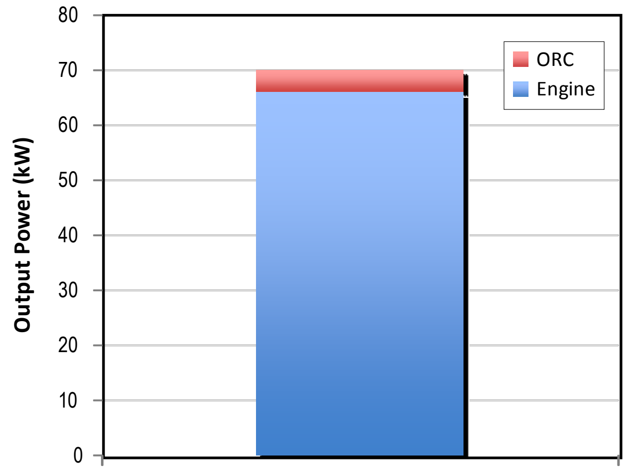

FIGURE 4. Combined Power Output of the Engine and ORC at 2,250 RPM and 18 bar BMEP

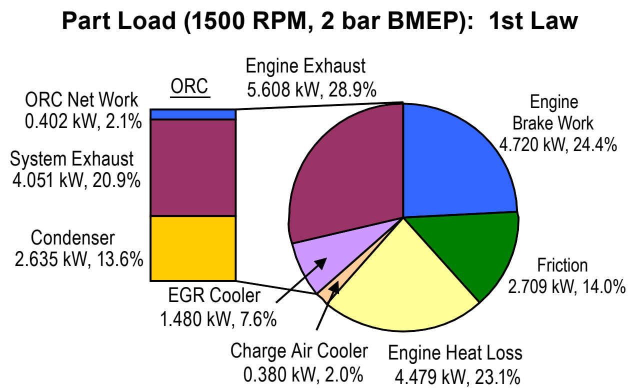

FIGURE 5. First Law Energy Balance of the Engine and ORC at 1,500 RPM and 2 bar BMEP

Conclusions

This activity has demonstrated the development, implementation, and demonstration of technologies for meeting Vehicle Technologies engine and efficiency milestones. Specific accomplishments are as follows:

- Demonstration of FY 2010 FreedomCAR milestone of 45% peak BTE on a light-duty diesel engine.
- Development and evaluation of an ORC through simulation and experiments on-engine.
- Thermal energy recovery being investigated on-engine and with realistic transient models using GT-SUITE.
- New insight into the thermodynamic availability of engine systems across the speed/load operational range of a light-duty diesel engine and estimated potential fuel economy improvements over the Federal Test Procedure drive cycle.

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3. R.M. Wagner, T.E. Briggs, K.D. Edwards, S.J. Curran, E.J. Nafziger, K. Cho, "Achieving and Demonstrating Vehicle Technologies Engine Fuel Efficiency Milestones", 2010 DOE Hydrogen and Vehicle Technologies Merit Review (Washington, D.C.; June 2010).

II.A.11 KIVA Development

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- Dr. Darrell W. Pepper, University of Nevada, Las Vegas, Las Vegas, NV

Objectives

- Continue developing code and algorithms for the advancement of speed, accuracy, robustness, and range of applicability of the KIVA combustion modeling software to higher-order spatial accuracy with a minimal computational effort. Plan and research for changes to underlying discretization to utilize an *hp*-adaptive characteristic-based split (CBS) or Petrov-Galerkin (P-G) finite element method (FEM).
- Extend KIVA-4 capability to predict heat transfer to and from the combustion chamber via conjugate heat transfer modeling. This for more accurate prediction in wall film and its effects on combustion and emissions.
- Ready the KIVA-4 parallel version for release. To supply the engine modeling community an efficient internal combustion engine solver.

Fiscal Year (FY) 2010 Accomplishments

- Developed *hp*-adaptive CBS and P-G finite element methods for all for flow regimes, from incompressible to high-speed compressible.
- Developed and verified the *hp*-adaptive FEM Framework that uses hierarchical basis.
- KIVA-4 capability has been extended to predict heat conduction and heat flux.
- KIVA-4 parallel version for release. Full version release after more testing and feedback.

Future Directions

- Continue developing the *hp*-adaptive FEM for multispecies flows in all flow regimes. Begin implementing this method to perform modeling of internal combustion engines, other engines, and general combustion. Develop comprehensive comparative results to benchmark problems and to commercial software as part of the verification and validation of the algorithms.
- Continue developing the Conjugate Heat Transfer Model, adding this model to the parallel version, KIVA-4mpi (message-passing interface).
- Develop overset grid method for moving and immersed actuated parts such as valves for robust grid movement.
- Include more appropriate turbulence models
- Continue developing cut-cell grid generation.

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Introduction

Los Alamos National Laboratory (LANL) and its collaborators are facilitating engine modeling by improving accuracy of the modeling, and improving the robustness of software. We also continue to improve the physical modeling methods. We are developing and implementing new mathematical algorithms, those which represent the physics within an engine. We provide software that others may use directly or that they may alter with various models e.g., sophisticated chemical kinetics, different turbulent closure models or fuel injection models.

Approach

Development of computational fluid dynamics (CFD) models and algorithms relies on basic conservation laws and various mathematical and thermodynamic concepts and statements including calculus of variations. The process encompasses a great many requirements including:

1. Knowledge of turbulent modeling for multiphase/multispecies fluid dynamics.
2. Knowledge of combustion dynamics and models.
3. Skill at implementing numerical methods for multi-physics CFD on complex domains.

Results

We proceed with the idea in mind that it is better to have algorithms which are more accurate at a given resolution and provide for higher resolution and accuracy only where and when it is required.

We recently began researching a CBS FEM, similar to that developed by Zienkiewicz and Codina [1]. This construction is a Galerkin-type finite element method that utilizes conservative momentum and energy transport. We are investigating use of the precise P-G stabilization [2] and the CBS method of discretized equation stabilization. Both algorithms are known as projection methods; methods now having great popularity in the finite element community. These methods, combined with higher order polynomial approximation for model dependent physical variables (*p*-adaptive) along with grid enrichment (locally higher grid resolution – *h*-adaptive) and overset grids for actuated and immersed moving parts will provide for highly accurate and robust solutions in the next generation of KIVA, particularly on complex domains. We have been developing this CBS algorithm for KIVA from our *hp*-adaptive FEM research code and formulating the process for implementing a KIVA combustion code [2-5].

Results from the algorithm simulating many validation problems (benchmarks) are shown in Figures 1 to 4. In Figure 1, turbulent convective flow modeled with the *k*-ω two-equation closure [2] over a backward-facing step at a Reynolds number (Re) = 28,000 is shown using two species to form the fluid (air). This Re corresponds to an inflow velocity of 17 m/s (Mach number ~0.05) and matches the experimental data. This velocity is near lower values in a typical internal combustion engine. Also, this is a problem current KIVA cannot do well. With the CBS FEM algorithm, nearly the exact solution is obtained with a recirculation length of 6.1 step heights (6.1 h).

KIVA-4 published solutions [6] for the driven cavity at this Re = 1,000 shows ~45,000 cells required to match benchmark data. As shown in Figure 2, that is an

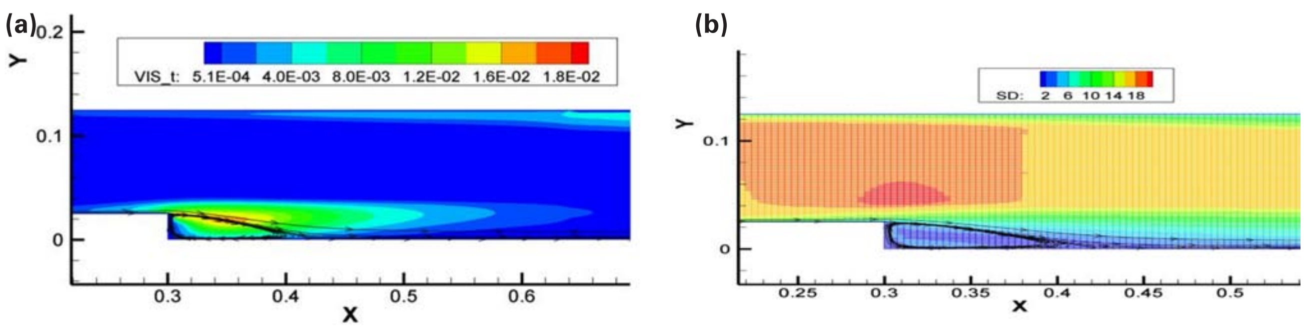

FIGURE 1. Two-dimensional (2-D) turbulent backward-facing step at Re = 28,000 using a k-*w* two-equation closure and *h*-adaptive P-G CBS FEM. a) Turbulent viscosity and streamlines b) Adapted grid, isotachs and streamlines.

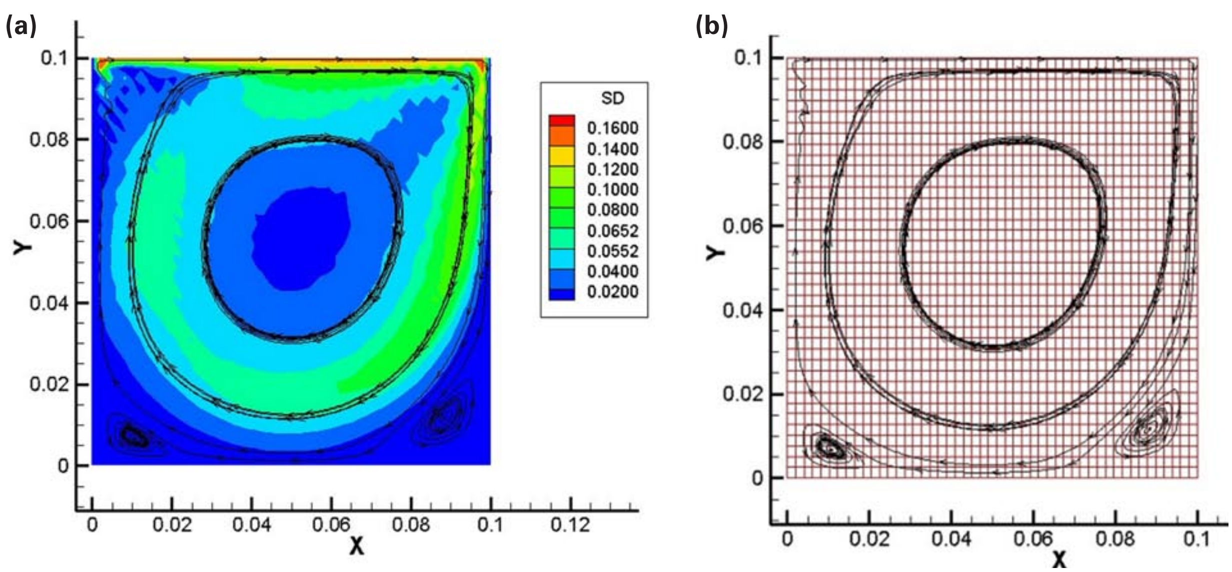

FIGURE 2. 2-D driven cavity at Re = 1,000 using an initial 40x50 mesh (2,000 cells). a) Isotachs and streamlines b) Grid and streamlines.

order magnitude more than with the CBS conservative formulated projection scheme using P-G stabilization.

Figure 3 shows the *h*-adaptive solution to two-dimensional (2-D) natural convection in a differentially heated cavity using the CBS algorithm and the P-G stabilizing at Rayleigh number of 1e06, showing good agreement with known solutions.

The *hp*-adaptive FEM framework incorporation hierarchical basis has been developed and verified (Table 1). The method uses a stress error indicator, different and more robust than the error indicator used in the simulations shown in Figures 1 through 3. Verification and results shown in Figure 4 are using an incompressible fractional step algorithm [6].

TABLE 1. Comparison of the *hp*-adaptive solution is shown to known benchmark data for Rayleigh number 10^5.

Comparison with Benchmark Data				
Case	Ra	Umax	Vmax	Nuave
3-D [7]	105	41.0	69.8	4.62
Present 3-D	105	40.8	69.2	4.58

3-D – three-dimensional

A conjugate formulation to predict heat conduction or conjugate heat transfer in the solid domain and spray combustion on the fluid domain was developed for multidimensional engine simulation using KIVA-4. Heat transfer through the wall affects the combustion

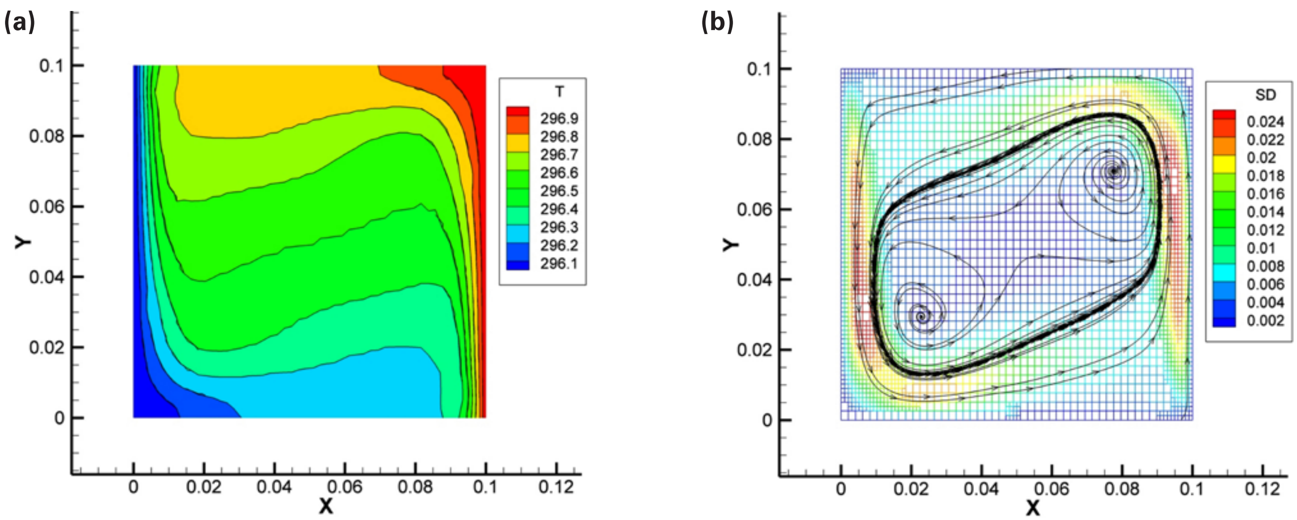

FIGURE 3. Natural convection in a 2-D cavity at Ra = 10^6 using an initial 40x50 mesh (2,000 cells). a) Isotherms b) The adapted grid, isotachs and streamlines.

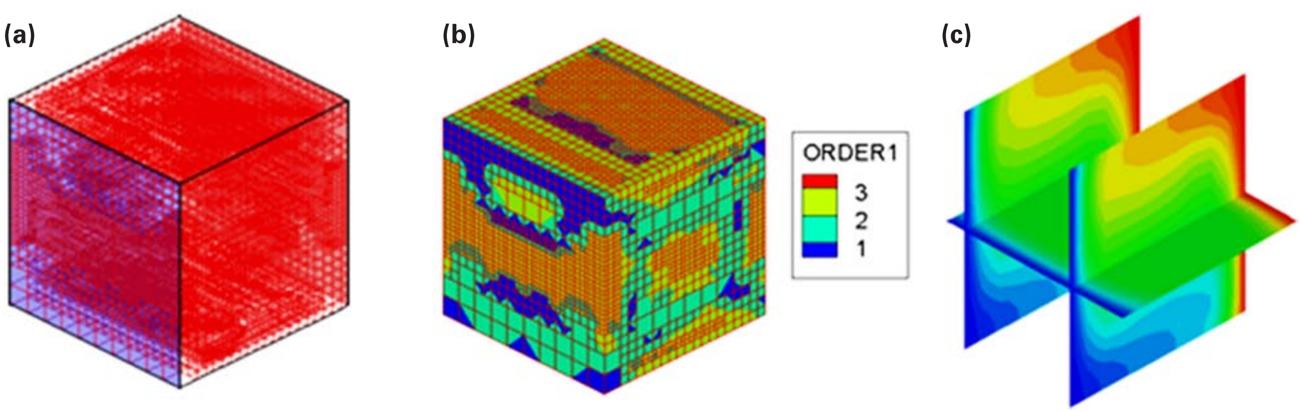

FIGURE 4. Natural convection in a 3-D differentially heated cavity using the *hp*-adaptive FEM Framework with the projection (incompressible) algorithm. a) Intermediate *h*-adaptive mesh, 12,634 elements and 11,718 degrees of freedom, b) Final *hp*-adaptive mesh, 12,634 elements and 29,108 degrees of freedom c) Isotherms.

process in the cylinder and the thermal loading on the combustion chamber surface. Detailed understanding of the wall heat flux is important in improving engine efficiency and durability. To account for the temporal and spatial variations of temperature on the combustion chamber surface, a fully coupled numerical procedure was developed and applied to calculate in-cylinder flow and solid component heat conduction simultaneously.

This work is based on KIVA-4 with the inclusion of solid computational domain of the cylinder head and piston. Unsteady heat conduction equations are implemented and solved for temperature distribution within the solid using a finite volume approach. Heat conduction (discretized with KIVA's finite volumes) is integrated into the solution algorithm. The new KIVA-4 was used to simulate the in-cylinder combustion and the heat conduction of a Caterpillar heavy-duty diesel engine. Results show that the present model is able to predict unsteady and non-uniform temperature distributions on the chamber's surface. The predicted surface temperature does approach a steady-state solution as the simulation progresses over numerous engine cycles as shown in Figure 5. The surface temperature can fluctuate by nearly 100 K within an engine cycle. The highest temperature on the piston surface occurs at the edge of the piston bowl along the spray axis at shown in Figure 6. Predicted global engine parameters including in-cylinder pressure, heat release rate, and emissions are in good agreement with the experimental data when the present model was used. The present coupling approach can further extend the capabilities of KIVA-4 to be used to improve engine design for optimal combustion and reduced thermal loading.

A newer version of KIVA-4, the parallel version, is being distributed. It is capable of utilizing many computers or processors via message-passing interface known as MPI [8]. These processors can be distributed on various machines or be local to a single machine. This distribution of the engine domain or geometry and accompanying discretization of the equations for mass, momentum and energy transport allows for a greater domain resolution to be solved in parallel, resulting in solutions in a shorter period of time.

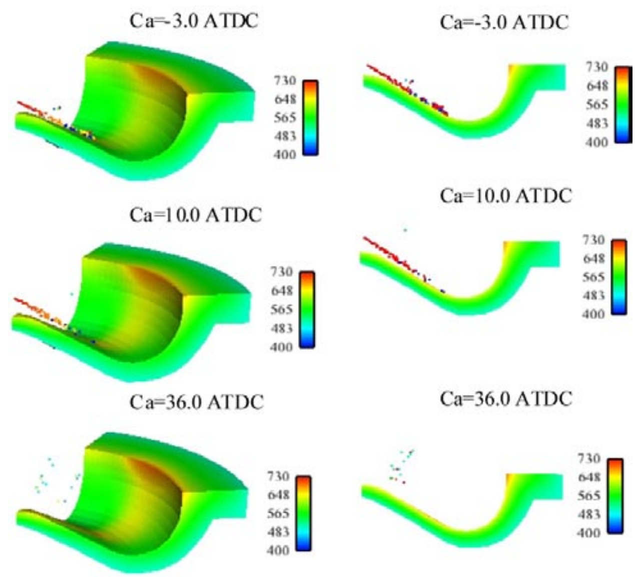

FIGURE 6. Piston surface distributions and temperature contours on a cut-plane within the piston together with spray drops at selected timings (start of injection, SOI = –7 after top dead center).

Conclusions

The following conclusions are drawn from the work described.

1. Development of an hp-adaptive CBS FEM for incompressible flow has been achieved. Compressible flow verification and validation is in progress. This projection method is a new solution algorithm for advancing the accuracy, robustness, and range of applicability of the KIVA combustion code. The system is one of higher-order spatial

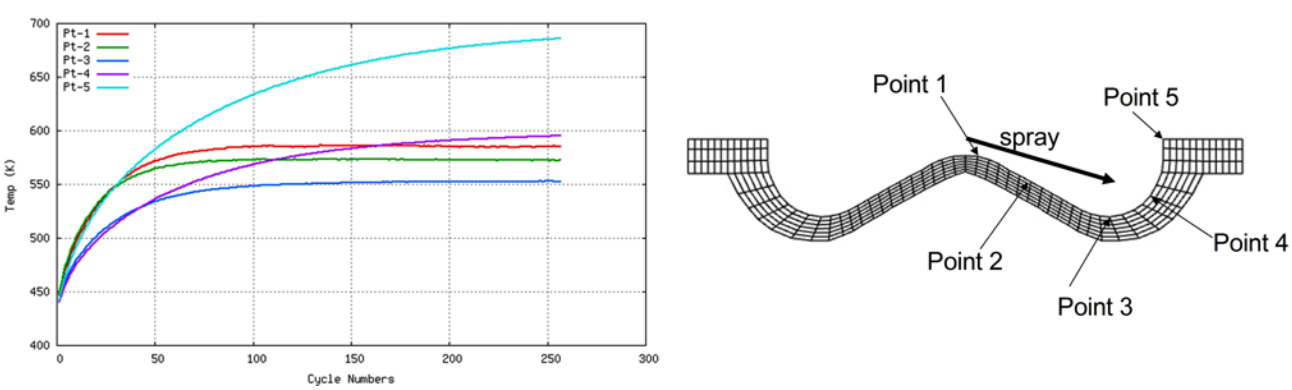

FIGURE 5. Variations of surface temperatures at selected locations over time as indicated in the grid diagram of the piston.

and temporal accuracy while providing a minimal amount of computational effort.

2. Extending KIVA-4 capability to predict heat conduction in solids, that is, in the combustion chamber, has been achieved. This will provide more accurate prediction of wall film wetting and subsequent evaporation. For example, to provide more accurate wall heat flux effects on combustion and emissions under premixed charge compression ignition engine conditions injected with fuel having wall impingement.
3. A KIVA-4 parallel version (beta version) is being distributed. This to supply the engine modeling community an efficient internal combustion engine solver and source code. Full version release after feedback from beta version. This is a great step forward in the ability of KIVA-4 and the KIVA project in general, providing for more rapid simulations on today's platforms, from smaller mini-super computers, small Linux systems, to the world's fastest computer.

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3. Carrington, D.B., "KIVA-4 Development," *2010 DOE/EERE Advanced Combustion Merit Review*, Washington, D.C., LA-UR-10-01879, June 2010.

4. Torres, D.J., Li, Y. H., Kong, S.-C., "Partitioning Strategies for Parallel KIVA-4 Engine Simulations," Computers and Fluids, Vol. 39, no. 2, p.301-309, 2010.

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II.A.12 Chemical Kinetic Models for HCCI and Diesel Combustion

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Objectives

- Develop detailed chemical kinetic models for fuel components used in surrogate fuels for diesel and homogeneous charge compression ignition (HCCI) engines.
- Develop surrogate fuel models to represent real fuels and model low-temperature combustion strategies in HCCI and diesel engines that lead to low emissions and high efficiency.
- Characterize the role of fuel composition on low-temperature combustion modes of advanced combustion engines.

Fiscal Year (FY) 2010 Accomplishments

- Developed first-ever primary reference fuel mechanism for gasoline and diesel fuels.
- Development of high- and low-temperature mechanisms for series of iso-alkanes that covers the entire distillation range of diesel fuel.
- Successfully simulated intermediate temperature heat release, which plays an important role in maintaining HCCI operation as the boost pressure is increased.
- Developed improved mechanisms for fuel components in gasoline fuels: toluene, pentenes, and hexenes.
- Developed a functional-group kinetics modeling approach for n-alkanes that greatly reduces the size of the mechanism for use in multidimensional engine simulations.

Future Directions

- Develop chemical kinetic model for a high molecular-weight aromatic to represent the aromatics chemical class in diesel fuel.
- Development of low- and high-temperature mechanisms for a new series of iso-alkanes to represent the iso-alkane chemical class in diesel fuel.
- Test surrogate mixture models for gasoline by comparison to HCCI engine and rapid compression machine experiments.
- Validate the chemical kinetic mechanism of 2-methyl heptane, a model iso-alkane.
- Develop a functional group method for iso-alkanes in diesel fuel so that the chemical kinetic mechanism can be greatly reduced in size for multidimensional engine simulations.

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Introduction

Predictive engine simulation models are needed to make rapid progress towards DOE's goals of increasing combustion engine efficiency and reducing pollutant emissions. These engine simulation models require chemical kinetic submodels to allow the prediction of the effect of fuel composition on engine performance and emissions. Chemical kinetic models for conventional and next-generation transportation fuels need to be developed so that engine simulation tools can predict fuel effects.

Approach

Gasoline and diesel fuels consist of complex mixtures of hundreds of different components. These components can be grouped into chemical classes including n-alkanes, iso-alkanes, cycloalkanes, alkenes, oxygenates, and aromatics. Since chemical kinetic models cannot be developed for hundreds of components, specific components need to be identified to represent each of these chemical classes. Then detailed chemical kinetic models for these selected components can be developed. These component models are subsequently merged to produce a "surrogate" fuel model for gasoline, diesel, and next-generation transportation fuels. This approach can create realistic surrogates for gasoline or diesel fuels that reproduce experimental behavior of the practical real fuels. Detailed kinetic models for surrogate fuels can then be simplified as needed for inclusion in multidimensional computational fluid dynamics (CFD) models or used in full detail for purely kinetic modeling.

Results

Iso-alkanes are present in diesel fuel in large concentrations [1] and are a chemical class that needs to be represented in a diesel surrogate model. During FY 2010, we have developed a chemical kinetic model for a whole series of iso-alkanes that covers the full distillation range of diesel fuel. It is important to represent the full distillation range in diesel to describe the complex behavior in evaporating and reacting diesel sprays. Ra et al. [2] have shown that lighter components are present in higher concentrations upstream in a simulated diesel spray and heavier components downstream. We have selected a series of 2-methyl alkanes as a starting point to represent the iso-alkanes in diesel fuel. We have developed a chemical kinetic model for all the 2-methyl alkanes from C_8 to C_{20} to cover the full distillation range. This was a very ambitious task, involving the estimation of thermodynamic properties for thousands of species and the assembly of thousands of reactions with their associated rate constants. Subsequently, we have obtained experimental data on one of the 2-methyl alkanes (2-methyl heptane) to help validate our chemical kinetic model [3]. Predictions of the model compare well with species concentration profiles measured in a counterflow diffusion flame for 2-methyl heptane. Further experimental validations are planned.

The interesting behavior of ignition of these iso-alkanes compared n-alkanes is given in Figure 1. The iso-alkanes are more resistant to ignition then the n-alkanes as shown by their longer ignition delay times. Also, the iso-alkanes show less low-temperature chemistry than the n-alkanes because the ignition delays are particularly longer temperature range 750 to 900 K. This is a critical temperature region for cetane number and these results indicate that the cetane numbers should be smaller for iso-alkanes compared to n-alkanes with the same carbon number which is consistent with available experimental information for cetane numbers [4]. Also Figure 1 shows the expected trend in ignition behavior with increasing carbon number for both the n-alkanes and iso-alkanes: as the carbon number of the alkane increases, the ignition delay time decreases. This trend is particularly apparent in the negative temperature coefficient region, a key region that influences fuel effects in diesel and gasoline engines.

Primary reference fuels (PRFs) are important for rating the ignition behavior of gasoline and diesel fuels. Detailed chemical kinetic models for primary reference fuels are needed to provide a reference point for comparison of the behavior of conventional and next-generation fuels. For the first time, we have developed a chemical kinetic mechanism for gasoline and diesel PRFs [5]. For gasoline PRFs, the mechanism describes the ignition of n-heptane and isooctane used to rate gasoline properties through the octane number. For diesel PRFs, our mechanism also describes the ignition of n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane used to rate diesel fuels through the cetane number test. The predicted ignition behavior of gasoline and diesel PRFs are shown in Figures 2 and 3. Predictions for the gasoline PRFs compare well with the experimental data from [6]. This mechanism provides engine designers and fuel scientists with a predictive tool to compare the behavior real fuels with reference fuels.

Chemical kinetic models for real fuels need to be reduced to allow their use in CFD engine simulation models. We have developed a new approach called the functional group approach, that greatly reduces the size of a chemical kinetic fuel mechanism and its accompanying computational requirements. Each fuel molecule is divided up into function groups based on the molecular structure of fuel. Each function group is represented in the chemical kinetic mechanism with its own set of intermediate species and associated detailed chemical kinetic reactions. Once the fuel molecules have eventually been broken down into fragments of C_4 or less, the chemical species are handled by our base C_1 to

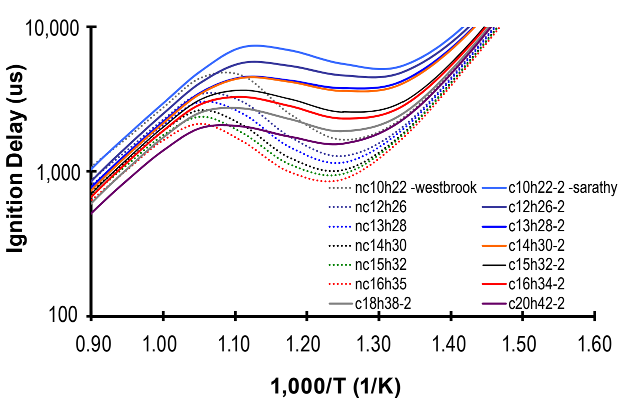

FIGURE 1. Prediction of the ignition behavior of 2-methyl alkanes compared to n-alkanes under representative diesel engine conditions (equivalence ratio of 3, 22 atm, and 1.4 % fuel in O_2/Ar). The region of negative slope is the negative temperature coefficient region.

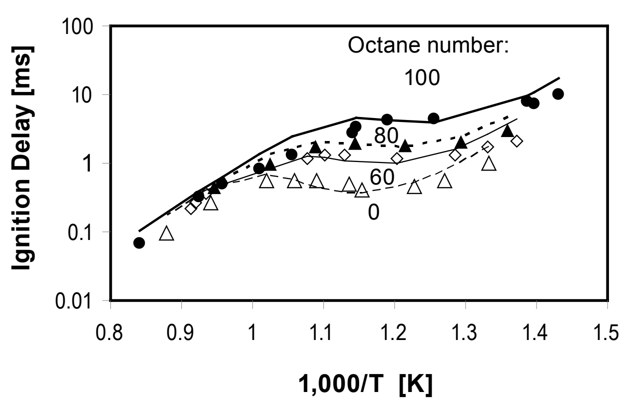

FIGURE 2. Computed and experimental ignition delay times for stoichiometric mixtures of gasoline PRF mixtures in air at 13 bar pressure over the low- and high-temperature range. (lines: predictions; symbols: experiments [6]). The numbers are the octane numbers of the PRF mixtures. (e.g. 80 means 80% iso-octane and 20% n-heptane).

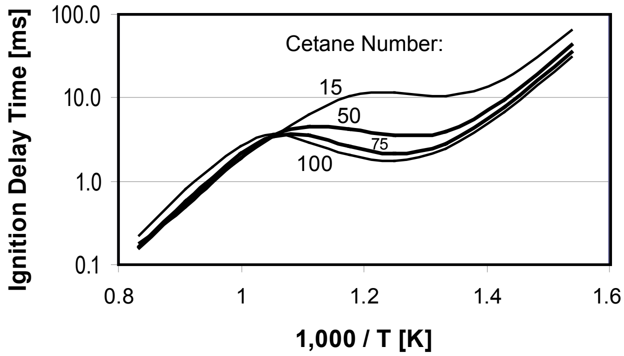

FIGURE 3. Computed ignition delay times [5] for stoichiometric diesel PRF mixtures in air at 13 bar pressure over the low- and high-temperature range. The numbers are the cetane numbers of the PRF mixtures.

C_4 mechanism. In the case of n-decane (Figure 4), the functional group approach has allowed a factor of four reduction in the number of species in the chemical kinetic model compared to a fully detailed approach. In the case of n-hexadecane, the number of species was reduced by factor of 10, greatly reducing computational requirements.

Dec et al. [7] found that intermediate temperature heat release is an important fuel behavior that allows retarded HCCI phasing and high load operation. We performed detailed kinetic modeling of intermediate temperature release and used their experimental data to provide further validation of our fuel kinetic model. We developed a methodology for formulating a gasoline surrogate model and developed a surrogate that contained n-heptane, isooctane, toluene, and 2-pentene, to simulate the 87 octane gasoline used in their experiments. As shown in Figure 5, we were able to back predict the temperature at bottom dead center required to reproduce combustion phasing in their HCCI engine. This comparison shows that our surrogate model is able to accurately predict HCCI combustion for 87 octane gasoline. We were also able to identify the source of the intermediate temperature release which was associated with the formation of HO_2 radicals and the oxidation of formaldehyde.

More accurate fuel component models are needed to formulate better surrogate models for real fuels. During FY 2010, we have improved our fuel component models for pentenes and hexenes to model the olefin chemical class and toluene to model the aromatic class in gasoline [8]. We have also improved the chemical kinetic model for benzene, an important intermediate in the oxidation of toluene and other aromatics. Our chemical kinetic models can now accurately predict ignition for these key gasoline components. In Figure 6,

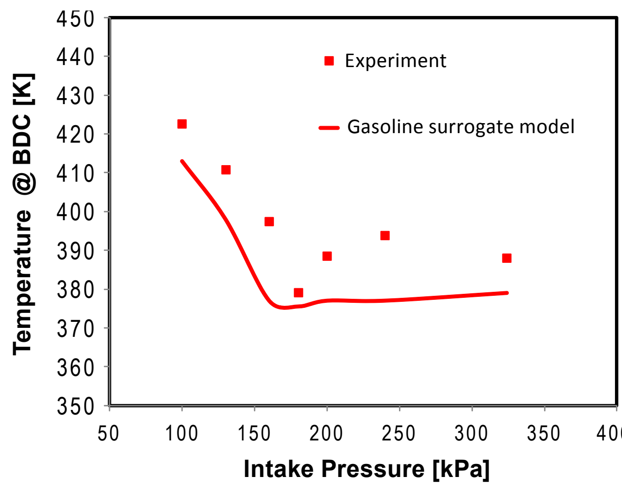

FIGURE 5. Gasoline surrogate model accurately back predicts bottom-dead center (BDC) temperature required to achieve HCCI combustion timing measured by Sandia National Laboratories.

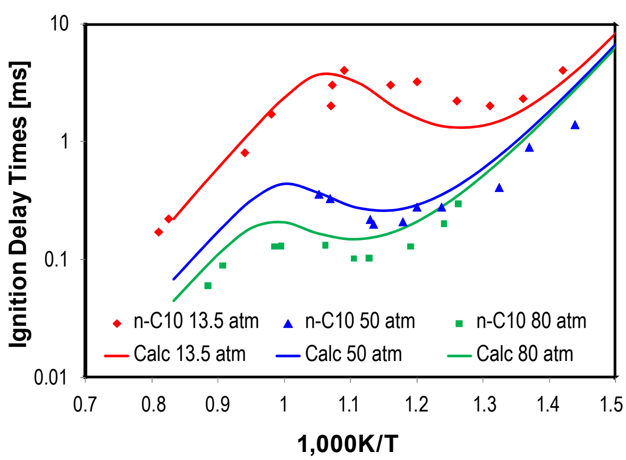

FIGURE 4. Ignition delay times for stoichiometric, n-decane/air mixtures, computed using a functional group approach (curves). The symbols are experimental ignition delay times from [9, 10].

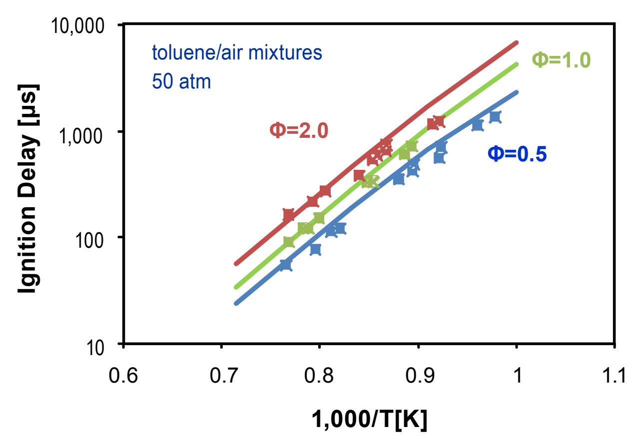

FIGURE 6. Computed (lines) [8] and experimental (symbols) [11] ignition delay times in a shock tube for different equivalence ratios of toluene in air over a range of temperatures and a pressure of 50 atm.

the computed ignition delay times for toluene-air mixtures are compared to those measured over a range of temperatures and for 50 atm, a pressure relevant to conditions in internal combustion engines.

Conclusions

- For the first time, a complete chemical kinetic mechanism for the PRFs of gasoline and diesel has been developed, providing engine developers and fuel scientists with a benchmark fuel model by which other fuels are compared.
- We have assembled a reaction mechanism for the high- and low-temperature oxidation of a series of 2-methyl alkanes that covers the entire distillation range of gasoline and diesel and can be used to represent the iso-alkane chemical class.
- A surrogate model for gasoline was developed and shown to accurately model HCCI combustion for 87 octane gasoline.

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1. W.J. Pitz and C.J. Mueller, "Recent Progress in the Development of Diesel Surrogate Fuels," Progress in Energy and Combustion Science (2010), in press, http://dx.doi.org/10.1016/j.pecs.2010.06.004.

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Special Recognitions

1. Charles Westbrook: Honorary Doctorate Degree, University of Nancy, France, 2010.

2. Charles Westbrook: President of the Combustion Institute.

3. William J. Pitz: Best paper of the year award 2009: Combustion Society Japan.

II.A.13 Hydrogen Free-Piston Engine

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Kellen Schefter

Objectives

- Study the effects of continuous operation (i.e. gas exchange) on indicated thermal efficiency and emissions of an opposed free-piston linear alternator engine utilizing homogeneous charge compression ignition (HCCI) combustion at high compression ratios (~20-40:1).
- Validate the concept of passively synchronizing the opposed free pistons via the linear alternators, providing a low cost and durable design.
- Demonstrate the principle of electronic variable compression ratio control, allowing optimized combustion timing and fuel flexibility, by means of mechanical control of bounce chamber air pressure.
- Provide a research tool to explore the free-piston engine operating envelope across multiple inputs: boost level, equivalence ratio, alternative fuels.

Fiscal Year (FY) 2010 Accomplishments

- Designed and fabricated piston lock-and-release mechanism intended to lock pistons in place for starting and release pistons simultaneously to ensure piston synchronization on the first stroke.
- Designed a full-scale test rig for the lock-and-release mechanism to determine force and velocity needed to remove the latch pin with an electric solenoid as well as investigate optimized designs of the latch pin (diameter, contact angle, material, and hardness).
- Latch pin testing revealed durability and performance issues with the lock-and-release mechanism.
- A compressed helium gas injection starting system was designed and simulated to show adequate performance.
- Bounce chamber cylinders, injection valves, vent manifolds, and pistons began fabrication in July 2010.
- Hardware for a helium starting system, bounce chamber air control (BCAC) motoring system, data acquisition, and other support systems has been received and installed.

Future Directions

- Complete assembly of research prototype engine, helium starting system and BCAC motoring system as well as associated support and data acquisition hardware.
- Quantify piston friction drag with engine fully assembled and lubricated but without magnets installed.
- Perform single-shot tests without fuel to characterize synchronicity of the compressed helium starting system.
- Initially run the engine under BCAC motoring mode only to test the stabilizing capability of the linear alternator coupling.
- Perform combustion experiments and measure indicated thermal efficiency at various compression ratios and equivalence ratios with both conventional and alternative fuels: hydrogen, natural gas, ethanol, biofuels, propane, gasoline, and other renewables.

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Introduction

As fuel efficiency of the typical American automobile becomes more important due to hydrocarbon fuel cost and availability issues, powertrain improvements will require smaller output engines combined with hybrid technologies to improve efficiency. In particular, the plug-in hybrid concept will require an electrical generator of approximately 30 kW output. Unfortunately, current crankshaft spark-ignition internal combustion engines with optimized power outputs of 30 kW have thermal efficiencies of less than 32%.

The free-piston generator of this project has a projected fuel-to-electricity conversion efficiency of 50% at 30 kW output. The project has progressed by conducting idealized combustion experiments, designing and procuring the linear alternators required for control and power conversion, and conducting computational fluid dynamics design of the inlet/exhaust processes. The design has evolved into a dynamically balanced configuration suitable for seamless incorporation into an automotive application or distributed power generator. The ultimate goal is to combine the developed components into a research prototype for demonstration of performance. Figure 1 shows the efficiency improvement of the free-piston engine based on single cycle experiments.

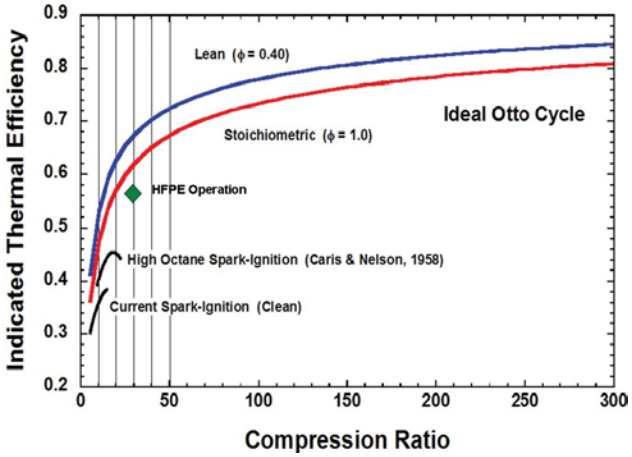

FIGURE 1. Indicated Efficiency as a Function of Compression Ratio (Sandia measured single cycle performance operation shown by diamond.)

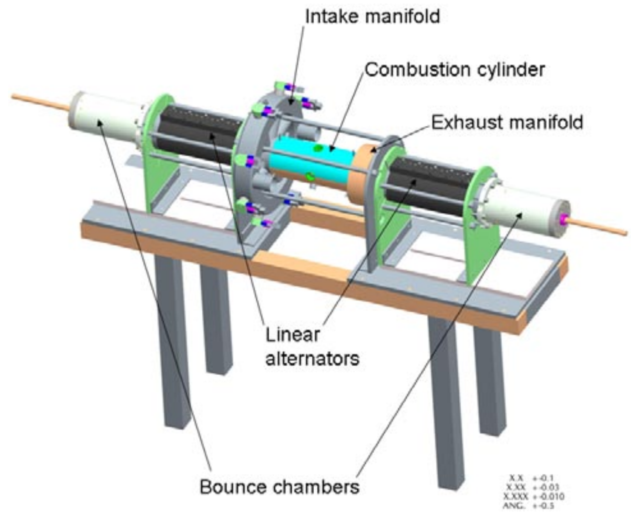

FIGURE 2. The Free-Piston Engine Research Prototype CAD Model

Approach

By investigating the parameters unique to free-piston generators (linear alternator, opposed-piston coupling, uniflow port scavenging) as separate entities, each piece can be used at its optimum design point. More importantly, upon assembly of a research prototype for performance demonstration (the goal of this project), understanding of the pieces in the device will allow quantifying the contribution of each component to the combined performance of the assembly.

Last year the major components of the research prototype engine were procured and assembled, along with the 1,000 psi air compressor required to power the BCAC motoring system. This year, the main focus has been on the starting device. A piston lock-and-release mechanism was designed for starting purposes but was found through modeling to be inadequate during validation testing. Compressed helium injection during the first stroke was found to be more suitable and easier to control. With the starting system design finalized, the remaining components needed to begin operation have been procured. In addition, collaboration with General Motors and the University of Michigan continues on a detailed model of the Sandia research prototype.

Results

Figure 2 shows the computer-aided design (CAD) model of the research device. Last year the major components of the experiment were procured and assembled, including the central combustion chamber, intake and exhaust manifolds, combustion pistons, back irons, magnets, linear alternators, load resistors, fuel injectors, lubrication system, and associated connections and support systems. In addition, the BCAC system was designed with the capability to start the piston oscillation and bring the motoring engine to the desired compression ratio before fuel is introduced. This is done by injecting controlled high-pressure air (up to 1,000 psi) through a piston-actuated valve in the bounce chamber cylinder head and venting it out ports in the bounce chamber cylinder into a controlled low-pressure (up to 50 psi) plenum. The BCAC system allows variable compression ratio control that will enable optimized combustion timing dependent upon fuel type, boost level, equivalence ratio, and mixture conditions.

Prior to having the bounce chamber cylinders, pistons, injection valves, and cylinder heads fabricated, it became necessary to determine how the BCAC motoring system would be started. In simulations of the BCAC system, the first stroke was started with both pistons locked at their respective outer ends (bounce chambers fully compressed). The bounce chambers were set to the appropriate pressure (the injection pressure corresponding to the desired compression ratio). The pistons were then released and the high-pressure air in the bounce chambers forced the pistons to compress the air in the combustion chamber to the desired compression ratio. Initially it was hoped that on the research prototype the pistons would not have to be locked and that the bounce chamber and injection valve volumes would be sufficiently small to quickly fill with high-pressure air. However, computational fluid dynamics simulations of the filling process showed inadequate fill times. With insufficient air injected on the first stroke, motion would stop after a few cycles. Thus, a piston lock-and-release mechanism was designed to lock the pistons in place for starting as shown in Figure 3. This mechanism features a cylindrical pin designed to latch into a plate attached to the crown of the bounce chamber pistons and lock the pistons in place. The bounce chambers would then be pressurized with the appropriate air pressure. Electric solenoids

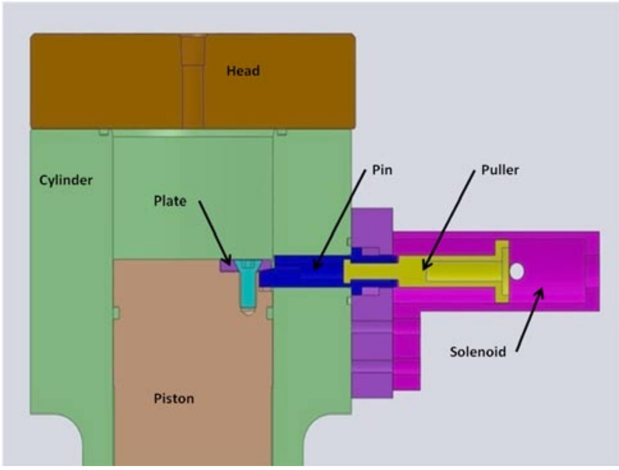

FIGURE 3. Bounce Chamber Piston Lock-and-Release Starting Mechanism

would simultaneously retract the latch pins into the bounce chamber cylinders, allowing the pistons to accelerate towards each other. The latch pins would remain retracted until the next start. This would ensure that both pistons remain synchronized during the first stroke.

In order to verify and optimize the latch mechanism design prior to final bounce chamber fabrication, a test stand was implemented with full-scale components as shown in Figure 4. Gas pressure of up to 1,100 psi was applied to a solid slug piston with equivalent mass of the prototype piston assembly. Free weights were then dropped from variable heights to determine the force and velocity needed to release the latch without interference. A linearly variable differential transformer was used to measure the velocity required for the solenoids to provide. Several design parameters were explored including latch pin diameter, latch plate thickness, pin/plate material and hardness, and contact angle between pin and plate. After several pin failures due to fracture, the pin size was increased. However, it quickly became apparent that a substantial force and velocity would be required to retract the pins without any grazing of the piston.

Due to the shortcomings of the latch mechanism design, an auxiliary compressed helium injection system for starting the BCAC motoring system was conceived. It consists of 150 cc helium storage tanks on each side charged to up to 3,600 psi. The tanks connect to the bounce chambers through electric solenoid valves and mechanical check valves via dedicated ports. The idea is to provide enough energy from the auxiliary helium system to power the first cycle and have the BCAC air motoring system take over for the remaining cycles. A model of the system was developed using the commercial code SINDA/FLUINT to determine the effects of different size storage tanks, the resulting

FIGURE 4. Latch Mechanism Test Stand

compression ratio and energy delivered, and the total number of strokes required for complete blow down. Ideally, the helium tanks would fully empty during the first stroke. Many runs of the model were performed, varying the tank size, time required for the solenoids to open and the head loss coefficient across the solenoids and check valves. It was determined that the helium system can supply enough energy to initiate BCAC motoring. High compression ratios on the first stroke can be achieved without large pressure vessels, and the tanks fully decompress during the first stroke. Solenoid opening time would not be an issue so long as a valve was chosen that could fully open in less than 10 ms. The head loss coefficient across the solenoids and check valves did not have a significant effect on the results so long as they did not change the orifice size of the system.

With the starting device design finalized, the remaining prototype engine components were sent out for fabrication at the beginning of July 2010. This includes the bounce chamber cylinder, head, injection valve, vent manifold and piston. These components are shown in Figure 5. In addition, the various parts needed for both the BCAC motoring system as well as the compressed helium starting system have also been purchased and installed. For the BCAC motoring system this includes the air injection and vent tanks, the regulators and valves, the line connections and associated transducers and sensors. Figure 6 shows these components as well as the layout of the research experiment. In addition, the implementation of a computer control and data acquisition system has already begun and should be ready prior to initial testing.

General Motors is funding work at the University of Michigan to assess the Sandia design's potential for improving vehicle fuel economy and emissions as well as stability and compression ratio control. The model is built in a MATLAB/Simulink framework and features a zero-dimensional thermodynamic model (including combustion kinetics, scavenging, heat transfer, and friction), a linear alternator model (using various linear alternator and load circuitry designs), a dynamic force balance model, and a BCAC model (to simulate start-up and motoring). The model will be validated by the experimental data of the Sandia experiment and then be used to explore other conditions beyond the experimental test matrix, such as different fuels and intake conditions.

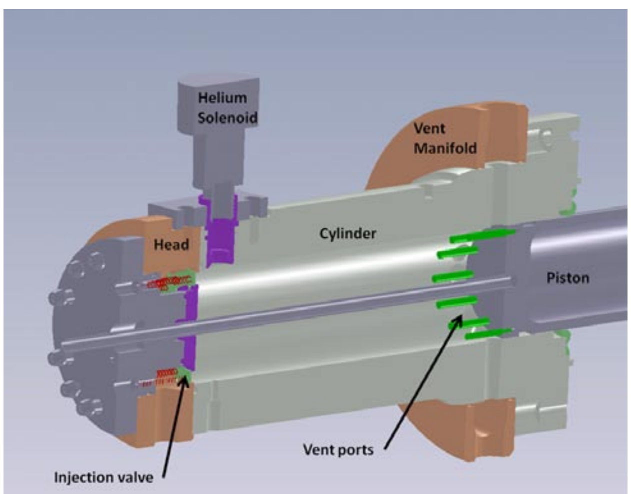

FIGURE 5. BCAC System with Piston-Actuated Injection Valve, Vent Ports and Manifold, and Helium Solenoid and Check Valve

FIGURE 6. The Sandia Research Prototype

Conclusions

- Piston lock-and-release mechanism design complete. Subsystem hardware testing on full-scale component model revealed durability and performance issues.
- Designed and simulated a compressed helium gas injection starting system with adequate performance.
- Procured final parts needed for the research prototype, BCAC motoring system, and helium starting system.
- Implemented a computer control and data acquisition system.
- Collaboration with General Motors and the University of Michigan on modeling of Sandia prototype engine and various alternator designs is ongoing.
- Project on track to start experimental tests in FY 2011.

II.A.14 Optimization of Direct Injection Hydrogen Combustion Engine Performance, Efficiency and Emissions

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Objectives

- Gain understanding of mixture formation and combustion process in hydrogen operation and develop advanced tools for their optimization.
- Quantify the engine efficiency potential of advanced hydrogen internal combustion engines with particular focus on direct injection.
- Optimize engine efficiency while reducing engine-out emissions of oxides of nitrogen (NOx).
- Assess potential of in-cylinder emissions reduction measures such as exhaust gas recirculation.

Fiscal Year (FY) 2010 Accomplishments

- Research engine upgraded to efficiency-optimized geometry.
- Fast-acting piezo injectors integrated in experimental setup to allow expansion of test regime and optimize mixture stratification.
- Three-dimensional computational fluid dynamics (3D-CFD) simulation validated against optical results from Sandia National Laboratories and subsequently used for injection strategy optimization.
- Indicated thermal efficiency levels increased by 6% (from 37% to 43%) over a wide load range through optimization of engine geometry.
- Peak brake thermal efficiency of 43.6% demonstrated at 3,000 RPM and 14.3 bar indicated mean effective pressure (IMEP) at engine-out NOx emissions levels below 100 ppm using turbocharging.

Future Directions

- Assess optimized injection strategies and injector nozzle designs through integration of experimental work with predictive 3D-CFD simulation.
- Estimate drive-cycle NOx emissions based on steady-state single-cylinder engine test results and determine requirements for in-cylinder emissions reduction.
- Demonstrate 45% peak brake thermal efficiency while meeting Tier II Bin 5 NOx emissions.

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Introduction

Hydrogen has been identified as a promising alternative fuel with the internal combustion (IC) engine as a transition technology to enable the introduction of a large-scale hydrogen infrastructure. Research is being conducted world-wide to assess the potential of hydrogen IC engines and hydrogen direct injection engines have been found to have particularly high potential [1]. The U.S. Department of Energy has set challenging targets for the performance and emissions behavior of hydrogen IC engine vehicles including a peak brake thermal efficiency of 45%, NOx emissions as low as 0.07 g/mile and a power density comparable to gasoline engines [2].

This report summarizes the efficiency improvements gained through an upgrade in engine geometry together with piezo actuated injectors, outlines the 3D-CFD validation and simulation activities and gives an outlook of the potential of turbocharged operation to maximize engine efficiencies with minimal NOx emissions.

Approach

Collaboration has proven to be the key to success for meeting DOE's challenging goals for hydrogen IC engines. Argonne National Laboratory operates a single-cylinder research engine that has been optimized to achieve highest engine efficiency. Optimization of the injection strategy including injector nozzle design is crucial for achieving the efficiency goal. At Argonne 3D-CFD simulation has been introduced as a diagnostic and cost-effective development tool. The 3D-CFD simulation tool has been carefully tested and validated against optical results from a hydrogen engine operated at Sandia National Laboratories. These close-coupled activities receive valuable guidance from experts at Ford Motor Company and also integrate hydrogen injector development at Westport Innovations Inc.

Results

Optimization of Engine Geometry and Injection Strategy

The single-cylinder research engine used to study the potential of hydrogen direct injection was upgraded with the intent to increase engine efficiencies. The specifications of the new single-cylinder research engine (GEN. 2) compared to its predecessor (GEN. 1) are shown in Table 1. The main changes to the geometrical specifications of the Gen. 2 single-cylinder research engine compared to its predecessor include an increase in compression ratio (CR) from 11.5 to 12.9 and a significant increase in engine stroke from 79.5 mm to 105.8 mm which also results in a larger engine displacement. With the modified engine stroke the bore/stroke ratio changed from an oversquare (1.12) to an undersquare (0.84) configuration. The GEN. 2 research engine is also equipped with a new injection system which now features a piezo activated injector. Due to the faster actuation of this new injector type compared to the solenoid driven injectors used in the GEN. 1 single-cylinder engine, the piezo system provides more flexibility for advanced direct injection strategies.

TABLE 1. Main Specifications of Upgraded Single-Cylinder Research Engine Compared to Baseline

Engine	GEN. 1	GEN. 2
Displacement [l]	0.5	0.66
Bore/Stroke [mm]	89/79.5	89/105.8
Bore/Stroke Ratio [-]	1.12	0.84
Compression Ratio [-]	11.5	12.9
Intake Valve Timing	IVO = 15 degCA BTDC IVC = 35 degCA ABDC	
Exhaust Valve Timing	EVO = 45 degCA BBDC EVC = 10 degCA ATDC	
Injector Actuation	Solenoid	Piezo

IVO - intake valve openging; IVC - intake valve closing; EVO - exhaust valve opening; EVC - exhaust valve closing; CA - crank angle
BTDC - before top dead center; ABDC - after bottom dead center;
BBDC - before bottom dead center; ATDC - after top dead center

The second engine generation with its higher CR and its longer stroke is expected to result in engine efficiencies superior to the previous generation. An initial comparison was performed using only early injection in order to minimize the influence of the different hydrogen injection systems on the efficiency and emissions performance of the two different engine configurations. With these early injection timings the difference in the mixture formation inside the combustion chamber at spark timing due to the different nozzle designs and different injector flow rates should be minimal. An analysis of losses for the two different engine configurations was performed and it can be stated that both main engine geometry modifications from GEN. 1 to GEN. 2 successfully contributed to a significant improvement in indicated thermal efficiency. Figure 1 shows a comparison of the experimental results for the two engine generations for different engine loads, early injection timing (start of injection [SOI]=140 °CA BTDC at 4 bar IMEP and 6 bar IMEP; SOI=120 °CA BTDC at 8 bar IMEP) and maximum brake torque (MBT) spark timing. A significant increase in indicated thermal efficiency for the second engine generation in the range of 6% can be observed regardless of engine load.

As can be seen from Figure 1, the indicated thermal efficiency of the GEN. 1 engine was 37-38% and 43% for its successor. In order to thermodynamically analyze this up to 6% increase in indicated thermal efficiency an analysis of losses was performed [3,4]. Figure 2 shows the analysis of losses for the 6 bar IMEP engine operating point for the two engine generations. Based on the in-cylinder pressure data an analysis of losses allows for a detailed assessment of partial losses. The efficiency of the ideal engine with real charge η_{IRC} of the GEN. 2 engine is 56.9% and about 2.8% higher than that of the first generation engine. Starting from this theoretical engine efficiency, individual losses due to injection during the compression stroke $\Delta\eta_{ICS}$, incomplete combustion $\Delta\eta_{IC}$, real combustion $\Delta\eta_{RC}$, wall heat $\Delta\eta_{WH}$ and gas exchange $\Delta\eta_{GE}$ are subtracted which results in the measured indicated efficiency η_i. A detailed description of the individual losses can be found in [5]. It is apparent from Figure 2 that the two major factors for the increased indicated efficiency of the GEN. 2 engine are the higher theoretical efficiency and reduced wall heat losses. The improvement in theoretical efficiency η_{IRC} is mainly caused by the increased CR as well as the slightly leaner air/fuel ratio at which the GEN. 2 is operated compared to the GEN. 1. The reduced wall heat losses mainly

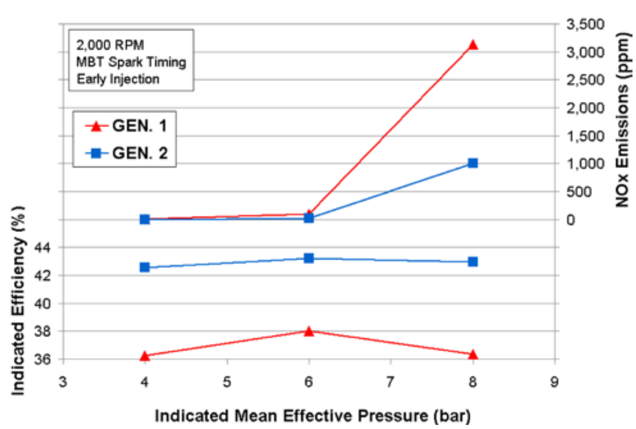
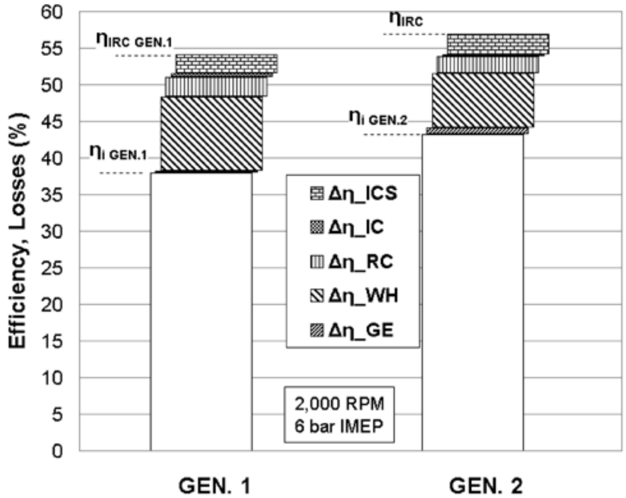


FIGURE 1. Comparison of Engine Efficiencies and Oxides of Nitrogen Emissions for Different Engine Loads



η_{IRC} – efficiency, ideal engine with real charge; η_i – indicated thermal efficiency; η_{ICS} – efficiency losses due to injection during the compression stroke; η_{IC} – efficiency of incomplete combustion; η_{RC} – efficiency of real combustion; η_{WH} – efficiency loss due to wall heat transfer; η_{GE} – efficiency loss due to gas exchange.

FIGURE 2. Analysis of Losses for the Two Engine Generations at Medium Engine Load

attributable to the optimized bore/stroke ratio are another major contributor to the overall improvement in indicated efficiency.

While the higher indicated thermal efficiency of the new engine was expected, the reduction of NOx emissions, also shown in Figure 1, in the extent shown by the experiments (more than two-thirds reduction from GEN. 1 to GEN. 2 at 8 bar IMEP) was not. The production of NOx is mainly a function of peak in-cylinder temperature and a higher CR was expected to shift the entire combustion process to a higher temperature and pressure level. The cause for the lower NOx emissions of the second generation engine can be found in the difference in the relative air/fuel ratio that is necessary to achieve the 8 bar IMEP (quality load control at wide-open throttle) for the two different engine configurations ($\lambda = 1.5$ for GEN. 1 vs. $\lambda = 1.9$ for GEN. 2). The relative air/fuel ratio has an important influence on the combustion temperature and hence on the NOx emissions. Almost no NOx emissions are produced in a hydrogen-fueled combustion engine (0.5 l engine displacement, CR 10.5, square bore/stroke ratio) with external mixture formation at relative air/fuel ratios above $\lambda = 2.2$, relative air/fuel ratios below this value lead to a sharp increase in NOx emissions reaching a maximum at about $\lambda = 1.3$ while a further λ-decrease results in a decrease of NOx emissions. Similar characteristics were found to be valid also for engine operation with early direct injection.

Validation of 3D-CFD Simulation

The computational code was validated against experimental data from an optically accessible single-cylinder engine at Sandia National Laboratories. In order to be able to follow the jet evolution during the entire compression stroke, early injection was analyzed. Accordingly, the SOI was set immediately after the IVC.

Figure 3 shows the comparison between numerical and optical data in terms of hydrogen mole-fraction for a single-injection at 100 bar. The maximum color-scale was progressively reduced to properly highlight the spatial distribution of hydrogen even for quasi-homogeneous mixtures (i.e. at late crank angles). A single-hole injector aiming at the intake quenching zone is used for the comparison. Hydrogen jet penetration, wall-impingement, overall evolution and final stratification at the spark timing were accurately predicted. Slight differences can be observed in terms of air entrainment (or, in other words, fuel dispersion), especially at late crank angles. Generally, gradients of fuel concentration in numerical results are sharper than in optical data.

A parametric analysis showed that the computational grid resolution has an influence only on jet penetration. A 1,400,000-cell (at bottom dead center) grid was used as it provided grid-independent results. To improve numerical predictions of fuel dispersion, the effect of "tuning" the turbulence model parameters was analyzed. The renormalization group (RNG) and realizable versions of the k-ε model were used and the turbulent number of Schmidt was varied

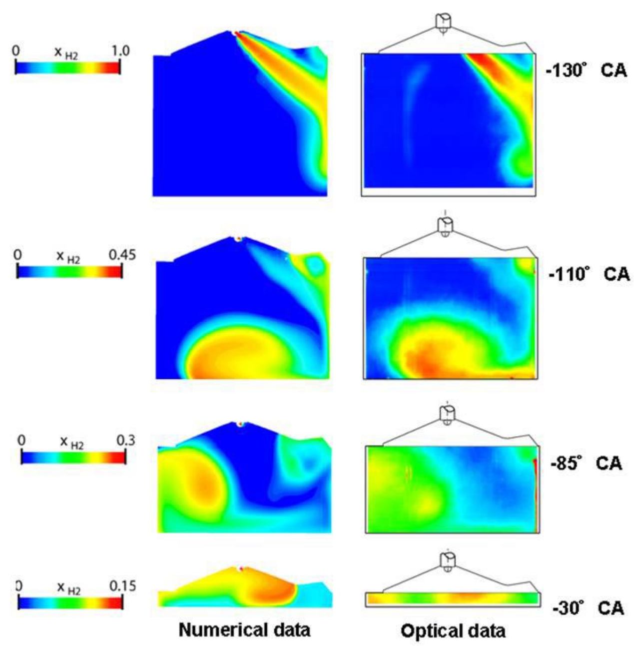


FIGURE 3. Validation of 3D-CFD Simulation Results with Optical Data

to evaluate its effect on the ratio between viscosity and diffusion and thus on the fuel mixing with surrounding air. Results showed that it is possible to provide an increased mixing, but only towards the end of the compression stroke. Reasons for this discrepancy between modeling and experiments in terms of local values of fuel concentration might depend on numerical (turbulence model, wall-treatment, injection law) and experimental (conversion of tracer fluorescence into actual fuel concentration) issues and are currently under investigation.

Potential of Turbocharging

Based on the promising results in naturally aspirated operation, initial tests with pressure conditions representative of turbocharged operation were performed. In an attempt to assess the brake thermal efficiency potential, the engine speed was increased to 3,000 RPM at which the combined losses due to wall heat transfer and engine friction should be at a minimum. Turbocharged operation on the single-cylinder research engine was replicated by simultaneously increasing intake (2 bar) and exhaust pressure (1.8 bar) based on real world test results from a turbocharged hydrogen port fuel injected engine. Early fuel injection (SOI=140 °CA BTDC) at an injection pressure of 100 bar was selected for these tests using a piezo operated 5-hole injector. Figure 4 shows the indicated thermal efficiency as well as NOx emissions results for combustion phasing sweeps at 11 bar and 14.3 bar IMEP.

In both cases efficiency-optimal combustion phasing with a 50 % mass fraction burned location around 8 °CA ATDC could be achieved without exceeding the maximum allowable cylinder pressure of 160 bar. As shown, for the lower load case, engine efficiency as well as NOx emissions decrease with later combustion phasing. At MBT spark timing and 11 bar IMEP a peak indicated efficiency of approximately 45.1% could be achieved with NOx emissions as low as 10 ppm. For the 14.3 bar IMEP point the indicated thermal efficiency further increased to a peak of 45.6% at a NOx emissions level of 90 ppm. Assuming friction values of a current production low friction engine (0.7 bar friction mean effective pressure) results in an estimated brake thermal efficiency of 43.4% for the higher load case. Further improvements in engine efficiency are expected with an optimized injection strategy and injector nozzle design. Due to unfavorable mixture stratification engine operation with more efficient, later SOI could not be achieved with the current nozzle design due to combustion instabilities.

3D-CFD simulation, validated in collaboration with Sandia National Laboratories [6,7] was employed to better understand the operational limitations with the current 5-hole injector and to develop optimized injector nozzle designs. Figure 5 shows an example

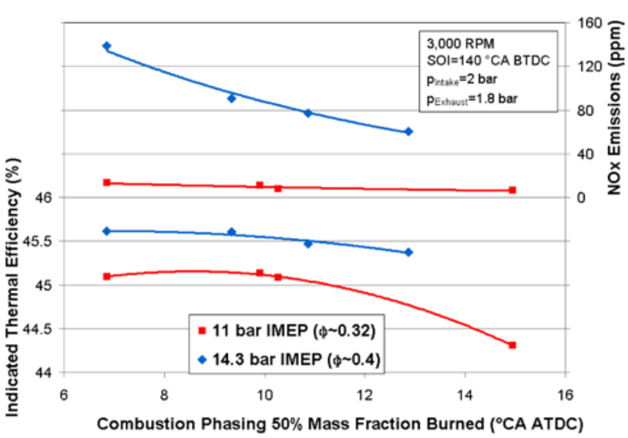


FIGURE 4. Indicated Thermal Efficiency and NOx Emissions In Turbocharged Operation

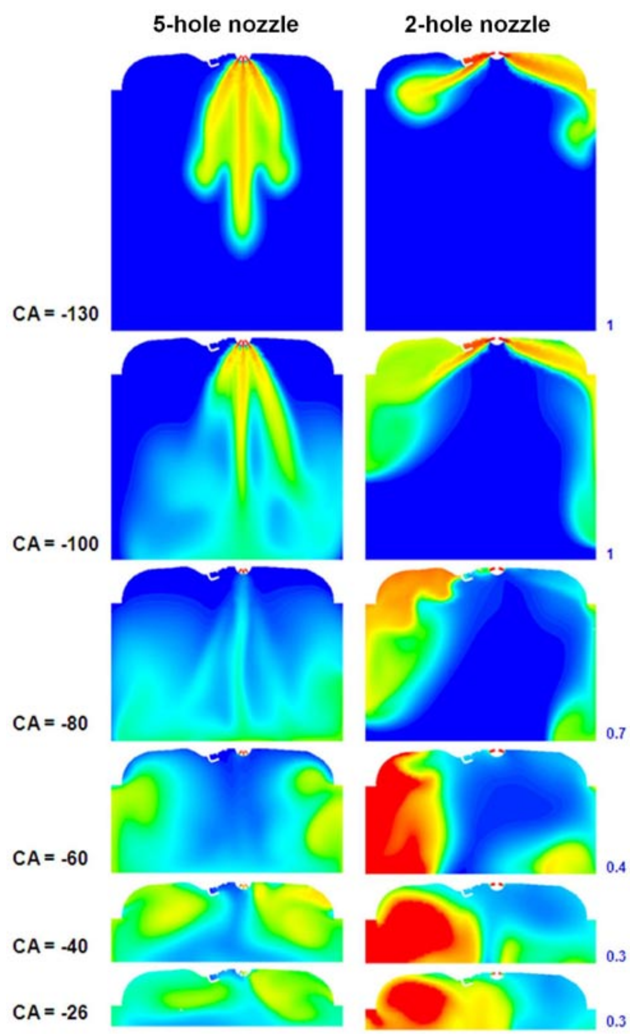


FIGURE 5. 3D-CFD Mixture Formation Results in Turbocharged Operation for Conventional 5-Hole Nozzle and Optimized Nozzle Design

result of 3D-CFD simulations for the turbocharged operating conditions at 3,000 RPM and 14.3 bar IMEP. The numbers to the right specify the maximum value of the air/fuel ratio scale. Red areas represent hydrogen air mixtures at the air/fuel ratio stated, blue areas are representative of air only. The mixture stratification resulting from injection with the 5-hole nozzle (left) shows lean zones around the spark plug. These results explain why stable engine operation could not be maintained with this injector configuration with later start of injection and extremely unstable combustion was observed.

In order to improve the mixture stratification in turbocharged operation and to possibly further increase engine efficiencies, various advanced injector nozzles were simulated for their potential to provide favorable mixture stratification. Figure 5 (right) shows the simulation results for a 2-hole injector. As can be seen, the mixture stratification around the spark plug is much richer compared to the 5-hole injector. In addition, zones closer to the cylinder liner are leaner which might further reduce wall heat losses.

Conclusions

A comparison of the two generations of hydrogen single-cylinder research engines showed up to 6% improvement in indicated thermal efficiency for a wide range of load points. It was found that the improvement is caused by an increased theoretical engine efficiency due to the higher CR as well as reduced wall heat losses due to the optimized bore/stroke ratio. Initial test runs at pressure conditions typical for turbocharged operation resulted in an estimated brake thermal efficiency of 43.4% with NOx emissions below 100 ppm. These tests were limited to early SOI and further improvements in engine efficiency are expected with an optimized injection strategy and nozzle design. In that respect, 3D-CFD simulation, which has been validated against hydrogen mixture formation results from an optical engine operated at Sandia National Laboratories, will provide invaluable input for designing optimized injector nozzles and identifying advantageous injection strategies.

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II.A.15 Advanced Hydrogen-Fueled ICE Research

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Objectives

The hydrogen internal combustion engine (H2ICE) project aims to provide the science base for the development of high-efficiency hydrogen-fueled vehicle engines. The technical focus is on direct-injection strategies, using laser-based in-cylinder measurements closely tied to numerical simulations, which are performed by both Sandia and external collaborators. Knowledge transfer to industry and academia is accomplished by publications, collaborations, and dedicated working-group meetings.

Specifically, at this point the goals of the project are to:

- Quantify the influence of injection strategies on pre-combustion in-cylinder mixing of fuel and air.
- Complement metal-engine research and development at Ford and single-cylinder engine research at Argonne National Laboratory (ANL).
- Provide data for and help in development of large eddy simulation (LES) as well as industrially applicable computational fluid dynamics (CFD) modeling.
- Investigate influence of charge stratification on the combustion event and nitric oxide formation.

Fiscal Year (FY) 2010 Accomplishments

- Characterized the pre- and post-injection in-cylinder flow-field in a direct-injection hydrogen engine (DI-H2ICE).
- Expanded the air/fuel mixing database by adding fuel concentration data from multi-hole nozzles to satisfy the critical needs of our simulation collaborators.
- Implemented a high-speed schlieren imaging system to visualize the hydrogen injection event and the flame propagation in the DI-H2ICE.
- Initiated the investigation of stratified hydrogen combustion in a DI-H2ICE.
- Distributed a "data package," including a solid model of the optical DI-H2ICE and relevant boundary conditions, to CFD collaborators.
- Established accuracy of KIVA and FLUENT simulations (performed at Lawrence Livermore National Laboratory [LLNL] and ANL, respectively) in predicting pre-ignition mixture formation for a single-hole nozzle.
- Published the first mixture formation data set and necessary documentation to initiate a simulation on the Sandia's Engine Combustion Network (ECN) [1].

Future Directions

- Complete the in-cylinder flow-field data with velocity measurements under the intake valves and in the pent-roof.
- Correlate the flame propagation characteristics with single-cycle heat release and performance parameters.
- Compare jet propagation using planar laser induced fluorescence (PLIF) and schlieren imaging for single and multi-hole nozzles.
- Coordinate meetings with LLNL and ANL to finalize the validation of the KIVA and FLUENT simulations, respectively.
- Upload air/fuel mixing data from multi-hole injectors to Sandia's ECN for easy access by modelers and finish the documentation of how to interpret and use the downloadable data posted on the ECN Web site.
- Wrap up project by documenting experiments and simulations findings in papers for journals and conferences.

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Introduction

H2ICE development efforts are focused on achieving an advanced hydrogen engine with peak break thermal efficiency greater than 45%, near-zero emissions, and a power density that exceeds gasoline engines. Such advanced engines can be part of a powertrain with efficiency similar to systems based on fuel cells [2]. With respect to these efforts, the DI-H2ICE is one of the most attractive options [3]. With DI, the power density can be approximately 115% that of the identical engine operated on gasoline. In addition, the problems of pre-ignition associated with port fuel injection can be mitigated. Lastly, in-cylinder injection offers multiple degrees of freedom available for controlling emissions and optimizing engine performance and efficiency.

The challenge with DI-H2ICE operation is that in-cylinder injection affords only a short time for hydrogen-air mixing, especially when start of injection (SOI) is retarded with respect to intake-valve closure (IVC) to reduce the compression work of the engine and to mitigate preignition. Since mixture distribution at the onset of combustion is critical to engine performance, efficiency, and emissions, a fundamental understanding of the in-cylinder mixture formation processes is necessary for optimizing DI-H2ICE operation. At the same time, predictive simulation tools need to be developed to be able to optimize injection and combustion strategies. Correct prediction of mixture formation before the onset of combustion is of great importance for any engine simulation. Quantitative imaging of this process in Sandia's optically accessible H2ICE can therefore provide a benchmark test for advanced and industrially applicable computations.

Approach

The engine in Sandia's H2ICE laboratory is a fully optically accessible, passenger-car sized single-cylinder engine with spark ignition and direct high-pressure injection of gaseous hydrogen. During the last fiscal year, a broad database of fuel concentration measurements from different nozzle designs was established. This fiscal year, the main focus has been on the characterization of the in-cylinder flow field and the use of high-speed schlieren imaging to study the hydrogen injection and flame propagation. Particle image velocimetry (PIV) enabled two-dimensional velocity measurements in the vertical symmetry plane of the cylinder. These measurements complement previous fuel distribution measurements from a single-hole nozzle with the jet oriented towards the intake valves (publication 3). This simple, yet instructive configuration has proven to be very valuable not only to gain a fundamental understanding of the physical processes involved in mixture preparation but also as a bench mark for initial simulation validation. In the second part of this year's effort, a high-speed schlieren imaging system, adapted to the optical engine, was used to achieve a fast qualitative assessment of the fuel injection and flame propagation. With this imaging tool, new nozzle designs can be quickly evaluated and the resulting jet propagation data can be used as a more suitable comparison for jet propagation validation. The flame propagation data on the other hand, can provide physical insight on how the in-cylinder flow-field and injection configuration affect engine performance.

To be consistent with the previous fuel concentration data, the engine was operated at a global equivalence-ratio of 0.25 and a speed of 1,500 rpm. Phase-locked measurements at several crank angles during the compression stroke allowed tracking the evolution of the in-cylinder flow-field with and without fuel injection. For the schlieren measurements, on the other hand, the data was continuously recorded during the compression and expansion strokes at every half crank angle degree (°CA).

In an effort to develop design optimization tools, the optical data is also being used for model development and validation by ANL and LLNL, using two different industry-type three-dimensional CFD codes. Sandia has supplied a data package including a solid model of the optical H2ICE and relevant boundary conditions for simulation initiation. The collaboration with ANL (principal investigator [PI]: Thomas Wallner) was initiated in FY 2009. ANL is using the commercial code FLUENT without any sub-models for the injection event, but a relatively fine mesh with about one million grid points. Complementing these calculations, work at LLNL (PI: Dan Flowers) has started in the second half of FY 2010. LLNL uses KIVA-3V with a jet model, derived from Lagrangian-droplet models for diesel jets, and initially a coarse mesh with about 80,000 grid points.

Results

As part of the flow-field characterization study, the intake ports were also modified by inserting a set of flow re-directing plates in order to create a pronounced tumble flow during air induction. The effect of this modified "high-tumble" flow on the mixture formation can be then compared to the one of the "low-tumble" flow from the unmodified configuration. Detailed results of this flow-field data complemented by previous fuel concentration measurements, imaged by PLIF, can be found in publications [2] and [8]. Since PLIF and PIV measurements were performed separately, it was not possible to establish an instantaneous correlation between fuel concentration and velocity. However, the mean hydrogen-molar fraction and velocity fields, shown in Figure 1, still provide a good overview of the mixture formation process.

At bottom dead center (-180°CA), the velocity flow fields indicate that for the low-tumble configuration there is not a single, well-defined tumble vortex. Instead, two counter-rotating vortices are observed: one with its center at the top left and another one at the bottom right. This pattern can also be seen in the classic results reported by Khalighi [4]. With the tumble plates inserted, on the other hand, a strong, well-defined tumble vortex is observed near the piston top, accompanied by a much weaker secondary one below the intake valves. The two-dimensional tumble ratio (TR), which is defined as the ratio of the solid-body angular speed of the flow to the engine speed, provides a further insight about the in-cylinder flow-field. Thus, Figure 2 indicates that the TR is four times greater for the high-tumble case than

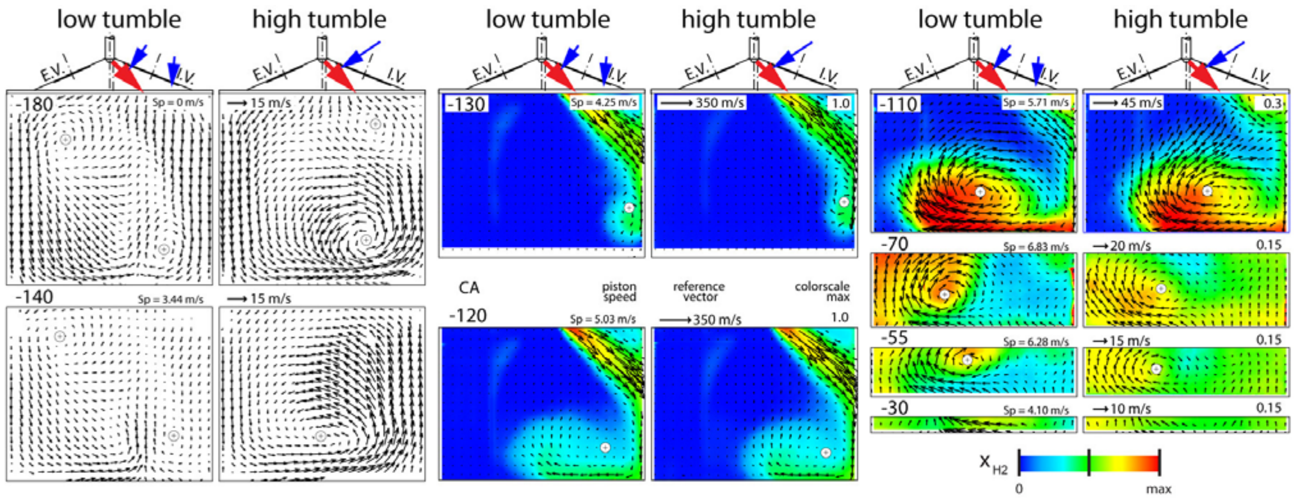

FIGURE 1. Mean velocity (arrows) and mean hydrogen mole-fraction (background color) for low and high tumble with SOI = -140°CA. The engine head with direction of injection and intake flow is shown schematically above each column. Above each image pair (left to right): crank angle, piston speed Sp, reference vector length, and peak of color scale for the mole fraction. For clarity, only every third velocity vector is plotted. The center of prominent vortices is marked by a white circle.

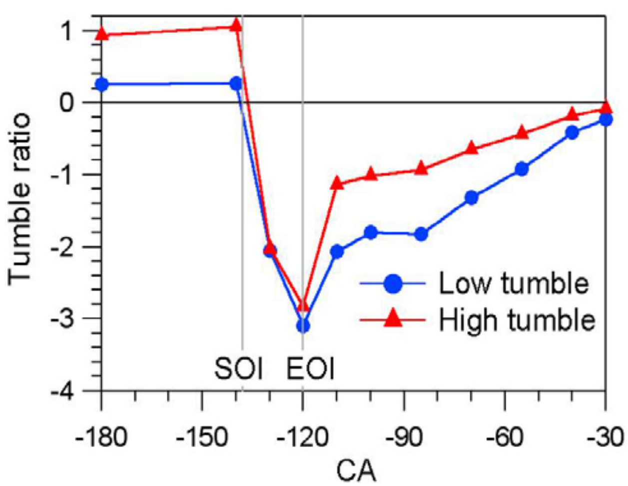

FIGURE 2. TR with injection into low- and high-tumble in-cylinder flow.

for low-tumble. This proportion is maintained up to just before the SOI, at -140°CA, despite the fact that the velocities for the low-tumble have decreased further than for the high tumble case.

At -130°CA, 10°CA after SOI, the fuel has impinged on the cylinder wall forming a wall-jet recirculation vortex. Typical centerline velocities within the free jet are measured to be about 300 m/s, more than one order of magnitude higher than typical velocities in the undisturbed flow field. Correspondingly, the TRs have been reversed in sign and increased in magnitude. While the free-jet velocities do not differ significantly between the two cases, the wall jet is already starting to show subtle influence of the intake-induced bulk flow. The lower part of the vortex head is pushed back slightly, and there is stronger back flow from this head vortex to the entrainment zone of the free jet. After the end of injection, the head of the wall-jet is the dominating feature in both scalar and velocity fields. During the remaining part of the compression stroke, the head of the wall jet moves down the liner, across the piston, and up the liner on the opposite side. In this progression, the differences between low and high tumble increase, as the fuel jet entrains intake-induced momentum. Consistent with conservation of momentum, the difference between the two tumble ratios is about the same as before injection, 0.5 to 1 unit. In a global view, the injection-induced vortex has completely absorbed the intake-induced tumble. The result is that at the end of the compression stroke the high-tumble case has a somewhat more homogeneous fuel distribution that could potentially affect the engine performance and emissions.

Another aspect of the present study is to assess the influence of the fuel distribution prior to ignition on the engine performance and emissions. As an initial attempt to explore this dependence, simultaneous flame propagation (by high-speed schlieren imaging) and cylinder pressure measurements were performed. Both fully homogeneous and stratified mixtures, for single and multi-hole nozzles, were evaluated. As an example, the results for the single-hole nozzle, with the jet pointing towards the intake valves, will be briefly described. Figure 3 shows typical single-cycle sequences of schlieren images, labeled by degrees after ignition, with the engine operating at maximum brake-torque spark timing. It is important to note that in the current engine configuration the hydrogen injector replaces the spark plug, and ignition using the spark plug is not possible. To overcome this limitation, the engine was fired by

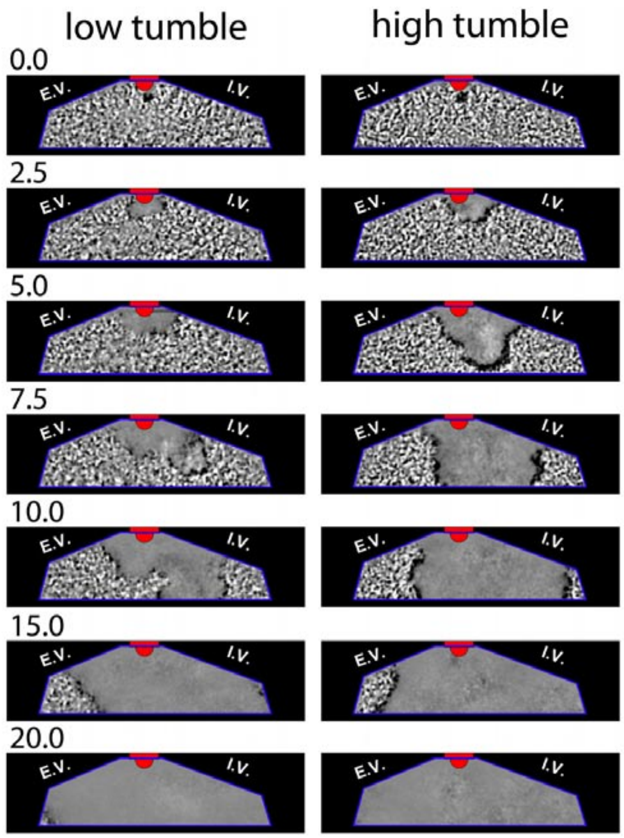

FIGURE 3. Flame propagation after hydrogen DI with SOI = -140°CA for low and high tumble. Typical single-cycle sequences of schlieren images are shown, labeled by °CA after ignition. Approximate locations of intake valves (IV) and exhaust valves (EV), and injector (red) with respect to the pent-roof windows are also shown.

creating a laser-induced plasma at the approximate location of the spark gap.

