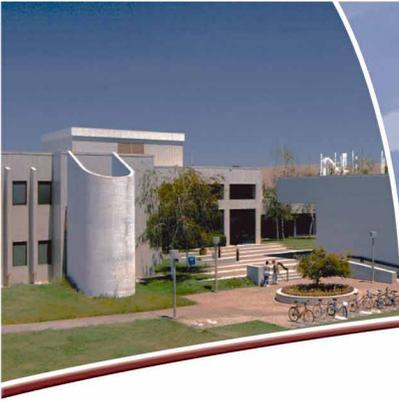


Combustion Research Facility NEWS



Laser-Induced Breakdown Spectroscopy (LIBS) Used to Evaluate Fiber Cane as Biomass Fuel in Hawaiian Power Generation Boiler

Laser-induced breakdown spectroscopy (LIBS) has been applied to the in situ detection of chemical elements in the boiler of a power generator in Maui, Hawaii. The effort was part of a DOE BioPower Program demonstration project headed by Hawaiian Commercial and Sugar Company (HC&S) to test the feasibility of using fiber cane as a boiler fuel. The Sandia team of Linda Blevins, Doug Scott, and Howard Johnsen and collaborators Lee Jakeway of HC&S, Scott Turn of the Hawaii Natural Energy Institute, and Bryan Jenkins and Rob Williams of the University of California, Davis, found that co-firing fiber cane with different fuels mitigated its tendency to form boiler deposits. This agrees with the findings from experiments performed at the CRF Multi-Fuel Combustor laboratory in support of the demonstration project.

HC&S currently burns bagasse, the fibrous residue left after sugar is extracted from sugar cane together with coal and fuel oil to provide steam and electricity for the sugar factory and the local electric company. Fiber cane (see Figure 1) potentially has better fuel characteristics than sugar cane and could be an attractive renewable energy alternative to fossil fuels. However, because fiber cane, unlike sugar cane, would be burned directly without first extracting sugar, the alkali metals and other inorganics that are usually leached from bagasse during sugar extraction could increase boiler deposition.

In the LIBS technique, a high-energy pulsed laser ionizes the gases and particles, and the ionic and atomic emission from the hot plasma is recorded. For the current tests, a newly acquired system



Figure 1. Harvested and chopped fiber cane drying on an airstrip between adjacent growing sugar cane fields. Drying prepares the fiber cane for combustion in a power generation boiler. Sugar making was bypassed, so there were questions about the fiber cane's propensity to form boiler deposits. Answers are being provided with LIBS data.

consisting of an intensified charge-coupled device (ICCD) camera coupled to an echelle spectrometer was used. The echelle spectrometer employs two gratings to allow detection of ultraviolet, visible, and near-infrared light in a single measurement. The LIBS system employed a Nd:YAG laser with a pulse width of 10 ns and pulse energy of 350 mJ. Spectra were collected at 5 Hz with a delay time of 10 μ s and a gate width of 50 μ s. For this 2-week field trial, 1000-point ensemble averages representing about 3 minutes of data were recorded for about 8 hours per day.

A three-foot-long, water-cooled, nitrogen-purged optics probe was designed and built for the project. The probe was

inserted into the boiler near the first bank of superheater tubes. Multimode fiber optics delivered light from the receiving optics to the ICCD, which was kept cool and clean in the power plant control room. Magnesium, silicon, titanium, iron, calcium, aluminum, sodium, and potassium were detected during the field trial. Potassium is a prime contributor to boiler deposition, and its LIBS-measured concentration was used to predict the likelihood that boiler deposits would form.

The CRF team took LIBS data from three fuel combinations: coal, bagasse/coal, and fiber cane/bagasse/coal. Fuel oil was added intermittently for boiler stabilization. For the co-firing cases, the fuel flows were estimated to be about

85% biomass by mass. The fiber cane constituted about 18% of its biomass fuel blend. Figure 2 shows a typical LIBS spectrum collected during fiber cane co-firing. LIBS signals were quantified using laboratory calibrations performed at Sandia after the field trial. In addition to LIBS, the team applied a variety of other diagnostics including a pitot tube, several deposition tubes, two continuous emissions monitors, an extractive wet-chemistry impinger, and various thermocouples. Samples of fuels and effluents were also collected for analysis. The resulting information comprises the most extensive data set ever collected during a biomass combustion field demonstration.

