ENERGY SCIENCE FOR A SEC SAND2011-5711P

COMBUSTION RESEARCH FACILITY
CRF
SANDIA NATIONAL LABORATORIES / CALIFORNIA

July/August 2011 • VOL. 33, NO. 4

Turbulent jet flame database generated for sooty fuels

The CRF has a long and distinguished history of performing laser diagnostic measurements in turbulent flames and documenting the processed data and corresponding boundary conditions in an online database accessible to modelers.

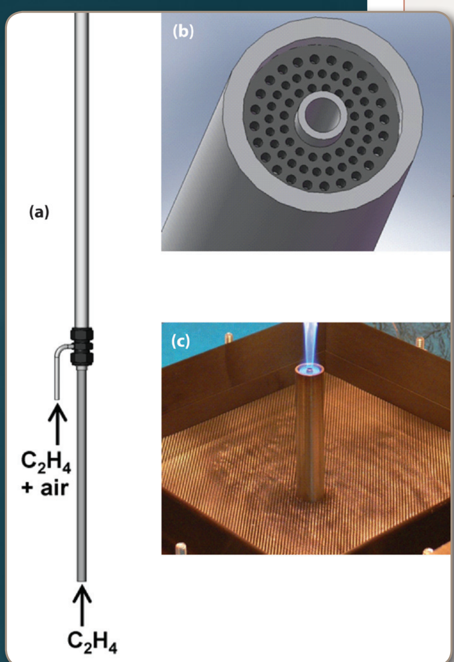

Figure 1. Design drawings of burner (a and b), showing the central fuel tube surrounded by a perforated plate that supports small pilot flames for stabilizing high-speed flames. Photograph (c) of pilot flames and the base of an ethylene jet flame.

Because of the desire for highly refined measurements of species concentrations and local temperature

(Continued on page 2)

Scrambling molecules with light

Isotopic labeling of chemical compounds is one of the most powerful techniques for understanding how chemical reactions proceed. Adding an extra neutron to an atom's nucleus [changing hydrogen (H) into deuterium (D) for example] doesn't usually change chemistry, but the extra mass of the heavier isotope allows scientists to track the position of this atomic label, often illuminating pathways of chemical reactions that might otherwise remain hidden. This technique is employed across a tremendous range of research, from astronomers studying the origins of the universe, to earth scientists studying historical temperature profiles, to biologists tracking lipid synthesis in bacteria. But new research shows such isotope labeling experiments can exhibit some unexpected twists.

An international team—directed by Meredith J. T. Jordan and Scott H. Kable (University of Sydney), and including David Osborn from the CRF's Combustion Chemistry Department and researchers from Argonne National Laboratory—recently published the results of a study investigating H/D scrambling in acetaldehyde near the energetic threshold for breaking the

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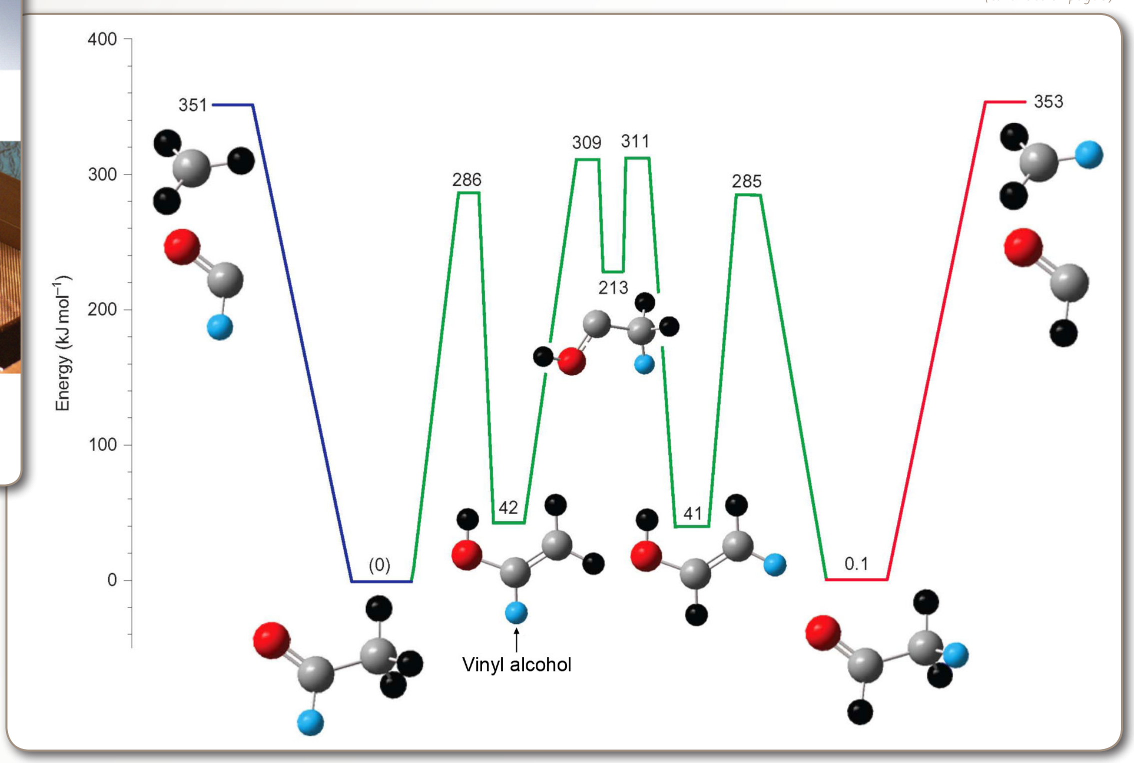