At ignition, 0°CA, a well-defined round-shaped plasma of similar size for both tumble configurations can be observed. This plasma then evolves into the developing flame kernel, which by 5.0°CA already shows a strong influence of the in-cylinder flow; i.e. the flame kernel has been elongated. Wrinkled borders, typical of a turbulent behavior, are also characteristic in both flames. As time progresses, the fuel and flow effects become more notorious and it is also clear that the flame propagates faster in the high-tumble case. This observation is consistent with results from an ensemble averaged heat release analysis (Figure 4), which also show a faster heat release rate during the initial part of the combustion process (up to around 20°CA) for the high-tumble flow. Although, visualization of the flame front during the second half of the combustion was not possible, the heat release analysis can still provide valuable information about the ongoing combustion process. Thus, contrary to the trend observed during the first part of the combustion, Figure 4 shows that

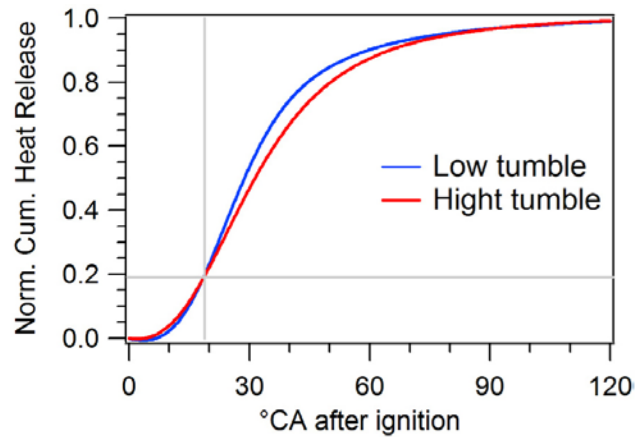

FIGURE 4. Cumulative heat release for low- and high-tumble in-cylinder flow.

after 20°CA the low-tumble case starts to release heat at a faster rate. Note also that the overall combustion duration is shorter for this case. It is well known in the literature [5], that the flame development is affected by the equivalence-ratio and flow around the flame kernel. Therefore, a plausible explanation for the trends observed above could be that while the presence of a richer fuel cloud dominates the early combustion, a stronger more turbulent in-cylinder flow overcomes the fuel effect during middle and late stages.

As it was mentioned before, we are actively collaborating with simulation groups at ANL and LLNL, who are developing industry-type simulation tools. The main accomplishments of this ongoing collaboration will be briefly discussed. Figure 5 shows an initial comparison of the simulations with the experimental results for the single-hole injector, with the jet pointing towards the intake valves. At -140°CA, before fuel injection, both FLUENT and KIVA predict relatively well the intake-induced flow field. However, subsequent to injection, the predictions of both codes are quite different. Thus the FLUENT simulation captures very well not only the jet penetration details but also the vortex roll-up. Quantitatively, on the other hand, this simulation consistently shows higher fuel concentration than the experiments at the center of the fuel cloud. In other words, the simulation predicts less fuel dispersion than what is actually measured. In contrast, the KIVA simulation does not capture the jet penetration and the subsequent vortex roll-up correctly. Although quantitatively the KIVA simulation shows better fuel dispersion than the FLUENT simulation the fuel cloud is still highly concentrated at the center and quite different from the experimental results. We suspect that the jet penetration problem at LLNL is mainly due to resolution. Computational time is an issue, but higher resolution needs to be considered, as well as the jet model should be adapted to operate properly after wall

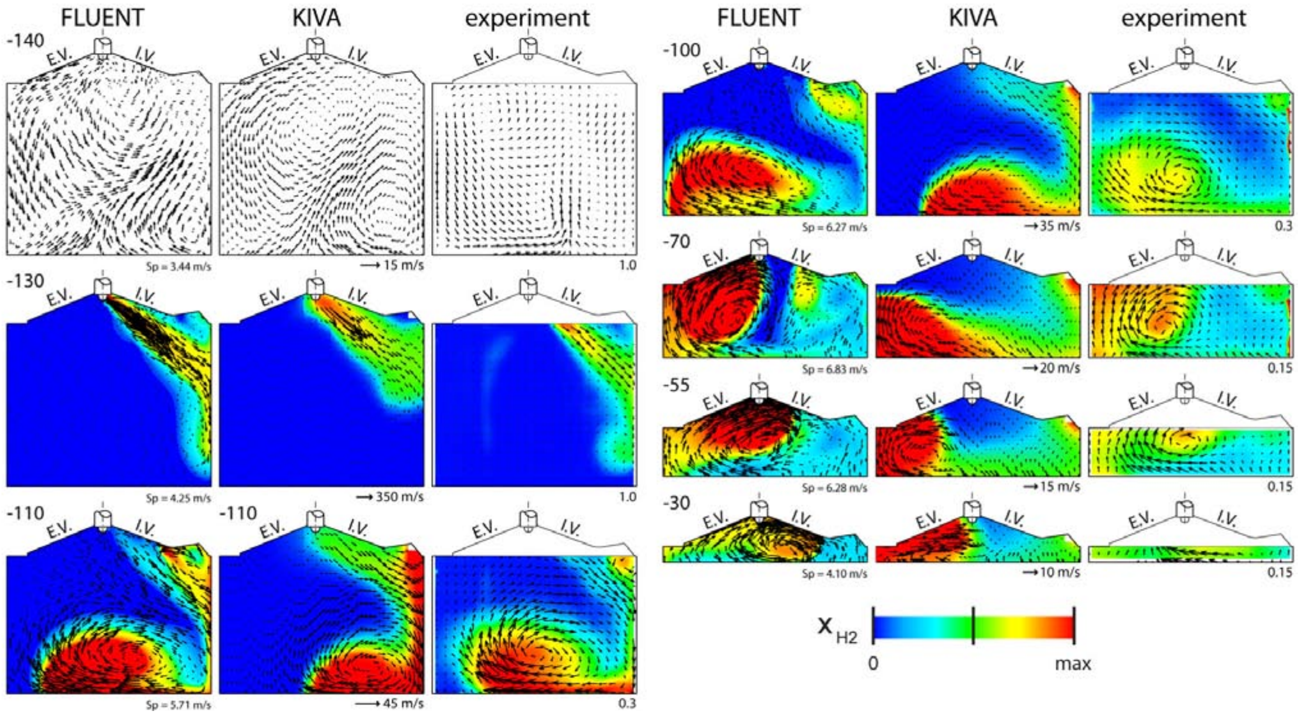

FIGURE 5. Numerical/experimental comparison of the mean velocity (arrows) and mean hydrogen mole-fraction for the unmodified intake ports with SOI = -140°CA. For the experiments the field of view spans the whole width of the cylinder bore and the full height to just below the fire deck, but not the pent-roof combustion chamber. The nomenclature follows the same convention as Figure1.

impingement. A more detailed comparison between experiments and the CFD simulation using FLUENT can be found in publication [11].

Our collaboration with simulations groups has taught us to appreciate the importance of efficient data sharing and the impact that a good data set can have beyond the immediate goals of the measurement campaign. Thus, the data from laser-based imaging and other information necessary to initiate and validate an in-cylinder engine simulation are progressively being incorporated into Sandia's ECN at http://www.sandia.gov/ecn/HE.php. Due to the simplicity of the fuel employed (gas-phase hydrogen), and the well-defined boundary conditions, our data are a very suitable complement for simple, yet insightful simulations in an engine. The hydrogen-engine database is expected to be widely used to validate future engine models, and is already being used at Iowa State University and the University of Pisa, Italy.

Conclusions

- PIV measurements of the in-cylinder flow field in the vertical symmetry plane of a direct-injection engine fueled with hydrogen were performed. The evolution of the flow field and mixture formation for two intake port configurations, generating low or high tumble, was investigated with and without fuel injection.
- In both tumble configurations, injection rapidly reverses the sign of the TR, which subsequently gradually decays in magnitude to near zero.
- As an initial attempt to study the hydrogen stratified combustion, the flame propagation has been visualized using a high-speed schlieren imaging system.
- Flame-front propagation and heat release analysis show that the intake induced flow field has a significant effect on the development of the combustion process.
- Sandia's H2ICE is being target of industry-type simulations by ANL and LLNL. The simulation at ANL is in an advanced phase and it is currently being used as a tool for injector optimization.
- The first data set from the H2ICE and relevant boundary conditions to initiate a simulation has been published into the Sandia's ECN. New data sets and supporting documentation are progressively being uploaded.

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II.A.16 Stretch Efficiency – Exploiting New Combustion Regimes

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Objectives

- Analyze and define specific advanced pathways to improve the energy conversion efficiency of internal combustion engines from nominally 40% to as high as 60%, with emphasis on opportunities afforded by new approaches to combustion.
- Implement proof-of-principle experiments for the identified pathways to stretch efficiency.

Fiscal Year (FY) 2010 Accomplishments

- Conducted detailed thermodynamic analysis on the fuel conversion efficiency impacts of several unconventional approaches to combustion, including chemical looping combustion (CLC), isothermal preheated gas phase combustion, and isothermal preheated gas phase combustion with thermochemical recuperation.
- Submitted peer reviewed journal manuscript on thermodynamic analysis of CLC and related concepts.
- Completed in-depth thermodynamic analyses of the impact of fuel type on ideal theoretical engine efficiency.
- Continued last phase of construction for the Regenerative Air Preheating with Thermochemical Recuperation (RAPTR) experiment.

Future Directions

- Complete construction and shakedown of RAPTR bench-top constant volume combustor.
- Experimentally demonstrate low-irreversibility combustion in the RAPTR bench-top apparatus. Measure time scales required for heat transfer, steam reforming, and oxygen carrier oxidation/reduction.
- Investigate feasibility of performing in-cylinder thermochemical recuperation (TCR) with a variable-valve-actuated (VVA) engine.
- Develop and implement detailed models for in-cylinder flow, heat transfer, and reforming in the VVA engine during exhaust heat recuperation.

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Introduction

In conventional single-stage internal combustion engines, most of the unutilized fuel energy ends up in the form of exhaust heat. Not all of this heat is available to produce work, because a significant portion (approximately 20-25% of the fuel exergy in conventional combustion) is converted to entropy by the thermodynamic irreversibility of the combustion process. The exergy in the exhaust heat cannot be utilized directly by the piston, but it can be converted into other forms which can be recycled and used to boost piston output. Two potential forms of exhaust heat recycling, steam generation and TCR, are of particular interest in this study. In the former, exhaust heat is used to convert liquid water into pressurized steam that generates additional piston work. In the latter, exhaust heat is used to chemically transform fuel into a higher exergy state. Under the proper conditions, the higher exergy fuel can be converted more efficiently to work by the piston. The goal of this project is to identify and demonstrate strategies that enable exhaust heat recuperation and transformation into forms that can be utilized to boost the thermodynamic efficiency of single-stage engines.

Approach

Our approach to improving internal combustion engine efficiency is based on developing a better understanding of the losses in current engines and then developing ways to mitigate them. Previous analytical studies of the exergy losses in current engines conducted in collaboration with Professors Jerald Caton (Texas A&M University) and David Foster (University of Wisconsin) identified the irreversibility of the combustion step as the largest single contributor to fuel exergy loss. In addition, these studies revealed that the thermal component of the exergy remaining in engine exhaust is not directly usable by the piston (i.e., it can't be effectively recycled to boost engine output), unless it is first transformed into a more suitable state.

Our current efforts are focused on development, analysis, and experimental evaluation of novel concepts that can accomplish such transformations of exhaust exergy, use the recycled exergy to boost engine output, and potentially reduce the inherent irreversibility of the combustion itself. In this regard, we are guided by combined input from industry, academia, and national labs, such as that summarized in the recently published report from the Colloquium on Transportation Engine Efficiency held last March at the USCAR meeting [1].

In previous years we analyzed three fundamental approaches for improving single-stage engine efficiency: counterflow preheating of inlet fuel and air with exhaust heat, TCR, and CLC. This year we began considering how these approaches, along with exhaust exergy extraction with liquid water vaporization, might be implemented using a novel 6-stroke engine cycle implemented on an advanced engine with VVA. We also began a more in-depth analysis of how variations in fuel properties can affect the theoretical efficiency of ideal internal combustion engines.

Counterflow preheating brings the air and fuel feeds closer to the temperature of the combustion process in as reversible a manner as possible, minimizing the entropy generation due to internal heat transfer. We previously considered the potential impact of counterflow preheating on combustion irreversibility [2]. TCR uses a steam reforming catalyst to convert thermal energy recuperated from the exhaust into chemical energy in the fuel reformate. In essence, exhaust heat is used to upgrade the fuel to a form with higher heating value (H_2 and CO) and higher pressure. Last year we began modeling efforts included detailed 1st and 2nd law thermodynamic analyses of the theoretical potential of TCR applied to an idealized internal combustion engine operating on various fuels [3].

This year we also completed an in-depth analysis of CLC, an approach that splits the combustion process into two steps through use of an oxygen carrier. In the first step, a solid material (often a metal) is oxidized by air, generating heat that can be used to perform work. In the second step, the oxidized solid is reduced back to its original state by a fuel, generating a stream of combustion gases undiluted by nitrogen. Typically, this process is realized through a combination of two fluidized bed reactors with the oxygen carrier solids circulating between them. CLC is an active area of research due to the benefits of a concentrated CO_2 stream in carbon sequestration, though several researchers have claimed potential efficiency advantages of CLC (see, for example, [4]). We conducted a detailed analysis of the fundamental aspects of CLC that potentially result in higher efficiency combustion, and compared it to other approaches that could exploit similar operational advantages.

Note that the three approaches listed above are not mutually exclusive. In fact, counterflow preheating is a prerequisite for high fuel conversion efficiency with either TCR or CLC. Further, one could envision a system that uses all three of these approaches, though whether or not the potential complexity and cost of such a system is justifiable is debatable. Because of the highly diverse nature of the developing fuel supply (e.g., from renewable sources), it is also recognized that the internal combustion engine efficiency variations among fuels may become a major consideration in selecting which fuels to produce in the future. Thus we have also begun including a broad range of fuels in our analysis of the thermodynamic limits of internal combustion engines to understand how fundamental fuel properties can affect those limits.

In parallel with these thermodynamic analyses, we are also developing an experimental platform (RAPTR) designed to experimentally evaluate the impacts of various approaches for recuperating exhaust exergy in more usable forms. In addition to providing a bench-top demonstration and validation of the approaches we have analyzed, we intend to use this platform to conduct investigations on the time scales of the heat transfer and chemical reaction steps at the heart of the different recuperation approaches. Armed with this data, we will develop more detailed models to investigate the efficiency and operational impacts of integrating these approaches into reciprocating internal combustion engines. We are specifically pursuing the use of a VVA engine capable of operating with a novel 6-stroke cycle for achieving the latter [5].

Results

Our fundamental thermodynamic analyses of CLC have been consolidated into an article submitted to a peer reviewed journal [6]. Some of the highlights are briefly summarized in the following. The main thermodynamic efficiency benefits of CLC depend on maintaining isothermal reaction (and associated heat release and work generation) and low-temperature-gradient heat exchange between the reactants and products of both the oxidation and reduction stages. In the absence of these features, CLC only provides a way of generating two exhaust-gas streams with different temperatures and compositions. While beneficial for carbon sequestration, exhaust-gas partitioning alone does not offer a significant exergy savings over conventional unconstrained combustion. CLC oxygen-carriers that support endothermic reduction reactions produce higher efficiencies because of the internal heat sink that is made available as an alternative to rejecting heat to the environment. For oxygen-carriers that involve exothermic reduction reactions, it is not generally possible to achieve a feasible equilibrium temperature in the reduction reactor. Nevertheless, it appears that the efficiency can still increase as the reduction reactor temperature increases, and the reaction becomes more irreversible. Thus it appears that closer approach to chemical equilibrium is not, by itself, sufficient to improve efficiency.

The traditional concept for CLC depends on transporting large masses of oxygen-carrier solids and small-temperature gradient heat exchange between counterflowing oxygen-carrier solids streams and between volumetrically unbalanced gas streams seems to be one of the biggest practical drawbacks in implementation of CLC. A modified form of CLC that utilizes a fixed bed of solids (referred to here as SCOT), overcomes the need for transporting solids. But SCOT suffers from a significant exergy penalty associated with heating and cooling the stationary oxygen carrier solids during each gas modulation cycle. It is not clear how this drawback can be overcome when endothermic and exothermic reactions at different temperatures are required.

Isothermal combustion with simultaneous work generation and carefully constrained heat exchange between products and reactants are the keys to achieving most of the efficiency benefits expected from CLC. It appears likely that these effects could be achieved without the need of circulating oxygen-carrier solids or utilizing impractical oxygen storage materials that have the endothermic properties required by CLC. One promising new approach (depicted in Figure 1) utilizes TCR combined with isothermal reaction. Like the endothermic reduction reaction in CLC, hydrocarbon reforming can provide an internal heat sink for generating work that does not result in external heat transfer to the environment. This version of TCR can theoretically achieve second law efficiencies 10-15% higher than are currently possible for ideal heat engines.

Since CLC and SCOT are not readily adaptable to existing architecture internal combustion engines,

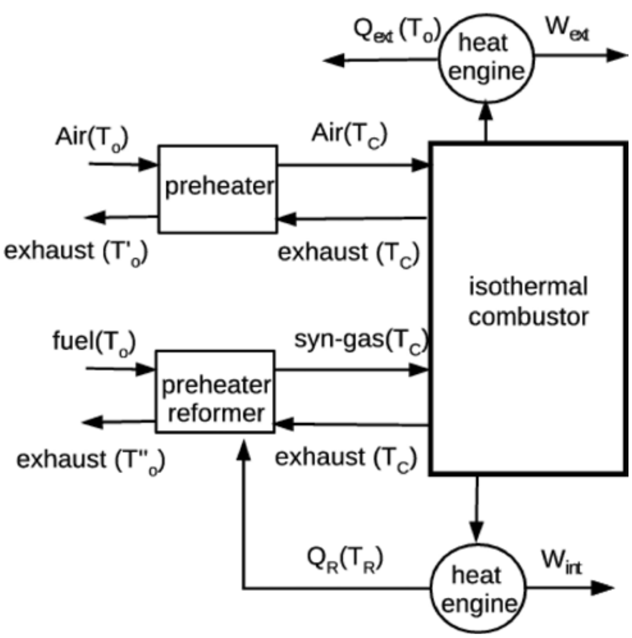

FIGURE 1. Conceptual schematic of an ideal TCR process combined with isothermal combustion. TCR implemented in this way provides an alternative approach for achieving some of the efficiency benefits of CLC.

neither of these approaches would appear to provide a transforming route to higher internal combustion engine efficiencies in the near future. However, utilization of oxygen carriers for storing and releasing exhaust energy as needed for assisting in the optimization of advanced combustion does appear to be a real possibility. A good example of this is in modulating the temperature of residual gases as needed for homogeneous charge compression ignition. Oxygen carrier materials located on or near the exhaust valve could be used to heat or cool recirculated exhaust by exposing them to excess fuel or air. Thus utilization of basic elements of SCOT for advanced engine control appears to us to be a promising area for future investigation.

As noted in last year's report, TCR appears to offer more near-term benefits to existing engines if the pressure boost generated by fuel reforming can be utilized. For an ideal stoichiometric engine fueled with methanol, TCR can increase the estimated ideal engine efficiency by about 5% of the original fuel exergy. For ethanol and isooctane the estimated efficiency increases for constant volume reforming are 9% and 11% of the original fuel exergies, respectively. The efficiency improvements from TCR are due to lower exhaust exergy losses and reduced combustion irreversibility with the reformed fuels. Currently, we are considering both extra-cylinder and in-cylinder approaches for implementing TCR. The 6-stroke implementation of in-cylinder exhaust heat recuperation is described in more detail in the following.

As discussed previously, the RAPTR experiment is designed to provide a test bed for measuring critical elements of exhaust gas heat recuperation and transformation. Construction of the RAPTR experiment is nearing completion. Remaining work includes additional wiring, insulation, and programming of the computer-based control system. Experiments planned for the near future include: quantifying post-combustion availability with and without TCR; measuring rates of gas/solid heat transfer; measuring rates of catalytic and non-catalytic steam reforming reactions; screening potential heat transfer materials and catalysts; and evaluating heat exchanger and catalyst configurations (packed bed, monolith, wire mesh, etc.). A photograph of the present setup is shown in Figure 2.

Studies of the 6-stroke cycle illustrated in Figure 3 have been initiated as a potential way to implement exhaust heat recuperation via both steam generation and TCR. The original version of the cycle with steam injection was conceived and modeled under an ORNL Laboratory Directed Research and Development project. With interest also growing in TCR, it became apparent that this approach could also lend itself to fuel reforming as well, either in combination with steam generation or separately. Experiments are being planned for the 2-liter experiment engine at ORNL with a Sturman VVA once preliminary modeling studies have been completed.

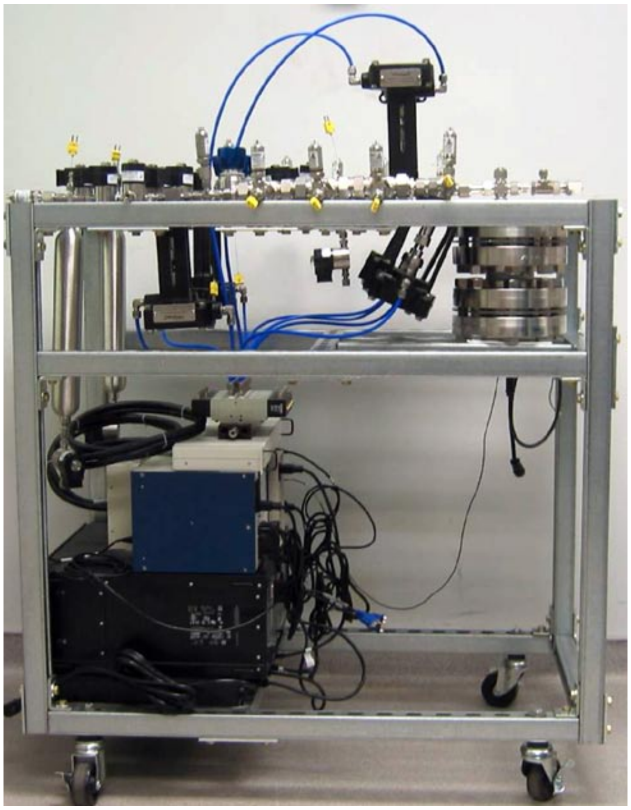

FIGURE 2. Side view photograph of the RAPTR apparatus assembly. The RAPTR apparatus provides a way to experimentally measure rates for heat and mass transfer and reforming reactions driven by recycled exhaust heat under controlled, constant volume conditions.

Conclusions

Inclusion of thermochemical fuel reforming appears to have the potential for making CLC a more practical reality. However, even in this form, CLC would probably not be feasible on existing internal combustion engine architectures. It appears instead that the greatest near-term value for the oxygen carrier concept used for chemical looping might be more directly utilized as a means for modulating advanced combustion modes on existing engines. On the other hand, exhaust heat recuperation via both thermochemical fuel reforming and vaporization of liquid water appear to have the potential for boosting the thermodynamic efficiency of existing single-stage internal combustion engines modified to include VVA. Implementation of both types of exhaust heat recovery require experimental and modeling studies of the associated rates of heat and mass transfer and, in the case of thermochemical recuperation, identification of appropriate non-catalytic and catalytic reforming kinetics. The RAPTR apparatus at ORNL is designed to provide a platform for making basic experimental measurements in support of these needs. Future modeling studies will require resolving physical details of these processes with multi-zone and computational fluid dynamics tools. The ultimate goal should be to demonstrate the benefits of exhaust heat recuperation on an experimental engine with 6-stroke cycle capability.

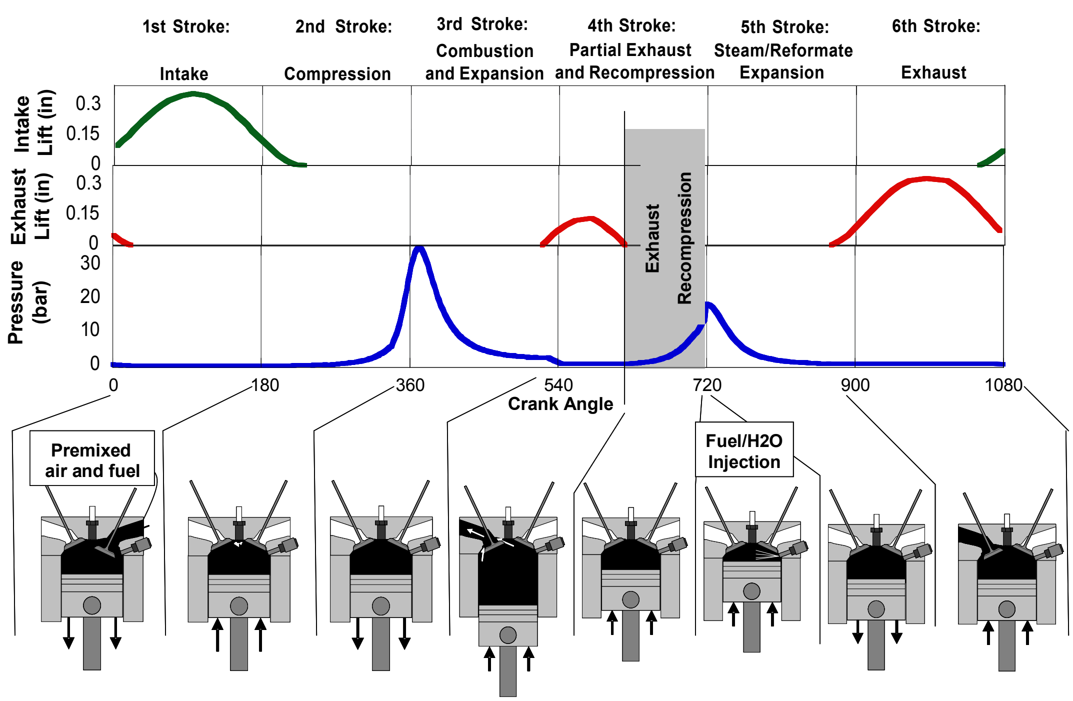

FIGURE 3. Illustration of the 6-stroke cycle concept for exhaust heat recuperation. One method suggested for implementing TCR with the 6-stroke cycle would involve designating a single cylinder in multi-cylinder engines for reformate production.

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II.A.17 Advanced Boost System Development For Diesel HCCI Application

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- ConceptsNREC, White River Junction, VT

Objectives

The overall objective is to support industry efforts of clean and efficient diesel engine development for passenger and commercial applications. More specifically:

- ConceptsNREC objectives: lead boost system design, optimization, computer-aided engineering (CAE) stress analysis and fabrication of prototypes as well as flowbench testing; provide turbocharger maps for various turbo technologies to support system level simulation/integration.
- Wayne State University objectives: lead computational fluid dynamics (CFD) analysis and analytical validation of various turbocharger concepts designed by ConceptsNREC.
- Ford Motor Company objectives: lead system integration, cascade system requirement, boost system development design target, and validation and demonstration of light-duty diesel engine fuel economy improvement.

Fiscal Year (FY) 2010 Accomplishments

Aerodynamic design, CFD validation and structure analysis of the turbocharger was completed. However, based on the findings from flow bench tests, additional design changes were made on compressor and turbine for potential 4-6% further performance enhancement. CFD validation, CAE structure analyses for high/low cycle fatigue durability compliance as well as flow bench test will be repeated in the next few months. The new design concepts will be migrated to smaller turbocharger development early in 2011.

Prototype fabrication and flow bench validation of the advanced boost systems were completed.

- The complete compressor wheel and mixed flow turbine were fabricated and integrated on a production BorgWarner BV70LF.
- The flow bench data indicated that the advanced compressor wheel has a substantial efficiency improvement over conventional compressors with similar size, especially at low mass flow area where most customer driving cycles are populated.
- A mixed flow turbine demonstrated anticipated efficiency improvement at low speed ratio area, along with 4% improvement in flow capacity with the similar inertia of a conventional radial flow turbine.
- During 2010, four presentations were made at the Society of Automotive Engineers Congress, Emissions2010 and Directions in Engine-Efficiency and Emissions Research conferences, respectively.

Future Directions

- Migrate the same technologies to a small turbocharger design/optimization to support light-duty diesel applications.
- Design and fabricate the actuation system for the advanced compressor for small chassis certification applications.

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Introduction

Diesel homogeneous charge compression ignition (HCCI) and low-temperature combustion (LTC) have been recognized as effective approaches to dramatically reduce diesel emissions. However, high levels of exhaust gas recirculation (EGR) are needed to achieve homogeneous or partially homogeneous combustion modes, which often drive the compressor and turbine into less efficient or even unstable operational areas.

This project focuses on complete and optimal system solutions to address boost system challenges, such as efficiency degradation and compressor surge, etc, in diesel combustion/emission control system development, and to enable commercialization of advanced diesel combustion technologies, such as HCCI/LTC.

Approach

There are several boosting concepts that have been seen in the literature and will potentially be helpful to extend operation range with decent efficiency. They are primarily single stage turbochargers so that they are cost effective, have small package space, small thermal inertia while providing enough EGR that is required by advanced combustion concepts such as HCCI/LTC.

This project will particularly focus on the following:

- Compressor variable inlet guiding vane – by varying the air rotational flow direction at the compressor inlet to have a better alignment with compressor blades, the compressor can work at a smaller mass flow without surge or stall. Similarly, an optimized casing treatment on the compressor housing can also re-align the re-circulated air flow to extend the surge margin.
- Variable geometry compressor – an optimized airfoil diffuser can push the surge line to a lower flow rate on the compressor map, often at the expense of efficiency in off-peak operation range and possibly reduce full flow capacity. A variable vane at compressor diffuser areas can maintain high compressor efficiency at a wide range of operation.
- Dual-sequential compressor volute/outlet – bifurcated volute that has a dual outlet and can be opened sequentially to match air exit velocity to compressor vane geometry. This method is an alternative design concept that is simpler, more economical and potentially more durable than a variable geometry compressor mentioned before since it has only one moving part: a switching valve.
- Mixed flow turbine is an attractive option to improve efficiency on the turbine side. Current turbine efficiency at light load and low speed is substantially lower than its peak efficiency. The target of this study will focus on high turbine efficiency at lower speed ratio to improve EGR pumping capacity and vehicle fuel economy on customer driving cycles.

These technologies have been fully investigated with well-validated numerical simulation methods. Some of them have been investigated via flow bench testing. The variable diffuser vane compressor was eliminated based on flow bench testing due to larger than expected operational range constraints; the variable inlet guide vane technology was considered non-compatible with our optimized impeller geometry and did not demonstrate further benefit; and the dual-sequential compressor volute has merit in efficiency and operational range enhancement based on numerical study. However, this technology has difficulty to be implemented in small turbochargers due to package space constraints. Therefore, current study on the compressor side is focused on advanced compressor impellers, and advanced casing treatment for high compressor efficiency over wide operation range; for the turbine the focus of the study is on a mixed flow turbine wheel, matched with a production variable geometry nozzle turbine center housing.

Results

1. Figure 1 is the fabricated parts of two compressor wheels and the mixed flow turbine wheel.
2. Figure 2 is the turbocharger assembly. Multiple compressor casing treatment inserts are replaceable for optimal performance.
3. Figure 3 shows that the advanced compressor efficiency has been improved over a wider operation range, compared with conventional centrifugal compressors.
4. Further improvements have been identified and numerically validated, as illustrated by Figure 4 and will be incorporated in the small chassis certification compressor design.
5. Figure 5 shows that the mixed flow turbine also demonstrated efficiency improvement during the hot flow bench test.

FIGURE 1. Mixed Flow Turbine and Compressor Wheels were Fabricated

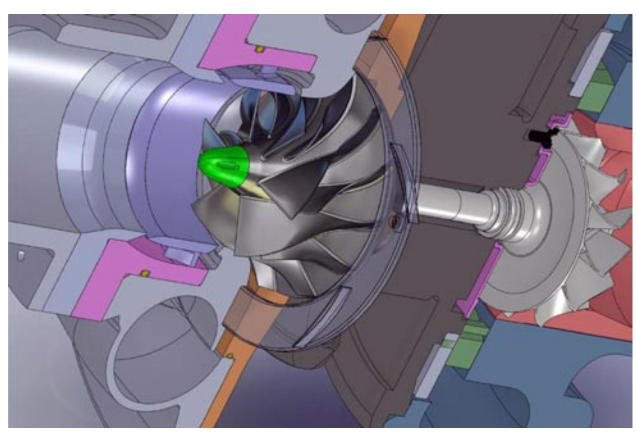

FIGURE 2. Turbocharger Assembly

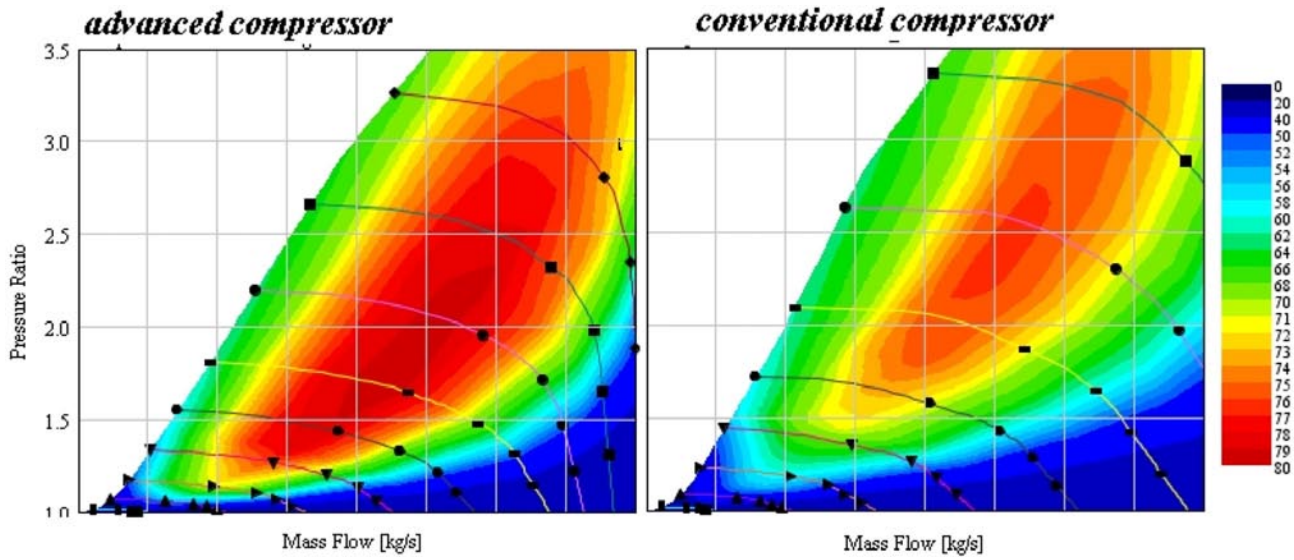

FIGURE 3. Compressor Efficiency Contour Plots, Advanced vs. Conventional Compressor

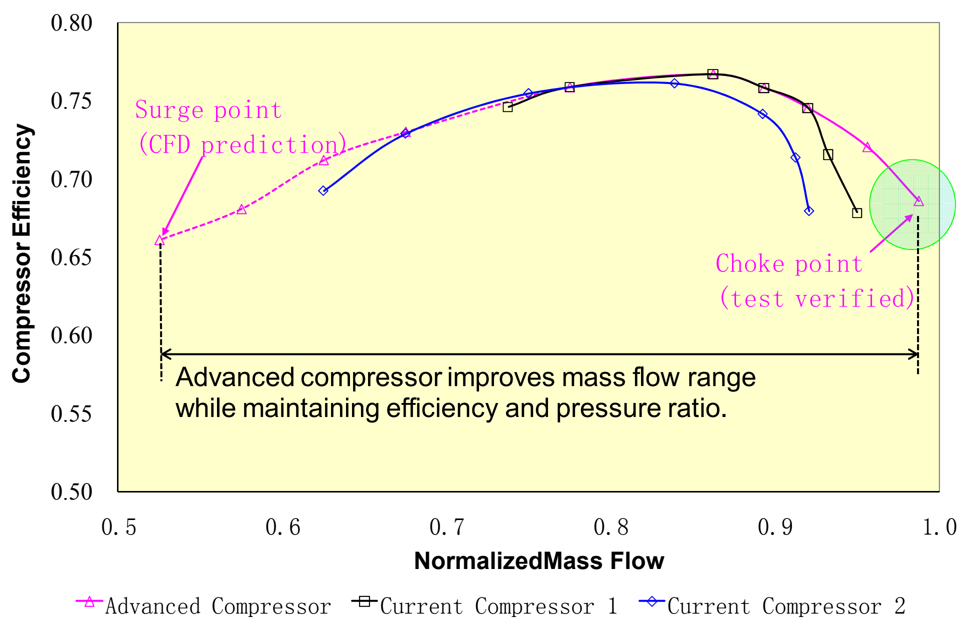

FIGURE 4. Further Improvement in Compressor Range Extension has been Demonstrated Numerically (on the surge side) and Experimentally (on the choke side)

Conclusions

The flow bench tests have demonstrated efficiency improvement on both the compressor and turbine, especially at low compressor mass flow and low turbine speed ratio areas where most customer driving cycle will be populated on. The compressor high efficiency area was extended by more than 25% compared with conventional centrifugal compressors. The test data also correlate very well with the prior numerical simulations, especially three-dimensional CFD predictions. The numerical analysis tools will continue to guide future design optimization for better efficiency and wider flow range on small chassis certification turbocharger applications. The next steps will include: fabrication of the redesigned compressor and turbine wheel for small turbochargers, development of an actuation system, and flow bench test validation and engine dynamometer tests.

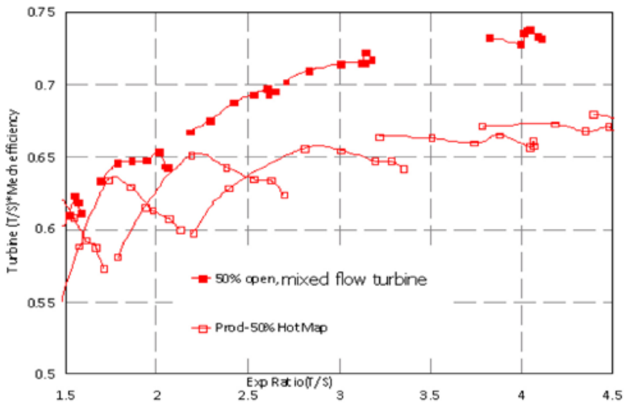

FIGURE 5. Efficiency Improvement of the Mixed Flow Turbine over the Radial Flow Turbine

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II.A.18 Visualization of In-Cylinder Combustion R&D

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Objectives

- Quantify the influence of low-cetane fuel ignition properties to achieve clean, high-efficiency combustion.
- Optimize the advanced controls available to create a combustion system that retains diesel-like efficiency while reducing oxides of nitrogen (NOx) and other criteria pollutants compared to conventional diesel.
- Demonstrate the use of combustion imaging techniques to aid in determining the operational boundaries of gasoline compression ignition operation.

Fiscal Year (FY) 2010 Accomplishments

- The General Motors (GM) 1.9 L turbodiesel engine, operating on 85 Research octane number (RON) gasoline, was successful in producing high power density (3,000 revolutions per minute, RPM - 16 bar brake mean effective pressure, BMEP), high efficiency (40% brake thermal efficiency, BTE at 2,750 RPM - 12 bar BMEP) and low NOx (less than 1 g/kW-hr at 2,750 RPM - 12 bar BMEP).
- Use of the injection system, combined with long ignition delay, to control the engine at a variety of speeds and loads with little difficulty (1,500 RPM - 2 bar, 2,000 RPM – 5 bar, 2,500 RPM – 8 bar and 2,750 RPM – 12 bar).
- Several types of low cetane fuels were operated successfully using this strategy; iso-paraffinic kerosene, 75 RON gasoline, and 65 RON gasoline.

Future Directions

- Evaluate the influence of lower compression ratio (CR) on successful ignition of gasoline in this engine (14:1, 15:1 and 16:1) compared to the stock 17.5:1 CR.
- Conduct experiments that will allow for transient operation of this combustion system to determine the suitability for application in an automobile.
- Optimize the operating parameters to provide for smooth transient operation while retaining the high efficiency and ultra-low emissions signature.

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Introduction

Current diesel engines already take advantage of the most important factors for efficiency – no throttling, high compression ratio and low heat rejection. However, diesel combustion creates a significant emissions problem. Mixing or diffusion combustion creates very steep gradients in the combustion chamber because the ignition delay of diesel fuel is extremely short. Particulate matter (PM) and NOx are the result of this type of combustion, requiring expensive after-treatment solutions to meet Environmental Protection Agency emissions regulations.

The current work seeks to overcome the mixing controlled combustion dilemma by taking advantage of the long ignition delay of gasoline to provide much more premixing of fuel and air before ignition occurs. This premixing allows for the gradients of fuel and air to be much less steep, eliminating the PM-NOx tradeoff of mixing controlled combustion.

Approach

The intent of this project is to utilize the long ignition delays of low cetane fuels to create an advanced combustion system that generates premixed (but not homogeneous!) mixtures of fuel and air in the combustion chamber. As reported in several articles, if the local equivalence ratio is below 2 (meaning at most, twice as much fuel as oxidizer) and the peak combustion temperature is below 2,000 K (usually using exhaust gas recirculation [EGR] to drop the oxygen concentration below ambient 21%, thereby slowing the peak reaction rates and dropping the peak combustion temperature), a combustion regime that is very clean and yet retains reasonably high power density is achieved. Figure 1 shows this contour plot, generated by Kitamura et al. [1].

The challenge to this type of combustion system is the metering of fuel into the combustion chamber needs to be precise, both in timing and amount. If too much fuel is added too early, a "knocking" type of combustion occurs, which creates unacceptably high combustion noise or worse. If not enough fuel is added, ignition may not occur

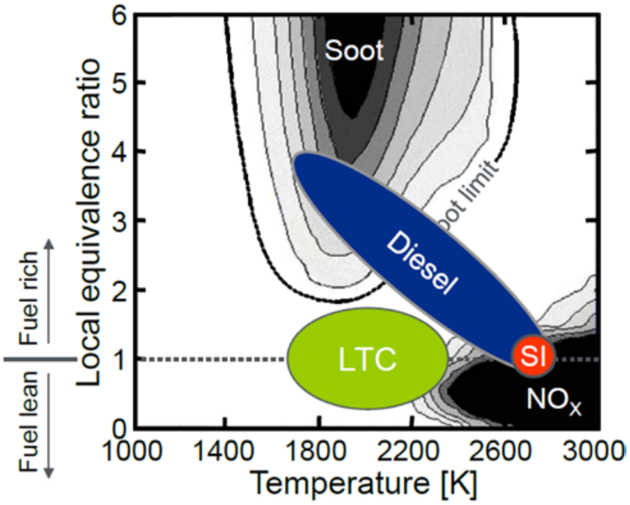


FIGURE 1. Soot and NOx as Function of Phi and Combustion Temperature

at all and raw hydrocarbons exit the exhaust. Control over the relevant operating parameters is very important.

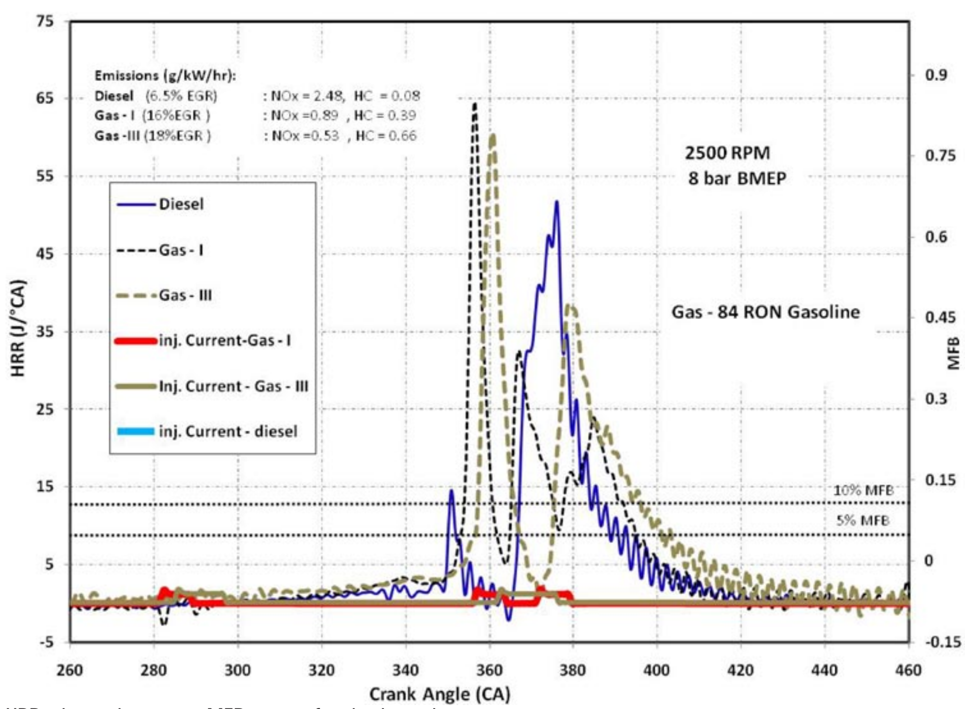
Results

Successful operation of several different points, provided by GM, was achieved using gasoline fuel. As can be seen in Figure 2 and Figure 3, the injections occur quite early compared to the diesel injections into the combustion chamber. The long ignition delay allows for significant premixing, leading to low PM formation. The NOx emissions decrease by a factor of 3-5, while hydrocarbon and carbon monoxide emissions only slightly increase under the same conditions.

Figures 2 and 3 also show that the primary control method for this type of combustion regime is injection timing, which is very desirable because injection timing can be adjusted very rapidly as engine conditions may change. Further work will be done to test the sensitivity of parameters like intake temperature, EGR level and boost to make this combustion system even more robust.

Conclusions

- Partially premixed charge compression ignition, using gasoline fuel, can be a very effective way to maintain power density and high efficiency while reducing NOx by up to 300-500%.
- The opportunity to utilize this combustion system is excellent, because of the high responsiveness of injection systems to changing engine conditions.
- The efficiency of this combustion system is close to double that of conventional spark-ignition gasoline, especially at low speeds and loads.



HRR – heat release rate; MFB – mass fraction burned

FIGURE 2. Injection Phasing and Heat Release for Gasoline and Diesel, 2,500 RPM – 8 bar BMEP

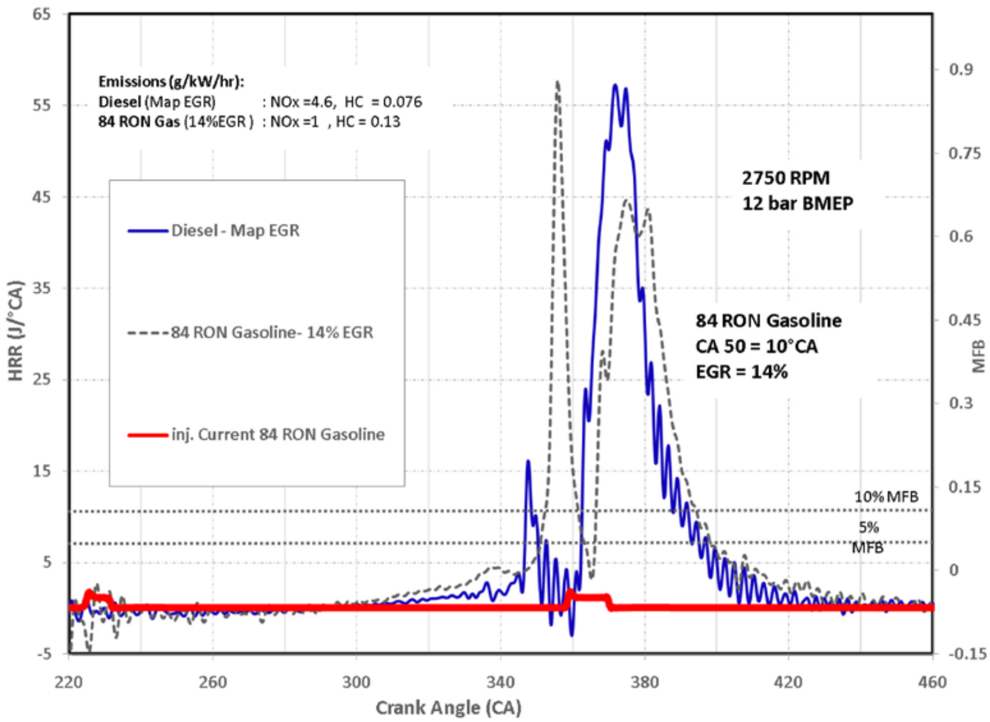


FIGURE 3. Injection Phasing and Heat Release for Gasoline and Diesel, 2,750 RPM – 12 bar BMEP

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FY 2010 Publications/Presentations

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II.A.19 Very High Fuel Economy, Heavy-Duty, Truck Engine Utilizing Biofuels and Hybrid Vehicle Technologies

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- Volvo Powertrain, Goteborg, Sweden
- Volvo Technology AB, Goteborg, Sweden
- University of California, Los Angeles, CA
- West Virginia University, Morgantown, WV

Objectives

- Develop a highly efficient engine system, including mild hybridization, to reduce CO_2 emissions from a long haul truck by >10%, in comparison to current production technology, while meeting U.S. 2010 emission levels.
- Develop an engine platform that is capable and tolerant of bio-diesel specifications.
- Develop multi-fuel vehicles and drivetrains that are compatible with the long-term use of combinations of fossil and bio-based diesel fuels.

Fiscal Year (FY) 2010 Accomplishments

- An MD13 engine has been developed and tested on a dynamometer at U.S. 2010 emission levels showing about 5% better fuel consumption than the current U.S. 2010 target. A seven-hole nozzle was compared with the current production injectors producing lower soot emissions at the same oxides of nitrogen (NOx) and fuel consumption levels. In addition, computational fluid dynamics (CFD) analysis and experiments have shown that high performance pistons can improve thermal efficiency by an additional 1%, giving a slight decrease in soot with other emission levels remaining unchanged.
- A parallel configuration for a Rankine cycle waste heat recovery (WHR) system comprised of an exhaust gas recirculation (EGR) sub-cooler and an exhaust stack heat exchanger has been selected, which also allows low-temperature EGR without an additional cooler. A binary mixture of ethanol-water will be used as the working fluid in conjunction with a stainless steel evaporator and a piston expander. With this configuration, the Rankine cycle power into the drivetrain is predicted to be 9.9 kW at the B50 point (~7% of engine power) and 24.5 kW at the C100 point (~8.5% engine power).
- Analyses of mechanical, electrical, and electromechanical transmission alternatives to connect a turbo-compound (TC) power turbine to the engine crankshaft indicate that a mechanical transmission is best in terms of fuel consumption. An improved mechanical transmission will be designed for use in the engine for the demonstrator truck.
- A powershift (PS) transmission has been used to evaluate powertrain functionality. Initial control software, including high functionality gearshift strategies, has been evaluated in a realistic hardware-in-the-loop test environment. Simulation indicates a much more continuous level of output engine torque and speed during acceleration as compared to a conventional manual transmission.
- The simulation is being employed to optimize the hybridization of the powertrain that will be implemented in the long-haul demonstrator. A new energy management strategy, employing a more aggressive discharge of the electrical storage system (ESS) and a different electric motor (EM) vs. internal combustion engine (ICE) torque distribution was used and showed a 0.6% improvement in fuel consumption. In addition, hybrid system simulations showed that increasing ESS and EM sizes/capacities above 200 kW results in no further gain in fuel consumption due to added hybrid system weight.
- An early biofuel endurance truck certified to U.S. 2010 emission levels and fuelled with a B20 biofuel-diesel blend (20% derived from soy oil, a fatty acid methyl ester [FAME] biofuel) was put into service by VPNA. Three weeks of soot loading were run prior to the start of road testing and weekly emissions conversion efficiency tests have been performed. The results indicate that the soot loading is consistent with pure diesel fuel. The emissions conversion tests have shown no significant decreases in the efficiency of the exhaust aftertreatment system during mileage accumulation.

Future Directions

- Phase 2: Continuation of the development of engine/transmission hardware/software design specifications and preparation for prototype procurement.
- Phase 3: Engine/transmission hardware/software development, testing and verification of components.
- Phase 4: System assembly and demonstrator vehicle verification using biofuels and blends.

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Introduction

This project, referred to as the Bilateral Program, is a cost-shared effort being conducted by the Volvo Powertrain North America division of Mack Trucks, Inc. (a unit of Volvo AB) and Volvo AB of Sweden. It is jointly funded by the U.S. Department of Energy and the Swedish Energy Agency. The overarching goals are the reduction of petroleum consumption and a reduction in both regulated emissions (hydrocarbons [HCs], CO, NOx and particulate matter [PM]) as well as greenhouse gases (GHGs), mainly CO_2, from heavy-duty diesel engines in the truck fleet. To that end, an extensive set of technologies is being studied and developed which can be implemented and integrated as a system into heavy-duty vehicles. The major areas of focus include the development of a very high efficiency powertrain system, including an engine equipped with a turbocompound unit, an automatic PS transmission and mild hybridization, as shown in Figure 1. An additional area of focus is the adaptation of the diesel engine for the use of biofuels, primarily FAME fuels, and blends of FAME biofuels with conventional petroleum-based diesel fuel.

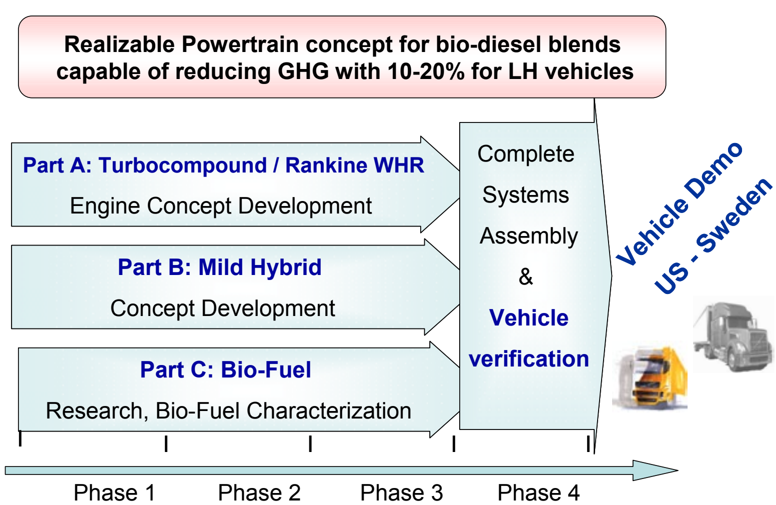


FIGURE 1. Bilateral Program Elements and Workflow

Approach

The effort directed at developing a highly efficient powertrain system includes fundamental combustion investigations such as the effect of diesel injection pressure and rate shaping to be implemented in an engine intended to operate within an optimized speed range, allowing further optimization of fuel efficiency and emission control. In addition to the development of the reciprocator itself, exhaust WHR is being utilized to further improve net engine output efficiency. Two different WHR concepts have been investigated – capturing exhaust energy through a turbine located in the hot exhaust stream (TC) and the use of a Rankine bottoming cycle, based on exhaust energy, to power a turbine. Both WHR systems can produce energy in either mechanical form or, using a conversion device, in electrical form for storage. Hybrid components and features are included in the powertrain concept allowing for engine shutdown at idle and the recovery of inertial energy of the vehicle during deceleration. Finally, an automatic PS transmission is used so that the engine can be more effectively operated under optimal conditions and, also, to reduce the losses in the driveline between the engine output and the production of tractive force at the tire-road interface. Figure 2 shows the targeted contributions to energy efficiency improvement from the various technologies which are incorporated.

Although a variety of fuels have been evaluated, the biofuel research has concentrated on the testing of FAME fuels, both pure and in blends with a standardized Swedish EC1 (Environmental Class 1) fuel, containing less than 10 ppm sulfur (by weight). Systematic single-cylinder tests have been carried out to determine thermal efficiency, combustion characteristics, regulated and unregulated emissions as well as the tradeoff between brake specific NOx and brake specific soot and between brake specific fuel consumption and brake specific NOx. These tests were conducted in parallel with injection simulation and combustion CFD calculations. In addition to the basic combustion work, particulate particle size distributions have been measured and, using specialized test equipment, the effects of biodiesel fuels and blends on the type of soot, the rate of soot combustion and the fraction ash formation were studied in order to assess the effect of these fuels on diesel particulate filter function and regeneration. Initial on-the road endurance tests with a 20% blend of soy oil in diesel fuel have been carried out in the U.S. showing no adverse in-cylinder emissions effects or deterioration of the exhaust aftertreatment system (EATS).

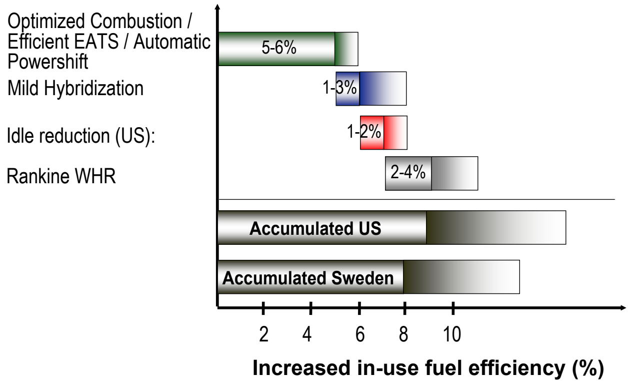


FIGURE 2. Targets for Improvements to Energy Efficiency from Technologies Employed in the Project

Selected Results

Rankine Cycle WHR System

A large number of system layouts and choices of the working fluid are possible. Extensive thermodynamic simulations were performed to select the optimum system. These simulations were carried out at the B50 engine operating point (cruise) and at the C100 point (grade). Among the simulation results that were used to select the best choice from the various alternatives were the WHR system power output, achievable EGR gas temperature, overall heat balance and heat exchanger pinch points. In addition, factors related to cost, packaging and safety were also carefully considered.

As a result, a parallel configuration for a Rankine cycle WHR system comprised of an EGR sub-cooler and an exhaust stack heat exchanger has been selected as shown in Figure 3. In addition to heat input into the bottoming cycle, this system also allows for low-temperature EGR without an additional cooler. A binary mixture of ethanol-water will be used as the working fluid in conjunction with a stainless steel evaporator and a piston expander. With this overall configuration, the Rankine cycle power into the drivetrain is predicted to be 9.9 kW at the B50 point (~7% of engine power) and 24.5 kW at the C100 point (~8.5% engine power).

Turbocompound Transmission System

The objective is to improve the overall efficiency of the engine and power turbine as a system.

Three different types of transmission connecting the power turbine and engine crankshaft have been investigated:

- Fully mechanical transmission with fixed speed ratio.
- Electric transmission, power flow through electric units with full variable speed ratio.
- Electromechanical transmission with mechanical-electrical power split.

The differential fuel consumption results shown in Figure 4 indicate that a fixed speed ratio fully mechanical system is most efficient. Therefore, further

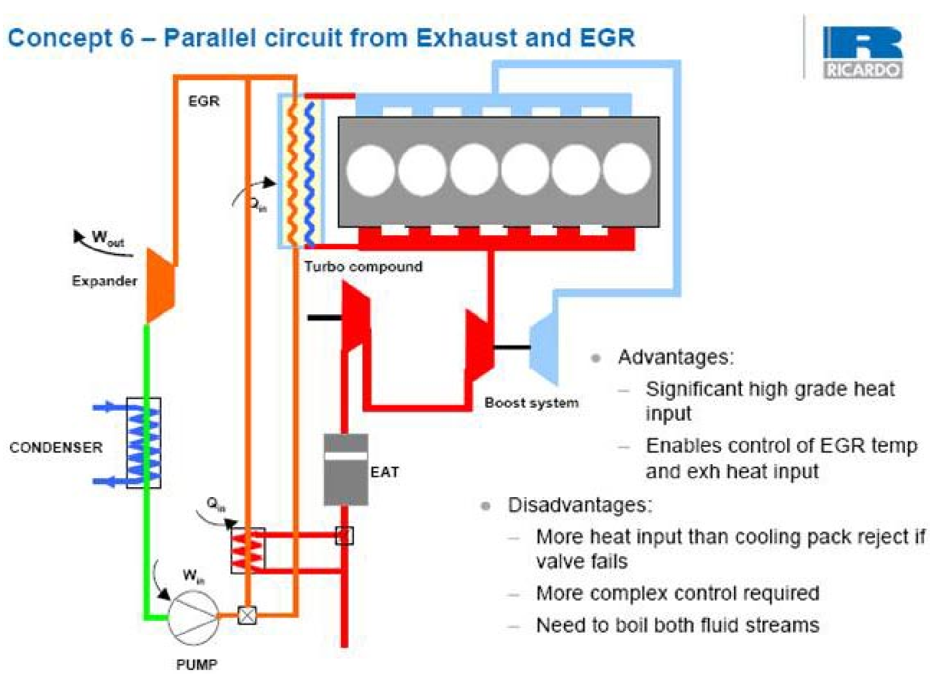
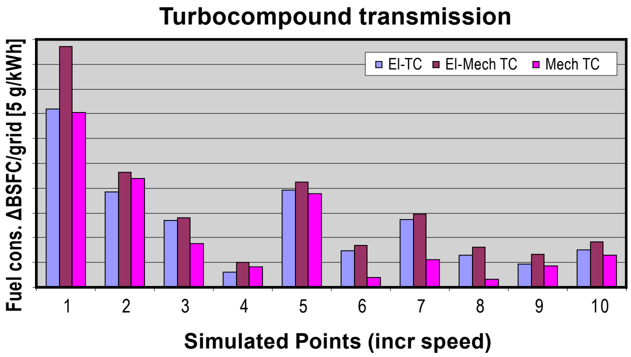


FIGURE 3. The Rankine Cycle WHR System of Choice – EGR and Exhaust Heat Exchangers in Parallel



BSFC - brake specific fuel consumption

FIGURE 4. Differential Fuel Consumption of a Turbocompound Engine System at Different Engine Operating Points Comparing Mechanical, Electrical and Electromechanical Power Turbine Transmissions

work will focus on design improvements to optimize and test this type of TC transmission.

PS Gearbox

The goal is to develop transmission-associated control software that will provide a highly functional and efficient link between the engine and the tire-road interface; and also allow efficient integration of the mild hybridization electric motor/generator truck components

Control software has been developed and evaluated in a hardware-in-the-loop environment and also in a truck. The automatic PS gearbox enables continuous engine torque during shifting as compared to the conventional gearbox with its associated torque interruptions. Also, engine speed variation while shifting is significantly less for the automatic PS.

Conclusions

Progress toward the project objectives has been achieved in all work areas:

- Development and test of a very high efficiency powertrain system, including speed control, TC, and a Rankine bottoming cycle WHR option, coupled to an automatic PS transmission.
- Development and optimization of a mild hybridization system, including EM and ESS components and control strategies.
- Determination of the combustion, emissions and aftertreatment effects of various biofuels and their blends with very low sulfur fossil-derived diesel fuel.

In accomplishing this work, analytical methods such as CFD and transient simulation have been combined with experimental testing to achieve better results within a shorter timeframe and at lower cost.

Specific conclusions include:

- A TC engine (based on a U.S. 2010 MD13 engine) with optimized injection and high performance combustion can decrease fuel consumption by ~6%.
- Application of an ethanol-water Rankine cycle WHR system to the ICE reciprocator shows potential for further fuel consumption gains.
- An optimized fully mechanical fixed-ratio power turbine transmission is more effective than either electrical or electromechanical alternatives.
- Hybrid components need to be sized carefully with respect to anticipated driving cycles to maximize fuel economy gains. Oversizing can result in excessive cost as well as decreased efficiency due to added weight.
- FAME biofuels and their blends have the potential to reduce soot emissions with no adverse efficiency impact. Early road endurance tests indicate no deterioration of the engine, emissions or EATS for low percentage blends of FAME biofuels (20% soy oil) in diesel.

II.A.20 Expanding Robust HCCI Operation with Advanced Valve and Fuel Control Technologies

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Kellen Schefter

Objectives

- Determine limits of conditions conducive to robust homogeneous charge compression ignition (HCCI) operation and the engine controls most effective at controlling HCCI using ORNL's single-cylinder research engine with fully-variable hydraulic valve actuation (HVA).
- Use experimental results from the single-cylinder HVA engine to develop a robust HCCI model in GT-POWER.
- Develop intake and exhaust HCCI camshafts for the Delphi 2-step cam-based valvetrain.
- Operate multi-cylinder engine with cam-based valvetrain under HCCI conditions, demonstrating the widest-possible HCCI operating regime.

Fiscal Year (FY) 2010 Accomplishments

Phase 1 of experimental studies using the ORNL single-cylinder HVA engine is complete:

- Parametric studies of engine controls to evaluate the effect on HCCI combustion.
- Experimental investigation of naturally-aspirated HCCI operation using negative valve overlap (NVO), fueled by unleaded 91 Research octane number gasoline.
- Experimental results, comprised by set of 367 data points, show engine operating sensitivities to control.
- Identified that gasoline direct injection timing is the most capable control parameter for single-injection HCCI.
- Demonstrated that substantially similar engine operation is possible over a range of NVO.

Future Directions

- Develop a robust GT-POWER model, to be calibrated using the Phase 1 experimental data from the ORNL HVA engine.
- Identify modeling needs and perform the second phase of experiments with the ORNL HVA engine.
- Investigate the effect of multiple fuel injection strategies.
- Develop cam profile for multi-cylinder HCCI.
- Demonstrate HCCI control on multi-cylinder engine.

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Introduction

HCCI combustion has a great deal of promise for improved efficiency and reduced emissions, but faces implementation barriers. This study aims to better understand the engine conditions that are conducive to HCCI combustion, and the engine operating sensitivities to engine controls. This information will then be used to develop cams for a production-intent valvetrain integrated into the Delphi 2-step system.

Approach

The approach taken in this project utilizes a combination of single-cylinder engine experiments, engine system modeling, and multi-cylinder engine experiments. The single-cylinder engine, shown in Figure 1, is equipped with a fully-variable HVA valvetrain which allows valve timing, duration, and lift as degrees of freedom during parametric studies. The single-cylinder engine is used to identify and characterize engine operating conditions that are conducive to HCCI combustion. Further, parametric studies of control parameters can identify the sensitivity and the controllability within the HCCI operating regime.

Results from the single-cylinder HVA engine will be used to develop and calibrate an engine model using GT-POWER. The model will be used to analyze the gas exchange phenomena and identify in-cylinder state conditions that are conducive to HCCI combustion, allowing for the development of HCCI cams in the

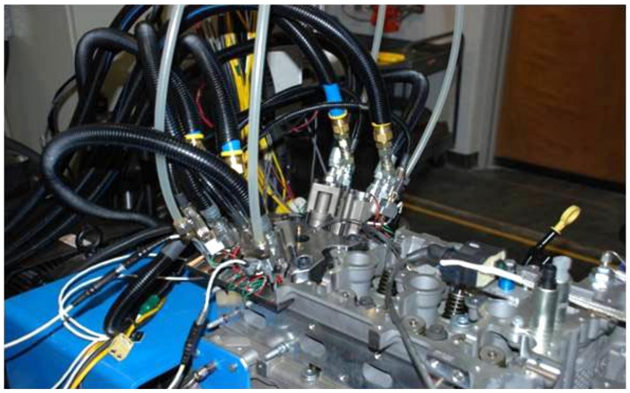


FIGURE 1. ORNL Single-Cylinder HVA Research Engine

Delphi 2-step valvetrain. Finally, we will demonstrate and map the operable HCCI regime on the flexible cam-based valvetrain.

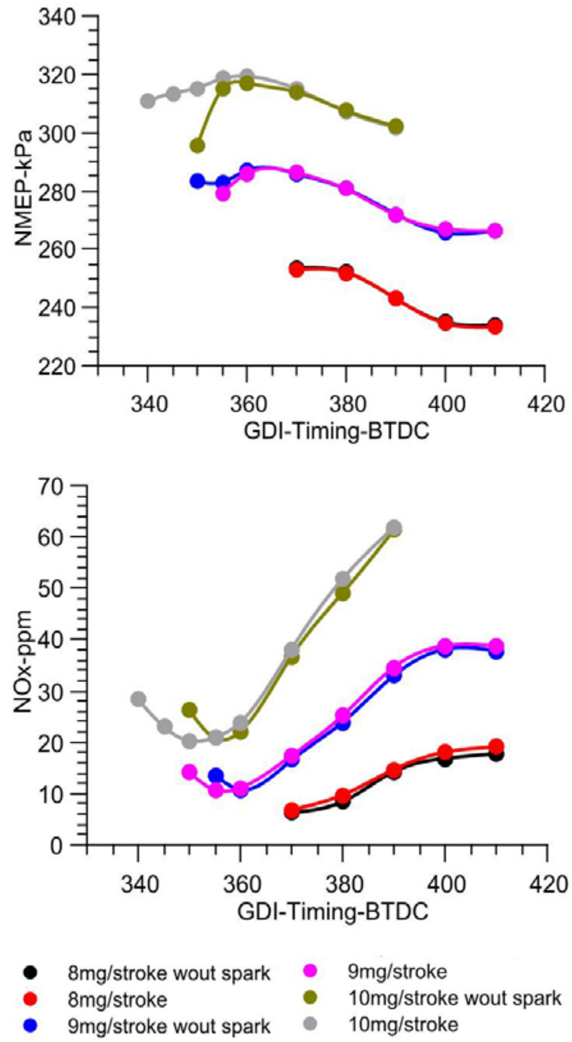
Results

The findings from Phase 1 of experimental work at ORNL show the sensitivities of HCCI combustion to the following engine controls: spark timing, direct fuel injection timing, cam duration at a constant NVO and NVO duration. These parametric sweeps were performed at 2,000 rpm and five different fueling rates, representing the operable load range.

The effects of fuel injection timing on engine load and oxides of nitrogen (NOx) emissions are shown in Figure 2 for three different fueling rates, both with and without spark. Fuel injection timing has a strong impact on combustion phasing and stability which impacts power, efficiency, and emissions. These sweeps show that each fueling rate has a different optimum fuel injection timing, but it also shows that fuel injection timing can be used to control combustion stability over a fairly wide range.

The effects of spark timing on engine load and NOx emissions for various fueling rates and NVO durations were also examined during this phase. The presence of the spark between 25 and 40 deg before top dead center did have a stabilizing effect over the combustion event, measurably reducing the coefficient of variance and increasing power depending on operating point characteristics. Nevertheless, for the majority of the operating map this was not required, instead it was found to be effective at increasing the operating range at the outside limits of the operating map.

To illustrate this, Figure 2 shows that for the most retarded fuel injection timing, the points are only operable when spark is present. Thus, while spark does not have a large impact on fuel consumption or emissions, it does act as a stabilizer that can enable a wider range of operation.



NMEP - net mean effective pressure; GDI - gasoline direct injection; BTDC - before top dead center

FIGURE 2. Engine Load and NOx Emissions as a Function of Fuel Injection Timing for three Different Fueling Rates, With and Without Spark

The effect of three different NVO durations on HCCI operating load and NOx emissions are shown in Figure 3. Knowing the range of NVO durations where a given engine point is operable is necessary to enable a cam-based valvetrain because valve lift durations are considerably less flexible compared to a HVA valvetrain. Figure 4 shows that the engine can achieve nearly identical operating load at a constant fuel rate for these three different NVO durations. Importantly, each NVO duration has a unique optimal fuel injection timing. While the trends in NOx emission are similar for the three NVO durations, the shorter NVO duration results in a lower concentration of NOx emissions.

Despite difference in engine load, NVO duration and fuel injection timing, the best indicated specific fuel consumption (ISFC) consistently collapses to the same value of approximately 225 g/kW-h, as shown

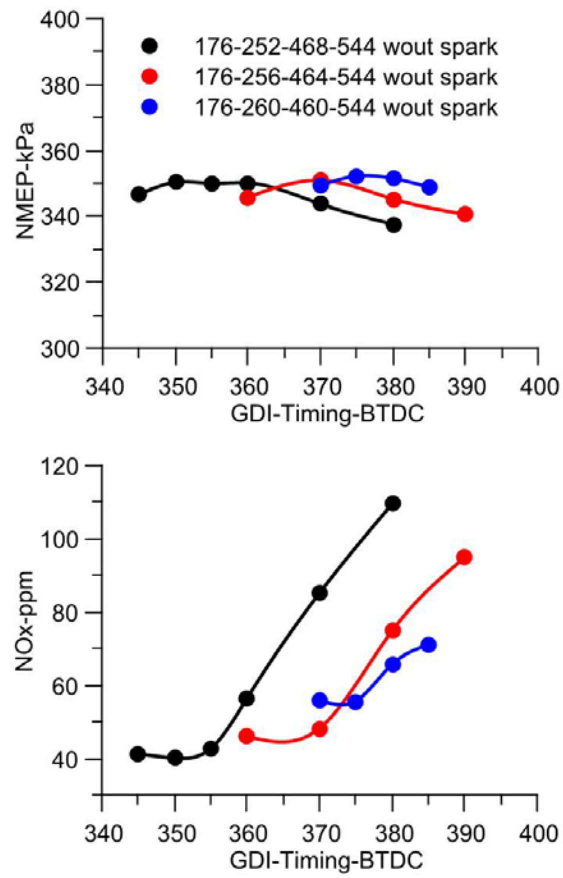


FIGURE 3. Effect of Fuel Injection Timing for Three Different NVO Durations at a Constant Fueling Rate of 11 mg/stroke

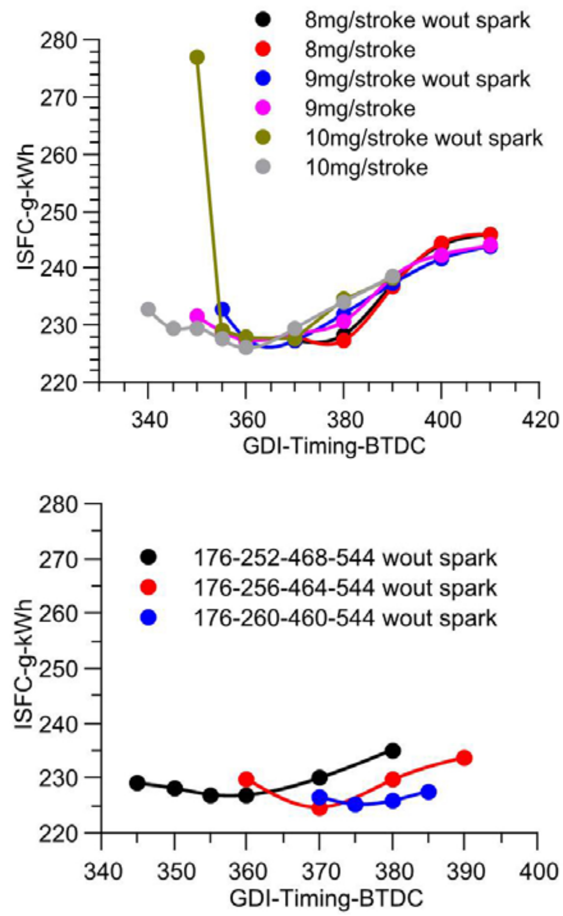


FIGURE 4. ISFC as a Function of Fuel Injection Timing for Fueling Rates of 8, 9 and 10 mg/stroke (top) and for Three Different NVO Durations at 11 mg/stroke (bottom)

in Figure 4. This is valuable information because it illuminates that by using fuel injection to control the combustion event, the engine efficiency is not degraded over the operable HCCI range of the engine.

Conclusions

The first phase of experimental HCCI work has been performed using the ORNL single-cylinder HVA research engine. The effort consisted of parametric studies to determine the operable regions of HCCI combustion, as well as the sensitivity to available engine controls. Results show that spark timing has only a minimal impact on engine load and emissions, and its effect is mainly to increased engine stability. Fuel injection timing exhibits a stronger control authority over HCCI combustion, and each engine operating condition has an optimal fuel injection timing for best efficiency. Importantly, many of the engine operating conditions can be reproduced with several different NVO durations, with each having its own optimal fuel injection timing.

This first phase of experimental data is being used to build and validate an engine model using GT-POWER software. The model will be used to analyze the engine gas exchange so that the same engine conditions can be reproduced on a cam-based valvetrain with custom cam profiles.

II.A.21 Light-Duty Vehicle Efficient Clean Combustion

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Objectives

- Improve light-duty vehicle (5,000 lb test weight) fuel efficiency over the Federal Test Procedure (FTP) city drive cycle by 10.5% over today's state-of-the-art diesel engine.
- Develop and design an advanced combustion system that synergistically meets Tier 2 Bin 5 oxides of nitrogen (NOx) and particulate matter (PM) emissions standards while demonstrating the efficiency improvements.
- Maintain power density comparable to that of current conventional engines for the applicable vehicle class.
- Evaluate different diesel fuel properties and ensure combustion system compatibility with commercially available biofuels.

Fiscal Year (FY) 2010 Accomplishments

- Can achieve 0.08 g/mi NOx on the FTP75 emissions certification cycle without NOx aftertreatment while improving the fuel efficiency by 4.5% relative to the 10.5% target.
- Can achieve 0.07 g/mi NOx on the FTP75 emissions certification cycle with selective catalytic reaction (SCR) NOx aftertreatment while improving the fuel efficiency by 9.1% relative to the 10.5% target.
- Completed the design and testing of a sequential 2-stage turbo to provide power density, minimize pressure drop, and deliver the targeted air/fuel (A/F) ratio and exhaust gas recirculation (EGR) rates.
- The design and testing of a combustion system (piston, fuel injector configuration, and intake swirl level) to extend the early pre-mixed charged, compression ignition (PCCI) combustion regime was completed.
- Integration of a piezo fuel system with steady-state calibration to demonstrate the ability to reduce PM emissions while meeting the noise, vibration, and harshness requirements for the light-duty vehicle application.
- Created and procured a novel variable valve actuation (VVA) design to provide intake and exhaust valve manipulation.
- Steady-state testing completed using a full-authority VVA system to demonstrate the potential fuel efficiency improvement and combustion stability associated with low temperature combustion.
- Closed-loop combustion controls implemented.
- Extended project to include SCR NOx aftertreatment architecture to meet the need for SFTP2 emissions certification.
- Selected an SCR NOx aftertreatment design for engine integration based on validated system modeling.

Future Directions

Phase 1 has been focused heavily on applied research as directed through the Analysis-Led-Design initiative. During Phase 2, Advanced Development, the emphasis on simulation will be reduced and experimental development and validation will become the primary focus. During 2010, we expect to:

- Perform multi-cylinder engine testing using the Phase 2 hardware (revised 2-stage sequential turbo, piezo fuel system, high capacity EGR, controls, and aftertreatment).
- Develop a detailed engine calibration using the Phase 2 technology to meet FTP75 and SFTP2 emissions certification.
- Incorporate a new SCR system design with full engine and aftertreatment calibration.
- Continue VVA testing and design refinement.
- Explore technology to enhance aftertreatment thermal management.
- Transient assessment of fuel efficiency improvements using test cell and software analysis procedure.
- Test biofuel blends to demonstrate compatibility.
- Assess suppliers of critical components for technology and commercial readiness to ensure the technologies required for the planned architecture will be available for production.

Introduction

Light-duty vehicles account for over 60% of all transportation energy consumption in the United States. Reducing petroleum fuel use and greenhouse gas emissions will require limiting the fuel consumed in light-duty vehicle engines. Today nearly all light-duty vehicles in the United States are powered by gasoline engines. Diesel engines have significant efficiency benefits over gasoline engines, and there are opportunities to further improve the diesel combustion system. If 30% of the light truck fleet in the United States were to transition to diesel engines, fuel consumption would be reduced by approximately 90 million barrels of oil per year. When fully implemented, developments proposed in this project will enable a 10.5% efficiency improvement, increasing potential fuel savings to 119 million barrels per year. The fuel savings associated with this project would reduce greenhouse gas emissions by eliminating the production of 11 million metric tons of CO_2 per year.

Cummins will develop and demonstrate combustion technologies for diesel engines that realize 10.5% efficiency improvements while meeting U.S. Environmental Protection Agency Light-Duty Emissions Standards (Tier 2, Bin 5) in a robust and cost-effective manner. The work integrates the areas of low temperature combustion, air handling, advanced fuel systems, and closed-loop controls to support high efficiency, low emission combustion concepts. Multiple steps are planned in the development process including analysis led design, concept integration, advanced system development and demonstration.

Approach

The project strategy is focused on the expansion of low-temperature combustion (LTC) to meet project objectives. LTC will result in very low engine-out emissions while achieving high efficiency. Two modes will be evaluated to expand the LTC region: smokeless rich combustion and early PCCI. Cummins believes these two modes offer the most opportunity for efficiency improvements while maintaining extremely low engine-out emissions.

As the engine transitions to higher speed and load operation, the combustion mode will transition to lifted flame diffusion-controlled combustion. Lifted flame diffusion-controlled combustion occurs when the diffusion flame is positioned further downstream of the liquid diesel fuel compared to conventional diffusion controlled diesel combustion. Anchoring the diffusion flame further downstream allows more air to be entrained into the combustion plume, resulting in lower equivalence ratios in the region of first stage reactions. The overall consequence is lower soot formation as the engine transitions from lower load PCCI combustion to high load engine performance.

Although the details are not yet finalized, the potential SFTP2 regulation proposes to mandate tailpipe-out emissions levels over the aggressive US06 drive cycle that are similar in magnitude to the levels required for the light load FTP75 urban drive cycle. This represents a significant risk for an in-cylinder NOx solution since the US06 drive cycle produces significant high-load, high-speed engine operation. As a result, both in-cylinder and advanced SCR solutions are being considered.

Results

The first phase of the project, Applied Research, has been focused primarily on Analysis-Led-Design. Combustion models have been used to analyze and optimize the combustion recipe. Engine cycle simulation models have been used to evaluate VVA, air handling and EGR components and to investigate preliminary architecture options. Controls algorithms and software have been developed and tested in the software simulation environment. Based on this work, preliminary engine architectures have been developed for both in-cylinder and advanced SCR solutions.

The preliminary architectures are designed to improve fuel efficiency by focusing on four main areas; closed-cycle efficiency improvements, air handling/ EGR systems, advanced controls, and aftertreatment. The major contributors to closed-cycle efficiency improvements include expansion of LTC, combustion system optimization, enhanced EGR cooling, and VVA. Air handling and EGR system improvements include high-efficiency two-stage variable-geometry turbocharging (VGT), advanced low-pressure drop EGR cooling systems, and VVA. Controls efforts are focused on closed-loop combustion control and model-based air handling controls. Both paths also include a reduction in fuel economy penalties associated with the diesel particulate filter (DPF) via reduced regeneration frequency and pressure drop.

Based on the analysis and engine data, an estimate of fuel efficiency improvements for the preliminary architectures has been developed. The estimated fuel efficiency improvements for the in-cylinder solution are shown in Table 1. The efficiency improvements shown are relative to the current baseline engine which is equipped with a lean-NOx trap (LNT) NOx aftertreatment system.

As shown in Table 1, the estimated fuel efficiency improvement for an in-cylinder NOx emissions solution is 11.5%, which exceeds the project goal of 10.5%. However, the most significant risk associated with an in-cylinder solution is that it will not be capable of meeting

TABLE 1. Estimated Improvements in Fuel Efficiency for an In-Cylinder NOx Emissions Solution Relative to an Architecture Employing an LNT NOx Aftertreatment System

Category	Major Technologies	Fuel Efficiency Improvement
Closed-Cycle	Expand LTC Optimize combustion system Enhanced EGR cooling VVA	3%
Air Handling/EGR	High-efficiency two-stage VGT turbocharging Low-pressure drop EGR VVA	2%
Controls	Closed-loop combustion control Model-based air handling controls	1.5%
Aftertreatment	Elimination of LNT Reduced DPF regeneration	5%
Total		**11.5%**

the emissions requirements required by the potential SFTP2 regulation. Hence, a high-efficiency SCR NOx aftertreatment solution is also being investigated. The estimated efficiency improvement for the SCR architecture, relative to the baseline LNT architecture, is similar to the in-cylinder solution. However, since the SCR solution enables high engine-out NOx over much of the drive cycle, closed-cycle efficiency improvement is expected to be slightly greater. Due to urea consumption and thermal management, efficiency improvements associated with aftertreatment are expected to be slightly less than the in-cylinder solution. During the next phase of the project, Advanced Development, efficiency improvements with be validated and optimized experimentally. A final architecture decision will be made based on the results of these experiments.

Conclusions

During 2010, all project milestones and deliverables were completed. All subsystem technologies (fuel system, turbomachinery, combustion system, aftertreatment, etc.) were integrated on a multi-cylinder engine. A summary of the achievements are listed based on limited engine testing and analysis:

- Can achieve 0.08 g/mi NOx on the FTP75 emissions certification cycle without NOx aftertreatment while improving the fuel efficiency by 4.5% relative to the 10.5% target.
- Can achieve 0.07 g/mi NOx on the FTP75 emissions certification cycle with SCR NOx aftertreatment while improving the fuel efficiency by 9.1% relative to the 10.5% target.
- Completed the design and testing of a sequential 2-stage turbo to provide power density, minimize pressure drop, and deliver the targeted A/F and EGR rates.
- Completed the design and testing of a combustion system (piston, fuel injector configuration, and intake swirl level) to extend the early pre-mixed charged, compression ignition (PCCI) combustion regime.
- Integration of a piezo fuel system with steady state calibration to demonstrate the ability to reduce PM emissions while meeting the noise, vibration, and harshness requirements for the light-duty vehicle application.
- Created and procured a novel VVA design to provide intake and exhaust valve manipulation.
- Steady-state testing completed using a full-authority VVA system to demonstrate the potential fuel efficiency improvement and combustion stability associated with LTC.
- Closed-loop combustion controls implemented.
- Extended project to include SCR NOx aftertreatment architecture to meet the need for SFTP2 emissions certification.
- Selected an SCR NOx aftertreatment design for engine integration based on validated system modeling.

II.B.1 CLEERS Aftertreatment Modeling and Analysis

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DOE Technology Development Manager:
Ken Howden

Objectives

- Lead and contribute to the Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) activities:
  - Provide project updates to the industry sub-team, solicit feedback, and adjust work scope accordingly.
  - Lead technical discussions, invite distinguished speakers, and maintain an open dialogue on selective catalytic reduction (SCR), lean-NO_x trap (LNT), and diesel particulate filter (DPF) modeling issues.
- Develop improved modeling capabilities for SCR and DPF through fundamental experiments.
- Develop a fundamental understanding of SCR and LNT catalysts with primary focus on reaction mechanisms and material characterization.

Fiscal Year (FY) 2010 Accomplishments

- Participated in monthly CLEERS teleconferences and coordinated the calls focused on SCR, LNT and DPF technologies.
- Investigated the hydrocarbon (HC) inhibition of a Fe-zeolite SCR catalyst through steady-state reactor tests and spectroscopic analysis in collaboration with Oak Ridge National Laboratory (ORNL).
- Developed a HC storage model and a single-site inhibition kinetic model to quantitatively describe the effects on various SCR reaction steps, such as NH_3 storage and NO oxidation.
- Published the first peer-reviewed study describing the oxides of nitrogen (NO_x) reduction performance of Cu-SSZ-13.
- Demonstrated that the sintering of Pt can be minimized through anchoring at penta-coordinated Al sites on the γ-alumina surface that we previously had identified using ultra-high field nuclear magnetic resonance (NMR) spectroscopy coupled with high resolution transmission electron microscopy.
- Eight publications and 19 public presentations (nine invited) during the past fiscal year.
- Co-organized sessions on emission control and modeling for the Society of Automotive Engineers World Congress and the American Society of Mechanical Engineers Internal Combustion Engine Conference.

