

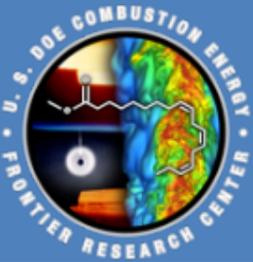


COMBUSTION ENERGY FRONTIER RESEARCH CENTER

**First Annual Conference of the
Combustion Energy Frontier Research
Center (CEFRC)**

September 23-24, 2010

Princeton



CONFERENCE SCHEDULE

Thursday, September 23

8:15am – 8:30 Announcements

8:30 – 9:00 Overview of the CEFRC (Chung K. Law)

9:00 – 10:30 Chemistry: Theory (William H. Green)

Multi-reference Correlated Wavefunction Calculations and Reaction Flux Analyses of Methyl Ester Combustion

Emily A. Carter, Princeton University

Computation of Accurate Thermochemical and Rate Parameters for Complex Combustion Reactions

Donald G. Truhlar, University of Minnesota

Theoretical Chemical Kinetics and Combustion Modeling

James A. Miller, Sandia National Laboratories

Theoretical Gas-Phase Chemical Kinetics

Stephen J. Klippenstein, Argonne National Laboratory

Constructing Accurate Combustion Chemistry Models

William H. Green, MIT

10:30 – 11:00 Break

11:00 – 12:30 Chemistry: Experiment and Mechanisms (Hai Wang)

Developing Fundamental Kinetics Database through Shock Tube Studies

Ronald K. Hanson, Stanford University

Combustion Studies of Alcohols, Esters, and Hydrogen Rich Fuels

Frederick L. Dryer, Princeton University

Chemical Kinetics Studies of Alternate Fuels

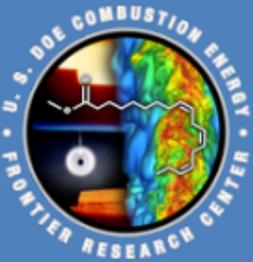
Chih-Jen Sung, University of Connecticut

Flame Chemistry and Diagnostics

Nils Hansen, Sandia National Laboratories

Chemical Kinetics of Combustion Processes

Hai Wang, University of Southern California



12:30 – 2:00 Lunch and Poster Presentations

2:00 – 3:30 Chemistry and Transport (Yiguang Ju)

Flame and Droplet Processes in Combustion
Chung K. Law, Princeton University

Flame Studies of Small Hydrocarbons and Oxygenated Fuels
Fokion N. Egolfopoulos, University of Southern California

Flame Chemistry, Dynamics, and Kinetic Model Reduction
Yiguang Ju, Princeton University

Direct Numerical Simulation of High Pressure, Mixed Mode Turbulent Combustion
Jacqueline H. Chen, Sandia National Laboratories

Predictive Turbulent Combustion Models for 21st Century Transportation Fuels
Stephen B. Pope, Cornell University

3:30 – 5:00 Open Discussion: The Role of CEFRC in Fuels Research
(Moderators: Tim Edwards, Chung K. Law, Wade Sisk)

5:00 MACCCR Review adjourn

5:00 – 7:00 Dinner

7:00 – 9:00 Discussion on Challenging Problems

Friday, September 24

8:00am – 8:30 Continental Breakfast

8:30 – 9:00 Overview and Charge (Chung K. Law)

9:00 – 11:00 Discussion of Future Work
Chemistry: Theory (William H. Green)
Chemistry: Experiment and Mechanisms (Hai Wang)
Chemistry and Transport (Yiguang Ju)

11:00 – 1:00 Breakout Sessions and Lunch
PIs of Disciplinary Working Groups: Coordination
Advisors: Preparation of report

1:00 – 2:00 Report from Advisors (Sarofim)

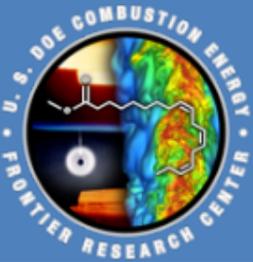
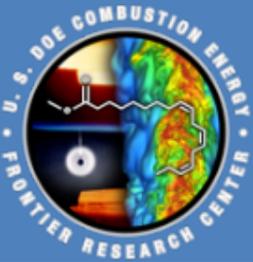


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ABSTRACTS

SUMMARY OF DISCIPLINARY WORKING GROUP. CHEMISTRY: THEORY

William H. Green

Progress

Carter and Truhlar made significant progress in computing potential energy surfaces and zero-point energies. Carter developed a new high-accuracy first-principles method suitable for studying bond-breaking in large molecules, and Truhlar developing empirically-corrected DFT methods which achieve high accuracy at very low CPU cost. Miller and Truhlar studied H-abstraction reactions from small alcohols and are preparing to tackle the butanols. Miller also studied the decomposition routes of the radicals formed from these H-abstractions. Green identified problems with the conventional independent-rotors approximation, and Green and Truhlar started to develop algorithms to try to avoid this approximation. Miller used trajectory studies to better understand the collisional energy transfer which is so important in determining pressure-dependent rate coefficients. Klippenstein made very detailed studies of important pressure-dependent reactions: the decomposition of methylhydrazine (with Law) and allyl + HO₂ and subsequent decomposition of allyloxy (with Green). Klippenstein also studied the H₂+O₂ system with Dryer. Green constructed a detailed chemical kinetic model for all 4 of the butanol isomers, and tested it against the literature data plus some new unpublished data measured by other members of the CEFRC team.

Learnings

On the positive side, the butanols model constructed base primarily on functional group estimates gave pretty good predictions for most experiments, particularly after a few of the most sensitive parameters were refined using quantum chemistry. The methods used appear to be viable (after some improvements in memory handling) for fuels with up to 10 or 12 carbon atoms, i.e. all of the gasoline range and getting in to the jet range. The “refine only the most sensitive numbers” approach appears to be viable, presuming we can determine which reactions will be most important under all engine conditions. However, research during Year 1 also highlighted some major challenges ahead, particularly if we seek general-purpose high-fidelity models:

- 1) A very large number of reaction coefficients used in the large kinetic models are probably significantly in error, but these errors are mostly invisible so far because none of the limited number of experimental data are sensitive to those particular rate coefficients. Almost every reaction studied in detail in Year 1 was found to be significantly different than the original estimates, and often very different than the numbers in the literature. (The situation is almost as bad for molecular properties such as thermochemistry and transport coefficients.) The implication is that hundreds or even thousands of rate coefficients really should be re-examined, implying the need to automate the high-accuracy rate-calculation methods.
- 2) Significant work needs to be done to improve the small-molecule kinetics. Most experiments are sensitive to the small-molecule reactions, and these do

not appear to be modeled in a way which will be correct over the full range of pressures important in combustion devices.

- 3) There is a fairly large unresolved discrepancy between experiment and the models for high-P ignition delays. There are speculations about which types of reactions are mis-modeled under these conditions, but this has not been resolved.
- 4) Three usually-neglected complications to rate-calculations were found to be much more important than previously thought. We made some progress towards computing these effects, but the issues are only partially resolved:
 - a. Transient H-bonding in transition states is unexpectedly important. This effect is missing in virtually all kinetic models.
 - b. Coupling between internal rotors is quite important in molecules with multiple functional groups which interact. In the past this has been almost always neglected. Team members made some progress towards developing practical algorithms for computing this effect, but at the time of this writing this is only incompletely resolved.
 - c. Roaming Radical reactions (which have been omitted from almost all kinetic models) appear to be significant in ignition chemistry. A method for computing these rates was developed by Klippenstein, but has only been applied to a handful of reactions so far.
- 5) After methods are developed for correctly handling problems a,b,c above, it seems likely that they will be complex and need to be automated.

Grand Challenge

The Grand Challenge identified by this working group was to develop reliable automated methods for automatically computing rate coefficients, handling all the issues raised above (plus some others discussed in the individual PI reports). The present pace of high-accuracy rate calculations (which currently involve a lot of human checking and double-checking) is at least an order of magnitude too slow to be satisfactory even for relatively simple fuels like butanol, and much too slow to compute all the rate coefficients needed for accurately modeling more complicated fuels such as hydroxymethyl furfural and methyl linoleate (not to mention real fuel mixtures). If these calculations could be reliably automated, it would be ideal to have them tied to the mechanism-construction process, either to refine the most sensitive rate coefficients, or (in the long term) to compute all rate coefficients (and transport properties and thermochemistry) in the final model.

There are many ways the multi-step calculations involved in computing an accurate rate coefficient can fail, giving incorrect results. Automation would require algorithms for identifying when the calculations were failing, and restarting them with some different initial guess or options. As a simple example, novices often have a great deal of difficulty in steering a quantum chemistry calculation to the correct saddle point for a rate calculation, but experts have much less trouble. This suggests the automated program might need to be an expert system, containing the knowledge gained by the expert quantum chemists.

MULTI-REFERENCE CORRELATED WAVEFUNCTION CALCULATIONS AND REACTION FLUX ANALYSES OF METHYL ESTER COMBUSTION

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A. Introduction

Biodiesel is a promising alternative fuel that is, ideally, carbon neutral because it is derived from plants.¹ Compared to conventional diesel fuels, biodiesel generates less particulate matter, due to the oxygen atoms anchored to the ester moiety of the alkyl esters. However, uncertainties exist in the kinetics and in the key mechanisms of biodiesel combustion. The molecules comprising biodiesel fuels are large alkyl esters containing between 18 and 20 heavy atoms. Understanding the relationship between the chemical structures of biodiesel compounds and the corresponding combustion properties represents a crucial challenge for finding the best biofuel in terms of both energetic and environmental advantages. To this purpose, kinetics modeling studies can have a paramount role. Thus, we aim to provide reliable *ab initio* thermochemical kinetics data, within chemical accuracy (*i.e.*, 1 kcal/mol error), that are needed as input to higher length scale predictive modeling of biodiesel combustion. Our objective is to accurately predict the energy required for bond scission and activation energies for pyrolysis and oxidation reactions of biodiesel molecules. Together with estimates for the pre-exponential factors, we will then evaluate the corresponding kinetic rate constants. Moreover, reaction flux analysis will provide us the conceptual framework of the complex biodiesel combustion mechanisms, from which we can identify the most important elementary reactions on which to focus our attention.

So far we mainly focused on bond dissociation energies (BDEs), which are unfortunately unavailable for a vast majority of combustion fuels. To achieve chemical accuracy when computing BDEs using quantum mechanics, electronic correlation needs to be included to the best extent possible and due to near-degeneracies that develop during bond breaking, a multireference wavefunction method must be used. Here, we use an integrated computational approach based on: correlated many-body wavefunction methods (*i.e.*, multi-reference single and double configuration interaction, MRSDCI, and multi-reference averaged couple paired functional, MRAPCF), a complete-basis-set extrapolation scheme, and computing structural and thermal effects using Hartree-Fock (HF) or density functional theory (DFT). We aim to address biodiesel molecules, for which no experimental data are available. Large molecules represent a numerical challenge for accurate post-HF treatment. However, we are able to compute accurate BDEs for these molecules by using our very fast, reduced scaling MRSDCI/ACPF code TIGERCI, which introduces local correlation, localized orthogonal virtual orbitals, and Cholesky decomposition of the two electron integrals.²⁻⁵

In the following sections we discuss the details of our approach and report results on (1) the validation of this method against accurate experimental BDEs for a wide range of chemical bonds, (2) BDEs for methyl butanoate and methyl-2-butenoate (two biodiesel surrogates), and (3) the reaction flux analysis of methyl decanoate, another biodiesel surrogate.

B. Methods

The BDE is defined as the difference between the energy of a molecule and the energies of the two molecular fragments generated by the homolytic fission of the bond under investigation. For a consistent accounting of the electronic correlation, here we consider the equilibrium structures of the molecule and of the super-molecular system with the bond in question extended to the dissociated limit (*i.e.*, 10 Å). To be comparable to experiments, *ab initio* BDEs should also account for zero point vibrational energy and thermal effects. Therefore, the BDE at room temperature, D_{298} , is given by

$$D_{298} = E(\text{dissociated limit}) - E(\text{equilibrium})$$

where

$$E(\text{species}) = \text{Electronic Energy} + \text{Zero Point Energy} + \text{Thermal Correction}$$

Our approach for achieving accurate BDEs consists of three steps: (1) calculation of the equilibrium structure, zero-point vibrational energy, and thermal correction for all species, (2) compute the electronic energies at the MRSDCI(MRAPCF) level of theory with different basis sets, and (3) extrapolation of the electronic energy to the complete basis-set limit (CBS).

For computing the equilibrium structures of the fuel molecule and the dissociated radical fragments, we employ HF and DFT with double- and triple-zeta basis-set from Dunning's and Pople's series. The DFT calculations here use the B3LYP⁶ hybrid HF-GGA exchange-correlation functional, which represents one of the most accurate and most exploited density functionals for molecules.

As a first rough test of HF and B3LYP for structural prediction, we considered four molecules, H₂O₂, CH₃OOH, CH₃CH₂OOH, and (CH₃)₃COOH, along with their corresponding ROO• radicals, using the cc-pVDZ basis set. We found that HF gave larger deviations from experimental values than B3LYP. For example, the experimental O-O bond length⁷ in H₂O₂ is 1.462 Å while the corresponding HF and B3LYP values are 1.391 and 1.452 Å, respectively.

We compute vibrational frequencies within the harmonic approximation at the same level of theory used for structural optimization. Anharmonicity is accounted for by applying commonly used scaling factors⁸⁻¹⁰ to normal mode frequencies. These scaled frequencies are then used for the zero point vibrational energy (ZVPE) and for the thermal correction, which is computed following the ideal gas Rigid-Rotor/(scaled-frequency)Harmonic-Oscillator model.

In order to set the best performing method of structural optimization and frequency calculation for BDE predictions, we tested four combinations of theory/ basis-sets/frequency scaling factors against experimental values: namely, HF/cc-pVDZ/0.908, HF/6-311G(2d,p)/0.899, B3LYP/cc-pVDZ/0.970, B3LYP/6-311G(2d,p)/0.990.

The electronic energy requires multiple steps to compute: first a complete active space self consistent field (CASSCF) calculation to obtain the reference wavefunction for the subsequent MRSDCI/MRACPF calculations. The CASSCF active space only includes the bonding and antibonding orbitals of the bond under investigation. All references within the CASCI for single bonds, and those that have CI coefficients above > 0.05 for double bonds, are used as the reference states from which to allow all single and double excitations in MRSDCI calculations. While MRSDCI is known to perform well for small molecules, it lacks size extensivity which becomes significant in large molecules. To correct for this, we also use the size extensive modification of MRSDCI known as MRACPF.

For both MRSDCI and MRACPF, we apply the dual basis set extrapolation scheme proposed by Truhlar¹¹ to extrapolate the electronic energies obtained with cc-pVDZ and cc-pVTZ to the CBS limit. In this scheme, the reference energy and the correlation energy are separately extrapolated with the formulas:

$$E_X^{CASSCF} = E_\infty^{CASSCF} + A^{CASSCF} X^{-\alpha} \quad \text{and} \quad E_X^{cor} = E_\infty^{cor} + A^{cor} X^{-\beta}$$

where $X=2$ and 3 for the Dunning type basis sets cc-pVDZ and cc-pVTZ, respectively.

The extrapolation parameters α and β were optimized by Truhlar for HF and coupled cluster singles and doubles (CCSD) levels of theory and they have values 3.4 and 2.4, respectively. We use the same unmodified parameters for the CASSCF and MRSDCI/MRACPF wavefunctions because we expect the basis set behavior of HF and our CASSCF wavefunction to be very similar since we use a small active space. Also, the MRSDCI/MRACPF and CCSD basis set behavior should be similar since they both primarily deal with single and double excitations.

C. Results and discussion

C.1 Bond Dissociation Energies

Methyl esters' BDEs reported in current literature¹²⁻¹⁷ exhibit scatter of up to 3 kcal/mol. These values were obtained with different methods, the simplest being based on some form of group additivity estimates.¹⁸ Osmont *et al.*^{14,15} computed BDEs for select bonds in a wide range of methyl esters by using the DFT-B3LYP level of theory with some additional empirical corrections. Our own studies demonstrated that B3LYP alone underpredicts BDEs by up to 10 kcal/mol in molecules for which experimental data are available. Moreover, the extent of the improvement made possible by the empirical correction on top of DFT energies is unclear since Osmont *et al.* provided no validation of their method against experimental data.

Recently, El Nahas *et al.*¹⁷ also reported ab initio BDEs in methyl butanoate and ethyl propanoate using the CBS-QB3 method in conjunction with isodesmic schemes. These are probably the most reliable values for these molecules to date. The authors cited a study¹⁹ which claims the CBS-QB3 method to be accurate within 1.43 and 1.49 kcal/mol in predicting ΔH and ΔG , respectively, for a series of deprotonation reactions (which is not the same of course as homolytic bond breaking). Aside from this, we found no systematic validation study determining how accurate this method is when compared against known experimental BDEs. Furthermore, the isodesmic reactions used by El-Nahas *et al.* are not unique, thereby leading to different possible estimates of some BDEs.

Therefore, to set the accuracy of our method, we performed a validation study considering a set of experimental BDEs reported by Blanksby and Ellison.²⁰ MRSDCI CBS-extrapolated BDEs were computed using HF and B3LYP structures, ZPVEs and thermal corrections. Such a validation set consisted of five different chemical groups, namely inorganic molecules, hydrocarbons, alcohols, alkyl hydroperoxides and aldehydes. Overall, the B3LYP/6-311G(2d,p) level of theory for structures and thermal effects performed slightly better than HF/cc-pVDZ: the mean absolute errors and standard deviations being respectively 1.2 and 1.0 kcal/mol for B3LYP and 1.4 and 1.0 kcal/mol for HF. Both the HF and B3LYP values appear to be better than the reported accuracy of CBS-QB3. Moreover, considering the uncertainties of BDEs' experimental determination, our reported mean errors are likely to be slightly overestimated. These considerations give us confidence in the reliability of our method for further studies of BDEs of biodiesel molecules.

As preliminary models of biodiesel fuel, we report BDEs computed for methyl butanoate (Figure 1) and methyl-2-butenoate (Figure 2), two biodiesel surrogates. For the first molecule, we have computed the BDEs at the MRSDCI level of theory with several basis sets up to the extrapolated CBS limit (cc-pV ∞ Z) with molecular structures, zero-point energies, and thermal effects computed by using the HF and B3LYP methods.

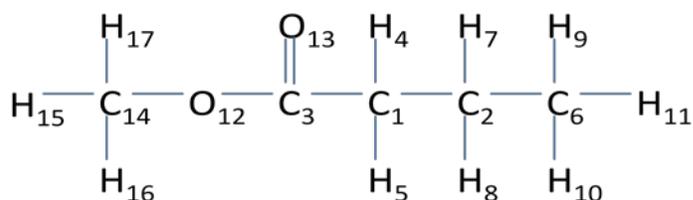


Figure 1. Methyl Butanoate

Our results are within 3 kcal/mol of the values reported by El-Nahas *et al.* So far we found a qualitative agreement between the BDEs computed with HF geometries, ZPVEs, and thermal corrections and the preliminary ones computed with the B3LYP counterpart. These last values are also qualitatively similar to the CBS-QB3 ones. Overall our data and the CBS-QB3 ones agree on predicting the C1_H4, C1_C2 and C14_O12 to be the weakest among C-H, C-C and C-

O bonds, respectively, and we also found the same relative energetic order among them: $\text{BDE}(\text{C1_C2}) < \text{BDE}(\text{C14_O12}) < \text{BDE}(\text{C1_H4})$. These bonds are the weakest of their cohort because of the π resonance-stabilized radical that forms upon cleavage in each case.

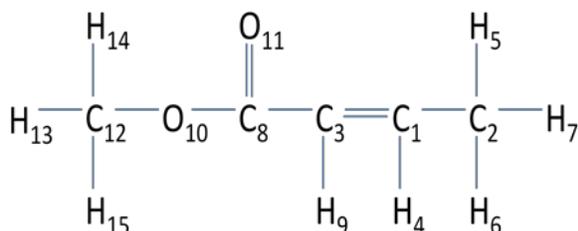


Figure 2. Methyl-2-Butenoate

Regarding methyl-2-butenate, the preliminary BDEs for hydrogen abstraction clearly show the C2_H5 to be the weakest bond, as expected since the resulting (allylic) radical is stabilized by extension of the delocalized π system.

C.2 Reaction flux analysis

We will also apply the methods here to the computation of activation energies in biodiesel reactions. Westbrook *et al.*²¹ developed a detailed mechanism for combustion of methyl decanoate, another biodiesel surrogate. However, many kinetic parameters in this mechanism came from analogous reactions for small species, leaving some uncertainties in the mechanism. In principle, it is crucial to improve the accuracy of those parameters for the important reactions in the mechanism, which contains 3012 species and 8820 elementary reactions. However, it is impossible to consider all the reactions in such a large mechanism. We therefore used the reduced mechanism by Sarathy *et al.*²² to perform a reaction flux analysis. The flux analysis was performed under conditions of a well mixed reactor for both high (1200 K) and low (650 K) temperatures. By analyzing these reaction fluxes, we found the most relevant reaction pathways. At high temperature, the main paths are through decomposition and β -scission reactions, which produce small hydrocarbon and methyl ester fragments. However, at low temperature, O_2 addition produces a more complex mechanism, and thus more uncertainties lie in this range. We are also working on the sensitivity analysis of this reduced mechanism under different conditions from 650 – 1200 K. With the reaction flux and sensitivity analysis, we will be soon able to determine which reactions to focus on for obtaining accurate thermochemical parameters in our future work.

D. Outlook and future work

In summary, we outlined a systematic approach for computing accurate BDEs. After validation against known experimental values, we provided preliminary results on methyl esters that represent surrogates of biodiesel molecules. Moreover, we also started to perform a statistical

analysis of combustion mechanisms for methyl decanoate, highlighting the key reaction steps and the uncertainties that need further investigation.

Our next step will be to expand the validation set for testing BDEs prediction schemes. We will compute BDEs for methyl butanoate and methyl-2-butenate using the MRAPCF method. These molecules are the largest size amenable to treatment at the exact (nonlocal) MRSDCI/MRAPCF levels of theory. Since, our goal is to model large biodiesel molecules, we will exploit our much faster TIGERCI code,²⁻⁵ which implements cost-saving approximations relying on the local (short-ranged) nature of electronic correlation; and we will validate the use of such approximations for accurate BDE and activation energy predictions as well. In earlier reports, we noted that we have already optimized structures for the actual large biodiesel molecules using Monte Carlo sampling and empirical force fields followed by structural refinement of the lowest energy conformers at the HF level. We will refine these structures again at the DFT-B3LYP level, since the latter structures appear to be more accurate for the smaller molecules we have tested thus far. We will then use our local MRSDCI/MRAPCF method to calculate the BDEs in the actual biodiesel fuel molecules, as well as determine activation energies and transition state theory rate constants for the important but uncertain reactions in methyl decanoate combustion. The structures of the transition states will be determined at the DFT-B3LYP level. Ultimately, we will calculate activation energies and rate constants for the most uncertain/most important reactions in the larger biodiesel molecules as well.

A grand challenge is how to automate the reaction flux and sensitivity analyses to automatically determine which reactions must be refined at the MRSDCI/MRAPCF level, and to automate the entire calculation process to output the refined energetics and rate constants. We hope to work with Bill Green and Don Truhlar to provide such a tool.

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Press, Corrected Proof.

Significant Appointments

Founding Director, Gerhard R. Andlinger Center for Energy and the
Environment, Princeton University, 2010 -
Chair, Energy Subdivision of the PHYS Division of the ACS, 2010-2011
Chair, DOE-BES Council on Chemical and Biochemical Sciences, 2010-2011
Vice-Chair, DOE-BES Council on Chemical and Biochemical Sciences, 2009-2010
Member, Board on Chemical Sciences and Technology, National Research
Council, National Academy of Sciences, 2010-2012

Major Lectures

2010 Coover Lecturer in Chemistry, Iowa State University
2010 Material Simulation Distinguished Lecturer, Penn State University
2010 Pelz Memorial Lecturer in Mechanical and Aerospace Engineering, Rutgers University
2010 Noyes Lecturer in Physical Chemistry, University of Texas, Austin
2010 Plenary Speaker at the 50th *Sanibel Symposium*, St. Simons Island, GA.
2009 Plenary Lecture at the 2009 *ETSF Workshop on Electronic Excitations*, Evora, Portugal

COMPUTATION OF ACCURATE THERMOCHEMICAL AND RATE PARAMETERS FOR COMPLEX COMBUSTION REACTIONS

Donald G. Truhlar
University of Minnesota
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SUMMARY/OVERVIEW

Our goal is to efficiently compute accurate thermochemistry and thermal rate coefficients over a wide temperature range (300 K–2400 K) for important reactions in the combustion of new and potential biofuels such as *n*-butanol. This requires calculating accurate potential energy surfaces for the minimum energy paths and tunneling swaths, accurate anharmonic partition functions for reactants and generalized transition states, including multiple conformations and torsions, and incorporating this information into practical methods for variational transition state theory with multi-dimensional tunneling. We use the high-performance Minnesota density functionals to calculate thermal rate coefficients via direct dynamics at the level of variational transition state theory with a curvilinear dividing surface and multidimensional tunneling. Many of the species generated in the combustion of *n*-butanol have multiple torsions, which, aside from being distinctly anharmonic, are often significantly coupled to one another and to external rotation, invalidating the usual procedures of obtaining partition functions from simple harmonic oscillator or separable one-dimensional hindered-rotor treatments. We are in the final stages of developing a practical multi-structural method for including torsional anharmonicity (MS-T) in the partition function for systems with multiple torsions giving rise to numerous structural conformers.

ACCOMPLISHMENTS

The initial collective focus of the CEFRC is to assemble a complete mechanism for the combustion of the potential biofuel *n*-butanol, which requires thermochemical and kinetic information about many important radical reactions and the intermediates generated, many of which are cyclic or have many torsions. We have recently provided rate coefficients obtained at the level of variational transition state theory with a curvilinear dividing surface and multidimensional tunneling for a key subset of such reactions — the hydrogen-transfer isomerization reactions of butoxyl radicals (Zheng & Truhlar, *PCCP* (2010) **12**, 7782). In this study, it was found that the M08-SO functional can predict the barrier heights and reaction energies for the various intramolecular hydrogen-shifts to well within the sub-kcal mol⁻¹ accuracy regime, and the study also brings out the need for a better accounting for multiple conformations and torsional anharmonicity.

Simple models relying on the separable treatment of normal modes corresponding to torsions as 1D hindered rotors are difficult to implement in systems with many coupled

torsions, as this coupling between torsions precludes the straightforward assignment of a particular normal mode to a specific torsion. Our attempts to compute accurate rate coefficients and thermochemistry for reaction systems involving species with multiple torsions have led to the development of a new method for accurately treating such systems, called the multi-structural torsion method (MS-T), that accounts for torsional anharmonicity in an efficient manner (Zheng, Yu, Papajak, Alecu, Mielke, & Truhlar, to be submitted to *JCP*).

The MS-T method circumvents the problem of associating certain normal modes with specific torsions by instead employing internal coordinates. The MS-T method is also very practical — it does not require any input information about the barriers along the torsional coordinates, eliminating the need for the expensive and labor-intensive geometry optimizations and frequency calculations of torsional saddle points or even unrelaxed scans along torsional coordinates. In this method, the number of conformers and their geometries, symmetries, frequencies, and relative energies are used to obtain the anharmonic partition functions, including the conformational contribution, over the whole range of temperature from the zero-point-dominated regime to the free-rotor limit.

Anharmonicity is also important for high-frequency modes. As a means of efficiently accounting for the effects of anharmonicity in the zero-point energies (ZPEs) of molecules or molecular radicals characterized by strong covalent interactions, we have compiled a database of accurate ZPEs for 15 species, and obtained the optimal scale factors for reproducing these ZPEs from the harmonic vibrational frequencies computed with 145 electronic model chemistries (Alecu, Zheng, Zhao, & Truhlar, *JCTC* accepted August 6, 2010). We also found that the ratios of the scale factor for ZPEs to that for fundamental vibrational frequencies and to that for harmonic vibrational frequencies are nearly independent of the electronic model chemistry used to calculate them, enabling the determination of all three scale factors at the cost of explicitly optimizing just one. Furthermore, we found that for molecules whose experimental fundamental frequencies are known, the use of these in conjunction with the appropriate scale factor ratio can lead to a highly-accurate prediction of the molecule’s ZPE.

We are exploring the prototypical reactions of the simplest alcohol, methanol, with the important hydroperoxyl and methyl radicals in an effort to devise an efficient and systematic approach for studying analogous reactions in the larger and more complex *n*-butanol reaction system (Alecu & Truhlar, in preparation for *JPC A*). We have split this project into a two-part study, the first part focusing on establishing accurate databases of accurate thermochemistry and barrier heights, searching for an efficient electronic model chemistry of benchmark quality, and identifying, through extensive validations, the most accurate DFT-based electronic model chemistry for use in the direct dynamics analysis based on variational transition state theory with a curvilinear dividing surface and multidimensional tunneling. In the first part of the study, we have found that single-reference formalisms based on coupled cluster theory with single, double, and at least a quasiperturbative treatment of connected triple excitations, when extrapolated to the complete basis set limit, provide benchmark-quality results for the methanol reactions investigated. Alternatively, the explicitly correlated CCSD(T)-F12a and CCSD(T)-F12b methods when used in conjunction with even a minimally-augmented valence triple-zeta basis set can also yield benchmark-quality results. It is shown that the M08-HX and M08-SO hybrid meta-GGA density functionals can achieve sub-kcal mol⁻¹ agreement with the

high-level *ab initio* results for both barrier heights and reaction energies, identifying these functionals as important potential candidates for direct dynamics studies on the rates of these and other homologous reactions systems.

PLAN FOR FUTURE WORK

In the near future, we plan to submit the second part of the study on methanol reactions for publication. The effects on the rate coefficient of multiple conformations, torsional anharmonicity (using the MS-T method), and weakly bound van der Waals complexes at the entrance and exit channels along the reaction coordinate are included in this second study.

We are presently working on fully automating the scale factor optimization process to further facilitate the procedure for obtaining scale factors for calculating zero point energies. We have recently written a FORTRAN code which implements a reduced scale factor optimization model that we introduced in our prior work (Alecú, Zheng, Zhao, & Truhlar, *JCTC*, accepted August 6, 2010). We are currently working on a PERL script that will set up, initiate, and then copy the results of Gaussian jobs to the FORTRAN program, which it then calls to execute and generate all three scale factors previously mentioned.

We have almost completed the development of a new version of variational transition state theory, called multi-structural variational transition state theory (MS-VTST), that allows for multiple conformations of the reactants and transition states in a practical yet realistic way. We are applying this method and our findings using the electronic structure methods discussed above to two important complex reactions: the 1,4-hydrogen shift isomerization of the pentyl radical (Yu, Zheng, & Truhlar, in preparation for *JCTC*) and the reaction of *n*-butanol with the hydroperoxyl radical, the latter of which the Green group's Reaction Mechanism Generator has identified to be a key process in the combustion of *n*-butanol at low temperatures. The reaction of *n*-butanol with the hydroperoxyl radical has also been identified as a key source of uncertainty in the *n*-butanol mechanism by Rex Skodje and the Argonne group of Mike Davis, Steve Klippenstein, and Larry Harding.

We will also return to the hydrogen-transfer isomerization reactions of butoxyl radicals, which can be calculated more realistically with the new methods.

JOURNAL PUBLICATIONS FUNDED BY CEFRC

- 1) Zheng, J. and Truhlar, D. G., "Kinetics of Hydrogen-Transfer Isomerizations of Butoxyl Radicals," *Phys. Chem. Chem. Phys.* 12, 7782-7793 (2010).
- 2) Alecú, I. M., Zheng, J., Zhao, Y., and Truhlar, D. G., "Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries," *J. Chem. Theory Comput.* (2010, accepted).

RECENT RECOGNITIONS AND HONORS

Elected to three-year term as officer of the Division of Chemical Physics of the American Physical Society: 2010-11, Vice Chair; 2011-12, Chair-Elect; 2012-13, Chair.

Doctor honoris causa of Technical University of Lodz, Poland, 2010, “for his contributions to the development of quantum chemistry and vivid collaboration with our and other Polish universities.”

Elected to the National Academy of Sciences, 2009 (induction ceremony in April 2010). Members are elected in recognition of their distinguished and continuing achievements in original research.

Dudley R. Herschbach Award for Excellence in Research in Molecular Collision Dynamics, 2009

Fellow of the Royal Society of Chemistry (UK), 2009

Elected to Fellowship in the American Chemical Society, 2009

MAJOR LECTURES

Moses Gomberg Lecture, University of Michigan, Ann Arbor, Michigan, February 12, 2009. "Recent Advances in Density Functional Theory"

Davidson Lectures, University of North Texas, Denton, Texas, March 5 and 6, 2009. “Quantum Photochemistry” and “Density Functional Theory: New Developments”

Milton Kahn Lectureship in Chemistry, University of New Mexico, Albuquerque, NM, Sept. 18, 2009. "Recent Advances in Density Functional Theory"

THEORETICAL CHEMICAL KINETICS AND COMBUSTION MODELING

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SUMMARY/OVERVIEW

Whether energy is generated by burning a conventional petroleum-based fuel or a biofuel, the key chemical reactions in combustion are rarely simple abstractions or other reactions commonly encountered in textbooks. Invariably they are complicated reactions that take place over multiple, interconnected potential wells with multiple sets of bimolecular products. Such reactions completely dominate our understanding of how aromatic compounds, polycyclic aromatic compounds (PAH), and soot are formed in flames. They are the critical steps in NO_x control strategies, and they play an important role in sulfur chemistry. They are also pivotal in predicting the chemistry of low temperature oxidation and ignition, cool flames, and engine knock. These reactions may be bimolecular (i.e. chemically activated), or they may be thermal dissociation/isomerization processes. Some of the former are effectively “collisionless” in that the intermediate complexes are so short-lived that they do not suffer a significant number of collisions under conditions that are normally of interest. However, intermediate complexes more commonly live long enough to suffer numerous collisions. In such cases, any of a number of stabilized or bimolecular products may result. These reactions (unimolecular or bimolecular), which dominate virtually all aspects of combustion chemistry, require a theoretical description in terms of a time-dependent, multiple-well master equation (ME).

