

# Western Spectroscopy Association Conference

The Western Spectroscopy Association hosted its 50th annual conference January 29-31, 2003 at Asilomar in Pacific Grove, California. Over 180 researchers attended the conference, which featured lectures by seven eminent scientists including two Nobel Laureates. A poster session with 90 posters covered a diverse range of topics within spectroscopy, including elementary gas phase reactions, microscopy of living cells, and decomposition of liquids on metal surfaces. Sandian David Osborn, who serves as the Secretary of the Western Spectroscopy Association, organized the event with the help of Susan Battles (Sandia) and Professor Geraldine Richmond (University of Oregon). Craig Taatjes (Sandia) serves on the executive committee of the Western Spectroscopy Association. Below is a picture of a lecture at the Asilomar chapel.



*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000*

Sandia National Laboratories  
 Mail Stop 9056  
 P.O. Box 969  
 Livermore, California 94551-0969  
<http://www.ca.sandia.gov/CRF/>

TEMP - RETURN SERVICE REQUESTED



RESORTED  
 FIRST CLASS  
 U.S. POSTAGE  
 PAID  
 MODESTO, CA  
 PERMIT NO. 16



# Combustion Research Facility NEWS

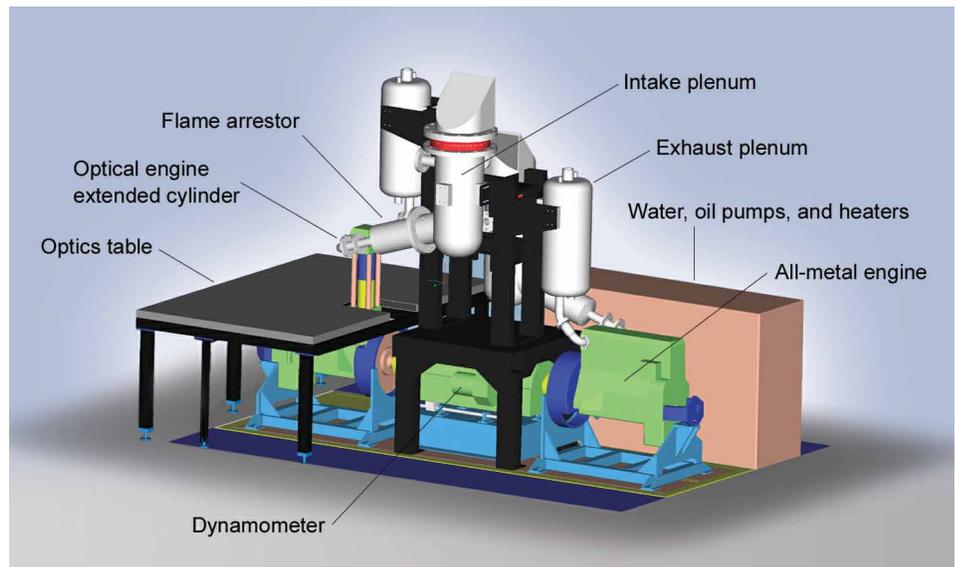


## Understanding Homogeneous Charge Compression Ignition Engine Combustion

Homogeneous Charge Compression Ignition (HCCI) is an alternative piston-engine combustion process that can provide diesel-like efficiencies, while producing ultra-low  $\text{NO}_x$  and particulate emissions. Because of the potential of this technique, automotive and diesel engine manufacturers worldwide are interested in developing these engines. However, several technical barriers, such as controlling ignition timing, reducing unburned hydrocarbon (HC) and carbon monoxide (CO) emissions, extending operation to higher loads, and maintaining combustion stability through rapid transients, must be overcome before HCCI engines will be practical for widespread application.

A new HCCI engine combustion laboratory has been built at the CRF to help develop the fundamental understanding needed to overcome these technical barriers. Research in this laboratory is being conducted in close cooperation with both the automotive and heavy-duty diesel industries. The new laboratory includes an optically accessible engine for the application of advanced laser diagnostics to in-cylinder processes, as well as a matching, all-metal HCCI engine used to establish operating points, investigate various fueling and control strategies, and measure emissions. Figure 1 shows a schematic of the facility.

