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2010 annual progress report

Fuels Technologies

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FY 2010 PROGRESS REPORT FOR FUELS TECHNOLOGIES

Energy Efficiency and Renewable Energy
Vehicle Technologies Program

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I. INTRODUCTION

I. Introduction

ADVANCED PETROLEUM-BASED, NON-PETROLEUM-BASED, AND RENEWABLE FUELS FOR A CLEAN AND SECURE HIGHWAY TRANSPORTATION SYSTEM

On behalf of the Department of Energy's Vehicle Technologies Program (VTP), we are pleased to introduce the Fiscal Year (FY) 2010 Progress Report for Fuels Technologies. The potential benefits of advanced fuels technologies include:

- Energy security: Advanced fuels enable more efficient engines that reduce fuel use, and non-petroleum-based fuels reduce the demand for petroleum fuel, much of which is imported.
- Environmental sustainability: Cleaner fuels enable efficient and durable emissions control technologies for reduced vehicle emissions. Advanced and non-petroleum-based fuels reduce the emissions of greenhouse gases.
- Economic improvement: A more diverse portfolio of fuels in transportation will improve the economy by reducing price volatility and stimulating new market activity in areas such as renewable fuels.

The Fuels Technologies subprogram supports fuels and lubricants research and development (R&D) to provide vehicle users with cost-competitive options that enable high fuel economy with low emissions, and contribute to petroleum displacement. Transportation fuels are anticipated to be produced from future refinery feedstocks that may increasingly be from non-conventional sources including, but not limited to, heavy crude, oil sands, shale oil, and coal, as well as renewable resources such as biomass, oils derived from plants and algae, and waste animal fats. The impact of changes in refinery feedstocks on finished fuels is an area of relatively new concern to engine manufacturers, regulators and users. Advanced engine technologies may be more sensitive to variations in fuel composition than were earlier engines, in addition to facing tightening emissions standards. The Fuels Technologies subprogram activities focus on the properties and quality of the finished fuels derived from these sources, not primarily on their production.

The Fuels Technologies subprogram consists of two activities: Advanced Petroleum-Based Fuels, and Non-Petroleum-Based Fuels and Lubricants. The goals are: (1) to enable post-2010 advanced combustion regime engines and emission control systems to be more efficient while meeting future emission standards; and, (2) to reduce reliance on petroleum-based fuels through direct fuel substitution by non-petroleum-based fuels. These activities are undertaken to determine the impacts of fuel and lubricant properties on the efficiency, performance, and emissions of current engines as well as to enable emerging advanced internal combustion engines, and are coordinated with and supportive of the Environmental Protection Agency's (EPA's) fuels and emissions-related activities, as mentioned in their strategic plan.

The Energy Independence and Security Act (EISA) of 2007 established aggressive goals for renewable fuel use that might require significant changes to the nation's fueling infrastructure. The EISA mandates the use of as much as 36 billion gallons annually by 2022 of renewable fuels, which will mainly be ethanol. The U.S. vehicle fleet consumed almost 10.8 billion gallons of ethanol in the first 10 months of 2010 (compared to 11.0 billion gallons in all of 2009), nearly all in the form of E10 (10% ethanol, 90% gasoline) sold as gasoline at fueling stations. The nation's 8.35 million flexible-fuel vehicles can operate on E85 (85% ethanol, 15% gasoline), but relatively few fueling stations are equipped to dispense E85. Because of E10 and E85's limited ability to absorb increases in U.S. ethanol production to meet the EISA goal of 36 billion gallons of annual renewable fuel consumption by 2022, a solution would be to require vehicles to use intermediate ethanol blends such as E15 (15% ethanol, 85% gasoline) or E20 (20% ethanol, 80% gasoline). The Fuels Technologies subprogram is examining the impact of intermediate blends on passenger vehicles, outdoor equipment, and generator sets, with research focusing on regulated and unregulated tailpipe emissions, fuel economy, and emission system durability. Materials compatibility, evaporative emissions, and vehicle driveability are also being investigated.

The Fuel Technologies subprogram is an integral part of the FreedomCAR government/industry partnership and a key means of pursuing the FreedomCAR mission to develop more energy-efficient and environmentally friendly highway transportation technologies that enable America to use less petroleum in transportation. The work in advanced petroleum-based fuels is conducted through joint programs with the energy and automotive industries and utilizes the expertise of DOE national laboratories and universities. Advanced petroleum-based fuels are even more important to the 21st Century Truck Partnership, which proposes to dramatically increase heavy-duty vehicle fuel economy while continuing emissions reduction. For heavy over-the-road trucks, combustion engines operating on liquid fuels are the only viable options for the foreseeable future based on our current transportation fuels distribution infrastructure. The Fuels Technologies subprogram works closely with the Advanced Combustion Engine R&D subprogram of the VTP, which is focused on removing critical technical barriers to commercialization of higher efficiency, advanced internal combustion engines in light-duty, medium-duty, and heavy-duty vehicles. Fuels Technologies subprogram activities are also coordinated with appropriate DOE/industry technical teams; the light-duty automotive, heavy-duty engine, and energy industries; and federal, state, and local government agencies. Some activities are undertaken in coordination with the Biomass Program, the Hydrogen Program, and the Office of Fossil Energy (via the Fuels Cross-Cut Team) to ensure maximum synergy and to avoid duplication of effort.

Goals

- By 2010, complete testing to determine if gasoline blended with 15% and 20% ethanol can be used interchangeably with existing fuels in passenger vehicles and small, non-road engines not specifically designed to run on these blends.
- By 2014, identify fuel and lubricant components and the interactions between these components and emission control systems that have significant impact on tailpipe and evaporative emissions.
- By 2014, determine the relative importance of hydrocarbon (HC) and nitrogen oxides (NOx) emissions to the formation of ground-level ozone to inform regulatory decision making.

To accomplish its goals, the Fuels Technologies subprogram collaborates with DOE's national laboratories and universities to advance basic fuel and combustion science and with industry partners–including auto and engine manufacturers, ethanol and biodiesel producers, and parts suppliers–to test and validate new technologies. The subprogram also works closely with other DOE programs (e.g., the Biomass Program) to ensure that fuels resulting from their R&D are compatible with existing infrastructure.

Transportation Fuels and Energy Security

Petroleum-derived fuels account for 97% of all fuel used in the U.S. highway transportation sector. Because of the lack of alternative sources of energy in this sector, a widespread disruption of petroleum supplies due to natural disaster, political maneuvering, market disruptions, or resource depletion has the potential to severely disrupt personal and commercial mobility in the U.S. This was vividly illustrated during the summer months of 2005 when several hurricanes hit the Gulf Coast of the U.S., disrupting at one point 28% of domestic crude oil production and 29% of U.S. refining capacity.

The Energy Information Administration believes that the following supply and demand fundamentals are the main drivers behind recent oil price movements:

1. Strong world economic growth driving growth in oil use,
2. Moderate non-Organization of the Petroleum Exporting Countries (OPEC) supply growth,
3. OPEC members' production decisions,
4. Low OPEC spare production capacity,
5. Organization for Economic Cooperation and Development inventory tightness,
6. Worldwide refining bottlenecks, and
7. Ongoing geopolitical risks and concerns about supply availability.

Barring a significant change in events going forward, it is likely that the U.S. will be faced with significantly higher transportation fuel prices than has been the norm for most of the 1980s and 1990s.

Petroleum currently supplies about 37% of all the energy used in the U.S., with 71% of this petroleum going to the transportation sector. The transportation sector alone consumes more petroleum than is produced in the U.S. Meanwhile, the increase in U.S. crude oil production in the Gulf of Mexico and elsewhere, combined with increasing biofuel, is expected to reduce the need for imports over the longer term. Vehicles and their refueling infrastructure will need to adapt to these changes in fuel resources.

Research sponsored by the Fuels Technologies subprogram focuses on tailoring petroleum-based fuels to accommodate and enable more efficient use, and on increasing use of renewable and non-petroleum-derived fuels. For example, oil-sand-derived fuels from Canada, Fischer-Tropsch fuels made from natural gas, and biofuels derived from fats and vegetable oils will play increasingly important roles as both replacements and extenders to conventional diesel fuel. Approximately 40% of the crude oil produced in Canada is from oil sands and production of oil sands liquids is projected to grow significantly over the next several years. Since Canada is our largest supplier of crude oil and we import between 80 and 90% of their production, it is likely that oil sands liquids will represent an increasing portion of our transportation fuel.

As previously mentioned, the EISA mandates increasing production of ethanol for use in transportation vehicles. Besides blending ethanol into gasoline, there are currently 8.35 million flexible-fuel vehicles that can use E85, gasoline, or any blend in between. These E85 vehicles are currently optimized for gasoline operation. The Fuels Technologies subprogram is sponsoring the development of engines for the next generation of flexible-fuel vehicles designed specifically to exploit the desirable fuel properties of E85, such as its high octane, which will increase the fuel economy of vehicles running on E85. Advanced controls and combustion systems are expected to enable these next-generation engines to operate at high efficiency regardless of ethanol concentration, achieving fuel savings beyond that of gasoline displacement alone.

Biodiesel is a popular renewable, non-petroleum fuel to displace diesel fuel. In addition, biodiesel tends to have beneficial effects on the regeneration of diesel particulate traps relative to use of pure diesel fuel. However, recent quality problems with biodiesel resulted in filter-clogging problems in many trucks. As a result of this and similar problems with the quality of U.S. biodiesel, the Fuels Technologies subprogram partnered with the National Biodiesel Board to improve ASTM (an international standards organization) biodiesel fuel specifications and ensure that suppliers adhere to the specifications. Surveys of marketed biodiesel conducted by the Fuels Technologies subprogram in 2005, 2007, 2008 and 2010 showed a large improvement in compliance with the ASTM standard over this period, including more consistent biodiesel concentration and reduced levels of impurities. The fuel-quality improvement resulted in increased willingness among engine manufacturers to endorse biodiesel use in their engines.

Transportation Fuels and the Environment

The combustion process used to convert the energy in petroleum fuels to propulsion for current highway vehicles creates criteria pollutants in large enough quantities to be detrimental to the environment and dangerous to human health, particularly in densely populated areas. Criteria pollutants include carbon monoxide (CO), NOx, particulate matter (PM), volatile organic compounds, and sulfur dioxide. The Fuels Technologies subprogram is evaluating advanced petroleum-based fuels and non-petroleum-based fuels for their impact on engine-out emissions and emission control system efficiency and durability. For example, detailed research is being conducted on biodiesel combustion to understand its impact on NOx emissions and its ability to enhance the performance of diesel particulate filters. Optimized engine designs are being explored to use E85 with high efficiency while achieving very low emissions.

Combustion of petroleum fuels also releases greenhouse gases (GHGs, primarily CO_2, plus nitrous oxide and methane) that are believed to contribute to global warming. Advanced petroleum-based fuels can reduce GHGs through more efficient combustion resulting in less fuel used per unit of work performed. Non-petroleum-based fuels can reduce GHGs not only through more efficient combustion, but also through use of renewable resources that consume CO_2 during their growth.

Emissions of harmful pollutants and greenhouse gases from combustion processes depend in large part on the conditions affecting combustion and on fuel properties. Among fuel properties, sulfur content has attracted the most attention due to its damaging effects on emission control devices. The Fuels Technologies subprogram led a government-industry collaboration in demonstrating that the sulfur content of diesel fuel had to be reduced to enable the use of advanced emission control systems. Diesel vehicles need these advanced emission control systems, such as lean-NOx catalysts, to meet stringent emissions standards. Fuels Technologies subprogram-sponsored research led the EPA to require that all highway diesel fuel contain a maximum of 15-ppm sulfur. Before this ruling went into effect in 2006, diesel fuel for on-road use contained an average of 350-ppm sulfur, with a legal maximum of 500 ppm.

Transportation Fuels and the Economy

The potential economic benefits of implementing advanced vehicle and fuels technologies in the U.S. are many. The value of petroleum products imported into the U.S. represents one-third of our entire trade deficit. Technologies that improve fuel economy will reduce the amount consumers spend on fuel, allowing consumers to spend more in ways that enhance their lives, and also reduces the trade deficit. Renewable fuels such as ethanol and biodiesel offer opportunities for expanding economic activity, especially in the agricultural sector; when used to replace or supplement petroleum fuels, they also improve the trade balance.

The Fuel Technologies subprogram is conducting research that will yield substantial benefits to the energy security of our country, to our environment, and to our economy. By cooperating with other DOE programs to leverage expertise, this subprogram greatly improves the prospects for advanced fuels and advanced vehicle technologies.

SUBPROGRAM LABORATORY CAPABILITIES

The Renewable Fuels and Lubricants (ReFUEL) Lab at the National Renewable Energy Laboratory (NREL) is dedicated to future fuels and advanced medium and heavy-duty vehicle powertrain research. It features a heavy-duty chassis dynamometer test cell capable of testing the performance and emissions of vehicles from 8,000 to 80,000 lbs, a 600 hp alternating current engine dynamometer test cell capable of certification-quality emissions testing and an altitude simulation system that provides conditioned air (temperature and humidity) at atmospheric conditions (pressure) from sea-level to the mile-high environment of Denver. The lab also includes a second engine test cell that accommodates a single-cylinder research engine that is used to develop advanced combustion strategies in support of DOE's Advanced Petroleum-Based Fuels activity.

The ReFUEL Laboratory also includes high-speed data acquisition systems that enabled the two engine test cells and the vehicle chassis dynamometer test cell to have the highest possible utilization factors to support simultaneous testing activities. A Horiba Mexa emissions analyzer as well as Fourier transform infrared and fast mobility particle sizer instruments are available to support ReFUEL's portfolio of measurement equipment to provide faster and more accurate emissions measurements as needed to support upcoming emissions regulations. The engine dynamometer is equipped with quick-disconnect hardware, a new universal wiring harness and new instrumentation and data collection protocols to allow for rapid removal and replacement of test engines. Currently a 2008 Cummins ISB engine is being used in the engine test cell to evaluate the interactions between a variety of biodiesel blends (including non-fatty acid methyl ester blended fuels) and advanced diesel engine emission control systems. Additionally, a significant number of chassis dynamometer test programs have recently been executed to evaluate fuel consumption and emission from medium and heavy-duty advanced technology vehicles and vehicles utilizing bio-fuels.

Sandia National Laboratories (SNL) has two engine labs focused on developing a fundamental understanding of the combustion and emission characteristics of advanced liquid petroleum-based, bio-derived, and synthetic fuels in engines employing various advanced combustion strategies. Engines employing these advanced combustion strategies are being aggressively researched and developed by

industry because of their potential for enabling high-efficiency, emission compliant engines. The first engine lab is the Advanced Heavy-Duty Fuels Laboratory. Research in this lab is conducted using a single-cylinder version of a Caterpillar® heavy-duty engine. The second is the Stratified-Charge, Spark-Ignition (SI) Light-Duty Engine lab, which is under development and nearing completion. Research in this lab will be conducted in a single-cylinder, direct-injection, light-duty SI engine, also extensively modified to provide optical access into the combustion chamber. In both labs, laser and imaging diagnostic techniques are used to observe combustion and emissions-formation processes through windows in the piston, the upper periphery of the cylinder liner and/or cylinder head. The optical measurements are complemented by heat-release analysis and quantification of engine-out emissions, including NOx, HC, CO, CO_2, and oxygen (O_2). These added measurements put the results into proper context with those acquired from industry partners and other research laboratories using non-optical prototype and production engines. Such observations are essential for understanding how fuel formulation affects engine efficiency and emissions, for discovering novel fuel-enabled strategies for high efficiency, clean engine technologies, and for creating accurate computer models to aid the development of such engines. Example accomplishments in FY 2010 included: 1) Identifying the key barriers to achieving mixing-controlled combustion that does not produce in-cylinder soot, a critical first step in using fuel-property and other changes to overcome these barriers. 2) Showing that over-penetration of liquid-phase fuel within the cylinder during early or late injections is the likely cause of lube-oil dilution observed when fueling with biodiesel blends, and that optimizing biodiesel composition can mitigate this effect and facilitate advanced injection strategies. 3) Demonstrated and explained the use of ethanol's strong vaporization cooling to enhance the in-cylinder thermal stratification, and thereby, lower the heat-release rate and extend the load range for homogeneous charge compression ignition (HCCI) combustion. New understandings such as these are providing engine designers the knowledge-base needed to develop more fuel-efficient engines for future fuels.

At Oak Ridge National Laboratory (ORNL), the Fuels, Engines, and Emissions Research Center (FEERC) is a comprehensive laboratory for internal combustion engine technology, specializing in research on paths to higher efficiency, emissions reduction, fuel effects, and emissions chemistry. Capabilities include catalyst spectroscopy laboratories, bench-top engine exhaust simulators, a range of engine dynamometer cells, and a 48-inch single-roll vehicle chassis dynamometer. In this facility, ORNL has developed several new diagnostic and analytical methods that allow greater definition of fuel combustion species and their spatial and temporal resolution in the emission control system. Among the recently updated capabilities are:

- Three General Motors 1.9-L multi-cylinder diesel engines are fully operational and support research on engine efficiency, fuel composition effects on advanced combustion, and methods for expanding high efficiency combustion.
- A modified General Motors 2.0-L Ecotec gasoline engine is fully operational and supports research on renewable fuels.
- A single-cylinder research engine with fully variable hydraulic valve actuation provides a highly flexible research platform for gasoline-like fuels research and has been used to explore efficiency with ethanol-blend fuels as well as spark-assisted HCCI combustion.
- A Ford-supplied multi-cylinder diesel engine is being used to study biodiesel effects on exhaust gas recirculation cooler fouling.
- A single-cylinder 3.0-L natural gas engine modeled after a Waukesha Advanced Power Generation engine is operational and supporting research on combustion and opportunity fuel sources.
- A new method for detecting fuel dilution of the engine lubricant in near-real time was developed in a Cooperative Research and Development Agreement (CRADA) with Cummins.
- A soot-capture and microreactor system was developed to assess how the constituents of biodiesel soot affect the oxidation kinetics as seen in soot-filter regeneration.

Numerous additional single-cylinder and multi-cylinder engines are also available to support fuels research. Many of these engines have open architecture engine controllers with research performed in close cooperation with on-going advanced combustion and aftertreatment research. Advanced

combustion modes under investigation include reactivity controlled compression ignition, premixed charge compression ignition, and high dilution stoichiometric gasoline direct injection.

The vehicle laboratory was recently upgraded with the installation of a new Burke Porter 48-inch single-roll dynamometer. Recent activities in the vehicle lab have included benchmarking European vehicles such as the Saab BioPower Flex Fuel vehicle and the lean-burn, direct-injection BMW 120i, supporting the Clean Cities program in conducting experiments to support the Driving Tips on fueleconomy.gov, and evaluation of mid-level ethanol blends in a wide range of vehicles.

Material compatibility with bio-renewable fuels is being explored with specially designed chambers. These chambers were designed to enable rapid exposure of material coupons to the desired test fluid. These chambers are sealed to maintain a constant environment (fluid and vapor) for extended periods. A motor is used to control the rate of fluid flow and to prevent thermal gradients and a heating jacket loop was added to enable precise and constant temperature control. Two chambers were constructed and used to expose polymer, metal, and sealant coupons. Material specimens, typical of gasoline dispenser components, were procured and evaluated using the stir chambers. The fuel types studied included Fuel C, CE10a, CE17a, and CE25a. The metal and alloy specimens did not exhibit significant corrosion. A range of elastomers were evaluated and their compatibility was assessed from volume swell, hardness and dynamic mechanical analysis measurement. The results have been reported and further studies (using the stir chambers) are being defined for FY 2011.

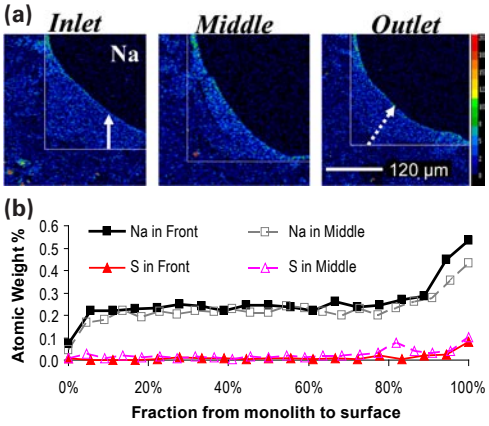
HIGHLIGHTS OF SIGNIFICANT FY 2010 ACCOMPLISHMENTS

The following presents highlights of the Fuels Technologies project accomplishments in 2010.

Fuels and Lubricants to Enable Efficient Engine Operation While Meeting 2007-2010 Standards

The objective of this subprogram activity is to identify fuel and lubricant properties that facilitate efficient engine operation and durable emissions control devices. This activity consists of three projects being conducted by ORNL.

- The impact of Na content in biodiesel on the performance and life of diesel engine emission control devices is being investigated. They found that that only ~5% of ash content in a field-aged diesel particulate filter (DPF) is due to Na in biodiesel. Confirmed minimal but measureable impact of ethylene, CO and NO oxidation over an aged diesel oxidation catalyst (DOC). Confirmed significant performance loss on the NO-reduction of the selective catalytic reduction (SCR) catalyst; when NO_2 is included, impact is significantly less. (Toops, ORNL)



(a) Electron probe microanalysis micrographs of accelerated-aged SCR catalysts and (b) their associated elemental line scans. Arrows in (a) indicate approximate location of the elemental line scans. (Toops, ORNL)

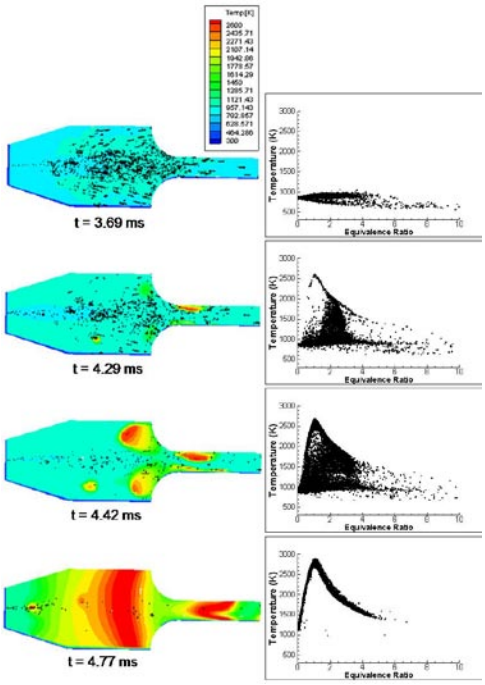
- Exhaust gas recirculation (EGR) system performance when using non-petroleum-based fuels is being quantified. They found that HCs participate in deposit formation until the deposit thickness builds to a point that the deposit temperature rises enough to reduce HC deposition. A second condition would be during cold-starts, when EGR is first utilized and the whole of the EGR cooler, including the deposits, has cooled to a near-ambient condition. A third condition, and one that is much more prevalent, is when an EGR cooler that is sized for high-flow conditions is exposed to low flow rates, such as would be the case at very low engine load conditions and idle. (Sluder, ORNL)

- The Fuels Technologies subprogram is investigating fuel formulations with increasingly higher levels of non-petroleum fuel components to reduce U.S. dependence on foreign oil. ORNL is attempting to improve the basic understanding of how non-petroleum-based fuels affect the performance of engine emissions controls and their associated fuel penalties. They completed analysis of oxidation kinetics for particulates generated on the ORNL Mercedes-Benz 1.7-L diesel engine with ultra-low sulfur diesel, B5, B10, B15, B20 and B100 fueling, and confirmed that high levels of biodiesel fueling produced particulate with higher volatiles and higher fixed carbon surface area. A general diesel particulate oxidation rate model is proposed that captures the combined effects of both fixed and volatile carbon components. (Daw, ORNL)

Fuel Property Effects on Advanced Combustion Regimes

The objective of this subprogram activity is to identify how fuel properties can be used to make combustion more efficient and lower emission.

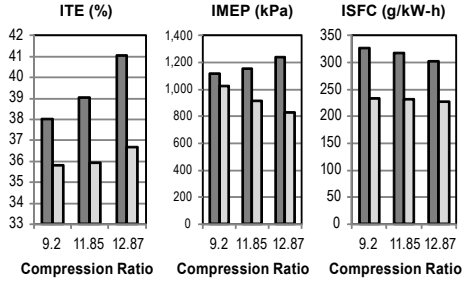
- ORNL is researching the relationships between fuel properties and high-efficiency clean combustion (HECC) modes. Fuels studied in 2010 include a repeat of the Fuels for Advanced Combustion Engines (FACE) diesel fuels in the diesel configuration, a study of surrogate diesel fuels designed to mimic the FACE diesel fuels, n-heptane and some special biofuels from non-traditional plant sources. Kinetic mechanisms were studied for fuel effects. (Bunting, ORNL)
- SNL is conducting measurements of liquid-phase fuel penetration (i.e., liquid length, LL) for single- and multi-component hydrocarbon and biodiesel fuels in a direct-injection (DI) engine when in-cylinder conditions and injection rate are time-varying. The relative importance of different parameters were quantified on the LL, including in-cylinder thermodynamic conditions, fuel volatility, injection pressure, and unsteadiness. Showed that longer LLs for biodiesels than for #2 diesel could help explain observed lube-oil dilution when fueling with biodiesel, but also that a properly formulated biodiesel could lead to improved performance under early-DI conditions. (Mueller, SNL)
- PNNL is developing detailed chemical kinetic reaction models for components of advanced petroleum-based and non-petroleum-based fuels. They developed detailed chemical kinetic models for two of the actual components in real biodiesel derived from either vegetable oil or animal fat. They also developed a reduced mechanism for a large biodiesel surrogate for use in computational fluid dynamics (CFD) codes and chemical kinetic models for three C5 esters that have molecular structures characteristic of biofuels. Chemical kinetic models were validated by comparing results from the chemical kinetic fuel models to experiments in stirred reactors, premixed flames and counterflow diffusion flames. (Pitz, PNNL)
- LLNL is working on development, testing and tuning of chemical kinetic models for fuel components and fuel surrogates of interest to industry and engine researchers; and modeling to test the applicability of chemical kinetic mechanisms at engine conditions. They developed a new methodology for chemical kinetic mechanism analysis by applying large-scale uncertainty and sensitivity analysis tools to analyzing low-temperature chemistry in HCCI combustion, and completed a 48-hour 2,000 processor



The role of autoignition is shown by the time evolution of the temperature contour plots (left) and the corresponding plots of temperature vs. equivalence ratio (right), which demonstrate that the onset of n-heptane combustion occurs primarily in the rich regions around $\phi = 2$. (Zigler, NREL)

dedicated run using our gasoline surrogate mechanism and multi-zone model to investigate low-temperature chemistry sensitivity. (Flowers, LLNL)

- NREL is addressing technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, emissions, and emission control systems. They continued development of Ignition Quality Tester-based research platform to characterize fuel ignition properties, supported development and utilization of research FACE fuels to determine relationships between fuel chemistry and engine combustion performance and emissions, and developed and utilized a spark-ignition direct-injection (SIDI) single-cylinder research engine facility to investigate fuel chemistry effects on advanced combustion and leverage links to NREL's biomass fuels research program. (Zigler, NREL)
- NREL is designing a standard set of research gasoline and diesel fuels to enable cross comparisons of results between different research and development organizations working on similar and different advanced combustion modes and engine designs. Nine diesel fuels were developed, which are currently available for purchase from Chevron-Phillips Chemical Company. Completed and published exhaustive advanced characterization of the nine diesel fuels, including application of novel techniques to fuel property characterization. (Zigler, NREL)
- ORNL is investigating the impacts of non-petroleum-based fuels on advanced combustion regimes for diesel and gasoline engines. They demonstrated high engine efficiency with low NOx and PM emissions using a dual-fuel reactivity-controlled compression ignition (RCCI) combustion strategy in coordination with the University of Wisconsin. They increased the operable load range for HCCI combustion for gasoline engine platforms using spark-assist and variable valve actuation, showing efficiency improvement with simultaneous emissions reduction under stoichiometric conditions. (Szybist, ORNL)
- SNL is exploring how emerging alternative fuels, with an initial focus on ethanol, will impact the new highly-efficient direct-injection spark ignition (DISI) light-duty engines being developed by the automotive industry. Comparisons with gasoline and other fuels reveal the unique characteristics of ethanol as a true single-stage fuel. As such, it has high sensitivity to changes of the charge temperature, but low sensitivity to changes of the boost pressure and oxygen concentration. Ethanol's strong vaporization cooling can be used to enhance the in-cylinder thermal stratification, which leads to a beneficial reduction of the peak heat release rate for HCCI operation. (Sjoberg, SNL)
- ORNL is investigating ways to improve engine efficiency when using ethanol-gasoline fuel blends in order to reduce the mile-per-gallon fuel consumption difference between gasoline and ethanol fuel blends. They found that thermal efficiency for 50 and 85% ethanol in gasoline (E50 and E85) fuels is 2-3 percentage points higher than for gasoline fuels under nearly identical operating conditions when spark advance is not knock-limited and that increasing compression ratio (CR) raises thermal efficiency when using E50 and E85, but E10 and gasoline experienced knock limitations. By using unconventional valve timing strategies, the fuel consumption gap between E85 and gasoline was reduced by 20% compared to a lower CR configuration and at the high-CR configuration, power with E85 is 33% higher than for gasoline. (Szybist, ORNL)



ITE - indicated thermal efficiency; IMEP - indicated mean effective pressure; ISFC - indicated specific fuel consumption

Comparison of Engine Performance of E85 (■) and Gasoline (■) at 1,500 rpm and Maximum Load using ORNL's Single-Cylinder Variable Valve Actuation Engine (Szybist, ORNL)

- ORNL is obtaining representative samples of new, unique, or emerging fuels and screening them with engine and laboratory analytical techniques to continue to add to a database of results and to develop tools for the rapid, efficient screening of new fuels and fuel components. (Bunting, ORNL)

Petroleum Displacement Fuels/Fuel Blending Components

The objective of this subprogram activity is to identify how non-petroleum-based fuels can be used by themselves and in blends to displace petroleum-based fuels.

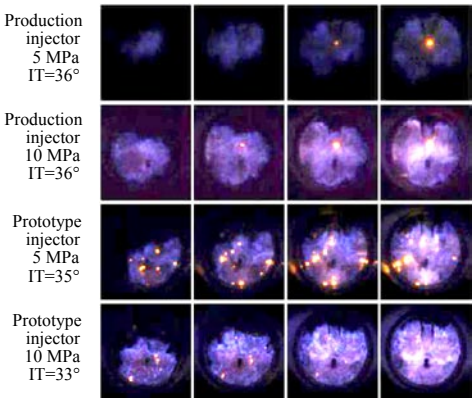
NREL is conducting a variety of projects relating to biodiesel and ethanol fuels:

- They are studying the impact of biodiesel metals content on the long-term durability of emission control systems found in modern diesel engines. They found that the ash loading onto the DPF from 150,000 miles of simulated operation is estimated to cause a 6.8% increase in exhaust backpressure. The thermal shock resistance of a cordierite DPF is compromised after 435,000 miles of B20 operation with a 69% decrease in the thermal shock resistance parameter of the substrate material. The DOC, placed upstream of the DPF, showed a loss in catalytic activity after 150,000 miles of operation with higher unburned hydrocarbon slip and lower NO_2 formation. (Williams)
- They conducted a survey of wintertime blends of biodiesel in diesel fuel in the range of 6-20% (B6-B20) quality in the United States, and collected a snapshot of so-called blender pumps in the midwest U.S. They found that the overall quality of biodiesel blends was high and a vast majority met the prevailing specifications. The snapshot of ethanol blender pumps in Midwest revealed that the blends contain slightly less ethanol than the pump labeling indicates, but have significantly higher vapor pressure than the maximum allowed by the FFV fuel specification for the time of year and region. (Alleman)
- They are revealing the fundamental causes of persistent (although rare) low-temperature operability problems that can occur when using biodiesel. They found that saturated monoglycerides where shown to increase the cloud point of biodiesel when the concentration is above a threshold or eutectic level. Additionally, above the eutectic the final melting temperature of the biodiesel increases and can be as much as 15°C or more above the cloud point. (McCormick)
- They are testing the compatibility of new and legacy fuel dispensing equipment with E15. They found that: (1) overall, results were inconclusive, with no apparent trends in performance related to E17 use; (2) hoses, hose assemblies, the flow limiter, and the submersible turbine pump largely demonstrated compliant results; (3) dispenser meter/manifold/valve assemblies performed poorly; (4) most failures occurred during performance testing; few leakages were observed during the conditioning phase of the test; and (5) improved results would be expected with the use of more appropriate seal materials and methods. (Moriarty)

B20/E85/E10 Dispenser (Moriarty)

- They are experimentally evaluating fuel tank headspace vapor flammability of various ethanol-blended fuels at various ambient temperatures. During the year, they developed the apparatus and methods needed to test the headspace vapor flammability of fuel samples and tested the flammability of in-use fuel blends including E85 samples from vehicle studies and field samples of E85, E10, E20, and E30 from commercial pumps. They also tested the flammability of a matrix of laboratory-prepared ethanol/gasoline blend samples consisting of three gasoline vapor pressure levels and blend levels of E0, E15, E55, E60, E68, E75, and E83, and the lean (low temperature) and rich (high temperature) flammability limits of denatured ethanol (E97). Mathematical models of flammability were developed and evaluated in comparison with the results of the experimental tests. A preliminary analysis of the flammability risks associated with vapor/air plumes emitted from fuel tanks during fueling was performed. (Clark)

- ORNL and NREL determined the effects of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on legacy vehicle emissions and emissions durability when aged with a dedicated fuel blend. They found that Tier 2 vehicles aged 63,000 to 120,000 miles did not show any increased exhaust emission deterioration due to aging with E15 fuel. Examination of powertrain components from Tier 2 vehicles aged with E15 and E20 showed no signs of increased corrosion or wear from the use of ethanol blends. Vehicles aged with ethanol blends did have higher intake valve deposit mass, however detergent additive concentrations were not adjusted in consideration of adding ethanol to the fuel. (West, ORNL)
- ORNL is developing and implementing analytical methods for the combustion products resulting from conventional and advanced combustion in order to further elucidate combustion properties of non-petroleum based fuels. In FY 2010, they developed a sampling and analysis method for exhaust condensates. Biofuel oxygenates can lead to corrosive exhaust condensate species that can affect EGR systems and other engine subsystems. They also developed one-step separation of aromatic poly-acids and anhydrides from soot. These compounds may represent up to 20% of the non-solid soot fraction. (Lewis, ORNL)
- General Motors is studying engine optimization for E85 fuel operation, while maintaining flex-fuel capabilities that enable engines to operate on a range of fuels from E85 to gasoline. They are employing cooled EGR, direct fuel injection, dual continuously variable intake and exhaust cam phasers, turbocharging, and a six-speed automatic transmission to improve vehicle fuel economy. (Wu, General Motors)
- MAHLE Powertrain LLC is demonstrating a new, commercially-viable engine concept that is optimized for E85 operation. A single-cylinder direct-injection spark-ignition optical engine has been used for in-cylinder combustion studies of different test fuels, (gasoline, E50 and E85) and three different injectors. Experiments have been performed at 1,500 rpm engine speed at part-load and full-load conditions. In-cylinder pressure data was recorded for combustion analysis that has been synchronized with imaging. (Thwaite, MAHLE)

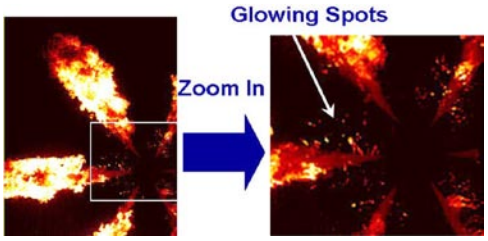


Flame Images of Gasoline (λ =1, Ignition Timing (IT) = Maximum for Best Torque (MBT) for each case) at Different Injection Pressures using the Bosch Production and Prototype Injectors (Thwaite, MAHLE)

- Ford Motor Company is develop a roadmap to demonstrate a minimized fuel economy penalty for an F-series FFV truck with a highly boosted, high compression ratio spark ignition engine optimized to run with ethanol fuel blends up to E85. They have completed data mapping at 9.5:1 compression ratio and investigated the use of twin-scroll turbochargers as a method to mitigate the effects of "exhaust blowdown interference" on the V8 engine to make the engine dynamometer results more generic and applicable to other engine configurations. They also evaluated the effects of combustion phasing retard on E85 consumption and vehicle range under towing conditions and the effect of the engine structural peak pressure limit on full-load performance with E85. Direct injection fuel pump and control strategies were upgraded to improve reliability and durability. (Bower, Ford Motor Company)
- Robert Bosch LLC has developed an optimized FFV, targeting substantial fuel economy improvement with minimum driveability and fuel consumption penalties using a direct injection turbocharged spark ignition engine. The flexible-fuel-optimized powertrain developed with a reduced final drive ratio of 2.90 running on E85 achieved 10% and 12% fuel economy improvements, as indicated by the simulation model correlated with engine/vehicle testing data, compared to the baseline vehicle over the city and highway cycles. This project is completed. (Yilmaz, Robert Bosch LLC)
- Delphi is developing an engine strategy optimized for ethanol operation using higher compression and compression management through valvetrain control. They found that cam optimization

E85 over the speed/load domain of 1,000-3,000 RPM using early intake valve closing, 1,000-4,000 RPM using late intake valve closing which provided a 5-12% improvement in ethanol fuel economy versus the baseline engine running on ethanol. Comparison of valve train control strategies from idle to peak load at 2,000 RPM for E85 and gasoline which identified 3-5% additional fuel economy improvement at loads <5 bar brake mean effective pressure. Cam and controls optimization utilizing single valve deactivation with early intake valve closing for total fuel economy improvement of 8-20% over baseline. (Confer, Delphi)

- The University of Illinois at Urbana-Champaign is optimizing diesel engine control strategies for biofuel combustion and reduced emissions and evaluating biofuel properties to ensure compatibility with mainstream engine technologies. They have enabled simultaneous reduction of NOx and soot emission up to 88.5% and 44.1%, respectively with combined heavy EGR and modified injection strategy comparing to the default engine control strategy. They also initiated optical experiments on spray and combustion characteristics for ternary blends of butanol, diesel and biodiesel with different blending ratios, studied the effects of fuel, ambient temperature and pressure on droplet micro-explosion, and evaluated and achieved stable water-containing emulsified fuel up to 20% volumetric ratio. (Lee, University of Illinois at Urbana-Champaign)



Potential micro-explosion phenomena observed in emulsified fuel combustion under low injection pressure. (Lee, University of Illinois at Urbana-Champaign)

- PNNL is developing and implementing analytical methods for the combustion products resulting from conventional and advanced combustion in order to further elucidate combustion properties of non-petroleum based fuels. They developed a sampling and analysis method for exhaust condensates and a one-step separation of aromatic poly-acids and anhydrides from soot. (King, PNNL)
- PNNL is providing analysis of international alternative fuel use which supports alternative fuel infrastructure development in the United States. In FY 2010 they profiled the development of alternative fuels in Thailand with a concentration on ethanol production and use. They found that E20 demand has been growing rapidly as all new cars in the Thai market are E20-compatible but limited options for FFVs and limited E85 pumps in the country have caused slow progress in increasing E85 production and consumption. (Bloyd, PNNL)
- PNNL is developing an agile decision-analysis tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies. The model predicts the need for sales of more flexible-fuel vehicles, with or without the recent E15 approval for new vehicles. (Bloyd, PNNL)

FUTURE ACTIVITIES

This section describes the activities that will be pursued in each portion of the Fuels Technologies subprogram in the next year.

Fuels and Lubricants to Enable Efficient Engine Operation While Meeting 2007-2010 Standards

Activities in the coming year in this portion of the Fuels Technologies subprogram will focus on how fuel sulfur and lubricating oil additives degrade exhaust catalysts, and how fuel properties can be exploited to optimize emission control system operation.

All these projects are focused on how emission control devices can be made more durable and efficient based on conventional fuels, non-petroleum-based fuels, and advanced-petroleum-based fuels.

- ORNL is identifying important deactivation mechanisms of emissions control devices that are impeding the implementation of efficient lean-burn technology. They plan to continue investigation of the impact of Na on emissions control devices and investigate impact of biodiesel oil dilution on lubrication properties and consumption. (Toops, ORNL)
- ORNL is quantifying EGR system performance when using non-petroleum-based fuels. Reducing fouling in general is still a critical need in terms of producing more efficient, reliable, cost-effective diesel engines in the United States. Experiments aimed at further understanding the fouling process with the goal of mitigating the problem posed by this phenomenon are planned in the coming year. (Sluder, ORNL)
- The Fuels Technologies subprogram is investigating fuel formulations with increasingly higher levels of non-petroleum fuel components to reduce U.S. dependence on foreign oil. ORNL is attempting to improve the basic understanding of how non-petroleum-based fuels affect the performance of engine emissions controls and their associated fuel penalties. In the coming year, they plan to collect diesel particulate samples from other experimental engines and compare their oxidation behavior with the behavior observed for the Mercedes-Benz engine particulate, measure particulate oxidation by NO_2, and incorporate the observed oxidation kinetics in DPF models and system simulations. (Daw, ORNL)

Fuel Property Effects on Advanced Combustion Regimes

The focus of this portion of the Fuels Technologies subprogram is on how fuels properties affect combustion and how they can be used effectively to enhance combustion modes such as HCCI and HECC where emissions of NOx and PM are extremely low. The pathway to accomplish this is not marked, and several different approaches are being taken. For example, SNL is studying the effects of fuel volatility and composition on transient liquid-phase fuel penetration, wall impingement, emissions, and efficiency under early direct-injection operating conditions with a narrow-included-angle injector nozzle using in-cylinder laser imaging techniques and an optical piston assembly. LLNL is developing detailed chemical kinetic reaction models for components of conventional, advanced petroleum-based and non-petroleum-based fuels. These models will allow quicker combustion analysis using commonly available computing power. NREL is working to correlate advanced ignition parameters with physical properties or compositional measurements of real fuels such as various biodiesels, Fischer-Tropsch fuels, and oil sands-derived diesel fuels, in an advanced combustion engine. ORNL is employing statistical techniques to correlate fuel properties with engine operating parameters to identify how engines can compensate for varying fuel properties and still achieve high efficiency and low emissions. A specific effort by ORNL is being conducted to improve engine efficiency with ethanol and ethanol-gasoline fuel blends.

- ORNL is researching the relationships between fuel properties and HECC modes. They will continue to screen new fuels as available in areas of alternate crude sources and biofuels through collaboration with University of Tennessee, Knoxville for biofuels, with the University of Maine for pyrolysis fuels, and with PNNL for oil shale fuels. (Bunting)
- SNL is conducting measurements of liquid-phase fuel penetration for single- and multi-component hydrocarbon and biodiesel fuels in a DI engine when in-cylinder conditions and injection rate are time-varying. They plan to study fuel and injection-parameter effects on mixing-controlled, high-efficiency, clean combustion strategies at injection pressures up to 300 MPa, and lead a team of researchers in the formulation and evaluation of diesel surrogate fuels, which are critical for enabling the computational optimization of future engines for emerging fuels. (Mueller)
- LLNL is developing detailed chemical kinetic reaction models for components of advanced petroleum-based and non-petroleum-based fuels. In the coming year they plan to develop: (1) detailed chemical kinetic models for three actual components in soy-based biodiesel: methyl palmitate, methyl lineate and methyl linolenate; (2) a chemical kinetic model for the four isomers of butanol, and (3) a chemical kinetic model for the iso-pentanol, a bio-derived fuel. (Pitz)

- LLNL is working on development, testing and tuning of chemical kinetic models for fuel components and fuel surrogates of interest to industry and engine researchers; and modeling to test the applicability of chemical kinetic mechanisms at engine conditions. They plan to apply newly available high-fidelity tools for multi-dimensional combustion simulation to investigate of high-efficiency and low-emissions advanced fuel engines, and characterize advanced fuel combustion regimes with judicious application of experiments and simulation. (Flowers)
- NREL is addressing technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, emissions, and emission control systems. They plan to continue expanding Ignition Quality Tester-based experimental and simulation research, and employ SIDI single-cylinder research engine study fuel chemistry impacts on advanced combustion, enabling NREL to study span of renewable fuels from fuel production and processing to engine performance and emissions. (Zigler)
- NREL is designing a standard set of research gasoline and diesel fuels to enable cross comparisons of results between different research and development organizations working on similar and different advanced combustion modes and engine designs. In the coming year, they plan to complete development and perform characterization of the gasoline fuel matrix and apply techniques developed in the diesel advanced characterization effort to address paucity of data for advanced alternative and renewable fuels. (Zigler)
- ORNL is investigating the impacts of non-petroleum-based fuels on advanced combustion regimes for diesel and gasoline engines. They will continue to pursue the RCCI combustion strategy to both incorporate ethanol fuel and to expand the operable engine points, and investigate the fuel effects of spark-assisted HCCI under stoichiometric conditions for ethanol and butanol blends. (Szybist)
- SNL is exploring how emerging alternative fuels, with an initial focus on ethanol, will impact the new highly-efficient DISI light-duty engines being developed by the automotive industry. They plan to perform experiments to assess DISI engine performance and efficiency, and the onset of knock as a function of ethanol/gasoline fuel blend, assess the influence fuel changes on the robustness of the spray-guided combustion system, and apply high-speed imaging of the flow field and fuel concentration to identify the in-cylinder processes that are responsible for sporadic misfire cycles. (Sjoberg)
- ORNL is investigating ways to improve engine efficiency when using ethanol-gasoline fuel blends in order to reduce the mile-per-gallon fuel consumption difference between gasoline and ethanol fuel blends. In the coming year, they will investigate particle emissions from multi-cylinder gasoline direct injection engines using ethanol blends. (Szybist)
- ORNL is obtaining representative samples of new, unique, or emerging fuels and screening them with engine and laboratory analytical techniques to continue to add to a database of results and to develop tools for the rapid, efficient screening of new fuels and fuel components. They plan to continue to screen new fuels as available in areas of alternate crude sources and biofuels and integrate statistical and kinetic modeling tools into routine workflow in order to obtain maximum usage and understanding of experimental results. (Bunting)

Petroleum Displacement Fuels/Fuel Blending Components

The focus of this portion of the Fuels Technologies subprogram over the next year will be on biodiesel, ethanol, and advanced petroleum-based fuels made from natural gas, and oil sands liquids. The objective is to identify how these fuels affect engine efficiency and emission control device performance by themselves or in blends with conventional petroleum fuels.

- NREL is conducting a variety of projects relating to biodiesel and ethanol fuels:
  - They are studying the impact of biodiesel metals content on the long-term durability of emission control systems found in modern diesel engines. Future work will be conducted to model and understand the role of alkali metal volatility on DPF and catalyst degradation. Future experiments will also be designed to determine an acceptable limit for these metal impurities. (Williams)

  - They plan to continue their survey of biofuels quality by conducting a larger sample of FFV fuel from blender pumps and conducting a survey of B100 fuels. (Alleman)
  - They plan to determine how minor components in biodiesel may affect the polymorphism of the monoglycerides and how this relates to cloud point and final melting temperature measurements. In addition, they hope to determine what effect blending the biodiesel into conventional diesel fuel with a range of properties will have on the polymorphic forms, cloud point and final melting temperature. (McCormick)
  - A government workshop with fuel dispensing manufacturers scheduled for January 2011 will provide guidance to testing the compatibility of new and legacy fuel dispensing equipment with E15. (Moriarty)
  - They will continue evaluating fuel tank headspace vapor flammability of various ethanol-blended fuels at various ambient temperatures. Further flammability studies of laboratory-blended fuel samples will be performed using a matrix that varies critical fuel blend parameters (e.g., ethanol content, vapor pressure, and hydrocarbon composition) systematically. Further tests are needed to adequately represent low vapor pressure blends which, according to the Coordinating Research Council National Survey of E85 Quality (2009), comprise a significant portion of in-use E85 fuels. The apparatus and experimental methods used in this study will be refined so they can be recommended as standard test practices. The development of the headspace vapor flammability model will be continued with the aim of achieving a practical means of predicting vapor flammability based upon readily available fuel property data. (Clark)

- ORNL and NREL determined the effects of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on legacy vehicle emissions and emissions durability when aged with a dedicated fuel blend. A final report will be published in FY 2011. (West, ORNL)
- ORNL is developing and implementing analytical methods for the combustion products resulting from conventional and advanced combustion in order to further elucidate combustion properties of non-petroleum based fuels. In the coming year, they plan to develop analytical methods for the determination of water-soluble organic compounds such as small alcohols and large carbonyls, and examine soot samples collected during advanced combustion modes for the absence or presence of poly-carboxylic acids and anhydrides. (Lewis)
- General Motors is studying engine optimization for E85 fuel operation, while maintaining flex-fuel capabilities that enable engines to operate on a range of fuels from E85 to gasoline. In the coming year, they plan to implement control strategies into the vehicle controller and commence calibration, review initial vehicle performance data and compare to dynamometer performance, implement optimized engine management functions, and fabricate and test integral system variants. (Wu, General Motors)
- MAHLE Powertrain LLC is demonstrating a new, commercially-viable engine concept that is optimized for E85 operation. In the coming year they plan to analysis combustion using a metal single-cylinder engine for candidate injectors and then optimize combustion through selection of compression ratios for blends of fuel. Additional gains using cooled EGR will be investigated. (Thwaite, MAHLE)
- Ford Motor Company is develop a roadmap to demonstrate a minimized fuel economy penalty for an F-series FFV truck with a highly boosted, high compression ratio spark ignition engine optimized to run with ethanol fuel blends up to E85. They plan to measure multi-cylinder full-load performance and fuel efficiency at vehicle mapping points for the E85-optimized dual-fuel engine at 12:1 compression ratio, evaluate vehicle level attributes for the FFV- and E85-optimized dual-fuel engines using the above engine dynamometer mapping point data as input to a vehicle level model, and develop a cold starting strategy for an E85-optimized dual-fuel 3.5-L EcoBoost™ engine on a transient dynamometer. (Bower, Ford Motor Company)
- Delphi is developing an engine strategy optimized for ethanol operation using higher compression and compression management through valvetrain control. In the coming year they plan to utilize instrumentation to improve soot measurement capability, optimize multi-pulse fuel injections to

minimize particulate emissions concentrating on gasoline and lower ethanol blends, and integrate transient control of new valvetrain strategies. (Confer, Delphi)

- The University of Illinois at Urbana-Champaign is optimizing diesel engine control strategies for biofuel combustion and reduced emissions and evaluating biofuel properties to ensure compatibility with mainstream engine technologies. They plan to apply butanol/diesel, butanol/biodiesel blends and emulsified fuel in a direct injection engine using optimized engine control strategy, and analyze the combustion and emission characteristics of water-containing emulsified fuel and explore the potential micro-explosion phenomena of fuel sprays in engines. (Lee, University of Illinois at Urbana-Champaign)
- PNNL is developing and implementing analytical methods for the combustion products resulting from conventional and advanced combustion in order to further elucidate combustion properties of non-petroleum based fuels. In the coming year they plan to conduct property analysis and performance tests of the oil shale-derived fuels and distillate streams and continue development of a refinery/blend model to predict fuel chemistry expected from unconventional hydrocarbon blends. (King, PNNL)
- PNNL will continue their analysis of ethanol use in Thailand to help the U.S. understand the issues and experiences associated with the introduction of alternative fuels in other countries, and help the U.S. in anticipation of potential problems, especially as the U.S. has been considering introducing higher blends of ethanol into the U.S. market. (Bloyd, PNNL)
- PNNL is developing an agile decision-analysis tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies. In the coming year they plan to: add DOE Vehicle Technologies Program projections for battery costs and other technology projections and learning curves, compare cellulosic ethanol and other advanced biofuels pathways, including "drop-in fuels" that need less distribution infrastructure, examine the portfolio effects of uncertainty results from research and development on biofuels, and expand the model of consumer preferences to reflect more intangible attributes in driving market share. (Bloyd, PNNL)

SPECIAL HONORS/RECOGNITIONS

1. The NREL Chairman's Award for Exceptional Performance was presented to Gina Ghupka for the work demonstrating that polymorphism of monoglycerides can lead to different crystal structures being present in biodiesel leading to solids that persist above the cloud point of the fuel. This phenomena can lead to fuel dispenser and filter plugging in cold weather for biodiesel and biodiesel blended with conventional diesel fuel.

2. Aaron Williams received the Biodiesel Technical Advancement Award, Presented by the National Biodiesel Board at the Biodiesel Technical Workshop, October 2009.

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

4. Charles K. Westbrook: 2008-2012 President of the Combustion Institute.

5. William Pitz received an award for best paper of the year from the Japanese Combustion Society.

6. S.M. Sarathy: Postdoctoral Fellowship from Natural Sciences and Engineering Research Council of Canada (PNNL).

7. Charles Mueller, SNL: Society of Automotive Engineers (SAE) 2009 John Johnson Award for Outstanding Research in Diesel Engines for SAE Technical Paper 2009-01-1792 entitled, "An Experimental Investigation of the Origin of Increased NOx Emissions When Fueling a Heavy-Duty Compression-Ignition Engine with Soy Biodiesel."

8. Charles Mueller, SNL: SAE Award for Excellence in Oral Presentation for presenting a paper at the 2009 SAE International Powertrains, Fuels and Lubricants meeting in Florence, Italy, on June 17, 2009.

9. Charles Mueller, SNL: Sandia National Laboratories Combustion Research Facility 2010 E. Karl Bastress Award for effective coupling of conservation-related programs to the needs of US industries.

10. Charles Mueller, SNL: Sandia National Laboratories 2010 Outstanding Mentor Award for mentorship of summer intern Peter M. Lillo from the University of California, Berkeley.

11. James Szybist of ORNL received an Outstanding Oral Presentation Award at the 2010 World Congress of the Society of Automotive Engineers for presenting "Investigation of Knock-Limited Compression Ratio of Ethanol Gasoline Blends."

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

13. 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 – November 2010.

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

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

16. LLNL signed a licensing agreement with Convergent Sciences, Inc. for their multi-zone model, September 2010.

Published Chapters in Books

1. Hansen, A.C., D.C. Kyritsis, and C.F. Lee: "Characteristics of biofuels and renewable fuel standards" in: "Biomass to Biofuels - Strategies for Global Industries" edited by A.A. Vertès, H.P. Blaschek, H. Yukawa and N. Qureshi, J. Wiley & Sons, 2010.

2. Hansen, A.C. C.E. Goering and A.S. Ramadhas: "Ethanol", Chapter 5 in textbook "Introduction to Alternative Fuels", CRC Press, Taylor & Francis Ltd., 2010.

PATENTS ISSUED

1. Patent Application 12/842169, An Exhaust Gas Recirculation System and Its Operation, Assignee: GM Global Technology Operations LLC, Inventor: Ko-Jen Wu.

2. Patent Application 12/884686, Integrated Exhaust Gas Recirculation and Charge Cooling System and Its Operation, Assignee: GM Global Technology Operations LLC, Inventor: Ko-Jen Wu.

3. Patent Application 12/884610, Integrated Cooling System for Boosted Engines Employing Recirculated Exhaust Gas, Assignee: GM Global Technology Operations LLC, Inventor: Ko-Jen Wu.

4. Pending US Patent, "Fuel Composition Recognition and Adaptation System", Serial Number 12/417240. (Robert Bosch LLC)

SUMMARY

The work being conducted in Fuels Technologies on conventional, non-petroleum-based, and renewable fuels complements the efforts to build advanced engines and fuel cells for use in transportation applications. High-efficiency prime movers such as advanced combustion engines need clean fuels with carefully defined properties to enable fuel-efficient light-duty and heavy-duty vehicles with the attributes that consumers demand. Highly fuel-efficient vehicles with very low emissions are essential to meet the challenges of climate change, energy security, and improved air quality. As the new fiscal year begins, we look forward to on-going and new cooperative efforts with the auto and energy industries to develop new and innovative fuels technologies for use in advanced transportation vehicles that are fuel-efficient, clean, and safe.

Kevin Stork
Technology Development Manager
Fuels Technologies
Vehicle Technologies Program

II. FUELS AND LUBRICANTS TO ENABLE HIGH EFFICIENCY ENGINE OPERATION WHILE MEETING 2007 - 2010 STANDARDS

II.1 Effects of Fuel and Lubricant Properties on Advanced Engine Emission Control; Development of Rapid Aging and Poisoning Protocols

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Objectives

- Identify important deactivation mechanisms of emissions control devices that are impeding the implementation of efficient lean-burn technology:
  - Includes issues arising from the introduction of renewable fuels such as biodiesel and ethanol.
- Develop and implement accelerated poisoning and aging protocols to provide:
  - Rapid evaluations of emissions control devices.
  - Deeper understanding of the mechanisms and chemistry affecting deactivation.
  - Input for modeling of deactivation processes and their impact on performance.
- Develop laboratory experiments to mimic field use:
  - Base protocol on analysis of the application and ways to accelerate.
  - Use extensive materials characterization.
  - Verify results by comparing to high mileage emissions control devices.
- Procedures and techniques developed in this project can also be used to evaluate field durability.

Approach

- Protocols are developed with significant industrial input to ensure that they are meaningful and relevant; when available, field-aged samples are used as a basis for comparison.
- Project uses industrially supplied emissions control devices:
  - Catalyst samples have multiple formulations and suppliers, including engine manufacturers.
  - Catalyst substrates and diesel particulate filters represented by multiple materials and suppliers.
  - Project has resulted in several projects sponsored by industry.
- Develop protocols for implementation using either a bench-flow reactor or a single-cylinder diesel engine with appropriately-sized emissions control devices.
- Current area of focus:
  - Biodiesel effects on emissions control devices.
- Using extensive materials characterization correlate materials changes to deactivation.
- Much research is conducted as the basis of graduate student thesis research at the University of Tennessee, Knoxville, using ORNL tools and techniques.

Fiscal Year (FY) 2010 Accomplishments

- Characterized several field-aged emissions control devices that have been operated with 20% biodiesel in diesel fuel (B20):
  - Determined that only ~5% of ash content in a field-aged diesel particulate filter (DPF) is due to Na in biodiesel. Based on measurements in a National Renewable Energy Laboratory (NREL) study it is estimated that the biodiesel used in the study contained ~1 ppm Na.
  - Ethylene, CO and NO oxidation over an aged diesel oxidation catalyst (DOC); confirmed minimal but measureable impact.
- Performed accelerated Na introduction using a single-cylinder engine and a DOC-selective catalytic reduction (SCR)-DPF emissions control system:
  - Confirmed significant performance loss on the NO-reduction of the SCR; when NO_2 is included, impact is significantly less.
  - Illustrated effect is on oxidation behavior rather than NH_3 storage or zeolite collapse.
- Initiated accelerated Na introduction with a DOC-DPF-SCR emissions control system and the single-cylinder engine.
  - Bench reactor measurements forthcoming.

Future Directions

- Continue investigation of the impact of Na on emissions control devices:

  - Working with NREL, Manufacturers of Emission Controls Association (MECA) and Ford to determine the appropriate limitation for the biodiesel specification of less than 5 ppm.
- If funding is restored to 2010 levels, investigate impact of biodiesel oil dilution on lubrication properties and consumption.

Introduction

The development and refinement of current emissions control devices on spark-ignition engines have allowed great advances in the efficiency of three-way catalysts (TWCs). These advances are due in part by the implementation of rapid-aging protocols that allow catalyst manufacturers to quickly and effectively evaluate their products for durability and functionality. The emissions control devices that are currently being installed on diesel vehicles do not have rapid-aging or poisoning protocols in place to enable the quick assessment of new formulations or designs. The development of these protocols will enable more rapid implementation of improvements in the emissions control devices currently being developed. There is also a significant additional benefit to establishing these protocols for lean-exhaust systems. Where improved efficiency for TWC systems will only lead to a reduced catalyst cost, improved efficiency of the diesel emissions control system will reduce costs and also enable decreased fuel consumption, since diesel emissions control systems have an associated fuel penalty–due to the high-temperature, rich operation for the desulfation of lean-NOx traps (LNTs) and high-temperature, lean operation for the regeneration of DPFs.

In 2010, diesel vehicles can require a DOC, a DPF, and an oxides of nitrogen (NOx) reduction device. Currently, urea-based SCR and LNTs are the leading solutions being employed for NOx control. In past years we have investigated the effects of lube-oil constituent effects on DOCs [1,2], ash accumulation in DPFs [3], and thermal aging of LNT and SCR catalysts [4-7]. In addition to these deactivation mechanisms that emissions control devices will incur during normal operation with petroleum-based fuel, the implementation of renewable fuel sources, such as biodiesel, introduces additional complications. One of the issues that we are addressing is the concern that has arisen from the presence of trace levels of Na in biodiesel–current specification is up to 5 ppm. To synthesize biodiesel–a fatty methyl ester–vegetable oils are reacted with methanol using a homogeneous base catalyst, typically NaOH. Since the products and catalysts are both liquids in this process, and the catalyst is not consumed, it is necessary to separate the NaOH from the biodiesel at the end of the manufacturing process. This results in trace levels of Na in the fuel, and even at the specification level of 5 ppm, there is a concern that this could impact the emissions control devices in modern diesel vehicles. Of particular concern is the deactivation of zeolite-based SCR catalysts and the generation of additional ash that would accelerate the blockage of DPFs, but deactivation of the DOC is also possible. In studying these processes we are hoping to either alleviate the concerns of the diesel vehicle industry or determine the deactivation mechanisms and suggest possible remedies. If the concerns can be alleviated it may be possible to increase the allowable biodiesel blend levels to 20% from the current 5% level. Additionally, biodiesel fuels have been shown to alter soot-burning characteristics that can affect DPF regeneration.

Approach

The development of the aging and poisoning protocols rely on two methodologies–one is engine-based and the other is bench-core reactor-based. A 517 cc Hatz single-cylinder diesel engine was modified to accommodate intake and exhaust manifold injection of lube oil or diesel fuel. For the biodiesel study, the fuel fed to the engine is mixed with elevated levels of Na to allow the introduction of a vehicle's lifetime of 5 ppm Na in very short time frames. The engine system is equipped with a full array of analytical systems to allow measurements of hydrocarbon, carbon monoxide, NOx conversions, as well as pressure drops and temperatures at various locations including the mid-bed of the emissions control devices. However, the simplicity of the engine does not allow a full evaluation of the emissions control devices, so core samples are typically removed from the engine-aged devices and evaluated on the bench reactor. The bench-core reactor allows precise control of the aging temperatures, the composition of the exhaust gases, and the duration of the rich and lean pulses. Simulated exhaust gas stream with a composition similar to the exhaust gas stream from a diesel engine is introduced into the bench-flow reactor system by means of mass flow controllers. The bench-core reactor is also fully equipped with gas analysis capabilities and utilizes up to six thermocouples to measure temperature variation along the catalyst axis. In addition to the aging experiments, bench-core reactor tests were used to obtain hydrocarbon and carbon monoxide light-off performance from samples cored from field service and engine-poisoned catalysts which provides evaluation under more controlled conditions than the engine bench allowed.

To fully understand the effects aging and poisoning have on the emissions control devices, the aged samples are sectioned and prepared for material characterization. Key materials characterization measurements that are needed are platinum group metal (PGM) crystallite

size, concentration of NOx storage sites, total surface area of the catalysts, elemental analysis of the devices including radial and axial profiles, and metal-oxide phase identification. These measurements can be achieved using the following techniques: Brunauer-Emmett-Teller physisorption, H_2 chemisorption, X-ray fluorescence, inductively coupled plasma techniques, scanning and transmission electron microscope, X-ray diffraction and electron probe microanalysis (EPMA). It is anticipated that the experimental results from the study can be used to determine the temperature range for the deactivation of LNTs by various thermal aging mechanisms, to correlate bench flow-aged catalysts to field-aged catalysts, and to extract deactivation kinetics from which theoretical models of thermal aging of LNTs can be formulated.

Results

Emissions control devices were aged by suppliers and at ORNL using accelerated techniques. Table 1 lists the emissions control devices that have been obtained or aged in this study. While each of the devices was aged in an engine-based system, the effect of Na contamination on the performance of DOCs, LNTs and Cu-zeolite SCR catalysts was investigated using a bench-core reactor; additionally, DPFs were characterized for ash build-up and elemental analysis. The LNT results were discussed last year (minimal impact of Na), and the devices aged in the DOC-DPF-SCR format have not been analyzed this FY.

TABLE 1. Listing of the Emissions Control Devices Obtained in this Study

Aging Routine	LNT	DOC	SCR	DPF
Field-Aged				
Supplier 1 (General Motors)		X		X
Supplier 2 (NREL/MECA)	X			
Accelerated-Aged				
DOC-SCR-DPF		X	X	X
DOC-DPF-SCR		X	X	X

DOCs

Both the field-aged and accelerated-aged parts were analyzed for the presence of Na using EPMA. The core samples were cut along the axis to allow the cross-sectional viewing of the inlet, middle and outlet (Figure 1). The field-aged sample was operated for 120,000 miles, the required light-duty durability range, and it can be seen that Na has deposited on the surface of the DOC washcoat in the inlet section; elemental analysis suggests the NA concentration is at 0.4 wt% at the surface. When compared to the accelerated-aged sample, which is targeting the Na exposure that would occur in a heavy-duty lifetime (435,000 mile equivalent), the Na layer at the washcoat surface is also observed at ~0.4 wt%. Although this higher dose is still mainly concentrated at the surface, there is some penetration into the washcoat and the Na is observed at similar levels in the outlet as the inlet (Figure 2). This suggests

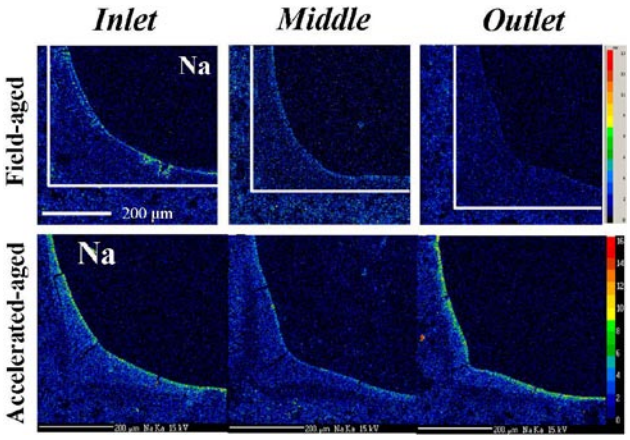

FIGURE 1. EPMA micrographs of field-aged (top) and accelerated-aged (bottom) DOCs with highlighted regions indicated location of Na.

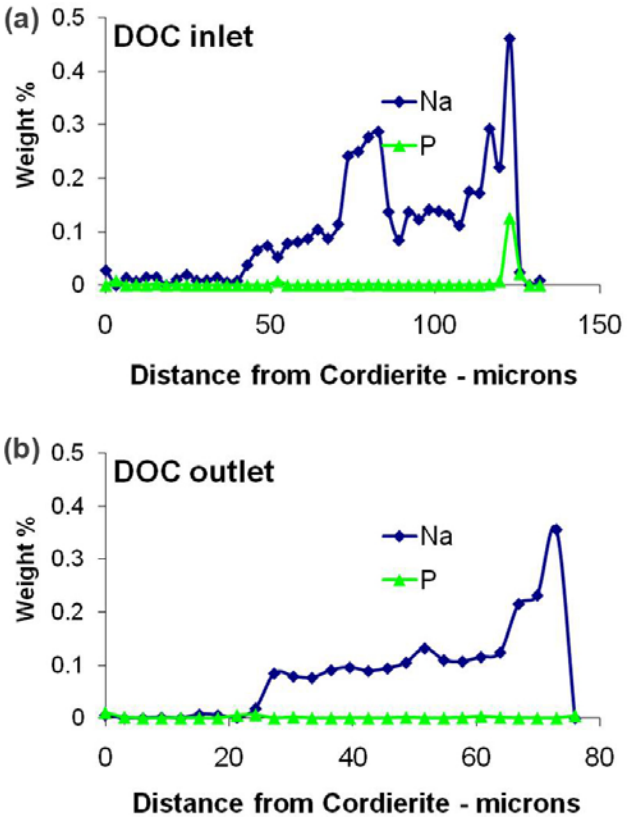

FIGURE 2. Elemental line scans of the accelerated-aged DOC illustrating the depth of penetration of the Na into the washcoat.

that the accelerated technique deposits the Na in a similar manor as the field-aged approach with respect to the DOC.

While identification of the Na in the device is important in confirming the approach, this contamination is only a concern if the reactivity of the DOC is impacted. Figure 3 shows the reactivity of ethylene and NO oxidation for the fresh and aged DOCs. There is a small but detectable decrease in ethylene oxidation activity for the aged samples between 200 and 300°C. Interestingly, there is a notable increase in NO to NO_2 oxidation on the aged samples and the increase is relatively consistent. The reason for this increase is not understood at this point but is still under investigation.

SCR Catalyst

The only SCR catalysts available for analysis were those that were aged using the accelerated approach for 435,000 mile equivalent at ORNL. The EPMA micrographs of this SCR catalyst show a layer of Na clearly visible on the washcoat surface and with a significant penetration into the washcoat (Figure 4).

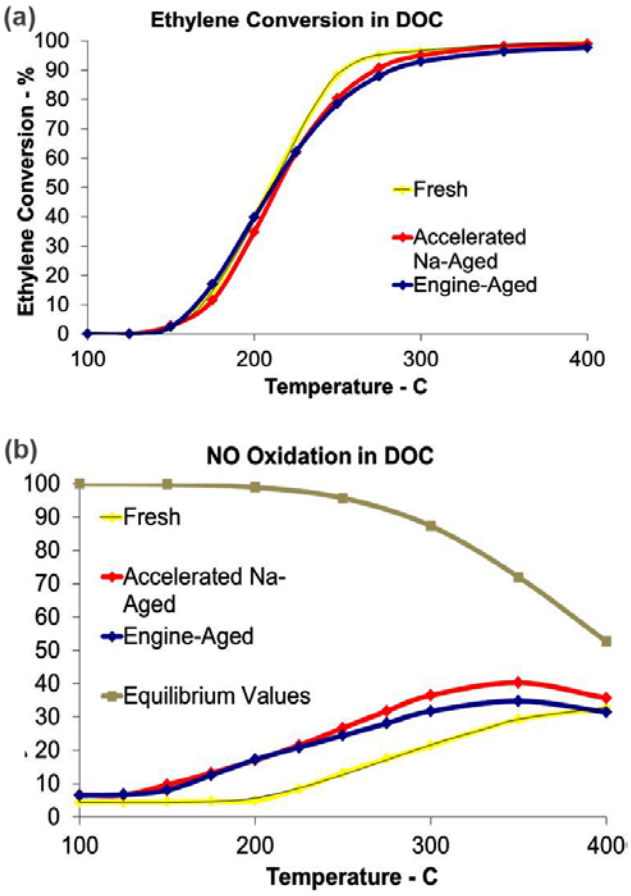

FIGURE 3. Fresh and aged DOC reactivity with respect to (a) ethylene and (b) NO oxidation.

