

Annual Progress Report

(Technical Accomplishments Excerpt)

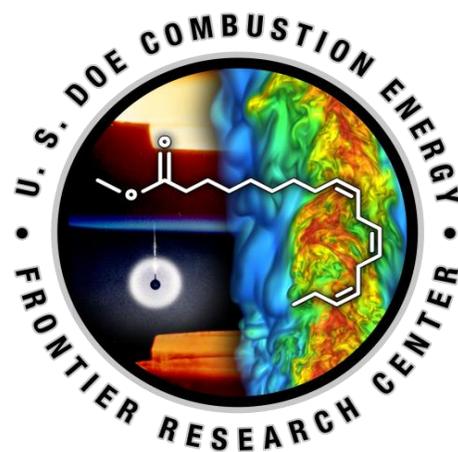
Combustion Energy Frontier Research Center

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1.0 Introduction and Highlights

Approaching the end of our first year in operation, the Combustion Energy Frontier Research Center (CEFRC) is simultaneously producing important results in research as well as settling into a consistent method of operations that allows us to coordinate and “glue” our research efforts leading to a unified outcome. We have spent time identifying and tackling the grand challenges in combustion research, and established the groundwork for maximizing the impact of our various outreach programs.

As a unified research effort, we have decided to initially use butanol as a target biofuel, based on which each PI would conduct his/her research. In particular, development of the reaction mechanism for butanol has already progressed to an advanced stage; it is anticipated that a comprehensive, predictive mechanism will be in place in the second year of operation. Furthermore, there have also been substantial activities on other fuels including biofuels that are of interest to transportation, accompanied by substantial progress on the fundamentals of combustion chemistry. The following are highlights of the research accomplishments.

- In quantum chemistry, a multi-reference single and double excitation configuration interaction method was developed to accurately treat molecules containing up to 50 non-hydrogen atoms.
- New methods for computing the thermochemistry of species with multiple hindered rotors were developed.
- Key elementary reaction rates of biofuel oxidation and pyrolysis were computed and measured, and kinetic mechanisms of butanol and isomers were created and cross-validated by using new experimental data on ignition, flame speed, and extinction.
- Kinetic and transport models of hydrogen and methyl butanoate were updated.
- A multi-timescale model reduction method was formulated to achieve efficient computation using detailed chemistry.
- Homogeneous charge compression ignition was modeled by using direct numerical simulation and several new flame regimes were identified.
- 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.

2.0 Technical Status

2.1 Technical Accomplishments

2.1.1. Quantum chemistry and thermochemistry: Development of high accuracy methods/models

Many promising alternative fuels are composed of fairly large molecules, making them computationally expensive to study using high-accuracy quantum chemical methods. We have developed a multi-reference single and double excitation configuration interaction (MRSDCI) method that can accurately treat molecules containing up to 50 non-hydrogen atoms. In addition, a comprehensive validation study of the linear scaling MRSDCI method is completed. These methods will be applied to biodiesel molecules.

The bond dissociation energies (BDEs) of biodiesel alkyl esters needed to determine which hydrocarbon radicals are most likely to form pyrolytically prior to oxidation were investigated. The thermochemistry of several intermediate species and radicals which are important in reactions of butoxyl and oxidation of butene were examined. Several new methods and approximations for computing the thermochemistry of species with multiple hindered rotors were developed. The new thermochemistry is particularly important for peroxy radicals relevant to the ignition chemistry of butanol, biodiesel, and Fischer-Tropsch diesel.

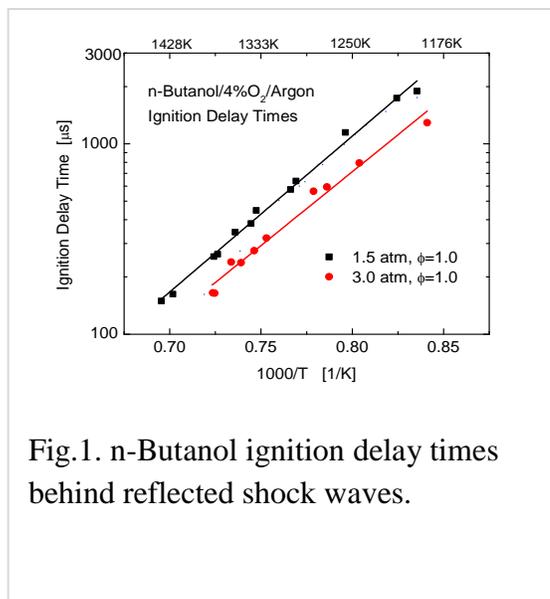


Fig. 1. n-Butanol ignition delay times behind reflected shock waves.

