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FUELS TECHNOLOGIES

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FY 2008/2009 PROGRESS REPORT FOR FUELS TECHNOLOGIES

Energy Efficiency and Renewable Energy
Office of Vehicle Technologies

Approved by Kevin Stork

Team Leader, Fuels Technologies
Office of Vehicle Technologies

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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) 2008/2009 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 are 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 billion gallons of ethanol in 2008, nearly all in the form of E10 (10% ethanol, 90% gasoline) sold as gasoline at fueling stations. The nation's seven 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).

However, before intermediate blends can be introduced into the nation's fueling infrastructure, their effects on the performance and emissions of vehicles and small non-road engines designed to run on gasoline with 0%–10% ethanol must be determined. 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. These disruptions caused the price of crude oil to spike up to over $70/bbl and retail gasoline prices to reach over $3/gal over most of the U.S. In July 2008, the price of crude oil reached $134/bbl due to speculative activity associated with the financial crisis that originated in the U.S. Since then, crude oil prices have declined to a range of $70-80/bbl as of January 2010. 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. The U.S. Energy Information Administration projects that net imports of U.S. crude oil and petroleum products will decline from 12.1 million bbl/day in 2007 to 8.3 million bbl/day in 2030. Growth in total U.S. petroleum consumption is expected to remain relatively flat out to 2030. Meanwhile, the increase in U.S. crude oil production in the Gulf of Mexico and elsewhere, combined with increasing biofuel and coal-to-liquids production, is expected to reduce the need for imports over the longer term. U.S. petroleum import dependence is projected to fall from 58% in 2007 to 40% by 2030. 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 over seven million flexible-fuel vehicles that can use E85 (85% ethanol and 15% gasoline), 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 should 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 and 2008 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 synergies, 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 heavy-duty vehicle research. It features a heavy-duty chassis dynamometer test cell for vehicle performance and emissions research, an engine dynamometer test cell capable of certification-quality emissions testing, and an altitude simulation system that provides conditioned air at atmospheric conditions from sea-level to the mile-high environment of Denver. In FY 2009 a second test cell was commissioned at ReFUEL to accommodate the installation of a single-cylinder research engine that will be used to develop advanced combustion strategies in support of DOE's Advanced Petroleum-Based Fuels activity.

In FY 2008/2009 the ReFUEL Laboratory completed several projects that have significantly enhanced testing capability and laboratory throughput. The laboratory undertook a project to modify the air-handling systems and acquired new 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 new Horiba Mexa emissions analyzer was added to ReFUEL's portfolio of measurement equipment to provide faster and more accurate emissions measurements as needed to support upcoming emissions regulations. The old engine dynamometer mule test engine was replaced with a new 2007 International Maxxforce engine and was subsequently used to evaluate the interactions between a variety of biodiesel blends (including some derived from algae) and advanced diesel engine aftertreatment systems. The engine dynamometer was 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. Additionally, a significant number of chassis dynamometer test programs were executed with funding from both DOE and research partners such as International, Eaton, Oshkosh Truck and the South Coast Air Management District.

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 2008/2009 included: 1) Showing the mechanisms by which liquid-fuel films can be formed on walls within the engine combustion chamber, and how the subsequent presence or lack of ignition of these films affects combustion and engine-out emissions. (This accomplishment won the prestigious Society of Automotive Engineers Horning Award for the most significant contribution to the field of engine and fuels research in 2008). 2) Determining that the cause of the NOx increase typically noted for biodiesel is related to reacting mixtures in the engine cylinder being closer to stoichiometric, leading to longer residence times at higher temperatures, and thereby, more thermal NOx formation. 3) Showing that increasing fuel volatility dramatically improves low-temperature combustion (LTC) by avoiding liquid impingement on cylinder walls, and thus associated combustion inefficiency and emissions. 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. The facility's capabilities include catalyst spectroscopy labs, bench-top engine exhaust simulators, a range of engine dynamometer cells, and a 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:

- General Motors 1.9 liter multicylinder diesel engine is fully operational and is in use for studies on engine efficiency, fuel effects on advanced combustion regimes, and methods to expand those regimes.
- A Ford-supplied multicylinder diesel engine is being used to study biodiesel effects on exhaust gas recirculation cooler fouling.

- A new method for detecting fuel dilution of the engine lube oil 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.

Using a two-cylinder variable compression ratio engine, ORNL researchers contributed new data on the ability to achieve homogeneous charge compression ignition (HCCI) modes with ethanol-based fuels (E85). The ignition characteristics of E85 were found to readily enable HCCI combustion. The results showed that the engine efficiency with E85 slightly surpassed that of gasoline at similar operating conditions, and the E85 NOx emissions were somewhat lower.

Additional HCCI fuel studies have included conventional diesel, oil sands-derived diesel, and B20 biodiesel fuels. HCCI combustion was found to prefer fuels with lower cetane and higher volatility for optimum performance. Cetane number remains the major factor for predicting ignition characteristics and is largely controlled by level of monoaromatics in HC fuels. High cycloparaffin concentrations in the oil sands fuels did not provide any unique benefits or problems. For biodiesels, fuel economy deteriorated because of fuel ignition characteristics and biodiesels from various vegetable sources required different control settings for optimized performance.

With support from the DOE Office of Biomass Program, a Saab Biopower flexible-fuel vehicle (FFV) was imported and its emissions and fuel economy on gasoline and E85 was extensively characterized. The vehicle is currently being exercised as a research platform for methods to improve the fuel efficiency of FFVs, such as lean-combustion.

HIGHLIGHTS OF SIGNIFICANT FY 2008/2009 ACCOMPLISHMENTS

The following presents highlights of the Fuels Technologies project accomplishments in 2008/2009.

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.

ORNL is studying the effects of fuel and lubricant properties on advanced engine emission control systems with the intent of development of rapid aging and poisoning protocols. Significant progress on the following issues was made: rapid phosphorus poisoning of diesel oxidation catalysts (DOCs); rapid ash loading of diesel particulate filters (DPFs); rapid thermal aging of lean-NOx traps (LNTs); rapid thermal aging of the DOC-selective catalytic reduction (SCR)-DPF system; and biodiesel effects on emissions control devices.

ORNL continued their study to identify fuels or fuel properties that may reduce the effectiveness of the exhaust gas recirculation (EGR) system through problematic deposit formation when using non-petroleum-based fuels. A study at low HC levels to examine the impacts of soot formed when using biodiesel blends on the EGR cooler fouling process was completed. Elevated HC levels were also examined to determine the impacts of different HCs on the fouling process. The deposit thermal conductivity was successfully measured in situ and identified deposit density as a key parameter. Experimental data were provided to two industrial organizations to aid in calibration of their models of the EGR cooler fouling process.

ONRL will continue to improve their understanding of fundamental particulate oxidation kinetics in DPF regeneration, in support of DPF modeling efforts. The oxidation kinetics for ultra-low-sulfur diesel (ULSD), B5, B10, B15, B20 and B100 particulate samples were evaluated and the impact of biofuel blend level on the combustion of particulate was determined, noting that B100 particulate reaches its peak oxidation rate ~70°C lower than ULSD particulate. The impact of the volatile fraction on the particulate combustion temperature was measured and total surface area evolution with burnout was measured for ULSD and B100 particulates. A general kinetic framework was proposed that includes dominant oxidation pathways for both fixed and volatile carbon.

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.

SNL is working to understand the extent to which fuel-volatility changes could help to enable early direct-injection (DI) high-efficiency clean-combustion (HECC) strategies and identify the primary combustion mechanism(s) responsible for the increased NOx emissions that typically are observed when fueling heavy-duty compression-ignition (CI) engines with biodiesel. They showed that increasing the volatility of diesel fuel can significantly improve engine efficiency and emissions under early-DI operating conditions by avoiding the formation of liquid-fuel films on in-cylinder surfaces. They also showed that while many factors may contribute to increased NOx emissions when fueling CI engines with biodiesel, the only mechanism that is consistent with all observed trends in our research is that fueling with biodiesel results in mixtures that are closer to stoichiometric during ignition and subsequent reaction. This leads to higher local temperatures earlier in the cycle, and hence increased thermal NOx production.

SNL is researching how emerging future fuels, with an initial focus on ethanol, will impact the new highly-efficient direct-injection spark-ignition (DISI) light-duty engines currently being developed by industry. The DISI engine design will be optimized to make the most efficient use of future fuels. In particular, there is incomplete understanding of the dynamics of fuel-air mixture preparation and ignition.

Lawrence Livermore National Laboratory (LLNL) is developing 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-sand-derived fuel, alcohol fuels and other advanced bio-based and alternative fuels. Detailed chemical kinetic models for two large unsaturated methyl esters: methyl-5-decenoate and methyl-9-decenoate, a detailed chemical kinetic model for a biodiesel surrogate that contains large saturated and unsaturated methyl esters characteristic of vegetable-oil-derived biodiesel, and a reduced mechanism for a large biodiesel surrogate for use in computational fluid dynamics codes were developed. LLNL is also developing surrogate chemical kinetic models for practical fuels (i.e., gasoline, diesel), testing and tuning chemical kinetic models at conditions of interest to engine researchers, and providing analytical support for fuel characterization experiments. They developed methodologies for testing and tuning gasoline surrogate chemical kinetic models and demonstrated a procedure for detailed modeling of NREL's Ignition Quality Tester (IQT).

NREL is supporting the simultaneous development of advanced fuel chemistries and advanced combustion engines by providing an experimental and modeling bridge between fundamental chemical kinetics and engines. NREL developed an IQT-based research platform and supported development and utilization of Fuels for Advanced Combustion Engines (FACE) to determine relationships between fuel chemistry and engine combustion performance and emissions. A DISI single-cylinder research engine facility was developed to investigate fuel chemistry effects on advanced combustion and leverage links to NREL's biomass fuels research program. Advanced speciation techniques were developed to analyze impact of advanced fuels on exhaust emissions.

ORNL and NREL are managing an effort to design a standard set 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. They assembled a cross-industry working team of subject matter experts through collaboration with the Coordinating Research Council (CRC), including stakeholder members from the energy/petroleum industry, automotive/engine manufacturers, universities, and national laboratories. Nine diesel fuels were developed, which are currently available for purchase from Chevron-Phillips Chemical Company. Exhaustive advanced characterization of the nine diesel fuels was completed, including application of novel techniques to fuel property characterization. Initial engine performance in pre-mixed charge compression ignition and HCCI operation was demonstrated with the diesel fuels.

ORNL is investigating the impacts of non-petroleum-based fuels on advanced combustion regimes for gasoline and diesel engines. Results were published demonstrating low emissions of multi-cylinder

HECC operation with biodiesel blends derived from soy and coconut oils. Numerical methods were used to analyze experimental results from separate fuel sets (biodiesel fuels, oil shale fuels, and oil sand fuels), allowing co-linear fuel properties to be correctly accounted for. Diesel HCCI results were published for oil sand fuels showing that the fuels with the best performance in this engine have high volatility and low cetane number. Kinetic modeling was utilized to identify a unique ignition characteristic of ethanol.

ORNL is investigating ways to improve engine efficiency with ethanol and ethanol-gasoline fuel blends in order to reduce the mile-per-gallon fuel consumption difference between gasoline and ethanol fuel blends. A single-cylinder research engine with variable valve actuation (VVA) showed that thermal efficiency for 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) 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%. Results from the single-cylinder engine demonstrate that with these methodologies, the fuel economy gap between E85 and gasoline can be reduced by about 20% at full load.

ORNL is helping to facilitate the development of modeling tools which will allow the accurate modeling of multiple fuel types in engine design and combustion modeling tools. Engine performance data for selected fuels and fuel surrogate compounds representing gasoline, diesel and alternative fuels, chosen by mutual agreement, on ORNL's HCCI research engine and other engines will be developed. To date, five sets of fuels have been run by ORNL on an HCCI research engine. These fuels cover gasoline and diesel fuels, both fully formulated and surrogate. The model fuels consortium modeling tools have been applied to these data sets to confirm the tools and to point out need for further development and improvement. This research has been documented in four SAE technical papers and two Diesel Engine Emissions Reduction (DEER) Conference presentations.

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:

- Work is being conducted to understand how biodiesel will impact the performance and durability of 2010 diesel engine aftertreatment technology, which is necessary to meet the EPA's stringent NOx emissions standards. A 2004 Cummins engine was retrofitted with a full aftertreatment system (DPF+SCR), representative of 2010 heavy-duty diesel engine aftertreatment technology. On average the use of B20 increased the NO_2:NOx ratio by 3%, decreased the catalyst temperature by 11% and caused no change in the catalyst space velocity. These small changes from biodiesel had no impact on the overall NOx conversion ability of the SCR catalyst. Bench-scale studies conducted by Ford showed that the SCR catalyst adsorbs more HCs from biodiesel (8.1 g/L) versus petroleum diesel (1.5 g/L). However, these tests revealed that the adsorbed diesel HCs begin to release from the catalyst at 400°C, whereas adsorbed biodiesel HCs begin to release at 200°C.
- Field fuel quality surveys of biodiesel and FFV fuel (primarily E85) commercially-available in the U.S. are being conducted. Reports on both biodiesel and FFV fuel quality were completed.
- Robust test methods are being developed and validated to characterize the trace components in biofuels and biofuel blends. A new ion chromatographic method was validated and applied to measure the amount of free and bound glycerin in biodiesel and biodiesel blends. A high performance liquid chromatographic (HPLC) method was implemented to determine the composition and trace components of biodiesel. A robust matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) technique was developed to allow rapid and complete analysis of the trace components in biodiesel.

- The extended in-use performance of B20 fuel at the St. Louis Metro transit fleet was evaluated. An 18-month evaluation of 15 transit buses with eight operating on B20 and seven operating on diesel fuel was completed. Fuel consumption and maintenance data were successfully analyzed, showing no significant different in fuel economy or in engine/fuel system maintenance costs. It was shown that fuel injector failures correlated to engine miles not fuel consumed.
- The cloud point (CP), cold filter plugging point (CFPP), and the low temperature flow test (LTFT) and actual heavy-duty vehicle performance at low temperatures for biodiesel blends were evaluated. A second objective is to validate that the cold soak filtration test (CSFT) is able to identify biodiesel that, in blends up to B20, causes fuel filter plugging at temperatures above the CP. It was found that that high CSFT B100 can cause low-temperature operability problems at temperatures above the CP for B20 blends. On average for all fuels combined, CP was found to be a conservative predictor of operability limit by about 1°C. CFPP tends to predict an operability limit higher than CP and may not be protective of the most severe vehicles. LTFT was protective of all vehicles but was very conservative for B20 from high CSFT biodiesel.
- The impact of biodiesel fuel blends on the performance of advanced emission control systems for light-duty diesels was evaluated. The engine-out NOx emission levels increased with the use of biodiesel up to 10% with B20 and the hydrocarbon emissions decreased, but the increase in engine-out NOx emissions did not translate into higher tailpipe emissions. The impact on NOx absorber catalyst or DPF regeneration events themselves was negligible. The SCR system performance did not change comparing the two fuels resulting in virtually identical tailpipe emissions.
- The toxic organic emissions from ULSD were compared with those from B20 and B100 soy biodiesel. It was demonstrated that a catalyzed, passively regenerated DPF was highly effective in oxidizing most organic exhaust emissions (1 to 3 orders of magnitude decrease). However, formaldehyde emissions increased post-DPF (except in the case of B100 fuel) and 1-nitropyrene conversion was less than 50% for all fuels tested.
- The compatibility of representative samples of in-use retail petroleum dispensing equipment is being evaluated with gasolines containing higher concentrations of ethanol than currently allowed, particularly blends in the range of 15-20% ethanol. A proposal was made to the International Codes Council (ICC) to amend the International Fire Code to require compatibility of fuel storage and dispensing equipment to be compatible with all blends of ethanol with gasoline up to 85% on a full system basis; tentatively accepted as a proposal by ICC. Immersion testing of parts is underway at ORNL; "failure testing" underway at Underwriters Laboratory.
- Fuel tank headspace vapor flammability of various ethanol-blended fuels is being experimentally evaluated at various ambient temperatures. The apparatus and methods needed to test the headspace vapor flammability of fuel samples were developed and the flammability of fuel blends were tested including E85 samples from vehicle studies; field samples of E85, E10, E20, and E30 from commercial pumps; laboratory samples of E55–E83; two types of gasoline; and denatured ethanol. Mathematical models of flammability and evaluated the models in comparison with the results of the experimental tests were developed and a preliminary analysis of the flammability risks associated with vapor/air plumes emitted from fuel tanks during fueling was performed.

NREL and ORNL are quantifying the immediate impacts of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on regulated tailpipe emissions and fuel economy. On average, regulated tailpipe emissions were found to be unaffected by ethanol content above 10%. Fuel economy was found to decrease with ethanol content, consistent with energy content of the fuel. Peak catalyst temperatures during power enrichment operation increased with increasing ethanol content for vehicles found to not apply learned-fuel trim at power-enrichment; about half the vehicles tested.

ORNL is studying the potential of improving the fuel economy of FFVs when using E85. Using a European-spec Saab BioPower FFV (the first FFV optimized for E85) lean-burn experiments with a novel hydrocarbon-selective catalytic reduction lean-NOx catalyst have been initiated.

ORNL is developing or 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. A microwave solvent extraction method for soot samples was developed that results in a 20-fold decrease in solvent usage and enhanced extraction efficiencies for polar compounds. Completed analysis of soot samples for novel oxygenated compounds, previously unknown in diesel soot, may account for up to 20% of the thermally-labile organic fraction in soot. An atmospheric pressure chemical ionization mass spectroscopy method was developed for the detection and quantification of urea and its major decompositions products on PM filter samples.

Five projects are being conducted to improve the fuel economy of FFVs when operating on E85 without degrading the fuel economy when using gasoline:

- General Motors is demonstrating the capabilities of a flexible-fuel turbocharged engine, which incorporates recirculated cooled exhaust gas along with other synergistic technologies, to achieve significant (15%) fuel economy benefit relative to conventional naturally aspirated engines operated on the same fuel. Dynamometer testing has demonstrated the fuel consumption benefits of cooled EGR for the downsized turbocharged engine over a broad operating range and the projected fuel economy gain over the combined urban and highway driving cycles is in the range of 13-17%.
- MAHLE Powertrain, LLC is demonstrating a new, commercially viable engine that is optimized for E85 operation. A vehicle simulation predicts that the shortfall in fuel economy on a state-of-the-art current engine between E85 to gasoline operation of ~30% can be reduced to about 10% with 55% from engine optimization and 45% from engine downsizing. These gains are achieved at the same time as significantly improving vehicle performance, reducing the 0 to 60 mph acceleration time from 8.3 seconds to 6.6 seconds.
- Ford is demonstrating the benefits of a dual-fuel (gasoline and E85) turbocharged engine which maximizes the efficiency 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. Optical and single-cylinder investigations of fuel spray pattern, piston bowl geometry and in-cylinder charge motion were completed and a multi-cylinder turbocharged dual-fuel engines capable of 150 bar peak pressure was prepared for testing. Preliminary vehicle level simulations of fuel economy and performance of single- and dual-fuel ethanol optimized engines and an initial baseline evaluation of a multi-cylinder engine at 9.3:1 compression ratio, exceeding performance targets were completed.
- Robert Bosch LLC is developing an optimized FFV, targeting substantial fuel economy improvement with minimum driveability and fuel consumption penalties using a direct injection turbocharged spark ignition engine. They predict that any optimized FFV engine could improve fuel efficiency with E85 by 3-4% without comprising performance on gasoline. The use of an optimized transmission shift pattern could further improve the fuel economy of FFVs up to 5%. Adaptive engine controls that adjust these parameters for the detected ethanol content could improve the fuel economy of ethanol fuels by 2-2.5%.
- Delphi will 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. An engine model was used extensively to evaluate valve lift profiles and cam phasing requirements for best performance on the modified compression ratio engine with gasoline and E85. Injector spray was modeled and the spray pattern was optimized. An optimized multi-cylinder engine was assembled including: custom fuel injectors, 2-step valvetrain for variable lift, extended range cam phasers, custom pistons for increased compression, and custom ground camshafts.

The University of Illinois at Urbana-Champaign is measuring and evaluating properties of pure biodiesel and biodiesel/diesel blends for LTC modeling. They found that without engine re-calibration, soot emissions reduced by 20% when burning biodiesel fuel. With optimized engine settings a 50% reduction in NOx emissions was found to be possible with biodiesel. They also found that variable spray angle can further reduce emissions and increase fuel economy by approximately 10% through optimized fuel spray location in the engine cylinder. Micro-explosions of a fuel spray were visualized for the first time with the technology developed at the University of Illinois. The result leads to a new fundamental understanding of the micro-explosion process and demonstrates the potential benefit of using micro-explosion in combustion.

Pacific Northwest National Laboratory (PNNL) will develop a fundamental understanding of 'fit for service' properties and the analytical tools to characterize fuels derived from unconventional hydrocarbons and chemistry-based predictive models to support future advanced combustion/emission technologies. They identified molecular structures utilizing advanced analytical techniques which have a significant influence on diesel fuel lubricity. They also investigated the influence of molecular structure and biodiesel blends on seal swell and established a preliminary seal swell correlation. Nine fuels were characterized and oil shale-derived crude was acquired to prepare stabilized distillate fuel in a #1 and #2 diesel fuel boiling point range which will be used to measure fuel properties.

PNNL is analyzing international alternative fuel use which supports alternative fuel infrastructure development in the United States. The development of alternative fuels in Thailand with a concentration on ethanol production and use was profiled.

PNNL is developing an agile decision analysis portfolio tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies. An initial prototype model was developed using the Analytica decision analysis support system. The initial model shows inputs, results, and intermediate computations for the prototype decision pathways and includes plug-in hybrid vehicles and biomass-to-ethanol for automobiles with flex-fuel internal combustion engines.

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.

ORNL is studying the effects of fuel and lubricant properties on advanced engine emission control systems with the intent of development of rapid aging and poisoning protocols. Work has been completed on rapid phosphorus poisoning of DOCs, rapid ash loading of DPFs, rapid thermal aging of LNTs, and rapid thermal aging of the DOC-SCR-DPF system. Work will continue on the investigation into the impact of Na from biodiesel on emissions control devices by identifying what catalyst sites are being affected by Na contamination, confirming that the Na:Ca ratio is on the order of 5% in field-aged ash plugs, and investigation of the impact of oil dilution by biodiesel on the rate of ash generation.

ORNL will conduct experiments to investigate the mechanism(s) by which HCs may play a role in increasing soot deposits that result in degradation of the EGR cooler thermal performance. The will also investigate pathways that show potential for reducing the impact of fouling on EGR cooler performance and overall engine system design.

ORNL will investigate B5 and B20 surface area trends to continue to improve their understanding of fundamental particulate oxidation kinetics in DPF regeneration. Bench reactor experiments with mini-DPFs will be completed to compare differential and device kinetics for models. NO_2 oxidation kinetics will also be investigated.

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.

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.

- SNL will continue study of how fuel-volatility changes could help to enable early direct-injection HECC strategies and identifying the primary combustion mechanism(s) responsible for the increased NOx emissions that typically are observed when fueling heavy-duty compression-ignition engines with biodiesel. In the coming year, SNL will continue study of fundamental fuel effects on liquid-phase fuel penetration under time-varying in-cylinder thermodynamic conditions. This research will help engine designers avoid the detrimental effects of liquid-fuel films. SNL will also lead a team of researchers in the formulation and evaluation of diesel surrogate fuels, which are critical for enabling computational optimization of future engines. A high-pressure common-rail fuel-injection system will be implemented in the optical engine, and use this system to study fuel and injection-parameter effects on mixing-controlled HECC strategies.
- SNL will finalize design of their DISI research engine with metal and optical configurations to research how emerging future fuels, with an initial focus on ethanol, will impact the new highly-efficient DISI light-duty engines currently being developed by industry. The DISI engine design will be optimized to make the most efficient use of future fuels and to assess the influence of intake boost, EGR, fuel/air-equivalence ratio, and fuel-vaporization cooling. The ethanol chemical-kinetics mechanism will be evaluated with regards to EGR, charge temperature, and fuel/air-equivalence ratio.
- LLNL will continue their development of detailed chemical kinetic reaction models for components of advanced petroleum-based and non-petroleum-based fuels. Detailed chemical kinetic models for actual components in soy-based biodiesel (methyl stearate and methyl oleate) will be developed as well as improved chemical kinetic models for fuel surrogate components and fuel blends to represent advanced petroleum-based fuels.
- LLNL is developing surrogate chemical kinetic models for practical fuels (i.e., gasoline, diesel), testing and tuning chemical kinetic models at conditions of interest to engine researchers, and providing analytical support for fuel characterization experiments. They will develop high-accuracy surrogate mechanisms for gasoline and diesel fuel, test chemical kinetic mechanisms at engine conditions, and characterize alternative fuel advanced combustion regimes through experiments and modeling.
- NREL is supporting the simultaneous development of advanced fuel chemistries and advanced combustion engines by providing an experimental and modeling bridge between fundamental chemical kinetics and engines. NREL will expand their IQT-based experimental and modeling research and continue collaboration with other DOE and Canadian national laboratories. They will employ DISI single-cylinder research engine study fuel chemistry impacts on advanced combustion, enabling them to study a span of renewable fuels from fuel production and processing to engine performance and emissions.
- ORNL and NREL are managing an effort to design a standard set 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. They will secure a fuel blender to manufacture and sell the gasoline test fuels and perform characterization of them. The techniques

developed during the diesel advanced characterization efforts will be applied to address the paucity of data for advanced alternative and renewable fuels. Development of a multi-component diesel surrogate with a full kinetic model, complementing the diesel fuel matrix will be completed.

- ORNL will continue to study the effects of non-petroleum-based fuels on advanced combustion by expanding the range of fuel properties, composition, chemistry, and fuel source material, including FACE fuels. A new single-cylinder research engine with hydraulic valve actuation will be used to study negative valve overlap HCCI for ethanol and butanol fuel blends. A deeper understanding of fuel effects will be developed by employing additional statistical analysis tools to design experiments and analyze data. ORNL is pursuing a dual-fuel combustion strategy for diesel engines (gasoline or ethanol with diesel). Discussions have been initiated with Professor Rolf Reitz from the University of Wisconsin to better understand the potential of the approach with production-like hardware. This effort is being leveraged with several other projects, including advanced petroleum-based fuel effects on advanced combustion, HECC, and Joule Milestone.
- ORNL will continue investigating ways to improve engine efficiency with ethanol and ethanol-gasoline fuel blends in order to reduce the mile-per-gallon fuel consumption difference between gasoline and ethanol fuel blends using a multi-cylinder research engine. This engine has direct fuel injection, a high mechanical CR of 11.85, and prototype cam-based VVA system will allow versatile parametric studies for ethanol optimization.
- ORNL is helping to facilitate the development of modeling tools which will allow the accurate modeling of multiple fuel types in engine design and combustion modeling tools. ORNL will verify surrogate modeling tools in terms of designing surrogates to mimic actual fuels through engine experimental and modeling; verify master mechanisms to model engine performance and to accurately reproduce fuel effects; and develop engine data related to particulate formation and characteristics to help support the development of particulate formation tools in CHEMKIN.

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:

- Work is being conducted to understand how biodiesel will impact the performance and durability of 2010 diesel engine aftertreatment technology, which is necessary to meet EPA's stringent NOx emissions standards. Additional testing will be done to understand the impact of biodiesel on Cu-zeolite-based SCR catalysts. Unlike Fe-zeolite catalysts used in research to date, Cu-zeolite is less susceptible to HC adsorption and will most likely be a leading technology used beyond 2010. Testing will also be done to understand how the alkali and alkaline metals found in biodiesel will impact aftertreatment systems through ash exposure.
- Field fuel quality surveys of biodiesel and E85 commercially-available in the U.S. are being conducted. NREL will conduct an additional B6-B20 survey in the U.S. comparing samples against ASTM D7467 specification and continue collaboration with CRC to conduct another FFV fuel survey in 2010. The CRC collaboration will be extended to sample ethanol blender pumps that dispense lower ethanol content fuels for FFVs.
- Robust test methods to characterize the trace components in biofuels and biofuel blends are being developed and validated. They will expand HPLC capability for analysis of impurities in biodiesel and other biofuels, more fully develop these chromatographic methods to reduce run times, improve separation, and reduce detection limits. The MALDI-TOF MS technique to investigate the nature of precipitates above the cloud point in biodiesel samples will be applied and methods for applicability to advanced biofuels such as cellulosic ethanol, biobutanol, and non-fatty acid methyl ester (FAME) biomass-based diesel fuel will be modified.

- The low-temperature flow performance of biodiesel blends will continue to be evaluated. The performance of additional high CSFT B100 will be evaluated. B20 and B5 blends from a biodiesel having CSFT between 200 and 360 seconds will be tested. Currently the faster 200 second CSFT is required for biodiesel to be blended in fuels with CP < -12°C, but many in the industry do not believe this is necessary.
- The toxic organic emissions from ULSD will be continued to be compared with those from soy biodiesel at concentrations of 20 and 100 percent (B20 and B100). Unknown nitro-compounds in existing PM extracts will be identified, robust sampling methods for volatile and semi-volatile nitro-compounds in exhaust downstream of the DPF will be developed, and DPF-out nitro-compounds from 2007 and 2010 diesel engines will be quantifyied.
- The compatibility of representative samples of in-use retail petroleum dispensing equipment will continue to be evaluated with gasolines containing higher concentrations of ethanol than currently allowed, particularly blends in the range of 15-20% ethanol. Failure tests on legacy dispensers, components, and hanging hardware with a test fuel representing 15% ethanol with a margin of error will be conducted and exposure testing of components and materials used in refueling station systems with various test and control fuels reflecting 0%, 10%, 15% and 20% ethanol with margins of error will be completed.
- Fuel tank headspace vapor flammability of various ethanol-blended fuels at various ambient temperatures will continue to be experimentally evaluated. Flammability studies using a matrix that varies critical fuel blend parameters (e.g., ethanol content, vapor pressure, and hydrocarbon composition) systematically will be performed. The apparatus and experimental methods used in this study so they can be recommended as standard test practices will be refined. Further studies of varied candidate E85 blends for which full hydrocarbon information is known so conclusions about the accuracy and reliability of flammability modeling can be drawn will be conducted. The flammability models to determine if tank safety could be predicted in a way simple enough for field use but more reliable than dry vapor pressure equivalent (DVPE) alone will be studied. A technique for extracting the necessary gasoline data from the distillation (D86) data of a low-alcohol blend so modeling is more accessible to others will be devised.

NREL and ORNL will continue quantifying the immediate impacts of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on regulated tailpipe emissions and fuel economy. A full-useful life vehicle study is underway to examine the long-term emissions impact of observed peak catalyst temperature increases with increasing ethanol content during power-enrichment.

ORNL will continue developing or 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 will conduct analyses with capillary electrophoresis of inorganic and organic acid anions in exhaust condensates and evaluate soot derived from non-petroleum-based fuel engine combustion for aromatic acids and anhydrides.

ORNL will continue studying the potential of improving the fuel economy of FFVs when using E85. Fuel economy and emissions limits of homogeneous-charge, spark-ignition, lean-burn engines and prototype lean-NOx catalysts will be established and additional technologies for enhancing efficiency, such as direct-injection, cylinder deactivation, variable valve timing, boosting, etc., will be explored.

Five projects are being continued to improve the fuel economy of flexible-fuel vehicles when operating on E85 without degrading the fuel economy when using gasoline:

- General Motors will continue demonstrating the capabilities of a flexible-fuel turbocharged engine, which incorporates recirculated cooled exhaust gas along with other synergistic technologies, to achieve significant (15%) fuel economy benefit relative to conventional naturally aspirated engines operated on the same fuel. Engine management system functions and optimize engine calibrations will be developed and demonstration vehicle build and testing will be completed.
- MAHLE Powertrain, LLC will continue demonstrating a new, commercially-viable engine that is optimized for E85 operation. Single-cylinder research and multi-cylinder engines will be developed and tested using E85. Vehicle fuel economy and emissions will be predicted.

- Ford will continue to demonstrate the benefits of a dual-fuel (gasoline and E85) turbocharged engine which maximizes the efficiency 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. The multi-cylinder engine dynamometer development will measure full-load performance and fuel efficiency at vehicle mapping points for the FFV and E85-optimized dual-fuel engines, evaluate dual-fuel performance and fuel economy at 12:1 compression ratio, and develop a cold starting strategy for E85-optimized dual-fuel engines. Vehicle level attributes for the FFV and E85-optimized dual-fuel engines will be evaluated.
- Robert Bosch LLC is developing an optimized FFV, targeting substantial fuel economy improvement with minimum driveability and fuel consumption penalties using a direct injection turbocharged spark ignition engine. They will demonstrate their proposed concepts at both engine and vehicle levels to confirm fuel economy improvements.
- Delphi will continue optimization of a production-based engine to take full advantage of ethanol's high octane and high latent heat of vaporization. The effects of enhanced intake charge motion will be studied and valvetrain, intake manifold and fuel injection targeting and timing will be varied to enhance charge motion. Effects of burn rate and combustion stability on fuel economy will be evaluated. A matrix of vehicle applications will be evaluated and optimized over representative drive cycles using a simulation model.

The University of Illinois at Urbana-Champaign is measuring and evaluating properties of pure biodiesel and biodiesel/diesel blends for LTC combustion modeling. They will evaluate the next generation biofuels, including biodiesel produced from micro-algae and bio-butanol blended biodiesel and diesel fuels, in terms of their properties, and combustion and emissions characteristics in LTC engines. Biodiesel LTC engine operating conditions with the multiple-cylinder engine and the optical engine will be optimized with the assistance of multi-dimensional computations. Optimizing variable spray angle injection with biodiesel and blends will be done to improve efficiency and lower emissions. The spray and combustion of butanol-biodiesel-diesel blends will be analyzed to understand the control mechanisms of micro-explosion phenomena, and explore the potential of using them to improve combustion and emissions of biodiesel-based fuels.

PNNL will use fuels data to investigate new correlations for bulk properties and 'fit for service' issues, e.g., lubricity and seal swell, and supporting other infrastructure and material compatibility issues, e.g., cold-temperature performance, crankcase oil compatibility and storage stability, that could be devastating to the introduction of fuels derived from unconventional hydrocarbon resources.

PNNL is analyzing international alternative fuel use which supports alternative fuel infrastructure development in the United States. They will conduct an analysis of E20 use in Thailand concentrating experiences which could benefit the introduction of E20 in the U.S.

PNNL is developing an agile decision analysis portfolio tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies. The prototype model will be made more general and modular so that it is easier to add new technologies and pathways simply by adding standard template modules. A model of automobile fleet turnover will be added that enables analysis of how long it might take for new technologies to obtain significant market share and achieve changes in results. Variations in battery cost and battery performance over time will be included as well as the use of both E15 and E20 versus E85 and compare cost for distributed infrastructure.

Special Honors/Recognitions

1. Salvador Aceves of LLNL was invited to serve as an opponent in Ph.D. exam, Chalmers University, Gothenburg, Sweden, September 2008.

2. Nick Killingsworth of LLNL was invited to deliver a seminar at the "Advanced Engine Control Symposium," Tianjin, China, November 2008.

3. Salvador Aceves of LLNL was invited to serve as an opponent in Ph.D. exam, University of Castilla La Mancha, Spain, March 2010.

4. Chuck Mueller of SNL received the Society of Automotive Engineers 2008 Harry L. Horning Award for the paper titled "Early Direct-Injection, Low-Temperature Combustion of Diesel Fuel in an Optical Engine Utilizing a 15-Hole, Dual-Row, Narrow-Included-Angle Nozzle," SAE Technical Paper 2008-01-2400.

5. Charles K. Westbrook of LLNL was elected to the 2008-2009 Class of Fellows of the Society of Automotive Engineers.

6. Charles K. Westbrook of LLNL received the 2008 Bernard Lewis Gold Medal award by the Combustion Institute.

7. Charles K. Westbrook of LLNL is serving as the 2008-2012 President of the Combustion Institute.

8. SCIENCEWATCH© identified Charles Westbrook and William Pitz of LLNL as in the top 25 most cited authors in the area of energy and fuels for the period of 1998 to 2008.

9. William J. Pitz of LLNL was invited to give the Plenary Lecture at the 2008 International Conference on Modeling and Diagnostics for Advance Engine Systems (2008 COMODIA), Sapporo, Japan.

10. William Pitz of LLNL received an award as co-author on the best paper of the year from the Japanese Combustion Society. The paper is "A Kinetic Modeling Study on the Oxidation of Primary Reference Fuel-Toluene Mixtures Including Cross Reactions between Aromatics and Aliphatics", Y. Sakai, A. Miyoshi, M. Koshi, W. J. Pitz, Proceedings of the Combustion Institute, 2009.

11. Magnus Sjoberg of SNL was the invited speaker at the 5th International SAOT Workshop on Optical Metrology, Erlangen, Germany, March 2009.

12. Brian West of ORNL received the SAE Excellence in Oral Presentation Award for the "Fuel Economy and Emissions of the Ethanol-Optimized Saab 9-5 BioPower" presentation at the Fall SAE Powertrain and Fluid Systems Conference (SAE 2007-01-3994), October 2007.

13. Brian West of ORNL received the Lloyd L. Withrow Distinguished Speaker Award at the 2009 SAE Congress, April 2009.

PATENTS ISSUED

1. Robert Bosch LLC pending US Patent, "Fuel Composition Recognition and Adaptation System", Serial Number 12/417240.

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
Office of Vehicle Technologies

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

Todd J. Toops (Primary Contact) and
Bruce G. Bunting
Oak Ridge National Laboratory (ORNL)
2360 Cherahala Blvd.
Knoxville, TN 37932

Ke Nguyen, D. William Brookshear,
Adam D. Youngquist, Adam L. Foster,
and Nathan A. Ottinger
University of Tennessee-Knoxville

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
University of Tennessee, Knoxville, TN

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 the manufacturers:
    - BASF, Fleetguard, Delphi/Umicore, Catalytic Solutions, and General Motors (GM).
  - Catalyst substrates and diesel particulate filters represented by multiple materials and suppliers:
    - Cordierite, SiC, and mullite substrates from NGK and Dow.
  - Project has resulted in several industrially sponsored projects.
- Develop protocols for implementation using either a bench-flow reactor or a single-cylinder diesel engine with appropriately-sized emissions control devices.
- Current areas of focus:
  - Rapid phosphorus poisoning of diesel oxidation catalysts (DOCs).
  - Rapid ash loading of diesel particulate filters (DPFs).
  - Rapid thermal aging of lean-NOx traps (LNTs).
  - Thermal aging of DOC-selective catalytic reduction (SCR)-DPF system focusing on SCR effects.
  - Biodiesel effects on emissions control devices.
- Extensive materials characterization conducted in all project areas.
- Much research is conducted as the basis of graduate student thesis research at the University of Tennessee-Knoxville, using ORNL tools and techniques.

Accomplishments

- Rapid phosphorus poisoning of DOCs:
  - Confirmed primary deactivation mechanism is due to soot layer rather than phosphorus.
  - Found effect of phosphorus on the oxygen storage capacity of the DOC:
    - Although this effect did not impact the performance, it could affect the ability of the DOC to oxidize CO and HCs during brief rich excursions.
- Rapid ash loading of DPFs:
  - Developed techniques to form plugs in the rear of the DPF channels or to form uniform ash layers along channel length:

    - Techniques are employed in other projects where ash layers and plugs are necessary part of aging evaluation.
- Rapid thermal aging of LNTs:
  - Determined that aging above 900°C introduces material changes that are not reflective of aging mechanisms observed at 700 and 800°C.
  - Identified effect of aging not only on oxides of nitrogen (NOx) reduction performance, but also on the relative reaction rates:
    - This has a large impact on the product speciation, such as increased NH_3 formation in aged samples.
    - Has an impact on the potential use of combined LNT-SCR combined systems.
- Rapid thermal aging of DOC-SCR-DPF system:
  - Using accelerated approach, replicated both deactivation mechanisms observed in field-aged samples.
  - Demonstrated that the use of the DOC to create high lean-exhaust temperatures can result in the volatization of a minute amount of platinum group metals (PGM) which can deposit on the SCR catalyst:
    - This results in non-selective NH_3 oxidation and drastically reduces performance.
- Biodiesel effects on emissions control devices:
  - Characterized several field-aged emissions control devices that have been operated with B20:
    - DOC and DPF obtained from GM.
    - LNT obtained from Umicore via the Manufacturers of Emission Controls Association and the National Renewable Energy Laboratory.
  - Determined that only ~5% of ash content is due to Na in biodiesel.
  - Determined that Na has minimal impact on LNT performance–as expected.
  - Initiated accelerated Na introduction with a DOC-SCR-DPF emissions control system and the single cylinder engine:
    - Measured significant performance loss on the NO-reduction of the SCR.
    - When NO_2 is included, impact is significantly less.

Future Directions

- Rapid phosphorus poisoning of DOCs:
  - Project completed; no further research planned.
- Rapid ash loading of DPFs:
  - Project completed; no further research planned.
- Rapid thermal aging of LNTs:
  - Publish final paper linking materials effects to performance observations. (To be submitted to Applied Catalysis B: Environmental.)
- Rapid thermal aging of DOC-SCR-DPF system:
  - Publish final paper linking materials effects to performance observations. (To be submitted to Catalysis Today.)
- Biodiesel effects on emissions control devices:
  - Continue investigation into the impact of Na on emissions control devices:
    - Identify what sites are being affected by Na contamination in the zeolite-based SCR catalysts.
    - Confirm that the Na:Ca ratio is on the order of 5% in field-aged ash plugs.
    - Investigate impact of oil dilution by biodiesel on the rate of ash generation.
  - Investigate impact of biodiesel oil dilution on lubrication properties.
- Interaction of ash components with catalyst washcoat during high temperature cycling from DPF or NOx trap regeneration.

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Introduction

The development and refining of current emissions control devices on spark ignition engines have allowed great advances in the efficiency of three-way catalysts (TWC). 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 LNTs and high temperature, lean operation for the regeneration of the DPFs.

In 2010, diesel vehicles can require a DOC, a DPF, and a NOx reduction device. Currently, urea-based SCR and LNTs are the leading candidates for NOx control and both are being implemented. All of these devices are susceptible to aging and poisoning to some degree. Phosphorus is a well-known catalyst poison that is derived from the zinc dialkyl-dithiophosphate (ZDDP) additive in lube oil used as an anti-wear agent. While in operation, an engine consumes lube oil, which results in phosphorus in the exhaust gases and subsequently the emissions control devices. The consumption of oil also leads to the formation of ash particulates which are trapped in the DPF; however, they remain in the filter until they are physically removed. The sulfur concentrations in ultra-low sulfur diesel (ULSD) fuel are still too high to avoid the inhibiting effect of SO_2, particularly in LNTs. Its effect can be reversed through periodic high temperature rich operation, but this process leads to irreversible catalyst aging mechanisms. It is the aim of this project to develop aging and poisoning protocols that address these key areas of deactivation in diesel emissions control devices that not only simulate the conditions in the field but also provide a deeper and more rapid understanding of the chemistry behind the deactivation. This understanding will guide future catalyst formulations, engine control strategies, and enable models to more accurately predict catalyst performance throughout the lifetime of the vehicle.

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 in this study is the concerns that have arisen from the presence of trace levels of Na in biodiesel, 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 liquid 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 new emissions control devices that are found in modern diesel vehicles. Of particular concern are the deactivation of zeolite-based SCR catalysts and the generation of additional ash that would accelerate the blockage of DPFs. 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 517cc Hatz single-cylinder diesel engine was modified to accommodate intake and exhaust manifold injection of lube oil or diesel fuel. Lube oil or specific lube oil additives can also introduced in the fuel or in the injection ports to further accelerate poisoning or simply used to increase the ash content of the exhaust. The fuel sprayed into the exhaust is either used to regenerate the LNT during typical operation for NOx conversion measurements or to induce an exotherm for high temperature thermal aging. Additionally, the fuel fed to the engine can be mixed with elevated levels of Na to allow the introduction of a lifetime of 5 ppm Na in very short time frames. The engine system is equipped with a full array of analytical systems to allow measurement of hydrocarbon (HC), carbon monoxide (CO), NOx conversions, as well as pressure drops and temperatures at various locations including the midbed of the emissions control devices.

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 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 (BET) physisorption, H_2 chemisorption, X-ray fluorescence (XRF), inductively coupled plasma (ICP) techniques, scanning and transmission electron microscope (SEM and TEM), X-ray diffraction (XRD) 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

Rapid Phosphorus Poisoning of DOCs

The deactivation of DOCs by soot contamination and lube-oil derived phosphorus poisoning was investigated. $Pt/CeO_2/\gamma\text{-}Al_2O_3$ DOCs were aged using three different protocols and compared to six high mileage field-service DOCs of similar formulation. The field-service and engine-aged DOCs were then evaluated for total hydrocarbon (THC) and CO oxidation performance using a bench-flow reactor. Collectively, these DOCs exhibit a variety of phosphorus and soot morphologies contributing to performance deactivation. To isolate and examine the contribution of each deactivation mechanism, performance evaluations were performed on each DOC "as received" and after subsequent surface soot oxidation in a high temperature oxidizing environment. In such a manner the deactivation contribution of soot contamination is de-convoluted from that of phosphorus poisoning. This is accomplished while preserving phosphorus (and to a lesser degree sulfur, calcium and zinc) chemistries and concentrations within the washcoat. Washcoat contaminant information and materials changes are characterized using EPMA, XRD, SEM-EDS, BET, oxygen storage capacity, XRF and ICP, from which the relative severity of each mechanism can be quantified. Results show that soot contamination from diesel exhaust severely degraded THC and CO oxidation performance by acting as a catalyst surface diffusion barrier (Figure 1, soot laden vs. soot oxidized). This results in a considerable increase of THC and CO light-off temperatures. In contrast, phosphorus poisoning, which is considered a significant deactivation mechanism in three-way catalysts, is shown to have minimal effect on DOC oxidation performance for the conditions studied here (Figure 1, fresh vs. soot oxidized). The aged catalysts do show the formation of both Ce(III-IV) and aluminum phosphates, but these phases do not significantly hinder the THC and CO oxidation in lean exhaust. This impact of phosphorus does impact the oxygen storage capacity of the ceria (Figure 2), but as shown in Figure 1 this impact does not affect the performance of the DOC. Although this did not impact lean DOC performance, it could affect the ability of the DOC to function during cyclic operation where the catalyst is exposed to brief rich excursions.

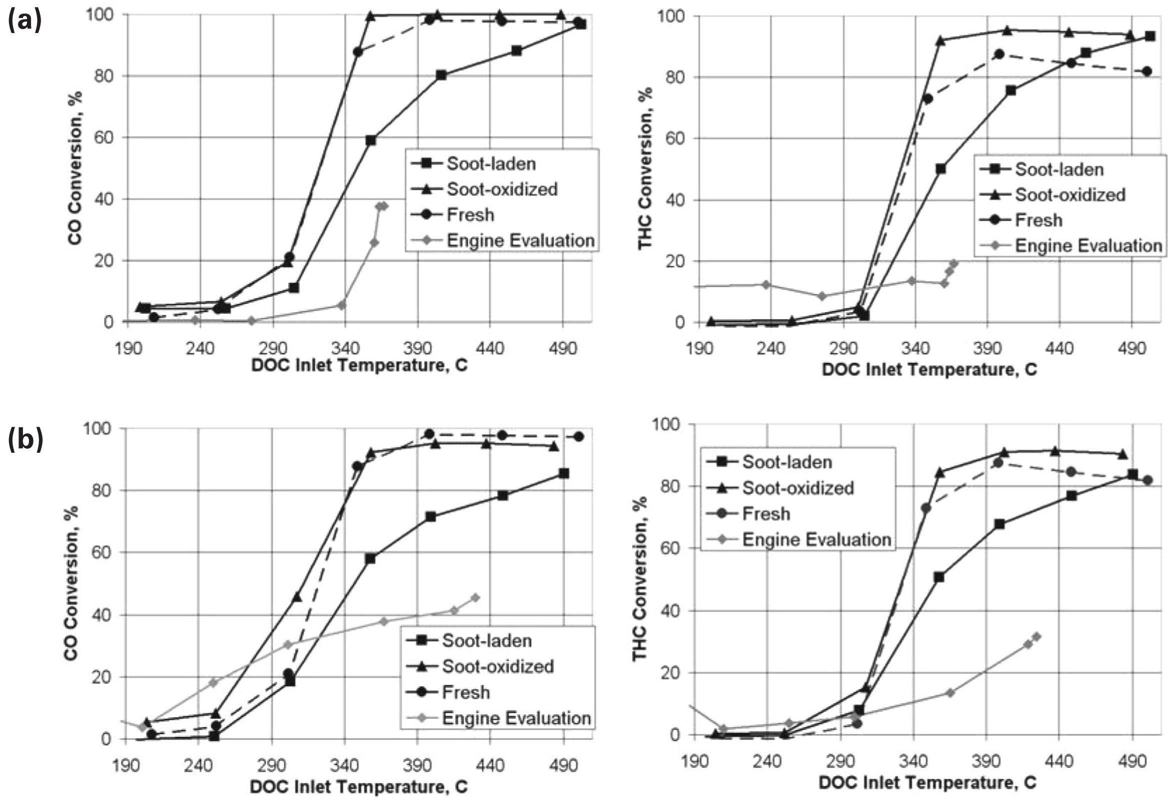


FIGURE 1. The inhibiting effect of a soot layer is illustrated in the CO and HC light-off curves of DOCs that have been aged a) using an accelerated aging protocol with elevated levels of ZDDP added to the fuel and b) in the field.

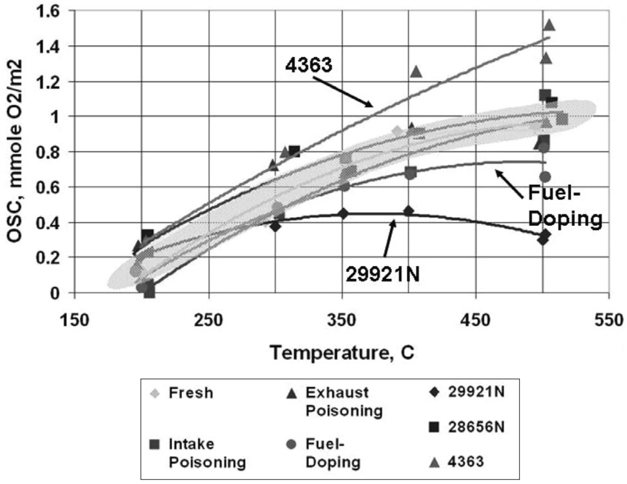


FIGURE 2. Oxygen storage capacity of fresh and aged diesel oxidation catalysts after surface carbon oxidation; shaded area encompasses response of typical fresh DOCs. The field-aged samples are represented by 29921N, 28656N and 4363 which are fully described elsewhere [1].

Rapid Ash Loading of DPFs

The accelerated ash loading of DPFs with DOCs mounted upstream by lube-oil derived products was investigated using a single-cylinder diesel engine and fuel blended with 5% lube oil. An ash loading protocol was developed which combines soot loading, active soot regeneration, and periodic shutdowns for cooling and filter weighing. Active regeneration was accomplished by exhaust injection of diesel fuel, initiated by a backpressure criterion and providing DPF temperatures up to 700°C. In developing this protocol, five DPFs of various combinations of substrates (cordierite, silicon carbide, and mullite) and washcoats (without PGM, low-PGM, and high-PGM) were evaluated. The initial backpressure and rate of backpressure increase with ash varied with each of the DPFs and ash was observed to have an effect on the active soot light-off temperature for the catalyzed DPFs. Multiple characterization techniques were performed on the ash layers, and ash distribution was found to be weighted towards the back of the DPFs with ash plugs apparent in the rear of the DPF channels (Figure 3). This profile is similar to the distribution of ash commonly observed in field aged samples [2-5]. As ash accumulates, the benefits of a catalyst for soot light-off are diminshed (Figure 4), and therefore, the full benefit of having a catalyst in the DPF may not be realized once an ash layer accumulates.

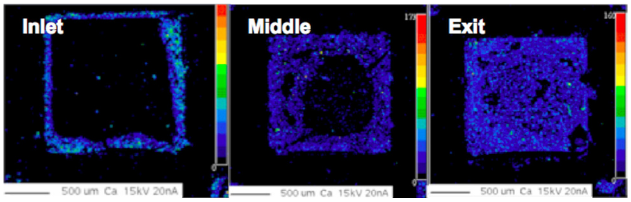


FIGURE 3. EPMA elemental maps of calcium for lightly-catalyzed cordierite substrate. The calcium is representative of ash accumulation in the channels of the DPF.

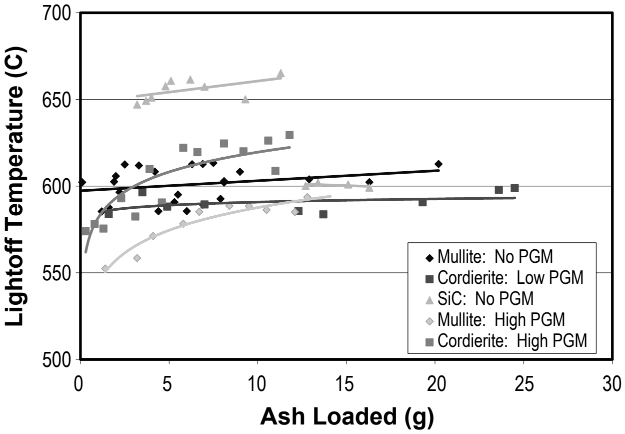


FIGURE 4. Impact of ash accumulation on light-off temperature associated with DPF regeneration.

Rapid Thermal Aging of LNTs

High-temperature deactivation of a fully-formulated LNT was investigated. Thermal aging was carried out in a bench-core reactor at 700, 800, 900, and 1,000°C using a long aging cycle–the cycle consists of a 130 s lean-phase and a 50 s rich-phase. After a prescribed number of lean/rich aging cycles, the NOx conversion of the aged LNT is evaluated at 200, 300, and 400°C using a short evaluation cycle consisting of a 60 s lean-phase and 5 s rich-phase as proscribed by the Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) protocol. The effects of aging on the LNT washcoat are determined with EPMA, XRD, STEM/EDS, and BET. Aging at 700 and 800°C has a minimal effect on LNT performance and material properties; however, at aging temperatures of 900 and 1,000°C reduction in surface area and sintering of PGM particles are observed, resulting in a drastic reduction in NOx conversion (Figure 5). Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) analysis was used to determine the effects of high temperature aging on surface chemistry and NOx storage. As PGM dispersion decreases with aging, the NO turnover frequency for NO oxidation at 200, 300, and 400°C was observed to increase. NOx storage and temperature programmed desorption experiments performed with DRIFTS at 200, 300, and 400°C indicate that a substantial amount of NOx is stored on Al_2O_3 as nitrates at 200 and 300°C before aging. However, almost no nitrates are observed on alumina after aging at 900 and 1,000°C, resulting in a significant reduction in NOx storage capacity. This is most likely due to a 45% reduction in total surface

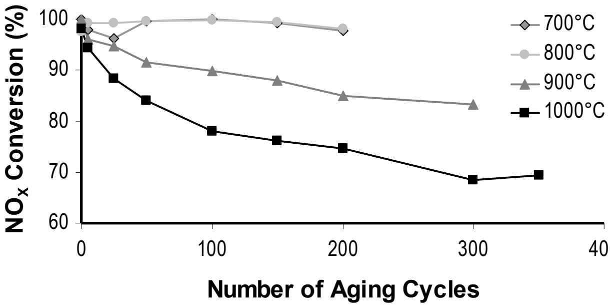


FIGURE 5. NOx conversion at 300°C after aging at the indicated nominal aging temperatures.

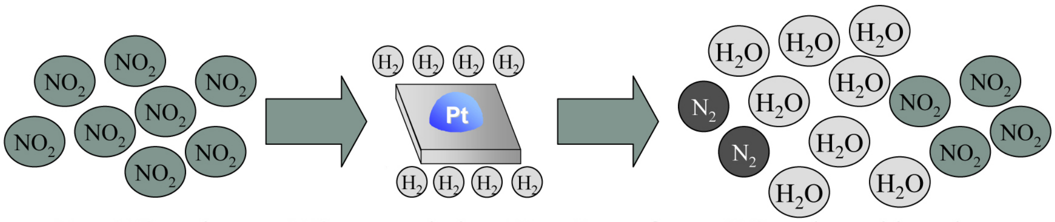
area and a high temperature redispersion of Ba over remaining alumina sites; no evidence of $BaAl_2O_4$ was observed with XRD. All of these results [6-7] point to an important finding from this effort: the fraction of stored NOx that was released and successfully reduced increases with aging. This occurs due to a slower release of more stable NOx species resulting from thermal aging. Subsequently, this significantly impacts the product speciation as additional NH_3 is expected from the aged samples (Figure 6).

Rapid Thermal Aging of DOC-SCR-DPF System

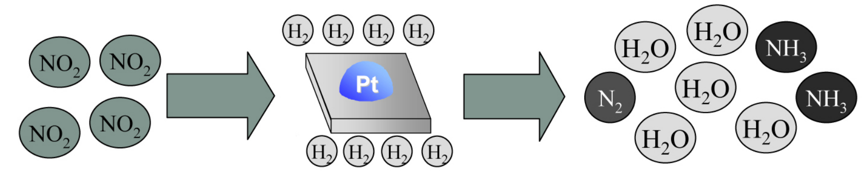
A single-cylinder diesel engine with an emissions control system–DOC, Fe-zeolite SCR catalyst, and DPF–was used to perform accelerated thermal aging of the SCR catalyst. Cyclic aging is performed at SCR inlet temperatures of 650, 750 and 850°C for up to 50 aging cycles. To assess the validity of the implemented accelerated thermal aging protocol, a field-aged SCR catalyst of similar formulation was also evaluated. The monoliths were cut into sections and evaluated for NOx performance in a bench-core reactor. While the rear section of both the field-aged and accelerated engine-aged SCR catalysts maintained high NOx conversion, 75-80% at 400°C, the front section exhibited a drastic decrease to only 20-35% at 400°C (Figure 7). This two-tiered deactivation was also observed for field-aged samples (Figure 7c). To understand the observed performance changes, thorough materials characterization was performed which revealed two primary degradation mechanisms. The first mechanism is a general Fe-zeolite deterioration which led to surface area losses, dealumination of the zeolite, and Fe_2O_3 crystal growth. This degradation accelerated above 750°C, and the effects were generally more severe in the front section of the catalyst. The second deactivation mechanism is linked to trace levels of Pt that are suspected to be volatizing from the upstream DOC and depositing on the front section of the downstream SCR catalyst [8-9]. Chemical evidence of this can be seen in the high levels of NH_3 oxidation (80% conversion at 400°C), which coincides with the decrease in performance.

Biodiesel Effects on Emissions Control Devices

Efforts since Fall 2008 have focused on both performance and materials characterization of field-aged and accelerated engine-aged emissions aftertreatment devices. In particular, the effect of Na contamination on the performance of DOCs, LNTs, and Cu-zeolite SCR catalysts was investigated using a bench-core reactor; additionally, field-aged DPFs were simply characterized for ash build-up and elemental analysis. To date the field-aged LNTs have not shown a significant deactivation mechanism that can be attibuted to biodiesel-based Na. Following desulfation, only minor performance differences are observed with the LNT



Fast NO_2 release…NO_2 overwhelms H_2 at Pt surface…NO_2 released in exhaust



Slow NO_2 release…H_2 overwhelms NO_2 at Pt surface…NH_3 formation possible

FIGURE 6. Schematic of how NOx reduction and its products depend on NOx release rate.

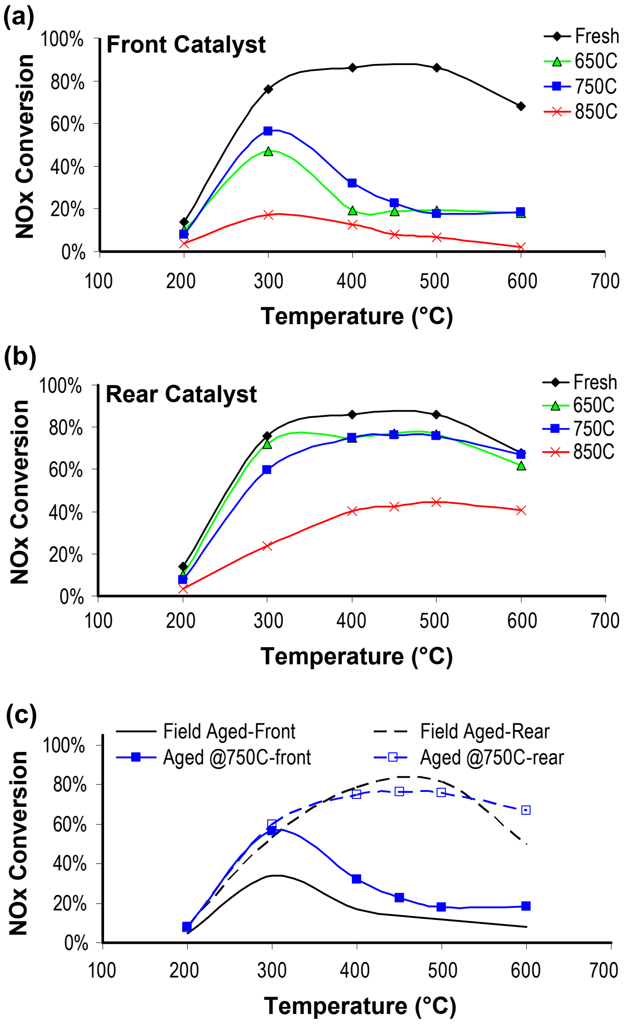


FIGURE 7. NOx conversion of the accelerated engine-aged Fe-zeolite SCR catalysts (a) front and (b) rear sections. (c) Field-aged samples show similar performance and deactivation mechanisms as the accelerated-aged samples (aged at 750°C for 50 cycles).

compared to the fresh sample. It is expected that this minor performance difference is simply due to PGM sintering common in aged samples; field-aged DOCs are currently under investigation. In the field-aged DPFs, a 50 mm ash plug is clearly visible in the rear of the inlet channels (Figure 8); as shown earlier, these ash plugs are expected in ULSD-fueled vehicles as well as biodiesel ones. Quantitative elemental analysis of the front section of this plug reveals that ~5% of the ash is constituted of Na. This level is not expected to significantly alter maintenance intervals. However, there have been reports that the use of B20 has lead to ash accumulation of up to twice as fast, so further studies are warranted to determine if this is occurring and if so, is it due to Na or is there another factor leading to increased oil consumption and subsequently increased ash accumulation.

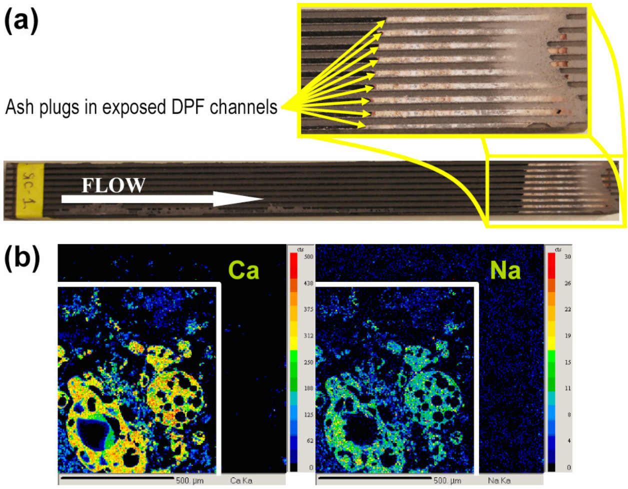


FIGURE 8. (a) Ash plugs apparent in field-aged DPF sample operated with B20. (b) Elemental analysis of front of ash plugs using EPMA showing the presence of Ca and Na; quantification of the analysis reveals that ~5% of ash plug is due to Na.

In addition to the evaluation and characterization of the field-aged samples, accelerated engine-aging was carried out in a 500cc single-cylinder diesel engine bench using B20 with an elevated concentration of Na. The EPMA micrographs of accelerated engine-aged SCR catalyst show a layer of Na clearly visible on the washcoat surface. The existence of a Na layer on the catalyst's washcoat has also been observed on field-aged LNTs and DOCs. However, unlike in the LNT results, Na appears to have a significant impact on the NO-reduction performance of the SCR as can be seen in Figure 9a. When NO_2 is included in the simulated exhaust, this impact is less severe (Figure 9b). The reasoning of this impact and its irreversibility will be the focus of future efforts.

Conclusions

- Rapid phosphorus poisoning of DOCs:
  - Soot layer is the dominant deactivation mechanism observed in both accelerated- and field-aged evaluations.
  - Impact of phosphorus observed on oxygen storage capacity, but at the conditions studied here it does not significantly impact CO or HC light-off.
- Rapid ash loading of DPFs:
  - Technique developed to accelerate ash loading in DPFs that achieves plugs in the rear of the channels.
  - Ash layer shown to diminish catalyst effects with respect to soot light-off temperature.

