Combustion Research Facility News

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Raman probe validates oxidation model in supercritical water

A team composed of Steve Rice, Dick Steeper, Russ Hanush, Tom Hunter, Jason Aiken, and visiting researcher Åsa Rydén (Lund University, Sweden) has been conducting experiments designed to test models of supercritical water oxidation (SCWO) that can illuminate the details of oxidation processes in this dense gaseous reaction environment. This research is supported by the DoD / DOE / EPA Strategic Environmental Research and Development Program (SERDP) to develop engineering design tools for large scale SCWO waste treatment equipment.

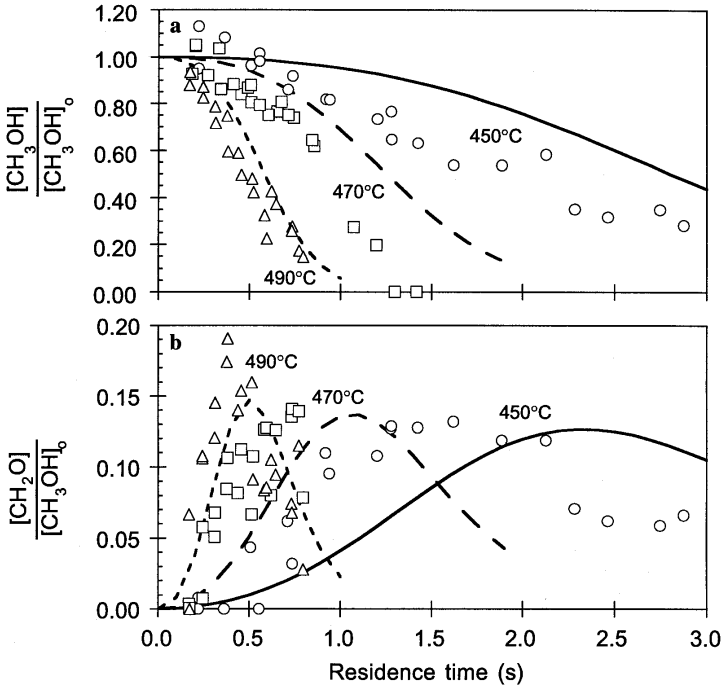
Supercritical water oxidation and related chemical processing applications operating at hydrothermal conditions are rapidly becoming practical technological solutions to industrial waste treatment issues. These technologies are designed to take advantage of rapid aqueous oxidation chemistry that occurs in water at pressures and temperatures above the critical point of water (22.1 MPa and 374°C).

Using Raman spectroscopy to monitor species concentration, recent results from experiments on methanol in the CRF's optically accessible supercritical water flow reactor have mapped the temperature dependence of the oxidation of methanol and the production of a key reaction intermediate, formaldehyde, at 24.1 MPa and 440 to 500°C.

The results of these quantitative measurements of formaldehyde and methanol are presented in the figure along with the predictions of an elementary reaction mechanism developed by Bill Pitz of Lawrence Livermore National Laboratory. The model, containing no adjustable parameters, reproduces experimental results for both species far better than do previous elementary reaction mechanisms, which typically underpredict reaction rates by nearly a factor of ten. The model uses Chemkin Real Gas, a modification of Chemkin II developed by Nina French and Barry Butler (University of Iowa), which treats mixtures of nonideal gases.

The detailed measurements reveal a temperature-dependent induction period characterizing the consumption of approximately 10% of the feed followed by reaction of the majority of the feed at an accelerated rate. During the peak of the oxidation rate, an appreciable concentration of formaldehyde is seen to be present. The elementary model accurately represents these features of the oxidation process. The model indicates that the length of the induction period in supercritical water is controlled by the rate of hydrogen abstraction reactions, but that the oxidation rate of the majority of the methanol, once the reaction is past the induction phase, is dominated by the dissociation rate of hydrogen peroxide.

These results, and those from similar research on the analogous system of isopropanol and acetone, are currently being used in separate engineering projects at Sandia for the design of full-scale reactors.



The observed fraction of methanol remaining as a function of time and the observed fraction of initial feed methanol present as formaldehyde accompanied by the predictions from the elementary reaction model (curves).

Methyl radicals detected in a flat flame using DFWM

Visiting researcher Volker Sick (University of Heidelberg) and Roger Farrow have demonstrated spatially precise detection of methyl (CH_3) by degenerate four-wave mixing (DFWM). DFWM is a coherent nonlinear spectroscopy that uses three incident laser beams to generate a fourth signal beam, with the measurement volume defined by the spatial overlap of the crossed laser beams.

