Mid-Term Report on the State of Combustion Energy Frontier Research Center (CEFRC)

Chung K. Law, Director

5th Annual MACCCR Fuels Summit
Sandia National Laboratory, Livermore, CA
September 17-20, 2012

Outline of Overview

- Mission, objectives & roadmap
- Organization & research structure
- Highlights of research
- Education, outreach & alliances
- Synergy

U.S. DEPARTMENT OF ENERGY | Office of Science

The Overarching Goal

- Workshop on Basic Energy Needs for Clean & Efficient Combustion of 21st Century Transportation Fuels (2007):

  *The development of a validated, **predictive**, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications*

- This is in resonance with message from the (plenary) Hottel Lecture at the 31st International Symposium on Combustion (2006): *Combustion has entered the era of quantitative **predictability***

U.S. DEPARTMENT OF ENERGY | Office of Science

Center Objectives

- To *advance* fundamental understanding and practice of *combustion and fuel science*
- To *acquire experimental databases* and validation platforms for kinetics, thermochemistry, transport processes, and flame structure
- To *develop methodologies for kinetic model generation* and reduction
- To *implement* validated, multi-scale, quantitative *prediction methods* for energy conversion of alternative fuels
- To *promote collaborations* with DOE/EFRC units as well as research community at large, and proactively disseminate Center-generated information to facilitate global progress
- To *train* the next generation of *combustion researchers*

Meeting BESAC Grand Challenges

1. How do we control material processes at the level of electrons?

   Design fuels with fundamentally new structures and properties through manipulation of the molecular structure at the level of electrons

2. How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?

   Develop a multi-scale approach to characterize the properties of matter at atomistic scales in terms of emergent properties

3. How do we characterize and control matter away – especially very far away – from equilibrium?

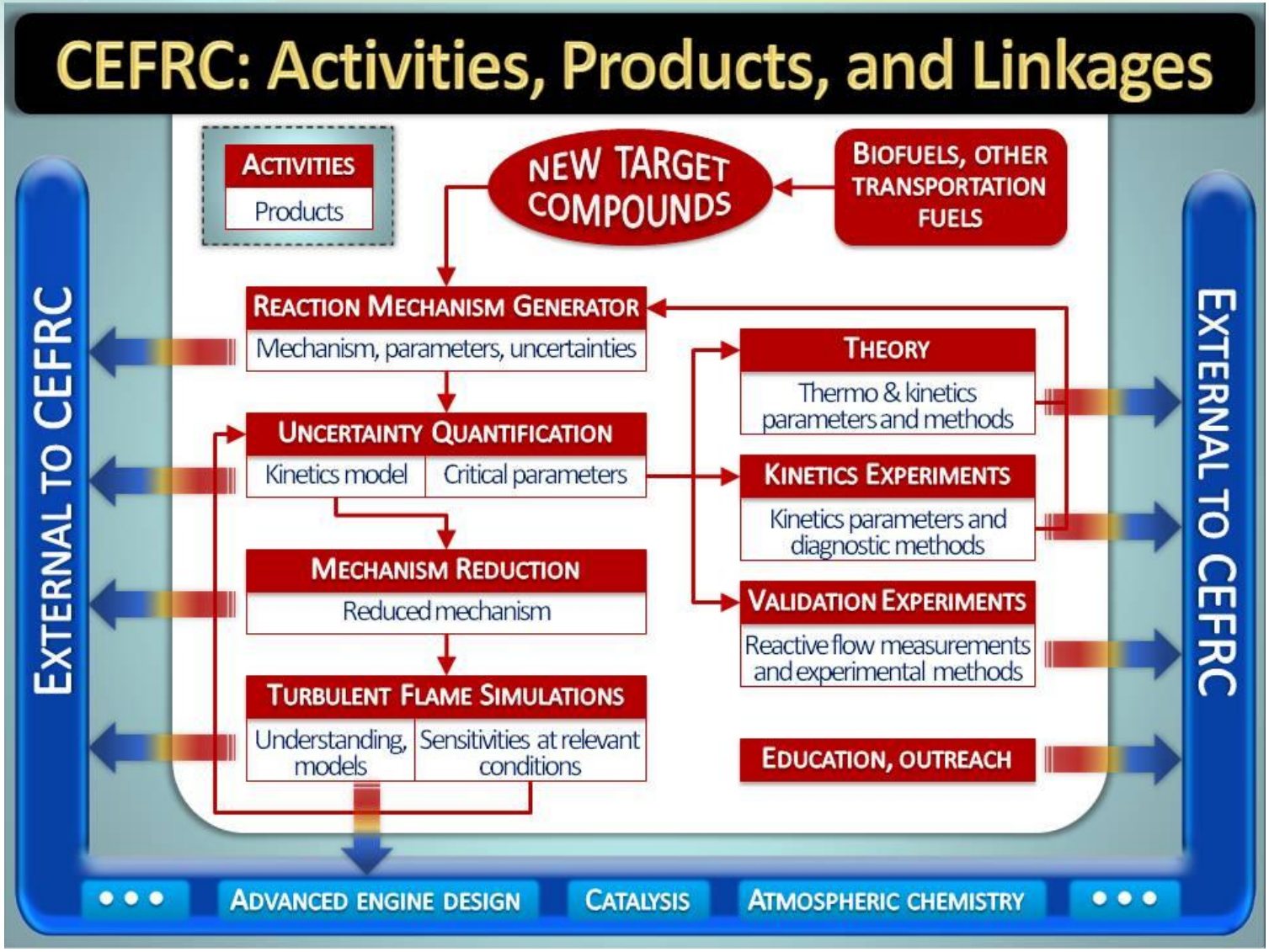
   Control reactions of fuels in situations far from equilibrium to produce clean and efficient energy using advanced devices

