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14. ABSTRACT <p>Experimental, theoretical, and computational studies of various combustion phenomena were carried out for a wide range of conditions. Flames of hydrogen, carbon monoxide, as well as neat and mixtures of gaseous and liquid hydrocarbons were studied experimentally. The experimental data were used as the basis for developing and validating reaction and molecular transport models. The following tasks were completed:</p> <p>(1) Development of a non-linear extrapolation technique for the determination of laminar flame speeds; (2) transport and kinetics effects on flame propagation and extinction in liquid hydrocarbon flames; (3) quantification of the effect of fuel blending on the flame response; (4) derivation of an extensive experimental flame database for C5-C12 n-alkane, cyclohexane, and mono-alkylated cyclohexane flames; (5) fundamental kinetic studies of elementary reactions; (6) refinement of USC Mech II to predict H2/CO combustion at pressures up to 500 atm; (7) development of detailed and simplified models for the oxidation of C5-C12 n-alkanes; (8) development of the method of uncertainty minimization by polynomial chaos expansion; and (9) gas-kinetic theory analysis of scattering between gas and molecular clusters with application in transport properties.</p>					
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Final Technical Report

EXPERIMENTS AND REACTION MODELS OF FUNDAMENTAL COMBUSTION PROPERTIES

(AFOSR Grant FA9550-07-1-0168)

(Period: April 1, 2007 – February 28, 2010)

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Summary/Overview

Experimental, theoretical, and computational studies of various combustion phenomena were carried out for a wide range of conditions. The parameters that were considered include the fuel type, reactant composition, flame temperature, pressure, and combustion mode. Flames of hydrogen, carbon monoxide, as well as neat and mixtures of gaseous and liquid hydrocarbons were studied experimentally in the counterflow configuration. The experimental data were used as the basis for developing and validating reaction and molecular transport models.

During the reporting period, the following tasks were completed (numbers correspond to the archival publications that are shown in Section 7.0 of Technical Discussion):

1. Development of a new non-linear extrapolation technique for the determination of laminar flame speeds [1];
2. Molecular transport and kinetics effects on flame propagation and extinction in liquid hydrocarbon flames [2];
3. Quantification of the effect of fuel blending on the flame response [3,4];
4. Derivation of an extensive experimental flame database for C_5 - C_{12} *n*-alkane, cyclohexane, and mono-alkylated cyclohexane flames [1,5];
5. Fundamental kinetic studies of elementary reactions critical to a predictive combustion reaction model [6,7];

6. Refinement of USC Mech II to predict H_2/CO combustion at pressures up to 500 atm [8];
7. Development of detailed and simplified models for the oxidation of C_5-C_{12} *n*-alkanes [1,9,10];
8. Development of the method of uncertainty minimization by polynomial chaos expansion (MUM-PCE) [11];
9. Gas-kinetic theory analysis of scattering between gas and molecular clusters with application in the transport properties of high molecular weight hydrocarbons in dilute gases [12].

Technical Discussion

1.0 Background

The three-year research program that was completed, aimed to provide insight into the physicochemical processes that control the burning behavior of fuels that are of relevance to high-speed air-breathing propulsion. This was achieved through combined experimental, theoretical, and detailed numerical studies of a number of fundamental combustion properties. Experimentally, the phenomena of flame ignition, propagation, and extinction of systematically chosen fuel/oxidizer mixtures were investigated. The studies considered both gaseous and liquid hydrocarbons in view of their importance towards the accurate description of the combustion behavior of practical fuels. The experimental studies expanded notably the parameter space of existing archival fundamental combustion data. The detailed modeling of the experimental data and existing ones in the literature, was performed by using well-established numerical codes and reaction and transport models that have been developed based on a novel approach. More specifically, the derivation of the kinetics models was based on the following four specific objectives: (a) to develop and test a suitable array of mathematical and computational tools that can be used to quantify the joint rate-parameter uncertainty space and in doing so, to facilitate the rational design of reaction models suitable for any given target fuel or mixture of these fuels; (b) to examine the applicability of the $H_2/CO/C_{1-4}$ reaction model, developed under the current and prior AFOSR support, to predict the phenomena of flame ignition, propagation, and extinction along with flame structures, (c) to examine the effect of inelastic collision on binary diffusion coefficients, and (d) to test the hypothesis that there exists a critical reaction model that

can be used as the quantitative kinetic foundation for modeling the combustion of high molecular weight hydrocarbons. The approaches to meet the objectives included quantum chemistry calculations, reaction rate theory, kinetic modeling, and large-scale optimization using the response surface method. The research that was completed not only produced a comprehensive reaction model suitable for air-breathing propulsion simulations, but it also generated a set of new approaches and computational tools for rational reaction model development and optimization. It was shown systematically, that not only the chemistry of hydrocarbons even at the C_2 level is not well described but that there are also notable uncertainties associated with the H_2/O_2 chemistry especially when attempts are made to predict simultaneously low-temperature and high-temperature flame phenomena. The latter is a rather important issue, as the H_2/O_2 kinetics are in general considered to be rather well understood and are a very important subset of the kinetics of all practical hydrocarbon fuels. The uncertainties of the H_2/O_2 kinetics can have a profound effect on the simultaneous prediction of ignition and vigorous burning of H_2 and hydrocarbons.

2.0 Experimental Approach

The experiments were conducted in the counterflow configuration as shown in Figs. 1 and 2, which allows for the establishment of steady, laminar, planar premixed or non-premixed flames and the measurement of laminar flame speeds, as well as ignition and extinction limits. From a practical point of view, these properties are measures of the ability of flames to be established and sustained under the extreme conditions encountered in engines. From a fundamental point of view, such data, being sensitive to the fuel's oxidation chemistry, can be used to compile/validate/optimize kinetic models.

An array of counterflow rigs were used and each one comprises of:

- A flow system that is appropriate for the handling of gaseous fuels as well as liquid fuels in their vapor phase
- Several pairs of variable-diameter heated burners opposing each other
- Either a digital particle image velocimetry (DPIV) or a laser Doppler velocimetry (LDV) system appropriate for velocity measurements
- Several thermocouple system appropriate for temperature measurements.

One set of counterflow burners is housed into a stainless steel chamber, shown in Fig. 3, which can operate from pressures well below atmospheric up to 10 atm and is equipped with the state-of-the-art, remotely controlled functions.

The vaporization system consists of a high-precision syringe pump that injects the fuels into a heated chamber surrounded by a flow of heated air or N_2 . The flow rates of all gases are measured using calibrated sonic orifices. The vaporization system has undergone several iterations to achieve optimum performance and reliability for heavy liquid fuels. The vaporization chamber is made out of glass chamber to prevent fuel cracking. Additionally, a quartz nebulizer with a flush capillary lapped nozzle was integrated into the system in order to introduce the fuel into the chamber as a fine aerosol; the details are shown in Fig. 4. Thus, rapid vaporization is achieved at relatively low chamber temperatures, allowing steady-state vaporization and minimizing the chances of fuel cracking. To prevent fuel condensation, the fuel delivery line is wrapped with electrically heated tapes, and its temperature is monitored by properly positioned thermocouples. The burners are heated with ceramic heating jackets to maintain the unburned mixture temperature, T_u , as high as 500 K.