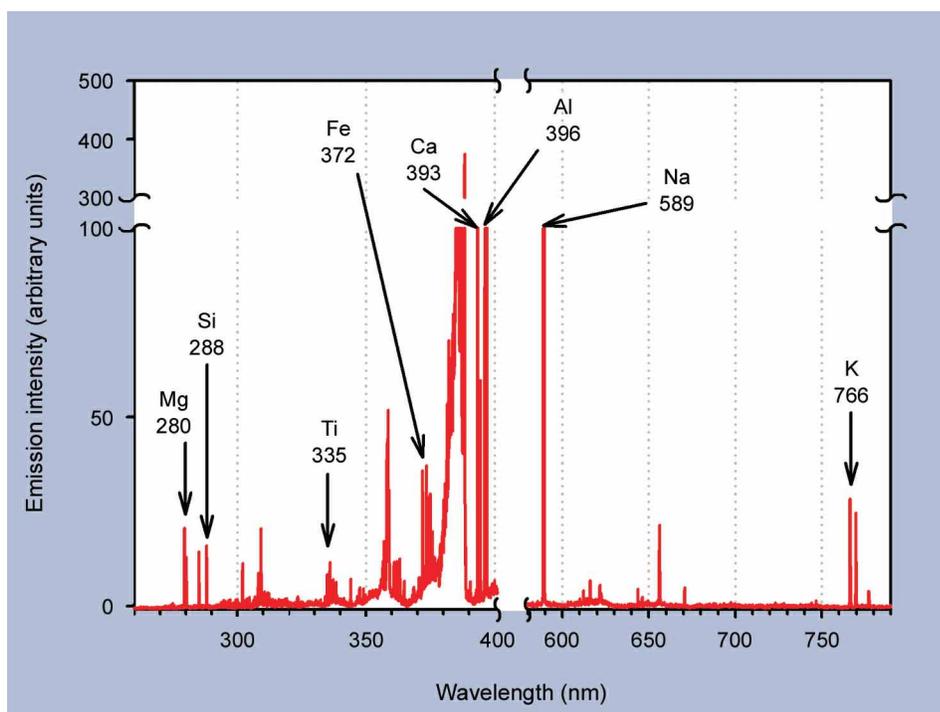


Figure 2. LIBS spectrum for fiber cane, bagasse, and coal co-firing in Hawaiian Commercial and Sugar Company's traveling grate boiler. The spectrum is a 1000-shot, three-minute ensemble average. Key species' peak locations are identified with detection wavelengths expressed in nanometers. The echelle spectrometer allows single-shot light collection between 200 nm and 900 nm.

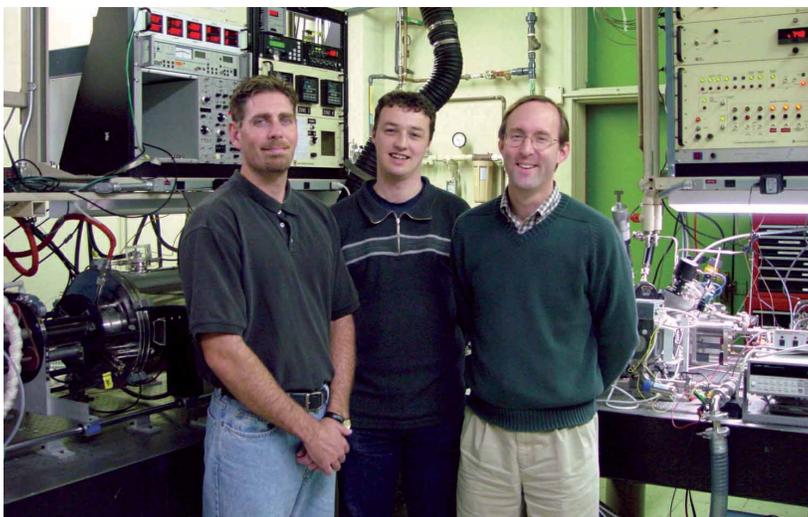
CRF Names New Department Heads



Wen Hsu and Sarah Allendorf have been named new CRF Department Heads. Sarah heads up the Combustion Chemistry group and Wen takes over the Diagnostics and Remote Sensing Group from Bob Gallagher, who moves on to Industrial and Combustion Processes. Sarah recently finished up a 6-year stint as leader for the steel sensors project. Wen comes to the CRF from the Systems Research Department at Sandia California's Center for Exploratory Systems and Development.