Figure 1. Schematic of the critical points on the global potential energy surface for C_2D_3HO. The reactant, CD_3CHO, can react to the left to form primary products (blue) or isomerize to the right through a maze of intermediate structures (green), which can continue to the final products (red) with exchange of H/D. The dominant pathway involves at least four isomerizations via H or D transfer. Key to atom colors: C, grey; O, red; H, blue; D, black. (Adapted from Heazlewood et al.)

Newsletter

Turbulent jet flame database generated for sooty fuels (Continued from page 1)

Figure 2. Photographs of JP-8 surrogate jet flame (left) and ethylene jet flame (right), both with a fuel jet Reynolds number of 20,000.

(using combined Rayleigh and Raman scattering), these measurements have always been performed in soot-free flames that allow for application of these laser diagnostic techniques.

However, some important combustion applications, notably traditional diesel engine combustion and aviation gas turbines, produce a considerable quantity of soot during the primary combustion phase, such that the amount of soot emitted in the exhaust creates a complicated interplay between the soot formation, turbulent mixing, and soot oxidation processes. Accurate predictions of soot emissions from these types of combustion systems require definitive datasets of experimental quantities in well-controlled flames for soot model development and validation.

Recently, Chris Shaddix and postdoctoral researcher Yao Zhang completed work on a project to develop such a database for the use of turbulent flame modelers. The work was supported by the Strategic Environmental Research and Development Program (SERDP), a Department of Defense research program that seeks solutions to environmental issues associated with U.S. military activities. In collaboration with other research program participants, Chris and Yao chose ethylene and a simple two-component surrogate consisting of *n*-dodecane and *m*-xylene for JP-8 (the standard U.S. military aviation fuel) as the two fuel systems to be researched. The first challenge of the project was to develop burner systems for these fuels that were amenable to both laser diagnostic measurements and turbulent flame modeling. Based on the previous success of the "Sydney burner" for piloted, non-premixed jet flames fueled by diluted methane, this burner design formed the basis for the ethylene and JP-8 surrogate burners. A design drawing of the burner exit plane of one of the new burners is shown in Figure 1, together with a photograph of the ethylene burner. For the liquid JP-8 surrogate, a flash vaporization and heated fuel vapor delivery system was developed.

Photographs of the canonical ethylene and JP-8 surrogate flames that were used for most of the experimental measurements are shown in Figure 2. Joint planar imaging of polycyclic aromatic hydrocarbons (PAH) and soot was performed to provide an understanding of where soot nucleation occurs in these flames. Similarly, joint imaging of hydroxyl radical (OH•) and soot was performed to show where soot oxidation occurs. The ethylene flame imaging showed soot layers that were always surrounded by OH•, and indeed no soot emission from that flame was visible, whereas the JP-8 surrogate flame showed quenching of the OH• layers and occasional release of soot near the top of the flame, consistent with the observation of soot in the exhaust. Figure 3 shows an example of joint OH• and soot imaging.

