Technical Highlights for June 2012

New Insights into Silver/Alumina Catalysts for the Selective Catalytic Reduction (SCR) of Nitrogen Oxide (NO_X) by Ethanol for Lean Gasoline Engine Emissions Control

Lean gasoline engines provide significant efficiency advantages over their stoichiometrically operated counterparts, but have yet not been able to meet United States (U.S.) emissions regulations for NO_X. Silver/alumina catalysts for the SCR of NO_X by ethanol could provide a low cost solution for NO_X reduction in lean gasoline engine exhaust that does not require precious metals or urea. Researchers at ORNL/FEERC performed experiments on a commercially relevant silver/alumina catalyst to quantify its performance and determine the mechanism for the reaction between NO and ethanol. Using E100 (100% ethanol) as the reductant, the catalyst achieved high NO_X conversions over a reasonably wide temperature window (300–500°C). It also generated significant quantities of on-board ammonia (NH_3) demonstrating the potential for a dual SCR system that utilizes a downstream NH_3 SCR catalyst to further reduce NO_X. By carefully tracking the consumption and formation of key species over the catalyst, we determined that the reduction of NO by ethanol proceeds through the formation of oxidized intermediates (NO_2 or surface nitrites/nitrates and acetaldehyde or surface acetate). Future experiments will focus on ethanol/gasoline blends to determine the effectiveness of the catalyst under more realistic fuel streams and the potential of ethanol to promote NO_X reduction by other hydrocarbons in those blends.

Coast Down Experiments Quantify Fuel Economy Effects of Drag

Coast down measurements at a subcontractor test track this month are being used to quantify fuel economy effects of vehicle alterations/modifications such as trailers, cargo boxes, tire pressure, and whether windows are open or closed. Ongoing experiments in the FEERC vehicle laboratory will quantify the fuel economy (miles per gallon [mpg]) changes from these variations. Preliminary data show that for a popular sport utility vehicle (SUV), the highway power requirement increases significantly for these conditions: opening all windows – over 5%, adding a cargo box to the roof rack – over 20%, and pulling a trailer – over 80%. Results will be summarized and used to update tips on the fueleconomy.gov website, which is managed by ORNL.

FEERC Contributes Important Updates to the fueleconomy.gov Website

Recent efforts by John Thomas, Shean Huff, and Brian West to quantify vehicle fuel economy for a range of highway cruising speeds have resulted in an update of the fueleconomy.gov website. Below is a generalized figure with a curve shape representative of the vast majority of light duty vehicles on the road today. This figure replaces an outdated curve based on nine vehicles from the 1990s. This new curve is based on data from 67 vehicles, including data for 51 vehicles from an original equipment manufacturer (OEM) partner and data for 16 vehicles collected at the ORNL vehicle research laboratory. This work is ongoing and will result in further updates and more detailed website information in the future.

Observe the Speed Limit
(New Information)

While each vehicle reaches its optimal fuel economy at a different speed (or range of speeds), gas mileage usually decreases rapidly at speeds above 50 mph.

You can assume that each 5 mph you drive over 50 mph is like paying an additional $0.26 per gallon for gas.

Observing the speed limit is also safer.

Fuel Effects on Diesel Engine Efficiency

A set of surrogate diesel fuels were designed using Reaction Design Model Fuels Consortium surrogate design tools to manipulate the performance of the Hatz diesel engine to the largest extent possible, within the constraints of available, verified surrogate compounds, and engine capability. The design matrix included cetane, threshold sooting index, and 50% distillation temperature, which were all parameters expected to affect ignition, flame luminosity, and mixing respectively. These fuels were run in the engine and analyzed for efficiency, emissions, and combustion performance. Indicated thermal efficiency was observed to be impacted by the fuel parameters at 4 bar indicated mean effective pressure (IMEP). IMEP is a measure of pressure work on the piston. At this engine condition, cetane number showed no effect on cylinder heat loss or thermal efficiency, threshold sooting index decreased thermal efficiency but did not change cylinder heat loss, and 50% distillation temperature had no effect. At 2 bar IMEP, a higher cetane number was observed to provide slightly improved efficiency and at 6 bar, a lower cetane provided slightly higher efficiency. Further data analysis is being completed, including kinetic modeling of results. These types of studies can provide rapid narrowing of fuel effects in a specific situation because of the ease of designing and blending surrogate fuels and direct link to kinetic modeling. A second round of fuels is being designed to study chemistry effects at constant sooting index.

FEERC Research in Diesel Emissions Control Catalysts was Featured in the Cover Story in the May 21 Issue of *Chemical and Engineering News* (C&EN), Vol. 90, Issue 21

In the article, the diesel catalyst research led by Bill Partridge and Jae-Soon Choi using a unique gas analysis technique developed by the FEERC team – Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS) – was highlighted as well as the increasing impact SpaciMS is making on the international catalyst research community (http://cen.acs.org/articles/90/i21/Ever-Cleaner-Auto-Exhaust.html).

