2005
Annual Progress Report

PROGRESS REPORT FOR FUELS TECHNOLOGIES

Less dependence on foreign oil, and
eventual transition to an emissions-free,
petroleum-free vehicle

FreedomCAR and Vehicle Technologies Program

U.S. Department of Energy
Energy Efficiency
and Renewable Energy
Bringing you a prosperous future where energy
is clean, abundant, reliable, and affordable

FreedomCAR & Fuel Partnership

21st CENTURY TRUCK PARTNERSHIP

U.S. Department of Energy
1000 Independence Avenue, S.W.
Washington, D.C. 20585-0121

FY 2005

Progress Report for Fuels Technologies

Energy Efficiency and Renewable Energy
Office of FreedomCAR and Vehicle Technologies

Approved by Stephen Goguen

January 2006

Acknowledgement

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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 Office of FreedomCAR and Vehicle Technologies (FCVT), we are pleased to introduce the Fiscal Year (FY) 2005 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.

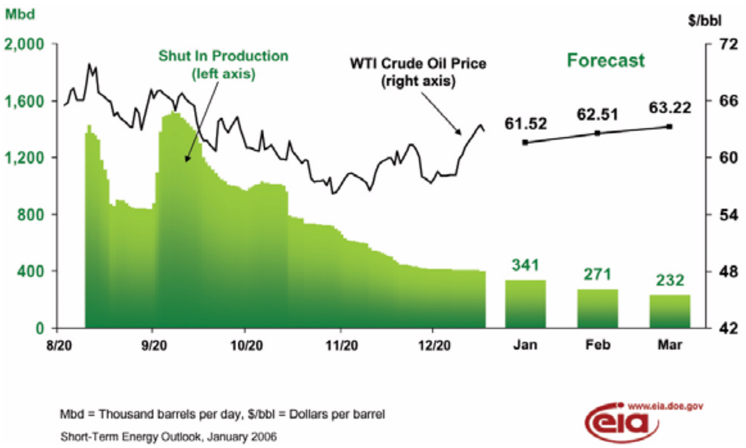
The Fuels Technologies Sub-Program is an integral part of the FreedomCAR government/industry partnership and a key component to achieving the FreedomCAR mission to develop more energy-efficient and environmentally friendly highway transportation technologies that enable America to use less petroleum 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 National Laboratories and universities. Advanced petroleum-based fuels are even more important to the 21st Century Truck Initiative that proposes to dramatically increase heavy-duty vehicle fuel economy while continuing to reduce emissions. For heavy over-the-road trucks, combustion engines operating on liquid fuels are the only viable options in the foreseeable future for these vehicles given our current transportation fuels distribution infrastructure. The Fuels Technologies Sub-Program works closely with the Advanced Combustion Engine R&D Sub-Program of FCVT, 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 Sub-Program 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, Fuel Cells and Infrastructure Technologies Program, and the Office of Fossil Energy via the Fuels Crosscut Team to ensure maximum synergy and to avoid duplication of effort.

Goals

- By 2007, identify fuel formulations optimized for use in 2007-2010 technology diesel engines that incorporate use of non-petroleum-based blending components with the potential to achieve at least a 5 percent replacement of petroleum fuels.
- By 2010, identify fuel formulations optimized for use in advanced combustion engines (2010-2020) providing high efficiency and very low emissions, and validate that at least 5 percent replacement of petroleum fuels could be achieved in the following decade.

Transportation Fuels and Energy Security

Petroleum-derived fuels account for 98% of all fuel used in the U.S. highway transportation sector. This sector includes private automobiles used for passenger transport and commercial trucks used for the transport of goods. Because of the lack of alternative sources of energy in this sector, a widespread disruption of petroleum supplies due to natural disaster, political maneuvering, 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. Overall, crude oil and gasoline prices rose about 50% from the beginning of 2005 to its end. The Energy Information Administration projects that crude oil and gasoline prices will stay at levels similar to those at the end of 2005 throughout most of 2006.



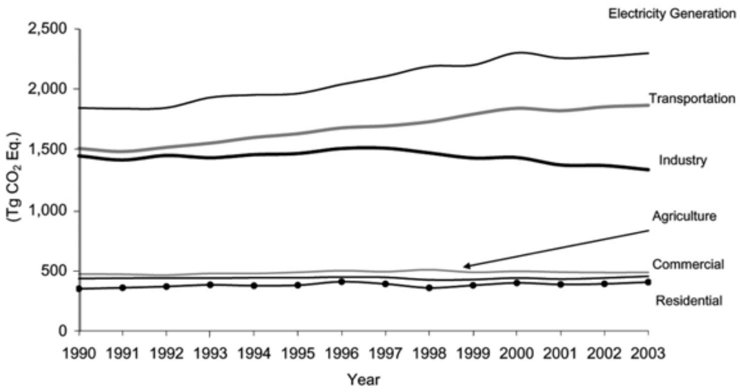
Shut-In U.S. Crude Production Due to Hurricanes in 2005
Source: U.S. Energy Information Administration

Petroleum currently supplies about 40% of all the energy used in the U.S., with 67% of this petroleum going to the transportation sector. The transportation sector alone consumes more petroleum than is produced in the U.S.; 67% of the petroleum consumed in the U.S. is imported. By 2025, the U.S. is expected to import as much as 77% of its petroleum, and the Organization of Petroleum Exporting Countries (OPEC) will need to increase oil production by 80% to satisfy not only increasing demands for petroleum in the U.S., but in the rest of the world as well, where demand is growing even faster. Such heavy dependence on non-indigenous energy sources leaves the U.S. vulnerable to petroleum price spikes and shortages, as well as related consequences.

Research sponsored by the Fuels Technologies Sub-Program 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 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. Likewise, in 2005, biodiesel production in the U.S. tripled from the 2004 level, and the number of plants planned to be built equals the number already in place. How the addition of these fuels impacts the physical and chemical characteristics of diesel fuel needs to be known to preserve and enhance the efficiency and emissions of advanced 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, oxides of nitrogen (NOx), particulate matter, ammonia, volatile organic compounds (VOCs), and sulfur dioxide. These pollutants are blamed with forming ozone and smog, causing acid rain, and contributing to a number of health issues – especially respiratory problems. Highway vehicles are responsible for 51% of all carbon monoxide emissions in the U.S., according to the U.S. Environmental Protection Agency (EPA). These vehicles also contribute 34% of all NOx emitted and 29% of all VOCs emitted—these are the two components necessary for ozone formation.



Transportation is the Second Largest Source of Greenhouse Gases in the U.S.

Source: U.S. Environmental Protection Agency

Combustion of petroleum fuels also releases greenhouse gases (primarily CO_2) that are believed to contribute to global warming. Highway vehicles emit 1,460 trillion grams of CO_2 equivalent greenhouse gases per year in the U.S. Transportation greenhouse gases have increased at a rate of about 1.7% per year since 1990. Increases in the number of vehicles and the miles traveled per year are responsible for this increase, as well as a general decline in average light-duty vehicle fuel economy. In the short term only minor adjustments can generally be made through consumer behavior (e.g., not driving as far for summer vacation). However, long-term adjustments such as increased vehicle fuel economy (i.e., more efficient engines and powertrains) and non-petroleum renewable fuels are needed to reduce highway transportation's contribution to greenhouse gas emissions.

Emissions of harmful pollutants and greenhouse gases from combustion processes depend in large part on the conditions used in combustion and on fuel properties. The fuel property that has attracted the most attention due to its damaging effects on emission control devices is sulfur content. Through a rulemaking in 2000, the EPA mandated that the sulfur content of highway diesel fuel be lowered to 15 ppm maximum by June 2006 to enable emission controls to reduce oxides of nitrogen and particulate matter from diesel engines. Engineering data to support the need for diesel fuel sulfur reduction to less than 15 ppm was generated by a previous DOE-led program, DECSE (Diesel Emission Control Sulfur Effects), and referenced in the EPA rulemaking. Though the sulfur reduction mandate is still 6 months away (retailers will be allowed to sell diesel fuel having up to 22 ppm sulfur through October 15 as part of the transition), some energy companies have been supplying ultra-low sulfur diesel fuel in certain areas where air pollution is a large concern.

In a separate rulemaking in early 2000, EPA required the amount of sulfur to be reduced in gasoline, down to a 30 ppm average by 2006, with a maximum cap of 80 ppm. Phase-in of this requirement began in 2004, but the final stage and largest change begins on January 1, 2006, as the sulfur level in gasoline is lowered from an average 300 ppm to a maximum average 30 ppm with the exception of some motor gasoline produced in the Rocky Mountain region. All motor gasoline must be in compliance by 2008.

Removal of MTBE as a blending component from motor gasoline, another pending change, will likely increase gasoline prices and possibly lead to greater price volatility. State concerns about potential water contamination are driving efforts to eliminate MTBE as a gasoline additive. Some MTBE removed from the gasoline pool may be replaced by the renewable fuel ethanol, which continues to grow in supply.

The Fuels Technologies Sub-Program is addressing sulfur reduction and mitigation strategies as well as other technologies to enable emission reductions. Fuel properties are being matched with combustion conditions and advanced combustion regimes to develop optimal systems with both high efficiencies and low emissions. Renewable and non-petroleum-based fuels are being pursued because they are generally sulfur-free and have desirable properties for lowering criteria emissions. Blends of renewable and non-petroleum fuels with petroleum fuels have much potential to decrease emissions and improve fuel properties in general. Renewable fuels have the added benefit of reduced greenhouse gas emissions.

Transportation Fuels and the Economy

Crude oil prices increased significantly over the past year, due primarily to strong worldwide demand, particularly in developing countries, but also from the disruption of U.S. crude oil production in the Gulf of Mexico due to hurricanes. As of late 2005, crude oil was about $67 per barrel, compared with $46 per barrel in December 2004. Crude oil spiked above $70 per barrel in 2005 based on concerns about economic and political stability in some oil producing countries, hurricane-induced production cut-backs, and concern that new discoveries were falling behind production. The value of petroleum products imported into the U.S. increased by 40% in 2005 compared to 2004, and represents about 31% of our entire trade deficit, up from 28% in 2004. While higher petroleum prices have not significantly affected the U.S. economy, their contribution to our growing trade deficit is worrisome.

The potential economic benefits of implementing advanced vehicle and fuels technologies in the U.S. are many. Technologies that improve fuel economy will reduce the amount consumers spend on fuel, allowing consumers to spend more in other areas of the economy. Reduced fuel spending also translates to reduced imports, improving 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 deficit.

The Fuels Technologies Sub-Program 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 Sub-Program greatly improves the prospects for advanced fuels and advanced vehicle technologies.

Sub-Program Laboratory Capabilities

The 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 for vehicle performance and emissions research, an engine dynamometer test cell capable of certification-quality emissions testing, and a fuel chemistry laboratory for performing precise studies of fuel properties, including ignition quality. In FY 2005, advanced facility capabilities, enhanced expertise, and new protocols were developed and utilized to lead and support fuels and heavy-duty hybrid vehicle research projects in support of DOE objectives and goals. Several test projects provided first-ever available data for new technologies and alternative fuels.

At Sandia National Laboratory (SNL), the Fuels Research Laboratory is focused on developing a fundamental understanding of the combustion characteristics of advanced liquid petroleum-based, bio-derived, and synthetic fuels. Research is conducted using the Sandia Compression-ignition Optical Research Engine (SCORE), which is a single-cylinder version of a Caterpillar® C-10 engine that has been modified at Sandia to provide extensive optical access into the combustion chamber. Advanced laser and imaging diagnostic techniques are used to observe combustion and emissions-formation processes through windows in the piston and the upper periphery of the cylinder liner. Such observations are important for understanding how fuel formulation affects engine efficiency and emissions. In FY 2005, experiments conducted in the Fuels Research Laboratory showed for the first time how fuel and combustion-regime changes can enable diesel combustion that simultaneously achieves 1) NOx and soot emissions compliant with EPA limits that will come into force in 2010, 2) uncompromised fuel economy, and 3) simpler combustion timing control and lower pressure-rise rates than those associated with homogeneous charge compression ignition (the prevailing advanced combustion approach to date).

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 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 added capabilities are:

- Second & third (non-proprietary) full-pass engine electronic control systems
- Electrospray mass spectrometry and negative chemical ion mass spectrometry for specific exhaust compounds and unregulated emissions
- “Gated bagger” for time-resolved emissions speciation
- Engine cell (sixth) area for single-cylinder engine research
- Engine models/codes (WAVE, etc.)
- Methods for “road-side” emissions measurements
- Variable compression ratio and variable valve actuation engines

An extensive study of fuel property effects on both gasoline-based and diesel-based HCCI performance and emissions was completed. The results were published showing that the fuel properties could in fact expand or shrink the HCCI operating space in the case of gasoline fuels. For diesel-like fuels, the results show how the cool-flame reactions are prominent in fuels with high cetane number. To more globally facilitate research in this area, ORNL conceived a vision to initiate a comprehensive project on how fuel properties affect advanced combustion processes like HCCI, and teamed with NREL to move the project plans forward. The effort will begin with design of a research fuel matrix via a working group of experts in this field convened under the auspices of the Coordinating Research Council. The project has been named “FACE” (fuels for advanced combustion engines).

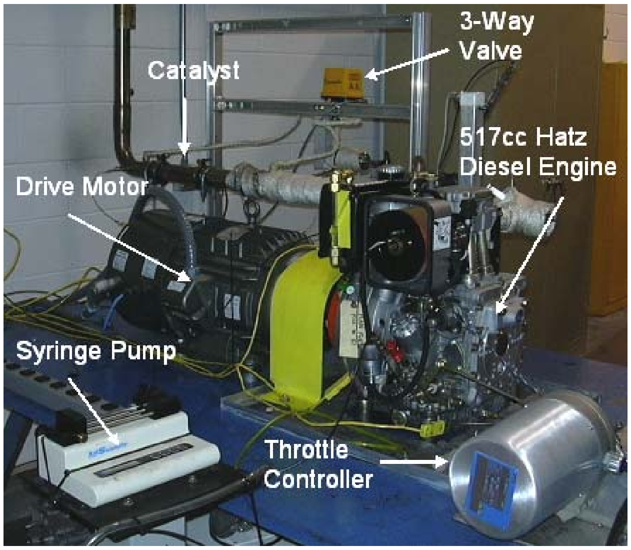
Highlights of Significant FY 2005 Accomplishments

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

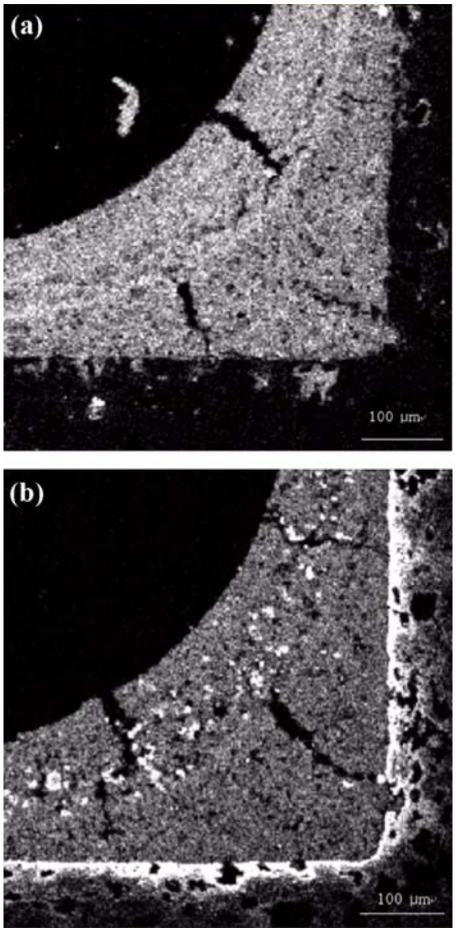
- In research of fuel sulfur effects on diesel emission control systems, 2200 hours of aging were completed using an advanced compression ignition direct injection (CIDI) passenger car engine equipped with a NOx adsorber catalyst and particulate filter. The testing showed that particulate emissions can be controlled over this time period to Tier 2 Bin 5 levels using a diesel particulate filter and 15 ppm sulfur fuel, while the NOx adsorber needs more work on durability and desulfation to meet emissions regulations. Similar testing over 2000 hours using an advanced CIDI engine sized for pickup trucks and SUVs using similar emission controls and the same fuels showed very similar results, i.e., Tier 2 Bin 5 particulate emissions could be achieved but the corresponding NOx emission level could not, despite high effectiveness. (NREL, FEV Engine Technology, Southwest Research Institute)

Light-Duty CIDI Test Engine Used in APBF-DEC Project (NREL, FEV Engine Technology)

- A novel in-cylinder fuel injection strategy was found to produce H_2 under net-lean engine operation at ORNL. A demonstration experiment revealed that highly accelerated hydrocarbon selective catalytic reduction (HC-SCR) catalyst light-off is possible using this technique. Future experiments will explore the capability of fuel-derived H_2 to promote catalytic NOx reduction. (ORNL)
- Southwest Research Institute (SwRI) aged two heavy-duty engine emission control systems comprising urea-selective catalytic reduction (SCR) and diesel particulate filters for a total of 6,000 hours each and retested them for emissions using 15-ppm sulfur fuel. The systems demonstrated that they could meet the 2010 emissions levels for heavy-duty engines using fuels with sulfur levels in the 0-30 ppm range. This project is now complete.
- ORNL studied the effect of phosphorous (derived from the zinc dialkyldithiophosphate additive in lube oil used for wear control) in diesel engine exhaust on oxidation catalyst, NOx adsorber, and catalyzed particulate filter poisoning. Phosphorus concentrations were found to be greatest at the catalyst surface, with a steep concentration gradient along the washcoat depth. Hydrocarbon and CO oxidation catalyst light-off temperatures increased between 50°C and 100°C, showing significant loss of performance from phosphorous contamination.
- In studies of the mechanisms of sulfur poisoning of emission controls, ORNL established protocols for rapid thermal aging experiments of lean NOx traps (LNTs) for both bench-flow reactors and engine benches. Rapid thermal aging of LNTs at aging temperatures of 900 and 1000°C using the bench-flow reactor was completed. The migration and accumulation of potassium at the interface of the washcoat and the cordierite substrate in aged high-temperature LNTs was observed as well as sintering of precious metal in all LNTs evaluated at high temperatures.
- Honeywell developed a sulfur removal filter and successfully demonstrated continuous sulfur removal at the 1 gallon scale. A 10 gallon version was constructed for engine testing. Loss of fuel lubricity was identified, and various fuel lubricants were studied.



ORNL Experimental Set-Up to Measure the Impact of Lubricating Oil Phosphorous on Catalyst Durability

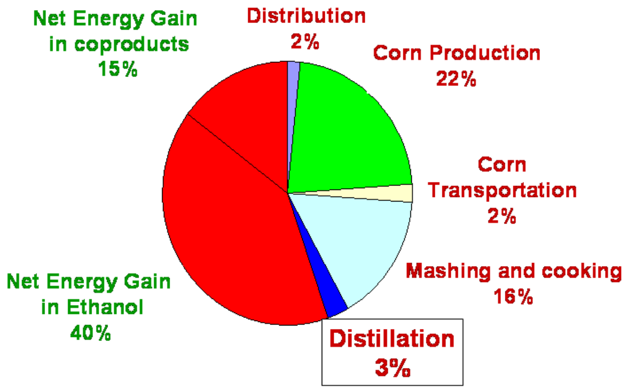


Electron Probe Microanalysis Images of Potassium Compounds Taken by ORNL (top: new; bottom: aged)

- The Advanced Petroleum-Based Fuel – Diesel Emission Control (APBF-DEC) Toxics and Unregulated Emissions team completed unregulated emissions sampling and analysis for three APBF-DEC projects: the heavy-duty selective catalytic reduction (SCR) project, the pickup/SUV NOx adsorber catalyst project, and the light-duty NOx adsorber catalyst project. The studies showed that diesel particulate filters appear to do a good job of removing the heavier polycyclic aromatic hydrocarbons from the engine-out exhaust, even under rich regeneration conditions and extensive aging. Conversely, naphthalene and methyl naphthalene increase with the NOx adsorber system and aging. Because these are gas-phase compounds, they are less likely to be retained by the diesel particulate filter.
- The ReFUEL Laboratory at NREL quantified and published the first known data on the performance impacts of biodiesel blends and synthetic GTL fuels on engines and vehicles equipped with advanced aftertreatment to meet 2007 requirements.

Fuel Property Effects on Advanced Combustion Regimes

- Using fuel changes (oxygenated fuel), SNL demonstrated a high-efficiency (>44% indicated efficiency), 2010-emissions-compliant (<0.2 g/hp-hr NOx, <0.05 filter smoke number) combustion strategy where ignition timing is simply controlled by injection timing, and peak pressure-rise rates are lower than for conventional diesel combustion.
- Lawrence Livermore National Laboratory (LLNL) completed models for chemical kinetics of combustion for two major fuel components, toluene and methyl cyclohexane, and for an oxygenated diesel fuel additive, dimethyl carbonate.
- LLNL conducted an analysis of a homogeneous charge compression ignition (HCCI) engine system that can work on highly hydrated ethanol while delivering high efficiency and low emissions. They found that HCCI engines can use highly hydrated ethanol which is less costly and energy intensive to produce than the anhydrous ethanol currently used for fuel purposes.
- NREL quantified ignition quality versus temperature using the Ignition Quality Tester (IQT™) for a base fuel and a matrix of four paraffinic fuels representing 3 boiling ranges and 3 derived cetane number levels. Very clean HCCI combustion was achieved using these fuels – brake-specific NOx emissions of 0.02 g/bhp-hr and undetectable levels of smoke for certain fuels and operating conditions.

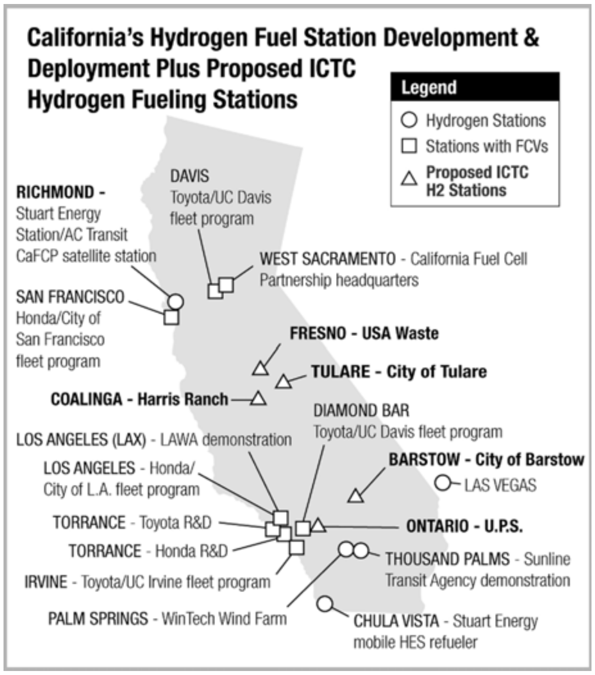


Net Energy Balance for Highly Hydrated Ethanol That Can Be Used in HCCI Engines

- ORNL and AVL determined that spark-augmented HCCI is a valid and useful mode of engine control, distinct from pure HCCI, and completed a set of parametric experiments to show the extent that gasoline-based fuel properties can further expand or shrink this multi-mode HCCI operating space.
- ORNL showed that fuels from a variety of feedstocks (oil-sands, petroleum, and vegetable oil) do exhibit high-efficiency clean combustion (HECC) behavior at a similar range of engine output and speed as conventional petroleum fuels. It was also shown that fuel properties within the limited range studied do not significantly expand the load/speed operating regime for HECC and that there is a strong influence of fuel properties on both particulate and hydrocarbon emissions in HECC modes.
- ORNL completed installation and conversion of a small diesel engine to HCCI combustion and conducted two fuel effects studies for diesel range fuels. HCCI performance was correlated to fuel chemistry and cetane values using commercial diesel fuels, blends of diesel secondary reference fuels, and biodiesel fuel.

Transition to Hydrogen Economy

- Cummins Westport Inc. completed development of a lean-burn 8.9L natural gas (NG) engine meeting EPA 2007 emissions standards for use in multiple vehicle platforms.
- NREL continued projects to develop and/or integrate the following NG engines meeting EPA 2007 emissions standards: 8.1L John Deere (John Deere Power Systems), 12L Mack/Volvo (Volvo Powertrain), and 15L Cummins (Westport Innovations).
- NREL continued projects to develop 11L Mack/Volvo (variable valve timing with Volvo Powertrain) and 8.9L Cummins Westport Inc. (with Cummins Westport) NG engines meeting EPA 2010 emissions standards.
- NREL initiated a project to develop a NG stochiometric engine for transit buses that meets EPA 2010 emissions standards.
- NREL published the final safety evaluation report of a NG home refueling appliance.
- An evaluation of opportunities to integrate hydrogen into natural gas vehicle (NGV) fueling stations of the Interstate Clean Transportation Corridor (ICTC) was completed.
- NREL held a Natural Gas Vehicle Technology Forum meeting in August 2005 and updated its Web site.
- Brookhaven National Laboratory demonstrated the viability of producing liquefied natural gas (LNG) on a small scale from landfill gas. Ten thousand gallons of LNG was produced and used to power the trucks hauling refuse to the landfill.



Map of Current Hydrogen Vehicle & Station Development Projects with Proposed ICTC Hydrogen Demonstration Projects Added

Petroleum Displacement Fuels/Fuel Blending Components

- An operability analysis of six months of fleet fueling and maintenance records demonstrated that heavy-duty fleet vehicles with diesel particulate filters using gas-to-liquid diesel fuel incur operational costs similar to those incurred using conventional diesel fuels (NREL).
- NREL completed a nationwide assessment of biodiesel (B20) quality and stability and identified peroxide formation and low water interfacial tension as issues when blending biodiesel to form homogeneous mixtures.
- NREL (ReFUEL) completed engine dynamometer testing of a modern 300 hp diesel engine, equipped with exhaust gas recirculation (EGR), variable geometry turbocharger (VGT), and high pressure common rail fuel injection with different B20 blends (20% biodiesel, 80% conventional diesel fuel). The study provided an evaluation of the emissions of a modern production engine with various B20 blends with biodiesel made from feedstocks including soy oil, yellow grease, canola oil, and beef tallow.
- NREL (ReFUEL) evaluated the effect of biodiesel on a 2004 compliant engine retrofitted with a catalyzed diesel particulate filter (DPF). The study compared emissions with and without the DPF system installed on reference ULSD fuel and B20 over the EPA transient certification test cycle as well as evaluating DPF regeneration performance with biodiesel compared to ULSD fuel.

- As part of a project to quantify the real-world operating costs and emissions impact of 20% biodiesel blend (B20), ReFUEL tested two MY 2000 in-use buses on B20 and conventional diesel fuel as a reference fuel. Use of the B20 fuel resulted in statistically significant reductions for all regulated emissions including nitrogen oxides (NOx), which were reduced by 4% on average, which is in contrast to many engine stand studies which have shown the NOx emissions to generally increase with biodiesel use. Testing also supports fleet study work being performed by NREL on the in-use performance and maintenance impacts of B20 use in the Boulder, Colorado transit bus fleet (NREL)
- ORNL utilized blended oil sands fuel for operation of a light-duty diesel equipped with a NOx adsorber catalyst using in-cylinder regeneration modes and found it to have very similar performance to a conventional petroleum diesel fuel with 15 ppm sulfur.
- ORNL developed a combination of electron impact and chemical ionization mass spectroscopic methods for identification of fuel components from oil sands crude.

New Technology Impacts

- NREL completed analysis of 1998-2002 or 2003 ambient ozone precursor and ozone data from many U.S. monitoring locations. A paper was submitted summarizing study results to the Journal of the Air & Waste Management Association for peer review and subsequent publication.

Future Activities

This section describes the activities that will be pursued in each portion of the Fuels Technologies Sub-Program 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 Sub-Program will focus on how fuel properties affect the durability of catalysts of all types, and what fuel-derived reductants can be made with and without fuel additives for use with HC-SCR catalysts (ORNL). The projects designed to assess the impact of 15-ppm sulfur diesel fuel on advanced diesel engine emission controls (light-duty and heavy-duty) to reduce NOx and PM emissions have been completed, and final reports will be issued (NREL, FEV, SwRI). It is known that sulfur has a deleterious impact on precious metal catalyst durability, even at ultra-low fuel sulfur contents that will exist starting in late 2006. An onboard filter that could remove the remaining sulfur would be highly desirable; Honeywell will conduct engine testing of their fuel sulfur removal filter and explore ways to decrease its size.

Catalyst durability testing at ORNL will include accelerated catalyst poisoning tests and measurements in order to better define phosphorus exhaust chemistry and resulting effects on catalyst performance. New engine oil additives and catalyst materials and types, such as lean NOx traps (LNTs) and diesel particulate filter (DPF) catalysts, will be included in testing. The techniques developed to assess catalyst poisoning will be extended to include effects of ash and soot loading in DPFs in addition to phosphorous poisoning. Thermal aging of LNTs at several different lean/rich aging cycles at 900 and 1000°C will be conducted to validate repeatability of data and to provide more samples for surface studies to identify the progression of K migration away from the washcoat, the transformation of $BaCO_3$ into other barium-mixed oxides, and sintering of the precious metal group.

Investigation of the potential to produce useful fuel-derived reductants from compression-ignition fuels with and without fuel additives will be continued using selected reductant and catalyst combinations. Durability and robustness of Ag-based and other HC-SCR catalysts will be addressed with industry partners. (ORNL)

The ReFUEL laboratory participates as part of the EPA/Engine Manufacturers Association (EMA) Calibration Standards Task Force which provides leadership and input for test methods and protocol specifications related to 2007-2010 EPA emissions regulations for vehicles and engines as published in the Code of Federal Regulations (CFR). As part of this group, ReFUEL has been selected to participate in a round-robin lab correlation study of a 2007 compliant engine to quantify and confirm lab-to-lab agreement and test methods between the nation's leading heavy-duty engine emissions laboratories on future technology engines with drastically reduced emissions. (NREL)

The APBF-DEC Toxics and Unregulated Emissions team will complete summary reports for each of the APBF-DEC projects and a final report on all APBF-DEC unregulated emissions activities including methods development.

Fuel Property Effects on Advanced Combustion Regimes

The focus of this portion of the Fuels Technologies Sub-Program will be 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. To this objective, SNL will investigate how fuels such as biodiesel, as well as Fischer-Tropsch paraffins by themselves and in blends with conventional diesel fuel, can facilitate very-low-emission combustion without loss of efficiency. As part of the modeling efforts to explain how fuels can be combusted very cleanly, LLNL will extend its current combustion model capabilities to additional classes of fuel components and continue development of increasingly complex surrogate fuel mixtures. ORNL will continue to study emissions as a means of furthering the understanding of the performance of fuels in advanced combustion modes, such as HECC.

Fuel properties are very important to HCCI combustion, and a primary objective is to expand the engine operating range where HCCI combustion is possible. To support this objective, ORNL will determine detailed chemistry effects of HCCI fuels in addition to bulk property effects such as octane, cetane, and volatility, and will continue to explore issues of stability and moving between various combustion regimes to determine if fuel chemistry can improve HCCI controllability and operating range. LLNL will modify the fueling system in an existing HCCI engine to demonstrate efficient and clean operation on wet ethanol. They will also investigate whether other marginal, low-grade fuels can be successfully utilized with HCCI engines, such as trash gas (natural gas with high concentration of carbon dioxide or other inert impurities). An evaluation will be performed to determine whether it is practical to generate HCCI additives (secondary fuels) onboard a vehicle to successfully control the engine. The Coordinating Research Council will conduct an experimental analysis of the impact of fuel properties on a light-duty HCCI engine.

Transition to Hydrogen Economy

Due to elimination of funding in this category of the sub-program, efforts to advance NG engine and vehicle technologies will be brought to an orderly conclusion in early FY 2006.

Petroleum Displacement Fuels/Fuel Blending Components

The focus of this portion of the Fuels Technologies Sub-Program will be on biodiesel, Fischer-Tropsch paraffins made from natural gas, and oil sands liquids.

The properties of biodiesel and Fischer-Tropsch paraffins have advantages over conventional diesel fuel for implementation of emission control technology for diesel engines. To further explore this potential, NREL will collect data from heavy-duty diesel vehicles using Fischer-Tropsch diesel fuel and advanced emission control technology to assess emission control efficiency and durability. NREL will also test heavy-duty diesel engines tailored to biodiesel and biodiesel blends by varying engine operating parameters such as injection timing, EGR rate, and others to assess the effect on performance of diesel particle filters and NOx adsorber catalysts.

A new nationwide survey of B100 and B20 quality and stability will be completed by NREL, applying lessons learned from 2004 and 2005 surveys. A detailed study of oxidation stability of B100, B20, and B5 will be completed with the objective of determining the best test method and specification limits.

The chemical analysis developed for oil sands liquids will be extended to several upgraded streams of oil sands fuels by ORNL. Engine performance with the same fuel streams in normal and advanced combustion modes will be evaluated to understand potential fuel chemistry effects from oil sands liquids. Other near-term non-petroleum-based fuels such as shale-derived fuels will be identified for analysis.

New Technology Impacts

DOE plans to support and participate in the Advanced Collaborative Emissions Study (ACES) in partnership with industry and the Health Effects Institute.

NREL will begin a proximate ozone modeling study in the southeast Michigan region in collaboration with state and local government groups and industry representatives in that area.

ORNL will continue data collection of air quality and heavy truck emissions in the vicinity of I-40 in Knoxville, Tennessee at the Watt Road Environmental Laboratory.

Special Honors/Recognitions

- Charles Mueller (SNL) received the Society of Automotive Engineers Lloyd L. Withrow Distinguished Speaker Award. This was one of 8 such awards presented in 2005 to recognize individuals who have received SAE’s Oral Presentation Award more than twice.
- Salvador M. Aceves (LLNL) invited to deliver a seminar at the SAE 2005 seminar on HCCI, September 2005, Lund, Sweden.
- Bruce Bunting (ORNL) was an invited speaker at the SAE Symposium on Homogeneous Charge Compression Ignition Combustion Engines in Lund, Sweden, September 2005. Dr. Bunting’s presentation was on fuel effects on HCCI.
- Doug Lawson (NREL) was appointed by the Colorado governor to serve a three-year term on the state of Colorado Air Quality Control Commission. Created in 1970 by the Colorado Legislature, the Air Quality Control Commission develops air pollution control policy, regulates pollution sources and conducts hearings involving violations of the state's air pollution laws.
- Doug Lawson (NREL) was invited to give the keynote presentation titled "The Weekend Ozone Effect: Reality vs. Conventional Wisdom" at the SAE Powertrain & Fluid Systems Conference in Tampa, Florida, October 2004.
- Doug Lawson (NREL) was invited to make a presentation to the 50 state air pollution control administrators at the Environmental Council of the States annual meeting in Portland, Maine, September 2005.
- Doug Lawson (NREL) was invited by the California Air Resources Board (ARB) to make a webcast presentation describing the results of DOE's Gasoline/Diesel PM Split Study at the ARB Chairman's Air Pollution Seminar in Sacramento, California, September 2005.

- Doug Lawson (NREL) was invited by the California Bureau of Automotive Repair to provide a webcast presentation describing DOE's Gasoline/Diesel PM Split Study and his research on EPA's high-mileage onboard diagnostics (OBD) study in Sacramento, California, September 2005.
- Charles Mueller (SNL) received the Society of Automotive Engineers Arch T. Colwell Merit Award, for paper entitled "Effects of Oxygenates on Soot Processes in DI Diesel Engines: Experiments and Numerical Simulations," SAE Technical Paper 2003-01-1791. This was one of 11 papers honored in 2004 for being most innovative and original out of approximately 2,500 papers published during the preceding year.
- Dr. Johney Green (ORNL) was selected as a *Science Spectrum* Trailblazer, Top Minority in Science.
- Bruce Bunting (ORNL) was an invited speaker and session co-chair at the 2005 International Conference for Automotive Technology in Vietnam in October 2005.

Patents Issued

- Controlling and Operating Homogeneous Charge Compression Ignition (HCCI) Engines, Daniel L. Flowers (LLNL), United States Patent 6,923,167, August 2, 2005.

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 compression ignition, direct injection 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.

Stephen Goguen
Team Lead
Fuels Technologies
Office of FreedomCAR and
Vehicle Technologies

Kevin Stork
Technology Development Manager
Fuels Technologies
Office of FreedomCAR and
Vehicle Technologies

II Fuels and Lubricants to Enable High Efficiency Engine Operation while Meeting 2007 - 2010 Standards

II.1 Development of a Passenger Car Test Platform to Evaluate NOx Adsorber/DPF Systems Using Ultra-Low Sulfur Fuels

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DOE Team Lead: Stephen Goguen

DOE Technology Development Manager: Kevin Stork

Other Participants:
American Petroleum Institute, Engine Manufacturers Association, Manufacturers of Emissions Control Association (MECA), U. S. Environmental Protection Agency (EPA), Oak Ridge National Laboratory, California Air Resources Board

Subcontractor:
FEV Engine Technology, Auburn Hills, MI

Objectives

- To use a systems approach to demonstrate the potential of NOx adsorber catalyst (NAC) technology in combination with diesel particle filters (DPFs), advanced fuels, and advanced engine controls to achieve low emission levels while maintaining high fuel economy. That is, to meet stringent Tier 2 Bin 5 light-duty vehicle emission standards with limits of 0.07 g/mi NOx and 0.01 g/mi particulate matter (PM).
- To help determine the necessary fuel sulfur level and other fuel properties that will enable these systems. The fuel sulfur levels tested were representative of those required to be available beginning June 2006 (<15 ppm S).

Approach

A model year 2001 Audi A4 Avant with a 1.9 liter TDI engine (100 KW at 4000 rpm) with a Bosch common rail second generation fuel injection system, integrated exhaust gas recirculation (EGR) and a Garett GT 17 V turbocharger was used as the test vehicle for this project. This vehicle was equipped with appropriately designed emission control devices and the necessary NAC regenerative control hardware and electronics to conduct this fuel study, which encompasses two primary tasks:

- Task A involved development of the test platform, including setup, integration, and optimization of the engine; rapid warm-up testing and thermal management; emission control system (ECS) and associated electronic controls; and baseline (engine-out) testing of regulated and unregulated (toxic) emissions.
- Task B involved system performance and aging tests using fuels with varying sulfur content (8 and 15 ppm S) and periodic evaluations of emissions over the Urban Dynamometer Driving Schedule (UDDS), US06, and Highway Fuel Economy Test (HFET) during aging tests up to 2200 hours of operation (full useful life equivalent, approximating 120,000 miles of operation). Two ECS architectures (A and B) were developed and tested, both being single-leg systems.

Accomplishments

- Completed Task A, the development of all control strategies related to the optimization of the ECS. This included the NAC regeneration strategy, DPF regeneration strategy, and NAC desulfurization strategy and the sampling and analysis of baseline engine-out emissions.
- Completed the sampling and analysis of the emissions for ECS-A and ECS-B with both 8- and 15-ppm sulfur fuels through 50 hours of aging.
- Completed Task B, the sampling and analysis of the emissions for ECS-B (the best-performing system) with 15-ppm sulfur fuel through 2200 hours of aging.

Future Directions

- Complete final report.

Introduction

The Advanced Petroleum Based Fuels – Diesel Emission Control (APBF-DEC) activity is a joint government/industry research effort to determine the best combinations of low-sulfur diesel fuels, lubricants, diesel engines, and emission control systems to meet projected emission standards for the 2002 to 2010 time period. The project leverages the participation of several multi-industry working groups that direct five individual projects.

This project aimed to demonstrate the viability of utilizing simultaneously NOx adsorber catalyst (NAC) and diesel particle filter (DPF) technologies in combination with clean fuels, advanced engines and electronic controls to achieve low emission levels while maintaining high fuel economy. Specifically, this project will identify the fuels needed to enable these technologies for use in light-duty vehicles. The goal for this platform is to meet Tier 2 Bin 5 light-duty emission standards with limits of 0.07 g/mi NOx and 0.01 g/mi PM.

Another critical focus of this project is the characterization of currently unregulated, but potentially toxic emissions.

Among the fuel variables to be studied, sulfur has been identified as most critical to this research. The Diesel Emission Control – Sulfur Effects (DECSE) project [1], a predecessor to this effort, examined the effect of sulfur on individual emission control devices including NACs, DPFs, diesel oxidation catalysts, and lean NOx catalysts. This testing showed that efficiency of NACs is significantly affected by sulfur in the diesel fuel [2]. This project provides a more thorough investigation of sulfur effects and uses modern hardware and robust electronic controls with systems incorporating both NOx and PM control devices. ECS performance over time, as a function of fuel sulfur exposure, was examined in tests up to 2200 hours in duration (approximating 120,000 miles of driving).

Approach

A model year 2001 Audi A4 Avant (Figure 1) with a 1.9 liter TDI engine (100 KW at 4000 rpm) (Figure 2) with a Bosch common rail second generation fuel injection, integrated exhaust gas recirculation (EGR) and a Garett GT 17 V turbocharger will be used as the test vehicle for this project. This vehicle was equipped with appropriately designed emission control devices and the necessary NAC regenerative control hardware and electronics to conduct this fuel study.
A significant reduction (80-90%) in tailpipe

Figure 1. Audi A4 Avant Test Vehicle

Figure 2. 1.9 L TDI Test Engine

emissions over the current European calibration for this vehicle was required for this project.

In order to make the goals of this project possible and limit the reduction efficiencies required by the ECS devices, significant modifications were made to the test engine by the subcontractor to lower engine-out emissions, including installation of common rail fuel injectors, addition of aluminum cylinder heads, and engine calibration changes (for lower engine-out NOx and more favorable exhaust temperature profiles). In addition, dual wall insulated exhaust components were used to retain heat for the ECS created by the engine. MECA provided emission control devices for two different ECS configurations (denoted as ECS-A and ECS-B), both single-leg systems. Figure 3 shows the basic configuration for both systems, with the key difference being the formulation of the pre-catalyst. In ECS-A the pre-catalyst will serve both a NOx adsorbing and oxidizing function, while in system ECS-B the pre-catalyst will only serve a NOx adsorbing function.

This project was comprised of two primary tasks:

Task A involved development of the test platform, including setup, integration, and optimization of the engine and vehicle, ECS and associated electronic controls, and development of thermal management strategies. This task included the design of post injection strategies that provided in-cylinder secondary fuel for NOx adsorber catalyst regeneration. The primary result of this task was the development of all control strategies related to the optimization of the ECS. This included the NAC regeneration strategy, DPF regeneration strategy, and NAC desulfurization strategy.

This task also included baseline tests to characterize engine-out emissions (no catalysts) during transient and steady-state operation. Baseline tests were conducted with DECSE 8- and 15-ppm sulfur fuels (referred to as D8 and D15) and a low-sulfur refinery fuel (referred to as BP15). The information and results from this task were included in previous years' reports and can be referenced in these reports or the publications listed at the end of this report [3].

Task B involved system performance and aging evaluations using fuels with varying fuel sulfur content. Performance evaluations on the UDDS, US06, and HFET driving cycles were conducted at 0 and 50 hours using 8- and 15-ppm S fuels. Aging continued on one of these systems for an additional 2150 hours using the 15-ppm S fuel to determine longer-term aging impacts. The results of these tests are included in the following section.

A full suite of emissions were measured during both Task A baseline testing and Task B aging tests. They included the following:

- NOx (oxides of nitrogen)
- CO (carbon monoxide)
- HC (hydrocarbons)
- CO_2 (carbon dioxide)

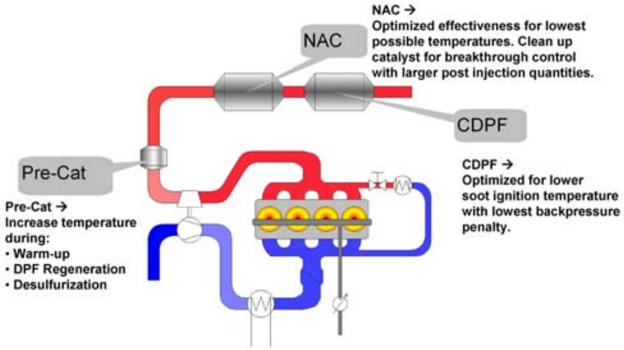

Figure 3. Emission Control System Architecture

  - PM (including detailed compositional analysis)
  - Benzene
  - 1,3 butadiene
  - Formaldahyde
  - Acetaldehyde
  - N_2O (nitrous oxide)
  - NH_3 (ammonia)
  - SO_2 (sulfur dioxide)
  - H_2S (hydrogen sulfide)
  - Nitroxyalkanes

Results

Once all of the ECS control features were incorporated into a final strategy, the refined calibration was applied to both ECS-A and ECS-B. Engine dynamometer tests were performed on the 1.9 liter TDI test engine over the cold- and hot-start USSD, US06, and HFET driving cycles. The UDDS, also known as the LA4, cycle is composed of Bag 1 and Bag 2 of the light-duty Federal Test Procedure (FTP) cycle. The US06 is a high speed/load aggressive test procedure, part of the supplemental FTP, and the HFET is the highway fuel economy test cycle.

All tests reported here were simulations of the actual driving cycles discussed above, performed by FEV in their engine test cell. The first test during each testing sequence was the FTP in its modified form (2 consecutive UDDSs). There were two (instead of three) bag and filter measurements taken per test. The calculation of the final result was a composite UDDS, algebraically equal to a standard FTP three-bag test (43% weighting on the cold-start UDDS and 57% weighting on the hot-start UDDS).

This discussion summarizes the aging results through 1220 hours of testing as they relate to NOx and PM emissions and NOx trends over the composite UDDS. One cold-start and multiple hot-start UDDS tests were run each day to accumulate operating time, since the engine would otherwise need to be force-cooled or soaked overnight between each cold-start test. These data are presented as averages of two or three tests at each evaluation point, including engine-out measurements shown on the left side of each figure. The majority of the evaluations were conducted with the DECSE 15 ppm sulfur fuel, denoted as D15, with occasional duplicate evaluations using a refinery run 15 ppm sulfur fuel, denoted as BP15. A distinction is made in all of the following figures when D15 versus BP15 fuel was used. In addition, the figures include the occurrence of a NOx adsorber desulfation event, indicated by vertical dashed lines; the 50,000-mile interim useful life Tier 2 Bin 5 emissions standard, indicated by the green dashed horizontal lines; and the 120,000-mile full useful life Tier 2 Bin 5 standard, indicated by the green solid horizontal lines.

During the course of aging, the catalyst system was evaluated frequently in order to assess its degradation in performance due to sulfur poisoning and thermal aging. The initial tests were performed at 0 hours with fresh catalysts. The subsequent test series were performed before and after the desulfurization events at 150 and 300 hours of aging. After the 300-hour mark, the desulfurization/evaluation cycle frequency was increased to every 100 hours up to 1600 hours of aging. Starting at 1600 hours, desulfurizations and evaluations were performed every 50 hours.

The average NOx emission results are displayed in Figure 4. Observations at the beginning and end of a single aging cycle are connected.

With the increased desulfurization frequency, the composite FTP tailpipe NOx emissions post desulfurization after 2200 hours could be maintained below the emission standard for 120,000 miles of 0.07 g/mile. A detailed statistical analysis of NOx emissions results from the test cell is discussed in the following section.

