Advanced Combustion Engine R&D

2003 Annual Progress Report

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

freedomCAR & 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

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FY 2003

Progress Report for Advanced Combustion Engine Research & Development

Energy Efficiency and Renewable Energy
Office of FreedomCAR and Vehicle Technologies

Approved by Gurpreet Singh

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I. INTRODUCTION

Developing Advanced Combustion Engine Technologies

On behalf of the Department of Energy's Office of FreedomCAR and Vehicle Technologies, we are pleased to present the Fiscal Year (FY) 2003 Annual Progress Report for the Advanced Combustion Engine R&D Sub-Program. The mission of the FreedomCAR and Vehicle Technologies Program is to develop more energy efficient and environmentally friendly highway transportation technologies that enable America to use less petroleum. The Advanced Combustion Engine R&D Sub-Program supports this mission by removing the critical technical barriers to commercialization of advanced internal combustion engines for light-, medium-, and heavy-duty highway vehicles that improve the brake thermal efficiency of internal combustion engines by

- 30 to 45 percent for light-duty applications by 2010
- 40 to 55 percent for heavy-duty applications by 2012

while meeting future Federal and state emissions regulations as well as cost and durability requirements. R&D activities include work on combustion technologies that improve efficiency, minimize in-cylinder formation of emissions, and reduce the energy penalty of aftertreatment technologies that further reduce exhaust emissions.

This introduction serves to outline the nature, current progress, and future directions of the Advanced Combustion Engine R&D Sub-Program. The research activities of this Sub-Program are planned in conjunction with the FreedomCAR and the 21st Century Truck Partnerships and are carried out in collaboration with industry, national laboratories, other government agencies, and universities. Because of the importance of clean fuels in achieving low emissions, R&D activities will be closely coordinated with the relevant activities of the Fuels Technologies Sub-Program, also within the Office of FreedomCAR and Vehicle Technologies.

Research is also being undertaken on hydrogen-fueled internal combustion engines, which will provide an interim hydrogen-based powertrain technology that promotes the longer range FreedomCAR Partnership goal of transitioning to a hydrogen-fueled transportation system. Hydrogen engine technologies being researched have the potential to provide diesel-like engine efficiencies with near-zero emissions.

Technology Status

The compression ignition, direct injection (CIDI) engine, an advanced version of the commonly known diesel engine, is the most promising advanced combustion engine technology for achieving dramatic energy efficiency improvements in light-duty vehicle applications, where it is suited to both conventional and hybrid-electric powertrain configurations. The CIDI engine is already the primary engine for heavy-duty vehicles because of its high efficiency and outstanding durability. However, implementation of the U.S. Environmental Protection Agency's (EPA's) Tier 2 regulations for light-duty vehicles taking effect in 2004 is imposing a significant barrier to further penetration of CIDI engines in U.S. light-duty vehicles beyond pick-up trucks and vans, unlike Europe where it represents approximately 45 percent of all new light-duty passenger car sales. Similarly, the implementation of heavy-duty engine emission standards for 2007 are predicted to cause a reduction in fuel efficiency due to the exhaust emission control devices needed in order to meet both the oxides of nitrogen (NO_x) and particulate matter (PM) emissions regulations.

The technology for controlling PM from CIDI engines is highly effective and is entering commercial markets in applications (mostly heavy-duty) where duty cycles and engine strategies can create adequately high exhaust temperature to ensure regeneration, and where low-sulfur fuel is available. Regeneration strategies for light-duty vehicles need further development before they can be considered market-ready. Several effective PM device designs are competing for use on both light- and heavy-duty vehicles with CIDI engines. Cost and durability are likely to be the important characteristics for choosing which PM control technology for a given application, though the type of NO_x control device used will also play a role in specifying a PM trap and where it will be placed.

Technology for control of CIDI engine NO_x is not nearly as mature as the technology for control of PM. Competing technologies include adsorbers, selective catalytic reduction (SCR), lean-NO_x catalysts (often called HC-SCR), and non-thermal plasma (NTP)-assisted catalysis. Of these technologies, SCR using urea as a reductant is the current leader in terms of having the lowest fuel penalty and highest durability. However, it faces the hurdle of needing a urea distribution infrastructure to supply the vehicles using it. Heavy-duty vehicle manufacturers in Europe have committed to urea-SCR and are supporting urea distribution and dispensing infrastructure implementation and standards to assure urea quality. Serious discussions of the willingness of U.S. heavy-duty vehicle manufacturers to implement urea-SCR emission control have been initiated. Urea-SCR is equally effective on light-duty CIDI vehicles, though development of urea distribution infrastructure is a more daunting prospect than for heavy-duty vehicles that primarily use truck stops for refueling. A system to refuel light-duty CIDI vehicles with both diesel fuel and urea using one coaxial hose has been demonstrated and shows much promise. However, no proposal has been developed to assure that urea will be available at sufficient numbers of the numerous refueling facilities serving light-duty vehicles. Heavy duty vehicles may not need as many urea supply outlets and the technology is in fact being implemented in Europe.

Development of NO_x adsorbers has shown rapid improvement to the point that they appear to be able to achieve the Tier 2 Bin 5 light-duty vehicle emission levels for a short period of time. NO_x adsorbers for heavy-duty vehicles are less well-developed based on the size of these units compared with engine displacement (being over twice as large as those required for light-duty vehicles). The durability of NO_x adsorbers is still in question (more so for heavy-duty vehicles than light-duty vehicles) since they are sensitive to even small amounts of sulfur (urea-SCR catalysts are less sensitive to sulfur). The other major concerns about NO_x adsorbers are their effect on fuel consumption and cost. NO_x adsorbers use fuel to regenerate instead of urea, and current fuel "penalties" for regeneration are in the range of five to ten percent of total fuel flow. This is exacerbated by the need to periodically drive off accumulated sulfur by heating the adsorber to high temperatures, again by using fuel. These concerns are raising serious questions as to the commercial viability of NO_x adsorbers.

Non-thermal plasma NO_x emission control has been researched for over ten years for its promise to be highly controllable and effective, but to date it has not demonstrated effectiveness sufficient to meet the light-duty or heavy-duty emission standards. One unique advantage of NTP systems is that the plasma does reduce PM emissions somewhat, enabling a smaller PM trap. The plasma can also produce highly reactive hydrocarbons such as aldehydes from fuel injected upstream, which improves the NO_x reduction efficiency of the catalyst. Challenges include making the window of operation wider, reducing coking of the catalyst, and reducing the power requirement of the plasma. The NTP-assisted catalyst systems have two forms of energy penalties, the electric plasma and the fuel-derived reductants. Some improvement in this area has been observed by "cascading" plasma reactors in series. Further development will be needed to make NTP competitive with urea-SCR and NO_x adsorbers.

Interest in lean-NO_x catalysis (hydrocarbon-SCR) is making a bit of a come-back for use on both light- and heavy-duty CIDI vehicles. Currently, lean-NO_x traps provide only 20-40 percent reduction in NO_x, but this may be sufficient when combined with measures to reduce engine-out NO_x such as EGR, low-temperature combustion, or homogeneous charge compression ignition (HCCI). Lean-NO_x catalysis may also be used as an interim step with heavy-duty engines as the 2007 standards are phased in. The advantages of lean-NO_x

catalysis include no core engine modifications, no fuel infrastructure requirements as for urea, some reduction of hydrocarbons and carbon monoxide, and it is amenable to retrofit applications. Remaining drawbacks include catalyst activity and durability, the need for a broader operating temperature window, and lower selectivity leading to a higher fuel penalty.

An optimum solution to CIDI engine emissions would be to alter the combustion process in ways that don't produce emissions at all. This is the concept behind new combustion regimes such HCCI and low-temperature combustion, which result in greatly reduced levels of NO_x and PM emissions (though emissions of hydrocarbons and carbon monoxide still exist but are easily controlled). Significant progress is being made in both types of combustion systems, and performance has been demonstrated over a limited portion of the speed/load engine map (at the low- to mid-range of load). The major remaining issues include fuel mixing, combustion control, and extension of the operating range. Control of fuel injection and valve opening independent of piston movement appears to be necessary for HCCI engines to be viable. The optimum fuel also is up in the air, though initial indications are that the trend to higher cetane number diesel fuel is not beneficial.

Complex and precise engine and emission controls will require sophisticated feedback systems employing new types of sensors. NO_x and PM sensors are in the early stages of development and require additional advances to be cost effective and reliable, but are essential to control systems for these advanced engine/aftertreatment systems. Much progress has been made, but durability and cost remain to be issues with these sensors.

Advanced fuel formulations and fuel quality are also crucial to achieving higher energy efficiencies and meeting emissions targets. The EPA rule mandating that sulfur content of highway diesel fuel be reduced to less than 15 ppm starting in 2006 will greatly benefit the effectiveness, durability, and life of emission control devices. The EPA has recently reported that based on pre-compliance reports, 95 percent of all the diesel fuel should be less than 15 ppm sulfur by June 2006.

Goals and Challenges

Quantitative targets have been developed for advanced engines in three major applications: passenger cars, light trucks, and heavy trucks. Light trucks here refer to pickup trucks, vans, and sport utility vehicles that are emissions-certified to the same standards as passenger cars, or generally "light-duty vehicles." Fuel efficiency improvement is the overarching purpose of this Sub-Program, but resolving the interdependent emissions challenges is a critical first step. The major challenges facing CIDI emission control systems across all three platforms are similar: durability, cost, and fuel penalty (or in the case of urea-SCR, urea infrastructure development). Full-life durability has yet to be demonstrated for either light- or heavy-duty systems. Nor have these systems demonstrated their ability to "bounce back" following exposure to fuel sulfur levels higher than 15 ppm which will occur periodically due to cross-contamination of fuels and outright fuel substitution mistakes. With significant progress made toward emission controls, attention will be turned more toward engine efficiency improvements by systematically attacking losses such as friction, exhaust energy, heat transfer, and parasitics.

The targets for passenger cars derived primarily by the FreedomCAR Partnership are shown in Table 1. Achieving emission compliance for CIDI engines in light-duty vehicles will provide a "quantum leap" (~30%) fuel efficiency improvement over port-fuel injected spark ignition engines. In the longer term, further advancement of engine efficiency along with reducing the emission control penalty will gain another 15-18% beyond today's technology.

Table 1. Technical Targets for Combustion and Emission Control Activity

Characteristics	Units	Fiscal Year 2004	Fiscal Year 2007	Fiscal Year 2010
FreedomCAR Goals				
ICE Powertrain				
Peak Brake Th. Eff. (CIDI)	%			45
(H_2-ICE: 2015)				45
Cost (CIDI)	$/kW			30
(H_2-ICE)				45
(H_2-ICE: 2015)				30
Reference Peak Brake Thermal Efficiency[a]	%	30	32	34
Advanced Combustion Engine Goals				
Target Peak Brake Thermal Efficiency/ Part-Load Brake Thermal Efficiency (2 bar BMEP[b] @1500 rpm)	%	43/29	45/32	46/35
Powertrain cost[c,d]	$/kW	30	30	30
Emissions[e]	(g/mile)	Tier 2, Bin 5	Tier 2, Bin 5	Tier 2, Bin 5
Durability[e]	Hrs.	5,000	5,000	5,000
Fuel economy penalty due to emission control devices[f]	(%)	<5	<3	<1

a Current production, EPA compliant engine
b Brake mean effective pressure
c High-volume production: 500,000 units per year
d Constant out-year cost targets reflect the objective of maintaining powertrain (engine, transmission, and emission control system) system cost while increasing complexity.
e Projected full-useful-life emissions for a passenger car/light truck using advanced petroleum-based fuels as measured over the Federal Test Procedure as used for certification in those years.
f Energy used in the form of reductants derived from the fuel, electricity for heating and operation of the devices, and other factors such as increased exhaust back-pressure, reduce engine efficiency.

While the light truck diesel engine R&D activity has already attained its targets for fuel economy increase, engine cost, and engine weight, it still has a way to go to achieve the 2004 targets for noise, vibration, and harshness (NVH), NO_x emissions, and durability (see Table 2).

Table 2. Technical Targets for Light Truck Diesel Engine R&D			
Characteristics	**Units**	**Fiscal Year**	
		2002 Status	2004
Engine power	hp	225-300	225-325
Fuel economy increase over equivalent gasoline vehicles	%	>50	>50
Engine cost (compared to equivalent gasoline engine)	%	<120	<120
Engine weight (compared to equivalent gasoline engine)	%	<110	<110
NVH (compared to equivalent gasoline engine)	db difference	<3	<1
NO_x emissions[a]	g/mile	<0.30	<0.07
PM emissions[a]	g/mile	<0.01, for 20 hrs. in test cell	0.01
Durability[b] (on lab dynamometer, computer simulated vehicle miles)	miles (equivalent)	>20,000	>100,000

a Projected full-useful-life emissions for a SUV (using advanced petroleum-based fuels with 15 ppm sulfur) as measured over the Federal Test Procedure as used for certification in those years.

b Projected full-useful-life durability, as measured over the Federal Test Procedure as used for certification.

Heavy truck engine R&D activities are focused on increasing heavy-duty diesel engine efficiency significantly above current levels as well as addressing efficiency penalties resulting from emission control technologies required to meet the increasingly stringent emissions standards. As seen in Table 3, heavy-duty truck engines will need to simultaneously increase thermal efficiency significantly while lowering emissions and doubling durability, all by 2005. By 2007, efficiency will need to be increased further while NO_x emissions are reduced and durability is doubled again. Achieving these technical targets will require sustained R&D activities along several fronts.

Table 3. Technical Targets for Heavy Truck Diesel Engine R&D				
Characteristics	**Fiscal Year**			
	2002 Status	2005	2007	2012
Engine thermal eff., %	>40	>45	>50	>55
NO_x emissions,[a] g/bhp-hr	<2.0	<1.2	<0.20	<0.20
PM emissions[a], g/bhp-hr	<0.1	<0.01	<0.01	<0.01
Stage of Development	commercial	prototype	prototype	prototype
Durability, miles (equivalent)	>100,000	>200,000	>400,000	

a. Using 15 ppm Sulfur diesel fuel

The Sub-Program is systematically addressing the emissions challenges facing both light- and heavy-duty CIDI engines as shown in Table 4.

Table 4. Key Challenges in CIDI Emission Compliance and Examples of Sub-Program R&D Projects Addressing Them
(Organizations Conducting Projects under the Sub-Program are shown in parentheses)

NO_x and PM Control Effectiveness over Wide Range of Operation	**Fuel Economy Penalty Due to Emission Controls**	**Need for Key Enablers Such as Sensors and Controls**	**Cost of Emission Control System**	**Aging of Emission Control Device to Thermal Effects and Poisons**
Emission control system development (DDC, Cummins, Ford)	Combustion R&D and modeling to reduce engine-out emissions (SNL, LLNL, LANL, ANL, ORNL)	PM sensor development (Honeywell, U. Minnesota)	Modeling tools to define most cost-effective system (CLEERS)	Sulfur poisoning mechanisms (PNNL) NO_x adsorber surface species and mechanisms (ORNL)
Development of modeling tools for emission controls (CLEERS)	NO_x adsorber regeneration strategies (ORNL)	NO_x sensor development (PNNL, Delphi, ORNL, Ceramphysics)	Combustion R&D to reduce engine-out emissions (SNL, LLNL, LANL, ANL, ORNL)	Exhaust sulfur trap development (PNNL, Caterpillar)
Urea decomposition phenomena at low temperatures (ORNL)	Modeling tools to define most cost-effective system (CLEERS)	Fast-response PM analysis tools (SNL, ANL)	NO_x adsorber surface species and mechanisms (ORNL)	NO_x adsorber regeneration and desulfation (ORNL)
Plasma-assisted catalysis (PNNL)	Nitrogen-enriched air for engine-out NO_x control (ANL)			
Catalyst discovery (SNL, LANL, GM)				

Recovery of energy from the engine exhaust represents a potential for 10 percent or more improvement in the overall engine thermal efficiency. More efficient turbochargers using variable geometry and electric assist are one approach. Turbocompounding and direct thermal-to-electric conversion could also improve the overall thermal efficiency. Semiconductor thermoelectric devices are currently 6 to 8 percent efficient, but recent developments in quantum well thermoelectrics suggest a potential improvement to over 20 percent is possible. The technical targets for the waste heat recovery R&D activities are listed in Table 4. Significant progress will be needed to meet the 2005 and 2008 targets.

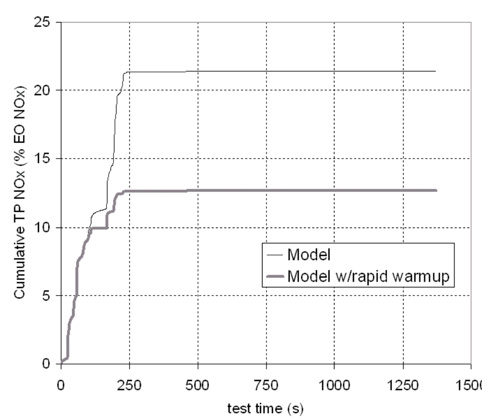
Table 5. Technical Targets for Waste Heat Recovery				
Characteristics	**Units**	**Fiscal Year**		
		2003 Status	2005	2008
Electrical turbocompound system				
Light-Duty Vehicles				
Power	kW	<2	>5	>10
Projected component life	Hrs.	<10	>2,000	>5,000
Class 7-8 trucks				
Fuel economy improvement	%	<1	>5	>10
Power	kW	<10	>20	>30
Projected component Life	Hrs.	<10	>5,000	>10,000
Thermoelectric Devices				
Efficiency • bulk semiconductor • quantum well	%	6-8	-- >10	-- >15
Projected cost/output (250,000 production volume)	$/kW	--	500	180

Project Highlights

The following projects highlight progress made in the Advanced Combustion Engine R&D Sub-Program during FY 2003.

The Capability of a Light-Duty Diesel Truck to Meet Tier 2, Bin 5 Emissions Using Urea-SCR is Defined

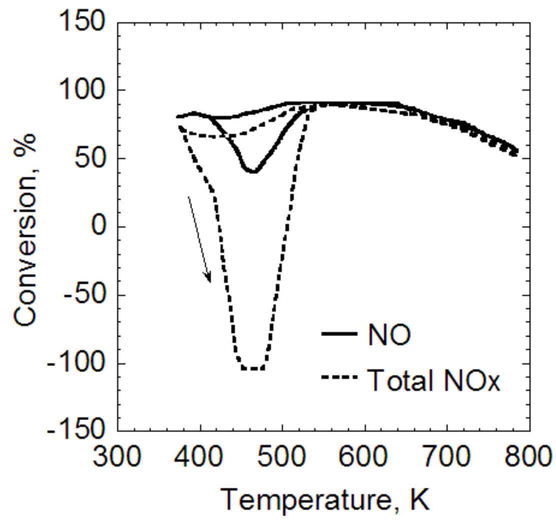
Ford has shown the capability for one of its F-250 light trucks to achieve Tier 2, Bin 5 emissions using urea-SCR to control NO_x emissions and a continuously regenerating filter to control PM emissions. The key to good NO_x control for this vehicle was found to be rapid warm-up of the catalyst following a cold-start. When warm, the NO_x catalyst was found to be capable of 90+ percent reduction of NO_x from the engine, which is required to meet Tier 2, Bin 5 regulations. While this system has been shown to be capable of meeting Tier 2, Bin 5 emissions, it has yet to demonstrate that it can do that over the full useful life of the vehicle. Other needs identified by Ford to make this system viable for production include accurate and durable NO_x and ammonia sensors, and further optimization of the aqueous urea injection strategy and hardware.



The Importance of Rapid Warm-Up on NO_x Emissions Is Illustrated by These Model Results

Plasma-Facilitated Lean-NO_x Catalysis for Heavy-Duty Diesel Emissions Control Makes Significant Advancements

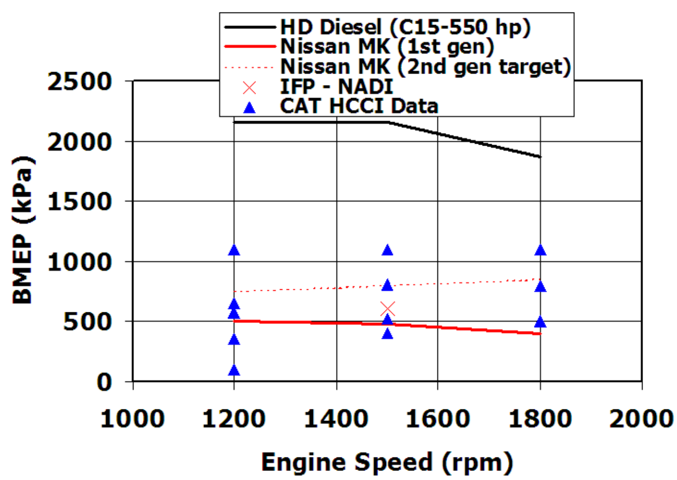
Pacific Northwest National Laboratory (PNNL), in conjunction with Caterpillar Inc., has demonstrated heavy-duty engine NO_x control using a plasma upstream of a lean-NO_x catalyst. The plasma facilitates conversion of NO to more reactive NO_2, and it oxidizes hydrocarbons injected for reduction to oxygenates, which are much more effective for NO_x reduction than unreacted hydrocarbons. These changes increase the efficiency of the lean-NO_x catalyst to reduce NO_x. While high conversion has been demonstrated, at low temperatures NO_x is desorbed from the catalyst where is it stored, resulting in release of unconverted NO_x. Further improvements that will be explored include applying the plasma only to the added hydrocarbons rather than the whole exhaust. This will significantly reduce the energy requirement of the plasma.



NO_x Conversion Showing Desorption of NO_x at Low Temperatures

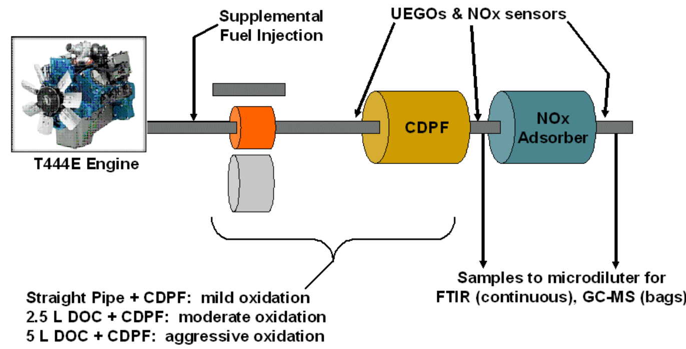
Caterpillar Demonstrates HCCI Performance at Higher Engine Loads

Caterpillar has assembled an HCCI development team including a unique mix of technical experts from the fields of controls, combustion fundamentals, engine design, engine development, and manufacturing. This team approach has resulted in a novel engine system that has achieved 1000+ kPa brake mean effective pressure (BMEP) while meeting future emissions standards. This achievement more than doubles the previously published power density and clearly advances HCCI as a potentially viable approach to meeting future regulatory and marketplace requirements. However, additional test stand evaluation, sensor development, and algorithm development is needed to address the challenges associated with controlling this novel combustion approach. Additional future efforts will include focus on identifying and developing a cost effective method of manufacturing the engine system, and development of an improved engine structure, enhanced air system capabilities, and improved combustion control.



Caterpillar HCCI Results Relative to Current Diesels and Other HCCI Engines

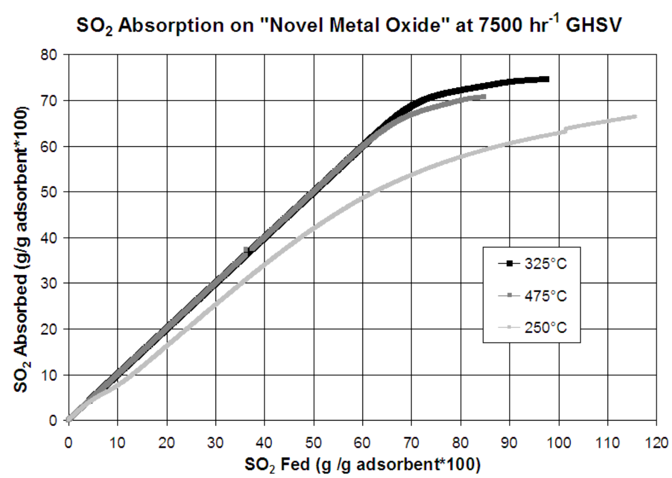
ORNL Explores and Improves NO_x Adsorber Regeneration Phenomena in Heavy-Duty Engines



Different Emission System Configurations Tested by ORNL

Oak Ridge National Laboratory (ORNL), in conjunction with International Truck and Engine Corporation, has developed NO_x adsorber regeneration and desulfation strategies for diesel aftertreatment systems. The effects of diesel oxidation catalysts and diesel particle filters on regeneration and desulfation efficiency are included. The strategies are implemented via a PC-based system developed by ORNL for transient electronic control of the intake throttle, EGR valve, wastegate, and reductant (fuel) delivery in-manifold (pre-turbo) and/or in-pipe (after turbo). Using this system, they have achieved 70% NO_x reduction at rated power with acceptable CO and hydrocarbon (HC) emissions. They confirmed the degree of fuel cracking in oxidation catalysts and observed improved NO_x adsorber performance with certain HC species. The potential for fuel savings using more aggressive in-pipe fuel reforming was shown. Future work activities include examining lower temperature conditions with in-pipe or in-manifold injection; speciating hydrocarbons at the adsorber inlet and outlet; confirming HC sensitivity at lower temperatures; developing desulfation strategies; and speciation of hydrocarbons for in-cylinder injection strategies.

PNNL Explores Materials Suitable for Sulfur Traps on Diesel Engines

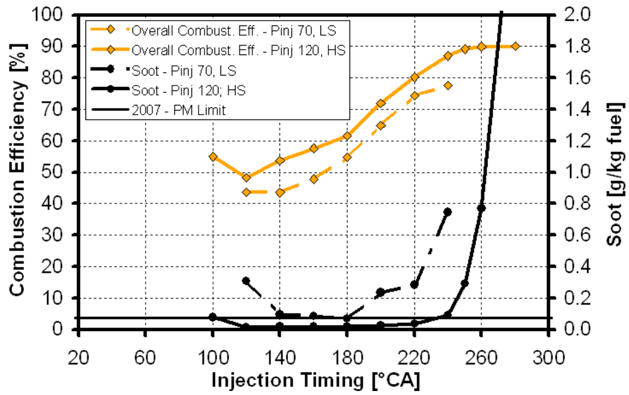


Performance of SO_2 Adsorbent Discovered by PNNL

Even though diesel fuel in the U.S. should have less than 15 ppm sulfur starting in 2006, most catalytic emission control devices would benefit from even less exposure to sulfur. An onboard sulfur trap would slow deterioration of emission control devices and guard against episodes of misfueling with high sulfur fuel or other calamities that result in inadvertently high fuel sulfur contents. PNNL is exploring a high-capacity SO_x adsorber trap in a self-contained canister placed in the exhaust stream that can be replaced at periodic service intervals. The adsorbent can then be regenerated off-line in a facility dedicated to such an operation. Replacement of the adsorbent would be approximately every 30,000 miles (oil change interval for heavy-duty trucks). A high-capacity adsorbent minimizes the weight and volume required. A target has been set at minimum 40 wt.% SO_2 capacity for the adsorbent. PNNL has identified a novel metal oxide adsorbent with capacity for SO_2 approaching 70 wt.%. Advantages of this adsorbent include: a separate SO_2 oxidation catalyst is not required; it maintains capacity from 250-475^{o}C; and, its capacity is not affected by NO, CO, or H_2O.

SNL Identifies the Effects of Fuel, Speed, and Heat Transfer on HCCI Combustion and Emissions

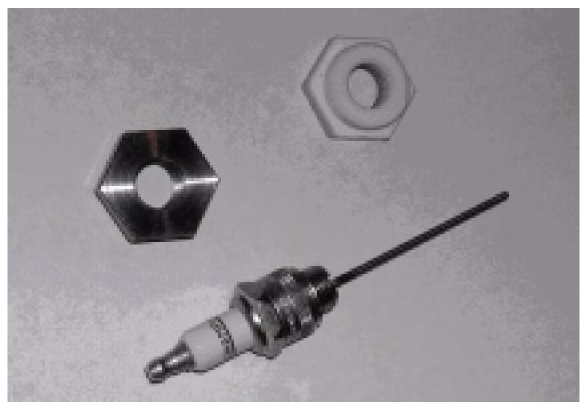
HCCI has a strong potential for reducing NO_x and particulate emissions from diesel engines, but mixture preparation can be difficult with a standard diesel injector. Sandia National Laboratories (SNL) found that a gasoline direct injection (GDI)-type injector appears to be well-suited for this application, and its potential for diesel-fueled HCCI was investigated. The effects of several operating parameters were assessed, including injection timing, injection pressure, intake-air temperature, air swirl, and fuel load. Overall, the GDI injector performed well, and its performance was found to improve with increases in both injection pressure and swirl. They found that the combination of increasing injection pressure and swirl significantly improved combustion efficiency and reduced soot emissions.



SNL Results Using a Gasoline Direct Injector to Control HCCI Combustion

Honeywell Develops Prototype Particulate Matter Sensor

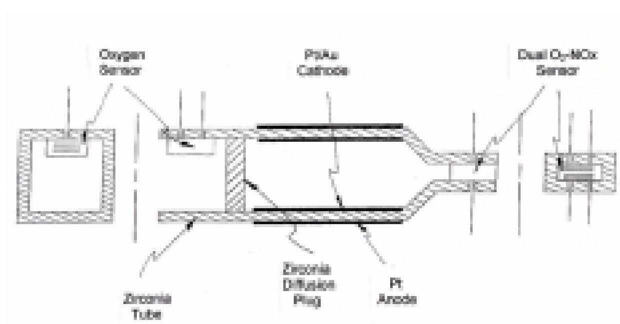
Honeywell has developed a prototype Diesel engine exhaust PM sensor that is low cost, has high speed and reliability, and is compatible with the harsh operational environment of diesel exhaust systems. The sensor probe is built on a commercial spark plug body. This platform is ideal for placement directly in the exhaust manifold as it withstands high pressure and temperature and is stable towards vibration and the gas composition found in that environment. They are currently developing prototype packaging for the sensor and its associated electronics with the goal of demonstrating a functional prototype in March 2004.



Honeywell Prototype PM Sensor

Development of a Small, Inexpensive Combined NO_x and O_2 Sensor

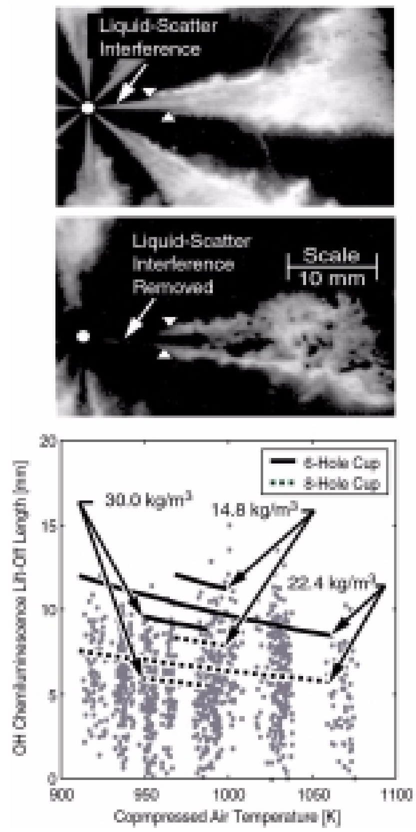
The basic concept of a miniature, inexpensive, amperometric NO_x sensor combined with an oxygen sensor has been demonstrated by CeramPhysics, Inc. The prospect of achieving a small, inexpensive NO_x + oxygen sensor that does not require a reference gas is now very promising, and such a sensor would serve an important diagnostic function onboard diesel vehicles to control NO_x emissions control devices. CeramPhysics is in the process of determining the Pt-Rh alloy for the electrodes of the NO_x sensor body.



Schematic of the Combined NO_x and Oxygen Sensor Being Developed by CeramPhysics

SNL Studies In-Cylinder Combustion Effects Using Laser Diagnostics

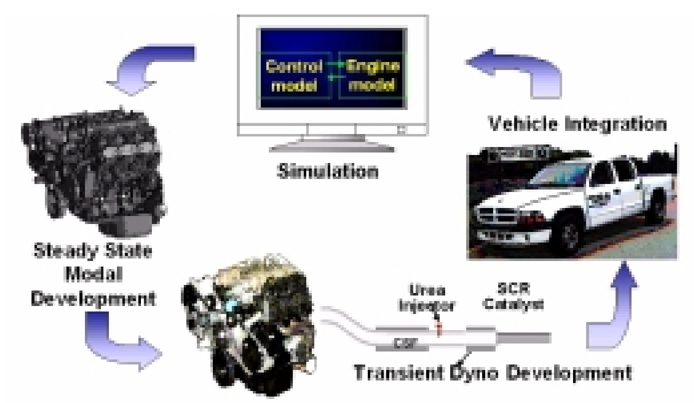
Using laser and imaging diagnostics, SNL is studying the influence of the in-cylinder environment on diesel flame lift-off length (LOL, the distance from the injector nozzle to the flame) to better understand the departure of flame lift-off behavior in the engine from that observed in single-jet, quiescent environments. SNL developed a new two-color, two-camera technique to more accurately measure the diffusion flame LOL using OH chemiluminescence. Using this technique, SNL found that in-cylinder swirl flow had a minor influence on the shape of the flame in the vicinity of the LOL, with a 7% longer LOL on the windward side of the jet, on average. Significant cycle-to-cycle variation was observed in the LOL data, even though the overall engine performance was very stable. Cycle-to-cycle variation in the LOL has important implications for soot reduction strategies that rely on more extreme operating conditions in order to achieve zero soot formation. SNL found that if the LOL is long enough, zero soot formation can be achieved in the jet. But high cycle-to-cycle variation requires longer average LOLs, which can be difficult to achieve.



SNL Data Showing Cycle-to-Cycle Variation in LOL

DDC Achieves Tier 2, Bin 6 Emissions for a Light-Duty Truck

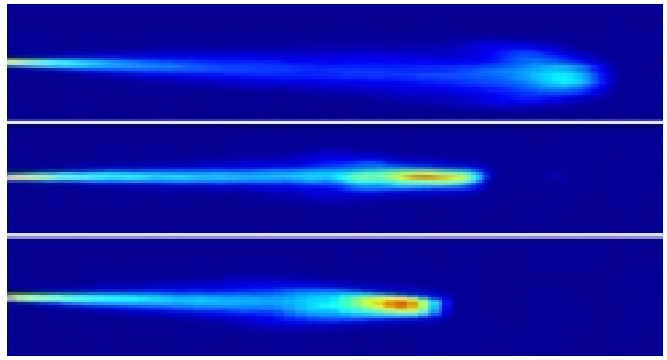
Detroit Diesel Corporation (DDC) is pursuing an integrated engine, aftertreatment and vehicle development roadmap to reduce emissions from light-duty vehicles while achieving large gains in fuel economy. This integrated experimental and analytical approach to technology development results in a shortened developmental cycle and substantially improved understanding of the NO_x-PM trade-offs and fuel economy improvements in both diesel engines and vehicles. Using a catalyzed PM trap and urea-SCR NO_x control, DDC has demonstrated Tier 2 Bin 6 emissions for a light-duty truck over the Federal Test Procedure (FTP) with a 45% fuel economy improvement compared to the baseline gasoline vehicle. By adding advanced urea injection control and vehicle integration system designs, DDC believes that they will be able to demonstrate tailpipe emissions below Tier 2 Bin 5 not only over the FTP, but over the high-speed US06 cycle as well.



DDC's Integrated Experimental and Analytical Approach to Technology Development

ANL Studies Diesel Fuel Spray Using X-Rays

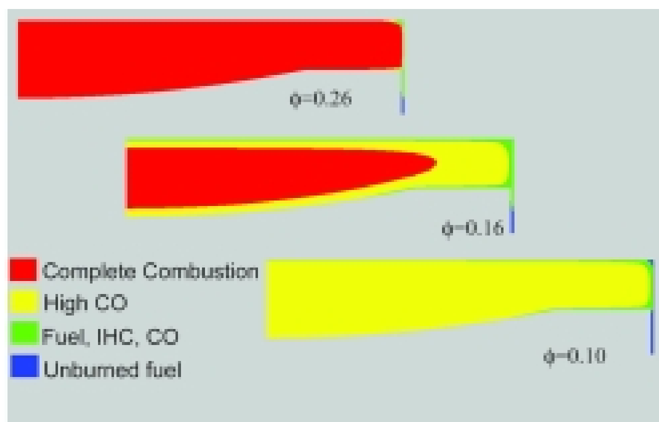
This effort originated out of an industry need for quantitative information about diesel fuel sprays in the near-nozzle region (within 10 mm of nozzle exit). Traditional optical or laser-based diagnostic techniques, such as Mie scattering, light extinction, or laser induced fluorescence have not been successful in providing quantitative information in this region. The tremendous intensity of synchrotron x-rays provides unprecedented access to fuel spray regions previously unexplored. The current technique relies upon x-ray absorption to provide information regarding fuel spray geometry and density that will assist in designing injectors that enable more efficient combustion. Over the past year, ANL has been developing an entirely new diagnostic technique that is undergoing continual refinement. In addition, a high-pressure test cell is being designed that will make the test environment more suitable for simulating fuel sprays in advanced diesel engines.



Fuel Spray Images Using the X-Ray Technique Developed by ANL

LLNL Models HCCI and PCCI Combustion and Multi-Cylinder HCCI Engine Control

LLNL has developed advanced methodologies that combine chemical kinetics with fluid mechanics to analyze HCCI and PCCI engines with accuracy never before achievable for other types of engines. They have also developed systems analysis models for HCCI engines that have allowed them to optimize operating conditions to obtain maximum efficiency with minimum emissions. This has been made possible by using both single-zone and multi-zone chemical kinetics models. In the past year, LLNL has extended their multi-zone model to include mixing between zones. This new model can be used as a framework to analyze engine operating conditions where the charge is not perfectly homogeneous (i.e. PCCI combustion). By using this model, LLNL has been able to demonstrate that mixing between zones is responsible for most of the production of carbon monoxide in an HCCI engine. This model has also allowed LLNL to perform a detailed analysis of experiments conducted at Sandia National Laboratory that studied the low power performance of HCCI engines. The results of this analysis demonstrate that during combustion at very low equivalence ratios even the central core of the cylinder (the hottest part of the combustion chamber) is too cold to react to completion, and instead it reacts partially into CO and intermediate hydrocarbons.



Combustion Prediction as a Function of Equivalence Ratio Using the LLNL Multi-Zone Model

Future Directions

Advanced Combustion and Model Development

Work in this area will focus on fuel injection spray characteristics, modeling of in-cylinder flow, combustion kinetics, and exploration of low-PM, low-NO_x combustion regimes. The following are some specific activities Advanced Combustion Engine R&D researchers will be doing in the coming year.

- ANL will expand their x-ray measurement of fuel sprays by increasing the ambient pressure to attain more realistic diesel engine conditions; expand the testing of injection parameters, such as orifice diameter and orifice finishing, to determine their influence upon fuel spray density distribution; and expand the use of the Pixel Array Detector (PAD), a technical innovation that allows for 2-D data acquisition.
- SNL will conduct detailed experiments quantifying the mixing behavior of low-temperature combustion regimes and the impact of swirl, injection pressure, multiple injection schemes, and bowl geometry/spray targeting.
- ORNL will continue exploring the potential of new approaches for achieving simultaneous low NO_x and PM emissions and will investigate the effects of fuel properties on achieving and exploiting low-emissions combustion regimes. ORNL will analyze opportunities of advanced combustion regimes to increase engine efficiency and validate with experiments.
- SNL will initiate a study of NO_x formation under conditions with long ignition delay, which is of interest for both conventional diesel combustion and advanced, multi-mode combustion strategies.
- ANL will build a nitrogen-enriched intake air (NEA) system suitable for a heavy-duty diesel engine and measure the impact on emissions. The NEA system will be tested for transient response and durability through an on-road test.
- SNL will extend their investigation of jet-wall interaction effects on soot production to include fast-response wall temperature measurements and quantitative laser extinction measurements in the wall jet region.

Emission Control Subsystem Technology Development

Work in this area will focus on making exhaust emission control systems more effective and durable.

- ORNL will continue their work to define NO_x adsorber regeneration strategies and quantify their impacts on engine torque, fuel consumption, and PM emissions. They will also quantify the effect of desulfation on NO_x adsorber integrity.
- PNNL will continue their work on exhaust sulfur traps by studying the compositional and structural variations and synthesis methods of the class of metal oxide absorbents they discovered. They will also measure sulfur absorption performance with simulated and real diesel emissions and initiate work to provide absorbents in monolith form.
- In ORNL's project with International Truck and Engine Corporation, they will examine lower temperature NO_x adsorber regeneration conditions with in-pipe or in-manifold hydrocarbon injection; speciate hydrocarbons at the adsorber inlet and outlet; confirm HC sensitivity at lower temperatures; and develop desulfation strategies and measure their effectiveness.

- Ford will continue development of their urea-SCR light truck emission control system by developing a rapid warm-up strategy, developing a 5000 hour durability test protocol, continuing testing of NO_x and ammonia sensors, and continuing to investigate concepts for onboard delivery of aqueous urea and its specifications.

NO_x Catalysts and Sensors

Projects in this area focus on development of NO_x reduction devices and sensors to control their operation.

- PNNL will measure the impact of sulfur on NO_x adsorbers by identifying the 'signatures' for catalyst deactivation.
- ORNL will continue identification of NO_x adsorber species in an effort to increase NO_x storage and decrease susceptibility to sulfur.
- PNNL will continue their work on non-thermal plasma-assisted catalysis of NO_x by investigating on-board production of reductants from fuel via partial oxidation reforming and evaluating catalyst combinations under transient conditions.
- Delphi will continue their efforts to design a viable NO_x sensor by improving the finish pump electrode, eliminating the Au contamination inside the NO_x measurement chamber, and achieving consistent and faster response time using pulse mode.
- PNNL will continue development of a NO_x sensor with Delphi by determining the effect of hydrocarbons, steam, carbon monoxide, carbon dioxide, and sulfur compounds on oxygen pumping and NO_x sensing electrode activity, selectivity, and lifetime.
- CeramPhysics will continue development of their combined NO_x and oxygen sensor by trying at least one more type of porous Rh-based electrode; continuing characterizations and long-term testing; determining the optimum operating temperature; designing and testing the measuring electronics; and completing testing at outside institutions.

Particulate Control Technologies and Instrumentation

This portion of the Sub-Program is focused on development of instrumentation to measure the mass and size of particulate emissions coming from diesel and gasoline engines.

- ANL will enhance the portable PM measurement instrument they designed by refining it for a minimum particulate detection of 0.1 mg/m^3; developing the capability to measure particle number density and mean aggregate size; and conducting tests to identify the sensitivity of the instrument to volatile organic fraction.
- SNL will refine the laser-induced desorption with elastic light scattering (LIDELS) PM measurement instrument to enable time-resolved measurements (~10 Hz data rate) and will continue commercialization efforts with Artium Technologies.
- Honeywell will continue development of their engine PM sensor by developing custom, cost effective prototype electronics for signal conditioning and real-time data interpretation, and will develop prototype packaging for the sensor and electronics with the goal of demonstrating a functional prototype in March 2004.

Homogeneous Charge Compression Ignition

The HCCI researchers will continue to expand the speed and load range of HCCI operation, identify the conditions necessary to initiate HCCI combustion for both gasoline and diesel fuel, and explore methods for controlling HCCI combustion.

- Lawrence Livermore National Laboratory (LLNL) will study partially stratified fuel charge (PCCI) as a possible solution to increase HCCI engine power output; identify satisfactory methods of starting HCCI engines under any environmental condition; and study of how interactions between cylinders can be used for successfully balancing and controlling combustion.
- SNL will initiate experiments to involve natural emission imaging of well-mixed and stratified combustion; investigate the effects of intake-pressure boosting on combustion and emissions for various fuel types and its potential to extend the load range; conduct a broader investigation of the effects of heat transfer and residuals on HCCI; and expand studies of mixture stratification by techniques such as late injection timing, multiple injections, and variation of injection parameters.
- The University of Wisconsin consortium will assess multiple injections of diesel fuel as a means of controlling HCCI combustion; analyze use of cylinder pressure-based and ion/optical sensing for engine control; and implement efficient methods for including detailed combustion kinetics in multidimensional models to make more accurate combustion predictions.
- The University of Michigan consortium will expand and refine current studies of mode transitions, thermal transients, and detailed heat transfer; continue shock tube and rapid compression experiments to improve models of gasoline combustion for engine simulation tools; and incorporate the latest reduced chemical kinetics and heat transfer mechanisms into an engine system code and validate with the transient engine data as it becomes available.
- SNL will apply planar laser-induced fluorescence (LIF) to measure HCCI fuel distribution as a function of fuel injection parameters; perform LIF measurements of the fuel mixing process under fired conditions for varying fuel-injection timings; and measure engine emissions and correlate with fuel-distribution measurements.
- Caterpillar will focus on achieving increased HCCI power density through an improved engine structure, enhanced air system capabilities, and improved combustion control; conduct additional test stand evaluation, sensor development, and algorithm development to develop practical engine controls; and will focus on identifying and developing a cost effective method of manufacturing HCCI engines.

Engine Components and Systems

Researchers in this portion of the Sub-Program will continue efforts to increase engine efficiency while lowering emissions through innovative engine designs and components.

- DDC will further develop a fuel economy improvement strategy via engine and aftertreatment integration and control; conduct integrated virtual engine and hardware tests to optimize the overall integrated engine-aftertreatment-powertrain-vehicle system; and refine CLEAN Combustion© technology via systematic subsystem enhancements and methodical integration.
- Cummins will continue in-cylinder development to reduce engine-out emissions and reliance on aftertreatment to control tailpipe emissions; reduce the fuel economy penalty for aftertreatment systems; and implement closed-loop air/fuel control for improved engine-out emissions and reduced variation.

- Envera will continue to explore variable compression ratio as a means of increasing the efficiency of internal combustion engines.
- Honeywell will complete a wider range of tests with a small electrically assisted turbocharger to fully quantify benefits and identify design issues; apply two small turbochargers to an SUV-size diesel engine to demonstrate feasibility and benefits; and design and build an electrically assisted turbocharger(s) sized for SUV diesel engines.

Honors and Special Recognitions

- Chris Aardahl, et. al. of PNNL were awarded a Federal Laboratory Consortium Award for their work on plasma-facilitated lean-NO_x catalysis for heavy-duty diesel engines in combination with other efforts at PNNL on a CRADA program with the LEP and a former program with Delphi.
- Three of LLNL's HCCI publications by Salvador Aceves, J. Ray Smith, Daniel Flowers, Joel Martinez-Frias, and Robert Dibble (University of California Berkeley) have been selected as "Landmark Research on HCCI Combustion" and published on an SAE bound volume "Homogeneous Charge Compression Ignition (HCCI) Engines: Key Research and Development Issues."
- SNL's work on HCCI combustion by John Dec et.al. was selected by the International Energy Agency as the most significant achievement in combustion for 2003 - out of submissions from all member countries.
- L.M. Pickett and D.L. Siebers of SNL were given the ASME Best Paper Award for their presentation at the ASME Internal Combustion Engine Fall 2001 conference.
- D.L. Siebers, L.M. Pickett and B. Higgins were given the DOE Advanced Combustion Engine R&D Award (May 2003) for providing fundamental new insights into the soot formation processes in diesel sprays. The recognition was given at this year's DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation.
- Richard Steeper of SNL was given the SAE speaker's award for Excellence in Oral Presentation for his paper given at the SAE 2002 World Congress; awarded August, 2002.
- One of the early publications on the "SpaciMS" instrument by ORNL's William P. Partridge, et al, "Time-Resolved Measurements of Emission Transients By Mass Spectrometry," Society of Automotive Engineers Paper 2000-01-2952, 2000, has been included in the permanent archive, Diesel Nitrogen Oxide Emissions - Landmark Research 1995-2001, John H. Johnson ed., SAE, ISBN 0-7680-1067-5, p.79-88, 2002.

Invention and Patent Disclosures

- Two invention disclosures, ANL-IN-99-056 (patent pending) and ANL-IN-02-036, were filed for the work of Sreenath Gupta and Raj R. Sekar on ANL's portable instrument for transient PM measurements.
- CeramPhysics, Inc. filed a patent disclosure on the invention of their small, inexpensive combined NO_x and O_2 sensor. They have also filed for patents on both their oxygen sensor and the combined NO_x + oxygen sensor.
- C.L. Aardahl (PNNL), J.W. Hoard, and P.W. Park filed a patent entitled "Mixture of Heavy-Duty and Light-Duty Catalysts for NO_x Control Using Plasma Assisted Catalysis" on August 28, 2002.
- Larry R. Pederson et.al. of PNNL filed a patent disclosure entitled "Novel Oxygen Pumping Electrode for NO_x Sensor" (2003) based on their work to develop a NO_x sensor.
- R.D. Reitz, C.J. Rutland and R. Jhavar of the University of Wisconsin filed a patent application entitled "Controlled Valve Actuation for Emissions Reduction," University of Wisconsin Alumni Research Foundation (WARF) Patent Application Ref. No. P03152US/09820263, January, 2003.
- Cummins has filed for two patents related to their light-duty truck diesel engine development efforts: "Air/Oil Coalescer with Improved Centrifugally Assisted Drainage," Patent No. 6,640,792; and "Valve Train with a Single Camshaft," Patent No. 6,390,046.

The remainder of this report highlights progress achieved during FY 2003 under the Advanced Combustion Engine R&D Sub-Program. The following 43 abstracts of industry and National Lab projects provide an overview of the exciting work being conducted to tackle tough technical challenges associated with R&D of higher efficiency, advanced internal combustion engines for light-duty, medium-duty, and heavy-duty vehicles. We are encouraged by the technical progress realized under this dynamic Sub-Program in FY 2003, but we also remain cognizant of the significant technical hurdles that lie ahead, especially those presented for CIDI engines to continue improving in efficiency while meeting the EPA Tier 2 emission standards and heavy-duty engine standards for the full useful life of the vehicles. In FY 2004, we look forward to working with our industrial and scientific partners to overcome many of the barriers that still stand in the way of delivering advanced, high efficiency internal combustion engines.

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Advanced Combustion Engine R&D
Office of FreedomCAR and Vehicle
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Kenneth Howden
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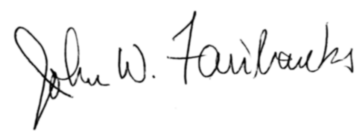

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SECTION II. ADVANCED COMBUSTION REGIMES AND MODELING FOR IMPROVED EFFICIENCY

II.A. Light-Duty Diesel Fuel Spray Research Using Advanced Photon Source

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DOE Technology Development Manager: Gurpreet Singh

Objectives

- Characterize fuel spray behavior of a light-duty diesel injector, especially in the near-nozzle region.
- Quantify the liquid mass flow of diesel injector nozzles as a function of space and time.
- Strive to create ambient conditions for these experiments as close to diesel engine-like as is practical.

Approach

- Design, test, and use pressure vessels that are compatible with the advanced photon source (APS) synchrotron environment to safely allow the testing of diesel injector nozzles. Vessels must be extremely robust to ensure the safety of the x-ray beamline and not disrupt other users.
- Run experiments to test several different injection parameters of interest to the engine community, such as orifice diameter, injection pressure, and ambient gas density.
- Analyze the acquired data to map fuel density of each configuration as a function of time and space.
- Determine the influence of independent variables upon fuel density distribution and correlate this information with the large knowledge base currently available.

Accomplishments

- Designed, built, and tested x-ray compatible pressure vessel (with x-ray permeable windows) to allow for the testing of diesel injectors under pressurized ambient conditions (Figure 1).
- Operated at pressurized ambient environments (up to 10 bar N_2) to display the influence of ambient pressure upon fuel density distribution.
- Conducted experiments using varied ambient N_2 pressures (1 bar, 2 bar, 5 bar, 10 bar) and two injection pressures (500 bar and 1000 bar), producing fuel density measurements as a function of space and time (Figure 2).
- Published industry papers describing experimental results, including a paper for the Institute of Liquid Atomization and Spray Systems (ILASS) entitled, "Effects of Ambient Pressure on Fuel Sprays as Measured Using X-ray Absorption."

Future Directions

- Continue to increase ambient pressure to attain more realistic diesel engine conditions. To expedite this process, several technique improvements will be explored, including modifying the fuel dopant to improve signal/noise ratio. A different dopant would allow the use x-rays with higher intensity and penetration, drastically reducing attenuation from the pressurized ambient gas.
- Expand the testing of injection parameters, such as orifice diameter and orifice finishing, to determine their influence upon fuel spray density distribution.
- Expand the use of the pixel array detector (PAD), a technical innovation that allows for 2-D data acquisition. Current data is acquired using a single-point detector, requiring numerous repetitions to cover the entire range of the fuel spray. Use of the PAD will facilitate the data acquisition and analysis process.

Introduction

In 1999, the first use of APS x-rays to study fuel sprays was undertaken. This effort originated out of an industry need for quantitative information about diesel fuel sprays in the near-nozzle region (within 10 mm of nozzle exit). Traditional optical or laser-based diagnostic techniques, such as Mie scattering, light extinction, or laser induced fluorescence (LIF), have not been successful in providing quantitative information in this region. The tremendous intensity of APS synchrotron x-rays provides unprecedented access to fuel spray regions previously unexplored. The current technique relies upon x-ray absorption to provide information regarding the fuel.

Project progress to date has been significant. An entirely new diagnostic technique has been developed and is undergoing continual refinement. X-rays are generally not used to study highly transient phenomena such as fuel sprays, requiring innovations in x-ray detection and beam refinement. In addition, improvements in creating a high-pressure ambient environment suitable for this work have been critical. Physicists and engineers attached to this project have teamed together to provide unique data that is unavailable elsewhere.

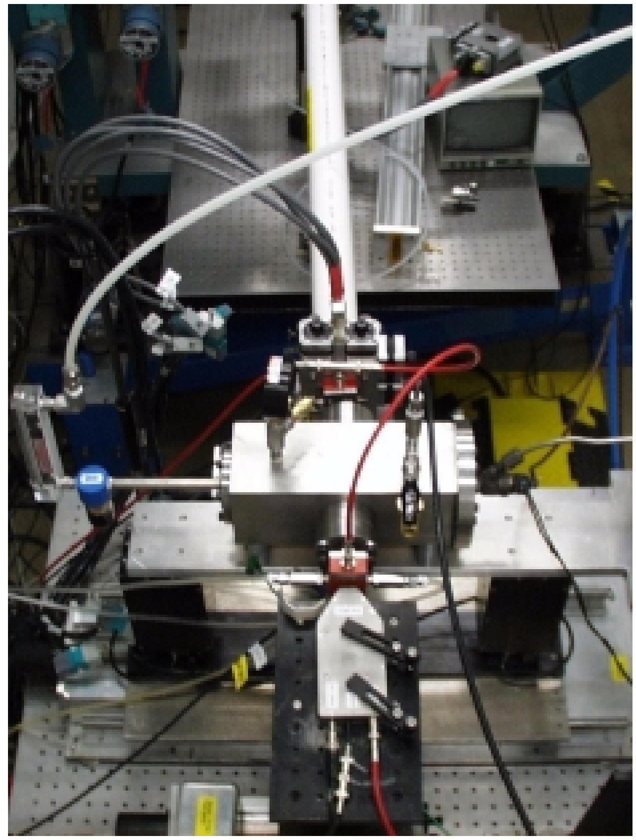

Figure 1. New Pressure Chamber Facilitates the Use of Synchrotron X-Rays to Study Fuel Sprays

Approach

The approach to this work has been multi-layered and requires communication between industry, DOE and ANL. The intent has always been to provide the manufacturers of fuel injection technology with data that is relevant to research and development of their products. Challenging emissions regulations enacted by the U.S. Environmental Protection Agency (EPA) have required all manufacturers to revisit every possible opportunity to reduce the production of harmful emissions from diesel engines. ANL has received tremendous support from Robert Bosch Company, the premier fuel injection technology manufacturer in the world, in the form of hardware and technical support. In addition, Daimler Chrysler, Delphi, and other manufacturers are interested in providing hardware to be tested using APS x-rays. The industrial collaborators have made it clear that they wish to see experimental results under more realistic

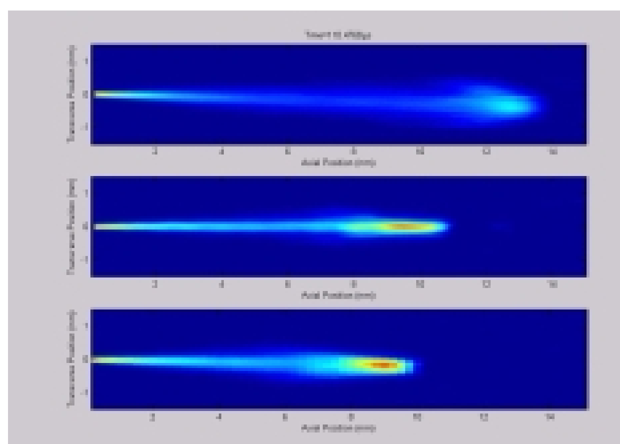

Figure 2. Fuel Spray Density and Penetration Differences as a Function of Ambient Pressure (N_2 gas at 1 atm, 2 atm, and 5.2 atm)

diesel engine ambient conditions, including high pressure and temperature.

As progress has developed, ANL has continued to seek collaboration with industrial partners and relationships with other national laboratories – especially Sandia National Laboratory. For example, a separate project that involves the use of heavy-duty injectors is done in collaboration with Sandia. The x-ray technique provides liquid density information that is not available using optical diagnostics, while Sandia's optical experiments provide complementary information, such as droplet sizing and fuel/air ratio.

Conclusions

- Ambient conditions used during the experiments progressed from 1 bar N_2 to 10 bar N_2, due to improved pressurized spray chamber.
- Significant differences were discovered in spray penetration and liquid density distribution as a function of ambient gas pressure.
- An increased number of samples are required to overcome x-ray signal attenuation as ambient pressure is increased.

FY 2003 Publications/Presentations

1. ILASS Americas 2003 Publication, "Effects of Ambient Pressure on Fuel Sprays as Measured Using X-ray Absorption," May 2003.
2. Presentation made at DOE Peer Review for Advanced Combustion and Aftertreatment, May 2003, Argonne, IL.
3. Presentation made for DOE Advanced Combustion CRADA Meeting, January 2003, Livermore, CA.

II.B. ANL-SNL Collaborative Research on Heavy-Duty Injector Spray Characteristics

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Objectives

- Study the mechanisms of spray atomization by making detailed, quantitative measurements in the near-nozzle region of sprays from heavy-duty injectors.
- Provide near-nozzle data that is crucial for the development of accurate spray models.
- Compare the data measured using the x-ray technique with existing data measured using conventional techniques at Sandia National Laboratory.

Approach

- Build a laboratory fuel injection system that is compatible with the x-ray technique based on the design of the existing system at Sandia.
- Test the fuel system for proper operation using visible light imaging techniques.
- Perform x-ray measurements of the fuel sprays generated from several different injector nozzle geometries.

Accomplishments

- Fuel system based on the Sandia design was constructed and successfully tested.
- First x-ray measurements of sprays from this heavy-duty injection system were completed in March 2003. In these studies, we measured the time-resolved mass distribution of sprays from three different nozzle geometries.
- Preliminary analysis of the x-ray data shows striking differences in the mass distributions from the different nozzle geometries. Unusual structures were observed in several of these sprays.

Future Directions

- Continue the analysis of the recently completed x-ray measurements. This will include measurements of the spray penetration and cone angles, as well as time-resolved measurements of the fuel mass distribution. We also hope to make model-based calculations of the time-resolved three-dimensional fuel density distribution of the spray.
- Perform further x-ray measurements on sprays under different conditions, including studying the effects of varying the injection pressure and ambient pressure.
- Compare x-ray data with conventional spray measurements at Sandia.
- Collaborate with spray modelers to develop more accurate models of the atomization process.

Introduction

Fuel injection systems are one of the most important components in the design of combustion engines with high efficiency and low emissions. A detailed understanding of the fuel injection process and the mechanisms of spray atomization can lead to better engine design. This has spurred considerable activity in the development of optical techniques (primarily using lasers) for measurements of diesel fuel injection systems. Some of these optical techniques have become commercially available and can be readily applied to the testing and development of modern injection systems. Despite significant advances in laser diagnostics over the last 20 years, scattering of light from the large number of droplets surrounding the spray prevents penetration of the light and limits such measurements to the periphery of the spray. This is especially true in the near-nozzle region of the spray, which is considered to be the most important region for developing a comprehensive understanding of spray behavior. Existing models of spray structure have to date only been compared with data acquired in the region relatively far from the nozzle. It is unknown how well these models apply in the crucial near-nozzle region. The limitations of visible light in the near-nozzle region of the spray have led us to develop the x-ray absorption technique for the study of fuel sprays. X-rays are highly penetrative, and measurements are not complicated by the effects of scattering. The technique is non-intrusive, quantitative, highly time-resolved, and allows us to make detailed measurements of the spray, even in the dense droplet region very near the nozzle.

Approach

This project utilizes a heavy-duty fuel injector designed and built as a prototype by Detroit Diesel Corp. with specially-fabricated single-hole nozzles. The injector and nozzles are similar to those which have been studied at Sandia National Laboratory over a wide range of conditions using a number of different measurement techniques [1,2,3]. Our approach is to make detailed measurements of the sprays from this injector using the x-ray technique. This will allow us to compare the x-ray results with the large body of existing data, and extend the existing knowledge into the near-nozzle region.

The x-ray measurements were performed at the 1BM-C station of the Advanced Photon Source at Argonne National Laboratory. A schematic of the experimental setup is shown in Figure 1; detailed descriptions of the experimental methods are given in [4] and [5]. The technique is straightforward; it is similar to absorption or extinction techniques commonly used in optical analysis. However, the x-ray technique has a significant advantage over optical techniques in the measurement of sprays: because the measurement is not complicated by the effects of scattering, there is a simple relation between the measured x-ray intensity and the mass of fuel in the path of the x-ray beam. For a monochromatic (narrow wavelength bandwidth) x-ray beam, this relation is given by

$$I/I_0 = \exp(-\mu_M M)$$

where I and I_0 are the transmitted and incident intensities, respectively; μ_M is the mass absorption constant; and M is the mass of fuel. The constant μ_M is measured in a standard cell, and the incident and transmitted intensities are measured as a function of time by the x-ray detector. This allows direct determination of the mass of fuel at any position in the spray as a function of time. It is the goal of our work to use the x-ray technique to measure sprays from our heavy-duty fuel injector at different injection pressures, different ambient pressures, and using different nozzle geometries. Our work will be compared to the existing data that has been acquired by Sandia National Laboratory using a similar injection system. This will allow us to extend the Sandia database into the region very near the nozzle,

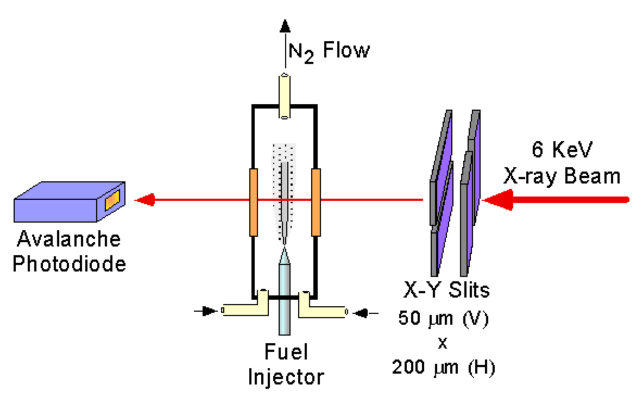

Figure 1. Schematic of the Experimental Setup

and we will be able to determine whether parameterizations that have been developed based on the Sandia data apply in this region. We will also collaborate with spray modelers to incorporate this previously unknown knowledge of the near-nozzle region of the spray into new models. This will lead to an increased understanding of the mechanisms of spray atomization and will facilitate the development of fuel injection systems designed to improve efficiency and reduce pollutants.

Results

X-ray measurements were performed on three different nozzles under otherwise identical conditions. The first nozzle had an orifice diameter of 180 μm and orifice length to diameter ratio (L/D) equal to four, the second had a diameter of 250 μm and L/D = 4, while the third had a diameter of 250 μm and L/D = 8. The measurements were made at an injection pressure of 1000 bar, the spray duration was 2.5 ms, and the ambient gas was N_2 at 1 bar pressure and 25°C.

Figure 2 shows images of sprays reconstructed from x-ray measurements of each of the three different nozzles; each image was measured 45 μs after the start of injection. Because the x-ray technique is quantitative, the images produced are not merely a measurement of the amount of light transmitted into the camera, but are two-dimensional projections of the mass of the spray. This allows the two-dimensional mass distributions to be compared between the images. The differences between sprays

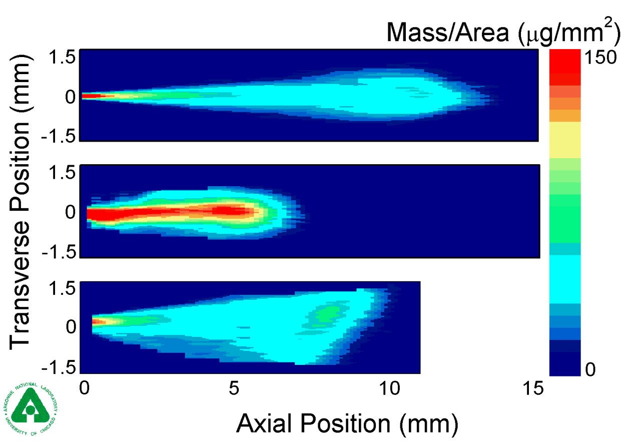

Figure 2. X-ray Image Reconstructions of Sprays from Three Different Nozzle Geometries

caused by the changes in nozzle geometry are striking. The spray from the first nozzle shows the greatest penetration, while the other two nozzles produced sprays that were moving more slowly. While each of the three sprays show a high density region near the nozzle orifice, the density quickly decreases as you move away from the nozzle in the top and bottom images, while this high density core persists out to 6 mm from the nozzle in the center image. While the upper two images appear to be nearly symmetric about the spray axis, the bottom image shows a very asymmetric fuel distribution. The relationship between these fuel distributions and the nozzle geometry is still under analysis, but the images show the power of the technique in resolving features of the spray in the near-nozzle region that cannot be observed with other techniques.

All of the measurements made using the x-ray technique are made as a function of time. This allows the dynamic features of the sprays to be studied and compared. Figure 3 shows the mass versus time plots at several different positions in the spray from a single nozzle. The uppermost plot shows the time evolution at a position along the central axis of the spray 0.2 mm from the nozzle. At the left of this plot, the measured mass is zero for the first 400 μs. This is the region when the fuel has not yet reached the measurement region 0.2 mm from the nozzle. At a time of about 400 μs, there is a sharp rise in the mass; this is the region where the leading edge of the fuel intersects the measurement region of the x-ray beam. Just after the sharp rise at the leading edge, the mass reaches a near-steady value of about 2.75 μg. Because this measurement is made only 0.2 mm from the nozzle, the flat mass versus time plot can be interpreted as the injector reaching a steady-state mass flow in this time region. This measurement made 0.2 mm from the nozzle can be compared with measurements made 0.8 and 2.0 mm from the nozzle. It can be seen in the latter two plots that the mass versus time is no longer flat, and that fluctuations increase as one moves farther from the nozzle. This indicates that some physical effect is causing fluctuations in the mass versus time, that this is taking place external to the nozzle, and that the effect is more prominent farther from the nozzle. Several possible mechanisms could cause this behavior, including air entrainment, variations in speed along the spray axis, and transverse motion of

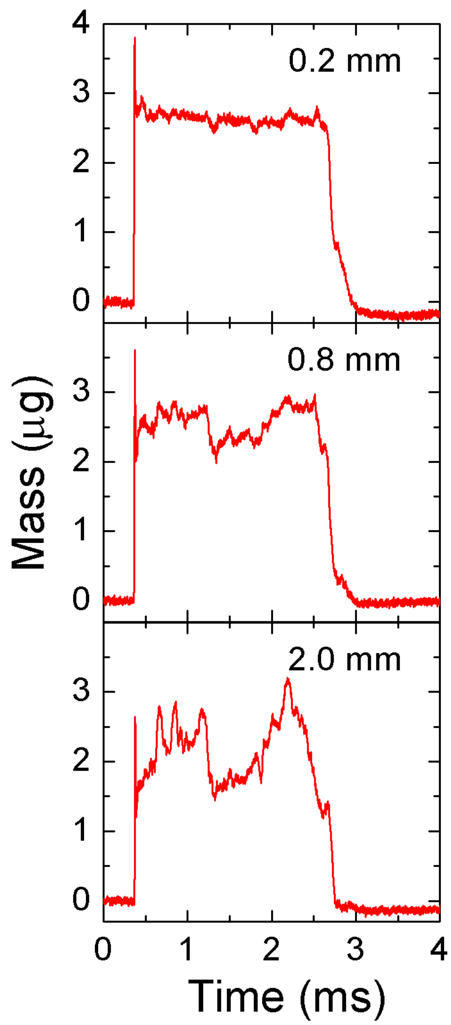

Figure 3. Time Evolution of the Mass Measured on the Central Spray Axis at Three Distances from the Nozzle

the fuel. Careful theoretical modeling may be able to reproduce the features shown in these plots and would be an important discovery in the study of the mechanisms of spray atomization.

Conclusions

- Testing has shown that the fuel system which we designed and built is operating as expected and is also compatible with measurements using the x-ray technique.
- The x-ray technique can be used to observe subtle changes in the spray structure resulting from different nozzle geometries. These changes are not apparent using other imaging techniques.
- The fuel mass distributions can be measured and compared between nozzles of different geometries. This may be a very useful diagnostic tool to fuel system manufacturers when designing and testing new injection systems.
- The time-dependent mass measurements show a change in the structure of the spray as it moves away from the nozzle. This may be a critical piece of information in the development of an accurate understanding of spray behavior. The quantitative measurements of this phenomenon that we have provided may help to elucidate the mechanisms of spray atomization. This could ultimately lead to the design of cleaner, more efficient engines.

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1. Presentation at DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation, Argonne National Laboratory, May 13-15, 2003.
2. Tentatively accepted for publication and oral presentation at SAE Powertrain & Fluid Systems Conference, October 27-30, paper 03FFL-212.

II.C. Light-Duty (Automotive) Diesel Combustion

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Subcontractors:
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Objectives

- Provide the physical understanding of the in-cylinder combustion processes needed to meet future diesel engine emissions standards while retaining the inherent efficiency and low CO_2 emissions of the direct-injection diesel engine.
- Improve the multi-dimensional models employed in engine design and optimization and validate the model predictions against in-cylinder measurements and tailpipe emissions.
- Investigate the effects of various combustion system parameters on engine performance and emissions, thereby generating a knowledge base for optimization efforts.

Approach

- Obtain measurements of flow and thermophysical properties in an optically-accessible engine using laser-based measurement techniques.
- Measure engine performance, fuel economy, and emissions in a non-optical test engine with the identical geometry.
- Compare in-cylinder measurements and engine emissions and performance to model predictions.
- Refine and improve models and engine operating strategies.

Accomplishments

- Experimentally identified dominant flow turbulence sources through direct measure of turbulence production. Compared with model predictions.
- Evaluated the evolution of the turbulent time scale within the combustion chamber. This scale is central to modeling of both the turbulence and the combustion processes.
- Evaluated linear and higher-order turbulent stress modeling relationships. Identified important aspects of flow physics not captured by the simpler (industry standard) models.
- Demonstrated that industry standard turbulence models overestimate the turbulence energy dissipation after injection.
- Investigated low-temperature combustion regimes; established necessity of high exhaust gas recirculation (EGR) levels (not merely premixing) for obtaining low emissions.

Future Directions

- Evaluate higher-order stress modeling relationships and turbulent time scales over a broad range of conditions, thereby enabling well-founded modeling recommendations.

- Attempt a direct measure of turbulent dissipation to enable quantitative model refinement.
- Conduct detailed experiments quantifying the mixing behavior of low-temperature combustion regimes and the impacts of swirl, injection pressure, multiple injection schemes, and bowl geometry/ spray targeting.

Introduction

Direct-injection diesel engines have the highest fuel efficiency and the lowest CO_2 emissions of any reciprocating internal combustion engine technology. This efficiency comes at the cost, however, of NO_x and particulate matter (soot) emissions, which are high in relation to proposed future emission standards. Reduction of these emissions through clean in-cylinder combustion processes is imperative if vehicles powered by these engines are to be available at a competitive cost. Recently, the potential of low-temperature combustion regimes to dramatically reduce NO_x and soot emissions has been demonstrated. These systems rely on high levels of EGR to increase the ignition delay (which allows greater premixing prior to the onset of combustion) and to reduce the combustion temperature. With high EGR levels, a larger quantity of the in-cylinder air/EGR mixture is needed to burn the fuel, and rapid mixing is required both during the ignition delay period (to minimize soot formation) and in the latter stages of combustion (to complete the fuel oxidation process).

Increased mixing early in the combustion process can be achieved through the use of increased injection pressure. Unfortunately, the increased mixing rates caused by the high pressure injection event decay rapidly and exert little influence on the late-cycle mixing. There are at least two promising methods, however, to influence the late-cycle mixing: 1) enhanced generation of late-cycle turbulence through control of the bulk flow structures and 2) use of multiple injection events. Understanding the process by which turbulence can be generated using these methods—and developing a predictive modeling capability—are crucial steps toward the development and optimization of low-emission engines and are the primary objectives of this work.

Approach

The research approach involves three parallel efforts in a closely coordinated project. Detailed flow and thermo-chemical property measurements are made in an optically-accessible laboratory test engine; emissions, performance and fuel consumption measurements are made in a traditional single-cylinder test engine; and computer simulations are performed and compared to the data obtained in both the optical and traditional test engines. Natural synergies emerge among these three efforts. For example, detailed measurements of the flow variables permit the evaluation and refinement of the computer models, while the model results can be used to clarify the flow physics—a process that is difficult if only limited measurements are employed. Similarly, traditional test engine measurements serve to identify interesting operating parameter trade-offs that bear further investigation either numerically or experimentally in the optical engine.

Results

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

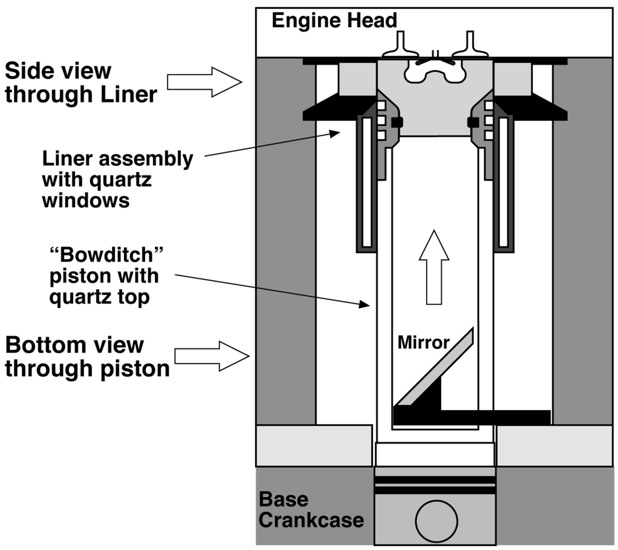

Figure 1. Schematic of the Optical Engine Facility

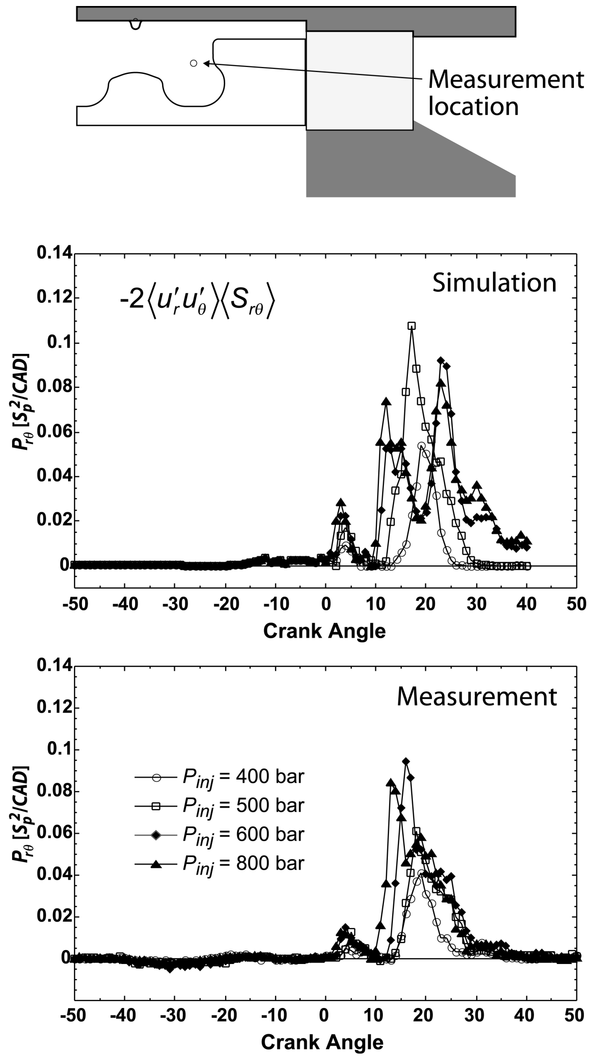

Figure 2. Measured and Simulated Turbulence Production within the Central Region of the Bowl at a Simulated Idle Condition

A major thrust of the research performed in FY 2003 was directed towards clarifying the sources of turbulence in the combustion chamber for the swirling flows typical of high speed direct injection (HSDI) diesel engines. Identifying and understanding the major sources of turbulence may suggest strategies for enhancing the turbulence and its associated mixing. To identify these sources, direct measurements of the turbulence production terms were obtained through measurement of the turbulent stresses and the appropriate mean velocity gradients. An example of the measured turbulence production in the horizontal (*r*-θ) plane is shown in Figure 2. For comparison, the predictions of the numerical simulation are also shown. Qualitatively, the measured and predicted turbulence production agree well. Both suggest that the swirling flow has little effect on the in-cylinder turbulence until after the fuel injection event, which disrupts the unproductive solid-body-like flow structure. However, there are significant differences in the details of the model predictions.

To investigate these differences further, we have investigated the applicability of the stress model formulation employed in the standard *k*-ε turbulence model. Here, the stress is assumed to be linearly related to the mean flow rate-of-strain. This simple relation is well founded in both theory and measurements, but breaks down when turbulent time scales are comparable to (or larger than) the mean flow time scales. In diesel engines, the mean flow time scales can become quite small, especially after the fuel injection event. To evaluate the stress modeling, the turbulent time scale and the appropriate mean flow gradients are measured, and the modeling hypothesis is applied directly to the measured quantities to predict the turbulent stress. The predicted stress is subsequently compared to the measured stress. Figure 3 shows a comparison between the measured stress and the stress obtained by applying the standard linear (*k*-ε) modeling hypothesis. Overall, the linear stress modeling performs well, but improvement is needed in the late compression stroke (between -45 and -15 crank angle

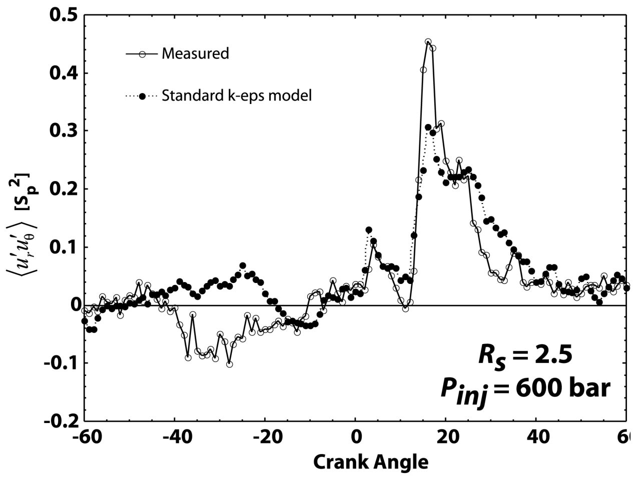

Figure 3. Comparison of the Measured Stress with the Predictions of the Linear Relationship Employed in the *k*-ε Turbulence Model (the measurement location is the same as is shown in Figure 2)

degrees [CAD]) as well as near the time of the peak measured late-cycle shear stress near 18 CAD.

To remedy the shortcomings seen in Figure 3—without introducing substantial speed, stability, and complexity penalties into the numerical models—we have investigated the use of higher-order relationships in which the stress is proportional to products of the elements of the mean flow rate-of-strain and rate-of-rotation tensors. A comparison of one such model (Reference 1) to the measured stress is presented in Figure 4. Note that the performance is substantially better in the late compression stroke, although the late-cycle stress prediction near 18 CAD has not been substantially improved. To improve on the stress modeling at this time, we find that a still higher-order stress relationship is required.

In addition to the turbulence measurements described briefly above, work in the traditional test engine has been focusing on low-temperature combustion regimes and the range of operating parameters under which these regimes can be realized. Figure 5 shows the behavior of NO_x emissions as both the injection timing (start of injection – SOI) and EGR rate are varied. Low NO_x emissions can be obtained under a variety of EGR/SOI combinations. However, if only a small penalty in fuel consumption is permitted, the low NO_x operating conditions corresponding to the latest

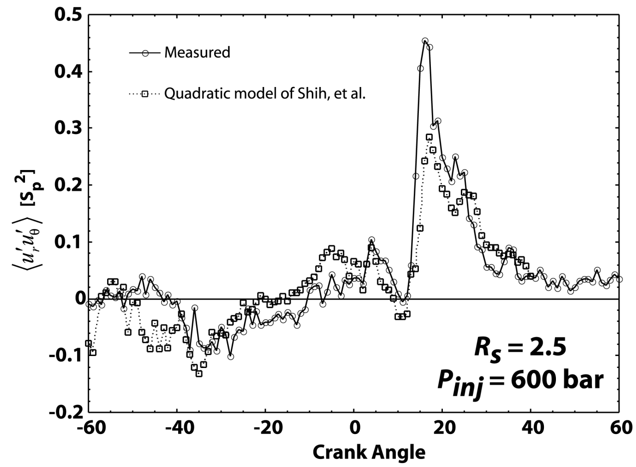

Figure 4. Comparison of a Higher-Order Stress Model to the Measured Shear Stress

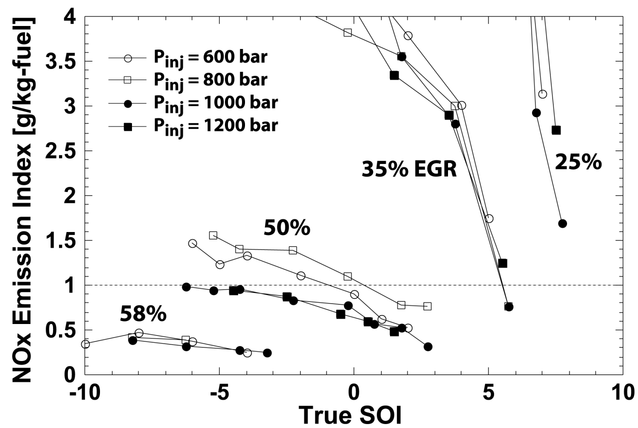

Figure 5. Variation of NO_x Emissions with Injection Timing and EGR Rate (1500 RPM, 300 kPa gross indicated mean effective pressure)

injection timings are eliminated. Accordingly, high EGR rates are required to meet the upcoming 2007 emissions standards (depicted by the dashed line shown in Figure 5).

Conclusions

- The dominant effect of flow swirl on turbulence generation within the combustion chamber occurs after the fuel injection process, which disrupts the unproductive solid-body-like flow.
- The numerical model qualitatively captures the turbulence generation associated with flow swirl,

but there are significant differences in the detailed profiles.

- Linear stress modeling performs reasonably well in these swirling flows, but significant improvements can be achieved by moving to higher-order turbulent stress models.

- Future (2007) emissions standards can be met at low-load operating conditions by a variety of SOI/EGR combinations. For small penalty in fuel consumption, however, high EGR rates (≈50%) are required.

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II.D. Effects of the In-Cylinder Environment on Diffusion Flame Lift-Off in a Heavy-Duty Diesel Engine

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Objectives

- The overall objective of this project is to advance the understanding of diesel engine spray, combustion, and emissions formation processes through the application of advanced laser-based and imaging diagnostics in an optically-accessible, heavy-duty, direct-injection diesel engine that is capable of operating under conditions typical of real diesel engines.
- Specific objectives for FY 2003 include:
  - Evaluate the influence of multiple factors present in a realistic diesel engine environment on the diesel flame lift-off length (LOL) and compare these measurements to those obtained from a single-hole injector in a simulated diesel engine environment.
  - Implement and characterize a modern, common-rail fuel injection system to update the laboratory facilities and facilitate future examination of advanced combustion strategies.

Approach

- Investigation of the influence of the in-cylinder environment on diesel flame LOL:
  - Improve an OH chemiluminescence-based LOL diagnostic to better reject elastic light scatter interference, and compare measurements to those obtained from OH planar laser-induced fluorescence (OH-PLIF) measurements to better evaluate both techniques.
  - Measure the in-cylinder diesel jet LOL over a range of charge temperatures and densities, using different injector nozzle configurations and imaging viewpoints, and use statistical data analysis to compare engine LOL data over a range of charge temperatures and densities to single-jet data from simulated diesel conditions.
- Implementation of modern, common-rail fuel injection system:
  - Work with industrial partners to design and implement modifications to the optical engine for retrofit installation of a modern, common-rail injection system, and demonstrate its performance.
  - Design, construct, and assemble a hole-specific, momentum-based rate-of-injection meter to characterize the spray dynamics of the common-rail injector.

Accomplishments

- Conducted a detailed investigation of the influence of the in-cylinder environment on the diesel flame LOL in a realistic engine environment.
  - Developed a two-color, two-camera OH chemiluminescence imaging technique to correct for laser elastic scatter interference and provide better measurements of the diesel flame LOL.

- Established that asymmetry in the shape of the diesel flame biases the LOL measurement from OH chemiluminescence to shorter values, and quantified the bias through comparison with OH-PLIF data.
- Demonstrated that coupling between adjacent jets likely shortens the LOL and lessens its dependence on in-cylinder temperature and density.
- Discovered significant cycle-to-cycle variation in the LOL even under very stable engine operating conditions, which has important implications for advanced soot reduction strategies that rely on manipulation of the LOL.
- Observed a strong influence of in-cylinder swirl flows on the shape of the diffusion flame, whereas nearby in-cylinder surfaces had little effect on flame shape.