Guiding Principles

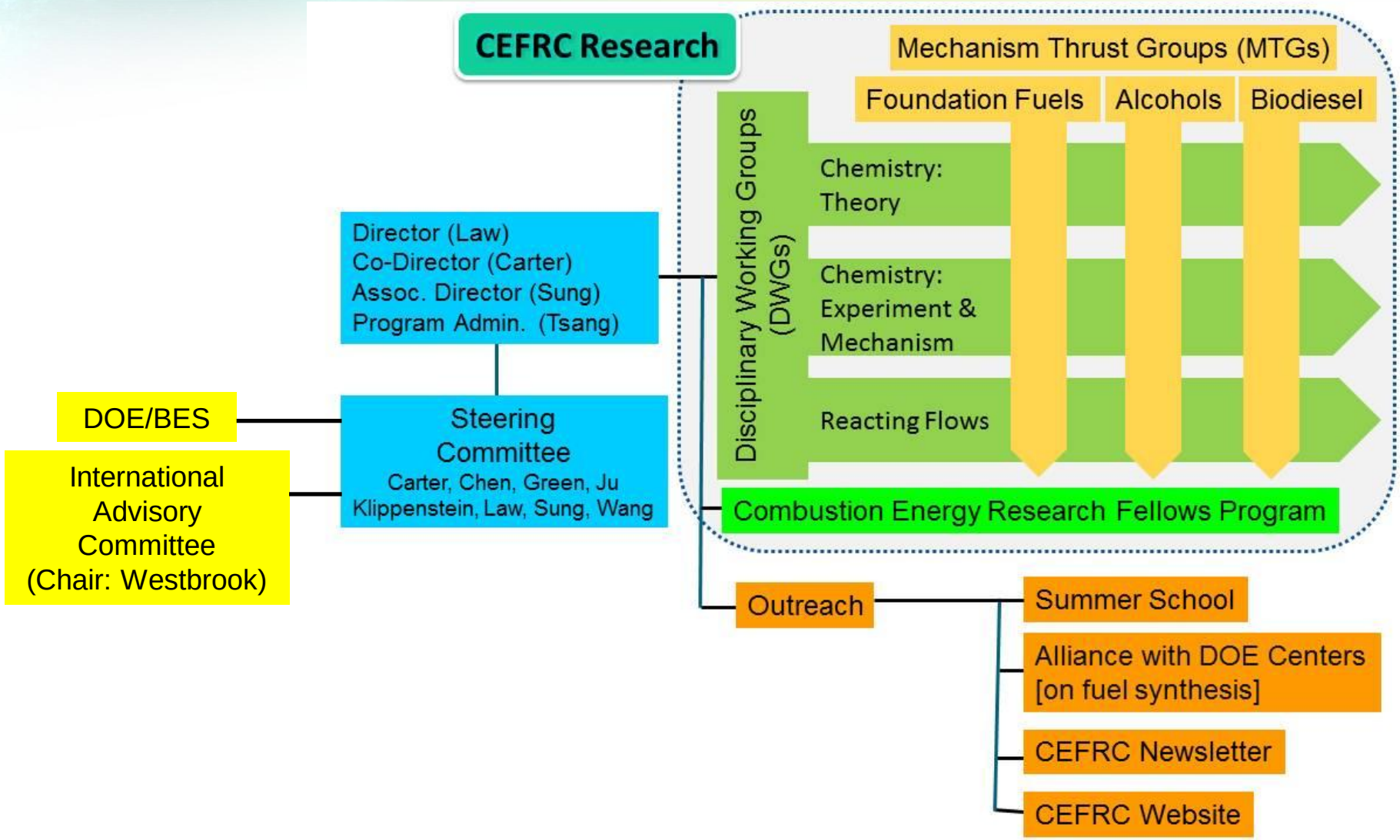
1. A DOE-BES grant: hence basic research
2. A center grant: hence the whole is greater than the sum of its parts
3. A long-term, five-year grant: hence need for nimbleness and perpetual rejuvenation
4. A community grant: hence service to the community at large in research and education