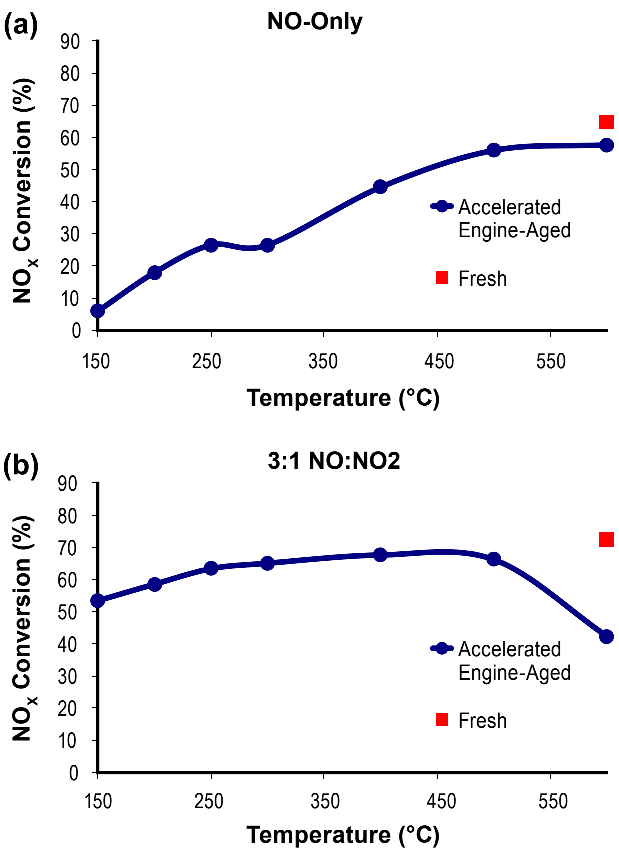


FIGURE 9. Impact of Na on the performance of zeolite-based SCR catalysts with (a) NO as the only NOx source in the flow and (b) a 3:1 ratio of NO:NO_2.

- Rapid thermal aging of LNTs:
  - Thermal effects greatly accelerate when aging above 900°C.
    - However effects are different than those observed at 700 and 800°C, so aging above 900°C is not recommended to accelerate effects observed at 700 or 800°C.
  - Thermally-aging LNTs effects both performance and speciation; more NH_3 observed on aged catalysts.
- Rapid thermal aging of DOC-SCR-DPF system:
  - Techniques employed for accelerating aging replicate field-aged samples with only 50 hours of engine operation.
  - Effects of Pt deposition on the SCR are observed as NOx reduction performance is dramatically reduced.
- Biodiesel effects on emissions control devices:
  - Na layer observed in all field-aged samples.
    - Performance of LNT and DOC does not appear to be affected by Na.
    - DPF ash plug is constituted of ~5% Na compared to 90+% Ca–indicates Na has only minor contribution to ash.
  - SCR appears to be most susceptible to Na
    - Results need to be confirmed and validated with field-aged samples when they become available.

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FY 2008/2009 Publications

1. T.J. Toops, K. Nguyen, A.L. Foster, B. Bunting, N. Ottinger, J. Pihl, E. Hagaman, J. Jiao, "Deactivation of Accelerated Engine-Aged and Field-Aged Fe-Zeolite SCR Catalysts", submitted to Catalysis Today.

2. N.A. Ottinger, K. Nguyen, B.G. Bunting, T.J. Toops, J. Howe, "Effects of Rapid High Temperature Cyclic Aging on a Fully-Formulated Lean NOx Trap Catalyst", SAE International Journal of Fuels and Lubricants 2:1 (2009) 217 (SAE 2009-01-0634).

3. J.A. Zandhuis, C.E.A. Finney, T.J. Toops, W.P. Partridge, C.S. Daw, T. Fox, "Nondestructive X-ray Inspection of Thermal Damage, Soot and Ash Distributions in Diesel Particulate Filters", SAE 2009-01-0289.

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5. A. Youngquist, K. Nguyen, B.G. Bunting, T.J. Toops, "Development of an Accelerated Ash Loading Protocol for Diesel Particulate Filters", SAE 2008-01-2496.

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2. N.A. Ottinger, K. Nguyen, B.G. Bunting, J. Howe, T.J. Toops, "Effect of High Temperature Lean/Rich Thermal Aging on NO oxidation and NOx storage in a Fully-Formulated Lean NOx Trap", Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Dearborn, MI, August 3–6, 2009.

3. D.W. Brookshear, K. Nguyen, B.G. Bunting, T.J. Toops, "Characterization and Evaluation of Field-Aged Emissions Control Devices using Biodiesel Fuel", Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Dearborn, MI, August 3–6, 2009.

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

C. Scott Sluder (Primary Contact),
John M.E. Storey, Samuel A. Lewis,
Michael J. Lance
Oak Ridge National Laboratory (ORNL)
2360 Cherahala Boulevard
Knoxville, TN 37932

DOE Technology Development Manager:
Kevin Stork

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.

Accomplishments

- Conducted discussions with Ford and General Motors engineers to obtain guidance for the direction of the project.
- Completed a study at low hydrocarbon (HC) levels to examine the impacts of soot formed when using biodiesel blends on the EGR cooler fouling process.
- Completed a study at elevated HC levels to examine the impacts of different HCs on the fouling process.
- Successfully measured the deposit thermal conductivity in situ and identified deposit density as a key parameter.
- Provided experimental data to two industrial organizations to aid in calibration of their models of the EGR cooler fouling process.

Future Directions

- Conduct experiments to investigate the mechanism(s) by which HCs may play a role in increasing soot deposits that result in degradation of the EGR cooler thermal performance.
- Investigate pathways that show potential for reducing the impact of fouling on EGR cooler performance and overall engine system design.

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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 the 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 unburned 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, for example, 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

The sampling system and engine necessary to support investigations of EGR cooler fouling were put in place during Fiscal Year 2007. During FY 2008 and FY 2009 studies were conducted to investigate the impact of 5% biodiesel (B5) and 20% biodiesel (B20) use on EGR cooler fouling. These studies focused on short-term experiments aimed at identifying differences in the fouling processes when different fuels are used. In FY 2008 the study focused on conditions where the HC content of the EGR stream was very low. Thus, the first study focused more on the potential impacts of different PM morphology. A second study was conducted in FY 2009 at higher HC levels to add information about the impact of HCs on the fouling process. The conditions for both studies (other than the HC concentration) were identical. The findings from these studies were published through SAE International [1-3].

Experiments were conducted using ultra-low sulfur diesel (ULSD) fuel, B5, and B20 blends. For each fuel, a series of experiments was conducted to examine the development of the fouling layer in the surrogate EGR cooler tubes at different time intervals from 0.5 up to 12 hours duration as well as at three coolant temperatures: 90°C, 70°C, and 40°C. The surrogate tubes for this study were 305 mm in length with a square cross-section of 6.35 mm per side. The tubes were composed of stainless steel with wall thickness of 0.51 mm.

The results showed that the fouling layer mass increased non-linearly with time, and that the loss of thermal performance by the tube was significant in only a few hours. The surrogate tubes in both studies initially exhibited a heat transfer effectiveness of ~60%, and were degraded to ~35% within 12 hours. Most of this degradation occurred in the first 3-4 hours. This level of degradation is quite severe. It is the buildup of deposit that results in the loss of heat transfer performance, and hence, it is useful to examine the relationship between these characteristics. Figure 1 shows the loss in heat transfer effectiveness versus the total mass of the deposit formed during each experiment conducted in the low-HC study. Data are included for ULSD, B5, and B20 fuels. The results under these experimental conditions do not demonstrate a significant difference in the fouling process for the three fuels studied. Similar trends were observed for the experiments conducted with higher levels of HC.

Fractionation of the deposit masses showed that most of the deposit mass was non-volatile, consistent with it being carbon soot. A significant portion of the deposits was found to result from semi-volatile HCs. In the low-HC experiments, the fraction of the deposit that was volatile was ~20% for ½ hour experiments and rapidly decreased with longer experiments to a near-steady level for each fuel. This result is shown in Figure 2. The near-steady fraction was about 5% for ULSD and was about 7% for B20. B5 resulted in a level very similar to ULSD. Experiments with higher HC conditions showed the same trend, but the steady levels of volatile fraction were ~2-3 times higher.

Both the low- and high-HC experiments showed similar results in terms of the impact of coolant temperature. In both cases, data was taken at a 2-hour experiment duration at lower coolant temperatures and compared with the baseline 90°C case at the same experiment length. The results showed that the lower coolant temperatures produced deposits of higher mass, but with effectiveness degradation comparable to the baseline condition. The deposits in these cases exhibited

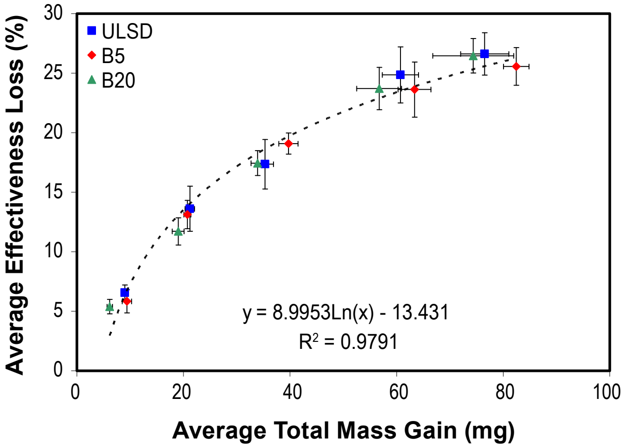

FIGURE 1. Heat Transfer Effectiveness Loss versus Total Deposit Mass

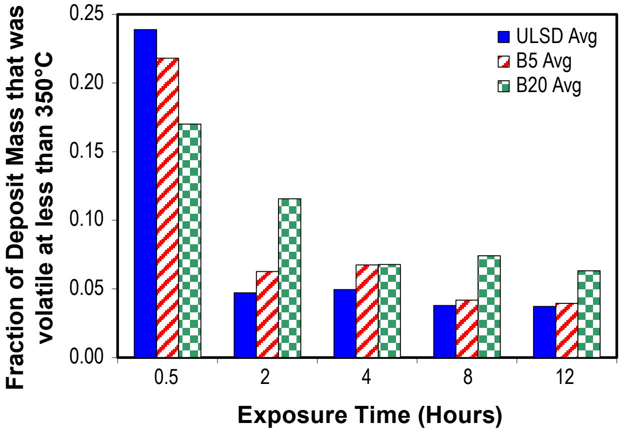

FIGURE 2. Volatile Fraction of the Deposit Mass

higher volatile fractions than the baseline case. HCs made up the increased mass of the deposit (within the error associated with the measurements), and did not significantly degrade the thermal effectiveness beyond the level observed for the higher-temperature baseline condition.

Several of the tubes with deposits were selected for microscopic analysis. These tubes were subjected to measurements of the deposit thickness, density, specific heat, and thermal diffusivity as well as microscopy. Thermal conductivity of the in situ deposit was determined directly from these measurements without the need to separate the deposit from the stainless steel tube surface. These measurements showed that the deposit was >95% porous, with a thermal conductivity of approximately 0.065 W/m^2K. This thermal conductivity is about an order-of-magnitude lower than typical HCs and approaches the thermal conductivity of many bulk insulating materials. The density of the deposit has the most impact on its thermal conductivity. The amount of HC mass needed to significantly impact the void volume is several times higher than the soot mass that formed the voids. Thus, the HC fractions observed in these studies do densify the deposit, but not significantly enough to impact the deposit thermal conductivity.

The results from these studies suggest that the soot fraction of the deposit is most responsible for degradation of the thermal performance of the EGR cooler. In fact, one experiment conducted with a particle filter upstream of the tubes showed that there was little, if any, decline in thermal performance. This finding has also been published by researchers at Southwest Research Institute® [4]. The impact of HCs in these results is confined to densification of the deposit layer. However, researchers at Ford showed that the presence of an oxidation catalyst upstream of the EGR cooler reduced the degradation in thermal performance associated with fouling [5]. This is most likely a result of oxidizing HCs. Hence, it appears that there is some mechanism by which HCs aid in the deposition of additional soot in the deposit. Future studies are aimed at identifying the mechanism by which HCs might participate in soot deposition and retention. Identifying this mechanism will enable more targeted studies to investigate the impact of non-petroleum-based fuels on this process.

Conclusions

Industrial partners have been consulted and have provided guidance for the project. A suitable engine, test cell, and supporting hardware and methods have been established and the project has generated substantial results. The results to date indicate that biodiesel blends up to B20 do not exhibit worse EGR cooler fouling characteristics than ULSD. This conclusion is based on short-term, steady-state data. Soot in the deposit is most responsible for degradation in thermal performance associated with fouling, with HCs playing an insignificant role. Industry data has shown an effect from HCs in longer term transient studies, hence, additional research is needed to understand this effect and to rule out any fuel-chemistry specific issues that could pose barriers to the increased use of non-petroleum-based fuels.

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

Andrea Strzelec, Stuart Daw (Primary Contact), Todd Toops
Oak Ridge National Laboratory
2360 Cherahala Blvd.
Knoxville, TN 37932

Academic Collaborators:
Professors David Foster and Christopher Rutland
Engine Research Center
University of Wisconsin-Madison

DOE Technology Development Managers:
Gurpreet Singh and Kevin Stork

Objectives

- Improve understanding of fundamental particulate oxidation kinetics in diesel particulate filter (DPF) regeneration, in support of DPF modeling efforts.
- Quantify effects of fuel properties on particulate nanostructure and oxidation kinetics, focusing on the effects of non-petroleum-based fuel (NPBF) species.
- Interact closely with Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) stakeholders.

Approach

- Investigate impact of hydrocarbons on particulate oxidation kinetics using a differential reactor.
- Measure fundamental oxidation kinetics of elemental carbon from ultra-low sulfur diesel (ULSD) and B100 fuel sources.
- Investigate NPBF blend level impacts on particulate nanostructure and surface area, relate to sample reactivity.
- Relate kinetics to DPF regeneration.

Accomplishments

- Evaluated oxidation kinetics for ULSD, B5, B10, B15, B20 and B100 particulate samples.
- Determined the impact of biofuel blend level on the combustion of particulate, noting that B100 reaches peak oxidation rate ~70°C lower than ULSD particulate.
- Measured the impact of the volatile fraction on the particulate combustion temperature; noted the persistence in the fuel impact on combustion temperature after the volatiles were removed, which suggests differences in the fixed carbon portion.
- Measured total surface area evolution with burnout for ULSD and B100 particulates; related particulate surface area to change in oxidation rate.
- Proposed general kinetic framework that includes dominant oxidation pathways for both fixed and volatile carbon.

Future Directions

- Investigate B5 and B20 surface area trends.
- Bench reactor experiments with mini-DPFs to compare differential and device kinetics for models.
- Investigate NO_2 oxidation kinetics.

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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 emissions regulations have made some type of diesel exhaust filtration an unavoidable necessity. Concurrently, the Fuels Technologies sub-program is investigating fuel formulations with increasingly significant amounts of non-petroleum-based fuel components to reduce U.S. dependence on foreign oil. However, there is currently inadequate data and modeling capabilities to predict the impact of alternative fuels 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 DPR 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 (FC) 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 often labeled mobile carbon (MC) since it can be separated from the FC. 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 complex nature of particulate formation and oxidation, this project will advance DPF device modeling for both conventional diesel particulate as well as NPBF derived particulate. These models will be able to better predict DPF regeneration behavior and allow for the design of control strategies to minimize the fuel penalty associated with high engine backpressure or too frequent regeneration.

Experimental Approach

All particulates studied so far in this project have been generated on a late model Mercedes-Benz engine, updated with a common rail fuel injection system, fueled with a range of biodiesel/ULSD blends. To date, work has focused on six different fuel blends (ULSD, 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.

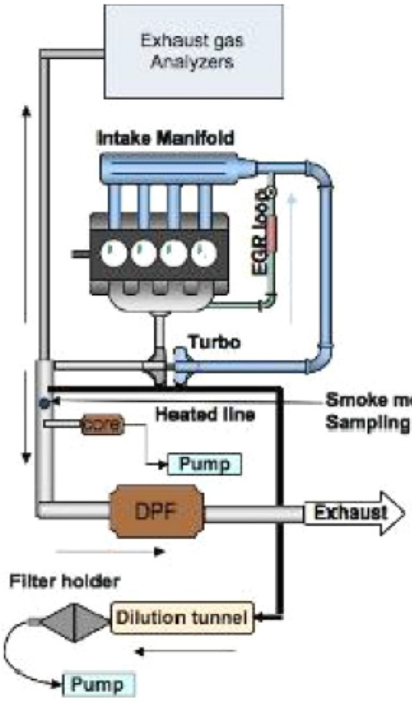

FIGURE 1. Engine and Sampling Setup

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].

These 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 Brunauer-Emmett-Teller (BET) technique. The measurement is made by flowing seven concentrations of Ar in He, estimating the adsorbed Ar at each point with the mass spectrometer. The estimated

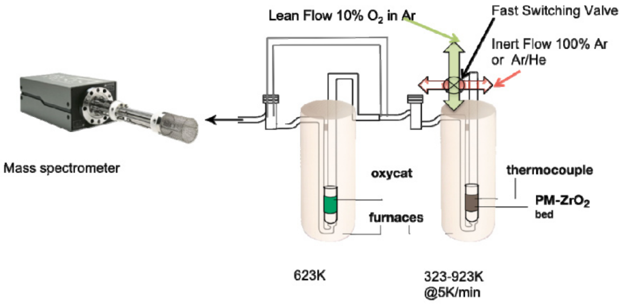

FIGURE 2. Microreactor Setup

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 (HR-TEM) 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 (GC-MS).

Results and Discussion

Based on the temperature-programmed oxidation (TPO) measurements, we found that the presence of adsorbed volatiles correlates closely with the temperature at which significant carbon loss begins to occur. This is illustrated in Figure 3, where the temperatures at which 10% of the nascent PM mass for different particulate samples has been depleted during TPO is plotted against the estimated volatiles present. The amount of volatiles, in turn, depends on the biodiesel blend level. Volatiles content generally goes up with biodiesel blend, but the relationship is more complex at low levels of biodiesel, where small amounts of biodiesel appear to suppress volatiles and low temperature mass loss.

One clue to the mechanism behind the complex trend in volatile content with biodiesel level is revealed in HR-TEM images such as Figure 4. Detailed inspection and analysis of these images suggest that high biodiesel blend percentage particulates have a more open nanostructure that allow more space for volatiles collection. This tendency for higher porosity appears to come from a disruption of the stacking of the underlying graphitic lamella that make up the backbone of the non-volatile carbon. The lamella lengths for high biodiesel particulate blend percentage also appear shorter, implying an increase in the ratio of edge to basal plane carbons. For the B5 particulate, however, this tendency for open nanostructure seems to be reversed, indicating there is some fuel component synergism in particulate formation that develops at low biodiesel blend ratios.

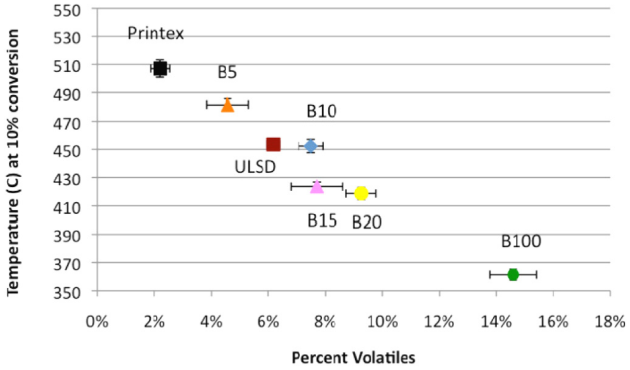

FIGURE 3. Temperature at 10% Mass Conversion of the Nascent Sample vs. Mass Percent Volatiles

Whatever the mechanisms responsible for the complex trends in volatiles content, it will be important for in-cylinder soot formation models to capture this nanostructure effect for small amounts of biodiesel if they are to be useful for predicting the effects of fuel blending strategies on DPF performance.

Results from the pulsed, isothermal oxidation measurements revealed that the oxidation rates of the individual devolatilized particulate samples can be readily fitted to global Arrhenius reaction rate parameters. Example Arrhenius plots are depicted in Figure 5 for both ULSD and B100 particulates. In this plot the higher apparent reactivity of B100 is evident as well as slight differences in the apparent activation energies (123 and 160 kJ/mol for ULSD and B100, respectively).

As noted above, we are able to track particulate surface area changes in the micro-reactor as burnout proceeds with the 7-point flowing BET method. This has revealed the interesting trends depicted in Figure 6. It appears that the initial stages of burnout increase the specific surface area of the particulate samples, perhaps by creating additional porosity in the samples, then after approximately 40% burnout, the surface area begins to plateau. The predicted behavior for a 'shrinking core' model is plotted for comparison, and it is evident that

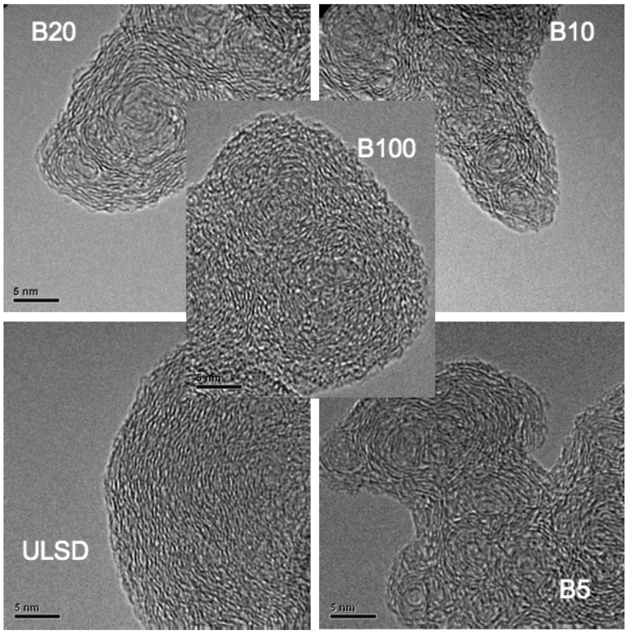

FIGURE 4. HR-TEM images of (clockwise from top left) B20, B10, B5, ULSD and B100 (center) Particles from a 1.7L Mercedes-Benz Engine at 1,500 rpm, 2.6 bar

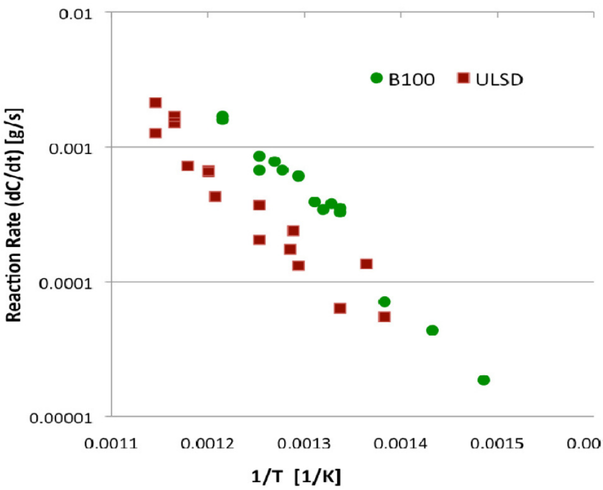

FIGURE 5. Arrhenius Plot of Devolatilized Oxidation Rates for ULSD and B100 Particulate

neither the ULSD nor the B100 particulates follow a shrinking core burnout trajectory.

We also found that appropriate inclusion of surface area makes it possible to reconcile the oxidation rates of the devolatilized ULSD and B100 particulates. When the observed oxidation rates are plotted as in Figure 7 (where the rate of carbon mass loss is normalized to the measured surface area), ULSD and B100 measurements converge, and there is an effective global activation energy of 113 kJ/mol for both particulates. This suggests that it may be possible to develop a single oxidation model for devolatilized diesel particulates from all types of fuel blends as long as surface area effects are properly accounted for.

Further analyses indicate that the observed TPO profiles for ULSD and B100 particulate can be modeled as the sum two terms: 1) a single area-normalized global rate described above for the non-volatile carbon component; and 2) a simple first-order rate model for the volatile component. Model predictions based on this approach are compared to the B100 data in Figure 8.

Conclusions

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

- High levels of biodiesel tend to increase particulate volatiles, but the trend is non-monotonic at low biodiesel levels.
- Oxidation reactivity of both nascent and devolatilized particulates increase monotonically with volatiles.

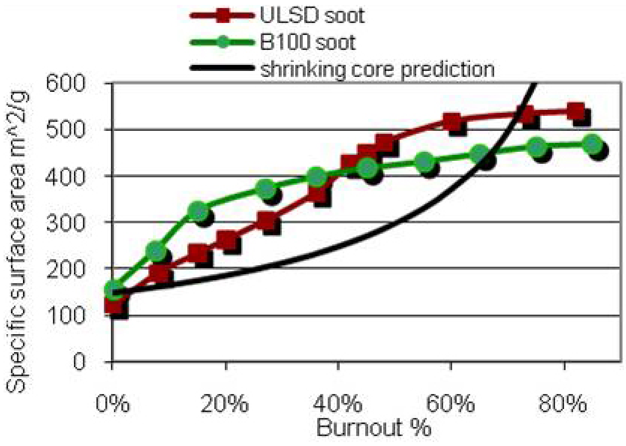

FIGURE 6. Specific Surface Area (area per gram of sample remaining) as a Function of Burnout for ULSD and B100 Soot

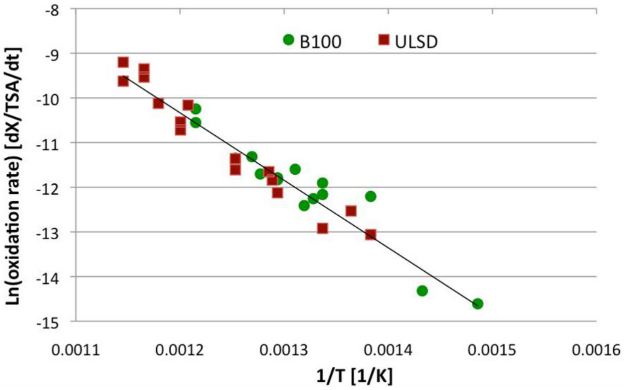

FIGURE 7. Arrhenius Plot of Devolatilized Particulate Reaction Rates Normalized to Surface Area for ULSD and B100

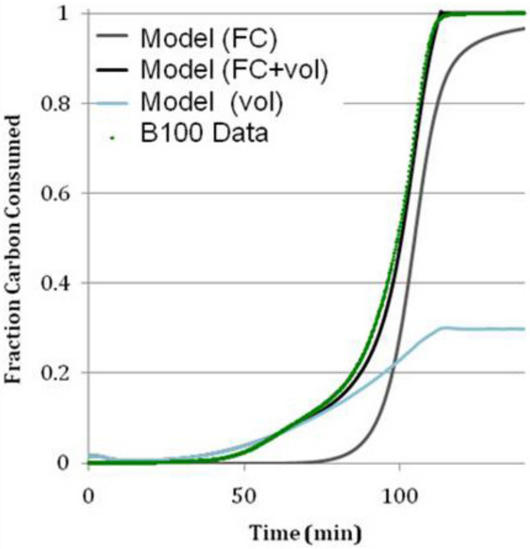

FIGURE 8. Data (colored circles) vs. model results for nascent particulate (black line) for B100. Also shown are the fixed carbon (grey line) and mobile carbon (blue line) components

- Neither ULSD nor B100 particulates follow a shrinking core burnout model.
- The oxidation rates of devolatilized particulates can be fitted with a single set of Arrhenius parameters if the rates are normalized to BET surface area.
- Oxidation of nascent particulate from both ULSD and B100 can be described by a general model that sums the contributions of the fixed and mobile carbon components.

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III. FUEL PROPERTY EFFECTS ON ADVANCED COMBUSTION REGIMES

III.1 Advanced Petroleum-Based Fuel Effects in Advanced Combustion Regimes

Bruce Bunting (Primary Contact), Scott Sluder, Jim Szybist, Robert Wagner, and John Storey
Oak Ridge National Laboratory (ORNL)
Fuels, Engines, and Emissions Research Center
2360 Cherahala Blvd.
Knoxville, TN 37932

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
Robert W. Crawford, Rincon-Ranch Consulting
Tucson, AZ

Objectives

- Quantify the effects of fuel chemistry and properties on advanced combustion regimes, including homogeneous charge compression ignition (HCCI) and partially premixed compression ignition (PCCI).
- Develop models for fuels and engines which will allow a greater understanding and extension of experimental results to new fuels, engines, or control strategies.
- Optimize fuels and controls of an engine to maximize fuel efficiency while meeting operability and emissions requirements.

Accomplishments

- Demonstrated that fuel effects are dependent on the details of the engine used to evaluate the fuels, in terms of how it is controlled and the control range available to compensate for fuels effects. In a PCCI engine, equivalent economy was achieved over the entire range of Coordinating Research Council (CRC) fuels for advanced combustion engines (FACE) fuels because of the control range available. In an HCCI engine, fuel economy deteriorated with increasing cetane number because of a limited ability to compensate for fuel ignition quality.
- Reproduced experimental cyclic stability effects using CHEMKIN kinetic modeling combined with variation in engine valve discharge coefficients to drive cyclic variation in cylinder residuals.
- Demonstrated that research octane number (RON) is of lower importance in a NVO (negative valve overlap) engine due to high bottom dead center (BDC) cylinder temperatures and that fuel responses are somewhat affected by stoichiometry and residual gases.

Future Directions

- Conduct engine experiments related to the use of fuels as a means to enable improved engine operation in high efficiency clean combustion (HECC) in a variety of engines.
- Evaluate effects of fuel formulation on advanced combustion regimes that offer lower emissions and the possibility of improved fuel economy, using petroleum-based fuels, as a companion to another project using non-petroleum-based fuels.
- Analyze the effects of fuel formulation on engine performance using a combination of experimental measurements, statistical analysis, and kinetic modeling in order to understand the simultaneous optimization of fuels and engine control.

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Introduction

Understanding the relationships between fuel properties and HECC is among the greatest needs as 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 our ability to fully exploit and implement these regimes in emerging engine technologies. Fuel composition impacts whether engines will operate in these regimes, 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 crude sources for the near-term future.

Approach

The primary goal of this research is to study the effects that fuel formulations can have on new combustion regimes and to exploit those properties for improved emissions and efficiency. Work at ORNL involves multiple test stands: two multi-cylinder common-rail engines with full pass control, a single-cylinder diesel research engine, a variable compression ratio gasoline engine, and a gasoline research engine equipped with variable valve timing. The effort covers a broad range of gasoline-based and diesel-based fuels. This research is based on experimental data from these engines with a variety of fully-formulated and surrogate fuels and subsequent analysis of this data using a variety of statistical, cycle, and kinetic modeling methods.

Results

Results have been obtained on multiple research platforms and will be discussed by type of engine and experiment, with an overall summary at the end. The diversity of the research is quite broad and it is somewhat difficult to combine findings in a single set of conclusions. The research conducted in 2008 and 2009 involves the study of fuel effects on advanced combustion engines and resulting emissions, fuel economy, and engine control considerations. Specifically, this research encompasses:

- Fuel effects on a diesel PCCI combustion strategy, as investigated on the General Motors multi-cylinder, 1.9 liter diesel engine operating under PCCI conditions and using the CRC FACE diesel fuels.
- Fuel effects on diesel HCCI combustion, as investigated on a single-cylinder research engine operating and using the CRC FACE diesel fuels.
- Fuel effects on combustion transition from conventional to HCCI combustion using NVO, in a modeling collaboration with Lawrence Livermore National Laboratory (LLNL) and partially supported by the Non-Petroleum-Based Fuels (NPBF) activity.
- Fuel effects on ignition under NVO, as a kinetic modeling study and also partially supported by the NPBF activity.

Multi-Cylinder PCCI Results

An experimental study was performed to understand fuel property effects on low-temperature combustion in a light-duty diesel engine, using the CRC FACE diesel fuels [1]. There are nine FACE fuels which cover a matrix range of 30 to 55 cetane, 20 to 45% aromatics, and 270 to 340°C T90 (temperature at 90% evaporated). An engine condition of 1,500 revolutions per minute (RPM) and 2.6 bar indicated mean effective pressure (IMEP) was choose to represent a typical light-duty operating point and early, single fuel injection combined with high exhaust gas recirculation (EGR) was used for engine control. Generally, the fuels grouped by cetane, with the low cetane fuels requiring earlier injection for equivalent combustion phasing. All fuels were capable of being tuned to the same brake thermal efficiency, with the low cetane fuels requiring both earlier injection timing and slightly earlier combustion phasing. Under these conditions, the low cetane fuels produced equivalent NOx, lower smoke, and higher hydrocarbons (HC) and carbn monoxide (CO). Higher aromatic fuels advanced ignition timing slightly for the low cetane fuels, but had no effect for the high cetane fuels. No effect for T90 was found for any of the fuels. As an example, Figure 1 shows how brake specific fuel consumption (BSFC) varies with injection timing for the fuels and indicates that fuels group mainly by cetane number.

Single-Cylinder HCCI Results

The same FACE diesel fuels were also run on a single-cylinder HCCI research engine which uses port atomization to achieve a homogeneous charge, intake heating for combustion phasing control, and intake throttling and boosting for lambda control [2]. The engine was exercised over a range of fuel rate, combustion phasing, and lambda. These operating ranges overlapped, but were different for each fuel and limited by the ability to achieve stable combustion combined with an acceptable rate of cylinder pressure rise. Data was fit with a statistical model, which was then exercised to perform a variety of parametric and optimization studies. Generally, response of this HCCI engine is mainly controlled by cetane number and resulting combustion phasing. Lower cetane fuels require higher intake temperatures, which reduces HC and CO emissions, increases NOx, and improves indicated specific fuel consuptiion (ISFC). High T90 fuels appear to have higher HC and CO emissions, and aromatics showed little effect when independent of cetane. Overall, the best fuel for this engine was one with both low cetane and low T90, providing one can accept an increase in NOx. When the crank angle where 50% of heat release has occurred (MFB50) is manipulated by changing lambda and

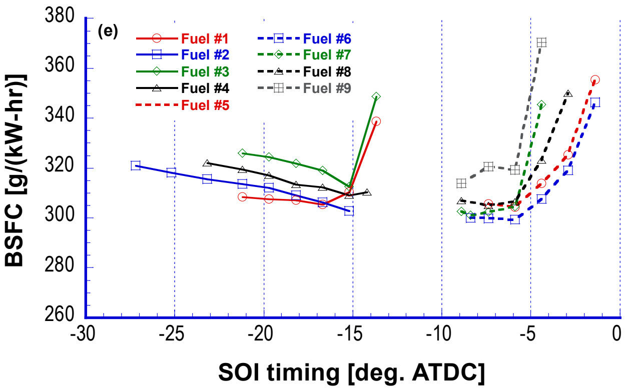

FIGURE 1. BSFC vs. Injection Timing for Fuels Grouped by cetane (low cetane = fuels 1 to 4, high cetane = fuels 5 to 8)

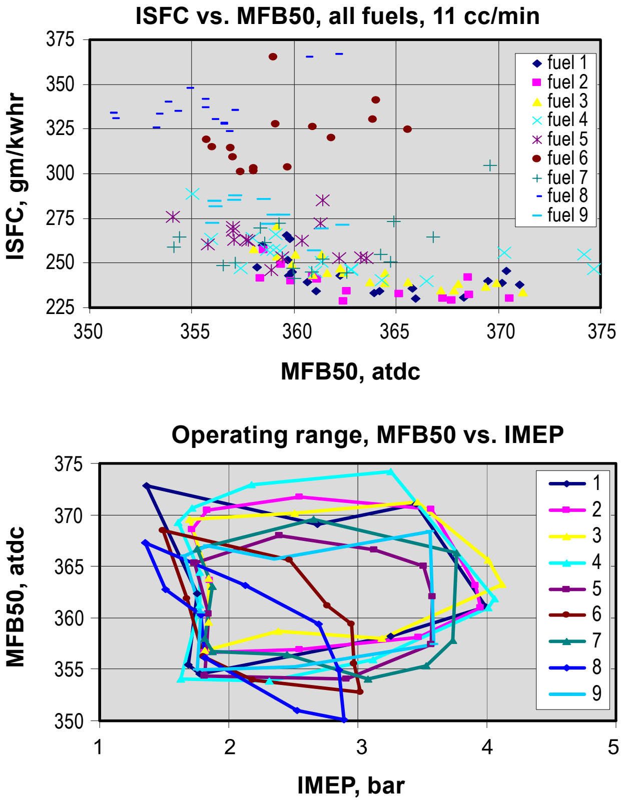

FIGURE 2. ISFC vs. MFB50 for constant combustion phasing and operating range as defined by MFB50 and IMEP. Fuels 1 to 4 are low cetane and fuels 5 to 8 are high cetane.

intake temperature independently, it appears that improved ISFC is achieved by higher lambda and lower intake temperature. For example, Figure 2 shows ISFC vs. MFB50 for all fuels at a constant fuel rate of 11 cc/minute. Fuels 1 to 4 are the low cetane fuels and provide improved fuel efficiency at more optimum combustion phasing. They also show a larger operating range of MFB50 and IMEP, as indicated in the second part of this figure.

Modeling Study of Conventional to HCCI Transition with NVO Gasoline Engine

ORNL is collaborating with LLNL to develop a CHEMKIN-based multi-zone model that simulates the expected combustion variations in a single-cylinder engine fueled with iso-octane as the engine transitions from spark-ignited (SI) combustion to HCCI combustion [3]. The model includes a 63-species reaction mechanism and mass and energy balances for the cylinder and the exhaust flow. For this study we assumed that the SI-to-HCCI transition is implemented by means of increasing the internal EGR at constant engine speed and that cyclic variation results from variation in amount and chemistry of residual cylinder gases from each cycle. This transition scenario is consistent with experimental measurements by ORNL on an experimental engine equipped with variable valve actuation. The model was able to reproduce many of the important experimental trends, including stable SI combustion at low EGR (~10%), a transition to highly unstable combustion at intermediate EGR, and finally stable HCCI combustion at very high EGR (~75%). Remaining differences between the predicted and experimental instability patterns indicate that there is further room for model improvement. Plans for Fiscal Year 2010 include additional experimental data using the ORNL variable valve actuation single-cylinder research engine. Results shown in Figure 3 indicate that it is possible to reproduce a wide range of cyclic variation with the model by varying discharge coefficients on a cycle-by-cycle basis for the engine intake and exhaust valves. This, in turn, varies residual fraction and results in cyclic instability as shown in these cycle n+1 vs. cycle n heat release maps.

Modeling of Fuel Effects in NVO

A modeling study was performed to investigate fuel-specific effects of EGR composition on HCCI combustion at conditions relevant to the NVO strategy using CHEMKIN-PRO [4]. Four single-component fuels were studied: n-heptane, iso-octane, ethanol, and toluene. These fuels were chosen because they span a wide range of fuel chemistries, and produce a wide composition range of complete stoichiometric products. The simulated engine conditions combined a typical spark ignition engine compression ratio (11.34) and high intake charge temperatures (500-550 K) that are relevant to NVO HCCI. It was found that over the conditions investigated, all the fuels had overlapping start of combustion (SOC) phasing, despite the wide range in octane number (RON = 0 to 120). The effect of the EGR components carbon dioxide (CO_2) and water (H_2O) was to suppress the compression temperature because of their higher heat capacities, which retarded SOC. For a concentration of oxygen (O_2) higher than the stoichiometric amount, or excess O_2, combustion phasing advanced for n-heptane, iso-octane, and toluene, but not for ethanol. Low-temperature heat release for n-heptane was also found to be highly dependent on excess O_2, and a mild endothermic reaction was observed for cases when excess O_2 was not present. As an example, Figure 4 shows how combustion phasing changes with an increase in excess oxygen. All fuels except ethanol show an advance with increasing oxygen except ethanol. The combustion phasing differences between fuels do not line up with RON.

Conclusions

The FACE fuels were run on two different engines, one a diesel PCCI and one a diesel HCCI. Fuel

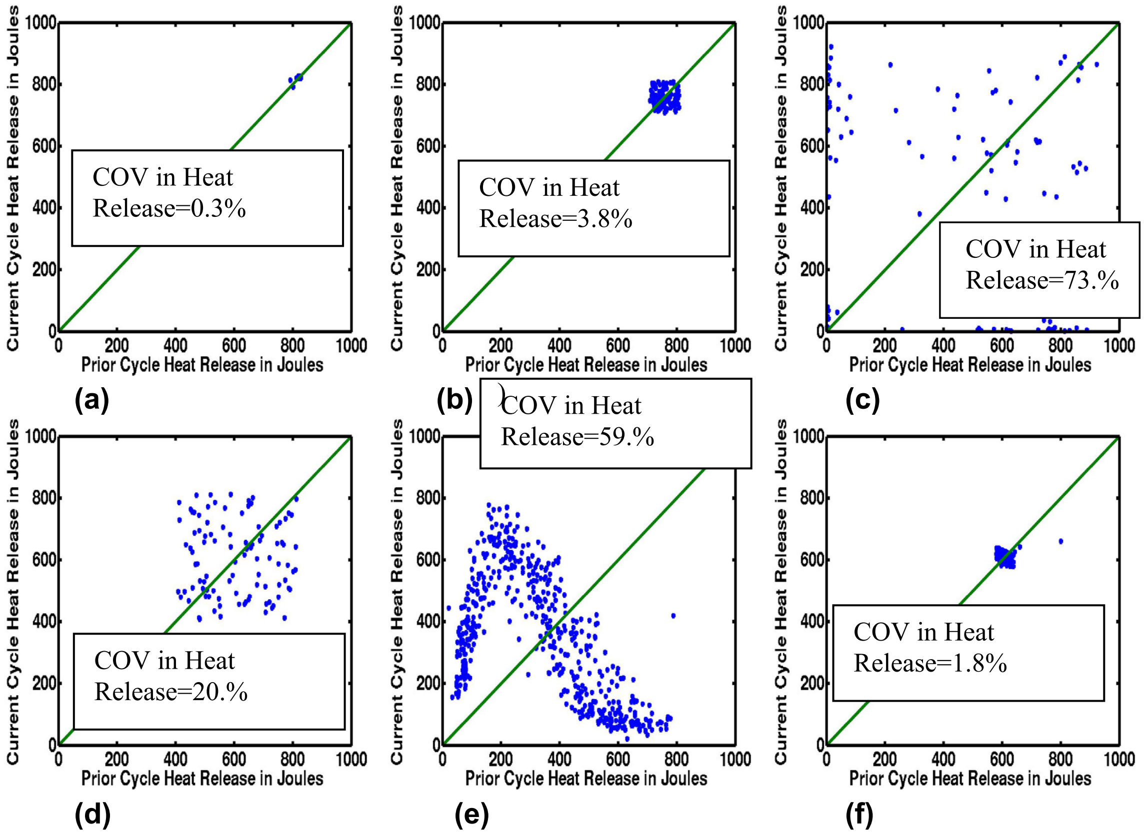

FIGURE 3. Cycle N+1 vs. cycle n return maps indicating different levels of combustion stability and matching trends found in experimental data. (COV - Coefficient of Variation)

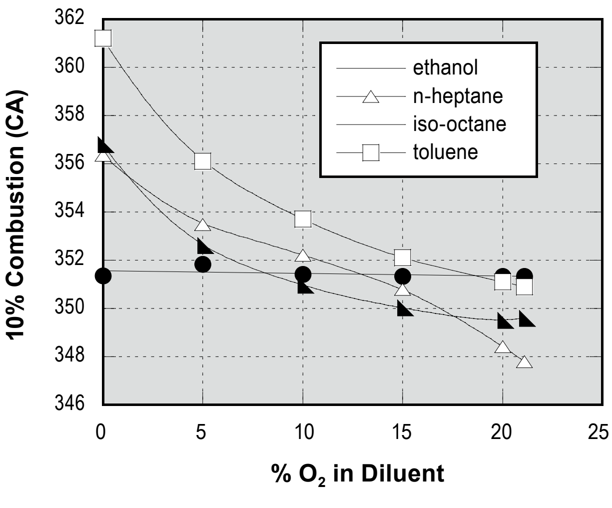

FIGURE 4. Effect of diluent O_2 concentration on 10% combustion at an intake temperature of 525 K.

response indicates that cetane is a major control variable and that aromatics or T90 provide some additional effect under certain operating conditions. Comparison of these results indicates that the response of an engine to fuel changes is governed by the fuel changes themselves, by how the engine is controlled, and by the ability of the engine to be controlled over a wide enough range to compensate for the fuel changes. In the PCCI engine, an equivalent BSFC could be achieved for all the fuels by changing both injection timing and resulting combustion phasing. In the HCCI engine, the higher cetane fuels produced the worst ISFC because the engine could not compensate for the higher cetane except with lower intake temperatures, which increased HC and CO emissions. For controls development, the engine must have a wide range of control available. For kinetics verification, HCCI provides a simple, easy to model situation and requires minimum fuel to run.

The modeling results indicate that robust models are being developed that will allow the further study of fuels and control changes and comparisons beyond the range of experimental data. Cyclic stability of an engine can be mimicked by manipulating the residual charge, in this case with valve discharge coefficients. Fuel effects are different depending on the situation in which they are run, with NVO minimizing RON effects and showing varying chemistry effects depending on stoichiometry and amount of EGR present.

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III.2 Optical-Engine Investigations of Advanced-Fuel Effects on Emerging and Conventional Combustion Strategies

Charles J. Mueller (Primary Contact),
Glen C. Martin†, Adelbert S. Cheng*,
Brian T. Fisher
Sandia National Laboratories
7011 East Ave., MS 9053
Livermore, CA 94550-9517
†Currently employed by Caterpillar Inc.
*Visiting professor from San Francisco State University

DOE Technology Development Manager:
Kevin Stork

Objectives

- Understand the extent to which fuel-volatility changes could help to enable early direct-injection (DI) high-efficiency clean-combustion (HECC) strategies.
- Identify the primary combustion mechanism(s) responsible for the increased oxides of nitrogen (NO_X) emissions that typically are observed when fueling heavy-duty compression-ignition (CI) engines with biodiesel.

Accomplishments

- Showed that increasing the volatility of diesel fuel can significantly improve engine efficiency and emissions under early-DI operating conditions by avoiding the formation of liquid-fuel films on in-cylinder surfaces.
- Showed that while many factors may contribute to increased NO_X emissions when fueling CI engines with biodiesel, the only mechanism that is consistent with all observed trends in our research is that fueling with biodiesel results in mixtures that are closer to stoichiometric during ignition and subsequent reaction. This leads to higher local temperatures earlier in the cycle, and hence increased thermal NO_X production.

Future Directions

- Study fundamental fuel effects on liquid-phase fuel penetration under time-varying in-cylinder thermodynamic conditions. This research will help engine designers avoid the detrimental effects of liquid-fuel films discussed below.
- 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.
- Implement a high-pressure common-rail fuel-injection system in the optical engine, and use this system to study fuel and injection-parameter effects on mixing-controlled HECC strategies.

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Introduction

Using advanced fuels to improve domestic energy security while at the same time reducing greenhouse gas and other undesired emissions from the transportation sector is a primary DOE objective. Two ways to improve energy security by reducing the consumption of imported petroleum are to: 1) improve engine efficiency and 2) use domestically produced renewable fuels. Compliance with current and future emissions legislation is a further requirement for the success of either of these strategies. Work in our laboratory over the current reporting period has focused on these issues. First, the effects of increasing diesel fuel volatility on early-DI low-temperature combustion (LTC) strategies were studied and found to significantly increase efficiencies while achieving emissions compliance. Second, the underlying mechanism(s) for the increased NO_X emissions often observed when fueling CI engines with biodiesel were identified. This is a key step toward developing strategies to mitigate these increases and will help remove a barrier to the increased penetration of this domestically producible, renewable fuel.

Approach

The experimental work is focused on using the Sandia Compression-ignition Optical Research Engine (SCORE) to investigate the relationships between fuel characteristics, in-cylinder processes, and engine-out emissions. The SCORE is a single-cylinder version of a modern-technology, heavy-duty, 4-stroke, compression-ignition direct-injection engine (CIDI) that has been modified by Sandia to provide extensive optical access to the combustion chamber [1]. A schematic of the SCORE is shown in Figure 1, and selected specifications are provided in Table 1. A large window in the piston bowl enables laser-sheet access and imaging of fuel vaporization and combustion processes within the engine during operation, as do additional windows in the upper

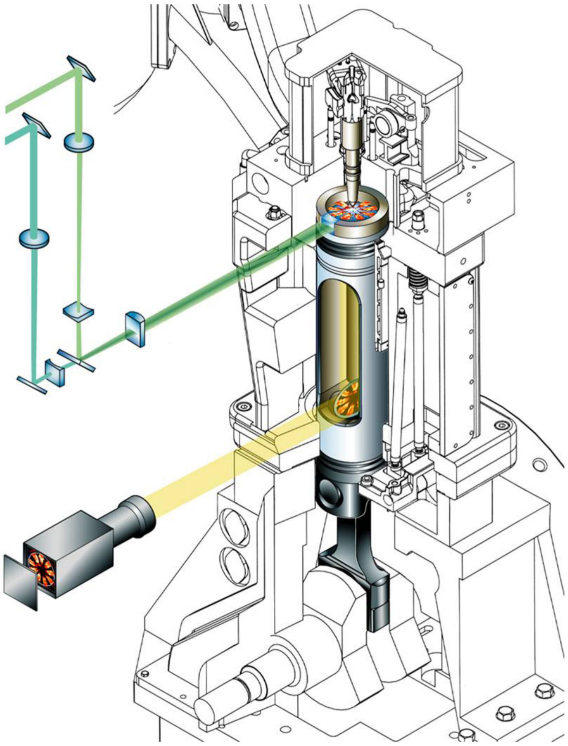

FIGURE 1. Schematic of Sandia Compression-ignition Optical Research Engine (SCORE)

TABLE 1. SCORE Specifications

Research engine type	Single cylinder
Cycle	4-stroke CIDI
Valves per cylinder	4
Bore	125 mm
Stroke	140 mm
Intake valve open[a]	32° BTDC exhaust
Intake valve close[a]	153° BTDC compression
Exhaust valve open[a]	116° ATDC compression
Exhaust valve close[a]	11° ATDC exhaust
Connecting rod length	225 mm
Connecting rod offset	None
Piston bowl diameter	90 mm
Piston bowl depth	16.4 mm
Squish height	1.5 mm
Swirl ratio[b]	0.59
Displacement per cyl.	1.72 liters
Fuel injector	Caterpillar® HEUI A
Max. injection pressure	142 MPa

[a] All valve timings are for lift ≅ 0.03 mm
[b] Measured at the Caterpillar Tech. Center using an AVL swirl meter
BTDC - before top dead center
ATDC - after top dead center
HEUI - hydraulically actuated electronic unit injection

periphery of the cylinder liner and the piston bowl-rim. The ability to use a wide range of advanced optical diagnostics, coupled with exhaust-gas analysis equipment to measure NO_X, smoke, unburned hydrocarbons (HCs), carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2), make the SCORE a versatile instrument for studying the details of fuel effects on in-cylinder processes and the corresponding impacts on efficiency and emissions.

Results

Part 1: Effects of Increased Diesel-Fuel Volatility on Efficiency and Emissions under Early-DI LTC Conditions

One way to achieve LTC in a diesel engine is to inject the fuel early (well before top-dead-center) in the compression stroke so that it has enough time before ignition to vaporize and premix to sufficiently fuel-lean conditions that emissions of NO_X and smoke are minimized. Collaborative DOE- and industry-sponsored work in our laboratory has shown that a principal barrier to success with this type of approach is the creation of liquid-fuel films on in-cylinder surfaces. These films form because fuel that is injected into the cooler, less-dense charge-gas early in the compression stroke is more difficult to vaporize, and can penetrate far enough through the combustion chamber to impinge on the piston or cylinder wall. This was found to be true even when an injector nozzle with a narrow included angle and small orifices was used to decrease the potential for wall impingement [2]. Since increasing fuel volatility should enhance vaporization and mitigate wall impingement, a follow-on study of fuel-volatility effects on efficiency and emissions was conducted using the same early-DI LTC strategy [3].

These optical-engine experiments were conducted using a conventional ultra-low-sulfur #2 diesel fuel (HV0), a high-volatility mixture of 20 vol% toluene with balance *n*-heptane (HV100), and blends of 28, 56, and 78 vol% of HV100 in HV0 (denoted HV28, HV56, and HV78, respectively) [3]. The HV100 was formulated to have approximately the same ignition quality as HV0 so that the results represent inasmuch as possible the effect of changing fuel volatility only (given the compositional differences between HV0 and HV100). Figure 2 shows selected frames from spray-visualization and natural-luminosity movies acquired with HV0 and HV100. Figure 3 shows the efficiency and emissions data for all of the fuels. The figures show that the absence of liquid-fuel impingement on in-cylinder surfaces is accompanied by substantial improvements in efficiency,

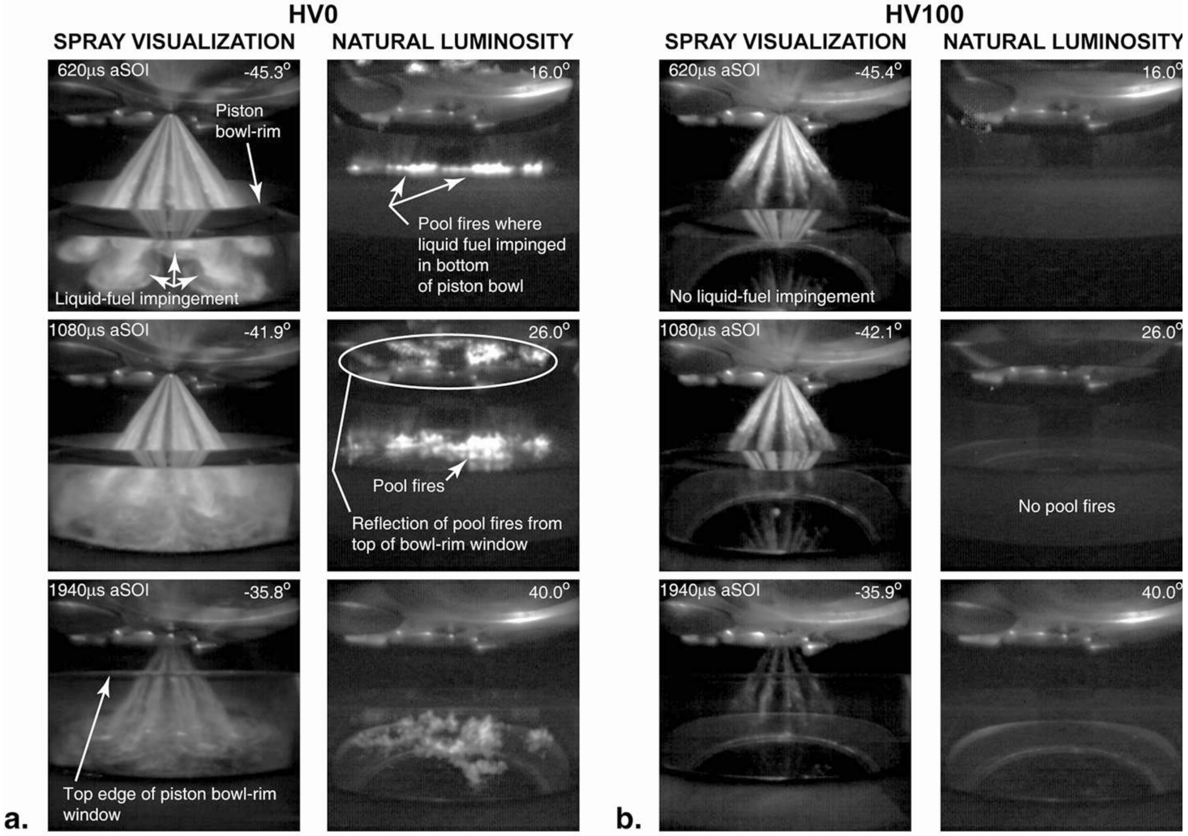

FIGURE 2. Images from spray-visualization (SV) and natural-luminosity (NL) movies acquired for: **a.** a conventional ultra-low-sulfur #2 diesel fuel (HV0), and **b.** a higher-volatility mixture of 20 vol% toluene with balance *n*-heptane (HV100). All images were acquired by viewing through a window in the cylinder wall. The SV images in **a.** show that the lower-volatility HV0 leads to impingement of liquid fuel on the top of the piston, and the NL images show that pool fires are observed later in the cycle at the impingement locations. In contrast, the images in **b.** show that the higher-volatility HV100 does not exhibit liquid-fuel impingement or pool fires. The crank angle after top dead center (ATDC) at which each image was acquired is shown in the upper-right corner of each image frame. The engine operating parameters for all images are: 1,200 rpm speed, 4.82 bar gross indicated mean effective pressure load, actual start of injection -50° ATDC, 42°C intake temperature, 1.42 bar intake manifold pressure (abs.), 50% EGR (simulated), 142 MPa injection pressure, and a dual-row injector tip with 15 orifices of 103-μm diameter (5 orifices at 35° included angle and 10 orifices at 70° included angle).

smoke, HC, and CO, while NO_X compliance with 2010 on-highway engine regulations (0.2 g/hp/hr) is achieved for intermediate injection timings.

The new insights gained through these experiments help unify fuel-effects trends reported in the literature into a simple conceptual understanding of the relationships among fuel films, efficiency, and emissions, as follows [2,3]. Liquid fuel films on in-cylinder surfaces should be avoided. For the conditions studied (which are representative of those proposed for future engine-operating modes), the formation of fuel films can occur, leading to incomplete combustion, which in turn can cause increased fuel consumption and dilution of the lubricating oil. In addition, if the fuel vapor above a film ignites to produce an intensely luminous pool fire, the fuel-rich combustion produces soot well into the expansion stroke when bulk-gas temperatures and mixing rates are insufficient to oxidize it, leading to elevated smoke emissions. Meanwhile, near-stoichiometric regions around the rich mixture can produce NO_X emissions. Radiative heat transfer from the pool fire to the fuel film enhances vaporization and combustion of the film, yielding lower HC and CO emissions than if an intensely luminous pool fire is not produced; nevertheless, HC and CO emissions are still high enough to require the use of an oxidation catalyst to meet emissions regulations. On the other hand, if an intensely luminous pool fire is not produced above a fuel-film, hot soot is not formed in the vapor region above the film. The lack of heat transfer to the film from radiating soot in a pool fire inhibits film vaporization and subsequent combustion, leading to even higher HC and CO emissions. NO_X emissions may be high or low in this latter case, since they are controlled primarily by the bulk-gas mixture (particularly in the absence of a pool fire). Using a higher-volatility diesel fuel can lead to substantial efficiency and emissions benefits by precluding the formation of fuel films (see Figure 3).

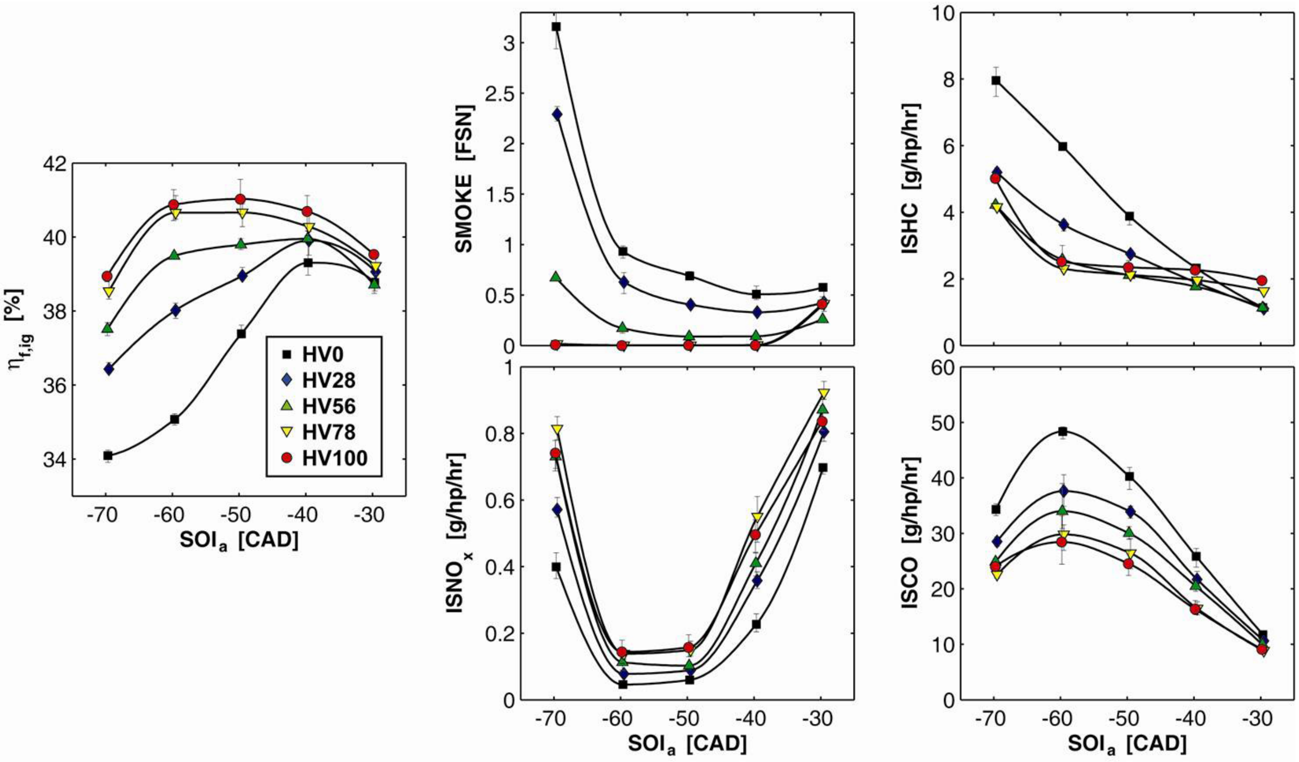

FIGURE 3. Gross indicated fuel-conversion efficiency ($\eta_{f,ig}$), smoke, and indicated-specific emissions of nitrogen oxides (ISNO$_X$), unburned hydrocarbons (ISHC), and carbon monoxide (ISCO) for HV0, HV28, HV56, HV78, and HV100 over a range of actual start-of-injection (SOI$_a$) timings. All other operating conditions are the same as those listed in the caption of Figure 2. In general, efficiency increases and smoke, HC, and CO emissions decrease as fuel volatility is increased, while NO$_X$ emissions for intermediate SOI$_a$ timings at this steady-state operating condition remain below the 0.2 g/hp/hr limit for 2010 on-highway truck engines.

The preceding understanding can assist engine designers and fuel producers in identifying improved operating strategies and fuel specifications for the future.

Part 2: Origins of the NO$_X$ Increase When Fueling CI Engines with Soy Biodiesel

It is generally accepted that fueling CI engines with soy biodiesel and its blends with petroleum diesel tends to result in increased NO$_X$ emissions. This NO$_X$ increase is a barrier to the widespread use of biodiesel in the U.S., limiting the ability of this important renewable fuel to displace imported petroleum. Many hypotheses have been proposed to explain the biodiesel NO$_X$ increase, but it has not been determined which (if any) of the prevailing hypotheses are most consistent with the reported data. The focus of our work was to conduct well-controlled experiments to evaluate a number of hypotheses, with an ultimate goal of elucidating the most important combustion mechanism(s) responsible for the biodiesel NO$_X$ increase [4].

In our study, the SCORE was operated using four fuels: 1) neat soy biodiesel, denoted B100; 2) B100 doped with a small amount of a 3-ring aromatic compound to increase soot formation and radiative heat losses from the flame, denoted B94; 3) a 45-cetane blend of diesel primary reference fuels, denoted CN45, with injection timing and ignition delay matched to B100 and B94; and 4) a 70-cetane blend of diesel primary reference fuels, denoted CN70, to provide insight into cetane-number effects. Steady-state engine operation was studied at a speed of 800 rpm and over a range of loads from 4 to 15 bar gross indicated mean effective pressure. Undiluted air and air diluted with simulated exhaust gas recirculation (EGR) were used to represent intake conditions in older-technology engines that remain in use today and newer-technology engines, respectively.

The primary combustion-related hypotheses to explain the biodiesel NO$_X$ increase are all ultimately due to increased NO$_X$ formation by the thermal mechanism. In general, any combustion change that leads to longer residence times at higher temperatures will lead to increased thermal-NO$_X$ formation. The following hypotheses to explain the combustion-induced NO$_X$ increase due to fueling with biodiesel were evaluated:

- Increased premixed-burn fraction leading to higher temperatures earlier in the cycle.
- Increased bulk-gas-average in-cylinder temperature.
- Increased adiabatic flame temperature.

- Increased actual flame temperature due to lower radiative heat losses (since biodiesel produces less soot and soot incandescence is the primary mechanism for radiative heat loss from in-cylinder combustion).
- Faster combustion leading to longer residence times at high temperatures.
- Autoigniting and reacting mixtures that are closer to stoichiometric, leading to higher local temperatures and faster combustion.

The results of the work can be summarized as follows (see [4] for details).

- Fueling with biodiesel increased load-averaged engine-out indicated-specific NO_X emissions: by 18% under conditions without EGR, and by 26% under conditions with moderate EGR.
- The 'increased premixed-burn fraction' hypothesis cannot explain the biodiesel NO_X increase at the conditions without EGR.
- The 'increased bulk-gas-averaged in-cylinder temperature' hypothesis cannot explain the biodiesel NO_X increase at high loads.
- The 'increased adiabatic flame temperature' hypothesis may be important under some conditions, but it cannot explain the reported NO_X differences between typical market #2 diesel fuels and B100. It also cannot explain the NO_X differences between B94 and B100 or between CN45 and CN70 in the present study.
- The 'increased actual flame temperature due to lower radiative heat losses' hypothesis is consistent with NO_X differences between B100 and B94, but it cannot explain the NO_X differences between the biodiesel fuels and the HC reference fuels.
- The 'faster combustion' hypothesis is consistent with higher NO_X emissions for all conditions, but a mechanism is required to explain why faster combustion would be expected for the biodiesel fuels.
- In-cylinder measurements and modeling show that a mechanism to explain the faster combustion is that biodiesel fuels produce autoigniting and reacting mixtures that are closer to stoichiometric, and are therefore hotter (due to higher flame temperatures and lower radiative heat losses). This appears to be the primary factor responsible for the biodiesel NO_X increase.