The evaluation of the PM filters showed the high degree of filtration efficiency of the DPF, as shown in Figure 5. There were two instances where the composite PM numbers were above the emission standard of 0.01 g/mi. These higher emission numbers were a result of a high soluble organic fraction on the cold UDDS filters. After a DPF failure during the 1000-hour vehicle tests, the DPF was replaced, and the aging testing was continued. The filtration efficiency for the new DPF remained on the high level as observed with the first DPF.

Statistical analyses were performed to characterize trends in emissions levels over the 2200 hours of testing. To account for the evaluations consisting of only the hot UDDS cycles, an imputation method was developed to estimate the cold UDDS and resulting FTP composite results. The statistical analysis is based on a combination of imputed and actual FTP composite results.

Figure 6 illustrates the degradation in catalyst performance between desulfurizations and the effectiveness of the desulfurization process at restoring performance. A log-linear model was fit to estimate average trends and evaluate statistical significance. The upper graph demonstrates that the average loss in NOx reduction efficiency (FTP composite) between desulfurizations varies between 15% and 35% prior to 1600 hours. After the desulfurization strategy changed at 1600 hours, the loss in NOx reduction efficiency was generally 10%. There was a slight drop between 1800 and 2000 hours that could not be explained.

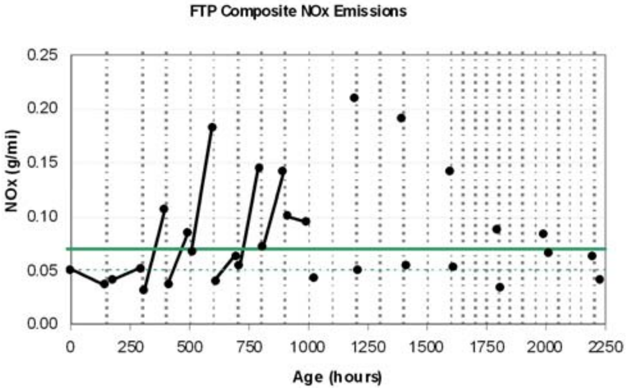

Figure 4. FTP Composite NOx Results during Aging Study (desulfation frequency is noted by gray dashed lines)

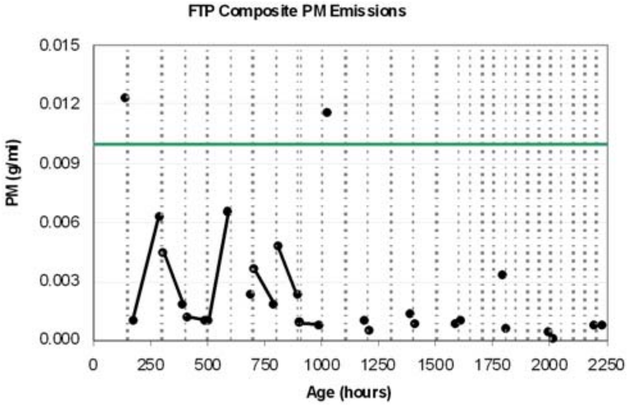

Figure 5. FTP Composite PM Results during Aging Study (desulfation frequency is noted by gray dashed lines)

The lower graph demonstrates that prior to 1600 hours there was an increase in average NOx reduction efficiency of 10% to 35% at each desulfurization event. After 1600 hours, there is on average a 10% improvement in NOx reduction efficiency at each desulfurization event, with a higher trend between 1800 and 2000 hours. Combined, these graphs indicate that the performance of the desulfurization process was relatively unstable with the 100-hour desulfurization strategy, but was quite consistent with the 50-hour desulfurization strategy.

The trends in FTP composite NOx reduction efficiency relative to engine-out emissions between

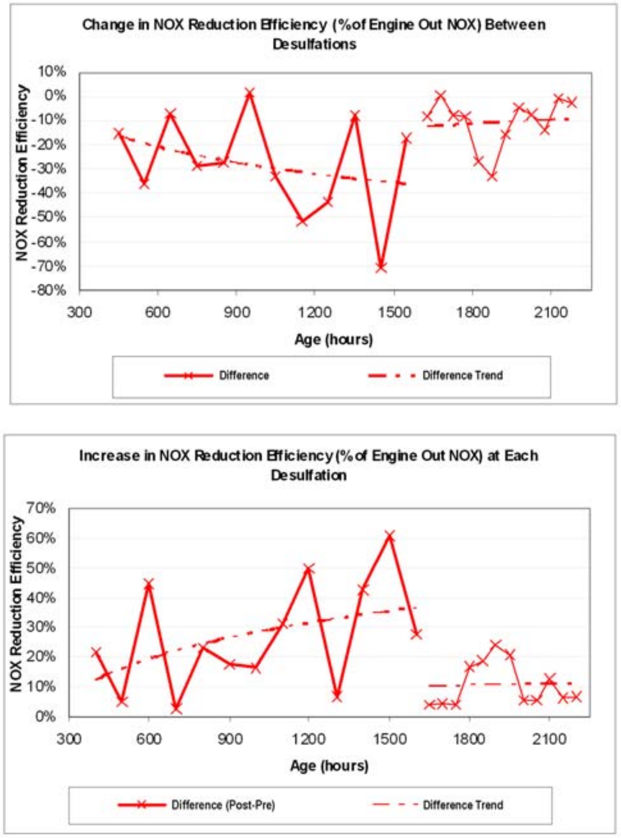

Figure 6. NOx Reduction Efficiency Behavior over Time

300 and 1600 hours and between 1600 and 2200 hours of aging are shown in Figure 7. To account for the effects of the desulfurization process, separate log-linear models were fit to three sets of NOx emissions data: (1) measurements made before a desulfurization event, (2) measurements made after a desulfurization event, and (3) the average of measurements made at the beginning (post-desulfurization) and end (pre-desulfurization) of each aging period. The latter results plotted at the midpoint of the aging period represent the best estimate of the average emissions over time; however, we could not verify that the increase in NOx emissions within an aging period is linear.

Both the average and pre-desulfurization log-linear regression lines shown in Figure 7, based on the 100-hour desulfurization data, were found to have statistically significant trends. However, because of the curvature in the trends, additional analyses were performed to address the question of whether the performance of the system stabilizes over time. This was accomplished by iteratively truncating the left-most data from each of the three data sets, then refitting the regression model and evaluating the significance of the regression slope parameter. Through this process, it was determined that the trends are not statistically significant after 700 hours of aging with a 100-hour desulfurization strategy. None of the regression lines shown in Figure 7, based on the 50-hour desulfurization data, were found to have statistically significant trends.

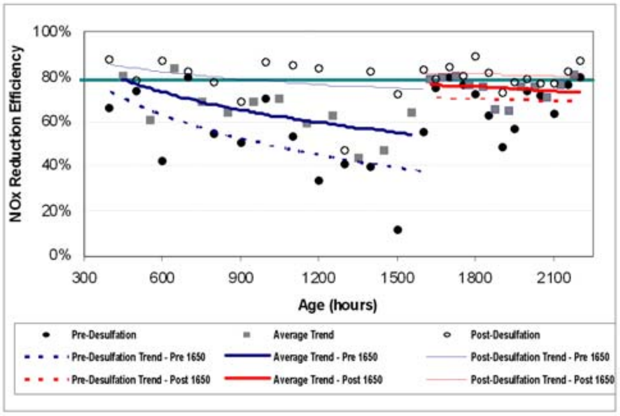

Figure 7. NOx Emission and Reduction Efficiency Trends over Time

Fuel consumption data were collected over the UDDS composite during the aging and evaluation events for this project. The average fuel economy for the baseline engine-out tests was 34.5 miles per gallon (mpg), compared with the average fuel economy during the ECS evaluation events of 32.5 mpg. This equated to a 5.8% fuel economy penalty for the NAC/DPF system. Despite this penalty, these data, combined with the NOx emissions data, indicate that a light-duty diesel can achieve low emissions while maintaining superior fuel economy. The adjusted EPA city cycle fuel consumption for the vehicle with the ECS is 29 mpg (54 mpg adjusted highway cycle), which is a 38% improvement over the gasoline version of the A4 Avant wagon (21 mpg adjusted city cycle) and a 26% improvement over a comparable SULEV (approximate Tier 2 Bin 5 vehicle) Honda Accord (23 mpg adjusted city cycle). Just as important, the fuel consumption has remained steady and has not shown any indication of increasing with ECS aging.

Subsequent to the UDDS tests, the US06 cycle was conducted. The US06 cycle was developed by the EPA to capture driving events not included in the FTP-75. Due to the aggressive nature of this test cycle, including steep accelerations and high vehicle speed, the emission numbers are higher than observed during the UDDS. However, the NOx emissions are still on a level of 0.2 g/mile and lower.

Due to the light load of the HFET (in conjunction with the hot-start), the emissions measured over this cycle are below the minimum detection level. All gaseous emissions are on a very low level.

A more complete set of results, including all pollutant emissions (i.e., criteria pollutant, toxic, and unregulated emissions), will be included in next year's final report for this project.

Conclusions

The developed integrated concept, which incorporates software and hardware solutions, shows considerable potential for meeting future emission standards. Important aspects during the development were the modifications of the test engine and the engine-out emissions optimization. With the adjusted engine-out emissions level, the exhaust ECS interventions were defined, developed, and refined. Due to the large portion of cold-start emissions, the rapid warm-up strategy, allowing fast catalyst light-off, was optimized. DPF desulfurization and regeneration strategies were developed focusing on catalyst long-term performance and fuel consumption. There are remaining challenges that need to be addressed, such as the increase in HC emissions over the catalyst life.

Test work associated with this activity is complete, and final data analysis and reporting will be published in 2006.

FY 2005 Publications/Presentations

1. Tomazic D., Tatur M., Tyrer H., Thornton M., McDonald J., "Tier 2 Intermediate Useful Life (50,000 miles) and 4000 Mile Supplemental Federal Test Procedure (SFTP) Exhaust Emission Results for a NOx Adsorber and Diesel Particle Filter Equipped Light-Duty Diesel Vehicle," SAE Paper 2005-01-1755, March 2005, Detroit, Michigan.
2. Information from this project was also presented at the Diesel Engine Emission Reduction (DEER) Conference in Chicago, Illinois, in August 2005.

References

1. http://www.ott.doe.gov/decse/
2. U.S. Department of Energy, Engine Manufacturers Association, Manufacturers of Emission Controls Association, "Diesel Emission Control – Sulfur Effects (DECSE) Program – Phase I Interim Data Report No. 2: NOx Adsorber Catalysts," October 1999.
3. Tomazic, Tatur, and Thornton, "Development of a Diesel Passenger Car Meeting Tier 2 Emissions Levels," SAE Paper 2004-01-0581, March 2004.

II.2 Development of a Pick-up/SUV Test Platform to Evaluate NOx Adsorber/DPF Systems Using Ultra-Low Sulfur Fuels

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DOE Team Lead: Stephen Goguen

DOE Technology Development Manager: Kevin Stork

Other Participants:
American Petroleum Institute, Engine Manufacturers Association, Manufacturers of Emissions Control Association (MECA), U. S. Environmental Protection Agency, Oak Ridge National Laboratory, California Air Resources Board

Subcontractor:
Southwest Research Institute, San Antonio, TX

Objectives

To use a systems approach to demonstrate the potential of NOx (oxides of nitrogen) adsorber technology in combination with diesel particulate filters, advanced fuels, and advanced engine controls to achieve low emission levels while maintaining high fuel economy. That is, to meet stringent Tier 2 Bin 5 light-duty emission standards with limits of 0.07 g/mi NOx and 0.01 g/mi particulate matter (PM). To help determine the necessary fuel sulfur level and other fuel properties that will enable these systems. The fuel sulfur levels tested were representative of those required to be available beginning June 2006 (<15 ppm S).

Approach

A 6.6 liter Duramax engine (300 HP at 3100 rpm) with a Bosch common rail fuel injection, integrated exhaust gas recirculation (EGR), charge air cooler, and a center mounted turbocharger was used as the test engine for this project. The vehicle was equipped with appropriately designed emission control devices and the necessary regenerative control hardware and electronics to conduct this study, which encompasses two major tasks:

- Task A involved development of the test platform, including setup, integration, and optimization of the engine, thermal management; emission control system (ECS) and associated electronic controls; and baseline (engine-out) testing of regulated and unregulated (toxic) emissions.
- Task B involved system performance and aging tests using fuels with 15 ppm sulfur content and periodic evaluations of emissions over the Federal Test Procedure (FTP), US06, and Highway Fuel Economy Test (HFET) driving cycles during aging tests up to 2000 hours of duration. One dual-leg ECS architecture was developed and tested during this task.

Accomplishments

- Completed Task A development of all control strategies related to the optimization of the ECS, which include the NOx adsorber catalyst (NAC) regeneration strategy, diesel particulate filter (DPF) regeneration strategy, and NAC desulfurization strategy.
- Completed Task B sampling and analysis of the emissions for the ECS with 15-ppm sulfur fuels through 2000 hours of aging.

Future Directions

- Complete final report.

Introduction

The Advanced Petroleum Based Fuels – Diesel Emission Control (APBF-DEC) activity is a joint government/industry research effort to determine the best combinations of low-sulfur diesel fuels, lubricants, diesel engines, and emission control systems to meet projected emission standards for the 2002 to 2010 time period. The activity leverages the participation of several multi-industry working groups that direct five individual projects.

This project aimed to demonstrate the viability of simultaneously utilizing NOx adsorber catalysts and DPF technologies in combination with clean fuels, advanced engines and electronic controls to achieve low emission levels while maintaining high fuel economy. Specifically, this project will identify the fuels needed to enable these technologies for use in light-duty vehicles. The goal for this engine/ECS test platform is to meet Tier 2 Bin 5 light-duty emission standards with limits of 0.07 g/mi NOx and 0.01 g/mi PM. Another critical focus of this project is the characterization of currently unregulated, but potentially toxic emissions.

Among the fuel variables to be studied, sulfur has been identified as most critical to this research. The Diesel Emission Control – Sulfur Effects (DECSE) project [1], a predecessor to this effort, examined the effect of sulfur on individual emission control devices, including NOx adsorber catalysts, DPFs, diesel oxidation catalysts, and lean NOx catalysts. This testing showed that the efficiency of NOx adsorber catalysts is significantly affected by sulfur in the diesel fuel [2]. This project provides a more thorough investigation of sulfur effects and uses modern hardware and robust electronic controls with systems incorporating both NOx and PM control devices. ECS performance over time, as a function of fuel sulfur content, was examined in tests up to 2000 hours in duration.

Figure 1. 6.6 L Duramax Test Engine

Approach

A 6.6 liter Duramax engine (300 HP at 3100 rpm) (Figure 1) with a Bosch common rail fuel injection, integrated exhaust gas recirculation (EGR), charge air cooler, and a center mounted turbocharger was used as the test engine for this project. This vehicle was equipped with appropriately designed emission control devices and the necessary regenerative control hardware and electronics to conduct this fuel study. A significant reduction in tailpipe emissions over the current California calibration for this engine was required for this project.

In order to make the goals of this project possible and limit the reduction efficiencies required by the ECS devices, significant modifications have been made to the test engine by the subcontractor in order to lower engine-out emissions, including installation of low-pressure EGR and engine calibration changes (for lower engine-out NOx and more favorable exhaust temperature profiles). In addition, secondary fuel injection, a diesel fuel burner, and dual wall insulated exhaust components were used for thermal

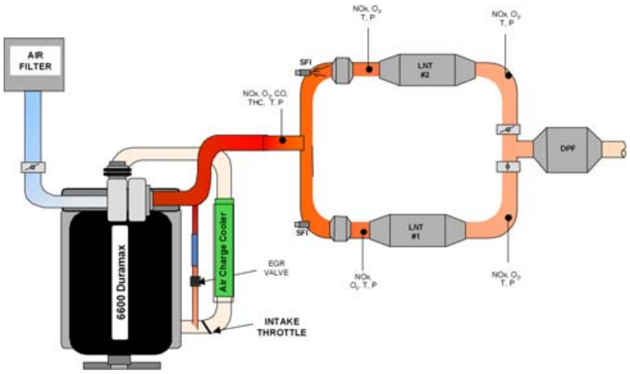

Figure 2. Emission Control System Architecture

management of the ECS. A MECA supplier provided emission control devices for the project dual-leg ECS configuration. Figure 2 shows the basic configuration for the system. This system minimized NOx breakthrough as well as the fuel penalties associated with NOx reduction, but was complex and expensive. This project is comprised of two major tasks:

Task A involved development of the test platform, including setup, integration, and optimization of the engine and vehicle, ECS and associated electronic controls, and development of thermal management strategies. This task included the design of post injection strategies that provide in-cylinder secondary fuel for NOx adsorber catalyst regeneration (3,4). This task also included baseline tests to characterize engine-out emissions (no catalysts) during transient and steady-state operation. Baseline tests were conducted with a DECSE 15-ppm sulfur fuel (referred to as D15) and a low-sulfur refinery fuel (referred to as BP15).

Task B involved system performance and aging evaluations using a 15-ppm sulfur fuel (D15 and BP15), with performance evaluations over the FTP, US06 and HFET driving cycles conducted every 50 hours up to 300 hours. Aging was continued on the ECS for an additional 1700 hours using the 15-ppm sulfur fuel to determine longer-term aging impacts.

A full suite of emissions were measured during Task A baseline testing and Task B aging tests. They include the following:

- NOx
- CO
- HC (hydrocarbons)
- CO_2 (carbon dioxide)
- PM (including detailed compositional analysis)
- Benzene
- 1,3 butadiene
- Formaldahyde
- Acetaldehyde
- N_2O (nitrous oxide)
- NH_3 (ammonia)
- SO_2 (sulfur dioxide)
- H_2S (hydrogen sulfide)
- Nitroxyalkanes

Results

Once all of the ECS control features were incorporated into a final strategy, the refined calibration was applied to the ECS configured engine. Engine dynamometer tests were performed on the 6.6 liter Duramax over the cold- and hot-start Urban Dynamometer Driving Schedule (UDDS), US06, and HFET driving cycles. The UDDS, also known as the LA4, cycle is composed of Bag 1 and Bag 2 of the light-duty FTP; the US06 is a high speed/load aggressive test procedure, part of the supplemental FTP; and the HFET is the highway fuel economy test cycle.

All tests reported here were simulations of the actual driving cycles discussed above, performed by Southwest Research Institute in their engine test cell. The first test during each testing sequence was the FTP in its modified form (2 consecutive UDDSs). There were two (instead of three) bag and filter measurements taken. The calculation of the final result was a composite UDDS, algebraically equal to a standard FTP three-bag test (43% weighting on the cold-start UDDS and 57% weighting on the hot-start UDDS).

This discussion summarizes the complete aging results through 2000 hours of testing as they relate to NOx and PM emissions and NOx trends over the composite UDDS. This was done as a time-saving method that would allow for multiple hot-start

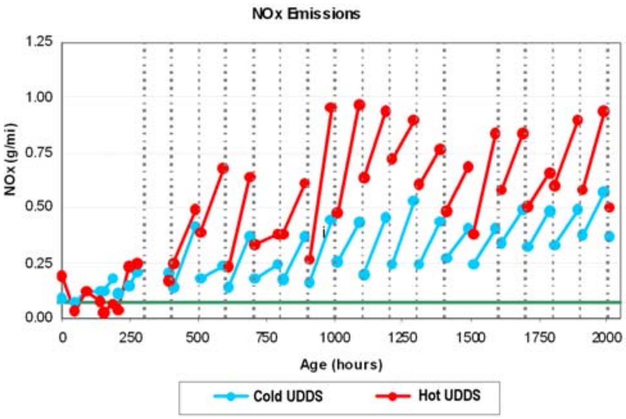

Figure 3. Cold- and Hot-Start UDDS NOx Emissions

UDDS tests to be run in a single day, since the engine would need to be force-cooled or soaked over night between each cold-start test. These data are presented as averages of two or three tests at each evaluation point. The majority of the evaluations were conducted with the DECSE 15-ppm sulfur fuel, denoted as D15, with occasional duplicate evaluations using a refinery run 15-ppm sulfur fuel, denoted as BP15. A distinction is made in all of the following figures when BP15 versus D15 fuel was used. The figures also include the occurrence of a NOx adsorber desulfation event, indicated by vertical dashed lines; the 50,000 mile interim useful life Tier 2 Bin 5 emission standard, indicated by the green dashed horizontal lines; and the 120,000 mile full useful life Tier 2 Bin 5 standard, indicated by the green solid horizontal lines.

During the course of aging, the catalyst system was evaluated frequently in order to assess its degradation in performance due to sulfur poisoning and thermal aging. The initial tests were performed at 0 hours with fresh catalysts. The subsequent test series were performed before and after the desulfurization events at 200 and 300 hours of aging. After the 300-hour mark, the desulfurization/evaluation cycle frequency was increased to every 100 hours through the remainder of the 2000 hours of aging.

The average NOx emission results are displayed in Figures 3 and 4. Observations at the beginning and end of a single aging cycle are connected. Cold- and hot-start UDDS cycles were performed at the aging marks depicted in Figure 3, and the composite FTP emissions are illustrated in Figure 4.

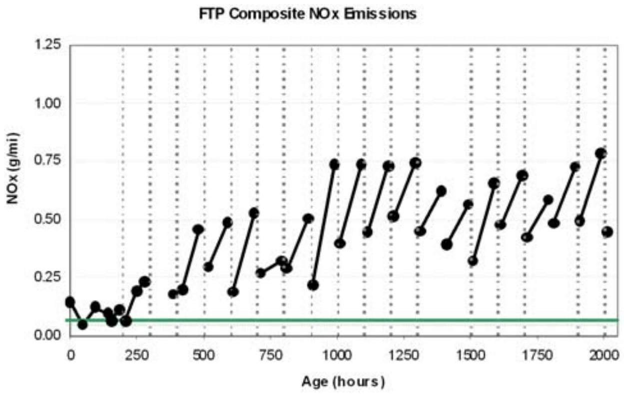

Figure 4. Composite FTP NOx Emissions

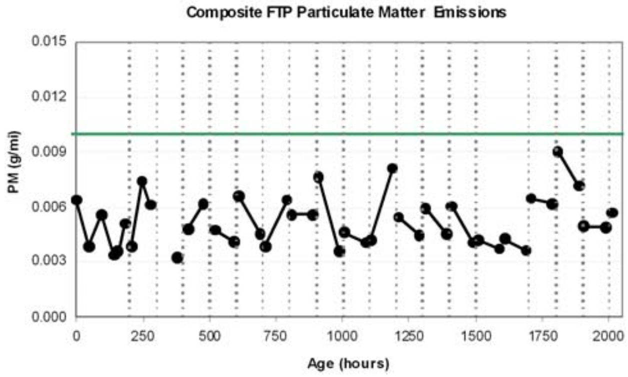

Figure 5. Composite PM Emissions

With the given desulfurization frequency, the composite FTP tailpipe NOx emission number post desulfurization after 2000 hours could not be maintained below the emission standard for 120,000 miles of 0.07 g/mile. A detailed statistical analysis of NOx emissions results from the test cell is discussed in the following section.

The evaluation of the PM filters showed the high degree of filtration efficiency of the DPF. In all instances throughout the aging, the average composite PM numbers were below the emission standard of 0.01 g/mi, as shown in Figure 5.

Statistical analyses were performed to characterize trends in emission levels over the 2000 hours of testing.

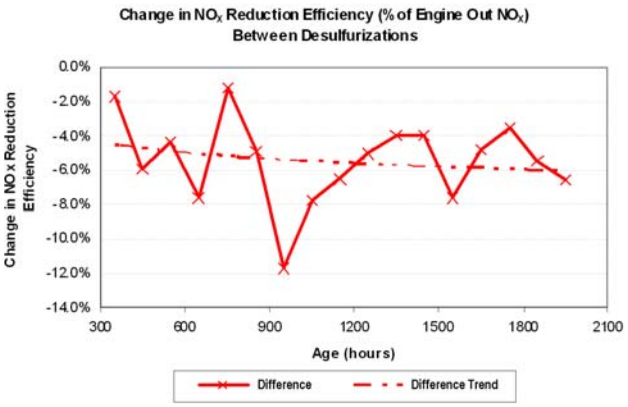

Figure 6. Change in NOx Reduction Efficiency Between Desulfurizations over Time

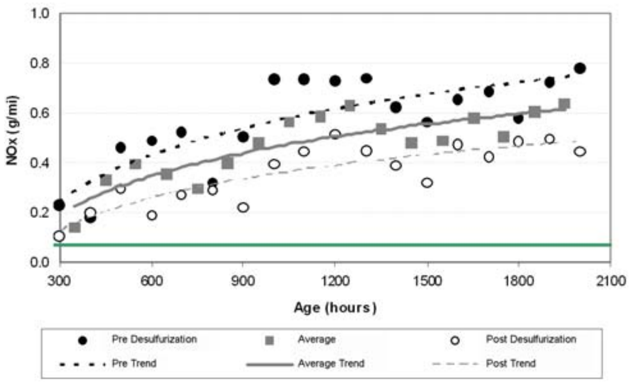

Figure 7. Increase in NOx Reduction Efficiency at Desulfurizations over Time

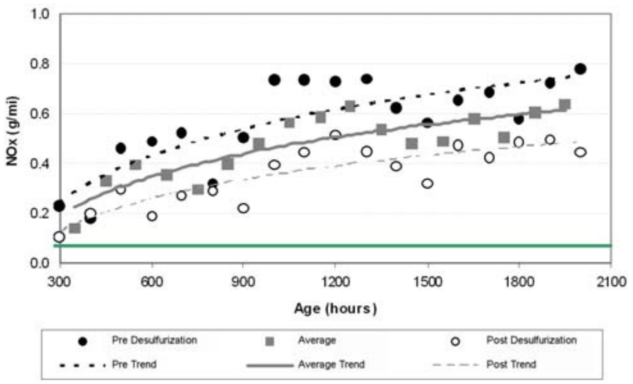

Figure 8. Emission Trends over Time

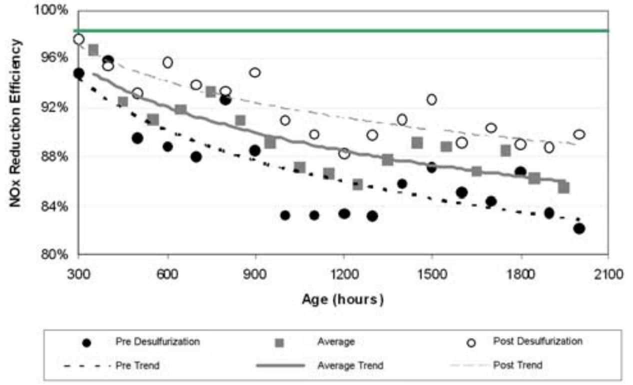

Figure 9. NOx Reduction Efficiency Trends over Time

Figure 6 illustrates the degradation in catalyst performance between desulfurizations. A log-linear model was fit to estimate average trends and evaluate statistical significance. The graph demonstrates that the loss in NOx reduction efficiency (FTP composite) between desulfurizations is generally about 6% of the engine-out without EGR, with a slight trend ranging between 4% and 6%. Figure 7 illustrates the effectiveness of the desulfurization process at restoring performance. There is a 6% improvement in NOx reduction efficiency at each desulfurization event, with a slight trend ranging between 3% and 6%. Although these trend lines show slight changes in NOx reduction efficiency, the slopes of the regression lines were not statistically different from zero. Combined, these figures indicate that the desulfurization process generally compensates for the increased degradation in catalyst performance between desulfurizations throughout the 2,000-hour test.

The trends in FTP composite NOx emissions between 300 and 2000 hours of aging are shown in Figure 8, and trends in FTP composite NOx reduction efficiency relative to engine-out between 300 and 2000 hours of aging are shown in Figure 9. To account for the effects of the desulfurization process, separate log-linear models were fit to three sets of NOx emissions data: (1) measurements made before a desulfurization event, (2) measurements made after a desulfurization event, and (3) the average of measurements made at the beginning (post-desulfurization) and end (pre-desulfurization) of each aging period. The latter results plotted at the midpoint of the aging period represent the best estimate of the average emissions over time; however, it could not be verified that the increase in NOx emissions within an aging period is linear.

The plots in Figures 8 and 9 show the performance stabilization for the systems over time. All three of the regression lines were found to have statistically significant trends at the 95% confidence level. However, because of the curvature in the trends, additional analyses were performed to address the question of whether the system stabilizes over time. This was accomplished by iteratively truncating the leftmost data from each of the three data sets, then refitting the regression model and evaluating the significance of the regression slope parameter. The trends are not statistically significant after 800 to 900 hours of aging.

Table 1 shows the average composite FTP emissions from the seven engine-out tests (six without EGR and one with EGR) and from the 18 tailpipe tests conducted prior to the first desulfurization at 200 hours, as well as the estimated FTP composite emissions results at 1950 hours as determined by the average trend line based upon measurements taken between 350 and 1950 hours. Emission reductions are calculated relative to engine-out with and without EGR. Emission reduction does not necessarily equate to NOx conversion because backpressure affects engine-out emissions by changing the amount of EGR in use.

The initial and 1950-hour estimated reductions in NOx, CO, and PM emissions due to the ECS were all statistically significant, as was the reduction in fuel

Table 1. Average Engine-Out, Initial, and Estimated 1950-Hour Tailpipe Composite FTP Regulated Emissions and Fuel Economy

Emission Parameter	EGR	Engine-Out	Tailpipe (0-200 Hours)		Tailpipe Average (Post-Pre)[5] (1950 Hours)		Regulated Emission Standard [4]
		Avg.[1]	Avg.[2]	Percent Reduction	Avg.[3]	Percent Reduction	
NO_x (g/mi)	Without	4.38	0.095	97.8%	0.616	85.9%	0.07
	With	2.12		95.5%		70.9%	
NMHC (g/mi)	Without	0.198	0.165	16.7%	0.372	-87.6%	0.09
	With	Missing		Missing		Missing	
THC (g/mi)	Without	0.204	0.463	-126.9%	0.730	-257.8%	N/A
	With	0.264		-75.1%		-176.2%	
CO (g/mi)	Without	2.02	0.258	87.2%	0.620	69.3%	4.2
	With	4.43		94.2%		86.0%	
PM (g/mi)	Without	0.065	0.005	91.6%	0.005	91.8%	0.01
	With	0.145		96.2%		96.3%	
FE (mi/gal)	Without	18.4	15.0	18.7%	15.5	16.0%	N/A
	With	18.0		16.7%		13.9%	

[1] Engine-out average without EGR is based on 6 tests; Engine-out average with EGR is based on 1 test

[2] Average of 18 tests performed prior to first desulfurization at 200 hours

[3] Estimate at 1950 hours based upon the trend of average results between 350 and 1950 hours

[4] Tier 2 Bin 5 Full Useful Life

[5] The average of the post-desulfurization measurement at 1900 hours and the following pre-desulfurization measurement at 2000 hours

N/A = Not applicable

economy (initially 18.7% relative to engine-out without EGR and 16.7% relative to engine-out with EGR). Although initially the average tailpipe NOx emissions of 0.095 g/mi were higher than the regulated emissions standard of 0.07 g/mi, the difference was not statistically significant. The 1950-hour estimate of 0.616 g/mi was significantly above the standard. Initial average non-methane hydrocarbon (NMHC) emissions of 0.165 g/mi were 83% higher than the applicable standard, and the estimated 1950-hour average NMHC emissions of 0.372 g/mi were over four times the applicable standard. Tailpipe emissions for total hydrocarbons (THC) were greater than engine-out THC emissions, and average PM emissions were 50% lower than the applicable standard throughout.

Fuel consumption data was collected for the composite UDDS during the aging and evaluation events. The average fuel economy for the baseline engine-out tests was 18.3 mpg, compared with the average fuel economy during the ECS evaluation events of 14.9 mpg. This equates to an 18.6% fuel economy penalty for the NAC/DPF system. This fuel economy penalty is large, but it should be noted that the majority of the total penalty (53%) is associated with the diesel fuel burner operation. With a smaller displacement engine and associated higher exhaust temperatures, less burner assist would be required, resulting in a lower fuel penalty. Indeed, the fuel penalty associated with the NAC regeneration over the composite UDDS is only 6%. The impact of the burner operation on the fuel penalty is further illustrated when the fuel consumption from the US06 cycles is considered. The US06 cycle is a more aggressive cycle than the UDDS, resulting in higher exhaust temperatures and, in turn, less need for the burner. The overall fuel penalty associated with the US06 cycle is only 5.2%.

Conclusions

During the course of this project, it was demonstrated that the NAC/DPF system evaluated, in conjunction with a 15-ppm sulfur fuel and appropriate control strategies and calibrations, could achieve high NOx and PM reduction efficiencies. After 2000 hours of on-engine aging, the NAC/DPF system demonstrated an average NOx reduction of 89% and PM reduction of 94% over the composite FTP. While the PM emissions were below the Tier 2 Bin 5 emission standard, the NOx emissions were outside of this limit after full aging. The desulfurization strategy employed was successful in recovering NOx adsorber performance, with some deterioration through 2000 hours of aging.

The ECS evaluated, in conjunction with 15-ppm sulfur fuel, achieved a high NOx reduction level over the course of 2000 hours of aging and was also able to achieve Tier 2 Bin 5 PM levels during early stages of aging.

Test work associated with this activity is complete, and final data analysis and reporting will be published in 2006.

FY 2005 Publications/Presentations

1. Information from this project was presented at the Diesel Engine Emission Reduction (DEER) Conference in Chicago, Illinois, in August 2005.

References

1. http://www.ott.doe.gov/decse/
2. U.S. Department of Energy, Engine Manufacturers Association, Manufacturers of Emission Controls Association, “Diesel Emission Control – Sulfur Effects (DECSE) Program – Phase I Interim Data Report No. 2: NOx Adsorber Catalysts,” October 1999
3. Webb C., Weber P., Thornton M., “Achieving Tier 2 Bin 5 Emission Levels with a Medium Duty Diesel Pick-Up and a NOx Adsorber, Diesel Particulate Filter Emissions System—NOx Adsorber Management,” SAE Paper 2004-01-0585, March 2004, Detroit, Michigan.
4. Weber P., Webb C., Thornton M., “Achieving Tier 2 Bin 5 Emission Levels with a Medium Duty Diesel Pick-Up and a NOx Adsorber, Diesel Particulate Filter Emissions System—Exhaust Gas Temperature Management,” SAE Paper 2004-01-0584, March 2004, Detroit, Michigan.

II.3 Fuel-Borne and Fuel-Derived Reductants for Diesel Exhaust NOx Reduction

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DOE Team Lead: Stephen Goguen

Objectives

- Explore methodologies for forming and utilizing fuel-borne and fuel-derived reductants to enable lean-NOx catalysis systems for diesel engines with high effectiveness and low energy penalty.

Approach

- Use a novel in-cylinder fuel injection strategy to produce H_2 under net-lean engine operation (leveraged with other research activities).
- Run experiments with a lean-NOx catalyst to quantify any beneficial effects of such H_2 production under lean conditions.

Accomplishments

- Efforts of previous years were embodied and published as an SAE paper. This work concerned broad performance mapping of a Ag-based catalyst, hydrocarbon selective catalytic reduction (HC-SCR) system (provided by Caterpillar, Inc.) under realistic conditions using 17 reductants.
- A modest HC-SCR Work for Others (WFO) research project equally funded by ExxonMobil Research & Development and Caterpillar Inc. was performed during the second quarter of FY 2005. This work was enabled by the earlier Ag-based catalyst effort performed in cooperation with Caterpillar, Inc. New types of catalyst were evaluated in the course of this work. The results of the WFO project are not presented here.
- Experiments were performed using a novel in-cylinder fuel injection strategy to produce H_2 under net-lean engine operation. A demonstration experiment revealed that highly accelerated HC-SCR catalyst light-off is possible using this technique.

Future Directions

- Investigate the potential to produce useful fuel-derived reductants from compression-ignition fuels with and without fuel additives.
- Experiment with selected reductant and catalyst combinations.
- Continue to work with industry partners.
- An open issue that could be addressed in the future is HC-SCR durability and robustness. This applies to Ag-based catalysts and other HC-SCR catalysts.

Introduction

One of the technology options for diesel exhaust NOx emission control is selective catalytic reduction (SCR) with hydrocarbons or urea. With SCR, a reductant is introduced into the oxygen-rich exhaust which then passes over a catalyst, and NOx is selectively reduced to N_2. To date, only urea SCR systems have adequate NOx control effectiveness to be considered as viable emission control systems, but this requires development of an onboard filling and storage system for the reductant that is entirely separate from the fuel system. This also means a separate delivery, storage, and dispensing infrastructure would need to be deployed, presumably at fuel filling stations. For the fuel-borne or fuel-derived reductant concept, the reductant is part of the fuel or can be produced from the fuel. No separate onboard system and infrastructure would be required.

Synthesis gas has been shown to be an effective reductant. Production of synthesis gas can be achieved with fuel reformers, but novel in-cylinder approaches may also produce similar species, in particular H_2. A reported application of reformate gas, and specifically H_2, is to enhance HC-SCR catalyst function [1-3]. Researchers have reported that H_2 significantly improves NO conversion over Ag/Al_2O_3 catalysts across a wide temperature range [1-3].

Approach

Previous efforts have been made to explore the in-cylinder production of reformate gas which includes significant H_2. The basic effort for development of these methods was performed as part of the DOE Advanced Combustion Engine Program and is reported in the FY 2005 Progress Report for Advanced Combustion Engine R&D. One of these previously developed methods is known as the delayed extended main (DEM) fuel injection strategy [4]. As the name implies, the main fuel injection is delayed and extended to create rich conditions late in the cycle in order to produce H_2. The approach used in this work is to apply a variation on the DEM strategy to enhance the effectiveness of HC-SCR.

Results

Fiscal year 2004 experimental efforts were devoted to performance mapping of a Ag-based HC-SCR catalyst provided by Caterpillar, Inc., which was designed to work well with ethanol as the reductant. In addition to ethanol, 16 reductants were tested under realistic conditions (exhaust from a 5.9 liter diesel engine), with 1-propanol and 1-butanol giving superior low-temperature results compared to ethanol. This FY 2004 work was embodied and published as an SAE paper in FY 2005. As a direct result of this HC-SCR work, Oak Ridge National Laboratory (ORNL) was approached to perform a modest WFO research project equally funded by ExxonMobil Research & Development and Caterpillar, Inc. This R&D effort was performed during the second quarter of FY 2005. New types of HC-SCR catalyst were evaluated in the course of this work, but the results are as yet unpublished.

Experiments using a 1.7 liter Mercedes-Benz diesel engine were performed to develop an in-cylinder fuel injection method which controls the combustion process such that reformate gas with significant H_2 is generated while maintaining a lean air-fuel ratio in the bulk exhaust gas. By operating only 1 of 4 engine cylinders in the DEM mode at any given time, significant amounts of reformate rich in H_2 can be generated while the bulk exhaust gases are oxygen rich. Which cylinder is operating in DEM mode can be changed in some pattern if desired to control wear and cylinder imbalance. This method of generating the H_2 is referred to as the individual-cylinder DEM strategy. It was demonstrated that exhaust containing up to 0.8% H_2, over 1% CO, and 3,000 ppm hydrocarbon (HC) with over 9% O_2 remaining could be produced. This reformate production strategy is reported with more detail in the FY 2005 Progress Report for Advanced Combustion Engine R&D.

Leveraging the Advanced Combustion Engine Program effort, a preliminary catalyst experiment was conducted with a commercial platinum HC-SCR catalyst core supplied by Manufacturers of Emission Control Association to examine the ability of reformate gas to accelerate catalyst light-off. Figure 1 shows a schematic of the experimental setup.

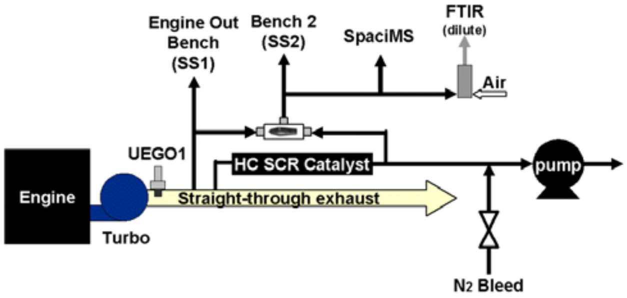

Figure 1. Experimental Setup Schematic Diagram

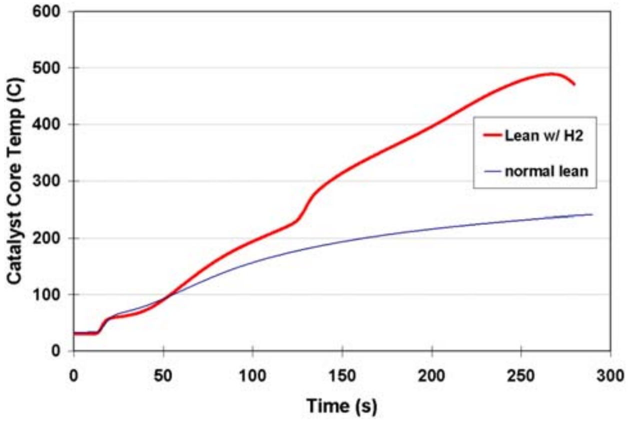

Figure 2. Catalyst Core Temperature-Time Trace for 30k hr^{-1} Space Velocity; Normal Lean Engine Operation Versus Individual-Cylinder DEM (lean with H_2)

Figure 2 compares the results for core catalyst temperature rise with normal operation versus using the individual-cylinder DEM strategy. The flow rates through the catalyst sample were the same in each case, and the exhaust temperature at the turbo-out location for each case was about 280-290°C. Both curves show a small but very steep rise in temperature when the flow through the catalyst first begins (the pump is started) at about the 15-second point in Figure 2. The warmup rates are similar until the core temperature reaches about 100°C, at which time the augmented warmup begins to take effect. At about 120 seconds, the catalyst lights off, its core temperature rapidly jumping about 50°C, then continuing to rise to nearly 500°C, at which point the augmentation (DEM) is stopped.

The augmented warmup is shown again in Figure 3 (with a different time axis), including the catalyst inlet, core and outlet temperature as well as engine-out (EO) and tailpipe (TP) NOx emissions. The light-off is seen at about 240 seconds in this figure. At this point, the core temperature exceeds that of the inlet temperature and continues to rise until the reformate production is aborted just before 400 s (as the core temperature approaches 500°C). The TP NOx is more than 100 ppm below the engine-out level, representing a 25% NOx reduction. Also note that the TP NOx remains lower even after normal combustion is resumed. Further experiments will be performed to determine if this phenomenon is repeatable.

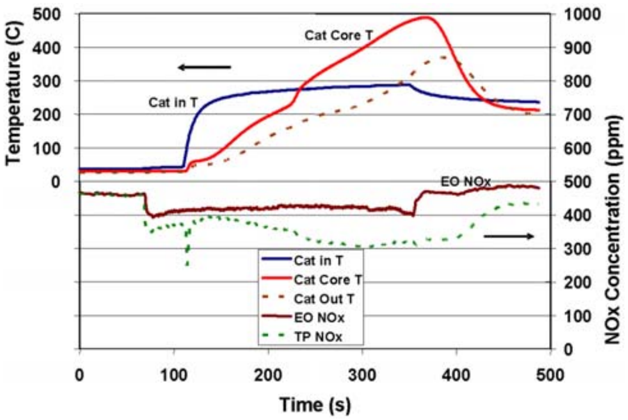

Figure 3. Catalyst Inlet and Outlet NOx Concentration, and Catalyst Inlet, Core, and Outlet Temperatures for Individual-Cylinder DEM Strategy

Conclusions

- Operating 1 of 4 cylinders with a rich DEM strategy can produce a continuous stream of up to 0.8% H_2, over 1% CO, and 3000 ppm HC in net lean exhaust with over 9% O_2 remaining.
- Preliminary catalyst experiments show that the presence of reformate in net-lean diesel exhaust can significantly accelerate catalyst light-off.
- Specific promotion of catalytic NOx conversion by H_2 during net lean operation has not been demonstrated. Future experiments are planned to explore this further on several catalyst formulations, in such a way that the hypothesis of NOx enhancement by H_2 can be examined.

Special Recognitions & Awards/Patents Issued

1. Patent application filed entitled "Stripping Ethanol from Ethanol-Blended Fuels for Use in NOx SCR," February 10, 2003.

FY 2005 Publications/Presentations

1. John F. Thomas, Bruce G. Bunting, Samuel A. Lewis, Sr., John M. Storey, Ron L. Graves, ORNL; Paul Park, Caterpillar, Inc., "Hydrocarbon Selective Catalytic Reduction Using a Silver-Alumina Catalyst with Light Alcohols and Other Reductants," SAE Paper Number 2005-01-1082, presented at SAE 2005 World Congress, Detroit, MI, April, 2005.

2. John F. Thomas, Bruce G. Bunting, Samuel A. Lewis, Sr., John M. Storey, Ron L. Graves, ORNL; Paul Park, Caterpillar, Inc., "Silver Alumina Catalyst Performance with Light Alcohols and Other Reductants," Proceedings: U.S. Department of Energy 10th Diesel Engine Emissions Reduction Conference, Coronado, California, August 29 to September 2, 2004. Paper sent April 2005, and is available on the web.

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4. Brian West, Shean Huff, James Parks, Sam Lewis, Jae-Soon Choi, William Partridge, John Storey, "Assessing Reductant Chemistry During In-Cylinder Regeneration of Diesel Lean NOx Traps," SAE Transactions - Journal of Fuels & Lubricants 4, 2004, 1975-1985, paper 2004-01-3023.

II.4 Effectiveness and Sulfur Tolerance of Selective Catalytic Reduction and Diesel Particle Filter Systems

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Objectives

- Demonstrate the low-emissions performance of advanced diesel engines operating on advanced fuels and equipped with low-pressure-loop exhaust gas recirculation (EGR) plus urea selective catalytic reduction (SCR) and diesel particulate filters (DPFs).
- Evaluate the sensitivities of the emission controls to fuel variables.
- Use a fuels matrix of five fuels, including four Diesel Emission Control Sulfur Effects (DECSE) fuels with sulfur levels of 3, 8, 15, and 30 ppm plus a refinery fuel of nominally 15 ppm sulfur, referred to as BP15.
- Determine the regulated and unregulated emissions with and without emission controls.
- Determine toxic and unregulated emissions levels.
- Examine the durability of the emission control systems.

Approach

- Set up a heavy-duty engine in an emissions test cell to optimize emissions reduction performance of two different emission control systems (referred to as System A and System B) utilizing urea SCR.
- Apply a low-pressure-loop EGR system to reduce engine-out NOx to ~ 2.0 - 2.5 g/hp-hr or less.
- Add emission control system(s), DPFs and SCR systems with urea injection, to reduce tailpipe emissions of both NOx and particulate matter (PM). (Two different emission control systems – Systems A and B – both comprised of DPFs and SCR catalysts, will be evaluated.)
- Integrate controls and optimize performance to reach the lowest possible emissions of NOx and PM for both systems.
- Perform 6,000-hour durability tests simultaneously with Systems A and B, checking emissions – regulated and unregulated – at 2,000-hour intervals.

Accomplishments

- By the end of FY 2005, all experimental work had been completed. Both systems had accumulated 6,000 hours of aging, and all emissions tests had been completed.
- Southwest Research Institute presented their final report of the project and handed over all files and data necessary for the working group to complete the Advanced Petroleum-Based Fuels Diesel Emissions Control (APBF-DEC) final report.

Future Directions

- All work has been completed on this project, a draft report has been submitted, and the final report is being prepared.