For applications in combustion, it is not sufficient to obtain the solution to the ME, which describes molecular processes on a collisional time scale. What is required is a description in terms of “emergent properties” on the longer, chemical time scale, i.e. a phenomenological description in terms elementary reactions and rate coefficients, $k(T, p)$. Systematic procedures or obtaining such a description have been proposed only in the last few years and are still under development. We propose to continue this development and to apply the methodology to critical problems in combustion chemistry. In the last year we have applied these methods to reactions involved in the combustion of propanol, in preparation for studying butanol combustion. In addition, we have taken the initial steps in placing the collisional energy transfer input to the ME on an equal theoretical footing with the reactive input. Results of these two efforts are discussed below.

ACCOMPLISHMENTS

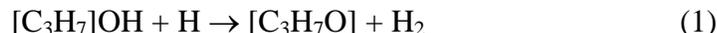
Kinetics of hydrogen abstraction from propanol and the subsequent unimolecular dissociation of the $\text{C}_3\text{H}_7\text{O}$ radicals (with Judit Zádor)

Butanol combustion is complicated because of the number of isomers arising from the parent molecules and the number of H-abstraction sites: there are 16 possible $\text{C}_4\text{H}_9\text{O}$ isomers. Calculations carried out on propanol (7 possible $\text{C}_3\text{H}_7\text{O}$ isomers) can serve as a benchmark for

future butanol calculations - there is probably enough experimental data available in the literature on the important elementary reactions of the former to be compared with our analysis.

Here we present high-level electronic structure calculations coupled to RRKM-based master equation (ME) methodology, including tunneling effects as well as internal-rotor hindering potentials, to study the initial steps of propanol combustion. The following reactions were studied:

H-abstraction by H, OH and HO₂



Unimolecular dissociation of the resulting radicals



where the [] means that all relevant isomers are considered.

Energetics of reactions (1)–(4) were determined at the QCISD(T)/cc-pV ∞ Z//B3LYP/6-311++G(d,p) level of electronic-structure theory. The results for the abstraction reactions are presented in Fig. 1, while the potential energy surface (PES) used for reaction (4) is essentially equivalent to the one presented in Figs 1 and 2 of our recent publication on propene + OH (Zádor, Jasper, and Miller, 2009, JPCA).

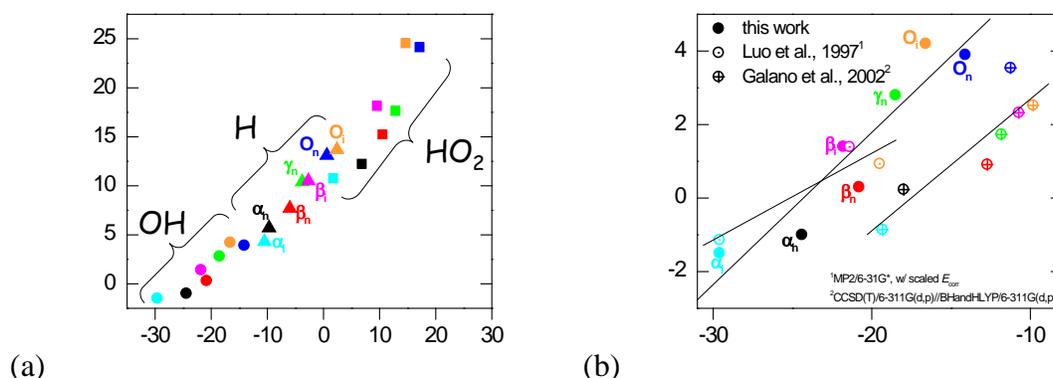


Figure 1. (a) ZPE-corrected QCISD(T)/cc-pV ∞ Z//B3LYP/6-311++G(d,p) energetics of the abstraction reactions (1)–(3). (b) Comparison to literature values in the case of reaction (2).

For reactions (2) and (3) weakly bound complexes exist on both the reactant and the product sides of the saddlepoint. From a kinetic point of view only the reactant complexes of reaction (2) are important, due to the low-lying or even submerged transition states leading to products. The well depth of the OH–propanol van der Waals complexes is ~ 7 kcal mol⁻¹. The channels leading to OH + propene in reaction (4) also feature submerged barriers and weakly bound complexes.

For the barrierless channels the E, J -resolved numbers of states were calculated variationally using the direct variable-reaction-coordinate transition-state theory, and the effective flux through the barrierless entrance channel, the van der Waals well, and the submerged barriers is represented by a two-transition-state model at the microcanonical, J -resolved level.

Our calculations on the temperature and pressure dependent unimolecular dissociation of the C₃H₇O radicals show that:

1. Catalytic dehydration of n/i -propanol via β -hydrogen abstraction by OH can take place above ~ 700 K. In this process the hydroxyl radical is regenerated, leading to increased reactivity

under low-temperature combustion conditions. The significant unimolecular dissociation rate coefficient above ~ 700 K also means a competition with the peroxy chemistry.

- Well-skipping channels persist even at high pressures. In this case, these channels do not originate from chemical activation, but from isomerization/dissociation reactions, where collisional stabilization in the intermediate wells is ineffective. e.g. the reaction $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O}$ takes place to a significant extent without stabilization in the intermediate propoxy well.
- Vinyl alcohol is formed from various dissociation channels. Vinyl alcohol has been identified as an intermediate in *n*- and *i*-propanol flames using electron ionization and VUV-photoionization molecular-beam mass spectrometry. The concentration of vinyl alcohol was reported (Kasper et al., 2009, CF) to be $\sim 10\times$ more in *n*-propanol flames compared to *i*-propanol ones, which is qualitatively in line with our dissociation and H-abstraction rate coefficients.

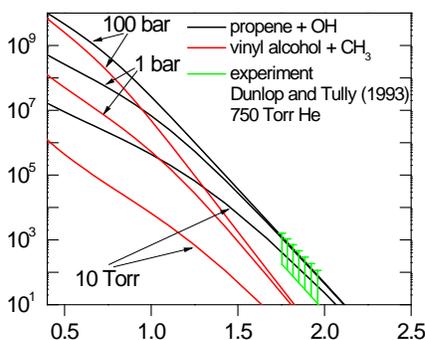


Figure 2. Rate coefficients of the 2-hydroxy-1-propyl radical's unimolecular dissociation.

Experimental data are available only in the case of the abstraction rate coefficients of the OH + *n/i*-propanol reactions, while branching fractions are available only for the OH + *i*-propanol reactions (Dunlop and Tully, 1993, JPCA). To achieve good agreement with the experiments, barrier-heights were modified by <1 kcal mol $^{-1}$. The remaining discrepancy requires further investigation. In doing so, we expect the kinetic isotope effects measured by Dunlop and Tully to be pivotal.

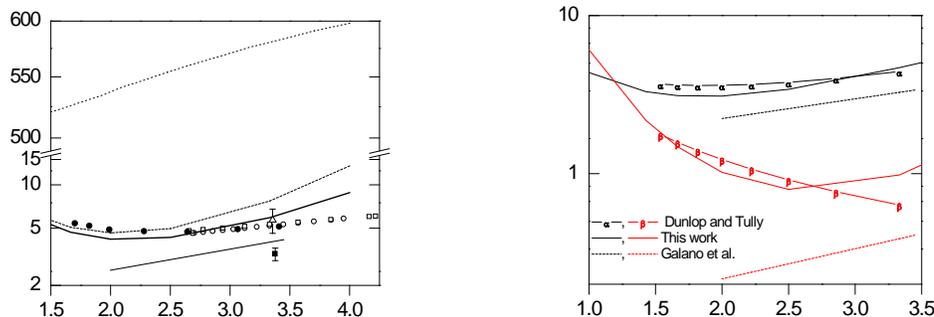


Figure 3. Overall and channel specific rate coefficients for the *i*-propanol + OH reaction compared to the available experimental data and to the calculations of Galano et al, 2002, PCCP.

Predictive Unimolecular Kinetics for $\text{CH}_4(+\text{M}) \rightleftharpoons \text{CH}_3+\text{H}(+\text{M})$ in Eight Baths: $\text{M}=\text{He, Ne, Ar, Kr, H}_2, \text{CO, N}_2,$ and CH_4 (with Ahren Jasper)

Collisional energy transfer plays an important role in controlling the rates of unimolecular reactions, both thermally and chemically activated ones. The low-pressure limiting rate coefficient for a thermal unimolecular dissociation reaction, for example, is proportional to the rate of activating collisions, i.e. to the rate at which molecules above the reaction threshold are produced from molecules below it. Pressure dependent kinetics may be fully characterized using the master equation (ME), which, in general, describes the time dependence of the microcanonical state populations of the reactants, products, and intermediates.

ME calculations require knowledge of the intramolecular potential energy surface (dissociation energies, isomerization barriers, vibrational frequencies, etc.), which may be obtained with known uncertainties from electronic structure calculations. Likewise, the required intramolecular isomerization and capture rate coefficients may be calculated via transition state theory, with well-validated, predictive strategies for treating barrierless reactions, tunneling, etc. In contrast, the models used for describing collisional energy transfer remain highly empirical. In many chemical kinetics calculations, these models are the dominant sources of uncertainty in the predicted rate coefficients.

We have used ensembles of classical trajectories to study collisional energy transfer in highly vibrationally excited species relevant to combustion chemistry (e.g., $\text{CH}_4, \text{C}_2\text{H}_3, \text{C}_2\text{H}_5$) for several bath gases. The current focus is on simple single-channel thermal dissociations. The goals of this ongoing work include the following:

- Validating and developing collisional energy transfer models for the ME,
- Quantifying the accuracy of classical trajectory calculations for studying energy transfer, with an emphasis on the sensitivity of the predicted results to the potential energy surface and the selection of the initial conditions for the ensemble, and
- Developing theoretical strategies involving quantum chemistry, transition state theory, and trajectory calculations for parameter-free predictions for pressure-dependent kinetics.

We have studied collisional energy transfer for CH_4 decomposition in eight bath gases: He, Ne, Ar, Kr, H_2 , N_2 , CO, and CH_4 (Jasper and Miller, *J. Phys. Chem. A* **113**, 5612 (2009); Jasper and Miller (2010)). Full-dimensional *ab initio* potential energy surfaces were used in direct trajectory calculations for $\text{M} = \text{He, Ne, H}_2,$ and CH_4 . The use of a separable approximation for the intramolecular (CH_4) and intermolecular ($\text{CH}_4\text{-M}$) potentials was tested against the full-dimensional calculations for He, Ne, and H_2 . Energy transfer was found to be very sensitive to the shape of the repulsive wall of the intermolecular potential, with an exponential repulsive wall required for

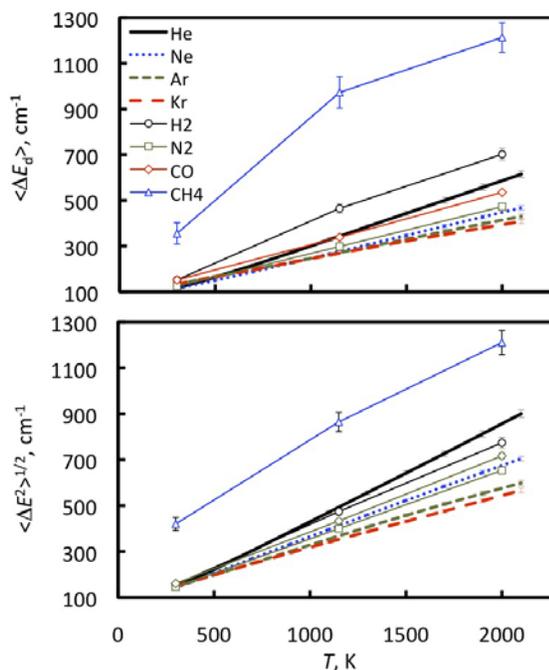


Fig. 4. The average downward and root-mean-squared energy transferred for CH_4 in eight baths.

quantitative predictions. For the diatomic baths, the separable pairwise approximation was unable to describe the orientation dependence of the interaction potential, and the ambiguity in the resulting parameterizations contributed an additional uncertainty to the predicted energy transfer averages of up to 50%. On the other hand, the energy transfer averages were found to be insensitive to the level of theory used to describe the intramolecular CH_4 potential, with a semi-empirical tight binding potential performing equally well as an MP2 potential.

In Fig. 4, the average energy transferred in deactivating collisions $\langle \Delta E_d \rangle$ and the root-mean-squared energy transferred $\langle \Delta E^2 \rangle^{1/2}$ are compared for eight baths. Both energy transfer averages are shown scaled to the Lennard-Jones collision rates. At room temperature, the calculated values of $\langle \Delta E_d \rangle$ for all the atomic and diatomic baths are similar, with $\langle \Delta E_d \rangle$ for Ar, Kr, and H_2 20% larger than $\langle \Delta E_d \rangle$ for He and Ne. At elevated temperature, the trend in the atomic baths is reversed, with relative differences of $\sim 30\%$. At all temperatures considered here, CH_4 is a qualitatively more efficient collider than the atomic and diatomic baths.

In Fig. 5, low-pressure and falloff rate coefficients for methane decomposition and $M = \text{Ar}$ are compared with several experimental results. The predicted low-pressure-limit results are within the scatter of the experimental results but are a factor of two lower than the recent recommendation of Baulch et al. (*J. Phys. Chem. Ref. Data* **34**, 757 (2005)). The falloff rates are similarly a factor of 2–3 lower than the measured rates of Barnes et al. (*J. Chem. Soc. Faraday Trans.* **85**, 229 (1989)). One source for this discrepancy may be the neglect of anharmonic effects when calculating the density of states and the partition function for CH_4 . In fact, Nguyen and Barker (T. L. Nguyen and J. R. Barker, *J. Phys. Chem. A* **114**, 3718 (2010)) recently calculated an anharmonic correction of 1.9 to the harmonic density of states for CH_4 at threshold. If we artificially increase the density of states at threshold by a factor of 1.9 but do not change the partition function for CH_4 , we can estimate an upper limit on the effect of anharmonicity on the predicted rates. These estimates (labeled “Scaled” in Fig. 5) are in closer agreement with the predicted and measured rates. This suggests that a quantitative treatment of pressure dependent kinetics likely requires accurate calculations of energy transfer parameters and anharmonic vibrational state densities.

Other ongoing energy transfer studies include the C_2H_3 and C_2H_5 systems, which feature lower dissociation thresholds and may therefore suffer less from anharmonic effects (C. M. Oana, A. W. Jasper, and J. A. Miller).

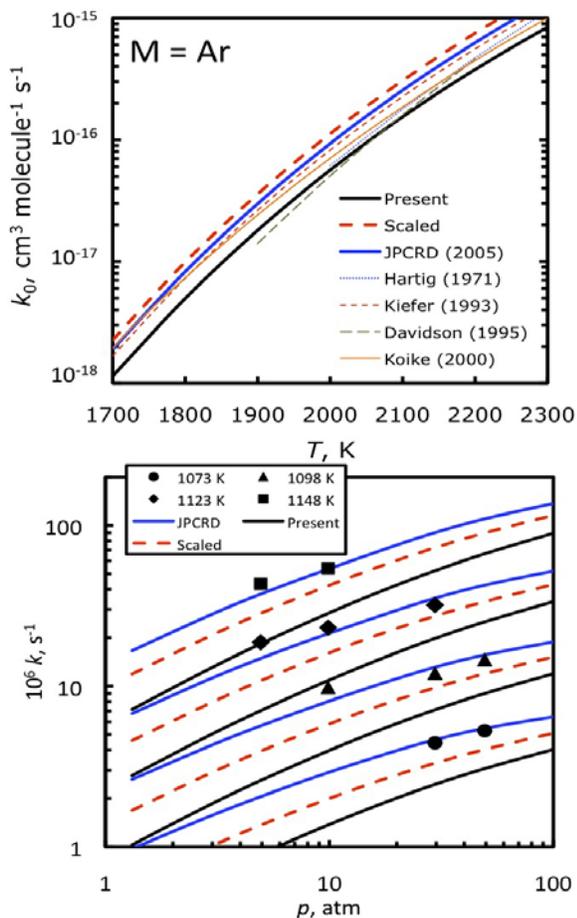


Fig 5. Low-pressure and falloff rate coefficients for CH_4 decomposition in Ar

PLANS FOR FUTURE WORK

1. We shall finish our work related to propanol combustion and move on to butanol. (in collaboration with **Judit Zádor**)
2. We shall continue the work on collisional energy transfer applied to unimolecular reactions. Our work so far is in its infancy. In the next year we shall continue to focus on simple single-channel dissociations, but we hope to begin to consider small-radical dissociations (C_2H_3 and/or C_2H_5) in detail and reactions involving more complicated intermolecular potentials (e.g. $HO_2(+H_2O)$). (in collaboration with **Ahren Jasper**)
3. We shall resume our study of elementary reactions leading to the formation of aromatic compounds containing one or two rings in flames burning aliphatic fuels. (in collaboration with **Stephen Klippenstein**)
4. We shall begin in earnest to explore the idea of using the Rate-Controlled Constrained-Equilibrium (RCCE) approach of Keck to model the formation of higher PAH in flames. This approach may also have promise as an alternative to the formulation of detailed mechanisms that involve thousands of reactions, virtually all of which are irrelevant.

THEORETICAL GAS PHASE CHEMICAL KINETICS

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SUMMARY/OVERVIEW

We have provided training in theoretical chemical kinetics calculations in a variety of ways. We provided a series of 9 lectures on the subject at the inaugural CEFRC summer school. We have provided individual instruction to Peng Zhang, a graduate student in the Law group at Princeton, and Franklin Goldsmith, a graduate student in the Green group at MIT, on the use of various aspects of our VaReCoF (for treating the kinetics of barrierless reactions) and VariFlex (for treating multiple well multiple channel master equations) codes. The interaction with Peng Zhang led to a publication on the kinetics of monomethylhydrazine decomposition.ⁱ The interaction with Franklin Goldsmith led to a publication on the reaction of allyl radical with HO₂.ⁱⁱ More importantly, this training should allow these students to perform useful kinetics calculations for a wide variety of related systems.

We have also interacted closely with Mike Burke from Fred Dryer's and Yiguang Ju's groups at Princeton, in the modeling of H₂/O₂ combustion at high pressure. A work in progress poster on this work was presented at the recent International Symposium on Combustion, and a manuscript is now in preparation.

ACCOMPLISHMENTS

1. Combustion Chemistry Course: Ab Initio Theoretical Chemical Kinetics

Our 9 lecture course on ab initio theoretical chemical kinetics was designed to introduce a diverse audience to the current state-of-the-art in ab initio theoretical chemical kinetics. There were roughly 120 students in attendance. Low level goals included (i) an illustration of the utility of current high level theoretical kinetics calculations, (ii) an understanding of the terminology employed in literature in this field, and (iii) the knowledge required to judge the quality and/or shortcomings of a given theoretical study. For the more advanced student, detailed comments were provided regarding the actual implementation of theory for various classes of reaction. The outline of the nine lectures was as follows:

1. Transition State Theory (TST)
2. Introduction to Electronic Structure Theory
3. Multi-Reference Electronic Structure Theory
4. TST for Abstractions and Simple Additions
5. TST for Radical-Radical Reactions
6. Multiple Transition States and Dynamics
7. Pressure Dependent Single Well Reactions
8. Multiple Well Time Dependent Master Equation - Theory
9. Multiple Well Time Dependent Master Equation – Examples

2. Ab initio kinetics for the decomposition of monomethylhydrazine (CH_3NHNH_2)

Monomethylhydrazine (MMH) is a commonly used bipropellant and monopropellant in rocket engines. Since MMH is prone to exothermically decompose upon contact with either a hot surface or an oxidizer, the thermal decomposition of MMH is an important issue related to fuel stability and storability. The decomposition kinetics of CH_3NHNH_2 (monomethylhydrazine) was studied with ab initio transition state theory-based master equation analyses. The simple NN and

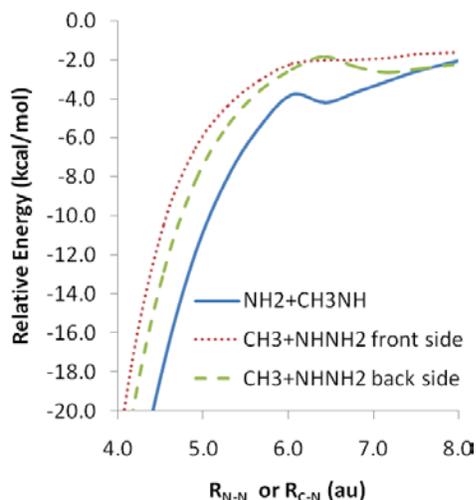


Figure 1. Potential curves for $\text{NH}_2 + \text{CH}_3\text{NH}$ (solid line), and the front (dotted line) and back (dashed line) sides of $\text{CH}_3 + \text{NHNH}_2$.

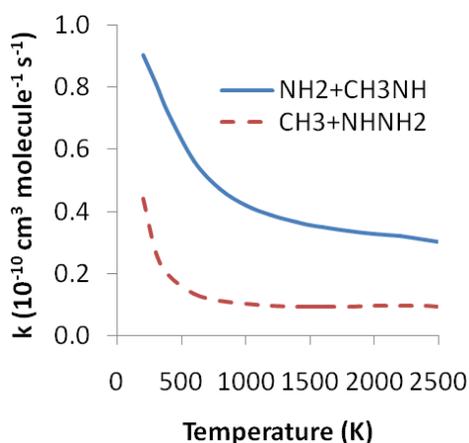


Figure 2. Temperature dependence of the high pressure recombination rate coefficients for $\text{NH}_2 + \text{CH}_3\text{NH}$ (solid line) and $\text{CH}_3 + \text{NHNH}_2$ (dashed line).

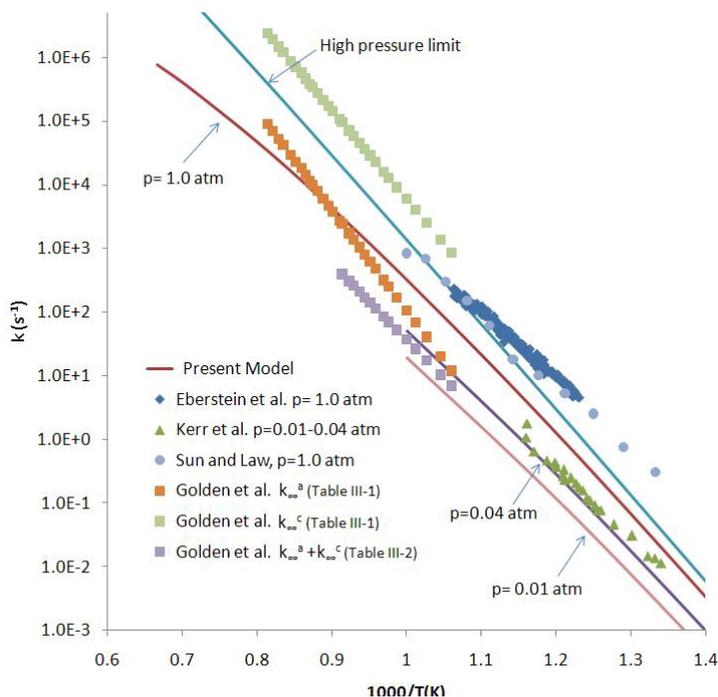


Figure 3. Comparison of the predicted total decomposition rate constant through $\text{MMH} \rightarrow \text{NH}_2 + \text{CH}_3\text{NH}$ and $\text{MMH} \rightarrow \text{CH}_3 + \text{NHNH}_2$ with previous experimental and simulation data for the overall thermal decomposition of MMH.

CN bond fissions to produce the radicals $\text{CH}_3\text{NH} + \text{NH}_2$ or $\text{CH}_3 + \text{NHNH}_2$ are expected to

dominate the decomposition kinetics. The transition states for these two bond fissions are studied with variable reaction coordinate transition state theory employing directly determined CASPT2/aug-cc-pVDZ interaction energies. Orientation independent corrections for limitations in the basis set and for the effects of conserved mode geometry relaxation are included. The bond dissociation energies are evaluated at the QCISD(T)/CBS//B3LYP/6-311++G(d,p) level. The transition state theory analysis directly provides high pressure dissociation and recombination rate coefficients. Predictions for the pressure dependence and product branching in the dissociation of CH_3NHNH_2 are obtained by solving the master equation.

3. Theoretical rate coefficients for allyl + HO_2 and allyloxy decomposition

Bimolecular reactions involving HO_2 with other radicals are important in ignition chemistry, particularly at moderate temperatures and high pressures. Although not a chain-branching reaction, $\text{R} + \text{HO}_2$ reactions can promote ignition by converting less reactive radicals into more reactive radicals through the following sequence: $\text{R} + \text{HO}_2 \rightarrow \text{RO} + \text{OH} \rightarrow \text{aldehyde} + \text{H} + \text{OH}$. Alternatively, the hydroperoxyl radical can transfer the H atom to the other radical, $\text{R} + \text{HO}_2 \rightarrow \text{RH} + \text{O}_2$, and thus act as a chain-terminating reaction. The relative rates of these competing chain-propagating and chain-terminating reactions are critical for accurate modeling of ignition chemistry.

The reaction of allyl + HO_2 shows up as a key reaction in various sensitivity analyses for alkane and alkene oxidation. For example, Heyberger et al. (B. Heyberger; F. Battin-Leclerc; V. Warth; R. Fournet; G. M. Come; G. Scacchi, *Combustion and Flame* **126**, 1780-1802 (2001).) demonstrated that the induction period of propene ignition in the temperature range of 500 – 800 K is highly sensitive to allyl + HO_2 kinetics, and that omitting this reaction increased the induction period by an order of magnitude. More recently, Hanson and coworkers (K. Y. Lam, Z. Hong, D. F. Davidson, and R. K. Hanson, *Proc. Comb. Inst.* **33**, doi:10.1016/j.proci.2010.06.131 (2010).) demonstrated a strong sensitivity to this reaction for the ignition delay of propane/ O_2 /Ar mixtures in a shock tube.

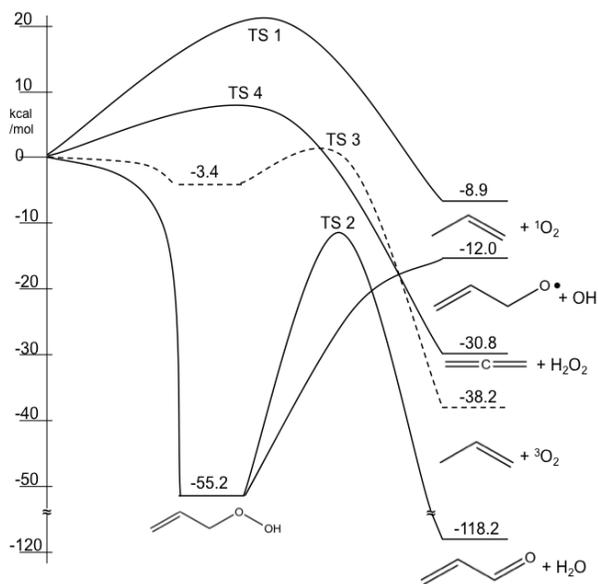


Figure 4: Potential energy surface for allyl + HO_2 .

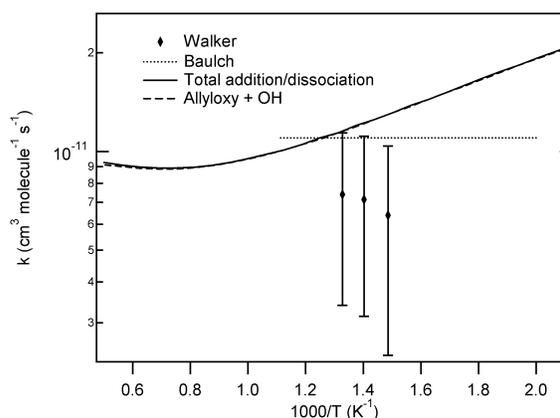


Figure 5: Allyl + $\text{HO}_2 \rightarrow \text{CH}_2\text{CHCH}_2\text{OOH} \rightarrow \text{products}$ rate coefficients in 60 Torr of N_2 .

The kinetics of the allyl + HO₂ bimolecular reaction, the thermal decomposition of C₃H₅OOH, and the unimolecular reactions of C₃H₅O were studied theoretically. High-level ab initio calculations of the C₃H₅OOH and C₃H₅O potential energy surfaces were coupled with RRKM master equation methods to compute the temperature- and pressure-dependence of the rate coefficients. Variable reaction coordinate transition state theory was used to characterize the barrierless transition states for the allyl + HO₂ and C₃H₅O + OH reactions. The predicted rate coefficients for allyl + HO₂ → C₃H₅OOH → products were in good agreement with experimental values. The calculations for allyl + HO₂ → C₃H₆ + O₂ underpredict the observed rate. The new rate coefficients suggest that the reaction of allyl + HO₂ will promote chain-branching significantly more than previous models suggest.

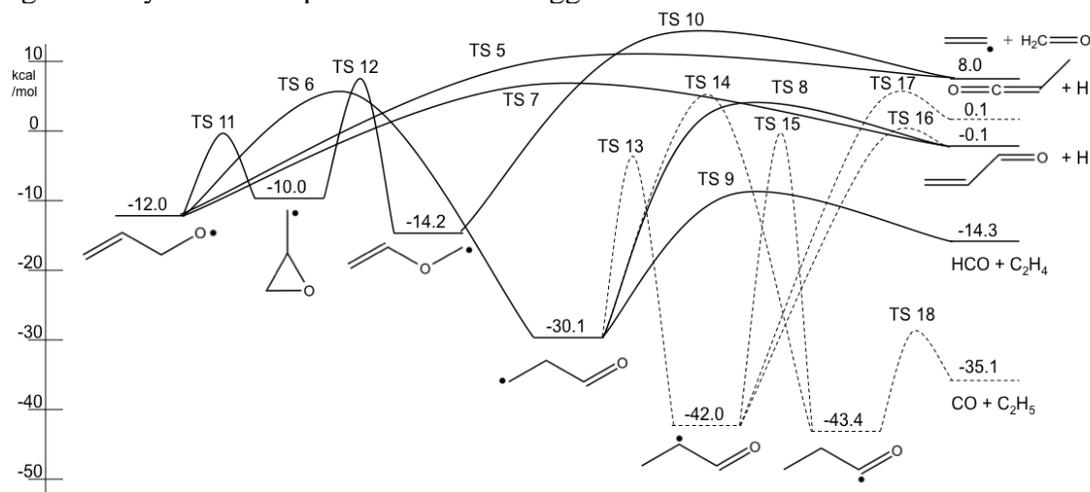


Figure 6: C₃H₅O potential energy surface. The energies are relative to allyl + HO₂ – OH. The dotted lines are omitted from the master equation calculations.

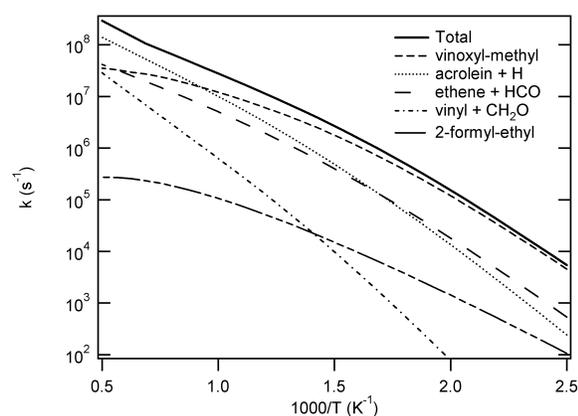


Figure 7: Computed rate coefficients for allyloxy decomposition in 60 Torr of N₂.

4. Updated H₂/O₂ Model to Address High-Pressure Flame Burning Rate Discrepancies

Knowledge of the H₂/O₂ oxidation mechanism is a fundamental issue in combustion. Accurate kinetic and transport models are necessary for computational design and optimization of gas turbine engines for syngas combustion as part of Integrated Gasification Combined Cycle processes. H₂/O₂ chemistry is a core subset of all hierarchically developed hydrocarbon

oxidation models. Most practical applications, particularly syngas combustion in GT engines, operate at high pressures (> 10 atm), frequently using lean conditions and/or dilution to lower flame temperatures to achieve low NO_x emissions. A number of recent studies have revealed substantial difficulties in accurately predicting flame behavior at high pressures and low flame temperatures. None of the kinetic models predict the pressure dependence across all conditions.

An updated kinetic model was constructed to incorporate recent improvements in rate constant determinations. Particular emphasis is placed on improving the treatment of reactions responsible for HO_2 production and consumption, which were found to be important in recent high pressure flame studies. Most notably, we have considered various aspects of the treatment for $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ including mixture rules and fall-off behavior as well as $\text{HO}_2 +$ radical reactions. Given that uncertainties in combustion predictions stemming from uncertainties in the elementary rate constants were still prevalent, minor adjustments were made to maintain reasonable fidelity to previous validation targets as well as improve predictions against more recent high-pressure, low-flame-temperature flame speed data of interest to practical syngas applications and other advanced engine technologies.

FUTURE WORK

We will continue to interact with others on the theoretical treatment of the kinetics of key combustion reactions. In collaboration with Franklin Goldsmith and Bill Green we are examining the kinetics of the $\text{C}_3\text{H}_6\text{OOH} + \text{O}_2$ reaction. This reaction is a key prototype to the second O_2 addition chemistry that plays an important role in low temperature combustion. We will continue to work with Peng Zhang, who is now a CEFRC Fellow. His efforts will focus on combustion at high and ultra-high pressures and we will contribute to the chemistry components of this work.

We have recently agreed to train Chongwen Zhou from Henry Curran's group in Ireland in various aspects of the theoretical calculations. This training will center around a treatment of the decomposition kinetics of n-butanol. We will work at extending this to the full range of butanol species.