A thermocouple is used to monitor the temperature at the center of the burner exit. Before each experiment, the entire system is allowed to equilibrate and reach steady state, typically within two hours.

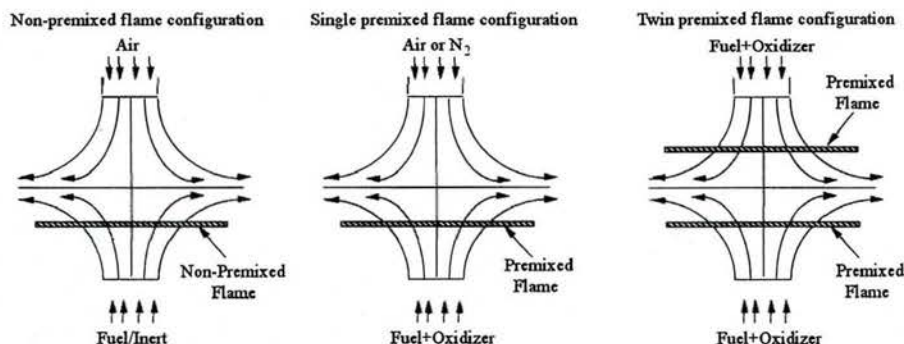


Figure 1. Flames that can be established in the opposed-jet configuration.

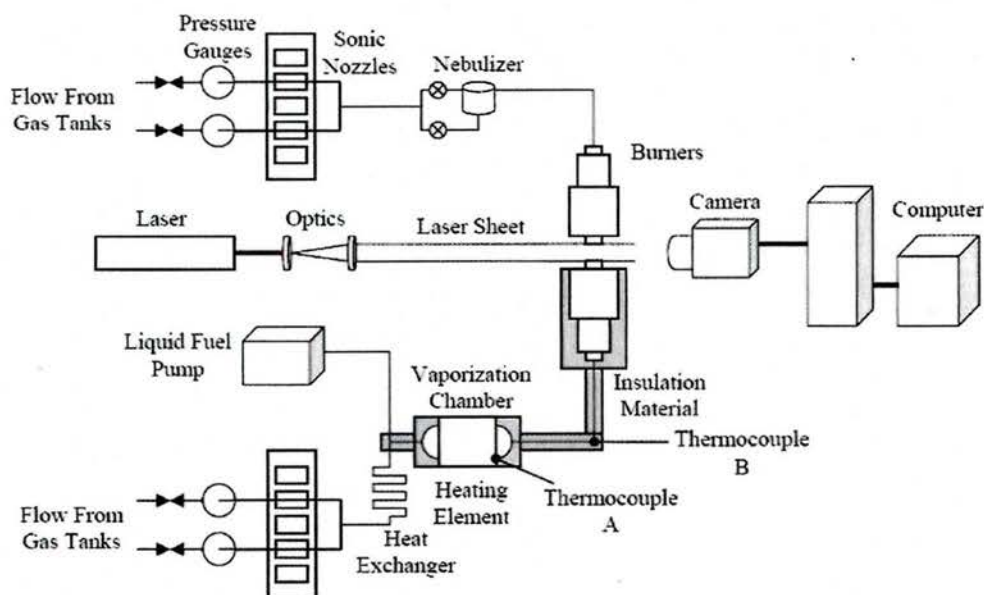


Figure 2. Schematic of a typical combustion rig.



Figure 3. High-pressure chamber equipped with counterflow burners and a state of the art DPIV system.

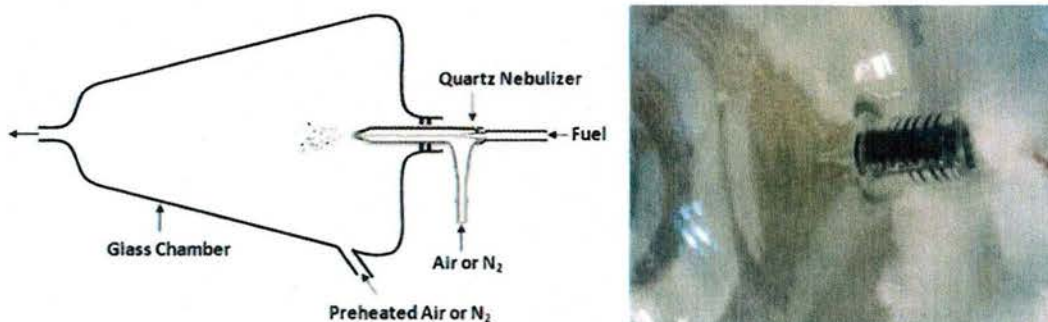


Figure 4. Schematic and picture of the updated liquid fuel vaporization system.

Flame ignition is achieved by heating air or N_2 in the upper burner at temperatures well exceeding 1000 K. To achieve this, the burner is replaced by a quartz tube equipped with independently controlled helicoidal internal (SiC) and external (Kanthal AI) electric heating elements that are capable of raising the temperature of air or N_2 up to 1600 K (Fotache et al. 1997). A temperature controller/power supply is used to operate the internal heater. Feedback to the temperature controller is provided by a B-type thermocouple (Pt-6% Rh/Pt-30% Rh) positioned in the heated air or N_2 stream within the quartz tube close to the surface of the inner heater. For a given reactant configuration and composition, the temperature at the quartz tube exit is increased and monitored via another B-type thermocouple, until flame ignition occurs, at

which point the tube exit temperature is defined as the ignition temperature, T_{ign} . Aspects of the ignition system are shown in Fig. 5.

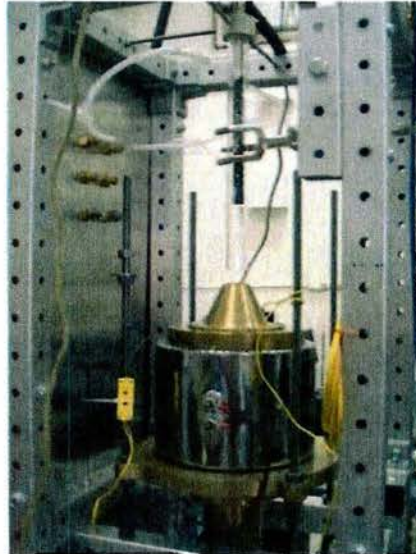


Figure 5. Ignition counterflow burner rig.