As in the accelerated-aged DOC the Na is also observed in the outlet of the SCR, and while there is more Na at the surface there is deep penetration of the Na to the cordierite wall. While there is an intentionally added sulfur component in the fuel in this accelerated approach, the elemental line scans illustrate that the Na that interacts with the SCR does not include sulfur.

Unlike in the DOC results, Na has a significant impact on the NO-reduction performance of the SCR as can be seen in Figure 5a. When NO_2 is included in the simulated exhaust, this impact is less severe (Figure 5b). This suggests that the Na is targeting a specific function of the SCR catalyst and when additional measurements were taken to investigate the NH_3 storage and NO oxidation behavior (Figure 6) only an impact on NO oxidation was observed. This reaction is typically associated with the metal-exchanged sites of the SCR catalyst, Cu in this case, and therefore, suggested that Na is exchanging with the Cu-exchanged sites.

DPFs

In the field-aged DPFs, a 50-mm ash plug is clearly visible in the rear of the SiC inlet channels. Since lube-oil consumption also leads to ash deposits, typically in the form of Ca or Zn, it is imperative to analyze the elemental components of these ash plugs. The elemental maps of Ca and Na are shown in Figure 7a and a quantitative elemental analysis of the front section of this plug reveals a 20:1 ratio of Ca to Na. Based on consumption rates indicated in a recent study [8], it is expected that the level of Na in the fuel used by the supplier was 1 ppm; therefore, although the ash accumulation from Na does not appear to be a large factor in this case, if

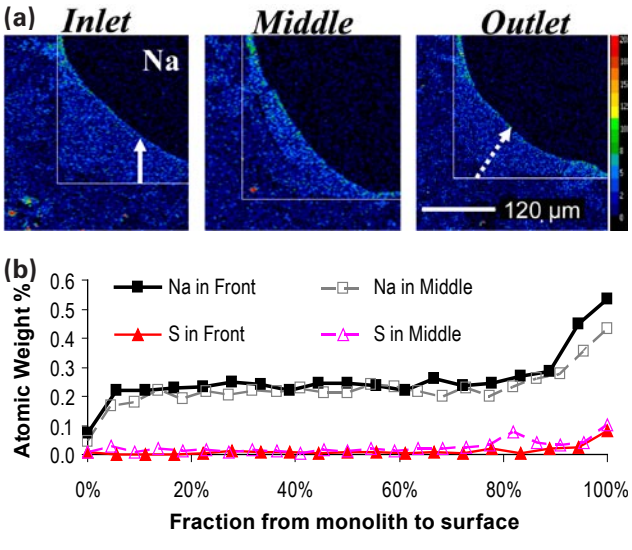

FIGURE 4. (a) EPMA micrographs of accelerated-aged SCR catalysts and (b) their associated elemental line scans. Arrows in (a) indicate approximate location of the elemental line scans.

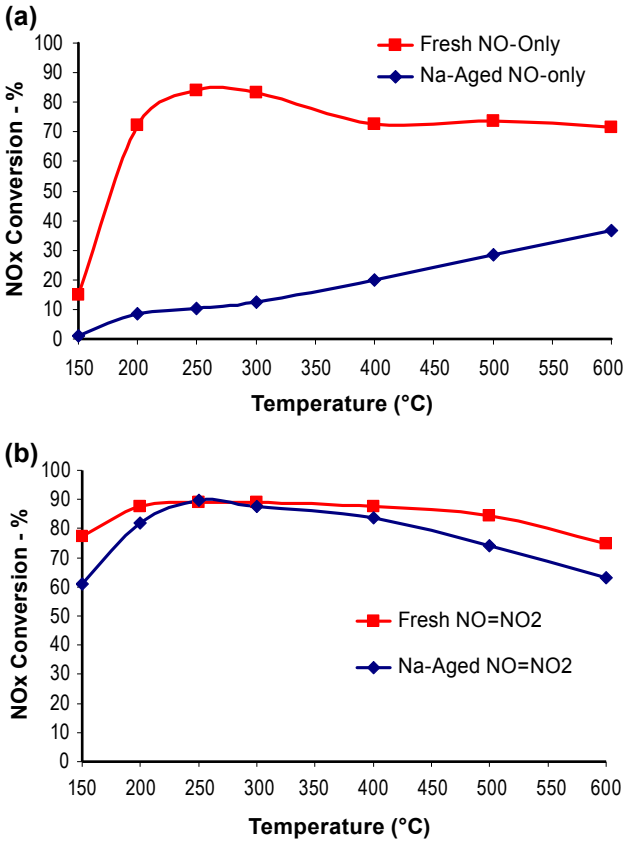

FIGURE 5. Impact of Na on the performance of zeolite-based SCR catalysts with (a) NO as the only NOx source in the flow and (b) a 1:1 ratio of NO:NO_2.

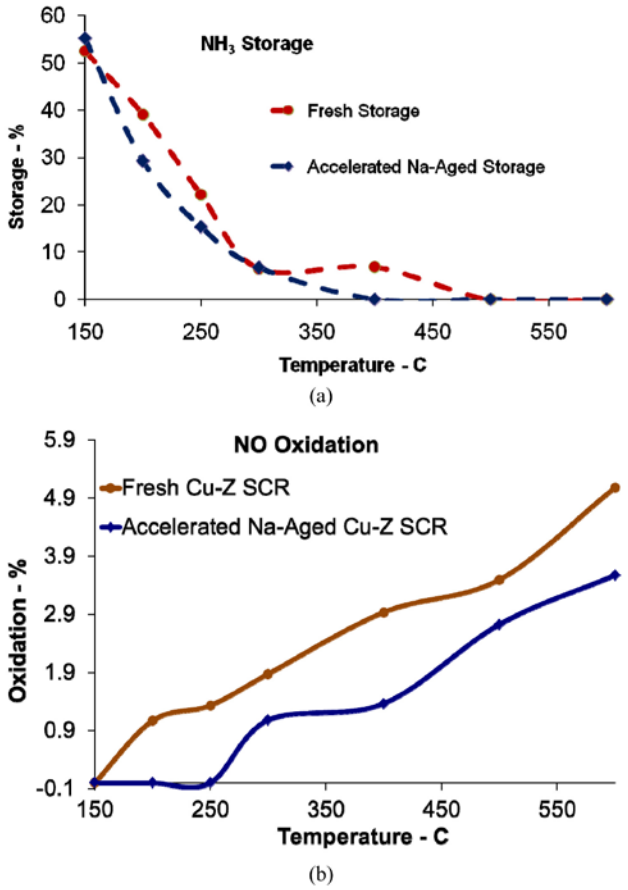

FIGURE 6. (a) NH_3 storage as a percent of the NH_3 introduced and (b) NO oxidation of the fresh and aged SCR samples.

there was five times more Na it could become a factor. As a comparison, Figure 7b shows the ash layer in the accelerated approach. No plugs formed in this study and the ash layer is primarily Na.

Conclusions

- Na layer observed in all emissions control devices:
  - Field-aged and accelerated-aged samples show similar Na layers relative to amount of Na introduction.
  - Performance of LNTs does not appear to be affected by Na.
  - Impact on DOCs is measurable, but impact is minor:
    - Ethylene oxidation decreases by 15%.
    - NO oxidation slightly improved.
  - Field-aged DPF ash plug constituted of ~5% Na compared to 90+% Ca:
    - Indicates Na has only minor contribution to ash when introduced at 1 ppm biodiesel level.
- SCR is the emissions control device most susceptible to Na:
  - NO-only reactivity drastically reduced over entire temperature range; NO+NO_2 (fast SCR) less impacted.
  - Reactivity differences suggest Na impact oxidation sites, i.e. metal-exchanged sites.

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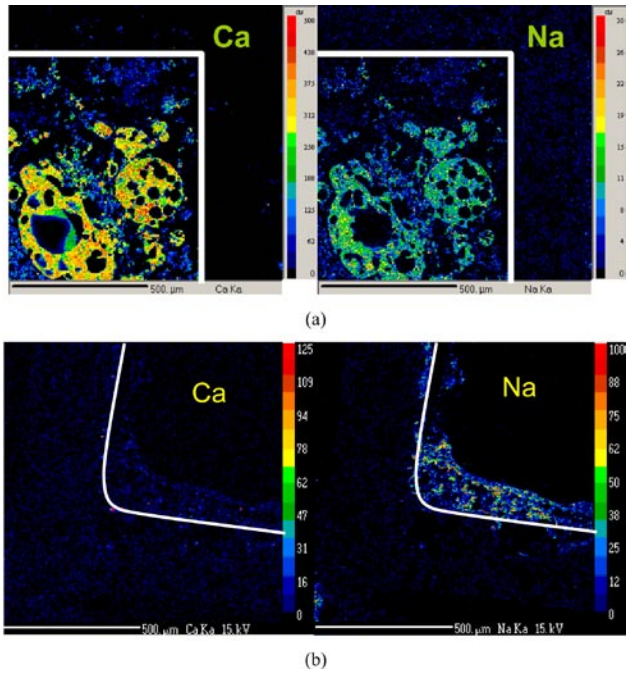

FIGURE 7. Elemental maps of (a) the field-aged ash plugs and (b) accelerated-aged ash deposits using EPMA. Ca-based ash is associated with lube-oil consumption while Na represents the biodiesel component.

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II.2 Non-Petroleum-Based Fuels: Effects on EGR System Performance

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Objectives

- Quantify exhaust gas recirculation (EGR) system performance when using non-petroleum-based fuels.
- Identify fuels or fuel properties that may reduce the effectiveness of the EGR system through problematic deposit formation.

Fiscal Year (FY) 2010 Accomplishments

- Upgraded apparatus to enable repeatable step-change flow transients during tube loading.
- Conducted experiments aimed at furthering the understanding of the role of unburned hydrocarbons (HCs) in deposit layer growth.
- Planned a series of experiments to be conducted in FY 2011 in partnership with Ford Motor Company to investigate surface treatments as a possible means of mitigating fouling.

Future Directions

Investigate pathways that show potential for reducing the impact of fouling on EGR cooler performance and overall engine system design.

Introduction

EGR is an oxides of nitrogen (NO_X)-reduction technology that utilizes engine exhaust recirculated to the engine intake and mixed with fresh air as a means of reducing combustion temperatures and engine-out NO_X emissions. As the quantity of EGR being used has increased and the conditions where EGR is used have broadened, EGR coolers have come to be a critical component of the EGR system. These coolers reduce the temperature of the EGR gases so that further NO_X reductions are possible. Increasingly stringent NO_X regulations have placed further importance on this approach. Commercial constraints, such as cost and packaging, place emphasis on compact, light-weight designs that are easily manufactured.

Unfortunately, the exhaust gases being cooled in the EGR cooler contain both particulate matter (PM) and chemical species such as HCs and in some cases acids derived from sulfur present in the fuel and nitrogen dioxide (NO_2) produced during combustion. PM is well-known to be deposited on surfaces where a temperature gradient exists, and when this occurs in EGR coolers the effectiveness of the cooler is degraded, resulting in hotter EGR gases at the cooler exit. HCs and acids may also contribute to this problem by creating an environment less conducive to removal of the PM by aerodynamic forces within the flow stream. This reduction in effectiveness of the EGR cooler is a critical problem because it may result in vehicles falling out of compliance with Environmental Protection Agency emissions regulations or, in severe cases, impacting driveability. Thus, manufacturers currently must over-design the EGR cooler, leading to increased cost and packaging issues.

Some non-petroleum-based fuels (such as biodiesel) have unique fuel chemistries and/or combustion behavior that may cause changes in the fouling tendencies of EGR coolers. If this is found to be the case, it represents a very significant technical hurdle that must be overcome if these fuels are to be successful in significant market penetration. The first step toward overcoming this hurdle is to gain an understanding of the scope of the problem.

Approach

ORNL has approached this problem from an experimental point-of-view. An engine and sampling system have been established to facilitate studies of surrogate EGR cooler tubes that can be extensively analyzed to examine the nature of the deposits caused by operation with non-petroleum-based-fuels. Examination of the deposits can provide insights into the fouling processes with these fuels and possible strategies to mitigate the problem.

Results

Experiments with both ultra-low sulfur diesel (ULSD) and 20% biodiesel in diesel fuel (B20) fuels were conducted at two different HC concentrations (50 and 100 PPM as C_1) and for several different lengths of time. The mass of both volatile and non-volatile portions of the deposits for each case were determined.

The masses were analyzed to produce a measure of the incremental HC deposition per unit time, and this was plotted against the exposure time, as shown in Figure 1. This data shows that deposition of HCs is rapid in the initial stages of deposit development, but quickly declines to a low, near-constant rate as the exposure time is increased. That is, HCs participate in the process more readily when the deposit is thin and relatively cool compared with the free-stream temperature of the EGR gases. As the deposit thickens, it becomes more thermally resistive and presents a large thermal gradient that reduces the heat exchanger effectiveness. As this happens, a larger fraction of the deposit cross-section becomes less conducive to the presence of trapped HCs because of its increased temperature.

The temperature regions where various portions of the fuel begin to participate in deposit formation are influenced by the pressure in the EGR system. Figure 2 shows data collected using n-decane (C_{10}) at various temperatures and a pressure of 10 PSIG. The decane was injected into a hot gas stream and the fraction of the decane that was trapped was noted at each temperature. Extrapolation of the data produces an estimate of the temperature where no trapping would occur of 165°F. Normal decane is a reasonable surrogate for the most volatile compounds present in diesel fuel; normal hexadecane (C_{16}) is typical of the center of the fuel distillation and is much less volatile. Experiments with C_{16} have thus far indicated that this species can be trapped in carbon deposits at 10 PSIG at temperatures of around 400°F. While no successful experiments have been conducted with compounds indicative of the top end of a typical diesel fuel distillation because of the difficulty in working with them, trends in the data of lower-carbon number compounds indicate that eicosane (C_{20}) could be trapped at most temperatures

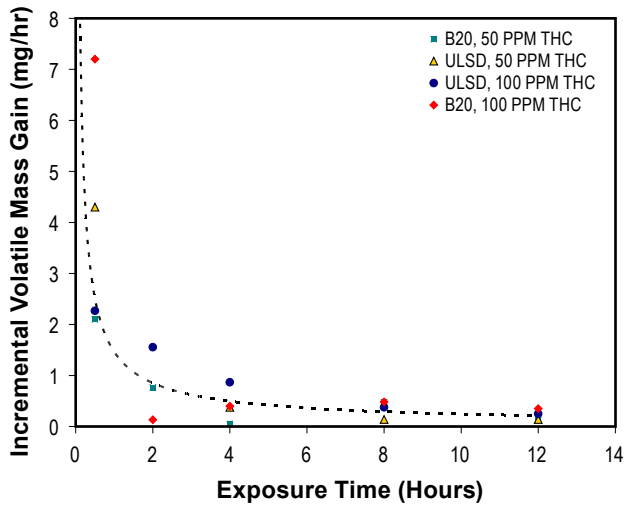

FIGURE 1. Rate of HC Deposition in EGR Cooler Deposits as a Function of the Length of Exposure to Exhaust

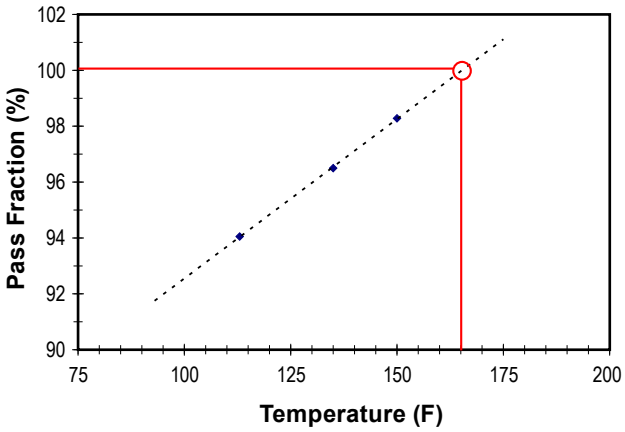

FIGURE 2. Pass Fraction Versus Temperature for Decane at 65 PPM_{C1} on Particulate at 10 PSIG

typical of light-duty EGR systems. In a previous study the profile of the HCs found in EGR cooler deposits was found to be bounded by C_{15} as the most volatile species of prevalence, with C_{19} as the species with the highest concentration. Species higher than C_{19} were present at lower amounts owing to limited amounts of these species being available in the exhaust stream [1]. The amount of fuel-range HCs present in engine exhaust is generally small compared with volatile species except during conditions requiring over-fueling, such as during regeneration of a diesel particulate trap. Thus, the amount of HCs that participate in deposit formation is low compared with the amount of HCs that do not contribute. As the deposit heats up due to thermal resistance, the amount of HC that can continue to participate in fouling is further reduced.

There is a small, but non-zero deposition of HCs even when the deposit is well-developed. This may result from two sources: very low volatility HCs in the exhaust, and diffusion of HCs into cooler portions of the deposit. Studies with carbon-based aerogels have shown that the mean-free-path for deposits made up of 1-micron particles is on the order of 600 nanometers [2]. This is an upper limit for EGR cooler deposits, which are similar, but should have a shorter mean-free-path given that the geometric mean particle diameter is much smaller, generally on the order of 0.1 microns. Since the deposit thickness under this condition is on the order of 200-500 microns, diffusion would be constrained to within about 0.5% or less of the deposit thickness from the gas-deposit interface. As this fraction of the deposit is at a relatively high temperature, this is unlikely to be the source of the continuing HC deposition. Very low volatility HCs (such as, for example, pyrene, a four-ring polynuclear aromatic hydrocarbon) might be the source of the ongoing HC deposition. Hydrocarbon species that have very low volatility are usually present in the exhaust gases individually at very low concentrations, but could collectively account for the

very low incremental HC mass deposition that has been observed. Furthermore, HCs of such low volatility can be in the particle phase during deposition, and only manifest themselves as volatile species during the post-experimental analysis of the tube deposits.

Conclusions

Experimental evidence to date points to the fact that HCs can only participate significantly in deposit formation when the deposit is rather cool relative to the exhaust gases. Importantly, this narrows the conditions where HCs play a significant role. One such condition is a relatively clean EGR cooler that is essentially free of deposits. In this case, the HCs participate in deposit formation until the deposit thickness builds to a point that the deposit temperature rises enough to reduce HC deposition. A second condition would be during cold-starts, when EGR is first utilized and the whole of the EGR cooler, including the deposits, has cooled to a near-ambient condition. A third condition, and one that is much more prevalent, is when an EGR cooler that is sized for high-flow conditions is exposed to low flow rates, such as would be the case at very low engine load conditions and idle. During these conditions, a portion of the EGR cooler is essentially unutilized because the gases have cooled to near the coolant temperature in the upstream portions of the cooler. The unutilized portion of the cooler, then, will experience near-zero heat transfer, meaning that deposits, if present, will also be near the coolant temperature and conducive to additional deposition by HCs. A similar circumstance would occur when the cooler is bypassed but experiences diffusion of gases into the cooler through imperfect valve seals that allow some leakage at very low flow rate.

Anecdotal evidence from discussions with manufacturers points to a higher incidence of cooler plugging in applications where idle and low-load operation are the dominant conditions. (For example, in airport shuttlebuses.) Plugging is a condition in which fouling has occurred to such an extent that deposits have obscured the gas flow path entirely, preventing the flow of EGR through the heat exchanger tubes. While no evidence has yet been uncovered of a direct connection between HC deposition and plugging, it can be observed that plugged coolers generally have a very tacky, tar-like deposit rather than dry soot as is most often the case when HCs do not contribute to fouling. It seems likely that extensive operation under conditions where HCs deposit readily increases the risk of EGR cooler failure through plugging. In these conditions, the use of an oxidation catalyst upstream of the EGR cooler could reduce the incidence of plugged coolers. However, in applications with higher-load duty cycles, an oxidation catalyst in the EGR system may be of less benefit, unless high-HC excursions are expected.

Reducing fouling in general is still a critical need in terms of producing more efficient, reliable, cost-effective diesel engines in the United States. Experiments aimed at further understanding the fouling process with the goal of mitigating the problem posed by this phenomenon are planned in the coming year.

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II.3 Non-Petroleum-Based Fuels: Effects on Emissions Controls Technologies

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Objectives

- Improve the basic understanding of how non-petroleum-based fuels (NPBFs) affect the performance of engine emissions controls and their associated fuel penalties.
- Quantify effects of NPBFs on diesel particulate nanostructure and oxidation kinetics and the impact of these effects on diesel particulate filter (DPF) performance.
- Interact closely with Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) stakeholders to maximize relevance and utilization of the research results.

Approach

- Collect representative samples of diesel particulate generated from conventional and biodiesel blended fuels with well-characterized multi-cylinder diesel engines operated under highly controlled conditions.
- Measure the oxidation kinetics of the particulate samples under precisely controlled conditions in laboratory reactors.
- Measure and correlate features of the particulate microstructure with fuel-related differences in oxidation reactivity.
- Relate particulate reactivity differences to expected impacts on DPF regeneration performance.

Fiscal Year (FY) 2010 Accomplishments

- Completed analysis of oxidation kinetics for particulates generated on the ORNL Mercedes-Benz 1.7-L diesel engine with ultra-low sulfur diesel (ULSD), B5, B10, B15, B20 and B100 fueling.
- Confirmed that high levels of biodiesel fueling produced particulate with higher volatiles and higher fixed carbon surface area.
- Determined that the observed differences in fixed carbon oxidation reactivity correlate directly with fixed carbon surface area differences. This was shown for ULSD, B5, B20 and B100.
- Confirmed that when fixed carbon oxidation rates are normalized with Brunauer-Emmett-Teller (BET) surface area, the oxidation kinetics can be modeled with a single set of Arrhenius parameters for particulates from all fuel blends evaluated.
- Proposed general diesel particulate oxidation rate model that captures the combined effects of both fixed and volatile carbon components.

Future Directions

- Collect diesel particulate samples from other experimental engines and compare their oxidation behavior with the behavior observed for the Mercedes-Benz engine particulate.
- Measure particulate oxidation by NO_2.
- Incorporate the observed oxidation kinetics in DPF models and system simulations.

Introduction

Increasing global energy demands have focused attention on energy efficiency and alternative energy sources. Compression ignition, diesel engines have traditionally been used in heavy-duty and off-road applications, but are experiencing growth in the passenger vehicle market due to their energy efficiency advantage over gasoline, spark ignition engines. As diesels grow in popularity, environmental concerns about pollution and greenhouse gases have meant increasingly strict regulatory constraints on diesel emissions in the United States, Japan and Europe. Particulate and nitrogen oxide emissions regulations have made diesel exhaust aftertreatment an unavoidable necessity. Concurrently, the Fuels Technologies subprogram is investigating fuel formulations with increasingly higher levels of non-petroleum fuel components to reduce U.S. dependence on foreign oil. However, there are currently inadequate data and modeling capabilities to predict the impact of these fuels and fuel blends on emissions and emissions control technologies.

Current DPFs utilize both mechanical filtration in a ceramic wall-flow monolith and subsequent combustion

to eliminate particulate matter (PM) from the tailpipe exhaust. The oxidation step is critical in order to minimize the impact of the DPF on engine backpressure, which has a negative impact on fuel efficiency. Understanding particulate oxidation kinetics is extremely important for diesel particulate filter regeneration.

Diesel particulates, produced as micron and submicron scale aerosols during the combustion process from unburned fuel residues, are typically comprised of a fixed carbon center with adsorbed partial combustion (fuel type) hydrocarbon products. The quantity of adsorbed hydrocarbons, here referred to by the process by which they were removed, soluble organic fraction (SOF), or volatile organic fraction (VOF), is sometimes labeled mobile carbon since it can be separated from the fixed carbon. The relative percentage and composition of the SOF/VOF is a function of engine, combustion type, speed-load point and fuel type.

By gaining further understanding of the links between non-petroleum fuels and fuel blends and the physiochemical and reactivity properties of their associated diesel exhaust particulates, this project will enhance our ability to assess the potential environmental and fuel economy impacts of alternate fuel options. Specifically, the information generated will make it possible to better predict the conditions and fuel consumption required to regenerate DPFs under realistic driving conditions.

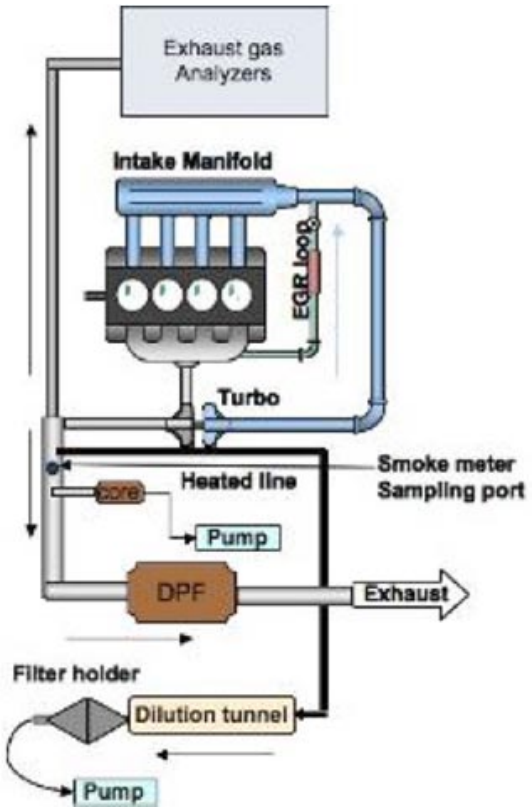

FIGURE 1. Engine and sampling setup used to collect diesel particulate.

Experimental Approach

Up through the present year, all particulates studied so far have been generated on a late-model Mercedes-Benz engine, updated with a common rail fuel injection system, and fueled with a range of biodiesel/ULSD blends. To date, work has focused on six different fuel blends (ULSD and five different blend levels of soy biodiesel B5, B10, B15, B20 and B100) at a single engine operating condition (1,500 rpm, 2.6 bar). As shown in Figure 1, particulate samples were collected directly from a non-catalytic DPF installed in the engine exhaust as well as from exhaust extracted through a dilution tunnel and filter. A small DPF 'core' was also installed parallel to the main DPF to collect particulate sample for analysis with solvent extraction. Additional details of the experimental setup and procedures can be found in [1]. In-cylinder pressure measurements made during particulate generation indicated that the global heat release rate profiles for all of the fuel blends evaluated so far have been similar.

Oxidation and volatilization behavior of the particulate samples are characterized in a differential micro-reactor coupled to a mass spectrometer (see Figure 2). Additional details can again be found in [1].

The micro-reactor measurements provide direct comparisons among particulates generated by different fuel blends as well as with other diesel particulates and reference materials reported in the literature [2,4,7-9]. In the temperature-programmed operating mode, samples are heated at a constant rate in the presence or absence of oxygen to measure oxidation and devolatilization activity, respectively. To better understand the mechanisms behind fuel blending effects, we measure the oxidation reactivity of both the nascent (as-collected) particulates as well as the residual solids left after volatiles have been removed by heating the sample to 650°C under inert gas.

In the pulsed, isothermal micro-reactor operating mode, previously devolatilized particulate samples are brought to a specified operating temperature under inert gas (Ar), and then oxygen is introduced in short pulses. This allows us to measure oxidation rates under effectively isothermal conditions at different stages of particle burnout. As explained below, these measurements make it possible to determine global Arrhenius reaction rate parameters and evaluate models for particle burnout.

Along with measuring oxidation reactivity as a function of particle burnout, we also measure specific surface area of the particulates in the micro-reactor using a 7-point flowing BET technique. The measurement is made by flowing seven concentrations of Ar in He, estimating the adsorbed Ar at each point

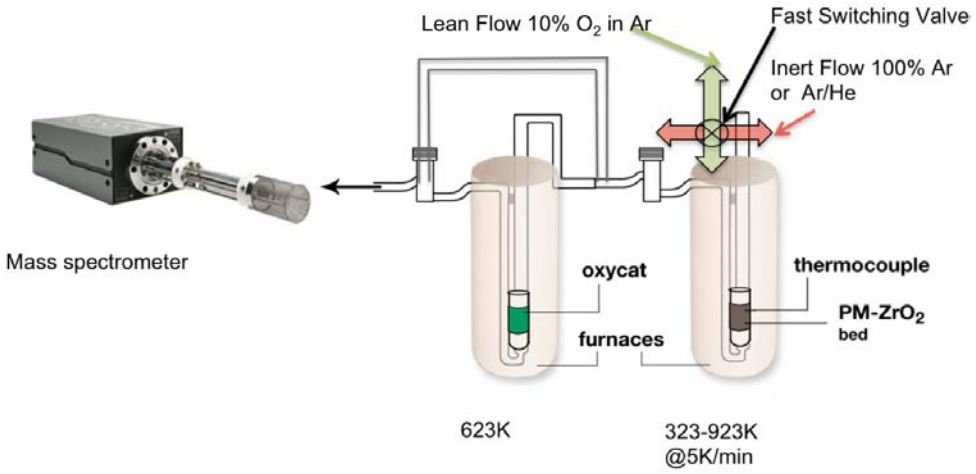

FIGURE 2. Micro-reactor setup used to measure devolatilization and oxidation of the particulate samples.

with the mass spectrometer. The estimated surface area is then determined from the estimated adsorbed Ar and standard BET theory [3].

Besides the micro-reactor, we use other standard methods of particulate characterization to detect changes associated with different fuel blends. The two principal methods we use are high resolution transmission electron microscopic imagining [5,6] and solvent extraction. For the latter, particulate from the DPF 'core' is extracted in a specialized microwave heated extractor, and the extract characterized with gas chromatography-mass spectroscopy.

Results and Discussion

Efforts this year focused on confirming differences observed previously for the ULSD and B100 particulates and clarifying the relative trends for the B5 and B20 intermediate blends. One particular issue raised in last year's report were apparent differences in oxidation reactivity (and the associated kinetic rate parameters) for the fixed carbon portion of the ULSD and B100 PM. This year we extended our observations to include the fixed carbon components of B20 and B5 PM. The Arrhenius plot in Figure 2 illustrates the resulting oxidation rate trends for the fixed carbon components of ULSD, B100, B20, and B5 PM samples all together. Note that the rates depicted in this figure are given on a unit mass basis and are clearly different for different samples at any given temperature. When depicted this way, the fixed carbon component of B100 PM appears more reactive than fixed carbon component of ULSD PM and B5 PM, and the effective activation energies (reflected in the slopes of the lines) also appear to be different. Such differences were noted previously for ULSD and B100 and are still present when B5 and B20 are included. It should be noted that the plot in Figure 3 only compares the oxidation rates at the point

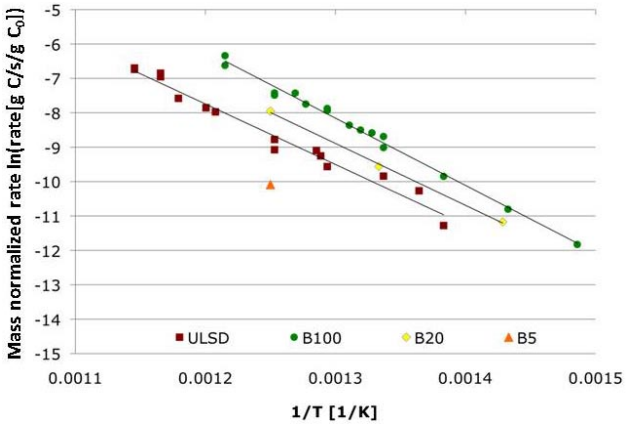

FIGURE 3. Observed oxidation rates at 40% conversion for the fixed carbon component of diesel particulates generated respectively by ULSD, B100, B5, and B20 fuel blends. Oxidation rates here are normalized by the initial particulate mass.

where 40% of the fixed carbon has been consumed (40% conversion). Similar plots made at other degrees of conversions show different trends and thus different effective Arrhenius parameters.

As noted previously, the special in situ BET measurement capabilities of the ORNL micro-reactor allow us to track specific surface area of the fixed carbon component as oxidation progresses. In this year's work, these measurements helped clarify the reasons behind the above apparent reactivity differences among the different PM samples and provided a new perspective on the oxidation mechanism. Example trends for the fixed carbon component surface area for the ULSD, B5, B20, and B100 PM samples are depicted in Figure 4 as functions of degree of oxidation. Initially, the specific areas for all the samples are relatively low (below 200 m^2/g) but all rise continually with oxidation and

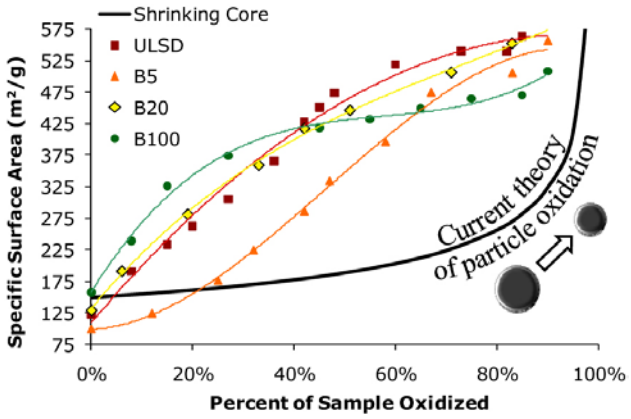

FIGURE 4. Evolution of BET surface area with degree of conversion for the fixed carbon components of ULSD, B100, B5, and B20 particulates. The solid black line is the expected profile for shrinking core oxidation.

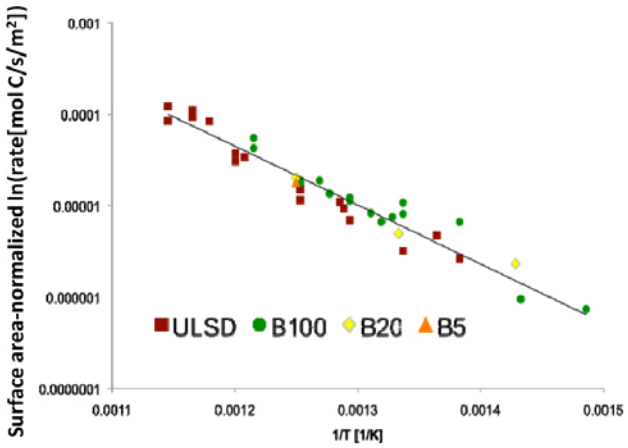

FIGURE 5. Arrhenius plot of the area normalized oxidation rates for the fixed carbon components of ULSD, B100, B5, and B20 particulates. The data depicted here include measurements for a range of conversions from 20 to 80%.

appear to approach maximum values of over 500 m^2/g as 100% conversion is reached. The different rates of area increase with oxidation suggest important differences in the oxidative evolution of the different particulates, but they are also all clearly distinct from the expected surface area profile for oxidation in the so-called shrinking core mode (also depicted in the figure). We are still attempting to understand what these profiles imply about the geometry of the fixed carbon oxidation process, but it is clear that some type of complex surface structure (e.g., branched pores or fractal pitting) is involved.

Another important result from the fixed carbon surface area measurements is depicted in Figure 5. In this case the observed pulsed oxidation rates for the different PM samples have been normalized to their respective BET surface areas and plotted on Arrhenius coordinates. The data here include measurements for a range of conversions from 20 to 80%. When the rates are transformed in this manner, the fixed carbon oxidation behavior of all the PM samples (for all stages of conversion) can be described by a single set of Arrhenius parameters. These surface normalized oxidation rates also compare very well with other recent data reported in the literature when the latter are transformed to the same area basis [2]. The resulting activation energy of 113±6 kJ/mole is consistent with Zone II burning, in which there is significant penetration of the particle surfaces by oxygen [10]. Taken together, all these observations imply that the differences among the devolatilized diesel particulates studied here are primarily due to variations in surface availability.

Based on the micro-reactor temperature-programmed desorption and temperature-programmed oxidation (TPO) measurements with nascent particulates, we found that the volatile release rates are consistent with a second-order polynomial function of temperature. This implies that at the slow heating rates involved in these experiments the volatiles slowly leave

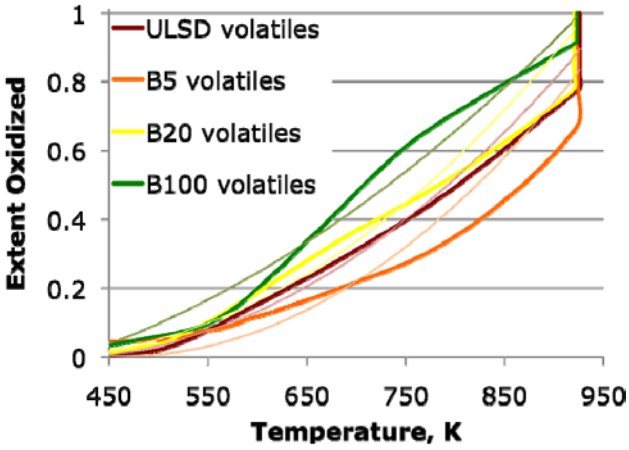

FIGURE 6. Integrated oxidation profiles for the volatile components from the different nascent particulates. Extent of oxidation is indicated as a fraction of the total measured volatiles in the sample versus temperature in the TPO experiment.

the particle surface according to their effective boiling point. Under TPO conditions, the released volatiles rapidly burn and contribute to the PM oxidation as illustrated in Figure 6. In future experiments we plan to determine whether this type of temperature-dependent volatiles release model still applies under conditions where the heating rate is much faster (such as might occur in a DPF undergoing rapid regeneration).

Combining the separate rate models described above for volatiles release/oxidation and fixed carbon oxidation, we find that the sum of these two rates is very close to what we observe experimentally during TPO of the nascent particulate. An example comparisons is illustrated in Figure 7 for B100 generated PM.

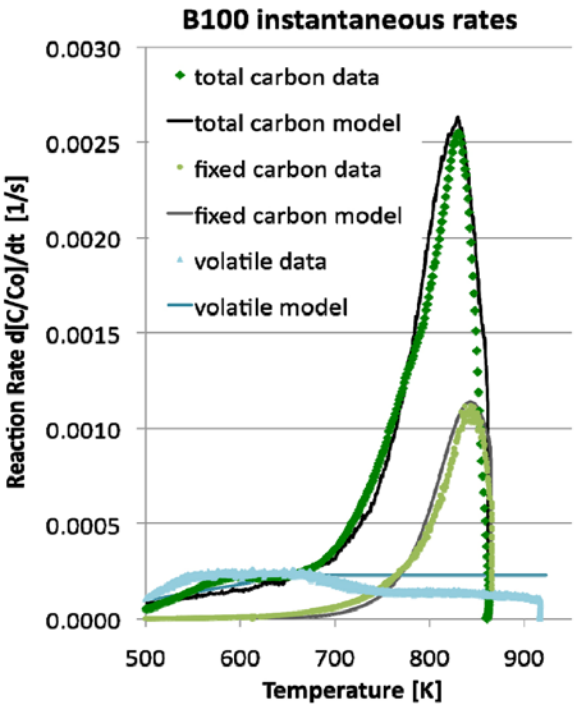

FIGURE 7. Illustration of the estimated relative contributions of volatiles and fixed carbon to the overall oxidation rate of nascent B100 particulate. Solid lines represent model predictions and points represent TPO measurements.

Conclusions

Characterization of exhaust particulate generated on a Mercedes-Benz engine fueled with a range of conventional and biodiesel blends has revealed the following:

- Additional evaluations of PM from B5 and B20 fuel blends confirm previous observations that high levels of biodiesel tend to increase particulate volatiles, but the trend is non-monotonic at low biodiesel levels.
- The devolatilized oxidation reactivity of all the particulates studied correlate closely with BET surface area.
- BET surface areas for devolatilized particles from all fuel blends are initially low and rise sharply with particle oxidation, finally approaching an apparent limiting value.
- The area-normalized oxidation rates of devolatilized particulates from all the fuel blends studied can be fitted with a single set of Arrhenius parameters, for all levels of particle conversion.
- Oxidation of nascent particulate generated from ULSD, B5, B20, and B100 can be described by summing the separate contributions of the fixed and mobile carbon components.

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2. Strzelec, A., Toops, T.J., Daw, C.S., Foster, D.E., and Rutland, C.J., "Diesel Particulate Oxidation Model: Combined Effects of Volatiles and Fixed Carbon Combustion," SAE 2010-01-2727 paper and presentation.

3. Strzelec, A., Lewis, S.A., Storey, J.M., Daw, C.S., Foster, D.E. and Rutland, C.J. Effects of Trans- Esterified Soy Oil Biodiesel Blending on Emissions from a Modern Light Duty Diesel Engine. SAE 2010-01-1273 paper and presentation.

4. Strzelec, A., Toops, T.J., Daw, C.S., Foster, D.E. and Rutland, C.J., "Kinetic Model Development for the Combustion of Particulate Matter from Conventional and Soy Methyl Ester Diesel Fuels," Proceedings of the 2010 Technical Meeting of the Central States Section of the Combustion Institute, Champaign-Urbana, March 21–23, 2010, paper and presentation.

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6. Strzelec, A., Bilheux, H.N., Finney, C.E., Daw, C.S., Foster, D.E., Rutland, C.J., Schillinger, B. and Schulz, M., "Neutron Imaging of Diesel Particulate Filters," SAE 2009-01-2735.

7. Strzelec, A., Toops, T.J., Daw, C.S., Foster, D.E. and Rutland, C.J., "Particulate Matter Oxidation Kinetics: Surface Area Dependence," 2010 CLEERS Workshop oral presentation, April 20–22, Dearborn, Michigan (www.cleers.org).

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III. FUEL PROPERTY EFFECTS ON ADVANCED COMBUSTION REGIMES

III.1 Fuel Effects on Advanced Combustion Engines

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2 Rincon Ranch Consulting, Tuscon, AZ (statistics)
3 AVL North America, Plymouth, MI, (statistics applied to combustion analysis)
4 University of Wisconsin, Madison, WI (kinetic modeling)

Objectives

- Obtain representative samples of new, unique, or emerging fuels and screen with engine and laboratory analytical techniques to continue to add to a database of results and to develop tools for the rapid, efficient screening of new fuels and fuel components.
- Develop and finalize statistical analysis tools which will allow study of fuel effects on engine control and engine performance (with Rincon Ranch Consulting and AVL).
- Determine extent that kinetic mechanisms can be reduced for efficient computational fluid dynamics (CFD) calculation while still showing fidelity to fuel changes (with University of Wisconsin, UW).
- Build an alliance with the University of Tennessee, Knoxville (UTK) and the Massachusetts Institute of Technology (MIT) in the area of lubrication research in support of 2011 DOE program goals in lubrication, friction, efficiency, and durability (with UTK, MIT, and MIT consortium on durable engines and aftertreatment).
- Build other alliances with industry, universities, or other labs which will advance an understanding of fuel chemistry and property effects on combustion and engine performance and help disseminate DOE research results.

Fiscal Year (FY) 2010 Accomplishments

- In addition to the homogeneous charge compression ignition (HCCI) engine which has been used for the last five years to study fuel effects, a single-cylinder diesel engine was also commissioned to allow more detailed study of the effects of fuel properties on mixing and combustion. Both engines have also been equipped with a new AVL Indicom combustion analysis system that incorporates slow-speed data channels, gas exchange, and energy balance analysis. This capability will allow much easier determination of residual fraction, true cylinder charge, and energy balances for more precise kinetic modeling.
- Fuels studied in 2010 include a repeat of the Fuels for Advanced Combustion Engines (FACE) diesel fuels in the diesel configuration, a study of surrogate diesel fuels designed to mimic the FACE diesel fuels, n-heptane (to provide data for developing and tuning kinetic models with very simple kinetic models), soy-biodiesel blends, and some special biofuels from non-traditional plant sources.
- In statistical analysis, our analysis strategy has been finalized and applied to several data sets and will be routinely used in future research. Our approach includes a generalized MATLAB tool for designing and interpreting principal components of fuel data and a generalized statistical toolbox (AVL Cameo) for modeling of fuel and engine data. We have moved from a 'study how to use statistics' to a 'use routinely' phase.
- In a project with UW, we are comparing two approaches to kinetic mechanisms for studying fuel effects. The first part of the study has been completed, an evaluation of UW's MultiChem approach to kinetic models, where more complex surrogates are used to define the physical processes of spray, evaporation, and mixing, and more simple kinetic models are used to represent chemistry and oxidation. This approach was applied very successfully to the FACE diesel fuels. The second approach, using Reaction Design's Model Fuels Consortium (MFC) large master mechanisms and tools for surrogate design and mechanism reduction is underway.
- We have been a participant in MIT's consortium for durable aftertreatment and engines since it began five years ago. Several years ago, we evolved from a paying member to a work-in-kind member and have assisted and shared our research in aftertreatment aging and poisoning and diesel particulate filter (DPF) ash effects. In 2010, we added an additional collaboration in the area of lubrication, tribology,

and engine efficiency and have leveraged this into a DOE funded project for 2011. The consortium provides a unique link to several lubricant and additive companies and engine and vehicle manufacturers in order to guide the research in the most effective directions.

Future Directions

- We plan to continue to screen new fuels as available in areas of alternate crude sources and biofuels; have established collaboration with UTK for biofuels, with the University of Maine for pyrolysis fuels, and with the Pacific Northwest National Laboratory (PNNL) for oil shale fuels.
- Rebuild collaboration with PNNL for fuels program in order to continue joint research into fuel analysis, engine performance, properties, chemistry, and fit-for-use tests, includinga second series of oil shale fuels and pyrolysis-derived fuels.
- Continue to integrate statistical and kinetic modeling tools into routine workflow in order to obtain maximum usage and understanding of experimental results.
- Conduct research in engine friction and lubrication through collaboration with UTK and MIT.
- We have begun collaboration with sp3h, a French company developing an on-board fuel quality sensor based on non-dispersive infrared to determine how to use fuel property and chemistry information for engine control. This collaboration also leverages our statistics work, since the sensor is based on principal component analysis (PCA) analysis of the non-dispersive infrared spectrum.

Introduction

Understanding the relations between fuel properties and high-efficiency clean combustion (HECC) modes is among the greatest needs expressed by engine, automobile, and fuel companies. ORNL and other organizations have found combustion operating regimes of simultaneous low oxides of nitrogen (NOx) and particulate matter (PM) using high dilution and optimization of fuel injection parameters. Under certain control strategies, these advanced combustion regimes have also demonstrated improved fuel efficiency. Fuel formulation has a substantial impact on our ability to fully exploit and implement these regimes in emerging engine technologies. Fuel composition impacts whether engines will operate in the regimes at all, and also influences the combustion rate, control, cycle-to-cycle consistency, and emissions. Although non-petroleum-based fuels are emerging and will play a larger role in future fuels, the bulk of diesel and gasoline fuels will continue to be derived from conventional and unconventional petroleum crude for the forseeable future.

Approach

The primary goal of this research is to study the effects that fuel formulation and emerging fuels can have on new combustion regimes and to exploit those properties for improved emissions and efficiency. Overall, fuels research at ORNL involves multiple test stands. This report is focused mainly on two single-cylinder engine platforms which operate in conventional or HCCI combustion, are capable of achieving results with a minimum of fuel, and are easy to control and kinetically model. Collaborations with other laboratories and universities are used to obtain unique or emerging fuels for evaluation, and results are studied with both statistical and kinetic modeling. We have extended our use of small engines and modeling to engine lubrication and efficiency for a new 2011 research topic, in collaboration with UTK and MIT.

Results

In the past, when comparing engine measurements to kinetic modeling results, we have been confronted with the situation of not having sufficient experimental measurements to fully define the boundary conditions for kinetic modeling. Areas most deficient have been residual fraction and true cylinder mass, charge temperature after induction into the cylinder, wall temperatures and heat loss, and true top dead center piston position and compression ratio. A major part of this year was spent integrating and commissioning a new AVL combustion analysis system which incorporates measurements and software necessary to eliminate or reduce all of these sources of uncertainty. The software also includes gas exchange analysis enabled by high-speed port pressure transducers and full energy balances.

Fuels studies this year include FACE fuels and surrogates for five of them run in diesel mode, n-heptane run to provide data for verification of kinetic models (diesel), soy-biodiesel blends, and non-traditional, hydrocarbon-related plant extracts (HCCI, to be repeated in diesel). It is interesting to contrast engine response in conventional diesel mode vs. HCCI mode, because HCCI is much more affected by fuel chemistry and properties and also more difficult to model statistically due to more non-linear responses. We will be investigating this further in 2011. We also had a difficult time obtaining additional samples of emerging biofuels, such as those derived from algae or thermochemical processing of biomass. However, we did set up collaboration with several groups to obtain such fuels for 2011 research.

Based on a merit review comment last year, we statistically modeled all of our diesel HCCI data, comprising five years of data and 95 fuels total. Conclusions are similar to those from the individual studies, with HCCI preferring lower cetane, lower boiling points, and no poly aromatics content. Oxygen-containing fuels, not containing nitrogen, showed some benefit in a smoke-constrained optimization. The study highlighted the benefits of revising the statistical models and selecting only portions of data to highlight specific fuel-related questions. The tools we have developed or acquired allow this to be easily done and will be applied routinely in future research. Additionally, this research emphasized the need to stay within experimental design space, which is not normally a simple orthogonal space, when exercising statistical models in parametric studies or optimizations of fuel effects, especially for low-temperature combustion.

It was our intent in 2010 to complete our statistics modeling methods development, and then use 2011 to verify methods and apply finishing touches. We were able to acquire a generalized principal components modeling tool, MATLAB-based, to generate vectors from any data set and to allow conversion of vector values to properties and chemistry or the reverse. This allows the PCA approach to be continued without custom programming each data set. Additionally, we acquired AVL Cameo, which is a statistically-based modeling and map generation tool for engine calibration. This software is very powerful in terms of generating, verifying, visualizing, and using statistical models for engine response data. In the software, fuel variables can be treated as if they are engine control variables in order to study engine response to fuels.

CFD modeling is widely used in engine design and optimization, generally with simple surrogate fuel models to promote faster calculations. Complex fuel mechanisms can be used, but they slow calculation time to the point that CFD is no longer practical for large engine design studies. Many groups are developing faster solvers, improved kinetic mechanisms, and more powerful mechanism reduction techniques to allow more complete modeling of fuel effects within CFD modeling. Because of our very large database of fuels, ORNL is well-equipped to participate in this development work. In this research, we have chosen to partner with the Engine Research Group at UW through a subcontract. They are modeling our FACE fuel data run on the HCCI engine and comparing two different surrogate mechanism strategies. A total of 32 data points are being modeled for the nine FACE fuels, pulled out of the ORNL data and covering the central or optimum operating portions of the ORNL experiments. The first technique, developed at UW, uses 14 pure compounds, with multiple choices of molecular weight and boiling point for each chemistry class (i.e., aromatics, iso-paraffins, etc.) in order to match physical properties of a fuel (distillation, density, energy content, cetane, cetane index, and H/C ratio) while maintaining the correct mix of chemistry. This complex surrogate is used only for calculation of physical processes of spray, mixing, and evaporation. For chemical reaction, only five surrogate compounds are used (n-heptane, n-tetradecane, iso-octane, toluene, and decalin) to represent each of the chemical classes in order to reduce mechanism size for the more complex chemistry and reaction calculations at each CFD time step. These compounds are combined in a skeletal mechanism of 90 species and 348 reactions. The second surrogate mechanism strategy is the use of the Reaction Design Model Fuels Consortium master diesel mechanism set, combined with MFC tools for surrogate design and mechanism reduction. In this case, the same surrogates are used to represent both the physical and the chemical characteristics of the fuels and can be designed using a user-selected set of chemistry and property targets with user selected weighting factors. This work has just begun, with ORNL having designed the surrogate blends from a pallet of nine pure components and starting on mechanism reduction.

The UW surrogate strategy is capable of matching the boiling points and properties of the FACE fuels within an absolute error of 10% or less, even for the FACE fuels with non-linear distillation curves, such as those shown in Figure 1. Figure 2 shows the match of cylinder pressure and heat release for three of the data points and the results are quite good. Figure 3 shows overall match for NOx (emissions), peak pressure (of interest for control and structural considerations), indicated specific fuel consumption (ISFC, fuel efficiency), and combustion phasing (of interest for control considerations). NOx matches well, although most of the points are near zero, typical of light-load HCCI. Peak pressure also shows a good match. ISFC is a little disappointing. Note that modeled ISFC is better because it does not include pumping losses for these simulations. Combustion phasing agrees quite well, indicating that the model is capable of mimicking the ignition characteristics of the individual fuels. This modeling work is complete, but further comparisons and drill down will be done in 2011. The next phase of this work is to repeat this modeling using the MFC surrogate and mechanism techniques for comparison. Due to budget cuts for 2011, this project has been reduced considerably and we will no longer be performing similar analysis for our gasoline or our diesel engine data. Completing this analysis within the MFC Cooperative Research and Development Agreement is one possibility and on the 2011 work planning ballot for the MFC.

In lubrication and effects on engine efficiency, we have a funded project from DOE for 2011. We have begun by borrowing a friction and wear machine from MIT. We will improve our motored engine friction rig with an improved torque meter, compression pressure measurement capability, and improved temperature

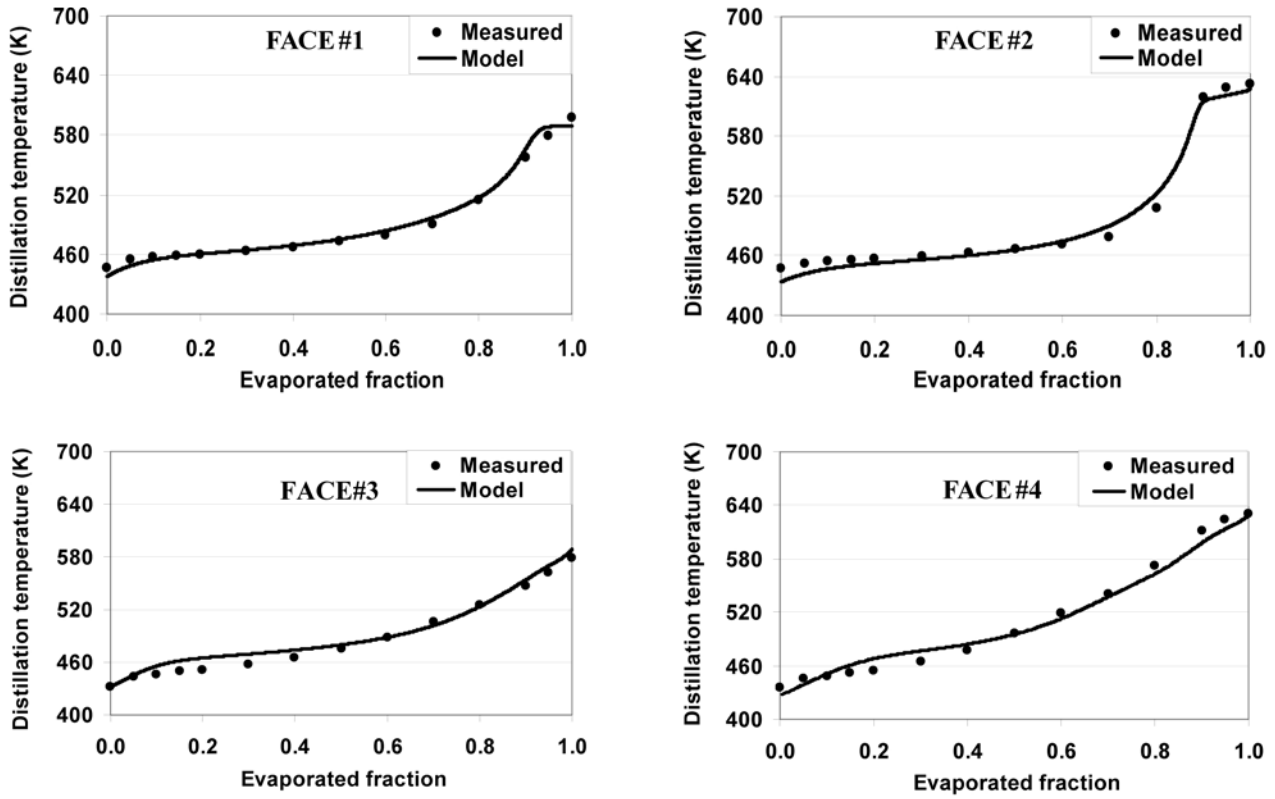
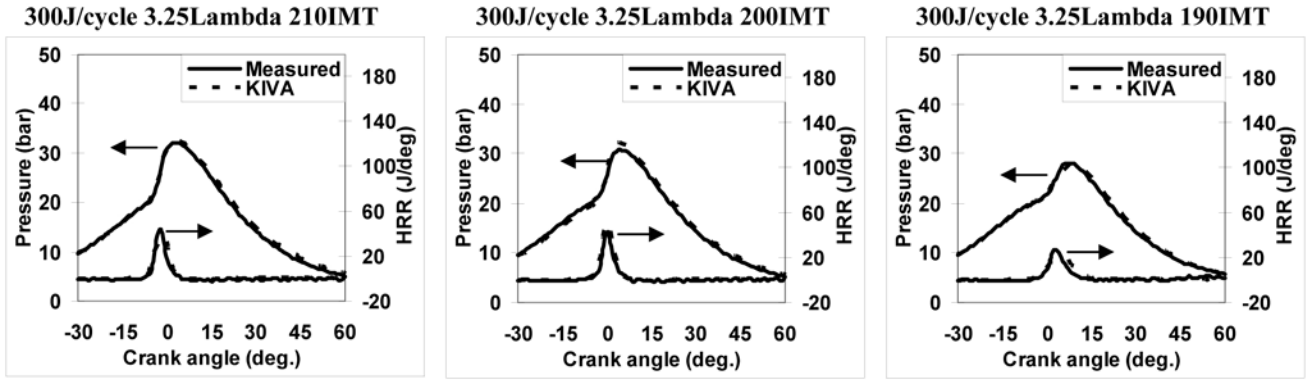


FIGURE 1. Comparison of Distillation Curves of FACE Fuels and FACE Surrogates for Four of Nine FACE Fuels



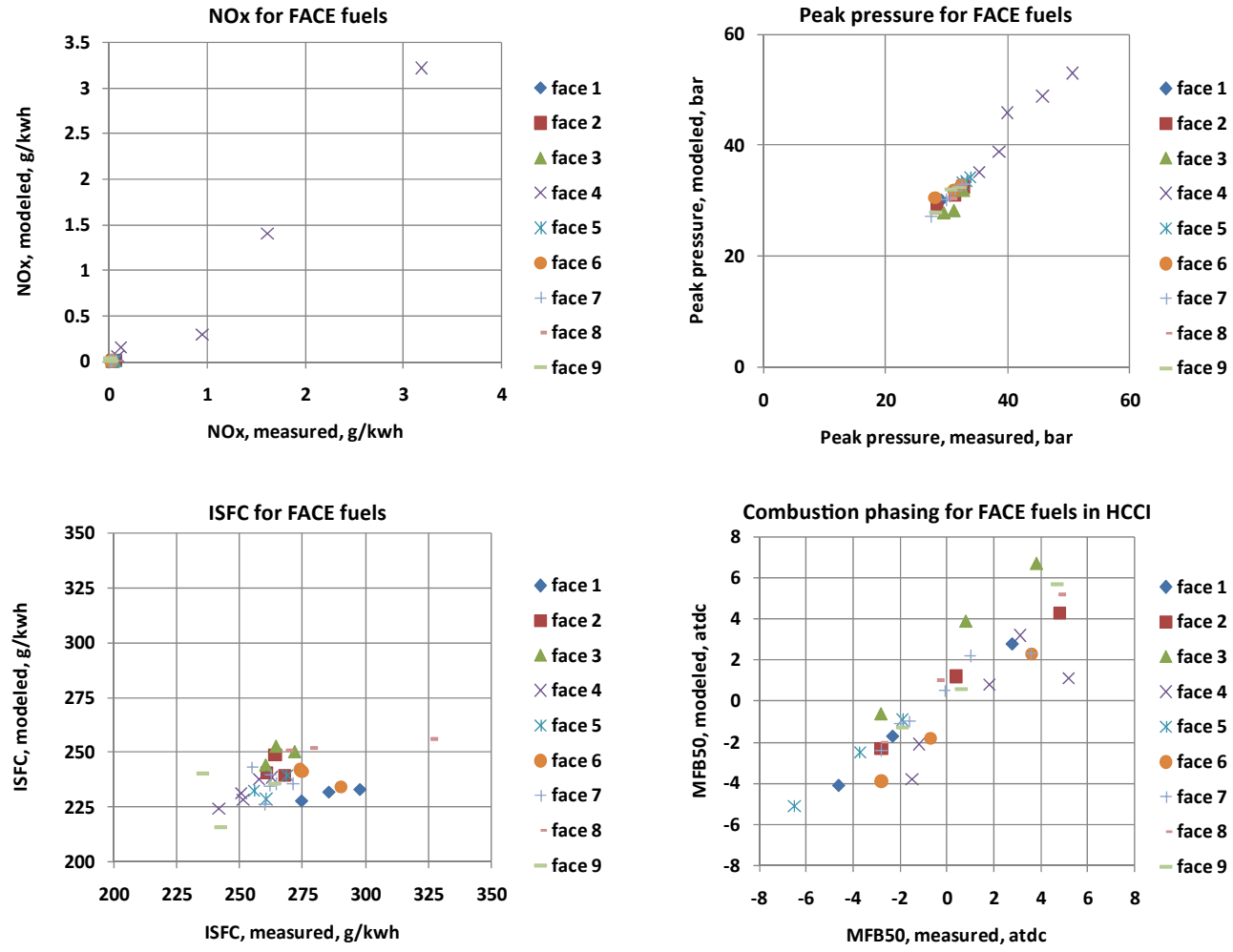
IMT - intake manifold temperature; HHR - heat release rate

FIGURE 2. Comparison of Measured and Modeled Cylinder Pressure and Heat Release for Three FACE Fuel #9 Operating Conditions

control. AVL Excite software has been acquired and will be used to link simple tribology measurements to total engine performance. The collaboration between ORNL, UTK, MIT, and AVL was described in a 2010 Directions in Engine-Efficiency and Emissions Research (DEER) conference poster noted in the references.

Conclusions

- Improved heat release including residual fraction and energy balance has been initiated through AVL hardware and software in order to provide improved definition of experimental conditions for kinetic modeling.
- A diesel configuration engine has been set up, in addition to the HCCI, and is being used to compare



MFB50 - 50% mass fraction burnt; atdc - after top dead center

FIGURE 3. Comparison of a Few Variables for Modeled vs. Experimental Data for FACE Fuels in HCCI, using KIVA and the UW MultiChem Kinetics Approach

fuel effects between HCCI and conventional combustion. Fuel sets run in 2010 included FACE diesel fuels and surrogate blends, n-heptane, non-traditional plant extracts, and soy biodiesel. Experimental results are shared between kinetic and statistical modeling and the model fuels consortium.

- Statistical tools are in place to allow this analysis to become a routine part of our experimental and analysis tool set, through a generalized PCA modeling tool and AVL Cameo software. We have begun applying these tools to more global studies of fuel effects than attempted previously.
- Kinetic modeling tools are being improved to the point that they can be used for global studies of fuel effects, but further development and verification are needed.
- A new lube oil/efficiency study was set up and received funding for 2011.

FY 2010 Publications/Presentations

1. Karthik V. Puduppakkam, Long Liang, Anthony Shelburn, Chitralkumar V. Naik, Ellen Meeks, and Bruce G. Bunting, Predicting Emissions Using CFD Simulations of an E30 Gasoline Surrogate in an HCCI Engine with Detailed Chemical Kinetics, SAE paper 2010-01-0362.

2. Bruce G. Bunting, Romain Lardet, and Robert W. Crawford, Statistical Overview of 5 Years of HCCI Fuel and Engine Data from ORNL, presentation at 2010 DOE DEER conference.

3. William F. Rohr, Ke Nguyen, Bruce G. Bunting, Jun Qu, Peter Blau, Sheng Dai, Huimin Luo, Greg Mordukhovich, Donald Smolenski, Wensheng Zhang, Tasfia Ahmed, Victor Wong, and Arthur Kariya, Validation of a Small Engine Based Procedure for Studying Performance of Engine Lube Oils, Ionic Liquids as Lubricants and/or Lubricant Additives, and Opportunities for Engine Friction

Reduction and Durable Design, triple poster presented at 2010 DOE DEER conference.

4. Bruce G. Bunting, Jim Szybist, Scott Sluder, John Storey, Sam Lewis, Robert Wagner, Jun Qu, Robert Crawford, FT01 – APBF Effects on Combustion (advanced petroleum based fuels, DOE project # 18546), presentation at 2010 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, June 7–10, 2010.

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III.2 Optical-Engine Investigations of Fuel and Operating-Condition Effects on In-Cylinder Liquid-Phase Fuel Penetration

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Objectives

- Conduct measurements of liquid-phase fuel penetration (i.e., liquid length, LL) for single- and multi-component hydrocarbon and biodiesel fuels in a direct-injection (DI) engine when in-cylinder conditions and injection rate are time-varying.
- Use measured results to elucidate effects of fuel-property changes, injection pressure, and in-cylinder thermodynamic conditions on LL so that the detrimental effects of wall impingement can be avoided with new fuels and combustion strategies.

Fiscal Year (FY) 2010 Accomplishments

- Completed a parametric study of LL over a range of in-cylinder conditions and injection pressures for five fuels with widely varying volatility characteristics: gasoline and diesel single-component primary reference fuels, two multi-component biodiesel fuels produced from different feedstocks, and a #2 diesel certification fuel.
- Quantified the relative importance of different parameters on the LL, including in-cylinder thermodynamic conditions, fuel volatility, injection pressure, and unsteadiness.
- Showed that ~20% longer LLs for biodiesels than for #2 diesel could help explain observed lube-oil dilution when fueling with biodiesel, but also that a properly formulated biodiesel could lead to improved performance under early-DI conditions.

Future Directions

- Study fuel and injection-parameter effects on mixing-controlled, high-efficiency, clean combustion strategies at injection pressures up to 300 MPa.
- Lead a team of researchers in the formulation and evaluation of diesel surrogate fuels, which are critical for enabling the computational optimization of future engines for emerging fuels.

Introduction

A number of advanced-combustion strategies and aftertreatment-system regeneration approaches proposed for use in future engines employ early and/or late DIs of fuel, i.e., injections that are at least 30 crank-angle degrees (CAD) from top dead center (TDC). Previous research in our optical-engine laboratory has shown that impingement of liquid-phase fuel on in-cylinder surfaces when employing early-DI strategies is a fundamental barrier to achieving the full benefits of premixed compression-ignition strategies with fuels in the diesel volatility range. This is because liquid-phase fuel films preclude proper mixture formation and combustion phasing, leading to significantly degraded efficiency and emissions [1].

Given the importance of liquid-phase fuel impingement as a barrier to achieving efficiency and emissions goals, recent research in our laboratory has focused on making high-speed measurements of maximum in-cylinder LLs under unsteady conditions encompassing those experienced when early- and late-DI strategies are used. The objective of the work is to enhance the fundamental understanding of fuel effects on LLs, to assist engine designers in avoiding the undesired effects of wall impingement. Whereas previous studies have focused on LLs under quasi-steady conditions (e.g., [2-6]), the current work is focused on determining the influences of fuel volatility and unsteady injection rate on LLs under the unsteady in-cylinder thermodynamic conditions produced by piston motion in operating engines.

Approach

The primary experimental apparatus used for the work is a single-cylinder version of a modern-technology, heavy-duty, 4-stroke, compression-ignition DI engine that has been modified by Sandia to provide extensive optical access to the combustion chamber [1]. As shown in Figure 1, LL measurements were made using 532-nm light from a diode-pumped Nd:YAG laser providing ~0.5-µs pulses at 50 kHz (i.e., every 0.2 CAD at 1,500 rpm engine speed) formed into an ~5-mm-thick sheet and passed through a window in the piston crown to illuminate one spray from the 2-hole injector

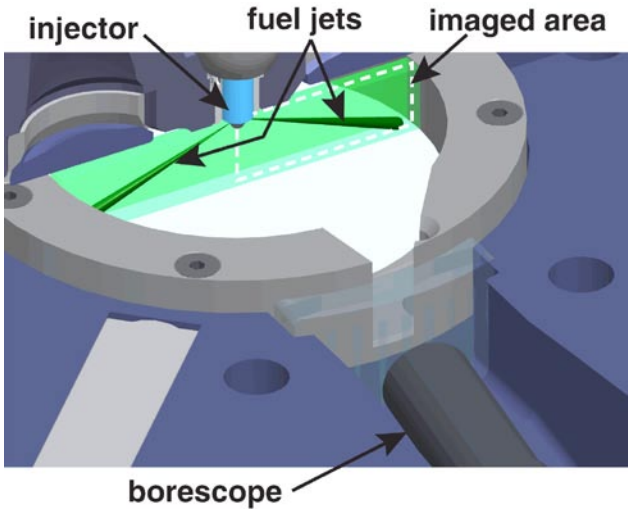

FIGURE 1. Schematic of imaging setup for LL measurements in the optical engine. Laser sheet passes upward through piston window and illuminates fuel jets. Elastically scattered light passes through notch in piston bowl-rim, window in cylinder liner, and borescope to be imaged by high-speed CMOS camera.

tip. Elastically scattered light from the liquid-fuel droplets was detected using a high-speed complementary metal-oxide semiconductor (CMOS) camera viewing through a custom borescope lens, a window in the upper periphery of the cylinder liner, and a cutout in the piston bowl-rim. Image corrections, specifics of the liquid-length measurement process, and further details of the experimental setup can be found in [7] and [8]. The fuel-injection rate was determined from measurements of fuel-jet momentum under static-engine conditions. A total of five fuels were tested: 2,2,4-trimethylpentane (TMP, i.e., iso-octane, a gasoline primary reference fuel); 2,2,4,4,6,8,8-heptamethylnonane (HMN, a diesel primary reference fuel); neat fatty acid methyl esters (FAME) derived from soybean oil (soy methyl ester, SME); neat FAME derived from Cuphea oil (CuME) [9]; and a 2007 #2 ultra-low-sulfur diesel certification fuel (ULSD).