In collaboration with Jim Miller we will study the kinetics of some of the key elementary reactions leading to the formation of aromatic compounds with one or two rings. This work will provide the primary focus for our efforts. Ultimately, we aim to have a nearly complete and accurate description of the kinetics of the first and second ring formation.

JOURNAL PUBLICATIONS

- i. Peng Zhang, Stephen J. Klippenstein, Hongyan Sun, and Chung K. Law, "Ab initio kinetics for the decomposition of monomethylhydrazine (CH_3NHNH_2)", *Proc. Comb. Inst.*, **33**, corrected proof in press, (2010); doi:10.1016/j.proci.2010.05.010.
- ii. C. Franklin Goldsmith, Stephen J. Klippenstein, and William H. Green, "Theoretical rate coefficients for allyl + HO_2 and allyloxy decomposition" *Proc. Comb. Inst.*, **33**, corrected proof in press, (2010); doi:10.1016/j.proci.2010.05.054.

RECENT RECOGNITIONS AND HONORS

Argonne National Laboratory Distinguished Performance Award

CONSTRUCTING ACCURATE COMBUSTION CHEMISTRY MODELS

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SUMMARY/OVERVIEW

We construct detailed chemistry models for fuel combustion and pyrolysis, and validate them with available experimental data (most of the data is measured by other CEFRC team members). We also work on improving model-construction methodology, so that we can build more accurate models for a broader range of fuels and conditions. Sensitivity analyses for those experimental conditions and also for proposed future engine conditions indicate which species and reactions need further study. We work to improve rate-coefficient and molecular-property estimates, using quantum chemistry, rate theory, and functional-group extrapolations. In Year 1 and early Year 2 we are focusing on the 4 isomers of butanol. We have several new fuels and new modeling methods we intend to pursue in future years.

ACCOMPLISHMENTS

We have constructed and published fairly accurate models for the combustion chemistry of 1-butanol, 2-butanol, and *tert*-butanol. These models agree fairly well with a very wide range of experimental data (fuel lean through pyrolysis; 800 K to 1800 K), so we believe they will be accurate over the whole range of conditions important for engine combustion. All the thermochemistry and rate coefficients in these models are derived from elementary-reaction experiments or quantum chemistry calculations, i.e. the model parameters were not tweaked to agree with the experimental data used for validation. This gives us greater confidence in making extrapolative predictions with the models e.g. to engine conditions. We are now building the model iso-butanol., and on making the models more accurate for low-T high-P ignition of the butanols. (Previous work in the literature and new RCM experiments by C.J. Sung's group suggest there are problems with all existing models at these conditions). With Stephen Klippenstein we also made and published a detailed study on the reaction $\text{HO}_2 + \text{allyl}$, an important reaction under low-T, high-P conditions, and with the decomposition of its dominant product, the allyloxy radical. This study revealed significant problems with existing kinetic models and with the literature on this 2-step reaction. Probably other resonantly-stabilized carbon-centered radicals react similarly.

The process of building and validating the butanol models revealed many methodological challenges as well as significant flaws in prior understanding of the chemistry. Special computer methods appear to be needed to make it practical to explore the millions of reactions which can occur at pre-ignition conditions; it is easy for the complexity of the chemistry to overwhelm the computer memory. This is particularly problematic for systems where a large number of low-energy isomers can be formed by chemically-activated reactions. We are creating new algorithms to address this problem.

Among the interesting chemical issues which were highlighted during the past year: 1) Serious problems with the conventional independent-rotors approximation for molecules which can form intramolecular H-bonds between functional groups (Sharma, Raman, & Green, JPCA (2010) **114**, 5689). This significantly affects both the thermochemistry and unimolecular reaction rates. 2) The role of bimolecular H-bonding in H-abstraction reactions by OH, which was brought to my attention by Simmie. Probably similar effects occur with HO₂ reactions. This high-T gas-phase transient H-bonding can significantly affect the selectivity i.e. which H is abstracted, and so which radical is formed, with major kinetic consequences; 3) the importance of enol intermediates and unimolecular dehydration reactions in the combustion of alcohols. This comes out clearly in the butanol kinetic models and in several experiments e.g. flow reactor studies by Dryer's group. 4) "Roaming Radicals": Klippenstein and Harding showed how to compute the rates of these strange but ubiquitous reactions. Early indications suggest that they are important in ROOH decomposition (in pre-ignition).

All these chemistry effects need to be systematically incorporated into combustion chemistry models; so far this has been done, if at all, on a somewhat *ad hoc* basis.

PLAN FOR FUTURE WORK

In the short term, we will continue our close cooperation with the team on the butanols, aiming to publish a joint article highlighting the team's accomplishments, and the benefits of team-integrated approach to chemical kinetics. We will also continue our collaboration with Stephen Klippenstein on a detailed study of the reaction $C_3H_6OOH + O_2$, an archetype for the many $QOOH + O_2$ reactions important in ignition. We will resolve the large-mechanism memory problem, and adjust our rate-estimation rules to try to account for the chemistry phenomena mentioned above. We have also performed high-accuracy quantum chemistry calculations to refine the thermochemistry of many small-molecule combustion intermediates, and we will publish these and incorporate them in the models. We look forward to Jim Miller's update of the small-molecule chemistry.

In the medium term, we will build models for new fuels and fuel mixtures (e.g. esters, furans, mixtures with fuel additives), use the fuel models in engine simulations, including simulations of new high-efficiency 2-fuel engine concepts, and better identify which fuel reactions / properties are really important for engine performance. This will involve reducing the size of the models, which we will do in collaboration with Ed Law. Certain fuels are more chemically-interesting than others, but the most important question is whether or not the fuel is likely to be deployed on a large scale. For nonvolatile fuels (e.g. biodiesel) it is possible that significant reaction occurs in the liquid phase, which we can treat by adding solvent effects to the kinetic model. Some of the interesting low-temperature chemistry (gas phase or liquid phase) can be measured directly at MIT using flash photolysis.

In the long-term, we would like to automate the process of computing $k(T)$ with quantum chemistry, so that the reaction rate coefficients could be accurately computed on-the-fly as the chemistry model is constructed. This would avoid the inaccuracy of long functional group extrapolations, and automatically capture phenomena such as intramolecular H-bonds, and steric effects on reactions through cyclic transition states, whose effects are hard to quantitatively estimate in absence of a full calculation. This will likely involve switching from the current "2-d" connectivity graph representation of molecules to a true "3-d" representation (which would provide a good initial guess geometry for quantum calculations).

This transformation from by-hand calculations of single reactions to automated calculations of millions of reactions would be a game-changer for the field of chemistry, and would be a good “Grand Challenge” target for the computational chemistry community. I believe the main technical challenge is developing a sort of “artificial intelligence” program which will help guide the saddle-point optimizer to a chemically-relevant TS geometry, though perhaps there are clever ways to accomplish this more efficiently. Note for example prior work by Irikura and Johnston [JPCA (2000), *104*, 2191] on automating searches for saddle points (even without any good initial guess geometry or specification of the products.)

JOURNAL PUBLICATIONS FUNDED BY CEFRC

- 1) Michael R. Harper, Kevin M. Van Geem, Steven P. Pyl, Guy B. Marin, and William H. Green, “Comprehensive Reaction Mechanism for n-Butanol Pyrolysis and Combustion”, *Combustion & Flame* (2010, accepted).
- 2) Kevin M. Van Geem, Steven P. Pyl, Guy B. Marin, Michael R. Harper, and William H. Green, “Accurate Reaction Networks for Alternative Fuels: Butanol Isomers”, *Industrial & Engineering Chemistry Research* (2010, accepted).
- 3) C. Franklin Goldsmith, Stephen J. Klippenstein, and William H. Green, “Theoretical rate coefficients for allyl + HO₂ and allyloxy decomposition”, *Proc. Combust. Inst.* (2010, accepted).

**SUMMARY OF DISCIPLINARY WORKING GROUP.
CHEMISTRY: EXPERIMENT AND MECHANISM**

Hai Wang

Accomplishments

The Mechanism and Experiment DWG uses four types of experimental apparatus to probe the combustion chemistry of fuels. Primary apparatus used include shock tube (Hanson/Davidson), variable-pressure turbulent flow reactor (Dryer), rapid compression machine (Sung), low-pressure burner stabilized flame coupled with synchrotron photoionization mass spectrometry (Hansen, Dryer), and atmospheric-pressure burner stabilized-stagnation flame (Wang), and premixed counterflow flames (Sung). These techniques allow us to access a wide range of pressure, temperature and stoichiometry for probing combustion reaction chemistry.

During the first year of the CEFRC effort, kinetic measurements were centered on bio-fuel derivatives including alcohols and esters.

Summary of experiments

Apparatus	Fuel/reactant	Data type	Conditions	Purpose
Shock tube	4 butanol isomers	ignition delay	1-42 atm, 1050-1600 K	model validation
Shock tube	<i>n</i> -butanol (oxidation)	OH & H ₂ O time histories	1430 K, 1.5 atm	model validation
Shock tube	butanols + OH → products	OH laser absorption	1100-1400 K 1-2 atm	rate constant
Shock tube	methyl esters	ignition delay absorption	1150-1350 K 7 atm	model validation
VPFR	<i>i</i> -propanol <i>t</i> -butanol	species time histories	3 and 12.5 atm 500-1000K	model development/ validation
VPFR	<i>i</i> -propanol	species time	3 and 12.5 atm, scavenger	H ₂ O elimination rate determination
VPFR	methyl formate (pyrolysis)	Species time histories	1000 K	rate constant, surface effects
RCM	<i>n</i> -butanol	ignition delay	15 & 30 atm	model validation
RCM	methanol	ignition delay	7, 15 & 30 atm	model validation
Premixed flame*	methyl formate	species profile	22-30 Torr $\phi = 1.0-1.8$	model development/ validation
Premixed flame*	<i>n</i> -butanol, <i>i</i> -butanol <i>i</i> -butane, <i>i</i> -butene	species profile		model development/ validation
Premixed flame ^{&}	<i>n</i> -butanol, <i>i</i> -butanol	soot PSDFs	1 atm, $\phi = 3.0$	model validation
Premixed flame	H ₂ /CO/H ₂ O	Flame speed	1 atm	model validation

* Molecular-beam synchrotron photoionization mass spectrometry. [&] Scanning mobility particle sizing

Additionally, experiments have been conducted which yielded motivating information about the kinetic interactions of butanol isomers with heptane (Dryer).

Reaction Mechanism Development

Reaction models of propanol isomers and methyl formate is under development by Dryer. An updated kinetic-transport model for the H₂/O₂ system is now available to account for burning rates at high pressures (Dryer). Reaction kinetics of isobutene and isobutane have been examined using USC Mech II (Wang). A wide range of validation tests have been conducted by DWG members using Green's reaction model of butanol isomers. The chemistry and kinetics of sooting processes in *n*-butanol and *i*-butanol is being examined (Wang). Additional accomplishments include an experimental and theoretical study on the products and their branching ratio for the reaction of benzene + O(³P) with an emphasis on the role of spin-state crossing on elementary reaction rates (Wang).

Future Work

Dryer: Studies leading to improved models for simple alcohols and esters. Provide elementary rate constants relevant to biofuel combustion chemistry and kinetic system validation data using flow reactor techniques, small molecule chemistry important to high-pressure reaction chemistry, including base sub-model species for <C₄ intermediate species.

Hansen: Studies of the oxidation chemistry and reaction paths in combustion of oxygenated, bioderived fuels combining the VUV photoionization mass spectrometer (with improved mass resolution) and state-of-the-art laser methods with detailed flame chemistry in laminar premixed flat flames and in a jet stirred reactor (currently under development with Ju).

Hanson/Davidson: Future work is divided into two parts: 1) complete rate coefficient measurements for all the isomers of butanol+OH; and 2) extend ignition delay time and species time-history measurements for large bio-derived methyl esters (including methyl stearate) using our 2nd generation aerosol shock tube. A longer-term goal would be to initiate studies of very-high-pressure and ultra-high-pressure ignition phenomena (up to 1000 atm) in conventional and new fuels using the Stanford high-pressure shock tube (HPST).

Sung: Provide data for autoignition delay for a large range of fuels, including butanol isomers, 2-buten-1-ol, *iso*-pentanol, gasoline/bio-alcohol blends, and syngas with speciation data using GC/MS, GC-FID and IR Spectroscopy. Carry out modeling study to test kinetic mechanisms against the data

Wang: Complete the development of an isobutanol model with its base model (isobutene/isobutane) validated. Develop fuel-rich chemistry of *n*-butanol and *iso*-butanol flames, including sooting chemistry. Provide diffusion cross section data for large molecules using a crossed molecule-particle beam apparatus. Understand the nature of aromatic π -diradicals and their role in soot nucleation/mass growth.

Major items of discussion for Thursday evening and Friday morning

- (1) Unifying and consolidating thermochemical data, transport coefficients and chemical kinetic models for small fuels.
- (2) Fuels to study for the future:
 - substituted five- and six-membered cyclic ethers
 - furan and its derivatives
 - others
- (3) Grand and less-than-grand challenge problems:

- high pressure reaction kinetics/transport
- parameter uncertainty quantification/propagation
- particulate formation: (the lack of fundamental) mechanism and kinetics
- transport properties of large molecules

DEVELOPING FUNDAMENTAL KINETICS DATABASE THROUGH SHOCK TUBE STUDIES

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SUMMARY/OVERVIEW

The Stanford group is developing a fundamental kinetics database for butanol chemistry (all four isomers) and large methyl esters using shock tube/laser absorption methods. This database currently includes high-temperature (1050-1600 K) ignition delay time measurements at pressures of 1-42 atm, species time-history measurements of OH, H₂O and 1-butanol during oxidation and pyrolysis, and rate coefficient measurements of n-butanol+OH. Preliminary ignition delay time and fuel time-history measurements for methyl decanoate (C₁₁H₂₂O₂) and methyl oleate (C₁₉H₃₆O₂) have also been performed. This study provides the first extensive kinetics data for these fuels, and will enable direct validation and refinement of butanol and methyl ester detailed mechanisms.

ACCOMPLISHMENTS

Current work is divided into two areas: butanol studies and methyl ester studies.

Butanol Studies

We have measured ignition delay times for the four butanol isomers over a pressure range of 1-42 atm and a temperature range of 1050-1600 K. In the case of 1-butanol ($\phi=1.0$), the ignition delay time varies with pressure at 1250 K as $P^{-0.67}$ over the entire pressure range studied. When compared with these data, the current Harper-Green/MIT/2010 detailed mechanism for 1-butanol recovers the measured low-pressure ignition delay fairly well, but at high pressures, the simulations consistently yielded times one-third shorter than the experiment. An inter-comparison of the ignition delay times for the four isomers reveals that 1-butanol has the shortest ignition delay times, typically about 50% shorter than 2-butanol and iso-butanol, but with the same approximate activation energy. tert-Butanol has the longest ignition delay times, typically about 2-3 times the values for iso- and 2-butanol, and with a significantly different activation energy. The MIT mechanism overpredicts the measured ignition delay times of tert-butanol at the highest temperatures, but underpredicts the ignition delay times of iso-butanol. Predictions for 1- and 2-butanol are in relatively good agreement with experiment.

We have applied our multi-wavelength, multi-species methodology to the study of 1-butanol pyrolysis and oxidation. Using this method, we have measured OH, H₂O and 1-butanol concentration time-histories. Preliminary comparisons of the Harper-Green/MIT detailed mechanism show that the time scales during pyrolysis are substantially longer in the model than the experiment; a similar effect is seen in the oxidation case as well.

Finally, measurements of the rate constant k_1 of the reaction of 1-butanol + OH were made over a temperature range of 1020-1270 K and pressures near 2 atm. Pseudo-first order experiments were performed by generating near-instantaneous ppm levels of OH behind reflected shock waves in a bath of 1-butanol and argon using tert-butyl hydroperoxide as an OH precursor. Representative results are shown in Figure 1. Excellent agreement is seen with the recent theoretical predictions by Zhou, Simmie et al. at NUI/Galway (2010).

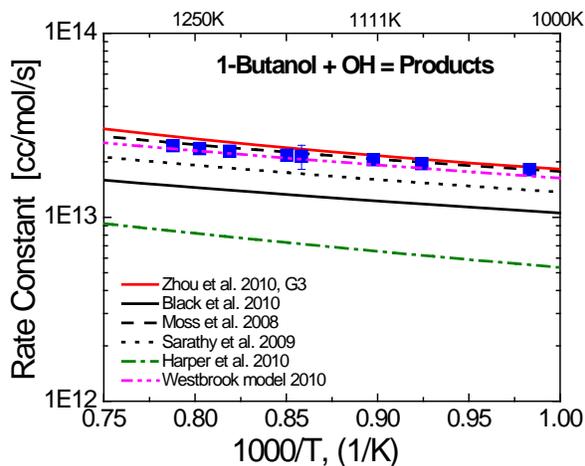


Figure 1. Arrhenius plot for OH+n-butanol.

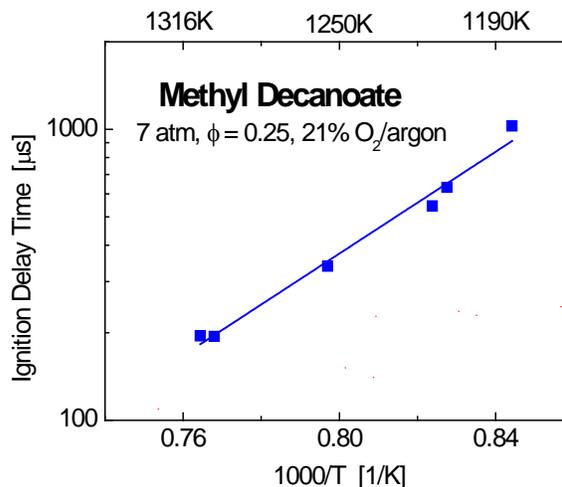


Figure 3. Preliminary ignition delay times for the bio-fuel surrogate, methyl decanoate, measured using the Stanford Aerosol Shock Tube.

Methyl Ester Studies

There have been very few shock tube kinetics studies of large bio-derived methyl esters, even though these substances are important components of bio-Diesel fuels and surrogates. This is primarily because these large methyl esters have very low vapor pressures and are difficult to load into conventional shock tubes even with pre-test heating. We have developed an aerosol shock tube methodology that enables the study of these and other low-vapor-pressure fuels.

The range of methyl esters that can be studied with an aerosol shock tube is significantly greater than that of a conventional shock tube. Figure 2 presents a performance map that shows the operating regimes of a conventional shock tube, both heated and unheated, and that of an aerosol shock tube with both heated and unheated nebulizers. As can be seen for this example case of a 10 atm, 1000 K ignition delay time experiment, the use of the aerosol shock tube extends the possible range of measurable ignition delay times for saturated methyl esters beyond $C_{10}H_{20}O_2$ (methyl nonanoate), which should be possible with a strongly-heated shock tube, to $C_{24}H_{48}O_2$ (methyl tricosanoate) or $C_{25}H_{50}O_2$ (methyl tetracosanoate, methyl lignocerate).

Shock Tube Access to Fuels: Saturated Methyl Esters

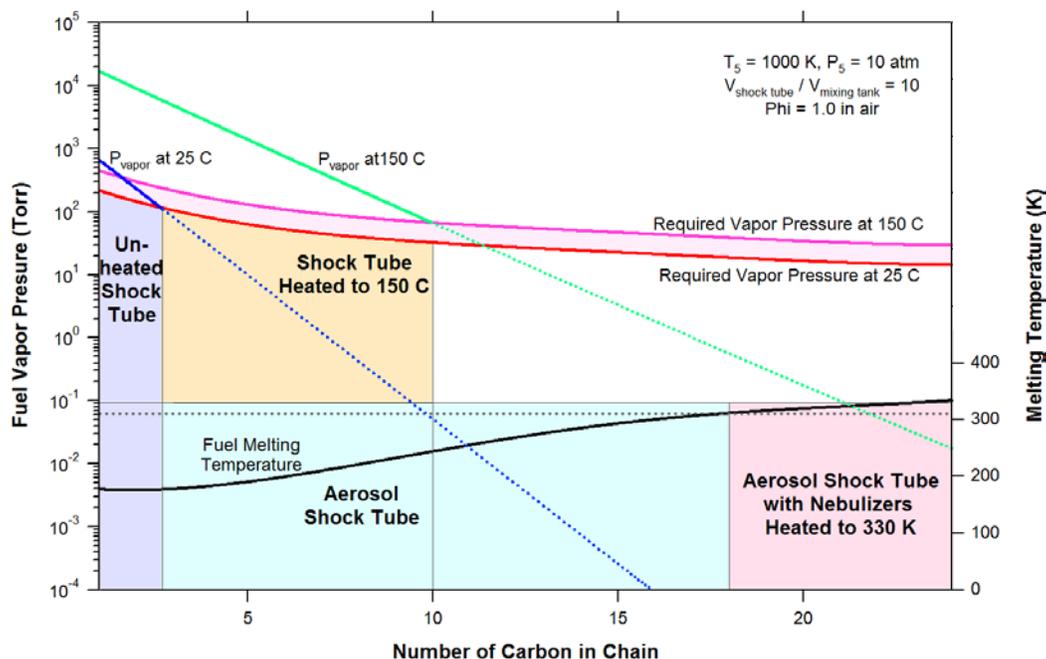


Figure 2. Shock tube operating regimes: methyl esters. Access up to $C_{25}H_{50}O_2$ (methyl tetracosanoate) should be possible with heated nebulizers.

We are currently using the Stanford Aerosol Shock Tube to investigate ignition delay times and species time histories for methyl decanoate ($C_{11}H_{22}O_2$, C10:0) and methyl oleate ($C_{19}H_{36}O_2$, C18:1). Preliminary ignition delay time results for methyl decanoate are shown in Figure 3. These represent the first ignition delay time measurements for this species.

PLAN FOR FUTURE WORK

Future work is divided into two parts: 1) complete rate coefficient measurements for all the isomers of butanol+OH; and 2) extend ignition delay time and species time-history measurements for large bio-derived methyl esters (including methyl stearate) using our 2nd generation aerosol shock tube. A longer-term goal would be to initiate studies of very-high-pressure and ultra-high-pressure ignition phenomena (up to 1000 atm) in conventional and new fuels using the Stanford high-pressure shock tube (HPST).

JOURNAL PUBLICATIONS

S. S. Vasu, D. F. Davidson, R. K. Hanson, D. M. Golden, "Measurements of the Reaction of OH with n-Butanol at High Temperatures," *Chem. Phys. Lett.* 487, 26-29 (2010).

S. S. Vasu, J. Zador, D. F. Davidson, R. K. Hanson, D. M. Golden, J. A. Miller, "High-Temperature Measurements and a Theoretical Study of the Reaction of OH with 1,3-Butadiene," submitted to *J. Phys. Chem. A*, May 2010.

COMBUSTION STUDIES OF ALCOHOLS, ESTERS AND HYDROGEN RICH FUELS

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SUMMARY/OVERVIEW

The overall areas to which the Fuels Combustion Research Laboratory is contributing to the CEFRC efforts encompass: a) generation of motivating fundamental experimental observations that elucidate the interactions of bio-derived molecular components and structures with components found in petroleum derived fuels; b) provision of experimental validation data for development and refinement of detailed kinetic models for esters and alcohols; c) experimental determination of elementary kinetic rates important to the decomposition and oxidation of hydrocarbons and hydrocarbon oxygenates. Over the past year, the laboratory has contributed to the following areas: 1) the practically relevant ignition properties of the isomers of butanol when mixed with gasoline components have been determined in an Ignition Quality Tester. These data show that additions of the normal-, secondary-, iso-, and tertiary-isomers depress the autoignition of n-heptane, and that the behavior of the tertiary isomer depression is uniquely different. Detailed chemical kinetic studies of tertiary butanol oxidation and pyrolysis (with and without the presence of a radical scavenger) have been undertaken employing the Variable Pressure Flow Reactor (VPFR). In collaboration with NUI-Galway, similar studies are underway on the isomers of propanol. 2) As part of a larger study on a series of small methyl esters, the flame oxidation and decomposition chemistry of methyl formate, the most basic methyl ester, has been studied by the development of a detailed chemical kinetic model. 3) An updated kinetic-transport model for the H_2/O_2 system has been constructed to incorporate recent improvements in rate constant expressions and transport properties and in response to the inability of currently published models to reproduce burning rate observations on hydrogen – oxygen and hydrogen – oxygen – methane mixtures.

ACCOMPLISHMENTS

1. Autoignition of Fuel/Butanol Blends in an Ignition Quality Tester

The isomers of butanol have been identified as promising candidates for 2nd generation biofuels; hence, much study has been devoted to determining the combustion properties of these isomers in their pure forms. However, much less work has been conducted to determine their behavior when in blends with conventional petroleum and/or its components, which is the likely end use scenario for these bio generated materials. Ignition Quality Tester (IQT) derived cetane numbers (DCNs) of blends of normal-, secondary-, iso-, and tertiary-butanols with both n-heptane and a real diesel fuel have been measured to explore the autoignition behavior of the mixtures at conditions relevant to transportation applications. Surprisingly, t-butanol, which has been shown in other studies to be the least reactive butanol as a pure component, shows the highest reactivity in blends (Fig 1). These DCN results additionally suggest that, subject to other constraints (e.g.

flashpoint), up to several percent t-butanol can be blended into distillate-grade fuels without substantially affecting cetane number.

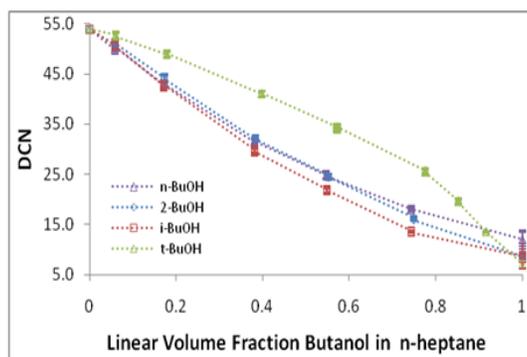


Figure 1. Butanol-n-heptane blend DCNs as a function of blend composition.

2. Chemical Kinetics of iso-Propanol and t-Butanol Pyrolysis and Oxidation

Alcohols such as methanol and ethanol have been extensively studied in terms of fundamental data and chemical kinetic modeling, while few studies exist on the so-called “next-generation” biofuels of higher molecular weight alcohols such as the propanols and butanols. Due to the relatively fewer experimental studies presently in the literature, the propanol and butanol isomers (particularly t-butanol) have been selected for detailed mechanistic study at conditions available in the VPFR.

Oxidation and pyrolysis studies (with and without the presence of a radical scavenger) have been conducted on these fuels in the temperature range 500-1000 K and at 3 and 12.5 atm pressure. At all pyrolytic conditions, all fuels are observed to form large and stoichiometric quantities of water and an olefin, propene in the case of the propanols and iso-butene in the situation of t-butanol. These observations are related to the prevalence of the molecular elimination reaction channel characteristic of simple alcohols. Experiments and analyses are currently under way with the use of radical trapping techniques to extract rate constant information from the data, Figure 2. In addition to experimentally isolating the dehydration reaction of iso-propanol and t-butanol, the overall oxidation behavior of both fuels has been studied, Figure 3. For both fuels, no low temperature reactivity characteristic of RO₂ chemistry was observed over the range of conditions available in the VPFR. Both fuels show the onset of oxidation at a low temperature of approximately 750K. Iso-butene and acetone are the observed major intermediate species derived in the oxidation of t-butanol, while iso-propanol oxidation is observed to form large quantities of propene and ethylene.

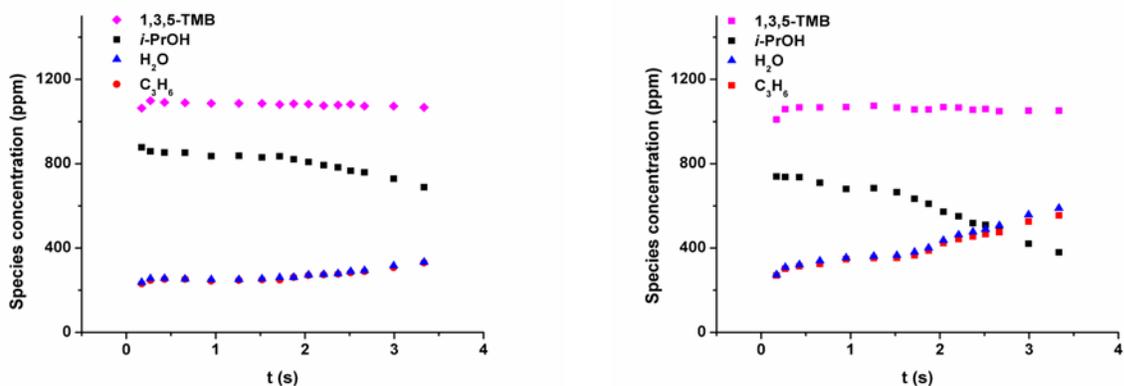


Figure 2. iso-propanol/mesitylene pyrolysis at 900K (LHS) and 950K (RHS)

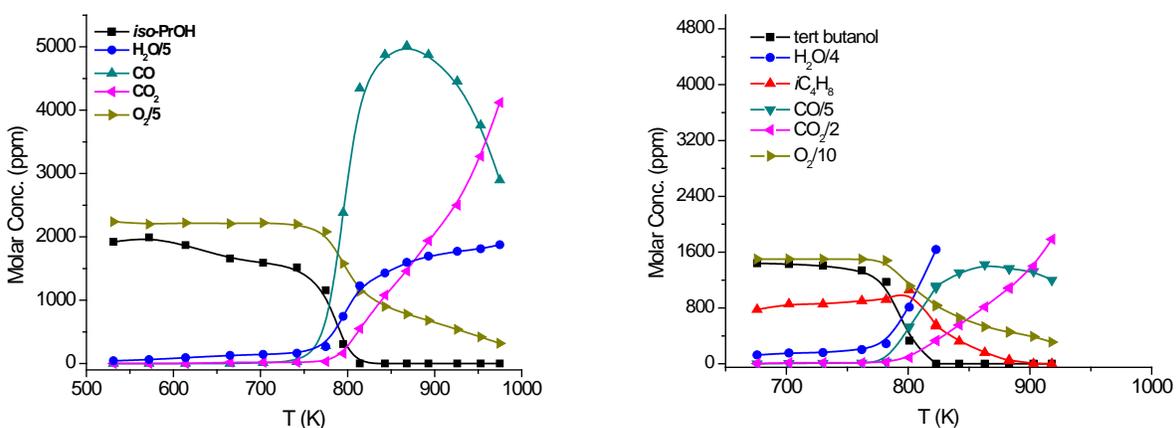


Figure 3. iso-Propanol oxidation reactivity analysis (LHS). t-Butanol reactivity profile oxidation ($\tau = 1.8$ sec, and 12.5 atm) (RHS).

3. An updated kinetic-transport model for the H₂/O₂

The hydrogen-oxygen sub-model is of central importance to combustion predictions for synthesis gas and more generally for all hydrocarbon and oxygenated fuels. In many advanced engine technologies, combustion occurs at high pressures to increase efficiencies and at reduced flame temperatures to control raw NO_x emissions. A number of recent studies have revealed substantial difficulties in accurately predicting flame behavior at high pressures and low flame temperatures, where the role of HO₂ formation and its subsequent reactions become prevalent throughout most of the flame structure.

An updated detailed kinetic-transport model based upon the earlier model of Li et al., 2004 (IJCK 36 pp. 566-575) has been developed to incorporate recent improvements in rate constant correlations and transport properties. Particular emphasis was placed on improving the treatment of reactions responsible for HO₂ production and consumption. For example, several aspects of the current treatment of $H + O_2 (+M) = HO_2 (+M)$ in kinetic models are reconsidered, including

the impact of nonlinear mixture rules for multi-component bath gases. More accurate expressions for the rate constant temperature dependence of $\text{HO}_2 + \text{X}$ ($\text{X}=\text{H}, \text{O}, \text{OH}, \text{HO}_2$) reactions based on recent experimental measurements and theoretical calculations have been incorporated. Consideration was also given to potential missing reaction pathways that could play a role under radical recombination-favored flame conditions. The updated model maintains reasonable fidelity to previous validation targets used by Li et al., as well as improves predictions against more recent high-pressure, low-flame-temperature flame speed data of interest to practical syngas applications, e.g. see Fig. 4.

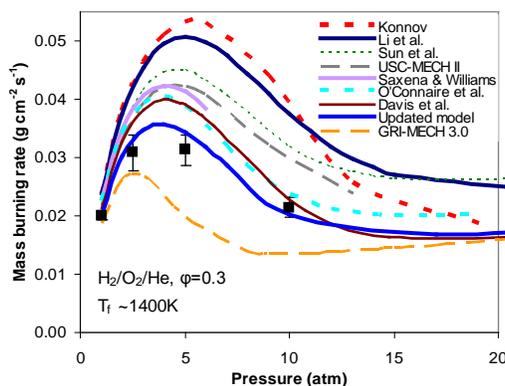


Figure 4. Comparison of measured and predicted mass burning rates for a lean, dilute H_2 flame as a function of pressure.

4. Methyl Formate Decomposition and Oxidation in Low Pressure Flames

In collaboration with Sandia National Laboratory and Cornell University, the oxidation of methyl formate (CH_3OCHO), the simplest methyl ester, has been studied in a series of burner stabilized laminar flames at pressures of 22–30 Torr and equivalence ratios (Φ) from 1.0–1.8 for flame conditions of 25–35% fuel. Flame structures are determined by quantitative measurements of species mole fractions with flame sampling molecular-beam synchrotron photo ionization mass spectrometry (PIMS). Methyl formate is observed to be converted to methanol, formaldehyde and methane as major intermediate species. Smaller amounts of ethylene and acetylene are also formed from methyl formate oxidation. Reactant, product and major intermediate species profiles are in good agreement with the computations of a recently developed kinetic model for methyl formate oxidation (Dooley et al., 2010; *IJCK*, 42, pp. 527–549) which shows that hydrogen abstraction reactions dominate fuel consumption under the tested flame conditions. Radical-radical reactions are shown to be significant in the formation of a number of small concentration intermediates, including the production of ethyl formate ($\text{C}_2\text{H}_5\text{OCHO}$), the subsequent decomposition of which is the major source of observed ethylene concentrations. The good agreement of model predictions with this set of experimental data provides a further validation of the proposed mechanism of methyl formate oxidation.