• Implemented and characterized a modern common-rail fuel injection system.

- The optical engine was modified as necessary to implement a state-of-the-art, production-ready, common-rail fuel injection system, and the performance of the system in the optical engine was demonstrated, enhancing the capabilities of the laboratory facility for investigation of advanced combustion strategies that are of interest to industry.
- Characterized the hole-specific spray dynamics of the common-rail injector so that future combustion and pollutant formation data obtained with the new system may be better interpreted.

Future Directions

• Implement a chemiluminescence-based nitrogen oxides (NO_x) measurement capability in the exhaust stream of the optical engine facility so that highly quantitative NO_x measurements may be correlated with optically-observable combustion phenomena to improve the understanding of NO_x formation processes in diesel engines.

• Initiate a study of NO_x formation under conditions with long ignition delay, which are of interest for both conventional diesel combustion and advanced, multi-mode combustion strategies.

• Investigate NO_x formation processes for advanced, multi-mode combustion strategies (e.g., pilot, post, and split injections).

Introduction

In diesel engines, the combusting in-cylinder diesel fuel spray is enveloped by a diffusion flame, which surrounds the downstream extent of the jet but does not propagate all of the way back to the injector. Rather, the upstream edge of the flame remains a finite distance from the injector nozzle, which is termed the “lift-off length” (LOL). Recent experimental studies conducted in a constant-volume combustion chamber capable of simulating the thermodynamic environment of diesel engines have revealed that the diffusion flame LOL has an important influence on in-cylinder soot formation [1-3]. Soot formation was found to decrease as premixing of fuel and air upstream of the LOL was increased, i.e., as the LOL increased [1]. Notably, soot formation in the diesel jets could even be reduced to essentially zero at very long LOLs [1]. Factors such as fuel injection pressure, fuel nozzle hole diameter, and in-cylinder gas temperature, density, and oxygen concentration were observed to affect the LOL, and thus affect soot formation [1,2,3]. More recently, similar measurements of the diesel flame LOL were obtained in the optically-accessible heavy-duty diesel engine of the current study, which is more representative of the in-cylinder environment typical of realistic diesel engines [4]. These measurements have revealed that the LOLs in the engine were much shorter than expected, based on correlations established at the same thermodynamic conditions in the single-jet, simulated diesel environment. In this more realistic diesel engine environment, additional factors, such as in-cylinder gas flows (swirl, squish, tumble) and the proximity of in-cylinder surfaces and adjacent jets may also affect the flame LOL.

It is the objective of the current study to examine the influence of factors present in a realistic engine environment on the diesel flame LOL. Such information will assist in the application of the valuable knowledge regarding diesel pollutant formation previously gained in well-controlled, well characterized simulated diesel environments to more realistic diesel engine environments. Additionally, to update the capabilities of the facility so that modern, advanced combustion strategies may be investigated in the near future, a common-rail fuel injection system was designed and implemented. The new injection system was also carefully characterized using a newly-constructed, momentum-based, hole-specific rate-of-injection meter. This investigation, and all of the work on this project, is conducted in cooperation with our industrial partners (including Cummins, Caterpillar, Detroit Diesel, Mack Trucks, International, John Deere, and General Electric), and the results are presented at Heavy-Duty Diesel CRADA and Advanced Engine Combustion Working Group meetings.

Approach

This project utilizes an optically-accessible, heavy-duty, direct-injection diesel engine for in-cylinder measurements of diesel spray, combustion, and pollutant formation processes. A cut-away cross-sectional schematic of the engine is shown in Figure 1. An extended piston with a large window located in the bowl of the piston provides primary imaging access to the combustion chamber. Additional access for imaging and/or laser diagnostics is provided by a window inserted in the cylinder head in place of one of the exhaust valves, and by five windows inserted in the cylinder wall. The engine is capable of operating under fired conditions over the full range of conditions typical of production diesel engines.

In the current study, the OH chemiluminescence imaging diagnostic previously developed to measure in-cylinder LOL [4] was improved to provide measurements that are more accurate. As shown in Figure 1, a two-color, two-camera technique was employed. Using appropriate spectral filters, the first camera recorded ultraviolet emission from OH chemiluminescence, with inherent light-scattering interference from the liquid fuel spray. The second camera used a different color-filter to primarily image soot emission, which is spatially separated (farther downstream) from the OH chemiluminescence. By subtracting the two images from each other, the light scattering interference in the OH chemiluminescence image could be removed without affecting measurement of the LOL.

A similar two-color, two-camera technique was used to measure the LOL in an alternative way, by using planar laser-induced fluorescence of OH (OH-PLIF). In these experiments, a laser beam was shaped into a thin sheet using lenses and directed into the engine so that it intersected the diesel jet along the spray axis. The OH molecules present in the flame were illuminated by the laser sheet, and the resulting images were used to measure the LOL along the jet axis. In a similar way as in the OH chemiluminescence technique, the second camera allowed elastic-scatter interference to be removed by image subtraction. Although the OH-PLIF technique could only be used for nozzles with exceptional side-optical access (widely spaced jets), the resulting LOL from both techniques were compared to quantify the experimental bias expected with the OH chemiluminescence technique.

To examine the influence of adjacent jets on the LOL, the flame LOL was measured for three different injector nozzle hole geometries having

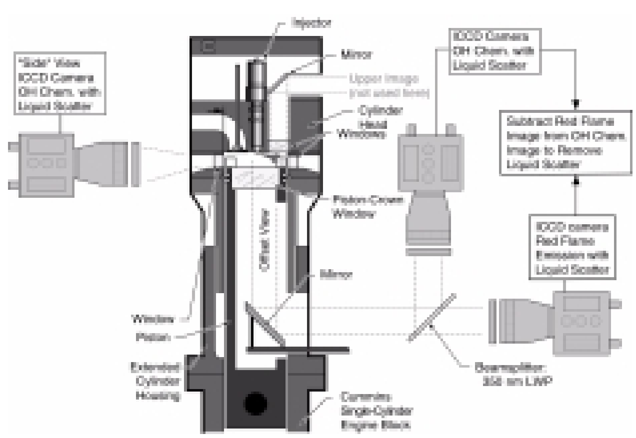

Figure 1. Schematic Diagram Showing Optical Engine and Two-Camera, Two-Color OH Chemiluminescence/OH-PLIF Diagnostic

different spacing between jets. Since significant cycle-to-cycle variation was observed in the LOL, many measurements were obtained over a range of charge temperatures and densities to generate a statistical database. The mean behavior of the LOL was extracted from the large dataset using statistical analysis techniques. To examine the influence of in-cylinder swirl flow on the shape of the flame, the LOL on each “side” of the jet was measured and compared over the same range of in-cylinder charge densities and temperatures. To examine the influence of in-cylinder surfaces (i.e., the firedeck) on the shape of the flame, the OH chemiluminescence was imaged from a side view, through one of the windows located in the cylinder wall (see Figure 1).

Results

Shown in Figure 2 are two pictures, each showing an image of OH chemiluminescence (in grayscale) overlayed by white contour lines showing the location of simultaneous OH-PLIF intensity at 20% of full scale, as viewed through the large piston window. Note that the camera field of view was adjusted so that it was “zoomed-in” on one of the jets and thus does not show the entire combustion chamber. The injector is located on the left of the images (white dot), and the curved white line on the right of the images represents the partial view of the edge of the piston bowl. For these experiments, a three-hole injector was employed to provide the optical access necessary for the OH-PLIF measurements. The grayscale OH chemiluminescence indicates the location of the diffusion flame, and the LOL is the distance from the injector to the most upstream extent of either the grayscale OH chemiluminescence or the OH-PLIF contour, as indicated in Figure 2.

In most of the images, the OH chemiluminescence and OH-PLIF images display the same LOL, as shown in the top image of Figure 2. In some images, however, the OH chemiluminescence image indicates a shorter LOL than the OH-PLIF measurement, as indicated in the lower image in Figure 2. Using statistical analysis, the mean LOL, measured using both techniques, was extracted from a large dataset acquired over a range of in-cylinder temperatures and densities. The graph on the bottom

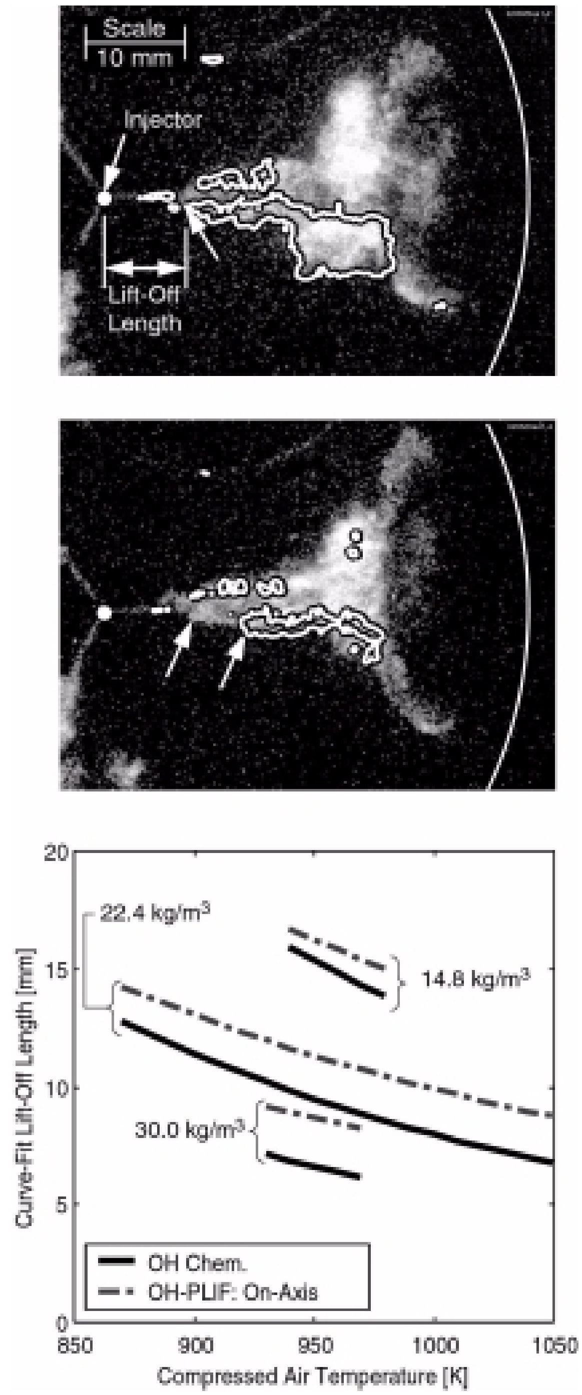

Figure 2. Top: Two simultaneous images of OH chemiluminescence (grayscale) overlayed by OH-PLIF contours at 20% of full-scale intensity. The edge of the piston bowl rim is indicated by the white arc on the right side of the images, and the white dot indicates the location of the fuel injector. Bottom: Variation of mean LOL with in-cylinder charge temperature and density for each diagnostic, as determined through statistical analysis.

of Figure 2 shows that on average, the OH-PLIF measurement indicates a 2 mm shorter LOL than the OH chemiluminescence technique. The difference between the two LOL measurements is due to asymmetries in the shape of the diffusion flame, which do not affect the on-axis OH-PLIF measurement but do affect the line-of-sight OH chemiluminescence imaging measurement. The effect of asymmetric flame shape is likely one of the reasons that the flame LOLs measured in the engine were shorter than those measured under similar thermodynamic conditions with a single-hole injector, but they are not large enough to account for the entire difference. Unfortunately, most realistic injector hole geometries do not allow sufficient optical access for on-axis OH-PLIF measurements of the flame LOL, so OH chemiluminescence measurements must be used, with the recognition that the measurement is somewhat biased to shorter values under conditions with irregularly-shaped flames.

Shown in Figure 3 are two grayscale images of OH chemiluminescence from the diffusion flame for two different injector nozzle hole geometries. The top image was acquired using a production 8-hole injector with a nominal spacing of 45° between adjacent jets. The bottom image was acquired using a special 6-hole injector having 90° between the jet of interest and the nearest adjacent jets. To illustrate the significance of liquid-scatter interference, the top image has not been corrected to remove liquid scatter interference, and the interference is noted on the image. In the lower image, the light-scattering interference off the liquid fuel has been removed using the second camera image.

Significant cycle-to-cycle variation in the lift-off data was observed, as shown by the individual data points in Figure 3. This rather large variation in the LOL data was observed even when the global engine performance was very stable. Previous experiments in the simulated diesel combustion environment, under conditions with much less cycle-to-cycle variation, have shown that as the LOL is increased, soot formation decreases, as shown in Figure 4 (solid black line). If the LOL is long enough, zero soot formation can be achieved in the jet. Conditions with cycle-to-cycle variation, however, will yield a distribution of LOLs about the mean value (dotted line), such as observed in the optical engine of the current study. Under such conditions, the threshold to achieve zero soot formation will be pushed to

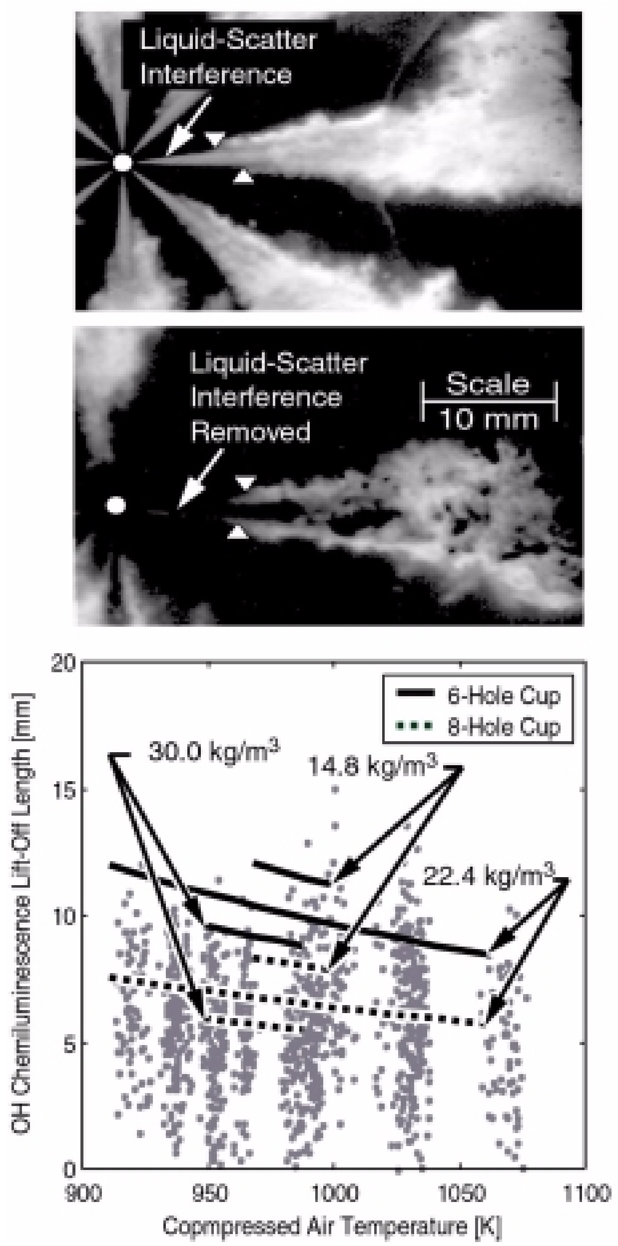

Figure 3. Top: Raw OH chemiluminescence image of diesel jet for 8-hole injector with 45° spacing between jets. Middle: OH chemiluminescence image of diesel jets for 6-hole injector with 90° spacing between jets of interest, corrected to remove light scattering from liquid fuel. Bottom: Variation of mean LOL with in-cylinder charge temperature and density for the two injector hole geometries, as determined through statistical analysis. The dots represent individual data points for the 8-hole injector.

longer LOLs (solid gray line), requiring more extreme conditions to yield a sufficient average LOL for zero soot formation.

Even though significant cycle-to-cycle variation was observed, the datasets could be statistically analyzed to uncover the underlying mean behavior. This analysis revealed that on average, the LOL for the more closely-spaced jets (e.g., top image) is about 35% shorter than that for the more widely-spaced jets (e.g., lower image), as shown in the graph of the mean behavior at the bottom of Figure 3 (solid *vs.* dotted lines). Thus, the proximity of adjacent fuel jets can have a significant influence on the LOL, accounting for a majority of the difference between the engine LOL data and the single-jet LOL data under simulated diesel conditions. Some data for a 3-hole injector showed contradictory trends, but this may be due to radical differences in the internal nozzle flow characteristics for the low-flow 3-hole injector tip, which was not properly sized for the high-flow injector. Measurements of the hole-specific spray momentum would have helped to resolve this issue, but the momentum-based rate-of-injection meter (see end of this section) was not yet constructed at the time these data were acquired.

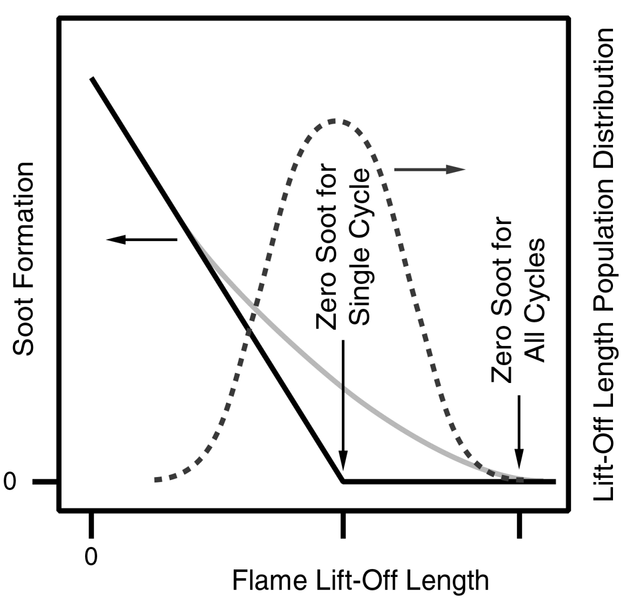

Figure 4. Dependence of average in-cylinder soot formation on mean LOL for zero cycle-to-cycle variation (solid black line) and high cycle-to-cycle variation (solid gray line) in the LOL. The dotted line represents the distribution of LOLs about the mean value for high cycle-to-cycle variation conditions.

To assess the influence of in-cylinder swirl flow on the upstream shape of the diffusion flame, the LOL on each "side" of the jet was compared under a condition with a moderate swirl ratio of about 0.5. As shown in Figure 5, individual images show varying degrees of asymmetry, from relatively equal LOLs (top image) to more asymmetric shapes (lower image). Statistical analysis of the data shows that on average, the LOL on the side of the jet that faces the swirl flow (windward side) is 7% longer than that on the other side (leeward side), as shown in the graph on the bottom of Figure 5.

The proximity of the in-cylinder surface of the firedeck (cylinder head) had little effect on the flame shape near the LOL. As shown in Figure 6, individual OH chemiluminescence images, acquired using the 3-hole injector cup from the side view, displayed some asymmetry in the flame shape. On average, however, the flame LOL near the firedeck was statistically equal to that on the opposite side.

To update the hardware and capabilities of the laboratory facility to reflect recent advances in fuel injection technology, a modern, production-ready common-rail fuel injection system was designed for retrofit installation in the optical engine. The injection system was implemented, and its performance in the engine was successfully demonstrated. Based on data from the current study (see above), the importance of differences in spray dynamics for each fuel hole of the injector on combustion processes was recognized. Accordingly, a new momentum-based, hole-specific rate-of-injection meter was designed, constructed, and utilized to characterize the spray dynamics of each hole of the new common-rail injector. Preliminary in-cylinder measurements have shown a strong correlation between hole-specific spray dynamics and differences in individual jet ignition characteristics with the common-rail injector.

Conclusions

Using laser and imaging diagnostics, the influence of the in-cylinder environment on diesel flame lift-off lengths (LOLs) was investigated in the

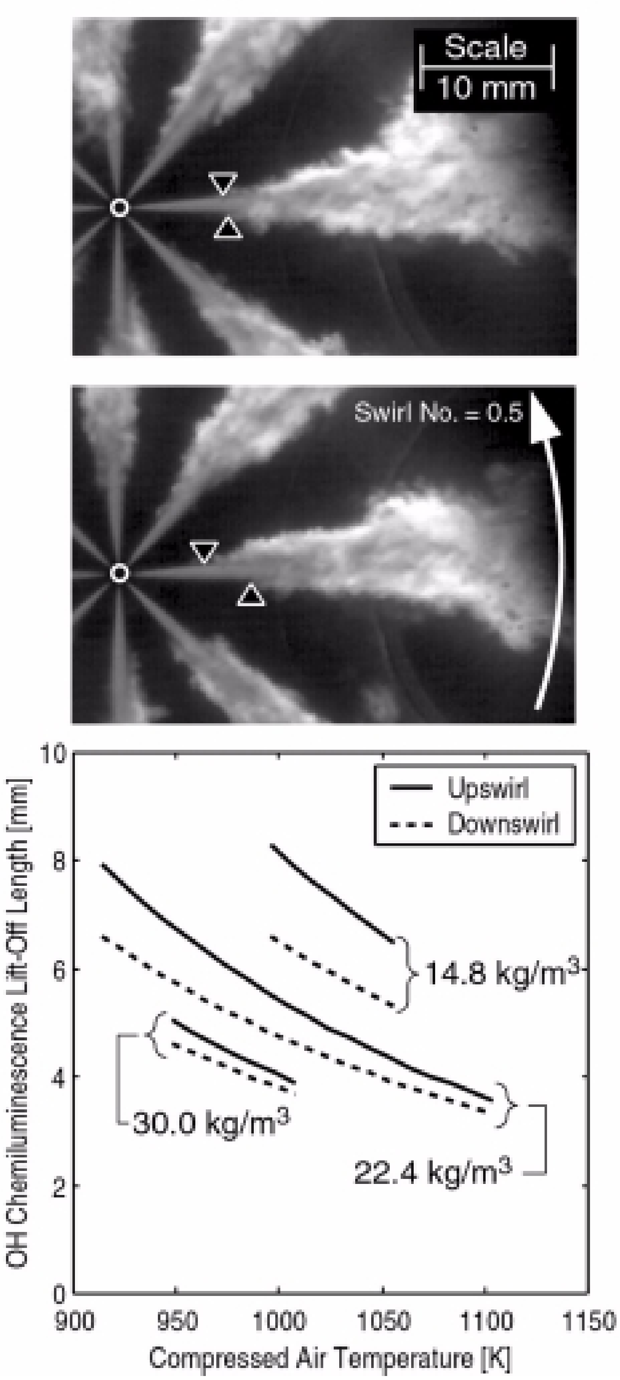

Figure 5. Top: Two raw OH chemiluminescence images showing examples of asymmetry in flame shape caused by in-cylinder swirl flow. Bottom: Variation of mean LOL on the upswirl and downswirl sides of the jet with in-cylinder charge temperature and density, as determined through statistical analysis, at a swirl ratio of 0.5.

current study to better understand the departure of flame lift-off behavior in the engine from that observed in single-jet, quiescent environments. A new two-color, two-camera technique was developed to more accurately measure the diffusion flame LOL using OH chemiluminescence.

- A comparison of flame lift-off data obtained from the OH chemiluminescence technique and an OH planar laser-induced fluorescence technique showed that the LOL, as measured from OH chemiluminescence images, is biased to shorter LOLs by about 2 mm for the somewhat irregularly-shaped flames of the current study.
- The LOL was observed to decrease by 35% as the spacing between adjacent jets was decreased from 90° to 45°, which accounted for much of the discrepancy between the engine data and the single-jet diesel simulation data.
- The in-cylinder swirl flow had a minor influence on the shape of the flame in the vicinity of the LOL, with a 7% longer LOL on the windward side of the jet, on average.
- The proximity of the firedeck to the jets had no effect on the shape of the diffusion flame, on average, though individual images did display some asymmetry in the shape of the flame.
- Significant cycle-to-cycle variation was observed in the LOL data, even though the overall engine performance was very stable. Cycle-to-cycle variation in the LOL has important implications for soot reduction strategies that rely on increased LOLs, requiring even longer LOLs with more extreme operating conditions to achieve zero soot formation.

A new, common-rail fuel injection system has been implemented and characterized in the optical engine using a newly-constructed, hole-specific rate-of-injection meter. This new injection system will facilitate investigations of advanced, multi-mode combustion strategies in the near future, including pilot, post, and split-injection strategies.

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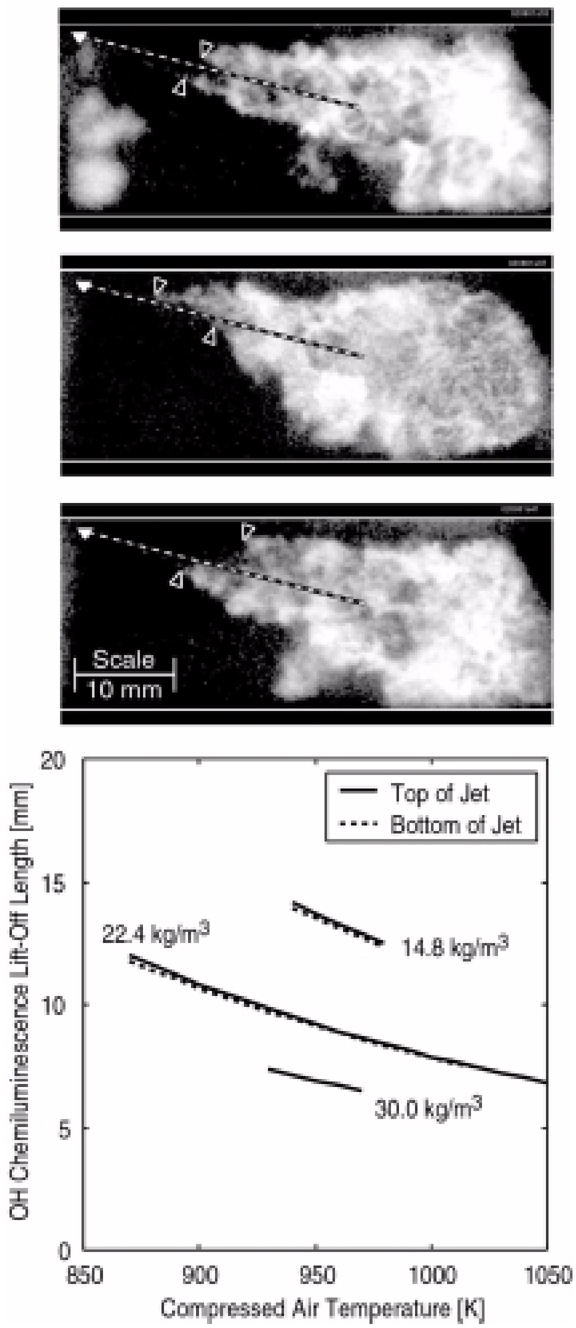

Figure 6. Top: Three OH chemiluminescence images, obtained through one of the cylinder-wall windows, showing three examples of flame shape near the firedeck. The firedeck is indicated by the white line at the top of the image, the tip of the injector is indicated by the white triangle at the top left of the image, and the nominal spray axis is indicated by the dashed white line. Bottom: Variation of mean LOL on the top and bottom of the imaged jet with in-cylinder charge temperature and density, as determined through statistical analysis.

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2. Musculus, M. P. B., Dec, J. E. and Tree, D. R., "Effects of Fuel Parameters and Diffusion Flame Lift-Off on Soot Formation in a Heavy-Duty DI Diesel Engine," SAE Paper 2002-01-0889, SAE International Congress and Exposition, Accepted for SAE Transactions, June 2003.

3. Musculus, M. P. B., "Effects of Fuel Parameters and Diffusion Flame Lift-Off on Soot Formation in a Heavy-Duty Diesel Engine," Department of Energy 2001 Annual Progress Report.

4. Musculus, M. P. B., "Effects of Fuel Parameters and Diffusion Flame Lift-Off on Soot Formation," Cross-Cut Diesel CRADA Meeting, January 2002.

5. Musculus, M. P. B., "Progress on Flame Lift-Off Measurements in a Realistic Heavy-Duty DI Diesel Engine Environment," Cross-Cut Diesel CRADA Meeting, June, 2002.

6. Musculus, M. P. B., "Effects of the In-Cylinder Environment on Diffusion Flame Lift-Off in a Heavy-Duty Diesel Engine," DOE National Laboratory Advanced Combustion Engine R&D Merit Review & Peer Evaluation, May 2003.

II.E. Nitrogen-Enriched Air for the Reduction of NO_x Emissions in Heavy-Duty Diesel Engines

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Technical Advisor: Steven Trevitz, Mack Trucks Inc., Hagerstown, Maryland

Objectives

- Evaluate the performance of nitrogen-enriched intake air (NEA) as an alternative to exhaust gas. recirculation (EGR) for NO_x reduction in heavy-duty diesel engines.
- Optimize NEA generation system using gas separation membranes.
- Test the NEA generation system installed on a heavy-duty diesel engine using an engine dynamometer.
- Demonstrate the NEA system's durability and effectiveness on a heavy-duty vehicle.

Approach

- Evaluate EGR data for baseline tests and relate target engine requirements to NEA performance.
- Develop parametric membrane model that accounts for bundle volume and fiber size.
- Characterize available gas separation membranes.
- Match membrane to target engine requirements.
- Test prototype on engine test stand (13 mode test).
- Test prototype performance in a vehicle (transient and durability testing).

Accomplishments

- The EGR engine tests (baseline tests) were performed and the data was evaluated. The target engine requirements were related to engine performance.
- A parametric membrane model that accounts for bundle volume and fiber size was developed.
- A gas separation membrane characterization bench was designed and built to provide data at higher flows and pressures required for heavy-duty diesel engines.
- Four of six gas separation membrane prototypes have been tested using the new membrane characterization bench.
- Three reports were delivered to Mack Trucks Inc., detailing the characterization results of four gas separation membranes.

Future Directions

- Characterize the remaining gas separation membranes.
- Evaluate the membrane characterization test data and optimize the gas separation membranes' form factor (fiber dimensions) using the membrane model.
- Analyze the model results and build a NEA system for use with heavy-duty diesel engines.

- Conduct a test of the NEA system on a heavy-duty diesel engine using the Environmental Protection Agency's (EPA's) 13 mode test.
- Conduct transient and durability testing on a heavy-duty vehicle.

Introduction

EGR has been used to reduce NO_x emissions for decades in spark-ignited engines. Recently, due to increasingly stringent emissions regulations, diesel engines are beginning to use this technology. EGR reduces NO_x emissions by adding CO_2 as a diluent to lower in-cylinder combustion temperatures. When used in a diesel engine, large quantities of exhaust gas are needed at low loads since the engine operates extremely lean at these points and the exhaust gas has a low percentage of CO_2 (see Figures 1 and 2). Large quantities of EGR must be cooled to keep the volumetric efficiency of the engine at normal levels. This increases the heat load of the radiator. A larger radiator is a problem for heavy-duty diesel vehicles; manufacturers have been trying to reduce the radiator size to lower aerodynamic drag. EGR in diesel engines also introduces particulate matter (PM) and acids into the cylinder which are corrosive and abrasive, increasing engine wear.

A solution to the problems inherent in EGR is to use nitrogen as a diluent. Nitrogen can be used to replace CO_2 to lower in-cylinder combustion temperatures and control NO_x emissions. Gas separation membranes can be used to remove oxygen from the intake air, making it nitrogen-rich. A gas separation membrane works by dividing the air into two streams: one is nitrogen-rich, and the other is oxygen-rich. The higher the driving pressures through the membrane, the higher the purity. Relatively low pressures are needed since the oxygen level only needs to be reduced from 21% to 17% (typical intake oxygen concentrations with EGR). Since exhaust gas is not used, PM is not introduced into the cylinder, decreasing engine wear. Also, since nitrogen is taken directly from the intake air and does not require extra cooling, there is no increased heat load to the engine.

Approach

Typically, the first step in a research project is to develop baseline data to use in evaluating the changes that occur during testing. For a baseline data set, a heavy-duty diesel engine was operated at four different EGR levels and 3 different beginning of injection (BOI) timings over a 13 mode test. The EGR data for baseline tests was evaluated, and target engine requirements were related to NEA performance. This data was used to develop a parametric membrane model that accounts for bundle volume and fiber size.

Previous studies have indicated that the best way to generate nitrogen onboard a vehicle is to use a gas separation membrane. Several gas separation membrane manufacturers were contacted, and prototype membrane bundles were requested. A new membrane characterization bench was developed since the heavy-duty diesel engine required higher

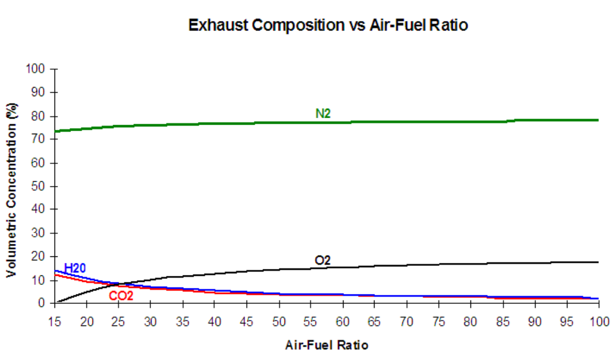

Figure 1. Exhaust Gas Composition at Different Air-Fuel Ratios

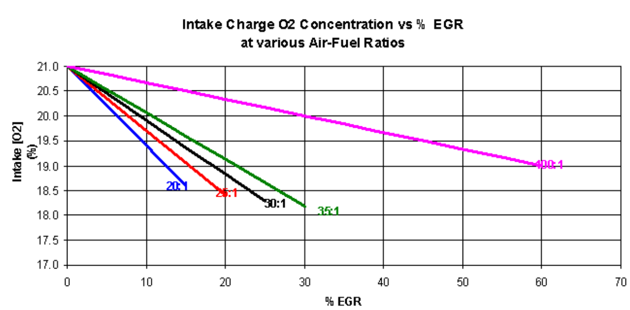

Figure 2. Amount of EGR Required to Lower Intake Air Oxygen Concentration at Different Air-Fuel Ratios

boost pressures than the previous bench could supply. Four of the six gas separation membranes have been characterized, and the remaining gas separation membranes will be characterized in the near future.

Once the membranes are characterized, the membrane data is evaluated using the model to match the gas separation membrane to target engine requirements. It is perceived that some form factors such as membrane thickness or fiber size may have to change to meet the engine requirements. After a suitable membrane is identified, a full-scale NEA unit will be built and evaluated using the 13 mode test on an engine test stand. At the conclusion of the engine tests, the NEA unit will be installed in a heavy-duty vehicle. Prototype performance in a vehicle with respect to transient response and durability will then be tested and evaluated.

Results

Five membrane manufacturers were willing to supply prototype membranes for this project. Because some suppliers requested anonymity, they will be designated as suppliers A, B, C, D and E. Analysis done by membrane manufacturer A concentrated on three different membrane variants from this supplier: a high selectivity membrane, a high permeability membrane and one of intermediate performance. Their initial conclusion was that their existing membrane technology required more energy than allowed and required more storage volume than available. They reviewed our feedback and concluded that they could develop an alternative module. However, it would have a higher permeability material with improved separation factor and it would cost a significant amount of money to produce. Therefore, they were not willing to spend the money required to produce this module variant due to other product priorities.

Membrane manufacturer B submitted a prototype for evaluation. The prototype was polymeric, consisting of bundled fibers, three elements (bundles) in a single chamber 7 inches in diameter x 40 inches long. These modules had been previously run in a high contaminant environment. The modules were tested under the following conditions: feed pressures to 40 psig, feed to retentate pressure differentials of less than 5 psi, permeate pressure at ambient conditions with ambient temperatures, and retentate flows up to 15 SCF/min. During testing, membrane module B achieved target nitrogen enrichment while remaining stable at elevated pressures and after repeated cycles of testing. However, the module required excess power and exceeded the module size limits.

Membrane manufacturer C supplied a low selectivity, high permeability, single-element polymeric, bundled fibers membrane in a container 5 inches in diameter x 20 inches long. Test conditions for membrane C were feed pressures to 50 psig, feed to retentate pressures less than 6 psi, permeate set at ambient pressure and temperatures, and retentate flows up to 25 SCF/min. Membrane C achieved the target nitrogen enrichment while slightly exceeding the power and size limits (see Figures 3 and 4). The membrane was chosen to be resized. Model results showed that if the low selectivity, high permeability membrane modules are sized at 18 inches in diameter and the maximum flow is corrected to 70 lb/min, two membrane bundles are needed if the fiber bore diameter is opened to twice its original size. With advanced coatings and optimization, this could be

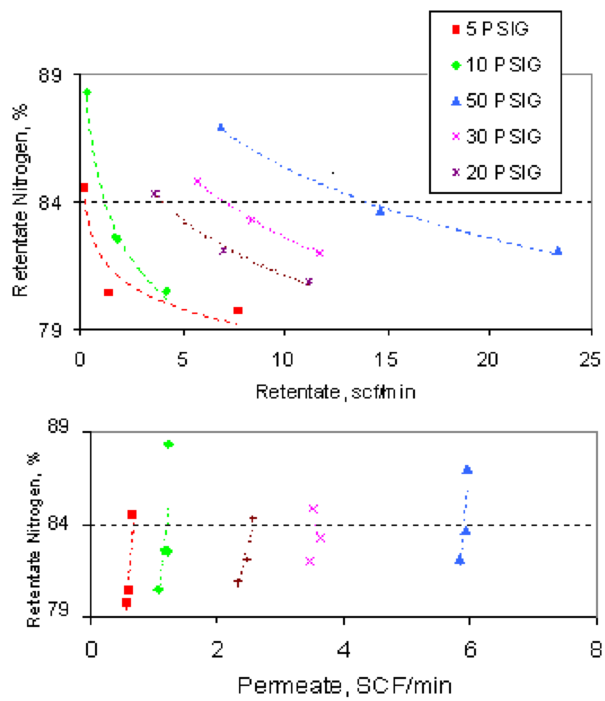

Figure 3. Retentate and Permeate Flows for Membrane C

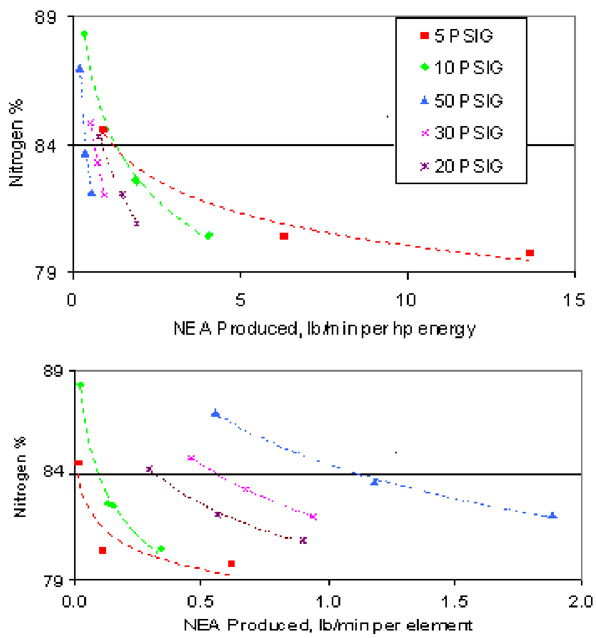

Figure 4. Power and Size Requirements for Membrane C

reduced to one bundle. A new bundle has been requested with a larger bore diameter.

Suppliers D and E have submitted modules that are currently being tested. Preliminary results at low pressures look promising.

Conclusions

- Membrane B achieved the required nitrogen enrichment but exceeded the power and size limits.
- Membrane C achieved the required nitrogen enrichment but slightly exceeded the power and size limits.
- Using the membrane model, membrane C was chosen to be resized and tested.
- Suppliers D and E have submitted modules that are currently being tested. Preliminary results at low pressures look promising.
- It is projected that a NEA system will be ready for engine testing on schedule.

FY 2003 Publications/Presentations

1. Presented "Nitrogen Enriched Air for the Reduction of NO_x Emissions In Heavy Duty Diesel Engines**"** at the 2003 DOE National Laboratory Advanced Combustion Engine R&D Merit Review Meeting.

II.F. Soot in Diesel Fuel Jets: Effects of Fuel Type, Wall Impingement and Low Flame Temperature

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Objectives

- Investigate the effect of fuel type on soot processes in diesel fuel jets.
- Investigate diesel fuel jet combustion and soot formation at low flame temperature conditions where nitrogen oxide (NO_x) emissions are expected to be low.
- Investigate jet-wall interaction effects on soot processes at diesel conditions.
- Provide a database for validating combustion and soot models in the multidimensional, computational models being developed for diesel engine design and optimization.

Approach

- Utilize advanced optical diagnostics coupled with a unique optically-accessible diesel combustion simulation facility (DCSF) to conduct the following investigations:
  - Measure soot concentrations and visualize soot distributions using line-of-sight extinction and laser-induced incandescence techniques.
  - Simultaneously with the soot measurements, acquire luminosity and OH chemiluminescence images to characterize the spray combustion region.
- Apply soot and combustion diagnostics in fuel jets using a wide range of fuels, including oxygenated, alternative, reference, and conventional fuels.
- Perform soot measurements at low flame temperature for a range of experimental conditions and with different fuels.
- Study jet-wall interaction effects on fuel jet soot and combustion in plane wall jet and "confined" wall jet configurations.

Accomplishments

- Completed a comprehensive database of soot, lift-off length, and ignition delay measurements for five different oxygenated, reference and conventional fuels.
- Showed that soot level and location in diesel fuel jets depend on the fuel molecular structure, as well as the fuel-air mixing upstream of the lift-off length.
- Demonstrated that diesel fuel jets produced from small orifice injector tips are non-sooting at typical mixing-controlled diesel combustion conditions AND that the fuel jets remain non-sooting at low flame temperature conditions.
- Showed that soot levels in a plane wall jet decrease compared to a free jet.
- Showed that soot levels in a confined wall jet increase compared to a free jet when the injection duration exceeds a critical value. Soot increases when redirected combustion gases shorten the lift-off length, thereby making the fuel-air mixture at the lift-off length more fuel-rich.

Future Directions

- Extend the investigation of jet-wall interaction effects on soot production to include fast-response wall temperature measurements and quantitative laser extinction measurements in the wall jet region.
- Evaluate the low temperature limits for mixing-controlled diesel combustion and soot processes at these conditions.
- Investigate injection rate modulation and orifice geometry effects on diesel combustion and emissions processes.

Introduction

Improving our understanding of in-cylinder combustion and emission formation processes in diesel engines is critical to developing advanced, low-emission diesel engines. During the previous year, a database of quantitative soot measurements in reacting fuel jets was completed for an extensive range of diesel operating conditions using a standard #2 diesel fuel. This year, the soot database was extended to include the effects of fuel type on the soot processes. Soot processes were specifically investigated at low flame temperature operating conditions that would be expected to produce minimal NO_x formation. In addition, an investigation of the effects of wall interaction on diesel fuel jet combustion and soot processes was initiated. The wall has an effect on the mixing and combustion processes of the fuel jet through redirection of the fuel jet, and the wall also confines the fuel jet such that it turns back on itself and interacts with the adjacent fuel jets. The effects of fuel type, wall interaction, and low flame temperature on the diesel fuel jet combustion and soot processes are important aspects in the development of computational models that simulate these phenomenon and ultimately for the design of low-emission engines.

Approach

The research was performed in the DCSF using a common-rail diesel fuel injector. Figure 1 shows a picture of the DCSF in operation. The experimental ambient and injector conditions are carefully controlled in this facility, thereby facilitating investigation of the effects of fundamental parameters on diesel combustion. The DCSF also has full optical access, allowing advanced soot and combustion measurements to be performed.

The effect of fuel type on soot processes was investigated using four fuel blends used in recent engine studies, including three oxygenates and one diesel reference fuel: (1) T70, a fuel blend containing the oxygenate tetraethoxy-propane; (2) BM88, a fuel blend containing the oxygenate dibutyl-maleate; (3) GE80, a fuel blend containing the oxygenate tri-

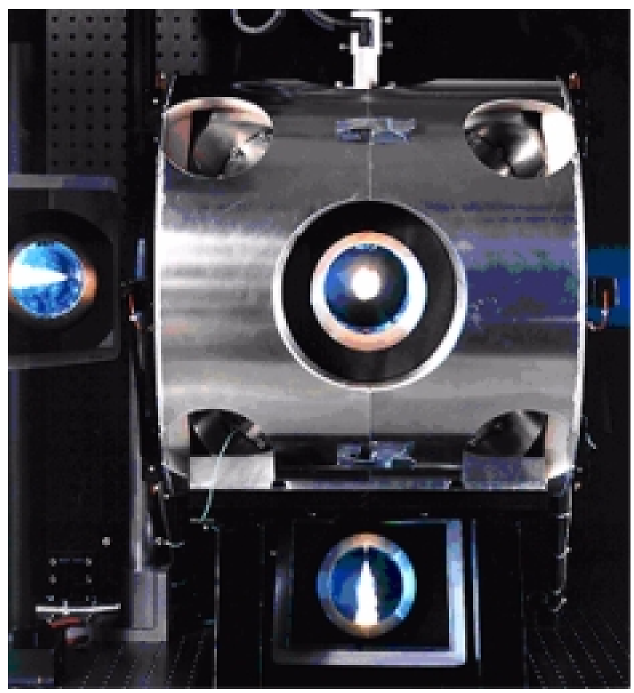

Figure 1. Photograph of the DCSF in operation demonstrating the optical access to the diesel spray. The bright spot in the center of the front window is a burning diesel spray penetrating toward the viewer. Mirrors at 45° next to the bottom and left-side windows show side views of the burning spray.

propylene-glycol-methyl-ether; and (4) CN80, a diesel reference fuel composed of an n-hexadecane and heptamethyl-nonane mixture [Pickett and Siebers, 2003]. Measurements of the soot distribution along the axis of quasi-steady fuel jets were performed using laser extinction and planar laser-induced incandescence (PLII) and were compared to previous results using a #2 diesel fuel (D2).

Methods of producing low flame temperature diesel combustion were investigated for single, isolated fuel jets that produced no soot at higher flame temperature [Pickett and Siebers, 2002].

The effects of jet wall interaction were investigated in the DCSF in two experimental configurations: a jet impinging on a plane wall without any additional geometrical constraints and a "confined" jet where the plane wall jet was constrained by a geometry that simulates the dimensions of an engine combustion chamber and the location where adjacent jet interaction occurs. In this way, the effect of adjacent geometry and jet interaction was separated from the effects of plane wall interaction.

Results

The effect of fuel type on diesel fuel jet soot is shown by the PLII images in Figure 2 and laser extinction optical thickness (*KL*) measurements shown at the same conditions in Figure 3. The experimental conditions were the same for each fuel. PLII images and laser extinction measurements were obtained by passing a laser from the side through the centerline of the fuel jet during mixing-controlled diesel combustion. The PLII images in Figure 2 are composite averages of all the images collected for each set of experimental conditions. The relative camera gain is indicated on the upper right of each image. The independently measured lift-off length is also indicated in each image by a vertical dashed line. Based on the PLII signal intensity and *KL* measurement (proportional to the mass of soot along the path of the laser), Figures 2 and 3 show that the soot level in decreasing order with respect to fuel composition is: D2 > CN80 > BM88 > T70 > GE80. The distance from the injector to the region of first soot formation has an inverse relationship to the sooting propensity given above. That is, the first-soot distance is longest for GE80 and shortest for D2. The order in sooting tendency is found at either fixed ambient and injector operating conditions, as is shown in Figures 2-3, or at equivalent fuel-oxygen mixtures at the jet lift-off length, confirming that fuel molecular structure effects are important to the soot processes at diesel conditions.

The soot measurements shown in Figures 2-3 show very high soot levels when using D2 fuel and a 180 µm injector orifice tip. However, our previous investigation showed that when the injector orifice tip is decreased to 50 µm and all other experimental conditions are the same as in Figures 2-3, there is no

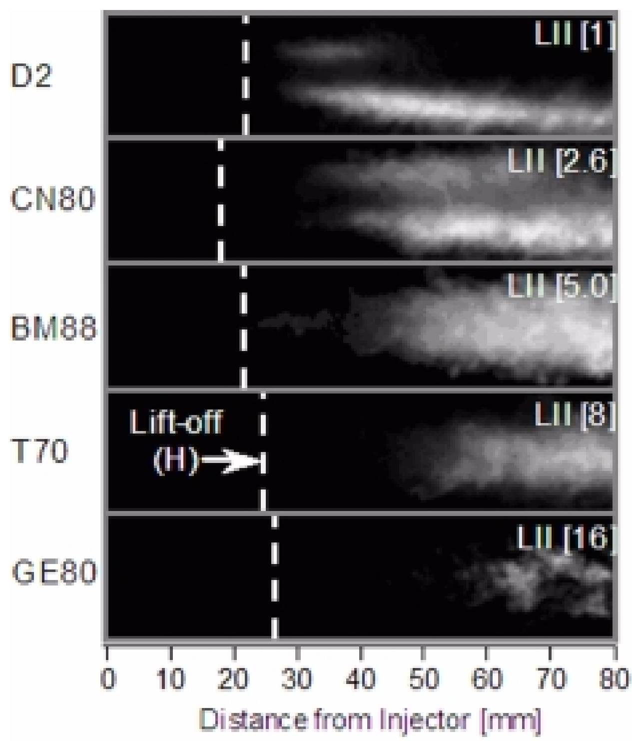

Figure 2. Composite-average PLII images at the central plane of the fuel jet for various fuel blends. PLII images were acquired during the mixing-controlled heat release phase of combustion. The ambient gas temperature and density were 1000 K and 14.8 kg/m^3. The injector orifice tip size and pressure drop were 180 µm and 138 MPa, respectively. The vertical dashed line in each image marks the lift-off length location. Relative PLII camera gain is given in brackets at the upper right of each image. An increased camera gain corresponds to a lower PLII intensity.

soot formation in the jet whatsoever using D2 fuel [Pickett and Siebers, 2002; Siebers and Pickett, 2002]. The disappearance of soot within the fuel jet was shown to occur as the air entrainment upstream of the lift-off length (relative to the amount of fuel injected) increased and the cross-sectional average equivalence ratio at the lift-off length was less than a value of two.

Methods of producing low flame temperature were investigated using the 50 µm injector tip referred to above. Figure 4 demonstrates two different ways that low flame temperature combustion was produced with a 50 µm injector tip and D2 fuel. Figure 4 shows time-averaged images of OH chemiluminescence with reduced ambient oxygen concentrations ranging from 21% to 10% (simulating the use of extensive EGR) and reduced ambient gas temperature of 850 K with 21% oxygen. Soot measurements performed at these conditions showed that the fuel jet remained non-sooting at all experimental conditions given in Figure 4. Figure 4 shows that the lift-off length increases with reduced ambient oxygen concentration. The increase in lift-off length compensates for the reduction in ambient oxygen concentration such that the equivalence ratio of the fuel-air mixture at the lift-off length does not change substantially with decreasing oxygen concentration [Pickett and Siebers, 2002] and, consequently, soot formation is avoided. With

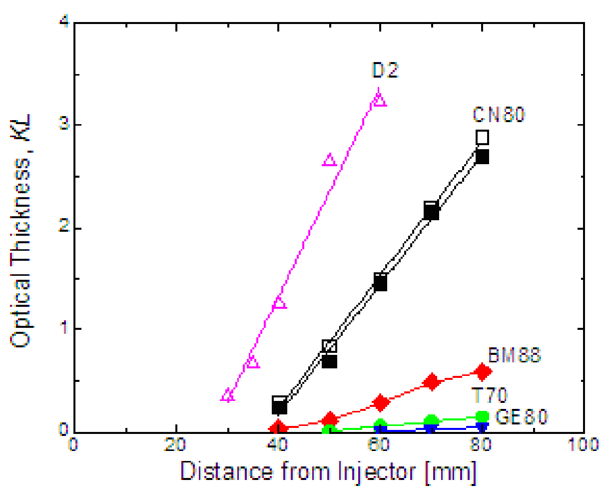

Figure 3. Average optical thickness, *KL*, as a function of axial distance for various fuel types. The experimental conditions are the same as those given in Figure 2.

reduced ambient gas temperature, Figure 4 shows that the lift-off length increases such that the fuel-air mixture at the lift-off length becomes fuel-lean, thereby avoiding the formation of a diffusion flame. Flame temperature calculations indicated in Figure 4 show that flame temperatures of approximately 2000 K were produced, compared to typical diesel flame temperatures of approximately 2700 K. The same low-temperature, non-sooting combustion, either with reduced ambient oxygen concentration or fuel-lean combustion, was also realized using T70 fuel and a 100 µm injector tip.

Jet-wall interaction effects on diesel fuel jet combustion and soot formation are demonstrated in

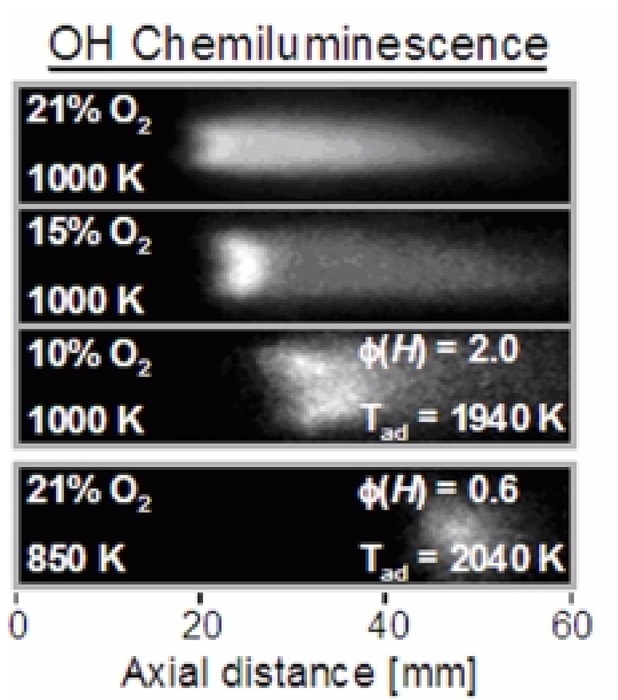

Figure 4. Time-averaged OH chemiluminescence images with various ambient oxygen concentrations and ambient gas temperatures. The injector orifice tip size and injection pressure were 50 µm and 138 MPa, respectively, and the ambient gas density was 14.8 kg/m^3. The fuel used was D2. The ambient gas temperature is shown at the lower left of each image. The adiabatic flame temperature, T_{ad}, and cross-sectional average equivalence ratio at the lift-off length, $\phi(H)$, are also given for low flame temperature conditions. All of the fuel jets were non-sooting at these experimental conditions.

Figure 5. The figure shows highly-sensitive photodiode measurements of fuel jet luminosity at two different injection durations (ID) for various wall-jet configurations. The sensitivity of the photodiode is such that, if soot formation occurs, the soot luminosity saturates the detector. Therefore, detectable levels of luminosity for the photodiode are due to chemiluminescence of non-sooting diesel combustion. Images of chemiluminescence are shown at the left of the figure for the "confined" jet configuration, where the wall jet was constrained by a transparent box-like geometry that simulates the dimensions of an engine combustion chamber and the location where adjacent jet interaction occurs. Figure 5 shows that the free jet and plane wall jet are non-sooting with an injection duration of 3.5 ms. However, the confined jet is non-sooting only with an injection duration of 1.4 ms. The time-sequence of chemiluminescence for the confined jet shows that combustion gases are redirected back towards the injector for extended injection durations. The redirected combustion gases cause the lift-off length to shorten, thereby making the fuel-air mixture at the lift-off length more fuel-rich. The time after the start of injection of soot formation corresponds to the time shortly after this time of jet interaction with redirected combustion gases. Figure 5 also shows that if the injection event is concluded prior to this jet interaction event, soot formation is avoided.

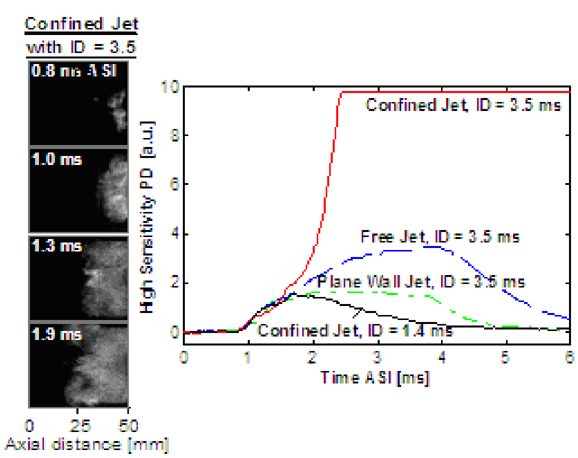

Figure 5. Luminosity images and time-resolved luminosity measurement for various wall jet configurations and injection durations (ID). The time after the start of injection (ASI) is indicated on the images.

Conclusions

The investigations of diesel fuel jet combustion and soot formation completed over the past year provide fundamental new information as to the effects of fuel type, low flame temperature, and wall interaction on diesel combustion. Soot levels are shown to depend strongly on fuel type. The non-sooting and low flame temperature mixing-controlled combustion realized using small orifice tips suggests that the use of small orifices offers the potential for a simultaneous soot and NO_x reduction in an engine. Mechanisms of jet-wall interaction and the effect on diesel fuel jet soot formation were identified.

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2. Pickett, L.M., Siebers, D.L., "An Investigation of Diesel Soot Formation Processes Using Micro-Orifices," Proc. Combust. Inst. 29:655-662, 29th International Symposium on Combustion, Sapporo, Japan, 2002.

3. Siebers, D.L., Pickett, L.M., "Injection Pressure and Orifice Diameter Effects on Soot in DI Diesel Fuel Jets," THIESEL 2002 Conference on Thermo- and Fluid-Dynamic Processes in Diesel Engines, Valencia, Spain, 2002.

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1. Pickett, L.M., and Siebers, D.L., "Fuel Effects on Soot Processes of Fuel Jets at DI Diesel Conditions," SAE Paper 2003-01-3080, submitted to SAE Powertrain and Fluid Systems Conference, 2003.

2. Pickett, L.M., and Siebers, D.L., "Soot in Diesel Fuel Jets: Effects of Ambient Gas Temperature, Ambient Density and Injection Pressure," submitted to Combustion and Flame, 2003. (Also appeared in the Proceedings of the Third Joint Meeting of U.S. Sections of the Combustion Institute, Chicago, IL, 2003.)

3. Pickett, L.M., and Siebers, D.L., "Fuel Effects on Soot Formation Downstream of the Lift-Off Length during Mixing-Controlled Phase DI Diesel Combustion," Proceedings of the Third Joint Meeting of U.S. Sections of the Combustion Institute, Chicago, IL, 2003. (Also "Soot Formation Downstream of the Lift-Off Length during Mixing-Controlled DI Diesel Combustion," in preparation for submission to International Journal of Engine Research, 2003.)

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2. Pickett, L.M., and Siebers, D.L., "Soot in Diesel Fuel Jets: Effects of Fuel-Type, Wall-Impingement and Low Flame Temperature," DOE Advanced Combustion Engine Annual Review, Chicago, IL, May 2003.

3. Pickett, L.M., and Siebers, D.L., "Effects of Ambient Gas Temperature, Ambient Density and Injection Pressure," Proceedings of the Third Joint Meeting of U.S. Sections of the Combustion Institute, Chicago, IL, March 2003.

4. Pickett, L.M., and Siebers, D.L., "Fuel Effects on Soot Formation Downstream of the Lift-Off Length during Mixing-Controlled Phase DI Diesel Combustion," Proceedings of the Third Joint Meeting of U.S. Sections of the Combustion Institute, Chicago, IL, March 2003.

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6. Pickett, L.M., and Siebers, D.L. "An Investigation of Diesel Soot Formation Processes Using Micro-Orifices," Proc. Combust. Inst. 29:655-662, 29th International Symposium on Combustion, Sapporo, Japan, August 2002.

Special Recognitions and Awards

1. ASME Best Paper Award for the best paper at the ASME Internal Combustion Engine Fall 2001 conference (awarded Fall 2002 to L.M. Pickett and D.L. Siebers).

2. DOE Advanced Combustion Engine R&D Award (given to D.L. Siebers, L.M. Pickett and B. Higgins, May 2003) for providing fundamental new insights into the soot formation processes in diesel sprays. The recognition was given at this year's DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation.

II.G. Exploring Low-NO_x, Low-PM Combustion Regimes

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DOE Technology Development Manager: Gurpreet Singh

Objectives

- Improve engine-system efficiency by lowering performance requirements for post-combustion emissions controls.
- Conduct detailed emissions characterization for improved understanding of combustion regimes and environmental impact.
- Extend load/speed envelope of low emissions advanced combustion regimes.

Approach

- Explore advanced diesel combustion regimes that exhibit low NO_x and low particulate matter (PM) emissions under light- and medium-load conditions.
- Perform detailed emissions characterization, including hydrocarbon (HC) speciation and PM characterization.
- Identify additional combustion regimes that exhibit low-NO_x, low-PM behavior.

Accomplishments

- Moved and commissioned engine cell at the National Transportation Research Center (NTRC).
- Performed extensive experiments under low- and medium-load conditions to characterize low-NO_x and low-PM combustion regimes.
- Performed HC speciation and detailed PM characterization under these advanced combustion regimes.
- Explored potential of several new approaches for achieving simultaneous low NO_x and PM emissions.
- Explored potential of recovering fuel penalty associated with these advanced combustion regimes.

Future Directions

- Continue analysis and interpretation of recent data.
- Continue exploring potential for recovering fuel penalty.
- Continue detailed analysis of HC and PM emissions.
- Continue exploring potential of new approaches for achieving simultaneous low NO_x and PM emissions.
- Investigate effect of fuel properties on achieving and exploiting low-emissions combustion regimes.

Introduction

Exhaust gas recirculation (EGR) has been used in recent years to reduce NO_x emissions in light-duty diesel engines and to a lesser extent in heavy-duty diesel engines. Actual EGR utilization in many production engines is typically less than optimal because of high unburned HC and PM emissions.

Recently, ORNL and other organizations have discovered non-traditional combustion regimes in which an order of magnitude reduction in NO_x is possible with a decrease in PM when EGR is pushed beyond normal production levels. ORNL is the only DOE laboratory to have successfully operated a multi-cylinder diesel engine in these novel regimes. In addition, ORNL observed these regimes under lean fueling conditions, whereas other organizations are reporting this behavior only for conditions rich of stoichiometric.

Extensive experiments have been performed this year to improve our understanding of engine operation under these combustion regimes. HC speciation and detailed PM characterization, including soluble organics analysis, have revealed information about the combustion process as well as the benefits of this type of combustion for utilizing advanced post-combustion emissions controls. Other activities this year include the demonstration of low-NO_x operation with minimal PM penalty under medium-load conditions and the discovery of new engine operating conditions that result in simultaneous low NO_x and low PM.

Approach

The primary objective of this work is to identify and characterize advanced combustion regimes where it may possible to achieve significant reductions in NO_x and PM emissions with only production-like parameters and controls. A combination of detailed emissions information, in-cylinder pressure data, and recent advances in combustion quality modeling is expected to supply the necessary information to exploit these kinds of regimes for production engine operation. A secondary objective is to investigate methods for recovering the fuel consumption penalty typically associated with operating in these advanced regimes. A method of minimizing penalties associated with these regimes must be developed and understood before this type of operation will be viable in a production system.

Numerous experiments have been performed on two Mercedes 1.7 liter common-rail diesel engines. Both engines can be operated on their factory engine control units or with rapid-prototype, full-pass engine controllers. Using the full-pass engine controllers, researchers have control over EGR, intake throttle, and fuel injection parameters (timing, duration, fuel rail pressure, etc.). Combustion regimes that exhibit a simultaneous reduction in NO_x and PM emissions were achieved using two approaches. The first approach utilizes a throttle to increase EGR rate beyond the maximum rate possible with sole use of the EGR valve for a particular engine condition. The second approach does not use a throttle, but rather uses a combination of EGR and manipulation of injection parameters. The second approach was investigated at both low- and medium-load conditions. Detailed emissions measurements made during the low-load conditions include HC speciation and an analysis of the soluble organic fraction in the PM.

Results

A detailed emissions analysis was performed for engine conditions that resulted in combustion behavior exhibiting simultaneous low NO_x and low PM emissions. Recall from the previous section that two approaches were used to enter the low-NO_x, low-PM combustion regime – Approach 1 relied heavily on EGR and throttling, and Approach 2 relied heavily on EGR and retarding injection timing. Typical results seen for Approach 1 are shown in Figure 1 for “road load” type conditions (1500 rpm, 2.6 bar brake mean effective pressure–BMEP). The diamond symbol represents the original equipment manufacturer (OEM) condition, which corresponds to a 22% EGR rate. A significant decrease in NO_x was observed with increasing EGR rate using Approach 1. PM emissions initially increase with EGR rate and then begin to decrease at approximately 47% EGR rate. The decrease in NO_x and PM was accompanied by an increase in brake specific fuel consumption (BSFC) (fuel penalty). Similar results were seen for Approach 2 at “road load” conditions, where NO_x and PM decreased and BSFC increased with retarding injection timing, as shown in Figure 2. Approach 2 was also applied to medium-load conditions (1500 rpm, 5.2 bar BMEP). Emissions trends were similar to those observed for the “road load” conditions.

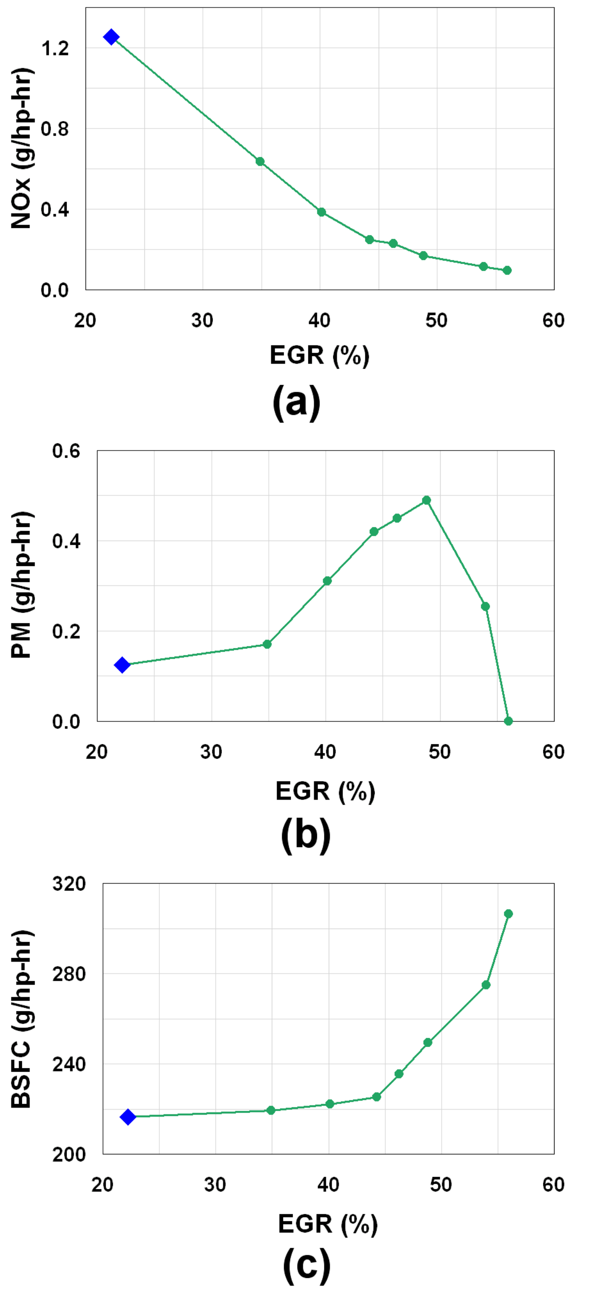

Figure 1. Low NO_x and Low PM Observed for Approach 1 with Base Conditions of 1500 rpm, 2.6 bar BMEP (Diamond symbol represents OEM conditions)

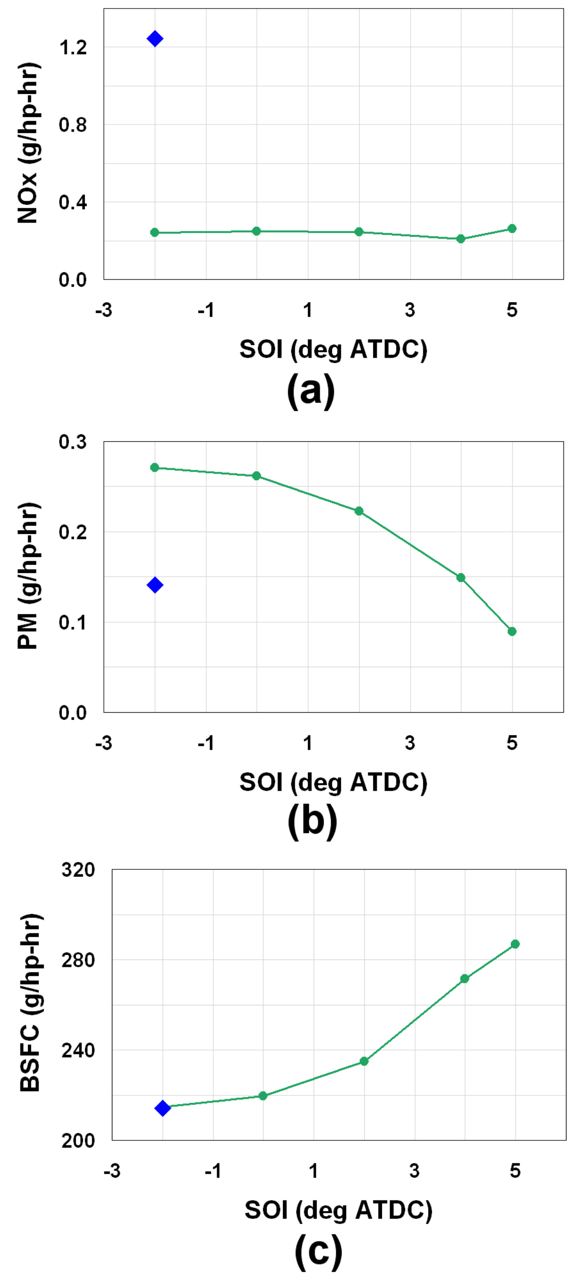

Figure 2. Low NO_x and Low PM Observed for Approach 2 with Base Conditions of 1500 rpm, 2.6 bar BMEP (Diamond symbol represents OEM conditions; SOI = start of injection; ATDC = after top dead center)

Characterization of the exhaust species from both Approaches 1 and 2 shows increased concentrations of partial combustion products relative to unburned fuel hydrocarbons. An example of this is shown in Figure 3, which shows a HC chromatogram for Approach 1 at 54% EGR as compared to a HC chromatogram for the fuel. There are clearly many short-chain HCs present in the engine exhaust which are not present in the fuel. Cyclopentene, a low-mass hydrocarbon compound not found in the fuel, exhibits a marked increase in concentration compared with baseline conditions, as

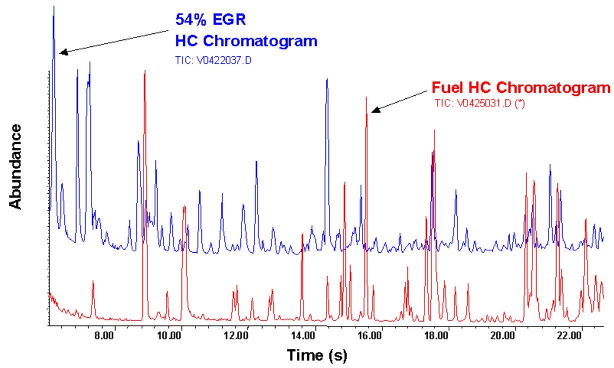

Figure 3. Gas Chromatography/Mass Spectroscopy (GC/MS) Analysis Shows High EGR Produces Many Short-Chain HCs Not Present in the Fuel (Approach 1 at 1500 rpm, 2.6 bar BMEP)

shown in Figure 4. The area counts in Figure 4 are normalized with respect to the OEM condition. For example, in Figure 4(a), cyclopentene increases by a factor of 95 for an EGR rate of 56% as compared to the OEM EGR rate of 22%. Analysis of the soluble organic fraction of the particulate emissions shows the presence of large amounts of carboxylic acids. These acids are the products of the first steps of the combustion process, which have survived to reach the exhaust stream. Interestingly, Approach 2 produces only about 1/3 the amount of cyclopentene and other partial oxidation components as Approach 1. As the NO_x and PM benefits from Approach 2 were not as great as those from Approach 1, the concentrations of partial oxidation components may provide an important insight into the character of the combustion process. It is important to discover whether these components are an enabling driver for the low-NO_x, low-PM condition or whether they are a result of it. Such knowledge will enable a more thorough understanding of means of accomplishing these combustion conditions reliably and will lead to their commercial viability.

Conclusions

A simultaneous reduction in NO_x and PM was observed under non-traditional conditions in the Mercedes 1.7 liter engine. Detailed HC speciation of these combustion regimes showed the presence of a significant concentration of partial oxidation components, and PM exhibited a high fraction of

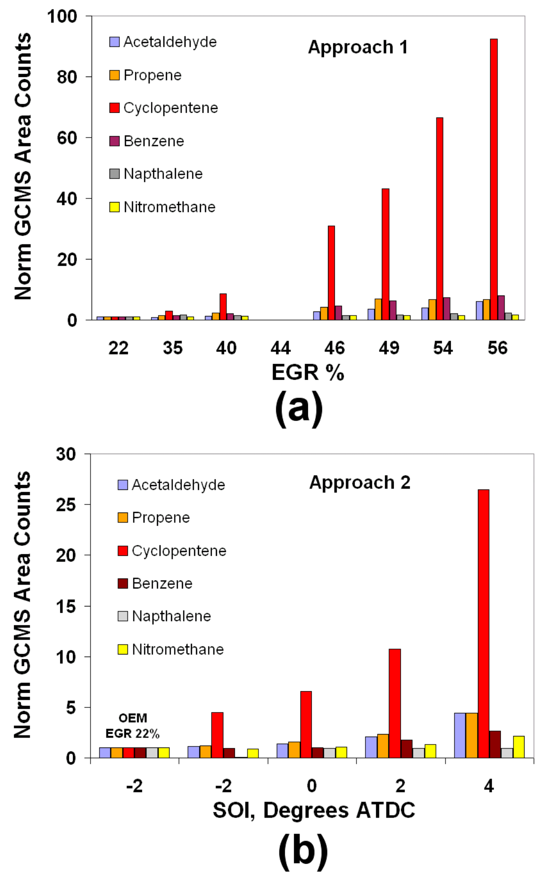

Figure 4. Increase in Partial Oxidation Products Was Observed for Approaches 1 and 2 for a Baseline Condition of 1500 rpm, 2.6 bar BMEP (The y-axis is normalized with respect to area counts for the OEM condition)

soluble organics. The concentrations were highest for Approach 1 as compared to Approach 2. We believe the majority of unburned HC and residual PM can be removed using a simple oxidation catalyst or may be useful for the regeneration of post-combustion emissions controls such as NO_x adsorbers.

FY 2003 Publications/Presentations

1. R. M. Wagner, S. Sluder, J. M. Storey, S. Lewis, "Exploring Non-Traditional Combustion Regimes for Diesel Emission Reduction", submitted for the 2004 SAE International Congress and Exposition (Detroit, MI, USA; March 2004).

2. R. M. Wagner, S. Sluder, J. M. Storey, S. Lewis, "Exploring Low-NO_x Low-PM Combustion Regimes", to be presented at Diesel Engines Emissions Reduction (DEER) Conference (New Port, RI, USA; August 2003).

3. S. Sluder, R. M. Wagner, J. M. Storey, S. Lewis, "Exploring Low-NO_x Low-PM Combustion Regimes", 2003 Advanced Combustion Engines Merit Review (Chicago, IL, USA; May 2003).

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II.H. Detailed Modeling of HCCI and PCCI Combustion and Multi-Cylinder HCCI Engine Control

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Subcontractor: University of California Berkeley, Berkeley, CA

Objectives

- Obtain low emissions and high efficiency operation of homogeneous charge compression ignition (HCCI) and premixed charge compression ignition (PCCI) engines.
- Advance our analysis techniques to learn the fundamentals of HCCI and PCCI combustion and to make accurate predictions of combustion and emissions.
- Determine and evaluate control and startability strategies for HCCI multi-cylinder engines.

Approach

- Conduct experiments on a 4-cylinder Volkswagen TDI engine and on a single-cylinder Caterpillar 3401 engine to evaluate startability and control strategies.
- Develop and use single-zone and multi-zone chemical kinetics models for analysis of HCCI and PCCI combustion and for evaluation of possible control strategies.

Accomplishments

Part 1. Analysis

- We have developed the most advanced and accurate analysis tools for HCCI combustion yet devised. During this year we have applied this capability to perform a detailed analysis of experiments conducted at Sandia National Laboratory, where the low power operation of HCCI engines has been studied. Our model can accurately predict hydrocarbon (HC) and carbon monoxide (CO) emissions as a function of equivalence ratio. The mechanisms of HC and CO formation at low power output have been demonstrated.
- We are conducting a detailed analysis of data from the Lund Institute of Technology, where two cylinder geometries were considered: a high turbulence cylinder with a square bowl in piston, and a low turbulence cylinder with a flat top piston. The purpose of the analysis is to determine the role of turbulence during HCCI combustion. So far we have analyzed the flat top piston geometry with good accuracy.
- We have extended our multi-zone model to include mixing between zones. This new model can be used as a framework to analyze engine operating conditions where the charge is not perfectly homogeneous (i.e. PCCI combustion).

Part 2. Experimental.

- We are developing methodologies for controlling and balancing combustion in a multi-cylinder HCCI engine. We are using an exhaust throttle as a low-cost surrogate for variable valve timing. Interaction between cylinders plays a major role for achieving balanced combustion in an HCCI engine. We are planning to conduct a detailed study of cylinder interaction to achieve optimum HCCI engine operation.

Future Directions

- The three fundamental problems of HCCI engines are the difficulty in controlling the engine, the low power achievable, and the difficulty in obtaining consistent timing in the different cylinders of a multi-cylinder engine. In this project, the analytical and experimental work is dedicated at solving these three problems.
- A possible solution to increase the engine power output and balance combustion is to partially stratify the charge (PCCI). We will develop analysis tools to accurately predict combustion and emissions under PCCI combustion.
- We will also use our analytical capabilities and experimental facilities to achieve a satisfactory method of starting the engine under any environmental condition that may exist.
- Our Volkswagen TDI engine is the ideal test bed for studying combustion balancing between the cylinders of a multi-cylinder engine. We are planning a detailed experimental and numerical study of how interactions between cylinders can be used to our benefit for successfully balancing and controlling combustion.

Introduction

This work supports the need to develop a new combustion concept that allows both high efficiency and low emissions for trucks and sport utility vehicles (SUVs). The high efficiency of diesel engines is highly desirable for improving the fuel economy of light-duty trucks and SUVs. However, diesel engines are well known as significant sources of NO_x and particulate matter emissions. The use of homogeneous charge compression ignition (HCCI) combustion systems represents a promising approach that needs further research and development.

Approach

Our work is a synergistic combination of analysis and experimental work. We have developed advanced methodologies that combine chemical kinetics with fluid mechanics to analyze HCCI engines with accuracy never before achievable for other types of engines. We have also developed systems analysis models for HCCI engines that have allowed us to optimize operating conditions to obtain maximum efficiency with minimum emissions. These analysis tools have been used to guide the experimental effort. We have a multi-cylinder Volkswagen TDI engine that allows us to work on balancing combustion between cylinders under controlled operating conditions. This is a crucial problem with HCCI combustion that has so far precluded commercialization of these engines.

Results

We have performed a detailed analysis of experiments conducted at Sandia National Laboratory [1] that studied the low power performance of HCCI engines. In these experiments, the fuel-air equivalence ratio was varied between 0.26 and 0.04 while the combustion timing was kept approximately constant. We have analyzed these experimental conditions with our multi-zone model. The results are shown in Figure 1. This figure shows that our model can accurately predict hydrocarbon and carbon monoxide emissions as a function of equivalence ratio. The results demonstrate that during combustion at very low equivalence ratios, even the central core of the cylinder (the hottest part of the combustion chamber) is too cold to react to completion, and instead it reacts partially into CO and intermediate hydrocarbons.

We are conducting a detailed analysis of experimental data from the Lund Institute of Technology, where two cylinder geometries were considered: a high turbulence cylinder with a square bowl in piston, and a low turbulence cylinder with a flat top piston [2]. The purpose of the analysis is to determine the effect of turbulence during HCCI combustion. So far, we have analyzed the flat top piston geometry with good accuracy. Figure 2 compares experimental and numerical pressure traces for the low turbulence cylinder. Excellent agreement is obtained between experimental and numerical results.

We have extended our multi-zone model to include mixing between zones [3]. We have used this model to demonstrate that mixing between zones is responsible for most of the production of carbon monoxide in an HCCI engine. In addition to being an important enhancement to our HCCI engine analysis tools, this new model can be used as a framework to analyze engine operating conditions where the charge is not perfectly homogeneous (i.e. PCCI combustion).

We are developing methodologies for controlling and balancing combustion in a multi-cylinder HCCI engine. We are using an exhaust throttle as a low-cost surrogate for variable valve timing. Our results for using an exhaust throttle in an HCCI engine show some unexpected results. Throttling the exhaust typically advances combustion in a single-cylinder engine due to the effect of hot combustion gases on HCCI combustion. However, in a multi-cylinder engine, throttling the exhaust of one cylinder delays combustion in this cylinder and advances combustion in the other cylinders. This is due to flow interactions between cylinders, as the exhaust throttle in a cylinder diverts the flow of the fresh charge to the other cylinders. Characterizing these effects is extremely important in obtaining satisfactory combustion in a multi-cylinder HCCI engine.

Conclusions

During the present year, we have achieved significant progress in evaluating HCCI combustion, both by analysis and experiments. In analysis, we have demonstrated that our multi-zone methodology can successfully predict the effect of engine geometry and operating conditions on HCCI engine combustion and emissions. We have also extended our multi-zone model to include mixing between zones, which provides a framework for analyzing partially stratified combustion (PCCI). In experimental work, we are testing operating modes for balancing and controlling combustion in multi-cylinder engines. Our future work is dedicated to studying the fundamentals of HCCI and PCCI combustion, identifying optimum strategies for HCCI engine control and startability, and increasing the engine power output.

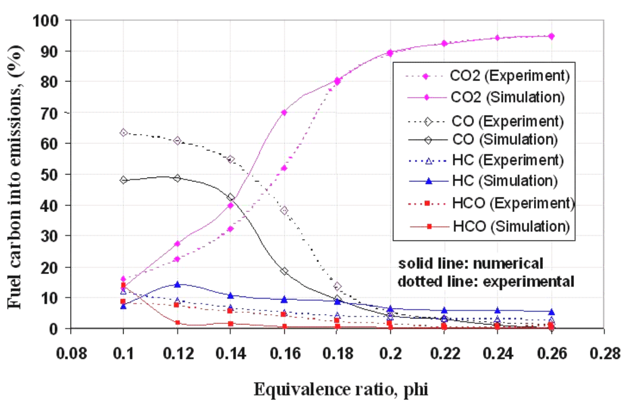

Figure 1. Comparison of analytical and experimental results for engine emissions for an HCCI engine running at low load [1]. The figure shows hydrocarbons, carbon monoxide, oxygenated hydrocarbons and carbon dioxide as a function of equivalence ratio. The figure shows good agreement between experimental and numerical results.

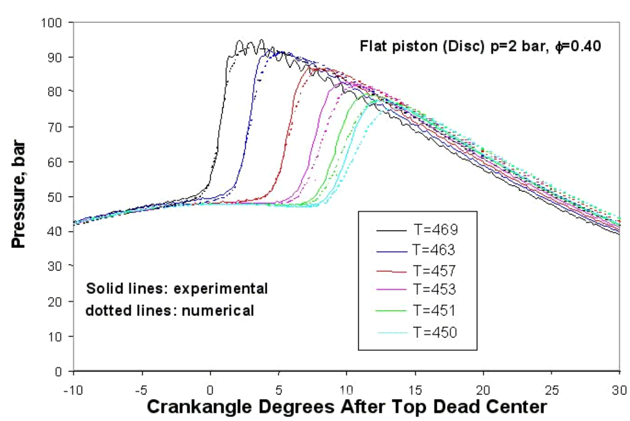

Figure 2. Comparison of pressure traces between an experimental HCCI engine [2] and a multi-zone numerical model, for an engine with a low turbulence geometry (flat top piston). The figure shows that there is a good agreement between numerical and experimental results.

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3. Daniel L. Flowers, Salvador M. Aceves, Joel Martinez-Frias, Randy Hessel, and Robert W. Dibble, 2003, "Effects of Mixing on Hydrocarbon and Carbon Monoxide Emissions, Predictions for Isooctane HCCI Engine Combustion Using a Multi-Zone Detailed Kinetics Solver," SAE Paper 2003-01-1821.

FY 2003 Publications/Presentations

1. **Effects of Mixing on Hydrocarbon and Carbon Monoxide Emissions, Predictions for Isooctane HCCI Engine Combustion Using a Multi-Zone Detailed Kinetics Solver**, Daniel L. Flowers, Salvador M. Aceves, Joel Martinez-Frias, Randy Hessel, and Robert W. Dibble. SAE Paper 2003-01-1821.

2. **Fuel and Additive Characterization for HCCI Combustion**, Salvador M. Aceves, Daniel Flowers, Joel Martinez-Frias, Francisco Espinosa-Loza, William J. Pitz, Robert Dibble, SAE paper 2003-01-1814.

3. **A Computer Generated Reduced Iso-Octane Chemical Kinetic Mechanism Applied to Simulation of HCCI Combustion,** Salvador M. Aceves, Joel Martinez-Frias, Daniel Flowers, J. Ray Smith, Robert Dibble, J.Y. Chen, SAE Paper 2002-01-2870.

4. **Piston-Liner Crevice Geometry Effect on HCCI Combustion by Multi-Zone Analysis**, Salvador M. Aceves, Daniel L. Flowers, Francisco Espinosa-Loza, Joel Martinez-Frias, Robert W. Dibble, Magnus Christensen, Bengt Johansson, Randy P. Hessel, SAE Paper 2002-01-2869.

Special Recognitions & Awards/Patents Issued

1. Three of our HCCI publications have been selected as “Landmark Research on HCCI Combustion” and published on a SAE bound volume “Homogeneous Charge Compression Ignition (HCCI) Engines: Key Research and Development Issues.”