2.1.2. Determination of elementary reaction rates of butanol, methyl formate, iso-butene and iso-butane oxidation and pyrolysis

Reaction rates of butoxyl radicals and its isomers were computed. Reactions such as allyl + HO₂ and the subsequent isomerization/dissociation and decomposition of the allyloxyl (CH₂CHCH₂O) radical, H-abstraction from propanol by H, OH and HO₂, and the rate of HO₂ + methanol were obtained using high-accuracy methods. The results show that HO₂ + alcohol is a key reaction in ignition. Moreover, the pressure-dependent unimolecular dissociation of hydroxypropyl radicals is studied. A method for computing the energy-transfer parameters needed to determine the pressure dependence of rate coefficients was developed. Methods for scaling vibrational frequencies to calculate accurate zero point energies, enthalpies, and free energies for reactants and for transition states were updated.

Measurements of time-resolved species concentration and ignition delay times for the validation of elementary reaction rates and kinetic mechanism were conducted by using the shock tube, flow reactor, and rapid compression machine (RCM). The overall rate coefficients of a series of reactions of butanol isomers with OH over temperatures of 1100-1400 K and pressures of 1-2 atm were measured by using laser absorption at 306.7 nm. Preliminary OH concentration time-history measurements during the high-temperature pyrolysis of n-butanol decomposition were

conducted. These data will be used to validate n-butanol oxidation and pyrolysis reaction mechanisms developed by us.

The shock tube experiments also acquired n-butanol ignition delay times for fixed oxygen concentration (4%) covering the temperature range of 1197-1438 K at two equivalence ratios (0.5 and 1.0) and two pressures (1.5 and 3.0 atm). Representative ignition delay time data are shown in Arrhenius form (Fig.1). Ignition delay times for the equivalence ratio of 1.0 follow a simple linear Arrhenius form with activation energy of 36.6 kcal/mol and pressure dependence of $P^{-0.56}$. Ignition delay time measurements were conducted for n-butanol and methanol oxidation in RCM, covering a wide range of conditions of pressure (7-30 bar), temperature (700-1100 K), and equivalence ratio (0.25-2.0). Comparison between simulations and experiments showed that available mechanisms for butanol are unable to reproduce the experimental results. The results also show that methanol exhibits longer ignition delays than n-butanol.

Methyl formate oxidation and pyrolysis were studied in the variable pressure flow reactor. Major intermediate and product species as functions of residence time at 3 atm, 900 K and 0.5% fuel concentration for oxygen/fuel stoichiometries of 0.5, 1.0 and 1.5 were determined. By comparing these data with the results of ignition delay in shock tube and flame speed data, it was shown that methyl formate is consumed exclusively through molecular decomposition in shock tube environments, while at flow reactor and freely propagating premixed flame conditions, there is significant competition between hydrogen abstraction and concerted elimination channels.

The gas-phase reaction of benzene with O(3P) is of considerable interest for the modeling of aromatic oxidation, a problem of importance to fuel rich combustion including that of biofuels. The reaction proceeds mainly through 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 isomerization, leading to several possible reaction products. 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 were examined. The reactions were initiated by pulsed-laser photolysis of NO₂ in