Uncertainties in the measurement and computation of low pressure flame sampling experiments are quantified and have been shown not to alter the kinetic or mechanistic conclusions provided by the kinetic modeling analysis. In particular, perturbations of the temperature profile by the

presence of the molecular beam sampling cone are shown to be inconsequential to kinetic mechanistic interpretations. However, such perturbations are shown to be responsible for the small disparities in species location between measurement and computation, Figure 5.

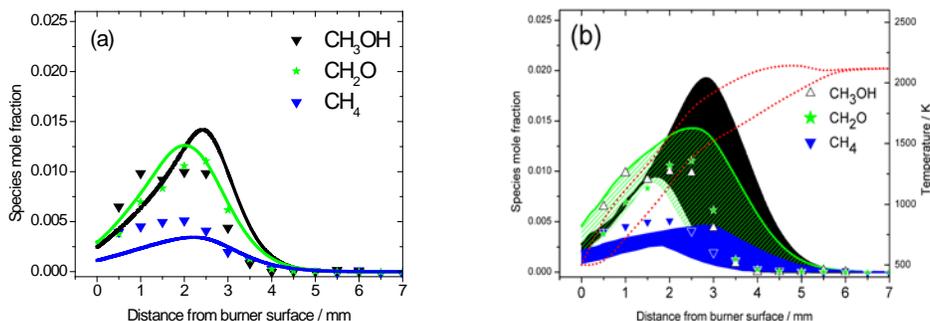


Figure 5. Major intermediate species measured (symbols) from methyl formate oxidation in a $\Phi=1.0$ burner stabilized flame at ~ 30 Torr and kinetic model [Dooley et al. IJCK 2010] computations. (a): unperturbed and (b) assuming perturbations of ± 200 K to measured temperature profile in reaction zone.

The unimolecular decomposition of methyl formate is shown to be important in the low pressure flame environment and previously shown to be controlling under autoignition conditions. The kinetics of the gas phase decomposition is a source of debate in the scientific literature, reported values of the Arrhenius activation energy vary extravagantly from 48-77 kcal mol⁻¹. In our previous work, a rate constant of $2.0 \times 10^{13} \text{ Exp}^{(-60,000 \text{ cal}/RT)} \text{ cm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ was measured for the reaction of $\text{MF}_{(g)} \leftrightarrow \text{CH}_3\text{OH}_{(g)} + \text{CO}_{(g)}$ by the flow reactor technique. The potential effect of wall catalytic reactions on this measurement has been evaluated by computational fluid dynamics large eddy simulation of the entire flow field of the reactor. The results show that heterogeneous surface perturbations cannot significantly affect the measurement of the gas phase reaction, Figure 6.

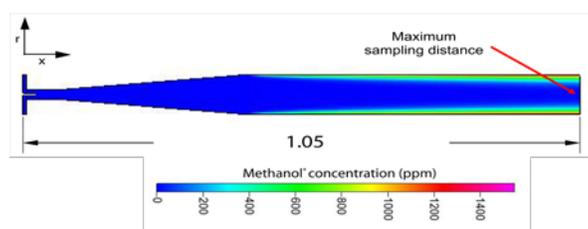


Figure 6. Calculated concentration of CH_3OH^* (product of wall catalytic reaction) in the Princeton flow reactor at 975 K, 3 atm, 14.344 g/s flow rate of 5000 ppm MF in N_2 .

FUTURE PLANS

In the coming year, we will be continuing our collaborations within and external to the CEFRC on improving models for simple alcohols and esters. We are continuing efforts to contribute elementary rate constant measurements and kinetic system validation data using flow reactor techniques. We are also planning on further contributions to the small molecule chemistry that is important to high pressure oxidation kinetics of these materials.

JOURNAL PUBLICATIONS

S. Dooley, **F.L. Dryer**, B. Yang, J. Wang, T. A. Cool, T. Kasper, N. Hansen “ An Experimental and Kinetic Modeling Study of Methyl Formate Low-Pressure Flames” *Combustion and Flame* in press.

CHEMICAL KINETIC STUDIES ON ALTERNATIVE FUELS

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SUMMARY/OVERVIEW

Using rapid compression machine (RCM), we have obtained autoignition delay data for *n*-butanol and methanol at elevated pressures. In addition, nanoparticle enhanced combustion of ethanol and JP-8 is explored and demonstrated. We have further implemented a system to obtain speciation data from the RCM using GC/MS and GC-FID/TCD. Using a counterflow twin-flame configuration, laminar flame speeds for moist syngas mixtures are measured over a range of hydrogen molar percentages in the hydrogen and carbon monoxide mixtures. Our next steps include investigation of the other three isomers of butanol, unsaturated butanols, *iso*-pentanol, and gasoline/bio-alcohol blends using the RCM with speciation data as well as *in situ* IR absorption spectroscopy. These studies are collectively designed to address the gaps in chemical kinetic knowledge, particularly combustion of alcohols under engine relevant conditions, and interactions between the chemistry of alcohols and traditional hydrocarbon fuels.

ACCOMPLISHMENTS

(1) *n*-Butanol Autoignition Delay Experiments

Autoignition delay experiments using the RCM are conducted for *n*-butanol/air mixtures for several equivalence ratios and compressed pressures of 15 and 30 bar. The experimental results show no NTC region and no two-stage ignition for the conditions studied. In addition, the experimental data are compared with four reaction mechanisms available in the literature. The simulations tend to take much longer to ignite than the experiments; for most cases, the discrepancy is at least one order of magnitude. Sensitivity analysis and reaction path analysis of one mechanism are used to help determine the cause of this discrepancy. The system is most sensitive to the reaction of *n*-butanol and HO₂, when the HO₂ abstracts a hydrogen atom from the carbon atom closest to the alcohol. The uncertainties in this rate suggest it as a good candidate for refinement. Reaction path analysis further illustrates several pathways which are not included in the mechanism. Adding these pathways may improve the comparison between experimental and simulated ignition delays.

(2) Methanol Autoignition Delay Experiments

Autoignition delay experiments using the RCM are conducted with methanol/oxidizer mixtures for several equivalence ratios and compressed pressures of 7, 15, and 30 bar. The experimental data are compared with simulated results from two mechanisms available in the literature. The simulations tend to ignite much more quickly than the experiments at the conditions tested in this study. To help determine the cause of the discrepancy, global sensitivity analysis is used to identify reactions which may be the controlling steps. At the condition studied, the reaction between methanol and HO₂ is found to be the most influential step. The rate for this reaction is

studied numerically, and it is found that reducing the rate of this reaction to a value suggested elsewhere in the literature would improve the comparison between experimental and simulated results. Furthermore, modifying the rate of this reaction in this way does not affect comparisons with high temperature data.

(3) Energetic-Nanoparticle-Enhanced Combustion of Liquid Fuels

The use of energetic nanoparticles offers a promising means of adjusting the reactivity of liquid fuels for enhanced combustion stability in next generation propulsion systems. With an aerosol rapid compression machine, the impact of energetic nanoparticles on reducing the ignition delay of liquid fuels is demonstrated using ethanol and JP-8. Fuel droplets are generated using an ultrasonic nozzle. The seeding of 50 nm aluminum nanoparticles in the liquid fuel is achieved by using a combination of chemical surfactants in addition to mixing in an ultrasonic bath. The autoignition delay is measured for neat and nanoparticle-enhanced mixtures at compressed conditions of 772–825 K and 15–28 bar in the RCM. The results show that significant changes in the ignition delay can be observed using a low concentration (2%-weight) of energetic nanoparticles. For ethanol and JP-8, ignition delays are reduced by 32% and 50%, respectively. This work is in collaboration with Michigan State University and University of Akron.

(4) Moist Syngas Laminar Flame Speed Measurements

Laminar flame speed measurements over a wide range of H_2/CO ratios are conducted to investigate the effect of water addition on flame propagation. CO-rich mixtures (i.e. small H_2/CO ratio) exhibit non-monotonic behavior of the laminar flame speed as water vapor is added to the mixture. For higher values of H_2/CO ratio, water addition monotonically reduces the laminar flame speed. There are two competing effects which cause this behavior. For high percentages of water addition, and for higher H_2/CO ratios, the addition of water causes a thermal effect because of the higher specific heat of water, which reduces the adiabatic flame temperature and the laminar flame speed. However, for lower percentages of water addition and CO rich mixtures, there is a chemical effect of water addition. Additional radicals are created which enhance the reactivity and increase the flame speed.

Computed laminar flame speeds compare well with experimental data at H_2/CO ratio equal to one; however, at higher H_2/CO ratios the mechanism tested under-predicts the laminar flame speed, while it over-predicts at lower H_2/CO ratios. The extent of the deviation becomes more pronounced as equivalence ratio is decreased. Reaction rate sensitivity analysis suggests that reducing the uncertainty for the rate constant for the reaction of $H_2+OH=H_2O+H$ could improve predictions, as well as improving the binary diffusion coefficients for several species pairs.

(5) Speciation using GC/MS and GC-FID/TCD

One particular interest in the RCM study is to perform quantitative measurements of stable reaction intermediates at different stages of oxidation, which not only will help to gain further insights into the oxidation chemistry of test fuels, but also can provide much needed experimental data for the development of high-fidelity, predictive chemical kinetic models for the oxidation of next-generation, non-petroleum-derived transportation fuels.

Two existing gas chromatographs have been refined and reconfigured to perform accurate speciation measurements. A Shimadzu QP2010 GC-MS system equipped with a split/splitless capillary injector and a 10-port sampling valve has been refined to perform qualitative analysis of stable reaction intermediates produced from the RCM experiments. The existing Shimadzu GC 2014-FID/TCD system has been upgraded and reconfigured for accurate quantification of hydrocarbon species and permanent gases. A new split/splitless capillary injection unit has been installed in the GC 2014. In addition, the 10-port sampling valve and flow configuration in the GC-FID/TCD system have been reconfigured. Identical capillary columns are used in both GC-MS and GC-FID so that hydrocarbon species identified via GC-MS can be accurately quantified using GC-FID. This system, combined with the planned IR spectroscopy system, is expected to provide insights into the low-temperature, high-pressure oxidation of fuels.

PLAN FOR FUTURE WORK

(1) Autoignition Delay of Butanol Isomers

The other three isomers of butanol (*iso*-, *sec*-, and *tert*-butanol) are receiving increased attention for several reasons. Some of the other isomers have higher octane rating than the normal isomer, which potentially makes them excellent additives for gasoline-based engines. In addition, the chemistry of the butanols may be able to be extended to higher alcohols. For these reasons, understanding the chemistry of the butanols is an important step forward.

(2) Autoignition Delay of 2-buten-1-ol

2-buten-1-ol is an important intermediate in the combustion of *n*-butanol, and has been found by several studies in the literature, especially under engine-relevant conditions. In addition, 2-buten-1-ol has some potential as an additive in, or replacement for, gasoline. Understanding the autoignition chemistry of this fuel is thus quite important. This work will be in collaboration with Bill Green of Massachusetts Institute of Technology.

(3) Autoignition of *iso*-Pentanol

iso-Pentanol produced from biological sources presents several advantages over ethanol and butanol including higher energy content and lower water solubility, which makes it a promising alternative to petroleum-derived gasoline fuels. Autoignition of *iso*-pentanol will be investigated using our rapid compression machine under both SI- and HCCI-relevant conditions over a wide range of pressure and temperature conditions.

(4) Autoignition of Gasoline/Bio-Alcohol Blends

As alcohol fuels will serve mainly as blending components in petroleum-derived gasoline fuels in the near future, it is necessary to investigate the autoignition behavior of gasoline/alcohol blends at different blending ratios. Moreover, it is important to achieve a fundamental understanding of the kinetic interactions between gasoline and alcohols during their co-oxidation. Therefore, it is of fundamental and practical interest to explore the autoignition

chemistry of the blends of gasoline with various alcohols (e.g., ethanol, 1-butanol, iso-pentanol, etc.) under engine-relevant conditions.

(5) Autoignition Delay of Syngas

Preliminary autoignition delay experiments using the RCM have been conducted with syngas for stoichiometric conditions at 30 bar. Several H₂/CO ratios are tested, as well as several levels of water addition. The results show an interesting trend as functions of both CO molar percent and water molar percent. For the case of pure hydrogen (i.e. CO molar percent = 0), the ignition delay first increases up to water addition level of 2.5% and then decreases as more water is added, up to 10%. For equal amounts of H₂ and CO, the same trend occurs above temperature of approximately 1050 K, but the ignition delay is monotonically decreasing as more water is added below that temperature. Further, for H₂/CO ratio of 5/95, the ignition delay decreases monotonically as more water is added, below about 1000 K, but for temperatures above 1000 K, the ignition delays for 0% water addition and 2.5% water addition are approximately equal before decreasing as more water is added.

In order to study the effect of compressed charge pressure, future work shall include investigation of higher and lower compressed charge pressures at stoichiometric condition, for H₂/CO ratio equaling 2, with 0%, 5%, and 10% molar percentage of water addition. It shall also include the study of fuel lean and fuel rich conditions at compressed charge pressure of 30 bar, for H₂/CO ratio equaling 2, with 0%, 5%, and 10% molar percentage of water addition, in order to investigate the effect of equivalence ratio.

(6) IR Spectroscopy in Rapid Compression Machine

In situ absorption spectroscopy of important species will be conducted in the RCM for various fuel systems. These species include H₂O₂ and CO. The evolution/consumption history of the species will be recorded and compared with reaction mechanism for better evaluation of the chemical kinetic model.

JOURNAL PUBLICATIONS

Allen, C., Mittal, G., **Sung, C.J.**, Toulson, E., and Lee, T., “An Aerosol Rapid Compression Machine for Studying Energetic-Nanoparticle-Enhanced Combustion of Liquid Fuels,” *Proceedings of Combustion Institute* **33**, in press.

Das, A., Kumar, K., and **Sung, C.J.**, “Laminar Flame Speeds of Moist Syngas Mixtures,” *Combustion and Flame*, in press.

Kumar, K. and **Sung, C.J.**, “Autoignition of Methanol: Experiments and Computations,” submitted.

Weber, B., Kumar, K., and **Sung, C.J.**, “Autoignition of *n*-Butanol at Low to Intermediate Temperature and Elevated Pressure,” submitted.

FLAME CHEMISTRY AND DIAGNOSTICS

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SUMMARY/OVERVIEW

The goal of the *Flame Chemistry and Diagnostics* program of the Combustion EFRC is to provide a rigorous basis for the elucidation of chemical mechanisms of combustion through a combination of experiments based on state-of-the-art diagnostics and detailed chemical kinetic modeling. The program concentrates on the development and application of combustion diagnostics for measuring the concentrations of key combustion intermediates in laboratory-based model flames. All experiments are designed to serve as benchmarks for the development and validation of detailed chemical kinetic models. In order to minimize transport issues, the experiments are carried out in low-pressure, one-dimensional laminar flames. For this configuration, well developed codes, such as the *Chemkin Premix* code, are available to simulate the underlying detailed combustion chemistry.

Recent work focused on the high-temperature oxidation chemistry in flames fueled by *n*-butanol, *iso*-butene and *iso*-butane. The chemical composition of various premixed flames was analyzed by flame-sampling molecular-beam mass spectrometry and the resulting mole fraction profiles were compared with flame chemistry model predictions. The acceptable and often very good agreement between experimental and modeled results allowed for an assessment of the importance of various fuel-decomposition pathways.

ACCOMPLISHMENTS

Premixed laminar low-pressure flames fueled by *n*-butanol, *iso*-butane, and *iso*-butene were used as benchmarks to develop detailed combustion chemistry models for the oxidation of the respective fuels. The flames, which were stabilized on a 6-cm-diameter stainless-steel McKenna burner, were analyzed using flame-sampling molecular-beam mass spectrometry (MBMS) and OH laser-induced fluorescence (LIF). The mass spectrometry experiments were carried out at the Chemical Dynamics Beamline at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory (LBNL), where the chemical structure of the flames was analyzed using flame-sampling MBMS in combination with photoionization (PI) by tunable synchrotron-generated vacuum-ultraviolet (VUV) radiation (Fig. 1).

The PI mass spectrometer, which allows intermediates to be detected with concentrations as low as one part-per-million (1 ppm), was used to collect data in two modes [1,2]. First, integrated and photon-current normalized ion signals were measured as a function of the photon energy. These so-called photoionization efficiency (PIE) spectra were used to identify the isomeric composition of the combustion intermediates. Second, ion signals were measured as a function of the distance to the burner and analyzed in order to produce quantitative mole fraction profiles for comparison with modeling results. In these measurements, isomers and species of near or equal mass were discriminated against one another according to their different ionization energies and PIE spectra. These isomer-specific differences allowed for the determination of the isomer-resolved mole fraction profiles.

The flame temperatures were measured with laser-induced fluorescence (LIF) using the frequency-doubled output of a dye laser near 306 nm to excite the OH A-X (0,0) transition [3]. The temperatures were recorded in the absence of the sampling probe and are therefore referenced to flame conditions unperturbed by the quartz cone. The measured temperature profiles were smoothed and subsequently used as input for the model calculations.

In collaboration with W. H. Green (MIT) and his student M. R. Harper, a chemical kinetic model is currently under development for the combustion of *n*-butanol at low pressure. This new model, which has been generated using the open-source software package *Reaction Mechanism Generator* (RMG), is based on a previously used set of reactions that successfully predicted autoignition delay times in shock tubes and mole fraction profiles in a jet-stirred reactor, an opposed-flow diffusion flame, and a doped methane diffusion flame [4]. This updated model includes additional pressure-dependent rate coefficients in order to reflect the experimental conditions below atmospheric pressure; the model was insensitive to these kinetic parameters for the previous validation targets.

The chemical kinetic model for the high-temperature oxidation of *iso*-butane and *iso*-butene is currently being developed in collaboration with H. Wang (USC) and our roving CEFRC fellow B. Yang. This model is developed on the basis of USC Mech V2.0, which is a comprehensive H₂/CO/C₁-C₄ mechanism assembled by Wang *et al.* for a wide variety of combustion scenarios [5].

In order to assess the quality and the predictive capabilities of the latest combustion chemistry models, the models' predictions were compared with the experimental mole fraction profiles of the major products and intermediate species (see Fig. 2 for examples). Although not presented here in any detail, the agreement between experimental mole fraction profiles and model predictions was quite favorable for the flames of interest. In other words, the combustion chemistry in flames of *n*-butanol, *iso*-butane, and *iso*-butene was reproduced satisfactorily by the

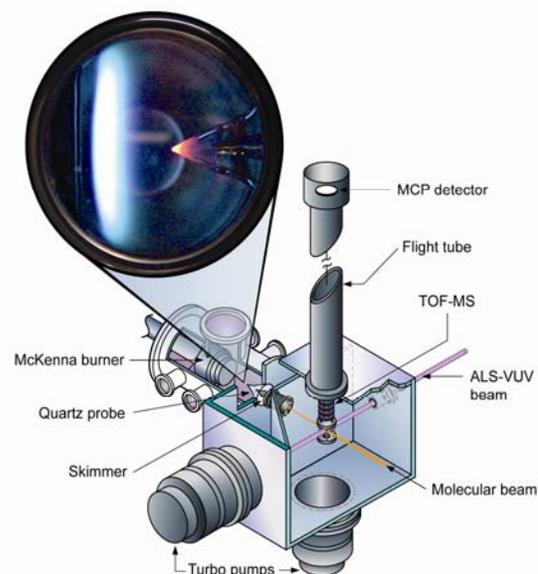


Fig. 1: Schematic of the Flame-Sampling Molecular-Beam Mass Spectrometer at the ALS

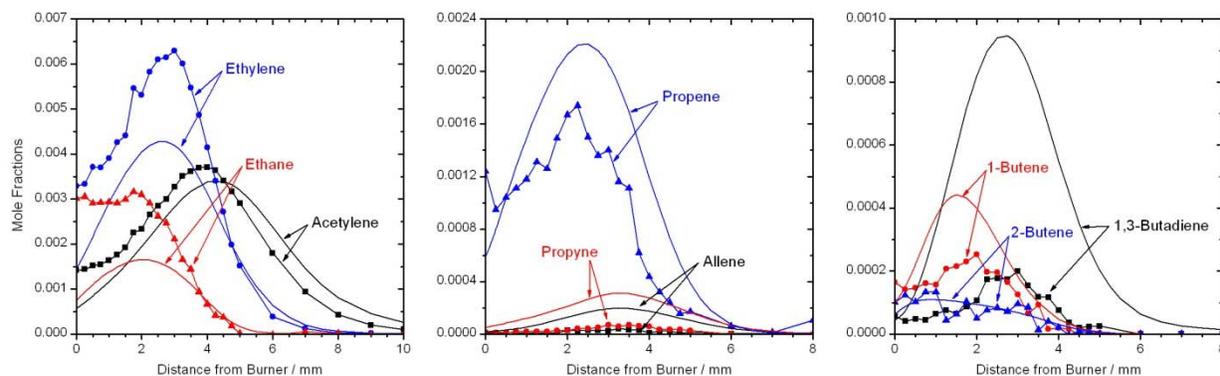


Fig. 2: Experimental (connected symbols) and modeled (lines) mole fraction profiles of selected C₂, C₃, and C₄ species in an *n*-butanol/H₂/O₂/Ar flame

current models and the predicted and experimentally observed profiles mostly, but not always, agreed within the expected error limits. This current level of accuracy allowed for a preliminary assessment of the importance of various fuel decomposition and other important reactions in low-pressure flames of *n*-butanol, *iso*-butane and *iso*-butene. Reaction paths and sensitivity analysis were performed for all flames studied, but only the results for an *n*-butanol/H₂/O₂/Ar shall be discussed here shortly.

In this flame, all paths towards the main products start from H-atom abstraction reactions by H, O, and OH producing any of the five isomeric forms of the C₄H₉O radical (Fig. 3). Within the group of these C₄H₉O radicals, the formation of the CH₃CH₂CH₂•CHOH radical seems to be slightly preferred. In subsequent steps, the different C₄H₉O radicals are likely to decompose rapidly by β-scissions or react with H, OH, and O₂ to form butanol isomers. For example, the CH₃CH₂CH₂•CHOH radical decomposes and produces CH₃CH₂CH₂CHO (butanal) + H or CH₃CH₂• (ethyl) + CH₂CHOH (ethenol). Other decomposition products include ethene, propene, formaldehyde, butenols, etc.

To date, the present results for the high-temperature oxidation chemistry of *n*-butanol, *iso*-butane, and *iso*-butene should be considered “preliminary” as work is still in progress to resolve larger discrepancies between experimental and modeled results. Future work on the *n*-butanol combustion chemistry should include re-examining the detailed enol chemistry, with its importance being overestimated by the current model.

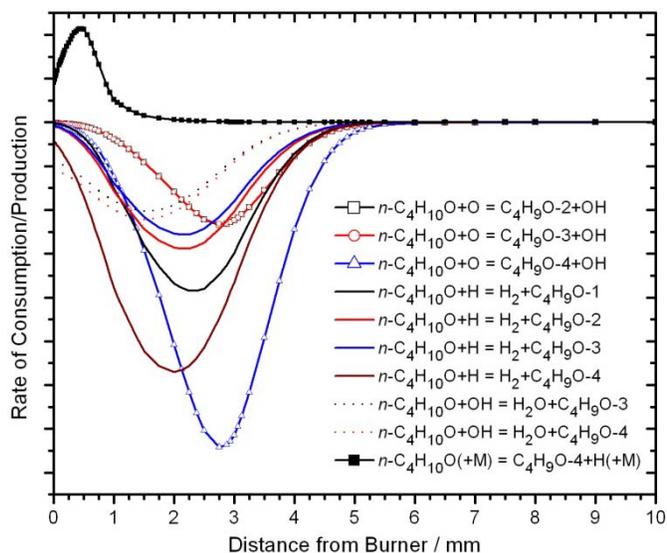


Fig. 3: The ten largest rates of consumption/production for *n*-butanol in an *n*-butanol/H₂/O₂/Ar flame at a reduced pressure of 15 Torr

PLAN FOR FUTURE WORK

Studies of the oxidation chemistry and reaction paths in combustion of oxygenated, bio-derived fuels will continue to be one of the dominant themes of this program. Combining the described VUV photoionization mass spectrometer and state-of-the-art laser methods with detailed flame chemistry, the complex combustion chemistry will be investigated in premixed laminar flat flames. The close collaborations with W. H. Green and H. Wang (through the CEFRC fellow B. Yang) have been proven to be very fruitful and will continue. The proposed work also includes a new experimental setup, which combines a jet-stirred reactor with MBMS employing single-photon ionization by tunable synchrotron radiation for the study of the low-temperature, high-pressure oxidation chemistry.

One key immediate task is the analysis of the large body of ALS data accumulated in the past year, which may compel further or confirmatory measurements during subsequent beam cycles. More experimental (and modeling) work will be performed on the determination of the absolute molar composition of flames fueled by the isomeric C₄H₉OH species *n*- and *iso*-butanol. Ongoing studies of the detailed flame chemistry of *iso*-butane and *iso*-butene will continue,

because future modeling work is likely to include re-examining the validity of the C₄ submechanisms. In this context, the work will be expanded to include flame studies of *n*-butane. The ALS-based experiments will be complemented by laser-based experiments, employing techniques such as laser-induced fluorescence (LIF) and resonantly enhanced multi-photon ionization (REMPI). The planned experiments will provide isomer-specific mole fraction profiles, which are thought to be a valuable basis for the mechanism developments under way in the groups of Green, Wang, and others.

The grand challenge is to consolidate the various mechanisms currently under development in different research groups. A serious, concerted effort should be undertaken to a) identify all important reactions, b) establish their most reliable rate constants over a wide range of pressure and temperature by reviewing the literature or through new quantum chemistry calculations and experimental measurements, c) actually include this information in *the* combustion chemistry mechanism, d) provide multiple types of experiments for testing of the model (flames, jet-stirred reactors, shock tubes etc.) and e) update the mechanism once new/better data becomes available. That is, the community should get together and assemble *the* comprehensive and predictive combustion chemistry mechanism.

Meanwhile, a variety of substituted five- and six-membered cyclic ethers, which can be found in biomass, are likely to be added to the fuel stream by transforming the biomass into suitable transportation fuels or fuel additives that retain these structures. In addition, cyclic ethers are formed during the autoignition of alkanes and alkenes by isomerisation of alkylhydroperoxide radicals. Therefore, it is of particular importance to study the combustion chemistry of cyclic ethers in molecular-level detail. Well suited as a model fuel to learn more about the characteristic combustion chemistry of cyclic ethers is furan. In collaboration with H. Wang and the CERFC fellow B. Yang, it is planned to develop a comprehensive understanding of the combustion chemistry of furan. We will apply the same experimental and modeling techniques successfully used for *n*-butanol, *iso*-butane, and *iso*-butene.

Specifically, flame-sampling molecular-beam mass spectrometry is a powerful tool for the investigation of combustion chemistry. It allows the study of mainly all stable and unstable species by using the same experimental procedure. As described above, the use of easily tunable synchrotron radiation for single-photon ionization makes this approach extremely effective. By funding through different programs at the DOE, the following modifications to the existing mass spectrometer are under way: a) The linear time-of-flight set-up will be replaced by a reflectron time-of-flight spectrometer. This modification will lead to a significant increase in mass resolution from currently $m/\Delta m \approx 400$ to $m/\Delta m \approx 2000$. Such an improved mass resolution will lead to a complete separation of most flame species, which is prerequisite for a more detailed analysis. b) A counter-flow diffusion flame system is currently being designed and built. Using a quartz microprobe to continuously withdraw gases from within such flames combined with mass spectrometry will be an ideal approach to study the fundamental combustion chemistry in diffusion flames.

With funds from the CEFRC, it is planned to expand the current capabilities to investigate the high-temperature oxidation chemistry at low pressure to enable studies of the oxidation kinetics at lower temperature and higher pressure. To this end, a new jet-stirred reactor (JSR), which is currently under development in the group of Prof. Ju at Princeton University, will be coupled to the existing molecular-beam mass spectrometer at the ALS. A JSR is a spherical quartz reactor in which a gas mixture is continuously flowing, and inside the reactor, the gas phase is well stirred, meaning the concentrations and temperature are homogenous. Such a JSR is an ideal system to investigate the chemical reaction kinetics in the low-temperature range of ~500-1200 K and elevated pressures of ~1-10 atm. However, in previous JSR experiments only stable products were detected and therefore, a lot of valuable chemical kinetics

information on all reactive intermediates and their concentration profile vs. reaction time were lost. Many previously developed reaction models based on JSR experiments consist of lots of well educated estimations rather than robust experimental observations. Only very recently, a JSR with molecular-beam sampling and coupling to an MBMS system has been described (see Fig. 4) [6]. This molecular-beam approach offers the advantage that concentration profiles vs. reaction time, temperature and pressure of all reactants, intermediates, and products can be identified and quantitatively measured. Such a setup will provide unprecedentedly detailed data that will be essential for the development of a predictive kinetic mechanism for low-temperature oxidation chemistry.

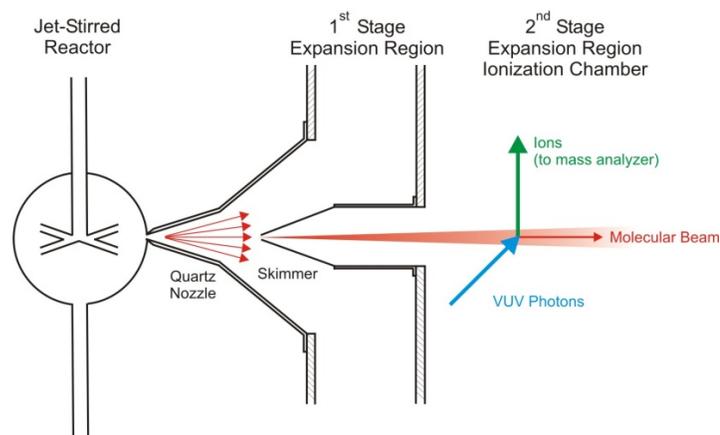


Fig. 4: Simplified illustration of the proposed experimental setup (adapted from Ref. [6])

Such a setup will provide unprecedentedly detailed data that will be essential for the development of a predictive kinetic mechanism for low-temperature oxidation chemistry.

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PUBLICATION

1. Dooley, S., Dryer, F. L., Yang, B., Wang, J., Cool, T. A., Kasper, T., Hansen, N., "An Experimental and Kinetic Modeling Study of Methyl Formate Low-Pressure Flames", *Combust. Flame*, in press.

CHEMICAL KINETICS OF COMBUSTION PROCESSES

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SUMMARY/OVERVIEW

During the reporting period, progress has been made in several aspects of research into the chemical kinetics of combustion processes. The products and kinetic rates of the multichannel benzene + O(³P) reaction were studied experimentally and theoretically, with a particular attention placed on the product branching ratio. A kinetic study of isobutanol combustion was initiated with a current focus on the reaction submodel of isobutanol oxidation. The sooting behaviors of *n*-butanol and *iso*-butanol were examined experimentally. A particle-molecule crossed beam apparatus is being developed to explore the collision cross section of large molecules. The role of π -diradicals in soot nucleation and surface growth was proposed.

ACCOMPLISHMENTS

Products of the Benzene + O(³P) Reaction

The gas-phase reaction of benzene with O(³P) is of considerable interest for modeling of aromatic oxidation, and also because there exist fundamental questions concerning the prominence of intersystem crossing in the reaction. While its overall rate constant has been studied extensively, there are still significant uncertainties in the product distribution. The reaction proceeds mainly through the addition of the O atom to benzene, forming an initial triplet diradical adduct, which can either dissociate to form the phenoxy radical and H atom, or undergo intersystem crossing onto a singlet surface, followed by a multiplicity of internal isomerizations, leading to several possible reaction products. In this work, we examined the product branching ratios of the reaction between benzene and O(³P) over the temperature range of 300 to 1000 K and pressure range of 1 to 10 Torr. The reactions were initiated by pulsed-laser photolysis of NO₂ in the presence of benzene and helium buffer in a slow-flow reactor, and reaction products were identified by using the multiplexed chemical kinetics photoionization mass spectrometer operating at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. As shown in Fig. 1, phenol and phenoxy radical were detected and quantified. Cyclopentadiene and cyclopentadienyl radical were directly identified for the first time. Finally, ab initio calculations and master equation/RRKM modeling were used to reproduce the experimental branching ratios, yielding pressure-dependent rate expressions for the reaction channels, including phenoxy + H, phenol, cyclopentadiene + CO, which are proposed for kinetic modeling of benzene oxidation.

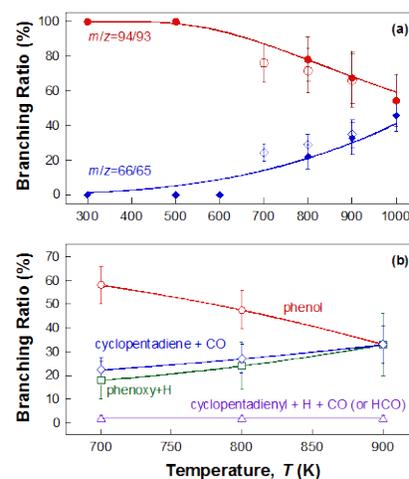


Figure 1. Branching ratios observed as a function of temperature at 4 Torr for (a) $m/z=94/93$ and $m/z=66/65$ by magnetic sector mass spectrometer (filled symbols) and time-of-flight mass spectrometer (open symbols), and (b) branching ratios determined by time-of-flight mass spectrometer. Lines are drawn to guide the eye. Error bars are 2 σ -standard deviations.