Results

In the first set of experiments [7], LLs were measured for the single-component fuels HMN and TMP. HMN has a normal boiling point (NBP) of ~240°C (diesel-range volatility), and TMP has an NBP of ~99°C (gasoline-range volatility). Data for HMN are shown in Figure 2 for a single-injection event during the compression stroke. The plot of LL vs. time and crank angle on the right shows evidence of turbulent fluctuations in LL throughout the injection, including the maximum at Point (b) that results from an "island" of liquid fuel that has separated from the core of the jet. The overall trend during this injection is a steadily decreasing LL, rather than the quasi-steady LL behavior that has been observed in previous work under quasi-steady ambient conditions (e.g., [2,4,5]). One possible explanation for this behavior is the unsteady injection rate. As shown in Figure 3, however, LL is not strongly affected by injection rate. This is particularly evident in the plot on the right, which shows average data for injection during the expansion stroke. In this case there is no peak in LL where the injection rate peaks, and LL steadily increases as injection rate decreases. Also, there is no significant difference in LLs measured at two different levels of maximum injection pressure (71 MPa and 142 MPa). This independence of LL with respect to injection pressure is consistent with previous studies (e.g., [2]).

As shown in Figure 4, the current results provide evidence that fuel volatility and instantaneous in-cylinder thermodynamic conditions largely determine the LL for a given fuel at a given crank angle. For each case, average LL traces for different injection timings have been pieced together, neglecting the ramp-up and ramp-down transients of each segment. The data show that LL for a given case decreases through the compression stroke as charge-gas temperature and density increase, then levels off near TDC, then increases through the expansion stroke as charge-gas temperature and density decrease. The two HMN cases further illustrate the influence of in-cylinder thermodynamic conditions. When intake pressure is increased, all charge densities are shifted to higher values and the entire liquid-length plot therefore shifts downward. The effect of fuel volatility is also apparent. For equivalent intake pressure, LLs at all engine crank angles are ~55% shorter for TMP (high volatility) than for HMN (low volatility). The direct influence of fuel volatility on LL has important implications for emerging fuels. For example, biodiesel fuels are typically less volatile than conventional diesel and therefore could have longer LLs.

The two biodiesels and ULSD were used in a second set of experiments to address this issue [8]. Figure 5a shows distillation data for the three multi-component fuels, and Figure 5b shows the LL increase of the two biodiesels with respect to the ULSD. Although the CuME has distillation temperatures nearly 100 K below those for SME up to ~60 vol% recovered, its LLs are nearly indistinguishable from those of SME. This is consistent with earlier work showing that the LL is governed by the least-volatile components of the fuel [6]. The fact that LLs are ~20% longer for the biodiesels could lead to more liquid-fuel impingement on in-cylinder surfaces and help explain observations of increased lube-oil dilution with biodiesel blends (e.g., [10]).

Figure 6 shows an unexpected potential benefit of the CuME fuel. Namely, the LL at -30° after top dead center (ATDC), when fuel might begin impinging on the top of the piston in a narrow-angle DI strategy, actually

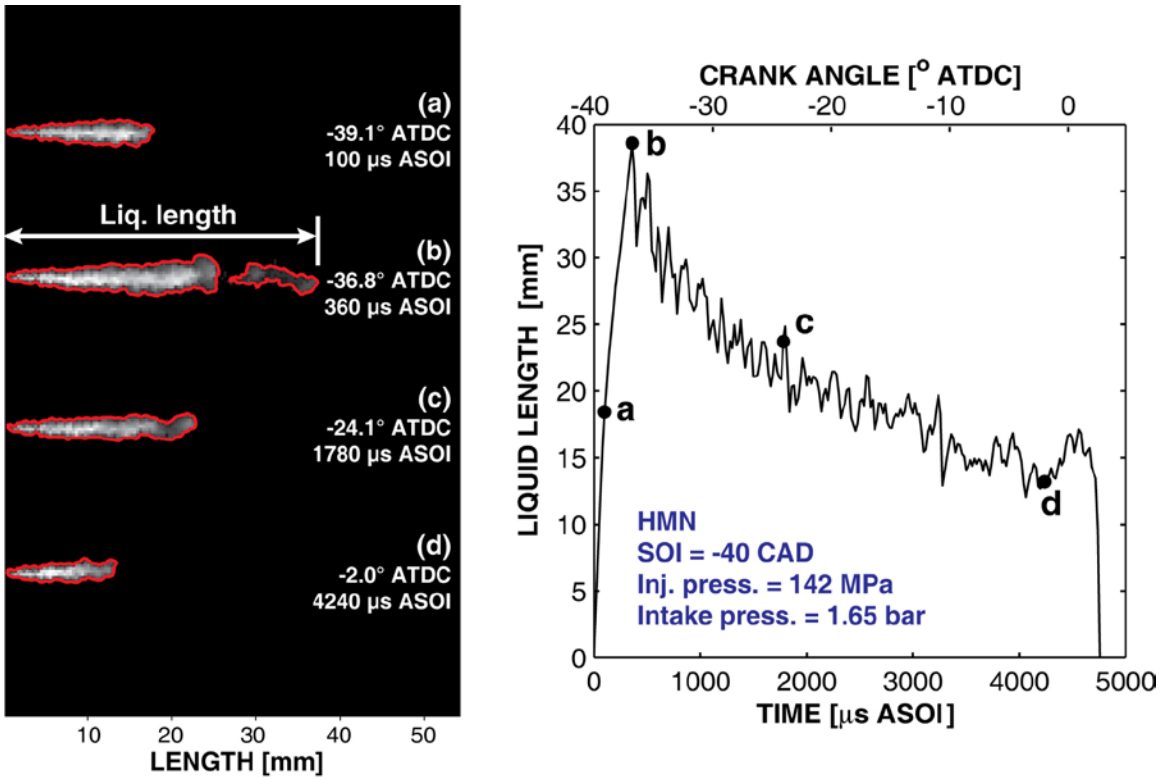

FIGURE 2. Sample data for a single HMN injection during the compression stroke. On the left is a set of images of elastically scattered light from HMN fuel droplets during injection. Images are oriented such that the fuel jet appears horizontal. Engine crank angle and time after start of injection (ASOI) are shown for each image frame. On the right is a plot of LL vs. time (bottom axis) and engine crank angle (top axis).

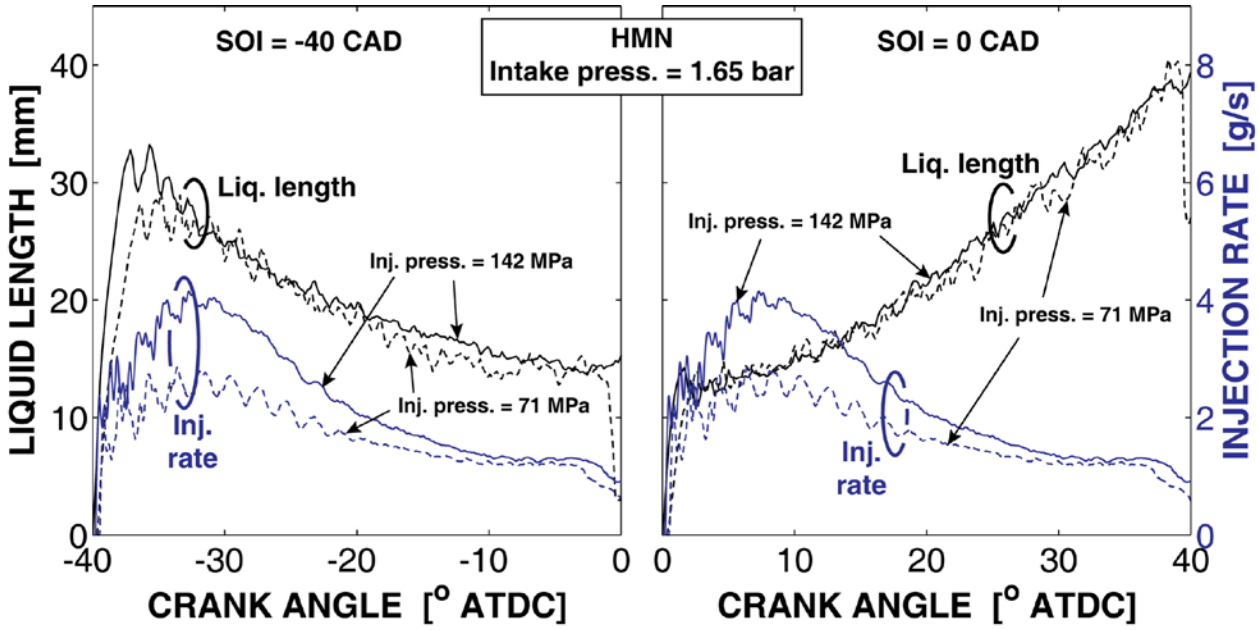

FIGURE 3. HMN LL (left axis) and injection-rate (right axis) data for two cases of maximum injection pressure. On the left are data for an injection during the compression stroke, SOI = -40 CAD. On the right are data for an injection during the expansion stroke, SOI = 0 CAD. All LL and injection-rate data are averaged over several injection events.

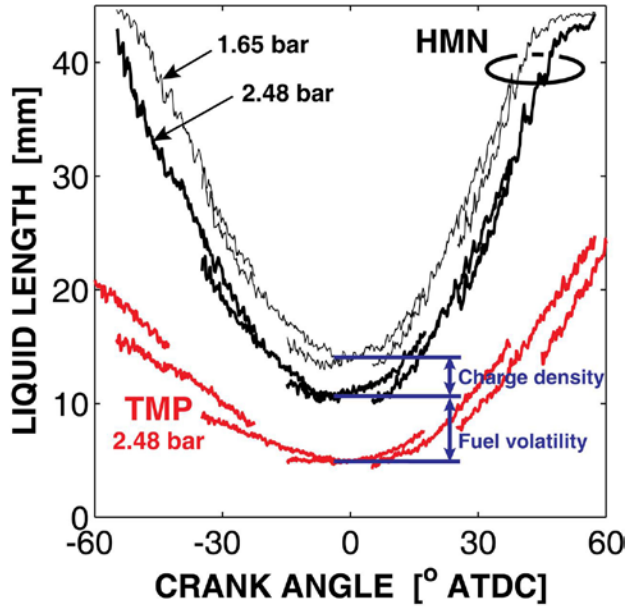

FIGURE 4. Overview plots of LL vs. engine crank angle. For each case, average LL data for different injection timings have been pieced together to form the overview plot. The effects of in-cylinder thermodynamic conditions are evident in the overall shapes of the plots and the downward shift in LL when intake-manifold pressure is increased from 1.65 to 2.48 bar. The effect of fuel volatility is evident in the downward shift in LL when changing from HMN (low volatility) to TMP (high volatility).

gets ~30% shorter as the start of injection (SOI) timing is advanced. Typically, earlier SOI timings are desired because they give more time for fuel/air premixing, but they also typically lead to longer LLs and more wall impingement. With CuME, an earlier SOI timing could actually lead to less wall impingement provided the piston is far enough away from the injector while the LL is long. This could facilitate early-DI strategies with CuME.

Conclusions

- Even under unsteady in-cylinder conditions, to first order, LLs are governed by fuel volatility (i.e., boiling point, heat of vaporization, and specific heat of liquid and vapor) and instantaneous in-cylinder density and temperature.
- Regardless of fuel type, injection pressure has little effect on LL.
- Consistent with previous work, the least-volatile fuel components appear to govern the LL.
- The presence of low-volatility compounds in the biodiesel fuels is correlated with them having ~20% longer LLs than the ULSD. This could lead to more liquid-fuel impingement on in-cylinder surfaces and help explain observations of increased lube-oil dilution with biodiesel blends.
- For single-component fuels, unsteadiness has little effect on LL. For multi-component fuels, unsteadiness can have a large effect on LL, especially for fuels that contain both high- and low-volatility components.
- These multi-component/unsteadiness effects lead to a synergy between the CuME fuel and early-DI injection strategies, yielding a 30% shorter LL at the same crank angle during the compression stroke as the SOI timing is advanced.

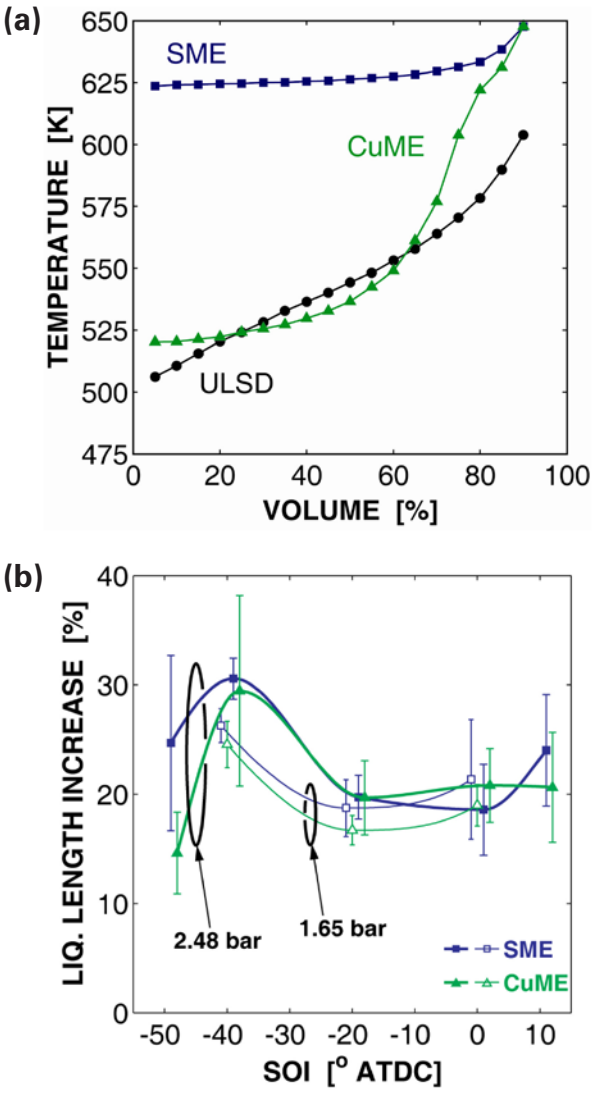

FIGURE 5. a) Advanced distillation curves for the three multi-component fuels: SME, CuME, and 2007 #2 ULSD. Data provided by Dr. T. Bruno of the National Institute of Standards and Technology. b) Increase in LL for SME and CuME relative to ULSD as a function of SOI timing for two intake-manifold pressures at an injection pressure of 142 MPa. Error bars represent ± one standard deviation of each time-averaged value.

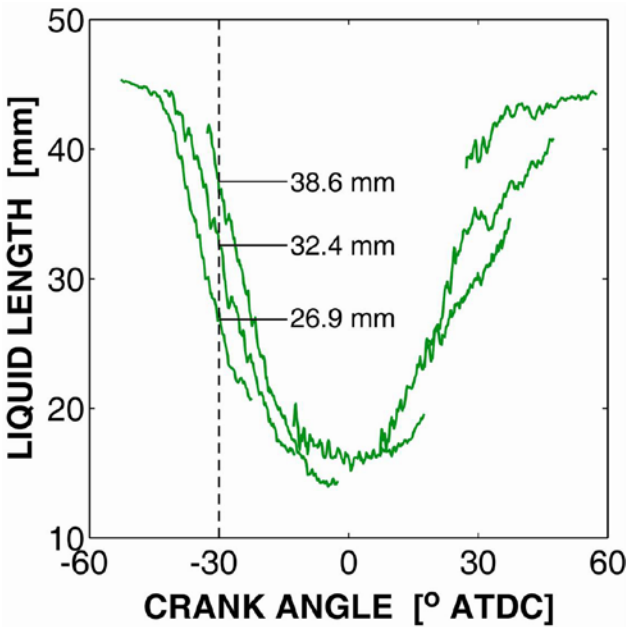

FIGURE 6. LL vs. engine crank angle for CuME. At a crank angle of -30° ATDC, the LL becomes ~30% shorter as the SOI timing is advanced from -40° ATDC to -60° ATDC. Intake-manifold pressure is 2.48 bar.

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2. Mueller, C.J., "Sandia/Caterpillar Collaborative Research: Past Results and Potential Future Directions," Caterpillar Technical Center, Peoria, IL (October 9, 2009).

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12. Fisher, B.T., "Optical Diesel Engine Studies of Conventional and Emerging Fuels to Understand Effects of Fuel Volatility on In-Cylinder Mixing and Combustion Processes," Sandia PReSS (Post-doctoral and Recent Staff Seminar), Livermore, CA (April 29, 2010).

13. Mueller, C.J., "Status Update on AVFL-18: Diesel Surrogate Fuel Development," CRC AVFL Committee Meeting, Detroit, MI (May 17, 2010).

14. Mueller, C.J., "Fuel Effects on Advanced Combustion: Optical Heavy-Duty Engine Research," 2010 DOE Vehicle Technologies Annual Merit Review, Washington, D.C. (June 8, 2010).

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18. Mueller, C.J., "Status Update on AVFL-18: Diesel Surrogate Fuel Development," CRC AVFL Committee Meeting, San Antonio, TX (September 15, 2010).

19. Mueller, C.J., "An Experimental Investigation of the Origin of Increased NO_x Emissions When Fueling a Heavy-Duty Compression-Ignition Engine with Soy Biodiesel," 2010 Diesel Engine Efficiency Enhancement and Emissions Reduction (DEER) Meeting, Detroit, MI (September 30, 2010).

Awards

1. Society of Automotive Engineers (SAE) 2009 John Johnson Award for Outstanding Research in Diesel Engines for SAE Technical Paper 2009-01-1792 entitled, "An Experimental Investigation of the Origin of Increased NO_x Emissions When Fueling a Heavy-Duty Compression-Ignition Engine with Soy Biodiesel."

2. SAE Award for Excellence in Oral Presentation for presenting above paper at 2009 SAE International Powertrains, Fuels and Lubricants meeting in Florence, Italy, on June 17, 2009.

3. Sandia National Laboratories Combustion Research Facility 2010 E. Karl Bastress Award for effective coupling of conservation-related programs to the needs of US industries.

4. Sandia National Laboratories 2010 Outstanding Mentor Award for mentorship of summer intern Peter M. Lillo from the University of California, Berkeley.

III.3 Chemical Kinetic Modeling of Advanced Transportation Fuels

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Objectives

- Develop detailed chemical kinetic reaction models for components of advanced petroleum-based and non-petroleum-based fuels. These fuel models include components from vegetable-oil-derived biodiesel, oil-sands-derived fuel, alcohol fuels and other advanced bio-based and alternative fuels.
- Develop detailed chemical kinetic reaction models for mixtures of non-petroleum and petroleum-based components to represent real fuels and lead to efficient reduced combustion models needed for engine modeling codes.
- Characterize the role of fuel composition on efficiency and pollutant emissions from practical automotive engines.

Fiscal Year (FY) 2010 Accomplishments

- Developed detailed chemical kinetic models for two of the actual components in real biodiesel derived from either vegetable oil or animal fat.
- Developed a reduced mechanism for a large biodiesel surrogate for use in computational fluid dynamics (CFD) codes.
- Developed chemical kinetic models for three C5 esters that have molecular structures characteristic of biofuels.
- Validated chemical kinetic models by comparing results from the chemical kinetic fuel models to experiments in stirred reactors, premixed flames and counterflow diffusion flames.

Future Directions

- Develop detailed chemical kinetic models for three actual components in soy-based biodiesel: methyl palmitate, methyl lineate and methyl linolenate.
- Develop a chemical kinetic model for the four isomers of butanol.
- Develop a chemical kinetic model for the iso-pentanol, a bio-derived fuel.

Introduction

Development of detailed chemical kinetic models for non-petroleum-based fuels is a difficult challenge because some of these fuels contain components that have not been considered in the past. Also, non-petroleum-base fuels are usually blended with petroleum-based fuels like diesel and gasoline that contain hundreds of components. It is important to develop detailed chemical kinetic models for these fuels since the chemistry models can be put into engine simulation codes used for optimizing engine design for maximum efficiency and minimal pollutant emissions. For example, these chemistry-enabled engine codes can be used to optimize combustion chamber shape and timing of single or multiple fuel injections in diesel engines. They also allow insight into how the composition of non-petroleum-based fuels affects engine performance characteristics. Additionally, chemical kinetic models can be used separately to interpret important in-cylinder experimental data and gain insight into advanced engine combustion processes such as homogeneous charge compression ignition (HCCI) and lean-burn engines.

Approach

Detailed chemical kinetic models are developed to represent the various components in non-petroleum-based fuels. These non-petroleum-based fuels include biodiesel, alcohol fuels, Fischer-Tropsch fuels and advanced bio-derived fuels. The components models are assembled into mixture or “surrogate” models to represent advanced fuels. Model calculations are carried out with these combined reaction mechanisms to compute ignition, soot precursor formation, and oxides of nitrogen (NOx) and other toxic species production under practical engine conditions. The mechanisms are then reduced for use in multidimensional CFD codes for simulating engine combustion. These chemistry-enabled CFD engine codes can be used to optimize engine design for new fuels for the best performance and engine efficiency and for minimum pollutants.

Results

Biodiesel fuel derived from vegetable and animal feedstocks contains saturated and unsaturated methyl esters that need to be included in a surrogate fuel

chemistry model for biodiesel. The five principal methyl esters in most vegetable oil-derived biodiesel are shown in Figure 1. In FY 2010, we developed a chemical kinetic model for two of these methyl esters, methyl stearate and methyl oleate [1]. This was a very ambitious task since it involved estimating thermodynamic data for thousands of species and describing thousands of reactions whose rate constants had to be estimated and assigned. Once the detailed chemical kinetic model had been built the combustion properties of the methyl esters could be computed. The ignition properties of the two methyl esters are compared in Figure 2. The methyl oleate ignites more slowly with longer ignition delay times than methyl stearate. This behavior can be expected due to the presence of a double bond in the carbon chain of methyl oleate (Figure 1) that inhibits low temperature chemistry. Normally, O_2 adds to the hydrocarbon chain and the radical site on the end of the O-O structure abstracts an H atom further down the chain. The presence of the double bond inhibits this process because the O-O structure is unable to "reach across" the double bond. This reaction is called an RO_2 isomerization and is a key chemical reaction in low temperature chemistry that enables low-temperature combustion modes in diesel and HCCI engines. The slower ignition of methyl oleate compared to methyl stearate is consistent with the derived cetane number of methyl oleate (59) compared to methyl stearate (96) [2]. The lower cetane number of methyl oleate indicates a longer ignition time than methyl stearate in the derived cetane number test. In Figure 2, we compare the ignition delay times of the two large methyl esters to ignition delay times of n-alkanes in a high pressure shock tube. A shock tube is an experimental device that allows testing of the fuels at pressures and temperatures similar to those found in internal combustion engines. We compare the methyl ester ignition to n-alkanes since there are no experimental data for these large methyl esters in a shock tube. The n-alkanes are n-hexane, n-decane and n-hexadecane, which have nearly the same carbon chain length as the methyl esters.

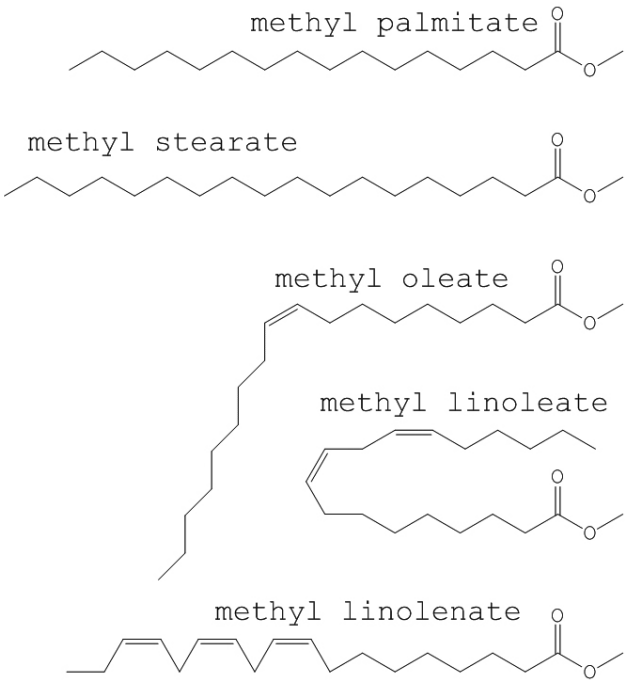

FIGURE 1. Molecular structures of the five principal methyl esters in most vegetable-derived biodiesel such as soybean-derived.

We further validated our chemical kinetic models for methyl stearate and methyl oleate by comparing computed results of the model to measurements in a jet-stirred reactor at elevated pressure [1]. A stirred reactor allows rapid mixing of fuel and air followed by reaction for a prescribe residence time and stable intermediate products can be observed. Comparison of the chemical kinetic fuel model with measured results from the stirred reactor allows one to assess that the calculated chemical pathways in the model are correctly reproducing experimentally-measured species concentrations. Figure 3 shows a comparison of the computed and experimentally-measured intermediate species concentrations in the stirred reactor at 10 bar for a stoichiometric ratio of 0.5 and a residence time of 1 sec. The experiments [3] were performed using methyl esters derived from rapeseed, the vegetable feedstock for most of the biodiesel produced in Europe. We compared measurements to predictions for the model using methyl stearate and methyl oleate as biodiesel surrogates. The agreement between the modeling and experimental results is quite good, giving us confidence in the models' accuracy (Figure 3).

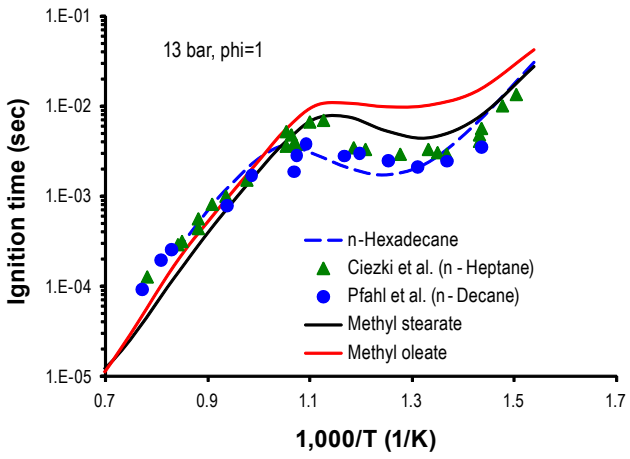

FIGURE 2. Ignition characteristics of methyl stearate and methyl oleate for stoichiometric fuel/air mixtures at 13.5 bar. Also for comparison are shown measured ignition behavior for n-alkanes (experimentally measured behavior for n-heptane/air [7], n-decane/air [8] and computed behavior for n-hexadecane [9]).

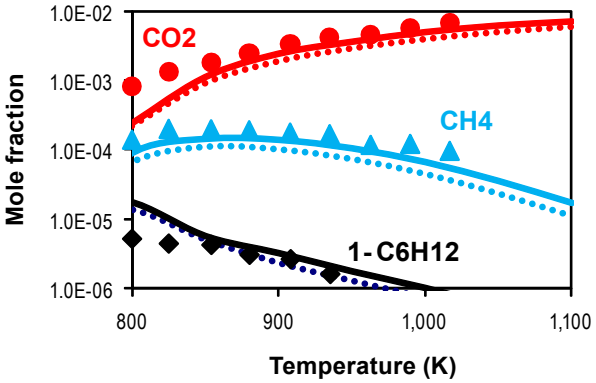

FIGURE 3. Predicted and measured intermediate species profiles in at stirred reactor at 10 atm and an equivalence ratio of 0.5. The measurements are for rapeseed-derived biodiesel methyl esters [3]. The curves are for biodiesel surrogates of methyl stearate (solid line) and methyl oleate (dotted line). Methyl stearate and methyl oleate are actual methyl esters found in most biodiesel. The species are CO_2 (carbon dioxide), CH_4 (methane) and 1-C_6H_{12} (1-hexene).

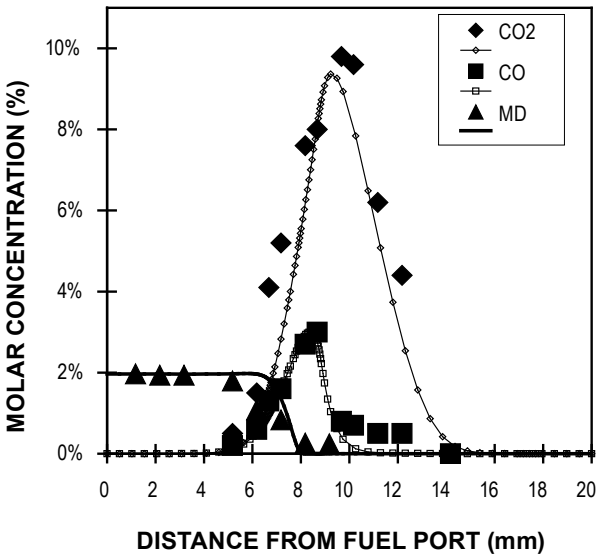

FIGURE 4. The measured and predicted concentrations of the fuel (MD) and intermediate species for the combustion of methyl decanoate, a biodiesel surrogate, in a counterflow flame [4]. The detailed methyl decanoate mechanism was greatly reduced for use in reacting flow codes.

It is important to reduce large chemical kinetic models, so that they can be used in multidimensional CFD codes for engine simulations. Detailed chemical kinetic models usually have too many species and reactions, and require too much computational resources to be included in engine codes. In FY 2010, we reduced our chemical kinetic mechanism for methyl decanoate, a large methyl ester that can be used as a surrogate for biodiesel and further validated our mechanism [4]. We collaborated with Prof. Lu at the University of Connecticut to reduce the mechanism using the directed relational graph (DRG) method that he developed [5]. The DRG method reduced the detailed mechanism of methyl decanoate from 3,012 species and 8,820 reactions down to 648 species and 2,998 reactions, almost a factor of 5 reduction in species. Since a conservation equation must be solved for each species considered in a reacting flow code, reducing the number of species greatly shortens code execution times. To validate the reduced mechanism, we compared results from the model to experimental results from a counterflow diffusion flame where fuel and air flow at each other in opposite directions. The counterflow diffusion flame incorporates fluid dynamic strain, molecular transport and fuel-air mixing, all of which are important processes found in diesel engine in-cylinder flows. Figure 4 shows the comparison between experimentally-measured and computed concentrations of fuel and intermediate species computed in the counterflow flame. The agreement between the model and experiment is very good.

It is important to validate the chemistry of new types of biofuels to ensure that the biofuel chemical kinetic models are accurate. In FY 2010, we developed the chemical kinetic mechanisms for three C5 esters with different molecular structures and validated the detailed chemical kinetic mechanisms by comparing computed results from the model with measurements in premixed laminar flames [6]. The structures of the three esters are shown on the top of Figure 5. The structures allow the assessment of the effects of methyl substitution on the hydrocarbon chain and the effect of including methyl or ethyl esters. Figure 5 shows the comparison of the computed and measured intermediate species profiles in the flames. The methyl esters produce more formaldehyde, while the ethyl ester produces more acetaldehyde. The computed and measured concentrations compare quite well. This validation of the models gives us confidence that chemical kinetic pathways in the models are accurately predicting the formation of experimentally measured species.

Conclusions

- New chemical kinetic component models of two large methyl esters actually found in real biodiesel have been developed, validated and published [1].
- Chemical kinetic models for three C5 esters with molecular structures characteristic of biofuels have been developed. Results of the models compare favorably to experimental results in premixed laminar flames.
- A reduced chemical kinetic mechanism for a biodiesel surrogate was developed and validated for use in a reacting flow code. Measured species profiles in a counterflow flame were accurately reproduced by the mechanism [4].

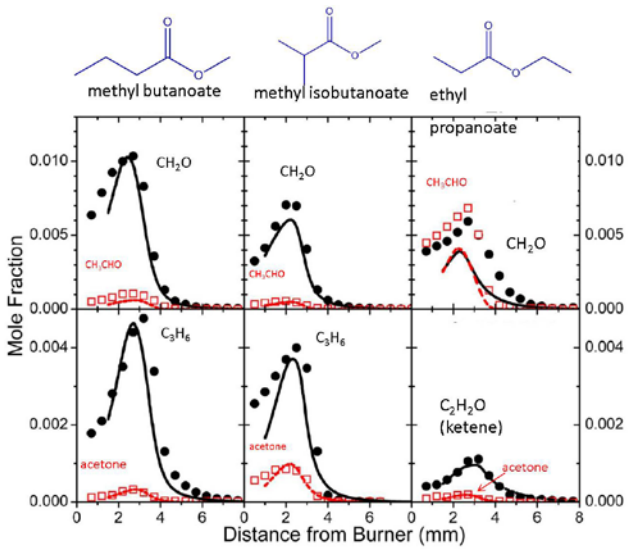

FIGURE 5. Comparison of experimental measurements and computed concentrations of selected oxygenated intermediates in premixed flames of methyl butanoate, methyl isobutanoate, and ethyl propanoate [6]. The measured and calculated species include CH_2O (formaldehyde), CH_3CHO (acetaldehyde), C_3H_6 (propene), ketene and acetone.

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2. S.M. Sarathy, M.J. Thomson, W.J. Pitz and T. Lu, "An Experimental and Kinetic Modeling Study of Methyl Decanoate Combustion," Proceedings of the Combustion Institute, 2010, in press, http://dx.doi.org/10.1016/j.proci.2010.06.058.

3. Naik, C.K. Westbrook, O. Herbinet, W.J. Pitz and M. Mehl, "Detailed Chemical Kinetic Reaction Mechanism for Biodiesel Components Methyl Stearate and Methyl Oleate," Proceedings of the Combustion Institute, 2010, in press, http://dx.doi.org/10.1016/j.proci.2010.05.007.

4. K. Kohse-Höinghaus, P. Oßwald, T.A. Cool, T. Kasper, N. Hansen, F. Qi, C.K. Westbrook and P.R. Westmoreland, "Biofuel Combustion Chemistry: From Ethanol to Biodiesel," *Angewandte Chemie International Edition* 49 (21) (2010) 3572-3597.

5. P.S. Veloo, Y.L. Wang, F.N. Egolfopoulos and C.K. Westbrook, "A comparative experimental and computational study of methanol, ethanol, and n-butanol flames," *Combust. Flame* 157 (10) (2010) 1989-2004.

Special Recognitions & Awards/Patents Issued

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

2. Charles K. Westbrook: 2008 - 2012 President of the Combustion Institute.

3. William Pitz received an award for best paper of the year from the Japanese Combustion Society.

4. S.M. Sarathy: Postdoctoral Fellowship from Natural Sciences and Engineering Research Council of Canada

III.4 Improving Advanced Fuel Utilization through Detailed Chemical Kinetic Combustion Modeling

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Subcontractor:
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Objectives

- Enhance understanding of advanced fuel combustion for application to clean and efficient engine technologies.
- Gain fundamental and practical insight into advanced fuel combustion through numerical simulations and experiments.
- Develop and apply numerical tools to analyze advanced fuel combustion regimes through multi-dimensional fluid mechanics with chemical kinetics.
- Improve the predictive capability of advanced fuel chemical kinetic mechanisms through analysis of advanced fuels in high efficiency combustion regimes.

Fiscal Year (FY) 2010 Accomplishments

- Conducted detailed simulations of combustion compared to Sandia National Laboratories (SNL) engine experiments using LLNL- and UCB-developed gasoline surrogate chemical kinetics.
- Developed a new methodology for chemical kinetic mechanism analysis by applying large-scale uncertainty and sensitivity analysis tools to analyzing low-temperature chemistry in homogeneous charge compression ignition (HCCI) combustion.
- Completed a 48-hour 2,000 processor dedicated run using our gasoline surrogate mechanism and multi-zone model to investigate low temperature chemistry sensitivity.

Future Directions

- Utilize the sensitivity and uncertainty analysis framework developed for improving predictive capability of chemical kinetic mechanisms for fuels and fuel surrogate combustion.
- Apply newly available high-fidelity tools for multi-dimensional combustion simulation to investigate high-efficiency and low-emissions advanced fuel engines.
- Characterize advanced fuel combustion regimes with judicious application of experiments and simulation.

Introduction

LLNL contributes to the efficient and clean utilization of advanced fuels through development of high-fidelity analysis tools. The work focuses on development, testing and tuning of chemical kinetic models for fuel components and fuel surrogates of interest to industry and engine researchers; and modeling to test the applicability of chemical kinetic mechanisms at engine conditions. We also develop and test concepts that may contribute to improved utilization efficiency of advanced fuels.

Approach

The growing interest in advanced fuels has brought with it a broad need for new fuel characterization under advanced combustion regimes. We contribute to this task by collaborating with industry, other national laboratories, and universities in identifying modeling needs for advanced fuels. Typically we team up with other institutions (foreign and domestic) that conduct experimental work, and we perform detailed analysis leading to the development, testing and tuning of new chemical kinetic mechanisms. The approach has proven very successful and our combustion models are widely used around the world.

Results

This year our work had a major focus on improving the low temperature chemistry predictive capability of chemical kinetic mechanisms applied to advanced fuels and combustion regimes. Low-temperature chemistry is partial reaction of fuel and air that typically occurs

at temperatures between 700 and 900 K. This is low temperature relative to the main autoignition that begins to occur at temperatures typically greater than 1,050 K. Between the low temperature and high temperature chemistry regime (900-1,050 K) is the so-called "negative temperature coefficient" regime where no heat release is apparent [1]. Some fuels exhibit little low-temperature heat release (e.g. methane), and other fuels exhibit significant low-temperature heat release (e.g. normal heptane, di-methyl ether).

Figure 1 demonstrates a persistent issue that chemical kinetic mechanisms are underpredictive of low-temperature heat release at highly supercharged and lean conditions. The top plot in Figure 1 shows the rate of heat release during the low-temperature portion of the cycle for SNL gasoline HCCI experiments at very lean (excess air relative to fuel) [2] and the bottom plot shows simulations conducted using the LLNL multi-zone model with a 197 species surrogate mechanism. Different curves show different intake manifold pressures. The temperature history from compression of the gas in the engine cylinder is relatively unaffected by elevated intake pressure, however the in-cylinder pressure history becomes amplified as intake pressure is increased. This temperature and amplified pressure trajectory of the reacting mixture significantly influence the ignition process.

Figure 1 shows that low-temperature heat release is observable in experiments for intake pressures of 180 to 190 kPa. In simulations the low-temperature heat release does not become apparent until intake pressures reach at least 250 kPa. While for unsupercharged to moderately supercharged conditions, the mechanisms are predictive, with greater level of supercharge the mechanisms will not capture the elevated level of low-temperature chemistry observed in engine experiments. Advanced engine combustion modes often involve elevated intake manifold pressures and very lean fuel-air ratios. The fundamental rapid compression machine and shock tube experiments upon which mechanisms are built tend to be at lower pressure and less lean fuel-air ratios than advanced engine operating modes demand. Figure 2 shows ignition delay simulations from UCB and LLNL mechanisms compared to experiments [3] for different surrogate combinations. The experimental data is all at stoichiometric fuel air ratio, while the operation of interest is at very lean conditions. It is very typical for kinetics experiments to be conducted at stoichiometric or mildly lean conditions far from the conditions of interest for some advanced engine modes. Figure 2 demonstrates another common occurrence in that the experimental data is reported for temperatures above the low-temperature chemistry range.

Mechanisms contain hundreds or thousands of individual reactions, but, excluding concentration effects, only some reaction rates in gas-phase hydrocarbon

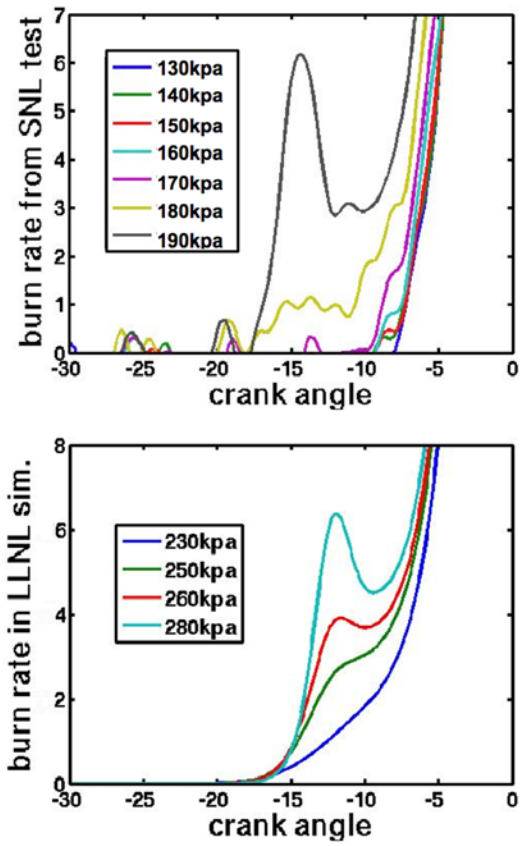

FIGURE 1. Comparison of SNL experimental rate of heat release to LLNL simulated rate of heat release. The low-temperature heat release portion of the combustion process is shown for various levels of supercharging (legend shows bottom dead center pressure). Experiments are gasoline HCCI at 0.16 fuel-air equivalence ratio [2]. Simulations use a 197 species surrogate gasoline reduced chemical kinetic mechanism developed in collaboration with Prof. J.Y. Chen at UCB.

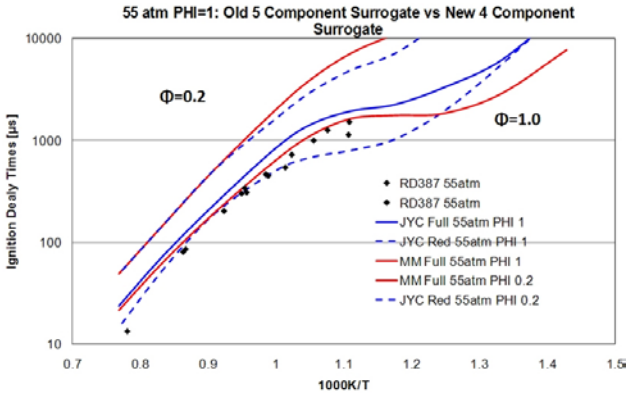

FIGURE 2. Comparison of surrogate and full mechanisms to experimental data for stoichiometric (ϕ=1.0) and lean operation (ϕ=0.2). Curves labeled "JYC" are for the UCB surrogate, curves labeled "MM" are for the Lawrence Livermore Mechanism, and RD387 is experimental data [3].

ignition have pressure sensitivity [1,3,4]. Since the mechanisms predict well at lower intake manifold pressures but do less well at higher intake manifold pressures, we focus our attention on reactions with pressure sensitivity. Pressure affects most reactions only through the concentration of involved species in a reacting mixture. However, certain types of reaction rates have strong pressure dependency. In hydrocarbon autoignition chemistry, third body reactions often have pressure dependent rate constants. An example of a pressure dependent third body reaction is the decomposition of hydrogen peroxide into two hydroxyl radicals [3].

$$H_2O_2+(M)\Leftrightarrow OH+OH+(M)$$

The participation of the enhanced third body "(M)" results in non-linear enhancement of the rate of this reaction as pressure increases. We can apply uncertainty quantification methods to the rate parameters of these third body reactions and investigate sensitivity of the occurrence of low-temperature chemistry.

PSUADE is a computational tool developed at Lawrence Livermore for large-scale studies of sensitivity analysis and uncertainty quantification [5 6]. We use PSUADE to apply Monte Carlo and Monte Carlo-like methods to uncertainty quantifications via exercising massive numbers of processors. PSUADE manages simulations where large numbers of parameters are uncertain, selecting combinations of values of these parameters so that as much of the parameter space is explored as possible with the limited number of runs available.

We identified 18 third body reactions, each with up to 10 pressure and temperature dependent parameters, giving approximately 150 total sensitivity parameters. PSUADE runs many engine cycle simulations with chemical mechanism parameters varied according to statistical methods. Our multi-zone model [4] is used for simulating the closed part of the engine cycle and each individual cycle simulation requires 30 minutes to 1 hour. To do a wide sweeping sensitivity study we applied for and were granted dedicated time on the Livermore Supercomputing facility, receiving access to 2,000 processors for 48 hours. This yielded nearly 100,000 simulations with different pressure dependent chemistry configurations, each simulation providing sensitivity information on the various third body reactions. All of these simulations were applied to a single experimental case, gasoline HCCI at a fuel air equivalence ratio of 0.16 and an intake manifold pressure of 1.9 kPa.

The PSUADE simulation exercise generated a substantial amount of data that is still being post-processed. However, we have preliminary results demonstrating pressure dependent reaction sensitivity.

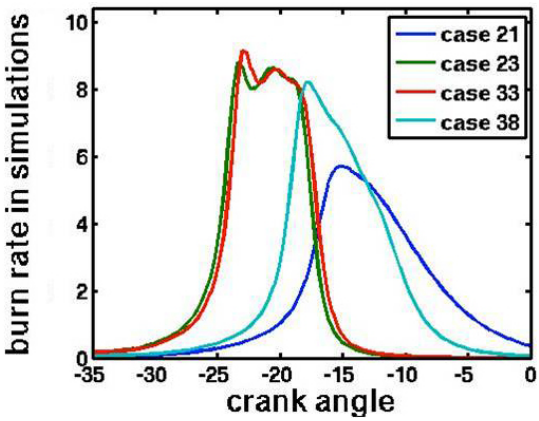

FIGURE 3. Rate of heat release in low-temperature heat release region for four different pressure dependent reaction realizations.

Figure 3 shows a comparison of heat release rate during the low-temperature heat release for four different parameterizations of the pressure dependent reaction. Depending on the combination of parameters, we can identify reaction parameters that have significant influence on low-temperature heat release. We can also identify reactions that have little influence and can be ignored.

This methodology is a powerful and systematic approach with promise to improve chemical kinetic mechanisms for engine combustion based on available engine data. This method will best be applied by looking at multiple engine operating conditions so that broad-based reaction sensitivity can be determined. Some reactions are common or similar between different mechanisms, so results from one mechanism may be able to be more widely applied to improving predictive capability of other hydrocarbon mechanisms.

Conclusions

- Our research and development project in advanced fuel combustion simulation focuses on gaining fundamental understanding of engine combustion processes with advanced fuels through high fidelity multi-dimensional simulations combining computational fluid mechanics and chemical kinetics.
- We are utilizing unique large-scale computing tools to find reaction parameters that better represent chemical kinetics observed in engine experiments.
- Sensitivity and uncertainty analysis tools available in our large-scale computing facility have great potential to improve the predictive capability of chemical kinetic mechanisms, especially for advanced combustion regimes.

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2. Mark Havstad, K. Dean Edwards, Robert Wagner, Salvador M. Aceves, Matthew McNenly, William Piggott, C. Stuart Daw, Charles E.A. Finney, "Detailed Chemical Kinetic Modeling of Iso-Octane SI-HCCI Transition," SAE Paper 2010-01-1087, 2010.

3. Matthew James McNenly, Mark Havstad, Salvador Aceves, William Pitz, "Integration Strategies for Efficient Multizone Chemical Kinetic Models," SAE Paper 2010-01-0576, 2010.

4. N.J. Killingsworth, Daniel Flowers, V.H. Rapp, S.M. Aceves, J.Y. Chen, and R. Dibble, "Increased Efficiency in SI Engine with Air Replaced by Oxygen in Argon Mixture", Proceedings of 33rd International Symposium on Combustion, Tsinghua University, Beijing, China, August 1–6, 2010.

4. R. Whitesides, R.P. Hessel, D.L. Flowers, S.M. Aceves, "Application of Gaseous Sphere Injection Method for Modeling Under-expanded H2 Injection", Combustion Theory and Modeling, In Press, 2010.

5. R. Whitesides, X. You, M. Frenklach, "Extended Simulations of Graphene Growth with Updated Rate Coefficients", Western States Section of the Combustion Institute Spring Technical Meeting, March 21–23, 2010, Paper 10S-50.

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Special Recognitions & Awards/Patents Issued

1. Signed licensing agreement with Convergent Sciences, Inc. for multi-zone model, September 2010.

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

3. 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 – November 2010.

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

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

III.5 Advanced Petroleum-Based Fuels Research at NREL

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DOE Technology Development Manager:
Kevin Stork

Subcontractor:
Colorado School of Mines, Golden, CO

Objectives

- Enable post-2010 advanced combustion regime engines and emission control systems to be more efficient while meeting future emission standards.
- Address technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, emissions, and emission control systems.
- Develop understanding of fuels/properties that enable furtherance of the Advanced Combustion Engines subprogram for high efficiency engines with cost-effective emission controls.

Fiscal Year (FY) 2010 Accomplishments

- Continued development of Ignition Quality Tester (IQT™)-based research platform to characterize fuel ignition properties, which:
  - Provided critical unique ignition data for low volatility fuels.
  - Evaluated and validated reduced kinetic mechanisms.
  - Bridged experimental void between fundamental ignition experiments and full engine testing.
  - Provided intermediate simulation development platform used by other DOE laboratories to evaluate optimized computational strategies.
- Supported development and utilization of research Fuels for Advanced Combustion Engines (FACE) to determine relationships between fuel chemistry and engine combustion performance and emissions.
- Collaborated with other DOE and Canadian national laboratories, along with corporate industrial partners via the Coordinating Research Council (CRC), to:
  - Expand fuels research to develop surrogate fuels with kinetic models.
  - Characterize advanced alternative and renewable fuel streams.
- Developed and utilized a spark-ignition direct-injection (SIDI) single-cylinder research engine facility to investigate fuel chemistry effects on advanced combustion and leverage links to NREL's biomass fuels research program.

Future Directions

- Continue expanding IQT-based experimental and simulation research to:
  - Develop broader understanding of fuel chemistry impacts on ignition.
  - Develop and validate improved kinetic model reductions.
  - Develop chemical kinetic models for fuel compounds, including biofuels.
  - Establish links between IQT-based ignition characterization and engine-based combustion performance and emissions.
- Collaborate with other DOE and Canadian national laboratories, along with corporate industrial partners via the CRC, to:
  - Expand fuels research to develop surrogate fuels with kinetic models.
  - Characterize advanced alternative and renewable fuel streams to address paucity of data relevant to engine research community.
- Employ SIDI single-cylinder research engine study fuel chemistry impacts on advanced combustion, enabling NREL to study span of renewable fuels from fuel production and processing to engine performance and emissions.

Introduction

Development of more energy-efficient and environmentally friendly transportation vehicles demand simultaneous increases in powertrain efficiency and reduction in vehicle emissions, which drive the need for significant advances in internal combustion engines. In turn, advances in engine combustion increasingly rely on thorough understanding of fuel physicochemical properties, especially ignition kinetics behavior. In addition, the need for petroleum displacement leads towards increased use of advanced alternative and renewable fuels, many of which behave much differently than traditional petroleum-based fuels. As a critical

enabler for advanced combustion engines and to eliminate barriers for alternative fuels, significant research is necessary to understand the relationships between fuel chemistry and engine performance and emissions. The DOE Vehicle Technologies Program's Fuels Technologies subprogram supports research and development to address this research need, including that of NREL's Advanced Petroleum-Based Fuels (APBF) research activity.

Approach

The focus of NREL's APBF research activity is the intersection of fuel physicochemical properties, ignition kinetics, combustion, and emissions. The overall research goal is to support the simultaneous development of advanced fuel chemistries and advanced combustion engines by providing bridging experiments and simulation between fundamental chemical kinetics and engine studies. This goal translates into APBF's research activities, which include:

- Development and characterization of research-grade reference fuels, surrogate fuels, and advanced alternative/renewable blending streams.
- Development of experimental and simulation research platforms to address barriers of inadequate knowledge to enable advanced efficient combustion and diversification in transportation fuel options.
- Support for development and validation of accurate, efficient kinetic models for fuel ignition and combustion.
- Use of engine-based testing to provide crucial correlation data to our experimental and simulation efforts, and expand combustion research capability to study fuel chemistry.

APBF's team members closely collaborate with relevant industry stakeholders (primarily through the CRC), academic researchers, and DOE and Canadian national laboratories colleagues. APBF participates in the DOE Advanced Engine Combustion Memorandum of Understanding, ensuring our work is in close alignment with and supports DOE Vehicle Technologies Program's Advanced Combustion Engines area. APBF engages the academic research community through these forums, in addition to directly funding fuel ignition kinetics research at Colorado School of Mines (CSM). The CSM collaboration was strengthened in 2010 with the beginning of a joint appointment for Prof. Greg Bogin at CSM and NREL.

Results

Ignition Kinetics Research

During FY 2010, APBF continued to develop methods to characterize fuel ignition properties to support kinetics-dominated advanced engine combustion strategies. This effort largely built upon prior research using the IQT, focusing on development of the IQT as an experimental research platform to quantify fuel autoignition behavior, allowing links to fuel physicochemical properties [1]. The rationale for using the IQT is illustrated using Figure 1. Fundamental ignition chemistry experiments are commonly performed with shock tubes, rapid compression facilities, and jet-stirred reactors, all of which generally employ premixed gas phase fuel/air mixtures. While extremely valuable in producing data for the development and validation of ignition kinetic models, not all of these devices operate in pressure, temperature, and characteristic ignition delay time regimes of interest to compression ignition engines, including low-temperature combustion engine concepts. Additionally, while improvements have recently been made by researchers, these devices are generally experimentally challenged with low-volatility, multi-component fuels. APBF's development of the

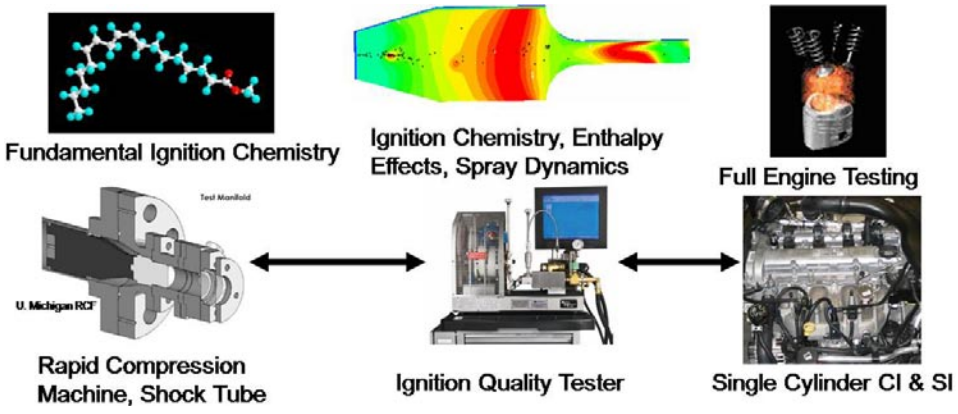

FIGURE 1. Conceptual Illustration of Linking Existing Experiments with Complementary IQT-Based Research Platform

IQT into a research platform provides an alternative, complementary source of experimental kinetics data, which is designed to operate with low-volatility, real fuels. Ignition kinetic studies with the IQT are complicated by the integration of physical effects (spray droplet breakup and evaporation) and chemical effects, but the IQT provides an intermediate research platform which is easier to characterize and control than full engine studies.

In FY 2008, APBF initially expanded IQT (Figure 2) operation beyond its intended operating point to measure ignition delay time and calculate Derived Cetane Number per ASTM D6890 [2]. This technique was applied to the nine fuels comprising the FACE diesel research fuel set [3,4], providing predictive Arrhenius ignition delay parameters over a range of pressure, temperature, and oxygen fraction. Expanding from that effort, APBF contracted with Prof. Tony Dean and Dr. Greg Bogin at CSM in FY 2009 to further develop the IQT platform further develop and validate kinetic ignition models for renewable fuel compounds, including alkanes and methyl esters. The collaboration with CSM resulted in significant progress in characterizing the IQT and understanding the unique critical experimental ignition data produced. Through valuable collaboration with Prof. J.Y. Chen at University of California, Berkeley, CSM and NREL developed a KIVA-3V ~65,000 cell computational fluid dynamics (CFD) model of the IQT injection and combustion process, coupling it with CHEMKIN to evaluate kinetic mechanisms, initially starting with n-heptane (Figure 3). The resulting experimental and computational development led to significant understanding of the IQT (illustrated in Figure 4), making it capable of providing critical ignition kinetics data. Additionally, APBF added significant exhaust speciation capability to the IQT, providing additional diagnostic markers against which to evaluate kinetics models.

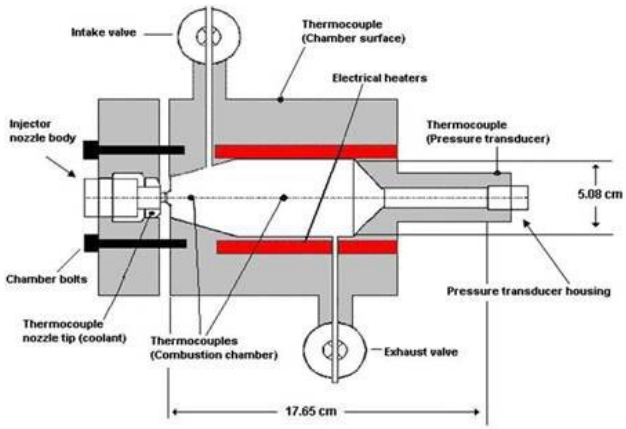

FIGURE 2. Schematic of IQT Combustion Chamber

In FY 2010, APBF significantly expanded simulation capability for the IQT through use of NREL's new dedicated supercomputing resources, Red Mesa and Red Rock. Significant reductions in computing time allowed APBF to explore turbulent chemistry effects and share simulation data with other DOE laboratories. Colleagues

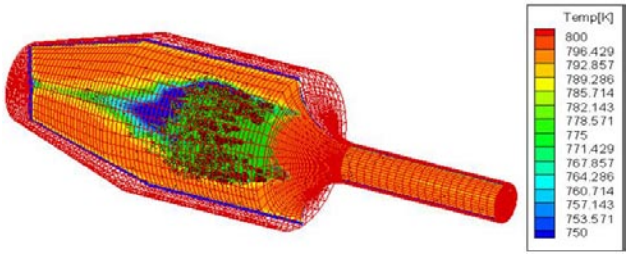

FIGURE 3. The KIVA-3V model (~65,000 cells) employs a Kelvin-Helmholtz Raleigh-Taylor spray breakup model and is linked with CHEMKIN to evaluate ignition kinetics in the IQT.

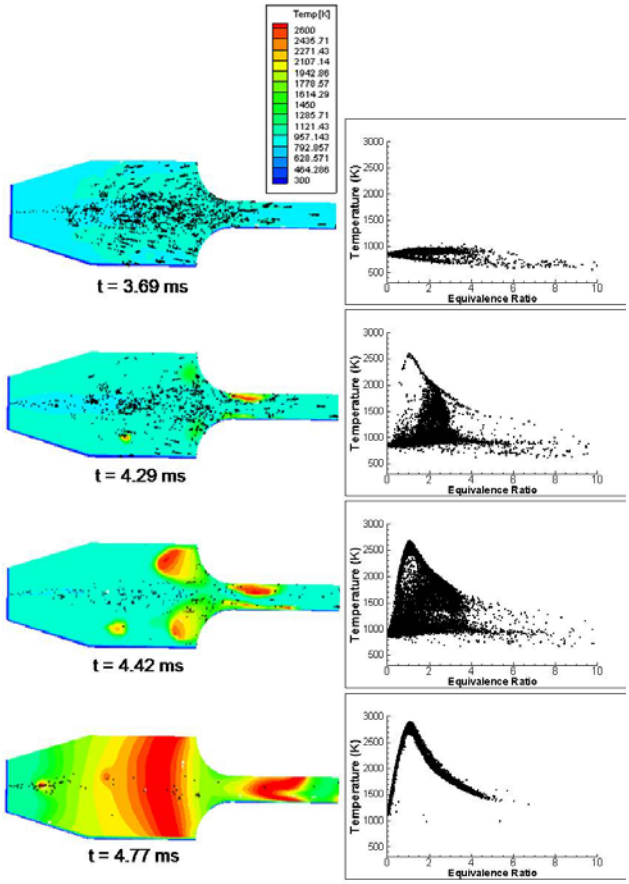

FIGURE 4. The role of autoignition is shown by the time evolution of the temperature contour plots (left) and the corresponding plots of temperature vs. equivalence ratio (right), which demonstrate that the onset of n-heptane combustion occurs primarily in the rich regions around $\Phi = 2$.

at Lawrence Livermore National Laboratory (LLNL) are now using NREL's IQT model for their research in multi-zone modeling to increase computational efficiency while maintaining full chemistry. APBF also regularly shares simulation and experimental data with other colleagues at LLNL for their development of chemical kinetics models for ignition.

Advanced Fuels for Advanced Combustion Engines

The APBF research activity actively participated in CRC committees and projects, collaborating with industry stakeholders and DOE and Canadian national laboratory colleagues. Details of much of this work is covered another Annual Progress Report chapter, covering "Fuels for Advanced Combustion Engine (FACE) – Development of Research Fuels Matrix". APBF's most significant contribution in this area in FY 2010 was to the AVFL-18 project to develop advanced diesel surrogates with full kinetic models [5], utilizing data and knowledge created in the FACE diesel research fuel set characterization effort. In FY 2010 APBF helped lead the AVFL-18 team to select candidate compounds, blend those compounds into candidate blends, and test the blends for ignition performance with the IQT.

Single-Cylinder Engine-Based Research Capability

In FY 2010 APBF completed commissioning of the new single-cylinder research engine facility based on a production General Motors 2.0-L SIDI turbocharged engine. The engine was thoroughly mapped as a multi-cylinder engine prior to conversion, including a series of experimental studies with various ethanol and iso-butanol blends. These unique data included valuable information regarding particle number (PN) emissions sensitivity to engine operating parameters and biofuel content [6-7]. After conversion to a more flexible single-cylinder configuration with full independent engine control, additional fuels studies focused on PN emissions with ethanol and iso-butanol blends. These studies complement the findings from the multi-cylinder configuration, which are of particular interest as SIDI engines are challenged in some operating regimes with increased PN emissions. The work completed in FY 2010 shows potential for PN reduction with biofuel content and demonstrates the flexibility of NREL's SIDI boosted single-cylinder research engine facility to conduct fuel chemistry effects studies on engine combustion, performance, and emissions. In addition, the new test cell enables DOE's Biomass and Vehicle Technologies Programs to leverage NREL's in-house capability to study the entire span from fuel processing (via NREL's National Bioenergy Center) to advanced combustion engine performance and emissions with alternative fuels.

Conclusions

NREL's APBF research activity made significant progress in supporting the simultaneous development of advanced fuel chemistries and enabling advanced combustion engines. The primary conclusions can be summarized as follows:

- APBF's continued development of an IQT-based experimental and simulation research platform allows ignition kinetics studies which provide unique, complementary data which are valuable in developing accurate, efficient chemical kinetics models.
- Collaborative efforts have produced well-characterized standardized research fuel sets which allow cross comparisons of results between different advanced combustion modes and engine hardware. These efforts enable the development of advanced surrogate fuels and characterization of advanced alternative and renewable fuels, which further benefit fuels and engine researchers.
- APBF demonstrated significant new engine-based research capability to both complement and expand studies of the intersection of fuel physicochemical properties, ignition kinetics, combustion, and emissions.

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III.6 Fuels for Advanced Combustion Engines (FACE) – Development of Research Fuels Matrix

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Objectives

- Bring together a collection of stakeholders.
- Design a standard set of research gasoline and diesel fuels to enable cross comparisons of results between different research and development (R&D) organizations working on similar and different advanced combustion modes and engine designs.
- Engage a fuels blender to manufacture and sell the fuels.
- Conduct extensive characterization of the fuels and make results publicly available.
- Champion use of the fuels by government laboratories, university researchers, and industry R&D groups.

Fiscal Year (FY) 2010 Accomplishments

- Assembled a cross-industry working team of subject matter experts through collaboration with the Coordinating Research Council (CRC), including stakeholder members from energy/petroleum industry, automotive/engine manufacturers, universities, and national laboratories.
- Leveraged CRC partnership with research collaboration between DOE and national laboratories, including:
  - Oak Ridge National Laboratory
  - Pacific Northwest National Laboratory (PNNL)
  - National Renewable Energy Laboratory
  - Lawrence Livermore National Laboratory
  - Sandia National Laboratories
  - CanmetENERGY
- Developed nine FACE diesel fuels, which are currently available for purchase from Chevron-Phillips Chemical Company (CPChem).
- Completed and published exhaustive advanced characterization of nine FACE diesel fuels, including application of novel techniques to fuel property characterization.
- Demonstrated initial engine performance in premixed charge compression ignition (PCCI) and homogeneous charge compression ignition (HCCI) operation with FACE diesel fuel matrix.
- Begun CRC-sponsored research study on HCCI operation in a light-duty diesel engine with FACE diesel fuels (CRC Advanced Vehicles Fuels and Lubricants [AVFL]-16 project).
- Nearly completed development of FACE gasoline matrix.
- Expanded effort to include evaluation of advanced alternative and renewable fuels (CRC FACE Working Group – Advanced Alternative and Renewable Fuels [AARF] Team).
- Applied output of FACE diesel fuels advanced characterization effort to facilitate development of a diesel surrogate with full kinetic model (CRC AVFL-18 project).
- Initiated plans to correlate existing PCCI and HCCI engine data using FACE diesel fuels with key fuel properties.

Future Directions

- Complete development and perform characterization of FACE gasoline fuel matrix.
- Apply techniques developed in FACE diesel advanced characterization effort to address paucity of data for advanced alternative and renewable fuels.
- Complete development of multi-component diesel surrogate with full kinetic model, complementing FACE diesel fuel matrix.

Introduction

There are many embodiments of advanced combustion processes for engines burning both gasoline-like and diesel-like fuels. These include HCCI, PCCI, and numerous related processes known by their own acronyms. In gasoline engines, advanced combustion

techniques such as those outlined above offer increased thermal efficiency without sacrifice of the traditionally low emissions offered by spark-ignited engines. In diesel engines, advanced combustion offers lower emissions of particulate matter (PM) and oxides of nitrogen (NOx) without the sacrifice of traditionally high thermal efficiency offered by compression-ignition engines. All of these processes generally focus on causing combustion to occur at a low enough temperature so that the formation of NOx is thermodynamically unfavorable and with enough air-fuel mixing to ensure low PM formation. In this way, the engine-out emissions of both pollutants are lowered simultaneously, without a trade-off relationship as had historically been the norm.

Advanced combustion techniques have been the focus of intense research at virtually every engine and vehicle manufacturer around the world for several years. As a result, there exists a breadth of specific techniques and hardware configurations, each aimed at determining the best path towards commercial viability. Some engines are known to use differing forms of advanced combustion as the speed and load demand on the engine change. The field is progressing rapidly, but at this point there is not one technology or hardware configuration that is universally more advantageous than others. Hence, it isn't possible to determine one "best" technology that can be used to study the importance of fuel properties on efficiency, emissions, and performance of advanced engines. However, if many research and development programs could utilize a common matrix of research fuels, the impact of fuel properties could be judged broadly across many specific applications of advanced combustion technology. The FACE program was conceived to bring together the stakeholders in industry together with researchers at universities and the national laboratories to begin the process of producing designed research fuels that can be used to fill this gap.

Approach

ORNL and NREL began to lay the groundwork for this program by assessing industrial interest and seeking the best forum in which to conduct it [1]. A goal from the outset was to engage the energy companies as well as the automotive sector in the process of designing the research fuels. Consequently, NREL and ORNL sought to form a working group under the auspices of the CRC as a forum to support the necessary interactions among the stakeholders. CRC was identified as a logical forum for this effort because it presented opportunities to bring the required stakeholders (energy companies, automobile manufacturers, engine manufacturers, universities, and national laboratories) together in an environment conducive to information sharing among the participants. The CRC FACE working group was chartered and a mission statement drafted and approved by CRC.

The mission of the FACE Group is to recommend sets of test fuels so that researchers evaluating advanced combustion systems may compare results from different laboratories using the same set (or sets) of fuels. Examples of advanced combustion systems are low-temperature combustion, HCCI, and high efficiency clean combustion (HECC).

The activities of the working group are focused and constrained by a well-defined and approved scope of work that is available on CRC's Web site.

The FACE working group is currently chaired by Bill Cannella of Chevron and co-chaired by Robert Wagner of ORNL and Brad Zigler of NREL. Invitations were extended to interested parties in the petroleum, automotive companies, engine manufacturers, universities, and research labs. The FACE working group roster includes 31 people representing 22 different organizations across industry, government, and academia. Working group members from many different organizations have participated actively in the process of designing proposed fuel matrices for both gasoline-like and diesel-like fuels. Subcommittees were formed to specifically focus on both gasoline-like fuels and diesel-like fuels.