U.S. DEPARTMENT OF ENERGY | Office of Science

Center Roadmap

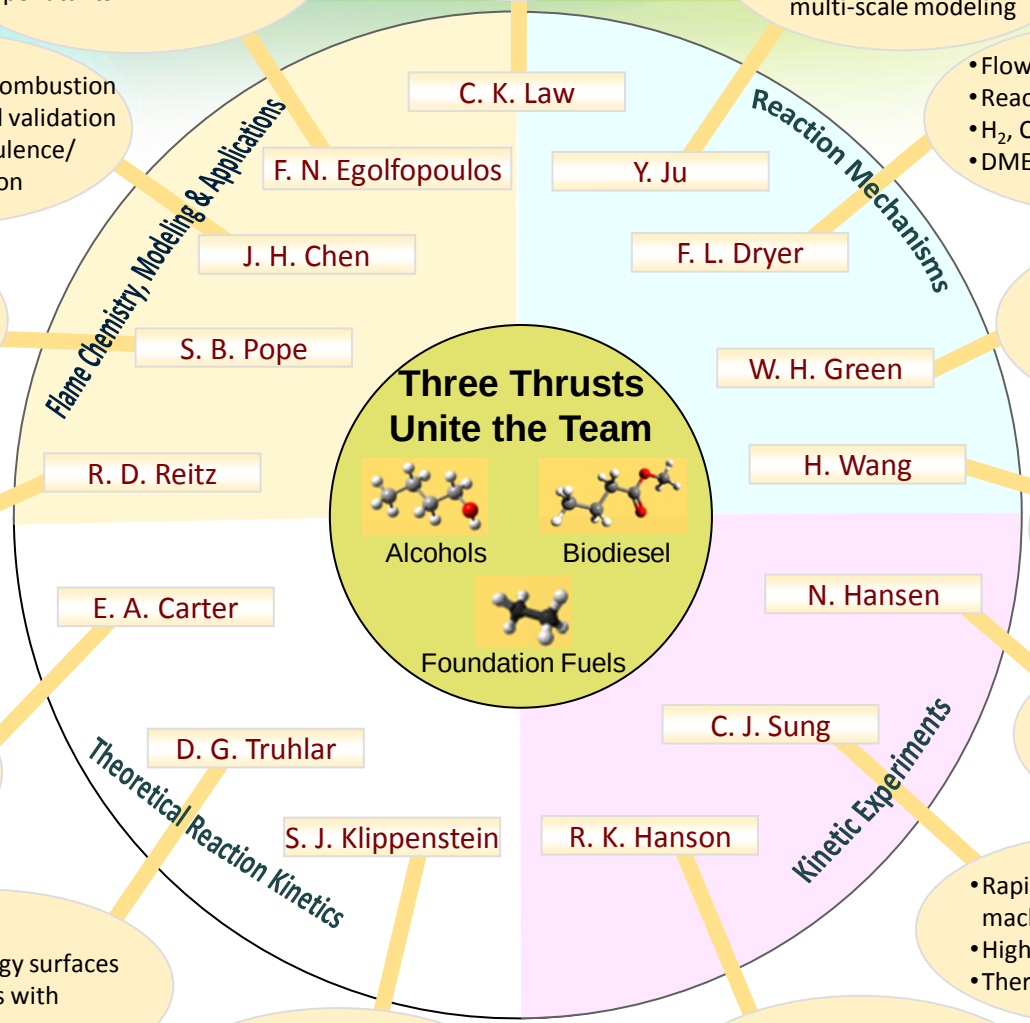


Organization Structure



U.S. DEPARTMENT OF ENERGY | Office of Science

Synergistic 2D Research Structure



- Laminar flame speeds, extinction and ignition, pollutants

- High-pressure flames
- Turbulent flames
- Droplet processes

- Flame chemistry
- Biodiesel kinetics
- Model reduction & multi-scale modeling

- DNS of HCCI/SACI combustion
- DNS data for model validation
- High pressure turbulence/ chemistry interaction

- Flow reactor experiments
- Reactivity and species history
- H_2, CO, small HC chemistry
- DME, small oxygenates

- LES/PDF/ISAT turbulent combustion
- Turbulence/chemistry

- Mechanisms of butanols
- Automatic mechanism generation

- Low-T combustion engines
- HCCI and RCCI CFD modeling
- Interface with DERC consortium

- Soot
- Small HC chemistry
- Transport properties
- UQ methods

- Ab initio methods
- Thermochemical kinetics
- Ester chemistry

- Flame species by Synchrotron MS
- Burner-stabilized flames

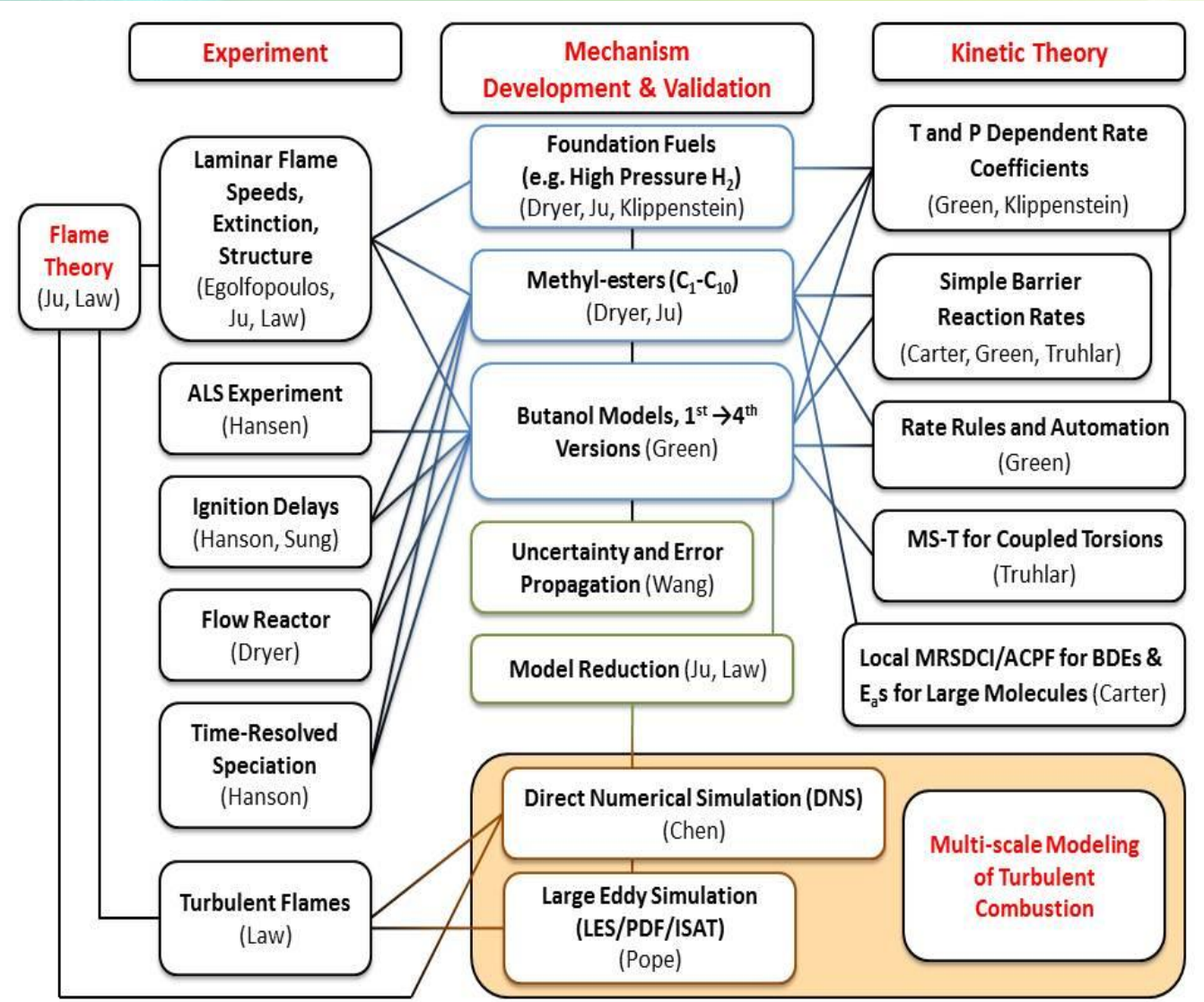
- Potential energy surfaces
- Rate constants with tunneling

