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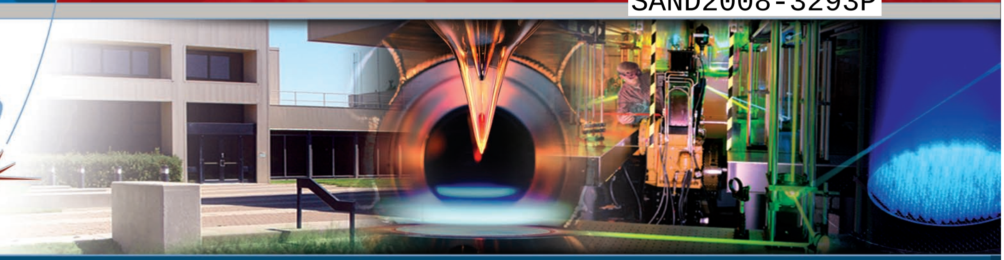
SAND2008-3293P

CRF NEWS



COMBUSTION RESEARCH FACILITY

Nov/Dec 2007 • VOL. 29, NO. 6

Exergy analysis explains the efficiency of H_2 production via steam-methane reforming

In his 2003 State of the Union address, President Bush declared, "With a new national commitment. . . the first car driven by a child born today could be powered by hydrogen and pollution-free." To fulfill this vision, the nation must first find ways to produce and distribute hydrogen.

This is a tall order. Energy companies use steam-methane reforming to produce large quantities of hydrogen for use in the refining process. However, since transporting hydrogen via trucks or pipelines is costly, one alternative is to take advantage of existing natural-gas or electricity infrastructures by producing hydrogen on-site via reforming or electrolysis.

DOE Technology Validation program

Prototype hydrogen stations are being built as a technology validation activity for the Department of

(Continued on page 5)

Spatial distributions of CO and UHC visualized in the cylinder of a light-duty diesel engine

Adoption of diesel engines in passenger cars and light-duty trucks is one path toward reducing consumption of hydrocarbon-based fuels and the concomitant CO2 emissions thought to be contributing to global climate change. However, conventional diesel engine technologies result in elevated emissions of NOx and particulate matter. Low-temperature diesel combustion technologies, employing high levels of recirculated exhaust gas and extensive pre-combustion mixing, have the potential to reduce these pollutant emissions, but can often result in high CO and unburned hydrocarbon (UHC) emissions. In addition to their environmental impact, CO and UHC emissions adversely affect fuel consumption. At the light loads that represent a large fraction of typical passenger car operation, CO and UHC emissions are particularly troublesome—and the low exhaust gas temperatures characteristic of light-load operation impede exhaust gas cleanup by aftertreatment devices. Understanding the mechanisms by which CO and UHC escape in-cylinder oxidation is thus crucial to the design of clean, fuel-efficient, light-duty diesel engines.