Offgas Sensors Installed at Two US Steel Plants

Sandia's Steel Team (Sarah Allendorf, David Ottesen, Bob Green, Ben Chorpening, Doug Scott, Shane Sickafoose, and Gary Hubbard) have successfully completed the installation of two real-time, offgas sensors for process control in commercial steelmaking. The first sensor prototype is a double-ended, tunable-diode-laser-based device that continuously measures the composition and temperature of gases emitted during electric arc steelmaking, and is installed at The Timken Company, in Canton, Ohio. The second system is a single-ended sensor that detects infrared emission from the offgas produced during basic oxygen steelmaking, and is installed at U.S. Steel's Edgar-Thomson plant outside Pittsburgh, Pennsylvania. Both instruments were installed during November, 2001, and are still functioning with occasional monitoring of their performance via long-distance computer control.



Dr. Ton van Mol of the Netherlands Organization for Applied Scientific Research (TNO) shown with staff members Tony McDaniel (left) and Mark Allendorf (right). Dr. van Mol is conducting experiments using a high-temperature flow reactor facility at the CRF to determine the oxidation kinetics for tin precursors used in the formation of tin oxide films on float glass. The project involves collaboration with PPG Industries, Inc. in Pittsburgh, PA.

SAE Presentation Award

Belated kudos to Chuck Mueller whose presentation of his paper "Glow Plug Assisted Ignition and Combustion of Methanol in an Optical Direct Injection Diesel Engine" won an award for Excellence in Oral Presentation at the SAE 2001 World Congress held in Detroit.

Rich Palmer

Friends and colleagues gathered at the CRF on January 31 to share reminiscences of Rich Palmer who passed away after a long illness. Rich started his 30-year Sandia career in Albuquerque after earning a Ph.D. in Physics from Princeton University. He came to the CRF in 1972 with an established reputation as a laser scientist and quickly added management and computer skills to that reputation. He worked in a number of different capacities at the California site, before returning to the CRF in 1998. While Rich was remembered in an astonishingly different number of ways by those present, it was his courage that seemed to touch everyone.

The reacting flow and diagnostics portion of the Department of Energy, Chemical Sciences program at the Combustion Research Facility was reviewed on March 4-6, 2002.

The participants included (Standing left to right) Dr. Chiping Li (Naval Research Laboratory), Professor Phil Johnson (SUNY, Stony Brook), Dr. William Kirchhoff (Department of Energy, Chemical Sciences), Professor Mike Heaven (Emory University), Dr. Allan Laufer (Department of Energy, Chemical Sciences), Professor Ann Karagozian (UCLA), Dr. Charles Romine (Department of Energy, MICS), Bob Carling, Wen Hsu, Sarah Allendorf, Bill McLean, Larry Rahn, and Dr. Heinz Pitsch (Stanford University).

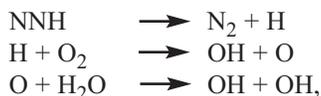


Direct Transition State Theory Analysis Explains Temperature Dependent Branching in $\text{NH}_2 + \text{NO}$ Reaction

Thermal De- NO_x is a noncatalytic process used to remove nitrogen oxides from flue gas by the addition of ammonia. While the process is complex, the overall mechanism is exquisitely sensitive to the branching of the $\text{NH}_2 + \text{NO}$ reaction between two product channels (a) and (b):



This sensitivity arises from the fact that reaction (b), followed by the sequence,



is chain branching, whereas reaction (a) is chain terminating.