Introduction and Approach

Southwest Research Institute (SwRI) was the subcontractor for this APBF-DEC project, and technical guidance was provided by the APBF-DEC working groups. Technical and programmatic oversight of the activities was accomplished with a technical team led by Oak Ridge National Laboratory, with an industry co-lead. Other team members represented automobile and engine manufacturers, suppliers, fuel and fuel additive companies, and government agencies. Caterpillar provided 12-liter engines for the project, and the Manufacturers of Emission Controls Association provided two exhaust emission control systems. Each emission control system included a diesel particulate filter combined with SCR catalysts. Low-pressure-loop EGR systems were provided by STT-EMTEC in Sweden, while Robert Bosch Company provided the urea injection systems.

The plan was to optimize emissions performance with two different catalyst systems (Systems A and B, each comprised of DPF and urea SCR catalysts). After optimization, the emissions performance was characterized with four different fuels: DECSE fuel with sulfur levels of 3, 8, and 15 ppm plus a BP refinery fuel with nominally 15 ppm sulfur. A limited test was performed with DECSE 30 fuel (30 ppm sulfur). Emissions were thoroughly characterized for these tests, including unregulated emissions of interest plus toxic and unregulated emissions compounds.

Following all the emissions tests with each system, the systems were set up in a test cell for aging the systems, where they underwent 6,000 hours of durability testing with emissions tests at the 2,000-, 4,000-, and 6,000-hour points.

Results

Optimization of emission control systems for both Systems A and B was completed in FY 2004. Aging of both systems for 6,000 hours and final emissions tests were completed in June 2005. During the period of aging, the systems were taken back to the emissions test cell for full emissions testing with the fuels matrix at intervals of 2,000 hours, 4,000 hours, and 6,000 hours each. The aging cycle was composed of repetitive ESC tests.

At the start of the aging cycle, PM emissions were well controlled by both systems over the U.S. transient cycle below the 2007-2010 requirement of 0.01 g/hp-hr. Very good control of PM throughout the aging period was maintained by both systems, and no problems with PM regeneration were encountered. That is, passive DPF regeneration occurred throughout the project and no active regeneration was needed. It is possible that this phenomenon is an artifact of the aging cycle used, and real-world operation may require some active control of DPF regeneration. Resolving this issue was beyond the scope of this project. The NOx level over the U.S. transient cycle at the start of aging was near the 2010 limit of 0.2 g/hp-hr for System A, but not as low for System B (~ 0.47 g/hp-hr). It should be noted that System B's SCR catalyst was of smaller volume than was that for System A. Good control of NOx emissions was maintained by both systems over the aging cycle.

With System A there was the appearance of a degradation of NOx control at the 2,000-hour test point over the transient emission test cycle. This result was later attributed to a phenomenon of urea overdosing during the aging cycle, and it was shown to be reversible with exposure to NOx. The presence of an ammonia sensor downstream of the catalyst system probably would have averted this problem. These phenomena with System A are not well understood at this time and were beyond the scope of research and of funding for this project to investigate thoroughly. Nevertheless, the results of the phenomena are evident in the figures to follow.

System B demonstrated good maintenance of NOx control (over the transient test cycle) during the entire 6,000-hour aging test, albeit that the system

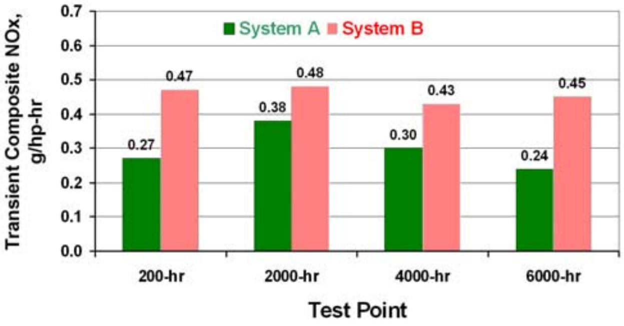

Figure 1. NOx Emissions on the Transient Cycle – Systems A&B – DECSE 8 ppm Fuel – Composite Results

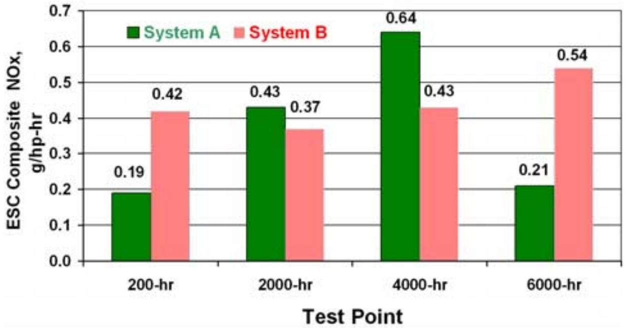

Figure 2. NOx Emissions on the Steady-State Cycle – Systems A&B – DECSE 8 ppm Fuel – Composite (Average 2 Cycles)

did not control NOx to levels as low as with System A. NOx and PM emissions results for both systems over the 6,000 hours of aging and for both the U.S. transient cycle and ESC steady-state cycle are illustrated in Figures 1-4.

Conclusions

Major conclusions from the project are as follows:

- Demonstrated the potential of low-pressure-loop EGR, diesel particulate filter, and urea SCR to achieve 2010 emissions levels for heavy-duty engines
- Demonstrated that these technologies are not sensitive to fuel sulfur level in the 0-30 ppm range

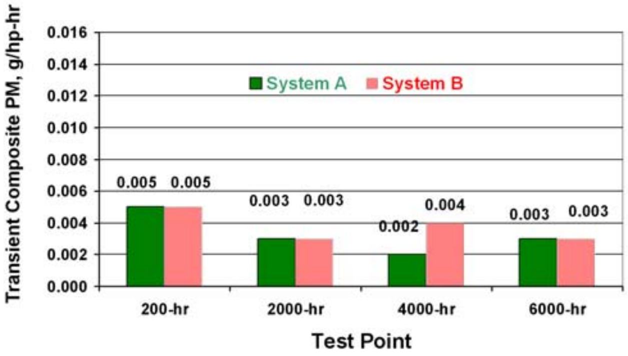

Figure 3. PM Emissions on the Transient Cycle – Systems A&B – DECSE 8 ppm Fuel – Composite Results

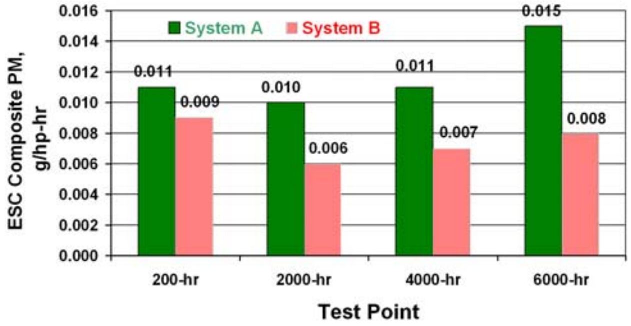

Figure 4. PM Emissions on the Steady-State Cycle – Systems A&B – DECSE 8 ppm Fuel – Composite (Average 2 Cycles)

- Demonstrated the stability of emission control systems over 6,000 hours of operation (on the ESC cycle)
- This project emphasized several issues important for commercialization of these technologies:
  - Importance of closed-loop control and of the need for integration of the emission control system and engine
  - Need to improve both the low-temperature conversion efficiency and the high-temperature catalyst efficiency and durability of SCR catalysts
  - Need to optimize boosting and EGR calibration to minimize fuel economy degradation
  - Need for ammonia sensors to be used in closed-loop controls

  - Need to examine long-term passive versus active regeneration of DPFs
  - Properly sizing the SCR catalyst to the engine so that the catalyst is large enough to effectively reduce NOx but not so large as to introduce large lags in both ammonia storage and NOx conversion

FY 2005 Publications/Presentations

1. "Final Update on APBF-DEC EGR/DPF/SCR Demonstration Project at SwRI," Chris Sharp and Magdi Khair, Southwest Research Institute, and Ralph McGill, Sentech, presented at the 2005 DEER Conference, Chicago, Illinois, August 2005

II.5 Phosphorus Poisoning of Diesel Oxidation Catalysts

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Subcontractor:
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Objectives

- Develop techniques for measuring the physical and chemical state of phosphorus in engine exhaust and determine its effects on diesel aftertreatment performance.
- Measure catalyst deactivation by phosphorus poisoning in accelerated tests and correlate to washcoat surface changes.
- Correlate accelerated poisoning tests to long-term and catastrophic poisoning of catalysts that occurs in field service.

Approach

- Conduct literature search to determine key parameters associated with phosphorus poisoning and measurement techniques.
- Design test rig and methodologies for exhaust chemistry measurement, catalyst poisoning and catalyst performance evaluation.
- Conduct experimental investigations of accelerated phosphorus poisoning techniques and surface characterization.
- Team with University of Tennessee at Knoxville in evaluating catalysts using a laboratory bench-flow reactor.

Accomplishments

- Compared characteristics of field service diesel oxidation catalysts with known deactivation mechanisms with similar catalysts poisoned by accelerated techniques.
- Compared performance and materials characteristics between the two catalysts.
- Evaluated exhaust phosphorus chemistry as a function of engine exhaust temperature and method of phosphorous introduction.

Future Directions

- Conduct further accelerated poisoning tests and measurements in order to better define phosphorus exhaust chemistry and resulting effects on catalyst performance.
- Identify absorbed phosphorus compounds using surface analytical techniques for the comparison of field service and accelerated catalyst poisoning.

- Apply techniques to new engine oil additives and catalyst materials and types, such as lean NOx traps (LNTs) and diesel particulate filter (DPF) catalysts.
- Extend techniques to DPFs and expand project to include effects of ash and soot loading in addition to phosphorous poisoning.

Introduction

Phosphorus is a well-known catalyst poison that is derived from the zinc dialkyldithiophosphate (ZDDP) additive in lube oil used as an anti-wear agent. While in operation, an engine consumes lube oil, and this results in the subsequent presence of phosphorus in the exhaust gases. The form and amount of phosphorous varies based on engine operating conditions. Phosphorus in the exhaust reacts with catalysts and causes a loss of performance through masking or chemisorption. Although the amount of ZDDP in lube oil is currently being reduced, a minimum amount appears to be necessary for adequate engine durability. Ways of reducing the effects of exhaust phosphorus on catalyst performance include reducing the amount of phosphorous, altering the chemical state of the phosphorus to a less damaging form, or formulating catalysts more resistant to phosphorous poisoning. To evaluate these solutions, it is necessary to measure the chemical state and compounds of phosphorus in diesel exhaust and the resulting changes in catalyst performance and material properties. Accelerated evaluation protocols allow such development to proceed more rapidly.

Approach

A 517cc Hatz single-cylinder diesel engine bench was utilized to provide a variety of pathways through which phosphorus can be introduced into the exhaust gases. The engine was modified to accommodate accelerated poisoning techniques including intake manifold injection, fuel doping, exhaust manifold injection and lube oil doping to simulate different engine and usage situations. A photograph of the engine bench is shown in Figure 1. Fresh commercial catalyst samples were compared to field service bus catalysts. Exhaust gases were collected during the experiment for each poisoning technique and analyzed using electrospray mass spectroscopy to determine the phosphorus species formed.

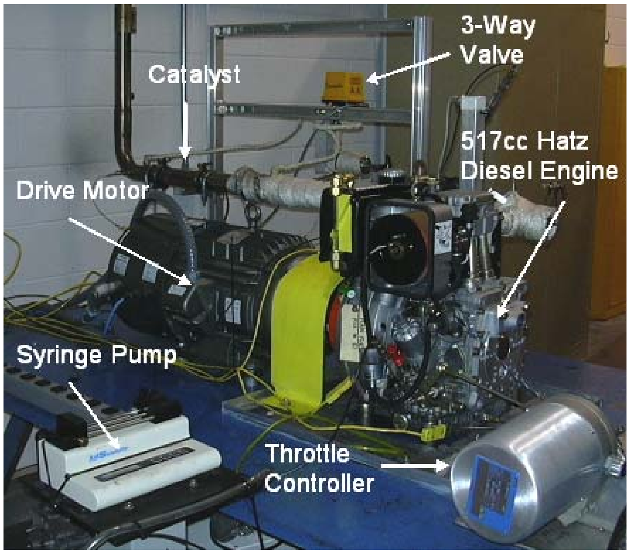

Figure 1. Photograph of engine bench used for accelerated poisoning and light-off evaluation of diesel oxidation catalysts.

Hydrocarbon and carbon monoxide oxidation light-off performance was measured using the engine bench for both the field and engine bench-poisoned catalysts. Samples were then sectioned and prepared for material characterization by X-ray fluorescence spectroscopy (XRF), X-ray photoelectron spectroscopy (XPS), and electron probe microanalysis (EPMA). In addition, bench-flow reactor tests were used to obtain hydrocarbon and carbon monoxide light-off performance from samples cored from field service and engine-poisoned catalysts. The bench-flow reactor was used to provide evaluation under more controlled conditions than the engine bench allowed.

Results

Commercial catalysts of similar formulation to the field service catalysts were poisoned using accelerated intake manifold injection of ZDDP-doped lube oil. The amount of phosphorus present in the injected lube oil was 0.5 grams P/50 cc oil. This correlates to 700 times normal phosphorous accumulation rate for a heavy-duty truck, when combined with the accelerated consumption rate used. Accelerated poisoning tests were conducted at different engine exhaust temperatures, and exhaust gas samples were collected during poisoning using an impinger. Catalyst temperatures for these tests were maintained at 165°C, 280°C and 420°C. Electrospray mass spectrometry was used to analyze exhaust gas species, and the results indicated that the ZDDP was completely combusted in the engine. The resulting chemical species derived from the ZDDP were phosphoric acid (H_3PO_4) and zinc sulfate ($ZnSO_4$). After poisoning, catalysts were sectioned and underwent materials characterization for comparison to the field service catalysts.

XRF analysis revealed that phosphorus and sulfur deposition was higher at higher catalyst temperatures. XRF results are listed in Table 1 and indicate that a maximum of 54% of the total phosphorus and 25% of the total sulfur were deposited in the catalyst during the accelerated poisoning. The maximum deposition found in the accelerated poisoning tests was 3.22 grams P and 4.57 grams S, which was of the same order as the field service catalysts. EPMA analysis performed at the ORNL High Temperature Materials Laboratory and the University of Tennessee confirmed the presence of phosphorus and sulfur and revealed that phosphorus was preferentially deposited at the front section of the catalyst while sulfur was evenly distributed along the catalyst length. Phosphorus concentrations were found to be greatest at the catalyst surface with a steep concentration gradient along the washcoat depth, and sulfur was found to disperse evenly throughout the washcoat. These findings were in agreement with analysis conducted on field service catalysts. Sample EPMA X-ray maps and line scan are shown in Figures 2 and 3, respectively. Catalyst samples are being further analyzed using XPS to identify phosphorus compounds deposited on the catalysts.

Table 1. Effect of catalyst temperature on phosphorus, sulfur and zinc (weight percent) deposited on engine-poisoned diesel oxidation catalysts by intake manifold injection as measured by XRF.

Temperature (°C)	Phosphorus Deposition (%)	Sulfur Deposition (%)	Zinc Deposition (%)
165	26.60	6.67	1.79
280	46.20	12.94	8.07
420	53.67	25.40	2.50

Hydrocarbon and CO light-off performance measurement was conducted using the engine bench at the National Transportation Research Center and the bench-flow reactor at UT for both the accelerated poisoning catalysts and the field service catalysts. For accelerated poisoning catalysts, light-off temperatures increase between 50°C and 100°C, showing significant loss of performance. Comparable loss in performance was found for the field service catalysts. Figure 4 shows the effects of phosphorus loading and deactivation methods on CO conversion for the engine-bench evaluation.

Conclusions

- Phosphorus and zinc chemistry is not dependent on engine load or exhaust temperature for accelerated intake manifold injection.
  - Phosphorus in the exhaust gases prior to the catalyst was found as phosphoric acid and adsorbed on the catalyst along with sulfur.
  - Zinc formed $ZnSO_4$ compounds, which passed through the catalysts with only minor adsorption.
- Higher exhaust temperatures during accelerated intake manifold injection poisoning result in more phosphorus deposition.
- Phosphorus compounds deposit preferentially on the front sections of both field service and accelerated poisoning catalysts, with similar phosphorus surface concentrations and washcoat penetration depths.
- Sulfur compounds deposit uniformly within the washcoat and along the catalyst length in both field service and accelerated poisoning catalysts, with more deposition on field service catalysts.
- Negligible zinc concentrations are found in both field service and accelerated poisoning catalysts.

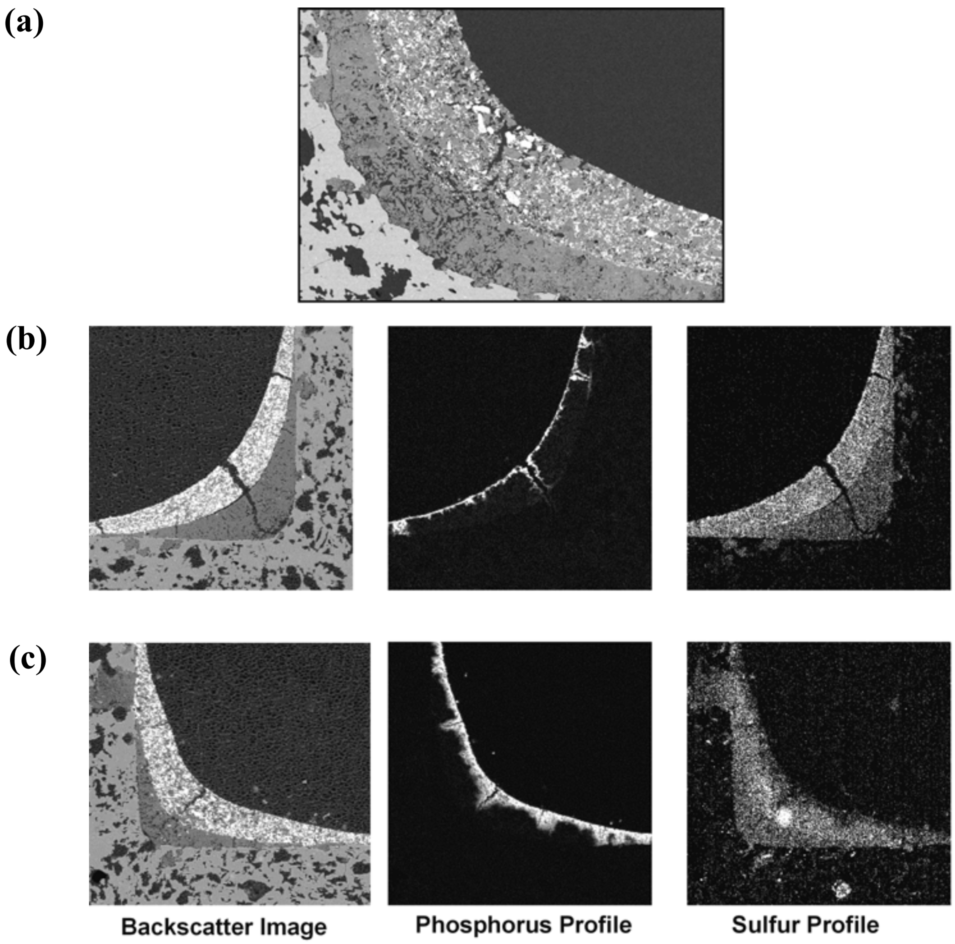

Figure 2. (a) EPMA backscatter image of the front section of a fresh commercial diesel oxidation catalyst. (b) EPMA backscatter and X-ray maps of the front section of a field service catalyst with phosphorus and sulfur deposition. (c) EPMA backscatter and X-ray maps of the front section of a bench-poisoned catalyst (poisoned via intake manifold injection) with phosphorus and sulfur deposition.

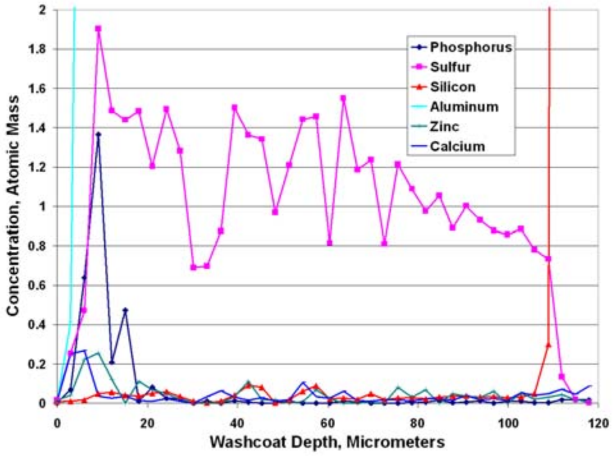

Figure 3. EPMA line-scan of the front section of a field service catalyst detailing elemental concentrations as a function of washcoat depth.

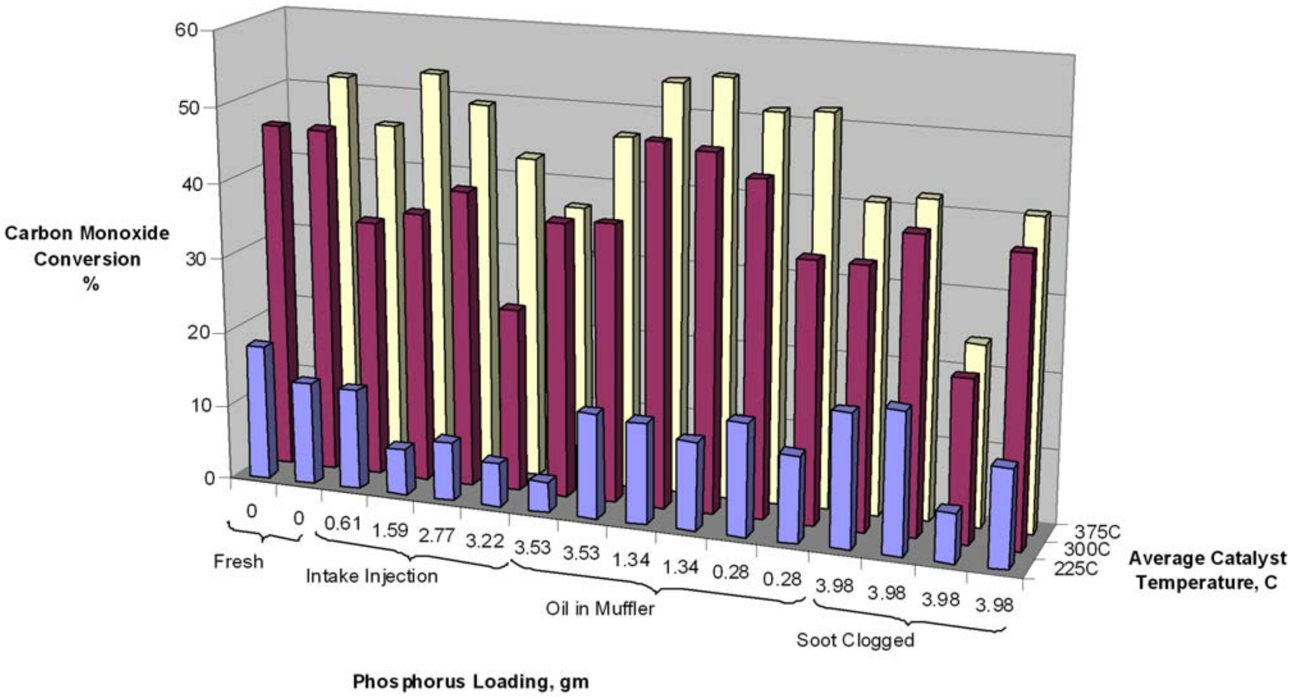

Figure 4. Engine-bench evaluation of carbon monoxide conversion of fresh commercial catalyst, intake manifold injection poisoned commercial catalysts and field service catalysts.

FY 2005 Publications/Presentations

1. Bunting, B.G., More, K., Lewis, S., and Toops, T., "Phosphorous Poisoning and Phosphorous Exhaust Chemistry with Diesel Oxidation Catalysts", SAE 2005-01-1758.
2. Bunting, B.G. and Nguyen, K., "The Development of Rapid Aging and Poisoning Protocols for the Verification of Combustion Engine Aftertreatment Devices", 2005 Vietnam International Conference on Automotive Technology for Vietnam, 10/05, paper 007.
3. Bunting, B.G., More, K., Lewis, S., Toops, T., Eaton, S., and Nguyen, K., "Transportation, Fate, and Impact of Lube Oil Phosphorous", DOE 2005 Fuels Technology Program Merit Review, 3/05.

II.6 Rapid Aging of Lean NOx Traps (LNTs)

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Objectives

- Develop protocols for rapid thermal aging of lean NOx traps (LNTs) to be used with a bench-flow reactor and an engine bench.
- Perform rapid thermal aging on various LNTs using bench-flow reactor.
- Extract deactivation kinetics from experimental results and formulate a simple theoretical model of thermal aging of LNTs.
- Compare bench-flow reactor-aged LNTs to engine bench-aged and field-aged LNTs.

Approach

- Conduct literature search for the LNT thermal deactivation mechanisms.
- Select appropriate surface characterization techniques.
- Perform rapid thermal aging experiments on LNT samples using bench-flow reactor and small engine bench.
- Perform surface characterization techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), and electron probe microanalysis (EPMA) to characterize the microstructure changes of LNT washcoat.

Accomplishments

- Established protocols for rapid thermal aging experiments for both bench-flow reactor and engine bench.
- Performed rapid thermal aging on LNTs at aging temperatures of 900 and 1000°C using the bench-flow reactor.
- Performed TEM, XRD, and EPMA studies on fresh and bench-flow reactor-aged LNTs.
- Observed the migration and accumulation of potassium at the interface of the washcoat and the cordierite substrate in aged high-temperature LNTs.
- Observed sintering of precious metal in all LNTs evaluated at high temperatures.

Future Directions

- Perform thermal aging at several different lean/rich aging cycles at 900 and 1000°C to validate repeatability of data and to provide more samples for surface studies.
- Perform additional thermal aging at 600, 700 and 800°C.

- Conduct TEM, XRD and EPMA to obtain the progression of K migration away from the washcoat, the transformation of $BaCO_3$ into other barium-mixed oxides, and sintering of the precious metal group (PGM).
- Incorporate experimental results into the theoretical model for predicting the thermal degradation of LNTs.
- Discuss results with catalyst suppliers to verify procedures and validity of data.
- Compare results to field-aged catalysts to verify mechanisms and to establish accelerated severity factors.

Introduction

The LNT is formulated with NOx storage components or trapping materials, usually alkali or alkaline earth metals such as barium, potassium, sodium and cesium, and precious metals such as Pt dispersed over a high-surface-area γ-alumina washcoat. During the period of lean operation, NOx in the exhaust gas stream is stored in the storage components in the form of nitrates. During the shorter period of rich operation, the stored nitrates are decomposed to NOx, which is subsequently reduced to N_2 by CO, H_2 and unburned hydrocarbons over the PGM. In order to be effective in reducing NOx emissions, a LNT has to be subjected to periodic regeneration and desulfurization. Since these two processes are carried out under fuel-rich conditions, high-temperature excursions can be produced which can lead to deactivation of the LNT. Three potential thermal aging mechanisms which lead to the deactivation of the LNT have been identified: (i) the loss of dispersion of the PGM and the NOx trapping materials, (ii) interactions between the trapping materials and the γ-Al_2O_3 to form less efficient NOx storage components, and (iii) the loss of surface area or porosity of the storage components and the washcoat. An understanding of these thermal aging mechanisms is critical in developing better LNT washcoat formulations as well as theoretical models of thermal aging of LNTs. Consequently, the objectives of the present study are to develop protocols for rapid aging of LNTs using a bench-flow reactor and a small engine and to determine the thermal aging mechanisms and the deactivation rates as a function of aging temperature and time for several LNT catalysts.

Approach

In the present study, the thermal aging of two LNTs was investigated by lean-rich cycling at elevated temperatures using a bench-flow reactor system as shown in Figure 1. The use of the bench-flow 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 with a composition similar to the exhaust gas from a diesel engine is introduced into the bench-flow reactor system by means of mass flow controllers. Water vapor is introduced into the system via the steam generator. By activating solenoid valves, lean and rich cycles of any duration can be achieved, and by adjusting the duration of rich cycle and the fuel ($CO+H_2$) to air ratio, it is possible to produce a range of aging temperatures inside the LNT sample. Prior to thermal aging, all LNTs were de-greened in a flowing environment of air and water vapor. The NOx conversion of the degreened LNTs was then evaluated at 400°C prior to aging. For thermal aging, the LNTs were subjected to two different aging temperatures of 900 and 1000°C in a number of pre-determined cycles. The thermal aging of LNTs was carried out with the bench reactor maintained at 400°C using a cycle of 130 seconds lean and 50 seconds rich. At a given aging temperature, the NOx conversions were measured at regular intervals in order to investigate the effect of

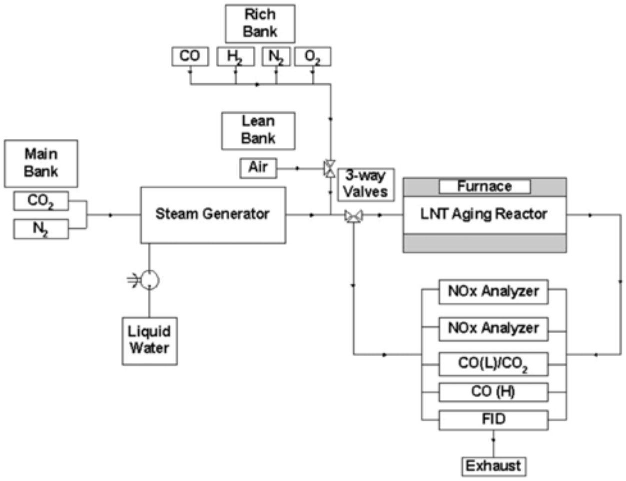


Figure 1. Schematic of Bench-Flow Reactor

lean/rich aging cycles on the thermal aging.

All bench-flow thermal aging and performance evaluations of LNTs were carried out at a NOx concentration of 1000 ppm and a gas hourly space velocity of 60,000 hr^{-1} to match engine bench conditions. The LNT performance deterioration as a function of aging temperature and number of lean/rich aging cycles and time was then obtained.

To determine the effect of thermal aging on the growth of Pt crystallites, NOx storage sites and γ-Al_2O_3, washcoat powder was extracted from fresh and aged catalysts and analyzed by TEM, XRD, and 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

Prior to the thermal aging experiments, the NOx conversion at different temperatures of the two fresh LNT catalysts was evaluated under lean/rich modulations with 20 s lean and 4 s rich. The LNT catalyst with a maximum NOx conversion at 350°C is referred to as the low-temperature LNT, whereas the other catalyst, with a maximum NOx conversion at 400°C, is referred to as the high-temperature LNT.

The effect of aging temperature and lean/rich aging cycles on the NOx conversion of the two LNTs is shown in Figure 2. As can be seen in the figure, a common feature of the thermal deactivation curves is that after an initial decrease, the NOx conversion begins to level out as the number of lean/rich aging cycles increases. In addition, the NOx conversion of the two LNT formulations was affected differently by the thermal aging. At an aging temperature of 900°C, the NOx conversion of the low-temperature LNT initially degrades at the same rate as that of the high-temperature LNT. As the number of lean/rich aging cycles increases, the NOx conversion of the high-temperature LNT appears to be stabilized while that of the low-temperature LNT is not stable. At an aging temperature of 1000°C, the low-temperature LNT degrades more severely than the high-temperature LNT. The difference in thermal degradation characteristics can be attributed to the different compositions of the NOx trapping materials in the washcoats of the two LNTs.

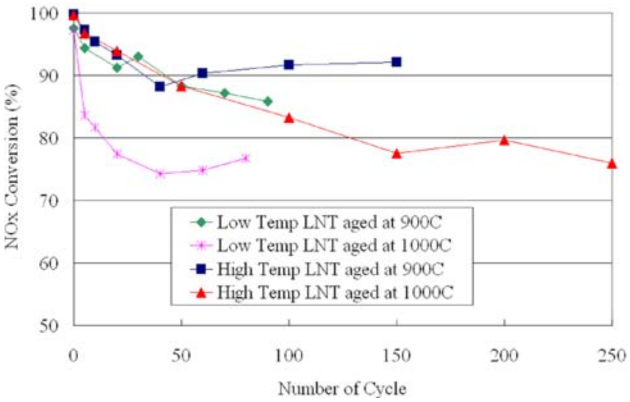


Figure 2. Effect of Aging Temperature and Aging Cycles on NOx Conversion of Low- and High-Temperature LNTs at a Gas Hourly Space Velocity of 60,000 hr^{-1}

Figures 3a and 3b show typical TEM images obtained from the powder of fresh and aged high-temperature LNTs, respectively. The dark, relatively round objects in these images are Pt particles. Both images display a rather wide distribution of Pt particle sizes. The sintering effect is clearly seen in Figure 3b for the high-temperature LNT aged at 900°C for 150 lean/rich aging cycles, in agreement with the XRD results (see Table 1).

Figures 4a and 4b show the region $2\theta = 15$-$85°$ of XRD spectra of fresh and aged high-temperature LNTs. Only the crystallite dimensions of Pt, γ-Al_2O_3 and $BaCO_3$ are evaluated from the full-width at half-maximum of the peaks in the XRD spectra of the fresh and aged high-temperature LNTs, and the results are listed in Table 1. The characteristic spectral lines of CeO_2, denoted as (•), at $2\theta = 28.5$, 33.3, 47.5 and 56.4° are observed in both samples. On the other hand, only a faint spectral line of CeO_3 at $2\theta = 30.6°$, denoted as (o), is observed in the fresh LNT sample, and none is observed in the aged sample. The spectral line at $2\theta = 29.41°$, denoted as (♦), is assigned to cerium mixed oxide, the composition of which has not been identified in the present study. Diffraction peaks corresponding to Pt, $BaCO_3$ and γ-Al_2O_3 were detected for both fresh and

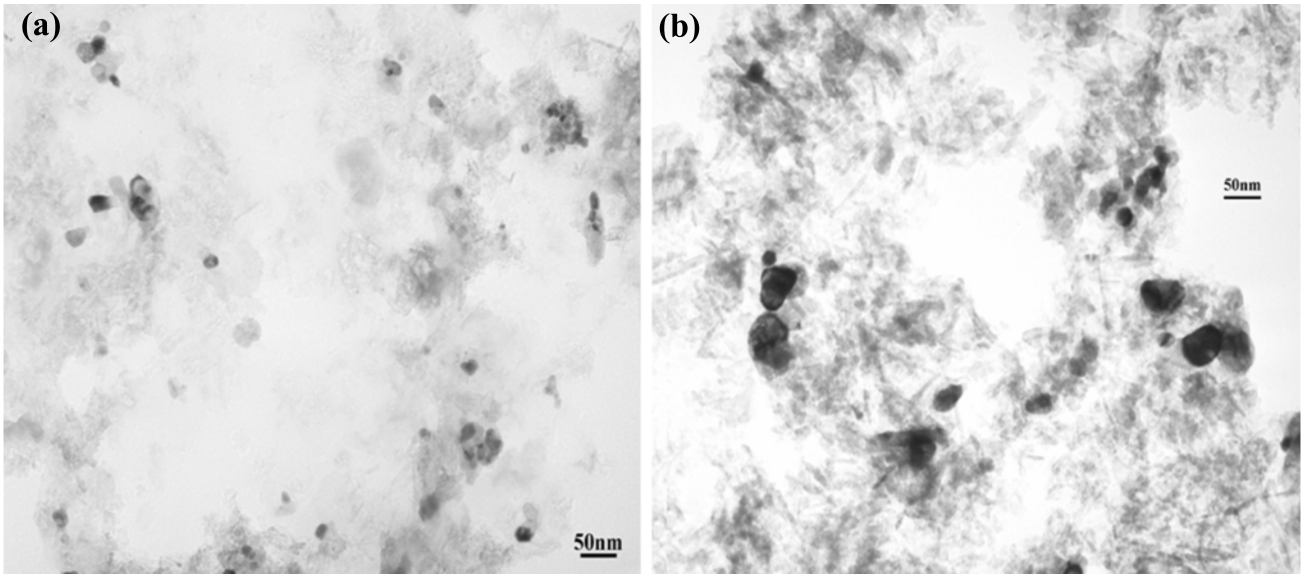
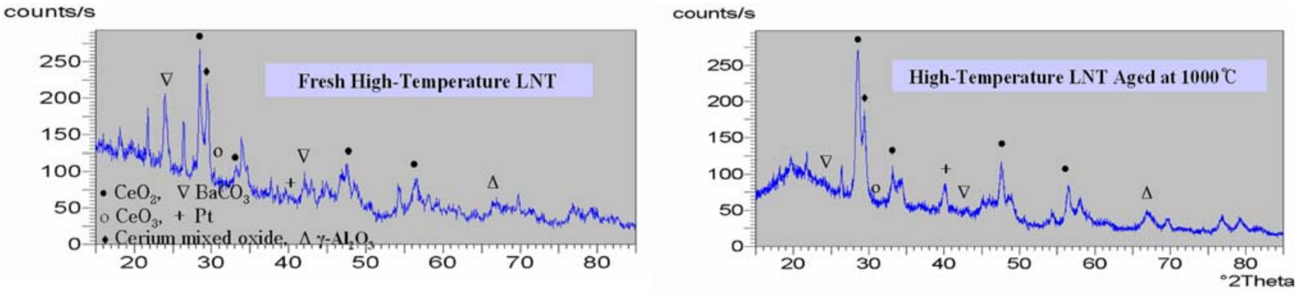


Figure 3. TEM Images of Pt Particles (a) Fresh High-Temperature LNT (100,000X Magnification) and (b) High-Temperature LNT Aged at 900°C (100,000X Magnification)



(a) **(b)**

Figure 4. XRD Spectra of (a) Fresh High-Temperature LNT and (b) High-Temperature LNT Aged at 1000°C

aged high-temperature LNTs. The average diameter of Pt crystallites in the fresh LNTs is not determined due to low peak intensities. The spectrum of the high-temperature LNT aged at 1000°C displays several remarkable differences with respect to that of the fresh sample. The diffraction peak of Pt at $2\theta = 39.8°$ becomes more discernable and intense and clearly indicates that the sintering of the Pt particles is due to the thermal aging. As seen in Table 1, the average Pt particle diameter increases from <2 to 12.5 nm on aging for the high-temperature LNTs subjected to 250 lean/rich aging cycles at 1000°C. However, the most notable result is the disappearance of the $BaCO_3$ peaks at $2\theta = 24.5$ and 42.1° at an aging temperature of 1000°C, not just for the high-temperature LNTs but for the low-temperature LNTs as well (see Table 1). This may be due to the transformation of $BaCO_3$ into a mixed oxide such as spinel-$BaAl_2O_4$, which is less efficient for NOx storage. Accordingly, further XRD and XPS analyses will be carried out in future studies to identify the exact composition of the newly formed barium mixed oxides.

To investigate the migration and accumulation of alkali metal trapping materials, EPMA images of fresh and 900°C-aged high-temperature LNTs were obtained. As seen in Figures 5a and 5b, Ba and K were well dispersed in the washcoat of fresh high-temperature LNTs, shown as bright spots in the EPMA image, and there was no evidence of either barium or potassium presence in the cordierite

Table 1. Average Diameter of Pt, $BaCO_3$, and γ-Al_2O_3 Determined from XRD for Fresh and Aged Low-Temperature and High-Temperature LNTs

XRD Sample	Element and Compound	P.D.(nm)	XRD Sample	Element and Compound	P.D.(nm)
Fresh Low-Temperature LNT	Pt	No Discernable Peak	Fresh High-Temperature LNT	$BaCO_3$	24.32
	$BaCO_3$	13.71		$BaCO_3$	24.32
	γ-Al_2O_3	5.63		γ-Al_2O_3	7.87
Low-Temperature LNT Aged at 900C	Pt	8.19	High-Temperature LNT Aged at 900C	Pt	9.83
	$BaCO_3$	No Discernable Peak		$BaCO_3$	21.34
	γ-Al_2O_3	5.76		γ-Al_2O_3	5.60
Low-Temperature LNT Aged at 1000C	Pt	14.68	High-Temperature LNT Aged at 1000C	Pt	12.49
	$BaCO_3$	No Discernable Peak		$BaCO_3$	No Discernable Peak
	γ-Al_2O_3	7.26		γ-Al_2O_3	6.18

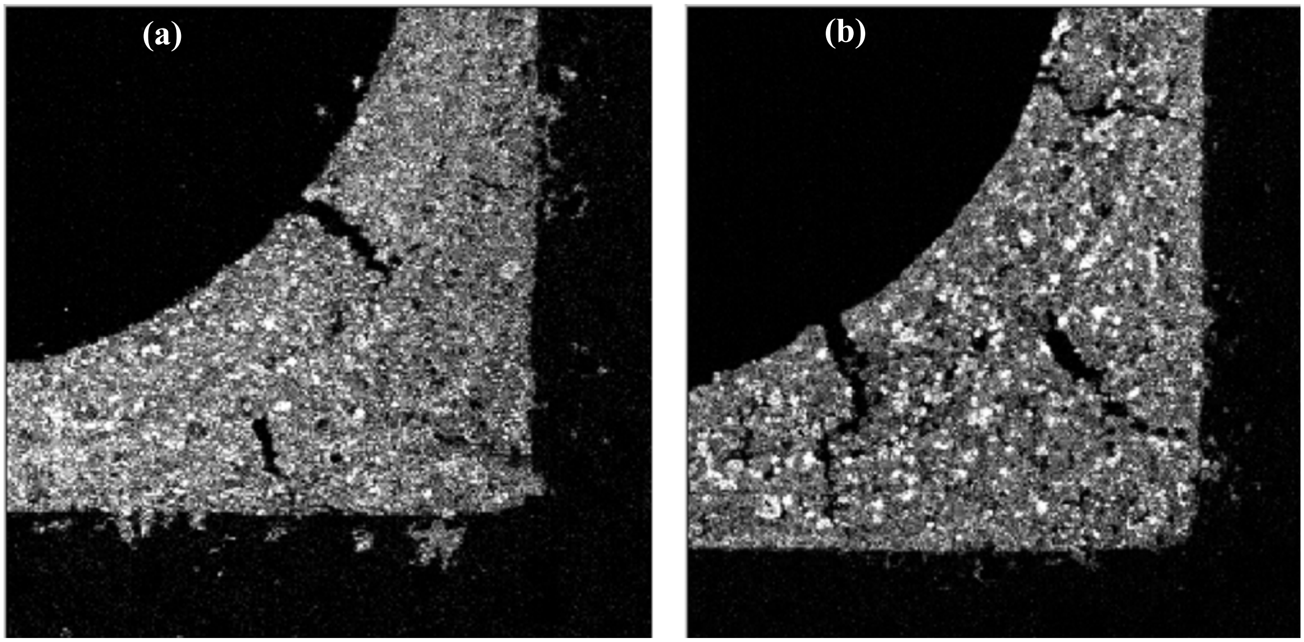


Figure 5. EPMA Images of Barium Compounds (a) Fresh High-Temperature LNT and (b) High-Temperature LNT Aged at 900°C

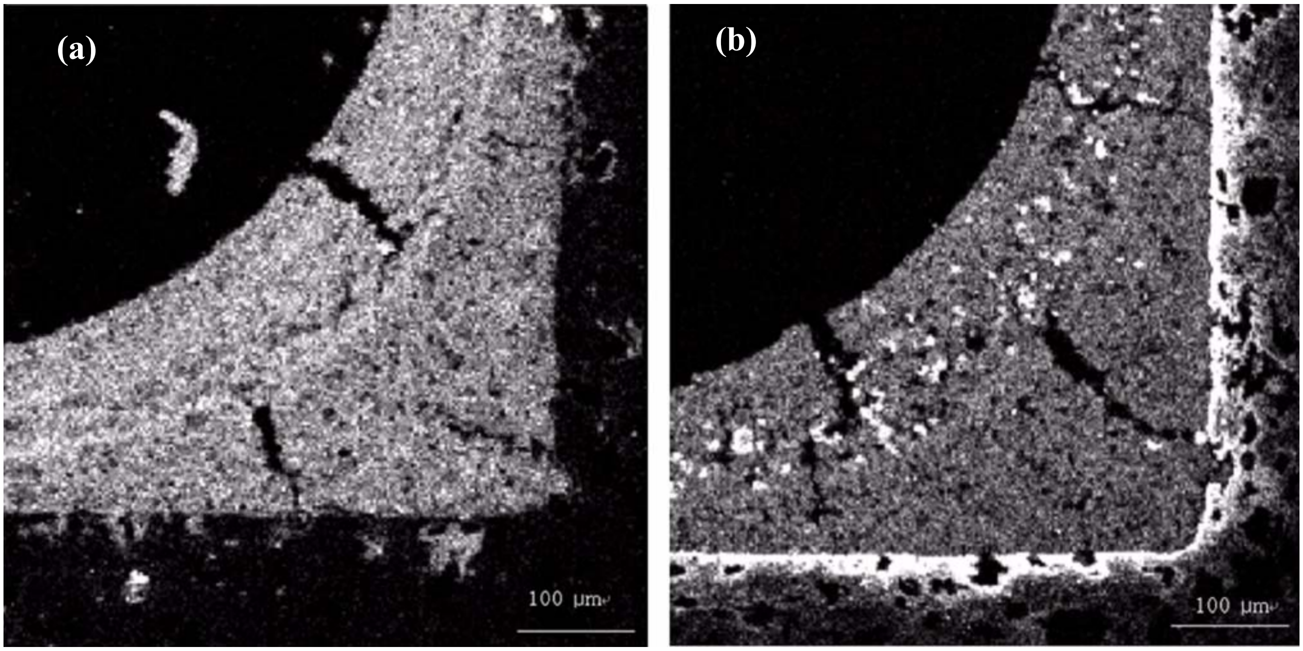


Figure 6. EPMA Images of Potassium Compounds
(a) Fresh High-Temperature LNT and (b) High-Temperature LNT Aged at 900°C

substrate. The Ba map in Figure 6a shows that the Ba crystallite size has been increased even though Ba was still well dispersed in the washcoat for the high-temperature LNTs subjected to 150 lean/rich aging cycles at 900°C. On the other hand, a significant amount of K originally in the washcoat migrated away from the washcoat and accumulated at the interface of the washcoat and the cordierite substrate, while the remaining K appeared as larger size particles in the washcoat, as evidenced in Figure 6b. Consequently, the sintering and the transformation of Ba and the migration of K into the cordierite substrate are the dominant mechanisms of thermal deactivation of alkali metal-supported LNTs. Preliminary results from EPMA clearly demonstrate that the loss of NOx conversion due to thermal aging can be minimized by suppressing the migration of K into the substrate.

Conclusions

- The thermal degradation of low-temperature and high-temperature LNTs increases as the aging temperature and the number of lean/rich aging cycles increase.
- Low-temperature LNTs are degraded more severely than high-temperature LNTs.
- The thermal degradation of LNTs can be attributed to:
  - The sintering of Pt particles and γ-Al_2O_3 crystallites
  - The transformation of $BaCO_3$ into less efficient NOx storage barium mixed oxides
  - The migration of K away from the washcoat and accumulation on the cordierite substrate in high-temperature LNTs

Publications and Presentations

1. Bunting, B.G. and Nguyen, K., "The Development of Rapid Aging and Poisoning Protocols for the Verification of Combustion Engine Aftertreatment Devices", Vietnam SAE International Conference on Automotive Technology, paper 007, October 2005.
2. Bunting, Toops, More, Nguyen, and Gopinath, "Rapid Aging of Lean NOx Traps for Diesel Applications", 2005 DOE Fuels Program Peer Review, March 2005.