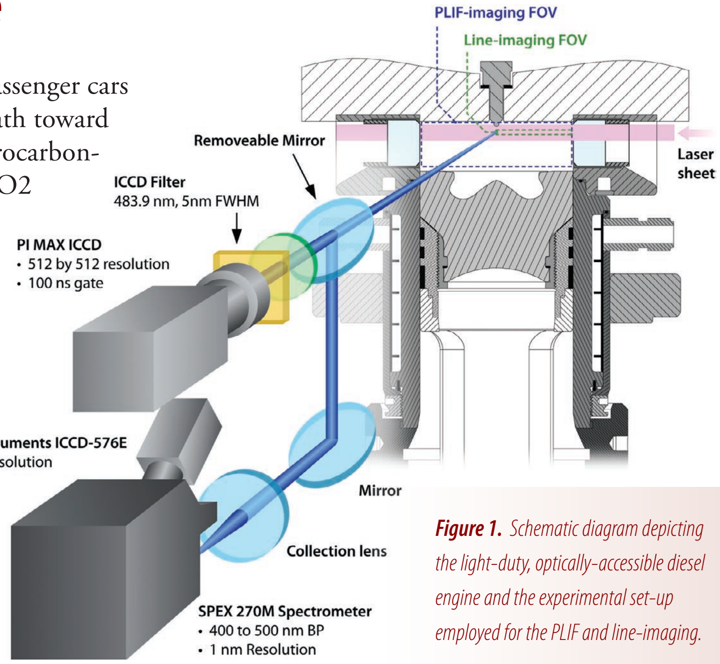


Figure 1. *Schematic diagram depicting the light-duty, optically-accessible diesel engine and the experimental set-up employed for the PLIF and line-imaging.*

(Continued on page 2)

Sandians at CRF and other colleagues remember Jürgen Warnatz

Jürgen Warnatz, Professor, University of Heidelberg, and outstanding leader and pioneering researcher in the field of reactive flows, passed away on December 22, 2007. The cause of death was lung cancer. Dr. Warnatz was a longtime friend and colleague at the CRF.

Robert Kee, former Sandian and now George R. Brown Distinguished Professor, Division of Engineering, Colorado School of Mines, began a long and productive collaboration with Jürgen Warnatz, beginning in 1983. At that time, Bob and Jim Miller were modeling a variety of flames and actively developing the Chemkin software capabilities. The initial versions of Chemkin handled complex chemical kinetics well, but we had not fully generalized the transport properties.

(Continued on page 3)

Sandia National Laboratories

Spactial distributions (cont.)

(Continued from page 1)

To better understand the sources of CO and UHC emissions, visiting researcher Duksang (Andy) Kim of Kookmin University, and CRF researchers Will Colban, Isaac Ekoto, and Paul Miles have measured the in-cylinder spatial distributions of CO and UHC using laser-induced fluorescence (LIF) techniques in an optically-accessible light duty engine, using a combination of planar LIF imaging and spectrally-resolved line-imaging (Fig. 1). They tuned their laser to near 230.1 nm, where a two-photon absorption process excites the B1Σ+ state of CO as well as various UHCs. This technique has been successfully employed in the study of laboratory flames (see CRF News, Vol. 25, No. 6, 2002), but had not been previously applied to diesel engine studies. As shown in Fig. 2, fluorescent emissions are collected in the blue region of the visible spectrum, and have contributions from both CO and from various unburned or partially-burned hydrocarbons—including a dominant broadband background from polycyclic aromatic hydrocarbons (PAHs). By tuning the laser just off the CO absorption line, only the emissions stemming from UHCs are observed. Due to the broadband PAH emissions, the emissions from CO and UHCs cannot, in general, be spectrally separated. An independent, off-line measurement—or spectrally-resolved information like that offered by a line-imaging experiment—is required to separate the distinct contributions from CO and UHC.

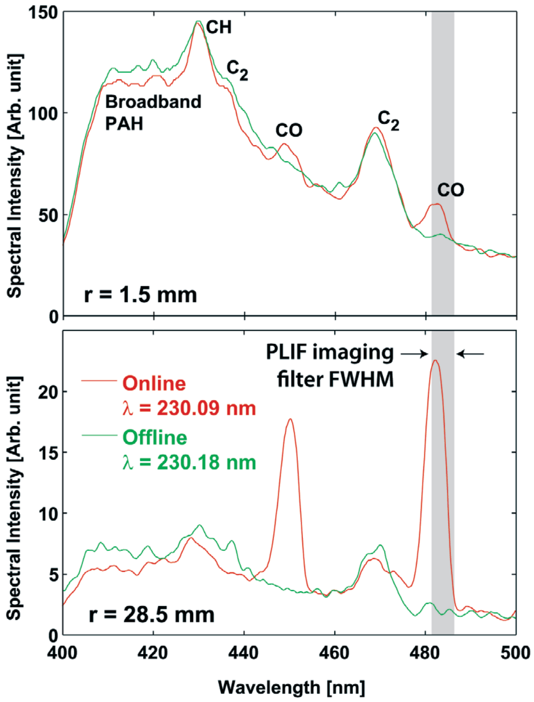


Figure 2. *Spectral characteristics of the fluorescence signal obtained with via line-imaging. The relative magnitude of the CO and UHC signals change significantly with spatial location within the cylinder.*

