COMBUSTION ENERGY
FRONTIER RESEARCH CENTER
(CEFRC)
FINAL TECHNICAL REPORT

(August 1, 2009 – July 31, 2016)

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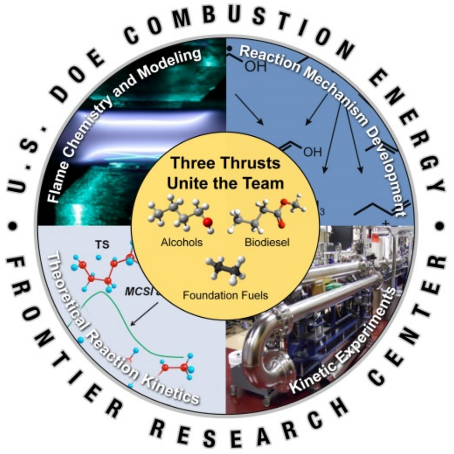

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EXECUTIVE SUMMARY

The Combustion Energy Frontier Research Center (CEFRC) was established to tackle the single overarching grand challenge of energy sustainability, energy security and global warming: to develop a "validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications," as identified in the DOE report on "*Basic Energy Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels*". The challenge is particularly daunting since energy conversion efficiencies and exhaust emissions are governed by coupled chemical and transport processes at multiple length scales ranging from electron excitation to molecular rearrangements to nanoscale particulate formation to turbulent fuel/air mixing. To tackle this challenge, the CEFRC assembled a world-class team of 15 principal investigators, with the objectives to: 1) develop and test theoretical models to predict elementary reaction rates, molecule thermalization rates, chemical bond dissociation energies, and nonequilibrium transport properties using quantum chemistry calculations that account for strong electron correlation and multiple electronic potential energy surfaces; 2) develop automated kinetic mechanism generation, reduction, and error control methods for predicting alternative fuel including biofuel oxidation, fuel droplet decomposition, and NO_x and particulate formation; 3) validate and improve the predictions of these models by measuring ignition delay times, species profiles, flame structures, burning limits, turbulence-kinetic coupling, and NO_x and soot emissions at high-pressures and near-limit conditions, by using advanced experimental diagnostic techniques including multiple laser techniques, molecular beam sampling and synchrotron photoionization, and by conducting the measurements in high-pressure shock tubes, jet-stirred and flow reactors, flame bombs, counterflow flames, and advanced-design rapid compression ignition instruments; and 4) develop a suite of validated petascale high-fidelity simulation and modeling capabilities to understand and predict chemistry-turbulence-radiation coupling for new fuels in new regimes, including the high pressure, low-temperature combustion in advanced engine and turbine designs, and 5) establish a knowledge highway between researchers and engineers in academia, national laboratories, and industry to facilitate the dissemination and exchange of knowledge on national and international levels, and enrich the talent pool and capabilities of the next generation of combustion scientists and engineers. The technical activities of the CEFRC were conducted through three Disciplinary Working Groups – *Chemistry Theory*, *Experiment and Mechanism*, and *Reacting Flows*, which coordinated the Center's research on the development of combustion chemistry of *Foundation Fuels* (C_0–C_4 hydrocarbons), *Alcohols*, and *Biodiesel* through three corresponding Mechanism Thrust Groups. Such a two-dimensional coordinated and tightly interwoven research structure has been proven to be highly effective in assuring the interplay between the developments of the fundamentals of combustion science and the utilization of the various categories of fuels. The Center has accomplished the above goals over the five year period (August 1, 2009 – July 31, 2014) with appropriated funding, followed by two additional no-cost-extension (NCE) years. The research results are documented in 230 journal publications, with six legacy review papers on the study of combustion chemistry using *shock tubes*, *flow reactors*, *rapid compression machines*, and *flames*, on *uncertainty quantification*, and on *theoretical reaction dynamics and chemical modeling of combustion.* A robust outreach program complemented these PI-led research activities, consisting of: 1) a roving post-doc program comprised of a corps of Center-appointed, co- or multi-sponsored post-doctoral fellows with rotating assignments to conduct seed projects initiated by at least two PIs, in residence with these

sponsoring PIs, to rapidly pursue new and high-risk, high-payoff interdisciplinary ideas; 2) an annual summer school on combustion heavily attended (~200) by senior graduate students and practicing researchers covering advanced topics on chemical kinetics, fluid mechanics, turbulent combustion, engine combustion, new technologies, etc.; 3) a robust open web-site providing Center and community information as well as the lecture videos and notes of the summer school; and 4) widely distributed biannual newsletters.

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I. MISSION AND GOALS

The report on "Basic Energy Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels", issued by the Department of Energy - Basic Energy Sciences, identified a single overarching grand challenge: to develop a *"validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications."* It is the goal of our Center to tackle this grand challenge head-on. To this end, we have assembled a world-class team of principal investigators with expertise in quantum chemistry, chemical kinetics, combustion theory and modeling, and corresponding experimentation. These principal investigators are chosen not only for their stature, but because their research covers all the myriad time and length scales that are involved in combustion, from the scale of the electron to those of the largest scales of turbulence. The Center has focused on the science underlying the development of non-petroleum-based fuels, including carbon-neutral biofuels, and their optimal use in transportation. This science intrinsically involves chemistry with transport at conditions far from equilibrium and at extreme pressures, the control of processes at the level of electrons, and a coordinated multi-scale approach for understanding and predicting emergent properties such as flame phenomena – three of the Grand Challenges identified in the BESAC report "Directing Matter and Energy: Five Grand Challenges for Science and the Imagination."

The urgent need for a concerted effort to develop non-petroleum-based fuels is abundantly substantiated by concerns over energy sustainability, energy security, and global warming. Drastic changes in the fuel constituents and operational characteristics of energy conversion systems are needed over the next few decades as the world transitions away from petroleum-derived transportation fuels. Conventional empirical approaches to developing new engines and certifying new fuels have only led to incremental improvements, and as such they cannot meet these enormous challenges in a timely, cost-effective manner. Achieving the required high rate of innovation will require computer-aided design, as is currently used to design the aerodynamically efficient wings of airplanes and the molecules in ozone-friendly refrigerants. The diversity of alternative fuels and the corresponding variation in their physical and chemical properties, coupled with simultaneous changes in energy conversion device and design/control strategies needed to improve efficiency and reduce emissions, pose immense technical challenges. These challenges are particularly daunting since energy conversion efficiencies and exhaust emissions are governed by coupled chemical and transport processes at multiple length scales ranging from electron excitation to molecular rearrangements to nanoscale particulate formation to turbulent fuel/air mixing. Fortunately, recent advances in quantum chemistry, chemical kinetics, reactive flow simulation, high-performance computing, and experimental diagnostics suggest that first-principles-based predictive tools for optimum integration of energy conversion/control methodologies and new fuel compositions are possible. The task is monumentally complex and demanding, requiring the *coordinated* effort of many researchers, including some of the best scientific minds that this nation has to offer, in order to ensure that research across all of the multi-scale endeavors is properly integrated.

Recognizing the challenges and opportunities, the goals of the CEFRC were the following:

1) *To advance* fundamental understanding and practice of combustion and fuel science. This includes the development of quantum chemistry methods for thermochemistry and kinetics at high pressures, the development of nonequilibrium transport models and

models of nanoscale particulate growth and oxidation, and the discovery and modeling of new phenomena of near-limit laminar and turbulent combustion.

2) *To create* experimental validation platforms and databases for kinetics, thermochemistry, transport, and flame structure through application of advanced *in situ* diagnostic methods.
3) *To enable* automated kinetic model generation and reduction.
4) *To implement* validated, *multi-scale*, prediction methods for energy conversion design/control concepts tailored to physical and chemical properties of 21st Century fuels.
5) *To establish* a knowledge highway connecting the CEFRC, academic and research institutions, and the transportation and fuel industries.
6) *To train* the next generation of combustion scientists with the multi-disciplinary background needed to tackle these immensely challenging combustion energy problems.

The research that was conducted at the CEFRC therefore directly addresses three of the BESAC Grand Challenges: (a) Designing fuels with fundamentally new structures and properties through the judicious manipulation of their molecular composition requires controlling matter at the level of the *electron*. (b) Controlling the reactions of these fuels to produce clean and efficient energy using advanced conversion devices requires characterizing and controlling matter *far from equilibrium*. (c) Developing a multi-scale approach to characterize the properties of matter at atomistic scales in terms of *emergent* properties at successively larger scales.

II. OBJECTIVES AND STRATEGY

The overall research objectives and strategy for the CEFRC are summarized in Fig. 1. In terms of broad categories of tasks we proposed to: 1) develop and test theoretical models to predict elementary reaction rates, molecule thermalization rates, chemical bond dissociation energies, and nonequilibrium transport properties using quantum chemistry calculations that account for strong electron correlation and multiple electronic potential energy surfaces. Most of the important processes occur at strongly nonequilibrium conditions, and many critical reactions proceed via non-Boltzmann intermediates; 2) develop automated kinetic mechanism generation, reduction, and error control methods for predicting alternative fuel oxidation, fuel droplet decomposition, and NO_x and particulate formation; 3) validate and improve the predictions of these models by measuring ignition delay times, species profiles, flame structures, burning limits, turbulence-kinetic coupling, and NO_x and soot emissions at high-pressures and near-limit conditions, by using advanced experimental diagnostic techniques including multiple laser techniques, molecular beam sampling and synchrotron photoionization. Measurements were to be made in high-pressure shock tubes, jet-stirred and flow reactors, flame bombs, counterflow flames, and advanced-design rapid compression ignition instruments; and 4) develop a suite of validated petascale high-fidelity simulation and modeling capabilities to understand and predict chemistry-turbulence-radiation coupling for new fuels in new regimes, including the high pressure, low-temperature combustion in advanced engine and turbine designs, and 5) establish a knowledge highway between researchers and engineers in academia, national laboratories, and industry to facilitate the dissemination and exchange of knowledge on national and international levels, and enrich the talent pool and capabilities of the next generation of combustion scientists and engineers.

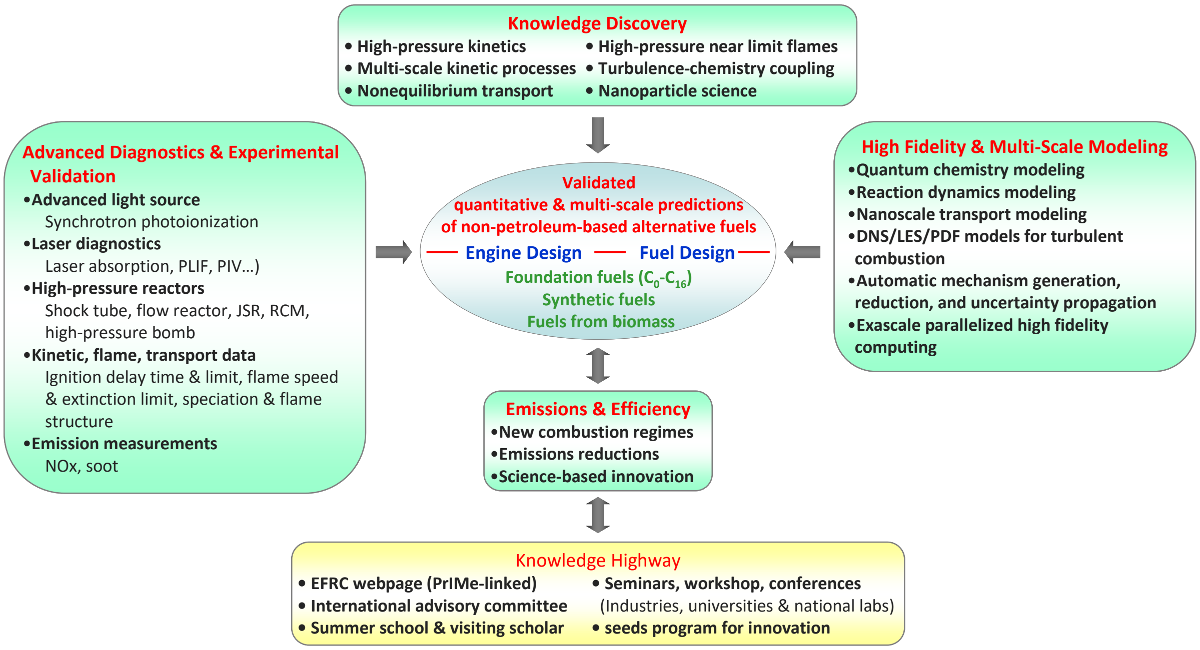

Figure 1. CEFRC Objectives and Strategy

III. ORGANIZATION, PI AND TASK STRUCTURES

A. Organization Structure

In order to accomplish the goals identified above, the CEFRC developed an organization structure shown in Fig. 2. Research was conducted through a novel two-core structure that, while retaining the meritorious aspects of time-tested, single-investigator-led mode of research, also facilitated cross-disciplinary interaction, promoted the exploration of new ideas through seed projects, and trained a team of post-doctoral researchers with strong multi-disciplinary experience. Specifically, a PI Core comprised the bulk of the Center's research effort, conducted by the PIs at their own institutions with their post-docs and graduate students. Coordination and effective communication, particularly through monthly and bi-monthly teleconferences, were instituted to ensure that the multiple linkages between the investigators and across disciplines and scales would lead to a scientific outcome that far exceeded the collection of the individual research efforts. Research in a Roving Post-doc Core was conducted by a team of Center-appointed, co- or multi-sponsored post-doctoral fellows with rotating assignments to conduct at least two PI-initiated seed projects, in residence with the sponsoring PIs, during a two-year appointment. This therefore provided a mechanism through which new and high-risk, high-payoff ideas could be rapidly pursued, with the Center post-docs being the agents and beneficiaries of cross-disciplinary collaboration and the cultivation of these new research ideas.