Quantitative, time-resolved measurements performed in these flames include soot volume fraction (from laser-induced incandescence), local soot temperature-concentration statistics (from simultaneous laser extinction and two-color pyrometry measurements with a ceramic probe), and local radiant emission intensity (from a calibrated thermopile with an anodized light tube). One of the complications in deducing the soot volume fraction in a turbulent, sooty flow is the existence of "signal trapping" (i.e., the loss of signal by optical extinction as it traverses soot layers between the location of signal excitation and the optical detector, outside of the flame). To correct for signal trapping, laser extinction measurements were performed on a time-average basis across the full width of the flame for a sequence of radial positions and heights, and then the results were interpolated to yield a 2D signal trapping correction for the entire flames. Processing of the experimental data is still in progress; when completed, it will be posted onto the CRF website (*https://share.sandia.gov/crf/*) for access by turbulent flame modelers.

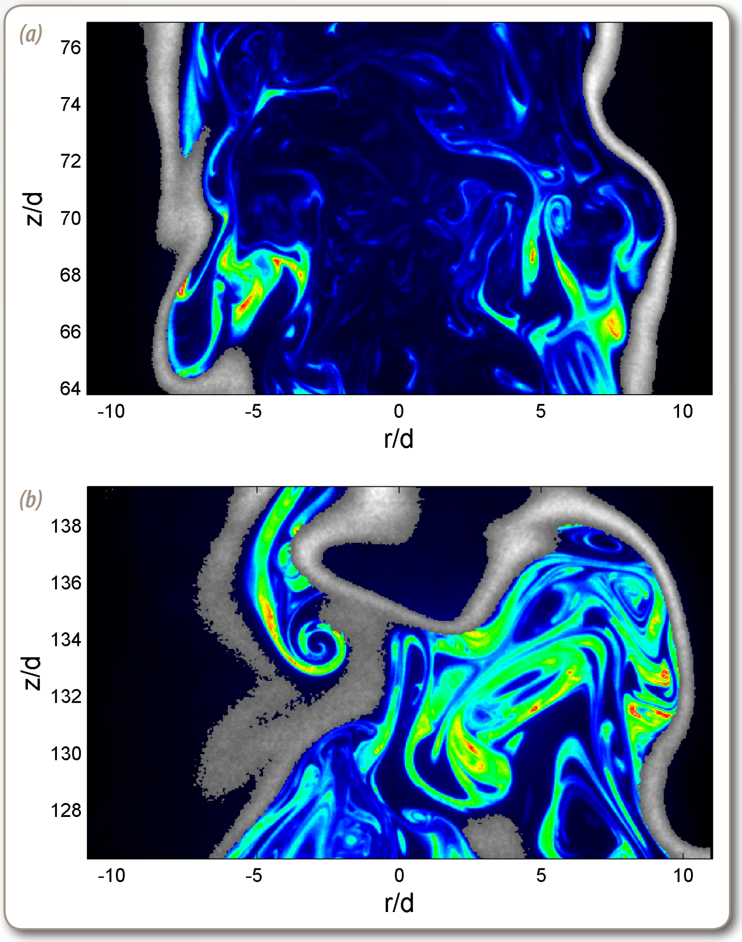
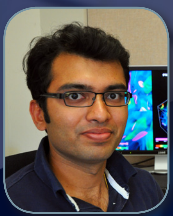


Figure 3. Overlay images showing OH• (in gray/white) and soot concentrations (color scale) at instantaneous moments in the ethylene jet flame. The top image (a) corresponds to a position one-third up the flame whereas the bottom image (b) is two-thirds up the flame.

Combustion Research Facility Visitor Program



Gaurav Bansal, post-doc with Jackie Chen

Gaurav's research was supported by the Combustion Energy Frontier Research Center. He worked on direct numerical simulation (DNS) of homogeneous charge compression ignition combustion with di-methyl ether, an oxygenated fuel, DNS of pulsating flame instabilities, and isometric mapping to identify reduced parameterizations in combustion. Gaurav has accepted a position with Intel Corporation in Oregon.

Michele Bardi, visitor with Lyle Pickett

Michele Bardi is visiting this summer from CMT Motores Térmicos at the Polytechnic University in Valencia, Spain. He is working to characterize the liquid penetration in vaporizing diesel sprays. The work is part of the Engine Combustion Network, which is performing comparative experiments in different high-temperature spray chambers applicable to engines, including those at CMT and Sandia.