Examples of planar images of in-cylinder CO and UHC distributions are shown in Fig. 3 for three different injection timings. At the baseline injection timing, CO is observed distributed throughout the squish volume. In contrast, UHC is found only near the cylinder wall, where it emanates from the top ring-land crevice. Although the LIF measurements cannot be quantitatively interpreted as proportional to CO or UHC number density, by examining trends in the signals it is possible to deduce a great deal about the mixture composition and progress of the combustion process. For example, increasing load at the baseline timing results in a decrease in both CO and UHC fluorescence, indicating that the mixture within the squish volume is fuel lean. Thus, the CO observed within squish volume is associated with the slow, final oxidation of CO to CO2—the partial oxidation of UHC has already been completed. Likewise, with advanced injection timing the increase in both CO and UHC seen in Fig.3 can be attributed to formation of fuel rich mixture, and the increased UHC but decreased CO observed with retarded timing is due to the existence of over lean mixtures in which even the initial UHC oxidation process is slow.

UHC is also observed in a second region, near the cylinder centerline, where CO does not appear until later in the cycle. The delayed appearance of CO, the spatial contraction of this region with increased load, and the detection of CH2O in this region all signify that, like similar regions observed in heavy-duty engines (see CRF News, Vol. 29, No. 2, 2007), this UHC stems from fuel lean regions.

Jointly, the measured CO and UHC distributions have led to significant insights into the mixture formation and processes in light-duty engines operating in low temperature combustion regimes. Comparison of these results to multi-dimensional numerical simulations, with the object of improving and validating our ability to model these engines, is in progress.

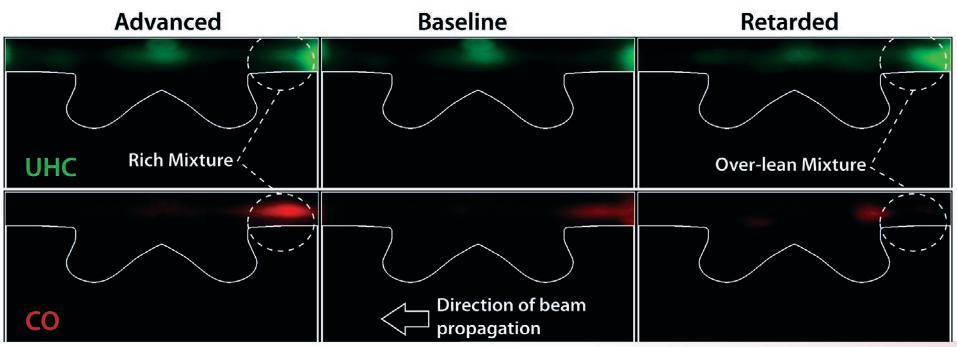
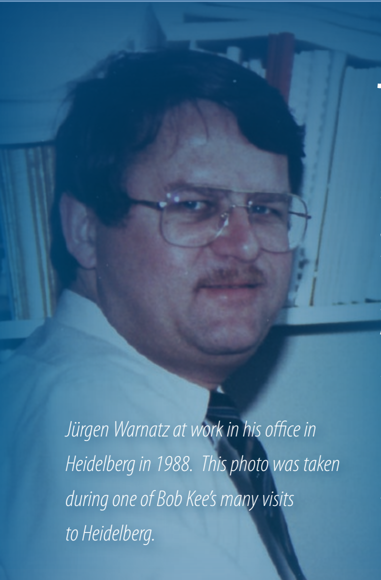


Figure 3. *Cycle-averaged spatial distributions of UHC and CO at 30° aTDC measured at a load of 3 bar indicated mean effective pressure, an engine speed of 1500 rpm, and an intake charge O2 concentration of 10%. Note the strong absorption of the laser beam, which restricts CO imaging to the RHS of the cylinder.*



Jürgen Warnatz at work in his office in Heidelberg in 1988. This photo was taken during one of Bob Kee's many visits to Heidelberg.