John Dec and Magnus Sjöberg have used the all-metal engine to investigate the source of CO and HC emissions during HCCI combustion. The graph in Figure 2 shows how the distribution of fuel carbon among the exhaust species varies as fuel loading is reduced from a moderate load (equivalence ratio  $\phi = 0.26$ ) down to fueling rates below those used for idle ( $\phi < 0.1$ ). Note that in an HCCI engine, the premixed charge reacts and burns volumetrically throughout the



**Figure 1.** Schematic of the new HCCI Engine Laboratory. The lab includes an optically accessible engine for use with advanced laser diagnostics, and a matching all-metal engine used to establish operating points, investigate various fueling and control strategies, and measure emissions. The six-cylinder engines have been converted to balanced, single-cylinder HCCI operation.

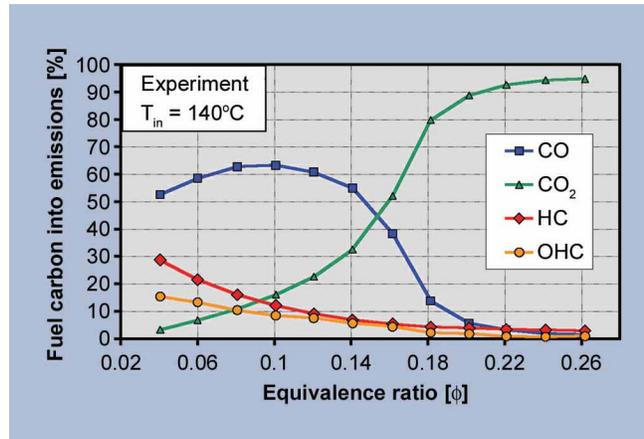
cylinder as it is compressed by the piston. This allows combustion of much leaner mixtures than can be burned by flame propagation as in a conventional engine, and it is the reason for many of the advantages of HCCI.

At the higher loads in Figure 2, more than 90% of the fuel carbon is completely oxidized to  $\text{CO}_2$ , and emissions of HC and CO are low. The piston in the Sandia all-metal engine has been designed to minimize crevice volumes, and the small piston ring-land crevice accounts for most of the emissions at these higher loads. However, as the fueling is reduced below  $\phi = 0.2$ , the CO emissions begin to rise rapidly followed by a more moderate increase in HC and partially oxygenated hydrocarbon (OHC) emissions. As a result, the combustion efficiency drops from 95% for  $\phi = 0.26$  to only 51% for  $\phi = 0.1$ .

To understand the reason for this reduction in combustion efficiency, the experimental data were compared with single-zone kinetic-rate modeling results, obtained using the Senkin application of CHEMKIN and the kinetic mechanism for iso-octane from Lawrence Livermore National Laboratory (LLNL). This analysis showed that the rise in CO emissions was due to incomplete combustion throughout the bulk gases. This occurs because the mixture is so lean that combustion temperatures are insufficient for completion of the CO-to- $\text{CO}_2$  reactions before expansion. Additional analysis indicated that HC and OHC emissions first begin to increase due to unburned fuel in boundary layer regions, followed by an additional increase due to incomplete bulk-gas reactions at lower loads.

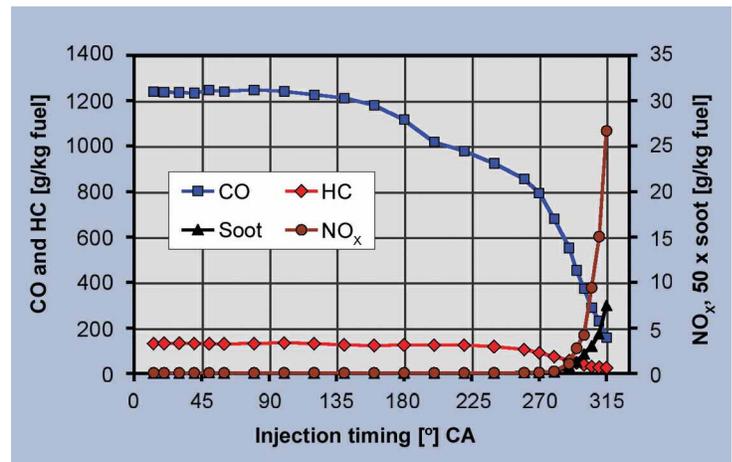
Based on this understanding, John and Magnus concluded that it should be possible to improve low-load combustion efficiency by stratifying the charge so that the fuel is more concentrated in the center of the chamber. This should reduce the amount of fuel reaching the piston ring-land crevice and raise the local equivalence ratio in the center of the chamber, increasing combustion temperatures.