Future Directions

- Update PNNL's SCR model for the state-of-the-art Cu-SCR catalyst, and develop models to describe the performance degradation due to HC inhibition and catalyst aging.
- Evaluate the accuracy of the unit collector model with respect to nano-sized particulates, and improve the accuracy of micro-scale model for prediction of soot-catalyst contact and soot penetration into the filter substrate.
- Conduct detailed characterization of the active sites of the Cu-SCR catalyst with emphasis on the catalyst deactivation.
- Complete studies of CO_2 and H_2O effects on BaO morphology changes and NO_x storage properties, and continue fundamental studies of novel high-temperature LNT formulations.
- Examine the interaction between catalysts in the integrated LNT-SCR or SCR-DPF system, including the passive regeneration of soot by base metal catalyst on advanced filter substrate.
- Develop advanced imaging techniques for substrate microstructure and soot loading analysis, such as neutron imaging and micro-computed tomography imaging.

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Introduction

CLEERS is a research and development focus project of the Diesel Cross-Cut Team. The overall objective is to promote the development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems. Three fundamental research projects are sponsored at PNNL through CLEERS: DPF, SCR, and LNT. Resources are shared among the three efforts in order to actively respond to current industrial needs. In FY 2010, more emphasis was placed on the

SCR and LNT activities because of urgent application issues associated with these technologies.

Approach

Among the catalysts for SCR technology, base metal exchanged zeolite catalysts are being considered for vehicle applications because of their high NO_x reduction efficiency over a wide temperature range [1]. However, the NO_x reduction efficiency at low temperatures continue to be a major challenge, because unburned HC and H_2O are known to inhibit NO_x reduction performance. Thus, we have investigated the effect of hydrocarbons on various SCR reaction steps over Fe-zeolite SCR, and developed a HC storage model and a single-site inhibition kinetic model to quantitatively describe the effects of water and toluene on various SCR reaction steps, such as ammonia adsorption and NO oxidation. In collaboration with ORNL, we also investigated the effect of toluene on the reaction intermediates using diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy.

In addition, as the industry began using the latest Cu-SCR technology, we also initiated the first open literature studies of the performance of the latest Cu zeolite catalyst. First, the SSZ-13 zeolite was synthesized using the methods recently published [2]. Cu ions were then exchanged into the zeolite in an aqueous ion-exchange process, using $Cu(NO_3)_2$ as precursor. After drying and calcination, the SCR activities of these powder catalysts have been examined in a flow reactor system.

The LNT technology is based on the ability of certain oxides, such as alkaline and alkaline earth oxide materials, to store NO_x under lean conditions and reduce it during rich engine operation cycles. Among the catalysts developed to date [3], the most extensively studied catalyst system continues to be based on barium oxide (BaO) supported on a high surface area alumina (Al_2O_3) material [4]. Our project is aimed at developing a fundamental understanding of the operation of the LNT technology especially with respect to the optimum materials used in LNTs.

We continued to utilize the state-of-the-art techniques, such as solid-state NMR [5], X-ray diffraction, transmission electron microscopy (TEM)/energy dispersive spectroscopy, Fourier transform infrared, Brunauer-Emmett-Teller surface area measurement, and temperature programmed desorption/temperature programmed reaction available at PNNL and ORNL, to probe the changes in physicochemical properties of the catalyst samples. The model LNT catalysts were prepared by the incipient wetness method, using an aqueous alkaline earth nitrate solution and a γ-alumina support, and the NO_x reduction performance was examined in a fixed bed reactor under lean-rich cycling conditions.

Results

Catalyst Model Development

SCR modeling activities focused on the development of sub-models for HC storage and inhibition on Fe-zeolite SCR catalysts, which had been developed in FY 2009. Steady-state surface isotherms were collected to generate the Langmuir isotherms, from which the rate parameters for NH_3 adsorption-desorption were determined. The rate parameters were then used in a one-dimensional SCR catalyst model, which simulates the gas phase and surface phase concentrations of NH_3 along the axial length of a catalyst. Kinetic parameters for various SCR reaction steps, such as NH_3 oxidation and NO oxidation, are included.

Similar to the H_2O inhibition model developed in FY 2009, a HC storage model was first developed using toluene. Assuming a single site for HC storage, a kinetic model was developed based on toluene adsorption and desorption experiments (shown in Figure 1). Some of the storage rate parameters were also derived from the slope and y-intercept of the Langmuir isotherms.

In the HC inhibition model, the rates of NO oxidation and NO_2 dissociation are defined as a function of equilibrium constant, and HC storage in the catalyst (as described by the equation below). Model parameters were tuned using the steady-state reactor test data, and the model was then validated against the temperature ramp test data (shown in Figure 2). In addition, a competitive adsorption model was developed to describe the competitive adsorption among different adsorbates, such as NH_3, H_2O and HCs. This model is currently being used to study the effects of n-dodecane on various SCR reaction steps over the commercial Fe-zeolite SCR catalyst.

$$r = \frac{k_{f,oxi}\left(c_{NO}c_{o_2}^{0.5} - \frac{c_{NO_2}}{K_{eq}}\right)}{1 + K_{tol}\frac{\theta_{tol}}{1-\theta_{tol}}}$$

Catalyst Fundamental Research

Among the factors than can influence the low-temperature performance of SCR catalysts, the effects of HCs on various SCR reaction pathways were examined using a commercial Fe-zeolite catalyst and four model HC species that can be present in the exhaust: ethylene and propane (engine-out HC species), toluene and

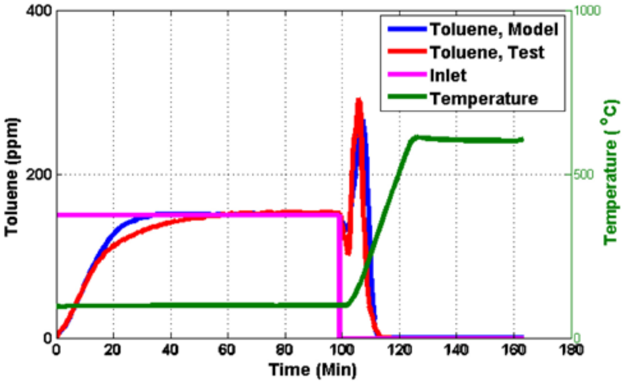

FIGURE 1. Single site toluene storage model validation with adsorption of 150 ppm toluene at 100°C, followed by temperature-programmed desorption.

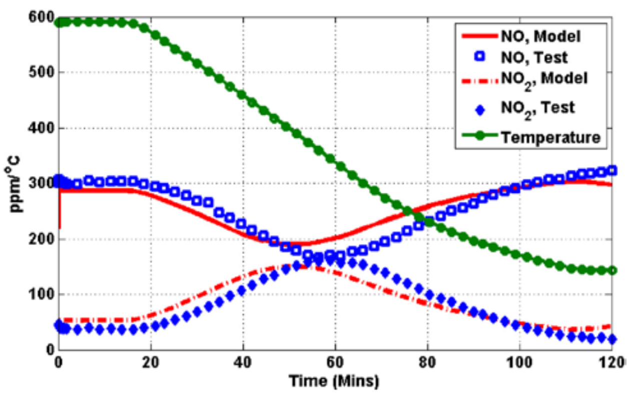

FIGURE 2. Comparison between the model prediction and experimental measurement of toluene inhibition of NO oxidation.

n-dodecane (fuel-component HC species). Among these HC species, the NO_x reduction efficiency was decreased in the presence of fuel-component HC species, such as toluene (shown in Figure 3). In particular, the standard SCR reaction ($NO+NH_3$) was more severely affected compared to the fast SCR reaction (NO/NO_2+NH_3), because of the suppressed NO oxidation step. Our collaborators at ORNL investigated the effect of toluene on reaction intermediates on the catalyst surface using DRIFT, and reported similar observations.

In the recent patent literature, Cu^{2+} ion-exchanged chabazite zeolite (Cu-SSZ-13) has been reported to exhibit excellent NO_x reduction efficiency and durability [6]. Thus, we initiated studies to understand the relationship between catalyst structure and reactivity, and have just published the first open literature paper on their performance [7]. Compared to extensively studied Cu-beta and Cu-ZSM-5 catalysts, it was found Cu-SSZ-13 is not only more active in the NO_x reduction performance (shown in Figure 4), but also more selective toward nitrogen formation, resulting in significantly lower N_2O formation and NH_3 slip.

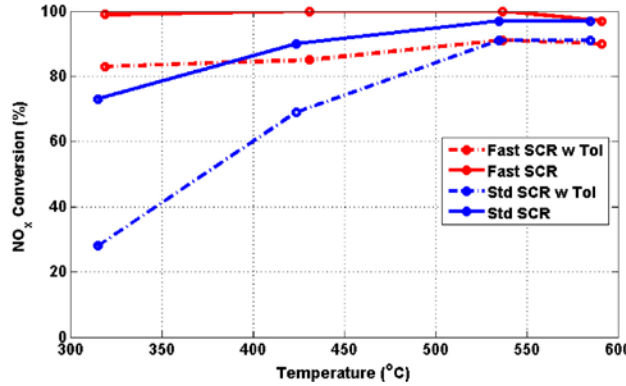

FIGURE 3. Effect of toluene on NO_x conversion over an Fe-zeolite SCR.

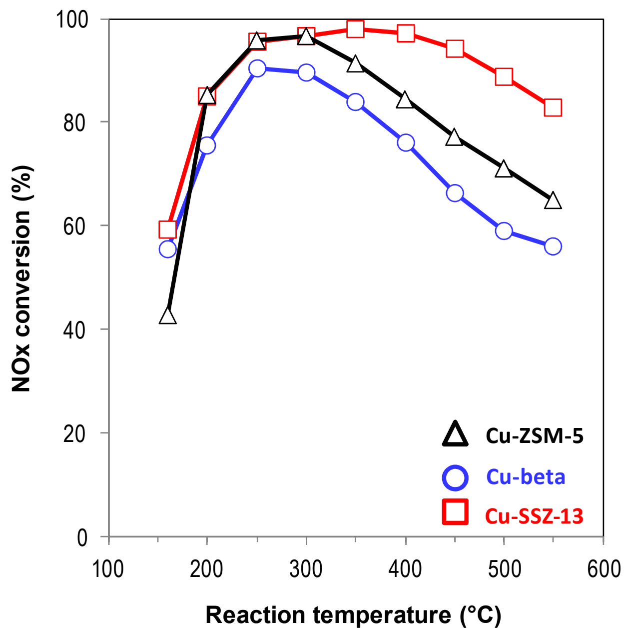

FIGURE 4. NO_x conversion performance of Cu-SSZ-13 (square), Cu-beta (circle) and Cu-ZSM-5 (triangle).

The interaction of metal particles with their oxide support can play a critical role in determining particle morphology and maintaining dispersion. Previously, we used a combination of ultra-high magnetic field, solid state magic angle spinning NMR spectroscopy and high-angle annular dark-field scanning transmission electron microscopy (STEM), coupled with density function theory (DFT) calculations, and reported that coordinatively unsaturated penta-coordinate Al^{3+} centers, present on the (100) facets of the γ-Al_2O_3 surface, anchor active phase of Pt [8]. At low loadings, the active catalytic phase is atomically dispersed on the support surface, whereas two-dimensional Pt rafts form at higher coverages. In FY 2010, we investigated the role of the penta-coordinated Al^{3+} sites on the γ-Al_2O_3(100) surface in the sintering of Pt metal particles.

Figure 5 shows high resolution STEM images of 1 and 10 wt% Pt/γ-Al_2O_3 samples after calcination at 300 (A and D) and 600°C (B, C, E and F). The the 300°C-calcined 1 wt% Pt/Al_2O_3 sample (A) clearly shows the almost exclusively atomic distribution of Pt on the γ-Al_2O_3 support, while two-dimensional clusters with an average size of ~1 nm are observed for the 10 wt% Pt/Al_2O_3 sample (D). Although Pt/Al_2O_3 catalysts sinter when calcined in air above 500°C, there was little sintering of Pt metals on 1 wt% Pt/Al_2O_3 after a 600°C calcination in dry air (B and C). In contrast, very large (>100 nm) Pt clusters (F) as well as a considerable amount of highly dispersed 1~2 nm Pt clusters with a two-dimensional (raft-like) morphology are seen for the 10 wt% Pt/Al_2O_3 sample after 600°C calcination (E).

We previously showed that at least some of the Pt atoms, even at high loadings, strongly interact with specific Al^{3+} sites on the γ-Al_2O_3(100) surface [8]. High level DFT calculations were conducted to investigate how these penta-coordinated Al^{3+} sites on the γ-Al_2O_3(100) surface can inhibit Pt sintering (shown in Figure 6). This inhibition was found to be both thermodynamic and kinetic due to the strong interactions of these sites with atomic Pt or Pt oxide species. Thus, it may be possible to stabilize the size and morphology of catalytically active metal particles on the support through this strong interaction.

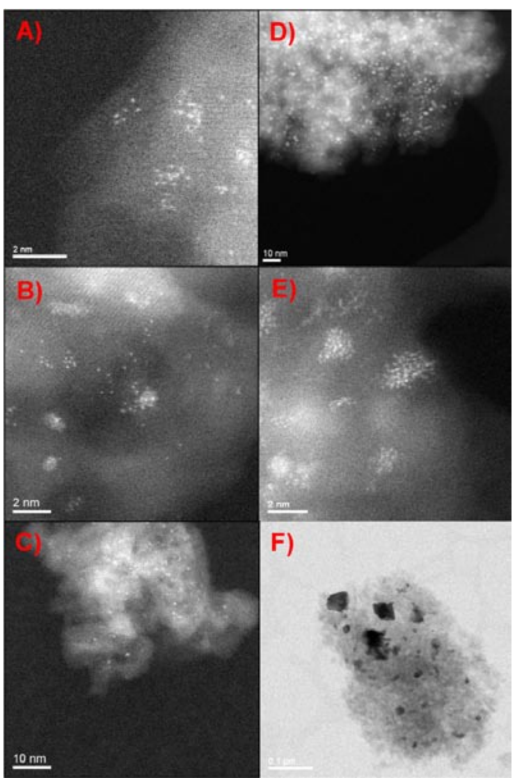

FIGURE 5. High Resolution STEM and TEM images of Pt/γ-Al_2O_3 samples after calcinations in dry air at 300 and 600°C. A) 1 wt% at 300°C; B) 1 wt% at 600°C; C) 1 wt% at 600°C; D) 10 wt% at 300°C; E) 10 wt% at 600°C; F) 10 wt% at 600°C.

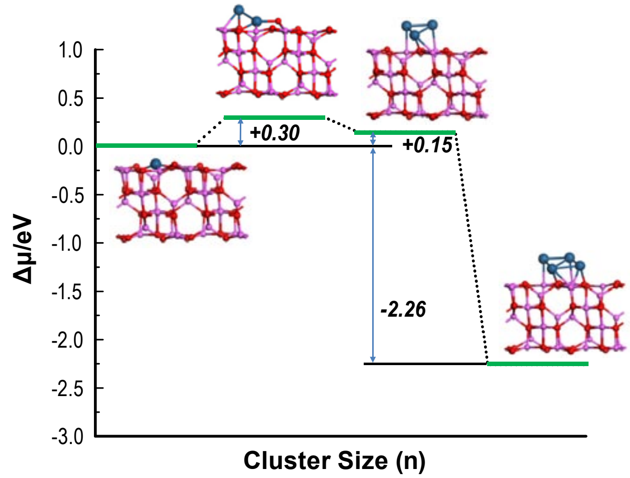

FIGURE 6. DFT calculated chemical potential differences (Δμ) for the sintering from Pt to Pt_4 on the γ-Al_2O_3(100) surface. A positive value of Δμ indicates the process is thermodynamically unfavorable.

Conclusions

- The effects of water and HCs on various NO_x reduction pathways were examined over a commercial Fe-zeolite SCR catalyst, and kinetic models were developed to quantitatively describe their impact.
- Among HC species found in the diesel engine exhaust, fuel-component HC species were found to suppress the NO oxidation and standard SCR reaction pathways over a commercial Fe-zeolite SCR catalyst.
- A new class of Cu-zeolite catalysts (Cu-SSZ-13) was prepared in-house and found to be more active and selective for the desirable nitrogen product during lab-reactor ammonia SCR measurements.
- Further investigation of interactions between LNT catalyst phases (Pt and Ba) and the support material, γ-Al_2O_3, showed that penta-coordinate Al^{3+} ions not only provide sites to 'anchor' Pt to the surface, but also minimize Pt sintering.

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FY 2010 Presentations

Invited

1. CHF Peden, "Fundamental Studies of Catalytic NOx Vehicle Emission Control."

- Advanced Light Source Annual Meeting, Berkeley, CA, October 2009.
- Washington State University, Pullman, WA, February 2009.

2. CHF Peden, "The Use of Ultrahigh Field NMR Spectroscopy to Study the Surface Structure and Catalytic Properties of Poorly Crystalline γ–Al_2O_3."

- Materials Research Society Fall Meeting, Boston, MA, December 2009.
- Eastman Chemical Company, Kingsport, TN, February 2009.
- 21st Canadian Symposium on Catalysis, Banff, Alberta, Canada, May 2010.

3. DR Herling, "CLEERS Aftertreatment Modeling and Analysis," DOE Annual Merit Review, June 2010.

4. CHF Peden, "The Surface Structure and Catalytic Properties of Poorly Crystalline γ–Al_2O_3 Surfaces: New Insights from Ultrahigh Field NMR Spectroscopy and Aberration-Corrected Transmission Electron Microscopy," Gordon Research Conference on Catalysis, New London, NH, June 2010.

5. CHF Peden, "Ultrahigh Resolution STEM and NMR Studies of Poorly Crystalline γ–Al_2O_3 Surfaces: New Insights From Imaging and Spectroscopy," Microscopy and Microanalysis 2010 Conference, Portland, OR, August 2010.

6. CHF Peden, "The Dispersion and Sintering of Pt on γ–Al_2O_3: The Role of Anchoring Penta-Coordinated Al^{+3} Sites," International Conference on Environmental Catalysis, Beijing, China, September 2010.

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1. DN Tran, RG Tonkyn, MN Devarakonda, JH Lee, DR Herling, "Effects of Hydrocarbons on NOx Conversion Performance of a Fe-zeolite Urea-SCR Catalyst," Pacific Coast Catalysis Society Annual Meeting, Seattle, WA, March 2010.

2. D Mei, Q Ge, JH Kwak, J Szanyi, CHF Peden, "Theoretical Investigations of NOx Storage on γ-Al_2O_3-Supported Barium Oxide Materials," ACS National Meeting, San Francisco, CA, March 2010.

3. DN Tran, RG Tonkyn, MN Devarakonda, JH Lee, DR Herling, "Effects of Hydrocarbons on NOx Conversion Performance of a Fe-zeolite Urea-SCR Catalyst," ACS National Meeting, San Francisco, CA, March 2010.

4. MN Devarakonda, RG Tonkyn, DN Tran, JH Lee, DR Herling, "Hydrocarbon Effect on a Fe-zeolite Urea-SCR Catalyst: An Experimental and Modeling Study," SAE World Congress, Detroit, MI, April 2010.

5. DH Kim, GG Muntean, CHF Peden, N Currier, A Yezerets, HY Chen, H Hess, "Studies of LNT Sulfation and Desulfation at PNNL," DOE CLEERS Workshop, Dearborn, MI, April 2010.

6. MN Devarakonda, RG Tonkyn, MN Tran, JH Lee, DR Herling, "Modeling Competitive Adsorption in Urea-SCR Catalysts for Enhanced Low Temperature NOx Control," DOE CLEERS Workshop, Dearborn, MI, April 2010.

7. G Li, DH Kim, D Hu, G Xia, ZC Zhang, and CHF Peden, "Catalyst characterization using operando Raman spectroscopy," ACS National Meeting, Boston, MA, August 2010.

8. MN Devarakonda, RG Tonkyn, MN Tran, JH Lee, DR Herling, "Modeling Species Inhibition of NO Oxidation in Urea-SCR Catalysts for Diesel Engine NOx Control," ASME Internal Combustion Conference, San Antonio, TX, September 2010.

9. X Wang, DH Kim, JH Kwak, CM Wang, J Szanyi, and CHF Peden, "Effect of Reductive Treatments on Pt Dispersion and NOx Storage in Lean NOx Trap Catalysts," International Conference on Environmental Catalysis, Beijing, China, September 2010.

10. MN Devarakonda, RG Tonkyn, DN Tran, DR Herling, JH Lee, J Pihl, S Daw, "The Effects of Hydrocarbons on NOx Reduction over Fe-based SCR Catalyst," Directions in Engine-Efficiency and Emissions Research Conference, Detroit, MI, September 2010.

FY 2010 Publications

1. D Mei, J Szanyi, JH Kwak, CHF Peden, "Catalyst Size and Morphology Effects on the Interaction of NO_2 with BaO/γ-Al_2O_3 Materials." *Catalysis Today* **151** (2010) 304-313.

2. Y Cheng, C Lambert, DH Kim, JH Kwak, SJ Cho, CHF Peden, "The Different Impacts of SO_2 and SO_3 on

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3. DN Devarakonda, DH Kim, JH Kwak, JH Lee, CHF Peden, ML Stewart, J Szanyi, RG Tonkyn, DN Tran, A Zelenyuk, and DR Herling, "CLEERS Aftertreatment Modeling and Analysis." FY 2009 Progress Report for Advanced Combustion Engine Research and Development, pp. 155-163.

4. D Mei, JH Kwak, J Hu, SJ Cho, J Szanyi, LF Allard, CHF Peden, "The Unique Role of Anchoring Penta-Coordinated Al^{+3} Sites in the Sintering of γ-Al_2O_3-supported Pt Catalysts." *Journal of Physical Chemistry Letters* **1** (2010) 2688-2691.

5. JH Kwak, RG Tonkyn, Y Wang, J Szanyi, CHF Peden, "Excellent Activity and Selectivity of Cu-SSZ-13 in the Selective Catalytic Reduction of NOx with NH_3." *Journal of Catalysis* **275** (2010) 187-190.

6. MN Devarakonda, RG Tonkyn, DR Herling, "Hydrocarbon Effect on a Fe-zeolite Urea-SCR Catalyst: An Experimental and Modeling Study." *SAE Papers* 2010-01-1171.

7. MN Devarakonda, GR Tonkyn, DN Tran, JH Lee, DR Herling, " Modeling Species Inhibition of NO Oxidation in Urea-SCR Catalyst for Diesel Engine NOx Control." *ASME Journal of Engineering for Gas Turbines and Power* (Accepted).

8. RG Tonkyn, DN Tran, MN Devarakonda, DR Herling, "Steady State and Thermal Transient Investigation of Toluene Inhibition of NO Oxidation on a Fe-zeolite Urea-SCR Catalyst." *Chemical Engineering Communication* (in review).

II.B.2 Enhanced High Temperature Performance of NOx Storage/Reduction (NSR) Materials

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Cooperative Research and Development Agreement (CRADA) Partners:
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- Hai-Ying Chen, Howard Hess - Johnson Matthey (JM)

Objectives

Identify approaches to significantly improve the high temperature performance and stability of the LNT technology via a pursuit of a more fundamental understanding of:

- The various roles for the precious metals.
- The mechanisms for these various roles.
- The effects of high temperatures on the precious metal performance in their various roles.
- Mechanisms for higher temperature oxides of nitrogen (NOx) storage performance for modified and/or alternative storage materials.
- The interactions between the precious metals and the storage materials in both optimum NOx storage performance and long term stability.
- The sulfur adsorption and regeneration mechanisms for modified and/or alternative storage materials.

Fiscal Year (FY) 2010 Accomplishments

- Three major research thrusts this year:
  - A quick survey of high-temperature NOx decomposition catalysts:
    - Candidate materials were prepared at PNNL and tested.
  - Fundamental studies of high-temperature lean-NOx trap (LNT) catalysts prepared by PNNL:
    - Initial examination of the effects of storage elements and various supports on the NOx storage activity via screening of the performance of the newly-prepared catalysts. Model catalysts prepared at PNNL are based on materials described in the open literature.
    - Initiated studies aimed at providing scientific explanations for the NOx storage process on these high-temperature storage materials.
  - Fully formulated high-temperature LNT catalysts supplied from JM:
    - JM-supplied materials are being used solely to provide baseline performance and stability data of a potential commercial high-temperature LNT catalyst. Materials characterization (e.g., composition, morphology, etc.) of these catalysts are not being performed.
    - Explored the storage behavior of a fresh sample as a function of temperature as a baseline for comparing performance of potential new LNT compositions optimized for high-temperature performance.
    - Initiated investigations of the effects of thermal aging and sulfation/desulfation on the NOx storage activity of the fully formulated material.
- Two public presentations and four manuscripts have been cleared for release by CRADA partners.

Future Directions

Studies aimed at determining performance limitations, sulfur sensitivity and desulfation behavior of candidate alternative support and NOx storage materials that provide improved high-temperature performance will continue. An overall goal of the work will continue to be to develop a deeper understanding of the mechanisms of NOx storage and reduction activity, and performance degradation of materials that have been reported to show good NOx storage reduction (NSR) performance at temperatures considerably higher than BaO/alumina-based materials. As have the initial studies to be described here, these fundamental studies will be carried out in conjunction with baseline performance and stability experiments on fully formulated catalysts provided by JM.

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Introduction

The NOx adsorber (also known as the lean-NOx trap, LNT, or NSR) technology is based upon the concept of storing NOx as nitrates over storage components, typically barium species, during a lean-burn operation cycle, and then desorbing and subsequently reducing the stored nitrates to N_2 during fuel-rich conditions over a precious metal catalyst [1]. This technology has been recognized as one of the most promising approaches for meeting stringent NOx emission standards for diesel vehicles within the Environmental Protection Agency's 2007/2010 mandated limits and, in fact is being commercialized for this application. However, in looking forward to 2012 and beyond with expected more stringent regulations, the continued viability of the NSR technology for controlling NOx emissions from lean-burn engines such as diesels will require at least two specific, significant and inter-related improvements. First, it is important to reduce system costs by, for example, minimizing the precious metal content while maintaining, even improving, performance and long-term stability. A second critical need for future NSR systems will be significantly improved higher temperature performance and stability. Furthermore, these critically needed improvements will contribute significantly to minimizing the impacts to fuel economy of incorporating the NSR technology on lean-burn vehicles. To meet both of these objectives, NSR formulation changes will almost certainly be necessary. Importantly, such material changes will require, at a minimum an improved scientific understanding of the following things:

- The various roles for the precious metals.
- The mechanisms for these various roles.
- The effects of high temperatures on the precious metal performance in their various roles.
- Mechanisms for higher temperature NOx storage performance for modified and/or alternative storage materials.
- The interactions between the precious metals and the storage materials in both optimum NOx storage performance and long term stability.
- The sulfur adsorption and regeneration mechanisms for modified and/or alternative storage materials.

The objective of this CRADA project is to develop a fundamental understanding of candidate next generation LNT materials for NOx after-treatment for light-duty lean-burn (including diesel) engines. The project will focus on characterizing and understanding the six issues described just above. Model catalysts that are based on literature formulations are the focus of the work being carried out at PNNL. In addition, the performance and stability of a realistic high-temperature LNT catalyst, supplied by JM, is being studied in order to provide baseline data for the model catalysts that are, again, based on formulations described in the open literature.

Approach

In a microcatalytic reactor system, LNT performance is evaluated in a fixed bed reactor operated under continuous lean-rich cycling. Rapid lean-rich switching is enabled just prior to the elevated temperature zone (furnace) where the LNT materials are contained in quartz tubing. After removing water, the effluent of the reactor can be analyzed by mass spectrometry and by a chemiluminescent NOx analyzer. For a typical baseline performance testing, the sample is heated to a reaction temperature in flowing He, the feed switched to a 'lean-NOx' mixture containing oxygen and NO, as well as CO_2 and/or H_2O. After an extended period (15 minutes or more), multiple rich/lean cycles of one and four minute duration, respectively, are run and NOx removal performance is assessed after at least three of these are completed. In the LNT technology, the state of the system is constantly changing so that performance depends on when it is measured. Therefore in studies at PNNL, we obtain NOx removal efficiencies as "lean conversion (30 minutes)", which measures NOx removal efficiencies for the first 30 minutes of the lean-period. We have established a reaction protocol, which evaluates the performance of samples after various thermal aging and sulfation condition. In this way, we could identify optimum de-sulfation treatments to rejuvenate catalyst activities.

Based on formulations described in the literature, PNNL prepared several candidate samples either for direct NO decomposition or LNT performance. Activity and performance stability measurements were performed. In addition, we investigated a more fully formulated catalyst for high temperature activity supplied from JM to provide baseline performance measurements. State-of-the-art catalyst characterization techniques were utilized to probe the changes in physicochemical properties of the PNNL-prepared model catalyst samples under deactivating conditions; e.g., thermal aging and SO_2 treatment.

Results

As noted above, work on this CRADA this past year has focused on three areas:

- High-temperature NOx decomposition catalysts
- High-temperature LNT catalysts prepared by PNNL.
- Fully formulated high-temperature LNT catalysts supplied from JM

1. Catalyst for Direct NO Decomposition

Since it has been reported that certain catalytic materials display some activity for direct NO decomposition (direct DeNOx), and that new compositions have been recently reported in the literature to show good performance, PNNL first prepared a number of candidate materials to determine if it was feasible to perform direct DeNOx at high temperatures in conjunction with a more standard LNT material. While lower performance NOx reduction could be acceptable for the direct DeNOx catalyst, it would still be necessary for it to show at least moderate performance under realistic conditions. One of the candidates considered by PNNL is BaO/MgO, which was initially reported by Lunsford et al. [2] a number of years ago. Figure 1 shows the activity of this catalyst for direct NO decomposition. With a reactant feed consisting of 0.5% NO in He and very low space velocities, NOx conversions is quite low (< 20%) over the entire temperature range studied here. More importantly, under more realistic reaction conditions of 200 ppm of NO and higher space velocity (five times that used to obtain data in Figure 1), NOx conversions were negligible. In addition, it is known that the presence of oxygen, not used here, inhibits the direct NO decomposition reaction. The direct DeNOx performance of a number of other mixed oxide materials recently reported in the literature was also assessed but none of these even closely matched the performance of the BaO/MgO material. Therefore, it was concluded that direct NO decomposition is not feasible for application in the high temperature removal of NOx removal under highly oxidizing conditions.

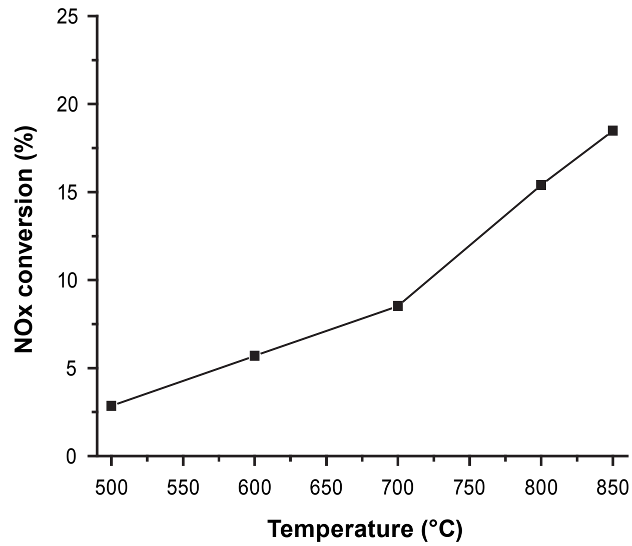

FIGURE 1. Direct NO decomposition rates obtained over a BaO/MgO catalyst (20 ccm, 0.5% NO in He).

2. High-Temperature LNT Catalysts Prepared by PNNL

In this last year, PNNL prepared several LNT catalysts to assess their high-temperature performance. The storage element was potassium, known to operate effectively at higher temperatures than Ba-based LNTs. However, very little has been published in the open scientific literature on the chemical/physical properties of K-based LNTs. As such, PNNL has initiated studies of these fundamental materials properties in order to provide scientific insight into their performance and stability. In particular, PNNL initiated investigations of the effect of alternative support materials and K loading on the NOx storage activity. As demonstrated in Figure 2, an Al_2O_3-supported K-based LNT shows higher NOx uptake than one supported on TiO_2, although the temperature where NOx uptake is maximized, 350-400°C, is essentially the same for both samples. These results clearly highlight a dependence of the NOx uptake performance on the support material. PNNL

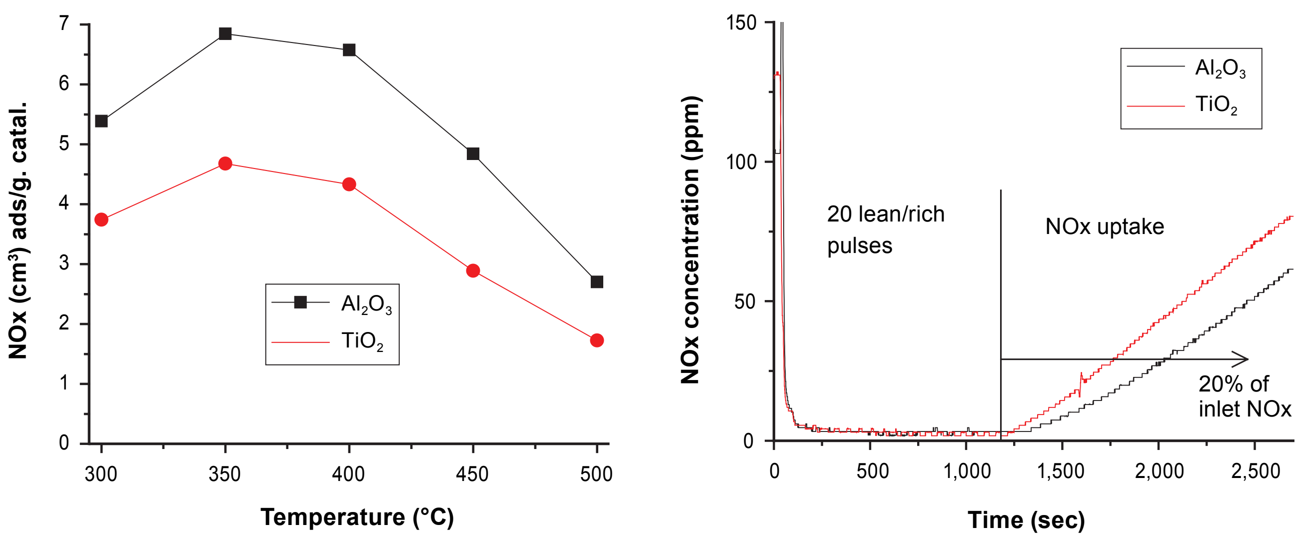

FIGURE 2. NOx uptake performance of Al_2O_3- and TiO_2-supported Pt-K NSR catalysts.

previously has shown that use of a $MgAl_2O_4$ support to prepare a Ba-based LNT gives rise to the shift in the temperature at which maximum performance is observed from 300ºC to 400ºC [3]. As such, PNNL prepared new K-based LNT materials using $MgAl_2O_4$ as the support material. For the case of this new Pt-K/$MgAl_2O_4$ sample, the maximum NOx uptake performance temperature (not shown here) shifted to 400ºC and 450ºC, in addition to providing larger total NOx uptake compared with the Al_2O_3-supported sample. Currently, PNNL is carrying out investigations of the characteristics of Pt-K/$MgAl_2O_4$ LNTs, such as K loading effects, NOx adsorption/desorption mechanisms, thermal aging, and SO_2 poisoning mechanisms.

The studies described above in Sections 1 and 2 are being pursued at PNNL in order to provide a more fundamental understanding of issues in LNT catalysts that have been shown in the open scientific literature to display improved high-temperature NOx storage/reduction performance relative to BaO/alumina-based materials. To provide a baseline for the overall performance as well as the stability of the materials being studied at PNNL, JM provided a fully formulated developmental catalyst. PNNL studies of this JM catalyst are limited to performance testing and performance stability measurements as described next.

3. Fully Formulated High-Temperature LNT Catalysts Supplied from JM

For a fully formulated sample supplied from JM, maximum NOx uptake is demonstrated around 400 and 450ºC as presented in Figure 3. Even at 500ºC, the NOx uptake performance is more than 60% of the maximum values. Small and incremental increasing amounts of SO_2 were then exposed to the catalyst, while continuing to measure NOx uptake at 400ºC. As demonstrated in Figure 4, full uptake monotonically decreases, indicating that even small amounts of SO_2 can deteriorate the NOx storage ability of this catalyst. For the sulfated sample, PNNL performed multiple desulfations aimed at removing the sulfur species by applying reductive treatments at elevated temperature, followed by additional NOx uptake measurements at 500°C. As shown in Figure 5, desulfation at 600°C gives rise to a small increase in the NOx uptake due to the removal of sulfur. However, further increases in the desulfation temperature up to 700°C resulted in a monotonic decrease in NOx uptake attributed, perhaps, to a more dominant thermal aging effect. Further investigations are aimed at determining optimum regeneration conditions.

Conclusions

PNNL and its CRADA partners from Cummins Inc. and JM have initiated a new CRADA project aimed at improving the higher temperature performance and stability of the LNT technology. Results obtained this year demonstrate that direct NO decomposition is not applicable for the real system. When K is used as storage element, the maximum temperature is shifted to 400ºC or higher, depending on the support. PNNL studies demonstrated that a $MgAl_2O_4$ support material provided especially promising NOx uptake performance. Additionally, the characteristics of a fully formulated LNT catalyst supplied from JM were investigated after applying SO_2 and thermal treatments. Overall, these studies are expected to provide valuable information for the development of durable LNT catalysts for high-temperature applications.

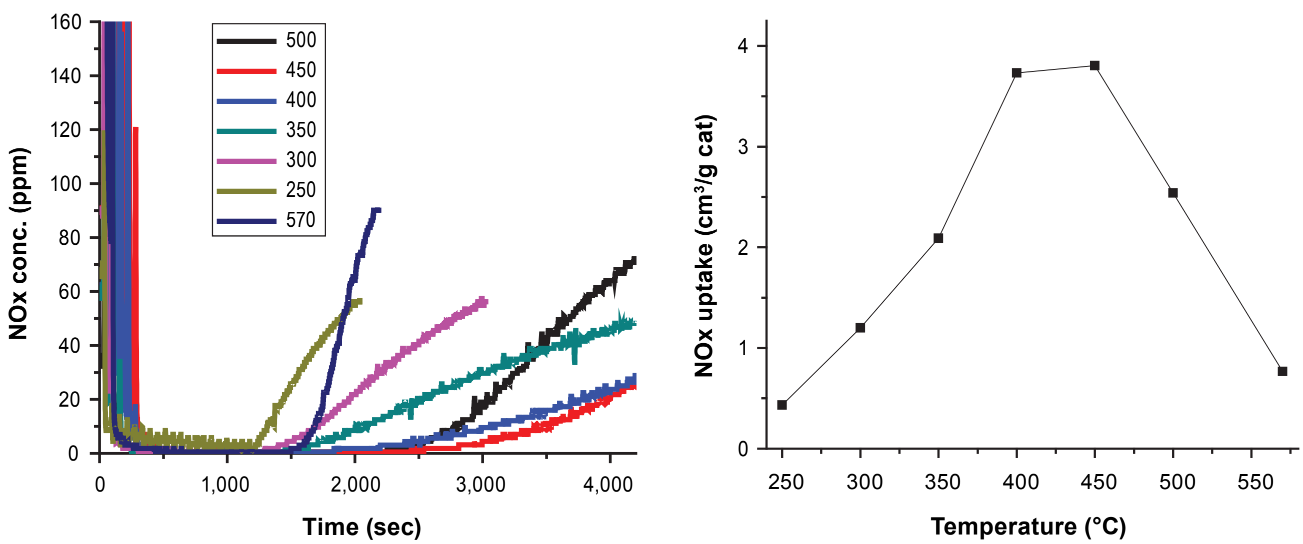

FIGURE 3. NOx uptake performance of a fully formulated NSR sample supplied from JM.

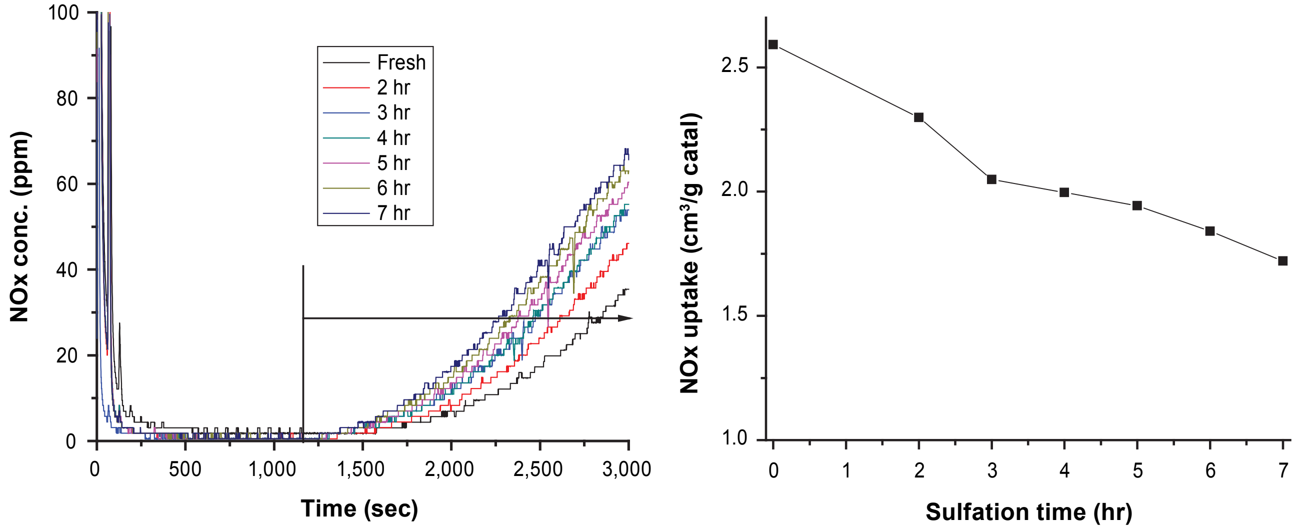

FIGURE 4. Changes in NOx uptake of the fully formulated NSR sample upon the exposure of SO_2 with time.

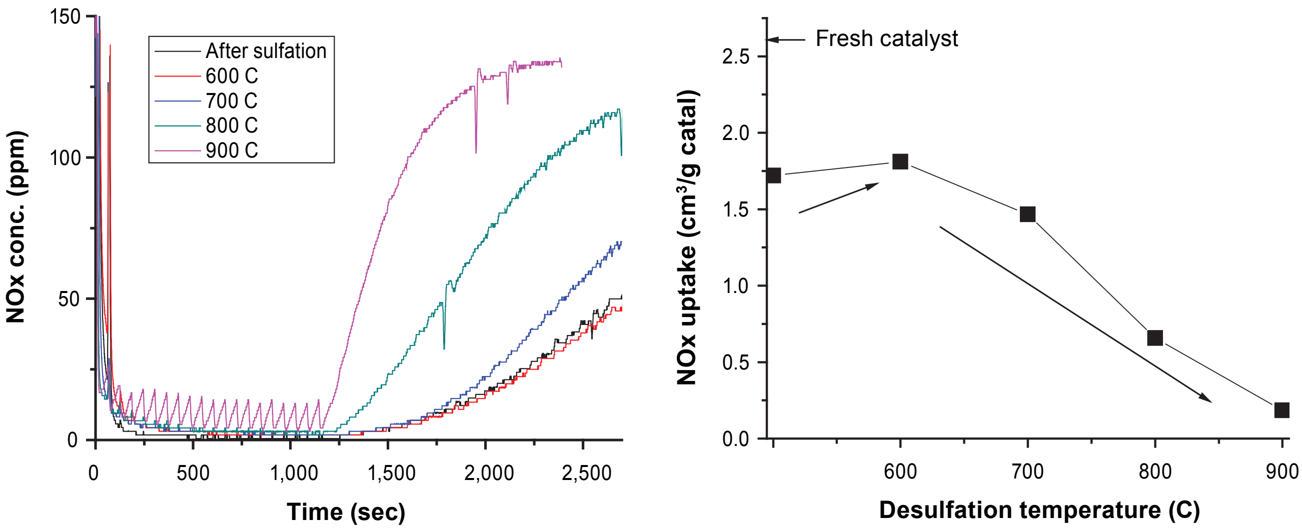

FIGURE 5. Changes in NOx uptake of a fully formulated NSR sulfated sample at 500°C after applying reductive desulfation treatments at elevated temperatures.

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1. Do Heui Kim, J.H. Kwak, J. Szanyi, X. Wang, M.H. Engelhard and C.H.F. Peden, "Promotional effect of CO_2 on the desulfation processes for pre-sulfated Pt-BaO/Al_2O_3 lean NOx trap catalysts", Topics in Catalysis 52 (2009) 1719.

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4. D.H. Kim, A. Yezerets, N. Currier, J. Li, H.-Y. Chen, H. Hess, M.H. Engelhard, G.G. Muntean, C.H.F. Peden, "Effect of sulfur loading on the desulfation chemistry over a commercial lean NOx trap catalyst." Ind. Eng. Chem. Res., submitted for publication.

5. D.H. Kim, X. Wang, G.G. Muntean, C.H.F. Peden, N. Currier, W.S. Epling, R. Stafford, A. Yezerets, H.-Y. Chen, and H. Hess, "Enhanced High Temperature Performance of NOx Storage/Reduction (NSR) Materials", presentation at the DOE Combustion and Emission Control Review, Washington, D.C., June, 2010.

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II.B.3 Emissions Control for Lean Gasoline Engines

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Objectives

- Assess and characterize catalytic emission control technologies for the reduction of oxides of nitrogen (NOx) from lean gasoline engines.
- Identify strategies for cost reduction of emission controls for lean gasoline engines.
- Characterize exhaust chemistry and the resulting evolution of chemistry in catalysts for lean gasoline engines.

Fiscal Year (FY) 2010 Accomplishments

Characterized the exhaust emissions from a modern lean gasoline engine vehicle including the reductant chemistry for lean-NOx trap (LNT) regeneration processes.

Future Directions

- Install a lean gasoline engine as a research platform for catalyst studies.
- Analyze NOx storage capacity challenges for LNT catalysts.
- Determine catalytic NH_3 production viability under rich engine operation for selective catalytic reduction (SCR) reactions.

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Introduction

Currently, the U.S. passenger car market is dominated by gasoline engine powertrains that operate at stoichiometric air-to-fuel ratios (sufficient fuel is mixed in air such that all of the oxygen in the air is consumed during combustion). Stoichiometric combustion leads to exhaust conditions suitable for three-way catalyst (TWC) technology to reduce NOx, CO, and hydrocarbon emissions to extremely low levels. Operating gasoline engines at lean air-to-fuel ratios (less fuel compared with air than for stoichiometric combustion) leads to less fuel consumption; however, the resulting oxygen in the exhaust prevents the TWC technology from performing. It is relatively straightforward to operate an engine lean at a good portion of the load and speed operating range; so, the largest challenge preventing fuel-saving lean combustion in gasoline applications is the control of emissions, primarily NOx. This project addresses that challenge.

Approach

FY 2010 was the first year for this project. Ultimately, this project will utilize a lean gasoline engine on an engine dynamometer to investigate catalytic emission control technologies to enable lean gasoline engines to meet NOx emission standards; however, for the first year, the project did not have such a platform in place. Instead, while efforts were begun to develop such an experimental platform, research was conducted on a lean gasoline engine vehicle on a chassis dynamometer to begin to characterize the emission challenges associated with the lean gasoline engine. A 2008 BMW 120i vehicle was studied under various driving cycles and steady-state operating conditions. The vehicle uses a 4-cylinder lean gasoline engine with two close-coupled TWCs and an underfloor LNT catalyst to manage emissions (Figure 1). Exhaust samples were analyzed with a variety of techniques to understand the NOx emission challenges as well as the reductants utilized for the LNT catalyst. The analytical tools utilized include: chemiluminescent NOx analyzers, non-dispersive infrared CO analyzers, magnetic-sector mass spectrometry for H_2 and O_2 measurements, and a Fourier transform infrared spectrometer for various gas species including NH_3, nitrogen oxide species, and hydrocarbons.

Results

The BMW 120i vehicle fuel economy was evaluated over three driving cycles: the Federal Test Procedure

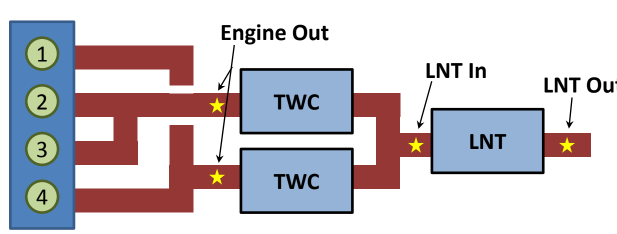

FIGURE 1. Schematic of the exhaust system of the BMW 120i vehicle showing the three-way and LNT catalysts.

(FTP), the Highway Fuel Economy Test (HFET), and the US06 Supplemental Federal Test Procedure (Figure 2). The vehicle operates lean to improve fuel economy and also utilizes start/stop and smart alternator power management to improve fuel economy. In all driving cycles, the largest fuel economy gains were due to the lean operation of the engine when compared to operation at stoichiometric conditions. The fuel economy improvements were between 4 and 15% due to lean operation with the most aggressive US06 driving cycle showing the lowest benefit. While lean operation enabled significant fuel savings, the NOx emissions observed at the tailpipe ranged from 0.11 to 0.35 g/mile for the driving cycles and were in excess of the U.S. Environmental Protection Agency (EPA) Tier II Bin 5 regulation level of 0.05 g/mile NOx at 50,000 miles. Figure 3 shows the tailpipe NOx emissions over the operating map of the vehicle with lean and stoichiometric operating zones defined; clearly, the highest NOx emissions occur during lean operation.

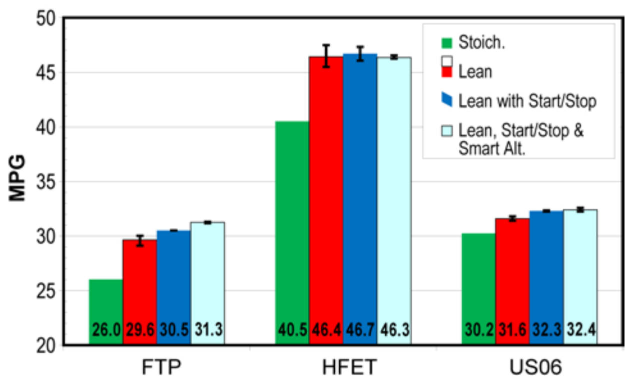

FIGURE 2. Fuel economy for three different drive cycles for combinations of the fuel saving technologies employed by the BMW 120i vehicle (as compared to stoichiometric-only operation).

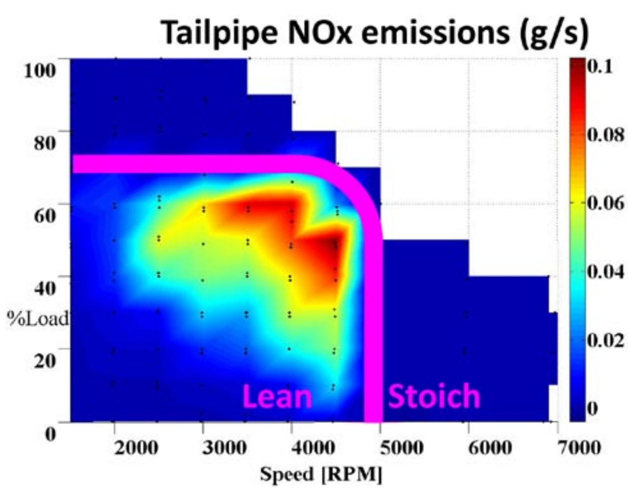

FIGURE 3. Tailpipe NOx emissions in g/s as a function of engine speed and load; lean and stoichiometric operating zones are defined by the pink curve.

The LNT catalyst requires periodic regeneration to reduce the stored NOx on the catalyst. For the BMW 120i vehicle, the regeneration process was performed by operating the engine at rich conditions (air-to-fuel = 12) for approximately 3 seconds. During the regeneration, H_2, CO, and NH_3 reductants were observed, in order of magnitude, at the LNT inlet position (Figure 4). The larger presence of H_2 as compared with CO is somewhat surprising based on experience from diesel engines with LNT technology. It was observed that the upstream TWCs play an important role in defining the LNT inlet reductant chemistry mixture as CO is converted to H_2 over the TWC during the rich conditions via the water-gas shift reaction (Figure 5).

Conclusions

Operation of gasoline engines at lean air-to-fuel ratio conditions can gain 4-15% improvements in fuel economy, but NOx emissions must be reduced to meet

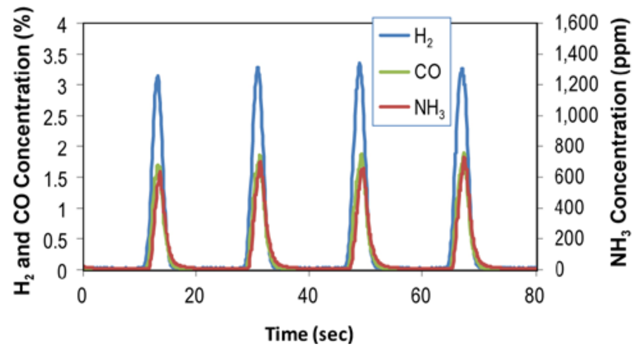

FIGURE 4. H_2, CO, and NH_3 reductant concentration as a function of time showing large peaks occurring during LNT regenerations. Note that the NH_3 scale is different than the H_2 and CO scale.

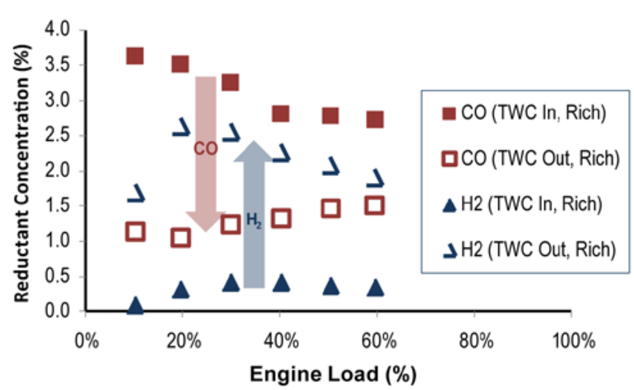

FIGURE 5. CO and H_2 concentration during the LNT regeneration event as a function of engine load at 3,500 rpm engine speed before and after the TWC; the TWC changes the ratio of CO:H_2 significantly.

U.S. EPA passenger car emission standards. A BMW 120i vehicle has been studied to characterize the NOx emission challenges associated with lean operation. The LNT technology on the vehicle is regenerated with a reductant mixture containing primarily H_2 and CO which is affected significantly by the upstream TWC.

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1. Jim Parks, Vitaly Prikhodko, Bill Partridge, Jae-Soon Choi, Kevin Norman, Paul Chambon, Shean Huff, "Lean Gasoline Engine Reductant Chemistry During Lean NOx Trap Regeneration", *SAE Technical Paper Series* 2010-01-2267 (2010).

2. Jim Parks, Vitaly Prikhodko, Bill Partridge, and Jae-Soon Choi, "Reductant Chemistry during LNT Regeneration for a Lean Gasoline Engine", *2010 Directions in Engine-Efficiency and Emissions Research Conference (DEER)*, September 27-30, 2010 (2010).

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II.B.4 Development of Chemical Kinetics Models for Lean-NOx Traps

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Objectives

- Identify a set of elementary (microkinetic) surface reactions that can account for the observed behavior of a lean-NOx trap (LNT) during a complete storage/regeneration cycle.
- Optimize the kinetic parameters associated with these reactions by matching model predictions with laboratory reactor data.
- Extend the mechanism to include reactions involving sulfur-containing species, with the aim of describing both catalyst degradation during normal operation and catalyst restoration during high-temperature desulfation.
- Use the validated reaction mechanism to suggest improvements in the usage of existing LNT materials and to help in the development of a new generation of catalysts.

Fiscal Year (FY) 2010 Accomplishments

- Modified our previously developed NOx storage and reduction (NSR) mechanism in order to account for N_2O formation during low-temperature cycles and to allow for complete catalyst regeneration during short (60 s/5 s) cycles under realistic concentrations of reductant.
- Developed the computational tools to simulate a complex sulfation/desulfation protocol described in the literature, along with a multipart objective function used in fitting the simulation results to key aspects of the experimental behavior.
- Developed a highly streamlined (nine-reaction) elementary mechanism for sulfation/desulfation that was nevertheless capable of reproducing the experimental data quite well.
- Formulated the thermodynamic relations necessary to extract temperature-dependent enthalpies and entropies for the surface species involved in the various mechanisms, and tabulated the results in CHEMKIN format.

Future Directions

- Account for the role of hydrocarbons and partial oxidation products as alternate reductant species during normal catalyst regeneration, as suitable experimental data becomes available.
- Enhance the transient plug flow reactor code with a complete energy balance equation, and use this to simulate the temperature excursions in conventional short storage/regeneration cycles, as these cannot be neglected or easily measured.
- Investigate the applicability of the techniques developed in this project to the modeling of selective catalytic reduction (SCR).

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Introduction

The increasingly strict constraints being placed on emissions from diesel and other lean-burn engines require the development of a new generation of aftertreatment technologies. LNTs represent one option for achieving the stated targets with regard to NOx emissions. In an LNT, NOx produced during normal lean engine operation is trapped and stored as nitrites and nitrates on alkaline oxide sites, and periodically this stored NOx is released and reduced to harmless N_2 on precious metal sites by imposing rich conditions for a short time. While this qualitative description is widely accepted, a detailed quantitative understanding of the underlying chemistry is not yet available. Such knowledge is needed in order to use the LNT concept to best advantage, so it is the principal goal of this project to develop an elementary reaction mechanism that describes both phases of LNT operation.

A complicating factor in the use of LNTs is that sulfur-containing contaminants in the fuel can lead to degradation in the catalyst performance over time, so periodic desulfation episodes are needed in addition to the ordinary regeneration (deNOx) excursions. Thus, a truly comprehensive mechanism must include reactions of sulfur-containing species alongside those describing storage, release, and reduction of NOx.

Clearly, a kinetics model with the ability to simulate all phases of LNT operation must account for the chemistry occurring on several kinds of catalytic sites: the metal oxide sites used to store NOx, additional oxide sites used (sometimes) for oxygen storage, and the precious metal sites involved primarily in the reduction of released NOx. While it is tempting to associate each of these kinds of sites with a particular part of the LNT cycle, it must be remembered that the desorption of NOx from the storage sites is an integral part of the regeneration process, while oxidation of NO on the precious metal sites is thought to be a key part of the storage phase. Nevertheless, it is possible to design experiments that isolate (to a large extent) a particular subset of the chemistry, and this has been used to facilitate model development in this project. Thus, work in early years led first to a tentative mechanism for the precious metal sites alone, and the basic mechanism was then completed by appending reactions for the storage sites. However, from time to time it has been necessary to revisit and refine this mechanism in order to overcome newly discovered deficiencies, as tends to occur when the mechanism is used under new circumstances. Ideally, work on the supplementary sulfation/desulfation chemistry proceeds via the addition of suitable reactions to a finalized NOx NSR mechanism, taking advantage of the fact that the roles of nitrogen- and sulfur-containing species are largely analogous. In reality, the sulfation/desulfation submechanism has undergone continuous refinement not only due to perceived flaws of its own, but also to account for changes in the underlying NOx chemistry.

Approach

Our basic approach to mechanism development is to assemble a candidate set of elementary reactions, generally with poorly known kinetic parameters, and then to optimize the parameters by fitting the results of reactor simulations to bench-scale experimental data provided by our collaborators at Oak Ridge National Laboratory. This process requires two principal pieces of supporting software: a reactor code to simulate flow through a single monolith channel using the proposed reaction mechanism (expressed in CHEMKIN format), and an optimization code to carry out the fitting process on a massively parallel computer. For the simulation of both storage/regeneration and sulfation/desulfation cycles, we have used a specially developed transient CHEMKIN-based plug flow code, and for the optimization we have adopted the Sandia APPSPACK code [1], which is ideally suited to this application.

As mentioned above, a tentative mechanism for the chemistry occurring on the precious metal sites was constructed and validated in previous years [2]. Our original intention was to incorporate this essentially without modification into the complete mechanism, thus minimizing the number of parameters to be determined on the basis of time-consuming transient simulations. However, it eventually became clear that this approach would lead to noticeable and avoidable errors, so the decision was made to treat the precious metal parameters once again as adjustable. A comprehensive LNT mechanism was then constructed by adding a set of candidate reactions for the storage sites, and the entire set of kinetic parameters was estimated by fitting simultaneously the experimental data (specifically, the exit gas concentrations) for not only a set of three long storage/regeneration cycles [3], but also the complete set of steady flow temperature sweeps used previously [2].

The experimental data used in optimizing the sulfation/desulfation mechanism were generated by a standard test protocol involving catalyst sulfation and periodic performance evaluation, both under continuous rapid cycling, and then desulfation by temperature-programmed reduction [4]. This led to an optimization process that was far more complex and time-consuming than that used for the NOx mechanism, but the basic approach was nevertheless the same.

In any mechanism development effort, a significant issue that must be addressed during the optimization process is that not all of the parameters can be varied independently if thermodynamic consistency is to be maintained. Thus, a number of well-defined relationships among the various parameters must be enforced; this reduces the size of the optimization problem, but it greatly increases the programming complexity. In addition, all of the activation energies, whether varied independently or computed from thermodynamic constraints, are required for physical reasons to be non-negative. Fortunately, the resulting inequality constraints are easily handled by APPSPACK.

A further complication in simulating LNT cycles is the issue of mass-transfer resistance within both the gas-phase boundary layer and the catalyst washcoat. A full treatment of these phenomena would result in a transient two-dimensional reactor model, which would be computationally prohibitive in light of the large number of simulations needed for parameter optimization. As an alternative, we have formulated and implemented a one-dimensional lumped-parameter description of mass transfer. Ultimately, however, we have found that the inclusion of a mass transfer resistance does not significantly improve the quality of the data fits. Because of this, and in light of the crudeness of this submodel, we have elected to abandon it and to pursue a purely kinetic description of LNT behavior.

Results

During the year we were able to overcome two drawbacks in our NSR mechanism, the first a longstanding issue with long-cycle simulations and the second an impediment to the simulation of real-world behavior. Specifically, our previous mechanism was unable to account for (1) the substantial production of N_2O immediately after the onset of regeneration during long cycles at 200°C, and (2) the complete regeneration of the catalyst during short (60 s/5 s) cycles at higher temperatures, this obviously being necessary for long-term NSR operation. The first of these problems was solved by postulating spillover reactions between stored nitrites and nitrogen atoms adsorbed on adjacent precious metal sites. As can be seen by comparing Figures 1 and 2, this was very successful in reproducing the observed behavior, although many other equally promising procedures had failed.

The ability of the NSR mechanism to simulate short cycles was, coincidentally, also achieved by adding spillover reactions involving stored nitrites, the co-reactants in this case being adsorbed reductants (H and CO). Similar reactions had previously been introduced to reduce nitrates to nitrites, but the new reactions were found to be crucial in reproducing the ability to regenerate the catalyst quickly by using high concentrations of reductant. The incompleteness of the old model was evidently masked in the long cycle analyses due to the low concentrations of reductant used. In any case, this advance was important not just

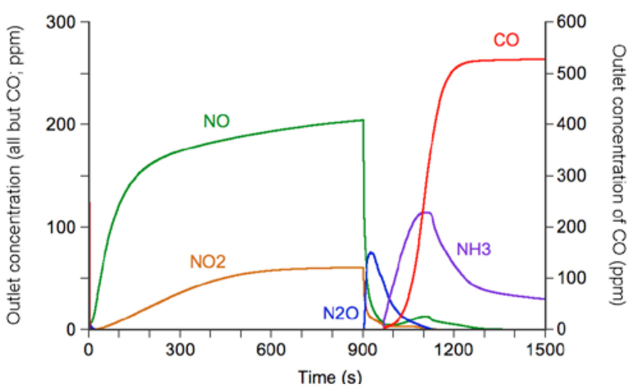

FIGURE 1. Simulated outlet concentrations for the benchmark long storage/regeneration cycle at 200°C.

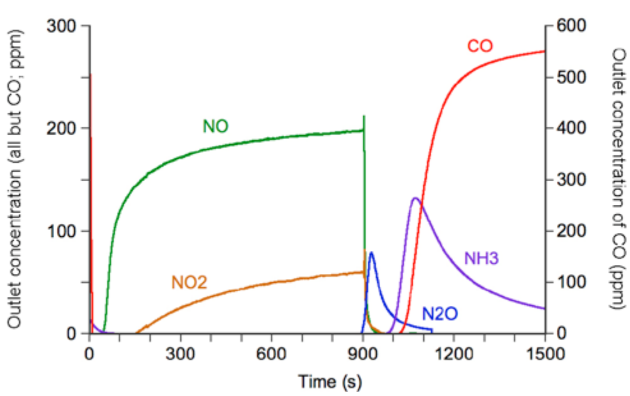

FIGURE 2. Experimental outlet concentrations for the benchmark long storage/regeneration cycle at 200°C [3].

for simulating normal NSR, but also for dealing with the effects of sulfation, as noted below.

Our continued development of a sulfation/desulfation mechanism involved not only changes in the reaction set itself, but also a vastly more comprehensive simulation of the relevant experiments. The latter involved two sets of 111 short NSR cycles with a small amount of SO_2 added to the feed, each set being followed by a sequence of SO_2-free cycles in order to gauge the effect of catalyst sulfation on NSR performance. The catalyst was then desulfated by ramping the temperature to a high value under a reductant flow. The simulation of this entire protocol proved to be extremely time-consuming, and this was a strong motivating factor to keep the number of adjustable kinetic parameters as small as feasible. Partly for this reason, the number of sulfur-specific reactions was reduced to a bare minimum of nine. A key simplification was to eliminate reactions describing the direct reduction (as opposed to simple decomposition) of SO_3 adsorbed on precious metal sites. On the other hand, a key addition was a reaction describing oxidation of SO_2 to SO_3 (the immediate sulfate precursor) on oxygen storage sites, as this was found to be the only way to produce SO_3 quickly enough to concentrate sulfate production at the front end of the catalyst.

The kinetic parameters in the streamlined mechanism were varied in an attempt to match five selected experimental observations: (1) the complete trapping of SO_2 during normal NSR functioning; (2) the plug-like sulfation of NOx storage sites; (3) the progressive degradation of NSR performance with increasing levels of sulfation; (4) the evolution of H_2S and SO_2 during desulfation by temperature-programmed reduction; and (5) the completeness of desulfation after a long high-temperature soak. The effect of sulfation on the NOx trapping efficiency of the catalyst is shown in Figure 3, and the agreement between simulation and experiment is quite encouraging. The effluent concentrations of the product gases H_2S and SO_2 during desulfation are shown in Figure 4. While the nature of the data precludes a direct quantitative comparison, the timing and the relative sizes of the peaks are clearly reproduced very well. Lastly, Figure 5 shows how the amount of sulfate on each of the two kinds of storage sites is predicted to fall off during desulfation. A key observation is that sulfur is bound more strongly to the NOx storage sites, in agreement with experiment. This feature was not incorporated into the objective function used in the parameter fitting process, so agreement of this kind provides significant support for the underlying chemical mechanism.

Finally, we devoted some effort this year to the extraction of thermodynamic properties for the various surface species involved in the mechanisms. Such properties are very difficult to compute directly, but

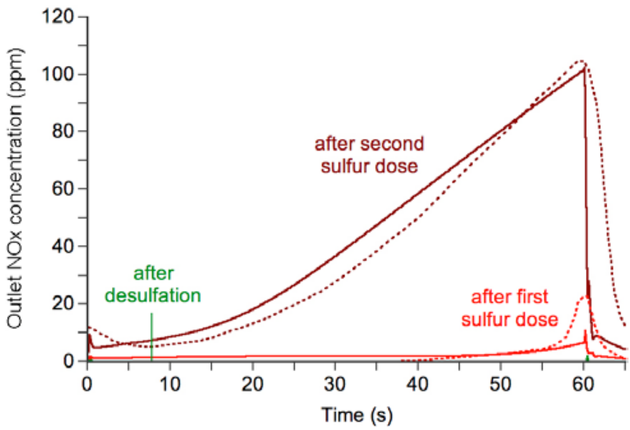

FIGURE 3. Outlet concentrations of total NOx during ordinary NSR cycling at 325°C for various degrees of sulfation. Solid lines are simulation results; dotted lines are experimental measurements [4].

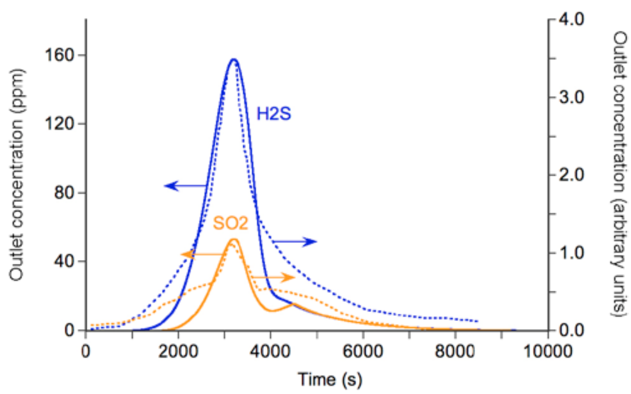

FIGURE 4. Outlet concentrations of evolved gases during desulfation by temperature-programmed reduction. Solid lines are simulation results; dotted lines are experimental measurements [4].

they can be inferred if a suitable number of equilibrium constants involving the desired species are known. The parameter optimization process provides the needed equilibrium constants, and the thermodynamic consistency relations guarantee that the properties of the surface species are determined uniquely. We have now formulated the necessary relations and computed properties for all of the surface species involved in the NSR mechanism. This information will be crucial in simulations that use an energy balance equation to compute the exotherms arising from the NSR reactions.

Conclusions

- Spillover reactions involving stored nitrites and reductant species on adjacent precious metal sites are crucial in explaining the behavior of an LNT during both long and short cycles.

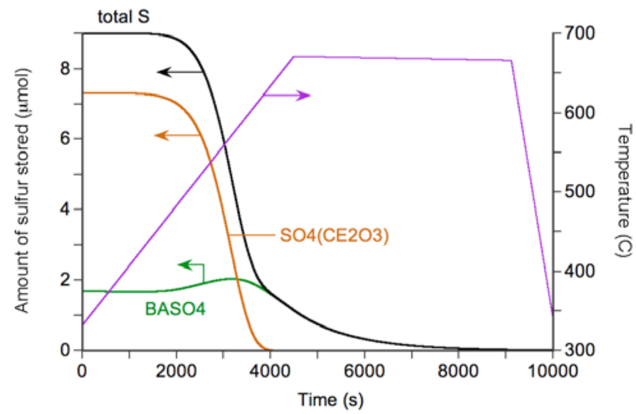

FIGURE 5. Simulation results for depletion of individual sulfate species and total trapped sulfur during desulfation by temperature-programmed reduction.

- The simulation of a standard sulfation/desulfation protocol, involving hundreds of short storage/regeneration cycles as well as a ramped-temperature desulfation regimen, is marginally feasible with current computing capabilities.
- The ability to simulate the plug-like sulfation of NOx storage sites in an LNT seems to require a pathway for the rapid oxidation of inlet SO_2 by stored oxygen.

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2. R.S. Larson, J.A. Pihl, V.K. Chakravarthy, T.J. Toops, and C.S. Daw, *Catal. Today* **136**, 104 (2008).

3. J.A. Pihl, M.S. Thesis, University of Wisconsin–Madison, 2005.

4. J.-S. Choi, W.P. Partridge, and C.S. Daw, *Appl. Catal. B* **77**, 145 (2007).

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1. R.S. Larson, V.K. Chakravarthy, J.-S. Choi, J.A. Pihl, and C.S. Daw, "Update on Microkinetic Modeling of Lean NOx Trap Chemistry," Thirteenth CLEERS Workshop, Dearborn, Michigan, April 22, 2010.

2. R.S. Larson, "Development of Chemical Kinetics Models for Lean NOx Traps," DOE Vehicle Technologies Program Annual Merit Review, Washington, D.C., June 10, 2010.

3. R.S. Larson, V.K. Chakravarthy, J.A. Pihl, and C.S. Daw, "Microkinetic Modeling of Lean NOx Trap Storage and Regeneration," journal paper under revision.

4. R.S. Larson, "Microkinetic Modeling of Lean NOx Trap Sulfation and Desulfation," journal paper in preparation.

II.B.5 Advanced Engine/Aftertreatment System R&D CRADA with Navistar, Inc.

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DOE Technology Development Manager:
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Objectives

- Develop engine/aftertreatment system configurations and control strategies that meet stringent emissions regulations while improving overall vehicle efficiency.
- Enhance fundamental understanding of diesel particulate filter (DPF) operating principles to facilitate fuel-optimal control strategy formulation.
- Develop experimental methods that probe the underlying chemical kinetics and changes in soot reactivity under carefully controlled DPF regeneration conditions.
- Exercise experimental methods to measure the reaction kinetics and operating parameters of DPFs needed in development of accurate simulation tools and detailed control strategies.
- Evaluate impact of non-traditional or non-optimal operating regimes on DPF fuel penalty and durability, including high soot loadings, partial regenerations, and alternate methods to achieve active regeneration temperatures.

Fiscal Year (FY) 2010 Accomplishments

- Provided ammonia selective catalytic reduction (SCR) catalyst evaluation protocol developed in FY 2009 to serve as a starting point for a new Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) transient SCR protocol.
- Transferred ammonia-SCR data collected in FY 2009 to separate DOE-funded project on "Experimental Studies for DPF and SCR Model, Control System, and OBD Development for Engines Using Diesel and Biodiesel Fuels" led by Michigan Technological University.
- Obtained miniature DPF samples from suppliers.
- Loaded miniature DPFs with soot in engine exhaust.
- Modified bench-scale flow reactor to handle high flow rates and backpressures required for DPF experiments and to enable liquid hydrocarbon injection.
- Conducted temperature programmed oxidation experiments on the soot-loaded miniature DPFs.

Future Directions

- Perform pulsed oxidation experiments to measure kinetic parameters for soot oxidation by both O_2 and oxides of nitrogen (NOx).
- Use kinetic data to improve Navistar DPF regeneration models.
- Investigate O_2 chemisorption method for in situ soot surface area characterization.

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Introduction

High-efficiency lean-burn combustion engines offer a promising strategy for reducing petroleum consumption. However, meeting increasingly stringent emissions standards with lean-burn engines has proven to be a challenge. The engine modifications and aftertreatment systems used to reduce exhaust emissions typically increase fuel consumption, eroding the efficiency advantages of lean-burn operation. These complex systems also increase costs, creating a barrier to penetration of lean-burn engines into new market segments.

Development of lean-burn engine systems that meet stringent emissions standards while improving overall vehicle efficiency requires simultaneous optimization of both engine and aftertreatment operating strategies. This optimization often relies heavily on simulation tools. Formulation of simulation tools and operating strategies is complicated by the presence of storage functions in aftertreatment devices (particulate filters store soot, lean-NOx traps store NOx, and SCR systems store NH_3), which precludes the use of the steady-state operating maps typically used for engine control. The focus of this CRADA is to assist Navistar in the development and calibration of detailed simulation tools that will be used in control strategy development. These efforts will help Navistar bring to market high-efficiency engine systems that reduce fuel consumption while complying with emissions regulations. The protocols and findings from this project will also provide useful insights to the engine aftertreatment research and development community as a whole.

Approach

During FY 2010 we shifted the focus of the CRADA from ammonia-SCR systems to DPFs. This shift was a logical consequence of Navistar's strategic decision to utilize in-cylinder NOx control, precluding a current need for NOx aftertreatment. While in-cylinder NOx control reduces or eliminates the need for NOx aftertreatment, it places more of a demand on the DPF due to increased particulate production and/or reduced passive filter regeneration by NOx. If not managed carefully, the resulting higher soot loading rates could require more frequent active regeneration events to avoid excessive filter backpressure or runaway regeneration events. Since active regeneration requires increasing the exhaust temperature (typically achieved through injection of excess fuel), more frequent regenerations could incur a larger fuel penalty and possibly impact filter durability. The goal of the current phase of the project is to measure relevant soot oxidation kinetics that will be integrated into Navistar's DPF regeneration control models.

Due to the complexities inherent in engine experiments, we decided to conduct our kinetic measurements on a bench-scale flow reactor system at ORNL. Navistar identified several DPF formulations of interest and obtained miniature (2.5 cm outer diameter by 7.6 cm long) particulate filter samples from suppliers. The formulations were based on three different substrate materials: cordierite, aluminum titanate, and silicon carbide. Half of the filters were washcoated with an oxidation catalyst; the other half were left uncoated. The filters were loaded with soot in an engine exhaust slip stream at a Navistar engine testing partner facility. The filters were subsequently sent to ORNL for detailed characterization of the regeneration process in an automated flow reactor. Flow reactor experiments conducted in FY 2010 focused on temperature programmed oxidations (TPOs). The TPO experiments consisted of loading a miniature DPF in the reactor, heating it to 200°C, starting the flow of a known composition of oxidant (O_2, NOx, or a mixture of the two) through the filter, and linearly increasing the filter temperature to 650°C. These controlled burnout experiments gave us an opportunity to characterize soot oxidation rates and pressure drop evolution over the course of a complete regeneration.

Results

Figure 1 shows the calculated soot oxidation rate (based on CO and CO_2 evolved) as a function of temperature for the O_2 TPO experiments on all six DPF formulations. To account for variations in total soot loading, the oxidation rates are normalized to the initial amount of soot on the fully loaded filter. The resulting rates plotted in Figure 1 can be interpreted as the fraction of soot burned per second. The oxidation rate profile is very similar for all three substrate materials in the absence of a catalytic washcoat. This is expected since, in the absence of a catalyst, the oxidation kinetics should be determined primarily by the properties of the soot, and all of the soot samples were collected under very similar engine operating conditions. Measurable oxidation by O_2 can be observed at around 300°C, but the reaction rate does not become significant until around 450°C. The peak burnout rate occurs at 600°C, after which the rapidly decreasing amount of soot on the filter causes a drop in CO and CO_2 evolved. The washcoat resulted in a slight increase in oxidation rate over the entire regeneration for cordierite and aluminum titanate, resulting in slightly lower peak burnout temperatures than for the uncatalyzed substrates. Interestingly, the presence of the washcoat on the silicon carbide substrate appeared to have a slightly negative impact on O_2 oxidation kinetics over the entire regeneration. The difference between the catalyzed and uncatalyzed silicon carbide filters was small, but the catalyst definitely did not have the positive impact on O_2 oxidations kinetics as seen in the other two substrate materials.

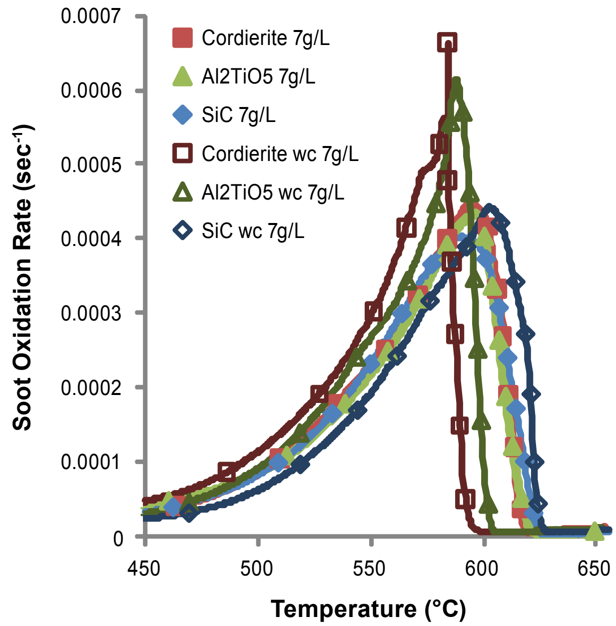

FIGURE 1. Soot oxidation rate as a function of temperature for O_2 (10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity) TPOs (200-650°C at 2°C/min) on miniature DPFs in a flow reactor. All samples were loaded in engine exhaust to approximately 7 g soot per liter of filter. "wc" indicates a filter coated with an oxidation catalyst.

The soot oxidation rates for the NOx + O_2 TPOs are shown in Figure 2. As expected, inclusion of NOx in the feed gas substantially increased the soot oxidation rate at low temperatures; measurable oxidation was observed as low as 200°C. As in the O_2 TPOs, the burnout curves for the uncatalyzed filters are fairly similar, but the presence of a catalytic washcoat introduces substantial differences between the substrate materials. In this case, the oxidation catalyst significantly increases the low temperature oxidation rates for all the substrates. Further, unlike the fairly simple burnout curves observed for the O_2 TPOs, the catalytic coating results in fairly complex NOx + O_2 oxidation rate behavior that changes significantly with substrate material. The apparent multiple bumps and peaks in the burnout profile suggest that different types of soot (or soot environments) exist within the filter.

Since the washcoat composition and loading was nominally the same for the three substrates, the differences in oxidation kinetics are most likely due to variations in washcoat location and distribution, which are caused by differences in substrate microstructure (porosity, monolith geometry, and affinity for the washcoat material). These variations in the washcoat could, in turn, result in different soot distributions within the filter (more soot in the cake layer as opposed to within the filter wall, for example).

Further evidence of possible spatial variations in soot loading and oxidation behavior can be seen in the filter backpressure evolution during the regeneration, shown in Figures 3 and 4. Both of these figures show filter pressure drop as a function of soot burnout (the fraction of the soot already oxidized). The fully loaded filter pressure drop changes based on the DPF formulation, since the filter microstructure depends on the substrate material and the presence or absence of a catalytic washcoat. For all three substrate materials, adding a washcoat increases the filter backpressure, probably due to occlusion of pores in the filter wall. Interestingly, for all of the formulations and operating conditions investigated, the filter pressure drop decreases to that of a clean filter by the time half of the soot has been oxidized. This observation highlights the inadequacy of pressure sensors for determining filter regeneration status: the pressure sensor would indicate a complete regeneration long before all of the soot in the filter has actually been consumed. It also illustrates the complex spatial dependence of the soot oxidation process. The soot that creates most of the filter pressure drop (located within the filter wall, for example) burns out faster than the soot located elsewhere. This effect is magnified when NOx is added to the feed gas (Figure 4): the backpressure drops after only a third of the soot has been oxidized. Why the NOx would be more selective

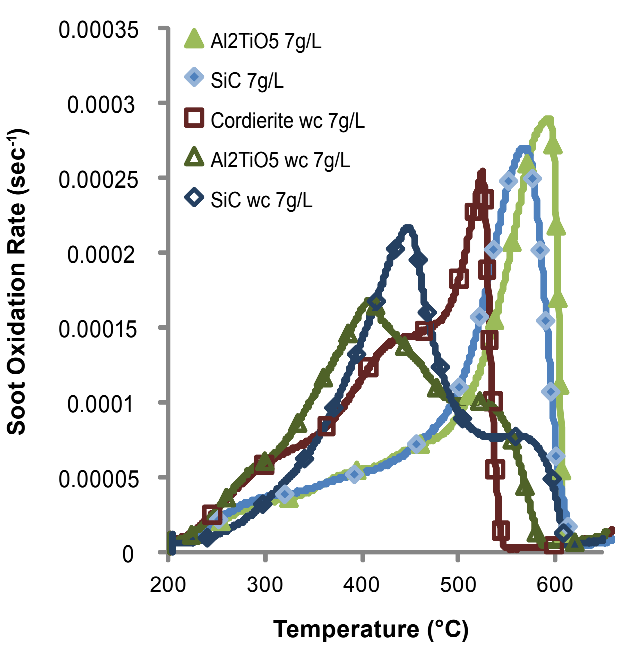

FIGURE 2. Soot oxidation rate as a function of temperature for O_2+NOx (75 ppm NO_2, 225 ppm NO, 10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity) TPOs (200-650°C at 2°C/min) on miniature DPFs in a flow reactor. All samples were loaded in engine exhaust to approximately 7 g soot per liter of filter. "wc" indicates a filter coated with an oxidation catalyst.

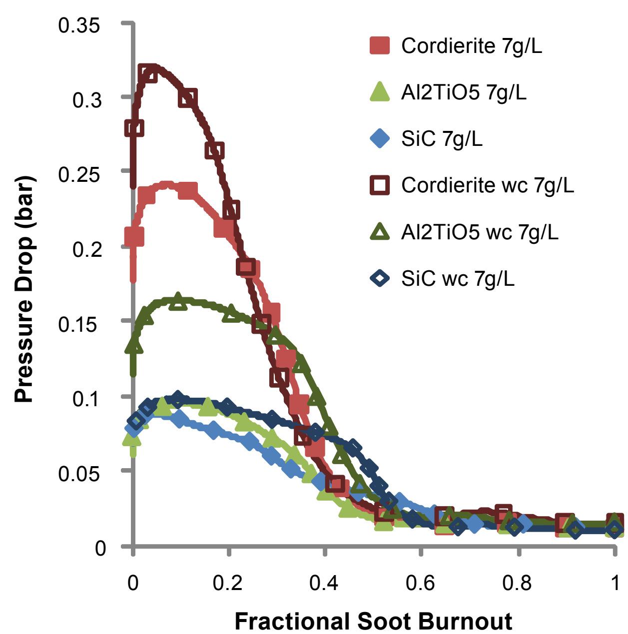

FIGURE 3. Filter pressure drop as a function of fractional soot burnout for O_2 (10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity) TPOs (200-650°C at 2°C/min) on miniature DPFs in a flow reactor. All samples were loaded in engine exhaust to approximately 7 g soot per liter of filter. "wc" indicates a filter coated with an oxidation catalyst.

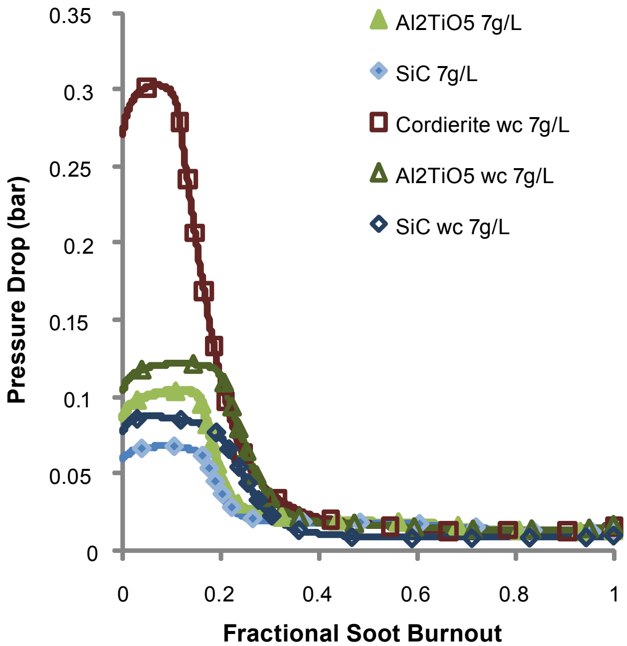

FIGURE 4. Filter pressure drop as a function of fractional soot burnout for O_2+NOx (75 ppm NO_2, 225 ppm NO, 10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity) TPOs (200-650°C at 2°C/min) on miniature DPFs in a flow reactor. All samples were loaded in engine exhaust to approximately 7 g soot per liter of filter. "wc" indicates a filter coated with an oxidation catalyst.