Jürgen Warnatz

(Continued from page 1)

In his habilitation thesis, Warnatz had developed theory and software to model transport properties for combustion species. In the Winter of 1983, Bob Kee went to Heidelberg for several weeks to learn more about Warnatz' efforts, and adapt his approaches into the Chemkin framework. The original Chemkin Transport Package was the result of this collaboration. In fact, much of this software is still in production today.

A second significant collaboration concerned early research on catalytic combustion. In 1993, Jürgen spent several months at the CRF working on a project to develop elementary reaction kinetics for heterogeneous combustion chemistry. The result of this effort, considering the hydrogen oxidation on platinum surfaces (Warnatz, Allendorf, Kee, and Coltrin, Combust. and Flame, 85:393-406, 1994), played an important role in developing the modeling approaches that are in wide use today for incorporating elementary chemical kinetics into applications such as catalytic combustion, catalytic converters, catalytic partial oxidation, and hydrocarbon reforming.

It is very appropriate to note Jürgen's enduring influence on the combustion community, through his former students and the strong collaborations established under his guidance. For example, Bob Kee maintains active collaborations with Prof. Olaf Deutschmann (Universität Karlsruhe) on heterogeneous catalysis and fuel cells. We interact regularly on fuel-cell and electrochemistry research with Dr. Wolfgang Bessler (Universität Heidelberg), who was Jürgen's last habilitation student.

Jürgen Warnatz and the International Energy Agency

In the late 1970s, the International Energy Agency (IEA) established a research program focused on efficiency improvements and emissions reductions in combustion systems. Under the leadership of Professor Jürgen Warnatz, Germany joined the program in 1987. Warnatz played an active role in the organization and leadership of the program from the beginning of his involvement, serving three terms as chair and three terms as vice chair of the program's Executive Committee (EXCo), last serving as chair during the 2006-7 program year. He also hosted several of the program's annual Task Leaders Meetings, the most recent in Heidelberg in 2006. In terms of attendance and the number and quality of papers presented, this was one of the most successful meetings in the three decades of the IEA combustion program's existence. Notable accomplishments that year included the successful submission of a request to IEA Headquarters that will carry the program into its fourth decade of combustion research.

For nearly all of its existence Sandia's CRF has served as the Operating Agent for the IEA's Combustion Program. As a result of the close collaborations that Warnatz established with CRF staff during this period, including Bob Gallagher and Jay Keller, he once estimated that he had spent a total of more than two full years in residence at the CRF as a visiting scientist.

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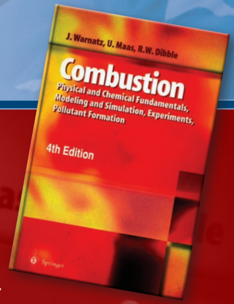

Combustion textbook in 6th edition

This ground breaking combustion textbook by J. Warnatz, U. Maas, and R. W. Dibble is now in its 6th edition

Following is the preface from the 1st edition

This book has evolved from a lecture series (of *J. Wa.*) on combustion at Stuttgart University. The lectures were intended to provide first-year graduate students (and advanced undergraduates) with a basic background in combustion. Such a course was needed since students of combustion arrive with a wide variety of backgrounds, including physics, physical chemistry, mechanical engineering, computer science and mathematics, aerodynamics, and atmospheric science. After a few years of improving printed matter distributed to the students, the lecture notes have been organized into a book, first in German, and later translated and augmented in an English version.