- Potential energy surfaces
- Reaction rate constants
- High pressure theories

- Shock tube/Laser diagnostics
- Ignition/Species histories
- Rate constants

- Rapid compression machine
- High-pressure ignition
- Thermometry and species

Research Activities and Synergy



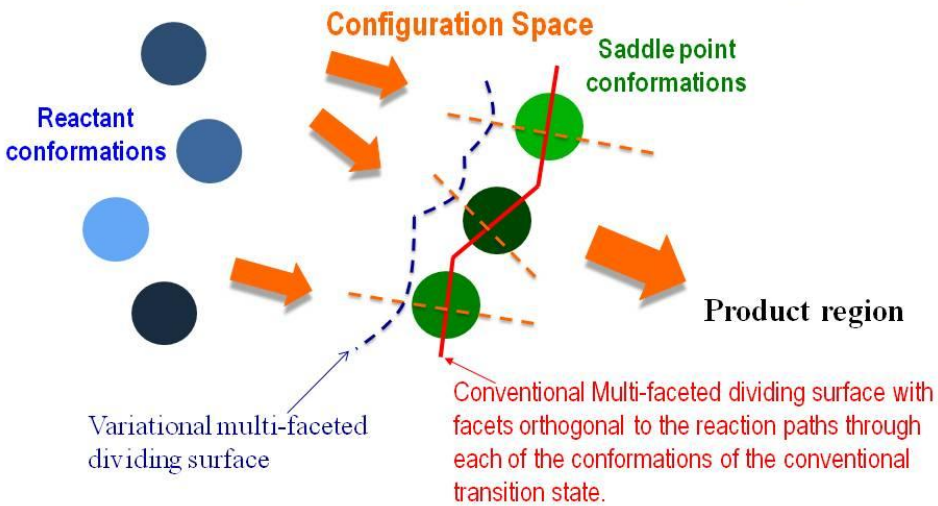
Selected Highlights of Research Capabilities, Methodologies & Results

U.S. DEPARTMENT OF ENERGY | Office of Science

Theories of Thermochemistry and Chemical Kinetics

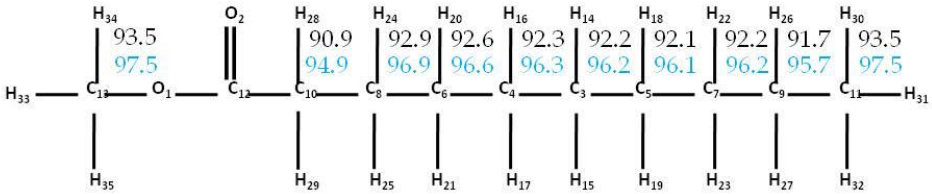
- Predicted thermochemical and kinetic properties of key combustion species
- Developed new methods to treat complex reactions
- Applied to reactions highlighted by the CEFRC modeling efforts
- Help formulate rate rules for RMG

Multi-Structural Multi-Path Variational Transition State Theory



Local MRSDCI Calculations of BDEs: Methyl Decanoate (MD)

Methyl decanoate D_{298} (kcal/mol)
Local MRSDCI/cc-pVDZ and B3LYP/6-311G(2d,p) geom. and freq.
Local MRSDCI/cc-pV∞Z (estimated)



New/Expanded Experimental Capabilities: Design, Methodologies, Extreme Conditions

Comprehensive array of experimental tools covering wide range of thermodynamic conditions

Homogeneous Chemistry

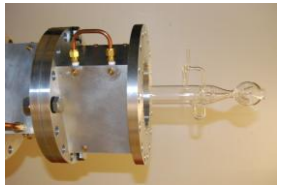
- VUV Photoionization Apparatus
- Variable Pressure Flow Reactor
- High Pressure Laminar Flow Reactor
- High Pressure Jet Stirred Reactor
- High Pressure Shock Tube
- Aerosol Shock Tube
- Rapid Compression Machine

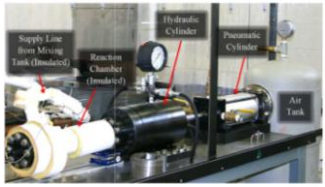
Flames

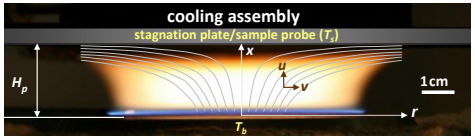
- Low-Pressure Flame Chamber
- High Pressure Counterflow Flame Facility
- Burner-Stabilized Stagnation Flame Facility
- High & Constant Pressure Expanding Flame Chamber: Laminar
- High & Constant Pressure Expanding Flame Chamber: Turbulent
- Droplet Combustion Facility