II.I. The Effects of Fuel Type, Speed, and Heat Transfer on HCCI Combustion and Emissions

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DOE Technology Development Manager: Gurpreet Singh

Objectives

Project Objective:

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

FY 2003 Objectives:

- Investigate the effects of fuel type and engine speed on engine performance and the completeness of bulk-gas combustion.
- Determine the potential of charge stratification for controlling ignition timing both for fuels that have “cool-flame” chemistry and those that do not.
- Conduct an initial study of diesel-fueled HCCI.
- Compare results with kinetic rate and multi-zone models.

Approach

- Improve all-metal engine facility to provide better control of air temperature and fueling.
- Build an optically accessible research engine for the application of advanced laser diagnostics to investigations of in-cylinder processes.
- Conduct well characterized experiments in the all-metal engine that isolate specific critical aspects of HCCI combustion.
  - Cover a wide range of engine speeds and fuel loads.
  - Investigate various fuel types, including gasoline, iso-octane, and primary reference fuel (PRF) mixtures.
  - Use a gasoline direct injection (GDI) injector with late injection timing for charge stratification.
- Perform a literature review of diesel-fueled HCCI and an initial investigation using a GDI-type fuel injector.
- Use CHEMKIN for single-zone kinetic rate modeling and compare with data. Also, support Lawrence Livermore National Laboratory (LLNL) in the application of their multi-zone model to our engine.

Accomplishments

- Improved metal engine facility with close-coupled air heater and accurate fuel-flow meter.
- Completed design and assembly of all major components for the optically accessible engine and began installation.
- Conducted metal engine experiments in the following areas:

- Studied the effects of fuel type, fuel load, and engine speed on HCCI ignition/combustion and emissions.
- Investigated charge stratification effects for iso-octane and PRF80 fuels.
- Investigated the potential of a GDI injector for diesel-fueled HCCI.

• Conducted a thorough literature review and wrote a chapter on diesel-fueled HCCI for a new book on HCCI that was subsequently published by the SAE.

• HCCI modeling:
- Conducted CHEMKIN kinetic rate modeling for iso-octane and PRF mixtures.
- Worked with LLNL to apply their multi-zone model to our engine.
- Initiated a cooperative modeling program with the University of Michigan.

Future Directions

• Complete setup and shakedown testing of optically accessible engine.
- Initial experiments are to involve natural emission imaging of well-mixed and stratified combustion.
- Later experiments will involve various laser-sheet imaging techniques.

• Investigate the effects of intake-pressure boosting on combustion and emissions for various fuel types, as well as its potential to extend the load range.

• Conduct a broader investigation of the effects of heat transfer and residuals on HCCI.

• Expand studies of mixture stratification by techniques such as late injection timing, multiple injections, and variation of injection parameters.

• Continue cooperative modeling work with both LLNL and the University of Michigan.

Introduction

Homogeneous charge, compression ignition (HCCI) is an alternative engine combustion process that can provide high, diesel-like efficiencies and very low emissions of NO_x and particulates. However, research is required to overcome the technical barriers to producing a practical HCCI engine, such as control of ignition timing over the load/speed map, control of hydrocarbon (HC) and carbon monoxide (CO) emissions, and extension of HCCI operation to higher loads. An understanding of how fuel characteristics affect HCCI ignition, combustion, and emissions is also critical.

The objective of this project is to develop the fundamental understanding necessary to overcome these barriers. To achieve this objective, an HCCI engine laboratory has been established and is being equipped with both an all-metal and an optically accessible HCCI engine of the same basic design. The metal engine is fully operational, and substantial progress has been made toward completion of the optical engine during this past year. Three studies were conducted using the all-metal engine, covering 1) fuel-chemistry effects for “gasoline-like” HCCI, 2) charge stratification, and 3) an initial investigation of diesel-fueled HCCI. In addition, the ignition/combustion process was modeled using a single-zone kinetic rate code (Senkin application of CHEMKIN) with kinetic mechanisms from Lawrence Livermore National Laboratory (LLNL), and a cooperative effort was established with LLNL for multi-zone modeling. This research is being conducted in close cooperation with both the automotive and heavy-duty diesel industries. Results are presented at bi-annual review meetings that provide for substantial discussion and feedback from industry.

Approach

The experiments were conducted in the all-metal engine of the HCCI engine laboratory. This versatile facility was designed to allow investigations over a wide range of operating conditions using various fuel-injection, mixing, and control strategies. In order to obtain the precisely controlled intake temperatures and fueling rates required for the current study, two improvements were made to the facility: 1) a close-coupled intake air heater was added to allow fine-tuning of the intake air temperature, and 2) the fuel system was equipped with a positive-displacement flow meter.

Because fuel ignition chemistry plays a major role in the performance of HCCI engines, four fuels with different ignition qualities were tested over a wide range of engine loads and speeds. The fuels consisted of a research-grade gasoline and three blends of the primary reference fuels (PRF) (iso-octane and *n*-heptane), including pure iso-octane, PRF80, and PRF60 (PRF blends with octane numbers of 80 and 60, respectively). At each operating condition, cylinder pressure and emissions data were acquired to determine the engine's performance. In addition to these studies at well-mixed conditions, stratified-charge operation was investigated for iso-octane and PRF80 to determine its potential for combustion timing and emissions control.

For diesel-fueled HCCI, creating a sufficiently homogeneous mixture without fuel wall-wetting can be challenging due to the low volatility of the fuel. Because the GDI injector appears to be well suited for this application, it was used for an initial study of diesel-fueled HCCI.

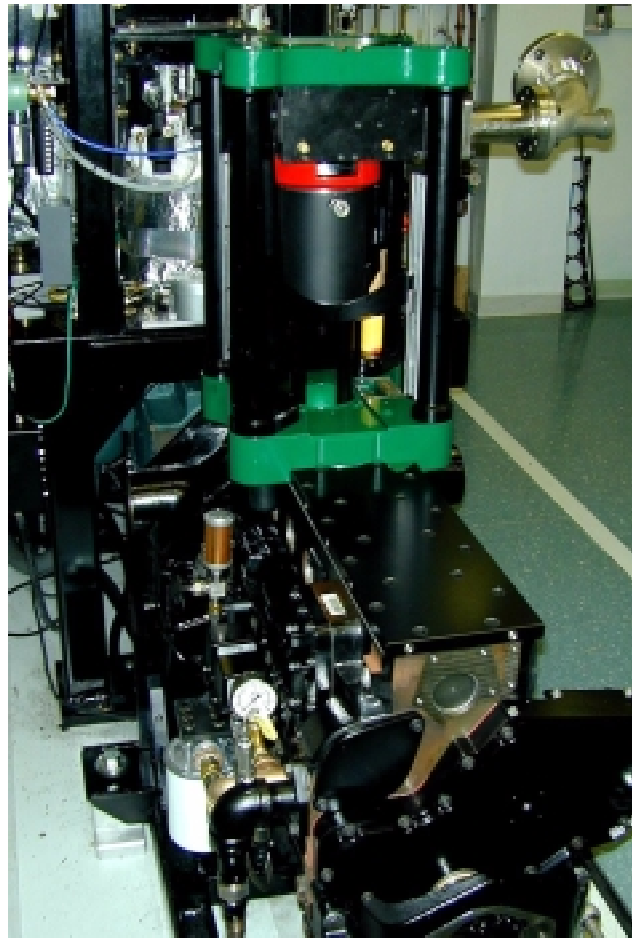

Figure 1. Photograph of the optically accessible engine. Both the optical and all-metal engines are derived from Cummins B-series diesel engines (0.98 liters/cyl.) and have been converted for balanced, single-cylinder, HCCI operation.

Results

Substantial progress was made on building an optically accessible HCCI research engine. Figure 1 is a photograph of the engine showing the extended cylinder for optical access. Fabrication and assembly of all major parts is complete, and installation is expected to be completed near the end of FY 2003.

The effect of fuel chemistry on "gasoline-like" HCCI is shown in Figures 2 - 4. Figure 2 shows a comparison of the CO_2, CO, and HC emissions for iso-octane and gasoline. For both fuels, as the equivalence ratio (ϕ) is reduced below about 0.2, CO_2 levels fall and CO levels rise dramatically, indicating the onset of incomplete bulk-gas reactions, as described in Reference [1]. Because incomplete bulk-gas combustion causes a serious loss of combustion efficiency, it is important to understand how it is affected by fuel type and engine speed. As evident in the figure, the behavior of gasoline is quite similar to that of iso-octane except that the rise in CO emissions is shifted to slightly higher fueling. The reason for this may be found in the difference in required intake temperatures for the two fuels, as shown in Figure 3. For both fuels, the intake temperature was adjusted so that the 50% burn point occurred at top dead center (TDC). Since gasoline autoignites more easily, a lower intake temperature was required, leading to lower combustion temperatures for the same fueling. Because completion of the CO-to-CO_2 reactions requires that combustion temperatures exceed a minimum value [1,2], slightly more fuel must be burned for gasoline to reach the same level of combustion completeness.

In contrast with the similarity of gasoline to iso-octane, the PRF mixtures show significantly different behavior. As shown in Figure 3, at low loads (ϕ<0.1), the required intake temperature for PRF80 approaches that of gasoline, but at higher loads, much lower intake temperatures are required. These low intake temperatures cause the onset of incomplete bulk-gas combustion, as indicated by the rapid rise in CO emissions, to shift to significantly higher fueling, as shown in Figure 4. PRF60 requires even lower intake temperatures, and TDC phasing could not be maintained above ϕ ≈ 0.17 because the required intake temperature was approaching ambient. These results show that the addition of *n*-heptane in the PRF mixtures significantly enhances the ignition, and that the enhancement increases with increasing equivalence ratio. Similarly, changes in engine speed had only a small effect on the required intake temperature or onset of incomplete bulk-gas reactions for iso-octane and gasoline, while they caused substantial changes in both intake temperature and emissions for PRF80 and PRF60. An examination of the apparent heat release rates (AHRR) shows that this enhanced ignition is due to low-temperature exothermic reactions ("cool-flame" chemistry) that occur with *n*-heptane. CHEMKIN single-zone model computations were conducted, and the trends were found to be in good agreement with the experimental data for iso-octane but not for

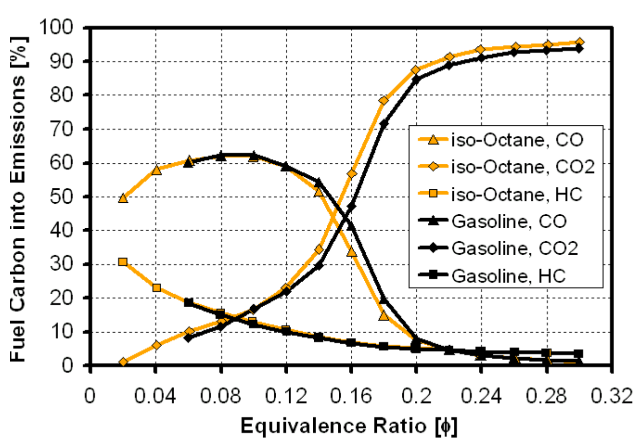

Figure 2. The fraction of fuel carbon into CO_2, CO, and HC emissions as a function of fuel loading for iso-octane and gasoline.

the PRF mixtures, suggesting that the kinetic mechanism for *n*-heptane is not yet accurate for HCCI conditions.

These results show that fuels with significant cool-flame chemistry, such as PRF80, require substantially more compensation to maintain combustion phasing with changes in load and speed than do iso-octane or gasoline. The large changes in intake temperature required to accomplish this (see Figure 3) could be difficult to achieve in the timescales of rapid transients in real automotive engines. Alternatively, the data in Figure 3 suggest that for fuels with cool-flame chemistry, it should be possible to adjust the phasing by varying the equivalence ratio. Figure 5 shows that with PRF80, making the fuel/air mixture locally richer by delaying injection [1] advances the combustion phasing for the same overall fueling rate. For a well-mixed charge

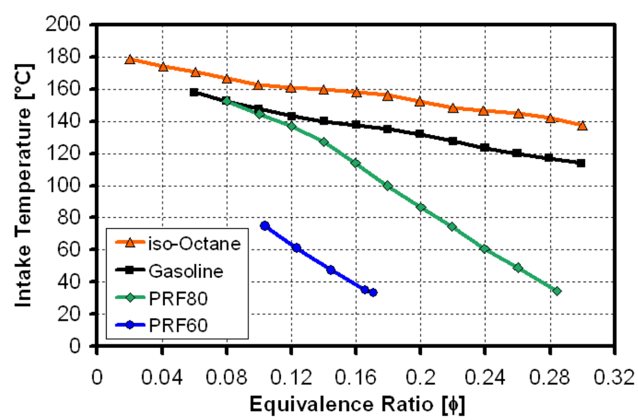

Figure 3. Intake temperature required to maintain the 50% burn phasing at TDC for various fuels.

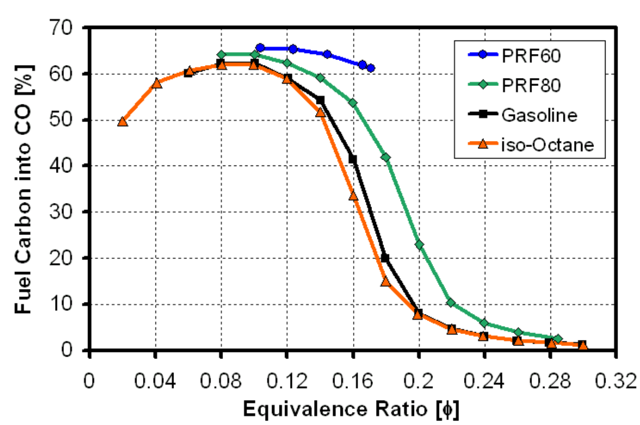

Figure 4. The fraction of fuel carbon into CO as a function of fuel loading (ϕ) for various fuels.

(injection at 40 - 100° crank angle [CA]), an intake temperature of 100°C is required for TDC combustion phasing, and reducing the temperature to 59°C causes the timing to be retarded by about 5° CA (see Figure 5). However, by delaying injection until 270° CA, the phasing can be shifted back to TDC with no change in intake temperature. Since injection timing can be easily varied from one engine cycle to the next, these results show that for fuels with cool-flame chemistry, charge stratification can rapidly and significantly shift the combustion phasing. In contrast, charge stratification has almost no effect on the combustion phasing for iso-octane, which has insignificant cool-flame chemistry at the conditions studied.

HCCI also has a strong potential for reducing NO_x and particulate emissions from diesel engines, but mixture preparation can be difficult with a standard diesel injector. A GDI-type injector appears to be well-suited for this application, and its potential for diesel-fueled HCCI was investigated. The effects of several operating parameters were assessed, including: injection timing, injection pressure, intake-air temperature, air swirl, and fuel load. Overall, the GDI injector performed well, and its performance was found to improve with increases in both injection pressure and swirl. Figure 6 shows that the combination of increasing injection pressure from 70 to 120 bars and increasing the swirl ratio from 0.9 to 3.2 significantly improved combustion efficiency and reduced soot emissions.

Conclusions

- Iso-octane is a good surrogate for the gasoline tested at the conditions investigated.
- There is a strong coupling between the ignition quality of the fuel and the intake temperature required to maintain combustion phasing. This in turn directly influences the completeness of combustion for a given equivalence ratio since it affects the combustion temperature.
- For iso-octane and gasoline, which have no significant cool-flame chemistry, changes in fuel load and engine speed have only a relatively small effect on the intake temperature required for TDC combustion phasing and on the onset of incomplete combustion. In contrast, for PRF80 and PRF60, which have significant cool-flame chemistry, both fuel load and speed strongly affect the required intake temperature and the onset of incomplete combustion.
- Stratification can significantly and rapidly shift combustion phasing for fuels with cool-flame chemistry such as PRF80, but not for fuels such as iso-octane that have no significant cool-flame activity.

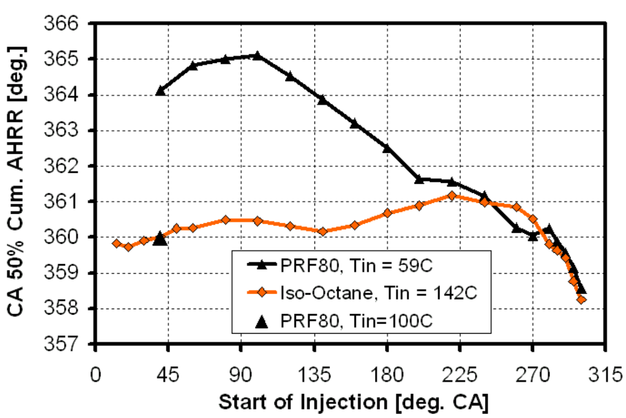

Figure 5. The effect of injection timing (charge stratification) on the 50% burn phasing for PRF80 (ϕ = 0.18) and iso-octane (ϕ = 0.14). 0° CA is TDC intake and 360° is TDC compression.

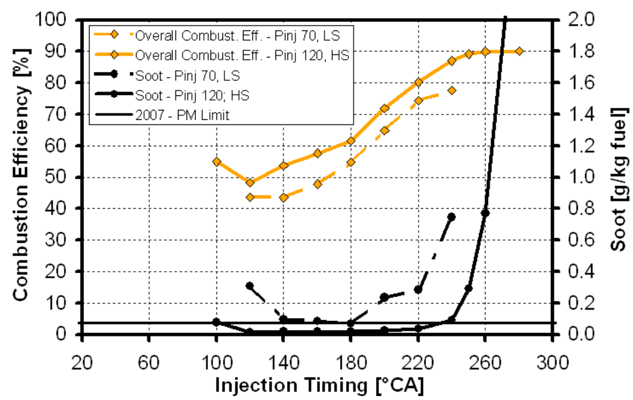

Figure 6. Combustion efficiency and soot emissions as a function of injection timing for diesel-fueled HCCI using a GDI fuel injector. Shown is a comparison of a moderate injection pressure (70 bar), low-swirl (LS) condition with a high injection pressure (120 bar), high-swirl (HS) condition (ϕ = 0.2).

- A GDI-type fuel injector has a strong potential for improving diesel-fueled HCCI. Higher injection pressures and air swirl were found to be advantageous.

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2. Dec. J. E., "A Computational Study of the Effects of Low Fuel Loading and EGR on Heat Release Rates and Combustion Limits in HCCI Engine," SAE paper no. 2002-01-1309, 2002.

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5. Sjöberg, M. and Dec, J. E., "Speed, Boost, and Heat-Transfer Effects on HCCI Combustion of Iso-Octane and Gasoline," Cross-cut Diesel CRADA Meeting, January 28-29, 2003.

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9. Sjöberg, M. and Dec, J. E., "Combined Effects of Fuel-Type and Engine Speed on Required Intake Temperature and Completeness of Bulk-Gas Reactions for HCCI Combustion," Advanced Engine Combustion Working Group Meeting, June 24-25, 2003.

10. Dec, J. E. and Sjöberg, M., "Isolating the Effects of Fuel Chemistry on Combustion Phasing in an HCCI Engine," Advanced Engine Combustion Working Group Meeting, June 24-25, 2003.

Special Recognitions & Awards/Patents Issued

1. Project was selected by the International Energy Agency as the most significant achievement in combustion for 2003 - out of submissions from all member countries.

II.J. Automotive HCCI Combustion Research

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DOE Technology Development Manager: Gurpreet Singh

Objectives

- Investigate in-cylinder processes to address technical challenges to automotive-scale homogeneous charge compression ignition (HCCI) combustion. The initial focus is to understand how in-cylinder fuel/air mixing affects combustion efficiency and emissions production.
- Interact with automotive industry to ensure continued focus on relevant HCCI issues. Coordinate research with Sandia's Dual-Engine HCCI program (J. Dec) to enhance progress of both projects.

Approach

- Apply planar laser-induced fluorescence (LIF) diagnostic to measure HCCI fuel distribution as a function of fuel injection parameters (motored optical engine).
- Compare the LIF equivalence ratio measurements with emissions measurements recorded under similar conditions (fired all-metal engine). Examine possible correlation between fuel mixing statistics and emissions during injection timing sweeps.
- Modify the light-duty optical engine facility to enable fired HCCI operation.

Accomplishments

- LIF diagnostic demonstrated to be effective for in-cylinder measurements at HCCI-like conditions.
- Fuel distribution measurements completed in motored engine for a selection of injection timings, equivalence ratios, injector types, and charge motion.
- Optical-engine LIF data and metal-engine emissions data compared to help explain the observed effect of injection timing on CO/NO_x emissions. An equivalence ratio limit applied to fuel probability density function (PDF) plots predicts CO emission trends during injection timing sweep.
- Lab modifications for fired HCCI operation completed.

Future Directions

- Debug the optical engine during fired HCCI operation. Establish repeatable, fired operating conditions.
- Perform LIF measurements of the fuel mixing process under fired conditions for varying fuel-injection timings.
- Measure engine emissions in the optical engine and correlate with fuel-distribution measurements.

Introduction

Understanding and controlling the preparation of HCCI fuel-air mixtures is an important step in the development of viable HCCI engines. As has been revealed by tests performed in metal engines at Sandia and elsewhere, emissions from HCCI engines are strongly coupled with injection timing. This dependence indicates the important role of fuel-air mixing on formation of emissions. Furthermore, control of ignition timing and combustion over a range of loads in the HCCI engine may well require advanced fuel-air mixing strategies (i.e., not necessarily homogeneous)–strategies that will require a better understanding and control of the fuel-air mixing process.

Approach

Two principal activities were pursued during FY 2002. First, a series of experiments were conducted to optically measure in-cylinder fuel distributions under typical HCCI light-load conditions. At the time of these experiments, our light-duty optical engine was not yet equipped for fired HCCI operation. Therefore, the tests were run under skip-fired (spark-ignited) conditions, with HCCI data collected during motored cycles. Data were collected for a range of fuel injection parameters including injector cone angles, flow rates, global equivalence ratios, and injection timings. In addition, the fuel distribution data were compared to emissions data recorded in Sandia's all-metal engine under similar operating conditions.

This year's second principal activity, begun after the completion of the above experiments, was the modification of the light-duty optical engine to allow fired HCCI operation. This work was begun in February and completed in June.

Results

Skip-fired operation enabled measurement of in-cylinder fuel distribution under HCCI-like conditions. The head was held at 70°C while in-cylinder surfaces were controlled to realistic temperatures using port-injected propane during fired cycles. During motored cycles, iso-octane (plus co-evaporating LIF tracers) was direct-injected at global equivalence ratios from 0.14 to 0.3. Two-dimensional LIF-tracer images were recorded near the end of the compression stroke and converted to fuel-equivalence-ratio images to provide quantitative measurements of fuel-air mixing. The collection of images from each operating condition were reduced to probability density function (PDF) plots that reveal the effects of varying operating parameters on fuel-air mixing.

The varied operating parameters included air charge motion, fuel spray cone angle, fuel injection rate, start-of-injection (SOI) timing, and global equivalence ratio. (The most significant of these parameters are, not surprisingly, SOI timing and equivalence ratio.) The PDF plots of fuel distribution vary dramatically as injection timing is retarded, as shown in Figure 1. The three plots are selected from an injection-timing sweep and represent early, mid, and late injection timings for an experiment with a low global equivalence ratio of 0.14. During early injection (Figure 1, top), there is plenty of time for mixing, and the resulting fuel-air mixture is homogeneous by the end of the compression stroke. Accordingly, the PDF curve indicates that the sampled mixture is represented by a narrow range of local equivalence ratio values. For injection at bottom dead center (Figure 1, middle), the mixing is less complete, and the resulting mixture PDF is broader and shorter. The PDF for late injection (Figure 1, bottom) reveals a very broad range of local equivalence ratios, indicating a heterogeneous, or stratified fuel-air mixture.

As a potential solution to high CO emissions from HCCI engines at low loads, many researchers have advocated using stratified, rather than homogeneous, mixing. Late injection is an obvious way to create a stratified charge, and data on the emissions from retarded injection are available. Figure 2 presents CO and NO_x emission trends as a function of injection timing. These data were recorded in Sandia's metal HCCI engine (see John Dec's annual report) under similar conditions to the above experiments (same injector, fuel, global equivalence ratio, and similar charge density at time of injection). Because the global equivalence ratio is so low, homogeneous mixtures produced by early injection do not burn hot enough to complete the conversion of CO to CO_2 — witnessed by the high CO levels for SOI < -250 crank angle degrees (CAD) in Figure 2. But the CO curve drops dramatically for later injection timing, indicating that locally richer mixtures are formed that burn hot enough to oxidize much of the CO.

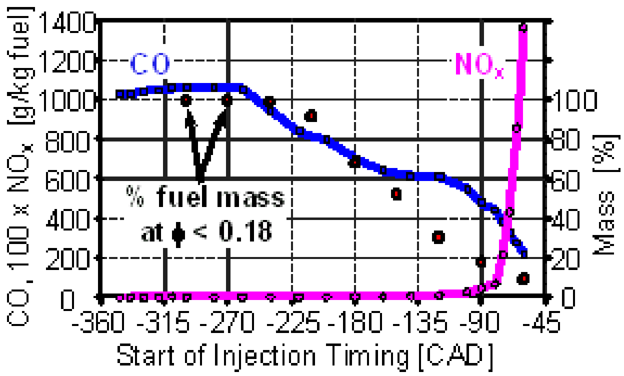

Figure 2. Emissions data recorded in all-metal engine under similar conditions to Figure 1. The curves report CO and NO_x emissions data for an injection timing sweep. The round data points are predictions derived from PDF plots by applying an equivalence ratio limit of 0.18.

Based on metal-engine emissions experiments, a global equivalence ratio of 0.18 was determined to be an approximate limit for good CO conversion. This limit has been superimposed on the PDF plots in Figure 1, with the idea that local equivalence ratios below this limit represent regions where CO will not be converted to CO_2. Thus, for early injection (Figure 1, top), all the fuel is at local ratios below the limit, while later injection is characterized by increasing mass of fuel at ratios above the limit. To determine whether the PDF-plot limit can predict CO emissions, fuel mass below the 0.18 limit was integrated for each SOI timing and plotted with the emissions data in Figure 2. The trends are similar enough to suggest that the LIF-generated data may prove a useful tool for predicting emissions, thus aiding the development of advanced injection strategies.

Conclusions

Skip-fired experiments in an optical engine enabled measurements of the fuel-air mixing process under simulated lean HCCI operation. LIF fuel-equivalence-ratio images captured near the end of the compression stroke were used to characterize charge preparation as a function of direct fuel injection timing. Equivalence ratio statistics from the data quantify the progression from homogeneous to stratified mixture as injection timing was delayed. A

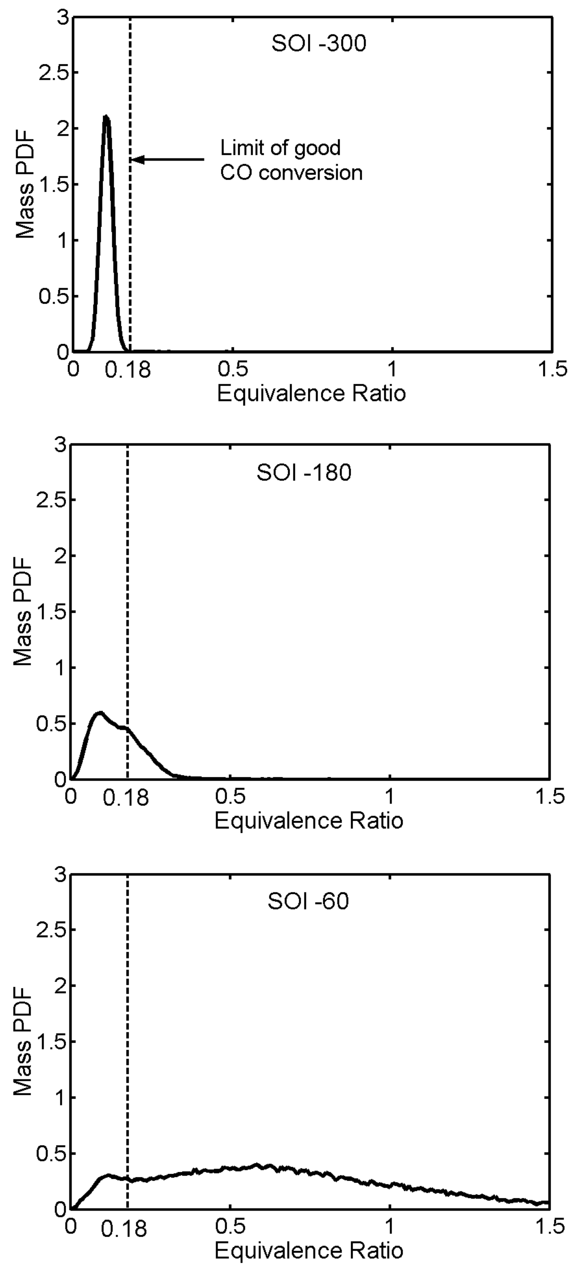

Figure 1. Fuel distribution data from LIF measurements recorded near the end of the compression stroke and reported as probability density functions. The global (overall) equivalence ratio, 0.14, represents low-load HCCI operation. Three timings from an injection timing sweep are presented. **Top:** Early injection timing of -300 CAD (60 CAD after top dead center of intake); **Middle:** Bottom dead center timing of -180 CAD; **Bottom:** Late injection timing of -60 CAD (60 CAD before top dead center of compression).

proposed method of predicting engine-out emissions using the LIF-based statistics proved successful in matching the trends of CO emissions measured in Sandia's metal HCCI engine under similar operating conditions.

Modifications to the direct-injection optical engine were completed, including a new crankshaft, camshafts, and intake-charge-handling system. The modifications enable fired HCCI operation in the engine at a compression ratio of 12 and intake air conditions up to 2 bar and 250°C.

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Awards

1. SAE speaker's award for Excellence in Oral Presentation at the SAE 2002 World Congress; awarded August, 2002.

II.K. HCCI Engine Optimization and Control Using Diesel Fuel

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Objectives

- Develop methods to optimize and control homogeneous charge compression ignition (HCCI) engines, with emphasis on diesel-fueled engines.
- Use engine experiments and detailed modeling to study factors that influence combustion phasing, unburned hydrocarbon and CO emissions.
- Provide criteria for transition to other engine operation regimes (e.g., standard diesel combustion).

Approach

- Use two fully-instrumented engines with prototype fuel injection systems and combustion sensors to map and define HCCI combustion regimes, and apply optimization techniques.
- Develop and apply engine performance models, including multi-dimensional, zero- and 1-D global models for control system development.
- Use homogeneous and stratified charge Cooperative Fuels Research (CFR) engine, and low and high injection pressure heavy-duty engine experiments to document fuel effects on HCCI ignition.
- Develop and apply modeling tools, including multi-dimensional codes (e.g., KIVA with state-of-the-art turbulent combustion and detailed and reduced chemistry models), to reveal combustion mechanisms.

Accomplishments

- Diesel engine operation with high injection pressures at both early and late start-of-injection timings has been shown to produce low emissions, with HCCI-like combustion. The time between the end of injection and start of combustion has been identified as a useful HCCI control variable.
- Low-pressure diesel fuel injection has been found to lead to significant wall fuel film formation that deteriorates engine performance.
- A multi-dimensional model has been developed and applied successfully to model low and high pressure injection cases.
- HCCI engine operating limits have been shown to be extended by operation with stratified combustion.
- Detailed combustion computations have been used to identify methodologies to increase mixing prior to ignition for emissions reduction.

Future Directions

- Use of multiple injections for diesel HCCI combustion control will be assessed.
- Use of cylinder pressure-based and ion/optical sensing for engine control will be analyzed.

- Ignition characteristics of diesel fuel will be explored in engine experiments.
- Efficient methods for including detailed kinetics will be implemented and applied in multi-dimensional models for more accurate combustion predictions.

Introduction

This project is in response to the Department of Energy (DOE) solicitation for research and development on homogeneous charge compression ignition (HCCI) diesel-fueled engines. Advantages of HCCI operation include significantly reduced NO_x and particulate emissions. However, there are significant challenges associated with the successful operation of HCCI engines. One of the major difficulties is controlling the combustion phasing—mainly the assurance of auto-ignition at appropriate timings over a wide range of operating conditions. Another obstacle of HCCI engine operation is the relatively high emissions of unburned hydrocarbons (HCs) and carbon monoxide (CO) due to incomplete combustion with low-temperature lean burn. The power output of the HCCI engine is also limited since the combustion can become unstable. The present research investigates methods to quantify and overcome these obstacles using a combined experimental and modeling approach.

Approach

In order to control the engine, it is necessary to know what variables to control. The five (5) technical tasks of the present work provide information about HCCI combustion mechanisms for use in knowledge-based engine control schemes. The experiments of Task 1 use a fully instrumented Caterpillar 3401 heavy-duty diesel engine that features electronically controlled fuel injection systems to map combustion regimes. Combustion sensors are being adapted for engine control, including acceleration (knock), spark plug ionization and fiber optic detectors. Combustion diagnostics include engine-out HC and other gaseous emissions measurements. Computer modeling, coupled with innovative engine experiments, is also being used to devise strategies for optimizing and controlling HCCI engine performance and reducing emissions over the speed-load range of interest in applications. The engine performance models also include zero- and one-dimensional global models for control system development (Task 2). Data for chemical kinetics model validation is obtained using a CFR engine operated on a variety of fuels (Task 4). The influence of turbulence and temperature and mixture inhomogeneities is revealed with highly resolved computational fluid dynamics (CFD) predictions (Tasks 5 and 6). (Note that Task 3, In-cylinder Species Measurements, was removed from the original proposal due to funding limitations.)

Results

Task 1: HCCI engine combustion optimization and regime mapping – The Caterpillar 3401 heavy-duty diesel engine has been tested over a wide range of speed and loads using the stock high-pressure electronic unit injector (EUI) injection system, and the time delay between the end of injection and the start of combustion has been shown to be a potential HCCI control parameter [1]. In the present effort, operation with a commercial gas direct injection (GDI) low-pressure (10 MPa) injector has been studied, including both single and split injections. Poor combustion performance was found at very early and at late injection timings using diesel fuel; however, significantly superior results were found using n-heptane. The companion multi-dimensional computer modeling has revealed that this is due to fuel impingement on the combustion chamber surfaces with the relatively non-volatile diesel fuel, and that minimum impingement occurs with injections close to intake valve closing (-120 degrees after top dead center [ATDC]), as shown in Figure 1. The modeling also shows that at higher boost conditions, the spray cone angle is reduced, leading to even more wall impingement. The modeling is being used to suggest optimum injection timings and spray geometries for both high and low injection pressures.

To enhance the computational efficiency of the multi-dimensional models, reduced chemical kinetic mechanisms that consist of limited numbers of species and reactions are being developed. A new, reduced mechanism has been generated based on an available n-heptane mechanism (40 species and 165 reactions). The procedure for generating the reduced mechanism includes eliminating unimportant species and reactions and adjusting kinetic constants in the new mechanism to improve ignition delay predictions. The current reduced mechanism consists of 33 species and 56 reactions and has been validated under both constant-volume and engine conditions. Results of HCCI engine combustion simulations using different reaction mechanisms are shown in Figure 2. The new, reduced mechanism gives cylinder pressure results similar to those of the detailed Lawrence Livermore National Laboratory (LLNL) mechanism at about 1/10 the computer time. The central processing unit (CPU) time of the current reduced mechanism is 55% of that of the base mechanism developed at Chalmers University (CU). Further development and validation of reduced mechanisms is under investigation.

Task 2: Combustion modeling and control – Modeling of a multi-cylinder, heavy-duty, turbocharged engine has been conducted using a global model to assess the potential of HCCI in applications. As has been documented previously, the HCCI operating regime is limited to moderate engine load due to the high rate of cylinder pressure rise at high loads and misfire and increased hydrocarbons at low loads. This presents a significant concern for application to on-highway trucks. Figure 3 presents full-throttle power at the rear wheels for a 350 HP truck engine. Also shown is the power required for level road operation, and for 1% and 2% up and down grades. As the vehicle experiences a grade, the engine can be operated anywhere underneath and up to the full-throttle

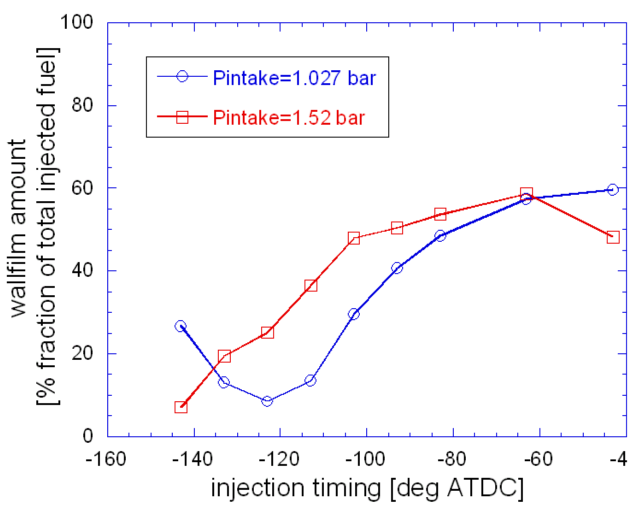

Figure 1. Predicted Amount of Fuel Impinged on Combustion Chamber Surfaces with Diesel Fuel as a Function of the Start-of-Injection Timing Using Low-Pressure GDI Injector for Naturally Aspirated and Boosted Operation

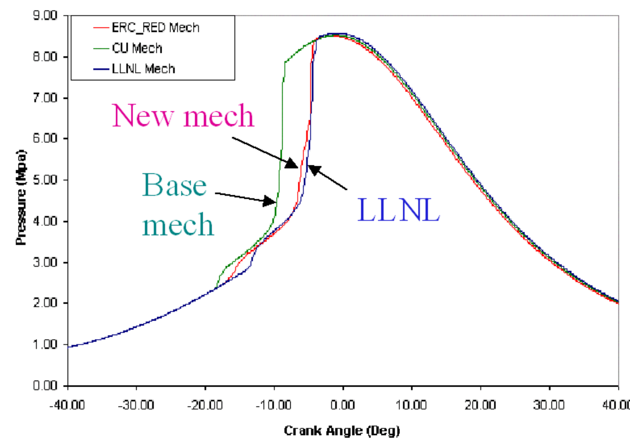

Figure 2. Predicted Cylinder Pressure for Early Injection Using the New (ERC) Reduced Chemistry, Baseline (CU) and Detailed (LLNL) Mechanisms

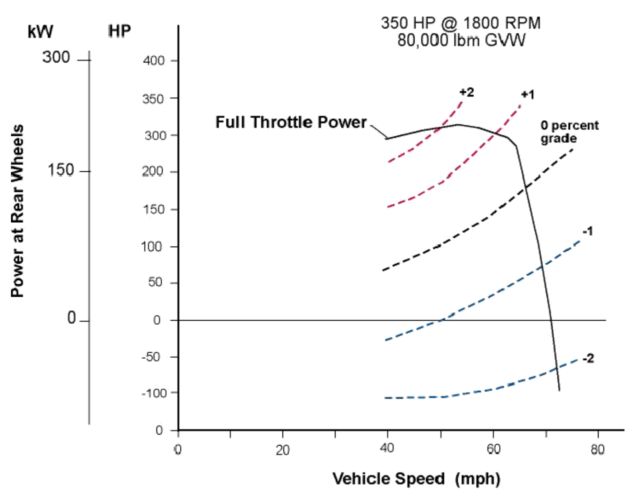

Figure 3. Heavy-Duty Truck Power Requirements as a Function of Grade Level and Speed

curve. As can be seen, at highway speeds, even a 1% uphill grade requires the 350 HP engine to operate at full load. Similarly, slightly more than a 1% downhill grade results in the engine being motored by the vehicle. Thus, with even slightly hilly terrain, the engine will be cycling between no load and full load, with relatively little time spent at the moderate loads most suited for HCCI operation. This suggests that while HCCI may be well suited for passenger car engines, its application to heavy-duty vehicles is problematic. Based on this finding, the multi-cylinder engine modeling effort is being focused on light-duty passenger car turbocharged diesel engines.

Task 4: Ignition chemistry – The CFR research engine has been run in the HCCI combustion mode over a wide range of temperatures and fuel compositions, and the effect of fuel composition on the ignition delay has been evaluated [3]. Recent work has been directed at evaluating whether the HCCI operating range can be extended via fuel charge stratification by direct injection of a portion of the fuel into the engine cylinder. The ratio of premixed to direct injected fuel was varied while the overall equivalence ratio was held constant. In addition, the timing of the direct injection of the fuel was varied. Optimal HCCI combustion was characterized by assessing the coefficient of variation of the indicated mean effective pressure (IMEP), the maximum rate of pressure rise, the combustion efficiency, emissions and the IMEP. A summary of the results is shown in Figure 4, which compares the ranges of HCCI operation obtained with homogeneous charge combustion to those obtained with stratified charge operation. In general, stratified charge operation does not offer potential for increasing the rich limit, or the highest load condition. However, stratified charge does provide more stable combustion and an extension of the lean limit, or low load operation. The potential for using stratified charge as a means of expanding and possibly controlling HCCI operation is being investigated further.

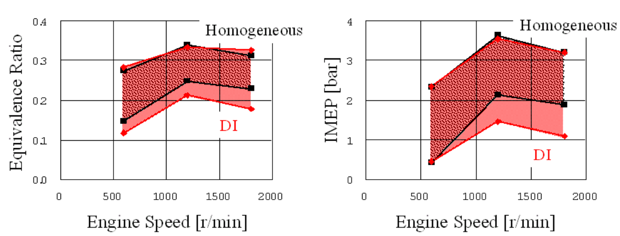

Figure 4. HCCI Operating Ranges for Complete Homogeneous Charge Mixtures and the Optimum Combination of Premixed and Direct Injected (DI) Fuel; Compression Ratio = 16.55, Fuel = PRF 92, Tintake = 107°C

Tasks 5 and 6: Multi-dimensional Modeling – Advanced combustion models are being developed for HCCI modeling [4]. As suggested from the work of Task 1, an important parameter is the time delay between the end of injection and the start of combustion. It has been shown that with a positive ignition delay, the diffusion burn is diminished and lower temperatures are achieved, resulting in less NO_x and soot formation [1]. Recent work has focused on understanding parameters including exhaust gas recirculation (EGR), intake temperature, ignition timing and valve actuation, and their effects on the local equivalence ratio and temperature distributions, soot formation and oxidation, intermediate species production/destruction and the variation in chemical and mixing timescales have been observed. Figure 5 shows predicted timescales for an early injection case where combustion begins around –20 deg. ATDC. K/E (turbulent kinetic energy/energy dissipation) is indicative of the turbulent (or mixing) timescale, and TAU is the combustion characteristic timescale. These parameters quantify the effect of mixing on the ignition delay and show how the start of combustion is controlled. They are being used to study the

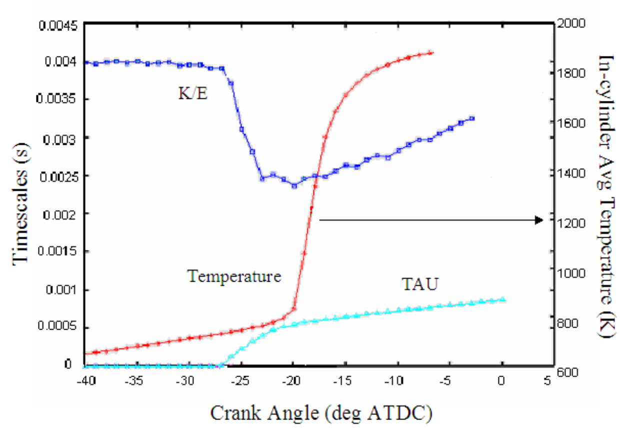

Figure 5. Variation of Turbulence (K/E) and Combustion (TAU) Timescales with Temperature for an Early Injection Diesel HCCI Engine Case

impact on the ignition delay of thermal effects (controlled by intake temperature and EGR rates) and mixing effects. They will also be used to study cases where intake valve actuation [2] is used to prolong the ignition delay.

Additional work has focused on the development of storage/retrieval-based chemistry-acceleration strategies to accommodate large chemical mechanisms in three-dimensional time-dependent CFD for practical engine configurations. The approach is being extended to stratified reactant mixtures, including direct-injection diesel autoignition using the in-situ adaptive tabulation (ISAT) method [5] and an improved method [6]. The new algorithm requires considerably less storage (one to three orders of magnitude) and yields speed-ups compared to direct integration even in highly non-homogeneous systems, as shown in Figure 6.

Conclusions

The present engine tests have shown that operation at both very early and very late start-of-injection timings is effective for low emissions using high-pressure diesel fuel injection. In particular, adequate dwell between the end of injection and the start of combustion allows time for fuel/air mixing. A combustion control criterion based on the ignition/injection time delay has been formulated and is being implemented in a control algorithm for low

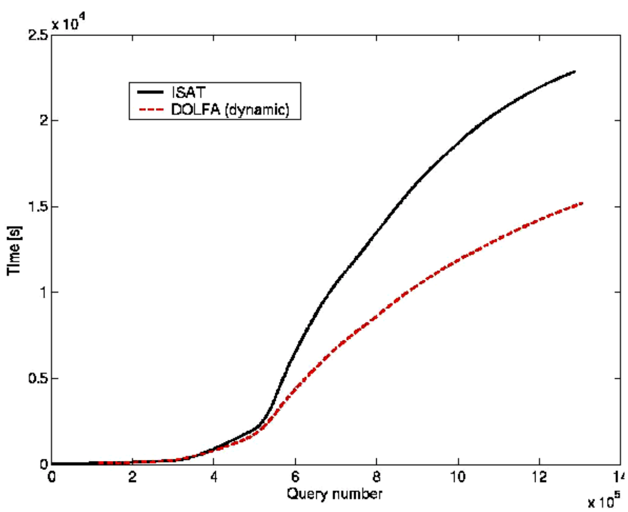

Figure 6. Cumulative CPU Time for a Direct-Injection Autoignition Case Using ISAT [5] and the New Storage/Retrieval Scheme [6]

emissions operation. With low-pressure fuel injection, significant fuel wall impingement occurs, and performance deteriorates. Multi-dimensional modeling has been applied successfully to help explain the experimental trends for both the high and low injection pressure cases. Fuel chemistry experiments show that HCCI ignition is controlled by effects beyond fuel octane or cetane number. This indicates that detailed and reduced chemical kinetic models will require further validation, and this is being achieved by comparison with the present engine experiments.

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Special Recognitions & Awards/Patents Issued

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II.L. HCCI Engine Optimization and Control Using Gasoline

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Objectives

- Develop a homogeneous charge, compression ignition (HCCI) engine control system.
- Develop full cycle modeling tools.
- Investigate chemical kinetics for modeling HCCI combustion.
- Carry out detailed modeling studies of mixing and sprays using computational fluid dynamics (CFD) codes and validate with optical diagnostics.

Approach

- Carry out experimental tests of available HCCI control methods.
- Develop a range of models of HCCI engines, from simple single-zone models to complex CFD codes, in order to incorporate and share the knowledge base on HCCI as it develops.
- Investigate critical chemical kinetic rates and mechanisms for gasoline, and develop and validate reduced kinetic mechanisms for computationally efficient use in these engine models.
- Validate models with engine experiments and combine models and experiments to develop a workable engine control system.

Accomplishments

- Demonstrated use of variable valve timing (VVT), exhaust back pressure, and exhaust rebreathing cams as means to achieve HCCI.
- Demonstrated spark ignited (SI)-to-HCCI mode change using VVT and used active control of backpressure to maintain combustion phasing during shift in intake temperature.
- A thermo-kinetic (TK) model of HCCI was developed for rapid computation in engine system simulations. This has been validated against HCCI engine data for three engines running on natural gas, propane and isooctane.
- Developed a multi-zone model of HCCI operation which is initiated by detailed CFD computations of the breathing process. The model shows significant mixing differences between two valve strategies for introducing recycled exhaust gas: negative overlap and rebreathing. These differences are likely to affect ignition behavior at the stability limits of engine operation.
- A Rapid Compression Facility (RCF) is now functional and has begun to generate combustion data for validating chemical kinetic mechanisms in a controlled environment.

- Developed a number of skeletal and reduced chemical kinetic mechanisms for isooctane and gasoline-like primary reference fuels (PRFs). Also developed an efficient solver which reduces computational times by up to a factor of 60.

Future Directions

- Engine control experiments will expand and refine current studies of mode transitions, thermal transients, and detailed heat transfer, critical features in HCCI combustion. Control algorithms will be developed and validated in engine experiments.
- Chemical kinetic and computational studies, along with shock tube and RCF experiments, will feed improved models of gasoline into the engine simulation tools.
- The thermo-kinetic engine model using the latest reduced chemical kinetics and heat transfer data will be incorporated into an engine system code and validated with the transient engine data as it becomes available. The combined model will be used to propose a workable control methodology for HCCI engine application.

Introduction

Homogeneous charge compression ignition (HCCI) has the potential to dramatically reduce NO_x emissions from gasoline internal combustion engines while achieving high thermal efficiencies characteristic of diesels, with lower particulate emissions. Because the ignition is not controlled by a spark plug as in conventional gasoline engines but occurs indirectly as a result of the compression heating of the charge, HCCI has been difficult to implement in practical engines. Therefore, the primary objective of this research project is to develop, through experiments and modeling, the understanding of physical and chemical HCCI processes necessary to develop and apply practical control strategies. To meet the project objectives, we have formed a Multi-University Research Consortium of experts in the areas of engine, optical diagnostics, numerical modeling, gas dynamics, chemical kinetics and combustion research from UM, MIT, SU, and UCB.

Approach

Our research project, now in its second year, combines experiments and modeling at various levels of complexity in order to acquire and utilize the knowledge and technology to develop a robust control system for HCCI engines. Both single-cylinder and multi-cylinder engine experiments are addressing issues such as injection strategy, mixture homogeneity, valve timing, exhaust gas recirculation (EGR), intake temperature, fuel properties, cooling strategy, transients and engine mode transitions (e.g. SI-to-HCCI). A range of models of HCCI engines and combustion, from simple single-zone to complex CFD codes, are being used in close coordination with the engine experiments to incorporate the experience gained as it develops. At the same time, extensive studies are underway to develop accurate and reliable chemical kinetic models for practical engine fuels. Together, the kinetics, engine models, and experiments will be used to identify HCCI operating ranges and limits and to develop viable control strategies.

Results

Development of an HCCI engine control system – At MIT, a single-cylinder engine has been set up with electromagnetic valve actuation. Initial testing has demonstrated successful transition from SI to HCCI engine mode in one cycle by dynamically changing exhaust valve opening time. University of California, Berkeley (UCB) researchers have shown that they can control the phasing of HCCI combustion by varying exhaust backpressure, thus changing the amount of hot residuals remaining in the cylinder. As shown in Figure 1, this control strategy has been successfully used to automatically maintain nearly constant ignition timing during an arbitrary intake temperature swing. During the next year, these results will be extended to cover a wide range of transitions and perturbations to provide both demonstration of feasibility and input to models.

Full cycle and system modeling tools – The existing thermo-kinetic (TK) engine simulation code at UM has been used to analyze experimental engine data and chemical kinetic schemes as they have become available from the project universities and partners. Figure 2 shows calculations comparing model results with experimental pressure data (Figure 2a) provided by Sandia National Laboratories for an HCCI engine operating with isooctane fuel, for a number of different equivalence ratios (relative mixture strength). As the mixture becomes stronger, the combustion advances and peak pressure rises. The model calculations shown in Figure 2b capture this trend with the exception of the richest mixture, which is somewhat retarded from the experimental trace. This is thought to be due to the fact that the model did not include the effect of increasing wall temperature with the richer mixtures and shows the extreme sensitivity of HCCI combustion to temperature.

Complementary experiments at UM are helping to understand the engine thermal environment with detailed studies of heat transfer in the engine cylinder of another HCCI engine. Figure 3 shows instantaneous wall temperature measurements (a) and heat flux measurement (b) for varying air/fuel (A/F) ratio; as expected, richer mixtures show higher temperatures and higher flux. An analysis of the data indicates that heat transfer in HCCI engines is different from normal spark ignited engines because of the absence of flames. The results of these measurements are being channeled to the model to improve the fidelity of the TK model.

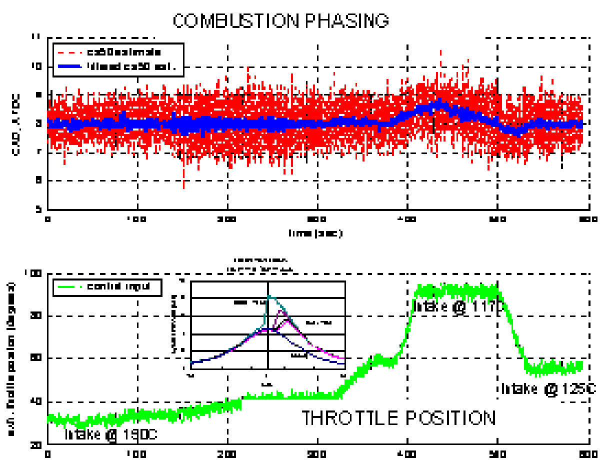

Figure 1. Experiments at UCB show automatic control of combustion phasing during swings of intake temperature by adjusting exhaust throttle position. (Inset shows phasing advance with increasing back pressure.)

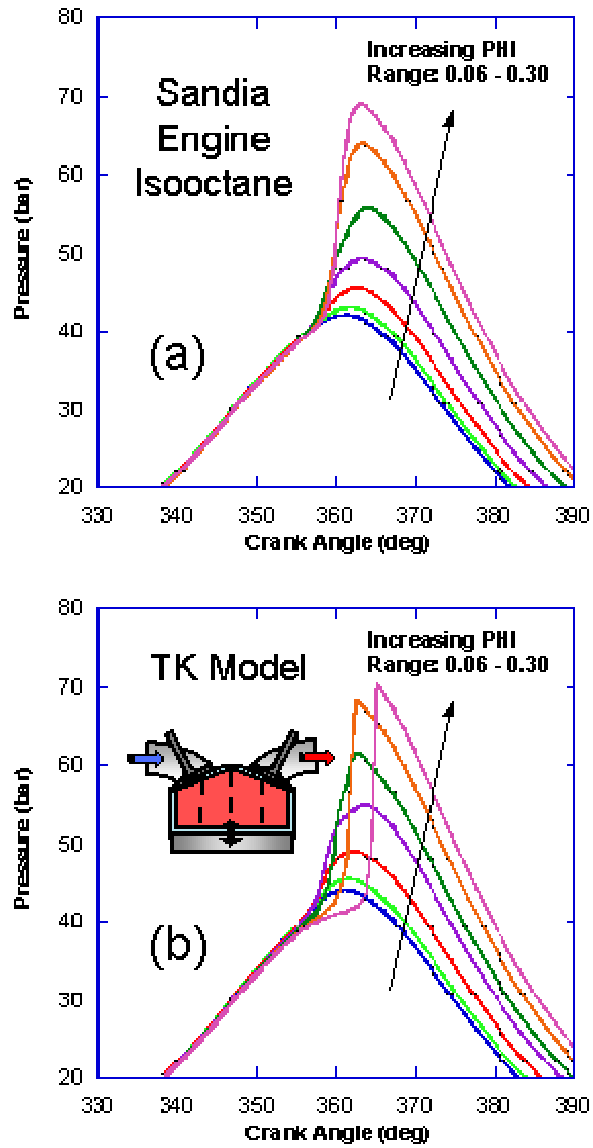

Figure 2. Effect of mixture ratio on combustion: (a) experimental data for isooctane fuel from Sandia National Labs HCCI engine; (b) TK model (UM) for same conditions. Note that effect of increasing wall temperature with richer mixtures was not modeled, explaining the retarding effect for the highest load.

Investigation of chemical kinetics for gasoline HCCI – Great progress has been made this year at UCB and at Stanford in developing and testing useable reaction mechanisms for isooctane, a gasoline surrogate fuel. Several skeletal and reduced mechanisms have been validated against the best available detailed mechanism currently available from Lawrence Livermore National Laboratory. We are just beginning to test these computationally faster mechanisms in the UM thermo-kinetic code. The initial results indicate that the reaction schemes have varying degrees of fidelity when used in the complex engine environment, and work is underway to systematically explore the sensitivities of the reaction schemes to normal engine operating parameters. At the same time, we will continue to test the candidate reaction mechanism against engine data.

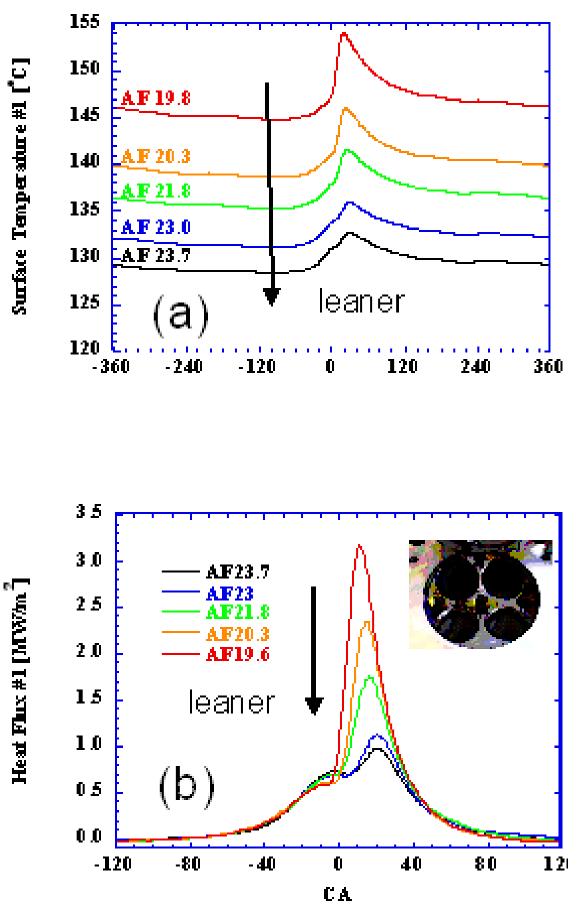

Figure 3. Wall temperature measurements (a) and heat flux measurements (b) in HCCI engine at UM for varying A/F ratio; richer mixtures show higher temperatures and higher flux. (Inset shows position of thermocouple on head surface.)

The experimental Rapid Compression Facility (RCF) at UM is now fully operational, and data is being compared with model predictions. Typical results are shown in Figure 4, where two chemical kinetic calculations of pressure rise are compared with data, again for isooctane fuel. Note that the predictions agree well in ignition timing; however, the final predicted pressure is higher than in the experiment due to the neglect of heat transfer in the calculations. The good agreement between the two mechanisms, one detailed, the other a much simplified skeletal mechanism, indicates that computation time saving of up to a factor of 10 may be possible by using the smaller mechanism.

Detailed modeling of reaction, mixing and spray dynamics using CFD code – Computational fluid dynamics (CFD) has been used to study the degree of mixing of in-cylinder residual gas, currently used by many researchers to induce HCCI operation. To analyze this process, CFD results for temperature and composition distribution just before combustion are fed to a multi-zone code developed at UM to carry out the actual combustion calculation with a much smaller number of zones. Figure 5 shows one such distribution of many thousands of points divided up into 12 zones. When the 12 zones are used to initialize the multi-zone combustion calculation, it is

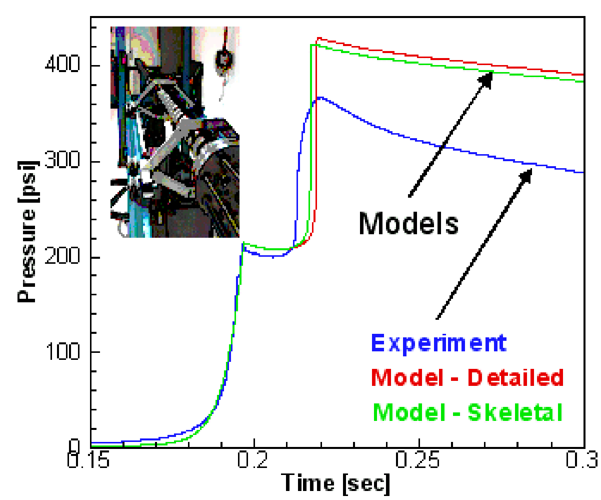

Figure 4. Pressure trace from UM RCF operating with isooctane-air. Model predictions of ignition time compare well with experimental pressure trace for two chemical kinetic mechanisms. (Heat transfer neglected in calculations. Inset shows RCF.)

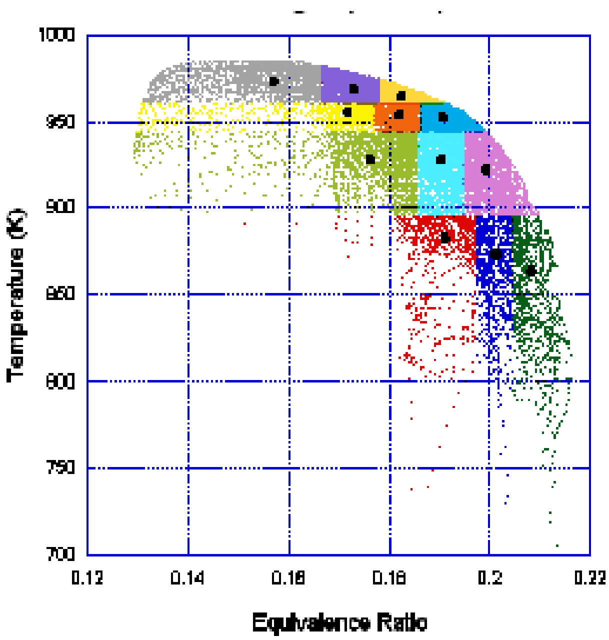

Figure 5. CFD-generated distribution of temperature and concentration just before ignition. Mass divided into 12 zones with centroids at the points indicated. The zones are input to the multi-zone combustion simulation at UM. The richer and hotter zones ignite first, while cooler and leaner zones ignite later, introducing a smoothing effect on pressure rise as observed in experiments.

found that they ignite at different times – the richer and hotter zones first, followed by the cooler and leaner zones. This spreads out the combustion in time, as is observed in experiments. The studies have also shown that different methods of achieving internal EGR by valve timing produce differing degrees of mixing and potentially could affect combustion and engine stability.

Conclusions

- Significant accomplishments have been achieved in FY 2003 through the linked efforts of the multi-university research team.

- Control of HCCI operation has been demonstrated on three engines in the consortium, each with a different strategy. Both static (low speed) control and dynamic (high speed mode change) control have been achieved. A fourth engine is providing detailed heat transfer and wall temperature data indicating that heat transfer in HCCI engines is different from normal spark ignited engines. This information is being fed to the engine modeling effort.

- Validation tests comparing data with a simple thermo-kinetic model show that the model is very sensitive to initial conditions, particularly those affecting the thermal environment. Further, this sensitivity varies greatly depending on the chemical kinetic mechanisms and the sub-models used for combustion. The engine model is being used to analyze data sets from all engines in the consortium and kinetic schemes as they become available from project partners. Validation and development of the model will continue in order to determine the best balance between computational cost and fidelity, with the intent of using the model as a basis for larger scale engine and vehicle system studies.

- Fundamental combustion data obtained in a Rapid Compression Facility is now being added to the shock tube data in the development and validation of chemical mechanisms for describing HCCI ignition and combustion. The focus is on isooctane and mixtures of isooctane and n-heptane, as surrogate fuels representing gasoline. Several skeletal and reduced mechanisms have been proposed in order to reduce computational time, which for multi-dimensional calculations is currently prohibitive. Initial testing of these models in the simulated engine environment of the TK model is delivering promising results.

FY 2003 Publications/Presentations

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II.M. Diesel HCCI Development

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Objectives

- Identify cost effective engine technology strategy to meet the stringent Tier 2 light-duty emissions standard.
- Identify cost effective engine technology strategy to meet the stringent 2010 heavy-duty emissions standard.
- Develop enabling technology to implement the engine technology strategy.

Approach

This research effort focuses on the development of an advanced combustion regime called homogeneous charge compression ignition (HCCI). HCCI holds the potential of meeting future emissions regulatory challenges for internal combustion engines while satisfying the needs of the marketplace. This multi-year development project focuses on the key challenges associated with implementing this technology. Specifically, the challenges are:

- Air - Fuel Mixture Preparation – To date, diesel fueled HCCI has been largely unsuccessful due to the difficulty of achieving the proper air-fuel mixture. The Caterpillar project has evaluated a number a technical approaches to achieve appropriate mixing.
- Power Density – To date, HCCI demonstrations have been limited to relatively low power density (circa 500 kPa BMEP). Higher power density (1500+ kPa BMEP) is required for a commercially viable technology. The Caterpillar project has evaluated a number of options to increase the power density.
- Combustion Phasing and Control – With HCCI, direct control of the combustion event is lost. The Caterpillar project will investigate the parameters that influence the control and identify a means to actively control combustion.

Accomplishments

Caterpillar's project has made significant progress in each of the key technical challenges associated with this technology.

- Caterpillar developed a novel engine system that successfully achieves the proper air-fuel mixture. The advent of this novel engine system virtually solves the mixture preparation challenge associated with HCCI, thereby facilitating the engine demonstration of 2007 Tier 2 light-duty and 2007-2010 heavy-duty emissions standards.
- Caterpillar achieved 1000+ kPa brake mean effective pressure (BMEP) while meeting the future emissions standard. This achievement more than doubled the previously published power density and clearly advances HCCI as a potentially viable approach to meeting future regulatory and marketplace requirements.
- Caterpillar started aggressive engine test stand evaluation of key performance parameters (boost level, injection event, intake manifold temperature, etc.) to better understand the parameters that impact and control combustion.

Future Directions

The Caterpillar team will utilize best in class design practices, advanced combustion modeling techniques, single-cylinder engine testing and multi-cylinder engine testing to advance the technology. Technology development continues in the following key areas:

- With the advent of the novel engine system, the air-fuel mixture issue is largely resolved. Future work will focus on identifying and developing a cost effective method of manufacturing the engine system.
- Caterpillar will continue to focus on the power density issue to achieve additional breakthrough results. The team will focus on achieving the results with improved engine structure, enhanced air system capabilities, and improved combustion control.
- Additional test stand evaluation, sensor development, and algorithm development is needed to address the challenges associated with controlling this novel combustion approach. Rapid control algorithm development tools will be utilized to expedite the development of this technology. In addition, novel combustion control mechanisms will be designed, analyzed and, if appropriate, evaluated on the engine test stand.

Introduction

Increasingly stringent air quality standards have driven the need for cleaner burning internal combustion engines. Many emissions reduction technologies adversely affect fuel consumption (and subsequently U.S. dependence on foreign oil). HCCI fundamentally shifts the traditional emissions and fuel consumption trade-off. This breakthrough emissions technology may enable compression ignition engines to effectively compete on cost in the automotive market, resulting in a dramatic improvement in fuel economy for that market segment. Additionally, this advanced combustion technology will reduce (or eliminate) the need for expensive NO_x aftertreatment devices which rely heavily upon imported precious metals.

Approach

The development team is utilizing a multi-discipline approach to resolving this complex engineering challenge. The development team has a unique mix of technical experts from the fields of controls, combustion fundamentals, engine design, engine development, and manufacturing. The team is concurrently developing the analytical tools to model and understand the fundamentals of combustion while delivering novel hardware to the test stand to validate the models, improve our understanding, and advance the technology. The unique team is utilizing best in class design practices, advanced combustion and engine system modeling techniques, rapid control strategy development tools, single-cylinder engine testing, multi-cylinder engine testing and over 70 years of experience delivering successful compression ignition engine technology to the marketplace.

Results

As stated above, Caterpillar has made significant progress in each of the key technical challenges associated with this technology. Figure 1 shows typical emissions data acquired on the single-cylinder test engine while operating in the advanced combustion regime. The emissions results were achievable due to the development of a novel engine system that successfully achieves the proper air-fuel mixture. Figure 1 illustrates the potential of this

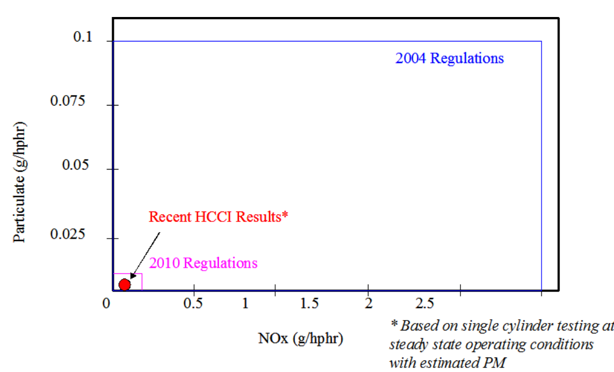

Figure 1. Breakthrough Emissions Results with HCCI

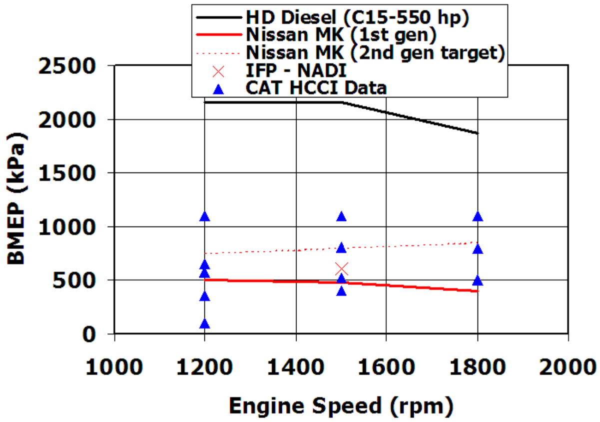

Figure 2. Breakthrough Power Density with HCCI

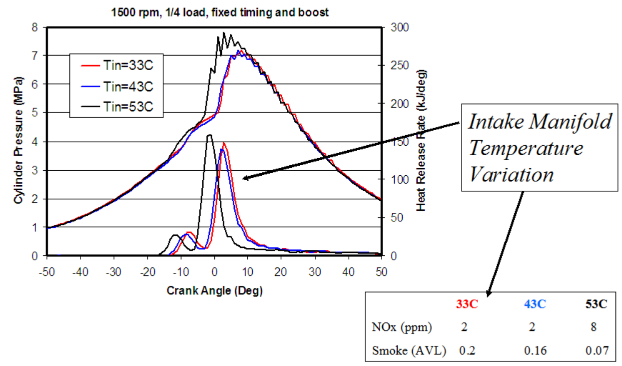

Figure 3. Combustion Control Challenges

technology relative to meeting the 2007 Tier 2 light-duty and 2007-2010 heavy-duty emissions standards. Figure 2 shows the power density achieved with HCCI. Caterpillar has made significant progress toward achieving the power levels required for a commercially viable technology. Additional work is needed to meet the expectation of the market place; however, the progress to date illustrates the exciting promise that this technology holds. Figure 3 illustrates the remaining control challenge associated with the combustion process. As Figure 3 illustrates, relatively minor changes in the ambient temperature will influence the combustion event, which subsequently affects the fuel consumption and emissions.

Conclusions

Caterpillar's aggressive HCCI development has resulted in significant technical progress against each of the key technical challenges. The progress has clearly positioned this advanced combustion technology as a potentially viable approach to meeting the regulatory and marketplace challenges of the future. This technology holds the promise of reducing the U.S. dependence on foreign oil and improving the trade balance.

II.N. Chemical Kinetic Modeling of Diesel and HCCI Combustion

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Objectives

- Characterize the role of diesel fuel composition on production of particulate matter (PM) emissions from diesel engines
- Develop detailed chemical kinetic reaction models for diesel fuel and additives
- Compare soot production mechanisms of different diesel fuels

Approach

- Identify individual diesel components and their molecular structure
- Develop kinetic reaction mechanism for diesel fuel components and additives
- Compute ignition and flame structure for diesel fuel and additive mixtures
- Compare predicted levels of PM and NO_x from different diesel fuel components and use detailed chemical models to determine the mechanisms for the changes

Accomplishments

- Predicted reductions in PM emissions for mixtures of diesel fuel with addition of oxygenated additives
- Demonstrated that newly proposed oxygenated additives suppress PM production at approximately the same rate as previous additives
- Developed and tested a molecular structure basis for predicting the effectiveness of many proposed oxygenated diesel fuel additives
- Developed computer model using molecular dynamics and kinetic Monte Carlo methods for soot growth based on fundamental chemistry formulations

Future Directions

- Extend model capabilities to additional diesel fuel components
- Continue development of soot growth chemistry simulations
- Increase collaborations with programs outside LLNL dealing with diesel fuel issues

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Introduction

Experimental diesel engine studies have indicated that when oxygen is added to diesel fuel, soot production in the engine is reduced. The soot reduction appears to be largely independent of the way oxygen is incorporated into the reactants, whether through entrainment of additional air into the reacting gases or direct inclusion of oxygen atoms into the diesel fuel molecules.

The present study continues our studies of diesel fuel chemistry to understand soot-producing characteristics. While previous studies have emphasized the effects of oxygenated diesel fuels and additives such as dimethyl ether, dimethoxy methane, and more complex molecules such as tri-propylene glycol monomethyl ether, our current focus is to understand and calculate the separate contributions of the major constituent chemical species in regular diesel fuels. This will lead to improved understanding of the interactions 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 computational fluid dynamics (CFD) models of engine combustion.

Approach

Chemical kinetic modeling has been developed uniquely at LLNL to investigate combustion of hydrocarbon fuels in practical combustion systems such as diesel and homogeneous charge compression ignition (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 [1-4] for diesel and HCCI engine combustion, providing understanding of ignition, soot production, and NO_x emissions from diesel engines in fundamental chemical terms.

The underlying concept for diesel engines is that ignition takes place at very fuel-rich conditions, producing a mixture of chemical species concentrations that are high in 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 [5] as a reasonable diesel fuel surrogate model, mixed with oxygenated additives. The impact of the additives on predicted levels of soot producing chemical species was then 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. However, HCCI ignition is overall very fuel-lean, so the chemical kinetics of the ignition are somewhat different. In particular, the premixing of fuel and air in the gaseous state produces no soot, and the lean combustion under HCCI conditions can lead to extremely low NO_x 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, NO_x and soot [6].

Results

We 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. The computed soot precursor evolution for this new oxygenated compound was entirely consistent with our previous findings, confirming again that the kinetic analysis of soot production is becoming more and more consistent and reliable.

In addition to the study of oxygenates, we continued numerical studies of soot growth [7] from tiny precursors into macroscopic soot particles. Figure 1 shows the carbon-rich structure that has

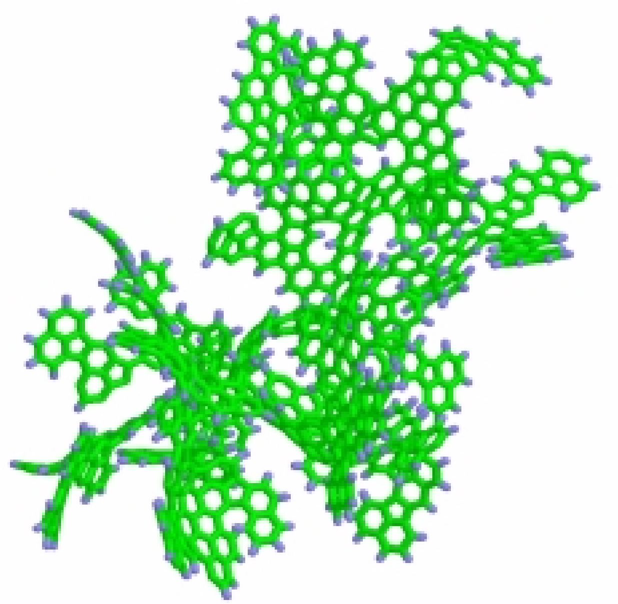

Figure 1. Soot particle during molecular growth period. The particle is built of aromatic rings and grows steadily by adding small fragments at the peripheral available bonding sites. Occasionally, free edges of the particle will link together, forming curved exterior surfaces.

grown from the 2- and 3-carbon fragments emerging from the rich premixed diesel ignition region. The power of this modeling capability is being able to relate the chemical properties of these soot particles based on very elementary physical principles.

Finally, we have continued computational studies of HCCI ignition. The multizone model [8] 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 approach to examine other operating regimes, such as operation with extensive amounts of exhaust gas recirculation or other forms of dilution with richer fuel/air mixtures.

Conclusions

Kinetic modeling provides a unique tool to analyze combustion properties of diesel 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 becoming an essential tool in engine research.

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II.O. KIVA Development

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Objectives

- Improve mass diffusion coefficients, thermal conductivity, and viscosity computations in the high pressure vaporization model.
- Compare single droplet vaporization with experimental results under high pressures.
- Continue to perform high pressure spray calculations.
- Evaluate KIVA-AC as a suitable parallel unstructured code to replace KIVA-3V. KIVA-AC is a parallel, unstructured version of KIVA proposed to replace KIVA-3V. KIVA-3V is the publicly available version of KIVA in circulation.
- Modify KIVA-3V directly to accommodate unstructured grids. Unstructured grids allow not only the use of hexahedra but also tetrahedra and prisms when generating a grid.

Accomplishments

- Correlations have been incorporated which more accurately describe thermal conductivities, viscosities, and mass diffusion coefficients. We can now accurately account for deviations from ideal behavior in both the liquid and gas phase in spray simulations.
- We compared our high pressure model with the experimental data of Stengele *et al*. Comparisons were conducted under a variety of conditions by varying the ambient pressure, ambient temperature, and droplet composition.
- Two-dimensional axisymmetric spray calculations were performed. We show a simulation that explores a non-ideal vaporization regime with n-heptane as a diesel surrogate using ambient conditions (422 K and 130 bar) under which departures from ideal behavior are significant.
- KIVA-AC's computational speed, parallel performance, and numerical solution schemes were evaluated. For a 3-D compression test, KIVA-AC (compiled to run on one processor) takes approximately 9 times longer than KIVA-3V. KIVA-AC scales well in parallel (i.e. the computational time is reduced by two if the number of processors is doubled). The unstructured and parallel solution strategy of KIVA-AC was documented in a report included in the Abstracts of the Thirteenth International Multidimensional Engine Modeling User's Group Meeting at the SAE Congress. Ways of improving KIVA-AC's efficiency were investigated. These ways included eliminating allocatable data (which improved the computational speed by 12%) and improving the computational speed of computationally expensive subroutines (which improved the computational speed by 10%).
- KIVA-3V subroutines which update species concentrations, velocity, temperature, pressure, and turbulence quantities have been successfully modified. The modified subroutines consume roughly 70% of the computational time in the code. The new unstructured version of KIVA-3V is only 10% slower than the structured version.

Introduction and Approach

A high pressure environment is different than an environment at normal or low pressure. Gases behave differently. Fuel droplets vaporize at different rates. In the past year, we have improved the high pressure version of the KIVA-3V code by improving the accuracy in the computation of mass diffusion coefficients, viscosity, and thermal conductivity near the droplet. The high pressure KIVA-3V code is capable of computing with a generalized equation-of-state and capturing deviations from ideal behavior in both the gas phase dynamics and the liquid vaporization. Such deviations can become significant at high pressures encountered in a diesel engine. We have sought to quantify these deviations and discern how important they are in a diesel environment using our high pressure version of KIVA-3V.

We have also devoted efforts to developing a parallel, unstructured version of KIVA-3V. Engine simulations require a grid. KIVA-3V requires the grid to be built from structured hexahedra, which can require much user interaction and time if the engine geometry is complex. In addition, grid-generation with KIVA-3V can consume a disproportionate amount of time compared to an actual simulation. KIVA-AC (AC stands for Arbitrary Connectivity) was proposed as a parallel, unstructured version of KIVA which would allow a user the flexibility to generate better quality, faster grids. We have evaluated KIVA-AC and determined that it lacks provisions for effective piston and valve movement, as well as a validated spray model. The code is also significantly slower than KIVA-3V. Taking into consideration these deficiencies of KIVA-AC, we decided to work directly with KIVA-3V. KIVA-3V can already accommodate pistons, valves, and spray. Our interest is in modifying KIVA-3V so it can compute on unstructured grids, thus enabling KIVA-3V to interface with grid-generation packages to create quality grids for engines quickly.

Results

Figure 1 shows a comparison of our single droplet vaporization model results with experimental results. Figures 2 and 3 show a 2-D axisymmetric spray calculation in a low temperature, high pressure regime where departures from ideal behavior are significant. Figures 4 and 5 demonstrate the increased accuracy that can be achieved by using an unstructured grid.

Figure 1 compares our model with the experimental results of Stengele *et al.* for a freely falling droplet in a 30 bar, 550 K pressurized chamber. The vertical axis plots the droplet diameter, and the horizontal axis plots the distance the droplet moves. The experimental results are displayed as a line with symbols while the model results are displayed only as a line. Four different results are shown. Each result differs in the initial percentage mixture (by mass) of pentane and nonane. Our model compares well with the experimental results except for minor deviations. Other comparisons have been made and are documented in our paper, "High Pressure Multicomponent Liquid Sprays: Departure from Ideal Behavior."

In Figures 2 and 3, 2000 particles (composed of n-heptane) are injected at 250 m/s into a 422 K, 130 bar chamber with a 14 degree solid cone angle. Injection ends at 1.4 milliseconds, at which time a total of 9.6 milligrams of fuel have been injected. Figures 2 and 3 show the total fuel vapor mass fraction (fuel mass divided by total mass) at 2.8 milliseconds. The brighter areas are indicative of more fuel vapor. Figure 2 uses the KIVA-3V model which does **not** account for deviations from ideal behavior, while Figure 3 uses the

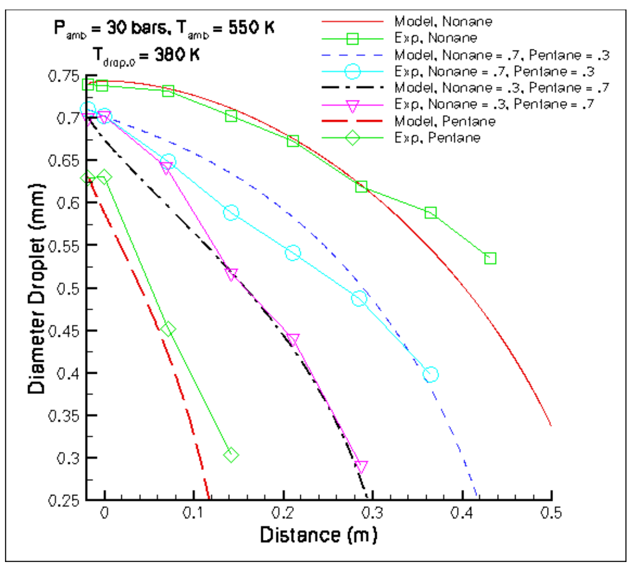

Figure 1. Comparison of Experimental and Model Results for Vaporizing Droplets in a High Pressure Chamber

revised KIVA-3V model. At higher pressures and low temperatures, differences in vaporization rates between the two models become significant, as evidenced by the brighter areas in Figure 3.

Figures 4 and 5 show the relative errors resulting from solving a mass diffusion equation in KIVA-3V using a structured and unstructured grid, respectively. A mixture of oxygen and nitrogen is distributed unevenly in a cylindrical disk. Concentrations of oxygen and nitrogen adjust themselves until spatial distributions of oxygen and nitrogen are uniform.

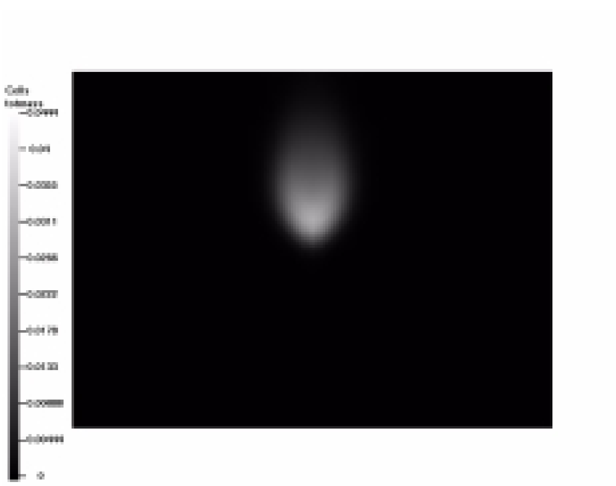

Figure 2. Total Fuel Mass Fraction for Injection into a 422 K, 130 Bar Chamber with KIVA-3V Model Which Does Not Account for Deviations from Ideal Behavior

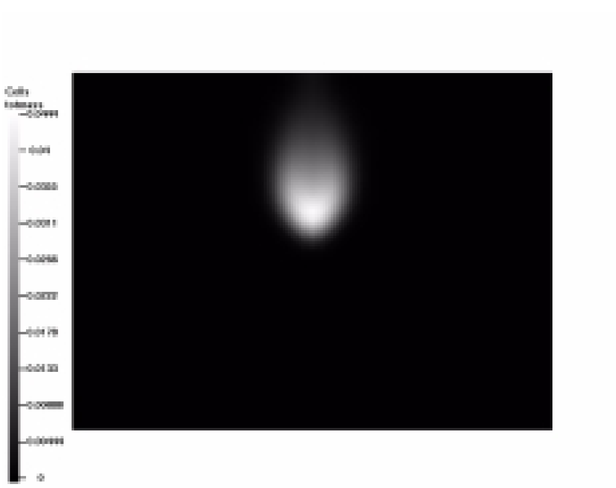

Figure 3. Total Fuel Mass Fraction for Injection into a 422 K, 130 Bar Chamber with KIVA-3V Model Which Does Account for Deviations from Ideal Behavior

The structured grid (Figure 4) uses near triangular cells at four corners of the mesh which are responsible for the resurgence of error near these corners. The unstructured grid (Figure 5) eliminates these triangular cells and reduces the numerical errors at these locations.