We intend that the book provides a common basis from which research begins. Thus, the treatment of the many topics is compact with much citation to the research literature and presents numerous exercises. Beyond this, the book expects that combustion engineers and researchers will increasingly rely on mathematical modeling and numerical simulation for guidance toward greater understanding, in general, and, specifically, toward producing combustion devices with ever higher efficiencies and with lower pollutant emissions. Spatially homogeneous combustion and laminar flame computer codes and selected sample data to run them are available on the internet at *http://reaflow.iwr.uni-heidelberg.de/software/*.

The actual fourth edition presents a completely restructured book: Mathematical formulae and derivations and the space-consuming reaction mechanisms have been removed from the text to appendices, a new chapter has been added to discuss the impact of combustion processes on the earth atmosphere, the chapter on auto-ignition is moved and has been extended to deal with combustion in Otto and Diesel engines, and the chapters on heterogeneous combustion and on soot formation have been heavily revised. The rest of the chapters is polished and extended to account for recent developments and new results.

Because this book is a research launching point, we expect it to be updated in a timely fashion. For this rerason, we invite the readers to contact our e-mail address (*juergen@warnatz.de*) for additional comments and constructive critical remarks that may be part of the next edition.

Heidelberg, Karlsruhe, Berkeley, in March 2006
J. Warnatz, U. Maas, R. W. Dibble

Visiting researcher leaves the CRF

Alejandro Molina

"Alejandro Molina, a visiting researcher with Chris Shaddix, will be leaving the CRF in February.


SAE

In Recognition of

Wontae Hwang

for Excellence in Oral Presentation

"Fuel Stratification for Low-Load HCCI Combustion: Performance & Fuel-PLIF Measurements"

Powertrain & Fluid Systems Conference and Exhibition
October 29-31, 2007

EMB Chair

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SAE Excellence in Oral Presentation

Wontae Hwang

Wontae Hwang, who won an SAE Excellence in Oral Presentation for his paper "Fuel Stratification for Low-Load HCCI Combustion Performance and Fuel-PLIF Measurements" This paper was presented at the SAE Powertrain & Fluid Systems Conference and Exhibition in Chicago, IL, October 29-31, 2007.


SAE

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Richard Steeper

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"Improving the NO_X-CO_2 Trade-Off of an HCCI Engine Using a Multi-Hole Injector"

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April 16 - 19, 2007

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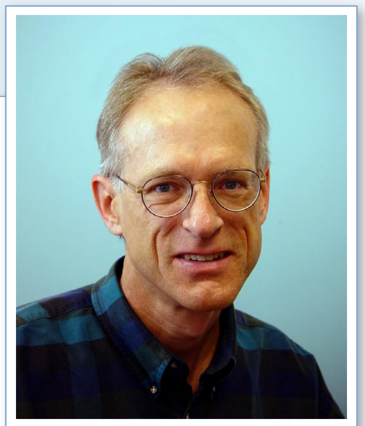


SAE Excellence in Oral Presentation

Richard Steeper

Richard Steeper, who won an SAE Excellence in Oral Presentation for his paper "Improving the NOX-CO2 Trade-Off of an HCCI Engine Using a Multi-Hole INjector" This paper was presented at the SAE World Congress & Exhibition in Detroit, MI, April 16-19, 2007.

Exergy analysis

(Continued from page 1)

Energy's (DOE's) Hydrogen, Fuel Cells, & Infrastructure Technologies (HFCIT) Program. To support the validation, CRF scientist Andy Lutz and graduate students Adam Simpson (Stanford) and Carl Mas (Berkeley) performed analyses to determine if the distributed production technologies can meet targets established by the HFCIT Multi-Year Program Plan. For distributed reforming, the 2007 target is 72% energy efficiency. (One kilogram of hydrogen has approximately the energy value of one gallon of gasoline.)