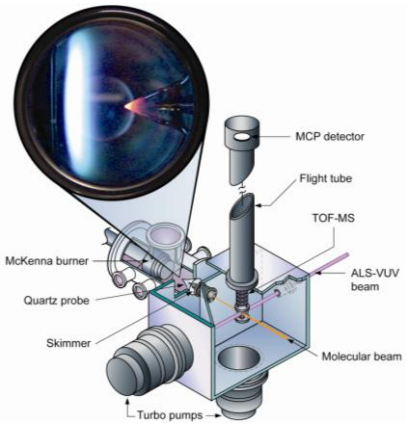
Advanced Diagnostics

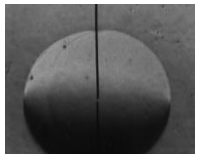
- Molecule-Particle Crossed Beams Apparatus
- Advanced Light Source
- UV Laser Absorption
- Mid- and Far-IR Absorption Spectroscopy
- Molecular Beam Mass Spectrometry

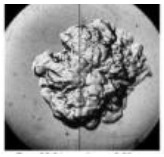






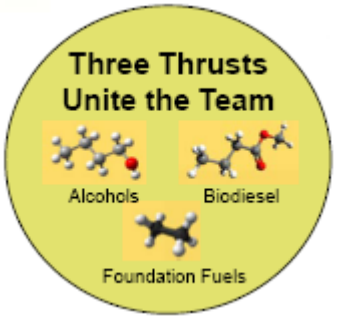






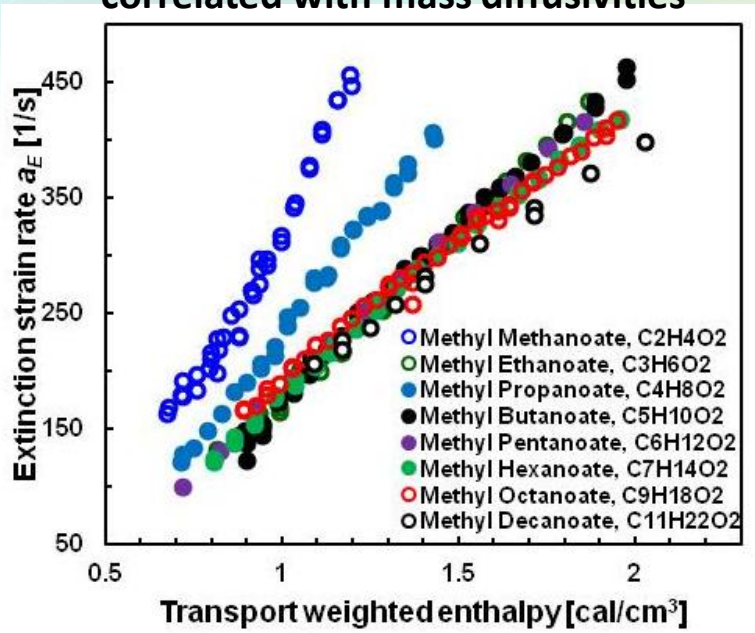
Systematic Approach Towards Developing Reaction Mechanisms of Thrust Fuels (from RMG to UQ/EP)

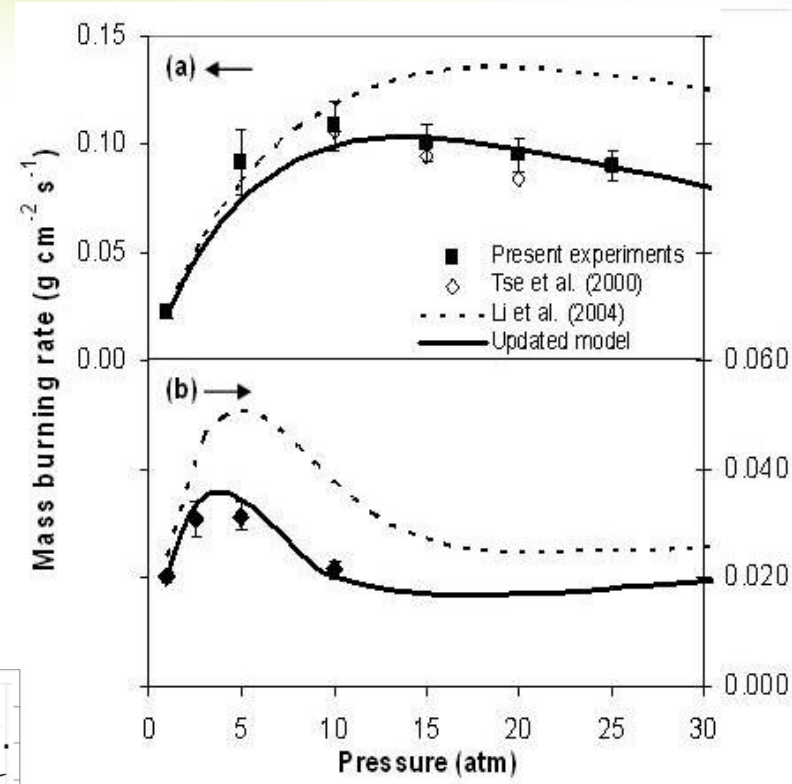
- Three mechanism thrusts represent three different levels of kinetic understanding; requiring different approaches
  - Foundation fuels: accuracy & precision, quantified uncertainty
  - Butanols: close to foundation fuels but still substantial unknown pathways & kinetic parameters; testing rules & theories of RMG
  - Biodiesel: distant from foundation fuels & butanols; few experimental data and kinetic parameters; requires *ad hoc* model
- Center effort will eventually bring all approaches and models together via the RMG/MUM-PCE platform into a single, self-consistent tool set and reaction model
- Uncertainty quantification methods are also used to better utilize the experimental data