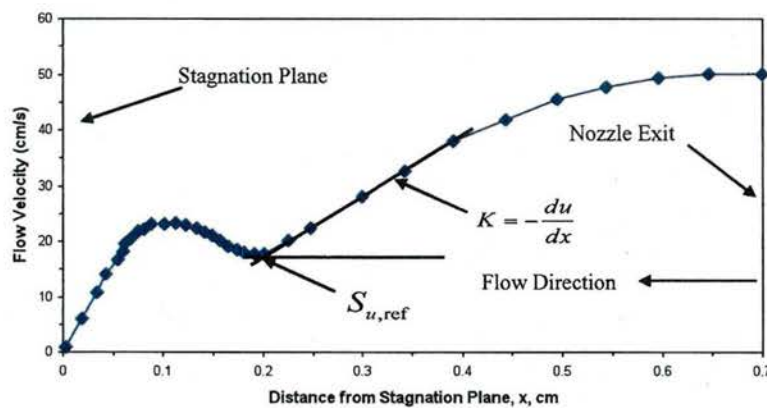


Figure 6. Axial velocity along the system centerline.

The measurements included axial flow velocities and temperature measurements. The axial flow velocities were measured along the stagnation streamline using either LDV or DPIV. The flow was seeded with 0.3- μm diameter, heated silicon oil droplets that were produced by a nebulizer. A typical axial velocity profile is shown in Fig. 6. The local strain rate, K , is defined as the maximum absolute value of the velocity gradient just upstream of the flame, as shown in

Fig. 6 (Law 1988). The minimum axial flow velocity just upstream of the flame is defined a reference flame speed, $S_{u,ref}$, as shown also in Fig. 6 (Law 1988).

3.0 Numerical Approach

The experiments were simulated directly by including detailed descriptions of chemical kinetics and molecular transport. Laminar flame speeds, S_u^o , extinction strain rates, K_{ext} , and T_{ign} were computed by utilizing CHEMKIN-based codes (Kee et al. 1985, 1986, 1988, 1989; Egolfopoulos & Campbell 1996). Those codes have been upgraded by the PIs to:

- Account for any type of combustion mode (Egolfopoulos 1994a; Egolfopoulos & Campbell 1996);
- Account for any type of boundary condition (Egolfopoulos 1994a; Egolfopoulos & Campbell 1996, Egolfopoulos et al. 1997);
- Account for thermal radiation (Egolfopoulos 1994b; Zhang & Egolfopoulos 2000);
- Solve around singular turning-points at the states of ignition and/or extinction (Egolfopoulos & Dimotakis 1998; Dong et al. 2005; Holley et al. 2006, 2009);
- Perform mathematically rigorous sensitivity analysis of all dependent parameters, including S_u^o , K_{ext} , and T_{ign} , on all rate constants and all binary diffusion coefficients (Dong et al. 2005; Holley et al. 2006, 2009).

Additionally, efficient post-processing codes have been developed to perform reaction path analysis, which, when combined with the sensitivity analyses, provide the required insight into the controlling kinetic pathways for each phenomenon that is investigated.

4.0 Results and Discussion

4.1 Development of a new non-linear extrapolation technique for the determination of laminar flame speeds

To determine S_u° , $S_{u,\text{ref}}$ and K need to be measured first, as shown in Fig. 6. Subsequently, plotting $S_{u,\text{ref}}$ against K , S_u° could be determined, in principle, by extrapolating linearly the $S_{u,\text{ref}}$ data to zero stretch, $K = 0$ (e.g., Law 1988). However, it has been shown (e.g., Tien and Matalon 1991) that as $K \rightarrow 0$ the variation of $S_{u,\text{ref}}$ may not be linear with respect to K because of the dilatation. Therefore, the linearly extrapolated values of S_u° have been shown to be higher than those obtained by using non-linear extrapolation (Davis & Law 1998) or by other more direct methods (Vagelopoulos & Egolfopoulos 1998).

A new non-linear extrapolation technique was introduced. Specifically, the variation of $S_{u,\text{ref}}$ with K is computed from first principles, i.e. using detailed description of chemical kinetics and molecular transport, over a range of K for which there is no heat loss to the burner boundary. In addition, the S_u° value, corresponding to $K = 0$, is computed in order to anchor the $S_{u,\text{ref}}$ -vs.- K correlation. The computed $S_{u,\text{ref}}$ and S_u° values are then fitted as a polynomial function of K . It was shown that small but finite uncertainties in rate constants and reactant transport coefficients have minimum effect on the shape of the $S_{u,\text{ref}}$ -vs.- K correlation. Thus, the polynomial function can be translated vertically to fit the experimental $S_{u,\text{ref}}$ best and determine S_u° . The sensitivity of the shape of the $S_{u,\text{ref}}$ -vs.- K correlation on kinetics was tested further by considering various kinetic models that predict reasonably well S_u° , and it was determined that the shape of the non-linear extrapolation curves were affected minimally by the choice of the model. This finding is physically reasonable. More specifically, the response of $S_{u,\text{ref}}$ to fluid dynamics is due to flame stretch and dilatation. In opposed-jet flames that are computed using similar transport parameters but two different kinetic models that predict similar S_u° values, the effects of stretch and dilatation is expected to be similar. Finally, a computed $S_{u,\text{ref}}$ -vs.- K correlation from first-principle, represents the experimental data better compared to asymptotic analysis in which one-reactant, one-step kinetics and over-simplified assumptions for the transport coefficients are used.

Similarly to previous studies invoking non-linear extrapolations (e.g., Davis & Law 1998; Yang et al. 2009), the present study confirmed that linear extrapolations result in higher S_u° values. Figure 7 depicts the percentage difference between linearly and non-linearly

extrapolated laminar flame speeds for atmospheric C_5 - C_{12} n -alkane flames. The results illustrate that the difference is about 5% for fuel-lean mixtures (equivalence ratio $\phi < 1.0$), but it rises to about 20% for fuel-rich mixtures ($\phi > 1.0$). Such differences are rather large if reaction kinetics are to be validated against S_u° data. The increasingly larger discrepancies towards fuel-rich mixtures relates to their sub-unity Lewis number for the fuels considered herein, given the large molecular weight discrepancy between the fuel and oxygen (e.g., Law 1988; Tien & Matalon 1991).

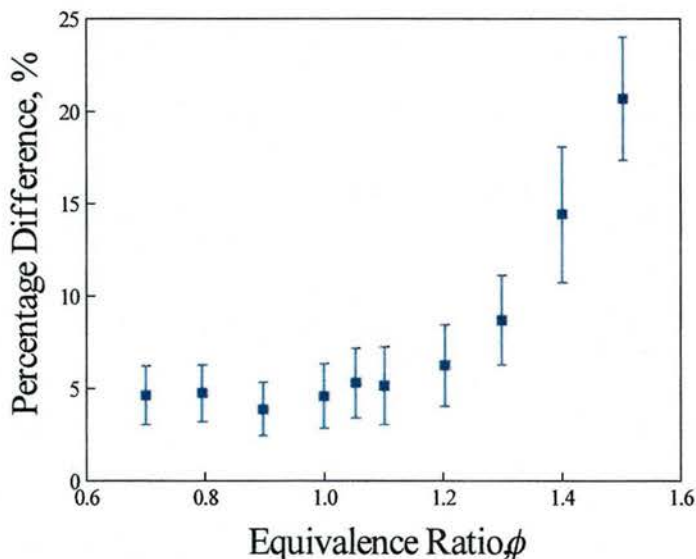


Figure 7. Average percentage difference between S_u° 's of atmospheric C_5 - C_{12} n -alkane/air mixtures as obtained by linear and non-linear extrapolations. Non-linear extrapolations result in lower S_u° values.