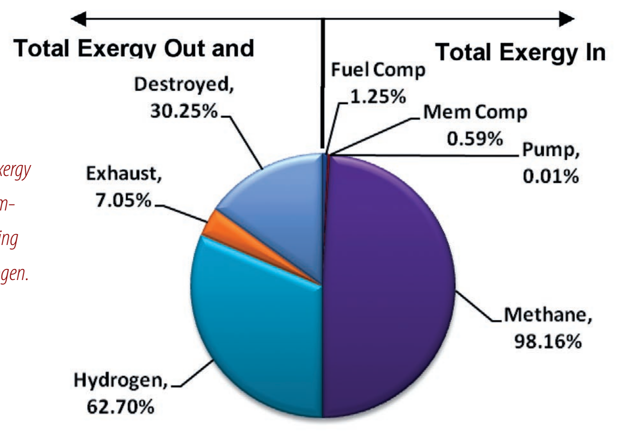


Figure 1. The exergy balance for steam-methane reforming to produce hydrogen.

Modeling energy efficiency

To analyze distributed hydrogen production stations, the CRF team developed H2Lib: a library of Simulink modules that model hydrogen components, such as reformers, electrolyzers, chillers, compressors, and fuel cells. The library approach and the palette-based Simulink framework provide the flexibility to adapt models to various systems. Modules for gas/liquid mixtures use CHEMKIN software to provide thermodynamic properties and solutions for equilibrium compositions.

The reformer model represents the catalytic reactor by chemical equilibrium and performs an internal energy balance with detailed heat integration to track exergy at state points in the process. Since the reforming is endothermic, heat is provided by a combusting the remaining fuel species (CH_4, CO, H_2) in the reformate mixture (after H_2 separation), which may require supplemental fuel from the methane input stream.

Parametric studies predict the maximum system efficiency to be 67%, based on 1st-law energy balances using lower heating values for hydrogen and methane, which occurs at 975 K and a steam-to-carbon ratio of 3.2 (by mole). This suggests that improvements to the system are necessary to reach the DOE target of 72%.

Exergy analysis

Exergy (2nd Law) analysis provides information about potential improvements in a process. Exergy, sometimes called available energy, is a thermodynamic state property that measures the maximum work that can be extracted from a resource at a given state with respect to the environmental. Exergy, like entropy, is not conserved. Exergy destruction occurs due to irreversibilities within a system and is proportional to the entropy generated during an irreversible process.

The model tracks the flow of exergy within the reforming model. Figure 1 shows the balance of exergy into the process (mostly methane) with that exiting (in the hydrogen and exhaust) and that which is destroyed. Simple energy (1st-law) analysis would conclude that unused energy is only that carried out in the exhaust. Exergy analysis provides the additional information that quantifies the destruction of useful energy, which in this example is significantly larger than what is unused in the exhaust.

To understand the potential for improving the efficiency of the process, Figure 2 breaks out the exergy that is unused in more detail. The majority of the exergy destruction occurs in the reformer, due to inherent irreversibilities of combustion, heat transfer, and mixing. Following the reformer, the next largest destroyers of exergy are the heat exchangers (HE). The heat exchange losses might be reduced by adjustments to the combustion air mixture and better thermal integration (more closely matching the temperatures of the two streams). The exhaust exergy is divided into two forms: thermomechanical (TM) and chemical. Thermomechanical exergy refers to the work that could be extracted from the exhaust due to the temperature and pressure being different than the environment; this work could be extracted by including a bottoming cycle. The chemical exergy of the exhaust is the work that could be extracted in bringing it to the composition of the environment; while the exhaust is in chemical equilibrium, theoretically, work could be extracted through a series of species-specific membranes while the exhaust species diffuse to their environmental partial pressures. Further discussion of the exergy analysis appears in the published paper: Simpson and Lutz, Int. J. of Hydrogen Engy., 32 (2007) 4811-4820.