Results

Diesel Fuel Matrix

The diesel subcommittee initially sought to determine the most important fuel properties that should be included in the fuel matrix. Recognition that keeping the number of fuels in the matrix to a manageable level demanded that many interesting and perhaps important fuel properties or characteristics be left to future studies. A measure of ignitability, a measure of fuel chemistry, and a measure of fuel volatility were selected as the most important variables for study if the fuel set were constrained to less than 10 fuels. Cetane number, aromatic content by volume, and the 90% recovery point of the fuel distillation were selected as the representative measures of the variables of interest (see Figure 1) [2]. The team recognized that these might not be the only or the best representative measures, but agreed that these would be the measures that a blender would be most successful in using to actually produce the fuels. Ranges of variation for the fuel properties to be studied were established. In order to keep the number of fuels manageable, only two levels for each variable were specified. The fuels were formulated by CPChem and have been made available for purchase by interested researchers. ORNL has facilitated distribution of the fuels from drums maintained by ORNL for those researchers who only require small volumes of the fuels. Research efforts have been conducted or are underway at ORNL, West Virginia University (under contract from

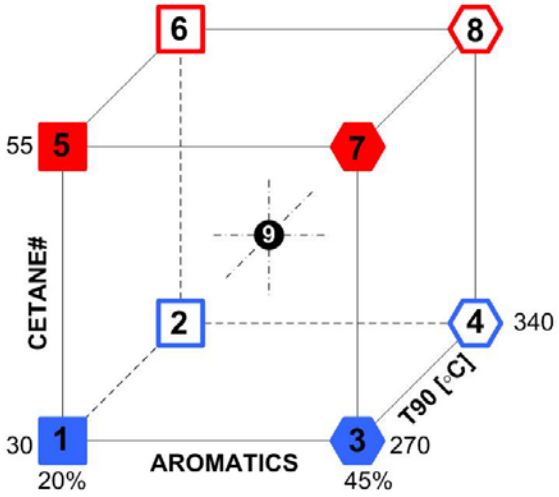

FIGURE 1. FACE Diesel Matrix

CRC), Pennsylvania State University, Sandia National Laboratories, National Research Council-Canada, NREL, and other locations using the fuels.

A CRC FACE Characterization team was formed to perform an exhaustive characterization of the nine FACE diesel fuels. This team included ORNL, Chevron, PNNL, NREL, and CanmetENERGY. The team focused on both the chemical and physical properties of the first production run of the FACE fuel set, as well as implementation of emerging state-of-the-art tools for fuel analysis. One motivation was to come up with a tractable parameter set, based on chemical composition, to relate to observed combustion behavior or physical properties. Advanced analysis techniques applied included:

- 1-dimensional gas chromatography-mass spectrometry (GC-MS).
- 2-dimensional (2-D) GC-MS.
- 2-D gas chromatography-flame ionization detection.
- 2-D GC-field ionization mass spectrometry (GC-FIMS) plus paraffins, isoparaffins, olefins, naphthenes, and aromatics.
- Ignition Quality Tester derivation of Arrhenius ignition parameters.
- ^{1}H and ^{13}C nuclear magnetic resonance (NMR).

Well-characterized fuel chemistry improves the possibility of developing robust predictive models for combustion behavior in both conventional and advanced combustion modes, whereby the predictive models could be applied to more complex fuel streams from non-traditional sources. The FACE team introduced the diesel research fuel set and preliminary characterization to the engine research community in SAE 2009-01-2769 [3], and published the exhaustive characterization details in a CRC report [4]. Figures 2 and 3 illustrate examples of advanced characterization performed for these fuels, which provide a significant correlation a resource for researchers studying advanced engine combustion [5,6].

Development of the FACE diesel matrix prompted its immediate use in studies of advanced combustion. ORNL employed the full set in fuel effects studies on HECC (SAE 2009-01-2669) [7], and on HCCI (SAE 2009-01-2645) [8]. Additionally, NREL and CRC began a joint study employing the FACE set to enable light-duty diesel advanced combustion regimes, as the AVFL-16 project. The unique knowledge gained in the advanced characterization study of the FACE diesel fuels also enabled CRC to begin the development of advanced diesel fuel surrogates with full kinetic models as another AVFL project (AVFL-18) [9]. Table 1 and Figure 4 illustrate how detailed compositional structural information from the FACE diesel set characterization

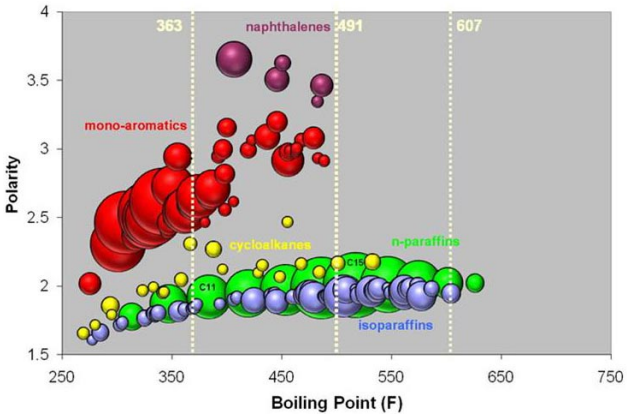

FIGURE 2. 2-D GC-MS Analysis of the Centerpoint FACE Diesel Fuel (FD-9A)

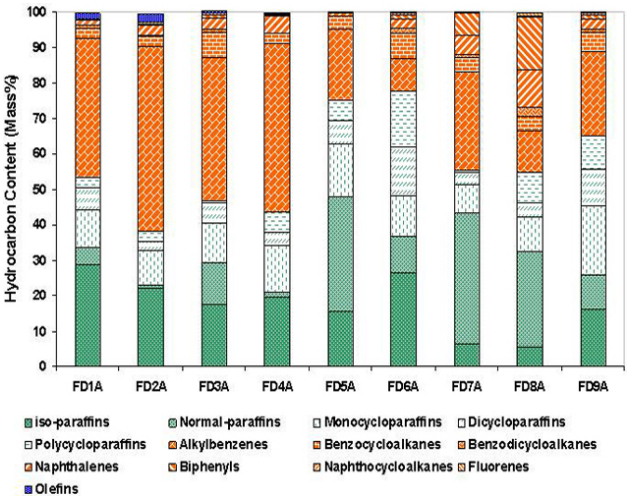

FIGURE 3. GC-FIMS and Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics Analysis of FACE Diesel Fuels

TABLE 1. ^{13}C and ^{1}H NMR-based Molecular Models

Carbon Type	Content (mole %)	
	Calculated	Measured
Aromatic	25	23
Cycloparaffinic	21	25
Branched Paraffin	15	17
Paraffin Chain (C1+)	40	36
Olefin	0	0
C=O*	0	0
Total	**100**	**100**
Parameter	**Calculated**	**Measured**
Ar Cluster Size (# carbons)	6	7
Cy Cluster Size (# carbons)	10	11
Chain Length	5	4.8

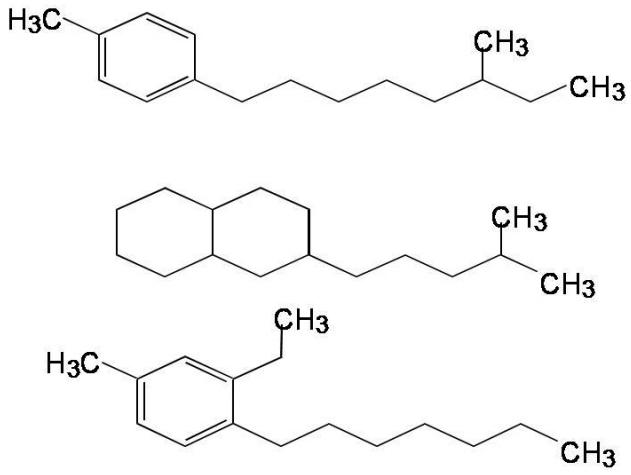

FIGURE 4. ^{13}C and ^{1}H NMR-based Molecular Models

allow modeling of surrogate molecules to match bulk fuel makeup, providing direction for the formulation of diesel surrogates [10].

Gasoline Fuel Matrix

The gasoline subcommittee identified four key parameters as being important to capture in a matrix of test fuels for advanced combustion engines. The initial design matrix targeted four key fuel properties:

- Research Octane Number (70-95)
- Sensitivity (0-12)
- N-paraffins content by volume (5%-25%)
- Aromatics content by volume (0%-50%)

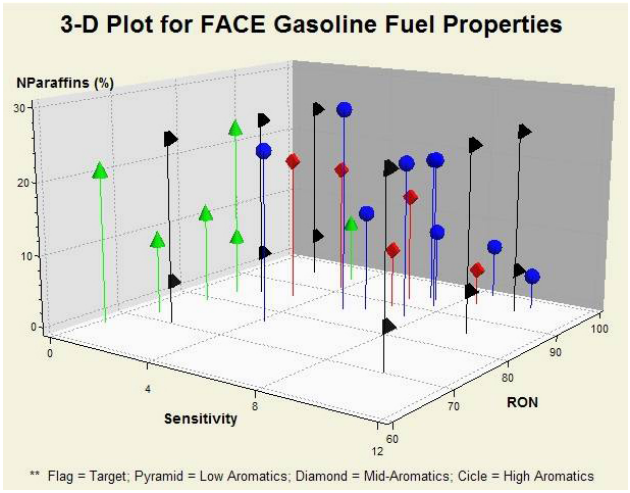

FIGURE 5. Proposed FACE Gasoline Fuel Matrix

The approach in the gasoline subcommittee was to ask the blender to use a blending model and small quantity hand blends to determine which fuel targets could be met. Then an assessment and statistical analysis was used to determine which fuels would be blended and available for distribution. CPChem worked with their blending model to determine which fuel targets can be met and where constraints need to be relaxed. In short, the initial design placed too many constraints for any reasonable number of fuels to be produced. For example, the range of sensitivity of 0 to 12 is extremely difficult to meet under any cases. Additionally, with normal paraffins, aromatics, and olefins constrained, the only remaining classes of chemical compounds to vary are cycloparaffins and isoparaffins. This makes it exceedingly difficult to reach the other target properties and can only even partially be met using large quantities of pure compounds (up to 85% by volume).

The gasoline subcommittee consulted with statistical experts at Battelle to steer how the design should be modified to target key fuel properties without placing too many constraints that make the fuels impossible to blend. Fifty-eight different fuel designs were modeled resulting in 37 candidate fuel blends. The 37 candidate blends were down-selected to 20 blendable recipes. Figure 5 illustrates an interim model of the FACE gasoline matrix design space. Physical properties of the 20 hand blends were analyzed and statistically studied by Battelle. Based on that input, a final matrix of 10 fuels was identified. The CRC FACE Working Group is currently working with CPChem to finalize and approve blends before producing the FACE gasoline matrix and offering those fuels for sale.

Advanced Alternatives and Renewable Fuels

The CRC FACE working group also began to expand work beyond the FACE petroleum-based diesel and gasoline research fuel sets. Increasing interest in advanced alternatives and renewable fuels led the team to consider the eventual need for standardized research fuel sets utilizing these blending streams. After consideration, the team decided to first address the paucity of fuel chemistry data for many of these blending streams. The lessons learned and techniques developed in the FACE diesel advanced characterization effort would provide valuable data regarding these fuels. The team, therefore, decided to first concentrate on this effort while not precluding the eventual development of advanced alternative and renewable fuels-based FACE research fuels.

The AARF sub-team was formed by the CRC FACE working group. Initial focus is on identifying and characterizing streams of interest for diesel-type fuels, giving careful consideration to avoid declaring advanced alternative and renewable fuel "winners" but rather provide critical fuel chemistry data to enable further research. While the list is not finalized, the AARF sub-team is currently considering the following blending streams:

- Second generation biofuels
  - Non-food sources
    - Jatropha
    - Algae
    - Lignocellulose
    - Other biomass-to-liquid
  - Advanced processing of edible feedstocks
  - Hydrotreated animal fat
  - Hydrotreated soy oil
- Oil shale
- Oil sands
- Other processing, including Fischer-Tropsch

Conclusions

The collaborative efforts of the DOE national laboratories and Canadian national laboratories, synergistically working with industry partners through the CRC have enabled development of standard sets of research gasoline and diesel fuels to enable cross comparisons of results between different R&D organizations working on similar and different advanced combustion modes and engine designs. In FY 2010, the FACE-related research effort has:

- Published the results of the exhaustive advanced characterization of the FACE diesel fuels.
- Fostered continued use of the FACE diesel research fuels in advanced engine combustion research.
- Planned work to correlate existing PCCI and HCCI engine data using FACE diesel fuels with key fuel properties.
- Continued development of the FACE gasoline matrix.
- Begun a project to identify advanced alternative and renewable fuel streams about which critical fuel chemistry data are lacking and characterize them, applying techniques developed in the FACE diesel characterization effort.

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III.7 Non-Petroleum Fuel Effects in Advanced Combustion Regimes

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Objective

- Investigate the impacts of non-petroleum-based fuels on advanced combustion regimes for diesel engine platforms.
- Investigate the impacts of non-petroleum-based fuel on advanced combustion regimes for gasoline engine platforms.

Fiscal Year (FY) 2010 Accomplishments

- Demonstrated high engine efficiency with low oxides of nitrogen (NOx) and particulate matter (PM) emissions using a dual-fuel reactivity-controlled compression ignition (RCCI) combustion strategy in coordination with the University of Wisconsin.
- Increased the operable load range for homogeneous charge compression ignition (HCCI) combustion for gasoline engine platforms using spark-assist and variable valve actuation, showing efficiency improvement with simultaneous emissions reduction under stoichiometric conditions.

Future Directions

- There is strong overlap between this project and a similar advanced petroleum-based fuels (APBF) fuels project, which is reported separately. The division of work between the two is somewhat arbitrary, because of where projects were started and where they currently reside. The APBF project will discuss advanced statistics, improved combustion measurements, kinetic modeling for fuel effects, and new collaborations which were begun in 2010. In 2011, both non-petroleum-based fuels and APBF have been merged into a single project.
- Continue to pursue the RCCI combustion strategy to both incorporate ethanol fuel and to expand the operable engine points.
- Investigate the fuel effects of spark-assisted HCCI under stoichiometric conditions for ethanol and butanol blends in conjunction with the following Joule Milestone:

  Characterize the potential for gasoline-like bio-fuels to enable efficiency improvements of at least 5% (compared to conventional spark-ignited operation with gasoline) within the Federal Test Procedure drive-cycle load range using the ORNL spark-assisted HCCI operating methodology.

Introduction

Advanced combustion strategies are being developed for both gasoline and diesel engine platforms as a means to increase fuel economy and/or reduce engine emissions to meet future regulations. Concurrently, alternatives to conventional petroleum-derived gasoline and diesel fuel are growing in both types of alternatives, and in total consumption. Non-petroleum fuels, such as ethanol, butanol and biodiesel, are largely compatible with conventional gasoline and diesel engine technologies. However, because advanced combustion strategies have less direct control over the start of combustion, they are more sensitive to differences in fuel composition than conventional gasoline and diesel combustion. The purpose of this research is three-fold: to identify fuel compositions that may pose compatibility challenges to advanced combustion regimes, to identify areas where non-petroleum-based fuels may offer an advantage over conventional petroleum-derived fuels and to help ensure that future engines will provide robust performance over the wide range of fuels expected worldwide either in efficiency, emissions, or the operating envelope that is achievable in advanced combustion modes.

Approach

Investigations of fuel effects on advanced combustion regimes are being performed using both single-cylinder and multi-cylinder engine platforms. The multi-cylinder engine platform is a 1.9-L General Motors diesel engine that is being used to investigate a dual-fuel RCCI combustion mode. For this strategy, the engine is equipped with port fuel injection of a gasoline-range fuel while the diesel fuel is introduced using the production common rail diesel injection system. The engine is controlled with a flexible engine controller that allows

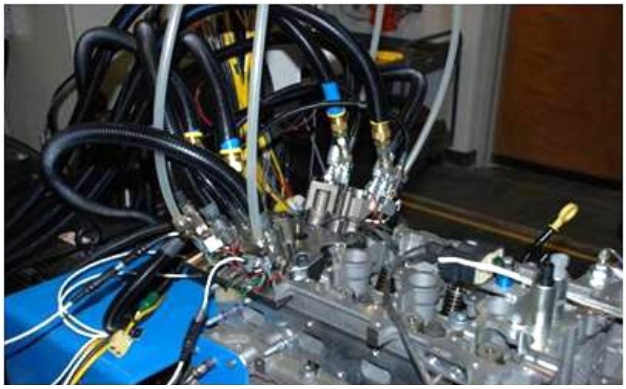

FIGURE 1. ORNL Single-Cylinder Hydraulic Valve Actuation Research Engine

for full control of both fuel injection systems, exhaust gas recirculation, swirl and other operating parameters. A close collaboration with the University of Wisconsin, who has developed expertise with the RCCI combustion concept, provides guidance and modeling support for the experimental engine operating points.

There are two single-cylinder engine platforms at ORNL being used for this project. The first is a single-cylinder gasoline engine shown in Figure 1. It is equipped with a fully variable hydraulic valve actuation valvetrain which allows valve timing, duration, and lift to be degrees of freedom during engine studies. The engine is an enabling tool for numerous advanced combustion regimes, and in FY 2010 the focus was on expanding the load range of HCCI by using spark assist and using intake valve closing angle to control the effective compression ratio. The other single-cylinder engine has a conventional diesel valvetrain, but has a modified piston and fuel injection system for HCCI combustion. Port fuel injection allows for fully premixed charges of fuel and air, and combustion of the fuel-air charges is controlled with an intake manifold heater. This research platform allows for straight-forward comparisons of the effects of fuel properties in relative isolation from confounding operational parameters. Although the combustion strategy used in this engine is not production-intent, results are very useful for kinetics modeling and statistical comparisons of fuels.

Results

Dual-Fuel Reactivity Controlled Compression Ignition Combustion

Stable dual-fuel RCCI combustion has been demonstrated on a multi-cylinder light-duty diesel engine at an operating condition of 5.5 bar net indicated mean effective pressure (NMEP) accomplished through port fuel injection of gasoline and direct injection of

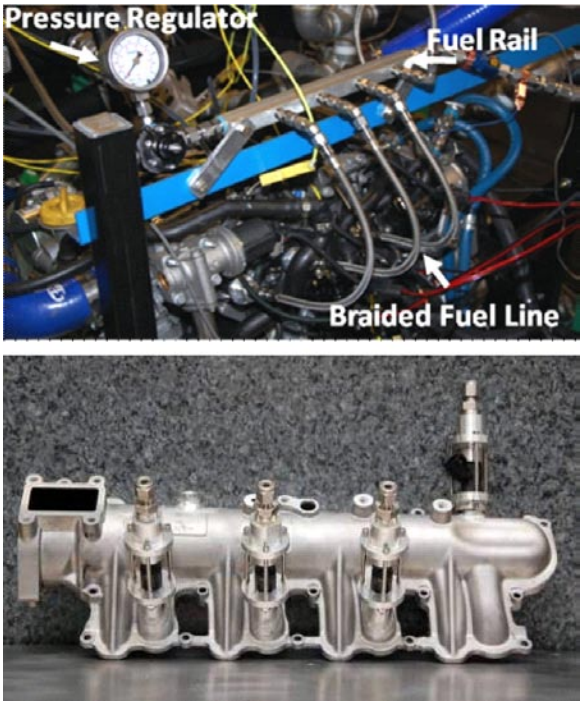

FIGURE 2. Modified Intake Manifold Installed on Engine (bottom) and with Gasoline Injectors Installed (top)

diesel fuel. The modified intake manifold equipped with the port fuel injection system is shown in Figure 2.

The initial experiments focused on the combustion characteristics and performance of dual-fuel RCCI as compared to a) the University of Wisconsin model, b) conventional diesel combustion at the same load and c) emissions characterization and catalyst effectiveness in dual-fuel RCCI mode as compared to conventional diesel combustion and diesel pre-mixed charge compression ignition (PCCI).

The ORNL multi-cylinder experiments mirrored the trends predicted by the University of Wisconsin modeling, shown in Figure 3. As compared to conventional diesel combustion at the same load, dual-fuel RCCI showed a 4.5% improvement in brake thermal efficiency, over a 90% reduction in NOx and nearly a 99% reduction in soot as measured by the filter smoke number. There were corresponding increases in carbon monoxide (CO) and unburned hydrocarbons (HCs) as well as lowered exhaust temperatures. These finding motivated the third part of the study examining the exhaust species including PM as well as investigating the effectiveness of a diesel oxidation catalyst at reducing the increased HC and CO. Favorable results were shown for reductions in particle number from RCCI, shown in Figure 4, and a diesel oxidation catalyst was shown to be effective at reducing HC and CO emissions even at the lower exhaust temperatures.

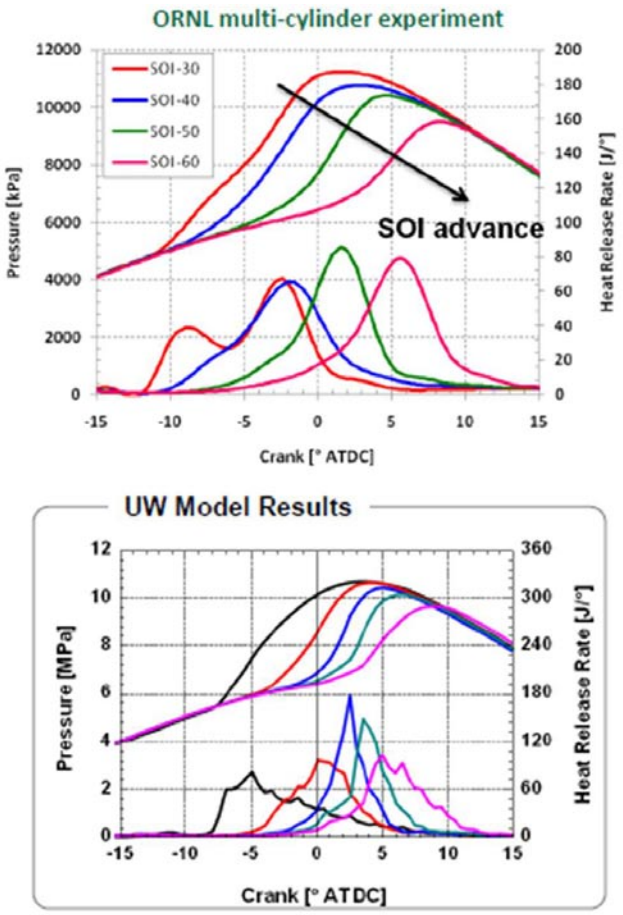

FIGURE 3. Comparison of ORNL Multi-Cylinder RCCI against University of Wisconsin Modeling

This activity is the result of collaboration across

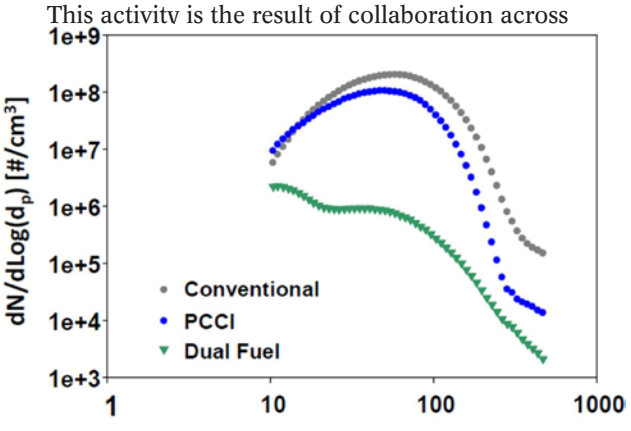

FIGURE 4. Comparison of Particle Size Distribution for RCCI, PCCI and Conventional Diesel Combustion

This activity is the result of collaboration among ORNL, universities, and industry. Internal ORNL activities include those focused on advanced combustion processes, aftertreatments, fuels, and various approaches to improve combustion efficiency. The progress and results of this work has been shared with external sources through government/industry technical meetings, professional conferences, and one-on-one interactions with industry teams.

RCCI work will be continued in FY 2011 and will focus on 1) using ethanol or an ethanol blend as the port-injected fuel instead of gasoline, and 2) expanding the demonstrated operation of RCCI combustion to higher engine loads.

Spark-Assisted HCCI

This work focuses on expanding the operable load range of advanced combustion techniques and the compatibility of the combustion strategy with different fuel blends. Numerous experimental investigations have shown that engine loads above ~4 bar NMEP are not possible with lean-burn HCCI combustion due to high rates of in-cylinder pressure rise. We show that by using advanced controls it is possible to reduce the engine noise and achieve engine loads of 7.5 bar NMEP from 1,000-3,000 rpm. By expanding the load range, real-world efficiency is increased because the engine spends more time in advanced combustion regimes.

Two distinct modes of heat release are present in this combustion process: 1) an initial slow spark-ignited mode of combustion, followed by 2) a volumetric HCCI-like mode of combustion. At low engine loads, volumetric heat release dominates the combustion event, so much so that at some operating points spark is not required. As engine load increases, a large fraction of the fuel energy is released during the spark-ignited mode combustion. With this dual-mode combustion, the rate of pressure rise and combustion noise is controlled by a combination of spark timing, which controls the start of combustion, and variable valve actuation, which can vary the effective compression ratio. Control of pressure rise rate with the intake valve closing angle is illustrated in Figure 5.

Compared to conventional spark ignition combustion, this combustion strategy reduces engine-out CO, HCs, and NOx emissions. While they are lower than spark ignition combustion, NOx emissions for this combustion strategy can still be substantial enough to require aftertreatment, which is why compatibility with a conventional 3-way exhaust catalyst was maintained by using a stoichiometric air/fuel ratio. Thus, rather than being a detriment to this combustion strategy, the NOx emissions can be easily treated and do not represent a barrier to implementation.

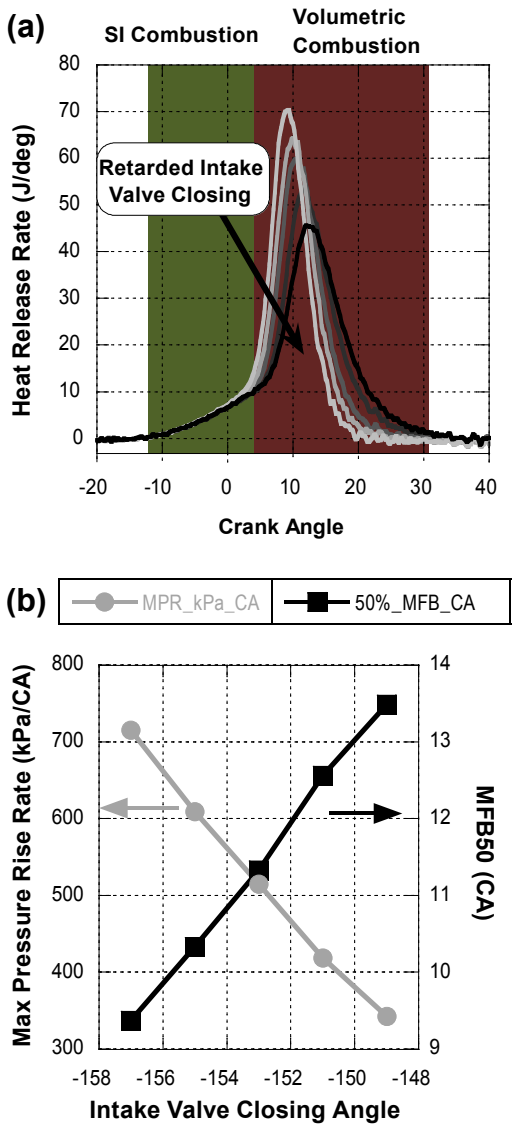

FIGURE 5. Effects of Intake Valve Closing Angle during Spark-Assist HCCI Combustion at 2,000 rpm and 500 kPa Indicated Mean Effective Pressure: (a) Effect of Intake Valve Closing Angle on Heat Release Rate, and (b) Effect of Intake Valve Closing Angle on Maximum Pressure Rise and 50% Mass Fuel Burned (MFB50)

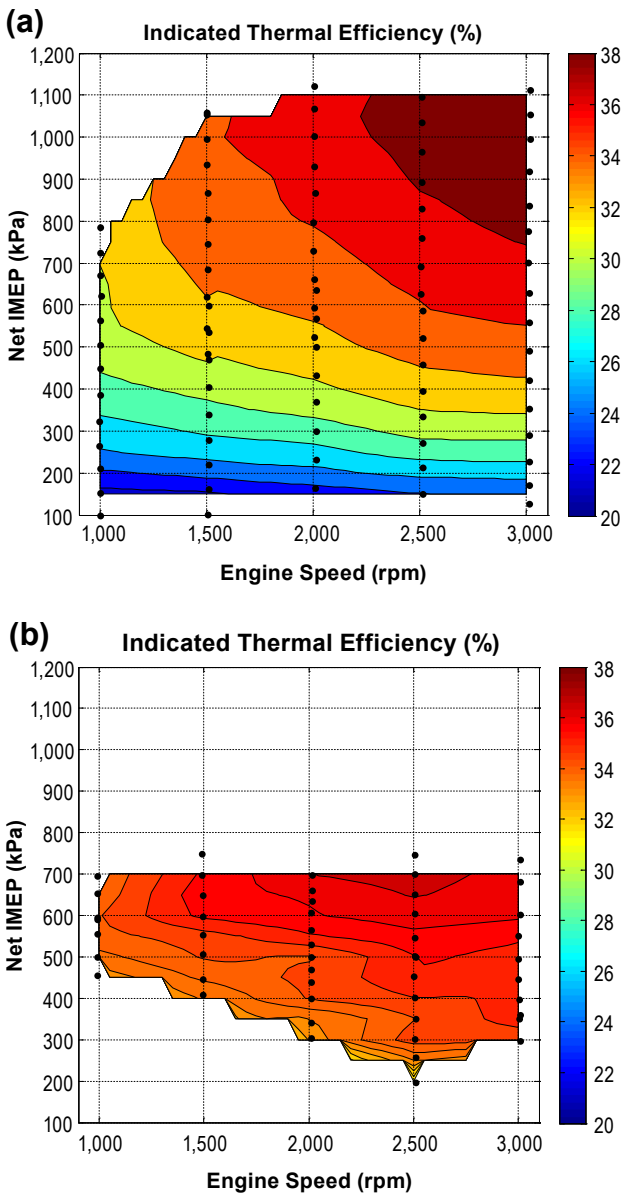

FIGURE 6. Indicated Thermal Efficiency for (a) Conventional Spark Ignition Combustion and (b) Spark-Assist HCCI Combustion

This combustion mode also provides an increase in engine efficiency compared to conventional spark ignition combustion, as shown in Figure 6. Efficiency improvements are realized at nearly all operating conditions, with the largest efficiency improvements occurring at the lowest engine loads and translating to a fuel consumption reduction of up to 9%. And importantly, the increase in engine efficiency is attained while producing no increase in tailpipe-out emissions because compatibility with 3-way catalyst technology is maintained.

The work in FY 2010 focused on the development of the spark-assist HCCI combustion process and its characteristics with a single certification gasoline. In FY 2011, continuing work will focus on the performance of ethanol blends, butanol blends and different octane gasoline fuels.

Conclusions

- Dual-fuel RCCI combustion can be performed on a multi-cylinder engine to simultaneously produce an efficiency improvement and a reduction in NOx and PM emissions compared with conventional combustion.

- Spark-assist and variable valve actuation can be used to expand the operating range for HCCI combustion:
  - Efficiency and emissions benefit compared with conventional combustion.
  - Stoichiometric air/fuel ratio to maintain compatibility with 3-way catalyst.

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III.8 Alternative Fuels DISI Engine Research

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Objectives

The overarching objectives are to provide the science-base needed to understand:

1. How emerging alternative fuels, with an initial focus on ethanol, will impact the new highly-efficient direct-injection spark ignition (DISI) light-duty engines being developed by the automotive industry.
2. How engine design can be optimized to make the most efficient use of future fuels.

To accomplish these longer-ranging objectives, we are:

A. Building an alternative fuels lab for advanced lean-burn DISI engine research:
   - Design and commission an optically-accessible DISI research engine.
   - Develop laser-based diagnostics for probing the in-cylinder processes.
   - Perform modeling of flame fundamentals.

B. Evaluating the characteristics of alternative fuels in the existing homogeneous charge compression ignition (HCCI) lab:
   - Determine the autoignition behavior of ethanol over wide ranges of operating conditions, including exhaust gas recirculation (EGR).
   - Assess the potential of ethanol's high heat of vaporization for enhancing the in-cylinder thermal stratification to smooth HCCI heat release.

Fiscal Year (FY) 2010 Accomplishments

A. Alternative fuels DISI engine lab:
   - Finished detailed engine design.
   - Successfully demonstrated motored operation.
   - Designed the optical layout for high-speed particle image velocimetry (PIV) and planar laser induced fluorescence (PLIF).
   - Procured high-speed laser for PLIF of in-cylinder fuel/air mixing.
   - Performed computational study of the flame speed of ethanol.

B. Fuel evaluation in HCCI lab:
   - Finished assessment of the autoignition characteristics of ethanol and gasoline, and compared with reference fuels.
   - Demonstrated the potential to smooth HCCI heat release with vaporization-cooling-induced thermal stratification using ethanol.

Future Directions

DISI engine research with all-metal and optical configurations:

- Complete the installation of the fueling system to allow fired operation.
- Perform experiments to assess DISI engine performance and efficiency, and the onset of knock as a function of ethanol/gasoline fuel blend.
- Assess the influence of fuel changes on the robustness of the spray-guided combustion system.
- Apply high-speed imaging of the flow field and fuel concentration to identify the in-cylinder processes that are responsible for sporadic misfire cycles.

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Introduction

In order to reduce dependence on dwindling petroleum and to reduce CO_2 emissions, it is important to both replace traditional gasoline with renewable fuels and to improve the thermal efficiency of automotive engines. Under the Energy Independence and Security Act of 2007, the volume of renewable fuel required to be blended into transportation fuel will increase from 9 billion gallons in 2008 to 36 billion gallons by 2022 [1]. At the same time, Federal Corporate Average Fuel Economy standards require substantial fuel economy improvements for model years 2012 through 2016 [2]. Thus, the industry is facing tough requirements to improve engine efficiency while the composition of gasoline-type fuels is changing.

One technique for increasing the efficiency of gasoline-type piston engines is to switch from traditional stoichiometric homogeneous-charge spark ignition (SI) combustion to stratified-charge SI combustion over a large portion of the engine-operating map. This allows operation that is overall lean and unthrottled, both of

which can contribute to 20% higher fuel efficiency. However, operating the engine in overall lean but stratified mode requires precise and robust control of the fuel/air mixing and charge preparation to ensure that an ignitable and flammable mixture exists around the spark-plug gap at the time of ignition. This is particularly challenging to accomplish for flexible-fuel engines since the fuel properties vary greatly between traditional gasoline and alternative fuel blends. For example, to obtain the same engine torque with E85, roughly 50% more fuel mass has to be supplied compared to operation on gasoline. To ensure high robustness and avoid the appearance of misfire cycles, additional understanding is needed of advanced, direct-injection stratified-charge SI engines. Therefore, the new Alternative Fuels DISI Engine Lab is being set up to enable a combination of performance testing and in-cylinder optical measurements. By contributing to the science base, the lab will support the automotive industry to overcome the challenges associated with the newly adopted fuels and fuel economy standards

Approach

The engine is based on a General Motors cylinder head and combustion system for an advanced spray-guided stratified-charge engine. This single-cylinder research engine has a bore of 86 mm and a stroke of 95 mm, for a swept volume of 0.55 liter. This corresponds to 2.2 liter swept volume in a potential 4-cylinder configuration.

The research will follow a staged approach. First, performance testing with an all-metal engine configuration will be done over wide ranges of operating conditions and alternative-fuel blends. Second, optical access will be used to apply laser-based diagnostics to probe the in-cylinder processes. This will develop the understanding needed to improve operating conditions that show less-than-desired robustness, performance, or efficiency. Modeling will be used to support the experiment and provide additional insights. Specifically, chemical-kinetics modeling will be performed of flame speed and autoignition for better understanding of the fundamentals that govern the combustion event.

Results

A. Alternative Fuels DISI Engine Lab

The detailed design of the research engine has been completed. This includes two configurations of the engine. For performance testing, one all-metal version with metal piston-ring pack, oil cooling of the piston, and lower cylinder for oil control will be used, see Figure 1. For optical diagnostics, one optical version with pent-roof windows, piston-bowl window, 45° mirror, and full optical cylinder will be used. Both

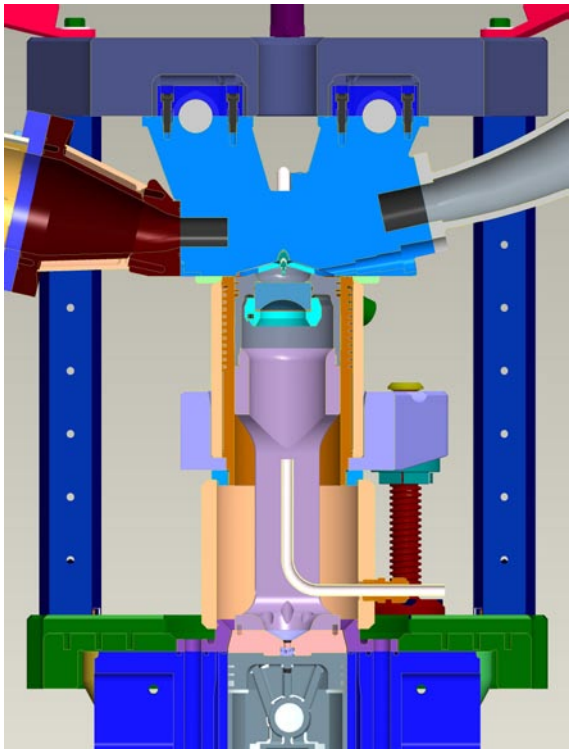

FIGURE 1. Computer-Aided Design Rendering of Engine Cross-Section for the All-Metal Version

engine configurations feature a drop-down cylinder for easy access to the piston top and combustion chamber.

All custom-design parts of the metal version of the engine have been manufactured. The engine has then been assembled (see Figure 2) and instrumented with pressure and temperature sensors in multiple locations. The initial motored tests were successful. Figure 3 shows in-cylinder pressure as a function of in-cylinder volume. Since no fuel was supplied, the gross indicated mean effective pressure ($IMEP_g$) was negative (-41 kPa), mainly due to normal heat losses and blow-by that occur around top-dead center (TDC). The timings of the two overhead camshafts were chosen to produce a small valve overlap, centered 7°crank angle (CA) after TDC during the gas exchange stroke (TDC_{exc}). These valve timings give very low flow resistance during the end of the exhaust stroke, so the amount of retained residuals is minimized. The pumping losses are also very low, rendering a pumping mean effective pressure (PMEP) of -2 kPa at 1,200 rpm.

The measurements of motored pressure demonstrate that the custom lab electronics has been finalized. To test the high-speed imaging capabilities, one of the existing high-speed cameras was synchronized with the engine shaft encoder and the valve motion was imaged. The resulting high-speed movie allows determination of the actual valve motion at full engine speed, which

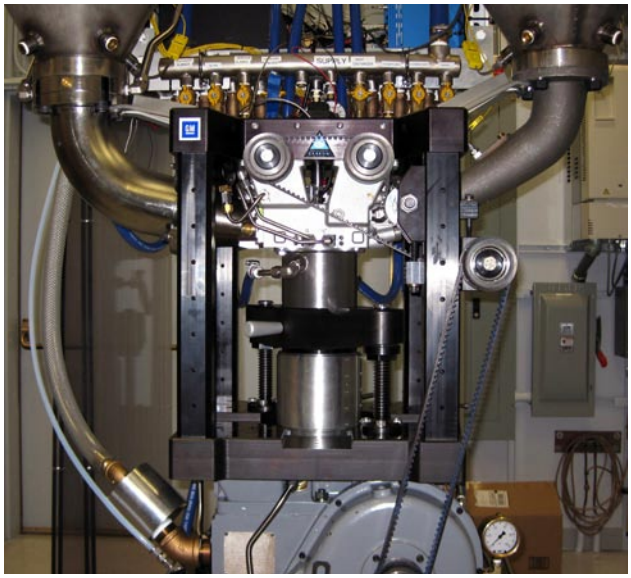

FIGURE 2. Picture of the Assembled Engine

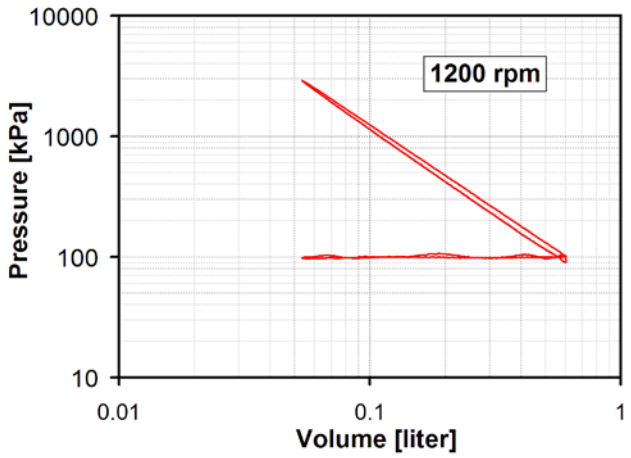

FIGURE 3. Motored Pressure Trace for Naturally Aspirated Operation with Compression Ratio=12

will be somewhat different from static measurements, in particular due to the dynamics of the hydraulic valve lifters (lash eliminators). Planned optical diagnostics of fired operation include PLIF of fuel concentration, PIV of the in-cylinder flow field, and direct chemiluminescence imaging of the combustion. For the PLIF measurements, a high-speed laser from Quantronix has been procured and successfully installed. A high-speed PIV laser will be procured during FY 2011.

Relating back to the Introduction, for a stratified charge engine it is important to avoid misfire cycles caused by inappropriate conditions near the spark gap. In particular, it is important that the early formed flame kernel propagates quickly to the fuel/air mixture

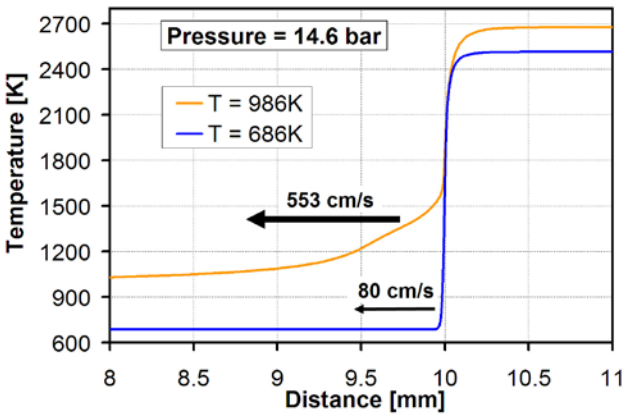

FIGURE 4. Computed Flame-Front Temperature Profile and Flame Speed for Stoichiometric Ethanol/Air Mixture at two Different Temperatures

in the piston bowl [3]. The laminar flame speed is one important indicator of the potential growth rate of the flame kernel. To guide the interpretation of engine data, it will be valuable to compare the robustness of the combustion with laminar flame speed. Unfortunately, most published experimental data of laminar flame speed are for atmospheric conditions. Therefore, to obtain laminar flame speed for conditions that prevail near TDC, it is necessary to perform modeling. During FY 2010 a computational study of flame-speed fundamentals for ethanol was conducted using CHEMKIN-PRO. Figure 4 shows one example of the results, demonstrating the strong influence of the charge temperature on the thickness and propagation speed of the flame front.

B. Fuel Evaluation Using HCCI Experiments

Since knock must be avoided when operating an SI engine on alternative fuels, it is essential to examine the autoignition characteristics of these fuels. Therefore, experiments in the HCCI and Stratified-Charge CI Engine lab (at Sandia) were performed over a wide range of conditions. These results have been published in Refs. [4,5], so only the EGR sweeps will be discussed briefly here. Of the five fuels tested, ethanol's autoignition timing has the lowest sensitivity to addition of clean EGR (i.e. EGR without unburned hydrocarbons or carbon monoxide). This low sensitivity stems primarily from ethanol's exceptionally low sensitivity to a reduction of the intake [O_2] in the 21–17% range, as shown in Figure 5. Chemical-kinetics modeling shows that ethanol is a stable molecule that does not break down until just prior to the hot-ignition point. Therefore, small changes of [O_2] does very little to influence the timing of the autoignition. The HCCI data also enable evaluation of the chemical-kinetics mechanisms. As reported in Ref. [5], the newly

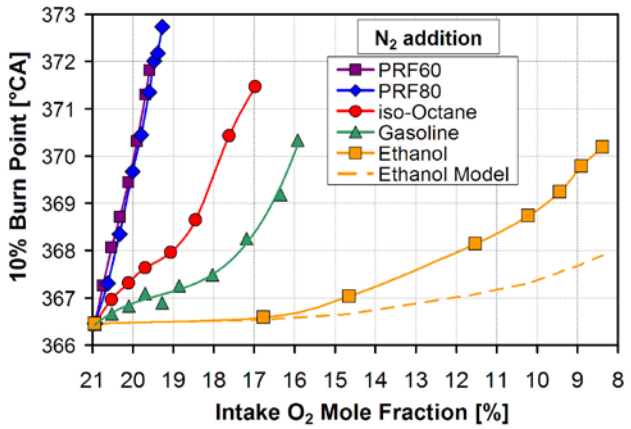

FIGURE 5. HCCI Experiments Showing the Effect of N_2 Addition on the 10% Burn Point

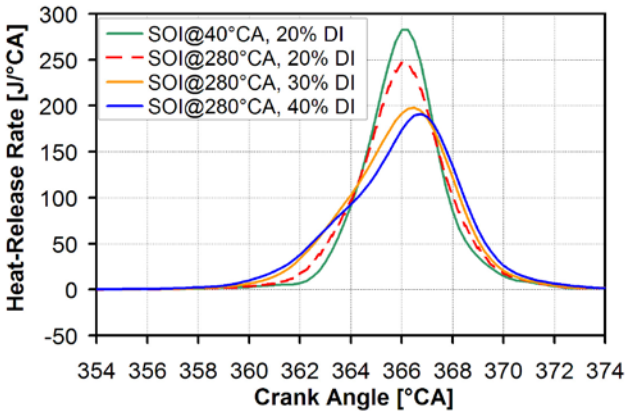

FIGURE 6. Reduction of Peak Heat-Release Rate of HCCI Combustion by Enhanced Thermal Stratification Caused by Vaporization Cooling Using Ethanol

developed chemical-kinetics mechanism for ethanol by Curran et al. [6] captures well the experimentally observed trends.

As discussed in conjunction with Figure 4 and in Ref. [5], the charge temperature has a strong influence on both laminar flame speed and autoignition. Therefore, HCCI experiments with direct injection have been performed to quantify the additional in-cylinder cooling that occurs when ethanol substitutes for gasoline. The measurements confirm thermodynamic theory and show that, when the engine load is maintained, the in-cylinder cooling due to vaporization increases by more than 400%. This explains some of the knock-suppression benefit associated with direct injection of ethanol in SI engines [7]. The strong vaporization cooling with ethanol also opens up the possibility to enhance the naturally occurring thermal stratification and in this way reduce the peak heat-release rate in HCCI engines. Experiments with partial-fuel stratification were performed to assess if this potential benefit can be realized in practice. The experiments were successful as Figure 6 shows. By increasing the fraction of the fuel that is supplied by an injection during the compression stroke, the combustion event is given a longer duration with a lower peak heat-release rate. This strong and beneficial effect of vaporization-cooling-induced thermal stratification can be realized not only because of ethanol's high heat of vaporization, but also because ethanol is a true single-stage ignition fuel [4,5].

Conclusions

The new Alternative Fuels DISI Engine Laboratory is nearly complete. The new engine will allow performance testing with an all-metal configuration over wide ranges of operating conditions (including high intake boost) and alternative fuel blends. For modes of operation that show less-than-desired performance or robustness, high-speed optical diagnostics will be applied for detailed insights. These measurements coupled with modeling will support industry to develop the highly efficient DISI engines that are needed to comply with future fuel-economy standards.

Measurements of ethanol autoignition have been performed in the HCCI and Stratified-Charge CI Engine Laboratory. Comparisons with gasoline and other fuels reveal the unique characteristics of ethanol as a true single-stage fuel. As such, it has high sensitivity to changes of the charge temperature, but low sensitivity to changes of the boost pressure and oxygen concentration. Ethanol's strong vaporization cooling can be used to enhance the in-cylinder thermal stratification, which leads to a beneficial reduction of the peak heat-release rate for HCCI operation.

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4. M. Sjöberg and J.E. Dec, "Effects of EGR and Its Constituents on HCCI Autoignition of Ethanol", in press for Proc. Combust. Inst. (2010), doi:10.1016/j.proci.2010.06.043.

5. M. Sjöberg and J.E. Dec, "Ethanol Autoignition Characteristics and HCCI Performance for Wide Ranges of Engine Speed, Load and Boost", SAE Paper 2010-01-0338.

6. H. Curran, Z. Serinyel, and W. Metcalfe, Combustion Chemistry Centre at NUI Galway, Ireland, personal communication, 2010.

7. J. Milpied, N. Jeuland, G. Plassat, S. Guichaous, N. Dioc, A. Marchal, and P. Schmelzle, "Impact of Fuel Properties on the Performances and Knock Behaviour of a Downsized Turbocharged DI SI Engine – Focus on Octane Numbers and Latent Heat of Vaporization", SAE Paper 2009-01-0324.

FY 2010 Publications/Presentations

1. J.E. Dec, M. Sjöberg, and W. Hwang, "Isolating the Effects of EGR on HCCI Heat-Release Rates and NO_x Emissions", SAE Paper 2009-01-2665. Presented at SAE 2009 Powertrains Fuels and Lubricants Meeting, Nov 2009, San Antonio, TX.

2. M. Sjöberg and J.E. Dec, "Ethanol Autoignition Characteristics and HCCI Performance for Wide Ranges of Engine Speed, Load and Boost", SAE Paper 2010-01-0338. Presented at SAE 2010 International Congress, April 2010, Detroit, MI.

3. M. Sjöberg, "Advanced Lean-Burn DI Spark Ignition Fuels Research", presented at the 2010 Annual Merit Review and Peer Evaluation Meeting, June 2010, Washington, D.C.

4. M. Sjöberg and J.E. Dec, "Effects of EGR and Its Constituents on HCCI Autoignition of Ethanol." Presented at the 33rd Symposium on Combustion, Aug 2010, Beijing, China, and in press for Proc. Combust. Inst. (2010), doi:10.1016/j.proci.2010.06.043.

5. Y. Yang, N. Dronniou, M. Sjöberg, and J.E. Dec, "Tailoring HCCI Heat Release Rates with Partial Fuel Stratification: Comparison of Two-Stage and Single-Stage Ignition Fuels." Presented at the 33rd Symposium on Combustion, Aug 2010, Beijing, China, and in press for Proc. Combust. Inst. (2010), doi:10.1016/j.proci.2010.06.114.

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III.9 Enabling High-Efficiency Ethanol Engines

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Objective

The purpose of this project is to investigate ways to improve engine efficiency when using ethanol-gasoline fuel blends in order to reduce the mile-per-gallon fuel consumption difference between gasoline and ethanol fuel blends.

Fiscal Year (FY) 2010 Accomplishments

Published experimental study using a single-cylinder research engine at ORNL with a fully variable valve actuation (VVA):

- Thermal efficiency for 50 and 85% ethanol in gasoline (E50 and E85) fuels is 2-3 percentage points higher than for gasoline fuels under nearly identical operating conditions when spark advance is not knock-limited.
- Increasing compression ratio (CR) raises thermal efficiency when using E50 and E85, but E10 and gasoline experienced knock limitations.
- By using unconventional valve timing strategies, compatibility with gasoline and E10 can be maintained without adversely impacting thermal efficiency compared to lower compression ratio conditions:
  - The fuel consumption gap between E85 and gasoline was reduced by 20% compared to a lower CR configuration.
  - At the high-CR configuration, power with E85 is 33% higher than for gasoline.

Completed installation of flexible-fuel multi-cylinder engine for ethanol optimization featuring a Delphi cam-based VVA system:

- New port fuel injection and multi-pulse direct fuel injection system capabilities added.
- Commenced experimental campaign to investigate the impact of ethanol content on gasoline particle emissions, and potential reductions in these particle emissions using various breathing and fueling strategies.

Future Directions

- Complete study investigating fuel effects on particle emissions from multi-cylinder gasoline direct injection (GDI) engines.
- This Cooperative Research and Development Agreement (CRADA) comes to an end in the second quarter, FY 2011.

Introduction

Several automakers currently sell vehicles compatible with E85 ethanol-gasoline blends, but in nearly all cases, these engines are optimized for gasoline. Using ethanol in these engines results in thermal efficiencies similar to gasoline, but because of the lower energy density of ethanol, fuel economy for consumers is reduced by about 30% with E85. Ethanol has several fuel properties that, if taken advantage of, may help to close the fuel economy gap between gasoline and E85. These fuel properties are a high octane number, which may allow the CR to be increased, and high latent heat of vaporization, which may help to cool the intake charge, thereby increasing volumetric efficiency and reducing the propensity for engine knock. In addition, it is becoming increasingly more likely that particle emissions from gasoline engines will be the subject of future regulation. Thus, it is essential to understand the impact of fuel composition on the particle emissions for ethanol fuels, and for the unconventional engine breathing strategies employed in this CRADA for efficiency optimization of ethanol fuels. In this CRADA project we have partnered with Delphi Automotive Systems to identify and demonstrate potential efficiency gains for ethanol fuels, and to investigate effect of fuels, engine breathing strategies, and fueling strategy on particle emissions.

Approach

Experimental engine studies are being investigated with two different research platforms combined with high-fidelity engine system modeling. Although the modeling effort is very much a part of this project, it is funded under a separate DOE agreement number, and is therefore not discussed in detail here.

The first experimental effort utilized a single-cylinder engine at ORNL equipped with a hydraulic VVA system to explore the knock limits of ethanol-containing fuels. A series of custom pistons were used to change the CR from 9.2 to 12.87 in order to investigate the extent that efficiency can be increased for fuels with high ethanol content. Ethanol-containing fuels are less prone to knocking than conventional gasoline fuels, and are able to operate at high CR. For gasoline and low ethanol blends which are prone to knocking, early and late intake valve closing (EIVC and LIVC) strategies were used to reduce the effective CR, thereby simultaneously mitigating knock and maintaining high efficiency, albeit at a de-rated engine load. The focus of this investigation was on thermal efficiency and the extent that the fuel economy gap between ethanol and gasoline can be reduced. Reporting for this experimental effort was completed during FY 2010.

The second experimental effort uses a research platform based on production technology, but fitted with a higher compression ratio, a cam-base VVA valvetrain featuring a 2-step system with high-authority phasing, and fully-flexible engine controls. The hydraulic VVA system on the single-cylinder engine is more versatile but has numerous implementation barriers. In contrast, the cam-based VVA system is a production-intent system. Modifications to the production engine to make it a highly versatile research platform were performed by our CRADA partner, Delphi, and the engine is shown in Figure 1. At ORNL, the engine has been modified further to include port fuel injection (PFI), as shown in Figure 2. The engine has been installed in a new engine test cell at ORNL that was renovated during FY 2008 and FY 2009. Investigations at Delphi using a companion engine platform have shown that smoke emissions with some fuels and some operating conditions can be problematic. Thus, experiments at ORNL are being focused on how particle emissions can be reduced by using ethanol fuel blends, differences in engine breathing (throttled, unthrottled with EIVC, and unthrottled with LIVC), and three different fueling techniques (single-injection GDI, multi-injection GDI, and PFI).

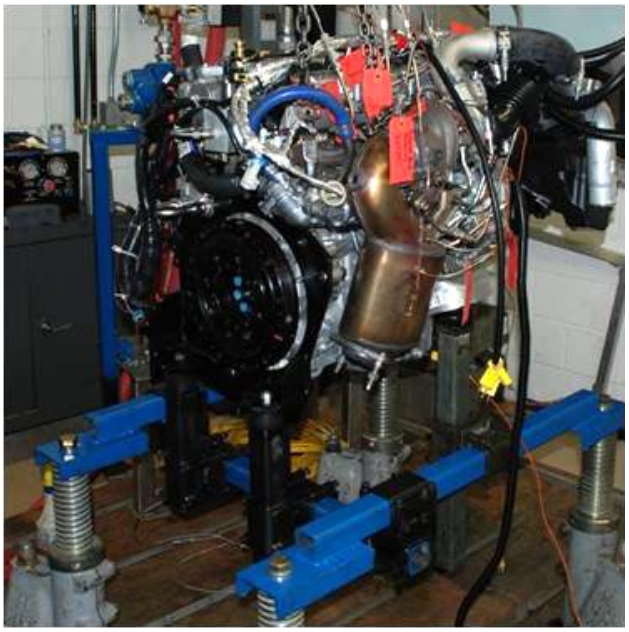


FIGURE 1. 4-Cylinder Research Engine for Ethanol Optimization Modified from a Production Engine by ORNL's CRADA Partner Delphi

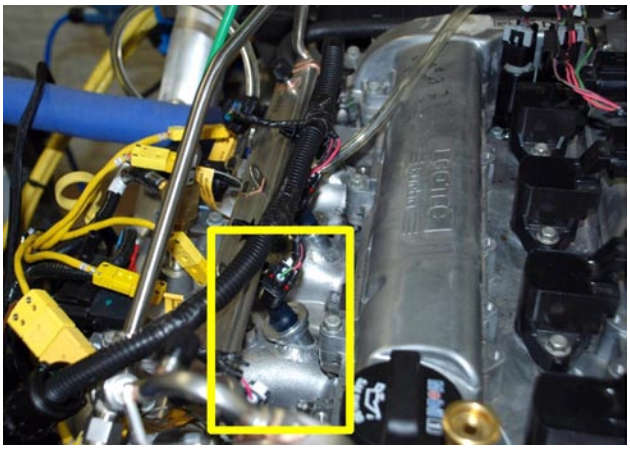


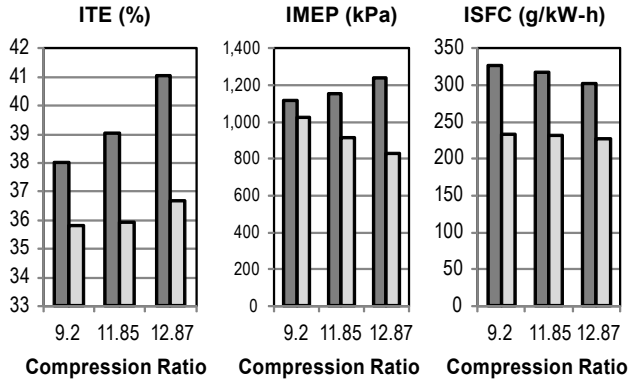
FIGURE 2. Modifications made by ORNL to add PFI Capabilities to the 4-cylinder GDI Research Engine

Results

Experimental Investigation 1: Effect of CR on a VVA Engine for Ethanol Fuels

The single-cylinder engine experiments show that as ethanol content increases, thermal efficiency and power both increase. However, the higher thermal efficiency for ethanol blends is not sufficient to offset the lower energy density compared to gasoline. Thus, the specific fuel consumption shows a substantial increase with ethanol-containing fuels.

For E50 and E85, fuels that are not knock-limited, efficiency and power continue to increase with increases in CR. However, in order to maintain compatibility at high CR with fuels that are prone to knocking, such as gasoline and E10, changes in operating strategy are required. EIVC and LIVC operating strategies were used to de-rate the engine at these conditions as a method of mitigating knock with a minimal efficiency penalty, or even an efficiency increase. This result is demonstrated in Figure 3, which compares maximum load at 1,500 rpm for E85 and gasoline as a function of CR. Thermal efficiency increases for both fuels as CR increases, but the increases for E85 are much higher. In contrast, engine power increases for E85 while decreasing for



ITE - indicated thermal efficiency; IMEP - indicated mean effective pressure; ISFC - indicated specific fuel consumption

FIGURE 3. Comparison of Engine Performance of E85 (■) and Gasoline (■) at 1,500 rpm and Maximum Load using ORNL's Single-Cylinder VVA Engine

gasoline. The net effect is that under these conditions, the fuel economy gap between E85 and gasoline can be reduced by about 20%. Additional details of this study can be found in the Society of Automotive Engineers paper listed in the publications section.

Experimental Effort 2: Particle Emissions from Ethanol Blends

Particle emissions can be problematic for GDI engines under some operating conditions, and is currently an emission source being evaluated for possible regulation. In an investigation on a companion engine installed at Delphi's facility, smoke emissions, measured by the filter smoke number, could be reduced at most operating conditions by optimizing fuel injection timing and increasing the swirl through valve deactivation, but smoke levels could not be reduced at all operating conditions.

Thus, the second experimental effort aims to expand the base of knowledge on particle emissions from a GDI engine. With guidance from our CRADA partner Delphi, the investigation will be focused on three particularly problematic speed/load engine operating conditions. We will evaluate the effect of fuel injection timing, fuel injection strategy (single-injection GDI, multi-injection GDI, and PFI), the effect of engine breathing (throttled, EIVC and LIVC) as well as the effect of ethanol content in the fuel. A heated 2-stage dilution system with an evaporator tube, shown in Figure 4, has been constructed in an effort to perform measurements only on solid particles in the engine exhaust. A scanning mobility particle sizer will be used to characterize the particle size distributions and number counts. Currently we have demonstrated that we are able to operate the engine under single-injection GDI, multi-injection GDI, and PFI operation, as shown in Figure 5. This experimental investigation is in the early

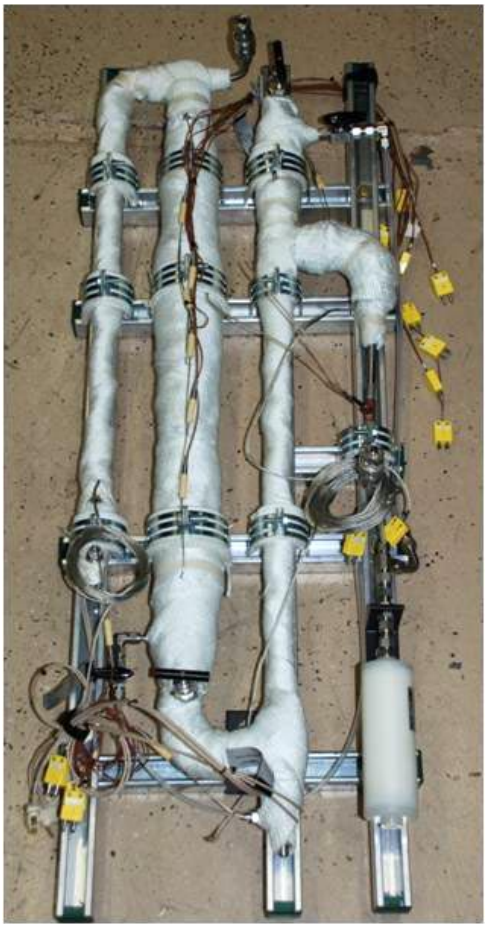


FIGURE 4. 2-Stage Dilution Tunnel Constructed at ORNL to Measure Particle Emissions with the Scanning Mobility Particle Sizer Instrument

stages, and is on-track to be completed in the second quarter of FY 2011.

Summary

An experimental study was performed demonstrating the ability of CR to increase thermal efficiency with ethanol fuels:

- Ethanol fuels increase thermal efficiency by 2-3 percentage points at comparable conditions when none of the fuels are knock-limited.
- Increasing CR to 12.87 does raise thermal efficiency for fuels that are not knock-limited. Neither E50 nor E85 were knock-limited under any operating condition investigated, whereas E10 and gasoline were frequently knock-limited.
- Using unconventional intake valve timing strategies, engine compatibility was maintained with knock-prone fuels at high CR with minimal impact on thermal efficiency. The maximum power output of these fuels was de-rated up to 33% compared to E85.

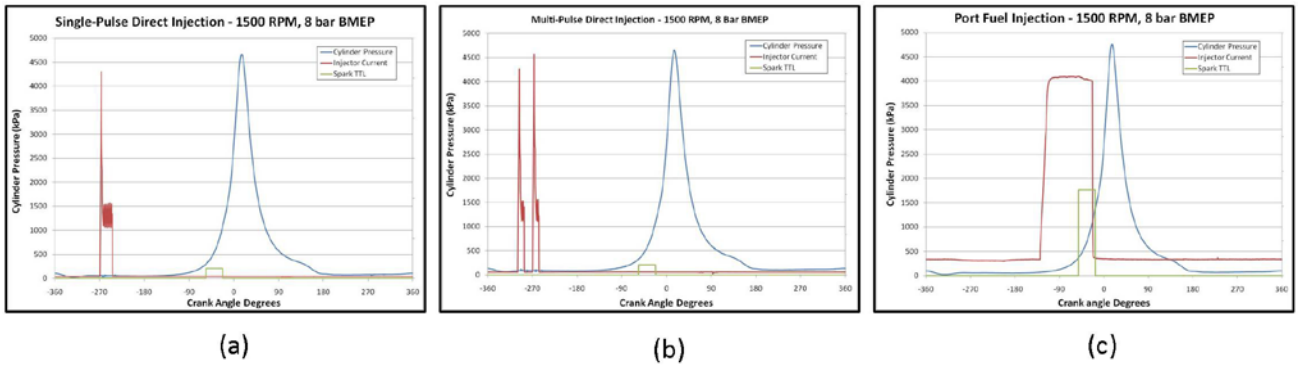


FIGURE 5. Cylinder Pressure and Injector Current of Engine Operations at 1,500 rpm and 8 bar Brake Mean Effective Pressure with (a) Single-Injection GDI, (b) Multi-Injection GDI and (c) PFI Operation

- Results demonstrate that with these methodologies, the fuel economy gap between E85 and gasoline can be reduced by about 20%.

A multi-cylinder research engine with cam-based VVA has been installed and is fully functional at ORNL:

- Modifications and additional capabilities have been added to perform an investigation of particle emissions:
  - PFI capability added at ORNL.
  - 2-stage dilution system constructed at to measure solid particle emissions in the exhaust.
- Experimental particle investigation will be complete during the second quarter of FY 2011.

FY 2010 Publications/Presentations

1. Szybist, J.P., A. Youngquist, R.M. Wagner, W. Moore, M. Foster, K. Confer. "Investigation of Knock Limited Compression Ratio of Ethanol Gasoline Blends" Society of Automotive Engineering, 2010, Technical Paper 2010-01-0619.

2. Szybist, J.P., A. Youngquist, R.M. Wagner, W. Moore, M. Foster, K. Confer. "Enabling High Efficiency Ethanol Engines" Presented at the AEC/HCCI Working Group Meeting February 25, 2010, Sandia National Laboratory.

Special Recognitions & Awards/Patents Issued

1. Outstanding Oral Presentation Award at the 2010 World Congress of the Society of Automotive Engineers for presenting "Investigation of Knock-Limited Compression Ratio of Ethanol Gasoline Blends."

III.10 CRADA with Reaction Design

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DOE Technology Development Manager:
Kevin Stork

Collaborators:
- **Reaction Design (RD), Inc.
- Reaction Design Model Fuels

Objectives

- Provide experimental engine data with combustion and emissions analysis for selected fuels and surrogates for evaluation of the Model Fuels Consortium (MFC) modeling tools and mechanisms. (ORNL)
- Use MFC modeling tools and mechanisms in ORNL research and provide feedback and suggestions regarding use, accuracy, and improvements. (ORNL)
- Provide ORNL access to MFC and RD tools with training and assist in setting up projects using these tools. Current tool set includes master mechanisms for gasoline and diesel fuels, multi-zone CHEMKIN model, and the RD FORTE computational fluid dynamics (CFD) model. (RD)

Fiscal Year (FY) 2010 Accomplishments

- Ran nine Fuels for Advanced Combustion Engines (FACE) fuels and five surrogate blends in conventional diesel combustion to provide data needed to develop and evaluate a kinetic model for particulate formation.
- Provided data of smoke point for above fuels to allow design of better surrogates.
- Provided additional data for n-heptane and soy biodiesel blends for mechanism and engine model development.
- Developed CFD models for both homogeneous charge compression ignition (HCCI) and diesel configuration using RD FORTE, which allows routine comparison of experimental and CFD results.
- Improved accuracy and comprehensiveness of combustion measurements to include gas exchange and residual analysis, heat loss, energy balance analysis, and additional experimental measurements.

Future Directions

- Provide additional diesel engine measurements with particular emphasis on particulate mass, number, and size distributions for verification of particulate formation and destruction models.
- Model all past data using MFC mechanisms and tools and RD FORTE CFD in order to provide a comprehensive database and tools for the study of fuel effects on combustion.

Introduction

The automotive and engine industries are in a period of very rapid change being driven by new emission standards, new types of aftertreatment, new combustion strategies, and the introduction of new fuels. The rapid pace of these changes has put more pressure on the need for modeling of engine combustion and performance, in order to shorten product design and introduction cycles. New combustion strategies include HCCI and partial-premixed combustion compression ignition (PCCI) which are being developed for lower emissions and improved fuel economy. New fuels include those derived from bio-materials such as ethanol and biodiesel and those derived from new crude oil sources such as gas-to-liquids, coal-to-liquids, oil sands, and oil shale. Kinetic modeling of the combustion process for these new combustion regimes and new fuels is necessary in order to allow modeling and performance assessment for engine design purposes.

Approach

The primary focus of this project is the extension of fuel kinetic models, modeling tools, and engine models to include the ability to model a wide variety of fuels. In this research, ORNL will be supplying experimental data related to engine performance with new fuels and new combustion strategies along with interpretation and analysis of such data and consulting services to RD related to engine and fuels analysis and technology. RD will perform additional analysis of this data in order to extract important parameters and to confirm newly-developed engine and kinetic models. The data generated

will be made available to the engine and automotive design communities through published reports of ORNL experimental data and through RD's MFC.

Results

In 2010, ORNL spent a large amount of effort improving experimental heat release measurements and accuracy in order to provide improved definition of experimental conditions for input to kinetic modeling tools. This was accomplished by the installation of a new AVL combustion analysis system, integration of low-speed and high-speed data acquisition, and AVL software that calculates wall heat losses, gas exchange and residual fraction, and overall energy balances. New measurements added to support these capabilities include improved cylinder pressure transducers, high-speed intake and exhaust port pressure transducers, cylinder liner and head thermocouples, and direct measurement of compression ratio and top dead center position. This capability was set up with both diesel and HCCI configuration engines and also required definition of valve lift, swirl, and injection rate. We will not present these capabilities in great detail in this report, because they will become apparent when used to analyze and present data in 2011.