Methyl is an important intermediate species in hydrocarbon combustion and in some types of chemical vapor deposition (*e.g.*, diamond-film growth). Because of strong predissociation in the electronic *B* state, purely optical methods for detecting trace amounts of CH_3 have been limited to absorption spectroscopy, a line-of-sight measurement.

Volker and Roger used a frequency-tripled tunable dye laser to excite the Herzberg β_1 band of CH_3 near 217 nm. A nearly phase-conjugate geometry was employed for the DFWM measurements. Each beam had an energy of ~20 μJ/pulse. Absorption measurements were performed with the same setup.

Figure 1 compares absorption spectra (upper curves) with a DFWM spectrum of the CH_3 β_1 band measured in a rich (equivalence ratio $\phi = 1.55$) methane/air flat flame. The absorption spectra are dominated by a sloping background (indicated by the dashed line) corresponding to ≈10% absorption in a 4-cm path length; the two broad features are assigned to the P/Q and R-branches of CH_3, respectively. Nearly indiscernible narrow peaks are assigned to Schumann-Runge lines of O_2. In the DFWM spectrum (lower curve) the two broad CH_3 features are clearly observed along with numerous sharp lines from O_2. The DFWM spectrum is nearly free of the broad background seen in absorption.

Differences in the relative intensities of spectral features between the absorption and the DFWM spectra can be attributed to the factor $(I/I_{sat})^2$ in the DFWM signal equation, where I and I_{sat} are the pump intensity and saturation intensity, respectively. For example, the team measured I_{sat} for the DFWM background to be roughly 50 times greater than that of CH_3 or O_2, explaining the relatively reduced background signal in DFWM compared to absorption. Different values of I_{sat} also explain the reversed DFWM intensities for the two CH_3 peaks compared to absorption.

To investigate the applicability of DFWM for obtaining spatial profiles, the laser frequency was tuned to the CH_3 signal in a region free of O_2 interference (46,185 cm^{-1}), and the signal was recorded as the burner was translated vertically. Subtracting a residual (≈15%) background signal and taking the square root of the result (to account for the quadratic DFWM signal dependence on number density) resulted in the filled circles in Fig. 2. The latter are compared to a CH_3 spatial profile calculated by postdoctoral scientist Mary Bui-Pham. Excellent agreement is observed for the shape and position of the profile. The sensitivity for CH_3 detection by DFWM is estimated to be ≈65 ppm in the current setup.

The results show that DFWM is a promising technique for measuring CH_3 concentrations with high spatial and temporal resolution and high sensitivity, and which can be used close to surfaces. Real-time concentration measurements using a single laser appear feasible provided that the sample temperature is known.

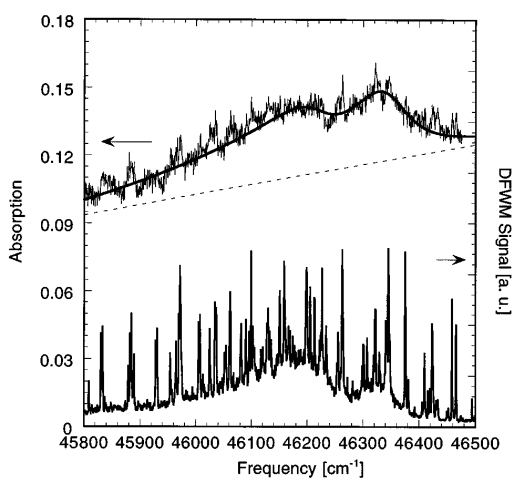


Figure 1. The upper trace shows a single-pass absorption spectrum of CH_3 measured 2.1 mm above the burner surface. A concentration of 650 ppm CH_3 radicals is measured for this flame position. The dashed line indicates a dominating background absorption, which has been added to the simulation of the spectrum (thick solid line). The lower trace shows a DFWM spectrum of CH_3 measured at the same position. The two underlying broad features result from CH_3. The overlapping narrow peaks result from O_2.

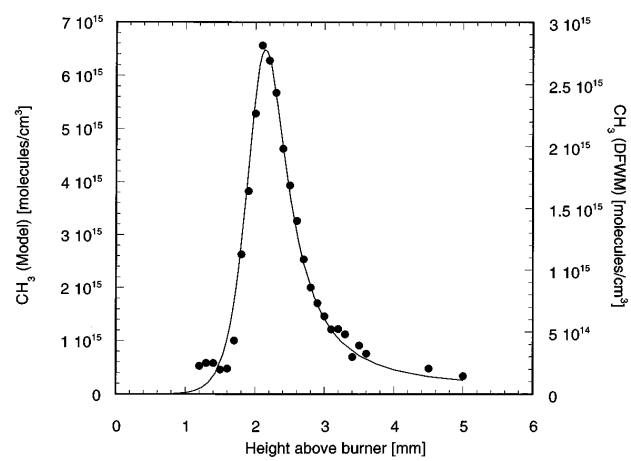


Figure 2. Spatial CH_3 profiles in a laminar methane/air flame at $\phi = 1.55$. The measured profile (dots) was obtained using DFWM, to which a vertical scaling factor was applied for purposes of comparison. Calibrated by absorption measurements, the absolute experimental concentrations were found to be about two times lower than the calculations, a difference within experimental and theoretical uncertainties.