To test this idea, John and Magnus used a direct gasoline injector, and injected the fuel progressively later in the engine cycle to allow less time for mixing before combustion. As shown in Figure 3, CO emissions begin to fall as injection timing is retarded beyond 140°. Beyond 260°, the decrease in CO becomes more rapid, and HC emissions fall as well. These emissions continue to decrease as the injection timing is further retarded. Eventually, the charge becomes so stratified that NO<sub>x</sub> and smoke emissions begin to arise, but a substantial improvement in combustion and emissions is realized before they become significant. For example, an injection timing of 290° increases combustion efficiency from 51% to 78% with very low NO<sub>x</sub> emissions of only 1 g/kg fuel. Even greater improvements are likely with further optimization of the fuel injection and mixing processes.



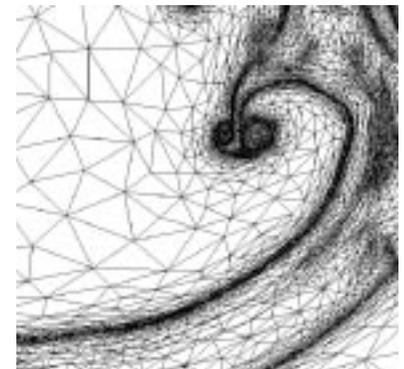
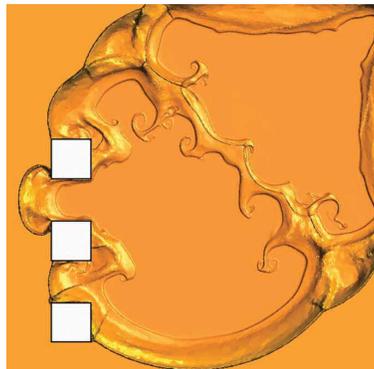
**Figure 2.** Emissions as a function of fuel loading. The fuel is iso-octane which has been shown to be a good surrogate for gasoline. Operating conditions are as follows: 1200 rpm;  $P_{in} = 120$  kPa;  $T_{in}$  was set to 140°C so that the 50% burn point occurred at TDC for  $\phi = 0.14$ . Carbon fractions for the exhaust species were computed for mole fraction measurements, obtained using standard exhaust-gas analysis instruments.

**Figure 3.** The effect of varying the injection timing for  $\phi = 0.1$  on the emissions. Operating conditions are as follows: 1200 rpm;  $P_{in} = 120$  kPa;  $T_{in} = 142$ °C. 0° CA is the start of the intake stroke.



## Meshing Workshop Held at the CRF

The Mesh Quality and Dynamic Meshing Workshop, organized by Philippe Pébay, was held at the CRF January 16-17, 2003. Sandians Habib Najm, Philippe Pébay, Kevin Long, and Patrick M. Knupp were among the ten speakers who covered a wide range of meshing topics. For more information and links to the papers presented, visit the Meshing Workshop website at [www.ca.sandia.gov/CRF/mqdm](http://www.ca.sandia.gov/CRF/mqdm)



Numerical simulation of a two-point Sedov blast-wave problem in 2-D (left) coupled with an adaptive mesh refinement and coarsening algorithm (right). The adaptive mesh refinement can improve the accuracy of the numerical scheme by several orders of magnitude.

## Engine Combustion Reviews Held at Sandia/CA

Sandia hosted the CRADA and HCCI Engine DOE Office of FreedomCAR and Vehicle Technologies Working Group Meetings on January 26-28, 2003. Meetings are held twice annually to discuss recent research results. The meetings were attended by more than 50 researchers from the engine manufacturing industry, universities, and national labs.