In order to advance beyond multi-zone kinetic modeling, which had been shown previously to not provide complete ability to mimic emissions responses due to lack of mixing during combustion, CFD models were developed for both the HCCI and the diesel engine configurations. Again, these will not be presented in detail in this report, but will be used to analyze and present data in 2011.

New fuel data run for 2010 was all run in the diesel configuration in order to provide realistic diesel particulate for verification of particulate and soot formation kinetic models. Four fuel sets were evaluated. In the first, all nine FACE fuels were run. In the second, surrogate blends of five of the FACE fuels were designed, blended, and evaluated under identical conditions. N-heptane was also evaluated, to provide data to rapidly check models because it well verified small, skeletal kinetic models for heptanes are available. Finally, blends of soy-derived biodiesel in diesel fuel in percentages of 0, 5, 10, 20 and 50 (B0, B5, B10, B20, and B50) were also evaluated. The purpose of evaluating these fuels was to provide data for the next step of model and mechanism development and verification, which will be done in 2011. As such, only preliminary data analysis will be included in this report.

Data analysis and comparisons between actual results and kinetic modeling can be divided into several questions. In this work we are trying to globally extend the application of kinetic modeling tools to the study engine response to fuels to allow fuel studies to be conducted over a wide range of chemistries and properties without first running the fuels in an engine to determine response. This work breaks down to several key questions:

1. How well can surrogate fuel blends represent real fuels?
2. What size kinetic mechanisms are needed to reproduce broad fuel effects?
3. How simple can CFD models be made to reduce calculation time and allow use of more complex kinetic mechanisms for fuels?
4. How well can CFD and multi-zone modeling, using surrogate fuels, represent the engine response to real fuels?

These questions will be the main focus of FY 2011 work, since we now have sufficient data and MFC tool development to allow addressing them. For this report, comparison will be made using graphs and statistics in order to explain some of the data trends.

Table 1 describes the surrogates designed using MFC tools, using eight pure compounds selected from a pallet of 25 possible starting compounds. The design process included matching cetane, percent aromatics, smoke point, temperature for 50% evaporated, and ignition delay (closed homogeneous reactor). These surrogates were blended and evaluated for properties and chemistry and a comparison for some of the variables is shown in Figure 1. Percent aromatics, cetane, and smoke point agree quite well. The temperature for 90% evaporated (T90) does not agree because the highest boiling point compound in the pallet is $C_{15}H_{34}$, which has a boiling point lower than the T90 of most of the FACE fuels. Figure 2 shows comparisons for selected important engine response

TABLE 1. Design of Surrogates for FACE Fuels, Using MFC Tools

component	surrogate 1	surrogate 3	surrogate 5	surrogate 8	surrogate 9
1-methyl naphthalene	0.000	0.103	0.063	0.244	0.128
n-propyl benzene	0.216	0.281	0.102	0.072	0.145
decalin	0.131	0.000	0.000	0.122	0.181
methyl cyclo hexane	0.000	0.169	0.198	0.025	0.099
hepta methyl nonane	0.470	0.213	0.111	0.083	0.073
n-decane	0.131	0.000	0.000	0.000	0.000
n-dodecane	0.052	0.000	0.211	0.000	0.000
n-hexadecane	0.000	0.234	0.314	0.455	0.375
	volume fractions				

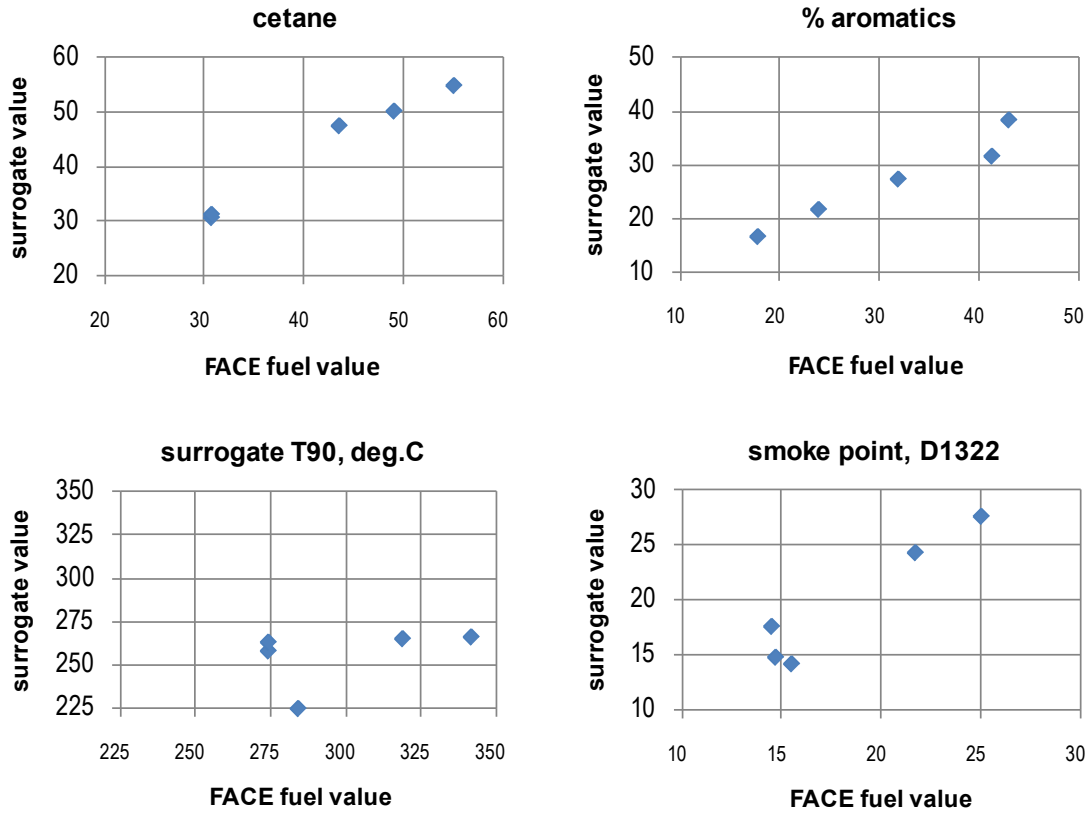
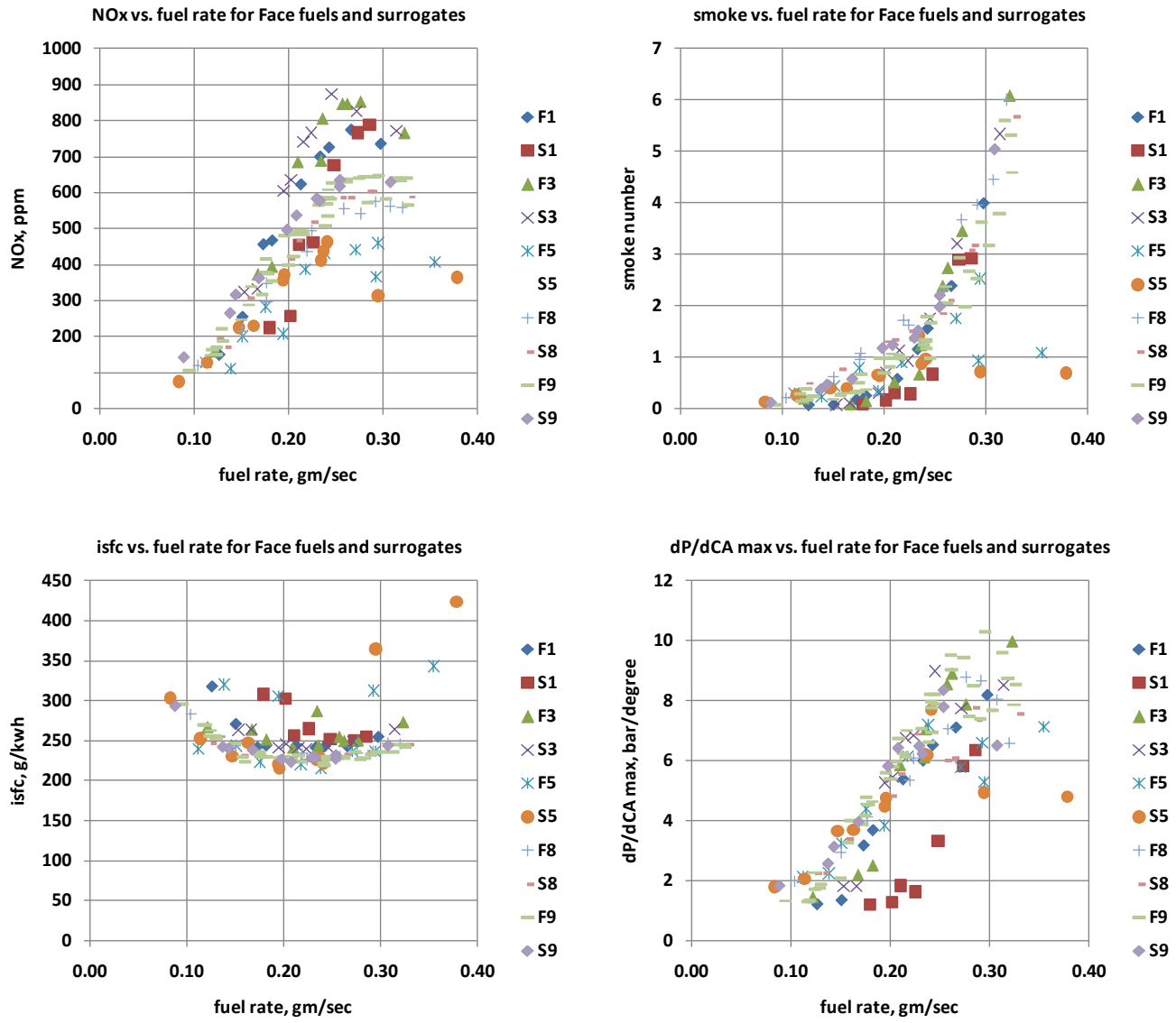


FIGURE 1. Match of Surrogate Properties to FACE Fuel Properties for Selected Variables

variables for the FACE fuels and surrogates, plotted against fuel rate. It is a little difficult to tell from these graphs, but generally a fuel and its matched surrogate fall in the same portion of the overall response band. Another good way to visualize the data is by looking at engine response vs. run order. In this case, each fuel is followed by its corresponding surrogate and was run in the same sequence of increasing and then decreasing throttle. Figure 3 shows engine response vs. run order for selected variables. Quick examination indicates that a surrogate's response generally matches that of the corresponding FACE fuel. Fuel 5 produces lower smoke and oxides of nitrogen (NOx) than the other fuels, but worse indicated specific fuel consumption. Fuels 8 and 9 both produced higher smoke and NOx than the other fuels. This data will be subject to further analysis in 2011, including examination of engine response vs. fuel properties and chemistry, comparison to previous data with these fuels run in HCCI, and ability to model the engine response and using CFD and MFC surrogate fuel mechanisms.

Conclusions

- Improvements in experimental measurement capabilities were made in 2010, including improved heat release measurements and calculations including residual fraction and energy balance, in order to provide better definition of the experiments for input to engine models. These improvements should reduce uncertainty and the need to tune models to engine data to achieve agreement.
- A new diesel engine was instrumented and installed to provide fuel response information for a second type of combustion and to provide more representative measurements for verifying particulate formation models.
- Data was completed for FACE diesel fuels and surrogates, for n-heptane, and for soy-based biodiesels. This data will form the basis of an extensive modeling effort in 2011 to compare and further develop kinetic modeling tools to experimental engine response.
- Although not presented in this report, CFD engine models have been completed for both the HCCI and diesel configuration to support this modeling effort.



isfc - indicated specific fuel consumption

FIGURE 2. Comparisons of Diesel Engine Response for Five FACE Diesel Fuels and Corresponding Surrogate Blends Designed Using MFC Tools

FY 2010 Publications and Presentations

1. Karthik V. Puduppakkam, Long Liang, Anthony Shelburn, Chitralkumar V. Naik, Ellen Meeks, and Bruce G. Bunting, Predicting Emissions Using CFD Simulations of an E30 Gasoline Surrogate in an HCCI Engine with Detailed Chemical Kinetics, SAE paper 2010-01-0362.

2. Bruce G. Bunting, ORNL Research on Behalf of Model Fuels Consortium, presentation to MFC 2010 mid-year meeting, 7/14/2010.

3. Bruce G. Bunting, Diesel Engine Measurements for MFC, presentation to MFC 2010 annual meeting, 11/2/2010.

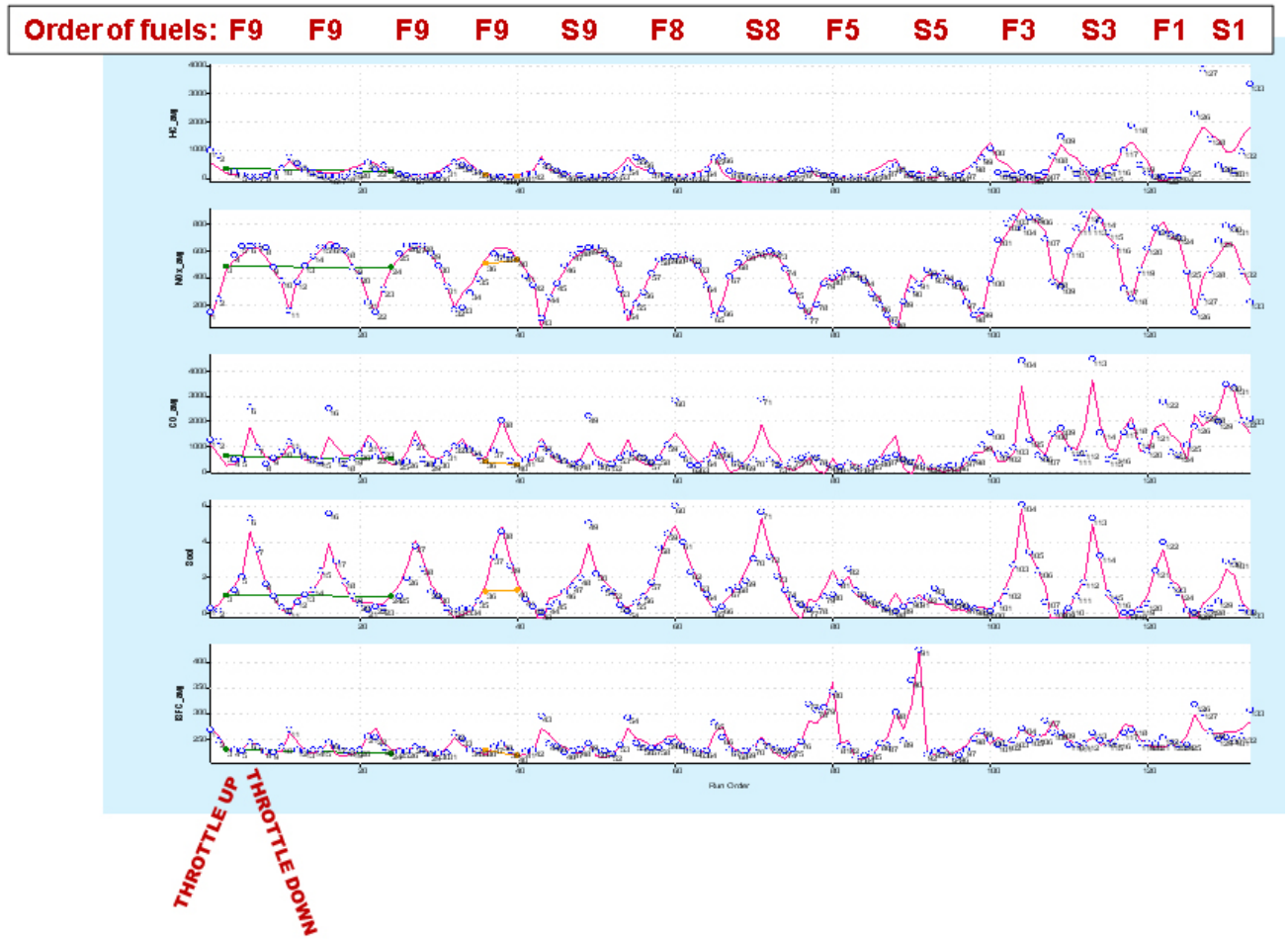


FIGURE 3. Engine Response vs. Run Order for Experiments Comparing FACE Fuels and Surrogate Blends

IV. PETROLEUM DISPLACEMENT FUELS/FUEL BLENDING COMPONENTS

IV.1 Biodiesel Impact on Performance and Durability of DOC and DPF Systems

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DOE Technology Development Manager:
Kevin Stork

Objectives

- Assess the impact of biodiesel on the long-term durability of emission control systems found in modern diesel engines.
- Determine if the current ASTM International specification limit for metal impurities in biodiesel is adequate to protect the catalytic activity or mechanical durability of diesel emission control systems.

Fiscal Year (FY) 2010 Accomplishments

- The impact of long-term biodiesel ash exposure was investigated for three different diesel particulate filter (DPF) substrate types (cordierite, aluminum titanate [AT], and SiC), as well as for a diesel oxidation catalyst (DOC).
- Estimates of DPF pressure drop indicate that the additional ash exposure from 150,000 miles of operation with 20% biodiesel in diesel fuel (B20) will result in a 6.8% increase in exhaust backpressure.
- The catalytic activity of a DOC was measured after simulated exposure to 150,000 miles of biodiesel ash. Results showed a significant drop in NO_2 formation selectivity to 21%, compared to 37% for a ultra-low sulfur diesel (ULSD)-aged DOC.
- The mechanical durability of cordierite, AT and SiC DPFs were measured after long-term exposure to biodiesel ash. There was no significant change in durability for any of the DPFs after simulated 150,000 mile exposure. There was a 69% decrease in thermal shock resistance of the cordierite DPF after simulated 435,000 mile exposure.

Future Directions

- Testing to date has shown that metal impurities found in biodiesel can have a severe impact on both the catalytic activity and mechanical durability of diesel emission control systems. Future work will be conducted to model and understand the role of alkali metal volatility on DPF and catalyst degradation.
- Future experiments will also be designed to determine an acceptable limit for these metal impurities.

Introduction

The biodiesel production process can result in small quantities of metal impurities in the fuel. These impurities are currently limited by ASTM D6751 to 5 ppm Na+K and 5 ppm Ca+Mg. While these limits are relatively low, these metals lead to ash accumulation in the exhaust and can have detrimental impacts on the emission control systems. Furthermore, the Environmental Protection Agency requires full-useful-life performance of 435,000 miles for the emission control system in heavy-duty engines. A study was conducted to determine if the current allowable limits for these impurities would have a negative impact on the performance and durability of diesel emission control systems after full-useful-life exposure.

Approach

An accelerated aging method was used to simulate long-term operation with a B20 fuel that is at the current ASTM limit for metal impurities. Accelerated aging tests matched the total amount of biodiesel ash and thermal exposure that you would expect to see in 150,000 and 435,000 miles of operation. The B20 test fuel was additized with higher levels of metal impurities to accelerate the ash exposure. The thermal aging of the catalysts was also accelerated. This was accomplished by operating the system at continuous high temperatures such as those experienced during a DPF regeneration event, with peak temperatures reaching 850°C.

Testing was conducted on a 2008 Caterpillar C9 engine shown in Figure 1. The engine was fitted with various emission control devices including three different DPF substrate types (cordierite, AT, and SiC), as well as DOC and selective catalytic reduction (SCR) catalysts. For each aftertreatment component type, a baseline test was conducted with ULSD followed by a test with B20 for comparison. Following the accelerated aging, post-mortem tests were conducted to investigate the impact on DPF backpressure, DPF thermo-mechanical properties and DOC and SCR catalytic activity.

FIGURE 1. Caterpillar C9 Retrofitted With Emission Control System

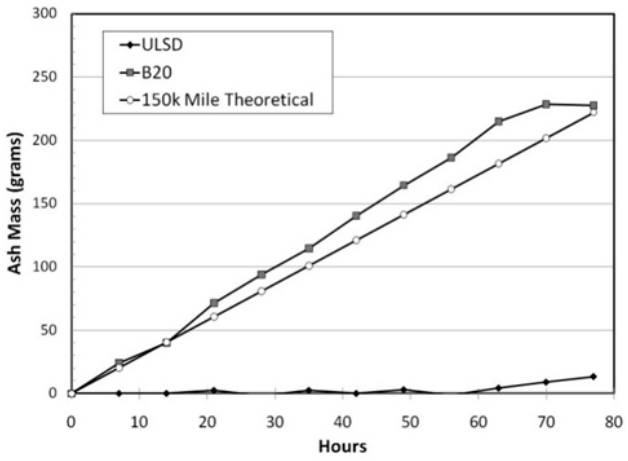

FIGURE 2. Cordierite DPF Ash Loading Tested to 150,000-Mile Equivalent

Results

Ash Loading

The accelerated aging test resulted in an ash accumulation on the DPF. The accumulated ash was measured by weighing the DPF throughout the test. For the B20 tests, the accumulation rates were similar to those expected by operating with a B20 at the current ASTM limit for metal impurities. For both the ULSD and B20 cases there was also a small amount of ash accumulation from the engine lubricant, however the ash accumulation from the lubricant oil was not accelerated. The ash accumulation on the two cordierite test filters operated to a simulated 150,000 miles is shown in Figure 2. The B20 DPF collected 228 grams of ash compared to 14 grams for the ULSD filter. This additional ash loading from biodiesel resulted in an estimated 6.8% increase in backpressure for a DPF at 150,000 miles.

DPF Thermo-Mechanical Durability

At the high temperatures experienced during DPF regeneration events the alkali metals found in biodiesel ash can react with the filter substrate. This could potentially change the thermo-mechanical properties of the material making the filter more susceptible to cracking. Resistance to thermal shock for a given material is defined by three material properties; bend strength, elastic modulus and coefficient of thermal expansion. A decrease in the bend strength of the material or an increase in the elastic modulus or the coefficient of thermal expansion will result in a lower thermal shock resistance parameter. These material properties, shown in Figure 3 were measured for the cordierite DPFs aged to 150,000 and 435,000 miles. After 435,000 miles there was a 69% decrease in the

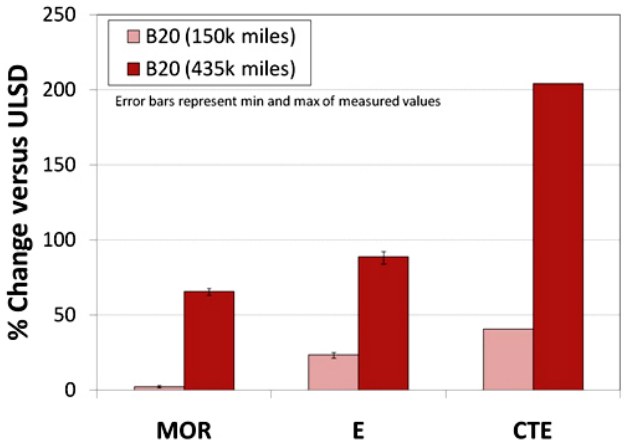

FIGURE 3. Thermo-Mechanical Properties for Cordierite DPF

thermal shock resistance for the B20 tested filter compared to the ULSD test piece.

DOC Catalytic Activity

In the accelerated aging tests a DOC is placed upstream of the DPF. This DOC has two primary functions for creating regeneration conditions for the DPF; 1) converting NO into NO_2 which is used to oxidize stored soot and 2) to burn fuel injected into the exhaust which is used to heat up the DPF. Any loss in catalytic activity from biodiesel ash exposure could hinder the performance of the DPF regeneration. The DOC's ability to convert injected fuel was measured over an eight-mode engine test. A comparison of the two DOCs showed higher unburned hydrocarbon slip for the biodiesel-aged part at all eight modes. The NO_2 formation from the DOCs was also measured across a range of catalyst temperatures. This was done by ramping the engine load from 0 to 100% at a steady-

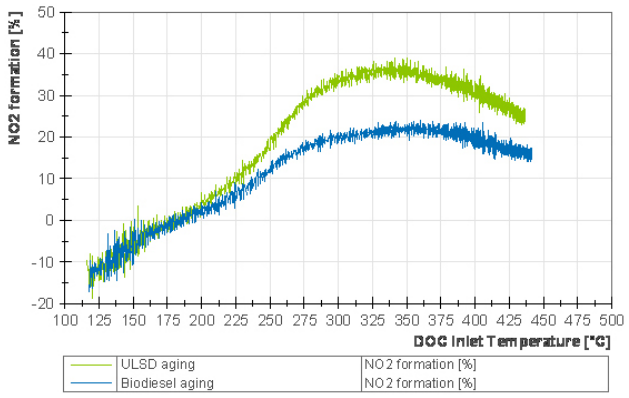

FIGURE 4. NO_2 Formation from DOCs Tested to 150,000-Mile Equivalent

state engine speed of 1,100 rpm. The results, shown in Figure 4 demonstrate a significant loss in catalyst activity for the biodiesel-aged DOC reducing the maximum NO_2 formation from about 37% for the ULSD DOC to 21% for the B20 DOC.

Conclusions

- Ash loading onto the DPF from 150,000 miles of simulated operation is estimated to cause a 6.8% increase in exhaust backpressure.
- The thermal shock resistance of a cordierite DPF is compromised after 435,000 miles of B20 operation with a 69% decrease in the thermal shock resistance parameter of the substrate material.
- The DOC, placed upstream of the DPF, showed a loss in catalytic activity after 150,000 miles of operation with higher unburned hydrocarbon slip and lower NO_2 formation.

FY 2010 Publications/Presentations

Presentations

1. Biodiesel Technical Workshop, October 2009 – San Antonio, TX.

2. 2nd International Congress on Biodiesel, November 2009 – Munich, Germany.

3. National Biodiesel Conference, February 2010 – Grapevine, TX.

4. DEER Conference, September 2010 – Detroit, MI.

Special Recognitions & Awards/Patents Issued

1. Aaron Williams received the Biodiesel Technical Advancement Award, Presented by the National Biodiesel Board at the Biodiesel Technical Workshop, October 2009.

IV.2 Biofuels Quality Surveys in 2010

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DOE Technology Development Manager:
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Objectives

- Survey and report on wintertime blends of biodiesel in diesel fuel in the range of 6-20% (B6-B20) quality in the United States.
- Collect snapshot of so-called blender pumps in the midwest U.S.
- In collaboration with Coordinating Research Council (CRC), assess the quality of U.S. ethanol fuel for flexible-fuel vehicles (FFVs) in 2010/2011.

Fiscal Year (FY) 2010 Accomplishments

- Completed wintertime B6-B20 quality survey demonstrating that the overall quality of biodiesel blends was high and a vast majority met the prevailing specifications.
- Completed snapshot of ethanol blender pumps in Midwest which revealed that the blends contain slightly less ethanol than the pump labeling indicates, but have significantly higher vapor pressure than the maximum allowed by the FFV fuel specification for the time of year and region. The vapor pressures of these blends do fall below the maximum allowable by the appropriate gasoline specifications.
- Initiated an ethanol fuel survey with CRC to examine the quality of ethanol fuel for FFVs across the U.S., collecting samples from each volatility class. Samples will be compared to ASTM International D5798-10 to assess compliance with the specification.

Future Directions

- Finalize and report on ethanol fuel for FFV quality with CRC.
- Collaborate with CRC for larger blender pump quality survey.
- Conduct B100 quality survey in 2011.

Introduction

The focus of this research area is on documenting the quality of biofuels, specifically B6-B20, ethanol fuel for FFVs (formerly known as E85 [85% ethanol and 15% gasoline]), and fuel dispensed from blender pumps. The goal of this work is to provide a snapshot of the quality of biofuels in the U.S., to determine if quality is changing significantly over time, and to provide data for on-going specification refinement and development. More common biofuels, like biodiesel blends and FFV fuels, have quality specifications in place. Emerging fuels, like those found in so-called ethanol blender pumps (a pump allowing the user to select one of several predefined blends of ethanol and gasoline between conventional gasoline and FFV fuel) do not yet have specifications or recommend practices governing their quality.

Approach

Two surveys were completed in 2010, one on B6-B20 and one on blender pump fuel quality. In each survey a contractor visited a publically accessible station to collect a fuel sample. Each survey was conducted independently, though the methodology and approach were similar.

The B6-B20 survey samples were collected between December 2009 and January 2010 to assess the wintertime performance and quality of these blends. All samples were collected from public stations with pumps labeled as selling biodiesel or biodiesel blends. The samples were then tested for critical properties in ASTM D7467-09, the specification for B6-B20 blends. In addition, other key properties were examined to fully assess the fuel quality. All properties tested are listed in Table 1.

Samples from ethanol blender pumps were collected in a single campaign in the wintertime of 2009. The blender pump samples are typically a blend of seasonal FFV fuel and conventional gasoline and intended for use in FFVs only. Samples were collected at each station spanning a range of blend levels. In an effort to examine the most extreme case, samples were collected during the Class 3 FFV season, with the lowest minimum ethanol content to determine whether the samples met the posted ethanol content. The properties tested are listed in Table 2.

We also published the results of an ethanol fuel for FFV study from samples collected throughout the U.S. in all three volatility classes. The study showed that on average, 74% of the samples did not meet the minimum vapor pressure requirements and 45% of the samples did

not meet the ethanol content requirements, most often due to excess ethanol content.

TABLE 1. Properties Measured for B6-B20 Blends

Property	Test Method	Specification Limit	Failure Rate, Cold States	Failure Rate, Warm States
Blend Concentration, vol%	ASTM D7371	6-20	27%	30%
Acid Value, mgKOH/g	ASTM D664	0.5, maximum	0%	0%
Oxidation Stability, hrs	EN15751	6, minimum	13%	40%
Flash Point, °C	ASTM D93	52, minimum*	3%	0%
Karl Fisher, ppm	ASTM D6304	Not Applicable**	Not Applicable	Not Applicable
Cloud point, °C	ASTM D2500	Not Applicable	Not Applicable	Not Applicable

*If a No. 1 diesel fuel is used in the blend, or the cloud point requirement is less than -12°C, the minimum flash point is 38°C.
**D7467-09 does not contain a specification for Karl Fisher or cloud point.

TABLE 2. Properties Measured for Ethanol Blender Pump Fuels

Property	Test Method	E10 Average, Standard Deviation	E20 Average, Standard Deviation	E30 Average, Standard Deviation	E50 Average, Standard Deviation
Ethanol Content, vol%	D5501	12.3 0*	18.4 1.4	27.9 0.54	44.8 0.59
Vapor Pressure, psi	D5191	9.61 0*	12.9 3.1	14.0 0.26	13.1 0.41
Sulfur, ppm	D5453	46.8 0*	58.6 44.2	51.6 36.5	44.4 32.1

* Single measurement

Results

B6-B20 Survey

Forty B6-B20 samples were obtained between December 2009 and January 2010 from around the U.S. Thirty samples were collected from states with a 10th percentile minimum ambient temperature of –12°C or less. The daily minimum ambient air temperature will on average not go below the monthly 10th percentile minimum ambient air temperature more than three days for a 30-day month. These temperatures are derived from the report by Doner [1] and are presented in ASTM D7467-09. The remaining samples were collected from states with December and January 10th percentile minimum temperatures greater than –12°C. The contractor took photographs of a majority of the pumps to provide information on labeling used in the field. Most of the pumps photographed provided some sort of indication to the consumer that the product dispensed was a biodiesel blend. Although some pumps had homemade labels, most used the Federal Trade Commission compliant blue and black label (Figure 1).

The results show that overall, biodiesel blends are of high quality and meeting the specifications. The results are presented in Table 1, alongside the specification limits and test methods. Averages for cold and warm states include all data collected. Because the samples in this survey had only a single analysis by a single lab, error bars were assigned using the ASTM or European Normalization method of reproducibility. This reproducibility is based on the round robin testing performed during the development of the test method and includes a statistically determined precision. For this survey, a sample has been determined to be on specification if either the absolute value of the measurement meets the specification or if the error bar determined by the method reproducibility is within the specification.

Ninety-eight percent of the samples were B20 or below (Figure 2), a vast improvement from previous surveys where a wide range of blend percentages were observed [2,3]. Almost 75% of the samples were within the range of B6-B20 (29 samples). The average biodiesel concentration in cold states was 12%, likely due to the need to reduce biodiesel content to meet cold weather operability requirements. The percent biodiesel rose to 19% in the warm states.

Focusing only on the B6-B20 samples (shown as circles in Figure 3), seven did not meet the oxidation

FIGURE 1. Federal Trade Commission compliant pump label for B6-B20 blends.

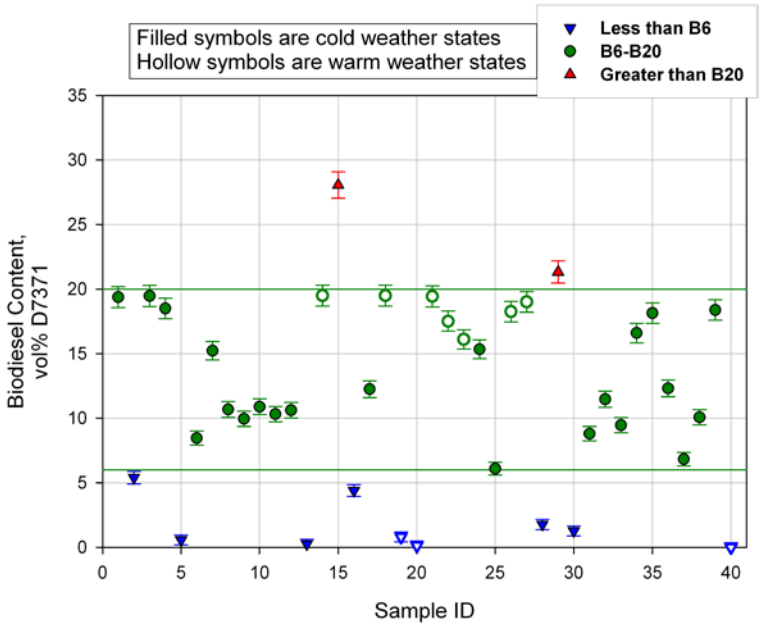

FIGURE 2. Average wintertime biodiesel content in wintertime B6-B20 survey.

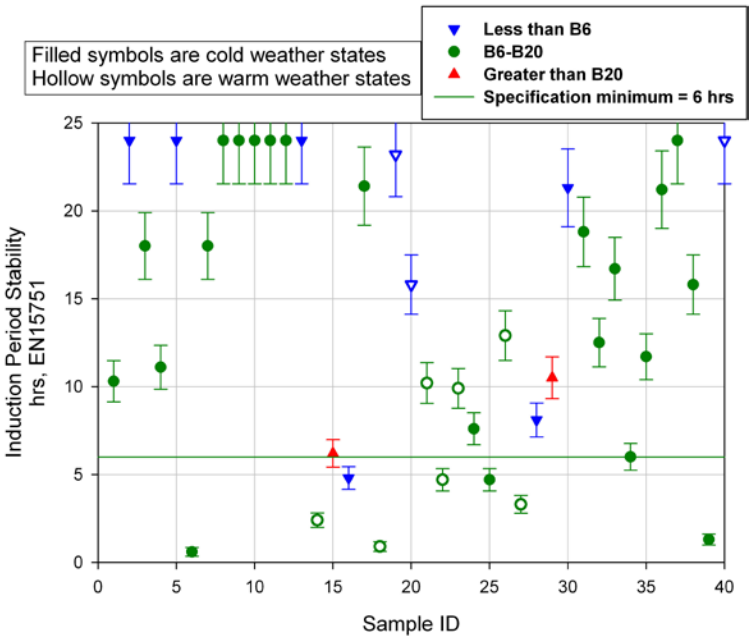

FIGURE 3. B6-B20 oxidation stability results.

stability minimum of 6-hours in D7467-09, 75% of the samples were on-specification (Figure 3). Oxidation stability is dependent on a number of factors, including sample age, and the presence of stability additives [4]. Previous work has also shown that a B100 with oxidation stability below two hours will result in a B5 blend with very low stability as well [5].

There was a difference between the cold and warm weather states and their oxidation stability results. In the cold weather states, 87% of the samples met the oxidation stability minimum in D7467-09, while in the warm weather states, only 60% of the samples met the 6-hour minimum. No other critical properties were found to be problematic.

Previous surveys have found that biodiesel was predominately produced from soybean oil [2,3,6,7]. This survey found that roughly half the samples contained biodiesel produced from soybean oil. This is likely due to the emphasis on cold state sampling (75% of the study), where ambient conditions require less saturated feedstocks than in warm weather or warm states. The remaining samples contained biodiesel that was a complex mixture of fats and oils. These mixtures represented a wide range of feedstocks, including soy, canola, and corn oils, as well as various animal fats, such as beef tallow, white grease, and poultry fat.

Blender Pump Snapshot Survey

Three stations were visited to collect a variety of samples to assess the properties of fuel dispensed by so-called ethanol blender pumps. These fuels are defined by ethanol content higher than conventional gasoline (10 vol% ethanol), but less ethanol than found in FFV fuels (minimum of 70 vol% ethanol at the time these samples were taken). These fuels are typically blends of FFV fuel and conventional gasoline and the samples were collected in the winter, when the FFV fuel may have the lowest ethanol content. No specification or standard exists for these fuels, so the average properties are simply reported here (Table 2).

Blender pump samples are most often sold in discrete intervals at the pump, rather than allowing the consumer to selected any blend. For the pumps sampled in this survey these intervals are E20, E30 and E50, representing 20, 30, and 50 vol% ethanol in gasoline, respectively. Three E20 samples, three E30 samples, and two E50 samples were collected in addition to one conventional gasoline (E10) sample.

All samples were tested for ethanol content to determine if the blends met the pump labeling. To ensure that accurate samples were collected, the one

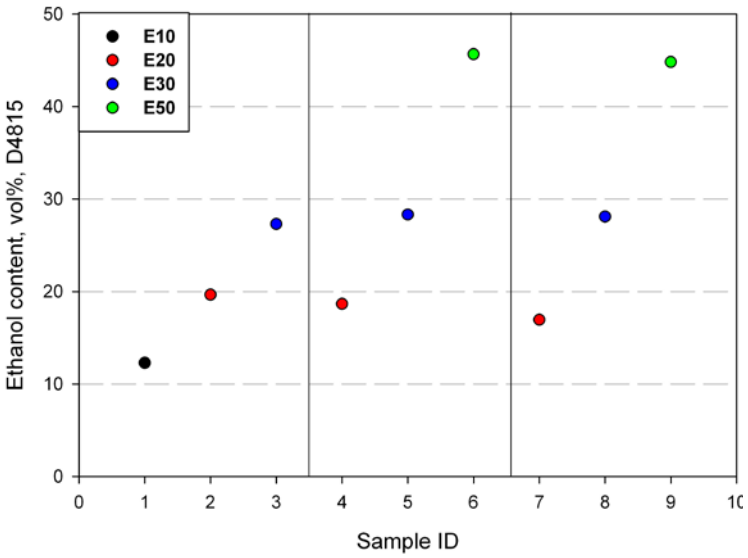

FIGURE 4. Ethanol content, in vol%, of blender pump samples.

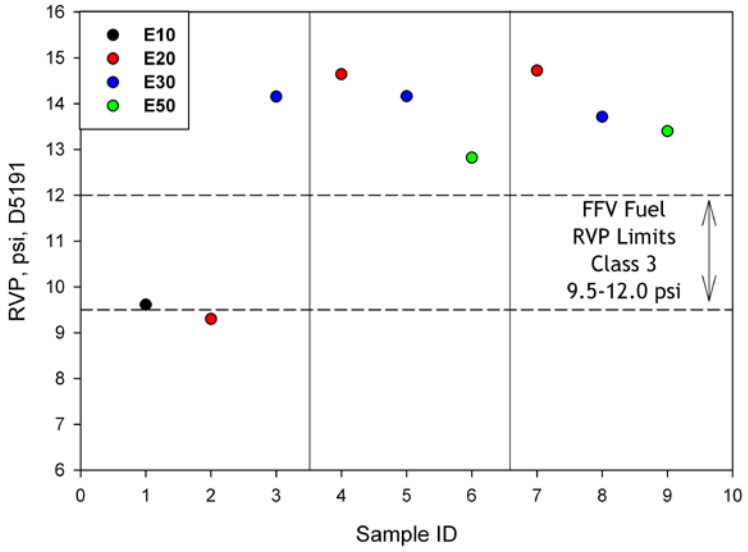

FIGURE 5. Vapor pressure, in psi, for samples collected in ethanol blender pumps.

gallon of the desired blend was flushed through the pump prior to collection. The samples showed ethanol content in the range of the blend selected. The E10 sample was actually 12 vol% ethanol, while the other samples were always slightly below the indicated blend level, see Figure 4 (i.e. the E20 samples ranged from 17-19 vol% ethanol).

Recently, blenders of FFV fuels have had difficulty in meeting the minimum vapor pressure requirements, particularly in Class 3 or wintertime fuels [8,9]. The impact of low vapor pressure has been well documented and includes difficulty of starting in cold weather and poor driveability. Since the blender pump samples are intended for use in FFVs, the samples were compared to the vapor pressure requirements for Class 3 FFV fuel, which specifies the fuels must fall between 9.5-12.0 psi. This limit is set specifically for FFV fuels, with their higher ethanol content, which drops the vapor pressure in the blend significantly. Because of the much higher gasoline content of the blender pump fuels relative to FFV fuel, they were typically above the 12.0 psi maximum set for Class 3 FFV fuels (Figure 5), but met the appropriate conventional gasoline volatility specifications from ASTM D4814. Based on this limited data set, these samples show that by reducing the ethanol content in FFV fuels, the vapor pressure can be increased. The E10 sample met the appropriate vapor pressure requirements for gasoline at the time of collection, however the E20 sample from the same state showed a slight drop in vapor pressure and was slightly below the minimum for FFV fuels, but still within the gasoline specification. It is worth noting that since no specification or guide exists to guarantee blender pump fuel quality, the samples collected in this survey cannot be deemed on or off-specification.

Conclusions

In 2010, the quality of wintertime biodiesel blends was sampled nationwide, with an emphasis on cold-weather states. The samples were tested and compared against ASTM D7467-09, the specification for B6-B20. Biodiesel content was lower in cold weather states, averaging 9 vol%, while warm states had biodiesel content around 19 vol%.

Overall, the quality of biodiesel blends sampled was high, with 87% of the samples in cold-weather states met the oxidation stability requirements, but only 60% of the samples in the warm states.

A small sampling of FFV fuels from blender pumps was conducted in 2010. Although these fuels are not covered under a specification or standard, pump labeling clearly indicates they are for use in FFVs. The ethanol content is slightly lower than the pump labeling in most cases. The vapor pressure is typically higher than the FFV fuel specification maximum limit, however the meets the applicable gasoline volatility class requirements.

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9. CRC Report No. 654; http://www.crcao.org/publications/performance/index.html.

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2. Alleman, T.L.; Fouts, L.; McCormick, R.L.; *Analysis of Biodiesel Blend Samples Collected in the United States in 2008*; NREL Report No. TP-540-46592; National Renewable Energy Laboratory, Golden, CO, March 2010; http://www.nrel.gov/docs/fy10osti/46592.pdf.

3. CRC Report No. E-85, http://www.crcao.org/publications/emissions/index.html.

4. Alleman, T.L.; Fouts, L.; McCormick, R.L.; *Quality Analysis of Wintertime B6-B20 Biodiesel Blend Samples Collected in the United States*; submitted September 2010 to *Fuel Processing Technology*.

IV.3 Understanding Biodiesel Low Temperature Operability Issues

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Objectives

To reveal the fundamental causes of persistent (although rare) low-temperature operability problems that can occur when using biodiesel. These low-temperature operability issues occur at temperatures above the fuel's cloud point (CP) and hence are not expected based on experience with petroleum-derived fuels where CP is a conservative predictor of the low-temperature operability limit. Field observations suggest that saturated monoglycerides (SMGs), an impurity present in biodiesel, are the cause of these problems. Thus a further objective of this project was to determine how SMG might cause fuel filter plugging above the CP.

Fiscal Year (FY) 2010 Accomplishments

- SMGs where shown to increase the CP of biodiesel when the concentration is above a threshold or eutectic level. Additionally, above the eutectic the final melting temperature (FMT) of the biodiesel increases and can be as much as 15°C or more above the CP.
- Experiments conducted under a controlled temperature microscope showed that SMG initially crystallized in one form, but that over time or under slow heating the SMG transformed to have a different crystal habit. We propose that the SMGs crystallize as the α-polymorph, and transform to the more stable and higher melting β-polymorph. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) results confirm that the higher melting crystals are the β-form. The formation of these stable and higher melting crystals on time scales longer than the CP measurement could explain the low-temperature operability issues.

Future Directions

Further study to address the following issues is underway:

- Determine how other minor components in biodiesel may affect the polymorphism of the monoglycerides and how this relates to CP and FMT measurements.
- Determine what effect blending the biodiesel into conventional diesel fuel with a range of properties will have on the polymorphic forms, CP and FMT.

Introduction

Low-temperature performance of biodiesel and biodiesel blended with conventional diesel, particularly B5, has sometimes been problematic in the field. Precipitate formation above the measured CP of the fuel, while relatively rare, has been an issue that has plagued biodiesel producers and users leading to plugging of engine and dispenser fuel filters. Impurities in biodiesel have long been thought to be the cause of these operability issues. One approach to limiting impurities has been a cold soak filtration test (in which the fuel is cooled to 4.5°C and maintained at that temperature for 16 hours, followed by timed filtration). Fuels with long filtration time are deemed to have levels of impurities high enough to cause low-temperature operability problems. This was confirmed in recent Coordinating Research Council studies, led by NREL, that tested trucks at low temperature on B5 and B20 blends from biodiesel with a range of cold soak filtration times [1,2]. As a result, cold soak filterability was added to the B100 ASTM International specification (D6751) in 2008.

The objective of this study was to understand mechanistically how impurities can cause operability problems above the CP and to begin to quantitatively identify these impurities. Selvidge and coworkers presented evidence that dispenser filters used with a 2.5 vol% soy biodiesel blend could become blocked by SMG as temperatures approached –18°C (0°F) for SMG content above about 0.07 w/w% [3]. The idea that SMG could cause filter plugging was also the conclusion of a low-temperature heavy-duty vehicle testing study [4]. Hence we have initially focused on how SMG in B100 behaving upon cooling to CP and below, followed by warming until all solids have melted.

Approach

- Biodiesel produced using vacuum distillation as a purification step has very low levels of SMG and other impurities. Distilled soy and animal-derived biodiesels were spiked with common monoglycerides monomyristin, monopalmitin and monostearin at levels ranging from 0.02 w/w% up to 1.0 w/w%. All samples were tested for CP and FMT using an apparatus that detects the presence of solids by diffusive light scattering and a Peltier effect cell to heat and cool the sample at precise rates.
- A set of samples were also tested using a controlled temperature microscope and the observed crystal habit was compared to the CP and FMT data. Crystals were analyzed by DSC and XRD.

Results

Tables 1 and 2 contain the CP and FMT results that were measured for the spiked samples. These results are an average of all runs performed on each sample. Results in bold type show a significant increase in CP or FMT relative to the neat biodiesel. Here we define a significant increase as a change in CP of 2°C or higher from the neat sample CP.

TABLE 1. Cloud Point (ASTM D5773) of Monoglycerides in B100

D5773 Cloud Point (Temp °C)						
	Soy			Animal		
w/w%	Myristin	Palmitin	Stearin	Myristin	Palmitin	Stearin
Neat	-0.9			13.7		
0.02%	-1.1	-0.8	-0.8	13.4	13.3	13.4
0.1%	-0.7	-0.6	**6.7**	13.4	13.3	13.4
0.2%	-1.3	**4.8**	**18.6**	13.3	13.6	**15.9**
0.6%	**18.4**	**29.7**	**30.0**	13.1	**18.6**	**28.6**
1.0%	**27.5**	**30.0**	**40.5**	**24.7**	**29.8**	**35.8**

TABLE 2. Final Melting Temperature of Monoglycerides in B100

Final Melting Temperature (Temp °C)						
	Soy			Animal		
w/w%	Myristin	Palmitin	Stearin	Myristin	Palmitin	Stearin
Neat	0.8			14.4		
0.02%	1.1	0.9	0.9	14.3	14.5	14.6
0.1%	0.8	0.7	**10.2**	15.2	14.8	15.0
0.2%	1.2	**10.0**	**37.0**	15.1	15.3	**16.8**
0.6%	**26.5**	**35.5**	**45.7**	**29.2**	**36.0**	**47.0**
1.0%	**34.8**	**43.0**	**49.5**	**34.5**	**44.5**	**48.5**

SMGs affect the CP of the neat biodiesels at fairly low concentrations. The effect begins at between 0.2 and 0.6 w/w% monomyristin in soy biodiesel and at above 0.6 w/w% in animal biodiesel, and at even lower concentrations for monopalmitin and monostearin. A typical U.S. biodiesel will have SMG content in the 0.1 to 0.3 w/w% range [5]. Cold soak filterability was measured for a set of soy biodiesel samples containing from 0.025 to 0.3 w/w% monostearin. These results are in Table 3. Filtration time began to increase at 0.075 w/w% monostearin and addition of 0.1 w/w% monostearin increased filtration time to over 720 seconds, suggesting that this biodiesel would have caused vehicle operability problems at temperatures above the CP [1,2]. The effect on soy biodiesel, with its lower CP, occurs at lower monoglyceride concentration than it does for animal fat biodiesel. There is only a small difference between CP and FMT of the neat biodiesels and for the samples with low concentrations of monoglycerides. Once the monoglyceride concentration exceeds a threshold level, the eutectic point, which is different for each monoglyceride/biodiesel pair, it affects both the CP and the FMT. The difference between the two can be quite large. For example, a 0.2 w/w% solution of monostearin in soy biodiesel has an FMT of 37.0°C, even though its CP was only 18.6°C. Even at 0.1 w/w%, the FMT–CP difference is nearly 4°C. Thus, the presence of SMG in sufficient quantities could cause the presence of precipitates above the CP in biodiesel.

During the FMT measurement of some of the samples, a very prominent signal increase was noted after an initial large decrease in signal in the light scattering plots. As an example, a plot of animal B100 with no added monoglyceride and plots of 0.6 w/w% monostearin and 0.6 w/w% monopalmitin in animal fat B100 are shown in Figure 1. In Figure 1a, where no SMG is added, the signal decreases rapidly until the FMT at approximately 15°C. In Figure 1b, there is an initial signal decrease, followed by an increase prior to the FMT being reached at approximately 40°C (for monostearin). Repeated experiments determined that this increase in signal was reproducible and present in several samples where the concentration of SMGs is above the eutectic point.

TABLE 3. Effect of Monostearin on Cold Soak Filterability (D6751 Annex Method) for the Soy Biodiesel

Monostearin (% w/w)	Filtration Time (sec)
Neat	93
0.025	80
0.05	85
0.075	291
0.1	720
0.3	208 mL at 720

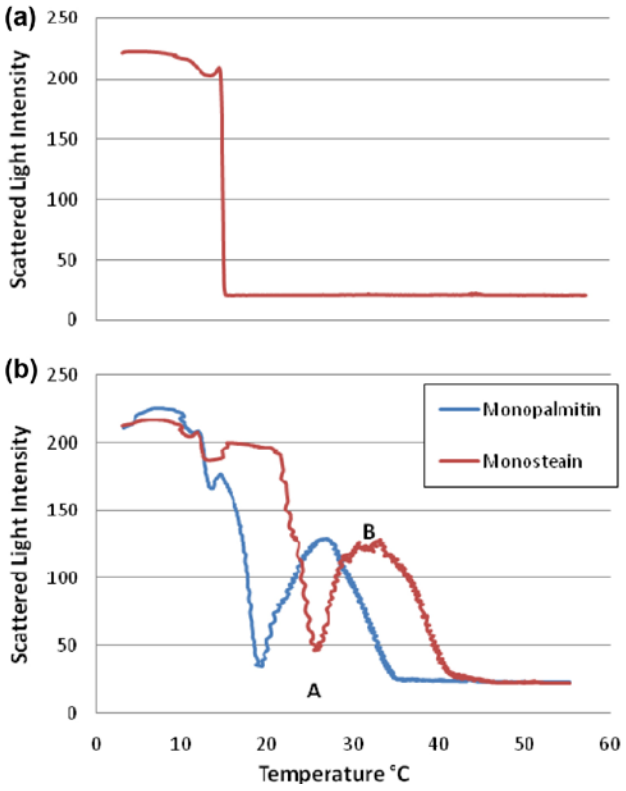

FIGURE 1. Diffusive light scattering FMT plots: a) neat tallow B100, and b) 0.6 w/w% monostearin and 0.6 w/w% monopalmitin in tallow B100.

To try to determine the cause of this feature, a hot stage microscope was used to visualize the 0.6 w/w% monostearin sample as it was heated and cooled. The microscope observations of this sample show a similar significant temperature difference between when the crystals formed on cooling and when they melt on heating. The microscope images also show the difference in the appearance of the crystals at different temperatures. Figure 2 shows images at various temperatures ranging from 25°C to 46°C. From these images, it is apparent that the crystals changed from a needle-like habit to a pinwheel or rosette habit between 25°C to 34°C. These temperatures coincide with the points marked "A" and "B" in Figure 1b. This was also observed when the sample was held at a constant temperature of 25°C for 20 minutes. Figure 3 shows one image taken during initial crystal formation (on cooling at 1.5°C/min) compared to an image taken 17 minutes later. SMG are well known to exhibit polymorphism: the ability of a solid material to exist in more than one crystalline form [6]. We propose that the SMG crystallize as the α-polymorph, and transform to the more stable and higher melting β-polymorph. DSC and XRD results confirm that the higher melting crystals are the β-form.

Conclusions

SMGs in B100 will raise the CP when present at concentrations above a critical (eutectic) value that is specific to the SMG/B100 pair – a pure (distilled) B100 with a higher CP can tolerate higher levels of SMG before CP is raised. Commercial biodiesel in the United States can have SMG concentrations that are in the same range as the measured eutectic concentration [5]. For concentrations above this eutectic point, there is an increasing difference between the FMT and the CP. For concentrations in this range, light scattering

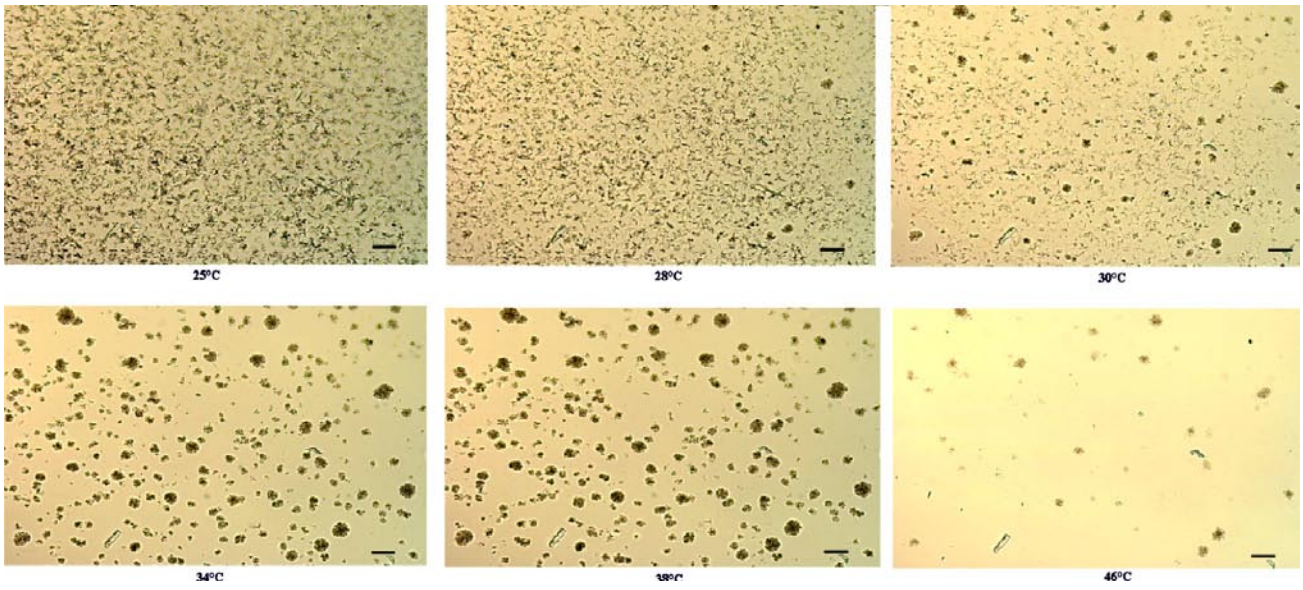

FIGURE 2. Monostearin crystals under microscope at various temperatures (0.6 w/w% monostearin in animal fat biodiesel).

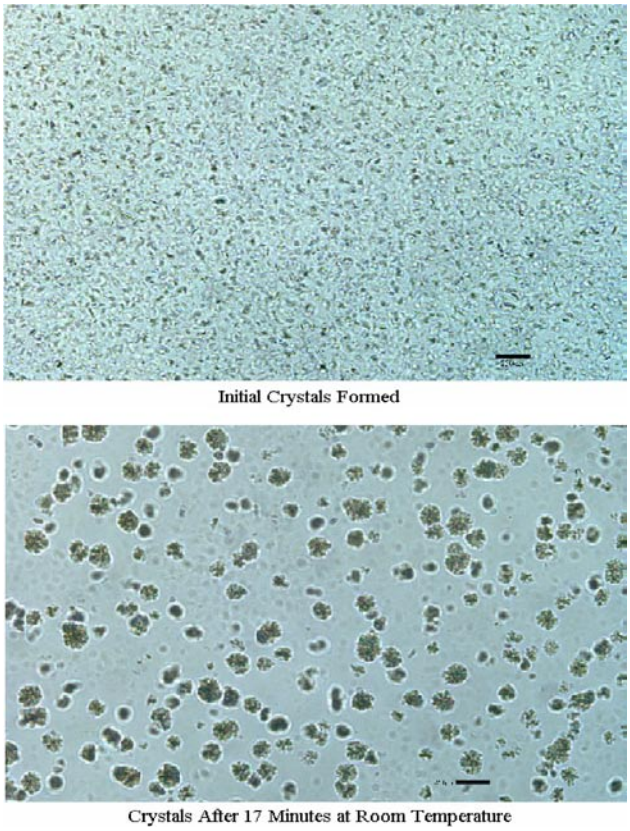

FIGURE 3. Monostearin crystals held at 25°C for 20 minutes (0.6 w/w% monostearin in animal B100). Scale bar in photos is 250 μm long.

shows that upon heating, crystals begin to dissolve, but then recrystallize and ultimately melt at a much higher temperature. Observation in a microscope shows a change in crystal habit occurring during this recrystallization. We propose that upon rapid cooling the initial form of SMG that precipitates is a lower melting temperature phase, which over time or upon slow heating can transform into a higher melting polymorph.

Consideration of the complex phase behavior of monoglycerides in biodiesel may explain some observations of precipitates above the CP. This work shows that monoglycerides in biodiesel can precipitate in different crystal forms, with different solubility. Transformation between these different crystal forms can occur in storage and upon slow warming, resulting in a difference between the crystallization temperature measured as the CP and the FMT. This could lead to fuel filter plugging at temperatures above the determined CP of the fuel.

Monoglyceride polymorphism is just one consideration in assessing the effects of impurities on the cold weather behavior of biodiesel. The presence of water, sterol glucosides, and other impurities has also been associated with the formation of precipitates above the initial measured CP of the fuel and will be the subject of future work.

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2. Chupka, G.M., Yanowitz, J., Chiu, G., Alleman, T.A., McCormick, R.L. "Effect of Saturated Monoglyceride Polymorphism on Low-Temperature Performance of Biodiesel" Energy&Fuels published online 12/3/2010 http://pubs.acs.org/doi/pdf/10.1021/ef1013743.

Special Recognitions & Awards/Patents Issued

1. The NREL Chairman's Award for Exceptional Performance was presented to Gina Ghupka for performance of this project.

IV.4 Advanced Chemical Characterization of Non-Petroleum-Based Fuels and Emissions for Understanding Effects on Combustion

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Objectives

- Develop, or implement analytical methods for the combustion products resulting from conventional and advanced combustion in order to further elucidate combustion properties of non-petroleum-based fuels (NPBFs).
- Identify fuel properties and specific combustion products that may limit the implementation of NPBFs.

Fiscal Year (FY) 2010 Accomplishments

- Developed a sampling and analysis method for exhaust condensates. Biofuel oxygenates can lead to corrosive exhaust condensate species that can affect exhaust gas recirculation (EGR) systems and other engine subsystems.
- Developed one-step separation of aromatic poly-acids and anhydrides from soot. These compounds may represent up to 20% of the non-solid soot fraction.

Future Directions

- Develop analytical methods for the determination of water-soluble organic compounds such as small alcohols and large carbonyls.
- Examine soot samples collected during advanced combustion modes for the absence or presence of poly-carboxylic acids and anhydrides.

Introduction

In studies of fuel effects on combustion and emissions, the measured results are typically correlated against a known fuel property. The methods for analyzing the fuel chemistry and emissions have been developed over many years for conventional petroleum fuels. These analysis methods were largely developed for the detection of non-polar compounds present in petroleum-based fuels and emissions. However, these methods can often be insensitive to oxygenated hydrocarbons and other compounds present in exhaust samples from engines operating on NPBF. For example, gas chromatography/mass spectrometry typically underestimate non-methane hydrocarbon concentrations for emissions containing oxygenated species. Thus, novel exhaust sampling and analytical methods which specifically target the oxygenated byproducts of NPBF combustion are required for understanding NPBF emissions and fuel effects.

The combustion of oxygenated fuels such as alcohols can lead to higher levels of both aldehydes, like formaldehyde and acetaldehyde, and carboxylic acids, such as formic acid and acetic acid. These acids can lead to corrosion of components such as EGR coolers, and intake valve seats. Sampling methods, which collect the exhaust condensates at relevant temperatures and in relevant locations, are important to understanding fuel effects on engine components. Additionally, the analysis of these condensates must include the inorganic acids such as sulfuric and nitric acid to determine the overall corrosion potential of the condensate.

Diesel particulate matter (PM) emissions contain a significant fraction of solvent-labile and thermally-labile species, often aggregated in the term “soluble organic fraction” or “organic carbon”. A more apt description may be “non-solid” carbon, to describe all carbonaceous compounds in the PM that are not part of the soot carbon framework. The non-solid carbon fraction is an important PM characteristic and plays important roles in EGR cooler fouling and diesel particulate filter (DPF) regeneration. In characterizing the non-solid fraction carbon of the PM, one can use both solvent extraction and thermal desorption methods, such as total gravimetric analysis. Previous attempts at reconciling the mass of organic species measured by solvent extraction with the mass of organic carbon measured by thermal evolution have been unsuccessful. The discrepancy between the two measurements may become more problematic for understanding the composition of NPBF emissions, since the organic carbon fraction is often higher for biofuel than conventional petroleum diesel PM emissions. In FY 2009, methods were developed by our group to help understand how the nature of organic compounds influence inconsistencies between conventional organic carbon measurements. In FY 2010, we show that the separation of the major

components, aromatic poly-anhydrides and aromatic poly-carboxylic acids, is possible with a single method.

Approach

Collection methods using both cold traps and condensers were developed. The condensers used a temperature-controlled bath to mimic various cooler temperatures. Many of the acids have dew points at higher temperatures than water; thus acids can be collected "dry" and then analyzed by washing out the condenser. A capillary electrophoresis method was developed to separate the anions of both inorganic acids and organic acids. This indirect absorption method incorporates the use of polymeric buffer solution allows a constant electroosmotic flow (the bulk flow) at a pH of 10. Normally, the electroosmotic flow is very low at pH 10, which results in poor separation conditions, but high pH is necessary to insure all acids are ionic and are not neutral. This method also incorporates an organic clean-up step and a concentration step to further improve the detection limit and the sample matrix variations.

To investigate the non-solid organic fraction of PM, PM deposits from EGR coolers and DPFs were sampled from the deposits and analyzed. The soot was extracted with a mixture of diethyl amine and methanol, which enables the removal of the tightly bound polar species. A new analytical method incorporates the use of a pre-coating treatment of the capillary used in the capillary electrophoresis separation. This method is more tolerant to residual diethyl amine used in the extraction procedure, which is needed to extract the organic acids and anhydrides.

Results

A capillary electropherogram for a 5 ppm solution of the most common exhaust acids is shown in Figure 1. A typical condensate from the EGR cooler on a diesel engine is shown in Figure 2. Gasoline exhaust condensates also typically have formic acid and acetic acid in similar or higher levels to the sulfuric acid. Levels of 5-50 ppm of all acids are common in exhaust samples collected in our studies. The pH of these condensates can then be as low as 3, causing concerns for materials.

For the investigation of thermally labile organic fraction of PM, compounds were selected based on preliminary direct thermal desorption experiments. Five aromatic acids and anhydrides shown were selected:

- 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA)
- 1,2,4,5-Benzenetetracarboxylic dianhydride (BTCDA)
- 1,8-Naphthalene anhydride (NA)
- 1,2,4,5-Benzenetetracarboxylic acid (BTCA)
- 1,8-Naphthalene- dicarboxylic acid (NDCA)

The separation of these compounds is complicated by the complex acid dissociation constants for the poly-carboxylic acids, as well as interactions with the diethyl amine solvent. Figure 3 shows how well the new CI-MS method works on these compounds.

The overall implication of this work is that a large fraction of the non-solid carbon in soot is made up of these complex carboxylic acids and anhydrides. An understanding of their formation and subsequent

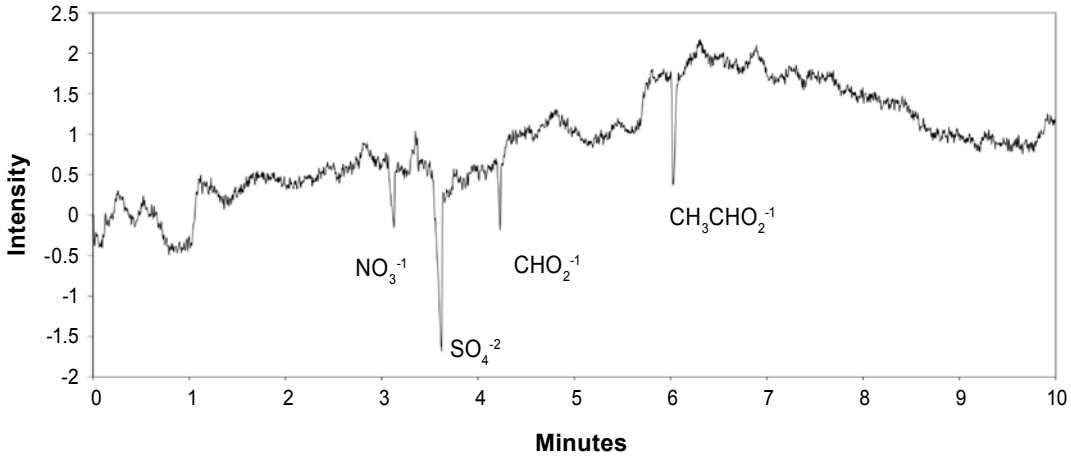

FIGURE 1. Capillary electropherogram of common acids in exhaust condensates showing the excellent separation made possible by the method.

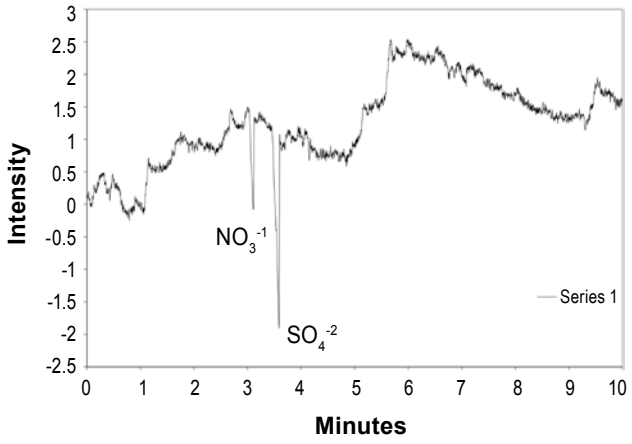

FIGURE 2. Capillary electropherogram of an actual condensate collected form a diesel EGR system cooler showing the presence of both nitric and sulfuric acid

behavior in the soot may lead to insights into soot particle formation, fouling in EGR systems, and the regeneration behavior in the DPF.

Conclusions and Future Effort

The advanced chemical characterization effort has focused on two areas: exhaust condensates and unique polar compounds that make up a large fraction of the non-solid carbon in soot. These methods will continue to be developed for application to direct injection spark-ignited engines as well as advanced combustion modes.

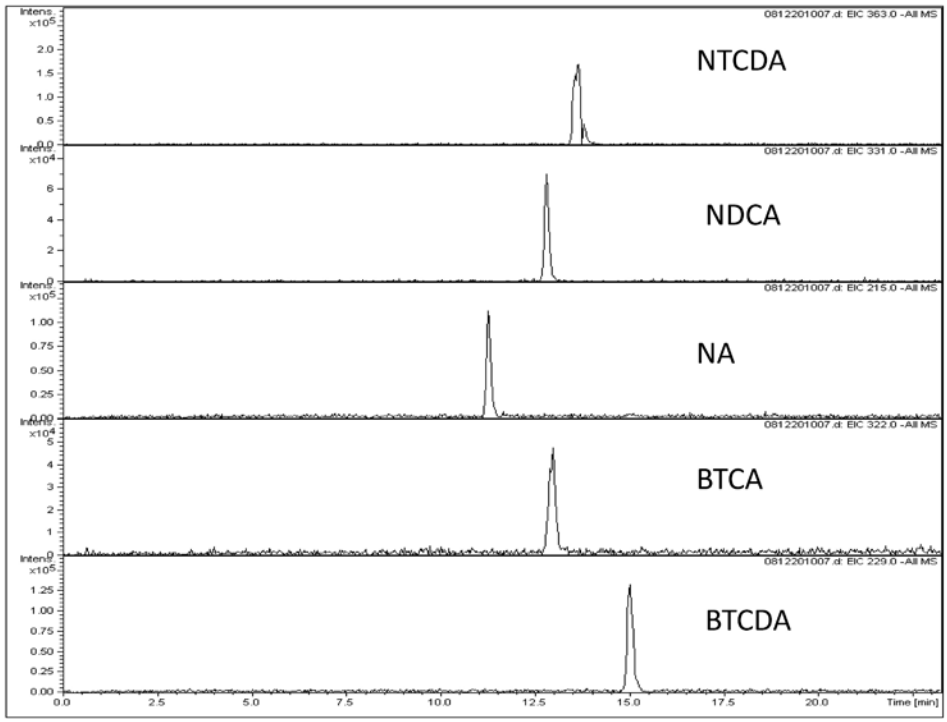

FIGURE 3. Separation of aromatic carboxylic acids and anhydrides with new method. Compounds as follows: 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA); 1,2,4,5-Benzenetetracarboxylic dianhydride (BTCDA); 1,8-Naphthalene anhydride (NA); 1,2,4,5-Benzenetetracarboxylic acid (BTCA); 1,8-Naphthalene-dicarboxylic acid (NDCA).