Kinetic Modeling Studies of Iso-butane and Iso-butene Combustion

Kinetic modeling of isobutanol combustion requires a reliable chemical kinetic submodel for the pyrolysis and oxidation of isobutene. To establish the validity of USC Mech II as a base model for isobutanol combustion, validation tests were performed for the oxidation of isobutane and

isobutene against a wide range of experimental observations. Over 50 sets of data were considered, including previously published data of laminar flame speeds, shock tube ignition delay, species concentrations in a jet stirred reactor and a new set of burner-stabilized premixed flame data. As examples, Figure 2 shows comparisons of the experimental and computed laminar flame speeds of isobutane- and isobutene-air mixtures. Figure 3 presents sample comparisons of ignition delay times for two isobutane-oxygen-argon mixtures. The results suggest that USC Mech II provides a reasonably good starting point for extension to iso-butanol combustion, though minor revisions and updates are required for the reaction chemistry of iso-butene pyrolysis and oxidation.

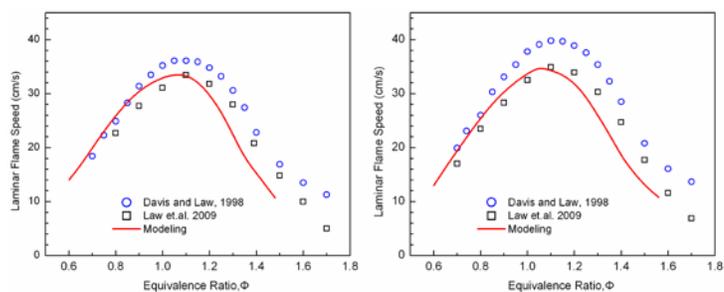


Figure 2. Laminar flame speeds of mixtures of isobutane-air (left panel) and isobutene-air (right panel) at 1 atm pressure and an unburned gas temperature of 300 K (symbols: experimental data [1, 2], lines: simulation).

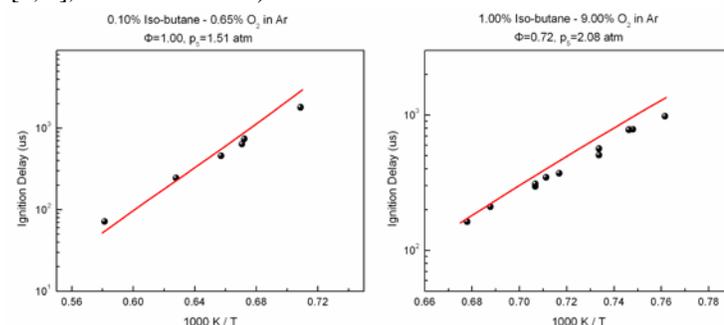


Figure 3. Experimental (symbols) and computed (lines) ignition delay times for isobutane-oxygen-argon mixtures behind reflected shock waves. The experimental data are taken from refs [3,4].

Sooting Behaviors of Isobutanol and *n*-Butanol Flames

Isobutanol and *n*-butanol are important candidates for the next generation of biofuels. The sooting behaviors of butanol flames must be characterized if these fuels are to be utilized at a large scale. Also, the examination of oxygenated fuels may reveal insights into mechanisms of soot nucleation and growth for all hydrocarbon fuels in general. In this work, we examined the evolution of particle size distribution function of nascent soot produced in atmospheric-pressure burner-stabilized stagnation (BSS) *n*-butanol and *iso*-butanol flames [5]. A sample for the evolution of particle PSDFs in an *iso*-butanol flame is presented in Fig. 4. The kinetic behaviors of soot nucleation and mass growth are similar in comparable *n*-butanol and *iso*-butanol flames. Both are characterized by exceedingly persistent particle nucleation during soot mass growth. The inception of soot particles in flames of both fuels requires a longer reaction time than in comparable ethylene flames. However, beyond particle nucleation, the soot volume fraction increases more dramatically in butanol flames than in ethylene flames.

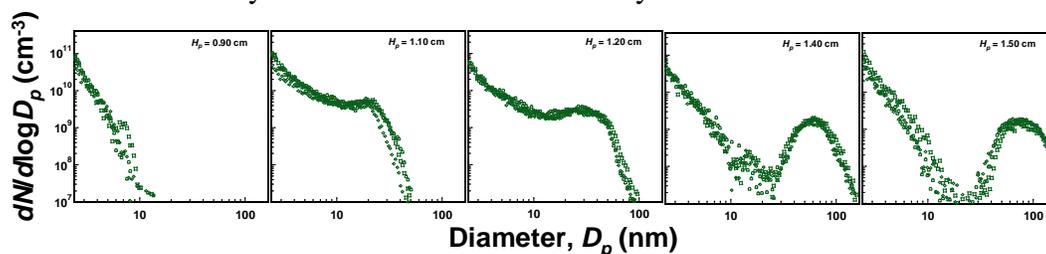


Figure 4. Detailed PSDFs measured at various burner-to-stagnation separation distances (H_p) of burner-stabilized stagnation 13.6% isobutanol-26.4% O_2 -Ar burner-stabilized stagnation flame with the cold gas velocity = 4.6 cm/s.

Development of a Molecule-Particle Crossed Beam Apparatus

We are developing a molecule-particle crossed beam apparatus suitable for determination of diffusion cross section of large molecules. This cross section measurement will aid the advance of a molecular transport property formulation beyond the Chapman-Enskog theory for large molecules where the approximation of spherical potential energy function fails. The apparatus is

composed of a particle beam crossing a molecular beam with a liquid helium cooled bolometer as a detector for the position and kinetic energy of the particle beam, as shown in Fig. 5. An example of the bolometer responses to molecular beams of argon and air is presented in Fig. 6, as a function of molecular density. It shows that the bolometer has a linear response to molecular density resulting from the beam intensity. Further investigations on the bolometer responses to molecular and particle beams are still needed to characterize the response of the bolometer to the incident particle beam. To aid the validation of the crossed beams apparatus, we plan to conduct experiments on the scattering behavior of helium with silver clusters and nanoparticles. Computationally, we carried out molecular dynamics simulations to examine the role of surface adsorption of helium on silver, resulting in apparent diffuse scattering as opposed to specular scattering [6,7].

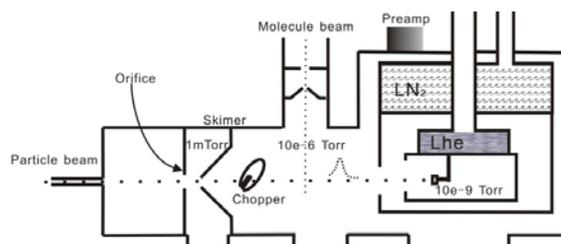


Figure 5. Schematic the molecule-particle crossed beams.

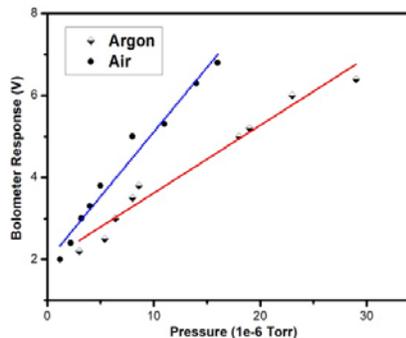


Figure 6. Bolometer responses towards molecular argon and air beams.

Aromatic π -diradicals in Soot Nucleation and Mass Growth

Our description of the sooting process is reaching a quantitative level for at least small model fuel compounds. Yet critical gaps remain, especially in our understanding of particle nucleation and mass growth. In this work, we identified some of these gaps and propose the roles of certain aromatic π radicals resulting from localized π electron structures in particle nucleation and subsequent mass growth of nascent soot. The existence of these free radicals provides a rational explanation for the strong binding forces needed for forming initial clusters of polycyclic aromatic hydrocarbons. They may also explain a range of currently unexplained sooting phenomena, including the large amount of aliphatics observed in nascent soot formed in laminar premixed flames and the mass growth of soot in the absence of gas-phase H atoms. While the above suggestions are inspired, to an extent, by recent theoretical findings reported within the materials research community, the work also demonstrates that the knowledge garnered through our longstanding interest in soot formation may well be carried over to flame synthesis of functional nanomaterials for clean and renewable energy applications. In particular, work on flame-synthesized thin films of nano-crystalline titania illustrates how our combustion knowledge might be useful for developing advanced yet inexpensive thin-film solar cells and chemical sensors for detecting gaseous air pollutants.

PLAN FOR FUTURE WORK

Future work will be focused on completing an iso-butanol reaction kinetic model with its base model well validated and the fuel-rich chemistry of *n*-butanol and *iso*-butanol flames, including their sooting behaviors. We will continue to develop the crossed beam apparatus into a critical tool for probing the diffusion cross section of large molecules and develop the molecular dynamics tools to analyze their scattering behavior upon collision with small gas molecules. We plan to explore the nature of aromatic π -diradicals experimentally and through electronic structure calculations. In addition, we will begin to explore some of the problems of relevance to the grand challenges identified below.

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SUMMARY OF DISCIPLINARY WORKING GROUP. CHEMISTRY AND TRANSPORT

Yiguang Ju

A. Summary

The overall goal of the flame chemistry working group is to obtain fundamental combustion and emission properties of low and high pressure flames, to validate kinetic and transport models, and to develop accurate and computationally efficient models capable of predicting turbulent combustion of future transportation fuels. In the first year, experimental data of laminar flame speeds, extinction/ignition limits, and soot/NO_x emissions were measured for hydrogen, C₁-C₇ hydrocarbons, C₁-C₄ alcohols, C₁-C₁₀ methyl-esters, and some important ethers, aldehydes, and ketones up to 25 atm. Kinetic models and transport properties of these fuels were validated and improved. Correlations for laminar flame speeds and extinction limits of blended fuels were developed. An efficient multi-timescale model reduction method was developed and applied to direct modeling of homogeneously charge compression ignition (HCCI). New flame regimes and singular critical temperature gradient for ignition and acoustic wave coupling due to negative temperature coefficient effect were identified. Effects of temperature gradient and fluctuation on the transition between multi-stage ignition and flame deflagration were investigated. A new combined method using large eddy simulation (LES), probability density function (PDF), and *in situ* adaptive tabulation (ISAT) to include the turbulence-chemistry interactions and to enable the efficient implementation of detailed mechanisms in turbulent flame simulations was developed. A comparative study between RANS, PDF, and direct numerical simulation (DNS) for turbulent lifted ethylene flames in preheated air was initiated. The role of auto-ignition at the flame base in a fuel-lean mixture for stabilization of the lifted jet flame was demonstrated.

B. Technical Accomplishments

1. *Measurements of combustion and emission properties and validations of kinetic and transport models*

The measurements of laminar flames speeds, and ignition and extinction limits of premixed and non-premixed C₁-C₄ alcohols (e.g. methanol, propanol, and butanol), dimethyl ether (DME), methyl-esters (e.g. methyl-butanoate, methyl-crotonate, and methyl-decanoate), H₂/CO, and C₁₋₄ *n*-alkanes at atmospheric and elevated pressures (up to 25 atm) were completed. The comparison between experimental data and predictions showed that the deficiencies of existing kinetic mechanisms including hydrogen and C₁-C₄ mechanisms become progressively larger as the pressure increases. Parent mechanisms were found not able to reproduce the flame properties of their major intermediate species. Model prediction of radical concentrations was unconstrained. The transport properties of fuels were found to have a great impact on flame extinction and

burning rates. Unfortunately, the transport properties for large oxygenated fuels, particularly at elevated temperatures, have large uncertainties. Kinetic and transport coupling for fuels with different functional groups were identified. Accurate prediction of radical pool concentration was found to be important to reproduce extinction limits of multi-fuel mixtures. A linear correlation parameter was identified for hydrogen blended hydrocarbon fuels. A new correlation of extinction limit with radical index was established. NO_x and soot emissions as well as micro explosion in biodiesel and ethanol flames were studied.

2. Development of model reduction methods and efficient ODE solvers for detailed mechanism

A new multi-timescale (MTS) model to achieve about one-order reduction of the computation time for both detailed and reduced kinetic mechanisms was developed. The robustness and accuracy of the method were demonstrated for the ignition and unsteady propagation of hydrogen, methane, methyl-butanoate, n-heptane, and n-decane flames. A multi-generation path flux analysis (PFA) method was developed also and integrated with MTS method to increase the computation efficiency further. A reduced mechanism of n-butanol was obtained also and compared with the detailed kinetic mechanism. The performance of four different ODE integration schemes was examined. An improved integration scheme for ISAT with error control was developed based on exponential integrators.

3. Development of LES/PDF methodology and modeling of homogeneous charged compression ignition combustion

An accurate, efficient and scalable LES/PDF turbulent combustion methodology was developed and examined by using a turbulent jet flame with a simple flamelet model. The LES/PDF method was demonstrated to be second-order accurate in space and time. Numerical consistency was demonstrated for mixture fraction between LES and PDF. Good agreement was observed between LES/PDF calculations and experimental data.

The effect of thermal stratification and fluctuations on the ignition and flame propagation in a lean homogeneous *n*-heptane/air mixture at HCCI conditions was investigated by direct numerical simulations (DNS) with a reduced kinetic mechanism. It was found that the mean heat release rate was more spread out with increasing thermal stratification regardless of the mean initial temperature. In addition, ignition delay was decreased with increasing thermal stratification for high mean initial temperature relative to the negative temperature coefficient (NTC) regime and was retarded with thermal fluctuation for relatively low mean initial temperature. Direct numerical simulation of the near field of a three-dimensional spatially-developing turbulent ethylene jet flame in highly-heated coflow was performed. The resultsshowed that auto-ignition in a fuel-lean mixture at the flame base was the main source of stabilization of the lifted jet flame. A DNS benchmark data set for lifted jet flame stabilization in an autoignitive coflow was established.

C. Technical challenges and future plan

Our future plan addresses the challenges of deficiency of existing kinetic mechanisms and transport properties, scarcity of flame and species data at high pressures and turbulent conditions, computational efficiency and accuracy of detailed mechanism, and accurate modeling of turbulent combustion with detailed mechanisms. We are planning to conduct,

- 1) Measurements of species concentrations, global flame properties, and emissions of oxygenated fuels at high pressures
- 2) New approaches to study high pressure fuel oxidation in premixed and non-premixed systems
- 3) Validation and improve performance of hydrogen and C₁-C₄ hydrocarbon fuel mechanisms
- 4) Turbulent flame experiments at high pressures (30-60 atm)
- 5) Transport properties and chemical kinetics at high pressure
- 6) Development of efficient and accurate ODE solvers with dynamic adaptive mechanisms
- 7) DNS modeling of high pressure lifted diesel-jet stabilization with DME and iso-butanol.
- 8) DNS of DME HCCI Combustion and topologic diagnostics of flame structures
- 9) Completion and validation of the implementation of the LES/PDF/ISAT methodology on large-scale computer systems and application to non-premixed flames.
- 10) A posteriori comparison of lifted ethylene-air jet flame with LES/PDF/ISAT with detailed mechanism

D. Discussion topics

1. Validation strategy for kinetic mechanism
2. Future fuel targets
3. Uncertainties of transport properties
4. New experimental methods for high pressure flames
5. Experimental uncertainty of laminar flame speeds and species concentrations
6. Validation approaches for turbulent combustion
7. Cross working group collaboration
8. Road map towards systematic mechanism construction

FLAME AND DROPLET PROCESSES IN COMBUSTION

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SUMMARY/OVERVIEW

Various aspects of flame and droplet processes in combustion were investigated experimentally and computationally, including: (1) Development of an accurate and computationally efficient fitting formula for the falloff curves of unimolecular reactions with tunneling effects; (2) determination and modeling of the nonpremixed ignition limit and laminar flame speeds of *n*-butanol, *iso*-butanol, and methyl butanoate; (3) determination and correlation of the laminar flame speeds of hydrocarbon fuels with hydrogen addition; (4) experimental investigation on the effects of biodiesel and ethanol blending in commercial diesel in terms of soot reduction and facilitated droplet atomization, respectively. Future work will involve: (1) Further determination of laminar flame speeds of biofuels of interest at high pressures, up to 30–60 atmospheres; (2) studies on soot formation in biofuels; (3) studies on turbulent spherical flame propagation at high pressures, up to 60 atmospheres; (4) liquid-phase reactions in gasifying high-boiling-point fuels.

ACCOMPLISHMENTS

1. A Fitting Formula for the Falloff Curves of Unimolecular Reactions with Tunneling Effects

Unimolecular and the reverse recombination reactions play an important role in many chemical reaction systems related to atmospheric chemistry and combustion. Evaluation of these reaction rates, especially for large reaction systems, is however computationally demanding because of their complicated pressure and temperature dependence, frequently expressed in transcendental functions. Approximate formulas of high accuracy, expressed in computationally simple mathematical forms, are therefore desired in the simulation of these systems. Previously we have approximated the fall-off curves of unimolecular reaction rate constants by proposing a fitting formula based on the Kassel integral. The enhanced performance of this formula was attained for all reactions tested except those affected by tunneling effects. In the present study we take into account effects of tunneling on the shape of the falloff curves of unimolecular reaction rate constants based on Troe's weak collision integral, developed a tunneling-affect fitting formula, and examined its performance for several tunneling-affected reactions. It is demonstrated that, compared to the widely used Troe's and Prezhdo's formulas, the present expression not only substantially enhances the accuracy in fitting for tunneling-affected reactions (Fig. 1), but it is also computationally more efficient in its evaluation.

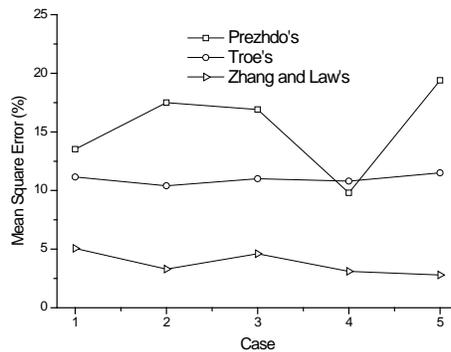


Figure 1. Mean square errors of the present formula with the three tunneling correction factors, as well as those of the present, Prezhdo and Troe formulas.

2. Nonpremixed Ignition, Laminar Flame Propagation, and Mechanism Reduction of *n*-Butanol, *iso*-Butanol, and Methyl Butanoate

The present study provides experimental data of three popular biofuels, namely *n*-butanol, *iso*-butanol and methyl butanoate, in two well-controlled combustion environments: nonpremixed ignition in a stagnation flow and laminar flame propagation of spherical flames. We first measured the nonpremixed ignition temperature of *n*-butanol, *iso*-butanol and methyl butanoate in a liquid pool assembly by heated oxidizer in a stagnation flow for system pressures of 1 and 3 atmospheres. Measurement of the axial velocity profile was conducted with LDV over local strain rates of 100 to 450/s (Figs. 2 - 4). We also determined the stretch-corrected laminar flame speeds of mixtures of air and *n*-butanol / *iso*-butanol/ methyl butanoate from outwardly propagating spherical flames at initial pressures of up to 2 atmospheres, for an extensive range of equivalence ratio (Figs. 5 - 6). The ignition temperature and laminar flame speeds of *n*-butanol and methyl butanoate were then computationally simulated with three recently developed kinetic mechanisms in the literature. Furthermore, using a Chemical Explosive Mode Analysis (CEMA) and sensitivity analysis, we have identified the dominant reaction pathways to ignition and flame propagation. We also performed mechanism reduction on the three detailed models employed in the simulation. The reduced mechanisms provided excellent agreement in both homogeneous and diffusive combustion environments and greatly improved the computation efficiency.

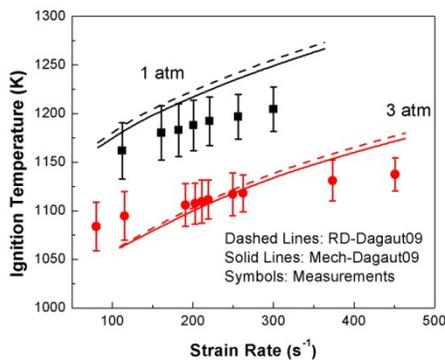


Figure 2 Ignition temperature of *n*-butanol versus density-weighted strain rate; $p = 1$ & 3 atm.

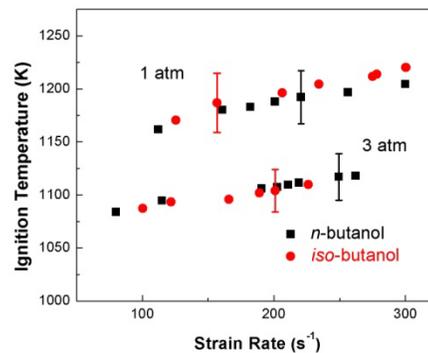


Figure 3 Ignition temperature of *n*-butanol and *iso*-butanol versus density-weighted strain rate; $p = 1$ & 3 atm.

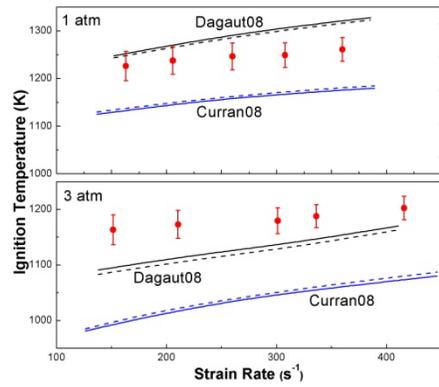


Figure 4 Ignition temperature of MB versus density-weighted strain rate; $p = 1$ & 3 atm.

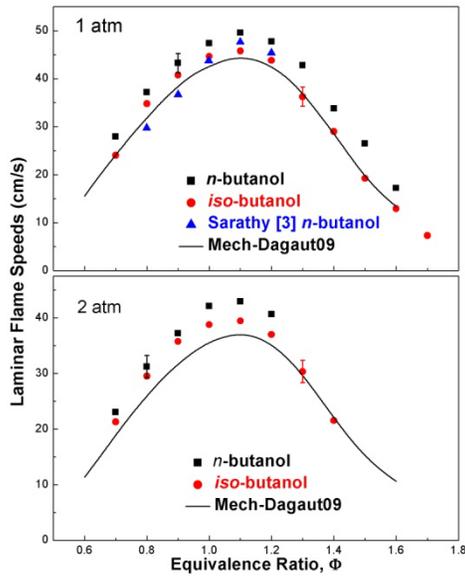


Figure 5 Laminar flame speeds of *n*-butanol and *iso*-butanol, $p=1$ & 2 atm, $T=353$ K.

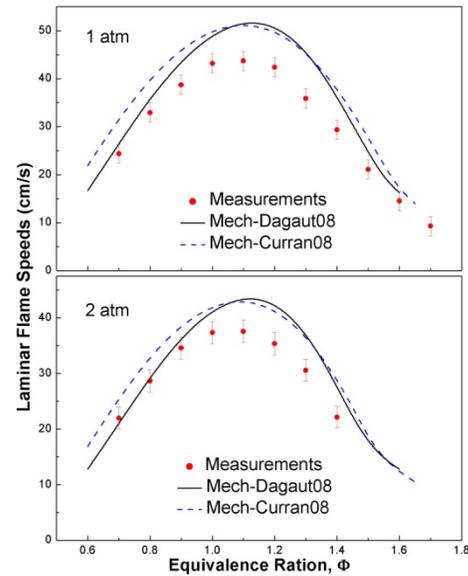


Figure 6 Laminar flame speeds of methyl butanoate, $p=1$ & 2 atm, $T=353$ K.

3. Effects of Hydrogen Addition on Laminar Flame Speeds of Hydrocarbon–Air Mixtures

A viable approach towards the utilization of hydrogen as a fuel source is to mix it with hydrocarbon fuels to facilitate the overall reactivity, especially for lean mixtures. In a previous experimental study, conducted in the 1980s, we showed that the laminar flame speeds of mixtures of methane and moderate amount of hydrogen can be approximately correlated linearly with the extent of hydrogen addition by using a parameter, RH. This parameter was proposed based on the concept that oxidation of the fuel mixture occurs in two stages, with complete consumption of the freestream hydrogen followed by the oxidation of methane. This result has enjoyed extensive follow-on work by others, ostensibly due to its usefulness and simplicity.

In the present study we have shown that the same linear correlation also approximately holds for the C_2 hydrocarbons as well as *n*-butane, not only experimentally but also through computational simulation. Typical results for *n*-butane are shown in Fig. 7. Furthermore, using sensitivity analysis we have demonstrated that the factors that are responsible for the increase in the flame speed with hydrogen addition are, in increasing importance, enhanced diffusivity, increased flame temperature, and enhanced reactivity.

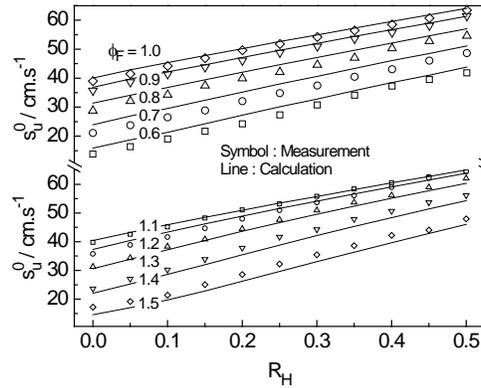


Fig. 7 Measured and calculated laminar flame speeds of mixtures of butane-air with hydrogen addition, as function of R_H .

4. Soot Reduction and Microexplosion in the Combustion of Diesel Droplets Blended with Biodiesel and Ethanol

While the primary interest in blending biodiesel and ethanol in diesel is the use of these biofuels without major engine modifications, we demonstrate herein that there are two additional benefits in the blending, namely soot reduction and enhanced atomization. Specifically, since many candidates of biodiesels are oxygenated fuels, such as the methyl esters, their sooting propensity has been demonstrated to be low. It is then reasonable to expect that when blended with diesel the overall soot formation will reduce. Second, since the boiling point of ethanol is much lower than that of diesel, the ethanol component within a blended droplet could undergo superheating as the droplet gasifies, leading to internal gasification and consequently violent rupturing of the droplet. This facilitates the atomization and thereby overall gasification rate of the liquid.

To explore and quantify the above possibilities, experiments were conducted for a downwardly-injected stream of droplets in a heated, oxidizing gas stream. The instantaneous droplet size, the extent of soot formation in the flame surrounding the droplet, and the instant of droplet explosion were determined as functions of the mixture composition. The upper panels of Fig. 8 show the flame streaks of: (a) diesel, (b, c) blends of diesel and biodiesel, (d) biodiesel, and (e) hexadecane, while the lower panels show the corresponding amount of soot collected on filter paper. Figure 9 shows quantitatively the amount of soot formed per droplet at various stages of the droplet burning. These results demonstrate that biodiesel indeed soots very little, and that the blending it in diesel also reduces the overall soot emission.

For ethanol blending in diesel and biodiesel, Fig. 10 shows the flame streaks of (a) diesel, (b, c, d) diesel/ethanol blend, and (e) pure ethanol, with the flame streak of ethanol being extremely faint. These flame streaks demonstrate two positive attributes of ethanol blending. First, being more volatile, the preferential gasification of ethanol suppresses soot formation during the early stage of burning when the flame size is large and soot emission is otherwise the most severe. Second, the blended droplet indeed explodes during burning, thereby reduces the overall gasification time. Figure 11 quantifies the instant of droplet explosion, showing that explosion occurs earlier in the droplet lifetime for the biodiesel, because of its higher boiling point than diesel, and that the explosion occurs the earliest for equal volume of the constituents, which is in accordance with existing theory on multicomponent droplet combustion.

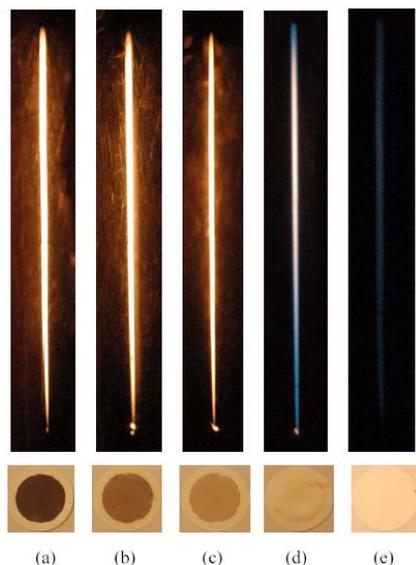


Figure 8. Flame streak images of burning droplets and the soot images on the filter papers of (a) diesel, (b) diesel/10% biodiesel, (c) diesel/20% biodiesel, (d) biodiesel, and (e) hexadecane. Yellow luminosity indicates soot formation, while blue flames indicate its absence.

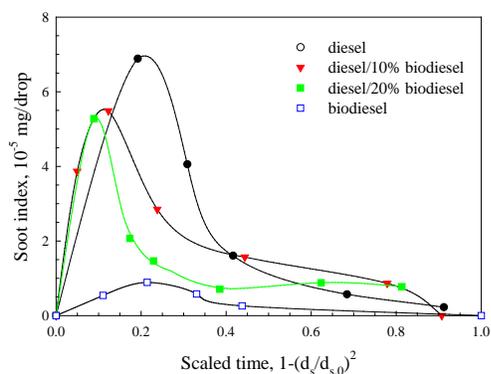


Figure 9. Variation of the soot index as a function of scaled time for diesel, diesel mixed with 10% and 20% biodiesel, and biodiesel.

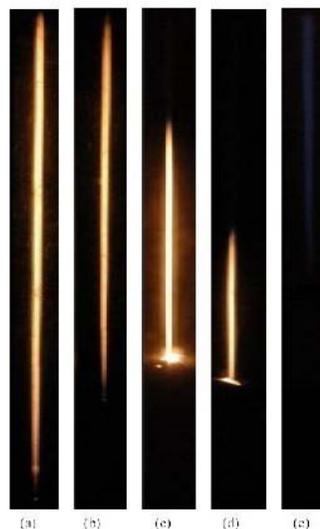


Figure 10. Flame streak images of diesel/ethanol mixtures: a) diesel b) diesel/25% ethanol, c) diesel/50% ethanol, d) diesel/75% ethanol, e) ethanol.

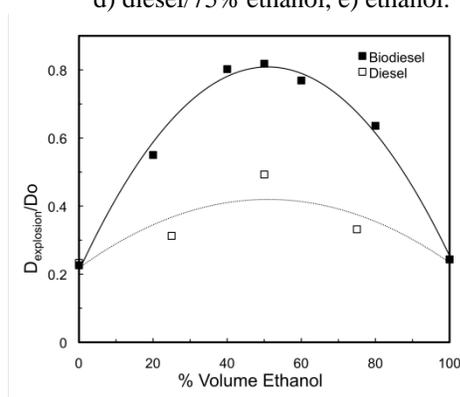


Figure 11. Normalized droplet diameter at droplet explosion as function of ethanol addition

PLAN FOR FUTURE WORK

1. Laminar Flame Propagation and Reduced Mechanisms of Biofuels

We shall continue with our effort towards the accurate determination of laminar flame speeds of various biofuels at elevated pressures. Recognizing that our current burner cannot accommodate fuels of high boiling points due to high-temperature and high-pressure structural limitations, we shall fabricate a third-generation burner that allows experimentation with fuel volatilities in the range of dodecane and hexadecane, and in the pressure range of 10 to 20 atmospheres.

We shall also continue with our development of computational algorithms for the automatic reduction of large reaction mechanisms with minimum loss of accuracy. In particular, on-the-fly reduction approaches will be explored.

2. Sooting Limits of Aerodynamically-Strained Diffusion Flames of Biofuels

It is now well established that the combustion of biofuels yields significantly less soot than commercial diesels. The propensity of soot formation in biofuels will therefore be experimentally quantified and then modeled. The experiment will involve impinging an oxidizing gas onto a pool of the liquid fuel, establishing a stagnation flame over the liquid pool, and identifying the critical strain rate at which soot luminosity is negligible. The elimination of the luminosity signal, if attributed to polycyclic aromatic precursors, yields a “sooting limit” that can be considered as condition for completely non-sooting flame. Through variations in flame temperature and oxidizer concentration, and with the use of additives, we shall develop understanding of soot production in biofuel flames.

3. Experiment and Modeling of High-Pressure Turbulent Spherical Flames

In this study we shall first experimentally determine the burning velocity and structure of spark-ignited turbulent outwardly propagating spherical premixed flames at high pressures, up to 60 atmospheres. Effects of the turbulent fluctuating velocity on the flame surface area, and the development of flamefront Darrieus-Landau hydrodynamic cells due to strong density gradients and small flame thickness typically under high pressures, will be measured using a high-speed PIV system. The experiment will be conducted in a unique, recently-constructed dual-chamber apparatus that extends the design of our current high-pressure spherical laminar flame burner to include fan-generated turbulence.

In addition to its fundamental importance, the turbulent flame speed so determined is also needed to close the averaged governing equations in modeling multidimensional turbulent premixed combustion. Though such models describe the phenomenology in details, one of the major roadblocks remain to be the lack of high quality experimental data and the lack of fundamental understanding of the behavior of turbulent flame speed over different turbulent premixed combustion regimes particularly at high pressures. Availability of high quality experimental data over such regimes and pressure could significantly augment analytical and reduced order modeling approaches. Quantifying the functional relationships between overall rms velocity and that in the flame neighborhood, stretch, curvature and flame generated turbulence could lead to a universal functional form of the turbulent flame speed for widespread application in turbulent premixed combustion models.

In parallel with the experimental effort, LES/PDF simulation of spherical flames in a turbulent environment will also be conducted in collaboration with Steve Pope. Extension of the LES/PDF turbulent flame modeling to high pressures, identifying the role of the Darrieus-Landau instability cells in the turbulent flame structure and propagation rate, and comparison with the experimental data, are aspects of focus.

4. Liquid-Phase Reaction within Gasifying High-Boiling-Point Droplets

Since the temperature within a gasifying droplet can approach the boiling point of the liquid in the high-temperature environment of a combustor, liquid-phase reactions can be initiated for high-boiling-point fuels, especially under elevated pressures because of the corresponding elevation of the boiling point. In extreme cases, such as the #6 heating oil, cenospheres are formed. Since the fuel components in the gas are those released from the gasifying droplet, it is

necessary to be able to describe the liquid-phase reactions in the high-temperature environment within the droplet.