The technical activities of the CEFRC were conducted through three **Disciplinary Working Groups (DWGs)** – *Chemistry Theory*, *Experiment and Mechanism*, and *Reacting Flows*, which coordinated the Center's research on the development of combustion chemistry of *Foundation Fuels* (C_0–C_4 hydrocarbons), *Alcohols*, and *Biodiesel* through three corresponding **Mechanism Thrust Groups (MTGs)**. Such a two-dimensional coordinated and tightly interwoven research structure was proven to be highly effective in assuring the interplay between the developments of the fundamentals of combustion science and the utilization of the various categories of fuels.

Matters related to research directions and resources was handled by a Steering Committee, consisting of the Director and Co-director of the Center, and representative PIs to coordinate the research efforts on chemistry, laminar flames and transport phenomena, turbulent flames, and oversight the experimental equipment and computational resources.

Accountability and dissemination of the research results was accomplished through publications, conference presentations, and an annual workshop that was open to the community at large. Special effort was made to invite representatives from government agencies and the fuel and transportation industries to attend the workshop.

The CEFRC also had a robust outreach program through an annual summer school, website, newsletter and alliance with other EFRCs. The summer school has proven to be especially popular, attracting ~200 participants of mostly senior graduate students and practicing researchers every year. This will be separately discussed later.

Oversight of the Center was provided by a high-level International Advisory Committee, consisting of members with various technical expertise and background to ensure adequate coverage of various aspects of the research program. Their role was to critique and provide guidance to the research program of the Center, and to provide advice to the sponsoring agency.

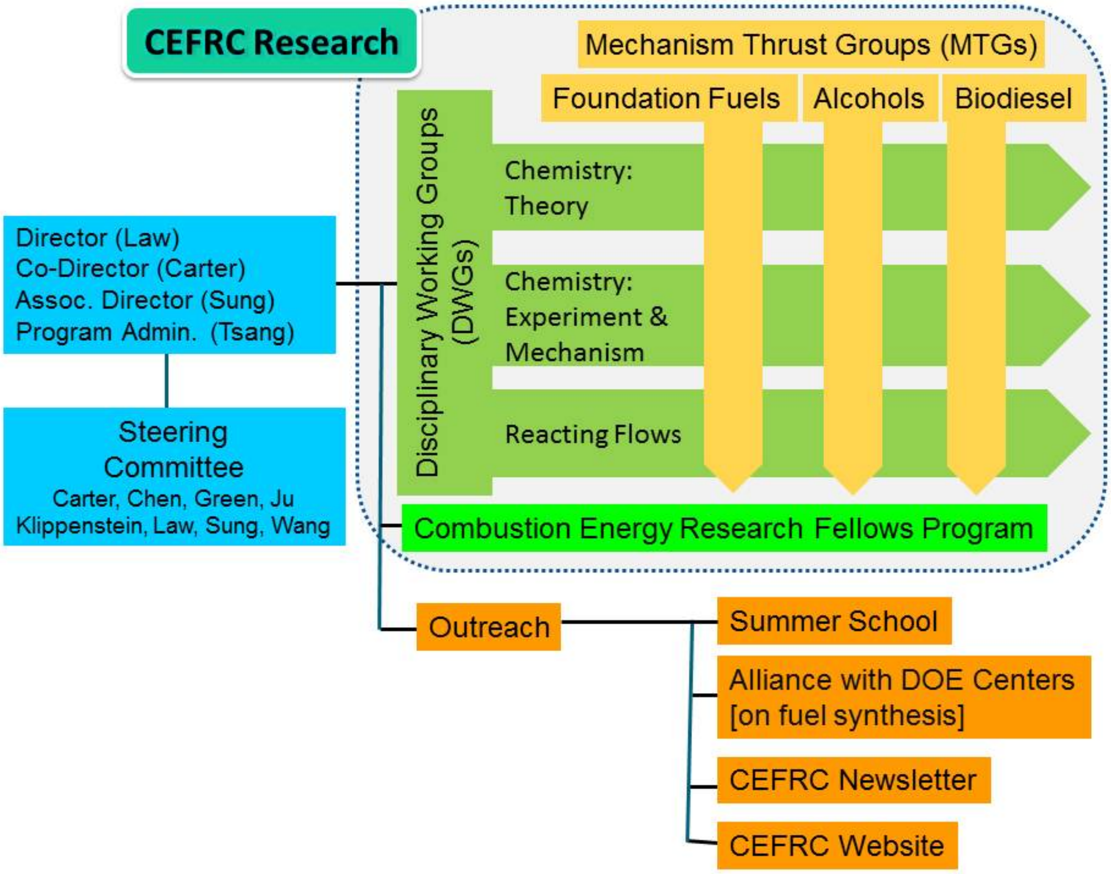

Figure 2. Organization Structure of the CEFRC

B. The Research Team

The world-class team that was assembled is uniquely qualified to address the challenging tasks in a balanced, concerted, and integrated manner. Their expertise covers the entire spectrum of combustion science, from quantum chemistry to turbulent combustion. The team consisted of the following 15 principal investigators, with their specific topical coverages shown in Fig. 3:

- Theoretical Reaction Kinetics: Emily A. Carter (Princeton), Stephen J. Klippenstein (Argonne), Donald G. Truhlar (Minnesota).
- Kinetic Experiments: Ronald K. Hanson (Stanford), Chih-Jen Sung (Connecticut), Nils Hansen (Sandia).
- Reaction Mechanisms: Fredrick L. Dryer (Princeton), William H. Green (MIT), Hai Wang (USC).
- Flame Chemistry, Modeling and Applications: Jacqueline H. Chen (Sandia), Fokion N. Egolfopoulos (USC), Yiguang Ju (Princeton), Chung K. Law (Princeton), Stephen B. Pope (Cornell), Rolf Reitz (Wisconsin),

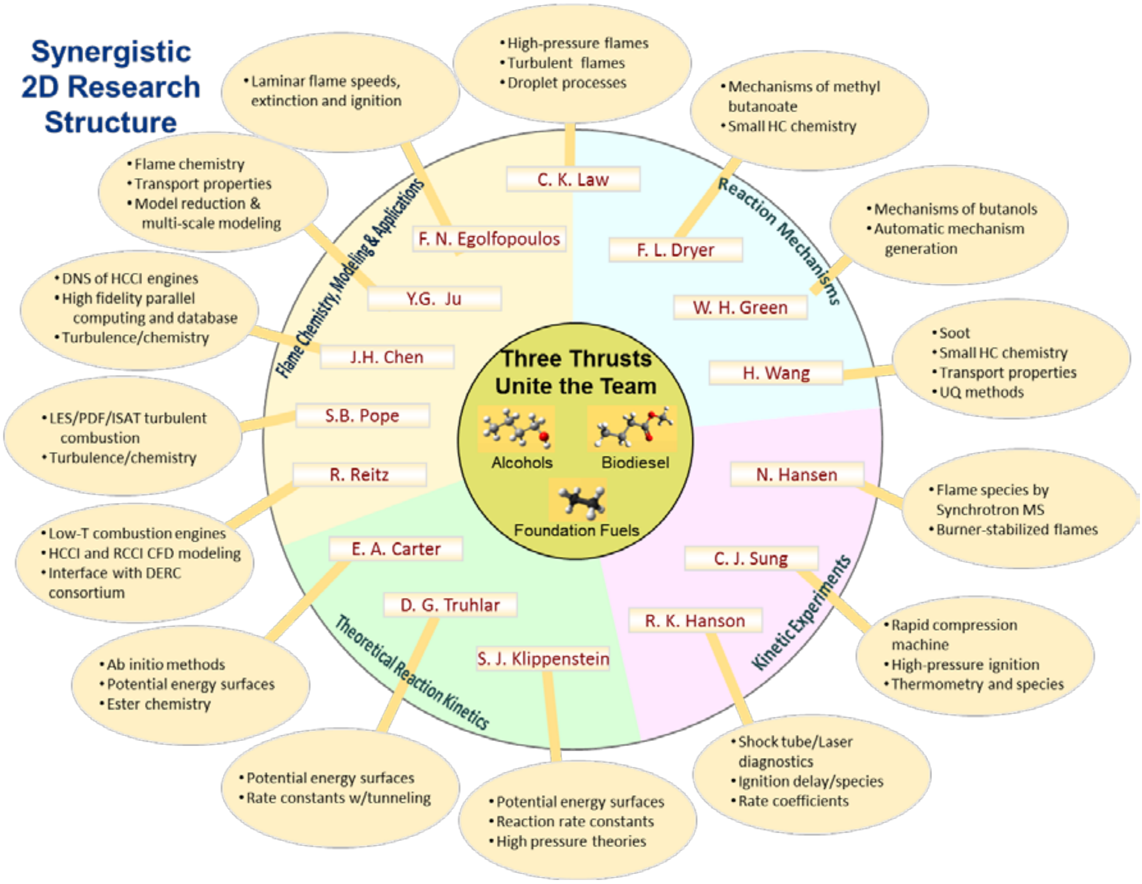

Figure 3. The CEFRC PI and Expertise Structure

These 15 team members are recognized for their scientific contributions and stature as: member of the NAE (4 members) and NAS (2), Fellow of the Royal Society (1), endowed chair professors in academic institutions and distinguished technical staff members of the DOE national laboratories (11), recipient of the NSF CAREER award (3) and the silver medal (5) and gold medal (4) of the Combustion Institute, and associate editor and editor-in-chief of premier journals in chemistry and combustion such as *Journal of the American Chemical Society*, *International Journal of Chemical Kinetics*, and *Combustion and Flame*.

C. The Research Roadmap

Figure 4 is the research roadmap of the CEFRC. Basically our goal is to understand the combustion chemistry of biofuels and other transportation fuels, and develop reaction mechanisms that can describe their pyrolysis and oxidation within various combustor environments with the associated combustion efficiency and pollutant emissions. This was achieved by determining the rate parameters of the individual reactions through high-level quantum mechanical computation, experimentation involving advanced instrumentation, and scrutiny through uncertainty quantification. Furthermore, since these mechanisms are usually extremely large and computationally stiff, it is essential that they are reduced in size and stiffness so that they can be integrated in large-scale computational codes, especially those involving turbulent combustion.

Figure 5 is the specific job sheet for the individual PIs, indicating his/her responsibilities and interactions with the rest of the team.