IV.5 Evaluating Compatibility of New and Legacy Infrastructure with E15

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Subcontractors:
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Objectives

- Determine compatibility of new fuel dispensing equipment with E15.
- Determine compatibility of legacy fuel dispensing equipment with E15.

Fiscal Year (FY) 2010 Accomplishments

- Completed conditioning and performance testing of all new and used fuel dispensing equipment.
- Published a technical subcontractor report and provided manufacturers with the results.
- Gathered additional information on the impact of testing conditions and test fluid on materials through spent fluid analysis.
- Initiated post mortem analysis, which is ongoing and provides insights into the various performance of equipment.
- Engaged National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), the U.S. Department of Energy (DOE), manufacturers, and industry groups in ongoing discussions to determine solutions, in response to unexpected test results.

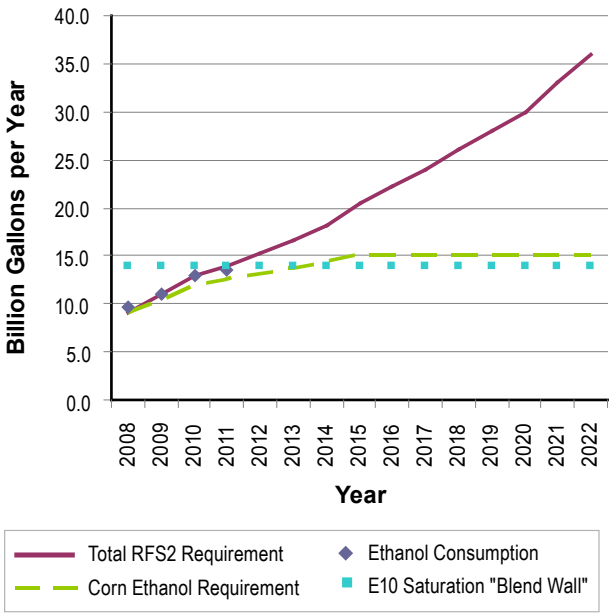
Future Directions

A government workshop with fuel dispensing manufacturers is scheduled for January 2011. Feedback from industry will highlight gaps in research and the best uses for funds in ongoing work. The completed work did not include repetitions or all equipment deployed in the marketplace; further work may involve testing additional products. We will review the potential for manufacturers to list products for E25 through the Underwriters Laboratory (UL) certification process. Development of dispenser retrofit kits to address materials-specific issues with ethanol are another possibility.

Introduction

The federal Renewable Fuel Standard dictates a steady increase in future use of renewable fuels, but rapid expansion of the E10 market leaves little opportunity to sell required volumes of renewable fuels (Figure 1). DOE's Mid-Level Blends Research activity began in 2007 and will continue into 2011. DOE has invested more than $45 million into this activity, with a portion allocated to infrastructure work. In March 2009, the ethanol industry submitted a Clean Air Act Waiver Request to the Environmental Protection Agency (EPA) to allow commercial sales of E15; EPA granted a partial waiver in October 2010, for model year 2007 and newer vehicles. Fuel impact on infrastructure is not a legal consideration for EPA Clean Air Act Wavier Requests. However, regulations unrelated to air quality require safe operation of fueling equipment. And prior to this study, the safety of E15 in existing equipment had not been tested.

DOE directed NREL to test new and used equipment to determine compatibility of existing infrastructure with E15. NREL entered into a contract with UL, which tests and certifies fuel dispensing equipment, to test new and used fuel dispensing devices using UL Testing Subject 87A for gasoline/ethanol



(source: EISA Title II Subtitle A, EIA MER Table 10.3)

FIGURE 1. Renewable Fuel Standard Requirements, Ethanol Consumption and Blend Wall

blends exceeding 10% ethanol. Equipment selection was based on market penetration.

Approach

Test Protocol: We used the Outline of Investigation for Power-Operated Dispensing Devices for Gasoline and Gasoline/Ethanol Blends with Nominal Ethanol Concentrations up to 85 Percent (E0-E85) known as UL Subject 87A [1]. This testing protocol was developed by UL in 2007 to create a certification path for E85 fuel dispensing equipment. Subject 87A was amended in 2009 to allow certification for mid-level ethanol blends between E11 and E25. Equipment is conditioned in a chamber at 60°C for 2,520 hours; fluids are replaced weekly, and a 50 psi leakage test is conducted. The conditioning phase is designed to simulate aging in equipment. Performance testing follows specific for each type of equipment.

One control and 16 spent fluid samples were collected and analyzed during the conditioning phase (spent fluid samples were collected from one new and one used dispenser of similar design). Spent test fluids were analyzed using a gas chromatography-mass spectrometer.

Test Fluid: Tests were conducted using CE17a: a blend of 83% ASTM International Reference Fuel C and 17% aggressive ethanol (Table 1). The fuel formula was obtained from Society of Automotive Engineers (SAE) Publication J1681 [2]. This fuel formulation was developed by the auto industry for testing flex-fuel vehicles and is accepted by EPA as the appropriate ethanol/gasoline test fluid. UL Subject 87A-E25 requires CE25a, which contains 25% ethanol; however, different percentages of ethanol blended into gasoline impact materials (e.g., elastomers and gaskets) differently. For example, E25 may impact materials differently than E15 does. Therefore, NREL selected CE17a as the test fuel formula. This ethanol volumetric concentration is representative of E15 while also accounting for variations in ethanol blending concentrations occurring in the marketplace.

Equipment: This test project covered above-ground equipment at service stations, with one exception: the submersible turbine pump, which conveys fluid from a tank to a dispenser. Equipment was selected based on market-penetration information provided by industry groups, manufacturers, large distributors, and buyers. UL tested one sample of each piece of equipment. Information on used dispensers was limited to date of manufacture and geographic location of use. No information was available on used hanging hardware (hoses, swivels, nozzles, and breakaways). The test list represents approximately 80% of equipment in the market place. At the conclusion of UL testing, ORNL began post mortem analysis; the work is ongoing and will be reported separately. Figure 2 highlights equipment tested.

TABLE 1. Test Fluid Formula

Component	Volume/Mass per liter of test fluid
Isooctane	415 milliliter
Toluene	415 milliliter
Synthetic Ethanol	168.6 milliliter
Deionized Water	1.378 milliliter
Sodium Chloride (solid, dissolved into solution)	0.68 milligram
Sulfuric Acid	0.002 milliliter
Glacial Acetic Acid	0.010 milliliter

(source: SAE Publication J1681)

Results

Results were inconclusive; no clear trends were established (Table 2). Overall, new equipment generally performed better (67% compliant with equipment safety standards) than used equipment (40% compliant). Results on new equipment were unexpected: it was anticipated that most new equipment would pass the

(source: NREL Photo Library)

FIGURE 2. Fueling Equipment

TABLE 2. UL Test Results

Equipment	Pass New	Pass Used	Pass Overall
Breakaways	2 of 5	1 of 4	3 of 9
Flow limiters	1 of 1		1 of 1
Hoses/Hose Assemblies	8 of 9	4 of 6	12 of 15
Meter/Manifold/Valve	0 of 2	0 of 4	0 of 6
Nozzles	3 of 6	1 of 4	4 of 10
Shear Valve	3 of 3		3 of 3
Submerisble turbine pump	1 of 1		1 of 1
Swivels	3 of 4	3 of 5	6 of 9

(source: http://www.nrel.gov/docs/fy11osti/49187.pdf)

test with compliant results. As for used equipment, in most cases it was already through its useful life (15 years for dispensers, three years for hanging hardware) and was subjected to a strenuous test designed for new equipment.

Nearly all problems impacting compliance occurred during performance testing; few leakages occurred during the conditioning phase. Non-compliant results were caused by the leaking or pulling apart of sealing materials. Elastomer and gasket materials may swell when exposed to ethanol/gasoline blends. This can impact long-term performance of sealing materials. No impacts on metal materials were observed during the test.

Hoses and hose assemblies generally performed well. The flow limiter, submersible turbine pump, and all shear valves were found to be compliant after testing.

Dispenser meter/manifold/valve assemblies performed poorly with all new and used samples leaking, resulting in noncompliance. This is significant, because dispensers cost approximately $15,000 and have life spans of about 15 years. Nozzles and breakaways also performed poorly; however, these parts are generally inexpensive (typically less than $100) with a short life (less than three years). Upgraded sealing materials and enhanced sealing methods would likely result in better performance.

Spent fluids from one new dispenser were analyzed; samples collected from one used dispenser were contaminated by kerosene and could not be analyzed. Dispenser 1 fluid samples contained leached phthalates; these are used in hoses, o-rings, and elastomers. The concentration of phthalates in test fluids is a function of test week sample, decreasing over the 15-week conditioning test. Fluid samples also demonstrated concentrated levels of fragmented polymers, which may interact with acid in the test fluid, causing structural damage to sealing materials.

The results do not offer a clear indication of how E15 will impact existing fuel dispensing infrastructure. Existing equipment at service stations is UL listed for E10; however, this equipment was listed under a different testing protocol with a different testing fluid. Therefore, a direct comparison between existing E10 data and the E17 data obtained in this study is not possible. The testing protocol and fluid (87A and SAEJ 1681) is expected to replace the legacy standards (Standard 87 and ASTM Fuel H) in the near future. Manufacturers will need to demonstrate that products comply with UL Subject 87A; in many cases this will require upgraded materials.

Conclusions

- Overall, results were inconclusive, with no apparent trends in performance related to E17 use.
- Hoses, hose assemblies, the flow limiter, and the submersible turbine pump largely demonstrated compliant results.
- Dispenser meter/manifold/valve assemblies performed poorly.
- Most failures occurred during performance testing; few leakages were observed during the conditioning phase of the test.
- Improved results would be expected with the use of more appropriate seal materials and methods.

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IV.6 Headspace Flammability of Gasoline/Ethanol Blends

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DOE Technology Deployment Manager: Dennis Smith

Subcontractors:
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- Nexum Research Corporation, Mallorytown, ON, Canada

Objectives

- Experimentally evaluate fuel tank headspace vapor flammability of various ethanol-blended fuels at various ambient temperatures.
- Develop mathematical models of the fuel tank tests, use the models to predict fuel flammability, and evaluate the utility of modeling to assess fuel tank combustion-hazard scenarios.
- Analyze the flammability risks associated with vapor/air plumes emitted from fuel tanks during fueling.

Fiscal Year (FY) 2010 Accomplishments

- Developed the apparatus and methods needed to test the headspace vapor flammability of fuel samples.
- Tested the flammability of in-use fuel blends including E85 samples from vehicle studies and field samples of E85, E10, E20, and E30 from commercial pumps.
- Tested the flammability of a matrix of laboratory-prepared ethanol/gasoline blend samples consisting of three gasoline vapor pressure levels and blend levels of E0, E15, E55, E60, E68, E75, and E83.
- Tested the lean (low temperature) and rich (high temperature) flammability limits of denatured ethanol (E97).
- Developed mathematical models of flammability and evaluated the models in comparison with the results of the experimental tests.
- Performed a preliminary analysis of the flammability risks associated with vapor/air plumes emitted from fuel tanks during fueling.

Future Directions

- Perform further flammability studies of laboratory-blended fuel samples using a matrix that varies critical fuel blend parameters (e.g., ethanol content, vapor pressure, and hydrocarbon composition) systematically. Further tests are needed to adequately represent low vapor pressure blends which, according to the Coordinating Research Council (CRC) National Survey of E85 Quality (2009), comprise a significant portion of in-use E85 fuels.
- Refine the apparatus and experimental methods used in this study so they can be recommended as standard test practices.
- Continue development of the headspace vapor flammability model with the aim of achieving a practical means of predicting vapor flammability based upon readily available fuel property data.

Introduction

DOE supports efforts to increase the use of ethanol-rich transportation fuels such as E85. However, the physical and chemical properties of ethanol-rich fuels are different from those of conventional transportation fuels and must be evaluated to ensure safety.

When a fuel tank is partially filled with liquid fuel, the remaining space (i.e., the "headspace") is filled with fuel vapors and air. Depending on the degree of tank filling, fuel type, and conditions (e.g., ambient temperature), the fuel vapors can be flammable or non-flammable. Vapors in fuel tanks containing pure gasoline generally are too rich (i.e., the ratio of fuel vapor to air is too high) to be flammable except when ambient temperatures are extremely low. However, fuels containing high percentages of ethanol blended with gasoline can be less volatile than pure gasoline and thus can produce flammable headspace vapors at common ambient temperatures. This project evaluated the effects of ambient temperature and fuel formulation on the headspace vapor flammability of ethanol/gasoline blends.

Approach

Experimental methods–including instrumented pressure chambers with a spark-ignition source (Figure 1)–were developed to test headspace vapor flammability under conditions corresponding to a tank 5% filled with liquid fuel at temperatures from below

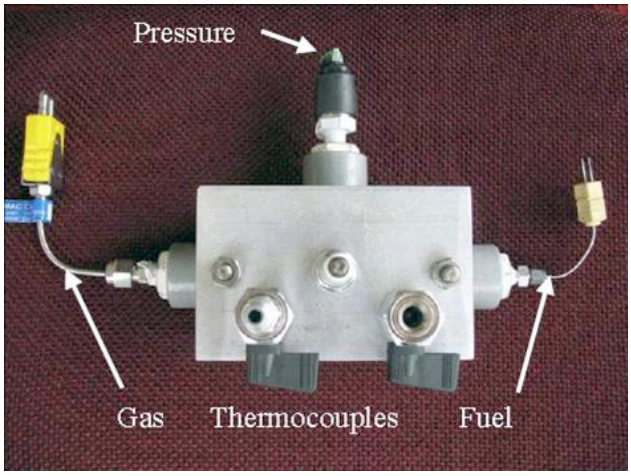

FIGURE 1. Flammability Test Chamber Used in the Study

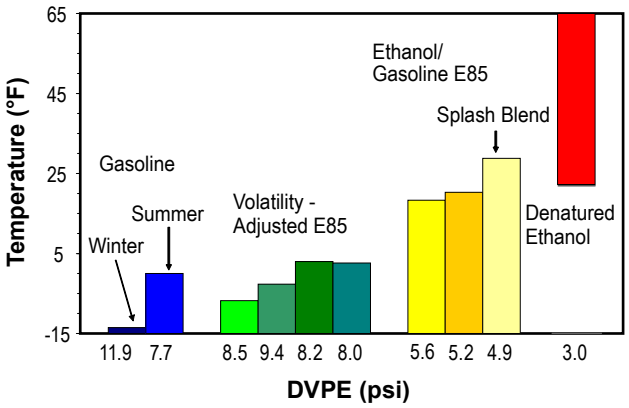

FIGURE 2. Flammability Limits of Fuel Tank Headspace Vapors (5% fill level) from Phase 1 of the Study

-30°C (-22°F) to room temperature. Measurements of the pressure rise and rate of pressure rise following ignition were used to determine the flammability limits for the fuel samples.

Mathematical models of flammability were developed based on the experimental tests. These models were used to predict flammability of the fuels tested in the experimental work and to evaluate the utility of such modeling to assess fuel tank combustion-hazard scenarios. In addition, a preliminary analysis was performed on the flammability risks associated with vapor/air plumes emitted from fuel tanks during fueling.

Results

In phase one of the project, the following were the temperatures at which the test fuels became flammable (Figure 2):

- Summer gasoline: -19°C (-2°F) and lower
- Winter gasoline: -25°C (-13°F) and lower
- Seven E85 blends: -2°C (28°F) to -22°C (-8°F) and lower
- Denatured ethanol: room temperature and all temperatures down to about -6°C (22°F)

As shown in Figure 2, the "volatility-adjusted E85" fuels had lower flammability limits than the standard ethanol/gasoline E85 blends. The volatility-adjusted fuels were composed of 69%–79% denatured ethanol blended with natural gasoline or 85% denatured ethanol blended with high-vapor-pressure gasoline/isopentane. The "splash blend" in Figure 2 is E85 resulting from the blending of denatured ethanol and pump gasoline without regard to the final blend's physical properties.

In phase two of the project, the headspace vapor flammability of two "real-world" E85 field samples, a "real-world" E10 sample and E20 and E30 blends produced by mixing the E10 blend with an E85 blend, and laboratory blends of E55–E83 (denatured ethanol blended with a single type of winter-volatility gasoline having a "typical" vapor pressure level) were compared.

One of the E85 field samples produced flammable vapors over the entire ASTM D 5798-09 Class 3 temperature range (-5ºC and below). The other produced flammable vapors at -10ºC and below. No significant differences were measured between vapor flammability limits of the E20 and E30 samples and the E10 sample from which they were produced. The flammability limits of the E55–E83 fuels showed a non-linear relationship with ethanol content and vapor pressure; reducing the ethanol content from typical E85 levels (80% or more) substantially reduced temperatures at which flammable vapors formed, while reducing the ethanol content below about 60% had a smaller impact on flammability limits. Figure 3 compares the phase 2 experimental and modeling results.

Although the ranking of flammability limit temperatures for the test fuels often could be predicted from their dry vapor pressure equivalent (DVPE), DVPE alone did not predict the ranking correctly in all cases. The properties of the hydrocarbon portion of the fuel must be considered as well. This observation was confirmed by the mathematical flammability modeling.

When basic properties of the base oxygenate-free gasoline are known, the mathematical model developed in this study can be used to compare the flammability characteristics of various gasoline/ethanol blends satisfactorily. The model requires ASTM D86 distillation data, D4052 specific gravity, and D5191 DVPE of the base oxygenate-free gasoline and the percentages of ethanol and gasoline in the blend.

The use of conventional flammability data leads to the prediction of higher rich-limit temperatures than those actually measured in this study. Although

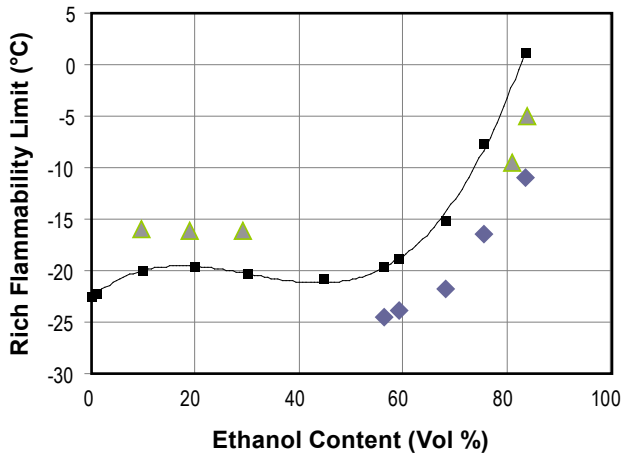

FIGURE 3. Comparison of Experimental and Modeling Results from Phase 2 of the Study

an adjustment might be made to better match the predictions to the measurements, this is unlikely to be worthwhile because it would be apparatus dependent and not necessarily applicable to other conditions. Rather, the model is useful in comparing blends to each other to assess their relative hazards.

In phase 3 of the project, further laboratory fuel blends of E55-E83 were produced and tested. These blends were composed of denatured ethanol and two types of gasoline representing the lowest and highest vapor pressure levels commonly encountered for winter gasoline. In addition, flammability tests were also carried out for E0 and E15 blends made from the low and high vapor pressure gasolines, and the typical vapor pressure gasoline from the phase 2 study.

The laboratory blends tested during phase 2 and phase 3 were accompanied by full hydrocarbon information which was used to refine and evaluate recent improvements to the mathematical model for flammability. Data from the E0 and E15 fuels was used to devise a technique for extracting the necessary gasoline data from the distillation (D86) data of a low-alcohol blend. Further tests were also carried out with denatured ethanol to examine both the lean flammability limit (experienced when the fuel is too cold to produce flammable vapors) and the rich flammability limit (the temperature above which the vapors are too rich to be flammable).

Phase 3 data analysis, modeling, and testing of denatured ethanol were still in progress at the time of writing of this report.

Conclusions

In general, E85 is flammable at low temperatures, whereas denatured ethanol is flammable at warmer temperatures. If both fuel types are stored in separate tanks at the same location, one or both of the tanks' headspace vapors will be flammable over a wide range of ambient temperatures. This is relevant to the issue of splash blending ethanol and gasoline at fueling stations and allowing consumers to blend ethanol and gasoline themselves. The field sample E85 test results indicate that at least some of the ethanol fuels currently available when and where Class 3 conditions (-5ºC and below) exist are likely to produce flammable vapors within the ambient temperature range where they are used.

No significant differences were measured between vapor flammability limits of the E20 and E30 samples and the E10 sample from which they were produced. This indicates that blends in this mid-range are unlikely to increase the risk of producing flammable vapors significantly versus the base gasoline used for the blends.

The laboratory fuel blends studied were produced from a "typical" winter-volatility gasoline (DVPE = 89 kPa). None of the blends produced from this gasoline could simultaneously meet the ASTM D 5798 requirements for minimum vapor pressure (66 kPa) and minimum ethanol content (70%). The vapor pressure data for the blends indicates that reducing ethanol content to about 65% would achieve the minimum vapor pressure specification. The flammability data trends suggest that blends with ethanol content in this region would provide a favorable trade-off between avoiding flammable vapor formation and maximizing ethanol content.

Existing mathematical models for gasoline hydrocarbons can be used for some alcohol blend comparisons, provided that both DVPE and distillation data of the model used are reasonable approximations of the actual hydrocarbon characteristics. Matching DVPE alone is insufficient.

Preliminary analysis of the flammability risks associated with vapor/air plumes emitted from fuel tanks during fueling showed that fuels that are more volatile produce longer vapor plumes and represent greater hazards. For the more dangerous situation of a flammable plume adjacent to flammable tank headspace vapors, the size and location of the plume is important. Some plumes might be long enough to present a serious hazard of ignition and tank explosion, whereas other plumes might be short enough to preclude ignition by typical ignition sources found near fueling equipment. This study did not assess this aspect in detail.

Phase 3 data analysis, modeling, and testing of denatured ethanol were still in progress at the time of writing of this report therefore conclusions will be presented in the next report.

Recommendations for Alternative Approach of Future Testing

The headspace flammability project has provided information both to guide the development of specifications for ethanol/gasoline blends, and to

reveal the potential hazards and consequences if such specifications are not adhered to. To this end, there has been some discussion of the possibility of obtaining additional "real-world" E85 samples (from a CRC survey, or otherwise) for comparisons with the laboratory fuel samples that have been evaluated thus far. However, examination of the 2008/2009 CRC survey shows that a very wide range of fuel properties were encountered in the field samples for all three classes of E85. Thus, no "typical" fuel existed, so a large number of these samples would need to be tested to properly characterize the headspace flammability of in-use fuels.

The following discussion presents part of the rationale for an alternative approach in which laboratory fuel blends would be used to represent the range of possible in-use fuel blends. The balance of the discussion may be found in the document titled "Recommendations Regarding Fuel Samples for Future Flammability Tests." It is proposed that further data obtained from a strategically chosen fuel matrix (with systematic variation of critical blend parameters) will ultimately provide the best value for enhancing knowledge about flammability hazards and facilitating the prediction of flammability characteristics through mathematical modeling.

The tests conducted so far with laboratory blends provided by Marathon Petroleum Company have covered three levels of base gasoline vapor pressure (nominally 12, 13, and 15 psi), intended to represent low, typical, and high values for winter gasoline. Figure 4 shows a comparison of the vapor pressure and ethanol content data for these laboratory blends and the Class 1 samples from the CRC survey. As expected, the Class 1 fuels have much lower volatility than the laboratory blends tested thus far. Such comparisons can be used to guide the formulation of future laboratory test blends in order to ensure that the full range of "real-world" fuel types is adequately represented in the study. Similar comparisons have shown that, based upon the CRC survey data, 10-15% of in-use Class 2 and 3 E85 fuels have substantially lower volatility than the laboratory blends.

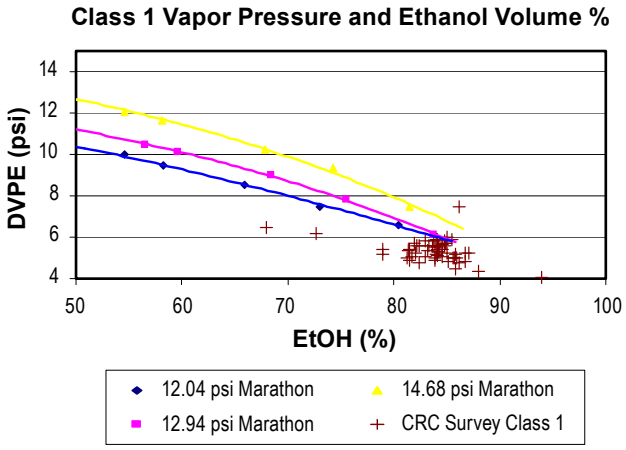

FIGURE 4. Comparison of Marathon Laboratory Blends and CRC Survey Class 1 Samples

Therefore, it is recommended that flammability testing be carried out on laboratory blends made with low vapor pressure gasoline such that the resulting blends fall within the range indicated by the least volatile Class 1 fuels shown in Figure 4, and the low volatility Class 2 and 3 samples identified in the CRC survey. These results will provide valuable information regarding the flammability hazards associated with the use of fuels which are non-compliant with seasonal volatility specifications, are used during a colder season than their intended volatility classification, or suffer from in-use volatility reduction due to unintentional vapor losses (weathering).

FY 2010 Publications/Presentations

1. Gardiner, D., Bardon. M., LaViolette, M., An Experimental and Modeling Study of the Flammability of Fuel Tank Headspace Vapors from Ethanol/Gasoline Blends; Phase 2: Evaluations of Field Samples and Laboratory Blends. NREL Report No. SR-540-47819, www.nrel.gov/docs/fy10osti/47819.pdf.

2. Gardiner, D., NREL Study on Flammability of Ethanol Blends in Tank Headspace. Presented at the 2010 American Petroleum Institute (API) Storage Tank Conference, Oct 18–21, 2010, San Francisco, CA.

3. Gardiner, D., NREL Study on Flammability of Fuel Tank Headspace Vapors from Ethanol/Gasoline Blends. To be presented at the ASTM D02 December 2010 meeting, December 5–9, 2010, Jacksonville, FL.

4. Gardiner, D., Recommendations Regarding Fuel Samples for Future Flammability Tests. Email to W. Clark NREL 11/29/2010.

IV.7 Mid-Level Ethanol Blends Vehicle Aging Program

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DOE Technology Development Manager:
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Objectives

- Determine effects of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on legacy vehicle emissions and emissions durability when aged with a dedicated fuel blend.
- Enable informed decision-making regarding Clean Air Act waiver application for increased ethanol in gasoline.

Fiscal Year (FY) 2010 Accomplishments

- Conducted testing of 82 vehicles for emissions durability at three subcontractor laboratories.
- Completed mileage accumulation and emissions testing of 47 Tier 2 vehicles aged with gasoline (E0), and blends of 10, 15 or 20% ethanol in gasoline (E10, E15, E20).
- Completed mileage accumulation and emissions testing of 11 pre-Tier 2 vehicles aged with E0, E15, or E20.
- Completed powertrain component inspection on six pairs of Tier 2 vehicles aged on E0 and E15.
- Provided critical data to the Environmental Protection Agency (EPA) prior to September 30, 2010 to enable informed decision-making on a fuel waiver application.

Future Directions

Complete data collection and analysis and publish report in FY 2011.

Introduction

The United States' Energy Independence and Security Act (EISA) of 2007 calls on the nation to significantly increase its production of renewable fuels to meet its transportation energy needs [1]. The law established a new renewable fuel standard (RFS) that requires 36 billion gallons of renewable fuel to be used in the on-road vehicle fleet by 2022. Given that ethanol is the most widely used renewable fuel in the United States, ethanol–both from corn and from cellulosic feedstocks–will likely make up a significant portion of the new renewable fuel requirements. The vast majority of ethanol currently used in the United States is blended with gasoline to create E10–gasoline with up to 10 volume percent (vol.%) ethanol.

In light of projected growth in ethanol production, as well as the new RFS, most analysts agree that the E10 market will be saturated within the next few years, possibly as soon as 2012. Although the U.S. Department of Energy (DOE) remains committed to expanding the flexible-fuel vehicle (FFV) fuel infrastructure, that market will not be able to absorb projected volumes of ethanol in the near term. Given this reality, DOE and others have been assessing the viability of using mid-level ethanol blends (blends of gasoline with up to 20 vol.% ethanol) in conventional vehicles as one way to potentially accommodate growing volumes of ethanol, thereby displacing petroleum and helping the country comply with EISA.

Approach

This work is a follow-on effort to previous DOE [2] and the Coordinating Research Council (CRC) [3] mid-level ethanol blend studies to investigate the effects of aging vehicles with mid-level ethanol blends. Vehicle testing has been conducted at three laboratories under subcontract to ORNL and NREL. Vehicles were aged using the Standard Road Cycle (SRC), the official EPA driving cycle used for aging whole motor vehicles for exhaust system durability [4], shown in Figure 1. Southwest Research Institute® (SwRI®, San Antonio, TX) and Environmental Testing Corporation (ETC, Aurora, CO) aged vehicles using the SRC on mileage accumulation dynamometers, while Transportation Research Center (TRC, East Liberty, OH) ran the SRC on their 7.5 mile test track[1]. Vehicles on the mileage accumulation dynamometers (MADs) are shown in Figure 2, while Figure 3 shows the TRC test track.

[1] All vehicles were aged using the SRC with the exception of the 2006 Nissan Quest vehicle set, which was switched to a series of steady-speed laps on the track part way through aging. DOE directed this change to accelerate mileage accumulation.

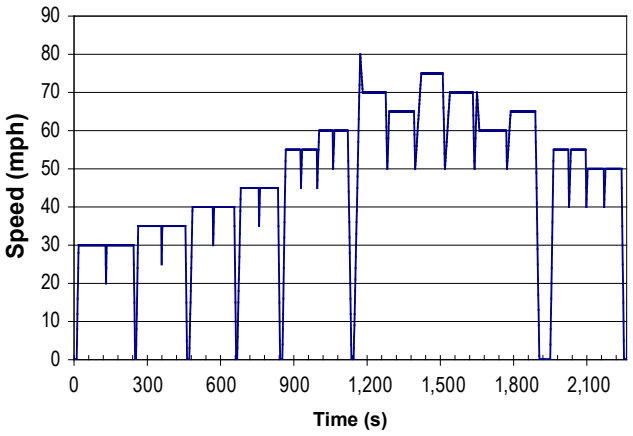

FIGURE 1. Standard Road Cycle for Vehicle Aging

FIGURE 2. Vehicles on Mileage Accumulation Dynamometers at ETC (top) and SwRI® (bottom)

Emissions tests on all vehicles were conducted using emissions certification gasoline (E0), and splash blends of this same fuel with denatured ASTM International D4806 ethanol to produce "certification grade" E10, E15, and E20. Vehicle aging was conducted with retail gasoline (RE0), and this same fuel splash blended with denatured ASTM D4806 ethanol to produce RE10, RE15, and RE20; the "R" denoting retail gasoline.

Vehicles were purchased in matched sets of two, three, or four vehicles with matching model year, engine family, evaporative emissions control family, powertrain

FIGURE 3. Test track at TRC

control unit calibration, transmission, wheel and tire size, etc. For vehicle sets of two, one vehicle was aged with RE0, and the second vehicle was aged with RE15. For vehicle sets of three, a third matched vehicle was acquired and aged on RE20. For vehicle sets of four, a fourth vehicle was acquired and aged on RE10. Five vehicle sets were aged on all four fuels, eighteen vehicle sets on three fuels (RE0, RE15 and RE20), and four vehicle sets on two fuels (RE0 and RE15). Figure 4 shows a sample schematic for a four-vehicle set, in which each colored rectangle represents one vehicle. Both new and pre-owned vehicles were purchased for the program, with Tier 2 model years ranging from 2005-2009, and pre-Tier 2 model years ranging from 2000-2003, as shown in Table 1.

Vehicles were emissions tested using the Federal Test Procedure at three or four points during the aging program; at the start of mileage accumulation, at one or two mid-mileage points in the program, and at the end of mileage accumulation. All of the 2009 vehicles were purchased new and were driven 120,000 miles (120k) during the program. Eight new vehicles at ETC were emissions tested at 4k miles (start of test), and 60k and 90k (intermediate test points), and at 120k (end of test). Twelve new vehicles at TRC were tested at 4k, 60k, and 120k, omitting the 90k test point due to time and budget constraints. Mileage accumulation for the pre-

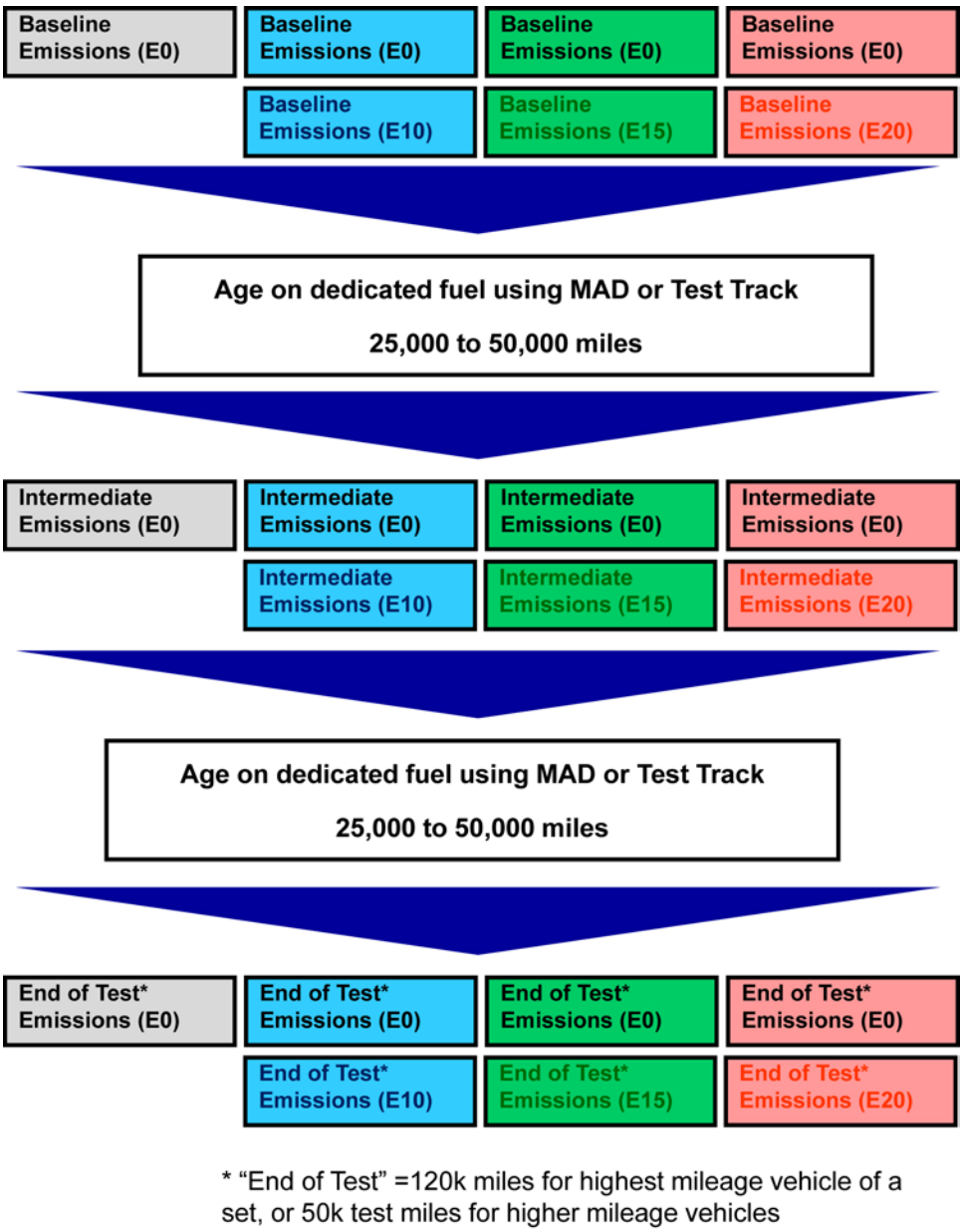

FIGURE 4. Vehicle Aging Program Schematic for One Matched Set of Four Vehicles

owned vehicles was determined based on actual vehicle odometers, ranging from 50k to 103k miles. All vehicles of a given set were driven the same distance in the test program.

Results

All Tier 2 vehicle results for the E0 and E15 vehicles were acquired before the end of FY 2010 and provided to EPA. Vehicle testing and data collection for the remaining vehicles are scheduled for completion by mid-January 2011. Results are being provided to EPA continuously throughout the program. A summary of the E0 and E15 vehicle results are shown in Table 2, taken from the Federal Register, which shows that three of the vehicle models aged with E0 exceeded their full useful life emissions standards at end of test (two for oxides of nitrogen [NOx], and one for non-methane organic gases), while two of the vehicle models aged with E15 failed for NOx emissions compliance. Emissions failures did not appear to be fuel-related. Based on these results and detailed statistical analysis, EPA determined that "E15 does not cause Tier 2 motor vehicles to exceed their exhaust emissions standards over their full useful life" [5].

TABLE 1. Test Vehicle Summary

Tier 2 Vehicles						
Southwest Research Institute (TX), Mileage Accumulation Dynamometers						
Year	**Vehicle**	**# veh.**	**Fuels**			
2006	Chevrolet Silverado	4	E0	E10	E15	E20
2007	Honda Accord	4	E0	E10	E15	E20
2008	Nissan Altima	4	E0	E10	E15	E20
2008	Ford Taurus	4	E0	E10	E15	E20
2007	Chrysler Caravan	4	E0	E10	E15	E20
2006	Chevrolet Cobalt	3	E0		E15	E20
2007	Dodge Caliber	3	E0		E15	E20
Transportation Research Center (OH), Test Track Aging						
2009	Jeep Liberty	3	E0		E15	E20
2009	Ford Explorer	3	E0		E15	E20
2009	Honda Civic	3	E0		E15	E20
2009	Toyota Corolla	3	E0		E15	E20
2005	Toyota Tundra	3	E0		E15	E20
2006	Chevrolet Impala	3	E0		E15	E20
2005	Ford F150	3	E0		E15	E20
2006	Nissan Quest	3	E0		E15	E20
Environmental Testing Corp (CO), Mileage Accumulation Dynamometers						
2009	Saturn Outlook	2	E0		E15	
2009	Toyota Camry	2	E0		E15	
2009	Ford Focus	2	E0		E15	
2009	Honda Odyssey	2	E0		E15	
Pre-Tier 2 Vehicles						
Southwest Research Institute (TX), Mileage Accumulation Dynamometers						
Year	**Vehicle**	**# veh.**	**Fuels**			
2000	Chevrolet Silverado	3	E0		E15	E20
2002	Nissan Frontier	3	E0		E15	E20
2002	Dodge Durango	3	E0		E15	E20
Transportation Research Center (OH), Test Track Aging						
2003	Toyota Camry	3	E0		E15	E20
2003	Ford Taurus	3	E0		E15	E20
2003	Chevrolet Cavalier	3	E0		E15	E20
Environmental Testing Corp (CO), Mileage Accumulation Dynamometers						
2000	Honda Accord	3	E0		E15	E20
2000	Ford Focus	3	E0		E15	E20

In addition to the emissions testing throughout the program, powertrain component inspections were performed on six of the vehicle sets at SwRI® at end of test. Results for the E0 and E15 vehicles were completed by September 30, 2010 with results compiled in a draft report and pre-published in the EPA docket [6]. Additional results for the E20 vehicles from those same vehicle sets are expected before the end of the calendar year. Powertrain component inspection included an evaporative emissions system leak check, evaporative canister working capacity test, cam lobe measurement, valve seat width and valve surface contour, valve stem height, intake valve deposit mass, engine oil analysis, fuel injector flow measurements, fuel pump flow measurement and fuel pump disassembly and inspection.

There were no significant differences in the powertrain components from vehicles aged on gasoline versus those aged on ethanol blends, with the exception of intake valve deposit (IVD) weight. Many of the vehicles aged on E15 or E20 showed significantly higher IVD than their E0 counterparts; an example is shown in Figure 5 for the 2007 Honda Accord. The gasoline used for vehicle aging was top tier gasoline[2], and this gasoline was splash-blended with ethanol to make the RE15 and RE20 blends. Dilution of the additive package would be expected to increase IVD formation, so these results are not surprising. In addition, E10 has been shown to be a more severe test fuel for intake valve deposits [5]. While the IVD was higher for the E15 vehicles, it does not appear to have lead to emissions increases on these vehicles.

About half of the 24 pre-Tier 2 vehicles completed testing in FY 2010, and the remainder will be completed early in FY 2011. Data analysis on the full suite of vehicle data will continue into FY 2011 and be detailed in a comprehensive report.

Conclusions

- Tier 2 vehicles aged 63k to 120k miles did not show any increased exhaust emission deterioration due to aging with E15 fuel.
- Examination of powertrain components from Tier 2 vehicles aged with E15 and E20 showed no signs of increased corrosion or wear from the use of ethanol blends. Vehicles aged with ethanol blends did have higher intake valve deposit mass, however detergent additive concentrations were not adjusted in consideration of adding ethanol to the fuel.

[2] Top tier gasoline is formulated to meet a particular level of deposit control per ASTM D 6201, "Standard Test Method for Dynamometer Evaluation of Unleaded Spark-Ignition Engine Fuel for Intake Valve Deposit Formation."

TABLE 2. Tier 2 E0/E15 Vehicle Pass/Fail Summary

Reproduced from Federal Register/Vol. 75, No. 213/ November 4, 2010/Notices				
RE0 End of Test results Compared to Tier 2 Standards (Vehicles aged on RE0)				
Year	**Vehicle**	**NOx**	**NMOG**	**CO**
2007	Honda Accord	Pass	Pass	Pass
2006	Chevrolet Silverado	Pass	Pass	Pass
2008	Nissan Altima	Pass	Fail	Pass
2008	Ford Taurus	Pass	Pass	Pass
2007	Chrysler Caravan	Pass	Pass	Pass
2006	Chevrolet Cobalt	Pass	Pass	Pass
2007	Dodge Caliber	Fail	Pass	Pass
2009	Honda Civic	Pass	Pass	Pass
2009	Ford Explorer	Pass	Pass	Pass
2009	Toyota Corolla	Pass	Pass	Pass
2009	Jeep Liberty	Pass	Pass	Pass
2005	Toyota Tundra	Pass	Pass	Pass
2006	Chevrolet Impala	Pass	Pass	Pass
2005	Ford F150	Pass	Pass	Pass
2006	Nissan Quest	N/A	N/A	N/A
2009	Saturn Outlook	Pass	Pass	Pass
2009	Toyota Camry	Pass	Pass	Pass
2009	Ford Focus	Fail	Pass	Pass
2009	Honda Odyssey	Pass*	Pass	Pass
Total Fails, RE0		**2**	**1**	**0**

RE15 End of Test results Compared to Tier 2 Standards (Vehicles aged on RE15)				
Year	**Vehicle**	**NOx**	**NMOG**	**CO**
2007	Honda Accord	Pass	Pass	Pass
2006	Chevrolet Silverado	Pass	Pass	Pass
2008	Nissan Altima	Pass	Pass	Pass
2008	Ford Taurus	Pass	Pass	Pass
2007	Chrysler Caravan	Pass	Pass	Pass
2006	Chevrolet Cobalt	Pass	Pass	Pass
2007	Dodge Caliber	Pass	Pass	Pass
2009	Honda Civic	Pass	Pass	Pass
2009	Ford Explorer	Pass	Pass	Pass
2009	Toyota Corolla	Pass	Pass	Pass
2009	Jeep Liberty	Pass	Pass	Pass
2005	Toyota Tundra	Pass	Pass	Pass
2006	Chevrolet Impala	Pass	Pass	Pass
2005	Ford F150	Pass	Pass	Pass
2006	Nissan Quest	Fail	Pass	Pass
2009	Saturn Outlook	Pass	Pass	Pass
2009	Toyota Camry	Pass	Pass	Pass
2009	Ford Focus	Fail	Pass	Pass
2009	Honda Odyssey	Pass	Pass	Pass
Total Fails, RE15		**2**	**0**	**0**

*Denotes that average of emissions tests were below the applicable full useful life standard, but had at least one test value above the applicable standard

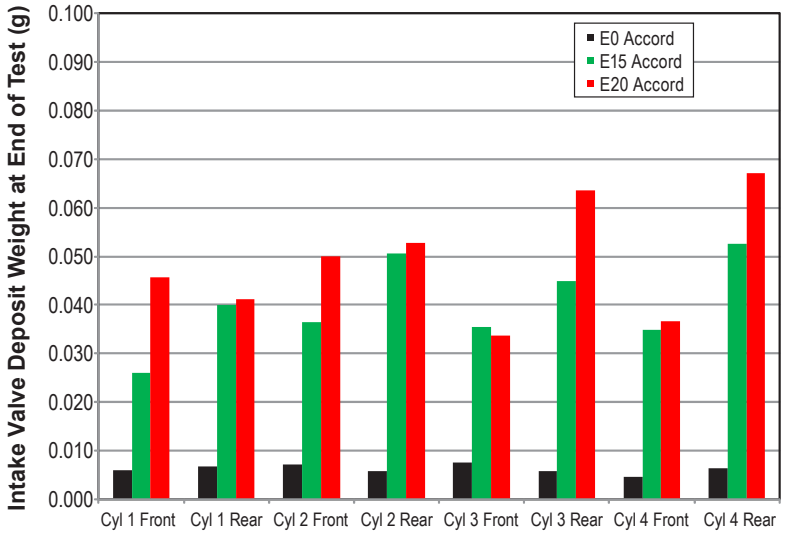

FIGURE 5. Intake Valve Deposit Weight for 2007 Honda Accords at End of Test

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1. Energy Independence and Security Act of 2007, H.R. 6, 110th Congress, 2007-2008.

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3. "Mid-Level Ethanol Blends Catalyst Durability Study Screening," CRC Report No. E-87-1, Coordinating Research Council, Alpharetta, GA, 2009.

4. Code of Federal Regulations, 40CFR Part 86, Appendix V.

5. Federal Register/Vol. 75, No. 213/ November 4, 2010/ Notices, "Partial Grant and Partial Denial of Clean Air Act Waiver Application Submitted by Growth Energy To Increase the Allowable Ethanol Content of Gasoline to 15 Percent; Decision of the Administrator"

6. Powertrain Component Inspection from Mid-Level Blends Vehicle Aging Study, available from EPA docket: http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2009-0211

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1. B. West et al., "DOE V4 and CRC E87-2 Project Status," Coordinating Research Council Emissions Committee Meetings, October 1, 2009; January 21, 2010; May 20, 2010.

2. K. Knoll, and W. Clark, "Mid-Level Ethanol Blends Vehicle Evaluations," Missouri Corn Grower's Association, January 26, 2010.

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6. K. Stork, R. Graves, ORNL and NREL Team, "Recent Work on Intermediate Ethanol Blends for Use in Conventional Vehicles," 15th Annual National Ethanol Conference, February 17, 2010.

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8. B. West, R. Graves, M. Kass, and T. Theiss, "Increasing Ethanol Utilization in the U.S.," Society for Industrial Microbiology, 32nd Symposium on Biotechnology for Fuels and Chemicals, April 20, 2010.

IV.8 The Use of Exhaust Gas Recirculation to Optimize Fuel Economy and Minimize Emissions in Engines Operating on E85 Fuel

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Kevin Stork

NETL Project Manager: Michael Ursic

Objectives

- Demonstrate the capabilities of a flex-fuel turbocharged engine, which incorporates recirculated, cooled exhaust gas along with other synergistic technologies, to achieve significant (15%) fuel economy (FE) benefit relative to conventional naturally-aspirated engines operated on the same fuel.
- Optimize the engine system through simulation and testing.
- Develop and optimize engine management system functions and calibrations to maximize FE of the demo vehicle.
- Develop viable aftertreatment technologies for achieving low emission vehicle (LEV) III super ultra-low emissions vehicle (SULEV) capabilities using three-way catalysts.

Fiscal Year (FY) 2010 Accomplishments

- Dynamometer testing has demonstrated the fuel consumption benefits of cooled exhaust gas recirculation (EGR) for the downsized turbocharged engine over a broad operating range and the projected FE gain over the combined urban and highway driving cycles is in the range of 13-17%.
- Cooled EGR vehicle is prepped and development testing and calibration commenced.
- The project team completed a technology integration review and formally expanded the scope of the project to include tasks to develop viable technologies for the flex-fuel turbocharged powertrain to meet the LEV III SULEV emissions standards – Turbo SULEV. A revision to the project SOPO (statement of project objectives) was recently submitted to DOE (Figure 1).
- Designs are complete for the Turbo SULEV development steps.
- Turbo SULEV Enhanced Base System hardware and initial testing was completed.

Future Directions

- Cooled EGR Vehicle Development
  - Implement control strategies into vehicle controller and commence calibration.
  - Review initial vehicle performance data and compare to dynamometer performance.

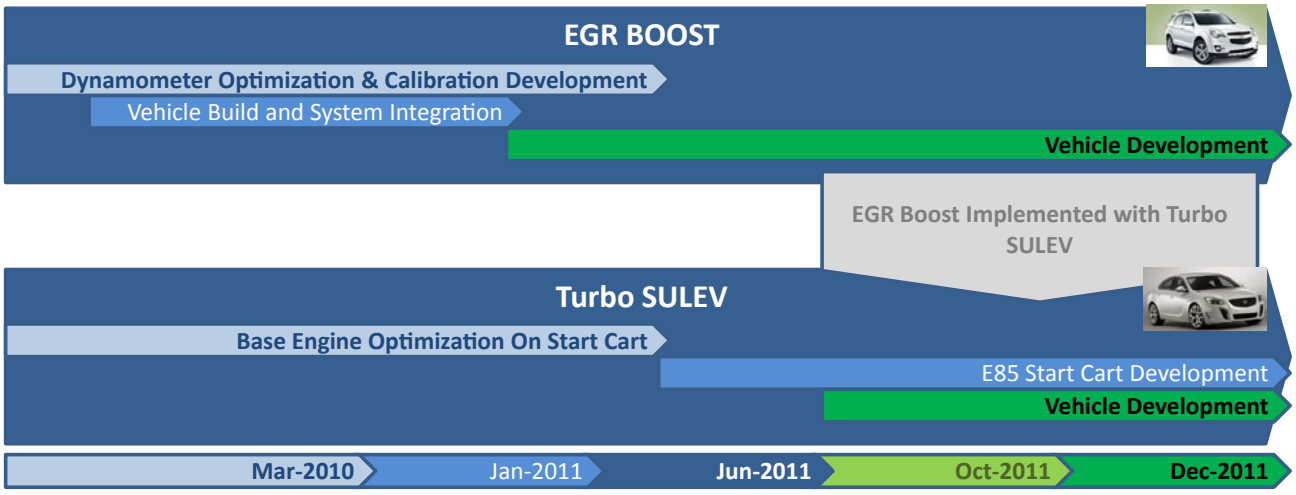


FIGURE 1. Revised SOPO Plan with Turbo SULEV

  - Refine and execute plan for controls refinement and vehicle calibration.
- Turbo SULEV Start Cart Development
  - Implement optimized engine management functions.
  - Fabricate and test integral system variants.

Introduction

In order to further the federal government's objective of U.S. energy independence, this project focuses on engine optimization for E85 fuel operation, while maintaining flex-fuel capabilities that enable engines to operate on a range of fuels from E85 to gasoline. Through development and integration of a number of advanced and novel engine technologies, the demo engine can achieve substantially improved fuel economy while operating with E85 and that is also production viable in the near- to medium-term. The key engine technology area under development is turbocharging, which is known to improve fuel economy through downsizing. This engine technology is in particular capable of exploiting ethanol fuel's characteristics of high octane number and high latent heat of evaporation. Revision to the SOPO this year enhanced the project by introducing emissions enabling technology of the Turbo SULEV.

Combined innovative technology steps integrated in synergy are:

- Cooled EGR
- Direct fuel injection
- Dual continuously variable intake and exhaust cam phasers
- Six-speed automatic transmission
- Integrated bifurcated exhaust manifold
- Integrated turbocharger

Cooled EGR development was conducted with simulation to demonstrate the viability of the technology and provide input to hardware design and system implementation. Confirmation testing in a development dynamometer facilitated optimization of hardware and control strategies and verified project targets. A vehicle was fitted with the optimized system and began strategy and calibration development. Vehicle calibration will be developed to demonstrate powertrain-related attributes including fuel economy, performance, driveability and NVH (noise, vibration, and harshness) while meeting emissions targets.

The Turbo SULEV project content was successfully adapted to this project. Presently running parallel to the Cooled EGR task, Turbo SULEV will be integrated together in the final segment of this project phase. The combined systems will demonstrate the feasibility of fuel economy and emissions aftertreatment.

Two vehicles are now included in the overall project:

- Cooled EGR for fuel economy demonstrator
- Turbo SULEV emissions demonstrator

Approach

Cooled EGR continues into the final phase, Phase 4 Vehicle Calibration. A vehicle is configured with the dynamometer optimized and demonstrated hardware, control strategies and calibration. Road and track calibration development will be conducted. Periodic performance and emissions characterization will be performed on an emissions-capable vehicle dynamometer.

Turbo SULEV Enhanced Base System results will drive fabrication and start cart testing of two integral hardware variants. Each variant will progressively characterize catalyst performance benefits from changes in thermal mass and exhaust path length from engine to catalyst (Figure 2). Systems are:

- System 1: Enhanced Base System
- System 2: 210 hp Integral System #1
- System 3: 260 hp Integral System #2

Aftertreatment system optimization for E85 will be conducted on an E85-optimized start cart to develop and evaluate control strategies and calibration as well as aftertreatment component optimization.

EGR dilution effects on cold start will be investigated on the start cart. Two options are elected for this project: low pressure and high pressure. Low-pressure EGR will be investigated first to determine cold-start tolerance to EGR dilution. Two low-pressure options are in consideration. If low-pressure EGR results are positive, then higher EGR dilution rates will be investigated. At this juncture the second,

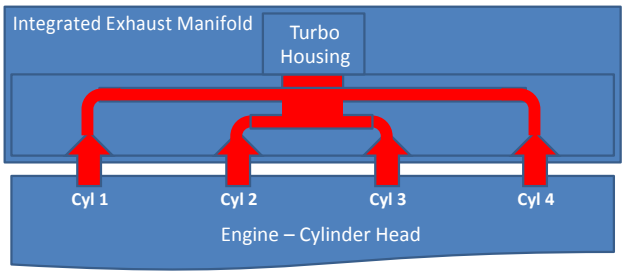


FIGURE 2. Turbo SULEV Integrated Bifurcated Exhaust Manifold

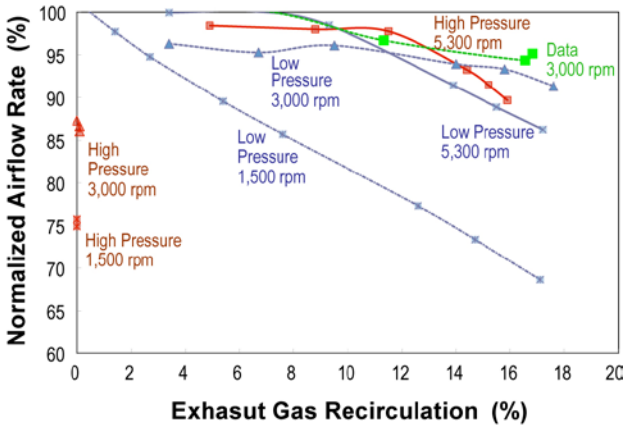


FIGURE 3. Cooled EGR Comparison between Data and Simulation Results

high-pressure EGR system will be introduced. This testing will define the envelope for cold-start EGR tolerance and determine optimum EGR rates and system architecture for this engine.

Results

Cooled EGR simulation results were compared to steady-state dynamometer results (Figure 3). Data demonstrates the benefit potential with a higher than expected EGR rate at 3,000 rpm.

Cooled EGR dynamometer testing confirmed a fuel economy benefit ranging from 13%-17% against a range of steady-state operating points of 1.3 bar brake mean effective pressure @ 650 rpm to 10.4 bar @ 1,338 rpm and 6.9 bar @ 2,366 rpm.

The Turbo SULEV Enhanced Base System was designed using computational fluid dynamics (CFD) to optimize exhaust flow from wastegate passages, which bypass the turbine wheel, to a close-coupled catalytic converter. In addition, the wastegate passages have significantly increased flow areas compared to traditional practices. Figure 4 shows the results from the CFD optimization.

Turbo SUELV Start Cart testing demonstrated directionally correct thermal benefits for aftertreatment catalyst operation. Assumptions for success of enhanced thermal rates are reduced thermal mass and intimate coupling of the hot-side exhaust. This is facilitated with the new integral system which features the GM integrated bifurcated exhaust manifold.

Temperatures are higher with the Enhanced Base System – data is compared as aftertreatment temperature correlated to tailpipe emissions, Figure 5. An improvement in tailpipe emissions correlates to catalyst efficiency improvement with increased temperature.

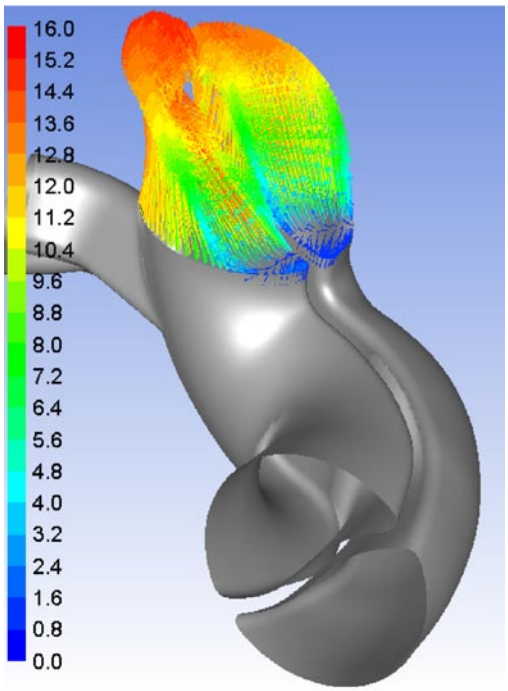
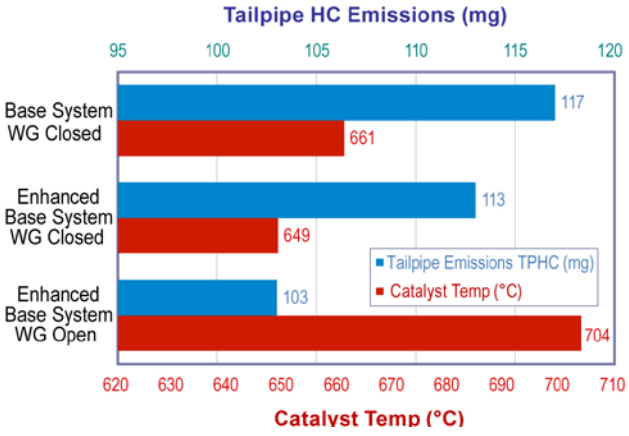


FIGURE 4. CFD Optimized Exhaust Velocity Vectors at Catalytic Converter Inlet



HC - unburned hydrocarbons; TP - tailpipe; WG - wastegate

FIGURE 5. Aftertreatment Temperature Correlated to Tailpipe Emissions at 20 s from Start

Analysis was employed to simulate Turbo SULEV system configuration designs at cold-start conditions. In the development system, EGR is routed to a pre-compressor location as opposed to conventional EGR introduction into the intake manifold. Figure 6 compares EGR architectures – intake manifold vs. turbo compressor. Simulation result suggests the pre-

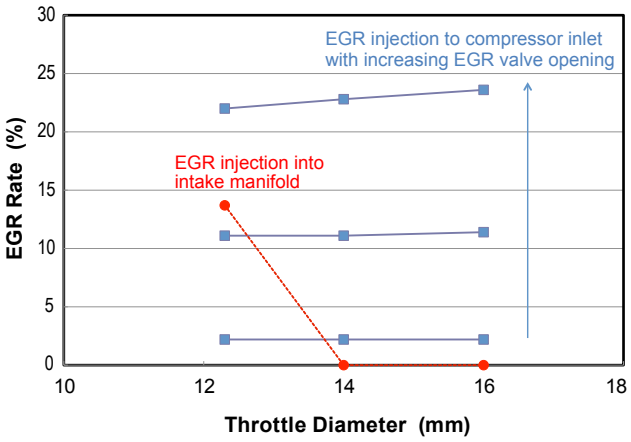


FIGURE 6. EGR Architecture Comparison: Intake Manifold vs. Turbo Compressor

compressor location is preferred due to its capabilities in providing a broader range of EGR flow.

Conclusions

- Cooled EGR assumptions and simulation results were confirmed in steady-state dynamometer testing.
- Cooled EGR demonstrates a positive advantage to fuel economy and emissions.
- Design and simulation for the Turbo SULEV proof-of-concept testing demonstrates a positive advantage to cold start and emissions.
- Faster thermal response is an enabler to three-way catalyst operation and reinforces the theory supporting an optimized integrated exhaust system.

Special Recognitions & Awards/Patents Issued

1. Patent Application 12/842169, An Exhaust Gas Recirculation System and Its Operation, Assignee: GM Global Technology Operations LLC, Inventor: Ko-Jen Wu.

2. Patent Application 12/884686, Integrated Exhaust Gas Recirculation and Charge Cooling System and Its Operation, Assignee: GM Global Technology Operations LLC, Inventor: Ko-Jen Wu.

3. Patent Application 12/884610, Integrated Cooling System for Boosted Engines Employing Recirculated Exhaust Gas, Assignee: GM Global Technology Operations LLC, Inventor: Ko-Jen Wu.

IV.9 Optimally Controlled Flexible Fuel Powertrain System

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- Argonne National Laboratory, Argonne, IL

Project Objectives

The project object is to demonstrate a new, commercially-viable engine concept that is optimized for E85 operation, exhibiting the following characteristics:

- Show minimum fuel economy impact of running on E85 when compared to gasoline.
- Show no degradation in vehicle emissions running on E85 when compared to gasoline.
- Allow the engine to run at various levels of ethanol fuel content up to 85 percent.
- Show minimal compromise of engine performance when running on gasoline.
- Demonstrate an engine with superior performance by fully exploiting the properties of E85.
- Help DOE promote the economy and social benefits of using E85 fuel to the nation.

Fiscal Year (FY) 2009/2010 Objectives

- Static and dynamic fuel injector spray characterization tests (bench tests).
- Compare penetration, spray angle, bend angle, droplet size distribution, static flow, dynamic flow and flow linearity for candidate injectors.
- Design and construct an ionization-based ignition system (to be utilized for closed-loop combustion control, CLCC) together with higher spark ignition energy requirements of the engine concept.
- Complete performance and emissions testing of comparator engine (2.2-L General Motors [GM] Ecotec) to provide baseline data.
- Assemble and break-in the multi-cylinder MAHLE R3 concept engine.
- Single-cylinder (optical engine) tests in conjunction with a high-speed camera to perform in-cylinder observations of the fuel injector performance with representative airflow and fluctuating in-cylinder pressures:
  - Study fuel spray impingement on cylinder walls and piston with various injectors.
  - Study split injection vs. single injection.
  - Study effect of fuel blend.
  - Study correlation of cold spray tests to combustion images.
- Single-cylinder (metal engine) firing tests to determine optimum injector selection, compression ratio for gasoline/ethanol blends, emissions measurements.

FY 2010 Accomplishments

- Injector spray performance characterization completed for three candidate injectors – spray imaging, dynamic flow and injector droplet size.
- Ignition system with CLCC designed, built and tested on single-cylinder engine.
- Comparator baseline engine (GM Ecotec 2.2-L) performance tests completed.
- Evaluated performance of injector candidates on single-cylinder engine and selected best injector candidate for R3 engine.
- Multi cylinder R3, 1.2-L engine assembled with final injector selection and single turbocharger. Break-in tests completed and correlation performance testing has begun.

Future Directions

- Combustion event analysis using metal single-cylinder engine for candidate injectors.
- Combustion optimization through selection of compression ratios for blends of fuel.
- Correlate GT-POWER engine model to R3 1.2-L engine test results.
- Complete R3 multi-cylinder 1.2-L engine final testing.
- Investigate additional gains using cooled exhaust gas recirculation.
- Confirm operation of ionization detection, fuel content determination and CLCC system and on the multi-cylinder R3 engine.
- Report R3 engine efficiency and fuel economy results compared to targets.
- Analysis of commercial feasibility of final design.

Introduction

Current flexible-fuel vehicles typically see a reduction in fuel economy of around 30%, when operating on 85% ethanol in gasoline (E85) compared to 100% gasoline. The purpose of this project is to demonstrate a flexible-fuel powertrain that is better optimized for E85, reducing the fuel economy penalty for E85 operation.

Approach

- Develop a flexible-fuel powertrain that provides volumetric fuel economy improvements when operating on E85, similar to, or better than, a current gasoline powertrain of similar performance. This project will develop the MAHLE 'R3' research engine (Figure 1), such that it is optimized for E85. The GM 2.2-L direct injection Ecotec engine is being used as the equivalent comparator engine.
- Use of existing technology, with suitable modifications, integration actions and tuning to realize a production- and commercially-viable solution.

Key enablers include:

- Downsizing: aggressive reduction in swept volume combined with direct injection and turbocharging.
- Increased compression ratio: takes advantage of ethanol's higher octane rating and increased heat of vaporization.
- Variable valve control for Atkinson cycle operation, cooled exhaust gas recirculation: allow optimization across the speed/load map, minimize pumping losses and optimize the combustion process.
- CLCC: enables fully flexible-fuel operation.

Development of the optimized powertrain will be accomplished by the following engineering methodologies:

- Simulation:
  - Combustion system (GT-POWER)
  - Vehicle effects (ADVISOR)
  - Social benefit (GREET)
  - High-level component requirements
- Combustion System Design:
  - Injector analysis (computational fluid dynamics) and modeling
  - Detailed 1-dimensional (GT-POWER)
  - Control system design (CLCC)
  - Optical engine design

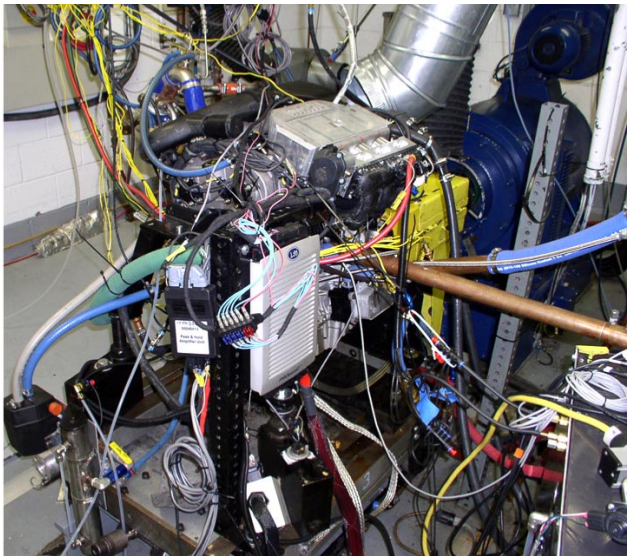

FIGURE 1. MAHLE R3 Engine in Test Cell

- System Assembly/Baseline:
  - Injector build, spray characterization tests
  - Optical single-cylinder tests
  - Ignition/control system build
  - E85-optimized engine build
  - Baseline engine tests (performance and emissions)
- System Development (E85-optimized engine tests):
  - Performance and emissions
  - Results analysis, model update
  - Commercialization study

Results

Bench testing and in-cylinder spray characterization tests have been completed utilizing the Mie Scattering method. A single-cylinder direct-injection spark-ignition optical engine has been used for in-cylinder combustion studies of different test fuels, (gasoline, E50 and E85) and three different injectors.

Experiments have been performed at 1,500 rpm engine speed at part-load and full-load conditions. In-cylinder pressure data was recorded for combustion analysis that has been synchronized with imaging. The following injection spray parameters were determined for n-heptane and E85 fuels:

- Penetration, spray angle, bend angle
- Droplet size, distribution
- Static flow, dynamic flow, flow linearity

Three types of fuel injectors have been evaluated as follows and Table 1 summarizes the results of the droplet size characterization:

TABLE 1. Fuel Droplet Size Comparison

Injector Type	Fuel	Pressure (MPa)	Dv10 (μm)	Dv50 (μm)	Dv90 (μm)	SMD (μm)	D43 (μm)
Visteon LPDI Injector	n-heptane	3	12.7	26.0	**44.0**	**20.1**	27.9
	E85	3	12.3	26.3	**49.2**	**20.8**	29.1
Production Bosch GDI Injector	n-heptane	3	10.4	23.6	**41.5**	**17.8**	25.2
	n-heptane	5	7.8	17.8	**29.0**	**13.3**	18.3
	n-heptane	10	5.3	12.3	**20.6**	**8.5**	12.8
	E85	3	11.5	24.9	**45.7**	**19.6**	27.3
	E85	5	8.7	20.1	**32.3**	**14.8**	20.5
	E85	10	6.1	15.3	**24.3**	**10.9**	15.4
Prototype Bosch GDI Injector	n-heptane	5	9.73	21.8	**48.39**	**16.88**	26.15
	n-heptane	10	6.63	14.61	**33.85**	**11.9**	17.38
	E85	5	10.92	25.45	**54.25**	**18.63**	29.6
	E85	10	7.06	14.67	**29.93**	**12.01**	16.98

LPDI – low-pressure, direct injection; GDI – gasoline direct injection

- Low-pressure Visteon production-intent injector with fuel pressure of 3 MPa.
- High-pressure Bosch production injector with fuel pressures of 5 and 10 MPa.
- High-pressure Bosch prototype injector with fuel pressures of 5 and 10 MPa. This injector had previously been specifically optimized for gasoline use in the MAHLE R3 research engine.