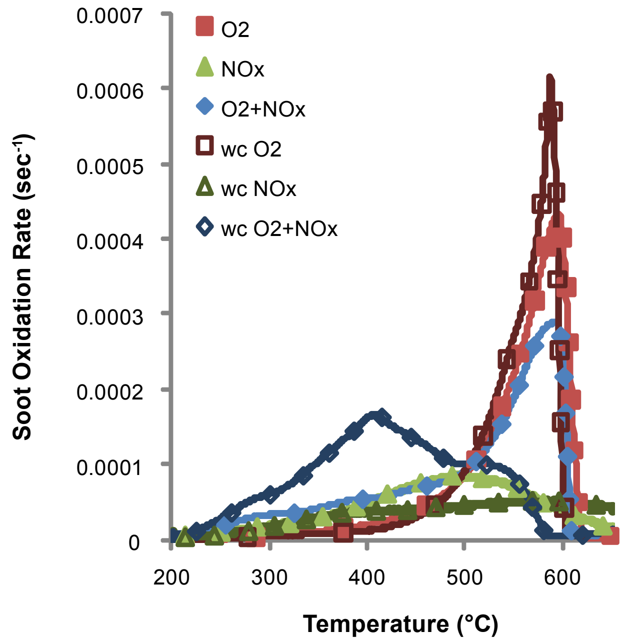

FIGURE 5. Soot oxidation rate as a function of temperature for O_2 (10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity), NOx (75 ppm NO_2, 225 ppm NO, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity), and O_2+NOx (75 ppm NO_2, 225 ppm NO, 10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity) TPOs (200-650°C at 2°C/min) on miniature aluminum titanate DPFs in a flow reactor. O_2 and O_2+NOx TPO samples were loaded in engine exhaust to approximately 7 g soot per liter of filter; NOx TPO samples were loaded to 3 g/L. "wc" indicates a filter coated with an oxidation catalyst.

in burning out the soot contributing to the backpressure (even in the absence of a catalytic coating) is unclear.

A clearer illustration of the effects of gas composition and catalytic coating on spatial variations in soot oxidation can be found in Figures 5 and 6, which show three different TPO experiments (O_2, NOx, O_2+NOx) conducted on aluminum titanate filters with and without a catalytic washcoat. Note that the NOx-only TPOs did not result in complete regeneration of the filter; upon completion of the temperature ramp, O_2 was introduced at 650°C to oxidize the soot completely and close the carbon balance.

The oxidation rate data in Figure 5 demonstrate the synergistic effect of O_2 and NOx over a catalyzed filter. On the uncatalyzed filter, the oxidation rate for the O_2+NOx experiment is roughly the sum of the runs with O_2 and NOx individually. However, on the catalyzed sample, the O_2+NOx TPO shows a substantially increased low temperature soot oxidation rate over either the individual catalyzed O_2 and NOx experiments or the uncatalyzed O_2+NOx TPO. The increase in low temperature oxidation rate is likely due to catalytic oxidation of NO to NO_2. NO_2 is a more reactive Figure 6 shows how the O_2+NOx feed gas results in a drop in backpressure at a much lower fractional soot burnout than in cases with just O_2 or NOx, implying that NO_2 is more selective in burning soot located in the filter wall. If exploited, these behaviors may lead to fuel optimal control strategies that achieve filter regeneration at lower temperatures or allow for less frequent regenerations. Developing such strategies will require DPF regeneration models that accurately capture these details. We are currently conducting carefully controlled pulsed oxidation experiments to measure the relevant kinetics needed for model development and calibration.

Conclusions

The goal of our current work is to reduce the fuel penalty associated with DPF regeneration by developing more accurate simulation tools which should lead to better control strategies. During FY 2010, the CRADA team obtained miniature DPFs with several different formulations from suppliers, loaded the filters in engine exhaust, and conducted temperature programmed oxidation experiments in a flow reactor. We observed complex variations in soot oxidation rate and pressure drop evolution for cases with O_2 and NOx in the feed gas, which could be explained by spatial variations in the regeneration process. Our work for FY 2011 will be focused on figuring out how to incorporate these behaviors in DPF regeneration models.

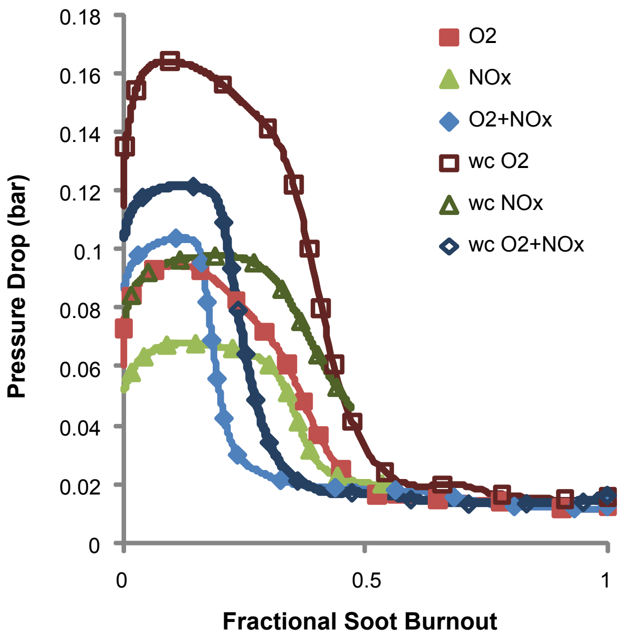

FIGURE 6. Filter pressure drop as a function of fractional soot burnout for O_2 (10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity), NOx (75 ppm NO_2, 225 ppm NO, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity), and O_2+NOx (75 ppm NO_2, 225 ppm NO, 10% O_2, 5% H_2O, balance N_2; 40,000/hr gas hourly space velocity) TPOs (200-650°C at 2°C/min) on miniature aluminum titanate DPFs in a flow reactor. O_2 and O_2+NOx TPO samples were loaded in engine exhaust to approximately 7 g soot per liter of filter; NOx TPO samples were loaded to 3 g/L. "wc" indicates a filter coated with an oxidation catalyst.

FY 2010 Publications/Presentations

1. J.A Pihl, T.J. Toops, V.O. Strots, E.M. Derybowski, "Advanced Engine/Aftertreatment System R&D – CRADA with Navistar Incorporated," 2010 DOE Vehicle Technologies Program Annual Merit Review & Peer Evaluation Meeting, Washington, D.C., June 10, 2010.

2. J.A. Pihl, T.J. Toops, V.O Strots, S.B. DeLand, G.G. Parker, J.H. Johnson, "Development & Implementation of Experimental Protocol for Steady-State and Transient SCR Kinetics," 2009 American Institute of Chemical Engineers Annual Meeting, Nashville, TN, November 12, 2009.

II.B.6 Fundamental Sulfation/Desulfation Studies of Lean NO_x Traps, DOE Pre-Competitive Catalyst Research

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DOE Technology Development Manager:
Ken Howden

Objectives

- Investigate methods for improving performance and/or durability of lean-NOx (LNTs):
  - Measure and characterize impact of changing LNT formulations.
  - Determine the optimum operating parameters.
- Improve the fundamental understanding of deactivation mechanisms that result during the regeneration of LNTs.

Approach

- Conduct pre-competitive LNT research.
- Investigate materials changes that can improve NOx reduction performance and/or desulfation behavior.
- Study deactivation and regeneration mechanisms fundamentally.
- Coordinate efforts with other projects to maximize knowledge findings.

Fiscal Year (FY) 2010 Accomplishments

- Demonstrated the use of ceria as a support of the Ba storage phase decreases the temperature required to desulfate the Ba phase by over 100°C.
- Demonstrated re-distribution of Ba-phase occurs during high temperature treatments.
- Presented results at 2009 Annual Meeting of the American Institute of Chemical Engineering, 13th Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, 2010 DOE Vehicle Technologies Annual Merit Review and 2010 Directions in Engine-efficiency and Emissions Research Conference.
- Published invited paper in a special issue of Catalysis Today.
- Prepared paper for submission to Applied Catalysis B.

Future Directions

- Investigate durability of Ca + Ba lattice to understand if the observed performance improvements withstand aging.
- Expand characterization of Ca + Ba to include diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and microscopy.
- Establish capability to measure the surface and gas-phase species simultaneously using newly developed DRIFTS reactor and spatially resolved capillary inlet mass spectrometer.

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Introduction

Increasingly stringent emissions regulations have necessitated the introduction of new catalytic emissions control devices for vehicles with lean-burn engines. While lean-burn engines are typically more fuel efficient than their stoichiometrically-operated counterparts, meeting these regulations requires the system to operate at non-optimum levels. In designing the controls to operate the system the manufacturer must make a decision between these extreme scenarios:

- Operate the engine at non-optimum conditions resulting in low emissions of oxides of nitrogen (NOx) and particulate and having minimal reliance on emissions control devices, or
- Operate the engine at peak efficiency and rely on the larger more robust emissions control systems to “clean-up” the exhaust.

Most of the vehicles on the road today operate somewhere between these two conditions. The implementation of the emissions control systems can also incur a “fuel penalty.” For example, LNT catalysts require periodic operation under fuel-rich conditions, increasing vehicle fuel consumption. The key to deployment of lean-burn engine technology lies in optimizing the emissions control system such that emissions regulations are met without substantially reducing fuel economy.

This project focuses on establishing a fundamental understanding of the underlying LNT chemistry to improve the accuracy of computer simulations used to design, develop, and control LNT aftertreatment systems. This includes identifying the roles of the catalytic phases of LNTs, investigating the impact of changes in catalyst formulations, elucidating reaction pathways, and determining the fate of sulfur in the catalyst. This effort is closely tied to the CLEERS kinetics activities and serves as guidance for the research undertaken in that project.

Approach

Our approach to understanding LNT fundamentals utilizes the unique capabilities and expertise developed in previous years of this project, i.e. the differential microreactor and the barrel-ellipse DRIFTS reactor. The microreactor is operated to minimize heat and mass transfer effects, enabling analysis of the underlying LNT reactions. The microreactor is capable of running a suite of catalyst characterization experiments, including surface area measurements through physisorption and chemisorption, quantification of reaction kinetics, characterization of catalyst performance under realistic operating conditions, and measurement of surface species stability through temperature programmed reactions. It was designed for relatively quick and easy sample loading, so several catalysts can be studied in a short period of time. In addition to the measurement of the reaction kinetics, it is important to understand the catalyst surface chemistry. The DRIFTS reactor enables these measurements at elevated temperatures and using simulated engine exhaust, including H_2O and CO_2. The ability to make these measurements under realistic conditions offers the ability to identify "real-world" reaction intermediates and thus confirm mechanistic models or suggest new reaction pathways.

Results

Significant effort was also put forth this year to understand the functionality of the individual components that are found in a commercially-available Umicore LNT. This complex catalyst, that is also the CLEERS LNT reference catalyst, has several distinct phases that have been thoroughly characterized in a recent publication [1]. A cross-section of the washcoated LNT with the primary phases identified is shown in Figure 1. The key features that distinguish this sample from many of the model systems being studied is that the Ba-storage phase is primarily supported on ceria-zirconia rather than alumina. This is a very important distinction since even the advanced model systems that do incorporate ceria typically employ a physical mixture of Pt/Ba/alumina and Pt/ceria-zirconia. Several studies have shown that the inclusion of ceria leads to an improvement in the low temperature NOx reduction capability [2,3], but few studies have reported the use of ceria-zirconia as the support. Efforts this year were focused on understanding the impact of using this support versus alumina, with a focus on the sulfation and desulfation behavior. The samples studied are listed in Table 1 and include Pt/Al_2O_3 (PA), Pt/CeO_2-ZrO_2 (PCZ), $Pt/Ba/Al_2O_3$ (PBA), and $Pt/Ba/CeO_2$-ZrO_2 (PBCZ).

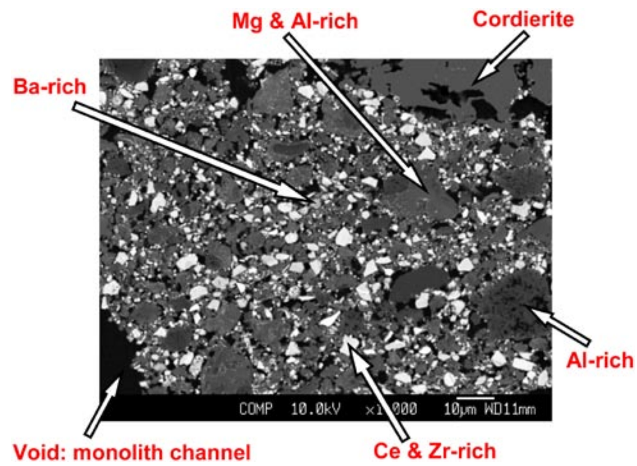

FIGURE 1. Cross-Section of Washcoated LNT that Identifies the Primary Phases of the Commercial Catalyst

TABLE 1. Component Contributions by Mass Percent

	Pt	Ba	Al_2O_3	CeO_2-ZrO_2
Pt/Al_2O_3	1.5	-	98.5	-
$Pt/Ba/Al_2O_3$	1.5	20	79.2	-
Pt/CeO_2-ZrO_2	1	-	-	99
$Pt/Ba/CeO_2$-ZrO_2	0.8	20	-	79.2

To investigate the sulfation behavior at 400°C the samples were exposed to typical lean-rich cycling conditions, 60 seconds lean (300 ppm NO, 10% O_2, 5% CO_2, 5% H_2O, balance Ar) and 5 seconds rich (0.71% H_2, 1.19% CO, 5% H_2O, 5% CO_2, balance Ar), with 15 ppm SO_2 flowing at all times. In comparing the individual supports PA and PCZ under these conditions (Figure 2a), it can be seen that PCZ is much more efficient at capturing the SO_2 being fed to the reactor; there is essentially no SO_2 escaping the PCZ reactor bed under these conditions while PA shows sulfur breaking through after 1,200 seconds. Interestingly the inclusion of Ba on these supports has a two-tiered effect. PBA has a later breakthrough compared to PBCZ, 2,000 seconds versus 1,300 seconds, but significantly more sulfur is released when switching from lean to rich. These results show spikes of 9 ppm at the end of the sulfation step compared to spikes of ~1 ppm for PBCZ. This specifically illustrates ceria-zirconia's ability to store sulfates under rich conditions, which is most likely due to its oxygen storage characteristic. While this ability to store and release oxygen can have a negative effect on fuel consumption, it may aid in the temporary protection of the Ba phase from sulfur.

A key contributor to the durability of LNTs is the requirement to go to high temperature to remove the sulfates and restore NOx storage capacity. The high temperatures typically result in sintering of expensive

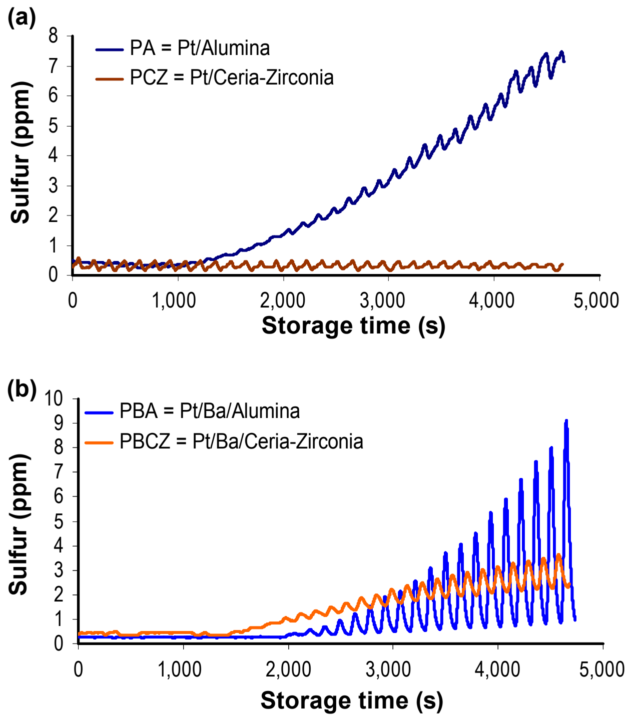

FIGURE 2. Sulfur measured in the effluent during lean-rich cycling at 400°C. Samples shown are for (a) the individual supports, PA and PCZ, and (b) those with the Ba-phase included, PBA and PBCZ.

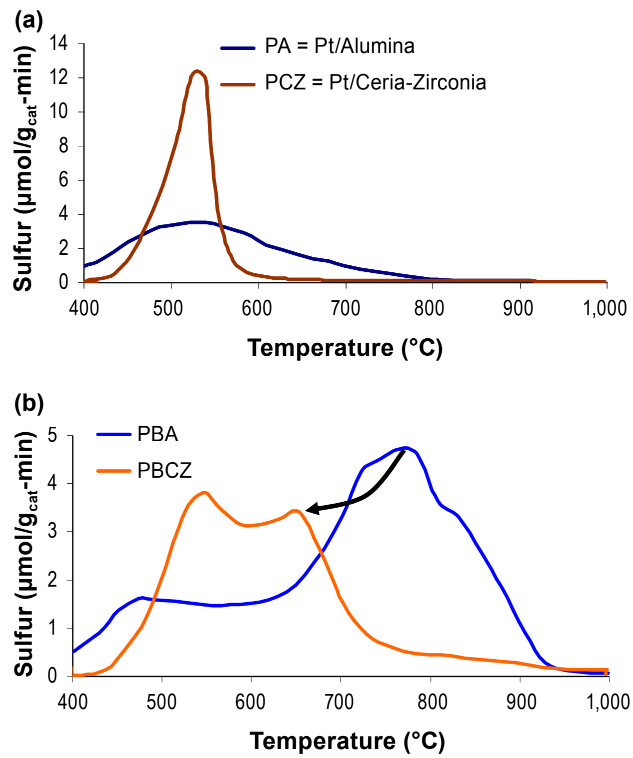

FIGURE 3. Sulfur measured during the temperature programmed reduction of the sulfated LNTs. Samples shown are for (a) the individual supports, PA and PCZ, and (b) those with the Ba-phase included, PBA and PBCZ.

TABLE 2. Peak Assignments (cm^{-1}) for Adsorbed NOx Species

Sample	Peak Position (cm^{-1})	Adsorbed Species
Pt/Al_2O_3	1000, 1030, 1245, 1290, 1545, 1575, 1600	NO_3 on Al_2O_3
Pt/CeO_2-ZrO_2	1010, 1244, 1527, 1542	NO_3 on Ce
$Pt/Ba/Al_2O_3$	1350, 1410	NO_3 on Ba
$Pt/Ba/CeO_2$-ZrO_2	1200	NO_2 on Ba
	1300, 1350, 1410	NO_3 on Ba
	1300, 1410	NO_3 on Ce

precious metals and also can lead to reduced storage capacity. The higher the temperature required for desulfation, the more pronounced the deactivation is, and the shorter the lifetime of the LNT is. In studying LNTs, it is common to only consider the formulation of the storage phase with respect to nitrate and sulfate stability and the required desulfation temperature. Thus a study of the impact of the underlying support is important. Figure 3a shows the desulfation behavior of the base supports following the sulfation step illustrated Figure 2a. Upon heating PA immediately begins releasing sulfur under reducing conditions, however the heterogeneity of sites on this γ-alumina support is illustrated by the very wide temperature of sulfate release; removal of 90% of the sulfates does not occur until 710°C. PCZ on the other hand, does not begin to release sulfates until 450°C, but has released 90% of the sulfates by 570°C. This comparison clearly shows that the supports have differing interactions with sulfur, which becomes even more pronounced with the inclusion of Ba. Comparing the sulfur release profile for PBA in Figure 3b to PA shows that there is some low temperature release of sulfur that appears to coincide with the alumina-phase, but the bulk is released at high temperatures peaking around 800°C. Similarly, in comparing PBCZ to PCZ it is clear there is some low-stability sulfur on the ceria-zirconia support, illustrated by the peak release near 540°C. However, the high temperature release observed with PBCZ peaks around 670°C rather than near 800°C. This clearly illustrates that the support dramatically impacts the sulfate release properties of Ba-based LNTs, and thus can affect the overall durability of the system. Furthermore, in a DRIFTS analysis of the nitrates samples (Figure 4) we can observe a profound impact on the location of the Ba-associated nitrates. Ba-nitrates on PBA are located at 1410 and 1350 cm^{-1}, while those on PBCZ are found at 1410 and 1300 cm^{-1}. These nitrates are clearly not associated with underlying support and further illustrates that the support affects the nitrate bonds and thus their stability. This type of understanding can be used to tailor the LNT components to a specific temperature operating window.

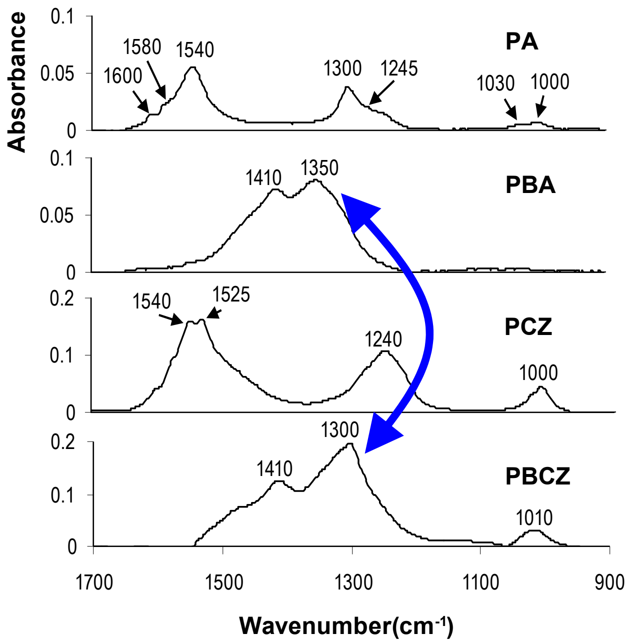

FIGURE 4. DRIFT spectra showing spectral location of the peaks associated with Ba nitrates for PA, PBA, PCZ and PBCZ. Ba-nitrates on PBA are located at 1410 and 1350 cm^{-1}, while those on PBCZ are found at 1410 and 1300 cm^{-1}, which illustrates that the support affects the nitrate bonds and thus their stability.

In moving forward with this study, it is often beneficial to expand our characterization techniques that we use to study these catalysts. This year we were able to gain access to the world class microscopy equipment available in the High Temperature Materials Laboratory at ORNL. Specifically we employed the aberration-corrected electron microscope (ACEM) to image catalyst samples which has allowed the observation of very fine Pt dispersions in dark-field imaging mode on our LNT samples (<1 nm particles with atomic resolution). Furthermore, energy-dispersive X-ray spectroscopy (EDS) on the ACEM allows elemental distributions to be mapped at the nanometer level, and when combined with the unique sample holder that allows in situ heating it is possible to track changes in Pt size and Ba storage phases during elevated temperature treatments. We were able to observe that heating under vacuum at 600°C leads to baria crystallite dispersion and thereby increased surface sites for storage, as shown in Figure 5. However, this does not hold true when heating in ambient air as the Ba phase is quite stable up to 800°C. These results illustrate the importance of studying these catalyst systems under realistic environments. It is our intent to further employ these techniques to gauge the Pt and even sulfate stability as a function of LNT composition. We are looking to apply this technique to analyzing the effect of adding dopants, such as Ca, in the Ba lattice of an LNT that have been a focus of past efforts in this project. Efforts are ongoing, but the results this year are still preliminary and thus not reported.

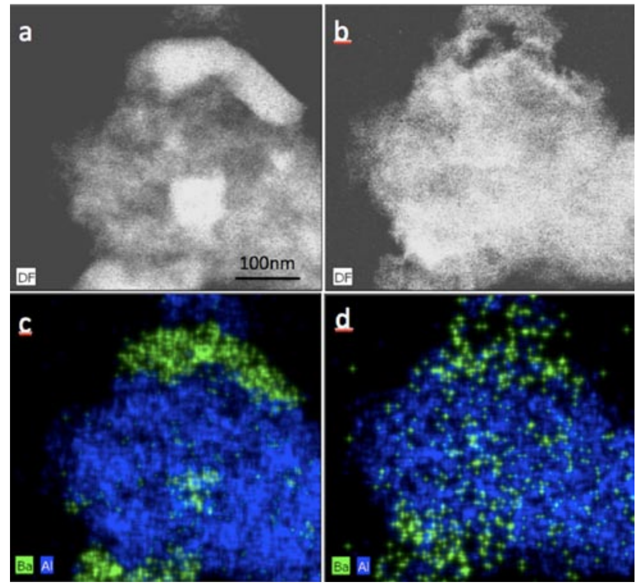

FIGURE 5. Dark-field images (a) before and (b) after heating catalyst for 10 min at 600°C in the ACEM vacuum chamber; the bright areas are the barium-rich phase. Elemental maps using EDS (c-d) show the dispersing of the barium-rich phase after heating.

Conclusions

- Ceria is a very effective adsorbant of sulfur. Its inclusion in catalyst formulations suggests that it could offer an initial level of protection from the Ba-phase.
- Using ceria-zirconia as a support for the Ba-storage phase has a large effect on sulfate stability as peak sulfur release decreases by ca. 100°C.
- Advanced characterization techniques have been developed to monitor the impact of thermal cycling on both Pt size and storage phase morphology under realistic conditions: the results illustrate the importance of using these real-world conditions to correlate materials effects on operating conditions.

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1. J.-S. Choi, W.P. Partridge, M.J. Lance, L.R. Walker, J.A. Pihl, T.J. Toops, C.E.A. Finney, C.S. Daw, "Nature and spatial distribution of sulfur species in a sulfated barium-based commercial lean NOx trap catalyst", Catalysis Today 151 (2010) 354.

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FY 2010 Publications/Presentations

1. N.A. Ottinger, T.J. Toops, J.A. Pihl, J.T. Roop, J.-S. Choi[1], W.P. Partridge, "Study of Nitrate and Sulfate Storage and Stability on Common Lean NOx Trap Components", submitted to Applied Catalysis B: Environmental.

2. T.J. Toops, N.A. Ottinger, C. Liang, J.A. Pihl, A. Payzant, "Impact of lattice substitution in Ba-based NOx storage reduction catalysts on sulfation, desulfation and NOx reduction performance", Catalysis Today (2010), in press, doi:10.1016/j.cattod.2010.08.009.

3. J.-S. Choi, W.P. Partridge, M.J. Lance, L.R. Walker, J.A. Pihl, T.J. Toops, C.E.A. Finney, C.S. Daw, "Nature and spatial distribution of sulfur species in a sulfated barium-based commercial lean NOx trap catalyst", Catalysis Today 151 (2010) 354.

4. J.-S. Choi, W.P. Partridge, J.A. Pihl, M. Lance, N.A. Ottinger, C.S. Daw, K. Chakravarthy and T.J. Toops, "Functionality of multi-component commercial NOx storage-reduction catalysts and the development of a representative model", Directions in Emissions and Efficiency Research (DEER) Conference, Detroit, MI, September 27–30, 2010.

5. T.J. Toops, N.A. Ottinger, J.A. Pihl, "Pre-Competitive Catalysis Research: Fundamental Sulfation/Desulfation Studies of Lean NOx Traps", 2010 DOE Annual Merit Review, Washington, D.C., June 7–11, 2010.

6. T.J. Toops, N.A. Ottinger, J.T. Roop, J.A. Pihl, J.-S. Choi, W.P. Partridge "Sulfate Storage and Stability on Lean NOx Trap Components", Presented at 13th Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Dearborn, MI, April 20–22, 2010.

7. T.J. Toops, C. Liang, J.A. Pihl, N.A. Ottinger, "Impact of Dopants in Ba-Based NOx Storage Reduction (NSR) Catalysts on Sulfation, Desulfation, and Performance", American Institute for Chemical Engineers (AIChE) Annual Meeting, November 8–13, 2009.

II.B.7 NO_x Control and Measurement Technology for Heavy-Duty Diesel Engines

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DOE Technology Development Manager:
Ken Howden

Objectives

- Improve diesel engine-catalyst system efficiency through better combustion uniformity, engine calibrations and catalyst control.
- Work with industrial partner to develop full-scale engine-catalyst systems to meet efficiency and emissions goals.

Fiscal Year (FY) 2010 Accomplishments

- Resolved induced cylinder-to-cylinder exhaust variations in heavy-duty diesel engine.
- Measured distributed NH_3 storage and reactions within Cu-zeolite and Fe-zeolite selective catalytic reduction (SCR) catalysts, for use to understand detailed catalyst chemistry and develop advanced control strategies for improved efficiency.
- Demonstrated complex nature of SCR thermal ageing; which for the case studied shifted reaction distributions, reduced overall oxides of nitrogen (NO_X) conversion, increased parasitic NH_3 consumption, but did not change the dynamic NH_3 storage distribution.
- Experimentally confirmed lean-NO_X trap (LNT)-catalyst conceptual model showing how sulfation increases effluent NH_3 by displacing the NO_X storage and reduction (NSR) zone, where NH_3 is generated, and correspondingly shortening the downstream oxygen storage capacity (OSC)-only zone and reducing the capacity to oxidize NH_3.
- Coordinated research effort with the Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) program for enhanced programmatic effectiveness.
- Established working partnerships with Chalmers University of Technology and Prague Institute of Chemical Technology and continued partnership with Queen's University Belfast which enhances programmatic effectiveness.
- Two archival publications.
- Fourteen presentations and posters.

Future Directions

- Quantify engine combustion non-uniformities and develop mitigation strategies.
- Enable development of self-diagnosing smart catalyst systems through:
  - Detailed characterization of the spatiotemporal relationship between natural and indicator chemical functions and catalyst properties throughout the catalyst operation and ageing.
  - Develop methods for in situ, on-engine-system assessment of catalyst state.

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Introduction

A combination of improved technologies for engine and aftertreatment control of NO_X and particulate emissions are required to efficiently meet 2013 emission regulations. These include advanced combustion and associated engine hardware and controls, improved catalyst systems, and overall system management improvements. There are specific needs in terms of reducing cylinder-to-cylinder and cycle-to-cycle combustion variations, and continuous catalyst-state monitoring. For instance, combustion variations mandate system-calibration tradeoffs which move operation away from optimum efficiency points. Combustion variations are amplified at high exhaust gas recirculation (EGR) conditions which are expected in advanced engine systems. Advanced efficiency engine systems require understanding and reducing combustion variations. Improved efficiency, durability and cost can be achieved through advanced control methodologies based on continuous catalyst-state monitoring; these advanced control methods reduce the fuel penalty associated with catalyst maintenance (e.g., desulfation, regeneration) and extend the lifetime of the catalyst by triggering maintenance events only when and for as long as required as indicated by real-time catalyst-state monitoring, as opposed to being preprogrammed based on end-of-life performance. Continuous catalyst-state monitoring also provides a solution for 2013 regulations which require identification of the specific component function (e.g., oxidation) responsible in the event that a component's (e.g., NO_X catalyst) performance falls outside the regulatory window. These engine, combustion and catalysis advances require development and application of enhanced diagnostic tools to realize these technology improvements.

Approach

Developing and applying minimally invasive advanced diagnostic tools to resolve spatial and temporal variations within operating engines and catalysts has been central to the historical successes of this Cooperative Research and Development Agreement (CRADA) partnership, and continues to be a key element of the project approach. These include small capillary and optical-fiber based technologies which are able to resolve spatiotemporal variations without changing the measurement environment or requiring significant hardware modifications for applications. Integral to this work are coating technologies to create localized fiber and capillary transducers to detect variations; e.g., species, temperature, pH, etc... The approach relies heavily on optical and mass spectrometry, but also includes other techniques such as electrical impedance spectroscopy. Diagnostics are developed and demonstrated on bench reactors and engine systems (as appropriate) at ORNL prior to field application at Cummins. In some cases discrete-sensor technology is a stepping stone and may be further developed and integrated in system components; e.g., to create self-diagnosing smart catalyst systems.

Diagnostics are applied at ORNL and Cummins to study the nature and origins of performance variations. In combustion studies, this may be manifested in cylinder-to-cylinder CO_2 variations due to non-uniform fueling, air and/or EGR charge, fuel spray, component tolerance stacking, or other variations. Detailed measurements can be used to identify and evaluate corrective measures; e.g., hardware and control changes. In catalyst studies, this may be spatial and temporal variations unique to each catalyst function (e.g., SCR, NH_3 storage and parasitic oxidation, NSR, OSC, water-gas shift) during operation and how these vary with ageing (e.g., thermal, hydrocarbon, sulfur). This detailed information is applied to understand how catalysts function and degrade, develop device and system models, and develop advanced control strategies.

Results

Combustion Uniformity

Cylinder-resolved variations in exhaust H_2O were quantified in a development V-8 engine at the Cummins Technical Center using rapid scanning optical-fiber based near-infrared laser spectroscopy. Figure 1 shows a schematic of the measurement location and results associated with single cylinder ('E') enrichment. These measurements provide insights into high-frequency engine variations in much greater detail than previously possible, and are being used to study the origins of and mitigation strategies for such variations. The CRADA team is pursuing high-speed measurement of other species and parameters associated with cylinder imbalance and variations. In addition to the CRADA objectives, these CRADA-developed technologies are being extended to the SuperTruck objectives via a separate project. Development and applications of these instruments will enable greater engine combustion uniformity and in turn engine control closer to optimum performance to achieve greater fuel economy and lower emissions.

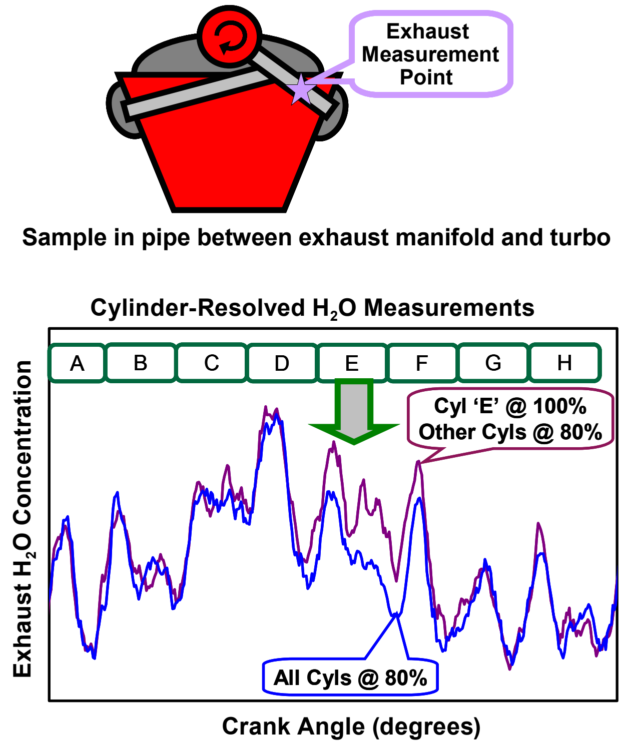

FIGURE 1. Sampling Point and Results Showing Cylinder-Resolved Exhaust H_2O Measurements from Application of Rapid Scanning Near-Infrared Laser Spectroscopy

Catalyst Chemistry Measurements and Insights

The distributed NH_3 utilization in a Umicore Fe-zeolite SCR catalyst was studied using the Cummins 4-Step protocol shown in Figure 2 [1]. The partitioning of NH_3 utilization between NO_X reduction, slip, dynamic capacity and other reactions (NH_3 decomposition or parasitic NH_3 oxidation) can be determined from the protocol Step 2. Figure 3 shows how this utilization varies in the front half of the catalyst. The green arrows indicate the amount of NH_3 used for NO_X reduction which is determined as the difference in the green curve

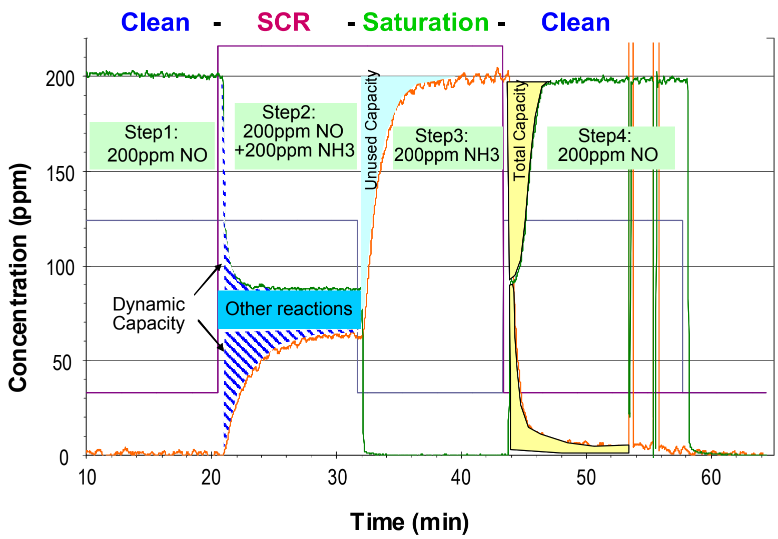

FIGURE 2. Cummins 4-Step Protocol for SCR Catalyst Performance Assessment

and the 200-ppm feed value; this amount increases over the front half of the catalyst. The NH_3 slip (orange arrows) decreases along the catalyst axis and is fully consumed by the half-catalyst location; thus with no remaining NH_3 slip there is no potential for further NO_X reduction. The other or parasitic NH_3 reactions (light-blue boxes) are less at the catalyst front and approximately constant beyond the quarter catalyst location. Figure 4 summarizes these results and shows the distribution of NH_3 utilization under steady-state SCR over the entire catalyst. Notably, ca. 55-80% of the NH_3 is used for NO_X reduction. However, a significant (ca. 15-20%) amount of the NH_3 is lost to other reactions and is not available for NO_X reduction use. Other results (not shown) indicate that the unused NH_3 capacity (Step 3) increases linearly along the catalyst length, the dynamic NH_3 capacity (Step 2) is concentrated in the front where SCR reactions occur, and the total capacity (Step 4) balances with the dynamic and unused capacities. These types of catalyst insights are necessary to understand how to better model, design and control SCR catalyst for better efficiency and durability; e.g., how to reduce the parasitic NH_3 consumption.

In addition to the Fe-zeolite catalyst described above, a model Cu-zeolite SCR catalyst was studied by the CRADA team in cooperation with Professor Louise Olsson at the Chalmers University of Technology. To support this effort, Chalmers doctorate student Xavier Auvray spent five months working with Dr. Partridge at ORNL. The distributed intra-catalyst performance of the model Cu-zeolite catalyst was characterized under standard and fast SCR conditions at three temperatures and two ageing states. This catalyst displayed different performance compared to the Fe-zeolite catalyst shown in the figures; for instance, parasitic NH_3 consumption appears to consist of both oxidation and N_2O-forming reactions. Thermal ageing brings about inhibition, an axial downstream shift in the SCR reaction distribution and lower overall NO_X conversion; for the specific conditions studied, the parasitic NH_3 consumption practically doubled, although the dynamic NH_3 storage

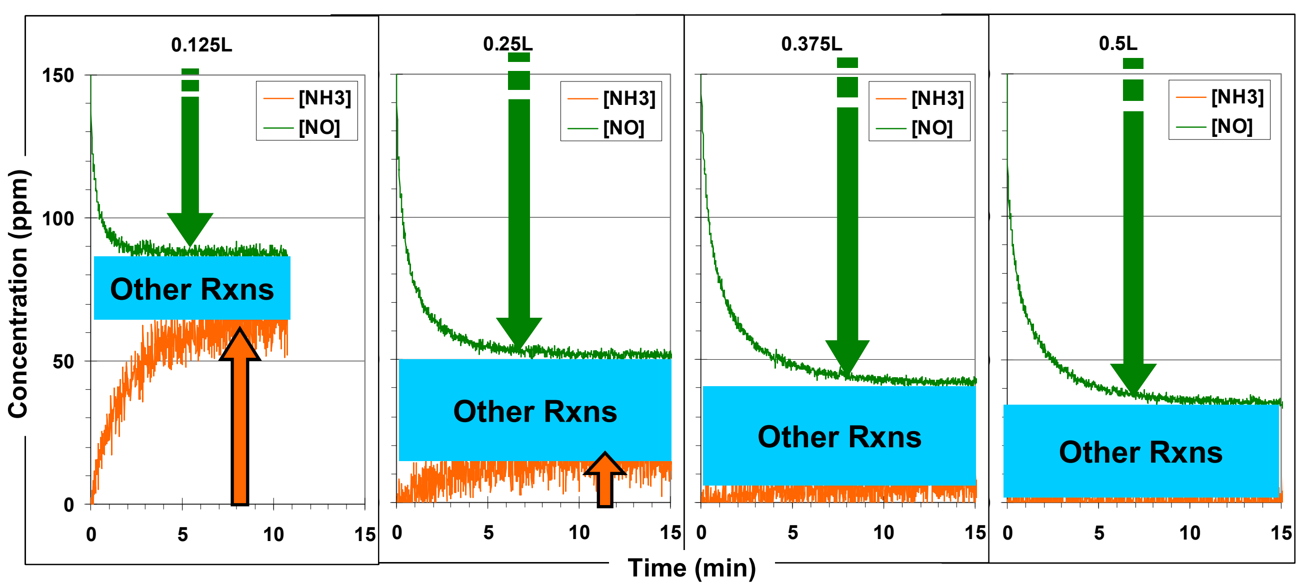

FIGURE 3. Variation in Step-2 NH_3 Utilization in the Front Half of the Catalyst

is not changed. This highlights the rich and varying impact ageing has on the different SCR-catalyst functions. Understanding these impacts is necessary for development, modeling and practical control of these devices.

The CRADA and CLEERS projects coordinated on experimental and numerical investigation of NH_3 formation and utilization during LNT-catalyst regeneration, and specifically the impact of sulfation on these reactions. This work confirmed our published [2] LNT-catalyst conceptual model showing how sulfation increases effluent NH_3, generated during regeneration in the NSR zone. The data verified that in unsulfated conditions the NSR zone is located at the catalyst front and is followed by a broad downstream OSC-only zone; NH_3 generated in the NSR zone is oxidized in the OSC-only zone resulting in little or no NH_3 slip in unsulfated conditions. However, progressive sulfation correspondingly displaces the NSR zone down the catalyst axis and reduces the OSC-only zone; consequently, the capacity to oxidize NH_3 slipping from the NSR zone is reduced and effluent NH_3 increases.

The CRADA team leveraged partnerships to enhance the effectiveness of the project. Via partnership with Dr. Alex Goguet at Queen's University Belfast (QUB) an archival publication and a poster related to work to resolve self-sustained CO oscillations within a monolithic catalyst (see paper 2 and poster 1) was prepared. This work was also relevant because of the application of computational fluid dynamics modeling to investigate the minimally invasive nature of spatially resolved capillary-inlet mass spectrometry (SpaciMS) sampling; this code will be further exercised by a QUB masters student in 2011 to investigate this non-invasive nature over a range of catalyst and sampling conditions. In conjunction with the CLEERS project, Dr. Petr Koci of the Institute of Chemical Technology in Prague spent a month at ORNL working to model CLEERS Protocol LNT experimental data with specific focus on NH_3 and N_2O formation during regeneration; this continues CRADA experimental work regarding formation and utilization of NH_3 during regeneration [3]. This partnership also produced insights to SpaciMS chromatography effects important to accurately assessing the timing of various intra-catalyst reactions; these are currently being investigated via experiments and modeling. In a second partnership with Dr. Olsson at Chalmers, master student Soran Shwan worked to model slow- and fast-cycling CLEERS protocol LNT data with focus similar to that of Dr. Koci. These partnerships are strengthening both the CRADA and CLEERS DOE projects by bringing additional modeling and experimental capabilities and insights, and expanding the use of corresponding project data and efforts.

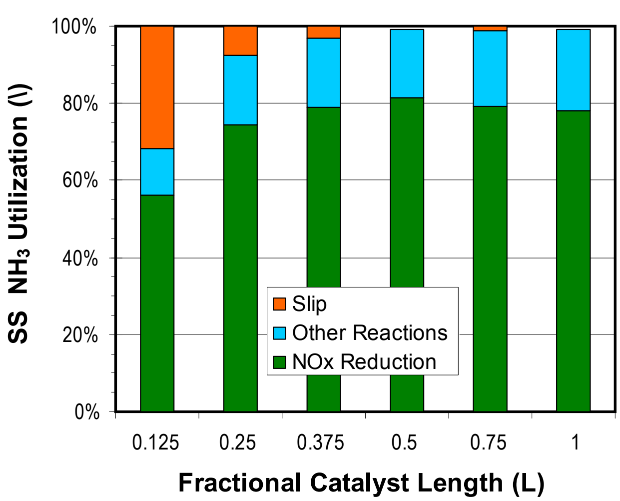

FIGURE 4. Distributed NH_3 Utilization at Steady-State (SS) SCR

Conclusions

Internal combustion engine cylinder and cycle uniformity and catalyst control are central issues to achieving high efficiency. This CRADA is squarely involved in development and application of measurement technologies related to these central issues; specifically, identifying the origins of combustion non-uniformity and assessing mitigation strategies, and developing self-diagnosing smart catalyst systems.

- Quantified induced cylinder-specific exhaust variations on heavy-duty diesel engine via in situ high-speed exhaust concentration measurements.
- Characterized distributed SCR catalyst reactions and effects of thermal aging; providing the basis for developing SCR design and control strategies to achieve improved efficiency and real-time on-board catalyst-state assessment.
- Experimentally verified validity of LNT conceptual model showing basis for increasing effluent NH_3 with progressive sulfation.
- Developed new insights into chromatography effects and non-invasive nature of SpaciMS capillary sampling via external partnerships.
- Improved insights into LNT chemistry via modeling work with external partnerships.

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FY 2010 Publications/Presentations

Papers

1. Jae-Soon Choi, William P. Partridge, Michael J. Lance, Larry R. Walker, Josh A. Pihl, Todd J. Toops, Charles E.A. Finney, C. Stuart Daw (2010). "Nature and spatial distribution of sulfur species in a sulfated barium-based commercial lean NOx trap catalyst," Catalysis Today 151, 354-361; doi:10.1016/j.cattod.2010.01.016.

2. Jacinto Sá, Daniel Luis Abreu Fernandes, Farid Aiouache, Alexandre Goguet, Christopher Hardacre, David Lundie, Wasif Naeem, William P. Partridge and Cristina Stere (2010). "SpaciMS: spatial and temporal operando resolution of reactions within catalytic monoliths," Analyst 135, 2260-2272; doi:10.1039/C0AN00303D.

Presentations

1. Jae-Soon Choi, William P. Partridge, Josh A. Pihl, Kalyan Chakravarthy, and C. Stuart Daw (2010). "Factors Affecting the NH_3 Selectivity of Lean NO_x Traps – Insights from Spatiotemporal Distribution of Reactions," ***Keynote Lecture***, 2nd International Symposium On Air Pollution Abatement Catalysis (APAC 2010), CRACOW, Poland, September 8, 2010. ***Invited***

2. W.P. Partridge, X. Auvray, N. Currier, L. Olsson, J.-S. Choi, A. Yezerets, K. Kamasamudram (2010). "Ammonia Storage & Reaction Distributions Within an Operating SCR Catalyst," 9th Annual Symposium of the Southeastern Catalysis Society, Asheville, SC, September 27, 2010.

3. Bill Partridge, Jae-Soon Choi, Josh Pihl, Todd Toops, Jim Parks, Nathan Ottinger, Alex Yezerets , Neal Currier (2010). "Advanced LNT DeSulfation Control via Understanding the Distributed Intra-Catalyst Impacts of Sulfation on Water Gas Shift, NO_x Storage & Reduction Reactions," DEER 2010 Conference, Emissions Control Technologies, Detroit, MI, September 28, 2010.

4. Jae-Soon Choi, William P. Partridge, Josh A. Pihl, Michael J. Lance, Nathan A. Ottinger, C. Stuart Daw, Kalyan Chakravarthy and Todd J. Toops (2010). "Functionality of Commercial NO_x Storage-Reduction Catalysts and the Development of a Representative Model," DEER 2010 Conference, Emissions Control Technologies, Detroit, MI, September 29, 2010.

5. Todd Toops, Nathan Ottinger, Justin Roop, Josh Pihl, Jae-Soon Choi, Bill Partridge (2010). "Sulfate Storage and Stability on Lean NO_x Trap Components," DEER 2010 Conference, Emissions Control Technologies, Detroit, MI, September 29, 2010.

6. Jae-Soon Choi, Bill Partridge, Josh Pihl, Kalyan Chakravarthy, Todd Toops, Stuart Daw (2010). "Spatial Distribution of Reactions: a Key to Understanding the Performance of Lean NOx Trap Catalysts," Korea Institute of Science and Technology, Seoul, Korea, July 1, 2010. ***Invited***

7. Jae-Soon Choi, William P. Partridge, Josh A. Pihl, V. Kalyana Chakravarthy, Todd J. Toops, C. Stuart Daw, "Spatial Distribution of Reactions: a Key to Understanding the Performance of Lean NOx Trap Catalysts", KIChE Discussions on Catalysis Research, Busan, Korea, June 23, 2010. ***Invited***

8. Jae-Soon Choi, Bill Partridge, Josh Pihl, Kalyan Chakravarthy, Todd Toops, Stuart Daw (2010). "Spatial Distribution of Reactions: a Key to Understanding the Performance of Lean NOx Trap Catalysts," Pohang University of Science and Technology, Pohang, Korea, June 22, 2010. ***Invited***

9. Jae-Soon Choi, Josh A. Pihl, William P. Partridge, V. Kalyana Chakravarthy, Todd J. Toops, C. Stuart Daw, "Factors Affecting LNT NH_3 Selectivity", 13th DOE Crosscut Workshop on Lean Emissions Reduction Simulation, Dearborn, Michigan, April 20-22, 2010.

10. Jim Parks, Bill Partridge (2010). "Laser-Induced Fluorescence Diagnostic for Fuel Dilution of Oil in Advanced Combusiton," ACE/HCCI Working Group Meeting, Sandia National Lab, February 25, 2010.

11. Bill Partridge, Jae-Soon Choi, Josh Pihl, Todd Toops, Jim Parks, Nathan Ottinger, Alex Yezerets , Neal Currier, "Understanding the Distributed Intra-Catalyst Impact of Sulfation on Water Gas Shift in a Lean NOx Trap Catalyst," AIChE National Meeting, Nashville, TN, November 13, 2009.

12. Jae-Soon Choi, Bill Partridge Nathan Ottinger, Todd Toops, Josh Pihl, Michael Lance, Charles Finney, Stuart Daw, "Types, Spatial Distribution, Stability, and Performance Impact of Sulfur on a Lean NOx Trap Catalyst," AIChE National Meeting, Nashville, TN, November 12, 2009.

Posters

1. Jacinto Sá, Alexandre Goguet, Cristina Stere, David Lundie, Daniel Fernandes, William P. Partridge, Farid Aiouache, Wasif Naeem and Christopher Hardacre (2010). "SpaciMS – the tool to unveil the behaviour within catalytic monoliths," Poster Presentation, TOCAT 6, Sapporo, Japan, July 19, 2010.

Special Recognitions & Awards/Patents Issued

The CRADA-developed Fuel-in-Oil technology received the 2009 Southeast Regional Award for Excellence in Technology Transfer presented annually by the Federal Laboratory Consortium for Technology Transfer. The award recognizes laboratory employees who have accomplished outstanding work in the process of transferring a technology developed by a federal laboratory to the commercial marketplace.

II.B.8 Efficient Emissions Control for Multi-Mode Lean DI Engines

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DOE Technology Development Manager:
Ken Howden

Objectives

- Assess the relative merits of meeting emission regulations via catalytic aftertreatment or advanced combustion for diesel engines capable of operating in multiple combustion modes ("multi-mode" engines).
- Determine the fuel efficiency of combinations of catalytic aftertreatment and advanced combustion modes.
- Characterize exhaust chemistry from advanced combustion and the resulting evolution of chemistry in catalysts for emissions control to improve the understanding of advanced engine and aftertreatment systems.

Fiscal Year (FY) 2010 Accomplishments

- Demonstrated a radio frequency (RF)-based sensor for on-board measurement of diesel particulate filter (DPF) particulate matter (PM) loading that more accurately tracks PM loading when compared with the common differential pressure (dP) sensor technique (coefficient of determination [R^2] of 0.9783 for the RF sensor vs. an R^2 of 0.4702 for the dP sensor where 1 is the ideal R^2).
- Characterization of emissions from reactivity-controlled compression ignition (RCCI) combustion and measurement of the effectiveness to control carbon monoxide (CO) and hydrocarbon (HC) emissions from RCCI with a diesel oxidation catalyst (DOC).
- Characterization of the hydrocarbon fouling of Cu- and Fe-zeolite selective catalytic reduction (SCR) catalysts during production engine and high-efficiency clean combustion (HECC) combustion.

Future Directions

- Extension of engine load and speed conditions for DOC control of emissions from RCCI combustion.
- Analysis of DOC control of emissions from low-temperature conditions for HECC combustion.

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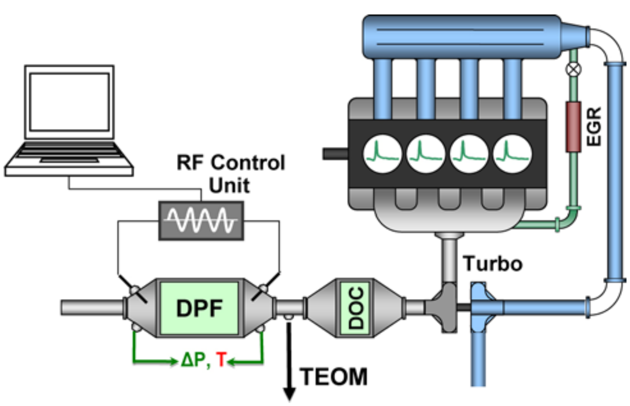
Introduction

New combustion regimes are being investigated as a means to increase the efficiency of, and to reduce the emissions from, diesel engines. The reduction of emissions during combustion is beneficial to the fuel efficiency of the system as a whole (engine plus emissions control system or "aftertreatment"). For example, lower engine-out oxides of nitrogen (NOx) emissions can remove some burden from post-combustion emissions controls, and can thereby reduce the fuel penalty associated with NOx reduction. Although new combustion techniques have been developed that offer advantages for both engine fuel efficiency and emissions, often the techniques are not attainable over the entire range of load and speed required for market acceptance. Thus, engines designed to implement the new combustion techniques often operate in a "multi-mode" fashion where, at certain loads, the engine is operated with advanced combustion techniques and, at other loads, the engine is operated with more traditional diesel combustion. While modern control systems enable switching between the multiple modes of operation, the optimization of the system for fuel efficiency and emissions becomes more complex. One particular challenge is optimizing the size, cost, and complexity of the emissions control system. This project is aimed at understanding the complex issues of efficiency and emissions management for multimode engines with advanced emission control systems. Characterization of combustion exhaust chemistry and catalytic control are conducted to assist industry in the design of multi-mode engine and emission control systems.

Approach

This research was conducted on a modern General Motors (GM) 1.9-liter 4-cylinder diesel engine on an engine dynamometer at ORNL. The production engine controller for the engine has been replaced with a full-pass control system made by Drivven that enables complete control of all engine operating controls such as fuel injection timing, exhaust gas recirculation levels, and intake manifold pressure. With this advanced control system, the engine is operated with unique advanced combustion strategies that achieve high efficiency and low emissions. The development of the advanced combustion strategies is conducted in other projects at ORNL and other collaborating entities; this project leverages those efforts by simply transferring the "recipes" for control to duplicate the advanced combustion. Advanced combustion strategies utilized in this project include: low-temperature combustion (LTC), HECC, and RCCI. All of these combustion strategies achieve extremely low NOx and PM emissions while maintaining low brake specific fuel consumption; however, in some cases CO and HC emissions increase. Formaldehyde emissions can increase as well; formaldehyde is classified as a mobile source air toxic by the Environmental Protection Agency. Thus, the burden of the emissions control system to control NOx and PM emissions is significantly reduced with advanced combustion, but higher CO and HC emission control is needed. Experiments are conducted to understand the synergies between advanced combustion and advanced aftertreatment with the objective of achieving high efficiency combined with low emissions and low cost. Commercial and prototype catalysts for the studies are obtained from a variety of vendors and representatives of the Manufacturers of Emission Control Association. Catalysts technologies include: catalyzed DPF, DOC, lean-NOx trap, urea-SCR, and HC-SCR.

In FY 2010, experiments conducted included studies of zeolite-based urea-SCR catalysts, DOC control of emissions from RCCI combustion, DOCs for low temperature CO and HC oxidation, and RF sensor technology for on-board diagnostics (OBD) of DPF PM loading. For this report, the technical results from the study of RF sensor technology for DPF diagnostics will be discussed. The RF sensor technology studied was developed by Filter Sensing Technologies and utilizes a spectrum of RF electromagnetic waves to detect resonances in the DPF filter via transmitter and receiver probes placed directly upstream and downstream of the DPF in the exhaust system (Figures 1 and 2). A DPF with the RF sensor installed was operated in diesel exhaust, and sensor signals were monitored during DPF loading and regeneration processes at various engine loads and speeds. Data related to PM on the DPF was also collected with a dP sensor (commonly used in vehicle applications now) and a tapered element oscillating microbalance (TEOM) lab instrument.



EGR – exhaust gas recirculation

FIGURE 1. Schematic of the experimental system showing the diesel engine, exhaust system with DOC and DPF, and RF sensor probes upstream and downstream of the DPF.

Results

The response of the RF sensor to PM on the DPF is shown in Figure 3. Resonance peaks in the RF signal transmitted through the DPF shift in magnitude

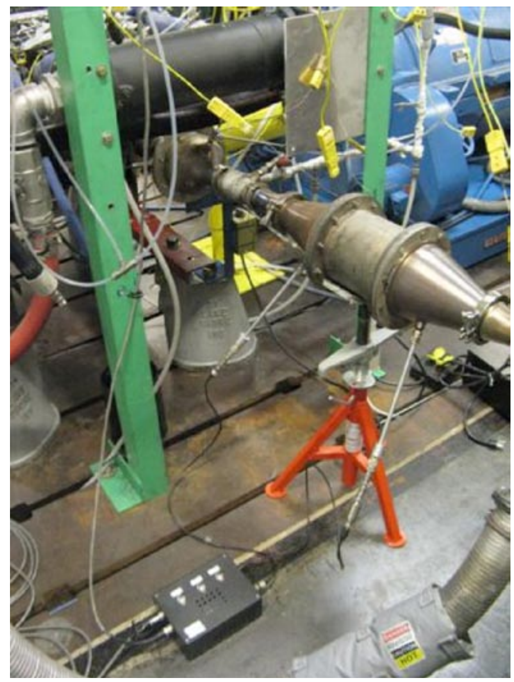


FIGURE 2. Picture of the engine exhaust system including the DPF with the RF sensor probes installed.

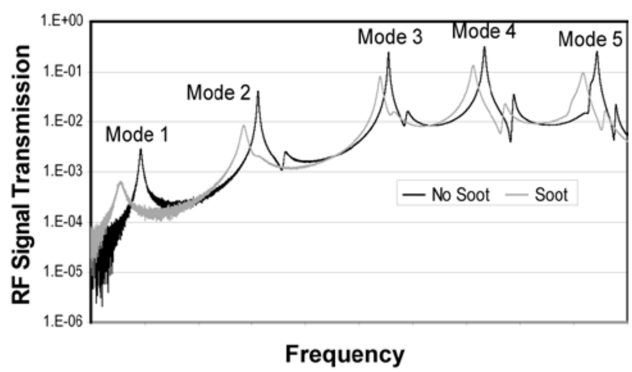


FIGURE 3. RF signal as a function of frequency for a DPF with and with out particulate (soot) loading; the resonance peaks shift in frequency and strength with particulate loading.

and center frequency with the additional loading of PM on the DPF. Thus, the spectral differences in the RF signal are used to measure PM loading. The engine was operated at various speed and load points sequentially to compare the RF sensor signal to the dP sensor and the TEOM lab instrument. Data from the same experiment is shown in Figures 4 and 5; in both cases the data is normalized to the data values at the start and end times. Figure 4 shows a comparison of the dP sensor to the TEOM data. The dP sensor shows large variations in the measurement due to changes in the exhaust flow rates and temperatures during the engine speed and load transitions. These variations are present even though a correction for varying flow rate was applied to the dP sensor data. In contrast, the RF sensor data compares very well with the TEOM data during the same experiment. The RF sensor is not sensitive to the flow rate changes due to the nature of the RF sensor operation. As a result, the RF sensor can more accurately measure PM loading on the DPF. A quantitative measure of the improved accuracy for the RF sensor can be obtained by the R^2 of the linear regression of the RF sensor data vs. the TEOM data; the same measure of accuracy can be used for the dP sensor. An R^2 of 0.9783 was found for the RF sensor, and an R^2 of 0.4702 was found for the dP sensor (where 1 is the ideal R^2).

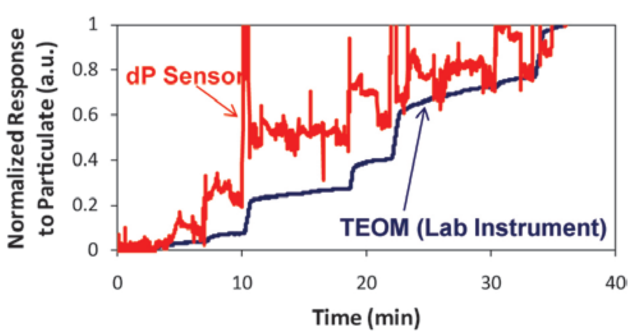


FIGURE 4. Comparison of the dP sensor signal with the TEOM measurement of PM (data normalized to the start and end data points).

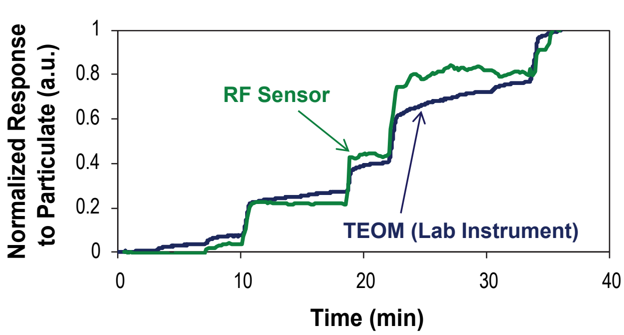


FIGURE 5. Comparison of the RF sensor signal with the TEOM measurement of PM (data normalized to the start and end data points).

Conclusions

A RF-based sensor technology developed by Filter Sensing Technologies was studied on a light-duty diesel engine with an exhaust system containing a DOC and DPF. When compared with the common dP sensor approach, the RF sensor showed more stable and accurate measurement of PM loading during experiments where engine loads and speeds varied. The RF sensor signal and TEOM lab instrument data compared well. The RF sensor's more accurate measurement of DPF loading will enable fuel consumption reduction from DPF regeneration processes as well as improved diagnostics for OBD requirements.

FY 2010 Publications/Presentations

1. Teresa L. Barone, Anshuman A. Lall, John M.E. Storey, George W. Mulholland, Vitaly Y. Prikhodko, Jennifer H. Frankland, James E. Parks, Michael R. Zachariah, "Size-Resolved Density Measurements of Particulate Emissions from an Advanced Combustion Diesel Engine: Effect of Aggregate Morphology", *submitted to Energy and Fuels* (2010).

2. Curran, S.J., Prikhodko, V., Wagner, R.M., Parks, J.E., Cho, K., Sluder C.S., Storey, J.M., Barone, T.L., and Lewis, S.A., "Combustion and Emissions Performance of Dual-Fuel Gasoline and Diesel HECC on a Multi-Cylinder Light Duty Diesel Engine", *2010 Directions in Engine-Efficiency and Emissions Research Conference (DEER)*, September 27-30, 2010 (2010).

3. Alexander Sappok, James Parks, and Vitaly Prikhodko, "Investigations of Diesel Particulate Filter Loading and Regeneration using a Novel Radio Frequency-Based Sensor", *2010 Directions in Engine-Efficiency and Emissions Research Conference (DEER)*, September 27-30, 2010 (2010).

4. Scott J. Curran, Vitally L. Prikhodko, Robert M. Wagner, James E. Parks II, Kukwon Cho, C. Scott Sluder, Sage L. Kokjohn, Rolf D. Reitz, "In-Cylinder Fuel Blending of Gasoline/Diesel for Improved Efficiency and Lowest Possible Emissions on a Multi-Cylinder Light-Duty Diesel Engine", *SAE Technical Paper Series* 2010-01-2206 (2010).

5. Vitaly Y. Prikhodko, Scott J. Curran, Teresa L. Barone, Samuel A. Lewis, John M. Storey, Kukwon Cho, Robert M. Wagner, James E. Parks II, "Emission Characteristics of a Diesel Engine Operating with In-Cylinder Gasoline and Diesel Fuel Blending", *SAE Technical Paper Series* 2010-01-2266 (2010).

6. Alexander Sappok, Leslie Bromberg, James Parks II, Vitaly Prikhodko, "Loading and Regeneration Analysis of a Diesel Particulate Filter with a Radio Frequency-Based Sensor", *SAE Technical Paper Series* 2010-01-2126 (2010).

7. Robert Wagner, Scott Curran, Vitaly Prikhodko, Eric Nafziger, Jim Parks, Scott Sluder, John Storey, and Teresa Barone, "Dual-Fuel Combustion Concept for Improved Efficiency and Emissions in a Multi-Cylinder Engine", *11th International Conference on Present and Future Engines for Automobiles*, Shanghai, China, June, 2010 (2010).

8. Alexander Sappok, Leslie Bromberg, Peter Koert, James Parks II, and Vitaly Prikhodko, "Advanced Sensors for Next Generation Diesel Particulate Filter Systems", *13th DOE Crosscut Workshop on Lean Emissions Reduction Simulation*, April 20-22, 2010 (2010).

9. James E. Parks II, Vitaly Prikhodko, John M. E. Storey, Teresa L. Barone, Samuel A. Lewis Sr., Michael D. Kass, and Shean P. Huff, "Emissions from premixed charge compression ignition (PCCI) combustion and affect on emission control devices", *Catalysis Today* **151** pp. 278-284 (2010).

10. Vitaly Y. Prikhodko and James E. Parks, "Implications of Low Particulate Matter Emissions on System Fuel Efficiency for High Efficiency Clean Combustion", *SAE Technical Paper Series* 2009-01-2709 (2009).

II.B.9 Cross-Cut Lean Exhaust Emission Reduction Simulation (CLEERS): Administrative Support

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DOE Technology Development Manager:
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Key ORNL personnel involved in this activity are Stuart Daw, Vitaly Prikhodko, and Charles Finney.

Objectives

Coordinate the CLEERS activity for the Diesel Cross-Cut Team to accomplish the following:

- Promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and associated emissions controls.
- Promote development of performance models for emissions control components such as exhaust manifolds, catalytic reactors, and sensors.
- Provide consistent framework for sharing information about emissions control technologies.
- Help identify emissions control research and development (R&D) needs and priorities.

Fiscal Year (FY) 2010 Accomplishments

- Continued co-leading the CLEERS Planning Committee and facilitation of the selective catalytic reduction (SCR), lean-NOx trap (LNT), and diesel particulate filter (DPF) Focus group telecoms with strong domestic and international participation.
- Continued co-leading the LNT Focus Group and refinement of the standard LNT materials protocol.
- Continued to advise and adjust current DOE national lab projects associated with CLEERS to bring them into closer alignment with the 2007 and 2008 CLEERS industry partner priority surveys.
- Provided regular update reports to DOE Diesel Cross-Cut Team.
- Organized 13th CLEERS workshop at University of Michigan, Dearborn on April 20-22, 2010.
- Maintained CLEERS Web site (www.cleers.org) including functionalities, security, and data to facilitate Web meetings and serve focus group interactions.
- Increased utilization of models and kinetic parameters produced by CLEERS projects in full system simulations of alternative advanced powertrain options.

Future Directions

- Continue co-leading CLEERS planning committee.
- Continue co-leading the LNT Focus Group and support the DPF and SCR Focus Groups as needed.
- Continue providing standard reference LNT materials, data, and kinetic modeling results for focus group evaluation.
- Organize and conduct the 2011 CLEERS workshop in the spring of 2011.
- Continue expanding basic data and model exchange between CLEERS and other Advanced Vehicle Technologies projects.
- Continue maintenance and expansion of CLEERS Web site.
- Continue providing regular update reports to the DOE Diesel Cross-Cut team.
- Conduct updated CLEERS survey of industry priorities for R&D in emissions and emissions controls simulations.

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Introduction

Improved catalytic emissions controls will be essential for utilizing high-efficiency lean-burn engines without jeopardizing the attainment of much stricter U.S. Environmental Protection Agency emission standards that will take effect in 2010 and beyond. Simulation and modeling are recognized by the DOE Diesel Cross-Cut Team as essential capabilities needed to achieve this goal. In response to this need, the CLEERS activity was initiated to promote improved computational tools and data for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems. Specific activities supported under CLEERS include:

- Public workshops on emissions control topics.
- Collaborative interactions among Cross-Cut Team members, emissions control suppliers, universities, and national labs under organized topical focus groups.

- Development of experimental data, analytical procedures, and computational tools for understanding performance and durability of catalytic materials.
- Establishment of consistent frameworks for sharing information about emissions control technologies.
- Recommendations to DOE and the DOE Cross-Cut Team regarding the most critical emissions control R&D needs and priorities.

ORNL is involved in two separate DOE-funded tasks supporting CLEERS:

- Overall administrative support.
- Joint development of benchmark LNT kinetics with Sandia National Laboratories and the Pacific Northwest National Laboratory (PNNL).

Approach

In the administrative task, ORNL coordinates the CLEERS Planning Committee, the CLEERS Focus groups, CLEERS public workshops, and the CLEERS Web site (http://www.cleers.org). The specific activities involved include:

- Coordination of the CLEERS Planning Committee and the LNT Focus Group.
- Organization of the annual CLEERS public workshops.
- Maintenance of the CLEERS Web site.
- Preparation and presentation of status reports to the Cross-Cut Team.
- Response to requests and inquiries about CLEERS from the public.
- Coordination of periodic Cross-Cut Team member surveys regarding R&D priorities for CLEERS.

Results

The 13th CLEERS workshop was held April 20–22, 2010 in the meeting facilities of the Institute of Advanced Vehicle Studies at the Dearborn campus of the University of Michigan (Figures 1 and 2). In spite of severe disruptions in travel from Europe due to eruption of a volcano in Iceland, more than 80 foreign and domestic attendees from equipment suppliers, engine and vehicle manufacturers, universities, software vendors, and consultants were present to hear and discuss 29 contributed and three invited presentations on experimental measurements and simulations of lean exhaust aftertreatment control systems. In addition, a special panel of seven experts from industry and academia (Gary Salemme and Neal Currier from Cummins, Paul Laing, Yisun Cheng, and Giovanni Cavataio from Ford, Yongsheng He from General Motors, and Chris Rutland from the University of Wisconsin) was convened on the afternoon of the second day to discuss experience in carrying out integrated simulations of vehicle emissions and emissions controls under realistic driving conditions. Details of the technical program and presentation downloads are available on the CLEERS Web site (http://www.cleers.org) under the 13th workshop heading.

FIGURE 1. Institute of Advanced Vehicle Studies Facility at the University of Michigan Dearborn campus where the 2010 CLEERS Workshop was held.

FIGURE 2. The CLEERS Workshop agenda is structured to include invited presentations, contributed presentations, and panel discussions about the latest developments in emissions controls and emissions controls modeling. Time is also set aside for informal one-on-one discussions.

Key observations from the workshop presentations included the following:

- Much progress has been made on measuring ammonia SCR kinetics but modeling ammonia storage and urea thermolysis/hydrolysis remains a major challenge.
- A CLEERS laboratory protocol for characterizing the transient response of ammonia-SCR catalysts has been proposed and is under review.

- The response time of nitrogen oxide (NOx) emissions to imposed ammonia injection transients might be used as an on-board diagnostic metric for catalyst aging.
- Dual silver-based catalysts for hydrocarbon and ammonia SCR might provide a low-cost, efficient way to meet Tier 2/Bin 5 and Tier 2/Bin 2 NOx standards.
- Micro-calorimetric methods have been developed for measuring heats of adsorption on SCR catalysts (a key kinetic parameter).
- Particulates from spark-ignited direct injection engines will be regulated in Europe starting with the 2011 Euro 5+ limits.
- Existing DPF models capture many key aspects of regeneration but PM reactivity variation is still poorly understood, especially in regard to the effects of biodiesel blending.
- Simulations and experiments reveal DPFs can experience thermal runaway when exhaust temperatures decrease (the so-called wrong-way effect), which can complicate DPF control strategies.
- New measurement techniques employing infrared thermography and capillary inlet mass spectroscopy are revealing important details about how reaction fronts relocate and change speeds within diesel oxidation catalysts and LNTs as the catalysts age.
- Recent demonstrations of in situ particulate loading measurements in DPFs using radio frequency absorption indicate that this might be a viable approach for real-time DPF monitoring and control.
- Recent simulations indicate hybrid LNT/SCR catalysts can significantly improve NOx control performance beyond that typically achieved with LNTs only.
- One specific feature that appears to be important for successful LNT models is the inclusion of at least two distinct types of NOx storage sites.
- Recently developed low-cost perovskite catalysts have shown very promising performance in LNTs compared to current noble-metal catalysts that are much more expensive.

Highlights from the panel discussion included the following:

- Multiple levels (scales) of simulation and analysis tools are needed to meet industry needs for system and vehicle integration.
- Most vehicle-level emissions simulation/control models need to be much lower order than those used to resolve catalyst kinetics.
- Universities/labs are better at developing basic understanding than at developing optimized integrated system models.
- A primary function of models should be to guide, reduce experimental scope and cost.
- Results from integrated systems simulations need to be fed back through the modeling chain to help guide fundamental studies.
- Industry/universities/labs need to maintain close communication regarding modeling needs.

Outside the workshop, the CLEERS Focus Groups have continued technical topic phone/Web discussion meetings at monthly or bi-monthly intervals throughout the year. Typical attendance has remained at 15-25 participants, with continued participation from Europe. This forum has turned out to be especially useful in keeping the U.S. members updated on recent developments in Europe.

Another CLEERS priority this year has been to identify and obtain new SCR reference catalysts for evaluation at the national labs. Acquisition of a new type of copper chabazite catalyst was strongly recommended by our industry partners due its recent commercial introduction by automotive manufacturers. These catalysts have been recognized as a breakthrough for urea-SCR NOx control because of their very good performance over a wide temperature range and low hydrocarbon sensitivity. Up till now, the CLEERS SCR data and models were based on beta-zeolite catalysts. During the summer both ORNL and PNNL were able to obtain samples of these new catalysts to include in future SCR studies.

Consistent with its mission, CLEERS is also continuing to assist in utilizing kinetic aftertreatment models developed at the national labs in carrying out vehicle systems simulations as part of other DOE projects, such as the studies of hybrid and plug-in hybrid vehicles under the Vehicle Systems Analysis Technology Team. An example of the kind of results produced with the CLEERS models is illustrated in Figure 3. This figure depicts the simulated fuel economy impact of different types of emissions control devices and levels of insulation on a diesel-powered passenger car hybrid electric vehicle (HEV) operated over many urban drive cycles. Energy consumption for a comparable gasoline HEV is also shown. Emissions controls are a major concern for HEVs because of the large number of engine restarts required by typical urban driving. Engines restarts require catalytic aftertreatment devices to repeatedly light-off and extinguish, reducing their efficiency.

Conclusions

CLEERS continues to provide a very effective mechanism for non-proprietary communication among emissions control researchers from industry, national labs, universities, and emissions controls

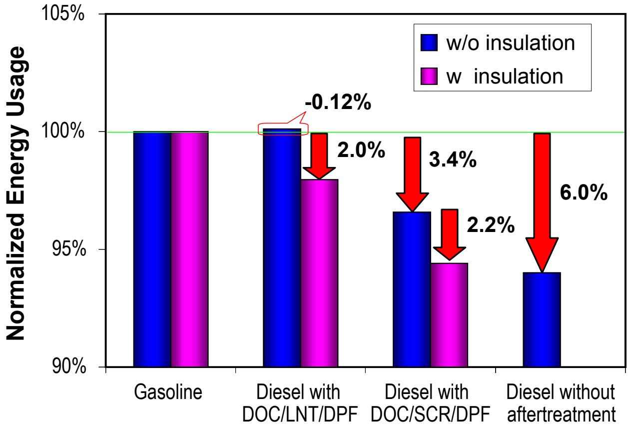

FIGURE 3. A major objective of this project is to promote utilization of models developed by CLEERS collaborations among the national labs and universities in vehicle simulations. This figure illustrates results from using CLEERS generated models and data to simulate the fuel economy impact of different emissions controls and thermal insulation for a 1,450 kg diesel-powered passenger HEV during urban driving. Energy usage for a comparable gasoline HEV is also shown on the left.

suppliers. This type of informal interaction helps keep industry more aware of the latest developments coming from fundamental research at the national labs and universities, and it helps keep national labs and universities more aware of the practical challenges faced by industry in getting the best transportation technology available into a marketable format. The success of CLEERS is most noticeable in the broad participation in the public workshops, the strong interest in the technical focus meetings, and the explicit feedback and guidance provided to DOE and the DOE Diesel Cross-Cut Team regarding the optimal use of their shared R&D resources.

FY 2010 Publications/Presentations

1. 13th CLEERS Workshop presentations at http://www.cleers.org.

2. "CLEERS Coordination & Joint Development of Benchmark Kinetics for LNT & SCR," J.-S. Choi et al, 2010 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review, Washington D.C., June 9, 2010.

II.B.10 Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS): Joint Development of Benchmark Kinetics

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DOE Technology Development Manager:
Ken Howden

Objectives

- Coordinate ORNL's collaboration with Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratories (SNL) in the development of kinetics information needed for aftertreatment component simulation through the following:
- Provide benchmark laboratory measurements of oxides of nitrogen (NOx) reduction chemistry and reaction rates in lean-NOx traps (LNTs) and selective catalytic reduction (SCR) catalysts under realistic operating conditions.
- Correlate laboratory measurements of LNT and SCR catalysts with test-stand/vehicle studies.
- Develop and validate global chemistry and (low order) models for LNT and SCR kinetics.

Fiscal Year (FY) 2010 Accomplishments

- Implemented a fully automated bench flow reactor with gas speciation of high temporal resolution to understand LNT chemistry and kinetic details under relevant fast lean/rich cycling conditions.
- Continued a systematic study of LNT regeneration chemistry with an emphasis on resolving spatiotemporal distribution of reaction:
  - Impact of reductant type and temperature.
  - NH_3 and N_2O selectivity.
  - Axial redistribution of NOx storage.
- Experimentally confirmed a conceptual model of how sulfation affects NH_3 generation and conversion in collaboration with the Cummins Cooperative Research and Development Agreement (CRADA) project.
- Implemented a global LNT cycling model which incorporates the intermediate roles of NH_3.
- Collaborated with the Prague Institute of Chemical Technology in global LNT modeling.
- Refined a detailed LNT cycling model in collaboration with SNL.
- Developed a new transient NH_3 SCR flow reactor evaluation protocol.
- Tested the SCR protocol on CLEERS reference Fe zeolite and new commercial Cu-zeolite SCR catalysts using the exhaust from a 2010 diesel truck.
- Obtained model zeolite powders exchanged with both Fe and Cu from an industrial partner.

Future Directions

- Resolve the impact of reductant composition on the effective fuel penalty and emissions performance for LNT catalysts.
- Confirm the roles of NH_3 storage and NOx redistribution on LNT catalyst performance.
- Benchmark CLEERS LNT and SCR reference catalysts against state-of-the-art commercial formulations.
- Quantify impacts of hydrocarbons and thermal aging on SCR catalyst kinetic parameters.
- Identify key surface species and associated catalyst sites in SCR zeolite catalysts through diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements.
- Utilize above results to improve models for simulating LNT and SCR NOx reduction performance under both laboratory and vehicle drive cycle conditions.

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Introduction

Improved catalytic emissions controls will be essential for utilizing high-efficiency lean-burn engines without jeopardizing the attainment of increasingly strict emission standards. Simulation and modeling are recognized by the DOE Diesel Cross-Cut Team as essential capabilities needed to achieve this goal. In response to this need, the CLEERS activity was initiated to promote improved computational tools and data for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems [1].

ORNL is involved in two separate DOE-funded tasks supporting CLEERS:

- Overall administrative support; and
- Joint development of benchmark LNT kinetics with SNL and PNNL.

Approach

In the benchmark kinetics task (covered by this report), ORNL is collaborating with SNL and PNNL to produce kinetic information for LNT and urea-SCR aftertreatment devices, both as individual and system integrated components. The results of this work are discussed with the LNT, DPF, and SCR Focus groups prior to publication to provide technical review and guidance to the labs. Specific activities involved include:

- Regular direct interactions among ORNL, PNNL, and SNL.
- Experimental measurements of LNT and SCR chemistry and reaction rates using laboratory reactors and prototype devices installed on engine test stands and vehicles.
- Analysis and reconciliation of experimental data from different sources with predictions from computer simulations.
- Publications in journals and presentations in public meetings and on the Web site.

Results

The ORNL bench-flow reactor used for LNT protocol measurements has been upgraded to allow more refined measurements of transient LNT chemistry under relevant fast lean/rich cycling conditions. In particular, a significant improvement has been realized on both hardware and software to equip the reactor with gas analytics of high temporal resolution. This enhanced temporal resolution of reactor effluent speciation complements the ORNL-developed spatially resolved capillary inlet mass spectrometer (SpaciMS) approach [2] in LNT research, and combined spatiotemporal information was instrumental in acquiring new insights into LNT process details for instance transient NH_3 chemistry. It is expected that the improved temporal resolution of this reactor will also be useful in understanding the high-speed dynamics of other types of catalysts (e.g., diesel oxidation catalysts).

A major goal of the LNT research this year was to expand our understanding of NH_3 formation, evolution and utilization processes to help improve the ability of LNT models to predict NH_3 behavior during relevant fast lean/rich cycling conditions. To this end, we initiated a series of cycling experiments with the CLEERS LNT catalysts in the bench flow reactor over a wide range of temperature and reductant types. Data were collected with H_2, CO, H_2/CO, and H_2/C_3H_6 as reductant over 150-550°C so far, and this effort will continue into the next year to cover a broader range of reaction conditions. These experiments show strong influence of temperature and nature of reductant on NH_3 and N_2O selectivity. Besides, temporally resolved species profiles have revealed several chemistry details not well recognized previously. For example, in addition to its formation during the regeneration phase, a significant amount of N_2O was found to evolve from the catalyst at the rich/lean transition and early lean phase. This second N_2O peak indicates possible NH_3 storage on the LNT surface during the regeneration phase; the oxidation of the adsorbed NH_3 during the next lean phase leading to the N_2O formation.

To further resolve NH_3 storage and conversion reactions, we performed complementary DRIFTS reactor experiments to study the transient catalyst surface chemistry under regeneration conditions. The results, as reported in Figure 1, confirm that a significant amount of NH_3, a byproduct of NOx reduction, can remain adsorbed on the LNT surface at the end of the regeneration phase. The adsorbed NH_3 is then oxidized

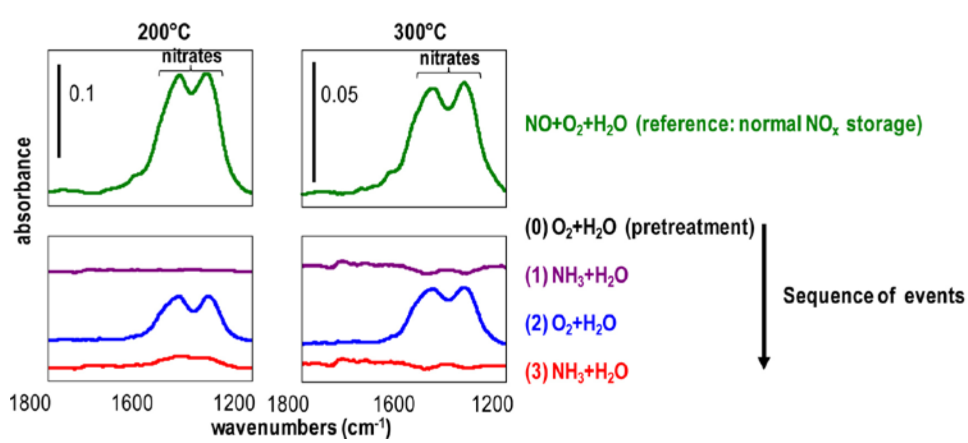

FIGURE 1. DRIFTS evidence of NOx storage via rich-phase adsorption of NH_3 followed by lean-phase oxidation on a Pt/Ba/Al_2O_3 model LNT catalyst at 300°C.

by O_2 at the inception of the subsequent lean phase leading to surface nitrates as well as N_2O breakthrough (as observed during the bench reactor study). This NH_3 formation/adsorption/oxidation sequence also implies downstream axial redistribution of stored NOx via conversion of released NH_3. As can be seen in Figure 2, almost all of the inlet NOx is stored within the first half of the LNT, while the NH_3 formed during regeneration attaches to the surface all along the LNT length. As revealed by DRIFTS, some of adsorbed NH_3 can convert back to nitrate under lean conditions, increasing the downstream extent of NOx storage. These observations reveal that measuring spatial profiles of gas-phase NO_x alone is not sufficient for developing fully accurate models of global LNT performance.

In conjunction with the ORNL-Cummins CRADA project, we confirmed our conceptual model on the sulfation-induced increase in LNT NH_3 selectivity [3] via direct measurements of spatiotemporal NH_3 profiles. As shown in Figure 3, the intermediate roles of NH_3 were first verified and quantified by studying the CLEERS LNT before sulfation. Ammonia, generated during regeneration, reacts with stored NOx and oxygen storage capacity (OSC) in the downstream portion of the catalyst. The result is significantly reduced NH_3 at the outlet of LNT. Sulfation of this commercial LNT displaces the NOx storage-reduction zone (confirmed by SpaciMS results not shown in this report), where NH_3 is generated, and correspondingly shortens the downstream OSC-only zone thereby reducing the capacity to oxidize NH_3. Hence, LNT NH_3 slip increases with increasing sulfation level.

We have implemented a global LNT model complementing the detailed micro-kinetics model developed in collaboration with SNL. The current version of the global model leads to NH_3 profiles in good agreement with the experimental results obtained at 300°C (Figures 2, 3). We plan to incorporate the DRIFTS and bench flow reactor experimental observations into the ORNL global LNT model to further enhance NH_3 prediction over a broad range of temperatures and reductant types. Moreover, ORNL has initiated collaboration with Prof. Milos Marek and Dr. Petr Koci at the Prague Institute of Chemical Technology to bring research synergy in modeling regeneration chemistry with global models.

We have collaborated with PNNL to improve the fidelity of SCR models under realistic operating conditions. These efforts have focused on the impact of transient operating conditions and hydrocarbon exhaust constituents. Our goal is to characterize the state of the catalyst active sites as functions of these two factors and quantify how changes in the active sites impact SCR reaction rates and surface storage capacities.