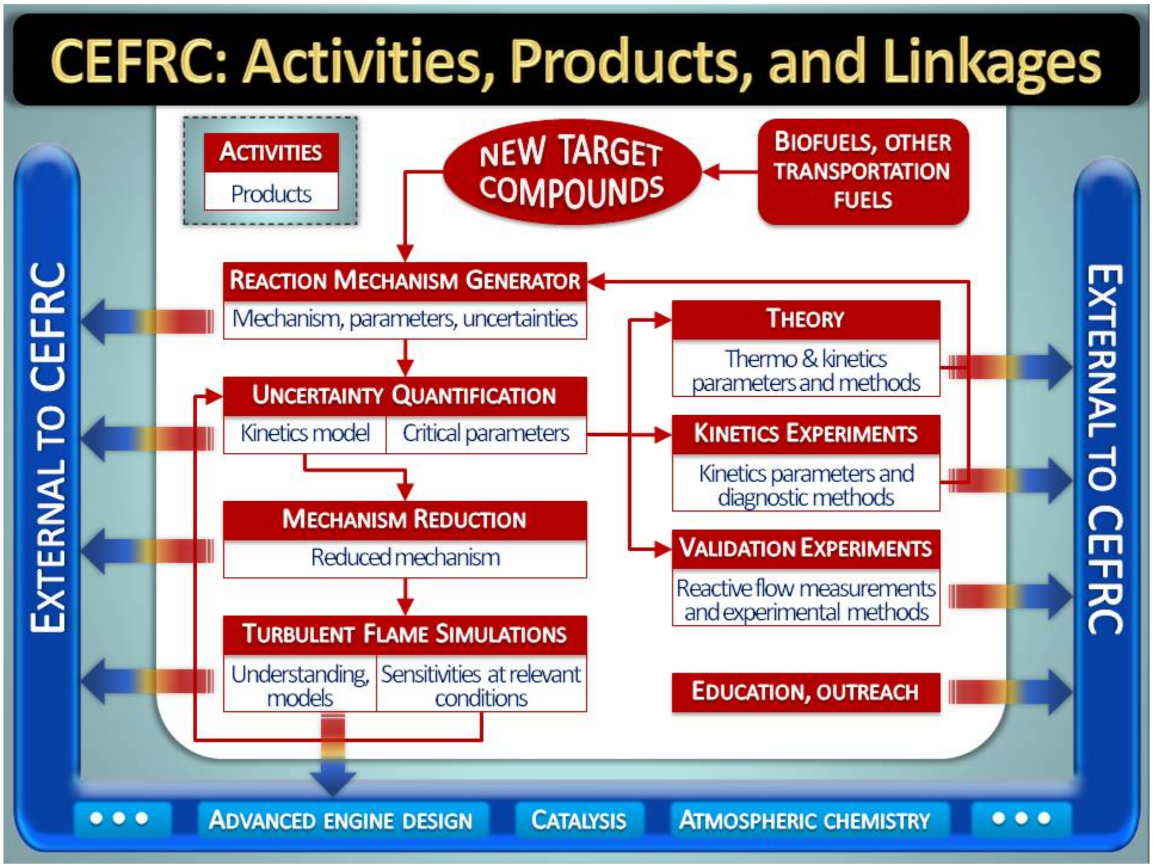

Figure 4. Research Roadmap of the CEFRC

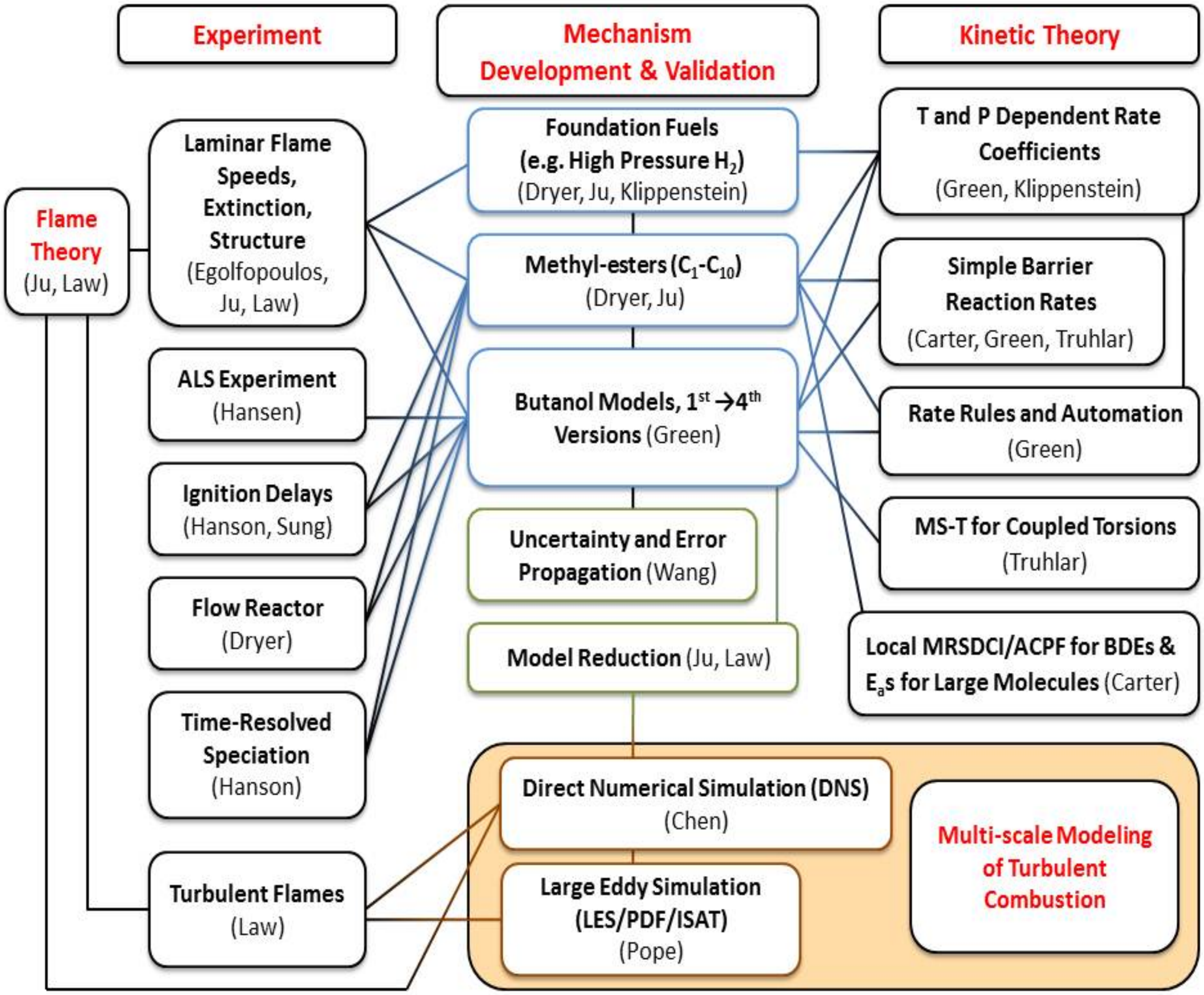

Figure 5: Task Network of the CEFRC PIs

IV. TECHNICAL ACCOMPLISHMENTS

A. Summary of Major Accomplishments

The Center has accomplished many scientific goals over the five year period (August 1, 2009 – July 31, 2014) during which the Center operated on the appropriated funding, and the two additional no-cost-extension (NCE) years during which no further funding was provided. The research results are document in 230 journal publications. The technical accomplishments can be largely grouped into the following four major categories, as: (1) developments in atomistic simulations and large-scale chemical kinetic models, (2) advancement in experimental apparatuses and diagnostic techniques, (3) laminar flame dynamics and chemistry, and (4) detailed experimental and computational studies of turbulence-chemistry interaction, and development of predictive sub-models in engineering simulations. In addition, six legacy review articles [1-6] were published. These major accomplishments are briefly presented in the following.

Development of Chemistry Theory and Chemical Kinetic Models

Butanol was selected for detailed study as it is representative of bio-alcohols produced by fermentation of biomass, and presents many of the challenges arising during the combustion of non-traditional, single-component fuels. The CEFRC has developed a detailed model for the combustion, pyrolysis, and oxidation of butanol isomers [7-11], based largely on high-accuracy quantum chemistry, rate theory, and master equation calculations of pressure dependence and chemical activation. The butanols model predictions have been tested experimentally in many ways, including some advanced techniques developed by our Center. This is one of the best examples in the literature of the accuracy of an alternative fuel model's predictions being comprehensively tested by experiments performed after the prediction is made. Through this large-scale example, it highlights both the strengths and the limitations of the current predictive modeling technologies, and learnings from this test case are informing our studies of other fuels. Building on this, the Center also created improved chemical models for esters, which are biodiesel surrogates [12, 13]. In addition, the chemistry of the gaseous foundation fuels (H_2, CO, C_1–C_4 hydrocarbons) was also revisited by the Center [14, 15].

To accomplish this we have developed and tested several new computational techniques, including a novel MS-T method for handling the strongly coupled rotors common in oxygenated fuel chemistry, automated methods for computing pressure-dependent rate coefficients and identifying important chemically-activated reaction channels, and methods for efficiently handling the many uncertainties in these large mechanisms and the corresponding complicated experiments. We also developed and tested the RPMD method for reliably computing high-accuracy rate coefficients. Fast algorithms developed for size-extensive modifications of multi-reference configuration interaction were also tested for high-accuracy quantum chemistry computations on large molecules.

One of our key findings is that the existing chemical mechanisms are still incomplete in crucial ways. As an example, we have discovered a new, general pathway that plays a role in the low-temperature oxidation chemistry of alkanes when the crucial, second O_2 addition step takes place, and predicted its rate from first principles [16]. This new pathway generates closed-shell, unreactive species instead of radicals, thus slowing autoignition, with additional consequences beyond combustion chemistry; in atmospheric chemistry for instance. Several important reactions were found to involve relatively large molecules with many torsional degrees of freedom, and to have rate coefficients that vary significantly over the normal laboratory-to-engine pressure range. The Center developed and applied new computational chemistry methods to efficiently, yet rigorously handle the large anharmonicities arising in molecules with coupled torsions [17-26], to achieve better accuracy in the thermodynamic parameters of large molecules [27], and to consistently treat multiple-well systems [28-30], where chemical activation, energy transfer, and hot reactive collisions can take place simultaneously.

Advancement in Experimental Apparatuses and Diagnostic Techniques

Scientific discovery advances rapidly when new types of measurements become possible. Through the Center's synergetic effort, a comprehensive array of experimental apparatuses and techniques covering a wide range of thermodynamic conditions were developed [e.g., 7, 31-38] to probe fuel combustion behaviors and high- and low-temperature chemistry of many hydrocarbons and their oxygenated analogs, which in addition facilitated very detailed tests of the computer models. Further, techniques with complementary analyses helped to elucidate the reaction mechanisms for important fuel components, by probing the rates of elementary reactions and by providing reliable experimental data such as ignition delay times, laminar flame speeds, flame structures, and species profiles. Some recent accomplishments are highlighted below.

A new Constrained-Reaction-Volume (CRV) strategy was developed to overcome the pressure and temperature changes behind the reflected shock. The near-constant-pressure ignition delay times provide a new database for low-temperature mechanism development [34]. Time-histories of H_2O, CO_2, and CO were determined using recently developed mid-IR laser diagnostics, with orders-of-magnitude greater detectivity than previously available [39]. In situ temperature and species concentration measurements using two-line laser absorption thermometry in a rapid compression machine (RCM) was developed and demonstrated up to compressed (pre-ignition) pressures of 20 atm [40,41], widening the use of the RCMs for understanding chemical kinetics. The first direct in situ measurement of HO_2 was made using mid-IR Faraday rotation spectroscopy [35], which offers a sensitivity of <1 ppmv over 398–673 K. Further studies extended the measurement to H_2O_2 [42]. Mole fraction profiles for > 40 flame species and the temperature profile were measured for various flames under 15–30 Torr [8, 37]. Molecular-beam mass spectrometry, coupled with single-photon ionization by synchrotron-generated vacuum-UV radiation with high energy resolution and/or electron ionization, was combined with a custom-built reflectron time-of-flight spectrometer to provide high mass resolution. The experimental datasets provide a wealth of information for the development of combustion chemistry models. Using Helium Ion Microscopy for the first time, the smallest soot nanoparticles were found to show structural diversity and inhomogeneity [43, 44], highlighting the deficiency in the basic understanding of the early stages of soot formation.

Laminar Flame Dynamics and Chemistry

The chemical kinetic models developed by the Center were coupled to laminar flow models to determine laminar flame speeds and understand flame ignition and extinction phenomena. Analytical and computational models were developed to quantify how radiation, heat loss, aerodynamic stretch, and radical quenching contribute to the uncertainties in measured laminar flame speeds in a high-pressure spherical bomb [45, 46]. In addition, the heat loss effect on the uncertainty of species sampling in low-pressure, multi-dimensional flat flames was investigated [47]. Measurements of high-pressure laminar flame speeds for the validation of kinetic models were conducted, including those of formaldehyde (CH_2O), dimethyl ether (DME), methyl esters, acetylene, and butene with H_2O/CO_2 dilutions up to 20 atm [48, 49]. By comparing with the experimental data, kinetic mechanisms of DME, methyl formate (MF), methyl acetate (MA), acetylene, and butene were updated and validated. In low- and high-pressure flame chemistry studies, species distributions in flames of DME, MA, and *iso*-butanol, *iso*-pentanol, and small prototypical esters were measured, providing important speciation data for kinetic model development and validation [8, 31].

Significant progress was made in understanding the effects of low-temperature chemistry on ignition to flame transition, through combined experimental and numerical studies of the effects of low-temperature chemistry on laminar flames. The dynamics of low-temperature ignition, high-temperature ignition, ignition transition to flames, knocking, and detonation was studied numerically for temperature and concentration stratified *n*-heptane mixtures [50]. Cool flames were observed and their stability diagram and structures were determined for the first time [51]. To facilitate computationally efficient modeling of multidimensional reacting flows, a method integrating correlated dynamic adaptive chemistry with multi-timescale algorithms was developed [50]. In addition, advances were made in computations of spherically expanding flames and multi-dimensional laminar flames using OpenFOAM [52].