The branched chain character of the process is important for predicting a number of its observed properties. The chain branching is also sensitive to the lifetime of the NNH radical.

In earlier work, Jim Miller and Peter Glarborg (Technical University of Denmark) constructed a satisfactory chemical kinetic model for Thermal De- NO_x by fitting the branching fraction, $\alpha(T)$, to the available experimental data and employing an NNH lifetime that was consistent with independent experimental measurements and theoretical predictions.

However, the temperature dependence of $\alpha(T)$ used in the Miller-Glarborg model was not consistent with the most reliable theoretical prediction of this parameter.

Extending their earlier theoretical analysis, Stephen Klippenstein and Jim

Miller of the CRF, together with Larry Harding of Argonne National Laboratory, have now provided an a priori theoretical explanation (from first principles without data fitting) for the temperature dependence of this branching. A schematic diagram of the potential energy surface governing this reaction is provided in Figure 1. The branching ratio is effectively determined by the ratio of the transition state partition function for trans-HNNOH \longrightarrow NNH + OH (ts8) to that for the cis-trans isomerization of HNNOH (ts3, ts4).

The barrierless nature of the reverse NNH + OH recombination presents difficulties for standard implementations of transition state theory.

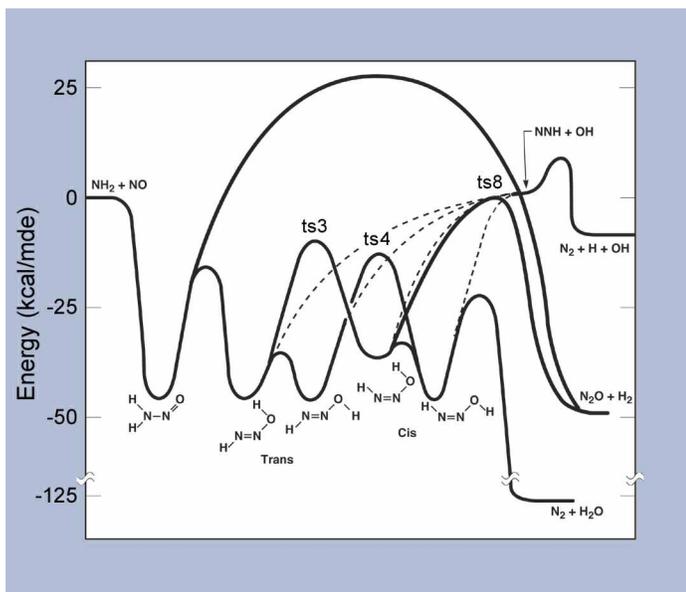


Figure 1. The reaction coordinate diagram for the reaction of NH_2 with NO . The dashed lines indicate the barrierless transitions that yield NNH + OH from each of the HNNOH conformers.