FEERC Researchers was invited to give a seminar at Massachusetts Institute of Technology (MIT)

Andreas Malikopoulos delivered a seminar at MIT entitled, "Average Cost Criterion in Controlled Markov Chains: Enabling Theoretical Framework for Optimal Solution Characterization," presenting new theoretical and algorithmic results in stochastic optimization

and control. The work presented is currently used in transportation related applications, and in particular, to develop power management control algorithms for plug-in electric vehicles (PEVs).

Invited Journal Article on Lean NO_X Trap (LNT) Catalysis Published in *Catalysis Today*

A manuscript by Jae-Soon Choi, William P. Partridge, Josh A. Pihl, Mi-Young Kim, Petr Kočí, and C. Stuart Daw entitled "Spatiotemporal Distribution of NO_X Storage and Impact on NH_3 and N_2O Selectivities during Lean/Rich Cycling of a Ba-based Lean NO_X Trap Catalyst," has been published in *Catalyis Today*, pp. 20–26, 184(1), April 2012. The study shows that the distribution of stored NO_X in an operating LNT catalyst changes continuously over space and time. The experimental results reported in the article demonstrate that the details of this spatiotemporal distribution of reactions are important for accurately understanding and modeling LNTs such as NO_X reduction performance and NH_3 and N_2O emissions.

ORNL Collaboration Supports Graduate at Chalmers University of Technology

Filipa Coelho presented her Master of Science (MS) thesis presentation on modeling steady state intra-catalyst distributed SCR performance June 29, 2012, at Chalmers University of Technology in Gothenburg, Sweden, with ORNL staff joining in via telecom. The MS presentation was titled "Kinetic Modeling of Ammonia Selective Catalytic Reduction for Cleaning Emissions from Vehicles." Ms. Coelho has been working with Professor Louise Olsson in the Department of Chemical Engineering, Competence Centre for Catalysis (KCK), Chalmers, to model the steady state SpaciMS SCR data acquired during Xavier Auvray's previous ORNL visit; Xavier is one of Professor Olsson's Ph.D. students and was supported by Dr. W. P. Partridge and Dr. J.-S. Choi of ORNL FEERC during that visit. Ms. Coelho received her BS from the Universidade do Porto in Portugal and has been working at Chalmers for the past five months via EuRopean Community Action Scheme for the Mobility of University Students (Erasmus) fellowship. Her work w/Prof. Olsson was coadvised by Dr. Partridge and Dr. Choi and is supportive of DOE programs including Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) and the Cummins Cooperative Research and Development Agreement (CRADA). Ms. Coelho's work represents the most recent step in a successful ongoing collaborative partnership between ORNL\FEERC and Chalmers\KCK, which leverages existing programs at each location to further strengthen and bring the most value to those programs. This collaborative team intends to publish the results of Ms. Coelho's research and further build on that work to investigate transient SCR performance and nature and dynamic NH_3 inhibition.

ORNL RCCI Paper Published in the *International Journal of Engine Research*, Special Issue on Fuel Efficiency

FEERC researchers Scott Curran, Robert Wagner and a visiting student from the University of Wisconsin, Reed Hanson, published a paper entitled, "Reactivity Controlled Compression Ignition on a Light-Duty Diesel Engine," was published in the June 2012 issue of the *International Journal of Engine Research's Special Issue on Fuel Efficiency*. The paper investigated RCCI operation with gasoline and diesel on a light-duty diesel engine with the stock diesel pistons. Significant findings from this paper include a new understanding of the robustness of the RCCI approach on multi-cylinder engines. This robustness allowed for the development of a systematic procedure for extrapolating modeling guidance to a wide range of engine speed/load conditions to allow for ultra-low NO_X emissions, near zero smoke emissions and high brake thermal efficiencies while minimizing increases in CO and HC emissions. This is

potentially an advantage over other single fuel low temperature combustion techniques which are more sensitive to in-cylinder charge conditions, more difficult to control, and require direct model guidance with minimal opportunity for extrapolation.

Progress Made in High Load Expansion of Homogeneous Charge Compression Igniation (HCCI)
An experimental effort to expand the high load limit of lean-burn HCCI combustion as part of a CRADA project with Delphi made substantial progress in June 2012. With the use of boost, external cooled exhaust gas recirculation (EGR), negative valve overlap (NVO), and direct fuel injection, ORNL researchers achieved an engine load of 6.5 bar $IMEP_{net}$ with low noise, single-digit ppm NO_X emissions, and net indicated efficiency of 41.4% (equivalent to an indicated specific fuel consumption (ISFC) of 199 g/kW-h for gasoline with a lower heating value of 43.7 MJ/kg). While others have achieved similar or higher HCCI engine loads in the past, this work provides new insights on the sensitivity of control parameters by including extensive parametric investigations of injection timing, NVO duration, boost, and external EGR. The current plans are to deliver a paper and presentation on this work at the 2013 Society of Automotive Engineers (SAE) World Congress.