Stewart Cant, visiting professor with Jackie Chen

Professor Stewart Cant, a long-term collaborator with the CRF, is visiting for three weeks this summer to work on analysis of our turbulent premixed flame direct numerical simulation data and *a priori* evaluation of flame surface density models for large-eddy simulation.

Katie Gabet, PhD student with Rob Barlow

Katie Gabet, a PhD student at Ohio State University, is working under Prof. Jeff Sutton to develop a Raman/Rayleigh scattering system for turbulent combustion measurements. She was here for one month to learn about our approach, including optical setup, calibration methods, data acquisition strategy, and methods of Raman/Rayleigh data analysis.

Dirk Geyer, visiting professor with Rob Barlow

Dirk Geyer is from Darmstadt, Germany, where he is a Professor at Hochschule Darmstadt and also collaborates closely with the combustion group of Prof. Andreas Dreizler at the Technical University of Darmstadt. Dirk's visit is part of a long-running collaboration between Sandia and TU Darmstadt directed at developing and applying state-of-the-art methods for multiscalar measurements in turbulent hydrocarbon flames.

Tang-Wei Kuo, liason from General Motors

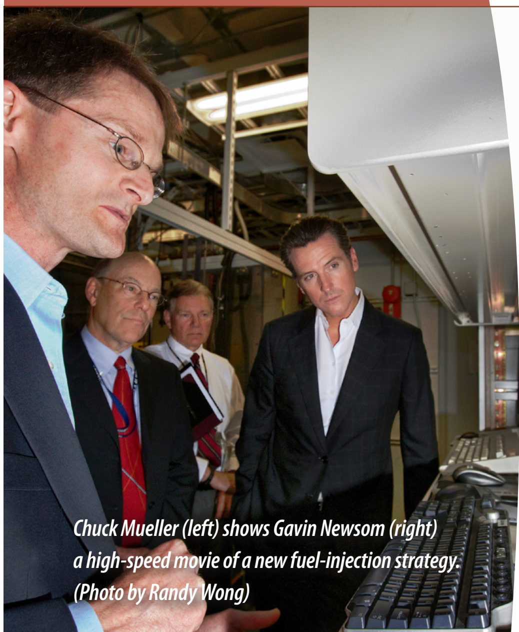
One year ago, GM and Sandia National Laboratories initiated a Strategic Alliance to strengthen mutual collaboration. To ensure close cooperation, a liaison position was created in which one person from GM was assigned to Sandia and one person from Sandia assigned to General Motors. Tang-Wei Kuo, thermosciences group manager in the Propulsion Systems Research Lab at GM, served as the GM liason, working primarily in the CRF.

Ajith Mascarenhas, post-doc with Jackie Chen

Ajith has been working on topological feature extraction and tracking methods applied to turbulent combustion. He worked closely with Gaurav Bansal to identify accurate low-dimensional manifolds (LDMs) embedded in high-dimensional (in phase space) turbulent combustion data using a novel technique based on Isomap. Isomap is a technique for dimensionality reduction that employs a distance metric locally to infer the underlying manifold of a dataset globally. Isomap can discover low-dimensional manifolds that may be nonlinearly embedded. Post-CRF, Ajith will be joining Google as software engineer in the Search Quality team.

Photos by Daniel Strong

CRF proves to be a popular destination



Chuck Mueller (left) shows Gavin Newsom (right) a high-speed movie of a new fuel-injection strategy. (Photo by Randy Wong)

This summer has been a busy one for staff members hosting graduate and undergraduate students, interns, and a myriad of visitors...

Government officials tour Sandia California

The On June 29, Gavin Newsom, Lieutenant Governor of California, visited Sandia to learn about current and emerging energy research at the site. Hosted by Vice President Rick Stulen, Newsom learned about Sandia's advanced modeling and simulation capabilities, research into advanced engine design, cybersecurity work, and the site's economic impact on the State of California. California State Assembly member Joan Buchanan visited the California site on July 18. Ms. Buchanan, who represents the 15th District including the Sandia California site, chairs the Select Committee on Innovation and the Bay Area Economy. And on July 28, 12 members of the Navajo Nation Energy Advisory Committee, including Ben Shelly, president of the Navajo nation, paid Sandia a visit in conjunction with the West Coast Regional Carbon Sequestration Partnership (WESTCARB). WESTCARB is a collaborative research project bringing together dedicated scientists and engineers from more than 90 public agencies, private companies, and nonprofits to identify and validate the best regional opportunities for keeping CO_2 out of the atmosphere.