The experimental apparatus is that used for the study of soot formation and droplet explosion. Here a steady stream of droplets is produced using the ink-jet printing technique, and downwardly injected into the post-combustion region of a flat-burner flame, for which the temperature is well defined. The droplets will be sampled through suction at various stages of burning, and chemically analyzed. The results will be compared with those calculated using existing mechanisms if they exist. Otherwise they will form the basis for mechanism development. The initial liquid temperature will be sufficiently high so as to minimize the effects of initial transient heating, but not high enough to trigger reaction.

It is noted that while this method is not as ideal as that involving a flow reactor, it does simulate the practical situation. Furthermore, the liquid is not in contact with a wall, hence eliminating any potential wall effect, while the possible formation of the solid-phase cenospheres can not be readily studied in flow reactors.

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3. Liu, W., Kelley, A.P., **Law, C.K.**, "Nonpremixed ignition, laminar flame propagation, and mechanism reduction of *n*-butanol, *iso*-butanol, and methyl butanoate," *Proceedings of Combustion Institute*, in press.
4. Tang, C.L., Huang, Z.H., **Law, C.K.**, "Determination, correlation, and mechanistic interpretation of effects of hydrogen addition on laminar flame speeds of hydrocarbon-air mixtures," *Proceedings of Combustion Institute*.
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HONORS AND AWARDS

Fellow, American Academy of Arts and Sciences (AAAS), 2010.

FLAME STUDIES OF SMALL HYDROCARBONS AND OXYGENATED FUELS

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SUMMARY/OVERVIEW

The primary goal of this research is to provide insight into the burning characteristics of oxygenated fuels in flames. The focus on oxygenated fuels is driven by the need to derive valuable scientific information regarding the underlying combustion kinetics and molecular transport for bio-derived fuels, which are expected to play a significant role in transportation at least for a good part of the 21st Century. Compared to hydrocarbon fuels, oxygenated fuels have been studied in notably lesser extent, with the exception being small molecular weight alcohols such as methanol and ethanol. The approach includes experimental and detailed modeling studies of flames of C₁-C₄ alcohols, dimethyl ether (DME), and C₁-C₁₀ methyl-esters. Additional compounds are also considered, such as H₂, CO, selected C₁-C₄ hydrocarbons, aldehydes, and ketones, whose kinetics can affect notably the oxidation of the target fuels such as, for example, butanol or biodiesel surrogate components. The parameter space of this research is quite extensive, with the only limitation being the maximum thermodynamic pressure that cannot exceed 8 atm. The flame properties considered are laminar flame speeds, ignition and extinction limits, as well as NO_x and soot volume fraction profiles, all in counterflow flames. The results obtained during Year 1, point to several deficiencies in both the kinetics and transport properties of flames of oxygenated fuels as well as the need of improving the understanding of the oxidation kinetics of H₂, CO, and various C₁-C₄ hydrocarbons. The results of this research aim to characterize the effect of the fuel molecular structure and in particular of the location and type of the O-containing functional group atom as function of the carbon number, on fundamental flame properties. This approach is expected to contribute towards the improved understanding of the burning characteristics of bio-derived fuels and towards better kinetic models of relevance to both conventional and alternative fuels. During Year 1, the following progress was made: (1) Studies of laminar premixed flames of neat and mixtures of H₂, CO, and CO₂ with C₁-C₄ hydrocarbons at atmospheric and high pressures; (2) Studies of flammability limits of CH₄/air flames at elevated pressures; (3) Studies of methanol, ethanol, and *n*-butanol flames at atmospheric pressure; (4) Studies of flames of butanol isomers at atmospheric pressure; (5) Comparative studies on the extinction of non-premixed DME and ethanol flames at atmospheric pressure; (6) Studies of NO_x formation in flames of model biodiesel flames at atmospheric pressure; (7) Studies of *n*-propanol, *iso*-propanol, and propane flames at atmospheric pressure; (8) Studies of C₄ and C₁₀ methyl-ester flames at atmospheric pressure. The plans for Year 2 and beyond will be guided by the present findings as well as by the need to achieve archival experimental data of fundamental value under conditions that either extreme, e.g. pressure, and/or under which state of the art kinetic models do not appear to perform satisfactorily.

ACCOMPLISHMENTS

1. Studies of laminar premixed flames of neat and mixtures of H₂, CO, and CO₂ with C₁-C₄ hydrocarbons at atmospheric and high pressures

The combustion characteristics of mixtures of air with H₂/CO/CH₄/C₃H₈/C₄H₁₀ were investigated. While individual fuel components as well as binary mixtures such as H₂/CO have been studied extensively both experimentally and numerically in the past, few studies have incorporated all components. The goal of this study was to provide additional experimental data

to quantify the effect of kinetic coupling between H₂, CO, CH₄, C₃H₈, and C₄H₁₀. The propagation as well as ignition and extinction limits were determined in a newly developed high-pressure counterflow facility over a wide range of unburned mixture temperatures, pressures, and equivalence ratios. The experiments were modeled using the USC Mech II kinetic model [Wang, H., You, X., Joshi, A.V., Davis, S.G., Laskin, A., Egolfopoulos, F.N. & Law C.K., “USC Mech Version II. High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds.” http://ignis.usc.edu/USC_Mech_II.htm, May 2007]. The fuel mixtures were chosen in order to gain insight into potential kinetic couplings during the oxidation of fuel mixtures. It was determined that when hydrocarbons are added to hydrogen flames as additives, flame ignition, propagation, and extinction are affected in a counterintuitive manner. More specifically, it was found that by substituting methane by propane or *n*-butane in hydrogen flames, the reactivity of the mixture is reduced both under pre-ignition and vigorous burning conditions. This behavior stems from the fact that propane and *n*-butane produce higher amounts of methyl radicals that can readily recombine with atomic hydrogen and reduce thus the rate of the $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ branching reaction. The USC Mech II kinetic model was determined to predict in general closely the experimental data except for H₂-rich fuel mixtures under ultra lean conditions. This work is reported in Journal Publication #1.

2. Studies of flammability limits of CH₄/air flames at elevated pressures

This study was conducted in collaboration with Tsinghua University and aimed to provide the first experimental flame extinction data for near-limit CH₄/air flames at elevated pressures. The experiments were carried out at the 3.5 s drop tower of the National Microgravity Laboratory of China. The experimental results showed for the first time that at a given strain rate, the fuel concentration at extinction varies non-monotonically with pressure, namely it first increases and subsequently decreases as pressure increases. The simulations confirmed the non-monotonic variation of flammability limits with pressure. Sensitivity analysis showed that for pressures between one and five atmospheres, the near-limit flame response is dominated by the competition between the main branching, $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, and the pressure sensitive termination, $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$, reaction. However, for pressures greater than five atmospheres it was determined that the HO₂ kinetics result in further chain branching in a way that is analogous to the third explosion limit of H₂/O₂ mixtures.

This work is reported in Journal Publication #2.

3. Studies of methanol, ethanol, and n-butanol flames at atmospheric pressure

Laminar flame speeds and extinction strain rates of premixed methanol, ethanol, and *n*-butanol flames were determined experimentally at atmospheric pressure and elevated unburned mixture temperatures. Additional measurements were conducted also to determine the laminar flame speeds of their *n*-alkane/air counterparts, namely methane, ethane, and *n*-butane in order to compare the effect of alkane and alcohol molecular structures on high-temperature flame kinetics. Two recently developed detailed kinetics models of *n*-butanol oxidation were used to simulate the experiments. The experimental results revealed that laminar flame speeds of ethanol/air and *n*-butanol/air flames are similar to those of their *n*-alkane/air counterparts, and that methane/air flames have consistently lower laminar flame speeds than methanol/air flames. The laminar flame speeds of methanol/air flames are considerably higher compared to both ethanol/air and *n*-butanol/air flames under fuel-rich conditions. Numerical simulations of *n*-butanol/air freely propagating flames, revealed discrepancies between the two kinetic models regarding the consumption pathways of *n*-butanol and its intermediates.

This work is reported in Journal Publication #3, and Fig. 1 depicts representative results.

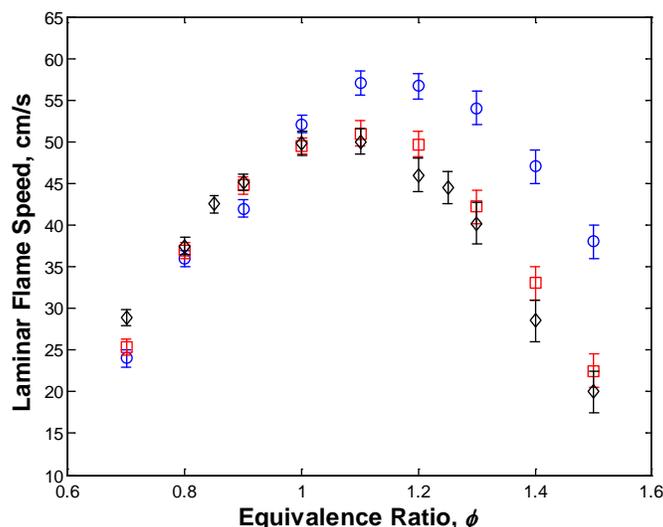


Figure 1. Experimentally determined laminar flame speeds of methanol/air, ethanol/air and, *n*-butanol/air flames at $T_u = 343$ K. (\circ) methanol/air; (\square) ethanol/air; (\diamond) *n*-butanol/air.

4. Studies of flames of butanol isomers at atmospheric pressure

An experimental and computational study was conducted on the propagation of flames of saturated butanol isomers. The experiments were performed under atmospheric pressure, unburned mixture temperature of 343 K, and for a wide range of equivalence ratios. The experiments were simulated using a recent kinetic model for the four isomers of butanol. Results indicate that *n*-butanol/air flames propagate somewhat faster than both *sec*-butanol/air and *iso*-butanol/air flames, and that *tert*-butanol/air flames propagate notably slower compared to the other three isomers. Reaction path analysis of *tert*-butanol/air flames revealed that *iso*-butene is a major intermediate, which subsequently reacts to form the resonantly stable *iso*-butenyl radical retarding thus the overall reactivity of *tert*-butanol/air flames relatively to the other three isomers.

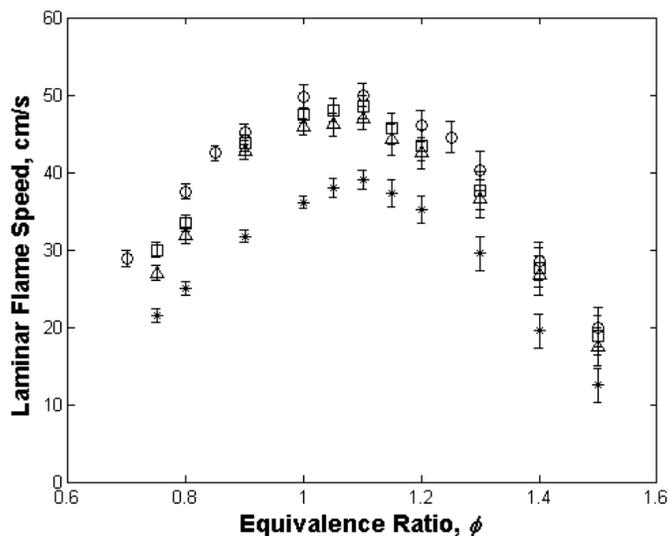


Figure 2. Experimentally determined laminar flame speeds of (\square) *n*-butanol/air [14], (Δ) *iso*-butanol/air, (\circ) *sec*-butanol/air, and ($*$) *tert*-butanol/air flames at $T_u = 343$ K.

Through sensitivity analysis, it was determined that the mass burning rates of *sec*-butanol/air and *iso*-butanol/air flames are sensitive largely to hydrogen, carbon monoxide, and C_1 - C_2 hydrocarbon kinetics and not to fuel-specific reactions similarly to *n*-butanol/air flames.

However, for *tert*-butanol/air flames notable sensitivity to fuel-specific reactions exists. While the numerical results predicted closely the experimental data for *n*-butanol/air and *sec*-butanol/air flames, they overpredicted and underpredicted the laminar flame speeds for *iso*-butanol/air and *tert*-butanol/air flames respectively. It was demonstrated further that the underprediction of the laminar flame speeds of *tert*-butanol/air flames by the model was most likely due to deficiencies of the C₄-alkene kinetics.

This work is reported in Journal Publication #4, and Fig. 2 depicts representative results.

5. Comparative studies on the extinction of non-premixed DME and ethanol flames at atmospheric pressure

The extinction characteristics of non-premixed dimethyl ether and ethanol flames were investigated in order to assess the effect of the molecular structure on the combustion behavior of two otherwise similar fuels. The experiments involved counterflowing streams of fuel diluted in nitrogen and pure oxygen. Extinction strain rates were determined at atmospheric pressure and elevated unburned mixture temperature, over a wide range of fuel to nitrogen ratios. Two recent chemical kinetic models were used to simulate the experiments. The Lennard-Jones potential parameters assigned to dimethyl ether in the transport databases of the models were evaluated, and the effect of their uncertainty on the prediction of extinction limits of non-premixed flames was assessed. Sensitivity analyses with respect to reaction rates and binary diffusion coefficients were conducted to provide insight into the controlling physico-chemical processes. Additionally, the high-temperature reaction pathways of dimethyl-ether and ethanol oxidation in non-premixed flames were identified and were used to interpret the results.

This work is reported in Journal Publication #5.

6. Studies of NO_x formation in flames of model biodiesel flames at atmospheric pressure

The combustion and pollutant formation characteristics of model biodiesel fuels were investigated. NO_x emissions of model biodiesel fuels, i.e. fatty acid methyl-esters (FAME), were experimentally determined for premixed and non-premixed flames. More specifically, the pollutant emission characteristics of flames of two C₄-type FAME, namely methyl-butanoate and methyl-crotonate, was considered and the results were compared against those obtained for *n*-butane and *n*-pentane flames. Methyl-butanoate/air flames were determined to produce significantly less NO_x than the two alkanes under both premixed and non-premixed conditions. These results indicate that the presence of oxygen in the fuel molecule can potentially result in lower NO_x emissions.

This work is reported in Journal Publication #6.

7. Studies of *n*-propanol, *iso*-propanol, and propane flames at atmospheric pressure

The phenomena of propagation and extinction of flames of saturated C₃ alcohols and propane were studied experimentally and numerically in order to assess the effects of the presence and location of the hydroxyl radical in the fuel molecular structure. The experiments were carried out under atmospheric pressure and for unreacted fuel-carrying stream temperature of 343 K. The simulations included detailed descriptions of molecular transport and chemical kinetics using a recently developed kinetic model for C₃ alcohols. The experimental results revealed that the laminar flame speeds and extinction strain rates of *n*-propanol/air and propane/air flames are close to each other whereas those of *iso*-propanol/air flames are consistently lower. Similar behavior was observed also for the extinction strain rates of non-premixed *n*-propanol and *iso*-propanol flames. It was shown through sensitivity and reaction path analyses that there are two major differences between the intermediates of *n*-propanol/air and *iso*-propanol/air flames. In *iso*-propanol/air flames there are notably higher concentrations of propene whose consumption pathway results in the relatively unreactive allyl radicals, retarding thus the overall reactivity. In

n-propanol/air flames there are notably higher concentrations of formaldehyde that reacts readily to form formyl radicals whose subsequent reactions enhance the overall reactivity. The kinetic model used in this study was found to overpredict the experimental results for rich *n*-propanol/air and propane/air flames. Analysis revealed that those discrepancies are most likely caused by deficiencies in the C₃ alkane kinetics. Through sensitivity analysis, it was determined also that the propagation and extinction of *n*-propanol/air and *iso*-propanol/air flames are sensitive largely to hydrogen, carbon monoxide, and C₁-C₃ kinetics and not to fuel-specific reactions. Finally, the relative sooting propensities of flames of these three fuels were assessed computationally.

This work is reported in Journal Publication #7, and Fig. 3 depicts representative results.

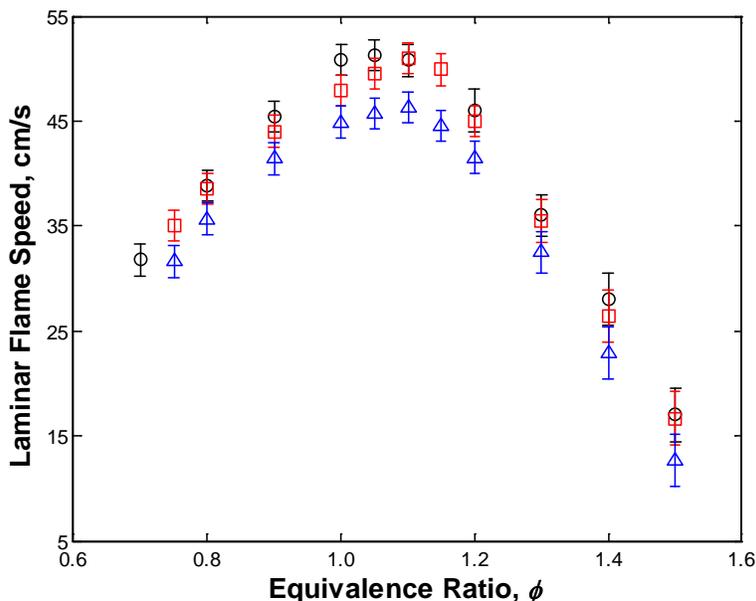


Figure 3. Experimentally determined laminar flame speeds of *n*-propanol/air (\square), *iso*-propanol/air (Δ), and propane/air (\circ) flames at $T_u = 343$ K.

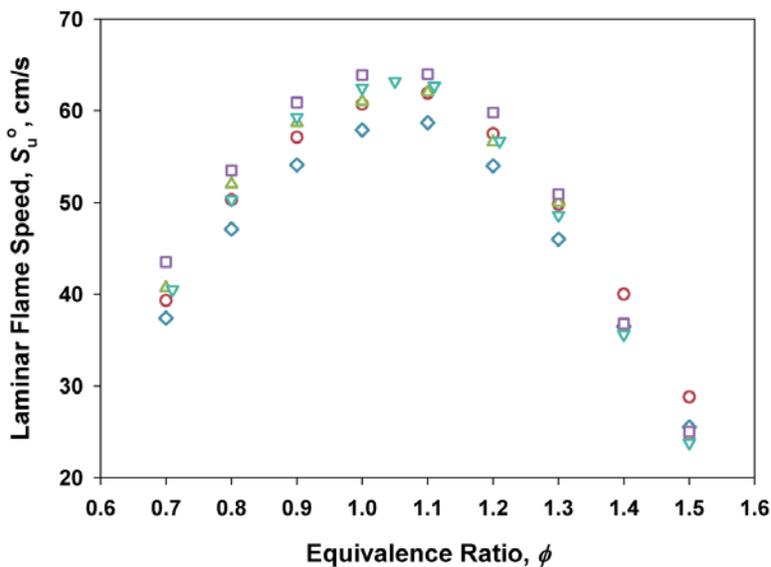


Figure 4. Experimentally determined laminar flame speeds of methyl-butanoate/air (\diamond), methyl-crotonate/air (\circ), methyl-decanoate/air (\triangle), *n*-C₄H₁₀/air (\square), and *n*-C₁₀H₂₂/air (∇) flames at $T_u = 403$ K.

8. Studies of C_4 and C_{10} methyl-ester flames at atmospheric pressure

The oxidation of three model biodiesel fuels, namely methyl butanoate, methyl crotonate, and methyl decanoate was investigated in laminar premixed and non-premixed flames. The experiments involved the determination of laminar flame speeds and extinction strain rates at atmospheric pressure, for a wide range of equivalence or inert-dilution ratios, and elevated reactant temperatures. The experimental data were compared against those derived for flames of n -alkanes of similar carbon number, in order to assess the effects of saturation, the length of carbon chain, and the presence of the ester group. Several recent chemical kinetic models were tested against the experimental data, and major differences were identified and assessed. The accuracy of the Lennard-Jones potential parameters assigned to the methyl esters in the transport databases of the different models was evaluated and new values were estimated. Insight was provided into the high-temperature kinetic pathways of methyl esters in flame environments. Additionally, the reduced sooting propensity of methyl ester flames compared to n -alkane flames was investigated computationally.

This work is reported in Journal Publication #8, and Fig. 4 depicts representative results.

PLAN FOR FUTURE WORK

The work of Year 1 established a framework based on which kinetic and transport models can be developed for oxygenated fuels and validated against experimental data obtained primarily for near-atmospheric conditions. The results have demonstrated clearly the deficiencies of existing kinetic and transport models as in most cases fail to predict satisfactorily even global flame properties such as laminar flame speeds and ignition/extinction limits, with the exception of the well-studied methanol and ethanol. Existing kinetic models can result in predictions that vary notably among themselves for two reasons. First, there are discrepancies regarding rate constants of fuel-related reactions, but more important there are discrepancies in the “foundation kinetics” of H_2 , CO, and C_1 - C_4 hydrocarbons that, in many instances, control the flame response and structure. Additionally, it has been determined that the kinetics of various intermediates of oxygenated fuel oxidation, including several unsaturated small hydrocarbons, need to be improved. Finally, much needs to be done towards the better understanding of the NO_x and sooting propensities of flames of oxygenated fuels as function of the carbon number and the extent of saturation.

The specific plan for future work includes the following:

1. Pressure effects

The measurements of laminar flame speeds, ignition/extinction limits, NO_x profiles, and soot volume fractions will be completed at atmospheric pressure and will be extended to the range of 0.5 to 8 atm that is appropriate for counterflow flames. The studies will be divided in two categories. The first one will involve data obtained in flames of key oxygenated fuels, e.g. those discussed earlier in this report as well as some additional ones to be discussed below. The experimental data for the proposed pressure range will impose additional constraints to kinetic and transport models validation. The second category will involve data obtained in flames for H_2 and selected small hydrocarbon flames, whose kinetics constitute the “foundation” of models for all oxygenated fuels considered. Additionally, studying flames of hydrocarbons with molecular structure similar to that of oxygenated fuels, will allow for the derivation of more conclusive insight into the effect of O-containing functional groups in the fuel molecule on fundamental combustion properties including the propensity for pollutant formation.

In addition to performing studies in the well-established counterflow configuration, efforts will be expended towards developing new approaches to study the oxidation kinetics of fuels in the presence of diffusion at extreme pressures. The development of such approaches will be based on three basic requirements. First, the experimental data need to exhibit particular

sensitivity to chemical kinetics. Second, the reacting configuration needs to be free of instabilities that are favored at high pressures. Third, the measurements need to be direct and free from as many assumptions as possible.

2. Reacting configurations and fuels

Both premixed and non-premixed reacting configurations will be considered based on the need to mimic the conditions that are encountered in practical combustors, which are different for different fuels, and to increase the sensitivity of the measured quantities on kinetics and molecular transport. In premixed configurations, most flame properties are sensitive largely to kinetics. In non-premixed configurations, on the other hand, the phenomena of ignition and extinction exhibit a notably higher sensitivity on reactant diffusion. Additionally, the type and concentration of the diluents will be chosen so that the validity of specific rate constants can be assessed with greater confidence. For example, adding water in lean hydrogen flames and raising the thermodynamic pressure can result in flames whose behavior is rather sensitive to the recombination reaction between H and O₂ and the subsequent HO₂ kinetic pathways. There is evidence that the HO₂ kinetics there are not well characterized under high-density conditions.

Although butanol and C₄ and C₁₀ saturated methyl esters are target fuels for model validation, C₁-C₅ or higher-carbon oxygenated fuels will be considered so that kinetic and transport models can be validated in a hierarchical fashion. Additionally, selected unsaturated oxygenated compounds will be considered for two reasons. First, such compounds are present in biodiesel fuels and it is essential that their kinetics are developed eventually. Second, the presence of unsaturated bonds could augment the sooting propensity and it is of interest to weigh this against the sooting suppressing effect of the atomic oxygen that is present in the fuel molecule. Finally, based on the results obtained in Year 1 the need to study flames of selected alkenes, aldehydes, and ketones was identified. The alkenes include propene, *l*-butene, 2-butene, and *iso*-butene. The aldehydes include propanal, butanal, and *iso*-butanal. The ketones include acetone and butanone.

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FLAME CHEMISTRY, DYNAMICS AND KINETIC MODEL REDUCTION

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A. SUMMARY

Our EFRC research focuses on fundamental understanding of flame chemistry and the kinetic/transport couplings between species with different functional groups; development of computationally efficient dynamic model reduction approaches; and direct numerical modeling of new flame regimes in homogeneously charged compression ignition (HCCI) system at high pressure and low temperature conditions. Specifically, the research achievements include: 1) the flame speed measurements and kinetic assessment of combustion of high hydrogen synthetic gas mixtures at high pressure (1-25 atm) and low temperature (1400-1800 K) were completed; 2) extinction limits of n-heptane/methyl butanoate diffusion flames were measured and updated kinetic and transport models were developed; 3) a dynamic multi-timescale (MTS) method integrated with a multi-generation path flux analysis (PFA) method were developed and tested; and 4) ignition and combustion regimes in HCCI combustion of n-heptane/air mixtures were modeled by using a detailed kinetic mechanism and the multi-timescale method. Six different flame regimes were identified. Singular dependence of the critical temperature gradient on temperature for ignition/acoustic coupling was identified in the negative temperature coefficient (NTC) region.

B. ACCOMPLISHMENTS

1. Flame Speed Measurements and Kinetic Validation of $H_2/CH_4/CO/O_2$ Flames at High Pressures and Low Flame Temperatures.

Biomass and coal derived high hydrogen syngas is one of the major solutions for energy security and CO_2 reduction. Furthermore, the H_2/O_2 reaction system forms the core subset of oxidation mechanisms of all hydrocarbon and oxygenated fuels. As such, development of a validated H_2/O_2 mechanism at high pressure and low temperature conditions is critical for quantitative prediction and optimization of practical power generation systems to achieve enhanced energy efficiency and low

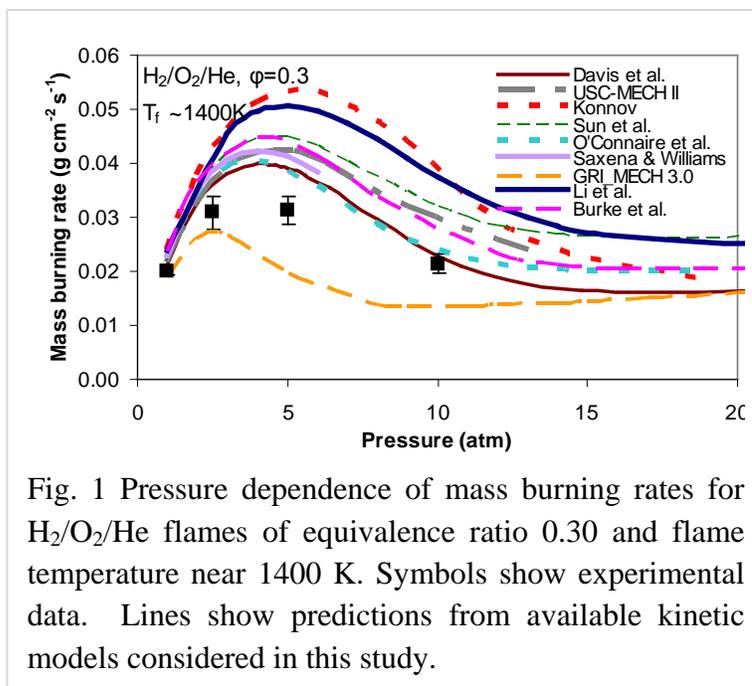


Fig. 1 Pressure dependence of mass burning rates for $H_2/O_2/He$ flames of equivalence ratio 0.30 and flame temperature near 1400 K. Symbols show experimental data. Lines show predictions from available kinetic models considered in this study.

emissions. In this study, experimental measurements of burning rates, analysis of key reaction and kinetic pathways as well as kinetic modeling studies were performed for $H_2/CH_4/CO/O_2$ flames spanning a wide range of fuel conditions: equivalence ratios from 0.30 to 3, flame temperatures from 1400 to 1800 K, pressures from 1 to 25 atm, CH_4/CO fuel fractions from 0 to 1. As shown in Fig.1, it is found that there is a negative pressure dependence of burning rate on high pressure when the pressure is higher than a critical value. In addition, the results show similar negative pressure dependence of the burning rates with CO and CH_4 at fuel fractions typical of synthetic gas mixtures.

Substantial differences between the predictions using the existing kinetic models and the experimental data are demonstrated. The deviations in model predictions themselves increase up to a factor of four as the pressure increases. None of the recent kinetic models can reproduce the measured pressure dependence of the mass burning rate for all diluent concentrations at high pressures. The results suggest that improvements of elementary reaction rates at high pressure involving HO_2 formation and destruction with H, O, and OH radicals are needed in hydrogen mechanism to reproduce the experimental data.

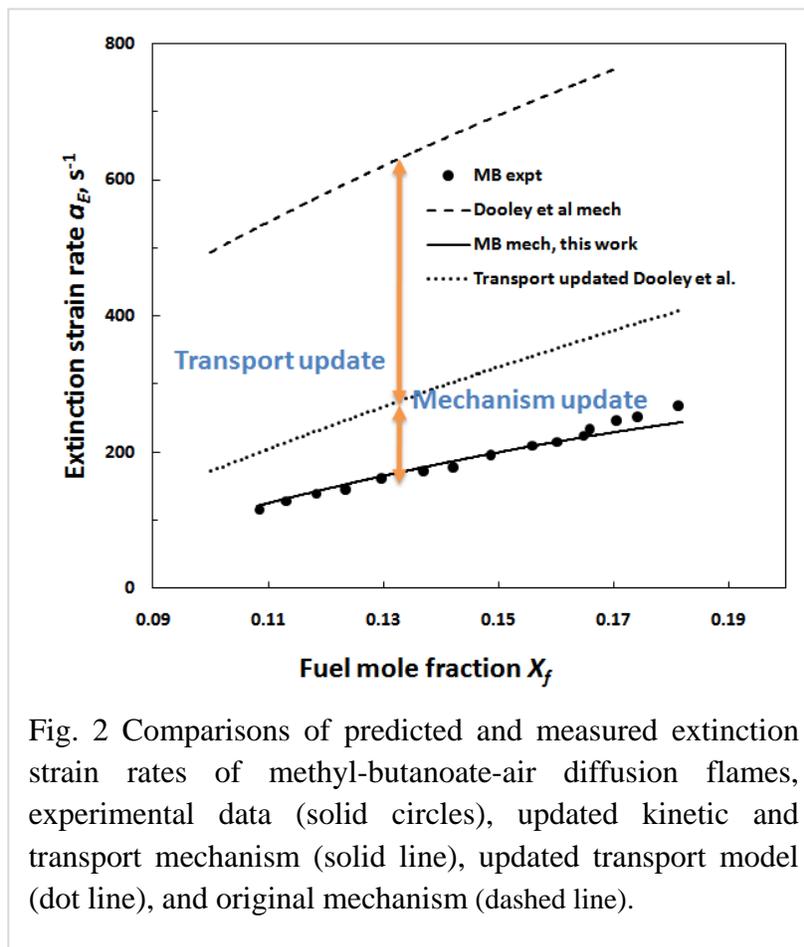


Fig. 2 Comparisons of predicted and measured extinction strain rates of methyl-butanoate-air diffusion flames, experimental data (solid circles), updated kinetic and transport mechanism (solid line), updated transport model (dot line), and original mechanism (dashed line).

2. Kinetic and Transport Couplings in n-Heptane/Methyl Butanoate Diffusion Flames

Bioderived fuels such as biodiesels and alcohols will have to be blended into petroleum derived fuels for ground transportation. However, biodiesels and alcohols have different transport properties and propensities in producing radicals and intermediate species, leading to dramatic changes in ignition and extinction properties for blended transportation fuels via kinetic and transport couplings between biofuels and petroleum derived fuels. In this study, the extinction limits of methyl butanoate and n-heptane diffusion flames have been measured as a function of fuel mole fraction with nitrogen dilution in a counterflow with air. The results show that methyl butanoate diffusion flames are observed to have a much lower extinction strain rate than n-

heptane diffusion flames and the extinction strain rate of n-heptane/methyl butanoate diffusion flames is observed to decrease significantly as the methyl butanoate fraction is increased. Moreover, as shown in Fig.2, the transport properties of species with ester functional group play an important role in the prediction of extinction limits. An update of the transport properties dramatically improves the prediction of the extinction limit. In addition, a detailed chemical kinetic model for the high temperature oxidation for mixtures of these fuels is assembled and tested. Numerical computations of extinction agree well with experimental results for the pure fuels as well as for mixtures. The path flux analysis reveals that the production formaldehyde and the hydroperoxy radicals of methyl butanoate at low temperatures destructs the radical production from n-heptane and narrows the extinction limit.

3. Development of Multi-Time Scale (MTS) and Multi-Generation Path Flux Analysis (PFA) Methods for Kinetic Model Reduction

Recently, significant progresses in detailed kinetic mechanism generation have been made in both hierarchical and automatic mechanism generation. However, a typical detailed kinetic mechanism for a large hydrocarbon or oxygenated fuel involves hundreds to thousand species. The large species number and the broad timescale distributions of reactions make direct numerical simulation extremely challenging.

In this study, a dynamic multi-timescale (MTS) method (Fig.3), which simulates each species at its own timescale, is developed to increase dramatically the computation efficiency involving multi-physical and chemical processes using detailed and reduced kinetic mechanisms. Furthermore, a hybrid multi-timescale (HMTS) algorithm is constructed by integrating the MTS method with an implicit Euler scheme, respectively, for species with and without the requirement of accurate time histories at sub-base timescales. The efficiency and the robustness of the MTS and HMTS methods are demonstrated by comparing with the Euler and VODE solvers for homogenous ignition and unsteady flame propagation of hydrogen, methane, n-heptane, and n-decane-air mixtures. A decrease computation time by about one-order with the same kinetic mechanism is demonstrated. Moreover, a multi-generation path flux analysis (PFA) method is developed and the MTS method is integrated with the PFA method. The MTS and PFA methods are used in adaptive computation of unsteady spherical flame propagation using detailed kinetic mechanisms.