Conclusions

Significant progress was made in answering technical questions that are important for achieving the DOE objective of enhancing energy security while assuring the emissions compliance of current and future engines. The primary conclusions can be summarized as follows:

- Increasing diesel-fuel volatility can significantly improve engine efficiency and emissions under early-DI operating conditions by avoiding the formation of liquid-fuel films on in-cylinder surfaces.
- The primary mechanism responsible for the biodiesel NO_X increase in this work is that fueling with biodiesel results in mixtures that are closer to stoichiometric during ignition and subsequent reaction. This leads to higher local temperatures earlier in the cycle, and hence increased thermal NO_X production.

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3. Mueller, C.J., “Non-Traditional Fuels for High-Efficiency, Clean-Combustion Engines,” **invited plenary presentation** at Fall Technical Meeting of Western States Sections of the Combustion Institute, Livermore, CA (Oct. 16, 2007).

4. Mueller, C.J., “Update on Chemical-Kinetics Activities within the FACE Working Group,” Fall 2007 CRC/FACE Working Group Meeting, Ann Arbor, MI (Oct. 22, 2007).

5. Cheng, A.S., “Investigation of Fuel Effects on Dilute, Mixing-Controlled Combustion in an Optical Direct-Injection Diesel Engine,” SAE Powertrain and Fluid Systems Meeting, Chicago, IL (Oct. 30, 2007).

6. Mueller, C.J., “Advanced Combustion and Emerging Engine Technologies,” **invited plenary** at 2nd Non-Petroleum-Based Fuels and Advanced Combustion Research Roadmap Workshop, Ottawa, Canada (Nov. 27, 2007).

7. Mueller, C.J., “Advanced Combustion Topical Area Summary,” 2nd Non-Petroleum-Based Fuels and Advanced Combustion Research Roadmap Workshop, Ottawa, Canada (Nov. 28, 2007).

8. Mueller, C.J., “A Status Report on Two Diesel Surrogate/Reference Fuels Research Efforts in the US,” **invited presentation** at Reaction Design Model Fuels Consortium Annual Meeting, Las Vegas, NV (Dec. 3, 2007).

9. Mueller, C.J., “Overview of Research Capabilities in the Sandia Advanced Fuels Laboratory,” Strategic Planning Meeting at Caterpillar Technical Center, Mossville, IL (Jan. 16, 2008).

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11. Mueller, C.J., “Fuel Effects on Advanced Combustion Engines,” DOE Office of Vehicle Technologies Annual Merit Review Meeting, Bethesda, MD (Feb. 27, 2008).

12. Mueller, C.J., “Radiative Heat Transfer and Other Effects on the Biodiesel NO_x Increase,” AEC Working Group Meeting, Livermore, CA (March 18, 2008).

13. Mueller, C.J., “Update on Diesel Surrogate Fuel Formulation,” FACE Working Group Meeting, Woodland Park, CO (May 29, 2008).

14. Mueller, C.J., “Advanced Combustion and Emerging Engine Technologies,” **invited plenary** at Transportation Technologies and Fuels Forum, Ottawa, Canada (June 2, 2008).

15. Mueller, C.J., “Sandia Optical-Engine HECC Research,” DOE HECC Annual Program Review, Peoria, IL (June 11, 2008).

16. Mueller, C.J., “Property Needs for Engine Design and Performance Evaluation,” **invited plenary** at NIST workshop entitled “Properties Needs for Biofuels and Blends: Production, Distribution, and End Use,” Boulder, CO (July 10, 2008).

17. Mueller, C.J., “Optical-Engine Study of a Low-Temperature Combustion Strategy Employing a Dual-Row, Narrow-Included-Angle Nozzle and Early, Direct Injection of Diesel Fuel,” 2008 Diesel Engine-efficiency and Emissions Research (DEER) Conference, Dearborn, MI (Aug. 6, 2008).

18. Mueller, C.J., “Fuel-Volatility Effects on an Early Direct-Injection, Low-Temperature Combustion Strategy in an Optical Engine Utilizing a 15-Hole, Dual-Row, Narrow-Included-Angle Nozzle,” AEC Working Group Meeting, Auburn Hills, MI (Aug. 19, 2008).

19. Martin, G.C., “Early Direct-Injection, Low-Temperature Combustion of Diesel Fuel in an Optical Engine Utilizing a 15-Hole, Dual-Row, Narrow-Included-Angle Nozzle,” SAE 2008 Powertrains, Fuels, and Lubricants Meeting, Rosemont, IL (Oct. 7, 2008).

20. Mueller, C.J., “Radiative Heat Transfer and Other Effects on the Biodiesel NO_x Increase,” 2008 Biodiesel Technical Workshop, New Orleans, LA (Oct. 22, 2008).

21. Mueller, C.J., “Biodiesel/Bioethanol Break-out Session Results,” National Algal Biofuels Technology Roadmap Workshop, Washington, DC (Dec. 10, 2008).

22. Mueller, C.J., "What Causes NO_x Emissions to Increase When Fueling with Biodiesel?" AEC Working Group Meeting, Livermore, CA (Feb. 10, 2009).

23. Fisher, B.T., "High-Speed Measurement of Liquid Penetration Length of Heptamethylnonane under Unsteady In-Cylinder Conditions," AEC Working Group Meeting, Livermore, CA (Feb. 10, 2009).

24. Mueller, C.J., "A Utilization Perspective on Current and Emerging Biofuels," **invited presentation** at Biomass 2009, Washington, DC (March 18, 2009).

25. Mueller, C.J., "The Transformation of Transportation Fuels and Engines: Sandia's HITEC Future," Sandia Division 8000 Tri-Level Meeting, Livermore, CA (April 16, 2009).

26. Mueller, C.J., "Status Update on AVFL-18: Diesel Surrogate Fuel Development," CRC AVFL Committee and Working Group Meeting, Detroit, MI (May 12, 2009).

27. Mueller, C.J., "Fuel Effects on Advanced Combustion: Heavy-Duty Optical-Engine Research," DOE Office of Vehicle Technologies Annual Merit Review, Washington, DC (May 19, 2009).

28. 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," SAE 2009 International Powertrains, Fuels, and Lubricants Meeting, Florence, Italy (June 15, 2009).

29. Boehman, A.L., "Investigation of the Origin of Increased NO_x Emissions in a Heavy-Duty Compression-Ignition Engine Fueled with Soy Biodiesel," ACS Fuel Chemistry Division Meeting, Washington, DC (August 2009).

Award

1. Society of Automotive Engineers 2008 Harry L. Horning Award for paper entitled "Early Direct-Injection, Low-Temperature Combustion of Diesel Fuel in an Optical Engine Utilizing a 15-Hole, Dual-Row, Narrow-Included-Angle Nozzle," SAE Technical Paper 2008-01-2400 (see "Publications" section above).

III.3 Chemical Kinetic Modeling of Advanced Transportation Fuels

William J. Pitz (Primary Contact),
Charles K. Westbrook, Olivier Herbinet,
Marco Mehl
Lawrence Livermore National Laboratory (LLNL)
P. O. Box 808, L-372
Livermore, CA 94551

DOE Technology Development Manager:
Kevin Stork

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-sand-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.

Accomplishments

- Developed detailed chemical kinetic models for two large unsaturated methyl esters: methyl-5-decenoate and methyl-9-decenoate.
- Developed a detailed chemical kinetic model for a biodiesel surrogate that contains large saturated and unsaturated methyl esters characteristic of vegetable-oil-derived biodiesel.
- Developed a reduced mechanism for a large biodiesel surrogate for use in computational fluid dynamics (CFD) codes.

Future Directions

- Develop detailed chemical kinetic models for actual components in soy-based biodiesel: methyl stearate and methyl oleate.
- Develop improved chemical kinetic models for fuel surrogate components and fuel blends to represent advanced petroleum-based fuels.

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Introduction

Development of detailed chemical kinetic models for advanced petroleum-based and non-petroleum-based fuels is a difficult challenge because of the hundreds of different components in these fuels and because some of these fuels contain components that have not been considered in the past. It is important to develop detailed chemical kinetic models for these fuels since the 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 fuel injection timing. They also allow insight into how the composition of advanced petroleum-based and non-petroleum-based fuels affect 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 advanced petroleum-based and non-petroleum-based fuels. These advanced fuels include biodiesel, oil-sand-derived diesel, alcohol fuels, Fischer-Tropsch fuels and new advanced bio-derived fuels. Then these component 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 NOx and other toxic species production under practical engine conditions. The mechanisms are then reduced for use in multidimensional fluid mechanics codes for simulating engine combustion. This approach has been used extensively for diesel and HCCI engine combustion, providing better understanding in fundamental chemical terms of ignition, soot production, and NOx emissions from these engines.

Results

Biodiesel fuel derived from vegetable feedstocks contains saturated and unsaturated methyl esters that need to be included in a surrogate fuel model. In Fiscal Year 2007, we developed a chemical kinetic model for methyl decanoate to represent large saturated methyl esters [2]. We also need a component model to represent unsaturated methyl esters. In FY 2008-2009, we developed chemical kinetic models for two large unsaturated methyl esters [1], methyl-9-decenoate and methyl-5-decenoate. The former methyl ester has a double bond on the end of the carbon chain and the later one a double bond in the middle so that we can examine the effect of the position of the double bond on combustion characteristics. The molecular structures of all three methyl esters considered here are shown in Figure 1. By comparing the saturated methyl ester (methyl decanoate) with the two unsaturated methyl esters, one can assess the effect of including a double bond in the carbon chain. Figure 2 shows the effect of the presence and position of a double bond in the carbon chain of the methyl esters on ignition behavior. The main difference in ignition between the different methyl esters lies in the low temperature region between 750-900 K, a region that is important for low-temperature combustion in diesel engines. Methyl-9-decenoate, with a double bond on the end of the carbon chain, has the shortest ignition delay time and is the most reactive methyl ester component. Methyl-5-decenoate with a double bond in the middle of the carbon chain has the longest ignition delay times. Methyl decanoate (with no double bond) has slightly shorter ignition delay times than methyl-5-decenoate. At low temperature, all three methyl esters ignite similarly. Our work shows that the position of a double bond in the alkyl chain of a fuel component is very important in determining its reactivity. By adjusting the amount of each of these components in a biodiesel surrogate mixture, the targeted reactivity of real biodiesel methyl esters can be achieved.

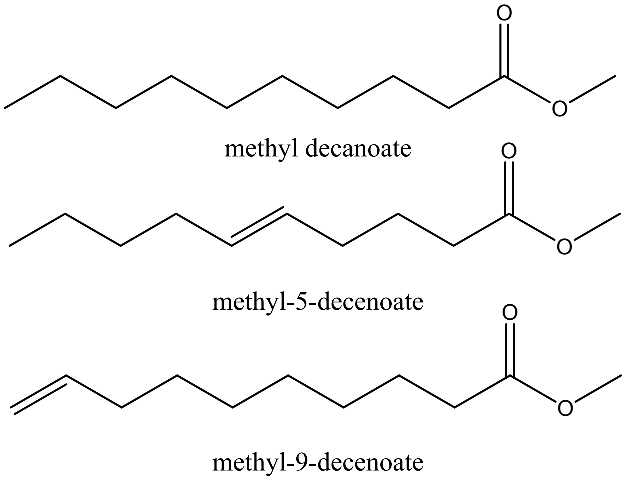

FIGURE 1. Molecular structures of the three C10 methyl esters considered as fuel surrogate components for biodiesel.

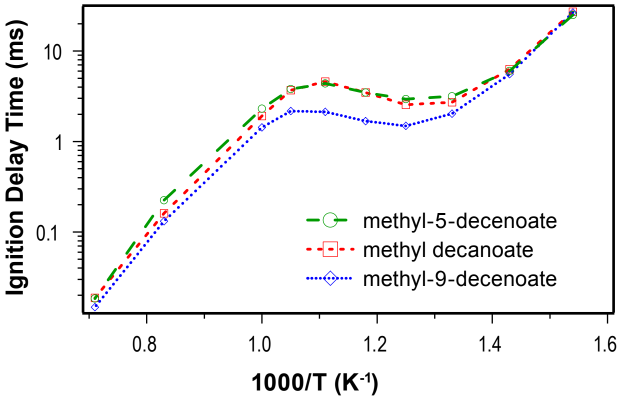

FIGURE 2. Ignition behavior of saturated and unsaturated C10 methyl esters for stoichiometric, fuel-air mixtures at 1 atm [1]. See Figure 1 for molecular structures of the esters.

The inclusion of unsaturated methyl decenoates and saturated methyl decanoate gives a more accurate and improved surrogate for biodiesel. However the long carbon chain on methyl decanoate (C10) is shorter than the typical of biodiesel methyl ester (C16-C19). Since the reactivity of a methyl ester component is attributed to the reactivity of the carbon chain, n-heptane (C7) was added to the surrogate mixture model as well, in order to compensate for the short carbon chain of the C10 methyl esters considered. The carbon chain length of n-heptane (C7) plus the length of the carbon chain of methyl decanoate (C10) gives a total carbon chain length in surrogate (C17) which is close to that of biodiesel methyl esters (C16-C19). We tested this surrogate mixture model by comparing computed results to experimental results from Dagaut et al. [3] of the oxidation of rapeseed-derived methyl esters in a stirred reactor at 10 atm. They measured the concentration of intermediate species in the reactor for a range of temperatures. We used a surrogate mixture model of 25% methyl decanoate, 25% methyl-9-decenoate and 75% n-heptane to simulate the rapeseed-derived methyl esters. Figure 3 compares concentrations of intermediate

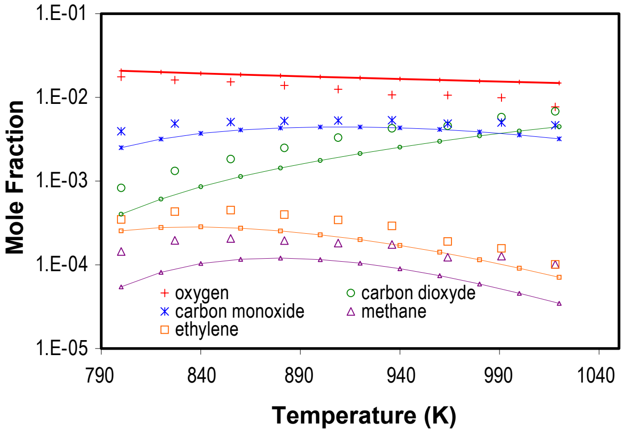

FIGURE 3. Comparison of an LLNL biodiesel surrogate model with rapeseed-based methyl esters. Concentration of intermediate species formed from the reaction of the rapeseed-based methyl esters are shown as a function of temperature in a jet stirred reactor at 10 atm, equivalence ratio of 0.5, and a residence time of 1 sec. The experiments (symbols) are from Dagaut et al. [3]. The symbols are from the LLNL detailed chemical kinetic surrogate model for biodiesel.

species predicted and measured in the oxidation of large methyl esters at a residence time of 1 second. The comparison shows that the concentrations of species predicted from the surrogate model and measured in the experiments agree relatively well.

A motored engine is a useful device for assessing reactivity of fuels under engine conditions. To obtain further confidence in the chemical kinetic model for unsaturated methyl esters, we compared the predictions of an unsaturated C10 methyl ester model to unsaturated C9 methyl ester measurements in a motored engine. No engine experiments of unsaturated C10 methyl esters were available for comparison. Specifically, we used the methyl-5-decenoate model to represent methyl-2-nonenoate in the engine. The comparison of carbon monoxide and carbon dioxide predictions and measurements [4] in the exhaust of the engine are shown in Figure 4. The CO_2 is quite well reproduced by the model and the CO is within a factor of 2 to 3. The profile shapes are also well simulated by the model.

It is important to reduce large chemical kinetic models so that they can be used in multidimensional CFD codes. Detailed chemical kinetic models usually have too many reactions and species, and require too much computational resources to be included in CFD codes. In FY 2008-09, we reduced our large chemical kinetic mechanism for a biodiesel surrogate so that it could be used in a reacting flow code. The work allowed us to test a new and promising method for mechanism reduction called the directed relational graph (DRG) method [5]. This method is a graphical technique that analyses the reaction paths in the mechanism and removes paths that do not affect the concentration of important species of interest. The DRG method reduced the detailed mechanism of methyl decanoate from 3,036 species and 8,555 reactions down to 125 species and 713 reactions. The number of species was reduced by a factor of 5, a dramatic reduction.

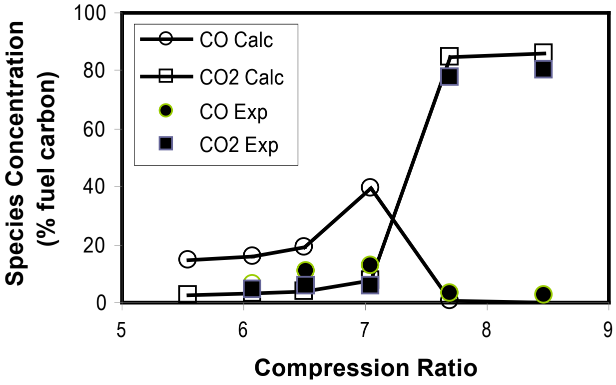

FIGURE 4. Comparison of predicted and measured [4] species from the exhaust of a motored engine (Fuel: methyl-5-decenoate [model], methyl-2-nonenoate [experiments]). The equivalence ratio is 0.25 and the engine speed is 600 rev/min.

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 employed a counterflow flame configuration which consists of fuel and air flowing in opposite directions, towards each other. When ignition occurs, a flame develops near the stagnation plane formed by the two flows. This flame configuration has relevance to diesel engines because the fuel and air are initially separate in the flame just as it is the case in a conventional diesel engine. Also, the counter-flow flame includes the effect of fluid dynamic strain, an effect also found in diesel engine flows. To compute this flame, a 1-dimensional reacting flow code that computes fluid flow, transport of energy and species, and chemical reactions is required [6]. Figure 5 shows good agreement between experimentally measured and computed ignition temperatures in the counter-flow flame. This work is published in the Proceedings of the Combustion Institute [7].

Conclusions

- New chemical kinetic component models of two large, unsaturated methyl esters have been developed and the mechanism published in Combustion and Flame [1].
- Using both saturated and unsaturated methyl ester components, a biodiesel surrogate mixture model has been developed and compared to experimental measurements of rapeseed-derived methyl esters used in biodiesel. Chemical kinetic models for the components and the surrogate mixture are available on the LLNL Web site [8].

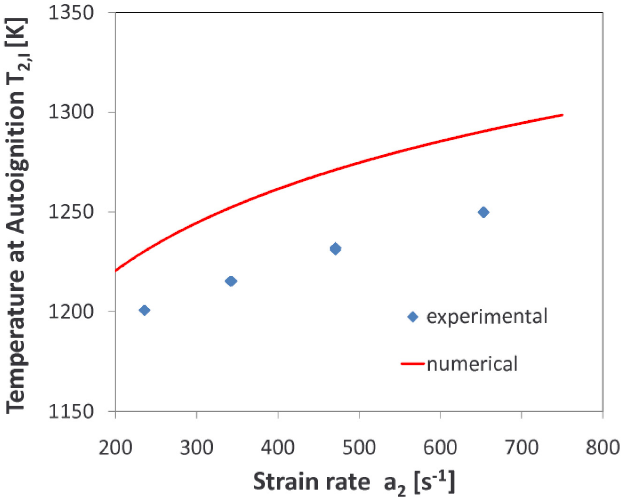

FIGURE 5. The measured and predicted temperature for autoignition in a counterflow flame [7]. The temperature of the air flow is increased slowly until ignition occurs. Autoignition temperatures are given at different strain rates which are controlled by the velocities of the reactant flows. (a_2: Strain rate based on air side of stagnation plane [s^{-1}]).

- A reduced chemical kinetic mechanism for a biodiesel surrogate was developed and validated for use in a reacting flow code.

Acknowledgements

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Special Recognitions & Awards/Patents Issued

1. Charles K. Westbrook: Elected to the 2008-2009 Class of Fellows of the Society of Automotive Engineers (SAE).

2. Charles K. Westbrook: 2008 Bernard Lewis Gold Medal award by the Combustion Institute.

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

4. SCIENCEWATCH© identified Charles Westbrook and William Pitz as in the top 25 most cited authors in the area of energy and fuels for the period of 1998 to 2008.

5. William J. Pitz: Invited Plenary Lecture at the 2008 International Conference on Modeling and Diagnostics for Advance Engine Systems (2008 COMODIA), Sapporo, Japan.

6. William Pitz received an award as co-author on the best paper of the year from the Japanese Combustion Society. The paper is "A Kinetic Modeling Study on the Oxidation of Primary Reference Fuel-Toluene Mixtures Including Cross Reactions between Aromatics and Aliphatics", Y. Sakai, A. Miyoshi, M. Koshi, W.J. Pitz, Proceedings of the Combustion Institute, 2009.

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

Daniel L. Flowers (Primary Contact),
Salvador M. Aceves, Mark Havstad,
JY Chen (UC Berkeley)
Lawrence Livermore National Laboratory (LLNL)
7000 East Avenue, L-792
Livermore, CA 94551

DOE Technology Development Manager:
Kevin Stork

Objectives

- Develop surrogate chemical kinetic models for practical fuels (i.e., gasoline, diesel).
- Test and tune chemical kinetic models at conditions of interest to engine researchers.
- Provide analytical support for fuel characterization experiments.

Accomplishments

- Developed methodologies for testing and tuning gasoline surrogate chemical kinetic models.
- Demonstrated a procedure for detailed modeling of the National Renewable Energy Laboratory's (NREL's) Ignition Quality Tester (IQT).

Future Directions

- Develop high-accuracy surrogate mechanism for gasoline.
- Develop high-accuracy surrogate mechanism for diesel fuel.
- Test chemical kinetic mechanisms at engine conditions.
- Characterize alternative fuel advanced combustion regimes through experiments and modeling.

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Introduction

Lawrence Livermore National Laboratory contributes to the efficient and clean utilization of alternative fuels through development of advanced 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. Test concepts are also developed that may contribute to improved utilization efficiency of alternative fuels.

Approach

The growing interest in alternative fuels has brought with it a broad need for new fuel characterization under advanced combustion regimes. Contribution to this task is done by collaborating with industry, other national laboratories, and universities in identifying modeling needs for alternative fuels. Teams are typically formed with other institutions (foreign and domestic) that conduct experimental work, and detailed analysis leading to the development, testing and tuning of new chemical kinetic mechanisms is performed. The approach has proven very successful and the resulting combustion models are widely used around the world.

Results

Accurate homogeneous charge compression ignition (HCCI)-based chemical kinetic mechanism testing and tuning has been demonstrated. As a chemically controlled process, HCCI combustion lends itself very well to chemical kinetic model development and validation. This characteristic will be taken advantage of in pursuit of improved model fidelity and predictive engine analysis capability.

The first component of the reported work focuses on demonstrating the use of a surrogate gasoline chemical kinetic mechanism that captures the changes in engine performance with changes in equivalence ratio, boost pressure and intake temperature. To date, a fully detailed gasoline mechanism is impractical because gasoline consists of far too many distinct chemical components and no surrogate gasoline kinetic mechanisms have performed well over a large or even modest range of boost pressures.

Surrogate mechanisms can take many forms. A surrogate is sought that is sufficiently compact for use with multi-zone engine simulations that realistically compute cylinder compressive work, heat loss, combustion driven mixing and kinetic heat release, particularly in the "low-temperature" regime. A reduced mechanism with 217 species and 800 steps is currently focused on, but the approach could be extended (at the expense of increased computational time) to large mechanisms that may now include thousands of species.

The reduced mechanism has been shrunk and tuned for improved pressure dependent kinetics while retaining the five key classes of gasoline components: aromatics, cycloalkanes, n-alkanes, iso-alkanes and alkenes. Simulations have been performed using a variety of candidate mixtures of these and the results have been compared to well-instrumented experiments performed on a research engine (John Dec's engine at Sandia Livermore [1]) running in HCCI mode at a compression ratio of 16.7 and an engine speed of 1,200 rpm. Intake pressure was swept from 60 to 190 kPa with equivalence ratio fixed at 0.2. Equivalence ratio was also swept from 0.08 to 0.30 with intake pressure fixed at 100 kPa. The results of these tests and single-zone simulations were previously reported [1] but the simulations did not capture the character of the dependence of combustion timing with varying intake pressure. Improving kinetic mechanisms in this regard is widely sought.

The initial multi-zone simulations of engine performance agree well with tests. In Figure 1 the cylinder pressure histories are compared for simulation and test for a central test configuration: 100 kPa intake pressure and 0.24 equivalence ratio. The cylinder charge used in the simulation matches the test as indicated by the good agreement at the crank angles preceding ignition. The kinetic mechanism performs very well in the simulation as indicated by the good match through the angles during combustion where pressure rise rate is severe and then declining. The simulation does an excellent job of matching cylinder heat loss and expansion work as indicated by the match through the crank angles after burn.

The simulations of the dependence of intake temperature (required for 50% burn at top dead center) on intake pressure (Figure 2) show an improved agreement with test over that in the prior work [1]. The strong fall off of bottom dead center temperature as intake pressure exceeds 150 kPa (caused by increased reactivity at high pressures) is almost fully captured by the new simulations.

The next steps are focusing on comparisons of measured and calculated burn fractions and hydrocarbon emissions. Further, comparisons between candidate gasoline surrogate mixtures can be performed to improve the comparisons to test. A detailed check of the performance of our reduced mechanism against a complete mechanism may be possible later in the year.

In a related task, we are modeling direct fuel injection experiments in NREL's IQT to characterize alternative diesel fuels based on their ignition characteristics. In addition to NREL, this activity is being conducted in collaboration with Colorado School of Mines.

The work focuses on simulating complex fuels in highly stratified regimes under diesel-like conditions. Simulations of these processes require expanding the capabilities of LLNL's KIVA3V-MZ-MPI (KIVA parallel multi-zone [2]) code to handle highly stratified operating regimes with the goal of developing a tool that can practically utilize large chemical kinetic mechanisms (thousands of species) for advanced fuels.

In addition to the KIVA multi-zone work, we are also modeling the IQT with an integrated chemical kinetics-fluid mechanics model that solves for chemical kinetics in each computational cell. The combination of the two approaches allows benchmarking of the

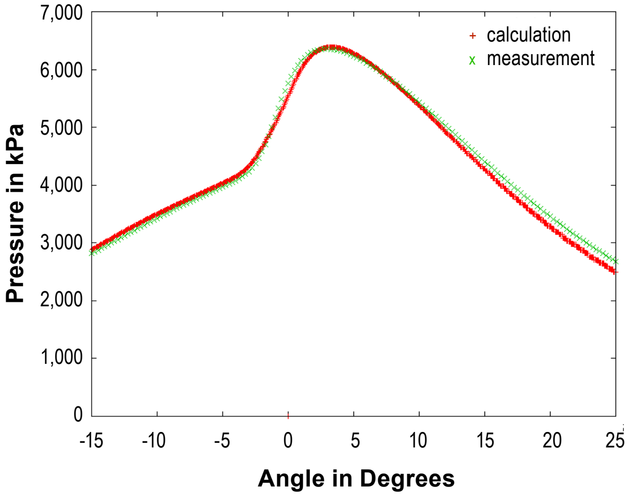

FIGURE 1. Cylinder Pressure Histories from Computation and Test for Equivalence Ratio of 0.24 and 100 kPa Intake Pressure

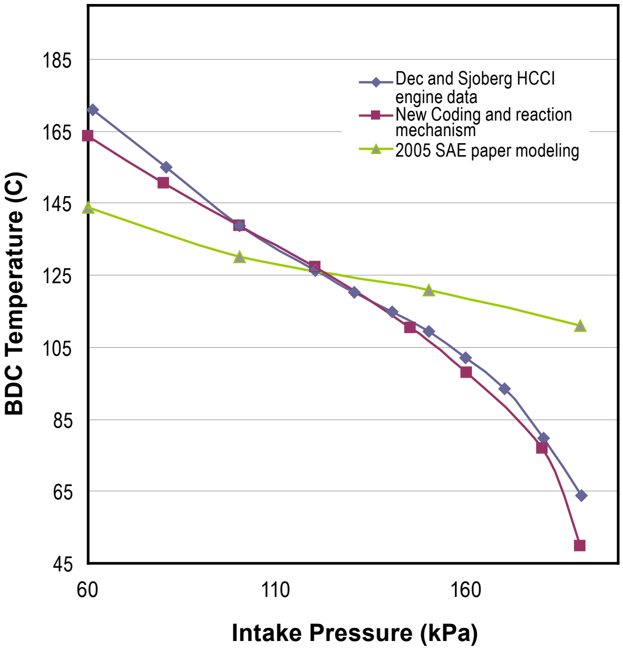

FIGURE 2. Comparison of Simulation and Test for Sweep of Boost Pressures

multi-zone model vs. the more comprehensive approach of fully linked fluid mechanics and chemical kinetics. Once benchmarked, the multi-zone model can be used for considerably faster solutions (or larger chemical kinetic mechanisms), because chemical kinetics is solved for ~100 zones vs. ~100,000 computational cells in the fully integrated solver.

Simulations show promise in predicting the direct-injected experiments in the IQT. Figure 3 shows visualization of simulation results for n-heptane fuel in a benchmark case where the KIVA multi-zone model is compared to the fully integrated solver. A refined cell-to-zone mapping strategy has been implemented and shows that the multi-zone model gives results consistent with the every cell simulation, giving confidence for application of the KIVA3V-MZ-MPI to simulations with more complex fuels.

Conclusions

- Detailed modeling of gasoline HCCI combustion has been performed. The reduced surrogate gasoline model accurately captures the increased reactivity that is observed at high intake pressures.
- LLNL's KIVA multi-zone model has been applied to model NREL's IQT with considerable reduction in computational time. The code is being benchmarked against a fully integrated fluid mechanics-chemical kinetics solver. The results show promise for computationally efficient and accurate IQT modeling.

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3. Modeling Iso-octane HCCI using CFD with Multi-Zone Detailed Chemistry; Comparison to Detailed Speciation Data over a Range of Lean Equivalence Ratios, Randy P. Hessel, David E. Foster, Salvador M. Aceves, M. Lee Davisson, Francisco Espinosa-Loza, Daniel L. Flowers, William J. Pitz, John E. Dec, Magnus Sjöberg, Aristotelis Babajimopoulos, SAE Paper 2008-01-0047, 2008.

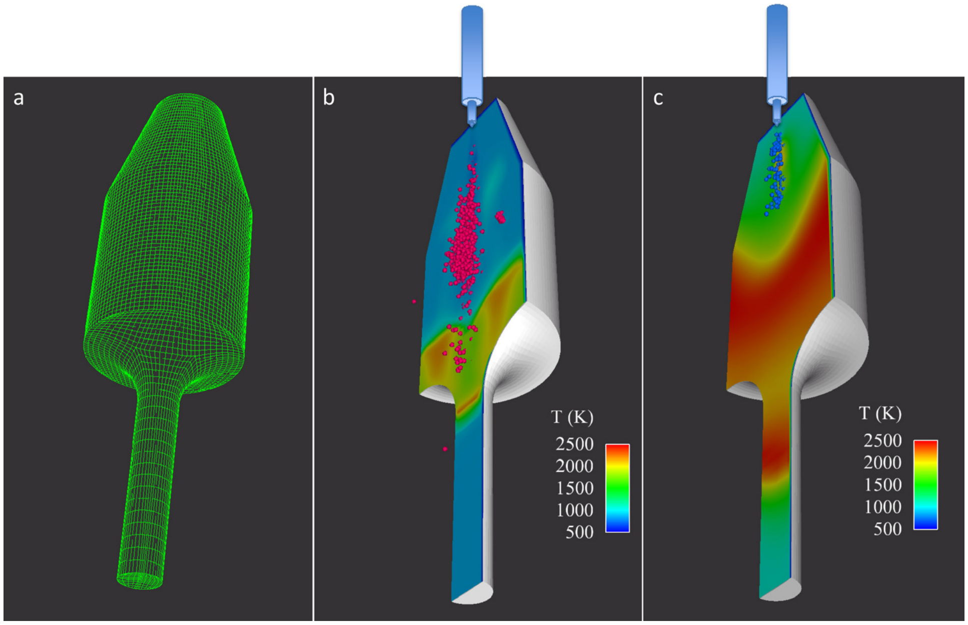

FIGURE 3. The KIVA multi-zone model is being expanded to handle highly stratified combustion in the IQT. Figure 3a) shows the KIVA3V mesh of the fluid domain of the IQT, 3b) shows the liquid spray (n-heptane) and contours of temperature on a mid-plane slice at a point when the fuel is just starting to react, and 3c) shows spray and temperature contours near the end of injection.

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

Special Recognitions & Awards/Patents Issued

1. Salvador Aceves invited to serve as an opponent in Ph.D. exam, Chalmers University, Gothenburg, Sweden, September 2008.

2. Nick Killingsworth invited to deliver a seminar at the "Advanced Engine Control Symposium," Tianjin, China, November 2008.

3. Salvador Aceves invited to serve as an opponent in Ph.D. exam, University of Castilla La Mancha, Spain, March 2010.

III.5 Advanced Petroleum-Based Fuels Research at NREL

Bradley Zigler (Primary Contact),
Matthew Ratcliff
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd., MS-1634
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Subcontractors:
- Colorado School of Mines, Golden, CO
- Coordinating Research Council, Alpharetta, GA

Objectives

- Address technical barriers of inadequate data and predictive tools for:
  - Fuel effects on combustion, engine optimization, emissions, and emission control systems.
  - Impact of lubricants on engine emissions.

Accomplishments

- Developed 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.
  - Bridges experimental void between fundamental ignition experiments and full engine testing.
- 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 a direct-injection spark-ignition (DISI) single-cylinder research engine facility to investigate fuel chemistry effects on advanced combustion and leverage links to NREL's biomass fuels research program.
- Developed advanced speciation techniques to analyze impact of advanced fuels on exhaust emissions.

Future Directions

- Expand IQT-based experimental and modeling research to:
  - Develop broader understanding of fuel chemistry impacts on ignition.
  - Develop and validate improved kinetic models.
  - 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 DISI single-cylinder research engine to study fuel chemistry impacts on advanced combustion, enabling NREL to study a span of renewable fuels from fuel production and processing to engine performance and emissions.

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Introduction

Development of more energy-efficient and environmentally friendly transportation vehicles demands 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 kinetic 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 to understand the relationships between fuel chemistry and engine performance and emissions is necessary. The DOE Vehicle Technologies Program's Fuels Technologies subprogram supports research and development (R&D) to address this 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 an experimental and modeling bridge between fundamental chemical kinetics and engines. This goal translates into APBF's research activities, which include:

- Development and characterization of research grade reference fuels, surrogate fuels, and advanced alternative and renewable blending streams.
- Development of experimental and modeling 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 APBF's experimental and modeling 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 laboratory colleagues. APBF participates in the Advanced Engine Combustion/Homogenous Charge Compression Ignition Consortium, ensuring our work is in close alignment with and supports DOE Vehicle Technologies' Advanced Combustion Engines R&D subprogram. APBF engages the academic research community through this forum, in addition to directly funding fuel ignition kinetics research at Colorado School of Mines (CSM).

Results

Ignition Kinetics Research

During Fiscal Year 2008 and FY 2009, APBF continued to develop methods to characterize fuel ignition properties to support kinetics-dominated advanced engine combustion research. These efforts 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. 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 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 (Figure 3) and calculate Derived Cetane Number per ASTM D6890-08 [2]. This

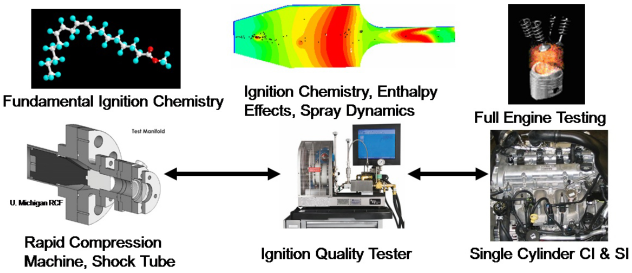

FIGURE 1. Conceptual Illustration of Linking Existing Experiments with Complementary IQT-Based Research Platform

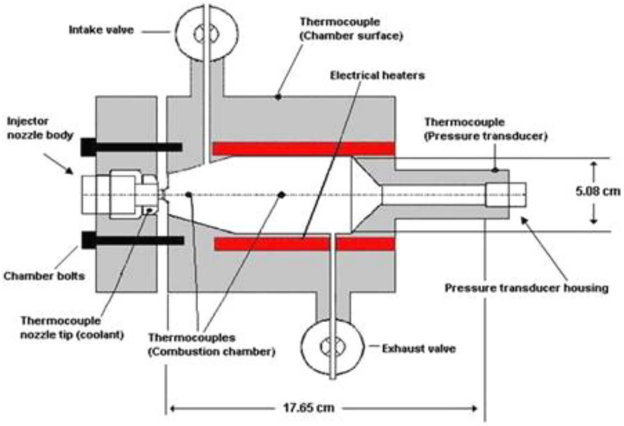

FIGURE 2. Schematic of the IQT Combustion Chamber

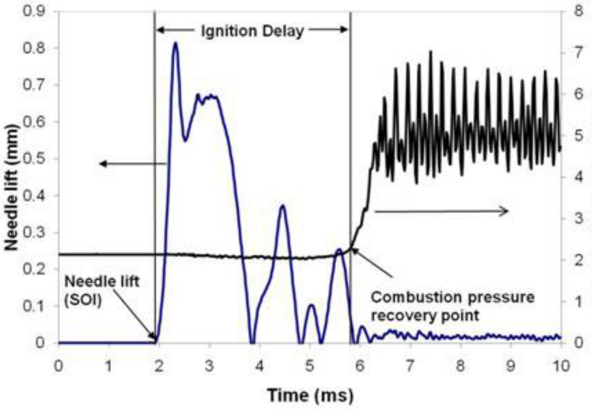

FIGURE 3. Combustion pressure and needle-lift traces used to determine ignition delay; n-heptane, m ≈ 72 mg/inj.

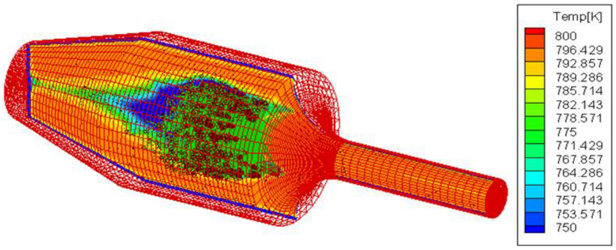

FIGURE 4. The KIVA-3V model (~65,000 cells) employs a Reitz Kelvin-Helmholtz Raleigh-Taylor spray breakup model and is linked with CHEMKIN to evaluate ignition kinetics in the IQT.

technique was applied to the nine fuels comprising the FACE diesel research fuel set [3], 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 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 a valuable collaboration with Prof. J.Y. Chen at University of California (UC), 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 4). The resulting experimental and computational development led to significant understanding of the IQT (illustrated in Figure 5), making it capable of providing valuable ignition kinetics data. This led to evaluation of single-step and reduced kinetic mechanisms for n-heptane, as shown in Figure 6. IQT experimental data was compared to the KIVA-3V/CHEMKIN model, using a

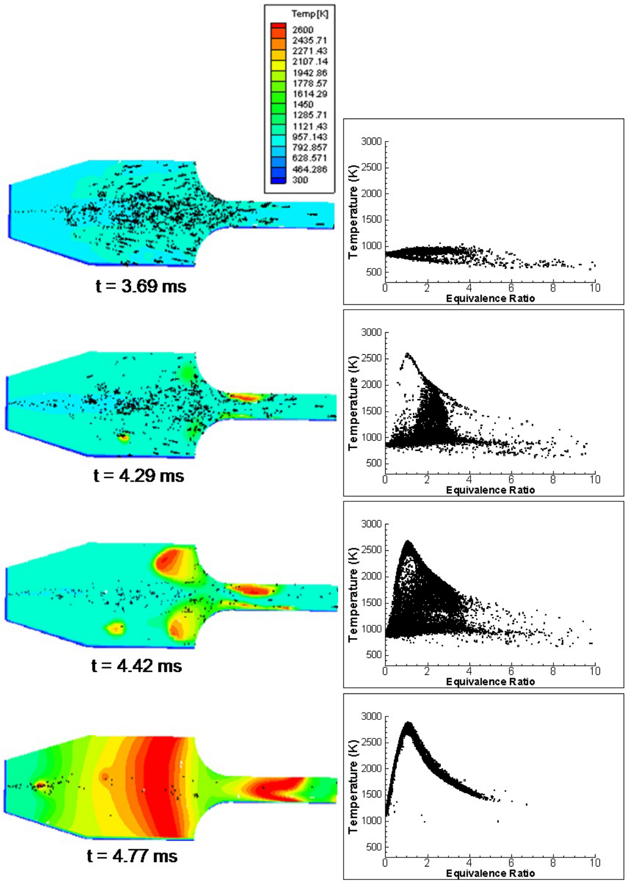

FIGURE 5. The role of autoignition is shown by the time evolution of the temperature contour plots (left) and the corresponding plots of temperature vs. equivalence ratio (right), which demonstrate that the onset of n-heptane combustion occurs primarily in the rich regions around $\Phi = 2$.

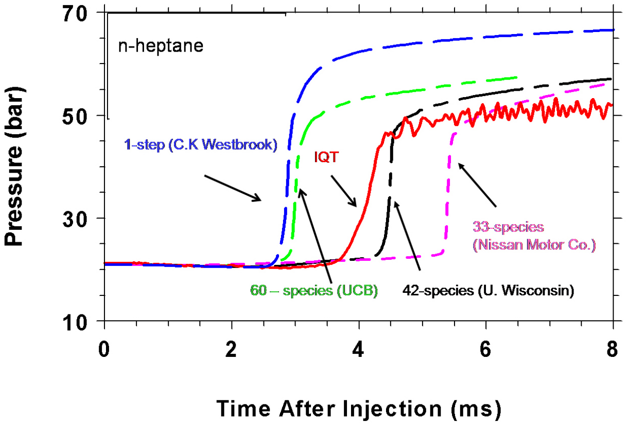

FIGURE 6. IQT experimental ignition delay versus model with reduced mechanisms for n-heptane. $P_{air} = 21$ bar, $T_{air} = 861$ K, overall $\Phi = 0.7$, $T_{fuel} = 50°C$, spray tip speed = 140 m/s with collision, and variable injection rate ~ pintle lift. One step chemistry is from C. Westbrook (Lawrence Livermore National Laboratory), 60-species mechanism is from J.Y. Chen (UC, Berkeley), 42-species mechanism is from R. Reitz (University of Wisconsin–Madison), and 33-species mechanism is from T. Tsurushima (Nissan).

60-species mechanism from J.Y. Chen at UC Berkeley, a 42-species mechanism from R. Reitz at the University of Wisconsin–Madison, and a 33-species mechanism from T. Tsurushima at Nissan [4-6]. Additionally, APBF added significant exhaust speciation capability to the IQT, providing additional diagnostic markers against which to evaluate kinetic models. This work serves as a foundation for continued IQT-based kinetics research.

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 are covered in another annual progress report chapter, titled "Fuels for Advanced Combustion Engine (FACE) – Development of Research Fuels Matrix". Highlights of ABPF's contributions during FY 2008 and FY 2009 include:

- Participation in the FACE Working Group to develop and characterize standardized research diesel and gasoline fuel sets, enabling cross-comparisons of results between different R&D organizations working on different advanced combustion modes and engine hardware.
- Leadership for the Advanced Alternatives and Renewable Fuels (AARF) sub-team to identify and plan a characterization effort for these blending streams, including:
  - 2nd generation biofuels
    - Non-food sources
    - Advanced processing of edible feedstocks
  - Oil shale
  - Oil sands
  - Other processing, including Fischer-Tropsch
- Leadership and co-funding for the AVFL-16 project to employ the FACE diesel research fuel set to enable light-duty diesel advanced combustion regimes.
- Significant contribution to the AVFL-18 project to develop advanced diesel surrogates with full kinetic models [7], utilizing data and knowledge created in the FACE diesel research fuel set characterization effort.

Single-Cylinder Engine-Based Research Capability

In FY 2008 and FY 2009, APBF used capital funding to add significant research capability to NREL's Renewable Fuels and Lubricants (ReFUEL) Research Laboratory with the addition of a single-cylinder research engine and test cell. The goal was to provide NREL in-house capability to investigate fuel effects on advanced combustion engine strategies utilizing spark-ignition type fuels. The new test cell equipment includes a 75 horsepower dynamometer capable of transient motoring and absorption operation, a custom high-pressure fuel handling system, additional emissions analysis equipment, and an independent engine control system. The engine was selected to position NREL's spark ignition engine research with an auto manufacturer production-based, leading technology combustion system which matches latest industry trends (i.e., direct-injected, variable valve timing, turbocharged, decreased displacement). A 2009 General Motors Ecotec "LNF" family 2.0L DISI turbocharged engine was chosen for conversion to single-cylinder operation. The most cost-effective and highest quality option available was to purchase a 2009 Chevrolet HHR-SS vehicle from which to pull the engine and all supporting ancillary, emissions, and controls equipment. This allowed the ReFUEL team to condition the engine and initially run it on the dynamometer in a configuration mimicking the vehicle, allowing for quality checks and mapping data to be shared with General Motors.

After initial characterization as a four-cylinder engine, fuels studies were initiated which would take advantage of the vehicle's emissions control system. Following that, conversion to dedicated single-cylinder operation was begun. The dynamometer and much of the test cell were configured to accommodate future addition of a compression ignition research engine with minimal effort. A custom high-pressure fuel handling system was constructed to replace the high-pressure fuel pump integral to the engine, which would have caused pressure and injection stability issues when the engine was converted to single-cylinder operation. The high-pressure fuel handling system was also protected for capability to handle a wide range of fuels, including renewables. Engine instrumentation was deliberately coordinated with General Motors Research & Development Center, allowing for sharing of data between the organizations.

The new single-cylinder research engine test cell serves as a bridge between APBF's fundamental combustion research and full engine/vehicle testing, allowing links with other research. Converting a production engine to single-cylinder operation provided a cost-effective means of investigating fuel chemistry effects on combustion system interactions, efficiency, and emissions with a production engine combustion chamber to enable hardware tie-points with other researchers. In addition to providing a research engine platform capable of advanced combustion regimes, 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:

- NREL's development of an IQT-based research platform allows ignition kinetics studies which bridge fundamental ignition chemistry studies and engine testing.
- 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 also enable the development of advanced surrogate fuels and characterization of advanced alternative and renewable fuels, which further benefit fuels and engine researchers.
- NREL added significant 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

Scott Sluder
Oak Ridge National Laboratory (ORNL)
National Transportation Research Center
2360 Cherahala Blvd.
Knoxville, TN 37932

Bradley Zigler
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd., MS-1634
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork
Phone: (202) 586-8306; E-mail: kevin.stork@ee.doe.gov

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.

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 manufacterers, universities, and national laboratories.
- Leveraged CRC partnership with research collaboration between DOE and Canadian national laboratories, including:
  - Oak Ridge National Laboratory
  - Pacific Northwest National Laboratory (PNNL)
  - National Renewable Energy Laboratory
  - Lawrence Livermore National Laboratory
  - Sandia National Laboratories
  - National Center for Upgrading Technology (Natural Resources Canada)
- Developed nine FACE diesel fuels, which are currently available for purchase from Chevron-Phillips Chemical Company (CPChem).
- Completed 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 the FACE diesel fuel matrix.
- Begun joint NREL/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).

Future Directions

- Secure a fuel blender to manufacture and sell the FACE gasoline fuel matrix.
- Perform characterization of FACE gasoline fuels.
- 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.

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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 project was conceived to bring together the stakeholders in industry together with researchers at universities and 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 project by assessing industrial interest and seeking the best forum in which to conduct it. 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 chaired by Ken Wright of Conoco-Phillips and co-chaired by Wendy Clark of NREL and Ron Graves of ORNL. Invitations were extended to interested parties in the petroleum, automotive companies, engine manufacturers, universities, and research labs. The FACE working group roster includes 25 people representing 22 different organizations across industry 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). 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 Chevron-Phillips Specialty Chemical Company and have been made available for purchase by interested researchers. ORNL has facilitated distribution of the fuels from drums maintained at ORNL for those researchers who only require small volumes of the fuels. Research efforts are underway at ORNL, West Virginia University (under contract from NREL), Pennsylvania State University, Sandia National Laboratories, and other locations using the fuels.

A CRC FACE Characterization team was formed to perform an exhaustive characterization of the nine

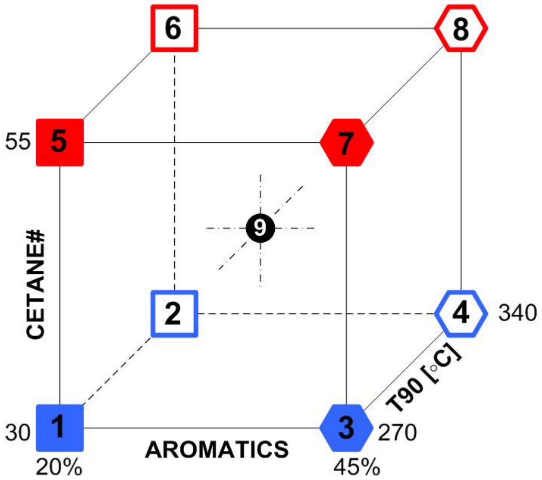

FIGURE 1. FACE Diesel Fuel Matrix

FACE diesel fuels. This team included ORNL, Chevron, PNNL, NREL, and Natural Resources Canada's National Center for Upgrading Technology. 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 (PIONA)
- 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, and published the exhaustive characterization details in a CRC report. 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.

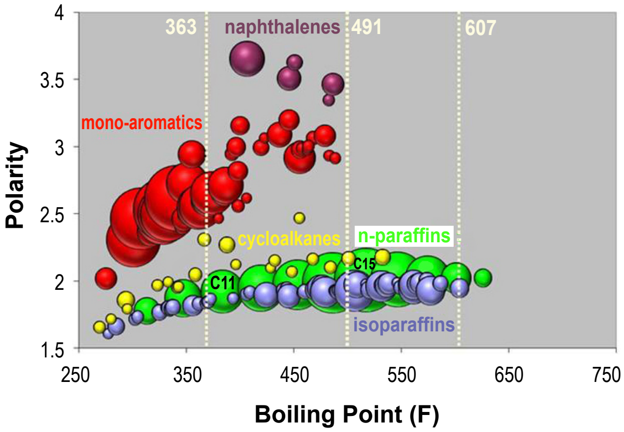

FIGURE 2. 2D GC/MS Analysis of the Centerpoint FACE Diesel Fuel (FD-9A)

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), and on HCCI (SAE 2009-01-2645). Additionally, NREL and CRC began a joint study employing the FACE diesel 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 Advanced Vehicles Fuels and Lubricants (AVFL-18) project. Table 1 and Figure 4 illustrate how detailed compositional structural information from the FACE diesel set characterization allow modeling of surrogate molecules to match bulk fuel makeup, providing direction for the formulation of diesel surrogates.

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%)

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

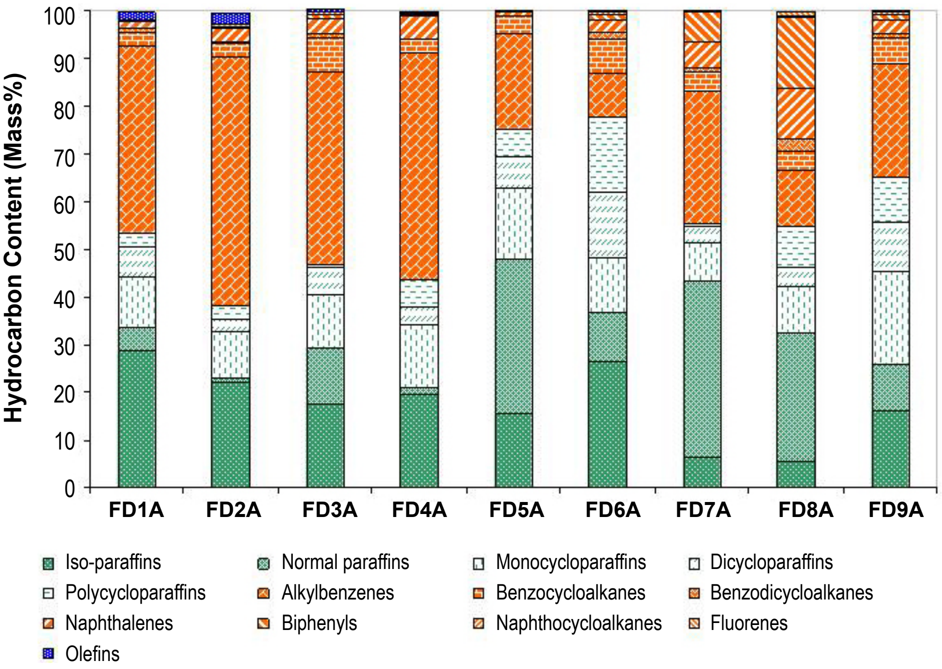

FIGURE 3. GC-FIMS and PIONA Analysis of FACE Diesel Fuels

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

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).

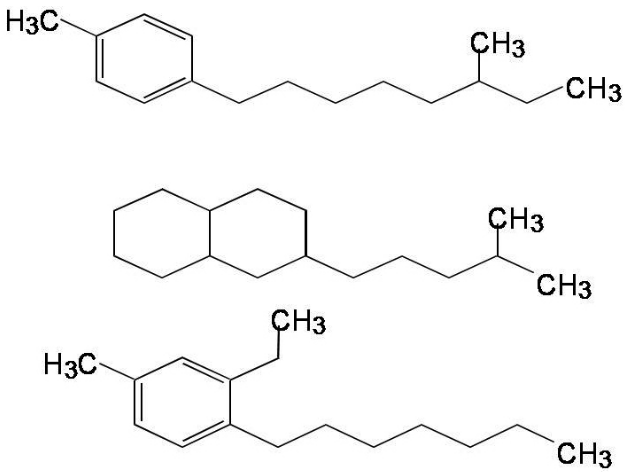

FIGURE 4. ^{13}C and ^{1}H NMR-based Molecular Models

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

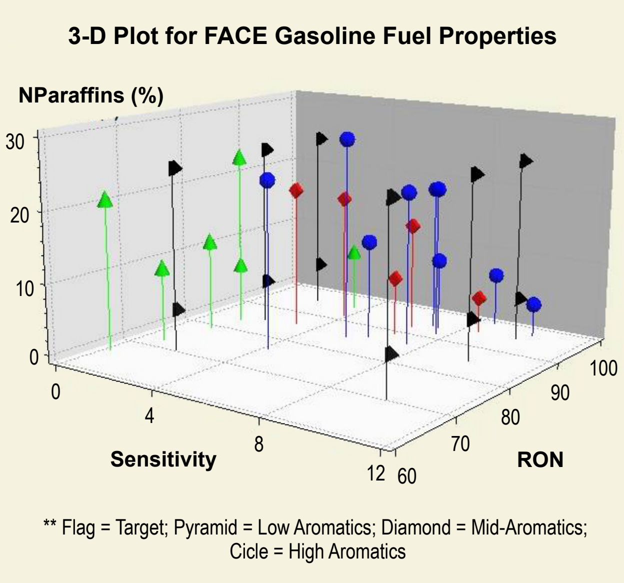

FIGURE 5. Proposed FACE Gasoline Fuel Matrix

is currently working to identify a fuel blender who will produce the FACE gasoline matrix and offer those fuels for sale.

Advanced Alternatives and Renewable Fuels

In Fiscal Year 2008 and FY 2009, the CRC FACE Working group 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:

- 2nd 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 procedures, including Fischer-Tropsch

Conclusions

The collaborative efforts of the DOE 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 2008 and 2009, the FACE-related research effort has:

- Developed the FACE diesel matrix of nine research fuels.
- Worked with a blending partner to produce the FACE diesel fuels and offer them currently available for sale to researchers.
- Performed an exhaustive advanced characterization of the FACE diesel fuels and published the results.
- Fostered initial use of the FACE diesel research fuels in advanced engine combustion research.
- Developed analytical techniques, produced critical data, and developed predictive models to enable development of advanced diesel surrogate fuels with kinetic models.
- Completed initial 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

Jim Szybist (Primary Contact), Bruce Bunting, Scott Sluder, Kukwon Cho, Manbae Han, Scott Eaton, Sam Lewis, Scott Curran, and Robert Wagner
Oak Ridge National Laboratory (ORNL)
2360 Cherahala Boulevard
Knoxville, TN 37932

DOE Technology Development Manager:
Kevin Stork

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.

Accomplishments

- Published results demonstrating low emissions of multi-cylinder high-efficiency, clean combustion (HECC) operation with biodiesel blends derived from soy and coconut oils.
- Used numerical methods to analyze experimental results from separate fuel sets (biodiesel fuels, oil shale fuels, and oil sand fuels), allowing co-linear fuel properties to be correctly accounted for.
- Published diesel homogeneous charge compression ignition (HCCI) results for oil sand fuels showing that the fuels with the best performance in this engine have high volatility and low cetane number.
- Kinetic modeling was utilized to identify a unique ignition characteristic of ethanol.

Future Directions

- Continue to study the effects of non-petroleum-based fuels on advanced combustion by expanding the range of fuel properties, composition, chemistry, and fuel source material, including the Fuels for Advanced Combustion Engines fuels.
- A new single-cylinder research engine with hydraulic valve actuation (HVA) will be used to study negative valve overlap (NVO) HCCI for ethanol and butanol fuel blends.
- Develop deeper understanding of fuel effects by employing additional statistical analysis tools to design experiments and analyze data.
- ORNL is pursuing a dual-fuel combustion strategy for diesel engines (gasoline or ethanol with diesel). Discussions have been initiated with Professor Rolf Reitz from the University of Wisconsin to better understand the potential of the approach with production-like hardware. This effort is being leveraged with several other projects, including advanced petroleum-based fuel effects on advanced combustion, HECC, and Joule Milestone.

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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 heavy crude-derived fuel, ethanol, 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 diesel fuel effects on advanced combustion regimes are being performed on two research platforms: a straight-forward single-cylinder diesel engine operated under HCCI conditions, and a multi-cylinder production diesel engine operating under a premixed charge compression ignition form of HECC. The single-cylinder research platform was used to perform investigations for biodiesel, oil-sands, and oil-shale fuel sets. It is equipped with a custom partial vaporization port fuel injector for fully premixed charges of fuel and air, does not use exhaust gas recirculation (EGR), and utilizes an intake manifold heater to control HCCI combustion. This research platform allows for simple comparisons of the effects of fuel properties in relative isolation from confounding operational parameters. The multi-cylinder platform was used to investigate B5 and B20 blends of soy- and coconut-derived biodiesel, and a study to quantify the oil dilution under HECC conditions was attempted. The multi-cylinder engine operates in a more realistic manner for production engines compared to the single-cylinder platform because the fuel injection pressure and timing can be controlled with the original equipment manufacturer (OEM) fuel injection equipment, and high levels of EGR are utilized.

The primary platform for gasoline-range fuel investigations had been a 2-cylinder variable compression ratio engine. During the course of an experimental study in Fiscal Year 2008 for Non-Petroleum-Based Fuel (NPBF) Task 2.6, Enabling High Efficiency Ethanol Engines, a major hardware failure occurred on this engine platform. This engine platform has since been replaced with a single-cylinder gasoline direct injection research engine equipped with fully variable HVA. Moving forward, this research platform will be used to study production-intent HCCI combustion strategies (both NVO and exhaust re-breathing). However, because of the equipment failure, the gasoline NPBF efforts during FY 2008 and FY 2009 were focused modeling efforts, specifically one study using CHEMKIN software, and another investigating spark-assisted HCCI. In the study using CHEMKIN, modeling was employed to investigate the behavior of ethanol and other fuel components under operating conditions relevant to NVO HCCI. The spark-assisted HCCI modeling uses a combination of reduced kinetic mechanisms and multidimensional modeling, and is leveraged with several other projects.

Results

Diesel Advanced Combustion: Single-Cylinder HCCI Engine

The effects of methyl ester fuel properties and chemistry on engine performance under HCCI engine conditions were investigated in a collaborative study with BP and Cummins. The performance and emissions of numerous biodiesel blends were investigated experimentally by using narrow-cut methyl esters that spanned the low and high limits of fuel properties possible for biodiesel-relevant methyl esters (molecular weight, volatility, saturation, oxygen content, and cetane number). The experimental results of this study were combined with a previous study that investigated B20 blends derived from soy, rapeseed, palm, coconut, and mustard oils. A statistical method, principal components analysis (PCA), was used to analyze the results. Analysis showed that performance, namely thermal efficiency, improved with lower boiling point methyl esters and with lower cetane numbers. Biodiesel blending appears to only affect performance to the extent that it alters the distillation characteristics and cetane number of the blend. It should be emphasized that the trends of improved performance with lower cetane number may be unique to this type of fully-premixed engine operation where ignition and combustion rate are entirely kinetically driven. Production-intent combustion strategies utilize control of mixing and combustion rate and therefore may actually benefit from improved ignition characteristics

A separate project to investigate the effects of oil sand-derived fuels was performed on this engine platform, in collaboration with NCUT, Shell Canada (now Royal Dutch Shell) and the Pacific Northwest National Laboratory (PNNL). Seventeen oil sand-derived refinery intermediates were studied, and all but one met the ultra-low sulfur diesel specification of 15 ppm sulfur. The samples were tested under HCCI conditions in the single-cylinder engine and analyzed using PCA. PCA was also used to analyze the fuel chemistry and properties. Results showed that the fuels could be equally well characterized using fuel chemistry or bulk fuel properties. The cycloparaffin content did not cause large differences in fuel properties or engine operation. Performance data showed that the best efficiencies were achieved for fuels with low temperature distillation curves and low cetane numbers. Cetane number of the fuels was strongly reverse correlated to % mono aromatics. As with the biodiesel fuels, these findings are influenced by the engine platform used in this study which may not be representative of the combustion strategy used in production-intent engines.

Finally, a set of seven oil shale-derived fuels were investigated using this engine platform in a continuing collaboration with NCUT, Royal Dutch Shell, and PNNL. An oil shale sample was heavily hydrotreated and subsequently separated into narrow distillations cuts from 100-360°C. Compared to oil sand samples, the oil shale fuels had higher olefins and aromatics, and lower cycloparaffins. Low boiling point cuts of the hydrotreated oil shale exhibited as much as 25% higher fuel economy than high boiling point cuts, which can largely be attributed to the ability to achieve optimal combustion phasing. The oil shale components also exhibited higher oxides of nitrogen (NOx) than diesel fuel and generated heavy engine deposits. The authors suggest that minimally processed fuels from heavy crudes are not suitable as fuels for advanced combustion engines, but fuels refined to market specs from the same crudes may operate in similar engines without problems.

Diesel Advanced Combustion: Multi-Cylinder HECC Engine

A study was performed to investigate whether HECC combustion was compatible with biodiesel produced from soy and coconut oil, and to examine differences in engine performance and emissions at 5 and 20 vol% blend levels. The experimental portion of this study was largely conducted in FY 2007 and was discussed briefly in the FY 2007 annual report. The analysis and publication of these results extended into FY 2008. Results of the analysis showed that both biodiesel derived from soy and coconut oil was compatible with HECC combustion at these blend levels, producing a composite reduction of both NOx and particulate matter (PM) on the order of 80-90% compared to the conventional OEM engine calibration. The HECC operation did cause a fuel consumption penalty of 1-4% for the various operating modes investigated, but the fuel consumption penalty was not dependent on fuel type. There was a biodiesel-NOx penalty observed for the soy-based biodiesel, not for the coconut biodiesel, and it was present for both the conventional OEM and HECC engine calibrations. It is unclear if the NOx increase with soy biodiesel is statistically significant under HECC engine conditions. Figure 1 and Figure 2 show the composite NOx and PM emissions for the fuels investigated in this study under both HECC operating conditions and the OEM engine calibration.

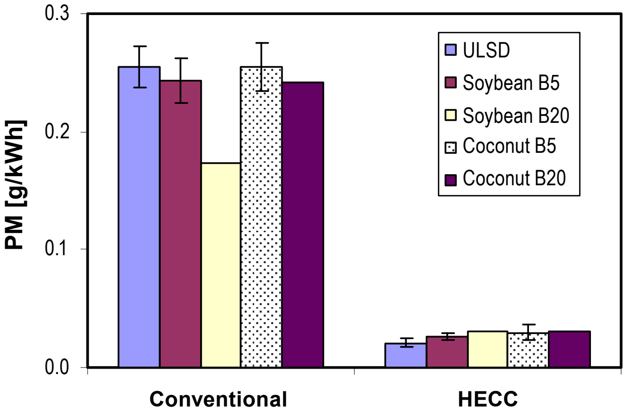

FIGURE 1. Composite PM Emissions from Conventional Diesel Combustion and HECC Modes

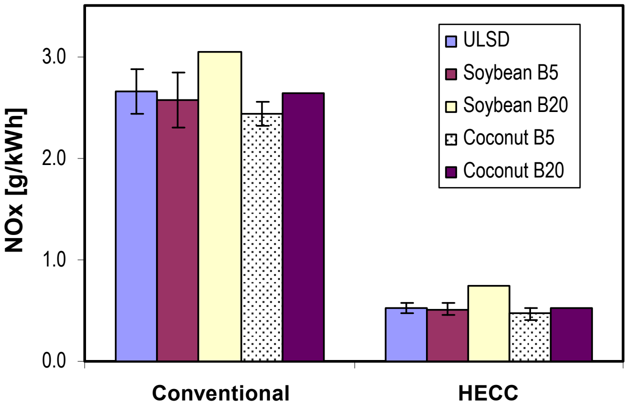

FIGURE 2. Composite NOx Emissions from Conventional Diesel Combustion and HECC Modes

Oil Dilution during HECC Operation with Biodiesel and Aged Biodiesel

An experimental study was performed to determine whether oil dilution would be problematic for advanced combustion engines when operating with in-spec biodiesel and with aged biodiesel. ORNL's 1.9 L General Motors diesel engine with full-pass control was used to accumulate 24 hours of HECC operation for conventional diesel, for in-spec B20, and for an aged B20. Unfortunately, several problems were encountered during the set of experiments, including with the engine controller, the fuel injectors, and the EGR cooler. The problems that were encountered prevented the completion of the experiments, and the data that was collected had poor control and repeatability. Thus, no conclusions can be made from the effort.