Figure 2 shows one of the comparisons of in-cylinder spray development with E85 for the Visteon LPDI injector at 3 MPa (left) and the Bosch production injector at 5 MPa (middle) and 10 MPa (right) (start of injection 240 before top dead center [BTDC] at 1,500 rpm full-load).

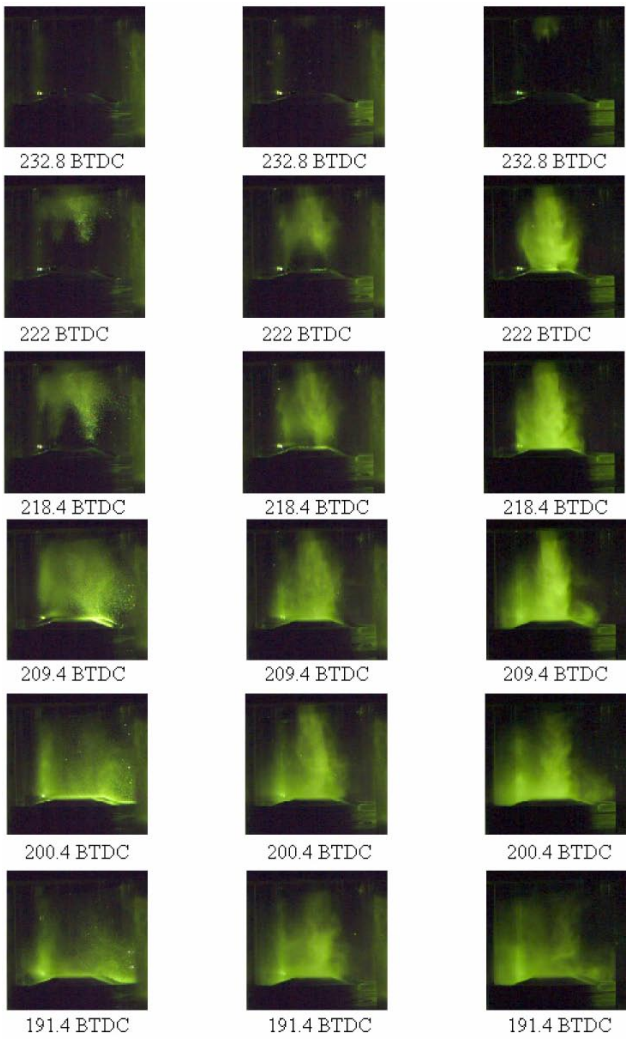

FIGURE 2. Comparison of In-Cylinder Injector Spray Development, for Visteon LPDI Injector @ 3 MPa and Bosch Production Injector at 5 MPa and 10 MPa Injection Pressures using E85 at 1,500 rpm Full-Load

The three injectors were used for tests which were conducted initially with a flat piston until the 'target design' pent roof piston was fabricated and available (Figure 3). The target piston effective compression ratio was 12.3:1. Poor performance, misfires and unrepeatable results were experienced using the Visteon LPDI injector with the target piston. Therefore subsequent tests focused on a comparison between two Bosch injectors with the target piston at 5 and 10 MPa injection pressures.

Injection Pressure Trends

- Figures 4 and 5 show images of stoichiometric gasoline combustion using the target optical piston. For both injectors, early flame growth is faster for the higher injection pressure. At 5 MPa the prototype injector exhibits much faster flame growth than the production injector. At 10 MPa, the growth rate appears to be equal for both injectors, however the Bosch prototype injector was less sensitive to pressure effects.
- The presence of many orange areas when using the prototype injector at 5 MPa are most likely droplets that have not fully atomized by the start of combustion and are impacting the piston face. These spots do not appear as vibrant in the 10 MPa case, pointing to better atomization of the fuel at this higher pressure and less piston face impingement.
- Peak in-cylinder pressure increased with higher injection pressure in all cases.
- Mass fraction burned curves show a generally faster burn rate with higher injection pressure, though the sensitivity is less pronounced with the prototype injector.

FIGURE 3. Target Optical Pent-Roof Piston

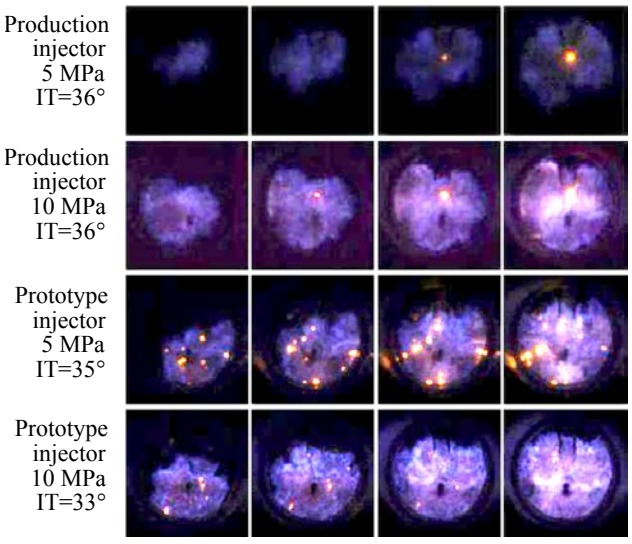

FIGURE 4. Flame Images of Gasoline ($\lambda = 1$, IT = MBT for each case) at Different Injection Pressures using the Bosch Production and Prototype Injectors

Injection Timing Trends Target Piston

- Production injector combustion images showed the fastest flame growth at 240° BTDC injection timing. The 180° and 210° injection timings showed nearly identical results

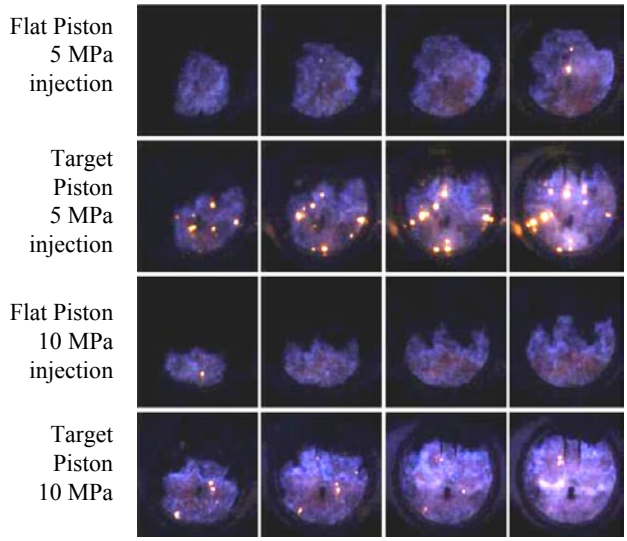

FIGURE 5. Flame Images of Gasoline Combustion, Flat vs. Target Piston at two Different Injection Pressures (MBT ignition timing for each case); Prototype Injector

- Prototype injector image results exhibited different flame growth trends. Growth was fastest with the earliest injection and slowest with the latest injection. Numerous hot spots visible with the 210° injection, were not visible at the other two injection timings indicating possible impingement issues at this timing. Steady operation was difficult to achieve with the 180° timing – numerous misfires were present, and flame growth appeared very uneven. Optimum timing was established at 240° BTDC.
- Burn durations decreased in general with the advancement of injection timing in most cases with the strong exception of the prototype injector with the flat piston, with which the 210° injection timing yielded significantly shorter burn duration.

Fuel Type Trends

- Combustion images showed that the flame growth rate increased with increasing levels of ethanol content in the fuel mixture and showed similar results for both Bosch injectors. It must also be noted though that ignition timing for maximum brake torque (MBT) was significantly later for the ethanol mixtures than for gasoline, which was reflected in the mass fuel burned (MFB) curves.
- E50 displayed many hot spots, likely from large droplets that did not mix fully. Ethanol blends displayed slightly faster initial flame growth, but similar overall burn duration compared to gasoline.
- The ethanol blends resulted in higher peak pressures but not necessarily higher indicated mean effective pressures (IMEPs) than gasoline. Using the

production injector, the drop in IMEP is likely due to the later MBT spark timing and the 10% burn and peak pressure points significantly retarded for ethanol compared to gasoline. However, IMEPs were the same for all fuel blends with the prototype injector indicating this injector produces more robust combustion.

- The Bosch prototype injector produced the smoothest running combustion with very little cycle to cycle variability for ethanol blends.

Injection Pulse Trends

- Investigations were conducted to establish the effects of using a split-injection strategy with a pilot pulse followed by a second injection for the candidate injectors and both types of piston. Gasoline test results using a split-injection strategy and the target piston produced visible hot spots and a very uneven and slower-developing flame with large cycle-to-cycle variations. E50 cases ran particularly unsteadily with split injection. A single-injection strategy was identified as the best option for the target piston and recommended injector.

Compression Ratio/Piston Design Trends

- The higher compression ratio target piston with the prototype injector led to faster initial flame development but overall longer burn durations and many more hot spots of possible piston impingement.
- Peak pressure increased and advanced in location with the target piston.

Conclusions

- Bench and in-cylinder spray testing indicate that the Bosch prototype injector is the best selection for the R3 engine.
- The prototype injector is superior to the production injector with ethanol blends and yields performance nearly on par with gasoline. Flame growth of E85 combustion with the prototype injector was noticeably more even than that of E50. Further validated will be completed during the metal single-cylinder engine tests.
- Piston type affects optimal injection timing (flat-210 BTDC vs. target 240 design), and a single-pulse injection strategy was optimal for the recommended injector. This needs to be further validated during the metal single-cylinder engine tests.

FY 2010 Publications/Presentations

1. Mittal, M., Hung, D.L.S., Zhu, G., and Schock, H.J., 2010, "A study of fuel spray visualization in a direct-injection spark-ignition engine with gasoline and ethanol-gasoline blended fuels," SAE Powertrains, Fuels and Lubricants Meeting, San Diego, California (October 25–27, 2010).

IV.10 E85 Optimized Engine

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NETL Project Manager: Michael C. Ursic

Subcontractors:
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- Ethanol Boosting Systems LLC, Cambridge, MA

Objectives

- Develop a roadmap to demonstrate a minimized fuel economy penalty for an F-series flexible-fuel vehicle (FFV) truck with a highly boosted, high compression ratio spark ignition engine optimized to run with ethanol fuel blends up to 85% ethanol in gasoline (E85).
- Develop and assess a dual-fuel concept for on-demand direct injection of E85.
- Reduce Federal Test Procedure 75 energy consumption by 15%-20% compared to an equally powered vehicle with a current production gasoline engine.
- Meet ultra-low emission vehicle (ULEV) emissions, with a stretch target of ULEV II/Tier II Bin 5.

Fiscal Year (FY) 2010 Accomplishments

- Completed mapping point data at 9.5:1 compression ratio. Used this data as input to refine vehicle level fuel economy and performance projections.
- Investigated the use of twin-scroll turbochargers as a method to mitigate the effects of "exhaust blowdown interference" on the V8 engine to make the engine dynamometer results more generic and applicable to other engine configurations.
- Evaluated the effects of combustion phasing retard on E85 consumption and vehicle range under towing conditions.
- Evaluated the effect of the engine structural peak pressure limit on full-load performance with E85.
- Upgraded direct injection fuel pump and control strategies to improve reliability and durability.

Future Directions

- Measure multi-cylinder full-load performance and fuel efficiency at vehicle mapping points for the E85-optimized dual-fuel engine at 12:1 compression ratio.
- Evaluate vehicle level attributes for the FFV- and E85-optimized dual-fuel engines using the above engine dynamometer mapping point data as input to a vehicle level model.
- Develop a cold starting strategy for an E85-optimized dual-fuel 3.5-L EcoBoost™ engine on a transient dynamometer.

Introduction

The project "E85 Optimized Engine" is a collaborative effort between the Department of Energy, Ford Motor Company, AVL Powertrain Engineering Inc., and Ethanol Boosting Systems LLC. The primary objective of this work is to demonstrate the benefits of a dual-fuel (gasoline and E85) turbocharged engine which maximizes the efficiency of usage of the primary gasoline fuel by allowing the engine to operate at high compression ratio and high levels of boost, and injecting ethanol only as needed to avoid engine knock. Gasoline turbocharged direct injection (GTDI) engines such as the Ford 3.5L EcoBoost™ are being introduced to improve the fuel economy of mainstream vehicles while maintaining or enhancing vehicle performance. The use of ethanol is a logical enhancement to these engines because the high octane and high heat of vaporization properties of ethanol vastly extend the knock-free engine operating range. However, ethanol has a low heating value per volume, which results in a dramatic reduction in vehicle range and volumetric fuel economy (mpg), which can be a cause for vehicle owner dissatisfaction.

The concept of the dual-fuel engine overcomes this issue with using ethanol. In this concept, port fuel injection of gasoline is combined with direct injection of E85 in the same engine, as shown in Figure 1. Gasoline is used at low to medium torques, and direct injection of E85 is used at high torque only in the amount required to prevent knock. Since knock is suppressed, the compression ratio and boost pressure can be increased. The resulting high torque levels allow downsizing of the engine and downspeeding (running lower rpm), which moves the operating regime of the engine in the vehicle to a more efficient part of the speed-load map. By enabling higher compression ratio, downsizing, and

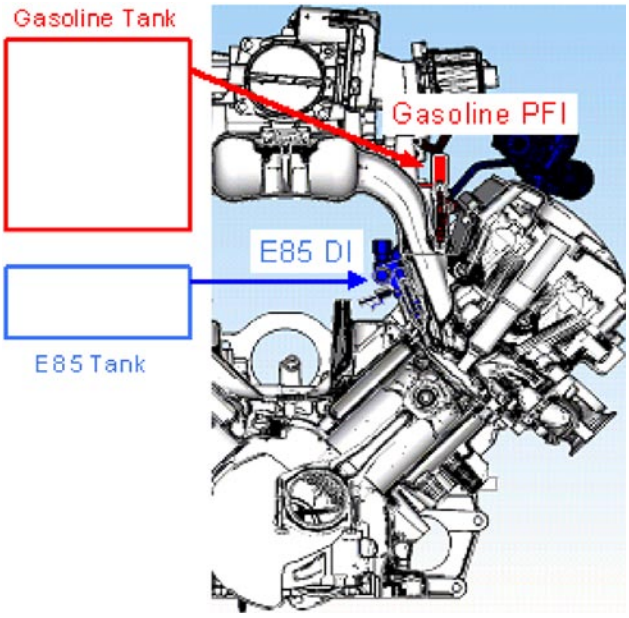

FIGURE 1. Cross-Section of E85-Optimized Dual-Fuel Engine

downspeeding, the dual-fuel engine uses gasoline more efficiently, thereby leveraging the benefit of ethanol in reducing the consumption of gasoline. The vehicle owner will realize high fuel economy because gasoline, with its high heating value per volume, is the fuel that is primarily used for most driving modes in an engine which operates at high efficiency in the vehicle [1].

Approach

This project builds on past knowledge and experience with turbocharged direct injection engine design and development at Ford and AVL. A combined analytical and empirical approach was utilized to develop a robust and durable design, optimized for efficiency with low emissions, and providing the required vehicle performance and fuel economy attributes.

As described in the 2009 report and in more detail in reference [2], the combustion system was initially developed on a conventional single-cylinder engine and a single-cylinder engine with optical access. The latter was used to validate conclusions drawn from the conventional single-cylinder test results and to ensure that there were no issues with fuel washing the lubricating oil from the cylinder bore or other fuel spray targeting related issues. Three 5.0-L V8 engines were then built with the combustion system specifications which were defined on the single-cylinder engine. A V8 is the preferred architecture for a GTDI engine to support the displacement required to compete with the Diesel engine in the F-Series and provide comparable torque and towing capability.

Results

Multi-Cylinder Development

A multi-cylinder dual-fuel engine tested at Ford's dynamometer labs has demonstrated a number of fundamental advantages for E85 compared to gasoline: absence of knock, near-zero particulate emissions, and no incidence of irregular combustion or pre-ignition, even at very high brake mean effective pressure (BMEP). Additionally and in contrast to the Diesel, the E85 engine operates at stoichiometry and uses a conventional three-way catalyst, so it can achieve stringent emission levels with low emissions aftertreatment cost.

Vehicle Projections of Fuel Economy and Performance

BMEP sweeps at various engine speeds were run on an engine dynamometer at 9.5:1 compression ratio. This data was then used as input to update and refine vehicle simulation projections for a 12:1 compression ratio E85-optimized engine. These projections indicate that an E85-optimized dual-fuel engine can achieve fuel economy similar to a Diesel on the metro-highway test cycles while providing enhanced vehicle performance as measured by gradeability, which is the maximum grade achievable in top gear at 65 mph (top plot of Figure 2). Additionally, the CO_2 emissions of the dual-fuel engine are significantly better than the Diesel (bottom plot of Figure 2).

Use of Twin Scroll Turbochargers to Mitigate V8 Blowdown Interference

"Blowdown interference" can occur on a multi-cylinder engine because the exhaust blowdown pulse from each cylinder propagates through the exhaust manifold and affects the in-cylinder pressure of other cylinders which have open exhaust valves. Depending on the firing interval between cylinders connected to the same exhaust manifold, this interference can affect the exhaust stroke pumping work and the exhaust pressure during overlap, which in turn affects the residual fraction [3]. In a twin-turbocharged V8 engine with uneven firing intervals on each bank (for inertia balance), blowdown interference can cause high residual fraction in some cylinders, which increases knock. This in turn increases the amount of E85 which is required to avoid knock in the dual-fuel engine.

To mitigate the effects of this "exhaust blowdown interference" on the V8 engine to make the engine dynamometer test results more generic and applicable to other engine configurations, the use of twin-scroll turbochargers was investigated. Twin scroll turbochargers significantly reduced the magnitude of blowdown interference (Figure 3). The interference

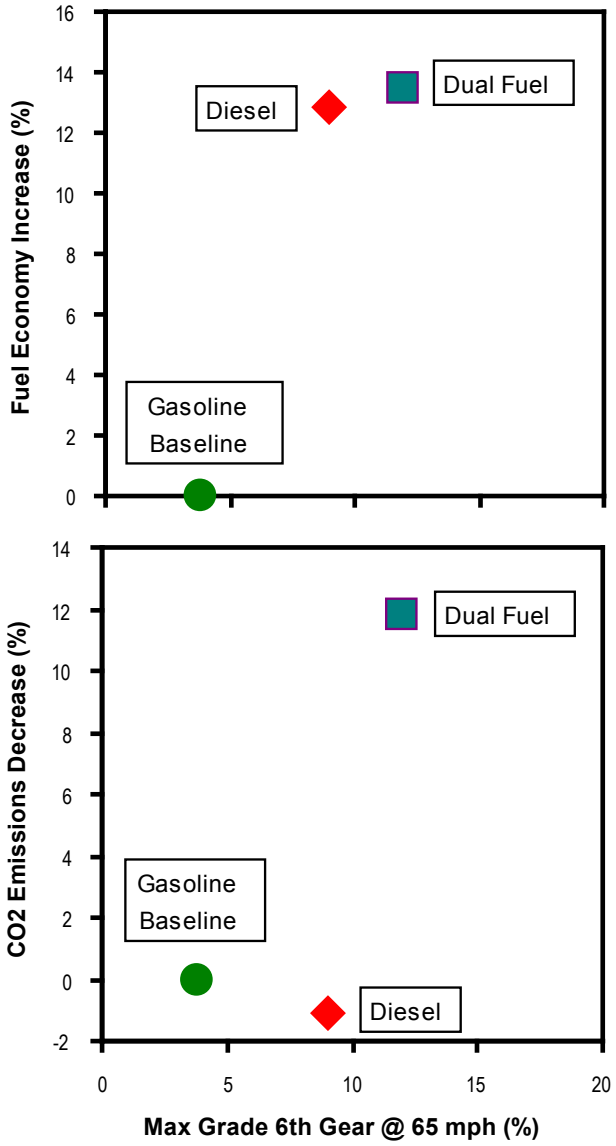

FIGURE 2. Dual-fuel Engine Compared to Gasoline Baseline and Diesel engines (top plot is fuel economy in mpg and bottom plot is CO_2 emissions)

is not completely eliminated due to the limited communication which exists between turbine scrolls. As a result of this investigation, it was decided to utilize twin-scroll turbochargers for the assessment of the dual-fuel E85-optimized engine at 12:1 compression ratio.

Effect of Combustion Phasing on Towing Range

The customer acceptance of a dual-fuel vehicle will require a reasonable range on the E85 tank before refueling is required, even under towing conditions. To reduce E85 consumption while towing, the effect of moderate retard of combustion phasing was investigated. Less E85 is required as combustion phasing is retarded

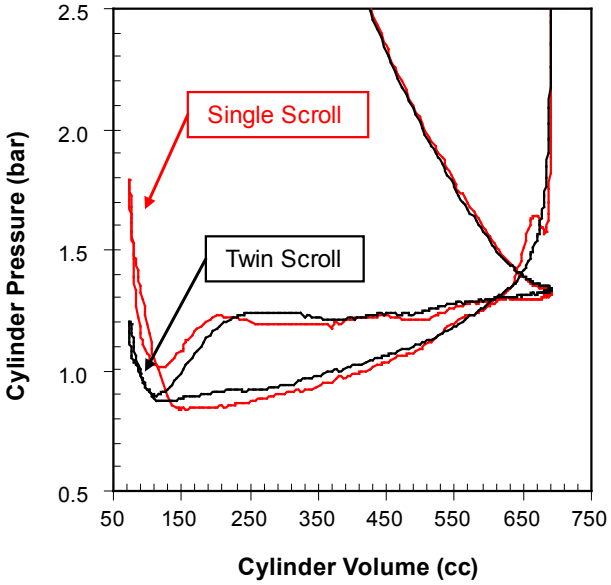

FIGURE 3. Effect of Twin-Scroll Turbochargers on Blowdown Interference on Cylinder 1

because the tendency to knock is reduced. As shown in the top two plots of Figure 4, E85 consumption is reduced by more than 50% by retarding combustion phasing by about 13° crank angle from the phasing corresponding to optimal brake thermal efficiency (combustion phasing is characterized by the crank angle location where 50% mass fraction of the charge is burned). As shown in the bottom plot of Figure 4, this amount of retard also results in approximately the minimum combined brake specific fuel consumption (BSFC) of gasoline and E85 (corresponding to the minimum combined fuel flow).

The engine speed and torque for the conditions of Figure 4 correspond to an F-Series pickup towing a 15,500 pound trailer at 70 mph. As an example, an F-series dual-fuel vehicle could have a 9 gallon E85 tank and a 27 gallon gasoline tank. Using retarded combustion phasing, the range on the E85 tank would be twice that of the gasoline tank, so the customer would only have to refill the E85 tank at every other fill-up of the gasoline tank under these very heavy towing conditions.

Effect of Peak Pressure Structural Limit on Full Load Performance

Typically, automotive gasoline engines are designed with an engine structure capable of withstanding about 80 to 100 bar peak cylinder gas pressure. Because E85 has very high effective octane, optimal spark timing can be used and boost pressure can be increased. These factors result in much higher peak cylinder pressures. The engine for this study was designed for 150 bar peak

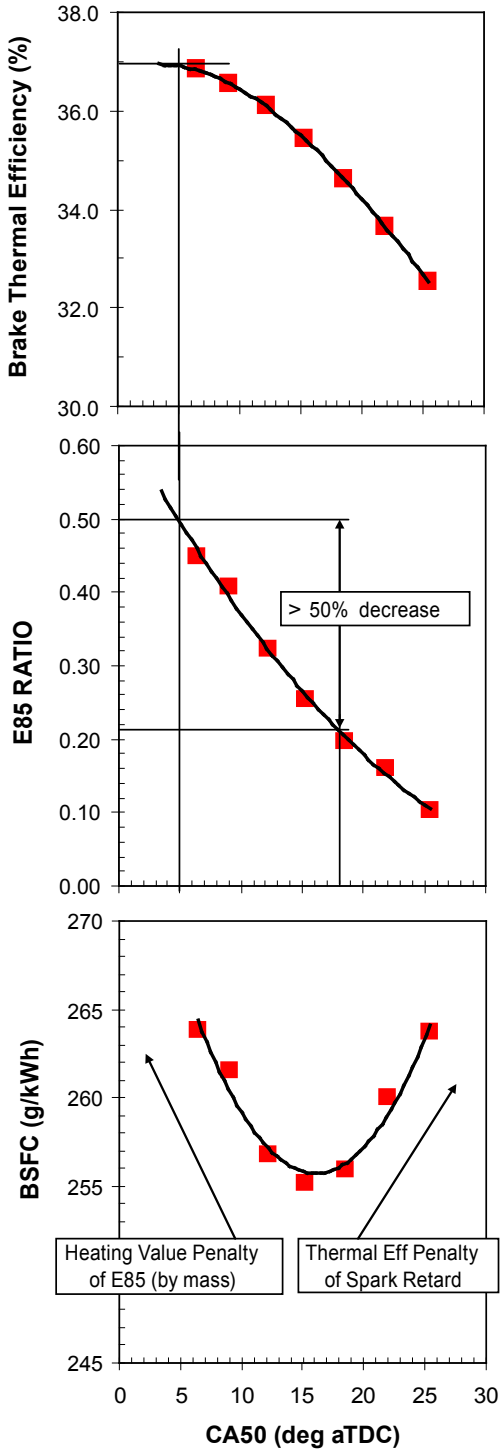

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FIGURE 4. Effect of Combustion Phasing Retard on Brake Thermal Efficiency, E85 Consumption, and BSFC under Heavy Towing Conditions

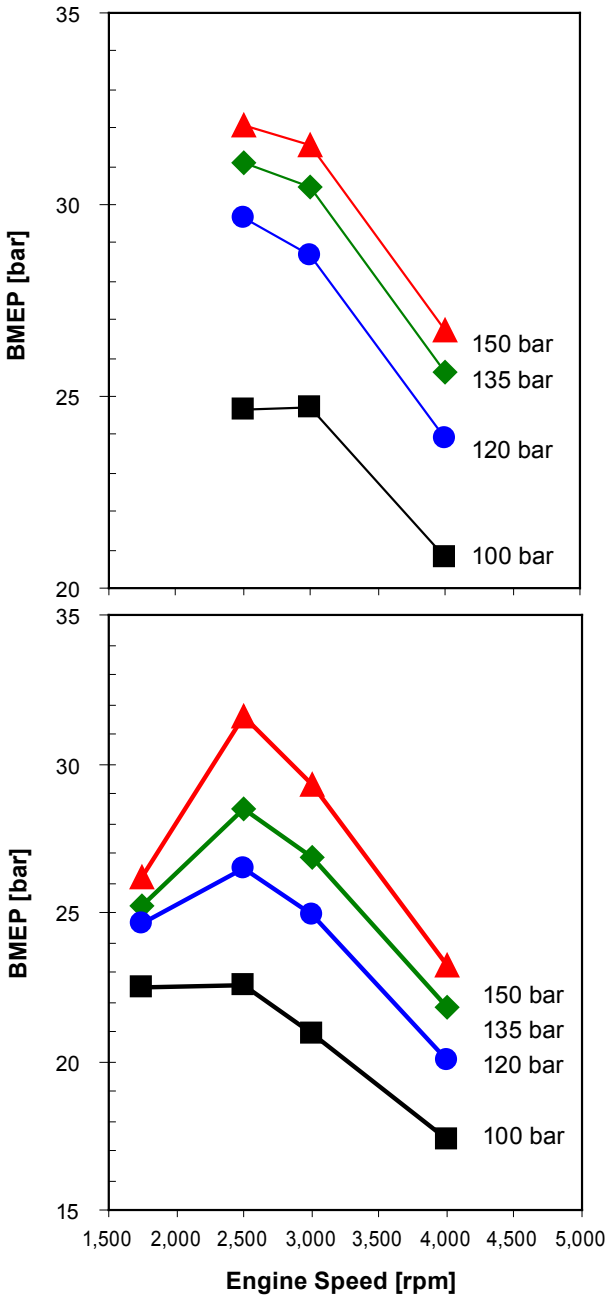

FIGURE 5. Effect of Peak Pressure Limit on Full-Load BMEP with E85 at Lambda 0.8 (top plot) and 1.0 (bottom plot)

pressure limit. However, there are trade-offs in terms of the peak pressure limit vs. the engine cost and possibly engine friction (due to larger bearing diameters, etc.). Additionally, modifying an existing engine to the dual-fuel concept may be limited in terms of the structural upgrades which can be implemented in the existing engine architecture. To investigate the effect of the peak pressure limit on full-load performance, data was acquired at various peak pressure limits at lambda values of 0.8 and 1.0 (Figure 5). As shown, there is a very large increase in full-load BMEP attained by increasing the peak pressure limit from 100 bar to 120 bar, and then lesser, but still significant increase in BMEP by further increasing the peak pressure limit.

Full-Load Performance Comparison of E85 to Gasoline at Stoichiometry

The full-load performance of E85 turbocharged direct injection (ETDI) was compared to that of GTDI at stoichiometry with a turbine inlet temperature constraint of 950°C and a peak pressure limit of 150 bar. At stoichiometry, ETDI provides about a 75% increase in BMEP across a broad speed range (Figure 6). At the lowest engine speeds, the BMEP for E85 was limited by the available boost of the turbochargers.

Conclusions

- Vehicle simulation results based on multi-cylinder engine data indicate that a dual-fuel engine can achieve fuel economy equivalent to a Diesel, but with lower CO_2 emissions and improved vehicle performance.
- Twin-scroll turbochargers significantly diminish the effects of V8 blowdown interference, and will be used for dual-fuel engine assessment at 12:1 compression ratio to make the results applicable to other engine configurations.
- Moderate combustion phasing retard substantially decreases E85 consumption of the dual-fuel engine and provides acceptable vehicle range under heavy towing conditions.
- The peak pressure limit of the engine structure directly affects the full-load performance which can be attained with E85.
- At stoichiometry and with a peak pressure limit of 150 bar, E85 provides about a 75% increase in full-load BMEP compared to gasoline.

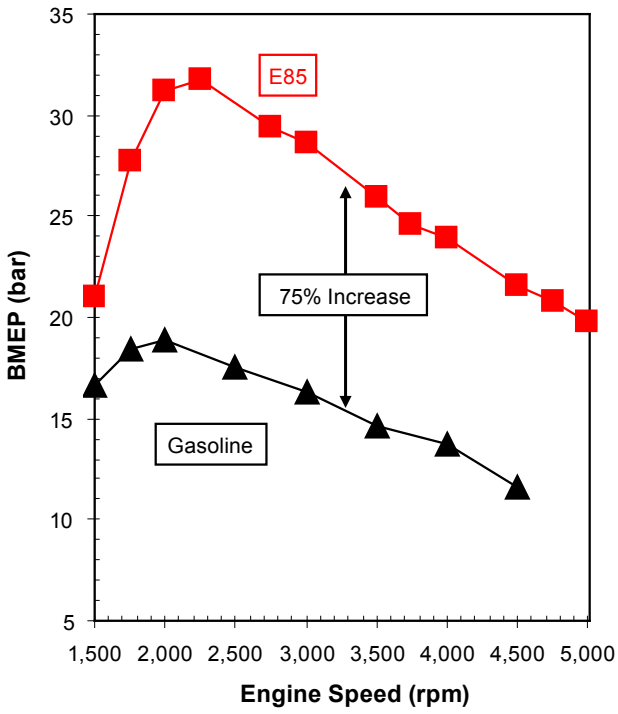

FIGURE 6. Full-Load BMEP Comparison Between ETDI and GTDI at Stoichiometry

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1. "Development of the Combustion System for a Flexible Fuel Turbocharged Direct Injection Engine", SAE Technical Paper 2010-01-0585.

2. 2010 DOE Merit Review.

IV.11 Optimally Controlled Flexible-Fuel Powertrain System

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Objectives

- Improve 85% ethanol in gasoline (E85) fuel efficiency by 10% with minimum performance penalties.
- Achieve low-emission vehicle (LEV)II and ultra-low emission vehicle (ULEV) level emissions with 100% gasoline and E85.
- Demonstrate flexible-fuel engine management system.

Fiscal Year (FY) 2010 Accomplishments

- The project has been completed successfully and the final report has been submitted.
- Optimized flexible-fuel engine achieved 420 N•m peak torque/295 hp peak power with E85 and 360 N•m peak torque/241 hp peak power with gasoline on an engine dynamometer.
- Optimized flexible-fuel powertrain approach resulted in 10% and 12% fuel economy improvement with E85 compared to baseline production-level engine in a city and highway drive cycle respectively as indicated by the simulation models correlated with prototype engine and vehicle test data.
- LEVII-ULEV emissions standards were achieved with E0 and E85 over the Federal Test Procedure (FTP)-75 drive cycle on a chassis dynamometer.
- Closed-loop spark control and combustion phasing optimization using extremum seeking via in-cylinder pressure sensor were developed for efficient combustion with various ethanol fuel blends.
- Ethanol detection and fuel system diagnosis via exhaust gas oxygen and in-cylinder pressure sensor fusion was developed.
- Proposed control algorithms were validated at engine dynamometer using rapid prototyping, and integrated into the Bosch MED17.3 engine control unit (ECU).

Future Directions

- The project demonstration vehicle will remain at Bosch for customer and media events to promote flexible-fuel concepts.
- Discussions with Oak Ridge National Laboratory are in progress to support their internal projects with the flexible-fuel vehicle (FFV) project prototype engine and Bosch's engine control/system expertise.

Introduction

Although today's FFVs are capable of running on gasoline-ethanol fuels, their powertrain and engine management systems are not designed to fully exploit the potential benefits from such fuel flexibility. Instead, the main goal of the current control calibration for FFVs is to improve the cold-start performance [1]. Apart from the cold-start problems, the lower combustion heating value of ethanol fuels results in higher fuel consumption (lower miles/gallon). Nevertheless, ethanol fuels also possess some advantageous properties such as higher octane number and the increased latent heat of vaporization (LHV) that could lead to higher knock resistance and stronger charge cooling effects, respectively. With a properly designed engine management system that can exploit these advantageous properties, the use of ethanol fuels in combination with the current development of turbocharged downsized engines, direct injection, and variable valve timing can improve vehicle performance and mitigate the fuel consumption penalties associated with high ethanol content fuels [2,3]. Therefore, the primary objective of this study is to develop an optimized FFV, targeting substantial fuel economy improvement with minimum driveability and fuel consumption penalties using a direct injection turbocharged spark ignition engine.

Approach

This project, through a four-phase approach, addresses the necessary engine optimization, modeling, control design and calibration, and vehicle-level implementation and verification.

Fuel Efficiency and Performance

In order to exploit the potential of the higher knock resistance in ethanol fuels, the engine simulation model was used to evaluate engine performance, such as output torque and knocking behavior, with different engine designs. As shown in Table 1, the flexible-fuel optimized engine has a higher compression ratio of 10.67:1 and an increased maximum cylinder pressure of 130 bar. Despite the benefits exploited from fuels with high ethanol content, the performance of an engine with a higher compression ratio will, in the mean time, suffer from more severe knocking with gasoline. In this study, a late intake valve closing strategy, realized by an intake cam phaser with increased authority of 100 degrees crank angle (degCA) and a modified intake cam profile with extended open duration, was employed to mitigate the associated knocking problem by reducing the effective compression. In addition, a vehicle-level simulation model was developed and correlated with prototype engine and vehicle testing data in order to exploit the fuel economy improvement potential of transmission optimization.

TABLE 1. Baseline Ecotec and Flexible-Fuel Optimized Engine Configuration

	Ecotec	Flexible-Fuel Optimized
Displacement	2.0 L	2.0 L
Compression Ratio	9.25:1	10.67:1
Maximum Cylinder Pressure	100 bar	130 bar
Intake Cam Phaser Authority	60 degCA	100 degCA
Intake Cam Open Duration	288 degCA	324 degCA

Emissions

Following the novel strategy proposed in [4], this project aimed to achieve LEVII-ULEV level emissions with the implementation of a multi-injection control strategy, the modification of piston bowl design and exhaust system layout, and the optimization of injection spray targeting. In addition, the potential of wastegate control for catalyst light-off performance improvement was also evaluated.

Advanced Engine Control Development

In order to compensate the effects of varying fuel properties on combustion, adaptive engine controls were developed to (a) estimate the ethanol content of a gasoline-ethanol fuel blend, and (b) optimize combustion for the detected fuel blend by adjusting critical control variables. Figure 1 illustrates the overall architecture and key domains of advanced development for flexible-fuel engine controls.

Control-Oriented Modeling: Control-oriented models of the flexible-fuel engine system were developed to capture the dynamics of the air and fuel paths, and the effects of spark timing and amount of internally recirculated exhaust gas on cycle-to-cycle combustion performance.

Combustion Controls: The proposed closed-loop combustion control strategy independently adjusts the spark timing of each cylinder so that the 50% mass fraction burned (CA50) position, estimated from cylinder pressure measurements, can located at the optimum value. In addition, an Extremum Seeking (ES) controller was developed to adapt the optimum CA50 position set-points, stored in the calibration map for feedforward control, to optimize combustion for various ethanol fuel blends.

Ethanol Detection: Inspired by the significant difference in the LHV between gasoline and ethanol, an approach was developed to extract a detection feature that could indicate the charge cooling effects of the injected fuel from the cylinder pressure measurements. In order to extract the charge cooling effects of the injected fuel, a unique injection mode that switches between single and split injection for a specific cylinder is introduced. During single injection, all the demanded fuel is injected during the intake stroke when the influences of the charge cooling effects on the cylinder pressure are compensated with additional air charge. During split injection, a fraction of the fuel is injected during the intake stroke, while the rest is injected during the compression stroke after the intake valve is closed. A detection feature, r_{LHV}, is then introduced to capture the difference in cylinder pressure evolution during single and split injections.

Fuel System Diagnosis: Derived from the fuel vaporization property, r_{LHV} provides an independent monitoring feature, in addition to stoichiometric air-to-fuel ratio, for fuel system diagnosis. Using the measurements from the cylinder pressure and exhaust gas oxygen sensors, a systematic algorithm was developed in this study to isolate a fuel system fault occurred during the conventional exhaust gas oxygen sensor-based ethanol detection process.

Results

Results that are accomplished in the areas of fuel efficiency and performance, emissions, and engine controls in this project are presented. A project prototype vehicle, as shown in Figure 2, was built to demonstrate the potential of the proposed flexible-fuel optimized powertrain technologies.

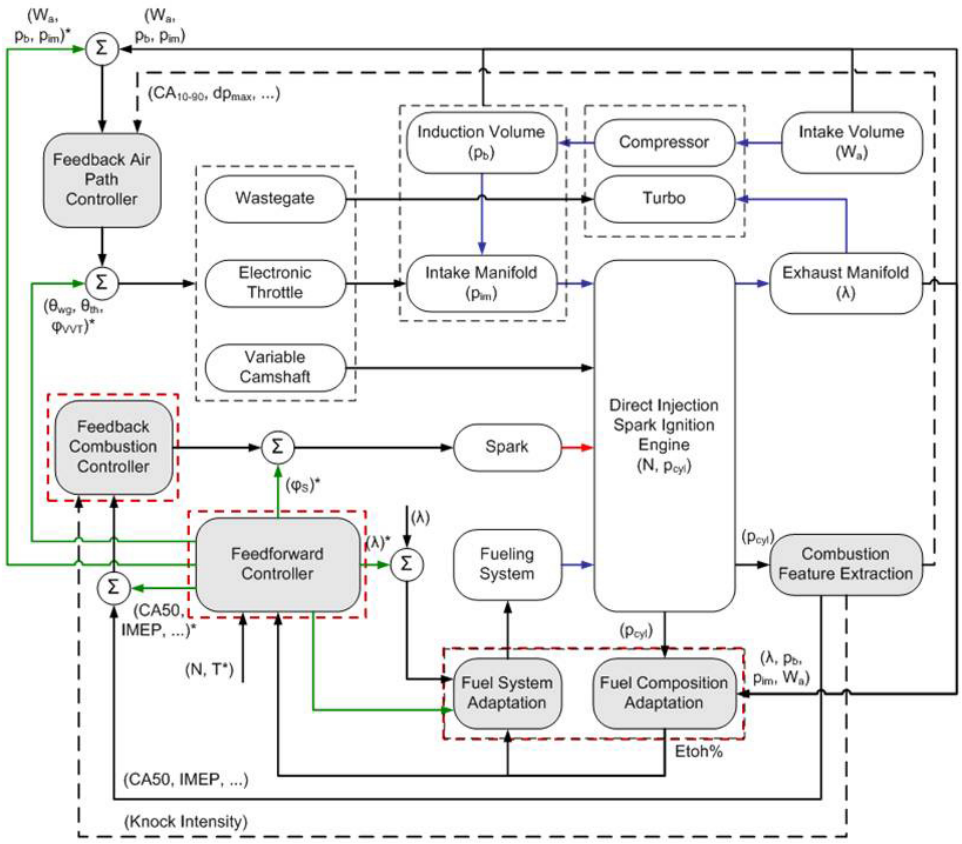

FIGURE 1. Block Diagram Illustrating the Proposed Engine Control Architecture

FIGURE 2. Advanced Flexible-Fuel Vehicle Project Demonstration Vehicle

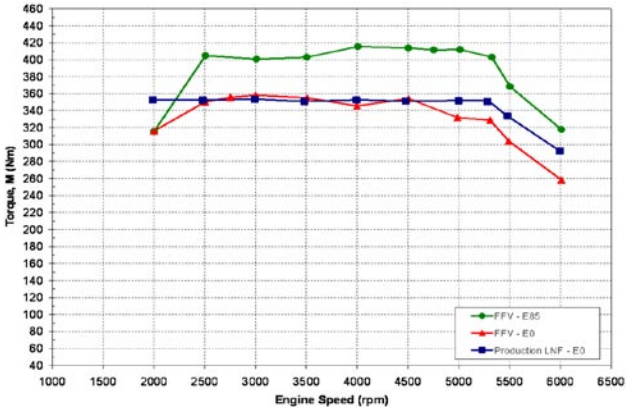

FIGURE 3. Flexible-Fuel-Optimized Engine Performance with Gasoline and E85

Fuel Efficiency and Performance

The flexible-fuel-optimized engine was calibrated for gasoline and E85 on the engine dynamometer at Bosch. Figure 3 illustrates the engine performance of the flexible-fuel-optimized optimized engine with E0 and E85, in comparison to the baseline Ecotec engine with gasoline, at full-load conditions. The flexible-fuel-optimized engine achieved 420 N•m peak torque/295 hp peak power with E85, and 360 N•m peak torque/241 hp peak power with E0 on an engine dynamometer.

In order to exploit the benefits of the improved full-load performance of the flexible-fuel-optimized engine, a powertrain optimization study was conducted using a vehicle-level simulation model for the target vehicle platform that was correlated with engine/vehicle

testing data. As shown in Table 2, the flexible-fuel-optimized powertrain along with the optimized engine and a reduced final drive ratio of 2.90 can still achieve a comparable vehicle performance running on E85. Due to the down-speeding effects associated with the reduced final drive ratio, the optimized powertrain is able to achieve 10% and 12% fuel economy improvement (Table 3), compared to the baseline vehicle with the Chevrolet HHR engine and final drive ratio of 4.05, during the FTP City and US06 Cycles, respectively.

TABLE 2. Vehicle-Level Performance Simulations for the Chevrolet HHR

		HHR*	HHR	HHR	FFV	FFV
		E0	E85/E0	E85/E0	E85	E0
Final Drive Ratio		4.05	4.05	2.90	2.90	2.90
0-60 mph	s	6.2	6.59	6.75	6.13	7.16
0-100 mph	s	15.1	15.63	16.00	13.87	16.82
1/4 mile	s	14.8	15.15	15.18	14.63	15.61
1/4 mile	mph	99	98.50	97.65	102.74	96.50

*EPA Published Data for 2008 HHR SS

TABLE 3. Potential Fuel Economy (FE) Improvement with Powertrain Optimization

	FTP City Cycle (mpg)		ΔFuel Economy (%)	US06 Cycle (mpg)		ΔFuel Economy (%)
	Optimized	Baseline		Optimized	Baseline	
E85	21.59	19.5	10.7	32.36	28.8	12.4
E0	29.83	27.5	8.5	44.62	40.2	11.0

Emissions

The flexible-fuel prototype vehicle was tested on the chassis dynamometer at Bosch to conduct an emissions study with California Phase 2 Gasoline, E85 and E77 using an aged super-low emission vehicle (SULEV) catalyst over the FTP City Cycle. The SULEV catalyst, provided by General Motors, is SULEV-capable and aged to full useful life (150,000 miles). The emissions results in Table 4 show that the flexible-fuel prototype vehicle achieved the project target of LEVII-ULEV standards. Moreover, the prototype vehicle demonstrates great potentials in achieving LEVII-SULEV standards.

Advanced Engine Control Development

Implemented in Simulink, the control-oriented models take the engine speed and critical control commands such as variable valve timings and spark timing as inputs. The developed model is able to capture the engine dynamics and the combustion behaviors.

TABLE 4. FTP Emissions for the Chevrolet HHR with Flexible-Fuel Optimized Engine

Catalyst	Test/Fuel	NMHC	CO	NOx	CO_2
		(g/mile)	(g/mile)	(g/mile)	(g/mile)
SULEV, Aged	20°C FTP/E77	0.021	0.281	0.010	333
LEVII-ULEV Standards		0.055	2.100	0.070	
LEVII-SULEV Standards		0.010	1.000	0.020	

Equipped with Kistler 6125B cylinder pressure sensors, the Bosch MED17.3 ECU provides real-time information of the combustion phasing (e.g. CA50) and output torque (e.g. indicated mean effective pressure). Using CA50 as the combustion phasing indicator, a closed-loop phasing indicator controller was implemented to adjust the spark timing based on the optimum CA50 set-points. In order to adapt the different combustion behavior of ethanol fuels, an ES controller was implemented to calibrate in real-time the optimum CA50 set-points for best fuel economy based on net specific fuel consumption. Figure 4 shows the ES controller behavior from one of the experiments during which the engine was operated at 2,000 RPM at varying load conditions and the spark was retarded to trigger the optimization. It can be observed that the ES controller is able to optimize the spark timing to achieve the minimum net specific fuel consumption in the presence of varying engine load.

It has been observed during the experiments that the LHV-based ethanol detection feature, r_{LHV}, has a monotonic correlation with the ethanol content over a wide range of commonly-visited operation points. In this study, a linear regression model was developed to capture such a correlation, in which parameters were mapped in terms of engine speed and load. Figure 5 illustrates the ethanol content estimation errors based on the LHV-based feature using the regression model at various engine conditions ranging from 1,500 RPM up to 2,500 RPM. Despite the saturation behaviors of r_{LHV} for fuels with less than 10% or more than 75% ethanol content, r_{LHV} provides a desired ethanol detection accuracy around 5%. Deriving from fuel vaporization behavior, r_{LHV} can also be employed to improve the fuel system reliability, especially during the ethanol content estimation process. Figure 6 illustrates a simulated experiment at the engine dynamometer when a 10% fuel injector drift occurred during the ethanol detection process with E55. To investigate the convergence behavior, the initial value of LHV-based ethanol detection algorithm was set to E0. It can be observed that with the integration of the LHV-based feature, the

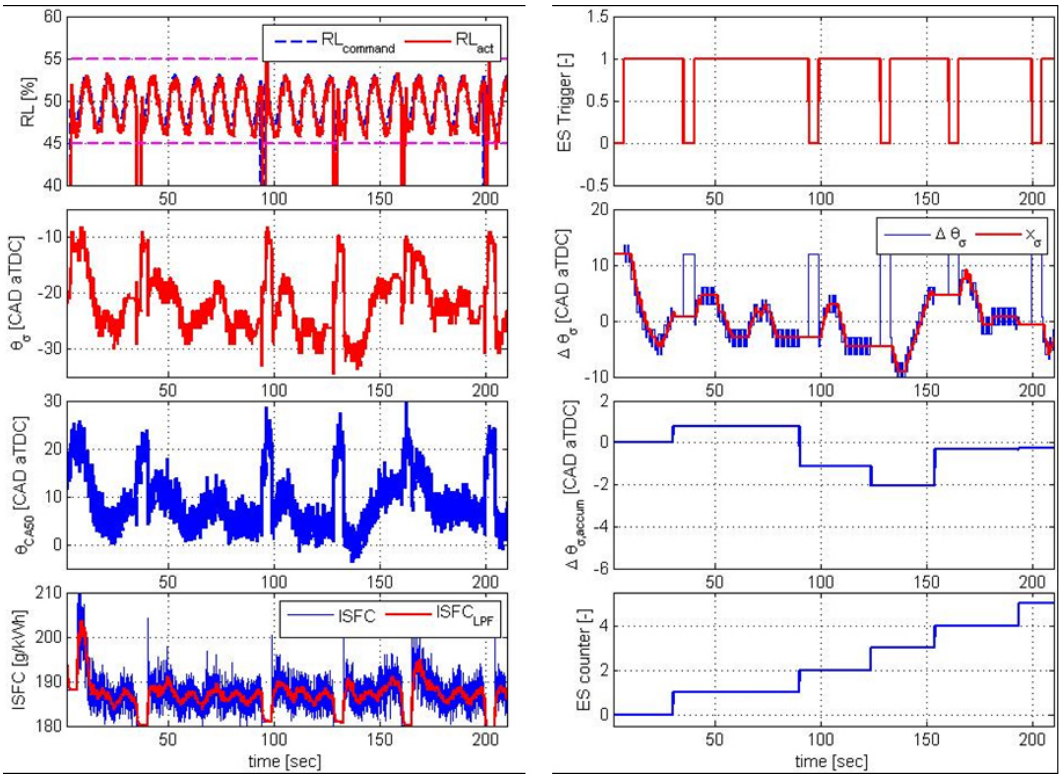

FIGURE 4. Extremum Seeking Controller Performance for Combustion Phasing Optimization

engine management system is able to better isolate the fuel system error from a fuel change.

Bosch Engine Control Unit Development

This study employs the latest Bosch MED17.3 ECU, capable of acquiring and processing real-time cylinder pressure measurements, in order to exploit the potentials of cylinder pressure sensing technologies and investigate the challenges in its implementation. Validated at the engine dynamometer using rapid prototyping techniques, the proposed combustion control and ethanol detection algorithms, along with the base flexible-fuel engine control functionalities, were integrated into the ECU software.

Conclusions

- The flexible-fuel-optimized engine with an increased compression ratio of 10.67:1, increased maximum cylinder pressure of 130 bar, and modified intake cam valvetrain for late intake valve closing strategy achieved 420 N•m peak torque/295 hp peak power with E85 and 360 N•m peak torque/241 hp peak power with gasoline at the engine dynamometer.
- The flexible-fuel-optimized powertrain with a reduced final drive ratio of 2.90 running on E85 achieved 10% and 12% fuel economy improvements, as indicated by the simulation model correlated with engine/vehicle testing data, compared to the baseline vehicle over the city and highway cycles.
- The flexible-fuel prototype vehicle achieved LEVII-ULEV standards with E0 and E85 over the FTP City Cycle.
- Advanced flexible-fuel controls including closed-loop spark control, combustion phasing optimization using extremum seeking, ethanol detection and fuel system diagnosis using LHV-based detection features were validated on an engine dynamometer.

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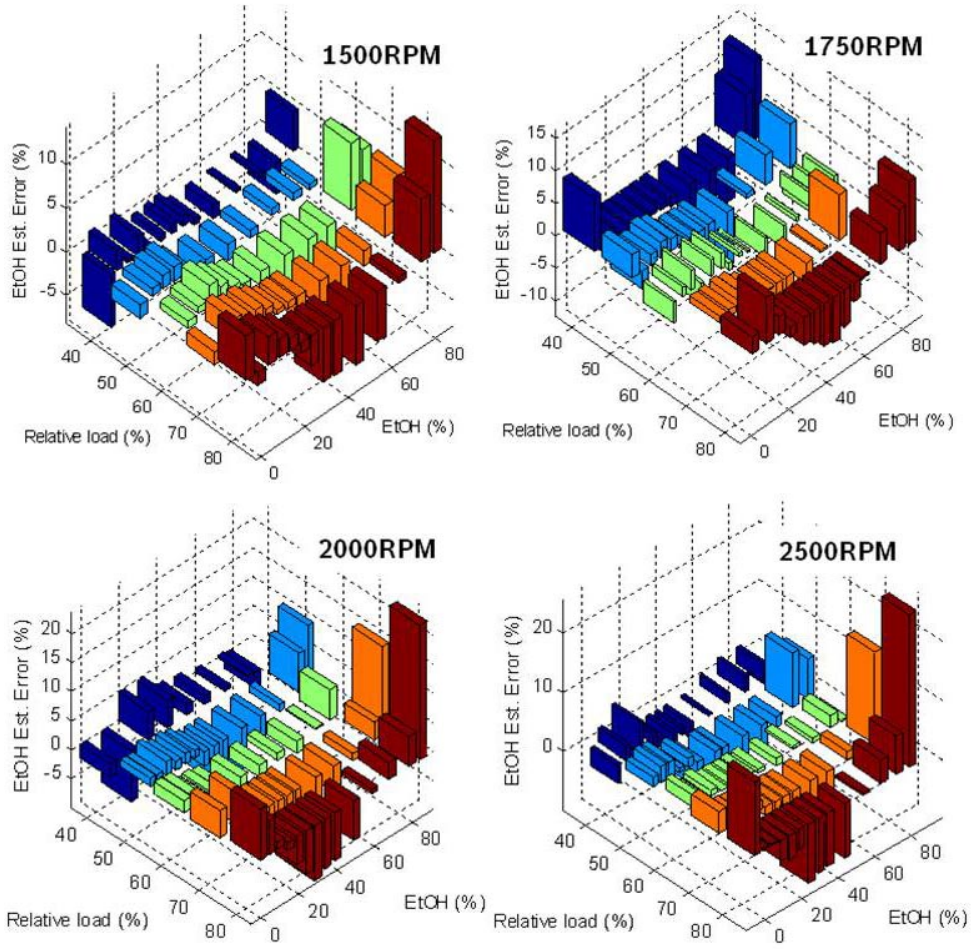

FIGURE 5. Ethanol Content Estimation Performance of LHV-Based Detection Feature

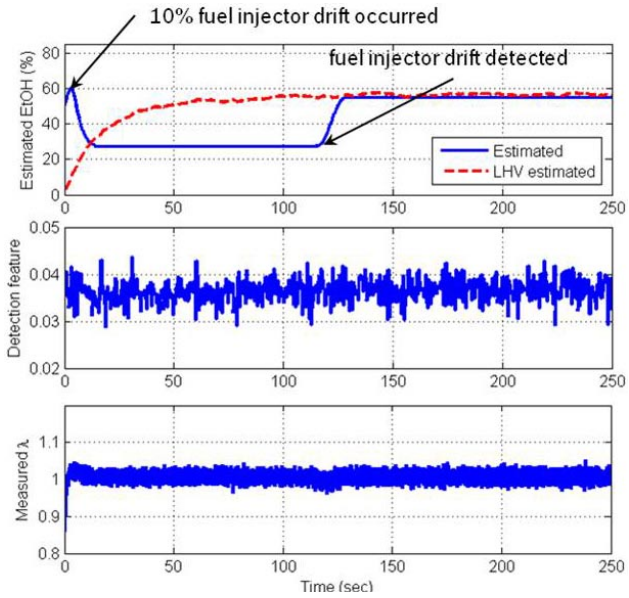

FIGURE 6. Fuel System Diagnosis Performance of LHV-Based Detection Feature

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2. D. Lee, L. Jiang, H. Yilmaz, A. Stefanopoulou, "Air Charge Control for Turbocharged Spark Ignition Engines with Internal Exhaust Gas Recirculation", In Proceedings of *2010 American Control Conference*, Baltimore, MD, June 30-July 2, 2010.

3. L. Jiang, K. Ahn, H. Yilmaz, A. Stefanopoulou, M. Christie, "Optimally Controlled Flex-Fuel Vehicle", In Proceedings of 10th Stuttgart International Symposium, Stuttgart, Germany, March 16-17, 2010.

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5. D. Lee, L. Jiang, H. Yilmaz, A. Stefanopoulou, "Preliminary Results on Optimal Variable Valve Timing and Spark Timing Control via Extremum Seeking", In Proceedings of *IFAC Symposium on Mechatronic Systems*, Cambridge, MA, September 13-15, 2010.

Special Recognitions & Awards/Patents Issued

1. Pending US Patent, "Fuel Composition Recognition and Adaptation System", Serial Number 12/417240.

IV.12 E85 Optimized Engine through Boosting, Spray-Optimized GDi, VCR and Variable Valvetrain

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Subcontractor:
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Objectives

- Develop an engine strategy optimized for ethanol operation using higher compression and compression management through valvetrain control.
- Identify interactions with subsystems for injection, ignition and valvetrain.
- Design and build engine hardware required.
- Develop controls strategies for the optimized engine.
- Demonstrate benefits of new hardware and refine engine operation.

Fiscal Year (FY) 2010 Accomplishments

- Testing was conducted on the multi-cylinder engine developed to utilize effective compression ratio management utilizing an advanced valvetrain. Two-step variable valve actuation with dual independent cam phasing provided effective load and compression ratio control. Accomplishments include:
- Cam optimization using 85% ethanol in gasoline (E85) over the speed/load domain of 1,000-3,000 RPM using early intake valve closing (EIVC), 1,000-4,000 RPM using late intake valve closing (LIVC) which provided a 5-12% improvement in ethanol fuel economy versus the baseline engine running on ethanol.
- Comparison of valve train control strategies from idle to peak load at 2,000 RPM for E85 and gasoline which identified 3-5% additional fuel economy improvement at loads <5 bar brake mean effective pressure (BMEP).
- Cam and controls optimization utilizing single valve deactivation with EIVC for total fuel economy improvement of 8-20% over baseline.
- Evaluation of injection timing optimization strategies for gasoline and soot-prone blends.
- Evaluation of the influence of single valve deactivation on efficiency and emissions for E0 and E20, providing up to 95% particulate reduction.
- Evaluation of intermediate ethanol blends on control optimization, emissions and performance.
- Computational fluid dynamics (CFD) evaluation of the mechanisms that produced improved combustion stability and reduced soot for valve deactivation at select operating conditions.
- Optical engine study of the in-cylinder charge motion and its influence on sprays for dual- and single-valve operation.
- Vehicle simulation of the fuel economy resulting from the improved E85 engine and from the additional engine down-speeding enabled by improved low end torque.
- Control system refinement to support multiple injections.

Future Directions

- Utilize instrumentation to improve soot measurement capability.
- Optimize multi-pulse fuel injections to minimize particulate emissions concentrating on gasoline and lower ethanol blends.
- Integrate transient control of new valvetrain strategies.

Introduction

E85-capable vehicles are normally equipped to run the higher levels of ethanol by employing modified fuel delivery systems that can withstand the highly corrosive nature of the alcohol. These vehicles are not however equipped to take full advantage of ethanol's properties during the combustion process. Ethanol has a much higher blend research octane number than gasoline and latent heat of vaporization. These properties allow the use of higher engine compression ratios and spark advance which result in more efficient engine operation. An engine that is optimized for operation on high concentrations of ethanol therefore will have

compression ratios that are too high to avoid spark knock (pre-ignition) if run on gasoline or a gasoline/ethanol blend that has a low percentage alcohol. The intent of this project is to optimize a production-based engine to take full advantage of ethanol's high octane and high latent heat of vaporization. The engine will however be capable of running gasoline/alcohol blends of E85 to E0 by employing variable effective compression ratio accomplished through cam phasing and variable valve actuation. The goals are therefore to demonstrate improved efficiency (minimized fuel consumption) while operating on E85 without losing capability of operating on any gasoline/alcohol blend and maintaining good drivability and ability to meet emissions requirements.

Approach

Improvements in E85 fuel economy are accomplished through increased compression ratio and variable valve actuation. A higher compression ratio is enabled by the high octane number of ethanol fuels as well as their high heat of vaporization. Early intake valve closing enables high efficiency and variable valve actuation provides unthrottled load control over 80-90% of the Federal Test Procedure (FTP). To avoid knock with gasoline caused by the higher compression ratio, the variable valve actuation mechanization is used to produce a lower effective compression ratio. The variable valvetrain system, comprised of Delphi's Dual Independent Cam Phasing and Delphi's 2-Step Valve Train, enable unthrottled operation for improved fuel economy as well as the lower effective compression ratio for the lower octane gasoline blends.

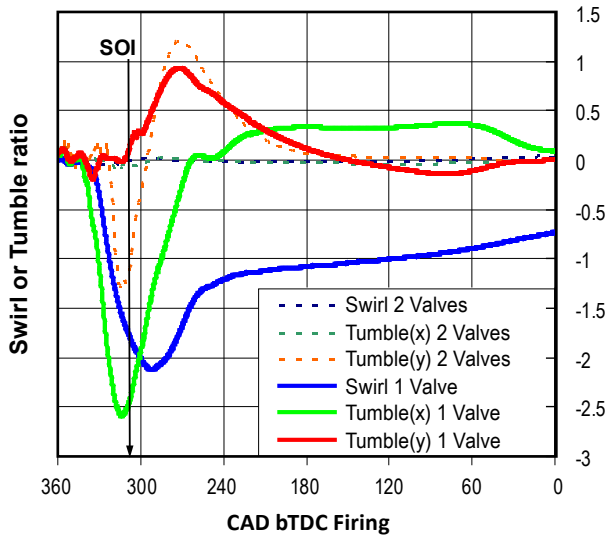
Results

CFD Simulation

The influence of valve deactivation was investigated with CFD to quantify the effect on in-cylinder charge motion, mixing and fuel interaction with the combustion chamber. Results indicate that valve deactivation provides significantly increased swirl and cross tumble (Figure 1) which results in spray deflection and reduced fuel films that lead to particulate and unburned hydrocarbon formation.

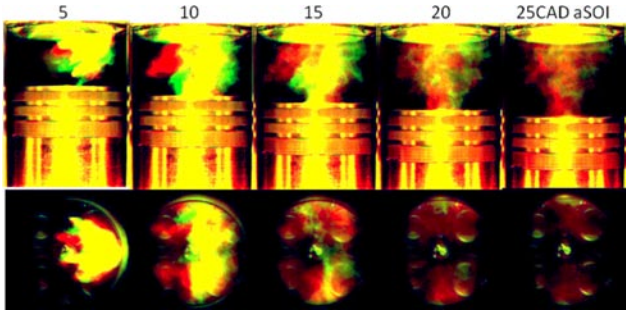
Optical Engine Testing

Optical engine test results compared the effects of valve deactivation on in-cylinder charge motion and spray development. Significantly more complex flow structures were observed which produced spray deflection (Figure 2) and reduced impingement under most conditions.



SOI - start of injection; CAD - crank angle degrees; bTDC - before top dead center

FIGURE 1. Dynamic Ratios EIVC 2,000 RPM 2 Bar BMEP



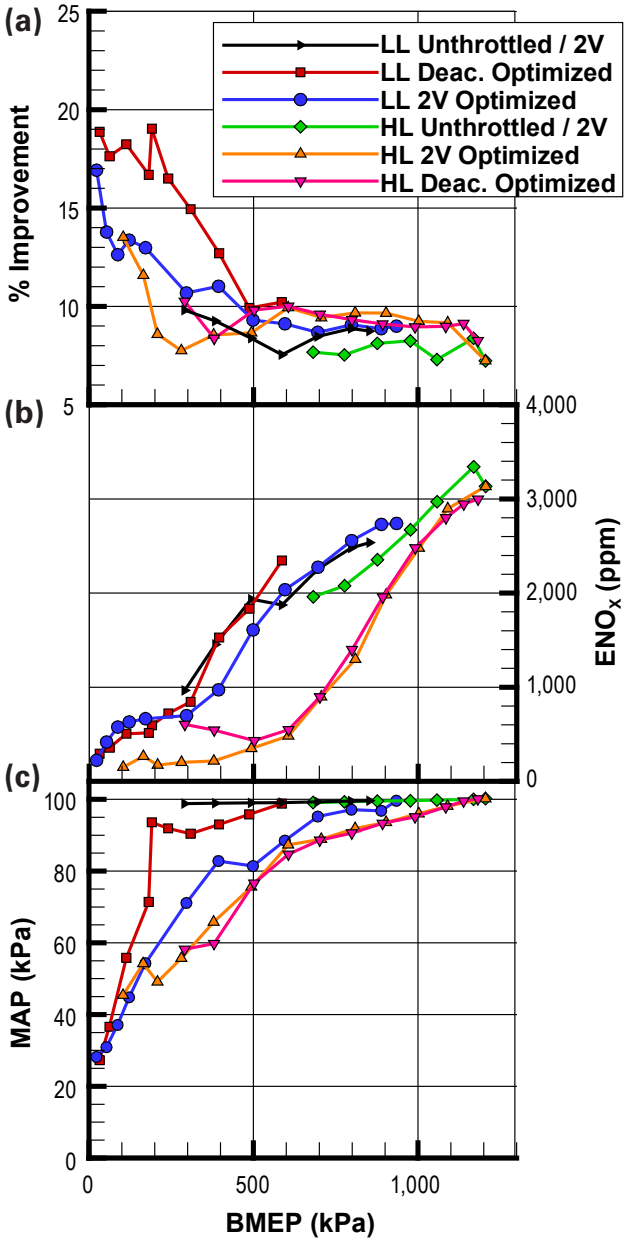
aSOI - after start of injection

FIGURE 2. False Color Comparison of Spray and Droplet Cloud, 2 Valves (Red), 1 Valve (Green)

Multi-Cylinder Engine Testing

To optimize engine efficiency and emissions, EIVC and LIVC were evaluated with and without valve deactivation. The preferred operating mode at low load (<6 bar) was EIVC with valve deactivation for E85 and gasoline. Two-valve LIVC operation optimized for internal residual control was preferred for E85 at high loads. Figure 3 shows a comparison of strategies using E85 at 2,000 RPM. A speed load map of the improvement in efficiency over the base engine with E85 is shown in Figure 4. Several areas at low load exceed 20% due to the reduction of throttling loses, residual management and injection timing optimization.

Unthrottled LIVC operation using gasoline at high loads to minimize internal residuals and combustion knock resulted in significantly higher oxide of nitrogen (NOx) emissions. Soot when using gasoline was also



LL - low load; HL - high load; 2V - two valve; MAP - manifold absolute pressure

FIGURE 3. 2,000 RPM Load Sweeps, E85 Fuel, Evaluation of Valvetrain Control Strategies: (a) Improvement in fuel consumption (thermal efficiency) over base engine; (b) NOx Emissions; (c) Map showing reduced throttling

an issue at high-load, low-speed operation. Valve deactivation with LIVC could be used to reduce soot.

Fuel Blend Evaluation

Fuel blends from gasoline up to E85 were evaluated for sensitivity to injection timing, exhaust gas recirculation tolerance, knock resistance and peak torque. By adjusting the effective compression ratio

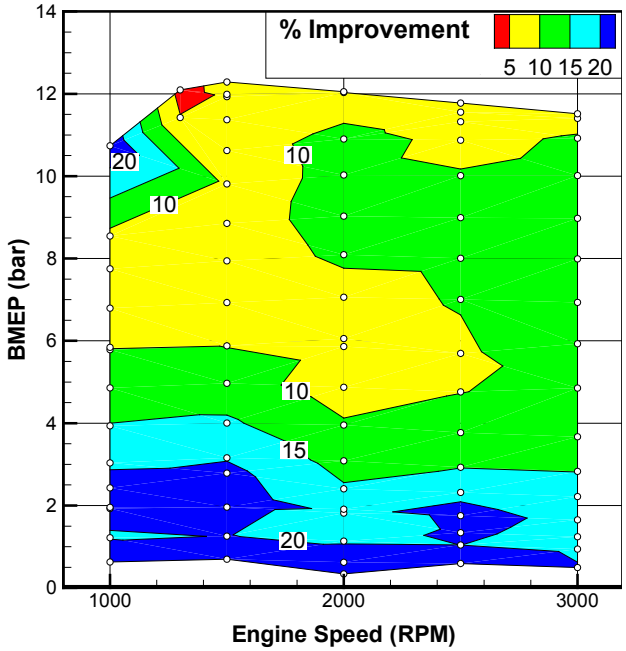


FIGURE 4. E85 Speed Load Map Showing Relative Thermal Efficiency Improvement over Base Engine Data

using the valvetrain, knock could be controlled for all fuels. Increasing ethanol content significantly increased the low-load, knock-limited torque of the engine. Figure 5 shows the knock-limited torque without spark retard and the knock-limited effective compression ratio. E50 and E85 did not knock under any conditions.

Vehicle Simulation

GT DRIVE was used to evaluate vehicle level fuel economy utilizing the test data from the E85 optimization. Transmission selection, final drive ratio and shift schedules were evaluated to best leverage the low-end torque capability of E85 through engine down-speeding. The reduction of fuel consumption was most significant under mild drive cycles and was reduced as loads increased, Figure 6.

Conclusions

System Optimization

E85 allowed knock-free operation at all operating conditions and enabled greater calibration optimization due to high resistance to soot formation and residual gas. The use of light throttling for internal residual control was preferential to unthrottled operation resulting in lower NOx and fuel consumption.