## Modeling the Physical Processes that Control Laser-Induced Incandescence from Soot

Growing concerns about adverse health and environmental effects of small particles has prompted strict regulations of fine particulate emissions and has intensified research on the formation and impact of combustion-generated particles. This research, however, is hindered by a lack of sensitive, accurate, noninvasive measurements of the physical characteristics of particles.

Laser-induced incandescence (LII)—a technique that involves heating particles with a laser and measuring the resulting blackbody emission—has been used extensively to make qualitative observations of temporal and spatial soot distributions in engines, engine exhaust, and flames. Recent studies indicate that LII can also be used to determine soot volume fraction and primary particle size quantitatively. Such quantitative measurements of volume fraction generally require accurate calibrations, whereas quantitative particle size measurements rely heavily on models of particle cooling rates. The results appear to be extremely sensitive to measurement conditions (e.g., ambient temperature and pressure, particle com-

position and morphology, laser beam spatial profile), and the general applicability of the technique has not been demonstrated conclusively. Primary particle sizing also depends on the accuracy of LII models, which exhibit significant discrepancies with experimental data.

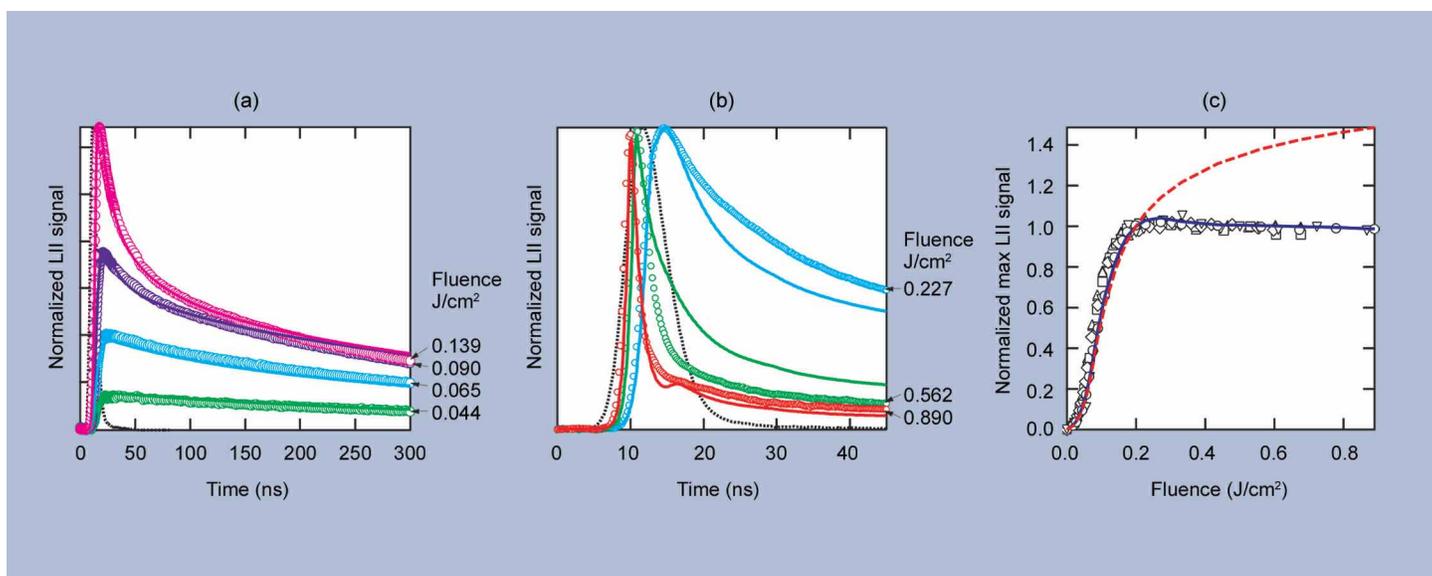
Hope Michelsen of Sandia has developed a model of the temporal response of LII to pulsed excitation to aid in assessing the applicability of LII for quantitative volume fraction measurements under a wide range of conditions. The most substantial advances in the new model over previous models are the inclusion of temperature-dependent thermodynamic parameters for calculating sublimation, conduction, and internal energy storage; wavelength-dependent optical parameters to describe absorption and emission; a thermal accommodation coefficient that is more appropriate for high-temperature conductive cooling; the introduction of a nonthermal photodesorption mechanism for evaporative heat and mass loss; and the influence of annealing (transformation of soot particles to a phase with a

more ordered microstructure) on absorption, emission, and sublimation.