4.2 Molecular transport and kinetics effects on flame propagation and extinction in liquid hydrocarbon flames

Lennard-Jones 12-6 potential parameters were estimated for n -alkanes and 1-alkenes with carbon numbers ranging from 5 to 14. These parameters, while somewhat uncertain, form the basis for a comprehensive analysis of the responses of various n -dodecane flame phenomena to kinetic and transport parameters. The logarithmic sensitivity coefficients on both reaction rates and binary diffusion coefficients were calculated for laminar flame speeds as well as extinction strain rates for premixed and nonpremixed flames. Results revealed that the response of premixed flames is generally insensitive to the fuel diffusivity. Coupled with the lack of

sensitivity to the reaction kinetics specific to the fuel molecule, the computational results explain satisfactorily the low sensitivity of the phenomena of flame propagation and extinction to the variation of the size of n -alkane fuels. In contrast, the extinction strain rates of nonpremixed flames were found to be highly sensitive to the fuel diffusivity, in that larger fuel diffusivities render the flames more resistant to extinction. Hence, the variation of K_{ext} of nonpremixed flames with the n -alkane size, as observed Holley et al. (2007), is explained satisfactorily by the variation of the mass diffusivity of the fuel.

Figure 8 illustrates a summary of the logarithmic sensitivity coefficients of the model responses of n -dodecane flames to key reaction rate parameters and binary diffusion coefficients. Laminar flame speeds (S_u° - ϕ) and extinction strain rates for premixed flames (K_{ext}° - ϕ) at several representative ϕ 's, and extinction strain rates for nonpremixed flames [$K_{\text{ext}}^{\text{fuel+nitrogen}}$ vs. oxidizer] were considered for conditions that are specified in Table 1.

Several observations can be made from the computational results. The overall influences of reaction rates and diffusion fluxes are about the same for the premixed flame responses. The sensitivity to diffusion originates primarily from the O_2 - N_2 binary diffusivity. Kinetically, the propagation rates of the premixed flames are found to be insensitive to the chemistry specific to n -dodecane as shown here, since its decomposition in the preheat zone of the flame is too rapid to be rate-limiting (You et al. 2009). Rather, the sensitivity spectrum includes only the rate coefficients found typically in H_2/CO and small hydrocarbon combustion. As shown in Fig. 8, these are mainly $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$, $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$, and $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$. The fact that the computed responses of premixed flames are insensitive to kinetic or diffusion parameters specific to n -dodecane suggests that the measured S_u° and K_{ext}° of premixed flames should be independent of the nature and size of the alkane fuel molecule. Note that under similar conditions, the decomposition kinetics of higher n -alkanes is similar to those of n -dodecane. Additionally, for smaller n -alkanes the larger diffusivities would cause the flame propagation rate to depend even less on the fuel diffusion rate.

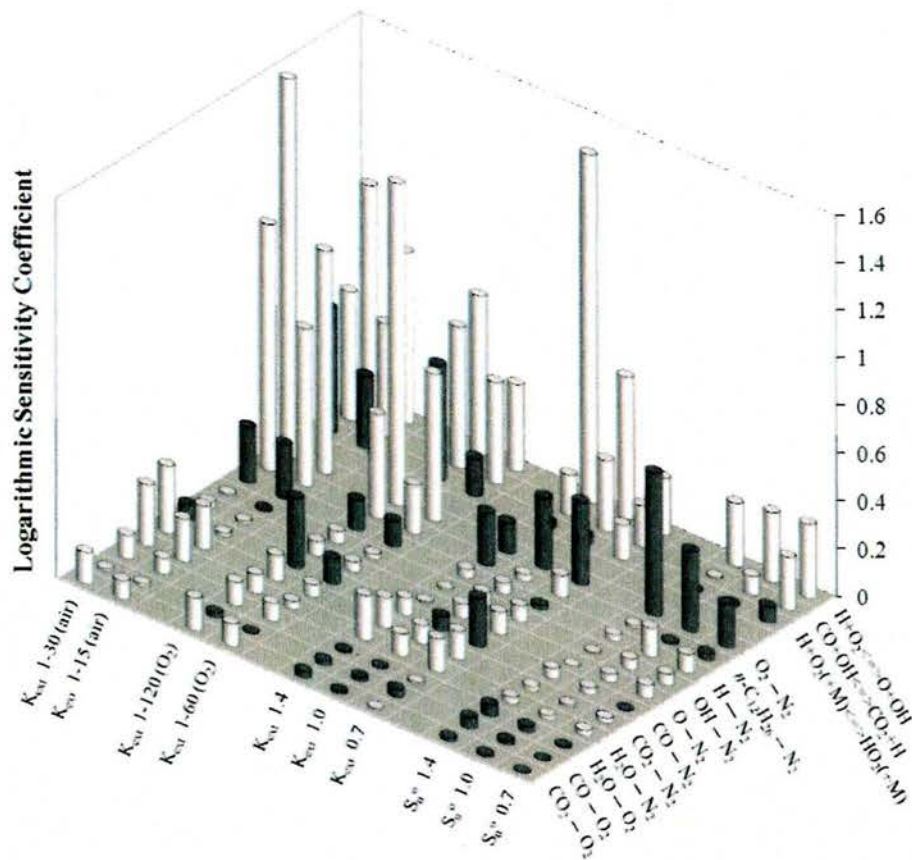


Figure 8. Logarithmic sensitivity coefficients on rate constants and binary diffusion coefficients. Light bars: positive values; dark bars: negative values.

Flame	Description
<u>Laminar Flame Speed ($T_u = 403$ K)</u>	
S_u° 1.4	$\phi=1.4$
S_u° 1.0	$\phi=1.0$
S_u° 0.7	$\phi=0.7$
<u>Extinction strain rate of premixed flame</u>	
K_{ext} 1.4	Fuel/air ($\phi=1.4$) vs. N_2
K_{ext} 1.0	Fuel/air ($\phi=1.0$) vs. N_2
K_{ext} 0.7	Fuel/air ($\phi=0.7$) vs. N_2
<u>Extinction strain rate of nonpremixed flame</u>	
K_{ext} 1-30 (air)	Fuel/ $N_2=1/30$ vs. air
K_{ext} 1-15 (air)	Fuel/ $N_2=1/15$ vs. air
K_{ext} 1-120 (O_2)	Fuel/ $N_2=1/120$ vs. O_2
K_{ext} 1-60 (O_2)	Fuel/ $N_2=1/60$ vs. O_2

Table 1. Conditions of computed results shown in Figure 8. For all cases, the fuel is *n*-dodecane, the pressure is atmospheric, and the temperature of the fuel-containing stream is 403 K. The oxidizer is air for premixed flames, and air or O_2 for nonpremixed flames. For nonpremixed flames the fuel stream consists of *n*-dodecane/nitrogen mixtures with varying molar ratios.