We developed a new CLEERS transient SCR flow reactor experiment protocol. The current SCR protocol (illustrated in Figure 4) includes multiple inlet gas transients to characterize NH_3 storage capacity, NH_3 uptake and release rates, reactivity of stored NH_3 for NOx reduction, and the impact of NH_3 coverage on SCR reaction rates. The protocol also measures rates of NH_3 and NO oxidation and SCR reaction kinetics under various NH_3/NOx and NO_2/NOx ratios. We have exercised the protocol on several SCR formulations, including the CLEERS reference Fe zeolite catalyst and a commercial Cu zeolite catalyst from a 2010 diesel vehicle (Figures 5 and 6). The Cu zeolite catalyst was obtained in response to industrial stakeholder recommendations to include one of the latest generation SCR catalysts in our investigations. The protocol

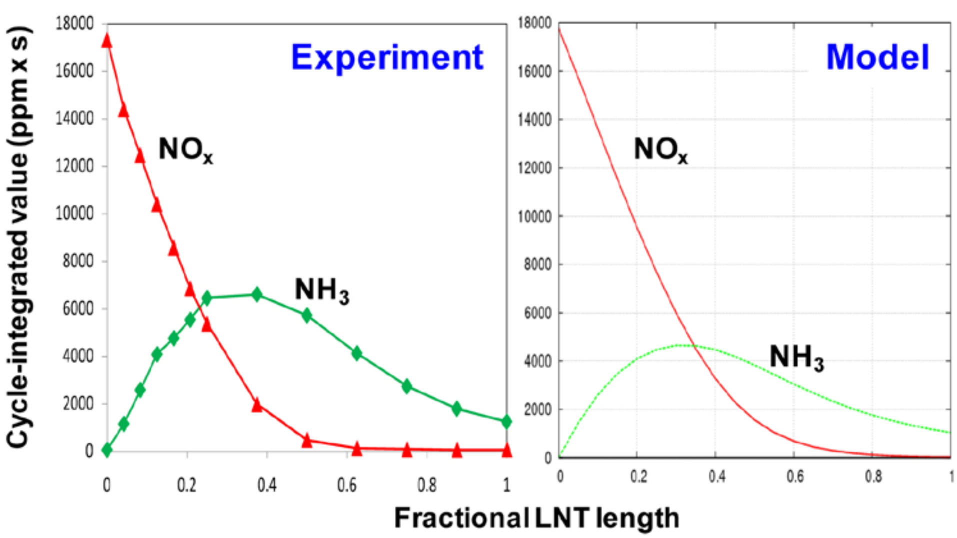

FIGURE 2. LNT NH_3 chemistry has been spatially resolved by combined use of bench-reactor experiments and modeling; 60/5-sec lean/rich cycling at 300°C with CLEERS reference LNT catalyst.

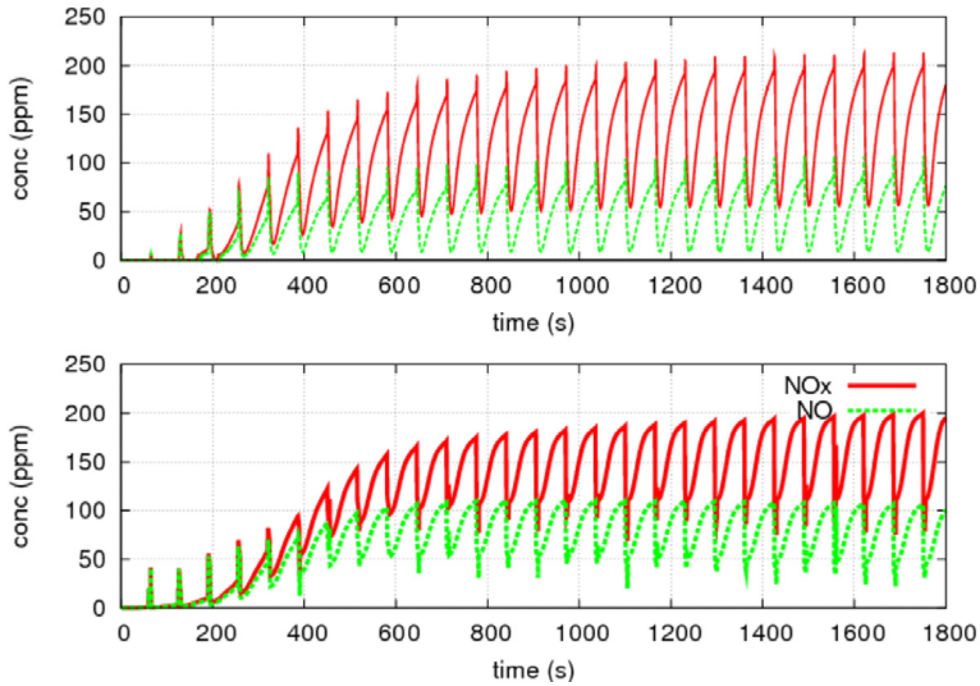

FIGURE 3. Comparison of measured (top) and predicted (bottom) NOx breakthrough profiles from a lean NOx trap during 60 sec lean, 5 sec rich cycling at 300°C starting from a fully reduced state.

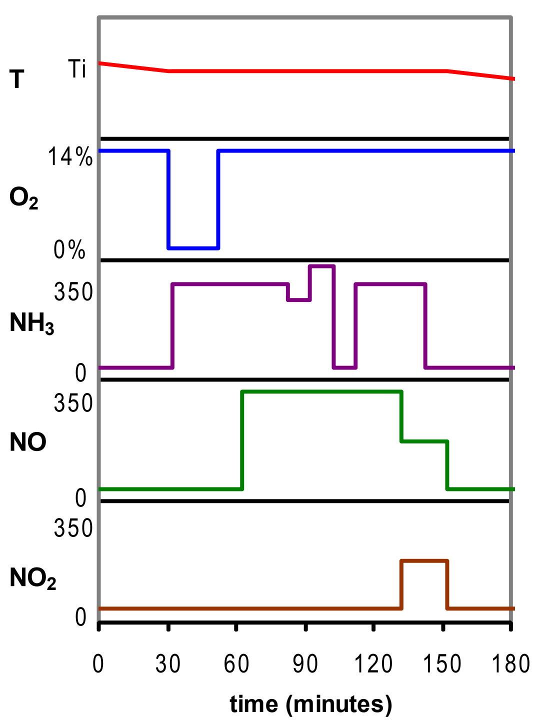

FIGURE 4. Schematic of the inlet gas transients during one temperature step of the CLEERS transient SCR reactor evaluation protocol.

data in Figure 5 reveal the performance limitations of both catalyst formulations. The Cu catalyst shows good low temperature NOx conversion, but the NOx reduction performance drops off at higher temperatures as NH_3 oxidation by O_2 begins to compete with the SCR reactions. The Fe formulation shows much more limited NO conversion at the lowest temperatures, but maintains good NOx conversion to higher temperatures, presumably due to the lower rate of NH_3 oxidation by O_2. With equimolar $NO+NO_2$ in the feed, the Fe formulation performs as well as the Cu catalyst at low temperatures. This performance enhancement with NO_2, which is observed with Fe but not Cu, is interesting given the very similar NO oxidation rates observed over the two catalysts. Figure 6 shows NH_3 storage capacities measured several different ways: NH_3 uptake under inert conditions, reduction of NOx by stored NH_3 under a subsequent SCR step, and NH_3 released and NO reduced by NH_3 stored during a previous SCR step with excess NH_3. As expected, the Cu zeolite has a much higher NH_3 storage capacity. However, a smaller fraction of the NH_3 stored on the Cu formulation is available for NOx reduction in subsequent protocol steps as compared to the Fe catalyst. For both samples, the saturation NH_3 storage capacity overpredicts the NH_3 on the surface under typical operating conditions, reinforcing the need for a transient protocol to measure NH_3 uptake and release under relevant operating conditions.

In addition to flow reactor experiments, we are also using DRIFTS to probe SCR catalyst surface chemistry. In FY 2009, we investigated the impact of hydrocarbons

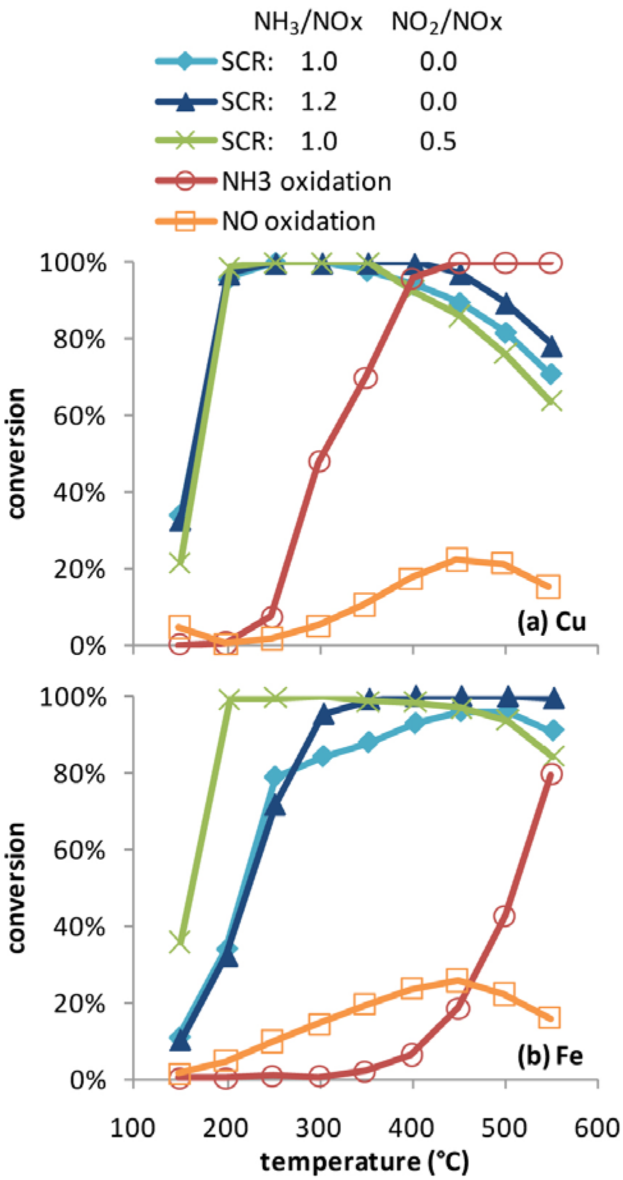

FIGURE 5. Variation of SCR NOx conversion with NH_3/NOx and NO_2/NOx, conversion of NH_3 by O_2 oxidation, and NO oxidation conversion all as a function of temperature for commercial (a) Cu and (b) Fe zeolite catalysts operated at a gas hourly space velocity of 30,000 hr^{-1}. All measurements included 14% O_2, 5% CO_2, and 4.5% H_2O. Total NOx was fixed at 350 ppm.

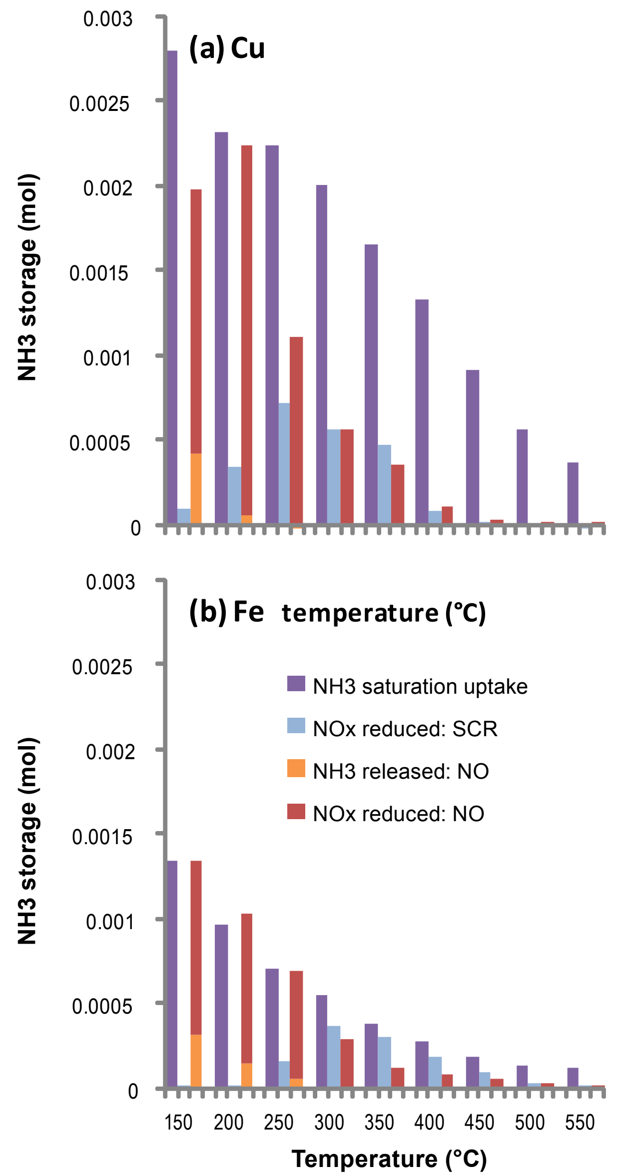

FIGURE 6. NH_3 storage capacity as a function of temperature measured for commercial (a) Cu and (b) Fe zeolite SCR catalysts by three independent methods from the CLEERS transient SCR evaluation protocol: total NH_3 uptake under inert conditions; subsequent conversion of NOx by stored NH_3 under SCR conditions; and NO converted by NH_3 stored during a previous SCR step with excess NH_3.

on the CLEERS reference Fe zeolite catalyst. While DRIFT spectra of the catalyst changed upon addition of certain hydrocarbons, the other components of the fully formulated washcoat complicated spectral interpretation. To avoid these complications, we worked with a catalyst supplier in FY 2010 to obtain model Beta and ZSM-5 zeolites in the ammonium form and exchanged with Cu and with Fe. We also submitted a user proposal to ORNL's Center for Nanophase Material Science to utilize their expertise and facilities in synthesizing a model SSZ-13 zeolite. Cu-SSZ-13 is a good model material for the latest generation of commercial zeolite SCR catalysts.

Conclusions

Strong research and development collaborations among ORNL, PNNL, and SNL continue to reveal new insights into the fundamental mechanisms controlling the performance of both LNT and urea-SCR catalysts for lean NOx control. The resulting kinetic parameters and device simulation models are providing critical information for guiding vehicle and system simulations studies as well as development of more fuel efficient, lower cost emissions control options for advanced combustion engines. Continuing industry input via the CLEERS groups and workshops is helping to insure practical relevance of the results.

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6. Jae-Soon Choi, William P. Partridge, Josh A. Pihl, V. Kalyana Chakravarthy, Todd J. Toops, C. Stuart Daw, "Spatial Distribution of Reactions: a Key to Understanding the Performance of Lean NO_x Trap Catalysts", invited lecture at the Korea Institute of Science and Technology, Seoul, Korea, July 1, 2010.

7. Jae-Soon Choi, William P. Partridge, Josh A. Pihl, V. Kalyana Chakravarthy, Todd J. Toops, C. Stuart Daw, "Spatial Distribution of Reactions: a Key to Understanding the Performance of Lean NO_x Trap Catalysts", invited lecture at the KIChE Discussions on Catalysis Research, Busan, Korea, June 23–25, 2010.

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11. Josh A. Pihl, Todd J. Toops, C. Stuart Daw, "Development of a CLEERS transient experimental protocol for urea/ammonia SCR," presented at the 2010 DOE Crosscut Workshop on Lean Emissions Reduction Simulation, Dearborn, MI, April 20–22, 2010.

12. Richard S. Larson, V. Kalyana Chakravarthy, Jae-Soon Choi, Josh A. Pihl, C. Stuart Daw, "Update on Microkinetic Modeling of Lean NO_x Trap Chemistry," presented at the 2010 DOE Crosscut Workshop on Lean Emissions Reduction Simulation, Dearborn, MI, April 20–22, 2010.

13. Zhiming Gao, V. Kalyana Chakravarthy, C. Stuart Daw, "Study of Aftertreatment Challenges in Hybrid Vehicles through System Simulations," presented at the 2010 DOE Crosscut Workshop on Lean Emissions Reduction Simulation, Dearborn, MI, April 20–22, 2010.

14. Jae-Soon Choi, William P. Partridge, Nathan A. Ottinger, Todd J. Toops, Josh A. Pihl, Michael J. Lance, Charles E.A. Finney, C. Stuart Daw, "Types, Spatial Distribution, Stability, and Performance Impact of Sulfur on a Lean NO_x Trap Catalyst", presented at the AIChE National Meeting, November 8–13, 2009, Nashville, TN.

Special Recognitions & Awards/Patents Issued

1. Invited keynote lecture by Jae-Soon Choi at the 2nd International Symposium on Air Pollution Abatement Catalysis, Cracow, Poland, September 8–11, 2010.

2. Invited lecture by Jae-Soon Choi at the KIChE Discussions on Catalysis Research, Busan, Korea, June 23–25, 2010.

II.B.11 Development of Advanced Diesel Particulate Filtration Systems

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Objectives

- Characterize the oxidation behavior of diesel particulate matter (PM) emissions in terms of heat release and oxidation rate.
- Quantify the amount of soluble organic compounds (SOCs, which are volatile components).
- Analyze ash particles.

Fiscal Year (FY) 2010 Accomplishments

- Measured the heat flow rates of diesel PM and dry soot samples.
- Measured oxidation rates of diesel soot.
- Measured the amount of SOCs.
- Visual analysis of residue particles after oxidation of diesel PM emissions.

Future Directions

- Define equations for the oxidation rates of diesel particulates.
- Characterize oxidation behaviors of diesel soot with different exhaust emission components.
- Improve pressure drop in filtration.
- Perform regeneration experiments and find quantitative data.

Introduction

Diesel particulate filters (DPFs) have been developed to remove PM emissions emitted from diesel engines, but better understanding of diesel PM oxidation mechanisms and thermo-physical properties of PM emissions (such as heat release and oxidation rate) are still required to effectively control an excess amount of heat release generated during DPF regeneration. For precise prediction of DPF performance and material failures by uncontrolled thermal reactions, numerical models also need detailed experimental information about heat release and oxidation rates of diesel soot.

In general, diesel PM emissions contain various complex components, such as SOCs, which are often dissolved in diesel PM emissions. The amount of SOCs in PM emissions usually depends on engine speed and load conditions [1-3]. A potential advantage of utilizing these particulates would be a low energy input required for DPF regeneration, because SOCs could enhance the ignition and oxidation of particulates.

In this experimental work, the researchers used thermal gravimetric analysis (TGA) to perform extensive oxidation experiments with diesel PM samples at different ambient conditions, and subsequently evaluated oxidation rates. These PM samples were collected directly from a filter membrane in a DPF system, which was connected to a diesel exhaust pipe. The measurement of oxidation rate at various isothermal conditions is rare in the literature. The researchers also measured the amount of heat release with oxidizing a small amount of PM samples collected from a lab-scaled DPF membrane, using a differential scanning calorimeter (DSC), which can eventually be used to predict a total amount of heat release generated during regeneration processes in a practical DPF system. Furthermore, the heat release from PM oxidation was characterized for different concentrations of SOC. Thus, the objective of this work is to characterize the thermo-physical/chemical properties of diesel PM emissions that can be used to find the efficient regeneration strategies of DPF systems.

Results

Diesel PM used in this research was collected from a non-catalyzed cordierite particulate filter membrane, connected to the main engine exhaust (see Figure 1). PM emissions were collected in the filter at various engine speed and load conditions for an extended time period to retain the same properties as those in practical DPF systems. The PM samples were kept in an environment controlled glove box till oxidation experiments.

As instrumentation, a DSC (temperature range between ambient and 550°C; temperature ramp rates 0.1-100°C/min; crucible size 50 µL) was used to measure heat flow rates from the oxidation of PM sample (or dry soot) under specific temperature profiles. A TGA (temperature range between ambient and 1,050°C; temperature ramp rates 0.1-100°C/min; crucible size 100 µL) measured the temporal variations of sample mass under specific temperature profiles, either by oxidation with air (60 ml/min) or evaporation in

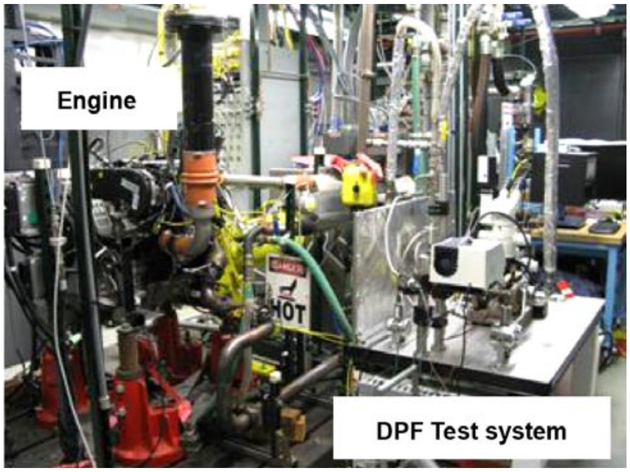

FIGURE 1. DPF Test System Connected to the Exhaust Pipe of a 1.9-L 4-Cylinder Light-Duty Diesel Engine

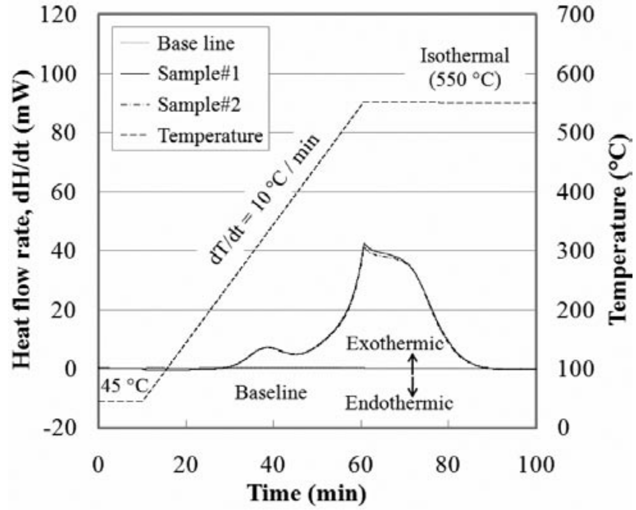

FIGURE 2. Temperature Profile and the Heat Flow Rate Measured In Oxidation of PM Samples with DSC

TABLE 1. Initial Sample Mass, Residual Mass, and Amount of Total Heat Released in the Oxidation of SOC-Containing PM Samples with DSC

Sample	M_o (mg)	M_r (mg)	M_o - M_r (mg)	Total Heat Release (kJ/g)
#1	4.197	0.323	3.874	14.67
#2	4.081	0.363	3.718	14.61

inert gas environment. Three different oxidation processes were used for TGA and DSC experiments at a temperature range of 500~600°C: (1) temperature-programmed isothermal oxidation with DSC (PM samples [or dry soot samples] were heated up to 550°C with a temperature gradient of 10°C/min in air and then maintained this temperature constant till the completion of oxidation), (2) SOC separation from diesel PM samples with DSC and TGA (PM samples were heated up to 550°C with a temperature gradient of 10°C/min in helium and then maintained this temperature constant for an hour), and (3) isothermal oxidation with TGA (dry soot samples were heated up to target temperatures [500°C, 550°C, or 600°C] with a temperature gradient of 10°C/min in helium and then oxidation proceeded at the isothermal conditions in air).

Results from the DSC experiments are illustrated in Figure 2, which presents the rate of heat flow evolved in the oxidation of PM samples in air under the given temperature profile. The heat flow rate curves indicate two characteristic regions: the first peak around 300°C is mainly due to the exothermic reaction by the oxidation of SOCs. The second peak at the start of isothermal conditions is associated mostly with the oxidation of dry soot. For each PM sample, the total amount of heat flow per unit sample mass was evaluated by integrating the data versus time, as given by:

$$q = \left[\int_{t_1}^{t_2} \frac{dH}{dt} dt \right] \cdot \left(\frac{1}{M_o - M_r} \right) \quad \text{Eq. 1}$$

where dH/dt is the heat flow rate, t is the time during oxidation, and M_o and M_r are the initial and residual mass of sample, respectively. The values of these parameters are listed for each sample in Table 1. The total heat release was calculated with respect to mass of soot only (i.e., M_o - M_r). It is noted that the magnitude of data for the total heat release per unit mass is almost identical between the two samples, suggesting a good repeatability in measurement.

Figure 3 represents results from a TGA experiment for the separation of SOCs in a PM sample. An initial sample mass of 4.184 mg was heated to 550°C at a temperature increase rate of 10°C/min in a helium environment, and then continued to be oxidized at the isothermal condition for an hour. During the extended isothermal condition, the volatile components of SOCs were completely removed, as indicated by no mass change with time. The reduction of PM mass corresponds to the mass of volatile components evaporated from the sample, which turned out to be 19.94 weight % with respect to the initial sample mass.

Measurement of transient heat release from oxidation of soot particles can predict the temporal distribution of thermal energy during regeneration in a DPF system and finally control thermal runaway taking place in oxidation of an excess amount of soot deposits. Figure 4 presents the temporal variation of the rate of heat released during the oxidation of SOC-containing PM (sample#1) and dry soot (sample#3).

As seen in the figure, the oxidation of dry soot sample exhibited just one peak point, while the

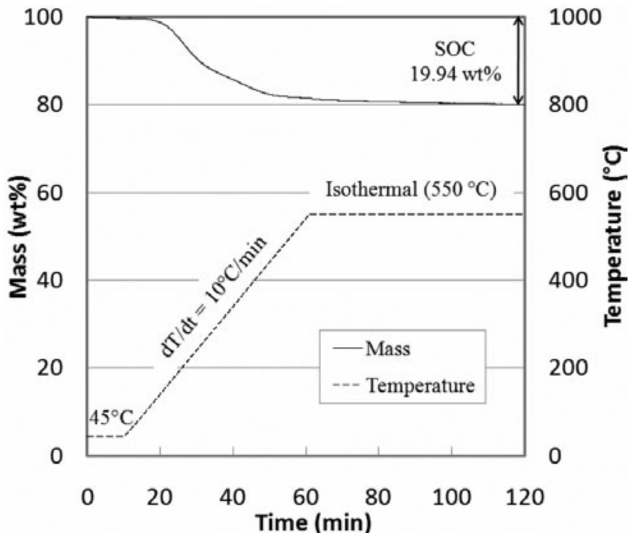

FIGURE 3. Change of PM Mass due to Evaporation of SOC Contents in Helium

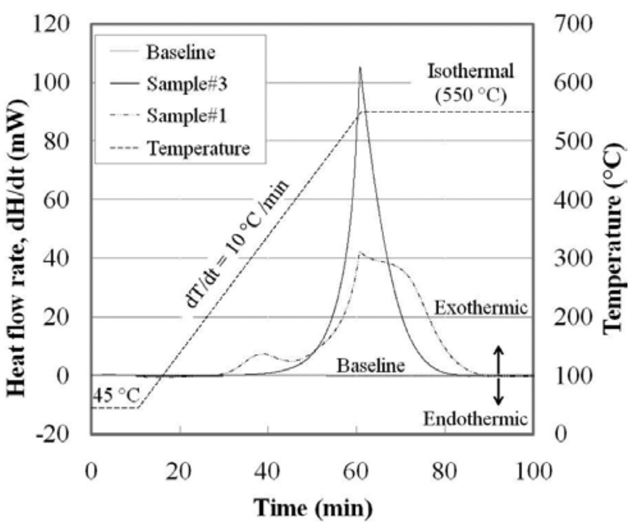

FIGURE 4. Rate of Heat Release Measured During the Oxidation of SOC-Containing PM Sample (sample#1) and Dry Soot (sample#3) Subjected to a Specified Temperature Profile in Air

oxidation of PM sample initially involved an exothermic reaction by the oxidation of SOCs (indicated by the first peak around t=40 min.) and then mainly the oxidation

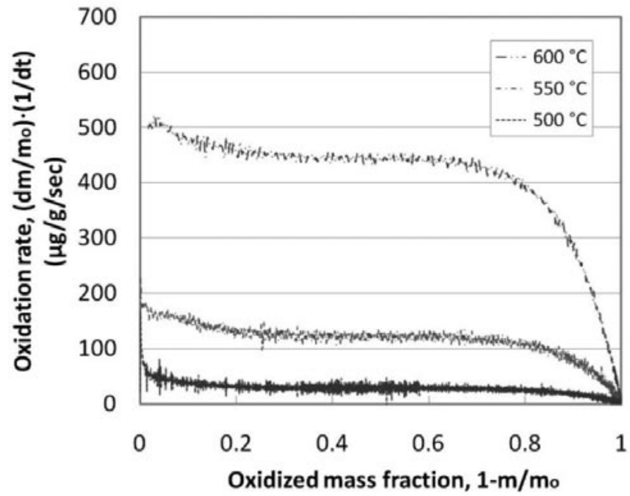

FIGURE 5. Rate of Oxidation with Respect to Oxidized Mass Fraction of Dry Soot at 500, 550 and 600°C

of dry soot (approximately t>50 min.). The total heat flows of two samples were evaluated by using Eq. (1) and the results were listed in Table 2. The heat release per unit mass of dry soot turned out to be 17.25 kJ/g.

The amount of heat flow released in the oxidation of SOC only (sample #1) can be calculated by

$$q_{SOC} = \frac{q_{PM} \cdot m_{PM} - q_{soot} \cdot m_{soot}}{m_{SOC}} \qquad \text{Eq. 2}$$

where q_{PM} and q_{soot} denote the amount of heat release per unit mass from the oxidation of PM and dry soot samples, respectively. m_{PM} denotes the mass of PM sample including SOCs but excepting the mass of residues, i.e., $(M_o – M_r)$, m_{SOC} the mass of SOCs, and m_{soot} the mass of dry soot, i.e., $(M_o - M_r - M_{soc})$. Finally, the heat release from the oxidation of SOCs was calculated to be 5.4 kJ/g.

Figure 5 displays the oxidation rates of dry soot at three different temperatures (500, 550 and 600°C) as a function of oxidized mass fraction $(1\text{-}m/m_o)$. The data for oxidation rates displayed two different reaction zones: a constant zone in x = 0 to 0.8 and the other zone in x = 0.8 to 1 where the oxidation rate rapidly decreased. The existence of two distinct reaction zones may be attributed to the differences of dry soot properties displayed with progress in soot oxidation.

TABLE 2. Mass and Amount of Heat Release Measured in the Oxidation of PM (#1) and Dry Soot (#3) Samples

Sample	M_o (mg)	M_r (mg)	M_{SOC} (mg)	$M_o - M_r$ (mg)	Heat release (kJ/g)	$M_o - M_r - M_{SOC}$ (mg)	Heat release by SOC only (kJ/g)
#1	4.197	0.323	0.84	3.874	14.67	3.034	5.4
#3	3.725	0.315	-	3.410	17.25	3.410	-

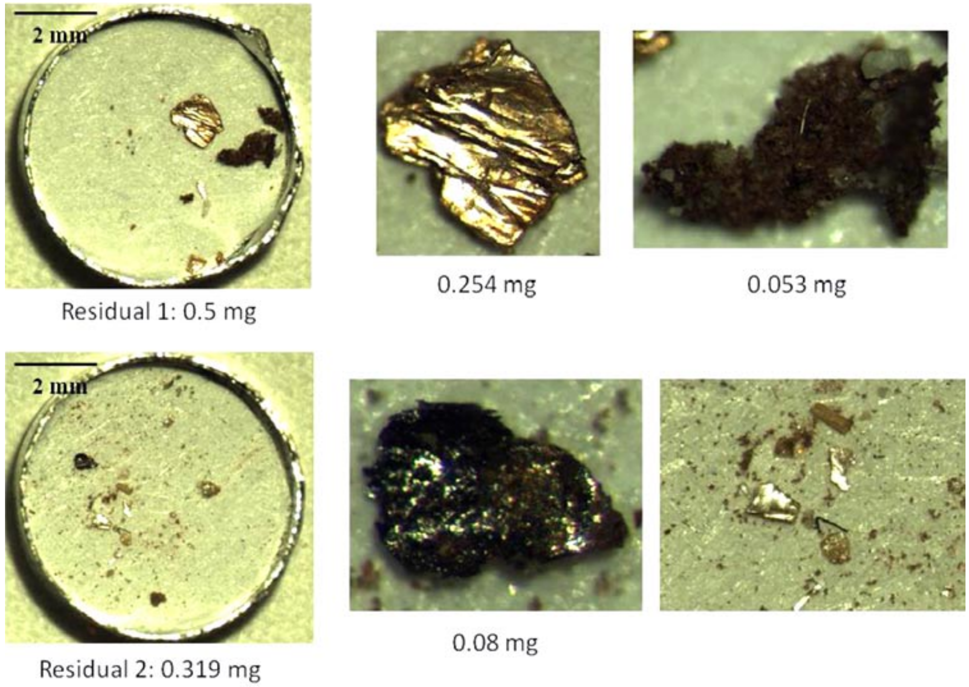

FIGURE 6. Images of Residues after the Complete Oxidation of Diesel PM Samples

Figure 6 shows the images of residues collected after the complete oxidation of PM sample. The amount of residue was measured to be 3~20 % in mass with respect to the initial PM sample mass. In this figure, the residues of 0.5 mg and 0.319 mg were obtained from the PM samples, of which initial mass was 4.271 mg and 4.552 mg, respectively. The residues appeared to consist of complex materials, such as metallic compounds (potentially metal oxides) and ash particles mixed with metal contents. The heavy metallic compounds and ash particles are originated typically from engine wear, pipe corrosion, or incomplete combustion of lube oils and fuel additives [4-6]. In general, diesel PM emissions are believed to contain various metallic elements, such as Zn, Mg, Pb, Fe, P, Ba, La, Si, Cu, Ni, Cd and Cr [4,6]. The gold-colored shiny object of 0.254 mg and the black/partially gold-colored one of 0.08 mg are the examples of a metallic compound and a mixture of a metallic compound and ash particles, respectively. The proportions of metallic compounds in the residues are significant.

Conclusions

In an effort of characterizing the thermo-physical and chemical properties of diesel PM emissions, the amount of heat release in diesel PM oxidation and the concentrations of SOCs were measured. Differences in soot oxidation behaviors were also observed for two different samples: a SOC-containing PM sample and a dry soot sample. The result drawn from our research can be summarized as follows:

- Heat release from the oxidation of PM and dry soot was evaluated to be 14.6±0.1 kJ/g and 7.25±0.03 kJ/g, respectively.
- The amount of SOCs (volatile components only) in PM turned out to be 19.9±0.2 % and the heat release from oxidation of SOCs to be 5.4±0.2 kJ/g.
- Two different zones of oxidation rate were observed from the oxidation of dry soot, which should be attributed to differences in soot properties, such as soot morphology or microstructures.
- The residues appeared to contain quite complex substances, such as metallic compounds, ash particles, and their mixtures. The amount of residue was measured to be 3~20% with respect to the initial PM sample mass.

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II.B.12 Combination and Integration of DPF-SCR After-Treatment

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Objectives

- Develop a fundamental understanding of the integration of selective catalytic reduction (SCR) and diesel particulate filtration (DPF) technologies for on-road heavy-duty application.
- Probe the interaction of steady-state and transient DPF-SCR couples in order to better understand the optimization of combining the two units with a view to proper function and greater integration.
- Determine system limitations and define basic design requirements for efficient on-board packaging and integration with the engine, in order to minimize fuel utilization or impact on vehicle efficiency.
- Develop the scientific understanding that will lead to the design and optimization of 4-way devices, which will address soot, hydrocarbons (HCs), carbon monoxide (CO), and oxides of nitrogen (NO_x) in a single unit.

Fiscal Year (FY) 2010 Accomplishments

- A literature review as well as a DPF substrate review were completed detailing state-of-the-art particulate filtration technology, state-of-the-art NO_x catalytic reduction technology, and current commercial DPF substrates, providing the knowledge base for initiating the integration effort, and identifying the path forward.
- A Fe/Zeolite Socony Mobil-5 (ZSM-5) SCR active phase catalyst was developed by PNNL with sufficient activity for employing in the integration effort.
- An effective washcoating technique was developed for incorporating SCR catalyst washcoat onto 1-inch diameter DPF core; ~19 wt% SCR catalyst was successfully integrated into the DPF wall flow filter.
- Soot-loading methodology was developed and quantitatively verified in the 1-inch core configuration for integrated system interrogation; protocol for passive regeneration capacity quantification was developed and verified.

Future Directions

- The Cooperative Research and Development Agreement (CRADA) between PNNL and PACCAR for this project has determined the necessity of including a catalyst supplier. This is being facilitated now, and appropriate agreements are being put in place. The integration effort will move forward employing the catalyst supplier's commercial SCR formulation, and leveraging the supplier's washcoating capabilities and experience.
- Future activities include the catalyst supplier integrating SCR catalyst with high porosity cordierite in various loadings and configurations, and PNNL:
  - Performing detailed washcoat interrogation including physical and elemental examinations.
  - Examining the effect of the washcoat on the dynamics of soot loading within the system.
  - Examining the effect of the washcoat on the kinetics of NO_x reduction (with and without varying levels of soot).
  - Examining the effect of the washcoat on the kinetics of soot oxidation (both passive and active).
- With an optimized integrated system, produce a large integrated SCR-DPF device for testing and examination on a diesel engine, including:
  - Steady-state and transient investigations.
  - Loading and regeneration investigation and strategy development.
  - Aging studies.
  - Subsequent physical and elemental analyses of substrate and washcoat.

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Introduction

Exhaust after-treatment is considered an enabler for widespread implication of higher fuel efficient diesel engines. In the last decade extensive research has resulted in the development and advancement of many after-treatment technologies: lean-NO_x traps (LNTs), urea-SCR, and DPFs are considered the most mature and top choices at present. Despite the extensive amount of research performed to develop and enhance the performance and durability of SCR and DPF technologies in the United States and Europe, there are still many unanswered questions that relate to how these technologies can work together synergistically versus in opposition. Furthermore, DPF is the only technology that addresses abatement of particulate matter (PM) from the exhaust stream; the others deal with NO_x reduction exclusively. As such, it is anticipated that for the 2010 model year and beyond diesel vehicle regulations will indeed require a combination of either SCR or LNT with a DPF unit. However, to-date research focused on combining these technologies into an integrated system has been relatively sparse.

Today and to a greater extent in the future there is a need to minimize the volume and mass of after-treatment systems on ever increasingly more complex truck platforms. At the same time diesel engine exhaust emissions are currently set to be regulated in the U.S. by 2010 to the levels of: PM <0.01 g/bhp-hr, NO_x <0.20 g/bhp-hr, non-methane hydrocarbons (NMHC) <0.14 g/bhp-hr. It is projected that in future years these regulations will move to even lower levels while striving to increase fuel efficiency of diesel engines. A research area ripe for exploration is the combination of current cutting edge emission control systems to discover and utilize synergies between the systems to drive improved performance and efficiency. With the inevitable need to consider how SCR and DPF technologies will function in synergy to reduce both NO_x and PM, as well as how CO and HCs need to be managed, an intergraded investigation and approach is essentially mandatory. The determination of important synergies will require study both under steady-state conditions and through transient conditions.

Approach

In three years PNNL and PACCAR will execute a project to understand the critical developmental gaps and subsequently close these for a single container DPF-SCR system. The new PM and NO_x removal system is to be tested on a yet to be designated PACCAR heavy-duty diesel engine platform in the third year of this CRADA under real exhaust conditions. As part of the collaborative thrust in research PACCAR via DAF will leverage their existing programs with the Universiteit Utrecht in the Netherlands.

The primary thrust in the project is to study the synergies of DPF-SCR systems in order to develop a pathway to a singular catalytic brick that combines the function of both a DPF-SCR. Within this project an emphasis on available volume in the truck of the future leads to solely considering a single-path emission system. It is not envisioned that a flow-through open monolith would have sufficient contact with PM in order to reach U.S. 2010 heavy-duty diesel engine PM emission regulations. As such wall flow substrates will be the focus of the study.

Results

A literature review was conducted providing a detailed review of the current state-of-the-art urea SCR catalyst and diesel particulate filtration technologies. The review examined closely the fundamental mechanisms and reactions that take place in each technology, with a two-fold focus: necessity and opportunity. The purpose of the review was to provide the fundamental knowledge base for planning the strategy of integration as well as adequately evaluating the success of integrating the technologies.

A substrate review was also conducted for the purposes of providing a detailed quantitative comparison of important substrate characteristics. Substrates examined included cordierite, silicon carbide (SiC), aluminum titanate, mullite, and silicon nitride. Parameters examined included pore structure and characteristics, thermal conductivity, heat capacity, micro-cracking, thermal shock parameter, melting point, mass, and cost. The result of the review was to focus on high porosity cordierite in the near-term, with SiC to be examined further along in the effort; both substrates do hold interest for the integration.

A Fe/ZSM-5 SCR catalyst was successfully developed by PNNL and its activity was verified on a PNNL active-phase test apparatus. The Fe/ZSM-5 catalyst was developed using the formulation provided by Long and Yang [1]. Figure 1 shows the activity of an 80-100 mesh sample of the Fe/ZSM-5 formulation at 400 L/g-hr space velocity, which is an appropriate space velocity that targets 20 weight percent loading of a wall-flow filter operating at 35,000 gas hourly space velocity. Significant barriers prevented the CRADA from acquiring a commercial SCR catalyst active phase

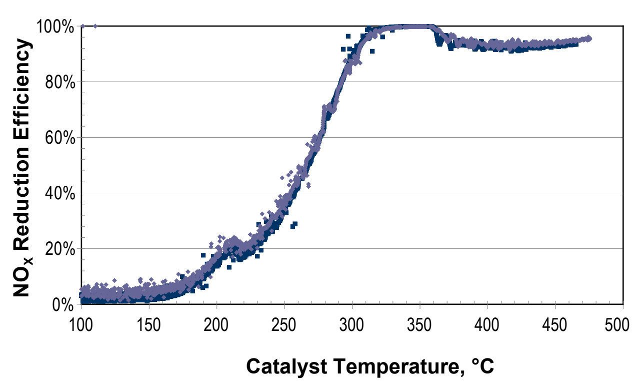

FIGURE 1. NO_x reduction performance for PNNL Fe^{2+} exchanged Fe/ZSM-5 SCR catalyst, 80-100 mesh sample tested at 400 L/(g-hr) space velocity.

from a commercial supplier. Thus, in the absence of a vendor-supplied commercial SCR catalyst formulation, this would provide an active catalyst phase that could be employed in the SCR-DPF integration effort.

A wash-coating technique for integrating the SCR catalyst into the DPF substrate was developed for the 1-inch core configuration. Employing a vacuum-suction method, an appropriate slurry rheology (i.e. solids concentration) was determined that was appropriate for the coating effort. Employing this washcoating method, a conventional porosity (~48%) cordierite substrate was successfully integrated with ~19 wt% Fe/ZSM-5 catalyst.

The strategy for scaling pressure drop of the integrated system was examined and developed out of Konstandopoulos and Johnson's device-scale model [2]. Konstandopolous and Johnson's device-scale model employs four general contributing factors in determining the total filter pressure drop, including contributions from: (1) entrance/exit effects, (2) inlet/outlet channels, (3) porous filter wall, and (4) soot. The contribution from the filter wall is the parameter affected by the integration, which is intimately a function of the wall permeability. Thus, scaling pressure drop measurements on the 1-inch core scale into predictions of pressure drop across full-size filters was accomplished by determining the quantitative effect of the washcoat on the filter wall permeability.

Quantitative prediction of diesel exhaust soot loading was successfully executed and implemented in the 1-inch filter configuration, and the path forward for passive regeneration feasibility analysis was determined for the system. Diesel exhaust soot from a 2003 Volkswagen Jetta TDI was employed for investigating the ability to quantitatively determine soot loading. An AVL 415 Smoke Meter was employed for estimating soot mass loading on the filters. In the 1-inch configuration, smoke meter measurements provided greater than 92% accuracy with mass measurements. With such good agreement, it is expected with this technique that smoke meter measurements will be able to be used to accurately predict soot loading mass for planned loading and regeneration activities.

Passive regeneration feasibility was investigated in the 1-inch configuration employing 1,000 ppm NO_2. With stepwise increases in temperature and subsequent exposure to five minutes of 1,000 ppm NO_2 flow, the concentration of NO in the effluent, together with filter pressure drop measurements, provided the ability to gauge the extent of passive regeneration in the system. Figures 2 and 3 show the NO concentration and pressure drop results from these stepwise investigations, respectively. Up to ~188°C, minimal passive soot oxidation is seen in the system from minimal increase in NO concentration along with minimal decline in the pressure drop across the filter over the course of the five minute exposure. At 235°C, a small increase in the NO concentration and a slight decrease in the filter pressure drop over the five minute NO_2 exposure are indicative of a small amount of passive soot oxidation taking place. Similarly, at 288°C, a larger increase in NO concentration and more significant decrease in filter pressure drop indicate more significant passive oxidation of soot in the 1-inch core filter. These tests demonstrate the ability to gauge passive regeneration feasibility, and the ability to evaluate the extent to which the presence of the SCR reaction will affect the passive regeneration capacity of the integrated system.

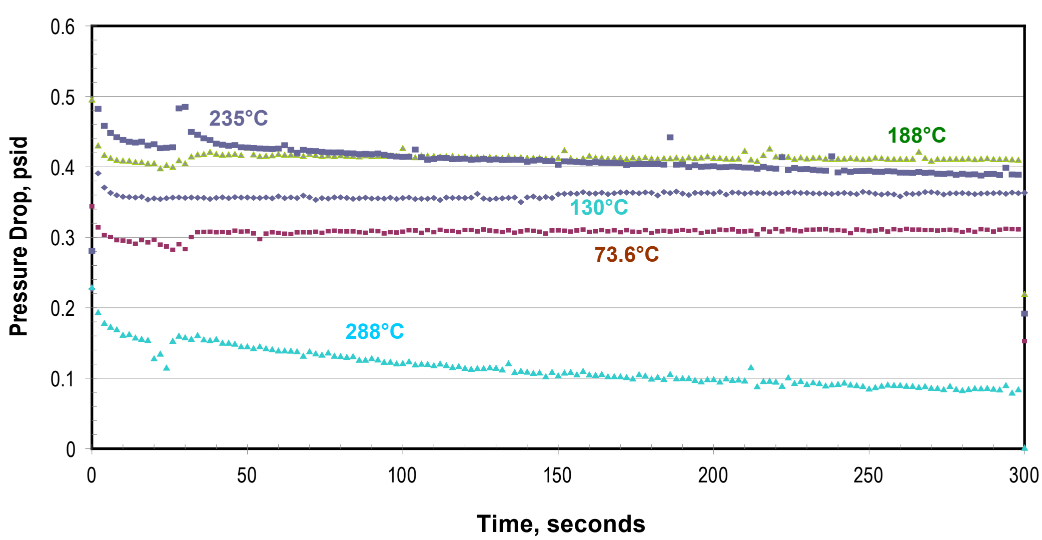

FIGURE 2. NO concentration out of DPF filter with loaded soot exposed to five minute pulses of 1,000 ppm NO_2 (in N_2) at 73.6°C, 130°C, 188°C, 235°C and 288°C.

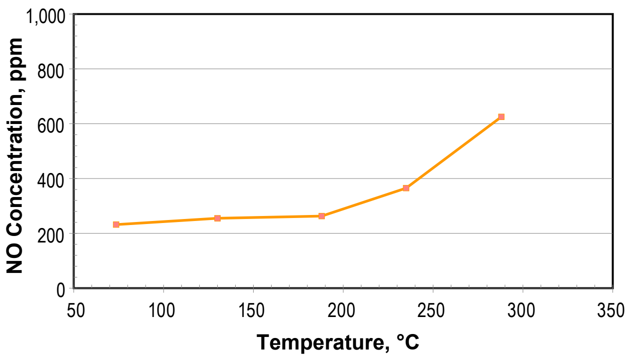

FIGURE 3. Pressure drop across DPF filter with loaded soot exposed to five minute pulses of 1,000 ppm NO_2 (in N_2) at 73.6°C, 130°C, 188°C, 235°C and 288°C.

Conclusions

This effort has made excellent progress towards laying the groundwork for developing a fundamental understanding of the integration of SCR and DPF technologies. A detailed literature review, combined with a close examination of the various DPF substrates has provided substantial direction for current and future activities in the effort. Additionally, as a result of high-quality technique development, soot investigations can now move forward with a high level of confidence and reliable predictability in both the expected mass of accumulated soot as well as the ability to gauge the passive regeneration capacity of the system.

PNNL also successfully developed, tested, and washcoated an SCR active catalyst phase that exhibited sufficient activity to warrant its use in the integration effort. However in light of bringing a catalyst supplier into the effort, it is expected this active phase will not be employed in the balance of the CRADA activities; it is much more preferable to employ the catalyst supplier's current commercial active phase in the integration effort. Thus, this will be the CRADA's preferred path forward as this presents the greatest opportunity for success of the integration effort.

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II.B.13 Degradation Mechanisms of Urea Selective Catalytic Reduction Technology

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Objectives

- Develop an understanding of the deactivation mechanisms of and interactions between the diesel oxidation catalyst (DOC) and the urea selective catalytic reduction (urea-SCR) catalyst used in diesel aftertreatment systems.
- Understand similarities and differences between actual field aging and aging under laboratory conditions, information essential in developing a rapid assessment tool for emission control technology development.
- Determine the role of the various aging factors impacting long-term performance of these catalyst systems, in order to provide information about what operating conditions should be avoided to minimize catalyst deactivation.

Fiscal Year (FY) 2010 Accomplishments

Two Major Thrusts this Year:

- Several state-of-the-art characterization tools were found to be useful for investigating degradation mechanisms of 'development' DOC and SCR catalysts. In particular, to date we have used:
  - Transmission electron microscopy/X-ray diffraction (TEM/XRD): to obtain structural and catalytic phase/morphology information.
  - X-ray photoelectron spectroscopy (XPS): to investigate chemical state of active catalytic phases.
- Based on a correlation of performance measurements (GM) and characterization results (PNNL) obtained to date, the following are indicated as the primary reasons for deactivation:
  - DOC catalyst: sintering of active alloy metal (Pt/Pd) particles and corresponding loss in the number of active sites.
  - SCR catalyst: structure destruction of the zeolite-based catalysts and agglomeration of ion-exchanged metal species.

Future Directions

- Applying project established techniques to vehicle-aged samples (135,000 miles).
  - Based on the evaluation of DOC and SCR catalysts, revised laboratory aging protocols are being compared.
- Continued evaluation of the most effective characterization tools in order to provide additional crucial information about materials changes in the support materials as well as active catalytic phases.
  - Several additional state-of-the-art characterization techniques will be applied to develop correlations between structural changes and the deactivation of catalyst materials, including:
    - In situ X-ray absorption near-edge spectroscopy, electron paramagnetic resonance and ^{27}Al nuclear magnetic resonance (NMR).
    - H_2 temperature programmed reaction and NO_2 temperature programmed desorption.

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Introduction

Diesel engines can offer substantially higher fuel efficiency, good driving performance characteristics, and reduced CO_2 emissions compared to stoichiometric gasoline engines. For these reasons along with favorable taxation policies, diesel-powered passenger vehicles have been gaining popularity in Europe in recent years. Despite the increasing public demand for higher fuel economy and reduced dependency on imported oil, however, meeting the stringent emission standards with affordable methods has been a major challenge for the wide application of these fuel-efficient engines in the U.S. light-duty vehicle market. Urea-SCR is one of the most promising technologies for oxides of nitrogen (NOx) emission control for diesel engine exhausts. Compared to the competing lean-NOx reduction technologies such as the NOx adsorber technology (lean-NOx trap, LNT, and NOx storage/reduction, NSR), urea-SCR offers a number of advantages, including excellent low-temperature NOx reduction efficiency, a wide temperature window of operation, and no platinum group metal (PGM) requirement, etc. Therefore, urea-SCR technology is being implemented by many automotive manufacturers as a primary path to meeting the emission standards for 2010 and beyond diesel vehicles. To ensure successful NOx emission control, a DOC and a urea-SCR catalyst with high activity and durability are critical for the emission control system. Because the use of this technology for mobile applications is new, the lack of experience makes it especially challenging to satisfy the durability requirements. Of particular concern is being able to realistically simulate the actual field aging of diesel aftertreatment catalysts under laboratory conditions, which is necessary as a rapid assessment tool for verifying improved performance and certifiability of new promising catalyst formulations. In addition, it is imperative to understand deactivation mechanisms to develop improved catalyst materials.

GM and PNNL are investigating fresh, laboratory- and engine-aged DOC and SCR catalysts in this CRADA project that began in January, 2009. These studies are intended to obtain a better understanding of various aging factors that impact the long-term performance of catalysts used in the urea-SCR technology, and improve the correlation between laboratory and engine aging in order to reduce emission control system development time and cost. Investigations of DOC catalysts will include oxidation of hydrocarbons and NO, and SCR catalysts for low-temperature NOx conversion activity, ammonia storage and slip at low temperatures and ammonia oxidation at high temperatures.

Approach

This project is focusing on the characterization of catalyst materials used in the urea-SCR technology with special attention to changes in the materials properties under conditions of laboratory (e.g., oven and laboratory reactor) and realistic (e.g., engine dynamometer and vehicle) aging protocols. In particular, a primary area of emphasis is on establishing the relevance of rapid laboratory catalyst aging protocols with the specific aging phenomena observed in realistic engine operating conditions. This information will aid in the development of improved catalyst formulations and the optimal integration of new catalyst formulations into GM's aftertreatment systems. More importantly, the information will also aid in understanding how catalyst degradation occurs in the field, and developing ways to improve the durability of catalyst materials.

GM has been providing both fresh and aged catalyst materials used in the DOC and urea-SCR technology and making experimental measurements of changes in the catalytic performance of these materials before and after the aging. PNNL has been utilizing state-of-the-art analytical techniques to investigate the surface and bulk properties of these catalysts as well as the changes in these properties induced by the aging process. In particular, catalyst characterization techniques such as XRD, XPS, TEM/EDS, Brunauer-Emmett-Teller/pore size distribution, and ^{27}Al solid state NMR are being utilized to probe the changes in physicochemical properties of DOC and SCR catalyst samples under deactivating conditions; e.g., hydrothermal aging at various temperatures. This work is being performed on a group of model and development catalysts. By developing a good understanding of performance degradation mechanisms during the catalyst aging, PNNL and GM expect to be able to provide a framework for developing robust DOC and urea-SCR catalyst systems, a better definition of the operational window for current materials, and perhaps also suggesting formulation changes that have potential to demonstrate improved performance and long-term durability.

Results

Physicochemical Investigations of the Degradation Mechanisms for DOC Catalysts

From this project's first year's studies, we found that a commercial DOC, consisting of noble metals deposited on an alumina-based support, suffered from the agglomeration of metal particles after they were hydrothermally aged at elevated temperatures. To understand the sintering process of DOCs containing Pt and Pd, we obtained a series of samples containing varying ratios of Pt/Pd such as 2/1, 5/1 and 10/1. We then exposed these samples to a heat treatment at 850°C for 48 hrs. XRD patterns of these samples, in the region where the main peaks of Pt or Pd phases are located, are shown in Figure 1. The main peak for the sample with the Pt/Pd ratio of 2/1 is located at 40.8°, while those of the samples with 5/1 and 10/1 ratios have peaks at lower 2θ. These results indicate that Pt-Pd alloys are formed in each sample, with compositions corresponding to the nominal amount of Pt and Pd, rather than simple sintering of individual crystalline particles of Pt and Pd. Also the peak in each case is very symmetrical, suggesting that homogeneous Pd-Pt alloy phases are produced as a result of the thermal aging applied here. The role of Pd in prohibiting the sintering of Pt-Pd alloy seems to be apparent, based on the relatively broader XRD peak in the sample with Pt/Pd of 2. The formation of homogeneous alloy phases corresponding to the initial ratio of Pt/Pd is also confirmed in TEM/EDX analysis as demonstrated in Figure 2. Clearly, there is a strong driving force for alloy formation under the oxidizing aging conditions used here.

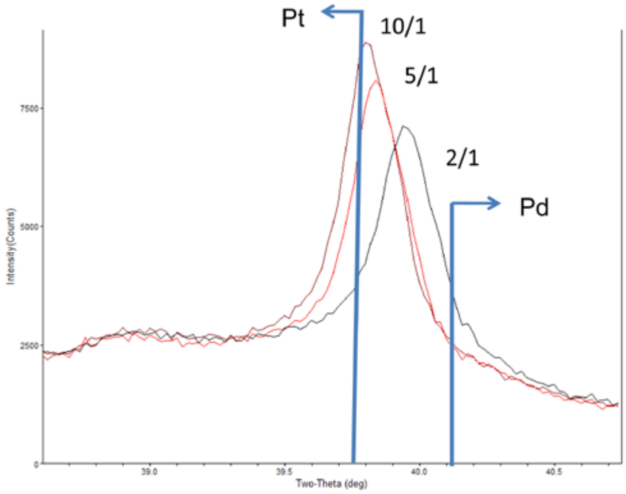

FIGURE 1. XRD patterns of Pt-Pd/Al_2O_3 catalysts with Pt/Pd ratios of 2/1, 5/1/ and 10/1 after thermal aging in laboratory air at 850°C for 48 hrs.

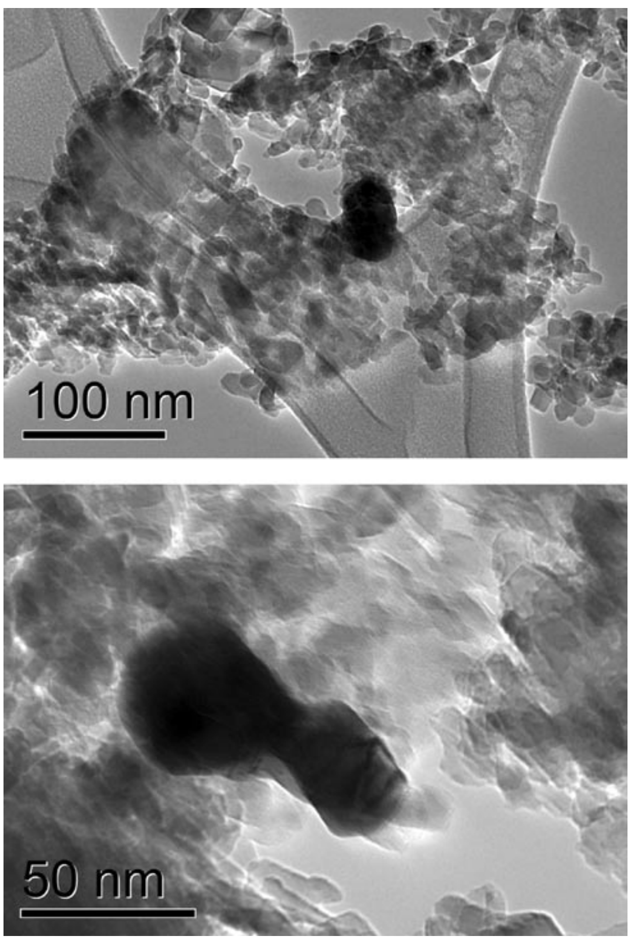

FIGURE 2. TEM pictures of Pt-Pd/Al_2O_3 with the ratio of 2/1 after hydrothermal aging at 850°C for 48 hrs.

Physicochemical Investigations of the Degradation Mechanisms for SCR Catalysts

A commercial SCR catalyst (base metal ion-exchanged zeolite) was thermally aged in a laboratory oven. Figure 3 shows GM-measured NOx conversions as a function of temperature at various aging times at 850ºC, where activity is shown to decrease slowly up to an aging time of 24 hr. However, there is a drastic decrease in NOx conversions from 24 hr to 48 hr for reaction temperatures between 300°C and 400°C, and almost no activity was observed after aging for 48 hr, implying nearly complete deactivation of the catalyst. Meanwhile, activity in the low-temperature region (~200°C) decreases rather linearly with aging time. We investigated the crystallinity of the zeolite structure by using XRD, and Figure 4 shows an intensity change of one of the zeolite structure peaks with aging time at 850°C. This figure clearly demonstrates that the zeolite morphology is gradually lost with aging time. In addition, agglomeration of metal clusters is clearly observed in both TEM and XPS analyses, also as a result of the thermal aging process. Combining XRD with activity results, the destruction of the zeolite structure correlates well with the gradual decrease in activity at lower temperature; however, there is not a good correlation with activity changes above 300ºC. Therefore it is necessary to investigate the hydrothermal aging of the catalysts further, especially focusing on the catalytically active sites in the material. In summary, the destruction of the zeolite structure and the agglomeration of active metal are indicated as the causes of severe SCR catalyst deactivation in good agreement

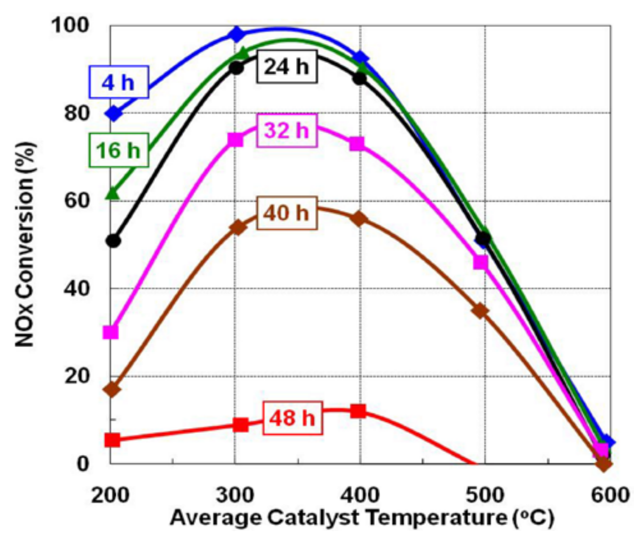

FIGURE 3. Changes in NOx conversion over thermally aged urea-SCR catalysts as a function of hydrothermal aging time at 850°C.

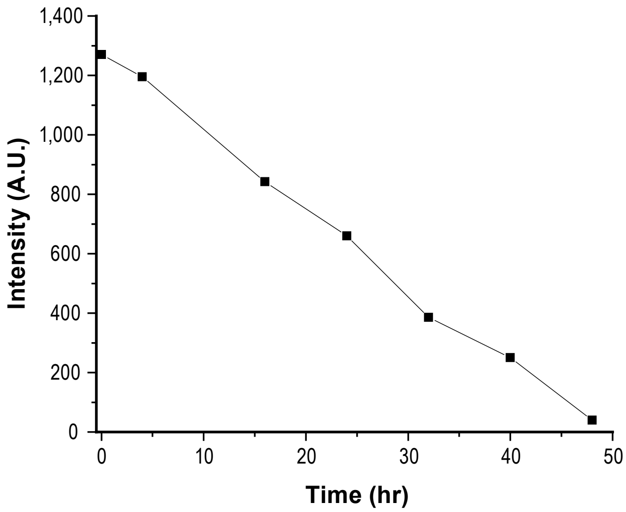

FIGURE 4. Changes in the intensity of an XRD peak due to the crystalline zeolite structure of the SCR catalyst after hydrothermal aging with time.

with previous studies [1]. Currently, in order to obtain a quantitative relationship between activity/adsorption and catalyst changes during the hydrothermal aging as a function of time and temperature, detailed catalyst characterization experiments focusing on molecular level active phase changes are underway.

Conclusions

PNNL and its CRADA partner GM are carrying out a project to study the mechanisms of deactivation of SCR and DOC materials arising from thermal aging. Results demonstrate that the growth and alloying of PGM in DOC catalysts are the primary materials changes and, thus, likely causes of deactivation. For the case of the urea-SCR catalyst, both the collapse of the zeolite structure and the growth of particles of the active metal are observed for a heavily-aged sample and certainly important causes of activity loss. Because the catalytically active sites certainly include isolated and very small (even mono-atomic) ion-exchanged metals in the zeolite cages, we are currently pursuing a molecular-level understanding of the deactivation mechanisms related to the activity degradation by using a number of state-of-the-art catalyst characterization techniques.

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II.C.1 Health Effects from Advanced Combustion and Fuel Technologies

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Objectives

- Understand potential impact of developing fuel, combustion, and aftertreatment technologies on air quality and, thereby, human health.
- Quantify particulate matter and other air toxic emissions from advanced technologies.
- Link emissions measured in laboratory setting to air quality impact, and thereby, health impact.

Fiscal Year (FY) 2010 Accomplishments

- Completed characterization of particulate matter (PM) emissions from both stoichiometric and lean-burn direct-injection spark ignition (DISI) vehicles operating on gasoline and ethanol blends (E0, E10 and E20):
  - Higher ethanol blends decreased cycle-based PM mass emissions.
  - Highest PM number emissions were associated with transient acceleration events; increased ethanol content reduced PM number emissions.
  - PM-associated elemental carbon decreased and organic carbon increased with increasing ethanol content.
- Completed measurements of aldehydes, ketones, and ethanol for both light-duty DISI vehicles:
  - Ethanol and acetaldehyde emissions were very low but increased with increasing ethanol content.
  - Formaldehyde and benzaldehyde decreased with increased ethanol content.
- Completed comparison of PM emissions from light-duty diesel engine in conventional, premixed-charge compression ignition (PCCI) and dual-fuel reaction controlled compression ignition (RCCI) operation:
  - The PM mass emissions for dual-fuel RCCI were much lower than that for conventional diesel combustion and were similar to that for PCCI.
  - The diesel oxidation catalyst (DOC) had a greater effect in reducing duel-fuel RCCI PM mass emissions than for conventional and PCCI.
  - The dual-fuel RCCI PM number concentration emissions were up to 100 times lower than PCCI and conventional diesel emissions, depending on particle size.
  - The DOC reduced the number concentration of 10 nm range dual-fuel particles.

Future Directions

- Determine lubricant contribution to PM emissions in DISI applications.
- Characterize DISI PM emissions from start-stop operations typical of hybrid vehicle operations.
- Examine effect of combustion phasing on PM emissions from a DISI engine operating on gasoline and ethanol blends.

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Introduction

Scientists and engineers at national laboratories, universities, and industrial companies are developing new fuels and energy efficient technologies for transportation, and the DOE is actively involved in this innovative research. However, care must be taken to insure that any new fuel or technology developed for transportation must not adversely affect public health in a direct way or through the contamination of the environment. To address this need, DOE sponsors research studies on the potential health impacts of advanced technologies for transportation including advanced fuels, combustion techniques, and emissions controls (also known as “aftertreatment” or, more commonly, “catalytic converters”). DOE sponsored health impact research activities at ORNL are presented in this report.

ORNL conducts research on advanced fuel, combustion and emissions control technologies at the Fuels, Engines, and Emissions Research Center. As research is conducted to evaluate advanced engine and vehicle performance, the potential adverse health effects of the technologies are assessed by the ORNL team for DOE’s health impacts subprogram. Results from ongoing ORNL studies in FY 2010 are presented here. A major focus has been the impact of ethanol blends on emerging gasoline vehicle technologies. PM and air toxic emissions were characterized for two light-duty DISI gasoline vehicles, one certified for use in the U.S.

and one certified for operation in Europe. The vehicles were operated on gasoline and gasoline-ethanol blends. A second focus has been on the impact of advanced combustion regimes on the emissions of PM. PM emissions from an engine operating in the advanced diesel combustion modes of PCCI and dual-fuel RCCI were evaluated. For dual-fuel RCCI, the use of gasoline and diesel blends in-cylinder dampens fuel reactivity and allows control of combustion phasing. This enables the extension of advanced combustion regimes to high load operation.

Approach

PM and Air Toxic Emissions from DISI Vehicles Fueled with Gasoline-Ethanol Blends

The U.S. DISI vehicle operated under stoichiometric conditions with a three-way catalyst and the European DISI vehicle operated primarily under lean-stratified conditions with a NOx trap catalyst. U.S. transient driving schedules (Federal Test Procedure, FTP, and US06 [1]), transient acceleration modes, and steady-state operation were used in the evaluation. PM mass and number concentration emissions were measured over the transient cycles; composition and size distributions were measured during steady-state operation. Aldehydes and ketones were collected during the FTP on dinitrophenylhydrazine cartridges. Ethanol emissions were collected in heated bags and analyzed with a photoacoustic analyzer.

PM Characteristics for a Diesel Engine Operating in Advanced Combustion Modes

The first studies of dual-fuel RCCI combustion were carried out on single-cylinder research engines [2,3]. In the current study, we extend the analysis to a 4-cylinder, General Motors production engine and investigate the aftertreatment effects of a DOC. For the study, the 1.9-L engine was operated at 2,300 rpm and 5.5 bar brake mean effective pressure (BMEP); particle emissions were sampled using a heated line and micro-tunnel dilution system. Particle number-size distributions were measured by a scanning mobility particle sizer and particle mass concentration by gravimetric analysis of Teflon®-coated quartz-fiber filters. We compared the particle emissions of dual-fuel PCCI, PCCI using diesel fuel only and conventional diesel combustion.

Results

PM and Air Toxic Emissions from DISI Vehicles Fueled with Gasoline-Ethanol Blends

The results from the two transient cycles, the FTP and US06, are shown in Figure 1 for both vehicles. The US06 is a more aggressive drive cycle with higher speeds and higher accelerations than the FTP and results in higher PM levels for both vehicles. By way of reference, the 2009 Tier 2 PM emissions standard for light-duty diesel vehicles is 10 mg/mile, the highest value on the scale. Particle size distributions were obtained at 30 MPH and 80 MPH steady-state operation. The results for the stoichiometric vehicle are shown in Figure 2, and the data indicate that increased ethanol reduces the overall number concentrations of particles across the size range. The size distributions for the lean-burn DISI vehicle showed similar trends, but an overall higher concentration of particles and smaller peak particle size.

PM number concentrations were investigated during transient operation; the results for wide-open throttle (WOT) accelerations with the stoichiometric vehicle are shown in Figure 3, along with the vehicle speed trace. Three particle sizes, 10 nm, 50 nm, and 100 nm, were selected for measurement over three repeat WOT accelerations. For E0, the 50 and 100 nm particles show an order-of magnitude increase during the acceleration phase that quickly drops off. The 10 nm particles, typically hydrocarbon droplets formed by nucleation, were removed by the three-way catalyst for both fuels. Strikingly, there is an absence of a particle burst during the WOT acceleration with the E20 fuel. This is consistent with the 45% decrease in PM mass emissions observed over the US06 cycle in Figure 1 for E20.

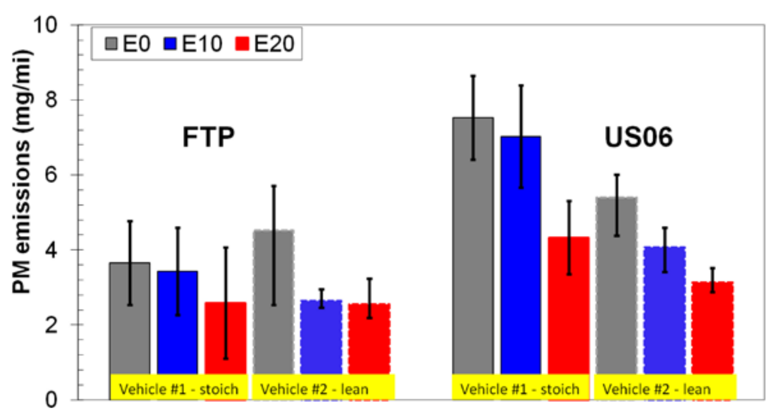

FIGURE 1. PM mass emissions for both study vehicles over the urban transient driving cycle (FTP) and a more aggressive cycle (US06) with three ethanol blends. Typical post-2002 port fuel-injected vehicles emit <1 mg/mile of PM and diesel vehicles with particulate filters emit 1-2 mg/mile over the FTP cycle.

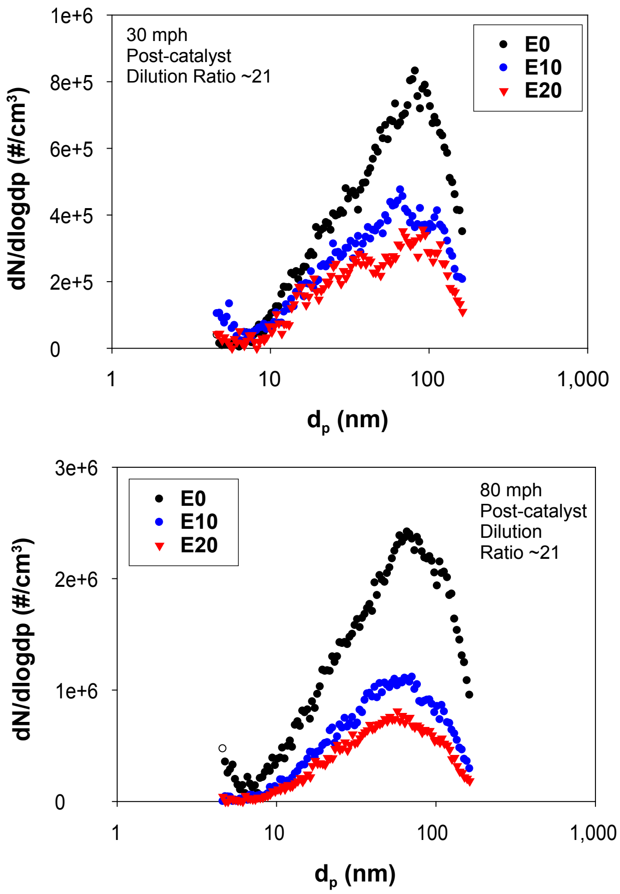

FIGURE 2. Particle size distributions for the stoichiometric DISI vehicle operating on gasoline and ethanol blends at two different steady-state speeds. Note that the scale for the 80 MPH case is 3X higher than the scale for the 30 MPH case.

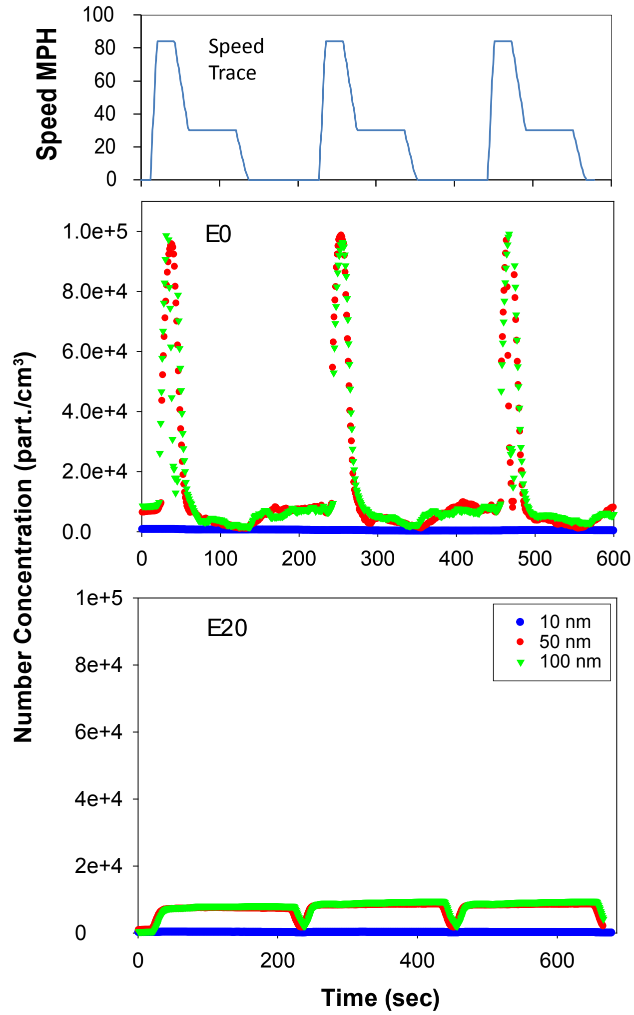

FIGURE 3. PM number concentrations for WOT accelerations at three different particle sizes: 10 nm; 50 nm; and 100 nm. Data for the stoichiometric DISI vehicle operating on E0 and E20 are shown.

Figure 4 shows that the aldehyde emissions were very low, and only occur in the first phase or "Bag" of the FTP which includes the cold start. The weighted aldehyde emissions for the entire FTP cycle would thus be much less than 1 mg/mile. By way of reference, a light-duty emissions standard for formaldehyde was promulgated in 2000 at 18 mg/mile [1]. Acetaldehyde emissions do increase with increasing ethanol content, as was seen in previous research in our laboratory [4].

PM Characteristics for a Diesel Engine Operating in Advanced Combustion Modes

The results of the study indicate the particle mass emissions for dual-fuel combustion (0.027 ± 0.007 g/hp-hr) are much less than that for conventional diesel (0.115 ± 0.016 g/hp-hr) but are similar to PCCI (0.028 ± 0.001 g/hp-hr). However, the DOC has a greater effect in reducing dual-fuel particle mass emissions (47 ± 9%) than PCCI emissions (9 ± 18%). In addition, the dual-fuel exhaust temperature was 161 ± 7°C cooler at the inlet of the DOC. The larger reduction

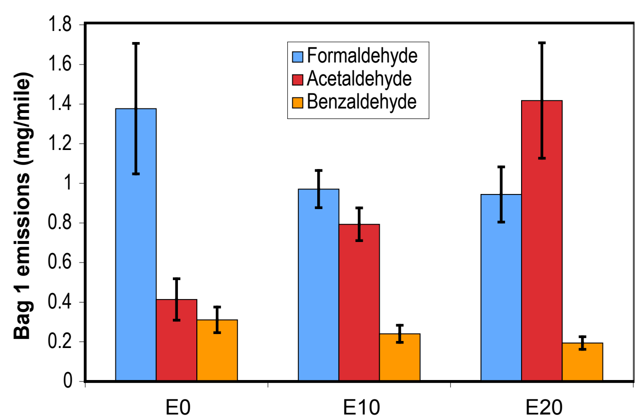

FIGURE 4. E10 and E20 lower formaldehyde and benzaldehyde emissions, but acetaldehyde increases with increasing ethanol content. Values are very low or these pollutants only occur in the first phase of the FTP which includes the cold start.

by the DOC for lower exhaust temperature suggests that dual-fuel emissions consist of more organic carbon. Some of the organic carbon may have been present as low-range nanoparticles, since the particle number-size distribution measurements show the DOC is effective in reducing the sub-20 nm particle number concentration (35 ± 6%) but does not have an effect on larger particles (Figure 5). Reduction of <20 nm particles is more important since their number concentration is similar to conventional diesel and PCCI values, while larger dual-fuel particles are approximately 100 times less (Figure 6). Thus, incorporating dual-fuel rather than conventional diesel or PCCI combustion in conjunction with DOC aftertreatment leads to fewer particle mass and number concentration emissions at high load.

Conclusions

Light-duty DISI vehicles operating on gasoline and gasoline-ethanol blends:

- Increasing ethanol content reduces PM mass and number concentration over transient and steady-state operation.
- Differences between lean-burn and stoichiometric vehicles are not great; the size distributions show smaller particles but higher concentrations for lean-burn operation.
- Aldehydes, ketones, and ethanol emissions were low for the stoichiometric vehicle with the three-way catalyst. Both acetaldehyde and ethanol increased with increasing ethanol content in the fuel.

Extending advanced combustion regimes to high load using dual-fuel reaction controlled compression-ignition:

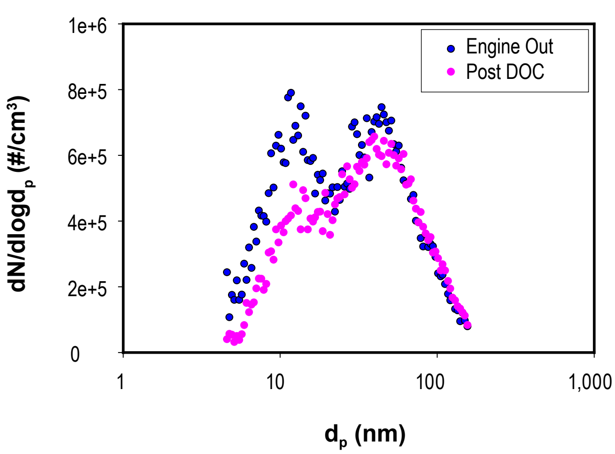

FIGURE 5. Dual-fuel RCCI particle number-size distributions for engine-out and post-DOC. The DOC has a greater effect in reducing sub-20 nm particles than the larger size range.

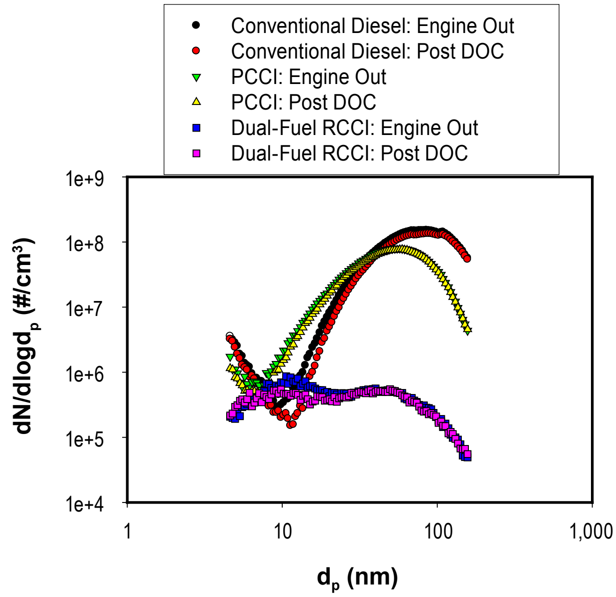

FIGURE 6. Comparison of particle number-size distributions for conventional diesel, PCCI, and dual-fuel RCCI combustion. The dual-fuel RCCI particle number concentration emissions were approximately 100 times lower for the >20 nm particles, but were similar to the conventional diesel and PCCI emissions for <20 nm particles.

- Dual-fuel RCCI operation enabled advanced combustion at high load while producing less particle mass and number concentration emissions than that of PCCI and conventional diesel combustion.
- There was an enhanced reduction in dual-fuel RCCI PM mass emissions by the DOC over the PCCI and conventional diesel emissions.

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1. Teresa L. Barone, John M. E. Storey, Scott J. Eaton, Bruce Bunting, Raynella M. Connaster, and Samuel A. Lewis ,"The Influence of Fuel Chemical Composition on Particle Emissions from an Advanced Combustion Engine," American Association for Aerosol Research (AAAR) 2009 Annual Conference, October 2009, Minneapolis, Minnesota.

2. John M.E. Storey, James E. Parks II, and Teresa L. Barone, "PM2.5, Air Toxics, And Crankcase Emissions In The Truck Stop Environment," *Oral Presentation* at the National Ambient Air Monitoring Conference in Nashville, TN in November, 2010.

3. John M.E. Storey, Teresa L. Barone, Samuel A. Lewis, Kevin Norman, and Brian West, "Ethanol Blend Effects On Direct-injection Gasoline Vehicle PM Emissions," *Oral Presentation* at the 20th CRC On-Road Vehicle Emissions Workshop, March 2010, San Diego, CA.

4. John M.E. Storey, Teresa L. Barone, Samuel A. Lewis, John N. Thomas, Shean P. Huff and Kevin Norman, "Measurement and Characterization of Unregulated Emissions from Advanced Technologies." *presented* at the 2010 DOE Annual Merit Review, June, 2010.

5. John M.E. Storey, "Greenhouse Gas Emissions from Advanced Diesel Technologies – What to Expect Now and in the Future," *EM: Environmental Manager*, July 2010.

6. John Storey, Sam Lewis, and Teresa Barone, "Ethanol Blend Effects On Direct Injection Spark-Ignition Gasoline Vehicle Particulate Matter Emissions," SAE Technical Paper no. 2010-01-2129. *accepted for presentation* at the SAE Powertrain, Fluids, and Lubricants Meeting, San Diego, CA. October 2010.

7. Teresa L. Barone, Anshuman A. Lall, John M.E. Storey, George W. Mulholland, Vitaly Y. Prikhodko, Jennifer H. Frankland, James E. Parks, Michael R. Zachariah, "Size-Resolved Density Measurements of Particulate Emissions from an Advanced Combustion Diesel Engine: Effect of Aggregate Morphology," In preparation.

II.C.2 Collaborative Lubricating Oil Study on Emissions (CLOSE) Project

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- Southwest Research Institute®
  6220 Culebra Road
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Objective

The objective of this project is to quantify the relative contributions of fuels and engine lubricating oil on particulate matter (PM) and semi-volatile organic compound (SVOC) emissions from in-use motor vehicles fueled with gasoline, E10, diesel, biodiesel, and natural gas while operating with fresh and used crankcase lubricants.

Fiscal Year (FY) 2010 Accomplishments

- Continued Cooperative Research and Development Agreement between NREL and the South Coast Air Quality Management District and the California Air Resources Board for project funding.
- Obtained internal funding from the National Renewable Energy Laboratory Strategic Initiatives Program for project support.
- The American Chemistry Council Petroleum Additives Product Approval Protocol Task Group provided new and aged engine lubricating oils for all vehicles tested in the project.
- Completed all heavy-duty vehicle emissions testing in June 2010. All vehicle emissions testing for the project has been completed.

Future Directions

A variety of light-, medium-, and heavy-duty vehicles have been tested over different driving test cycles at room (72°F) and cold (20°F) temperatures on chassis dynamometers. The test matrix depicting the vehicles and test conditions is shown in Table 1. The entire CLOSE Project, including review and delivery of the project final report, will be completed during FY 2011.

The engine lubricating oil used in the project is labeled with deuterated hexatriacontane ($C_{36}D_{74}$). This tracer, along with other naturally occurring compounds found in lubricating oil such as hopanes and steranes, and metals used as lubricant additives, are being used to quantify the relative contributions of PM and SVOC formed from the fuels and the lubricants in the vehicles in the CLOSE Project. In addition, detailed hydrocarbon speciation of compounds found in fuels and lubricants, will be used to identify the portions of exhaust produced by fuels and lubricants, which are the "parent materials" of species found in vehicle pollution.

TABLE 1. CLOSE Project Test Matrix

Test Temperature	72°F				20°F			
Test Lubricant	Fresh		Aged		Fresh		Aged	
Vehicle/Sample Number	1	2	1	2	1	2	1	2
LD gasoline ("normal" PM emitter)	√	√	√	√	√	√	√	√
LD gasoline (high PM emitter)	√	√	√	√	√	√	√	√
LD E10 ("normal" PM emitter)	√	√	√	√	√	√	√	√
LD E10 (high PM emitter)	√	√	√	√	√	√	√	√
MD diesel ("normal" PM emitter)	√	√	√	√	√	√	√	√
MD diesel (high PM emitter)	√	√	√	√	√	√	√	√
MD biodiesel ("normal" PM emitter)	√	√	√	√	√	√	√	√
MD biodiesel (high PM emitter)	√	√	√	√	√	√	√	√
HD CNG ("normal" PM emitter)	√	√	√	√				
HD CNG (high PM emitter)	√	√	√	√				
HD diesel ("normal" PM emitter)	√	√	√	√				
HD diesel (high PM emitter)	√	√	√	√				

LD – light-duty; MD – medium-duty; HD – heavy-duty

"Normal" and high-emitting vehicles representing gasoline, diesel, and compressed natural gas (CNG)-powered vehicles have been tested. Lubricants used in each technology are representative of those currently on the market, with both new and aged lubricants being tested. The fuels used in the vehicles were gasoline containing no ethanol, E10, Texas-mandated low-emission diesel, biodiesel, and CNG. Room temperature and cold temperature testing were conducted on all of the light- and medium-duty vehicles. Cold temperature testing was not conducted on the heavy-duty vehicles due to funding limitations.