Turbulence-Chemistry Interactions and Predictive Sub-Models in Engine Simulations

One of the unique hallmarks of this Center's research activities on turbulent combustion is its triad of experimentation, DNS, and LES, designed and operating in tandem, to understand and predict the behavior of combustion processes, particularly on issues related to turbulence-chemistry interactions. Using this coupled approach, we have developed a high-fidelity large-eddy simulation framework based on probability density function and in situ adaptive tabulation (LES/PDF/ISAT) methodology [53], and have successfully applied it to a variety of well-designed turbulent laboratory scale flames [54, 55]. Moreover, through a relatively new approach of *a posteriori* comparisons against DNS jet flame data [56, 57], we have assessed multi-scalar reactive mixing closures [58, 59]. Experimentally, multi-scalar measurements of species concentrations and temperature were made in a series of highly turbulent dimethyl ether jet flames [60] to investigate turbulence-chemistry interaction under high-Reynolds-number flame conditions, in addition to providing new benchmark data for assessment and validation of turbulent combustion simulation tools developed within the Center. Direct numerical simulations were performed to understand the effects of composition and thermal gradients on ignition timing and combustion rates in spark-assisted compression ignition (SACI) with lean ethanol/air [61] and multi-stage homogeneous charge compression ignition with *n*-heptane [62].

Furthermore, much of the Center's contributions in the fundamental understanding of fuel chemistry and its behavior in aero-thermo-chemical engine environments are relevant to premixed charge compression ignition (PCCI) engine strategies, which offer the potential for high diesel-like efficiency without the incumbent NO_x and soot emissions. One PCCI strategy, namely dual-fuel reactivity controlled compression ignition (RCCI), has been developed [63]. The RCCI concept uses in situ blending of either dual fuels with distinct auto-ignition characteristics or a fuel and a cetane improver additive to attain controlled high-efficiency clean combustion. Closer to the application, experiments and CFD simulations were conducted on diesel engines using a variety of fuels to help evaluate chemistry mechanisms generated by the Center and other researchers, with focus on the concept of dual-fuel RCCI operation [63, 64]. The combustion performance of oxygenated fuels in RCCI engines with validated CEFRC mechanisms against CFD and methanol/diesel RCCI engine experiments was determined. RCCI combustion simulations made with alternative bio-alcohol fuels (methanol, ethanol, and butanol isomers) confirmed that RCCI combustion can be realized by applying alternative fuels with a cetane improver, which further extends the fuel flexibility of RCCI combustion [65]. The accurate butanol models we developed were successfully used by CEFRC members to predict the performance of butanols in advanced RCCI engines and to identify how these new alternative fuels could be used effectively [65]. It was found that the experimental trends in engine performance with the various fuels were well captured by the CFD simulations.

B. Specific and Coordinated Group Accomplishments (August 1, 2009 to July 31, 2014)

In the following we present the specific and coordinated accomplishments of the three Disciplinary Working Groups (**DWG**s) and the three intersecting Mechanism Thrusts Groups (**MTG**s), during the five-year period of the appropriated funding.

Chemistry Theory DWG

The overarching goal of the chemistry theory group is “to develop methods for accurately predicting thermochemistry and rate coefficients, and to apply these methods to reactions of importance to the development of accurate chemical models for combustion”. The research focused on studies of alcohol chemistry especially butanol chemistry, ester chemistry, and oxidation chemistry.

The work on alcohol chemistry has proceeded along many correlated fronts. We have: (1) computed all the important thermochemistry for three of the butanol isomers (*n*-butanol, *iso*-butanol, and *tert*-butanol), as well as for *n*-pentanol and *iso*-pentanol; (2) computed the product branching ratios for the OH abstraction of the various H atoms in *iso*-butanol, paying particular attention to the role of anharmonicity [7]; (3) built an excellent, well-tested mechanism for *iso*-butanol [8], and partially validated mechanisms for the butanol isomers, *iso*-butane, *iso*-butene, and two pentanol isomers. Some of the tests have included the formation of aromatics in pyrolysis, leading towards soot, with a good degree of accuracy. Furthermore, in an effort to conduct the full soot-in-flame calculation, we have developed a new flame solver, using a new operator-splitting method that we developed, which is excellent for time-marching-to-steady-state [9].

Our work on ester chemistry also proceeded along many correlated fronts. We have: (1) completed the computation of accurate bond dissociation energies of alcohols [10] and biodiesel surrogate fuels [11,12]; (2) calculated the high-pressure-limit rate constants of methyl acetate (MA) and methyl propanoate (MP) H abstraction reactions and pressure-dependent rate constants for the unimolecular dissociation reactions of MA and MP radicals [13]. These rate coefficients are directly incorporated in the mechanisms developed for MA and methyl formate (MF). For MF, the mechanism development efforts led to new rate calculations for the CH_3O system [14], for CH_3OH+OH, and for the reaction of H with CH_2OCHO. Studies were also conducted on the kinetics of methyl butanoate (MB), methyl crotonate, and methyl decanoate.

We have carefully examined the weaknesses in the current thermochemistry and rate-calculation methodology, and identified several paths forward. Particularly interesting and important is how anharmonicity, especially those associated with large-amplitude motions such as torsions, significantly affect both rate and thermochemistry. We have continued to develop improved methods for the treatment of torsional motions in kinetics analyses [15]. We released a new version of *MSTor*, our multitstructural based program for treating torsional anharmonicity, and integrated this with POLYRATE and GAUSSRATE [16]. A key challenge for the future is to make rate calculations more automatic. As a first step, we have been developing a software package that automatically searches for saddle points for H-abstraction reactions.

Experiment and Mechanism DWG

This DWG has made significant advances in measurements of global and detailed kinetic properties of a range of bio-related fuels. Specifically, we have completed the measurement of high-pressure ignition delay times using the new constrained-reaction-volume (CRV) technique for all four butanol isomers [17]. Using multi-species shock tube/laser absorption technique, an improved reaction mechanism was developed for 3-pentanone oxidation and pyrolysis based on the measured OH, CO, CH_3, and H_2O species histories [18], with the concomitant identification of the key reaction pathways in ethyl ester pyrolysis [19]. Additionally, ignition delay time measurements were made for several low vapor-pressure biodiesel surrogates, including methyl laurate, methyl myristate, and methyl palmitate [20]. Furthermore, flow reactor and jet stirred reactor (JSR) experiments were conducted on methyl esters [13], while significant progress was made in the measurement of OH and HO_2 during dimethyl ether oxidation using the mid-IR FRS method [21,22].

In rapid compression machine (RCM) studies of fuel oxidation chemistry, the ignition delays of *iso*-butanol, higher alcohols, methyl esters, syngas mixtures, and propene were measured. The published data for the *iso*-pentanol data cover a range of equivalence ratios at a pressure of 40 bar [23], while results for *iso*-butanol were also measured at compressed pressures of 15 and 30 bar [24,25]. The autoignition behavior of methylcyclohexane was investigated [26] experimentally and computationally, and ignition delay measurements were made for two alkane-rich research gasolines and their surrogates, emphasizing on conditions where peroxy radical chemistry is dominant [27]. In addition, an experimental protocol was developed to probe species concentrations from RCM for GC/MS analyses.

Regarding flame-based investigations, the absolute composition of burner-stabilized flames of *iso*-butanol, *iso*-pentanol, and small prototypical esters were measured [28]. Data were also taken for methyl-pentanoate, methyl-hexanoate, methyl-hex-3-enoate, and 2-methylbutanol flames. Significant progress was made to couple JSR with molecular beam synchrotron photoionization mass spectrometry to enable studies of the mechanism of fuel oxidation. In collaboration with several international research groups, data were taken and analyzed with focus on the low-temperature oxidation of *n*-butane, dimethyl-ether (DME), *n*-heptane, and 2-methylhexane. In particular, in collaboration with colleagues at the Bielefeld University in Germany, the morphology of nascent soot down to 3 nm in size was examined, for the first time, by using a newly available Helium Ion Microscope [29, 30]. A coupled burner-stabilized stagnation flame and flow reactor was developed to follow the oxidation kinetics of nascent soot [31].

Reacting Flows DWG

Substantial advances were made in the understanding and quantitative predictability in chemically reacting flows, as follows. (1) Uncertainty quantification of flame speed and species measurements: Analytical and computational models to quantify the uncertainties of radiation, heat loss, stretch, and radical quenching on flame speeds in a high pressure spherical bomb were developed [32, 33]. In addition, heat loss effect on the uncertainty of species sampling in low-pressure flat flames was investigated [34]. (2) Measurements of high-pressure flame speeds for the validation of kinetic models: Flame speeds of CH_2O, DME, methyl esters, acetylene, and butene with H_2O/CO_2 dilutions up to 20 atm were measured [35, 36]. Kinetic mechanisms of DME, MF, MA, acetylene, and butene were updated and validated. (3) Low- and high-pressure flame chemistry studies: Species distributions in low-pressure flames of DME, MA, and *iso*-butanol, *iso*-pentanol, and small prototypical esters were measured, providing important speciation data for kinetic model development and validation [13, 28]. (4) Understanding the effects of low-temperature chemistry on ignition to flame transition: Significant progress was made in experimental and numerical studies of the effects of low-temperature chemistry on laminar and turbulent flames. The dynamics of low-temperature ignition, high-temperature ignition, ignition transition to flames, knocking, and detonation was studied numerically for temperature and concentration stratified *n*-heptane mixtures [37]. Cool flames were observed and their stability diagram and structures were examined for the first time [38]. (5) Development of computationally efficient methods for multidimensional modeling: Correlated dynamic adaptive chemistry model with integration to multi-timescale method developed [37, 39]. In addition, advances were made in computations of spherically expanding flames and multi-dimensional laminar flames using OpenFOAM [40]. A new parallelization strategy using the graphics processing unit (GPU) for the chemistry terms of a reactive-flow solver and the CPU for the simulation and transport was developed [41, 42]. (6) Development of turbulent flame experiments and theory: Experimental study of low-temperature ignition on turbulent flame speeds conducted, and joint experiment and DNS study of a turbulent DME jet flame undergoing local extinction and re-ignition performed [43]. (7) New DNS and LES/PDF calculations to investigate turbulence-chemistry interactions in engine relevant environments: Detailed computational simulations were performed for the DNS of ignition of lean PRF/air mixtures with temperature inhomogeneities under high pressure and intermediate temperature, DNS of lifted high-pressure DME jet flames [44], CFD and chemical kinetics model validations using CEFRC mechanisms and methanol/diesel RCCI engine experiments, LES/PDF and PDF modeling of DME jet flames, and RCCI combustion simulations with alternative bio-alcohol fuels (methanol, ethanol, butanols) [45].

Foundation Fuels MTG

Using shock tube/laser diagnostics, propene ignition delay times and the OH time-histories during ethylene oxidation were determined, and the reactions of acetaldehyde and formaldehyde were studied. Mechanism refinement was made for methanol and MF oxidation and pyrolysis based on the measurements of CH_3OH and CO concentration time-histories [46]. RCM experiments were conducted to observe the autoignition behavior of propene under compressed pressures of 10 and 40 bar and over a range of equivalence ratios and level of dilution. Together with the shock tube work, these studies form the basis for extending the current C_0–C_2 chemistry to the lesser constrained C_3–C_4 chemistry.

The C_0–C_2 model has undergone extensive development. The trial model was compiled and validated against 200 sets of data, ranging from shock tube ignition delay and multispecies time histories, to flame speeds and species profiles in flow reactors describing the pyrolysis and combustion of H_2, CO/H_2, CH_4, CH_2O, and C_2H_6. Among the validation datasets, 148 data points were chosen as targets for model uncertainty minimization. A majority of the response surfaces were developed for the targets. The Method of Uncertainty Minimization by Polynomial Chaos

Expansions (MUM-PCE) was extended to uncertainty quantification and minimization for mechanism reduction [47].

Alcohols MTG

The goals and accomplishments for this thrust are as follows. (1) Thermochemistry of butanols and related radicals: We have performed advanced calculations using MR-ACPF, CCSD(T)-F12, and advanced methods for handling anharmonicity, and quantified the residual errors in these *a priori* computations [7,10]. (2) Calculation of rate coefficients for reactions of importance to butanol chemistry: Full model was constructed based largely on quantum calculations. We discovered and computed key low-temperature reaction of ketohydroperoxides [48]. High-accuracy calculations on key steps [7, 49] were also completed. (3) Pyrolysis and oxidation studies of *iso*-propanol, *n*-butanol, *tert*-butanol, and measurements of rates of unimolecular reactions: We have measured these species in the flow reactor in both pyrolytic and oxidative conditions [24, 25, 50], as well as the butanols in advanced shock tube pyrolysis experiments [51]. We also collaborated with NIST and Ghent in additional shock tube and flow reactor measurements and their interpretation [8, 49]. (4) Ignition delay measurements for butanol isomers in the shock tube using the new CRV method: Significant low-temperature data were obtained [17, 52, 53]. This CRV dataset partially overlaps with that measured using RCM, confirming the results. (5) Accurate chemistry models for butanols, butanes, and butenes which predict flame measurements: We have completed high accuracy model for *iso*-butanol, which accurately predicted flame data measured and all existing experimental data with T>750 K [8]. Good models for the other butanol isomers, butanes, and butenes were constructed. (6) Measurement of concentration profiles in *iso*-butanol and *iso*-pentanol flames: Very detailed datasets (~40 species including radicals and reactive enols) were obtained [28]. We have also measured the concentration profiles of another pentanol isomer, 2-methylbutanol [54]. (7) Turbulent flame modeling of *iso*-butanol using LES and comparison with DNS: Originally we planned to use *iso*-butanol as the test fuel, but the team decided to instead focus on DME, facilitating detailed experimental measurements. (8) Effects of alternative bio-alcohol fuels in an advanced engine (RCCI): Butanols and smaller alcohols were shown to all work well with cetane improvers [45].