Prominent Chemistry & Transport Effects in Flames

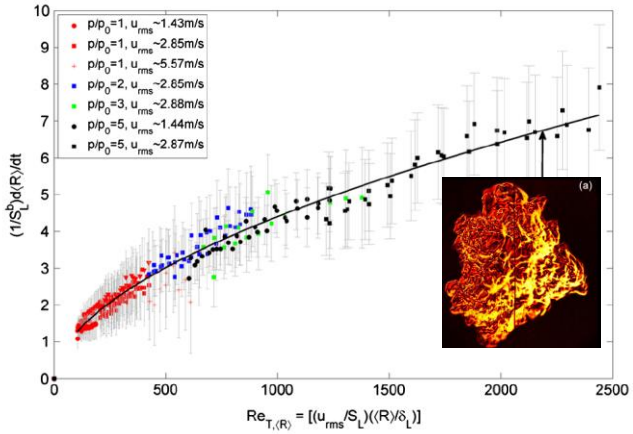
Extinction strain rate of various methyl esters correlated with mass diffusivities





Successful theoretical & experimental correlation of turbulent flame speeds

$$\frac{S_{T,0}}{S_L} \sim O(1)\sqrt{\frac{u_{rms}}{S_L}\frac{\lambda_I}{\delta_L}}$$

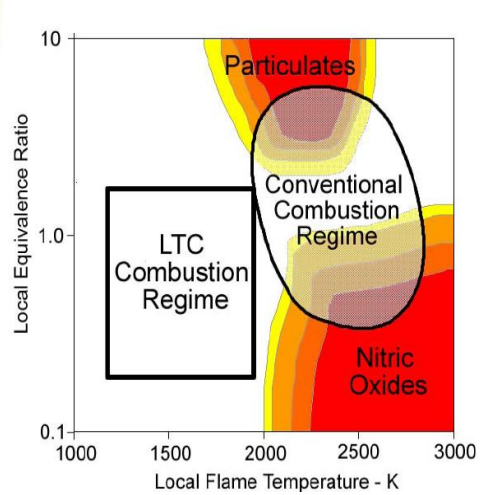


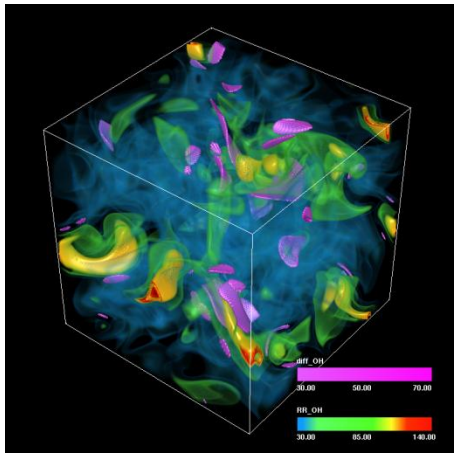
Experimental high-pressure flame burning rate agrees well with new H_2/O_2 mechanism: ϕ = 0.85 (a), 0.3 (b)

U.S. DEPARTMENT OF ENERGY | Office of Science

DNS of Autoignition in Stratified DME/Air Turbulent Mixtures

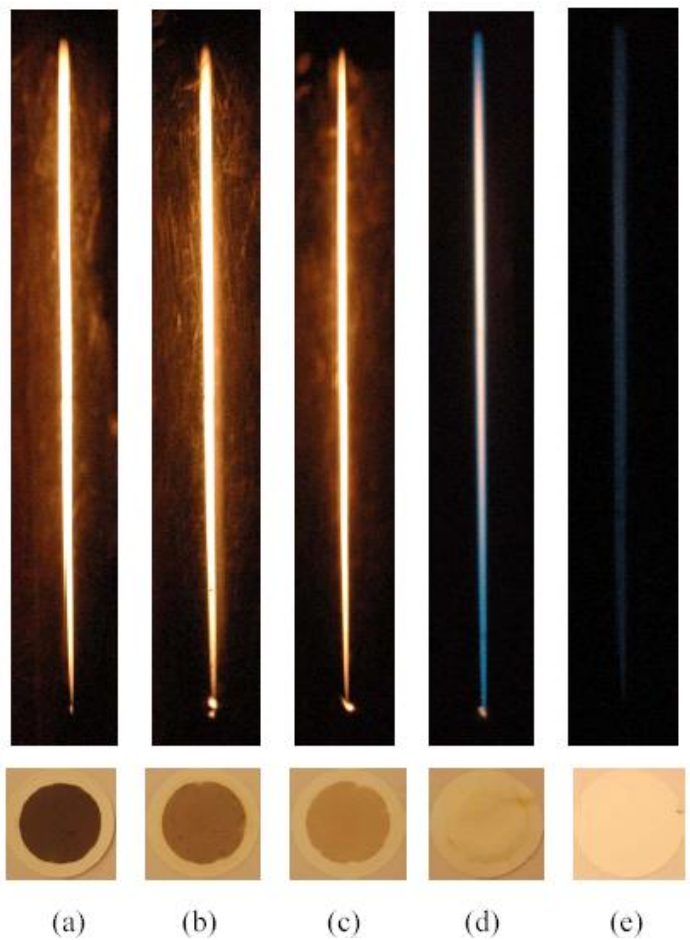
- Operating fuel-lean and at low temperatures reduces soot and NO_x and increases efficiency
- Mixture inhomogeneities reduce peak heat release rates and pressure rise rates
- DNS: 170M grid points; 10M CPU hours
- Results show ignition occurs in three distinct stages
  - 1st Stage: low-temperature chemistry
  - 2nd Stage: spontaneous ignition fronts
  - 3rd Stage: premixed flame
  - 2nd and 3rd stages can occur in close physical proximity