4.3 Quantification of the effect of fuel blending on the flame response

S_u^o 's, K_{ext} 's, and T_{ign} 's were computed Laminar flame speeds as well as ignition and extinction limits of mixtures of air with hydrogen, carbon monoxide, and C₁-C₄ saturated hydrocarbons were studied both experimentally and numerically. The fuel mixtures were chosen in order to gain insight into potential kinetic couplings during the oxidation of fuel mixtures. The experiments were modeled using the USC Mech II kinetic model (Wang et al. 2007). 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 $H + O_2 \rightarrow O + OH$ branching reaction. The kinetic model predicts closely the experimental data for flame propagation and extinction for various fuel mixtures and pressures. On the other hand, it underpredicts, in general, T_{ign} 's.

Additionally, S_u^o 's of mixtures of air with 80% *n*-dodecane + 20% methylcyclohexane and 80% *n*-dodecane + 20% toluene, on a per volume basis, were determined over a wide range of ϕ 's, at atmospheric pressure, and $T_u = 403$ K. The choice of the fuel blends was dictated by their anticipated compositions in surrogates of jet fuels. Phenomenological analysis revealed that S_u^o 's of binary fuels mixtures can be estimated using S_u^o 's and adiabatic flame temperatures of flames of the neat components. The propagation rates of flames of the various binary fuels blends were computed using detailed descriptions of chemical kinetics and molecular transport and were found to be in good agreement with the estimations. Although the initial fuel initial consumption pathways and the resulting intermediates and radicals may be different for each neat component, the propagation of flames of binary fuels was found to be mostly sensitive to the flame temperature through its influence on the main branching reaction $H + O_2 \rightarrow OH + O$. Thus, kinetic couplings resulting from the presence of two different fuels appear to have minor effect on flame propagation.

4.4 Derivation of an extensive experimental flame database for C_5 - C_{12} *n*-alkane, cyclohexane, and mono-alkylated cyclohexane flames

S_u° 's and K_{ext} of premixed C_5 - C_{12} *n*-alkane flames were determined over a wide range of ϕ 's, at atmospheric pressure, and elevated T_u 's. S_u° 's were obtained using the aforementioned in Section 4.1 non-linear extrapolation technique. Compared to linearly extrapolated values, the laminar flame speeds obtained using non-linear extrapolations were found to be 1 to 4 cm/s lower depending on ϕ . It was determined that S_u° 's of all *n*-alkane/air mixtures considered in this investigation are similar to each other and sensitive largely to the H_2/CO and C_1 - C_4 hydrocarbon kinetics. Additionally, the resistance to extinction decreases as the fuel molecular weight increases. Simulations of the experiments were performed using the recently developed JetSurF 0.2 reaction model (Sirjean et al. 2008) consisting of 194 species and 1459 reactions. The experimental S_u° 's were predicted with good accuracy for all the *n*-alkanes. The experimental K_{ext} 's were predicted closely by the model for fuel-lean mixtures. For stoichiometric and fuel-rich mixtures, the computed K_{ext} 's were approximately 10% lower than the experimental values. Insights into the physical and chemical processes that control the response of *n*-alkane flames were provided through detailed sensitivity analyses on both reaction rates and binary diffusion coefficients. Figures 9 and 10 depict the experimental and computed S_u° 's.

S_u° 's were measured in the counterflow configuration for cyclohexane/air, methylcyclohexane/air, ethylcyclohexane/air, *n*-propylcyclohexane/air, and *n*-butylcyclohexane/air mixtures, at atmospheric pressure, $T_u = 353$ K, and for a wide range of ϕ 's. It was determined that cyclohexane/air flames propagate somewhat faster than mono-alkylated cyclohexane/air flames. Flames of mono-alkylated cyclohexane compounds, i.e. methyl-, ethyl-, *n*-propyl-, and *n*-butyl-cyclohexane, were found to have similar S_u° 's, suggesting that the different alkyl groups have a secondary effect on flame propagation. The experimental data were modeled using JetSurF 1.1 (Sirjean et al. 2009), a detailed reaction model for the combustion of cyclohexane and its derivatives, and satisfactory agreements were found. Based on the analysis of the modeling results, the somewhat lower rates of mono-alkylated cyclohexane flame propagation were attributed to the greater production of propene and allyl and the increased H-atom scavenging by these C_3 intermediates. Though these fuel-specific reaction kinetic features do not limit the overall oxidation rates, the distribution of the cracked products

exert influences on flame propagation, leading to the subtle differences in S_u^o 's that were observed experimentally. Figure 11 depicts the experimental and computed S_u^o 's.

