Technical Highlights for December 2011

Fuels Program Collaboration with Pacific Northwest National Laboratory (PNNL)
A conference call was held with PNNL in December to discuss further collaborations in emerging fuels research. This collaboration will continue in four areas and also includes participation by the National Center for Upgrading Technology (NCUT) and the National Renewable Energy Laboratory (NREL). The first is engine experiments and characterization of oil shale derived fuels from PNNL. These fuels have been made and distributed and research will begin this quarter. The second is analysis and engine experiments of upgraded pyrolysis oil being made under contract with the University of Georgia. These fuels should be completed in March. Third is analysis and mining of past data for oil shale fuels and Fuels for Advanced Combustion Engines (FACE) diesel fuels for relationships between properties, chemistry, and engine performance. This task is still under discussion. Forth, we are exploring the possibility of obtaining additional upgraded pyrolysis oil samples from the PNNL biomass program.

ORNL Completes Analysis of Elastomer and Plastic Compatibility to Higher Ethanol Fuel Blends
Fueling infrastructure material properties obtained from the CE50a and CE85a exposures were analyzed and compared to the results obtained from previous studies. The results showed that the intermediate levels of ethanol produced the highest volume swell for the majority of the elastomers. Fluid permeation decreased dramatically with higher ethanol concentration, and for several NBR specimens, exposure to 85% aggressive ethanol did not produce noticeable swelling. Interestingly, even though permeation of CE85a into the NBRs was low, it was enough to extract plasticizers and degrade performance. In contrast, the majority of plastic materials were not significantly impacted with exposure to the test fuels, but a few did exhibit noteworthy changes. (For instance, the nylon 12 specimen shrank by 8 percent after drying, and the vinyl ester and polyester resins swelled to over 20% with exposure to CE25a.) A formal request was made by industry for ORNL to present the latest findings and a Webinar was scheduled for January 5. The Petroleum Equipment Institute issued an announcement of the upcoming webinar to their members on their website and, based on feedback, over 100 attendees will be participating. These attendees will include representatives from the dispenser and material industries, Department of Defense, and other government agencies. Mike Kass and Tim Theiss will formally deliver the results.

ORNL has Completed Analysis of Elastomer and Plastic Compatibility to Higher Ethanol Fuel Blends
ORNL has completed analysis of elastic and plastic material performance to ethanol-blended test fuels of CE25a, CEE50a, and CE85a. The results from this analysis will be compiled in a future report and a formal industry request was made to present this data on January 5, 2012 in a webinar organized by Kristi Moriarty of NREL. Over 100 attendees will be participating with representatives from the dispenser and material industries, Department of Defense, and other government agencies. Mike Kass and Tim Theiss will formally deliver the results.

The University of Georgia Pyrolysis Upgrading Contract Update
The University of Georgia is approximately 50% complete on a research contract funded under the fuels program to provide samples of upgraded pyrolysis oil for ORNL engine experiments. For this research, pyrolysis oil was supplied by UOP and the University of Georgia experiments consist of autoclave hydrotreating with various catalysis and operating conditions and up to three stages. They have not succeeded in obtaining a clean hydrocarbon (HC) phase and have only achieved a reduction to about 20% oxygen content, which appears to be about the lower limit with reasonable yield and hydrogen consumption. We are going to do some blending experiments with diesel fuel to see if this will break the remaining emulsion of water, catalyst, coke, and HCs and yield a clean fuel blend for engine tests. After further analysis and a few more operating trials, the goal is to produce two one-liter samples through multiple runs. These will be run at ORNL in diesel fuel blends and shared with PNNL, NREL, and NCUT for characterization.

Transient Spaci-IR (Infrared) Measurements of Spatial On-Board Ammonia (NH_3) Storage Distributions in a Commercial Small Pore Copper Zeolite under Selective Catalytic Reduction (SCR) Operating Conditions
Researchers at ORNL's Fuels, Engines, and Emissions Research Center (FEERC) used a newly developed transient Spaci-IR technique to map the NH_3 surface coverage inside a commercial small pore copper zeolite under SCR operating conditions. To our knowledge, this is the first time such measurements have been performed on state-of-the-art commercial copper zeolite catalysts. The maps of NH_3 coverage reveal where the NH_3 is located within the catalyst in relation to where the SCR reactions occur. This information provides insights into the relative rates of NH_3 storage and consumption, and informs development of both simulation tools and SCR operating strategies. Our

partners at Michigan Technological University will use the data sets to validate the spatial NH_3 storage distributions predicted by their SCR catalyst models.

FEERC Researcher Delivers Distinguished Lecture at Georgia Southern University

Bruce Bunting visited Georgia Southern University in late November to present a talk entitled "Transportation Fuels: Markets, Trends, Biofuels, and Related Research," for their distinguished lecture series to visit laboratories, meet faculty, and discuss possible future collaboration. Georgia Southern University combines a strong, practical mechanical program, a strong biology department, and high minority enrollment. Over the last few years, they have also built up an engine laboratory and biofuels research laboratory, funded partially with the Department of Energy (DOE) and National Science Foundation (NSF) equipment grants. Future collaborations may include partnering on proposals and student internships at ORNL.