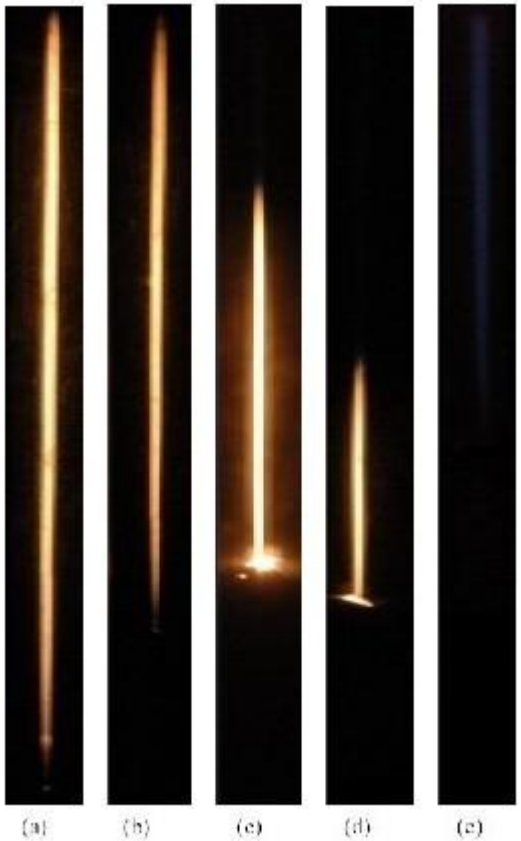
Blending Strategy for Biofuels

Biodiesel Blending: Soot Reduced



Blending ratio
(a) Neat diesel
(b) 10% biodiesel
(c) 20% biodiesel
(d) Neat biodiesel
(e) hexadecane

Ethanol Blending: Soot Reduced and Droplet Exploded (Hence Gasified)



Blending ratio
(a) Neat diesel
(b) 25% ethanol
(c) 50% ethanol
(d) 75% ethanol
(e) Pure ethanol

Education, Outreach & Alliances

Combustion Energy Research Fellows (aka Roving Post-Docs)

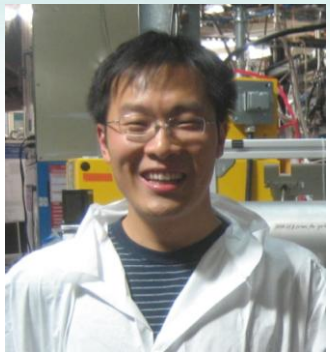
The Program

- Four to five appointments per year for two-year appointment, co-sponsored by two (or more) PIs
- Roving assignment on-site of sponsoring PIs, working on joint projects
- Appointees benefited from expanded exposure & career opportunities

The Merits

- Facilitates collaboration between sponsoring PIs
- Responds to new developments to ensure nimbleness
- High-risk, high-payoff projects
- Competition for slots ensures robust program

Combustion Energy Research Fellows

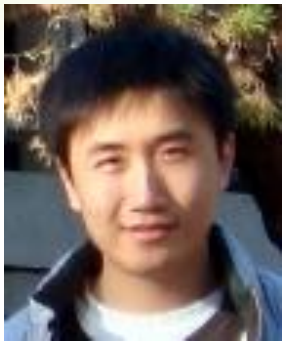


Bin Yang
Starting: 02/2010
PIs: Hansen/Wang

Jay Uddi
Starting: 05/2010
PIs: Ju/Sung

John Alecu
Starting: 07/2010
PIs: Green/Truhlar

Peng Zhang
Starting: 08/2010
PIs: Klippenstein/Law/Pope



Yue Yang
Starting: 03/2011
PIs: Chen/Pope

Bret Windom
Starting: 05/2011
PIs: Egolfopoulos/Ju

Gbenga Oyedepo
Starting: 09/2011
PIs: Carter/Truhlar

Damir Valiev
Starting: 09/2011
PIs: Chen/Law

Yury Suleymanov
Starting: 12/2011
PIs: Green/Klippenstein

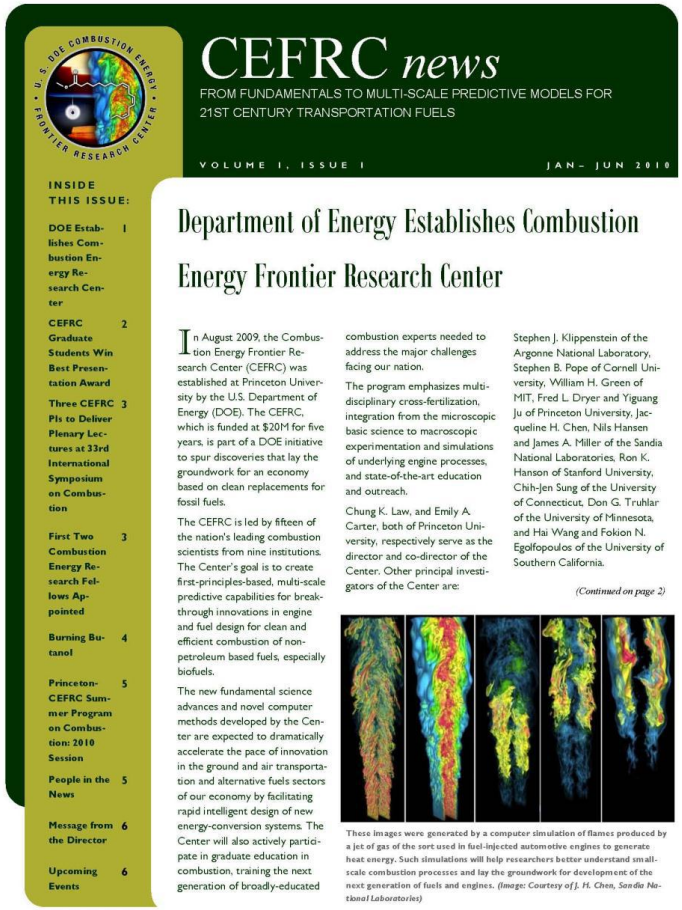
Enoch Dames
Starting: 06/2012
PIs: Green/Hanson/Wang