Invited Talks and Presentations

FEERC Researcher Gave an Invited Presentation Entitled "Lean NO_X Trap Regeneration Chemistry Studies" to the Research and Development (R&D) Staff of Heesung Catalysts in Korea
Heesung Catalysts Corporation, a joint venture between Heesung Group and BASF Catalysts, is a major supplier of automotive catalysts. Jae-Soon Choi visited the company's R&D Center near Seoul and had technical discussion with their R&D staff in particular on lean emissions control and collaboration opportunities.

ORNL has Strong Showing at the Advanced Engine Combustion (AEC)/HCCI Working Group Meeting
Scott Curran and Jim Szybist from ORNL delivered presentations at the June meeting of the AEC/HCCI Working Group held June 19, 2012, in Southfield, Michigan. Scott's presentation entitled, "Recent Advancements in Multi-Cylinder RCCI Combustion," focused on experimental results that were used to meet the FY2012 second and third quarter Joule Milestones on efficiency and engine mapping targets for multi-cylinder RCCI combustion. Dr. Szybist's presentation entitled, "The Impact of Low Octane Hydrocarbon Blending Streams on "E85" Engine Optimization," focused on the combustion impact of a recent American Society for Testing and Materials (ASTM) specification that allows the ethanol content of "E85" to be as low as 51%. Both presentations were well-received and generated a significant amount of discussion with colleagues from industry, academia, and other national laboratories. Robert Wagner from ORNL was also in attendance at the meeting.

FEERC Presents on the Challenges and Opportunities of the Next Generation of Internal Combustion Engines
Robert Wagner delivered two presentations at the recent Emissions 2012 conference held June 12–13, 2012, in Ypsilanti, Michigan. The first presentation was delivered during the keynote session and titled "Enabling the Next Generation of High Efficiency Engines." This

presentation focused on the opportunities and challenges of an ever increasing parameter space for enabling advanced engines. The second presentation was focused on the control and dynamics of advanced combustion strategies and titled "Walking the Edge of Stability with Low Temperature Combustion." The Emissions 2012 conference is sponsored by the Global Automotive Management Council with the purpose to provide a forum for engineers, managers, scientists, academic researchers, and industry executives to exchange advances in emission technology and management systems.

FEERC Researcher attended the 2012 Stochastic Networks Conference

Andreas Malikopoulos attended the 2012 Stochastic Networks Conference held in Boston, Massachusetts. Stochastic networks is a multifaceted area of research dealing with the modeling, stability, control, performance, approximation, and design of stochastic networks. It gives rise to challenging and subtle mathematical problems, whose solution often requires a combination of ideas and techniques from several branches of mathematics including probability theory, stochastic processes, analysis, optimization, algorithms, combinatorics, and graph theory. Research in this area is strongly motivated by applications in diverse domains, ranging from the traditional areas of transportation to service operations, biological and social networks, revenue management, and health care. Like its predecessors, the 2012 Stochastic Networks Conference emphasized new model structures and new mathematical problems that are motivated by contemporary developments in various application domains, as well as new mathematical methods for stochastic network analysis.

FEERC Researcher Presents at the Integrated Instrumentation Symposium

At the Integrated Instrumentation Symposium of the International Society for Automation held June 4–7 2012, in La Jolla, California, Dr. Jon Yoo presented his work, performed under Dr. William Partridge, on fast intake CO2 measurements to achieve combustion uniformity improvements in advanced engines. Dr. R. Maggie Connatser presented progress, also helmed by Dr. Partridge, on high temperature sensing of ammonia using materials-modified optical fibers for enhanced aftertreatment catalyst diagnostics. Separate discussions on rapid battery aging diagnostics were also conducted with a team representing Montana Tech, University of Connecticut, and the private entity Qualtech.

Awards

FEERC Researcher joins the American Society of Mechanical Engineers (ASME) Internal Combustion Engine Division (ICED) Board of Associates

The Executive Committee of the ASME ICED approved the nomination of Andreas Malikopoulos to serve on the Board of Associates as an ICED Associate.

FEERC Research Invited to be Associate Editor of International Journal

Robert Wagner was invited to be an Associate Editor of the SAE International Journal of Engines. This journal includes peer reviewed and authoritive papers on in-depth work in engine research. Topics span low temperature combustion, conventional gasoline and diesel combustion, controls, sensors, fuel economy, etc.