Conclusions

We have made improvements to the high pressure model in KIVA-3V, validated it with single droplet experimental comparisons, and continued to use it to study spray injection. Deviations from ideal behavior are significant at low temperatures and high pressures. We have evaluated KIVA-AC and decided

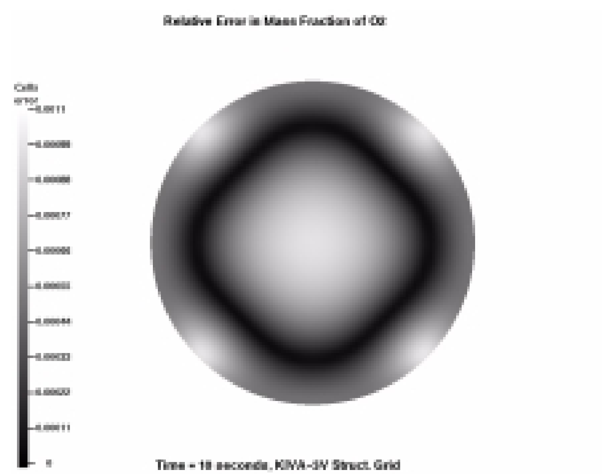

Figure 4. Relative Error in the Mass Fraction of O_2 for a Structured Grid

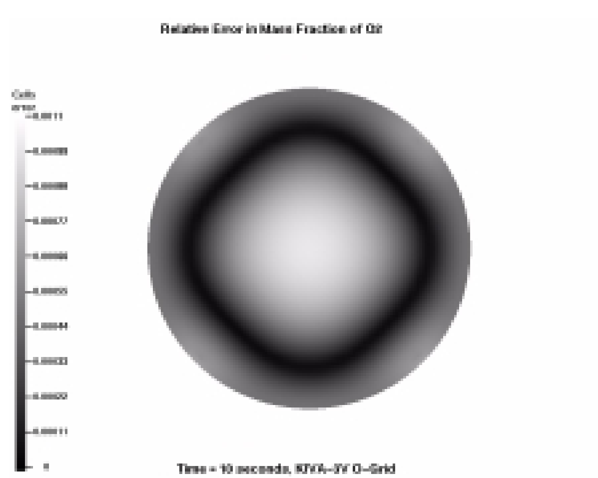

Figure 5. Relative Error in the Mass Fraction of O_2 for an Unstructured Grid

to implement unstructured capability directly into KIVA-3V. KIVA-AC lacks provisions for effective piston and valve movement and is significantly slower than KIVA-3V. We have made significant progress in enabling KIVA-3V to accommodate unstructured grids.

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SECTION III. ENERGY EFFICIENT EMISSION CONTROL TECHNOLOGIES

III.A. Measurement and Characterization of NO_x Adsorber Regeneration and Desulfation

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Industrial Partner: Ford Motor Company

DOE Technology Development Manager: Kevin Stork

Objectives

- Characterize candidate NO_x adsorbers for performance and degradation by assessing various in-cylinder regeneration and desulfation strategies
- Characterize H_2, CO, and hydrocarbons (HCs) generated by the engine and utilized by the NO_x adsorber catalyst
- Examine NO_x adsorber materials in the DRIFTS (diffuse reflectance Fourier transform infrared spectroscopy) and benchflow reactors
- Develop stronger link between bench and full-scale system evaluations in order to be able to evaluate a new formulation on the bench and then predict how it will behave on an engine

Approach

- Establish a relationship between exhaust species and various regeneration strategies on a fully controlled engine
- Characterize effectiveness of in-cylinder regeneration strategies
- Develop and execute rapid sulfation/desulfation experiments
- Develop experiments for bench-scale work to further characterize adsorber monoliths, wafers, and/or powders

Accomplishments

- Engine cell experimental setup complete and experiments underway
- Examined three regeneration strategies at 300°C NO_x adsorber bed temperature
- Measured instantaneous H_2 and CO generation during regeneration sequences
- Generated gas chromatograph/mass spectrometer (GC/MS) traces detailing similarities and differences in HC species formed by various regeneration strategies

Future Directions

- Complete development of regeneration strategies at three NO_x adsorber temperatures
- Quantify torque, fuel consumption, and particulate matter (PM) effects of each regeneration strategy
- Speciate HCs at adsorber inlet/outlet for each strategy and various catalyst formulations
- Conduct in-situ H_2 measurements with H_2-SpaciMS (hydrogen calibrated spacially resolved capillary inlet mass spectrometer)

- Characterize catalysts after sulfation and during desulfation
- Examine samples in bench-scale reactors

Introduction

As part of the Department of Energy's strategy to reduce imported petroleum and enhance energy security, the Office of FreedomCAR and Vehicle Technologies has been researching enabling technologies for more efficient diesel engines. NO_x emissions from diesel engines are very problematic, and the U.S. Environmental Protection Agency (EPA) emissions regulations require ~90% reduction in NO_x from light- and heavy-duty diesel engines in the 2004-2010 timeframe. An active research and development focus for lean-burn NO_x control is in the area of NO_x adsorber catalysts. NO_x adsorber catalysts adsorb NO_x very efficiently in the form of a nitrate during lean operation, but must be regenerated periodically by way of a momentary exposure to a fuel-rich environment. This rich excursion causes the NO_x to desorb and then be converted by more conventional three-way catalysis to N_2. The momentary fuel-rich environment in the exhaust is created by injecting excess fuel into the cylinder or exhaust and/or throttling the intake air. The controls methodology for NO_x adsorbers is very complex, and there is no clear understanding of the regeneration mechanisms. NO_x regeneration is normally a 2-4 second event and must be completed approximately every 30-90 seconds (duration and interval depend on many factors; e.g., load, speed, and temperature).

While NO_x adsorbers are effective at adsorbing NO_x, they also have a high affinity for sulfur. As such, sulfur from the fuel and possibly engine lubricant (as SO_2) can adsorb to NO_x adsorbent sites (as sulfates). Similar to NO_x regeneration, sulfur removal (desulfation) also requires rich operation, but for several minutes, at much higher temperatures. Desulfation intervals are much longer, on the order of hundreds or thousands of miles, but the conditions are more difficult to achieve and are potentially harmful to the catalyst function. Nonetheless, desulfation must be accomplished periodically to maintain effective NO_x performance. There is much to be learned with regard to NO_x adsorber performance, durability, and sulfur tolerance.

Different strategies for introducing the excess fuel for regeneration can produce a wide variety of hydrocarbons and other species. One focus of this work is to examine the effectiveness of various regeneration strategies in light of the species formed and the adsorber formulation. Another focus is to examine the desulfation process and examine catalyst performance after numerous sulfation/desulfation cycles. Both regeneration and desulfation will be studied using advanced diagnostic tools.

Approach

A 1.7-L Mercedes common rail engine and a motoring dynamometer have been dedicated to this activity (Figure 1). The engine is equipped with an electronic engine control system that provides full bypass of the OEM (original equipment manufacturer) engine controller. The controller is capable of monitoring and controlling all the electronic devices associated with the engine (i.e., fuel injection timing/duration/number of injections,

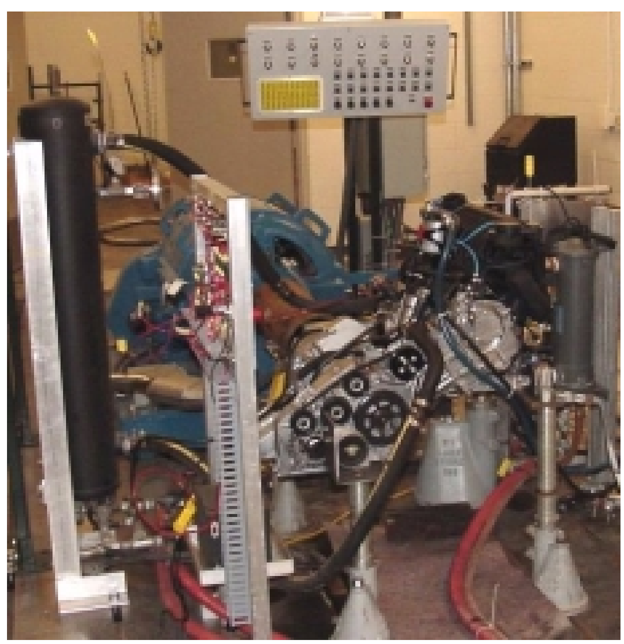

Figure 1. Experimental Setup Including Engine, Control System, Motoring Dyno, and Exhaust System

fuel rail pressure, turbo wastegate, electronic throttle, and electronic exhaust gas recirculation [EGR]).

Various regeneration strategies are being developed with the goal of introducing a broad range of species to the NO_x adsorber catalysts. Advanced tools such as H_2-SpaciMS and GC/MS are being used to characterize the species produced in the engine or in upstream catalysts. The H_2-SpaciMS will be used for both in-pipe and in-situ measurements within the catalyst monoliths. In addition, catalysts and exhaust species will be characterized after rapid sulfation and during desulfation. Some NO_x adsorber catalysts will be provided by Ford under a CRADA, while others will be provided by some Manufacturers of Emission Controls Association members. “Model” catalysts will also be characterized. Catalysts are being studied under quasi-steady conditions, i.e., steady load and speed but with periodic regeneration, as shown in Figure 2.

Finally, bench-scale work will be used to further characterize adsorber monoliths, wafers, and/or powders using our bench-scale reactor and the DRIFTS reactor. Results and characteristics of the engine experiments will be used to help define more meaningful bench scale studies. In some cases, the exact same catalyst formulation we are characterizing on the engine stand will also be examined in the bench studies.

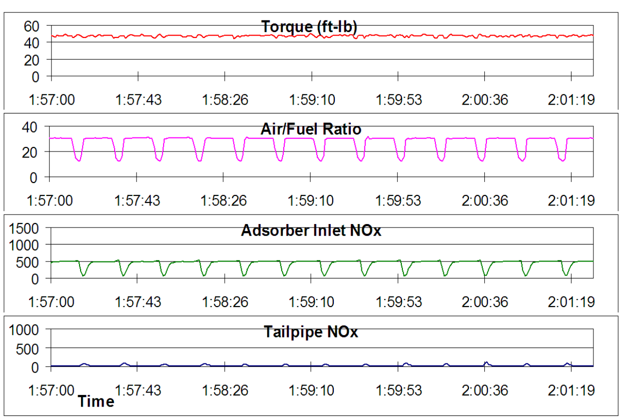

Figure 2. Quasi-Steady State NO_x Adsorber Regeneration Trace

Results

We have measured H_2, CO and speciated HC compounds for several regeneration strategies. Previous work has shown that H_2 and CO are excellent reductants for NO_x adsorber regeneration. Using ORNL’s H_2-SpaciMS, we have quantified the hydrogen in the exhaust with both time- and space-resolved measurements. Also, GC/MS determines the HC species that are generated in the engine or consumed in the catalysts. Using these unique instruments in conjunction with conventional gas analysis, we are developing a portfolio of regeneration strategies that will provide a wide range of NO_x adsorber inlet species to help understand the catalyst mechanisms.

The three strategies developed thus far include “Delayed and Extended Main” (DEM), “Post,” and “Extended Main” (EM). All three strategies use 15%-20% EGR during lean operation and intake throttling during the rich excursion to reduce airflow.

Figure 3 shows an oscilloscope trace of the DEM strategy. The main pulse width is increased to transition from lean to rich, and the start of injection (SOI) is retarded or delayed to maintain the torque level. (Increasing fuel would tend to increase torque, while retarding the injection timing would decrease torque.) EGR is cycled off during DEM regenerations to avoid intake fouling. The EM

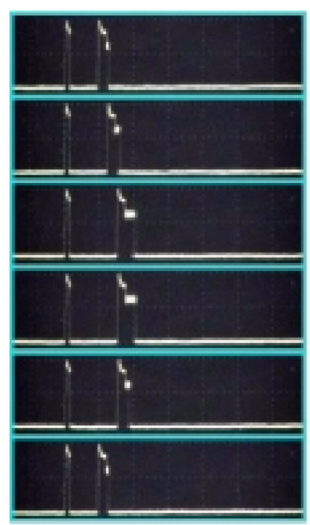

Figure 3. Oscilloscope Trace of "Delayed Extended Main" Regeneration Strategy

strategy uses a combination of larger main injection with increased EGR to transition from lean to rich.

The Post strategy is shown in Figure 4. An additional late cycle (post) injection is added to transition from lean to rich, and the main injection is modified to maintain torque. EGR is cycled off during Post regenerations to avoid intake fouling.

Figure 5 shows chromatograms for engine-out species and raw fuel species. The GC/MS separates HC species by molecular weight. The x-axis is time, and each peak on the chart is an individual compound. Note that there are several light HCs being produced during combustion that are not in the raw fuel. The extent of this fuel cracking in-cylinder can be tailored to some degree by the regeneration strategy.

H_2 and CO data collected during the Post injection timing sweep are shown in Figure 6. The average peak concentration for several regenerations is plotted as a function of injection angle (ATDC = after top dead center). Because H_2 and CO are excellent reductants, there is a need to understand how to control the amount of these species that is produced during regeneration, as well as to balance H_2 and CO production with PM formation and fuel penalty. We've shown that H_2 is produced in-cylinder, and we can quantify the amount of H_2 and CO produced by different strategies. Additionally, the H_2-SpaciMS allows us to measure intra-channel H_2, permitting determination of how the hydrogen is utilized, and in conjunction with the GC/MS information, what HC species are the best hydrogen precursors. It is also interesting to note that with comparable H_2 and CO levels, the Post, DEM, and EM fuel penalties were 5½ %, 4%, and 2% respectively.

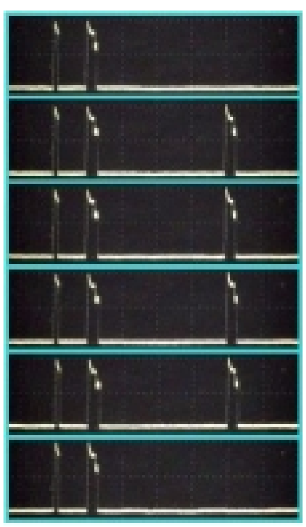

Figure 4. Oscilloscope Trace of "Post" Regeneration Strategy

Conclusions

- Regeneration strategies can be tuned to produce different HC pools and amounts of H_2 and CO.
- The CO to H_2 ratio is consistently near 2:1 for each regeneration strategy.

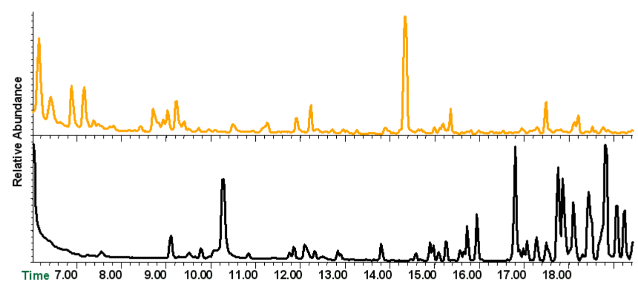

Figure 5. GC/MS Trace Showing Light Hydrocarbons Produced In-Cylinder

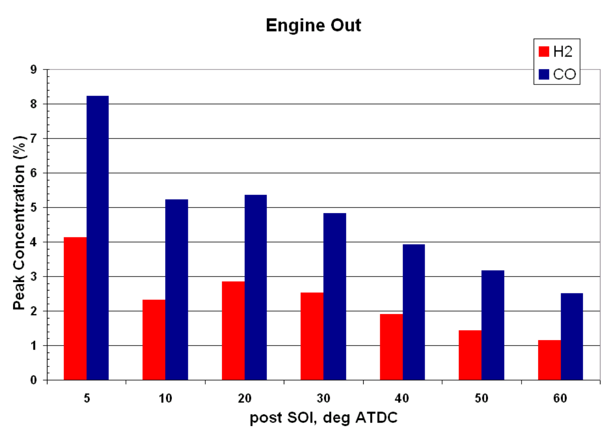

Figure 6. H_2 And CO Produced In-Cylinder for Post Timing Sweep

- Considerable fuel cracking occurs during in-cylinder combustion and can be quantified with GC/MS.
- Tradeoffs must be considered between a regeneration strategy's effectiveness and its impact on fuel consumption and PM.

III.B. Dedicated Sulfur Trap For Diesel Emission Control

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CRADA Partner: Caterpillar Inc.

Objectives

- Develop methodology providing quantification of SO_x uptake on solid adsorbents (both SO_2 and SO_3) by gas chromatography
- Quantify capacity of candidate adsorbers for SO_2 and SO_3, including materials requiring pre-oxidation catalyst as well as materials that adsorb SO_2 without need for pre-oxidation step
- Identify adsorber having 40 wt.% uptake capacity (as SO_2)

Approach

- Develop a chromatographic analysis for SO_2 and SO_3 using sulfur chemiluminescent detection
- Evaluate several types of adsorbers for SO_2 and SO_3 capacity
  - Conventional transition metal oxides in high surface area form, with and without added SO_2 oxidation catalyst
  - Oxide or mixed oxide materials having redox capacity
  - Copper as adsorption promoter (SO_2 oxidant) as possible additive
- Determine composition of spent adsorbers

Accomplishments

- The objectives for FY 2003 have been achieved on this project
- A chromatographic method has been developed for quantitative measurement of both SO_2 and SO_3 using sulfur chemiluminescent detection
- SO_2 and SO_3 capacities have been measured for several typical metal oxide adsorbents
- A novel metal oxide absorbent has been identified with capacity for SO_2 approaching 70 wt.%, operating over a broad temperature range, without use of a separate SO_2 oxidation catalyst

Future Directions

- Continue investigations of newly discovered class of metal oxide absorbents having high SO_2 capacity
  - Compositional and structural variations
  - Synthesis methods
- Measure SO_x absorption performance with simulated and real diesel emissions
- Initiate work to provide absorbents in monolith form
- Continue to evaluate other candidate materials

Introduction

The U.S. Environmental Protection Agency (EPA) has promulgated stringent on-road emission standards for heavy-duty diesel trucks that regulate the amount of NO_x, particulates, and non-methane hydrocarbons that can be emitted. Although sulfur oxides emissions are currently not regulated, their presence in the diesel exhaust adversely affects technologies that are being developed to handle the regulated emissions. As a result, a reduction in sulfur content in diesel fuel to 15 ppm has been mandated over this same time period. Even these low sulfur levels are anticipated to poison and cause long term deactivation of NO_x reduction catalysts currently under investigation. The development of a dedicated SO_x trap therefore can provide flexibility to the overall emissions control system.

Methods that propose to trap sulfur and periodically regenerate these traps on-vehicle suffer from system complexity, the requirement for two traps (one operating and one regenerating), and the possibility that generation of concentrated SO_x emissions evolved during the regeneration might be environmentally unacceptable. A more viable approach, which provides the basis of this project, is to develop a high capacity SO_x adsorber trap, in a self-contained canister, that can be replaced at periodic service intervals. The adsorbent can then be regenerated off-line in a facility dedicated to such an operation. Replacement of the adsorbent would be at approximately every 30,000 miles (oil change interval). A high capacity adsorbent minimizes the weight and volume required. A target has been set at minimum 40 wt.% SO_2 capacity for the adsorbent.

Approach

The sulfur emissions from diesel engines occur primarily as SO_2 (1). The removal of this SO_2 from the exhaust stream has been generally carried out using an oxidation catalyst (such as platinum) that first converts SO_2 to SO_3 (2). SO_3 is readily adsorbed on many metal oxides as the sulfate. Determination of the total capacity of an adsorbent for SO_3 has only been accomplished by post-analysis, since an analytical method for SO_3 detection has been unavailable. Without an analysis for SO_3, it is impossible to determine the breakthrough capacity of the adsorbent for SO_3, as well as how much SO_3 passes through the adsorber before it reaches saturation. Our approach has been to develop an analytical method for the detection of SO_3, enabling better understanding and quantification of the real-time performance of the adsorber. This approach is based on use of a gas chromatograph (GC) and a sulfur-specific detector to quantify SO_3 that is not taken up by the adsorber. With the analytical system in place, the approach will be to evaluate several types of metal oxide adsorbers for adsorption of both SO_2 and SO_3. Many metal oxides have significant adsorption capacity toward SO_3. However, to produce the SO_3 requires use of a precious metal oxidation catalyst. It is therefore desirable to identify adsorbers that have high capacity for SO_2 as well. This minimizes the cost of precious metal recovery from the spent adsorber and may also improve sulfur oxide recovery at low temperatures where the precious metal oxidation catalyst can only incompletely convert SO_2 to SO_3. Therefore, we have also explored metal oxides having redox properties, such as cerium oxide. Such materials can carry out both the oxidation of SO_2 and adsorption as the sulfate (3).

Results

Our initial work focused on quantification of SO_2. We were able to detect SO_2 with the sulfur chemiluminescent detection method readily, producing sharp peaks and near-linear response as a function of concentration (see Figure 1). Detection of SO_3 proved to be more challenging. This is because SO_3 is a highly reactive molecule, and it is readily adsorbed on the walls of tubing, fittings, and sample valves, so that frequently the SO_3 molecule never gets to the detector. We approached this problem through minimizing all tubing and fittings, heat tracing all lines, conditioning the system for long periods in SO_3, and using a short uncoated silica capillary to provide the separation of SO_2 from SO_3. We used a Pt/SiO_2 catalyst to oxidize SO_2 to SO_3 (the silica support was chosen to eliminate SO_3 adsorption on the oxidation catalyst itself). A broad peak is detected in addition to the SO_2 signal and corresponds to SO_3, as shown in Figure 2. We verified the presence of SO_3 by bubbling the gas exiting the catalyst bed through a solution containing barium nitrate. The formation of barium sulfate precipitate was confirmed by x-ray diffraction, and no barium sulfate precipitate formed when the SO_3 peak was absent from the chromatographic trace. By varying the conversion level of SO_2 to SO_3 and using our previous calibration for SO_2, we were able to determine the SO_3 concentration by difference. SO_3 detection was linear over the concentration range 80-230 ppm SO_3, with less linear response at lower SO_3 concentrations. However, the strong detection signal for SO_3 readily allows determination of SO_3 breakthrough capacity of the adsorbent.

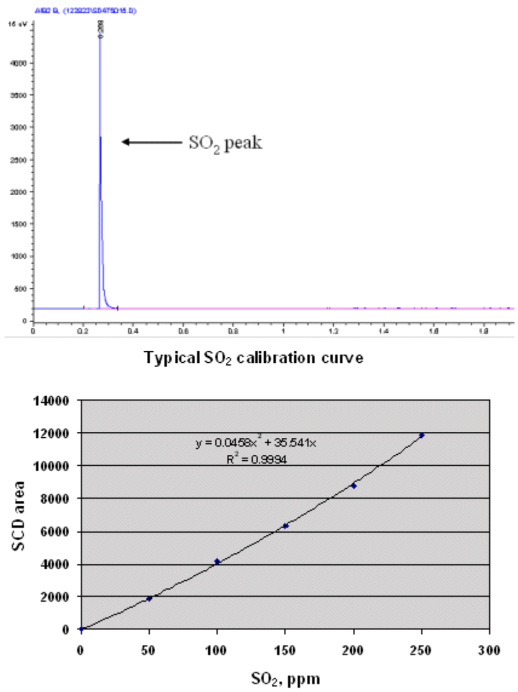

Figure 1. SO_2 signal using gas chromatography with sulfur chemiluminescent detection: (upper) GC output showing 250 ppm SO_2 signal; (lower) calibration curve showing near linearity of response with SO_2 concentration.

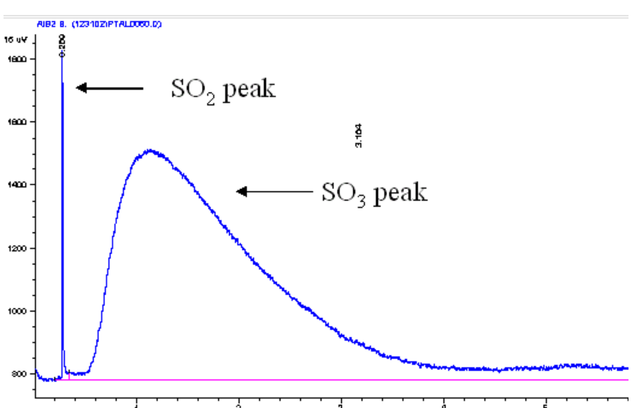

Figure 2. Gas chromatographic traces showing both SO_2 and SO_3 signals. The SO_3 signal is the large, broad signal following the sharp SO_2 peak.

For adsorption studies, we typically used a gas composition of air containing 250 ppm SO_2. This high concentration is not representative of actual emissions concentration but was employed to reduce the duration of the experiment to 1-2 days. The adsorption progress was monitored by sample injection every three minutes throughout the course of the experiment. Figure 3 shows the adsorption of SO_2 and SO_3 over gamma alumina (γ-Al_2O_3), a typical metal oxide adsorber. In the absence of the Pt/SiO_2 catalyst, uptake of SO_2 by alumina at 325°C is low, with breakthrough capacity of 1.0 wt.%. Upon addition of the oxidation catalyst, adsorption increased substantially to a breakthrough capacity at 325°C of 11 wt.%. A higher total capacity is achieved (see Figure 3), but it is unlikely that the target 40 wt.% SO_2 uptake can be achieved with this

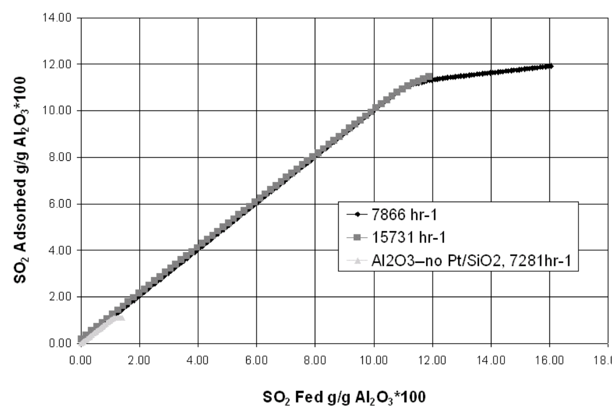

Figure 3. Comparative SO_2 and SO_3 adsorption by γ-Al_2O_3 at 325°C. The plot compares SO_2 taken up by the adsorbent with SO_2 fed to the adsorbent. Uptake is calculated on a SO_2 basis, regardless whether SO_2 or SO_3 is actually adsorbed. The legend provides the gas hourly space velocity (GHSV) employed. Breakthrough is observed when the initial uptake line departs from the 1:1 correspondence between SO_2 fed and adsorbed. The total capacity measured is given by the end point of the curve. For the SO_3 measurement, a Pt/SiO_2 catalyst was utilized to oxidize SO_2 to SO_3.

material, even at long periods of exposure. Figure 4 shows the adsorption of SO_2 over a zirconia-ceria-lanthana adsorbent. This material is capable of adsorbing SO_2 without the need for a separate SO_2 oxidation catalyst. The breakthrough and total capacity for SO_2 adsorption increases with increasing temperature, which reflects the activity of the adsorbent for SO_2 oxidation (facilitated by the ceria component in the adsorber) followed by SO_3 adsorption. At the highest adsorption temperature, SO_3 is detected in the effluent after the breakthrough point has been achieved, indicating that the sulfated material remains active for SO_2 oxidation at this temperature. The capacity of this material is insufficient to achieve the target value of 40 wt.% SO_2 uptake.

Figure 5 shows the uptake of SO_2 from 250-475°C over a novel metal oxide material that also has redox properties and therefore does not require a separate SO_2 oxidation catalyst. At 325°C and above, this material has a SO_2 breakthrough capacity of nearly 60 wt.% and a total SO_2 capacity of nearly 70 wt.%. The breakthrough point is lower at 250°C, but total capacity is still quite high with this material. Separate experiments have shown that the uptake capacity for SO_2 is unaffected by the presence of CO, NO, or H_2O. X-ray diffraction analysis shows that the material converts virtually completely to the metal sulfate. Based on this formation of a bulk sulfate, this process is better described as absorption rather than adsorption.

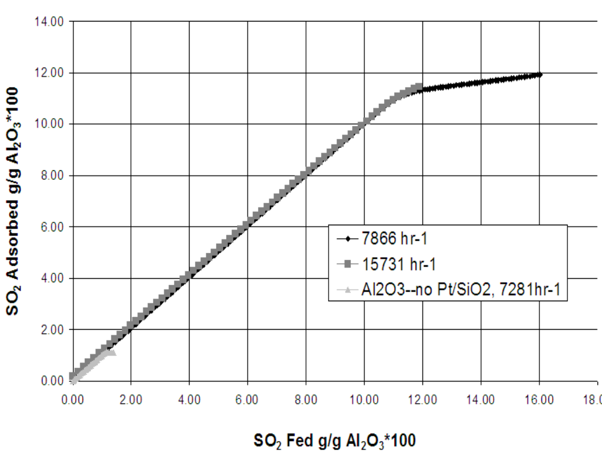

Figure 4. Adsorption of SO_2 by ZrO_2-CeO_2-La_2O_3 mixed oxide adsorber over a range of temperatures. Traces show increasing capacity with increasing temperature. No separate SO_2 oxidation catalyst was employed. At 475°C, SO_3 was observed exiting the adsorbent bed, indicating SO_2 oxidation capability of this material at elevated temperatures.

Conclusions

- A methodology has been developed for measurement of both SO_2 and SO_3 uptake by solid adsorbents using gas chromatography with sulfur chemiluminescent detection.
- SO_2 and SO_3 capacities have been measured for typical metal oxide adsorbents.
  - Gamma alumina, a typical metal oxide adsorber, has little capacity for SO_2 but moderate capacity (10-15 wt.%) for SO_3.
  - Cerium-zirconium mixed oxides exhibit modest capacity toward SO_2 without a separate oxidation catalyst, a result of their redox properties.
- A novel metal oxide absorbent has been identified with capacity for SO_2 approaching 70 wt.%.
  - Separate SO_2 oxidation catalyst is not required.
  - Capacity is maintained from 250-475°C.
  - Capacity is not affected by NO, CO, or H_2O.

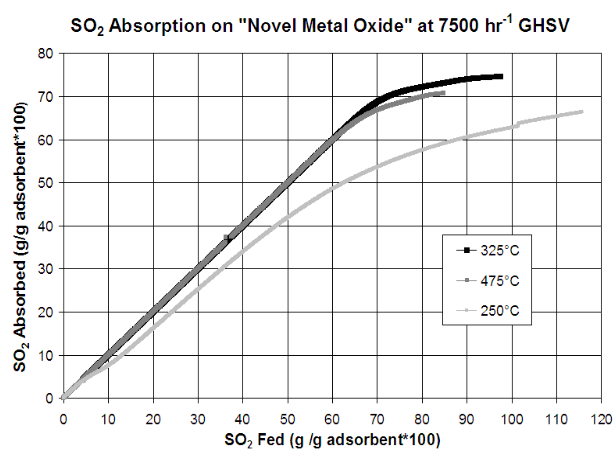

Figure 5. Effect of temperature (250-475°C) on SO_2 absorption behavior with novel metal oxide absorbent. No separate SO_2 oxidation catalyst was employed.

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1. D. L. King and Liyu Li, "Dedicated Sulfur Trap for Diesel Emissions Control", presented at DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation, Argonne National Labs, May 2003.

III.C. NO_x Adsorber Regeneration Phenomena in Heavy-Duty Applications (CRADA with International Truck and Engine Corporation)

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Industrial Partner:
Xinqun Gui, Shouxian Ren
International Truck and Engine Corporation

DOE Technology Development Manager: Gurpreet Singh

Objectives

- Develop NO_x adsorber regeneration and desulfation strategies for diesel aftertreatment systems, including effects of diesel oxidation catalysts and diesel particle filters.
- Improve understanding of role/fate of different exhaust hydrocarbons in advanced diesel aftertreatment systems for various reductant delivery systems. International Truck and Engine Corporation will focus on in-cylinder strategies while ORNL examines in-manifold and in-pipe strategies.

Approach

- NO_x adsorber regeneration strategies will be developed for several steady-state conditions. Electronic control of the intake throttle and exhaust gas recirculation (EGR) valve will be used to lower air:fuel ratio prior to reductant delivery.
- System performance will be measured for a variety of regeneration conditions. Hydrocarbon speciation and other advanced ORNL analytical tools will be used to improve understanding of the system.

Accomplishments

- Developed PC-based system for transient electronic control of intake throttle, EGR valve, wastegate, and reductant (fuel) delivery in-manifold (pre-turbo) and/or in-pipe (after turbo).
- Developed strategy for regenerating NO_x adsorber at NTE (not-to-exceed) rated load condition; measured hydrocarbon (HC) species entering and exiting NO_x adsorber for mild, moderate, and aggressive reductant oxidation schemes.
- Achieved 70% NO_x reduction at rated power, with acceptable CO and HC emissions.
- Confirmed degree of fuel cracking in oxidation catalysts; observed improved NO_x adsorber performance with certain HC species.
- Showed potential fuel savings with more aggressive in-pipe fuel reforming.

Future Directions

- Examine lower temperature conditions with in-pipe or in-manifold injection; speciate hydrocarbons at adsorber inlet and outlet; confirm HC sensitivity at lower temperatures.
- Develop desulfation strategies; measure H_2S, SO_2.
- Speciate hydrocarbons for in-cylinder injection strategies.

Introduction

Heavy-duty emissions standards call for a 90% reduction in NO_x and particulate emissions by 2010, as shown in Figure 1. These new regulations include certification at any and all engine operating conditions, whereby emissions may not exceed 150% of the emissions standard. This regulation is known as not-to-exceed (NTE) and includes steady operation at the rated load condition (or any engine condition). The NO_x adsorber catalyst is a promising technology to help meet these stringent new NO_x standards, but there are many open issues that must be resolved prior to commercialization. The (lean-burn) diesel engine does not readily run rich, but rich exhaust conditions are required to regenerate the NO_x adsorber catalyst. With more flexible fueling systems and other advanced engine control schemes, engineers are devising means to run these engines rich during "normal" operation to regenerate NO_x adsorber catalysts. However, the NTE points can include operating conditions at which rich engine operation could be detrimental to the engine and/or aftertreatment system. Producing these rich exhaust conditions is not only challenging, but doing so can also potentially cause durability problems, excessive fuel consumption, and excess particulate matter (PM), HC, and/or CO emissions.

Additionally, the NO_x adsorber catalyst is very sensitive to sulfur in the exhaust; therefore, effective sulfur management schemes must be developed that will ensure full useful life of the aftertreatment systems. This Cooperative Research and Development Agreement (CRADA) aims to help resolve some of the problems and unknowns with NO_x adsorber technology.

Approach and Results

International Truck and Engine will pursue late-cycle, in-cylinder injection of fuel to achieve rich exhaust conditions for adsorber regeneration. Complementary experiments at ORNL are focusing on in-manifold (pre-turbo) and in-pipe (after turbo) fuel injection. ORNL has developed a PC-based controller for transient electronic control of EGR valve position, intake throttle position, and actuation of fuel injectors in exhaust manifold and downstream pipe locations (Figure 2). Aftertreatment systems consisting of different diesel oxidation catalysts (DOCs) and NO_x adsorbers in conjunction with catalyzed diesel particle filters will be evaluated for a variety of regeneration strategies at steady-state conditions.

Experiments in FY 2003 focused on the rated load condition. A catalyzed diesel particulate filter (CDPF) was installed just upstream of the NO_x adsorber catalyst for all experiments, as shown in Figure 3. Mild, moderate, and aggressive oxidation conditions were examined by using the CDPF alone and in conjunction with a 2.5 liter or 5.0 liter oxidation catalyst, respectively. Gas chromatograph mass spectrometry (GC/MS) and Fourier transform

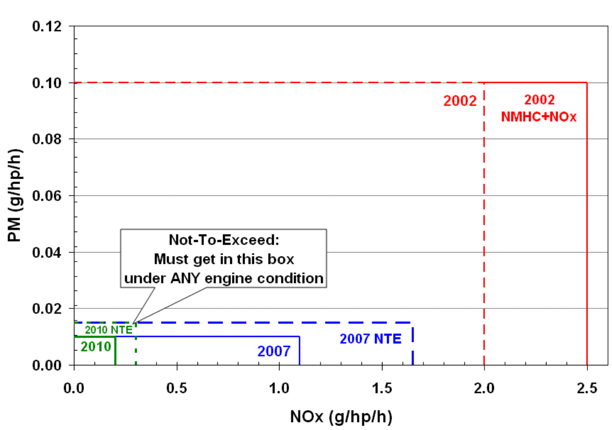

Figure 1. Impending Heavy-Duty Emissions Standards

Figure 2. Post-Engine Fuel Injection for NO_x Adsorber Regeneration

infrared (FTIR) spectroscopy were used to speciate the hydrocarbons entering and exiting the NO_x adsorber catalyst. Figure 4 shows the GC/MS data for a CDPF-only case and CDPF plus oxidation catalyst. Many light HC species are produced in the oxidation catalyst. By comparing the hydrocarbon species produced in the upstream catalysts and those exiting the NO_x adsorber catalyst, we can determine which species, if any, are preferentially utilized by the NO_x adsorber. Light alkenes are not present in raw diesel fuel, but are formed in the oxidation catalyst and readily utilized by the NO_x adsorber. Figure 5 shows the presence of high concentrations of pentenes and butenes at the adsorber inlet, and the very low concentrations at the adsorber outlet. Likewise, propene is formed in the oxidation catalyst and readily utilized. Mono-aromatics have also been found to be well-utilized by the NO_x adsorber, while branched alkanes are less preferred.

The benefits of fuel cracking in the diesel oxidation catalyst are clearly shown in Figure 6. The supplemental fuel fraction on the x-axis is the amount of fuel used for regeneration, expressed as a fraction of the fuel used for normal lean operation. Note that 10-20% less fuel is needed when an oxidation catalyst is added upstream of the CDPF to net a comparable level of NO_x reduction. Emissions of CO and HC for all experiments to date have been below the NTE limit for 2010.

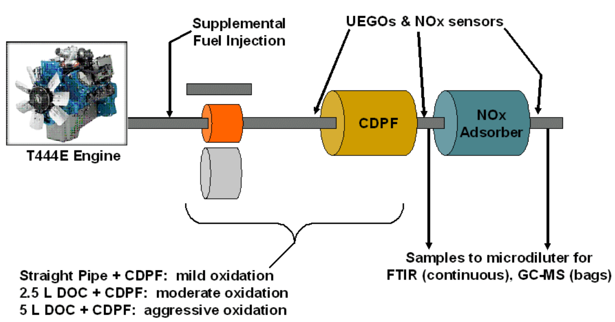

Figure 3. Aftertreatment System Schematic Diagram (UEGO = universal exhaust gas oxygen)

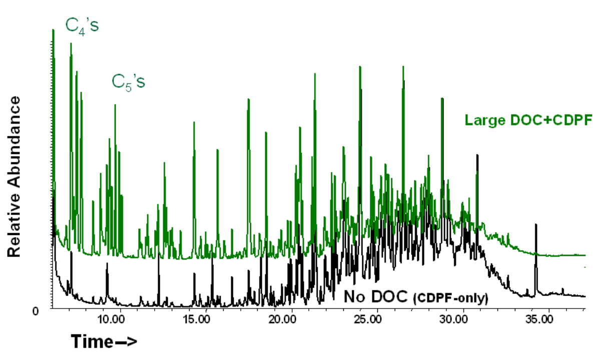

Figure 4. Gas Chromatogram Showing Extensive HC Cracking in DOC, as Compared to the CDPF-Only Case (NO_x Adsorber Inlet)

Conclusions

Cracking of raw fuel with diesel oxidation catalysts can provide the NO_x adsorber catalyst with HC species other than those in the raw fuel. Observations from experiments to date include the following:

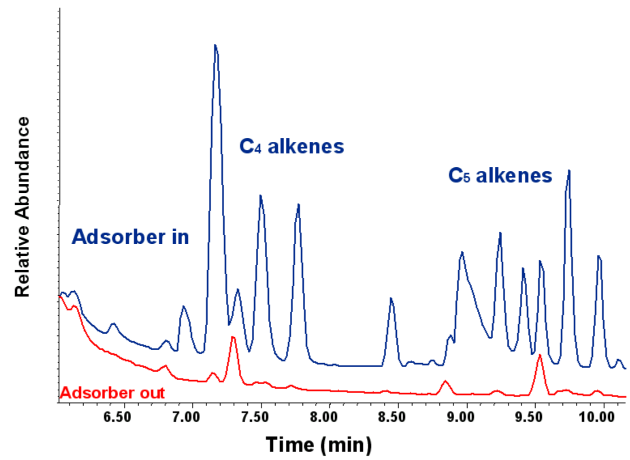

Figure 5. Gas Chromatogram Showing Light HCs at Adsorber Inlet and Outlet

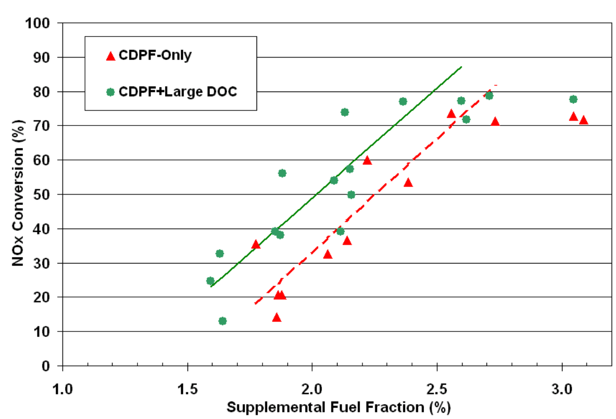

Figure 6. NO_x Conversion Versus Supplemental Fuel Fraction

- Providing the NO_x adsorber with preferred HC species can lower the fuel penalty associated with NO_x adsorber regeneration for a given level of NO_x reduction.
- Mono-aromatics and light alkenes have been found to be readily utilized by the NO_x adsorber catalyst.
- This work underscores the difficulty in meeting the heavy-duty not-to-exceed regulations. For 70% NO_x reduction to be adequate in the 2010 timeframe, engine-out NO_x emissions will have to be reduced to below 1.0 g NO_x/hp/h.

FY 2003 Publications/Presentations

1. West, Brian H., John Thomas, Mike Kass, John Storey, and Sam Lewis, "NO_x Adsorber Regeneration Phenomena in Heavy-Duty Applications," U.S. Department of Energy Advanced Combustion Engines Merit Review, May 13-15, 2003, Argonne, IL.

2. West, Brian H., John F. Thomas, Mike Kass, John Storey, and Sam Lewis, "NO_x Adsorber Regeneration Phenomena In Heavy Duty Applications: ORNL/ITEC CRADA," presented at 9th Diesel Engine Emissions Reduction Workshop, August 2003.

III.D. Cross-Cut Lean Exhaust Emission Reduction Simulation (CLEERS)

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Industrial Partner: DOE Diesel Crosscut Team
Website: www.cleers.org

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Objectives

- Promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems;
- Promote development of performance models for emissions control components such as exhaust manifolds, catalytic reactors, and sensors;
- Provide a consistent framework for sharing information about emissions control technologies; and
- Identify R&D needs and priorities.

Approach

- Coordinate with the CLEERS subcommittee to plan and implement public topical workshops on key issues in emissions control simulation.
- Assist in coordinating focused technical discussion groups composed of DOE Diesel Crosscut members.
- Maintain a website for the CLEERS activity that will include announcements for upcoming workshops, summaries and presentations from past workshops, and data libraries and model information for the performance of emission control technologies and systems. Some information on the website will be public, but controlled access to restricted data will also be established for crosscut team members and members of technical focus groups.
- Coordinate among Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratories (SNL) to provide experimental and analytical input to the focus group discussions and CLEERS database.

Accomplishments

- Provided summary report and recommendations based on the results of the public CLEERS workshops in 2001 and 2002 to DOE and the Diesel Crosscut Team.
- Restructured the CLEERS workshops plan to create discussion focus groups composed of Crosscut Team members and public workshops at a reduced frequency (e.g., once or twice annually).
- Defined the Lean NO_x Trap (LNT) and Diesel Particulate Filter (DPF) Focus Group members and began monthly web meetings.
- Updated and expanded the CLEERS database of experimental aftertreatment and engine performance data and fundamental physical properties of aftertreatment materials.
- Initiated LNT experiments at ORNL to develop key benchmark rate and performance data needed for the LNT Focus Group discussions.

- Initiated kinetics studies at SNL and PNNL to develop kinetic understanding needed by the LNT and DPF Focus Groups.

Future Directions

- Provide leadership and assistance to the LNT and DPF Focus Groups and assist in the redefinition of the Selective Catalytic Reduction (SCR) Group.
- Provide data and kinetics analysis benchmarks for the LNT and DPF Groups.
- Continue expanding the CLEERS database on LNT, DPF, and SCR kinetics and critical properties.
- Coordinate future CLEERS public workshops.
- Facilitate more direct interaction between original equipment manufacturers (OEMs) and emissions controls suppliers.

Introduction

The CLEERS activity is carried out under the auspices of the DOE Diesel Crosscut Team and is intended to provide the following benefits:

- A framework for collaboration among OEMs, emission controls suppliers, national labs, and universities
- A collective forum for identifying critical technology bottlenecks and demonstrating simulation value
- A mechanism for sharing non-proprietary basic data/understanding among the community
- A mechanism for direct industry feedback to DOE R&D
- A definition of common technical terminology/ standards to facilitate communication (e.g., between researchers, between OEMs and suppliers)

CLEERS is not intended as a system for funding the development of simulation software, but rather as a way for participants to develop improved understanding of the physics and chemistry of aftertreatment devices and engine-aftertreatment systems that can be utilized in their own in-house or commercial simulation codes.

The initial stages of CLEERS focused on the organization of public workshops that could be used to better define the collective sense of priorities among the OEMs, suppliers, national labs, and universities that should be addressed for improving performance predictions for advanced emissions controls. Each workshop had 70-80 attendees that included representatives from OEMs, component/ software suppliers, labs, and academia. The format involved invited and contributed presentations, review panel discussions, and wrap-up/conclusion discussions, and the results were summarized in detailed reports to the Diesel Crosscut Team.

The initial workshop in May of 2001 identified that the greatest needs for collaborative work on simulation development were in the areas of lean NO_x traps (LNTs), diesel particulate filters (DPFs), and urea/ammonia selective catalytic reduction (SCR). As a result, subsequent workshops were held in 2001 and 2002 on LNTs, DPFs, and urea and non-urea SCR. These workshops identified the following critical priorities for each technology area:

<u>LNTs</u>

- Aging/sulfur poisoning
- NO_x reduction/adsorption kinetics
- Desulfation chemistry (including the heat and mass transfer effects)

<u>DPFs</u>

- Particle morphology, oxidation characteristics
- Particulate matter spatial distribution and impact on maximum temperature
- Ash creation, composition, and transport vs. operation
- Gas emissions during regeneration

<u>SCR</u>

- Non-urea
  - Non-Pt catalyst additives

- Non-standard hydrocarbon reductants
- NO_x and reductant storage
- Engine-out speciation
- Fuel reformer kinetics

- Urea/ammonia
- Ammonia storage
- Urea decomposition
- Catalyst degradation
- Effects of NO/NO_2 split
- NO_x reaction pathways, rate

These workshops also identified several crosscutting issues that are common to all the emissions control technologies. These issues included:

- Global kinetic rates for the heterogeneous catalytic reactions of all key emissions species;
- Single-step (elementary) reaction rate kinetics;
- Separation of chemical kinetics from physio-chemical solid phase processes;
- Homogeneous gas phase kinetics for reactions in and before catalytic reactor components;
- Controlled lab measurements of both homogeneous and heterogeneous kinetics;
- Accurate transient engine-out data with 1 s resolution;
- Adaptive computation of multi-step kinetic rates; and
- Standard software/data interfacing.

Approach and Results

In the fall of 2002, a plan was developed for restructuring the CLEERS workshops plan into regular meetings of three highly targeted Focus Groups. The three Focus Groups target lean NO_x adsorbers/traps, diesel particulate filters, and urea/ammonia selective catalytic reduction, respectively, and are organized based on the specific high needs identified in the public workshops held in FY 2001 and 2002. Discussion topics are selected from the list of prioritized simulation and modeling needs identified in these workshops. A description of the Focus Groups is also available on the CLEERS website (www.cleers.org). Co-leaders and initial members of the LNT and DPF groups have been identified. The LNT group began meeting in March, and the DPF group began in June. Both groups use a phone conference/web meeting format for the monthly meetings. Summary reports of these meetings are provided to the Diesel Crosscut Team.

Public CLEERS workshops continue to be held but at a reduced frequency from FY 2001 and 2002 (e.g., once or twice annually). The next planned public workshop will be held in September 2003.

The LNT Focus Group (Dick Blint and Stuart Daw, co-leaders) has provided prototype experience for the other groups. Group members include Kevin Sisken (Detroit Diesel), Neal Currier (Cummins), Ed Jobson (Volvo-Mack), Josh Driscoll (Caterpillar), John Hoard (Ford) and Tony McDaniel (SNL). Co-leaders for the DPF Group are Cornelius Opris (Caterpillar) and George Muntean (PNNL). Regular members are Alex Yezerets (Cummins), Kevin Sisken (Detroit Diesel), Yongsheng He (General Motors), Chuck Salter (Mack), Kalayana Chakravarthy (ORNL) and Chris Rutland (University of Wisconsin). There is still some uncertainty regarding the scope and membership of the SCR group, and this is being addressed in discussions with the Crosscut Team and the CLEERS committee.

The CLEERS database has been considerably expanded and the search capabilities enhanced. There are nine data categories and nine technology areas covered. The typical content for each dataset includes:

- Experimental setup information;
- Public information for catalyst materials and/or engines used;
- A summary of relevant operating parameters; and
- Transient and/or steady-state measurements of relevant performance variables in text and/or Excel file format.

Examples are provided to illustrate the data requirements. There is currently a large backlog of experimental LNT data being processed.

In mid-FY 2003, additional funding became available for experimental and modeling work in direct support of CLEERS activities. Specifically, ORNL, PNNL, and SNL were funded to collect experimental data and perform kinetics modeling that would provide direct input to the technical questions under discussion by the LNT and DPF Focus Groups. The ORNL LNT bench flow experiments began in February, but the work at PNNL on DPF modeling and at SNL on LNT kinetics was delayed until June. Key observations from the ORNL experiments so far include the following:

- Evidence suggests there are multiple types of sorbent sites where the nitrates are formed. Some of these sites appear less stable than others and may contribute disproportionately to losses of unreduced NO_x during regeneration.
- Many of the features of LNT function during lean phase capture appear to be consistent with the classical behavior of sorbers used in the chemical industry. This is expected to simplify analysis and provide a convenient way for characterizing data that has not been utilized so far.
- One key lean phase feature is the formation of concentration fronts or waves that propagate down the axis of the LNT. The overall performance of the device depends on the relative speed and dispersion of these waves.

Example characteristics of these concentration waves are illustrated in Figure 1, which depicts the separation of the NO and NO_2 fronts as they move through the LNT at different speeds. We observe that at low temperature, NO_2 breaks through more slowly than NO, probably reflecting the fact that NO_2 is the primary form of NO_x that is formed from nitrates, and NO must first be converted to NO_2 before it can be stored. Under these low temperature conditions, higher Pt loading increases the effective storage capacity (slows the wave speed), suggesting that Pt is important for NO oxidation. At higher temperature, the NO/NO_2 differences and effect of Pt loading appear to be much diminished. Thus, it should be possible to use less Pt without suffering much of a performance penalty as long as the temperature is sufficiently high. The optimal capacity appears to be between 300° and 400°C, where the breakthrough wave speed is minimum.

Many such characterizations of LNT sorbent materials are planned for the ORNL experiments, both with model materials (i.e., specially manufactured, non-proprietary sorbents) as well as commercial materials supplied by Manufacturers of

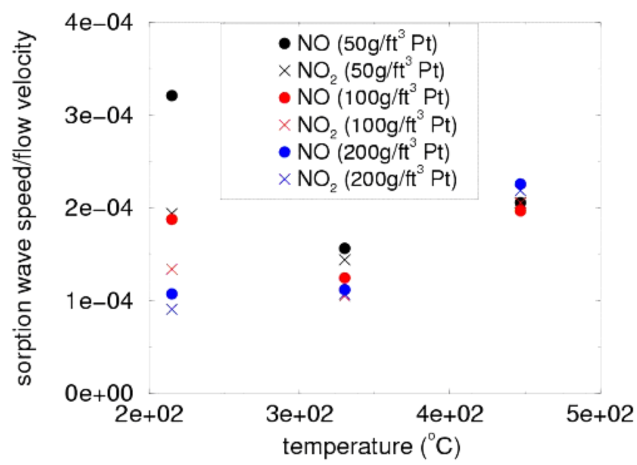

Figure 1. Breakthrough wave speed for a sorbent composed of $Pt/K/Al_2O_3$ with various Pt loadings. The simulated lean exhaust gas at the inlet contains 300 ppm NO, 12% O_2, 5% H_2O, 5% CO_2, N_2 (balance). Breakthrough at the exit was measured after initially removing all nitrate from the sample monolith core with exposure to simulated rich exhaust containing hydrogen and then switching to the simulated lean exhaust.

Emissions Controls Association (MECA). The intention is to produce benchmark data that can be used to resolve basic but critical questions of the functioning of LNT devices and to improve simulations of performance and durability.

Conclusions

The CLEERS sponsored public workshops have helped to better identify the high priority needs to development of improved simulation capabilities for emissions controls of advanced high-efficiency engines. These priorities have led to the formation of focused discussion groups among the DOE Diesel Crosscut members that are facilitating the solution of common simulation problems among the community. The focus groups are also providing a direct mechanism for better coordinating efforts among national labs and industry.

FY 2003 Publications/Presentations

1. C. S. Daw, K. E. Lenox, V. K. Chakravarthy, W. Epling, G. Campbell, "Phenomenology of NO_x Adsorber Catalysts, Part 1: Lean-Phase

Operation," Chemical Reaction Engineering IX, Engineering Conferences International, Quebec City, Canada, June 29-July 4, 2003.

2. C. S. Daw, Kalyana Chakravarthy & K.E. Lenox, "A Simple Model for Lean NO_x Adsorber Catalysts," Third joint meeting of the section of the Combustion Institute, Chicago, March 16-19, 2003.

III.E. Advanced CIDI Emission Control System Development

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DOE Technology Development Manager: Ken Howden

Subcontractors:
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ExxonMobil Research and Engineering Company (EMRE), Paulsboro, NJ

Objectives

Develop and demonstrate a highly efficient exhaust emission control system for light-duty CIDI engines to meet 2007 Tier 2 emissions standards (0.07 g/mi NO_x, 0.01 g/mi PM) with minimal fuel economy penalty and 120,000 miles of durability. Tier 2 standards require 90+% NO_x and particulate matter (PM) conversion.

Approach

- Establish baseline emission control system.
- Conduct parallel engine dynamometer and vehicle testing.
- Continue research to identify the most active and durable catalysts and PM filters.
- Continue research to determine the most selective and durable exhaust gas sensors.
- Use a very low sulfur diesel fuel to represent U.S. fuel of 2007 and beyond.
- Assist in the development of a feasible aqueous urea delivery system for diesel vehicles.

Accomplishments

- Second year of the project was completed.
- Engine-out emissions data were collected on a Ford F-250 truck equipped with a mid-sized diesel prototype engine. The baseline emission control system using SCR (selective catalytic reduction) and aqueous urea injection achieved about 80% NO_x conversion on the FTP cycle and 90+% NO_x conversion during the hot, stabilized portion of the test (Phase 2).
- Hydrocarbon (HC) conversion on the FTP improved from 90% to 96% after the oxidation catalyst volume was enlarged and the precious metal loading was increased. The ratio of NO_2/NO_x entering the SCR catalyst improved from about 30% to almost 60%.
- High NO_x and HC conversions were maintained on the F-250 after the diesel fuel was switched from Swedish-type fuel to U.S.-type, project fuel produced by ExxonMobil. Both fuels were very low in sulfur but had significantly different cetane and aromatic content. The engine calibration was modified to partially compensate for the higher engine-out HC and NO_x emissions resulting from the lower cetane and higher aromatic content of the project fuel.
- Another vehicle with a similar exhaust system to the F-250 maintained very high NO_x conversion after 22,500 miles of on-the-road driving.
- Automatic regeneration of a catalyzed diesel particulate filter (CDPF) under both city and highway driving conditions was successfully completed at FEV.

- An ammonia sensor was obtained and tested onboard the F-250 with favorable results.
- Developed onboard diagnostics for identifying possible system malfunctions and improved the adaptiveness and robustness of the control model.
- The negative impact of HC and sulfur on SCR NO_x conversion and the conditions required to regain high NO_x conversion were quantified in the laboratory at Ford.
- Improved second generation EMRE SCR catalysts to achieve high (90%+) degreened conversion at low temperatures over a broad range of NO_x feed gas compositions.
- EMC-9 showed improved hydrothermal durability compared to initial EMRE high activity SCR catalysts.
- Successful discussions took place between EMRE and a major nozzle supplier on modifications to the Ford-designed, diesel/urea co-fueling nozzle for improved durability and reliability.
- A major dispenser manufacturer provided equipment for an EMRE co-fueling demonstration.

Future Directions

- Develop rapid warm-up strategy for cold-start to achieve 90+% FTP-75 NO_x conversion.
- Integrate NO_x and PM control functions into one emission control system.
- Develop aging cycle to be used in the durability phase of the program, and select final catalyst formulations to be used in durability phase.
- Continue vehicle testing of NO_x and ammonia sensors, testing for reproducibility and durability.
- Continue laboratory testing of NO_x sensors, with the aim at developing a better model of their response.
- Continue laboratory testing/development of ammonia sensing technologies and determination of their value in an urea/SCR diesel aftertreatment system.
- Improve sulfur durability of EMRE SCR catalysts.
- Continue to investigate concepts for onboard delivery of aqueous urea and its specifications. Diesel/ urea dispenser and nozzle will be tested under both summer and winter climate conditions.

Introduction

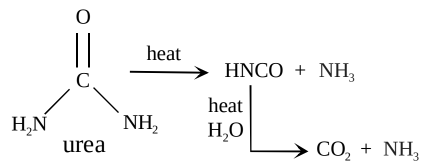
Reducing particulate matter (PM) and NO_x emissions are primary concerns for diesel vehicles required to meet 2007 Federal Tier 2 and California LEV II emission standards (Table 1). These standards represent a 90-95% reduction from current Federal Tier 1 diesel standards.

Table 1. 2007 Emission Standards (passenger cars and light-duty vehicles)

	50k mi		120k mi	
Standard (g/mi)	NO_x	PM	NO_x	PM
LEV II	0.05	-	0.07	0.01
Tier 2, Bin 5	0.05	-	0.07	0.01

The high oxygen content of diesel exhaust makes onboard NO_x control complicated. The available technologies for high NO_x reduction in lean environments include selective catalytic reduction (SCR), in which NO_x is continuously removed through active reductant injection over a catalyst, and lean NO_x traps (LNT), which are materials that adsorb NO_x under lean conditions and require periodic regeneration under rich conditions to reduce NO_x to N_2. The technology with the most potential to achieve 90+% NO_x conversion with minimal or no fuel economy penalty is SCR with an ammonia-based reductant such as aqueous urea. Ammonia-SCR has been used extensively for stationary source NO_x control [1]. Its high selectivity and reactivity with NO_x in high O_2 environments makes SCR attractive for diesel vehicle use. The main reactions are as follows:

urea decomposition:



NO_x reduction:

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$$
$$2NH_3 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O$$

Compared to ammonia, aqueous urea is much safer for onboard vehicle use. Feasibility has been proven by past work at Ford [2], Volkswagen [3] and Mack Truck [4].

Control of diesel PM is accomplished with a periodically regenerated ceramic filter. The filter may be washcoated with precious metal to help oxidize HC and collected soot. A diesel oxidation catalyst (DOC) may also be placed upstream of the filter to further aid in filter regeneration.

Approach

At Ford, supplier catalysts are tested in a laboratory flow reactor and ranked for fresh and aged conversion levels. SCR catalyst formulations are developed at EMRE, and the most durable are sent to Ford for evaluation. Full-size monoliths of the most promising formulations are installed in the engine dynamometer and onboard the vehicle and tested in parallel. Modeling is used to help choose the catalyst configuration with the highest potential to meet the emission standards. Since cold-start plays an important role in emission control system functionality, special emphasis is placed on rapid warm-up strategies. Appropriate exhaust gas sensors and control strategies are used for durable system function. Schemes for delivery of aqueous urea to diesel vehicles are explored.

Results

A 14,000 gallon batch of ultra low sulfur (<15 ppm S) diesel was manufactured for use in the optimization and long term durability portions of the project. Fuel properties were selected to approximate the product quality anticipated in the 2006 market. The resultant fuel also meets the EPA certification fuel standards for 2007.

An F-250 truck with a mid-size prototype diesel engine was tested with an oxidation catalyst, aqueous urea injection system and a base metal/zeolite SCR catalyst. A maximum NO_x conversion over the FTP-75 of about 65% was achieved using a baseline aqueous urea injection strategy in conjunction with a NO_x sensor. Results indicated that the injection system needed to more effectively distribute the reductant over the entire SCR catalyst. Mixing devices were added to the exhaust system that improved cycle NO_x conversion to over 80%. Lengthening the entrance cone to the SCR catalyst was also found to be beneficial. The oxidation catalyst upstream of the SCR catalyst was enlarged, and the precious metal loading was increased. This resulted in 96% total hydrocarbon (THC) conversion over the cycle and a favorable average NO_2/NO_x ratio entering the SCR catalyst of almost 60%. The final exhaust system is shown in Figure 1.

NO_x conversion could not be improved further due to the cold-start. NO_x performance was modeled with and without rapid warm-up, as shown in Figure 2. The SCR catalyst must be warmed to 200°C during the first minute of the test cycle to achieve 90+% cycle NO_x reduction.

The negative impact of HC on SCR NO_x performance was investigated in a laboratory flow reactor using the primary base metal/zeolite catalyst formulation. A mixture of HC containing an alkene, a long-chain alkane and an aromatic was fed into the flow reactor while the catalyst was converting NO_x

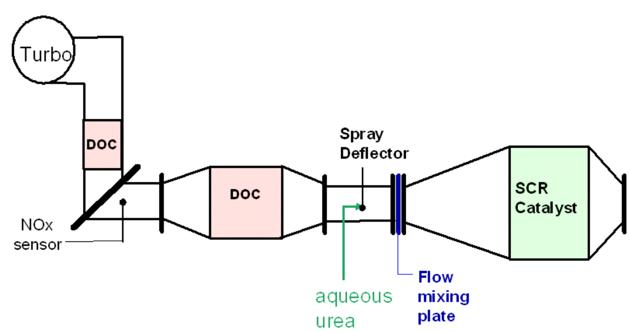


Figure 1. Exhaust System Schematic of the F-250 Vehicle

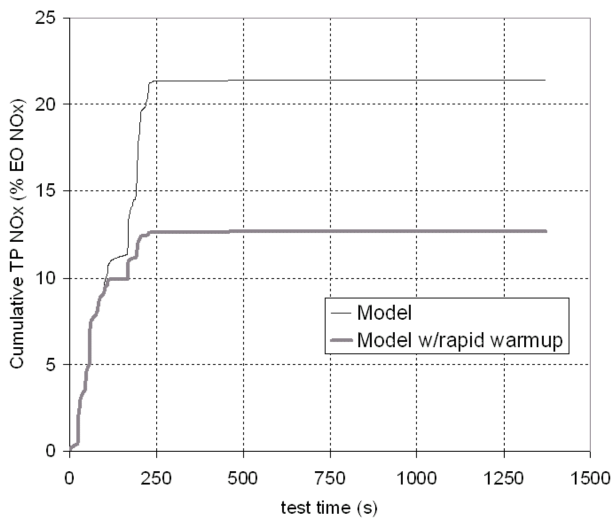


Figure 2. Modeling Results of Urea SCR NO_x Performance on the FTP-75

with NH_3 in simulated diesel exhaust gas. An inlet NO_2/NO_x ratio of 20% was used. The NO_x conversion was allowed to degrade from 90+% to 50% at 250°C and 30,000 h^{-1}, after which the temperature was raised. It was found that at least 425°C was required to regain high NO_x conversion at 250°C.

The negative impact of sulfur on SCR NO_x performance was investigated separately under similar test conditions to the HC experiments with the primary catalyst formulation. A catalyst core was exposed to enough flowing SO_3 to represent 120k miles assuming a diesel fuel sulfur level of 10 ppm. Low temperature NO_x conversion degraded significantly but could be completely regained by exposing the catalyst to 650°C under lean conditions. Testing will be conducted to confirm if a lower temperature is adequate.

At EMRE, a catalyst formulation was identified that had very good hydrothermal stability but poor resistance to sulfur, especially under NO-rich conditions. Work continued to identify variations in the formulation to improve the sulfur resistance.

The gas response and sensitivity of several types of ammonia sensors were studied. One sensor, believed to be the most reliable to date, was tested on the F-250 with favorable results. Laboratory testing of multiple NO_x sensors in dry conditions demonstrated that their sensitivity to ammonia was a complex function of temperature, gas constituents and gas concentration. However, the anomalous effects were greatly reduced when water was present. These tests also demonstrated that the sensitivity to NO_x was lowered by roughly 10% in the presence of 100 ppm of ammonia, and vice-versa. Vehicle testing of the NO_x sensors demonstrated some small cross-sensitivity to oxygen.

Work on the engine dynamometer included improved urea spray distribution, FTP-75 cycle development and automated CDPF regeneration. Using a spray target, a steady-state NO_x conversion of 98% was achieved with no ammonia slip. Simulation of the FTP-75 was successful. Oxidation catalyst volume to be used upstream of a CDPF was optimized. A CDPF was fully instrumented with thermocouples to determine internal temperature distribution during regeneration. The filter can was modified to allow for weighing of the filter before and after regeneration. Automated regeneration was investigated under both city and highway driving conditions.

Work on urea infrastructure has focused on evaluating urea solutions for the optimum mixture and discussing the prototype nozzle designs with a major nozzle manufacturer. Nozzles must be durable and ensure no urea contamination of diesel fuel. A key dispenser manufacturer has offered assistance on the urea co-fueling equipment.

Conclusions

Rapid warm-up of the exhaust system during a cold-start is key to achieving 90+% NO_x conversions required to meet the light-duty Tier 2 Bin 5 standards. Further optimization of the aqueous urea injection strategy and hardware is required to allow full utilization of the reductant by the SCR catalyst, thus improving NO_x conversion. Continued research on NO_x and NH_3 sensors is needed for better selectivity and durability.

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3. A.K. Prasad, P.I. Gouma, D.J. Kubinski, J.H. Visser, R.E. Soltis and P.J. Schmitz, "Reactively Sputtered MoO_3 Films for Ammonia Sensing," Thin Solid Films, 436 (1) 2003, pp 46-51. Also presented at the 2002 Semiconducting Gas Sensor Conference, Ustron, Poland (September), and the 2003 American Ceramic Society Meeting, Nashville (April).

4. A.K. Prasad, D.J. Kubinski and P.I. Gouma, "Comparison of Sol-gel and Ion Beam Deposited MoO_3 Thin Film Gas Sensors for Selective Ammonia Detection," Sensors and Actuators B: Chemical, 93 (1-3) 2003, pp 25-30. Also presented at the 2002 International Meeting on Chemical Sensors, Boston (July).

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III.F. Development of Improved Selective Catalytic Reduction Catalysts

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CRADA Partners: Low Emissions Technologies Research and Development Partnership
(Member Companies: DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation)

DOE Technology Development Manager: Kevin C. Stork

Objectives

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

Approach

- Discover and develop new catalyst materials for reducing NO_x emissions in lean-burn exhaust environments by greater than 90% in the 200 to 400°C temperature range using ammonia as a reductant. Materials for study include:
  - Hydrous metal oxide (HMO) or other oxide-supported catalysts and
  - Microporous materials-supported catalysts, including zeolites.
- Using identical protocols, compare and contrast the efficacy of these two catalyst types.
- Evaluate new catalyst materials in both bulk powder and monolith forms, including short-term durability testing under hydrothermal conditions and in the presence of SO_2/SO_3.
- Scale up synthesis and processing of promising catalyst formulations to enable fabrication of prototype catalytic converters for CIDI engine dynamometer testing.
- Transfer technology of the most promising catalyst formulations and processes to designated catalyst suppliers via the Low Emissions Technologies Research and Development Partnership (LEP).
- Evaluate performance of small monoliths (with bench flow reactors) through full-scale catalyst bricks with engine laboratory facilities at ORNL. Use microscopy capabilities as appropriate to evaluate catalyst structure on a monolith both before and after exposure to engine exhaust.

Accomplishments

- LANL implemented new, more stringent catalyst screening protocols (higher space velocities, testing as a function of NO/NO_2, more realistic accelerated aging with SO_3 vs. SO_2).
- LANL screened 26 new monolith catalysts and 4 powder catalysts; 60% of these catalysts have passed the criteria for all of the activity and short-term aging protocols.
- LANL catalyst screening efforts and research on NO_x reduction mechanisms have led to the discovery of ‘hybrid’ oxidizer-SCR (selective catalytic reduction) monolith catalysts having remarkable low temperature NO_x activity.
- LANL has filed an invention disclosure on the new ‘hybrid’ catalyst systems.
- LANL has completed preliminary scoping work on zeolite-catalyzed decomposition of urea.
- LANL had one journal paper published, one patent issued, and one patent disclosure filed on lean NO_x catalysts.
- SNL tested over 153 new materials (powder samples, NO_2:NO_x = 50%, space velocity = 30,000 h^{-1})
  - 43 met activity criteria: >90% NO_x conversion at 200 - 400°C
  - 17 (of 27 tested) passed short-term durability test
  - 6 (of 9 tested) passed SO_2/SO_3 aging test.
- SNL monolith tested for hydrothermal aging and SO_2 tolerance.
- SNL monolith tested at Ford Motor Company.
- SNL catalysts that passed all criteria in LEP staged acceptance protocol were tested across a range of $NO:NO_2$ ratios.
- New catalyst developed at SNL shown to have decreased sensitivity to $NO:NO_2$ ratio.
- New catalyst shown to have high tolerance to model hydrocarbons under SCR conditions.
- Monolith development and optimization underway.
- SNL has filed a technical advance for new catalyst materials. Patent application submitted.
- SNL switched catalyst testing system to include testing powders at higher space velocities.
- ORNL has begun engine-based experiments to study urea decomposition in the exhaust with a particular emphasis on the low-temperature regime where urea decomposition can be incomplete.

Future Directions

- LANL and SNL will continue to synthesize, characterize, and test new catalyst compositions as ammonia SCR catalysts.
- LANL will proceed with a more detailed exploration of ‘hybrid’ catalyst concepts and explore ‘dual-bed’ catalyst systems.
- LANL will explore in more detail the fate of the urea residues that remain after contact with zeolite catalysts at high temperatures.
- LANL will initiate transient studies of the effects of hydrocarbons and CO adsorption at low temperatures over the most promising catalysts.
- SNL will continue to optimize most promising catalysts and develop monolith fabrication techniques.
- SNL hydrothermal and sulfur durability tests on monoliths will be continued.
- SNL will continue to give samples to CRADA partners for comparison testing.
- SNL will continue to investigate the effect of hydrocarbons on deNO_x performance.
- LANL and SNL will transfer the most promising candidates to suppliers via LEP.
- ORNL will complete the study of urea decomposition and will issue a report to the partners on the findings.
- ORNL will also provide microstructural evaluations with electron microscopy as required for SNL and LANL catalyst materials.

Introduction

This multi-partner effort has been continued under the sponsorship of the Office of FreedomCAR and Vehicle Technologies and involves separate CRADAs between three national laboratories (Los Alamos National Laboratory [LANL], Oak Ridge National Laboratory [ORNL], and Sandia National Laboratories [SNL]) and the Low Emissions Technologies Research and Development Partnership (LEP, composed of DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation). Each of these CRADAs is scheduled to run through 2003. The project addresses reduction of CIDI engine NO_x emissions using exhaust aftertreatment – identified as one of the key enabling technologies for CIDI engine success. The overall CRADA efforts are currently focused on the development of urea/ammonia selective catalytic reduction (SCR) processes for reducing NO_x emissions, specifically targeting the selection of appropriate catalyst materials to meet the exhaust aftertreatment needs of light- and medium-duty diesel engines. Infrastructure issues notwithstanding, this process has the greatest potential to successfully attain the >90% NO_x reduction required for CIDI engines to meet the new EPA Tier II emission standards scheduled to be phased in starting in 2004.

Los Alamos National Laboratory (LANL) Efforts

Approach

During FY 2003, work at Los Alamos National Laboratory was focused on implementing new, more stringent catalyst screening protocols for the catalyst discovery effort. A particular focus of the LANL catalyst discovery effort was in developing new materials having improved activity under the low temperature operation regime. This regime requires high catalyst activity under conditions of high NO/NO_2 ratios below temperatures of 200°C. LANL's history of participation in this CRADA has centered on the use of microporous catalysts, particularly zeolite-based catalysts using base metals as the active component. With over 1000 different microporous base-metal catalysts in the LANL lean NO_x catalyst library, our effort in FY 2003 has been to focus on a small subset of these materials and modify them to achieve low temperature activity. Our new testing protocols, arrived at through extensive discussions with representatives of the LEP, put a particular emphasis on low temperature activity as well as on accelerated aging in steam and in SO_3; see Table 1.

Table 1. New Testing Protocols

	Standard Test Conditions	Hydro-thermal Aging	SO_3 Aging*
Temperature	**450 - 125°C**	**700°C, 14 hr**	**355°C, 15 hr**
Space Vel. (hr^{-1}) (monolith)	**30K, 120K (powders)**	**30K**	**30K**
NO (ppm)	175; 280	175	-0-
NO_2 (ppm)	175; 70	175	-0-
NH_3 (ppm)	350	350	-0-
O_2 (%)	14	14	35
CO_2 (%)	5	5	15
H_2O (%)	4-5	5-7	4-5
SO_3 (ppm)	0	0	45
Balance	He	He	He

* Equivalent to 120,000 miles at 21 mpg with 10 ppm sulfur in fuel.

Results

During FY 2003, the LANL research effort has been focused on low temperature activity of lean NO_x reduction using ammonia as reductant. It is now well-known that the kinetics of the SCR reaction is a strong function of the NO_2/NO_x (NO_x = NO + NO_2) ratio in the feed gas, and that the fastest rate is found at 50% NO_2, *i.e.*, conditions of equal concentrations of NO and NO_2. It is anticipated that for automotive applications, there will be a diesel oxidation catalyst (DOC) between the engine and the SCR catalyst to oxidize hydrocarbons and some particulates. The engine-out NO will also be oxidized to NO_2 over the DOC in the presence of excess oxygen, and the extent of oxidation of NO to NO_2 is a function of temperature. A plot of NO oxidation over a Pt catalyst similar to a DOC is shown in Figure 1.

Figure 1 shows that a typical Pt catalyst similar to a DOC oxidizes NO to NO_2 at too low a rate at low temperatures to achieve the optimal 1:1 ratio necessary to attain the highest rates of SCR catalysis. Therefore, our strategy has been to focus our discovery efforts on catalysts that assist the DOC to provide a higher degree of engine-out NO oxidation at low temperatures.

This strategy has led to the discovery of new ‘hybrid’ oxidizer-SCR catalysts that have vastly improved low temperature activity compared to the best commercially available catalyst. As shown in Figure 1, we have been able to increase the rate of NO oxidation at low temperatures over the ‘hybrid’ catalysts. This leads to an improvement in the low temperature SCR activity for conversion of NO-rich feed gas (20% NO_2, 80% NO), as shown in Figure 2. These materials are highly active under conditions of 50% NO_2, 50% NO, converting well in excess of 95% of the NO_x between 200 and 400°C (data not shown).

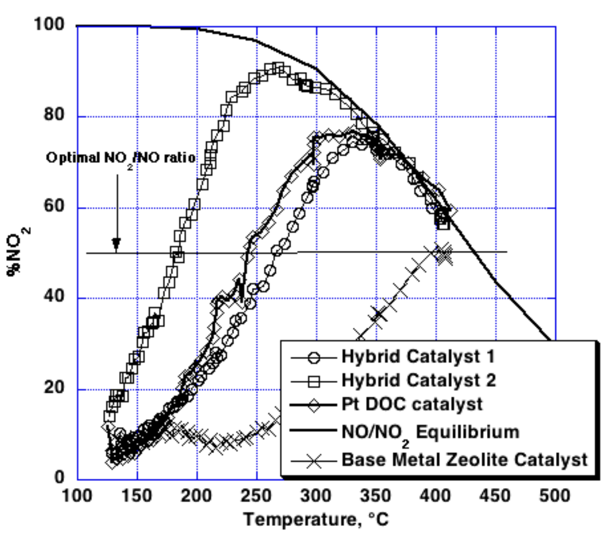

Figure 1. Plot of the oxidation of NO over various monolith catalysts. The bounding line is the calculated NO-NO_2 equilibrium. The horizontal 50% conversion line denotes the optimal NO_x ratio for the highest rate of the SCR reaction. Conditions: 190 ppm NO, 12% O_2, 5% steam, GHSV 30,000 h^{-1}.

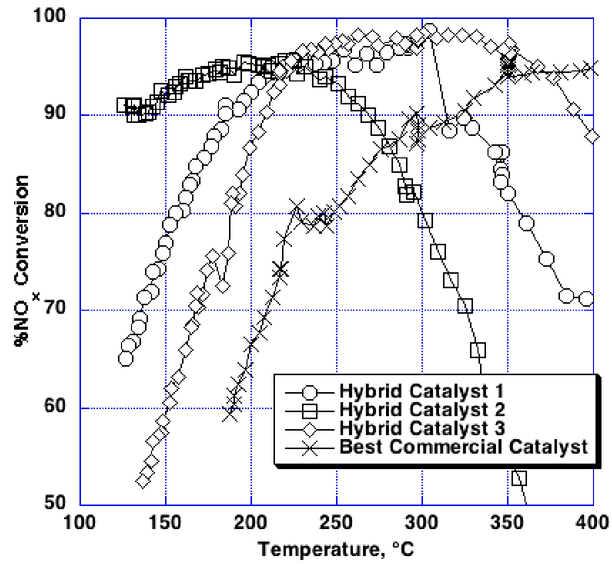

Figure 2. Comparison of three hybrid monolith catalysts with the best commercially available base metal zeolite catalyst. Conditions: 20% NO_2, GHSV 30,000 h^{-1}, 5% steam, 350 ppm NO_x, 350 ppm NH_3.

The ‘hybrid’ oxidizer-SCR catalysts have been subjected to preliminary accelerated aging test conditions. After aging in 45 ppm SO_3 for 15 hours at 355°C, the catalyst still achieves 85% NO_x conversion between 200 and 400°C with only 20% NO_2 in the feed. This exceeds all of the LEP activity criteria.

The ‘hybrid’ oxidizer-SCR catalysts are such potent oxidants that they combust NH_3 at temperatures above around 250°C. This can be countered by feeding 10-15% more ammonia at these temperatures, as is shown for the SO_3-aged catalyst in Figure 3. In fact, this is generally true for all of the hybrid catalysts, in that the activity at high temperature can be dramatically improved simply by feeding additional ammonia beyond what is combusted by the catalyst.

Conclusions

Our strategy of understanding the mechanism of SCR has led to new catalyst formulations that are exceedingly active at low temperatures and with only 20% NO_2 in the feed. At higher temperatures, the

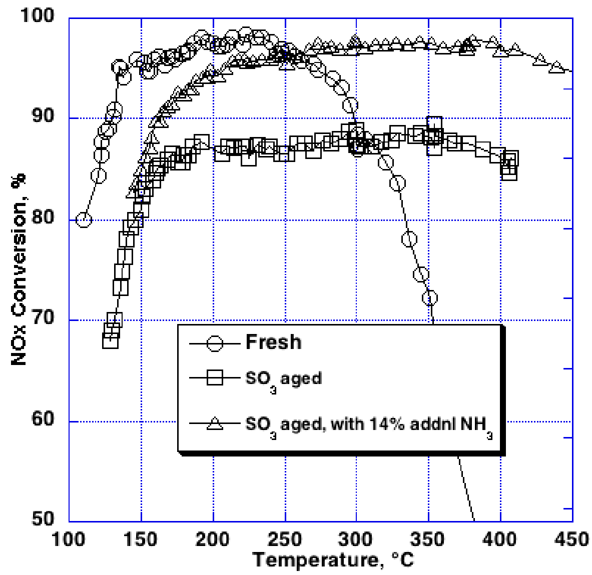

Figure 3. Effect of SO_3 accelerated aging on the activity of a hybrid oxidizer-SCR catalyst. Conditions as given in Figure 2.

catalysts are active for ammonia combustion at the expense of NO_x conversion. This may be countered by the addition of additional ammonia. The influence of sulfur is deleterious to the catalyst activity, but not to the extent that the catalysts fail the activity criteria. Because of the excellent activity these catalysts have under low temperature conditions and their resistance to sulfur, the new 'hybrid' catalyst approach will be investigated in more detail in our future work.

Sandia National Laboratories (SNL) Efforts

Approach

SNL continues to develop hydrous metal oxide (HMO) and other oxide-supported catalysts. We have been investigating the use of promoters to improve catalyst activity and catalyst durability. During FY 2003, we have focused on testing catalysts under more stringent testing conditions, with particular attention paid to the development of catalysts with high activity for a wide range of $NO:NO_2$ ratios. We are also investigating the effects of hydrocarbons on catalytic activity. In addition to materials discovery and testing of powders, we are also working on optimizing our monolith fabrication procedures.

Results

In FY 2002 we reported on a catalyst (Catalyst B with promoter) that showed excellent activity, hydrothermal stability, and tolerance to SO_2 with $NO_2:NO_x$ = 50%. This catalyst has been tested under a variety of $NO_2:NO_x$ ratios by keeping the total NO_x (NO + NO_2) constant at 350 ppm and varying the amount of NO_2 from 0 to 350 ppm. Catalyst activity was found to drop off significantly when the $NO_2:NO_x$ ratio diverged from 50%. These results were verified by testing performed at Ford Motor Company (Figure 4). The catalyst in monolith form was aged for 64 hours at 670ºC with water and 28 ppm SO_2 present. With $NO_2:NO_x$ = 50%, greater than 90% conversion of NO_x was achieved at 200-400ºC. However, with $NO_2:NO_x$ = 80%, there was a significant drop off in low temperature activity.

With $NO_2:NO_x$ = 50%, six SNL catalysts had passed all the stages in original selection criteria (>90% NO_x conversion between 200 and 400ºC at 30,000 h^{-1}). Several of these catalysts were re-screened using a variety of $NO_2:NO_x$ ratios. In most cases, similar results were seen as with promoted Catalyst B. However, it was found that one type of catalyst (Catalyst C) exhibited dramatically decreased sensitivity to the amount of NO_2 in the feed when a promoter was included in the

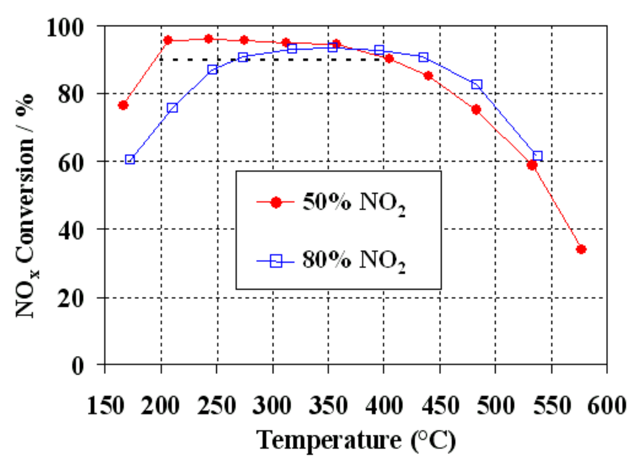

Figure 4. The effect of $NO_2:NO_x$ on promoted Catalyst B monolith. Monolith was aged for 64 hours at 670ºC in 4.5% steam, 28 ppm SO_2, 5% CO_2, 14% O_2, balance N_2 with a space velocity of 30,000 h^{-1} prior to testing. Data from catalyst testing at Ford Motor Company.

formulation. Figure 5 shows the effect of the NO_2:NO_x ratio for Catalyst C without and with a promoter. Without the promoter, NO_x conversion was less than 40% at 200ºC with NO_2:NO_x = 0% (NO only feed); however, with the promoted Catalyst C, 90% NO_x conversion was achieved at 200ºC using the same feed.

Catalyst C with promoter was also tested for hydrothermal durability and SO_2 tolerance. With a space velocity of 30,000 h^{-1}, promoted Catalyst C passed all the LEP criteria with almost no loss of activity after 16 hours at 600ºC in 5% water and a very minor loss of activity after aging with 20 ppm SO_2 for 24 hours (not shown).

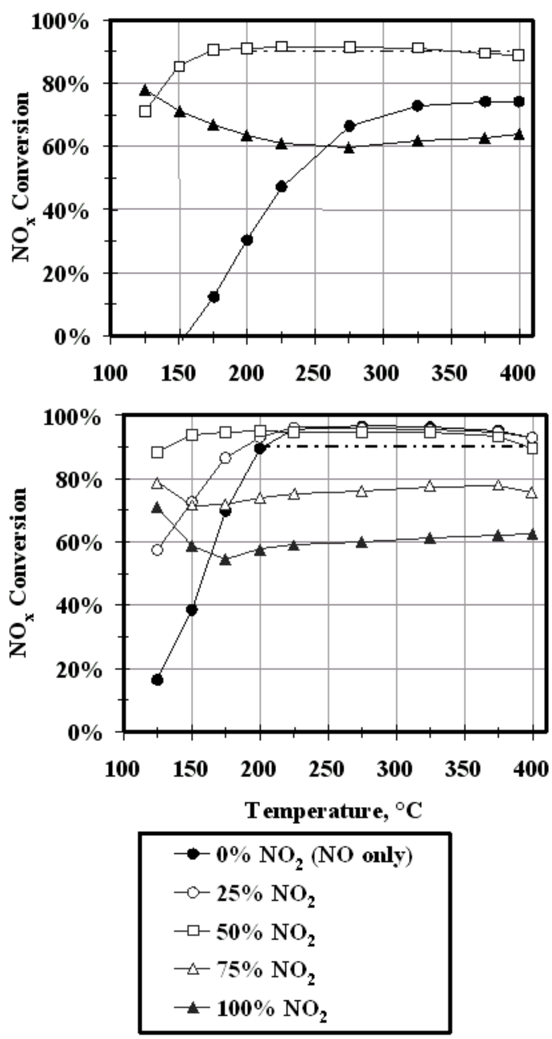

Figure 5. The effect of NO_2:NO_x on powder Catalyst C without promoter (top) and with promoter (bottom).

In light of the excellent results achieved with the powder form of Catalyst C with promoter, the development of a monolith form of Catalyst C with promoter has been undertaken. A slurry-coating technique with an alumina binder was found to be the most reliable preparative technique. Monolith activity was tested with both NO_2:NO_x = 50% and NO_2:NO_x = 20%. By increasing the catalyst loading, the activity of the catalyst could be improved significantly (Figure 6). At the highest loading tested (16 wt % washcoat), good activity was achieved. Most commercial catalysts used in automobile application have a washcoat loading of approximately 25%; as a result, it is reasonable to assume that further increases in activity are possible for this catalyst. Hydrothermal durability and sulfur tolerance studies are underway for this catalyst.