Kinetic Modeling of Ethanol HCCI

A modeling study was performed to investigate fuel-specific effects of EGR components on HCCI combustion at conditions relevant to the NVO combustion strategy using CHEMKIN-PRO. The kinetics of ethanol were compared to three hydrocarbon fuel components: n-heptane, iso-octane, and toluene. These fuels were chosen because they span a wide range of fuel chemistries, and produce a wide compositions range of complete stoichiometric products. The simulated engine conditions combined a typical spark ignition engine compression ratio (11.34) and high intake charge temperatures (500-550 K) which are relevant to NVO HCCI. It was found that over the conditions investigated, all the fuels had overlapping start-of-combustion (SOC) phasing, despite the wide range in octane number (Research Octane Number = 0 to 120). The effect of the EGR components CO_2 and H_2O was to suppress the compression temperature because of their higher heat capacities, which retarded SOC. Excess O_2 in the intake charge (i.e. an O_2 concentration higher than the stoichiometric requirement) caused the SOC to advance for n-heptane, iso-octane, and toluene, but SOC for ethanol was not advanced, as shown in Figure 3. It was concluded that the ethanol initial ignition reactions differ from hydrocarbon fuels in that under these conditions the rate-limiting step is not dependent on the concentration of O_2 in the reaction environment.

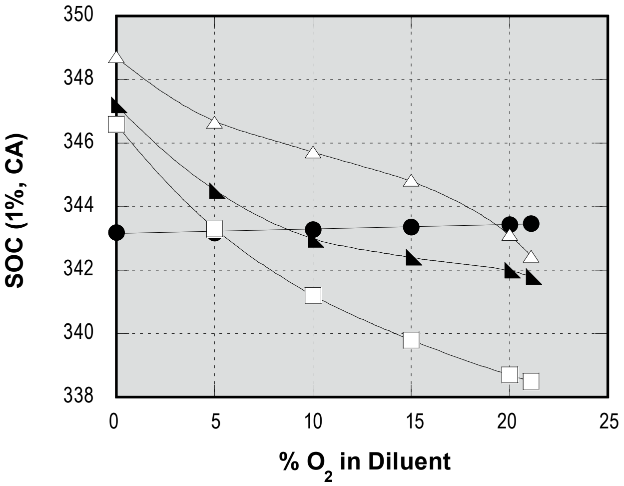

FIGURE 3. Effect of diluent O_2 concentration on the start of combustion predicted by CHEMKIN for a start of compression temperature of 550 K for (□) toluene, (●) ethanol, (◣) iso-octane, and (△) n-heptane.

Spark-Assisted HCCI (SA-HCCI)

Spark assist for controlling HCCI combustion and expanding the operating envelope was investigated through system-level and multi-dimensional combustion models. Additionally, this activity was leveraged with other investigations in partial support of the development of a single-cylinder research engine with continuously variable valve actuation. The experimental setup will be used in FY 2010 for model validation and improved understanding of the instability mechanisms which govern and often limit HCCI operation. A system-level model developed at the University of Michigan (UM) was validated for conventional spark-ignition operation and is being expanded to include SA-HCCI. This model is based on an HCCI combustion correlation developed at UM and will serve as a basis for future models to understand the effect of valve events, geometric compression ratio, and ultimately fuel chemistry on HCCI stability and operational range. ORNL also worked closely with Lawrence Livermore National Laboratory in FY 2009 to make use of a CHEMKIN-based multi-zone model to better understand the effect of fuel chemistry on SA-HCCI. The initial investigation makes use of a 63-species reaction mechanism for iso-octane to explore the transition from spark-ignition to SA-HCCI as well as the cycle-to-cycle interactions. The results of this study have been accepted for publication at the 2010 International SAE Congress.

Conclusions

- Biodiesel methyl ester chemistry affects performance under HCCI conditions, with low cetane number and low distillation curve temperatures leading to high efficiency.
- Low cetane number and low boiling point oil sand fuels exhibited best efficiency in a diesel HCCI engine.
- HECC combustion is compatible with soy and coconut biodiesels up to levels of 20 vol% and resulted in a substantial NOx and PM reduction.
- Kinetic modeling study revealed that under NVO HCCI conditions, ethanol differed from hydrocarbon fuels in that for the initial ignition processes, the rate-limiting reactions were not dependent on the concentration of ambient O_2 in the mixture.

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III.8 Advanced Lean-Burn DI Spark Ignition Fuels Research

Magnus Sjöberg
Sandia National Laboratories
MS9053, PO Box 969
Livermore, CA 94551-0969

DOE Technology Development Manager:
Kevin Stork

Objectives

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

1. How emerging future fuels, with an initial focus on ethanol, will impact the new highly-efficient direct-injection spark-ignition (DISI) light-duty engines currently being developed by 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 a future fuels lab for advanced lean-burn DISI engine research.
  - Design an optically-accessible DISI research engine.
  - Install and commission the engine in the future fuels lab.

B. Evaluating ethanol for spark-ignition (SI) and homogeneous charge compression ignition (HCCI) operation, utilizing the existing HCCI fundamentals lab.
  - Determine the autoignition characteristics of ethanol over ranges of loads, speeds, and intake-pressure boost.
  - Evaluate the latest ethanol chemical-kinetics mechanism from Lawrence-Livermore National Laboratory (LLNL)/National University of Ireland (NUI) - Galway.

Accomplishments

A. Future fuels DISI lab.
  - Finished designing the laboratory that houses the new DISI research engine.
  - All lab infrastructure has been finalized.
  - Designed and installed an engine-test stand with excellent vibration isolation.
  - A high-performance alternating current induction motor that controls the engine speed and absorbs load has been installed.
  - The crankcase of the existing CLR research engine has been modified to accommodate the new optical setup with an extended-piston arrangement.
  - To ensure a well-balanced single-cylinder engine, the balancing shafts have been modified with added tungsten.
  - Completed preliminary design of combined all-metal/optical engine.

B. Initial fuel evaluation for DISI operation.
  - Performed tests in the HCCI lab to assess ethanol and gasoline autoignition characteristics (as related to knock and flame speed for SI).
  - Evaluated/validated the latest ethanol chemical-kinetics mechanism from LLNL/NUI - Galway.

Future Directions

A. Finalize design of DISI research engine with metal and optical configurations.
  - Complete the fabrication of parts for all-metal configuration.
  - Assemble and commission the engine to allow performance testing.
  - Perform experiments to assess DISI engine performance and efficiency, and the onset of knock as a function of ethanol/gasoline fuel blend and compression ratio (CR).
  - Assess the robustness of the stratified spray-guided combustion system as the fuel composition and intake-boost pressure change by continuously monitoring for misfire cycles.
  - Apply advanced optical diagnostics (including high-speed imaging) to identify the in-cylinder processes that are responsible for sporadic misfire cycles.
  - Focus on the conditions prevailing near the spark gap (fuel concentration and flow field) and the ensuing early flame growth.

B. Continue evaluation of ethanol and gasoline over a wide range of conditions.
  - Particularly assess the influence of intake boost, exhaust-gas recirculation (EGR), fuel/air-equivalence ratio (ϕ), and fuel-vaporization cooling.
  - Evaluate the ethanol chemical-kinetics mechanism with regards to EGR, charge temperature, and ϕ.

– Use the PREMIX flame model to investigate the influence of EGR, ϕ, and intake boost on the laminar flame speed in the DISI engine.

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Introduction

In the U.S., transportation accounts for most of the petroleum usage. A reduction of oil imports is important for energy independence. Therefore, it is imperative both to increase engine efficiency and to replace conventional petroleum-based fuels with renewable fuels. In addition, the U.S. and most industrialized countries are committed to substantial reductions of carbon dioxide (CO_2) emissions in order to reduce the risk of irreversible damage to the planet due to global climate change. Ethanol is the most widespread renewable fuel today with a 5% contribution to the energy needs of gasoline-type powered vehicles in the U.S. [1,2], and its use is rapidly increasing as mandated by the Renewable Fuel Standard (RFS) set forth in the Energy Independence and Security Act of 2007.

One technique for increasing the efficiency of gasoline-type piston engines is to switch from traditional stoichiometric homogeneous-charge 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% or more higher fuel efficiency. However, for such stratified operation, it is important to minimize the engine-out emission of NO_X, because NO_X exhaust aftertreatment is less efficient when oxygen is present in the exhaust due to the overall lean operation. Engine-out NO_X can be decreased by applying EGR. However, the potential reduction of NO_X with EGR is limited by the appearance of misfire cycles. Thus, there is a trade-off between engine-out NO_X and combustion robustness. To improve the robustness and avoid the appearance of misfire cycles, additional understanding is needed of advanced, direct-injection (DI) stratified-charge SI engines. Given the current trends of increased usage of ethanol and engine downsizing/turbocharging, the project focus will be on boosted operation with ethanol. In particular, there is incomplete understanding of the dynamics of fuel-air mixture preparation and ignition. It can be noted that ethanol has a stoichiometric air/fuel ratio (AFR_{st}) that is substantially lower than gasoline (9.0:1 vs. 14.6:1). With a lower AFR_{st}, ethanol requires a larger injected fuel mass for the same power, which influences the fuel stratification and therefore also the ignition and combustion.

Approach

The lab and engine hardware will be based off existing and well-proven engine labs and optical engines at Sandia National Laboratories, and then improved to accommodate the unique requirements of advanced DISI engine fuels research. Our collaboration with General Motors (GM) allowed us to acquire the latest generation single-cylinder engine head and piston designed for stratified-charge SI research, thus ensuring highest relevance to industry. The engine has a spray-guided stratified charge SI combustion system and optical access to the pent-roof combustion chamber.

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 diagnostics will be applied to 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, detailed chemical-kinetics modeling will be performed of flame speed and autoignition for better understanding of the fundamentals that govern the combustion event. The chemical-kinetics mechanism will be validated against experiments in Sandia's HCCI fundamentals lab. In addition, collaboration with DISI computational fluid dynamics modeling teams will be developed.

Results

A: Future Fuels DISI Lab

The laboratory build-up started from an empty room. Consequently, all room infrastructure and engine test stand had to be developed. An engine-test stand was designed based on an assembly of heavy steel plates suspended on AirMounts, see Figure 1. The combination of a large mass (2,700 kg) and a low natural frequency (2.8 Hz) prevents engine vibrations from reaching sensitive lasers and other measurement devices. The laboratory room has been finished, including electrical supply, ventilation, cable trays, and shelves over engine and laser table. A high-performance electric motor has been installed, and it is controlled by a 55 kW variable-frequency drive.

The engine assembly is based off an existing CLR research engine. This single-cylinder engine needed dynamic balancing of reciprocating masses. Therefore, the two original counter-rotating balancing shafts were redesigned to account for the extra weight of the extended optical piston. Computations showed that addition of tungsten could provide complete balancing of 1st order forces, as is custom. The modified balancing shafts have been installed and additional modifications have been made to prepare the base of engine for the extended piston and the optical assembly. The design and manufacturing of the upper portion of the engine is in progress. The engine will have a bore of 86 mm and a stroke of 95 mm. Thus, the swept volume of this single-

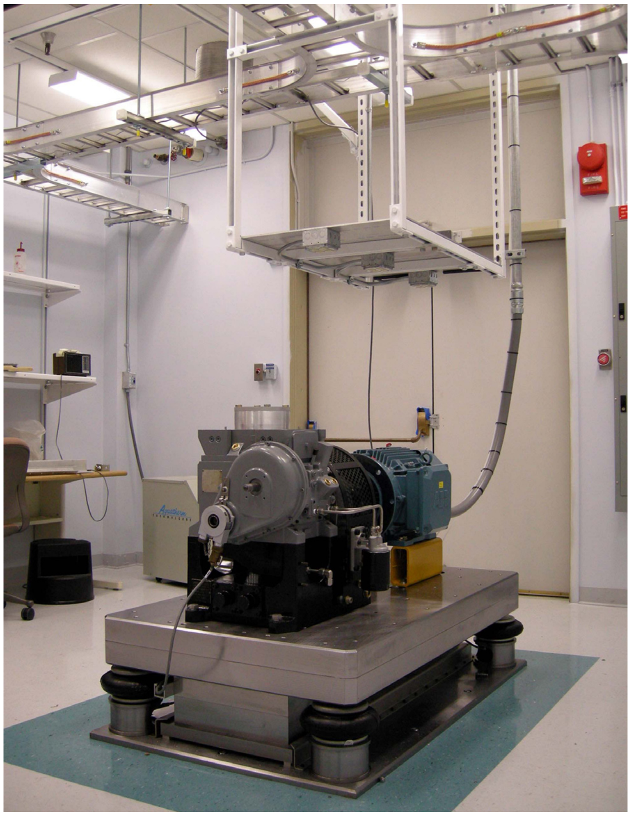

FIGURE 1. Engine Test Stand with Base of Engine and Load-Absorbing Electric Motor

cylinder engine will be 0.55 liter, corresponding to a 2.2 liter 4-cylinder engine.

Two configurations of the engine are being prepared. For performance testing, one all-metal version with metal piston-ring pack and oil cooling of the piston (including lower cylinder for oil control) will be used, see Figure 2. For optical diagnostics, one optical version with pent-roof windows, piston-top window, 45° mirror, spacer-ring windows, and endoscope access will be used, see Figure 3. Both engine configurations feature a drop-down cylinder for easy access to the piston top and combustion chamber. Planned optical diagnostics include planar-laser-induced fluorescence (PLIF) of fuel concentration, particle image velocimetry (PIV), and direct chemiluminescence imaging of the combustion.

Figure 4 shows a schematic of the room layout (with a mock-up engine top). To facilitate working on the engine, the optics tables are placed such that the engine can be accessed freely from three directions. This is accomplished by separating the main laser table (center-left in Figure 4) from the engine. To link the laser beams to the optical engine, a movable and hinged optical bridge will be used. For non-optical experiments, the optical bridge will be raised, as illustrated in Figure 4.

When operational, the new future fuels DISI lab will enable cutting-edge research that supports industry to develop highly efficient combustion technologies, thereby significantly contributing to DOE's goal of 25% fuel economy improvement for gasoline-type engines. These DISI engines show promise to deliver the targeted efficiency at a lower cost than diesel engines, allowing extensive market penetration in the passenger-car segment.

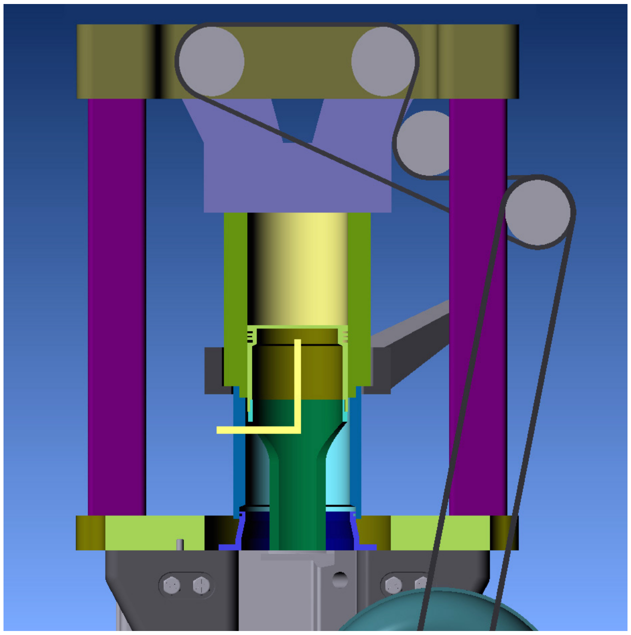

FIGURE 2. Schematic of the Engine in its All-Metal Performance Configuration with Lower Oil-Control Cylinder and Oil-Jet Cooling of Piston

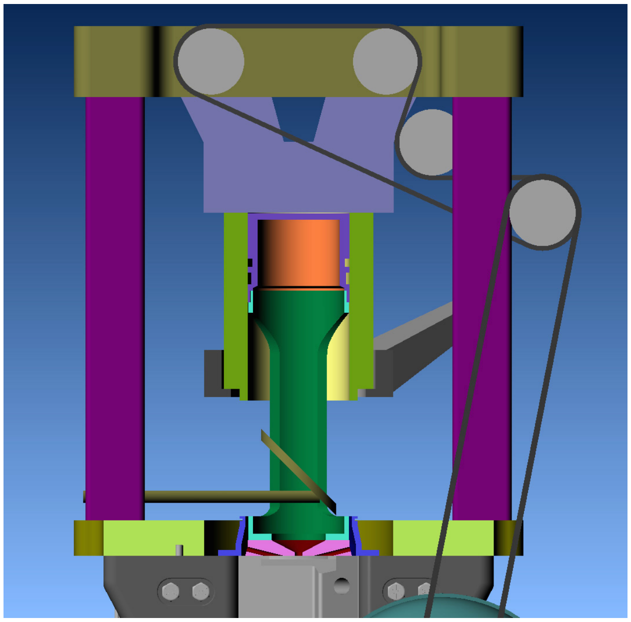

FIGURE 3. Schematic of the Engine in its Optical Configuration with 45° Mirror Inside the Extended Piston

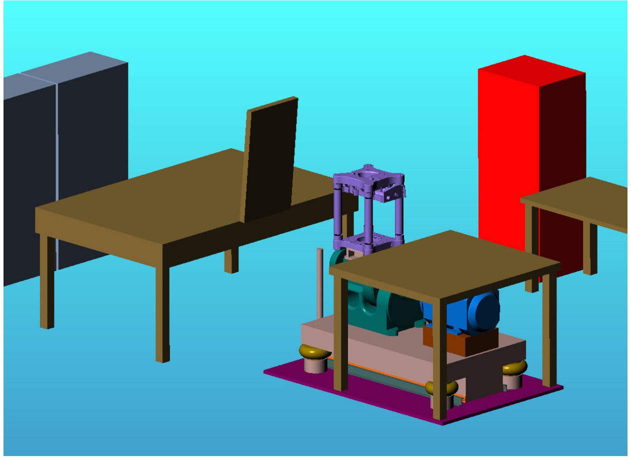

FIGURE 4. Schematic of Engine-Test Stand and Optics Tables

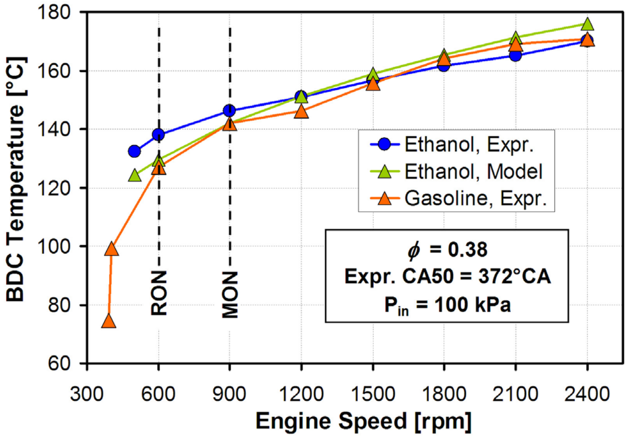

FIGURE 5. Required T_{bdc} for Maintaining CA50 = 372°CA as Engine Speed is Changed Using Ethanol and Gasoline ($RON_{ethanol}$ = 107, $RON_{gasoline}$ = 90.8, $MON_{ethanol}$ = 89, $MON_{gasoline}$ = 83.2)

B: Initial Fuel Evaluation for DISI Operation

The first fuels to be examined in the new DISI research engine are gasoline and ethanol, and various blends of the two. Since engine knock must be avoided when operating with alternative fuels, it is essential to examine the autoignition characteristics of these fuels. Consequently, experiments in the HCCI fundamentals lab were performed to assess gasoline, and especially, ethanol autoignition characteristics over a wide range of conditions. During the time period covered by this report, engine-speed, intake-boost pressure, and ϕ sweeps have been performed, and the first two will be discussed here. Additional tests will address the influence of the charge temperature and EGR rate. The acquired data allow the autoignition characteristics of gasoline and ethanol to be compared, and it also allows comparisons with reference-fuel blends containing iso-octane and n-heptane. Importantly, the data also enable evaluation of the fidelity of both existing and newly developed chemical-kinetics mechanisms, which are used for modeling knock onset and flame speed at conditions relevant for DISI operation.

To provide an example of the results obtained, Figure 5 shows data from engine-speed sweeps with gasoline and ethanol. For controlling the combustion timing, an electric heater near the intake was used to adjust the incoming charge temperature, which directly influences the charge temperature before compression begins, i.e., the bottom-dead-center temperature (T_{bdc}). Figure 5 compares the T_{bdc} requirements for ethanol and gasoline across a wide speed range. It can be seen that for either fuel, the T_{bdc} requirement increases monotonically with speed. This is expected since the autoignition reactions have to occur in less time as speed increases in order for the combustion timing (50% burn point – CA50) to occur at the correct crank angle. In this case, CA50 was maintained at 372°CA (crank angle degrees), which corresponds to 12°CA after top dead center (TDC = 360°CA). Furthermore, the T_{bdc} requirements are very similar for engine speeds of 1,500 rpm and higher. This shows that the autoignition reactivities of gasoline and ethanol are nearly identical in this speed range. Figure 6a plots the heat-release rate (HRR) for operation at 1,500 rpm. As can be seen, the HRR traces are also very similar at this engine speed.

The nearly identical autoignition reactivities at the higher speeds are perhaps surprising given the higher octane numbers of ethanol compared to gasoline (see caption of Figure 5). However, it should be taken into account that the traditional research octane number (RON) and motor octane number (MON) tests are conducted at 600 and 900 rpm, respectively. Therefore, these standard octane tests do not directly reveal how reactivities of fuels will compare at higher engine speeds. In fact, a comparison of the data points at 600 and 900 rpm in Figure 5 with the RON and MON numbers given in the figure caption reveals that the current HCCI measurements with ethanol and gasoline are consistent with the SI-based RON and MON tests for the same fuels. Furthermore, for engine speeds below 600 rpm, the curves in Figure 5 diverge distinctly. This happens because this gasoline starts to develop low-temperature heat-release (LTHR), which increases its reactivity and requires a strong reduction of T_{bdc} to maintain CA50 at 372°CA. One example of the LTHR that develops is shown in Figure 6b. In contrast, ethanol remains a single-stage ignition fuel even for engine speeds below 600 rpm. The lowest engine speed plotted in Figure 5 for ethanol is 500 rpm. To determine if ethanol possibly could develop any LTHR for operation with an intake pressure (P_{in}) of 100 kPa, 300 rpm was also tested using a low T_{bdc}. However, no tendency to develop LTHR was detected for this naturally aspirated operation, and this supports the assessment that ethanol is a true single-stage ignition fuel.

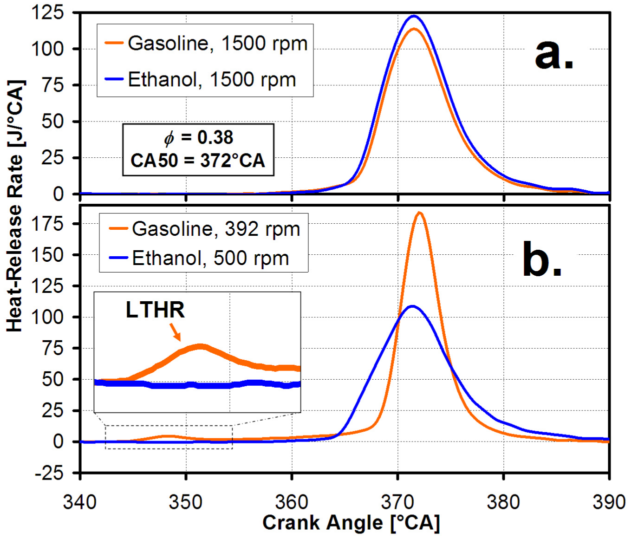

FIGURE 6. HRR Traces for Ethanol and Gasoline at 1,500 rpm (a) and at Low Engine Speed (b)

The latest ethanol mechanism from LLNL/NUI - Galway [3] was evaluated against the data using a single-zone CHEMKIN model. The mechanism has 55 species and 350 reactions. It is developed to be an integrated part of a gasoline surrogate mechanism [4]. This much larger gasoline surrogate mechanism is a joint effort between NUI - Galway (Curran, Serinyel, and Metcalfe) and LLNL (Pitz and Mehl). For this model evaluation, it was beneficial to compare the T_{bdc} required to achieve the same start of combustion (SOC) as engine speed changes. As can be seen in Figure 5, at 1,200 rpm the BDC temperatures match nearly perfectly for the ethanol model and experiment. The good match was obtained without any tuning of the model, so this indicates that the model predicts well the autoignition reactivity for this operating point. However, there is a difference in slope between the two ethanol curves in Figure 5. This suggests that the mechanism is not sufficiently reactive at high engine speeds, and vice versa at low engine speeds. Future work is planned to better understand this apparent shortcoming of the mechanism.

Experiments also show that the autoignition reactivity of ethanol has a very low dependence on intake-pressure boost (not plotted here). In contrast, gasoline exhibits a strong increase of its reactivity with intake boost [5]. For gasoline, the increased reactivity happens partly because LTHR develops at higher pressures. However, LTHR does not develop for ethanol, which remains a single-stage ignition fuel even for boosted conditions. This is consistent with the proven anti-knock properties of ethanol for boosted SI operation. Modeling shows that the ethanol mechanism has slightly too-low boost sensitivity. However, given that no tuning of the mechanism was performed, it can be concluded that the ethanol model overall performs well.

Conclusions

Significant progress has been made to commission a new advanced future fuels research engine laboratory. The design is nearly complete for an optically-accessible research DISI engine with all-metal performance-testing capability. The engine has a spray-guided stratified-charge SI combustion system. Strong collaboration with GM on hardware is ongoing. The new engine will allow performance testing with an all-metal engine 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, advanced high-speed optical diagnostics will be applied for detailed insights. When the lab is fully operational, it will support industry to develop the highly efficient DISI engines that are needed to comply with future fuel-economy standards.

An initial assessment of the autoignition characteristics of ethanol and gasoline has been performed using data acquired in the HCCI Fundamentals lab. It was found that ethanol remains a true single-stage ignition fuel, even for boosted operation. In contrast, gasoline developed two-stage ignition with LTHR at both low engine speeds and for boosted operation. These HCCI data are also very valuable for the planned DISI research as they enable model validation. It was found that the latest ethanol mechanism from LLNL/NUI-Galway captures autoignition well over ranges of engine speed and intake boost, making the mechanism useful for future modeling that will support the interpretation of experimental DISI data.

References

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2. International Energy Agency, www.iea.org .

3. Curran H., Serinyel, Z., and Metcalfe, W., Combustion Chemistry Centre at NUI Galway, Ireland, personal communication, 2009.

4. Mehl, M., Pitz, W.J., Sjöberg, M., and Dec, J.E., "Detailed Kinetic Modeling of Low-Temperature Heat Release for PRF Fuels in an HCCI Engine," SAE Paper 2009-01-1806, 2009.

5. Silke, E.J., Pitz, W.J., Westbrook, C.K., Sjöberg, M., and Dec J.E., "Understanding the Chemical Effects of Increased Boost Pressure under HCCI Conditions", SAE Paper 2008-01-0019, 2008.

FY 2008/2009 Publications/Presentations

1. Silke, E., Pitz, W.J., Westbrook, C.K., Sjöberg, M., and Dec, J.E., "Understanding the Chemical Effects of Increased Boost Pressure under HCCI Conditions", presented at and published in the proceedings, AIChE Annual Meeting, Salt Lake City, UT, November 2007.

2. Silke, E., Pitz, W.J., Westbrook, C.K., Sjöberg, M., and Dec, J.E., "Understanding the Chemical Effects of Increased Boost Pressure under HCCI Conditions", SAE paper 2008-01-0019, 2008 SAE International Congress, Detroit, MI, April 2008.

3. Sjöberg, M., "Advanced Lean-Burn DI Spark Ignition Fuels Research", 2009 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, May 2009.

4. Mehl, M., Pitz, W.J., Sjöberg, M., and Dec, J.E., "Detailed Kinetic Modeling of Low-Temperature Heat Release for PRF Fuels in an HCCI Engine", SAE Paper 2009-01-1806, SAE Powertrains, Fuels and Lubricants Meeting, Florence, Italy, June 2009.

Special Recognitions & Awards/Patents Issued

1. Invited speaker at the 5th International SAOT Workshop on Optical Metrology, Erlangen, Germany, March 2009.

III.9 Enabling High Efficiency Ethanol Engines

Jim Szybist (Primary Contact),
Adam Youngquist, and Robert Wagner
Oak Ridge National Laboratory (ORNL)
2360 Cherahala Boulevard
Knoxville, TN 37932

Wayne Moore (Primary Contact), Matt Foster,
and Keith Confer
Delphi Automotive Systems
3000 University Drive
Auburn Hills, MI 48326

DOE Technology Development Manager:
Kevin Stork

Objective

- The purpose of this project is to investigate ways to improve engine efficiency with ethanol-gasoline fuel blends, up to 85% ethanol (E85), in order to reduce the mile-per-gallon fuel consumption difference between gasoline and ethanol fuel blends.

Accomplishments

- Completed experimental study using a new single-cylinder engine at ORNL with variable valve actuation (VVA):
  - Results show that thermal efficiency for 50% ethanol (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) 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 10% ethanol (E10) and gasoline were frequently knock-limited.
  - By 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%.
  - Results demonstrate that with these methodologies, the fuel economy gap between E85 and gasoline can be reduced by about 20% at full load.
- A new engine test cell at ORNL with a motoring engine dynamometer has been completed and a multi-cylinder research engine designed for ethanol optimization is being installed for experiments to be carried out during Fiscal Year 2010.
  - The highly versatile 4-cylinder research engine from Delphi is onsite at ORNL. Direct fuel injection, high mechanical CR of 11.85, and prototype cam-based VVA system will allow versatile parametric studies for ethanol optimization.

Future Directions

- Experimental effort for FY 2010 will be focused on ethanol optimization on the multi-cylinder research engine. An identical engine is installed at the Delphi facility, and experiments conducted at the two locations will be complementary, and will both expedite and validate findings.
- A modeling effort has been initiated at ORNL to understand the efficiency advantage of fuels with high ethanol concentrations, and will be pursued throughout FY 2010. The investigation is using CHEMKIN kinetic modeling software to investigate the fuel-specific effects of ethanol on an ideal Otto cycle.

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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 its lower energy density, fuel economy for consumers is reduced by about 30% with E85. Ethanol has several fuel properties that are advantageous, and 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 this Cooperative Research and Development Agreement (CRADA) project we have partnered with Delphi LLC to identify and demonstrate these potential efficiency gains using a combination of high-fidelity engine modeling and engine experiments on multiple engine platforms.

Approach

Efficiency gains for ethanol engines are being investigated with two different engine 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 through the Vehicle Systems sub-program, and is therefore not discussed in detail here.

The first experimental effort utilized a single-cylinder engine at ORNL equipped with a VVA system to explore the knock limits of ethanol-containing fuels. A series of custom pistons was used to change CR from 9.2 to 12.87 in order to investigate the extent that efficiency can be increased for fuels with high ethanol content, which are not prone to knocking. For fuels that are prone to knocking, early and late intake valve closing (EIVC and LIVC) strategies are used to mitigate knock while 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. This experimental effort was completed during FY 2009.

The second experimental effort uses a research platform based on production technology, but fitted with a higher CR, more versatile cam phasing, and fully flexible engine controls. Modifications to the production engine to make it a highly versatile research platform were performed by our CRADA partner, Delphi, and at the time this report was written had recently been delivered to ORNL. The engine is being installed in a new engine test cell at ORNL that was renovated during FY 2008. Experimental investigations will be conducted to determine the engine conditions that lead to the highest thermal efficiency for ethanol blends during FY 2010.

Results

Experimental Effort 1:

Figure 1 shows thermal efficiency, power, and fuel consumption at the same operating condition for the production CR configuration for a series of ethanol blend levels. 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 fuel consumption is substantially increased for ethanol-containing fuels.

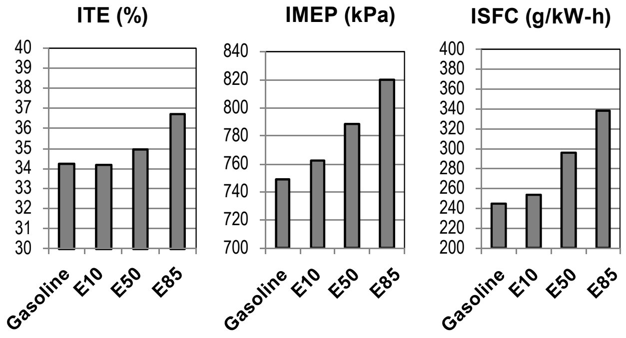

FIGURE 1. Indicated thermal efficiency (ITE, %), indicated mean effective pressure (IMEP, kPa), and indicated specific fuel consumption (ISFC, g/kW-h) at 1,500 rpm, 80 kPa intake manifold pressure, and spark timing for best torque. Original equipment manufacturer compression ratio of 9.2, and spark advance is not knock-limited for any fuel.

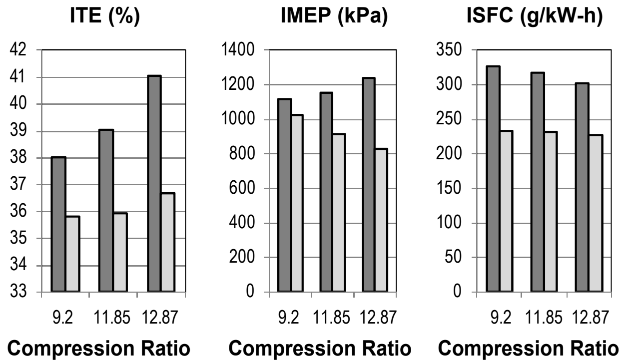

FIGURE 2. Comparison of engine performance of E85 (■) and gasoline (□) at 1,500 rpm and maximum load.

For E50 and E85, fuels that are not knock-limited, efficiency and power continue to increase with increase 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 conditions are required. Early and late intake valve closing 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 2, 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. Engine power increases for E85 but decreases for 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 SAE paper listed in the publications section.

Experimental Effort 2: Optimization of a Flexible Research Platform for Ethanol Fuels

The second experimental effort is to optimize a highly-flexible multi-cylinder research platform for operation on ethanol fuels. A production engine was modified by our CRADA partner, Delphi. Modifications include increasing the CR to 11.85 from the production engine CR of 9.2, using a more flexible cam technology that allows greater manipulation of valve events than production technology, full engine instrumentation, and integration of a fully-open engine controller. At the time this report was written, the engine had recently been delivered to ORNL and installation was in-progress. The engine is being installed into a new engine dynamometer test cell at ORNL. Major renovations of the facility were conducted during FY 2008, and the test cell is currently fully operational. A picture of the engine is shown in Figure 3.

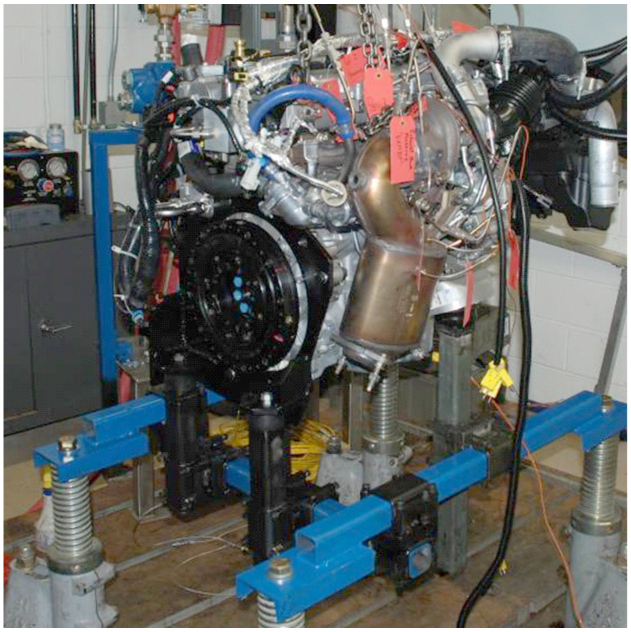

FIGURE 3. 4-cylinder research engine for ethanol optimization modified from a production engine by ORNL's CRADA partner Delphi.

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%.
    - Results demonstrate that with these methodologies, the fuel economy gap between E85 and gasoline can be reduced by about 20%.
- A production engine was modified by CRADA partner Delphi to be a highly flexible engine research platform for efficiency optimization of ethanol fuel blends:
    - The engine has been delivered and will be used for ethanol optimization experiments during FY 2010.

FY 2008/2009 Publications/Presentations

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

III.10 Reaction Design CRADA

Bruce Bunting
Oak Ridge National Laboratory (ORNL)
Fuels, Engines, and Emissions Research Center
2360 Cherahala Blvd.
Knoxville, TN 37932

DOE Technology Development Manager:
Kevin Stork

Objectives

- Help facilitate the development of tools which will allow the accurate modeling of multiple fuel types for combustion and engine design.
- Develop engine performance data for selected fuels and fuel surrogate compounds representing gasoline, diesel and alternative fuels, chosen by mutual agreement, on ORNL's homogeneous charge compression ignition (HCCI) research engine and other engines.
- Compile and analyze data for the purpose of determining data quality and to allow access to data by the Reaction Design technical team for further analysis.
- Analyze ORNL engine data in order to determine relevant trends and characteristics for the development and verification of engine modeling and combustion simulation software and kinetic modeling parameters with particular emphasis on fuel effects.

Accomplishments

This project began in August 2007 and runs through December 2011, with this report covering activities in 2008 and 2009.

- To date, five sets of fuels have been run by ORNL on an HCCI research engine. These fuels cover gasoline and diesel fuels, both fully formulated and surrogate.
- The model fuels consortium (MFC) modeling tools have been applied to these data sets to confirm the tools and to point out need for further development and improvement. This research has been documented in four SAE technical papers and two Diesel Engine Emissions Reduction (DEER) Conference presentations (Directions in Engine Efficiency and Emissions Research).
- Interaction with the MFC has provided ORNL with access to the MFC master kinetic mechanisms and to a CHEMKIN multizone and Forte computational fluid dynamics (CFD) model of the HCCI engine for kinetics and combustion research.

Future Directions

Efforts for the remainder of the Cooperative Research and Development Agreement (CRADA) will center around three areas:

- Verification of surrogate modeling tools in terms of designing surrogates to mimic actual fuels through engine experimental and modeling.
- Verification of master mechanisms and Forte CFD to model engine performance and to accurately reproduce fuel effects.
- Development of engine data related to particulate formation and characteristics to help support the development of particulate formation tools in CHEMKIN.

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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 emphasis on 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 Reaction Design related to engine and fuels analysis and technology. Reaction Design 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 a Reaction Design's MFC.

Results

In 2008/2009, ORNL conducted several HCCI fuel studies in direct support of the model fuels consortium, modeled the data using CHEMKIN multizone and the MFC master mechanisms, and conducted two additional fuel studies which will be analyzed in 2010 to support efforts in verifying the processes for designing surrogate fuels and for soot formation. The goals of these studies were to measure detailed hydrocarbon chemistry in the exhaust, which might give some indication of combustion intermediates or pathways and to conduct the first detailed particulate studies on this engine. These experiments were run in a single-cylinder HCCI engine using port atomization of the fuel and intake air heating to assist combustion. This engine should be familiar since it has been used in previous studies and more detail is provided in references 1 to 6. This engine can run a very wide range of fuels, has a nearly homogeneous fuel and air charge and depends completely on kinetics for ignition. The engine is not quite homogeneous, however, and we do see some fuel volatile effects and high hydrocarbon (HC) emissions (typical of HCCI) from wall quenching. We have been working diligently on improving measurement accuracy and are currently installing a new combustion analysis system and improved measurements of fuel and air rates. In 2009, engine-wise, we found that about 90% of the HC emissions of this engine are composed of unburned fuel with the fuel chemistry profile preserved, that combustion intermediates do appear in the exhaust in the form of light HCs and oxygenated species, and that particulates consist of volatile, condensed products to a much larger extent than conventional diesel engines.

The first series of fuels (1, 2, 3) consisted of an 87 research octane number (RON) primary reference fuel, an 87 RON toluene reference fuel (TRF), and the TRF blend + 30 vol% ethanol (RON=105). Data consisted of combustion phasing sweeps controlled by intake air temperature run at a single fuel rate of 9 gm/minute. There were six points per fuel, or 18 points total. Data consisted of heat release, gaseous emissions, smoke, scanning mobility particle size analyzer (SMPS), Fourier transform infrared (FTIR), and a number of absorptive/extraction techniques to measure determine heavier HC and oxygenated species emissions. All the fuels produced formaldehyde and acetaldehyde in about a 1.5-3 to 1 ratio and the TRF also produced benzaldehyde and benzoic acid from the toluene. Smoke and particulate emissions were low (smoke 0.02 to 0.06 units) and particle emissions were in the size range of 13 to 30 nm and most likely volatile aerosols. Ignition characteristics were different among the three fuels, with the TRF requiring the highest intake temperatures and the ethanol blend requiring the lowest. The phasing characteristics of the three fuels are indicated in Figure 1 and Table 1 indicates the overall ranges of emissions measured. More detailed information is included in the references.

The second series of fuels covered diesel range surrogates and the fuels were Coordinating Research Council fuels for advanced combustion engines (FACE) fuel #9 (a refinery-based fuel of 44 cetane), and two surrogate fuels of the same cetane, one a blend of n-hexadecane and hepta methyl nonane and one a blend of n-hexadecane and a-methylnaphthalene. The goal was to compare emissions between the base fuel and surrogate blends with and without the aromatic component, a-methylnaphthalene. The experiments consisted of combustion phasing sweeps controlled by intake air temperature at three levels of fuel rate (8, 10, and 12 grams per minute or about 2.5, 3.5, and 4.5 bar indicated mean effective pressure, IMEP) and three

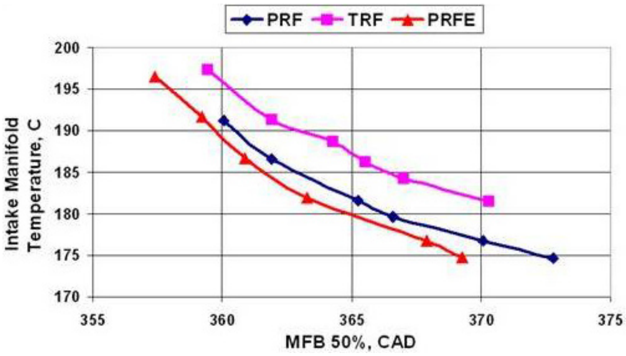

FIGURE 1. Combustion Phasing Characteristics of Gasoline Surrogates (PRF – Primary Reference Fuel; TRF – Toluene Reference Fuel; PRFE – TRF + 30 Vol% Ethanol; MFB – Mass Fuel Burned)

TABLE 1. Range of Emissions from Gasoline Surrogates

Method	Measurement	Range of Measurements		
		PRF	TRF	PRF + Ethanol
NDIR	CO (ppm)	600 - 1650	600 - 1650	550 - 2000
NDIR	CO_2 (%)	4.7 - 5.1	5 - 5.5	4.1 - 4.7
Chemiluminescence	NO_x (%)	5 - 65	5 - 70	5 - 35
FID	THC_1 (ppm)	2300 - 3850	3050 - 4650	2050 - 3800
Paramagnetic	O_2 (%)	13.4 - 14.0	13.7 - 14.3	14 - 14.9
AVL smoke meter	Smoke Number	0.02 - 0.05	0.02 - 0.06	0.02 - 0.04

NDIR - Non-dispersive infrared
FID - Flame Ionization Detecter
THC - Total hydrocarbons

levels of lambda (3.25, 2.75, and 2.4, controlled by intake throttling or boosting). Three combustion phasing points were run for each combination of fuel rate, lambda, and fuel and covered a range for MFB50 of about 5 deg before top dead center to 5 deg after top dead center. Measurements included gaseous emissions, smoke, particulate characterization by SMPS, and light HC and oxygenated HC species by FTIR. A limited number of transmission electron microscope (TEM) grids were also taken to further define particulate characteristics. In general, smoke increased with both fuel rate and IMEP and oxides of nitrogen (NOx) increases at higher IMEP, relating mainly to the rate of cylinder pressure rise. The hepta methyl nonane (HMN)/n-hexane fuel produced the highest smoke and the FACE fuel produced the least, although this result appears to mainly relate to intake temperatures required to achieve a selected combustion phasing. When plotted against intake temperature, smoke ranked (lowest to highest) HMN/n-hexane, alpha methyl naphthalene (AMN)/n-hexane, and FACE 9, as shown on Figure 2. In this graph, intake temperature variations result from fuel characteristics, fuel rate, and desired combustion phasing.

This HCCI engine produces significant amounts of oxidized HC emissions, mainly butadiene, formalydehyde, and acetaldehyde, with all three fuels being similar and increasing at retarded timing. Further details of emissions and engine performance are given in reference 5.

Particulates were examined with both dilute SMPS and TEM grids. Particulate count ranged from 10^6 to $5x10^8$ counts/cm^3 and showed weak trends of increasing with load and smoke. The full boiling range fuel, FACE 9, had a higher particle count than the two surrogate fuels, perhaps because of the higher boiling point range of the fuel. This engine operates with a nearly homogeneous charge and HC emissions arise mainly from wall quenching due to the low combustion temperatures. As such, the particulate is mainly volatile condensed HC rather that carbon-based chain agglomerates, as produced by a conventional diesel engine. Figure 3 shows TEM images of the particulate for several operating conditions. These images also show a progression of time in the TEM (vacuum and electron beam) from left to right which indicates evaporation and verifies the volatile nature of these particulate. The formation of these particulates no doubt begins in cooler portions of the combustion chamber and continues in the exhaust system and the mini dilution tunnel used for SMPS measurements and grid collection. There are differences in emissions between the fuels, but because our goal is to provide data for comparison to kinetic modeling, these will not be further explained here.

For comparison to kinetic modeling results, a simple five-zone model was used. The quench zone (zone 1) was set up to approximately match HC emissions and the core zone was set up to match ignition time and NOx, with zone details shown in Table 2.

The fuels were defined by the surrogate compounds used, and fuel air ratio was matched to experimental data. Intake temperature and wall temperature were also set based on experimental measurements and pressure at start of compression was adjusted to match total charge mass. There is a total of 51 data points

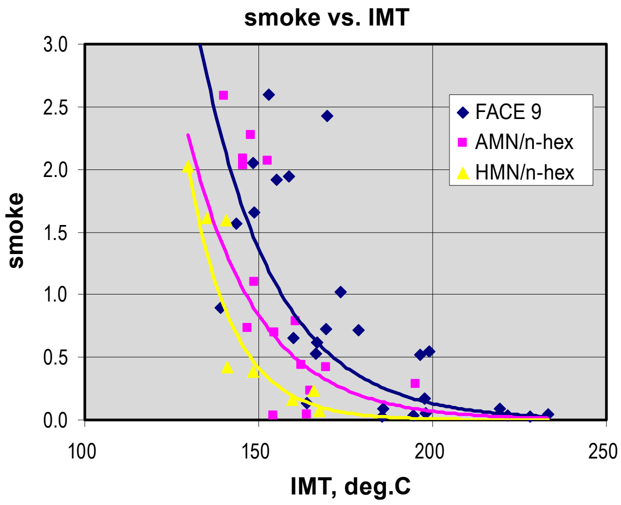

FIGURE 2. Smoke vs. Intake Temperature (IMT) for Diesel Fuel and Diesel Surrogates

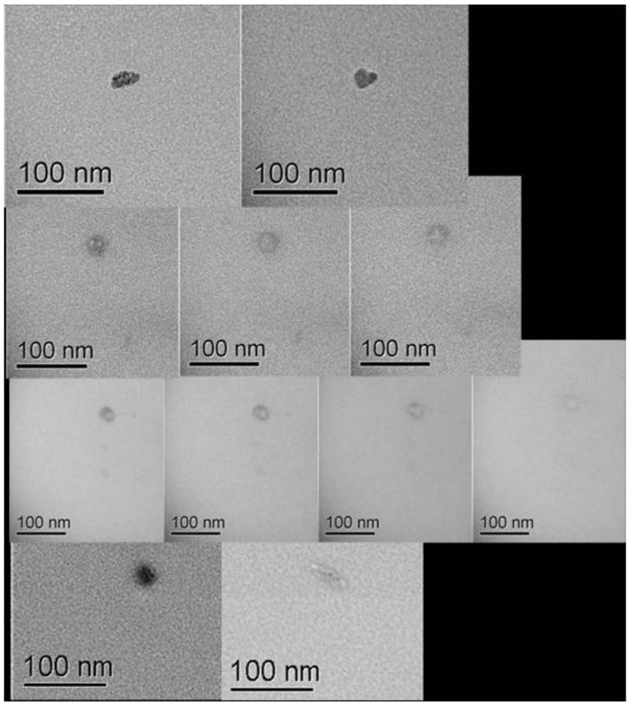

FIGURE 3. TEM Images of Exhaust Particulate Showing Non-Diesel Soot Characteristics and Volatility in Microscope

TABLE 2. Zone Setup for Multi-Zone Kinetic Model

ZONE	% MASS	% AREA
1	5	45
2	15	25
3	20	15
4	25	10
5	35	5

covering five fuels, three of gasoline range and two of diesel range. All were modeled using CHEMKIN MFC with the 2008 complete master mechanisms. Comparison between modeling and experiment is demonstrated by plotting modeled value vs. experimental value for various measurements. These results are shown in Figure 4 for cycle work, NOx, and MFB50.

Conclusions

In general, Chemkin did a fairly good job of modeling work and MFB50, except for one fuel and showed differences in NOx between fuels. HC, CO, and detailed HC species (not shown) were not successfully modeled. Based on detailed examination of the results, it appears that the main reason for differences is inability of a simple, fixed-zone model to mimic the mixing and quenching processes of the engine.

In 2010, similar experimental work to above, combined with re-analysis of existing data, will be completed. Modeling will be conducted using a Forte CFD model of the engine, which appears to be much more capable of reproducing detailed emissions effects. Emphasis will be placed on use of the surrogate blend optimizer to reproduce actual fuels, in verifying a wide range of surrogate blends, and in more particulate measurements for verification of the soot formation model. Some results will also be obtained from a real diesel engine, to study the formation of more normal diesel-like soot.

FY 2008/2009 Publications/Presentations

1. Bruce G. Bunting, Scott Eaton, Chitralkumar V. Naik, Karthik V. Puduppakkam, Chen-Pang Chou, and Ellen Meeks, A Comparison of HCCI Ignition Characteristics of Gasoline Fuels Using a Single-Zone Kinetic Model with a Five Component Surrogate Fuel, SAE paper 2008-01-2399.

2. Karthik Puduppakkam, Long Liang, Chitralkumar Niak, Ellen Meeks, and Bruce Bunting, Combustion and Emissions Modeling of a Gasoline HCCI Engine Using Model Fuels, SAE Paper 2009-01-0669.

3. Bunting, Eaton, and Crawford, Performance Evaluation and Optimization of Diesel Fuel Properties and Chemistry in an HCCI Engine, SAE Paper 2009-01-2645.

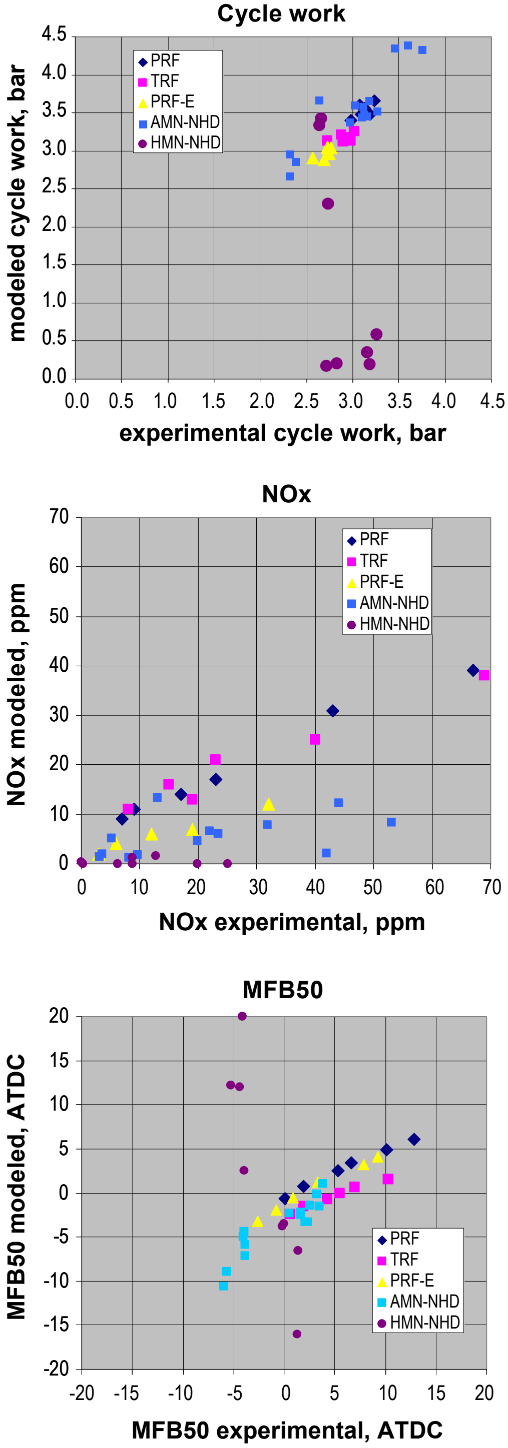

FIGURE 4. Match between Modeling and Experimental Values for Five Surrogate Fuels for Cycle Work, NOx, and MFB50

4. 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.

5. Bunting, Eaton, Storey, Lewis, Barone, and Connatser, Detailed HCCI Exhaust Speciation – ORNL Reference Fuel Blends, 2009 DOE DEER Conference, Dearborn, MI, August 3–6, 2009.

6. Bunting, Eaton, Taylor, Nguyen, Puduppakkam, and Meeks, A Comparison of HCCI Engine Performance Data and Kinetic Modeling Results over a Wide Range of Gasoline Range Surrogate Fuel Blends, 2009 DOE DEER Conference, Dearborn, MI, August 3–6, 2009.

IV. PETROLEUM DISPLACEMENT FUELS/ FUEL BLENDING COMPONENTS

IV.1 Biodiesel Performance with 2010 Diesel Engine Aftertreatment Technology

Aaron Williams (Primary Contact),
Robert L. McCormick, Matt Ratcliff,
Dan Pedersen, John Ireland,
Giovanni Cavataio*, Justin Ura*,
Howard Fang**
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd, MS1633
Golden, CO 80401
*Ford Motor Co.
**Cummins Inc.

DOE Technology Development Manager:
Kevin Stork

Other Participants:
- National Biodiesel Board
- Cummins Inc.
- Ford Motor Co.

Objectives

- The overall objective of this work is to understand how biodiesel will impact the performance and durability of 2010 diesel engine aftertreatment technology, which is necessary to meet the EPA's stringent oxides of nitrogen (NOx) emissions standards.
- The first specific goal of this work is to measure biodiesel's impact on variables which are critical to selective catalytic reduction (SCR) performance as well as biodiesel's impact on overall NOx reduction.
- A second goal of this work is to evaluate the potential for unburned biodiesel in the exhaust to adsorb onto the reaction sites of an SCR catalyst, thus hindering its ability to reduce NOx emissions.

Accomplishments

- A 2004 compliant Cummins ISB was retrofitted with a full aftertreatment system (diesel particulate filter [DPF]+SCR), representative of 2010 heavy-duty diesel engine aftertreatment technology.
- Engine testing at eight different engine modes was conducted to determine the impact of B20 on critical variables for SCR performance. On average the use of B20 increased the NO_2:NOx ratio by 3%, decreased the catalyst temperature by 11% and caused no change in the catalyst space velocity. These small changes from biodiesel had no impact on the overall NOx conversion ability of the SCR catalyst.
- Bench-scale studies conducted by Ford showed that the SCR catalyst adsorbs more hydrocarbons (HCs) from biodiesel (8.1 g/L) versus petroleum diesel (1.5 g/L). However, these tests revealed that the adsorbed diesel HCs begin to release from the catalyst at 400°C, whereas adsorbed biodiesel HCs begin to release at 200°C.
- Furthermore, engine tests indicate that, overall, the SCR system has a faster recovery from HC masking with biodiesel which is partially due to a reduction in exhaust HCs with the use of biodiesel.

Future Directions

- Additional testing is needed to understand the impact of biodiesel on Cu-zeolite based SCR catalysts. Unlike Fe-zeolite catalysts used in our research to date, Cu-zeolite is less susceptible to HC adsorption and will most likely be a leading technology used beyond 2010.
- Additional testing is also needed to understand how the alkali and alkaline metals found in biodiesel will impact aftertreatment systems through ash exposure.

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Introduction

In support of the U.S. Department of Energy Fuels Technologies Program Multiyear Program Plan goal of identifying fuels that can displace 5% of petroleum diesel by 2010, NREL, in collaboration with the National Biodiesel Board (NBB), Cummins, and Ford, performed testing of a DPF+SCR aftertreatment system. The objective of this work was to determine biodiesel's impact on the performance and durability of an Fe-zeolite SCR catalyst. Engine and bench-scale studies were designed to determine biodiesel's impact on NOx reduction and HC adsorption.

Approach

The first step of this study was to retrofit a 2004 emissions compliant Cummins ISB with a full aftertreatment system, including a DPF followed by an SCR catalyst. Urea injection for the SCR catalyst was properly tuned to achieve maximum NOx reduction. Testing was conducted in two phases. The first phase included measurement of biodiesel's impact on the key variables which impact the performance of an SCR catalyst. The temperature, space velocity, NO_2:NOx ratio and overall NOx conversion of the SCR catalyst was measured at eight steady-state engine modes. Comparisons were made between a petroleum-based ultra-low sulfur diesel (ULSD) and a soy-based B20 blend of biodiesel.

The second phase of testing included measurement of the adsorption of unburned HCs by the SCR catalyst and the subsequent impact on NOx conversion. This was achieved through engine testing, by operating at a low exhaust temperature condition long enough to allow the catalyst to adsorb unburned exhaust HCs. Following HC adsorption the engine was operated at higher temperature conditions while monitoring the NOx conversion of the SCR catalyst. Similar tests were conducted on a bench-scale reactor with more precise control over temperature conditions and HC exposure. Comparisons were made between a petroleum-based ULSD and a soy-based biodiesel.

Results

Testing at the eight steady-state engine modes revealed biodiesel's impact on variables known to influence SCR performance including; catalyst temperature, catalyst space velocity and the NO_2:NOx ratio. B20 resulted in an average 11% decrease in catalyst temperature, a 3% increase in NO_2:NOx ratio and did not change catalyst space velocity. Of these three variables, catalyst space velocity proved to be the dominant parameter effecting overall SCR performance. Thus with B20 having no impact on space velocity, the overall NOx conversion of the SCR system is unchanged with the use of B20. Figure 1 shows the NOx conversion achieved at each of the eight test modes with both ULSD and B20. On average ULSD had a 0.3% higher NOx conversion, a difference which is not statistically significant.

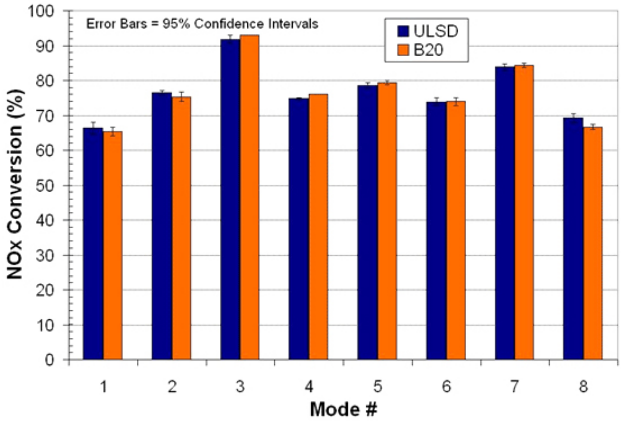

FIGURE 1. ULSD vs B20 NOx Conversion

Flow reactor experiments were conducted to show the potential for the SCR catalyst to adsorb unburned HCs in the exhaust. When exposure to unburned fuel occurs at higher temperatures (250°–400°C), the catalyst is able to adsorb a greater mass of HCs from biodiesel than of ULSD. In the worst case (400°C), the catalyst adsorbs 8.1g/L of HC from biodiesel compared to 1.5g/L of HC from ULSD. Flow reactor experiments indicate that for a catalyst free of HC exposure, NOx conversion begins between 100° and 200°C (see the clean catalyst data in Figures 2 and 3). Experiments show that when the catalyst is masked with ULSD, NOx conversion is inhibited until it is heated to 400°C (see Figure 2). However, when masked with biodiesel, NOx conversion is observed to begin at temperatures as low as 200°C (see Figure 3). Engine test results also show low-temperature recovery from HC storage with the use of biodiesel (see Figures 4 and 5). Engine tests indicate that, overall, the SCR system has a faster recovery from HC masking with biodiesel. This is at least partially due to a reduction in exhaust HCs, and thus total HC exposure with biodiesel.

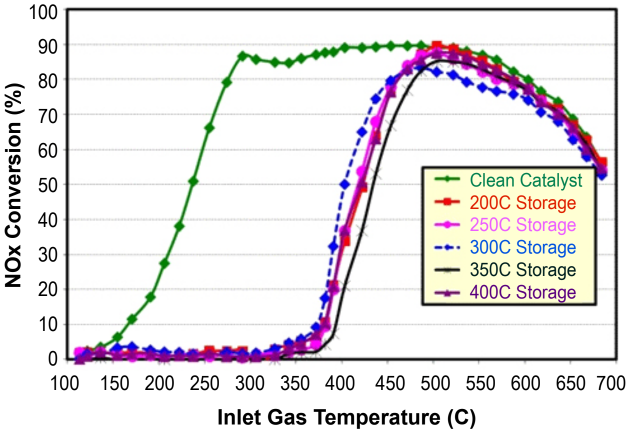

FIGURE 2. ULSD HC Mask

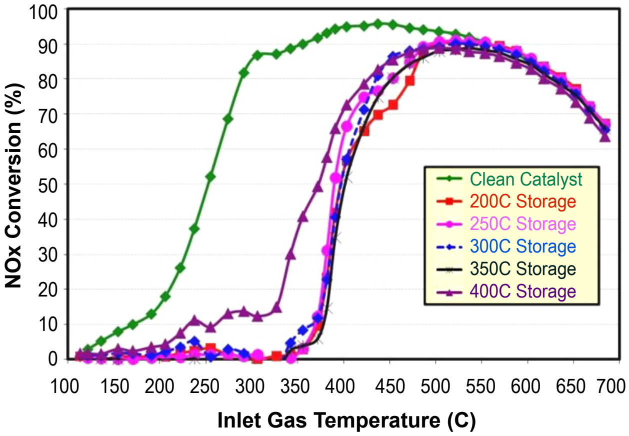

FIGURE 3. Biodiesel HC Mask

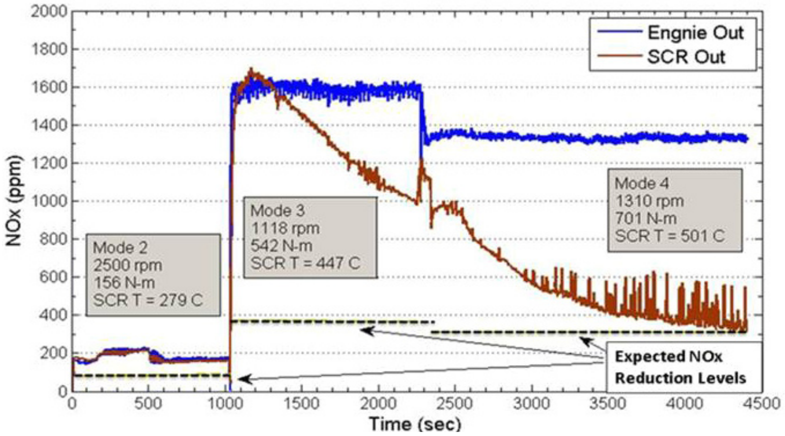

FIGURE 4. Engine Testing – ULSD HC Mask

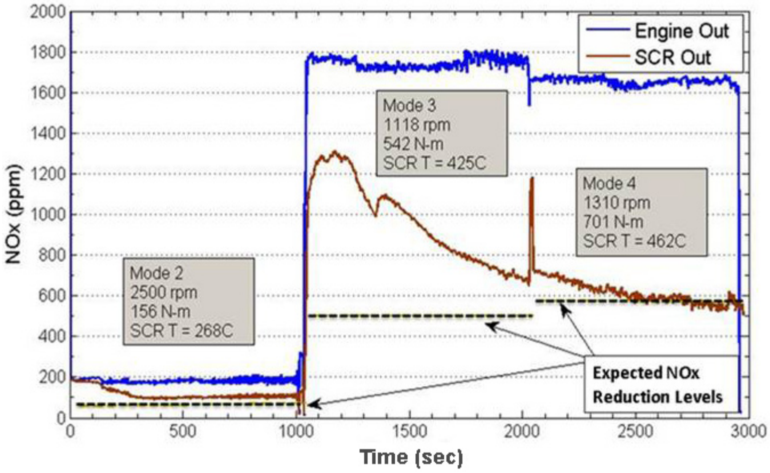

FIGURE 5. Engine Testing – Biodiesel HC Mask

Conclusions

- Compared to ULSD, the use of a B20 leads to a slight increase in the NO_2:NOx ratio, a slight decrease in SCR catalyst temperatures and no change in catalyst space velocity. These small changes did not lead to a change in the overall NOx reduction capability of the SCR catalyst.
- Bench-scale studies conducted by Ford showed that the SCR catalyst adsorbs more HCs from biodiesel (8.1 g/L) versus petroleum diesel (1.5 g/L).
- Bench-scale tests also revealed that the adsorbed diesel HCs begin to release from the catalyst at 400°C, whereas adsorbed biodiesel HCs begin to release at 200°C.
- Furthermore, engine tests indicate that, overall, the SCR system has a faster recovery from HC masking with biodiesel which is partially due to a reduction in exhaust HCs with the use of biodiesel.