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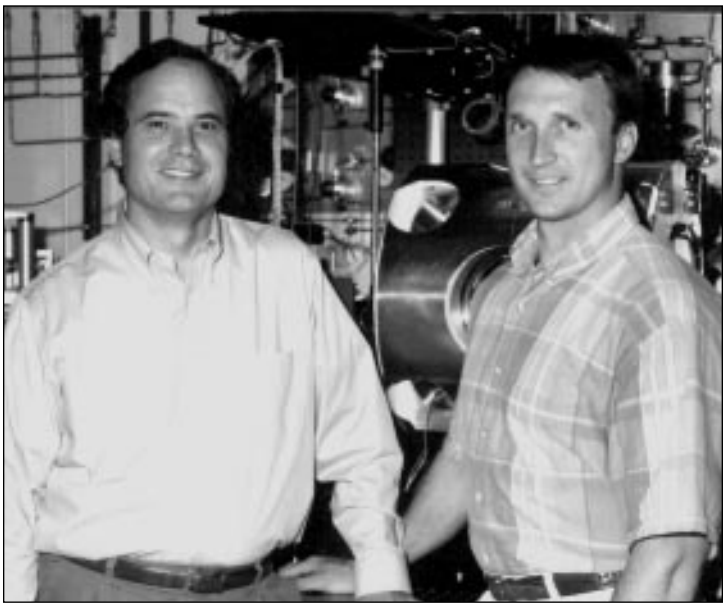
Adams and Bastress Awards presented

David Rakestraw (right) received the O. W. Adams Award for 1995 during an informal ceremony in February. The citation read, in part, "for making the CRF the paradigm for government-sponsored 'user' facilities." Dave has been a leader in the development and use of laser-based diagnostics for combustion science. His major contribution has been the extension of degenerate four-wave mixing spectroscopy to the remote detection of trace chemical species. Dave has also helped employ the laser expertise developed at the CRF in applications to analytical chemistry by coupling laser spectroscopy with advanced separation techniques.

At the same ceremony, Donald Hardesty (left) was presented the E. K. Bastress Award. Don was selected for his "significant contribution to a strong and effective coupling of combustion research programs to the needs of United States industries." Don has provided outstanding leadership and technical contributions to achieve an effective coupling between DOE research capabilities and industrial needs. Don's contributions have ranged over a broad spectrum of scientific/industrial collaboration. His work with the coal industry, specifically, and most recently with the nascent biomass industry provides clear examples of his major contributions.

Postdoc completes investigations

Jeff Naber (right) recently completed a postdoctoral fellowship, working with Dennis Siebers (left). Jeff carried out several experimental studies of diesel combustion processes, including investigations of natural gas and hydrogen combustion under diesel conditions and the effects of high in-cylinder pressures on diesel combustion. He is currently employed by Motorola Corporation, Dearborn, MI.



AISI project review held

The CRF recently hosted the second annual review of Sandia's project with the American Iron and Steel Institute (AISI) on the development of optical sensors and controls for improved operation of basic oxygen furnaces (BOF) used in steelmaking. The project aims to develop a suite of optical sensors for on-line, real-time measurement of gaseous species in the BOF exhaust products as well as properties of the steel melt including temperature, carbon content, trace species, and bath height. The project is jointly sponsored by the AISI and DOE's Office of Industrial Technologies.

In attendance at the meeting were: (seated) Larry Kavanagh (AISI program manager) and George Lee (Rouge Steel); (standing, l to r) Bill Kent, Howard Johnsen, Don Hardesty (project manager), Al Salmi, Lois Johnston, Sarah Allendorf, Phil Stelts (Bethlehem Steel), Dave Ottesen, Beth Fuchs, and Mike Bonin (INSITEC).