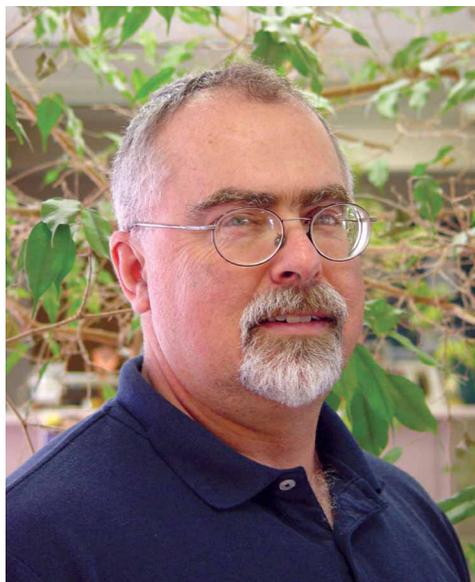
In collaboration with Peter Witze of Sandia, Simone Hochgreb of the University of Cambridge, and David Kayes, a former Sandia postdoctoral researcher, Hope has compared this model with measurements made in a laminar ethene diffusion flame over a range of laser fluences.

Representative results are shown for low fluences in Figure 1(a) and for moderate and high fluences in Figure 1(b).

The new model reproduces the shapes of the temporal profiles significantly better than previous models. At low fluences, better agreement is attributable to the estimated reduction in the emissivity of the particles with annealing and a more appropriate thermal accommodation coefficient. At intermediate fluences, annealing reduces the sublimation rate and leads to a slower decay rate, which is too fast when thermodynamic properties for graphite are assumed. At high fluences, the photodesorption mechanism for heat and mass loss allows the model to reproduce the fast decay during the laser pulse. This mechanism also allows the model to reproduce the fluence dependence of the magnitude of the signal, as shown in Figure 1(c).



**Figure 1.** Comparisons of model results with measured LII temporal profiles at low fluence (a) and moderate and high fluences (b). Profiles are shown for selected fluences. Measurements are represented by circles, and model results by lines. The dotted line shows the measured laser temporal profile. (c) Fluence dependence of the magnitude of the peak LII signal. Experimental results (symbols) are compared with model results including (solid blue line) and excluding (dashed red line) the photodesorption mechanism for energy and mass loss. Each data set is normalized to one at  $-0.5 \text{ J/cm}^2$ ; the model results are scaled to the mean experimental value at  $0.2 \text{ J/cm}^2$



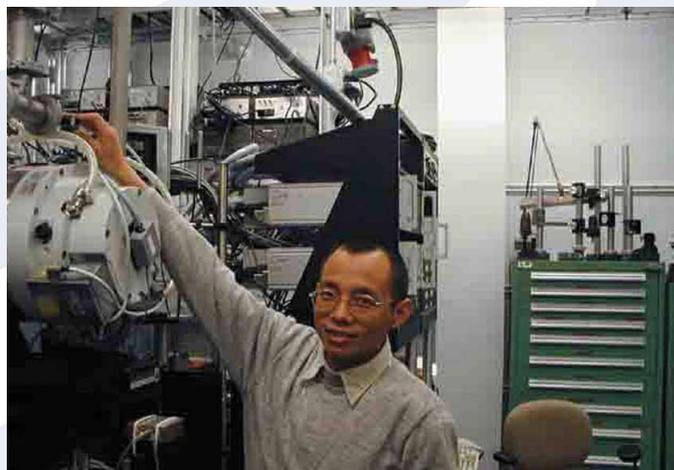
## People People

### Dave Chandler Returns from Research Leave

Dave Chandler recently returned from the University of Leiden in the Netherlands, where he spent six months working with Professor Thomas Schmidt. While at Leiden, Dave worked on the use of single-molecule fluorescence resonance energy transfer (FRET) to study messenger-RNA folding. Wide-field fluorescence microscopy was utilized for imaging the FRET processes.