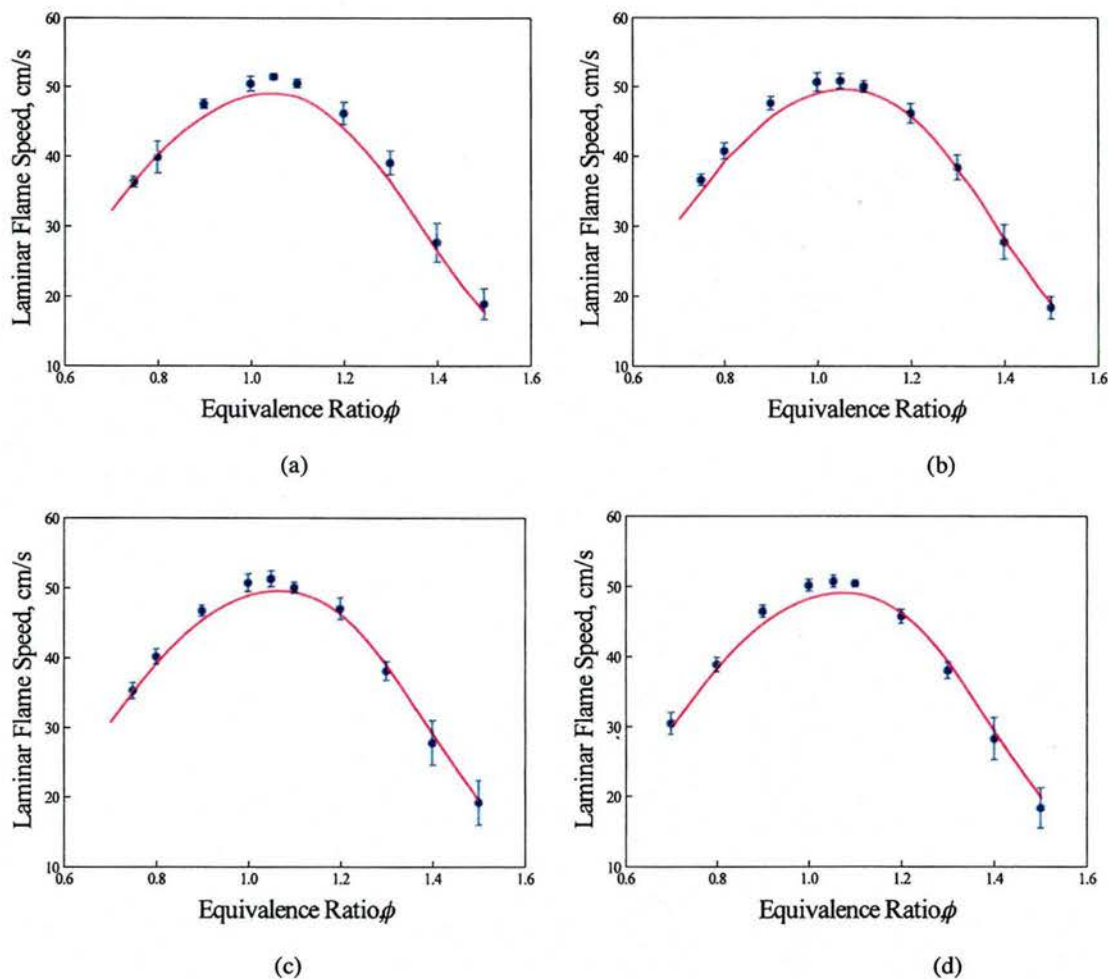


Figure 9. Experimentally and computed S_u^o 's at $T_u = 353$ K. (a) $n\text{-C}_5\text{H}_{12}$, (b) $n\text{-C}_6\text{H}_{14}$, (c) $n\text{-C}_7\text{H}_{16}$, and (d) $n\text{-C}_8\text{H}_{18}$ /air mixtures. Symbols: present experimental data obtained with non-linear extrapolation; Lines: simulation results using the JetSurF 0.2 kinetic model.

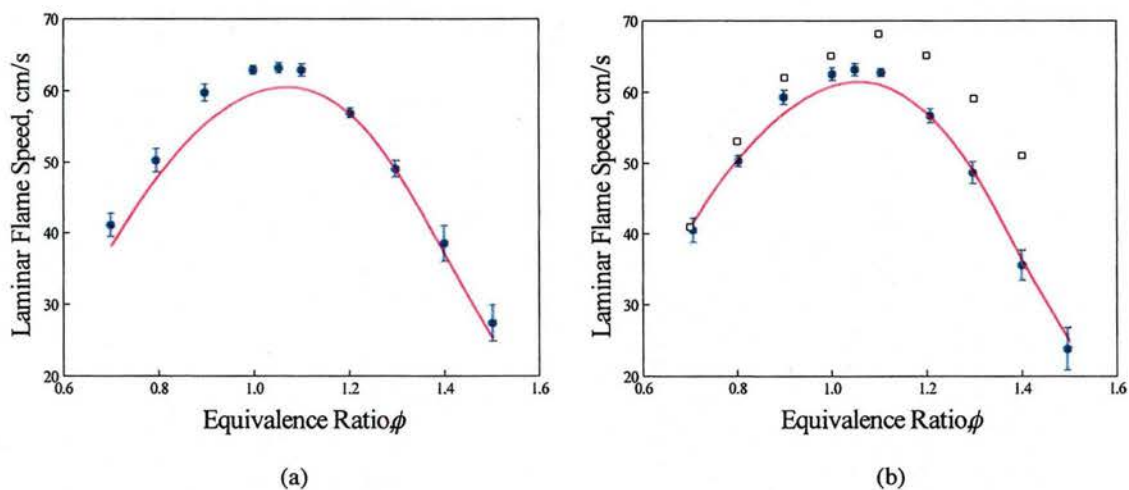


Figure 10. Experimentally and computed S_u° 's at $T_u = 403$ K. (a) n -C₉H₂₀/air mixture, (●) Present experimental data obtained with non-linear extrapolation; (b) n -C₁₀H₂₂/air mixture, (●) Present experimental data obtained with non-linear extrapolation; (□) Experimental data of Kumar & Sung (2007); Lines: simulation results using the JetSurF 0.2 kinetic model. The error bars indicate 2- σ standard deviations.

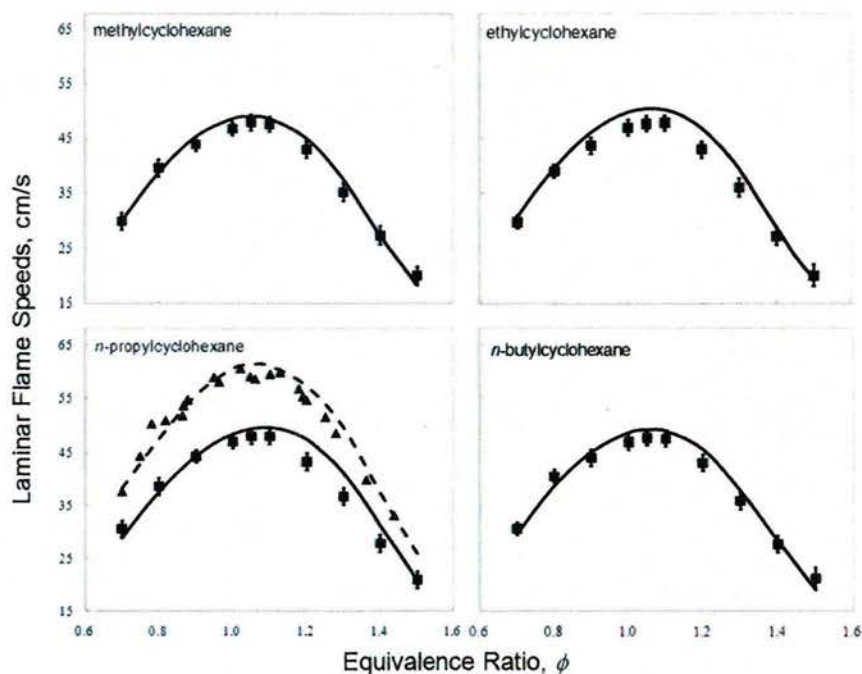


Figure 11. Experimental and computed S_u° 's of methyl-, ethyl, n -propyl, and n -butyl-cyclohexane/air flames at $p = 1$ atm. Symbols: (■) present experimental data at $T_u = 353$ K, (▲) DuBois et al. (2009). Lines: (—) simulation using Model I (JetSurF 1.1) at $T_u = 353$ K, (---) simulation using Model I (JetSurF 1.1) at $T_u = 403$ K. The error bars indicate 2- σ standard deviations.

4.5 Fundamental kinetic studies of elementary reactions critical to a predictive combustion reaction model

The kinetics of the reaction



was studied using a combination of *ab initio* electronic structure theory, transition state theory, and master equation modelling. The potential energy surface was examined with the coupled cluster CCSD(T) method and complete active space CASPT2 methods. The classical energy barriers were computed, as shown in Fig. 12. The energy barriers were found to be 18 and 19 kcal/mol for CO + HO₂• addition following the *trans* and *cis* paths, respectively.