FY 2008/2009 Publications/Presentations

Publications

1. Aaron Williams, Robert L. McCormick, Dan Pedersen, John Ireland and Howard Fang. "Effect of Biodiesel Blends on Urea Selective Catalytic Reduction Performance with a Medium Duty Engine" SAE Techn. Pap. No. 2008-01-2484.

2. Aaron Williams, Robert L. McCormick, Matt Ratcliff, Dan Pedersen, Giovanni Cavataio and Justin Ura. "Effect of Unburned Methyl Esters on the NOx Conversion of an Fe-zeolite SCR Catalyst" *SAE Techn. Pap. No.* 2009-01-2777.

Presentations

1. National Biodiesel Conference and Exp. Orlando, FL. February 4, 2008.

2. Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop. Dearborn, MI. May 13, 2008.

3. SAE Powertrain, Fuels and Lubricants Meeting. Chicago, IL. October 6, 2008.

4. NBB Technical Workshop. New Orleans, LA. October 21, 2008.

5. National Biodiesel Conference and Expo. San Francisco, CA. February 2, 2009.

6. Directions in Engine Efficiency and Emissions Reduction (DEER). Dearborn, MI. August 3, 2009.

7. SAE Powertrain, Fuels and Lubricants Meeting. San Antonio, TX. November 4, 2009.

8. AOCS 2nd International Congress on Biodiesel. Munich, Germany. November 16, 2009.

IV.2 Biofuels Quality Surveys in 2008 and 2009

Teresa L. Alleman (Primary Contact),
Robert L. McCormick
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd., MS1634
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
Southwest Research Institute®, San Antonio, TX

Objectives

- Conduct and report on B20 quality in the United States (U.S.) in 2008.
- In collaboration with Coordinating Research Council (CRC), assess U.S. flexible-fuel vehicle (FFV) fuel quality in 2008/2009.

Accomplishments

- Completed and reported on B20 survey.
- Published NREL-CRC collaborative report on E85 quality.

Future Directions

- Conduct additional B6-B20 survey in the U.S. comparing samples against ASTM D7467 specification.
- Continue collaboration with CRC to conduct another FFV fuel survey in 2010.
- Build on CRC collaboration to sample ethanol blender pumps that dispense lower ethanol content fuels for FFVs.

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Introduction

The utilization of biofuels is dependent on many factors, including fuel production, quality, and availability to the consumer. This report will focus on the key question of biofuel quality. As the biofuel market continues to expand, there must be fit-for-purpose and ideally use must be transparent to the public. A portion of the public may suffer through growing pains as biofuels go from niche markets to widespread distribution, but a majority expects a completely fungible product.

The goal of this work is to take a snapshot of the biofuel markets in the U.S. to understand if these fuels are meeting the quality expectations set through specifications by ASTM International. Currently, only biodiesel (sold as a blended fuel termed Bxx, where xx is the volume percentage of biodiesel) and FFV fuel (sometimes referred to as E85, a blend of 70% to 83% by volume ethanol with gasoline) are commercially available in appreciable quantities. These biofuels were sampled across the U.S. and quality was compared to the respective quality specifications in 2008 and 2009.

Approach

In each survey, Southwest Research Institute® visited station locations distributing the appropriate fuel. Each survey was an independent effort, though methodology was similar.

The B20 samples were collected in the summer of 2008. The contractor visited public B20 stations and a small number of centrally-refueled fleets. The samples were then tested using ASTM methods for critical properties that would impact engine operability. The survey was conducted prior to the adoption of D7467, the specification for B6-B20 fuels, so the samples could not be termed "on-specification" or "off-specification". The fuels were tested for key properties of interest, outlined in Table 1.

The FFV fuel survey was conducted in four campaigns throughout 2008 and 2009. The properties specified in ASTM D5798 vary with geographic location and ambient conditions and are separated into three distinct classes, with the ethanol content and vapor pressure changing with class (Table 2). The survey goal was to collect 50 samples in each of these three seasons. A secondary sampling (10 samples) of Class 1 fuels was conducted in the summer of 2009. The fuels were analyzed for select properties (Table 3).

Results

B20 Survey

Thirty-two B20 samples were collected around the U.S. in 2008. Seven samples were collected from fleets using B20, while the remaining 25 samples came from public pumps. The results have been presented in Table 1, alongside the specification limit in D7467. The samples were collected prior to the adoption of D7467 and did not have to meet the specification at the time

TABLE 1. B20 Survey Test Methods

Property, Units	Test Method, ASTM unless otherwise noted	D7467-08 Specification	Average*	Percent that would fail D7467 specification
Acid number, mgKOH/g, max	D664	0.3	0.08	5%
Flash point, °C, min	D93	52[a]	138	0%
Cloud point, °C	D2500	Report[b]	-12	NA
Sulfur, ppm, max	D5453	15[c]	7.4	5%
Cetane number, min	D613	40	48	0%
Biodiesel content, vol%	D7371	6.-20.	19.8	0%
Oxidation stability, h, min	EN14112	6	8.4	31%
Group I and II metals, ppm	D7111	No Limit	0.5	NA
Karl Fisher, ppm	D6304	No Limit	130	NA
Particulate contamination, mg/L	D6321 or D7321	No Limit	6.3 on D6321 14.2 on D7321**	NA
Interfacial tension, mN/m	D971	No Limit	12.3	NA
Free and total glycerin, mass%	In-house method	No Limit	0.002 free glycerin*** 0.101 on total glycerin***	NA

* Average determined only from samples that are nominally B20.
** Fewer samples were tested on D7321 and average is influenced by one outlier with a value of 75 mg/L.
*** Extrapolated to B100.
[a] If No.1 diesel fuel is used in the blend or a cloud point of less than -12°C is specified, the flash point minimum is 38°C.
[b] Cloud point is based on operability limits and time of year where the blend will be used.
[c] All samples were on-road and must meet the 15-ppm maximum sulfur limit.
NA - not applicable

TABLE 2. Seasonal Requirements for the Three Grades of FFV Fuel Specified in ASTM D5798-08

Property	Class 1	Class 2	Class 3
Ethanol content, vol %	79-83	74-83	70-83
Vapor pressure, psi	5.5-8.5	7.0-9.5	9.5-12.0
Sulfur, ppm, maximum	210	260	300

of the survey. However, the percentage of samples that would fail to meet the specification is presented.

Sixty percent of the samples were nominally B20, defined as 18 vol% to 22 vol% biodiesel. Only two samples contained excess biodiesel content, with the remaining samples having lower biodiesel contents, typically B10, B5, and B2.

The induction period stability and acid value of biodiesel and biodiesel blends are key parameters used to gauge quality. Twenty-five percent of the samples failed to meet the then-proposed 6-hour minimum for induction period stability, though the overall average was 8.4 hours (Table 1). It is well documented that the induction period stability drops as fuel ages [1]. The fuel “freshness” also impacts the acid value. In this study, every sample but one met the proposed acid value specification of 0.3 mgKOH/g. Previous B100 survey work has shown similar compliance with these specifications [2].

One of the goals of this survey is to provide data on properties not included in the blend specification but still relevant for fuel performance. The current B6-B20 specification has a combined free water and sediment requirement. Previous surveys have shown that this method does not discriminate sufficiently to yield useful information about the quality of biodiesel and biodiesel blends. Karl Fisher water content and particulate contamination have recently been suggested as more discriminatory methods for biodiesel and biodiesel blends. The Karl Fisher water content of B100 is between 1,200 and 1,500 ppm [3], while diesel fuel is between 50 and 100 ppm [4]. This work has shown that the average Karl Fisher water for B20 is 130 ppm, about 30% higher than diesel fuel. Typically, particulate contamination is low for these fuels, with only two samples having greater than the 10 mg/L cited as acceptable by the engine manufacturers [5].

FFV Fuel Survey

FFV fuel is typically known as E85, although the ethanol content can range from 70 to 83 vol% depending upon season and location. Fuel quality is specified under ASTM D5798. The specifications, including

TABLE 3. ASTM D5798-07 Specification Limits and Average E85 Results, Except Where Noted

Property	ASTM Method	Notes	Specification	Average
Ethanol and methanol, vol%	D5501	All samples	See Table 2	See Table 4
Dissolved water, mass%	D6304	All samples	1.0 max	0.590
Vapor pressure, psi	D5191	All samples	See Table 2	See Table 4
Sulfur, ppm	D5453	All samples	See Table 2	8.61
Washed gums, mg/100mL	D381	All samples	5 max	0.605
Unwashed gums, mg/100 mL	D381	All Samples	20 max	3.80
pHe	D6423	All samples	6.5-9.0	7.70
Inorganic chloride, ppm	D7328	All samples	1	0.245
Inorganic sulfate, ppm	D7328	All samples	No Limit	0.821
Appearance	D5798	All samples	Clear and Bright	Clear and Bright
T90 Distillation, °C	D86	Select samples	No Limit	80.7
Density/API Gravity	D4052	Select samples	No Limit	0.780
NACE corrosion	TM0172-2001	Select samples	No Limit	A
RON/MON	D2699/D2700	Select samples	No Limit	101/90
Peroxides, ppm	D3703	Select samples	No Limit	0.93
Oxidation stability, min	D525	Select samples	No Limit	1440
Silver corrosion	D4814 Annex	Select samples	No Limit	0

seasonal variations are given in Table 2. The goal of this project was to collect 50 samples in each of the three distinct classes, with 10 additional samples collected in the 2009 Class 1 season. Overall, these samples were off-specification for containing excess ethanol and having low vapor pressure (Table 4). The difficulty meeting the vapor pressure specification, especially in Class 3, has recently been cited by Marathon Petroleum Company in their decision to halt FFV fuel sales [6]. Beyond the ethanol content and vapor pressure, these samples readily met the other specifications. The acidity specification was most often not met in this survey, although the failure rate was only 5%.

TABLE 4. Vapor Pressure and Ethanol Content Compliance with D5798-07

		Vapor Pressure			**Ethanol Content**		
D5798 Class	**# of Samples**	**Below Minimum, %**	**Above Maximum, %**	**On Specification, %**	**Below Minimum, %**	**Above Maximum, %**	**On Specification, %**
1 (2008)	47	53.2	0	46.8	4.3	89.4	6.3
1 (2009)	10	90.0	0	10.0	10.0	10.0	80.0
1 (All Data)	57	60.0	0	40.0	5.3	66.7	28.0
2	26	61.5	7.7	30.8	3.8	38.5	57.7
3	40	87.5	0.4	12.1	12.0	5.0	83.0
All	*123*	*73.1*	*0.7*	*26.2*	*7.5*	*35.7*	*56.8*

Conclusions

- In 2008, the quality of B20 was sampled nationwide, prior to the publication of ASTM D7467, the specification for B6 to B20 blends. An issue with pump labeling may have existed at this time as 60% of the samples were nominally 20 vol% biodiesel content, with the majority having lower biodiesel content. The main issue noted with these samples is that 25% would not have met the D7467 requirement for oxidation stability.
- The quality of FFV fuel was sampled in 2008 and 2009 across the U.S. in collaboration with CRC. Regardless of volatility class, the E85 samples had low vapor pressure and excess ethanol content. Failure rates for other properties were very low.

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IV.3 Advanced Test Methods for Biofuels

Teresa L. Alleman (Primary Contact),
Gina Chupka, Robert L. McCormick,
Casey McAlpin*, Kent Voorhees*
National Renewable Energy Laboratory (NREL)
1617 Cole Boulevard
Golden, CO 80401
*Colorado School of Mines
1500 Illinois Street
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Objectives

To develop and validate robust test methods to characterize the trace components in biofuels and biofuel blends.

Accomplishments

- Validated and applied a new ion chromatographic method to measure the amount of free and bound glycerin in biodiesel and biodiesel blends.
- Implemented a high performance liquid chromatographic (HPLC) method to determine the composition and trace components of biodiesel.
- Developed a robust matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) technique to allow rapid and complete analysis of the trace components in biodiesel.

Future Directions

- Expand HPLC capability for analysis of impurities in biodiesel and other biofuels, more fully develop these chromatographic methods to reduce run times, improve separation, and reduce detection limits.
- Apply MALDI-TOF MS technique to investigate the nature of precipitates above the cloud point in biodiesel samples.
- Modify methods for applicability to advanced biofuels such as cellulosic ethanol, biobutanol, and non-fatty acid methyl ester (FAME) biomass based diesel.

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Introduction

New fuels can contain minor components that are not present in conventional fuels, and for which there are no established methods of chemical analysis. These impurities can, in some cases, cause significant issues with fuel handling or vehicle operability. In Fiscal Years 2008-2009 the focus was on some specific issues for biodiesel. One of the largest technical barriers facing biodiesel utilization is the impact of trace components on performance in cold weather. Several groups have recently reported dispenser and vehicle fuel filter clogging issues related to impurities, and possibly caused by monoglycerides precipitating from biodiesel blends [1,2]. Unfortunately the ASTM method for glycerides is currently limited to neat biodiesel (B100) and is extremely sensitive to the presence of diesel fuel so new methods need to be explored. Other impurities such as steryl glucosides have also been shown to affect biodiesel low-temperature performance.

In a vast majority of field issues, the parent fuels are not available for analysis. Thus, there was a practical limit to the information available when field problems occurred. The new ion chromatography technique allows for better diagnostic of glycerides in biodiesel blends without the need for the parent fuels.

The technical literature has multiple examples for trace component analysis in biodiesel using techniques as varied as gas chromatography (GC), HPLC, nuclear magnetic resonance spectroscopy (NMR), and Fourier Transform Infrared Spectroscopy (FTIR) [3]. There is little consensus on the best method to analyze these components.

To analyze biodiesel for steryl glucosides, as well as for individual glycerides and other components, an HPLC method was developed. A method originally developed by the United States Department of Agriculture (USDA) was used as a starting point, which can be found in Reference 4. The method provides excellent separation of multiple species in biodiesel in a single chromatogram. The technique can be applied to fuels, laboratory-created filter extracts, or material found in the field in plugged filters.

Mass spectrometry has most often been used as a detector on traditional chromatographic methods. Advanced mass spectrometric techniques, while commonly used for lipids and other complex systems, have rarely been applied to biodiesel. The applicability of advanced mass spectrometry to analyze trace components in biodiesel was examined. The MALDI-TOF approach eliminates the chromatographic interface, allowing a wide variety of samples to be analyzed without solvent or background effects and eliminating the need for complex chromatographic separations.

Approach

Through its parallel 20% biodiesel (B20) survey work in 2008, NREL was able to provide a wide variety of real-world samples to validate the robustness of the ion chromatography method. The free glycerin in Bxx blends is extracted using water and analyzed directly on the ion chromatograph. The total glycerin must first be converted into free glycerin in a separate step prior to analysis.

The USDA method provides a single method to analyze sterols, glycerides, glucosides, FAME, and free fatty acids. The first step was to purchase pure components and validate the method at NREL. Next, the HPLC method was optimized to improve the chromatography, minimize solvent use, and decrease analysis time. Filters collected during cold-soak filtration testing were extracted and analyzed using this HPLC method.

The difficulty with volatilizing components in biodiesel led to the development of a MALDI-TOF MS method. Several pathways were explored, in particular the literature showed the efficacy of using different matrices for analyzing the various lipids [5,6,7]. By combining these matrices in equimolar ratios, the wide range of components thought to be in biodiesel can be analyzed. Pure component mixtures were analyzed for proof-of-concept. In MALDI-TOF MS, a range of adducts are observed, making compound identification more difficult. These adducts form through the ionization pathway and can include sodium adducts ($M+Na^+$), potassium adducts ($M+K^+$), and hydrogen adducts ($M+H^+$). The use of sodium iodide has been shown to enhance the formation of sodium adducts, making compound identification easier [8]. Adding 10 mM NaI to the ionization matrix increased the sodiated ions in this experiment and aided in positive identification of the compounds from the mixture (Figure 1).

The MALDI-TOF MS technique was successfully applied to three various palm-derived B100s and illustrated the differences between these samples.

Results

The robustness of the ion chromatography method was demonstrated using samples collected under NREL's 2008 B20 survey [9]. The free and total glycerin of these samples were measured and reported (Figure 2). Using the blend content, measured by ASTM D7371, the glycerin of the parent B100 was extrapolated. The results from the samples collected show that in 2008, the B100 used to make the B20 blends met the glycerin specification. The low level of glycerin failures is similar to what was observed in NREL's 2007 B100 survey [10].

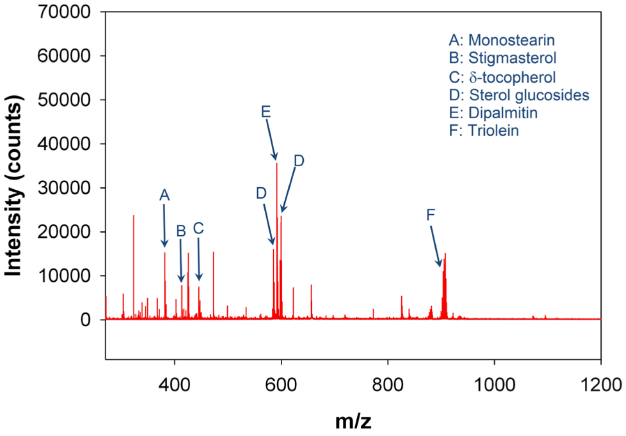

FIGURE 1. Standard mixture of biodiesel components analyzed through MALDI-TOF MS using mixed matrix and NaI doping.

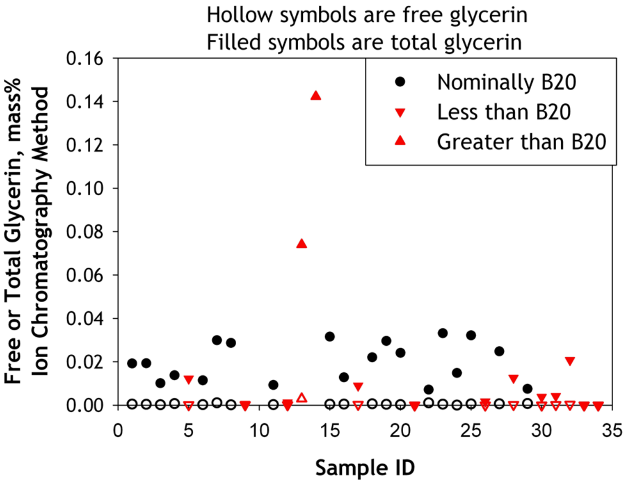

FIGURE 2. Free and total glycerin of the 2008 B20 survey blends as measured by ion chromatography.

The method is currently being balloted to become an ASTM method. At the current time, there is no intent to add a glycerin specification to the B6-B20 specification (D7467); the method can be extremely useful for diagnostic purposes when problems occur in blended fuels. In these scenarios, the parent B100 and diesel fuel are almost never available and methods to characterize the key properties from these blends are critical.

HPLC can be used to give a broader picture of the components of biodiesel, and in particular to quantify sterol glucosides content. Both trace components and composition of the FAME can be measured using one method. HPLC also eliminates the need to derivatize samples prior to analysis, as is required in some GC methods for trace components. Most often the trace components in biodiesel are non-volatile making GC a less efficient method for this type of analysis. An example chromatogram from the HPLC showing the different types of components that can be analyzed using this method is shown in Figure 3.

The HPLC technique was used to analyze the compounds present in the solids captured on filters during the cold-soak filtration test. The cold-soak test was introduced into D6751 to identify potential problems with cold weather operability in B100s. The collected filters were extracted by different solvents in increasing polarity (heptane, 9:1 chloroform/methanol, and pyridine). The technique showed some differences between the extracts, although the major component found was FAME.

To validate the MALDI-TOF MS technique on real-world systems, three palm biodiesels were analyzed. The B100s met the D6751 specification, but were produced using widely different processes. The first sample was distilled to remove as many non-FAME components as possible. The second sample had average quality and the third sample was barely on specification. Figure 4 shows the substantial differences in trace components between these fuels. The spectrum of the distilled fuel is lacking peaks, showing the distillation was highly effective at removing non-FAME components. The average palm showed some glyceride species (monoglycerides, average m/z ca. 258 g/mol, diglyceride species with average m/z ca. 625 g/mol), which is typical of non-distilled B100. The final palm biodiesel showed significant peaks in the mono- and di-glyceride regions, indicating the highest percentage of non-FAME components of the samples. The analysis of these real world samples demonstrates the applicability of this method to biodiesel analysis.

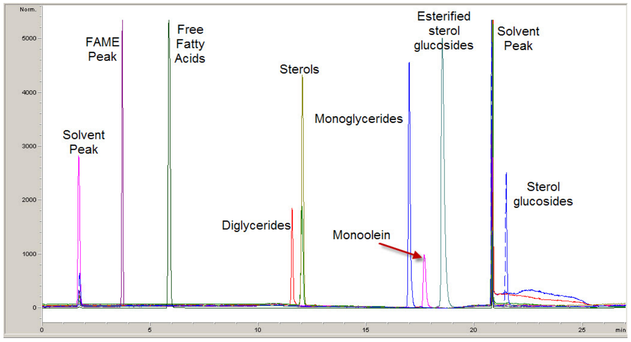

FIGURE 3. Chromatogram using the USDA HPLC method for a multi-component standard mixture.

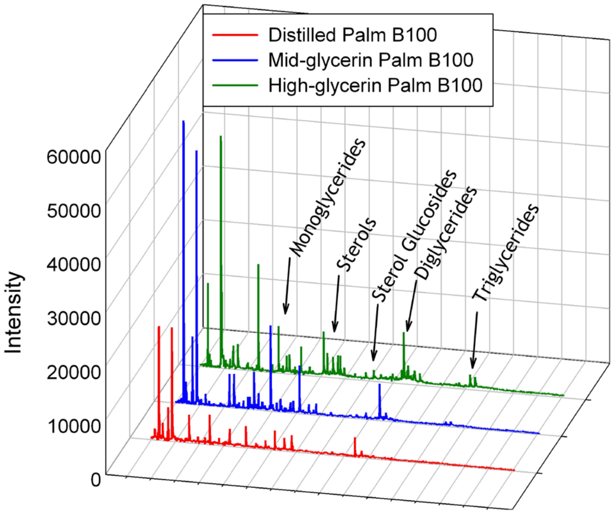

FIGURE 4. Comparison of trace components in three palm-derived biodiesel samples using mixed-matrix and NaI-doping in MALDI-TOF MS.

Both the HPLC and MALDI-TOF MS methods will be applied to future work to determine the root cause of cold-weather problems with biofuels. Once key compounds are identified, a dose response study will be conducted to prove cause and effect.

Conclusions

The ability of biofuels to become near-fungible in the current fuels infrastructure is a key barrier to increased utilization. Recently, low-temperature operability issues have impacted biodiesel blend utilization significantly. This problem is particularly difficult to overcome as no single root cause has been identified, partly due to the lack of robust analytical test methodology. NREL has validated and applied several new analytical techniques to help quantitatively understand the cold-weather operability of biodiesel blends. These methods are briefly summarized as follows.

- Ion chromatography method for glycerin determination in Bxx blends: this method is critical to understanding real world Bxx blend fuel quality.
- HPLC method to analyze trace components in B100 and Bxx blends: a deeper understanding of the chemical composition of trace components can be achieved.
- MALDI-TOF MS provides a research based tool to rapidly screen fuels for trace components.

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IV.4 Evaluation of B20 Usage in the St. Louis Transit Bus Fleet

Mike Lammert (Primary Contact),
Robb Barnitt, Robert McCormick
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd.
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Objectives

- Evaluate the extended in-use performance of B20 fuel at the St. Louis Metro transit fleet.
- Document fuel economy, maintenance costs, reliability, fuel quality, and lube oil performance.
- Quantify differences due to B20 fuel use.

Accomplishments

- Completed 18-month evaluation of 15 transit buses with eight operating on B20 and seven operating on diesel fuel.
- Successfully analyzed fuel consumption and maintenance data, showing no significant different in fuel economy or in engine/fuel system maintenance costs.
- Showed that fuel injector failures correlated to engine miles not fuel consumed.

Future Directions

No additional work is planned with buses or other vehicles of this vintage. Future studies will focus on B20 performance with 2007 and later model year systems using advanced emission controls.

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Introduction

The Fleet Test and Evaluation and Non-Petroleum-Based Fuels teams worked with the National Biodiesel Board and St. Louis Metro (Metro) to test and evaluate the extended in-use performance of B20 in transit buses. Fifteen 40-foot, model year 2002 transit buses manufactured by Gillig and equipped with Cummins ISM engines were evaluated in this project; eight operated on B20, while seven ran on ultra-low sulfur diesel (USLD).

Approach

The B20-fueled study buses are driven on the 11 Chippewa route out of the Brentwood garage, while the ULSD-fueled study buses are operated on the 32 Wellston route from the Debaliveire garage. Average speed is an accurate representation of real-world driving severity and was therefore the defining metric in selecting these two routes for comparison. Rack-blended (in-line proportional blending) B20 was delivered to Brentwood by Hartford Wood River Terminal. ULSD was delivered to Debaliveire by Energy Petroleum. Each bus is scheduled to fuel every other day. As the bus enters the fueling island area, a radio frequency connection is established between the bus, the fueling dispenser, and Metro's M5 electronic database. The bus is recognized, and the odometer reading, fueling volume, and lube oil requirements are uploaded to the database. These fueling records were transferred to NREL for evaluation and analysis.

For the purposes of this analysis, data received from Metro indicating that a road call (RC) occurred was recorded as such, regardless of its relative severity. Maintenance events in the form of labor hours and parts costs are captured electronically by M5 and were submitted to NREL, where they were reviewed for accuracy and analyzed for a maintenance cost per mile comparison of the B20 and diesel groups. Maintenance cost per mile figures were calculated for specific vehicle subsystems that could be impacted by B20 fuel use.

Results

BUS USE - The overall 18-month average monthly miles per bus for the B20 buses was about 3.7% higher than for the ULSD buses at Debaliveire. Based on a two-tailed, paired t-test, the difference between the two groups is not statistically significant with a high degree of confidence ($P = 0.13$). The average mileage accumulated per bus during the study is also very similar for the two groups. The average usage of the buses declined slightly during the evaluation period, in which the B20 and ULSD study bus groups accumulated 590,042 and 497,654 miles, respectively.

FUEL ECONOMY - The calculated 18-month average fuel economy for the B20 buses is 1.5% lower than that of the ULSD buses. This difference is expected because of the approximately 2% lower energy content in a gallon of B20; however, based on a two-tailed, paired t-test, the difference between the two groups is not statistically significant with a high degree of confidence ($P = 0.2$).

VEHICLE RELIABILITY ANALYSIS - Figure 1 shows the cumulative miles between road calls (MBRC) for all RCs for the ULSD and B20 groups. Average MBRC values over the evaluation period were 2,690 and 2,694 for ULSD and B20 groups, respectively, a difference that is not statistically significant based a two-tailed, paired t-test (P = 0.95). In addition, reliability as measured in MBRCs is assessed for the engine and fuel systems. Figure 2 shows the cumulative MBRC for all engine and fuel system RCs for the ULSD and B20 groups. The ULSD group had a three-month run of exceptionally high MBRC numbers, creating a spike, but that was followed by a few months of a high number of road calls that dragged the cumulative average below that of the B20 group for seven months. For the last four months of the 18-month evaluation, the B20 buses and ULSD buses were comparable, with cumulative engine and fuel system MBRC values of 8,435 and 8,310 for the ULSD and B20 groups, respectively, at the end of the evaluation period. Based on a two-tailed, paired t-test, this difference is not significant (P = 0.8).

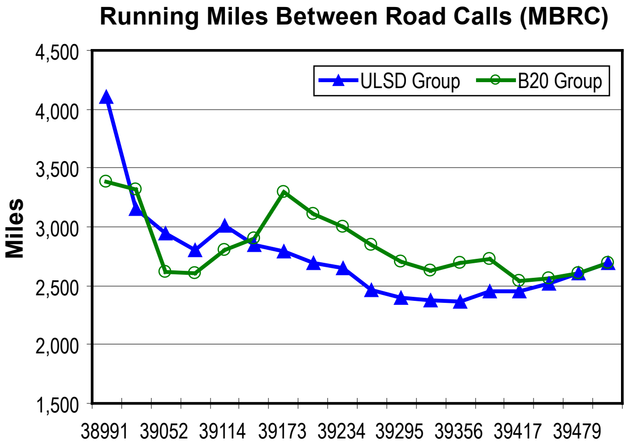

FIGURE 1. Cumulative MBRCs

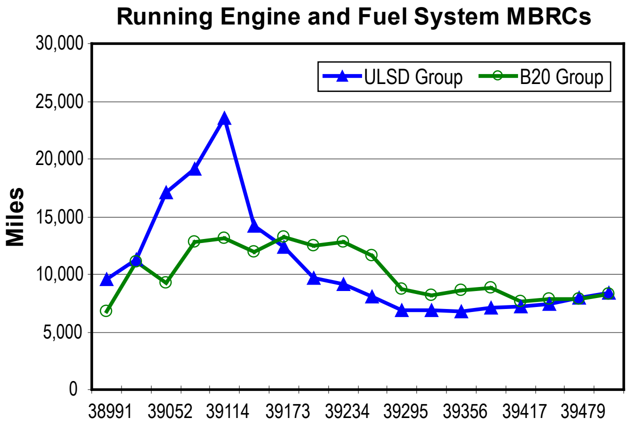

FIGURE 2. Cumulative MBRCs, Engine and Fuel System

MAINTENANCE COST ANALYSIS - The total maintenance cost includes the cost of parts and assumes an hourly labor cost of $50 per hour, but it does not include warranty costs. The labor rate has been arbitrarily set at a constant rate of $50 per hour which does not directly reflect Metro's current hourly mechanic rate.

The monthly and running average of maintenance costs for the diesel and B20 groups are compared in Figure 3. The total maintenance cost per mile was 4.4% higher for the B20 buses than for the ULSD buses ($0.027/mile higher), a difference that is not significant based on a two-tailed, paired t-test (P = 0.48). Maintenance costs are initially higher for the B20 group, but ultimately they gain parity with the diesel group by the ninth month of the evaluation. Parity is maintained for the remaining nine months despite increased volatility in the monthly data.

Bus maintenance costs related to the engine and fuel system during the evaluation period make up only 4% to 5% of the total maintenance costs. The engine and fuel system maintenance cost per mile was $0.03/mile higher, or about 50%, for the B20 (P = 0.03 based on a paired t-test). Engine- and fuel system-related maintenance was not a significant driver of the total maintenance cost, but it does appear to be the primary difference between the groups. Fuel filters are replaced at 6,000-mile intervals, but Metro changed B20 bus fuel filters every 2,000 miles for the first two months to avoid RCs caused by fuel filter plugging. This is a common practice for fleets beginning to use B20. The B20 group also used more filters during unusual winter cold snaps when the outside temperature dropped below the cloud point of the fuel. The diesel group did not experience this issue. Neither group experienced fuel pump failures. The B20 group experienced more fuel injector failures, but they relate to bus mileage rather than to the fuel used as explained below.

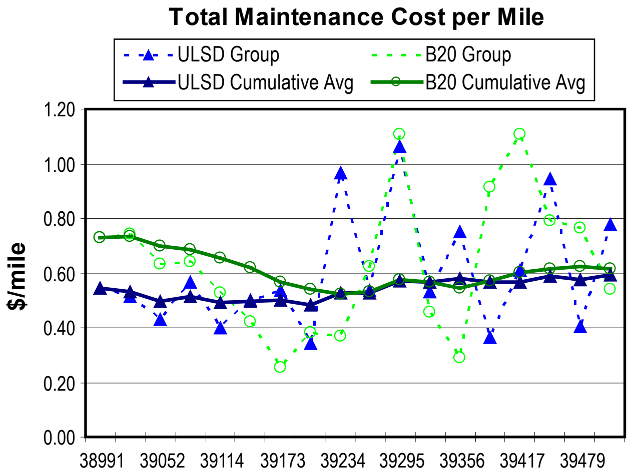

FIGURE 3. Total Maintenance Costs

One way to compare the populations is to consider the lifetime fuel injector failures rather than just the 18-month study period on B20 and see if the populations are different. Figure 4 shows a comparison of cumulative injector failures for each bus group at given mileages from new through March 2009. The groups had a comparable rate of failures through 200,000 miles which confirms that the fuel injector failures correlate to bus miles rather than exposure to a specific fuel. The injector failure events below 200,000 miles were compared and found to be not significant, based on a two-tailed, paired t-test (P = 0.3). The corrected B20 series has been multiplied by 7/8 to better compare with the seven buses of the ULSD group. Even uncorrected, the B20 group had fewer injector failures at 200,000 miles than the ULSD group did. Based on these considerations that fuel injector failures relate to higher bus miles rather than to B20 fuel, there is not a significant difference between the two bus groups in maintenance costs for the engine and fuel system.

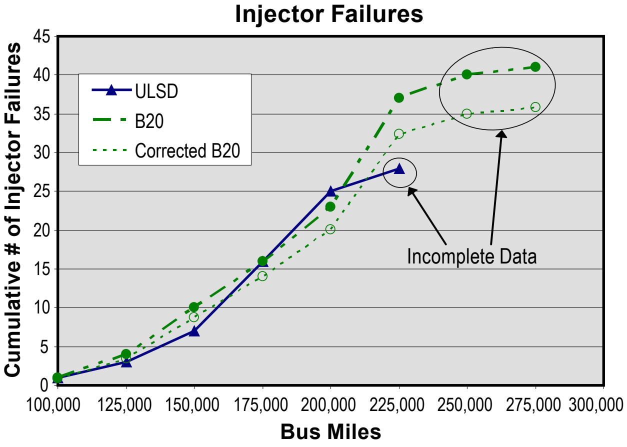

FIGURE 4. Fuel Injector Failure Mileages

Conclusions

In comparison to buses running on ULSD, the following observations can be made for buses running on B20:

- No statistical difference in fuel economy. With similar usage and duty cycle, the B20 study group exhibited a 1.5% lower fuel economy than the ULSD study group did. However, the difference is considered to be not statistically significant (P = 0.19).
- No statistical difference in MBRC or engine and fuel system MBRC. The reliability of the B20 study group was similar (as measured in MBRC) to that of the ULSD study group.
- No statistical difference in total maintenance cost per mile between the two study groups.
- Engine- and fuel-system-related maintenance was the same for the two groups after we corrected the ULSD group data to equivalent mileage.
- The B20 study group had a higher number of fuel filter replacements because of low-temperature operability problems caused by unseasonably low temperatures. Operators of fleets fueled with B20 need to be aware of the potential for low-temperature operability problems to be more severe for B20 during unseasonable weather.
- Lube oil analysis indicates reduced soot loading and wear metals for B20. Viscosity decay and lead corrosion was increased for B20, and there was no difference in total base number deterioration.

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IV.5 Ensuring Biodiesel Blend Low-Temperature Performance

Robert L. McCormick (Primary Contact) and
Teresa L. Alleman
National Renewable Energy Laboratory (NREL)
1617 Cole Boulevard
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
Imperial Oil Company, Sarnia, Ontario

Funding partners:
- Engine Manufacturers Association
- National Biodiesel Board

Objectives

- Evaluate cloud point (CP), cold filter plugging point (CFPP), and low temperature flow test (LTFT) and actual heavy-duty (HD) vehicle performance at low temperatures for biodiesel blends.
- Validate that the cold soak filtration test (CSFT) is able to identify biodiesel that, in blends up to B20, causes fuel filter plugging at temperatures above the CP.

Accomplishments

- Four B100 fuels were tested as B5 and B20 blends in three Class 8 trucks, each believed to represent approximately 30% of the North American Class 8 market. For each fuel/truck combination, we experimentally determined a minimum operating temperature. These results were compared to the predicted operability limit based on CP, CFPP, and LTFT.
- Three of the B100 fuels exhibited an average CSFT of less than 200 seconds, while the fourth had a CSFT >720 seconds. This study showed that high CSFT B100 can cause low-temperature operability problems at temperatures above the CP for B20 blends.
- On average for all fuels combined, CP was a conservative predictor of operability limit by about 1°C. CFPP tends to predict an operability limit higher than CP and may not be protective of the most severe vehicles. LTFT was protective of all vehicles but was very conservative for B20 from high CSFT biodiesel.
- Results were presented at ASTM in June of 2008 leading to the passage of ballots adding the cold soak filtration requirement to the B100 specification (D6751), allowing up to 5% biodiesel in conventional diesel fuel meeting the D975 requirements, and the creation of a new specification for B6 to B20 blends, D7467.

Future Directions

Further study to address the following issues is underway:

- Evaluate the performance of additional high CSFT B100.
- Test B20 and B5 blends from a biodiesel having CSFT between 200 and 360 seconds. Currently the faster 200 second CSFT is required for biodiesel to be blended in fuels with CP < -12°C, but many in the industry do not believe this is necessary.

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Introduction

Like other fuels, diesel fuels must perform under a range of environmental conditions throughout the year. To accomplish this, petroleum-derived diesel is formulated to have a lower CP during colder months, with significantly lower CP fuels required in northern tier states and colder areas. Tenth percentile minimum ambient air temperatures are shown in an appendix to the ASTM D975 Standard Specification for Diesel Fuel Oils [1] and are used to estimate low-temperature operability requirements. This is most commonly done by ensuring that fuel CP is below the tenth percentile minimum ambient air temperature. Note that for petroleum-derived diesel fuels flow improver additives allow operability at temperatures significantly below the CP.

Biodiesel blend operability may be complicated by the observation that some biodiesel blendstock can form precipitates at temperatures above the CP. The objectives for this study were to validate a cold temperature performance test to identify biodiesel that, in blends up to B20, shows precipitate formation and fuel filter plugging at temperatures above the CP. This cold temperature performance test is known as cold soak filterability or CSFT. In this test, a B100 sample is held at 4°C for 16 hours, allowed to warm to room temperature, and filtered under specified conditions. D6751 currently requires all biodiesel to filter in less than 360 seconds, and biodiesel to be used in blends with the CP less than -12°C to filter in less than 200 seconds. A further objective of the study was to evaluate the correlation between bench test results (CP, CFPP, and LTFT) and actual HD vehicle performance at low temperatures for biodiesel blends. This study was performed in collaboration with the Coordinating Research Council, the Engine Manufacturers Association, and the National Biodiesel Board.

Approach

- Testing of nine fuels in three HD vehicles; vehicle data provided in Table 1. Fuels include B5 and B20 blends from four biodiesels plus one base fuel. The four B100s were derived from different feedstocks, cover a range of CP from 0.8°C to 11.7°C, and include one sample with long cold-soak filtration time. A No. 2 diesel fuel with CP of -28.6°C was used to prepare the B5 blends; and a 50/50 by volume blend of this No. 2 and a No. 1 diesel, with a blend CP of -37.5°C, was used to prepare the B20 blends.
- The biodiesels were characterized for quality by multiple labs. Base fuel and blends were characterized for CP, CFPP, LTFT and other low temperature operability parameters by multiple labs.
- Vehicles were cooled to test temperature (initial test temperature was the CP) overnight then started and driven on an all-weather dynamometer simulating 80,000 lb of vehicle inertia. In subsequent tests, temperatures were adjusted to try to define an operability limit. Testing protocol was similar to that used in previous studies [2,3].

TABLE 1. Class 8 Trucks Procured for this Project

Test Vehicle:	Model Year	Engine	Inlet fuel heated at filter by:
International	2003	Caterpillar C-12	Return fuel
International	2005	Cummins ISM	Return fuel
Freightliner	2003	Detroit Diesel Series 60	Electric

Results

Table 2 shows CSFT results from different laboratories for the four B100 samples. There is generally good agreement between labs and the results indicate that B100 A fails both the 200 second and 360 second CSFT requirements that are currently in D6751. B100 B, C, and D show average CSFT times of less than 200 seconds indicating that they should be appropriate for blending of fuels with CP < -12°C.

CP for the B5 blends is compared with CFPP and LTFT in Figure 1. The B5 results are those clustered between CP of -23°C and -25.3°C; thus, addition of 5% biodiesel caused a 3°C to 5°C increase in CP. CFPP is equal to or slightly below CP, while LTFT is equal to or slightly above CP. This is in line with expectations because the LTFT test was developed to predict performance with the most challenging vehicle fuel systems.

TABLE 2. Cold Soak Filtration Test Results for B100 Samples

Lab	CSFT, sec			
	B100A	B100B	B100C	B100D
F	>720	95	179	185
G	>720	92	118	167
K	>720	126	170	296
L		93	105	112
Average	**>720**	**102**	**143**	**190**

B20 blends were prepared from each B100 by blending with a 50/50 (volume) blend of the No. 1 and No. 2 diesel fuel. Additionally, B100B was blended with both the No. 1 and No. 2 diesel fuels to make two additional B20 blends. Recall that the CP of the 50/50 No. 1/No. 2 diesel blend was -37.5°C. Blending of 20% biodiesel causes an increase of CP by 12 to 15°C. Figure 1 also shows a comparison of CP with CFPP and LTFT results for the B20 blends. Trends are as expected with the exception of test fuel (TF) #5, which was prepared from B100A having a high CSFT. For this blend LTFT averages -1.5°C while CP is -17.9°C.

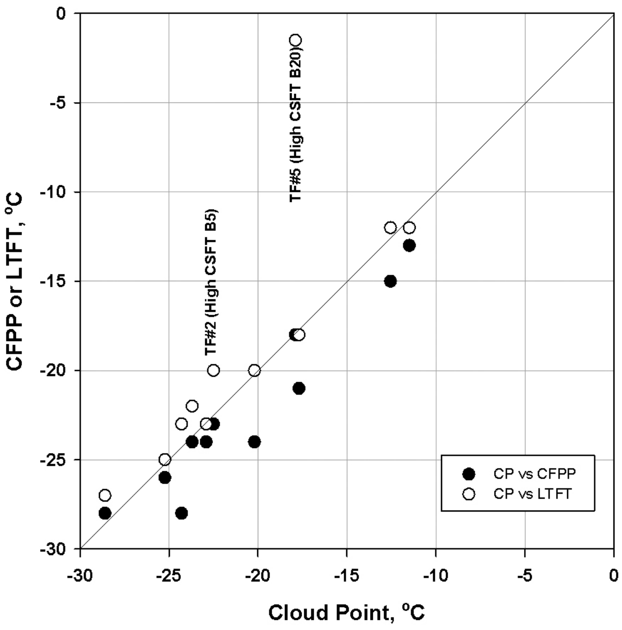

FIGURE 1. Comparison of CP with CPFF and LTFT for B5 and B20 Blends

Based on the vehicle operability data it is possible to define an estimated minimum operability temperature (EMOT). The difference between the lowest pass temperature and the highest fail temperature was calculated and the EMOT was defined as one-third of the temperature difference above the maximum fail temperature or two-thirds below the lowest passing test. Results of this estimation are shown in Table 3. In cases where the result is listed as "greater than," no passing test was obtained. In cases where the result is listed as "less than," no failing test was obtained; in general, these results are at temperatures below the fuel CP.

TABLE 3. Estimated Minimum Operating Temperature, °C

	B100/ Diesel	Blend Level	Truck A	Truck C	Truck D
TF #1	No. 2	0	-28.8	-29.2	-28.7
TF #2	A/No. 2	5	-25.4	<-25.8	<-25.9
TF #3	B/No. 2	5	-25.9	-25.4	<-26
TF #4	C/No. 2	5	-25.2	-25.4	-25.3
TF #5	A/(50/50)[a]	20	>-15.4	-18.8	-17.9
TF #6	B/(50/50)	20	-23.3	-23.3	-23.2
TF #7	C/(50/50)	20	<-13.4	-14.4	-14.4
TF #8	B/No. 2	20	>-19.8	-20.7	<-20.7
TF #9	D/No. 2	5	-23.4	-23.6	<-24.2
TF #10	D/(50/50)	20	-12.6	-11.9	-13.0
TF #11	B/No. 1	20	-24.2	-24.1	<-24.8

[a] 50/50 denotes a 50/50 by volume blend of No. 1 and No. 2 diesel was used.

Figure 2 shows a comparison of EMOT and CP. In this figure the color (white, black, or grey) of a symbol indentifies the truck. If the symbol is a circle, then an operability limit was determined. If the symbol is a triangle pointing up, then no passing test was obtained and the operability limit is greater than this value, and similarly for a triangle pointing down. Figure 2 shows that CP is a slightly conservative predictor of EMOT in almost all cases. The one exception is TF#5, the B20 blend produced from the high CSFT B100A which produced failing results at 3°C above CP. A regression line suggests that on average CP was conservative by about 1°C over the full range of CP.

Conclusions

Overall, biodiesel blends produced from B100 with CSFT of less than 200 seconds performed as predicted by CP or LTFT measurements. These fuels were also clear and bright above CP and did not cause significant fuel filter blockage and pressure drop at or above CP. In many cases these fuels could operate at temperatures 1°C to 2°C below CP. CFPP tends to predict an operability limit lower than cloud and may not be protective of the most severe vehicles.

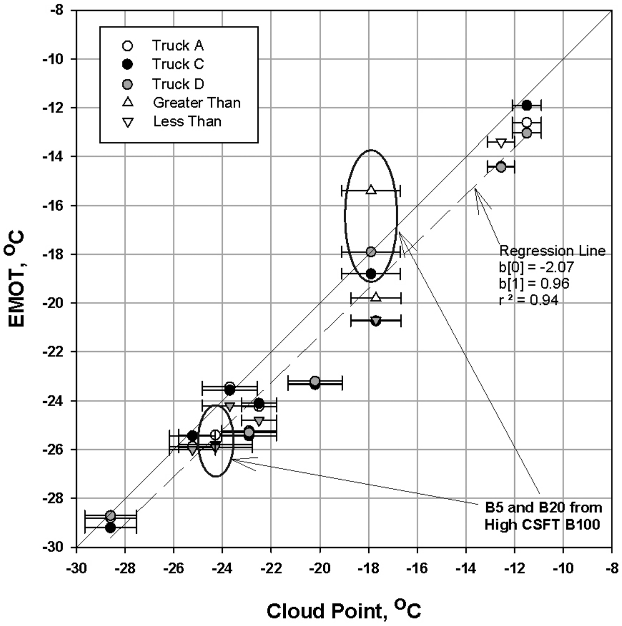

FIGURE 2. EMOT as a Function of CP for all Fuels Tested (95% confidence interval shown for CP)

The B20 blend prepared from the high CSFT B100 was slightly cloudy at -15°C and showed obvious precipitates at -17°C, yet the CP of this fuel was -18°C where the fuel appears almost milk-white. Failing tests were obtained in Truck A at all temperatures tested, up to 3°C above CP. This truck manufacturer represents roughly 30% of the North American Class 8 truck market, implying that B100 with high CSFT may cause unanticipated low-temperature operability problems.

It was shown that movement of the trucks could result in mixing of the vehicle fuel tank and suspension of materials that had precipitated to the bottom causing a failing test. The effects found for stirring of the fuel tank may indicate that vehicle dynamometer tests do not capture all failure modes that can be experienced in actual vehicle operation.

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IV.6 Biodiesel (B20) Performance with Light-Duty Vehicle Advanced Emission Control Devices

Matthew Thornton
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
FEV Engine Technology Inc., Auburn Hills, MI

Objectives

- Evaluate the impact of biodiesel fuel blends on the performance of advanced emission control systems for light-duty diesels, (e.g. conversion efficiencies, regeneration effects for both NOx adsorber catalyst (NAC)/diesel particle filter (DPF) and selective catalytic reduction (SCR)/DPF systems).
- Understand effects over time (emission control system aging to full useful life).
- Assess engine and fuel system operation impacts at end of project (e.g. combustion chamber, fuel injections system, fuel pump, oil dilution, etc.).

Accomplishments

- Vehicle and engine procurement and baseline testing complete.
- Worked with the Manufacturers of Emissions Controls Association to develop emission control system configurations and set-up in a test cell and on a vehicle for both emission control systems.
- Completed computational fluid dynamics modeling of selective catalytic reduction system urea spray, evaporation, and ammonia distribution for test bed optimization.
- Completed system optimization for both NAC/DPF and SCR/DPF systems with 20% biodiesel fuel blend.
- Aging and performance evaluations for NAC/DPF systems with 20% biodiesel blend is complete (accelerated aging to represent 2,100 hours of operation or approximately 120,000 miles or full useful life) completed.
- Aging and performance evaluations for SCR/DPF systems with 20% biodiesel blend is complete (accelerated aging to represent 2,100 hours of operation or approximately 120,000 miles or full useful life) completed.
- Catalyst post mortem, engine and fuel system durability analysis, and oil dilution analysis complete.

Future Directions

- Project complete.

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Introduction

Due to advancements in diesel engine technology light-duty diesel-powered vehicles are becoming more popular in the U.S. In addition to the increased interest in light-duty diesel vehicles the stringent Tier 2 emissions standards for this vehicle class has lead to the necessity of emissions control systems (ECS) on these vehicles. Concurrently, increasing fuel prices and energy security goals have focused interest on bio-fuels, such as biodiesel, as a means to displace demand for petroleum-derived fuels.

SCR with urea and NACs are the leading technologies for meeting the Tier 2 NOx emission standards for light-duty diesel vehicles. Extensive research has been conducted over the past decade focusing on the performance and durability of these technologies in conjunction with conventional fuels [1-8]. Little research has been performed with the intent of gaining an understanding of the impact of bio-fuels, or more specifically biodiesel, on these ECSs. In addition, biodiesel fuel blends can create potential problems affecting vehicle operation through accelerated dilution of the oil by the fuel affecting the compatibility of the fuel with other vehicle components.

Biodiesel is a renewable fuel derived from vegetable oil, animal fat, or waste cooking oil, and it consists of the methyl esters of fatty acids. It is typically used as a diesel blending component at levels up to 20% by volume. Life-cycle analysis indicates that the use of biodiesel can help displace imported petroleum in the United States and resource assessments have indicated that biodiesel has the potential to displace 5% or more of petroleum diesel over the next decade [9,10]. However, little is known about the potential impacts of these fuel blends on the life and performance of ECSs and because biodiesel has a relatively higher distillation temperature and boiling point, when it is present in post-injected fuel it tends to dilute the oil on a level disproportionate to its blend ratio in the fuel [11,12,13]. This leads to an additional concern about oil dilution.

Approach

The intent of this project was to assess the emissions performance of a NAC system, combined with a diesel oxidation catalyst (DOC) and DPF, and an SCR system, combined with a DOC and DPF; both while operating on ultra-low sulfur diesel (ULSD) and a blend of ULSD and 20% biodiesel (B20). A consideration of SCR and NAC chemistry suggests several areas where biodiesel blends may perform differently than pure petroleum-derived fuels. This project included an initial look at these potential areas.

Before the start of the ECS development, the engine-out emissions were recalibrated to result in required NOx and hydrocarbon (HC) conversion efficiencies of approximately 80% from the ECS. The achieved target level was in the range of 0.35 g/mile NOx emissions over the Federal Test Procedure.

Based on the experience gained during the APBF-DEC light-duty vehicle development efforts [1,2,4,7,8], the development team decided to start the activities with the implementation and calibration of the NAC system. The hardware configuration was defined as close-coupled DOC and NAC combination allowing the fastest possible catalyst light-off after cold start. The SCR system was designed around the vehicle body constrains with a close-coupled DOC and an underfloor SCR–DPF allowing sufficient mixing length after the point of injection for urea.

Results

All ECS parts were aged to an equivalent of 120,000 miles or full useful life. In order to accomplish this, the engine and ECS were exposed to an equivalent useful lifetime of fuel in the engine dynamometer test cell. To keep the aging time at a reasonable level, the aging duration for each ECS was set to be accomplished after 700 hours. The following assumptions regarding the fuel consumption for the system were used:

- Highway cycle fuel economy at 55 mpg.
- City cycle fuel economy at 33 mpg.
- Split of ¾ highway and ¼ city cycle.

These assumptions resulted in an average fuel economy of 49.5 mpg. At 120,000 miles this equates to 2,424 gallons or 7,708 kg of fuel. With the available 700 hours of aging time an average fuel consumption of approximately 11 kg/hr was established. Three operating phases were established to reflect real in-use operating modes:

1. NAC operation using the systems efficiency control algorithms to determine the frequency of regeneration events.
2. DPF regeneration (300 times for full useful life).
3. Desulfurization (25 times for full useful life for NAC system only).

Table 1 shows the detailed operating conditions and durations for the chosen durability cycle. In Phase 1 the engine operating conditions are changed between two operating points (OP1 and OP2) for 120 minutes. In the second phase the system transitions into the DPF regeneration mode with a DPF inlet temperature setpoint of 650°C. Once the DPF regeneration is completed the system returns into the Phase 1 operation. This sequence is repeated until a total runtime of 28 hours is obtained. After the 28 hours the system is forced into the desulfurization mode with a setpoint temperature of 700°C and frequent lean-rich transitions. In addition to the operating point discussion, the table also contains temperature information for the different emission control components as well as the fuel flow rates for each state.

TABLE 1. Durability Cycle Operating Conditions

	Operating point	Duration	Reps	Fuel consumed
	[rpm], [Nm]	[min]	-	[gallons]
OP 1	2,000 rpm, 210 Nm	5		0.262
OP 2	2,600 rpm, 160 Nm	5		0.287
Phase 1	(OP 1 + OP 2) x 12	300	120	6.234
Phase 2	DPF regeneration 2,600 rpm, 110 Nm	20	300	1.062
Total per cycle	Phase 1 + Phase 2	140	300	7.296
Phase 3	Desulfurization 2,200 rpm, 75 Nm	20	25	0.668

After completion of the durability testing with each ECS, the components were installed on the project vehicle and underwent the same test sequence as with the parts during the development phase. All of the vehicle tests were conducted at EPA's National Vehicle and Fuel Emissions Laboratory. The vehicle was tested using a 48-inch-diameter, single-roll, electric chassis dynamometer. The tests showed that Tier 2 Bin 5 emission levels could be met with the NAC ECS. However, the performance of the SCR system degraded to a point at which Tier 2 Bin 5 limits could not be met. Figure 1 and Table 2 show the system performance at the beginning and end of the aging process for both ECS.

Although the desired NOx and non-methane HC emission levels for the SCR system were not met, the researchers believe that this was the result of degradation of the SCR catalyst from thermal shock due to HC adsorption and loss of cold-start performance, and not a result of fuel or fuel oil dilution impacts. The

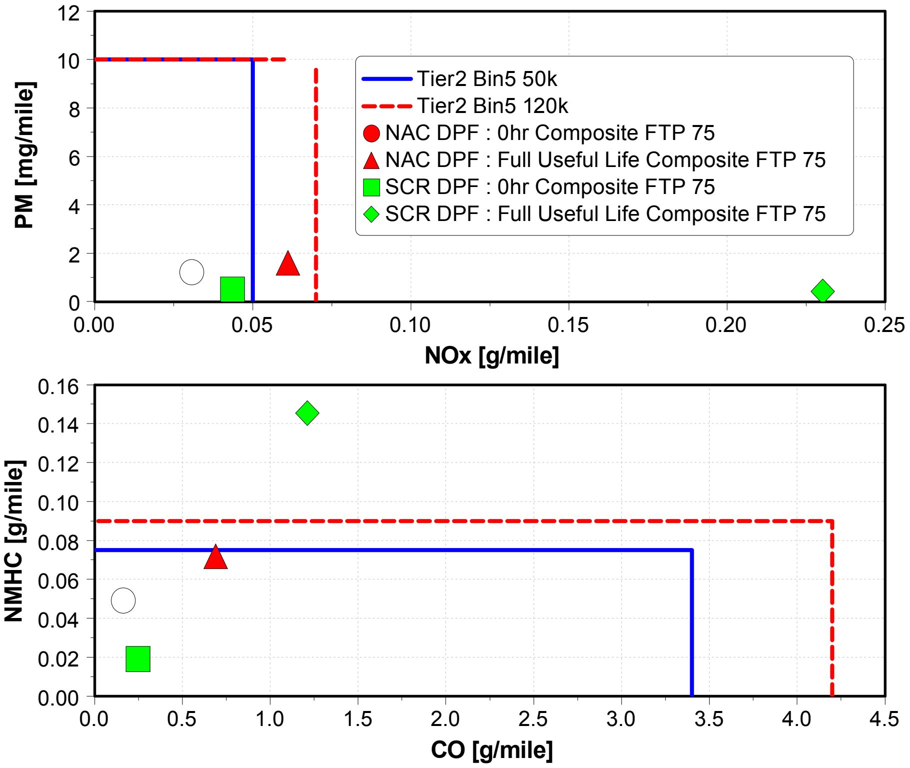

FIGURE 1. Emission Results with New and Useful Life Aged Components, Federal Test Procedure (g/mi)

TABLE 2. Emission Results with New and Useful Life Aged Components, Federal Test Procedure (g/mi)

System	NOx	PM	CO	NMHC
NAC 0 hr	0.031	.0012	0.163	0.149
NAC 700 hr	0.061	.0016	0.690	0.072
SCR 0 hr	0.044	.0005	0.247	0.019
SCR 700 hr	0.230	.0004	1.212	0.145

Tier 2 Bin 5 emission levels could be met with the SCR system for PM and CO.

For the NOx storage system (which requires a late in-cylinder fuel injection for regeneration), biodiesel oil dilution levels ranged from 5%-10%. For the SCR system (which used a urea solution as the reductant and late in-cylinder fuel injection for diesel particle filter regeneration), biodiesel oil dilution ranged from <4%-8%. These observations were made over typical oil drain intervals. Despite these observed biodiesel oil dilution levels, there were no observed impacts on performance of the engine or the emission control systems.

Conclusions

The following are the main conclusions derived from the presented work to date.

The complete project which resulted in the integrated engine–ECS configuration was conducted in the following main steps:

- Baseline measurement of the existing production hardware.
- Recalibration for lowered engine-out level.
- Implementation and calibration of the NAC system.
- Implementation and calibration of the SCR system.
- Aging of the NAC system.
- Aging of the SCR system.

The used engine hardware as well as the engine control strategy and calibration resulted in an engine-out NOx increase under biodiesel operation which came along with small improvements in fuel economy of about 2%. The engine-out NOx emission levels increased with the use of biodiesel up to 10% with B20. The hydrocarbon emissions decreased. The increase in engine-out NOx emissions did not translate into higher tailpipe emissions. The NAC system performance was at a higher rate comparing the B20 and ULSD fuels; this was a result of a more optimal exhaust temperature especially during the Federal Test Procedure. The overall NOx conversation rates exceeded 80% for the un-aged systems allowing the Tier 2 Bin 5 emission standards for all emission constituents to be met. The impact on NAC or DPF regeneration events themselves was negligible. The SCR system performance did not change comparing the two fuels resulting in virtually identical tailpipe emissions.

The durability tests with both emission control systems proved that the NAC system provided sustainable conversion efficiencies over the useful life while there was significant system performance degradation of the SCR system which is attributed to the deactivation of the iron-zeolite through thermal shock resulting from HC adsorption.

Biodiesel fuel blends from any feedstock that meet the D6751 specifications will have similar composition compared to the tested fuel and should result in similar performance characteristics.

Finally there was no biodiesel-related wear or engine mechanics deterioration found after the hardware was exposed to an accelerated aging protocol of twice the useful life.

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IV.7 Speciation of Toxic Organic Emissions from Biodiesel Combustion

Matthew Ratcliff (Primary Contact),
John Dane*, Robert McCormick and
Kent Voorhees*
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
*Colorado School of Mines, Golden, CO

Objectives

- Develop improved analytical methods to measure nitro-polynuclear aromatic hydrocarbons (NPAH) and polynuclear aromatic hydrocarbons (PAH) associated with diesel particulate matter (PM).
- Compare the toxic organic emissions from ultra-low sulfur diesel (ULSD) with those from soy biodiesel at concentrations of 20 and 100 percent (B20 and B100).
- Quantify the effects of a catalyzed diesel particle filter (DPF) on toxic organic emissions with these three fuels.

Accomplishments

- Demonstrated that a catalyzed, passively regenerated DPF was highly effective in oxidizing most organic exhaust emissions (1 to 3 orders of magnitude decrease).
- Formaldehyde emissions increased post-DPF (except in the case of B100 fuel) and 1-nitropyrene conversion was less than 50% for all fuels tested.
- Demonstrated that an advanced electron monochromator-mass spectrometer (EM-MS) has unique advantages for selectively analyzing NPAHs in organics extracted from diesel PM.
- Improved methods for extracting and cleaning the soluble organic fraction (SOF) of diesel PM were developed.

Future Directions

- Identify unknown nitro-compounds in existing PM extracts.
- Develop robust sampling methods for volatile and semi-volatile nitro-compounds in exhaust downstream of the DPF.
- Quantify DPF-out nitro-compounds from 2007 and 2010 diesel engines.

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Introduction

The effects of biodiesel blending with diesel fuel on regulated exhaust emissions are well documented. In general, emission rates of total hydrocarbons, carbon monoxide and PM decrease as the concentration of biodiesel increases. In contrast, emissions of oxides of nitrogen (NOx) can either slightly increase or slightly decrease, depending on the engine or vehicle and test cycle used [1]. The installation of a DPF is extremely effective in reducing PM and has been required for all on-road diesel vehicles since 2007. However, detailed knowledge of non-regulated emissions exiting a DPF, and the interactions of biodiesel with a DPF are not well understood. To address concerns for potential unintended consequences of DPFs, this study was performed which characterized unregulated (and in many cases toxic) emissions.

Approach

A Cummins ISB engine with 2004 calibration was retrofitted with a catalyzed continuously regenerated trap (CCRT) type DPF from Johnson Matthey. The engine was operated on three fuels: ULSD, soy biodiesel (B100) and a 20% blend (B20), using a modified AVL-8 steady-state test cycle designed to emulate the heavy-duty Federal Test Procedure (FTP) [2]. PM and carbonyl emissions were sampled from a dilution tunnel, while gas phase organics were sampled directly from the raw exhaust.

The PM samples were subjected to an extraction and clean-up procedure to obtain the SOF. The SOF was then analyzed by gas chromatography (GC) employing a unique JEOL Inc. EM-MS. The EM-MS uses low energy electron capture ionization allowing highly sensitive and selective analysis of NPAH. A second GC-EM-MS analysis using higher energy electron impact ionization quantified the PAH.

Carbonyl compounds were captured in Waters Sep-Pak cartridges as dinitrophenylhydrazones (DNPH). These were eluted from the cartridges with acetonitrile and the solutions were analyzed by an Agilent 1200 high pressure liquid chromatograph (HPLC) using a gradient of acetonitrile/water solvent buffered to a pH of 2.5. Compound detection was by ultraviolet absorption.

Raw exhaust gas samples were collected in evacuated 3.2L fused silica coated canisters. The samples were analyzed with an Agilent 6890 gas chromatograph/5975 mass spectrometer (GC-MS) detector. The inlet to the GC-MS was an Entech 7100 cryogenic pre-concentrator, using a cold-trap dehydration method to concentrate the volatile and semi-volatile compounds in the exhaust sample, and then injected them onto the GC column.

Results

GC-MS analysis of post-DPF exhaust gases indicated very high DPF conversion efficiency for the C_3-C_{11} hydrocarbon species, typically below detection limits. Selected unburned fuel hydrocarbons and products of incomplete combustion in the engine-out exhaust are compared in Figure 1. The amounts are averages of triplicate engine tests/samples with error bars ± one standard deviation. Expected decreases of diesel fuel hydrocarbons decane and undecane were observed as more biodiesel was incorporated into the fuel. Most products of incomplete combustion (e.g. isobutylene and toluene) also decreased with increasing biodiesel concentration. These trends across fuels are consistent with measurements made by Sharp et al. [3] using a similar engine tested with the transient heavy-duty FTP. However, benzene emission appears to be insensitive to the changes in fuel chemistry, consistently measuring ~150 ng/L concentration. Because aromatics are not present in biodiesel, benzene likely forms from 1,3 butadiene and acetylene precursors arising from olefinic carbons within soy biodiesel. Similar reactions evidently led to the formation of naphthalene which was measured in the PM samples. The highest amount of naphthalene came from B100, at more than double the level from ULSD.