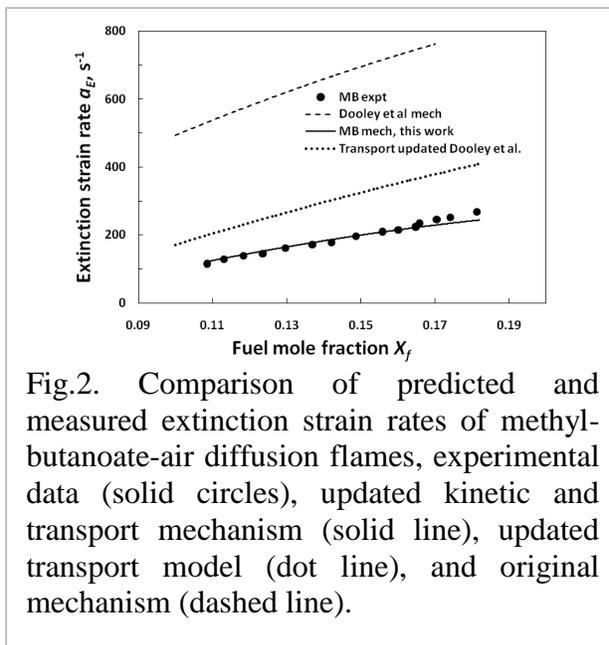


Fig.2. Comparison of predicted and measured extinction strain rates of methylbutanoate-air diffusion flames, experimental data (solid circles), updated kinetic and transport mechanism (solid line), updated transport model (dot line), and original mechanism (dashed line).

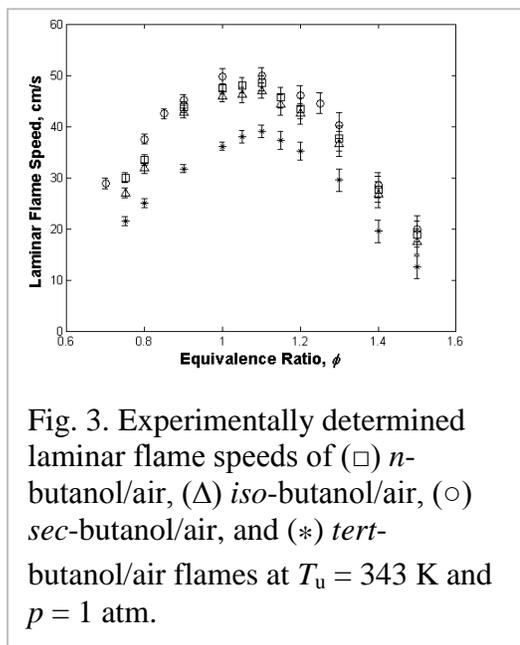


Fig. 3. Experimentally determined laminar flame speeds of (\square) n-butanol/air, (Δ) iso-butanol/air, (\circ) sec-butanol/air, and ($*$) tert-butanol/air flames at $T_u = 343$ K and $p = 1$ atm.

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. Phenol and phenoxy radical were detected and quantified, and 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.

2.1.3. Development of chemical kinetic and transport models: n-butanol/isomers, methylbutanoate, and H₂/O₂/Syngas

Kinetic models for the combustion chemistry of n-butanol, 2-butanol, and tert-butanol were constructed. Specifically, an updated methyl butanoate kinetic and transport model was developed. The resulting model is found to reproduce the measured extinction limits of butanoate/n-heptane mixtures with good accuracy (Fig.2). Analyses of the kinetic model simulation show that the inhibitive effect of methyl butanoate addition is due to the production of large amounts of formaldehyde and hydrogen peroxide from the oxidation of the methyl ester moiety. It is demonstrated that the uncertainty of transport properties of esters has a great effect on the over-prediction of extinction limits (Fig.2). Hydrogen-oxygen chemical kinetics, which are essential in modeling the oxidation chemistry of all hydrocarbons and hydrocarbon oxygenates, were investigated. Experimental measurements of burning rates, analysis of key reactions and kinetic pathways, and modeling studies were performed for H₂/CH₄/O₂/CO/CO₂ diluent flames spanning a wide range of fuel-lean conditions: equivalence ratios from 0.30 to 1.0, flame temperatures from 1400 to 1800K, pressures from 1 to 25 atm, CH₄ fuel fractions from 0 to 0.1. The experimental data show negative pressure dependence of burning rate at high pressure, low flame temperature conditions for all equivalence ratios. It is demonstrated that none of the existing kinetic mechanisms reproduce the measured pressure dependence for very lean mixtures. Elementary reaction rates and uncertainties of H+O₂(+M)=HO₂(+M) and HO₂ reactions with O, OH, H, and HO₂ were analyzed. Methane addition was shown to influence the pressure dependence mainly through reactions of CH₃ with H and HO₂. The effect of the presence of water vapor on the hydrogen/CO mechanism was studied by using the counterflow twin-flame configuration. It is found that the laminar flame speed varies non-monotonically with addition of water for carbon monoxide rich mixtures.