The data collected throughout the study are being chemically analyzed with detailed speciation to quantify the relative importance of the fuel and lubricant to PM and SVOC emissions from these vehicles under the variety of testing conditions specified in the study design.

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Introduction

Air quality studies conducted in Denver, Phoenix, Washington D.C., Pittsburgh, Portland, and the Vehicle Technologies Program's Gasoline/Diesel PM Split Study in Los Angeles have shown that PM from gasoline engines is a more significant contributor to ambient air quality than PM from diesel engines [1]. For example, data collected in Washington, D.C., over a ten-year period suggest that PM from gasoline exhaust is 10 times more important to the emission inventory than diesel exhaust, as shown in Figure 1 [2,3].

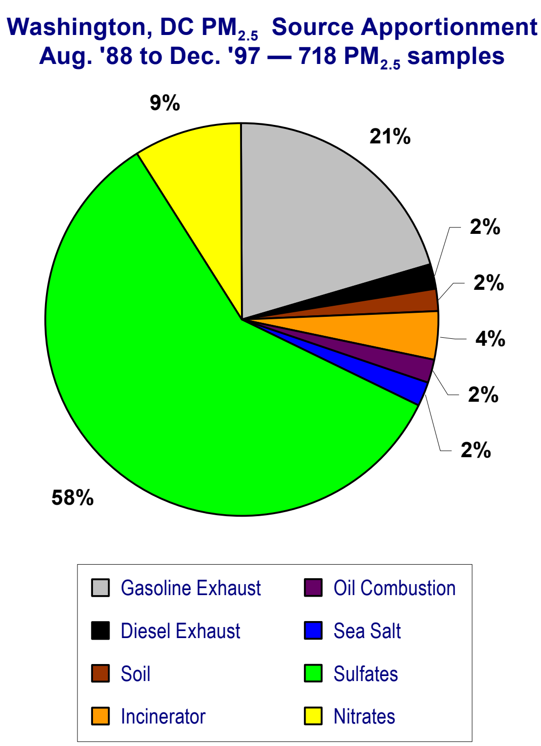

FIGURE 1. Source Apportionment of $PM_{2.5}$ in the Washington, D.C. Area, Ambient Air Quality Samples Collected between 1988 and 1997

The Vehicle Technologies Program's Comparative Toxicity Study demonstrated that the toxicity from gasoline exhaust on a per-unit-mass basis is at least as toxic as that from diesel exhaust, and that high emitters' toxicity is even greater than that from normal emitters [4].

Because PM and SVOC emissions from both gasoline and diesel exhaust are so important to human health and ambient air quality, it is important to understand their source – whether it derives from the fuel, the lubricant, or both, and to understand the engine operating conditions that are responsible for PM emissions. That is the objective of the CLOSE Project.

Approach

The CLOSE Project is conducting extensive chemical and physical characterizations of PM and SVOC emissions from vehicles fueled with gasoline, E10, diesel, biodiesel, and natural gas while operating on fresh and used crankcase lubricants in an effort to improve our current understanding of the impact of crankcase lubricant formulations on vehicle emissions. In-use light-, medium- and heavy-duty vehicles were recruited, including both "normal" and high-PM emitters, and operated on chassis dynamometers at room temperature (72°F) and cold temperature (20°F). Gaseous (total hydrocarbons, non-methane hydrocarbons, carbon monoxide, and oxides of nitrogen) and real-time particle emissions were measured, and PM and SVOC samples were collected for subsequent chemical analyses. Physical exhaust PM characterizations – including total particle number and particle size distributions – were measured over the various driving test cycles for the different vehicles run on the chassis dynamometers.

Results

At the time of this report, all CLOSE Project vehicle testing has been completed for all "normal" and high-emitting vehicles. Figure 2 shows the "high-emitting" natural gas heavy-duty bus that was procured by the South Coast Air Quality Management District (one of the project sponsors) and tested in the CLOSE Project, while Figure 3 shows the sampling ports and equipment used in the dilution exhaust sampling tunnel.

Conclusions

There is much national interest in the results coming from the CLOSE Project. In FY 2008, the Environmental Protection Agency asked for a presentation of the CLOSE Project at its Mobile Source Technical Review Subcommittee meeting in Arlington, VA, and additional presentations have been made to the Health Effects Institute, Coordinating Research Council, and the 2010 DOE Merit Review Meeting since that

FIGURE 2. Heavy-Duty High-Emitting CNG-Powered Heavy-Duty Bus Tested in the CLOSE Project

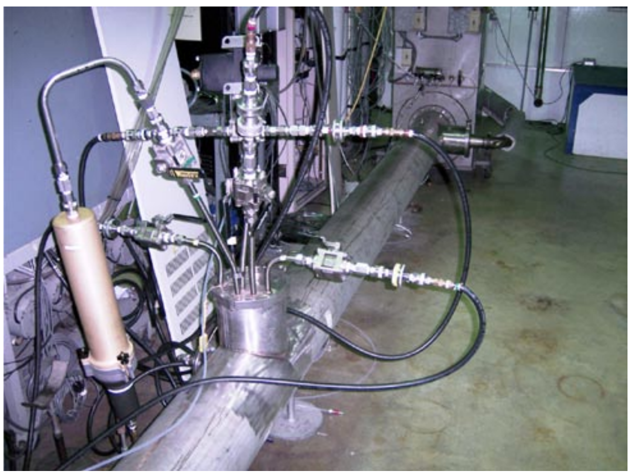

FIGURE 3. Sampling Probes used to Collect Exhaust Emissions Samples from the Dilution Tunnel

time. Because this project is not completed, there are no conclusions at the time of this report. The CLOSE Project will be completed by April 2011, and results will be available at that time.

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2. Kim, E. and P. K. Hopke. Source Apportionment of Fine Particles in Washington, DC, Utilizing Temperature-Resolved Carbon Fractions, *J. Air & Waste Manage. Assoc.*, Vol. 54, pp. 773-785 (2004)

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FY 2010 Publications/Presentations

1. "The Collaborative Lubricating Oil Study on Emissions (CLOSE) Project," progress reports presented at CRC AVFL program review meetings February, May and October 2010.

2. "The Collaborative Lubricating Oil Study on Emissions (CLOSE) Project," presented at DOE Annual Merit Review Meeting, Washington, D.C.; June 2010.

3. "Role of Fuel and Lubricating Oil on Particulate Matter and Semivolatile Organic Compound Emissions from Normal- and High-Emitting Light-Duty Vehicles," E.M. Fujita, B. Zielinska, J. Carroll, K. Whitney, L. Smith, and D.R. Lawson, submitted to CLOSE Project sponsors for review, September 2010.

II.C.3 The Advanced Collaborative Emissions Study (ACES)

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- Lovelace Respiratory Research Institute (LRRI), Albuquerque, NM

Objectives

- Phase 1: Extensive emissions characterization at Southwest Research Institute® (SwRI®) of four production-intent heavy-duty diesel engine and control systems designed to meet 2007 standards for particulate matter (PM) and nitrogen oxides (NOx). One engine/aftertreatment system will be selected for health testing.
- Phase 2: Extensive emissions characterization of a group of production-intent engine and control systems meeting the 2010 standards (including more advanced NOx controls to meet the more stringent 2010 NOx standards).
- Phase 3: One selected 2007-compliant engine will be installed and tested in a specially-designed emissions generation and animal exposure facility at LRRI (Phase 3A) and used in chronic and shorter-term health effects studies to form the basis of the ACES safety assessment (Phases 3B and 3C). This will include periodic emissions characterization during both a core 24-month chronic bioassay of cancer endpoints in rats and biological screening assays in both rats and mice (Phase 3B) as well as emissions characterization during a set of shorter animal exposures and biological screening using accepted toxicological tests after the end of the chronic bioassay (Phase 3C). (NOTE: Only the emissions characterization and biological screening activities during Phase 3 are components of the DOE ACES contract.)

Fiscal Year (FY) 2010 Accomplishments

Key Accomplishment

Completed detailed emissions and exposure characterization of one selected 2007-compliant engine after installation at the health testing facility (Phase 3A) and initiated animal inhalation exposures for chronic and shorter-term bioscreening studies (Phase 3B). Prepared a draft report with results of Phase 3A and completed the shorter-term exposures in rats and mice; toxicological analyses are well underway.

General Oversight

- Held conference calls with the HEI ACES Oversight and Advisory Committees and the LRRI team to discuss the Phase 3A report and remaining hurdles to starting Phase 3B, if any. Reached a final decision to go ahead with Phase 3B, pending approval from the engine manufacturer (which was subsequently obtained) (November 2009).
- Finalized with the engine manufacturer and Oversight Committee members the requirements for analyses of fuel batches shipped to LRRI and finalized the list of spare parts to purchase for the dynamometer and engine control systems (January 2010).
- Reached a decision to initiate the Phase 3B short-term exposures in mice and communicated the decision to LRRI (January 2010).
- Held two ACES meetings at the HEI Annual Conference, one for the ACES Phase 3B investigators, and one for the ACES Advisory and Oversight Committees to discuss progress in ACES and plans for health testing (April 2010).
- Launched planning with the CRC for Phase 2 – the detailed emission characterization for 2010 engines. It has become apparent that this will provide critical information given a wide array of new and innovative NOx control technologies (April 2010).
- Reviewed the performance of the exposure system during the first month of Phase 3B mouse exposures and reached a decision to initiate the long-term exposures in rats and communicated the decision to LRRI (May 2010).
- Conducted a site visit by the Engine Manufacturers Association and other sponsors to LRRI to view the engine facilities in operation (June 2010).
- Held a conference call with the ACES Oversight Committee to initiate investigator and stakeholder workshops to discuss progress in Phase 3B (September 2010).

Phase 1

- Completed draft manuscript on emissions characterization in Phase 1 to be published in the peer-reviewed literature (April 2010).
- Posted the complete data set for Phase 1 on the CRC Web site (April 2010).
- SwRI® investigators submitted revised Phase 1 manuscript to the Journal of the Air & Waste Management Association (revision submitted October 2010).

Phase 2

- Held monthly conference calls with CRC, its Technical Panel, and the engine manufacturers to start planning Phase 2 (August-October 2010).

Phase 3

- Completed detailed emissions and exposure chamber characterization of the back-up engine B' at LRRI in Phase 3A in anticipation of the start of the chronic bioassay in Phase 3B. Received a draft final report on Phase 3A (November 2009).
- Finalized protocols and standard operating procedures for the chronic bioassay in Phase 3B (December 2009) with further revisions in Spring 2010.
- Started phase 3B short-term mouse exposures in February 2010 and completed them in June 2010.
- Finalized necropsy procedures with pathology experts at LRRI and the ACES Oversight Committee during a site visit to LRRI (April 2010).
- Internally reviewed the Phase 3A report and communicated requests for revisions to LRRI investigators (April 2010).
- Started exposures of rats for the chronic inhalation study (May 2010).
- Completed the first of four detailed chemical characterizations of exposure atmospheres at LRRI (May 2010).
- Completed contract negotiations with the investigators selected under Request for Applications 06-2 to conduct additional biological screening (August 2010).
- Received a revised draft report with results from Phase 3A and sent it to external reviewers (August 2010).
- Distributed samples from the short-term exposures to investigators for toxicological analyses (summer and fall 2010).

Future Directions

Phase 1

- Publish Phase 1 results in the Journal of the Air & Waste Management Association (Fall/Winter 2010).

Phase 2

- Continue planning and initiate Phase 2 characterization of 2010-compliant engines. The expectation is that 2010-compliant engines will be made available for testing in Spring 2011.

Phase 3

- Expose rats for 24 months at three selected diesel exhaust exposure concentrations (high, medium, and low) or clean (2011 and part of 2012).
- Receive draft final reports from biological screening in rats and mice from all Phase 3B investigators and submit them to HEI's rigorous independent review process (Winter/Spring 2011).
- Receive a further revised report with results from Phase 3A (characterization of engine emissions and exposure atmospheres in the inhalation chambers at LRRI) and issue it as an HEI publication (Winter 2010/2011).
- Conduct combined investigator and stakeholder workshops to discuss progress in Phase 3B.

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Introduction

The ACES is a cooperative, multi-party effort to characterize the emissions and assess the safety of advanced heavy-duty diesel engine and aftertreatment systems and fuels designed to meet the 2007 and 2010 emissions standards for PM and NOx. The ACES is being carried out by HEI and the CRC. It is utilizing established emissions characterization and toxicological test methods to assess the overall safety of production-intent engine and control technology combinations that will be introduced into the market during the 2007-2010 time period. This is in direct response to calls in the U.S. Environmental Protection Agency (EPA) Health Assessment Document for Diesel Engine Exhaust [1] for assessment and reconsideration of diesel emissions and health risk with the advent of new cleaner technologies.

The characterization of emissions from representative, production-intent advanced compression ignition (CI) engine systems will include comprehensive analyses of the gaseous and particulate material, especially those species that have been identified as having potential health significance. The core toxicological study will include detailed emissions characterization at its inception, and periodically throughout a two-year chronic inhalation bioassay similar to the standard National Toxicology Program bioassay utilizing two rodent species. Other specific shorter-term biological screening studies also will be undertaken, informed by the emissions characterization information, to evaluate these engine systems with respect to carefully selected respiratory, immunologic, and other effects for which there are accepted toxicologic tests. It is anticipated that these emissions characterization and studies will assess the safety of these advanced CI engine systems, will identify and assess any unforeseen changes in the emissions as a result of the technology changes, and will contribute to the development of a database to inform future assessments of these advanced engine and control systems.

Approach

Experimental work under ACES is being conducted in three phases, as outlined in the objectives. Detailed emissions characterization (Phases 1 and 2) is performed by an existing engine laboratory (SwRI®) that meets the U.S. Environmental Protection Agency specifications for 2007 and 2010 engine testing. In Phase 1, emissions from four 2007-compliant engine/control systems have been characterized. One engine has been selected for health testing in Phase 3. In Phase 2, emissions from four 2010-compliant engine/control systems will be characterized. In Phase 3, the selected 2007-compliant engine/control system has been installed in a specially designed emission generation facility connected to a health testing facility at LRRI to conduct a chronic inhalation bioassay and shorter term biological screening in rats and mice. During the 2-year bioassay, emissions will be characterized at regular intervals throughout the testing.

The emissions characterization work is overseen by CRC and its ACES Panel. The health effects assessment is overseen by HEI and its ACES Oversight Committee (a subset of the HEI Research Committee augmented by independent experts from several disciplines), with advice from an Advisory Committee of ACES stakeholder experts. The overall effort is guided by an ACES Steering Committee consisting of representatives of DOE, engine manufacturers, EPA, the petroleum industry, the California Air Resources Board, emission control manufacturers, and the Natural Resources Defense Council. Set-up of the emission generation facility at LRRI (for Phase 3) and establishment of periodic emissions characterization throughout Phase 3 has been done with input from the team of investigators who conducted Phase 1 and the CRC ACES Panel.

Results

The results obtained during this reporting period pertain to (1) Phase 3A characterization of engine emissions and inhalation chamber exposure atmosphere prior to the start of Phase 3B at LRRI and (2) preliminary data for the exposure atmosphere characterization during the ongoing Phase 3B animal exposures.

Phase 3A. Emissions characterization of engine B (main engine) was completed in July 2009. Basic emissions and operating specifications were met and approved by the engine manufacturer. Initial testing of the exposure atmosphere in the animal inhalation chambers (without animals present) was conducted at a target NO_2 concentration of 4.2 ppm (lowest dilution level or highest diesel engine exhaust concentration), 0.8 at the mid level and 0.01 ppm at the highest dilution level. Testing continued during summer and fall 2009 with engine B' at all dilution levels with additional room cooling in place to reduce the exposure chamber temperature. A decision was made to conduct the Phase 3B health testing with engine B' because it is a newer version of engine B with updated emission controls and has a larger share in today's marketplace. Thus, the remaining inhalation chamber characterization was done with engine B' and was completed in November 2009 (Table 1). Subsequently, the data were reviewed and a decision was made to go ahead with animal exposures in Phase 3B in January 2010.

It was found that one to two diesel particle trap regenerations were observed during each 16-hr engine cycle, consistent with what was found in Phase 1. The majority of the particle number and mass was observed

TABLE 1. Exposure Chamber Atmosphere at Three Dilution Levels (no animals present; engine B' operated on 15 consecutive days using a 16-hr cycle)

	High Diesel Engine Exhaust							Mid Diesel Engine Exhaust			Low Diesel Engine Exhaust		
	CO_2 (ppm)	CO (ppm)	THC (ppm)	PM chamber (μg/m³)	PM inlet (μg/m³)	NO (ppm)	NO_2 (ppm)	PM chamber (μg/m³)	NO (ppm)	NO_2 (ppm)	PM chamber (μg/m³)	NO (ppb)	NO_2 (ppb)
Avg.	2885	3.1	0.1	9.7	12.5	2.9	4.0	1.7	0.5	0.7	0.8	35.8	98.5
Stdev.	166	0.6	0.1	2.8	2.9	0.4	0.4	0.9	0.3	0.4	0.6	30.0	50.7

Avg. – average; Stdev – standard deviation; THC – total hydrocarbons

TABLE 2. Average Daily Exposure Concentrations during July 2010 (animals present; engine B' operated 5 days/week using a 16-hr cycle)

	High Diesel Engine Exhaust						Mid Diesel Engine Exhaust			Low Diesel Engine Exhaust		
	SO_2 (ppm)	CO (ppm)	HC (ppm)	PM ($\mu g/m^3$)	NO (ppm)	NO_2 (ppm)	PM ($\mu g/m^3$)	NO (ppm)	NO_2 (ppm)	PM ($\mu g/m^3$)	NO (ppb)	NO_2 (ppb)
Avg. in chamber	21.47	10.34	0.56	25	4.88	3.31	30	1.33	0.86	25	0.17	0.13
Avg. at inlet				11			3			1		

during the trap regenerations, and the composition of the PM was mostly organic carbon and sulfate. All measured particles were less than 500 nm in diameter, and varied substantially throughout the engine cycle. Overall, the emissions characteristics reflected normal engine function and demonstrated successful commissioning of the engine test facility for the chronic bioassay.

Phase 3B. The LRRI investigators are continuously monitoring the exposure atmospheres during the Phase 3B animal exposures, which started in February 2010. Table 2 presents an overview of preliminary data collected during July 2010. In regular progress reports, the LRRI investigators have indicated that the system has been operating reliably, although some minor modifications have been necessary to maintain this.

Conclusions

Characterization of emissions of engine B' and the exposure atmosphere at LRRI in Phase 3 was successfully completed, which allowed the main health effects testing during Phase 3B to go forward in early 2010. During spring and summer of 2010, the short-term mouse and rat exposures were successfully completed. Toxicological analyses are well underway with the first results expected in early 2011. All this work has been conducted with input from the ACES stakeholders.

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1. U.S. Environmental Protection Agency. 2002. Health Assessment Document for Diesel Engine Exhaust. EPA/600/8-90/057F. U.S. Environmental Protection Agency, National Center for Environmental Assessment, Office of Research Development, Washington, D.C.

FY 2010 Publications/Presentations

1. Poster presentation at the CRC On-Road Vehicle Emissions Workshop in San Diego CA, March 2010: "ACES: Characterization of Exposure Atmospheres and System Performance for a Chronic 2007 Compliant Diesel Exhaust Inhalation Study".

2. Platform and poster presentations at the HEI Annual Conference in Alexandria VA, April 2009:

- "Micronucleated Reticulocytes as an Indicator of Genotoxicity Following Exposure to Cyclophosphamide and Its Application to the Evaluation of Diesel Exhaust" (PI Bemis)
- "Effects of Diesel Emissions on Vascular Inflammation" (PI Conklin)
- "Assessment of the Genotoxicity of Diesel Exhaust/Diesel Exhaust Particulates from Improved Diesel Engines" (PI Hallberg)
- "Status of ACES Phase 3: Chronic Inhalation Bioassay" (PI Mauderly)
- "Diesel Exhaust Exposure and Cardiovascular Dysfunction: Part of ACES Phase 3" (PI Sun)
- "Lung Cell Gene Transcription Responses to Diesel Particulate" (PI Veranth).

3. Platform presentation at the annual DOE Vehicle Technologies Program Annual Merit Review, Washington, D.C., June 2010: "Advanced Collaborative Emissions Study (ACES)."

4. Platform presentation at AK Fasern Stäube, Dortmund, Germany, September 2010: "Current Status of the Toxicology of Diesel Engine Exhaust – and the ACES Project."

5. Platform presentation at the Directions in Engine-Efficiency and Emissions Research (DEER) conference in Dearborn MI, September 2010: "Advanced Collaborative Emissions Study (ACES): Phase 3."

III. SOLID STATE ENERGY CONVERSION

III.1 High-Efficiency Thermoelectric Waste Energy Recovery System for Passenger Vehicle Applications

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NETL Project Manager: Carl Maronde

Subcontractors:

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- Ford Motor Company, Detroit, MI
- Faurecia, Troy, MI

Fiscal Year (FY) 2010 Objectives

The primary objectives of 2010 are to complete the preliminary design of a cylindrical thermoelectric generator (TEG) subsystem, build and test the prototype TEG on a test bench at BSST followed by integration and test with a BMW engine on a dynamometer test stand at the National Renewable Energy Laboratory (NREL). The design of the TEG subsystem was changed from a planar configuration in Phase 3 to a cylindrical configuration in Phase 4 to simplify manufacturing, improve thermal and electrical interfaces and to reduce overall system size, weight and volume at the vehicle level. Through computer modeling and hardware bench testing it is predicted that the TEG will enable a reduction in fuel consumption by as much as 5% in the near term and 10% (anticipated) with improved materials and system improvements. Objectives for 2010 also include:

- Improving TEG manufacturing readiness for commercialization.
- Integrating exhaust system inlet/outlet sections with the TEG, including a coaxial exhaust gas bypass valve.

FY 2010 Accomplishments

A prototype high-temperature (600^{0}C inlet gas temperature), cylindrical TEG was designed, built and tested at BSST. Due to problems associated with assembly processes and tooling, the TEG under-performed and was not suitable for dynamometer testing at NREL.

Following extensive test and characterization of performance, countermeasures were developed and are in the process of being implemented into the TEGs at the time of this report. Integration into BMW and Ford vehicle exhaust systems is scheduled for the first quarter of 2011.

The Phase 5 cylindrical TEG subsystem packaging design has been completed including inlet/outlet sections with a coaxial bypass valve in preparation for BMW X6 and Ford Fusion vehicle exhaust system installation.

The MATLAB®/Simulink® model was updated to predict performance in the cylindrical TEG form factor. The upgraded model was used to identify sources of performance deficiencies in the bench prototype cylindrical generator. The model was also used to identify design upgrades that provide countermeasures to the deficiencies.

Future Directions

In the first quarter 2011, BSST and partner Faurecia will integrate the high-temperature cylindrical TEG subsystem into BMW and Ford vehicle exhaust systems for test and evaluation.

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TEG Design Introduction and Approach

The initial prototype TEG design is shown in Figure 1. Exhaust gas enters from the left, passes through the TEG system, and exits to the right. In normal operation, the valve on the outlet side (right) is closed so that gas is prevented from passing through the central (bypass) region of the heat exchanger subassembly. At high flow rates passing all the exhaust gas through the heat exchanger would raise backpressure above the limit for optimal engine operation and expose the thermoelectric (TE) materials to potentially harmful temperatures. The valve allows excess exhaust gas flow to bypass the heat exchanger reducing backpressure to within allowable limits. The valve, designed and implemented by project partner, Faurecia, has proportional control so that the maximum available thermal power in the exhaust stream can be utilized. Similarly, the valve position is adjusted to prevent the TE system from exposure to the excess temperatures experienced during extreme driving

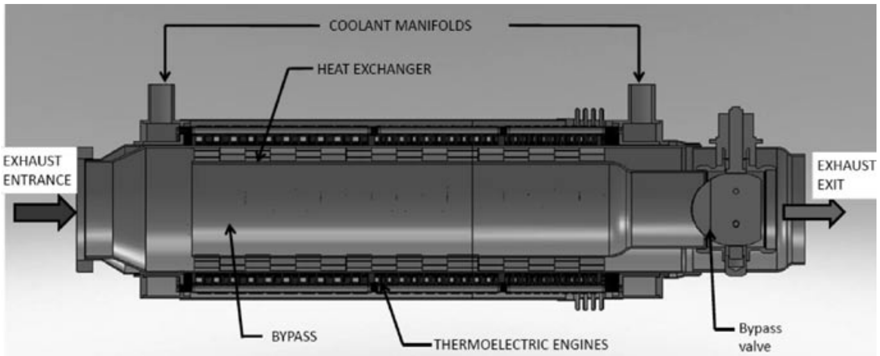

FIGURE 1. Cross-Sectional View of Waste Heat Recovery TEG

conditions. The thermal power collected by the heat exchanger fins is conducted through the cylinder wall to hot side shunts. The shunts are electrically isolated from the cylinder. Thermal power flows from the hot side shunts through the TE elements to the cold side shunts. Sleeve assemblies transfer waste thermal power to the coolant through tubes which are electrically isolated from the cold side shunts. The coolant enters a manifold at the right side, passes through an array of tubes and is collected at the left before exiting the system. Generally, the coolant is an ethylene glycol mixture and is part of the vehicle's engine coolant loop.

Electrical power generated by the assembly passes through terminals at the right and left sides. In the present design, each ring of TE engines are electrically in parallel and the rings themselves are electrically in series. Thus the assembly has a series-parallel arrangement, providing a high level of electrical redundancy. The nominal voltage current characteristics of the device are shown in Figure 2 as a function of cold inlet temperature.

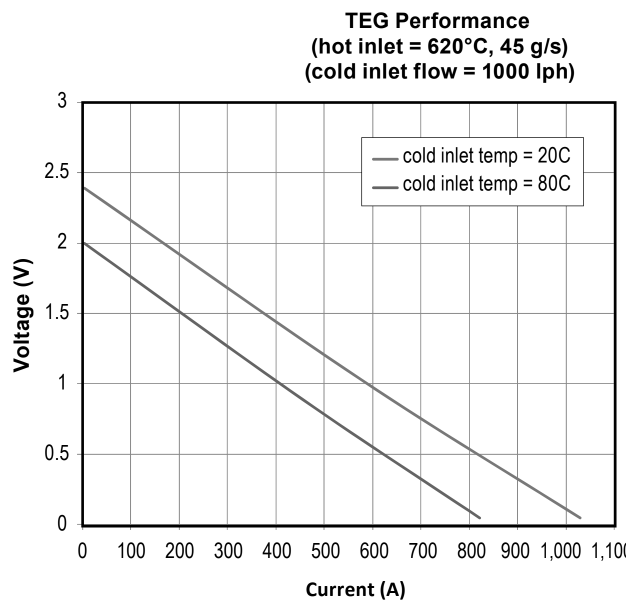

FIGURE 2. Current-Voltage Curve for a Nominal TEG Operating at a Hot Inlet Temperature of 620°C

Results

Thirty-six copper rings were fabricated and attached to a stainless steel tube as described previously. Thermoelectric engines were inserted at 15 positions around the circumference of the copper rings. Three TE engine designs were built corresponding to the average hot side temperature predicted in three zones at the nominal operating condition. Figure 3 shows three typical TE engines.

The high-temperature engines operate at the hottest (inlet) temperatures, the mid-temperature engines in the middle of the TEG and the low-temperature engines near the exhaust exit. Both the high- and mid-temperature engines are segmented with Half Heusler hot sides and Bi_2Te_3 (BT) low-temperature segments. The low-temperature engines are BT only. Output characteristics of each engine type are given in Figure 4.

FIGURE 3. From Left to Right, Typical High-, Medium- And Low-Temperature TE Engines

Each engine, consisting of two P- and two N-type TE elements, are connected in series in the geometry shown in Figure 5.

The TEG assembly was completed and installed in a hot air test bench at BSST's laboratory in Irwindale,

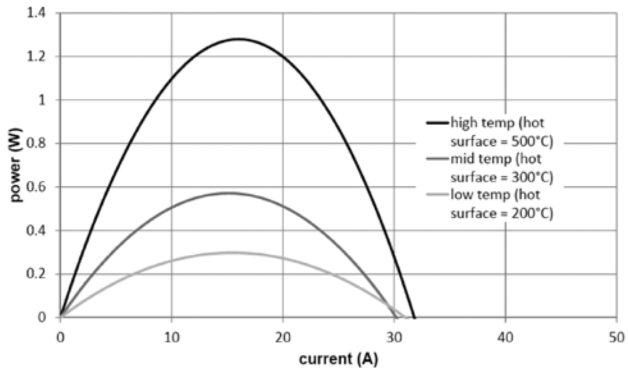

FIGURE 4. Performance of TEG High-, Mid- And Low-Temperature Engines at a Nominal Operating Condition

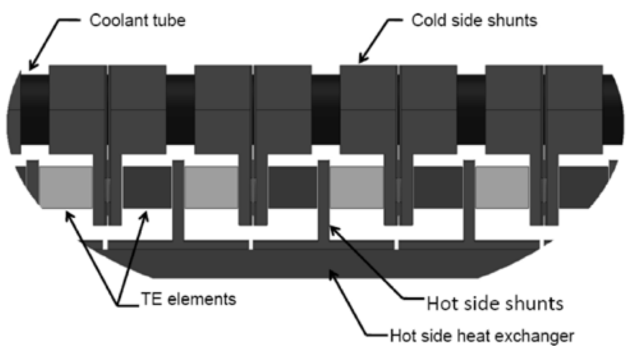

FIGURE 5. TE Engine General Arrangement — P and N TE Elements are Connected in Series Separated by Cold- and Hot-Side Shunts — the Current Produced Flows from Right to Left

CA. Many tests were performed to characterize the performance of the TEG and to validate the performance predictions made using MATLAB/Simulink. The performance of the completed TEG operated with gas inlet temperature = 586°C and water temperature = 25°C is shown in Figure 6. At this operating point, the model predicted a TEG power output of approximately 500 watts. As can be seen below, the TEG underperformed and produced a peak power of approximately 200 watts.

An analysis of the TEG performance was made to determine the loss mechanisms. Measurements of hot-side shunt temperature, cold-side shunt temperature and interfacial electrical resistance were taken to correlate with the inputs used as a basis for the model's predicted power. It was discovered that due to inadequate prototype tooling and assembly processes, the thermal and electrical interfaces did not perform to the level predicted in the model resulting in lower performance.

As a result of the underperformance, the dynamometer test at NREL was not completed, and a TEG redesign effort was undertaken to address the TEG interface issues. The performance of the full-scale, high-temperature TEG with countermeasures to the issues

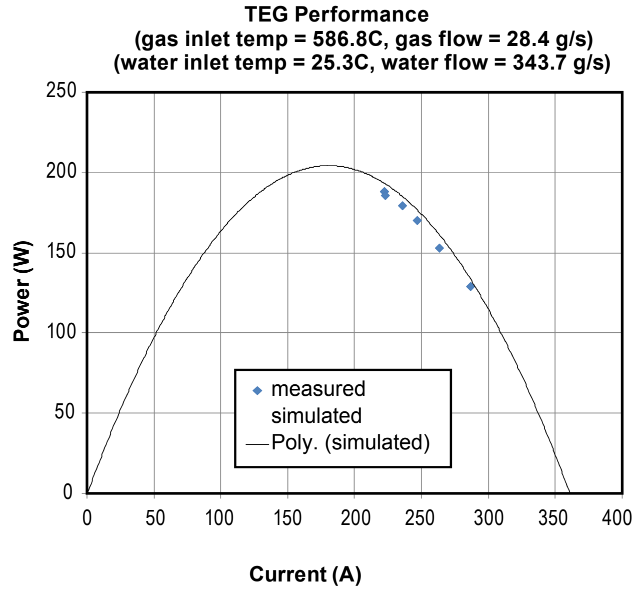

FIGURE 6. TEG Performance Results — Simulated Curve uses Adjusted Parameters to Match the Measured Results, and in doing so, Identify Opportunities for Performance Improvement

noted in the Phase 4 testing will be evaluated in Phase 5 before vehicle testing.

Conclusions

- A full-scale cylindrical TEG subsystem was designed, built and tested at BSST in 2010. The TEG underperformed due to inadequate assembly tooling and processes and subsequent testing on the engine dynamometer at NREL was not performed. The factors contributing to TEG underperformance were quantified, and countermeasures were designed and are in the process of being implemented. The evaluation of the full-scale TEG with countermeasures is scheduled for the first quarter of 2011 in bench testing at BSST followed by vehicle installation and evaluation by BMW and Ford.
- In preparation for the vehicle installations, Faurecia designed, built and tested prototype bypass valve assemblies and modified the existing design systems to accept the TEG subsystem.

FY 2010 Publications/Presentations

1. Lon E. Bell, John LaGrandeur, Douglas T. Crane, "Thermoelectrics Goes Automotive", IAV Conference, Berlin, Germany, 9–10 December 2010.

2. Crane, D.T., "An Introduction to System Level Steady-State and Transient Modeling and Optimization of High Power Density Thermoelectric Generator Devices Made of Segmented Thermoelectric Elements", International Thermoelectric Conference, Shanghai, China, July, 2010.

3. LaGrandeur, J.W., Crane, D.T. and Bell, L.E., "Status of a Cylindrical Waste Heat Power Generator for Vehicles Development Program ", Directions in Engine-Efficiency and Emissions Research DEER Conference, September 29, 2010, Dearborn, Michigan.

Special Recognitions & Awards/Patents Issued

1. 2010 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting R&D Award, presented to John LaGrandeur, BSST.

2. International Conference on Thermoelectrics, July, 2010, Shanghai Chine, Best Technical paper award to Dr. Douglas Crane, BSST.

III.2 Thermoelectric Conversion of Waste Heat to Electricity in an IC Engine Vehicle

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Subcontractors:
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- Tom Shih, Iowa State University, Ames, IA
- Todd Sheridan, Cummins Engines, Indianapolis, IN

Objectives

- Using a thermoelectric generator (TEG), provide a 10% improvement in fuel economy by converting waste heat to electricity used by an over-the-road (OTR) truck.
- Show how advanced thermoelectric (TE) materials can provide a cost-effective solution for improving fuel economy and idle reduction for an OTR truck.
- Determine steps necessary to demonstrate a 1 kW TEG:
  - Develop a TEG fabrication protocol for module and system demonstration using non-heritage, high-efficiency TE materials.
  - Determine heat exchanger requirements needed for building efficient TEGs.
  - Design and demonstrate power electronics for voltage boost and module fault by-pass in a TEG.

Fiscal Year (FY) 2010 Accomplishments

- Systems for material synthesis, powder processing, hot pressing, leg and skutterudite module fabrication are operational at MSU (ingot to couple with 95% utilization of material).
- Major issues that impede advanced TEG implementation identified.
- Couple bypass technology (CBT) developed and demonstrated – permits electrical series configuration for numerous modules and greatly improves generator reliability.
- Better material reliability and longevity enabled by functionally-graded material at hot side interfaces.

Future Directions

- Build a TEG using an advanced skutterudite material with aerogel insulated modules: output >100 Watts, voltage >14 V, modules will feature couple bypass technology.
- Scale up 100 Watt TEG to make a 1 kW generator for an OTR truck. First viable application may be as an electrical recovery system auxiliary power unit (ERS-APU) for trucks and buses (one and three year payoffs for 1 and 5 kW units, respectively).
- Develop stable hot-side interfaces which for skutterudite systems.
- Analyze electrical and thermal resistive losses to translate couple level performance into module level performance.
- Work to improve reproducibility and uniformity of fabricated legs by looking at different fabrication techniques.

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Introduction

As efforts to improve engine efficiency continue, one area that holds considerable potential for improvement is the exhaust system. As much as 40% of the energy generated by the engine can escape out the tailpipe as waste heat, creating a significant opportunity to reclaim energy. One way to accomplish this is to incorporate the use of thermoelectrics into the exhaust system. Thermoelectrics utilize the Seebeck effect to convert waste heat into electrical energy via a temperature gradient.

The cost savings potential for thermoelectrics is achieved by reducing brake specific fuel consumption by powering the vehicle electronics with the electrical energy generated by the TEGs, rather than with the battery, which must be recharged by the alternator. Previous cost estimate studies place the payback period for a 1 kW ERS-APU installed on a Class 8 OTR truck at approximately one year [1,2]. To be economically viable then, the ERS-APUs must exhibit uncompromising reliability and durability. However, the extreme environment in which TEGs operate poses a significant risk to the integrity of the thermoelectric legs. The focus of this phase of the project has been on improving the physical and electrical reliability of the TEGs over several thermal cycles, while continuing to make improvements to the TE material itself. Minimizing material failures while maintaining electrical power output is crucial to the success of cost-effectively implementing TE technology to improve overall engine efficiency.

Approach

To improve the physical and electrical reliability of the TEGs, improvement efforts have focused on two areas: minimizing breakages and mitigating failures.

Minimizing Breakages:

The interface between the skutterudite material and the metallization layers in the thermoelectric leg is prone to high levels of local stress during operation, due to unequal coefficients of thermal expansion. Analysis of couples that broke during testing revealed a high percentage of couples that failed at this interface. A functionally graded material (FGM) methodology was developed to provide a more gradual transition between the skutterudite material and the metallization layers. MSU has filed a patent disclosure on this technology.

Mitigating Failures:

As the modules are wired in series, a single failure jeopardizes the overall power of the entire generator. If just one couple in the series fails, it breaks the electric circuit for the other couples in the circuit, negating the power they produce. Higher voltage requirements necessitate connecting even more modules in series, which further increases the negative effect of a broken couple. To mitigate the detrimental effects of even a single broken couple, CBT was developed.

In addition, ongoing research of TE materials continues to provide improvements in both thermal and electrical properties. Improvements were made to the n-type skutterudite, which saw a figure of merit (ZT) increase of 25% to 1.2. Current efforts are also underway to make significant improvements to the ZT of the p-type skutterudite by homogenizing the p-type skutterudite and measuring the transport properties. If successful, up to a 25% gain over the current generator power output can be expected.

Results

To investigate the effect of FGM on local stress concentrations, a cuboid representative of the TE module leg geometry was modeled in Abaqus. Three variations of the TE leg were constructed: a leg with pure material layers; a leg with discrete layers comprised of 50% of each material, and a leg with a graded layer (Figure 1). While the first two variations have been fabricated here at MSU, the third variation is a theoretical concept, and is used to investigate the trends of using graded layering. Finite element analysis (FEA) was used to investigate the thermo-mechanical properties of these leg variations.

As is seen in Figure 2, the leg with a theoretical graded layer will experience smoother and lower stress

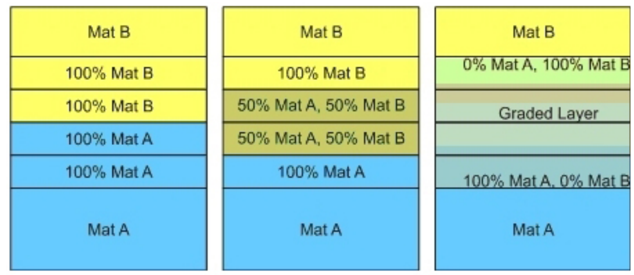

FIGURE 1. FGM Leg Variations

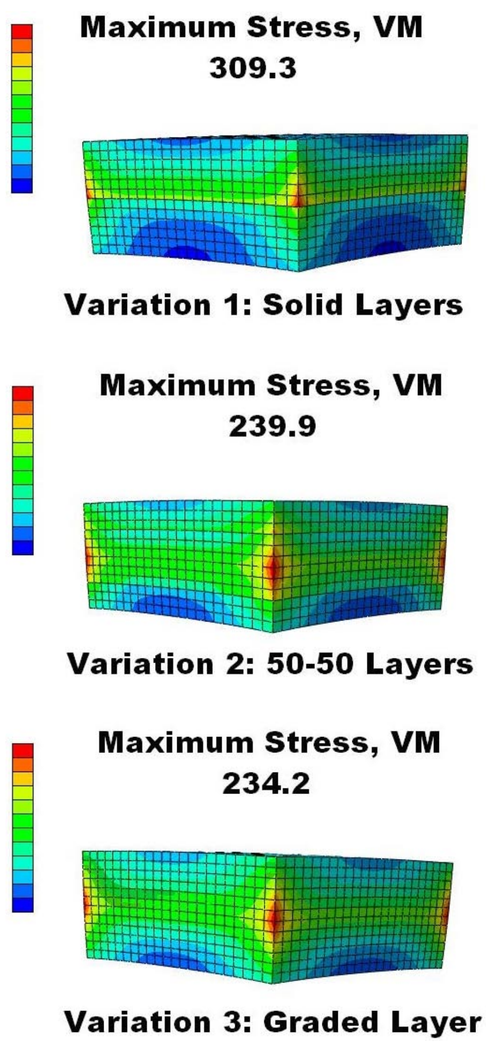

FIGURE 2. FEA Results: Von Mises (VM) Stress

concentrations across the interface. Similarly, the 50-50 layer leg variation exhibits a smoother stress profile across the interface and a maximum Von Mises stress concentration of, 22% less than the pure layer leg variation. Preliminary testing indicates an improvement in total leg success rates during operation from 79% to 98% as a result of FGM and other design improvements.

While FGM is important in reducing the number of couple failures, CBT mitigates the negative effect of a failed couple. CBT is an electronic solution that incorporates the use of metal oxide semiconductor field effect transistors (MOSFETs) to electrically bypass couple failure locations (Figure 3). When a particular MOSFET is activated, it short-circuits the corresponding thermoelectric couple, excluding it from the electric circuit. This enables the circuit to bypass a failed couple and utilize the power produced by the other non-broken couples in the series. MOSFET activation requires power, which is approximately equivalent to the power produced by a single TE couple. Thus, if one couple fails, the power produced by another couple is needed to activate the MOSFET to bypass the failed couple. Figure 4 shows the power required to activate the MOSFET versus the circuit current.

Under our current configuration, TE modules are constructed by assembling 10 TE couples wired in series. Utilizing CBT allows recovery of 80% of the original module power in the event of a single couple failure. In the same way, 60%, 40% and 20% of the original module power can be recovered in the event of a double, triple or quadruple couple failure, respectively. While any degree of couple failures is undesirable, using CBT to mitigate the effects of a failed couple is an important step in developing TE technology to the point of being economically feasible.

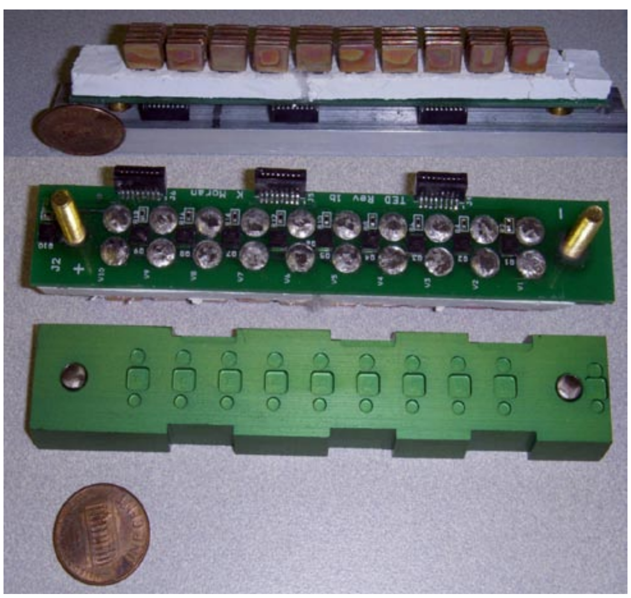

FIGURE 3. 10-Couple Module with CBT

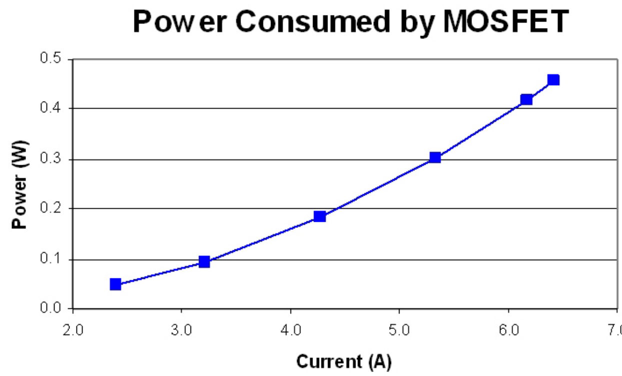

FIGURE 4. MOSFET Power

Conclusions

This year has seen significant improvements in the reliability of the TE couples, as well as improvements to the skutterudite material itself. Specific accomplishments include:

- Development of FGM methodology (and other design improvements) resulting in an 80% reduction of leg failures during operation.
- Development of CBT, capable of recovering up to 80% of electrical power otherwise lost on account of couple failure.
- Improvements made to N-type skutterudite, increased ZT by 25% to 1.2.

References

1. Estimate of Fuel Use by Idling Commercial Trucks, Paper No. 06-2567, 85th Annual Meeting of the Transportation Research Board, Washington, D.C., Jan. 22–26, 2006.

2. Roadmap and Technical White Papers, USDOE-EERE, 21CTP-0003, Dec. 06.

FY 2010 Publications/Presentations

1. Harold Schock, Jeff Sakamoto, Thierry Caillat, Jean-Pierre Fleurial, Ed Timm, Tom Shih, Ryan Maloney and Trevor Ruckle, "Thermoelectric Conversion of Waste Heat to Electricity in an IC Engine Powered Vehicle," Direction in Engine-Efficiency and Emissions Research (DEER) Conference (Detroit, MI; September 2010).

2. Harold Schock, Jeff Sakamoto, Thierry Caillat, Jean-Pierre Fleurial, Ed Timm, Tom Shih, Ryan Maloney and Trevor Ruckle, "Thermoelectric Conversion of Waste Heat to Electricity in an IC Engine Powered Vehicle," DOE Merit Review (Washington, D.C.; June 2010).

3. Trevor Ruckle, Jeff Sakamoto, Harold Schock, Thierry Caillat, Jean-Pierre Fleurial, Ed Timm, Tom Shih and Ryan Maloney, "Thermoelectric Conversion of Waste Heat to Electricity in an IC Engine Powered Vehicle," Global Powertrain Congress (Troy, MI; November 2010).

4. Jeff Sakamoto, Harold Schock, Thierry Caillat, Jean-Pierre Fleurial, Ed Timm, Tom Shih, Ryan Maloney and Trevor Ruckle, "Thermoelectric Conversion of Waste Heat to Electricity in an IC Engine Powered Vehicle," Materials Research Society Meeting (San Francisco, CA; April 2010).

III.3 Improving Energy Efficiency by Developing Components for Distributed Cooling and Heating Based on Thermal Comfort Modeling

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- University of California, Berkeley (UCB), CA
- University of Nevada, Las Vegas (UNLV), NV

Objectives

- Identify distributed cooling and heating strategies that can efficiently augment or replace a vehicle's central heating, ventilation and cooling (HVAC) system by delivering localized cooling/heating of key human body segments that strongly influence an occupant's perceived thermal comfort.
- Develop local cooling/heating HVAC components that utilize thermoelectric (TE) technology to implement these energy-saving strategies.
- Evaluate the effectiveness of distributed cooling and heating strategies for providing thermal comfort to vehicle occupants.
- Prioritize the development of individual local cooling/heating HVAC components and optimal combinations of these strategies based on their impact to human comfort and practical considerations about their implementation within a vehicle.
- Develop computer-aided engineering (CAE) tools that support the inclusion of local cooling/heating HVAC components in future energy-efficient vehicle designs.
- Investigate new TE material systems for waste heat recovery (parallel effort with the "Develop Thermoelectric Technology for Automotive Waste Heat Recovery" project).

Fiscal Year (FY) 2010 Accomplishments

- A set of distributed cooling and heating strategies were identified that can strongly influence an occupant's perceived thermal comfort.
- Computational fluid dynamics (CFD) analysis was used to model and refine the local cooling/heating HVAC components in a computer-aided design version of the target vehicle.
- Test procedures and simulation systems for local cooling/heating HVAC components were developed for mock-up vehicle testing at the UCB and mule vehicle testing at Delphi.
- Simulated local cooling/heating HVAC components were extensively evaluated by human test subjects and a thermal mannequin during mock-up vehicle testing in the UCB environmental test chamber and during mule vehicle testing in the Delphi climatic wind tunnel.
- Initial revisions for localized cooling/heating were made to the Thermal Comfort model and the CAE tool, and resulting simulations had good correlation with actual test results.
- Research on new TE materials with improved efficiency was conducted.

Future Directions

- Further evaluate the effectiveness of distributed cooling and heating strategies for providing energy-efficient thermal comfort to vehicle occupants.
- Identify the set of distributed cooling and heating strategies that will be developed into prototype HVAC components for localized cooling/heating.
- Develop initial prototype local HVAC components that utilize TE technology to deliver energy savings.
- Continue to develop CAE tools that support the inclusion of local cooling/heating HVAC components in future energy-efficient vehicle designs.
- Continue to investigate new and improved TE materials for automotive waste heat recovery.

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Introduction

The primary project objective is to reduce the fuel used for passenger thermal comfort by 30% through the application of TE technology to provide localized cooling and heating of vehicle occupants. The project will revise UCB's existing Thermal Comfort model to quantify the impact from locally cooling and heating specific body segments. The updated Thermal Comfort model will be incorporated into computer-aided engineering tools that will accommodate the design of local cooling/heating HVAC components into future energy-efficient vehicles. In addition, a secondary project objective is to improve the efficiency of TE generators for directly converting engine waste heat to electricity by developing new and improved TE materials.

Approach

The main goal of this project is to develop distributed cooling and heating strategies and components that efficiently supplement the central HVAC system and then to integrate and test them in a demonstration vehicle. This aspect of our three-year project is divided into four phases. During the first 18 months, only the first project phase is active with its primary objective to develop a Thermal Comfort model of human responses to localized cooling/heating of various body segments. UCB uses regression analyses of the overall whole body sensation, the local body sensations, and the comfort votes from the human subject tests to arrive at the overall sensation and comfort models (see Figure 1). During the second 18 months, the other project phases will develop the most effective strategies into prototype local HVAC components, and then integrate and test them on a demonstration vehicle.

For the first project phase, work was divided among four major activities: (1) identify potential locations for distributed HVAC components, (2) perform testing of the automotive mock-up in the UCB environmental test chamber, (3) perform testing of the mule vehicle in the Delphi climatic wind tunnel, and (4) update the UCB Thermal Comfort model and the GM Virtual Thermal Comfort Engineering CAE tool. The team used knowledge of human physiology to brainstorm distributed cooling and heating strategies with high potential for positively influencing a person's perception of thermal comfort. CFD analyses of the selected mule vehicle, a Cadillac SRX crossover, were used to set a range of operating parameters for these cooling/heating locations. In their environmental test chamber, UCB constructed a vehicle mock-up that simulated the local cooling/heating HVAC components. Human test subjects and a thermal mannequin entered the mock-up vehicle to provide subjective and objective assessments of these strategies (see Figure 2). The UCB test results and further CFD analyses were used to set a refined range of operating parameters for localized cooling/heating during mule vehicle testing. Delphi designed and constructed systems to simulate the local cooling/heating HVAC components (see Figure 3); these systems and extensive instrumentation were installed in the mule vehicle. Following a procedure derived from the UCB test protocol, human test subjects and the thermal mannequin entered the mule vehicle to further evaluate the distributed cooling and heating strategies in the Delphi climatic wind tunnel (see Figure 4). In parallel with this work at Delphi, GM incorporated a revised Thermal Comfort model in its Virtual Thermal Comfort Engineering CAE tool (see Figure 5). This tool was used to simulate the testing performed at UCB, and the simulated results were compared to the actual test results.

For the secondary project objective, the basic physics and chemistry of new and breakthrough TE materials were studied at GM. This fundamental

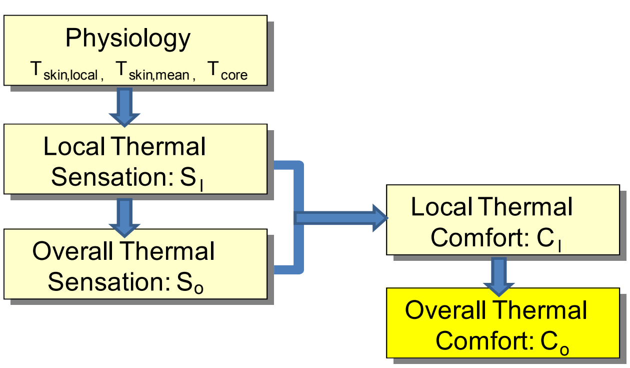

FIGURE 1. Flow Chart Showing How the UCB Thermal Comfort Model is Developed

FIGURE 2. Thermal Mannequin Inside the Mock-Up Vehicle in the UCB Environmental Test Chamber

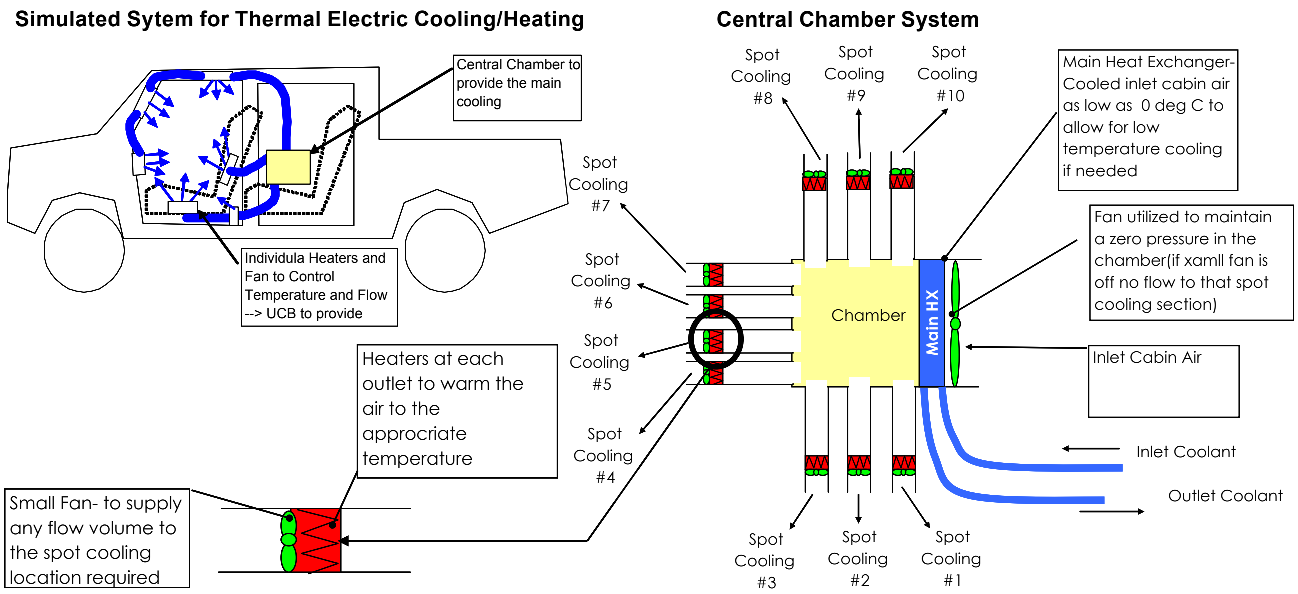

FIGURE 3. Design of the TE Device Simulation System at Delphi

FIGURE 4. Instrumented Mule Vehicle in the Delphi Climatic Wind Tunnel

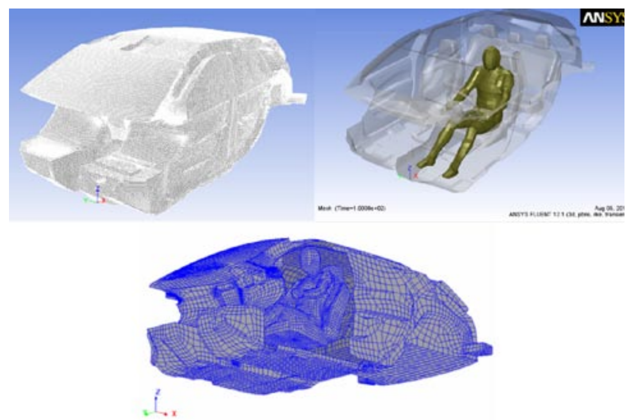

FIGURE 5. GM Passenger Compartment Model used in the Simulation of Thermal Comfort

research of new materials was assisted by theoretical work performed at UNLV.

Results

The project team made significant progress towards successfully achieving the overall project objectives. A set of distributed cooling and heating strategies were identified. These strategies were translated into local cooling/heating HVAC components for our target application, and their operating parameters were developed and refined. Computer-controlled systems that simulate local cooling/heating HVAC components were developed at UCB for the mock-up vehicle and at Delphi for the mule vehicle. Human test subjects and a thermal mannequin provided extensive assessments of simulated local cooling/heating HVAC components during mock-up vehicle testing in the UCB environmental test chamber and during mule vehicle testing in the Delphi climatic wind tunnel. Preliminary test results indicated that localized cooling/heating effectively influences an occupant's perceived thermal comfort and that certain combinations of these strategies work well together to positively affect human comfort. Clear preferences regarding the operating parameters of the local cooling/heating HVAC components have emerged from the collected human subject test data. These preferences will guide further refinement of the operating parameters and the selection of a final set of strategies to be implemented in prototype hardware. Initial revisions for localized cooling/heating were made to the Thermal Comfort model and the CAE tool, and the resulting simulations had good correlation with actual test results. The analysis also demonstrated that localized cooling strategies are capable of delivering sufficient overall thermal comfort at potentially lower air conditioning energy consumption.

We continue to explore new TE materials and to optimize existing materials at GM. This work includes collaboration with UNLV, on fundamental theoretical research involving new computational approaches for determining lattice thermal conductivity, phonon densities of states, nano-cluster doping, and electronic band structure of doped skutterudites. Our aim is to investigate and understand the very low thermal conductivities and the power factor enhancements seen experimentally for some TE materials.

Conclusions

During this initial year of the project, the project team made significant progress towards successfully achieving the overall project objectives. Based on knowledge about how the temperature sensations of various body parts influence a person's perception of thermal comfort, we identified distributed cooling and heating strategies with high potential to augment or replace a vehicle's central HVAC system. Simulated implementations of these strategies were evaluated and refined during mock-up vehicle testing in the UCB environmental test chamber and during mule vehicle testing in the Delphi climatic wind tunnel. Preliminary human subject results and CFD analyses indicate that these strategies can positively affect thermal comfort and reduce energy consumption. Our continued fundamental material research aims to further improve TE material properties and to further explore new materials.

FY 2010 Publications/Presentations

1. Meisner, G.P.; "Improving Energy Efficiency by Developing Components for Distributed Cooling and Heating Based on Thermal Comfort Modeling," Vehicle Technologies Program Annual Merit Review Meeting, U.S. Department of Energy, Washington, D.C., June 2010.

2. Meisner, G.P.; "Develop Thermoelectric Technology for Automotive Waste Heat Recovery," Vehicle Technologies Program Annual Merit Review Meeting, U.S. Department of Energy, Washington, D.C., June 2010.

3. Meisner, G.P.; "Thermoelectric Generator Development for Automotive Waste Heat Recovery," 16th Directions in Engine Efficiency & Emissions Research (DEER) Conference, Detroit, MI, September 2010.

4. Yang, J.; "Advanced Materials for Future Propulsion". 2010 Frontiers of Renewable Energy Sciences & Technologies Conference, Harvard University, Cambridge, MA, September 2010 (Invited).

Special Recognitions & Awards/Patents Issued

1. "Thermoelectric Generators for Waste Heat Recovery from Engine Exhaust," Meisner, G. P.; Yang, J.; P012262, U.S. Patent Application filed September 2010.

III.4 Ford Thermoelectric HVAC Project

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- BSST LLC, Irwindale, CA
- National Renewable Energy Laboratory, Golden, CO
- Ohio State University, Columbus, OH
- Amerigon Inc., Northville, MI
- ZT::Plus, Azusa, CA

Objectives

- Identify technical and business approaches to accelerate deployment of automotive thermoelectric (TE) heating, ventilation and air conditioning (HVAC) technology.
- Demonstrate TE HVAC device coefficient of performance (COP) of 1.3 in cooling and 2.3 in heating.
- Demonstrate reduction in air conditioning (AC) compressor power consumption of 33%.
- Develop higher efficiency TE materials for heating and cooling.
- Deliver a vehicle with a zonal TE HVAC system to demonstrate the ability to meet customer comfort needs at reduced power consumption levels.

Fiscal Year (FY) 2010 Accomplishments

- Completed development of metrics to be used for measuring and demonstrating technical performance against objectives in order to measure COP and HVAC system efficiency.
- Established thermal comfort and vehicle performance criteria and targets through analytical computer-aided engineering (CAE) and baseline vehicle testing in a climate wind tunnel under representative operating conditions.
- Evaluated and built several TE heat pump designs to study manufacturing and performance trade-offs.
- Discovered that Sn is a resonant level in Bi_2Te_3 and made progress in showing performance enhancements in commercial p-type alloys.

Future Directions

- Analyze performance HVAC system architectures to be evaluated using the empirical and analytical tools developed in the previous phase.
- Validate performance of a subscale prototype liquid-to-air TE HVAC subsystem using transient modeling to provide directional performance of devices that will be integrated into the full vehicle demonstration.
- Test TE device performance in a calorimeter to determine COP in heating and cooling.
- Model the estimated energy reduction benefit for a demonstration vehicle equipped with a TE HVAC system.
- Conduct research on n-type TE materials to determine a resonant level or other mechanism to boost power factor or reduce lattice thermal conductivity.
- Develop system controls that allow for achieving a 33% reduction in AC compressor power consumption using environmental weighting factors.

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Introduction

Current light-duty vehicles provide passenger thermal comfort primarily through the use of a centralized HVAC unit that distributes conditioned air to vent locations throughout the vehicle. Powertrain energy is used to generate hot or cold working fluids that are subsequently used to condition the entire cabin and certain surrounding structures. Because of this, the majority of the power expended by today's automotive HVAC systems does not directly contribute to occupant thermal comfort. This is not an overwhelming issue in today's vehicle design criteria, but as pressure builds to improve powertrain and vehicle efficiency, the energy available to provide occupant comfort will decrease. As an example, AC systems in vehicles today are sized to enable rapid cooling of the cabin under the most extreme environmental conditions. This means that under more moderate operating conditions, the capacity of the system is much larger than necessary, which reduces efficiency.

Approach

A phased approach is being used to quantify anticipated benefits through detailed design and modeling prior to building and testing subsystems. The first phase of the project has progressed through the initiation of a system architecture study, modeling to predict fuel efficiency, and occupant thermal comfort modeling for baseline and distributed system options. Design requirements have been developed to provide a starting point for detailed hardware design and build activities. Research efforts into more efficient TE materials and the design of liquid-to-air TE devices for distributed heating and cooling were started in the first phase of the project, and will continue to be refined and optimized in subsequent phases. This early design work and establishment of test metrics and methods is critical to set guidelines which the team will use in future phases of the project to develop, design, build, and validate the performance of the TE HVAC system.

In the second phase, key subsystems including TE modules, the means for distribution of hot and cold working fluids, power management, and system controls will be independently modeled, designed, built, and tested. System performance predictions will be updated according to subsystem test results. Engineering and systems specifications will be developed to guide hardware design. Vehicle package studies will be performed to identify long-lead vehicle modifications required. The team will also initiate a business cost analysis to predict commercialization pathways. In the third phase of the project, initial system characterization will be conducted, and hardware prototypes for integration into the target vehicle will be designed and fabricated. The vehicle-intent hardware prototypes will be tested and results compared to initial prototypes to assist predictions of in-vehicle performance. Advanced materials will begin to be selected for development and incorporation into early next-generation prototype devices. The subsystem level hardware will be evaluated to validate model-based comfort predictions. The team will finalize the business cost analyses. In the final phase, all of the subsystem hardware fabrication will be completed and the subsystems will be incorporated into the test vehicle. A formal system test, based on the developed test conditions, will be performed to quantify system benefits and performance compared to the baseline system. Technical results, fuel savings, emission reductions, other potential benefits, and commercialization potential and planning will be analyzed and a demonstration vehicle delivered to DOE for further evaluation.

Results

Development of Test Protocols and Performance Metrics

Key technical criteria were established, including vehicle availability, computer-aided design (CAD) data, baseline test data, ability to package thermoelectric devices, and ability to supply power and controls to the system. The vehicle selected for this project was a 2010 model-year Ford Fusion hybrid electric vehicle (HEV). Operating condition metrics involved analysis of regional weather data from the U.S. Weather Service, population trends from the U.S. Census Bureau, and driving patterns from the Oak Ridge National Laboratory National Highway Transportation Survey database. These data were combined to determine when and how average occupants use their vehicles. This information was concatenated and used to establish the conditions under which the vehicle will be evaluated. Basic operating requirements, environmental operating conditions, and comfort metrics were established early in the first quarter of 2010. A summary of the conditions established is shown in Table 1.

HVAC and Thermal Comfort Modeling

Vehicle CAD model data was used to develop a parametric CAE model used in vehicle cabin modeling work. Initial vehicle cabin CAE models were run to validate cabin boundary conditions. Sample results are shown in Figure 1. The AC pull-down data was used to establish results of an Occupant Thermal model. The National Renewable Energy Laboratory (NREL) task of assessing the integrated CAE/Occupant

TABLE 1. Test conditions and energy weighting factors used to determine overall climate system performance against project objectives.

	Hot Test 1	Hot Test 2	Hot Test 3	Cold Test 3	Cold Test 2	Cold Test 1
Ambient Conditions	43°C (104°F) 40% RH 1,000 W/m^2 Solar	32°C (90°F) 70% RH 850 W/m^2 Solar	28°C (82°F) 70% RH 750 W/m^2 Solar	5°C (41°F) No Solar	-5°C (23°F) No Solar	-18°C (0°F) No Solar
Energy Consumption Weighting Factor	6%	13%	31%	33%	11%	6%
Comfort Target	5 Comfortable	6 Slightly Warm	5 Comfortable	5 Comfortable	4 Slightly Cool	5 Comfortable

RH - relative humidity

Comfort tools was initiated, is being closely coordinated between the CAE teams and is focused on providing a recommendation for best practices in performing a fully-coupled computational fluid dynamics/radiation/thermal comfort CAE analysis which will ultimately be correlated to vehicle-level and subjective testing in the fourth quarter of 2010 and the first quarter of 2011.

Vehicle-level requirements for the project were developed during the second quarter of 2010 and were used in establishing extensive parametric CAE models of the test vehicle interior. These models were used to validate the accuracy of the test results obtained during vehicle wind tunnel testing and to feed data to the NREL-led task for evaluating and developing advanced thermal comfort models. Heater and AC performance modeling carried out in 2Q10 were re-run using test data from the baseline vehicle. A representative result is shown in Figure 2. Model refinement continues to be conducted and extended to other aspects of the vehicle and HVAC system, such as adding the use of one-dimensional AC and heater simulation to drive register outlet conditions. These additions improve the fidelity and accuracy of the models at additional locations critical to developing good occupant thermal comfort predictive models.

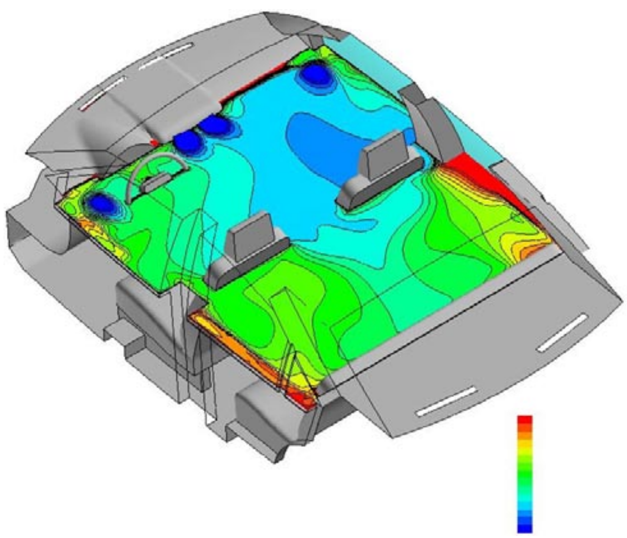

FIGURE 1. Parametric model of vehicle cabin interior indicating air temperature at breath level.

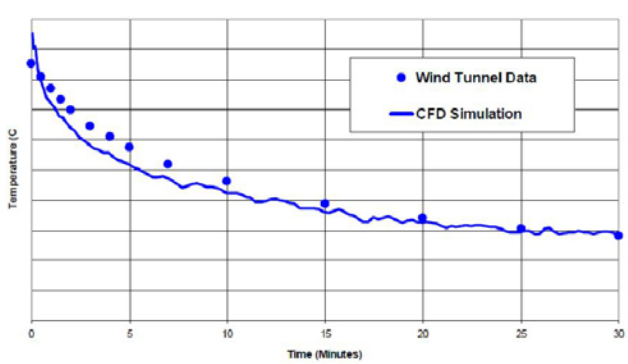

FIGURE 2. Correlation of wind tunnel test data and computational fluid dynamics simulation results for breath level temperatures during an AC pull-down.

TE Heat Pump Development

Engineering analysis of a concept TE device and extensive modeling the performance of a TE device in a transient thermal environment were conducted throughout the first project phase. Several device configurations were constructed using various build techniques to evaluate performance, manufacturability, and durability. An example of one prototype device is shown in Figure 3. Extensive work was done with solder and solder processes to enable the manufacturing of high capacity TE engines. These developments will be used to advance the performance of the next generation devices. A flow calorimeter bench to characterize device performance underwent final calibration in the third quarter of 2010 and testing is scheduled to begin in the fourth quarter of 2010 in order to characterize the performance of the TE concept device and validate with the transient model. A trade-study on commercially available TE pellets was conducted and determined that no commercial materials exist that are substantial improvements over what is currently in production.

TE Materials Research

Scoping of the advanced TE materials research at Ohio State University, with support from ZT::Plus, was initiated in the fourth quarter of 2009 and initiated in the first quarter of 2010. Advanced TE materials work was continued in the third quarter of 2010. The work focused on developing high-performance p-type materials. Seebeck measurements conducted in this work are shown in the Pisarenko plot shown in Figure 4,

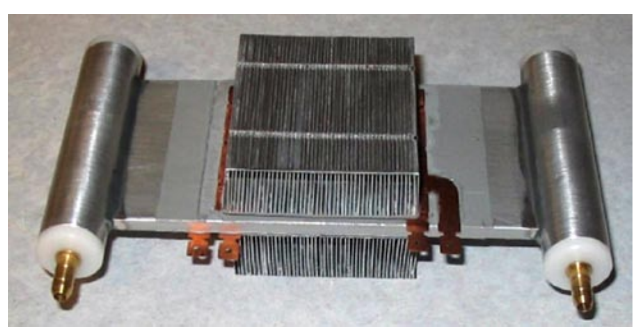

FIGURE 3. Prototype liquid-to-air TE heat pump design used for validation testing of various manufacturing methods.

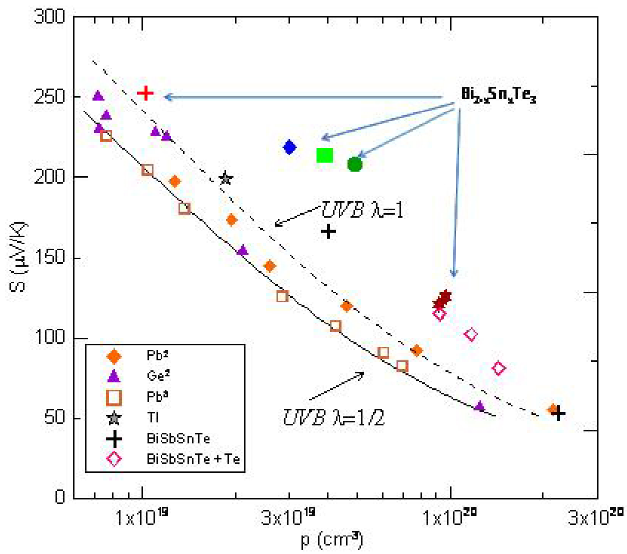

FIGURE 4. Pisarenko plot for Bismuth Telluride showing the increase in Seebeck coefficient when Sn is added.

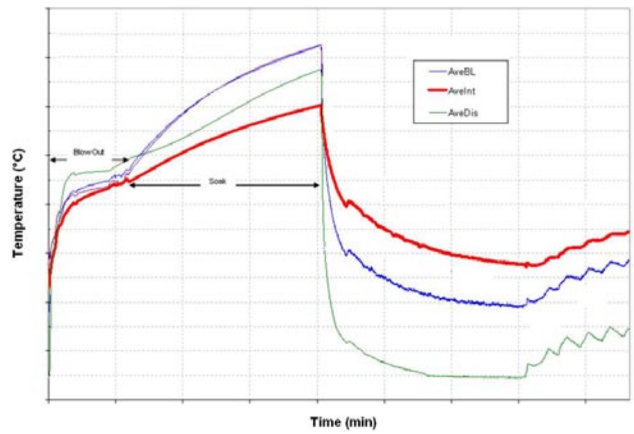

FIGURE 5. Wind tunnel test data showing cabin soak temperatures for the discharge air, front seat breath level, and average interior temperature. Ripples in temperature at the end of the test are due to engine cycling during the idle portion of the test.

and indicate Sn as a resonant level. Focus on Sn as a resonant level in the commercial Bi_2Te_3 continues to be the focus for this effort for p-type materials. Other doping elements will be considered for n-type material development in the next project phase.

Vehicle Testing and Architecture Development

A test vehicle was instrumented in the second quarter of 2010 and a substantial amount of the baseline vehicle testing was performed in the third quarter of 2010. Tests at 43°C, 32°C, and 28°C were performed in a wind tunnel that was configured to include solar lamps. Test results typical of this test sequence are shown in Figure 5. The nozzle-flow evaluation chamber, constructed in the second quarter of 2010 at the Visteon facility began to be used for evaluating various test configurations. The chamber has allowed a highly modular controlled environment to be used in developing correlation between trained climate systems subject jurists, thermal mannequins, and CAE thermal comfort tools.

Development of a vehicle systems-level model was substantially completed in the third quarter of 2010 for the baseline case (current-production 2010 Fusion HEV). Baseline vehicle climate control energy loads and impacts on fuel consumption are being developed, in part, using data from baseline wind tunnel testing. The testing is anticipated be completed early in the fourth quarter of 2010 and final modeling assessments can be run once the data is obtained and analyzed. HVAC power profiles from proposed architectures will be run once suitable system architectures are finalized for analysis.

Conclusions

Substantial progress has been made in establishing the baseline vehicle HVAC system performance and in developing appropriate test conditions and performance metrics to be used in assessing progress against the project objectives. Early TE heat pump prototypes have been developed to investigate design trade-offs that impact performance and manufacturability. A unique test system has been designed and built to evaluate system architecture configurations. This early work lays the critical groundwork necessary to move into the next phase of the project where specific architecture and hardware specifications will be established.

FY 2010 Publications/Presentations

1. C.W. Maranville, et al., "Development of a High-Efficiency Zonal Thermoelectric HVAC System for Automotive Applications", 2009 DEER Conference, Dearborn, MI, August 5, 2009.

2. C.W. Maranville, "Thermoelectric Opportunities in Light-Duty Vehicles", 2009 Thermoelectric Applications Workshop, San Diego, CA, September 30, 2009.

3. C.W. Maranville, "Thermoelectric Opportunities in Light-Duty Vehicles", Global Powertrain Congress, Troy, MI, November 4, 2009.

4. C.W. Maranville, "Thermoelectric HVAC & Waste Heat Recovery: Project Update", Presented at USCAR ACEC working group meeting, Southfield, MI, March 10, 2010.

5. C.W. Maranville, "Thermoelectric HVAC for Light Duty Vehicles", Presented at DOE Annual Merit Review, Washington, DC, June 11, 2010.

6. C.W. Maranville, et al., "Progress towards Development of a High-Efficiency Zonal Thermoelectric HVAC System for Automotive Applications", Proceedings of the 2010 DEER Conference, Detroit, MI, September 29, 2010.

III.5 Advanced Thermoelectric Technology for Automotive Waste Heat Recovery

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- University of Nevada, Las Vegas, NV

Objectives

- Construct and assemble thermoelectric (TE) generator heat exchanger subassemblies.
- Acquire and install electronics and control systems in test vehicle.
- Install and test a prototype TE generator (TEG) in our test vehicle.
- Fabricate skutterudite-based TE modules.
- Investigate new TE material systems.

Fiscal Year (FY) 2010 Accomplishments

- Completed fabrication of heat exchanger and TEG subassemblies.
- Completed installation of electronics for integrating the TEG output power into the vehicle electrical system.
- Assembled a prototype TEG and installed it on a Chevrolet Suburban test vehicle.
- Collected preliminary data to verify proper functioning of subassemblies and components (e.g., the bypass valve for over temperature/back pressure protection, the TE modules for electrical output, and the direct current (dc)/dc converter for power conditioning and integration).
- Investigated and developed metal layer contacts for electrical connections to the skutterudite components of the TE modules.
- Fabricated n- and p-type TE elements with new diffusion barrier processing parameters.
- Designed tooling for fabricating ceramic headers for the thermoelectric modules.
- Determined optimized material composition and processing parameters for fabrication of skutterudite materials for use in TE modules.
- Produced a large number of n- and p-type skutterudite ingots for TE module fabrication.
- Conducted neutron scattering experiments on PbTe and Bi_2Te_3 samples to assess their usefulness for measuring residual and thermal stresses in TE modules.
- Combined computational and experimental studies of thermodynamic and transport properties for several chalogenide-based and Zn-Sb-based TE materials to better understand their very low thermal conductivities and superior TE performance.
- Conducted research on new TE materials with improved efficiency.

Future Directions

- Complete vehicle testing of the preliminary prototype TEG with Bi-Te-based modules.
- Complete fabrication skutterudite modules and validate their performance.
- Assemble, install, and integrate a skutterudite-based prototype TEG into the test vehicle.
- Collect and analyze performance data for the TEG in the test vehicle.
- Investigate new TE materials for automotive waste heat recovery.

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Introduction

During the past year, we have focused on fabrication, assembly, and implementation of a working TEG for automotive waste heat recovery. Our specific engineering design has now been implemented as a prototype TEG and is installed on a production Chevrolet Suburban test vehicle. Vehicle modification and integration is complete and includes adapting the exhaust system for the TEG and installing the power electronics and control systems for interfacing the TEG output to the vehicle electrical system. Vehicle drive testing, data collection, and analysis are underway and provide quantitative results on the actual performance of our prototype TE automotive waste heat recovery system. The development and fabrication of new TE modules to operate at higher temperature has focused on skutterudites. Successful fabrication of working modules requires good TE material properties while achieving material compatibility with electrical and thermal contacts within the modules, and requires thermal and chemical stability in the harsh environment of the vehicle exhaust system. A large quantity of both n- and p-type skutterudite has been synthesized for production of modules that will be used for a second, higher temperature prototype TEG. Our continued fundamental material research aims to further improve TE material properties and mechanical strength, and to further explore new materials.

Approach

The scope of this project has ranged from the basic physics and chemistry of new and breakthrough TE materials, to the modeling and design of a waste heat recovery device for automotive applications, and finally to the engineering, assembly, integration, and testing of a working TEG. Existing and newly developed TE materials were carefully studied. Experimental results for material properties were validated by Oak Ridge National Laboratory to help avoid any potential pitfalls associated with material stability and performance at the elevated and cyclical temperatures typical of an automotive exhaust system. Fundamental research on these and other new materials was assisted by the theoretical work at the University of Nevada, Las Vegas. Electron microscopy and mechanical property measurements have been conducted at Oak Ridge National Laboratory on the TE materials selected for this project in order to identify strength-limiting flaws and provide critical insight for improving the material composition and processing procedures to achieve better mechanical performance. These results were incorporated into the TEG design and optimization. TE module development and fabrication by Marlow has focused on compatibility, durability, and robustness of the mechanical, thermal, and electrical contacts and connections. Vehicle level electrical and thermal management algorithms have been developed to optimize potential fuel economy gains. The design and modeling engineers worked closely with vehicle engineers to ensure that accurate vehicle level information was used for developing subsystem models and generator design, and this enabled the actual engineering and fabrication of the TEG. Throughout this project, we have incorporated costs associated with materials, modules, subsystems, and integration into the selection criteria for all of the aspects of the final generator design and implementation. The cost per watt of electrical power generated was used as one of the primary metrics for design optimization. We use this approach not only as a guide for balancing technology options, but also for providing consumer benefits.

Results

General Motors has now implemented its TEG design in the form of an assembled and integrated prototype unit incorporated into the exhaust system of the Chevy Suburban test vehicle, and Figure 1 is a view from underneath the vehicle. In the fabrication and assembly, special attention was paid to ensure that the generator parts were machinable and could be assembled, and that the TEG was mechanically compatible with automotive components and vehicle systems. Preliminary tests indicate that the bypass valve and controller are working correctly to ensure that the TEG remains within required temperature and backpressure limits. Improvements in the thermomechanical design of the generator are continuing. A new heat exchanger design incorporates skutterudite modules and will allow operation at higher temperatures. A new exterior case was designed and installed to give more room inside the TEG to accommodate the wiring of the TE modules into series and parallel strings, and for connecting the module strings to the output electrical wires.

For skutterudite module development, we continued to apply a metal diffusion barrier to p-type material using our previously developed die process. In order to improve the yield on n-type material we developed a new die process that allows for the higher pressing temperatures required for bonding metal layers to n-type skutterudites. Synthesis of a large quantity of n- and p-type skutterudite material was completed at

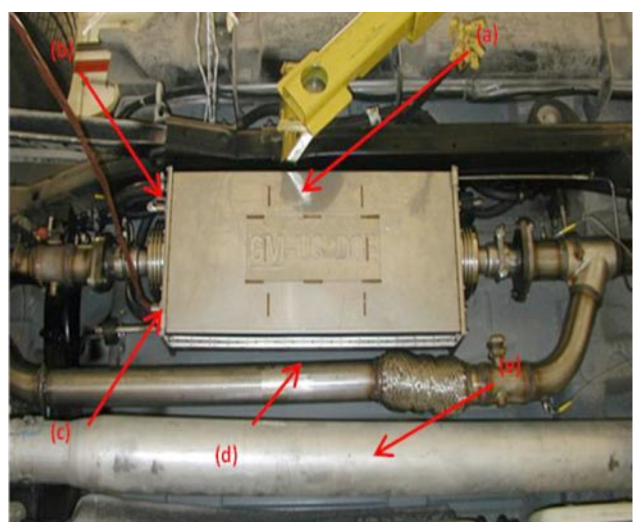

FIGURE 1. The prototype TEG (a) installed on the test vehicle. Feed-through connections for TE power (b) and thermocouples (c) are on the downstream end of the TEG, and exhaust gas bypass pipe (d) prevents over heating of the TE modules. The grey cylinder (e) is the drive shaft.

General Motors Global R&D. Figure 2 shows a set of completed skutterudite billets ready to be sliced up for module fabrication. Wafers have been sliced from the billets and analyzed to confirm that no unacceptable defects were present, and transport properties were tested to confirm acceptable TE performance. These skutterudite materials are being processed into finished modules. In addition to excellent TE performance, TE materials require high fracture strength and resistance to thermal shock in order to meet durability requirements for automotive waste heat recovery applications. Finite element analysis, Figure 3, and fracture strength testing results, Figure 4, indicate that thermal tension stresses are on the order of 130 MPa at $\Delta T = 500°C$, and that skutterudites can withstand tensile stresses of over 140 MPa.

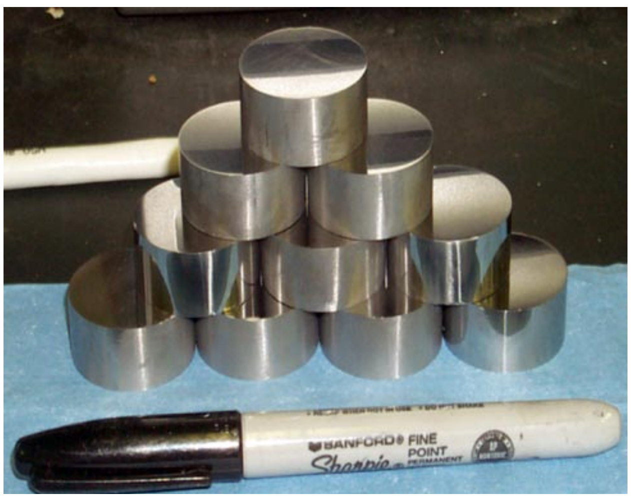

FIGURE 2. Billets of skutterudite material ready to be sliced into parts for TE module fabrication.

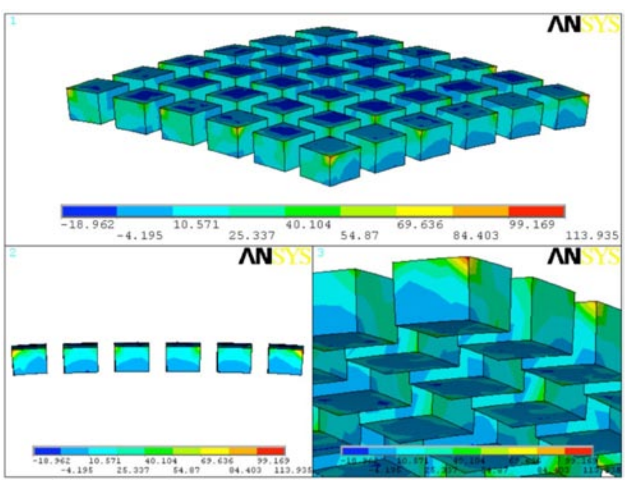

FIGURE 3. Finite element analysis finds internal stresses ≥130 MPa for $\Delta T = 500$ K.

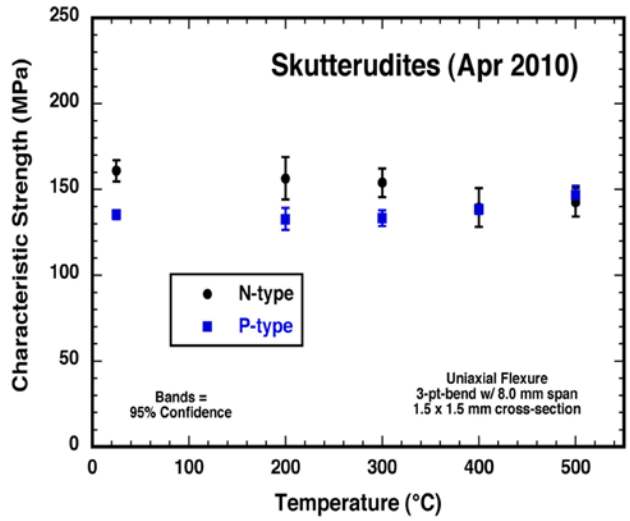

FIGURE 4. Fracture strength tests indicate skutterudites can withstand stresses of over 140 MPa.

We continue exploring new TE materials and optimizing the existing materials at General Motors Global R&D. This work includes collaboration with the University of Nevada, Las Vegas, on fundamental theoretical research involving new computational approaches for determining lattice thermal conductivity, phonon densities of states, nano-cluster doping, and electronic band structure of doped skutterudites. Our aim is to investigate and understand the very low thermal conductivities and the power factor enhancements seen experimentally for some TE materials.