II.7 Ultra-Low Sulfur Reduction Emission Control Device

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DOE Team Lead: Stephen Goguen

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Subcontractors
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Johnson Matthey, Malvern, PA
Marathon Ashland Petroleum, Catlettsburg, KY
American Wastes Industries, Maywood, IL

Objectives

To develop and demonstrate proof-of-concept for an “on-vehicle” desulfurization fuel filter for heavy- and light-duty diesel engines.

- Define the most relevant chemistries available that would be suitable for sulfur reduction.
- Modify the most promising chemistries to the requirements for the system.
- Demonstrate the efficacy on an engine test.

Approach

- Phase I: Develop a concept design and analysis, and resolve technical barriers concerning removal of sulfur-containing species in low-sulfur fuels.
- Phase II: Implement high-throughput screening techniques for chemistry selection and dynamic testing.
- Phase III: Prototype design and testing; adapt research concept into a practical filter module and test its efficacy; produce prototype(s).
- Phase IV: Life cycle studies; study life cycle and regeneration options for spent filters.
- Phase V: Validation testing; conduct engine testing with NOx adsorber and test prototype filter on a heavy-duty diesel engine for efficacy; complete system testing and component integration.

Accomplishments

- Successfully completed Phases I, II, III and IV. Awaiting completion of the engine test in Phase V. The project has been delayed due to scheduling issues with the engine test at Mack Trucks.
- From over 4,000 candidate chemistries tested for sulfur removal, one approach was chosen to go forward with.
- Successfully demonstrated continuous sulfur removal at the 1 gallon scale.
- Studied the fuel sensitivity of the sorbent and identified key components in the fuel which affect the sorbent’s performance.
- Completed construction of a 10 gallon vessel for the engine demonstration.
- Studied various fuel lubricants and characterized the loss of lubricity of the fuel after sulfur removal.

- Characterized the mechanism of action of the sorbent to remove sulfur and identified key operational factors.
- Began the optimization of the sorbent to improve its capacity, which will result in lower overall volume.
- Screened available ultra-low sulfur diesel (ULSD) fuels.
- Identified a new sorbent with 20% greater capacity and the potential to achieve a 3 gallon footprint.

Future Directions

- Complete the optimization of the sorbent to achieve a lower bed volume.
- Integrate the NOx adsorber into the Mack engine and have it operate successfully.
- Carry out the Mack engine validation.
- Continue to screen sorbents for the new approach in order to meet the criteria.
- Compile the final report.

Introduction

The goal of this project is to develop an emission control device that can enable engine manufacturers to comply with the new Environmental Protection Agency (EPA) emission standards, including Tier II Bin 5 for light-duty engines and the new '2007 Rule' for heavy-duty diesel engines. The '2007 Rule' includes a new diesel fuel sulfur limit that has a maximum cap of 15 ppm. Successful integration of the sulfur removal component into a heavy-duty diesel vehicle coupled with a post-combustion NOx adsorber catalyst device will, by default, be applicable to light-duty diesel engines.

The sulfur removal device developed by this project can expedite implementation of the new emissions standards by reducing the need for diesel fuels to attain the ultra-low sulfur levels required to ensure optimal performance of NOx adsorber technologies under development. This should be accomplished at relatively modest cost to the end-user because the sulfur removal device will be an add-on to the existing fuel system and will be packaged in a conventional engineering format. It is anticipated that the cost of the proposed sulfur removal device to the consumer will represent no more than a low multiple of the current cost of a standard fuel filter.

Approach

Since the end of the last reporting period we have down-selected a single sorbent for engine testing. It has the highest sulfur removing capacity of over 4,000 candidate reagents we have studied during this project. It is a commercially produced material of modest cost and with properties attractive for building a commercial product. It does not suffer from any health, safety, or environmental issues and its disposal, if that is the ultimate fate, will be not unlike that of the other components of traditional fuel filters. These factors and its high sulfur absorbance capacity have made it the sorbent of choice for proceeding with the project.

Results

Fuel Sensitivity

Throughout this project we have been testing various ULSD fuels for their ability to be desulfurized using our sorbent. These fuels have shown a range of sulfur levels from 4.5 to 9 ppm. Figure 1 shows the range in performance of the sulfur sorbent with these ULSD fuels. The Chevron Texaco fuel will be the fuel which Mack will use in the engine test. Two samples of this fuel have been obtained, and their sulfur removal profiles are described in this figure.

In order to determine what properties in the fuel are controlling this variation, the aromatics content was measured and is presented in Figure 2. As can be seen, the lower the levels of higher polynuclear aromatics, the better the sulfur performance. This is consistent with the competitive binding that we have measured in the past for both 1-ring and 2-ring aromatics. These components in the fuel, which are at higher levels compared to the sulfur, compete for the same sites on the sorbent.

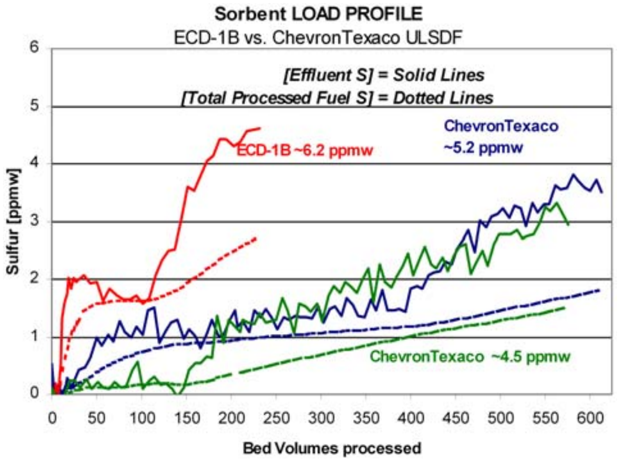

Figure 1. Fuel Sensitivity

The sulfur distribution was measured for the Chevron Texaco fuel and compared to that of the BP fuel (Figure 3). As can be seen, the Chevron Texaco fuel has lighter sulfur components but also has the higher molecular weight sulfur species like the BP fuel. The BP fuel which we are testing here is over 1 year old, and since then a cleaner fuel more like the Chevron Texaco fuel is available.

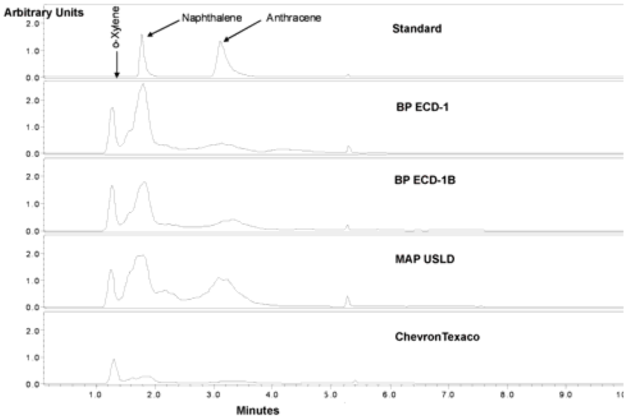

Figure 2. Distributions of Aromatics in Various Fuels

Lubricity Loss

From our earlier studies on fuel properties, we had seen a decrease in the fuel lubricity after passing through the sulfur adsorber. The reduction in lubricity was to a value below specification for the fuel. We now confirm this to be an issue even in column testing and at all stages in the life of the sulfur adsorbent. Either the sulfur which is being removed during the desulfurization is responsible for

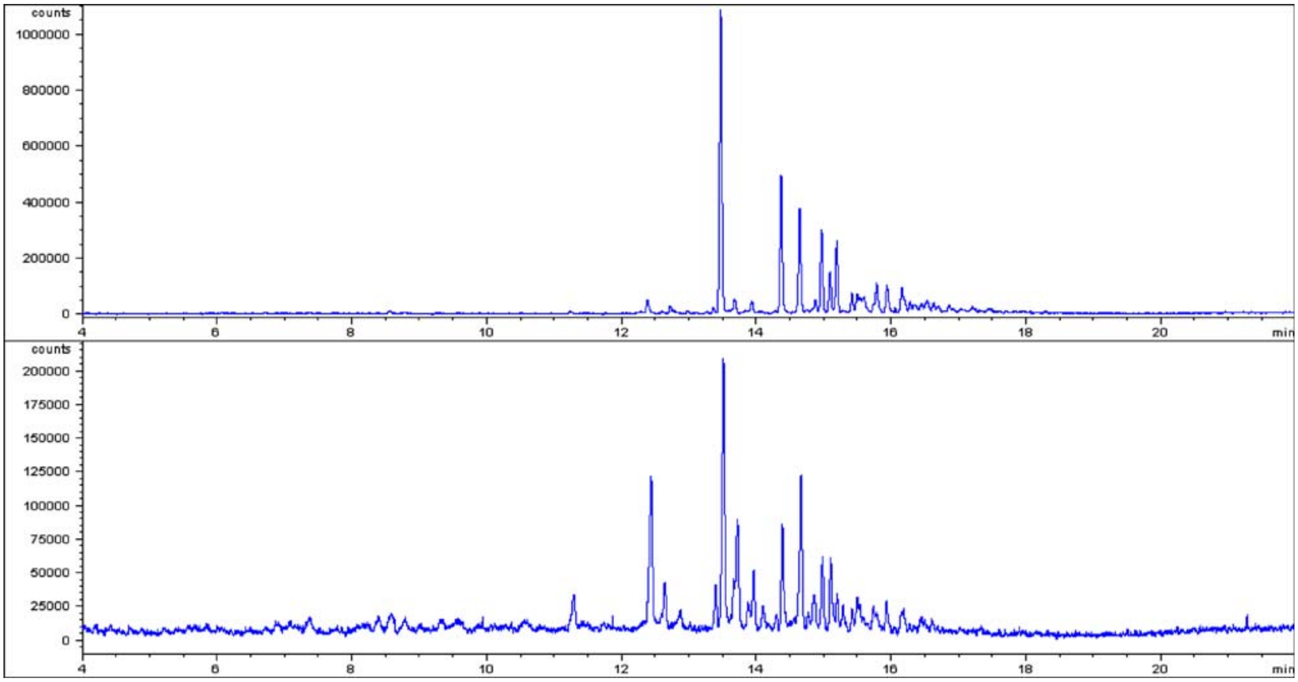

Figure 3. Sulfur Speciation

Table 1. Fuel Properties

Chemistry	Notebook Ref	Copper Corrosion D130	Viscosity @40C D445 (cSt)	Cetane No. D613	Bromine No. D1159	Cloud Point D2500 (deg C)	Total Aromatics in Diesel D5186 (mass %)	Mono Aromatics (mass %)	Poly Aromatics (mass %)	Lubricity D6079 (mm)	Thermal Stability D6468 (%)
Control (BP ECD1)	40065-13	1A	2.446	55.6	0.4	-6	23.3	20.7	2.6	0.465	98
Sorbent A	40059-24	1A	2.451	50.5	0.41	-6	22.9	20.4	2.5	0.625	100

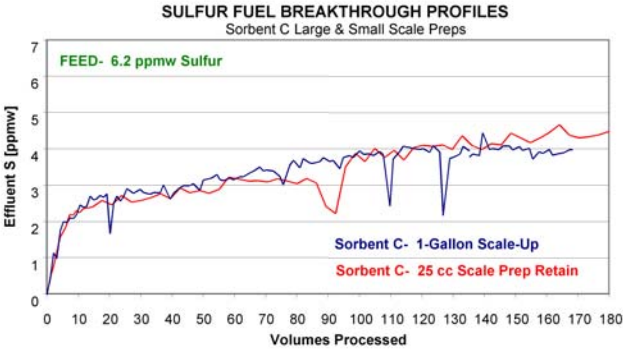

Figure 4. Performance Comparison of Scale-Up

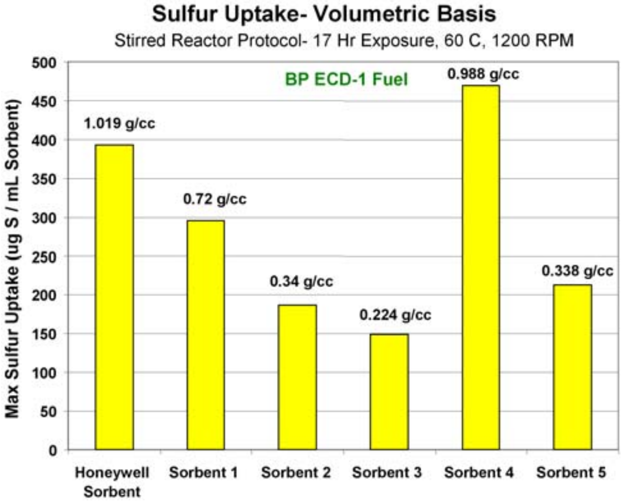

Figure 5. Sorbent Screening

the lubricity loss or the added lubricant is being removed by the sorbent. Table 1 shows the properties of the fuel before and after desulfurization.

Scale-up

The final stage of this project involves the scale-up of the sorbent. A prototype engineering design of the filter has been completed and the temperature control installed with a volume of 10 gallons. We have found that the scale-up performance from the 25 mg to 1 gallon size has been consistent (see Figure 4). This closeness in performance after a scale transition of this magnitude gives us confidence that at the 10 gallon size it will function similarly.

Sorbent Screening

We are continuing to both optimize the sorbent as well as search for better sorbents in order to improve the sulfur removal capacity, which will lead to a smaller bed size. Figure 5 contains data on some promising new sorbents. As can be seen from Figure 5, we have a new sorbent which yields a 20% improvement in sulfur removal performance. We are working with the vendor to try to further improve this and some other sorbents. We will still use our previous best candidate sorbent for the Mack engine test due to the overwhelmingly larger amount of experience we have with it.

Conclusions

- An approach to polish the sulfur from ULSD fuels has been identified. All the components necessary for the engine test are complete.
- A unique sorbent has demonstrated the greatest promise to reduce sulfur in diesel fuel for this application.
- The sorbent has been optimized to remove any external or internal diffusional barriers.
- A successful large-scale activation procedure has been developed which is reproducible.
- Successful scale-up of sulfur sorbent from 25 mg to 1 gallon has been achieved.

- The sorbent removes lubricant from fuel, resulting in a loss of lubricity, requiring readditization of lubricant.
- The source of fuel sensitivity of the sorbent has been identified as the presence of higher polynuclear hydrocarbons.
- The operation of the sorbent has been elucidated.
- Progress has been made on improving the sorbent's sulfur capacity and lowering its footprint, but more work is necessary to achieve a <3 gallon size.

FY 2005 Publications/Presentations

1. "**Diesel Desulfurization Filter",** 11th Annual Diesel Engine Emission Reduction (DEER) Conference, Chicago, Illinois, August 22, 2005.

II.8 Fuel and Emission Control System Effects on Unregulated Emissions

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DOE Technology Development Manager: Kevin Stork

Subcontractors:
Southwest Research Institute, San Antonio, TX
Desert Research Institute, Reno, NV

Objectives

- Develop and/or specify analytical methods for the determination of unregulated emissions specific to advanced diesel aftertreatment systems
- Quantify unregulated emissions from Advanced Petroleum Based Fuels – Diesel Emissions Control (APBF-DEC) projects collected over transient and steady-state cycles

Approach

- Convene advisory group to decide on test protocols and methods for unregulated emissions measurement
- Develop sampling and analytical methods for urea decomposition products
- Develop sampling and analytical methods for nitroxy-alkane products
- Analyze samples from APBF-DEC engine/aftertreatment projects

Accomplishments

- Completed unregulated emissions sampling and analysis for the APBF-DEC heavy-duty selective catalytic reduction (SCR) project
- Completed unregulated emissions sampling and analysis for the APBF-DEC pickup/SUV NOx adsorber catalyst (NAC) project
- Completed unregulated emissions sampling and analysis for the APBF-DEC light-duty NAC project

Future Directions

- Complete unregulated emissions summary reports for each of the APBF-DEC project reports
- Complete final report on all APBF-DEC unregulated emissions activities including methods development

Introduction

The APBF-DEC Toxics and Unregulated Emissions team was formed to address issues and provide guidance to the APBF-DEC project teams on toxics and unregulated emissions measurement. It was recognized that urea-SCR and NOx adsorber systems can produce byproducts as a result of the complex reactions that occur in their respective NOx reduction pathways. The original equipment manufacturers (OEMs) and suppliers were eager to avoid any unpleasant surprises from the widespread adoption of these technologies. For instance, urea can decompose with heat and recombine to form a series of chemical compounds and complexes that may or may not be a cause for concern. NOx adsorber systems may form alkyl nitrates and nitrites, some of which have known toxicity. Because of the periodic fuel-rich operation during regeneration, NOx adsorbers may emit unburned hydrocarbons (HCs) since the oxidation catalysts are inoperable under fuel-rich conditions. Furthermore, lubricant additives designed to replace sulfur compounds may also cause unwanted emissions or may poison the catalytic emission control systems.

An analytical methods development project was selected as the first activity since reliable methods for analyzing exhaust samples for the unusual compounds had not been developed yet. This project was awarded to a team from Oak Ridge National Laboratory (ORNL) which had extensive experience in this type of work for a variety of environmental and forensic samples. The second activity for the Toxics and Unregulated Emissions team is the analysis of samples from the APBF-DEC Lubricants project. The third activity is the analysis of samples from the urea-SCR project and the three NOx adsorber projects.

Approach

The technical team was led by ORNL with an industry co-chair. Members included representatives from engine and vehicle manufacturers, suppliers, and energy companies. The technical team met several times during FY 2005 to discuss analysis results from the ongoing analyses of the APBF-DEC samples. Polyaromatic HCs (PAHs) and nitro-PAHs were collected on large filters and polyurethane foam substrates and analyzed by Southwest Research Institute. Metals and other elemental analyses were conducted by Desert Research Institute on filter samples. Data flowed through the Statistics and Data Analysis Team led by Battelle. The team co-chairs participated in final project meetings for the light-duty and medium-duty NOx adsorber projects as well as the heavy-duty urea-SCR project. The heavy-duty NOx adsorber project finished during FY 2004. Examples of the results are presented below.

Methods were developed in FY 2004 for detecting and measuring the possible urea decomposition products as shown in Figure 1 [1]. These compounds were not detected in any of the heavy-duty SCR exhaust samples. The high exhaust temperatures and "clean-up" oxidation catalyst after the SCR unit were expected to destroy any remaining urea or urea decomposition products. Additional information on these compounds, including examples of their presence in light-duty diesel exhaust, can be found in reference 2.

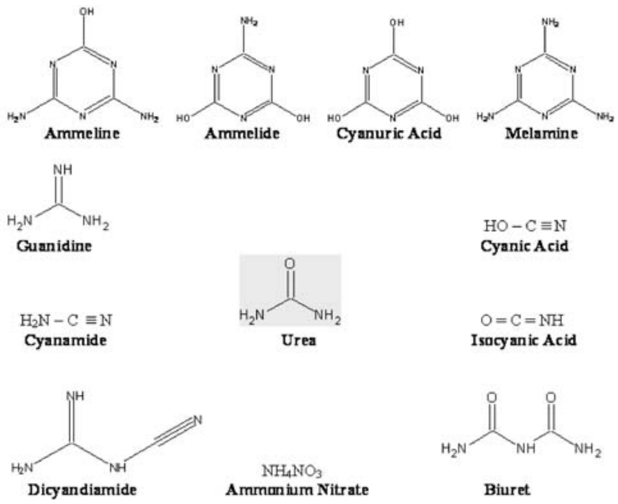

Figure 1. Urea Decomposition Products

Methods were also developed for detecting and measuring nitroxy-alkanes. These compounds include organic nitrates (R-NO_3), organic nitrites (R-NO_2) and nitro-alkanes (NO_2-R). All of these compounds have the potential to form in the NOx adsorber environment, where there are active NO_2 species and organics in contact. Each NAC team collected dilute exhaust samples on solid-phase extraction cartridges prepared by the ORNL team, refrigerated the samples and sent them back to ORNL for analysis. An analysis method based on gas chromatography with a nitrogen-specific chemiluminescence detector (N-CLD) was used to analyze the samples. Results for the light- and medium-duty NOx adsorber catalysts showed the presence of nitroxy alkanes, but the levels were not consistent between triplicate cycles, probably due to the low levels (<1 μg/mile). The salient feature of this effort is that nitroxy-alkanes do not appear to be a significant sink for NOx in NOx adsorber systems.

Results

Example results of the unregulated organic emissions analysis show extensive destruction by the catalyst systems of typical engine-out emissions.

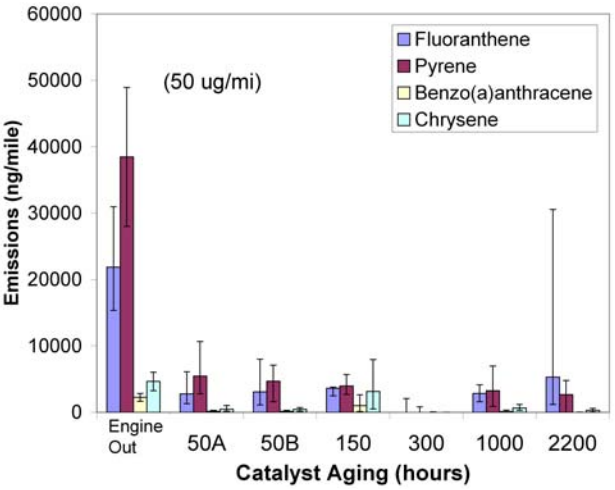

Figure 2. Effective Destruction of 4-ring PAHs by the Light-Duty NOx Adsorber and Diesel Particulate Filter Not Affected by Aging (light-duty NOx adsorber project)

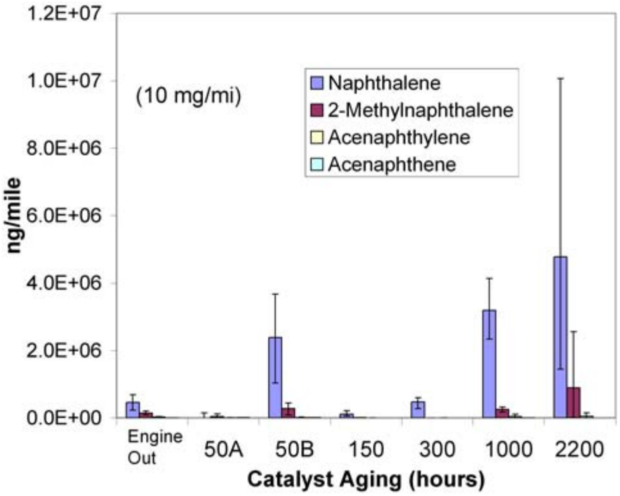

Figure 3. Gas-Phase PAHs Show Increasing Emissions with Aging (light-duty NOx adsorber project)

Figure 2 shows results for the four-ring PAH removal by the light-duty NOx adsorber system. The implications of this are that the diesel particulate filter appears to do a good job of removing the heavier PAHs from the engine-out exhaust, *even under rich regeneration conditions and extensive aging.* Conversely, Figure 3 shows that naphthalene and methyl naphthalene increase with the NOx adsorber system and aging. Because these are gas-phase compounds, they are less likely to be retained by the diesel particulate filter.

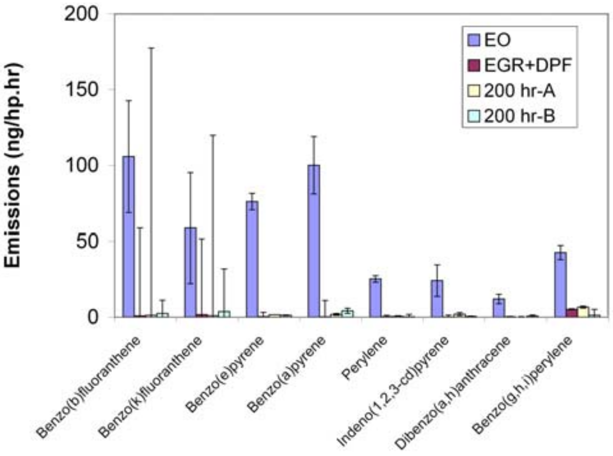

Figure 4. 5 and 6-ring PAHs Treated Effectively by Both Systems A and B (heavy-duty SCR project)

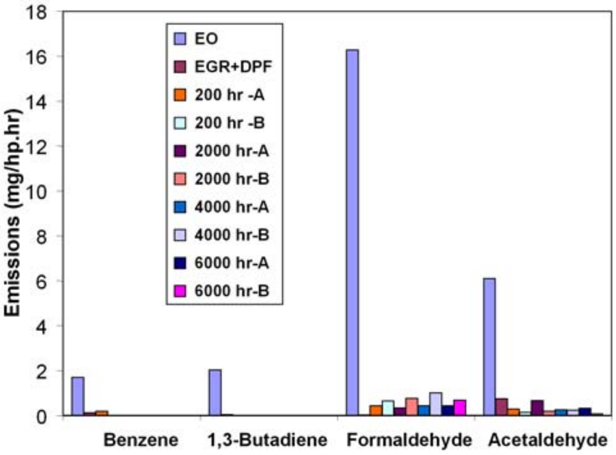

Figure 5. Heavy-Duty SCR System Shows Good Destruction of MSATs even after 6000 Hrs of Aging (heavy-duty transient test results)

Figure 4 shows how both heavy-duty SCR systems treat the highest molecular weight PAHs effectively. The long-term aging appears to have little effect on the ability of the diesel particulate filter to treat these particulate-phase compounds. Furthermore, Figure 5 shows that even the lightest HC compounds examined, the mobile source air toxics (MSATs), benzene, 1,3 butadiene, formaldehyde and acetaldehyde, show high levels of destruction with these systems and little aging effect.

Conclusions

The FY 2005 APBF Toxics and Unregulated Emissions team accomplished the objectives for the year, including the conclusion of the analyses for the samples from the projects. The remaining analysis of the data from the projects will be wrapped up in FY 2006 and final reports finished.

FY 2005 Publications/Presentations

1. Storey, J.M. and S.A. Lewis. "Unregulated Emission Measurements from the APBF-DEC SUV Project," Advanced Petroleum Based Fuel meeting at Southwest Research Institute, San Antonio, TX. March 2005.
2. Storey, J.M. and S.A. Lewis. "Unregulated Emission Measurements from the APBF-DEC Heavy-Duty SCR Project," Advanced Petroleum Based Fuel meeting at Southwest Research Institute, San Antonio, TX. July 2005.

References

1. Ball, James C., "A Toxicological Evaluation of Potential Thermal Degradation Products of Urea", Technical Report Number SRR-1999-0134.
2. Storey, J. M. E., Sluder, C.S., Lewis, S.A., and Lewis, L.A., "Urea Decomposition and Storage under Light-Duty Operating Conditions," *presented* at the 8th Annual CLEERS Workshop, Dearborn, MI. May 2005. Can be found at http://www.cleers.org/workshop8/presentations/storey.pdf.

II.9 Testing at the ReFUEL Laboratory

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DOE Team Lead: Stephen Goguen

DOE Technology Development Manager: Kevin Stork

The ReFUEL Laboratory was further established this year as one of the premier laboratories for testing and research on heavy-duty engines and vehicles. Advanced facility capabilities, enhanced expertise, and new protocols were developed and utilized to lead and support fuels and heavy-duty hybrid vehicle research projects in support of DOE objectives and goals. Several test projects provided first-ever available data for new technologies and alternative fuels. Project-specific highlights for several of the major test projects performed at ReFUEL during fiscal year 2005 are summarized below.

Accomplishments

B20 Experimental Study Completed

ReFUEL completed engine dynamometer testing of a modern 300 hp engine, equipped with exhaust gas recirculation (EGR), variable geometry turbocharger, and high-pressure common rail fuel injection with different B20 blends (20% biodiesel, 80% conventional diesel fuel). The study provided an evaluation of the emissions of a modern production engine with various B20 blends with biodiesel made from feedstocks including soy oil, yellow grease, canola oil, and beef tallow. (Project Partners: Cummins, Inc.)

ReFUEL Completes Fischer-Tropsch Fuel Blend Project

ReFUEL completed a study on the effects of Fischer-Tropsch (FT) diesel fuel blended with conventional refinery diesel fuels on emissions over the Environmental Protection Agency (EPA) transient certification test with a modern 300 hp (2004 emissions certified) production engine. The study quantified the emission reductions of blending FT at levels of 10%, 20% and 30% in typical refinery fuels, compared to a specialty Tier 2 ultra-low sulfur diesel (ULSD) refinery fuel that is formulated for low emissions. Results show a reduction in particulate matter for the FT blends, although they did not reduce emissions to the specialty Tier 2 ULSD level, at blend levels up to 30%. There was no significant effect of the FT blends on nitrogen oxide emissions. (Project Partners: Syntroleum, Valero)

ReFUEL Studies Biodiesel Effects on Diesel Particulate Aftertreatment System Performance as Part of a Cooperative Research and Development Agreement with Cummins Inc.

ReFUEL evaluated the effect of biodiesel on a 2004 compliant engine retrofitted with a catalyzed diesel particulate filter (DPF). The study compared emissions with and without the DPF system installed on reference ULSD fuel and B20 over the EPA transient certification test cycle as well as evaluating DPF regeneration performance with biodiesel compared to ULSD fuel. Transient test results showed that measured particulate matter (PM) emissions were approximately 67% lower with B20 fuel vs. ULSD fuel with the DPF aftertreatment system installed, as compared to a 25% measured PM reduction with B20 when no DPF aftertreatment system is present (Figure 1). Steady-state DPF regeneration testing showed significant measurable benefits from biodiesel vs. ULSD fuel, resulting in lower DPF balance point temperatures with biodiesel and significantly higher DPF regeneration rates at the same operating conditions for B20 vs. ULSD (Figure 2). (Project Partners: Cummins, Johnson Matthey)

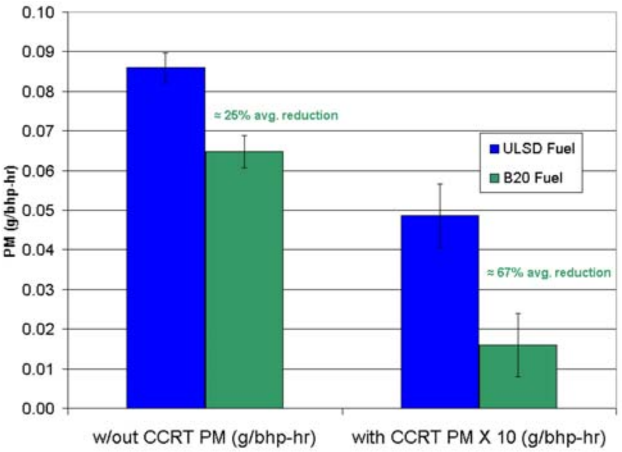

Figure 1. Heavy-Duty Transient Test – PM Emissions, B20 vs. ULSD Fuel, with and without a Catalytic Continuously Regenerating Trap (CCRT) Particulate Aftertreatment System

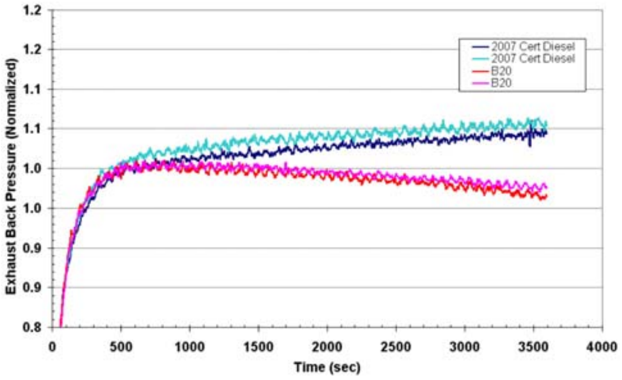

Figure 2. DPF Back Pressure – Regeneration Slope Test (1700 rpm, 250 ft-lb) Comparing B20 vs. Baseline 2007 Certification Diesel Fuel

ReFUEL Completes Transit Bus Biodiesel Testing

As part of a project to quantify the real-world operating costs and emissions impact of 20% biodiesel blend (B20), ReFUEL tested two MY 2000 in-use buses on B20 and conventional diesel fuel as a reference fuel. Use of the B20 fuel resulted in statistically significant reductions for all regulated emissions. Average total hydrocarbons (THC), carbon monoxide (CO) and particulate matter (PM) emissions with B20 were lower than with the conventional diesel by 29%, 24%, and 18%, respectively (Figure 3). Average measured emissions of nitrogen oxides (NOx) were reduced by 4%, which is in contrast to many engine stand studies which have shown the NOx emissions to generally increase with biodiesel use. Fuel economy on a mpg basis was measured to be approximately 2 -3% lower for the biodiesel blend (B20) due to the lower energy density of the fuel. Testing also supports fleet study work being performed by NREL on the in-use performance and maintenance impacts of B20 use in the Boulder, Colorado transit bus fleet. (Project Partners: Regional Transportation District)

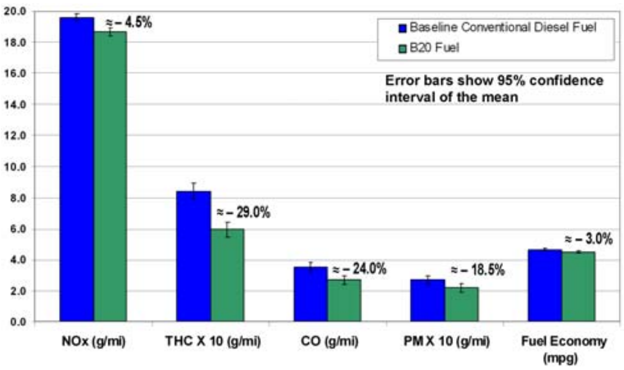

Figure 3. Transit Bus Test Results – B20 vs. Conventional Diesel Fuel

Chassis Testing of Bus with PM Retrofit Aftertreatment System and Biodiesel Blends

ReFUEL completed a series of chassis dynamometer tests to evaluate the emissions benefits of a retrofit particulate matter (PM) aftertreatment system and B20 on buses which operate at the Cheyenne Mountain Air Force Base. This project provided the first known chassis dynamometer data on biodiesel blends and PM aftertreatment on an in-use bus. The study provided data to support decisions for implementation of the aftertreatment system and use of B20 at the base. (Project Partners: Center for Environmental Research & Technology, University of California Riverside, Naval Facilities Engineering Service Center, Tetra Tech)

Baseline Testing Completed for Eaton/ International Truck and Oshkosh Refuse Hauler to Support Advanced Heavy Hybrid Development

ReFUEL completed a thorough study of the fuel economy, emissions, and performance of a medium-duty truck and a commercial refuse hauler as the foundation for an evaluation of the benefits of hybridization. The vehicles tested will be used as a baseline reference for comparison with prototype hybrid vehicles as part of the Advanced Heavy Hybrid Program. This activity will allow an accurate assessment of the benefits of hybridization and model validation to accelerate development of hybrid technology in heavy-duty vehicles. The medium-duty truck was tested on standard drive cycles while the OshKosh refuse hauler was tested over 5 custom refuse hauler drive cycles developed for the vehicle based upon operational field data. (Project Partners: OshKosh, McNeilus, Ohio State University, Eaton, International Truck and Engine)

ReFUEL Evaluates Hybrid Transit Bus

ReFUEL evaluated the performance, emissions, and fuel economy of a production 60 ft. hybrid bus developed by GM-Allison, as well as a conventional baseline vehicle, over 4 different test cycles. This test project enabled the first known direct comparison of the effects of hybridization on measured fuel economy and emissions, with both vehicles utilizing identical make and model engines. The work included several advanced elements, notably the use of a custom test cycle derived from in-use data gathered from the King County bus fleet in Washington, which also incorporates grade. Work also included evaluating the effects of the air conditioning auxiliary loads. By examining effects of both grade and auxiliary loads, the research breaks new ground in heavy-duty chassis testing. The production hybrid bus tested will also serve as a baseline for comparison of planned future testing of an advanced prototype hybrid bus. (Project Partners: GM – Allison)

Future Directions

Several of the projects completed in FY 2005 have led to future work that is planned at the ReFUEL laboratory. Specific planned efforts are as follows:

- Continued study of biodiesel effects on DPF aftertreatment system performance is planned to include various biodiesel blend levels, including B5, and detailed particulate sampling and characterization studies to understand the differences in properties between biodiesel and biodiesel blend PM vs. PM from ULSD fuel.
- Testing of 4 – 6 heavy-duty vehicles on the chassis dynamometer with B20 vs. reference fuel will be done to add to the scant collection of existing published data regarding B20 effects on the performance and emissions of heavy-duty vehicles over chassis dynamometer test drive cycles that simulate real-world duty cycles. This work is to be performed as part of a cooperative research and development agreement with the National Biodiesel Board.
- ReFUEL has plans to expand its transient altitude simulation testing capabilities to enable transient testing of engines and vehicles at sea level conditions as well as Denver altitude. Current capabilities only allow for lower-altitude simulation during steady-state testing.
- The ReFUEL laboratory participates as part of the EPA/Engine Manufacturers Association Calibration Standards Task Force, which provides leadership and input for test methods and protocol specifications related to EPA regulations for vehicles and engines as published in the Code of Federal Regulations. As part of this group, ReFUEL has been selected to participate in a round-robin lab correlation study of a 2007 compliant engine to quantify and confirm lab-to-lab agreement and test methods between the nation's leading heavy-duty engine emissions laboratories on future-technology engines with drastically reduced emissions.
- The ReFUEL laboratory will also continue to conduct heavy-duty hybrid vehicle tests in FY 2006 in support of the projects discussed above and is participating in an EPA-led heavy-duty vehicle test procedure development effort to enable quantification of fuel savings and emission benefits of heavy-duty hybrid vehicles to support tax credit requirements and state implementation plans for air quality improvement.

FY 2005 Publications/Presentations

Peer-reviewed Publications

1. "Regulated Emissions from Biodiesel Tested in Heavy-Duty Engines Meeting 2004 Emission Standards," 2005 SAE Fuels and Lubricants Meeting, Paper No. 2005-01-2200, Robert L. McCormick, Christopher J. Tennant, R. Robert Hayes,

Stuart Black, John Ireland, Tom McDaniel, Aaron Williams, Mike Frailey (NREL); Christopher A. Sharp **(**Southwest Research Institute)

2. "Achievement of Low Emissions by Engine Modification to Utilize Gas-to-Liquid Fuel and Advanced Emission Controls on a Class 8 Truck," 2005 SAE Powertrain and Fluids Systems Conference, Paper No. 2005-01-3766, Teresa L. Alleman, Christopher J. Tennant, R. Robert Hayes (NREL); Matt Miyasato, Adewale Oshinuga (SCAQMD); Greg Barton (ATL); Marc Rumminger (Cleaire Advanced Emission Controls); Vinod Duggal, Christopher Nelson (Cummins Inc.); Mike May (Ricardo Inc.); Ralph A. Cherrillo (Shell Global Solutions (US) Inc.)

Presentations

1. "Emissions Testing of a RTD Bus", Bob Hayes, presented to 2005 Biodiesel Technical Workshop, November 9-10, Denver, CO
2. "Biodiesel and DPF Operation in an EGR Engine", Bob Hayes, presented to 2005 Biodiesel Technical Workshop, November 9-10, Denver, CO
3. "Testing of Biodiesel Fuels and Blends in a Modern Production Medium-Duty Engine", presented to Fuels Technologies Merit Review, Denver, CO, March 2005

III Fuel Property Effects on Advanced Combustion Regimes

III.1 Using Non-Traditional Diesel Fuels and Optical Diagnostics to Understand and Optimize In-Cylinder Processes

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DOE Technology Development Manager: Kevin Stork

Objectives

- Determine whether fuel changes can enable an efficient, 2010-emissions-compliant combustion strategy that is not limited by difficulties with controlling ignition timing (at all loads) and with excessive pressure-rise rates (at high loads). Avoiding such difficulties has been challenging with homogeneous charge compression ignition (HCCI), the prevailing strategy to date.
- Introduce a parameter that accurately quantifies the proximity of a reactant mixture to its stoichiometric condition when fuel molecules contain oxidizer elements or when oxidizer molecules contain fuel elements. Such a parameter is important for understanding mixture stoichiometry effects on low-temperature combustion processes by quantifying mixture stoichiometry once reactions have begun; it is also important when oxygenated fuels are used.

Approach

- Upgrade experimental facility to enable the simulation of high exhaust gas recirculation (EGR) rates. Select a highly oxygenated fuel with a short ignition delay for testing. Conduct engine experiments with oxygenated fuel at high EGR rates to determine whether high-efficiency, emissions-compliant operation is achievable when employing a mixing-controlled combustion strategy.
- Develop a clear understanding of why conventional parameters for the quantification of mixture stoichiometry can be inaccurate when fuel molecules contain oxidizer elements or when oxidizer molecules contain fuel elements. Derive a parameter that properly quantifies mixture stoichiometry under these conditions. Show the relationship between the new parameter and existing parameters such as the equivalence ratio. Quantify the errors involved when the equivalence ratio is used outside of its range of validity.

Accomplishments

- Both objectives were achieved.
- Fuel changes were used to enable a high-efficiency (>44% indicated efficiency), 2010-emissions-compliant (<0.2 g/hp-hr NOx, <0.05 filter smoke number) combustion strategy where ignition timing is simply controlled by injection timing, and peak pressure-rise rates are lower than for conventional diesel combustion. Insight into the important in-cylinder processes was gained through the application of optical diagnostics. This accomplishment directly supports DOE objectives of identifying and enhancing the understanding of high-efficiency, clean combustion modes. The strategy could be an attractive alternative to HCCI, or it could be used at low- and high-load conditions with HCCI at moderate loads.
- A parameter was derived that accurately quantifies mixture stoichiometry after reactions have begun or when oxygenated fuels are used. This accomplishment directly supports the DOE objective of developing

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[1] Currently employed at General Motors Research and Development Center in Warren, Michigan.

the fundamental science base required to understand and optimize high-efficiency, clean combustion modes.

Future Directions

- Determine the extent to which the high-efficiency, clean combustion alternative to HCCI identified in FY 2005 research activities can be achieved with more-traditional fuels such as #2 diesel, biodiesel, and Fischer-Tropsch paraffins.
- Continue investigations into the reasons for higher NOx emissions when biodiesel is used in conventional diesel combustion systems.
- Demonstrate the first successful application of two-photon laser-induced fluorescence detection of NO within an operating engine.

Introduction

Emissions regulations coming into force in 2010 for heavy-duty on-highway engines, combined with increasing concerns over the stability of imported petroleum supplies, are driving the development of cleaner, more efficient engine technologies. One promising approach to meeting these challenges without costly exhaust aftertreatment systems is low-temperature combustion (LTC). In LTC, in-cylinder temperatures are low enough that high nitrogen oxide (NOx) emissions are avoided, and high particulate matter (PM) emissions are avoided by premixing the fuel/oxidizer mixture to overall lean conditions and/or decreasing in-cylinder temperatures below those required for soot formation. The fundamentals of LTC are not yet well understood, however, and this has been a barrier to it being successfully employed in production engines. For example, implementation of HCCI (the prevailing LTC strategy to date) has been slow due to challenges with controlling ignition timing and limiting peak pressure-rise rates at high loads. It is known that fuel properties, fuel/oxidizer mixture preparation, and exhaust gas recirculation (EGR) level are important, but it is not yet known how to use these parameters to optimally employ LTC in engine applications.

Work in our laboratory has been focused on providing experimental and theoretical results to support the development of a fundamental science base of fuel and mixture-preparation effects on LTC to 1) employ LTC operating strategies with improved performance characteristics, 2) determine the extent to which fuel changes can facilitate operation in LTC regimes, and 3) provide theoretical tools necessary to better understand the effects of mixture stoichiometry on LTC processes.

Approach

The approach to developing the science base of fuel and mixture-preparation effects on LTC includes both experimental and theoretical components. The experimental work has been focused on using advanced diagnostics in the Sandia Compression-ignition Optical Research Engine (SCORE) to investigate the relationships between fuel characteristics, in-cylinder processes, and engine-out emissions. The theoretical work has concentrated on understanding mixture stoichiometry under non-trivial conditions, such as once reactions have begun or when oxygenated fuels are used, so that this important LTC control parameter can be properly quantified and its effects understood.

The SCORE is a single-cylinder version of a modern-technology, Caterpillar® 4-stroke direct injection (DI) diesel engine that has been modified by Sandia to provide extensive optical access into the combustion chamber [1]. The SCORE is based on the Caterpillar 3176/C-10 engine family. A schematic of the SCORE is shown in Figure 1. A large window in the piston bowl enables laser-sheet access and imaging of combustion processes within the engine during operation, as do additional windows in the upper periphery of the cylinder liner and the piston bowl rim. Specifications of the SCORE are provided in Table 1. The ability to use a wide range of advanced optical diagnostics, coupled with exhaust-gas analysis equipment to measure

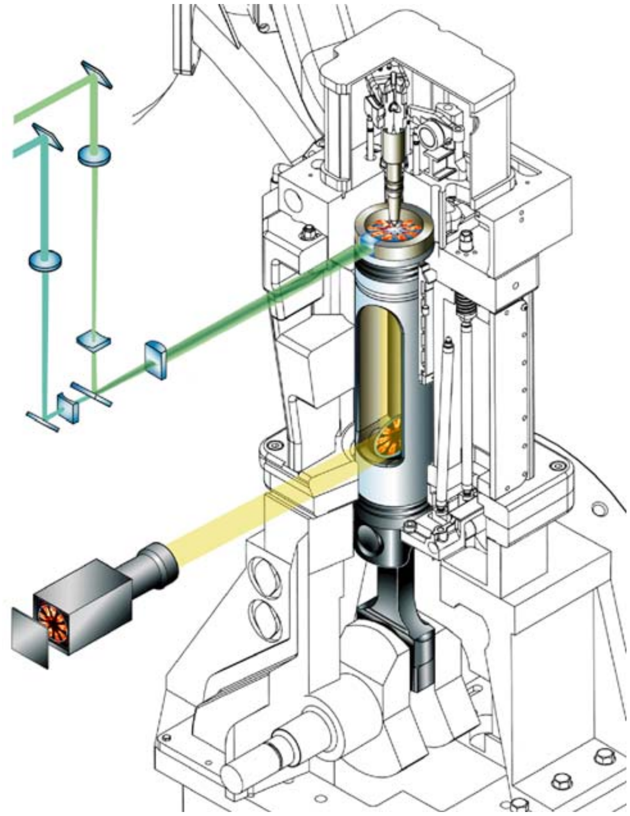

Figure 1. Schematic of Sandia Compression-Ignition Optical Research Engine (SCORE)

Table 1. SCORE Specifications

Research engine type	1-cyl. vers. of Cat 3176/C-10
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
Geometric compr. ratio	11.27:1
Simulated compr. ratio[c]	16.00:1

[a] All valve timings are for lift @ 0.03 mm

[b] Measured at the Caterpillar Tech. Center using an AVL swirl meter

[c] TDC temperature, pressure, and density in the production engine are matched in the optical engine by preheating and boosting the pressure of the intake air

NOx, smoke, HC, CO, CO_2, and O_2, makes the SCORE a versatile instrument for studying the details of fuel effects on in-cylinder processes and corresponding impacts on emissions. Optical-engine data also complement measurements from multi-cylinder production engines tested over standard driving cycles, and can be used to verify the accuracy of computational fluid dynamics models.