Sandia's Summer Institute: technology and policy tools for energy in an uncertain world

On August 8, Sandia launched a new cross-discipline week-long research program for top graduate students from the nation's premier universities. At the Sandia Summer Institute (SSI), twenty-one enthusiastic graduate students met to collaborate in small teams, working side-by-side with leading scientists from Sandia to solve challenging problems in a fast-paced, collegial work environment. The Institute addresses technical topics of national interest through hands-on projects using world-class facilities and is led by top scientists and engineers. It also offers networking opportunities with the best and brightest scientists and students in the nation. For more information on the SSI, see ***http://www.sandia.gov/summer_institute/.***

Future Physics Study Tour welcomed

Each year, the Vereniging voor Technische Physica (VvTP), the student association for Applied Physics students at Delft University of Technology in the Netherlands, organizes an extended tour of top universities, high-technology multinationals and start-ups, and world-renowned research facilities. As part of this year's tour, 29 undergraduate students and two professors visited the CRF on July 21. The group was first welcomed by David Chandler. The students broke into smaller groups for CRF laboratory tours and then reconvened for a briefing on Coal and Biomass Utilization. Magnus Sjoberg, Nils Hansen, Judit Zador, and Isaac Ekoto gave informational talks in each of their respective laboratories.

Student interns return to the CRF

The Summer Technical Student Internship Program at Sandia National Laboratories provides opportunities for undergraduate and graduate students majoring in science, math, engineering, and other technical fields to integrate their academic program with work-related experience during their summer break. The CRF offers students training and practical work experience in the operation of state-of-the-art equipment and instruments. Interns work under the direction of a mentor, in a variety of technical and business disciplines. This summer's interns include (left to right) Romina Rodiguez, Nathan Greco, Daniel Nilson, Cassandra Janakos, Alexander Lloyd, Calvin Ball, Mari Sanchez, and Matthew Morabito (not pictured).

Information on Sandia National Laboratories' intern program can be found at ***http://sandia.gov/careers/stu-interns.html***

Scrambling molecules with light (Continued from page 1)

formyl C–H bond (Heazlewood et al., "Near-threshold H/D exchange in CD_3CHO photodissociation," *Nature Chemistry*, 23 May 2011, http://www.nature.com/nchem/journal/v3/n6/full/nchem.1052.html).

In this study, the research team first replaced three of the hydrogen atoms in acetaldehyde molecules with their heavier isotope, deuterium. They then applied laser light with energies slightly higher than that needed to break the chemical bonds (called the threshold energy), and made the surprising discovery that the deuterium atoms were scrambled throughout the molecule despite the relatively meager amount of energy supplied. Comparisons with chemical models have provided an explanation of how this scrambling happens.

Why study reaction pathways near their threshold?

As the energy available to a chemical reaction is reduced, the number of reaction pathways open to the energetic molecule also reduces. In principle, interpreting the reaction outcome should also become simpler. However, as the chaff of multiple high-energy pathways is removed, careful investigation can reveal details about chemical mechanisms and pathways that either were not suspected or were hidden previously. An analogy can be made to a waterfall: when the water flow is high, underlying structures of the cliff face behind the fall can be very difficult to discern. However, as the flow of water slows to a trickle, a detailed study of the cliff can be undertaken. Likewise with chemical reactions—at energies near threshold, the forces that control the breaking of chemical bonds and the formation of new bonds can be studied in much more detail than is possible at higher energies.

> *"The photo-excitation wavelengths employed in this study are characteristic of those from the solar spectrum that reach the troposphere—raising the specter that the present findings may have implications for atmospheric chemistry models."*
>
> *(M. Ashfold and D. Glowacki, "Photochemistry: Scrambled by the sun?" Nature Chemistry, 23 May 2011, **http://www.nature.com/nchem/journal/v3/n6/full/nchem.1058.html**)*

Photo-excitation experiments reveal unexpected complexity

Once the torrent of acetaldehyde reaction pathways was reduced to a metaphorical trickle and studied, several fascinating phenomena were observed. The team studied acetaldehyde-d_3 (CD_3CHO) molecules in which all the hydrogens of the methyl group were substituted with deuterium atoms. The expected photochemical products of this reaction were the simple cleavage of the carbon–carbon bond, which forms CD_3 + HCO. However, the experiments showed that up to 17% of the radical products underwent H/D-exchange to yield CD_2H + DCO.