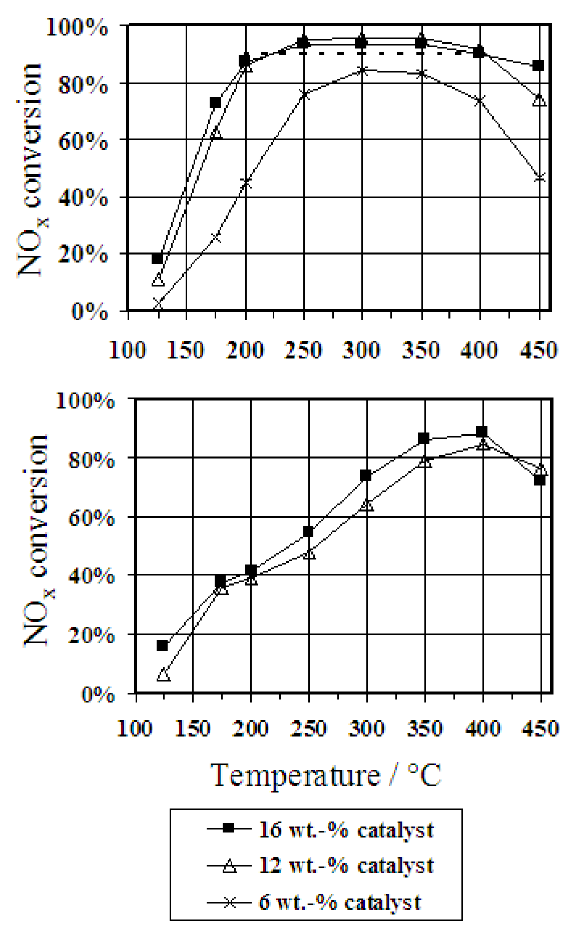

Figure 6. The effect of washcoat loading on activity of promoted Catalyst C monoliths. (top) NO_2:NO_x = 50%; (bottom) NO_2:NO_x = 20%.

In addition to hydrothermal durability and sulfur tolerance, it is important that catalysts in lean NO_x environments maintain activity in the presence of residual hydrocarbons. To test the effect of hydrocarbons on Catalyst C with promoter, 34 ppm propylene and 38 ppm n-octane (equivalent to 390 ppm C_1) were co-fed into the reactor during an SCR run. Results are shown with and without hydrocarbon in the feed with NO_2:NO_x = 20% (Figure 7). Only a small decrease in activity was seen at temperatures greater than 300ºC. This decrease in activity corresponds to the light-off temperature of the hydrocarbons. The investigation of the effects of hydrocarbons on catalyst

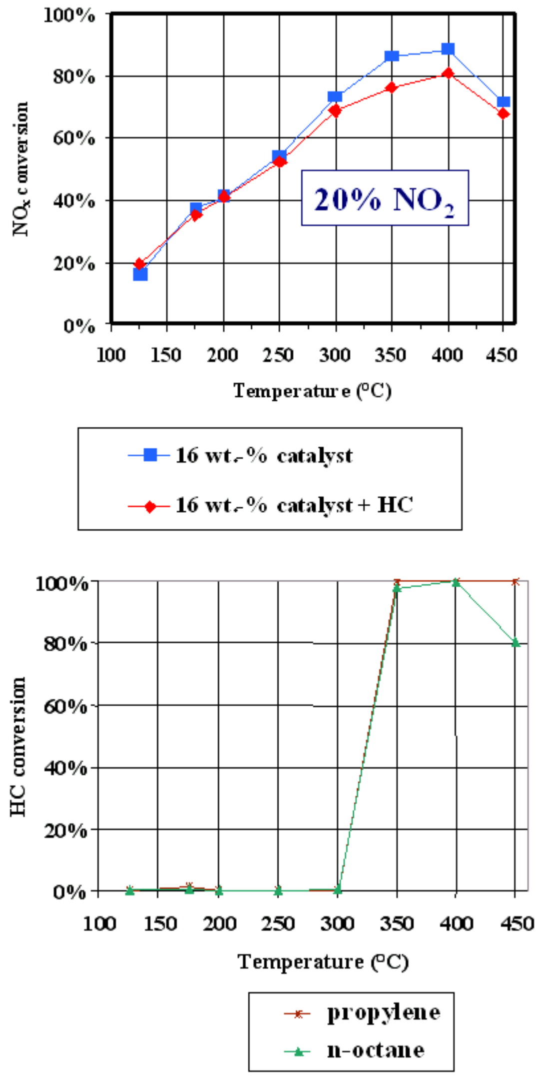

Figure 7. The effect of hydrocarbons on NO_x reduction with promoted Catalyst C monolith. (top) NO_x conversion; (bottom) hydrocarbon conversion.

performance will be continued. In particular, future testing will involve aromatic hydrocarbons, whose interactions with the catalyst may be stronger.

Conclusions

A new catalyst, Catalyst C with promoter, has been developed that shows good activity for a range of NO_2:NO_x ratios, good hydrothermal stability, and SO_2 tolerance. Techniques to translate this performance to a monolith catalyst have been developed. Initial results are promising, and further improvements are anticipated with continued optimization. Samples of this catalyst will be given to our CRADA partners for comparison testing. The transfer of this technology to the catalyst suppliers is one of our short-term goals. Materials discovery will continue in an effort to develop other new and promising catalyst formulations.

Oak Ridge National Laboratory (ORNL) Efforts

The early work plan for ORNL for FY 2003 called for vehicle-based studies of urea decomposition in the low-temperature regimes of vehicle operation. It is thought that in those regimes the urea might not completely decompose into ammonia and water and that this phenomenon would have detrimental effects on SCR catalyst performance and unregulated emissions. The plan was to use one of Ford's Focus vehicles with urea SCR already installed on the vehicle. This was to be supplemented with engine-based studies of the same phenomena in a dynamometer laboratory at ORNL.

Scheduling the availability of the Ford Focus became an issue, and it appeared that this portion of the study might have to be eliminated. In the second quarter of the FY this decision was taken, and the planned study was modified so that it focused entirely on engine-based experiments, which are just underway.

Ford provided the urea injection hardware. A catalyst manufacturer has provided oxidation and urea SCR catalysts. ORNL is employing a Mercedes 1.7 liter, turbocharged, 4-cylinder diesel engine, which was in-house. This engine has associated with it a Rapid Prototyping Engine Control System providing very flexible engine controls for experimental work such as this project. A number of potentially relevant unregulated emissions have been identified earlier as emissions of interest for urea SCR systems, and these will be investigated in this study. A schematic diagram of the experimental setup is shown in Figure 8.

Parameters to be varied during the tests include exhaust temperature and space velocity, and the ratio of NO to NO_2 into the SCR catalyst were monitored to try to ensure an equal balance between the two as much as possible. Early results from these experiments showed that there is no evidence of ammonia in the exhaust stream prior to the catalyst at temperatures below 200°C. Evidence pointed to urea storage on the catalyst rather than ammonia storage at those temperatures. Nevertheless, there was reasonably good NO_x conversion at temperatures below 200°C as illustrated in Figure 9. The red curve represents NO_x conversion data for the lower space velocity. All other points and curves in the figure are for the higher space velocity. The exhaust temperature was controlled by varying the engine

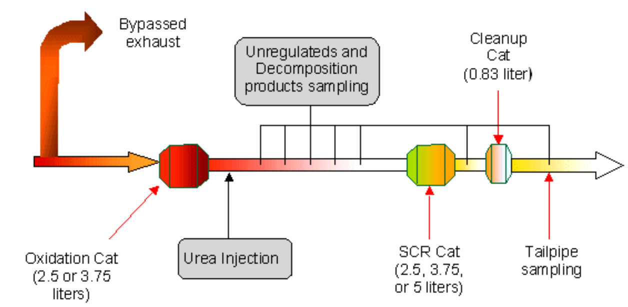

Figure 8. Schematic Diagram of Urea Decomposition Experiment.

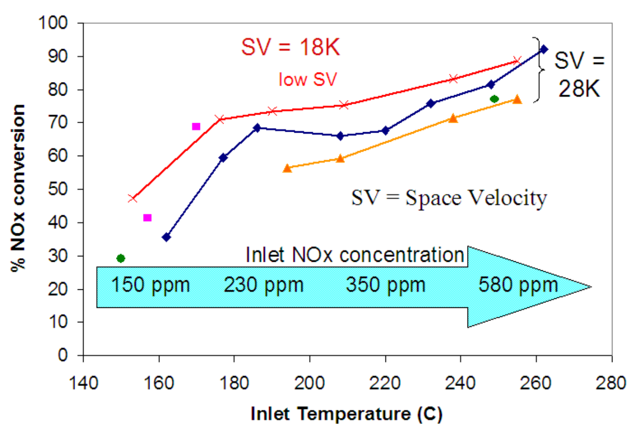

Figure 9. NO_x Conversion as a Function of Exhaust Temperature, Space Velocity, and Catalyst Inlet NO_x Concentration - Urea SCR System

load, and the NO_x increased with engine load. The arrow with the NO_x concentrations illustrates the rising NO_x concentration with exhaust temperature (and, indirectly, with engine load).

There was additional evidence of nitrogen compounds forming in the pre-catalyst stream, but the identities of those compounds is not yet known. Additional work will be performed on this issue before the end of calendar year 2003.

FY 2003 Publications/Presentations

1. K. C. Ott, C. Macomber, J. A. Rau, "Reduction of NO_x Emissions for Lean-Burn Engine Technology," Presentation at the 2003 National Laboratory CIDI and Fuels R&D Review, Argonne, IL, May 2003.

2. E. N. Coker, "Reduction of NO_x Emissions for Lean-Burn Engine Technology," Presentation at the 2003 National Laboratory CIDI and Fuels R&D Review, Argonne, IL, May 2003.

3. K. C. Ott, N. C. Clark, J. A. Rau, "Hysteresis in Activity of Microporous Lean NO_x Catalysts in the Presence of Water Vapor," Catal. Today, 73, 223, 2002.

4. K. C. Ott, N. C. Clark, M. T. Paffett, "Catalysts for Lean Burn Engine Exhaust," U. S. Patent 6,514,470, February 4, 2003.

5. K. C. Ott, "Hybrid Catalysts for Lean NO_x SCR," Patent Disclosure, Docket # S100,615 (LANL).

6. D. L. Mowery-Evans, T. J. Gardner, L. I. McLaughlin, "Method of Selective Catalytic Reduction of Nitrogen Oxides", Patent Application, Docket #S100325 (SNL).

7. J. Storey, N. Domingo, R. McGill, S. Sluder, D. Blom "Urea decomposition process and products, and catalyst microstructure" Presentation at the 2003 National Laboratory CIDI and Fuels R & D Review, Argonne, IL, May 2003.

8. D.L. Mowery-Evans, J.E. Miller, E.N. Coker, R.M. Ferrizz, R.S. Sandoval, J. Cesarano III and J.N. Stuecker, "Catalyst development at Sandia National Laboratories for automobile applications" Materials Science Seminar at Colorado School of Mines, Golden CO, February 27, 2003.

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

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CRADA Partner: Low Emissions Technologies Research and Development Partnership (LEP - Member Companies: Ford Motor Company, General Motors, and DaimlerChrysler Corporation)
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Byong Cho and Steven Schmieg, General Motors R&D Center
David Brooks, DaimlerChrysler Technology Center

This project also includes a plasma-reactor materials development effort with the following personnel: Steve Nunn
Oak Ridge National Laboratory (ORNL)
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Oak Ridge, TN 37831-6087

Objectives

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

Approach

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

Accomplishments

- Conducted five weeks of engine testing at FEV facility in Pontiac, Michigan.
  - DaimlerChrysler funded test facility at FEV.
  - Achieved 90+% conversion with hexane and 70+% conversion with diesel fuel as reductants.
  - Resolved many problems encountered during prior testing; identified new problems.
- Synthesized new catalyst material that provides an average 20% improvement in NO_x conversion and a much wider ‘temperature window’.

- Contributed 11 publications, 6 with PNNL as lead authors. Made 15 presentations at scientific meetings, including DEER and SAE conferences. Filed 1 new patent, and 1 additional patent is still being prosecuted.
- Initiated studies of catalyst coking when this problem was identified in FY 2003 engine dynamometer testing.
- Nitrogen and carbon balance continue to be routinely obtained in our laboratory measurements.
- Joint studies of catalysts for light- and heavy-duty diesel vehicles, performed with researchers on the DOE-funded PNNL/Caterpillar CRADA, continued to show good results.
- This project received national recognition with the 2003 Federal Laboratory Consortium (FLC) Award for Technology Transfer on May 7, 2003.

Future Directions

This project is slated to end by October 1, 2003. Despite this, several important areas for continued R&D can be identified:

- There is a need for more consistently available engine dynamometer time for realistic testing that should include studies of transient performance (e.g., Federal Test Procedure [FTP] cycles);
- Improved methods to prepare realistic coated monoliths with laboratory synthesized catalyst materials are needed for fair testing of performance;
- Continued and focused (e.g., resistance to coking) development of catalyst materials and plasma reactors is needed; and
- Continued fundamental studies of NO_x adsorption and reaction on and deactivation (e.g., coking) of oxide catalyst materials (zeolite- and alumina-based catalysts for plasma-enhanced hydrocarbon selective catalytic reduction [SCR], NO_x adsorber materials, urea SCR catalysts) is needed.

Introduction

In this project, we have been developing a novel plasma/catalyst technology for the remediation of NO_x under lean (excess oxygen) conditions, specifically for compression ignition direct injection (CIDI) diesel engines that have significant fuel economy benefits over conventional stoichiometric gasoline engines. Our previous work has shown that a non-thermal plasma in combination with an appropriate catalyst can provide NO_x emission reduction efficiency of 60-80% using a simulated diesel exhaust [1]. Based on these levels of NO_x reduction obtained in the lab, a simple model was developed in this project that allows for the estimation of the fuel economy penalty that would be incurred by operating a plasma/catalyst system [2]. Results obtained from this model suggest that a 5% fuel economy penalty is achievable with the then-current (FY 2000) state-of-the-art catalyst materials and plasma reactor designs.

Figure 1 is a conceptual schematic of a plasma/catalyst device, which also shows our current best understanding of the role of the various components of the overall device for reducing NO_x from the exhaust of a CIDI engine. When this project was initiated, it was not at all clear what the plasma was doing and, as such, what class of catalyst materials might be expected to produce good results. With the understanding of the role of the plasma (as depicted in Figure 1) obtained in this project, faujasite zeolite-based catalysts were developed and shown to produce high activity for NO_x reduction of plasma-treated exhaust in a temperature range expected for light-duty diesel engines. These materials are the subject of a pending patent application and were recognized with a prestigious R&D100 Award in FY 2002.

In this last year, we have continued to focus on (1) improving the catalyst and plasma reactor efficiencies for NO_x reduction, (2) studies to reveal important details of the reaction mechanism(s) that can then guide our catalyst and reactor development efforts, and (3) evaluating the performance of prototype systems on real engine exhaust. While studies of the effects of the plasma on PM in real diesel engine exhaust are meant to be part of the project, this year we did not conduct any experiments along these lines due to the major effort required to carry out the engine testing.

FY 2003 Results

Our catalyst development efforts in FY 2003 have continued to focus on 1) the 'optimum' cation substitution (type and amount) into zeolite-Y; 2) whether the zeolite structure is necessary for creating the 'active catalytic sites' and, if yes, what is the 'optimum' structure; and 3) whether the addition of other metal dopants, reported to be good partial hydrocarbon oxidation catalysts, could increase the yield of desirable aldehyde species. In last year's annual report, we showed NO_x conversions over a variety of alkali-metal and alkaline-earth exchanged Y-zeolite (Y,FAU) catalysts that address issue 1). We learned in this last year that one must be very careful in making such comparisons because of the need to fully exchange the substituted cation (see next paragraph) [3], and because we observed a significant batch-to-batch variation in the performance of the commercial Na-Y starting material [4]. Carrying out a careful comparative study produced the results that are summarized in Figure 2. As can be seen in the figure, Ba-Y is clearly the best of this series of materials [4]. In the comparison shown in Figure 2, NO_x conversion activity for the various catalysts is plotted as a function of charge density (charge/ionic radius; e/r). In this presentation of the activity data, there are clear trends for both sets of catalysts studied here, *i.e.*, the activity increases with decreasing e/r. This correlation seems to emphasize again the importance of the basic character of the catalysts in the plasma-assisted NO_x reduction process. Although there is correlation

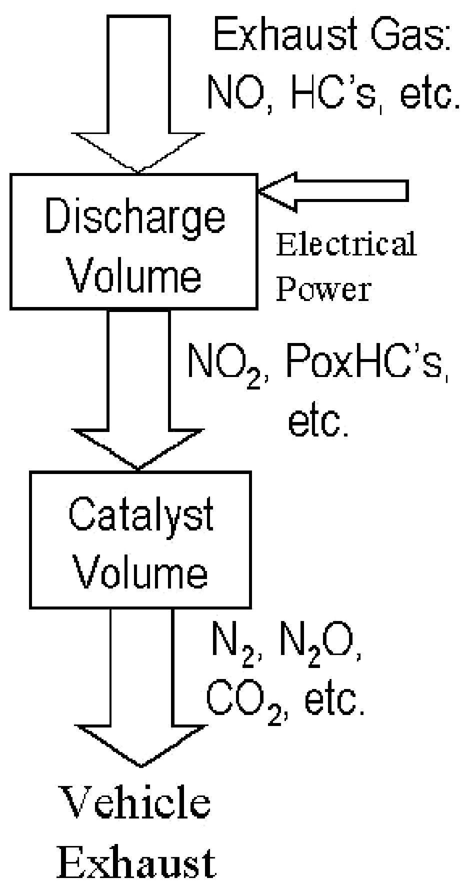
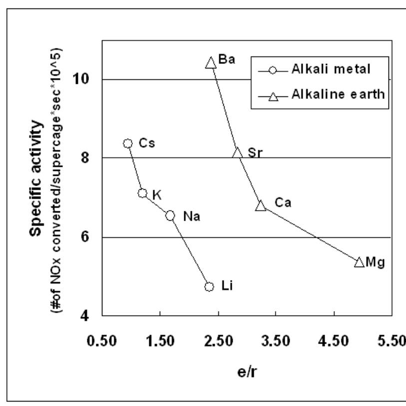


Figure 1. Schematic of a two-step discharge/catalyst reactor used for reducing NO_x and PM from the exhaust of CIDI engines. Note especially the current understanding of the effect of the plasma "discharge volume" in producing NO_2 and partially oxidized hydrocarbons (PoxHC's).



Ionic radius(Å)	
Li^+	0.68
Na^+	0.95
K^+	1.33
Cs^+	1.69
Mg^{2+}	0.65
Ca^{2+}	0.99
Sr^{2+}	1.13
Ba^{2+}	1.35

Figure 2. Specific NO_x reduction activity, given as turn-over frequencies (TOFs, defined as the number of NO_x converted/supercage•sec•100000), as a function of charge density around the charge compensating cations in the Y,FAU framework. Activities are compared at a reaction temperature of 473 K, with gas flow rates that yield a 12,000 hr^{-1} space velocity, and with a plasma-reactor energy of 9 J/L. The simulated diesel exhaust gas feed was 8% O_2, 2% H_2O, 210 ppm NO, 520 ppm (C_3) C_3H_6, balance N_2.

between activity and e/r for each set of catalysts, there is a disconnect between the two sets of catalysts. This suggests that charge density around the charge compensating cation is not the only factor influencing the overall NO_x reduction activity.

The effects of some aspects of catalyst preparation on the NO_x reduction activity of a series of Ba-Y,FAU zeolites were investigated in detail during this last year. As clearly shown in Figure 2, the introduction of Ba^{2+} ions into Na-Y,FAU results in a large increase in their non-thermal plasma-assisted NO_x reduction activity. The NO_x reduction activities of Ba-Y,FAU catalysts were found to increase with increasing Ba^{2+} concentration in the aqueous ion exchange solutions, which translated into increased Ba^{2+}/Na^+ ratios in the resulting materials. Consecutive ion exchange procedures at a given Ba^{2+} concentration in the aqueous solution, however, did not improve the NO_x reduction activities of Ba-Y,FAU catalysts, i.e. the activity of the four times ion exchanged material was the same as that of the one that was ion exchanged only once. In contrast, as shown in Figure 3, a significant increase in NO_x reduction activity was observed when a 773 K calcination step was implemented after each solution ion exchange. Also note the

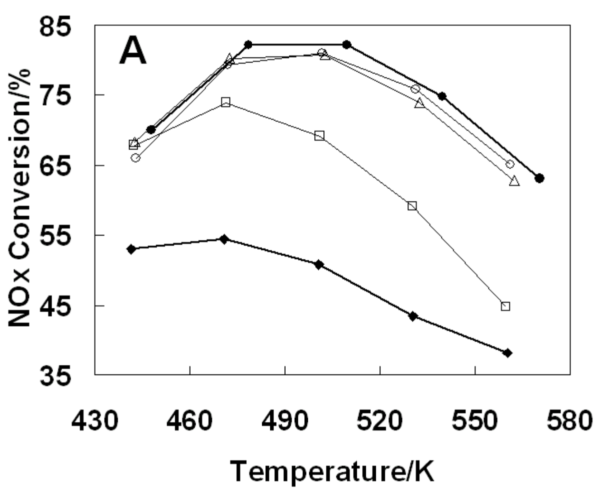


Figure 3. The effect of multiple ion exchanges/ calcination on the NO_x conversion over Ba(Na)-Y,FAU catalysts. Filled diamonds: Na-Y; open squares: Ba-Y(1-1); open triangles: Ba-Y(2-2); open circles: Ba-Y(3-3); filled circles: Ba-Y(4-4) – (# of solution ion exchanges-# of calcinations).

considerable increase in the 'temperature window' of operation. These results represent a *major* improvement in the catalyst materials for plasma-enhanced hydrocarbon SCR for light-duty applications. The results can be understood by noting that the calcination following each ion exchange step seems to allow for a further increase in the Ba^{2+}/Na^+ ratio in the zeolite.

In collaboration with personnel working on a PNNL/Caterpillar CRADA aimed at the development of plasma-assisted catalysis for NO_x emission control from 'heavy-duty' diesel engines, we have been studying the synergistic effects of using two classes of catalysts, zeolite-based for low temperature (<300°C) and alumina-based for high temperature operation [5]. Results from this work are described in the PNNL/ Caterpillar program's annual report, and a patent application that identifies the optimum catalyst configurations has been filed [5b].

Our more fundamental studies have continued to utilize Fourier transform infrared (FTIR) spectroscopy to identify important details of the reaction mechanism, including the reaction intermediates and their reaction pathways. The adsorption of NO and NO_2 and the reaction between NO and O_2 were investigated on a Na-Y,FAU zeolite [6]. The interaction between NO and Na-Y is weak, and no infrared (IR) absorption feature is seen upon room-temperature adsorption. On the other hand, several NO_x species were identified as a result of the adsorption of NO_2. For example, Figure 4 shows a series of room-temperature IR spectra recorded at different NO_2 pressures in the 1200-2300 cm^{-1} spectral range. At very small NO_2 doses, a doublet with band positions at 1370 and 1420 cm^{-1} appears, and a peak develops at 2017 cm^{-1} with a high frequency tail. The intensities of the features in both of these spectral regions increase with increasing NO_2 doses. After the bands in the 1370-1420 cm^{-1} region reach their maximum intensities, they become significantly broadened as additional NO_2 aliquots are added to the system. At the highest NO_2 pressure applied (1.9 Torr), a single unresolved broad band covers the entire spectral range between 1200 and 1500 cm^{-1}. The intensity of the 2017 cm^{-1} band first increases with the introduction of additional NO_2 aliquots. It then reaches a maximum, followed by a decrease in intensity, and finally, it completely disappears at high NO_2 doses. Parallel to the decrease of the 2017 cm^{-1} peak is the development of a new absorption feature at 2170 cm^{-1}. At higher NO_2 doses, the intensity of this band becomes very high, and a shoulder develops on its high frequency side as the presence of gas-phase N_2O_4 becomes evident in the IR spectrum. As the amount of NO_2 increases in the cell, the IR features of gas-phase NO_2 and N_2O_4 at ~1616 cm^{-1} and 1748 cm^{-1}, respectively, become clearly visible, and they grow with the addition of further NO_2 doses. A number of adsorbed NO_x species can account for these various spectral changes; specifically, we've identified NO_2 bonded to Lewis acidic (NO_3^-, NO_2^-) and basic (NO^+ and $[NO^+][NO_2]$ and $[NO^+][N_2O_4]$) sites. A series of reaction and isotopic substitution ($N^{15}O$ and $O^{18}{}_2$) experiments were conducted to unambiguously assign the IR features in the 2000-2120 cm^{-1} spectral range. The bands in this region were assigned to NO^+ adsorbed onto framework O^- sites as charge compensating cations.

In last year's report, we provided an update of the collaboration between PNNL (S. Barlow) and Steve Nunn at ORNL that has been refining the design and fabrication of ceramic parts for a plasma reactor in order to reduce part number and complexity. This year, we have participated in the planning for a test of the prototype device on an engine test stand at ORNL. This engine dynamometer test was planned for later this fiscal year or early next year.

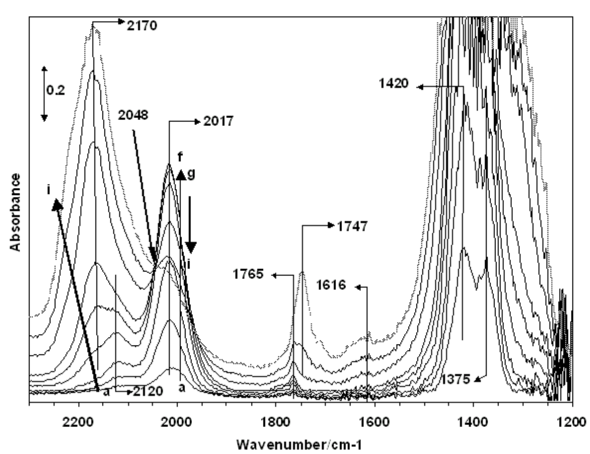


Figure 4. FTIR Spectra Taken Following NO_2 Adsorption on Na-Y,FAU at 300 K (n_{NO2}(min) $=2.5*10^{-7}$ mol; n_{NO2}(max)$=2.0*10^{-4}$ mol)

Engine testing of prototype plasma/catalyst devices has been an important element of our project to provide a ‘calibration’ of where the technology is, both relative to the alternatives and with respect to meeting the overall goals of the project. We have previously described the first of these engine tests (at ORNL) that demonstrated as much as 50% reduction with an estimated total fuel economy penalty of 6% (see FY 2000 Annual Progress Report). In last year’s report, we described the design of a vastly improved and flexible test unit that was used in engine dynamometer testing using a diesel engine at FEV in Detroit during the month of November, 2001. Excellent overall activity was observed even when utilizing diesel fuel as the added reductant necessary to carry out plasma catalysis. However, there were notable problems with regard to catalyst temperature and power delivery that prevented the attainment of optimum operating conditions for the system. These problems were largely eliminated for this fiscal year’s recent series of tests conducted at FEV in November of 2002. As before, we utilized a DaimlerChrysler prototype 1.9 L diesel engine operated mostly at a single load point of approximately 45-50 Newton-meters torque at 2000 RPM with 25-30% exhaust gas recirculation (EGR). The exhaust flow through the prototype plasma-catalysis emission control system was ~50 m^3/hr, and it contained 150-200 ppm of NO_x (~90% NO) engine-out. The plasma energy was held below 9 Joules/liter, and the catalyst temperature varied between 150°C and 250°C during the tests.

Figure 5 compares the NO_x reduction levels initially measured using either hexane or Fisher-Tröpsch diesel fuel as the added reductant. The figure shows that with hexane reductant added to the exhaust, we observed over 90% NO_x reduction. Somewhat lower levels (75-80%) of NO_x reduction were achieved with Fisher-Tröpsch diesel fuel. However, with a low-sulfur diesel or Fischer-Tröpsch reductant, the catalyst efficiency dropped off with time. Heating the catalyst in air removed a brown deposit from the surface and restored the conversion efficiency. This suggests that the catalysts deactivated due to ‘coking’, as also indicated by post-mortum characterization of the catalysts performed subsequent to the engine tests. Brunauer-Emmett-Teller (BET) surface area decreased, and temperature programmed desorption (TPD) revealed significant storage. This storage appears to be partly unburned diesel fuel that can be removed by heating to around 250-300°C, and partly hydrocarbons bonded to the surface that remain in place until 450-500°C.

To assess the progress based on this year's engine tests, we directly compared the results to those obtained in the two previous series of engine tests. Figure 6 shows this comparison. In the figure, highlights in red indicate areas in which the test was more demanding. As can be seen, in most cases the recent FEV tests provided more challenges to the plasma catalysis concept than did the first series of tests performed at ORNL several years ago. Despite this, overall performance was excellent and has continued to improve. As in any tests of this type, realization of optimum performance is extremely difficult without a major systems engineering activity. One of the major 'caveats' to this year's

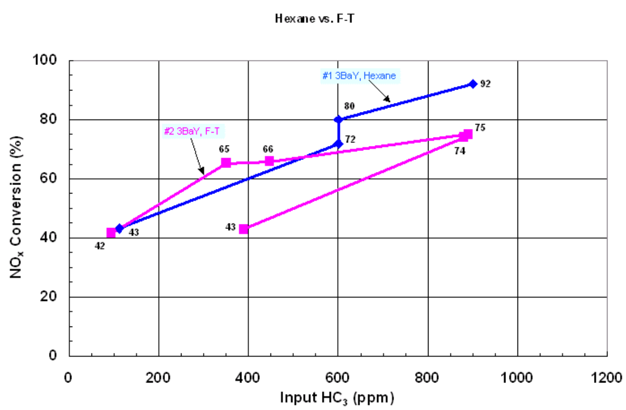


Figure 5. Comparison of the % NO_x Conversion vs. Added Hydrocarbon Using Both Hexane and Fisher-Tröpsch (F-T) Diesel Fuel as Reductants

	ORNL	FEV 1	FEV 2
Space Velocity (over all catalysts)	12,500 hr^{-1}	7200 hr^{-1} (but catalyst volume not nearly filled)	7200 hr^{-1} (but many monolith channels blocked)
Soot Filter?	No	Yes	Yes
Catalyst Temperature	Likely Optimum	160-180C	In the optimum range
Power Delivered to Plasma Reactors	Not measured but estimated to be high	Not measurable but probably not nearly as high	0-5 J/L
Catalyst	BaY	NaY	NaY and BaY
Reductant	Propylene	Fisher-Tropsch Diesel	Fisher-Tropsch Diesel
Coatings	PNNL	Johnson/Matthey	Johnson/Matthey and PNNL
NOx Conversion	60%	60%	70-95%
Stable Activity?	Deactivated Over Time	Seems reasonably stable	Deactivated Over Time

Figure 6. Comparison with FY 2000 ORNL and FY 2002 FEV Engine Tests

tests was that the catalyst-coated cordierite monoliths had significant blockage due to the relatively poor coating process utilized by the catalyst manufacturer. Some of the monoliths had greater than 60% blockage of the channels, and all had a significant amount of blockage. Thus, higher to much higher performance can be expected should better catalyst monoliths be used. Furthermore, it should be noted that for this year's tests, we did not use our current best catalyst formulation that is described above.

Conclusions

PNNL and its LEP CRADA partners from Ford, General Motors and DaimlerChrysler have been developing a plasma-assisted catalyst system that is showing great promise for treating emissions of NO_x and PM from the exhaust of 'light-duty' CIDI engine-powered vehicles. High NO_x conversions have been demonstrated over a wide temperature range on simulated diesel exhaust. Furthermore, high conversions have been demonstrated in engine tests utilizing real diesel exhaust and diesel fuel as the added reductant. The results obtained in the last year provide good evidence that the overall project targets of 90% NO_x reduction with less than a 5% fuel-economy penalty are within reach.

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List of Publications

1. S. Barlow, J.-H. Kwak, C. Peden, R. Tonkyn, K. Epping, J. Hoard, B. Cho, S. Schmeig, D. Brooks, S. Nunn, P. Davis, "Plasma Catalysis for NO_x Reduction from Light-Duty Diesel Vehicles", Combustion and Emission Control for Advanced CIDI Engines, FY 2002 Progress Report (2002) 68-75.

2. J.W. Hoard and P.W. Park, "Temperature Transient Effects in Plasma-Catalysis", Proceedings of the 2002 DEER Workshop, San Diego, CA, August, 2002.

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9. J. Szanyi, J.-H. Kwak, and C.H.F. Peden, "The Adsorption and Reaction of NO_2 and the $NO+O_2$ Reaction on Na-Y,FAU: an *in-Situ* FTIR Investigation", Physical Chemistry and Chemical Physics, submitted for publication.

10. S.J. Schmieg, B.K. Cho, and S.H. Oh, "Selective Catalytic Reduction of Nitric Oxide with Acetaldehyde over NaY Zeolite Catalyst in Lean Exhaust Feed", Applied Catalysis B, submitted for publication.

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List of Patents

1. C.L. Aardahl, J.W. Hoard, and P.W. Park, "Mixture of Heavy-Duty and Light-Duty Catalysts for NO_x Control Using Plasma Assisted Catalysis", U.S. Patent Filed, August 28, 2002.

List of Presentations

1. J.W. Hoard and P.W. Park, "Temperature Transient Effects in Plasma-Catalysis", Proceedings of the 2002 DEER Workshop, San Diego, CA, August, 2002.

2. J.W. Hoard, "Plasma-Catalysis", Ford Research Laboratory, Dearborn, MI, January, 2003.

3. C.H.F. Peden, "The Adsorption and Reaction of NO_x on Selected Oxide Surfaces – Implications for HC-SCR of NO_x in Oxygen-Rich Environments", 2003 Mesilla Workshop on "Environmental Chemistry at Interfaces: Advances through Molecular-Level Insight", Las Cruces, NM, February, 2003, **INVITED**.

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9. J.W. Hoard, "Plasma-Catalysis", Ford Diesel R&A, Aachen, Germany, March, 2003.

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15. G.G. Muntean and C.H.F. Peden, "Diesel Engine Emission Control Science at Pacific Northwest National Laboratory", Ford Scientific Research Laboratories, June, 2003, **INVITED**.

Special Recognitions and Awards/Patents Issued

1. 2003 FLC Award for Technology Transfer.

III.H. Fuel Reformation for Vehicle Emissions Aftertreatment

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DOE Technology Development Manager: Kevin Stork

Objectives

- Develop technology suitable for the on-board reforming of fuel for the reduction of lean burn engine emissions
  - Show proof of concept for reformer production of reductants suitable for the reduction of NO_x
- Develop methods for the on-board generation of reductants
  - Examine and understand reductant interactions with NO_x catalysis
  - Investigate reforming of gasoline and diesel fuel to:
    - Generate reductants for lean NO_x catalysis
    - Produce hydrogen for regeneration of NO_x adsorbers and particulate traps
    - Optimize reformer operation and outlet composition for NO_x reduction (hydrogen, CO, propene)
  - Advance reforming technology for suitability for on-board vehicle applications
    - Durability
    - Start-up
    - Vehicle integration (air and water feed/sources)

Approach

- Examine catalytic partial oxidation for on-board conversion of gasoline and diesel fuel to produce reductants for:
  - Selective hydrocarbon reduction of NO_x
  - Regeneration of NO_x adsorbers or particulate traps
- Measure reduction of NO_x over lean NO_x catalysts as a function of:
  - Reformer operating conditions: temperature, fuel/air ratio, fuel composition, reformate injection flowrate
  - Lean NO_x catalyst type and temperature

Accomplishments

- Demonstrated use of reformate to successfully reduce NO_x in oxidizing environment over lean NO_x catalyst
- Evaluated NO_x reduction with reformer reformate
  - Examined effect of reformer temperature on NO_x reduction
  - Measured effect of reformate bleed flowrate
  - Tested two lean NO_x catalysts
- Evaluated hydrocarbon constituents in reformate stream and their effect on NO_x reduction

Future Directions

- Evaluate and improve diesel reformer / NO_x reduction durability
  - Delineate reformate effect on lean NO_x catalyst durability
  - Analyze lean NO_x catalysts after use with diesel reformate to evaluate hydrocarbon effect on lean NO_x catalyst morphology
- Evaluate other lean NO_x catalysts (such as BaZeoliteY)
- Develop reformer for cyclic operation
  - Evaluate reformer operation for regeneration of NO_x adsorbers
  - Couple NO_x adsorber with reformer operation

Introduction

The reduction of NO_x in the oxidizing atmosphere of a lean-burn engine exhaust is a chemically challenging task. Two methods used for the reduction of NO_x are selective catalytic reduction over a catalyst with a hydrocarbon reductant (Hydrocarbon SCR) and adsorption on a NO_x adsorber followed by regeneration (potentially by hydrogen). Both reducing hydrocarbons and hydrogen reductants can be generated onboard a vehicle by reforming of the available fuel such as diesel or gasoline. This task is to develop technology for onboard reforming of fuel to produce these reductants and to demonstrate NO_x reduction by integration of a reformer with a lean NO_x catalyst system.

Approach

This task involves the design, operation, and optimization of a reformer to generate NO_x reductants and the demonstration of its effectiveness with a NO_x reduction catalyst. A partial oxidation (POx) reformer was designed and built to investigate effects on the product composition of the operating temperature, fuel/air feed ratios, and fuel composition. Diesel fuel was reformed by catalytic partial oxidation over a noble-metal catalyst. Partial oxidation produces a mixture of hydrogen, carbon monoxide, and hydrocarbons, as shown by Equation 1, for atomic oxygen to atomic carbon ratio of less than 1 (O/C < 1).

$$C_nH_{(2n+2)} + (m/2)O_2 \rightarrow mCO + C_{(n-m)}H_{2(n-m)} + H_2 \quad (1)$$

The product composition affects the lean NO_x catalyst performance. Small, unsaturated hydrocarbons such as propene are some of the most effective NO_x reductants. The reduction of NO_x was demonstrated and investigated by integrating the POx reformer with lean NO_x catalysts. The experimental setup extracted a product slipstream from the reformer, mixed that stream with a simulated diesel exhaust, and then supplied that stream to a lean NO_x catalyst test system. With this system, NO_x reduction can be investigated as a function of reformer operating conditions, reformate bleed flow rate, and temperature, and residence time of the lean NO_x catalyst can be investigated.

Results

The feasibility of generating reductants for NO_x reduction using onboard reforming was demonstrated by comparing the NO_x reduction with a bottled reductant gas mixture to that with the reformate stream from a POx reactor operating on kerosene. Figure 1 shows the reduction of NO_x over a Co-beta-zeolite catalyst first using a bottled reductant mixture (1576 ppm C_3H_8, 523 ppm C_3H_6, 390 ppm H_2 in N_2) followed by a switch to using kerosene reformate at a similar flowrate. The inlet NO_x concentration of 263 ppm was reduced to about 100 ppm using the bottled reductant, while the reductants in the kerosene reformate reduced the NO_x to a level of 50 ppm. With no reductant injection, NO_x reduction was not observed. The Co-beta-zeolite catalyst was maintained at 500ºC, and the simulated exhaust flowrate corresponded to a 30 to 100 msec residence time over the catalyst.

NO_x reduction as a function of reformate bleed injected into simulated diesel engine exhaust (flow at 3500 sccm) is shown in Figure 2. NO_x reduction increased with increasing reformate bleed flowrate. Higher reformate flowrates correspond with increasing fuel use and, thus, increasing fuel penalty.

Figure 3 shows NO_x reduction as a function of reformer temperature for three fuel compositions, iso-octane, iso-octane/15% xylene/5% methylcyclohexane, and methylcyclohexane/1% pyridine. For all three fuel mixtures, NO_x reduction was higher at lower reformer temperatures but did not show a significant dependence on the fuel composition. Pyridine is a nitrogen-containing hydrocarbon which has been show to yield a measurable amount of ammonia (NH_3) during the reforming process.[1] It does not appear that the relatively small concentration of ammonia formed during the reforming process significantly helped the conversion of NO_x via ammonia SCR.

To determine why reformer temperature affected NO_x reduction, the reformate composition was analyzed for the various operating conditions. Figure 4 shows gas chromatograms of the reformate for different operating conditions and levels of NO_x reduction. The GC (gas chromatograph) chromatograms correspond to reformer temperatures and NO_x reduction conversions of (A) 873°C, 7% NO_x conversion; (B) 822°C, 14%; (C) 770°C, 62%; and (D) 758°C, 73%. The residence times for H_2, N_2, CO, CO_2, CH_4, C_2H_6 (ethane), C_2H_4 (ethylene) C_3H_8 (propane), C_3H_6 (propylene), C_3H_4 (propadiene), and the region where C_4 compounds are labeled. At the higher reformer temperatures (A and B), nearly full conversion to H_2 and CO was observed with little resultant NO_x reduction. As the

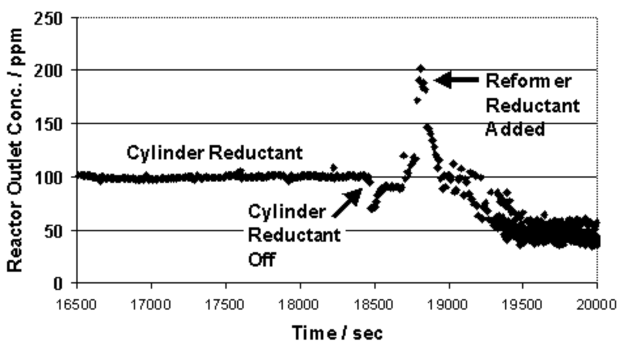

Figure 1. Comparison of NO_x Reduction over Lean NO_x Co-Beta Catalyst Using Hydrocarbon Reductant from Cylinder (1576 ppm C_3H_6, 523 ppm C_3H_8, 390 ppm H_2) and Fuel Processor Reformate Stream

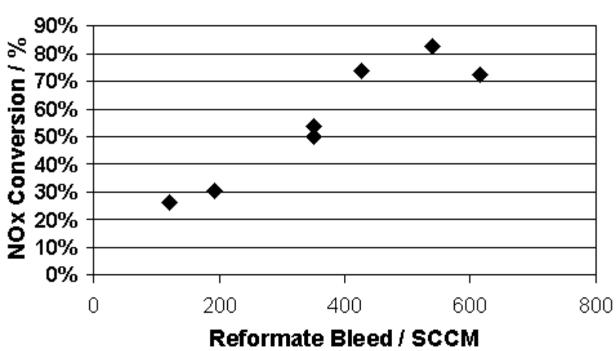

Figure 2. Diesel Reformate Bleed Effect on NO_x Conversion

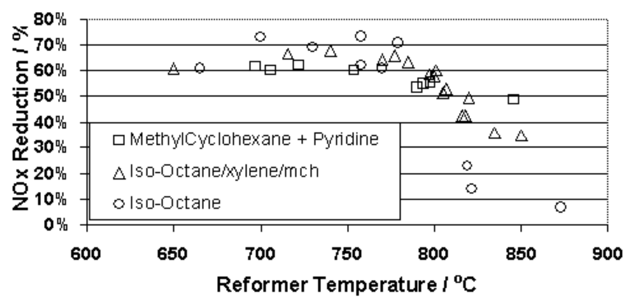

Figure 3. NO_x Reduction as a Function of Reformer Temperature for Various Gasoline Fuel Components

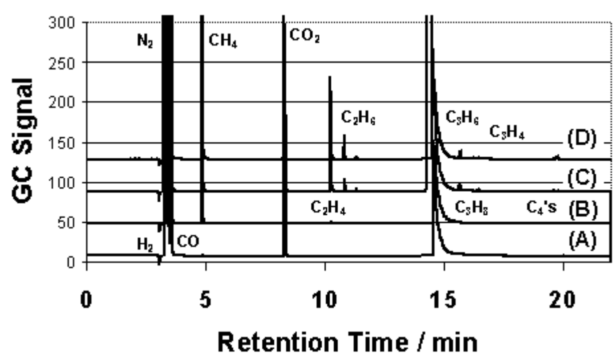

Figure 4. Chromatogram Delineating Reformate Composition Under Various Reformer Operating Conditions Showing Variation in NO_x Reduction

reformer temperature was decreased (by reducing the operating O/C ratio), an increase in unconverted hydrocarbon was measured. This increase in hydrocarbon concentration corresponded to an increase in the NO_x reduction. These measurements indicate that hydrocarbons show much higher NO_x reduction activity than hydrogen/carbon monoxide over the Co-Beta lean NO_x catalyst.

The fuel penalty for NO_x reduction was calculated based on measured $C_3H_6 + C_2H_4$ outlet concentrations from the reformer. Assuming that NO_x conversion proceeds via

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

and a NO_x reductant stoichiometry of 2.0 is required (meaning that 2 propylene molecules are required to reduce 9 NO molecules from equation 2), the theoretical fuel penalty is 1.6%. Experimentally, the fuel penalty was measured to be between 3 and 5%, based upon the fuel input to the reformer and reductant flow to the NO_x reduction reactor.

A Co-Ferrite (Co-FER) lean NO_x catalyst has shown promising results with bottled reductant. However, this catalyst showed a rapid (<10 min) decrease in activity to zero conversion with reformate from the reforming of kerosene. Figure 5 shows a time history of NO_x conversion over a Co-FER catalyst. The initial period of operation showed essentially 100% NO_x conversion using bottled reductant. Upon introduction of the kerosene reformate, the NO_x conversion rapidly decreased to zero NO_x conversion within 10 minutes. After switching back to bottled reductant, the catalyst activity only returned to 20% NO_x conversion. After recalcination of the catalyst, the NO_x conversion with the bottled reductants returned to 100%.

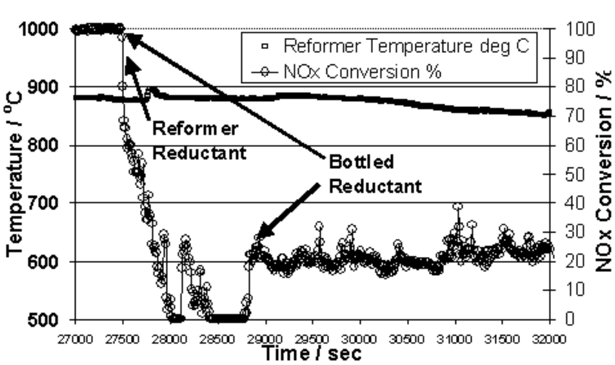

Figure 5. NO_x Reduction with Co-FER Lean NO_x Catalyst

Conclusions

NO_x reduction over a lean NO_x catalyst using reductants generated by the reforming of liquid hydrocarbons has been demonstrated. The level of reduction depended upon the operating conditions of the reformer; specifically, lower temperature with lower hydrocarbon conversion yielded higher NO_x reduction. Changes in various fuel components showed little effect on NO_x reduction. NO_x conversion over Cobalt-beta zeolite catalysts showed good NO_x reduction, while Cobalt-Ferrite catalysts were quickly poisoned by the reformer reformate. A theoretical fuel penalty for NO_x conversion is about 1.6%, while experimental measured fuel penalties were between 3 and 5%.

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FY 2003 Publications/Presentations

1. Diesel Reforming Effect on the Reduction of NO_x, in preparation

III.I. Mechanisms of Sulfur Poisoning of NO_x Adsorber Materials

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Objectives

- Utilize information obtained from detailed, state-of-the-art catalyst characterization and activity testing on pre-treated NO_x adsorber materials to develop mechanistic models that account for adsorber performance degradation.
- Ultimately, apply the new knowledge for the development of new NO_x adsorber materials formulations with high sulfur tolerance for the lean-NO_x trap (LNT) technology.
- Verify improved performance of new formulations through continued materials characterization and laboratory and engine testing.

Approach

- In collaboration with Johnson Matthey researchers, synthesize and process (via various thermal aging and SO_2 treatment protocols) model and realistic NO_x adsorber materials.
- Utilize PNNL's state-of-the-art surface science and catalyst characterization capabilities, such as x-ray diffraction (XRD), transmission electron microscopy (TEM)/energy dispersive spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD)/thermal gravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET)/pore size distribution, as well as performance testing facilities to examine the NO_x storage chemistry and deactivation mechanisms on the model and more fully formulated materials.

Accomplishments

- Initiated project with first two catalysts (model $Pt/BaO/Al_2O_3$ material and a more fully formulated sample) provided by Johnson Matthey.
- Developed surface science and catalyst characterization experiments specifically for probing physiochemical properties of the model catalyst and fully formulated materials. This includes XRD, TEM/EDS, XPS, TPD/TGA and BET experiments.
- Performed initial experiments aimed at the study of deactivation of the model and fully formulated materials under severe thermal aging and SO_2 treatment.
- Designed and initiated construction of a NO_x adsorber reactor system able to perform a full range of aging or sulfation/nitration protocols on the samples.

Future Directions

- Complete construction of and initiate experiments on the NO_x adsorber reactor system.

- Identify the 'signatures' for catalyst deactivation on the differently prepared samples (nitrated or sulfated) by using the established characterization techniques in PNNL correlated with performance measurements.
- Characterize the effect of sulfur on these steps, especially focusing on the regeneration process and its effect on the long-term stability.

Introduction

The lean-NO_x trap (LNT) technology is based upon the concept of storing NO_x as nitrates over storage components, typically barium species, during a lean-burn operation cycle and then reducing the stored nitrates to N_2 during fuel-rich conditions on a precious metal catalyst. This technology has been recognized as perhaps the most promising approach to meet stringent NO_x emission standards for diesel vehicles within the Environmental Protection Agency's (EPA's) 2007/2010 mandated limits. However, problems arising from thermal and/or SO_2 deactivation must be addressed to meet durability standards. Therefore, an understanding of these processes will be crucial for the development of the LNT technology.

This project is focused on the identification and the understanding of the important degradation mechanism(s) of the catalyst materials used in LNTs. A model $Pt/BaO/Al_2O_3$ catalyst and more fully formulated samples are being investigated. In particular, the changes in physicochemical properties of these LNT materials, due to the effects of high temperature operation and sulfur poisoning, are the current focus of the work.

This report describes selected preliminary results obtained in the first three months of this project that was initiated in March, 2003.

Approach

In parallel with an effort to construct a microcatalytic reactor system for continuous lean-rich cycle operation and material treatments, several state-of-the-art catalyst characterization techniques such as XRD, XPS, TEM/EDS, BET/pore size distribution, and temperature programmed desorption (TPD) are being utilized to probe the changes in physicochemical properties of the catalyst samples under deactivating conditions: *e.g.*, thermal aging and SO_2 treatment. Thermal aging experiments were conducted in an oven under ambient conditions at 500°C, 700°C and 900°C, while the SO_2 aging experiments were performed under flows of 50 ppm SO_2, 10% CO_2, 10% H_2O and N_2 balance at 300°C.

By comparing model $Pt/BaO/Al_2O_3$ with fully formulated materials, we try to understand the role of various additives on the deactivation processes. However, this report covers only the results obtained to date on the model $Pt/BaO/Al_2O_3$ materials for proprietary reasons.

Results

Effect of thermal aging. Figure 1 shows XRD patterns of a model $Pt/BaO/Al_2O_3$ material obtained subsequent to thermal treatments to various temperatures. The as-received sample contains γ-Al_2O_3 and a mixture of orthorhombic and monoclinic $BaCO_3$ phases. Upon calcination at 700°C, diffraction peaks ascribed to both $BaCO_3$

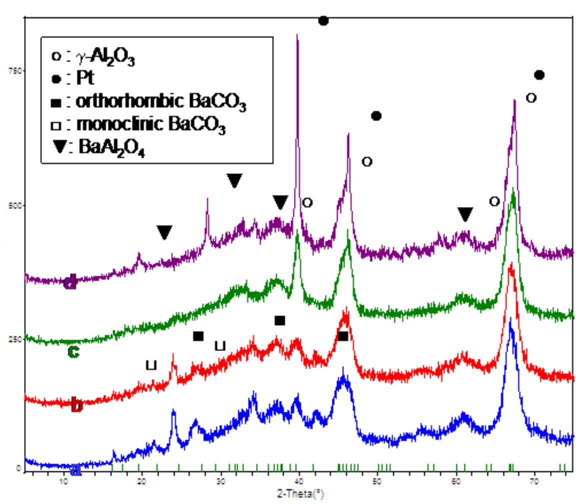

Figure 1. XRD Patterns of the Model $Pt/BaO/Al_2O_3$ Sample: (a) as-received and calcined at (b) 500°C, (c) 700°C, and (d) 900°C

species disappear. Indeed, no diffraction patterns associated with any Ba-containing phases are detected. Instead, a metallic Pt phase appears. XRD spectra on a sample aged at 900°C for 10 hours shows diffraction peaks ascribed to $BaAl_2O_4$ and metallic Pt. The presence of a $BaAl_2O_4$ phase indicates an interaction of BaO with the Al_2O_3 support. In addition, a growth in the size of the diffraction peaks for metallic Pt and their sharpening is direct evidence for sintering of Pt to form large aggregated metallic Pt crystallites upon aging at elevated temperatures. Interestingly, formation of $BaAl_2O_4$ phase does not alter the textural properties of the materials. For example, BET analysis of the model sample before and after the thermal treatment (not shown here) shows negligible changes in surface area and pore size distributions.

TEM micrographs of the model Pt/BaO/Al_2O_3 as-received and calcined at 900°C are shown in Figure 2. For the as-received sample, Pt particles between 2 and 4 nm are clearly seen. On the other hand, thermal aging at 900°C gives rise to the formation of Pt particles larger than 100 nm, which corresponds well to the XRD results described above. The fact that Pt separates from the support to form large crystalline particles may have a negative effect on the NO_x storage-reduction process; previous studies suggest that an intimate interaction between Pt and Ba species is crucial for good performance [1].

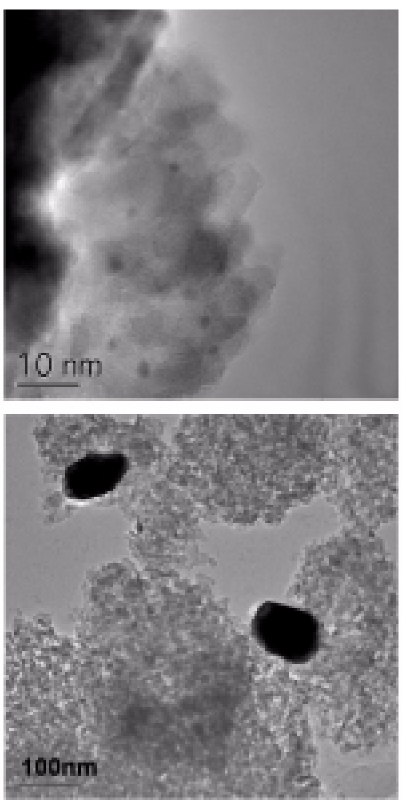

Figure 2. TEM Micrographs of the Model Pt/BaO/Al_2O_3 Sample: (top) as-received and (bottom) after calcination at 900°C

Figure 3 shows TPD spectra obtained following room temperature NO_2 adsorption on the model Pt/BaO/Al_2O_3 material calcined at 500°C (top) and 900°C (bottom). As concluded in previous work [2], TPD peaks of NO_2/O_2 at 380°C and NO/O_2 at 500°C in Figure 3 (top) can be attributed to the decomposition of bidentate Ba nitrate and ionic Ba nitrate, respectively. Comparison of two TPD spectra in Figure 3 indicates that thermal aging leads

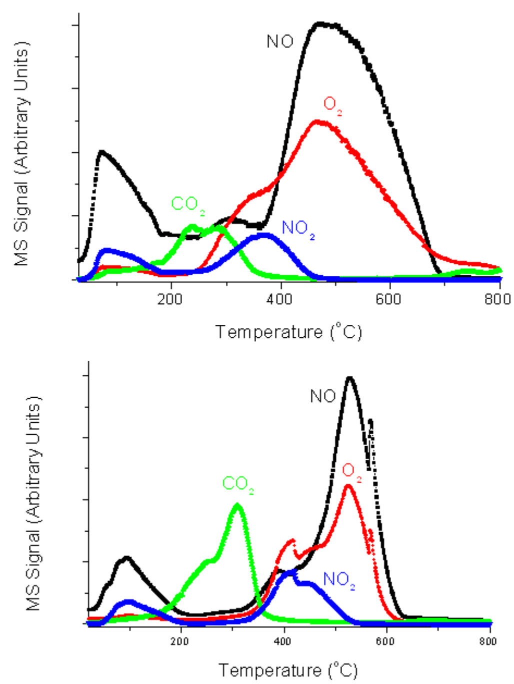

Figure 3. NO_2 TPD spectra obtained from a model Pt/BaO/Al_2O_3 sample calcined at 500°C (top) and 900°C (bottom). TPD experiments were performed after adsorbing NO_2 at room temperature, followed by evacuation under high vacuum prior to linearly increasing the temperature to 800°C at 8°C/min while measuring the desorbing gases with an electron impact ionization mass spectrometer (MS).

to the formation of more stable bidentate nitrates and ionic nitrates species. Considering the fact that Pt catalyzes the decomposition of barium nitrates [2], the segregation between Pt and Ba species may explain the higher nitrate decomposition temperatures observed in Figure 3 (bottom). Formation of these stable nitrates species on the material may not be desirable in a dynamic NO_x storage-reduction system, since stable nitrates species require higher temperatures for regeneration.

Table 1 shows the changes in the XPS binding energy and the relative surface concentration of Pt with respect to the thermal aging estimated on the basis of the XPS data. A calcination up to 700°C does not affect the oxidation state of PtO; however, a thermal treatment to 900°C results in the formation of metallic Pt. Another phenomenon evident in the XPS data is the decrease in the Pt/Al ratio with respect to the thermal aging. The lower surface concentration of Pt is likely related to the growth of Pt particles observed in the TEM and XRD data.

Effect of SO_2 treatment. The model $Pt/BaO/Al_2O_3$ LNT material, treated with SO_2 at 300°C, still contains mainly $BaCO_3$ phases, as shown by the XRD patterns in Figure 4. As the sulfation 'aging' treatment increased from 1 g/L to 10 g/L SO_2 exposure, the peak assigned to $BaCO_3$ decreased slightly; however, there is little, if any, evidence in the XRD for the formation of sulfur-related phases such as $BaSO_4$ and $Al_2(SO_4)_3$. Despite this result, it seems likely that the crystalline $BaCO_3$ phases are consumed by reaction with SO_2 during the sulfation process, yet the XRD results would then suggest the formation of amorphous sulfur-containing phases. Indeed, XPS data clearly show the existence of sulfur species in the form of sulfate (SO_4^{2-}), as summarized in Table 2, in agreement with a previous study [3].

Table 1. The Pt $3d_{5/2}$ Binding Energies (eV) and the Relative Pt Surface Concentrations of the Model $Pt/BaO/Al_2O_3$ Sample Calcined at 500°C, 700°C and 900°C

	500 °C	700 °C	900 °C	Notes
Pt $3d_{5/2}$ (eV)	316.1	315.7	313.8	Pt: 314.0 PtO: 316.0
Pt/Al*	0.076	0.0580	0.055	

*: arbitrary units

As evidenced by changes in relative surface concentrations listed in Table 2, the model $Pt/BaO/Al_2O_3$ samples show a gradual decrease in Pt/Al and Ba/Al ratios upon sulfation, while the ratio of sulfur to Al increases as expected.

Conclusions

PNNL and its CRADA partners from Cummins Engine Company and Johnson Matthey have initiated a project to study the mechanisms of deactivation of the materials proposed for use in lean NO_x traps arising from thermal aging and SO_2 poisoning. Early results demonstrate that thermal aging gives rise to the formation of $BaAl_2O_4$ and the growth of Pt particles, resulting in the segregation of the support and Pt particles. Such phenomena are expected to

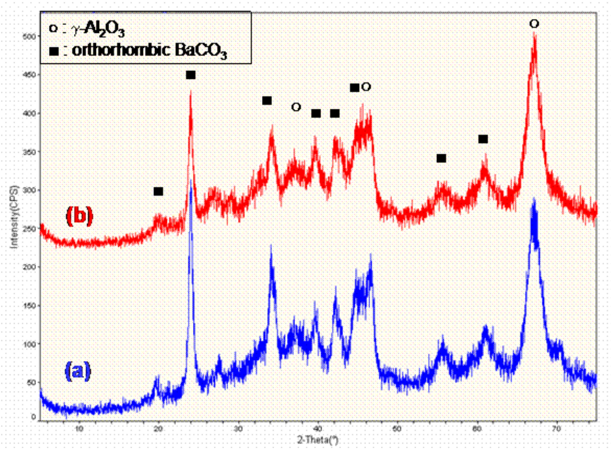

Figure 4. XRD Patterns of the Model $Pt/BaO/Al_2O_3$ Sample After SO_2 Treatments of (a) 1 g/L and (b) 10 g/L

Table 2. The S 2p Binding Energies (eV) and the Relative Pt, Ba, and S Surface Concentrations of the Model $Pt/BaO/Al_2O_3$ after SO_2 Treatment

	500 °C	1g/L	10g/L	Notes
S 2p (eV)	-	169.2	169.2	$BaSO_4$: 168.8
Pt/Al*	0.076	0.054	0.037	
Ba/Al*	1.131	0.907	0.734	
S/Al*	-	0.002	0.014	

*: arbitrary units

have a negative effect on the chemistry of NO_x adsorption/desorption. Sulfur is deposited on the LNT materials in the form of sulfate, likely modifying the BaO surface and, thus, blocking both Ba sites important for NO_x storage.

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2. F. Prinetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi and P. Forzatti, "FT-IR and TPD investigation of the NO_x storage properties of BaO/Al_2O_3 and $Pt\text{-}BaO/Al_2O_3$ catalysts", J. Phys. Chem. B **105** (2001) 12732.

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1. D.H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, L. Broering, R. Stafford, J. Stang, H.-Y. Chen, B. Cooper, H. Hess and D. Lafyatis, "Mechanisms of Sulfur Poisoning of NO_x Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Argonne, IL, May, 2003.

2. G.G. Muntean and C.H.F. Peden, "Diesel Engine Emission Control Science at Pacific Northwest National Laboratory", Ford Scientific Research Laboratories, Dearborn, MI, June 2003, INVITED.

III.J. Quantitative Identification of Surface Species on NO_x Adsorber Catalysts

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Objectives

- Determine what surface species form on a model NO_x adsorber catalyst, $Pt/K/Al_2O_3$, and elucidate the roles of the catalyst's constituent parts, i.e. Pt, K, and γ-Al_2O_3.
- Quantify the surface species to show the temporally resolved amount of NO_x adsorbed in terms of $\mu mols/m^2_{catalyst}$.
- Demonstrate quantification routine in the presence of H_2O and CO_2 and evaluate their effects.

Approach

- Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) reactor is used to evaluate surface species on the catalysts. It is capable of *in-situ* measurements up to 500°C and is designed to allow up to 10% H_2O in the feed. All tests in this study were conducted at 250°C.
- To determine the constituent effects of $Pt/K/Al_2O_3$, the following catalysts were studied: γ-Al_2O_3, 1% Pt/γ-Al_2O_3, 8% K_2CO_3/γ-Al_2O_3, and 1% Pt/8% K_2CO_3/γ-Al_2O_3.
- The spectral features from the DRIFTS reactor were calibrated with CO_2 and NO_2 chemisorption, which respectively allowed the quantification of carbon- and nitrogen-based species on the Al_2O_3 and K surfaces.

Accomplishments

- Successfully developed technique to quantify catalyst surface species temporally.
- Identified primary and intermediate surface species on potassium phase, and demonstrated the contribution from the Al_2O_3 support.
- Demonstrated importance of fundamental analysis with H_2O and CO_2 in the feed.
- Presented work at several conferences and industrial seminars, including the 2003 DOE Advanced Combustion Engine Merit Review.

Future Directions

- Conduct quantification experiments for 150-400°C.
- Perform post-reactor gas analysis of products for analysis of catalyst regeneration.
- Investigate the poisoning effects of sulfur.
- Investigate the Group I and Group II elements for their potential use as NO_x adsorber catalysts.

Introduction

A solution to the stricter Environmental Protection Agency (EPA) NO_x emissions regulations has not been fully realized, and research efforts are continuing. A leading solution was first published by Miyoshi *et al* [1] and is based on the ability of alkali and alkaline elements to trap NO_x under lean conditions in the form of a nitrate. The stored nitrate is then reduced by H_2 or hydrocarbons in a brief rich cycle to obtain the benign products N_2 and H_2O. To work effectively, these catalysts require an oxidation component–typically a noble metal like Pt, a storage component–commonly Ba, and a high surface area support like γ-Al_2O_3. Potassium is another element that has shown potential as a storage component [2], especially in conjunction with Ba [3-4]; however, reports on the specific contributions of potassium are scarce.

This study explores the contribution of K during the NO_x storage phase in a Pt/K/Al_2O_3 powder using *in-situ* DRIFTS. When DRIFTS is used in conjunction with CO_2 and NO_2 chemisorption measurements, the nitrate and carbonate spectral features on this catalyst can be quantified in terms of surface loading (µmol adsorbate/m^2 catalyst). Each catalyst component, i.e. γ-Al_2O_3, Pt/γ-Al_2O_3, and K/γ-Al_2O_3, is also studied to better understand its contributing factor. Work is performed in the presence of CO_2 and H_2O to probe the effects of these common exhaust stream components.

Approach

A DRIFTS reactor is used to evaluate surface species on the catalysts: γ-Al_2O_3, 1% Pt/γ-Al_2O_3, 8% K_2CO_3/γ-Al_2O_3, and 1% Pt/8% K_2CO_3/γ-Al_2O_3. Feed streams consisting of NO, NO with O_2, or NO_2 were introduced to the reactor at 250°C to illustrate the effect of the catalyst's constituents on NO_x adsorption. Uptake was monitored throughout the first hour of experimentation and intermittently until saturation of the catalyst was determined.

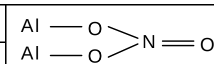
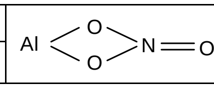
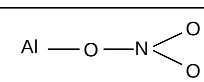
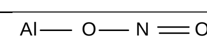
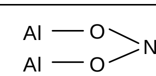
The spectral features from the DRIFTS reactor were calibrated with CO_2 and NO_2 chemisorption, which respectively allowed the quantification of carbon- and nitrogen-based species on the Al_2O_3 and K surfaces. The DRIFTS response is linear (based on Beer's Law); therefore, only one calibration point was necessary for each spectral feature. This process established response factors that relate the area of a DRIFTS peak with a normalized uptake.

After establishing the species that formed during NO_x adsorption and their respective response factors, the effects of CO_2 and H_2O were investigated on Pt/K/Al_2O_3. Adsorption spectra of NO and O_2 were compared to experiments with NO and O_2 and either CO_2, H_2O, or CO_2+H_2O.

Results

The γ-Al_2O_3 support demonstrates NO_x storage at 250°C in the presence and absence of O_2. The nitrates formed initially are primarily bidentate nitrates, with unidentate nitrates dominating as the surface becomes saturated; nitrites are only apparent in the absence of O_2. These adsorbates are illustrated in Table 1 for Alumina and Pt/Alumina. Alumina's ability to store nitrates is limited by its inability to oxidize NO to NO_2, e.g. 0.030 µmole/m^2 adsorbed after 10 minutes with NO+O_2 in the feed versus 0.40

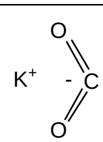
Table 1. Assigned Frequencies (cm^{-1}) for Al_2O_3 and Pt/Al_2O_3

Peak	Infrared Vibration	Structure
bridging bidentate nitrate		
1610	N=O stretch	
1210	NO_2 asymmetric stretch	
chelating bidentate nitrate		
1590	N=O stretch	
1297	NO_2 asymmetric stretch	
unidentate nitrate		
1550	NO_2 asymmetric stretch	
1527	NO_2 asymmetric stretch	
linear nitrite		
1460	N=O stretch	
bridging bidentate nitrite		
1302	NO_2 asymmetric stretch	
1230	NO_2 asymmetric stretch	

μmole/m^2 with NO_2 in the feed. The addition of 1% Pt does not alter the peak locations of the nitrates, and there is no detectable nitrite formation even in the absence of O_2. The oxidation step is significantly enhanced such that the stored nitrate after 10 minutes with NO+O_2, 0.63 μmole/m^2, is comparable to that of NO_2, 0.53 μmole/m^2; however, Pt does not affect nitrate storage capacity once NO_2 has formed, as noted by the similarity of nitrate loading between γ-Al_2O_3 and Pt/γ-Al_2O_3 when flowing NO_2.

After determining the role of the support, K/γ-Al_2O_3 was examined to determine the adsorption behavior of the alkali phase. NO_2^- and NO_3^- ions are the predominant spectral features with alumina nitrates and potassium carbonates also contributing; these features are illustrated in Table 2. Similar to γ-Al_2O_3 without Pt, K/γ-Al_2O_3 adsorbs nitrates more slowly with NO and O_2, 0.14 μmole/m^2 after 10 minutes, than with NO_2 in the feed, 0.23 μmole/m^2. The NO_3^- ion is the primary nitrate adsorbed on Pt/K/Al_2O_3, specifically on K, and the rate of formation is greatly enhanced for both feed combinations; after 10 minutes, 2.8 μmole/m^2 are adsorbed with NO and O_2, and 2.6 μmole/m^2 are adsorbed with NO_2 only. Pt/K/Al_2O_3 was further studied by introducing steam and carbon dioxide into the feed gas with NO and O_2.

Table 2. Assigned Frequencies (cm^{-1}) for Pt/K/Al_2O_3

Peak	Infrared Vibration	Structure
Nitrogen-based adsorbates		
free nitrite ion		
1255	asymmetric stretch	NO_2^-
free nitrate ion		
1380	asymmetric stretch	NO_3^-
1750	combination band	
Carbon-based adsorbates		
carboxylate ion, CO_2^-		
1599	CO_2 asymmetric stretch	
1310	CO_2 symmetric stretch	

Concentrations of 5% H_2O and CO_2 individually reduce the total NO_x storage rate by 16% and 44%,

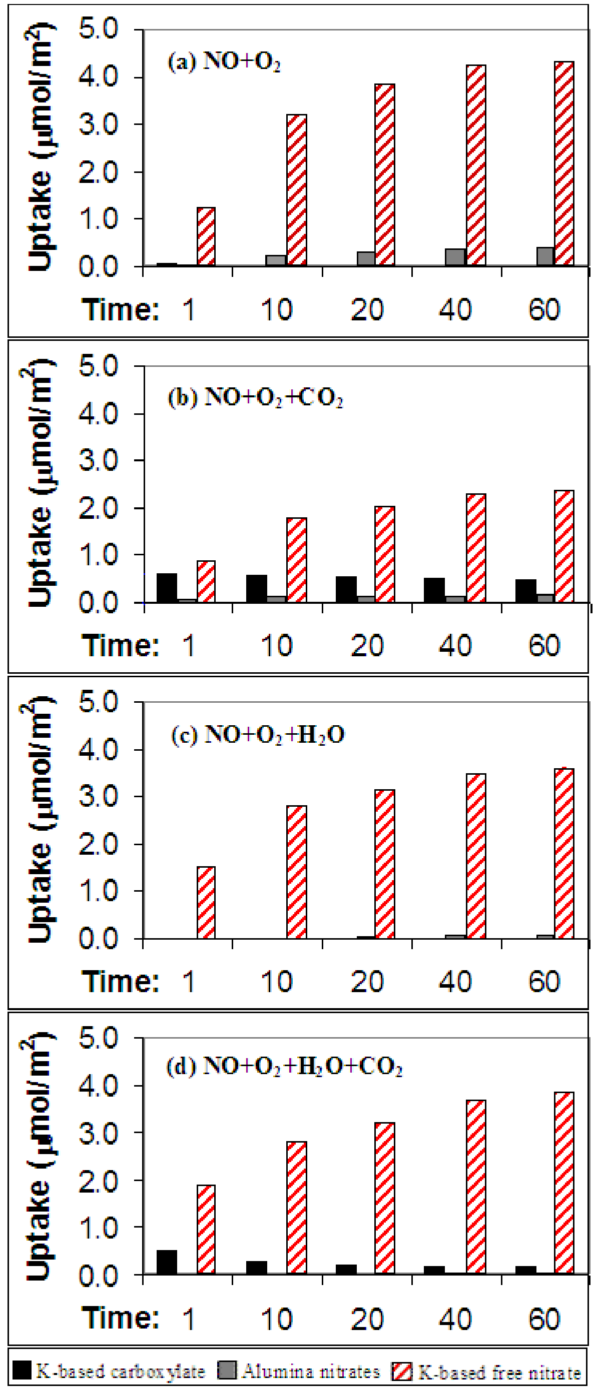


Figure 1. Temporal NO_x Uptake on Pt/K/Al_2O_3 at 250°C with (a) 300 ppm NO and 12% O_2; (b) 300 ppm NO, 12% O_2, and 5% CO_2; (c) 300 ppm NO, 12% O_2, and 5% H_2O; and (d) 300 ppm NO, 12% O_2, 5% CO_2, and 5% H_2O. Flow rate was 50 sccm with N_2 as the balance.

respectively, and when both CO_2 and H_2O are in the feed, the nitration rate decreases by 16%. These results are summarized in Figure 1. CO_2 immediately forms a carbonate on potassium, 0.61 µmole/m^2 after 1 minute, which only decreases by 19% during the first hour. Flowing only steam with NO and O_2 shows a dramatic increase in the hydroxyl stretching region, and while only decreasing the nitrate formation marginally on the K-phase, the Al_2O_3-phase nitrates are greatly mitigated—0.006 µmole/m^2 after 10 minutes compared to 0.12 µmole/m^2 without water. The combination of H_2O and CO_2 in the feed shifts the nitrate/carbonate equilibrium towards nitrate formation, and the carbonate feature decreases by 69% after an hour.

Conclusions

- Technique successfully developed to quantify dynamic catalyst surface species on both potassium and alumina surfaces.
- The primary stored nitrates are potassium-based NO_3^- ions with an ionic nitrite, NO_2^-, as the probable intermediate; covalently bound nitrates exist on alumina and are significantly abundant after 10 minutes of adsorption in the absence of H_2O.
- H_2O mitigates the deleterious effect CO_2, and only 11% reduction is observed, which illustrates the importance of having both CO_2 and H_2O in the test feed stream.

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2. "Quantified in-Situ NO_x Adsorption on Pt/K/γ-Al_2O_3 and the Effects of CO_2 and H_2O", Todd J. Toops, D. Barton Smith, William S. Epling, Jim E. Parks, William P. Partridge, in preparation for submission to Applied Catalysis B.
3. "Quantified in-Situ DRIFTS Analysis of NO_x Adsorption on Pt/K/Al_2O_3 in the Presence of CO_2 and H_2O", presented at the 18th North American Meeting of The North American Catalysis Society, Cancun, Mexico, June 2003.
4. "NO_x Adsorption on Pt/K/$A1_2O_3$ and the Quantitative Effects of H_2O and CO_2", Todd J. Toops, D. Barton Smith, William S. Epling, Greg Campbell, Jim E. Parks, and William P. Partridge, presented at the Third Joint Meeting of the U.S. Sections of The Combustion Institute, Chicago, IL, March 2003.

III.K. Plasma-Facilitated Lean NO_x Catalysis for Heavy-Duty Diesel Emissions Control

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DOE Technology Development Managers: Kevin Stork, Gurpreet Singh

Objectives

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

Approach

- Develop active catalyst formulations for plasma-facilitated lean NO_x operation
- Design and test concepts for on-board reductant production
- Investigate interplay between catalyst mixtures and reductant-catalyst systems

Accomplishments

- Completed investigation of silver loading effects on reduction efficiency for catalyst-reductant combinations in preparation for FY 2004 engine testing
- Demonstrated preliminary efficacy for NO_x reduction based on reformer-assisted lean NO_x catalysis
- Demonstrated broad temperature coverage using catalyst mixtures

Future Directions

- Evaluate catalyst combinations under transient conditions
- Continue investigation of on-board production of reductants from fuel via partial oxidation reforming
- Prepare full-scale catalysts and assemble full-scale plasma reactor
- Conduct full-scale transient engine test

Introduction

Non-thermal plasma-assisted catalysis (PAC) is an effective method for reducing NO_x emissions in diesel exhaust; however, further advances in plasma system efficiency and catalyst development are needed for vehicle applications. Research in FY 2003 has focused on an extensive set of laboratory experiments, process engineering, and formulation to prepare for transient engine testing in FY 2004. Formulation has focused on Ag-doped γ-alumina and, in particular, on optimizing this material for fuel-type hydrocarbons. We have also continued two high profile tasks in the Cooperative Research and Development Agreement (CRADA). The first is a catalyst exchange with the Low Emissions Technologies Research and Development Partnership (LEP) CRADA, where mixtures of light-duty and heavy-duty catalysts are used to broaden the applicable temperature range of the PAC technology. The second activity is based around plasma reformation (partial oxidation) of hydrocarbons in order to produce oxygenates and other more reactive molecules for NO_x aftertreatment catalysis.

Approach

Plasma-assisted catalysis for NO_x reduction is a two-step process. First, the exhaust is treated in a non-thermal electrical discharge. Such treatment facilitates the conversion of NO to more reactive NO_2. In addition, a portion of hydrocarbon that is added to the stream is partially oxidized to form oxygenate species. In the second step, the plasma-treated exhaust is passed over a lean NO_x catalyst. Plasma treatment is beneficial for two reasons: (i) on many catalysts, NO_2 is more easily converted to N_2, and (ii) partially oxidized hydrocarbons participate in NO_x reduction chemistry more readily than alkanes or alkenes.

An aftertreatment system involving a non-thermal plasma reactor in conjunction with a catalytic reactor is being developed to reduce NO_x emissions from heavy-duty engines. In this endeavor, a partnership between Pacific Northwest National Laboratory (PNNL) and Caterpillar Inc. has been formed. PNNL is responsible for plasma system design, process engineering, plasma bench testing, and catalyst development and characterization. Caterpillar is responsible for catalyst development and characterization, lean-NO_x bench testing, and engine cell testing.

In FY 2003, efforts focused on continuing preparation for a transient engine demonstration in FY 2004. Silver-doped γ-alumina was optimized for fuel hydrocarbon reduction. Catalyst combinations were further examined to obtain broad temperature coverage in engine testing. Limited transient measurements on this two-catalyst system were completed to assess how the catalyst system might perform in transient operation. Lastly, hydrocarbon reformation was attempted on a separate stream from the exhaust to determine whether fuel penalty could be reduced by creating oxygenates prior to injection of hydrocarbon into the exhaust stream.

Results

In FY 2002, PNNL completed a set of experiments to determine how optimal silver loading changes for γ-alumina catalysts when the hydrocarbon speciation in the exhaust is altered. The general trend showed that silver loading increased with a high thermal stability of the hydrocarbon. This is expected because higher metal loading results in a great degree of hydrocarbon activation by the catalyst. An optimal loading is obtained for a given hydrocarbon due to the balance between activation for NO_x reduction and the tendency of the catalyst to burn hydrocarbon if the metal loading is too high. In FY 2003, we focused on the effect of catalyst aging on this trend. Earlier work on the In_2O_3/γ-alumina system showed that sulfur can impact optimal metal loading. In general, slightly higher metal loading is needed on aged catalysts to obtain optimal operation. For example, with propene, optimal loading for the aged system is above 2%, whereas with the fresh catalyst system, the optimum is between 1 and 2%. We are currently wrapping up these experiments and preparing a report of the investigation for *Appl. Catal. B.*

Work in FY 2003 also involved continuing collaboration with the LEP CRADA in the area of catalyst combinations. Ordering of the catalysts was reported in FY 2002 as a critical feature to obtain the highest NO_x reduction performance. This year, data collected at Ford Research Laboratories was used to understand the mechanism. Figure 1 shows a trace of formaldehyde level over the optimal catalyst

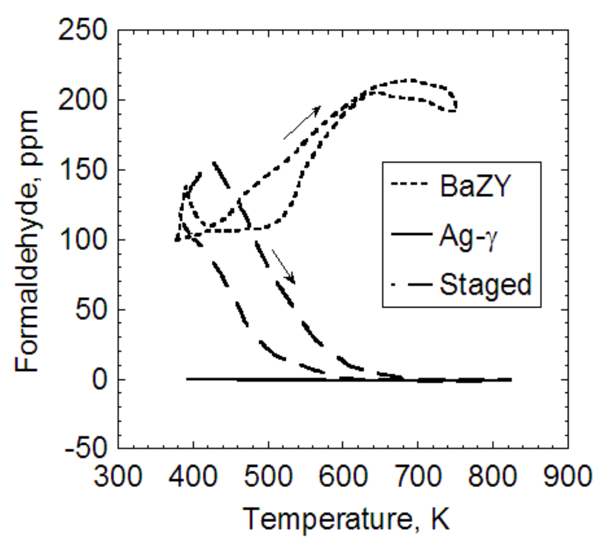

Figure 1. Formaldehyde concentration exhausted from the catalyst as a function of temperature. Staged indicates Ba/zeolite Y in front of γ-alumina. Arrows indicate direction of increasing temperature for thermal cycling of the catalyst at 10 K/min.

configuration. Notice that if Ba/zeolite Y is used alone, formaldehyde is produced in the catalyst. Using a combination of this catalyst preceding Ag/γ-alumina, formaldehyde is utilized to a much greater degree. Therefore, the principle mechanism by which this system is most efficient is hydrocarbon utilization, and the catalysts must be ordered in this manner to achieve the lowest fuel penalty. This combination was also used to examine transient effects in the system. Data are shown in Figure 2, where NO_x reduction is plotted versus temperature. Cycle average NO_x conversion was 70%, but notice the large spike of NO_x that desorbs from the catalyst during heating at low temperature. This presents a challenge for light-duty operation, as the catalyst tends to store NO_x below about 180^{o}C. For very cold transient cycles, exhaust heat-up can cause large NO_x slip through the system. For heavy-duty operation, where temperatures are expected to remain above 200^{o}C, the storage phenomenon is expected to be less of a concern.

The last area of emphasis in FY 2003 was in the area of plasma reforming of fuel. Previous work in this program and the LEP program indicate that oxygenated species have the capability of reacting effectively with NO on lean NO_x catalysts; therefore, if fuel hydrocarbons can be converted to oxygenates, it is possible that the entire exhaust would not need plasma treatment. A schematic of such a *reformer-facilitated* lean NO_x approach is shown in Figure 3. Here, a small side-stream of fuel is plasma-treated prior to injection upstream of the catalyst. Initial results using this technique are shown in Figure 4. Plasma reformation of the hydrocarbon is clearly beneficial over a wide temperature range. When this strategy is applied to the dual catalyst system, we expect much higher conversions across the temperature range of interest for heavy-duty emissions control.

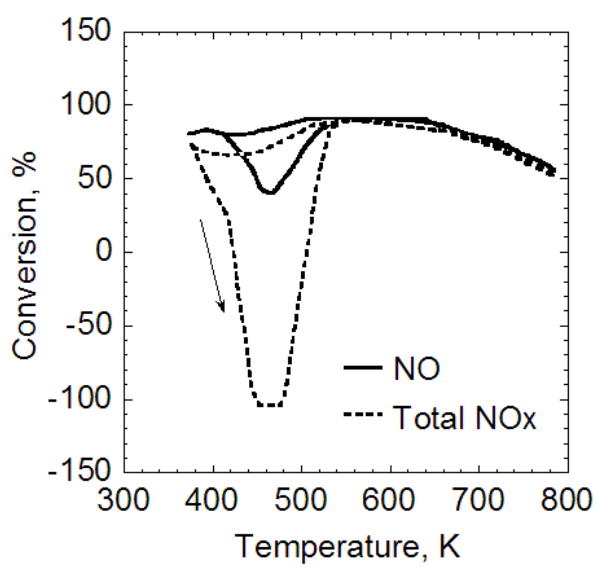

Figure 2. NO_x conversion as a function of temperature for the staged catalysts. Arrows indicate direction of increasing temperature for thermal cycling of the catalyst at 10 K/min.

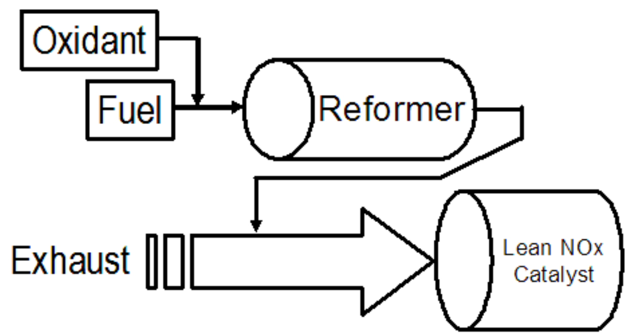

Figure 3. Schematic of the reformer-assisted lean NO_x approach.

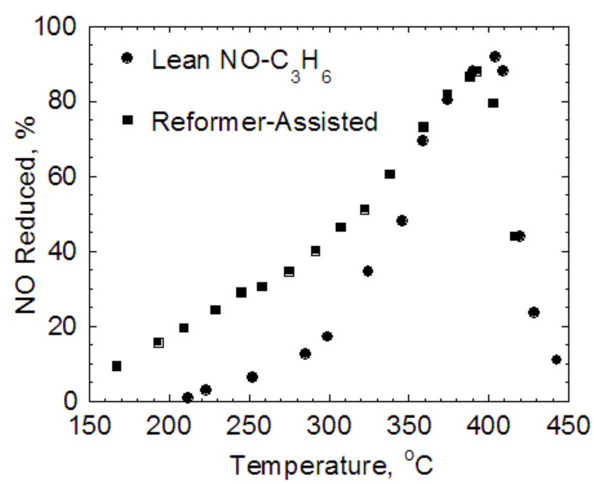

Figure 4. NO_x conversion as a function of temperature for traditional lean NO_x and reformer-facilitated lean NO_x catalysis.

Conclusions

- Silver loading on γ-alumina must be increased to obtain maximum conversion with fuel hydrocarbons.
- Catalyst combinations offer broad temperature coverage, particularly when staged.
- Transient operation of staged catalyst showed significant NO_x storage between 100 and 180°C. This could greatly impact transient performance on light-duty engines but should not be a significant issue for heavy-duty performance.
- Reformer-assisted lean NO_x catalysis was demonstrated. Initial results are promising, but additional effort is needed to approach plasma-catalysis performance.

FY 2003 Publications/Presentations

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9. CL Aardahl (2003) Plasma-facilitated NO_x reduction for heavy duty diesel emissions control. Presentation given at the DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation, May 2003, Argonne National Laboratory, IL.
10. CL Aardahl, JW Hoard, PW Park, CHF Peden (2003) ENV-17: Combination of Ba/Y zeolite and Ag/γ-alumina catalysts for reduction activity over a broad temperature range using plasma-facilitated lean NO_x catalysis. Presentation given at the 18th North American Meeting of the North American Catalysis Society, June 2003, Cancun, Mexico.