FEERC Researcher Attends Greenhouse Gases, Regulated Emissions, and Energy use in Transportation (GREET) Workshop at Argonne National Laboratory (ANL)

FEERC researcher Scott Curran attended a GREET workshop hosted at ANL on December 7–8, 2011. Other workshop attendees included researchers, scientists, and policy makers from private industry, other national laboratories, and universities. GREET has been used for a number of analyses at ORNL and the recent major updates to the model will allow researchers at ORNL to have a stronger capability for life-cycle analysis in transportation systems.

FEERC Researcher Attends Model Fuels Consortium Annual Meeting

Bruce Bunting attended the Reaction Design Model Fuels Consortium Annual Meeting November 14th and presented a talk entitled "ORNL Fuels Research on Behalf of Reaction Design Model Fuels Consortium." This consortium is entering the seventh year and has recently released the following tools to members: master kinetic mechanisms for diesel, gasoline, and gaseous fuels including oxygen containing species, flexible target surrogate blend design tools, tools for mechanism reduction, and tools for calculating particulate mass (engines) and size distribution (burner rigs). In the final year of this collaboration we will be applying these tools to the task of modeling all past ORNL engine data. This task will confirm these tools and will provide practical experience relative to their application with the goal of being able to model fuel behavior prior to running engine experiments.

FEERC Study Shows Limitations for Use of Leak-Down Tests to Monitor Engine Degradation

A study recently published by ORNL FEERC entitled, "Limitations and Recommendations in the Use of Compression and Leak-Down Tests to Monitor Gradual Engine Degradation," pp. 2767–2777 in the December 2011 issue of *The Society of Automotive Engineers (SAE) International Journal of Engines* shows that the variability of the leak-down test is problematic for monitoring gradual changes in engine wear. The study was completed as a part of the mid-level ethanol blends program and examined results from 68 individual vehicles that were each driven between 50,000–100,000 miles on the standard road cycle (SRC), an emissions durability cycle. Compression and leak-down measurements were conducted at start, middle, and end of aging. The results showed that the leak-down tests could have 95% confidence intervals of nearly 3% leak-down indicating low statistical confidence in changes below 3%. Modern engines typically have very low leakage, most often less than 10%, and thus the confidence interval is large relative to most measured results. The data showed no correlation between compression tests and leak-down tests. Comparison of the difference in leakage from start to end of the program showed that over 80% of the results could not be considered significant; hence, the study concluded that the leak-down test, in its current form, is not well-suited to monitoring gradual engine degradation, though it remains a useful method for diagnosing gross failures of power cylinders.

FEERC Researcher Delivers Invited Presentation to the American Society for Testing and Materials (ASTM) Fuels Corrosivity Workshop

Mike Kass gave an invited presentation entitled "Material Compatibility of Fueling Infrastructure Materials in Ethanol Blended Fuels," to the Fuel Corrosivity Workshop on December 8th in New Orleans. This workshop was sponsored by the ASTM Committee D02.14 Stability and Cleanliness of Liquid Fuels. Co-authors include Tim Theiss, Chris Janke, and Steve Pawel. This paper was well received and afterwards the head of the Corrosion and Degradation Division of the National Institute of Technology (within the Ministry of Science and Technology of Brazil) stated that these results explained the compatibility issues with automotive seals that Brazil experienced with E22 fuels.

FEERC Researchers and Underwriters Laboratories Present to the 21st International Conference on Fluid Sealing

Edwin Yang of the Underwriters Laboratories gave a joint ORNL-UL paper entitled "Elastomer Compatibility to a Gasoline Standard Containing Intermediate Levels of Ethanol" to the 21st International Conference on Fluid Sealing on December 1st in Milton Keynes, United Kingdom. ORNL/FEERC co-authors were Mike Kass, Tim Theiss, Chris Janke, Steve Pawel, and Sam Lewis. This paper was extremely well received and afterwards the lead editor for *The Journal of Sealing Technology* requested two papers based on the presented work.

FEERC Staff Recognized at ORNL Partnerships Award Ceremony

FEERC staff members Bill Partridge, Jim Parks, Sam Lewis and Maggie Connatser were recently recognized for their recent contributions and successes at the ORNL Partnerships Award Ceremony. Bill Partridge and Jim Parks received dual recognition for their CRADA-developed Fuel-in-Oil (FiO) technology; one for receiving the FiO patent (US 7,839,492 B2; Nov. 23, 2010; Laser Induced Fluorescence Fiber Optic Probe Measurement of Oil Dilution by Fuel), and the other for receiving the 2011 FLC National Award for Excellence in Technology Transfer. The Federal Laboratory Consortium for Technology Transfer (FLC) award recognizes laboratory employees who have accomplished outstanding work in the process of transferring a technology developed by a federal laboratory to the commercial marketplace. The FiO was developed in a DOE-funded CRADA between ORNL and Cummins Inc. and has been licensed for commercial development to Da Vinci Emissions Services. Sam Lewis and Maggie Connatser were recognized for a patent related to Raman imaging of fingerprints; US 7,869,031 B2; January 11, 2011, Detection of Latent Prints by Raman Imaging. This patent was issued based on ORNL work led by Dr. Linda Lewis which enables detection of fingerprints which could not be resolved with conventional methods.