Biodiesel MTG

The goals and accomplishments for this thrust are as follows. (1) Accurate calculations and measurements of elementary reaction rates of small methyl ester oxidation: The bond dissociation energies (BDES) of biodiesel surrogate fuels and accurate estimates of elementary reaction rates were calculated [11, 12]. A quantum anharmonic umbrella mode treatment and quantum and semi-classical multidimensional torsional treatments were adopted in the master equation codes, whose additions allowed more accurate rate estimate for systems such as the decomposition of MF. Accurate rate constants of H-abstraction reactions of MF, MA, and MP, and pressure-dependent unimolecular dissociation reactions of MF, MA, MP, and methanol radicals were calculated. The predicted rates agreed well with available experimental rate constants. (2) Kinetic studies of methyl ester oxidation in flow reactor, JSR, RCM, and shock tube: Pyrolysis and oxidation of MF, MA, and MP in a flow reactor between 500 and 1100 K were measured. JSR experiments were conducted to understand the effects of double bond on fuel oxidation [13]. The RCM experiments for MA, MP, and MB were conducted under high pressures (up to 75 bar). First quantitative measurements of CH_3OH time-histories in shock tube experiments were performed. Key reaction pathways in ethyl ester pyrolysis were identified by using multi-species shock tube/laser absorption measurements. The first ignition delay time measurements for very low pressure biodiesel surrogates including methyl laurate, methyl myristate, and methyl palmitate were conducted [20]. (3) Species and flame speed measurements of methyl ester oxidation in flames: Flame speeds of MF, MA, and MP and flame structures of MP and methyl hexanoate measured. These data were used to validate the kinetic mechanisms of esters [13]. (4) Development of updated, pressure-dependent methyl ester kinetic mechanisms: Mechanism refinement for methanol, MF and MA has been completed based on theoretical calculations and experimental results. Mechanism refinement of larger methyl esters including MP and MB is in progress.

Legacy Review Papers

A major Center goal throughout the funding period is to develop a collection of legacy review/position papers on combustion chemistry, aiming to summarize the key achievements of the Center as well as elsewhere, and point to the deficiencies in current methodologies and findings that would require serious and coordinated remediation. This suite of papers is a concrete and useful deliverable to account for the support that we received. Consequently, five review articles on the study of combustion chemistry by using *shock tubes* [1], *flow reactors* [2], *rapid compression machines* [3], and *flames* [4], and on *uncertainty quantification* [5] were prepared and published in the highly-regarded journal *Progress in Energy and Combustion Science*, which has an Impact Factor exceeding 16. In addition, a review paper on *theoretical reaction dynamics and chemical modeling of combustion* [6] was delivered as a plenary lecture at the 35th International Combustion Symposium and published in the symposium proceedings. It is clear that through the CEFRC team effort, together with renowned US and international colleagues who are external to the Center, we have significantly advanced the science of combustion energy, and have pointed the way to the future.

C. Accomplishments during No-Cost-Extension Period (August 1, 2014 to July 31, 2016)

While funding for the CEFRC was terminated on August 31, 2014, the Center PIs have continued to work on projects along the stated goals of the proposal, being sustained by minimal residue funds and in some instances leveraged with other sponsored programs. Consequently, research was conducted on extreme combustion characterized by high-pressure, low-temperature chemistry and transport, on near-limit laminar and turbulent flames, on the determination of thermochemistry and thermochemical kinetics of alcohols, biodiesel and foundational fuels, on the development of detailed and reduced-order reaction models of biofuels, on soot formation in biofuels, on uncertainty quantifications of foundational fuels chemistry, and on various topics that are of general interest to the mission of the CEFRC. Research papers of high quality were prepared and published in leading journals, and our PIs continued interacting with each other and advocating what we learnt through the CEFRC experience to the combustion community in general. Furthermore, the Summer School on Combustion has been continuously offered every year, with alternate sources of funding. The following is an accounting of the research progress that has been made during this extraordinary period of operation, sustained by our dedication and devotion to the science that we love, and our obsession to do something meaningful for the society.

Scaling Relation for High-Temperature Biodiesel Surrogate Ignition Delay Times

High-temperature Arrhenius ignition delay time correlations are useful for revealing the underlying parameter dependencies of combustion models, for simplifying and optimizing combustion mechanisms for use in engine simulations, for scaling experimental data to new conditions for comparison purposes, and for guiding in experimental design. We have developed a scaling relationship for Fatty Acid Methyl Ester (FAME) ignition time data taken at high temperatures in 4%O_2/Ar mixtures behind reflected shocks using an aerosol shock tube.

Additionally, we have combined our ignition delay time data for methyl decanoate, methyl palmitate, methyl oleate, and methyl linoleate with other experimental results in the literature in order to derive fuel-specific oxygen-mole-fraction scaling parameters for these surrogates. We also determined the significance of the parameter values and compared our correlation to others found in the literature for different classes of fuels, and contrast the above expression's performance with correlations obtained using leading FAME kinetic models in 4%O_2/Ar mixtures.

Pyrolysis and Oxidation of Methyl Acetate in a Shock Tube: A Multi-species Time-history Study

High-temperature methyl acetate (MA) pyrolysis and oxidation were studied behind reflected shock waves using laser-absorption species time-history measurements of CO, CO_2, OH and H_2O. The shock tube experiments covered a temperature range of 1401-1605 K for MA pyrolysis (0.2% MA/Ar) and 1423-1674 K for MA oxidation (0.4% O_2, $\phi = 1$), and pressures around 1.5 atm. A recent kinetic mechanism developed originally for interpreting the flow reactor and low-pressure flame data was adopted in this work to simulate and compare with the current experiments. The dominant sensitivity of CO_2 concentration to the MA unimolecular decomposition reaction (MA $\leftrightarrow CH_3 + CH_3 + CO_2$) enables the shock tube determination of its rate coefficient by monitoring the CO_2 time-history during MA pyrolysis. Excellent agreement was found between several of recent theoretical calculations and our current measurements. The measured CO and CO_2 time-histories during MA pyrolysis were well predicted, showing that MA is mainly consumed via two unimolecular decomposition pathways to produce CO_2 directly, or CH_3OH+CH_2CO leading eventually to CO. A relatively complete description of MA oxidation behavior was given by measuring CO, CO_2, OH and H_2O time-histories at the same temperature and pressure (1480 K, 1.5 atm). Despite the over-prediction of MA ignition delay times by 18-40% between 1623-1423 K, the kinetic model is able to well capture the plateau levels and the peak values of all the measured species profiles, as well as to predict the characteristic two-stage formation of CO_2 in an excellent way.

Diffusive Ignition of Butanol Isomers at Atmospheric and Elevated Pressures

Critical to the development of predictive combustion models is a robust understanding of the coupled effects of chemical kinetics and convective-diffusive transport at both atmospheric and elevated pressures. A new variable-pressure non-premixed counterflow ignition experiment was designed to address the need for well-characterized reference data to validate such models under conditions sensitive to both chemical and transport processes. A comprehensive characterization of system behavior was provided to demonstrate boundary condition and ignition quality as well as adherence to the assumption of quasi-one-dimensionality, and suggest limitations and best practices for counterflow ignition experiments. This effort revealed that the counterflow ignition experiment requires special attention to ignition location in order to ensure that the assumption of quasi-one-dimensionality is valid, particularly at elevated pressures. This experimental tool was then applied to the investigation of butanol isomers for pressures of 1-4 atm, pressure-weighted strain rates of 200-400 s^{-1}, and molar fuel loading in nitrogen-diluted mixtures of 5-25%. Comparison of the parametric effects of varied pressure, strain rate, and fuel loading amongst the isomers facilitates a comprehensive evaluation of the effect of varied structural isomerism on transport-affected ignition. The experimental results were simulated using isomer-specific skeletal mechanisms developed from two comprehensive butanol models available in the literature, and were used to validate and assess the performance of these models. Comparison of the experimental and computational results revealed that while both models largely capture the trends in ignition temperature as functions of pressure-weighted strain rate, fuel loading, and pressure, both models over-predict the experimental data to an appreciable extent for all isomers. In addition, neither model captures the experimentally-observed ignition temperature rankings. While the nonpremixed counterflow system is found to exhibit large sensitivities to changes in the fuel diffusivity, within reasonable bounds errors in the transport model cannot account for disparities between the experimental and numerical results. Further sensitivity and path analyses reveal that significant differences exist between the fuel breakdown descriptions of the two butanol models, suggesting that further work is required to better define these pathways, particularly the branching ratios from the hydroxybutyl radicals and the breakdown chemistry of the butene isomers.

Soot and PAH Formation of Butane and Butanol Isomers

An investigation of soot and polycyclic aromatic hydrocarbons (PAHs) formation in counterflow non-premixed flames was carried out using non-intrusive in-situ optical diagnostics measurement techniques, including Laser Induced Incandescence, Planar Laser Induced Fluorescence (PLIF) and Light Extinction. These measurements aid in better understanding of the soot and PAH formation processes. Considering these, the soot and PAH formation processes for butane and butanol isomers (C_4 fuels) were studied. Under the investigated conditions, butane isomers were observed to form more soot than butanol isomers, thereby showing the effect of the hydroxyl group. The effects of isomeric structural differences on sooting propensity were also observed within the butane and butanol isomers. In addition, while soot volume fraction is seen to increase with increasing fuel mole fraction, the ranking of sooting propensity for these C_4 fuels remained unchanged. For the conditions studied, the sooting tendency ranking generally follows *n*-butane > *iso*-butane > *tert*-butanol > *n*-butanol > *iso*-butanol > *sec*-butanol. The counterflow non-premixed flames were also simulated using the gas-phase chemical kinetic models available in the literature to compute the spatially-resolved profiles of soot precursors, including acetylene and propargyl. For these C_4 fuels, the PAHs of the various aromatic ring size groups (2, 3, 4, and larger aromatic rings) were characterized and compared in non-premixed combustion configuration. In particular, the formation and growth of the PAHs of different aromatic ring sizes in these counterflow flames was examined by tracking the PAH-PLIF signals at various detection wavelengths. PAH-PLIF experiments were conducted by blending each of the branched-chain isomers with the baseline straight-chain isomer, in order to study the synergistic effects. The fuel structure effects on the PAH formation and growth processes were also analyzed by comparing the PAH growth pathways for these C_4 fuels. A chemical kinetic model available in the literature that includes both the fuel oxidation and the PAH chemistry was also used to simulate and compare the PAH species up to A_4 rings.

Mechanism of Soot Formation

A series of studies were conducted to examine a range of fundamental questions concerning the mechanism of soot formation. Using the Helium Ion Microscopy, we showed for the first time that nascent soot is not structurally homogeneous. They were found to be far more reactive towards oxidation by molecular oxygen than mature soot. An ethylene flame for probing soot formation, from nucleation to size growth was developed and is currently serving as a benchmark flame for many models of soot formation. The uniqueness of the study is that the evolution of soot size distribution was reproduced quantitatively in three separate research facilities and over four different burners. Additionally, the mass density of nascent soot was determined for the first time, showing drastically smaller density than the value traditionally assumed in all reaction models of soot formation.

Autoignition Response of *n*-Butanol and Its Blends with Gasoline PRFs

Fundamental ignition data from a rapid compression machine were studied for *n*-butanol blended with key gasoline components, including *n*-heptane and *iso*-octane. This fundamental database provides a reliable validation set for chemical kinetic models of *n*-butanol with *n*-heptane and *iso*-octane. Additionally, the experimental results give insight into how *n*-butanol affects the autoignition chemistry of *n*-heptane and *iso*-octane which are representative of the *n*-alkane and *iso*-alkane chemical classes in gasoline. The present ignition data show that the addition of *n*-butanol to *n*-heptane leads to a decrease in overall reactivity as manifested by the increase in both the first-stage and the total ignition delays. The addition of *n*-butanol to *iso*-octane is found to lead to shorter total ignition delays under fuel lean conditions important for HCCI combustion. Ignition response was also studied under stoichiometric conditions by keeping the charge temperature at the end of compression approximately constant while varying blending ratios, where an unusual behavior was seen when a clear two-stage ignition is present. Under these conditions, addition of *n*-butanol to *iso*-octane decreases the second-stage ignition delay time (τ_2) while addition to *n*-heptane increases τ_2. An *n*-butanol/PRF mechanism was also generated by a systematic merger of previously reported chemical kinetic schemes for individual constituents in the literature. This mechanism was found to generally well predict the qualitative and quantitative trends for the autoignition of the binary fuel blends studied in this work, while some discrepancies between experiments and simulations for *n*-butanol/*iso*-octane blends were noted. The present new measurements represent targets for the next generation of chemical kinetic models which will require more accurate rate constants and thermodynamic properties.