One can envision simple pathways to exchange a D atom from the left side of the molecule with an H atom from the right side. However, calculations showed that none of these simple routes were energetically feasible. Further calculations suggested that a more complicated (but lower-energy) pathway, depicted in Figure 1, could explain the results. The degree of scrambling, quantified by the percentage of the unexpected DCO product produced, was the key observation from the experiments that this calculation reproduced. The calculations further showed that the H/D exchange involved at least four and, on average, up to 20 isomerizations, statistically breaking every CH/CD bond in the molecule en route. The "simple" dissociation of CH_3CHO into CH_3 + HCO is in fact not simple at all, but was simply obscured because all the hydrogen atoms are indistinguishable in the normal (unlabeled) version of acetaldehyde.

Scrambled by the sun?

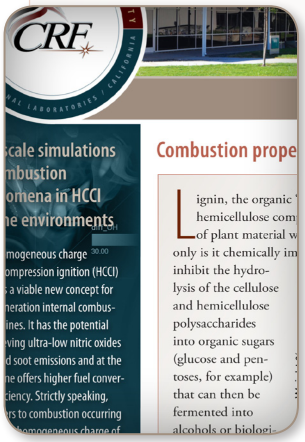
The fact that complete isotopic scrambling could occur at such low energies could complicate the interpretation of isotope-labeling experiments. In addition, this research implies that new pathways for the degradation of acetaldehyde in the earth's atmosphere, where it is a key species in long-range transport of pollution, should be considered. The first intermediate formed in the scrambling reaction, vinyl alcohol, is an isomer of acetaldehyde (as shown in Figure 1). Based on the scrambling experiments, the team predicted that acetaldehyde, absorbing ultraviolet radiation from the sun, will convert to vinyl alcohol. Vinyl alcohol, on the other hand, does not absorb sunlight, which eliminates the possibility that sunlight will convert it back to acetaldehyde. What is the fate of vinyl alcohol in the atmosphere? The answer is not known. Atmospheric models do not currently include this class of compounds, known as enols, just as combustion models did not contain enols until CRF researchers discovered them in flames several years ago. (See "CRF scientists discover new combustion intermediates in hydrocarbon flames," *CRF News*, July/August 2005.)

Caribbean Picnic

On August 4, the CRF and Transportation Energy Center hosted a Caribbean-themed intern and team celebration. This annual event, which highlights the Student Intern Program, brings together Center employees, interns, contractors, visitors, and their families at a local park for some non-work-related fun and food.

This year's event was held at Robert Livermore Community Center, with dinner catered once again by Cabana Dave's. Guests made good use of the water balloons, Frisbees, pools, athletic fields, and volleyball courts. The onsite water slide proved to be especially popular with younger researchers studying the acceleration of a gravity-driven projectile traveling along a near-frictionless ramp into a chaotic fluid environment. After a suitable drying-off time, the results of these experiments will be submitted for publication in a peer-reviewed journal.

Announcing the launch of *CRF News* 2.0



After nearly 32 years of publication history, the CRF News will be moving to a new, interactive, online publishing format this fall. While this bi-monthly newsletter will no longer be printed and mailed to subscribers after the July/August issue, continually updated news, stories, technical articles, and information will be available at the CRF website: ***https://share.sandia.gov/crf/.***

If you would like to receive occasional news and updates from the CRF, please send an email with the subject: **CRF News** to ***crfnews@sandia.gov*** to be included in our confidential subscriber database. We hope that the *CRF News* has been a good source of information and thought-provoking technical articles on a variety of subjects. Our new web-based format will be be a convenient and easy-to-use way to keep up with the latest goings-on at the CRF. Thank you for your support over the years!

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CRF News is a bimonthly publication of the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.
ISSN 1548-4300

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Subscriptions are free. Subscriptions and address changes to crfnews@sandia.gov

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.