Progress in the hierarchical mechanism construction for transportation fuels was also made. The concept that the hydrocarbon oxidation model should be understood and developed in a hierarchical fashion has been a major driving force in kinetics research for decades. The

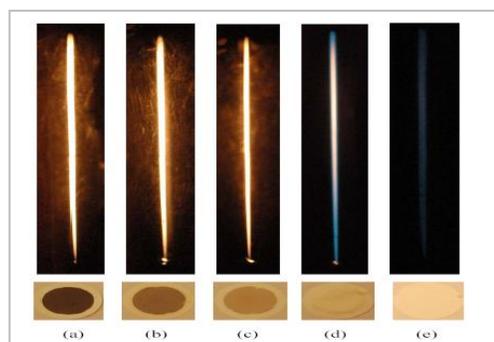


Fig.4. Upper panel: Time-exposed photographic images of the flame streaks of burning droplets of (a) diesel, (b) diesel/10% biodiesel, (c) diesel/20% biodiesel (d) biodiesel, and (e) hexadecane. Yellow flames indicate soot formation, while blue flames indicate its absence; Lower panel: Soot samples collected on filter papers from the burning droplets.

question how this hierarchical strategy works at a quantitative level, however, has never been addressed. In this work, we used ethylene and propane combustion as examples and explore the question of hierarchical model development quantitatively. The Method of Uncertainty Minimization (MUM-PCE) is utilized to explore the relationships among the combustion chemistry of hydrogen/carbon monoxide, ethylene and propane. We extended MUM-PCE to quantify the amount of information that a particular combustion experiment contributes to the model, and thereby the relative contribution of each data set. The method developed herein will be utilized to analyze the relationship between the predictive capabilities of reaction models developed for the butanol isomers to the fundamental kinetic knowledge needed for butanol reactions as well as the base H₂/CO/C₁-C₄ oxidation kinetics.

2.1.4. Measurements of combustion and emission properties and kinetic validations

Measurements were performed for the ignition, flames speeds, and extinction limits of all C₁-C₄ alcohols, 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 20 atm (Fig. 3) The research provides new experimental data for flame chemistry and transport of oxygenated biofuels and foundation fuels of small hydrocarbons. Comparisons between experimental data and kinetic prediction demonstrate that the oxygen containing molecular structure of biofuels has a distinctive impact on chemical kinetics, transport properties, ignition, flame speeds, and emissions. The results show that the current chemical kinetic models for biofuels fail to reproduce the global flame properties. In particular, it is also found that the hydrogen and C₁-4 kinetics play a dominant role in biofuel combustion and have a large uncertainty at low temperature and high pressure associated with the HO₂/H₂O₂ reaction pathways. A linear correlation parameter identified for hydrogen addition to all hydrocarbon fuels is identified. Furthermore, experimental studies of soot emission in burning biodiesel droplets demonstrate clearly that soot formation in biodiesel is substantially less than that of diesel (Fig.4).

2.1.5. Development of reduced kinetic mechanisms and model reduction methods

A new multi-timescale model to achieve about one-order reduction of the computation time for both detailed and reduced kinetic mechanisms is developed. The robustness and accuracy of the method are demonstrated for hydrogen, methane, butanoate, n-heptane and n-decane ignition and