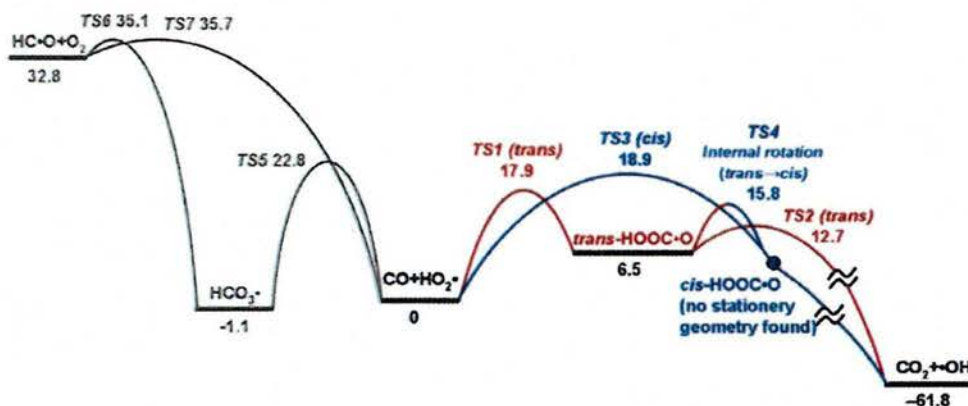


Figure 12. Potential energy diagram for CO + HO₂• → products. For CO + HO₂• → CO₂ + •OH, the energy values were determined using the CCSD(T)/CBS method, and included zero-point energy corrections. For CO + HO₂• → HC•O + O₂, the energy values were taken from Martínez-Ávila et al (2003).

For the *cis* path, rate constant calculations were carried out with canonical transition state theory. For the *trans* path, master equation modelling was also employed to examine the pressure dependence. Special attention was paid to the hindered internal rotations of the HOOC•O adduct and transition states. The theoretical analysis showed that the overall rate coefficient is independent of pressure up to 500 atm. The computed rate coefficient was found to be substantially smaller than some of the rate recommendations in the literature, as shown in Fig. 13. Based on the current theoretical calculations, the following rate expression was recommended for reaction R1

$$k_1(\text{cm}^3/\text{mol} - \text{s}) = 1.57 \times 10^5 T^{2.18} e^{-9030/T}$$

for $300 \leq T \leq 2500$ K with the uncertainty factor equal to 8, 2 and 1.7 at temperatures of 300, 1000, and 2000 K, respectively.

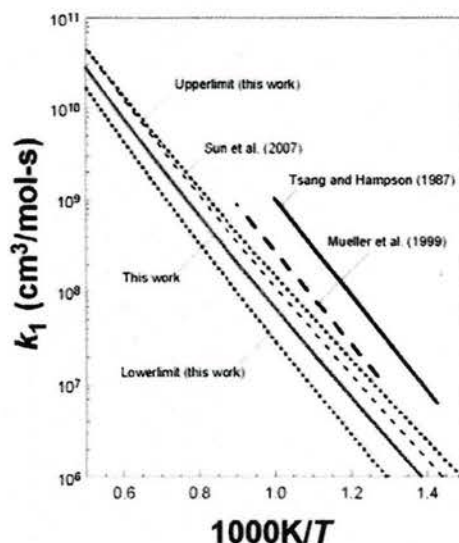


Figure 13. Rate coefficient of reaction R1.

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, still there are 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, the product branching ratios of the reaction was studied 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 NO_2 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. Phenol and phenoxy radical were detected and quantified. Cyclopentadiene and cyclopentadienyl radical were identified directly 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, and

cyclopentadiene + CO, as shown in Fig. 14. These computed rate coefficients were used to update the USC_Mech II reaction model (Wang et al., 2007) so that predictions of aromatics combustion are improved.

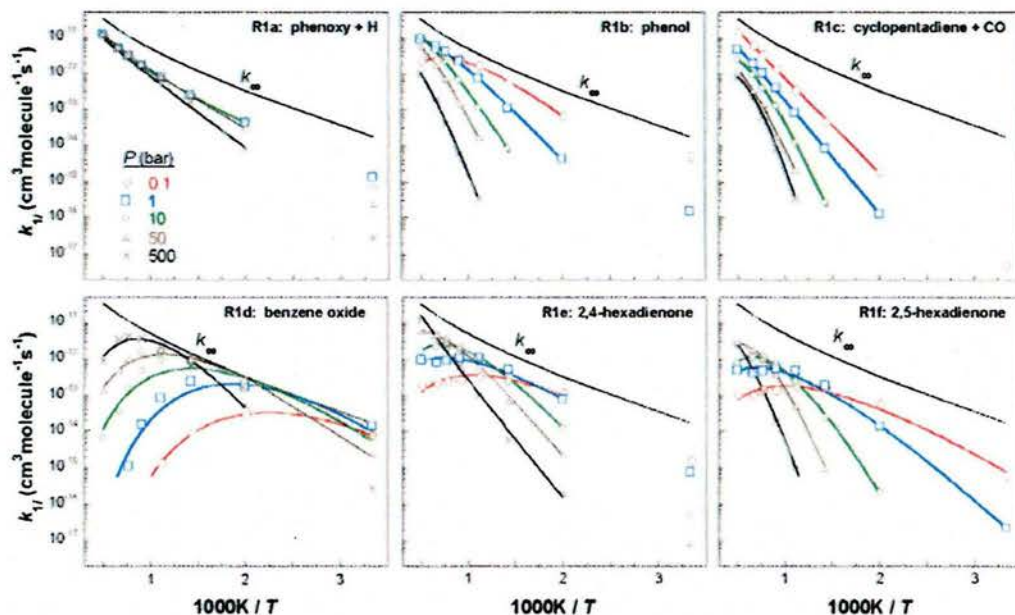


Figure 14. Arrhenius plots for the reaction channels leading to (a) phenol, (b) phenoxy + H, (c) cyclopentadiene + CO, (d) benzene oxide, (e) 2,4-cyclohexadienone, and (f) 2,5-cyclohexadienone. Symbols are rates computed with Monte Carlo RRKM/master equation modeling and lines represent fitted Arrhenius expressions.

4.6 Refinement of USC Mech II to predict H_2/CO combustion at pressures up to 500 atm

The high-pressure oxidation of inert-diluted CO/O_2 mixtures doped with 150-200 ppm of H_2 was studied behind reflected shock waves in the University of Illinois at Chicago high-pressure single pulse shock tube. The experiments were performed for stoichiometric ($\phi = 1$) and fuel lean ($\phi = 0.5$), over the temperature and pressure ranges of 1000-1500 K and 21-500 bar respectively. Stable species sampled from the shock tube were analyzed by gas chromatographic (GC) and GC/mass spectrometric techniques. The experimental data were simulated using the USC Mech II kinetic model (Wang et al. 2007). These simulations showed that within the experimental uncertainty, USC Mech II was able to capture the experimental trends for the lower pressure data sets (average nominal pressures of 24 and 43 bars). However the model underpredicted the CO and O_2 decay and subsequent CO_2 formation for the higher-pressure data sets (average nominal pressures of 256 and 450 bars). The elevated pressure data sets span a previously unmapped regime and have served to probe HO_2 radical reactions, which appear to be among the most critical reactions under the experimental conditions that were considered. With updated rate parameters for a key HO_2 radical reaction, USC Mech II was shown to reconcile the elevated pressure data sets thereby extending the model predictability to an extreme range of conditions.