Results

Experimental study of new LTC strategy – As described above, a primary objective of FY 2005 activities was to study mixing-controlled reaction under high-EGR conditions as a means to achieve high-efficiency, clean combustion while avoiding the control problems and excessive pressure-rise rates that can occur with HCCI. We have called this strategy dilute clean diesel combustion (DCDC). DCDC can be viewed as traditional diesel combustion that has been shifted into the LTC regime by the use of high EGR levels, and in this way it is similar to "smokeless rich combustion" [2,3], but DCDC also uses a "clean" fuel to suppress PM emissions. The control problems of HCCI are avoided because with DCDC, as with traditional diesel operation, combustion phasing is controlled by fuel-injection timing. Figure 2 shows results from DCDC experiments that were run at steady-state conditions using neat diethylene glycol diethyl ether (DGE), a short-ignition-delay, oxygenated fuel. Emissions are plotted as a function of the mole fraction of oxygen in the intake charge. NOx emissions are below the 2010 limit for intake oxygen mole fractions less than approximately 14%, and smoke emissions are well below 0.05 filter smoke number (FSN) over the range of oxygen concentrations in the study. High fuel-conversion efficiency (defined as the product of thermal

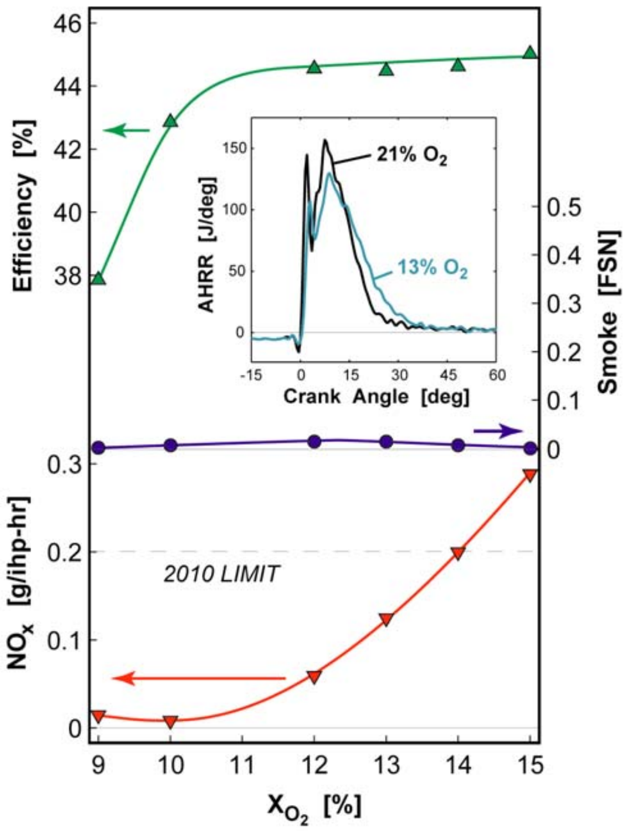

Figure 2. Engine-out NOx and smoke emissions, indicated fuel-conversion efficiency, and apparent heat-release rate data (inset) for DCDC operation. Data obtained at 1200 rpm and an engine load of 7.0 bar indicated mean effective pressure, for intake temperature and pressure of 25°C and 2.23 bar (abs.), respectively. EGR was simulated with nitrogen gas.

efficiency and combustion efficiency [4]) is maintained at intake oxygen concentrations as low as approximately 11%, indicating that there is a substantial window for desirable DCDC operation. The inset shows that heat-release rates are even lower under DCDC conditions than for traditional diesel combustion, which should lead to quieter engine operation. Longer flame lift-off lengths and more diffuse combustion are observed as dilution level increases (see Figure 3). The total natural luminosity signal intensity drops by two orders of magnitude as the intake oxygen concentration is lowered from 21% to 9%, indicating significant decreases in soot volume fraction and/or temperature under DCDC operation. Results have been acquired at up to 18 bar indicated mean effective pressure, which represents 3/4-load operation. See Refs. [5,6] for further details about DCDC operation.

Theoretical study of quantification of mixture stoichiometry – A parameter called the oxygen equivalence ratio, denoted ϕ_Ω, was derived to accurately quantify mixture stoichiometry in situations where fuel molecules contain oxidizer elements or oxidizer molecules contain fuel elements. The oxygen equivalence ratio is defined as the amount of oxygen (moles or mass) required to convert all fuel elements to saturated stoichiometric products (SSPs), divided by the amount of oxygen present in the given mixture. The oxygen equivalence ratio can be expressed mathematically as:

$$\phi_\Omega = \frac{2n_C + \frac{1}{2}n_H}{n_O}$$

where n_C, n_H, and n_O are the numbers of carbon, hydrogen, and oxygen atoms, respectively. An SSP is defined as a product species with no net charge, each of whose constituent atoms has a saturated (i.e., filled or closed-shell) valence orbital. Atoms that are initially bound in SSPs in the reactants are neglected in the calculation of the oxygen equivalence ratio. The oxygen equivalence ratio is a valid measure of mixture stoichiometry in any mixture for which the SSPs are CO_2, H_2O, N_2, and/or noble gases. See Ref. [7] for details about the oxygen equivalence ratio.

Conclusions

- Fuel changes were found to enable a high-efficiency (>44% indicated fuel-conversion efficiency), 2010-emissions-compliant (<0.2 g/hp-hr NOx, <0.05 filter smoke number) combustion strategy where ignition timing is simply controlled by injection timing, and peak pressure-rise rates are lower than for conventional diesel combustion. Insight into the important in-cylinder processes was gained through the application of optical diagnostics. This accomplishment directly supports DOE objectives of identifying and enhancing the understanding of fuel effects on high-efficiency, clean combustion modes.

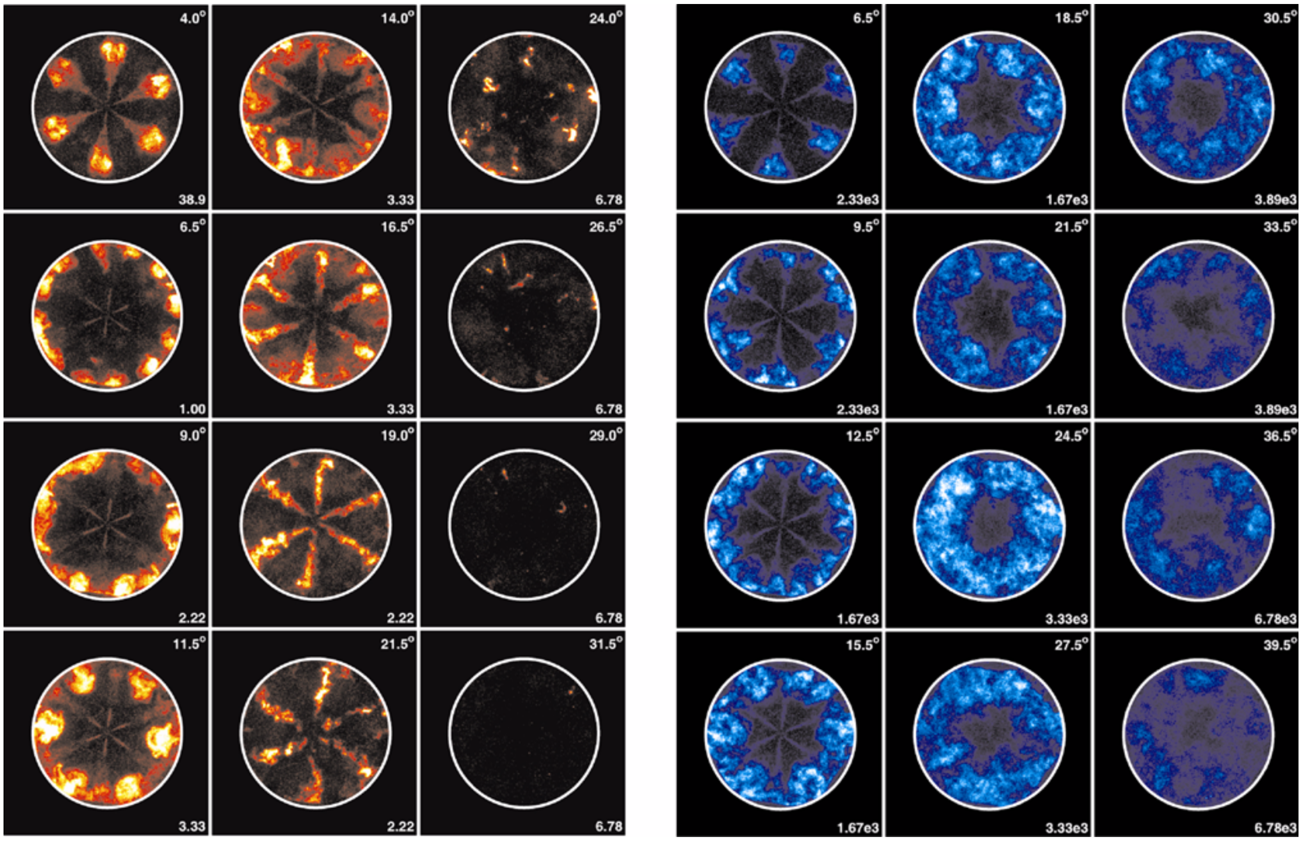

Figure 3. Natural luminosity images for combustion at (left) 21% oxygen (i.e., undiluted) and (right) 9% oxygen at same speed, load, and intake conditions as Figure 2. Numbers in upper- and lower-right corners of each image indicate crank angle at which image was acquired and camera gain, respectively. Higher camera gain = fainter luminosity signal. Images of undiluted combustion (left) show high signal levels due to soot incandescence; images for dilute case (right) show more diffuse combustion and are typically 1000 times dimmer, indicating that hot soot is no longer present.

- A parameter was derived that accurately quantifies mixture stoichiometry after reactions have begun or when oxygenated fuels are used. This accomplishment directly supports the DOE objective of developing the fundamental science base of fuel and mixture-preparation effects required to understand and optimize high-efficiency, clean combustion modes.

Special Recognitions & Awards

1. Society of Automotive Engineers ***Arch T. Colwell Merit Award***, for paper entitled "Effects of Oxygenates on Soot Processes in DI Diesel Engines: Experiments and Numerical Simulations," *SAE Technical Paper 2003-01-1791*. This was one of 11 papers honored in 2004 for being most innovative and original out of approximately 2,500 papers published during the preceding year.
2. Society of Automotive Engineers ***Lloyd L. Withrow Distinguished Speaker Award***. This was one of 8 such awards presented in 2005 to recognize individuals who have received SAE's Oral Presentation Award more than twice.

FY 2005 Publications

1. Upatnieks, A. and Mueller, C.J., "Clean, Controlled DI Diesel Combustion Using Dilute, Cool Charge Gas and a Short-Ignition-Delay, Oxygenated Fuel," *SAE Paper 2005-01-0363*.
2. Upatnieks, A., Mueller, C.J., and Martin, G.C., "The Influence of Charge-Gas Dilution and Temperature on DI Diesel Combustion Processes Using a Short-Ignition-Delay, Oxygenated Fuel," *SAE Paper 2005-01-2088*.
3. Mueller, C.J., "The Quantification of Mixture Stoichiometry When Fuel Molecules Contain

Oxidizer Elements or Oxidizer Molecules Contain Fuel Elements," *SAE Paper 2005-01-3705*.

4. Mueller, C.J., Martin, G.C., Briggs, T.E., and Duffy, K.P., "An Experimental Investigation of In-Cylinder Processes under Dual-Injection Conditions in a DI Diesel Engine," *SAE Transactions*, Vol. 113, Sect. 3, 2004.
5. Buchholz, B.A., Mueller, C.J., Upatnieks, A., Martin, G.C., Pitz, W.J., and Westbrook, C.K., "Using Carbon-14 Isotope Tracing to Investigate Molecular Structure Effects of the Oxygenate Dibutyl Maleate on Soot Emissions from a DI Diesel Engine," *SAE Transactions*, Vol. 113, Sect. 4, 2004.
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7. Mueller, C.J., "In-Cylinder Processes under Early Direct-Injection Diesel HCCI Conditions," *Proc. of DOE Advanced Engine Combustion, Emission Control, and Fuels Program Review*, Argonne National Laboratory, Argonne, IL, 2004.
8. Martin, G.C., Mueller, C.J., and Lee, C.F., "Two-Photon Laser-Induced Fluorescence of Nitric Oxide in a Diesel Engine," submitted for presentation at SAE World Congress, 2006.
9. Martin, G.C., Mueller, C.J., and Lee, C.F., "Two-Photon NO LIF Measurements in a Diesel Engine," submitted to *Applied Optics*, 2005.
10. Cheng, A.S., Upatnieks, A., and Mueller, C.J., "Investigation of the Impact of Biodiesel Fueling on NOx Emissions Using an Optical DI Diesel Engine," submitted to *International Journal of Engine Research*, 2005.

FY 2005 Presentations

1. Mueller, C.J., "Dilute Clean Diesel Combustion Achieves Low Emissions and High Efficiency While Avoiding Control Problems of HCCI," *Caterpillar 10/4 Tech Team Meeting*, Mossville, IL (September 27, 2005).
2. Mueller, C.J., "Dilute Clean Diesel Combustion Achieves Low Emissions and High Efficiency While Avoiding Control Problems of HCCI," *Advanced Engine Combustion Working Group Meeting*, Detroit, MI (September 13, 2005).
3. Mueller, C.J., "Dilute Clean Diesel Combustion Achieves Low Emissions and High Efficiency While Avoiding Control Problems of HCCI," *11th Annual Diesel Engine Emissions Reduction (DEER) Conference*, Chicago, IL (August 22, 2005).
4. Mueller, C.J., "Emerging Trends in Engine Combustion," invited plenary address at *Oil-Sands Chemistry and Engine Emissions Workshop*, Edmonton, Canada (June 6, 2005).
5. Mueller, C.J., "Optical-Engine Studies of Fuel Effects on Low-Temperature Combustion Processes: Sandia Diagnostics and Activities," *Caterpillar/ExxonMobil/Sandia HECC Project Teleconference* (May 19, 2005).
6. Upatnieks, A., "The Influence of Charge-Gas Dilution and Temperature on DI Diesel Combustion Processes Using a Short-Ignition-Delay, Oxygenated Fuel," *SAE Spring 2005 Fuels and Lubricants Meeting*, Rio de Janeiro, Brazil (May 11, 2005).
7. Mueller, C.J., "Engine Combustion Research at the CRF," *Sandia Energy PDS Meeting*, Livermore, CA (May 4, 2005).
8. Upatnieks, A., "Clean, Controlled DI Diesel Combustion Using Dilute, Cool Charge Gas and a Short-Ignition-Delay, Oxygenated Fuel," *SAE 2006 World Congress*, Detroit, MI (April 11, 2005).
9. Mueller, C.J., "Optical-Engine Studies of Fuel Effects on Low-Temperature and CIDI Combustion Processes," *DOE Fuels Technology R&D Program Review*, Golden, CO (March 8, 2005).
10. Mueller, C.J., "The Quantification of Mixture Stoichiometry When Fuel Molecules Contain Oxidizer Elements or Oxidizer Molecules Contain Fuel Elements," *HCCI University Working Group Meeting*, Livermore, CA (February 3, 2005).
11. Mueller, C.J., "An Investigation into Causes of Increased NOx Emissions with Biodiesel Fueling," *Advanced Engine Combustion Working Group Meeting*, Livermore, CA (February 1, 2005).
12. Upatnieks, A., "Dilute Clean Diesel Combustion Using a Short-Ignition-Delay, Oxygenated Fuel," *Advanced Engine Combustion Working Group Meeting*, Livermore, CA (February 1, 2005).

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3. Pickett, L.M. and Siebers, D.L., “Non-Sooting, Low Flame Temperature Mixing-Controlled DI Diesel Combustion,” SAE Paper 2004-01-1399, *SAE Trans.*, Vol. 113, Sect. 4, 2004.
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6. Upatnieks, A., Mueller, C.J., and Martin, G.C., “The Influence of Charge-Gas Dilution and Temperature on DI Diesel Combustion Processes Using a Short-Ignition-Delay, Oxygenated Fuel,” SAE Paper 2005-01-2088, *SAE Trans.*, Vol. 114, Sect. 4, 2005.
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III.2 Chemical Kinetic Modeling of Combustion of Automotive Fuels

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DOE Technology Development Manager: Kevin Stork

Objectives

- Develop detailed chemical kinetic reaction models for components of fuels, including oxygenated species and additives used in diesel, spark-ignition and homogeneous charge compression ignition (HCCI) engines
- Develop surrogate mixtures of hydrocarbon components to represent real fuels and lead to efficient reduced combustion models
- Characterize the role of fuel composition on production of emissions from practical automotive engines

Approach

- Identify individual fuel components and their molecular structures
- Develop kinetic reaction mechanisms for fuel components and additives
- Compute ignition and flame structure for fuel components under diesel, spark-ignition and HCCI conditions
- Compute ignition and flame structure for surrogate mixtures of fuel components under diesel, spark-ignition and HCCI conditions

Accomplishments

- Completed models for chemical kinetics of combustion of two major fuel components, toluene and methyl cyclohexane, and of an oxygenated diesel fuel additive, dimethyl carbonate
- Continued development of surrogate mixtures to describe HCCI ignition
- Identified specific chemical species contributing to problems in providing an optimal surrogate
- Continued past studies of mechanisms by which oxygenated diesel fuel components reduce soot production

Future Directions

- Extend model capabilities to additional classes of fuel components
- Continue development of increasingly complex surrogate fuel mixtures
- Increase collaborations with programs outside Lawrence Livermore National Laboratory (LLNL) dealing with automotive fuel issues

Introduction

Automotive hydrocarbon fuels consist of complex mixtures of hundreds or even thousands of different components. These components can be grouped into a number of structurally distinct classes, including n-paraffins, branched paraffins, cyclic and branched cyclic paraffins, olefins, oxygenates, and aromatics (see Figure 1). The fractional amounts of

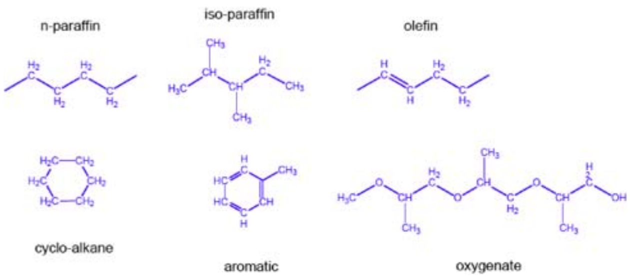

Figure 1. Examples of the major classes of hydrocarbon species present in practical transportation fuels. These specific examples are n-hexane, 2,3-dimethyl pentane, 2-hexene, cyclo-hexane, toluene, and tri-propylene glycol monomethyl ether (TPGME).

these components are quite different in gasoline, diesel fuel and jet fuels, which contributes to the very different combustion characteristics of each of these types of combustion systems.

To support large-scale computer simulations of each kind of engine, it is necessary to provide reliable chemical kinetic models for each of these fuel classes. However, few specific hydrocarbon components of some of these fuel classes have been modeled. For example, although models for benzene and toluene have been developed, models for few if any larger aromatic compounds such as naphthalene or styrene currently exist. Similarly, detailed models for small n-paraffins such as propane, n-heptane and even n-octane have been developed, but detailed models do not yet exist for the much larger versions characteristic of diesel fuels, such as n-hexadecane. A current approach to this problem is to construct a detailed model containing one or more representatives of each class of components to serve as a surrogate mixture. In order for such a surrogate mixture model to be useful, each component must have a well-tested detailed kinetic model that can be included. This high-level approach can create realistic substitutes for gasoline or diesel fuel that reproduce experimental behavior of the practical real fuels, but these substitutes, or surrogates, will also then be reproducible in both experiments and modeling studies. Detailed kinetic models for groups of fuels can then be simplified as needed for inclusion in multidimensional computational fluid dynamics (CFD) models or used in full detail for purely kinetic modeling.

Our recent studies continue to address soot-producing characteristics of diesel fuels. The kinetics of oxygenated chemical species and their effects on sooting remain a major goal, and we have added several new species to the list of available oxygenates, but our current focus is to understand and calculate the separate contributions of the major constituent chemical species on sooting by regular diesel fuels. This will lead to improved understanding of the effects of these diesel fuel components on engine performance and pollutant formation and to development of efficient simplified chemical models for diesel fuel for use in multidimensional CFD models of engine combustion. Other applications to ignition and pollutant formation in HCCI engines have also been pursued, using a multizone spatial model for this type of engine and using suitable surrogates for both diesel fuel and gasoline.

Approach

Chemical kinetic modeling has been developed uniquely at LLNL to investigate combustion of hydrocarbon fuels in practical combustion systems such as diesel and HCCI engines. The basic approach is to integrate chemical rate equations for chemical systems of interest, within boundary conditions related to the specific system of importance. This approach has been used extensively for diesel and HCCI engine combustion, providing better understanding of ignition, soot production, and NOx emissions from these engines in fundamental chemical terms.

The underlying concept for diesel engines is that ignition takes place at very fuel-rich conditions, producing a mixture with high concentrations of species such as acetylene, ethene, propene and others which are well known to lead to soot production. Some changes in combustion conditions reduce the post-ignition levels of these soot precursors and reduce soot production, while other changes lead to increased soot emissions. The LLNL project computes this rich ignition using kinetic modeling, leading to predictions of the effect such changes might have on soot production and emissions.

Kinetic reaction models were developed for the oxygenated additives proposed by a DOE/industry panel of experts. We then computed diesel ignition and combustion using heptane as a reasonable diesel fuel surrogate model, mixed with oxygenated additives. The impact of the additives on predicted levels of soot-producing chemical species could then be assessed.

Ignition under HCCI engine conditions is closely related to that in diesel engines, since both are initiated by compression ignition of the fuel/air mixtures. In very fuel-lean HCCI ignition, the premixing of fuel and air in the gaseous state results in no soot and extremely low NOx production. Kinetic modeling has proven to be exceedingly valuable in predicting not only the time of ignition in HCCI engines, but also the duration of burn and the emissions of unburned hydrocarbons, CO, NOx and soot.

Results

Our kinetic models assume that soot production in diesel combustion occurs from reactions of chemical species created in fuel-rich ignition near the fuel injection location. Because there is insufficient oxygen in this region to burn the fuel completely, the hydrocarbon species remaining there react instead to produce soot. Our kinetics calculations show that when the fuel itself contains some oxygen, that oxygen helps convert more of the ignition products into chemical species that do not contribute to soot production.

During the past year, the LLNL project has examined additional oxygenated hydrocarbon species that have been proposed as possible diesel fuels or additives, specifically dimethyl carbonate, which includes significant amounts of oxygen imbedded in the primarily hydrocarbon fuel molecule. A detailed chemical kinetic reaction mechanism has been developed for this fuel, and the resulting model was used to assess its sooting tendency. We have also been able to distinguish between the soot-reducing abilities of different oxygenated hydrocarbons, based on the location of the O atoms within that molecule. Some structural factors, including some that are typical of biodiesel fuel species, actually reduce the effectiveness of such species in reducing sooting. Our recent publication summarizing several years of experimental and kinetic modeling work describing the mechanisms by which oxygenated additives influence sooting was selected as a winner of the Society of Automotive Engineers Arch Colwell Award of Merit for 2005.

We have completed and submitted for publication kinetic mechanisms for the large olefin di-isobutylene, which is closely related to iso-octane, and for methyl cyclohexane, which is a very important cyclic paraffin. These non-aromatic cyclic hydrocarbons are expected to become increasingly important because they are present in particularly large quantities in diesel fuels derived from Canadian oil sands, currently estimated to be the world's second largest petroleum resource. We have identified new reaction pathways in methyl cyclohexane that have large impacts on its ignition (see Figure 2).

Finally, we have continued computational studies of uses of surrogate gasoline mixtures to describe HCCI ignition. The multizone model has been shown to reproduce nearly all of the important features of engine performance and emissions characteristics when the engines are operated in the normal, fuel-lean regime. We are using the same

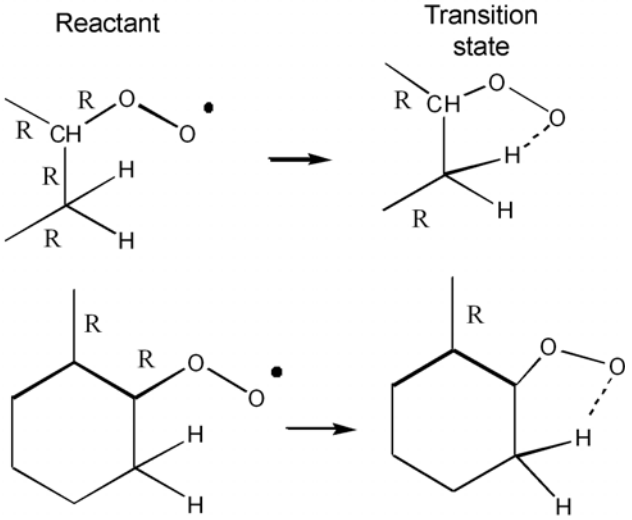

Figure 2. Two related H atom transfer reactions in n-heptane and methyl cyclohexane, showing how the cyclic structure alters the number of free rotors (indicated as R above) differently in the two reactions. These differences produce different rates of what otherwise appears to be the same reaction, leading to different rates of ignition.

approach to examine other operating regimes, such as operation with extensive amounts of exhaust gas recirculation or other forms of dilution but with richer fuel/air mixtures.

Conclusions

Kinetic modeling provides a unique tool to analyze combustion properties of diesel, spark-ignition and HCCI engines. A kinetic model can be very cost-effective as an alternative to extended experimental analyses and as guidance for more efficient experimentation, and computations can also provide a fundamental explanation of the reasons for the observed results. LLNL kinetic models are providing this valuable capability for engine research at many university and industrial facilities in the United States and are essential tools in engine research.

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III.3 Improving Ethanol Life Cycle Energy Efficiency by Direct Combustion of Wet Ethanol in HCCI Engines

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Objectives

- Demonstrate the possibility of using wet ethanol as a fuel for homogeneous charge compression ignition (HCCI) engines.
- Quantify the benefit of directly using wet ethanol on the overall energy balance for ethanol.

Approach

- Analyze an HCCI engine system that can be used to evaporate and successfully combust wet ethanol at high water concentration (50% by volume or higher).
- Analyze the overall energy balance for ethanol to determine the energetic cost of every step in ethanol manufacture and processing.
- Analyze different ethanol-water compositions as fuel for HCCI engines to minimize the need for distillation and dehydration.

Accomplishments

- Conducted an analysis of an HCCI engine system that can work on highly hydrated ethanol while delivering high efficiency and low emissions.
- Performed an evaluation of energy needs for ethanol processing and production.
- Calculated energy use in distillation as a function of the final ethanol-water composition of the distilled mixture.

Future Directions

- *Experimental demonstration*: Modify the fueling system in an existing HCCI engine to demonstrate efficient and clean operation on wet ethanol.
- *Use of other marginal, low-grade fuels*: Evaluate the utilization of other marginal fuels that can *only* be successfully utilized with HCCI engines, such as trash gas (natural gas with high concentration of carbon dioxide or other inert impurities).
- *Analysis of fuel additives*: Evaluate whether it is practical to generate HCCI additives (secondary fuels) onboard a vehicle to successfully control the engine.

Introduction

Dependence on foreign oil and climate destabilization are very serious issues that threaten the economy and environment. Ethanol has been promoted as a domestically produced biofuel that can reduce dependence on foreign oil as well as CO_2 emissions. However, a lively debate exists on the actual benefits of ethanol production and consumption. Ethanol critics have reported that up to 70 percent more energy is required to produce ethanol than the energy it contains [1].

Environmental consequences of ethanol production, such as soil degradation, have also been described and quantified. The high cost of ethanol production has also been criticized, and it is typically recognized that ethanol production is dependent on government subsidies to be competitive. Ethanol utilization is also promoted through legislation that mandates the use of oxygenated and alternative fuels.

The energy balance of ethanol has been studied in considerable detail by multiple researchers. Recent publications [2,3] have reported a slight energetic advantage from producing and using ethanol from corn (Figure 1). The net gain in making ethanol from corn is estimated at only 21% of the total energy of ethanol and coproducts, and the remaining 79% of the energy is spent in different stages of the process. New technologies that improve the ethanol energy balance may help in delivering the ethanol promise of improved energy security and reduced global warming.

Approach

A possibility for improving the energy balance of ethanol is to develop new utilization techniques that may allow a reduction in the processing necessary for converting ethanol to a useful form. Figure 1 shows that the biggest fraction of the energy necessary for making ethanol is spent in distillation and dehydration (37% of the total energy in ethanol and co-products). It is therefore clear that substantial improvement in the energy balance of ethanol can be obtained by using wet ethanol directly, possibly with only partial distillation as necessary, and with no dehydration. While many applications may demand neat ethanol, finding a practical application for wet ethanol may make the energy balance of ethanol much more attractive.

A new option for prime mover in transportation and stationary applications is HCCI engines. Automobile and engine manufacturers are interested in HCCI engines due to their potential for high efficiency and low emissions. HCCI combustion is fundamentally different from combustion in spark-ignited (SI) engines and diesel engines. HCCI combustion is a thermal autoignition of a premixed fuel-air mixture, with no flame propagation (as in SI engines) or mixing-controlled combustion (as in diesel engines) [4]. HCCI engines are intrinsically fuel-flexible. Any fuel can be used as long as it can be evaporated and then heated by compression to a temperature high enough for autoignition (approximately 1100 K [5]). The operating limits for HCCI are therefore set by the requirement to evaporate the fuel and not by the need to propagate a flame across the combustion chamber. Also, fuel evaporation can be done outside the engine in a vaporizer heated by exhaust gases so that the cooling effect of water vaporization does not have a negative effect on ignition, as it does in a diesel engine. Water-ethanol mixtures can therefore be burned in an HCCI engine that cannot be burned in either diesel or SI engines.

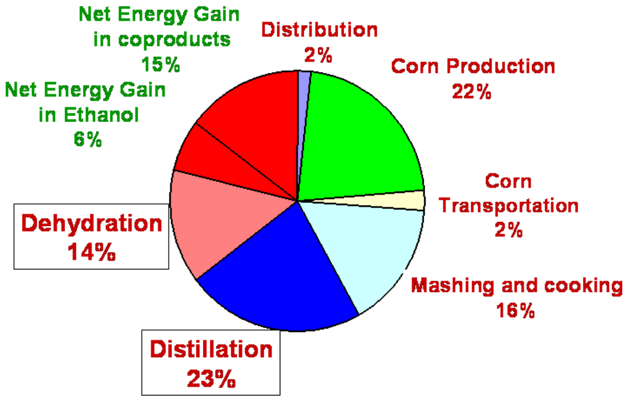

Figure 1. Net energy balance for ethanol. The full circle represents the energy of ethanol and coproducts. The figure shows energy consumption in all stages of ethanol production from corn, as a percent of the heating value of ethanol and coproducts. The energy that remains after accounting for all the energy consumption is the net energy gain, and it has two components: net energy in the ethanol and net energy in the coproducts.

Results

We have conducted a detailed thermodynamic analysis of an HCCI engine running on wet ethanol. The engine and heat recovery system is shown in Figure 2 and consists of a regenerator and a vaporizer in addition to the typical engine system components (turbocharger, catalytic converter). The purpose of this work is to determine the maximum concentration of water in ethanol that can be used while maintaining high performance in the HCCI engine.

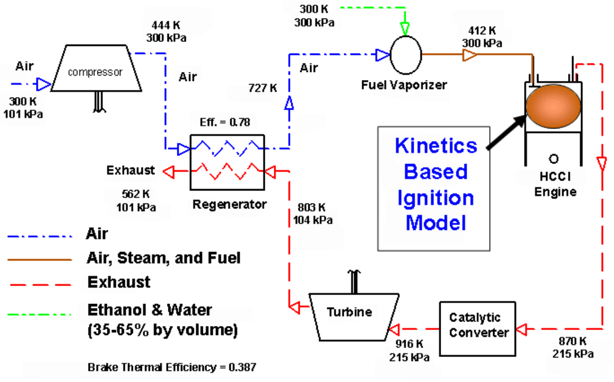

Figure 2. Schematic of the HCCI engine system operating on wet ethanol. The numbers in the figure show pressures and temperatures for operation with a 35-65% volumetric mixture of ethanol and water.

The analysis indicates that a 35% ethanol-water mixture by volume can sustain efficient combustion in an HCCI engine. Figure 2 shows the thermodynamic conditions at all points in the HCCI engine system using 35% ethanol as a fuel. The compressor delivers air at 300 kPa and 444 K. The air temperature is further increased at the regenerator by exchanging heat with the exhaust gases. This hot air (727 K) is mixed with the wet ethanol in the fuel vaporizer, cooling down as the fuel and water evaporate. The mixture of ethanol, steam, and air at 300 kPa and 412 K enters the HCCI engine. The charge mixes with the hot residual gases and the temperature of the gases in the combustion chamber at the beginning of the compression stroke increases to 420 K. After combustion, exhaust gases enter the catalytic converter at 870 K and leave the catalytic converter at 916 K due to combustion of unburned hydrocarbons and CO in the catalyst. Gases from the catalytic converter (215 kPa and 916 K) go to the inlet port of the turbine. The turbine provides all the work needed for the compressor to increase the inlet pressure to the desired level (300 kPa, in this case). After circulating through the turbine, the exhaust gases exchange heat with the intake air in the regenerator and they leave the system at ambient pressure and 562 K. The engine system model predicts a 38.7% brake thermal efficiency for the wet ethanol HCCI engine. Emissions of NOx are predicted at 1.6 parts per million, low enough to meet any existing or oncoming standards for stationary and transportation applications.

The wet ethanol HCCI engine combines high efficiency and low emissions, with the additional advantage of considerably improving the energy balance for ethanol. The HCCI engine on wet ethanol is more efficient than typical SI engines, which are limited to ~35% peak brake thermal efficiency due to the low compression ratio of SI engines necessary to avoid knock [6]. Diesel engines are more efficient, but they have high emissions of NOx that restrict their applicability to markets without strict emissions standards.

Finally, it is important to determine how the use of wet ethanol affects the overall energy balance of ethanol production and utilization. Figure 1 shows that the net energy balance of ethanol is positive but small, with only 21% net energy gain, and 15% of this coming from coproducts. Being able to use ethanol at 35% volume fraction (14.3% mole fraction) considerably reduces the energy required for ethanol distillation, from 23% of the total energy in ethanol and coproducts to only 3%. The energy required for dehydration is reduced from 14% to zero, as use of wet ethanol avoids the need for any dehydration. The final energy balance for wet ethanol is shown in Figure 3. The figure shows that using ethanol at 35% volume concentration increases the ethanol net energy gain from 6% to 40%. Total net energy gain (including coproducts) is now 55%, showing a much more favorable energy balance for ethanol. It is considered that wet ethanol utilization in an HCCI engine may be a path to improve the energy balance of ethanol, contributing to climate stabilization and improving energy security.

Conclusions

We have conducted an analysis that indicates that direct combustion of wet ethanol in a homogeneous charge compression ignition (HCCI) engine can result in a considerable improvement in the energy balance for ethanol. HCCI engines are a relatively new technology in which combustion occurs due to global autoignition of the fuel and air mixture. Combustion in HCCI engines is limited by the need to evaporate the fuel, and not by the need to propagate a flame across the combustion chamber (as

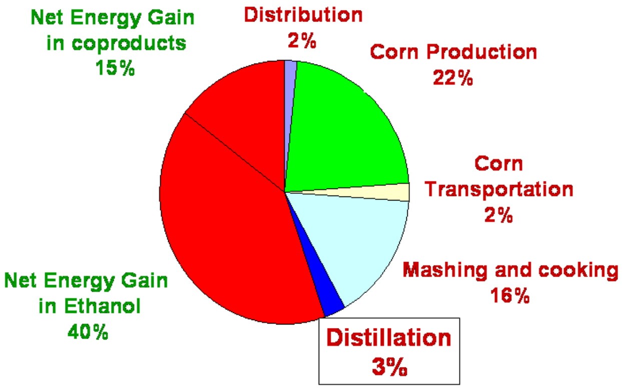

Figure 3. Net energy balance for ethanol, considering that ethanol is used as a 35-65% mixture of ethanol and water. The figure shows energy consumption in all stages of ethanol production from corn, as a percent of the heating value of ethanol and coproducts. The energy that remains after accounting for all the energy consumption is the net energy gain, and it has two components: net energy in the ethanol and net energy in the coproducts.

in a spark-ignited engine). Therefore, it is expected that HCCI engines can run on wet ethanol with high concentration of water. Considering that much of the energy required for processing the ethanol is spent in distillation and dehydration, direct use of wet ethanol in an HCCI engine considerably shifts the energy balance in favor of ethanol.

Special Recognitions & Awards/Patents Issued

1. Salvador M. Aceves invited to deliver a seminar at the SAE 2005 HCCI symposium, September 2005, Lund, Sweden.
2. **Controlling and Operating Homogeneous Charge Compression Ignition (HCCI) Engines**, Daniel L. Flowers, United States Patent 6,923,167, August 2, 2005

FY 2005 Publications/Presentations

1. Analysis of Homogeneous Charge Compression Ignition (HCCI) Engines for Cogeneration Applications, Salvador M. Aceves, Joel Martinez-Frias, Gordon M. Reistad, Proceedings of the ASME Advanced Energy Systems Division, 2004, Accepted for Publication, Journal of Energy Resources Technology.
2. A Fully Integrated CFD and Multi-zone Model with Detailed Chemical Kinetics for the Simulation of PCCI Engines, Aristotelis Babajimopoulos, Dennis N. Assanis, Daniel L. Flowers, Salvador M. Aceves, and Randy P. Hessel, International Journal of Engine Research, Vol. 6, pp. 497-512, 2005.
3. Improving Ethanol Life Cycle Energy Efficiency by Direct Combustion of Wet Ethanol in HCCI Engines, Joel Martinez-Frias, Salvador M. Aceves, Daniel L. Flowers, Paper IMECE2005-79432, Proceedings of the ASME International Mechanical Engineering Congress and Exhibition, 2005.
4. Development and Testing of a 6-Cylinder HCCI Engine for Distributed Generation, Joel Martinez-Frias, Daniel Flowers, Salvador M. Aceves, Francisco Espinosa-Loza, Robert Dibble, Paper ICEF2005-1342, Proceedings of the 2005 Fall Technical Conference, ASME Internal Combustion Engine Division, October 2005.
5. Experimental and Kinetic Investigation of Effect of Fuel on Ion Sensor Signal to Determine Combustion Timing in HCCI Engines, Parag Mehresh, Jason Souder, Daniel Flowers, Uwe Riedel, Robert W. Dibble, International Journal of Engine Research, Vol. 6, pp. 465-474, 2005.
6. Effect of the Di-Tertiary Butyl Peroxide (DTBP) Additive on HCCI Combustion of Fuel Blends of Ethanol and Diethyl Ether, J. Hunter Mack, Daniel L. Flowers, Bruce A. Buchholz, Robert W. Dibble, SAE paper 2005-01-2135.
7. Source Apportionment of Particulate Matter from a Diesel Pilot-Ignited Natural Gas Fuelled Heavy Duty DI Engine, H. L. Jones, G. McTaggart-Cowan, S. N. Rogak, W. K. Bushe, S. R. Munshi, B. A. Buchholz, SAE paper 2005-01-2149.
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9. Investigation of HCCI Combustion of Diethyl Ether and Ethanol Mixtures Using Carbon 14 Tracing and Numerical Simulations, J. Hunter Mack, Daniel L. Flowers, Bruce A. Buchholz, Robert W. Dibble, Proceedings of the Combustion Institute, Vol. 30, 2004.
10. Measuring the Effect of Fuel Structure and Blend Distribution on Diesel Emissions Using Isotope Tracing, B. A. Buchholz, R. W. Dibble, C. J. Mueller, A. S. Cheng, Proceedings of the Western States Section of the Combustion Institute, Davis, CA, March 2004.

11. Tracing Fuel Component Carbon in the Emissions from Diesel Engines, B. A. Buchholz, C. J. Mueller, G. C. Martin, A. S. Cheng, R. W. Dibble, B. R. Frantz, Nucl. Instrum. Methods Phys. Res. Sect. B, Vol. 223-4, 837-841, 2004.
12. Analysis of Premixed Charge Compression Ignition Combustion with a Sequential Fluid Mechanics-Multizone Chemical Kinetics Model, Salvador M. Aceves, Daniel L. Flowers, Francisco Espinosa-Loza, Aristotelis Babajimopoulos, Dennis Assanis, SAE Paper 2005-01-0115, SAE Transactions, 2005.
13. A Detailed Chemical Kinetic Analysis of Low Temperature Non-Sooting Diesel Combustion, Salvador M. Aceves, Daniel L. Flowers, SAE Paper 2005-01-0923, SAE Transactions, 2005.
14. Spatial Analysis of Emissions Sources for HCCI Combustion at Low Loads Using a Multi-Zone Model, Salvador M. Aceves, Daniel L. Flowers, Francisco Espinosa-Loza, Joel Martinez-Frias, John E. Dec, Magnus Sjöberg, Robert W. Dibble and Randy P. Hessel, SAE Paper 2004-01-1910, SAE Transactions, Journal of Fuels and Lubricants, 2004.
15. Analysis of the Effect of Geometry Generated Turbulence on HCCI Combustion by Multi-Zone Modeling, Salvador M. Aceves, Daniel L. Flowers, Francisco Espinosa-Loza, Joel Martinez-Frias, Magnus Christensen, Bengt Johansson, Randy Hessel, SAE Paper 2005-01-2134.
16. Thermal Management for 6-Cylinder HCCI Engine: Low Cost, High Efficiency, Ultra-Low NOx Power Generation, Joel Martinez-Frias, Daniel Flowers, Salvador M. Aceves, Francisco Espinosa-Loza, Robert Dibble, Paper ICEF2004-930, Proceedings of the 2004 Fall Technical Conference, ASME Internal Combustion Engine Division, October 2004.
17. The Use of Hydrogen Combustion for Power Generation, D. Walther, C. Fernandez-Pello, and R. Dibble, S. Aceves and D. Flowers, Paper AIAA-2005-5753, 3rd International Energy Conversion Engineering Conference and Exhibit, San Francisco, California, Aug. 15-18, 2005.

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III.4 Fuels for Diesel HCCI Engines

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DOE Team Lead: Stephen Goguen

Subcontractors:
Volvo Powertrain (Mack Trucks), Hagerstown, Maryland

Objectives

- Identify favorable physical properties of synthetic fuel surrogates in homogeneous charge compression ignition (HCCI) engines.
- Quantify the effects of fuel ignition quality and volatility on emissions and efficiency in an HCCI engine.

Approach

- Design a matrix of test fuels of varying ignition quality and boiling range.
- Develop an HCCI engine test platform with a flexible valvetrain and exhaust gas recirculation (EGR) capabilities to test fuels.
- Investigate each test fuel in the HCCI engine test platform to quantify effects of fuel properties on emissions and efficiency.

Accomplishments

- Quantified ignition quality versus temperature using the Ignition Quality Tester (IQT™) for the base fuel and a matrix of four paraffinic fuels representing 3 boiling ranges and 3 derived cetane number (DCN) levels.
- Achieved very clean HCCI combustion with brake-specific NOx emissions of 0.02 g/bhp-hr and undetectable levels of smoke for certain fuels and operating conditions.

Future Directions

- No further subcontracted work will occur under this project.
- This engine was loaned to the National Renewable Energy Laboratory (NREL) and will be set up at the ReFUEL Laboratory for continued testing of fuels for HCCI.
- A similar project on a light-duty HCCI engine will be conducted over the next fiscal year in collaboration with the Coordinating Research Council.

Introduction

Homogeneous charge compression ignition (HCCI) engines have the potential to achieve very low pollutant emissions with diesel-like engine efficiency. It is likely that future compression ignition direct injection (CIDI) engines will employ HCCI combustion for at least part of their operating range. However, conventional diesel fuel is a poor fuel for HCCI combustion, largely due to its low volatility and high ignition quality. Other fuels with differing physical properties may be better suited for HCCI combustion, while still maintaining adequate CIDI combustion properties so the fuel could be used in a mixed-mode engine. The goal of this project was to investigate a matrix of fuels with varying volatility and ignition quality to identify how these properties can improve HCCI performance in a heavy-duty (diesel) engine.

Approach

The overall approach was to develop a matrix of fuels and test them on a sophisticated HCCI engine platform. The matrix of fuels was designed to include three levels of ignition quality and three boiling ranges. The ignition quality was specified by cetane number for the purposes of designing the matrix, but ignition quality was measured versus temperature using the IQT™. The fuel matrix included a base fuel (EPA Certification fuel) and four mixtures of straight-chain and branched alkanes. Using mixtures of normal and iso-paraffins, we could vary the ignition quality independently from the boiling range by changing the relative proportions. These mixtures also minimize any other variations of physical properties among the test fuels. Figure 1 shows the boiling ranges and cetane levels of the fuels used.

The matrix of fuels was tested in a heavy-duty Mack 12L engine equipped with Sturman Industries' Hydraulic Valve Actuation (HVA) system, shown in Figure 2. The Sturman HVA system allows flexibility in the valve control, which enables internal (hot) EGR and Miller cycle operation (variable effective compression ratio). In this study, we chose to conduct a parametric study of each fuel operating in HCCI mode at one operating point of 1200 rpm and 2 bar brake mean effective pressure (BMEP). This modest load condition was chosen because HCCI combustion was achievable using the conventional diesel fuel under all conditions tested. The parametric study included two levels of compression ratio, external EGR, boost, and injection timing. No control over start of reaction timing was employed in this study.

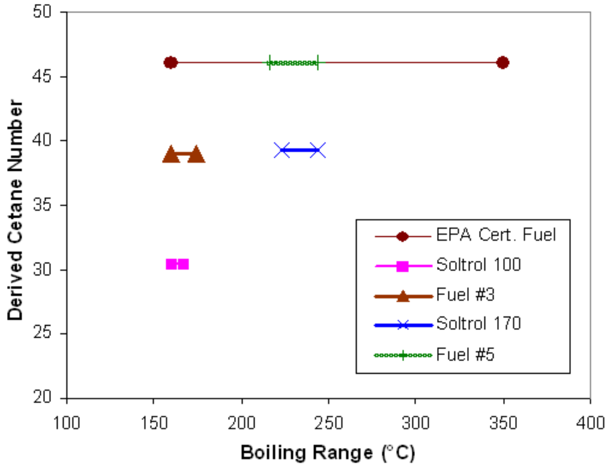

Figure 1. Ignition Quality and Boiling Range of the Test Fuels

Results

The ignition delay was measured as a function of charge temperature for each of the test fuels, and the results are shown in Figure 3. The temperature dependence of the ignition delay differs for each of the fuels in the matrix. For example, two of the test fuels (Fuel #3 and Soltrol 170) have a DCN of 39 but have different boiling ranges and degrees of branching. The IQT™ measurements show that ignition delay of Fuel #3 has a higher dependence on temperature (steeper slope) than that of Soltrol 170. This is because of the higher normal paraffin content, since isoalkanes have lower activation energy for ignition than normal alkanes. Similarly, the certification fuel and Fuel #5 have the same DCN of 46 but show different temperature dependence. Since the composition of the cert fuel is not as well defined, it is difficult to describe the reason for this on a molecular level. However, we can assume that aromatics and naphthenes in the certification fuel contribute to the higher activation energy than the (primarily) isoalkanes in Fuel #5.