Special Recognitions & Awards/Patents Issued

1. A Federal Laboratory Consortium (FLC) Award was awarded to this work in combination with efforts at PNNL on a CRADA program with LEP and a former program with Delphi.

III.L. Clean Diesel Engine Component Improvement Project

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Objectives

- Design, develop and demonstrate components that can be integrated into a non-thermal plasma (NTP) aftertreatment system (Figure 1) for removal of over 90% of the NO_x from the exhaust of a 60-kW diesel engine (Figure 2).
- Certify the performance of the NTP components on a bench test rig (Figures 3,4,5).
- Design and build a NTP system for a 60-kW engine that can achieve over 90% NO_x reduction.
- Conduct third party test of the 60-kW NTP system.

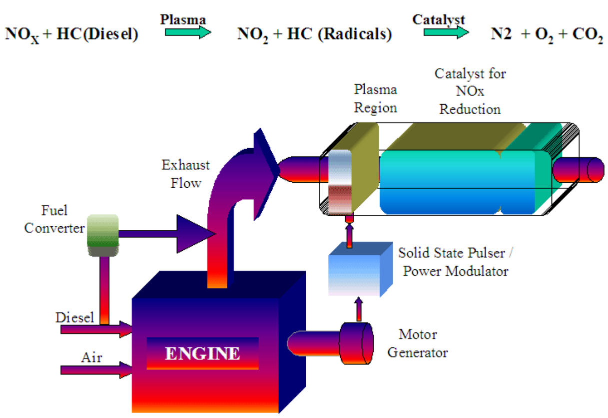

Figure 1. Plasma Assisted Catalyst System Schematic.

Figure 2. NTP System for 60-kW Diesel Engine

Figure 3. Advanced Noxtech Solid State Pulser

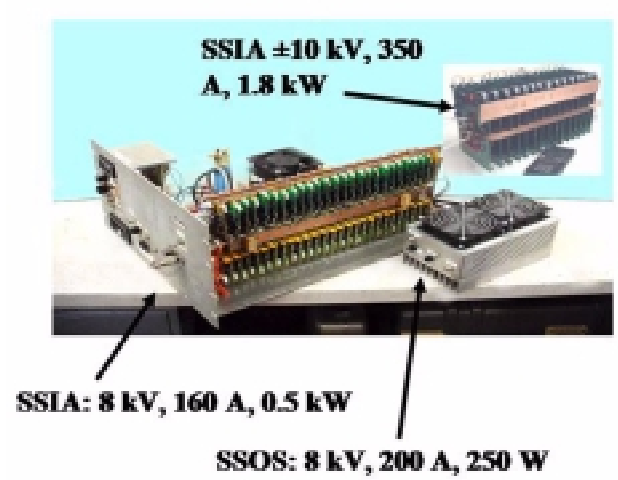

Figure 4. Solid-State Pulsers

Approach

- Design, build and demonstrate components required to fabricate a NTP system capable of successfully removing over 90% of the NO_x from the exhaust of a 60-kW engine. Make significant modifications and improvements in the NTP process to improve the practicality, cost and operating performance of the NTP system.
  - Redesign the plasma reactor (smaller and lower power) to go outside the exhaust to generate ozone and decompose diesel fuel for injection into the exhaust to form NO_2 and hydrocarbon fractions.
  - Complete the design and demonstration of a small, efficient, and tunable solid state pulser in conjunction with our industrial partners.
  - Design, build and demonstrate an advanced plasma reactor to go into the exhaust of the engine for NO_x reduction. This reactor would be more efficient, easier to fabricate and more cost-effective to build than the coaxial reactor.
  - Design, build and demonstrate practical (size, cost and performance) plasma and catalytic fuel converters using plasma and/or catalytic cracking to produce an optimum reductant from diesel fuel.
  - Work with Alcoa, Sud-Chemie and Catalytic Solutions to improve the surface availability and surface selectivity, incorporate use of monoliths, and enhance catalyst composition to reduce the volume of catalyst needed and minimize/eliminate by-product emissions.
- Evaluate the improved bench-scale components individually and as an integrated system on a pilot rig using actual diesel exhaust to determine their performance (NO_x reduction, parasitic requirements, operating range, etc.).
- Use the designs and data from the bench tests and test components to design and build a NTP unit capable of reducing over 90% of the NO_x from the exhaust of a 60-kW diesel engine.

Figure 5. Plasma Reactor for 60-kW Diesel Engine

Accomplishments

- Major improvements (costs, ease of fabrication, efficiency, operating temperature range and NO_x reduction capability) were made in the design and performance of the components and integrated NTP system that produced over 90% NO_x reduction for diesel exhaust.
- Unique and creative enhancements and modifications were made to and demonstrated (on a bench scale) on the NTP process that resulted in a major improvement in practicality and performance while maintaining over 90% NO_x reduction.

- The plasma system was moved out of the exhaust stream, reducing its size and power consumption significantly. A slipstream from the exhaust was passed through this device to generate ozone and active reductants from diesel fuel injection and reinjected into the exhaust for NO_x reduction.
- A catalytic cracker was demonstrated on a bench scale that could form partially oxidized hydrocarbon species that were injected into the exhaust to produce high levels of NO_x reduction over the NO_x catalyst. This eliminated the need for a plasma reactor completely, significantly reducing the system's complexity and cost.

- A bench-scale, integrated NTP system demonstrated excellent performance capability using real diesel exhaust: over 90% NO_x reduction; 2.5% (of engine output) parasitic loss; operating temperature range of 225°C - 500°C; no loss of activity from fuel sulfur poisoning; and the ability to generate active reductant species using a catalytic cracker.
- A NTP system (with the exception of a NO_x catalyst) capable of treating the exhaust from a 60-kW diesel engine was fabricated. The planned third party test could not be completed because the catalyst supplier could not provide sufficient quantities of the proven NO_x catalysts (from the bench tests) in time to perform this test.

Future Directions

- Complete the 60-kW engine third party NTP test after acquiring sufficient quantity of catalyst from supplier.
- Use the data generated from designing and testing the 60-kW integrated NTP unit and its components to design, build and evaluate a NTP unit capable of reducing over 90% of the NO_x from a 275-hp high-speed diesel engine.
- Continue to improve the performance, cost, ease of fabrication, operating range and efficiency of the NTP system components and integrated system.

Introduction

Emission standards in the U.S. will require reduction of emissions from light- and heavy-duty diesel powered vehicles by as much as 90% from current levels in the 2005-2010 time frame. Achieving these levels with acceptable durability will be very difficult for this industry. Catalyst poisoning, thermal cycling and the need for generation of a practical reductant make the performance and life of NO_x adsorbers and lean NO_x catalysts problematic. Non-thermal plasma (NTP) is a promising alternative to exhaust aftertreatment for reduction of NO_x from diesel exhaust since it does not have the sensitivity to fuel sulfur levels and operating temperature excursions that is exhibited by the traditional catalyst-based systems.

Approach and Results

Noxtech has developed and demonstrated (at its facilities) the technical viability of its earlier design of a non-thermal plasma system (NTS) with the cooperation and support (technical and financial) of the DOE. That NTP system, although demonstrating a very high level of NO_x reduction (94%) for diesel exhaust, had several practical problems and issues that needed resolution and improvement in order to be considered a viable option for commercial application. During this project, Noxtech successfully implemented the improvements in component/process design and performance to enhance the NTP system's commercial potential.

The approach or path Noxtech adopted to achieve its primary objective of demonstrating its NTP system in a practical fashion on a 60-kW diesel engine was to first resolve the problems and issues with the components and NTP process from its previously demonstrated system:

- **Reductant supply system:** Most of our prior work used thermally cracked and fractionated diesel fuel as the reductant. Over a period of time, the heavy hydrocarbons in cracked diesel fuel coated the NO_x catalyst, causing a loss of activity. Noxtech resolved this issue by formulating and demonstrating cracking catalysts from one of its catalyst suppliers that would produce partially oxidized reductants that achieved high levels of NO_x reduction with and without the use of an in-line plasma reactor. In addition, Noxtech built a compact external plasma reactor that would produce partially oxidized hydrocarbons from diesel fuel as well as ozone for NO_2 conversion.

- **NOx catalysts:** Noxtech has demonstrated excellent NO_x reduction performance using unique NO_x catalysts wash coated onto monolithic substrates. However, it has been discovered that the wash coat process was poorly understood and produced active catalysts in only about 50% of the prepared catalysts. In addition to addressing the monolith coating issue, there is a need and opportunity to enhance the performance (efficiency, effective temperature, selectivity, etc.) through the manipulation of the surface area, pore structure and dopant levels of the base catalyst. It was decided to work with the pure catalyst spheres instead of the monoliths to achieve these objectives.

Noxtech, working with its catalyst suppliers, formulated and demonstrated a significantly improved NO_x catalyst that would produce over 90% NO_x reduction under these conditions:

- 50,000 hr^{-1} space velocity
- 225→550°C
- sulfur tolerance at over 200 hours of operation
- nominal by-product formation
- customized response to type reductant used and the form of NO_x being treated

- **Pulser:** Noxtech had already jointly designed and demonstrated a solid state pulser/driver for its plasma reactor. Its efficiency and size needed to be improved further. A new design was developed for this project that would reduce the size (cost) by 60%. However, funds were not available to complete this unit. Noxtech planned to use the previously demonstrated unit for the 60-kW engine third party demonstration.

- **Plasma reactor:** The existing Noxtech coaxial corona plasma reactor will be used in conjunction with the European-built solid state pulser for the demonstration test. This system is not as efficient or effective as the more advanced plasma reactor that has been designed to match the advanced pulser. However, the advanced plasma reactor and solid state pulser will not be available for this test since Noxtech did not have the funds to complete the fabrication of the advanced pulser.

Noxtech integrated and pre-tested the improved components previously designed and demonstrated individually, on a bench-scale test facility. The bench-scale NTP system functioned reliably and achieved the high levels of NO_x reduction specified for the 60-kW engine demonstration test.

Noxtech designed and built an NTP system for the 60-kW engine third party test. However, the NO_x catalysts needed for this test could not be supplied in the quantity needed in time to perform the demonstration test this year. In any event, Noxtech had selected an outside testing company to conduct performance/evaluation testing of its NTP system for the removal of NO_x from the exhaust of a 60-kW diesel generator powered by a mid range "B" series Cummins Engine. These tests would have been conducted at two steady state load points that cover the load and exhaust temperature ranges for this engine. Thorough measurements would have been made of all operating parameters for this system, including exhaust emissions, temperatures, reductant flows and engine loads (Figure 6). Specifically, NO_x would have been measured by chemiluminescence, hydrocarbons using a flame ionization detector (FID)/single beam Fourier transform infrared (FTIR) spectrometer, CO by non-dispersive infrared spectrometer (NDIR) and O_2 by polaragraph. The Hoard test would be conducted using an oxidation catalyst to test the treated exhaust downstream from the catalyst for false positive NO_x reduction as a result of potential complexing of NO_x with hydrocarbons during the NTS treatment process. The demonstration test is

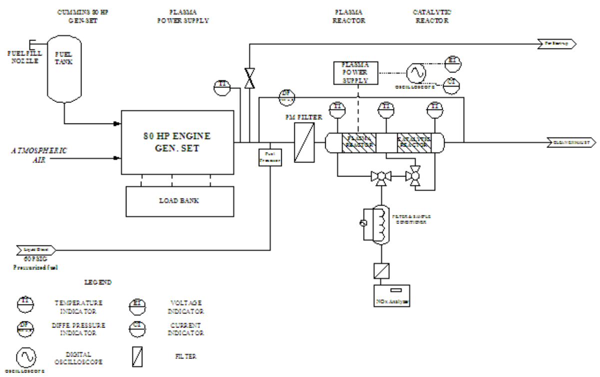

Figure 6. 6.60-kW Engine Test Schematic

not scheduled to be performed until 2004, after receipt of the NO_x catalyst.

Conclusions

It is clear that the NTP system is a unique NO_x aftertreatment system for diesel engines. It has, based on our bench tests, the capability to achieve over 90% NO_x reduction in diesel exhausts without the issues associated with the other systems being developed for this purpose. If the needed resources are devoted to this technology expeditiously, it is anticipated a superior NO_x reduction system for mobile diesel-powered vehicles will be available within 1 to 2 years.

FY 2003 Publications/Presentations

1. "Noxtech's Plasma-Assisted Catalyst System Development and Demonstration", presented at the U.S. Department of Energy 9th Diesel Engine Emissions Reduction (DEER) Conference, August 24-28, 2003.

III.M. NO_x Sensor for Direct Injection Emission Control

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Subcontractors: Delphi Delco, Kokomo, IN; SRI International, Menlo Park, CA

Objectives

- Develop an electronics control circuit for the NO_x sensor.
- Develop the packaging for the electronic controller.
- Develop the sensing element structure based on integrating zirconia and alumina ceramics and planar element technology.
- Develop the interconnection method to carry power and signal to and from the NO_x measurement device.
- Develop the necessary materials and process refinements in support of the ceramic sense element.

Approach

- Use alumina and zirconia ceramic tapes and thick film screen-printed pastes to form the necessary control and measurement cells. Integrate the heater on the co-fired substrate.
- Initiate development using simple configuration test samples and coupons. Continue to evolve the design and test samples into a fully functional NO_x measurement sense element.
- Confirm the operation of the sense element using bench and engine testing.
- Use set-based concurrent engineering (SBCE) to develop at least two different techniques to interconnect the power and signal wires to the sense element substrate. Use accelerated engine and environmental testing to establish the optimum interconnection approach.
- Use existing sensor packaging technology to house and protect the sense element.

Accomplishments

- Designed and built an initial NO_x sensor development breadboard controller.
- Tested the NO_x decomposition of various concentrations of doped Platinum/Au electrodes and determined initial stability.
- Developed a 4-cell sense element based on a NO_x function model.
- Developed control point parameters for the individual cells in the sense element.
- Evaluated the initial NO_x cell sense elements.

- Evaluated sensor response capability for continuous mode and pulse mode measurements.
- Evaluated cell performance durability with long-term diesel exhaust exposure.
- Successfully built 4-cell sense elements without delaminations and micro defects using inert atmosphere for de-bindering.
- Successfully demonstrated multiple direct ultrasonic welding and mechanical connection technologies.

Future Directions

- Measure sense element performance using continuous and pulse mode control techniques.
- Continue refinements in the separation electrode and evaluate long-term stability.
- Eliminate Au contamination or design around it.
- Develop an electronic controller for pulse mode operation.
- Determine the electrode and design parameters that produce fast response under pulse mode control.
- Select the optimum interconnection technique and test for durability.
- Recommend packaging options for electronics.

Introduction

This project continues to develop the remaining technologies needed to deliver a robust NO_x sensor for use in closed-loop control of NO_x emissions in lean-burn engine technologies (particularly CIDI engines). At least two applications for NO_x sensors have been identified: (1) for engine-out control, requiring a high NO_x range of zero to 1500 ppm NO_x; and (2) for aftertreatment control and diagnostics, requiring a low NO_x range, less than about 100 ppm NO_x.

This activity builds on existing and developing Delphi technology in multi-layer and exhaust sensor ceramics, as well as work performed under a separate CRADA with Pacific Northwest National Laboratory (PNNL). This project is administered by Electricore, Inc., a 501 c 3 advanced technology development consortium.

Approach

The Delphi-led team will leverage the electrochemical planar sensor technology that has produced stoichiometric planar and wide range oxygen sensors as the basis for development of a NO_x sensor. Zirconia cell technology with an integrated heater will provide the foundation for the sensor structure. The re-use of proven materials and packaging technology will help to ensure a cost-effective approach to the manufacture of this sensor.

The electronics technique and interface is considered to be an area where new strategies need to be employed to produce higher signal-to-noise (S/N) ratios of the NO_x signal with emphasis on signal stability over time for robustness and durability. Both continuous mode and pulse mode control techniques are being evaluated.

Packaging the electronics requires careful design and circuit partitioning so that only the necessary signal conditioning electronics are coupled directly in the wiring harness, while the remainder is situated within the electronic control module (ECM) for durability and cost reasons.

The sense element is based on the amperometric method utilizing integrated alumina and zirconia ceramics. Precious metal electrodes are used to form the integrated heater, as well as the cell electrodes and leads. Inside the actual sense cell structure, it is first necessary to separate NO_x from the remaining oxygen constituents of the exhaust without reducing the NO_x. Once separated, the NO_x will be measured using a measurement cell. Development or test coupons have been used to facilitate material selection and refinement, as well as cell, diffusion barrier, and chamber development.

The sense element currently requires eight interconnections. To facilitate a robust, durable connection, at least two techniques are being evaluated using the SBCE approach. One technique will be mechanical, while the second will be a metallurgical connection. Due to the anticipated low NO_x signal levels, there may also be a need to “passivate” the lead interconnections to obtain the required isolation and durability. Materials and process refinements continue to play an important role in the development of this sensor and are integrated into this project accordingly.

Results

A NO_x sensor development controller was designed and constructed and is shown in Figure 1. This controller operates each of the sense elements (4 cells) and the heater, as well as the necessary interface and diagnostics of the sensor. The controller has been evaluated and functions according to plan, but continues to undergo small refinements to improve its capability and performance.

A key feature of the NO_x sensor is the requirement for pumping oxygen without reducing the NO_x component in diesel or automotive exhaust gas. Figure 2 shows the NO_x decomposition performance of pure platinum and platinum electrode materials doped with increasing amounts of Au. The doped electrodes delay or prevent NO_x decomposition even at elevated temperatures compared with the pure platinum electrode. These materials were re-tested after aging at temperatures as high as 950°C for 96 hours. The best electrodes were those processed in a slightly reducing atmosphere; they demonstrated excellent stability throughout the aging experiment.

The 4-cell functional model (Figure 3) provided the foundation for a newly designed 4-cell NO_x sensing element. This model illustrates 4 functional cells and the necessary features for this sensor to operate. There is a primary oxygen pump cell and a reference cell to control this rough pump located in the first chamber. A small diffusion path connects the first chamber to a second chamber. Inside the second chamber exists a secondary or finish oxygen pump and the NO_x measurement cell. Air channels provide an oxygen reference and remove the pumped oxygen from the chambers. The functional diagram

Figure 1. NO_x Sensor Development Breadboard Controller

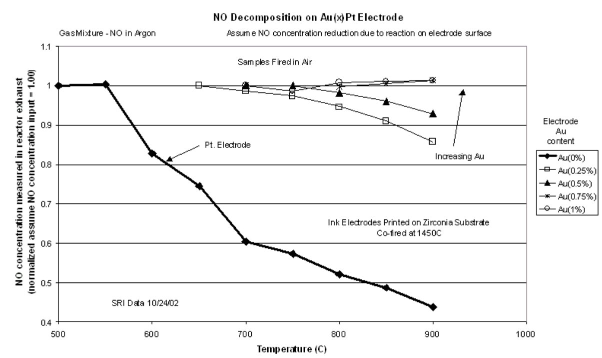

Figure 2. NO_x Decomposition vs. Temperature

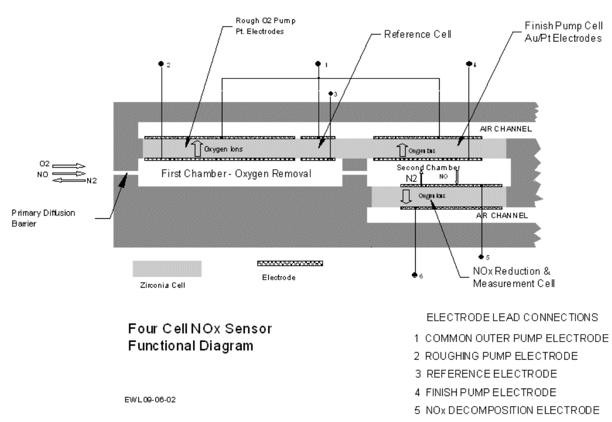

Figure 3. NO_x Four Cell Functional Diagram

is very useful for discussing the basic function of the sense element but is not meant to indicate the actual design of the sense element.

Previous work under this contract indicated that doping the platinum electrodes with Au severely diminishes the oxygen pump capacity of the electrode, thus rendering it unusable to perform the required separation of oxygen and NO_x. Figure 4 shows the performance of a cell controlled in such a way that it pumps oxygen without reducing NO_x. It is controlled by monitoring the reference cell and operating the rough pump at a voltage condition where little or zero NO_x is reduced. The control point is shown on the chart by the maximum amount of oxygen pumped without reducing NO_x (proposed control point). Using this technique, most of the oxygen can be removed without the NO_x being reduced. The balance of oxygen and NO_x is free to continue to the second chamber, where the finish pump electrode can pump the remaining oxygen without reducing the NO_x.

Figure 5 shows the initial performance of a NO_x measurement cell. NO_x reduction current is plotted versus applied voltage. The NO_x levels were varied between 0 and 500 ppm NO. The NO_x measurement can be obtained at a cell operating voltage of about 750 mV and is directly proportional to the NO_x levels. Continued refinements to the NO_x electrodes and element design and control parameters should allow for improvements in current limiting of the cell, thus increasing sensor resolution and accuracy. To achieve these initial results, this data was collected without heat-treating the sense element. In the past, heat-treatment of the sense element has dramatically improved the finish pump NO_x selectivity by moving a concentration of Au to the surface. Therefore, the initial finish pump separation was poor, but the NO_x measurement cell was performing adequately. After heat-treating the sense element, the finish pump cell performance was markedly improved. A problem was discovered in that the NO_x measurement cell performance was severely degraded due to contamination by Au. It was determined that some of the Au from the finish pump electrode had migrated to the NO_x cell during sintering. The Au came to the surface and degraded the performance of the cell only after the heat treatment. This issue needs to be resolved either by material, process, or design changes.

Sense elements were tested in both continuous and pulsed modes. Sensor response rates were highly variable under pulsed mode over a number of sensor builds, designs, and configurations. It is believed that sensor electrode parameters such as concentration, thickness, surface area, porosity, etc., are responsible for this variation. It is estimated that the response for a single pulse needs to approach that of about 50 mS for this technique to be useful. The best combination to date has been measured at ~100 mS.

The 4-cell functional diagram shown earlier is only part of the sense element design. In addition to the four cells, a heater is incorporated into the current sense element design. The structure is made by screen-printing the individual features for each layer of the device (leads, electrodes, diffusion channels, chambers, and air channels), followed by laminating the layers together with pressure and temperature.

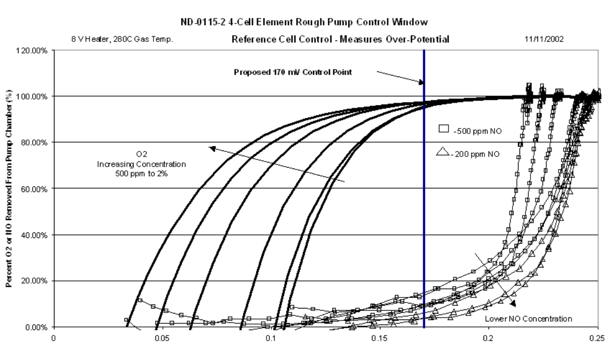

Figure 4. NO_x Rough Pump Control Window

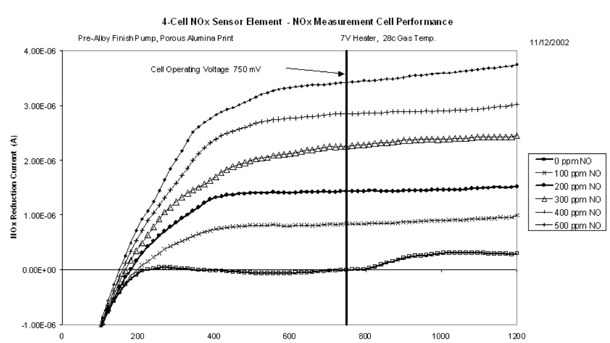

Figure 5. NO_x Measurement Cell Initial Data

The individual sense elements are then singulated and sintered. During the sintering operation, the binders and organics are first removed, and then the component undergoes densification during the remainder of the sintering cycle. Figure 6a indicates the difficulty of sintering such a complex structure. Lengthwise delaminations are easily seen on the sense elements pictured. This is a result of excessive stresses during the de-bindering (initial stages of sintering) of the component. A study of the weight loss of the sense element using therma-gravimetric analysis indicated that the organics were evolving at a much lower temperature and higher percentage then originally thought. Effective solutions were either to significantly extend the binder removal period by carefully decreasing the rate of temperature rise in the high loss regions, or to de-binder in an inert atmosphere such as Argon to avoid combustion processes that cause high stress on the part. It was found that to achieve success with a slower rate of de-bindering was counterproductive, since it increased the overall sintering cycle by days. This technique was also only useful in removing the gross delamination flaws. Many of the micro defects were still present in the device. De-bindering first in Argon, followed by air, minimized the stresses involved and produced defect-free components (Figure 6b). Not only were the gross delaminations eliminated, but micro flaws in the product were also reduced or eliminated. The parameters of this process are being refined and optimized to be production capable.

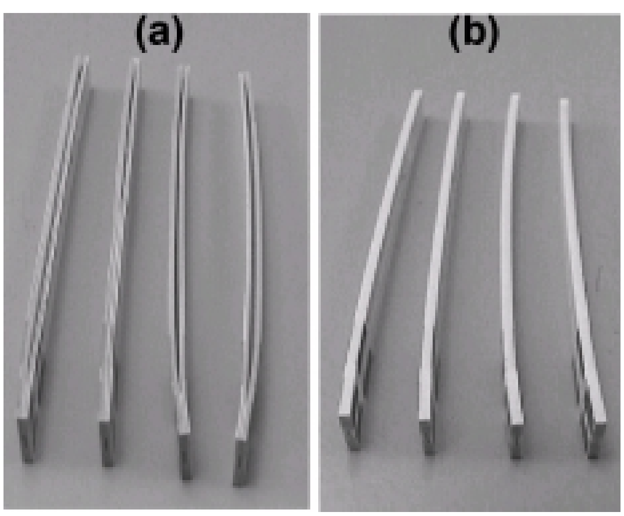

Figure 6. Sense Elements Showing Lengthwise Delamination (A) and No Delamination (B)

Interconnection has progressed with both of the SBCE designs. The mechanical interconnection design has been tested and successfully passed an accelerated 150,000 mile durability test. The direct ultrasonic welding process has continued to develop and demonstrated that multiple welds can be achieved with this technique (Figure 7). But the complexity of this process and tooling makes it highly unlikely as a production solution. An alternative interconnection technique is being evaluated as a backup to the mechanical approach. Brazing of terminals to the platinum pads is a technique that is being developed. The interconnection terminal design is complete, and braze materials are being selected for evaluation.

Conclusions

- NO_x sense elements have been designed, fabricated, sintered, and tested. Each of the sensor cells was tested for its performance compared to the design intent. Many of the features and cells of the element are operating as intended. Improvements are required in the finish pump electrode, Au contamination inside the NO_x measurement chamber must be eliminated, and consistent and faster response time using pulse mode is needed.

- A NO_x sensor development controller was designed, built, and tested. The basic functionality of the controller has been met. The controller development continues to evolve with small changes as needed.

- A much higher degree of control of the de-bindering of the complex sense element structure

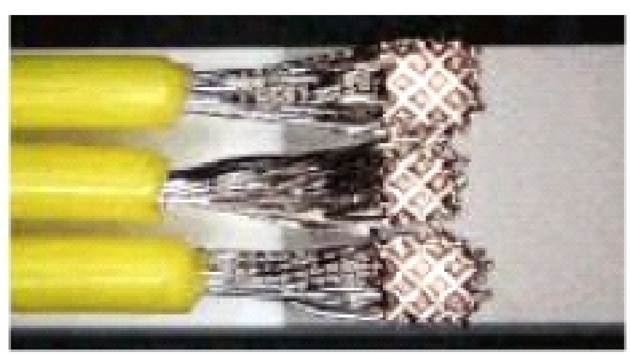

Figure 7. Direct Ultrasonic Welding Of Multiple Wires

is required to achieve a defect-free product. This has been achieved by the addition of an inert atmosphere gas during the early stages of sintering. The inert gas serves to prevent combustion processes from reaching thermal run-away or extreme stress conditions.

- Continued refinements are being made to materials (especially electrode) and interconnections to support the NO_x sense element development.

III.N. Small, Inexpensive Combined NO_x and O_2 Sensor

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DOE Technology Development Manager: Roland Gravel

Subcontractors:
MRA Laboratories, Adams, MA
RJS Electronics, Columbus, OH

Objectives

- Demonstrate miniature, amperometric, inexpensive NO_x sensor body in the form of a multilayer ceramic capacitor.
- Demonstrate microprocessor-based measuring electronics.
- Supply sensors and measuring electronics for testing at Rosemount Analytical and Visteon, Inc.

Approach

- Measure NO_x sensing characteristics of a matrix of sensor bodies manufactured from stabilized zirconia in the form of multilayer capacitors with porous, Rh-based electrodes.
- Determine optimum electrodes, operating temperature range, and long-term stability of NO_x sensor bodies.
- Design and breadboard microprocessor-based measuring electronics and characterize.
- Prepare sensors and measuring electronics and supply these to Rosemount and Visteon, Inc. for testing.

Accomplishments

- Capacitor-type sensor bodies successfully manufactured with two types of porous Rh-based electrodes.
- NO_x sensitivity demonstrated with sensor bodies having both types of Rh-based electrodes.
- Operating temperature range determined.
- Measuring electronics designed.

Future Directions

- Try at least one more type of porous Rh-based electrode.
- Continue characterizations and long-term testing of NO_x sensor.
- Determine optimum operating temperature.
- Breadboard and qualify measuring electronics.
- Complete testing at outside institutions.

Introduction

The need exists for an inexpensive, reliable, on-board sensor to monitor NO_x emissions of vehicles to meet state and federal regulations. This NO_x sensor project builds on a recent successful project supported by DOE to develop a miniature, amperometric *oxygen sensor* which is manufactured from stabilized zirconia as a multilayer ceramic capacitor with porous Pt electrodes which catalyze oxygen molecules to oxygen ions. The basic concept of the oxygen (and NO_x) sensor is illustrated in Figure 1. Oxygen ions are "pumped" from the (-) to the (+) electrodes across the zirconia ceramic layers under an applied voltage, and this amperometric current provides a measure of the oxygen partial pressure in the surrounding gas. The porosity of the Pt electrodes provides the necessary diffusion limitation, and there is no need for a reference gas. The sensitivity of this sensor is shown in Figure 2, and the output current is in the milliamp range. The sensor body contains eleven active ceramic layers and is approximately 2 mm x 3 mm x 5 mm. The established manufacturing methods for ceramic capacitors make this a very low cost sensor body (~ $1).

It is well known that Rh catalyzes NO_x to nitrogen and oxygen. If porous *Rh electrodes* are substituted for the porous Pt electrodes above, the resulting sensor will have an amperometric current output due to the oxygen released from the NO_x and thereby provide a NO_x measurement. A schematic illustration of a *combined* oxygen and NO_x sensor is shown in Figure 3. The oxygen sensor is mounted in the open end of the zirconia tube to measure the oxygen in the exhaust

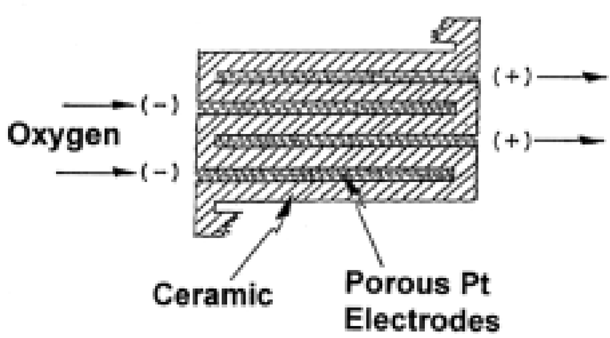

Figure 1. Schematic illustration of the capacitor-type amperometric sensor body showing the porous electrodes. The ceramic layers are stabilized zirconia and the electrodes are Pt in this example.

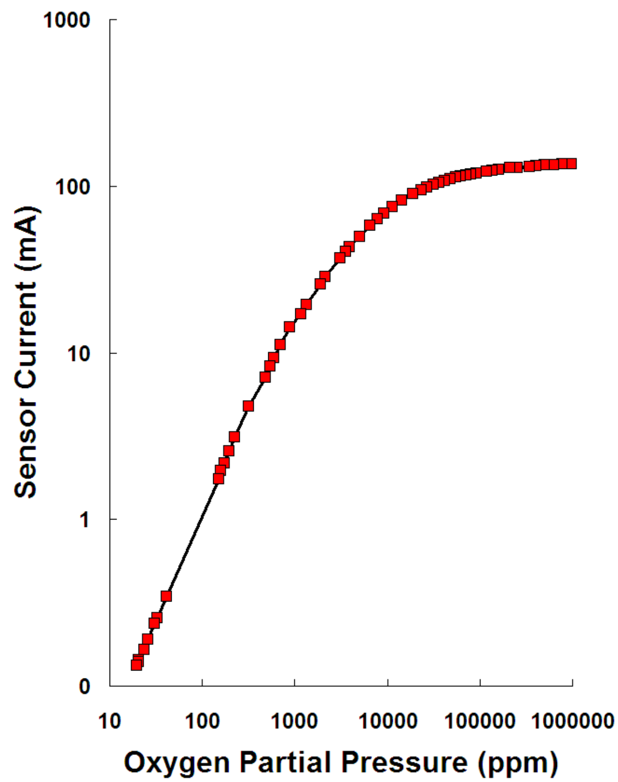

Figure 2. Oxygen sensitivity of the previously developed amperometric oxygen sensor (0.1 V direct current applied).

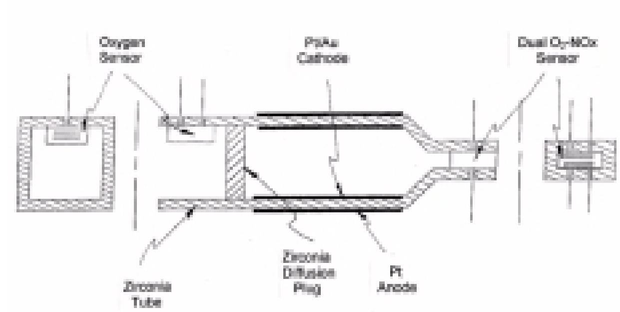

Figure 3. Schematic illustration of the combined sensor for measuring both the oxygen partial pressure and NO_x content of an exhaust gas. The exhaust gas diffuses through the zirconia diffusion plug and the oxygen level in the inner chamber is pumped to a small, residual level by applying a voltage to the Pt/Au cathode and Pt anode electrodes.

gas, and a dual oxygen-NO_x sensor is mounted in the closed end. Exhaust gas diffuses through a zirconia diffusion plug into the inner chamber, where the oxygen in the gas is pumped to a low, residual level by a voltage applied across the Pt anode and the Pt/Au cathode. The dual sensor has *two* sets of electrodes – Pt electrodes for measuring the residual oxygen and Rh-based electrodes for measuring NO_x and the residual oxygen. The difference in these two measurements is then a measure of the NO_x content of the exhaust gas. It is estimated that this combined sensor would be about 2.5 cm long and 1.3 cm in diameter, and parts costs would be $5 - $9.

Approach and Results

The capacitor manufacturer made zirconia sensor bodies with Rh electrodes and three active ceramic zirconia layers, 0.008 cm thick to conserve material. The first step involved measuring the NO_x sensitivity as a function of sintering temperature because, as with the oxygen sensor, the porosity of the electrodes decreases with increasing sintering temperature. Sintering temperatures in the range 1200 - 1300°C were used, and the optimum temperature is 1200°C. The basic concept of sensing NO_x was demonstrated in these tests, and in Figure 4 is shown a typical NO_x sensitivity curve. The amperometric currents are in the microamp range but can be increased by at least an order of magnitude by increasing the number of active layers and using thinner layers.

However, a fundamental problem arose in that the Rh slowly *oxidizes* in the 600 - 800°C operating range, and the amperometric current degrades with time. As the oxidation goes to completion, the associated volume change causes the sensor body to delaminate. Therefore, the emphasis shifted to using a Rh-Pt alloy for the electrodes to inhibit electrode oxidation, and the manufacturer made sensor bodies with these electrodes. Once again, the NO_x sensitivity was examined as a function of sintering temperature to optimize the porosity of this new alloy electrode, and 1200°C remained the temperature of choice. A NO_x sensitivity plot for a sensor using the alloy electrode is shown in Figure 5. It was demonstrated that this alloying significantly decreased the rate of oxidation without adversely affecting the NO_x sensitivity. The rate of change of the resistance of the Rh-Pt alloy compared to the pure Rh electrodes as a function of temperature is shown in Figure 6 on an Arrhenius plot. Measuring the change in resistance is equivalent to measuring the oxidation rate. The kinetics of oxidation of this alloy were analyzed, and it is estimated that the sensor would have a useful lifetime of several years at 600°C. Tests with another Pt-Rh alloy electrode

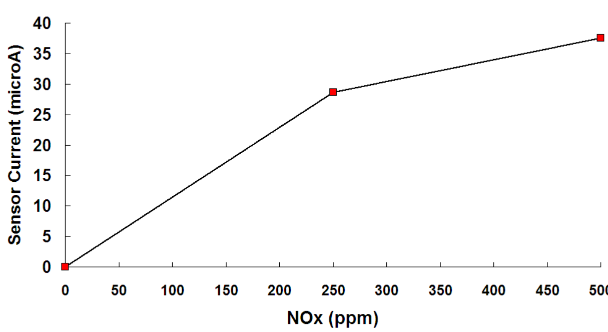

Figure 4. NO_x sensitivity of a sensor body with pure Rh electrodes at 600°C.

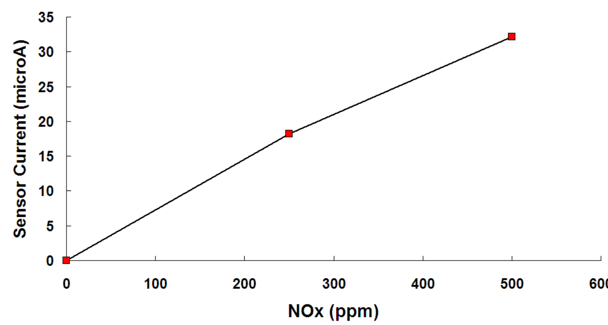

Figure 5. NO_x sensitivity of a sensor body with a Pt-Rh alloy electrode at 600°C.

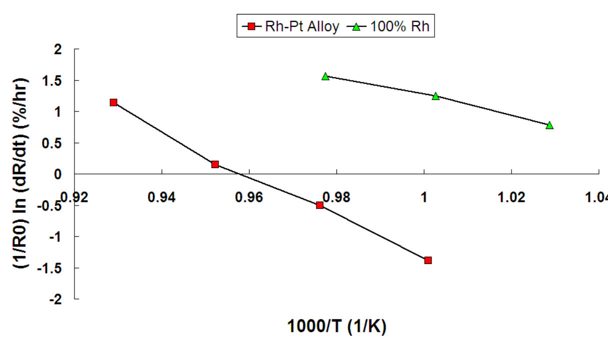

Figure 6. The rate of change of resistance (oxidation rate) of two types of Rh electrodes as a function of temperature.

aimed at further reducing the rate of oxidation are planned.

The measuring electronics have been designed in collaboration with the subcontractor.

Conclusions

The basic concept of a miniature, inexpensive, amperometric NO_x sensor *has been demonstrated*, and this is the *key* element in the combined oxygen and NO_x sensor illustrated in Figure 3 (the accompanying oxygen sensor has been developed previously). The prospect of achieving a small, inexpensive NO_x + oxygen sensor that does not require a reference gas is now very promising, and such a sensor would serve an important diagnostic function for emissions control onboard trucks and other vehicles.

The Pt-Rh alloy for the electrodes of the NO_x sensor body has not yet been optimized, but the methods for determining this alloy are straightforward, although time-consuming and expensive.

Patents

1. Patent applications have been filed for both the oxygen sensor and the combined NO_x + oxygen sensor. A patent disclosure on the invention was submitted to the patent office prior to receipt of this DOE contract.

III.O. Development of an Advanced Automotive NO_x Sensor

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DOE Technology Development Manager: Kevin Stork

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Objectives

- In collaboration with Delphi Corporation, develop an electrochemical NO_x sensor that meets performance targets for sensitivity, range, accuracy and resolution, transient response, cross-sensitivity, lifetime and cost.
- Develop active, selective and stable oxygen pump and NO_x sensing electrode compositions and structures.
- Address materials processing issues in producing multistage ceramic sensor structures.
- Model prototype device response characteristics.

Approach

- Establish rates of electrochemical decomposition for oxygen and NO_x for selected electrode/electrolyte combinations as a function of temperature and partial pressures of oxygen, NO_x and other exhaust gases.
- Refine ceramic material processing steps to minimize the appearance of physical defects in fired sensor assemblies.
- Using experimentally derived electrochemical properties and sub-component physical parameters, model expected sensor response characteristics.

Accomplishments

- Determined electrochemical activity and selectivity of Pt and Au/Pt oxygen pump electrodes in mixtures of oxygen and NO_x.
- Studied Au segregation to the surface of dilute Au/Pt alloys under conditions pertinent to sensor thermal processing and operation.
- Identified a new Pt alloy that exhibits substantially improved activity and selectivity as an oxygen pump electrode compared to Au/Pt.
- Modeling results show that sensor design is consistent with transient response targets.

Future Directions

- Determine effect of hydrocarbons, steam, carbon monoxide, carbon dioxide, and sulfur compounds on oxygen pumping and NO_x sensing electrode activity, selectivity, and lifetime.
- Provide modeling support to sensor configuration refinements.

Introduction

Advanced diesel engines, while offering significant advantages with respect to fuel economy, will require after-treatment of exhausts to lower NO_x to acceptable levels. After-treatment approaches include the use of selective catalytic reduction, NO_x absorbers, and/or plasma-catalyst systems. Sensors that can accurately assess NO_x slip are a necessary part of any exhaust treatment strategy. An increase in fuel economy related to the use of a NO_x sensor in a closed loop control mode is estimated to be between 0.5 and 1%. Thus, the NO_x sensor is a key enabling technology in after-treatment and control devices, applicable to both heavy- and light-duty diesel applications.

In the 2000 DOE Sensor Workshop, NO_x sensors were identified as a high priority need for CIDI/SIDI (spark ignition direct injection) engines (Glass, Milliken, Sullivan and Howden 2000). Performance requirements for a NO_x sensor were recommended: 20-300±5 ppm sensitivity range for diesel fuel; 100-200±20 ppm sensitivity for gasoline; 600-1000^oC operating range; 10 year lifetime (150,000 miles for autos, 500,000 miles for trucks); 1 second response time; provide separate measurements for NO and NO_2; and be immune to soot, sulfur, and ammonia. Noting that ceramic NO_x sensors are currently available, improvements needed include sensor durability, cost, response time, drift, and ammonia interference.

Approach

This project aimed at developing a reliable NO_x sensor is conducted in collaboration with Delphi Corporation. A multi-stage, amperometic approach is being followed, shown in Figure 1, which is believed to provide superior sensitivity, selectivity, and durability. Research and development performed at PNNL focuses on electrochemical properties, ceramic processing issues, and device modeling. These activities support Delphi Corporation's efforts to design and develop sensor elements, packages and associated electronics; building of prototype sensors on a pilot scale; dynamometer and vehicle testing of prototype sensors; and evaluation of degradation processes.

Electrochemical impedance spectroscopy and direct current methods are used at PNNL to establish rates of electrochemical decomposition for oxygen and NO_x for selected electrode/electrolyte combinations as a function of temperature and partial pressures of oxygen, NO_x and other exhaust gases. Models are developed to correlate sensor performance to electrode and electrolyte materials properties and to physical parameters of sensor sub-components.

Results

The oxygen pumping electrode(s) are needed to selectively remove oxygen from the diffusion chambers shown in Figure 1 without simultaneous decomposition of NO_x. Because oxygen is typically 1000-fold more concentrated in the exhaust than NO_x, this is a challenging requirement. Platinum alloys containing small concentrations of Au are favored for use as the oxygen pumping electrode. Gold has been found to segregate extensively to the surface of the dilute Au/Pt alloy electrodes during thermal processing and operation of the device. As shown in x-ray photoelectron spectroscopy results of Figure 2, the Au was 25 to 35 times more concentrated on the surface than in the bulk and was relatively insensitive to treatment temperature. Skelton et al. (2001) have proposed that selectivity of Au/Pt alloys for oxygen over NO_x derives from Au segregation to the stepped edges of the electrocatalyst, thus blocking active NO_x decomposition sites.

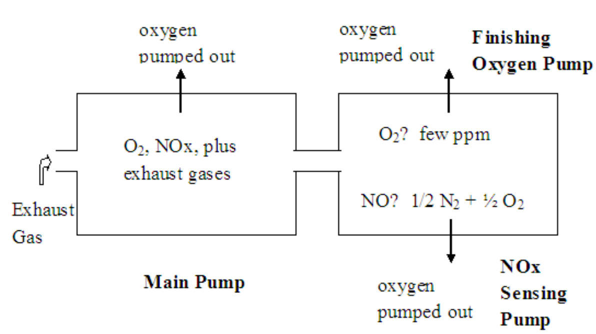

Figure 1. Functional diagram of an amperometric NO_x sensor being developed by the Delphi Corporation.

Oxygen pumping rates of the dilute Au/Pt electrode are lowered by the addition of NO_x to a gas mixture. In Figure 3, pumping currents containing a constant oxygen concentration decreased with increased NO_x concentration, believed due to competitive adsorption between oxygen and NO_x. Even though NO_x is not readily decomposed on this electrode, this molecule adsorbs on surface sites, thereby partially blocking oxygen adsorption and decomposition. This effect must be taken into account if the sensor is to be used simultaneously as a wide range oxygen sensor and NO_x sensor.

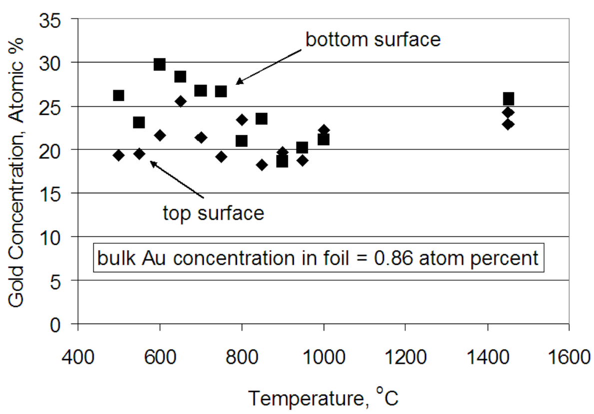

Figure 2. Gold surface concentration determined by x-ray photoelectron spectroscopy versus treatment temperature for a foil containing 0.86 atomic percent Au, balance Pt. High Au surface concentrations provide high selectivity of this electrocatalyst for oxygen versus NO_x.

At relatively high NO_x concentrations, the presence of low concentrations of oxygen served to promote NO_x decomposition. As shown in Figure 4, minor NO_x decomposition was found for oxygen concentrations less than 500 ppm. The opposite effect was noted for high oxygen concentrations, especially greater than 1000 ppm. Competitive adsorption of oxygen and NO_x are responsible for observed trends. At high oxygen concentrations, NO_x is displaced from the electrocatalyst surface. In contrast, similar measurements for pure Pt electrodes showed high electrocatalytic activity but no selectivity for oxygen over NO_x.

A new Pt alloy electrocatalyst was identified that provides an approximate 10-fold improvement in electrocatalytic activity for oxygen pumping while maintaining high selectivity for oxygen over NO_x. Families of current density versus potential curves for a constant oxygen concentration of ~2000 ppm with varied NO_x concentration are given in Figure 5. A key advantage of the new electrode composition is that much reduced cell potentials could be used to achieve the same oxygen pumping rate, which also improves electrode selectivity. Further research is needed to characterize the stability of this new electrode composition in realistic environments.

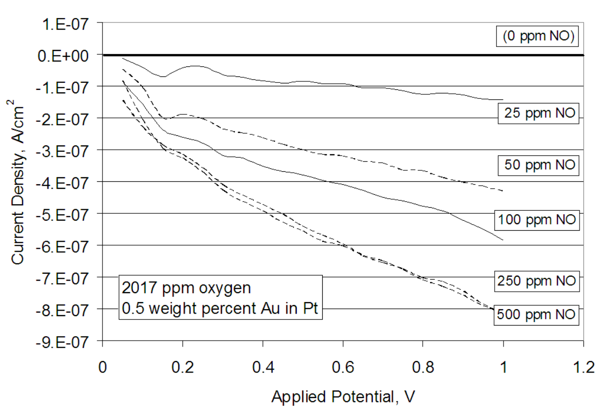

Figure 3. Incremental current densities associated with NO_x addition versus applied potential at constant oxygen partial pressure. Oxygen pumping currents are lowered by the presence of NO_x, the result of competitive adsorption.

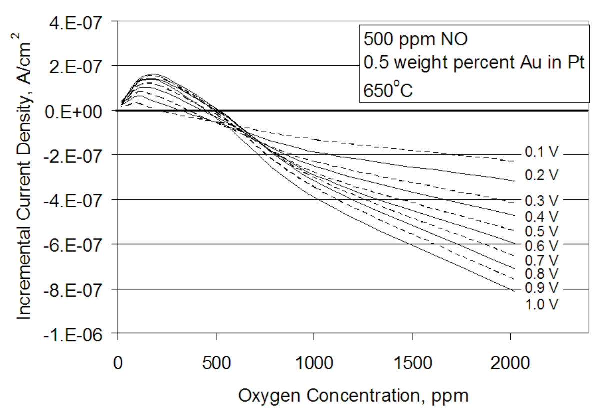

Figure 4. Incremental current densities associated with the addition of 500 ppm NO_x versus oxygen partial pressure at various cell potentials. Minor NO_x decomposition was apparent for low oxygen partial pressures when competition for surface sites between oxygen and NO_x was low.

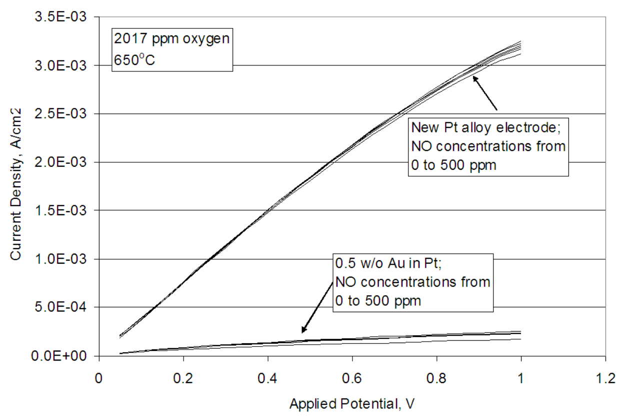

Figure 5. Comparison of pumping currents for a dilute Au/Pt electrode and a new Pt alloy electrode at a constant oxygen concentration of 2017 ppm. The new Pt alloy was ~10-fold more active while retaining similar oxygen selectivity.

A model was constructed using Lattice-Boltzmann methods that predicted oxygen partial pressures in prototype sensor configurations as a function of oxygen pumping rates, diffusion channel geometry, and other parameters. The model provides a means to predict sensor response times for different sensor configurations. Calculations showed that prototype sensor designs are capable of meeting response time targets of less than 1 second. As expected, response times were critically dependent on the dimensions of the diffusional aperture.

Conclusions

High selectivity for oxygen over NO_x for Au/Pt oxygen pumping electrodes derives from extensive segregation of Au to the surface of the alloy. The extent of segregation varies little with temperature, despite a relatively high mobility of Au in Pt at temperatures required for thermal processing and sensor operation. Oxygen pumping is partially inhibited by the competitive adsorption of NO_x. Platinum electrodes showed high electrocatalytic activity but no selectivity for oxygen over NO_x.

A new Pt alloy electrode was identified that provides significantly higher pumping currents than dilute Au/Pt electrodes under identical conditions, yet retains high selectivity for oxygen over NO_x. Use of this new electrode composition would allow lower cell potentials to be applied, which further improves selectivity. Further research is needed to show that the new electrode system is appropriately durable in exhaust gases.

A model was developed using Lattice-Boltzmann methods that provides a prediction of oxygen partial pressures in the sensor as a function of pumping currents, sensor geometry, and other parameters. The model is being used to predict sensor response times for different device configurations.

References

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2. Skelton, D. C., Hong Wang, R. G. Tobin, David K. Lambert, Craig L. DiMaggio, and Galen B. Fisher. “Suppression of Nitrogen Oxide Dissociation by Gold on Pt(335),” J. Phys. Chem. 105, 204-209 (2001).

Special Recognitions & Awards/Patents Issued

1. Patent disclosure: Novel oxygen pumping electrode for NO_x sensor (2003).

III.P. Portable Instrument for Transient Particulate Matter Measurements

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DOE Technology Development Manager: Gurpreet Singh

Objectives

- Define targets for future particulate measuring instrumentation based on current and future engine technologies and the corresponding particulate emission regulations.
- Develop an instrument to measure particulate emissions in real-time while meeting the above targets.
- Demonstrate the performance of such an instrument for particulate matter (PM) measurements on current light-duty and heavy-duty diesel engines.

Approach

- Performed a survey to identify the current and future PM measurement needs.
- Identified laser induced incandescence (LII) as a technique that satisfies the above needs.
- Performed computer modeling of the LII phenomena to identify various operational parameters.
- Developed an instrument called TG-1 with real-time particulate measurement capability.
- Tested the performance of TG-1 against that of commercially available TEOM 1105 through measurements performed on various diesel engines.

Accomplishments

- Modeled the LII phenomena to identify key operational parameters.
- Developed the mechanical, optical and electronic designs and the related software. Finally, these components were integrated into a portable instrument (the TG-1).
- Refined the performance of TG-1 to enhance portability and ease of use.
- Tested the instrument at Caterpillar and Cummins technical centers for validation and comparison against current particulate measurement practices.

Future Directions

- Further refine the design for a minimum particulate detection of 0.1 mg/m^3.
- Develop the capability to measure particle number density and mean aggregate size.
- Conduct tests to identify the sensitivity of the instrument to volatile organic fraction.

<u>Introduction</u>

Three issues remain regarding particulate emission measurement from current and future diesel engines:

- With emission regulations becoming stricter over time, the particulate emissions from current and future engines are so low that they are comparable to the minimum detection limits of current instrumentation. As a result, instrumentation needs to be developed with finer resolution and lower detection limits.
- Current and future particulate emission regulations are based on transient cycles in

addition to steady-state operation. Considering the fact that most of the particulate emissions occur during engine transients, a real-time measurement capability is very important.

- With health effects in perspective, future regulations may be based on particle number density, N (#/m^3), and size, D (nm), in addition to the particulate mass. Accordingly, a capability to measure these quantities additionally is very desirable.

A survey was performed to determine the functional requirements of future particulate measurement instrumentation. These are listed below:

- Minimum detection level ~ 0.1 mg/m^3
- Time response ~ 0.1 sec
- Time resolution < 0.5 sec
- Dynamic range ~ 3-4 orders of magnitude

Additionally, the instrument must be portable and able to perform measurements in real-time, should be able to measure independent of engine size and should be reasonably affordable.

Approach

Laser induced incandescence (LII) was identified to be the technique of choice. LII has a minimum detectivity of ~ 0.001 mg/m^3 and has a wide dynamic range. Additionally, this technique can be combined with laser Rayleigh scattering to obtain particle size and number density information.

Computer modeling of the LII phenomenon was performed to identify some of the key operational parameters. Remaining parameters were identified through lab-scale experiments. After the technique was refined for optimal performance, a prototype instrument was developed. After a few iterations optimizing the optical, mechanical, and electronic and software aspects, a prototype instrument was integrated (Figure 1). Subsequently, the instrument was tested for performance on a light-duty and a heavy-duty diesel engine.

Results

Initial tests were performed at Argonne National Laboratory on the exhaust of a Mercedes Benz 1.7 L engine coupled to a low-inertia dynamometer. Steady-state tests spanning over the engine map showed that the instrument's mass concentration (MC) measurements had excellent linearity and agreed with measurements performed with a scanning mobility particle sizer (SMPS) instrument to within ±12% (Figure 2). Also, it was noted that this prototype instrument, using a 10-Hz pulsed Nd:YAG laser, had a time resolution of 0.3 sec (Figure 3). Comparative measurements performed for a step change in engine operation (Figure 4) show

Figure 1. A Photograph of the TG-1 Instrument

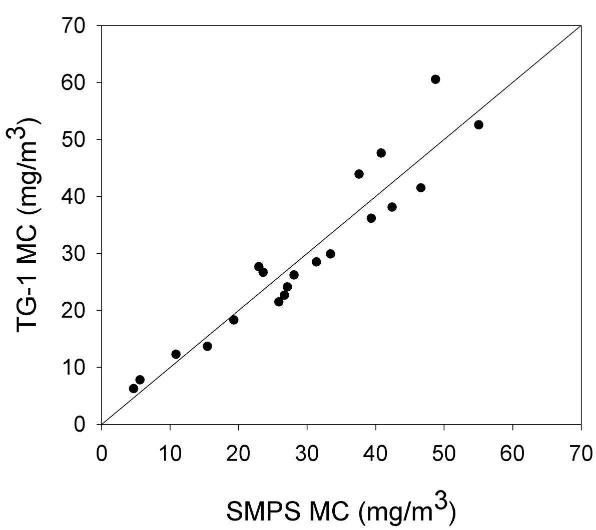

Figure 2. TG-1 Exhibits a Linearity of ±12% Full-Scale When Compared With a SMPS for Steady-State Measurements

that TG-1 has better performance with an ability to capture transients that might otherwise be missed while using the standard TEOM 1105. Subsequent measurements performed over an urban driving cycle showed TG-1 to track the PM emission levels accurately during transient operation.

Measurements were performed on the exhaust of a CAT-C10 heavy-duty engine at Caterpillar Technical Center by partial sampling of the engine exhaust. As shown in Figure 5, particles are emitted from this engine in spikes coincident with rapid accelerations. Such spikes could be 2-3 orders of magnitude larger than the levels emitted during steady-state operation. Similar transient measurements were also performed in a full-flow dilution tunnel while using a Cummins ISC-280 transit bus engine. Gravimetric measurement of particles collected over the heavy-duty transient cycle are compared in Figure 6 with those measured using the TG-1.

Conclusions

The prototype LII-based instrument developed here showed excellent performance for particulate

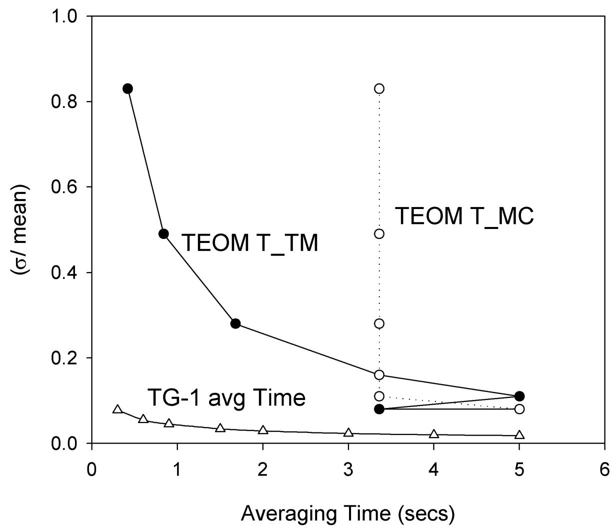

Figure 3. For Comparable (σ/mean) Values, TG-1 Requires Just 0.3 sec Average, Whereas a TEOM 1105 Requires Over 5 sec Average

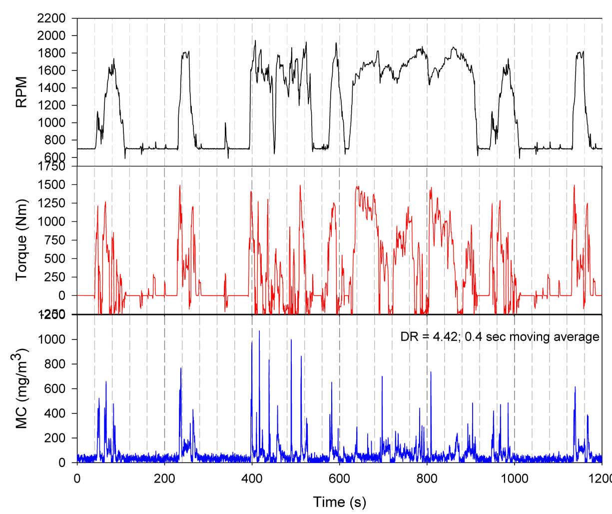

Figure 5. Tests on Environmental Protection Agency Heavy-Duty Engine Dynamometer Cycle

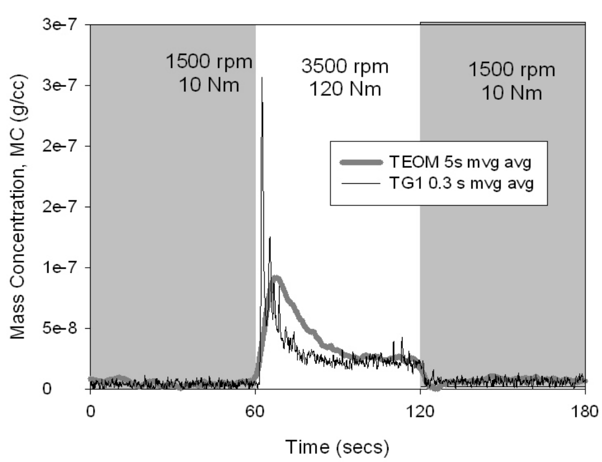

Figure 4. Operation Over a Step Change in Engine Operation

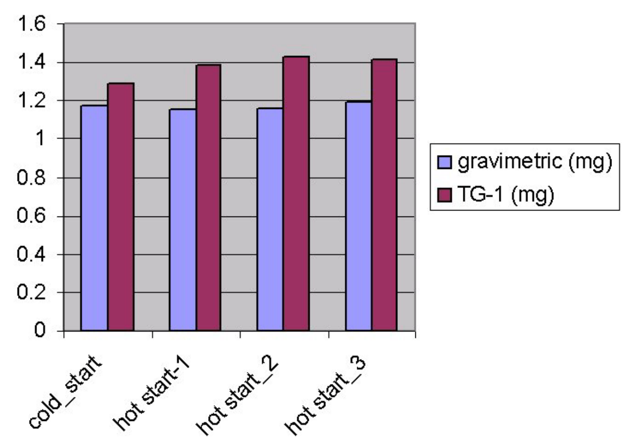

Figure 6. Gravimetric and TG-1 Response Integrated Over a Heavy-Duty Engine Dynamometer Transient Cycle

measurements during engine steady-state and transient operations. Most importantly, measurements performed over an engine transient cycle showed that particle emissions occur in spikes over certain engine operating conditions. It is envisioned that the transient measurement capability facilitated by the present instrument will help identify such high-emitting transients, with a view to developing particulate mitigation strategies. Also, such a quick measurement capability can prove instrumental in fuel formulation analysis and in the development of aftertreatment systems.

FY 2003 Publications/Presentations

1. S. Gupta, TG-1: Instrument to measure diesel exhaust particulate emissions in real-time, 6th ETH Conference on Nanoparticle Measurement, August 2002.

2. Poster presented at 13th CRC meeting.

3. Presentation at the Advanced Combustion Engine National Laboratory R&D Merit Review 2003.

4. SAE 2003-01-3155, SAE Powertrain and Fluids Conference, October 2003.

Special Recognitions & Awards/Patents Issued

1. Invention disclosure ANL-IN-99-056 (patent pending)

2. Invention disclosure ANL-IN-02-036

III.Q. High-Energy, Pulsed Laser Diagnostics for the Measurement of Diesel Particulate Matter

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DOE Technology Development Manager: Gurpreet Singh

Objectives

- Develop real-time, engine-out particulate matter (PM) diagnostics for measuring size, number density, volume fraction, aggregate characteristics, volatile fraction, and metallic-ash species and concentration.
- Transfer resulting technology to industry.

Approach

- A scanning mobility particle sizer (SMPS) is used as the reference standard for particle size distributions.
- Laser-induced incandescence (LII) is used to measure the soot volume fraction and primary particle size.
- Laser-induced desorption with elastic light scattering (LIDELS) is used to measure the volatile fraction of the PM.
- Laser-induced breakdown spectroscopy (LIBS) is used to measure metallic-ash species and concentration.
- Simultaneous measurements of LII and elastic light scattering (ELS) will be used to obtain the following PM aggregate parameters using the Rayleigh-Debye-Gans polydisperse fractal aggregate (RDG-PFA) approximation:
  - particle volume fraction
  - diameter of primary particles
  - number density of primary particles
  - geometric mean of the number of primary particles per aggregate
  - geometric standard deviation of the number of primary particles per aggregate
  - mass fractal dimension
  - radius of gyration of the aggregated primary particles
- Off-the-shelf components are used to build a measurement system that can be easily duplicated by industry partners.
- Artium Technologies Inc., Sunnyvale, California, is commercializing the resulting technology.

Accomplishments

- Time-resolved LII measurements of PM volume fraction have been obtained for engine startup/shutdown and exhaust gas recirculation (EGR) and throttle transients and compared with SMPS measurements.
- Time-resolved LII measurements obtained for a variety of vehicles during FTP-75 have been compared with tapered element oscillating microbalance (TEOM) and electrical low pressure impactor (ELPI) measurements. LII was shown to be sensitive to better than 0.5 mg/mi.

- Real-time LIDELS measurements of the volatile fraction of diesel PM have been obtained for load and EGR sweeps.
- A collaborative LII investigation of the effects of EGR on PM was conducted with the Combustion Research Group at the National Research Council (NRC) of Canada.
- Measurements of the calcium in lube-oil ash have been obtained using LIBS.
- A mobile, high-energy laser diagnostics (HELD) system has been built for use in other Sandia engine laboratories and off-site with industrial collaborators. The system was at Ford's Vehicle Emission Research Laboratory for two weeks in February and is scheduled for a week-long visit at Cummins in July, followed by three weeks at Oak Ridge National Laboratory (ORNL).
- Artium Technologies' prototype commercial LII instrument was successfully tested at Sandia in March and was exhibited at the JSAE/SAE International Fuels & Lubricants Meeting in Yokohama in May.
- A Particulate Matter Collaboratory web page (www.ca.sandia.gov/pmc) has been established as a part of the DOE Diesel Collaboratory Project. Members are Sandia, NRC, and Artium Technologies.

Future Directions

- Extend the LIDELS technique to enable time-resolved measurements (~10 Hz data rate) from its current real-time performance of approximately one minute per measurement.
- Extend the LIBS technique to enable time-resolved measurements using inexpensive analog detectors (rather than a spectrometer with an intensified camera).
- Develop experimental and modeling capability for RDG-PFA approximation for aggregate characterization.
- Continue the collaboration with Artium Technologies toward commercialization of HELD instrumentation for PM measurements.

Introduction

LII is a well-established technique for the measurement of PM volume fraction and primary particle size. Light from a high-energy pulsed laser is used to heat the PM to its vaporization point, resulting in thermal radiation that is proportional to the PM volume fraction; the cooling rate of the PM following laser heating is a measure of primary particle size. Simultaneous measurements of ELS from the particles at several discrete angles relative to the incident laser beam can be used to obtain additional information regarding the characteristics of PM aggregates using the RDG-PFA approximation.

LIDELS is a new technique we have developed for the real-time measurement of the volatile fraction of diesel PM. Laser energy is used to desorb the volatile matter from the diesel PM, and ELS measurements obtained before and after desorption give the volatile fraction. Conventional procedures require collection on filter paper and subsequent analysis that requires from several hours to several days to obtain a measurement. Our current LIDELS procedure requires approximately one minute to obtain a measurement, and we have plans for an upgrade that will permit 10 Hz data rates.

LIBS is a fairly well-established technique for measuring metallic ash. A focused laser beam is used to ionize the ash, resulting in atomic emissions that identify the species and their concentrations.

A single HELD system can perform all of the above tasks. Its main advantage over conventional PM measurement techniques is that it can be applied in any environment (e.g., hot or cold, undiluted or diluted, etc.); it responds in real time and is very sensitive to low PM concentrations (e.g., the lower limit for LII is estimated to be one part per trillion, or about 0.5 mg/mi).

Approach

The complete HELD system has been assembled on a mobile cart of dimensions 2' x 4', as shown in Figure 1. The only external connections required for use are the sample line for the diesel exhaust, a return vent line, and 110 V power. The optical setups for LII, ELS, and LIDELS can coexist, whereas LIBS requires the installation of an additional focusing lens. The cabling connections to the data-acquisition oscilloscope are unique for each HELD technique. However, once properly connected, all HELD applications are totally PC controlled, providing essentially "hands-off" operation.

Each time we develop a new HELD technique, or make a significant improvement or application of an existing one, we publish the procedures and results in an archived technical article. To further assist the transfer of HELD technologies to outside users, we are pursuing two parallel paths. Because off-the-shelf components are used whenever possible, the expedient approach is to "clone" the system from a shopping list of parts; the PC software and ancillary drawings and schematics are all in the public domain. The alternative is to purchase a commercial unit provided by Artium Technologies, Inc., of Sunnyvale, California. We are working directly with Artium on a no-fee basis to develop commercial products. At this time, Artium is marketing an LII instrument, but neither LIDELS nor LIBS are currently available other than by a development contract.

Figure 1. Mobile HELD System at Ford's Vehicle Emission Research Laboratory, Dearborn, MI

Results

The LIBS spectra for calcium from lube oil in diesel exhaust is shown in Figure 2. The line labeled Ca is for the neutral calcium atom, whereas Ca^+ is the singly-ionized atom. While the results shown required a 30 second average of a spectrograph, time-resolved LIBS measurements are feasible, permitting direct measurement of the lube oil contribution to diesel PM emissions during engine transients.

Shown in Figure 3 are LII measurements of PM emissions from a 1998 Volkswagon Beetle for bag 1 of FTP-75. These measurements were obtained during a two-week visit of the HELD system to Ford's Vehicle Emission Research Laboratory in Dearborn. The excellent temporal response of the LII technique is clearly evident. In Figure 4 we show the LII measurements for bag 2 compared with concurrent measurements made with a tapered

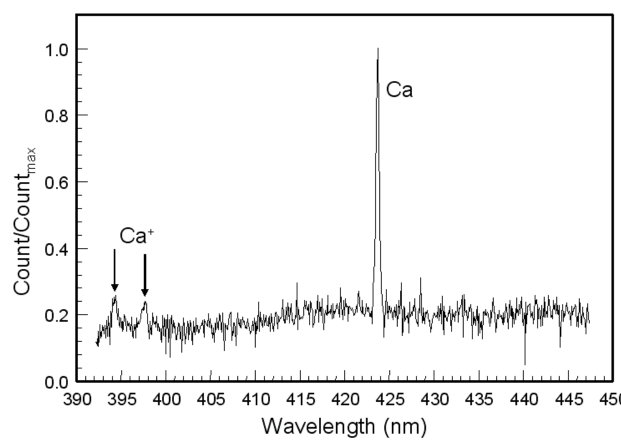


Figure 2. LIBS Measurement of Calcium in Lube-Oil Ash

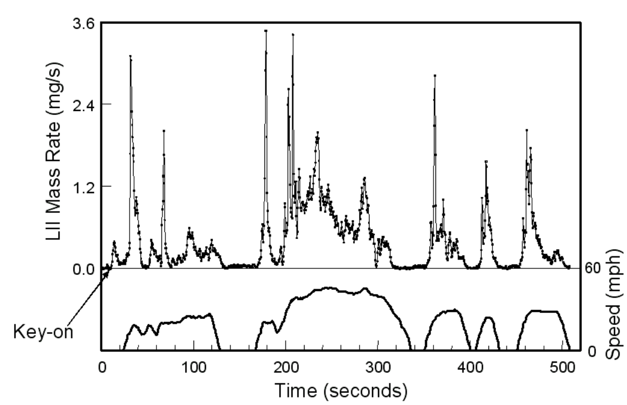


Figure 3. LII Measurements for Bag 1 of FTP-75

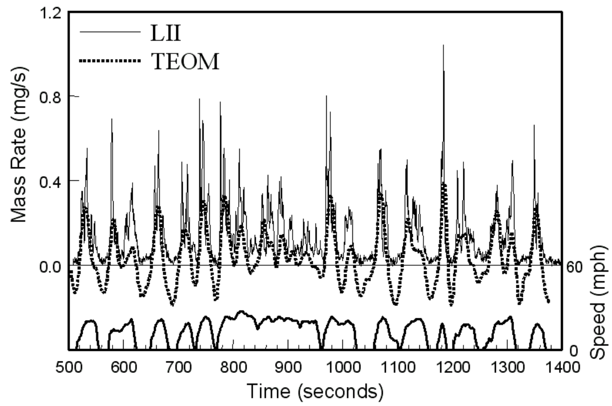


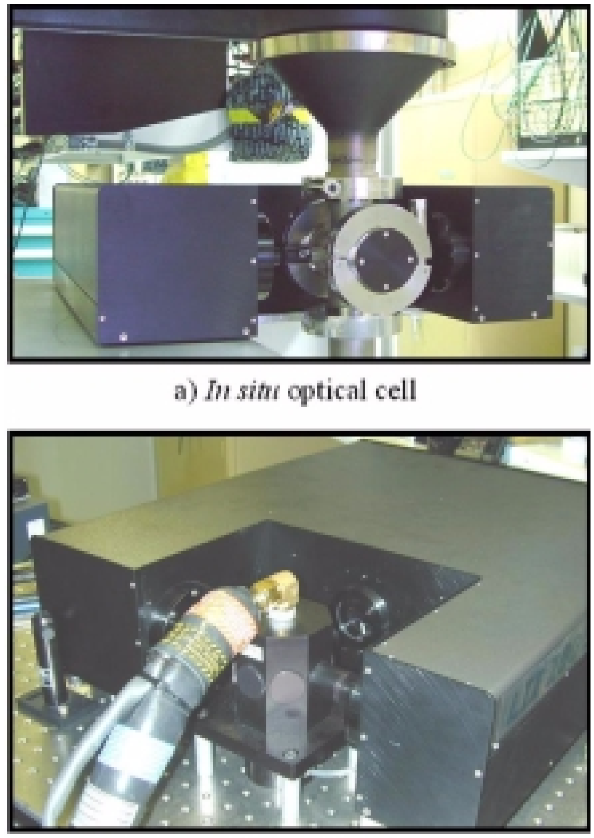
Figure 4. Comparison of LII and TEOM Measurements for Bag 2 of FTP-75

element oscillating microbalance (TEOM). The TEOM is currently the most widely accepted instrument for making transient PM measurements, but its sensitivity to water condensation and evaporation results in significant periods of negative emission rates. LII does not have this problem because it is sensitive only to the elemental carbon in the PM.

The Artium Technologies prototype LII instrument underwent evaluation testing at Sandia this past March. The prototype is shown in Figure 5a positioned to make *in situ* measurements with an in-line optical cell, and in Figure 5b with an external cell for extracted-sample measurements. The instrument box shown houses the laser, optics, detectors, and electronics. Necessary ancillary equipment include the laser power supply, PC, and extraction pump for the external cell. In Figure 6 we compare the *in situ* and extracted measurements for a free-acceleration transient, where the latter have been phase-shifted to account for the transit time through the extraction line. The agreement between the two measurements is excellent, confirming that extraction does not bias the measurement.

Conclusions

- LIBS has sufficient sensitivity to accurately measure the oil contribution to diesel PM. The real-time measurements presented were obtained in approximately one minute, but time-resolved measurements are feasible.


a) *In situ* optical cell

b) External optical cell

Figure 5. Artium Prototype LII Instrument Positioned for (a) In Situ and (b) Extracted-Sample Measurements

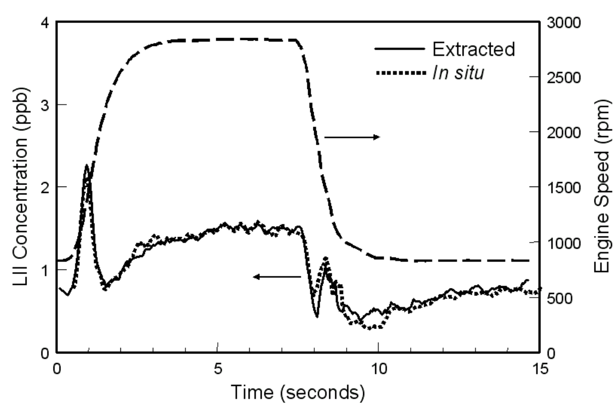


Figure 6. Comparison of In Situ and Extracted-Sample LII Measurements for a Snap-Acceleration Test (The results have been phase-shifted to account for the transit time through the extraction line.)

- LII is sensitive to better than 0.5 mg/mi and is superior to time-resolved TEOM measurements at low PM concentrations because LII is unaffected by water condensation.
- A direct comparison between LII measurements obtained *in situ* and by extraction to an external cell revealed virtually identical results, confirming that there is no penalty for the simpler approach of extraction.
- Artium Technologies' prototype LII instrument performed according to expectations during evaluation testing and is now being marketed worldwide.

FY 2003 Publications/Presentations

1. H. A. Michelsen, P. O. Witze, S. Hochgreb, and D. Kayes, "Time-Resolved Laser-Induced Incandescence of Soot: The Influence of Experimental Factors and Microphysical Mechanisms," accepted by *Applied Optics*, 2003.
2. G. J. Smallwood, D. Clavel, D. Gareau, R. A. Sawchuk, D. R. Snelling, P. O. Witze, B. Axelsson, W. D. Bachalo, and Ö. L. Gülder, "Concurrent Quantitative Laser-Induced Incandescence and SMPS Measurements of EGR Effects on Particulate Emissions from a TDI Diesel Engine," SAE Paper No. 2002-01-2715, accepted for *SAE Transactions, Journal of Fuels & Lubricants*.
3. P. O. Witze, "Real-Time Measurement of the Volatile Fraction of Diesel Particulate Matter Using Laser-Induced Desorption with Elastic Light Scattering (LIDELS)," SAE Paper No. 2002-01-1685, accepted for *SAE Transactions, Journal of Fuels & Lubricants*
4. P. O. Witze, "High-Energy Pulsed-Laser Diagnostics for the Measurement of Diesel Particulate Matter," *DOE Annual Progress Report, 2002.*
5. P. O. Witze, H. A. Michelsen, G. J. Smallwood, and W. D. Bachalo, Particulate Matter Collaboratory Web Page, www.ca.sandia.gov/pmc.
6. P. O. Witze, "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Reciprocating Engine PM Emissions," DOE/OTT CRADA Working Group Meeting, Livermore, CA, January 28-29, 2003.
7. P. O. Witze, "Feasibility of Laser-Induced Incandescence for On-Road Measurements of Particulate Matter Emissions," 13th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April 7-9, 2003.
8. P. O. Witze, "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Reciprocating Engine PM Emissions," DOE/OTT Merit Review and Peer Evaluation, Argonne, IL, May 13-15, 2003.
9. P. O. Witze, "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Reciprocating Engine PM Emissions," DOE/OTT AEC Working Group Meeting, Detroit, MI, June 24-25, 2003.
10. P. O. Witze, "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Reciprocating Engine PM Emissions," 8th Diesel Engine Emissions Reduction Conference, San Diego, CA, August 24-28, 2003.
11. P. O. Witze, "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Reciprocating Engine PM Emissions," International Energy Agency Task Leaders Meeting, Swindon, UK, September 7-10, 2003.

III.R. Particulate Matter Sensor for Diesel Engine Soot Control

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DOE Technology Development Manager: Roland Gravel

Subcontractors:
Univeristy of Minnesota, Minneapolis, MN
Honeywell Control Products, Freeport, IL

Objectives

- Develop diesel engine exhaust particulate matter (PM) sensor prototypes that have low cost, high speed, reliability, and are compatible with the harsh operational environment.
- Install the sensor prototypes in an appropriate engine test and compare test results to results of other reference instrumentation.
- Use test results to improve sensor concepts and to develop compatible sensor packages.
- Develop associated sensing electronics and signal processing hardware.
- Demonstrate prototype sensor to the DOE by 2Q, 2004.

Approach

The project has three main steps in order to accomplish the research:

- PM Sensor Development - We will design and build several prototypes of PM sensors utilizing high-temperature materials for operation directly in the exhaust stream. Honeywell will develop different readout electronic circuits to monitor the sensor and interface to data acquisition equipment and/or engine controllers.
- Sensor Testing - We will establish a diesel engine test bed that will include reference particulate measuring instrumentation and potentially other gas sensing instrumentation. A data acquisition system will be established that will be used to record the testing results for further data analysis. These tests will be conducted at the University of Minnesota's Center for Diesel Research and will utilize equipment from their Particle Measurement Laboratory. Gas concentration and particle size distribution information will be recorded to compare to sensor test results.
- Sensor Packaging - Staff members of Honeywell Labs and Sensing and Controls Division will develop suitable sensor packages for the PM sensors. Packaging materials should provide protection to the sensor as well as the ability to withstand the harsh operational environment. Sensor packages will be exposed to high temperatures and corrosive and potentially condensing environments. Destructive and nondestructive testing of the sensor package will be completed.

Accomplishments

- We have established our test facilities at the University of Minnesota using three commercial diesel engines. The first is a John Deere 4540T engine typical of medium-duty off-road applications, the second is a Caterpillar engine typical of heavy-duty on-road applications, and the third is a Volkswagen TDI (Euro IV) engine typical of passenger car applications.

- We have established our preferred technical approach and demonstrated the feasibility of monitoring particulates from each combustion event in real-time on a cylinder-by-cylinder basis.
- We have established the feasibility of monitoring the particulates directly in the exhaust manifold without pretreatment or dilution and without sensor fouling due to accumulation of particulate matter.

Future Directions

- We have recently begun an effort to develop custom, cost effective prototype electronics for signal conditioning and real-time data interpretation.
- We will shortly begin an effort to develop prototype packaging for the sensor and electronics with the goal of demonstrating a functional prototype in March 2004.

Introduction

Emission regulations worldwide emphasize reducing fine particulate matter emissions. Recent studies have shown that fine particles are more strongly linked with adverse health effects than are larger particles, and engines are an important source of fine particles.

Particles in the nucleation mode and in the accumulation mode appear to be formed by different mechanisms. Accumulation mode particles are primarily carbonaceous and are associated with rich combustion and poor subsequent oxidation during the engine cycle. Most nucleation mode particles are not even formed until the exhaust dilutes and cools. They consist of a complex, poorly understood mix of sulfuric acid and partially burned fuel and lubricating oil. Formation of these two types of particles likely occurs under different engine operating conditions with:

- Heavy loads favoring carbonaceous accumulation mode particles, and
- Light loads most likely favoring the formation of vapor phase precursors of nucleation mode particles. These precursors may not undergo gas to particle conversion until the exhaust cools and dilutes in the atmosphere.

In order to meet future emission standards, future diesel engines will have to be fitted with sophisticated combustion control systems and, almost certainly, an aftertreatment system including particle filters or traps. An effective exhaust particulate sensor would not only lead to a reduction of particulate emissions from the engine itself, but would also make traps and other aftertreatment devices more feasible. Particulate traps are now commercially available and are likely to be applied in high volume in the future. They are large, expensive, and impose a significant fuel economy penalty. The particulate sensor would help reduce the amount of particulate matter created through better engine control. It could also be used to monitor particulate loading or breakthrough on downstream traps. Thus, the particulate trap could potentially be made smaller, or regenerated less often.

Approach

Solid particles present in diesel engine exhaust carry a significant electrical charge (Kittelson et al., 1986a, 1986b; Moon, 1984). We examined several types of sensors based on measurement of particle charge such as an ionization sensor, an image charge sensor, and sensors based on alternating current (AC) conductance and capacitance of the exhaust. Our preferred approach is an image charge sensor based on design simplicity, speed, and ruggedness.

The sensor probe is built on a commercial spark plug body as seen in Figure 1. This platform is ideal for placing directly in the exhaust manifold, as it withstands high pressure and temperature and is stable towards vibration and gas composition found in that environment. The probe is mounted directly in the exhaust pipe just downstream of the turbocharger as seen in Figure 2. The electronics are remote from the sensor probe.

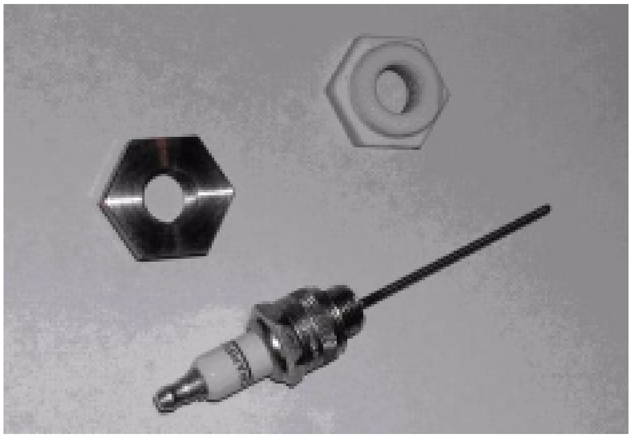

Figure 1. Honeywell PM Sensor Probe and Mounting Collars

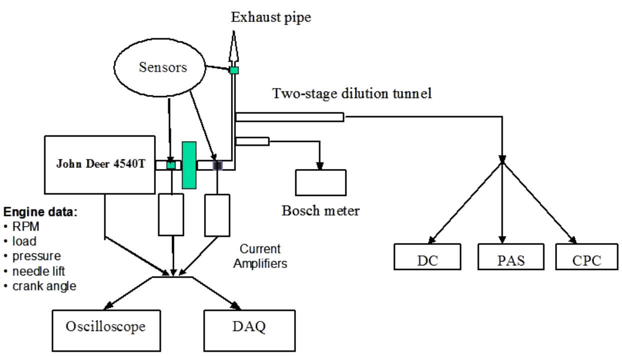

Figure 2. Sensor Mounting Locations on the John Deere 4540T Test Engine with Additional Particulate Reference Instrumentation

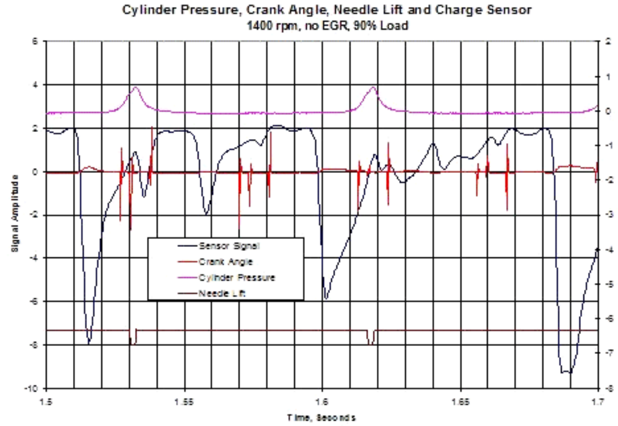

Figure 3. Typical real-time waveforms of sensor signal, cylinder pressure, crank angle, and needle lift. Data was taken on a John Deere 4540T test engine running at 1400 rpm, with no EGR, and 90% load.