Furthermore, the laminar flame speeds and ignition temperatures of nonpremixed counterflow were measured experimentally for the butene isomers at normal and elevated pressures. Results show that the flame speed increases in the order of isobutene, trans-2-butene, and 1-butene. In addition, isobutene has the highest ignition temperature, while those of trans-2-butene and cis-2-butene are quite similar to each other and are slightly higher than that of 1-butene. These results indicate that the reactivities of the butene isomers increase in the order of isobutene, 2-butene, and 1-butene. Furthermore, the critical reaction paths for butene isomer oxidation during ignition were analyzed by sensitivity analysis and a new kinetic model was developed with updated rate coefficients from *ab initio* calculation and kinetic theories. Simulations with the present kinetic model agreed well with the measured laminar flame speeds, counterflow ignition temperatures as well as recent laminar flame speciation and ignition delay times for all butene isomers.

Studies on Low-Temperature Chemistry and Cool Flames

Various aspects of the low-temperature chemistry, negative-temperature coefficient (NTC), and cool flame responses were studied. We first examined the controlling mechanisms of the upper turning point of the NTC curve. Using *n*-butane, *n*-heptane and *iso*-octane as representative fuels exhibiting the NTC behavior, it was found that the global behavior of the turnover states exhibits distinctive thermodynamic and kinetic characteristics under different pressures, in that the ignition delay at the turnover states shows an Arrhenius dependence on the temperature T and an approximate inverse quadratic power law dependence on the pressure P. These global behaviors imply that the temperature and pressure of the turnover states are not independent and can be correlated by an Arrhenius dependence, as $\ln P \propto 1/T$. Further theoretical analyses demonstrated that such turnover states result from the competition between the low-temperature chain branching reactions and the decomposition of the intermediate species, and therefore correspond to a critical value, α, of the ratio of OH production from low-temperature chemistry. In addition, the ignition delay at the turnover state can be well correlated by the analytical expression derived by Peters, with the further demonstration that the pressure dependence of the turnover ignition delay mainly results from the H_2O_2 decomposition reaction. Comparison of the present results with the literature experimental data of *n*-heptane ignition delay time showed very good agreement.

We then investigated the NTC-affected ignition and low-temperature flames in nonpremixed DME/air counterflow. In particular, the presence of low-temperature chemical reactivity was detected nonintrusively by using a photomultiplier tube combined with a filter to capture the chemiluminescence of HCHO, which is a characteristic intermediate species formed in low-temperature chemistry. Furthermore, the ignition temperature was determined through high-sensitivity infrared imaging with proper discrimination of the background signal. Experimental results showed that the transport-coupled low-temperature, NTC chemical reactivity is enhanced with smaller strain rate, higher air boundary temperature, and is insensitive to the fuel concentration. These findings agree well with those obtained from computation using detailed chemistry, leading to further identification of the controlling chemistry.

We next note that since the low-temperature chemical kinetics is promoted at elevated pressures, the ignition and extinction of nonpremixed cool flame at elevated pressures were experimentally and computationally investigated in the counterflow. Specifically, the hysteretic ignition and extinction behavior of the nonpremixed cool flame was for the first time observed and quantified. S-curve analysis was conducted to demonstrate the thermal and chemical structure of the cool flame and to elucidate the dominant chemical pathways during the ignition and extinction processes. The dominant low-temperature chemical reactions shift from those responsible for radical runaway to exothermic reactions that sustain the cool flame. Increasing the ambient pressure and/or the oxygen concentration in the oxidizer stream promote the heat release from the cool flame, and hence, result in an extended hysteresis temperature window between ignition and extinction. It is further noted that while the observed cool flame ignition temperatures were well predicted by computation, significant discrepancies existed for the extinction temperatures based on the well-adopted reaction mechanism used. Possible reasons were discussed to facilitate further cool flame studies and the development of the low-temperature chemistry.

A Direct Numerical Simulation of Cool-flame Affected Autoignition

In this study, a two-dimensional direct numerical simulation (DNS) is conducted to provide a fully resolved description of ignition at diesel engine-relevant conditions. The DNS was performed at a pressure of 40 atmospheres and at an ambient temperature of 900 K using dimethyl ether (DME) as the fuel, with a 30 species reduced chemical mechanism. At these conditions, similar to diesel fuel, DME exhibits two-stage ignition. The focus of this study is on the behavior of the low-temperature chemistry (LTC) and the way in which it influences the high-temperature ignition. The results show that the LTC develops as a “spotty" first-stage autoignition in lean regions which transitions to a diffusively supported cool flame and then propagates up the local mixture fraction gradient towards richer regions. The cool-flame speed is much faster than can be attributed to spatial gradients in first stage ignition delay time in homogeneous reactors. The cool-flame causes a shortening of the second-stage ignition delay times compared to a homogeneous reactor and the shortening becomes more pronounced for richer mixtures. Multiple high-temperature ignition kernels were observed over a range of rich mixtures that are much richer than the homogeneous most reactive mixture and most kernels form much earlier than suggested by the homogeneous ignition delay time of the corresponding local mixture. Overall, the results suggest that LTC can strongly influence both the timing and location in composition space of the high-temperature ignition.

Polybrachial Structures in Dimethyl Ether Edge-flames at NTC Conditions

The structure and stabilization mechanism of partially premixed, laminar, dimethyl ether (DME) flames were investigated using two-dimensional DNS. The simulations were performed at a pressure of 40 atmospheres and at oxidizer temperatures of 700, 900, 1100, 1300, and 1500 K, while keeping the lift-off length approximately fixed by varying the inlet velocity. At this pressure, DME exhibits two stage ignition below approximately 1100 K and a negative temperature coefficient (NTC) regime from approximately 800–1100 K. The DNS results were investigated by considering the thermochemical structure of the flames and by applying a transport budget analysis to key chemical species. The results show a transition from a lifted flame stabilized by conduction and diffusion-assisted flame propagation to a flame stabilized by autoignition with increasing temperature. At 700 K, the flame has a classical tribrachial structure similar to freely propagating edge flames at non-autoignitive conditions. The intermediate temperature cases reveal a complex transition involving multiple heat release pathways upstream of the stabilization point. At 900 K, the flame consists of a main-tribrachial structure and an additional upstream branch due to low temperature chemistry, constituting a tetrabrachial flame. At 1100 and 1300 K, two upstream branches were observed in addition to the main tribrachial structure, one due to low temperature chemistry and the other due to high temperature chemistry, which initiates autoignition and stabilizes the flame, hence constituting a pentabrachial flame. At 1500 K, the low temperature upstream branch is suppressed, so there is only one upstream branch due to high temperature chemistry which proceeds to autoignition, this flame has a tetrabrachial structure, but one which is different from that observed in the 900 K case.

Systematic Extraction of Laminar Flame Speeds

Spherically expanding and counterflow flame configurations are used extensively to determine laminar flame speeds. Significant advances have been made over the years with both the theoretical and experimental aspects of these standard experiments. However, discrepancies still persist in reported laminar flame speed data, hence raising the question of accuracy and consistency. Among the probable reasons that the discrepancy among reported data is that laminar flame speed is a derived and not a directly measured physical quantity, leaving thus room for interpretations that typically introduce additional uncertainties. In the present investigation, a combined experimental and modeling study was carried out in both configurations. Ethylene and *n*-heptane flames were considered and the flow velocities were measured using particle image velocimetry. The accuracy and consistency of the results were assessed by comparing directly measured and directly computed physical properties. It was shown that the directly measured data in both configurations are consistent based on comparisons against the results of direct numerical simulations.

Direct Numerical Simulations of Probe Effects in Low-Pressure Flame Sampling

Speciation studies of low-pressure flames using intrusive sampling and molecular beam mass spectrometry analysis are essential towards developing and validating combustion models. In order to assess potential probe-induced effects, direct numerical simulations of a realistic experimental configuration were carried out using a finite-volume fully compressible code as well as detailed descriptions of chemical kinetics and molecular transport. A 50 mbar rich propene/oxygen/argon flame was modeled for which experimental data are available. The effects of the probe and supporting flange, non-adiabaticity, sampling location, and compressibility when there is suction through the sampling orifice were assessed. Results showed that even under adiabatic conditions, the presence of the probe-flange assembly affects the flow field two-dimensionally. Furthermore, effects of heat loss and compressibility were found to be significant at the sampling location. Important radicals for fuel oxidation such as OH and HCO, and for soot formation such as C_3H_3 are affected by the sampling procedure and their concentrations at the sampling location can differ notably compared to unperturbed one-dimensional flames.

Uncertainty Quantification of Foundational Fuels Chemistry

A review article was published summarizing the current state of knowledge in the kinetic uncertainty of foundational fuel chemistry and the methods of uncertainty quantification. Foundational Fuel Chemistry Model (FFCM-1) is available online (http://web.stanford.edu/group/haiwanglab/FFCM1/pages/releasenotes.html). The primary objective is to advance a reaction model for the combustion of small hydrocarbon fuels using up-to-date kinetic knowledge and with well-defined predictive uncertainties. One key focus of the current work is to analyze and understand the knowledge gaps in the foundational fuel chemistry for combustion. To this end, discussions about future work critical to achieving quantitative kinetic predictions are perhaps more important than the FFCM-1 reaction model itself. In particular, optimization and uncertainty evaluation provide useful guidance for future experimental and theoretical studies of specific reaction kinetics and combustion responses. Details can be found at the model release web site. Experimental data evaluation and reaction model reduction are also of relevance to kinetic uncertainty quantification and propagation. Studies were conducted to examine the impact of model reduction on model uncertainties using *n*-butane combustion as an example, and to explore the methods to rationally quantify the combustion experimental data uncertainties.

Uncertainty Quantification and Minimization in Spherical Expanding Flame Experiments

The spherically expanding flame method is the only approach for measuring laminar flame speeds at thermodynamic states that are relevant to the high-pressure environments within internal combustion engines. In the present study, a comprehensive evaluation of data obtained under constant pressure and constant volume conditions was carried out through experiments, development of a mathematically rigorous method for uncertainty quantification and propagation, and advancement of numerical models that describe the experiments accurately. With the aid of direct numerical simulations, an approach was proposed to derive laminar flame speeds in constant pressure experiments by eliminating the need for using extrapolation equations developed on simplifying assumptions, which are known to be susceptible to major errors under certain conditions. The propagation of spherical flames under constant volume conditions was investigated through experiments carried out in a spherical chamber and the use of two numerical models. The first involves the solution of the fully compressible one-dimensional conservation equations of mass, species, and energy. The second model was developed based on thermodynamics similarly to existing literature, but radiation loss was introduced in the optically thin limit and approximations were made to allow for re-absorption. It was shown that neglecting radiation in constant volume experiments could introduce errors as high as 15%.

The uncertainties associated with the extrapolation of stretched flames to zero stretch in flame speed measurements were further investigated, using expanding spherical flames. Direct numerical simulations of time evolution of expanding spherical flames from a small ignition kernel to a propagating front with sufficiently large radius provide the relations between stretched flame speed and stretch rate that can be used to assess the uncertainty of extrapolation models. It was found that the uncertainties of flame extrapolation largely depend on the mixture Lewis numbers. While the uncertainty is minimized for stoichiometric H_2/air and *n*-heptane/air flames, the uncertainty can be as high as 60% for lean H_2/air mixtures, and 10% for lean and rich *n*-heptane/air mixtures. The present findings show that the weakly stretched flame assumption fails for lean hydrogen mixtures, and give a good explanation to the discrepancies between experiments and model predictions for H_2/air as well as the discrepancies between measurements of *n*-heptane/air using spherical and counterflow flames. A relation between extrapolation uncertainties and the product of Markstein number and Karlovitz number is provided, which can be useful for uncertainty quantification of future and existing measurements.