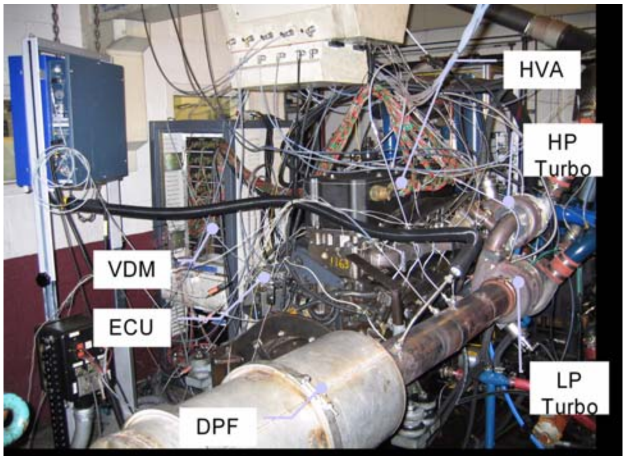

Figure 2. Mack 12L Engine Equipped with Sturman HVA System

In the initial stages of testing, two methods to vary the start of reaction were tested using the Sturman HVA system. In the first method, the effective compression ratio was varied using either early or late intake valve closing. Start of reaction is retarded by reducing the effective compression ratio, as expected. In comparing the two means of achieving reduced compression ratio (early or late intake valve closing), we found that early intake valve closing was a better method. When late intake valve closing is employed, charge air is introduced into the cylinder during intake (where it heats up from the cylinder liner) and then is pushed back into the intake manifold at the beginning of the compression stroke. Over time, the temperature in the intake manifold increases, resulting in a higher initial charge temperature. This higher initial charge temperature advances HCCI ignition further and is therefore a less desirable method (for these fuels). The second set of experiments was investigating the effect of internal EGR by closing the exhaust valve late. Internal EGR causes two competing effects on start of reaction. Dilution of charge air with exhaust should retard ignition, whereas increasing charge temperature should advance ignition. We found that the charge temperature effect dominated, and increasing internal EGR advanced start of reaction. Since during HCCI testing start of reaction typically occurred significantly before top dead center, internal EGR was not included in our parametric study as it would overly advance ignition.

Parametric HCCI testing at a single operating point of 1200 rpm and ~2 bar BMEP included two EGR levels (0 and 45%), two boost levels (1.0 and 1.3 bar), two compression ratios (17:1 and 15:1), and two injection timings (-66° and -76°). Each fuel was tested at all 16 combinations of these four parameters. At each test point, emissions of CO, hydrocarbons, NOx, and smoke were measured. Additionally, fuel consumption and ignition timing (reported as CA50 crank angle at 50% heat release) were measured.

One of the main results from this testing was that NOx emissions primarily depend on ignition timing (CA50) for a particular operating point. Figure 4 shows brake-specific NOx emissions versus CA50 for two operating points. All five fuels fall on an exponential curve of brake-specific NOx versus CA50 for all 16 points. The ignition timing depends primarily on derived cetane number. So given that NOx emissions depend on ignition timing, fuels that allow for ignition close to top dead center perform best in this HCCI engine. Another important observation from Figure 4 is that reducing effective compression ratio delays ignition, but does not improve brake-specific NOx emissions. This is

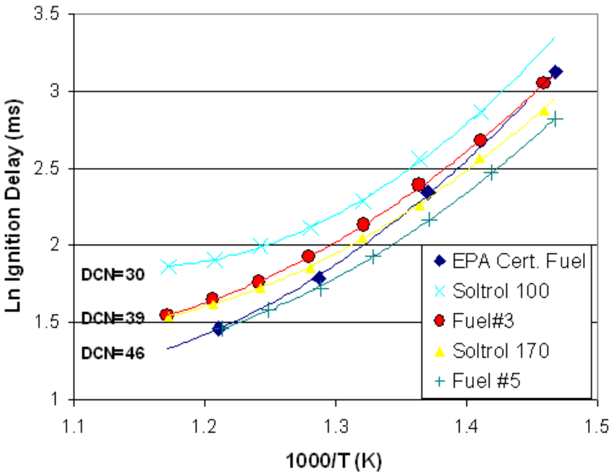

Figure 3. Ignition Delay Versus Temperature for the Test Fuels

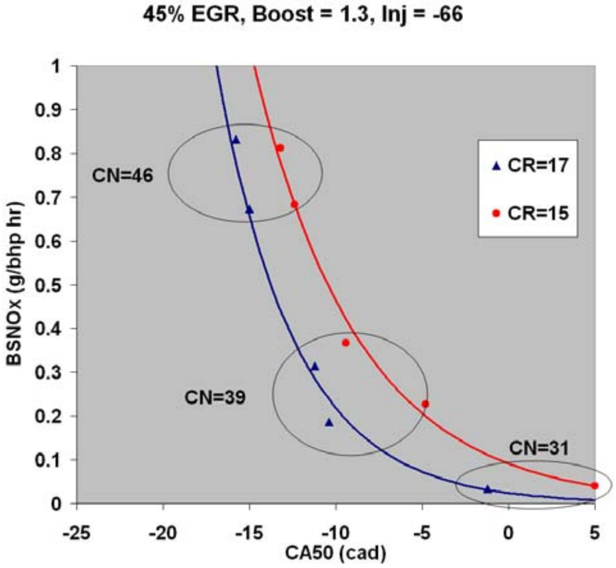

Figure 4. NOx Emissions at Two Compression Ratios for the Test Fuels

because closing the intake valve early reduces the quantity of charge air trapped in the cylinder. The result is a richer overall mixture and a higher local peak temperature. So although Miller cycle operation shifts the ignition timing toward top dead center, it is not an effective way to achieve very low NOx emissions.

Other results from this project are summarized in the following bulleted list:

- Increasing EGR level was the most effective way to achieve very low NOx emissions and shift CA50 toward top dead center (see Figure 5).
- Fuel consumption generally improved as ignition timing moved toward top dead center. Conditions with low boost and high EGR showed the best fuel consumption.
- Fuel consumption was generally poor relative to conventional CIDI combustion. This was likely due to the unit injectors used, which are not optimal for HCCI injection. Over time, significant fuel quantities were detected in the lube oil. However, several operating points with certain fuels had comparable brake-specific fuel consumption to CIDI operation with significantly reduced NOx emissions.
- Hydrocarbon emissions decrease with increasing EGR and are higher for fuels with higher volatility.

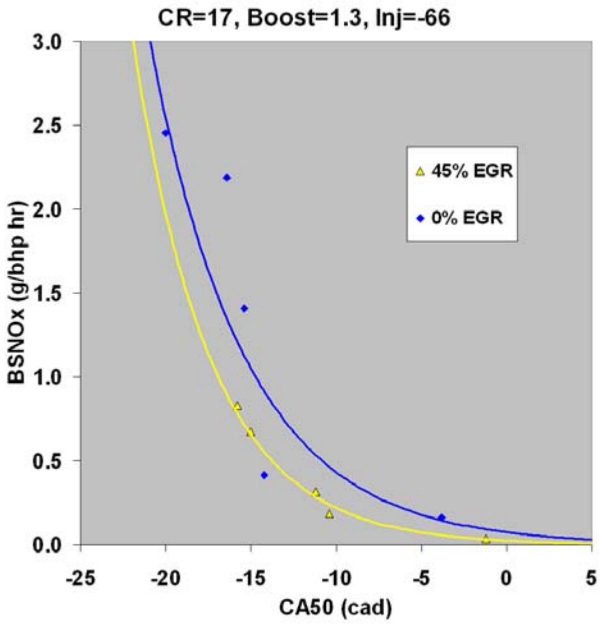

Figure 5. NOx Emissions at Two EGR Levels for the Test Fuels

Conclusions

- Ignition timing is the best indicator for emissions in HCCI combustion. Fuels that allow ignition timing close to top dead center for the largest operating range will allow for the widest range of HCCI operation in a mixed-mode engine.
- Fuels with lower ignition quality than conventional diesel fuel perform better in HCCI modes due to their resistance to early ignition.
- Miller cycle operation improves ignition timing, but does not improve NOx emissions due to reduced charge air. EGR is a more effective means of controlling start of reaction and reducing NOx emissions.

FY 2005 Publications/Presentations

1. "HCCI with Synthetic Fuels of Varying Boiling Range and Ignition Quality" presented at DOE Fuels Program Merit Review. Golden, CO, March 7-9, 2005.
2. "Fuels Ignition Chemistry and Fuel Challenges for HCCI Engines" presented at National Reseach Council – Canada. Ottawa, Canada, April 19, 2005.

III.5 Fuel Effects on Gasoline-Based HCCI Performance and Emissions

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Subcontractors:
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Battelle, Columbus, Ohio

Objectives

- Quantify the effects of fuel properties on homogeneous charge compression ignition (HCCI) combustion relative to ignition and combustion characteristics, emissions, and fuel efficiency.
- Define combustion characteristics of a selected HCCI engine platform to provide a baseline for continuing fuels evaluations.
- Demonstrate the potential for fuel economy improvement from a combination of advanced combustion, engine controls, and fuel properties.

Approach

- Select research subcontractor with appropriate HCCI engine to maximize experimental results early in the project.
- Develop partnership with major oil company in order to procure fuels for evaluation and technical support in test planning and data interpretation.
- Evaluate performance of the fuels and correlate results to relevant fuel properties.
- Launch HCCI engine capability for gasoline and diesel range fuels at Oak Ridge National Laboratory (ORNL).

Accomplishments

- Established sub-contract relationship with AVL Powertrain and research partnership with ExxonMobil.
- Demonstrated that spark-augmented HCCI can achieve about 12% fuel economy improvement over conventional spark-ignited combustion in back-to-back tests for a simulated driving cycle while achieving 95% NOx reduction.
- Determined that spark-augmented HCCI is a valid and useful mode of engine control, distinct from pure HCCI.
- Correlated HCCI performance to fuel chemistry and octane values using an expanded set of fuels supplied by ExxonMobil.
- Installation and conversion of gasoline range HCCI engine utilizing variable compression ratio is nearly complete at ORNL.

Future Directions

- Construct on-line fuel blending system to enhance research capability and flexibility with HCCI fuels.
- Commission ORNL research engine for gasoline range HCCI and continue diesel range HCCI studies.

- Determine detailed chemistry effects of HCCI fuels in addition to bulk property effects such as octane, cetane, and volatility.
- Continue to explore issues of stability and moving between various combustion regimes to determine if fuel chemistry can improve HCCI controllability and operating range.

Introduction

In HCCI, the fuel and air are pre-mixed prior to combustion and ignition is initiated by kinetic reactions which occur during the compression stroke. Ignition occurs when a threshold temperature is reached, and the timing of ignition is controlled by setting the cylinder conditions at the start of the compression stroke. The cylinder charge of fuel and air is also diluted with excess air or with exhaust gas. The purpose of this dilution is to lower the peak flame temperature to reduce NOx and to eliminate rich zones which can generate particulate matter. The dilution also helps control ignition by changing cylinder conditions during compression and helps regulate the rate of burning after combustion begins. Fuel economy improvement found in some HCCI engines is due to a combination of faster heat release, reduced heat transfer, and reduced throttling losses.

Since the ignition process is kinetically driven, fuel properties have a large effect on combustion characteristics and timing. Fuel octane characteristics regulate the tendency of a fuel to ignite in an HCCI engine, and fuel volatility can impact fuel mixing and evaporation and the degree of homogeneity achieved. Fuel chemistry may have a large effect because of the various pre-flame reactions required for successful ignition in HCCI. Conditions supportive of the compression ignition of fuels (mainly temperature) can be brought about through combination of a variety of engine parameters of temperature, compression ratio, air-fuel (A/F) ratio, boost pressure, internal or external exhaust gas recirculation (EGR), and supplemental ignition assist. Fuel chemistry and properties may interact differently depending on the engine conditions used to promote ignition.

Approach

The experiments discussed in this report were run on a single-cylinder research engine located at AVL Powertrain, in Plymouth, Michigan, under sub-contract to Oak Ridge National Laboratory. In current configuration, the engine displaces 500 cc with an 11.34 compression ratio. The engine has spark ignition and gasoline port fuel injection. The engine uses a single intake and single exhaust valve with fully flexible hydraulically actuated variable valve timing. In the work reported here, HCCI ignition is initiated by early exhaust valve closing and symmetric late intake valve opening combined with spark augmentation to assist ignition. This valve control strategy results in the retention of exhaust in the cylinder (internal EGR) and increased pressure and temperature during compression leading to auto-ignition of the fuel charge.

Results

This research was begun in FY 2004 and continued in FY 2005. An additional 7 fuels were blended by ExxonMobil in support of this project and evaluated at AVL. Generally, our goal was to produce fuels with similar octane values (research octane number, RON, or motor octane number, MON) to the indolene base fuel with widely varying chemistry. Several exploratory fuels were also blended, including a primary reference fuel, a high-volatility fuel, and a fuel with 10% ethanol. The fuels were blended using combinations of 19 pure compounds in the gasoline range. Details of the blends are shown in Table 1, and the individual blend recipes are given in reference 1. A wide range of properties and chemistries were obtained, with some dependence between properties. One important interdependence is between total paraffins, aromatics, and octane sensitivity. Fuels with the same RON and MON may behave as if they have a different octane value if evaluated at conditions apart from the RON or MON rating conditions. HCCI engines are expected to represent a significant departure from the rating conditions. The engine used in this study was shown to be "beyond MON" because of the high temperatures used for ignition combined with natural aspiration and the relatively light loads used in this study.

Table 1. Fuel Properties and Chemistries for Fuel Blends

PROPERTY (components in volume%)	**FUEL DESIGNATION**												
	Indo-lene-0	**F1 98-80**	**F2 98-87**	**F3 98-98**	**Indo-lene-1**	**F4 PRF80**	**F5 VOL**	**F6 P**	**F7 POA**	**Indo-lene-2**	**F8 PO**	**F9 PA**	**F10 EtOH**
RON	96.5	97.4	99.5	96.3	96.6	80	80.1	95.8	95.2	96.6	95.5	94.9	95.9
MON	88	80.9	86.8	94.5	88.3	80	77.3	85.1	85.2	88	85.6	86.2	85
sensitivity	8.5	16.5	12.7	1.8	8.3	0	2.8	10.7	10	8.6	9.9	8.7	10.9
T10 (°C)	55.6	79.3	85.1	98.1	52.2	98.1	36.6	65	69.3	55	69.8	63	58.4
T50 (°C)	106.7	101.1	97.7	98.1	105.5	98.3	38.2	82.4	86.6	105	94.1	90.3	107.4
T90 (°C)	160.7	108.5	102.1	98.2	162.2	98.4	43.5	99	102.3	161	97.5	102	162.8
n-paraffins	6.4	10	5.8	1.5	xx	20	40	0	0	6.2	0	2.2	6.7
iso-paraffins	29.3	0	49.3	98.5	xx	80	60	30	50	28.2	80.4	56.3	43.4
cycloparaffins	11.3	10	5	0	xx	0	0	70	0	10.3	0	16.4	0
total paraffins	66.5	20	60.1	100	67.3	100	100	100	50	66.9	80.4	74.9	50.1
olefins	5	20	10	0	0.4	0	0	0	25	0.8	19.4	0	20
aromatics	28.5	60	30	0	32.3	0	0	0	25	32.3	0	25	20
oxygenates	0	0	0	0	0	0	0	0	0	0	0	0	10

Each fuel was operated at 5 speed/load combinations and at a variety of combustion phasings, controlled with early exhaust valve closing. Engine variables analyzed include peak cylinder pressure (CP), pressure rise rate, combustion duration, coefficient of variation in indicated mean effective pressure, exhaust closing angle, 50% burn point (MFB50), fuel consumption, and emissions. Fuel variables included octane numbers, boiling point values, and fuel composition. A large number of plots and relationships were determined and are shown in the references. A typical plot is shown in Figure 1, which shows peak combustion pressure vs. combustion phasing for the 5 speed/load conditions. This type of data contains both speed/load information and also fuels information. Statistical analysis of this data was carried out by Battelle under sub-contact to ORNL because of the complex interrelationships of the data and in order to sort out the statistical effects from data variability. The statistical analysis indicated that the combustion variables of combustion duration, peak cylinder pressure, and pressure rise rate all correlated to octane sensitivity, with higher sensitivity resulting in faster, higher-pressure combustion. A higher T50 was also shown to increase hydrocarbon emissions slightly, showing a volatility or mixing effect. Fuel sensitivity was shown to be the best predictor of combustion phasing when normalized to the nominal or mid-point combustion phasing from this study.

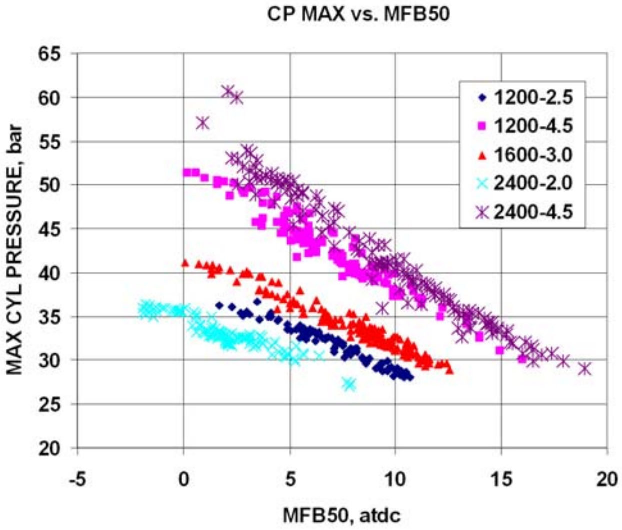

Figure 1. Relationship of Peak Cylinder Pressure to Combustion Phasing for Each Speed-Load Combination

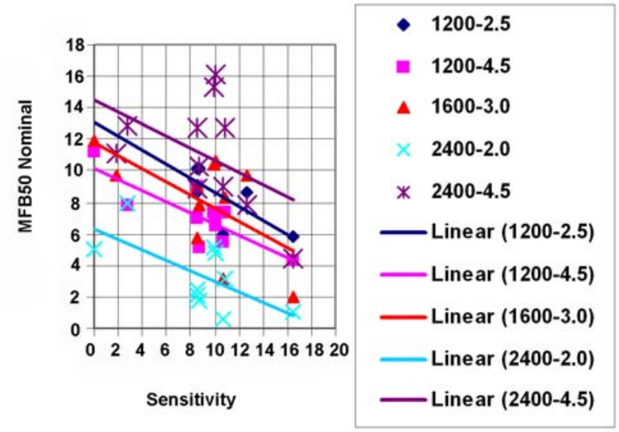

Figure 2. Relationship of MFB50 at Nominal Exhaust Valve Timing to Fuel Sensitivity for Each Speed-Load Combination

This relationship is shown visually in Figure 2, and correlation coefficients for this data ranged from -0.46 to -0.80 for each of the speed/load combinations.

In this study, fuel sensitivity was determined statistically to be the most important fuel variable for correlation to engine performance. Fuel sensitivity indicates the response of a fuel to the different conditions of the RON and MON rating tests and is also an indication of a fuel's chemical makeup. HCCI engines achieve combustion when cylinder conditions reach a temperature of ignition for the fuel, but this temperature can be reached through various combinations of initial pressure, initial temperature, and cylinder wall temperature. Naturally aspirated HCCI engines such as we used achieve combustion through high cylinder temperatures and relatively low cylinder pressures. This type of operation is classified as "beyond MON". Figure 3 shows how apparent octane number varies for our test fuels as a function of temperature during compression and indicates that high octane sensitivity (slope in these lines) can result in a low effective octane number at our operating conditions. A low octane number, in turn, indicates easier ignition under HCCI combustion. This results in faster and more rapid combustion, which are characteristics we found in the data.

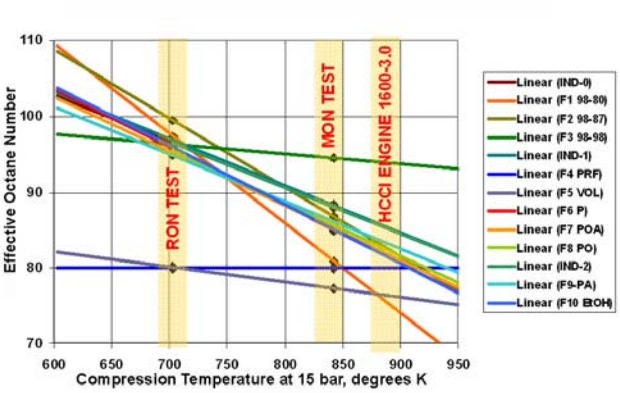

Figure 3. Relationship of Effective Octane Number to Compression Temperature at 15 Bar for Fuels Showing Conditions for RON and MON Tests and for HCCI Engine Operation

Conclusions

A series of gasoline range fuels encompassing both fuel property and fuel chemistry variables have been successfully run in a spark-assisted HCCI engine using a negative valve overlap with a high retained exhaust fraction to trigger HCCI. The addition of spark assist to an HCCI engine was useful to allow starting, to improve transitions to HCCI, to help stabilize HCCI, and to expand the operating range of HCCI. Within our ability to determine between fuels, octane sensitivity emerged as the major fuel variable which correlated to engine performance under both fixed combustion phasing (MFB50) and fixed compression conditions (exhaust valve closing angle). The HCCI engine used in this study is characterized as being 'beyond MON' due to the high compression temperatures and relatively low pressures resulting from naturally aspirated operation combined with a high retained EGR fraction. This condition results in high-sensitivity fuels behaving as lower octane fuels, which results in earlier or easier ignition and faster combustion. The experimental trends combined with the work of others support this conclusion. There is still the possibility that some other fuel property or chemistry variable may have an effect on HCCI combustion. More focused experiments and modeling are planned for FY 2006 to more fully answer this question.

FY 2005 Publications/Presentations

1. Bunting, B.G., COMBUSTION, CONTROL, AND FUEL EFFECTS IN A SPARK-ASSISTED HCCI ENGINE EQUIPPED WITH VARIABLE VALVE TIMING, offered for presentation at 2006 SAE International Congress, 06P-638.
2. Bunting, B.G., FUEL CHEMISTRY AND CETANE EFFECTS ON DIESEL HCCI PERFORMANCE, COMBUSTION, AND EMISSIONS, presentation at 2005 SAE HCCI Symposium, Lund, Sweden, 9/05.
3. Bunting, B.G., Wildman, Szybist, Lewis, and Storey, FUEL CHEMISTRY AND CETANE EFFECTS ON HCCI PERFORMANCE, COMBUSTION, AND EMISSIONS, presentation at 2005 DOE DEER Conference, 8/05.
4. Bunting, B.G., EFFECTS OF FUEL COMPOSITION AND PROPERTIES IN GASOLINE HCCI AND SPARK AUGMENTED HCCI, presentation at 2005 DOE MOU Review, 2/05.
5. Bunting, B.G., SPARK ASSISTED LOW TEMPERATURE COMBUSTION, presentation at 2005 Advanced Combustion Engine Merit Review, 4/05.
6. Bunting, B.G., FUEL EFFECTS ON GASOLINE BASED HCCI PERFORMANCE AND EMISSIONS, presentation at 2005 Fuels Technology Program Merit Review, 3/05.
7. Szybist, J.P., and Bunting, CETANE NUMBER AND ENGINE SPEED EFFECTS ON DIESEL HCCI PERFORMANCE AND EMISSIONS, SAE 2005-01-3723.
8. Lewis, S.A., Storey, Bunting, and Szybist, PARTIAL OXIDATION PRODUCTS AND OTHER HYDROCARBON SPECIES IN DIESEL HCCI EXHAUST, SAE 2005-01-3737.
9. Bunting, B.G., GASOLINE FUEL PROPERTY AND CHEMISTRY EFFECTS ON SPARK STABILIZED HCCI COMBUSTION, seminal presentation to Penn State University Department of Energy and Geo-Environmental Engineering, 10/05.

III.6 Fuel Effects on Diesel-Based Advanced Combustion Regimes

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DOE Technology Development Manager: Kevin Stork

Objectives

- Investigate the impacts of petroleum, non-petroleum, and bio-derived diesel fuel properties on the emissions from high-efficiency clean combustion (HECC) combustion modes.

Approach

- Utilize a Mercedes 1.7L diesel engine at Oak Ridge National Laboratory (ORNL) as a research platform equipped with full-pass electronic control.
- Using production-like hardware and control strategies, transition the engine from normal to advanced combustion.
- Characterize the performance and emissions from the engine when using several fuels.
- Analyze the resulting data to determine fuels impacts on advanced combustion regimes.

Accomplishments

- Showed that fuels from a variety of feedstocks (oil-sands, petroleum, and vegetable oil) do exhibit HECC behavior at a similar range of engine output and speed.
- Showed that fuel properties within the limited range studied do not significantly expand the load/speed operating regime for HECC.
- Showed that there was a strong influence of the fuel properties on both particulate and hydrocarbon emissions in HECC modes.

Future Directions

- For fiscal year 2006, adopt common fuel matrices with other research programs as appropriate and available. Continue to study emissions as a means of furthering the understanding of the performance of fuels in advanced combustion modes.

Introduction

Diesel-based advanced combustion regimes are combustion regimes that result in much lower oxides of nitrogen (NOx) and particulate matter (PM) emissions than traditional combustion processes. They can generally be achieved by reducing the quantity of fuel that burns in a hot diffusion flame. Most methods focus on reducing the diffusion burn by increasing the amount of fuel burned in a pre-mixed combustion event. This type of combustion generally does not lead to the formation of problematic pollutants. Formation of a fuel-lean, pre-mixed region inside the fuel jet may be influenced by several fuel properties, including the oxygen content, viscosity, and boiling range. Initiation of combustion inside such a region may also be influenced by fuel properties such as the cetane number. Hence, utilizing fuel property effects may represent a means of improving the combustion process if the impacts of these properties can be understood.

Approach

A Mercedes 1.7-liter diesel engine at ORNL was utilized for this study. The engine was fueled with three hydrocarbon fuels plus two blends using a soybean-based biodiesel fuel. The three petroleum-based fuels were termed fuels A, B, and C, and the two oxygenated blends were termed fuels A_O and C_O. Fuel A was an off-the-shelf certification diesel fuel. Fuel B was a low-sulfur diesel fuel derived from Canadian oil-sands reserves. Fuel C was an off-the-shelf low-aromatic, low-sulfur diesel fuel. Fuels A_O and C_O were blends of fuels A and C, respectively, that contained 5% by volume soy-methyl ester biodiesel. (See Table 1 for additional fuel properties.)

Table 1. Fuel Properties

Characteristic	Fuel A	Fuel B	Fuel C
Spec. Gravity	0.8453	0.8377	0.8299
Sulfur (PPM-wt)	386	8.4	13.2
Viscosity (cs 40 °C)	2.3	2.27	2.32
Carbon (wt%)	86.85	86.04	86.14
Hydrogen (wt%)	13.11	13.78	13.86
Net Heating Value (MJ/kg)	42.754	42.752	43.142
Cetane Number	47.3	47.9	49.9
Aromatics (Vol%)	30.6	15.07	9.0
Olefins (Vol%)	0.8	2.0	0.3
Saturates (Vol%)	68.6	82.3	90.7
Polynuclear Aromatics (wt%)	10.0	0.7	1.3
Distillation (°C)			
IBP	177	168	191
T10	207	195	214
T20	223	209	224
T30	236	223	233
T40	248	235	240
T50	258	248	246
T60	268	260	251
T70	277	273	257
T80	287	288	267
T90	302	308	292
T95	314	324	327
EP	328	336	343

The engine utilized only production-like hardware to achieve HECC. The exhaust gas recirculation (EGR) rate was increased to target 14-15% intake O_2 concentration. The fuel injection parameters were adjusted to provide a higher fuel rail pressure that allowed injection of the fuel charge in one short pulse at approximately 6 – 8 crank angle degrees before top dead center. The fueling strategy was held constant for each of the fuels. The brake output of the engine was also very similar given the close agreement among the heating values of the fuels (within 1% for fuels A, B, and C).

Results

Engine Operating Conditions – The results showed that fuels A, B, and C could achieve HECC conditions at the 1,500 RPM/2.80 bar brake mean effective pressure (BMEP) and 2,500 RPM/2.00 bar BMEP points, but failed to do so at the 2,000 RPM/2.90 bar BMEP point due to high PM emissions despite exhibiting very low NOx emissions. This provides an opportunity to compare the fuel effects both at conditions where HECC could be achieved and at the limits of engine operation for HECC where differences in fuel behavior are more likely to be significant. The brake engine output and fuel rates were held constant from baseline to HECC operation at each condition, meaning that the brake engine efficiency was not compromised from its baseline levels by operation in HECC modes.

Particulate Emissions – The PM mass emissions (from filtration) are shown for each of the three engine conditions for each of the 3 fuels (A, B, C) in Figure 1. The results are shown in column pairs for each fuel, with the baseline condition on the left and HECC condition on the right for each fuel. The HECC conditions for both the 1,500 RPM point and the 2,500 RPM point exhibit lower PM emissions than the baseline case for each fuel. The 2,000 RPM data show that none of the 3 fuels achieved HECC at that condition, since the "HECC" PM emissions are higher than baseline. The data show that fuel A had the highest PM emissions at baseline and under HECC at all conditions. Fuels B and C demonstrated lower PM emissions at baseline and under HECC at all conditions, with fuel C being the lowest. The data at 2,000 RPM show that the PM increase for fuel A

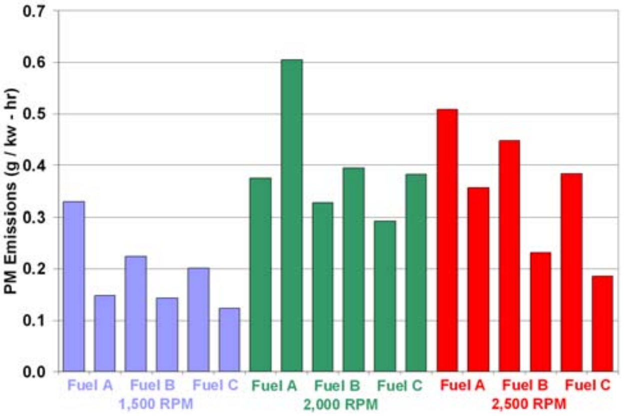

Figure 1. PM Emissions for Fuels A, B, and C (Normal mode is the left column and HECC mode the right column of each pair.)

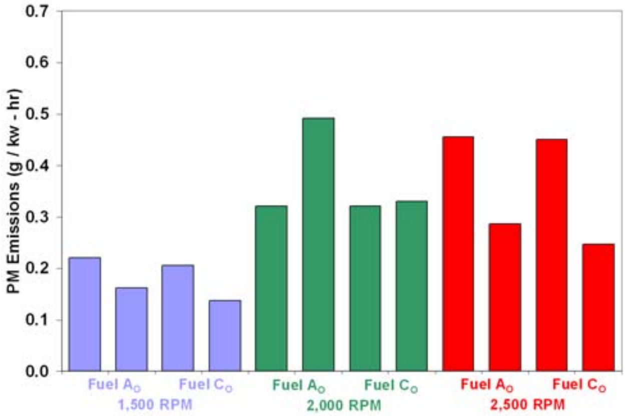

Figure 2. PM Emissions for Fuels A_O and C_O (Normal mode is the left column and HECC mode the right column of each pair.)

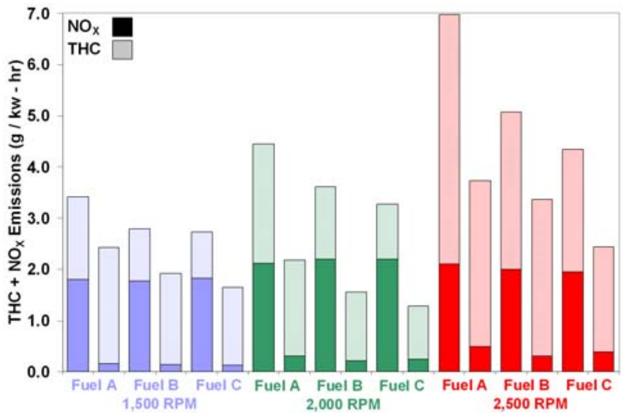

Figure 3. NOx and THC Emissions for Fuels A, B, and C (Normal mode is the left column and HECC mode the right column of each pair.)

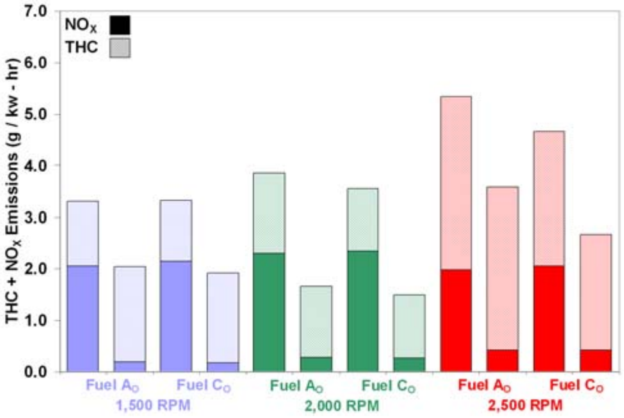

Figure 4. NOx and THC Emissions for Fuels A_O and C_O (Normal mode is the left column and HECC mode the right column of each pair.)

was highest, while those of fuels B and C were lower and comparable to each other. This suggests that while none of the fuels achieved HECC at the 2,000 RPM point, fuels B and C approached HECC more closely than did fuel A. Figure 2 shows the PM emissions results (from filtration) for the two oxygenated fuels, A_O and C_O. The PM emissions for fuel A_O are lower than those of fuel A. However, oxygenation of fuel C with 5% biodiesel does not improve its PM emissions at baseline conditions or under HECC conditions. The 2,000 RPM results show that oxygenation does allow both fuels to approach HECC more closely than the non-oxygenated fuels. In fact, fuel C_O exhibits only marginally higher PM than did fuel C, perhaps indicating a transitional condition very close to HECC conditions.

Unburned Hydrocarbon and NOx Emissions – The total hydrocarbon (THC) and NOx emissions for the 3 petroleum fuels are shown in Figure 3, with the results from the oxygenated fuels in Figure 4. The results for the three petroleum fuels show that the NOx emissions are not significantly dependent upon the fuel. The NOx emissions exhibit a marked reduction of more than 70%, with reductions approaching 90% at the 1,500 RPM condition. The NOx emissions for the oxygenated fuels were marginally higher than those for the non-oxygenated fuels at baseline conditions. The NOx emissions for the oxygenated fuels were very similar to those of the non-oxygenated fuels in the HECC modes. The NOx was approximately 25% NO_2 in baseline modes. The NO_2 fraction was observed to increase in the HECC modes, achieving fractions as high as 60% at some conditions. N_2O emissions remained constant at baseline levels, demonstrating a dependence upon neither the combustion mode nor the fuel.

THC emissions indicate a dependence upon both the combustion mode and the fuel. THC emissions generally increase in the HECC modes relative to baseline. The rate of increase is dependent upon the engine load and speed conditions, with higher speed conditions generally showing a smaller (or no) increase in THC emissions. The THC emissions increase at the 2,000 RPM condition was lower than for the 1,500 and 2,500 RPM conditions for all three fuels. At each engine speed condition, the THC emissions followed the same trend noted for the PM emissions. That is, the emissions were highest for fuel A and lowest for fuel C in both the baseline and HECC modes. In fact, the THC emissions for fuel C in the HECC modes at both 1,500 and 2,500 RPM were lower than the THC emissions for fuel A in the baseline modes.

Carbon Monoxide Emissions – The CO emissions for all 3 of the petroleum-based fuels increased in HECC mode compared with baseline, with the exception of fuels A and B at the 2,500 RPM condition. The CO emissions increase at the 2,000 RPM condition was lower than at the 1,500 and 2,500 RPM conditions. The data suggest a trend towards lower CO emissions for fuel C compared with fuel A, but the increases from baseline to HECC mode do not exhibit a strong correlation to the fuel.

The data also suggest that oxygenation of the fuels yielded mixed results in terms of CO emissions. In general, fuel A benefited from oxygenation while fuel C did not, at least in terms of CO emissions.

Conclusions

- Fuel properties in the ranges studied with the 5 fuels reported did not expand the HECC operating envelope significantly, but did have marginal impacts.
- Blends of 5% biodiesel with petroleum-based fuels were observed to exhibit HECC modes similar to those observed without biodiesel blending.
- EGR effects on NOx emissions in HECC modes overwhelmed any fuel effects on NOx emissions.
- Hydrocarbon emissions in HECC modes were strongly dependent upon the fuel burned. In general, fuels that produced less PM in normal modes produced less HC emissions in HECC modes.
- PM emissions in HECC modes were dependent upon the fuel burned, but less so than the PM emissions in normal modes.

FY 2005 Publications/Presentations

1. "Fuel Property Effects on Diesel High-Efficiency Clean Combustion," Presented at the 2005 DOE Fuels Technology Program Merit Review.
2. "Fuel Property Effects on Emissions from High-Efficiency Clean Combustion in a Diesel Engine," Paper in review for publication at the 2006 SAE International Congress and Exhibition.

III.7 Fuel Effects on Diesel-Based HCCI Performance and Emissions

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DOE Team Lead: Stephen Goguen

DOE Technology Development Manager: Kevin Stork

Objectives

- Quantify the effects of fuel properties on homogeneous charge compression ignition (HCCI) combustion relative to ignition and combustion characteristics, emissions, and fuel efficiency.
- Baseline performance and combustion characteristics of a selected HCCI engine to provide a stable platform for continuing fuels evaluations.
- Demonstrate the potential for fuel economy improvement from a combination of advanced combustion, engine controls, and fuel properties.
- Evaluate alternate fuels such as those containing biodiesel or oil sands derived components for performance characteristics.

Approach

- Establish HCCI engine capability and acquire diesel range fuels.
- Evaluate fuel performance in engine tests and correlate results to relevant fuel properties.

Accomplishments

- Completed installation and conversion of small diesel engine to HCCI combustion and conducted two fuel effects studies for diesel range fuels.
- Correlated HCCI performance to fuel chemistry and cetane values using commercial diesel fuels, blends of diesel secondary reference fuels, and biodiesel fuel.

Future Directions

- Determine detailed chemistry effects of HCCI fuels in addition to bulk property effects.
- Conduct studies to help define performance characteristics of biodiesel blends and effects of cetane number on effective load range.
- Continue to explore issues of stability and moving between various combustion regimes to determine if fuel chemistry can improve HCCI controllability and operating range.
- Interact with Cummins, Inc. and BP regarding fuel effects to achieve high-efficiency and low-emission combustion.

Introduction

In HCCI, the fuel and air are pre-mixed prior to combustion, and ignition is initiated by kinetic reactions which occur during the compression stroke. Ignition occurs when a threshold temperature is reached, and the timing of ignition is controlled by setting the cylinder conditions at the start of the compression stroke. The cylinder charge of fuel and air is also diluted with excess air or with exhaust gas. The purpose of this dilution is to lower the peak flame temperature to reduce NOx and to eliminate rich zones which can generate particulates. The dilution also helps control ignition by changing cylinder conditions during compression and to regulate the rate of burning after combustion begins. The improvement in fuel efficiency found in some HCCI engines is due to a combination of faster heat release, reduced heat transfer, and reduced throttling losses.

Since the ignition process is kinetically driven, fuel properties have a large effect on combustion characteristics and timing. Fuel cetane characteristics regulate the tendency of a fuel to ignite in an HCCI engine, and fuel volatility can impact fuel mixing, evaporation, and the degree of homogeneity achieved. Fuel chemistry may have a large effect because of the various pre-flame reactions required for successful ignition. Conditions supportive of the compression ignition of fuels (mainly temperature) can be brought about through combination of a variety of engine parameters such as temperature, compression ratio, air/fuel ratio, boost pressure, internal or external exhaust gas recirculation (EGR), and supplemental ignition assist. Fuel chemistry and properties may interact differently depending on the engine conditions used to promote ignition.

Approach

The experiments discussed in this report were conducted on a single-cylinder research engine located at Oak Ridge National Laboratory (ORNL). This engine was converted from a single-cylinder Hatz industrial diesel engine. The engine was modified by lowering the compression ratio from 20:1 to 10.5:1, by removing the conventional diesel injection system, by adding a 6 kW intake air heater, and by adding port fuel injection. The port fuel injection consists of an ORNL-designed heated atomizer which allows port injection of diesel fuel and provides a very uniform fuel/air mixture. The engine operates un-throttled, and combustion is regulated by intake air temperature. Figure 1 shows the engine and test rig, and Figure 2 shows details of the heated atomizer. Fuels are evaluated by conducting a timing sweep controlled by intake air temperature to vary combustion phasing.

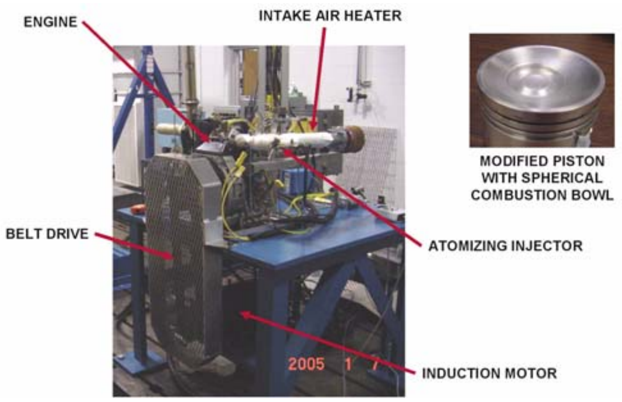

Figure 1. HCCI Engine and Test Rig

- Standard tube fittings
- 400 watt cartridge heater
- Slight air purge
- Operated at 375 deg.C
- Mounted between air heater and intake port
- Fuel controlled by laboratory metering pump
- Provides very uniform fuel mixing

Figure 2. ORNL Heated Atomizer

As temperature is increased, timing advances, and this advance is limited by maximum rate of cylinder pressure rise. As temperature is decreased, timing is retarded, and this retard is limited by combustion variability.

Results

Optimum combustion phasing was shown to vary with fuel cetane number. To achieve maximum power output, higher-cetane fuels required more advanced fuel introduction than lower-cetane fuels. Fuels below 40 cetane possessed no low-temperature heat release (LTHR), while fuels above 40 cetane had increasing amounts of LTHR. Higher-cetane fuels also had a longer combustion duration (CA 10-90) than low-cetane fuels because of their increasing LTHR. Optimal timing and combustion duration are shown in Figure 3 as a function of cetane number. As timing was retarded for all the fuels, hydrocarbon (HC) and CO emissions increased, with CO increasing more rapidly for the high-cetane fuels. This indicates the sensitivity of

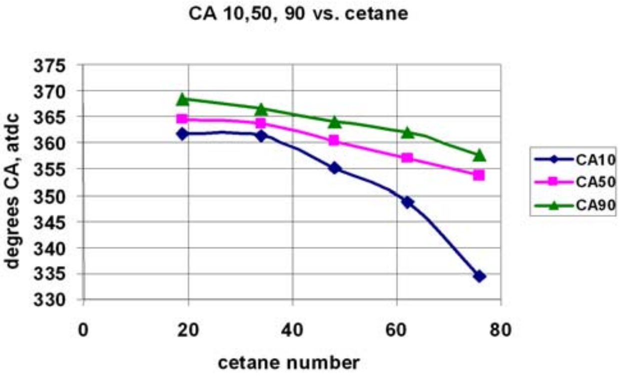

Figure 3. Relationship of Cetane Number to Optimum Combustion Phasing

LTHR to quenching effects and the generation of partial oxidation products during LTHR. NOx was low for all fuels in the range of optimal timings (below 10 ppm) and increased for all fuels as a function of rate of cylinder pressure rise for more advanced combustion timing, as shown in Figure 4. Increasing fuel aromatic content had a weak effect on increasing the rate of cylinder pressure rise, HC emissions, and NOx. It appeared that fuels with about 40 to 45 cetane number were optimum for maximum power output. As cetane number was increased from this, it became difficult to control combustion phasing late enough. With lower-cetane fuels, higher intake temperatures were needed for ignition, which tended to drive the engine into knock as fuel rate was increased.

Conclusions

Results from this study indicate that as cetane number increases, the optimum combustion phasing advances, low-temperature heat release increases, and NOx decreases slightly. Higher cetane resulted in a faster rate of cylinder pressure rise and higher NOx and HC emissions. Generally, NOx emissions were related to the maximum rate of cylinder pressure rise. Biodiesel operated differently from the petroleum-based fuels, exhibiting higher emissions, faster heat release, and less low-temperature heat release. All fuels operated successfully at the loads used for these experiments, and the heated atomizer proved to be a good way to simplify fuel delivery. In our mode of engine control, fuel rate is kept constant and intake heating is used to control to maximum power output. Changing intake air temperature also changes combustion chamber temperature and fuel air ratio. Further defining these effects is a subject for future research along with further fuel and fuel blend studies.

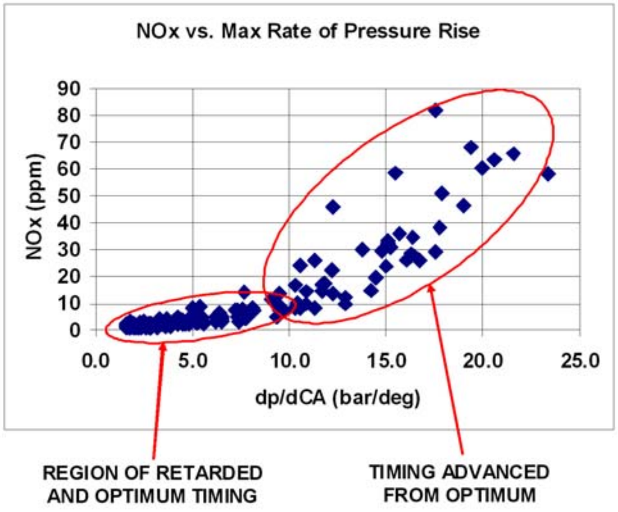

Figure 4. Relationship of NOx to Rate of Cylinder Pressure Rise

FY 2005 Publications/Presentations

1. Bunting, B.G., FUEL CHEMISTRY AND CETANE EFFECTS ON DIESEL HCCI PERFORMANCE, COMBUSTION, AND EMISSIONS, presentation at 2005 SAE HCCI Symposium, Lund, Sweden, 9/05.
2. Bunting, B.G., Wildman, Szybist, Lewis, and Storey, FUEL CHEMISTRY AND CETANE EFFECTS ON HCCI PERFORMANCE, COMBUSTION, AND EMISSIONS, presentation at 2005 DOE DEER Conference, 8/05.
3. Szybist, J.P., and Bunting, CETANE NUMBER AND ENGINE SPEED EFFECTS ON DIESEL HCCI PERFORMANCE AND EMISSIONS, SAE 2005-01-3723.
4. Lewis, S.A., Storey, Bunting, and Szybist, PARTIAL OXIDATION PRODUCTS AND OTHER HYDROCARBON SPECIES IN DIESEL HCCI EXHAUST, SAE 2005-01-3737.
5. Wildman, C.B., and Bunting, A COMPARISON OF BIODIESEL COMBUSTION PERFORMANCE WITH THAT OF THREE OTHER DIESEL FUELS IN A HOMOGENEOUS CHARGE COMPRESSION IGNITION ENGINE, offered for presentation at 2006 ACS Biofuels for Transportation Symposium, Atlanta, GA., 4/06.