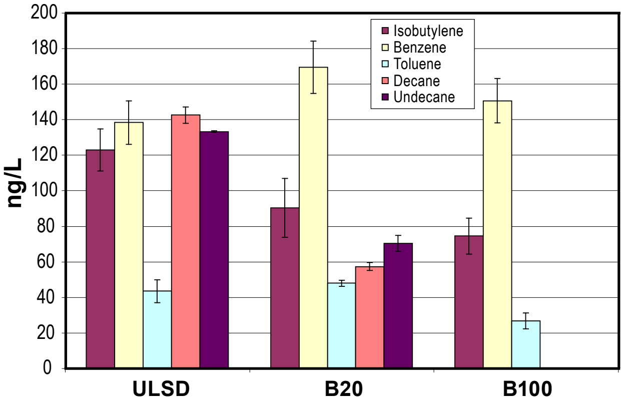

FIGURE 1. Selected Non-Methane Hydrocarbons Measured in Raw Engine-Out Exhaust

A product of incomplete combustion unique to biodiesel is methylacrylate which is the most intense signal in Figure 2, a gas chromatogram of B100 engine-out exhaust. Because the GC detector was a mass spectrometer, it is not warranted to assume methylacrylate's concentration was higher than that of benzene, but it is on the same order. Methylacrylate was

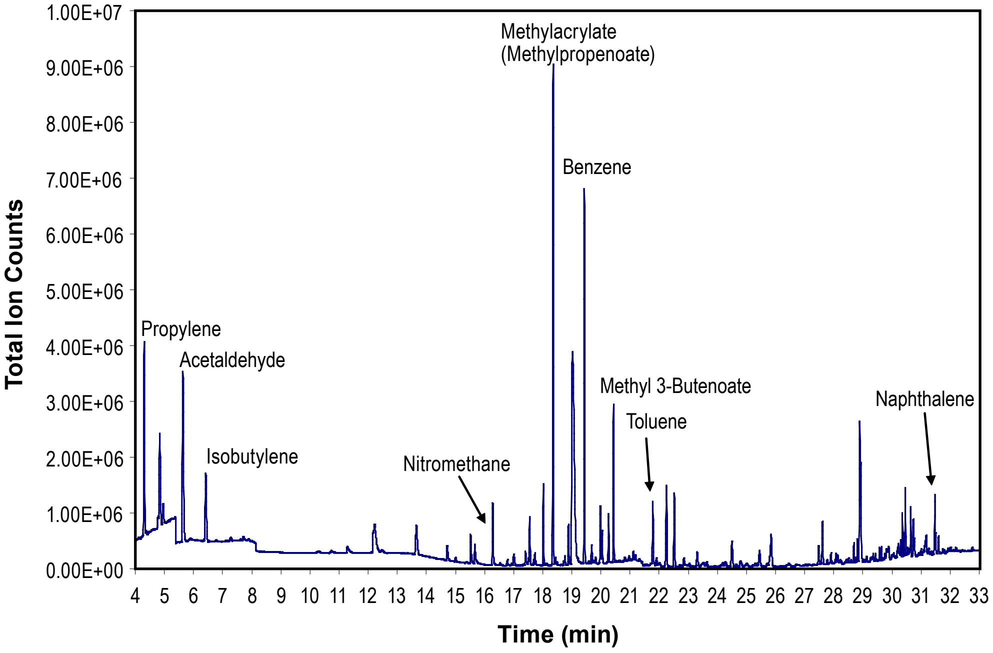

FIGURE 2. Gas Chromatogram of Raw Engine-Out Exhaust from B100

also detected in the engine-out exhaust from B20 tests, but none was present in the exhaust from ULSD tests, thus it appears to be clear indicator of methyl esters in the fuel.

It is postulated that methylacrylate formation arises in the combustion process via a two-step reaction mechanism, where first a labile hydrogen atom on the carbon alpha to the carbonyl is abstracted by hydroxyl radical, followed by beta-scission. This mechanism yields methylacrylate and an alkyl or alkenyl radical (R·), depending on whether R is saturated or unsaturated, respectively. Similar reactions at the carbon beta to the carbonyl could lead to methyl-3-butenoate, and R-1· alkyl or alkenyl radical, also seen in Figure 2. The persistence of methylacrylate in the engine-out exhaust may be explained by its conjugated structure which resists further oxidation by hydroxyl radicals. Supporting evidence for this comes from methylacrylate's high autoignition temperature of 468°C [4], which far exceeds the autoignition temperature of 200-220°C for alkanes in diesel fuel.

Aldehyde emissions in the engine-out exhaust were insensitive to fuel chemistry. In all cases formaldehyde dominated at ~150 ng/L, similar to the concentration of engine-out benzene. Acetaldehyde was next highest in concentration in the 40-50 ng/L range. The DPF effectively oxidized most carbonyl compounds. However, it was ineffective for formaldehyde, producing a net increase in formaldehyde emission from ULSD and B20 as shown in Figure 3. Only in the case of B100 was a net decrease in formaldehyde observed. The hypothesized explanation is that formaldehyde was formed within the DPF from other aldehydes and hydrocarbons as their oxidation progressed, and under the prevailing DPF temperatures during the test cycle, the oxidation of formaldehyde was inhibited.

Mass emission rates for the four major NPAHs extracted from the engine-out PM samples are compared in Figure 4, illustrating that biodiesel blending leads to significant reductions of NPAHs, especially 1-nitropyrene. Blending biodiesel at the 20% level reduced NPAH emissions approximately 50%. The furthest right-hand columns in Figure 4's NPAH groups are the amounts of 1-nitropyrene extracted from the DPF-out PM. Comparisons with the engine-out 1-nitropyrene data demonstrates the DPF's poor conversion efficiency for this NPAH. The DPF was effective for oxidizing the other NPAHs as illustrated qualitatively by the overlaid GC-EM-MS nitro-chromatograms (traces are the nitro-group's unique mass 46 ion signal only) in Figure 5. However in the case of B100, nitrobenzene and several unidentified nitro-compounds between 8 and 11 minutes are evident.

Conclusions

A catalyzed, passively-regenerated DPF was found to be very effective for oxidizing most organic exhaust emissions from a Cummins ISB diesel engine, including benzene, PAHs and many NPAHs. However:

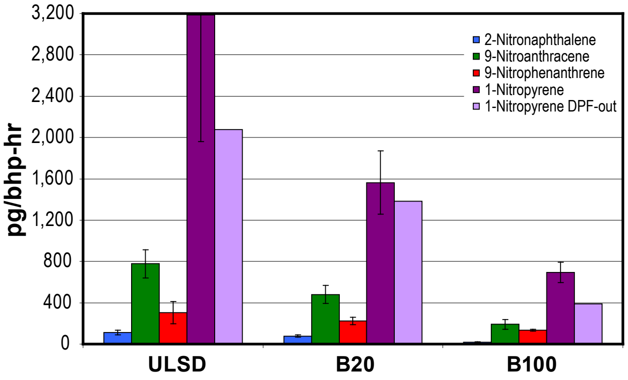

FIGURE 4. Major Engine-Out NPAHs and Comparison with 1-Nitropyrene Post-DPF

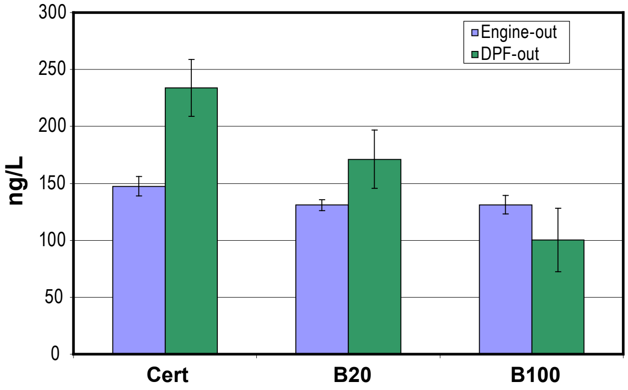

FIGURE 3. Formaldehyde Emissions before and after the DPF

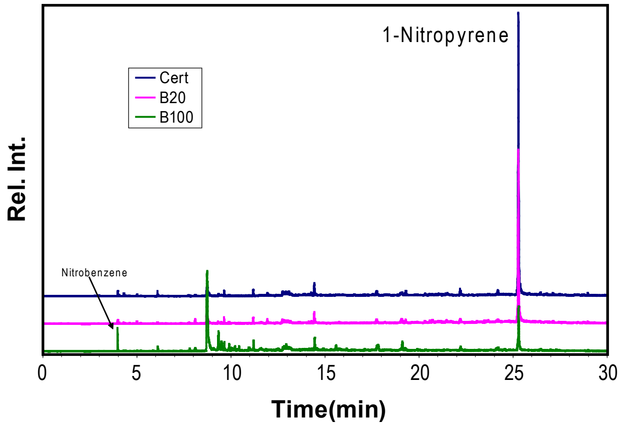

FIGURE 5. Overlaid Nitro-Compound (mass = 46) Chromatograms of SOF from ULSD, B20 and B100

- Formaldehyde emissions were found to actually increase after the DPF, except in the case of B100.
- The DPF's conversion efficiency for 1-nitropyrene was less than 50% for all fuels.
- Furthermore, the combination of B100 fuel and the DPF was not effective for oxidizing nitro-benzene and naphthalene. This combination also produced some unidentified nitro-compounds.

Because of the lack of PM after the DPF, and consequently a lack of surface area, it can be assumed that the capture efficiency of semi-volatile species (e.g., nitrobenzene) on the PM filters used in this study was low, and that the DPF-out results may be underestimated. Therefore, further sampling methodology development is required to ensure high capture efficiency of PAH and NPAH species from DPF-out exhaust.

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IV.8 Advanced Chemical Characterization of Non-Petroleum-Based Fuels and Emissions for Understanding Effects on Combustion

John M.E. Storey (Primary Contact),
Samuel A. Lewis, Sr., Raynella M. Connatser,
Teresa Barone
Oak Ridge National Laboratory
P.O. Box 2008, MS 6472
Oak Ridge, TN 37831-6472

DOE Technology Development Manager:
Kevin Stork

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.

Accomplishments

- Developed microwave solvent extraction method for soot samples that results in a 20-fold decrease in solvent usage and enhanced extraction efficiencies for polar compounds.
- Completed analysis of soot samples for novel oxygenated compounds, previously unknown in diesel soot, may account for up to 20% of the thermally-labile organic fraction in soot.
- Developed atmospheric pressure chemical ionization mass spectroscopy (APCI–MS) for the detection and quantification of urea and its major decompositions products on particulate matter (PM) filter samples. Nitrogen species from diesel particulate filter (DPF)-urea selective catalytic reduction (SCR) systems account for up to 50% of measured PM emissions from 2010-compliant heavy-duty engines.

Future Directions

- Conduct analyses with capillary electrophoresis of inorganic and organic acid anions in exhaust condensates.
- Evaluate soot derived from NPBF engine combustion for aromatic acids and anhydrides.

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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 fuels and emissions have been developed over many years for conventional petroleum fuels. It is likely that better methods are emerging now to correlate combustion performance, and in particular the analytical methods should be reassessed for NPBFs. Many NPBFs contain oxygenated functional groups which makes analytical methods oriented toward non-polar compounds ineffective. In fact, criteria pollutants such as non-methane hydrocarbons, typically measured with a flame ionization detector will be inaccurate for emissions containing oxygenated species. In support of the studies of fuel effects on combustion, new analytical procedures will be used (developed as needed) to find improved predictive correlations.

PM derived from diesel combustion contains a significant fraction of thermally-labile species, often aggregated in the term "organic carbon". The organic carbon fraction is an important soot characteristic and plays a role in exhaust gas recirculation (EGR) cooler fouling, and DPF regeneration behavior, among other key operations of the engine system. Previous attempts at reconciling the mass of extracted organic species with the mass of organic carbon have been unsuccessful. In NPBF combustion, particularly of biofuels, the organic carbon fraction is often higher than for conventional petroleum diesel combustion. In the studies described in the following, our laboratory developed methods to help understand what species may make up the missing fraction of organic carbon in PM.

Approach

Because the extraction of organic compounds from diesel PM is one of the most time-consuming and difficult challenges, an accelerated extraction method was developed. Using Environmental Protection Agency Method 3546 [1] as a basis, different solvent systems were investigated for their extraction efficiency of diesel range organic compounds including n-alkanes, polycyclic aromatic hydrocarbons (PAHs), as well as fatty acid methyl esters (FAME). PM filters were spiked with solutions of the compounds, extracted and analyzed.

To investigate the thermally-labile fraction of PM, PM from EGR coolers and DPFs was captured and analyzed. Early in the process, the poor response of the compounds was noted in conventional gas chromatography–mass spectrometry (GC-MS) with electron impact ionization, so significant efforts were made to enhance detection in the mass spectrometer. Furthermore, application of the microwave soot extraction method with a new solvent system resulted in enhanced extraction of these tightly bound compounds.

For urea deposit/byproduct analysis, samples of urea deposits from exhaust pipes and catalysts were dissolved in water/formic acid systems and analyzed by electrospray ionization–mass spectrometry (ESI-MS) in both positive and negative ion modes. Additional PM filter samples came from West Virginia University's 2010-compliant heavy-duty engine. In comparison to DPF-out filter samples, West Virginia University had observed weight gain on the sample filter after the whole DPF-urea SCR system. The solvent extraction samples were extracted in a similar solution and also analyzed.

Results

Microwave extraction with a mixture of 50:50 acetone and hexane yielded excellent recovery of the diesel range organics. Recoveries between 80% and 104% were observed for n-alkanes from tridecane (C_{13}) to pentacosane (C_{25}). Recoveries for PAHs also had similar values. The method uses many times less solvent, resulting in much lower disposal costs. Furthermore, by tailoring the solvents in the process, different compounds can be targeted for extraction including very polar compounds such as carboxylic acids.

For the investigation of thermally-labile organic fraction of soot, compounds were selected based on some preliminary direct thermal desorption experiments. Five aromatic acids and anhydrides shown in Figure 1 were selected:

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

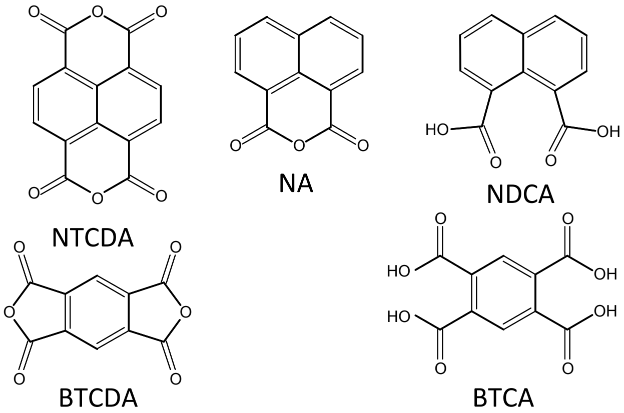

FIGURE 1. Five aromatic acids and anhydride were selected for study: 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA); 1,2,4,5-Benzenetetracarboxylic dianhydride (BTCDA); 1,8-Naphthalene anhydride (NA); 1,2,4,5-Benzenetetracarboxylic acid (BTCA); 1,8-Naphthalene- dicarboxylic acid (NDCA).

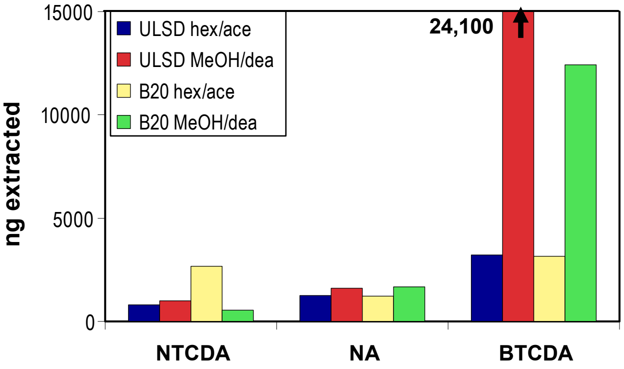

FIGURE 2. Extraction in methanol:diethylamine better than standard solvent systems for the aromatic anhydrides. Response factors reveal low ionization efficiency for compounds in the GC-MS leaving them unseen in typical soluble organic fraction extract analyses. Note the lower amounts of BTCDA in the B20 soot.

Using the microwave extraction method on spiked soot samples from an engine running on ultra-low sulfur diesel (ULSD) and 20% biodiesel in ULSD (B20), solvent systems were investigated and methanol:diethylamine was selected as having the best efficiency. Nascent soot samples collected in DPF cores and in EGR cooler experiments were then extracted and analyzed with GC-MS in negative chemical ionization mode. Extraction of actual soot samples showed that a single anhydride compound, BTCDA, made up 2.4% of the total mass of soot (1 mg) as shown in Figure 2. Note that less of the BTCDA was found in the B20 soot. In addition, the extraction of the dicarboxylic acid NDCA showed that it also comprised a large amount of the soot mass as shown in Figure 3, but B20 appeared to suppress the formation of the NDCA in the soot. In addition to the five compounds noted above, soot from the B20 contained substantial amounts of the C_{16} carboxylic acids that result from the FAME present in the fuel. Finally, the fifth compound in the list, BTCA, proved intractable to detection by GC-MS, even at very high amounts, so new methods using ESI-MS are being developed for detection. The overall implication of this work is that a large fraction of the organic carbon in soot is made up of these complex carboxylic acids and anhydrides. An understanding of their formation and

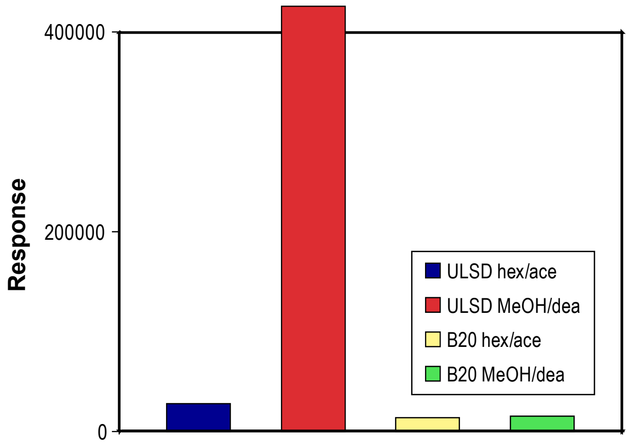

FIGURE 3. The aromatic carboxylic acids were more difficult to analyze by GC-MS. Analysis of soot samples did reveal the presence of NDCA in the matrix. Again, B20 appeared to suppress the formation of the compound in the soot.

subsequent behavior in the soot may lead to insights into soot particle formation and soot regeneration behavior in the DPF.

Urea-SCR has emerged as the most prevalent choice for NOx control of heavy-duty engines meeting the 2010 regulations. As part of ongoing investigations into urea decomposition products, ORNL analyzed some exhaust pipe deposits collected downstream of a urea injection system. Because of the refractory nature of the deposit, it was difficult to dissolve into most solvents. By using a combination of formic acid and water with and without acetonitrile, it was possible to create solutions which could be nebulized into the mass spectrometer, and then analyzed by APCI-MS. Positive and negative ionization modes also enhanced selectivity of the method. Species such as melamine and urea had high responses to positive ionization and almost no response to negative ionization. Cyanuric acid had a strong negative ionization response and a low positive ionization response (Figure 4). Thus, by alternating ionization, it was possible to identify many of the species in the deposits.

In addition to urea deposits in exhaust pipes, our laboratory analyzed sample filters collected downstream of a DPF-urea SCR system operating on a 2010-compliant heavy-duty engine [2]. By way of comparison to filters collected downstream of the DPF, but upstream of the SCR, the filters collected downstream of the DPF-SCR had additional mass, presumably generated in the urea-SCR system. The additional mass was not large enough to make the engine non-compliant with the 2010 PM standard. The filters were extracted in water:formic acid and also in water:formic acid:acetonitrile and analyzed by positive and negative ion APCI-MS. Results showed that the majority of the mass was unconsumed urea with some biuret and melamine also observed. As engine systems for 2010 and beyond are optimized, the ability to analyze these compounds will be critical.

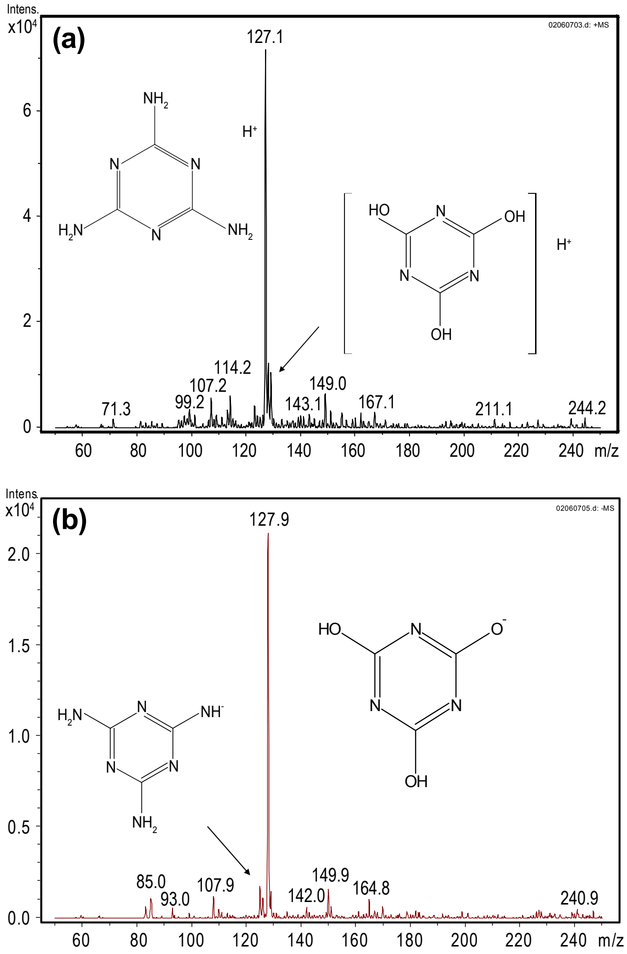

FIGURE 4. (a), APCI positive ion of 50:50 melamine and cyanuric acid. (b) APCI negative ion of 50:50 melamine and cyanuric acid. There is excellent discrimination between the two compounds.

Conclusions and Future Effort

The advanced chemical characterization effort has focused on two areas: soot organic carbon analysis and byproducts associated with urea-SCR systems. The soot extraction and characterization efforts have led to the identification of compounds that make up a large fraction of the organic carbon. Future efforts will focus on the separation of both the acids and anhydrides in one analysis. The urea byproduct analyses are ongoing for both deposit identification and identification of the contribution from the urea-SCR system to overall PM mass. Close collaboration with manufacturers and others on the urea-SCR analysis will lead to additional insights into urea decomposition processes and should result in better performance of the systems with less fouling.

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IV.9 Evaluating the Compatibility of Legacy Refueling Infrastructure with E15/E20

Wendy Clark (Primary Contact),*
Kristi Moriarty,* Marc Goodman,** Tim Theiss,†
Mike Kass.†
* National Renewable Energy Laboratory (NREL)
1617 Cole Blvd. MS #1633
Golden, CO 80401
** New West Technologies, LLC (NWT)
† Oak Ridge National Laboratory (ORNL)

DOE Technology Managers: Kevin Stork,
Dennis Smith

Subcontractor:
Ken Boyce and Tom Chapin, Underwriters Laboratory
(UL), Northbrook, IL

Objective

To evaluate the compatibility of representative samples of in-use retail petroleum dispensing equipment with gasolines containing higher concentrations of ethanol than currently allowed, particularly blends in the range of 15-20% ethanol.

Approach

- Assemble interagency team with diverse backgrounds reflecting range of knowledge.
- Consult with industry representatives regarding issues to be evaluated, equipment and materials to be tested, test fuels to be used, test methodologies.
- Determine reasonable data collection and test methodology options that can provide the most meaningful information.
- Determine test fuel to be used.
- Determine equipment and materials to be tested.
- Obtain materials and equipment to be tested, including harvesting legacy equipment actually in use or coming out of use.
- Perform laboratory tests on equipment, components, and materials.
- Record observations and evaluate results.
- Present data and proposed conclusion to interagency group for review and comment.
- Prepare report for release to public and to code and standard setting bodies.
- Identify areas for further investigation.

Accomplishments

- Steps shown in bullets 1-6 of Approach completed.
- Proposal made to International Codes Council (ICC) to amend the International Fire Code to require compatibility of fuel storage and dispensing equipment to be compatible with all blends of ethanol with gasoline up to 85% on a full system basis; tentatively accepted as a proposal by ICC.
- Test methods determined; equipment, materials and test fuels selected and obtained.
- Immersion testing underway at ORNL; “failure testing” underway at UL.

Future Directions

- Additional data needs to be determined based on results of tests underway.
- Possible need to perform tests with additional test fuels.
- Possible additional research on underground equipment systems.
- Possible related research projects, such as issues relating to ethanol blender pumps.

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Introduction

Although current regulatory requirements of the U.S. Environmental Protection Agency (EPA) limit blending of ethanol for use in conventional vehicles to 10% ethanol concentration, there have been numerous proposals in recent years for EPA to raise that limit. The renewable fuel use required by the Renewable Fuel Standard (RFS) would exceed the volume possible within the 10% limit by sometime in the 2010-2012 time frame. Meeting the requirements of RFS 2 appears to depend on the ability of refiners to blend ethanol in concentrations above the current limit. This raises concerns as to what impacts such blends may have on existing refueling infrastructure, particularly that of older manufacture, including potential for leaks and spills and other safety and environmental concerns, and conformity with codes and standards. Therefore, starting in the latter half of 2008, DOE’s Vehicle Technologies Program (VTP) and Biomass Program came together to organize sponsorship of this project to identify and evaluate concerns relating to the impacts of E10+ blends on refueling infrastructure.

Approach

In late 2008 and early 2009, an interagency team was assembled reflecting background knowledge on a wide range of possible impacts on infrastructure associated with potential introduction of higher levels of ethanol. The team included staff from VTP's Clean Cities and Fuels Technologies team, the Biomass Program, NREL (lead manager), ORNL, appropriate lab support contractors and subject matter experts, EPA's Office of Mobile Sources, Office of Underground Storage Tanks, and Office of Research and Development and UL. A meeting was held on March 3, 2009 to further identify issues and determine the contours of a project for testing the compatibility of infrastructure. A process of ongoing consultation with bi-weekly conference calls was established.

In preliminary testing, ORNL, in consultation with UL, NREL, and DOE, performed some tests exposing materials believed to be used in fuel dispensers to a blend of 25% ethanol. The color of the test fluid changes dramatically with prolonged exposure to the materials (see Figure 1). Hydrocarbons have been determined to have leached into the test fluids exposed to elastomers, presumably including fluorinated hydrocarbons. These could reflect loss of additives used to impart desired properties to the elastomers. Metallic corrosion products have leached into the test fluids exposed to metals, with hundreds to thousands of ppms of total metals (though these samples were exposed under accelerated aging conditions representing greater periods than would be normal exposure for dispensers).

Initially interest focused on potential use and testing of E20 including a margin of safety so that test fuels might be in the range of 25% denatured ethanol. At the March meeting, however, some participants noted that a lower concentration, possibly E15, seemed to be getting recent attention. On March 6, three days after this meeting, EPA received a petition from Growth Energy, representing the ethanol industry, to grant a waiver allowing use of E15 in gasoline. This led to a refocusing of the priorities of this project on initial testing to reflect possible use of E15 blends, and the group ultimately agreed to do most of the initial testing with a test fuel at 17% ethanol, representing E15 with a blending margin of 2%.

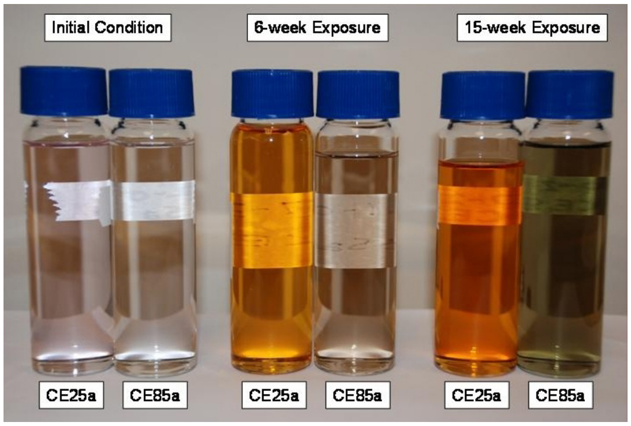

FIGURE 1. Discoloration of Ethanol Blend Test Fuels after Exposure to Materials

A process of consultation with industry groups was established, including meetings sponsored by the American Petroleum Institute (API). API and its members will sponsor some testing additional and complementary to the DOE work. Additional consultation was also held with staff and members of the Petroleum Equipment Industry Association (PEI).

As a result of the meetings and other communications in the first half of 2009, it was resolved that a test project would:

- focus on testing to address legacy equipment, including equipment harvested from use as well as the most representative samples of equipment in use in infrastructure today;
- focus on above-ground refueling systems (dispensers, components, seals and gaskets, hanging hardware and materials[1]), although some testing of materials from underground systems would be done[2] and there would be continuing consultation with EPA on its research related to underground systems;
- include harvesting and testing on legacy dispensers, components and hanging hardware for "failure testing" over a 22-24 week period with "aggressive" test fuel to simulate effects of longer term use; and
- include dynamic immersion testing (also using aggressive test fuels to simulate longer term exposures) for some new components and for samples of the types of elastomers, metals, and plastics likely to be exposed to fuels in refueling operations.

Specific models of equipment to be harvested and tested were identified as those most likely to be in widespread use through the consultations with PEI, API and other industry sources. (See Figure 2 for selected components). The failure testing at UL will use 17% ethanol in an aggressive test blend (CE17a). The immersion testing at ORNL will be with various test fuels, including Reference Fuel C (50% iso-octane/50% toluene), CE10a (aggressive 10% ethanol), CE17a (aggressive 17% ethanol to represent E15 with margin of error) and CE25a (aggressive 25% ethanol reflecting

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[1] Hanging hardware refers to nozzles and the hoses, valves and fittings that connect the nozzle to the dispenser.

[2] It was determined to be desirable to perform testing on submerged turbine pumps since their failures could substantially affect interfaces with consumers.

FIGURE 2. Examples of Dispenser System Components under Test at UL

what is believed to be the worst case fuel range for elastomers).

In September and October of 2009, ORNL obtained the components and materials for immersion testing and initiated the first round of tests in its two "stir tanks" in October of 2009 (see Figure 3). Tests on plastics and metals are being run for four week periods with the various test fuels; there will be one run of 16 weeks with elastomers and some metals on the CE17a test fuel. That first round of tests was completed in December 2009 and observations have been recorded, with data expected to be available in early 2010. During this same period, NREL identified dispensers (four) of the models previously selected coming out of service in various locations and arranged to have them harvested and shipped to UL's Northbrook, IL laboratory, while a contract to perform the testing was simultaneously executed with UL. That testing began in January of 2010.

FIGURE 3. Stir Tanks Being Used for Materials Compatibility Testing

Results

Results of the testing are not available as of end-December 2009 but will become available in 2010. All results of the current round of testing should be available by fall of 2010.

Summary

A project of testing and evaluation of the potential effects of mid-level ethanol blends (blends greater than 10% ethanol, particularly in the 11-20% range) has begun and is being guided by an interagency working group organized by and headed by DOE. The initial testing includes:

- failure tests on legacy dispensers, components, and hanging hardware (being conducted on subcontract by UL) with a test fuel representing 15% ethanol with a margin of error; and
- exposure testing of components and materials used in refueling station systems with various test and control fuels reflecting 0%, 10%, 15% and 20% ethanol with margins of error.

Results on this testing should be available by fall of 2010.

FY 2008/2009 Publications/Presentations

1. "Preliminary Compatibility Assessment of Metallic Dispenser Materials for Service in Ethanol Fuel Blends", ORNL-TM-2009-286.

2. A joint proposal was made by UL, NREL, and the Clean Vehicle Education Foundation, resulting from the collaboration sponsored by DOE and the working group, to the ICC to amend the International Fire Code (Chapters 22 and 24) to provide that equipment be compatible for blends of ethanol above 10% (to 85%) and to cover the entire system in the requirements. The proposal was accepted by the ICC and public comment is being sought before it becomes final.

3. Presentation on the mid-level blends research and issues made by Wendy Clark and Ken Boyce at the annual retreat of Clean Cities coordinators in November 2009.

4. Presentations on the mid-level issues and research were made at the PEI Education Session "E15: Are We Ready?" in November 2009 by Wendy Clark, Andrea Barbery (EPA) and Tom Chapin.

5. Technical paper "Compatibility Assessment of Fuel Dispenser Metals and Elastomers in an Aggressive E20 Fuel," by Mike Kass, Tim Theiss, Wendy Clark, Tom Chapin, Ken Boyce, et al. to be presented at the Materials Challenges in Alternative & Renewable Energy Sources 2010 conference in February 2010.

IV.10 Headspace Flammability of Gasoline/Ethanol Blends

Wendy Clark (Primary Contact),
David Gardiner (Nexum Research Corporation),
Doug Horne (Clean Vehicle Education Foundation)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401

DOE Technology Deployment Manager:
Dennis Smith

Subcontractors:
- Clean Vehicle Education Foundation, Acworth, GA
- Nexum Research Corporation, Mallorytown, Ontario, 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.

Accomplishments

- Developed the apparatus and methods needed to test the headspace vapor flammability of fuel samples.
- Tested the flammability of fuel blends including E85 samples from vehicle studies; field samples of E85, E10, E20, and E30 from commercial pumps; laboratory samples of E55–E83; two types of gasoline; and denatured ethanol.
- 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 flammability studies using a matrix that varies critical fuel blend parameters (e.g., ethanol content, vapor pressure, and hydrocarbon composition) systematically.
- Refine the apparatus and experimental methods used in this study so they can be recommended as standard test practices.
- Conduct further studies of varied candidate E85 blends for which full hydrocarbon information is known so conclusions about the accuracy and reliability of flammability modeling can be drawn.
- Study use of the flammability models to determine if tank safety could be predicted in a way simple enough for field use but more reliable than dry vapor pressure equivalent (DVPE) alone.
- Devise a technique for extracting the necessary gasoline data from the distillation (D86) data of a low-alcohol blend so modeling is more accessible to others.

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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 -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.

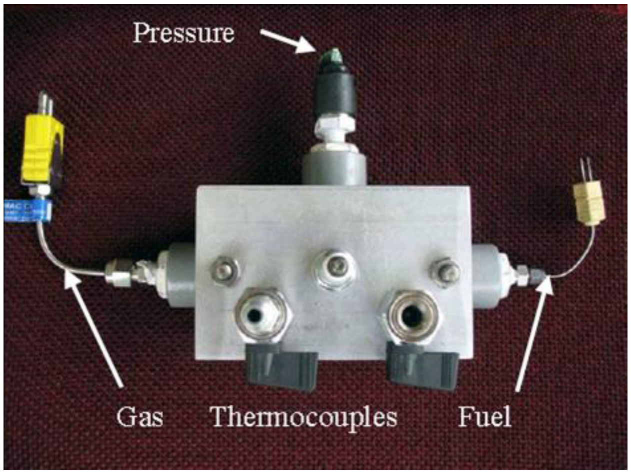

FIGURE 1. Flammability Test Chamber Used in the Study

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) were compared.

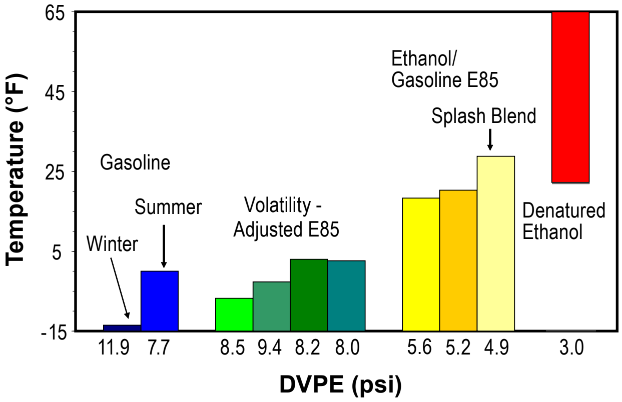

FIGURE 2. Flammability Limits of Fuel Tank Headspace Vapors (5% fill level) from Phase 1 of the Study

One of the E85 field samples produced flammable vapors over the entire ASTM D 5798-09 Class 3 temperature range (-5°C and below). The other produced flammable vapors at -10°C 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 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 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.

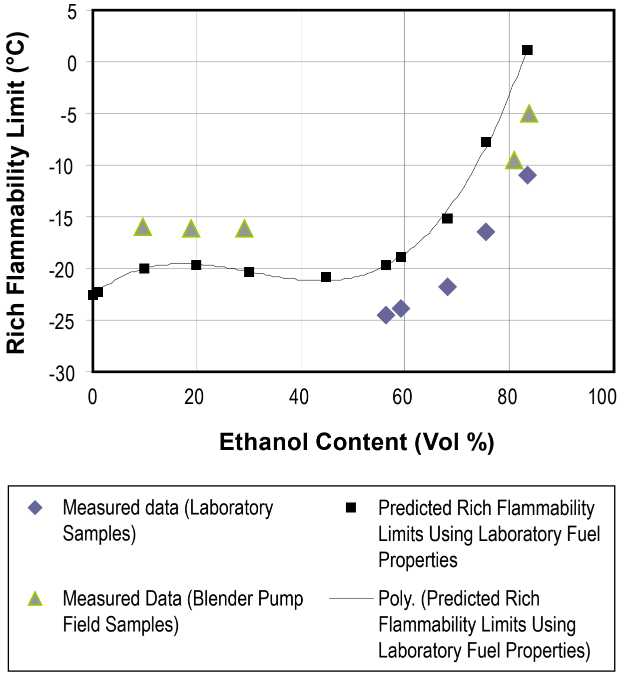

FIGURE 3. Comparison of Experimental and Modeling Results from Phase 2 of the Study

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 (-5°C 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.

FY 2008/2009 Publications/Presentations

1. Gardiner, D.; Bardon, M.; Pucher, G. 2008. An Experimental and Modeling Study of the Flammability of Fuel Tank Headspace Vapors from High Ethanol Content Fuels. NREL Report No. SR-540-44040, www.nrel.gov/docs/fy09osti/44040.pdf.

IV.11 Ethanol Engine and Vehicle Efficiency Improvement

Brian West (Primary Contact), Shean Huff,
John Thomas
Oak Ridge National Laboratory (ORNL)
2360 Cherahala Blvd.
Knoxville, TN 37932

DOE Technology Development Manager:
Kevin Stork

Objectives

- Enable reduction of petroleum imports through more efficient use of ethanol.
- Address market barrier of reduced fuel economy with ethanol use in flex-fuel vehicles (FFVs).
- Exploit properties of ethanol for more optimized engines.

Accomplishments

- Imported and baselined a European-spec Saab BioPower FFV, the first FFV optimized for 85% ethanol, 15% gasoline (E85).
- Mined Environmental Protection Agency (EPA) database to compare Saab fuel economy and emissions to U.S.-legal FFVs.
- Initiated lean-burn experiments with Saab vehicle in lean-burn mode with a novel hydrocarbon-selective catalytic reduction (HC-SCR) lean-NOx catalyst.

Future Directions

- Establish fuel economy and emissions limits of homogeneous-charge, spark-ignition, lean-burn engines with Saab vehicle and prototype lean-NOx catalysts.
- Explore additional technologies for enhancing efficiency, such as direct-injection, cylinder deactivation, variable valve timing, boosting, etc.

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Introduction

Increased use of ethanol to displace petroleum fuels is receiving renewed priority within the Department of Energy as well as nationally. In the U.S., FFVs can operate on gasoline or E85, or any blend of the two. Traditionally, these FFVs are optimized for gasoline and made to be ethanol tolerant. That is, the manufacturers have not tuned the engines to take advantage of some of ethanol's favorable properties. Power output for current FFVs on E85 fuel is typically on par with the gasoline rating, and the vehicles suffer a considerable 25-30% loss in "tank mileage" when running on E85 due to its lower energy density. Despite equivalent or slightly improved fuel efficiency (distance per unit energy), this range shortfall is considered a significant obstacle to wide-spread consumer acceptance of FFVs. Ethanol has several properties that make it attractive as a spark-ignition engine fuel, such as high octane, flammability limits at leaner air:fuel ratios than conventional gasoline, high latent heat of vaporization, and it is a very effective reductant for certain types of lean NOx catalysts. Engines specifically designed to take advantage of ethanol's properties should be capable of improved thermal efficiency, and thus improved vehicle fuel economy, thereby reducing the tank mileage loss with E85 use, as well as further reducing petroleum imports.

The Saab BioPower vehicle is an FFV than can burn gasoline or E85, but it is optimized for use with E85. Through higher turbocharger boost pressures and more advanced spark timing (enabled by E85's higher octane rating), the engine's power rating is 20% higher with E85 fuel. ORNL acquired a new Saab BioPower for benchmark evaluation in 2007. Applicable European regulations (Euro 4) only require FFVs to meet emissions standards on gasoline. As this vehicle was reportedly performance-optimized for E85 operation, there was interest in determining what effect, if any, this performance tuning had on emissions or fuel economy, and whether such tuning might be the basis for improved ethanol tank mileage on future vehicle designs. Following the benchmark exercise, the Saab became the platform for researching means to improving FFV fuel economy through lean-combustion.

Approach

Chassis dynamometer experiments are being conducted to accomplish this work. The vehicle is driven over standard transient drive cycles such as the Federal Test Procedure (also known as Urban Dynamometer Driving Schedule), the Highway Fuel Economy Test, and the high-speed, high-load US06 test (also referred to as Supplemental Federal Test Procedure). Emissions and fuel consumption on each of these cycles are measured for both gasoline and E85 fuel, and results can then be compared with data from similar tests on other, comparable vehicles.

Lean-burn experiments are conducted by forcing the engine control unit (ECU) to command less than the necessary fuel for stoichiometric operation. Modern vehicles operate in a closed-loop mode most of the time, by monitoring oxygen content in the exhaust. The "switching type" oxygen sensor detects rich or lean conditions in the exhaust and the ECU dithers the air:fuel ratio slightly rich to slightly lean, maintaining a net stoichiometric air:fuel ratio.

Lean-burn experiments on the Saab were conducted in a closed-loop mode by installing a wide-range oxygen sensor next to the factory switching sensor. The factory sensor signal to the ECU was intercepted and replaced with a biased signal based on the wide-range sensor. In this way, a desired air:fuel ratio could be achieved and controlled in a closed-loop mode by the factory ECU. The air:fuel ratio is on a mass basis (grams air per gram of fuel), but a non-dimensional term is often preferred, this term is lambda, also known as the excess air factor. Lambda is defined as the actual air:fuel ratio divided by the stoichiometric air:fuel ratio; thus lamda = 1.0 is stoichiometric, and lambda>1.0 indicates the degree of enleanment.

Prototype catalysts capable of NOx reduction in an overall lean environment were installed downstream of the factory catalysts. An in-pipe ethanol spray system was developed for introducing reductant to the lean-NOx catalysts for NOx reduction.

Results

In 2007, a Saab 9-5 BioPower was imported and benchmarked against U.S.-legal FFVs under the auspices of the Office of the Biomass Program. A comprehensive discussion of the benchmarking of this European FFV is too detailed to discuss here, but can be found in a recent SAE publication [1]. In summary, the vehicle emissions were found to be within U.S. limits (although not tested at full useful life), the relative fuel economy on E85 and gasoline was found to be on par with, or slightly better than U.S.-legal FFVs, and the 20% power increase with E85 was confirmed and found to offer about a 1 second quicker acceleration to 60 mph over that with gasoline fuel.

Following the completion of the Saab benchmark, modifications to the vehicle were made to enable closed-loop lean operation. The intercept control system developed successfully allows the vehicle to operate in a closed-loop mode at a target lambda other than 1.0. Initial drive cycle experiments have been successfully run with lambda as high as 1.4. Figure 1 shows the first 500 seconds of the FTP driving cycle for two experiments, one with factory air:fuel ratio control at stoichometry (lambda=1.0), and a second demonstrating the closed-loop operation at lambda 1.3. Fuel shut-off during deceleration is evident in both curves when lambda goes above 1.5 (lambda actually goes to infinity, but the sensor is setup to read only to 1.5). Using this intercept control, repeated hot-start city driving tests were conducted at various target lambda values. Figure 2 shows that enleanment nets a fuel economy improvement up to lambda of 1.15, but fuel economy quickly drops off at higher lambda. The intercept control can adjust lambda, but the factory spark timing is still retained. Advancing spark timing as lambda is increased would improve the fuel economy at higher lambda.

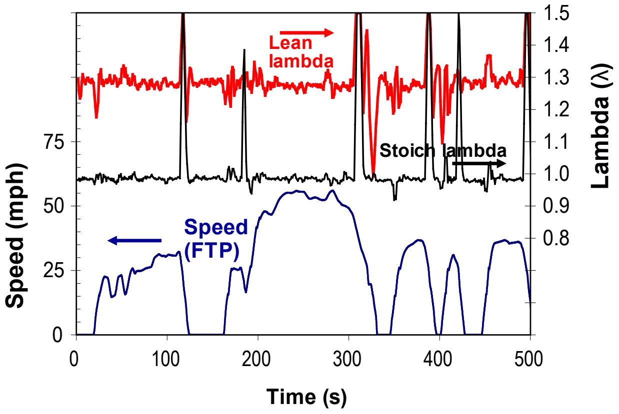

FIGURE 1. Segment of Federal Test Procedure showing factory closed-loop control at stoichiometry and intercept control at lambda 1.3.

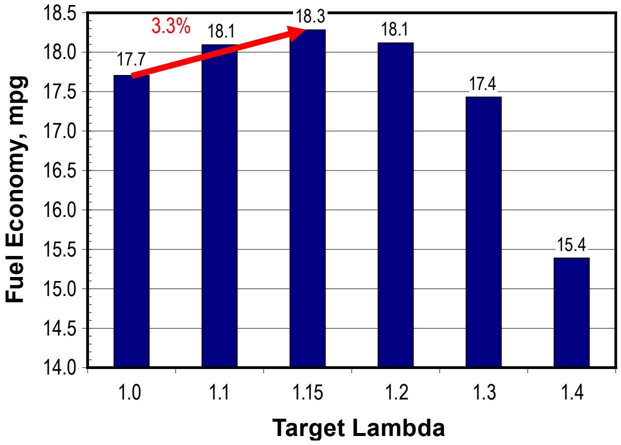

FIGURE 2. Fuel economy on hot-start city tests versus target lambda.

A novel lean-NOx catalyst was procured through an industrial partner (Catalytic Solutions). This silver-alumina (Ag/Al_2O_3) formulation is known to be particularly well-suited to NOx control in lean environments with ethanol or other alcohols as reductants [2,3]. As shown in Figure 3, preliminary steady-state experiments show excellent NOx conversion at two realistic space velocities, temperatures, and at low hydrocarbon to NOx ratios. Space velocity (gas flow rate divided by catalyst volume, units hr^{-1}) is a measure of the "changeovers per hour" in the catalyst. The higher the space velocity, the higher the flow rate through the catalyst. Lambda for these experiments ranged from 1.2 to 1.3, and the reductant used was

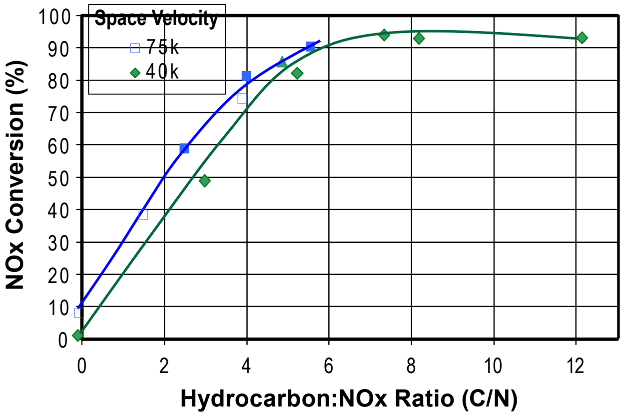

FIGURE 3. NOx conversion versus hydrocarbon:NOx ratio for two exhaust conditions. Gas temperature for 75k space velocity 420-430°C; for 40k space velocity 290-300°C.

E85 fuel. Unburned fuel emissions at the tailpipe were noted, however. Oxidation catalysts for tailpipe "clean up" have been procured for follow-on experiments. Despite the modest fuel economy improvements through enleanment without spark control, the vehicle provides a robust platform for investigating the efficacy of the novel silver-alumina lean-NOx catalysts for lean ethanol-fueled applications.

Conclusions

- Saab BioPower FFV imported and compared to U.S.-legal FFVs. Findings include:
  - Power increase with E85 use confirmed through acceleration tests.
  - E85 fuel efficiency slightly better than U.S.-legal FFVs on the city test.
  - Emissions on U.S. cycles are within Tier 2, Bin 5 levels.
- Closed-loop, lean operation achieved through intercept control (without spark control) yields modest fuel economy improvement.
  - Lean-burn platform well-suited to assessing advanced lean-NOx catalysts.

References

1. West, Brian H., Alberto J. Lopez, Timothy J. Theiss, Ronald L. Graves, John M. Storey, and Samuel A. Lewis, "Fuel Economy and Emissions of the Ethanol-Optimized Saab 9-5 BioPower", SAE Paper No. 2007-01-3994, October 2007.

2. Kass, Michael D., John F. Thomas, Samuel A. Lewis, John M. Storey, Norberto Domingo, Ron L. Graves, Alexander Panov, "Selective Catalytic Reduction of NOx Emissions from a 5.9 Liter Diesel Engine Using Ethanol as a Reductant," SAE Paper No. 2003-01-3244.

3. John F. Thomas, Samuel A. Lewis, Bruce G. Bunting, John M. Storey, Ronald L. Graves, Paul W. Park, "Hydrocarbon Selective Catalytic Reduction Using a Silver-Alumina Catalyst with Light Alcohols and Other Reductants," SAE Paper No. 2005-01-1082.

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1. West, Brian H., Alberto Lopez, Tim Theiss, Ron Graves, John Storey, and Sam Lewis, "Fuel Economy and Emissions of the Ethanol-Optimized Saab 9-5 BioPower", SAE Paper No. 2007-01-3994, *SAE 2007 Transactions, Journal of Engines*, Section 3 - Volume 116, pp 1191-1200.

2. West, Brian, Shean Huff, John Thomas, Robert Wagner, Jim Szybist, Dean Edwards, "Enhanced Ethanol Engine and Vehicle Efficiency," Office of Vehicle Technologies Annual Merit Review, Bethesda, MD, February 2008.

Special Recognitions & Awards/Patents Issued

1. Brian West received the SAE Excellence in Oral Presentation Award for the "Fuel Economy and Emissions of the Ethanol-Optimized Saab 9-5 BioPower" presentation at the Fall SAE Powertrain and Fluid Systems Conference (SAE 2007-01-3994), October 2007.

2. Brian West received the Lloyd L. Withrow Distinguished Speaker Award at the 2009 SAE Congress, April 2009.

IV.12 Effect of Mid-Level Ethanol Blends on Conventional Vehicle Emissions

Keith Knoll
National Renewable Energy Laboratory
1617 Cole Blvd., MS1634
Golden, CO 80401

Brian West
Fuels, Engines and Emissions Research Center
Oak Ridge National Laboratory
2360 Cherahala Blvd.
Knoxville, TN 37932

DOE Technology Development Manager:
Kevin Stork

Objectives

- The primary objective of this work was to quantify the immediate impacts of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on regulated tailpipe emissions and fuel economy.
- Secondary objectives were to explore potential areas of concern – beyond immediate emissions impacts – that may require further investigation; such as increased catalyst temperature, malfunction indicator light illumination, solvency (i.e., filter plugging), and driveability.

Accomplishments

- Sixteen vehicles were tested on the LA92 drive cycle operating on E0, E10, E15, and E20.
- On average, regulated tailpipe emissions were found to be unaffected by ethanol content above 10%. Fuel economy was found to decrease with ethanol content, consistent with energy content of the fuel.
- Tailpipe emissions were found to differentiate according to power-enrichment fuel trim strategy. Vehicles that did not apply learned-fuel trim at power-enrichment showed decreases in hydrocarbon and carbon monoxide (CO) emissions and increases in oxides of nitrogen (NO_X) emissions as ethanol content increased. Vehicles that applied learned-fuel trim at power-enrichment showed no significant change in regulated emissions with ethanol content.
- Peak catalyst temperatures during power enrichment operation increased with increasing ethanol content for vehicles found to not apply learned-fuel trim at power-enrichment; about half the vehicles tested.

Future Directions

- A full-useful life vehicle study is underway to examine the long-term emissions impact of observed peak catalyst temperature increases with increasing ethanol content during power-enrichment.

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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 establishes 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 DOE remains committed to expanding the flexible-fuel vehicle fuel infrastructure (i.e., E85), that market will not be able to absorb projected volumes of ethanol in the near term. Given this reality, DOE and others have begun 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

Vehicle testing was conducted using the LA92 drive cycle, also known as the Unified Cycle [2], executed as a three-phase test similar to the regulatory Federal Test Procedure (FTP). Composite emissions were calculated using the same weighting factors as specified for the FTP. Regulated emissions were measured via full-flow dilution per Code of Federal Regulations 40 part 86 guidelines using standard laboratory measurement techniques. Aldehydes were measured using dinitrophenylhydrazine cartridges with post-processing via high-performance liquid chromatography. Ethanol emissions were measured using the Innova Photoacoustic Multi-Gas Analyzer. Vehicles were instrumented with universal exhaust gas oxygen sensors to monitor fuel:air equivalence ratio. Some vehicles were also instrumented via the assembly line data link to monitor long-term and short-term fuel trim data.

Sixteen vehicles were chosen for this study using a database purchased from R. L. Polk & Co. which characterized the population of registered, light-duty vehicles in the U.S. fleet in 2007. Selection was based primarily on sales volume, but also considered vehicle manufacturer and engine configuration (number of cylinders and displacement). Vehicle model years were chosen to span the regulatory periods of interest including Tier 1 (1996 thru 1999), Tier 2 transitional (2000 thru 2004), and full Tier 2 compliance (phased in from 2004 thru 2007). A list of test vehicles is shown in Table 1.

Results

COMPOSITE EMISSIONS - AGGREGATE VEHICLE SET – Aggregate vehicle emissions trends for the 16 vehicles are shown in Figures 1 and 2. Figure 1 shows percent-change in regulated tailpipe emissions and fuel economy versus E0, while Figure 2 shows the magnitude-change of ethanol and percent-change of acetaldehyde and formaldehyde emissions relative to E0. Ethanol mass emissions are multiplied by 10 to allow for common y-axis scaling. Individual data points represent individual vehicle results, while bars indicate changes for all vehicles on average. Darker shaded bars (and asterisks along x-axis), indicate statistically significant results. Lighter shaded bars indicate results that are not statistically significant.

Non-methane hydrocarbons (NMHC) and CO both showed statistically significant reductions of about 10% to 15% with increasing ethanol content. This change occurred primarily with 10% ethanol addition; E15 and E20 showing no further reduction. Fuel economy showed a statistically significant reduction with increasing ethanol content, closely matching the energy content of the fuel. NMOG and NO_X emissions showed no statistically significant trend. Ethanol and acetaldehyde emissions showed statistically significant increases for all ethanol concentrations above E0. Formaldehyde emissions showed statistically significant increases for all ethanol concentrations above E0, but no significant change beyond 10% ethanol addition.

POWER-ENRICHMENT – During high-load conditions, such as wide-open-throttle (WOT), a modern vehicle's engine control unit switches from closed-loop stoichiometric operation to power-enrichment (i.e., fuel-enrichment) mode to reduce exhaust gas temperatures, protecting both engine and exhaust emission control components from thermal damage. Two fuel trim strategies are commonly employed during power-enrichment: those that apply previously learned long-term fuel trim (LTFT) to power-enrichment fueling and those that do not [3].

TABLE 1. Test Vehicle List

Manufacturer	Model	Model Year	Engine (Displacement, Cylinders)	Initial Odometer (Miles)	EPA Engine Family	Emission Standard
Honda	Accord	2007	2.4 L, I4	11,400	7HNXV02.4KKC	Tier 2, Bin 5
Nissan	Altima	2003	3.5 L, V6	53,300	3NSXV03.5C7A	LEV
Toyota	Camry	2003	2.4 L, I4	72,800	3TYXV02.4HHA	ULEV
Toyota	Camry	2007	2.4 L, I4	26,440	7TYXV02.4BEB	Tier 2, Bin 5
Honda	Civic	1999	1.6 L, I4	79,680	XHNXV01.6TA3	Tier 1
Toyota	Corolla	1999	1.8 L, I4	96,400	XTYXV01.8XBA	Tier 1
Ford	Crown Victoria	1999	4.6 L, V8	50,900	XFMXV04.6VBE	ULEV
Ford	F150	2003	5.4 L, V8	57,000	3MFXT05.4PFB	Tier 1, LEV
Ford	F150	2007	5.4 L, V8	28,600	7FMXT05.44H7	Tier 2, Bin 8
VW	Golf GTI	2004	1.8 L, I4-T	32,900	4ADXV01.8356	Tier 2, Bin 8
GM (Buick)	LeSabre	2003	3.8 L, V6	78,000	3GMXV03.8044	Tier 2, Bin 8
GM (Buick)	Lucerne	2007	3.8 L, V6	10,000	7GMXV03.9146	Tier 2, Bin 5
Chrysler	PT Cruiser	2001	2.4 L, I4	93,400	1CRXV02.4VD0	NLEV
GM (Chevrolet)	Silverado	2007	4.8 L, V8	12,800	7GMXT05.3379	Tier 2, Bin 8
Ford	Taurus	2003	3.0 L, V6	89,600	3FMXV03.0VF3	Tier 2, Bin 8
Chrysler	Town & Country	2007	3.3 L, V6	35,000	7CRXT03.8NEO	Tier 2, Bin 5

LEV - low emission vehicle; ULEV - ultra low emission vehicle; NLEV - national low emission vehicle

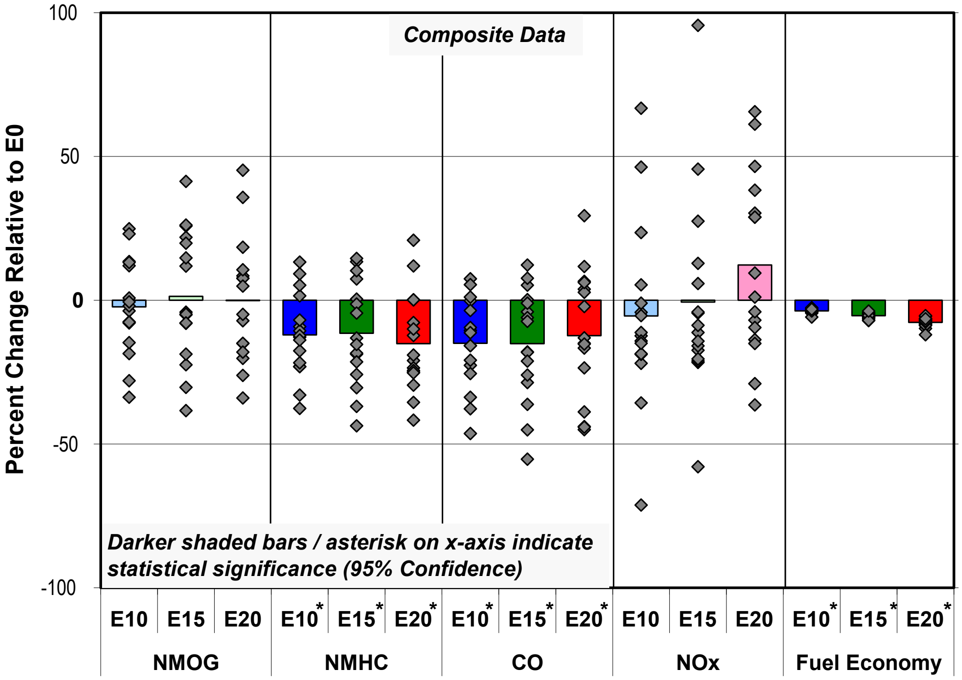

FIGURE 1. Average Percent Change in Emissions and Fuel Economy Relative to E0

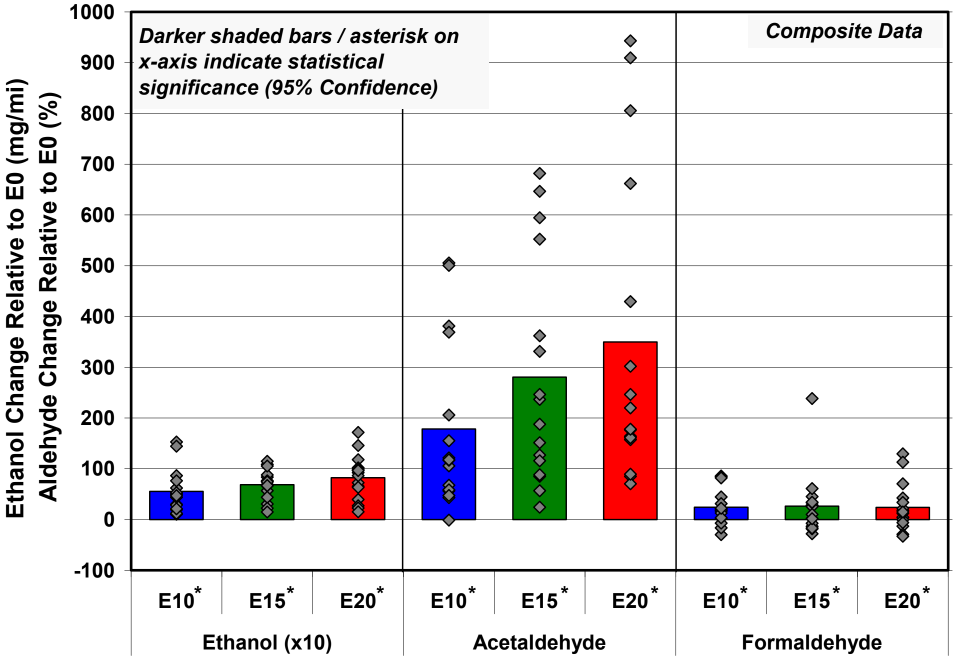

FIGURE 2. Average Change in Ethanol and Aldehyde Emissions Relative to E0

Of the 16 vehicles included in the current study, seven were determined to not apply LTFT to power-enrichment operation. For these vehicles, the decreased fuel:air equivalence ratio observed during power-enrichment at WOT roughly corresponded with the increased oxygen content of the ethanol containing fuels. For the balance of vehicles tested (9 of 16), the fuel:air equivalence ratio remained nearly constant during power-enrichment operation as ethanol content in the fuel increased.

POWER-ENRICHMENT EFFECT ON EMISSIONS – Figures 3 and 4 show composite emission trends for the 16-vehicle fleet with average values separated according to power-enrichment fueling strategy. Red and pink shaded bars (left bar of each pair) indicate average values for vehicles which did not apply LTFT during power-enrichment, while blue and light blue bars (right bar of each pair) indicate average values for vehicles which applied LTFT during power enrichment. Darker shaded bars (and asterisks along x-axis) indicate statistically significant results at the 95% confidence level. Individual data points show individual vehicle results.

Figure 3 shows regulated emissions and fuel economy as a percent change relative to E0. Figure 4 shows ethanol and aldehyde emissions change relative to E0; ethanol as a magnitude change, acetaldehyde and formaldehyde as a percent-change. Vehicles that applied LTFT to power-enrichment operation showed no statistically significant change in non-methane organic gases (NMOG), NMHC, CO or NO_X emissions for any ethanol content through E20 relative to E0. Vehicles that did ***not*** apply LTFT to power-enrichment operation showed no statistically significant change in NMOG emissions. NMHC and CO both showed statistically significant reductions as ethanol content increased from E0 while NO_X emissions for this vehicle subgroup showed a statistically significant increase for E20. These trends were generally consistent with earlier results found by EPA for Tier 0 vehicles [4].

As shown in Figure 4, ethanol and acetaldehyde emissions exhibited statistically significant increases for both vehicle subgroups when compared with E0. Statistically significant formaldehyde increases were observed only for vehicles that applied LTFT to power-enrichment operation and only for E10 and E20 fueling.

CATALYST TEMPERATURE EFFECTS – Ethanol effects on peak catalyst temperature during WOT acceleration are shown in Figure 5. As expected, vehicles that did not apply LTFT to power-enrichment conditions were found to exhibit higher peak catalyst temperatures during WOT operation as fuel-ethanol content increased. For E20 fueling, peak catalyst temperatures were seen to increase by an average of 30°C over the E0 values. Vehicles that were found to apply LTFT during WOT acceleration showed no significant change in peak catalyst temperature with ethanol content.