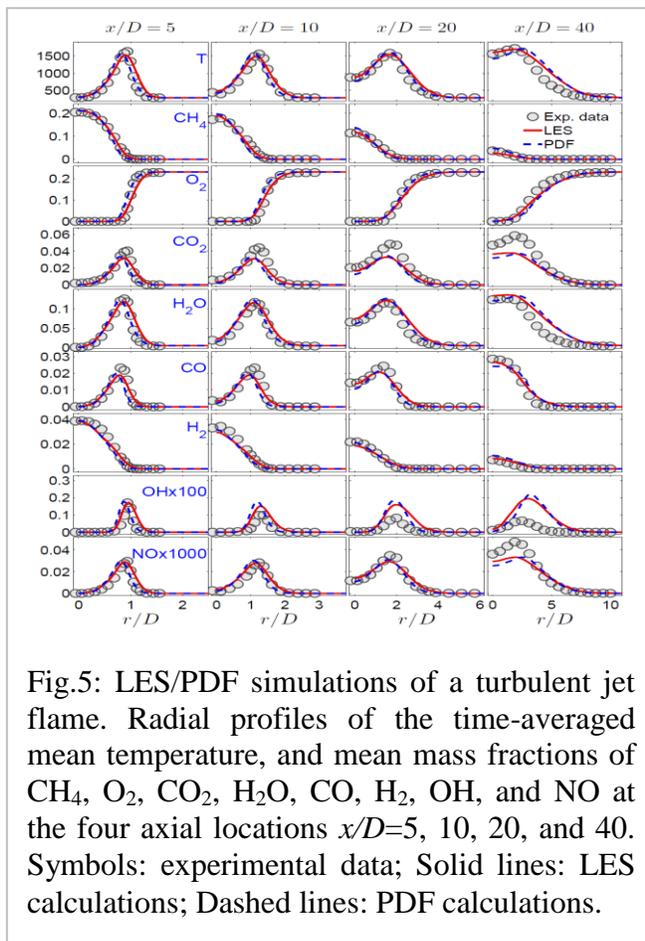


Fig.5: LES/PDF simulations of a turbulent jet flame. Radial profiles of the time-averaged mean temperature, and mean mass fractions of CH₄, O₂, CO₂, H₂O, CO, H₂, OH, and NO at the four axial locations $x/D=5, 10, 20,$ and 40 . Symbols: experimental data; Solid lines: LES calculations; Dashed lines: PDF calculations.

unsteady flame propagation. A multi-generation path flux analysis is also developed and integrated with the multi-timescale method to further increase the computation efficiency. A reduced mechanism of n-butanol is also obtained and compared with the detailed kinetic mechanism. The model reduction approach is used successfully in direct numerical simulations of HCCI combustion involving detailed and reduced chemistry.

2.1.6. Development of LES/PDF methodology and modeling of homogeneous charge compression ignition process

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 is demonstrated to be second-order accurate in space and time. Numerical consistency is demonstrated for mixture fraction between LES and PDF. Good agreement is observed between LES/PDF calculations and experimental data (Fig.5).

The multi-timescale model was employed to compute the flame regimes and ignition to detonation transition of n-heptane-air mixtures for spark assisted HCCI combustion. Six flame regimes involving negative temperature coefficient combustion were identified (Fig.6). The results showed that low temperature combustion has a significant impact on the flame regimes of HCCI combustion and the ignition to detonation transition. It was found that the dependence of the critical temperature gradient for ignition to detonation transition on temperature became singular in the negative temperature coefficient combustion region. The effect of thermal stratification on the ignition of a lean homogeneous n-heptane/air mixture at HCCI conditions was further investigated by direct numerical simulation (DNS) with a 58-species reduced kinetic mechanism. The influence of the mean and fluctuations in the initial temperature field and the ratio of turbulence to ignition delay time scales on multi-stage ignition of lean n-heptane/air mixture were studied. It was found that the mean heat release rate is more spread out with increasing thermal stratification regardless of the mean initial temperature. In addition, ignition delay is decreased with increasing thermal stratification for high mean initial temperature relative to the negative temperature coefficient (NTC) regime and is retarded with thermal fluctuation for relatively low mean initial temperature. The results suggest that control of initial mean temperature and the critical degree of thermal stratification are required for smooth operation of HCCI engines.

Direct numerical simulation of the near field of a three-dimensional spatially-developing turbulent ethylene jet flame in a highly-heated coflow was performed to understand the stabilization mechanism (Fig.7). The DNS was performed at a jet Reynolds number of 10,000 with over 1.29 billion grid points. Results show that auto-ignition in a fuel-lean mixture at the flame base is the main source of stabilization of the lifted jet flame. It was also observed that the present lifted flame base exhibits a cyclic 'saw-tooth' shaped