IV Transition to Hydrogen Economy

IV.1 Advancing Gaseous Fuel Vehicle and Infrastructure Technology

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DOE Technology Development Managers: Dennis Smith and David Hamilton

Subcontractors:
Clean Vehicle Education Foundation, Acworth, GA
Cummins Westport Inc., Vancouver, BC, Canada
Gladstein, Neandross & Associates, LLC, Santa Monica, CA
John Deere Power Systems, Waterloo, IA
Mack Trucks Inc., Hagerstown, MD
Westport Innovations

Objectives

- Promote reduction of U.S. petroleum consumption via advancement of gaseous fuel vehicle and infrastructure technologies
- Develop technologies to expedite the transition to the hydrogen-based transportation of the future
- Reduce emissions of pollutants compared with conventional fuel vehicles

Approach

- Engine & Vehicle Platform Development: Develop commercially viable gaseous fuel vehicles (GFVs) that compare favorably with conventional counterparts in terms of cost, reliability, performance, and adherence to Environmental Protection Agency (EPA) emission standards.
- Infrastructure Enhancement: Reduce costs and improve availability and reliability of gaseous fuel refueling.
- Hydrogen Transition Technology Development: Develop technologies and infrastructure that exploit the synergy between hydrogen and natural gas (NG) vehicles, promoting the transition to hydrogen-based transportation.
- Technology Transfer: Provide technical assistance to GFV adopters and introduce hydrogen technologies.

Accomplishments

Engine & Vehicle Platform Development

- Completed project to develop a Cummins Westport Inc. (Cummins/Westport or CWI) lean-burn 8.9L NG engine and integrate it into multiple vehicle platforms*
- Continued projects to develop and/or integrate the following NG engines: 8.1L John Deere, 12L Mack/Volvo, and 15L Cummins/Westport*
- Continued projects to develop 11L Mack/Volvo (variable valve timing) and 8.9L Cummins/Westport NG engines**
- Initiated project to develop a NG stochiometric engine for transit buses**

  *(*2007 EPA emission standards; **2010 EPA emission standards)*

Infrastructure Enhancement

- Published final safety evaluation report of NG home refueling appliance

Hydrogen Transition Technology Development

- Completed evaluation of opportunities to integrate hydrogen into natural gas vehicle (NGV) fueling stations of the Interstate Clean Transportation Corridor (ICTC)

Technology Transfer

- Held Natural Gas Vehicle Technology Forum (NGVTF) meeting in August 2005 and updated its Web site
- Held Transit Users Group (TUG) meeting in November 2004
- Actively participated in California NGV Partnership
- Provided leadership for codes and standards development

Future Directions

- Advance NG engine and vehicle technologies, including the following:
  - High-pressure direct injection (HPDI)
  - Digital camless variable valve timing
  - Three-way catalysts for heavy-duty stoichiometric engines
  - Lean air/fuel ratio, exhaust gas recirculation, and advanced aftertreatment
  - Hybridization of NGVs
  - Variable hydrogen compressed natural gas (HCNG) blend lean-burn engines
- Develop synergy between NG and hydrogen vehicle and infrastructure technologies
- Expand partnerships to advance and transfer gaseous fuel technologies; leverage R&D funding with additional partners

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Introduction

The National Renewable Energy Laboratory (NREL) advances gaseous fuel vehicle (GFV) and infrastructure technology in support of two major U.S. Department of Energy (DOE) goals: 1) reduce petroleum consumption and 2) provide a transition to hydrogen-based transportation. GFVs can also reduce emissions of regulated pollutants compared with gasoline- and diesel-fueled vehicles. Gaseous fuels include natural gas, hydrogen, and hydrogen-natural gas blends.

Approach

NREL employs an integrated strategy—from research to demonstration—to advance technology for commercially viable GFVs and related infrastructure, primarily for the medium- and heavy-duty sectors (Figure 1). These efforts fall into four

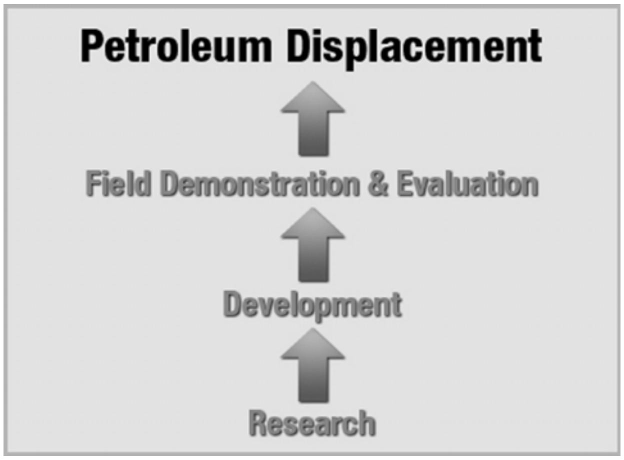


Figure 1. NREL's Integrated Strategy for Advancing Gaseous Fuel Vehicle and Infrastructure Technology

categories: engine & vehicle platform development, infrastructure enhancement, hydrogen transition technology development, and technology transfer.

To leverage resources, NREL forms partnerships with industry and government.

Results

Engine & Vehicle Platform Development

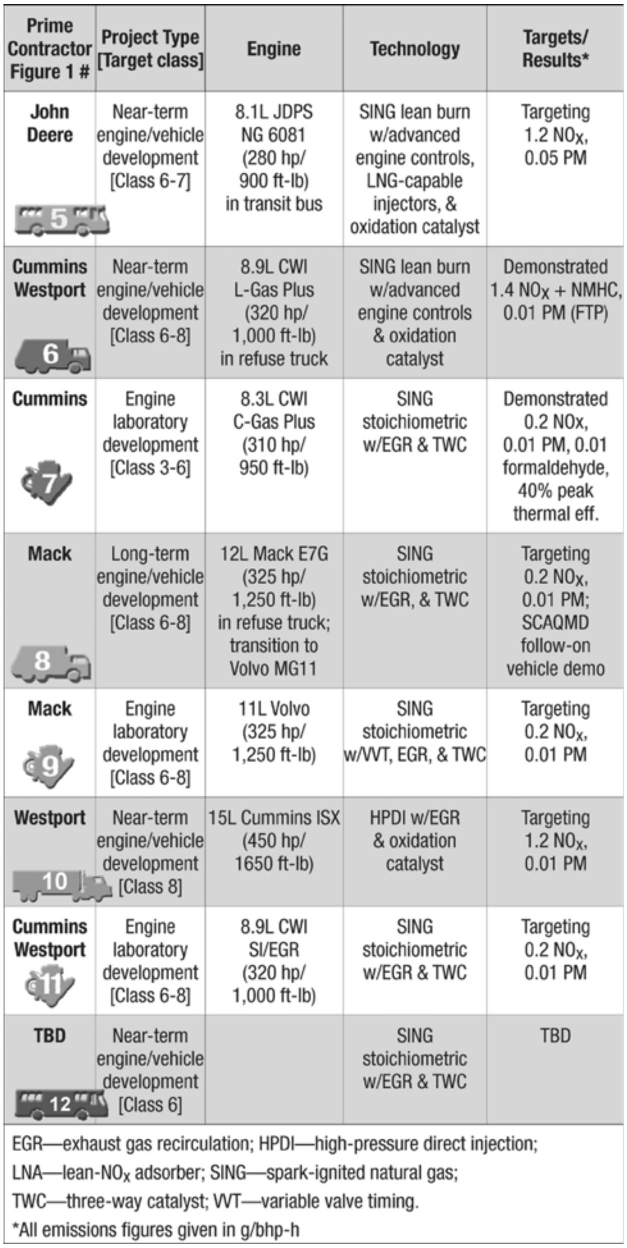
NREL carries out most of its engine and vehicle platform development as part of the Next Generation Natural Gas Vehicle (NGNGV) activity. The NGNGV activity is supported by DOE's FreedomCAR & Vehicle Technologies Program, South Coast Air Quality Management District (SCAQMD), and the California Energy Commission. In FY 2005, NREL had eight NGNGV projects (Table 1 and Figure 2).

NREL completed development and vehicle integration of a Cummins/Westport 8.9L NG engine that complies with the EPA 2007 emissions standards (1.2 g/bhp-hr NOx, 0.01 g/bhp-hr PM) for refuse trucks.

NREL continued to integrate three other EPA 2007-compliant NG engines into various platforms. A John Deere 8.1L engine was certified to target NOx levels, demonstrated in transit and school bus fleets, and is planned to be developed into a 9.0L engine to meet 0.2 g/bhp-hr NOx levels in a follow-on procurement action. A liquefied natural gas (LNG) pump and tank was designed, and certification is underway for an EPA 2007-compliant 15L Cummins/Westport engine for tractor-trailer platforms. Finally, an EPA 2007-compliant Mack/Volvo 12L engine was integrated into a refuse truck platform and is ready for demonstration under a follow-on activity funded by SCAQMD.

NREL also continued to develop NG engines capable of achieving EPA 2010 emission standards of 0.2 g/bhp-hr NOx and 0.01 g/bhp-hr PM for medium- and heavy-duty vehicle applications. A Mack/Volvo 11L engine under development uses variable valve timing to increase combustion and cycle efficiency and decrease emissions. A "concept" 8.9L Cummins/Westport engine is now operational and ready for demonstration.

Table 1. Next Generation Natural Gas Vehicle Engine & Vehicle Platform Development FY 2005 Projects



Prime Contractor Figure 1 #	Project Type [Target class]	Engine	Technology	Targets/ Results*
John Deere 5	Near-term engine/vehicle development [Class 6-7]	8.1L JDPS NG 6081 (280 hp/ 900 ft-lb) in transit bus	SING lean burn w/advanced engine controls, LNG-capable injectors, & oxidation catalyst	Targeting 1.2 NO_X, 0.05 PM
Cummins Westport 6	Near-term engine/vehicle development [Class 6-8]	8.9L CWI L-Gas Plus (320 hp/ 1,000 ft-lb) in refuse truck	SING lean burn w/advanced engine controls & oxidation catalyst	Demonstrated 1.4 NO_X + NMHC, 0.01 PM (FTP)
Cummins 7	Engine laboratory development [Class 3-6]	8.3L CWI C-Gas Plus (310 hp/ 950 ft-lb)	SING stoichiometric w/EGR & TWC	Demonstrated 0.2 NOx, 0.01 PM, 0.01 formaldehyde, 40% peak thermal eff.
Mack 8	Long-term engine/vehicle development [Class 6-8]	12L Mack E7G (325 hp/ 1,250 ft-lb) in refuse truck; transition to Volvo MG11	SING stoichiometric w/EGR, & TWC	Targeting 0.2 NO_X, 0.01 PM; SCAQMD follow-on vehicle demo
Mack 9	Engine laboratory development [Class 6-8]	11L Volvo (325 hp/ 1,250 ft-lb)	SING stoichiometric w/VVT, EGR, & TWC	Targeting 0.2 NO_X, 0.01 PM
Westport 10	Near-term engine/vehicle development [Class 8]	15L Cummins ISX (450 hp/ 1650 ft-lb)	HPDI w/EGR & oxidation catalyst	Targeting 1.2 NO_X, 0.01 PM
Cummins Westport 11	Engine laboratory development [Class 6-8]	8.9L CWI SI/EGR (320 hp/ 1,000 ft-lb)	SING stoichiometric w/EGR & TWC	Targeting 0.2 NO_X, 0.01 PM
TBD 12	Near-term engine/vehicle development [Class 6]		SING stoichiometric w/EGR & TWC	TBD

EGR—exhaust gas recirculation; HPDI—high-pressure direct injection; LNA—lean-NO_X adsorber; SING—spark-ignited natural gas; TWC—three-way catalyst; VVT—variable valve timing.
*All emissions figures given in g/bhp-h

Infrastructure Enhancement

NREL published a final report about its independent safety evaluation of FuelMaker's home refueling appliance (HRA), which is designed to refuel compressed natural gas (CNG) vehicles inside residential garages. The report is being used to educate local code officials during initial deployment of the HRA.

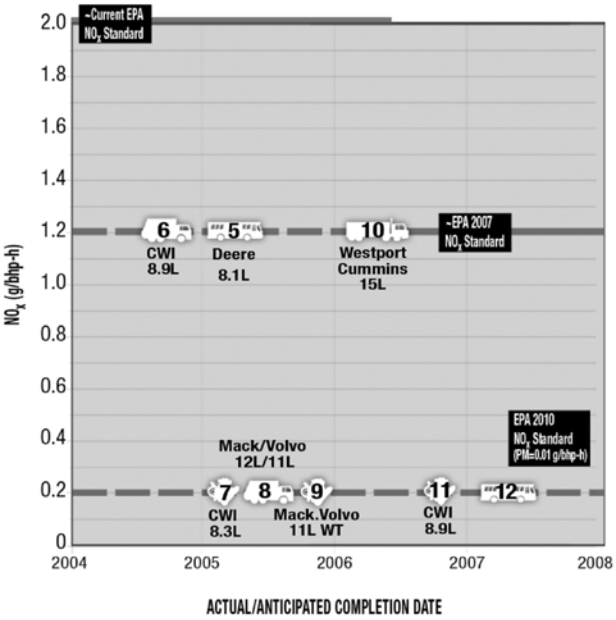


Figure 2. Next Generation Natural Gas Vehicle Engine & Vehicle Platform Development Projects

Hydrogen Transition Technology Development

NREL completed a project with Gladstein, Neandross & Associates to investigate establishing combined hydrogen-NG stations along the Interstate Clean Transportation Corridor (ICTC) (Figure 3). The ICTC is a network of CNG and LNG stations in California and surrounding states.

ICTC project findings and recommendations have been presented in a report for future planning.

Technology Transfer

NREL leads DOE's Natural Gas Vehicle Technology Forum (NGVTF) to facilitate communication and leverage resources among its stakeholders, including those who will play a key role in proliferating hydrogen vehicle technology. Around 80 people attended the NGVTF meeting held August 2-4, 2005, in Washington, DC. Participants included representatives of original equipment manufacturers, vehicle/infrastructure packagers, national laboratories, federal/state/local governments, industry/trade associations, consultants, utilities, fuel distributors, and fleet operators.

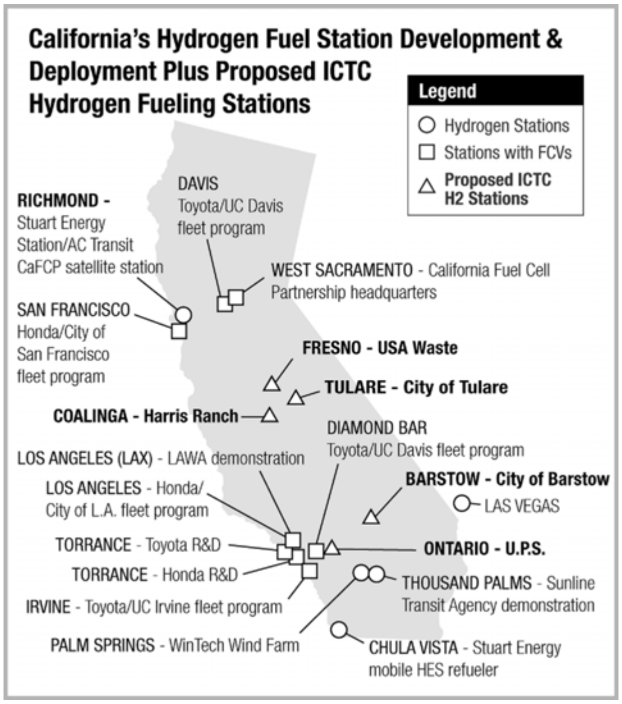


Figure 3. Map of Current Hydrogen Vehicle & Station Development Projects with Proposed ICTC Hydrogen Demonstration Projects Added

As part of the NGVTF, NREL leads DOE's Natural Gas Transit Users Group (TUG). A TUG meeting was held in November 2004 in Anaheim, California, in conjunction with an American Public Transit Association Workshop.

NREL provided leadership and direction for codes and standards development related to NGV technology development. NREL and its subcontractors actively participated in meetings hosted by the National Fire Protection Association, Society of Automotive Engineers, and the DOE Hydrogen Codes & Standards Committee.

Conclusions

As much as 800 million gallons of diesel fuel could be displaced annually if NGVs replaced diesel vehicles in half of all transit buses, school buses, refuse trucks, and demand-response vehicles. DOE/NREL-sponsored engines are already displacing as much as 72 million gallons of diesel fuel each year. NG transit buses continue to be the single largest niche application (Figure 4),

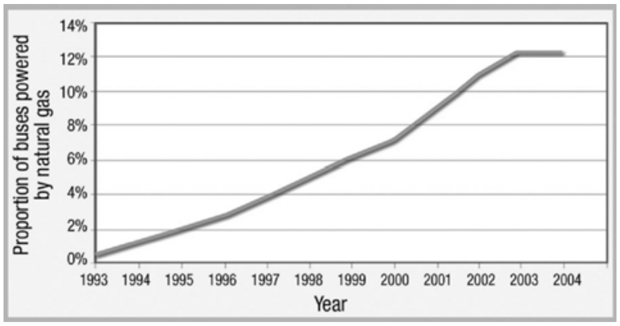


Figure 4. Proportion of U.S. Transit Buses Powered by Natural Gas (Source: American Public Transportation Association)

constituting approximately 25% of all new transit buses ordered in 2004 (4). TUG remains an effective forum for this critical sector.

Current medium- and heavy-duty NGVs typically exhibit lower emissions (particularly NOx) compared with their diesel counterparts. NREL has developed engines that meet EPA 2007 emissions standards and demonstrated those that meet EPA 2010 emissions standards. Meeting these stringent emissions standards promotes the use of NGVs.

NREL continues to explore synergistic opportunities between hydrogen and NG, regarding both engine development and fuel infrastructure. NREL has investigated combined hydrogen-NG fueling stations as a way to expedite the transition of a hydrogen-based transportation network.

FY 2005 Publications

1. Safety Evaluation of the FuelMaker Home Refueling Concept: Final Report http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/36780.pdf
2. Evaluating the Safety of a Natural Gas Home Refueling Appliance http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/037333ng_refuel.pdf
3. Assisting Transit Agencies with Natural Gas Bus Technologies http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/037921ng_bus.pdf
4. Strategy for the Integration of Hydrogen as a Vehicle Fuel into the Existing Natural Gas Vehicle Fueling Infrastructure of the Interstate Clean Transportation Corridor Project http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/38720.pdf
5. Heavy-Duty Waste Hauler with Chemically Correct Natural Gas Engine Diluted with EGR and Using a Three-Way Catalyst http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/38222.pdf

FY 2005 Presentations

1. NGNGV Presentation at the Faster Freight-Cleaner Air 2004 Conference, December 2004 http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/37406.pdf
2. Alternative Fuels and Systems for Refuse Trucks, Presented to the Municipal Waste Management Association, March 2005 http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/37843.pdf
3. NGVTF Meeting Presentations, August 2005 http://www.nrel.gov/vehiclesandfuels/ngvtf/tech_comm_mtg_aug05.html

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1. *Energy Information Administration Annual Energy Review* (U.S. Department of Energy), 2002, www.eia.doe.gov/emeu/aer/contents.html.
2. *Transportation Energy Data Book*, Edition 23, Oak Ridge National Laboratory (U.S. Department of Energy), 2001, www-cta.ornl.gov/data/Index.html.
3. *U.S. Environmental Protection Agency Air Pollutant Emission Trends Web Site*, 2001, www.epa.gov/ttn/chief/trends/index.html.
4. *Assisting Transit Agencies with Natural Gas Bus Technologies* (U.S. Department of Energy), 2005, http://www.nrel.gov/vehiclesandfuels/ngvtf/pdfs/037921ng_bus.pdf.

IV.2 Recovery of Natural Gas from Renewable Resources

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Upton, New York 11973

DOE Technology Development Manager: Dennis Smith

Subcontractors:
Mack/Volvo; Allentown, PA
Acrion; Cleveland, OH
Air Products; Allentown, PA
Chart Industries; Burnsville, MN
Waste Management; Houston, TX

Objectives

- Support R&D projects to identify vehicle fuel quality issues when liquefied natural gas (LNG) is produced from landfill gas (LFG) which is derived from renewable sources.
- Develop LNG recovery from LFG technologies in order to displace over 3 million gallons of diesel fuel per year per landfill.
- Address climate change issues by minimizing methane release and improving overall system efficiency by integrating LFG collection, clean-up, and liquefaction with LNG storage and delivery.

Approach

- Install a 10 gallon per hour process development unit (PDU) at the Burlington, New Jersey, landfill for converting LFG into LNG.
- Produce 10,000 gallons of LNG from LFG for vehicle fuel quality evaluation.
- Disassemble and analyze for premature failures refuse truck engines that were fueled with LNG derived from LFG.

Accomplishments

- Performed regularly scheduled commercial collection of refuse using trucks fueled with the 10,000 gallons of continuously produced LNG from LFG.
- Trucks experienced no downtime related to fuel quality issues during the 600-hour road tests.
- Disassembly and examination of the engines indicated no evidence of premature wear, performance degradation, or the presence of compounds that could adversely affect engine operation, durability or reliability.
- Increased LNG production rate from 9.6 gallons per hour to 14.0 gallons per hour by allowing the CO_2 concentration in the LNG to increase while still keeping it below solubility limits.

Future Directions

No additional work is currently planned, but the following work could be considered if funds become available in the future.

- Gas separation studies could further improve the production rate of LNG from LFG. Figure 1 shows a 45.8% increase in production rate by better controlling the carbon dioxide and methane separation process.
- A LNG from LFG project costs from $10 to 15 million dollars. By issuing a $1 million dollar cost share request for proposal, DOE could direct this activity towards a "no atmospheric methane release" strategy in the recovery/use of LNG from LFG.
- Conduct a technical feasibility analysis to determine the number of active landfills and related refuse handling trucks & equipment in the U.S. that are good candidates for this technology. Identify potential project partners for an expanded field test or demonstration project.

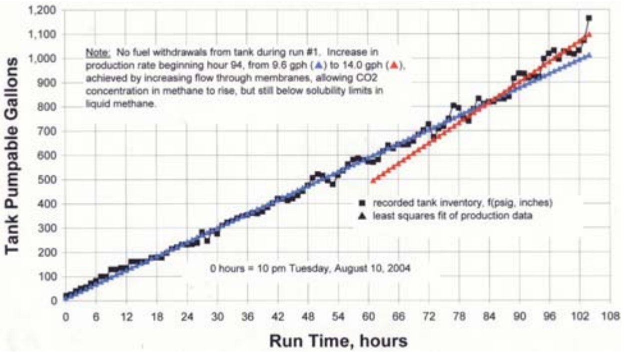

Figure 1. Liquid Methane Production Run #1 – August 10 to August 15, 2004

Introduction

This project reports the first sustained production and utilization of liquid methane from landfill gas which is derived from renewable resources. (LNG from LFG is more accurately referred to as liquid methane, since its composition is very low in the higher hydrocarbons such as ethane, propane, etc., when compared to LNG from pipeline natural gas.) Through the process of making LNG, the diluents in landfill gas such as CO_2 and N_2 are removed which lower heating value and limit its usefullness to non-transportation applications. The LNG production process removes virtually all the contaminants such as sulfur oxides associated with landfill gas. By making LNG, a low-value fuel is upgraded to an ultra-clean high value fuel suitable for transportation vehicles and heavy-duty equipment.

This new achievement in landfill gas processing took place at the Rutgers N.J. EcoComplex, located adjacent the Burlington County Landfill, Columbus, New Jersey. The landfill-derived LNG powered two Mack dedicated natural gas-powered refuse trucks owned and operated by Waste Management, Inc. The trucks saw daily service from the Burlington County Landfill to the Fort Dix Army Base and the McGuire Air Force Base. Each truck accumulated more than 600 hours of service and consumed about 10,000 gallons of LNG.

Approach

Acrion Technologies, Inc. has investigated production of liquid methane from landfill gas for more than a decade. During the past several years, with direction from Brookhaven National Laboratory and funding from DOE, these investigations have noticeably raised the confidence level of industrial stakeholders in the viability of Acrion's LFG cleanup technology. For example, the accomplishments listed in this report were a cooperative effort of Mack Trucks, Acrion, Waste Management, Air Products, Chart Industries, and the Burlington County, N.J., EcoComplex. The approach has been guided by Acrion's past successes. In 2001, an independent testing lab (Atlantic Analytical Laboratory, Whitehouse, N.J.) verified that Acrion's cleanup technology removed halogenated compounds, siloxane, sulfur and non-methane organic contaminates from landfill gas to levels below one part per million (ppm) aggregate (Table 1). At the request of Mack Trucks, these results were replicated in 2002. In 2003, Acrion designed and installed CO_2 removal and methane liquefaction to its PDU at the EcoComplex and first produced liquid methane from LFG on May 16, 2003. Upon the successful completion of these performance trials, the next step was the production of sufficient quantities of liquid methane using Acrion's technology. The goal is to operate refuse trucks for 600 hours in order to verify no adverse effects on the engines from running on LNG from LFG.

Table 1. Summary of Analytical Testing Performed by Atlantic Analytical Laboratory

Sample ID	Truck Fuel	Raw LFG	Truck Fuel	Truck Fuel
Sample Date	13 Aug 04	2 Dec 04	2 Dec 04	13 Jan 05
AAL Number	1352	2527-1rev	2527-2rev	2982
Test Performed				
Non Condensable Gases	3	3	3	3
Volatile Hydrocarbons	3	3	3	3
Siloxanes (by GC/MS)		3	3	
Volatile Sulfur Compounds	3			3
GC/MS TO-14 Target List	3			3
GC/MS Non TO-14 Target List	3			3
Toxic Substances Sub-17 Extended List	3			3
Analysis Overview				
Methane, CH_4	94.05%	57.13%	99.19%	98.55%
Carbon Dioxide, CO_2	0.12%	42.2%	ND	480 ppm
Nitrogen, N_2	5.81%	0.43%	0.73%	1.18%
Siloxanes	NA	1.2 ppm	ND	NA
Other	ND	390 ppm	10 ppm C_3	13 ppm C_3 3.2 ppm TX

Notes: NA not analyzed; ND not detected; TX toluene xylene

Results

Two dedicated natural gas refuse haulers ran daily service from October 19th, 2004, through January 27th, 2005, on LNG from the Burlington County Landfill. Each truck accumulated more than 600 hours engine time and consumed 10,000 gallons of LNG. Average fuel consumption in daily refuse collection service was about 7.5 gallons liquid methane per hour of engine operation. The trucks experienced no downtime related to fuel quality issues, and the drivers' comments were positive on several accounts: no odor, no smoke and reduced noise. LFG typically contains siloxanes that form silicates when burned in the combustion chamber, resulting in hard silicate plating on exhaust components. The silicates will accelerate engine wear if siloxanes are not removed from the LFG. Disassembly and examination of these engines produced no evidence of premature wear, performance degradation, or accumulation of deposits that could adversely affect engine operation, durability or reliability. Chlorinated hydrocarbons are also found in LFG that form acids and can attack engine bearings. No chlorinated hydrocarbons were found in the oils taken from these engines. Finally, it should be noted that the engine control system was operating as intended. This would suggest that there was no contamination to the fuel system or other sensor systems from using the processed LFG. Following the inspection, Mack engineers then reassembled the engines such that they retained the same warranty as new natural gas engines.

Conclusions

The first objective of demonstrating vehicle fuel quality of LNG from LFG was met. These results, when combined with diesel fuel prices exceeding $2.00 a gallon, have created a market-driven interest in using landfill gas derived from renewable resources to power LNG vehicles. The metric of "vehicles converted to alternative fuels" has been used in the past to assess the viability of DOE's alternative fuel program. The future metric is likely to be petroleum displaced. The conversion of 300 landfills to produce LNG can result in the displacement of over 1 billion gallons of diesel yearly. DOE also has the responsibility to see that this emerging LFG to LNG technology reduces and doesn't add to climate change concerns. Designs of LNG refueling stations must take into account that LNG is a "use it or lose it" fuel, and the atmospheric venting of methane by either the vehicle or refueling station has to be addressed before this technology can be successfully commercialized. Lastly, LNG from LFG has international appeal. DOE can, through its existing international partnerships, further develop and transfer a sustainable energy technology that is environmentally acceptable.

V Petroleum Displacement Fuels/ Fuel Blending Components

V.1 Operability Results of Class 6 Vehicles Operating on GTL Fuel with Catalyzed DPFs

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DOE Team Lead: Steve Goguen

DOE Technology Development Manager: Kevin Stork

Project Partners:
South Coast Air Quality Management District, Diamond Bar, CA
International Truck and Engine Corporation, Melrose Park, IL
Johnson Matthey, Inc., Malvern, PA
Shell Global Solutions (U.S.) Inc., Houston, TX
Yosemite Waters, Fullerton, CA

Objectives

- Assess real-world impact of gas-to-liquid (GTL) diesel fuel combined with catalyzed diesel particle filters (DPFs) on emissions, operability, and operating costs in a heavy-duty truck fleet, including fuel economy and maintenance costs.

Accomplishments

- Completed six-month operability analysis from fleet fueling and maintenance records.
- Demonstrated that a heavy-duty fleet vehicle using GTL fuel with a DPF has similar maintenance costs to such a vehicle using conventional fuels.

Future Directions

- Use successes from this project as basis for future projects evaluating larger fleets and new technology engines and emission control systems.

Introduction

Gas-to-liquid (GTL) fuel is a near-zero-sulfur and high-cetane diesel fuel that can be substituted for conventional diesel fuel. GTL fuel is an attractive alternative diesel fuel due to these premium fuel properties and the fact that the fuel can be produced from renewable and/or domestic resources like coal, biomass and natural gas.

Several studies have shown the emission reduction potential of GTL fuel in light- and heavy-duty engines and vehicles [1]. Emission control systems, which have been tested with GTL fuels, are expected to play an integral role in meeting upcoming emission regulations.

While the emission reductions for this fuel have already been proven, the impact on fleet operating costs has yet to be quantified. By collecting fleet fueling and maintenance records, the impact of the fuel on operations can be quantified.

Approach

A fleet of six vehicles was selected to participate in the project. The vehicles operated on a variety of city, suburban, and freeway routes delivering 5-gallon water bottles to residential and commercial customers. The vehicles were nominally identical and powered by 2001 model year International DT466 engines (195 hp and 525 ft-lb peak torque). Half of the vehicles were operated as-is on California Air Resources Board (CARB) specification diesel fuel with no emission control devices; half the vehicles were fueled exclusively with GTL fuel and retrofit with Johnson Matthey Catalyzed Continuously Regenerating Technology (CCRT™) DPFs. The fleet was operated from January to July, 2004.

Fleet maintenance and fueling records were collected and analyzed to determine maintenance costs for the fuel/filter technologies. Comparison and analysis of the records was used to determine if any fuel or filter related maintenance was experienced by the fleet. Additionally, the real-world fuel economy was determined through the fueling records. Emissions have been previously reported [2].

Results

Fueling records detailing the amount of each fill and miles traveled between fills were collected for analysis. The records were scrutinized for accuracy, and erroneous entries were purged from the data set. A confounding factor for the fuel economy for this fleet was the dedicated duty cycles for the vehicles. Each vehicle operated over a dedicated route with varying amounts of freeway and city driving, which influenced the fuel economy. On average, the fuel economy from the GTL-fueled vehicles was similar to that of the CARB diesel-fueled vehicles over the study period (Figure 1). Driver feedback on the GTL-fueled vehicles was overwhelmingly positive; the drivers noted similar performance characteristics with the GTL fuel and DPFs.

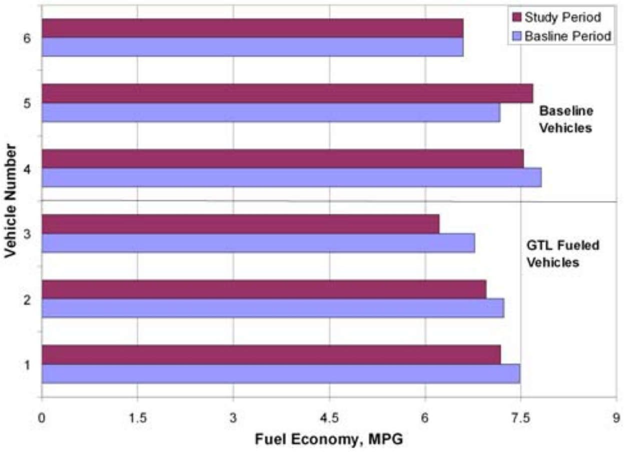

Figure 1. Fuel Economy for the Test Vehicles over the 6-Month Study Period

The fleet maintenance records were also evaluated, including preventative maintenance, unscheduled maintenance, and warranty events. The most significant event during the study period was the replacement of the starter in one of the vehicles. The starter for this vehicle was replaced twice during the study period. The cause of the failure was not related to the fuel or filter technology; therefore, costs associated with this repair were omitted from the data analysis. Beyond this event, four warranty items occurred which were remedied at no cost to the fleet. The results from the analysis indicated that the cost to maintain the CARB-fueled vehicles was \$0.03/mile and the cost to maintain the GTL fueled vehicles was \$0.02/mile. Start-up costs, such as filter procurement, and fuel costs were not considered in this analysis. Given the size of the vehicle fleet tested and the precision of fleet maintenance data, the costs to operate the CARB-fueled and GTL-fueled vehicles are similar.

Conclusions

A fleet of vehicles participated in a fleet test to determine the operating cost of GTL fuel with a DPF. These vehicles were compared to current in-use technology vehicles operating on CARB specification diesel fuel with no emission control systems. The fleet was evaluated for a period of six months, with chassis emissions data collection (previously reported). The results from the operability analysis indicate that the maintenance costs and fuel economy were similar for both groups of vehicles. Thus, the analysis indicates that exclusive of fuel costs, the cost of operating these vehicles with GTL fuel and DPFs is similar to the cost with conventional fuels and technology. The emissions and operability impact of GTL fuel on current technology vehicles has been proven. Future research should verify similar results for vehicles with advanced technology meeting future emissions standards.

FY 2005 Publications/Presentations

1. "Performance of GTL Fuels: Fuel-Engine Compatibility and Achieving Low Emissions", presented to Fuels Technologies Merit Review, Denver, CO, March 2005.
2. "Comparison of Two Rounds of Chassis Emission Testing from a Fleet of Class 6 Trucks with GTL Fuel and Catalyzed DPFs", poster presentation at 15th CRC On-Road Emissions Workshop, San Diego, CA, April 2005.
3. Alleman, T.L., Barnitt, R., Eudy, L., Miyasato, M., Oshinuga, A., Corcoran, T., Chatterjee, S., Jacobs, T., Cherrillo, R.A., Clark, N., Wayne, W.S., "Final Operability and Chassis Emissions Results from a Fleet of Class 6 Trucks Operating on Gas-to-Liquid Fuel and Catalyzed Diesel Particle Filters", SAE Technical Paper No. 2005-01-3769, 2005.

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2. Alleman, T.L., Eudy, L., Miyasato, M., Oshinuga, A., Allison, S., Corcoran, T., Chatterjee, S., Jacobs, T., Cherrillo, R.A., Virrels, I., Nine, R., Wayne, S., Lansing, R., "Fuel Property, Emission Test, and Operability Results from a Fleet of Class 6 Vehicles Operating on Gas-to-Liquid Fuel and Catalyzed Diesel Particle Filters", SAE Technical Paper No. 2004-01-2959, 2004.

V.2 Biodiesel Quality and Stability

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DOE Technology Development Manager: Dennis Smith

Subcontractors:
Magellan Midstream Partners, Kansas City, Kansas
Southwest Research Institute, San Antonio, Texas

Objectives

- Insure that biodiesel is of adequate quality and stability.

Approach

- Conduct a nationwide survey of biodiesel blend (B20) quality and stability.

Accomplishments

- Completed nationwide assessment of biodiesel (B20) quality and stability.
- Identified a significant issue with blending of biodiesel to form homogeneous mixtures.
- Identified potential issues with peroxide formation and low water interfacial tension that require further investigation.

Future Directions

- Complete nationwide survey of B100 and B20 quality and stability, applying lessons learned from 2004 and 2005 surveys.
- Complete a detailed study of oxidation stability of B100, B20, and B5 with the objective of determining the best test method and specification limits.

Introduction

Biodiesel consists of fatty acid methyl esters produced from vegetable oils, animal fats, and waste cooking oil via transesterification with methanol. The primary feedstocks for biodiesel in the United States are soybean oil and waste cooking oil (yellow grease). Approximately 94 million liters (25 million gallons) of biodiesel were consumed in the United States during 2001 [1], with estimates of current consumption in the range of 75 million gallons annually. The current annual production potential for biodiesel based on feedstock supplies is estimated at 5.8 billion liters (1.5 billion gallons) [2] from an analysis assuming high petroleum fuel prices that create strong demand for a renewable replacement. Life cycle analysis indicates that biodiesel is truly renewable and its use, therefore, produces real reductions in petroleum consumption and carbon dioxide emissions [3]. Thus, biodiesel holds the potential to displace on the order of 5% of on-road diesel fuel, consistent with the Office of FreedomCAR and Vehicle Technology (OFCVT) program goals for fuels R&D.

To insure adequate fuel quality, biodiesel (B100) intended for blending in the United States must meet the requirements of American Society for Testing and Materials (ASTM) Standard D6751. However, at present there is no quality specification for 20%

biodiesel blends (B20), the current most common blend level. This study examined the quality of B20 samples collected nationwide in order to provide data relevant to development of a new ASTM specification.

Approach

Fifty sites using B20 from across the country were selected to participate in the B20 quality survey. The basis of selection was two-fold: to represent the range of weather-related operating environments across the U.S. and to represent all of the U.S. major (greater than one million gallon annual production) biodiesel producers. However, samples were collected in August and September of 2004, so the survey does not reveal properties relevant to wintertime operation.

The test plan consisted of tests or properties to be measured for the B20 samples, as shown in Table 1. Magellan Midstream Partners performed all tests except oxidation stability by Rancimat. Robert Bosch Corporation and Southwest Research Institute supplied replicate Rancimat data sets. In addition, Parker-Racor supplied interfacial tension measurements. The National Biodiesel Board's B20 Fleet Evaluation Team, a committee of primarily automotive industry technical experts, proposed this list of tests.

Table 1. Tests conducted for B20 samples

Property	Test Method
Water and Sediment[a]	ASTM D2709
Visual Appearance	ASTM D4176 Procedure 2
Acid Number	WLS-102 (Field Acid Number)
Kinematic Viscosity	ASTM D445
Silver Strip Test	IP227
Peroxide Number	ASTM D3703
Oxidation Stability	EN14112 (Rancimat)
Water Extraction	GM Test Method
Density	ASTM D4062
Carbon Residue	ASTM D524
Biodiesel Content	FTIR Method
Cloud Point	ASTM D2500
Distillation (T90)	ASTM D86
Sulfur Content	ASTM D5453 or D2622, as appropriate

[a] Test to be conducted only if D4176 haze rating is significant

Results

Results for the following tests showed no reason for concern (i.e., they met D975 requirements for No. 2 diesel or were otherwise within normal range): Water and Sediment, Visual Appearance, Kinematic Viscosity, Silver Strip Corrosion, Density, Acid Number, Cloud Point, and Carbon Residue. The results for the balance of the tests conducted are discussed in more detail below, with full results available at NREL's website [4].

Biodiesel Content

Figure 1 shows results of biodiesel content determination for the 50 B20 quality survey samples. Thirty-two of the samples were nominally B20 (between 18 and 22 percent biodiesel), while the remaining 18 samples exhibited biodiesel content from 7% to 98%. We believe that this indicates a serious issue with biodiesel blending practices.

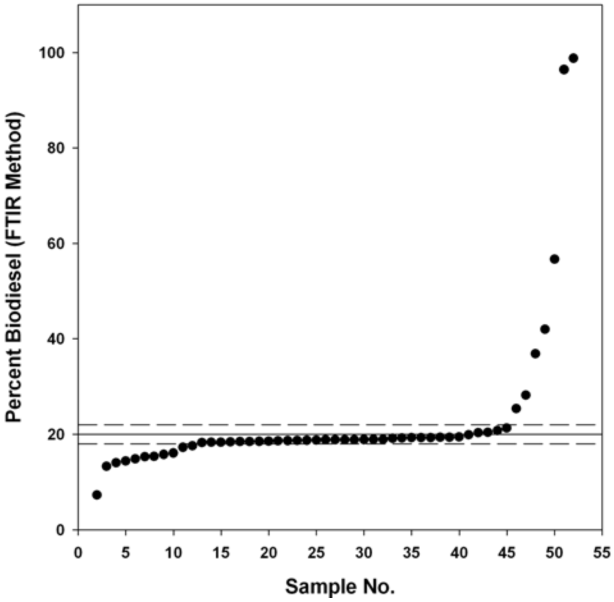

Figure 1. Percent Biodiesel Content for B20 Quality Survey Samples

However, it should be noted that no specific protocol was followed for the collection of these samples. Most blenders prepare blends by so-called splash blending, where the blends are prepared by pumping biodiesel and petroleum diesel sequentially into a tank (typically a transport truck or storage tank). Apparently, in many cases, a homogeneous mixture of biodiesel and petroleum diesel is not being obtained. Because B100 is slightly more dense than petroleum diesel, a poorly blended tank will have a high biodiesel content on the bottom of the tank and a low biodiesel content at the top of the tank.

While the use of blends containing less than 20% biodiesel is not a concern from a maintenance and durability standpoint, the use of blends with dramatically high biodiesel content can cause serious issues. The National Biodiesel Board is currently working with biodiesel producers and blenders to make sure that proper blending procedures are followed. These primarily involve insuring that adequate splashing or turbulence is occurring during blending. As the industry grows, a transition from splash blending to in-line blending should occur and will eliminate this problem.

Distillation

Figure 2 shows 90% recovery distillation temperatures (T90) for the survey samples. Many of the B20 samples meet the 338°C (640°F) upper limit for No. 2 diesel fuel, but a significant fraction do not. This suggests that any future B20 quality specification will require a slightly higher T90 limit than is currently used for No. 2 diesel.

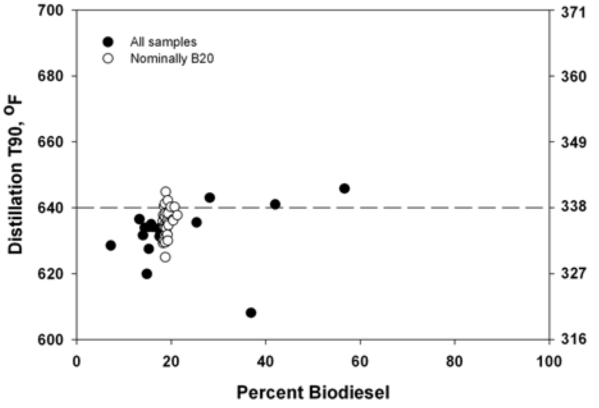

Figure 2. Distillation Results (ASTM D86) for B20 Quality Survey Samples (horizontal dashed line shows upper T90 limit for No. 2 diesel fuel)

Peroxide Value

Figure 3 shows results of peroxide value measurements for the quality survey samples. Peroxides can form as a result of biodiesel or petroleum diesel oxidation, and ultimately can decompose yielding aldehydes, acids, and polymers. They are of concern because of the potential to form acids and deposits, and also because certain fuel system plastics and elastomers may degrade in the presence of certain types of peroxides. The results show a broad range of peroxide content from values less than 10 which are not of concern to values of several hundred.

While these high peroxide values may raise significant issues, there are a number of unanswered questions that must be answered in order to understand their significance. First, we do not know the peroxide content of a typical diesel fuel, nor do we know the tolerance of diesel fuel system elastomers/plastics to diesel fuel derived peroxides. Second, this method for measuring peroxides was not developed specifically for biodiesel or biodiesel blends but for testing of gasoline and jet fuel. Thus, it is possible that the reported high peroxide values are an experimental artifact of applying this method to a substance for which it was not intended and that peroxide levels are not, in fact, this high. Research to answer these questions is currently ongoing. Additionally, in the near future, the B100 quality specification will be modified to include an oxidation stability requirement. This will presumably prevent or limit the potential for peroxide formation.

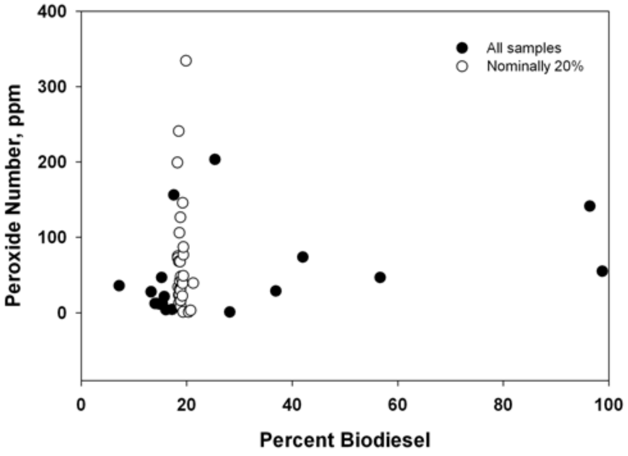

Figure 3. Peroxide Value (or number) Determined by ASTM D3703 for Quality Survey Samples

Interfacial Tension

Parker-Racor kindly supplied the results for interfacial tension. These tests were conducted using ASTM D971 Interfacial Tension of Oil Against Water by the Ring Method. Results of water interfacial tension (IFT) measurements are shown in Figure 4. Having an adequately high interfacial tension is required for on-board vehicle water separators that operate based on coalescence. A coalescer that operates in the upper 95% efficiency range in high interfacial tension fuel (around 30 dynes/cm) may show a decrease in efficiency by up to 30% as the IFT decreases below 25 dynes/cm depending on the type of medium being used in the coalescer (per SAE J1488). So, coalescence as a mechanism for water separators (which most water separators depend on) is highly influenced by fuel chemistry (i.e., IFT).

Of the 33 samples analyzed, only six displayed interfacial tensions above 15 dynes/cm. There were 13 samples that had IFTs at or below 10 dynes/cm. Of the six samples that had IFTs over 15 dynes/cm, the highest was only 19.5 dynes/cm. Water separation from diesel fuel begins to become unpredictable below 25 dynes/cm. In areas where there is not much water in fuel, it would probably not be noticed. In areas where there is often water in diesel fuel, this could lead to higher injector maintenance costs, over long periods of time, than previously experienced using diesel fuels with higher interfacial tension.

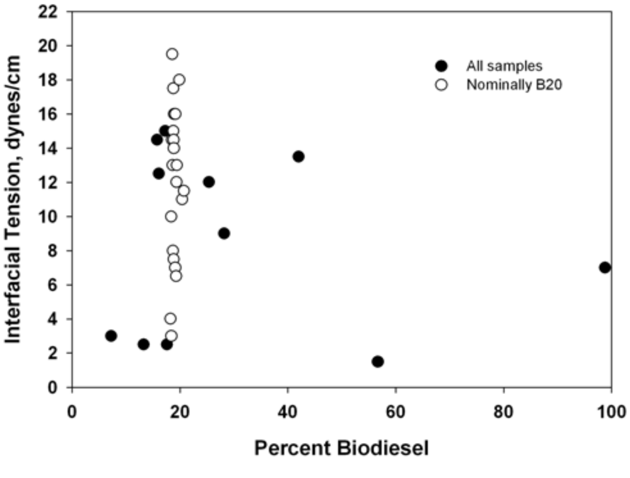

Figure 4. Results of Water Interfacial Tension Measurements by ASTM D971 for B20 Survey Samples

Thus, these results are a serious concern, but there are a number of outstanding questions. It is possible that the low IFT is caused by highly polar compounds in the biodiesel blends such as the peroxides noted above. Implementation of an oxidation stability requirement would be expected to mitigate the problem of low IFT as well. Also, it is possible that other types of coalescer media and other types of water removal devices could be implemented. This might include the installation of specifically designed water separation filters/devices at the fuel dispenser nozzle for separation of water prior to pumping into the vehicle fuel tank.