### Fei Qi Completes His Postdoctoral Appointment at the CRF

Fei Qi has completed his postdoctoral appointment with Andy McIlroy in the Flame Chemistry and Diagnostics Laboratory. Fei was instrumental in building the new low-pressure-flame sampling molecular beam mass spectrometer using single photon ionization at the Lawrence Berkeley National Laboratory (LBNL) Advanced Light Source (ALS) as part of a collaboration between LBNL, Sandia, Cornell University, and the University of Massachusetts, Amherst. At Sandia and the ALS, Fei studied the molecular weight growth chemistry in 1,3-butadiene doped hydrogen/oxygen/argon flames as well as ethylene and benzene combustion.



### Will and Michelle Medlin Leave the CRF



Will and Michelle Medlin left the CRF in December 2002. Will completed his stay as a postdoctoral associate working with Mark Allendorf on heterogeneous catalysis and with Tony McDaniel and Bob Bastasz on sensors for gas analysis. Michelle created and managed Mark Allendorf's website, Thermochemical Databases and Models for High-Temperature Materials Processing, Combustion, and Corrosion. Will has taken a position as an Assistant Professor of Chemical Engineering at the University of Colorado, and Michelle will continue her job as web manager from their new home in Boulder, Colorado.

The CRF News is Published bimonthly by the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.

**Director:** William J. McLean, Mail Stop 9054

**Editor:** Jessica Matto, Email: [jmatto@sandia.gov](mailto:jmatto@sandia.gov)

**Graphic Artist:** Daniel Strong

## Numerical Simulation Reveals the Effect of Product Enrichment on Chemical Response of Premixed Flames

In practical combustors, turbulent premixed flames may undergo enough intense stretching and wrinkling to create disruptions in the flame front, particularly in regions that are highly curved towards the reactants. In these regions, chemically crucial radical species like H atom are defocused until their concentration is too low to consume fuel locally. Consequently, hot product gases may diffuse through breaks in the flame front, mix with fresh reactants, and return to the flame. Additionally, large-scale unsteady fluid motions may re-circulate hot products back to the flame sheet. Models thus far do not account for the flame response to product gas enrichment.

Jackie Chen and Shiling Liu have been studying the premixed flame response to product enrichment using direct numerical simulation (DNS) with detailed methane/air chemistry provided by GRI-mech 3.0. They have studied a model problem in which a freely propagating premixed flame is perturbed upstream by a mixture of hot products and reactants. Product/flame interactions were studied for premixtures of nitrogen-diluted methane/air spanning fuel-lean to fuel-rich conditions.

Numerical simulations of a flame/vortex interaction were performed to study the chemical response of a diluted premixed methane/air flame to hot product enrichment. The simulation results show that the flame response depends upon the competition between transport of heat to the preheat zone of the flame (inert convective-diffusive layer ahead of the reaction zone) and mixing of the upstream products and reactants. If mixing rates are sufficiently fast compared to the time required for the preheat temperature to increase significantly, then the flame response to the product perturbation is minimal. On the other hand, if heat conduction from the flame and the upstream product perturbation is fast relative to mixing-time scales, then the flame response can be significant.

The chemical response of a rich premixed flame to product perturbation by a vortex pair is shown in Figure 1 in terms of its instantaneous OH mass fraction. The corresponding temporal sequence, taken at the

centerline of the vortex/flame interaction (Figure 2), reveals a 12-fold increase in the peak OH mass fraction and a comparable increase in the burning velocity (not shown) over 2 ms. The increase in OH originates on the sides of the flame near the cusps and eventually shifts to the centerline.