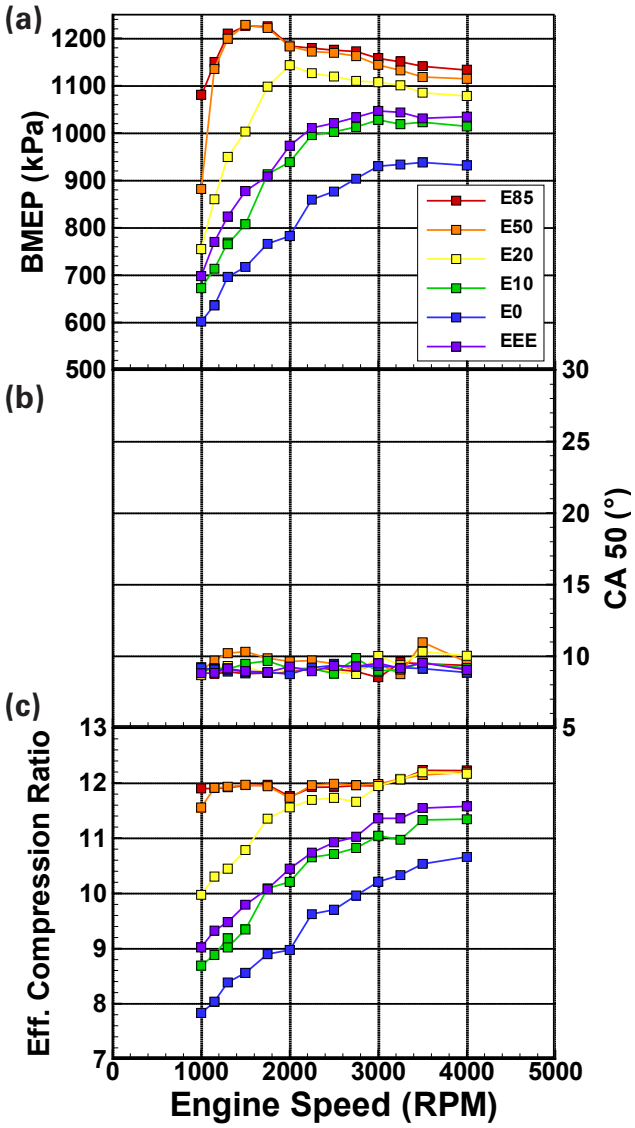


FIGURE 5. 1,000-4,000 RPM, LIVC Cam: (a) Knock limited load; (b) Combustion phasing (CA50); (c) Knock-limited compression ratio

Valve Deactivation

The use of valve deactivation enabled improved efficiency at loads <6 bar BMEP with EIVC. Valve deactivation at higher loads with LIVC was effective at reducing particulate and unburned hydrocarbon emissions with gasoline and E20 blends.

Intermediate Ethanol Blends

- E85 was resistant to soot formation allowing earlier injection timings.
- Gasoline and intermediate blends up to E50 had similar injection timing constraints due to soot formation.

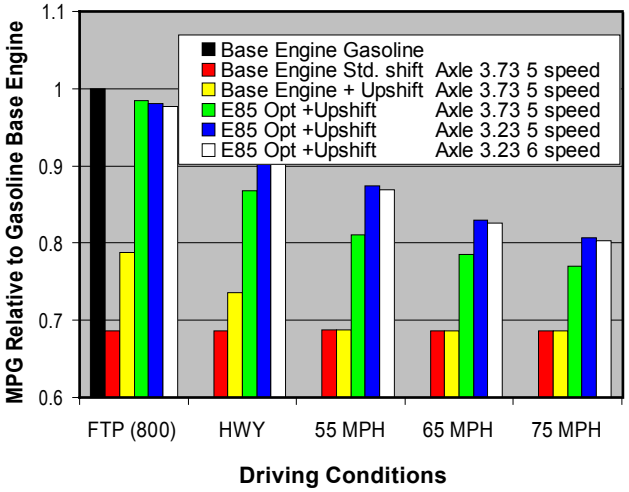


FIGURE 6. Relative Fuel Economy to Base Engine Operating on E85 for Various Operating Modes and Effect of Transmission, Axel Ratio and Shift Strategy

- Unburned hydrocarbons and NOx formation were reduced with increasing ethanol content.
- E20 provided significant knock resistance with minimal energy penalty providing the lowest BSFC at high loads.
- E20 provided 97% of the peak torque capability of E85 with a favorable energy tradeoff allowing improved performance with equivalent or better fuel economy.
- Increasing ethanol content allowed the use of higher internal residual trapping to reduce NOx without knock.

Vehicle simulation

Low-load operation, (FTP City cycle) with aggressive down-speeding can offset the majority, (80% +) of the E85 energy density penalty. For higher loads and speeds the reduction in the energy penalty was less than 50%.

FY 2010 Publications/Presentations

1. A paper was written on the CFD, optical engine and multi-cylinder engine work. It will be presented at SAE Congress in 2011: *Charge motion benefits of valve deactivation to reduce fuel consumption and emissions in a GDi, VVA engine.*

2. A paper was written on the projects multi-cylinder engine work and will be presented at SAE Congress in 2011: *Engine Efficiency Improvements Enabled by Ethanol Fuel Blends in a GDi VVA Engine*

IV.13 Investigation of Biodiesel-Fueled Engines under Low-Temperature Combustion Strategies

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Objectives

- Study the effects of spray angle on engine performance and emissions.
- Optimize engine control strategies for biodiesel/diesel blends with the concept of low-temperature combustion (LTC).
- Investigate, using experiments and numerical simulations, the potential benefits of using ternary blends of n-butanol, diesel and biodiesel.
- Exploit properties for water emulsified fuel for engine application.
- Develop a subset of physical properties from ASTM International standards and safety considerations for evaluating blends of biofuels and petroleum diesel fuel.

Fiscal Year (FY) 2010 Accomplishments

- Enabled simultaneous reduction of oxides of nitrogen (NO_x) and soot emission up to 88.5% and 44.1%, respectively with combined heavy exhaust gas recirculation (EGR) and modified injection strategy comparing to the default engine control strategy.
- Initiated optical experiments on spray and combustion characteristics for ternary blends of butanol, diesel and biodiesel with different blending ratios.
- Studied the effects of fuel, ambient temperature and pressure on droplet micro-explosion.
- Evaluated and achieved stable water-containing emulsified fuel up to 20% volumetric ratio.
- Determined which properties are most vital for a fuel to work within the design constraints of a fuel injection system allow guidelines to be set for formulating blends of biofuels and petroleum diesel fuel that still meet ASTM standards.

Future Directions

- Apply butanol/diesel, butanol/biodiesel blends and emulsified fuel in a direct injection engine using optimized engine control strategy.
- Seeking combined technology in terms of both engine control and fuel properties to further reduce engine emissions.
- Analyze the combustion and emission characteristics of water-containing emulsified fuel and explore the potential micro-explosion phenomena of fuel sprays in engines.
- Develop micro-explosion model(s) for heterogeneous nucleation.
- Evaluate the fuel property limits set from ASTM standards by measuring the physical properties of blends of biofuels and petroleum diesel fuel and by combusting these fuels in an engine to analyze combustion and emission phenomena.

Introduction

Due to the concern with the possible energy crisis in the future from the current high level of consumption of non-renewable fuels as well as more stringent emission regulation enforced by the governments around the world, the share of biofuels in the automotive fuel market is expected to grow rapidly over the next decade. The utilization of current and future biofuels is required to meet exhaust gas emission standards (European standard: EURO 5/6 [1] and U.S. standard: Tier 2 Bin 5 [2]) and be produced in a technically and economically efficient way, i.e. with high conversion rates and costs which are competitive with fossil fuel [3], therefore optimization of the biofuel application in the engine is crucial to its future usage.

Our research falls mainly into two categories: optimizing engine control strategies for biofuel combustion and reduced emissions and evaluating biofuel properties to ensure compatibility with mainstream engine technologies. Conventional EGR has been proved to reduce NO_x emissions effectively, but will cause higher soot emissions, known as the soot-NO_x tradeoff. The LTC concept has been introduced by using heavy EGR combined with modified injection strategies so that the fuel will be injected into a much lower ambient temperature environment, thus reducing NO_x and soot emission simultaneously. Numerical simulations were also applied to study the effects

of different fuel injection and operation strategies. Meanwhile, the selection of the biofuel is of great importance. Traditional fuel injectors limit flexibility in designing injection strategy. Therefore, the application of a variable cone angle spray was examined and its effects on engine performance analyzed.

Butanol is of particular interest as a renewable biofuel, since it is less hydrophilic and has higher heating value, higher cetane number, lower vapor pressure, and higher miscibility than ethanol or methanol, making it preferable to ethanol or methanol for blending with diesel fuel in a direct injection engine. The addition of butanol to diesel fuel, however, also reduces fuel density, viscosity, and cetane number. In order to maintain a stable mixture and acceptable properties for use in diesel engines, biodiesel was added to effectively compensate for these property changes. Therefore, the ternary blends of n-butanol, diesel and biodiesel were studied. As the volatilities and boiling points of butanol and diesel/biodiesel are significantly different, micro-explosions, which improve the atomization process, can be expected in the mixture. A numerical model of micro-explosions for multi-component biofuel droplets was developed.

Approach

Steady-state engine dynamometer experiments were performed on four different biodiesel-diesel blends in a production compression-ignition engine to determine optimized engine control module (ECM) settings for each fuel. The work focused on a combination of EGR ratio and start of injection timing, as these parameters were easily modified and had significant effects on engine emissions. Tests were run at low to moderate engine load at different engine speeds.

The investigations of the spray and combustion characteristic of the ternary blends of n-butanol, biodiesel and diesel were conducted in a constant volume chamber at various ambient conditions with different laser diagnostic methods applied. Mie scattering was used for liquid penetration and spray cone angle measurement, natural flame luminosity was used to provide insights into flame structure and lift-off while forward illumination laser extinction was used to generate a two-dimensional time-resolved soot distribution during the combustion process. Emulsified fuel containing water was also prepared and studied by adding multi-surfactant and water for the investigation of micro-explosion phenomena. The water-in-oil bubble diameter was measured with a 400X microscope.

A modified three-dimensional KIVA combustion modeling code was also used to simulate engine operations under various fuel injection and operational conditions. The fuel library was extended to include the properties of soybean biodiesel, determined with BDProp. The multi-component model was incorporated, thus allowing computations of fuel blends. LTC and ignition were described by the Shell model. A micro-explosion model describing the three crucial steps in micro-explosion of a droplet: bubble generation, bubble growth and breakup, was developed.

Results

Optimizing Engine Operation: With the ECM's default settings, higher blends of biodiesel tended to result in higher NO_x emissions and lower soot emissions. Also, increasing the EGR ratio to account for the different stoichiometric air-fuel ratio of biodiesel was effective in bringing NO_x emissions to similar or lower levels compared with those of petroleum diesel. At low-load conditions, improved fuel economy could be achieved by advancing the start of injection relative to the ECM default timing. By using an objective function, the optimal engine operation conditions under different engine speed, engine load, and fuel blends were determined from the and experimental and simulation results. Different EGR ratios and injection timings were tested to optimize the engine performance. The tradeoff between NO_x emission and fuel consumption was evaluated and optimal injection timing was established for various fuel compositions.

Pure soybean biodiesel was run with high rates of EGR and modified injection schemes in order to achieve simultaneous reduction of NO_x and soot emissions consistent with LTC. At low-load conditions, increasing the EGR ratio to high levels was sufficient to achieve very low NO_x and soot emissions. As engine load increased, high levels of EGR brought NO_x emissions to very low levels, but soot emissions increased substantially. The amount of EGR was increased to the point of combustion deterioration without causing a reduction in soot emissions. Thus, the engine's default injection strategy needed to be modified in order to achieve LTC. Effective strategies were a reduced amount of pre-injection, later main injection timing, and a combination of the two. With these strategies, LTC was achieved through a moderate range of engine load. Figure 1 demonstrates the trade-off of soot and NO_x emissions for pure biodiesel, confirming that optimizing engine control can reduce soot and NO_x simultaneously. Modifications to the injection strategy were found to be beneficial at different engine speeds.

Variable Spray Angle Injection Technology Application: Further improvements in combustion and the reduction of emissions were achieved by altering the spray angle. Combustion from the initial injection was consistently predicted by KIVA for all the fuel blends using variable cone angle injection with a micro-variable circular orifice (MVCO) due to faster evaporation of fuel and better combustion as shown in Figure 2 and in improved indicated specific fuel consumption (ISFC),

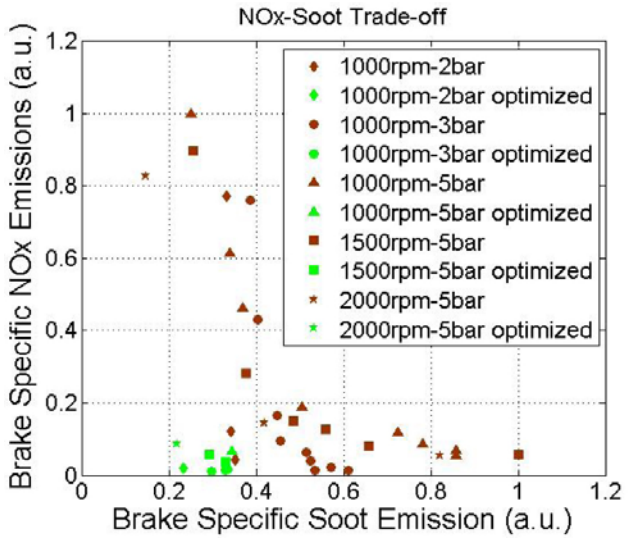

FIGURE 1. Normalized soot and NOx trade-off under various engine load and speed.

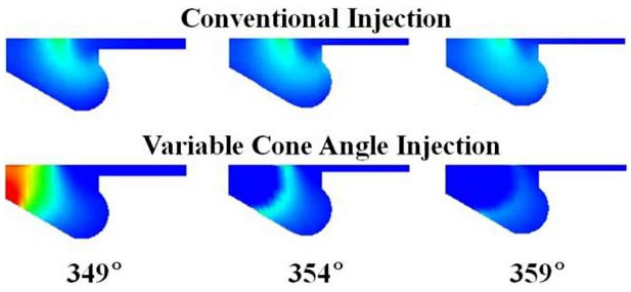

FIGURE 2. In-cylinder fuel distributions at 349°, 354° and 359° crank angles for both conventional and variable cone angle injections for main injection at 360° crank angles. Red color indicates high concentration of fuel vapor.

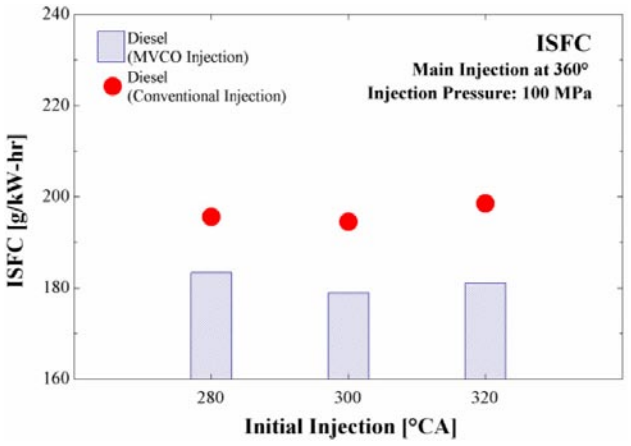

FIGURE 3. Comparison of indicated specific fuel consumption with conventional and variable cone angle injections for main injection at 360°.

as shown in Figure 3. The magnitudes of the initial heat release for biodiesel and its blends were lower than that of diesel. Therefore, main combustion occurred at a lower ambient temperature within the combustion chamber upon main injection. Consequently, lower NO_x emissions were realized. Soot emission was reduced and the trend was consistent with the general observation. With better fuel economy and lower emissions, further investigation of operating the engine using variable cone angle injection injectors and blends of biodiesel could be conducted for possible low-emission operations.

Micro-Explosion of Biofuel-Diesel Blends:
The spray and combustion images acquired by laser diagnostic methods indicate that the liquid penetration decreased with the increase of ambient temperature and n-butanol volume percentage. A sudden drop of the spray tip penetration, which might be related to micro-explosion, was observed in the spray evolution at low cylinder temperature of 800 K and 900 K for certain fuel blends. The heat release rate demonstrated the transition from total mixing controlled combustion at high ambient temperature to premixed combustion mode at low ambient temperature. At lower cylinder temperature, the increasing n-butanol volume in blends resulted in longer ignition delays due to the lower cetane number of butanol while virtually no difference was observed at the high cylinder temperature condition since the elevated chemical reaction became the dominant factor. Also, the total soot emissions increased as cylinder temperatures increased. By adding n-butanol, soot emissions were significantly reduced and mainly concentrated at the near downstream for the entire cylinder temperature range compared with neat diesel as shown in Figure 4, though the n-butanol additive reduced soot emissions more effectively at higher temperature.

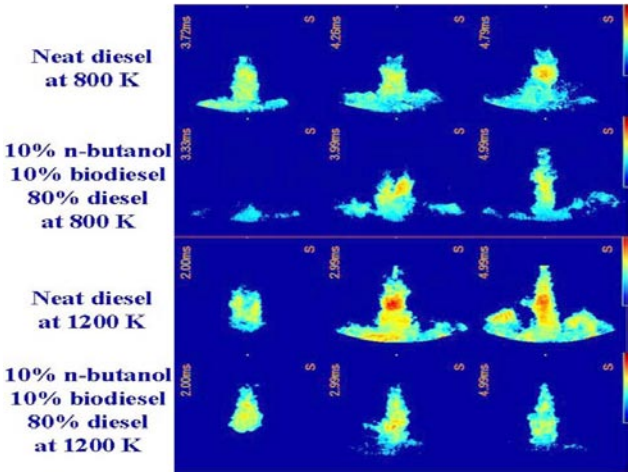

FIGURE 4. Soot distribution for different fuel under different cylinder temperature conditions.

Micro-explosions are known to enhance atomization and reduce both soot and NO_x emissions [4]. To confirm the micro-explosion phenomena in the fuel jet, the prepared water-containing emulsified fuel was tested in the same optical chamber. Broadband flame luminosity images with low injection pressure revealed glowing spots exploding from the liftoff at the near downstream of the fuel jet (Figure 5) which were very likely caused by the micro-explosion. Such glowing spots were observed neither in neat diesel combustion, nor with emulsified fuel combustion at high injection pressure, which indicated that lower injection pressure might favor micro-explosion in a fuel jet. Further investigations are currently underway. A set of calculations was done on butanol-biodiesel, and butanol-biodiesel-diesel droplets at different conditions. Figure 6 shows the effect of ambient pressure on micro-explosion. Two different fuel blends are tested: 20% butanol-80% soybean biodiesel (B20S80) and 20% butanol-60% soybean biodiesel-20% diesel (B20S60D20). The ambient temperature is 2,300 K, which is the typical adiabatic flame temperature of hydrocarbon. The normalized onset radius (NOR), the ratio of droplet radius at the onset of micro-explosion to the initial droplet radius, characterizes the onset of micro-explosion. A large NOR implies that micro-explosion is more likely to take place and vice versa. The droplet size decreases upon evaporation while the nucleation process is initiated. Therefore, micro-explosion can be characterized by the NOR, assuming that the time elapsed between the onset and final breakup of the droplet is negligible relative to the droplet lifetime. The NOR represents the possibility of micro-explosion: micro-explosion is likely to occur with large NOR. It is seen, from Figure 6, that the optimal cylinder pressure is about 10 atm for both butanol-biodiesel and butanol-biodiesel-diesel blends under the specified conditions. The slope of the curve decreases as pressure increases and eventually becomes negative at very high pressure. Bubble nucleation may be suppressed at very high ambient pressures that suppresses the likelihood of micro-explosion. Figure 6 shows that for the same amount of butanol composition, increasing soybean biodiesel favors micro-explosion because of the higher boiling point of biodiesel. Therefore, as shown in the figure, replacing soybean biodiesel with petroleum-based diesel diminishes the possibility of micro-explosion, i.e. NOR reduces. It is concluded from additional calculations that micro-explosion is less likely to occur for droplets evaporating at high ambient temperature because of the rapid evaporation of droplet. The minimal initial droplet radius to undergo micro-explosion will decrease with increasing ambient pressure and ambient temperature, and it also confirms that micro-explosion is possible in the typical engine operation condition based on this model..

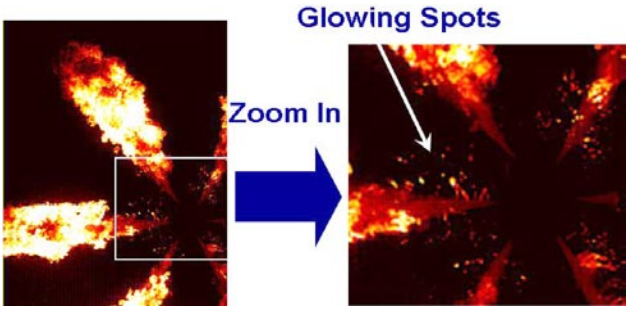

FIGURE 5. Potential micro-explosion phenomena observed in emulsified fuel combustion under low injection pressure.

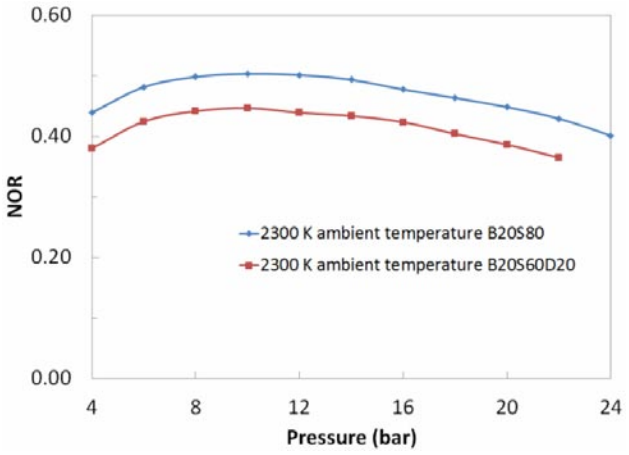

FIGURE 6. Effect of cylinder pressure on micro-explosion for a fuel droplet with 300 μm initial radius, 2,300 K ambient temperature.

Biofuels Property Measurements: The fuel blending properties selected from ASTM standards that are critical to evaluating the suitability of a fuel for use in a diesel engine encompass several areas of importance. These include handling and safety, cold flow, blend stability, material compatibility, wear prevention, and combustion. For biodiesel fuel, the kinematic viscosity, cloud point, pour point, cetane number, and boiling point all show an interesting trend tend to be higher than for diesel fuel, while the alcohols tend to be lower than diesel fuel. Blending of biodiesel with alcohols should be beneficial in being able to balance the properties of these fuels. The energy content of a fuel blend containing any oxygenated biofuel will typically be lower than that of petroleum diesel fuel. In addition, outside of materials compatibility, corrosiveness, and lubricity, butanol appears to be a more favorable fuel when compared to ethanol. The properties of butanol show it is more closely aligned to diesel fuel than ethanol.

Conclusions

- Through adjusting the EGR ratio and start of injection, the engine control strategies were

optimized for different biodiesel-diesel blends under a variety of operating conditions. Trade-offs of NO_x and soot emissions, and brake specific fuel consumption were evaluated.

- LTC conditions were reached by coupling a high rate of EGR with modified injection strategies which lowered both NO_x and soot emissions.
- The optimal EGR ratio and injection timing under different engine operating conditions are given based on the objective function calculation. Further improvements are possible by using variable cone angle injection.
- Combustion of the ternary blend of n-butanol, biodiesel and diesel showed significant reduction in soot emissions compared with neat diesel.
- Micro-explosion might occur in the ternary blends, improving atomization and reducing emissions. The combustion of water emulsified fuel could potentially help prove the existence of micro-explosion in a fuel jet.
- ASTM fuel standards for petroleum diesel fuel can be used to develop property criteria that can be used to determine the suitability and blending limits of biofuels.
- Comparing the properties of diesel fuel, butanol, ethanol, and biodiesel showed that the properties of the biofuels can differ significantly from diesel fuel and will put a limit on how much biofuel can be used in an engine with current design specifications.

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3. Huo, M. and C.F. Lee, "Spray/Wall Impingement inside the Needle Orifice Nozzle of an Expansion Valve," Proceedings of the 13th Annual Conference on Liquid Atomization and Spray Systems-Asia, Wuxi, China, Oct. 2009.

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IV.14 Unconventional Hydrocarbon Fuels

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Objectives

- Ensure a transparent transition of fuels derived from unconventional hydrocarbons into the market by developing a fundamental understanding of 'fit for service' properties.
- Develop analytical tools to characterize fuels derived from unconventional hydrocarbons, and chemistry-based predictive models to support future advanced combustion/emission technologies.

Fiscal Year (FY) 2010 Accomplishments

- Continued work identifying molecular structures utilizing advanced analytical techniques, e.g., nuclear magnetic resonance (NMR), gas chromatography field ionization mass spectrometry (GC-FIMS) and 2-dimensional gas chromatograph (2D-GC) analysis, which have a significant ability to correlate with diesel-range fuel lubricity.
- Sourced oil shale-derived crude and established a contract with Intertek to provide a stabilized distillate fuel in a #1 and #2 diesel fuel boiling point range which will be used to support the alternative fuels subcommittee commitment to the Coordinating Research Council (CRC) Fuels for Advanced Combustion Engines (FACE) project.
- Carried out initial work at Intertek with raw oil shale to determine our ability to catalytically stabilize the product with mild hydrotreating. Began utilizing the advanced analytical techniques described above to characterize the stabilized shale oil for degree of unsaturation and other properties.
- Completed NMR characterization of nine FACE fuels in conjunction with NMR, GC-FIMS and 2D-GC/mass spectrometer analysis by Oak Ridge National Laboratory (ORNL) and Natural Resources Canada laboratories. Samples were submitted for engine tests.
- Worked to develop the working relationship with JM Consulting to develop the 'Fit for Service' refinery/blending model, which incorporates chemistry-based 'fit-for-service' correlations with a refinery model which identifies issues with the use or blending of unconventional distillate streams or fuel products with conventional products.

Future Directions

- Produce oil shale-derived distillate #1 and #2 diesel-like fuels for the CRC FACE alternative fuel subcommittee; measure lubricity and seal swell.
- Conduct property analysis and performance tests of the oil shale-derived fuels and distillate streams.
- Continue development of a refinery/blend model to predict fuel chemistry expected from unconventional hydrocarbon blends.
- Continue to coordinate the interaction between Canada Centre for Mineral and Energy Technology and Natural Resources Canada on analytical correlation of fuel properties and material compatibility investigations.
- Continue collaborative work with the CRC alternative fuels FACE subcommittee.
- Begin acquisition of biomass-derived pyrolysis oil samples to extend the analysis and correlation chemistry to bio-based fuels.

Introduction

The objective of this project is to ensure that our chemical knowledge of future, unconventional fuels is sufficient to support advanced combustion research as well insure compatibility, i.e., 'fit for service' with existing engine technology. Future diesel fuels derived from unconventional resources, e.g., oil sands, oil shale, Fischer-Tropsch coal-to-liquid/gas-to-liquid and biomass, can exhibit significantly different chemistries and molecular structures from conventional hydrocarbon resources. Because of strict fungibility requirements for pipeline transportation, distribution of unconventional hydrocarbon fuels will possibly be limited to regional areas, resulting in high concentrations of fuels with various combinations of unconventional hydrocarbons entering the fuel market. A preliminary investigation into bulk properties, e.g., cetane, have shown correlations based on conventional fuels to be unreliable predictors for unconventional

fuels. Therefore, chemistry and structural differences can result in unpredictable problems with engine and fuel system components, as well as impact the understanding of advanced combustion and after-treatment research. PNNL will investigate NMR correlations for bulk properties and 'fit for service' issues of these unconventional fuels, e.g., lubricity and seal swell, along with other infrastructure and material compatibility issues such as cold temperature performance, crankcase oil compatibility and storage stability, that could be devastating to the introduction of fuels derived from unconventional hydrocarbon resources. This will eliminate industry's dependence on costly and empirically-derived engine and rig tests which have poor predictive capabilities with regard to material performance in new engine fluids.

Approach

This project was initiated by collaborative workshops between DOE and Canadian national laboratories to discuss the introduction of unconventional hydrocarbon fuels [1]. The workshops identified areas for collaboration based on key knowledge gaps and application of the expertise and analytical tools at national laboratories to gain fundamental insight. PNNL focused on $^{1}H/^{13}C$ NMR analysis which provides very specific structural information regarding hydrocarbon mixtures which then can be related to both physical and chemical properties of the fuel. Since NMR can quantitatively resolve specific carbon types, e.g., methyl (CH_3), the data can be easily adapted to additive functional group correlations which should be more robust with respect to a broad range of chemistries and molecular structures.

First, distillate fuels from unconventional hydrocarbon resources have been or will be acquired and upgraded as appropriate. Oil sands-derived distillate fuel streams have previously been obtained from Shell Canada. Oil shale samples have been obtained from Red Leaf, Inc. Distillate streams from this oil shale will be obtained by stabilizing the oil shale-derived crude and subsequently hydrotreating to a finished diesel-like product. Sources of hydrotreated biomass-derived pyrolysis oil feedstocks will be identified, and multiple gallon quantities acquired in FY 2011.

These fuels will be analyzed by both ^{1}H and ^{13}C NMR and the results combined with other advanced analytical techniques to develop new property correlations based on these data. Proprietary algorithms have been developed that allow hydrocarbon mixtures to be characterized by various molecular descriptors. In the literature these descriptors have been correlated with combustion properties, e.g., cetane and octane. However, the correlations, currently in the literature, may only be valid for the range of chemistries used to establish the correlation. To gain full benefit from the various analysis tools it is necessary to: 1) incorporate all analytical data sets into one format to assist advanced engine development and for fuel blending modeling; 2) establish property correlations to ensure engine system compatibilities with existing engines; and 3) expand molecular-based blending models to ensure the transparency of fuels from alternate feedstocks into the market.

Results

Stabilization of Shale Oil Fraction

Oil shale from Red Leaf was received by Intertek and exposed to mild catalytic hydrotreatment. This treatment was sufficient to stabilize the sample by removing the majority of olefinic and diolefinic species. The treatment was insufficient to remove S and N which would require more severe conditions and longer residence time. The olefinic CH/CH_2 species were removed by approximately 90% as revealed by NMR analysis. The stabilized material was distilled and separated into several cuts for NMR analysis.

NMR Analysis of the Stabilized Oil Shale Fractions

The processed shale oil samples in different boiling point ranges were provided by Intertek to PNNL. The samples were analyzed by PNNL and Process NMR Associates and characterized by ^{1}H and ^{13}C NMR. A sample ^{13}C spectrum derived from the stabilized shale oil is shown in Figure 1.

Lubricity

Lubricity was raised as a focal point as early as 2005 'fit for service' in advanced engines. The NMR and GC analytical techniques were used to gain additional insight into contradictory conclusions. High frequency reciprocating rig (HFRR) tests had been conducted on various oil sands-derived streams at conditions, i.e., 60°C/100 g load, which were less severe than the requirements established by the engine and fuel system manufacturers. However, HFRR tests conducted on selected fuels at 80°C/200 g load showed similar results. The GC-FIMS data showed a strong correlation with the high molecular weight (chain length) of the paraffins and isoparaffins in the distillate. The NMR data suggested a similar correlation to chain length and a negative influence from the number of branches (iso-paraffiins). The 2D-GC/MS analysis, which separates compounds by boiling point and polarity, provided the opportunity to investigate the influence of aromatics without the confusing direct relationship with paraffinic components. The 2D-GC/MS data showed a strong correlation with high molecular weight paraffinic structures. However, the correlation was improved significantly with the ratio

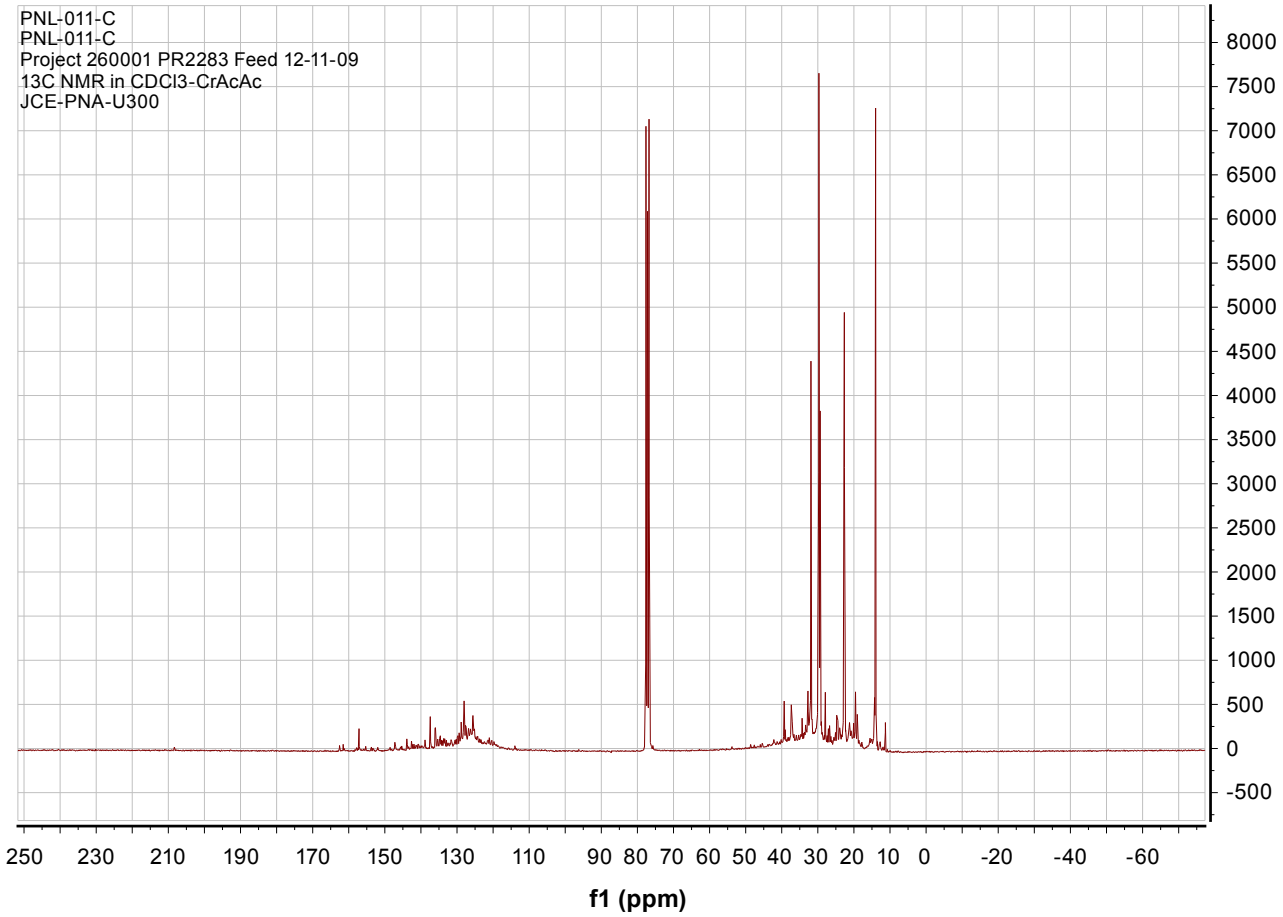

FIGURE 1. ^{13}C NMR of Shale Oil Sample following Stabilization Treatment to Remove Olefinic Species

of the paraffinic concentration/polar components. It is believed that the polar components are more strongly partitioned from the mixture to the metal surface. As a result the polar components successfully compete with the paraffinic components. If the polar components have poor lubricity properties it will diminish the lubricity of the fuel. However, as with additives, highly polar components with good lubricity properties, e.g., long paraffinic chain length, can enhance the lubricity of the fuel. These studies on lubricity of oil sands samples will be extended by similar correlations to the oil shale samples.

Conclusions

- Work on characterizing lubricity of diesel range fuels has been carried out using a combination of NMR, 2D-GC, and GC/MS techniques for samples derived from oil sands. This work is now being extended to unconventional fuels derived from shale oil.
- Advanced chemical analysis techniques identified high molecular weight paraffins as having a significant influence on lubricity; however, polar compounds can have either a negative or positive impact on lubricity.

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IV.15 Alternative Fuels Infrastructure Development

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Objective

To provide analysis of international alternative fuel use which supports alternative fuel infrastructure development in the United States.

Fiscal Year (FY) 2010 Accomplishments

Profiled the development of alternative fuels in Thailand with a concentration on ethanol production and use.

Future Directions

Conduct an analysis of 20% ethanol in gasoline (E20) use in Thailand concentrating on experiences which could benefit the introduction of E20 in the U.S.

Introduction

Gasohol has been commercially produced and sold in Thailand since 2001. The first product was E10. On January 1, 2008, E20 was introduced to the Thai market, and in the third quarter of 2008, E85 was available for consumers. The Thai government has set an aggressive target to increase ethanol production and its utilization as a fuel mix in order to reduce the country's importation of oil and petroleum products. Several measures have been put in place to encourage increased production of ethanol as well as increased consumption of ethanol content products. This research will help the U.S. understand the issues and experiences associated with the introduction of alternative fuels in other countries, and help the U.S. in anticipation of potential problems, especially as the U.S. has been considering introducing higher blends of ethanol into the U.S. market.

Approach

This research reviews the status of alternate transportation fuels development and utilization in Thailand.

Results

As of July 2010, there are a total of 19 commercial ethanol plants in Thailand, with total installed capacity of 2.925 million liters per day. This is 0.65 million liters per day more than last reported in October 2009, and 1.35 million liters per day more than what was reported in August 2008. Four additional ethanol plants are under construction with an additional capacity of 1.620 million liters per day with expected commencing dates between 2010 and 2011. The main feedstock for ethanol production in Thailand is molasses. Cassavas and sugar cane are also used, but in much lesser amounts.

The current blends of ethanol with gasoline in the Thai market are E10 with octane numbers of 91 and 95, E20 with octane number of 95, and E85 (85% of ethanol with 15% gasoline) with octane number of 95. Sales of gasohol in Thailand have been increasing continually since it was available in the market. The average sales of gasohol in 2009 were 12.21 million liters per day as compared to 9.22 million liters per day in 2008. The average gasohol sales from January to June 2010 were about 11.84 million liters per day (see Table 1). While sales of gasohol have continued to increase in the country, sales of gasoline have continued to decline. All gasoline sold in Thailand is unleaded with octane numbers of 91 and 95 (ULG 91 RON and ULG 95 RON). ULG 95 RON has been replaced by Gasohol 95 due to a large price difference between these two products. At present only the gas stations owned by Esso and Thai Oil are selling ULG 95 RON. Other gas stations replaced it with Gasohol 95.

TABLE 1. Gasohol Sales in Thailand (including E10, E20, and E85)

	Million Liter	Million Liter/ Day	% Change of Sales Per Day
2004	59.50	0.16	
2005	690.23	1.89	1081%
2006	1,279.30	3.50	85.2%
2007	1,762.76	4.83	38.0%
2008	3,391.73	9.22	90.9%
2009	4,456.44	12.21	31.4%
January-June 2010	2,141.16	11.84	

Source: Department of Energy Business (latest update in August 2010)

About 29.028 million liters of E20 were sold in 2008, and 83.4 million liters in 2009. The sales of E20 in 2010 from January to July were at a total of 72.5 million liters, or about 0.342 million liters per day, as compared to 0.228 million liter per day in 2009.

A total of 0.021 million liters of E85 were sold in 2008. Sales of E85 in 2009 were reported to be at 0.3 million liters. The latest information in 2010 recorded a total sale of E85 from January to July at 0.8 million liters, or about 0.004 million liter per day in 2010 as compared to about 0.001 million liter per day in 2009.

PTT and Bangchak are the major suppliers of gasohol in Thailand. As of July 2010, there are a total of 7,306 gasohol pumps across the country, 325 additional pumps from August 2009. The majority of these gasohol pumps are for E10 Octane 95 (4,131 pumps), and 2,787 pumps are for E10 Octane 91. Pumps for E20 increased from 234 in August 2009 to 381 in July 2010, and those for E85 increased from four in August 2009 to seven in July 2010 [1].

The government has structured oil pricing to make retail prices of gasohol lower than retail prices of gasoline, and gasohol with higher ethanol contents is less expensive than gasohol with lower ethanol contents. For example, Gasohol 95 is about 10 baht cheaper than gasoline of the same octane; the retail price of E85 is less than half of the retail price of gasoline ULG 95 RON; and the retail price of E85 is over 30% lower than the retail price of Gasohol 95. The retail prices of E10, E20 and E85 as compared to prices of gasoline selling in Bangkok and vicinity areas are shown in Table 2.

TABLE 2. Prices of Gasohol in the Bangkok Metropolitan Areas
Unit: Baht/Liter

	Oct 17, 2009	Sept 1, 2010
Gasohol 91 (E10 Octane 91)	29.74	29.14
Gasohol 95 (E10 Octane 95)	30.24	30.64
E20 (Octane 95)	28.24	28.34
E85 (Octane 95)	18.72	18.42
ULG 91 RON (Gasoline Octane 91)	34.24	34.44
ULG 95 RON (Gasoline Octane 95)	39.94	40.44

Note: On October 17, 2009, $1=33.385 baht, and on September 1, 2010, $1=31.288 baht
Source: Petroleum and Petrochemical Policy Bureau, Energy Policy and Planning Office, www.eppo.go.th/retail_prices.html

In 2009, E20 was recommended to be used on specific car models as suggested by the manufacturers, and only six automobile companies sold E20 capable cars–Ford, Honda, Mazda, Nissan, Mitsubishi and Toyota. As of September 2010, all new cars in the Thai market are E20-compatible, which made the demand of E20 increase rapidly. Gasohol suppliers are thus currently focusing their production and sales on E20 instead of E85. Effective since January 1, 2008, excise tax rates have been reduced for the cars capable of utilizing E20. More than 300,000 E20-compatible vehicles have been sold in Thailand so far.

As of August 2010, there are a total of 2,179 flexible-fuel vehicles (FFVs) being used in Thailand. Volvo has imported its FFV model, C30 1.8 F, to Thailand since the beginning of 2008. In November 2008, Volvo began to manufacture another FFV model, Volvo S80 2.5 FT, in Thailand. Mitsubishi launched an FFV, the Lancer EX, in Thailand in October 2009. Presently, FFVs are subject to an excise tax at the same rate as E20-compatible cars. The new measure under consideration is to waive the import duty on FFV auto parts.

E85 consumption has increased slowly considering the efforts from the government in keeping its price low. The slow increase of E85 consumption was due to the lack of FFV options in the country. Consumers also complained about insufficient E85 pumps which made it inconvenient for them to drive an FFV. Although FFVs can be fueled by E10 and E20, the consumers said that prices of FFVs especially the Volvo are too high that the savings from using E10 and E20 could not make up for the high prices of FFVs.

While consumers complained about insufficient E85 pumps, the gasohol suppliers complained that there was not enough demand of E85 for them to invest in more pumps at present, and they would increase more E85 pumps as E85 demand grew.

Conclusion

Thailand has continued to work to promote increased consumption of gasohol especially for high-ethanol content fuels like E85. The government has confirmed its effort to draw up incentives for auto makers to invest in manufacturing E85-compatible vehicles in the country.

The price subsidy and price control policies of the government have guaranteed gasohol prices to be below prices of gasoline, and made gasohol consumption increase continuously.

E20 demand has been growing rapidly as all new cars in the Thai market are E20-compatible.

Limited options for FFVs and limited E85 pumps in the country have caused slow progress in increasing E85 production and consumption. The government stopped tax privileges for imported FFVs, but confirmed its effort in promoting more domestically-manufactured FFV models. The high ethanol-content products like E85 are a prime focus of the government in order to meet their target of ethanol production of 9 million liter per day by 2022 as stated in the 15 Year Ethanol Development Plan (2008-2022).

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IV.16 Decision Analysis Tool to Compare Energy Pathways for Transportation

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Objectives

- To develop an agile decision-analysis tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies.
- To evaluate fuel and vehicle technologies on multiple criteria, including, greenhouse gas emissions, cost of transportation, energy security, and criteria pollutant emissions.

Fiscal Year (FY) 2010 Accomplishments

- A prototype model, Analytica Transportation Energy Analysis Model (ATEAM), was developed using the Analytica decision modeling environment, visualizing the structure as a hierarchy of influence diagrams.
- It enables evaluation of a wide-range of user-modifiable vehicle designs, including conventional internal combustion, flexible-fuel vehicles, hybrid-electric, plug-in hybrids (PHEVs), battery-electric vehicles, and hydrogen fuel cells.
- It includes a model of the U.S. vehicle fleet, and endogenous projection of market share among vehicle technologies based on their relative costs.
- It has demonstrated insightful results on the question of how many flexible-fuel vehicles need to be sold to consume the ethanol mandated by the Renewable Fuel Standard (RFS2), and the effect of the recent Environmental Protection Agency (EPA) approval of E15 for newer vehicles.
- It provides rapid definition and comparison of scenarios, sensitivity, and uncertainty analysis to identify which assumptions matter to the results and why.

Future Directions

- Add DOE Vehicle Technologies Program projections for battery costs and other technology projections and learning curves.
- Compare cellulosic ethanol and other advanced biofuels pathways, including “drop-in fuels” that need less distribution infrastructure. Examine the portfolio effects of uncertainty results from research and development on biofuels.
- Expand the model of consumer preferences to reflect more intangible attributes in driving market share.
- Explore responses to “surprises”, such as sudden spike in oil price, changes in consumer preference for larger vehicles, and breakthroughs in battery or fuel cell technologies.

Introduction

New biofuels, PHEVs, and light-weighting are just a few of the new automotive technologies being developed, with the goal of reducing greenhouse gas emissions, transportation costs, and oil imports. Given the time it takes for the U.S. vehicle fleet to turn over, and interactions among these innovations in the market place, it can be difficult to assess the scale and timing of their impacts.

In this project, we have developed ATEAM (Figure 1) as a scenario decision-analysis tool to assist policy makers, program managers, and others to more rapidly explore and understand these issues. ATEAM is designed to be agile and transparent to support easy definition and comparison of scenarios and to explore the sensitivities to find out what assumptions matter and why.

Our goal is to make the model public domain, open source, and extensible, so that interested groups from government, academe, industry, and non-governmental organizations can use ATEAM to explore and compare their perspectives on these important, and sometimes controversial issues.

Approach

The ATEAM prototype model focuses on selected issues and pathways from field or well to wheel. The initial pathways include: biomass to ethanol to automobile with flexible-fuel internal combustion engine, biomass-fueled combined cycle electrical power

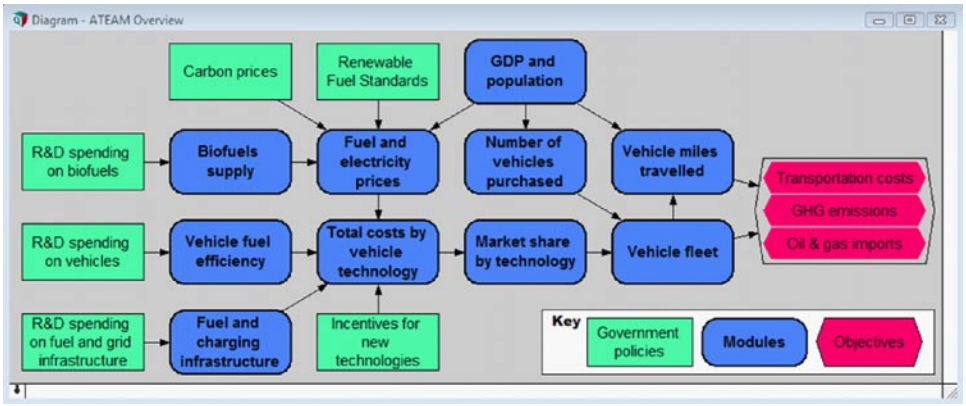

FIGURE 1. Top Level ATEAM Influence Diagram as User Interface

generation and plug-in hybrids. The framework can be expanded over time to add pathways, technologies, and additional detail. The model uses generic templates for fossil and renewable energy sources, energy-conversion devices and pathways. It uses a logit model to project market share as a function of relative costs of technologies and fuels. This structure will make it relatively easy to add new technologies and pathways as the model is expanded. ATEAM builds on a variety of existing models and studies, including the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model, PSAT (vehicle simulation), and the Stochastic Energy Deployment System. It enables direct comparison with scenarios from DOE's Annual Energy Outlook, National Academy of Science reports, and other sources.

Results

The ATEAM prototype enables comparison of a wide-range of vehicle designs and technologies. Users can select fuels, engine technology, electric-only ranges for PHEVs and battery electric vehicles, and light-weighting. It provides comparison of selected vehicle designs, using a breakdown of levelized cost per mile, including purchase cost, fuel cost, operating costs, costs and credits imposed by government policies (see Figure 2). It projects the changing market share among technologies over time (Figure 3), and hence the resulting make-up of the U.S. vehicle fleet. It projects energy usage by fuel type (Figure 4) for multiple scenarios. It evaluates results in terms of greenhouse gas emissions per kilometer, total cost per kilometer (or month), and reduction in oil imports. We are also exploring a simple physics model of energy usage in vehicles, to enable rapid analysis of sensitivities to major changes in vehicle design parameters (Figure 5). A major focus has been on the use of ethanol, and the question of how the U.S. fleet can consume the quantity of ethanol mandated to be produced by the RFS2 (Figure 6). ATEAM has been used to explore how many

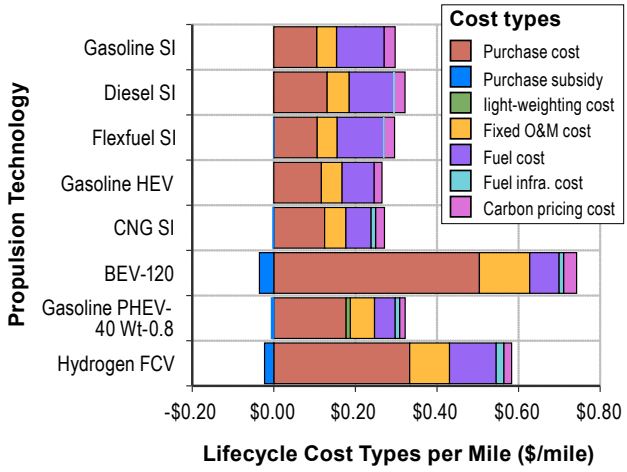

FIGURE 2. Comparison of Selected Technology as Levelized Cost per Mile Broken Down into Cost Elements

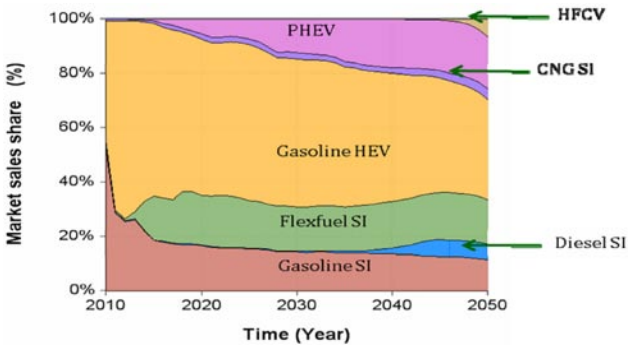

FIGURE 3. Projected Market Shares by Technology from Selected Scenario S1

flexible-fuel vehicles would be needed, with assumptions on deployment of blends of 85% ethanol and 15% gasoline (E85) infrastructure and fueling stations, and the effect of the recent EPA proposal to permit use

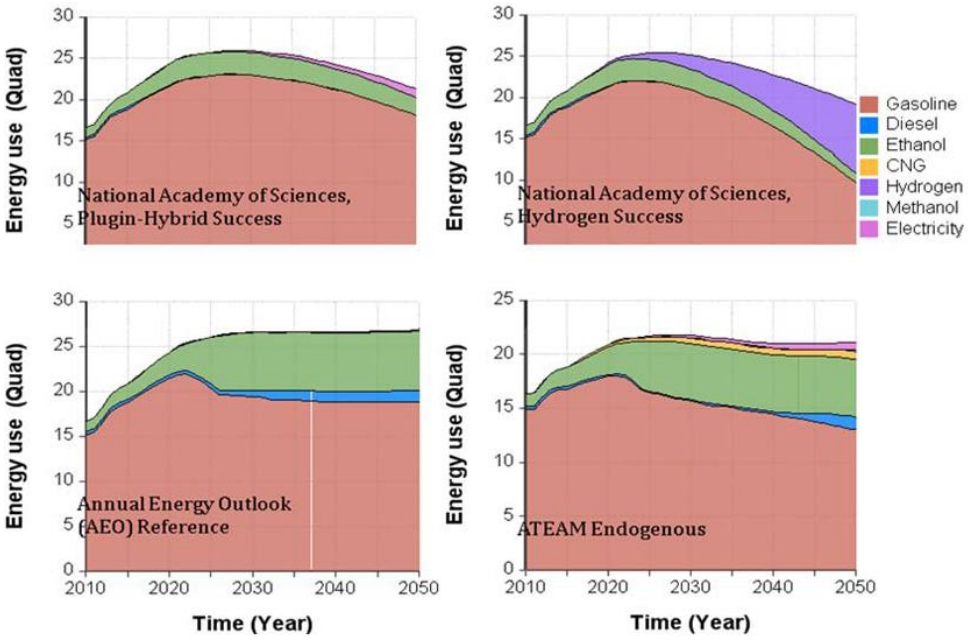

FIGURE 4. Energy Consumption by Fuel Type, Comparison of Four Scenarios

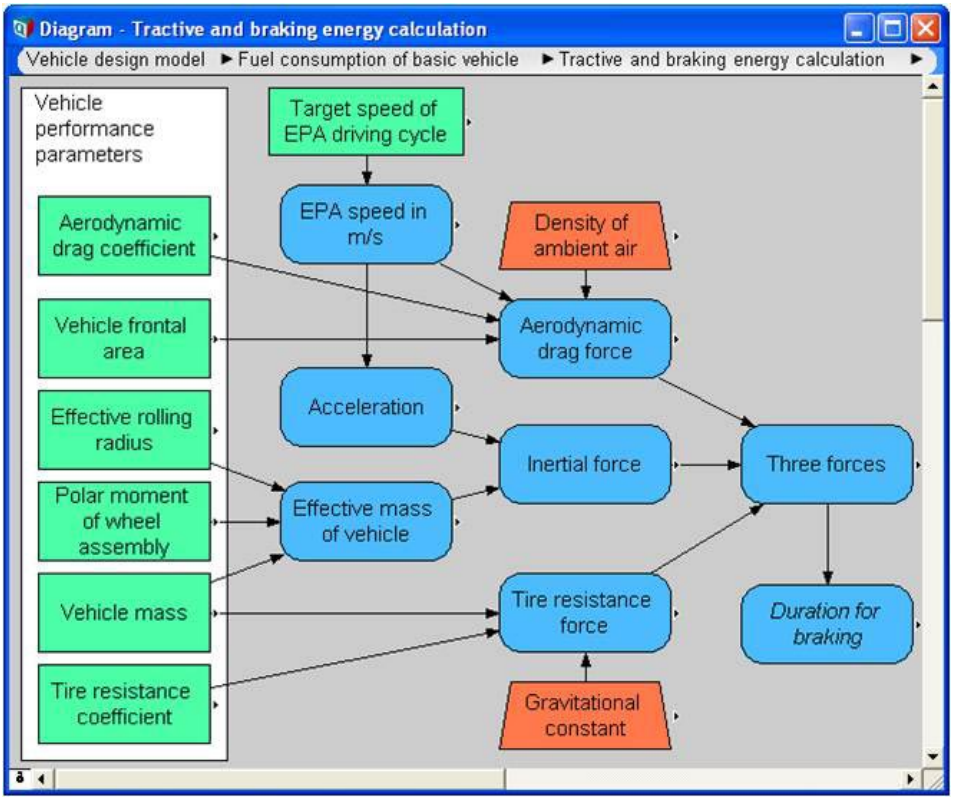

FIGURE 5. Influence Diagram Showing Elements of a Simple Physics Model of Forces and Energy Use in a Vehicle

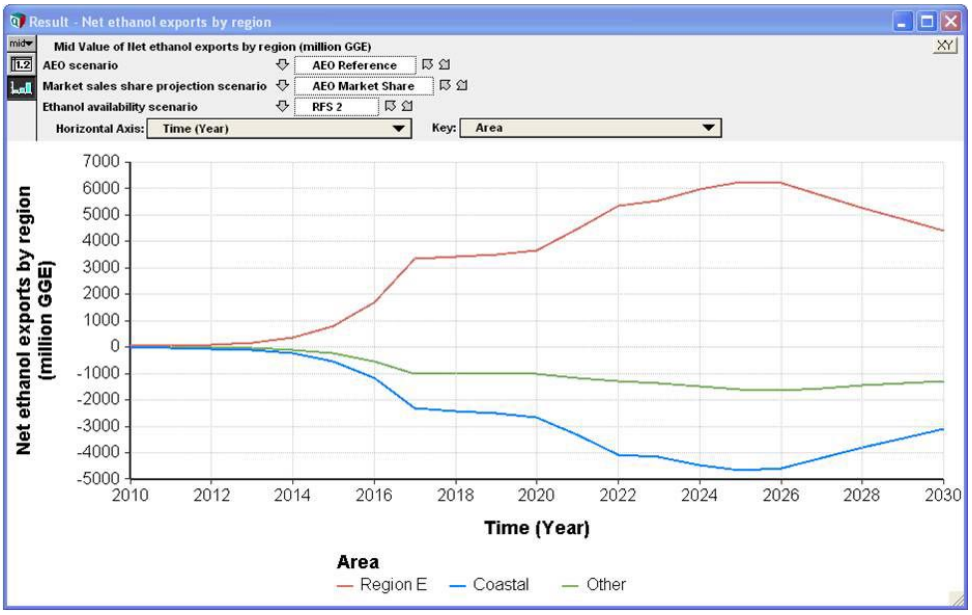

FIGURE 6. Exports (or Imports) of Ethanol by U.S. Region Required for RFS2

of E15 for newer vehicles. ATEAM has been run on a regional basis, comparing export of ethanol from ethanol-producing states to other states that will be net consumers of ethanol.

Conclusion

- The ATEAM prototype enables exploration of the effects of a wide range of new fuel and vehicle technologies on the U.S. vehicle fleet.
- ATEAM has demonstrated some interesting insights into the effects of the RFS2, its requirements for sales of more flexible-fuel vehicles, with or without the recent E15 approval for new vehicles.
- The prototype can assess sensitivities and the effects of uncertainty on key model parameters.

FY 2010 Publications/Presentations

1. *ATEAM User Guide*, Version 0.9, Sep 30, 2010. Lumina Decision Systems, Inc.

2. *Exploring Biofuels and Technology Changes to the US Vehicle Fleet*, Xirong Jiang, Max Henrion, Surya Swamy, Presentation at INFORMS, Austin, TX., November 9–12, 2010.

3. *Expecting the Unexpected: Surprises in Past and Future Energy Forecasts*, Max Henrion, Presentation at INFORMS, Austin, TX., November 9–12, 2010.

4. *Projections for US Flex-fuel Vehicle Structure and Renewable Fuel Standard*, Surya Swamy, Max Henrion, Xirong Jiang, Costa Samaras, Presentation at INFORMS, Austin, TX., November 9–12, 2010.

5. *ATEAM Project Review*: At PNL Offices, Max Henrion, Xirong Jiang, Surya Swamy, & Cary Bloyd, December 1, 2010.

V. NEW PROJECTS

V.1 Collaborative Lubricating Oil Study on Emissions (CLOSE) Project

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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.

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].

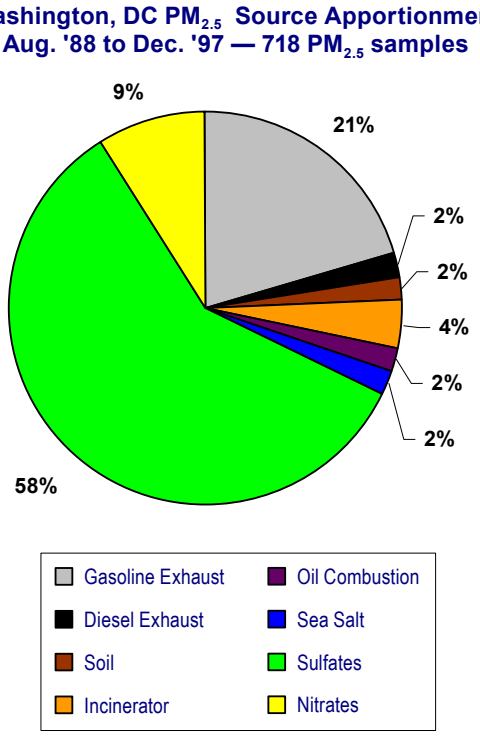

FIGURE 1. Source Apportionment of $PM_{2.5}$ in the Washington, D.C. Area, Ambient Air Quality Samples Collected between 1988 and 1997

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,

FIGURE 2. Heavy-Duty High-Emitting CNG-Powered Heavy-Duty Bus Tested in the CLOSE Project

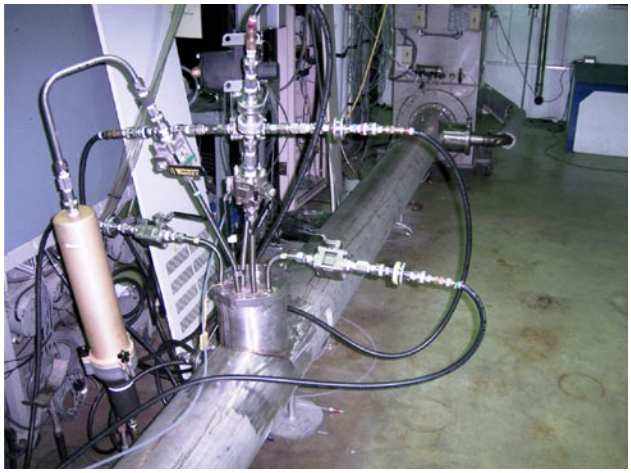

FIGURE 3. Sampling Probes used to Collect Exhaust Emissions Samples from the Dilution Tunnel

and the 2010 DOE Merit Review Meeting since that 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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1. Fujita, E.M., D.E. Campbell, W.P. Arnott, B. Zielinska, J.C. Chow. Evaluations of Source Apportionment Methods for Determining Contributions of Gasoline and Diesel Exhaust to Ambient Carbonaceous Aerosols, *J. Air & Waste Manage. Assoc.*, Vol. 57, pp. 721-740 (2007).

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)

3. Lough, G.C. and J.J. Schauer. Sensitivity of Source Apportionment of Urban Particulate Matter to Uncertainty in Motor Vehicle Emissions Profiles, G.C. Lough and J.J. Schauer, *J. Air & Waste Manage. Assoc.*, Vol. 57, pp. 1200-1213 (2007).

4. McDonald, J.D., I. Eide, J.C. Seagrave, B. Zielinska, K. Whitney, D.R. Lawson, J.L. Mauderly. Relationship between Composition and Toxicity of Motor Vehicle Emission Samples, Environ. Health Persp., Vol. 112, pp. 1527-1538 (2004).

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.

VI. Acronyms, Abbreviations and Definitions

ϕ	Fuel/air-equivalence ratio
°F	Degrees Fahrenheit
1-D	One-dimensional
2-D	Two-dimensional
AARF	Advanced Alternative and Renewable Fuels
APBF	Advanced petroleum-based fuels
ASOI	After start of injection
ASTM	ASTM International, a standards setting organization
AT	Aluminum titanate
atdc, ATDC, aTDC	After top dead center
ATEAM	Analytica Transportation Energy Analysis Model
a.u.	Arbitrary units
AVFL	Advanced Vehicles Fuels and Lubricants
B100	100% biodiesel
B20	20% biodiesel
B6	6% biodiesel
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.
BMEP	Brake mean effective pressure
BSFC	Brake specific fuel consumption
BTCA	1,2,4,5-Benzenetetracarboxylic acid
BTCDA	1,2,4,5-Benzenetetracarboxylic dianhydride
BTE	Brake thermal efficiency
Bxx	Biodiesel blend containing xx volume percent biodiesel
CA50	Crank angle at which 50% of the combustion heat release has occurred
CFD	Computational fluid dynamics
CI	Compression ignition
CLCC	Closed-loop combustion control
CLEERS	Cross-Cut Lean Exhaust Emissions Reduction Simulations
CMOS	Complementary metal-oxide semiconductor
COV	Coefficient of variation
CP	Cloud point
CPChem	Chevron-Phillips Chemical Company
CR	Compression ratio
CRADA	Cooperative Research and Development Agreement
CRC	Coordinating Research Council
CSM	Colorado School of Mines
CuME	FAME derived from Cuphea oil
degCA	Degrees crank angle
DI	Direct-injection
DISI	Direct-injection spark ignition
DNPH	2,4-dinitorophenylhydorazine
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
DRG	Directed relational graph
DRIFTS	Diffuse reflectance infrared Fourier-transform spectroscopy
DSC	Differential scanning calorimetry
DVPE	dry vapor pressure equivalent, i.e., vapor pressure at 100°F in the ASTM standard apparatus used for that test
E15	15% ethanol, 85% gasoline fuel blend
E20	20% ethanol, 80% gasoline fuel blend
E50	50% ethanol, 50% gasoline fuel blend
E85	85% ethanol, 15% gasoline fuel blend
ECM	Engine control module
ECU	Electronic control unit
EGR	Exhaust gas recirculation
EISA	Energy Independence and Security Act of 2007
EIVC	Early intake valve closing
EPA	Environmental Protection Agency
EPMA	Electron probe microanalysis
ES	Extremum Seeking
ETC	Environmental Testing Corporation
ETDI	E85 turbocharged direct injection
Exx	xx% ethanol, 100-xx% gasoline fuel blend
FACE	Fuels for Advanced Combustion Engines
FAME	Fatty acid methyl ester

FE	Fuel economy
FFV	Flexible-fuel vehicle; flex-fuel vehicle
FMT	Final melting temperature
FTP	Federal Test Procedure
FTP-75	Federal Test Procedure for LD vehicles
GC	Gas chromatography
GC-FIMS	Gas chromatography field ionization mass spectrometry
GC-MS	Gas chromatography – mass spectrometry
GDI	Gasoline direct injection
GHG	Greenhouse gases
GTDI	Gasoline turbocharged direct injection
HC	Hydrocarbons
HCCI	Homogeneous charge compression ignition
HD	Heavy-duty
HECC	High-efficiency clean combustion
HFRR	High frequency reciprocating rig
HMN	Heptamethylnonane (2,2,4,4,6,8,8-heptamethylnonane, a diesel primary reference fuel)
HPLC	High-performance liquid chromatography
HRR	Heat release rate
IMEP	Indicated mean effective pressure
$IMEP_g$	Indicated mean effective pressure, gross
IQT™	Ignition Quality Tester
ISFC	Indicated specific fuel consumption
$ISNO_X$	Indicated-specific emissions of nitrogen oxides
IT	Ignition timing
ITE	Indicated thermal efficiency
IVD	Intake valve deposit
KIVA	Combustion analysis software developed by Los Alamos National Laboratory
LEV	Low emission vehicle
LHV	Lower heating value; latent heat of vaporization
LIVC	Late intake valve closing
LL	Liquid length
LPDI	Low-pressure, direct injection
LTC	Low-temperature combustion
MBT	Minimum (spark advance) for best torque; Maximum brake torque
MECA	Manufacturers of Emission Controls Association
MFB	Mass fuel burned
MFB50	Crank angle where 50% of heat release has occurred
MFC	Model Fuels Consortium, a consortium run by Reaction Design to improve kinetic modeling tools and fuels and engine modeling tools.
MIT	Massachusetts Institute of Technology
MVCO	Micro-variable circular orifice
NA	1,8-Naphthalene anhydride
NBP	Normal boiling point
NDCA	1,8-Naphthalene-dicarboxylic acid
NMEP	Net indicated mean effective pressure
NMHC	Non-methane hydrocarbon
NMOG	Non-methane organic gases
NMR	Nuclear magnetic resonance
NOR	Normalized onset radius
NPBF	Non-petroleum-based fuel
NTCDA	1,4,5,8-Naphthalenetetracarboxylic dianhydride
NVO	Negative valve overlap
OEM	Original equipment manufacturer
PAH	Polycyclic aromatic hydrocarbon
PCA	Principal component analysis
PCCI	Pre-mixed charge compression ignition
PFI	Port fuel injection, port fuel injected
PGM	Platinum group metal
PHEV	Plug-in hybrid electric vehicle
PIV	Particle image velocimetry
PLIF	Planar laser induced fluorescence
PM	Particulate matter
PMEP	Pumping mean effective pressure
PN	Particulate number
RCCI	Reactivity-controlled compression ignition
RExx	xx% ethanol, 100-xx% retail gasoline fuel blend
RFS	Renewable Fuel Standard
RFS2	Renewable Fuel Standard 2
RON	Research octane number
RPM, rpm	Revolutions per minute
SCORE	Sandia Compression-ignition Optical Research Engine
SCR	Selective catalytic reduction
SIDI	Spark ignition direct injection
SME	Soy methyl ester
SMG	Saturated monoglyceride
SMPS	Scanning mobility particle scanner
SOC	Start of combustion; soluble organic compound
SOF	Soluble organic fraction

SOI	Start of injection
SOPO	Statement of project objectives
SRC	Standard Road Cycle
SULEV	Super ultra-low emissions vehicle
T90	Temperature for 90% evaporated
TDC	Top-dead center
TDC_{exc}	Top-dead center (of gas-exchange strokes)
THC	Total hydrocarbon
TMC	2,2,4-trimethylpentane (iso-octane)
TPO	Temperature-programmed oxidation
TRC	Transportation Research Center
TWC	Three-way catalyst
UL	Underwriters Laboratory
ULEV	Ultra-low emission vehicle
ULG 91 RON	Unleaded gasoline 91 Research octane number
ULG 95 RON	Unleaded gasoline 95 Research octane number
ULSD	Ultra-low-sulfur diesel
UTK	University of Tennessee, Knoxville
VOF	Volatile organic fraction
vol%	Volume percent
VVA	Variable valve actuation
WOT	Wide open throttle
XRD	X-ray diffraction
XRF	X-ray fluorescence

VII. Index of Primary Contacts

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