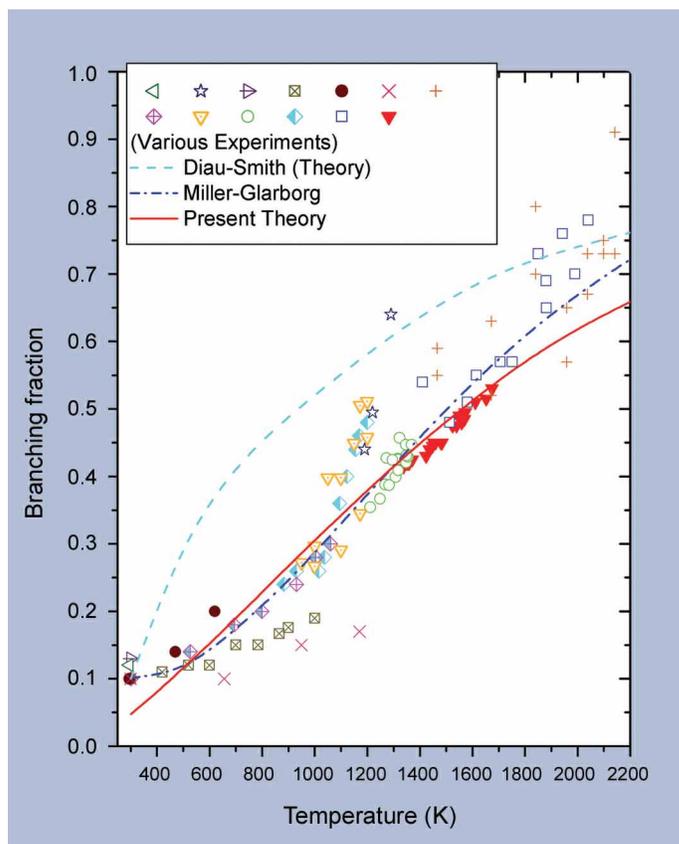


Figure 2. Comparison of recent theoretical predictions of the branching ratios with experiment and with prior theoretical results. The solid line represents the reference case with the NNH + OH reaction endothermicity reduced to 0.9 kcal/mol and the ts3, ts4 barrier height reduced by 4 kcal/mol.

In recent work, Klippenstein and Harding have developed a novel implementation of transition state theory specifically designed to provide accurate a priori theoretical predictions for such barrierless reactions.

This implementation directly couples ab initio quantum chemical simulations with the transition-state partition function evaluations, and includes a variable definition of the reaction coordinate. This direct variable reaction coordinate transition state theory analysis was applied to the partition function for ts8, with the

interaction energies determined at a high level of electronic structure theory (CAS+1+2/cc-pvdz).

This analysis for ts8 was coupled with more standard evaluations for the other transition states including ts3 and ts4, but again employing state-of-the-art ab initio quantum chemical properties, to yield estimates for $\alpha(T)$. A reduction by 1.6 kcal/mol in the endothermicity of channel a, and by 4.0 kcal/mol in the energies of ts3 and ts4, yields theoretical predictions for $\alpha(T)$ that are in quantitative agreement with the experimental measurements and

the Miller-Glarborg model, as illustrated in Figure 2. Importantly, such revisions in the thermochemistry are within the error bounds of quantum chemical estimates. Thus, experiment, theory, and the Miller-Glarborg model are now in complete accord for this key reaction in Thermal De-NO_x. This work has been published in *Faraday Disc.*, 119, 207-222, (2001).

RDX Decomposition Studies Point to the Formation of Nonvolatile Residue as an Emergent Phenomenon

The capability to accurately predict the response of a system containing energetic compounds RDX or HMX to improper storage or to exposure, such as a fire, is invaluable from a safety standpoint. A prediction requires the existence of a robust model that

can answer several fundamental questions pertaining to the 'damaged' energetic material. The Behrens Cycle is a scheme developed at the CRF to make such predictions (see CRF News, Vol 23, No.2). The scheme attempts to account for all the products and rates by dividing thermal decomposition into five cycles: solid phase, NO cycle, Nonvolatile Residue (NVR), Nitroso, and CH₂O/NO₂. Most recently, Sean Maharrey, Deneille Wiese-Smith, and Rich Behrens have devoted a major effort to studying the NVR cycle for RDX and found that this cycle has the characteristics of an emergent phenomenon.

The NVR reaction cycle initiates within the solid-phase reaction cycle and involves reactions of secondary products from the RDX decomposition. It dominates when the gaseous decomposition products are confined under high-pres-

sure. The NVR reaction-cycle becomes the main rate-controlling reaction cycle as the amount of NVR increases.

The NVR reaction cycle is responsible for what has been called the 'autocatalytic' behavior often observed in thermal

decomposition experiments. Autocatalytic behavior is often attributed to reaction intermediates formed within a sequential reaction mechanism that act to catalyze the already existing reaction without being consumed by the reaction. The overall NVR process, however, also involves a precursor formation step and subsequent decomposition upon depletion of RDX.