We have also examined a seemingly trivial issue in the representation of the concentration dependence of laminar flame speeds, namely the apparently large scatter found for the laminar flame speeds of fuel-rich mixtures as compared to those of lean mixtures. Using the hydrogen/air flame speed at atmospheric pressure as an example, it is demonstrated that this perceptive notion is based on a rather uninformed data presentation. It is shown that the cause for the notion has little to do with the data itself, but it is the result that the flame speed data are customarily plotted against the equivalence ratio, which by its asymmetric definition, compresses the data for lean mixtures and expands the data for rich ones. When plotting the flame speed against the symmetrized equivalence ratio defined as $\overline{\phi} \equiv \phi/(1+\phi)$, it can be readily shown that the flame speed data have, in fact, similar uncertainties across the entire range of stoichiometric mixtures tested thus far. A statistical analysis of an extensive set of flame speed data further illustrates the above point, namely, a nearly invariant confidence interval across the same range of stoichiometry. This result, coupled with a similar statistical analysis performed for a representative set of shock-tube ignition delay time, highlights the importance of the systematic treatment of the uncertainty in these global, yet fundamental combustion property measurements in aiding reaction model development and testing. For this purpose, an impact factor is proposed for combustion experiments, by combining the sensitivity of the response to rate parameters with the inherent uncertainty of the experiment. It is demonstrated that with the exception of some extreme cases, the impact factors of the flame speed and shock tube ignition delay data are quite close to each other, making both indispensable for model testing. Overall the study illustrates that as a quantitative science, fundamental combustion property measurements must consider inherent experimental uncertainty and require a careful analysis of the uncertainty in order to yield useful results.

Reduced-Order Description of Chemistry and Transport

We have developed reduced-order formulations of the chemistry and transport that can greatly simplify the computational calculation of flames. Regarding the former, skeletal reaction models for *n*-butane and *iso*-butane combustion were derived from a detailed chemistry model through directed relation graph (DRG) and DRG-aided sensitivity analysis (DRGASA) methods. It is shown that the accuracy of the reduced models can be improved by optimization through the method of uncertainty minimization by polynomial chaos expansion (MUM-PCE). The dependence of model uncertainty on the model size is also investigated by exploring skeletal models containing different number of species. It was shown that the dependence of model uncertainty is subject to the completeness of the model. In principle, for a specific simulation the uncertainty of a complete model, which includes all reactions important to its prediction, is convergent with respect to the model size, while the uncertainty calculated with an incomplete model may display unpredictable correlation with the model size.

Regarding the transport, the diffusion models for multicomponent mixtures were investigated in planar premixed flames, counterflow diffusion flames, and ignition of droplet flames. Discernable discrepancies were observed in the simulated flames with the mixture-averaged and multicomponent diffusion models, respectively, while the computational cost of the multicomponent model is significantly higher than that of the mixture-averaged model. A systematic strategy is proposed to reduce the cost of the multicomponent diffusion model by accurately accounting for the species whose diffusivity is important to the global responses of the combustion systems, and approximating those of less importance. The important species in the reduced model are identified with sensitivity analysis, and are found to be typically among those in high concentrations with exception of a few radicals, e.g. H and OH, that are known to participate in critical reactions. The reduced model was validated in simulating the propagation of planar premixed flames, extinction of counterflow non-premixed flames and ignition of droplet flames. The reduced model was shown to feature similar accuracy to that of the multicomponent model while the computational cost was reduced by a factor of approximately 5 for an *n*-heptane mechanism with 88 species.

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V. OUTREACH ACTIVITIES

A. Combustion Energy Research Fellows

A signature component of the CEFRC, unique among the DOE's Energy Frontier Research Centers (EFRCs), is the Combustion Energy Research Fellows program, also known as the Roving Post-doc program. In this program each fellow is sponsored by two or more of the Center PIs, splits his/her time approximately equally at the sites of the PIs, and works on new problems that arise since formation of the Center and that are inherently collaborative in nature between the sponsoring PIs. This structure therefore promotes synergy, ensuring the outcome of the Center's research is greater than the sum of the parts of the individual PIs, and provides the Center with nimbleness in responding to new developments. The program is strictly merit based, with each fellow and the proposed study competitively selected, and is highly demanding on the fellows as it requires either frequent commuting or relocation between the sites of the sponsoring PIs. It is therefore particularly gratifying that the program has attracted some of the brightest and most dedicated young combustion researchers, who rose to the challenge and in turn were richly benefitted through this unique research experience. A total of 12 Combustion Research Fellows were sponsored.

B. CEFRC Website

The CEFRC website (www.princeton.edu/cefrc) displays the Center's major research activities, mission statement, details of the PIs, information on postdoctoral fellowship, combustion summer school, and recent news and highlights. Beside the details of current session, the webpage on summer school also contains information of previous sessions, including the lecture notes and links for lecture videos. Together they constitute a comprehensive collection of lecture materials on various topics of combustion. These study materials are open source and widely viewed and referred by students across the world.

C. CEFRC Newsletters

The CEFRC issued biannual newsletters that were electronically distributed throughout the combustion and DOE-EFRC communities. It features news on the research activities and discoveries by members of the Center, brief review articles on timely topics, professional activities and honors of members of the CEFRC. The following is the front page of an issue.

CEFRC *news*

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

VOLUME 3 ISSUE 1 FEB—AUG 2012

INSIDE THIS ISSUE:

Computational Modeling of Turbulent Combustion

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Computer modeling is playing an increasing role in engineering design, including the design of combustion devices, such as internal combustion (IC) engines and gas turbine combustors. If a model can reliably and accurately predict the performance of a proposed design, then the expensive and time-consuming testing of prototypes can be greatly reduced. Such models are possible only when the underlying physics and chemistry are adequately understood, and the resulting modeled equations can be tractably solved on current computers.

Turbulent combustion, which occurs in practical combustion devices, poses formidable modeling and computational challenges. Among these are (1) the large number of chemical species (2) the large range of length and time scales, and (3) the combination of highly non-linear chemical kinetics and large turbulent fluctuations of temperature and species concentrations. As now described, in the CEFRC we have developed a modeling approach which goes a long way to meeting these challenges.

Models for the chemistry of hydrocarbon fuels can involve over 7,000 different chemical species. However, a variety of dimension-reduction techniques have been developed which allow several hydrocarbon fuels to be accurately represented by between 20 and 180 species; and computationally-efficient tabulation procedures have been developed to make feasible the use of models with up to 40 species. This is an active area of research within the CEFRC, and we expect to close the gap between the 40 species now tractable and the 180 species needed for the accurate representation of the combustion of some fuels.

The length scales involved range from the size of the combustion device (e.g., 5 cm for an IC engine) down to the smallest scales of the turbulence (e.g., 20 microns) or to the possibly smaller scales of chemical reaction zones. This large range of scales (a dynamic range of 2,500 in the example given) poses a huge challenge to the approach of "direct numerical simulation" (DNS), since all length and time scales have to be resolved within the three-dimensional, unsteady, turbulent flow field. While DNS is an extremely important research tool of increasing value, the range of scales that are currently computationally tractable are significantly less, and it will be several decades before computer power will allow the direct application of DNS to IC engines.

Currently, the usual approach to circumvent the problem of the large range of scales is to use "large-eddy simulations" (LES) in which only the large-scale, unsteady, turbulent motions are explicitly represented. As a consequence, processes occurring at smaller, unresolved scales must be modeled. For turbulent combustion this modeling is crucial, since the important processes of molecular diffusion coupled with chemical reactions occur below the resolved scales.

To model these processes we use a "probability density function" (PDF) method, in which the turbulent fluctuations are fully represented in terms of the joint PDF of the species. The combined LES/PDF method is implemented computationally as a particle/mesh method.

(Continued on page 2)

D. Princeton-CEFRC Summer School on Combustion

Combustion science is an interdisciplinary field and plays a critical role in providing modern society's needs for combustion technology. At the present juncture of technological development, the need for transformative advances in combustion has never been greater as we wrestle with the twin challenges of energy sustainability and climate change. By further recognizing that combustion is intrinsically an interdisciplinary science, with wide ranging topics from chemical kinetics to fluid mechanics, and that the students and practitioners are frequently trained in only a single discipline, the progress of combustion science has been severely handicapped by the paucity of professionals who are conversant in both chemistry and fluid physics. Hence, the goal of the annual Princeton Summer School on Combustion is to provide the current and next generation of combustion researchers and graduate students with advanced graduate level knowledge in combustion science and technology, covering such foundational courses as combustion physics, combustion chemistry, turbulent combustion, combustion modeling, experimental combustion techniques, engine combustion and more. In particular, the program aims to provide the participants with a comprehensive, interdisciplinary knowledge base needed to make fundamental discoveries in the relevant disciplines that encompass the broad landscape of combustion, particularly that of combustion energy science. The program also provides networking opportunities for the participants, and hence facilitates future career development and collaborative research. The academic program consists of four to five15-hour courses delivered over a five-day period. Seven sessions have been conducted, starting from 2010. Since the inaugural session, more than 1,200 participants have attended the summer school, with the current annual participation being about 200. They are mostly senior graduate students and practicing researchers in combustion, and come from more than half of the states of the country, as well as internationally. The cost is $50 for registration for the US students and the Summer School provides free room and board. The corresponding cost for industrial and non-US participants is also minimal. The lectures are delivered by world-renowned experts in combustion who are also inspirational lecturers. All lectures were videotaped, and together with the lecture notes, are freely available to the public. The response from the participants has been overwhelmingly positive and enthusiastic, validating the present model for the Summer School. Adopting a similar model other summer schools in Asia and Europe were held recently. In particular, the Tsinghua-Princeton Summer School on Combustion, held at Tsinghua University in Beijing, China has been offered annually since 2012, with upwards of 400 participants annually. The Combustion Institute has also adopted this model in sponsoring summer schools internationally. Since termination of funding for the CEFRC, the Princeton Summer School has continued, with funds solicited from various sources. The following is the poster and the participant group picture for the 2014 Summer School.

PRINCETON-CEFRC

2014 SUMMER SCHOOL

JUNE 22 – JUNE 27, 2014

https://www.princeton.edu/cefrc/

Combustion Theory and Applications in CFD

***Heinz Pitsch**, RWTH Aachen University*

Combustion and Fuels Chemistry

***William H. Green**, MIT*

Reciprocating Engines

***Rolf D. Reitz**, University of Wisconsin-Madison*

Unsteady Combustor Processes

***Timothy C. Lieuwen**, Georgia Institute of Technology*

New Developments in Combustion Technology

***George A. Richards**, NETL, DOE*

ORGANIZED BY
THE COMBUSTION ENERGY FRONTIER
RESEARCH CENTER

Director, Chung K. Law

U.S. DEPARTMENT OF ENERGY | Office of Science

VI. SUMMARY AND RECOMMENDATIONS

The Combustion Energy Frontier Research Center has accomplished many scientific goals, which include developments in atomistic simulations and large-scale chemical models, advancement in experimental apparatuses and diagnostic techniques, detailed simulation of turbulence-chemistry interaction, and development of predictive sub-models in coarse-grained engineering simulations.

As representative highlights of our accomplishments, the Center has developed detailed chemical models for the high-temperature combustion of representative biofuels, such as the butanol isomers, which are produced by fermentation of biomass and presents many of the challenges arising during the combustion of non-traditional, single-component fuels. Concurrently, the chemistry of the gaseous foundation fuels (H_2, CO, C_1–C_4 hydrocarbons) was also rigorously studied by the Center. One of our key findings is that the chemical mechanisms are still incomplete in crucial ways. As an example, we discovered a new, general pathway that plays a role in the low-temperature oxidation chemistry of alkanes when the crucial, second O_2 addition step takes place, and predicted its rate from first principles.

The chemical models were coupled to 1D laminar flame propagation and 3D direct numerical simulations (DNS) of turbulent flames and compression ignition incorporating accurate reduced mechanisms for bio-alcohol fuels. These studies demonstrated the importance of temperature and dilution with exhaust gas recirculation on modulating the combustion phasing and heat-release rate. Further *a posteriori* comparisons between DNS and large-eddy simulation coupled with a transported probability density function model revealed shortcomings in turbulent mixing closures in the presence of local extinction. The DNS data were also used to identify new empirically reduced nonlinear manifolds for representing detailed chemistry accurately in turbulent flows.

Scientific discovery advances rapidly when new types of measurements become possible. During our CEFRC effort, a comprehensive array of experimental apparatuses and techniques covering a wide range of thermodynamic conditions were developed to probe fuel combustion behaviors and high- and low-temperature chemistry of many hydrocarbons and their oxygenated analogs, which in addition facilitated very detailed tests of the computer models. For example, the new techniques developed by Hanson enabled the study of chemical reactions in shock tubes at well-defined conditions that were not possible using conventional measurement strategies, while Ju’s technique provided access to HO_2 radicals in reacting environments.

Because of the CEFRC, our ability to predict the behavior of new fuels in new combustion environments improved significantly, and we laid the foundation for future work in fuel design and utilization. Based on the accomplishments and lessons learned from the Center as well as advances in the combustion and fuels community at large, we have identified the major directions for further impactful research. We first recognize that most previous work has been on pure fuels, while almost all real fuels are mixtures. Fuel performance has a complicated dependence on composition, and often, small amounts of fuel additives can significantly change the performance. Such behavior is modeled in industry by empirical nonlinear “blending rules”. It is therefore recommended that research is needed to further understand and reliably predict fuel blending phenomena, building on the fundamental approaches developed in our studies.