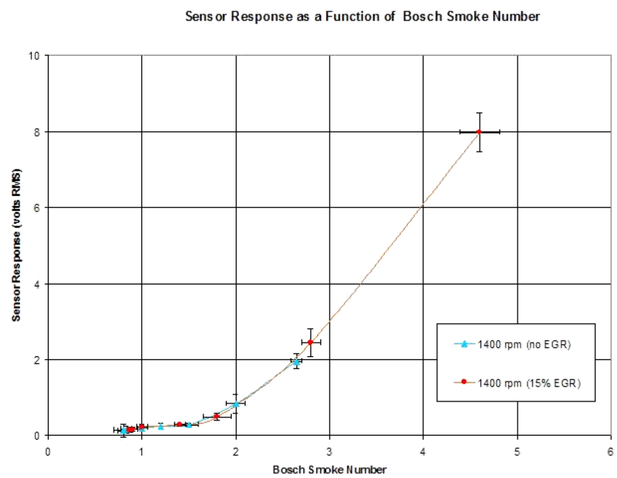

Figure 4. Correlation of the sensor average output (as measured by RMS voltage) to Bosch Smoke Number. Error bars are for repetitive measurements. The limit of sensitivity of the Bosch Meter was approximately 1.5.

Results

The John Deere engine being used has one cylinder (cylinder number 4) that is instrumented with cylinder pressure, fuel injector needle lift, and a flywheel crank-angle pick-up (Hall Effect, three pulses per revolution, one of which corresponds to top-dead-center on cylinder number 4). Figure 3 shows the basic real-time sensor signal with corresponding traces of cylinder pressure, crank angle and fuel injector needle lift. About two engine cycles (four crank revolutions) are shown. The sensor signal clearly shows variations corresponding to individual cylinder firings. These individual variations and the average sensor output (RMS output) are well correlated to smoke concentrations measured with a standard Bosch smoke meter as seen in Figure 4, an optical scattering meter as seen in Figure 5, and an aethelometer. The sensor output shows minimal correlation to temperature and pressure. The output signal from the PM sensor has shown no effect to fouling from accumulated particulate matter. The variations in peak height are real variations in smoke being produced in each cylinder on each combustion cycle. Similar effects

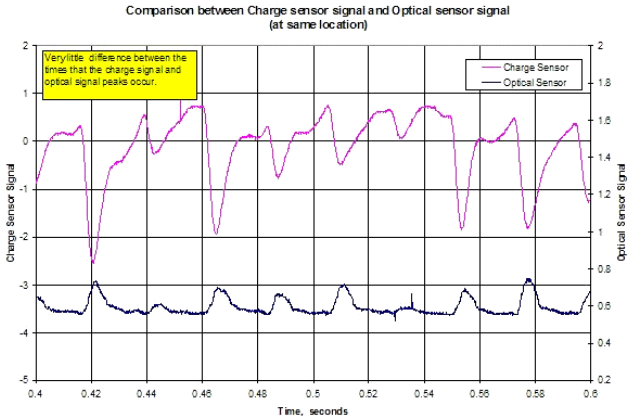

Figure 5. Correlation of individual smoke pulses to an optical scattering meter co-located in the exhaust stream with the PM sensor. Note that the PM sensor signal increases downwards while the optical sensor signal increases upwards.

have been observed on the Caterpillar engine (showing 6 smoke peaks present for the 6 cylinders). For this engine, the PM sensor peak heights are smaller, as it is a cleaner-burning engine and cylinder-to-cylinder variations are much lower, presumably due to a more efficient electronic fuel injection system. The Volkswagen engine is currently being set up for testing.

Conclusions

In conclusion, we have made considerable technical progress during FY 2003. Namely, we have:

- fabricated and tested several concept prototype sensor probes based on a very simple, manufacturable foundation;
- developed an adequate test bed and data logging capabilities that allow us to examine sensor behavior across multiple engine types and under varying engine conditions;
- verified that the charge sensor approach gives us a reproducible signal that is correlated to exhaust smoke as characterized by several reference methods;
- observed that the sensor probe response does not degrade due to soot build-up or temperature over several hundred hours of operation; and
- observed that on the Deere 4540T engine there is considerable variation in the sensor response from cylinder to cylinder and from cycle to cycle. This variability appears to be real variations in engine behavior and not artifacts of the sensor signal.

SECTION IV. ADVANCED ENGINE SUB-SYSTEMS R&D

IV.A. Heavy Truck Engine Project

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DOE Technology Development Manager: Roland Gravel

Objectives

- **Phase I -** Demonstration of 45% brake thermal efficiency (BTE) at cruise conditions while meeting 2002 U.S. Environmental Protection Agency (EPA) emission standards. (Demonstration made in January of 2002.)
- **Phase IIA -** Demonstration of 45% brake thermal efficiency at cruise conditions while meeting 2007 emission standards. (Demonstration due in Q1 of 2004.)
- **Phase IIB -** Demonstration of 50% brake thermal efficiency maximum while meeting 2010 emission standards. (Demonstration due in Q1 of 2006.)

Approach

Phase I tasks are complete. Approach to Phase IIA and IIB tasks is as follows:

- Engine Development
  - Define advanced combustion systems for best NO_x / fuel economy tradeoff for 2007/2010.
  - Perform analysis of data and sub-model development.
  - Identify optimal combustion system design options.
  - Define controls architecture for an advanced combustion system.
  - Specify air handling / exhaust gas recirculation (EGR) architecture.
  - Assemble prototype fuel system for advanced combustion single-cylinder engine testing.
  - Define and demonstrate subsystem architecture for 2007/2010.
- Analysis/Development of NO_x & Particulate Matter (PM) Aftertreatment Systems
  - Develop system architecture.
  - Procure engine and provide test support (adsorber/PM filter system).
  - Develop and validate model (adsorber/PM filter system).
  - Develop adsorber subsystem.
  - Develop soot filter subsystem.
  - Integrate aftertreatment subsystem.
  - Optimize aftertreatment subsystem.
  - Demonstrate aftertreatment subsystem integrity.
- Exhaust Conditioning for NO_x & SO_x Regeneration
  - Analyze and test in-cylinder exhaust conditioning.
  - Evaluate advanced common-rail fuel system for exhaust conditioning.
  - Develop engine management strategy for NO_x, SO_x, and diesel particulate filter (DPF) regeneration and exhaust stream conditioning.

- Development & Integration of Control System
  - Define controls architecture and modeling.
  - Develop aftertreatment sensor.
  - Define control architecture for 2007/2010.
  - Demonstrate control architecture for 2007/2010.
- Vehicle Demonstration
  - Demonstrate adsorber/PM filter system in a heavy truck.
  - Demonstrate 45% BTE @ typical cruise conditions @ 2007 emissions (PH IIA).
  - Demonstrate 50% BTE maximum @ 2010 emissions (PH IIB).

Accomplishments

- Defined combustion system to address 2007 emissions limit requirements.
- Achieved Phase IIA deliverable performance with unit injector fuel system.
- Evaluated the benefits of the flexible fuel system.
- Performed modeling to determine the benefits of homogeneous charge compression ignition (HCCI) combustion.
- Evaluated flexible fuel system performance against the Phase IIA deliverable.
- Evaluated particulate filter operation in a heavy-duty vehicle.
- Designed and examined improved models of engine-aftertreatment systems.
- Improved closed crankcase ventilation system performance.
- Initiated studies of waste heat recovery and optimum heat rejection methods with two academic research partners.

Future Directions

- **Phase IIA** – Demonstration of 45% brake thermal efficiency while meeting 2007 EPA emission standards:
  - Perform vehicle demonstration with Phase IIA configuration engine using both a unit injector fuel system and a high-pressure common-rail fuel system.
  - Analyze and evaluate parasitic load reduction techniques: electric accessory drive for the coolant and oil pumps, optimized lubricants, etc.
- **Phase IIB** – Demonstration of 50% brake thermal efficiency while meeting 2010 EPA emissions standards:
  - Determine viable in-cylinder and aftertreatment technology solutions and conduct modeling studies to verify their performance potential.
  - Define and acquire critical system components to verify model results and identify performance limits.
  - Evaluate NO_x sensor to determine durability and robustness to support heavy-duty vehicle applications.

Introduction

Cummins Inc. is working to develop and demonstrate advanced diesel engine technologies to improve diesel engine thermal efficiency while meeting future emissions requirements. The effort meets the objectives outlined by the Department of Energy, which include two major phases. In Phase I (completed), Cummins worked to demonstrate, by January, 2002, engine efficiency equal to or greater than 45% while complying with emissions regulations of 2.5 g/bhp-hr NO_x-hydrocarbon (HC) and 0.10 g/bhp-hr particulate matter, as stated in the EPA/Department of Justice Consent Decree with the diesel engine manufacturers. In Phase IIA, Cummins is working to demonstrate, in early 2004, brake thermal efficiency of 45% in a multi-cylinder engine while complying with 2007 EPA emission regulations of 1.2 g/bhp NO_x-HC and 0.01 g/bhp-hr particulate matter. In Phase IIB, Cummins will work to demonstrate, by early 2006, brake thermal efficiency of 50% in a multi-cylinder engine while complying with the 2010 EPA emission regulations of 0.2 g/bhp NO_x-HC and 0.01 g/bhp-hr particulate matter.

These project goals are challenging and require intensive research and development. Emissions reduction by traditional means will have a negative impact on brake thermal efficiency. The engine and emissions performance technologies advanced in this project will accelerate the development of high efficiency, low emission diesel engines.

Approach

Cummins' approach to these program objectives continues to strive for analysis-led design in nearly all aspects of the research. An emphasis is placed on modeling and simulation results to lead the way into feasible solutions.

For the deliverable in each phase, a configuration matrix study is planned to determine appropriate, feasible solutions. Engine system solutions include various air handling schemes, control system approaches, and aftertreatment system combinations. Based on extensive model/simulation data, previous testing experience, or verifiable supplier information, a best-choice solution set of system components is selected. A variety of laboratory tests are conducted to verify performance and to tune system functions. Often, different portions of the system are pre-tested independently to quantify their behavior, and their data is analyzed in a model-based simulation before combined test cell testing is conducted. Concurrent to laboratory testing and tuning, planning and preparation for a vehicle system demonstration is conducted. Once satisfactory test cell system performance is verified, the vehicle demonstration is conducted.

Results

The major accomplishments in 2003 are as follows:

- **Defined combustion system to address 2007 emissions limit requirements.**

System integration configuration matrices (SICM) were utilized to determine the most appropriate technology pathway toward achieving the objectives for Phase IIA. The matrices created for heavy-duty applications included the possible engine/aftertreatment combinations of technology available at present. From the initial matrix, a subset of viable options was identified through a weighting-based decision exercise.

The engine/aftertreatment system recipe found to be most appropriate for this contract and its deliverables was an engine incorporating the next generation of cooled EGR, optimized fuel system, enhanced combustion and air handling design and particulate aftertreatment.

- **Achieved Phase IIA deliverable performance with unit injector fuel system.**

An ISX engine equipped with a particulate filter and a prototype high capacity EGR system was assembled and tuned to demonstrate emissions performance. After several weeks of tuning in the steady-state performance test cell, the engine was moved into a transient emissions test cell, where steady-state gaseous emissions were evaluated at many speeds and loads across the torque curve. Analysis of the cycle included interpolation of the results at the non-idle points from the 13 mode emissions test, plus the three corners of the not-to-exceed (NTE) zone. Figure 1 presents typical operating points for that test.

These steady-state emissions results are very encouraging since they are well within the Phase IIA objective of 1.0 g/hp-hr NO_x and the 2007 legislated limit for HC of 0.14 g/hp-hr.

A second type of cycle was created based on the Federal Test Procedure (FTP) transient cycle. In order to achieve sufficient particulate loading on the filter, three consecutive FTP cycles were run back to back on a single filter without turning off the engine between cycles

The transient PM emissions were well below the 0.01 g/hp-hr standard but will likely increase with the addition of cold engine starting to the test cycle. Also, these data need to be repeated to determine the capability of the measurement system at such low particulate loading levels.

The engine system used for the emissions testing was demonstrated in a steady-state test cell and achieved good efficiency performance when constrained within the NTE zone emissions limits. Exploration of operation past these limits indicated the engine was capable of higher thermal efficiency.

- **Evaluated rate-shaped and multi-pulse fuel injection.**

The installation of a flexible fuel system capable of running various rate shapes was completed. The system generated different injection rate shapes, as shown in Figure 2, depending on when an amplifier piston was actuated relative to the main injection event.

Note the relatively square shape of the (-1300) trace, when the amplifier was fired well before the start of injection, versus that of the (300) trace, when the amplifier was fired significantly after the start of injection. The (-1300) trace would be typical of most high-pressure common-rail fuel systems.

The (-800) and (-250) traces show the injection rate when the amplifier was fired very close to the start of injection, yielding a shape similar to that expected from a cam-driven electronic unit injector.

Figure 3 shows the results obtained when running a series of points with swings of injection timing and several air handling parameters.

While the lower NO_x achieved with the (300) rate shape was apparently an improvement over the other rate shapes, note the unacceptable increase in smoke. It is believed the slower rate shape was effectively retarding the timing, the ranges of which were held constant for each rate shape. One could argue that the results from testing with each of the four rate shapes lie approximately on the same NO_x / smoke curve and that there is no significant impact due to rate shaping.

Multi-pulse injection strategies were also evaluated during 2003. This testing was carried out on an engine equipped with a high-capacity EGR system. Post injection is particularly interesting,

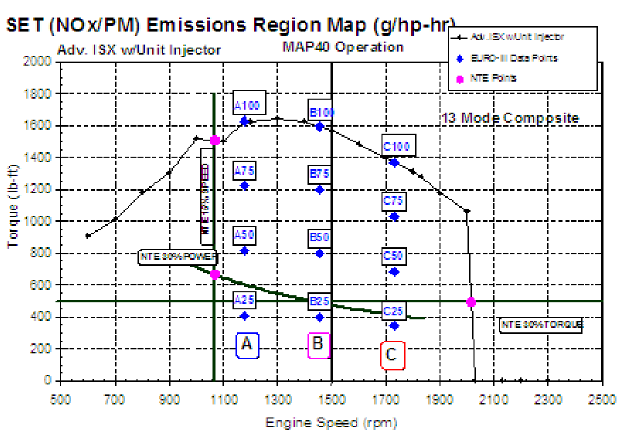

Figure 1. Steady-State, SET Map Performance

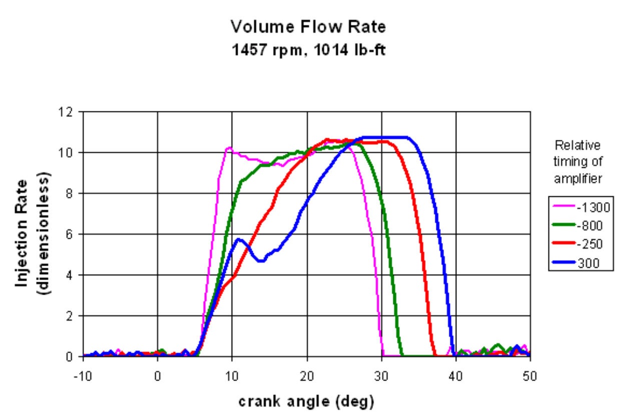

Figure 2. Rate-Shaped Injection Data

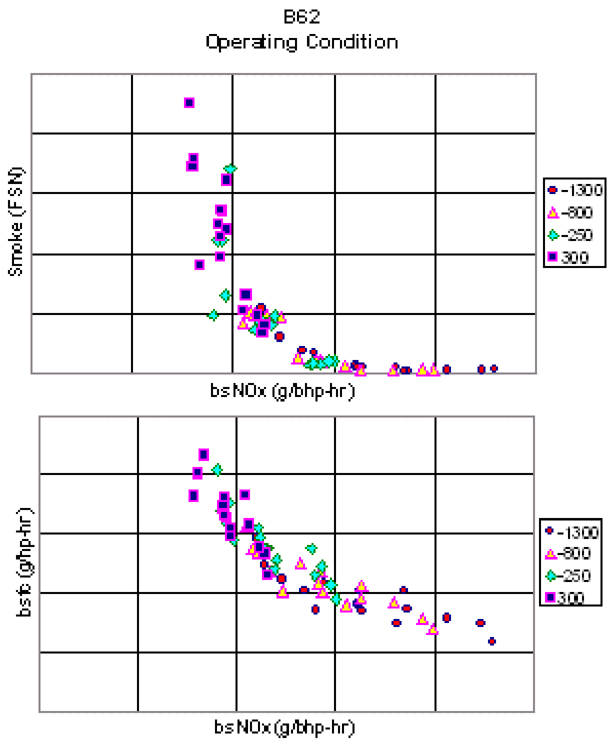

Figure 3. Rate-Shaped Injection Data Showing Related Effects Between Smoke, Brake Specific Fuel Consumption (BSFC), and Brake Specific NO_x ($BSNO_x$)

since it offers the potential of smoke reduction at high EGR rates.

The multi-pulse tests were run in the form of a designed experiment. Regression and optimization of the results yielded trend lines at constant smoke levels for fuel consumption vs. NO_x. Figure 4 shows the significant benefit of post injection at the C speed, 100% load point from the 13 mode test protocol.

- **Performed modeling to determine the benefits of HCCI combustion.**

Modeling the ignition and combustion in diesel cycle HCCI is considerably more difficult than with conventional diesel combustion. The ignition delays are typically much longer, and the fuel burns primarily in a premixed mode. Development of a reliable combustion model is a key step in being able to perform cycle simulation and optimization work. The model under development is a phenomenological model. It is a parcel-based model that uses

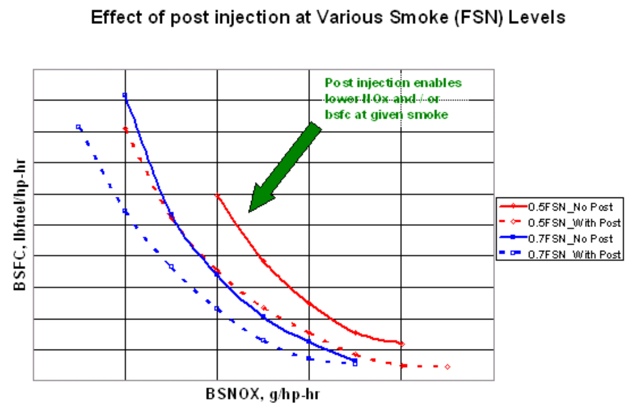

Figure 4. Effect of Post Injection at Various Smoke (Filter Smoke Number – FSN) Levels

the Sandia spray model to simulate mixing and uses techniques developed in our earlier HCCI work to simulate the ignition and burning processes. In early testing with 8 operating conditions comprising a timing sweep and EGR variations, the model did an excellent job predicting ignition and a good job predicting combustion duration. The goal now is to expand the range of conditions over which the model is useful.

- **Installed flexible fuel system and conducted system testing to evaluate performance against the Phase IIA objective.**

The first engine with a prototype flexible fuel system and a breadboard advanced air handling system was evaluated to determine the ability of this configuration to achieve increased brake thermal efficiency (BTE) while meeting the 2007 emissions targets. The investigation was carried out over the 5 most common emission-cycle operating points. Figure 5 shows the trend between fuel efficiency and NO_x emissions for different smoke levels.

Results from this breadboard engine assembly provided valuable experience with fuel system and air handling hardware while identifying critical control characteristics. The capability offered by a flexible fuel system clearly indicated a design direction toward achieving our Phase IIA objectives. The refinement of this system toward a vehicle-capable design and assembly was also a significant outcome.

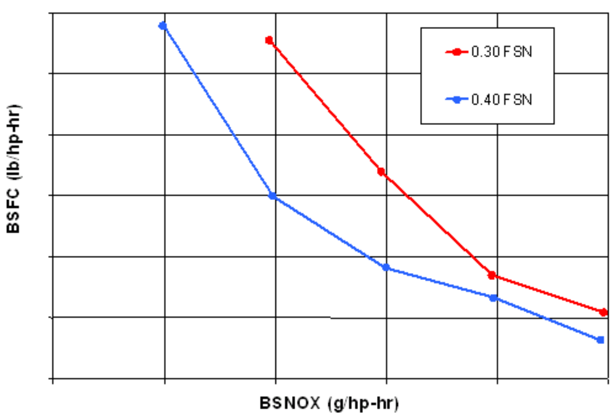

Figure 5. BSFC/NO_x Tradeoff with FSN Limit Difference

A new engine configuration with a flexible fuel system and advanced air handling components was built during the third quarter. The newer, more integrated system has been designed with the experience gained from the first, prototype engine. Testing with this new hardware is expected to begin in the fourth quarter and will continue into 2004.

- **Evaluated particulate filter operation in a heavy-duty vehicle.**

- **Designed and examined improved models of engine-aftertreatment systems.**

Particulate filters have continued to improve during the advanced engineering phase during 2003. The overall system architecture has been updated through virtual build reviews. We have designed and procured engineering samples for vehicle integration in support of our Phase IIA objective. System integration work is progressing, and concept design reviews of the vehicle system were completed using computer models of the aftertreatment system and vehicle chassis. In addition to the modeling, initial concept vehicle testing was completed in a heavy-duty truck and a medium-duty truck as a part of a field test experiment. In order to meet the 0.01 gm/hp-hr particulate target in the Phase II A objective, soot filters remain a key technology for the engine emission architecture. We used data from concept vehicle systems to calibrate and verify engine and aftertreatment dynamic system models that have been developed in Matlab / Simulink. These models allow us to assess the impact of factors such as vehicle duty cycle and cold weather over a wider range of conditions than could be tested through empirical methods. This approach was identified based on previous experience with introducing diesel aftertreatment and recent experience with EGR technology introduction on heavy-duty trucks. Results of this work will allow us to identify gaps within the system against the following attributes:

- Minimum performance or service impact
- Minimum cost and size
- Ability to regenerate in any application
- Self monitoring for problems or service
- Ease of application to a wide variety of vehicles
- Reliability / durability

Aftertreatment concept reviews used Pro-E computer models of the vehicle chassis and the aftertreatment technology in order to support the initial integration. This approach allowed us to integrate the aftertreatment system closer to the engine in order to conserve exhaust temperature and reduce regeneration fuel consumption. Based on the results of the reviews, the design team continued with physical hardware builds in support of our Phase IIA vehicle demonstration. As with prior field testing, test vehicles are equipped with data-logger systems including a global positioning system (GPS). This will allow us to quantify the functional responses of the particulate filter system as well as assess our ability to control regeneration temperatures during on-road operation.

- **Improved closed crankcase ventilation system performance.**

During 2003 significant progress was made toward achieving a successful closed crankcase ventilation system design. The system was evaluated from a durability and robustness standpoint, and a number of improvements were made to electrodes and power supplies. Arcing issues were resolved, thus improving the durability and reliability of the parts. On-vehicle system evaluation was conducted in a field test environment.

- **Initiated studies of waste heat recovery and optimum heat rejection methods at two academic research partners.**

Research agreements were reached during 2003 with two academic institutions to support the Phase IIB objectives. One was awarded a research sub-contract to perform studies of various waste heat recovery systems. As an example to demonstrate the opportunity of energy recovery, Figure 6 presents an analysis of heat rejection from a heavy-duty diesel engine.

As can be seen, the most obvious choices to recover otherwise wasted energy appear to be the exhaust gas and the coolant (radiator heat). The quality of heat energy (heat recoverable to perform work) from these sources varies widely during engine operation. A modeling and simulation study will seek to identify opportunities to recover energy along with a system designed for demonstration purposes.

A second university was awarded a research sub-contract to perform studies of optimized heat rejection systems. Future combustion systems which rely upon increasing amounts of cooled EGR will require upsized heat exchangers to eliminate heat. To achieve the Phase IIB vehicle demonstration, a means to allow cooling through currently sized heat exchangers and vehicle systems will be required. This study seeks to minimize or eliminate the need to upsize vehicle coolers to accommodate the Phase IIB demonstration.

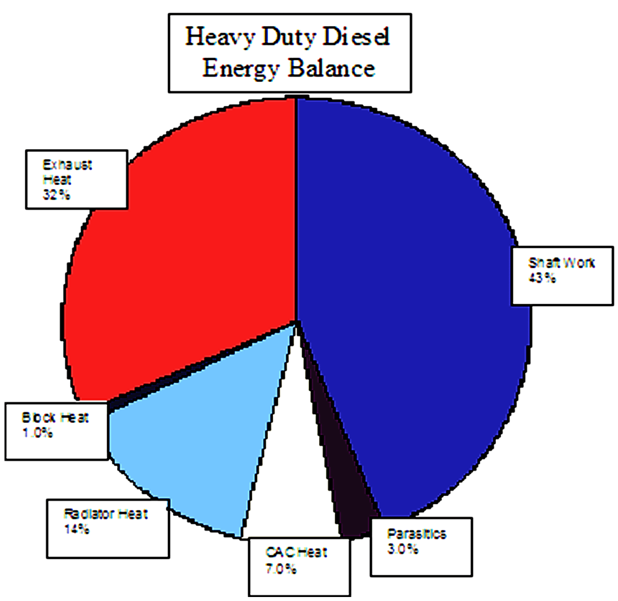

Figure 6. Example First Law Energy Balance for a Heavy-Duty Diesel Engine

Conclusions

- In 2003, we identified an engine system to meet the Phase IIA demonstration objective.
- Extensive system modeling was conducted to identify the engine system chosen for the Phase IIA objective, and model results were verified in actual performance testing.
- Aftertreatment system choice was settled. Controls to optimally regenerate the aftertreatment system were developed, and field testing was conducted.
- The aggressive emissions targets of the Phase IIA demonstration were achieved through test cell testing using a unit injector fuel system and a flexible fuel system. Engines with advanced air handling systems were installed in two heavy-duty vehicles for evaluation. Heat rejection analysis from each vehicle was conducted.
- Closed crankcase ventilation has been developed for adequate system performance and robustness. Designs for manufacturability will focus on reliability. These systems have been shown to be effective in greatly reducing emissions from this previously uncontrolled source. This work is considered complete.
- Research to achieve the Phase IIB demonstration objective was pursued through the year. Academic research partners were brought on board and have begun studies to identify waste energy recovery opportunities and heat rejection optimization techniques.

IV.B. Improvement in Heavy-Duty Engine Thermal Efficiency While Meeting Mandated 2007/2010 Exhaust Gas Emissions

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DOE Technology Development Manager: Roland Gravel

Objectives

- Demonstrate aggressive thermal efficiency targets (+45%) at 2004 engine-out emissions levels (Phase 1).
- Demonstrate 50% thermal efficiency at 2007/2010 mandated emissions (Phase 2).

Approach

- Identify direct fuel economy functions, fuel economy enabling functions and reliability functions for future key engine/aftertreatment systems.
- Use integrated analytical and experimental means to screen and evaluate alternative engine and aftertreatment approaches for downselection.
- Implement Phase 1 results into already-initiated development of technology building blocks for Phase 2.
- Leverage developed engine/vehicle aftertreatment models to spearhead selection and screening of fuel-efficient and viable future diesel technologies.

Accomplishments

Overall Project

- Achieved milestone of 45.3% thermal efficiency at 2004 engine-out emissions without use of aftertreatment devices (11% improvement). Built foundation for development of future technologies that show affinity to increased thermal efficiency.
- Experimentally validated technical roadmap by achieving sub-0.8 g/hp-hr engine-out NO_x composite ESC cycle (steady state 13 mode emissions test) with prototype design.

Combustion

- Validated tools for combustion design, such as KIVA and transient cycle simulation, at 0.5 g/hp-hr NO_x at high loads.
- Experimentally developed CLEAN Combustion© concepts at 0.2 g/hp-hr engine-out NO_x at critical operating regimes.
- Screened transient combustion system parameters and downselected toward the most promising package. Advantages include 30-50% and 45% reductions in particulate matter (PM) and heat rejection, respectively, at same brake-specific fuel consumption (BSFC), or 50% NO_x reduction at same PM and heat rejection levels.
- Developed competing low mixing rate / high mixing rate transient combustion concepts for downselection.

Air System

- Developed high-fidelity analytical tools for the study of exhaust gas recirculation (EGR) mixing, distribution and flow efficiency.
- Analytically screened six air system configurations for Phase 2 goals and identified options featuring high thermal efficiency.
- Experimentally investigated and improved EGR and variable geometry turbocharger (VGT) valve actuation via electronic actuation.
- Tested multiple options for exhaust temperature and air-fuel ratio (AFR) control for diesel particulate filter (DPF) regeneration with minimum fuel economy penalty.

Fuel System

- Applied common-rail injection with four injection events/cycle/cylinder for Phase 1, achieving 45.3% thermal efficiency at 2004 emissions.
- Applied prototype fuel system toward Phase 2 goals, demonstrating lower PM and significant liner temperature reduction.

Diesel Particulate Filter

- DPF technical evaluation developed silicon carbide and sintered metal filter concepts with competing designs for downselection.

Engine/Aftertreatment Dynamic Controls

- Demonstrated the advantages of the model-based approach over conventional controller technology.
- Developed critical virtual sensors, such as a virtual EGR sensor that replaces a hardware sensor and improves thermal efficiency while reducing backpressure requirements.
- Developed increasingly complex air/EGR control strategies, culminating with the transient demonstration of the last-generation controller. Demonstrated control features that reduce transient PM by 50% at same NO_x.
- Conceptualized DPF regeneration strategy and developed Phase A controller.

Future Directions

- Starting from Phase 1 results, quantify thermal efficiency degradation at 1 g/hp-hr engine-out NO_x.
- Leverage Pacific Northwest National Laboratory (PNNL) work and other aftertreatment models to simulate thermal efficiency at 0.2 g/hp-hr tailpipe-out NO_x.
- Based on previous milestones, develop technical package for 45% thermal efficiency for Phase 2.
- Evolve DPF regeneration strategies to Phases B and C, and validate experimentally.
- Complete the characterization of the physiochemical nature of urea selective catalytic reduction (urea-SCR), storage and release mechanisms. Investigate and capitalize on SCR aftertreatment technology's advantage for vehicle fuel economy.
- Investigate additional high-risk / high-thermal-efficiency reward technologies such as homogeneous charge compression ignition (HCCI) combustion, advanced exhaust recovery concepts (such as turbocompound), transient aftertreatment regeneration, next generation fuel system, etc.

Introduction

DDC is conducting the Heavy Truck Engine Project under a DOE cooperative agreement to develop viable technologies that will enable significant fuel economy improvements for future emission-compliant engines.

Approach

DDC has followed a philosophy of simultaneously targeting (1) significant engine and vehicle-based sub-system developments and improvements through blending of analytical and experimental means, and (2) integration and demonstration of such engine and aftertreatment systems at different maturity levels. Sub-system development activities were initiated at the beginning of the project as technology building blocks and are continuing with refinements and added degrees of complexity that impart an even better performance. System integration is a continuous effort that results in systems of increased complexity being added to the engine test-bed. In parallel, the development of aftertreatment controls has commenced and it is in the building-block phase. A significant milestone in systems integration was achieved by completing the "Phase 1 Demonstration" (Figure 1).

The core of this building-block/integration approach features the following technological main thrusts:

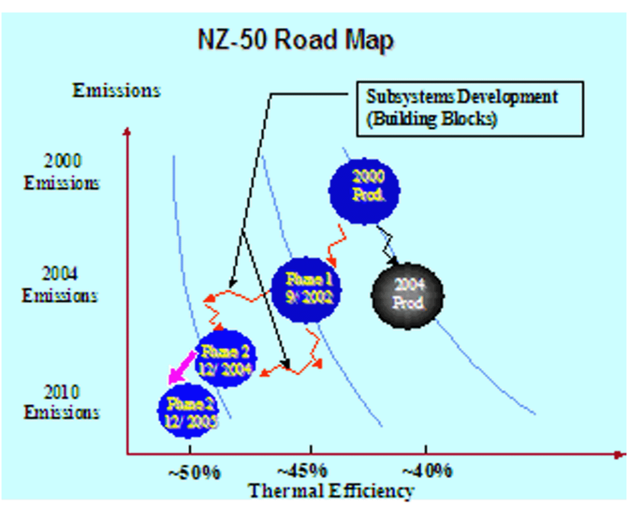

Figure 1. Programmatic Roadmap

- Advanced combustion (including transient, CLEAN Combustion© and other novel concepts)
- Fuel systems (focusing on determining the salient features of common rail and common-rail-like injection that impart improved efficiency and integration to the air, combustion and aftertreatment systems)
- Air systems (for efficient EGR flow and advanced concepts of exhaust gas recovery)
- Aftertreatment technology (requires integration to engine systems from early design stages and complementary control algorithms, as well as mitigation of adverse fuel economy effects of regeneration requirements)
- Engine/aftertreatment dynamic controls (the pinnacle of efficient operation of the integrated systems)

Results

The project demonstrated 45.3% thermal efficiency at 2004 engine-out emissions (i.e. without using aftertreatment devices at that point), thus nurturing engine-based systems for future progress and downselecting fuel-efficient technologies for Phase 2 (Figure 2).

The success of the Phase 1 Demo was the result of well planned and executed technical tasks, including integration of an advanced cylinder head with specially designed components, an optimized EGR circuit, a matched air system and a fuel injection system capable of up to five injection events per cycle.

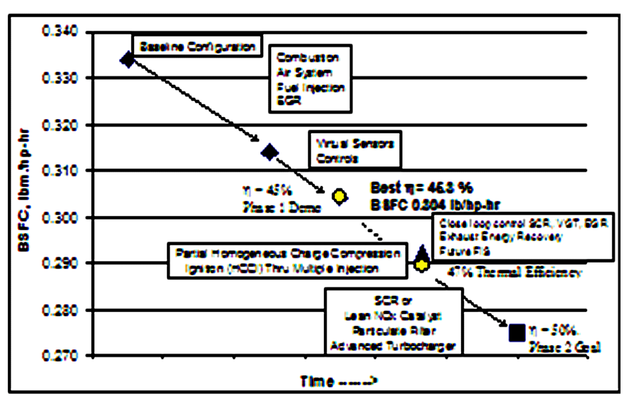

Figure 2. Technical Roadmap and Fuel Economy Demonstrator Progression

Building on the success of Phase 1 technology developments, another key milestone was achieved by reaching sub-0.8 g/hp-hr NO_x and sub-0.07 g/hp-hr PM emissions with prototype technology (Figure 3). This places us within striking distance to Phase 2 targets and allows more and earlier focus on fuel economy enhancement technologies.

Experimental and analytical tools, developed or perfected in-house during the tool development and validation phase, were used to guide the EGR-optimized combustion strategy development. They helped in the identification of two fundamentally different combustion mechanisms that aim at the same overall goal of efficient EGR combustion, but have their own advantages and disadvantages.

Recent experience and additional in-depth use of KIVA analytical simulation tools coupled with targeted selected experiments yielded two main concepts tuned for transient combustion strategies aiming at improving the in-cylinder fuel economy during heavy use of EGR in transient mode, thus fulfilling the transient combustion roadmap requirements (Figure 4). One concept has good potential for NO_x-soot tradeoff, less heat rejection and no loss in fuel economy when compared to the baseline design. The other strategy has a better potential for NO_x-fuel economy tradeoff, similar heat rejection, but higher PM that requires management. The integration of engine (including combustion system) with aftertreatment technology will identify the preferred option for Phase 2.

Significant progress was also achieved in demonstrating CLEAN Combustion©'s salient features in a heavy-duty combustion environment (Figure 5). Current effort focuses on leveraging the unique features of this type of combustion to alleviate the negative impact of DPF regeneration on vehicle fuel economy. CLEAN Combustion© and possibly HCCI have potential as bases for a regeneration strategy that minimizes the frequency of active regeneration events.

The combustion and aftertreatment technologies also influence the operating balance point soot load and are critical for improving the system's BSFC by minimizing the equilibrium soot load over the operational range of the engine.

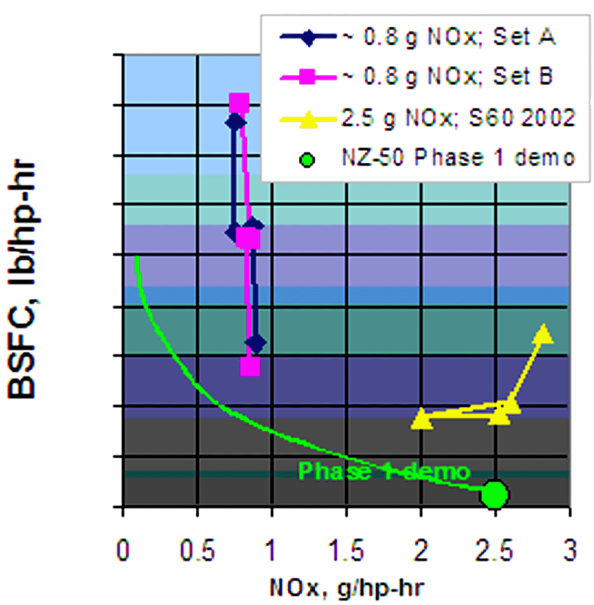

Figure 3. Sub-0.8 g/hp-hr NO_x with Prototype Technology

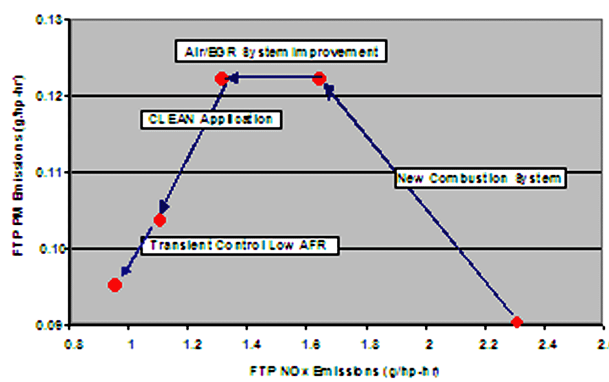

Figure 4. Roadmap to Achieving 2007/2010 Transient Engine-Out Emissions

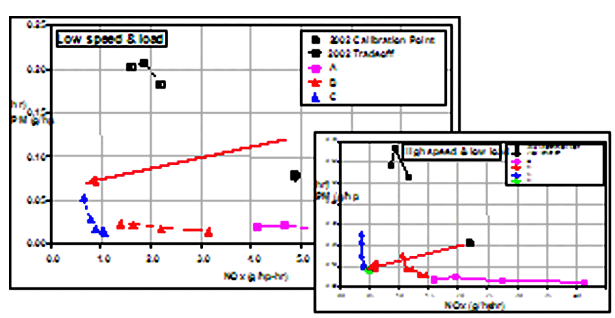

Figure 5. Heavy-Duty CLEAN Combustion© Results

The combustion system's integration and interoperability with the in-cylinder air delivery and quality of the injected fuel require an optimum symbiosis with the air and fuel injection systems. To this end, analytical investigation of the most promising air/EGR systems was conducted with the goal of downselecting systems capable of delivering the required air, EGR, air-fuel ratio and appropriate backpressure.

In addition, specific requirements for the injection system were addressed. Experimental tests conducted with prototype systems led to very promising advantageous BSFC-emissions and NO_x-PM trade-offs.

A new level of complexity for the combustion system design resides in the new requirements for aftertreatment operation and regeneration. In order to meet the Phase 2 objectives, elements of the diesel particulate filter technology requirements were embedded in the initial combustion system basic design and combustion strategy.

The DPF technology introduces additional degrees of freedom to the integrated engine-aftertreatment system that tend to mostly negatively impact the fuel efficiency (Figure 6). DPF technology filters soot particles from the engine exhaust, thereby increasing engine backpressure. The referenced example shows the effect of variable soot loading, soot emission and exhaust gas temperatures on fuel economy. The simulation employs DPF computer models, significantly improving the value added during the Phase 2 design phase.

Parallel investigations related to DPF technology include air/EGR/fuel system investigations for creating adequate conditions for DPF regeneration with minimum fuel penalty. Validation testing will identify a total system technical recipe having the best fuel economy.

A key aspect of the addition of aftertreatment regeneration consists in the dynamic control requirements. While a certain strategy for the control of the EGR/VGT/fuel system is permissible during normal engine operation, optimum operation with aftertreatment can derive great advantages from this alternative and more sophisticated approach. Meeting Phase 2 objectives requires sophisticated and integrated model-based controls focused on sub-system optimization for 50% thermal efficiency. This strategy is shown in Figure 7.

As an example, the progression from conventional technology-based EGR controller to more accurate and stable predictive strategies is shown in Figure 8. The development of virtual sensors is crucial for the EGR/VGT control and also for aftertreatment control. Among the advantages of these types of sensors are the minimization of engine-to-engine variation, compensation for engine drift, and non-intrusive measurements.

As a summary of the control development during the reporting period, the predictive EGR/VGT/fuel controller offers accurate transient emission control

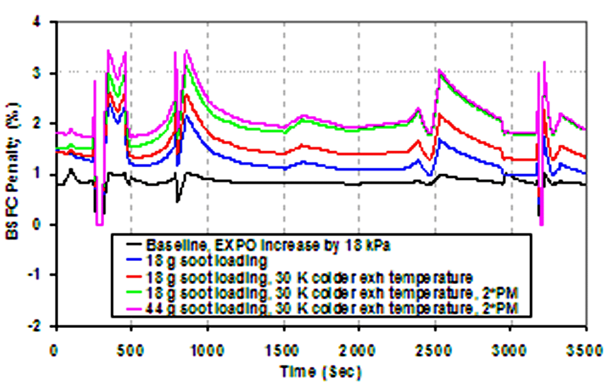

Figure 6. Quantification of Vehicle Fuel Economy Penalty Due to Prototype DPF Technology

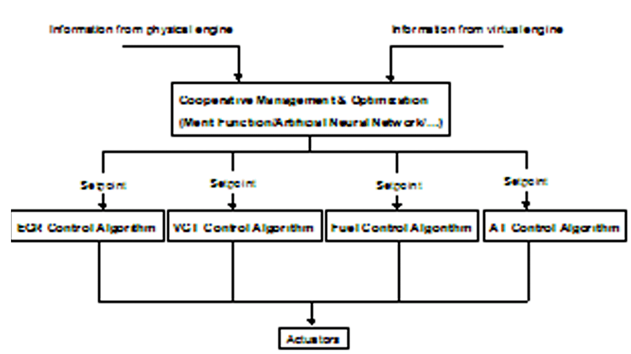

Figure 7. Model-Based Engine and Aftertreatment Controls Logic

that translates to a more favorable fuel economy-emissions tradeoff without loss in drivability.

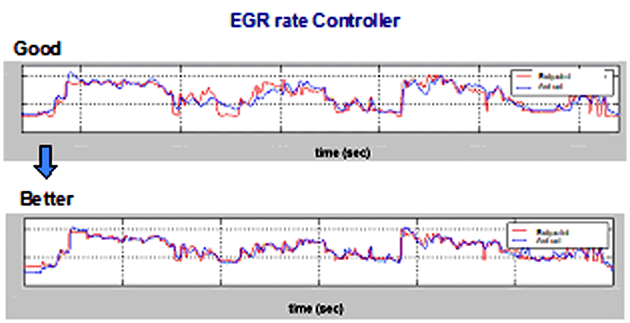

Figure 8. Continuous Improvement of EGR Rate Controller

Conclusions

- The project is on target considering the experimental validation of the Phase 1 and the development status of the Phase 2 sub-system technology building blocks.
- Leveraging of aftertreatment simulation models will allow more efficient screening of next generation technologies and coordination of development efforts.
- High-risk, high-reward technologies such as exhaust energy recovery (turbocompund), HCCI combustion and aftertreatment control optimization have been identified and are proposed for evaluation during the next reporting period.

IV.C. Development of Electrically Assisted Turbocharger for Diesel Engine/ Vehicle Applications

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DOE Technology Development Manager: John Fairbanks

Objectives

- Demonstrate the benefits and feasibility of electrically assisted turbocharging for use in sport utility vehicle (SUV)-size diesel engine/vehicle applications.
- Design and build electrically assisted turbochargers to apply to SUV-size diesel engines.
- Demonstrate fuel economy, emissions and response benefits of electrically assisted turbocharging.

Approach

- Build a mathematical model of an electrically assisted turbocharging system applied to an engine/ vehicle system. Correlate the model with experimental data.
- Design and build prototype electrically assisted turbochargers for application to small diesel engines and demonstrate feasibility and benefits. Define critical acceptance criteria and demonstrate that the design meets these criteria on small diesel engines/vehicles.
- Apply prototype turbochargers to SUV-size diesel engines/vehicles to demonstrate benefits and define critical acceptance criteria that might be unique to this size engine.
- Design and develop electrically assisted turbochargers specifically for SUV-size diesel engines/ vehicles.

Accomplishments

- Successfully built, demonstrated and verified a mathematical model of the electrically assisted turbocharger system on an engine running a vehicle.
- Used surrogate hardware to clearly define the benefits of electrically assisted turbocharging.
- Clearly defined success criteria to be met before electrically assisted turbocharging technology can be considered feasible.
- Developed new technology (induction motor/generator) with a supplier and designed a small turbocharger to demonstrate that this design meets the critical success criteria.

Future Directions

- Complete a wider range of tests with small electrically assisted turbocharger to fully quantify benefits and identify any design issues.
- Apply two small turbochargers to an SUV-size diesel engine to demonstrate feasibility and benefits.
- Design and build an electrically assisted turbocharger(s) sized for SUV diesel engines.

Introduction

Diesel engines offer 30-50% improvement in fuel economy compared to gasoline engines of similar power. Turbocharging is essential technology for the successful application of diesel engines, both for fuel economy and for emissions control. However, low-speed torque deficit and poor turbocharger response can impact the acceptability of diesel engines. Electrically assisted turbocharging appears to be an effective way to eliminate any response lag and further improve the fuel economy benefits offered by a turbocharged diesel engine.

Approach

Early simulations of electrically assisted turbocharging have shown great promise. As a first step, it was necessary to refine these simulations, verify them with actual data and use the simulation tool to optimize the design.

There are several options of electrically (motor/generator) assisted turbocharger design, including permanent magnet, switch reluctance and induction. In addition to conventional criteria such as performance, cost, durability, and packaging, there are additional critical acceptance criteria for this new technology. Based on early experience with preliminary designs, these criteria were defined as:

- High-speed motor/controller system to provide up to 1.4 kW mechanical power at speeds up to 175,000 RPM; total system efficiency > 70%.
- Turbocharger bearing system to carry the extra mass and length while still retaining acceptable shaft rotor-dynamic behavior up to 225,000 RPM.
- Turbocharger and motor cooling system to protect the motor from the extreme turbocharger thermal environment as well as from self-heating.
- Compressor aerodynamics to deliver the extra boost without suffering from surge (“stall”) during transients.

The next step was to select and execute a design that best met these critical criteria and build prototypes for application to small engines in order to more readily demonstrate feasibility and establish benefits. After successful demonstration in a small engine, design optimization and specific designs adapted to larger SUV-size diesel engines could proceed. In the process, any additional success criteria specific to large SUV-size diesel engines could also be developed.

Results

A Matlab-Simulink based model of an electrically assisted turbocharged engine/vehicle system was successfully constructed and verified, as shown in Figure 1.

Using a gasoline engine as a test bed and an e-Charger™ (electrically driven compressor) in series with a turbocharger, the benefits of electrical assist were clearly established, as shown in Figure 2.

A supplier of electrical machinery was selected as a partner to work on electrically assisted turbocharging. Induction motor/generator technology was selected in order to cost effectively meet the critical criteria set forth above. An electrically assisted turbocharger suitable for a small 2-liter engine was designed and built using this technology. Figures 3 through 5 show that the design meets critical acceptance criteria.

The design was tested over city, mountain, highway and country road duty cycles to verify that it

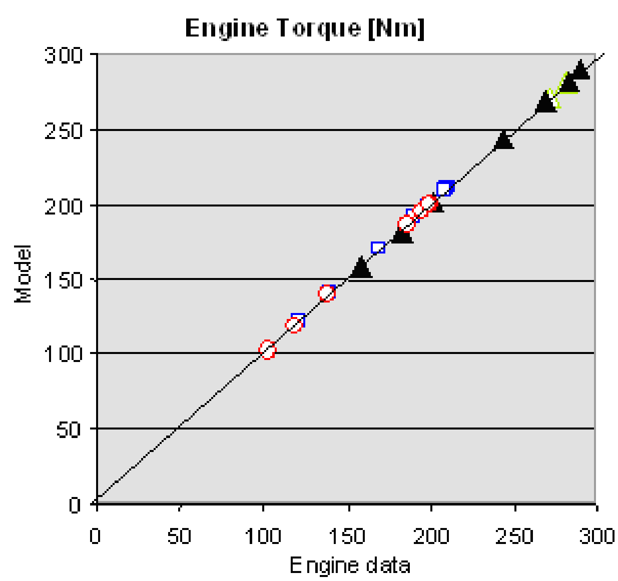

Figure 1. Comparison of Model Calculations and Engine Data over a Wide Range of Conditions

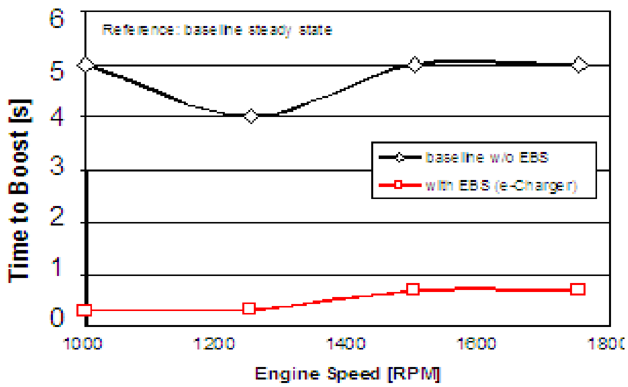

Figure 2. Demonstrating that Electrical Assist Turbocharging Reduces the Time to Achieve Boost

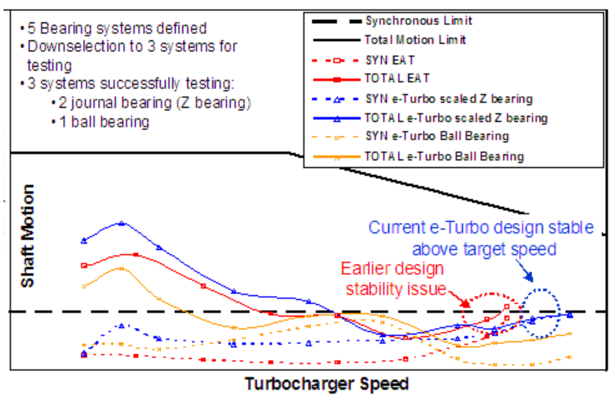

Figure 3. Current e-Turbo Design Meets the Critical Criterion of Shaft Stability at High Speed

meets the critical cooling criterion required, as shown in Figure 4.

Figure 5 shows a selected set of results illustrating how the model can be used for design optimization.

Conclusions

- System models have been developed, validated, and used to set development targets.
- Testing and simulation have validated the potential benefits (fuel economy, engine/vehicle response) of engine downsizing using electrically assisted turbocharging.

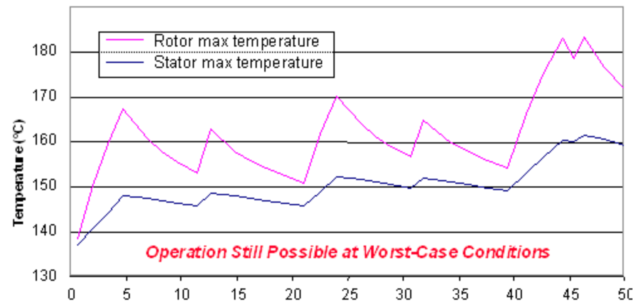

Figure 4. Current e-Turbo Design Successfully Meets Critical Cooling Criterion

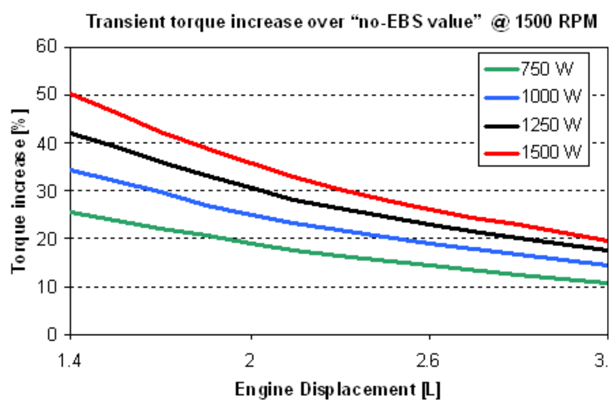

Figure 5. Use of Computer Simulation for Design Optimization Studies

- Key technical challenges have been identified: rotor bearing subsystem stability at high speed, cooling system (motor temperature under severe duty cycle conditions), motor efficiency, and compressor aerodynamics; solutions have been found.

Future Directions

- Develop next-generation prototype encompassing latest technical solutions and performance targets.
- Perform engine and vehicle testing to validate performance and downsizing potential.
- Assess total installed system cost and packaging.
- Scale up to SUV-size engine.

IV.D. Diesel Engine Waste Heat Recovery Utilizing Electric Turbocompound Technology

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DOE Technology Development Manager: John Fairbanks

Subcontractor: Switched Reluctance Drives Ltd., Harrogate, UK

Objectives

- Demonstrate technical feasibility on a laboratory engine
- Improve fuel economy with goal of 5% cycle improvement from exhaust energy recovery
- Improve driveability
- Reduce emissions

Approach

- Develop turbocharger and system design from concept design to preliminary design and final design
- Specify turbomachinery and electrical machinery
- Conduct structural and performance analysis of components
- Design and analyze control system

Accomplishments

- Complete turbocharger hardware has been procured
- Turbocharger has been preassembled
- The crankshaft and turboshaft motor/generator (M/G) have been designed, assembled and tested
- The control system has been developed and tested
- Gas stand preparation for turbo performance test has been completed

Future Directions

- Test turbocharger performance on gas stand
- Validate characterization of turboshaft M/G on gas stand between 30,000 rpm and 60,000 rpm
- Commission control system of electrical turbocompound (ETC) system on gas stand
- Commission engine and ETC control system in engine test cell
- Performance test turbocompound system on Caterpillar C15 on-highway truck engine in engine test cell

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Introduction

The principle of turbocompounding is not new to the industry. It is a known technology for reducing fuel consumption. Research projects for truck-size diesel engines revealed a potential of 5% brake-specific fuel consumption (bsfc) improvement [1]. Diesel engines for ship propulsion and stationary power generation have shown bsfc improvements in the same order. However, those systems consisted of a turbocharger plus an additional power turbine, which was mechanically connected to the crankshaft.

Research efforts at Caterpillar are now focusing on the development of an electrical turbocompound (ETC) system for heavy-duty on-highway truck engines. The efforts cover concept, design and test. This project is aimed at demonstrating electric turbocompound technology on a Class-8 truck engine.

The goal is to demonstrate the level of fuel efficiency improvement attainable with an electric turbocompound system. The system consists of a turbocharger with an electric M/G integrated into the turboshaft. The generator extracts surplus power at the turbine, and the electricity it produces is used to run a motor mounted on the engine crankshaft, recovering otherwise wasted energy in the exhaust gases. The electric turbocompound system also provides more control flexibility in that the amount of power extracted can be varied. This allows for control of engine boost and thus air/fuel ratio. The research work covers turbocharger design, system and component analysis, control system development, engine simulation, electrical machinery development and system and component test.

Approach

A multi-discipline approach has been used in order to address the following key development areas: aero design, electrical machine design, engine performance, control system, and structural analysis.

The layout of the turbocharger was based on a PUGH analysis. It was shown that a mid-mount configuration, i.e. electrical machine between compressor and turbine, is the most promising design (see Figure 1). The compressor wheel has been scaled down from an existing and proven design used in gas turbine engines. The turbine was chosen from a basic study on radial and mixed flow turbines. Performance and inertia lead to the choice and further refinement of a radial type turbine.

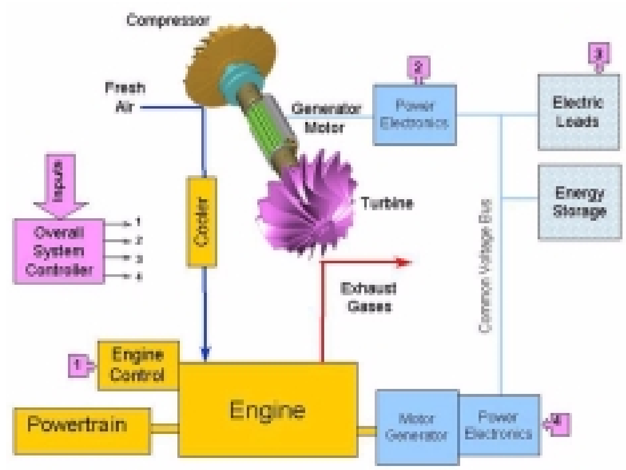

Figure 1. Cross Section of ETC Turbo

The selection of the electrical machine was mainly driven by high shaft speeds and packaging constraints. Three basic machine types were compared: switched reluctance (SR), synchronous reluctance and brushless permanent-magnet. Constraints of shaft speed, rotor outside diameter, low centrifugal stresses, rotor inertia and cost lead to the choice of a SR machine.

The control system targets power flux management and communication between the engine and the ETC control systems. Recovery of energy from the diesel engine exhaust is done electrically. A schematic of the system is shown in Figure 2. When the power produced by the turbocharger turbine exceeds the power requirement of the compressor, this surplus power is converted into electrical power by the electrical machine located on the turbocharger shaft. Surplus power at the turbine can be recovered by the ETC system through an electric motor mounted on the crankshaft, which assists the engine. The result of this process is an increase in system efficiency. Alternatively, the surplus power can be used to drive other electrical on-board devices or truck electrical loads, or it can be stored. To improve vehicle driveability, the system can be run in turbo assist mode, i.e. to accelerate the turboshaft.

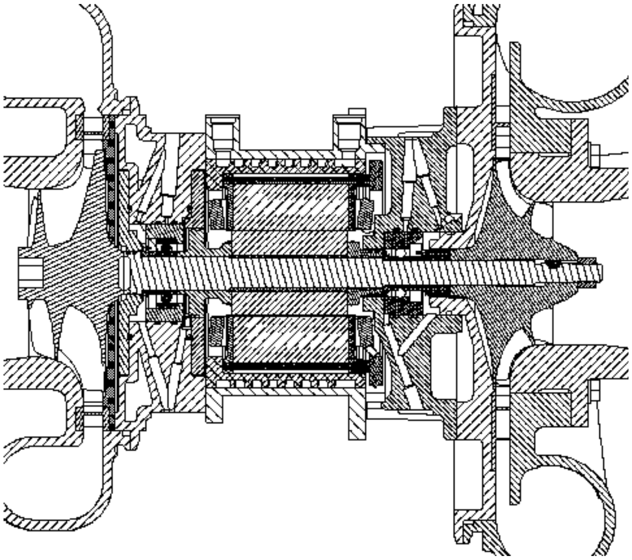

Figure 2. Electric Turbocompound Schematic

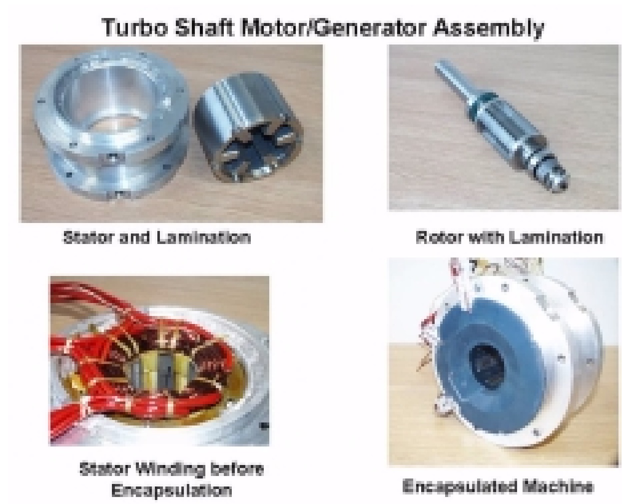

Figure 3. Parts and Assembly of Turboshaft M/G

Results

After having completed design and structural analysis of turbo and electrical machinery, Caterpillar has made progress in procurement and testing. All turbocharger parts, turbine and compressor wheel and cover, bearing housing and shaft assembly have been procured, inspected and preassembled.

The crankshaft M/G has been procured, assembled and tested (see Figure 3). Characterization has been carried out at 340 Vdc in the motoring and generating modes up to 60 kW and 2400 rpm. Independent of the turbocharger, the turboshaft M/G has been procured, assembled and tested on a separate test rig. Thermal tests and characterization were carried out in the motoring and generating modes.

For the control system, a fault mode control algorithm has been developed in order to conduct safe gas stand testing; loss of controller area network communication or any machine or sensor malfunctioning can trigger the shutdown immediately. This prevents the turbo from over speeding. The control, diagnostic and communication software components have been tested individually. The necessary screens for testing and monitoring have been designed and tested.

Conclusions

A turbocharger and ETC system has been designed and built. Compared to a mechanical system, Caterpillar's novel ETC system offers more flexible engine operation, e.g. air/fuel ratio control and turbo assist mode. Performance predictions indicate 5 to 10% improvement in fuel consumption. The system offers the potential for reduced emissions and improved driveabilty through improved air system response using the turbo assist capability.

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FY 2003 Publications/Presentations

1. Hopmann, U. and Algrain, M.C.: "Diesel Engine Electric Turbocompound Technology." SAE Future Transportation Technology Conference, Costa Mesa, June 23-25, 2003.

2. Algrain, M.C. and Hopmann, U.: "Diesel Engine Waste Heat Recovery Utilizing Electric Turbocompound Technology." DEER Conference, Newport, RI, August 25-28, 2003

IV.E. Clean Diesel Engine Component Improvement Program Diesel Truck Thermoelectric Generator

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DOE Technology Development Manager: John Fairbanks

Subcontractor: PACCAR

Objectives

- The objective of the project is to develop a cost-effective thermoelectric generator that will be powered by diesel engine exhaust heat.
- The thermoelectric generator, by generating electrical power, will reduce fuel consumption and emissions.
- Greater onboard generation of electricity could help satisfy the demand for power needed by most exhaust emission control devices being developed for diesel engines.
- Development of the next generation of thermoelectric technology called multi-layer quantum well films (MLQWF) should improve the thermoelectric conversion from the 5% to 6% available today to 20% to 30%.

Approach

- Design a 2 ½-watt quantum well (QW) module suitable for the 1-kW diesel truck thermoelectric generator (DTTEG).
- Test the 2 ½-watt QW module.
- Analyze results, design and test additional QW modules of increasing wattage.
- Plot achievement on calculated efficiency curve.
- Retrofit the 1-kW DTTEG with QW modules.

Accomplishments

- Achieved >1 kW in a test cell with a DTTEG containing 72 HZ-14 (14 watt) bulk material (BiTe) modules.
- Achieved >400,000 equivalent miles road test of DTTEG.
- Achieved 14% conversion efficiency in a QW couple.
- Prepared specifications and obtained quotation on 34-inch sputtering machine with 200 times current rate of sputtering.

Future Directions

- Accelerate QW development; buy or lease the quoted 34” internal diameter (ID) sputtering machine (2003), and execute contract with JDS Uniphase/OCLI (or others) to produce QW film for QW modules (2003).
- Test 2½-watt QW module (2003).

- Produce and test one 10-watt QW module (2004).
- Test a 100-watt QW DTTEG with ten 10-watt QW modules (2004).
- Design a 2-kW QW DTTEG (2005).
- Test a 2-kW QW DTTEG (2006).
- Improve deposition rate for QW film to approach 25% conversion efficiency (2006).

Introduction

Hi-Z Technology, Inc. (Hi-Z) is currently developing three different auxiliary generator designs that are used to convert waste heat from the truck engine directly to electricity. The first activity is the development of a 1-kW generator for heavy-duty diesel trucks. The second is a 300-W generator to be used on a light-duty gasoline engine truck or automobile. The third is a 200-W generator to be used on a light-duty diesel hybrid truck.

The 1-kW generator project [1] has been ongoing for several years and is now being tested for its response to over-the-road shock and vibration in a Class VIII Kenworth truck. Currently, the generator has logged in excess of 400,000 equivalent miles on PACCAR's test track.

The current focus of the 1-kW project has shifted from generator testing to the development of quantum well thermoelectric modules to replace the currently used bulk thermoelectric modules in the generator so that its output can be increased to about 4 kW.

Approach

The 1-kW DTTEG is currently funded by DOE with corporate participation from PACCAR and Hi-Z; it is shown mounted underneath the truck in Figure 1. Figure 2 shows the truck on PACCAR's test track. The 300-W generator is being funded by the New York State Energy Research and Development Authority (NYSERDA) and DOE, and the work is being done for Clarkson University with corporate support from General Motors and Delphi. This generator is shown in Figure 3. The 200-W generator rework is being funded by DOE, and the work is being done for Ohio State University.

All three of the above-mentioned generators currently use conventional BiTe alloy thermoelectric modules. The material in these modules has a value of ZT [figure of merit (Z) times its mean absolute operation temperature (T)] of about 1. The value of ZT has hovered around 1 since the mid-1950s, when

Figure 1. 1-kW DTTEG on PACCAR Truck

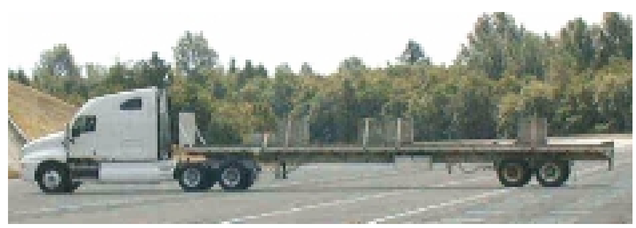

Figure 2. DTTEG Mounted on Truck at PACCAR's Test Track

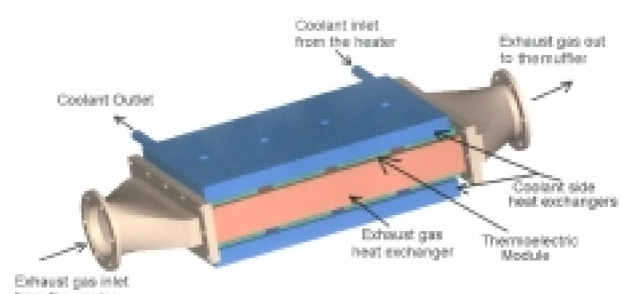

Figure 3. Rendering of 300-Watt Generator

semiconductor materials were introduced into thermoelectric conversion. In the late 1990s, new materials, including quantum well materials, started to increase the value of ZT to about 4 with some promise that even higher values can be obtained as development continues.

The figure of merit (Z) for a thermoelectric material is obtained from its electric and thermal properties by

$$Z = \forall^2 / \Delta * 6$$

where ∀ is the Seebeck coefficient of the material, v/K; Δ is its resistivity, ohm-cm; and 6 is its thermal conductivity, W/cm K. Efforts to improve the value of Z for a bulk material often fail because as one increases ∀, the values of Δ and/or 6 usually also increase so that the resulting value of Z either remains the same or decreases.

In 1992 Hicks and Dresselhouse [2] of MIT suggested that quantum wells should be a good candidate for thermoelectric energy conversion. This was confirmed in 1998 when Ghamaty and Elsner of Hi-Z [3] measured the thermoelectric properties of Si/SiGe quantum well films produced by both the University of California Los Angeles (UCLA) and the Navy for purposes other than thermoelectric energy conversion. Since then, several investigators around the country have confirmed the improved thermoelectric properties of quantum well films.

Quantum well films have been made by several methods. The Navy films measured by Hi-Z were made by molecular beam epitaxy (MBE). Currently, Hi-Z is making its films by magnetron sputtering. Several other methods of film fabrication are possible. While magnetron sputtering does not result in quantum well films with thermoelectric properties quite as good as films made by MBE, they can be made much more quickly and therefore have the potential for much lower cost.

A quantum well film is formed by alternating thin (~100 Å) layers of two materials with differing electron band gaps such as Si and SiGe. When done correctly, all three of the thermoelectric properties improve, i.e., ∀ increases and Δ and 6 decrease. This results in a much improved Z and therefore an improved conversion efficiency (η), which is defined by the equation:

$$\eta = \frac{T_H - T_C}{T_H} \; x \; \frac{M - 1}{M + \frac{T_C}{T_H}}$$

where the matching factor, M, is given by:

$$M = \sqrt{1 - \frac{Z}{2}\,(T_C + T_H)}$$

where T_C and T_H are respectively the cold and hot junction absolute temperatures. Note that the first term of the efficiency equation is the Carnot efficiency.

Results

Thermoelectric Generator (TEG) Mod 2 is scheduled to be installed on a test truck in late November at PACCAR's test facility to attain the remaining 100,000 of the planned 500,000 equivalent miles.

On June 19, 2003, DOE approved the internal shifting of funds within previously approved funding limits to allow Hi-Z to lease a used sputtering machine for the accelerated development of QW thin films.

The work on the Clarkson University Phase II AETEG is continuing in Hi-Z's shops. Assembly of the hot wall epitaxy test unit for development of QW film is continuing.

Quotes on a 34" sputtering machine for development of QW film are being assembled. Leasing brokers are being contacted for final terms on leasing. Hi-Z recently proposed to DOE, the National Aeronautics and Space Administration (NASA), the National Energy Technology Laboratory (NETL) and the Naval Sea Systems Command (NAVSEA) that a shared portion of currently available funding from all four contracts be utilized to purchase the machine in the government's name.

A quantum well film useful in a thermoelectric module is made by stacking many periods of alternating 100-Å layers. These layers are typically formed on a substrate such as silicon, which can remain as part of the film. If the substrate does remain, it becomes a parasitic loss in the system. This problem is discussed later.

The first quantum well couple was reported in 2002 [4]. Unfortunately, it was accidentally destroyed by overheating.

A second quantum well couple was completed recently. This couple, shown in Figure 4, consists of B_4C/B_9C for the P leg and Si/SiGe for the N leg. Both films were a total of 11 μm thick and were deposited on a 5-μm thick Si substrate. Figure 5 is a graph of the uncorrected module conversion efficiency as a function of the hot junction temperature and shows a conversion efficiency of over 14% at a T_H of 250°C. No corrections were made for heat loss through the leads, by radiation, or through the substrate.

Table 1 presents the raw data taken at a T_H of 250°C and T_C of 70°C both for the quantum well couple and a calibration couple made of bulk bismuth-telluride alloy taken on the same test rig.

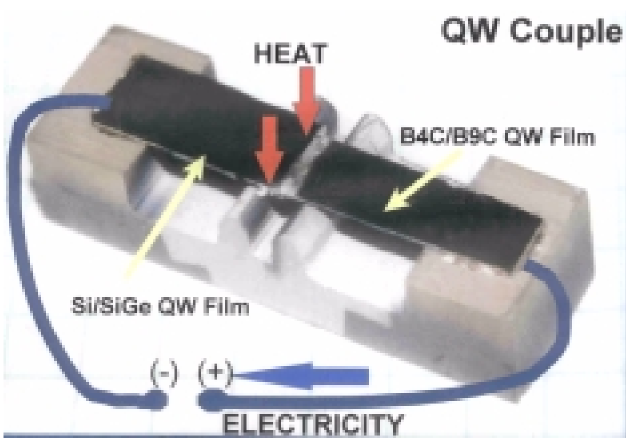

Figure 4. Experimental Quantum Well Couple

As previously mentioned, the substrate used will cause parasitic losses. Figure 6 presents a graph of the calculated quantum well conversion efficiency as a function of film thickness for films deposited on a 5 Fm Si substrate for a T_H of 250°C and a T_C of 50°C. The curve appears to become asymptotic to about 25%

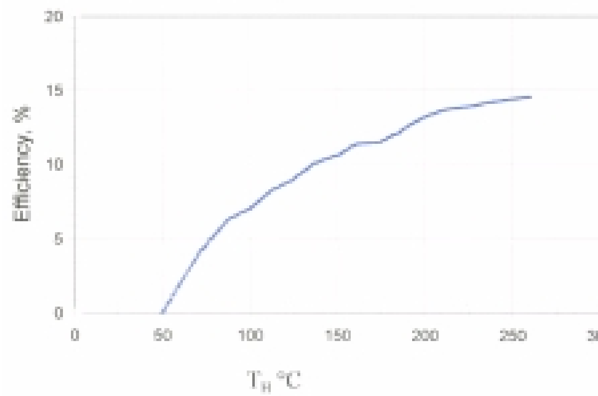

Figure 5. Measured QW Couple Efficiency Versus Temperature

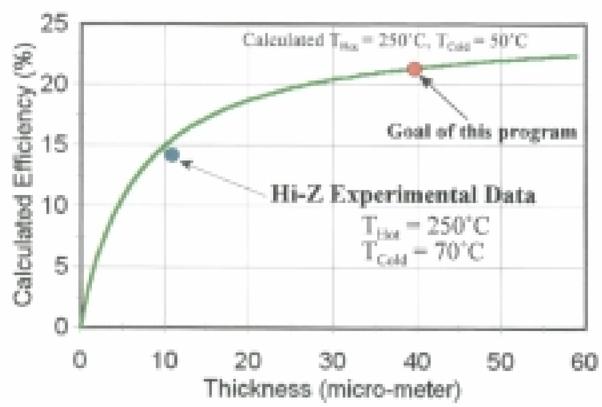

Figure 6. Calculated Efficiency of a B_4C/B_9C-SiC/SiCGe

Table 1. QW Device Raw Test Data for 11 Fm Thick B_4C/B_9C and Si/SiGe on 5 Fm Si at T_{cold} = 70°C and T_{hot} = 250°C

	Power Into Heater			Power Out From Couple			Efficiency
	Voltage	Current	Power	Voltage	Current	Power	
B_4C/B_9C-Si/SiGe	0.1413 V	47.1 mA	6.657 mW	0.365 V	2.608 mA	0.952 mW	14.30%
Calibration: Bi_2Te_3 Alloys	2.510 V	0.836 A	2.098 W	0.034 V	3.15 A	0.107 W	5.10%

efficiency for an infinitely thick film. Also shown on the graph are the data from the test couple and a point that we plan to achieve of over 20% conversion efficiency at a film thickness of 40 Fm.

Hi-Z has also been depositing quantum well films of Si/SiC. This is an N-type quantum well and can be used with the B_4C/B_9C P-type film for higher temperature applications. Table 2 presents the physical properties data obtained for several Si/SiC film samples of various thicknesses. These data were taken at room temperature.

Table 2. Thermoelectric Properties of Newly Fabricated Multi-layered QW Si/SiC Sputtered Film

Samples at Room Temperature	Thickness (Å)	Δ, Resistivity (mΣ-cm)	∀, Seebeck Coefficient (V/°C)
03-01	400	2.15	-750
03-02	800	2.16	-755
03-03	1000	2.14	-745
03-04	1000	2.12	-753
03-05	1600	2.15	-754
03-06	1600	2.11	-758
03-07	1400	2.17	-760
03-08	1400	2.14	-750
03-09	1600	2.12	-752
03-10	1600	2.14	-755

Conclusions

- The DTTEG passed 400,000 equivalent miles on PACCAR's test track, and 500,000 miles are within reach this year.
- QW modules achieved 14% conversion efficiency.
- QW modules with 20-25 micron film thickness can achieve 20% conversion efficiency.
- A larger, faster sputtering machine (34" diameter) is needed to be able to process eight 6" diameter substrates simultaneously.

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3. Elsner, N.B., Ghamaty, S., Normal, J.H., Farmer, J.C., Foreman, R.J., Summers, L.J., Olsen, M.L., Thompson, P.E. and Wang, K., 1994, "Thermoelectric Performance of $Si_{0.8}Ge_{0.2}$/Si Hetrostructures by MBE and Sputtering", Proceedings, 13th International Conference on Thermoelectrics, AIP Press, Kansas City, MO.

4. Ghamaty, S., 2002, "Quantum Well Thermoelectric Devices", Proceedings, DARPA/ ONR/DOE High Efficiency Thermoelectric Workshop, Coronado, CA.

FY 2002 Publications/Presentations

1. Three (3) Quarterly Reports for DTTEG Program
2. DEER '03 Conference: "Recent Progress in the Development of High Efficiency Thermoelectrics".

Special Recognitions & Awards/Patents Issued

1. Hi-Z has been awarded 16 patents: four apply to QW materials, two apply to TEGs.

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

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DOE Technology Development Manager: Ken Howden

Main Subcontractor: Engelhard Corporation

Objectives

- Demonstrate technologies that will achieve future Federal Tier 2 emissions standards.
- Demonstrate production-viable technical targets for engine-out emissions, efficiency, power density, noise, durability, production cost, aftertreatment volume and weight.

Approach

- Develop and use emerging combustion technologies combined with advanced aftertreatment to pursue integrated engine, aftertreatment and vehicle system technical targets.
- Develop aftertreatment simulation models and integrate them with engine simulation tools for emissions prediction, engine control and total system design.
- Select and evaluate system(s) (vehicle + engine + aftertreatment) using an integrated experimental and simulation methodology.
- Conduct system performance, emissions and limited durability evaluation.

Accomplishments

- Developed an integrated CIDI engine and emissions-control system (diesel particulate filter [DPF] + selective catalytic reduction [SCR]) for passenger car and light-duty truck applications.
- Demonstrated Tier 2 Bin 6 emissions target over FTP75 on a light-duty truck using a DPF + SCR system without ammonia slip, synergizing efforts with another project. A 45% fuel economy improvement was achieved compared to the equivalent gasoline engine. Using similar technology, Tier 2 Bin 3 emissions were achieved earlier in a passenger car application.
- Refined "CLEAN Combustion©" with added focus on fuel economy recovery strategies, while also providing lower engine-out NO_x emissions and simultaneously improving aftertreatment NO_x reduction over transient emissions tests, especially at low temperatures.
- Developed the first generation of lean-NO_x trap (LNT) + DPF system that is being applied to a 4.0 L engine. Demonstrated over 90% NO_x reduction over several critical FTP75 relevant driving modal steady-state points.
- Developed and validated individual digital lab aftertreatment simulation models, and integrated them with existing engine and vehicle simulations tools.
- Applied integrated simulation tool featuring engine, aftertreatment, and vehicle models to provide design and testing directions. New strategies for urea injection control and particulate matter (PM) regeneration are being developed.

Future Directions

- Apply next-generation SCR and LNT aftertreatment systems to the 4.0 L engine. Harvest synergy from other sport utility vehicle/light-duty truck (SUV/LDT) engine technology programs into a SUV/LDT application, addressing the technology scalability issues.
- Demonstrate Tier 2 Bin 5 integrated engine, combustion and aftertreatment system performance over the (high temperature) US06 test as well as current (low temperature) FTP75 tests in a LDT vehicle.
- Refine CLEAN Combustion© technology via systematic subsystem enhancements and methodical integration, investigating potential to reduce or simplify aftertreatment options to achieve Tier 2 emissions targets for SUV/LDT applications.
- Develop an integrated engine/aftertreatment system that can effectively and passively perform PM regeneration with low NO_x/PM ratio and with minimum fuel economy penalty.
- Further develop fuel economy improvement strategy via engine and aftertreatment integration with robust control strategy for future aftertreatment systems, and feasible DPF PM regeneration strategies.
- Conduct integrated virtual + hardware tests aimed at optimizing the overall integrated engine-aftertreatment-powertrain-vehicle system.

Introduction

DDC is conducting the Low Emissions Aftertreatment and Diesel Emissions Reduction (LEADER) program under a DOE project entitled: "Research and Development for Compression-Ignition Direct-Injection Engines (CIDI) and Aftertreatment Subsystem." LEADER is to develop emissions control technologies on vehicles and demonstrate scalability to various vehicle classes. The ultimate objective of this program is to achieve aggressive vehicle emissions targets for 2007 and beyond.

Approach

DDC has developed a proven concept and methodology of combining experiments with analytical tools (Figure 1) in pursuing an integrated engine, aftertreatment and vehicle development roadmap. The core of this integrated approach features DDC's CLEAN Combustion© strategy for engine combustion development and state-of-the-art analytical tools covering 0-D for real-time control, 1-D for system integration, and 3-D for component optimization. This system approach benefits substantially from an integrated experimental and analytical approach to technology development, resulting in a shortened developmental cycle, substantially improved understanding of the NO_x-PM trade-off, and fuel economy improvement in both engines and vehicles.

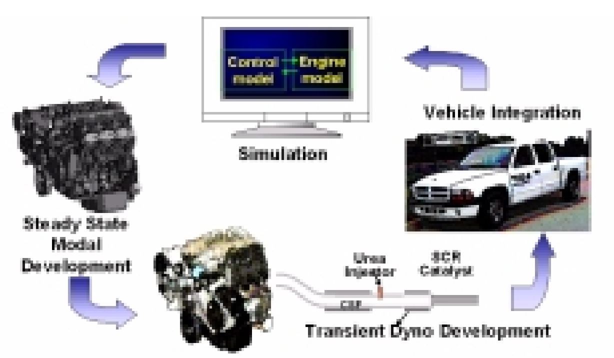

Figure 1. DDC "System Development" Methodology

Results

The DDC team has implemented a first-generation integrated system (DPF + SCR) into a Partnership for a New Generation Vehicle (PNGV)-type mule Neon vehicle, achieving Tier 2 Bin 3 emissions goals in 2002 (Bolton, Hakim, and Zhang, 2002). Further developing this technology and leveraging other programs, a similar type of DPF + SCR aftertreatment system was applied to a LDT Dakota vehicle powered by a 4-liter DELTA engine. This system demonstrated Tier 2 Bin 6 emissions goals over FTP75 transient tests with a 45% fuel economy improvement compared to the baseline gasoline (Figure 2). Figure 2 presents DDC 's roadmap for LDT FTP75 emissions. Integrated engine and passive aftertreatment technologies are targeted to achieve near Bin 9 emission levels without urea injection. Adding advanced urea injection control and vehicle integration system designs will allow tailpipe emissions below Tier 2 Bin 5.

The success of the LDT application was the result of well planned and executed technical tasks, featuring integration of experimental and analytical tools as indicated in Figure 1. This process can be illustrated in the combination of analytical tools and experiments that were utilized to study and improve the exhaust/urea mixing and to optimize ammonia and NO_x distribution entering the SCR catalyst as shown in Figures 3, 4, and 5. Figure 3 shows bench test results on the urea injection system, specifically investigating the injector hole-to-hole urea flow variability. This figure clearly shows that there is a significant deviation in the hole-to-hole flow distribution for a urea doser designed for LDT applications. A 3-D flow simulation model was then applied to this urea distribution to further understand the nature of the urea/exhaust mixing caused by the non-uniform spray distribution, specifically at the catalyst inlet face. As Figure 4 indicates, the urea doser system and exhaust system geometry of the catalyst both have a strong impact on the mixing.

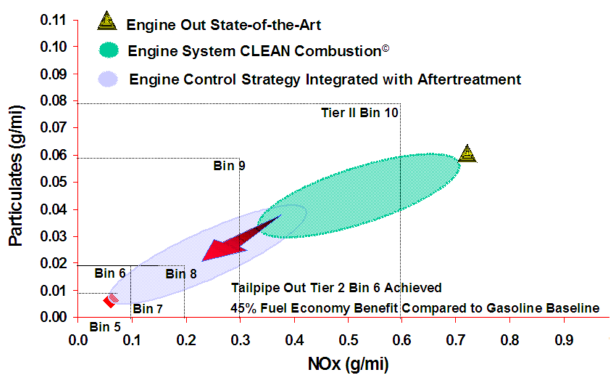

Figure 2. Light Truck Program Integrated Emissions Vehicle Chassis Dynamometer Results

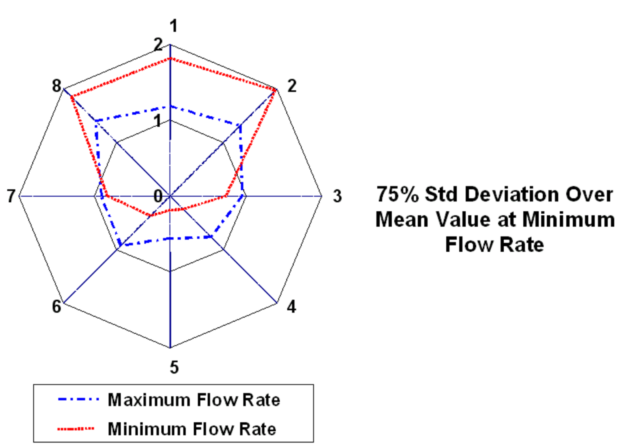

Figure 3. Spray Pattern for a Urea Injection System High Hole-to-Hole Variability

Using these analytical tools to guide system enhancements to the ammonia/NO_x distribution, the low-temperature exhaust gas chemistry, the urea injection controls and reduced engine-out NO_x, Tier 2 Bin 5 (or lower) NO_x targets will be achieved over FTP75 vehicle tests. The application of the integrated experimental and analytic approach further provides valuable design and testing directions for the urea injection and mixing system development. DDC also utilized its recently developed 0-D and 1-D virtual lab tools to investigate ammonia storage characteristics and control-related issues. Figure 5 shows the application of a 1-D SCR model to look into the effect of urea injection control strategy on SCR performance over a transient hot 505 cycle. Control strategies "X" and "Y" were developed, and with proper controls on urea injections, the control strategy "Y" demonstrated significant NO_x reduction without noticeable ammonia slip. These analytically-derived control strategies are crucial to

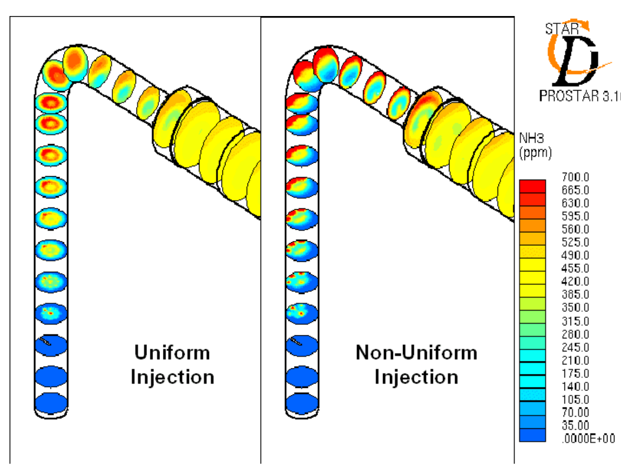

Figure 4. NH_3 Distribution for an Elbow Configuration

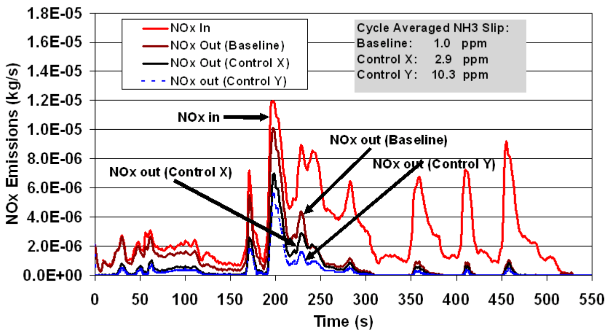

Figure 5. Urea Control Strategies over the Hot 505 Transient Cycle Using Simulation Tool

eventual reductions in tailpipe-out NO_x over low-temperature FTP75 vehicle tests.