The precursor step involves thermal initiation of surface active sites that readily promote the formation of the NVR. A multistep nucleation and growth process begins with sintering of the individual RDX crystals into a bulk agglomerate. Then transport and

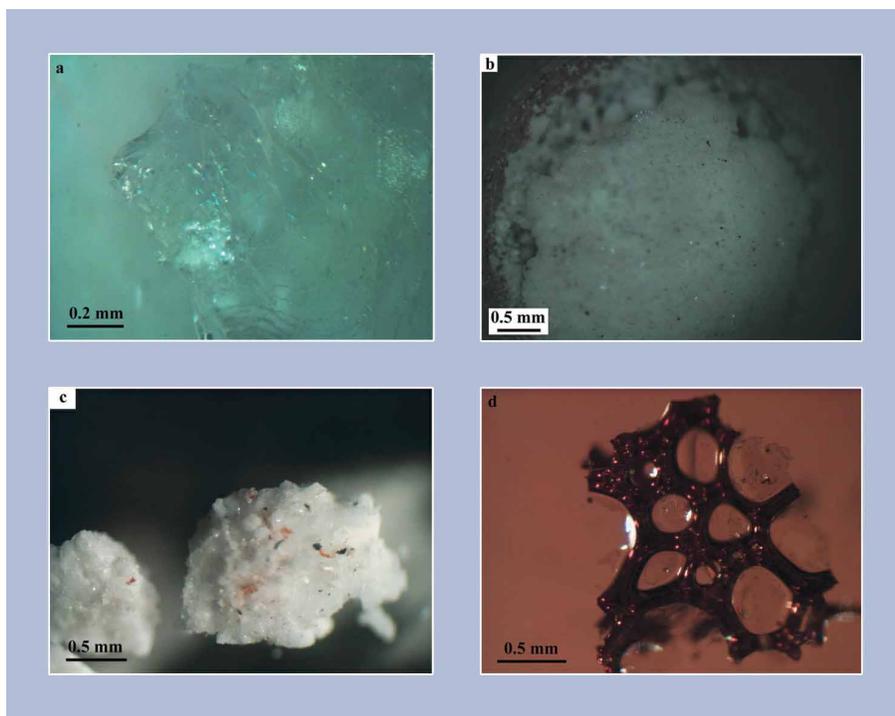


Figure 1. This series of optical micrographs shows the NVR formation process. At the top left (a) is the starting RDX sample. At ~ 3 % RDX decomposition (b), the RDX crystal has started to sinter. At ~ 30% decomposition (c), the RDX particles have been completely covered by the sintered surface, and the black spots have grown in size and number. Isolated black spots show the appearance of grainy, orange patches on their surface, while close-lying black spots have developed grainy, orange threads connecting them. In (d), the individual orange threads are shown to have combined to form the red, translucent NVR.

reaction of RDX on this sintered surface results in localized decomposition sites on the surface. Secondary reactions on the decomposition sites produce either elongated NVR 'strands' between close lying decomposition sites or NVR patches on isolated sites, followed by the growth of these isolated strands and patches into the bulk, amorphous NVR. Figure 1 depicts the overall decomposition through the complex reaction pathways that couple the NVR reaction cycle to the other reaction cycles.

This complex coupling of the solid-phase reaction cycle, the NVR reaction cycle and subsequent decomposition of the NVR, renders the 'autocatalytic' label an insufficient description of the process. An emergent phenomena, as described in

the nonlinear system science community, is a process whereby a closed system, left to itself, will seek its own path to a desired final product or an intermediate, which can itself alter the emergent phenomena process. Factors that tend to influence the emergent phenomena include initial environmental factors, such as heat and mass transport between the system and its environment before becoming closed, initial state of 'damage' to the system and distribution of this 'damage' throughout the system, past history of the system before onset of the emergent phenomena, and formation of intermediates within the system by the emergent phenomena that can create new 'feedback' loops within the system and influence or even alter the emergent phe-

nomena process. Scientists like Nobel Laureate physicist Bob Laughlin believe that emergent phenomena are prevalent in the mesoscale, or the region where matter is from 10 to 10,000 angstroms: bigger than a molecule, but smaller than a living cell.

Thus, the overall NVR process, nucleation and growth through the solid-phase reaction cycle, 'autocatalysis' through the NVR reaction cycle, and NVR reaction/decomposition by the coupling pathways, when taken together, describe a complex process that is more accurately described by the emergent phenomena process than the simpler 'autocatalysis' label.

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