The lower value of OH at the centerline early on is due to the competitive effects of strain and diffusion in transporting hot products to the preheat zone. The OH in stoichiometric and lean mixtures does not increase because the diluted rich flame response is much faster, and therefore, competitive with the mixing time scales chosen, whereas the leaner mixtures are not. (Given a long enough residence time of the hot products, the leaner mixtures would eventually also respond). The faster response of the diluted rich flame is due to its broader thermal thickness, and therefore, its higher initial temperature in the preheat zone prior to the product perturbation at a fixed spatial location.

These results may have implications for the design of lean premixed swirl-stabilized combustors, where large residence times exist in the corners near the base of the burner.

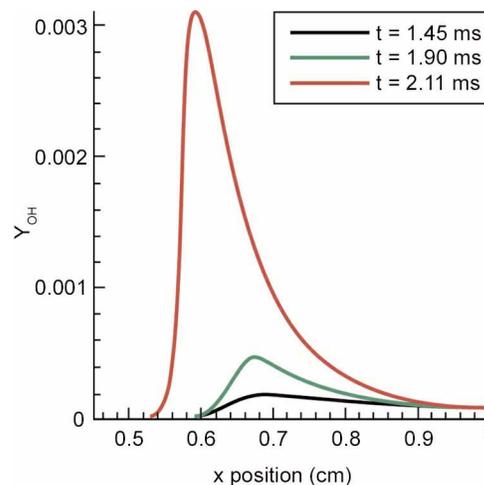


Figure 2. Temporal evolution of OH mass fraction at the centerline of the flame/vortex interaction.

The re-circulation of the heated products there may interact with the lean flame, resulting in a larger radical pool and higher temperature at the base of the burner. While this may help stabilize the flame, it could have a negative impact on NO production locally. Jackie and Shiling are currently extending this study to include the response of pollutants to product enrichment.

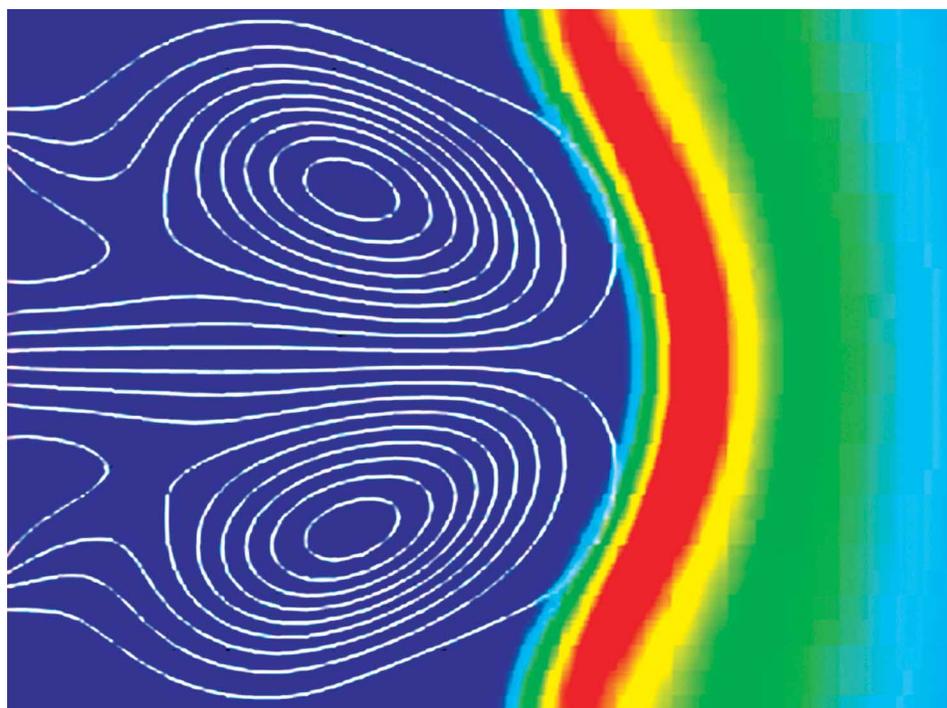


Figure 1. OH mass fraction and vorticity magnitude isocontours for the rich premixed methane/air flame at  $t=1.90$  ms.