Conclusions

- On average, increasing ethanol content from 0% to 20% resulted in no significant impact on composite emissions of NMOG and NO_X. NMHC and CO both decreased, however, ethanol, acetaldehyde and formaldehyde emissions increased.
- Vehicles that applied LTFT to power-enrichment operation showed no significant effect of ethanol content on LA92 composite emissions for NMOG,

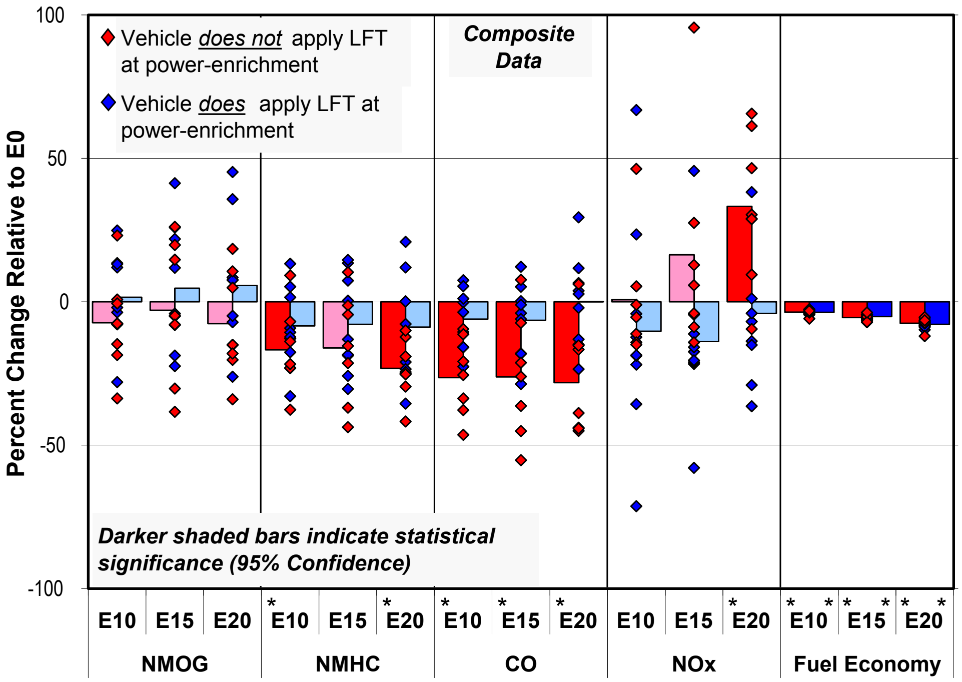

FIGURE 3. Average Percent Change in Emissions and Fuel Economy Relative to E0 Differentiated by Power-Enrichment Fuel Trim Strategy

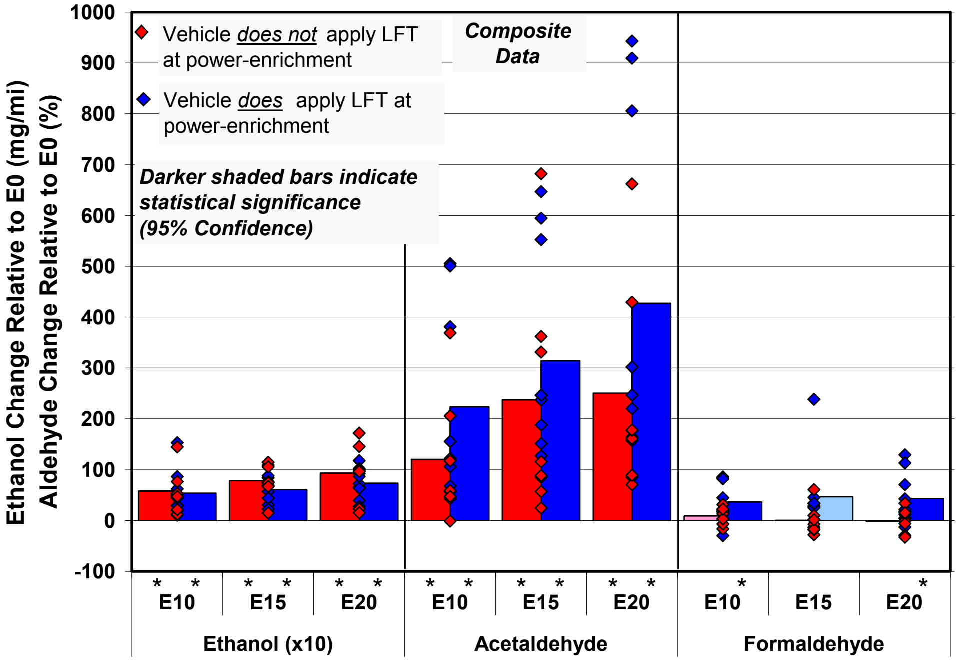

FIGURE 4. Average Change in Ethanol and Aldehyde Emissions Relative to E0 Differentiated by Power-Enrichment Fuel Trim Strategy

NMHC, CO, or NO_X. Composite emissions of ethanol, acetaldehyde and formaldehyde, however, increased with increasing ethanol content.

- Vehicles that did not apply LTFT to power-enrichment operation showed reductions in NMHC and CO and increases in NO_X, ethanol, and acetaldehyde with increasing ethanol content. Formaldehyde emissions were mostly unchanged.

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1. K. Knoll, B. West, S. Huff, J. Thomas, J. Orban, C. Cooper, "Effects of Mid-Level Ethanol Blends on Conventional Vehicle Emissions, SAE Technical Paper 2009-01-2723, 2009.

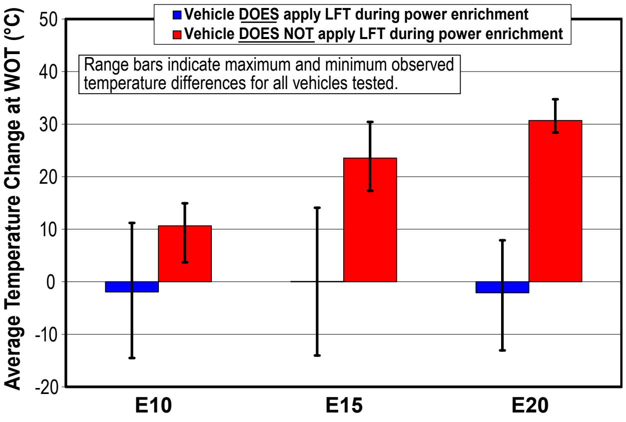

FIGURE 5. Change in Catalyst Temperature versus Fuel Type for WOT Power-Enrichment Conditions

2. K. Knoll, B. West, W. Clark, R. Graves, J. Orban, S. Przesmitzki, T. Theiss, "Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines, Report 1 – Updated," NREL/TP-540-43543 and ORNL/TM-2008/117, February 2009.

FY 2008/2009 Presentations

1. 19th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, March 23–25, 2009.

2. SAE Powertrains, Fuels and Lubricants Meeting, San Antonio, TX, November 2–5, 2009.

IV.13 The Use of Exhaust Gas Recirculation to Optimize Fuel Economy and Minimize Emissions in Engines Operating on E85 Fuel

Ko-Jen Wu
General Motors Powertrain
895 Joslyn Avenue
Pontiac, MI 48340

DOE Technology Development Manager:
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 thru simulation and testing.
- Develop and optimize engine management system functions and calibrations to maximize FE of the demo vehicle.

Accomplishments

- Simulation capabilities have been developed to help select, design and optimize exhaust gas recirculation (EGR) systems for flex-fuel turbocharged applications.
- Dynamometer testing has demonstrated the fuel consumption benefits of cooled 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%.

Future Directions

- Develop engine management system functions and optimize engine calibrations.
- Complete demo vehicle build and testing.

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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 FE 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 FE thru downsizing. This engine technology is in particular capable of exploiting ethanol fuel's characteristics of high octane number and high latent heat of evaporation. Additional synergistic FE technologies include:

- Cooled EGR which enables the engine to operate more frequently at stoichiometric air-fuel ratios with favorable spark timings for lower fuel consumption and the use of a conventional three-way catalyst for exhaust aftertreatment.
- Direct fuel injection.
- Dual continuously variable cam phasers for both intake and exhaust valves.
- Six-speed automatic transmission.

Approach

The research/development approach is to apply state-of-the-art simulation tools in conjunction with engine testing to address each of the project challenges so an optimized engine that is capable of achieving the objectives of the project can be developed and demonstrated in a vehicle. The simulation tools have been extensively used to size components and to guide initial engine design by translating the results into design specifications for the engine system for dynamometer testing, to compare performance of different engine system configurations, to select test points for steady-state dynamometer testing, and to investigate the transient behaviors of the engine in the demo vehicle.

The project is divided into separate, but interrelated, phases. By iterating between simulation and testing, the simulation tools have been further refined by correlating the predicted results to data and then applied to design parts of refined specifications to be used to build the demo vehicle.

Results

Two common ways of recirculating exhaust gas in a turbocharged engine are illustrated in Figure 1 for the four-cylinder engine used for this project. As the names imply, exhaust gas flows from a post-turbine location to a pre-compressor location in the low-pressure EGR system and from a pre-turbine location to a post-compressor location in the high-pressure EGR system.

The performance of each of the EGR systems was evaluated with a commercially-available GT Power simulation tool [1] at three key engine speeds of 1,500, 3,000 and 5,300 rpm under full-load conditions. The predicted tradeoffs between airflow, normalized by flow rate without EGR for each engine speed, and EGR rate are shown in Figure 2.

At 5,300 rpm, which is about the peak power engine speed, both systems can perform quite well for up to about 12% EGR by modulating the wastegate. Beyond that, airflow rate starts to decrease with increasing EGR rate as more and more air is displaced by exhaust gases.

At either 3,000 or 1,500 rpm, however, EGR flow cannot be established with the high-pressure system due to the lack of correct pressure drops with the turbo system on this engine.

The engine was predicted to perform quite well at 3,000 rpm with the low-pressure EGR system. At 15% EGR rate, the predicted air flow loss is about 5%.

At 1,500 rpm, the engine air flow suffers substantial degradation with the low-pressure EGR system. Air flow decreases with increasing EGR at a rate substantially steeper than the previous two engine speeds as air is displaced by exhaust gases.

The performance of the low-pressure EGR system was further investigated by simulation for its operation in the intended demo vehicle during launch from standstill. The sample results shown in Figure 3 for the first 3 seconds of vehicle behavior suggests that the low-pressure EGR system is capable of meeting the performance requirement of delivering 15% as the engine torque exceeds 300 N-m.

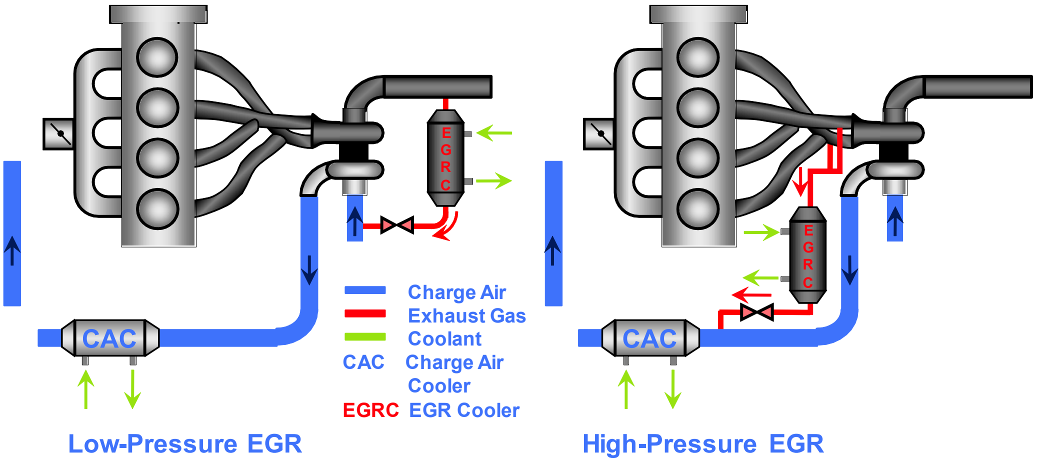

FIGURE 1. Schematics of Low- and High-Pressure EGR Systems

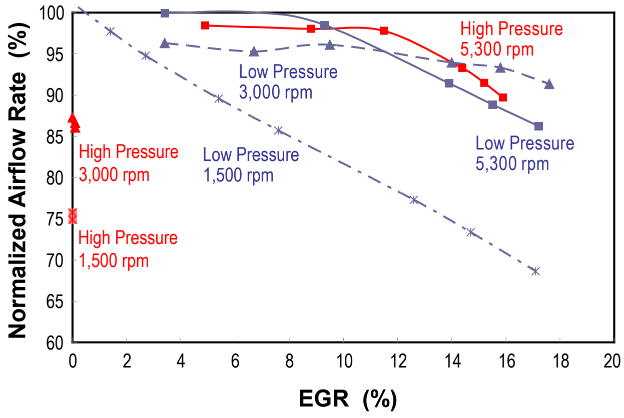

FIGURE 2. Comparison of Predicted Steady-State Performance between Low- and High-Pressure EGR Systems

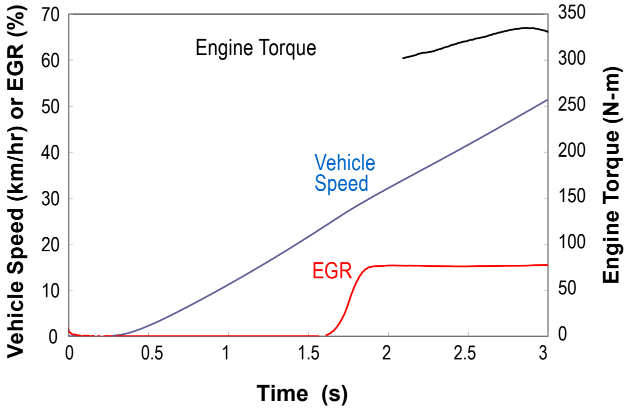

FIGURE 3. Predicted Launch Transient Response of the Optimized EGR Engine System in the Demo Vehicle

Judging from the simulation results, the low-pressure EGR system was chosen for the subsequent dynamometer evaluation and vehicle controls and calibration development.

Figure 4 shows sample fuel consumption and brake thermal efficiency (BTE) data at 1,355 rpm and 134 N-m of torque for both E85 and gasoline (EEE) fuels. As expected, brake specific fuel consumption (BSFC) for E85 decreases with increasing EGR rate until about 25% EGR rate where it reaches a minimum. BSFC for gasoline shows similar characteristics, although the absolute values are substantially lower due to the difference in energy content between the two fuels. The improvements in BSFC between the best EGR case and no EGR are 4.9 and 4.3% for E85 and gasoline, respectively.

When the comparison is made in BTE, using E85 fuel results in slightly higher thermal efficiency than gasoline on an equal EGR basis.

The steady-state fuel consumption data was further analyzed to project the demo vehicle's FE over the combined urban and highway cycles. The predicted FE improvements over several V6 engines are shown in Figure 5 for both E85 and gasoline fuels. With EGR, the FE gain is in the range of 13-17%, for either fuel, suggesting the potential of meeting the project's FE target. Among the predicted FE gains, about 1.5% results from cooled EGR.

A flex-fuel powertrain system, that incorporates a turbocharged engine with the optimized low-pressure EGR system and a six-speed automatic transmission for front wheel drive installation, was further refined to package in the intended demo vehicle. Figure 6 illustrates the design of the powertrain.

Conclusions

- Simulation capabilities have been developed to help select, design and optimize EGR systems for the flex-fuel turbocharged engine.
- Cooled EGR is as effective for E85 as for gasoline in lowering the flex-fuel turbocharged engine's fuel consumption over a broad range of operation.
- FE gain predicted from dynamometer data at conditions selected to represent the combined urban and highway driving cycles is in the range of 13-17%.

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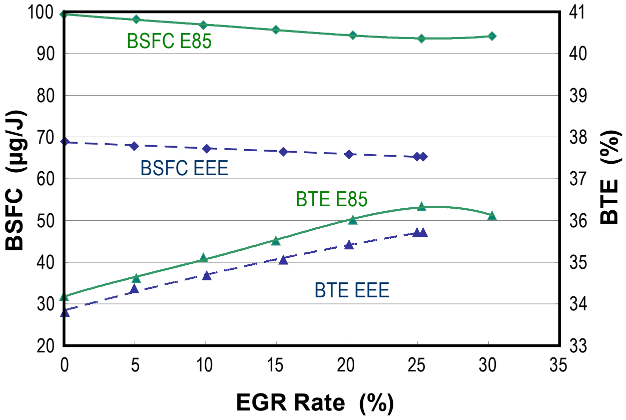

FIGURE 4. Steady-State Fuel Consumption and Thermal Efficiency Data at 1,355 rpm and 134 N-m Torque

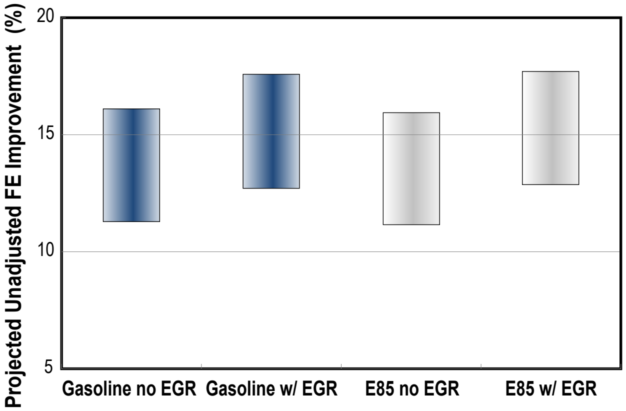

FIGURE 5. Predicted Combined Urban and Highway FE Gains for E85 and Gasoline Fuels over Several V6s

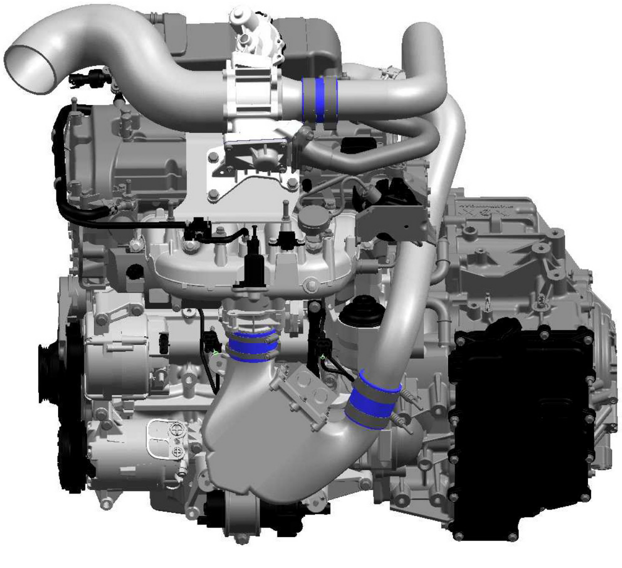

FIGURE 6. Turbo Powertrain System for EGR Demonstration Vehicle

Special Recognitions & Awards/Patents Issued

Two patent applications are being prepared.

IV.14 Optimally Controlled Flexible Fuel Powertrain System

Paul Kilmurray
MAHLE Powertrain, LLC
41000 Vincenti Court
Novi, MI 48375-1921

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager: Michael Ursic

Subcontractors:
- Michigan State University, Lansing, MI
- Argonne National Laboratory, Argonne, IL
- Visteon Corporation, Van Buren Township, MI

Project Objectives

The overall project object is to demonstrate a new, commercially-viable engine 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 level 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 to the nation of using E85 fuel.

Fiscal Year 2008 and 2009 objectives were as follows:

- Perform a detailed simulation of the proposed I-3 engine with optimization.
- Compare simulated benefits to an existing equivalent comparator engine.
- Perform social benefit analysis of potential fuel savings.
- Complete detailed MAHLE R3 engine design update and ordering of tooling changes and major components for revised flex-fuel engine variant.
- Design and fabrication of a single-cylinder optical access engine (for combustion and in-cylinder flow studies).
- Update fuel injector design.
- Design of ionization-based ignition system (to be utilized for closed-loop combustion control - CLCC).
- Complete control system design (engine control system including capabilities for both direct injection [DI] and CLCC).
- Base comparator engine procurement and instrumentation (typical gasoline engine used to provide baseline data).
- Perform a detailed simulation and analysis for the proposed I-3 study engine and a baseline 2.2 L DI engine for both gasoline and ethanol blends. Using GT-Power (engine) and ADVISOR (engine in vehicle) modeling, provide comparisons of fuel economy and performance.
- Initial assessment of the hardware technical and economic viability.
- Social Benefits Analyses – for fuel saving and emission reduction for U.S. from ‘oil well to pump’.
- In-cylinder computational fluid dynamics (CFD) modeling (injector spray).
- Procurement of test engine parts.
- Mean value engine model development.

Accomplishments

- Engine modeled and vehicle simulations completed with gasoline and E85. The MAHLE R3 (see Figure 1) and General Motors (GM) 2.2 L Ecotec engine models were simulated within a

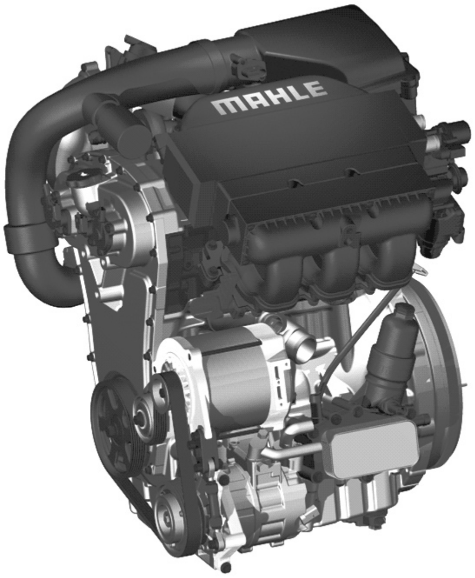

FIGURE 1. The MAHLE R3 Engine

vehicle model paramerized as a Chevrolet Cobalt. The R3 vehicle running on E85 was found to have 10% worse fuel economy (volumetric) than the 2.2 L Ecotec running with gasoline. This compares favorably with the typical ~30% reduction in volumetric fuel economy seen when a flex-fuel vehicle (FFV) is operated with E85 compared to gasoline. The E85 fuelled R3 was also found to have a 20% improvement in vehicle performance (0–60 mph wide-open throttle acceleration) compared to the Ecotec with gasoline.
- Greenhouse gas reduction of 33% predicted, compared to an equivalent gasoline engine.
- Single-cylinder optical test engine designed and under construction for combustion analysis.
- CFD model for injector spray characteristics and combustion.
- A mean-value engine model has been developed, validated and implemented into a dSPACE hardware-in-the-loop (HIL) simulator, for control validation.
- Initial hardware designed and ordered for DI, ignition and CLCC systems.
- Modeling adherence to 140 bar cylinder pressure limit and low exhaust temperatures for fuel blends indicate that an optimized E85 R3 engine is viable.
- Optical engine design complete.

Future Directions

- Finalize injector design/selection.
- Fabrication of injectors.
- Injector spray characterization (with optical engine).
- Evaluate performance of single-cylinder optical engine with blends of E85 and gasoline.
- Cold-flow injection tests with varying boost and injection timing.
- Combustion tests with varying injection timing, boost pressure, ignition energy and timing.
- Evaluate performance of the single-cylinder metal engine.
- Fuel economy and emission tests for blends of E85 and gasoline.
- E85 tests including cold start.
- Assemble optimized MAHLE R3 engine.
- Assemble control system.
- Complete break-in dyno tests.
- Test optimized R3 engine.
- Performance and emissions tests for E10, E85 and ethanol blends.
- Cold-start capability tests.
- Estimate drive cycle fuel economy, based on dyno tests.
- Results, analysis and reporting.
- Report engine efficiency and fuel economy results, compared to targets.
- Analysis of commercial feasibility of final design.

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Introduction

Current FFVs typically see a reduction in fuel economy of around 30%, when operating on E85 compared to gasoline. The purpose of this project is to demonstrate a flex-fuel powertrain that is optimized for E85, reducing the fuel economy penalty when using E85.

Approach

The overall approach is as follows:

- Develop a flexi-fuel powertrain that provides volumetric fuel economy, 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, such that it is optimized for E85. The GM 2.2 L DI Ecotec engine will be used as the equivalent comparator engine – refer to Table 1 for specifications.
- 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:
  - DI
  - Turbocharging
- Increased Compression Ratio: Takes advantage of ethanol's higher octane rating and increased heat of vaporization.
- Variable Valve Control, Exhaust Gas Recirculation: Allow optimization across the speed/load map, minimize pumping losses and optimize the combustion process.
- CLCC: Enables fully flexible fuel operation.
- Low-Pressure DI: Offers reduced parasitic losses.

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

- Simulation:
  - Combustion system (GT-Power)
  - Vehicle effects (ADVISOR)

TABLE 1. Specifications of Engines under Study

	GM Ecotec Comparator	Initial Gasoline MAHLE R3	Proposed FFV MAHLE R3
Displacement	2198 cc	1200 cc	1200 cc
Cylinders	4	3	3
Bore / Stroke	86.0 mm / 94.6 mm	83.0 mm / 73.9 mm	83.0 mm / 73.9 mm
Fuel Injection	Direct	Direct	Direct
Aspiration	Naturally Aspirated	Turbo	Turbo
Max Power	114 kW @ 5600 RPM 155 PS @ 5600 RPM	132 kW @ 6000 RPM 180 PS @ 6000 RPM	132 kW @ 6000 RPM 180 PS @ 6000 RPM
Specific Power	51.9 kW / Liter 70.5 PS / Liter	110.8 kW / Liter 150 PS / Liter	110.8 kW / Liter 150 PS / Liter
Max Torque	220 Nm @ 3800 RPM	286 Nm @ 3000 RPM	286 Nm @ 3000 RPM
Compression Ratio	12.0 : 1	9.25 : 1	12.5 to 14.5

  - Social benefit (GREET)
  - High-level component requirements
- Combustion System Design:
  - Injector analysis (CFD)
  - Ignition system design
  - Detailed 1-dimensional (GT-Power)
  - Control system design (CLCC)
  - Optical engine design
- System Assembly/Baseline:
  - Low-pressure DI injector build, spray tests
  - Ignition/control system build
  - E85 optimized engine build
  - Optical single-cylinder tests
  - Baseline engine tests (performance and emissions)
- System Development (E85 optimized engine tests):
  - Cold-start
  - Performance and emissions
  - Results analysis, model update
  - Commercialization study

Results

- The fuel economy of an internal combustion engine operating on E85 can be significantly increased through the application of downsizing and optimization techniques.
- Optimization provides the majority of the fuel economy benefit, primarily through the use of higher geometric compression ratio.
- Downsizing is also a major contributor to fuel economy improvement.
- E85 leads to lower exhaust temperatures allowing stoichiometric operation over entire operating envelope.
- The target ignition system specifications are determined to provide at least 37 kV (@25 pF) and spark energy of 45 mJ. Multi-strike techniques can be used to increase the ignition energy to over 80 mJ.
- A multi-hole injector nozzle is required to improve injector performance to meet the more challenging demands of E85 fuel. In-cylinder CFD modeling of 6- and 8-hole injector nozzles suggest that the 8-hole injector is better suited to the target engine design, resulting in a more uniform concentration of homogeneous charge within the cylinder. These results will be experimentally verified in Phase 3, via optical injector spay imaging methods.
- The developed mean value real-time engine model can be executed in the dSPACE-based hardware-in-the-loop simulator with a sample period of 1.5 ms.
- The developed Opal-RT engine controller is capable of crank-based signal sampling at one degree resolution, which is critical for closed-loop combustion control. The controller can also sample the engine knock signal at 250 kHz sample rate. This enables future software-based engine knock detection and control, which is required for the target engine due to compound boost and high compression ratio.
- Based upon the GT-Power simulation results of the developed dual-stage turbo engine model, it was found that a midsize single stage turbo (such as BorgWarner K03) could provide similar performance to a dual-stage system.

Conclusions

The overall target of this project is to achieve the same volumetric fuel economy between the proposed, E85-optimized engine running on E85 vs. that currently achieved by the state-of–the-art naturally aspirated, DI engine operating on gasoline. The data show that the existing shortfall in fuel economy on a state-of-the-art current engine between E85 to gasoline operation of ~30% can be reduced to about 10%. Further areas for improvement have been identified that are expected to eliminate this 10% deficit to achieve to goal of comparable fuel economy for both E85 and gasoline operation.

It can also be calculated from the data above that the gains in fuel economy have been achieved as follows:

- Approximately 45% from downsizing
- Approximately 55% from optimization

These gains were achieved at the same time as significantly improving vehicle performance, reducing the 0 to 60 mph acceleration time from 8.3 seconds to 6.6 seconds

Computer aided engineering CFD modeling established a favored 8-hole fuel injector design for initial optical engine verification in Phase 3.

The ionization sensing ignition system has been designed and initially proven on the GM comparator engine. The necessary CLCC system hardware has been acquired and assembled and initial progress has been made in developing the engine control algorithms with a mean value engine model, implemented in a dSPACE-HIL system.

FY 2008/2009 Publications/Presentations

1. Department of Energy Merit Review, Arlington, VA, February 28th 2008.

2. Department of Energy Merit Review, Arlington, VA, May 19th 2009.

IV.15 E85-Optimized Engine

Apoorv Agarwal (Primary Contact),
Paul Whitaker, Robert Stein
Ford Motor Company
2101 Village Road, MD 3629
Dearborn, MI 48124

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager: Michael Ursic

Subcontractors:
- AVL Powertrain Engineering, Inc., Plymouth, MI
- 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 E85.
- Develop and assess a dual-fuel concept for on-demand direct injection of E85.
- Reduce Federal Test Procedure 75 drive cycle 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 emission levels.

Accomplishments

- Completed optical and single-cylinder investigations of fuel spray pattern, piston bowl geometry and in-cylinder charge motion (July 2008).
- Completed design, procurement and build of multi-cylinder turbocharged dual-fuel engines capable of 150 bar peak pressure (August 2008).
- Installed and started testing a multi-cylinder engine in a dynamometer test cell (January 2009).
- Completed preliminary vehicle level simulations of fuel economy and performance of single- and dual-fuel ethanol optimized engines (June 2009).
- Completed initial baseline evaluation of a multi-cylinder engine at 9.3:1 compression ratio, exceeding performance targets (December 2009).

Future Directions

- Optimize cam timing by completing multi-cylinder engine dynamometer development for both FFV and dual-fuel engines.
- Measure multi-cylinder full-load performance and fuel efficiency at vehicle mapping points for the FFV and E85-optimized dual-fuel engines.
- Evaluate dual-fuel performance and fuel economy at 12:1 compression ratio.
- Develop a cold starting strategy for E85-optimized dual-fuel engines.
- Evaluate vehicle level attributes for the FFV and E85-optimized dual-fuel engines.

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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 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 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. A further concern with the use of ethanol is that the supply of ethanol will continue to be constrained until the production of cellulosic ethanol reaches a large commercial scale.

The concept of the dual-fuel engine overcomes these issues with using ethanol. In this concept, port fuel injection (PFI) of gasoline is combined with direct injection (DI) 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

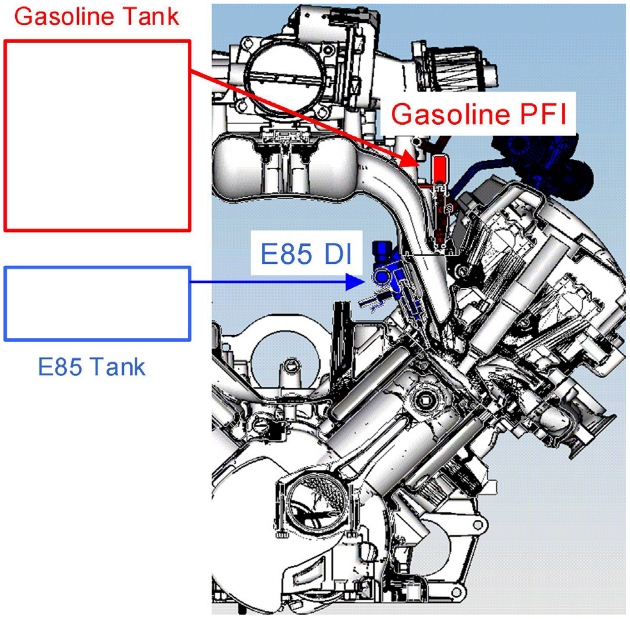

FIGURE 1. Cross-Section of E85-Optimized Dual-Fuel Engine

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 down-speeding (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 down-speeding, the dual-fuel engine uses gasoline more efficiently, thereby leveraging the benefit of the limited supply 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.

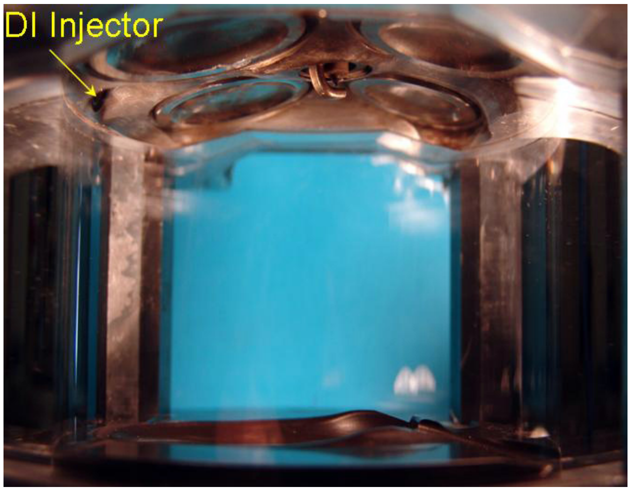

FIGURE 2. Optical Engine with Transparent Quartz Liner for Optical Access

The combustion system was initially developed on a single-cylinder engine which enabled the main combustion system specifications to be efficiently defined months before multi-cylinder engine hardware could be available. A single-cylinder engine with optical access (Figure 2) was used to validate conclusions drawn from the 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 multi-cylinder engines were then built with combustion system specifications defined on the single-cylinder engine.

Results

Design

The combustion system is a 4-valve per cylinder pent roof design with variable cam timing for both intake and exhaust valves. In order to ensure that the in-cylinder tumble air motion generated by the intake ports was not only of the magnitude required, but symmetric and centered, intake port development was conducted in a Laser Doppler Anemometry port development laboratory at AVL. Each cylinder has both DI and PFI fuel injectors to support dual fueling.

Turbochargers are utilized to generate boost pressure to improve specific torque and power output (and take advantage of the very high effective octane of E85), and were appropriately sized for fast transient response using 1-dimensional (1D) cycle simulation.

Single-Cylinder Engine Development

Two different direct injector spray designs were tested and three in-cylinder air motion tumble ratios were tested under part-load, full-load, and cold-starting conditions.

Figure 3 compares single-cylinder full-load performance on 91 research octane number gasoline versus E85 at the same compression ratio of 9:1. E85 allows knock-free operation at very high torque

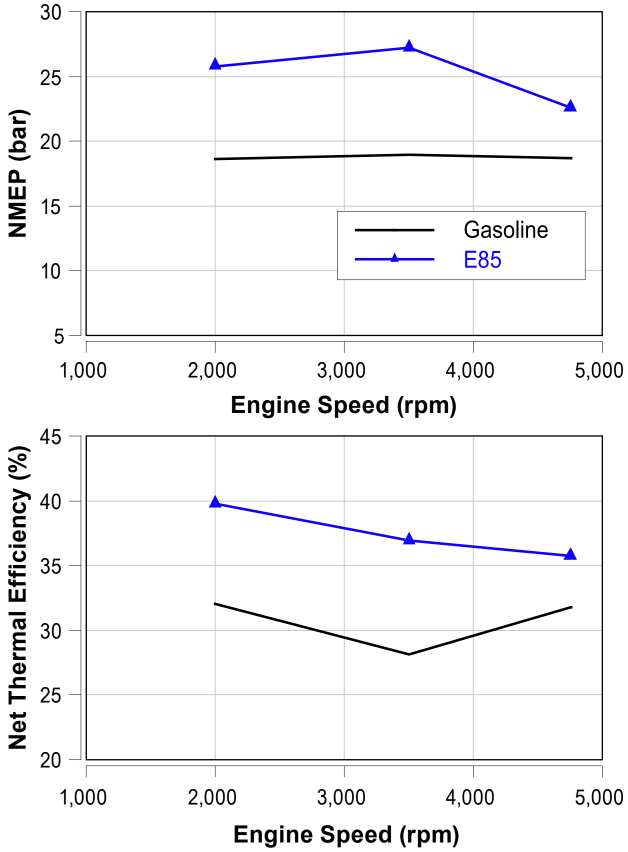

FIGURE 3. Comparison of E85 and 91 Research Octane Number Gasoline at Full-Load on a Single-Cylinder Engine

as combustion stability is excellent due to optimal combustion phasing, allowed by the very high effective octane rating of E85.

The limiting factors for performance on E85 are thermal and mechanical loading on the base engine and airflow capability which is defined by the turbocharger match. This single-cylinder engine operated at 26, 27, and 22 bar net mean effective pressure (NMEP)[1] at 2,000, 3,500 and 4,750 rpm, respectively. The above NMEP levels correspond to the target full-load torque levels of the multi-cylinder engine. The engine ran without knock at all of these conditions.

With E85 the engine could be operated at stoichiometry, but with gasoline, even though the torque was significantly lower, enrichment was required at 3,500 rpm and above to control exhaust temperatures. On a thermal efficiency basis (work output per unit of fuel energy input), E85 showed 32% higher thermal efficiency than gasoline at 3,500 rpm (37% vs. 28% for gasoline). At 2,000 rpm net thermal efficiency was 41% for E85. It could be increased further by increasing compression ratio which will be investigated on the multi-cylinder engine during 2010.

Operating the engine in dual-fuel mode at 2,000 rpm and full load, it was found that only 50% E85 was required to maintain optimum ignition timing (minimum for best torque, MBT) at 18.5 bar NMEP, and 70% E85 was required for MBT at 26 bar NMEP. When the E85 fraction is reduced from these levels, combustion phasing has to be retarded to avoid knock, thermal efficiency deteriorates, and exhaust temperatures increase.

These preliminary results were measured at 9:1 compression ratio. They confirm the benefit of the dual-fuel approach and show that less than 100% E85 is required at the highest load conditions, with the quantity of E85 required to suppress knock decreasing with load. The impact on dual-fuel operation at 12:1 compression ratio on a multi-cylinder E85-optimized engine will be investigated in detail in 2010.

Optical Engine Results

Figure 4 shows results from studies performed on the optical engine. The top row of pictures shows statistical flame images taken on the optical engine at 100 crank angle degrees after top dead center for cold-start conditions on E85 and gasoline.

With gasoline, sooting flames were measured (denoted by red), especially in the region close to the piston where fuel impingement would have created a fuel film. When the engine was operated on E85 at the same conditions, the sooting flames disappeared and only premixed combustion flames were observed (denoted by yellow). As ethanol is oxygenated, oxygen contained in the fuel reduces or eliminates soot formation in rich regions. Also, E85 is a mixture of ethanol (a single component fuel with a boiling point of 78.3°C) and high volatility gasoline components (to aid cold starting). Gasoline is a multi-component fuel with a range of boiling temperatures for its various constituents, typically with boiling points up to 180°C. Therefore it is likely that more complete evaporation of an E85 fuel film on a hot piston crown will occur than for gasoline, and that the heavier components that do not evaporate as readily are the source of sooting flames with gasoline. This shows another benefit of E85 operation which will be advantageous for meeting future particulate emissions standards.

The lower row of pictures of Figure 4 shows optical engine fuel spray measurements for operation on E85 at 2,000 rpm and full load. At these conditions, even with the dual-fuel system, the majority of the fuel delivered is E85 in order to suppress knock, and due to the high load and reduced energy content of E85, this leads to increased injection duration and a higher

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[1] NMEP is a measure of torque produced at the piston per unit of cylinder displacement, and is commonly used for single-cylinder engines.

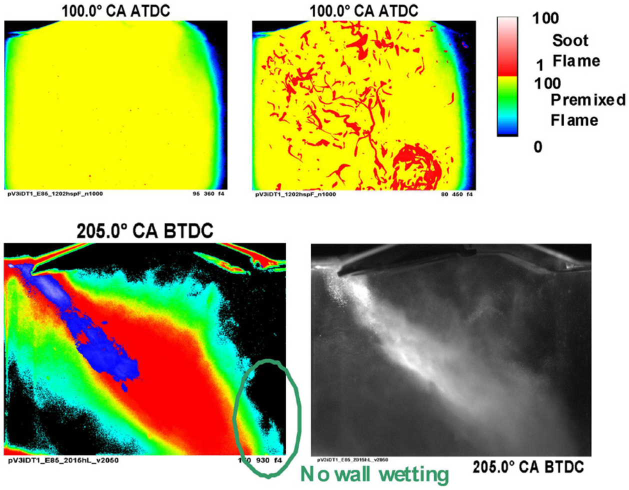

FIGURE 4. Optical Engine Results

penetrating fuel spray, causing concern over bore washing. However, when the fuel is injected at the time when there is a strong air motion interaction, the air motion deflects the fuel and prevents cylinder liner wetting. These images validate that this requirement of the combustion system design was met.

Multi-Cylinder Development

A multi-cylinder E85 optimized dual-fuel engine tested at Ford's dynamometer labs has demonstrated three 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 torque levels equivalent to 32 bar brake mean effective pressure (BMEP). These BMEP levels exceeded the project targets and are much higher than for a modern diesel engine (Figure 5). 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 simulation projections for a 12:1 compression ratio E85-optimized engine (based on data from a 9.3:1 compression ratio multi-cylinder engine) were performed (see Figure 6).

These projections indicate that a high compression ratio E85-optimized dual-fuel engine can achieve diesel fuel economy while providing enhanced vehicle performance as measured by gradeability (maximum grade achievable in top gear at 65 mph).

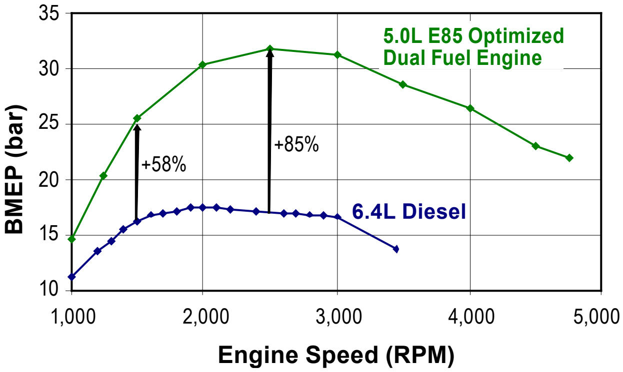

FIGURE 5. BMEP Comparison of Multi-Cylinder Ethanol Engine to 6.4L Diesel Engine

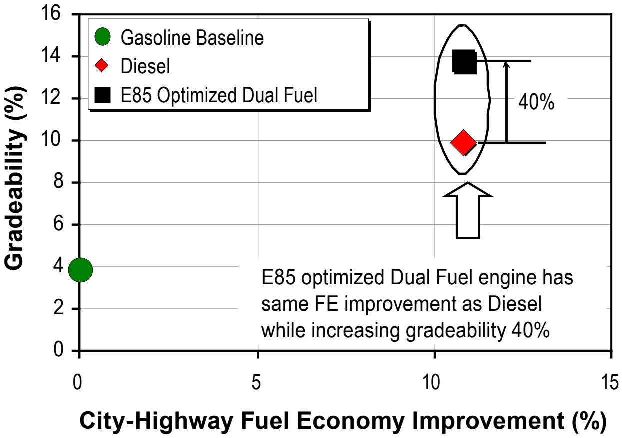

FIGURE 6. E85-Optimized Engine Compared to Gasoline Baseline and Diesel Engines

Conclusions

- Using E85 in a direct injection boosted engine allows knock-free operation at very high torque, enabling aggressive downsizing of engine displacement and high compression ratio.
- The high torque levels demonstrated on the multi-cylinder engine significantly exceeded the initial project targets.
- The dual-fuel concept performed as expected demonstrating that it is possible to use direct injection of E85 only as needed to suppress knock, improving the efficiency of the engine in using gasoline.
- Optical engine studies showed that there are no issues with cylinder bore washing with E85 as the high tumble air motion deflects the fuel spray from the liner. Also, E85 operation in a direct injection engine results in a significant reduction in smoke (particulates) under cold-start conditions.

- Vehicle simulation results based on multi-cylinder engine data have shown that it is feasible for a dual-fuel engine with the appropriate level of downsizing and high compression ratio to achieve fuel economy benefits equivalent to a diesel engine relative to the baseline gasoline engine.

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FY 2008/2009 Publications/Presentations

1. 2008 DOE Merit Review.

2. 2009 DOE Merit Review.

IV.16 Optimally Controlled Flexible Fuel Powertrain System

Hakan Yilmaz (Primary Contact) and Li Jiang
Robert Bosch LLC
38000 Hills Tech Drive
Farmington Hills, MI 48331

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager: Michael Ursic

Subcontractors:
- Ricardo Inc., Van Buren Township, MI
- University of Michigan, Ann Arbor, MI

Objectives

- Improve fuel efficiency with E85 by 10% with minimum performance penalties.
- Achieve ultra-low emission vehicle (ULEV) level emissions with all fuel blends E0…E85 and investigate the potential measures to reach super ultra-low emissions vehicle (SULEV) levels.

Accomplishments

- A prototype engine with flex-fuel optimized design has been built to explore the potential benefits of E85 while achieving 3-4% fuel efficiency improvement due to a higher compression ratio.
- Optimal transmission shift pattern is predicted to improve the fuel efficiency with E85 by up to 5%.
- Effects of varying fuel properties on control parameter settings for optimal ethanol combustion have been identified, based on which a 2-2.5% fuel efficiency improvement could be achieved with E85.
- Fuel system specification and engine design is completed for improved emissions.
- A sensor-less ethanol detection strategy using the existing exhaust gas oxygen sensor and the additional combustion pressure sensor is proposed to improve the estimation robustness and accuracy.

Future Directions

- Calibrate the engine and vehicle performance to achieve the proposed targets.
- Integrate developed flex-fuel functionalities with the Bosch production software packages into the MED17 engine control unit (ECU).
- Demonstrate the proposed concepts at both the engine and vehicle levels.

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Introduction

Although today's flex-fuel vehicles 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 flex-fuel vehicles is to improve cold-start performance [1]. Apart from the cold-start problems, the lower combustion heating value of ethanol results in higher fuel consumptions (miles/gallon). Nevertheless, ethanol also possesses some advantageous properties such as higher octane number and increased latent heat of vaporization 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 turbocharging, downsizing, 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 flex-fuel vehicle (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 capture the combustion characteristics of ethanol fuels and their impacts on the optimum control parameter settings, dynamometer testing was conducted following an advanced design of experiment (DoE) method on a state-of-the-art gasoline-optimized engine running on E0, E24, E55, and E85. Engine and vehicle simulation models were then developed based on the collected data to explore the potential benefits of ethanol fuels to enable engine design and transmission shift pattern optimization studies.

Emissions: Following the novel strategy proposed in [4], this project aims to achieve ULEV level emissions with the implementation of a multi-injection control strategy, modification of the piston bowl design and exhaust system layout, and the optimization of injection spray targeting.

Control Design: In order to compensate for the effects of varying fuel properties on combustion, adaptive engine controls that can (a) estimate the ethanol content of a gasoline-ethanol fuel blend, and (b) optimize combustion for the detected fuel blend by adjusting the critical control variables.

Modeling: Control-oriented models of the flex-fuel engine system are developed to capture the dynamics in the air and fuel paths, and the effects of spark advance and amount of internally recirculated exhaust gas on the cycle-to-cycle combustion performance.

Ethanol Detection: Inspired by the significant difference in the latent heat of vaporization (LHV) between gasoline and ethanol, an approach is developed to extract a detection feature that could indicate the charge cooling effects of the injected fuel from the cylinder pressure measurements. An ethanol detection strategy is proposed to integrate the LHV-based detection feature with one derived based on the stoichiometric air-to-fuel ratio of the combusted fuel from the exhaust gas oxygen sensor measurements.

Combustion: The proposed closed-loop combustion control strategy independently adjusts the spark advance of each cylinder based on the deviation of the location of 50% mass fraction burned (CA50) from the optimum value. In this project, the cylinder-individual CA50 locations are estimated from the cylinder pressure measurements on a cycle-to-cycle basis. To improve the transient response of the controller, the spark advance set-point values, stored in the calibrated maps for feed-forward control, are adapted online in terms of engine operation conditions.

Implementation: The latest Bosch MED17 ECU, equipped with the capability of collecting and processing real-time cylinder pressure measurements, is used in this project. Validated flex-fuel control functionalities will be integrated with the production-level Bosch software packages for vehicle-level calibration and demonstration.

Results

Results that are accomplished in the areas of fuel efficiency and performance, emissions, and engine controls during the last three phases are presented as follows.

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 the engine performance, such as output torque and knocking behavior, with different engine designs. As shown in Figure 1, with a higher tolerable maximum cylinder pressure of 150 bar, the engine is predicted to be capable of achieving a maximum torque of 500 N•m over 2,500-4,000 RPM when running on E85. 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. Therefore, advanced variable valvetrain strategies, such as the late intake valve closing, is employed to mitigate the associated knocking problems by reducing the effective compression ratio. As shown in Figure 2, the engine with a higher compression ratio, when running on gasoline, is predicted to be capable of matching the same torque curve of the gasoline-optimized engine using a modified intake cam profile. In addition, the DoE study for the effects of varying fuel properties on optimum engine parameter settings indicates in Figure 3 that a more complicated calibration scheme for all critical control variables could improve fuel

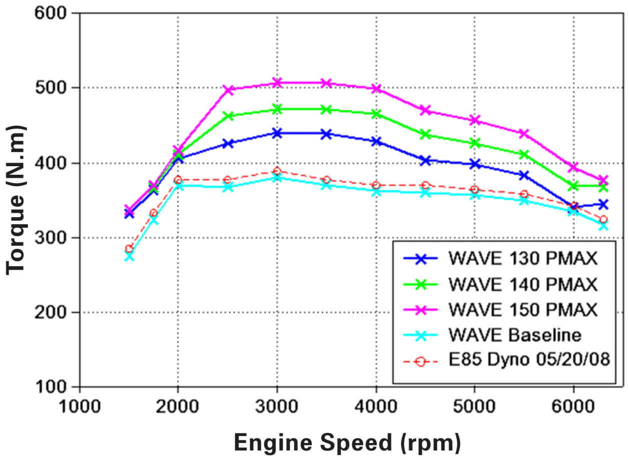

FIGURE 1. Predicted output torque of an engine, running on E85, with a higher tolerable maximum cylinder pressure ranging from 120 bar up to 150 bar.

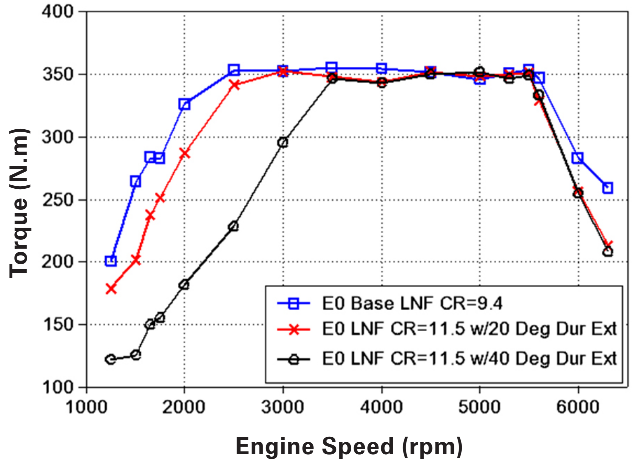

FIGURE 2. Predicted output torque of an engine, running on E0, with a higher compression ratio and two intake cam profiles.

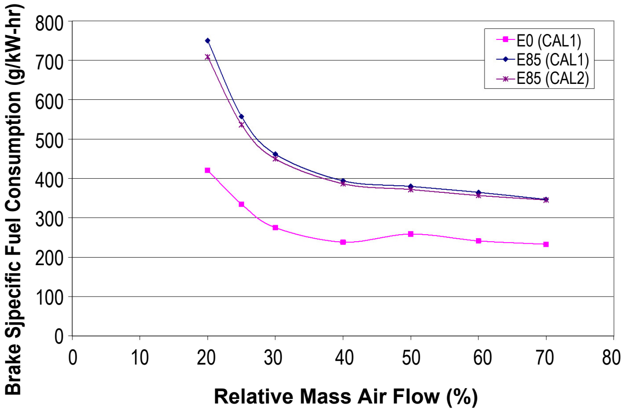

FIGURE 3. Brake specific fuel consumption under conventional calibration strategy (CAL1) for spark and injection timings, and a more complicated strategy (CAL2) for all critical control variables at 2,000 RPM.

efficiency by another 2-2.5% depending on the engine operation conditions. Furthermore, vehicle performance simulations indicate that the optimization of the transmission shift pattern for varying fuel properties could further improve the fuel efficiency by 2.7% with gasoline and 4.7% with E85.

Engine Controls: Implemented in Simulink, the control-oriented models take the engine speed and critical control commands such as variable valve timing and spark advance as inputs. As shown in Figure 4, the developed model is able to capture the dynamics in the air path system with the intake mass air flow rate and the pressures in various manifolds, and the cycle-to-cycle combustion behavior with the indicated mean effective pressure and CA50. Such a model is used to investigate the dependence of CA50, the selected combustion phase indicator, on the commanded spark advance and the influences of engine operation, such as variable valve timing on the cycle-to-cycle combustion variations. The understanding of the correlation among these variables enables the adaptation of feedback combustion controllers.

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

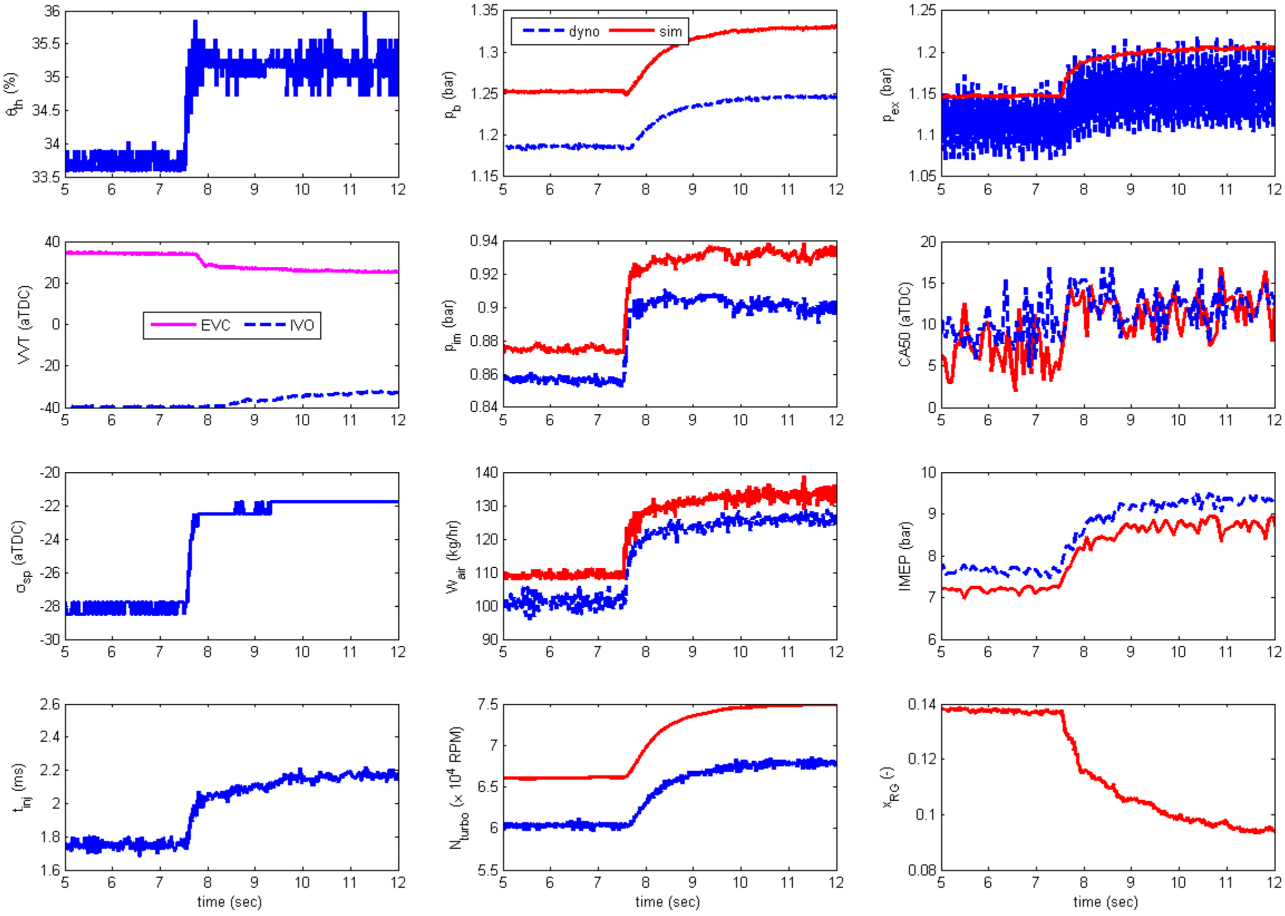

FIGURE 4. Modeling performance of the control-oriented model during the transients of a throttle step change at the speed of 2,500 RPM with E0.

demanded fuel is injected during the intake stroke when the influence of the charge cooling effects on 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, *residue*, is then introduced to capture the difference in cylinder pressure evolution during single- and split-injections. As illustrated in Figure 5, there exists a significant difference between the *residue* evolution for E0 and E85 at the same engine operation point. The higher *residue* values associated with E85, in fact, indicate stronger charge cooling effects due to its higher LHV and the higher fuel injection quantity at stoichiometric combustion. The monotonic correlation between LHV-based detection and ethanol content has been observed at specific operational conditions during dynamometer testing. For example, as shown in Figure 6, ethanol detection using the LHV-based detection feature results in an ethanol content estimation error of around 5 ethanol volumetric percentage. Moreover, due to the lower sensitivity of the LHV-based detection feature to the injected fuel amount, ethanol detection using such a feature can achieve better estimation accuracy, compared with that using the detection feature based on the stoichiometric air-to-fuel ratio (SAFR), during 10% fuel injector drifts. The different sensitivity of the LHV- and SAFR-based detection features to the injected fuel amount suggests the potential of integrating both features to improve ethanol content estimation accuracy and robustness.

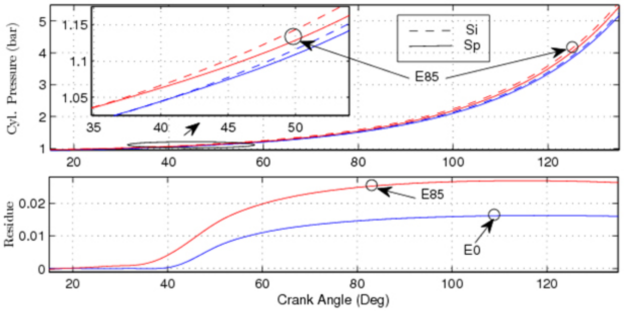

FIGURE 5. Cylinder pressure and residue evolution during the compression stroke at the engine speed of 2,500 RPM and intake mass air flow rate of 170 kg/hr. (Si = single injection; Sp = split injection)

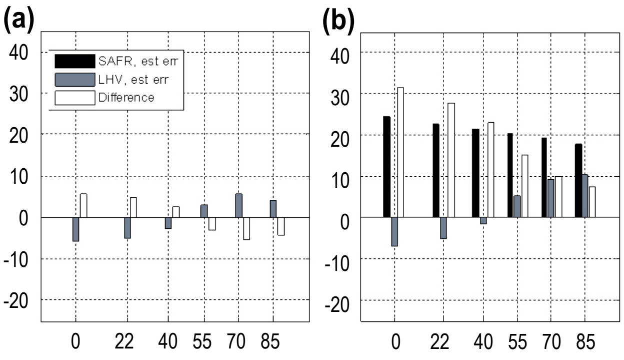

FIGURE 6. Ethanol content estimation errors using SAFR- and LHV-based detection features under (a) Left: fault-free conditions and (b) Right: 10% fuel injector drifts at the engine speed of 2,500 RPM and intake mass air flow rate of 130 g/hr.

Conclusions

- A flex-fuel optimized engine design with a higher compression ratio of 11.25:1 and a maximum tolerable cylinder pressure of 140 bar in combination with the advanced variable valvetrain strategies such as late intake valve closing could improve the fuel efficiency with E85 by 3-4% without compromising performance with gasoline.
- The use of a transmission shift pattern optimized for the corresponding fuel could further improve the fuel economy of FFVs up to 5%.
- Due to the influences of the varying fuel properties on optimum control parameter settings, adaptive engine controls that adjust these parameters for the detected ethanol content could improve the fuel economy of ethanol fuels by 2-2.5%.
- The LHV-based detection feature extracted from cylinder pressure measurements has a comparatively lower sensitivity, compared with the SAFR-based detection feature, to the injected fuel amount, which suggests the potential of integrating these two detection features for a more robust ethanol detection strategy.

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7. 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.

Special Recognitions & Awards/Patents Issued

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

IV.17 E85 Optimized Engine through Boosting, Spray-Optimized GDI, VCR and Variable Valvetrain

Keith Confer (Primary Contact), Wayne Moore
Delphi
3000 University Drive
Auburn Hills, MI 48326

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager: Michael Ursic

Subcontractor:
Dr. Ming-Chia Lai, Wayne State University, Detroit, MI

Objectives

- Develop an engine approach 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 an optimized engine.
- Demonstrate benefits of new hardware and refine engine operation.

Accomplishments

- An engine model was completed using GT Power. The model has been used extensively to evaluate valve lift profiles and cam phasing requirements for best performance on the modified compression ratio engine with gasoline and E85.
- Designs for various compression ratio combustion chambers have been evaluated for the chosen engine.
- A dynamic computational fluid dynamics (CFD) model was constructed to study spray patterns and spray characteristics of various injector geometries under the varying conditions of simulated engine operation. The injector model was correlated to initial bench test data of the production injector.
- Fuel injector spray targeting was prescribed and seat design completed.
- Fuel injector spray experiments for realistic temperature and pressure conditions were performed. Spray chamber and thermal capabilities were updated to enable study of spray characteristics using high-speed spray images.
- A multi-cylinder engine head was fitted to an existing optical engine. High-speed Mie-scattering movies have been used to compare the new vs. the old designs.
- Hardware was constructed for an optimized multi-cylinder engine: custom fuel injectors, 2-step valvetrain for variable lift, extended range cam phasers, custom pistons for increased compression, custom ground camshafts.
- The multi-cylinder engine with E85 optimized hardware was operated in an unthrottled condition to evaluate the domain of load control enabled by the Delphi valve train strategy. Various parameters, speed load maps, brake specific fuel consumption and coefficient of variation of indicated mean effective pressure for E85 and gasoline were compared.
- Fuel consumption was reduced up to 12% for stoichiometric operation. Further improvement due to vehicle level optimization to leverage the improved low-end torque should increase potential.

Future Directions

- Effects of enhanced intake charge motion will be studied using the optical engine.
- Effects of enhanced intake charge motion will be studied using the multi-cylinder engine. Valvetrain, intake manifold and fuel injection targeting and timing will be varied to enhance charge motion. Effects of burn rate and combustion stability on fuel economy will be evaluated.
- Multiple pulse fuel injection will be evaluated.
- A matrix of vehicle applications will be evaluated and optimized over representative drive cycles using a simulation model.

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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. This allows the use of higher engine compression ratios and spark advance which result in more efficient engine operation. Ethanol's latent heat of vaporization is also much higher that gasoline. This higher heat of vaporization cools the engine intake charge which also allows the engine compression ratio to be increased even further. 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. 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 both the unthrottled operation for improved fuel economy as well as the lower effective compression ratio for the lower octane gasoline blends. Figure 1 shows the test engine on the dynamometer.

Results

Simulation

The engine was modeled using commercially-available one-dimensional engine simulation tools. The results yielded specifications for the 2-step valve train design, compression ratio and phasing requirements that can improve fuel economy. Further, it confirmed that phased intake valve lift profiles can be used to control load over a wide range and is more efficient than using a throttle.

Injector Spray Experiments

The high-speed Schlieren visualization technique applied to the spray chamber provided an effective tool to characterize vaporizing direct injection sprays from E0 to E100 fuels (see Figure 2). The results confirmed that higher injection pressure resulted in better vaporization at the spray tip region. As ambient and fuel temperature increase, flash boiling was observed for lower ambient pressure cases. This resulted in plume collapse and enhanced penetration with a more focused spray angle. This phenomenon was not observed with higher ambient pressure. It was also noted that sprays injected from holes with smaller length to diameter ratio developed slower and wider. During the piston impingement testing, it was observed that poorly defined injector spray targeting and piston bowl geometry may produce wall wetting which is a source of unburned hydrocarbons and soot. CFD simulation agreed fairly well with the experimental data in terms of overall shape and penetration, but further modification is required for more accurate calculation results.