Hydrogen investigated as a fuel for a low NO_X DI engine

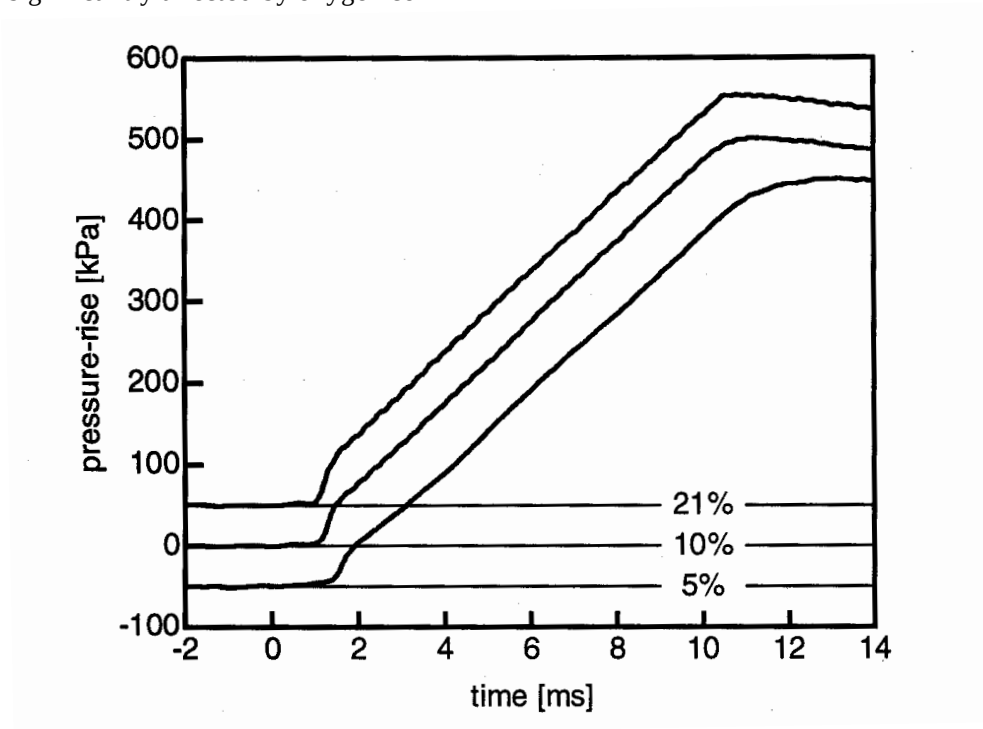
Jeff Naber and Dennis Siebers recently investigated the combustion characteristics of hydrogen under late-cycle, compression-ignited, direct-injection (DI) engine conditions. The measurements were part of Sandia's ongoing program on hydrogen utilization in internal combustion engines.

A major thrust of the program is to develop a low emission, hydrogen fueled engine optimized for use in a hybrid, automotive propulsion system. Direct injection of hydrogen offers potential efficiency, power density, and safety advantages over the more developed premixed hydrogen engine option. Stumbling blocks to the DI approach, however, are NO_X emissions and a poor understanding of gaseous fuel combustion at typical DI engine conditions.

The experimental investigations were performed in a high-pressure combustion facility that permits the study of DI engine combustion processes over a wide range of thermodynamic conditions. The hydrogen was injected with an electronically controlled high-pressure gas fuel injector (35 MPa). Measurements were made of the effects of injection parameters and ambient gas thermodynamic conditions on the ignition and combustion of hydrogen. Emphasis was placed on determining the effects of reduced oxygen concentration on DI hydrogen combustion, since intake charge dilution through exhaust-gas-recirculation (EGR) is a potential method for achieving the same ultra low NO_X emission levels previously noted for lean-burn premixed hydrogen engines (*e.g.*, Van Blarigan and Green, *CRF News* 17:1).

Some of the more important results are shown in the figure, a comparison of the combustion pressure histories for injection of hydrogen into three different ambient gas oxygen concentrations: 5%, 10% and 21%. The figure shows that the rate of combustion (indicated by the rate of pressure-rise) and the ignition delay (indicated by the start of the pressure-rise) are not significantly affected by oxygen concentration. The figure implies that high levels of EGR can be utilized in a DI hydrogen engine without affecting the combustion timing or duration.

Estimates of NO_X production from DI hydrogen combustion in ambient gas with a 10% oxygen concentration and thermodynamic conditions appropriate for compression-ignition indicate that a reduction in NO_X of more than two orders of magnitude can be achieved as a result of the lower combustion temperature at the lower oxygen concentration.



Combustion of hydrogen injected at a pressure of 21 MPa into ambient gas with oxygen concentrations of 5, 10, and 21%. (The 21 and 5% oxygen conditions are offset by 50 kPa for clarity.) The ambient gas density and temperature were 20.5 kg/m^3 and 1100 K, respectively.

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