Oxidation Stability by Rancimat

Southwest Research Institute performed the Rancimat test and provided 20 replicate results for a peanut oil standard showing a mean of 5.04 hr, standard deviation of 0.22 hr, and 95% confidence interval of +/-0.1 hr. A striking feature of these results is evident from the frequency plot of Figure 5. Twenty-one out of the thirty-six samples tested exhibited induction times of less than 2.5 hr. Much longer induction times were anticipated based on the very long times typically reported for petroleum derived diesel fuel, which makes up a large fraction of the composition of these samples. The short induction times may have been observed because of the age of these samples when tested. The samples were collected in September and October of 2004 and most analyses were conducted soon after. However, the Rancimat measurements were made in March and April of 2005, roughly 6 months later.

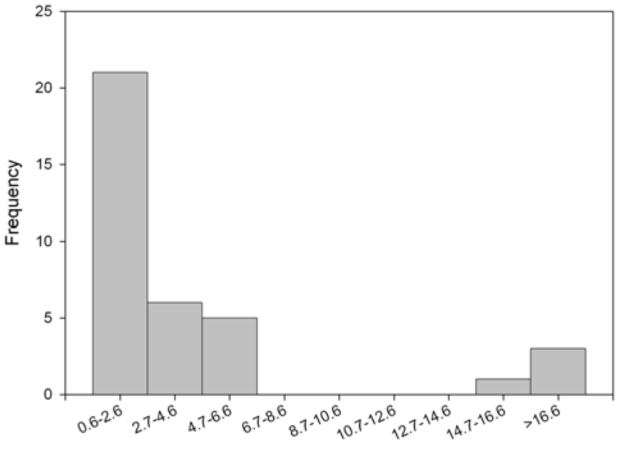

Figure 5. Frequency Distribution for B20 Rancimat Stability Test Results

Although these small samples were stored in an air-conditioned laboratory environment in sealed containers, the "oxidation reserve" of these samples may have been depleted during this time. It is recommended that in future quality surveys all tests be conducted within one month of sample collection.

Conclusions

Because no fuel quality specification currently exists for B20, we cannot compare the results of this survey to standard requirements. Most of the properties examined showed acceptable levels for use in diesel engines. However, the survey data point to a number of issues and potential issues. Chief among these is the biodiesel content of the supposedly B20 samples. Only 32 out of the 50 samples contained nominally 20% biodiesel. The cause of this is believed to be inadequate mixing during splash blending of these fuels. This result is being made widely known to the biodiesel industry in hopes that education on proper blending procedures can solve this problem.

Additionally, many of the B20 samples exhibited high levels of peroxides. This is of concern because certain vehicle fuel system components are made of materials that may not be compatible with peroxides. However, this contention is based on experience with gasoline, and the peroxides that form in biodiesel are chemically much different, having a much higher molecular weight. It is not known if biodiesel peroxides will produce the same effects on fuel system materials. Furthermore, it is widely agreed that the B100 specification, and perhaps the B20 specification, should include an oxidation stability requirement. Should such a requirement be implemented, it seems highly likely that antioxidant additives would be used to meet it, resulting in much lower potential for peroxide formation.

The B20 samples exhibited low interfacial tension with water when tested using the ring method. A minimum level of interfacial tension is required for the proper performance of water separators that are used in engine fuel systems to protect the engine from water in the fuel. There are a number of potential causes of this problem, including the presence of highly polar materials such as peroxides in the biodiesel. Thus, this is another issue that might be resolved by implementation of an oxidation stability requirement.

The B20 samples were tested for oxidation stability by the Rancimat method. Many of the samples exhibited induction times of less than 2 hours; however, the samples had been stored for on the order of 6 months prior to the oxidation stability measurements. Thus, it is not clear if the short induction times are intrinsic properties of these samples or are caused by the relatively long storage time where the samples' capacity to resist oxidation was consumed.

Future surveys of B20 quality should insure that all tests are conducted within one month of sample collection. Additionally, future surveys should include other oxidation stability tests such as ASTM D2274.

FY 2005 Publications/Presentations

1. McCormick, R.L., Alleman, T.L., Moens, L., Ratcliff, M., Lawrence, R. "Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004," National Renewable Energy Laboratory, NREL/TP-540-38836, October 2005 http://www.nrel.gov/docs/fy06osti/38836.pdf.

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4. McCormick, R.L., Alleman, T.L., Moens, L., Ratcliff, M., Lawrence, R. "Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004," National Renewable Energy Laboratory, NREL/TP-540-38836, October 2005 http://www.nrel.gov/docs/fy06osti/38836.pdf.

V.3 Resolving Barriers and Showing Incentives for Non-Petroleum Fuels in Near-Term Uses – Oil Sands Fuels Characterization

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Objectives

- Research and experiments will be conducted to clear any barriers to use of non-petroleum based fuels (NPBF) in the near-term
- Develop or implement analytical methods for identifying unique components of NPBFs, including fuels from the Athabascan Oil Sands

Approach

- Establish relationships with Canadian counterparts for research on fuel properties
- Develop separation methods for cycloparaffinic compounds
- Develop identification methods for cycloparaffins and other unique compounds
- Determine fuel chemistry and property effects on engine performance, including combustion, lubricity, and emissions controls performance

Accomplishments

- Utilized blended oil sands fuel for operation of a light-duty diesel equipped with a NOx adsorber catalyst using in-cylinder regeneration modes
- Separated oil sands fuel fractions with large column chromatography
  - Urea crystallization used to remove alkanes
- Developed a combination of electron impact (EI) and chemical ionization (CI) mass spectroscopic (MS) methods for identification of fuel components
- Utilized oil sands blend in advanced engine and emissions systems

Future Directions

- Extend chemical analysis to several upgrader streams of oil sands fuels
  - Relate to parallel characterization at other national laboratories
- Research engine performance with the same fuel streams in normal and advanced combustion modes to understand potential fuel chemistry effects
- Identify other near-term NPBFs such as shale-derived fuels for analysis
- Report in the literature on findings

Introduction

As a key ingredient of national energy security, DOE wishes to utilize NPBFs to the extent possible. However, if substitution is hurried and problems arise with engines or vehicles, the substitution process can be set back. Some properties of NPBFs may actually be found that provide incentive for their use. An emissions benefit from an NPBF additive would be an example. However, regulated and unregulated emissions from NPBFs must be evaluated to ensure that no new toxic emissions are produced. Reliable, thorough data regarding the benefits and issues of NPBFs need to be developed before these fuels will be adopted.

As an example of a NPBF, the synthetic crudes derived from Athabascan heavy crude are already making an impact on the Nation's energy supply. Canada is the largest supplier of crude oil to the U.S. and their present production of Athabascan heavy crude represents around 40% of their total crude oil production. Canada exports between 80 and 90% of their crude oil production to the U.S. and it is likely that oil sands liquids will represent an increasing portion of our transportation fuel..

The composition of Athabascan heavy crude differs from other crude oil sources, most notably in the large percentage of unsaturated hydrocarbon and aromatic species present in the heavy crude. This requires the crude to be hydro-treated before shipment to U.S. refineries. This treatment results in a higher-than-normal concentration of cycloparaffins among other products. The high percentage of cycloparaffins affects downstream refining procedures and fuel quality, generally increasing energy requirements for fuel production. If, instead, combustion parameters can be modified to exploit the cycloparaffins, then less refining energy would be required. A thorough chemical understanding of fuels derived from heavy crude can help guide optimization of combustion in future engine designs. Basic chemical composition of diesel fuel can be classified into four groups: paraffins, isoparaffins, cycloparaffins and aromatics. The determination of the types and quantity of cycloparaffin configurations in this diesel fuel is an important variable and should be considered when characterizing this fuel.

Approach

We propose the following protocol for the quantification and identification of cycloparaffins.

Separation of Cycloparaffins: Because cycloparaffins have the same molecular weight and similar boiling points as straight-chain alkanes and alkenes, it can be challenging to separate and identify these compounds in a complex mixture such as diesel fuel. Using ASTM Method 2549-91, diesel fuel is separated into two groups: paraffins and aromatics. The paraffin mixture can be further separated into n-paraffins, isoparaffins and cycloparaffin groups. The differences in solubility of cycloparaffins and paraffins in solutions of urea and thiourea can be exploited to separate the compound classes [1]. The crystallization of urea from solution selectively removes paraffins. The remaining solution of isoparaffins and cycloparaffins can be further separated using thiourea.

Identification of cycloparaffins: Cycloparaffins can be identified by mass spectroscopy (MS) or nuclear magnetic resonance (NMR) spectroscopy. MS is the most promising method due to the flexible ionization techniques and small sample volumes required. Using a soft ionization technique such as chemical ionization, the molecular weights of these cycloparaffins may be determined. A higher-energy ionization technique, such as electron ionization, would result in fragmentation patterns that provide insight into the molecular structure. MS analysis would also relax separation requirements due to the uniqueness of mass spectrum or molecular weight for different groups of these compounds. Due to differences in ionization efficiency, quantification using standards of the compounds of interest must be done.

With NMR, the determination of the chemical structure could be accomplished by proton or ^{13}C probes, and the quantity could be calculated by integrating the area of the signal. Problems with the NMR technique may lie in the typical concentrations needed for detection. Typically, a concentration in the high parts per million is required. An additional drawback is associated with the difficulty in interpreting mixtures possessing the same basic structure, although the newest, high-resolution NMRs may overcome this challenge.

As part of the determination of near-term suitability of NPBFs, Oak Ridge National Laboratory (ORNL) will evaluate the performance of NPBFs in advanced engine systems, including homogeneous charge compression ignition (HCCI) engines, and advanced diesel aftertreatment systems. Engine experiments with full-size catalysts will feature hydrocarbon (HC) speciation to characterize different regeneration and desulfation strategies and their effects on the NOx adsorber performance.

Results

Thus far, the urea crystallization separation and analyses with gas chromatography (GC)/MS have been completed for a blended oil sands fuel. Figure 1 illustrates the total ion chromatograms for the oil sands fuel and ECD1, a low-sulfur test fuel produced by BP Amoco between 2001 and 2003. Note that the envelope and boiling range look very similar for these fuels. The difference between the fuels is that the oil sands fuel has cycloparaffins whereas the ECD1 has mainly branched alkanes in addition to the *n*-alkanes. In Figure 2, the same fuels are compared after urea encapsulation, which removes the *n*-alkanes. Note that the envelope of the ECD is much smaller due to its paraffinnic content being removed, where as the extended envelope of the oil sands fuel indicates a broader base of compounds.

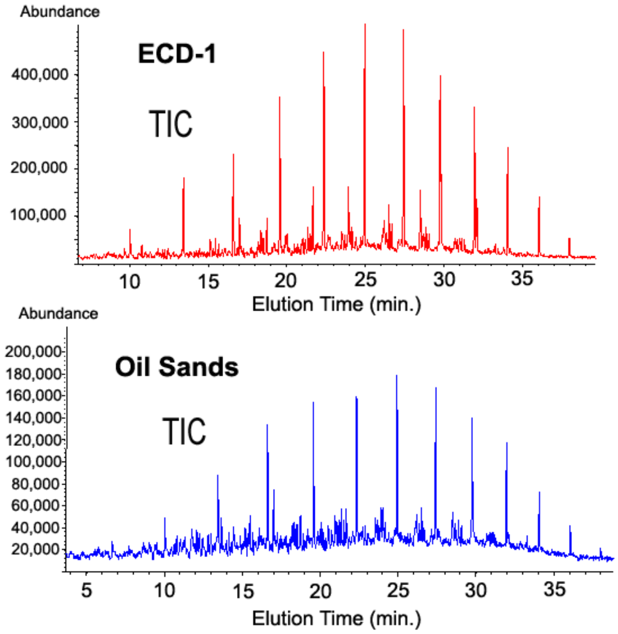


Figure 1. Gas chromatograms of (a) ECD1, a low-sulfur refinery fuel from petroleum sources, and (b) an oil sands blend provided to ORNL by Natural Resources Canada. TIC is total ion counts, indicating the combined signal of all of the ions measured by the mass spectrometer.

These chromatograms were obtained with the MS in electron impact (EI) ionization mode.

Because the cycloparaffins can have the same base molecular mass as olefins, it was necessary to distinguish between them. Chemical separation can be effected with thiourea crystallization, but it was desirable to use an analytical technique that directly distinguished without further preparatory steps. By using a mass spectrometer in positive chemical ionization (CI) mode with CH_4, the two classes of compounds produced different molecular ions. CI of cycloparaffins produces a strong $(M-1)^+$ peak, that is, a molecular ion with a mass 1 less than the molecular weight of the compound. CI of olefins produces a strong $(M+1)^+$ peak, a molecular ion with a mass 1 greater than its molecular weight [2]. Figure 3 illustrates the importance of the distinction. Note that the EI spectra of the two adjacent peaks, representing two distinct compounds, have the same molecular ion of 166. The fragmentation patterns are different, but the first peak could still represent a branched olefin, for instance. The CI spectra show the differences, with the first peak having a $(M-1)^+$ ion of 165, and the second peak having a $(M+1)^+$ ion of 167 present. The first peak is a cycloparaffin, dimethyl decalin, while the second peak is an olefin with two double bonds. Figure 4 shows the different molecular structures of decalins found in the oil sands blend.

The differences in molecular structure notwithstanding, the oil sands blend has similar fuel properties to many of the hydrogen-rich fuels

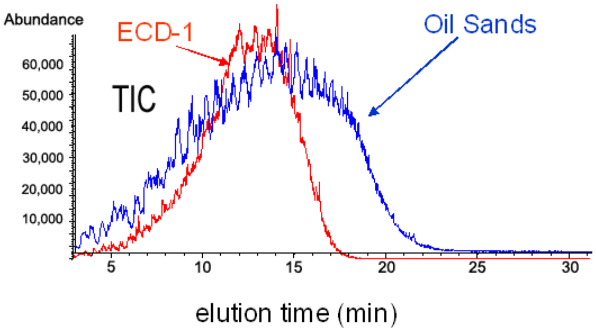


Figure 2. A comparison of ECD1 and the oil sands fuel after treatment by urea encapsulation to remove *n*-alkanes.

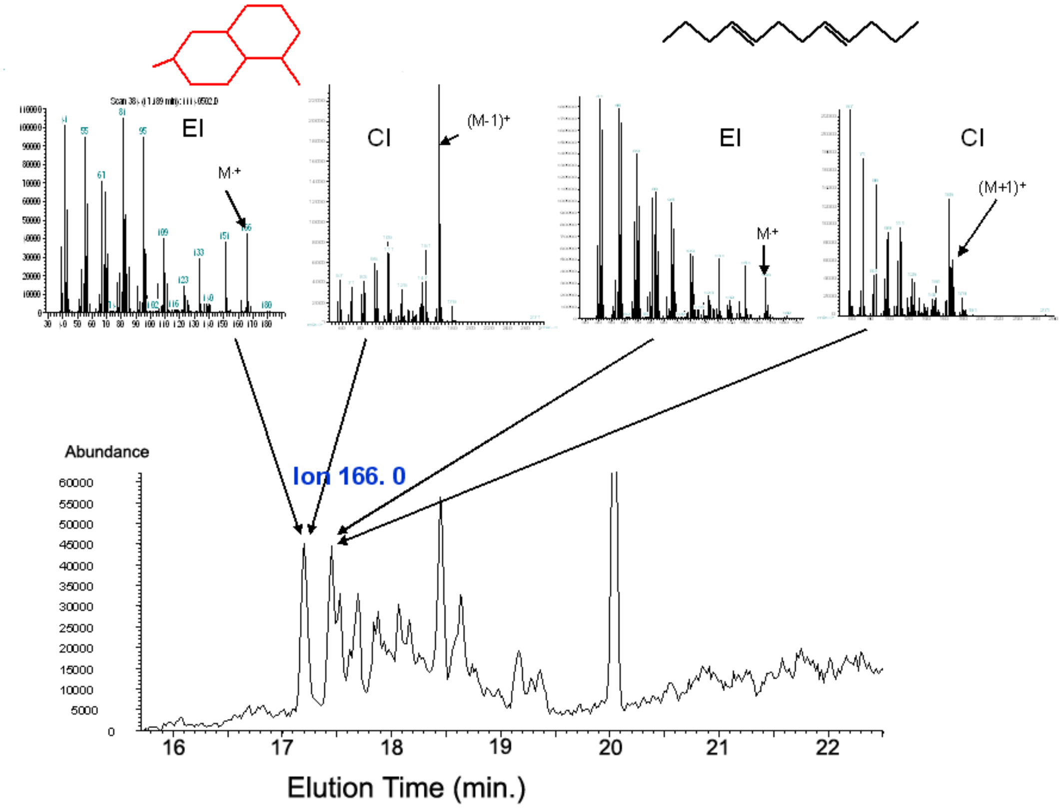
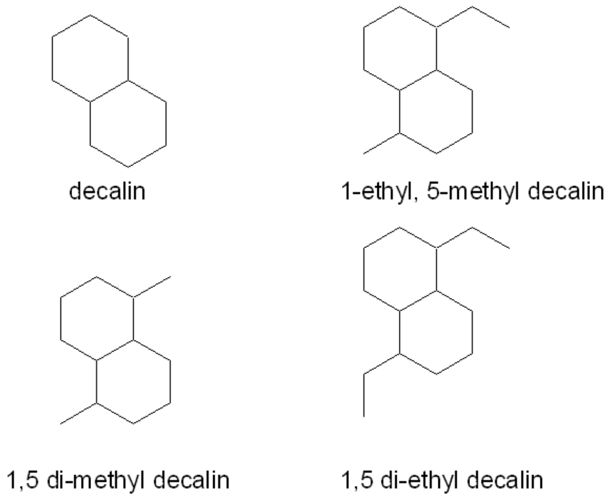


Figure 3. A comparison of EI and CI spectra of two compounds in the oil sands fuel. The compounds are of the same molecular weight.

expected to meet the 2006 standard for S content. At ORNL, this fuel was used in a single-cylinder research engine as part of a study of cetane effects on HCCI combustion. The performance of the fuel in this engine was consistent with traditional petroleum-based fuels of similar cetane number.



decalin

1-ethyl, 5-methyl decalin

1,5 di-methyl decalin

1,5 di-ethyl decalin

Figure 4. Substituted Decalins Found in the Oil Sands Fuel

The oil sands fuel was also used in a 1.7L four-cylinder diesel engine operating in high-efficiency clean combustion (HECC) modes. It behaved similarly to the BP15 test fuel, which has similar distillation properties, cetane and sulfur level under these combustion conditions. In a third ORNL study, the oil sands blend was incorporated into a fuels study of NOx adsorber regeneration. During the "rich" regeneration period of a NOx adsorber system, ORNL has shown that different fuel chemistries generate different exhaust species [3], and the question was whether or not these differences affected NOx reduction performance. Under the particular engine conditions studied, the oil sands fuel was found to perform very similarly to BP15 for two different rich-lean regeneration intervals. Figure 5 illustrates the comparison for short and long regeneration intervals at the same steady-state operating point.

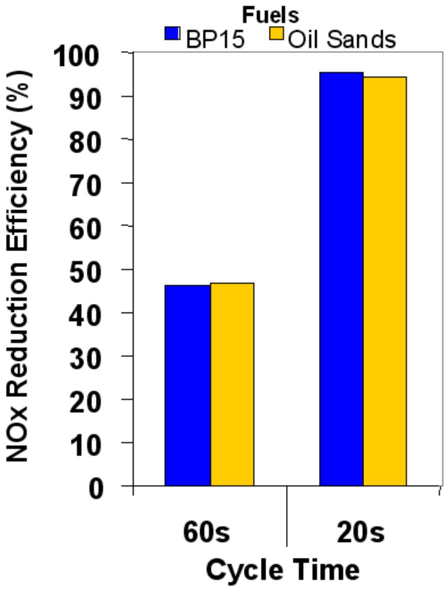


Figure 5. A comparison of NOx conversion performance for a light-duty engine equipped with a NOx adsorber system for two different ultra-low sulfur fuels.

Conclusions and Future Effort

The fuels analysis work demonstrated a reasonable method for determining the cycloparafinnic compounds in fuels derived from the Athabascan Oil Sands. Several derivatives of decalin, the base 10-carbon cycloparaffin, were identified. Additional methods using multi-dimensional chromatography as well as derivatization for liquid chromatographic separations will be investigated.

In terms of near-term usage in advanced engine systems, the oil sands blends tested performed in close accordance with bulk fuel properties such as cetane and distillation range in a single-cylinder HCCI engine, during HECC modes in a four-cylinder engine, and during NOx regeneration studies. Our continuing combustion projects plan to include oil sands and other NPBFs in the matrix.FY 2005 Publications/Presentations

FY 2005 Publications/Presentations

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VI New Technology Impacts

VI.1 Weekend Ozone Effect Studies

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Objectives

- Ambient ozone (O_3) levels in southern California are about 50% higher on Sundays than on mid-week days. The objective of this study is to identify whether this phenomenon exists in other parts of the U.S. that experience violations of the national ambient air quality standard for ozone.
- This project will characterize day-of-week differences in:
  - ambient concentrations of primary pollutants, including nitric oxide (NO), oxides of nitrogen (NOx), speciated volatile organic compounds (VOCs), carbon monoxide (CO), and black carbon (BC);
  - ambient concentrations of ozone and particulate matter (PM) nitrate;
  - responses of ozone and PM nitrate concentrations to changes in the ambient concentrations of primary pollutants.

The principal focus is on the gas-phase species NO, NOx, CO, VOCs, ozone, and PM nitrate.

Approach

The analyses were carried out at ambient air quality monitoring sites in ozone problem areas in 23 states: the Northeast corridor (including the New York-Northern New Jersey-Long Island, Philadelphia-Wilmington-Trenton, and Baltimore-Washington metropolitan areas); the Gulf of Mexico coast (including the Houston-Galveston-Brazoria and Beaumont-Port Arthur and Baton Rouge metropolitan areas); Dallas-Fort Worth; Phoenix; and the Colorado Front Range area (including Denver, Colorado Springs, Boulder, and Fort Collins). Previous work carried out for the Atlanta area and for six Midwestern states (Ohio, Michigan, Indiana, Illinois, Missouri, and Wisconsin) was also incorporated in this study. The time period analyzed was 1998 through 2002 (or 2003 where data were available).

Accomplishments

- Completed analysis of 1998-2002 or 2003 ambient ozone precursor and ozone data from many U.S. monitoring locations.
- Wrote and sent draft report to air quality staff in the regions/states studied for technical comments and peer review. The report was sent to the states of Arizona, Texas, and Colorado; Northeast States for Coordinated Air Use Management; Mid-Atlantic Regional Air Management Association; and the Lake Michigan Air Directors Consortium.
- Submitted paper summarizing study results to the *Journal of the Air & Waste Management Association* for peer review and subsequent publication.

Future Directions

- Began proximate ozone modeling study in southeast Michigan region in November 2005, in collaboration with state and local government groups and industry representatives in that area.

Introduction

The occurrence of generally comparable – or even higher – ambient concentrations of ozone on Saturdays and Sundays than on other days of the week is commonly known as the "weekend effect for ozone," or, simply, the "weekend effect." Because emissions of ozone precursors, including volatile organic compounds (VOC), oxides of nitrogen (NOx), and carbon monoxide (CO), are lower on weekends than on weekdays, the weekend ozone effect is counterintuitive. To provide a better understanding of the implications of the weekend effect, a thorough analysis of weekday and weekend precursor concentrations and composition is needed. Observed in air quality data from the mid-1960s and early 1970s, the weekend effect in California recently has been studied at length. Fujita et al. [1] and Lawson [2] conclude that weekend reductions of NO emissions are the most important factor leading to higher weekend ozone, allowing ozone to accumulate earlier in the day and to reach higher concentrations compared with weekdays, and that proposed alternative hypotheses are not supported by ambient data and do not explain the weekend effect in southern California. In contrast, Croes *et al*. [3] considered the available air quality data and photochemical models inadequate to conclusively determine the causes of the weekend ozone effect in southern California.

This study provides further analysis of the weekend ozone effect in areas of the United States outside California. The weekend ozone effect provides air quality managers and scientists the opportunity to make empirical observations of the kind that are so important in testing hypotheses by asking "What if" questions regarding emission reductions that are needed to reduce ambient O_3 levels. Seldom are such opportunities available using ambient data regarding how the atmosphere actually responds to changes in emissions because most air quality regulations provide small incremental benefits and take effect over long periods of time.

Approach and Results

Ambient air quality monitoring data were analyzed to evaluate the differences between mean day-of-week ambient concentrations of ozone precursors (NO, NOx, CO, and VOC) using 1998-2003 ambient air-pollutant data from monitoring sites in 23 states in New England, the Midwest, the mid-Atlantic, and isolated urban areas in the western and southern U.S. During the months of March through October, median decreases of NO, NOx, and CO at 6 a.m. Sundays compared with 6 a.m. Wednesdays were 71, 58, and 42 percent, respectively, as shown in Figure 1. The median

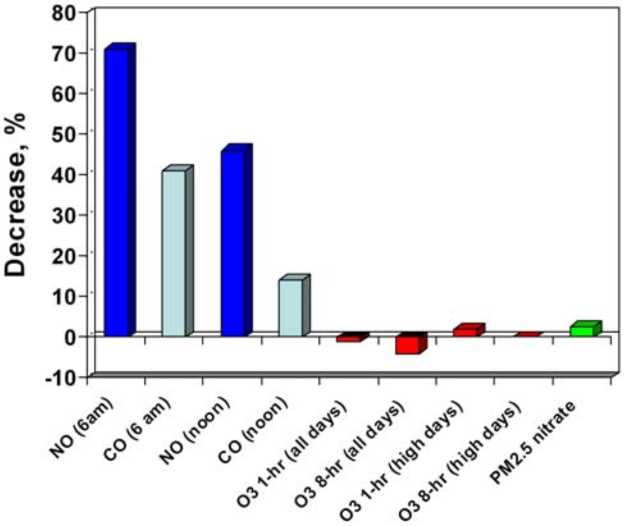

Figure 1. Median ambient pollutant concentration decreases from Wednesdays to Sundays. Results are shown for morning and noon concentrations of NO, NOx, and CO (March – October), and for 1-hour and 8-hour peak ozone concentrations on all ozone-season days (March – October) and on high-ozone days (top three peak days per day of week per year). PM nitrate levels are obtained from 24-hour sampling periods. Positive values represent higher Wednesday concentrations; negative values indicate that concentrations were higher on Sundays than on Wednesdays. The time period analyzed was 1998 through 2003.

declines of NO, NOx, and CO at 12 noon Sundays compared with 12 noon Wednesdays were 46, 40, and 12 percent, respectively. The Wednesday/Sunday PM nitrate median decline at 69 sites was 2.6%, with the difference statistically significant at only one location.

The large reductions in ambient concentrations of ozone precursors on weekends did not produce meaningful reductions of ambient ozone levels. To the contrary, median 1-hour and 8-hour ozone daily maxima on Sundays increased by 1 and 3 percent, respectively, from their mean peak levels on Wednesdays. When restricted to high-ozone days, the median 8-hour ozone daily maxima were unchanged on Sundays compared with Wednesdays, while the median 1-hour peak ozone levels decreased by 2 percent from Wednesdays to Sundays.

The changes observed in weekend ozone levels relative to weekday concentrations were the net result of weekday/weekend differences in a number of processes affecting ozone formation, including emissions, ozone transport, and local ozone formation:

- Ozone accumulation began about one hour earlier on Sundays than on Wednesdays. Ozone can accumulate only after NO concentrations fall to low levels.
- Regional ozone levels contributed the majority of the peak ozone concentrations measured downwind of four urban areas where ozone transport was studied in detail (Atlanta, Chicago, Dallas-Fort Worth, and Phoenix).
- Statistically significant day-of-week differences in ozone levels did not occur at either upwind or downwind locations. Ozone concentrations averaged about 5 to 10 ppbv lower on Sundays than on Wednesdays upwind of Atlanta, Chicago, and Phoenix; none of these differences were statistically significant, and no day-of-week transport differences were observed for Dallas-Fort Worth. Data from the Houston area are depicted in Figure 2.

Conclusions

The weekend ozone effect provides a natural experiment for understanding how urban ozone and PM nitrate respond to large reductions in ozone precursor emissions. The data suggest that, for ozone problem areas in and downwind of urban U.S. locations, VOC emission reductions reduce ozone, while NOx emission reductions increase ambient ozone levels. Despite large weekend reductions of NO emissions, there is little change in PM nitrate concentrations on weekends. The findings from this study may require a rethinking of present control strategies to reduce urban ozone and PM nitrate exposure and ozone transported downwind of urban locations in the U.S.

We interpret the observed absence of differences between weekday and weekend ozone levels, in combination with significantly lower ambient levels of NOx, as an indication that ozone formation in our study areas is VOC-limited. Our analyses of weekday/weekend differences in ozone precursor emissions show that different emission reductions of ozone precursors than normally take place on weekends will be required before significant reductions in ambient ozone can be achieved. Yet, in relative magnitudes, the emission changes that are projected to occur between now and 2010 more closely resemble the weekend reductions that we report here than the historical emissions trends, in which VOC emission reductions have exceeded reductions of NOx emissions on a relative basis. Our results call into question the rates of future progress in reducing peak ozone levels in major metropolitan areas in the United States.

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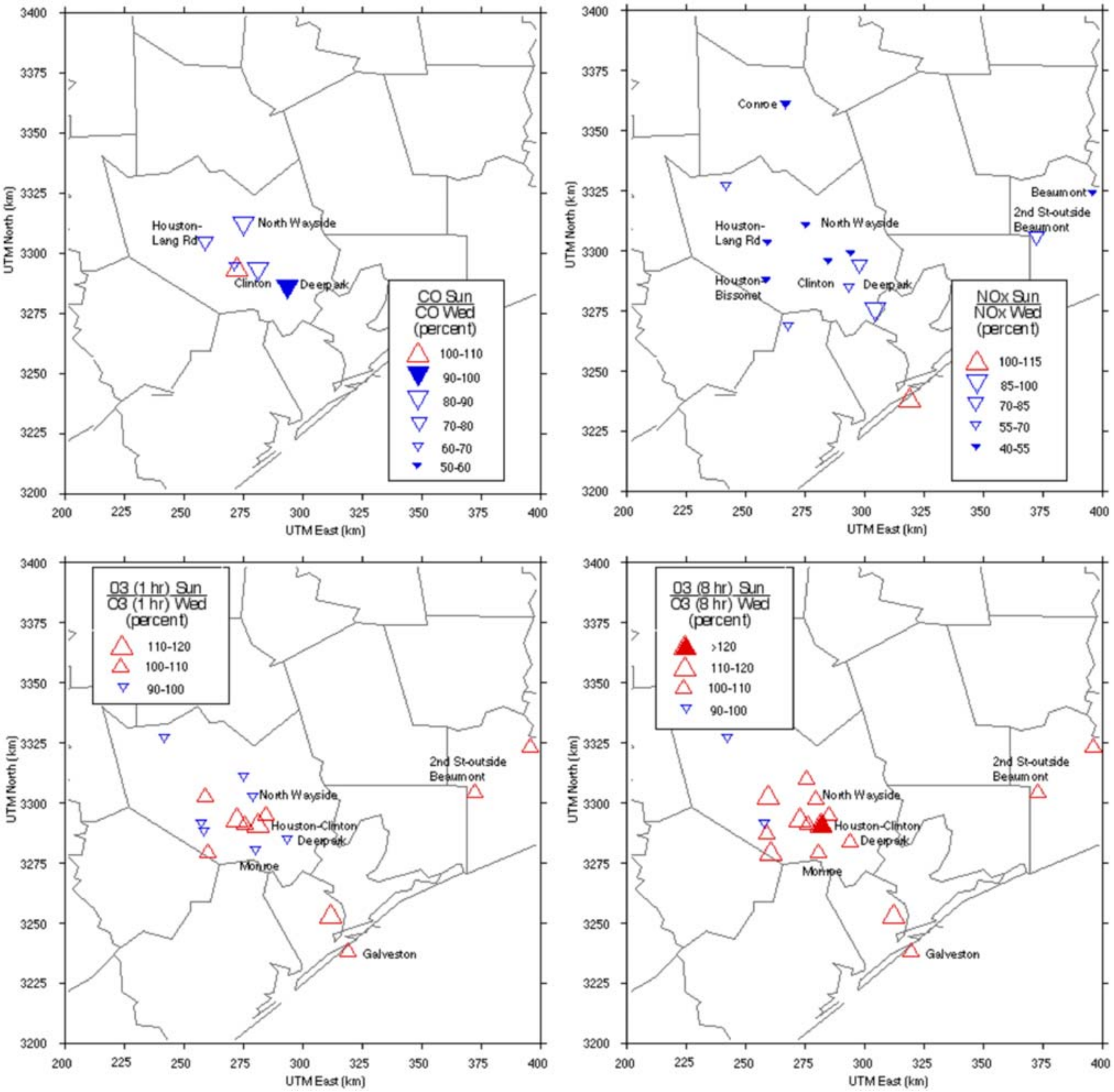

Figure 2. Geographical comparisons of mean Sunday to mean Wednesday daytime (6 a.m. through 3 p.m.) concentrations of CO and NOx and mean peak daily one-hour and eight-hour ozone in southeastern Texas. The differences were determined from all days, March-October 1998-2003.

VII Abstracts of Newly Awarded Projects

VII.1 Natural Gas Vehicle Cylinder Safety, Training and Inspection

Clean Vehicle Education Foundation

The overall object of this project is to increase the understanding of the safe and proper use and maintenance of vehicular compressed natural gas (CNG) fuel containers. There is a large and growing number of CNG-powered vehicles on the road in North America today. The high-pressure fuel containers they use require periodic inspection and maintenance to insure safe and proper operation. This project will identify and address CNG cylinder needs related to existing law, codes and standards, available training and inspection programs, and assure coordination among vehicle users, public safety officials and training providers.

Methodology: The project is composed of six separate phases:

I Public and Industry Awareness Campaign

II Training Scholarships or Tuition Assistance

III Evaluation of Current Training and Testing Practices

IV CNG Cylinder Safety Monitoring and Investigation Activities

V CNG Cylinder Recertification

VI Compressed Hydrogen/HCNG Cylinder Safety Considerations

The information generated by this project will assess current high-pressure fuel container inspection and maintenance and provide the basis for potential future changes to existing codes and standards. This information will also be useful in assessing the adequacy of codes and standards for high-pressure fuel containers for compressed hydrogen and mixtures of compressed hydrogen and natural gas.

VII.2 Natural Gas Vehicle Roadmap and Data Collection Effort

Clean Vehicle Education Foundation (CVEF)

This project will develop a comprehensive roadmap for targeted development of natural gas refueling infrastructure projects (compressed natural gas [CNG], liquefied natural gas [LNG] and/or a combination of the two) to support successful deployments of light- and heavy-duty natural gas vehicles in niche markets. The project will involve public and private stakeholders utilizing the already established CVEF Market Advisory Committee as the primary working group. This working group will address the drivers and barriers to the successful deployment of natural gas vehicles, research and document the lessons learned from existing projects, and develop criteria that allow decision-makers to focus limited resources. Also included in the effort is the development and implementation of a plan for the collection of natural gas (CNG and LNG) vehicle fuel sales information. A review of the several external efforts currently on-going that collect national and state estimates where feasible for CNG/LNG fuel use data in the transportation sector will be made. The work addressed will not only be a check and balance of those efforts, but will add the most value by concentrating on fuel use data collection efforts for CNG/LNG niche markets (e.g., transit buses, school buses, airport taxis and shuttles, short- and long-haul freight carriers, and refuse haulers) and aggregating and reporting the collected data at the state and national levels. Both retail and wholesale sales from private and public pumps will be included.

The Natural Gas Vehicle Roadmap will document the drivers and barriers to the successful deployment of natural gas vehicles (technical and market based), which includes, at a minimum, identifying regional differences and opportunities and the role for new natural gas vehicle and fuel technologies in meeting energy and environmental goals; documenting lessons learned from existing projects; describing potential fleet and niche market applications; developing criteria that allow decision-makers to focus limited resources and leverage investments through partnerships; documenting roles and opportunities for local gas distribution companies, fuel providers, and other industry stakeholders (including implementation steps and outreach required for public acceptance); and documenting the potential for natural gas infrastructure to build a foundation for future hydrogen infrastructure. Electronic versions of the Roadmap will be distributed via websites; a limited number of printed copies will be made available.

The natural gas vehicle fuel use data collection activity will focus on niche market applications (e.g., transit buses, school buses, airport taxis and shuttles, short- and long-haul freight carriers and refuse haulers). The data collected will be aggregated to the state and national levels, and, as feasible, attributable to Clean Cities jurisdictional boundaries. Both retail and wholesale sales from private and public refueling stations will be included. A protocol will be established so that data can be updated on an annual basis.

VII.3 Investigation of Bio-Diesel Fueled Engines under Low-Temperature Combustion Strategies

University of Illinois

This project will investigate the combustion characteristics of bio-diesel under low-temperature combustion (LTC) conditions. Bio-diesel has been found to be a very promising alternative to petroleum diesel fuel. It is renewable and is rich with oxygenates which have been shown to reduce soot emissions significantly. However, its utilization has been limited to some extent by its higher NOx emissions relative to petroleum diesel under conventional direct injection (DI) diesel engine combustion operation. LTC has the potential to dramatically reduce NOx emissions while keeping similar fuel efficiency as DI diesel engines. Using bio-diesel in LTC engines has the potential to achieve both high efficiency and very low exhaust emissions.

Meeting the challenge of developing and optimizing the combustion processes of bio-diesel fueled LTC engines will require a new level of the understanding of the physical phenomena that are common to the DI diesel engines and low-temperature combustion engines, which will be strongly affected by the different fuel properties, which in turn affect fuel/air mixture preparation, combustion and emissions. In particular, the liquid droplet vaporization process in the cylinder is highly transient and complicated due to the multi-component fuel effects and the interaction with the in-cylinder turbulent flow and combustion processes. It is difficult to evaluate (or control) the impact of the bio-diesel fuel on emissions without detailed knowledge of the in-cylinder fuel/air mixing. To date, little if any in-cylinder measurements have been made on such bio-diesel fueled LTC engines. The objective of this project is to provide detailed information on (1) bio-diesel fuel properties; (2) the effects of bio-diesel fuel properties on fuel-air mixing, ignition, combustion, and emissions in LTC engines; (3) knowledge of NOx, soot, hydrocarbon and CO emissions formation in bio-diesel LTC engines; (4) the effects of engine operating parameters on the efficiency and emissions of bio-diesel LTC engines; and (5) the strategies for reducing exhaust emissions and increasing the efficiency of bio-diesel LTC engines.

A multi-cylinder diesel engine will be used for measuring emissions and performance. A single-cylinder research engine based on the same engine geometry, modified for optical access using a Bowditch piston arrangement, will be used to study in-cylinder processes using the latest laser diagnostic and multi-dimensional modeling techniques. The combined experimental and modeling efforts will provide the useful physical insight and detailed quantitative information needed to optimize engine performance and minimize emissions.

VIII Acronyms

°C	Degrees Celsius
ACS	American Chemical Society
A/F	Air-fuel ratio
Ag	Silver
Al_2O_3	Aluminum oxide; alumina
ANL	Argonne National Laboratory
APBF-DEC	Advanced Petroleum-Based Fuels - Diesel Emission Control
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATDC, atdc	After top dead center
AU, a.u.	Arbitrary units
B20	A blend consisting of 20% biodiesel and 80% conventional diesel
B100	Neat (100%) biodiesel
Ba	Barium
$BaCO_3$	Barium carbonate
BC	Black carbon
BMEP	Brake mean effective pressure
BP	British Petroleum
$BSNO_x$	Brake-specific oxides of nitrogen
BTDC	Before top dead center
CA	Crank angle
cad	Crank angle degree(s)
CaFCP	California Fuel Cell Partnership
CARB	California Air Resources Board
cc	Cubic centimeter(s)
CCRT	Catalytic continuously regenerating trap
CeO_2	Ceric oxide
CFD	Computational fluid dynamics
CH_4	Methane
CI	Chemical ionization
CIDI	Compression ignition direct injection
cm	Centimeter
CN	Cetane number
CNG	Compressed natural gas
CO	Carbon monoxide
CO_2	Carbon dioxide
CP	Cylinder pressure
CR	Compression ratio
CRC	Coordinating Research Council
CRF	Combustion Research Facility
CVEF	Clean Vehicle Education Foundation
CWI	Cummins Westport Inc.
DCDC	Dilute clean diesel combustion
DCN	Derived cetane number
DECSE	Diesel Emission Control Sulfur Effects
DEER	Diesel Engine Emissions Reduction
deg	Degrees
DEM	Delayed extended main
DGE	Diethylene glycol diethyl ether
DI	Direct injection
DOE	U.S. Department of Energy
DPF	Diesel particulate filter, diesel particle filter
ECD	Emission control device
ECS	Emission control system
EGR	Exhaust gas recirculation
EI	Electron impact
EO	Engine-out
EP	End point
EPA	U.S. Environmental Protection Agency
EPMA	Electron probe microanalysis
ESC	European 13-mode, steady-state engine test procedure; also known as the OICA/ACEA cycle
FCV	Fuel cell vehicle
FE	Fuel economy
FID	Flame ionization detector
FSN	Filter smoke number
FT	Fischer-Tropsch
FTIR	Fourier transform infrared
ft-lb	Foot-pound
FTP	Federal Test Procedure
FTP-75	Federal Test Procedure for light-duty vehicles
FY	Fiscal year
g	Gram(s)
g/bhp-hr	Gram(s) per brake horsepower-hour
g/cc	Gram(s) per cubic centimeter
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectroscopy
g/hp-hr	Gram(s) per horsepower-hour
g/ihp-hr	Gram(s) per indicated horsepower-hour
g/mi	Grams per mile
GFV	Gaseous fuel vehicle
g/kw-hr	Gram(s) per kilowatt-hour
GM	General Motors
gph	Gallons per hour

GTL	Gas-to-liquid
H_2	Diatomic hydrogen
H_2S	Hydrogen sulfide
HC	Hydrocarbon
HCCI	Homogeneous charge compression ignition
HCNG	Hydrogen compressed natural gas
HC-SCR	Hydrocarbon selective catalytic reduction
HECC	High-efficiency clean combustion
HFET	Highway Fuel Economy Test
hp, HP	Horsepower
HP	High-pressure
HPDI	High-pressure direct injection
hr	Hour
HRA	Home refueling appliance
HVA	Hydraulic valve actuation
IBP	Initial boiling point
ICTC	Interstate Clean Transportation Corridor
IFT	Interfacial tension
IQT	Ignition quality tester
J	Joules
JSAE	Japan Society of Automotive Engineers
K	Kelvin
K	Potassium
km	Kilometer(s)
kPa	Kilopascal
L	Liter
LANL	Los Alamos National Laboratory
LFG	Landfill gas
LLNL	Lawrence Livermore National Laboratory
LNG	Liquefied natural gas
LNT	Lean NOx trap
LP	Low-pressure
LTC	Low-temperature combustion
LTHR	Low-temperature heat release
MECA	Manufacturers of Emission Controls Association
MFB50	Crank angle for 50% completion of combustion
mg	Milligram(s)
µg	Microgram(s)
mi	Mile(s)
min	Minute(s)
MJ/kg	Megajoule(s) per kilogram
ml, mL	Milliliter(s)
µm	Micrometer(s)

mm	Millimeter(s)
MON	Motor octane number
MOU	Memorandum of Understanding
mpg	Mile(s) per gallon
ms	Millisecond(s)
MS	Mass spectrometer
MSAT	Mobile source air toxic
MY	Model year
N_2	Diatomic nitrogen
N_2O	Nitrous oxide
N/A	Not applicable
NAC	NOx adsorber catalyst
N-CLD	Nitrogen-specific chemiluminescence detector
NETL	National Energy Technology Laboratory
ng	Nanogram(s)
NG	Natural gas
NGNGV	Next Generation Natural Gas Vehicle
NGV	Natural gas vehicle
NGVTF	Natural Gas Vehicle Technology Forum
NH_3	Ammonia
nm	Nanometer
NMHC	Non-methane hydrocarbon
NMR	Nuclear magnetic resonance
NO	Nitric oxide
N_2O	Nitrous oxide
NO_2	Nitrogen dioxide
NOx	Oxides of nitrogen
NPBF	Non-petroleum based fuel
NREL	National Renewable Energy Laboratory
O_2	Diatomic (molecular) oxygen
O_3	Ozone
OEM	Original equipment manufacturer
OFCVT	Office of FreedomCAR Vehicle Technologies
ORNL	Oak Ridge National Laboratory
P	Phosphorus
P	Pressure
PAH	Polyaromatic hydrocarbon
PCCI	Premixed charge compression ignition
PDU	Process development unit
PGM	Platinum group metal
PM	Particulate matter
PM2.5	Fine particles smaller than 2.5 µm
PNNL	Pacific Northwest National Laboratory
ppbv	Parts per billion by volume
ppm, PPM	Parts per million

ppmw	Parts per million by weight
Pt	Platinum
R&D	Research and development
RON	Research octane number
RPM, rpm	Revolution(s) per minute
s	Second(s)
S	Sulfur
SAE	Society of Automotive Engineers
SCAQMD	South Coast Air Quality Management District
SCORE	Sandia Compression-ignition Optical Research Engine
SCR	Selective catalytic reduction
sec	Second
SI	Spark ignition
SING	Spark-ignited natural gas
SNL	Sandia National Laboratories
SO_2	Sulfur dioxide
SpaciMS	Spatially resolved capillary inlet mass spectrometer
SSP	Saturated stoichiometric product
SULEV	Super ultra low emission vehicle
SUV	Sports utility vehicle
SwRI	Southwest Research Institute
T	Temperature
T50	Temperature where 50% of a fuel is evaporated during distillation
TDC	Top dead center
TDI	Turbocharged direct injection
TEM	Transmission electron microscopy
THC	Total hydrocarbon
TIC	Total ion count
TP	Tailpipe
TPGME	Tri-propylene glycol monomethyl ether
TUG	Transit Users Group
TWC	Three-way catalyst
UC	University of California
UDDS	Urban Dynamometer Driving Schedule
UEGO	Universal exhaust gas oxygen
ug	Micro-gram(s)
ULSD	Ultra-low sulfur diesel
U.S.	United States
US06	An aggressive chassis dynamometer emissions test procedure, part of the Supplemental Federal Test Procedure
USDA	United States Department of Agriculture
UTM	Universal Transverse Mercator (mapping projection methodology)
V	Volt
VGT	Variable geometry turbocharger
VOC	Volatile organic compound
Vol%	Volume percent
VVT	Variable valve timing
wt	Weight
wt%	Weight percent
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy
yr	Year
ZDDP	Zinc dialkyldithiophosphate

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