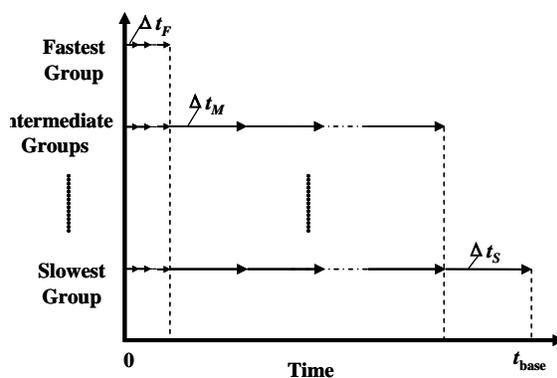


Fig.3 Diagram of multi timescale (MTS) method. Δt_F is the time step of the fastest group, Δt_M is the time step of an intermediate group, Δt_S is the time step of the slowest group, and t_{base} is the base time step.

4. Modeling of Flame Regimes and Ignition/Acoustic Wave Coupling in Low Temperature Homogeneous Compression Ignition (HCCI) of n-Heptane-Air Mixtures

Homogeneous charge compression ignition (HCCI) engines are currently under development to achieve a dramatic increase in energy conversion efficiency. However, the emissions and engine performance are strongly controlled by chemical kinetics at low temperatures. As such, it is necessary to understand the flame regimes and the ignition/acoustic wave coupling using detailed kinetic mechanisms. In this study, by using the HMTS method, HCCI combustion of n-heptane/air mixtures in a one-dimensional, non-adiabatic closed cylinder is modeled. A detailed kinetic model for n-heptane with 1,034 species is reduced by using the path flux analysis method. The MUSCL-Hancock scheme is adopted to enable shock capturing capability. The initial pressure and equivalence ratio are 20 atm and 0.4, respectively. The initial temperature is varied between 600 K and 1100 K. As shown in Fig.4, it is found that there exist at least six different combustion regimes. It is found that the critical temperature gradient for ignition and acoustic wave coupling becomes singular in the negative temperature coefficient (NTC) region. In addition, the results demonstrate that both the NTC effect and the acoustic wave propagation in a closed reactor have a dramatic impact on the ignition front and acoustic interaction.

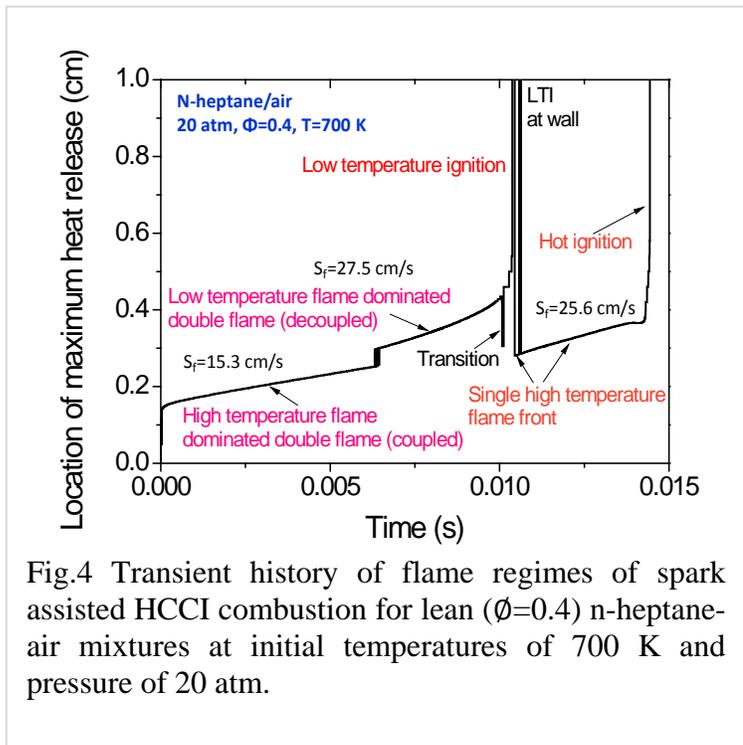


Fig.4 Transient history of flame regimes of spark assisted HCCI combustion for lean ($\phi=0.4$) n-heptane-air mixtures at initial temperatures of 700 K and pressure of 20 atm.

C. FUTURE CHALLENGES AND RESEARCH PLAN

1. Challenges

The state of the art quantum computation of elementary reaction rates still has a large uncertainty and is limited to small fuel molecules. Computation of internal multi-freedom thermalization via collisional energy transfer at high pressure remains challenging. Therefore, accurate experimental data are needed to constrain and validate quantum computations. However, today's experimental measurements of species in flames are still limited to low pressure or dominated by intrusive methods. Laser diagnostics for quantitative species measurements are limited to few species compared to thousands species involved in kinetic mechanisms. Direct and accurate measurements of elementary reaction rates even for the most important reactions remain challenging. Extraction of global and local flame properties such as flame speeds and species still have large uncertainties. The C_0 - C_4 mechanism has not been well validated at high pressures. Accurate transport properties at elevated temperatures and pressure are not available. Correlations for kinetic coupling between fuels with different functional groups remain unclear.

Flame regimes at high pressure with low temperature chemistry have been rarely studied. Large scale turbulent modeling is still constrained by the uncertainty, size, and stiffness of kinetic mechanisms. Quantitative prediction of turbulence-kinetic interactions at high pressures remains challenging.

2. Future Work

Experimentally, we will develop new laser based diagnostic and molecular beam mass spectroscopy systems to measure important intermediate species in flames at elevated pressures. We will also develop a high pressure jet stirred reactor to study fuel pyrolysis and oxidation as well as species isomerization at low temperatures. Computationally, we will develop algorithms for dynamic multi-timescale modeling with adaptive chemistry and gridding. These methods will be used to understand ignition and flame regimes in HCCI engines at the NTC region. In Theory, we will develop methods to reduce the uncertainty in experimental measurements of global flame properties and develop correlations for kinetic coupling between fuels with different functional groups.

D. PUBLICATIONS

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DIRECT NUMERICAL SIMULATION OF HIGH-PRESSURE, MIXED-MODE TURBULENT COMBUSTION

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SUMMARY/OVERVIEW

The objective of this research is to perform direct numerical simulation (DNS) with detailed chemistry to couple high pressure, low temperature kinetics with turbulent transport. The DNS is used to understand ‘turbulence-chemistry’ interactions at high pressure in mixed-modes of combustion relevant to the utilization of 21st Century transportation fuels. DNS complements experimental data in providing statistics at moderate Reynolds numbers needed to develop and validate other more approximate modeling approaches at high pressure. In the past year DNS were performed of two canonical configurations relevant to homogeneous charge compression ignition (HCCI) combustion and lifted flame stabilization in vitiated hot environments encountered in diesel combustion. In collaboration with Steve Pope and roving postdoc, Andrew Garmory, *a posteriori* comparisons were made of the RANS PDF approach with the latter configuration. Future plans involve comparisons of the DNS data with the LES/PDF approach. In the following sections highlights of these accomplishments are presented, followed by discussion of future plans.

ACCOMPLISHMENTS

1. DNS of Turbulent Ethylene Lifted Jet Flame in Heated Air Coflow

Direct numerical simulation (DNS) of the near field of three-dimensional spatially-developing turbulent ethylene [Yoo et al. 2010] jet flame in highly-heated coflow was performed with a reduced mechanism to investigate the stabilization mechanism. The DNS was performed at a jet Reynolds number of 10,000 with over 1.29 billion grid points. Figure 1 shows instantaneous images of several scalar fields - scalar dissipation rate, mixture fraction, and hydroperoxy, methyl and hydroxyl intermediates - obtained from the DNS data. The results showed that auto-ignition in a fuel-lean mixture at the flame base is the main source of stabilization of the lifted jet flame.

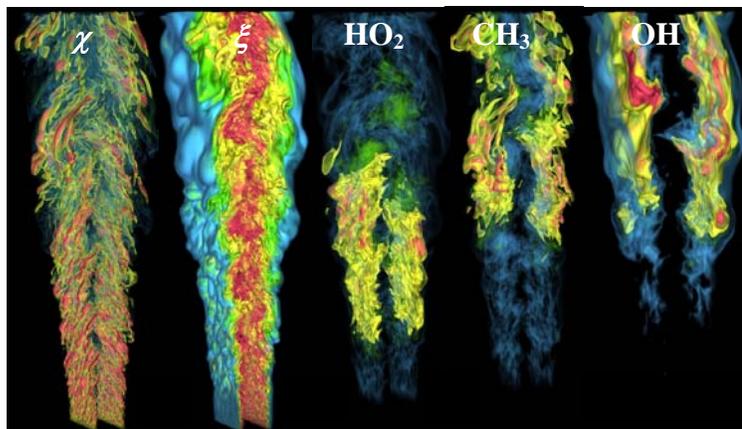


Figure 1. Instantaneous volume rendering of scalar dissipation rate χ , mixture fraction ξ , HO_2 , CH_3 and OH radicals in a lifted ethylene/air jet flame ($\text{Re}=10,000$) in a hot coflow.

This was verified by applying several diagnostics to the lifted jet flame DNS including the development and application of a chemical explosive mode (CEM) analysis [Lu et al. 2009, 2010], a Damköhler number defined by the CEM and the local scalar dissipation rate [Yoo et al. 2009, Lu et al. 2010], and by Lagrangian tracking of key scalar and velocity statistics at the stabilization point [Yoo et al. 2010].

2. Effects of Thermal and Composition Stratification in HCCI Combustion with Oxygenated and Diesel Surrogate Fuels

HCCI combustion offers the potential of high diesel-like efficiencies with low NO_x and particle emissions. It achieves this by burning overall lean and dilute, largely through volumetric autoignition in the absence of flames. As a viable alternative to spark-ignited engines, an important issue that needs to be resolved is controlling the rapid rate of pressure rise and energy release at high loads. One proposed method is to control the rate of pressure rise through mixture and thermal stratification due to non-uniformities that exist either intrinsically in the charge or due to externally imposed stratification. These non-uniformities are thought to exist due to heat transfer from the charge to the cylinder walls during compression, to the presence of hot residual pockets from previous cycles, or due to direct injection and fuel vaporization.

In a previous DNS study of hydrogen/air ignition in a constant volume [Sankaran et al. 2005, Chen et al. 2006, Hawkes et al. 2006] multiple combustion modes were identified ranging from sequential autoignition down a temperature gradient to deflagrative propagation, and the ignition front speed and thermal gradients were found to be key controlling parameters of the combustion mode. In the following two studies, we have performed DNS of turbulent multi-stage ignition with thermal and concentration stratification. The objective is to determine the effect of different mean and root-mean-square temperature and concentration distributions, particularly spanning the negative temperature coefficient (NTC) regime, on the transient evolution of ignition of fuel-lean *n*-heptane and dimethyl ether mixtures at high pressure in a constant volume. In particular, the influence of scalar gradients, and dilution with exhaust gas recirculation (EGR) on ignition front propagation and structure are determined as a function of the initial temperature and concentration stratification, the mean temperature and pressure, and turbulence characteristics.

2.1 Effect of Thermal Stratification on Ignition of a Lean *N*-Heptane/Air Mixture at High Pressure and Constant Volume

The effect of thermal stratification on the ignition of a lean homogeneous *n*-heptane/air mixture at constant volume and high pressure was investigated by DNS with a new 58-species reduced kinetic mechanism [Yoo et al. 2010] developed for very lean mixtures from the detailed LLNL mechanism [Curran et al. 2002]. DNS were performed in a fixed volume with a two-dimensional isotropic velocity spectrum and temperature fluctuations superimposed on the initial scalar fields [Yoo et al. 2010]. The influence of variations in the initial temperature field, imposed by changing the mean and variance of temperature, and the ratio of turbulence to ignition delay timescale on the multi-stage ignition of a lean *n*-heptane/air mixture was studied. In general, it was found that the mean heat release rate increases more slowly with increasing thermal stratification regardless of the mean value of the initial temperature. Ignition delay decreases with increasing thermal stratification for high mean initial temperature relative to the negative temperature coefficient (NTC) regime. It is, however, retarded with thermal fluctuation for relatively low mean initial temperature due to longer overall ignition delays of the mixtures. Analyses of the displacement speed and Damköhler number reveal that a high degree of thermal stratification induces deflagration rather than spontaneous ignition at the reaction fronts, and

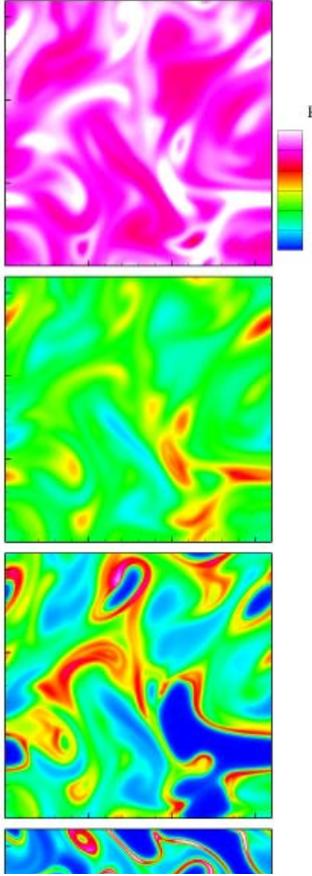


Figure 2: Isocontour of normalized heat release rate for $T_0 = 934\text{K}$, $T' = 15, 30, 60, 100\text{K}$ (from top to bottom) at $t/\tau_{0\text{ig}} = 1.0, 0.96, 0.88,$ and 0.60 , respectively.

hence, the mean heat release rate is smoother after thermal runaway occurs at the highest temperature regions in the domain. Chemical explosive mode analysis (CEMA) also verified that diffusion counterbalances chemical explosion at the reaction fronts for cases with large temperature fluctuation. It was also found that if the ratio of turbulence to ignition delay timescale is short, resultant diminished scalar fluctuations cause small increases in ignition delay. However, the overall effect of turbulence is negligible compared to the effect of thermal stratification. These results suggest that the critical degree of thermal stratification for smooth operation of homogeneous charge compression-ignition (HCCI) engines depends on both the mean and fluctuations in initial temperature which should be considered in controlling ignition timing and to prevent a too rapid rate of pressure rise in HCCI combustion.

Figure 2 shows isocontours of heat release rate for an initial mean temperature, T_0 , of 934K (in the NTC region) and for several different initial temperature fluctuations, T' , ranging between 15 and 100K. approximately at each ignition delay, τ_{ig} , normalized by the corresponding maximum heat release rate during the homogeneous ignition. It is readily observed from the figure that, for small levels of temperature fluctuations, T' (e.g. 15K, top frame), the heat release rate occurs simultaneously throughout the domain, largely as spontaneous ignition. However, for large values of T' , regions of high heat release rate are confined to narrow flame-like regions, although there still exists regions where relatively low heat release rate also occurs in a much larger area. Hence, the combustion mode changes with T' ; *i.e.*, the spontaneous ignition mode is predominant for small T' and the mixed mode of deflagration and spontaneous ignition is predominant for large T' .

A detailed analysis pertaining to the propagation characteristics of deflagration and spontaneous ignition modes was also performed. The ratio of the density-weighted displacement speed, S_d^* , to the laminar flame speed, S_L , was adopted to distinguish between deflagrations and spontaneous ignition fronts. In the present study, the isocontour of $Y_c = Y_{\text{CO}_2} + Y_{\text{CO}} = 0.04$ was chosen to evaluate the displacement speed. This particular isocontour coincides approximately with the location of maximum heat release rate. Figure 3 shows the temporal evolution of the front speed, S_d^* , for the two-dimensional DNS cases with different T_0 and T' . Nominally, the curves exhibit a ‘U’ shape, also observed in previous studies [Chen et al. 2006, Hawkes et al. 2006]. Note that overall, combustion is enhanced with increasing T' for cases with $T_0 = 934$ and 1008 K but retarded for cases with $T_0 = 850$ K. Note also that, for all cases, during incipient thermal runaway, S_d^* of the nascent ignition kernel is significantly larger than the laminar flame speed, S_L . Note that S_d^* is unbounded in the nascent ignition kernel since the scalar gradient, $|\nabla Y_k|$ vanishes. Similarly, burnout of the remaining charge results in an abrupt thermal runaway due to compression heating and thus, S_d^* is also unbounded there. Between the two singularities in S_d^* , however, deflagration of relatively constant speed is

predominant for cases with large T' , and hence, S_d^* exhibits values approaching S_L with increasing T' .

Figure 3 also shows that the duration of deflagration is increased with increasing T' , suggesting that combustion at the reaction waves occurs primarily by deflagration rather than by spontaneous ignition. On the contrary, for cases with small T' , the front speed is always much greater than S_L . These results suggest that a critical degree of thermal stratification for smooth operation of HCCI engines depends on both the mean initial temperature T_0 and T' .

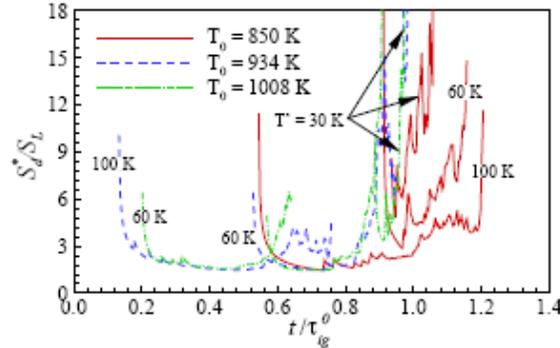


Figure 3. Temporal evolution of the mean front speed S_d^* for two-dimensional DNS cases with different $T_0 = 850, 934,$ and 1008 K and $T' = 30, 60,$ and 100 K.

2.2 HCCI with an Oxygenated Fuel: Di-methyl Ether (DME)

As an oxygenated fuel with a high cetane number (55-56), DME is an interesting fuel for HCCI combustion, for example, as an additive to a fuel blend such as natural gas, to regulate ignition timing. Because of its low ignition temperature and high oxygen content it has the potential to burn more efficiently and cleaner than diesel or bio-diesel fuels. The chemical mechanism for DME used in this study was obtained via a reduction procedure [Lu and Law 2008, Bansal et al. 2010] applied to a detailed mechanism [Zhao et al. 2008] and consists of 30 species and 26 reaction steps. As with the n-heptane HCCI DNS study described above, the goal of this study is to identify the relative importance of various heat release modes including homogeneous autoignition, spontaneous ignition front, premixed deflagration, and triple flames which are known to be present when combustion occurs in thermally and compositionally stratified mixtures.

The computational configuration corresponds to either a two-dimensional constant-volume square or a three-dimensional constant volume cube, with the turbulent velocity field initialized using a turbulence energy spectrum. Inhomogeneous temperature and fuel mass fraction fields were initialized by incorporating insights gained from optical engine experiments performed elsewhere [Dec et al. 2009a, Dec et al. 2009b]. Since, most of the fuels used in engines exhibit a negative-temperature coefficient (NTC) regime at the engine operating conditions, a non-negligible fraction of the total heat release rate occurs at temperatures below 900 K. To accurately capture the low-temperature heat release phenomenon that generally occurs when the piston is moving up in the compression stroke, mass addition source terms were added to the governing equations to mimic the isentropic compression effect due to piston motion. Several two-dimensional DNS cases were performed this past year to identify the parameter space for which three-dimensional DNS will be conducted.

2.2.1 Non-Reacting Mixing Simulations

Non-reacting mixing simulations were first conducted to investigate how the temperature fields evolve due to imposed turbulence starting from an initial inhomogeneous mixture. The objective of these simulations was to investigate how the temperature gradients change if the initial integral length scale of temperature inhomogeneities is increased. For this purpose, three different cases with different initial integral length scales of temperature field were simulated. The initial temperature field was imposed using a scalar spectrum similar to the turbulence spectrum and consists of hot and cold pockets of reactant mixture. The domain length, L , for the three cases was 4 mm, 8 mm, and 16 mm. All the cases had the same initial RMS of temperature fluctuation, T' , and same turbulence integral time scale. Fig. 4 shows the evolution of maximum temperature gradients within the domain for the three cases. It is clearly seen that after one turbulence integral time ($= 1$ ms) the maximum gradient in the domain becomes comparable for the three cases. The physical justification of this is simply given in Eq. 1 below, which essentially states that turbulence dissipation equals production (in an average sense):

$$\overline{2D|\nabla T|^2} = \frac{\epsilon_T}{\tau_t} T'^2 \quad (1)$$

Therefore, if the turbulence integral time scale (τ_t) and temperature RMS (T') are kept fixed, then the temperature gradient ($|\nabla T|$) also remains fixed. The DNS was initialized with values of τ_t and T' similar to that in a real engine. Since temperature gradient is the key variable controlling the mode of heat release [Sankaran et al. 2005], it is reasonable to expect that the combustion behavior observed in DNS will also be relevant to practical engines. Moreover, the chemical time scale is also comparable in the DNS and in real engines (both equal to the ignition delay time of ~ 2 ms);

therefore, turbulence-chemistry interactions are also expected to be similar in the DNS and real engines.

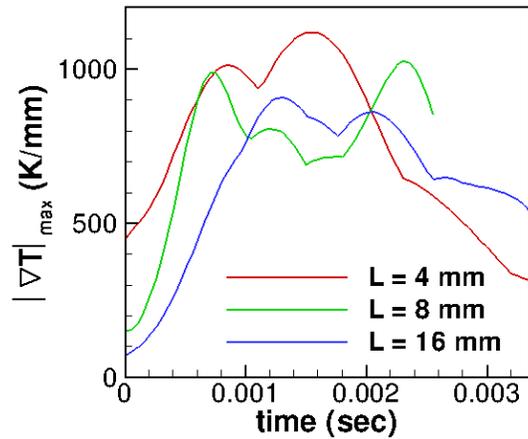


Figure 4. Maximum temperature gradient evolution in time for the three cases.

2.2.2 Thermal Stratification with Isentropic Compression

Reacting DNS were performed with mass addition source terms added to the governing equations to mimic isentropic compression effects due to piston motion in a real engine. Fig. 5 shows plots of average temperature, and average heat release rate (HRR) vs. time and also an

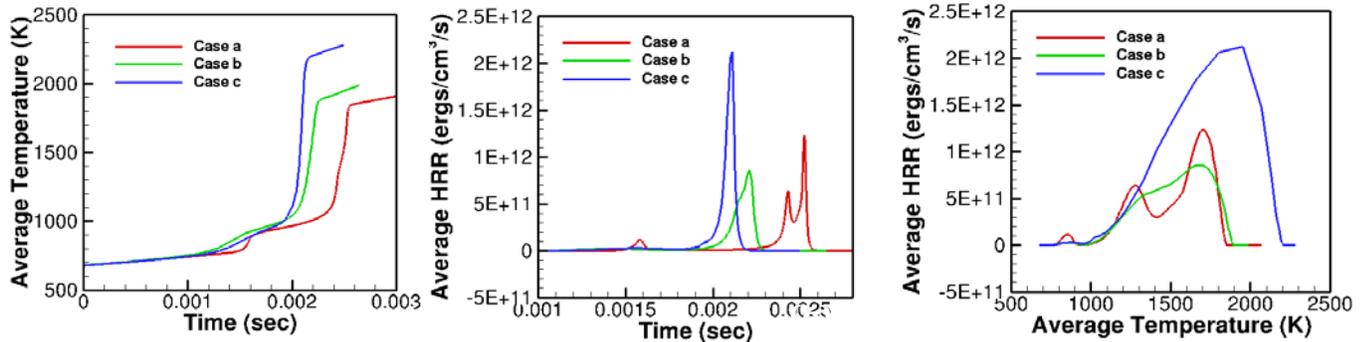


Figure 5. Left: Average temperature vs. time; Middle: Average HRR vs time; Right: Average HRR versus temperature. Case a: 0D simulation; Case b: Thermally stratified case; Case c: Thermally and compositionally stratified case

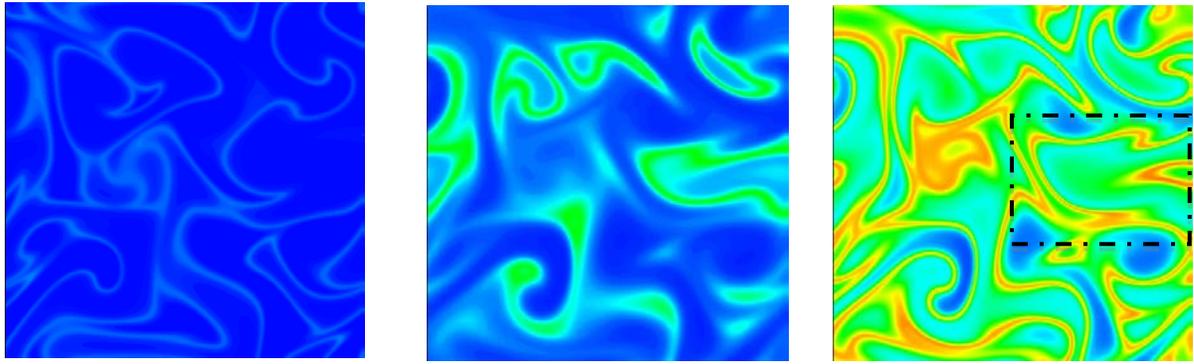


Figure 6. Heat release rate field for case b (blue - 0; red - $1e12$ ergs/cm³/s). (a) $t = 1.4$ ms; (b) $t = 2.075$ ms; (c) $t = 2.135$ ms.

Arrhenius plot of HRR vs. temperature. Case a is a 0D simulation with initial temperature equal to the average initial temperature of the thermally stratified 2D DNS case (case b). Case c is a 2D DNS in which there is stratification in both temperature and equivalence ratio initially (case c is discussed in section 2c below). From the left plot it is observed that as stratification is added the first stage temperature rise becomes smoother. The average HRR plot shows that heat release occurs in three distinct stages corresponding to low (LTC), intermediate (H_2O_2 decomposition), and high ($H+O_2$ branching) temperature ignition pathways (more clearly seen in the Arrhenius plot on the right). For cases b and c, there is some degree of overlap between the intermediate and high-temperature ignition stages. The initial enthalpy for Case c is high, and therefore, the total heat release for case c is higher.

Fig. 6 shows the heat release rate fields for Case b at three different times. Fig. 6(a) shows the low temperature heat release. It is interesting to observe that LTC heat release occurs in thin reaction zones. In Fig. 6(c), some overlap in time between the intermediate- and high-temperature ignition stages is observed for the reaction layers inside the rectangle shown. The outer layer is the intermediate-temperature ignition wave and the inner layer is the high-temperature ignition wave. For all the points inside the rectangle a scatter plot between CH_3 mass fraction and temperature is shown in Fig. 7. Different colors correspond to different times

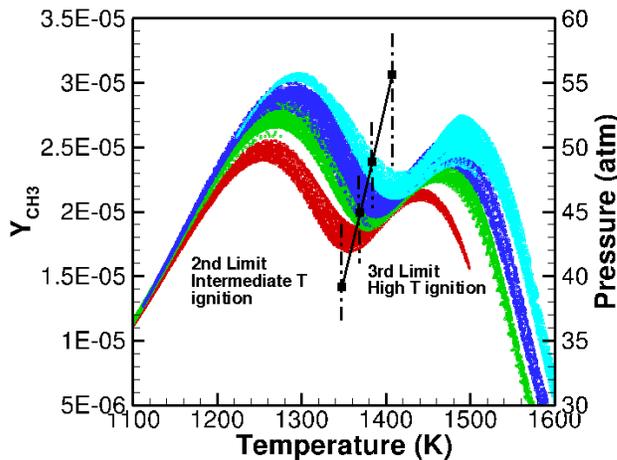


Figure 7. Scatter plot of Y_{CH_3} with temperature for points within the rectangle shown in Fig. 3 (c). Different colors show different times and pressures. The line in the middle of the figure shows the crossover between the second and third limits of ignition.

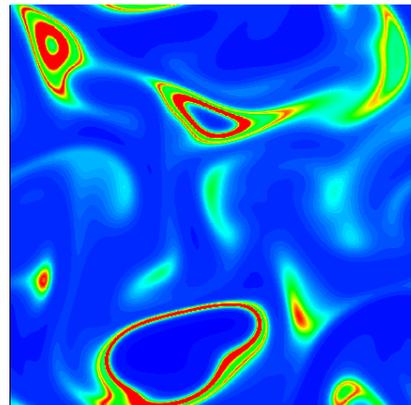


Figure 8. Heat release rate field at time = 2.02 ms for case c (blue - 0; red - $1.5e12$ ergs/cm³/s).

(red: early time (lower pressure), cyan: later time (higher pressure)). Two distinct peaks are observed at intermediate- and high-temperature conditions. The peaks also move towards the right as the system pressure is increased. The solid line in the middle is the computed crossover temperature [Law 2006] line for the mechanism employed in this study. The symbols on the line show the pressures corresponding to the different colors. The crossover line clearly demarcates intermediate- and high-temperature limits of ignition pathways.

Thermal and Compositional Stratification with Isentropic Compression

Direct fuel injection is thought to be a viable option in reducing the peak heat release rates in HCCI engines [Yang et al. 2010]. Late fuel injection causes the fuel to be stratified inside the cylinder. To simulate this using DNS, stratification in both temperature (T) and equivalence ratio (ϕ) fields is initially imposed. The initial T- ϕ fields are uncorrelated. Case c in Fig. 5 shows the evolution of average temperature and average HRR for this case. There is a very strong overlap between the intermediate- and high-temperature stages of ignition and the average HRR plot only reveals an overall two-staged ignition evolution. However, HRR field plots in Fig. 8 show a very interesting two-ringed structure associated with the reaction fronts. The intermediate- and high-temperature ignition waves occur very close to each other both spatially and temporally. This two-ringed structure is observed for most of the ignition kernels. Due to this proximity, it is highly likely that transport of heat/radicals from one stage affects the evolution of the other ignition stage. Analysis of this case is currently underway.

PLAN FOR FUTURE WORK

1. DNS of Lifted Autoignitive Turbulent Jet Flames (DME, Iso-Butanol)

a. A posteriori Comparison of Lifted Ethylene-Air Jet Flame with LES/PDF

The performance of the LES/PDF approach developed by Steve Pope of Cornell University will be assessed via *a posteriori* comparisons with DNS in turbulent lifted jet flames and HCCI simulations focusing on alternative fuels for transportation under engine conditions. To facilitate this interaction we have submitted a nomination package for an EFRC roving postdoc to replace Andrew Garmory who has recently left the CEFRC.

b. Effects of DME as an Additive to regulate Lift-Off Height in DME/Methane/Air Jet Flames in Hot Coflow

The use of DME as an additive to methane will be explored in DNS of a turbulent lifted methane/air jet stabilized in a heated air coflow. It has been shown that small amounts of DME added to methane can substantially impact the ignition delay, or equivalently lift-off distance in a reactive jet flame. The stabilization characteristics may change depending upon the concentration of DME in the fuel stream compared with the rate at which the fuel and air streams mix. Furthermore, the presence of oxygen in the fuel stream may also have a significant impact on flame stabilization and blowout.

c. High Pressure Lifted Diesel-Jet Stabilization with DME and Iso-Butanol

Multi-stage ignition processes representative of diesel engine combustion using an oxygenated fuel, DME, at engine pressures (40-50 atm.) will be explored with DNS. At these pressures and at low temperatures (< 900K), DME exhibits 'cool flame' behavior. A cool flame results from the transition between the first-stage low-temperature ignition to intermediate-temperature ignition, as the reactions are weakly exothermic and result in

the formation of intermediate species. The presence of cool flame behavior may facilitate transition to high-temperature ignition and the establishment of a flame or the faster propagation of a flame through a reactive mixture. DNS of a turbulent DME fuel jet issuing into heated quiescent air at constant pressure will provide unprecedented detail into the lifted diesel stabilization process. As reduced mechanisms for iso-butanol become available in the Center, DNS of this configuration with iso-butanol will also be performed.

2. DNS of DME HCCI Combustion

a. Diagnostics using topological methods

Statistics of individual ignition kernels will be extracted using topological methods that detect and track the local maxima of an intermediate ignition species marker. This will provide important information about how these ignition kernels evolve in a turbulent medium in comparison with 0D homogeneous ignition.

b. Principal component analysis (PCA) and chemical explosive mode analysis (CEMA)

In this highly transient mixed-mode combustion system conventional definitions of reaction progress variables are not applicable. PCA will be applied to the DNS database to obtain the most important reaction coordinates. CEMA will also be applied to the ignition features identified by the topological method to identify the distinct combustion modes and the associated chemical kinetics and tracked in time.

c. Extension to 3D

Three-dimensional turbulence behaves in a fundamentally different way compared to two-dimensional turbulence. Therefore, to get a more realistic picture of the stratified HCCI combustion phenomenon, 3D DNS will be conducted in a configuration similar to the 2D cases.

d. *A-priori* investigation of subgrid turbulent combustion models for stratified HCCI combustion

Using the DNS database obtained in this study, *a-priori* and *a posteriori* evaluations of subgrid closure models based on the transported PDF approach as well as the conditional moment closure (CMC) approach will be conducted to identify the best models for stratified HCCI combustion in both RANS and LES contexts. This is a good benchmark for the validation of the LES/PDF approach by Steve Pope in capturing mixed-mode combustion regimes at high pressure.

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C. S. Yoo, E. S. Richardson, R. Sankaran, and J. H. Chen, “A DNS Study of the Stabilization Mechanism of a Turbulent Lifted Ethylene Jet Flame in Highly-Heated Coflow,” *Proc. Combust. Inst.* (2010) doi:10.1016/j.proci.2010.06.147 (In press).

T. Lu, C. S. Yoo, E. S. Richardson and J. H. Chen, “Chemical Explosive Mode Analysis for a Turbulent Lifted Ethylene Jet Flame in Heated Coflow,” submitted to *Combust. Flame* (2010).