Princeton-CEFRC Summer School on Combustion: 2012 Session

- **Academic program**: 15-hour courses over 5 days
- **Registrants: ~ 200** (120 students, 80 professionals**)**; 24 states; 17 countries; 54 universities, 9 US government and industry labs.; 5 international labs.
- Lecture notes and video-taped lectures publicly available

Dissemination of Technical Information

- An active web-site
- Biannual newsletter
- Free online Summer School lecture notes and videos
- Pre-publication release/dissemination of research data and results



CEFRC *news*

FROM FUNDAMENTALS TO MULTI-SCALE PREDICTIVE MODELS FOR 21ST CENTURY TRANSPORTATION FUELS

VOLUME 1, ISSUE 1 JAN – JUN 2010

INSIDE THIS ISSUE:

DOE Establishes Combustion Energy Research Center 1
CEFRC Graduate Students Win Best Presentation Award 2
Three CEFRC PIs to Deliver Plenary Lectures at 33rd International Symposium on Combustion 3
First Two Combustion Energy Research Fellows Appointed 3
Burning Butanol 4
Princeton-CEFRC Summer Program on Combustion: 2010 Session 5
People in the News 5
Message from the Director 6
Upcoming Events 6

Department of Energy Establishes Combustion Energy Frontier Research Center

In August 2009, the Combustion Energy Frontier Research Center (CEFRC) was established at Princeton University by the U.S. Department of Energy (DOE). The CEFRC, which is funded at $20M for five years, is part of a DOE initiative to spur discoveries that lay the groundwork for an economy based on clean replacements for fossil fuels.

The CEFRC is led by fifteen of the nation's leading combustion scientists from nine institutions. The Center's goal is to create first-principles-based, multi-scale predictive capabilities for breakthrough innovations in engine and fuel design for clean and efficient combustion of non-petroleum based fuels, especially biofuels.

The new fundamental science advances and novel computer methods developed by the Center are expected to dramatically accelerate the pace of innovation in the ground and air transportation and alternative fuels sectors of our economy by facilitating rapid intelligent design of new energy-conversion systems. The Center will also actively participate in graduate education in combustion, training the next generation of broadly-educated combustion experts needed to address the major challenges facing our nation.

The program emphasizes multi-disciplinary cross-fertilization, integration from the microscopic basic science to macroscopic experimentation and simulations of underlying engine processes, and state-of-the-art education and outreach.

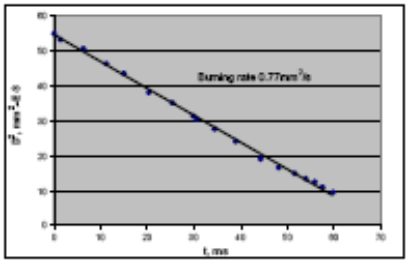
Chung K. Law, and Emily A. Carter, both of Princeton University, respectively serve as the director and co-director of the Center. Other principal investigators of the Center are: Stephen J. Klippenstein of the Argonne National Laboratory, Stephen B. Pope of Cornell University, William H. Green of MIT, Fred L. Dryer and Yiguang Ju of Princeton University, Jacqueline H. Chen, Nils Hansen and James A. Miller of the Sandia National Laboratories, Ron K. Hanson of Stanford University, Chih-Jen Sung of the University of Connecticut, Don G. Truhlar of the University of Minnesota, and Hai Wang and Fokion N. Egolfopoulos of the University of Southern California.

(Continued on page 2)

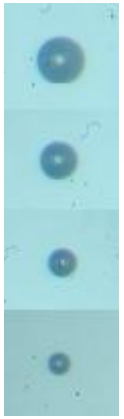
These images were generated by a computer simulation of flames produced by a jet of gas of the sort used in fuel-injected automotive engines to generate heat energy. Such simulations will help researchers better understand small-scale combustion processes and lay the groundwork for development of the next generation of fuels and engines. *(Image: Courtesy of J. H. Chen, Sandia National Laboratories)*

Alliance with DOE Centers on Fuel Synthesis

- Alliance with three major DOE-sponsored centers that synthesize biofuels
  - Catalysts Center for Energy Innovation
  - Center for Advance Biofuels Systems
  - National Alliance for Advanced Biofuels and Bioproducts



D^2-Law of DMF demonstrated



- The CEFRC performs combustion tests and analysis of the biofuels synthesized by the alliance centers to provide feedback on fuel viability and design

U.S. DEPARTMENT OF ENERGY | Office of Science

Summary on Synergy: Center-wide

- Inherent coordination through DWGs on fundamental science (theory, experiment, fluid physics) and MTGs on mechanism development
- Trans-scale information transfer including error propagation and uncertainty quantification
- Chemistry overlaps in the three thrust mechanisms
- Young associates group
- Monthly telecons for DWGs, MTGs, steering committee & young associates
- Roving post-doc program

Summary on Synergy: Community-wide

- Alliance with sister EFRC & DOE bio-fuel centers
- Proactive, including pre-publication, release of CEFRC-generated data and knowledge
- Summer School on Combustion, including publicly-accessible lecture notes and videos
- Active website
- Newsletter
- Advocacy through leadership in scientific community

U.S. DEPARTMENT OF ENERGY | Office of Science