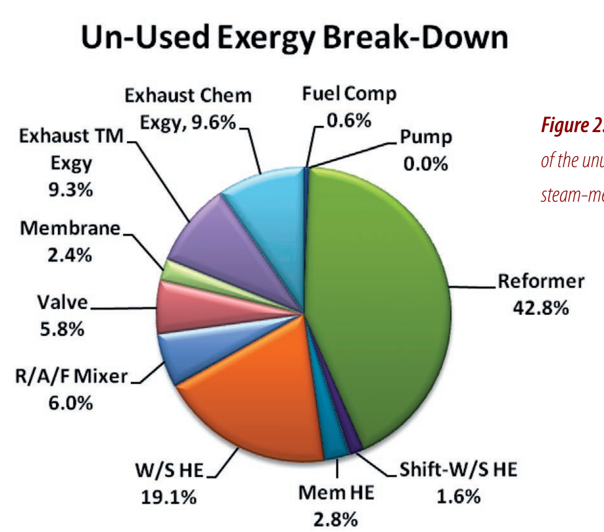
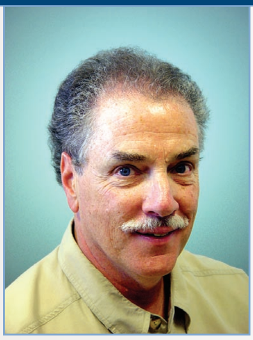


Figure 2. Breakdown of the unused exergy in steam-methane reforming.



Words from former CRF Director Bill McLean

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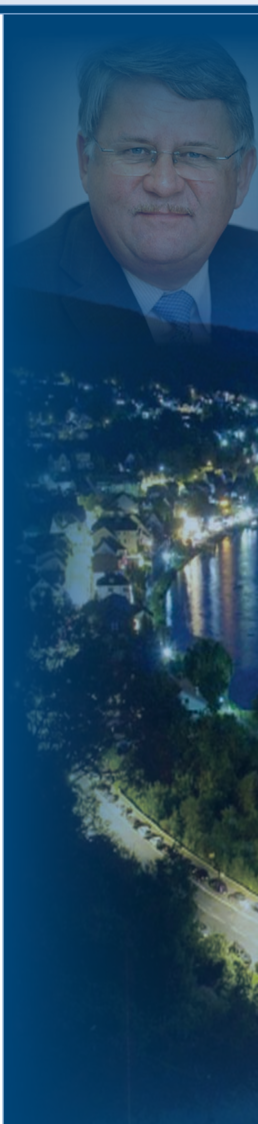
Former CRF Director Bill McLean recalled some of Jürgen's early visits to CRF. Bill noted, "You know Jürgen was truly one of our CRF family. He visited often and on several occasions he was in residence for significant periods of time." Bill recalled a visit, Juergens' first extended stay at CRF in the early '80's. It seems that Jürgen and his wife Christel and their two quite small children arrived in Livermore one afternoon after a long trip from Germany only to discover that arrrangements had not been made for their housing during Jürgen's leave at Sandia. Bill was the manager of the combustion chemistry group at that time and it fell to him to support the Warnatz family in quickly learning their way around in the Livermore area and in locating and moving into a suitable apartment. "There was some confusion and tension with the sudden arrival and we hadn't developed the smooth functioning CRF visitor support system we have today," noted Bill. In the end it worked out well and the visit was a real success and led to many more working visits by Jürgen to CRF.

Bill comments: *"We mourn the loss of such a long standing colleague. It is a personal loss for me and a loss for the entire combustion modeling community. We shall truly miss Jürgen Warnatz."*



Memorial Colloquium to honor Professor Jürgen Warnatz

The Interdisciplinary Center for Scientific Computing of the University of Heidelberg and the German Section of The Combustion Institute will jointly sponsor a Memorial Colloquium for Professor Warnatz on Saturday, May 31, 2008.

Among the notable speakers on the program is Professor R. W. Dibble, Combustion Analysis Laboratory, University of California, Berkeley, co-author with Dr. Warnatz and Dr. Ulrich Maas of their well-known combustion textbook, Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation (Springer-Verlag: Berlin, Heidelberg, New York), now in its fourth edition. Dr. Dibble will speak on the topic, "The Combustion Textbook, Past and Future.

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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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Photography .... Daniel Strong/Various Photographers

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