PREDICTIVE TURBULENT COMBUSTION MODELS FOR 21st CENTURY TRANSPORTATION FUELS

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SUMMARY

The overall goal of the project is to develop and demonstrate turbulent combustion models capable of predicting in detail the chemical effects occurring in turbulent flames of future transportation fuels. The methodology being developed combines: large-eddy simulation (LES) to treat the flow and turbulence; probability density function (PDF) methods to treat the turbulence-chemistry interactions; and *in situ* adaptive tabulation (ISAT) to enable the computationally-efficient implementation of the chemistry of transportation fuels. The research to date has concentrated on the final stages of the development of a new LES/PDF/ISAT methodology, and its implementation on large-scale computer systems. In addition, model calculations have been performed of a turbulent non-premixed jet flame (DLR-A), and of a lifted ethylene flame studied at Sandia using direct numerical simulation (DNS). Future work includes continued collaboration with Sandia to exploit DNS data to develop and test LES/PDF models; and an emphasis on premixed and stratified combustion, including in opposed jet burners.

ACCOMPLISHMENTS

1. Development of the LES/PDF Methodology

Although LES/PDF has been implemented in several previous works (e.g. [R1-3]), numerically solving the PDF equation adequately remains to be investigated and validated. A new Monte Carlo particle code (called HPDF) suitable for RANS/PDF and LES/PDF studies has been developed as a platform for studying numerical algorithms and for practical turbulent combustion modeling. Accurate numerical schemes have been developed and implemented in the code to advance the particles in physical and composition spaces to ensure overall second-order numerical accuracy in both space and time. In contrast, all previous LES/PDF studies achieve only first-order accuracy in the time advancement [R4]. In addition, the code has the following attributes: scalable up to at least 4096 cores with MPI parallelization; supporting Cartesian and cylindrical coordinate systems; parallelizable by domain decomposition in two dimensions; and having a general interface to facilitate coupling to different existing LES (or RANS) codes.

The HPDF code has been verified comprehensively with a wide range of manufactured test cases, and has been initially combined with an LES code developed by Pierce [R5]. The first set of LES/HPDF simulations has been performed for the DLR-A flame [1]. For simplicity and computational economy, the flamelet model is used to compute the thermochemical properties based on the mixture fraction. A single scalar (the mixture fraction) is solved for the particles. In this initial study, the following issues are discussed: the verification of the HPDF code; the effect of the LES grid resolution; the consistency between LES and PDF; and, the performance of different time-integration schemes (first-order and second-order). Second-order accuracy of the code in space and time is verified by a manufactured 1D test case. Strong grid-dependency is found for DLR-A. In order to study consistency, the numerical solutions of the mixture fraction

are duplicated in LES and HPDF. At the level of the governing equations, the first two moments of the mixture fraction are consistent in the LES and PDF approaches, so that any discrepancy between their simulation results is due to numerical errors. The results of the mixture fraction fields from LES and HPDF agree well with each other, indicating good numerical consistency. The effect of first and second order time integration schemes are also compared in the flame simulations, and negligible difference is observed due to the very small local CFL number in the flow downstream. The numerical results are compared to the experimental data, and overall good agreement is observed for the velocity, turbulence and scalar fields (see Figure 1), which demonstrates the capability of the new code.

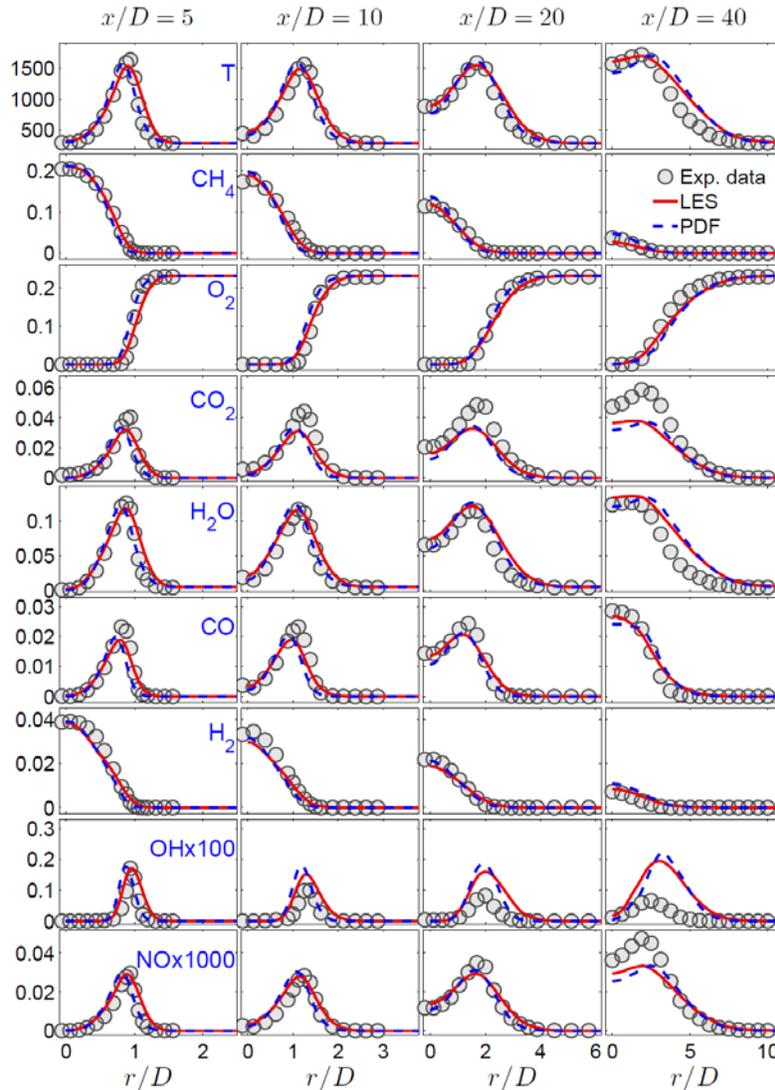


Figure 1: Radial profiles of the time-averaged mean temperature, and mean mass fractions of CH_4 , O_2 , CO_2 , H_2O , CO , H_2 , OH , and NO at the four axial locations $x/D=5, 10, 20,$ and 40 . Symbols: experimental data [R9]; Solid lines: LES calculations; Dashed lines: PDF calculations.

2. Efficient Integration of ODEs for Chemical Kinetics

For homogeneous systems, or in the splitting schemes used in LES/PDF and other methods, the computational problem presented by chemical kinetics amounts to the integration of a stiff set of ordinary differential equations (ODEs). In a full-scale LES/PDF calculation, this ODE integration needs to be performed of order 10^{12} times, e.g., for each of 10^8 particles on each of

10^4 time steps, and hence it is crucial to be able to obtain accurate solutions efficiently. Solutions can be obtained either directly using an ODE solver, or by using *in situ* adaptive tabulation (ISAT), which itself relies on an ODE solver. To an extent, since the 1980s, the numerical integration of ODEs has been a solved problem. However, given its importance in LES/PDF and the recent development of “exponential integrators” [R6-7] we have re-visited two aspects of the problem.

For ODE integrators, as with all other numerical methods, the control of numerical errors is essential. We have compared the performance of four ODE integration schemes and compared their computational speed as a function of the error tolerances and of the incurred error. As may be seen from Figure 2, the incurred error can be substantially different from the specified error tolerance. At a given incurred error, the DVODE scheme is the most efficient and about twice as fast as DDASAC (Figure 3).

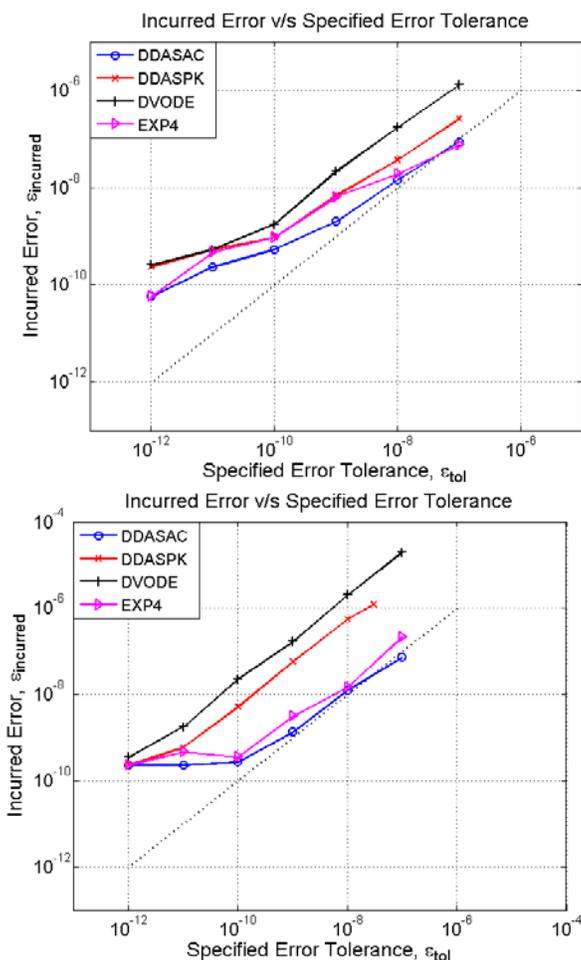


Figure 2: Incurred error ($\epsilon_{incurred}$) as a function of the specified error tolerance (ϵ_{tol}) for four different ODE integrators, with the 31-species GRI-Mech 1.2 mechanism (Argon removed) for methane combustion (left), and the 111-species mechanism¹ for ethylene combustion (right).

¹ Provided by Prof H. K. Chelliah (University of Virginia)

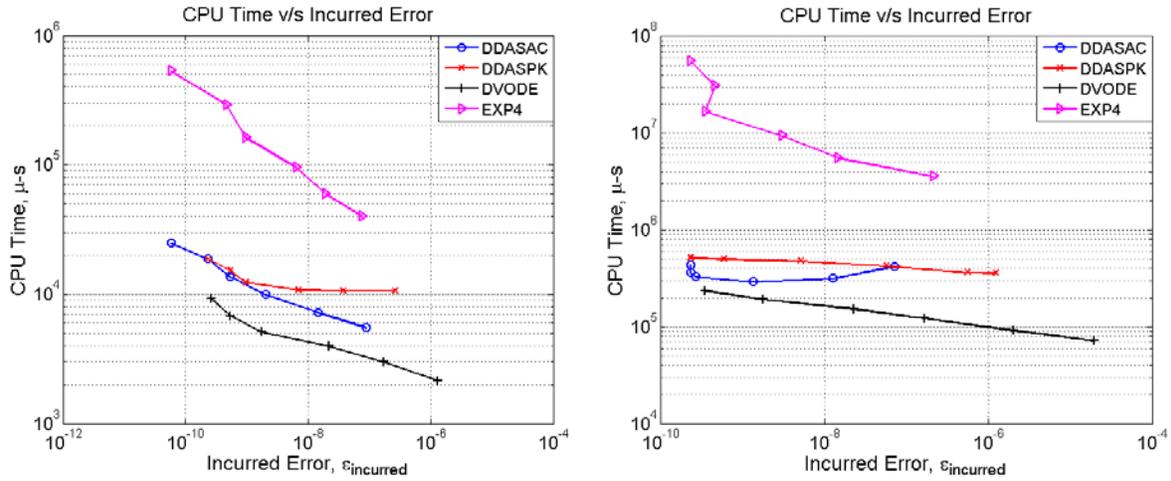


Figure 3: CPU time (μ -s) as a function of the incurred error ($\epsilon_{\text{incurred}}$) for four different ODE integrators, with the 31-species GRI-Mech 1.2 mechanism (Argon removed) for methane combustion (left), and the 111-species mechanism¹ for ethylene combustion (right).

The second topic is the integration used in ISAT for the sensitivity coefficients of the ODE solution with respect to the initial conditions. With there being n species, this amounts to solving the ODE system

$$\frac{dA(t)}{dt} = J(t)A(t), \quad A(0) = I,$$

where A is the $n \times n$ sensitivity matrix, and J is the $n \times n$ Jacobian matrix. If $J(t)$ were constant, then the solution would be $A(t) = e^{Jt}$. Currently, in ISAT, this observation is used to obtain A based on the Jacobians already evaluated in the ODE integrator. We have devised, and are currently implementing, an improved scheme with error control based on exponential integrators [R6-8].

3. PDF Calculations of Turbulent Flames

A study was initiated to apply PDF methods to the lifted slot flames studied experimentally at Sandia by Dr. J.H. Chen and others. This was a preliminary investigation, prior to a full LES/PDF study. The PDF code HYB2D was successfully modified to accommodate the required geometry and boundary conditions, and the calculations correctly yielded a lifted flame, in at least qualitative agreement with the DNS data. We are hoping for the appointment of a new roving post-doc to continue the investigation of these flames.

4. Other Activities

In January 2010, the PI visited Dr. J.H. Chen at Sandia to discuss the CEFRC collaboration and to present a seminar. In July 2010, two Cornell students (on support by the CEFRC) attended the CEFRC Summer School at Princeton. In August 2010, the PI and Dr. Haifeng Wang attended the TNF Workshop and the Combustion Symposium in Beijing. During this funding period, the PI was elected to the National Academy of Engineering, and was awarded the Fluid Dynamics Prize of the American Physical Society. He presented the Otto Laporte lecture at the annual meeting of the APS Division of Fluid Dynamics.

FUTURE PLANS

The principal topics of future research are:

1. Completion of the implementation of the LES/PDF/ISAT methodology on large-scale computer systems. This includes new methodologies for implementing molecular mixing and diffusion, including differential diffusion, and new variance reduction methodologies.
2. Application of the methodology to non-premixed flames exhibiting chemical effects (e.g., lift off, extinction, ignition). This includes the turbulent flames in the TNF series, and new measurements with DME.
3. Application of the methodology to premixed and stratified flames (which have not been studied using LES/PDF). This includes collaboration with Princeton on statistically-spherical premixed flames at atmospheric and elevated pressures.
4. Continued collaboration with Sandia on using DNS to study LES/PDF modeling issues.

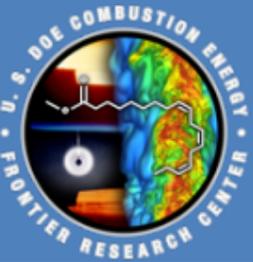
As chemical mechanisms for future transportation fuels become available within the CEFRC, and as turbulent combustion experiments or DNS are performed using these fuels, then we shall apply the LES/PDF /ISAT methodology to these flames.

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CHALLENGING PROBLEMS

E.A. Carter, Princeton University

Reaction flux and sensitivity analyses mapping

A grand challenge is how to automate the reaction flux and sensitivity analyses to automatically determine which reactions must be refined at the MRSDCI/MRACPF level, and to automate the entire calculation process to output the refined energetics and rate constants.

F.N. Egolfopoulos, University of Southern California

Accurate description of rate constants and transport properties

This problem is known and has been identified by all co-PIs of CEFRC. Elaborating on the need for additional experimental data including at high pressures, would be a redundancy as it is recognized by all. However, it is essential to consider approaches in reacting configurations in which the transport properties of the fuel can be validated with confidence. Experimental data on the diffusivities of fuels of interest to CEFRC are scarce and sometimes inconsistent. It has been shown that such inconsistencies can falsify kinetic rates upon validation against flame data.

High pressure combustion

This problem is also known and has been identified by several co-PIs of CEFRC. In addition to their practical importance in engines, experimental data at high pressures are critical for the validation of chemical kinetics for conditions that matter at the end. While experiment data can be obtained in homogeneous systems (e.g. shock tubes, flow reactors) at high pressures without significant complications at least in theory, this is not the case for flames. The only exception to that is the spherically expanding flame configuration that is used for the determination of laminar flame speeds. Such flames though are susceptible to various instabilities that can complicate the measurements under certain conditions. While laminar flame speeds are essential for developing kinetic models, experimental data on flame ignition and species profiles are not available at high pressures. Thus, there are no sufficient constraints that could reduce the uncertainty of not well-characterized rate constants of various reactions that control the overall oxidation process at high pressures. Thus, there is need to develop new approaches, e.g. by thinking “outside the box,” to tackle this problem. The development of such approaches must be based on three basic requirements. First, the experimental data need to exhibit particular sensitivity to chemical kinetics. Second, the reacting configuration needs to be free of instabilities that are favored at high pressures. Third, the measurements need to be direct, non-intrusive, and free from as many assumptions as possible.

N. Hansen, Sandia National Laboratories

Kinetic mechanisms consolidation

The grand challenge is to consolidate the various mechanisms currently under development in different research groups. A serious, concerted effort should be undertaken to a) identify all important reactions, b) establish their most reliable rate constants over a wide range of pressure and temperature by reviewing the literature or through new quantum chemistry calculations and experimental measurements, c) actually include this information in *the* combustion chemistry mechanism, d) provide multiple types of experiments for testing of the model (flames, jet-stirred reactors, shock tubes etc.) and e) update the mechanism once new/better data becomes available.

That is, the community should get together and assemble *the* comprehensive and predictive combustion chemistry mechanism.

Meanwhile, a variety of substituted five- and six-membered cyclic ethers, which can be found in biomass, are likely to be added to the fuel stream by transforming the biomass into suitable transportation fuels or fuel additives that retain these structures. In addition, cyclic ethers are formed during the autoignition of alkanes and alkenes by isomerisation of alkylhydroperoxide radicals. Therefore, it is of particular importance to study the combustion chemistry of cyclic ethers in molecular-level detail. Well suited as a model fuel to learn more about the characteristic combustion chemistry of cyclic ethers is furan. In collaboration with H. Wang and the CERFC fellow B. Yang, it is planned to develop a comprehensive understanding of the combustion chemistry of furan. We will apply the same experimental and modeling techniques successfully used for *n*-butanol, *iso*-butane, and *iso*-butene.

Specifically, flame-sampling molecular-beam mass spectrometry is a powerful tool for the investigation of combustion chemistry. It allows the study of mainly all stable and unstable species by using the same experimental procedure. As described above, the use of easily tunable synchrotron radiation for single-photon ionization makes this approach extremely effective. By funding through different programs at the DOE, the following modifications to the existing mass spectrometer are under way: a) The linear time-of-flight set-up will be replaced by a reflectron time-of-flight spectrometer. This modification will lead to a significant increase in mass resolution from currently $m/\Delta m \approx 400$ to $m/\Delta m \approx 2000$. Such an improved mass resolution will lead to a complete separation of most flame species, which is prerequisite for a more detailed analysis. b) A counter-flow diffusion flame system is currently being designed and built. Using a quartz microprobe to continuously withdraw gases from within such flames combined with mass spectrometry will be an ideal approach to study the fundamental combustion chemistry in diffusion flames.

With funds from the CEFRC, it is planned to expand the current capabilities to investigate the high-temperature oxidation chemistry at low pressure to enable studies of the oxidation kinetics at lower temperature and higher pressure. To this end, a new jet-stirred reactor (JSR), which is currently under development in the group of Prof. Ju at Princeton University, will be coupled to the existing molecular-beam mass spectrometer at the ALS. A JSR is a spherical quartz reactor in which a gas mixture is continuously flowing, and inside the reactor, the gas phase is well stirred, meaning the concentrations and temperature are homogenous. Such a JSR is an ideal system to investigate the chemical reaction kinetics in the low-temperature range of ~ 500 - 1200 K and elevated pressures of ~ 1 - 10 atm. However, in previous JSR experiments only stable products were detected and therefore, a lot of valuable chemical kinetics information on all reactive intermediates and their concentration profile *vs.* reaction time were lost. Many previously developed reaction models based on JSR experiments consist of lots of well educated estimations rather than robust experimental observations. Only very recently, a JSR with molecular-beam sampling and coupling to an MBMS system has been described (see Fig. 4) [6]. This molecular-beam approach offers the advantage that concentration profiles *vs.* reaction time, temperature and pressure of all reactants, intermediates, and products can be identified and quantitatively measured. Such a setup will provide unprecedentedly detailed data that will be essential for the development of a predictive kinetic mechanism for low-temperature oxidation chemistry.

R.K. Hanson, Stanford University

Low-vapor-pressure fuels

- 1) Investigation of low-vapor-pressure fuels using Aerosol Shock Tube (AST) methodologies. These fuels could include large bio-derived diesel surrogates such as the larger methyl esters (methyl stearate etc.) and intermediates from thermal or catalytic cracking of biomass (such as 2,5-dimethyl furan and related compounds). The extended capabilities of the AST now enable studies of this type that were not previously possible.

Multi-species time-histories

- 2) Measurement of multi-species time-histories using multi-wavelength, laser absorption techniques to study the oxidation and pyrolysis of new fuels. Recent advancements in multi-wavelength laser absorption measurements in shock tubes now enable the acquisition of multi-species data sets at near constant-volume conditions. These datasets present a new paradigm for mechanism validation and refinement.

Fuel chemistry at very-high and ultra-high pressures

- 3) Studies of fuel chemistry at very-high and ultra-high pressures (to 1000 atm). The Stanford 5 cm diameter High-Pressure Shock Tube (HPST) would permit the study of fuels at very high pressures using standard (or heated) shock tube techniques. This facility will allow the accurate determination of temperature using new direct laser methods, rather than older indirect methods using chemical thermometers. Very little if any shock tube data is available for any fuel at pressures above 250 atm, and new data sets for both conventional fuel components and new designer fuels will provide insight into the chemistry of these fuels at extreme conditions.

Y. Ju, Princeton University

High Pressure Kinetic Mechanisms

The state of the art quantum computation of elementary reaction rates still has a large uncertainty and is limited to small fuel molecules. Computation of internal multi-freedom thermalization via collisional energy transfer at high pressure remains challenging. Therefore, accurate experimental data are needed to constrain and validate quantum computations. However, today's experimental measurements of species in flames are still limited to low pressure or dominated by intrusive methods. Laser diagnostics for quantitative species measurements are limited to few species compared to thousands species involved in kinetic mechanisms. Direct and accurate measurements of elementary reaction rates even for the most important reactions remain challenging. Extraction of global and local flame properties such as flame speeds and species still have large uncertainties. The C₀-C₄ mechanism has not been well validated at high pressures. Accurate transport properties at elevated temperatures and pressure are not available. Correlations for kinetic coupling between fuels with different functional groups remain unclear. Flame regimes at high pressure with low temperature chemistry have been rarely studied. Large scale turbulent modeling is still constrained by the uncertainty, size, and stiffness of kinetic mechanisms. Quantitative prediction of turbulence-kinetic interactions at high pressures remains challenging.

S.J. Klippenstein, Argonne National Laboratory

Determination of the foundational mechanisms for H₂, C₁, and C₂ chemistry to sufficient accuracy for current engine design efforts.

Sensitivity analyses of combustion properties are almost invariably most sensitive to the fuel decomposition kinetics and to some key reactions in the core mechanisms describing the hydrogen and C₁, C₂ oxidation chemistry. For this reason, it is extremely important to obtain foundational mechanisms that are of the highest accuracy possible. Recent research at high pressures has clearly demonstrated that there are shortcomings even for the H₂/O₂ system. One component of this challenge should involve a clear description of what kind of accuracy is actually needed. Obtaining a mechanism with sufficient accuracy will likely require a concerted effort in theory, experiment, and modeling.

The development and incorporation in mechanisms of an accurate description of the chemistry of the second O₂ addition for a range of fuels, temperatures, and pressures.

The chemistry of the second O₂ addition plays an important role in negative temperature coefficients and other aspects of low temperature combustion behaviour. The detailed understanding of a given reaction can be obtained from ab initio transition state theory multiple well master equation simulations. However, there is currently no useful procedure for taking such results and using them to predict the kinetics as a function of temperature and pressure for related system. Furthermore, essentially no mechanisms currently include a proper treatment of the pressure dependence of these reactions.

The development of an accurate model for soot formation.

There are many stages in soot formation: First and second ring formation, growth of larger PAHs, dimerization of PAHs to form stacked PAHs, coagulation into larger particles, etc. Essentially all of these stages remain very poorly determined.

The development of an automated approach to theoretically predicting the temperature and pressure dependent chemical kinetics for an arbitrary set of reactants.

It is now widely accepted that high level theory is capable of providing kinetic data of sufficient accuracy for most combustion modeling purposes. However, the generation of such accurate theoretical predictions requires concerted effort by competent theoreticians. As a result, the impact of theory is still rather limited. An automated, or nearly automated, procedure for predicting the kinetics directly from the reactants would greatly facilitate the development of accurate mechanisms.

The development of a simple approach for treating the transformation from fuel and fuel radicals to C₁ and C₂ hydrocarbons.

In general, there is little sensitivity of combustion properties to the decomposition and oxidations of intermediates in the decay process from fuel radicals to small hydrocarbons. This lack of sensitivity suggests the feasibility of an approach to modeling that does not consider every intermediate. Instead, what seems to matter is simply the distribution of small hydrocarbons that arises. A modeling approach that ignores the intermediate details would be of immediate benefit as we move to the modeling of ever more complex fuels and surrogate mixtures of fuels. Currently models simply ignore much of the cross chemistry in mixtures. I expect that much better assumptions, which still retain some limit on the number of species considered, are both possible and needed for quantitative predictive modeling.

C.K. Law, Princeton University

Mapping of the Fuels Genome

Systematic development of reaction mechanisms for combustion systems started in the late 1970s, with path-breaking works by Fred Dryer, Charlie Westbrook, and Jurgen Warnatz. For a while it seemed that the mechanisms for such simple fuels as methane were largely in place. However, throughout the years we would see the continuous updating of these mechanisms, and now there is the belief that even aspects of the hydrogen oxidation are not reliable. So when can we reach closure, even in an approximate sense? Thinking back, there has clearly been a lot of wasted effort in rushing to get a mechanism while the state of the art (understanding, experimental data, accuracy of calculations, etc.) was not ready. But are we now at the stage that a serious, concerted assault can be meaningfully mounted through say quantum chemistry calculations and experimental measurements (shock tube, flow reactor, RCM, laminar flame speeds and structure, etc.)? If this is the case then should the community get together and construct the roadmap to achieve closure of the reaction mechanisms of hydrocarbon fuels? The task may be horrendously large, but spread out over “reputable” groups internationally to avoid inferior work (which not only is a waste of resources but can also cause confusion, leading to further waste of efforts by others trying to duplicate and/or disprove.) and unnecessary duplication, and done in a sustained manner, perhaps we can close the problem (i.e. map the fuels genome) once and for all in, say, the next 10 to 20 years (assuming realistically that the world will still be burning hydrocarbons way beyond that time frame).

Dynamic Reduction of Reaction Mechanisms

Having mapped out the fuels genome is not of much help unless the reaction mechanisms developed can be used, especially in computational simulation. At present and in the foreseeable future, this is a daunting and almost impossible task for fuels of moderate size and for flows beyond the simplest. The approach at present is to develop reduced mechanisms of smaller sizes and reduced stiffness. In order to be comprehensive in their description in terms of the temperature, pressure and composition of a reacting mixture, there is a limit on the extent of reduction. However, since the local (space and time) reacting state depends only on the local thermodynamic state, much of the information contained in the reduced mechanism is not needed for a local evaluation and as such the corresponding evaluation is wasted. Thus the computational demand on the chemical description of reacting flows would cease to be an issue if an on-the-fly, dynamic reduction algorithm can be developed. In other words, the fidelity in the simulation of a reacting flow will now only be limited by the accuracy in simulating the flow aspects and the detailed reaction mechanism supplied. Consequently, developers of detailed mechanisms would not be too concerned about their size, while simulations can divert more computational resources to the description of the flow, which is still a huge challenge for turbulent flows.

Molecular Transport, Chemical Kinetics, and Turbulent Flame Modeling at High and Ultra-High Pressures

Motivation: Internal combustion engines operate at very high pressures; from over 50 atmospheres in diesel engines to several hundred atmospheres in rocket engines. Furthermore, the leading-order parameter governing their thermal efficiency is the compression ratio. Thus much improvement in the combustion efficiency can be achieved if new concepts in engine design and operation allowing

combustion at higher compression ratios can be identified. Fundamentally, very little has been done for various combustion-related processes at high and ultra-high pressures.

The Team: A CEFRC fellow, Peng Zhang, performs theoretical and computational studies under the supervision of CEFRC PIs: Klippenstein, Law, Pope and Wang; (b) a CEFRC post-doc, Swetaprovo Chaudhuri, performs experimentation on high-pressure turbulent flames under the supervision of Law

The Program

1. Turbulent flame modeling up to tens of atmospheres (Pope and Law): challenges are increased computational demand for high Reynolds numbers and reduced flame thickness and hence characteristic dimension; reduced flame thickness also triggers hydrodynamic cells which need to be considered.
2. Turbulent flame experiments (Law): study structure and propagation speed of outwardly propagating flames in a high-pressure (~30 - 60 atm.) environment with fan-generated turbulence.
3. Molecular transport at ultra high pressures (Law and Wang): implement dense gas effects on equation of state and the classical kinetic theory of gases.
4. Chemical kinetics at ultra high pressures (Klippenstein and Law): effects of bath molecules on unimolecular reaction rate theories and effects of high pressure on the Master Equation.

A. Starikovskiy, Princeton University

Thermally Non-equilibrium Chemistry

Motivation:

Modern gas turbines, RAMJets and SCRAMJets operate at ultra-lean conditions and high flow velocities. To stabilize the flame propagation under such conditions various gasdynamic methods are used. Unfortunately all these approaches lead to significant efficiency decrease. That is why alternative methods of ignition and flame stabilization were proposed. Among them there are plasma-assisted ignition, laser initiation, microwave radiation flame stabilization etc. All these methods are based on the non-equilibrium excitation of internal degrees of freedom of the gas followed by system relaxation and chemical reactions under non-Boltzmann conditions. It was shown that plasma-assisted ignition may be two-three orders of magnitude more efficient than thermal excitation. Unfortunately, kinetic models and quantitative experimental data for thermally non-equilibrium excitation and chemistry are available only for few simplest systems in very limited range of parameters.

The Program

1. Theory development of non-equilibrium excitation of chemically-active media. Further theory development of chemical reactions under nonequilibrium conditions and non-thermal gas excitation with dissociation, ionization and excitation of internal degrees of freedom.
2. Experimental investigations of ignition development under independent variation of translational-rotational temperature of the gas and internal degrees of freedom excitation. Data for ignition threshold shift vs initial gas temperature, mixture composition and non-equilibrium excitation.

D.G. Truhlar, University of Minnesota

Computation of accurate thermochemical and rate parameters for complex combustion reactions

- 1) To develop a version of VTST that is suitable for complex molecules with multiple conformations. VTST has been widely applied to barrier reactions in the gas phase, barrierless reactions in the gas phase, and reactions at gas-solid interfaces, in solid, in liquid solutions, and in enzymes, and the most appropriate formalism is different for each case. In the present project we recognize a distinction between two kinds of gas-phase barrier reactions, which are may loosely categorize as small molecules reactions and complex molecule reactions. In the former case the reactants and transition states have one conformation or more than one conformation, but we need to consider only one. An example with only one conformation for both reactant and transition state would be $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$. The previous formulation of VTST for gas-phase reactions with a barrier is applicable to this kind of case. An example of a complex reaction would be the isomerization of 1-pentyl radical to 2-pentyl radical. Here the reactant has 15 distinguishable conformations, and the transition state has 2. We label these conformations as “structures”. It is a grand challenge, that we propose to solve, to develop a multi-structural version of VTST theory including them. This will be called multistructural variational transition state theory (MS-VTST).
- 2) To calculate the reaction rates for hydroperoxyl radical from each of the sites of each of the butanols, taking full account of all the torsional conformations and torsional anharmonicity of all reactants and all transition states by using a high level of electronic structure theory combined with multistructural variational transition state theory (MS-VTST), either by using interpolated VTST by mapping or by using multiconfiguration Shepard interpolation., or both.
- 3) Same for abstraction by triplet oxygen atom, by hydroxyl radical, and by methyl radical.
- 4) To complete the development of the multistructural method for torsional anharmonicity and to incorporate it in a portable computer code that can be used by the entire combustion community. Many methods for correcting harmonic partition functions for the presence of torsional motions employ some form of one-dimensional torsional treatment to replace the harmonic contribution of a specific normal mode. However, torsions are often strongly coupled to other degrees of freedom, especially overall rotations, other torsions, and low-frequency bending motions, and this coupling can make assigning torsions to specific normal modes problematic. It is a grand challenge, that we propose to solve, to develop a new class of methods that circumvents the need for such assignments by instead adjusting the harmonic results by torsional correction factors that are determined using internal coordinates. It is even more challenging to incorporate these methods in a portable, well documented code for use by the entire combustion community, and we propose to do that as well.

H. Wang, University of Southern California

High-pressure reaction kinetics

High-pressure reaction kinetics coupled with molecular transport—the validity of the current mathematical formulations of laminar combustion processes are limited to conditions in which the reacting gas is in the free molecule regime and the probability of reaction upon molecular collision

is negligible. For the mean free path falling into the length scale typical of a covalent chemical bond or for highly reacting flows (e.g., plasma), both assumptions become invalid. At present, there is no chemical kinetic, gas-kinetic and transport theories that can adequately describe the outcome of collisional processes under this condition. New and more general mathematical formulations are needed to address this fundamental limitation.

Method of reaction mechanism development

The current method of reaction mechanism development is outdated. In general, we are still practicing a one-reaction-at-a-time approach. For predicting the global combustion properties of hydrocarbon or other fuels, this approach may be fine, but for other problems including soot formation, the reaction pathways can be exceedingly sensitive to fuel structure and local flame condition, to an extent that the number and the nature of reaction pathways cannot be predicted *a priori*. We are in need of a new theoretical approach to screen high-dimensional gibbs free energy surfaces and determine the relevant reaction pathways “on the fly.” This approach will hopefully yield a robust method to describe the reaction process as “molecular structural flows” on potential energy surfaces, rather than treating the reactions as from a set of local potential energy minima to others.

The mechanism of soot nucleation

The mechanism of soot nucleation and mass growth remains illusive. The principal difficulty of the current models of soot formation is that they are largely phenomenological and cannot account for many of the experimental observations on the basis of fundamental reaction kinetics and thermodynamics. The issues have been discussed in detail in a recent review paper, and a solution to the problem will have to come when there is a concerted experimental and theoretical effort directed at addressing the critical problems, including the nature of PAH binding in a high-temperature environment.