Conclusions

We have made substantial progress on developing, validating, and testing a TEG for waste heat recovery from a vehicle exhaust system. This includes advances in the design, engineering, and integration of a prototype device, improvements in TE material performance, and advances in TE module design and fabrication processes.

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2. Shi, X.; Yang, Jiong; Bai, S.Q.; Yang, Jihui; Salvador, J.R.; Wang, H.; Chi, M.; Zhang, W.Q.; Chen, L.; Wong-Ng, W. "On the Design of High Efficiency Thermoelectric Clathrates through a Systematic Cross-substitution of Framework Elements", Adv. Funct. Mater. **20**, 755 (2010).

3. Beekman, M., Shi, X., Salvador, J.R., Nolas, G.S., and Yang, J., "Characterization of delafossite-type $CuCoO_2$

prepared by ion exchange", J. Alloys Compounds **489**, 336 (2010).

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5. Shi, X.; Cho, J.; Salvador, J.R.; Yang, J.; Wang, H.; "Thermoelectric properties of polycrystalline In_4Se_3 and In_4Te_3", Appl. Phys. Lett. **96**, 162108 (2010).

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7. Meisner, G.P.: "Materials and Engineering for Automotive Thermoelectric Applications," Global Powertrain Congress, Troy, MI, November 2009 (Invited).

8. Salvador, J.R.; "Engineering and Materials for Automotive Thermoelectric Applications," U.S. Car, Troy MI, March 3, 2010 (Invited).

9. Yang, J.; "Neutron Scattering Studies of Thermoelectric Materials for Automotive Applications" American Physical Society Meeting, Portland, OR, March 2010. (Invited).

10. Yang, J.; "Thermoelectric Materials by Design," 29th International Conference on Thermoelectrics, Shanghai, China, May 2010 (Invited).

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12. Meisner, G. P.; "Improving Energy Efficiency by Developing Components for Distributed Cooling and Heating Based on Thermal Comfort Modeling," Vehicle Technologies Program Annual Merit Review Meeting, U.S. Department of Energy, Washington, D.C., June 2010.

13. Meisner, G.P.; "Develop Thermoelectric Technology for Automotive Waste Heat Recovery," Vehicle Technologies Program Annual Merit Review Meeting, U.S. Department of Energy, Washington, D.C., June 2010.

14. Meisner, G.P.; "Thermoelectric Generator Development for Automotive Waste Heat Recovery," 16th Directions in Engine Efficiency & Emissions Research (DEER) Conference, Detroit, MI, September 2010.

15. Yang, J.; "Advanced Materials for Future Propulsion". 2010 Frontiers of Renewable Energy Sciences & Technologies Conference, Harvard University, Cambridge, MA, September 2010 (Invited).

16. Salvador, J.R.; "Engineering and Materials for Automotive Thermoelectric Applications," Global Powertrain Congress, Troy, MI, November 2010 (Invited).

17. Yang, J. Shi, X.; Wang, H.; Chi, M.; Salvador, J.R.; Yang, Jiong; Bai, S.; Zhang, W.Q.; Chen, L.; Copley, J.R.; Leao, J.; Rush, J.J.; "Are Skutterudites Phonon Crystals or Phonon Glasses," Materials Research Society Fall Meeting, Boston, MA, December 2010 (Invited).

18. Meisner, G.P.; "Progress on Thermoelectric Generator Development for Automotive Exhaust Gas Waste Heat Recovery," Materials Research Society Fall Meeting, Boston, MA, December 2010.

19. Salvador, J.R.; "Mechanical and Elastic Property Evaluation of n and p-type Skutterudites," Materials Research Society Fall Meeting, Boston, MA, December 2010.

20. Cho, J.Y.; Salvador, J.R.; Wang, H.; Wereszcak, A.A.; Chi, M.; 'Thermoelectric Properties of Diamond-like Compounds $Cu_2Ga_xGe_{1+x}Se_3$ ($x = 0 \sim 0.1$)," Materials Research Society Fall Meeting, Boston, MA, December 2010.

Special Recognitions & Awards/Patents Issued

1. "Filled Skutterudites for Advanced Thermoelectric Applications," Yang, J.; Meisner, G.P.; U.S. Patent 7648552 Issued January 19, 2010.

2. "Optimal power determination for a Thermoelectric Generator by setpoint dithering," Reynolds, M.G.; Cowgill, J.D.; P011627, Record of Invention submitted January 29, 2010.

3. "Algorithms for Bypass Valve and Coolant Flow Controls for Optimum Temperatures in Waste Heat Recovery Systems," Meisner, G.P.; P012265, Record of Invention submitted April 8, 2010.

4. "Method of Controlling Temperature of a Thermoelectric Generator in an Exhaust System." Prior, G.P.; Reynolds, M.G.; Cowgill, J.D.; P011519, U.S. Patent Application filed April 2, 2010.

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6. "Formation of Thermoelectric Elements by Net Shape Sintering" Salvador, J.R.; Yang, J.; Wereszczak, A.A.; P009885-R&D, U.S. Patent Application Filed June 4, 2010.

7. "Thermoelectric Generators for Waste Heat Recovery from Engine Exhaust," Meisner, G.P.; Yang, J.; P012262, U.S. Patent Application filed September 2010.

IV. UNIVERSITY RESEARCH

IV.1 University Consortium on Efficient and Clean High-Pressure Lean-Burn (HPLB) Engines

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Subcontractors:
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Objectives

- Explore new HPLB combustion that can enable future gasoline engines with 20-40% improved fuel economy.
- Determine the fuel economy benefits of engines and engine cycles designed to utilize advanced combustion modes.

Fiscal Year (FY) 2010 Accomplishments

- A thermodynamic cycle analysis was carried out confirming the merit of the HPLB strategy for increased fuel economy for gasoline engines.
- Spark-assisted compression ignition (SACI) was demonstrated in the UM fully-flexible valve actuation (FFVA) engine, enabling load extension up to 7.5 bar net mean effective pressure (NMEP) under naturally aspirated operation by decreasing the peak heat release rates.
- A computational fluid dynamics (CFD) model of SACI has been completed, integrating turbulent flame and autoignition models, with full chemical kinetics. The model reproduces the moderation of burnrate experimentally observed in SACI operation.
- A comprehensive analytical exploration of laminar flame propagation has been carried out for spark-assist conditions at high dilution level and high unburned temperature. A flame speed correlation has been developed for use in modeling turbulent SACI flame propagation.
- Experimental testing of a microwave-assisted spark plug (MWASP) at UCB has demonstrated stability improvements in homogeneous charge compression ignition (HCCI) combustion in a CFR engine under lean conditions with potential application to SACI.
- The computational singular perturbation (CSP) technique has been used to classify ignition regimes encountered in turbulent stratified conditions, according to the relative importance of spontaneous and deflagrative ignition.
- Speciation studies of intermediates formed during ignition of methylbutanoate and air mixtures have provided quantitative insight into the reaction pathways important during ester combustion and have been used to improve available kinetic models.
- Gasoline/diesel blends were tested in a small automotive diesel engine under partially premixed compression ignition (PPCI) conditions. The improved mixing and increased time delay relative to diesel fuel resulted in lower soot emissions.

Future Directions

- Expand thermodynamic and system analyses of new mixed combustion modes, and use new modeling tools to assess the potential benefit of lean/dilute burn, high pressure engine operation.
- Explore fuel and thermal stratification and its interaction with fuel properties and heat transfer for improving and controlling combustion. Along with continuing modeling work, begin experiments as test facility upgrades are completed.
- Now that initial feasibility experiments have been carried out on SACI and MWASP, conduct detailed study of multi-mode ignition and combustion and compare with recently developed models.
- Explore opportunities for improved engine efficiency through chemistry and properties of novel fuels.

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Introduction

Low-temperature combustion (LTC) is a desirable thermodynamic regime that can provide improved fuel efficiency in gasoline engines, because the properties of the working fluid are best at low temperature and because oxides of nitrogen (NOx) emissions are reduced. Unfortunately, practical and reliable combustion under these dilute conditions has traditionally been unattainable due to ignition limits. HCCI is one method to achieve good combustion in this regime and has been the subject of much recent research. Because of the limited loads possible with HCCI, turbocharging is actively being considered as a potential solution.

Figure 1 shows brake efficiencies simulated with GT-POWER® for various methods of load control over a range of boost pressure levels. Except for the throttled condition, intake pressure equals exhaust pressure. The results show significant gains by moving from current throttled engines to unthrottled, dilute operation at 1 bar. Further gains are possible under boosted conditions up to 3 bar intake pressure, largely because the effect of friction does not rise as fast as the engine load (brake mean effective pressure, BMEP). Overall brake efficiency gains from the mid 20% to the low 40% are potentially possible. The vertical arrows identify the conditions of optimal thermodynamic efficiency. These correspond to mixtures diluted from 30-60% with either air or exhaust gas recirculation (EGR) solid or dashed respectively. Combustion under HPLB conditions is the focus of the consortium effort, and supports the Advanced Vehicle Technologies goal of 20-40% fuel economy gain.

Achieving reliable combustion under HPLB conditions presents a number of challenges. At the extremely low loads (up to 4-5 bar BMEP), compression ignition as in HCCI can enable good ignition and combustion. Above this range, HCCI combustion is too rapid and knock occurs. Significantly higher loads are required before normal spark ignition (SI) can be used. HPLB conditions lie between HCCI and SI. The mixture is either too lean or dilute for normal SI, or not dilute enough to avoid the knocking combustion of HCCI. The overall goal of the consortium is to investigate methods of initiating and controlling combustion in this region.

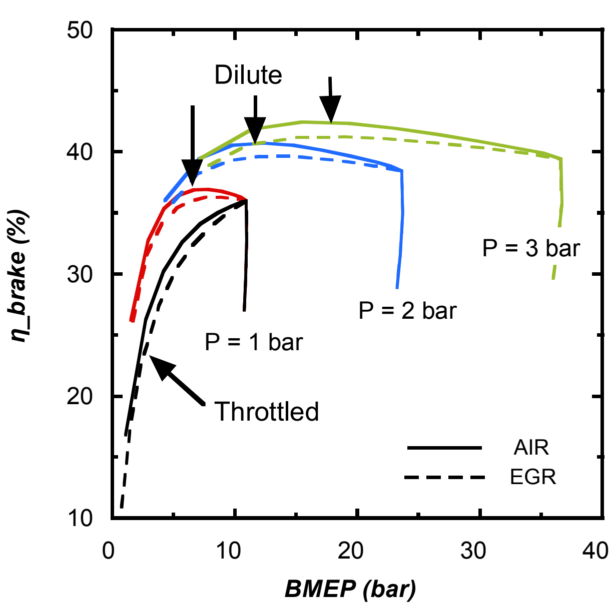

FIGURE 1. Effect of dilute (either with air or EGR), high pressure combustion on engine brake efficiencies simulated with GT-POWER® and equal intake and exhaust pressure.

Approach

Our research project, now at the end of its first year, combines experiments and modeling at three university research centers in order to acquire the knowledge and technology to explore the HPLB combustion regime, which is key to achieving optimal fuel economy. To accomplish this, both single-cylinder and multi-cylinder engine experiments are being used to investigate direct fuel injection strategies, fuel and thermal stratification, turbo/supercharging, advanced ignition and combustion modes as well as the ignition characteristics of alternate fuels and blends with gasoline.

At the same time an array of modeling tools are being developed and refined, and brought to bear on the specific limit problems of importance. These models cover a range of detail from system models for engines and after-treatment devices, through fully-coupled CFD/kinetic models, to detailed and reduced chemical mechanisms. Our intent is to take advantage of the broad range of capabilities of the university partners and the collaborative relationships among them.

The overall technical approach is focused on light-duty automotive engine application using primarily gasoline and gasoline blends with alcohols as the fuel. The research agenda addresses the following areas:

1. Thermodynamics of engines and engine cycles operating in advanced combustion modes.
2. Fuel and thermal stratification and its interaction with fuel properties and heat transfer.
3. Advanced multi-mode ignition and combustion.
4. Novel fuel opportunities for improved efficiency.

Results

Thermodynamic Conditions for Optimal Engine Efficiency

GT-POWER® was used to perform a parametric study exploring the thermodynamic conditions necessary for best engine efficiency. The idea was to identify these conditions taking into account heat transfer, friction and pumping losses, dilution (air or EGR), and boosting, and so, link the final brake output to the desired in-cylinder conditions. A constant fixed burn rate was assumed, leaving to a future study the question of whether viable combustion can be achieved at these conditions. On an indicated basis, leaner or more dilute conditions were always best. However, when friction losses were taken into account an optimum condition was observed as a result of the fact that friction losses make up a smaller proportion of the power when the engine is operating at higher BMEP. Results for air and EGR dilution were similar when compared using a "dilution" equivalence ratio defined as $Ø' = Ø\,(1–EGR)$. As shown in Figure 1, optimal brake efficiencies were obtained over a range $0.4 \le Ø' \le 0.6$ for operation up to 3 bar manifold pressure. These conditions are intermediate between traditional HCCI and SI regimes, and are the subject of much of the work of the consortium.

Fuel Economy Assessment Tool

A model-based framework has been developed for evaluating fuel-economy improvements of new engine technologies and control strategies. The framework has been demonstrated through a comparative fuel-economy study of dual-mode SI-HCCI operation. The framework is comprised of three key components: first, an improved experimental heat release analysis and model validation tool, designated MGT-HR, was created by coupling a locally developed heat release analysis software program to a GT-POWER® engine cycle simulation, capable of evaluating both SI and HCCI combustion behavior. Then, the validated GT-POWER® SI/HCCI model was used to generate full engine load and fuel-consumption maps. Finally, an integrated vehicle modeling and drive-cycle simulation procedure was developed for fuel economy evaluation by coupling MATLAB®/Simulink® and GT-SUITE, and employing SI and HCCI engine maps developed for the present work. A comparative drive-cycle fuel-economy study for three SI and HCCI engine configurations was then carried out and it was found that HCCI can provide substantial fuel-economy benefits on the order of 15% for the combined city and highway cycles.

Charge Stratification Studies

The objectives of this task are first to experimentally study stratification strategies for HPLB engines and the interaction between fuel properties, heat transfer and stratification, and second to develop advanced simulation tools to predict the combustion characteristics in the presence of temperature and composition inhomogeneities arising from stratified charge, exhaust/residual gas recirculation, and wall heat loss.

Relating to composition stratification, the effect of diluent on the ignition properties of gasoline has been investigated at MIT using the rapid compression machine. Under the same compressed condition (temperature, molar density, and equivalence ratio), both the ignition delay and the heat release time scale increase with the increase of dilution by CO_2. The effect is more pronounced at a lower compression temperature.

Significant progress has been made at UM in analytical efforts to model turbulent stratification effects. The CSP technique was applied as an automated diagnostic tool to classify ignition regimes encountered in HCCI engines. Various model problems representing HCCI combustion were simulated using high-fidelity computation with detailed chemistry for a hydrogen–air system. The simulation data were then analyzed by CSP. The active reaction zones were identified by the locus of minimum number of fast exhausted time scales (based on user-specified error thresholds). Subsequently, the relative importance of transport and chemistry is determined in the region ahead of the reaction zone. A new index I^T, defined as the sum of the absolute values of the importance indices of diffusion and convection of temperature to the slow dynamics of temperature, serves as a criterion to differentiate spontaneous ignition from deflagration regimes. These diagnostic tools were applied to one-dimensional and two-dimensional ignition problems under laminar and turbulent mixture conditions, respectively, allowing automated detection of different ignition regimes at different times and location during the ignition events. Figure 2 shows examples of four modes of ignition.

Experiments in Multi-Regime Ignition Strategies

SACI was used in the UM FFVA engine to extend the high load limit of HCCI to near 7.5 bar NMEP. The

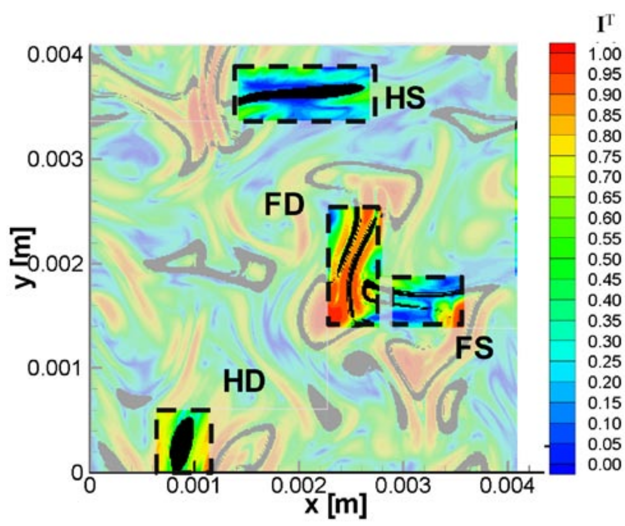

FIGURE 2. Analysis of direct numerical simulation results for ignition of a two-dimensional turbulent H_2-air field. The importance index, I^T is used to identify four regimes of ignition (HS: homogeneous region spontaneously igniting; HD: homogeneous ignition kernel leading to deflagration; FS: front in spontaneous ignition mode; FD: front in deflagration mode).

strategy was to employ a stoichiometric equivalence ratio diluted with cooled EGR. Combustion phasing and pressure rise rates were controllable using negative valve overlap and spark assist. The results are shown in Figure 3.

The heat release for several engine loads within the SACI regime were investigated in detail and are shown in Figure 4 for five points with crank angle at 50% burned of 10 deg after top center. As can be seen in the figure, the curves show a distinct period of flame propagation with relatively low heat release rate, followed by rapid auto-ignition of the remaining charge characterized by a much higher heat release rate. With proper control of the combustion variables, the relative time spent in flame propagation can be increased as load is increased, so that combustion eventually resembles conventional spark-ignited combustion. Spark assist provided control over combustion phasing while at the same time it reduced the maximum heat release during the autoignition portion of the combustion event permitting the increased maximum engine load without exceeding the ringing index limit.

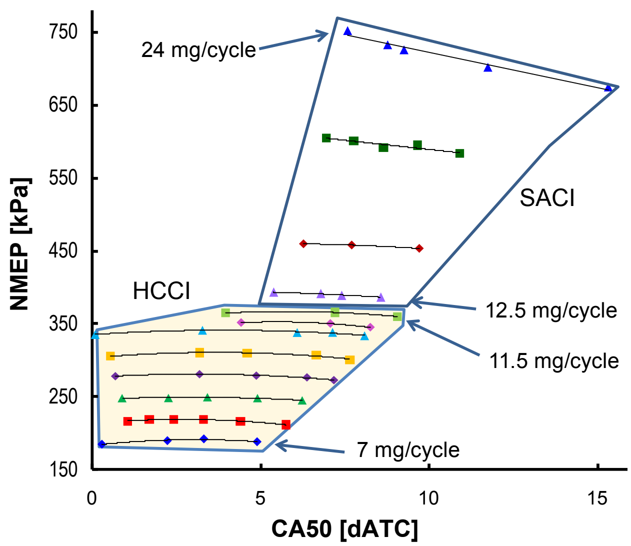

FIGURE 3. Combustion regimes in the FFVA engine, showing extension of maximum load to 7.5 bar NMEP through the use of SACI.

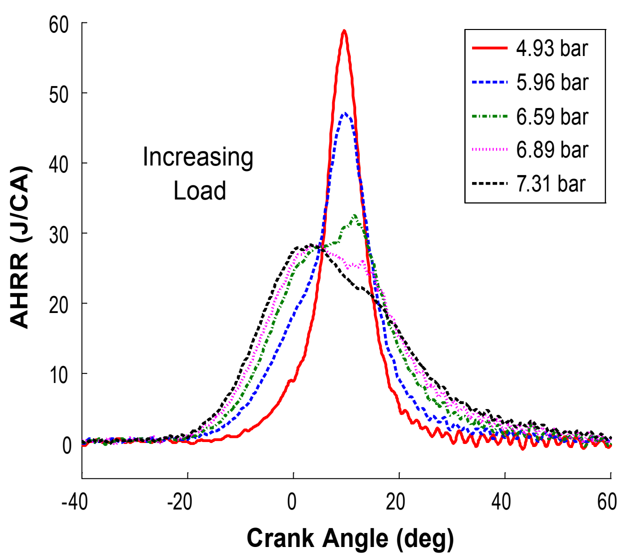

FIGURE 4. Moderating effect of SACI on heat release rates as load is increased at constant CA50 = 10 degrees after top center. Operating points are within the SACI regime shown in Figure 3.

CFD Modeling of SACI

Culminating several years of development, a CFD model of SACI has been assembled. A sub-grid model was developed capable of capturing SI flame propagation, HCCI autoignition modes and intermediate SACI modes, and integrated into KIVA-3V, designated as KIVA-CMFZ (KIVA Coherent Flamelet Multi-Zone). A key requirement in this work was the development of laminar flame speed data in the range of SACI (high preheat – high dilution), a range for which little or no experimental data is available. A large number of simulations were carried out with the transient flame code (Hydrodynamics, Chemistry, Thermodynamics Code) for both air and EGR dilution, and the results correlated for use in the KIVA model. Using the laminar burning velocity and front thickness correlations, KIVA-CFMZ uses the Coherent Flamelet model for modeling the turbulent reaction front propagation and the fully coupled KIVA-CMFZ model for detailed chemical modeling of end gas autoignition.

Figure 5 shows a sequence of simulated results from KIVA-CFMZ compared with experimental combustion images. The first column shows a side cut through the chamber while the middle is a horizontal cut. The right column shows images captured in the UM optical engine through a transparent piston under similar conditions. The first three rows show an orderly flame development beginning with a small kernel which is established just after the spark (top). The last row shows the transition from flame to autoignition.

A parametric study of the effects of spark timing and intake manifold temperature under highly dilute conditions showed moderated heat release results consistent with the experimental observations made in the FFVA engine shown in Figure 4.

MWASP

Tests in a single-cylinder engine at UCB show that microwave enhancement eliminates misfire in lean conditions, but stable engine operation is still limited by partial-burn. For gasoline, methane, ethanol and wet ethanol fuels, MWASP was found to be effective at increasing the lean flammability limits under

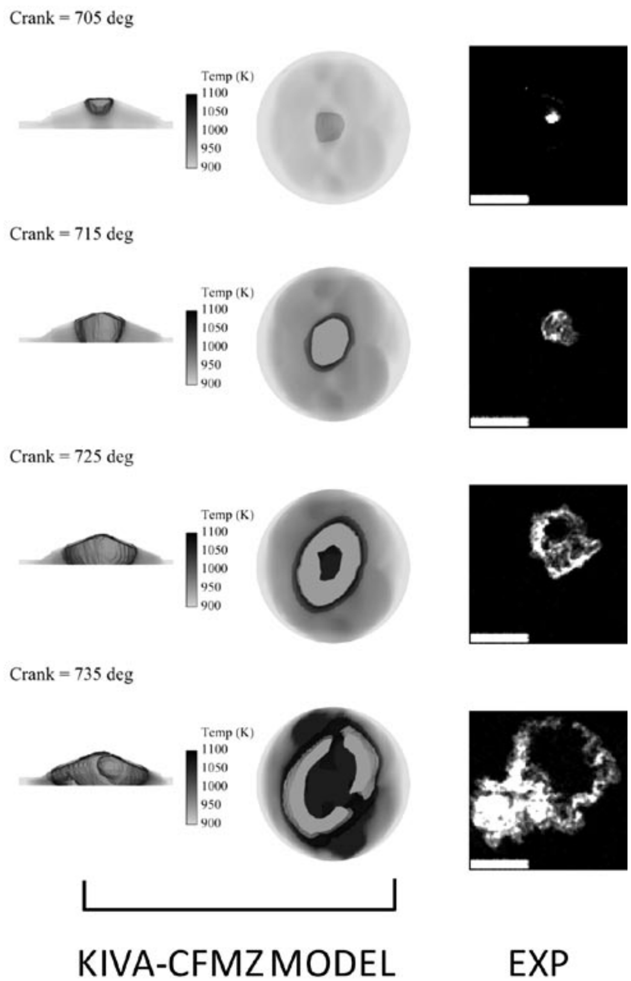

FIGURE 5. Sequence (top to bottom) of SACI combustion simulations from KIVA-CFMZ model on the left, compared with images on the right obtained in the UM optical engine under similar conditions. The transition from flame to autoignition is beginning in the bottom row.

normal SI engine conditions. Future work will aim at demonstrating the effect in the SACI regime.

Chemical kinetic modeling of plasma-assisted combustion now includes evolution of electron energy. Current results show that adding energy to the electrons in a reacting mixture will accelerate combustion much more than adding an equivalent amount of energy to the gas molecules in the mixture. Related experimental work with potassium acetate added to ethanol fuel in small concentrations (<720 mg/L) increases ion signals to acceptable levels, even at equivalence ratios as low as 0.20.

Fuel Chemistry for Improved Engine Efficiencies

A single-cylinder engine study was carried out at UM with diesel/gasoline blends to investigate how a fuel's resistance to auto-ignition and volatility affect the load limits of PPCI under low-temperature combustion conditions. Three fuels were tested: 100% diesel fuel, 80/20 diesel gasoline mixture and 60/40 diesel gasoline mixture. It was found that the increased ignition delay and higher volatility gasoline blends produce a more homogeneous fuel air mixture before the start of combustion, extend smokeless combustion to higher loads, and produce lower NOx emissions. Engine boosting was found to move both the high and low limits of LTC to higher engine loads. It was found that increased ignition delay with more gasoline not only causes soot emissions to remain at a low level but also to become insensitive to changes in intake oxygen concentration. A higher gasoline fraction causes the effect of injection pressure to become limited because improved mixing avoids locally fuel-rich regions.

In the UM rapid compression facility, measurements of ignition delay have been extended to n-butanol. We have acquired speciation data which provide quantitative understanding of the pathways important during combustion of alcohols at conditions directly relevant to advanced engine strategies. Analysis of the experimental results has identified several species which are not captured well by current reaction models of n-butanol, including aldehydes which are important to quantifying the potential adverse emission effects of alcohol fuels. Work also continues on the chemistry of larger hydrocarbon and oxygenated hydrocarbon species, relevant to model development at Lawrence Livermore National Laboratory and elsewhere.

Conclusions

The work of the consortium has made considerable progress towards bringing together the knowledge and tools needed to achieve the fuel economy goals of the Advanced Vehicle Technologies Program for gasoline engines.

- The HPLB combustion regime has been identified as the most suitable for achieving optimal engine fuel economy. The regime includes lean mixtures $0.4 < \phi < 0.6$ for air or equivalent EGR dilution of stoichiometric mixtures, a region inaccessible to normal homogeneous SI engines.
- Engine experiments have demonstrated the use of SACI in bridging the gap between upper limit HCCI and lower limit SI combustion, and identified the potential utility of MWASP.
- A new KIVA-CFMZ model has been developed incorporating both flame and autoignition mechanisms for describing SACI combustion.
- Analytical work with direct numerical simulation modeling has developed a methodology for identifying small scale ignition regions in turbulent stratified mixtures.

- Speciation work in a rapid compression facility with n-butanol ignition is being applied to the development of improved chemical kinetic models. Other experiments have shown the effect of EGR on ignition time.

FY 2010 Publications/Presentations

1. Assanis, D., "A University Consortium on High Pressure, Lean Combustion for Efficient and Clean IC Engines," presentation at the 16th Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, Michigan, September 27–30, 2010.

2. DeFilippo, A., Saxena, S., Rapp, V.H., Ikeda, Y., Chen, J-Y, Dibble, R.W., "Extending the lean flammability limit of gasoline using a microwave assisted sparkplug," submitted to 2011 SAE World Congress Meeting.

3. Gupta, S., Im, H.G., Valorani, M., "Classification of Ignition Regimes in HCCI Combustion using Computational Singular Perturbation," *Proceedings of the Combustion Institute*, v. 33, in press (2010).

4. Han, D., Ickes, A., Assanis, D.N., Zhen, H., Bohac, S.V., 2010, "The Attainment and Load Extension of High-Efficiency Premixed Low-Temperature Combustion with Dieseline in a Compression Ignition Engine," *Energy & Fuels*, 24, pp. 3517-3525.

5. Han, D., Ickes, A., Bohac, S. V., Zhen, H., Assanis, D. N., 2010, "Premixed Low-Temperature Combustion of Blends of Diesel and Gasoline in a High Speed Compression Ignition Engine," *Proceedings of the Combustion Institute*, v. 33, in press (2010).

6. Keros, P.E., Assanis, Dimitri, Schlechtweg, J.A., and Wooldridge, M.S., "Flame Speed Measurements Based on High-Speed Imaging of HCCI and Spark Assisted HCCI Ignition Events," ASME ICE Fall Technical Conference, San Antonio, TX September 12–15th 2010.

7. Manofsky, L., Vavra, J., Babajimopoulos, A., and Assanis, D. (2011) Bridging the Gap between HCCI and SI: Spark-Assisted Compression Ignition. Submitted to 2011 SAE World Congress Meeting.

8. Martz, J.B., Kwak, H., Im, H.G., Lavoie, G.A., Assanis, D.N., "Combustion Regime of a Reacting Front Propagating into an Auto-Igniting Mixture," *Proceedings of the Combustion Institute*, v. 33, in press (2010).

9. Martz, J.B., Middleton, R.J. Lavoie, G.A. Babajimopoulos, A., Assanis, D.N., (2010), A Computational Study and Correlation of Premixed Isooctane Air Laminar Flame Properties under Spark Ignited and Spark Assisted Compression Ignition Engine Conditions, *Combustion and Flame* (in press).

10. Ortiz-Soto, E., Assanis, D., and Babajimopoulos, A. (2010) A Comprehensive Engine to Drive-Cycle Modeling Framework for the Fuel Economy Assessment of Advanced Engine and Combustion Technologies. *International Journal of Engine Research,* (submitted).

11. Saxena, S., Chen, J-Y, and Dibble, R.W., (2010) "Increasing the signal-to-noise ratio of sparkplug ion sensors through addition of a potassium acetate fuel additive", *Proceedings of the Combustion Institute*, 33, DOI: 10.1016/j.proci.2010.07.046.

12. Saxena, S., Chen, J-Y, Dibble, R.W., "Maximizing power output in an automotive scale multi-cylinder HCCI engine," submitted to 2011 SAE World Congress Meeting.

13. Saxena, S., Rapp, V.H., Chen, J-Y, Dibble, R.W., "A numerical study of ultra-high efficiency combustion of a hydrogen-oxygen-argon mixture in HCCI engines", Presented at the Western States Meeting of the Combustion Institute, March 2010.

14. Walton, S.M., Karwat, D.M., Teini, P.D., Gorny, A., and Wooldridge, M.S., "Speciation Studies of Methyl Butanoate Ignition," submitted to *Fuel*, July 22, 2010.

15. Zigler, B.T., Keros, P.E., Helleberg, K.B., Fatouraie, M., Assanis, Dimitri, and Wooldridge, M.S., "An Experimental Investigation of the Sensitivity of the Ignition and Combustion Properties of a Single-Cylinder Research Engine to Spark-Assisted HCCI," submitted to the *International Journal of Engine Research* May 5, 2010, revised and resubmitted October 2010.

IV.2 Optimization of Advanced Diesel Engine Combustion Strategies

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Objectives

- Development of high efficiency internal combustion engines with goals of improved fuel economy by 20-40% in light-duty (LD) and 55% brake thermal efficiency in heavy-duty (HD) engines.
- Develop methods to further optimize and control in-cylinder combustion processes, with emphasis on compression ignition engines.

Fiscal Year (FY) 2010 Accomplishments

- Optimum spray and combustion chamber design recommendations have been made for improved efficiency of (HD) and (LD) diesel engines. Greater than 55% thermal efficiency achieved using dual fuel reactivity-controlled compression ignition (RCCI) combustion in HD engines over wide load range with Environmental Protection Agency 2010 oxides of nitrogen (NOx) and soot levels met in-cylinder (i.e., without need for after-treatment).
- Guidelines established for engine control methodologies under light- and high-load operating conditions with consideration of fuel property and mixture preparation effects.
- Validated combustion and realistic fuel vaporization submodels developed for biofuels and gasoline/diesel surrogates to be used for further optimization and combustion system concept evaluation.
- Methodology formulated for efficient engine system transient control strategies appropriate for engine speed/load mode transitions.

Future Directions

- Methods to further increase fuel efficiency while maintaining low emissions will continue to be explored.
- Low temperature combustion (LTC) strategies on HD and LD engines will be further demonstrated.
- Optimized injection strategies, matched with piston geometry and fuels, will be developed.
- Transient control strategies for mixed mode combustion will be demonstrated and tested.

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Introduction

This work addresses the DOE's Vehicle Technologies Program goals of a 20-40% improvement in fuel efficiency in a LD vehicle and the attainment of 55% brake thermal efficiency in HD engine systems. To achieve these goals, both the efficiency of the internal combustion engine and the exhaust heat recovery and air system efficiencies must be increased, and it is necessary to improve the efficiency of expansion work extraction. This requires optimized combustion phasing and minimized in-cylinder heat transfer losses. There is also a need to minimize the fuel used for diesel particulate filter (DPF) regeneration, and thus it is necessary to minimize soot emissions.

Significant challenges must be solved to achieve viable high thermal efficiency engine combustion. It is generally agreed that conventional diffusion controlled combustion might be still be needed to reach full load, possibly with low-sooting lifted flames. LTC (e.g., homogeneous charge compression ignition and early premixed charge compression ignition, HCCI/PCCI) offers increased thermal efficiency with low NOx and reduced requirements for DPF regeneration for light-load operation. However, the inability to adequately control combustion phasing and to avoid liquid fuel impingement on combustion chamber surfaces with the use of high cetane number, low-volatility fuels such as diesel, limits the practical load range and thermal efficiency benefits of HCCI/PCCI combustion. In addition, reduction of combustion noise due to high rates of pressure rise, reduction of high levels of exhaust carbon monoxide and unburned hydrocarbons (which negatively impact fuel efficiency), and the need for optimizing mixture preparation is required to extend the light-load operating range. These issues are addressed in the present research by using novel fuel injection and fueling strategies.

Approach

The project focuses on advanced combustion research in low-temperature combustion and lean-burn strategies, and in advanced modeling and control of vehicle emissions reduction (after-treatment) devices. The work is divided into four main tasks with 12 subprojects, featuring experimental and modeling components:

A. Combustion strategies for increased thermal efficiency;
B. Fuels as an enabler for fuel efficiency improvement;
C. Multi-scale predictive tools for understanding combustion and emissions; and
D. System-level engine optimization (air, fuel, emissions, after-treatment).

A main focus of Tasks A, B and C is to improve fundamental understanding to overcome the technology barriers that control fuel efficiency. The impact of advanced combustion technologies on engine performance linked with the after-treatment system is also considered in Tasks C and D. Fully instrumented light- (General Motors [GM] 1.9 L) and heavy-duty (Caterpillar 3401) research diesel engines are used to reveal combustion fundamentals and to explore methods of controlling and optimizing fuel efficient combustion under steady-state and transient operation. Information from the engine experiments is incorporated into comprehensive multidimensional computational fluid dynamics (CFD) codes (KIVA3V and KIVA4 with large eddy simulation [LES] turbulence models and detailed chemistry using CHEMKIN) and system models (GT-POWER and WAVE codes and their associated control algorithms). The developed models and experimental methods are used to explore methods to optimize diesel engine fuel efficiency while maintaining low emissions.

Results

Task A: Combustion Strategies for Increased Thermal Efficiency

The potential of operating a HD compression ignition engine fueled with *conventional gasoline* in the partially premixed combustion mode has been demonstrated previously experimentally using the ERC Caterpillar 3401 single-cylinder engine. This combustion regime offers high thermal efficiency and low emissions [1]. To further optimize the engine, computer modeling was conducted this year using the updated KIVA-3V code. The simulations used genetic algorithm optimization techniques coupled with the CFD, and revealed that the high-load condition is quite constrained by ringing intensity considerations. Low NOx and good thermal efficiency operating points were found, but peak pressure and soot emissions were challenging [2]. Simulations have also been performed for the LD GM 1.9 L engine. The modeling indicates that engine operation up to 20 bar indicated mean effective pressure (IMEP) conditions is achievable with a compression ratio of 13.9. In addition, exhaust gas recirculation (EGR) and injection parameter variations have been studied and used to provide guidelines for the companion experimental studies [3].

The HD engine was also chosen to study high power mode switching and cycle-by-cycle analysis of load transition cases. Full engine CFD computations were conducted using the ERC's LES model integrated with the KIVA-3V code and the ERC n-heptane chemistry mechanism. Single-cycle mode switching from conventional diesel to PCCI combustion at high-load conditions has been considered. A mode switch strategy was developed that introduces a gradual injection schedule change, and provides a better fuel-air distribution and avoids engine knock (high pressure rise rates), as shown in Figure 1 [4].

Experiments have also been conducted using dual fuel RCCI on the Cat® 3401 HD research engine. Fuel effects have been explored from low- to high-load operation (4.5-17 bar gross IMEP and 1,300 rev/min) [5]. The experiments use gasoline or E85 (85% ethanol, 15% gasoline) as the low reactivity fuel and ultra-low sulfur diesel as the high reactivity fuel. A second set of tests used gasoline as the low reactivity fuel, and gasoline blended with ~3% by volume of the cetane improver additives ethyl-hexyl-nitrate or di-tert-butyl-ether as the reactive fuel. The results indicate that the use of low concentrations of the additive effectively replicates diesel fuel's combustion performance [6,7]. Figure 2 demonstrates that RCCI allows greater than 55% gross indicated thermal efficiency, while meeting 2010 soot and NOx mandated levels in-cylinder (i.e., without after-treatment) [7].

An experimental investigation of combustion chamber design, fuel injection, intake boosting and fuel properties has also been conducted in the LD GM 1.9 L engine. This subtask explores interactions between engine geometry and operation strategies with a set of widely different fuels and evaluates their effects on emissions, efficiency, and noise at LTC-like conditions. Engine operating conditions recommended by the CFD modeling have been tested for different fuel blends, including bio-fuels. Current testing has explored the sensitivity of the onset of combustion and combustion stability to the composition of the exhaust residual to provide validation data for the simulation results. In addition, the sensitivity of the engine operating regimes to variation in injection pressure has been studied. The results in Figure 3 show that engine operable regions are sensitive to the injection pressure and the details of the injection timings and amounts [3].

Task B: Fuels as an Enabler for Fuel Efficiency Improvement

The ability of chemical changes, through the fuel composition, to extend the ignition delay to promote

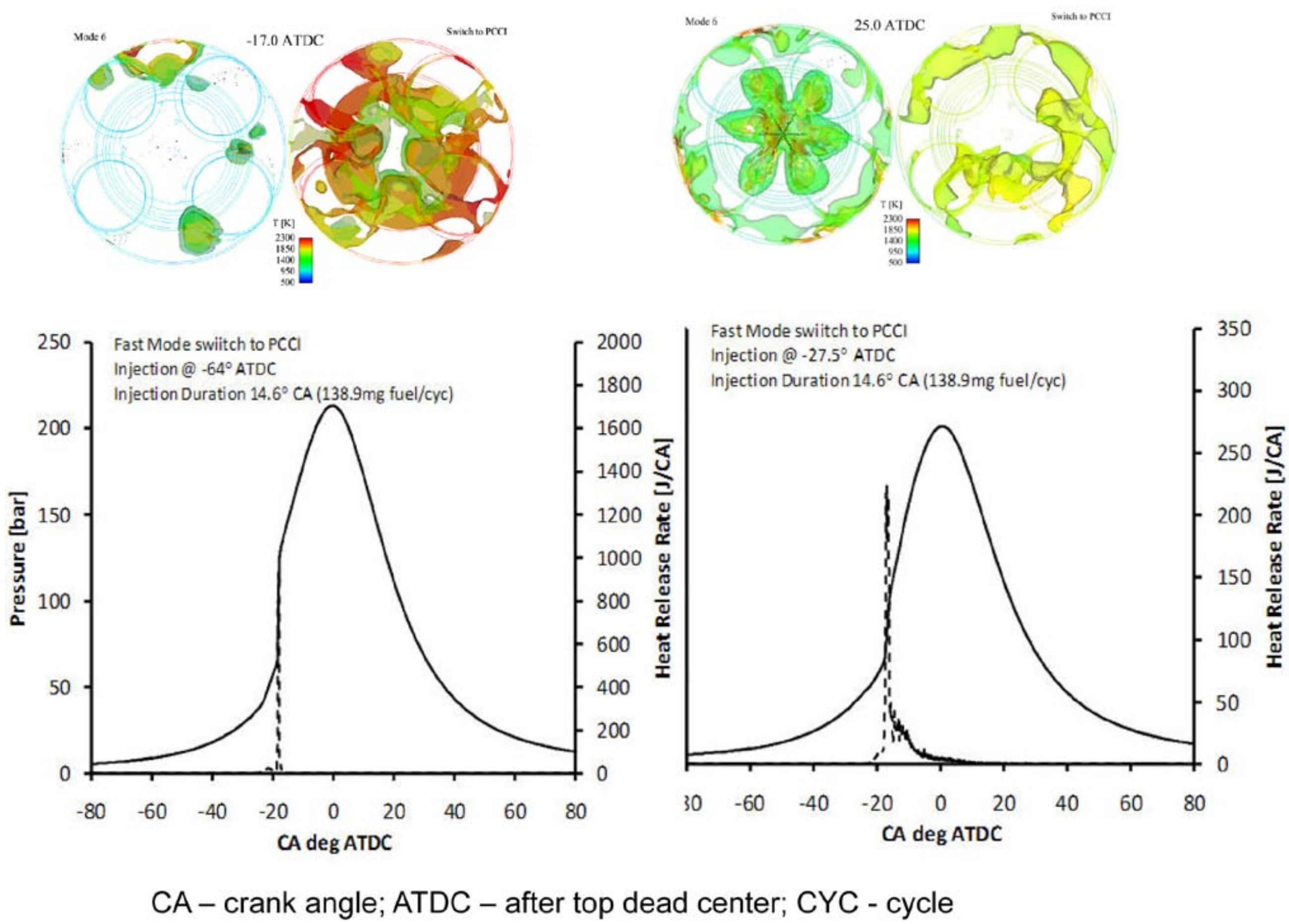

FIGURE 1. Single-cycle mode switching from conventional to PCCI combustion at high load. Left: Fast mode switch strategy, Right: gradual injection schedule change. Top – Predicted in-cylinder OH contours at -17° and 25° ATDC), Bottom - pressure and heat release rate.

volumetric combustion is studied in this task. The focus of the study includes combustion visualization using an optical engine that has the same geometry as the LD 1.9 L GM diesel engine. The optical engine has been run using dual-fuel, or RCCI combustion. The engine operating parameters were determined experimentally with guidance from both the computational and metal-engine experiments performed in Task A. The low reactivity fuel, i.e. gasoline, was injected far upstream of the engine and was well-mixed with the intake air prior to the engine. The high reactivity fuel, i.e., diesel fuel, was directly injected using a single injection. The diesel injection timing and the mass split ratio between the two fuels were optimized, and the resulting conditions were similar to those of the metal engine. Testing has also been performed using n-heptane injected during the intake stroke, and the combustion was found to be completely non-luminous. Current dual-fuel experiments are being conducted using both visible and ultraviolet light imaging and will provide further understanding of RCCI combustion mechanisms.

In-cylinder laser/optical diagnostics are also being used to investigate extended-lift-off combustion (ELOC). The diagnostics include planar laser-induced fluorescence measurements of the fuel distribution, planar laser-induced incandescence measurements of the soot distribution, and hydroxyl (OH) chemiluminescence and/or OH planar laser induced fluorescence (PLIF) measurements, and high-speed natural luminosity and chemiluminescence imaging. An optically accessible piston and head has been designed that features indexable shrouded valves and an injector that allows single-spray plumes to be viewed, as well as interacting plumes. Baseline operating conditions will use n-heptane and isooctane mixtures and will provide information about the conditions for sootless ELOC combustion.

Task C: Multi-Scale Predictive Tools for Understanding Combustion and Emissions

The goal of this sub-task is to develop and apply predictive, detailed-chemistry-based models to improve understanding of the combustion and emission formation processes for future efficient engines. A combustion model that can model auto-ignition,

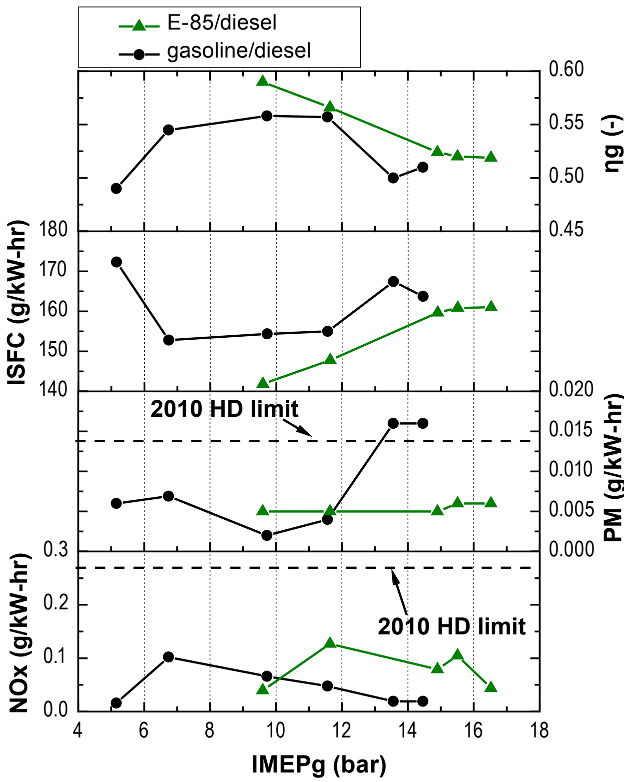

FIGURE 2. RCCI performance with diesel/gasoline and diesel/E85 fuel in the HD engine over wide load range at 1,300 rev/min.

flame propagation, and premixed and non-premixed combustion is required to be able to study combustion processes that range from conventional diesel (non-premixed), HCCI/PCCI (premixed), lifted flames, and mixed-mode regimes that conceivably all occur in the same engine cycle in advanced combustion concepts. The chemistry is described using reduced reaction mechanisms for surrogate fuels, and will be extended to consider multi-component fuels and multi-mode (e.g., PCCI/flame propagation) combustion.

A multi-component fuel vaporization model has been developed for use with KIVA-3V [8]. This year the thermophysical properties for biodiesel were added to the model, including for the five main components of soy biodiesel, which are methyl palmitate ($C_{17}H_{34}O_2$), methyl stearate ($C_{19}H_{38}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), and methyl linolenate ($C_{19}H_{32}O_2$) [9]. Bio-fuel sprays have been modeled under non-reacting conditions and the model was found to be able to describe the varying amounts of fuel vapor of each component. The vapor distribution was found to strongly depend on the fuel composition with methyl linoleate and methyl oleate contributing the most vapor [9].

Advanced spray and fuel film models for selective catalytic reduction after-treatment are also being developed in this subtask. Calculations have been performed of urea-water solution sprays and their subsequent vaporization, solidification and urea decomposition. The decomposition of solid urea is a highly temperature-sensitive process, and a model has been developed that simulates the heat transfer and melting dynamics for a single particle. Predictions of the mass fraction ratio of ammonia and nitric oxide have been made, and the target is to obtain a homogenous distribution of this mixture (slightly below the stoichiometric value) at the entrance to the catalyst to enhance the performance of the NOx conversion process.

Measurement of turbulence mixing in engine flows is being explored, and the results are being utilized for LES turbulent combustion model development and validation. Turbulent mixing is a controlling feature in LTC where the goal is to premix, to as large an extent as possible, the fuel and air prior to ignition. The goal of the project is to obtain optically full resolution of all relevant turbulent scales using laser-induced fluorescence. Initial measurements have been acquired during the intake stroke, and the mixing between the flow through the two intake valves has been quantified, where one of the streams was doped with a fluorescent tracer. The current effort extends the measurements to times late in the compression stroke by injecting a small amount of nitrogen seeded with a fluorescent tracer is injected into the cylinder, as shown in Figure 4. Dissipation spectra have been found to be relatively constant with respect to injection timings in the end of injection (EOI) range of 30-60 degrees before top dead center and a suitable delay between EOI and the image acquisition time.

Crank-angle-resolved species and temperature measurement diagnostics are being developed for improved understanding of chemistry and mixing in fuel-efficient, low-emission combustion regimes. This information is crucial for validating advanced models used to develop concepts that expand HCCI operation. Previous work in this subtask developed an emission Fourier transform infrared (FTIR) technique that has been applied to in-cylinder RCCI measurements [10]. The method has been extended to backscatter-based engine FTIR probes as well as for back-reflection-based probes. The results show that backscatter-based probes typically achieve signal-to-noise ratios of only 20-30 even after averaging over hours of steady engine operation. On the other hand, reflection-based probes can achieve excellent signal-to-noise ratios of >1,000 even in short total test times like 10 seconds. Accordingly, in-cylinder absorption FTIR spectrometry is currently being pursued using reflection-based probes.

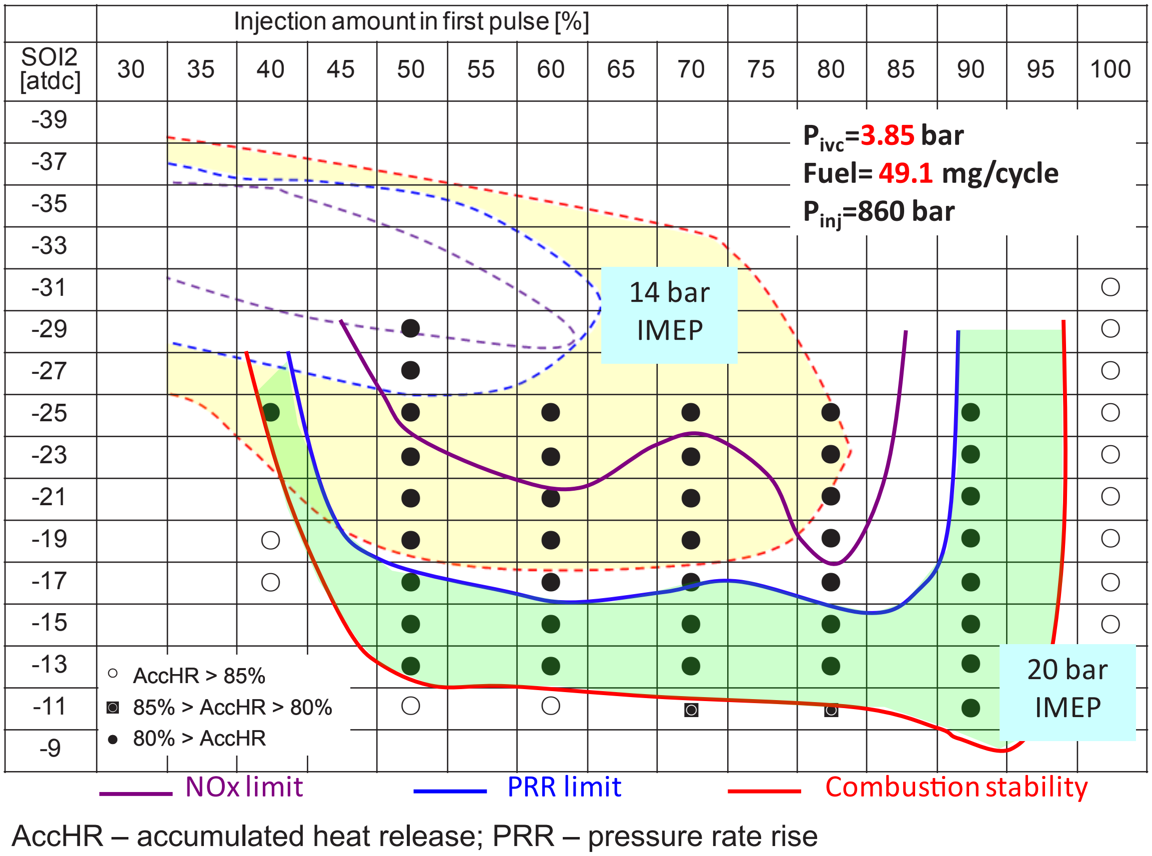

FIGURE 3. Comparison of operable conditions (shaded regions) of gasoline direct injection compression ignition combustion in the LD engine with compression ratio = 13.9 at 14 and 20 bar IMEP.

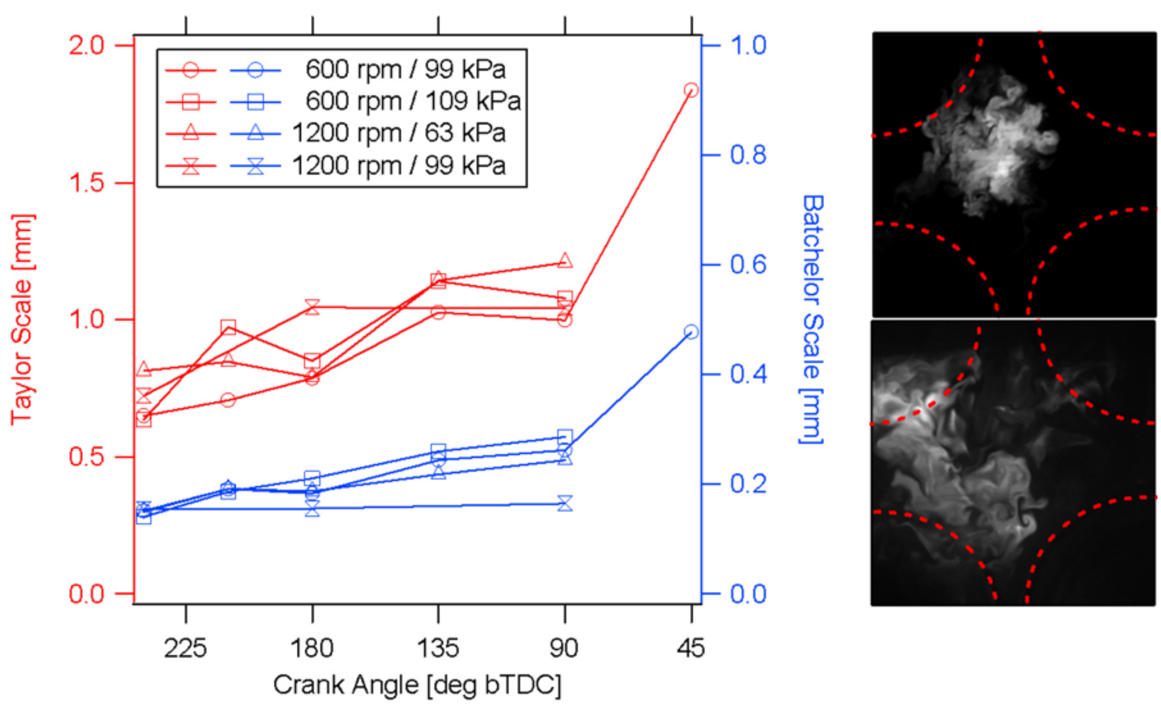

FIGURE 4. In-cylinder gas injection methodology developed for mixing measurements in the late compression stroke. Turbulence length scales measured late in the compression stroke.

Task D: System-Level Engine Optimization (Air, Fuel, Emissions, Aftertreatment)

Interactions between high- and low-pressure EGR systems with mixed-mode operation under load and speed transients are being evaluated to understand the requirements for LTC combustion phasing control. A low-pressure EGR loop has been incorporated to expand the load range. New hybrid EGR systems exhibit cooler EGR temperatures, higher EGR flow rates at low loads, higher turbo speeds and boost pressure, and improved high-pressure EGR response. The capability of meeting Tier II Bin 5 NOx emissions has been demonstrated on the multi-cylinder GM 1.9 L with comparable brake specific fuel consumption to the EURO4 calibration, but with lower emissions.

Transient load experiments have shown a decrease in NOx followed by a recovery to a level slightly higher than when the transient started. This is due to the combination of the momentary decrease in the airflow, while fuel flow is held constant, with the attendant decrease then increase in inlet O_2 concentration. These trends are also consistent with the measured progression of CA50 during the transient and the hydrocarbon emissions. The results indicate that a key aspect of controlling the emissions and performance during transient operation is controlling the response of the in-cylinder O_2.

Engine and after-treatment optimization modeling is being used to guide the engine experiments and to study engine and after-treatment options for low fuel consumption. System-level models capable of simulating multiple cycles and operating transients have been formulated based on GT-POWER coupled with purpose-written emissions submodels. The models have been implemented and validated and describe both high- and low-pressure EGR systems in a multi-cylinder engine model. The after-treatment component models contain diesel oxidation catalyst converter (DOC), DPF and advanced controllers, which have been validated individually, and are used to explore advanced active DPF regeneration strategies. Previous studies indicated that pulsed DPF regenerations (especially for two or three hydrocarbon pulsed injections upstream of DOC) show promise to achieve efficient, safe and reliable regenerations of a DPF [11].

To further optimize the pulsed regeneration strategies, two-stage pulsed regeneration has been studied this year. The idea for two-stage pulsed regeneration is to burn enough soot during stage one (the first pulse) at intermediate target temperatures so that the remaining soot can be burned more efficiently at higher temperatures but without the risk of a runaway regeneration. During stage two, the second pulse uses a high regeneration temperature to maintain high fuel efficiency. The peak temperature occurs in this more aggressive second stage regeneration, but are limited since there is not a large amount of soot in the DPF. The split soot fraction (f_split) is used to determine the contributions of the first stage and the second stage regenerations. Figure 5 shows that regeneration characteristics (fuel efficiency and DPF maximum wall temperature) can be adjusted by controlling the split soot fraction.

Conclusions

- Novel diagnostics, fuel-types, injection concepts, optimized piston geometries with advanced CFD models have been used successfully, and have been coordinated with engine experiments to explore efficient LTC concepts.
- The present study has shown that advanced combustion regimes with optimized control of fuel/air/diluent mixture preparation and control of fuel reactivity distributions can offer transformational improvements in engine efficiency (>50% thermal efficiency over a wide engine operating range) while meeting emissions mandates without the need for after-treatment.

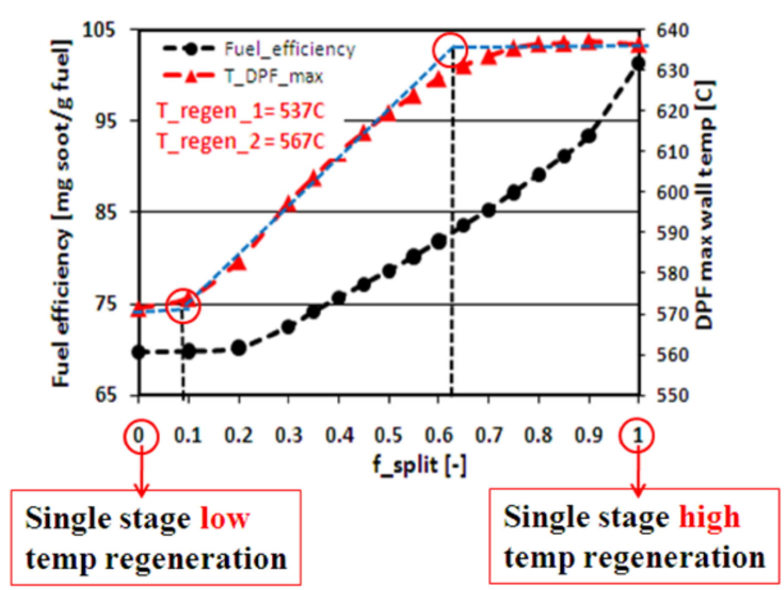

FIGURE 5. Fuel efficiencies and DPF maximum wall temperatures at different soot split factors for two-stage pulsed regenerations at T_tar_1 = 537°C and T_tar_2 = 567°C (f_split indicates how much of total soot is combusted during the second stage [high temperature] regeneration).

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IV.3 Flex-Fuel Optimized SI and HCCI Engine

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Objectives

- Demonstrate a spark ignition (SI) and homogeneous charge compression ignition (HCCI) dual combustion mode engine for a blend of gasoline and E85 (85% ethanol and 15% gasoline) for the best fuel economy.
- Develop a cost-effective and reliable SI and HCCI dual combustion mode engine.
- Develop a control oriented (real-time) SI, HCCI and SI-HCCI combustion model and implement it into a hardware-in-the-loop (HIL) simulation environment.
- Develop model-based combustion mode transition control strategies for smooth mode transition between SI and HCCI combustions.
- Utilize closed-loop combustion control to minimize efficiency degradation with satisfactory engine out exhaust emissions under any blend of gasoline and E85.

Fiscal Year (FY) 2010 Accomplishments

- Finalized the target SI and HCCI dual-mode combustion engine design and its specifications by working with our industrial partner Chrysler Group LLC.
- Real-time control oriented SI, HCCI, and SI-HCCI hybrid combustion engine model has been developed and calibrated using the GT-POWER simulation results. The developed model has been implemented into the dSPACE HIL simulator.
- The SI combustion optical engine has been designed and fabricated, and the base line SI combustion tests are underway. The HCCI combustion optical engine design with two-step valve lift and electrical cam variable valve timing (VVT) is underway.
- The hybrid combustion simulations show that steady-state operational parameters are not optimized for mode transient control and model-based control is necessary for a smooth combustion mode transition.

Future Directions

- Analyze SI-HCCI hybrid combustion characteristics through optical engine cold flow and combustion studies.
- Develop closed-loop combustion control strategy based upon the control oriented engine model calibrated by GT-POWER and experimental data.
- Evaluate the developed control strategy for smooth mode transition between SI and HCCI combustions in the HIL simulation environment.

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Introduction

To obtain the benefit of high efficiency of compression ignition engines and low emissions of SI engines, there has been a rekindled interest in HCCI engines in recent years. The major advantage of HCCI engines is realized by eliminating the formation of flames and results in a much lower combustion temperature [1-5]. As a consequence of the low temperature, the formation of oxides of nitrogen (NOx) is greatly reduced. The lean-burn nature of the HCCI engine also enables un-throttled operation to improve vehicle fuel economy. The main challenge of HCCI engines is the accurate control of the start of combustion and combustion duration. The practical application of the HCCI principle to gasoline engines is envisioned in a dual-mode combustion engine concept. At partial-load conditions, the engine would operate under an un-throttled HCCI combustion mode; and at low- or high-load conditions, the engine operation needs to transit to the conventional SI combustion mode to avoid engine misfire or knocking. The objective of this project is to demonstrate a SI and HCCI dual-mode combustion engine for a blend of gasoline and E85. The operating efficiencies shall be obtained through closed-loop combustion control, which will result in minimal efficiency degradation when E85 fuel or any blend of gasoline and E85 are used.

Approach

This research activity adopts model-based control approach to develop control strategies for smooth mode transition between SI and HCCI combustions with the support from our industrial partner, Chrysler Group

LLC. The following methodology is and has been used in this research activity:

- Understand and optimize the HCCI and SI-HCCI hybrid combustion process through optical engine study.
- Develop a control-oriented SI, HCCI, SI-HCCI combustion model as well as the entire engine model, and calibrate it based upon GT-POWER simulation results and optical/metal engine experiments.
- Utilize the developed control-oriented engine model to study SI and HCCI combustion modes as well as SI-HCCI hybrid (spark-assist) combustion mode during combustion mode transition.
- Develop the closed-loop combustion control strategy for hybrid combustion and SI to HCCI combustion mode transition under a blend of gasoline and E85 and validate it through HIL simulations.
- Validate the developed control strategy on the multi-cylinder metal engine for smooth mode transition between SI and HCCI combustions.

Results

Selection of the target SI and HCCI dual-mode engine that represents the future production engine platform has been finalized. The target engine will be the Chrysler 2.0 L turbocharged inline 4-cylinder with dual-VVT and direct injection. Chrysler has delivered the target engine components to be used for construction in the optical engine at MSU. The target engine head will be modified to fit two-step lift valves and electrical VVT actuators for SI and HCCI combustions.

A single-cylinder GT-POWER engine model, representing the target engine, has also been delivered by Chrysler to MSU and engine simulations were conducted. The simulation results obtained from this model were used to calibrate the developed control oriented engine model [6]. A GT-POWER injector flow model was also developed to accurately model the fuel injection process.

A two-zone combustion mode transition model between SI and HCCI operations was developed at the beginning of the first fiscal year [6], see Figure 1. This two-zone combustion model has been further refined to improve the estimation accuracy of the in-cylinder temperature. The developed two-zone model has been implemented into the HIL simulation environment (see Figure 2) to evaluate the benefits of smooth mode transition between SI and HCCI combustion modes [7], see Figure 3. The simulation results show that the SI-HCCI hybrid combustion mode can be used to reduce engine output torque variation during combustion mode transition, see Figure 3. The simulation results also show that the transient performances of the mode transition between SI and HCCI combustions is heavily dependent of the model-based mode transition control strategy. This is due to the fact that the steady-state control parameters for SI-HCCI hybrid combustion are not optimal for the transient SI-HCCI combustion operation and the model-based control is a necessity.

Optical engine design has been completed, where a Hatz engine crank case was used as the base of the optical engine and the Chrysler target 4-cylinder engine head was modified to fit on to the optical engine. A Bowditch optical piston of the target engine

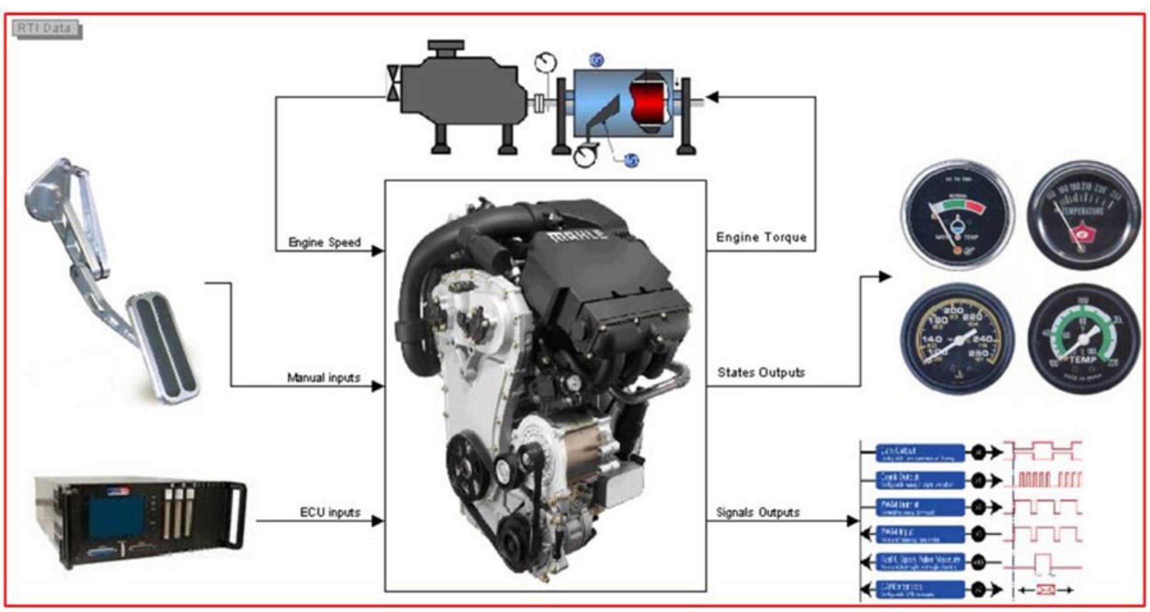

FIGURE 1. Simulink Model of the Two-Zone Combustion Engine Model

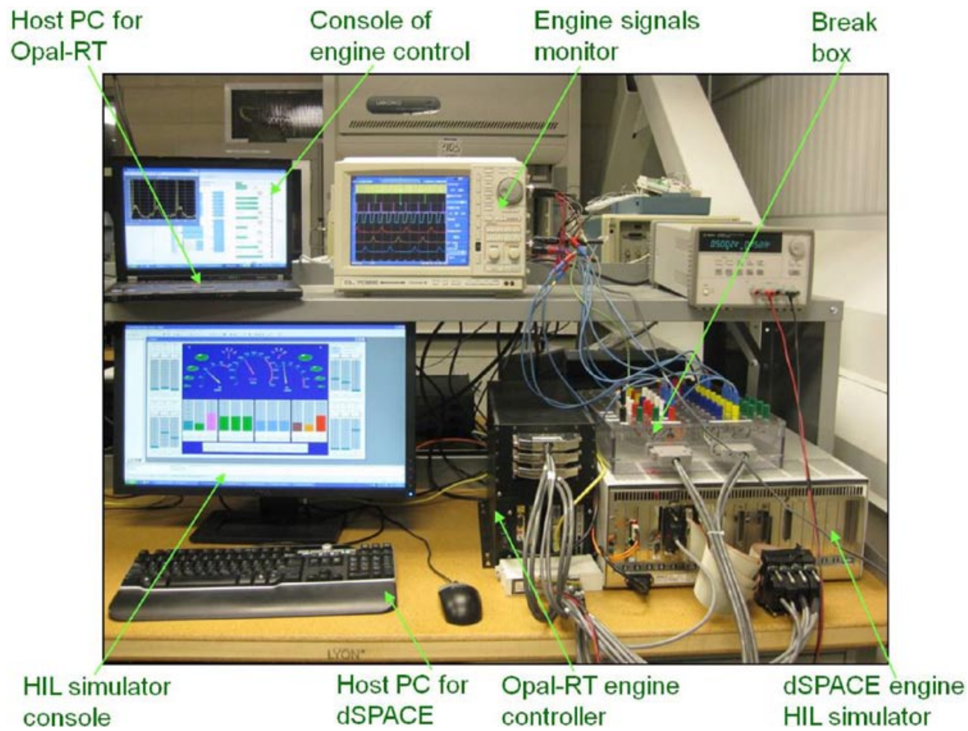

FIGURE 2. HIL simulation Bench for the Control Oriented Engine Model

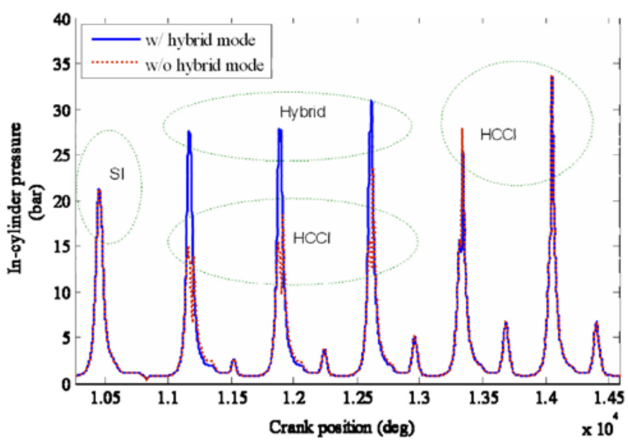

FIGURE 3. Simulation Comparison of One-Step and Proposed Mode Transition From SI To HCCI Combustion

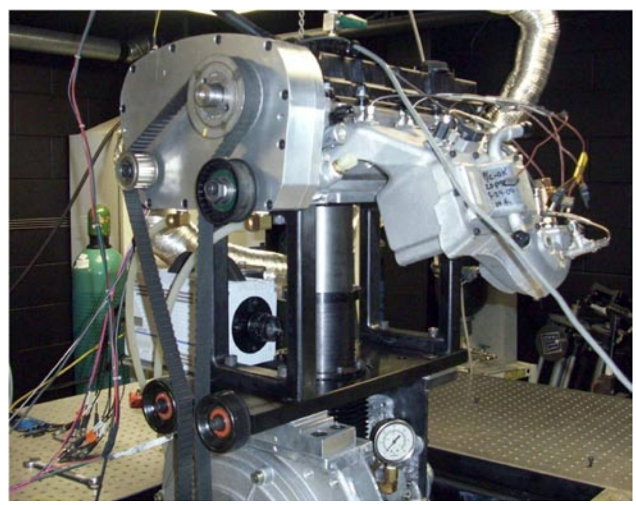

FIGURE 4. Optical Engine Assembly

was designed, along with the flat piston lens. The Hatz engine crankshaft and connecting rod has been redesigned to meet target engine specifications. The optical engine fabrication has been completed (see Figure 4), where a Bowditch optical piston of the target engine was fabricated as well as the flat piston lens. The crank shaft and connecting rod of the optical engine have also been fabricated. A preliminary SI combustion optical engine tests have been conducted; see Figure 5 for a combustion image.

During this fiscal year, we worked closely with Chrysler and selected suppliers for both two-step lift valve and electrical cam phase actuators of the target engine. Feasibility study of implementing the selected two-step lift valve systems into the target engine head was also conducted by Chrysler, and the lift height optimization was conducted at MSU through intensive GT-POWER simulations that provides a 4.4 mm low lift (HCCI combustion mode) specification for both intake and exhaust valves with the intake valve timing centered

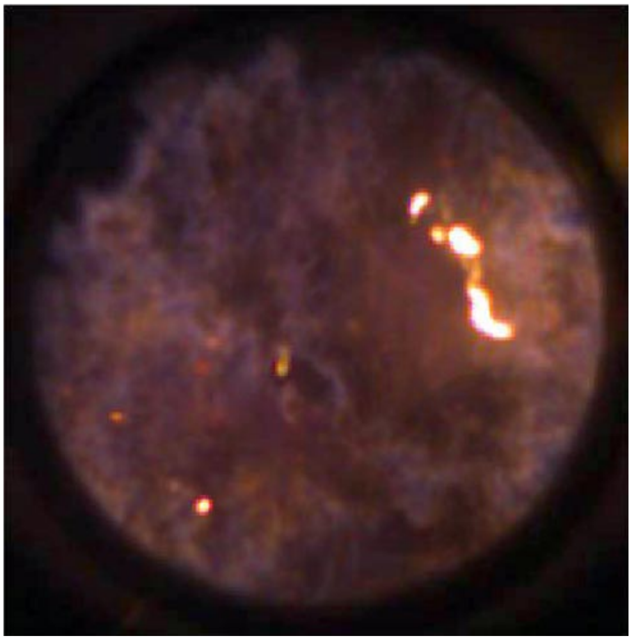

FIGURE 5. SI Combustion Image from Optical Engine Tests

at 450 degrees after combustion top dead center and the exhaust valve at 250 degrees. The GT-POWER simulation also requires the electrical cam phase system to have a range of 80 crank degrees for both intake and exhaust valves. A dynamic model of the electrical variable valve timing systems has been developed in this fiscal year [8]. This model will be used for model based control development and validation.

The control oriented engine model with the two-zone combustion model has be implmented into MATLAB/Simulink environment and validated by off-line simulations using calibrations from the GT-POWER simulations. The validated Simulink engine model was implemenetd into the MSU dSPACE HIL simulation environment.

The development of the prototype engine controller got started in the past fiscal year. The target engine controller consists of an Opal-RT prototype controller and an engine controller in-out box.

Conclusions

This research activity has shown the progress toward the development, implementation, and demonstration of the proposed technology. Specific accomplishments are listed below:

- Target demonstration engine has been selected.
- It is shown that a control-oriented engine model can be developed for combustion mode transition simulations between SI and HCCI combustion and is feasible to be implemented into a HIL simulation environment.
- The HIL simulation results also demonstrated that the transient performance of the mode transition between SI and HCCI combustions is heavily dependent of the mode transition control strategy, and the steady-state control parameters for SI-HCCI hybrid combustion are not optimal for the transient SI-HCCI combustion operation. As a consequence, the model-based control is a necessity
- An optical engine of target engine has been designed and fabricated and a preliminary SI combustion tests were completed.
- Two-step valve lift and electrical cam phase range studies have been completed.

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IV.4 Development of Optimal Catalyst Designs and Operating Strategies for Lean NOx Reduction in Coupled LNT-SCR Systems

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Objectives

The overarching goal of this project is to identify the oxides of nitrogen (NOx) reduction mechanisms operative in lean-NOx traps (LNTs) and in situ selective catalytic reduction (SCR) catalysts, and to use this knowledge to design optimized LNT-SCR systems in terms of catalyst architecture and operating strategies. The project is split into three phases. Activities to date have concentrated on Phase 1 and 2 objectives, which are as follows.

Phase 1

- Elucidate the mechanism of the non-NH_3 pathway for NOx reduction by means of bench-scale reactor, in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) reactor, and temporal analysis of products (TAP) reactor studies.
- Map LNT selectivity to NH_3 as a function of catalyst composition (ceria content and type) and relevant process parameters (NOx loading, purge duration, purge lambda and space velocity).
- Develop a microkinetic LNT model that takes into account the catalyst composition (storage component such as ceria and barium loading as well as precious metal such as Pt loading/dispersion) and H_2, CO, and C_3H_6 reductants.
- Develop low-dimensional models for the LNT and the coupled LNT-SCR unit for different catalyst architectures incorporating microkinetics.

Phase 2

- Determine optimum ceria type and content in model LNT catalysts to achieve best net NOx conversion in serial LNT-SCR catalysts.
- Determine the level of platinum-group metal (PGM) reduction possible in the serial LNT-SCR catalyst system while providing equivalent performance to the corresponding LNT-only system.
- Establish the optimal operating strategy of serial- and double-layer catalyst systems with respect to NOx conversion level and fuel penalty.
- Develop microkinetic SCR model that includes non-NH_3 mechanism.
- Carry out experimental optimization study of segmented LNT-SCR catalyst configurations.
- Establish sulfur evolution on serial- and double-layer LNT-SCR systems.
- Perform simulations of the LNT and coupled LNT-SCR unit using the low-dimensional models to examine the performance features and to identify optimal periodic operation and how it depends on the axial and transverse distribution of the catalytic components.

Fiscal Year (FY) 2010 Accomplishments

The project is on track versus its objectives. During the first year of the project very good progress has been made on Phase 1 activities with some progress on Phase 2. Highlights of accomplishments are as follows.

- LNT/SCR experiments have been conducted that investigate the coupling of a LNT and SCR in series.
- A combination of bench-scale and vehicle experiments confirms the existence of an important non-NH_3 pathway for NOx reduction. This pathway primarily involves olefins which adsorb on the SCR catalyst with subsequent reduction of NOx.
- A microkinetic model for NOx storage and reduction chemistry using H_2 and NH_3 as reductants has been refined and applied to experimental data obtained in a TAP reactor.
- TAP experiments have confirmed an earlier estimate of the diffusion of stored NOx species during regeneration of LNT catalysts.
- Bench-scale data of the CO/NO/H_2O reaction system on model LNT catalysts quantify the pathways for H_2 and NH_3 production. The data show that both a water-gas shift and isocyanate pathways are both important for generating NH_3.
- A crystallite-scale model for NOx storage and reduction has been extended to enable the simulation of the complete cycle. The model can accommodate LNT catalysts of variable loadings of Pt and BaO.

- Spatially resolved capillary inlet mass spectrometer (SpaciMS) experiments for the LNT system provide comprehensive information of the effect of various operating parameters on the generation of NH_3 using H_2 as the reductant. The experiments will enable a direct use of the crystallite-scale model.
- Comprehensive steady-state and transient bench-scale experiments have been conducted for a Fe-Zeolite Socony Mobil (ZSM)-5 catalyst for NH_3-based SCR. Mechanistic-based kinetic models have been developed that capture the main features of the reaction system. A comparison of Fe- and Cu-based catalysts is underway.

Future Directions

Selective Catalytic Reduction Studies:

- We will continue to converge on the mechanism for the non-NH_3 mechanism dominated primarily by the breakthrough of hydrocarbons and conditions for which breakthrough occurs.
- We will complete the mechanistic studies of NH_3 SCR on Fe-based and Cu-based BASF SCR catalysts which will include both steady-state and transient experiments.
- Complete kinetic models will be constructed for NH_3 reduction of NO/NO_2 based on steady-state and transient experiments. These kinetic models will be incorporated into reactor models to evaluate LNT/SCR configurations.

LNT Studies:

- We will complete DRIFTS measurements during typical regeneration conditions on the BASF catalyst. Parametric study of LNT performance in terms of NH_3 formation will be completed.
- Bench-scale studies of NH_3 formation via $NO/CO/H_2/H_2O$ mixtures will be completed and quantified. The kinetics of the main reactions will be determined.
- Continued work will be carried out on the microkinetic modeling of the LNT. The focus will be on incorporating NH_3 chemistry as well as CO and olefins as reductants.
- A crystallite-scale LNT model of NOx storage and reduction with H_2 as reductant will be completed.
- SpaciMS experiments will be conducted to generate data that are compatible with the crystallite-scale model that describes the spatio-temporal evolution of NH_3. Additional experiments will be conducted to map the spatial gradients in the LNT for different feeds and temperatures.
- The SpaciMS will be used to conduct sulfation/desulfation LNT experiments in order to elucidate the formation of SO_2 and H_2S. These experiments will be carried out first with the LNT and then with the LNT/SCR, the latter of which will assess the effect of the SCR.

LNT/SCR Studies:

- Experimental work will commence in evaluating the LNT/SCR reactor system. We will examine different segmented designs and the double-layer catalyst in terms of NOx conversion and the effect of various operating conditions such as temperature, reductant type, lean-rich timing, etc.
- A global reaction-based LNT/SCR model will be further developed to predict the main features of NH_3 generation and NOx SCR as a function of the main reactor and catalyst parameters.
- The effect of PGM and ceria loadings on LNT and LNT/SCR performance will be determined in bench-scale reactor experiments.
- Synthesis of double-layer LNT/SCR monolith catalysts will be completed.
- Kinetic models will be incorporated into low-dimensional LNT and SCR models. Simulations of experiments will be carried out in order to identify deficiencies in the models and to elucidate the trends in the data. This will be an ongoing effort as new bench-flow and TAP data are generated and model improvements are made.

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Introduction

The effective removal of NOx from lean exhaust represents a continuing challenge to the automotive industry. The LNT is a promising technology, particularly for light-duty diesel and gasoline lean-burn applications. Recent studies have shown that the performance of the LNT can be significantly improved by adding an in situ SCR catalyst in series downstream. SCR catalysts promote the selective reduction of NOx with ammonia (NH_3) in the presence of excess oxygen. An in situ SCR catalyst refers to a system where the NH_3 is generated in the upstream LNT and subsequently stored on the SCR catalyst where it reacts with NOx that breaks through the LNT.

Central to this project be the development of microkinetic descriptions of the catalytic chemistry incorporated into monolith reactor models. Mechanistic, kinetic and performance data from bench-scale, DRIFTS, and TAP reactors will be utilized to build the reactor models containing predictive kinetics of the main chemistries. Using vehicle tests, the optimal operating strategy for LNT-SCR systems will be validated with respect to NOx conversion level and fuel penalty. The bench-scale and vehicle tests will be extended to include aged LNT-SCR systems, with the aim of assessing system durability.

Approach

The project activities encompass catalyst synthesis and characterization, kinetics and reactor modeling, vehicle testing, and systems integration (Figure 1). In Phase 1 of the project, the studies focus on two main goals: first, elucidating the mechanism of the non-NH_3 pathway for NOx conversion in LNT-SCR systems and second, developing a microkinetic model which describes the dependence of LNT selectivity to NH_3 as a function of relevant process parameters and catalyst composition (important for subsequent modeling of the NH_3 pathway for NOx conversion). In Phase 2, efforts are directed at establishing the optimal catalyst architecture (Figure 2) and operating strategy of LNT-SCR catalyst systems, with the goal of maximizing NOx conversion level at minimum fuel penalty. A low dimensional LNT-SCR model is being developed that first incorporates the NH_3 reduction pathway and second incorporates the non-NH_3 NOx pathway. The LNT-SCR model is to be used to assist with the system optimization. One aspect of the optimization is to assess prospects for PGM reduction in LNT-SCR catalyst. The LNT-SCR sulfation-desulfation behavior will also be studied. In Phase 3 of the project, the microkinetic model developed in Phase 2 will be completed and will be experimentally verified based on bench reactor and vehicle tests. LNT-SCR system aging will also be studied at the bench reactor and vehicle level, with the aim of assessing system durability and identifying limits on rich exposure and maximum desulfation temperature.

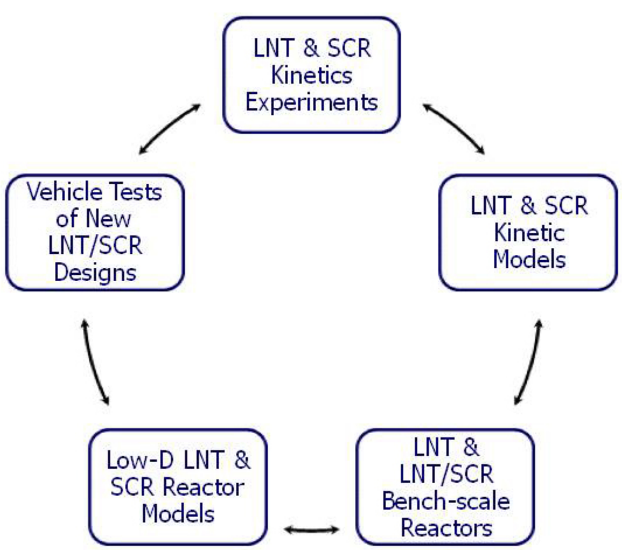

FIGURE 1. Organization of Activities Carried Out by the Project Team

Results

Selected results are provided here to illustrate the various activities that are underway.

Steady-state and transient NOx storage and reduction experiments have been carried out to determine mechanistic pathways and to quantify kinetics of the $NO/CO/H_2O$ on $Pt/BaO/Al_2O_3$ reaction system. The results clearly show the production of NH_3 does not require H_2 as a reductant, with NH_3 forming by the hydrolysis of an adsorbed nitrogen-carbon-oxygen intermediate and by the generation of H_2 via the water-gas shift reaction. Figure 3 shows the evolution of conversion and product distribution as the feed concentration of CO is varied in a mixture containing

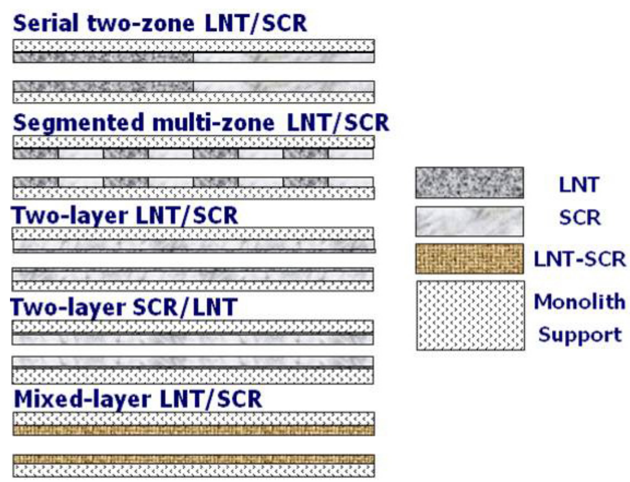

FIGURE 2. Several Catalyst Formulations and Architectures to be evaluated in this Project

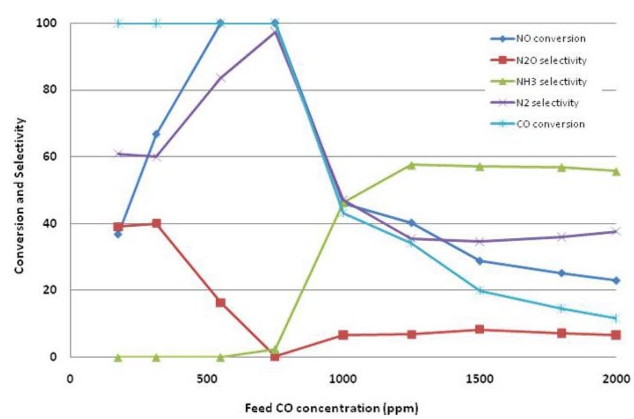

FIGURE 3. Dependence of Conversion and Product Selectivity during NO Reduction for a Feed Containing CO (varied concentration), NO (500 ppm), and H_2O (4%) at a Fixed Temperature of 270°C

CO, NO, and H_2O. As the CO/NO ratio increases, the N-containing product switches from N_2O to N_2 and finally to NH_3. At high CO concentration the inhibition of CO significantly reduces the overall conversion. These results have implications for the optimization of the LNT to generate NH_3.