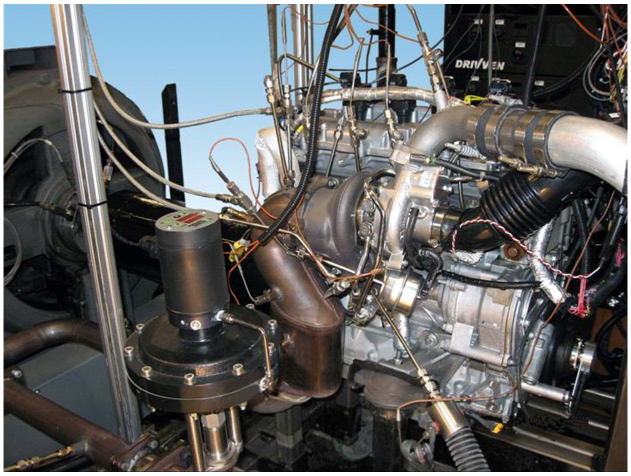
FIGURE 1. Multi-Cylinder Dyno Engine

Multi-Cylinder Engine Testing

A multi-cylinder engine was operated on E85 and gasoline fuels to confirm the operating range provided by the advanced valvetrain system. The low-lift cam which operates using an early intake valve closing (EIVC) strategy was able to provide unthrottled load control from 2-9 bar brake mean effective pressure (BMEP) using E85 fuel. The high-lift cam which utilizes a late intake valve closing (LIVC) strategy was able to control the load from 7-12.7 bar BMEP under unthrottled naturally aspirated conditions on E85. Regular gasoline was also evaluated. Peak torque was reduced about 10% relative to E85. Gasoline was prone to knock which could be reduced with spark retard or reduced effective compression ratio (CR). The high-lift (LIVC) strategy allows effective CR control from the geometric CR of 11.85 down to 8.5. Figure 3 shows the torque curves for E85 fuel under unthrottled operation. The EIVC and LIVC domains are illustrated and the switch point

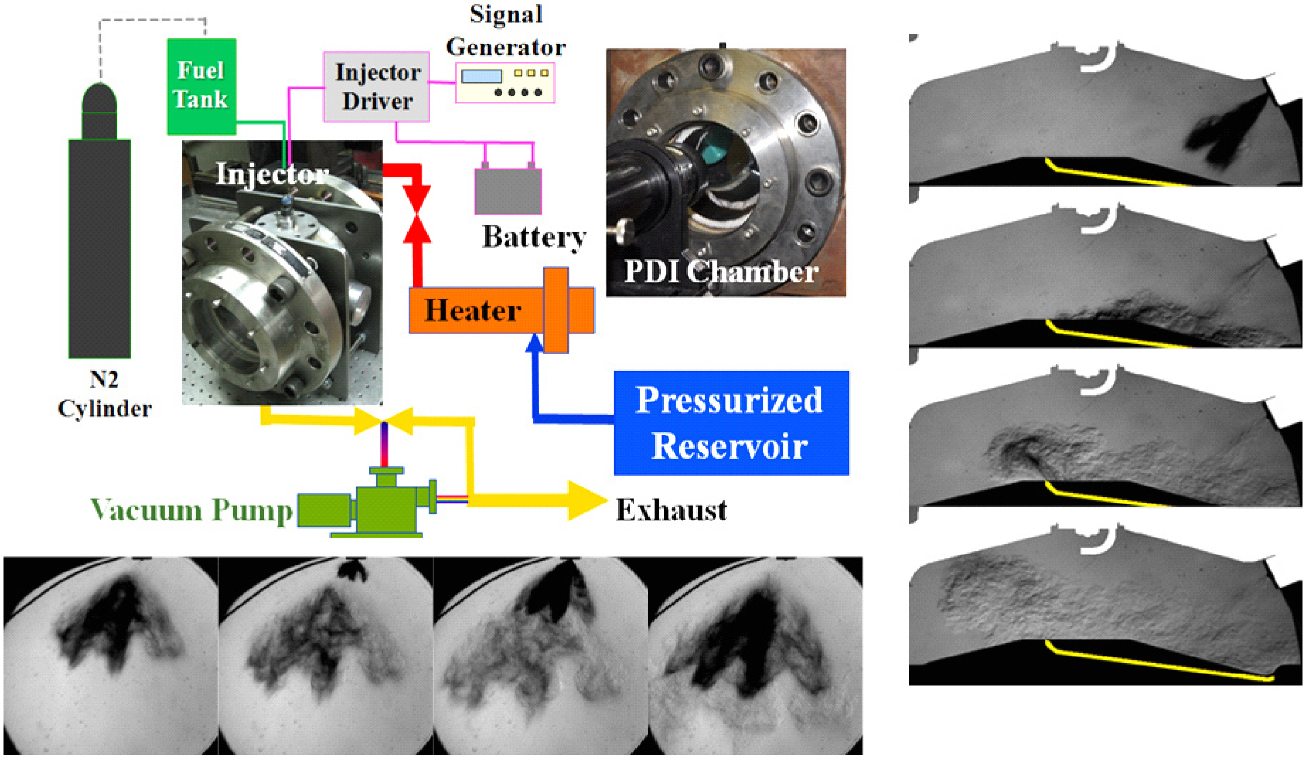

FIGURE 2. High-Speed Schlieren Spray Visualization

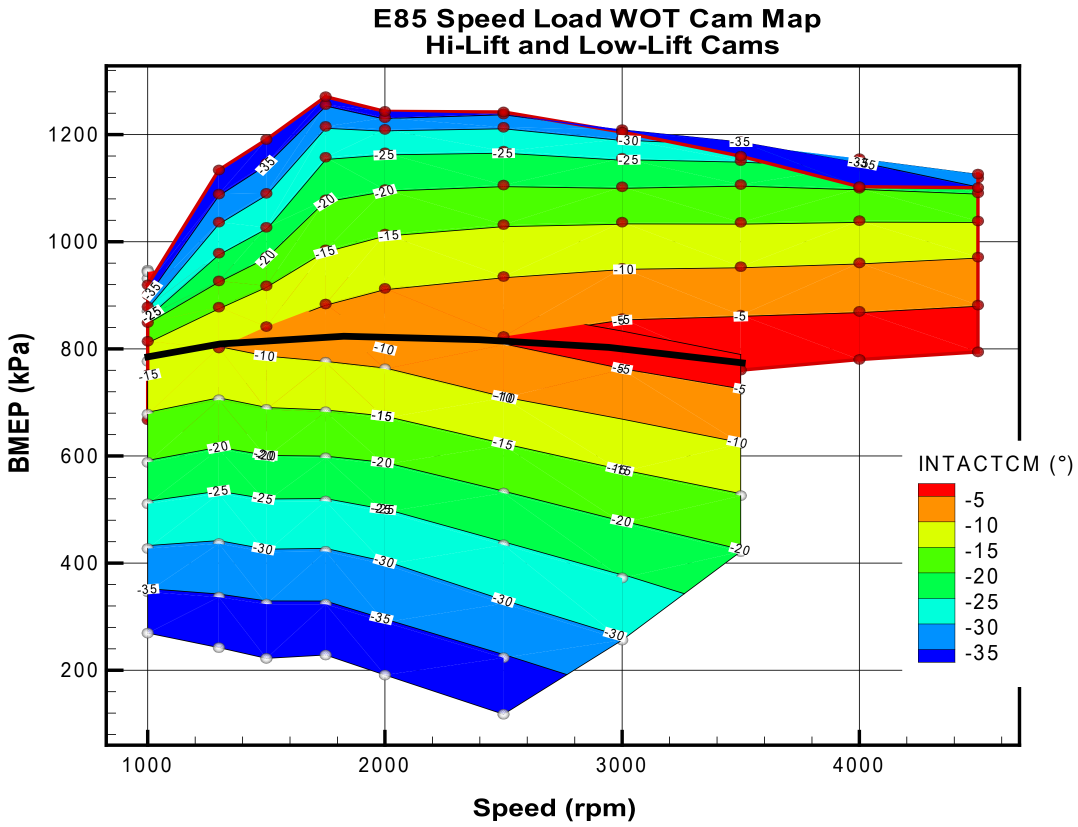
E85 Speed Load WOT Cam Map
Hi-Lift and Low-Lift Cams

FIGURE 3. E85 Torque Curve (WOT - wide open throttle)

to eliminate torque differences is also shown. Good low-end torque without need for spark retard is achieved with E85 fuel. Guided by simulation results indicating efficiency potential of internal exhaust gas recirculation (EGR), valvetrain optimization was able to further reduce fuel consumption at low loads of 3 to 5 bar BMEP as shown in Figure 4.

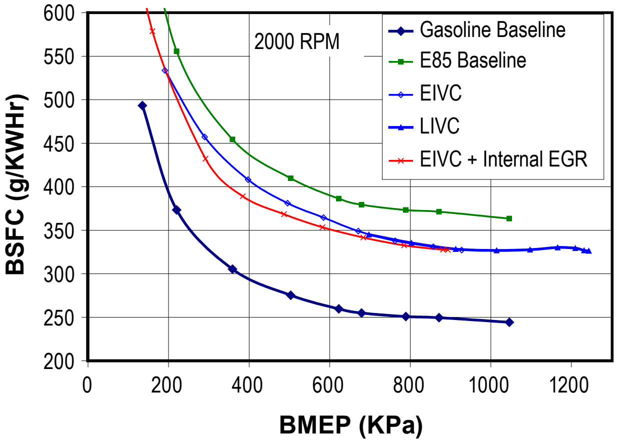

FIGURE 4. Fuel Economy Gain

Conclusions

Variable Valvetrain

- LIVC strategy provides effective CR control with cam phasing.
- EIVC strategy provides unthrottled load control for 80-90% over the Federal Test Procedure.
- EIVC needs improved charge motion to extend fuel economy potential.
- There are only minor differences in spray characteristics between E100 and E0 with the same injected mass, but when energy content of injected fuel was fixed, longer penetration and slower vaporization of E100 spray were documented.
- High temperature and low pressure of the air charge and hot fuel promoted flash vaporization.

System Improvements

- Improved engine demonstrated 12% reduction in fuel consumption.
- Low-speed torque without spark retard enables efficient down-speeding using E85.

FY 2008/2009 Publications/Presentations

1. SAE paper 2010-01-1203 was written on the simulation portion of the project and will be presented at SAE Congress 2010: *A Simulation Method to Guide DISI Engine Redesign for Increased Efficiency using Alcohol Fuel Blends.*

2. SAE paper 2010-01-0601 was written on the fuel injector portion of the project and will be presented at SAE Congress 2010: *Spray Characterization of Ethanol-Gasoline Blends and comparison to a CFD Model for a Gasoline Direct Injector.*

IV.18 Investigation of Biodiesel-Fueled Engines under Low-Temperature Combustion Strategies

Chia-Fon Lee (Primary Contact),
Alan C. Hansen
University of Illinois at Urbana-Champaign
1206 West Green Street
Urbana, IL 61801

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager: Michael Ursic

Objectives

- Measure and evaluate properties of pure biodiesel and biodiesel/diesel blends for low-temperature combustion (LTC) combustion modeling.
- Quantify the impact of biodiesel fuel properties on combustion and emissions in LTC engines.
- Create fundamental knowledge about emissions formation from biodiesel in LTC engines with the aid of combustion modeling and engine testing.
- Optimize LTC engine operating parameters with biodiesel.
- Develop and demonstrate new technologies and strategies for reducing emissions and increasing efficiency from biodiesel combustion.

Accomplishments

- Forty publications over two years in journals and conference proceedings featuring biofuels and engine technologies accessible to a broad range of researchers and equipment manufacturers.
- Quantified impact of fatty acid composition of source materials on biodiesel properties from which renewable oils including those from micro-algae can be screened in the future to ensure their compatibility with diesel engines.
- Without engine re-calibration, soot emissions reduced by 20% when burning biodiesel fuel. With optimized engine settings a 50% reduction in oxides of nitrogen (NOx) emissions was found to be possible with biodiesel.
- Variable spray angle injector technology demonstrates a new strategy for further reducing emissions and also increasing fuel economy by approximately 10% through optimized fuel spray location in the engine cylinder.
- Micro-explosions of a fuel spray were visualized for the first time with the technology developed at the University of Illinois. The result leads to a new fundamental understanding of the micro-explosion process and demonstrates the potential benefit of using micro-explosion in combustion.

Future Directions

- Evaluate next generation biofuels, including biodiesel produced from micro-algae and bio-butanol blended biodiesel and diesel fuels, in terms of their properties, and combustion and emissions characteristics in LTC engines.
- Optimize biodiesel LTC engine operating conditions with the multiple-cylinder engine and the optical engine with the assistance of multi-dimensional computations.
- Increase fuel economy and lower emissions further by optimizing variable spray angle injection with biodiesel and blends.
- Analyze further the spray and combustion of butanol-biodiesel-diesel blends to understand the control mechanisms of micro-explosion phenomena, and explore the potential of using them to improve combustion and emissions of biodiesel-based fuels.

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Introduction

In accordance with meeting DOE technical targets this research is aimed at developing and optimizing new fuel injection technologies and strategies for the combustion of clean-burning renewable fuels in diesel engines. In addition a simultaneous minimum 20% improvement in fuel economy is targeted with the aid of this novel advanced combustion system. Biodiesel and other renewable fuels have unique properties that can be leveraged to reduce emissions and increase engine efficiency. This research is an investigation into the combustion characteristics of biodiesel and its impacts on the performance of a LTC engine, which is a novel engine configuration that incorporates technologies and strategies for simultaneously reducing NOx and particulate emissions while increasing engine efficiency.

Generating fundamental knowledge about the properties of biodiesel and blends with petroleum-derived diesel and their impact on in-cylinder fuel atomization and combustion processes was an important initial step to being able to optimize fuel injection strategies as well as introduce new technologies. With the benefit of this knowledge experiments were performed on both optical and metal LTC engines in which combustion and emissions could be observed and measured under realistic conditions. With the aid these experiments and detailed combustion models strategies were identified and applied in order to improve fuel economy and simultaneously reduce emissions.

Approach

The research was divided into three phases with the first phase focusing on performing experimental studies to quantify and predict biodiesel blend fuel properties to be used in an existing computational combustion model that was modified to account for the differences in biodiesel fuel combustion characteristics. An LTC metal engine and optical engine were also set up in this first phase to be ready for testing. The second phase focused on acquiring data from both the metal and optical engines so as to fully characterize the combustion and emissions processes. In parallel with these tests the computational model was used to explore the in-cylinder processes which were compared with the engine tests in order to provide a fundamental understanding of the impact of biodiesel and blends on combustion and emissions in an LTC engine. In the third phase the knowledge generated from the first two phases was to be used in further engine experiments to establish the optimum operating conditions and settings for the LTC engines to achieve the desired reductions in emissions and improvement in fuel economy.

Results

Biodiesel Fuel Property Measurement and Computation for Combustion Modeling: Biodiesel can be manufactured from a wide range of source materials which include oils from soybeans, canola (rapeseed), palm, coconut and more recently micro-algae. The relative proportion of saturated and unsaturated fatty acids in the oil plays a major role in defining the properties of the fuel related to ignition quality, oxidation stability and effect of cold weather conditions. It was also found that adiabatic flame temperature, which is the maximum possible temperature generated from combustion, was strongly correlated with regulated NOx emissions. Figure 1 shows the variation of flame temperature with carbon chain length and degree of unsaturation of the fatty acid. Soybean and rapeseed biodiesel fuels contain high quantities of long-chain, unsaturated methyl esters that raise the adiabatic flame temperature and may lead to increases in NOx emissions. Coconut and palm biodiesel fuels contain shorter chain, saturated methyl esters that lower adiabatic flame temperature and can lower NOx emissions. Fatty acid composition of micro-algae oil is strongly dependent on the algae species and these oils contain unique acids not found in vegetable oils, the effect of which is unknown.

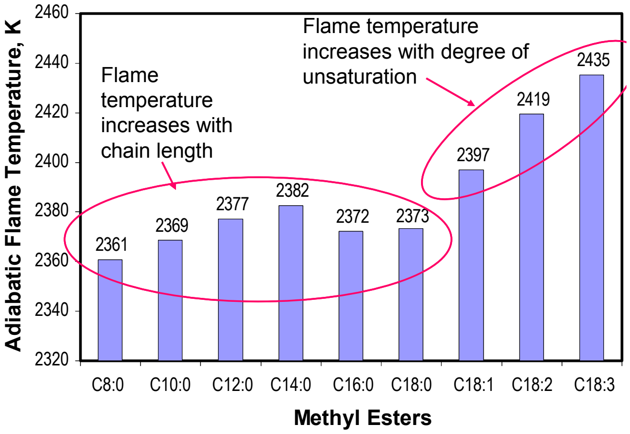

FIGURE 1. Impact of Biodiesel Fatty Acid Composition on Adiabatic Flame Temperature

Biodiesel LTC Engine Computations and Experiments: A modified KIVA program was improved to include a fuel library for bio-fuels, a multi-component vaporization model for fuel blends, and LTC and ignition models for biodiesel fuels. The effects of dual injections of biodiesel in a multi-cylinder direct injection engine were examined both experimentally and numerically. The improved KIVA code accurately predicted the major combustion characteristics, including ignition delay, peak combustion pressure and peak heat release rate for both diesel and biodiesel as shown in Figure 2. Figure 3 shows that KIVA also accurately predicted the trends of nitrogen oxide emission for both diesel and biodiesel. Biodiesel produces higher NOx emissions as expected for all injection scenarios and it asserts a greater effect at higher engine speed. Increasing engine speed tends to increase NOx emissions.

Optical LTC Engine with Biodiesel: Effects of injection timing and different biodiesel blends were studied for low-load conditions in the optical high-speed direct injection (HSDI) diesel engine [1]. The results showed that maximum heat release rate can be reduced by retarding fuel injection. Ignition and peak heat release rate were both delayed for fuels containing more biodiesel. Retarding the injection to post-top-dead center (TDC) time lowered the peak heat release and flattened the heat release curve. It was observed that LTC effectively reduced NOx emissions because less thermal NOx was formed. Although biodiesel combustion produced more NOx for both conventional and late injection strategies, with the latter leading to a LTC mode, the levels of NOx of B20, B50 and B100 with post-TDC injection were lower than pure European low-sulfur diesel using the conventional injection scenario (Figure 4). The results also showed simultaneous reduction of NOx and soot was feasible with a low-

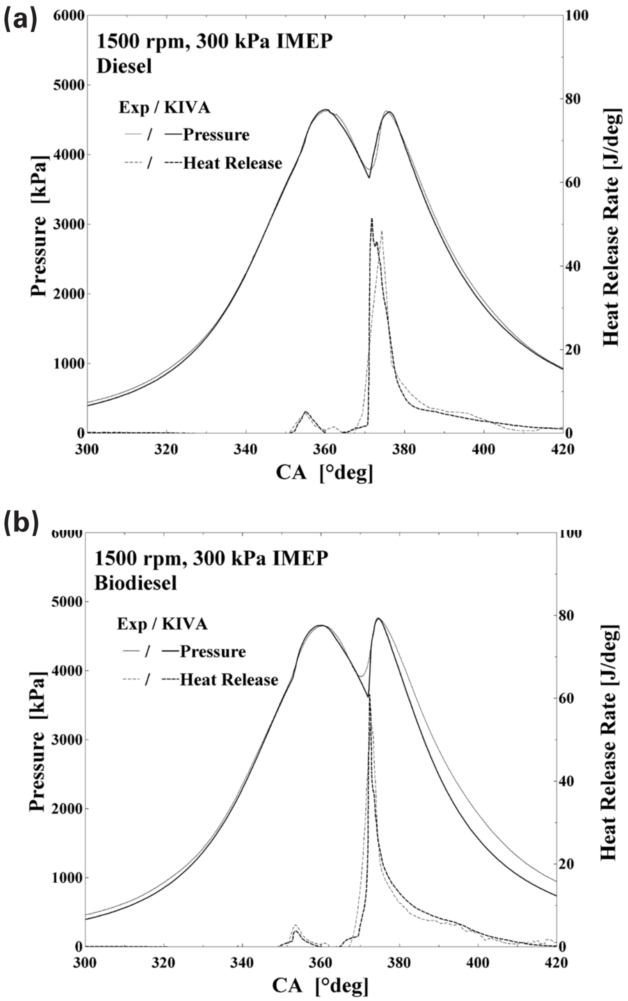

FIGURE 2. Comparison of pressure and heat release rate for (a) diesel and (b) biodiesel combustion in a direct injection engine operating at 1,500 rpm.

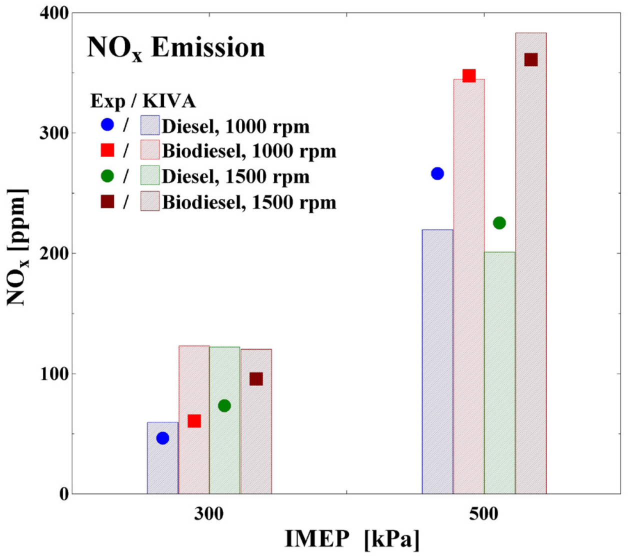

FIGURE 3. NOx Emission from the Multi-Cylinder Direct Injection Engine

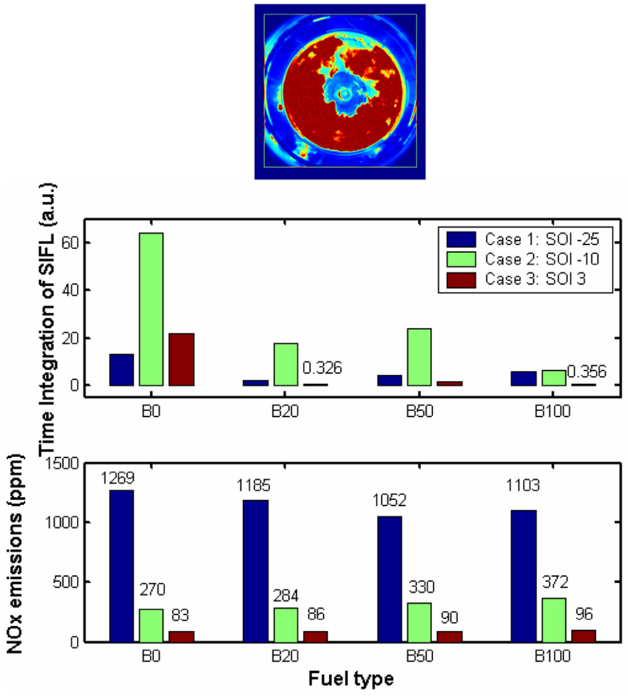

FIGURE 4. A typical in-cylinder flame luminosity picture (top) for B0 near TDC for Case 2 which is one of the pictures used in the time integration of spatially integrated flame luminosity (SIFL), that is closely related to soot, and NOx emissions of the 12 cases using different injection strategies and fuel blends.

temperature HCCI-like combustion mode. Problems associated with biodiesel NOx emissions therefore can be solved using LTC.

Variable Spray Angle Injection (VSAI) Technology Application: Simulations were done to study the operation characteristics of the HSDI optical engine with variable spray angle injection (VSAI). Various schemes were considered, with simulations conducted over blends of biodiesel and diesel. The VSAI injector extended the range of injection timings over conventional injectors by allowing very early injection. Combustion from the initial injection was always observed for all the fuel blends using VSAI. Initial combustion consisted of LTC and the breakdown of the fuel molecules into smaller radicals, generating a favorable environment for fuel evaporation and ignition during the main injection. This was reflected as an improvement in fuel economy. VSAI may lead to up to 10% in indicated thermal efficiency improvements [2,3]. Biodiesel (and its blends) was shown to lengthen the ignition delay over diesel for initial injection. The magnitude of the initial heat release for biodiesel and its blends tended to be lower than that of diesel. Therefore, main combustion occurred at a lower ambient temperature within the combustion chamber upon main injection. Consequently, lower NOx emission was realized. Soot emissions from biodiesel blends were also lower. Diffusion combustion was observed in all the cases considered. However, faster burning rate and shorter combustion duration were found to be proportionally varying with the amount of biodiesel in the blends.

Lift-off Length of Soybean Biodiesel Spray Combustion: Figure 5a shows the measured and predicted lift-off length for 20% biodiesel blend, and 50% biodiesel blend, together with those of pure diesel and pure biodiesel at different temperatures. KIVA predicted the lift-off length for the entire cases well. Ambient temperature showed dominating influence on lift-off length for the fuels considered. The lift-off length reduced with lower ambient temperature. Biodiesel increased the lift-off length under all ambient temperatures considered in this study due to its higher density and viscosity. Longer lift-off length would improve soot emission since more air is entrained into the spray prior to ignition, thus avoiding rich combustion of the fuel, which is verified by Figure 5b, which shows soot emissions. Note from the figure that soot emission from biodiesel is significantly lower than diesel. KIVA prediction (Figures 5b and 5c) of soot emission matched with experimental data well for all the fuel blends considered.

Micro-Explosion of Butanol-Biodiesel-Diesel Sprays: Blends of butanol-biodiesel-diesel were tested inside a constant volume chamber to investigate liquid spray and combustion of the fuels using laser diagnostics. Various ambient temperatures and fuel composition were investigated. When the spray penetration of the butanol-biodiesel-diesel blends is compared to that of the biodiesel-diesel blends, under non-combusting environment, a sudden drop in continuous liquid jet penetration length is observed at 1,100 K while the droplets penetrate faster for the butanol-biodiesel-diesel blends due to the micro-explosion effects. As shown in Figure 6, the tip of the spray jet erupts into a plume sometime after injection for the butanol-biodiesel-diesel blend. This phenomenon is not seen with the biodiesel-diesel blend at the same ambient temperature, neither at lower or much higher ambient temperature. It was concluded that micro-explosion can occur under certain conditions for the butanol-biodiesel-diesel blend, and the results were consistent with our previous theoretical study [4]. Butanol is much more volatile than biodiesel and diesel. With the significant differences in volatilities and boiling points among butanol, biodiesel and diesel, micro-explosion can occur in a butanol-biodiesel-diesel mixture. Micro-explosion leads to faster vaporization and better fuel/air mixing which in turn results in faster combustion.

Conclusions

- Biodiesel fuel properties relevant to combustion are strongly affected by the fatty acid composition of

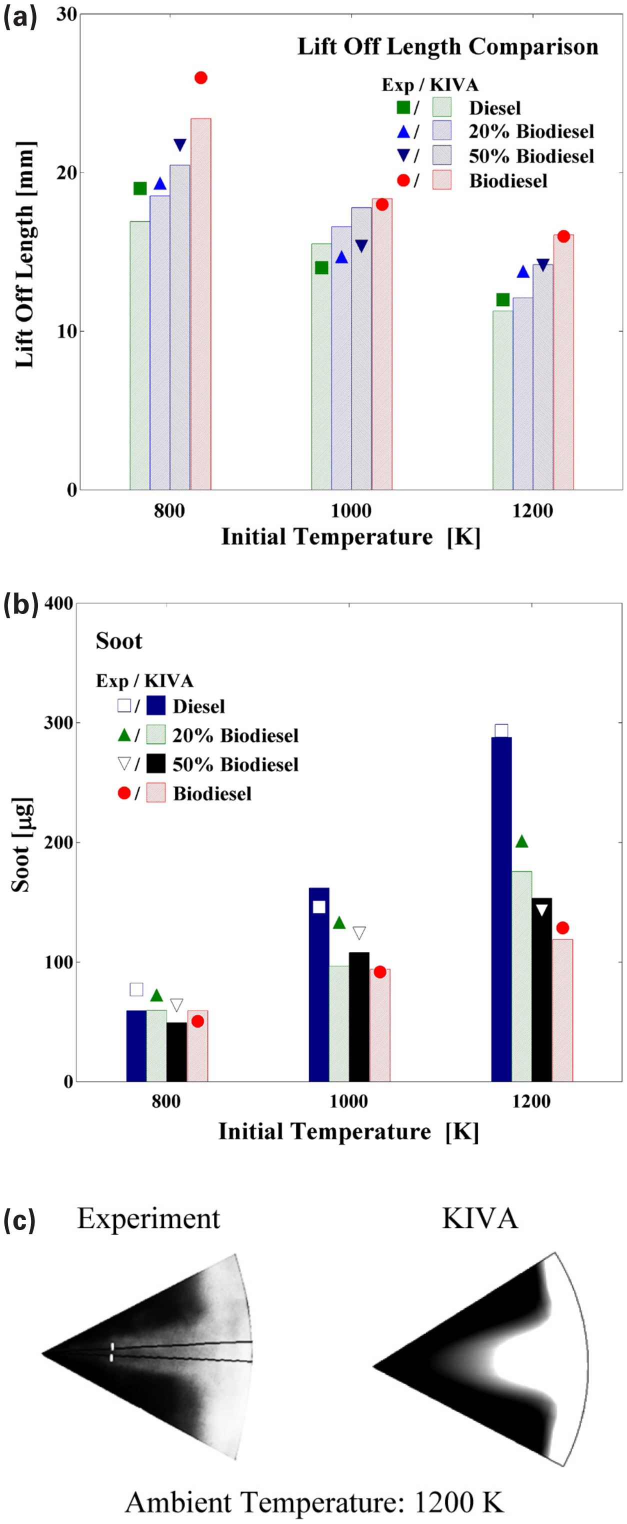

FIGURE 5. (a) Lift-off lengths and (b) soot emissions for the diesel, 20% biodiesel, 50% biodiesel and pure biodiesel. (c) An example of measured and computed hydroxyl radicals for 50% soybean biodiesel blend used in the lift-off length measurement.

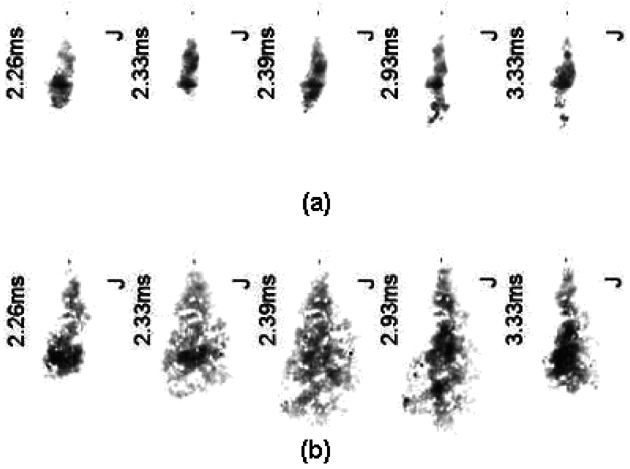

FIGURE 6. Spray jet penetration images at ambient temperature of 1,100 K for (a) Biodiesel 10% and Diesel 90%; (b) Butanol 10%, Biodiesel 10%, and Diesel 80% illustrating micro-explosion effects.

the source material, analogous to the hydrocarbon composition of petroleum-based fuels. A large percentage of mono-unsaturated fatty acids is preferable, followed by a balance in saturated and poly-unsaturated acids to ensure sufficient ignition quality without compromising oxidation stability and cold temperature properties.

- Both electronic control unit calibration and fuel effects influence the performance and emissions of the biodiesel engine pointing to the need for optimized calibrations with biodiesel fuels and diesel blends.
- Numerical predictions of spray penetrations, combustion characteristics and emissions match well with experimental measurements. Sub-models have been successfully modified to predict the experimental data.
- Narrow angle direct injections provide more flexibility in injection strategy optimization for LTC.
- Studies of the VSAI injector in the same engine show promising potential of the new injector on the performance and emissions of biodiesel LTC engines.
- Laser diagnostics of biodiesel LTC in the chamber provide excellent data for model improvement and fundamental understanding.
- Visualization of spray and combustion of butanol-biodiesel-diesel blends shows micro-explosions can occur under certain conditions for the blends. Micro-explosion leads to faster vaporization, better fuel/air mixing, and faster combustion. Mixture composition of bio-fuels can potentially be an effective way to improve combustion and emissions.

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IV.19 Unconventional Hydrocarbon Fuels

Thomas R. Gallant,
James A. Franz (Primary Contact)
Pacific Northwest National Laboratory (PNNL)
P.O. Box 999
Richland, WA 99352

DOE Technology Development Manager:
Kevin Stork

Subcontractors:
- Intertek USA, Pittsburgh, PA
- JM Consulting, Pittsburgh, PA

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.

Accomplishments

- Identified 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 influence on diesel fuel lubricity. The results, not previously reported in the literature, help explain many of the conflicting correlations and establish a new correlation which can be used in blending models to predict changes in lubricity.
- Investigated the influence of molecular structure and biodiesel blends on seal swell and established a preliminary seal swell correlation for a typical fuel-resistant nitrile seal material based on GC-FIMS data.
- Completed NMR characterization of nine Fuels for Advanced Combustion Engines (FACE) in conjunction with NMR, GC-FIMS and 2D GC/mass spectrometer (MS) analysis by Oak Ridge National Laboratory (ORNL) and Natural Resources Canada (NRCan) laboratories.
- Established a contract with JM Consulting to develop a 'fit for service' refinery/blending model to incorporate chemistry-based 'fit for service' correlations to identify issues with the use or blending of unconventional distillate streams or fuel products with conventional products.
- 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 support the alternative fuels subcommittee commitment to the Coordinating Research Council (CRC) FACE project.

Future Directions

- Characterize oil shale-derived distillate #1 and #2 diesel-like fuels for the CRC FACE alternative fuel subcommittee and measure lubricity and seal swell.
- Continue development of a refinery/blend model to predict fuel chemistry expected from unconventional hydrocarbon blends.
- Continue characterization work with the CRC alternative fuels FACE subcommittee to investigate future unconventional hydrocarbon-derived fuels, distillate streams and blends.

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Introduction

The objective of this project is to ensure that our chemical knowledge of 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 NMR correlations to bulk properties, e.g., cetane, have shown correlations based on conventional fuels to be unreliable predictors. 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 aftertreatment research. PNNL will use the data to investigate new NMR correlations for bulk properties and 'fit for service' issues, e.g., lubricity and seal swell, and supporting other infrastructure and material compatibility issues, e.g., cold temperature performance, crankcase oil compatibility and storage stability, that could be devastating to the introduction of fuels derived from unconventional hydrocarbon resources.

Approach

This project was initiated by collaborative workshops between DOE and NRCan national laboratories to discuss the introduction of unconventional hydrocarbon fuels [1]. The workshops identified areas for collaboration based on key knowledge gaps identified at the workshops and application of the expertise and analytical tools at national laboratories to gain fundamental insight. PNNL focused on ^1H / ^{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 need to be procured or developed. Oil sands-derived distillate fuel streams were obtained from Shell Canada. Oil shale distillate streams will be obtained by stabilizing an oil shale-derived crude from Red Leaf, Inc. and then hydrotreated to a finished diesel-like product. Other unconventional hydrocarbon fuels will be obtained through the Alternative Fuel subcommittee of CRC. These fuels will be analyzed by both ^1H and ^{13}C NMR and combined with other advanced analytical data to develop new property correlations based on NMR 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 to 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

1. Lubricity

Lubricity being a focal point for the 2005 'fit for service' issues, advanced analytical techniques were used to gain additional insight into the contradictory conclusions. High frequency reciprocating rig (HFRR) tests were 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 the same. The GC-FIMS data showed a strong correlation to 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 by the number of branches, (iso-paraffiins). Figure 1 shows the strong correlation to *n* and *iso* paraffinic structures with correlation factors consistent with experimental results using *n* and *iso* pure paraffinic molecules [2]. 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 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 over 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.

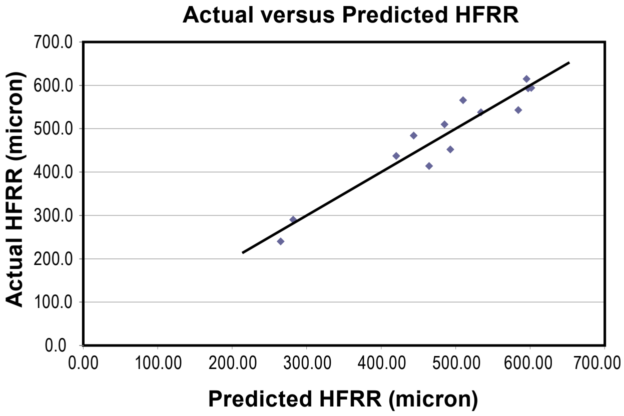

FIGURE 1. GC-FIMS-based HFRR Correlation

2. Nitrile Seal Swell

Seal swell was measured using a technique developed by the University of Dayton Research Center [3]. Two oil sands derived distillate streams, ultra-low sulfur diesel and 10 and 20% blends with soy- and rapeseed methyl ester-based diesel fuel. The high volume swell character of the blends apparently arises from a higher concentration of unsaturated cyclic hydrocarbons and complex aromatics. Furthermore, the volume swell is moderated by the relatively low solubility of the alkanes present in the fuel. The blending soy and rapeseed methyl ester increase the volume swell character of these fuels. The propensity of rapeseed methyl ester to swell nitrile seals is similar to that of soy methyl ester.

Conclusions

- 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.
- Nitrile seal swell is influenced by both cycloparaffins and mono-aromatics and soy and rapeseed methyl ester blends were shown to increase seal swell of the unconventional hydrocarbon fuels.

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IV.20 Alternative Fuels Infrastructure Development

Cary Bloyd
Pacific Northwest National Laboratory
902 Battelle Blvd., Box 999
Richland, WA 99352

DOE Technology Development Manager:
Kevin Stork

Objectives

To provide analysis of international alternative fuel use which supports alternative fuel infrastructure development in the United States.

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 with 80% gasoline (E20) use in Thailand concentrating on experiences which could benefit the introduction of E20 in the U.S.

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Introduction

Thailand imports about 90% of the crude oil and petroleum products used in the country. Thailand is an agro economy producing several biofuel feedstocks. The Royal Thai government thus has aggressively implemented energy policies to promote biofuel production in the country with an attempt to lower the amount of oil imports. Biofuel programs have been under development in Thailand for the past three decades, drawing upon inspiration originated from the Royal Projects by His Majesty the King after the first oil crisis in 1973. Thailand was the first country in Asia to announce national policies for both bioethanol and biodiesel. The Royal Thai government signed cabinet resolutions to promote bioethanol on September 19, 2000 and to promote biodiesel on July 10, 2001. These were followed by several measures such as investment promotion, biofuel standardization, biofuel price incentives, vehicle specifications and tax incentives, research and development programs, and the proposal for cooperation among the Association of Southeast Asian Nations economies.

An understanding of the issues and experiences associated with the introduction of alternative fuels in other countries can help the U.S. in anticipation of potential problems as it introduces new automotive fuels. Thailand is of particular interest since it introduced E20 to its commercial market in 2007 and the U.S. is now considering introducing E20 into the U.S. market.

Approach

This research reviews the status of alternate transportation fuels development and utilization in Thailand.

Results

As of June 2009, there are a total of 15 commercial ethanol plants, with total installed capacity of 2.275 million liters per day (see Table 1). This is 0.7 million liters per day more than reported in August 2008 as four more ethanol plants started operation in 2009. Eight additional ethanol plants (mainly using cassava as a feedstock) are being constructed with an additional capacity of 3.42 million liters per day. As of April 2009, 47 more ethanol plants received construction permits with total production capacity of 12.295 million liters per day.

The current blends of ethanol with gasoline in the Thai market are E10 (10% ethanol with 90% gasoline) in Octane 91 and Octane 95, E20 in Octane 95, and E85 in Octane 95 (85% of ethanol with 15% of gasoline). Sales of gasohol in Thailand have been increasing continually since the start in 2004. The most recent available data of gasohol sales in Thailand was for the month of January 2009 at 390.01 million liters or 12.581 million liters per day (as compared to the sales of gasohol in January 2008 at 220.84 million liters or 7.124 million liters per day).

Production and sales of E10 increased drastically in 2008 as compared to 2007. The production of E20 began in 2007, and the production of E85 began in 2008 as seen in Table 2.

As of August 2009, there are a total of 6,981 petro stations across Thailand selling gasohol. The majority of them are selling E10 Octane 95. Since E20 and E85 were introduced to the market in 2008, the petro stations offering these products are still limited and are mainly located in the Bangkok Metropolitan Area (see Table 3). However, both PTT and Bangchak have plans to open more petro stations for E20 and E85 all over the country to meet future growing demand.

TABLE 1. Existing Ethanol Plants in Thailand (June 2009)

Company	Installed Capacity (L/day)	Feedstock	Province	Commencing Date
1. Pornwilai International Group	25,000	Molasses	Ayuddhaya	Oct 03
2. Thai Alcohol	200,000	Molasses	Nakhon-Pathom	Aug 04
3. Thai Agro Energy	150,000	Molasses	Suphanburi	Jan 05
4. Thai Nguan Ethanol	130,000	Cassava	Khon Khan	Aug 05
5. Khon Khan Alcohol	150,000	Sugarcane/Molasses	Khon Khan	Jan 06
6. PetroGreen	200,000	Sugarcane/Molasses	Chaiyaphoom	Dec 06
7. Thai Sugar Ethanol	100,000	Sugarcane/Molasses	Kanchanaburi	Apr 07
8. KI Ethanol	100,000	Sugarcane/Molasses	Nakhon Ratchasima	Jun 07
9. PetroGreen	200,000	Sugarcane/Molasses	Kalaseen	Jan 08
10. Ekarat Pattana	200,000	Molasses	Nakhonsawan	Mar 08
11. Thai Rung Ruang Energy	120,000	Sugarcane/Molasses	Saraburi	Mar 08
12. Ratchaburi Ethanol	150,000	Cassava/Molasses	Ratchaburi	Jan 09
13. ES Power	150,000	Molasses/Cassava	Sakaew	Jan 09
14. Maesawd Clean Energy	200,000	Sugarcane	Tak	May 09
15. SupThip	200,000	Cassava	Lopburi	May 09
Total	**2,275,000**			

Source: www.dede.go.th/dede/fileadmin/upload/pictures_eng/pdffile/Existing_Ethanol_Plant.xls

TABLE 2. Production and Sales of Gasohol in 2007 and 2008

Unit: Million Liters

	Production		Sales	
	2007	**2008**	**2007**	**2008**
E10-Octane 91	248.160	928.730	244.256	923.501
E10-Octane 95	1,516.133	2,435.466	1,518.507	2,439.182
E20	0.047	29.395		29.028
E85		0.037		0.021
	1,764.34	3,393.628	1,762.763	3,391.732

Source: www.doeb.go.th/information/info_conclude51.htm

TABLE 3. Numbers of Petro Stations Selling Gasohol (August 2009)

	E10 Octane 91	E10 Octane 95	E20	E85
PTT	801	1,133	117	3
Bangchak	804	720	117	1
Shell	375	584		
Esso	336	550		
Chevron	191	418		
Petronas	76	116		
Siam-Sahaborikan		143		
Others	98	398		
Total	**2,681**	**4,062**	**234**	**4**

Source: www.doeb.go.th/information/stat/stat_gasohol.xls

PTT was the first company selling E20 and used the commercial name of "PTT E20 Plus". Later on Bangchak entered the E20 market and was the second producer and distributor of E20 in Thailand.

A total of 29.028 million liters of E20 were consumed in 2008. Of the total, 61.8% or 17.931 million liters was the PTT E20 Plus by PTT. It was reported that in 2009 PTT's sales of E20 are about 2.7 million liters per month, which almost doubles from 1.494 million liters per month in 2008.

E20 is recommended to be utilized on specific car models as suggested by their manufacturers. At present, six automobile companies are selling E20 capable cars. Those include:

- Ford–Focus and Escape 3000 CC
- Honda–Accord, CR-V, Civic and City
- Mazda–Mazda 3
- Nissan–Tida and Teana
- Mitsubishi–Space Wagon and Lancer
- Toyota–Corolla, Vios, Yaris, Altis, and Camry

The Ford Focus and Ford Escape 3000 CC have been available in the Thai market since 2005, while the other models have been sold since 2008. The government has provided guidelines which specify that cars manufactured for E20 can also be fueled by gasoline octane 95 and E10 octane 95. About 60,000 of E20 capable cars were sold in Thailand in 2008. The Thailand Automobile Institute forecasts that there will be 610,000 E20 compatible vehicles on the street in 2011.

At present there are 234 petro stations selling E20 across the country–of which half are owned by PTT and the other half are owned by Bangchak.

The Thai government is implementing various policies to support E20 as well as E20 capable cars. As an incentive for people to use more E20, the retail price of E20 is set to be 2.0 baht per liter lower than the retail price of E10 Octane 95 (Gasohol 95) and 6 baht per liter lower than that of gasoline 95. For example, the retail price of E20 on October 20, 2009 was 28.24 baht per liter, and those of Gasohol 95 and gasoline 95 on the same day were 30.24 baht and of 34.24 baht per liter, respectively.

Conclusions

- Thailand has been a leader in introduction of a wide range of alternative transport fuels.
- The introduction of E20 at commercial stations was accompanied by the introduction of E20 compatible cars.
- There are currently six brands of E20 cars now being sold and operated in Thailand.
- An examination of the experience of utilizing E20 in Thailand could benefit the U.S. alternative fuel program.

FY 2008/2009 Publications/Presentations

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IV.21 Decision Analysis Tool to Compare Energy Pathways for Transportation

Cary Bloyd
Pacific Northwest National Laboratory
902 Battelle Blvd., Box 999
Richland, WA 99352

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
Lumina Decision Systems, Inc.
Los Gatos, CA

Objectives

- To develop an agile decision analysis portfolio tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies.
- To evaluate technologies on multiple criteria, including, greenhouse gas emissions, cost of transportation, energy security, and criteria pollutant emissions.

Accomplishments

- An initial prototype model was developed using the Analytica decision analysis support system.
- The initial model shows inputs, results, and intermediate computations for the prototype decision pathways.
- Initial prototype model includes plug-in hybrid vehicles and biomass-to-ethanol for automobiles with flex-fuel internal combustion engines.

Future Directions

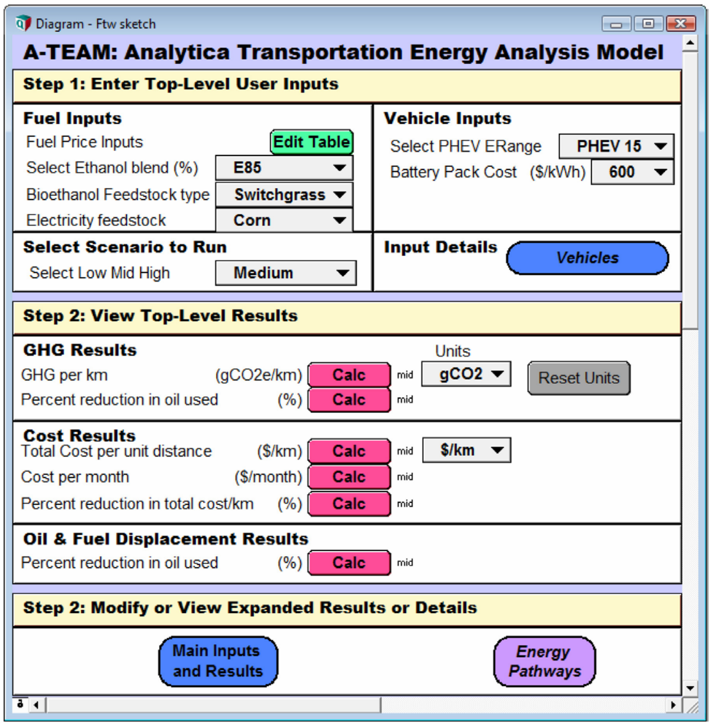
- Make the prototype model more general and modular so that it is easier to add new technologies and pathways simply by adding standard template modules.
- Add a model of automobile fleet turnover that enables analysis of how long it might take for new technologies to obtain significant market share and achieve changes in results.
- Include variations in battery cost and battery performance over time.
- Include the use of both E15 and E20 versus E85 and compare cost for distributed infrastructure.

* * *

Introduction

With the goals of reducing greenhouse gas emissions, oil imports, and energy costs, a wide variety of automotive technologies are proposed to replace the traditional gasoline-powered internal combustion engine (g-ICE). Biomass is seen as an important domestic energy feedstock, and there are multiple pathways in which it can be linked to the transport sector. Contenders include the use of cellulosic ethanol from biomass to replace gasoline or the use of a biomass-fueled combined cycle electrical power generation facility in conjunction plug-in hybrid electric vehicles (PHEVs).

This project is to develop a scenario decision analysis tool to assist policy makers, program managers, and others to obtain a better understanding of these uncertain possibilities and how they may interact over time. The tool is provisionally named A-TEAM for Analytica Transportation Energy Analysis Model (Figure 1). A-TEAM will evaluate pathways and technologies in terms of their effects on the three Es:



A-TEAM: Analytica Transportation Energy Analysis Model

Step 1: Enter Top-Level User Inputs

Fuel Inputs
Fuel Price Inputs: Edit Table
Select Ethanol blend (%): E85
Bioethanol Feedstock type: Switchgrass
Electricity feedstock: Corn

Vehicle Inputs
Select PHEV ERange: PHEV 15
Battery Pack Cost ($/kWh): 600

Select Scenario to Run
Select Low Mid High: Medium

Input Details: Vehicles

Step 2: View Top-Level Results

GHG Results (Units: gCO2; Reset Units)
GHG per km (gCO2e/km): Calc mid
Percent reduction in oil used (%): Calc mid

Cost Results (Units: $/km)
Total Cost per unit distance ($/km): Calc mid
Cost per month ($/month): Calc mid
Percent reduction in total cost/km (%): Calc mid

Oil & Fuel Displacement Results
Percent reduction in oil used (%): Calc mid

Step 2: Modify or View Expanded Results or Details

Main Inputs and Results
Energy Pathways

FIGURE 1. User Interface for A-TEAM

environmental (greenhouse gas [GHG] emissions), economics (capital and energy costs), and energy security (oil imports). It will allow users to rapidly define and compare scenarios with alternative assumptions about key uncertainties and policy variables. It will support explicit probabilistic treatment of the many other uncertainties. The model is designed to be as simple, transparent, and extensible as possible – consistent with addressing the most important questions of interest.

Approach

This project will build an initial prototype computer model that focuses on just a few important issues and pathways from field or well to wheel. The initial pathways include, biomass-to-ethanol for automobiles with flex-fuel internal combustion engines, biomass-fueled combined cycle electrical power generation and PHEVs. The framework will be developed so that it can be expanded over time to add pathways and other kinds of detail. The model will be created with generic templates for fossil and renewable energy sources, energy-conversion devices and pathways, and market components, using a logit model to project market share as a function of relative prices of competitive fuels. This structure will make it relatively easy to add new technologies and pathways as the model is expanded.

Results

A prototype model was developed which compares vehicles one of each type (or assuming all vehicles of the same type). Initial pathways are shown in Figure 2. The prototype model does not yet include a model of fleet turnover and market penetration of each technology. The initial model was expanded, including adding estimates from the energy numbers wiki, adding results, and criteria to compare vehicle technologies, including GHG emissions per kilometer, total cost per kilometer (or month), and reduction in oil imports. It was assumed that any change in usage of gasoline (or other oil-derived fuel) would result in a corresponding reduction in oil imports. Simple range sensitivity (Figure 3) analysis was also added showing for a range of key input parameters, what the effect on each criterion result is of varying each parameter from a low to high value, while keeping all other parameters at their nominal mid-value. A result was also added to compare vehicle technologies in terms of the percentage change (increase or decrease) on each criterion (GHG emissions, cost, and oil imports) compared to a base vehicle – typically, a g-ICE as shown in Figure 4.

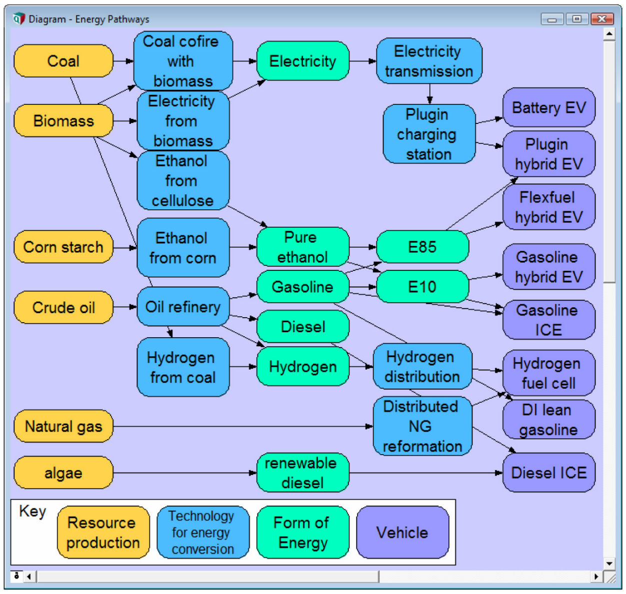
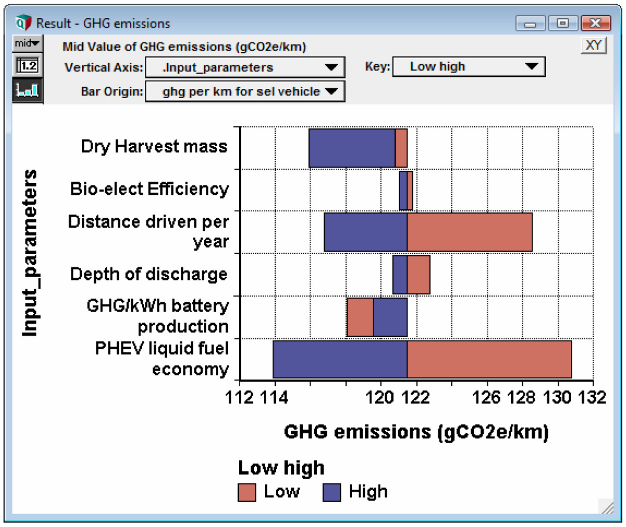


FIGURE 2. Selected Energy Pathways for Analysis from Resource Production to Vehicle Technology


Result - GHG emissions

Mid Value of GHG emissions (gCO2e/km)

Vertical Axis: .Input_parameters

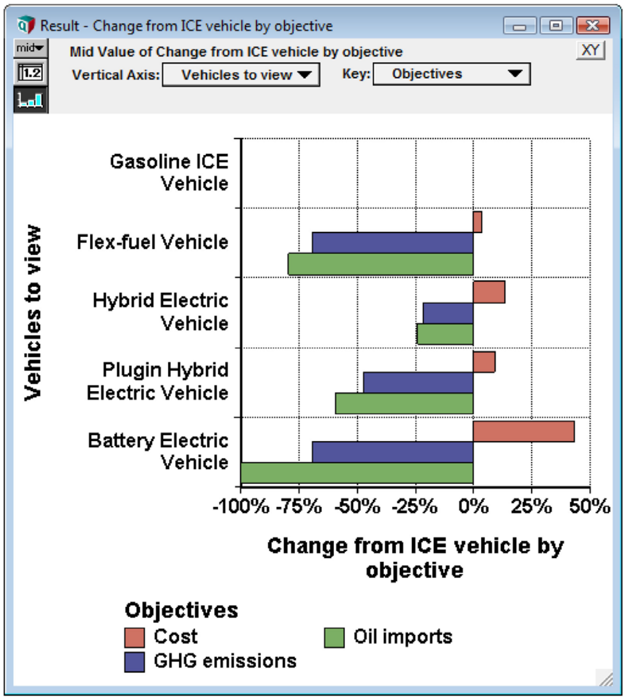
Key: Low high

Bar Origin: ghg per km for sel vehicle

FIGURE 3. Range sensitivity analysis comparing the effect of changing selected input parameters from low to high levels on the GHG emissions.

Conclusion

- A prototype decision analysis tool to compare energy pathways for transportation was developed.
- The prototype compared biomass to ethanol for flex-fuel vehicles and electricity linked to PHEVs.
- The prototype has the capability to model the impacts of uncertainty on key model parameters.
- Future directions for the prototype model development were identified.



Result - Change from ICE vehicle by objective

Mid Value of Change from ICE vehicle by objective

Vertical Axis: Vehicles to view

Key: Objectives

FIGURE 4. For selected vehicle technologies, estimate of percent change on key objectives relative to a conventional g-ICE.

FY 2008/2009 Publications/Presentations

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V. NEW PROJECTS

V.1 Collaborative Lubricating Oil Study on Emissions (CLOSE) Project

Dr. Douglas R. Lawson
National Renewable Energy Laboratory (NREL)
1617 Cole Boulevard
Golden, CO 80401

DOE Technology Development Manager:
Kevin Stork

Subcontractors:
- Southwest Research Institute®, San Antonio, TX
- Desert Research Institute, Reno, NV

Objective

The objective of this project is to quantify the relative roles 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, 10% ethanol in gasoline (E10), diesel, biodiesel, and compressed natural gas (CNG) while operating on fresh and used crankcase lubricants.

Accomplishments

- Continued Cooperative Research and Development Agreement between NREL and the South Coast Air Quality Management District (SCAQMD) and the California Air Resources Board for project funding.
- Obtained additional funding from the Coordinating Research Council (sponsored by the automotive and petroleum industries), Lubrizol and the SCAQMD 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 medium-duty vehicle ("normal" and high emitter) emissions testing in September 2009. Heavy-duty vehicle testing will begin in October 2009.

Future Directions

A variety of light-, medium-, and heavy-duty (LD, MD, HD) vehicles are being 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 complete vehicle and emissions testing project will be completed during Fiscal Year 2010.

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, is used to quantify the relative contributions of PM formed from the fuels and the lubricants in the vehicles in the CLOSE Project.

TABLE 1. CLOSE Project Test Matrix

Test Temperature	72°F (nominal)				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)	√	√	√	√				

"Normal" and high-emitting vehicles representing gasoline, diesel, and CNG-powered vehicles are being tested. Lubricants used in each technology are representative of those currently on the market, with both new and aged lubricants being tested in the project. The fuels used in the vehicles will be gasoline containing no ethanol, E10, TxLED diesel, biodiesel, and CNG. Room temperature and cold temperature testing will be performed on all of the light- and medium-duty vehicles. Cold temperature testing will not be 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 Office of Vehicle Technology's (OVT'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 [1,2]. For example, data collected in Washington, D.C., over a ten-year period suggest that PM from gasoline exhaust is ten times more important to the emission inventory than diesel exhaust, as shown in Figure 1 [3].

OVT's comparative toxicity studies have also shown 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 CNG 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- and heavy-duty vehicles are being recruited, including both "normal" and high-PM emitters, and operated on chassis dynamometers at room temperature (72°F nominal) and cold temperature (20°F). Gaseous (total hydrocarbons, non-methane hydrocarbons, carbon monoxide, oxides of nitrogen) and real-time particle emissions are being measured, and PM and SVOC samples are being collected for subsequent chemical analyses. Physical PM characterization is being conducted to obtain data on particle size and count, which will be investigated over the various driving test cycles run on the chassis dynamometers.

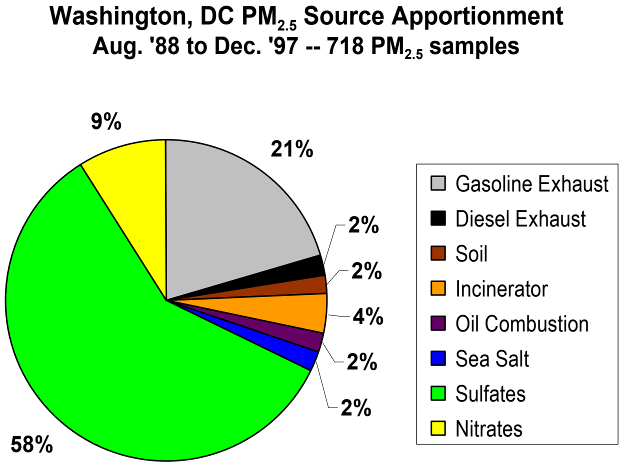

FIGURE 1. Source apportionment of $PM_{2.5}$ in the Washington, D.C., area, samples collected between 1988 and 1997 [3].

Results

At the time of this report, vehicle testing has been completed on the light-duty and medium-duty "normal" and high-emitting vehicles. Figures 2 and 3 show the "normal" emitter vehicle on the dynamometer, along with the sampling ports and equipment used in the 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, in May 2008, and additional presentations have been made to the Health Effects Institute and the annual DOE Merit Review Meeting. Because this project is not completed, there are no conclusions at the time of this report. The CLOSE Project will be completed by August 2010, 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).

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3. Kim, E. and P. K. Hopke. Source Apportionment of Fine Particles in Washington, D.C., Utilizing Temperature-Resolved Carbon Fractions, *J. Air & Waste Manage. Assoc.*, Vol. 54, pp. 773-785 (2004).

FIGURE 2. Light-duty "normal" emitter tested in the CLOSE Project, a 2006 Chevrolet Impala.

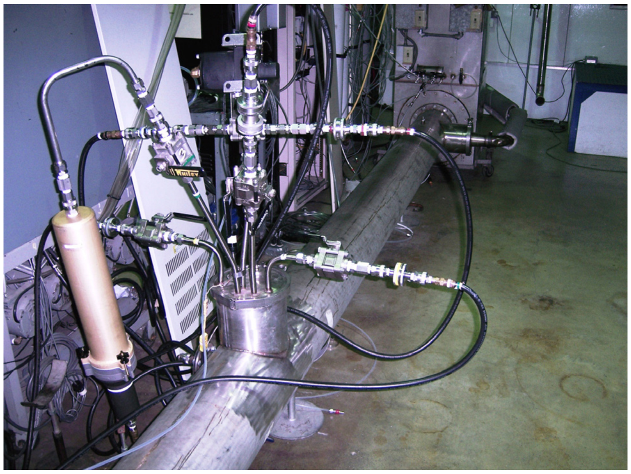

FIGURE 3. Sampling probes used to collect exhaust emissions samples from the dilution tunnel.

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 2009 Publications/Presentations

1. "The Collaborative Lubricating Oil Study on Emissions (CLOSE) Project," progress reports presented at CRC AVFL meetings and at Infineum, February, May and October 2009.

2. "The Collaborative Lubricating Oil Study on Emissions (CLOSE) Project," presented at DOE Merit Review Meeting, Arlington, VA; May 2009.

VI. Acronyms, Abbreviations and Definitions

ϕ	Fuel/air-equivalence ratio
$\eta_{f,ig}$	Gross indicated fuel-conversion efficiency
°F	Degrees Fahrenheit
1-D	One-dimensional
2D GC	2-dimensional gas chromatograph
2-D	Two-dimensional
AFCI-MS	Atmospheric pressure chemical ionization mass spectroscopy
AFR_{st}	Stoichiometric air/fuel ratio
AMN	Alpha methyl naphthalene
API	American Petroleum Institute
ASTM	ASTM International, a standards setting organization
atdc, ATDC, aTDC	After top dead center
A-TEAM	Analytica Transportation Energy Analysis Model
a.u.	Arbitrary units
B5	5% biodiesel
B6	6% biodiesel
B20	20% biodiesel
B100	100% 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
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
CCRT	Catalyzed continuously regenerated trap
CFD	Computational fluid dynamics
CFPP	Cold filter plugging point
CI	Compression ignition
CLCC	Closed-loop combustion control
CLEERS	Cross-Cut Lean Exhaust Emissions Reduction Simulations
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
CSFT	Cold soak filtration test
CX	A fuel molecule with X carbon atoms
DEER	Diesel Engine Emissions Reduction
DNPH	2,4-dinitorophenylhydorazine
DOC	Diesel oxidation catalyst
DoE	Design of experiment
DPF	Diesel particulate filter
DRG	Directed relational graph
DRIFTS	Diffuse reflectance infrared Fourier-transform spectroscopy
DVPE	dry vapor pressure equivalent, i.e., vapor pressure at 100ºF in the ASTM standard apparatus used for that test
E10	10% ethanol, 90% gasoline fuel blend
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
ECS	Emission control system
ECU	Electronic control unit
EGO	Exhaust gas oxygen
EGR	Exhaust gas recirculation
EISA	Energy Independence and Security Act of 2007
EIVC	Early intake valve closing
EM-MS	Electron monochromator-mass spectrometer
EMOT	Estimated minimum operability temperature
EPMA	Electron probe microanalysis
ESI-MS	Electrospray ionization–mass spectrometry
Exx	XX% ethanol, 100-XX% gasoline fuel blend
FACE	Fuels for Advanced Combustion Engines

FAME	Fatty acid methyl ester
FC	Fixed carbon
FFV	Flexible-fuel vehicle; flex-fuel vehicle
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
GHG	Greenhouse gases
g-ICE	Gasoline internal combustion engine
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
HPLC	High-performance liquid chromatography
HRR	Heat release rate
HR-TEM	High-resolution transmission electron microscopic
HSDI	High-speed direct injection
HVA	Hydraulic valve actuator
ICC	International Codes Council
ICP	Inductively coupled plasma
IMEP	Indicated mean effective pressure
IQT™	Ignition quality tester
ISFC	Indicated specific fuel consumption
$ISNO_x$	Indicated-specific emissions of nitrogen oxides
ITE	Indicated thermal efficiency
LHV	Lower heating value; latent heat of vaporization
LIVC	Late intake valve closing
LTC	Low-temperature combustion
LTFT	Low temperature flow test; long-term fuel trim
LTHR	Low temperature heat release
MALDI-TOF MS	Matrix-assisted laser desorption/ ionization time of flight mass spectrometry
MBRC	Miles between road calls
MBT	Minimum (spark advance) for best torque; Maximum brake torque
MC	Mobile carbon
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.
NAC	NOx absorber catalyst
NDCA	1,8-Naphthalene-dicarboxylic acid
NL	Natural-luminosity
NMHC	Non-methane hydrocarbon
NMOG	Non-methane organic gases
NMR	Nuclear magnetic resonance
NPAH	Nitro-polynuclear aromatic hydrocarbons
NVO	Negative valve overlap
OEM	Original Equipment Manufacturer
OSC	Oxygen storage capacity
PAH	Polycyclic aromatic hydrocarbon
PCA	Principal component analysis
PCCI	Pre-mixed charge compression ignition
PEI	Petroleum Equipment Industry Association
PFI	Port fuel injection, port fuel injected
PHEV	Plug-in hybrid electric vehicle
PIV	Particle image velocimetry
PLIF	Planar laser induced fluorescence
PM	Particulate matter
RC	Road call
RFS	Renewable Fuel Standard
RON	Research octane number
RPM, rpm	Revolutions per minute
SA	Spark assist
SAFR	Stoichiometric air-to-fuel ratio
SCORE	Sandia Compression-ignition Optical Research Engine
SCR	Selective catalytic reduction
SEM	Scanning electron microscopy
SIDI	Spark ignition direct injection
SIFL	Spatially integrated flame luminosity
SMPS	Scanning mobility particle scanner
SOC	Start of combustion; soluble organic compound
SOF	Soluble organic fraction
SOI	Start of injection
SULEV	Super ultra-low emissions vehicle
SV	Spray-visualization
T_{bdc}	Bottom-dead-center temperature
TDC	Top dead center

TEM	Transmission electron spectroscopy
TF	Test fuel
THC	Total hydrocarbon
TPO	Temperature-programmed oxidation
TRF	Toluene reference fuel
TWC	Three-way catalyst
ULEV	Ultra-low emission vehicle
ULSD	Ultra-low sulfur diesel
VOF	Volatile organic fraction
VSAI	Variable spray angle injection
VVA	Variable valve actuation
WOT	Wide open throttle
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZDDP	Zinc dialkyl-dithiophosphate

VII. Index of Primary Contacts

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