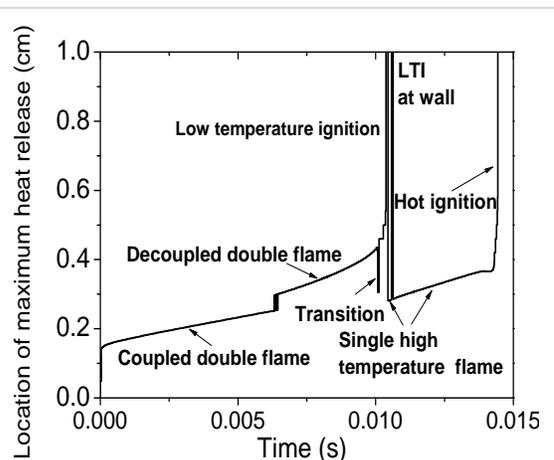


Fig. 6: Transient history of flame regimes of spark assisted HCCI combustion for lean ($\phi=0.4$) n-heptane-air mixtures at initial temperature of 700 K and pressure of 20 atm.

movement marked by rapid movement upstream and slower movement downstream. A DNS benchmark data set for lifted jet flame stabilization in an autoignitive coflow was established.

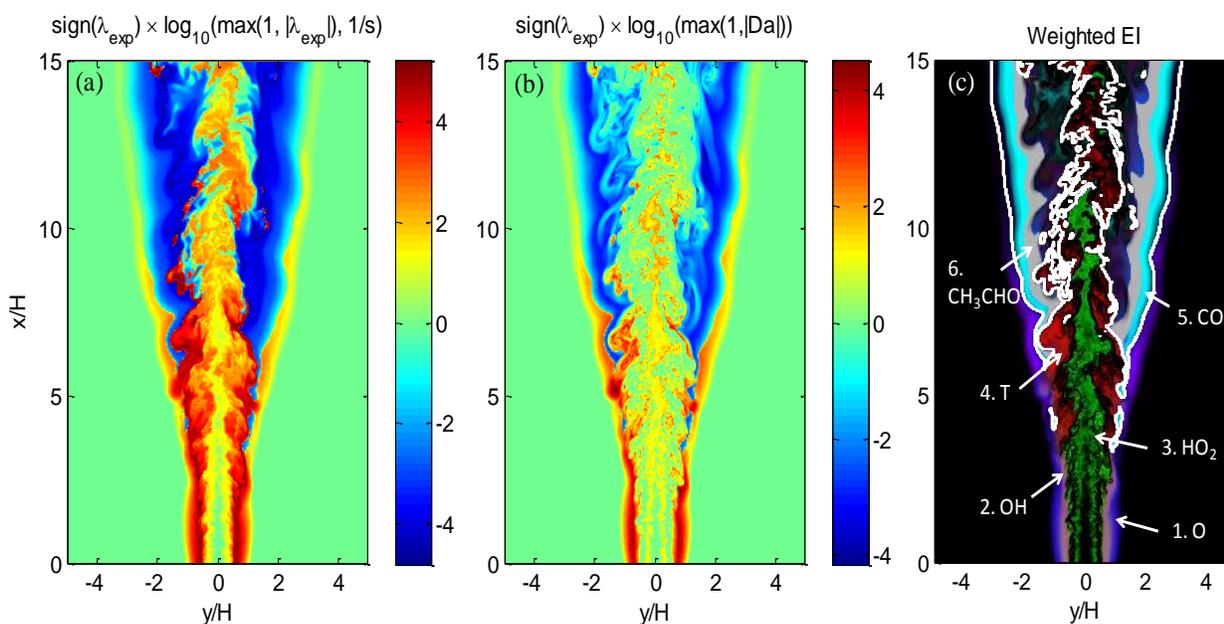


Fig.7. Structure of the lifted ethylene jet flame in a heated air coflow DNS, obtained by chemical explosive mode (CEM) analysis: (a) time scales of CEM or the decaying mode evolved from a CEM. Red hues indicate unburned mixture (eigenvalue of chemical explosive mode, $\lambda_{exp} > 0$) and blue indicates burned mixture ($\lambda_{exp} < 0$); (b) isocontour of Damköhler number, Da , with red indicating auto-igniting zones and blue indicating the diffusion flame zone; (c) controlling variables, temperature and species, identified by explosion index, weighted locally by normalized Da . The white isocontour shows the partially premixed flame fronts, where $\lambda_{exp} = 0$, identified in (a).