An experimental study was carried out of steady-state and transient SCR of NO with NH_3 on both commercial and in-house synthesized Fe-ZSM-5 (MFI-type zeolite structure). Experiments included NH_3 uptake and temperature-programmed desorption, steady-state and transient NO and NH_3 oxidation and standard SCR ($NO+NH_3+O_2$) reaction studies. The data clearly suggest that the oxidation of NO is the rate determining step for NH_3-based SCR. A mechanistic-based Langmuir-Hinshelwood kinetic model is proposed in which NH_3 reacts with surface bound NO_2 and nitrous acid via a NH_4NO_2 intermediate. In the absence of NH_3 these species serve to inhibit the adsorption of NO and/or O_2 during NO oxidation. Experiments on monoliths with different washcoat thicknesses conclusively show the appearance of washcoat diffusion limitations at higher temperatures (≥350°C). Figure 4 compares the NOx conversion for two catalysts with the same total catalyst loading but with different lengths and wash coat loadings. The feed contains an equimolar mixture of NO and NO_2 (1,000 ppm each), 1,000 ppm NH_3, and 5% O_2.

Bench-scale reactor studies employing SpaciMS have been carried out to map the conditions for which ammonia is generated in the NOx trap catalyst. Figure 5 shows typical data obtained with the SpaciMS, i.e., three-dimensional plots of NH_3 concentrations measured as a function of time and position along the length of the catalyst monoliths during a single regeneration event. In both cases the regeneration event commenced at around 26 s and lasted 5 s. The catalyst samples were 1" (25.4 mm) in length; hence, the profiles corresponding to 25.4 mm represent the NH_3 concentration measured at the outlet face of the monolith. For both catalysts the NOx storage–reduction zone is largely confined to the front of the catalyst. This is evidenced by the corresponding NO release profiles which show that the maximum gas-phase NOx concentration is attained near the front of the catalyst (data not shown). Consequently, the gas-phase NH_3 concentration increases along the length of the NOx storage-reduction zone, attaining its peak value towards the end of the zone (close to the middle of the catalyst in the axial direction). Subsequently, the NH_3 concentration diminishes due to its consumption by reaction with released NOx that re-adsorbs on the catalyst downsteam of the reductant front and with stored oxygen in the rear of the catalyst.

A combination of vehicle experiments and laboratory tests has been carried that confirm a non-

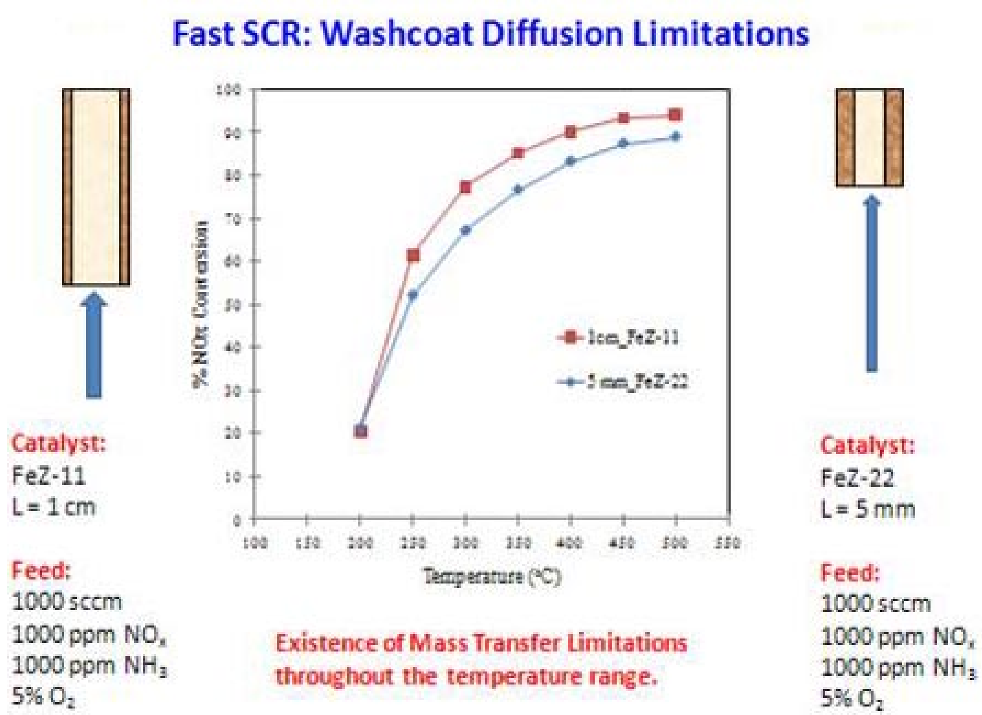

FIGURE 4. Comparison of NO Conversion Obtained During the Standard SCR Reaction for Catalysts with the Following Two Different Dimensions: a) washcoat loading by (wt% of entire piece): 11%, length = 2 cm, and b) washcoat loading by (wt% of entire piece) 22%, length = 1 cm, inlet feed: 500 ppm NO, 500 ppm NH_3, 5% O_2, total flow rate: 1,000 sccm, balance gas: Ar

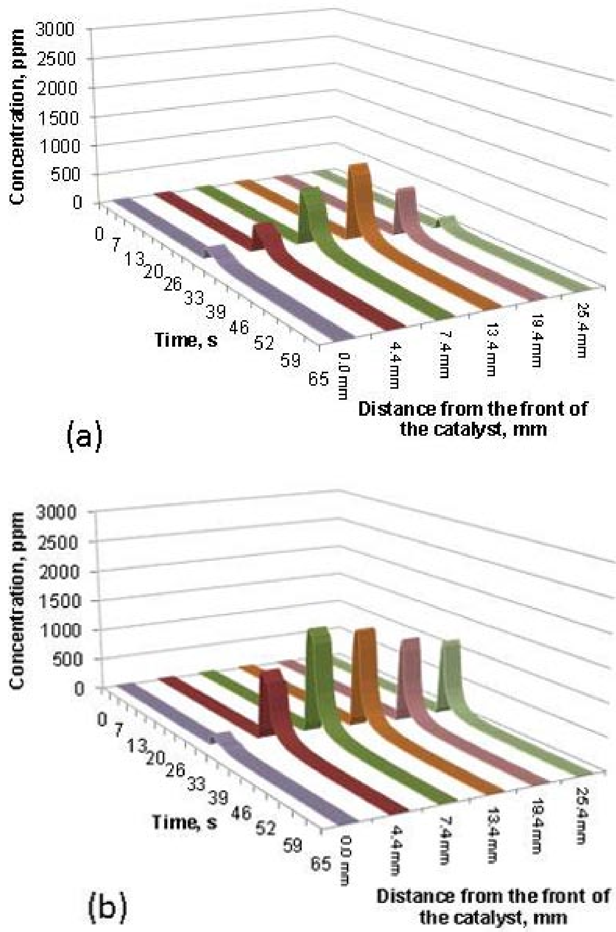

FIGURE 5. Evolution of Intracatalyst NH_3 Concentrations during Rich Phase Regeneration at 200°C; (a) C-100 (containing 100 g CeO_2/L); (b) C-0 (catalyst without CeO_2)

NH_3 pathway for NOx reduction. This pathway is associated with the presence of hydrocarbons. To investigate the ability of SCR catalysts of this type to utilize different reductants, steady-state NOx reduction experiments were conducted using ethene, propene and a CO/H_2 mixture. As shown in Figure 6, the catalyst is able to utilize each of these reductants for NOx reduction, to varying degrees. As expected, propene is a more active reductant than ethene, while somewhat surprisingly, CO/H_2 is an even better reductant under these conditions (although only in the absence of oxygen). This is a critical issue because operation of the LNT should be optimized to provide the reductant consumed in the downstream SCR. The data reveal the existence of the non-NH_3 pathway in pre- and post-LNT gas phase composition measurements during LNT regeneration with downstream NOx reduction on a commercial Cu-based zeolite SCR catalyst.

Quantitative studies of the behavior of ethylene as the only reductant during rich purge of the LNT/SCR

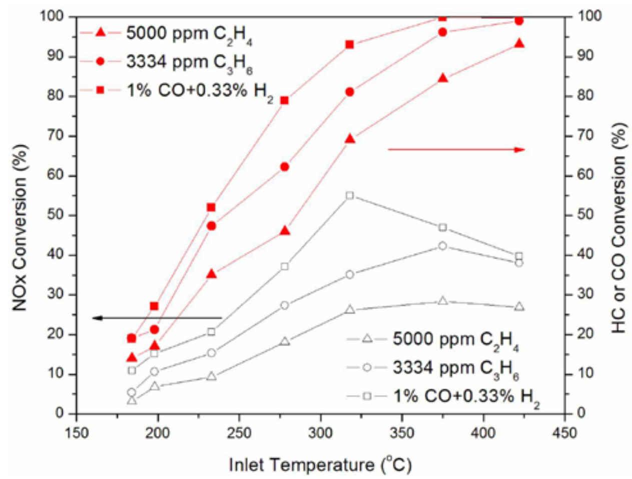

FIGURE 6. Steady-State NOx Reduction over Commercial Cu-zeolite SCR Catalyst Using Different Reductants: feed gas: 300 ppm NO, 5% CO_2, 5% H_2O, N_2 balance, gas hourly space velocity = 30,000 h^{-1}, reductant as shown

has clearly measured the ethylene rich purge of the LNT and the subsequent lean-SCR performance observed for various lengths of time in a combined LNT/SCR system. The SpaciMS system was used to measure gas compositions in all potential locations (pre LNT, within the LNT, post-LNT, within the SCR, and post SCR) for key reactants and products: e.g., NH_3, C_2H_4, NO, NO_2, etc. Some more specific findings are as follows:

- Ethylene is a useful reductant for LNT purging and is also stored in the commercial SCR catalyst (BASF) and behaves as an ammonia surrogate in lean-SCR in this formulation.
- The data collected to date supports the hypothesis that ethylene and propylene enjoy a temperature window that favors their use as an LNT purge reductant and their ability to act as lean-SCR reductants in a Cu-based SCR system using zeolite materials of a proprietary nature.

A crystallite-scale monolith reactor model has been upgraded to simulate the complete cycle of NOx storage and reduction. The model captures the interaction between the precious metal and the storage functions of a Pt/BaO catalyst. The trapping of NO_2 occurs via a spillover mechanism and through the gas phase. Simulations are underway which show how the stored NOx distribution evolves during multiple storage/regeneration cycles.

Conclusions

The project is on track versus its objectives. A combination of bench-scale reactor experiments of LNT, SCR, and LNT/SCR systems, which includes the use of SpaciMS, is providing a database for subsequent refinement of reactor models containing kinetic models with varying degrees of complexity.

FY 2010 Publications/Presentations

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2. Xu, J., A. Kumar, M.P. Harold, and V. Balakotaiah, "Microkinetic Modeling of NOx Storage and Reduction with H_2 as the Reductant," ISCRE 21, Philadelphia, PA June, 2010.

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6. Crocker, M., V. Easterling, J. Wang, M. Dearth, R. McCabe, J. Theis, "Laboratory Product Speciation Studies of the LNT + in-situ SCR NOx Emission Control Concept", oral presentation at the 2010 Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, September 27-30, 2010.

7. Wang, J., Y. Ji, M. Crocker, "The Effect of Regeneration Conditions on the Selectivity of NOx Reduction in a Fully Formulated Lean NOx Trap Catalyst", oral presentation at the 6^{th} International Conference on Environmental Catalysis, Beijing, September 12–15, 2010.

8. Ji, Y., V. Easterling, C. Fisk, M. Crocker, J.-S. Choi, "Effect of Aging on the NOx Storage and Regeneration Characteristics of Fully Formulated Lean NOx Trap Catalysts", poster presentation at the 6^{th} International Conference on Environmental Catalysis, Beijing, September 12–15, 2010.

9. Harold, M., M. Crocker, R. McCabe, M. Dearth, J. Theis, V. Balakotaiah, D. Luss, J.-S. Choi, and C.Z. Wan, "Studies of LNT/SCR," poster presentation at the 2010 Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, September 27–30, 2010.

IV.5 Three-Dimensional Composite Nanostructures for Lean NOx Emission Control

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Fiscal Year (FY) 2010 Objectives

- Synthesize three-dimensional (3D) metal oxide nanowire/nanodendrite arrays on both planar and monolith substrates.
- Fabricate 3D mesoporous metal oxide/perovskite composite structured nanowire/nanodendrite arrays on both planar and monolith substrates.
- Characterize the chemical, morphology and structure of the grown metal oxide and metal oxide/perovskite composite nanostructures using a wide array of electron microscopy and spectroscopy techniques.

FY 2010 Accomplishments

- Synthesized and characterized metal oxide nanowire/nanodendrite arrays (such as ZnO, Ga_2O_3, Zn_2SnO_4 and TiO_2) on various planar substrates such as silicon, glass and monolith substrates such as ceramic honeycomb.
- Fabricated and characterized mesoporous composite nanowire/nanodendrites such as ZnO/(La,Sr)MnO_3 (LSMO), ZnO/(La,Sr)CoO_3 (LSCO) and TiO_2/LSMO, etc. by pulsed laser deposition (PLD),sputtering process and wet chemical method.
- Found the high activity of $LaMnO_3$ (LMO) systems for O involving reactions arising from its ability to support partially O covered surfaces.

Future Directions

- Conduct systematical optimization of 3D composite nanowire/nanorod arrays based on metal oxides (ZnO, Ga_2O_3, Zn_2SnO_4 and TiO_2) and perovskite (LSMO, LSCO).
- Load precious metal nanoparticles (Pt, Au, Pd) before and after barium oxide and perovskite nanofilm loading on metal oxide nanowire/nanodendrite arrays.
- Optimize the catalysis evaluation system and evaluate the catalytic performance of 3D composite nanowire/nanorod arrays on NOx storage and reduction performance.
- Calculate reaction barriers for various elementary steps involved in the oxygen dynamics on the MnO_2-terminated (001) LMO surface. Then incorporate NO and NO_2 interactions.

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Introduction

Nowadays, lean-burn engines are attracting more and more attention than conventional gasoline engines due to their higher fuel efficiency and lower CO_2 emission [1-6]. However, under lean-burn conditions, the nitrogen oxides (NO_x) exhaust emissions cannot be efficiently reduced over the classical three-way catalysts in the presence of excessive O_2 [1,4,7]. The NO_x emissions have multi-fold hazards on the atmosphere, environment and human health, due to the formation of fine particles, ozone smog, acid rain and eutrophication [8]. NO_x storage/reduction (NSR) technology is regarded as the most practical technology for lean-burn gasoline and diesel vehicles. Our overall project objective is to synthesize, characterize and model a new class of oxide-based 3D composite nano-catalysts for the NO_x storage, and NO_x reduction, hydrocarbon (HC) and carbon monoxide (CO) oxidation, and particular matter filtering under lean-burn conditions.

Approach

In the calculation part, we use the first principles thermodynamics approach to construct surface phase diagrams of (001) AO and BO_2- terminated ABO_3 perovskite surfaces and choose gaseous O_2 as the principal source of surface oxygen. In the experiment part, we use chemical vapor deposition, carbothermal, and hydrothermal methods to synthesize metal oxide nanowires/nanorods array and perovskite nanoparticles. PLD, sputtering and sol-gel spin coating methods were also used to combine with the hydrothermal method or other methods to fabricate a metal oxide/perovskite composite nanostructure array. Annealing was used to improve the crystallinity and dispersity of 3D composite nanostructures.

Results

During the past year, we focused on and initiated our research work toward the successful synthesis of nanowire/nanodendrite arrays of metal oxides (ZnO, Ga_2O_3, Zn_2SnO_4 and TiO_2) and perovskite(LSMO, LSCO). We have achieved ZnO nanowires and nanorods array by both chemical vapor deposition (CVD) and hydrothermal methods. ZnO nanowires or nanodendrite arrays at relatively low temperature (~500-700°C), using a CVD process facilitated by graphite. For example, two types of pure ZnO nanodendrites have been grown at ~700°C (Figure 1a): single crystal nanodendrites and nanocombs (Figure 1c). Figure 1d shows the cross-section scanning electron microscopy (SEM) images of ZnO nanorod arrays grown by the hydrothermal method. The growth of ZnO nanorod arrays is hexagonally patterned and vertically aligned on the Si substrate. The diameter and length of the ZnO nanorods are very uniform with an average diameter and length of 80 nm and 1 µm, respectively. Figure 1e is an SEM image showing the Zn_2SnO_4 (ZTO) nanowires grown on an Ag-coated SiO_2/Si substrate by the CVD method. High yield of ZTO nanowires grew uniformly with ~50-200 nm in diameter and tens of micrometers in length on the substrate. The insets in Figure 1e revealed a 1 mm×1 mm substrate successfully deposited with uniformly grown ZTO nanowires and the closer view of zigzag periodic nanowires.

Besides ZnO and ZTO, we also successfully synthesized TiO_2 nanorods array on silicon, glass and ceramic honeycomb substrates. Figures 2a and 2b show the SEM images of the synthesized TiO_2 nanorod arrays on ceramic honeycomb substrate by the hydrothermal method. Figures 2c and 2d depict the transmission electron microscopy (TEM) image and the selective area electron diffraction (SAED) pattern of the corresponding nanorod, respectively. TEM results suggested that the TiO_2 nanorods arrayed as synthesized are single crystals. Figure 2e shows a typical SEM image revealing the morphology of Ga_2O_3 nano-feathers grown from Au-coated Si substrate using carbothermal method.

Based on the metal oxide nanowire arrays, metal oxide nanowire/perovskite nanofilm composite materials were fabricated. Figure 3a shows the top view of LSMO/ZnO core-shell nanorod arrays. Figure 3b and 3c show the bright field and dark field TEM images of a typical as-deposited ZnO/LSMO nanorod, respectively. The diffusive ring pattern can be found in the inset in Figure 3b in addition to the dot pattern that corresponds to ZnO single crystal. Therefore, the LSMO nanofilm coated on ZnO nanorod is polycrystalline but with poor crystallinity. In Figue 3c we can see clearly the core-shell structure of ZnO/LSMO nanorod. Figures 3d and 3e depict the TEM image and energy-dispersive X-ray (EDX) spectrum of TiO_2/LSMO nanorods before annealing. EDX spectrum results confirmed the formation of TiO_2/LSMO core-shell nanorods.

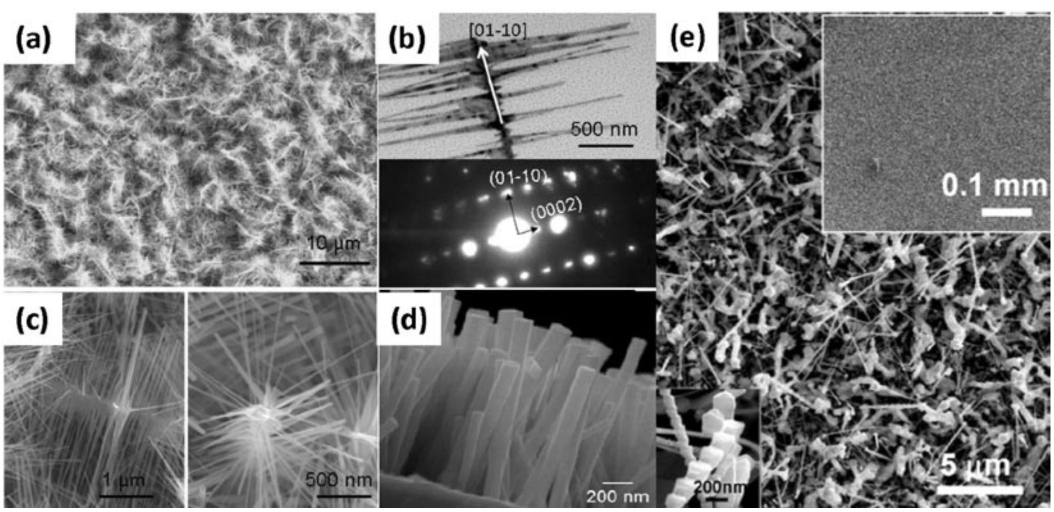

FIGURE 1. a) A top-view SEM image of self-catalyzed ZnO nanodendrites grown on Si substrate at ~700°C. b) A TEM image showing a nanocomb with single-crystal structure, inset is the corresponding selected area electron diffraction pattern. c) ZnO nanodendrites and nanocombs with (left) and without (right) exhibiting certain core-branch crystal symmetry. d) A cross-sectional view SEM image of ZnO nanorod arrays on Si substrate by the hydrothermal method; e) a top view SEM image of ZTO periodic nanowires, with insets displaying the millimeter-scale uniform deposition of ZTO and the closer view of ZTO nanowires.

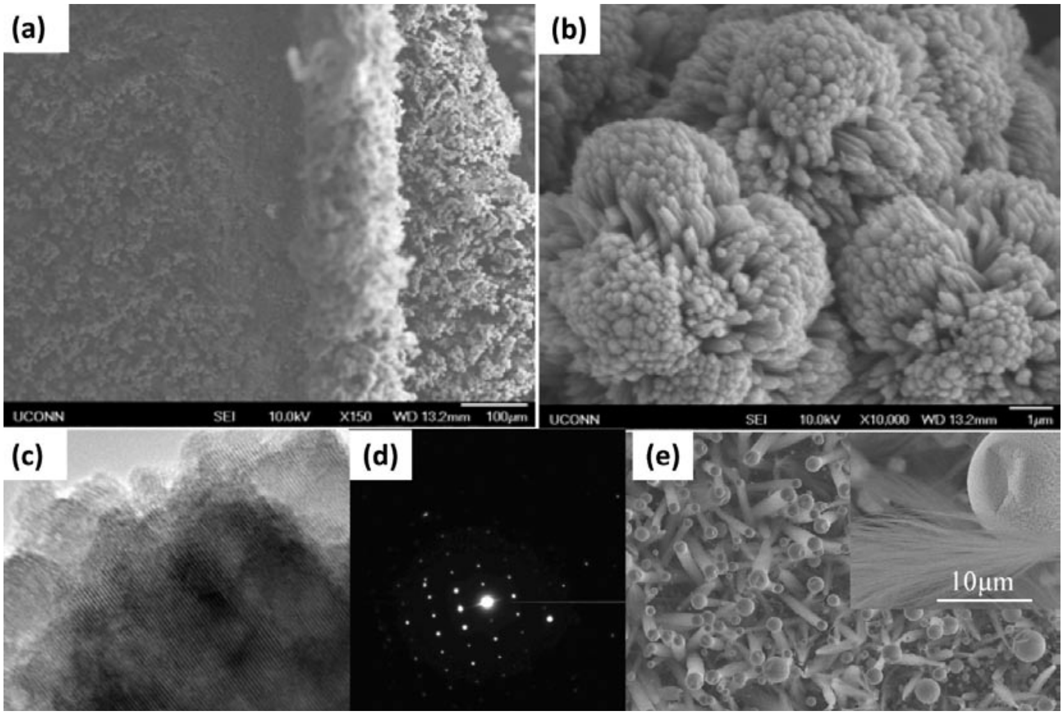

FIGURE 2. Low (a) and high (b) magnification SEM images of TiO_2 nanorod arrays on ceramic honeycomb substrate. (c) and (d) are TEM image of TiO_2 nanorods and the corresponding SAED pattern, respectively. (e) A typical low magnification SEM image of Ga_2O_3 nanofeathers grown on Au-coated Si substrate. The inset shows the zoom-in detailed morphology of an individual Ga_2O_3 nanofeather.

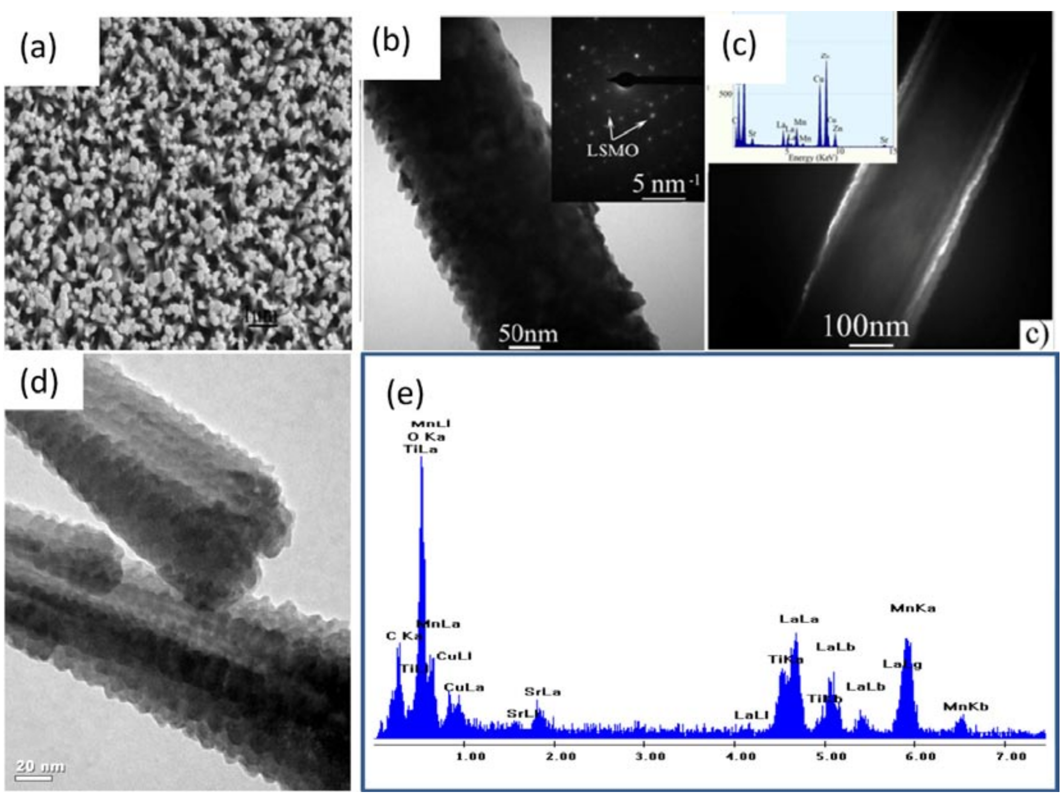

FIGURE 3. (a) A top-view SEM image of LSMO/ZnO nanofilm-nanorod arrays; typical TEM images of a LSMO/ZnO composite nanowire: b) bright field and c) dark field. (e) TEM image and EDXS spectrum of TiO_2/LSMO nanorod.

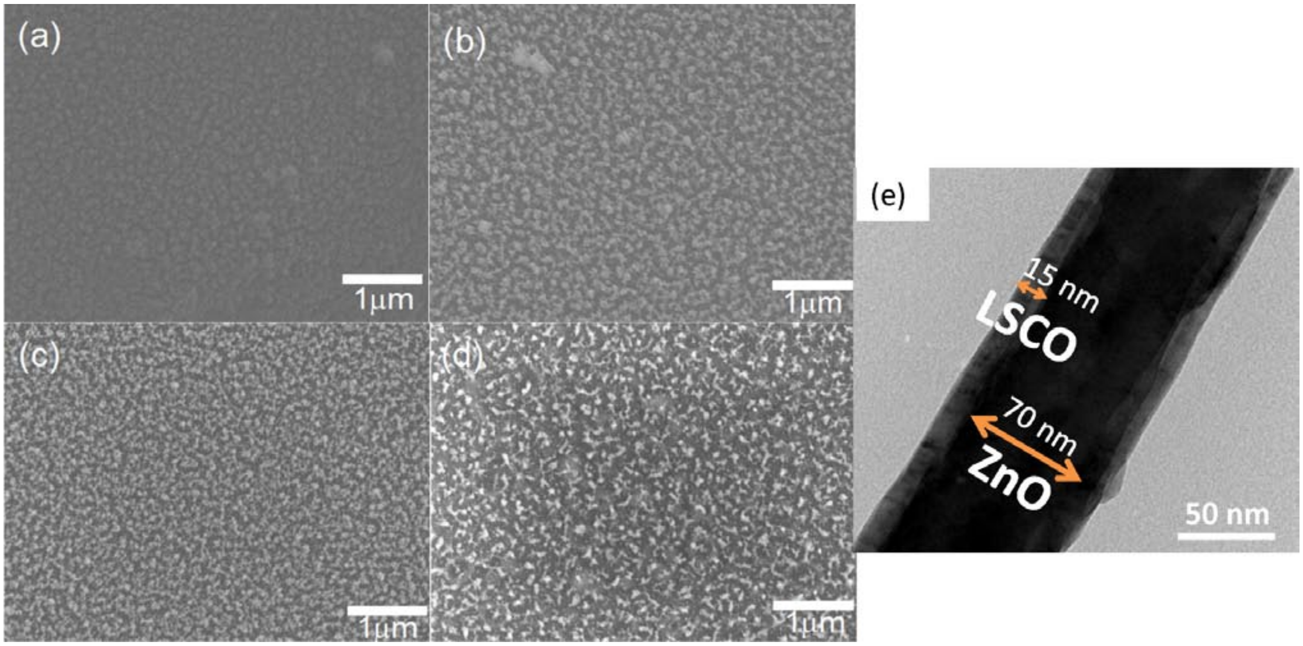

FIGURE 4. LSCO films deposited at room temperature on Si substrate (a) as made, and annealed at different temperatures: (b) 350°C, (c) 550°C, and (d) 750°C for 2 hours in air. e) TEM image of LSCO deposited on ZnO nanowire at 750°C for 10 minutes.

Figures 4a-d are the SEM images of the LSCO on Si substrates grown at room temperature, which show that highly porous structured films could be obtained. The porosity of the films increases with the annealing temperature. At high annealing temperatures, increased atomic mobilities result in clustering of the small islands. At high growth temperatures (>550°C), a uniform and condensed LSCO film is formed. Figure 4e shows the TEM image of an LSCO film on a ZnO nanowire grown at 750°C for 10 minutes, which indicates that ZnO nanowires can be uniformly coated with LSCO.

Meanwhile, a schematic of the resulting surface phase diagram using the first principle thermodynamics analysis using density functional theory (DFT) is shown in Figure 5, which shows the stability of various surface phases (O vacancies, O ad-atoms and clean surface) as a function of temperature and O_2 partial pressure. Most notably, it can be seen that the clean

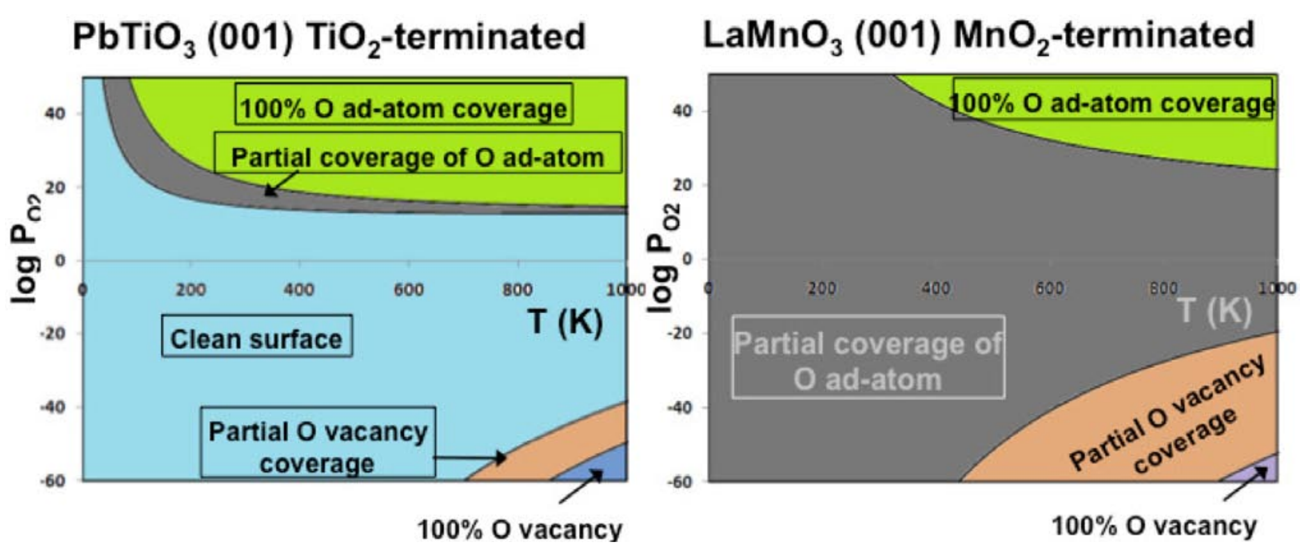

FIGURE 5. A DFT calculated pressure-temperature phase diagram for $PbTiO_3$ and LMO surfaces at thermodynamic equilibrium under various O_2 gaseous environments.

stoichiometric surface is stable under a wide range of achievable temperature and pressure conditions in the case of $PbTiO_3$, making this system catalytically inactive. In contrast, the partially oxygen covered surface is more stable in the case of LMO under a wide range of achievable temperature and pressure conditions, making this system an active catalyst for reactions involving oxygen. These conclusions are consistent with expectations.

Conclusions

In FY 2010, we have successfully advanced the project according to the projected timeline and reached the project milestones. Main accomplishments are listed as follows:

- Successful synthesis and characterization of ZnO, Ga_2O_3, Zn_2SnO_4 and TiO_2 nanowire/nanodendrite arrays on various substrate such as silicon, glass and ceramic honeycomb substrate.
- Successful fabrication and characterization of 3D composite nanostructures (such as ZnO/LSMO, ZnO/LSCO and TiO_2/LSMO) by PLD, sputtering process and wet chemical methods.
- Identification of the high activity of LMO systems for O involving reactions arising from its ability to support partially O covered surfaces by calculation.

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7. P. Shimpi and P.X. Gao, *Large scale synthesis of ZnO nanodendrites using in-situ carbothermal method and their ethanol sensing property*, ACS National Meeting, Boston, August, 2010.

8. W.J. Cai, and P.X. Gao, *Investigation on the contradictory gas sensing behaviors of ZnO and Zn_2SnO_4 crystalline nanowires arrays*, ACS National Meeting, Boston, August, 2010.

9. W.J. Cai, P. Shimpi, D.L. Jian, and P.X. Gao, *Chemical and thermal stability, and gaseous catalytic and sensing behaviors of ZnO/(La,Sr)CoO_3 composite nanowire arrays*, ACS National Meeting, Boston, August, 2010.

9. P.X. Gao, *Three-dimensional Composite Nanostructures for Lean NO_x Emission Control,* DOE Vehicle Technology Program Annual Merits Review Meeting, Washington, D.C., June 10, 2010.

10. P.X. Gao, *Three-dimensional Composite Nanostructures for Lean NO_x Emission Control,* DOE Headquarters, Washington, D.C., March 31, 2010.

11. P.X. Gao, *Hierarchical Composite Nanostructures for Energy, Environmental and Sensing Applications,* Materials Science and Engineering Program, Worcester Polytechnic Institute, Worcester, MA, March 19, 2010.

12. P.X. Gao, *Composite nanowire catalysts for energy, environmental and sensing applications,* Gordon Research Conference - Catalysis, Colby-Sawyer College in New London NH, June 27 – July 2, 2010.

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15. P. Shimpi and P.X. Gao, *A universal growth process for various functional nanowire architectures without using* *metal catalysts*, Materials Research Society Fall Meeting, Boston, December, 2009.

16. P. Shimpi and P.X. Gao, *Controlled annealing induced structure and photoluminescence property evolution in solution-processed Mg–alloyed ZnO nanowires,* Materials Research Society Fall Meeting, Boston, December, 2009.

17. M. F. Sarac, J. A. Mackey, P. Shimpi, D.S. Kim, and P.X. Gao, *Lateral heterojunction micro-networks of semiconductor nanowires/nanofilms*, Materials Research Society Fall Meeting, Boston, December, 2009.

18. W.J. Cai, and P.X. Gao, *Investigation on the contradictory gas sensing behaviors of ZnO and* Zn_2SnO_4 *crystalline nanowires arrays*, Materials Research Society Fall Meeting, Boston, December, 2009.

19. W.J. Cai, P. Shimpi, C. Brooks, and P.X. Gao, *Chemical and thermal stability, and gaseous catalytic and sensing behaviors of ZnO/(La,Sr)*CoO_3 *composite nanowire arrays*, Materials Research Society Fall Meeting, Boston, December, 2009. (oral)

Special Recognitions & Awards/Patents Issued

1. Research on Ag_2O/Zn_2SnO_4 hybrid nanowires and their unique reversible catalytic multi-gas sensing is highlighted as the front cover story on *Journal of Materials Chemistry, Volume 20, issue 25,* June 2010.

IV.6 Experimental Studies for DPF, and SCR Model, Control System, and OBD Development for Engines Using Diesel and Biodiesel Fuels

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DOE Technology Development Manager:
Ken Howden

Subcontractors:
- Oak Ridge National Laboratory (ORNL), Oak Ridge, TN
- Pacific Northwest National Laboratory (PNNL), Richland, WA

Objectives

- Experimentally validated reduced order models and state estimation algorithms.
- Increased knowledge of particulate matter (PM) maldistribution, loading and NO_2/PM ratio effects on passive regeneration, bio-fuel blends, and aging for diesel particulate filters (DPFs).
- Increased knowledge of NH_3 storage behavior, optimal NH_3 loading, hydrocarbon (HC) poisoning, and aging for selective catalytic reduction catalysts (SCRs).
- Understanding effect of sensor type/configuration on state estimation quality.
- Optimal reductant strategies for SCR operation and DPF regeneration.

Fiscal Year (FY) 2010 Accomplishments

The most significant accomplishments of this project to date are:

- Developed a new procedure to measure a DPF's passive oxidation rate as a function of NO_2 concentration, temperature and PM filter loading, NO_2/PM ratio and exhaust flow rate.
- Developed SCR models for the Fe-zeolite ORNL reactor data.
- Created a reduced order model of a diesel oxidation catalyst (DOC) suitable for internal state estimation and a high-fidelity simulation of the DPF.
- Prepared the project test cell including two production engines, aftertreatment systems, an integrated data acquisition system, and a suite of both commercial off-the-shelf and prototype sensors.

Future Directions

- Calibrate reduced order models with experimental data and quantify the effect of model reduction compared to high-fidelity models.
- Develop state estimation strategies, and understand the effects of different sensor combinations/types.
- Conduct fundamental studies in DPF PM oxidation kinetics and SCR NO_X reduction kinetics.

Introduction

To meet future heavy-duty diesel emission standards for oxides of nitrogen (NOX) and PM, engine manufacturers will likely use a combination of exhaust aftertreatment devices, including DOCs, DPFs, and SCR. Both the DPF and the SCR require injection into the exhaust stream of reductants – diesel fuel for DPF PM regeneration and urea for SCR NOX reduction. Closed-loop control of reductants is envisioned to ensure high PM and NOX conversion while minimizing expensive reductant usage. Being able to estimate the internal operating state of all the devices in an aftertreatment system can facilitate advanced closed-loop control strategies and improve strategies used for on-board diagnostics (OBD).

The focus of this project is to develop experimentally validated DOC, DPF and SCR models with real-time internal state estimation strategies that support future OBD, advanced control system, and system optimization objectives for DOC-DPF-SCR aftertreatment systems that minimize the energy penalty of meeting emission regulations. Studying the effects of sensor type and combinations on state estimate quality is an inherent aspect of the estimator design process. State estimate quality is ultimately limited by the accuracy of the device and sensor models. Thus, two additional phases of this work focus on developing SCR and DPF models in specific, high-impact areas. The DPF research includes PM maldistribution, PM loading and passive regeneration over large NOx/PM ranges for engines using both diesel and biodiesel-diesel fuel blends, and optimal active regeneration. The SCR research will examine ammonia distribution, optimal ammonia loading, and hydrocarbon poisoning as a function of engine and fuel type.

Approach

This project uses a consortium-like structure to leverage the unique experience of engine manufacturers, sensor developers, catalyst suppliers, and national laboratories to achieve the project goals. This ensures development of fundamental knowledge with a system-level focus not typically seen in user-specific research projects that concentrate only on the sensor, or the catalyst, or the engine.

The approach to achieving the goal of DOC, DPF, and SCR state estimation strategies uses a mix of simulation-based analysis and experimental studies with a combination of off-the-shelf and prototype sensor technologies. Using both engine test cell and reactor data, high-fidelity model calibrations can be used as the basis for reduced order model forms, suitable for state estimation strategy development. Because all three devices exhibit nonlinear, dynamic behavior, nonlinear state estimation strategies will be developed and used to examine postulated sensor type and combination scenarios. During this simulation/experimental process studies will be carried out to uncover key fundamental phenomena important for device modeling.

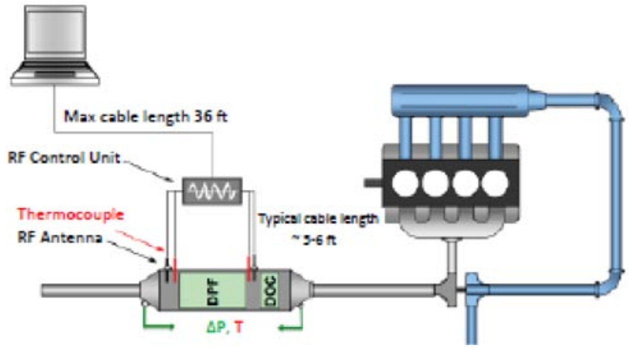

FIGURE 1. Schematic shows the installation approach for the Filter Sensing Technologies radio frequency DPF mass retained sensor.

Results

The experimental engine test facilities are vital to several aspects of the project – model calibration, fundamental DPF oxidation and biodiesel behaviors, and development of state estimation strategies based on both commercial-off-the-shelf and prototype sensors. Once repeatable calibrations and models are established these sensors could have a dramatic impact on the DPF model approach used for state estimation. The existing test facilities at Michigan Tech were modified to accommodate the unique aspects of this project including installation of:

- Cummins 2007 ISL 365/450 hp and 2010 ISB 330 hp engines and aftertreatment systems.
- Two prototype, wide-range, PM concentration sensors.
- Incorporation of a prototype radio-frequency DPF mass retained sensor (Figure 1 and Figure 2).
- Four NO_X sensors integrated into the test cell to monitor the NO_X and O_2 concentrations at different locations of the exhaust system in real time.
- Watlow inline exhaust heaters (25 kW) integrated into the exhaust system to provide independent/ wider range of exhaust temperatures.
- A reconditioned dynamometer.
- Serviced components of an AVL/Pierburg gas analyzer.
- An AVL Fourier transform infrared analyzer.

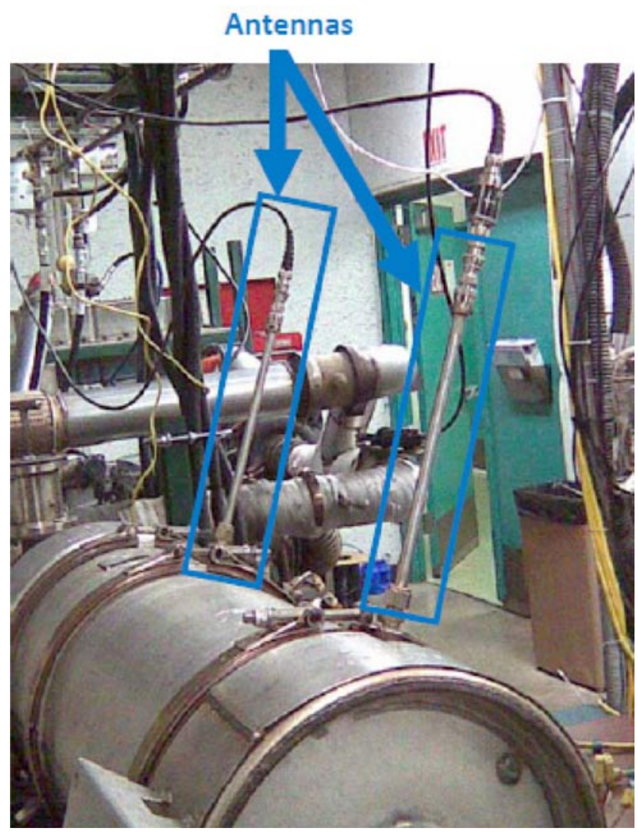

FIGURE 2. DPF Mass Sensor Antennas

- A unified data acquisition hardware and software system.
- A new fuel building.

Using test data supplied by Michigan Tech, Watlow completed design of a novel exhaust gas heating system. To our knowledge the heaters are a new engine test cell concept and will permit controlled, independent variation of exhaust gas temperature while keeping the gas concentrations, dictated by the engine's speed/load/ exhaust gas recirculation settings, relatively constant.

The most significant result of this project is the passive oxidation rates from the ISM and ISL engines have been modeled using the one-dimensional (1-D) catalyzed particulate filter (CPF) high fidelity model using a single set of kinetic parameters. Being able to model the passive NO_2 oxidation of accumulated PM in the DPF is critical to creating accurate state estimation strategies. Understanding the effect of fuel type (ultra-low sulfur and biodiesel blends) and the effect of DPF loading level on oxidation kinetics are primary goals. Test plans, protocols and analysis procedures were developed to calibrate passive oxidation kinetics from engine test cell data.

Figure 3 shows the model predicted reaction rates as a function of temperature conditions for seven different conditions. It can be observed that the model predicted reaction rates show a linear trend with temperature on a logarithmic scale with slopes of 71 kJ/mol for the passive and 125 kJ/mol for thermal which compares to 73 kJ/mol and 125 kJ/mol, respectively, that were used in the 1-D model.

Reduced order models for the DOC are important since outputs of the DOC estimator are inputs to the DPF and SCR estimator. The low fidelity DOC model is derived from an already existing high fidelity model and was developed using MATLAB®/Simulink® with the capability of optimization based calibration. The reactions considered in both the high- and low-fidelity models are the carbon monoxide (CO), nitric oxide (NO) and hydrocarbon oxidation (C_3H_6). The reduced order model consists of one bulk gas temperature state and five bulk species states (CO, NO, NO_2, C_3H_6 and O_2) for each axial element. This is in contrast to using two species states in each element – one for the bulk flow and one for the gas concentration near the catalyzed substrate surface.

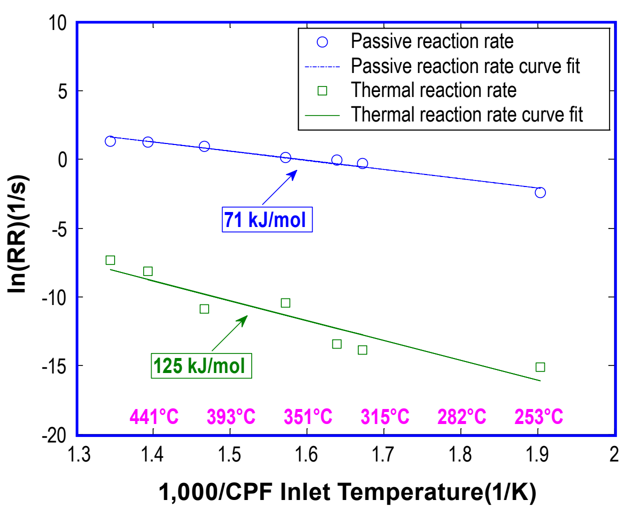

FIGURE 3. Arrhenius plot of model-predicted passive and thermal oxidation reaction rates. The passive oxidation reaction rates are normalized by the NO_2 mole fraction.

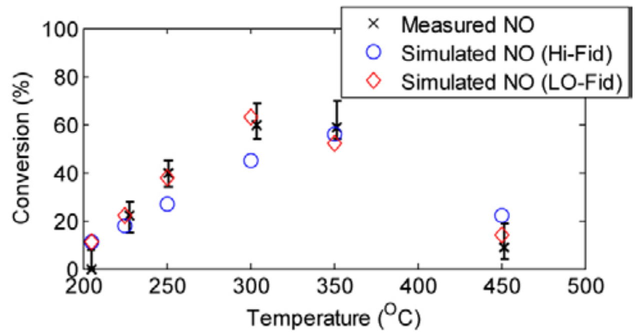

FIGURE 4. Comparison of the high fidelity, low fidelity and measured NO conversion efficiencies.

The measured CO and HC conversion efficiencies of the DOC are almost 100% across the temperature range and the model is able to predict the conversion efficiencies within the measurement uncertainty. Figure 4 shows the comparison of the NO conversion efficiency between the low-fidelity model, high-fidelity model and measured values from a similar DOC, but not the same, as ISB DOC. Except at 300°C and 350°C, the NO to NO_2 conversion efficiency predicted by the low-fidelity model is within the measurement uncertainty. Instead of trying to refine this calibration more, data for the ISB engine's DOC is being accumulated and will be used for final calibration and model reduction evaluation.

It should be noted that in a DOC, the reactions take place almost instantaneously and temperature is the slowest transient. A second approach to a low-fidelity DOC model is being worked on which consists of two temperature states and quasi-steady reactions for each element.

A 1-D CPF high fidelity model development has continued based on discussions with industry partners. The catalyst sub-model has been undergoing significant improvement specifically in being able to model the actual location of the catalyst as shown in Figure 5, and tailoring the domain of gaseous oxidation reactions to the catalyst location. In addition, the PM oxidation calculations have been integrated into the catalyst sub-model so as to use local oxidant (O_2 and NO_2) concentrations in the PM cake and substrate wall in determining PM oxidation reaction rates.

Conclusions

This project has shown progress toward the development of experimentally validated DOC, DPF, and SCR models with real-time internal state estimation strategies that support future OBD, advanced control system, and system optimization objectives for DOC-

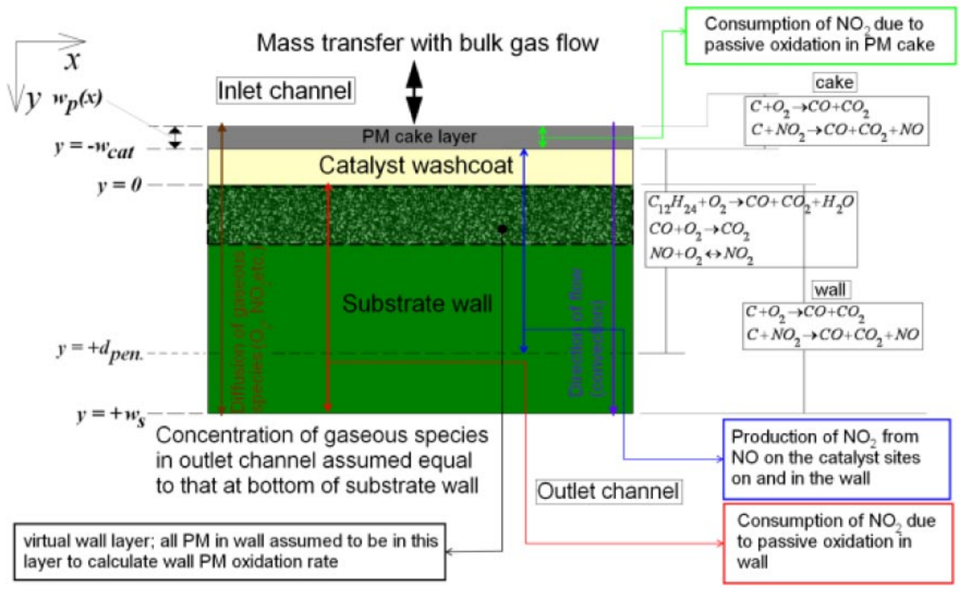

FIGURE 5. Schematic showing reaction scheme and domains used in the PM cake + catalyst washcoat + wall element in the CPF model.

DPF-SCR aftertreatment systems that minimizes the energy penalty of meeting emission regulations.

Specific conclusions are as follows:

- The new procedure to measure a DPF's passive oxidation rate as a function of NO_2 concentration, temperature and PM filter loading, NO_2/PM ratio and exhaust flow rate is an advancement in determining passive oxidation rates.
- The reduced order model of the DOC is suitable for internal state estimation.
- The high-fidelity simulation model of the DPF will provide a good basis for developing the reduced order model.
- The project test cell including two production engines, aftertreatment systems, an integrated data acquisition system, and a suite of both commercial off-the-shelf and prototype sensors is an excellent set-up for experimental research on this project.

FY 2010 Publications/Presentations

1. Oral Presentation: G. Parker, "Experimental Studies for DPF, and SCR Model, Control System, and OBD Development for Engines Using Diesel and Biodiesel Fuels," 2010 DOE Vehicle Technologies Annual Merit Review, Washington, D.C.

2. Surenahalli, H.S., Premchand, K.C., Johnson, J.H., and Parker, G.G., "Modeling Study of Active Regeneration of a Catalyzed Particulate Filter Using One-Dimensional DOC and CPF Models," submitted to SAE for review.

V. NEW PROJECTS

The following are brief abstracts of newly instituted Advanced Combustion Engine R&D projects. These projects were selected under the Recovery Act – Systems Level Technology Development, Integration, and Demonstration for Efficient Class 8 Trucks (SuperTruck) and Advanced Technology Powertrains for Light-Duty Vehicles (ATP-LD) Funding Opportunity Announcement, and have not been in effect a sufficiently long period of time to accumulate results worthy of reports similar to those in the previous sections. These projects will have full-length reports in the FY 2011 Annual Progress Report. Also included are new projects co-funded under the partnership developed between the Department of Energy's Vehicle Technologies Program and the National Science Foundation's Thermal Transport Processes Program. The goal of the Partnership is to leverage the complementary missions of deployment and commercialization (DOE) and fundamental research and education (NSF) to advance the science and technology of thermoelectrics for converting waste heat generated in vehicles to electricity. The nine projects funded under this partnership are primarily university-based and include collaborators from industry.

AMERICAN RECOVERY AND REINVESTMENT ACT FUNDED NEW PROJECTS

V.1 Technology and System Level Demonstration of Highly Efficient and Clean, Diesel-Powered Class 8 Trucks

Cummins, Inc.

PI: Don Stanton

The objective of this project is to develop and demonstrate technologies capable of 68% or greater increase in vehicle freight efficiency over a 24-hour operating cycle to include a highly efficient and clean diesel engine capable of 50% or greater brake thermal efficiency (BTE) including an advanced waste heat recovery system as well as an aerodynamically efficient Peterbilt tractor-trailer combination with reduced rolling resistance tire technology, dual-clutch transmission, and an efficient solid oxide fuel cell auxiliary power unit for idle management. In order to maximize fuel efficiency, each aspect associated with the energy consumption of a Class 8 tractor and semi-trailer vehicle will be addressed through the development and integration of advanced technologies. In addition, Cummins will develop and demonstrate technologies for a 55% BTE engine system. The vehicle demonstration will be accomplished via an integrated tractor-trailer vehicle demonstration of 50% freight efficiency improvement for operation over the Vernon drive cycle utilizing a 50% or greater BTE engine system. Key partners include Peterbilt, Eaton, Delphi, Bridgestone, Modine, Purdue University, and U.S. Xpress.

V.2 Systems Level Technology Development and Integration for Efficient Class 8 Trucks

Daimler Trucks North America LLC

PI: David Kayes

The objective of this project is to develop and demonstrate a 50% improvement in overall freight efficiency on a heavy-duty Class 8 tractor-trailer measured in ton-miles per gallon and will include the development of an engine capable of achieving 50% brake thermal efficiency. A secondary objective is to identify, through modeling and analysis, key pathways to achieving long-term goal of developing a 55% efficient heavy-duty diesel engine. Engine work shall include component and integrated system level development of innovative fuel injection systems; next generation model-based controls; engine downsizing; turbocharger technologies; turbo-compounding; air and exhaust gas recirculation technologies; emission aftertreatment systems; thermal management systems; electrified accessories; and waste heat recovery systems. Vehicle work shall include research and development of tractor/trailer aerodynamic improvements; next generation hybrid drivetrains and integrated engine-drivetrain systems; lightweight chassis, cab, and tractor components; improved transmissions, drivelines, and tires; predictive technologies; improved route planning and eco-driver feedback; and improved idle reduction technologies and integrated power generation systems.

V.3 Lean Gasoline System Development for Fuel Efficient Small Cars

General Motors Company

PI: Stuart Smith

The objective of this project is to accelerate the development and synergistic integration of four cost-competitive technologies to improve fuel economy of a light-duty vehicle by at least 25% while meeting Tier 2 Bin 2 emissions standards. These technologies can be broadly implemented across the U.S. light-duty vehicle product line between 2015 and 2025 and are compatible with future and renewable biofuels. The technologies in this project are; lean combustion, innovative passive selective catalyst reduction lean after-treatment, 12 volt stop/start and active thermal management. The technologies are initially developed on engine dynamometers, further refined on development vehicles, fully integrated and then calibrated in a mid-size sedan for final demonstration to compare fuel economy and emissions to a baseline production model.

V.4 A MultiAir®/Multi-Fuel Approach to Enhancing Engine System Efficiency

Chrysler Group LLC

PI: Ron Reese

The objective of this project is to develop and demonstrate an integrated suite of technologies to improve fuel economy of a light-duty vehicle by at least 25% while meeting Tier 2 Bin 2 emission standards. The technologies for this project include MultiAir® technology, turbocharging, cooled exhaust gas recirculation, novel ignition system, and multi-fuel technology to include gasoline, E85, and diesel micro-pilot. This fuel economy improvement will be demonstrated on a Chrysler minivan while maintaining comparable vehicle performance to the state-of-the-art gasoline port fuel-injected 4.0 L V6 baseline reference engine. Key partners include Delphi, Argonne National Laboratory, and Ohio State University.

OTHER NEW PROJECTS

V.5 Development and Demonstration of a Fuel-Efficient Class 8 Tractor and Trailer

Navistar, Inc.

PI: Dennis Jadin

The objective of the project is to develop, design, and demonstrate a diesel tractor and trailer combination that achieves at least a 50% ton-miles per gallon increase when compared to a Navistar baseline ProStar Tractor and Wabash National standard 53-foot trailer. An engine capable of at least 50% brake thermal effi ciency will also be demonstrated. Vehicle technology development areas include tractor aerodynamics, trailer aerodynamics, accessory system electrifi cation and weight reduction, chassis and trailer weight reduction, drivetrain parasitic friction reduction, smart axles, regenerative braking and hybrid powertrain. Engine technology areas include combustion and effi ciency improvements, air system modifi cations, waste energy recovery, friction reduction and insulation, variable valve actuation, and dualfuel. Fuel economy increase will be demonstrated on a chassis dynamometer and test track. Aerodynamic development will utilize full-scale tractor/trailer wind tunnel tests. Engine effi ciency will be verifi ed on an engine dynamometer. Arvin Meritor is a key partner in the project in support of hybrid and other powertrain component design and analysis.

V.6 Gasoline Ultra Fuel Efficient Vehicle with Advanced Low-Temperature Combustion

Delphi Automotive Systems, LLC

PI: Keith Confer

The objective of this project is to develop, implement and demonstrate fuel consumption reduction technologies which are focused on reduction of friction and parasitic losses and on the improvement of thermal efficiency from in-cylinder combustion. The project will be executed in two phases. The conclusion of each phase is marked by an on-vehicle technology demonstration. Phase I concentrates on short-term goals to achieve technologies to reduce friction and parasitic losses (including variable valve lift to reduce pumping losses). The duration of Phase I will be approximately two years. The recipient is targeting a 20% fuel economy improvement over the baseline for the Phase I demonstration vehicle. Phase II is focused on the development and demonstration of a breakthrough low-temperature combustion scheme called gasoline direct compression ignition. The duration of Phase II will be approximately four years. The target is greater than 35% fuel economy improvement over the baseline for the Phase II demonstration vehicle.

V.7 Advanced Gasoline Turbocharged Direct Injection (GTDI) Engine Development

Ford Motor Company

PI: Dan Rinkevich

The objective of this project is to develop a suite of vehicle subsystem technologies and then design, integrate, build, and demonstrate an integrated vehicle that achieves greater than 25% fuel economy vehicle performance improvement in comparison to a 3.5 L V6 port fuel injection production sedan while not exceeding Tier 2 Bin 2 emission standards. Technology development areas include engine downsizing and boosting, advanced boost systems, advanced fuel systems, cooled exhaust gas recirculation, advanced ignition, advanced valvetrain, lean homogeneous combustion, hydrocarbon-trap and advanced lean-NOx trap and selective catalytic reduction aftertreatment, assisted direct start (start-stop), noise, vibration and harshness actions, and electric power steering. Fuel economy will be measured and reported using Federal Test Procedure cycles. The majority of the project will be performed at the Ford Research and Innovation Center with engine dynamometer testing at Ford's Engine Dynamometer Building, both in Dearborn, MI. Engine builds will be performed at Ford Engine Manufacturing Development Operations in Allen Park, MI. Vehicle testing will be done at the Allen Park Test Laboratory in Allen Park, MI. Michigan Technological University will support combustion research as a key subcontractor in the project.

V.8 Advanced Combustion Controls - Enabling Systems and Solutions (ACCESS) for High Efficiency Light-Duty Vehicles

Robert Bosch

PI: Carrie Morton

This project has the primary objective of developing highly capable and flexible advanced control concepts with enabling system, sub-system and component level solutions for the management of multi-mode/multi-fuel combustion events in order to achieve at least 25% fuel economy improvement in a gasoline-fueled light-duty vehicle without compromising its performance and remaining in compliance with future emission standards. The work will focus on further developing state-of-the-art combustion concepts and automotive technologies such as spark ignited combustion with high compression ratio and high boost, cooled external exhaust gas recirculation, homogenous charge compression ignition assisted with controlled boost, external exhaust gas recirculation and fueling strategies for operation range extension, port-assisted direct-injection – dual injection system for combining the benefits of port fuel injection and direct injection, enabling dual-fuel system approach for high compression ratios and extreme downsizing on boosted engines, and multi-hole direct injectors with individual nozzle geometry design for improved mixture preparation and combustion efficiency.

V.9 Cummins Next Generation Tier 2 Bin 2 Diesel

Cummins, Inc.

PI: Michael Ruth

The objective of the project is to develop a suite of vehicle subsystem technologies and then design, integrate, build, and demonstrate a pickup truck that achieves greater than 40% fuel economy vehicle performance improvement in comparison to a Nissan Titan full-size pickup equipped with a gasoline 5.6 L dual overhead camshaft 32-valve V8 engine while not exceeding Tier 2 Bin 2 emission standards and maintaining market comparable vehicle performance and drivability when compared to the baseline vehicle. The work shall integrate advances in the areas of combustion, air handling, fuel systems, closed-loop controls and aftertreatment to create a high-efficiency, low-emission diesel engine, suitable for both consumer and commercial applications. Work shall also be conducted for the development of system architecture to accommodate on-board diagnostic regulations from the design stage to better enable product commercialization. Cummins will design and develop the engine and emission control system for ease of integration into the vehicle build process, further enabling the feasibility of commercialization. The integrated vehicle demonstration will occur on a chassis roll dynamometer at the Cummins Technical Center, Columbus, IN. Dow Chemical Company, Johnson Matthey, and NxtGen are key partners in the project. Dow Chemical Company research and development activities will be performed at the Midland, MI plant. Engine catalyst development will be performed at the Johnson Matthey North American Technical Center, Wayne, PA and the Vehicle Testing and Development facility in Taylor, MI. NxtGen will develop and test emission control technologies at their technical center in Richmond, British Columbia, Canada.

V.10 Project SEEBECK: Saving Energy Effectively By Engaging in Collaborative research and sharing Knowledge

Ohio State University

PI: Joseph Heremans

This project will investigate the effect of material type, durability, and the role of interfaces on thermal management of thermoelectric (TE) modules that incorporate earth-abundant, elements and compounds made from PbSe and Mg_2Si-Mg_2Sn. The effort will include substituting selenium for tellurium in lead-salt-based materials, and expanding to silicides and stannides. Hot side contacts and bonds that mitigate thermal stresses will be investigated starting from porous flexible sintered nanopastes of silver along with simultaneously addressing bonding and metallization. Materials characterization will include thermal impedance spectroscopy and electrical contact resistance measurements to characterize interfaces. The TE device will incorporate the targeted materials in a design in which the TE elements are stacked along the direction of the electrical flow of current, in contrast to conventional approaches in which the TE device is comprised of alternating p and N type pellets aligned thermally in parallel and electrically in series. The project is a collaboration among Ohio State University, Northwestern University, Virginia Tech and includes industrial partners from ZT Plus and BSST.

V.11 Thermoelectrics for Automotive Waste Heat Recovery

Purdue University

PI: Xianfan Xu

This project is a collaboration between Purdue University and General Motors to develop the fundamental understanding and technology improvements needed to make viable the efficient conversion of waste heat in automotive exhaust systems to electricity. The project will include materials development, heat exchanger design, system level thermal modeling, and fabricating and testing of a thermoelectric (TE) module. The materials to be investigated include misch-metal filled skutterudites; nanowire and nanocrystalline TE materials; and titanate and cobalt-based materials with embedded nanowires (to improve their typically low figure of merit which is less than 0.3). Also included will be design of a heat exchanger that incorporates offset strip fins to enhance heat transfer from the hot gas to the TE materials; systems-level thermal management analysis that includes the effect of thermal interface resistances between the various materials and contacts; and construction of a prototype TE generator and measurements to evaluate its performance.

V.12 Automotive Thermoelectric Modules with Scalable Thermo- and Electro-Mechanical Interfaces

Stanford University

PI: Kenneth Goodson

The purpose of this project is to develop nanostructured thermal interface materials (TIM) to enhance transport and bonding between thermoelectric materials and the substrates on the hot and cold sides to which they are attached. The TIMs will be nanostructured and include carbon nanotube (CNT) pellet films for enhanced thermal conductivity and reduced contact resistance. An in situ infrared thermometry technique will be developed for measuring the figure of merit of thermoelectric modules that also includes the interface contribution and properties. The TIM of stand-alone CNT films will be thermally and electrically characterized. System design optimization will also be carried out by combining all thermal, fluidics, stress, electrical and thermoelectric components for realistic gas flow conditions. The deliverables will include a code for modeling thermal/fluid transport in thermoelectric modules, material and transport properties of CNT TIMs and development of materials and techniques for integration of CNT TIMs into thermoelectric devices. The team includes Stanford University, University of South Florida and an industrial partner from Robert Bosch.

V.13 Integrated Design and Manufacturing of Cost-Effective and Industrial-Scalable TEG for Vehicle Applications

Stony Brook University

PI: Lei Zuo

This project will investigate the viability of thermal spray and laser micromachining technologies to fabricate thermoelectric materials directly onto cylindrical surfaces that emulate exhaust pipe components. The performance of the materials will be evaluated by measurements of the thermoelectric figure of merit. The materials will consist of filled skutterudites, Mg_2Si and $FeSi_2$. The materials will contain controlled nanocrystalline inclusions. The research will include non-equilibrium synthesis of thermoelectric materials, fabrication of thermoelectric structures, a demonstration of an integrated design process, and performance characterization. The team is a collaboration with faculty at Stony Brook, Brookhaven National Laboratory and Hi-Z and the New York City Transit Authority.

V.14 Inorganic-Organic Hybrid Thermoelectrics

Texas A&M University

PI: Sreeram Vaddiraju

This project concerns demonstrating a thermoelectric figure of merit >3 using large-area hybrid thermoelectric devices comprised of single-crystalline inorganic skutterudite and antimonide nanowires with sub-10 nm diameters, and functionalized conducting polymer thin films. The focus will be on two material systems: $CoSb_3$ and InSb in the temperature range of 25-800°C. The effect of linker molecule chemistry on performance will be examined along with the effect of contact resistance at the metal-hybrid interfaces. The tasks will include employing organic linker molecules as wires for the fabrication of large-scale integration of inorganic nanowires either to themselves or to thin conducting polymer films. The tasks will include measurement of thermoelectric performance of individual wires and molecularly wired nanowire assemblies will be accomplished, microscopic and spectroscopic analysis of interface-engineered junctions, fabrication and performance measurement of conducting polymer-inorganic nanowire hybrid devices, a systematic study of the metal-hybrid junction contact resistance using the transfer length method, and fabrication and evaluation of thermoelectric modules comprised of many thermoelectric cells.

V.15 Advanced Nanocomposite Materials and Interfaces for Thermoelectric Vehicle Waste Heat Recovery

University of California, Los Angeles (UCLA)

PI: Yongho Ju

This project will focus on developing thermoelectric materials that can withstand thermal cycling and mechanical vibrations such as encountered in automotive applications. The materials will have a metal-matrix nanocomposite structure consisting of iron and magnesium silicide. The emphasis will be on nanostructuring the composites to achieve tailorable coefficients of thermal expansion (CTE) as small as 5 ppm/K. The materials will include a filler material with an isotropic negative thermal expansion (NTE). NTE fillers, such as ZrW_2O_8 powders may be able to offset the high CTE of the metal phase without significantly degrading the electrical conductivity. Material characterization will include measuring the thermoelectric figure of merit using metrology appropriate to the scale of the material samples to be investigated. Modeling of thermoelectric modules incorporating the composites will be carried out to optimize composition and functional grading, and the interfaces will be examined to test their compatibility with the composites. UCLA will team with the Jet Propulsion Laboratory for materials characterization and cross-checking of data.

V.16 High Performance Thermoelectric System Based on Zintl Phase Materials with Embedded Nanoparticles

University of California, Santa Cruz

PI: Ali Shajouri

This project focuses on developing thermoelectric materials with a figure of merit greater than 1.3 in the temperature range most relevant to automotive waste heat recovery applications. This objective will be met by developing non-toxic zintle-phase magnesium silicide alloys embedded with nanoparticles; and to optimize the matrix alloy composition for maximum. The tasks will include material synthesis, and thermal and structural characterization. Measurements to be made include the power factor and thermal conductivity. The data will be used to develop strategies for modifying the alloy composition, nanoparticle sizes and concentration. Comparisons will be made with similar data to obtained by the industrial partners (BSST and the Jet Propulsion Laboratory). The deliverables will include codes for analyzing thermoelectric transport that include embedded nanoparticle thermoelectric materials.

V.17 High-Performance Thermoelectric Devices Based on Abundant Silicide Materials for Vehicle Waste Heat Recovery

University of Texas at Austin

PI: Li Shi

The goal of this project is to increase the figure of merit (ZT) of thermoelectric (TE) materials fabricated from magnesium silicide compounds to >1.5 by nanostructuring the materials. A position-dependent doping concept will be employed that targets reducing the lattice contribution of the thermal conductivity to achieve the targeted ZT value. System and device-level computational tools will be developed in conjunction with experiments to maximize the hot-side temperature and enhance heat transfer to the TE devices, as well as to control the exhaust after-treatment catalyst temperature under transient exhaust flow conditions. Several interface materials will be studied to achieve low electrical and/or thermal interface resistances between the metal interconnects and the TE materials. Metrology will be developed for characterization of temperature- and position-dependant transport properties of the TE and interface materials. The tasks will also include testing silicide-based TE modules incorporated on the exhaust manifold of a 6.7-liter Cummins diesel engine. The project is a collaboration between teams at the University of Texas (Austin) and the University of Wisconsin. The team has access to characterization facilities at Oak Ridge National Laboratory via a user agreement to allow for cross-checking of measurements (e.g., Seebeck coefficient, electrical conductivity and thermal conductivity).

V.18 Efficient, Scalable, and Low-Cost Thermoelectric Waste Heat Recovery Devices for Vehicles

Virginia Tech

PI: Scott Huxtable

The objective of this project is develop efficient thermoelectric generator (TEG) systems that can be manufactured at high volume and low cost, through advances in materials, heat sinks, thermal management, and interfaces. The team will investigate silicide and skutterudite thermoelectric (TE) materials and appropriately scaled TE elements, development of heat exchanges using minichannels and swirl-jet impingement, system-level modeling forpredicting device performance and development of a benchtop TE generator and performance evaluation. The tasks will include using three-dimensional (3-D) aerosol deposition for rapid growth of textured 3-D materials, formation of scaled elements from TE powders using isotatic pressing, and prototype testing of a TE generator system for a vehicle. The project team include Virginia Tech and industrial partners from Romney Scientific.

VI. Acronyms, Abbreviations and Definitions

η_g	Gross indicated thermal efficiency
ϕ	Fuel air equivalence ratio
°C	Degrees Celsius
°CA	Degrees crank angle, 0° = TDC intake
°F	Degrees Fahrenheit
1-D	One-dimensional
2-D	Two-dimensional
3-D, 3D	Three-dimensional
ABDC	After bottom dead center
AC	Alternating current
AC	Air conditioning
AccHR	Accumulated heat release
ACEM	Aberration-corrected electron microscope
ACES	Advanced Collaborative Emissions Study
A/F	Air to fuel ratio
a.k.a.	Also known as
Al	Aluminum
Al_2O_3	Aluminum oxide
AMT	Automated manual transmission
ANL	Argonne National Laboratory
APU	Auxiliary power unit
ASME	American Society of Mechanical Engineers
atdc, ATDC, aTDC	After top dead center
atm	Atmosphere
a.u.	Arbitrary units
Avg.	Average
B	Boron
Ba	Barium
$BaAl_2O_4$	Barium aluminate
$Ba(NO_3)_2$	Barium nitrate
BaO	Barium oxide
bar	unit of pressure (14.5 psi or 100 kPa)
BBDC	Before bottom dead center
BCAC	Bounce chamber air control
BDC	Bottom dead center
BET	Named after Brunauer, Emmett and Teller, this method for determining the surface area of a solid involves monitoring the adsorption of nitrogen gas onto the solid at low temperature and, from the isotherm generated, deriving the volume of gas required to form one monolayer adsorbed on the surface. This volume, which corresponds to a known number of moles of gas, is converted into a surface area though knowledge of area occupied by each molecule of adsorbate.
bhp-hr	Brake horsepower hour
BMEP	Brake mean effective pressure
Bsfc, BSFC	Brake specific fuel consumption
bsNOx, BSNOx	Brake specific NOx emissions
BT	Bi_2Te_3
BTDC, btdc	Before top dead center
BTE	Brake thermal efficiency
$C_{36}D_{74}$	Deuterated hexatriacontane
CA	Crank angle
CA50	Crank angle at which 50% of the combustion heat release has occurred
CAD	Crank angle degrees, computer-aided design
CAE	Computer-aided engineering
CBS	Characteristic-based split
CBT	Couple bypass technology
cc	Cubic centimeter
CCD	Charge coupled device
CDI	Compression direct injection
Ce	Cerium
CeO_2	Cerium oxide
CFD	Computational fluid dynamics
CH_4	Methane
CI	Compression ignition
CIDI	Compression ignition direct injection
CLC	Chemical looping combustion
CLEERS	Cross-Cut Lean Exhaust Emissions Reduction Simulations
CLOSE	Collaborative Lubricating Oil Study on Emissions
cm	Centimeter
cm^3	Cubic centimeters
CMOS	Complementary metal–oxide–semiconductor
CN	Cetane number
CNG	Compressed natural gas
CO	Carbon monoxide
CO_2	Carbon dioxide
COP	Coefficient of performance
COV	Coefficient of variation
CPF	Catalyzed particulate filter
cpsi	Cells per square inch

CPU	Central processing unit
Cr	Chromium
CR	Compression ratio
CRADA	Cooperative Research and Development Agreement
CRC	Coordinating Research Council
CRF	Combustion Research Facility
CSOI	Commanded start of injection
CSP	Computational singular perturbation
Cu	Copper
CVD	Chemical vapor deposition
DC, dc	Direct current
deg	Degrees
DeNOx	NO decomposition
DFT	Density function theory
DI	Direct injection, direct-injected
DI-H2ICE	Direct-injection hydrogen internal combustion engine
DNS	Direct numerical simulation
DOC	Diesel oxidation catalyst
DOE	U.S. Department of Energy
DOHC	Double overhead camshaft
dP	Differential pressure
DPF	Diesel particulate filter
DPNR	Diesel Particulate NOx Reduction
DRIFTS	Diffuse reflectance infrared Fourier-transform spectroscopy
DSC	Differential scanning calorimeter
E10	10% ethanol, 90% gasoline fuel blend
E15	15% ethanol, 85% gasoline fuel blend
E20	20% ethanol, 80% gasoline fuel blend
E85	85% ethanol, 15% gasoline fuel blend
EC1	Swedish Environmental Class 1 diesel fuel (<10 ppm sulfur, by weight)
ECM	Electronic control module
ECN	Engine Combustion Network
ECU	Electronic control unit
EDS	Energy-dispersive spectroscopy
EDX	Energy dispersive X-ray
EERE	Energy Efficiency and Renewable Energy
EEVO	Early exhaust valve opening
EGR	Exhaust gas recirculation
ELOC	Extended-lift-off combustion
EM	Electric motor
EOI	End of injection
EPA	U.S. Environmental Protection Agency
ERC	Engine Research Center
ERS-APU	Electrical recovery system auxiliary power unit
ESS	Electrical storage system
EV	Exhaust valve
EVC	Exhaust valve closing
EVO	Exhaust valve opening
EWHR	Exhaust waste heat recovery
FAME	Fatty acid methyl ester
Fe	Iron
FEA	Finite-element analysis
FEM	Finite-element method
FFVA	Fully-flexible valve actuation
FGM	Functionally graded material
fmep	Friction mean effective pressure
FSN	Filter smoke number
FTIR	Fourier transform infrared
ft-lb	Foot-pound
FTP	Federal Test Procedure
FTP-75	Federal Test Procedure for LD vehicles
FY	Fiscal year
g, G	Gram
g/bhp-hr	Grams per brake horsepower-hour
GC	Gas Chromatography
GC-FID	Gas chromatograph combined with a flame ionization detector
GC-MS	Gas chromatography – mass spectrometry
GDI	Gasoline direct injection
g/hphr	Grams per horsepower-hour
GHSV	Gas hourly space velocity
gIMEP	Gross indicated mean effective pressure
GM	General Motors
g/mi	Grams per mile
GP-GPU	General purpose graphical processing unit
H_2	Diatomic (molecular) hydrogen
H2ICE	Hydrogen internal combustion engine
H_2O	Water
HC	Hydrocarbons
HCCI	Homogeneous charge compression ignition
HC-SCR	Hydrocarbon selective catalytic reduction
HD	Heavy-duty
HECC	High-efficiency clean combustion
HEV	Hybrid electric vehicle
HFPE	Hydrogen free-piston engine
HHV	Higher heating value
HIL	Hardware-in-the-loop

hp	Horsepower
HPL	High pressure loop
HPLB	High-pressure, lean-burn
hr	Hour
HR	Heat release
HRR	Heat release rate
HSDI	High-speed direct-injection
HVA	Hydraulic valve actuation
HVAC	Heating, ventilation and air conditioning
HWFET	Highway Fuel Economy Test
Hz	Hertz
IC	Internal combustion
I/C	Intercooler
ICCD	Intensified charged-coupled device
ICE	Internal combustion engine
IMEP	Indicated mean-effective pressure
$IMEP_g$	Indicated mean effective pressure, gross
INCITE	Innovative and Novel Computational Impact on Theory and Experiment
IR	Infrared
ISFC	Indicated specific fuel consumption
ITHR	Intermediate temperature heat release
IV	Intake valve
IVC	Intake valve closing
IVO	Intake valve opening
J	Joule
k	thousand
K	Kelvin
K	Potassium
kg	Kilogram
kHz	Kilohertz
KIVA	Combustion analysis software developed by Los Alamos National Laboratory
KIVA-CMFZ	KIVA Coherent Flamelet Multi-Zone
kJ	Kilojoules
kJ/L	Kilojoules per liter
kJ/m^3	Kilojoules per cubic meter
kPa	Kilopascal
kW	Kilowatt
L	Liter
LANL	Los Alamos National Laboratory
lb ft	Pound foot
lb/min	Pounds per minute
lbs	Pounds
lbs/sec	Pounds per second
LD	Light-duty
L/D	Length-to-diameter ratio
LDT	Light-duty truck
LES	Large eddy simulation
LHV	Lower heating value
LIF	Laser-induced fluorescence
LII	Laser-induced incandescence
LLNL	Lawrence Livermore National Laboratory
LMO	$LaMnO_3$
LNT	Lean-NOx trap
LSCO	$(La,Sr)CoO_3$
LSMO	$(La,Sr)MnO_3$
LTC	Low-temperature combustion
m^2	Square meters
m^2/gm	Square meters per gram
m^3	Square meters
mA	Milliamps
mbar	Millibar
MBT	Minimum (spark advance) for best torque; Maximum brake torque
MD	Medium-duty
Mg	Magnesium
mg/cm^2	Milligrams per square centimeter
mg/mi	Milligram per mile
mg/mm^2	Micrograms per square millimeter
mg/scf	Milligrams per standard cubic foot
mi	Mile
µs	Micro-second
µm	Micrometer
min	Minute
mm	Millimeter
mmols	Micro-moles
Mn	Manganese
Mo	Molybdenum
mol	Mole
mol/s	Moles per second
MOSFET	Metal oxide semiconductor field effect transistor
MPa	Megapascals
mph	Miles per hour
MPI	Message-passing interface
ms	Millisecond
MS	Mass spectrometry
MSATs	Mobile source air toxics
MSU	Michigan State University
MTU	Michigan Technological University
MWASP	Microwave-assisted spark plug
N_2	Diatomic nitrogen
N_2O	Nitrous oxide
Na	Sodium

NETL	National Energy Technology Laboratory
NH_3	Ammonia
NIR	Near-infra-red
nm	Nanometer
Nm	Newton meter
NMEP	Net mean effective pressure
NMHC	Non-methane hydrocarbon
NMOG	Non-methane organic gases
NMR	Nuclear magnetic resonance
NO	Nitric oxide
NO_2	Nitrogen dioxide
NOx, NO_X	Oxides of nitrogen (NO and NO_2)
NRE	NOx reduction efficiency
NSE	NOx storage efficiency
NSR	NOx storage and reduction
NVO	Negative valve overlap
O_2	Diatomic (molecular) oxygen
OBD	On-board diagnostics
OC	Organic carbon
OEM	Original Equipment Manufacturer
OH	Hydroxyl
OH PLIF	Planar laser-induced fluorescence of OH
ORC	Organic Rankine Cycle
ORNL	Oak Ridge National Laboratory
OSC	Oxygen storage capacity
OTR	Over-the-road
P	Pressure
PA	Pt/Al_2O_3
PAH	Polycyclic aromatic hydrocarbon
PBA	$Pt/Ba/Al_2O_3$
PBCZ	$Pt/Ba/CeO_2$-ZrO_2
PCCI	Premixed charge compression ignition
PCI	Premixed compression ignition
PCZ	Pt/CeO_2-ZrO_2
PDF	Probability density function
P-G	Petrov-Galerkin
PGM	Platinum-grade metal, platinum group metal
PIV	Particle image velocimetry
PLD	Pulsed laser deposition
PLIF	Planar laser induced fluorescence
PLII	Planar laser-induced incandescence
PM	Particulate matter
PME	Palm methyl ester
PNNL	Pacific Northwest National Laboratory
ppb	Parts per billion
PPC	Partially premixed combustion
PPCI	Partially premixed compression ignition
ppi	Pores per square inch
ppm	Parts per million
PRF	Primary reference fuel
PRF80	PRF mixture with an octane number of 80 (i.e., 80% iso-octane and 20% n-heptane)
PRR	Pressure rise rate
PSAT	Powertrain Systems Analysis Toolkit
psi	Pounds per square inch
psig	Pounds per square inch gauge
Pt	Platinum
PTO	$PbTiO_3$
PV	Pressure-volume
R&D	Research and development
RAPTR	Regenerative Air Preheating with Thermochemical Recuperation
RAPTOR	SNL massively-parallel LES solver
RCF	Rapid compression facility
Re	Reynolds number
Rf	Radio frequency
Rh	Rhodium
RME	Rapeseed methyl ester
RON	Research octane number
RPM, rpm	Revolutions per minute
RT	Room temperature
S	Seebeck coefficient
S	Sulfur
SA	Spark assist(ed)
SAED	Selective area electron diffraction
SAIC	Spark-assisted compression ignition
RCCI	Reactivity-controlled compression ignition
sccm	Standard cubic centimeters
SCF/min	Standard cubic feet per minute
SCORE	Sandia Compression-ignition Optical Research Engine
SCOT	A modified form of chemical looping combustion that utilizes a fixed bed of solids
SCR	Selective catalytic reduction
sec	Second
SEM	Scanning electron microscopy
Si	Silicon
SI	Spark ignition, spark-ignited
SiC	Silicon carbide
SIDI	Spark ignition direct injection
SFC	Specific fuel consumption
SFTP	Supplemental Federal Test Procedure

SLPM	Standard liters per minute
SME	Soy methyl ester
SNL	Sandia National Laboratories
SO_2	Sulfur dioxide
SOC	Start of combustion; soluble organic compound
SOI	Start of injection
SOF	Soluble organic fraction
SO_x	Oxides of sulfur
SpaciMS	Spatially resolved capillary inlet mass spectrometer
STEM	Scanning transmission electron microscopy
SULEV	Super ultra low emissions vehicle
SUV	Sports utility vehicle
SVOC	Semi-volatile organic compound
SwRI®	Southwest Research Institute®
T	Temperature
T_{90}	90% volume recovered temperature
TAP	Temporal analysis of products
TC	Turbocompound
TCR	Thermo-chemical recuperation
TDC	Top dead center
TDL	Tunable diode laser
TE	Thermoelectric
TEG	Thermoelectric generator
TEM	Transmission electron spectroscopy
TGA	Thermal gravimetric analysis
TGM	Thermoelectric generator module
THC	Total hydrocarbon
TPD	Temperature-programmed desorption
TPO	Temperature programmed oxidation
TPR	Temperature-programmed reduction or reaction
TP-XRD	Temperature programmed X-ray diffraction
TR	Tumble ratio
TS	Thermal stratification
TWC	Three-way catalyst
TxLED	Texas-mandated low-emission diesel
UDDS	Urban Dynamometer Driving Schedule
UEGO	Universal exhaust gas oxygen
UHC	Unburned hydrocarbons
ULSD	Ultra-low sulfur diesel
UM	University of Michigan
US06	Supplemental Federal Test Procedure (SFTP) drive cycle
UV	Ultraviolet
UW	University of Wisconsin
UW-ERC	University of Wisconsin Engine Research Center
V	Volt
VCR	Variable compression ratio
VDC	Volts – direct current
VGC	Variable geometry compressor
VGT	Variable geometry turbocharger
VVA	Variable valve actuation
VVT	Variable valve timing
W	Watt
WGS	Water-gas shift
WHR	Waste heat recovery
WOT	Wide-open throttle
wt%	Weight percent
WTT	Well-to-tank
XAFS	X-ray aborption fine structure
XANES	X-ray absorption near-edge spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
yr	Year
YSZ	Ytrria-stabilized zirconia
Zn	Zinc
Zr	Zirconium
ZSM-5	Zeolite Socony Mobil-5
ZT	Dimensionless thermoelectric figure of merit; equal to: (electrical conductivity)(Seebeck coefficient)^2(temperature)/(thermal conductivity)
ZTO	Zn_2SnO_4

VII. Index of Primary Contacts

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