The chemical models built herein needs to be further improved because, while our predictions of fuel chemistry are consistent with a wide variety of data, our research revealed gaps in the fundamental understanding of “pre-ignition” low-temperature oxidation chemistry.

This is critical for understanding knock in gasoline engines, ignition and emission problems in diesel engines, and the performance of advanced engines including RCCI.

Furthermore, we have identified new opportunities in the investigation of soot formation. The early chemistry leading towards PAH formation and ultimately soot is relatively well described in the literature, but it is largely unknown how the gas-phase PAH molecules rapidly turn into the toxic particulate emissions correlated with human mortality; the existing models which try to match soot observations are phenomenological to an extent and contain unphysical aspects.

In addition to the chemistry areas in need of further research, next-generation engines are expected to function closer to the limits of stable operation, to maximize efficiency and minimize emissions. However, this makes them susceptible to fluctuations, and even the small local fluctuations caused by turbulence found in all practical engines can be amplified by the sensitive pre-ignition chemistry leading to undesirable fluctuations in power, pressure, and emissions and, in extreme cases, to a misfire or knock event. For this reason the stochastic nature of in-cylinder processes has been identified as a key research area.

Near-limit combustion is characterized by previously unexplored mixed-regimes of combustion, e.g., a flame propagating into a pre-igniting mixture. A particularly important fundamental challenge that was identified is how to develop and validate regime-independent turbulence-chemistry sub-models from coordinated DNS simulations and experiments on a few configurations that isolate low-temperature, high-pressure near-limit combustion at conditions far from equilibrium. This generalization would represent a major advancement in scientific understanding, and would be practically useful in accelerating innovation, making accurate affordable coarse-grained large eddy simulation (LES) or Reynolds-averaged Navier-Stokes (RANS) simulations of real engine geometries with real fuels possible.

Our research has also demonstrated that it is now possible to predict complicated fuel chemistry, and to embed detailed chemistry within solvable 3D turbulent combustion simulations. A key research area is generating reliable error bars for the predictions of combustion simulations, and more importantly, to understand the sources of uncertainty. Uncertainty quantification (UQ) must play a central role within and across the scales (micro to macro), disciplines (turbulence, chemistry) and methods (experiments, theory and modeling) in future research to drive scientific discovery and help constrain remaining systematic errors.

APPENDIX I: PUBLICATIONS
(2009 – 2017)

A. PUBLICATIONS SOLELY SUPPORTED BY THE CEFRC

B. COLLABORATIVE PUBLICATIONS SUPPORTED BY THE CEFRC AND OTHER PROGRAMS

A. PUBLICATIONS SOLELY SUPPORTED BY THE CEFRC

(Total Count: 70)

1. Oyeyemi, V. B.; Pavone, Michele; and **Carter, Emily A.** “Accurate Bond Energies of Hydrocarbons from Complete Basis Set Extrapolated Multi-Reference Singles and Doubles Configuration Interaction”, *ChemPhysChem*, **12**, 3354-3364 (2011). [10.1002/cphc.201100447]

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APPENDIX II

Legacy Review Papers*

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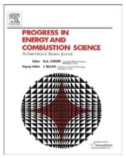

Review

Recent advances in laser absorption and shock tube methods for studies of combustion chemistry

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ABSTRACT

Recent advances in laser absorption and shock tube methodologies for studies of combustion chemistry are reviewed. First the principles of shock tube operation are discussed, and then an overview of shock tube diagnostic methods and experiments is covered. Recent shock tube developments include the use of driver inserts to counteract the small pressure gradient seen in conventional reflected shock wave experiments and the use of a constrained-reaction-volume strategy to enable the implementation of near-constant-pressure gasdynamic test conditions during energetic processes. Recent laser absorption developments include the use of a CO_2 laser absorption sensor to accurately monitor temperature during shock wave experiments, the use of multi-wavelength laser absorption strategies to simultaneously monitor multiple species time-histories, and the used of isotopic labeling strategies to identify individual reaction sites during the measurement of elementary reaction rate constants. The improved ability to accurately constrain the test conditions in shock tube experiments, combined with non-intrusive, species-sensitive and quantitative laser absorption diagnostics, is enabling experimenters to provide a new generation of high-quality experimental kinetics targets for combustion chemistry model validation and refinement. The paper concludes with a brief discussion of newly emerging laser-diagnostic techniques and a summary of future research directions.

Contents

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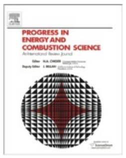

Review

Interpreting chemical kinetics from complex reaction–advection–diffusion systems: Modeling of flow reactors and related experiments

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Uncertainty quantification
Interpretive uncertainty

ABSTRACT

The present discourse is directed toward the community that wishes to generate or use flow reactor data from complex chemical reactions as kinetic model development and validation targets. Various methods for comparing experimental data and computational predictions are in evidence in the literature, along with limited insights into uncertainties associated with each approach. Plug flow is most often assumed in such works as a simple, chemically insightful physical reactor model; however, only brief qualitative justifications for such an interpretation are typically offered. Modern tools permit the researcher to quantitatively confirm the validity of this assumption. In a single complex reaction system, chemical time scales can change dramatically with extent of reaction of the original reactants and with transitions across boundaries separating low temperature, intermediate temperature, and chain branched (high temperature) kinetic regimes. Such transitions can violate the underlying assumptions for plug flow interpretation. Further, uncertainties in reaction initialization may confound interpretation of experiments for which the plug flow assumption may be appropriate. Finally, various methods of acquiring experimental data can also significantly influence experimental interpretations. The following discussions provide important background for those interested in critically approaching the relatively vast literature on the application of flow reactors for generating kinetic validation data. The less frequently discussed influences of reactor simulation assumptions on modeling predictions are addressed through examples for which the kinetic behavior of specific reactant combinations may cause experimental observations to depart locally from plug flow behavior.

Contents

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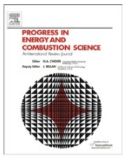

Review

Using rapid compression machines for chemical kinetics studies

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A B S T R A C T

Rapid compression machines (RCMs) are used to simulate a single compression stroke of an internal combustion engine without some of the complicated swirl bowl geometry, cycle-to-cycle variation, residual gas, and other complications associated with engine operating conditions. RCMs are primarily used to measure ignition delay times as a function of temperature, pressure, and fuel/oxygen/diluent ratio; further they can be equipped with diagnostics to determine the temperature and flow fields inside the reaction chamber and to measure the concentrations of reactant, intermediate, and product species produced during combustion.

This paper first discusses the operational principles and design features of RCMs, including the use of creviced pistons, which is an important feature in order to suppress the boundary layer, preventing it from becoming entrained into the reaction chamber via a roll-up vortex. The paper then discusses methods by which experiments performed in RCMs are interpreted and simulated. Furthermore, differences in measured ignition delays from RCMs and shock tube facilities are discussed, with the apparent initial gross disagreement being explained by facility effects in both types of experiments. Finally, future directions for using RCMs in chemical kinetics studies are also discussed.

Contents

1. Introduction

Rapid compression machines (RCMs) are considered an important experimental device for understanding low-to-intermediate temperature autoignition chemistry under idealized engine-like conditions. RCMs are able to interrogate the region responsible

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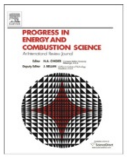

Review

Advances and challenges in laminar flame experiments and implications for combustion chemistry

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Laminar flames
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ABSTRACT

The state of the art and the further challenges of combustion chemistry research in laminar flames are reviewed. Laminar flames constitute an essential part of kinetic model development as the rates of elementary reactions are studied and/or validated in the presence of temperature and species concentration gradients. The various methods considered in this review are the flat, low-pressure, burner-stabilized premixed flame for chemical speciation studies, and the stagnation, spherically expanding, and burner-stabilized flames for determining the global flame properties. The data derived using these methods are considered at present as the most reliable ones for three decades of pressures ranging from about 50 mbar to over 50 bar. Furthermore, the attendant initial and/or boundary conditions and physics are in principle well characterized, allowing for the isolation of various physical parameters that could affect the flame structure and thus the reported data. The merits of each approach and the advances that have been made are outlined and the uncertainties of the reported data are discussed. At the same time, the potential sources of uncertainties associated with the experimental methods and the hypotheses for data extraction using each method are discussed. These uncertainties include unquantified physical effects, inherent instrument limitations, data processing, and data interpretation. Recommendations to reduce experimental uncertainties and increase data fidelity, essential for accurate kinetic model development, are given.

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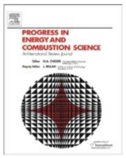

Review

Combustion kinetic model uncertainty quantification, propagation and minimization

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ABSTRACT

The current interest in the combustion chemistry of hydrocarbon fuels, including the various alcohol and biodiesel compounds, motivates this review of the methods and application of kinetic uncertainty quantification (UQ). Our intent is to provide a self-contained review about the mathematical principles and methods of uncertainty quantification and their application in highly complex, multi-parameter combustion chemistry problems. We begin by outlining the reasons why the kinetic uncertainty must be considered and treated as a part of the combustion chemistry development in order to make progress. This is followed by a brief discussion about the sources and classification of kinetic uncertainties and the meanings and definitions of model verification and validation. We discuss the histories of UQ studies with an emphasis on how the combustion community has a long tradition of UQ consideration through standard sensitivity analysis. Such efforts have motivated the advancements of UQ methods specifically tailored to combustion chemistry. They also led to the recent growing interests in applying UQ methods as a part of our recommended long-term solution to the chemical kinetic problem of combustion. We then review and classify the various UQ methods and illustrate their applications for problems involving forward uncertainty quantification and propagation, and as an inverse problem leading to model uncertainty constraining. For the inverse problem, the focus of discussion is in the use of methods originating from Bayes' Theorem. We show that, for combustion chemistry problems, while UQ alone cannot produce precise, individual rate parameters, it can be instrumental in measuring the progress of our understanding of combustion chemistry and in utilizing fundamental combustion property data beyond a simple "agree–disagree" statement. When treated as a Bayesian inference problem, UQ also aids the development of predictive kinetic models in two ways: the use of fundamental combustion property data, global or local, to provide a better constrained kinetic model, and along with forward kinetic uncertainty propagation, to yield estimates for the confidence of a model to make predictions outside of the thermodynamic regimes where the model has been tested. We provide several examples to illustrate the utility of the UQ methods discussed and to demonstrate that, in the field of combustion chemistry, further progress will be better achieved through a combination of fundamental studies of reaction rates through well-defined and designed experiments and *ab initio* theoretical calculations, and of analyses of global experimental measurements. These studies together must be supplemented by UQ analyses, in such a way that a measurable progress can be made over time.

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From theoretical reaction dynamics to chemical modeling of combustion

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Abstract

The chemical modeling of combustion treats the chemical conversion of hundreds of species through thousands of reactions. Recent advances in theoretical methodologies and computational capabilities have transformed theoretical chemical kinetics from a largely empirical to a highly predictive science. As a result, theoretical chemistry is playing an increasingly significant role in the combustion modeling enterprise. The accurate prediction of the temperature and pressure dependence of gas phase reactions requires state-of-the-art implementations of a variety of theoretical methods: ab initio electronic structure theory, transition state theory, classical trajectory simulations, and the master equation. In this work, we illustrate the current state-of-the-art in predicting the kinetics of gas-phase reactions through sample calculations for some prototypical reactions central to combustion chemistry. These studies are used to highlight the success of theory, as well as its remaining challenges, through comparisons with experiments ranging from elementary reaction kinetics studies through to global observations such as flame speed measurements. The illustrations progress from the treatment of relatively simple abstraction and addition reactions, which proceed over a single transition state, through to the complexity of multiwell multichannel reactions that commonly occur in studies of the growth of polycyclic aromatic hydrocarbons. In addition to providing high quality rate prescriptions for combustion modelers, theory will be seen to indicate various shortcomings in the foundations of chemical modeling. Future progress in the fidelity of the chemical modeling of combustion will benefit from more widespread applications of theoretical chemical kinetics and from increasingly intimate couplings of theory, experiment, and modeling.

Keywords: Theoretical chemical kinetics; Ab initio electronic structure theory; Transition state theory; Master equation; Combustion chemistry

1. Introduction

Recent years have seen an explosion in the number of studies using kinetic models to explore the chemistry of combustion. A survey of the 2015 volume of Combustion and Flame finds studies implementing kinetics models for biofuels (*methanol, ethanol, n-butanol, isobutanol, 2-methylbutanol, n-pentanol, 2- and 3-pentanol, dimethyl ether, tetrahydrofuran, 2,5-dimethylfuran, tetrahydropyran, diethylcarbonate, and tripropyleneglycol mono-methyl*

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