Conclusions

Integration of combustion, aftertreatment, and vehicle technologies allowed the DDC team to demonstrate state-of-the-art performance and emissions levels for both passenger car and SUV/LDT applications. Project targets have been met for passenger car applications, and intermediate performance and emissions milestones related to engine and aftertreatment technologies have been achieved for the LDT vehicle. The ultimate challenge is integration of these diverse aftertreatment, control and engine technologies into a prototype vehicle demonstrating 2007+ Tier 2 emissions and performance targets during all operational modes and driving cycles.

References

1. Brian Bolton, Nabil Hakim and Houshun Zhang, "Demonstration of Integrated NO_x and PM Emissions for Advanced CIDI Engines," FY 2002 Progress Report for Combustion and Emission Control for Advanced CIDI Engines, U.S. Department of Energy, November, 2002.

IV.G. Light Truck Clean Diesel Engine Progress Report

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DOE Technology Development Manager: John Fairbanks

Objectives

To develop a diesel engine for light trucks and sport utility vehicles (SUVs) with the following attributes:

- Improved fuel economy – 50% fuel economy improvement over the gasoline-powered vehicle it replaces.
- Emissions capable of Tier 2, Bin 5 full useful life of 0.07 g/mi NO_x and 0.01 g/mi particulate matter (PM).
- Equal or exceed the positive attributes of gasoline performance:
  - Noise
  - Acceleration
  - Cold start and warm up
  - Serviceability
  - Weight

Approach

- Fully analyze the overall combustion and performance of new smaller diesel engines using practical tools including computational fluid dynamics (CFD), combustion kinetics, stress and heat transfer finite element analysis, and overall transient performance simulation.
- Establish bench tests to confirm the above models.
- Optimize the complete system design using the above models.
- Build and test complete system prototypes.

Accomplishments

- Completed design and procurement of a complete diesel engine meeting size and weight goals.
- Successfully repowered a standard gasoline-equipped vehicle without having to modify "hard points" of vehicle construction.
- Demonstrated fuel economy improvement of 50% over gasoline-powered equivalent vehicle.
- Achieved engine-out emissions of less than 1.0 g/mi NO_x and 0.1 g/mi PM on standard (currently available) diesel fuel, satisfying Tier 1 vehicle emissions requirements.
- Demonstrated engine managed solution for active aftertreatment regeneration.
- Integrated active aftertreatment controls into engine controls architecture.
- Demonstrated Tier 2, Bin 5 emissions with engine managed aftertreatment regenerations on fresh "degreened" catalyst system.
- Developed analytical/computational methods for design of the intake port geometry to meet flow and motion requirements.

- Demonstrated increased power goals through use of a variable geometry turbocharger and efficient intake porting.
- Demonstrated vehicle to four major automotive manufacturers.

Future Directions

- Develop proper aging protocol for diesel aftertreatment systems.
- Reduce fuel economy penalty for aftertreatment systems.
- Demonstrate emissions on fully aged aftertreatment systems.
- Revise engine architecture to accommodate potential customer packages.
- Implement closed loop lambda (air/fuel) control for improved engine-out emissions and reduced variation.
- Develop controls to recognize and complete sulfur desorption of emission control system.
- Develop engine and aftertreatment OBD (on-board diagnostic) algorithms that meet standards required for vehicle emissions certification.
- Continue in-cylinder development to reduce engine-out emissions and reliance on aftertreatment to control tailpipe emissions.
- Demonstrate reliability goals for critical engine components:
  - Cylinder head
  - Pistons
  - Emission control devices (on engine)
  - Valve train

Introduction

Beginning in the mid 1980's, the light truck and SUV market share has steadily increased from 30 percent of all new light vehicles sold in the U.S. to what is now over 50 percent share of a 14 million vehicle per year market. As this market has shifted from cars to trucks, the U.S. fleet average fuel economy has decreased. The increase in fuel consumption has driven the need to increase imported oil, affecting the overall trade balance and economy (and eventually, national security). This Department of Energy (DOE)-funded project is aimed at reducing America's dependence on foreign oil while not compromising America's choice of available vehicles. Diesel-powered vehicles will not require a massive change in the fuel distribution infrastructure, vehicle designs, or vehicle usage.

Diesel engines have long been known for efficiency, reliability and durability. Unfortunately, due to the nature of the physics involved, the emissions of oxides of nitrogen (NO_x) and particulates (PM) are significantly higher than legislated limits for light vehicles. America's limited knowledge of light vehicle diesels requires that a saleable product must not only meet the legislated parameters, but must exceed the positive attributes of gasoline-powered vehicles without exceeding the threshold market pricing. This project includes development of a diesel power package that will not require vehicle design changes, will not require unrealistic fuel specifications, and will not require the end user to modify driving or maintenance practices.

Approach

This diesel power package has been developed with a production design intent in mind since inception. This is evident in the use of high-volume, gasoline production accessories and components. Also notable in the design is the use of modern, design for manufacturing initiatives, such as integrated components and reduced bracketry.

The base architecture is designed specifically for light-duty use, as opposed to an adaptation of an industrial or medium-duty engine. This ensures the lightest design methods without compromise for varied applications. This also ensures the design can be optimized for the important customer attributes, including NVH (noise, vibration, and harshness), weight, and cost.

Development of this diesel power package has considered the use of the latest technology for emission controls. High-pressure, common-rail diesel fuel systems in high-volume production from European applications are being utilized. Due to emissions requirements, advanced aftertreatment devices are being used. Engine-out emissions development continues to reduce the engine-out emissions levels, thereby reducing the volume (displacement), total material used, and cost of the aftertreatment device or catalyst. Catalysts are typically loaded with expensive precious metals such as platinum, palladium and rhodium. The cost target for the aftertreatment system is to be equivalent with that of an equal emitting gasoline emission control system.

Results

The diesel power package developed by Cummins Inc. has achieved numerous objectives for this project (see Table 1). The basic design architecture of the engine lends itself to one overriding objective of a production intent project; that is low cost. The engine design utilizes integrated components that allow subassemblies to be assembled and tested prior to final engine assembly. These subassemblies, or modules, reduce final assembly time and material handling in a production environment.

Computer design techniques have been developed and used on several systems of this engine. The intake ports were developed via computational fluid dynamics techniques. The objective for the design of the ports was to maintain swirl for in-cylinder emission control while reducing pressure drop for high flow at high power, reducing pumping losses. The successful design of these ports aided in reaching the increased power goals for the engine (see Figures 1 and 2).

Table 1. Engine Goals and Status

Description	Actual (status)	
	V6	V8
Emissions	Tier 2 Interim Demonstrated, Tier 2 Bin 5 Final, Met in Vehicle	
Noise, dBa	72.7, Bare Engine in Test Cell	49.7 Interior Idle Park Ram1500 Pickup
Fuel Economy, MPG	22.1 Combined, Durango (+60%)	21.7 Combined, Ram1500 (+60%)
Quality/Reliability	Current Work Focus	
Rated Speed	4000 rpm (5000 max.)	
Useful Life km(mi)	8000 hr Total Development Testing (equivalent usage >1.9M(1.2M)	
Performance	10.7 sec, 0-60 mph, 5500 # PTW	9.6 sec, 0-60 mph, Ram1500, 6000 # PTW
Displacement, liter	4.2	5.6
Power, kW(hp) @ rpm	177(237) @ 3600 WG 201(270) @ 3800 VNT	224(300) @ 4000 Interim target met.
Torque Peak, Nm(ft-lb)	584(430)	623(460)
Warm-Up	34C in 200 sec @ -10C	Future Work
Serviceability	No Adjustments Diesel fuel filter added.	
Cold Start	3.2 sec (10 sec glow) @ -10C	Future Work
Weight, kg(lb)	301(663)	357(788)

Meets Goal   Partially Meets Goal; Plan in Place

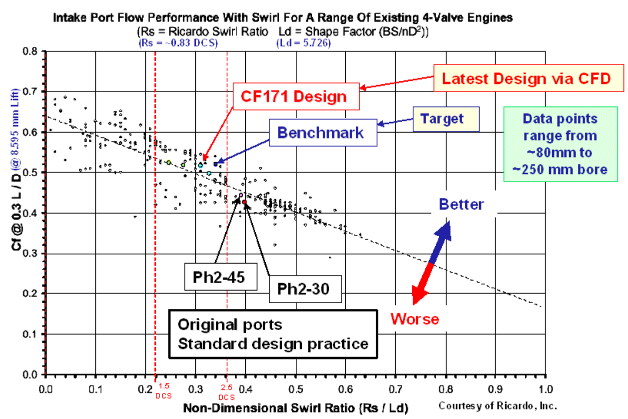

Figure 1. Swirl vs. Flow Trade-Off Curve

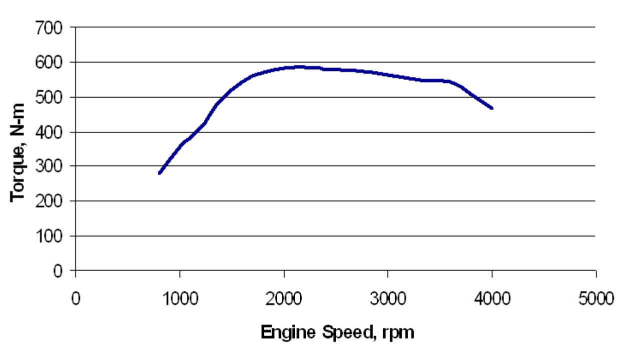

Figure 2. V6 Performance Results

Integration of the aftertreatment controls into the base engine and emission controls has been a major effort in this project. The NO_x aftertreatment device requires periodic conditions of fuel-rich exhaust stoichiometry in order to regenerate, or reduce the stored emissions of NO_x (see Figure 3) to elemental components of nitrogen and oxygen. This rich operation is not normal for diesel engines that typically only operate under lean conditions. Major emphasis was placed on being able to operate the cylinder under rich conditions to avoid adding additional hardware devices such as an additional injector in the exhaust piping. Also, maintaining the original objectives set for this project, development had to focus on not inducing torque or noise fluctuations during these fuel-rich excursions. The successful integration of these controls, along with advanced catalysts, made possible the demonstration of Tier 2, Bin 5 emissions (see Table 2).

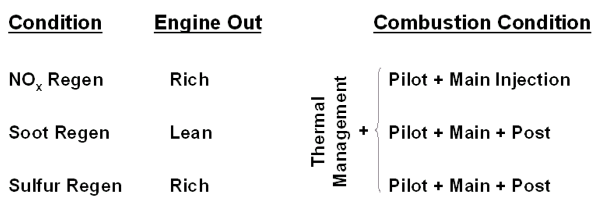

Figure 3. Regeneration Strategy

Table 2. Demonstrated Emission Results for 5000 lb Vehicle With Automatic Transmission

Test	NO_x (g/mi)	NMHC* (g/mi)	CO (g/mi)	PM (g/mi)	Fuel Economy (mpg)
Tier 2, Bin 5 Limits	0.07	0.09	4.2	0.01	-
FTP	0.033	0.089	0.399	0.006	20.32
HFET	0.005	0.00	0.122	0.006	32.8
US06	0.158	0.011	0.138	0.023	22.53
SC03	0.009	0.00	0.229	0.013	21.16
* NMHC = non-methane hydrocarbon					

The emissions tests have been done using Phillips 66 “DECSE” fuel and relatively fresh “degreened” only catalyst system. The “DECSE” fuel has very low sulfur content (<4 ppm). Sulfur poisons the NO_x-adsorbing catalyst, resulting in poor performance as the catalyst ages. Fuel specifications for future diesel fuels include a maximum sulfur content of 15 ppm. While the low sulfur content of future fuels should aid in reducing catalyst poisoning, catalysts will eventually fail due to poisoning by sulfur. Future work will include desulphation development and related catalyst durability enhancement.

Conclusions

- It is possible to create a reducing atmosphere for NO_x storage catalysts using only in-cylinder air and fuel management.
- Rich cylinder excursions can be achieved without affecting power production or noise from the engine.
- The use of advanced aftertreatment controls does enable the diesel engine to meet emissions requirements while realizing a significant fuel consumption reduction.
- The engine provides a viable business case for light truck diesels.

FY 2003 Publications/Presentations

1. DOE Diesel Engine Emission Reduction Workshop, Newport, RI, August 2003.

Special Recognitions & Awards/Patents Issued

1. Air/oil coalescer with improved centrifugally assisted drainage, Patent No. 6,640,792.
2. Valve train with a single camshaft, Patent No. 6,390,046.

IV.H. Variable Compression Ratio Engine Analysis

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Subcontractor: Cosworth Technology Ltd., Northampton, England

Objectives

- Using variable compression ratio (VCR), demonstrate potential for attaining over 38% efficiency with a spark ignition engine running at a lambda of 1.0.
- Achieve 150 horsepower per liter (hp/L) maximum power output.

Approach

- A VCR 2-cylinder engine block was built and tested by Envera LLC for DOE in 2001. The VCR mechanism was proven to be structurally robust and reliable. A donor cylinder head from an Acura Integra Type-R was used for durability testing. The donor cylinder does not have a compact combustion chamber shape or high enough compression ratio (18:1) necessary for demonstrating the objective high engine efficiency value of 38%. To demonstrate high peak efficiency capability running at a lambda of 1.0 concurrent with a high horsepower per liter capability, a new cylinder head was designed, built, and tested. The gas path geometry and cam timing values needed for attaining a high peak efficiency were also produced.

Accomplishments

- A VCR engine with a high compression ratio cylinder head was designed, built and successfully tested.
- Indicated fuel efficiency values demonstrated potential for attaining a peak efficiency of over 38% using high octane pump gasoline (93 octane) running at a lambda of 1.0 for effective reduction of emissions using proven 3-way catalytic converter technology.

Future Directions

- Investigate potential diesel engine fuel economy and emissions benefits that can be attained with VCR.
- Investigate potential further gains in spark-ignition engine efficiency that may be attainable with VCR.
- Demonstrate potential for manufacture at commercially acceptable cost.

Introduction

A high-efficiency cylinder head for an existing 2-cylinder VCR engine was designed, built and tested. The cylinder head is designed to provide a compression ratio range of 8.5:1 to 18:1 and a power output capacity of 150 hp/L. The cylinder head also includes adjustable valve control that may be used for throttle-free power control.

VCR project goals were redirected to the FreedomCAR Program in 2002. The new goals are technically more challenging. In particular, to attain the former Partnership for a New Generation Vehicle (PNGV) 80 mpg target, a peak engine efficiency of approximately 35% was required when combined with aggressive engine downsizing (1). While engine downsizing is recognized as being of high value for improving fuel economy, the FreedomCAR Program emphasizes peak energy conversion efficiency. To attain a higher peak efficiency, the gas path and cam timing were optimized using GT-Power software. The new VCR cylinder head was dynamometer tested in November, 2002. Indicated fuel consumption data showed that a naturally aspirated peak efficiency of approximately 38% is attainable, a significant improvement over the PNGV target. Turbocharging is expected to further increase peak engine efficiency; however, boosted testing was beyond the scope of the project.

Approach

A cylinder head for the 2-cylinder VCR engine was designed, built and tested by Envera LLC and Cosworth Technology Ltd. Major design goals included design of a high compression ratio combustion chamber, high-performance intake and exhaust ports, 150 hp/L capacity to support aggressive engine downsizing, adjustable valve timing to enable throttle-free engine operation and/or further efficiency optimization, and calibration and tuning for a high peak efficiency. Table 1 shows specifications for the engine.

Table 1. VCR Engine Specifications

Cylinders	2
Valves per cylinder	4
Valve included angle	20.1 degrees
Valve actuation	Tappet (Both exhaust valves)
	Tappet (First intake valve)
	Rocker (Second intake valve)
Bore spacing	90 mm
Bore	81 mm
Stroke	90 mm
Bore/stroke ratio	0.90
Displacement	928 cc
Rod center length	171 mm
Balance shaft	Single primary
Bore off-set	15.5 mm
Compression ratio	18:1 maximum
	8.5 minimum
Fuel	93 octane (98 RON + 87.7 MON)/2
Engine management	PFI Motec
Emission control	3-way catalyst
VCR actuator type	Hydraulic
Specific Power Output	150 hp/L
Bottom end design speed	8000 rpm

A compact, high compression ratio combustion chamber was attained by using a narrow valve-included angle of 20.1 degrees and a small bore-to-stroke ratio of 0.90. A small, 1.0 mm high piston dome was required to attain a maximum compression ratio of 18:1.

The intake ports were designed by Envera LLC using GT-Power software from Gamma Technologies to determine the cross-sectional area for optimum tuning and an Excel spreadsheet for skeletal shaping. The intake port approach angle and lower bend radius details for attaining target tumble values were determined using parametric modeling from Cosworth Technology (2). The final geometry was created in ProE software. Steady-state computational analysis of the final port design was conducted by Cosworth Technology using Star Cd software. Coefficient of drag flow values exceeded expectations.

Throttle-free power control is provided by phase-shifting one of the two intake valves per cylinder to control the amount of intake charge trapped in the engine cylinders. Small power levels are attained by closing one intake valve late, so that much of the intake air charge is pushed back into the intake manifold during the early part of the compression stroke. The two exhaust valves per cylinder and one of the intake valves are driven by a first camshaft, and a second phase-shifted camshaft drives the remaining intake valve per cylinder.

Engine tuning and peak efficiency calibration was conducted by Envera LLC using GT-Power. Excel was used to track over 1000 optimization test runs. Multi-variable optimization was conducted as part of the optimization strategy. The GT-Power model, which displayed exceptional accuracy, was used during dynamometer testing to design test runs in real time.

Peak engine efficiency was tested at Cosworth Technology in November, 2002. Indicated efficiency values are shown in Table 2. Brake specific fuel consumption values are projected using friction mean effective pressure (fmep) values that are representative of good production 4-cylinder engine capability.

Table 2. Efficiency Projected from Dynamometer Test Results

Engine speed	2350 rpm
Fuel to air mixture ratio	Stoichiometric, lambda 1.0
Fuel	93 octane
Fuel lower heating value	42.58 MJ/kg
Indicated mean effective pressure	10.7 bar
Projected friction mean effective pressure, fmep	1.10 bar
Brake mean effective pressure with assumed fmep	9.60 bar (imep – fmep)
Brake specific fuel consumption with assumed fmep	220.7 g/kWh
Brake efficiency with assumed fmep	38.3%

Conclusions

A VCR engine with a high compression ratio cylinder head was designed, built and successfully tested. Indicated fuel efficiency values from dynamometer testing demonstrated potential for attaining a peak efficiency of over 38% using high octane pump gasoline (93 octane) running at a lambda of 1.0 for effective reduction of emissions using proven 3-way catalytic converter technology. The potential of lowering diesel engine emissions with VCR should be explored, as well as the potential for further improving spark-ignited engine efficiency.

References

1. Ricardo Technical Report No. D99-0498, June 4, 1999.
2. Blaxill, H.; Downing, J. et. al: A Parametric Approach to Spark-Ignition Engine Inlet-Port Design, SAE paper no. 1999-01-0555, pub. 1999.

IV.I. Development of Metal Substrate for $DeNO_x$ Catalysts and Particulate Trap

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Objectives

- Develop advanced metallic catalyst substrate materials and designs for use in off-highway applications.
- Increase durability, reduce flow resistance, decrease time to light-off, and reduce cost relative to cordierite substrates.

Approach

- Define the requirements of the catalyst substrate.
- Determine the properties of alternative materials for application in the diesel exhaust environment.
- Test alternate materials.
- Model new designs.
- Validate models.
- Fabricate new metallic substrates.
- Evaluate new material and design in diesel engine exhaust environment and off-highway environment.

Accomplishments

- Material down-selection occurred.
- Modeling of new design options started.
- Determination of material coatability started.

Future Directions

- Validate computational fluid dynamics (CFD) model and optimize the foil folding geometry.
- Optimize coating formulation.
- Determine acceptable joining techniques.
- Begin fabrication of full-scale device.

Introduction

To meet estimated Tier 2 and Tier 3 EPA emission targets on off-highway vehicles, it may be necessary to add aftertreatment. Two technologies under consideration are $DeNO_x$ catalysts and particulate traps. Current aftertreatment technologies utilize a packaged cordierite honeycomb catalyst support. This package performs well in on-highway applications; however, off-highway applications are much more harsh. Ceramic material properties are not expected to be adequate for the severe conditions found in off-highway applications, such as the high vibration loads (>10 x gravity). Additionally, the ceramic matrix requires relatively thick walls between cells, causing high flow resistance, which translates to increased engine exhaust backpressure and approximately a 2-3% fuel consumption increase. Because metallic substrates have superior mechanical properties over ceramics in this application, they are a possible solution to both durability and flow resistance issues. Metallic substrates are expected to be a key enabler for durable, commercially viable off-highway exhaust aftertreatment.

Approach

The development of the metal catalyst substrate is focused in two areas: materials and design. The materials aspects are investigating metals that are more applicable to the diesel exhaust environment. Current metallic catalyst substrates are made from higher cost alloys that have properties that are necessary for the automotive market. Since diesel applications are less demanding, in terms of maximum temperature, than the automotive market, the search for a less costly material is a major driver. The material selected must have a few key qualities: good oxidation resistance at diesel exhaust gas temperatures, catalyst coatability and adhesion, and good formability.

On the design side, the investigation is moving to alternative design shapes and packages. Current commercially available catalyst supports have straight channel passages. The current work looks to optimize the flow path, thereby increasing catalyst efficiency and potentially reducing necessary catalyst volume. The approach relies on computation methods to give design direction. The package shape is also critical since off-highway vehicles have severe space limitations on additional equipment. The work will investigate the applicability of package shapes alternative to cylindrical or rectangular.

Results

Materials selection for a suitable metallic catalyst substrate involves characterizing the oxidation behavior of each material to find a material that forms a stable and adherent oxide that is capable of being coated with a catalyst. A number of potential alloys were identified and investigated for use in this application. Many were eliminated due to lack of oxidation resistance, poor oxide formation, poor manufacturability, and high cost. Significant investigation was performed on three alloys. Material C exhibited oxidation resistance similar to material A and better resistance than material B, as shown in Figure 1. Material B has low aluminum content and is capable of forming an aluminum oxide scale at high temperatures. The alumina scale is desirable not only for its very good oxidation resistance properties but also for its good catalyst coatability. Because material C has less than half of the aluminum content as material A, it is a much easier alloy to roll into thin foil sections down to 50 μm. Foils of each material were exposed in air at temperatures ranging from 800°C to 1000°C for times up to near 90 hours. Resulting oxides were characterized with the scanning electron microscope (SEM). Mass gain and oxide thickness as a function of oxidation time and temperature were also measured.

The top two candidates for the metal substrate applications are material A and material C. Figure 2 is a comparison of the oxides that are grown on the surfaces of each alloy. The oxide whiskers on material C are approximately 10 times smaller than those grown on material A for a comparable time and

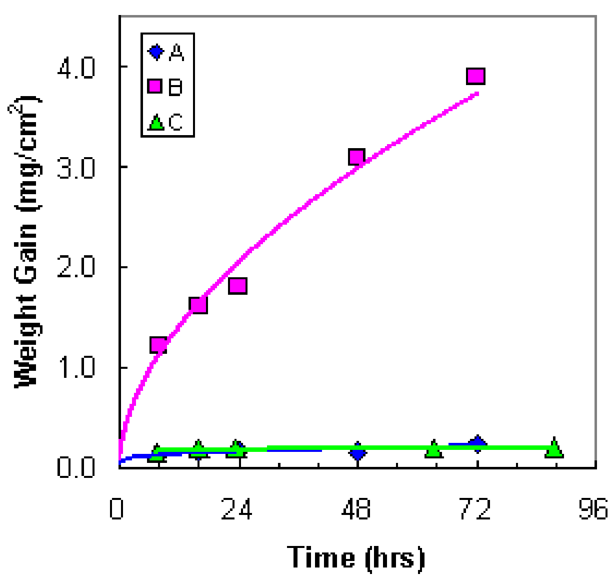

Figure 1. A Comparison of High Temperature Oxidation Properties for Three Different Materials

temperature; however, they appear to be much more dense. The difference in size would explain the ease with which material A is coated. With the much larger oxide particles, the coating is accepted onto the surface very well and causes the coating to have very good mechanical integrity.

One of the drawbacks of material C is found in the alloy's reluctance to nucleate the oxide whisker structure exhibited in Figure 2. A study to optimize the process heat-treating to achieve a suitable oxide layer is currently underway.

New Design Development. The project has undertaken a task to perform CFD modeling to determine the effect of geometry changes on the flow through the channel of a substrate. The designs focus on limiting pressure drop through the metal catalyst support while maximizing gas mixing within the support structure, thereby increasing catalytic performance without hindering engine performance. The CFD model will be utilized to obtain the optimum geometry more quickly than through trial and error. Initial geometries have been selected on which investigations will build.

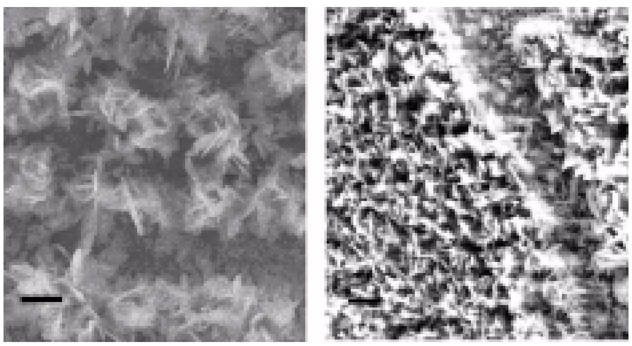

Figure 2. SEM photomicrographs depicting the surface morphology of surface oxides on material A (left) and material C (right) that were oxidized in air at above 800^{o}C for the same amount of time. Note the shape and size of the oxide for each material. The markers are 2 mm in length.

Coat Support with Catalyst. To determine the ability of a material to be washcoated, the new metal substrate materials were initially coated with an aqueous suspension of gamma alumina. This initial assessment of material B and material A proved to be very informative. Material B was more difficult to coat than material A, and the coating on material A was more durable. The differences in adhesion are presumed to be due to the large difference in surface oxide shape. Material A oxide grows as rosettes on the surface, while the material B has small cuboidal crystals. The rosettes will act as large anchors for the alumina washcoat, resulting in a resistance to spalling during drying and calcining. Acceptable catalyst coatings were achieved on both material A and material C.

Conclusions

The catalyst substrate material has been selected from a number of alloys. The new alloy has comparable oxidation properties to the alloy currently used in commercial metal substrates.

IV.J. Off-Highway Heavy Vehicle Diesel Efficiency Improvement and Emissions Reduction

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DOE Technology Development Manager: Gurpreet Singh

Objectives

- Design combustion systems that meet Tier 3 emission requirements with comparable fuel economy to Tier 2 engines
- Improve combustion system design tools
- Improve calibration development tools

Approach

- Use combustion computational fluid dynamics (CFD) to design combustion systems for Tier 3 engines
- Incorporate improved submodels in the KIVA-RIF code
- Improve optimization tools for selecting combustion systems
- Develop and incorporate a global model for calibration development

Accomplishments

- Combustion system design completed on one engine platform
- Fuel economy close to Tier 2 value
- Combustion system design in progress on three other programs
- Improved KIVA-RIF submodels incorporated and validated
- Calibration improvement model developed for steady-state calibrations

Future Directions

- Continue to develop energy efficient combustion system designs
- Continue with combustion tool development
- Continue with calibration tool development
- Focus combustion design on Tier 4 emission requirements

Introduction

Cummins Inc. is a world leader in the development and production of diesel engines for on-highway vehicles, off-highway industrial machines, and power generation units. Cummins Inc. diesel products cover a 50-3500 HP range. The power range for this project includes 80-750 HP engines that must achieve the U.S. Environmental Protection Agency's Tier 3 emission levels of 4.0 gm/kW-hr NO_x+NMHC (non-methane hydrocarbon) and 0.2 gm/kW-hr PM (particulate matter). Cummins' anticipated product offerings for Tier 3 regarding this topic include midrange, heavy-duty, and high horsepower engines.

Cummins has extensive experience with meeting tough emission standards for on-highway engines. The key strategies involve retarded timing and using cooled and un-cooled exhaust gas recirculation (EGR). EGR is an effective strategy for on-highway applications because they utilize ram-air, operate under light load factors, typically utilize standard drive-line configurations, and operate in clean environments. Variable geometry turbo-charging also works effectively in this environment. A typical on-highway installation is illustrated in Figure 1.

Conversely, off-highway applications are diverse (see Figure 2), operate under extreme ambient and duty cycle requirements, will typically require a hydraulic cooler, and do not benefit from ram-air cooling. For example, a hydraulic excavator is a highly transient (speed) stationary application that is hydraulically driven through a gearbox which incorporates multiple hydraulic pumps for propulsion, boom operations, etc. The installation

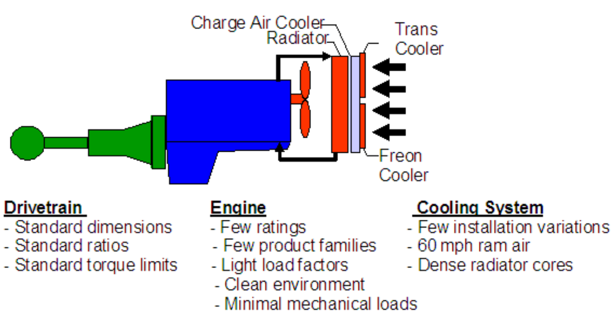

Figure 1. On-Highway Installation

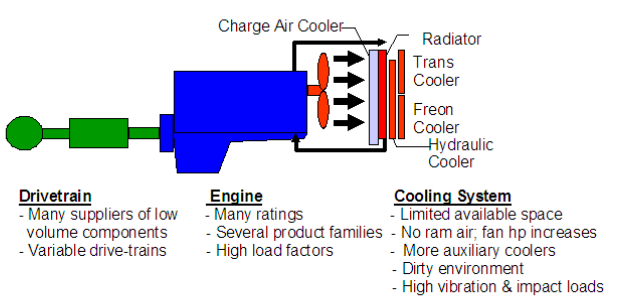

Figure 2. Off-Highway Installation

may incorporate one or multiple engines (2) and utilize multiple cooling fans for engine and hydraulic cooling. High horsepower mining applications of an excavator will require it to operate in a wide range of ambient conditions (-40°F to 130°F and above), and the environment is typically dusty/muddy, which fouls radiators easily. A three-shift, 22 hr/day operation is typical. Whereas a midrange engine in an excavator application may experience the same transient performance requirements, the duty cycle and usage will typically be lower. However, in both applications, the cooling systems and installations are extremely complex and involve up to five or more coolers (fuel, hydraulic, freon, engine coolant, charge air cooler) and complex air system and hydraulic plumbing routing and connections. The successful application of cooled or un-cooled EGR and/or a comparable technology that negatively impacts installations will be extremely difficult.

Utilization of EGR in off-highway applications is problematic because of the significant installation limitations. Using a timing retard strategy only will result in significant fuel economy penalties (5-10%) and will increase the particulate matter emissions. Both of these shortcomings are unacceptable, which is why an in-cylinder solution for Tier 3 is so important. With the short time line available, an in-cylinder solution can only be developed with advanced analytical tools.

Cummins' goals also include a minimal impact to machine installations and systems. Engine characteristics of key concern to customers installing engines in new applications include start-ability, altitude capability, transient response, idle torque, engine envelope, cooling systems, air flow (intake and exhaust), and fuel system requirements. Any significant change to any of the aforementioned characteristics may lead to a loss in productivity, lack of competitiveness, or require a larger engine to achieve current (Tier 2) performance at Tier 3 emission levels.

During the past fiscal year (2003), work accomplished on this project included the design and verification of combustion systems for several of the above platforms. An in-cylinder solution was developed that meets Tier 3 emissions while minimizing fuel consumption. In addition, the tools for designing combustion systems and developing calibrations were significantly improved.

Approach

An analysis-led approach was used for this project. Cummins has developed a combustion computational fluid dynamics (CFD) capability based on the KIVA software program. This code has been improved by incorporating several new submodels. The code has also been integrated with cycle simulation, fuel system simulation, and optimization routines to create a design tool as shown in Figure 3. A rigorous design and validation process was followed using this tool as shown in Figure 4.

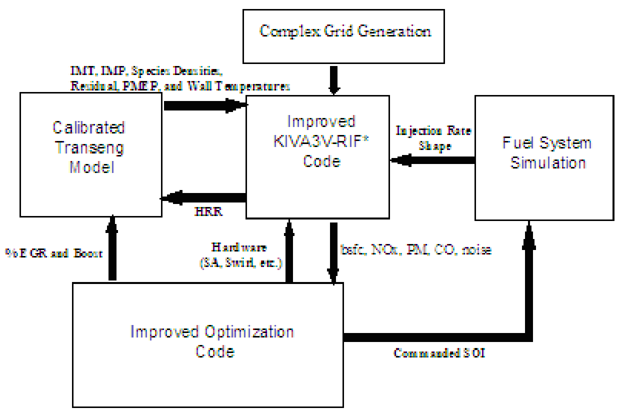

Figure 3. Combustion CFD Design Tool

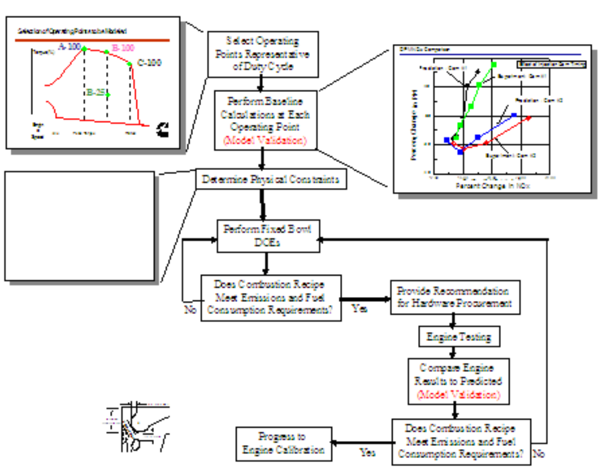

Figure 4. Combustion Design Process

This analysis-led approach enabled a much larger design space to be covered within the mechanical and customer constraints for these engines as well as the project time and cost constraints. The resultant designs will provide more energy efficient engines than could have been developed using past experimental techniques. The objective of the project is to define engine configurations capable of meeting Tier 3 emissions with a minimum fuel economy impact relative to Tier 2 engines.

Once the fundamental building block of the combustion design is defined, the flexibility of the electronic controls must be managed. To that end, a new method of developing engine calibrations was initiated. This method moves away from traditional methods of optimizing engine parameters at a speed and load to a global approach that incorporates a space-filling design of experiments. This methodology is expected to reduce the time required to develop a calibration by over 50%.

Results

During fiscal year 2003, the following improvements to the KIVA code were incorporated and validated:

- NO_x Transport Model
- Combustion Model
- Spray Model
- Combustion Noise
- Complex Grids

The global optimization methodology for steady-state calibration development was defined, and several data sets were gathered for validation.

The combustion design was completed and validated on several engine platforms and initiated on several other platforms. The CFD design tool is working quite well in defining optimized combustion configurations. Some limitations to the tool were also defined and are being addressed so that improved future designs are possible.

Figure 5 contains a NO_x-PM plot of one of the engine platforms. This plot shows the effect of swirl on engine performance for the combustion geometry chosen. It shows that proper selection of swirl was a key part of finding a combustion configuration that

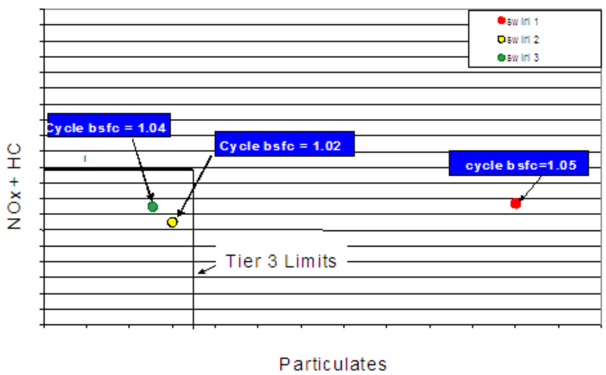

Figure 5. Tier 3 Engine Performance

meets Tier 3 emissions with only a 2% increase in fuel economy over Tier 2 fuel economy levels.

Conclusions

- In-cylinder solutions for Tier 3 engines have been defined.
- Combustion design tool improvements have been validated.
- An improved calibration development methodology has been defined.
- The analysis-led approach was successfully used to define fuel efficient combustion designs.

IV.K. Exhaust Aftertreatment and Low-Pressure Loop EGR Applied to an Off-Highway Engine

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Objectives

- Demonstrate that 4 g/kWh NO_x + HC (hydrocarbons) and 0.02 g/kWh PM (particulate matter) emission levels can be achieved over the ISO 8178-test cycle using cooled low-pressure loop exhaust gas recirculation (EGR) and a diesel particle filter (DPF). This will require optimizing the EGR strategy for NO_x reduction and also optimizing the engine for best brake specific fuel consumption (BSFC).
- Measure the exhaust particle size distributions for both baseline and with the EGR/DPF emission control system over several engine operating conditions.
- Determine the steady-state loading curves. This data will then be incorporated into the Michigan Technological University (MTU) aftertreatment model.

Approach

- Review current literature on EGR and DPF.
- Write specifications and order unique parts (DPF, SMPS, engine, EGR valves, etc.).
- Install engine and incorporate the SMPS (scanning mobility particle sizer) into the test cell.
- Collect baseline data.
- Install the EGR and DPF system and debug.
- Optimize the EGR strategy.
- Determine DPF loading curves for various conditions.
- Determine DPF balance point regeneration temperatures.
- Collect data with EGR and DPF.
- Modify and incorporate data into MTU model.
- Write final report.

Accomplishments

- The low-pressure loop EGR system has been optimized, and the goal of less than 4 g/kWh NO_x and less than 0.02 g/kWh PM over the ISO 8178 eight-mode test was achieved.
- Test cell changes have been made to enable particle size distribution measurements to be collected before and after the diesel particle filter.
- MTU continues to make progress on the DPF model. They have completed the NO to NO_2 conversion model of the diesel oxidation catalyst portion of the continuously regenerating DPF (CR-DPF).

Future Directions

- The particle size distribution data before and after the DPF will be collected along with the pressure drop loading curves, and this data will be provided to MTU.
- MTU will continue to work on the model and will verify their model once the data is delivered.

Introduction

This project evaluates the feasibility of using a low-pressure loop EGR system in combination with a high efficiency DPF to reduce both the oxides of nitrogen (NO_x) and particulate emissions. By removing the EGR gas downstream of the DPF, the clean gas can be routed to the upstream side of the turbocharger, and because the exhaust is free of particles, there is no abrasive wear on the turbo compressor wheel or fouling of the engine's intercooler (see Figure 1). With this emission control strategy, the overall engine efficiency is greater than if a high-pressure loop EGR system was incorporated. A study by Moser et.al., 2001, indicated that the BSFC in a low-pressure loop EGR system with a DPF was 3.5% percent better than in a high-pressure loop system with a DPF.

The major driving force for the research is to meet the future off-road diesel emission standards. The off-road Tier 3 standards take effect in 2006, and the Tier 4 standards begin in 2012. The technology gained from this project will contribute to meeting both the Tier 3 and Tier 4 standards.

Approach

A John Deere 6081H 175-kW engine is being used for this research. The engine's displacement is 8.1 liters, and it is turbocharged and intercooled. It incorporates the latest high-pressure common rail fuel injection system and is fully electronic. A continuously regenerating diesel particle filter (CR-DPF) is placed downstream of the turbocharger, and downstream of the particle filter, a portion of the exhaust gas is routed to the intake system. An EGR cooler is incorporated to cool the EGR exhaust gas, which maximizes the NO_x benefit.

The test project began with obtaining baseline data with no aftertreatment or EGR over the ISO 8178 test cycle. An EGR strategy was then determined, and additional tests were conducted with EGR and the CR-DPF. Several additional operating conditions have been identified which will be used for loading the DPF without regenerating. These conditions are necessary so that the steady-state loading curves can be obtained when the DPF is installed. This data will be used to validate the MTU model.

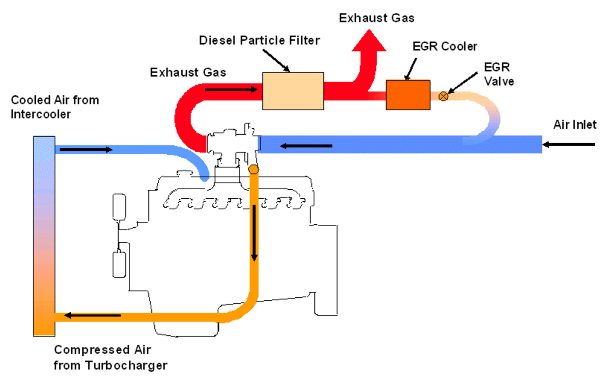

Figure 1. Low-Pressure Loop Exhaust Gas Recirculation Schematic

Results

The initial data was collected over the ISO 8178 eight-mode test cycle. The 8 modes are shown in Table 1 along with the weighting factors for each mode.

Table 1. ISO 8178 Eight-mode Test Cycle

Mode	Speed	%Load	Wt Factor
1	2200	100	0.15
2	2200	75	0.15
3	2200	50	0.15
4	2200	10	0.10
5	1400	100	0.10
6	1400	75	0.10
7	1400	50	0.10
8	1400	10	0.15

Table 2 compares the results between the baseline data and the low-pressure loop EGR with the CR-DPF over the 8178 test cycle. The low-pressure loop EGR system reduced the NO_x emissions an average of 28%. The CR-DPF reduced the PM and HC emissions over 94%. Figure 2 shows the percent reduction of both PM and HC for each of the eight modes. The NO_x plus HC standard for Tier 3 is 4.0 g/kWh for this power engine, and the values obtained provide an acceptable margin for meeting the standards. The data also indicate that break specific fuel consumption improved slightly over the baseline data.

Table 2. Summary of the ISO 8178 Data

Data in g/kWh	NO_x	HC	NO_x+HC	PM	BSFC at FLRS
Baseline, no EGR	5.22	.51	5.73	.132	211.9
With EGR	3.74	.03	3.77	.008	208.9

The regeneration of the CR-DPF is highly dependent on the NO_2 concentration in the exhaust and the exhaust temperature. MTU has completed modeling the conversion of NO to NO_2 in the diesel oxidation catalyst that is part of the CR-DPF system. The data shown in Figure 3 is without using EGR. Additional data will be collected with EGR to verify the model. Figure 3 indicates that at temperatures above 275°C, over 50% of the NO is converted to NO_2, and the model agrees well with the experimental data. The NO_2 reacts with the collected carbon in the DPF; therefore, it is necessary to know the NO_2 concentration in order to predict when regeneration will occur. This model will eventually be incorporated into the overall MTU model to better predict DPF operation.

The next phase of the project will be collecting the exhaust particle size distribution data before and

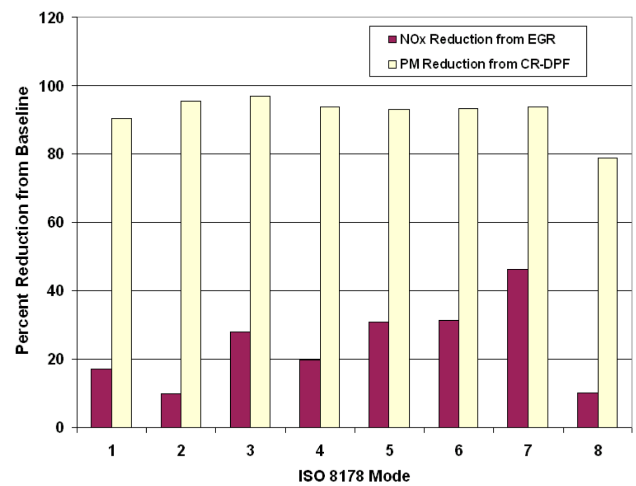

Figure 2. Percent NO_x and PM Reductions Using EGR and a DPF over the ISO 8178 Test Cycle

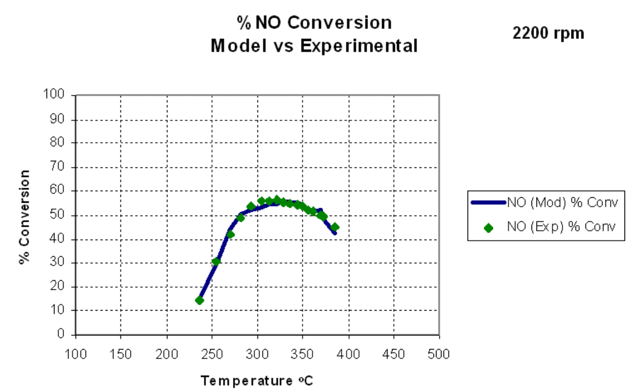

Figure 3. NO to NO_2 Conversion Efficiency of the Diesel Oxidation Catalyst as a Function of Exhaust Temperature

after the CR-DPF along with the pressure drop data, and this data will also be used to verify the MTU DPF model.

Conclusions

- The low-pressure loop EGR and CR-DPF system reduced NO_x emissions by 28%, HC emissions by 94% and PM emissions by 94%.
- The fuel economy was improved slightly with this technology.
- The MTU diesel oxidation catalyst model properly predicted the conversion of NO to NO_2 as a function of exhaust temperature.

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IV.L. Advanced Fuel-Injection System Development to Meet EPA Emissions Standards for Locomotive Diesel Engines

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Major Technical Objectives of Phase I

- Demonstrate, via engine combustion testing and emissions modeling, Tier 2 emissions-compliance capabilities utilizing an advanced fuel-injection system;
- Design and build a prototype advanced fuel-injection system suitable for a single-cylinder locomotive diesel engine; and
- Conduct demonstration tests on the single-cylinder locomotive diesel engine to validate new fuel-injection system design and injection strategies with reoptimized engine hardware and operating conditions.

Approach

- Set up appropriate analytical (engine and combustion) models and conduct parametric studies to analyze the effects of various injection strategies.
- Develop conceptual designs of the injection system, system layout, and the electronic control strategy for a single-cylinder locomotive diesel engine.
- Choose designs based on analytical predictions and structural and hydraulic analyses of selected hardware components.
- Test the new injection system with various engine hardware configurations for performance and emissions characteristics.
- Study fuel spray behavior and cavitation phenomena using appropriate analytical tools and optical methods.

Accomplishments

- Evaluated a number of fuel injection strategies with existing (Tier 1) hardware using engine system-level models (1-D) and detailed combustion (3-D computational fluid dynamics [CFD]) models.
- Optimized engine geometry and operating conditions to better match the injection profiles of the injection system under development.
- Developed design concepts for key hardware components and system layout of the new fuel-injection system.
- Carried out structural and hydraulic analyses of selected preliminary injector/pump designs.
- Preliminary results from analytical modeling showed that the new fuel-injection system can potentially meet Tier 2 goals with favorable NO_x-BSFC-particulate matter (PM) tradeoff characteristics.

Future Directions

- Test the new injection system on a single-cylinder diesel engine and demonstrate Tier 2 performance and emissions potential.
- Conduct fuel spray bench tests to analyze spray characteristics and help in understanding cavitation behavior. Other future plans, not within the scope of Phase I of this project, include:
  - Develop a complete fuel-injection system for a full-size locomotive diesel engine and verify single-cylinder test results using a multi-cylinder engine,
  - Conduct demonstration tests using a prototype locomotive unit with a Tier-2-equipped engine,
  - Conduct altitude tests using a Tier 2 prototype locomotive unit for performance acceptance, and
  - Perform manufacturing build verification of the new injection system.

Introduction

A railroad and locomotive technology roadmap workshop sponsored by the U.S. Department of Energy in January, 2001, identified the critical research and development (R&D) needs of locomotive diesel engines for reducing fuel consumption and exhaust emissions while maintaining or enhancing system performance [1]. This workshop set the stage for a cooperative R&D effort among the railroads, suppliers, original equipment manufacturers of locomotives, and the federal government to further improve railroad efficiency and lower exhaust emissions. During this workshop, a number of key technical areas were identified, and recommendations were made for R&D to remove the technical barriers in each of these areas. The key areas for suggested R&D activity include improvements in fuel-injection technology and combustion geometry to achieve potential fuel savings and meet the Environmental Protection Agency's (EPA's) Tier 2 (and beyond) emissions regulations [2]. The other research topics that were identified to help meet the above goals include exhaust gas recirculation, advanced combustion strategies and numerical models, alternative fuels, and thermal barrier coatings.

As a result of the railroad and locomotive technology roadmap workshop, a cooperative agreement was reached between the U.S. Department of Energy and the Electro-Motive Division of General Motors Corporation (EMD) in October, 2002. The first phase of this cooperative R&D effort involves developing advanced fuel-injection technology and demonstrating its potential benefits towards meeting fuel savings goals and the EPA Tier 2 emissions standards while continuing to meet the reliability and durability requirements of railroad operations. Figure 1 shows the pump-line fuel-injection system (also known as Unit Pump System) that is currently in production for Tier 1 locomotive diesel engines. The alternative fuel-injection systems [3] that are considered for the present study are depicted in Figure 2.

Approach

To achieve the delineated project goals, we plan to approach Phase I of the project in terms of four

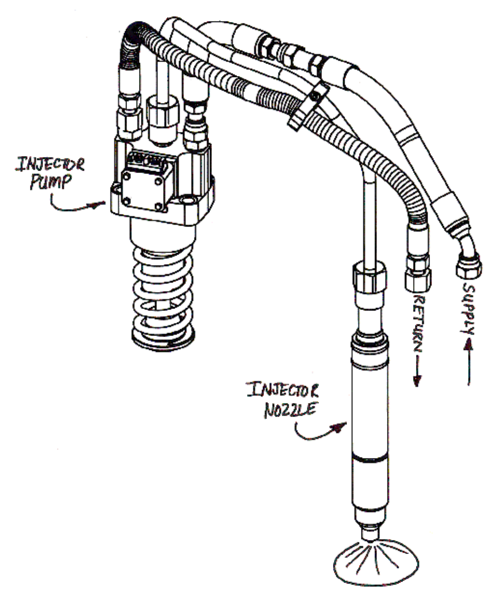
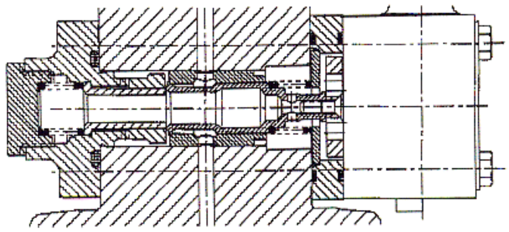
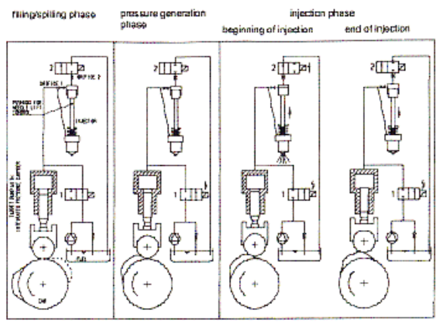


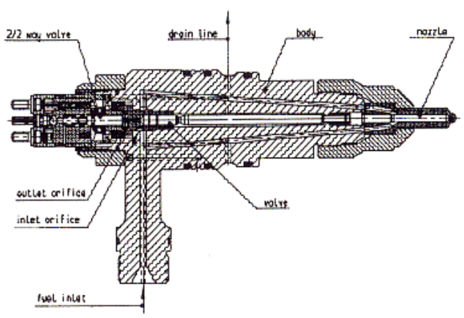
Figure 1. Current Unit Pump Fuel Injection System for Four-Stroke Locomotive Diesel Engines



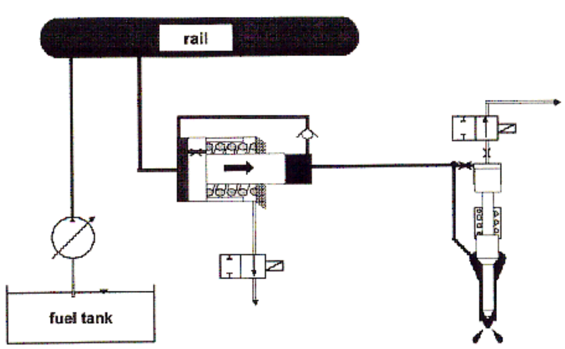
Current-controlled rate shaping (CCRS)



Advanced Unit Pump System (AUPS)



Common Rail System (CRS)



Amplifier Piston Common Rail System (APCRS)

Figure 2. Alternative Fuel-Injection Systems for Medium-Speed Diesel Engines

major technical tasks, which are briefly summarized below:

Task 1: Identify an alternate injection system and injection strategies while optimizing the injection system in conjunction with engine geometry and operating conditions.

Task 2: Design and build a prototype fuel-injection system with appropriate electronic controls.

Task 3: Conduct bench tests with the prototype system and examine fuel spray characteristics.

Task 4: Conduct single-cylinder engine tests and demonstrate potential benefits.

Task 1 involves analytical investigations by means of validated engine combustion and emissions (1-D engine, 3-D CFD) models. Factors including injection parameters (timing, peak pressure, rate shaping), combustion chamber geometry, turbocharging, valve/port timing, residual gas fraction, port design, and charge cooling will be explored. Recently developed computational design methodologies, such as the genetic algorithm and the response surface method, will be utilized to aid the analytical efforts. The goal of this task is to identify an optimal combination of design and operating parameters that can reduce regulated emissions and improve brake-specific fuel consumption (BSFC). Analytical models will also be used to predict nozzle flow behavior and cavitation under different injection conditions. Our subcontractor for this project, Wayne State University, will carry out the cavitation modeling effort.

Task 2 consists of mechanical design of the injector system assembly and development of the electronic control strategy. This task is a joint effort between EMD and the fuel-injection equipment supplier. EMD will integrate the injection system design and prepare appropriate design modifications to the engine assembly. The final goal of this task is to develop a working injection system with an associated electronic control unit that is suitable for testing in a single-cylinder diesel engine.

Task 3 involves test-bench component evaluations as well as an investigation of fuel spray characteristics using established optical diagnostic techniques. **Task 4** comprises implementation and testing of the prototype injection system in a single-cylinder engine. This work will utilize EMD's test facilities at Argonne National Laboratory. Analytical results will be used to guide the engine tests. A decision will be made on the basis of the engine test results to extend the demonstration of this technology to include a series of locomotive engines; this work is for Phase II of the program.

Results

A comprehensive engine system model was built using the AVL-Boost (1-D) code, and a combustion (valves closed period) model was built into the KIVA3v2 (3-D CFD) code. Figure 3 shows a graphical representation of both 1-D and 3-D CFD sector mesh models built for a 16-cylinder locomotive diesel engine. Both models were calibrated for performance and emissions with engine hardware and operating conditions representative of EPA Tier-1-complaint locomotives. The boundary conditions for the CFD model were obtained from the 1-D engine system model. Because the CFD runs would be time consuming with complete combustion geometry, only a sector of the combustion chamber was considered for emissions predictions. Initially, the emphasis was placed on evaluating the effects of injection characteristics while keeping all other engine hardware (piston, cam, turbochargers, and aftercoolers) the same as in the Tier 1 package. Statistical techniques for multivariant optimization, such as the Taguchi method and the Micro-Genetic algorithm, were considered in reducing the number of CFD runs during the optimization of injection parameters. Efforts were made towards developing a hydraulic simulation model using Easy-5, a 1-D model for flow analysis of the injection system, to examine flow behavior and injector output characteristics. An appropriate modeling capability was developed for structural analyses of fuel injection system hardware (piping, pumping element, injector body, and injector holder) using the ANSYS software package.

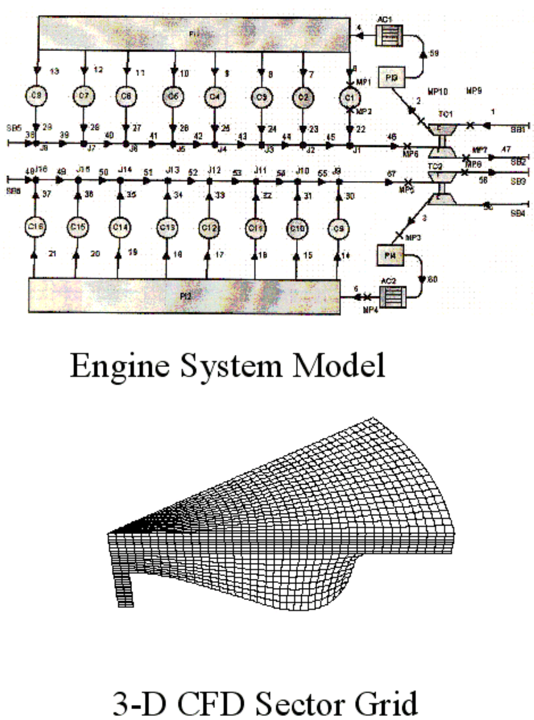


Figure 3. Engine Combustion and Emissions Models Developed for Evaluating Different Injection Strategies

The internal flow characteristics of a locomotive injector were modeled using commercially available 3-D CFD codes (Fluent and Star-CD) at Wayne State University. The key differences between these two codes in predicting nozzle internal flows involve treatments of fuel viscosity and surface tension. Star-CD code considers the effects of surrounding bubbles and offers the option of two different sub-models for predicting cavitation – barotropic and bubble two-phase flow (BTF) cavitation sub-models. Efforts were also made to predict the flow behavior of the cavitation and non-cavitation nozzles using Fluent and Start-CD codes. Parameters such as nozzle discharge coefficient and amplitude factor are used to characterize the internal flow though the nozzle orifices. Figure 4 shows the comparison of cavitation predictions using two different 3-D CFD model approaches from a locomotive injector.

Variations in injection parameters, such as nozzle geometry (orifice aspect ratio, number of orifices, orifice geometry), injection timing, and injection quantity, were investigated using a 3-D CFD model. The emission trends were found satisfactory and were documented. On the basis of predicted in-cylinder pressure from the CFD model, a multi-cylinder engine system model was employed to estimate the brake-specific fuel consumption. Thus, the effects of any single injection variable or combination of variables can be represented in the NO_x-BSFC-PM tradeoff chart. From the current analytical investigations, we have identified the sensitivity of different variables and the range of these variables that can yield favorable NO_x-BSFC-PM characteristics. Figures 5 and 6 show the predicted performance and emissions tradeoffs with different injection strategies in combination with different engine hardware at the full-load engine condition. Most analytical work was done at the full-load engine condition because of its importance in locomotive diesel engine operation regarding performance and emissions. Further, the emissions at full load contribute a majority of the federal emissions duty-cycle average, particularly for line-haul locomotives. The predicted NO_x, particulates, and BSFC show the potential of the advanced injection system under development in meeting Tier 2 emissions and performance goals.

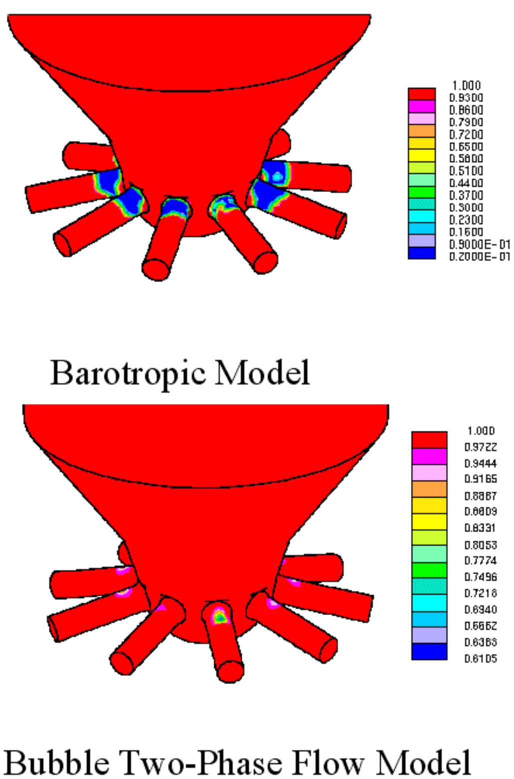


Figure 4. Modeling Approaches for Studying Locomotive Injector Nozzle Cavitation

The design phase of the injection system capable of generating the desired injection characteristics was completed as a joint effort between EMD and the fuel injection equipment supplier. Product cost and reliability considerations led to the selection of certain components from the state-of-the-art fuel injection technologies that are currently being mass-produced for various medium-speed and heavy-duty diesel engines. A general layout of the injection system suitable for a multi-cylinder locomotive diesel engine was also developed. Currently, a prototype injection system suitable for testing on a single-cylinder diesel engine is being developed.

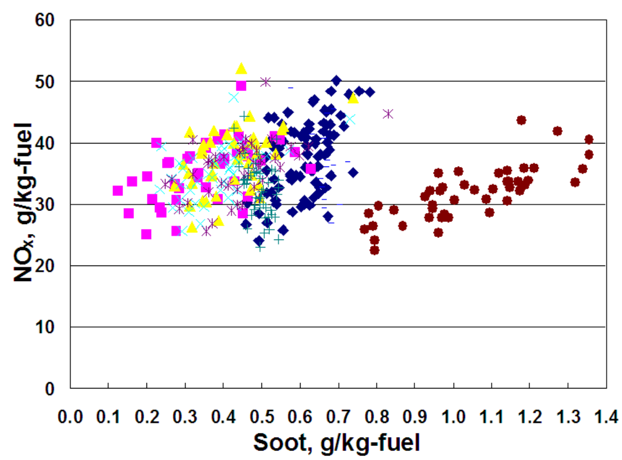


Figure 5. Analytical Predictions of NO_x-Particulates Tradeoff Characteristics with Different Injection Strategies

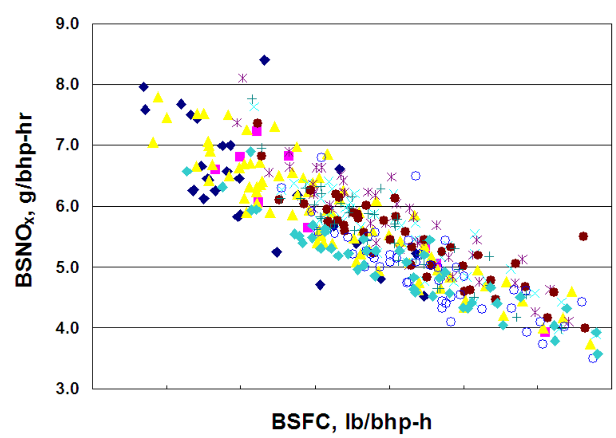


Figure 6. Analytical Predictions of NO_x-BSFC Tradeoff Characteristics with Different Injection Strategies

Conclusions

- An extensive analytical modeling capability was developed to study and optimize fuel-injection characteristics for improving locomotive diesel engine performance and emissions. A number of injection strategies were evaluated in terms of performance and emissions with existing Tier 1 hardware using these calibrated analytical tools.
- An injection system was identified that has the capability of generating the desired injection characteristics. Analytical model data showed that this new, advanced fuel-injection system has the potential to meet Tier 2 goals with favorable NO_x-BSFC-PM tradeoff characteristics.
- Preliminary design concepts of the new injection system were developed, its key components and system layout were defined, and structural and hydraulic analyses were carried out on selected hardware components.
- Working with the fuel equipment manufacturer, a prototype injection system was developed for testing on a single-cylinder diesel engine and for bench-level testing for fuel spray analysis.

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FY 2003 Publications/Presentations

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IV.M. 21st Century Locomotive Technology: Advanced Fuel Injection and Turbomachinery

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Objectives

- Develop and demonstrate an advanced fuel injection system targeting Tier 2 emissions levels and maximum possible specific fuel consumption (SFC) improvement.
- Validate electrically assisted turbocharger unit to full speed and power and develop conceptual design for multi-cylinder engine.
- Demonstrate turbocharger efficiency improvement using abradable seals on the compressor and turbine.

Approach

…for Objective 1

- Develop combustion model for locomotive engine and verify model via test data.
- Use combustion model to optimize fuel injection strategy.
- Implement advanced fuel injection system on single-cylinder locomotive engine.
- Determine optimized fuel injection parameters via experiments, using model predictions as a guide.

…for Objective 2

- Install electrically assisted turbocharger and test over operating range in motoring and generator mode.
- Measure performance and dynamic stability characteristics.
- Identify key areas of improvement.
- Develop conceptual design for multi-cylinder engine.

…for Objective 3

- Perform clearance tests to determine possible efficiency improvement.
- Specify and develop seal material candidates.
- Perform rub tests to identify best choice(s).
- Implement abradable seals on full-scale turbocharger and characterize performance.

Accomplishments

…for Objective 1

- Calibrated and commissioned the computational fluid dynamics (CFD) combustion model at the University of Wisconsin – Madison.

- Started assembly of the common rail fuel injection system.

…for Objective 2

- Installed and commissioned the hybrid electric turbocharger.
- Obtained preliminary data on turbocharger performance in generator and motoring modes from idle to full speed.
- Identified system vibration resonance and encoder issues.

… for Objective 3

- Completed literature search on polymeric abradable materials.
- Identified candidate materials for the compressor and turbine casings.
- Prepared polymer test coupons for rub test evaluations.

Future Directions

…for Objective 1

- Run genetic algorithm optimization on the combustion model.
- Operate the advanced fuel system on a bench test, separate from the single-cylinder engine.
- Install the advanced fuel system on the single-cylinder engine.
- Experiment with the advanced fuel system, complete baseline and then optimize hardware and strategy.

…for Objective 2

- Complete testing of the electrically assisted turbocharger for different modes of operation.
- Implement solutions for the vibration resonance and encoder issues.
- Evaluate performance in motoring mode at high ramp rates.
- Develop conceptual design, including packaging, for the larger Tier II turbocharger in preparation for multi-cylinder engine tests.

… for Objective 3

- Determine turbocharger boundary conditions (e.g. metal temperatures, hot running clearances).
- Perform rub tests of aluminum compressor wheel against polymer seal material samples.
- Evaluate compressor performance as a function of clearance on a full-size turbocharger.
- Evaluate turbine performance using abradable seals on the turbocharger shroud.

Introduction

As with cars, trucks, and buses, the exhaust emissions of locomotives are now under regulatory control. The first emission standards for locomotives (Tier 0) were enforced in 2000, limiting NO_x, particulate matter (PM), and unburned hydrocarbon (HC) emissions. In 2002, more stringent Tier 1 regulations took effect. Yet again, in 2005, a tighter set of regulations will lower the permitted emission levels. As this trend of decreasing emissions continues, researchers must determine the best way to reach the targets. Traditional methods to reduce NO_x and PM emissions in a diesel engine increase fuel consumption, incurring higher costs on the railways. General Electric is committed to bringing technology to the locomotive industry to achieve both low emissions and low fuel consumption.

The goals and objectives of the Department of Energy and General Electric's 21st Century Locomotive Program are to develop freight locomotives that are 25% more efficient by 2010, while meeting Tier 2 emission standards. General Electric (GE) proposes to dramatically advance the technology at both the diesel engine and locomotive system levels. This document describes the technology at the diesel engine level, which involves improving the brake specific fuel consumption by development of advanced fuel injection and turbocharger systems.

Approach

The approach of the engine-related technology project varies by task. The methods by which GE will reach targets in the area of advanced fuel injection, electrically assisted turbomachinery, and the turbocharger abradable seals are discussed below.

Advanced Fuel Injection: A Bosch common rail system will be implemented on a locomotive single-cylinder research engine. The system will be capable of up to four injection events per cycle and will produce injection pressures above 1600 bar. During optimization testing, the injection schedule and nozzle configuration will be varied to establish the best performance. To better understand the combustion phenomena and prepare for experimental testing, CFD (KIVA) analysis is progressing in collaboration with the University of Wisconsin – Madison. The combustion code has been calibrated to predict the performance of the locomotive engine. The mesh has been developed to maximize usefulness for a given computation time. The genetic algorithm optimization process will be used to identify the optimum combination of fuel spray cone angle and injection schedule. The KIVA modeling work provides input and guidance for the experimental study on the single-cylinder engine.

Electric-Assist Turbocharger: An electrically assisted turbocharger has been designed and built. The advanced turbomachinery will be tested at full scale in the Global Research Center (GRC) turbomachinery laboratory to identify its performance potential. The opportunity to transfer energy between the electrical system and the intake and exhaust flow streams provides an added degree of freedom for efficiency optimization. Modeling studies will be used to predict performance gains given optimum airflow and pressure at the various locomotive notch settings (engine speed-torque combinations) of interest. Significantly improved transient engine response is expected in motoring mode at low notches, and up to 150 KW additional energy recovery is expected in generating mode at higher turbocharger speeds.

Turbocharger Abradable Seals: The application of abradable seals to the aluminum compressor wheel will be investigated in the literature. Materials that show potential for the temperature, speed, and blade material compatibility requirements of the compressor will be selected and tested in a dedicated rub test facility. High-temperature metallic abradable seals will be selected for test on the turbine end of the turbocharger. Promising candidate materials will be down-selected for test in a full-scale locomotive turbocharger. The turbocharger tests will be performed in the turbomachinery laboratory at GRC.

Results

The major accomplishments pertaining to the advanced fuel injection are the hardware integration and the modeling progress. Figure 1 shows the common rail fuel system hardware on hand, including the pump, fuel injector, accumulator, and high-pressure lines. These components are currently being assembled for system testing. The CFD combustion model, which has the capability of multiple injections (Figure 2), predicts engine combustion very well. Figure 3 shows the

Figure 1. Common Rail Fuel System Components: (Left) High-pressure fuel pump. (Right) Accumulator, high-pressure fuel line, and injector.

experimental versus predicted heat release rate (HRR). The curves match well, implying that the model is calibrated correctly. The model can then be used for optimization studies.

The electrically assisted turbocharger has been constructed (Figure 4) and successfully operated over a range of conditions in both motoring and generator mode. The system has been run from idle to full speed with no issues encountered regarding structural integrity, or rotor dynamics of the combined turbocharger, drive shaft and motor/generator. The system has met the design rating of 150 KW in generator mode at maximum rated turbocharger speed. Preliminary transient testing in motoring mode has indicated the potential for significant improvement in turbocharger load rate. Useful design data have been obtained regarding the vibration characteristics of the system, the efficiency of the compressor, and system surge limits. Optimization and characterization of the system are ongoing. Modifications to the system to correct a casing resonance in the middle of the speed range are being investigated. An improved encoder will be installed on the motor.

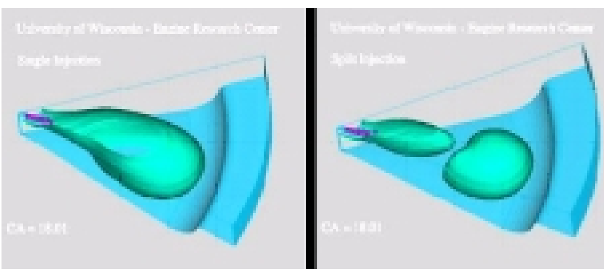

Figure 2. Modeling Results from CFD (KIVA) at the University of Wisconsin-Madison Engine Research Center (Left figure shows single injection, right figure shows split injection)

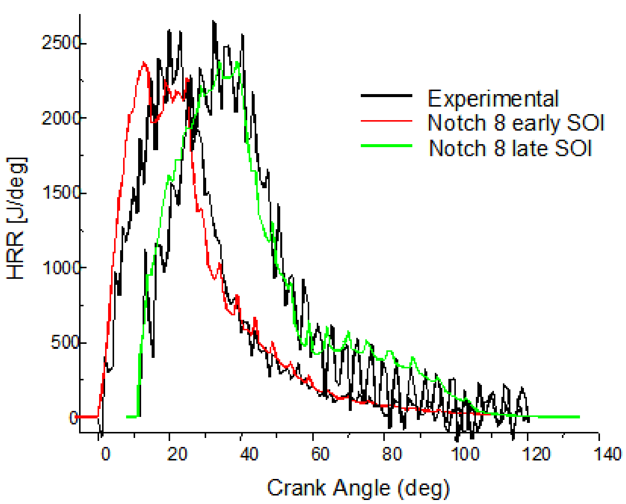

Figure 3. Predicted Heat Release Rates (illustrated in red and green) Show Good Agreement with the Experimental Data (Examples are presented for two different start-of-injection [SOI] timings)

Candidate abradable seal materials have been identified for the turbocharger compressor and turbine shrouds. Polymeric samples for the compressor have been prepared for bench scale qualification testing. A design of experiment approach was used to optimize the thermal spray parameters for the polymer materials using a minimum number of trials. A dedicated rub rig, shown in Figure 5, will be used to evaluate the performance of these test coupons against the actual aluminum wheel material under varying temperatures, speeds, and incursion rates. The most promising candidates will be down-selected for application to the turbocharger for full-scale testing. Micrographs of the polymer samples after spray optimization look promising.

Two metallic-based coatings have been selected for application to the turbine shroud. Tests are planned to determine the hot running clearance between the turbine blisk and stationary shroud for selection of initial coating thickness. A local vendor

Figure 4. Electric Turbocharger Installed on Test Stand

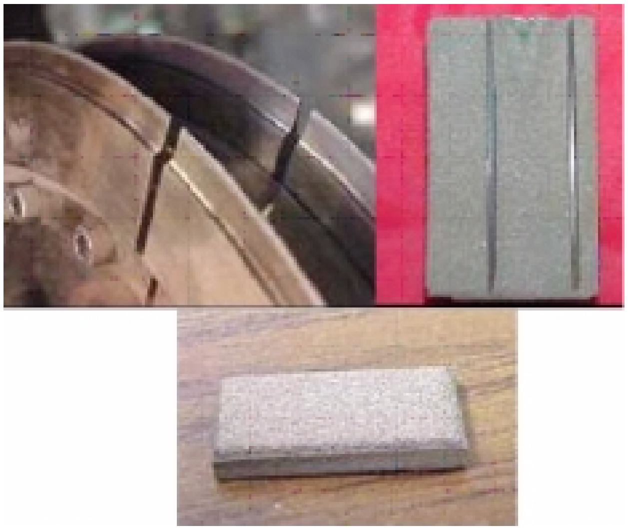

Figure 5. Experiments to Simulate Impact from Turbomachinery on Material Coupons are Performed to Evaluate Materials for Abradable Seals (Upper left) Rub-rig wheel testing apparatus (Lower center) Material sample before test (Upper right) Material sample after test

has been qualified to spray the two coatings selected for evaluation.

Conclusions

- The CFD combustion model can predict engine performance adequately once calibrated.
- The genetic algorithm approach is an appropriate tool to optimize injection parameters.
- The electrically assisted turbocharger is expected to meet performance goals; however, there are system vibration issues that are being addressed.
- Polymeric test coupons of abradable seal candidates have been successfully sprayed using a thermal spray process optimized through a design of experiments approach.

ACRONYMS

1-D	One-dimensional
2-D	Two-dimensional
3-D	Three-dimensional
A	Ampere
Å	Angstrom
AC	Alternating Current
A/F or AFR	Air/Fuel Ratio
Ag	Silver
AHRR	Apparent Heat Release Rate
Al	Aluminum
Al_2O_3	Aluminum Oxide
$Al_2(SO_4)_3$	Aluminum Sulfate
ANL	Argonne National Laboratory
APCRS	Amplifier Piston Common Rail System
APS	Advanced Photon Source
ASI	After Start of Injection
ASME	American Society of Mechanical Engineers
ATDC	After Top Dead Center
atm	Atmosphere
Au	Gold
AUPS	Advanced Unit Pump System
Ba	Barium
$BaCO_3$	Barium Carbonate
BaO	Barium Oxide
$BaSO_4$	Barium Sulfate
BaZY	Barium/zeolite Y
BET	Brunauer-Emmett-Teller particle surface area and pore-size measurement method
bhp-hr, bhp-h	Brake horsepower-hour
BMEP	Brake mean effective pressure
BOI	Beginning of Injection
BSFC	Brake specific fuel consumption
$BSNO_x$	Brake specific oxides of nitrogen
BTDC	Before Top Dead Center
BTE	Brake Thermal Efficiency
BTF	Bubble Two-Phase Flow
°C (also C)	Degrees Celsius
Ca	Calcium
CA	Crank Angle
CAD	Crank Angle Degrees
cc	Cubic centimeter
CCRS	Current-controlled rate shaping
CDPF	Catalyzed diesel particulate filter
CeO_2	Ceric Oxide
CFD	Computational Fluid Dynamics
CFR	Coordinating Fuels Research
CH_4	Methane
C_2H_4	Ethylene
C_2H_6	Ethane
C_3H_4	Propadiene
C_3H_6	Propylene
C_3H_8	Propane
CHEMKIN	Name of Chemical-Kinetic Code
CI	Compression Ignition
CIDI	Compression Ignition Direct Injection
CLEERS	Cross-Cut Lean Exhaust Emission Reduction Simulation
cm	Centimeter
cm^2	Square centimeter
Co	Cobalt
CO	Carbon Monoxide
CO_2	Carbon Dioxide
Co-FER	Cobalt-Ferrite
CPU	Central Processing Unit
CRADA	Cooperative Research & Development Agreement
CR-DPF	Continuously Regenerating Diesel Particulate Filter
CRS	Common Rail System
Cs	Cesium
CU	Chalmers University
DC	Direct Current
DCSF	Diesel Combustion Simulation Facility
DDC	Detroit Diesel Corporation
DECSE	Diesel Emission Controls Sulfur Effects
DEER	Diesel Engine Emissions Reduction Workshop
deg	Degrees
DEM	Delayed and Extended Main
DI	Direct Injection
DOC	Diesel oxidation catalyst
DOE	Department of Energy
DPF	Diesel Particulate Filter
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
ECM	Electronic Control Module

EDS	Energy Dispersive Spectroscopy
EGR	Exhaust Gas Recirculation
ELPI	Electrical Low Pressure Impactor
ELS	Elastic Light Scattering
EM	Extended Main
EMD	Electro-Motive Division of General Motors Corporation
EMRE	ExxonMobil Research & Engineering Company
EPA	Environmental Protection Agency
ERC	Engine Research Center, University of Wisconsin-Madison
ESC	Steady state 13 mode emissions test cycle
ETC	Electrical Turbocompound
EUI	Electronic Unit Injector
°F	Degrees Fahrenheit
FEV	FEV Engine Technology, Inc.
FID	Flame Ionization Detector
FLC	Federal Laboratory Consortium
fmep	Friction mean effective pressure
FSN	Filter Smoke Number
Ft^3	Cubic feet
FTIR	Fourier Transform Infrared
FTP	Federal Test Procedure
FY	Fiscal Year
g (or gm)	Gram
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
GDI	Gasoline Direct Injection
GE	General Electric
GHSV	Gas hourly space velocity
GPS	Global Positioning System
GRC	General Electric's Global Research Center
GVW	Gross Vehicle Weight
h	Hours
H_2	Diatomic Hydrogen
H_2O	Water
H_2S	Hydrogen sulfide
H_2-SpaciMS	Hydrogen-calibrated spacially resolved capillary inlet mas spectrometer
HC	Hydrocarbon
HCCI	Homogeneous Charge Compression Ignition
HELD	High-Energy Laser Diagnostics
HMO	Hydrous Metal Oxide
hp or HP	Horsepower
hphr or hp-hr	Horsepower-hour
hr	Hour
HRR	Heat release rate
HS	High swirl
HSDI	High Speed Direct Injection
Hz	Hertz
ICCD	Intensified charge-coupled device
ICE	Internal Combustion Engine
ID	Inner Diameter
ID	Injection Duration
ILASS	Institute of Liquid Atomization and Spray Systems
IMEP	Integrated Mean Effective Pressure
In_2O_3	Indium oxide
IR	Infrared
ISAT	*in-situ* adaptive tabulation
J	Joule
K	Kelvin
K	Potassium
K_2CO_3	Potassium carbonate
kg	Kilogram
kJ	Kilojoule
kPa	Kilopascal
kV	Kilovolt
kW	Kilowatt
kWh	Kilowatt-hour
L	Liter
LANL	Los Alamos National Laboratory
La_2O_3	Lanthanum Oxide
lb	Pound
lb-ft	Pound-foot
lbm	Pound-mass
LBNL	Lawrence Berkeley National Laboratory
Ld	Shape Factor
L/D	Length to Diameter Ratio
LDT	Light-Duty Truck
LEADER	Low Emissions Aftertreatment and Diesel Emissions Reduction
LEP	Low Emissions Technologies Research and Development Partnership
LEV	Low Emission Vehicle Program
Li	Lithium
LIBS	Laser-Induced Breakdown Spectroscopy
LIDELS	Laser-Induced Desorption with Elastic Light Scattering
LIF	Laser-Induced Fluorescence
LII	Laser-Induced Incandescence

LLNL	Lawrence Livermore National Laboratory
LNT	Lean NO_x Trap
LOL	Lift-off length
LS	Low swirl
m	Meter
m^2	Square meter
m^3	Cubic meter
mA	Milliampere
MC	Mass concentration
MECA	Manufacturers of Emissions Controls Association
µg	Microgram
Mg	Magnesium
mg	Milligram
M/G	Motor/Generator
mi	Mile
min	Minute
MIT	Massachusetts Institute of Technology
MJ	Megajoule
µm	Micron
mm	Millimeter
µmol	Micromole
MoO_3	Molybdenum trioxide
MPa	Megapascal
mpg	Miles per gallon
mph	Miles per hour
MS	Mass Spectrometer
µs	Microsecond
mS	Millisiemens
ms	Millisecond
msec	Millisecond
MTU	Michigan Technological University
mV	Millivolt
MW	Megawatts
N_2	Diatomic Nitrogen
N_2O	Nitrous Oxide
N_2O_4	Nitrogen Tetraoxide
Na	Sodium
Nd:YAG	High Power Pulsed Laser Source
NDIR	Non Dispersive Infrared
NEA	Nitrogen-enriched Intake Air
NH_3	Ammonia
nm	Nanometer
Nm	Newton meter
NMHC	Non-methane Hydrocarbon
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_x	Oxides of nitrogen
NRC	National Research Council
NREL	National Renewable Energy Laboratory
NTE	Not-to-exceed
NTP	Non-Thermal Plasma
NTRC	National Transportation Research Center
NTS	Non-Thermal Plasma System
NVH	Noise, Vibration, and Harshness
O_2	Diatomic oxygen
OBD	On-Board Diagnostic
O/C	Oxygen to Atomic Carbon Ratio
OD	Outer Diameter
OEM	Original Equipment Manufacturer
OFCVT	Office of FreedomCAR and Vehicle Technologies
OH	Hydroxyl radical
ORNL	Oak Ridge National Laboratory
P	Pressure
PAC	Plasma-Assisted Catalysis
PAD	Pixel Array Detector
PC	Personal computer
PCCI	Premixed Charge Compression Ignition
PDF	Probability Density Function
PLIF	Planar Laser-Induced Fluorescence
PLII	Planar Laser-Induced Incandescence
PM	Particulate Matter
PNGV	Partnership for a New Generation of Vehicles
PNNL	Pacific Northwest National Laboratory
POx	Partial Oxidation
PoxHC's	Partially Oxidized Hydrocarbons
ppb	Parts per billion
ppm	Parts per million
PRF	Primary Reference Fuel
psi	Pounds per square inch
psia	Pounds per square inch absolute
psig	Pounds per square inch guage
Pt	Platinum
Q	Quarter (e.g. 2Q, 2003 denotes second quarter of 2003)
R&D	Research and Development
RCF	Rapid Compression Facility
RDG-PFA	Rayleigh-Debye-Gans polydisperse fractal aggregate
Rh	Rhodium
RPM or rpm	Revolutions Per Minute
Rs	Ricardo Swirl Ratio

s	Second
S	Sulfur
SA	Surface area
SAE	Society of Automotive Engineers
SBCE	Set Based Concurrent Engineering
sccm	Standard cubic centimeters per minute
SCF	Standard cubic feet
SCR	Selective Catalytic Reduction
sec	Second
SEM	Scanning electron microscopy/ microscope
SFC	Specific fuel consumption
SI	Spark Ignition
SICM	System Integration Configuration Matrix
SIDI	Spark Ignition Direct Injection
SiO_2	Silicon Dioxide
SMPS	Scanning Mobility Particle Sizer
S/N	Signal to Noise Ratio
SNL	Sandia National Laboratories
SO_2	Sulfur Dioxide
SO_3	Sulfur Trioxide
SO_4	Sulfate
SOI	Start-of-Injection
SO_x	Oxides of Sulfur
Sr	Strontium
SR	Switched Reluctance
SU	Stanford University
SUV	Sport Utility Vehicle
T	Temperature
TDC	Top Dead Center
TDI	Turbocharged Direct Injection
TEOM	Tapered Element Oscillating Microbalance
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
THC	Total Hydrocarbons
TK	Thermo-kinetic
TOF	Turn-over frequency
TPD	Temperature Programmed Desorption
UCB	University of California, Berkeley
UEGO	Universal Exhaust Gas Oxygen
UHC	Unburned Hydrocarbon
UM	University of Michigan
U.S.	United States
USCAR	U.S. Council for Automotive Research – umbrella organization of DaimlerChrysler, Ford, and General Motors
UW ERC	University of Wisconsin Engine Research Center
V	Volt
VCR	Variable Compression Ratio
Vdc	Volts - direct current
VGT	Variable Geometry Turbocharger
VVA	Variable Valve Actuation
VVT	Variable Valve Timing
W	Watt
WSU	Wayne State University
Wt	Weight
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
Y,FAU	Y-zeolite
ZrO_2	Zirconium Dioxide