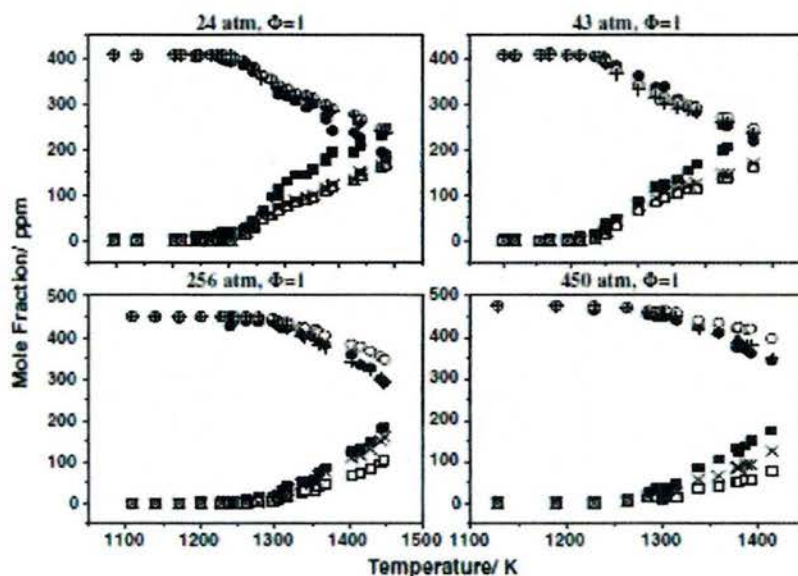


Figure 15. Experimental data for CO (\bullet) and CO_2 (\blacksquare) measured by shock heating of a mixture containing 500 ppm CO , 200 ppm H_2 , O_2 and argon with the equivalence ratio equal to 1.0. The computational results are \square : base USC Mech II, \times : updated USC Mech II.

4.7 Development of detailed and simplified models for the oxidation of C_5 - C_{12} n -alkanes

A detailed kinetic model was proposed for the combustion of n -alkanes up to n -dodecane and for temperatures above 850 K. The model was validated against experimental data, including fuel pyrolysis in plug flow and jet-stirred reactors, laminar flame speeds, and ignition delay times behind reflected shock waves, with n -dodecane being the emphasis. Selected model validation results are shown in Figs. 16 and 17. The model was used as the basis for JetSurF 0.1 and 1.0 with a wider range of validation tests reported on the JetSurF web site (Sirjean et al. 2008; 2009) and in Figs. 9 and 10.

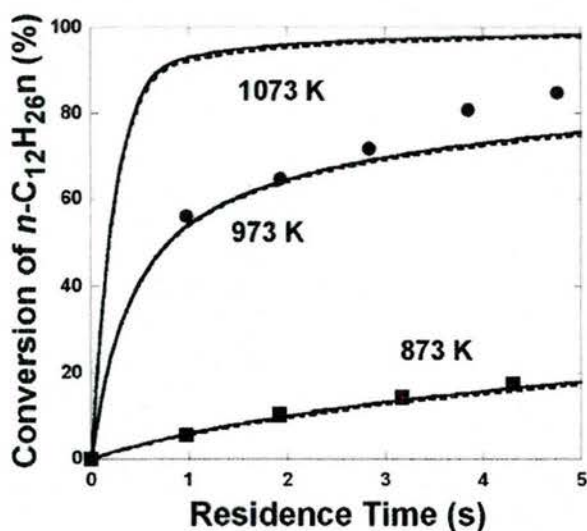


Figure 16. Experimental (symbols: Herbinet et al. 2007) and computed (solid line: detailed model; dashed line: simplified model) conversions of n -C₁₂H₂₆ as a function of the residence time for the pyrolysis of 2% n -C₁₂H₂₆ in He in a jet-stirred reactor ($p = 1$ atm).

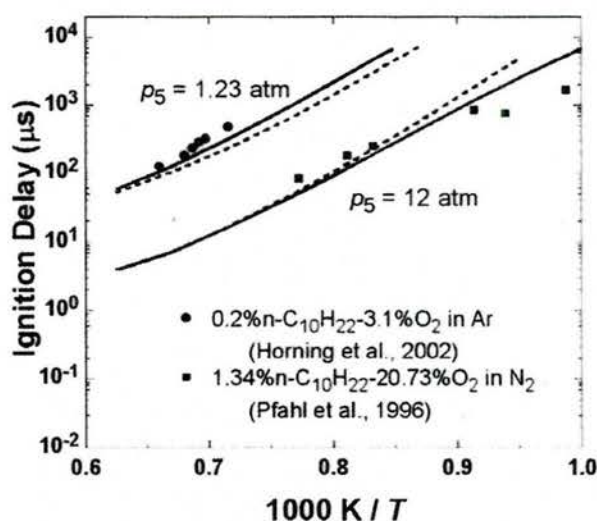


Figure 17. Experimental (symbols) and computed (solid line: detailed model; dashed line: simplified model not shown here) ignition delay times for n -C₁₀H₂₂ oxidation behind reflected shock waves.

Analysis of the computational results revealed that for a wide range of combustion conditions, the kinetics of fuel cracking to form smaller molecular fragments is fast and may be decoupled from the oxidation kinetics of the fragments. Subsequently, a simplified model containing a minimal set of 4 species and 20 reaction steps was developed to predict the fuel pyrolysis rate and product distribution. Combined with the base C₁-C₄ model, the simplified model predicts fuel pyrolysis rate and product distribution, laminar flame speeds, and ignition delays as close as the detailed reaction model.

4.8 Development of the method of uncertainty minimization by polynomial chaos expansion

The ability of a reaction model to predict the combustion behavior of a fuel relies on the rigorous quantification of the kinetic rate parameter uncertainty. Although the accuracy of a detailed kinetic model may be ensured, in principle, by a multi-parameter optimization, the inherent uncertainties in the fundamental combustion targets used for optimization cause the derived optimized model to be characterized by a finite kinetic parameter space. In this work, spectral expansion techniques were developed and employed to quantify these uncertainties. The resulting method, called the Method of Uncertainty Minimization by Polynomial Chaos Expansion (MUM-PCE) was used to analyze a detailed, $H_2/CO/C_1-C_4$ kinetic model for ethylene combustion. Uncertainty was quantified for both the as-compiled model and the optimized model, and was propagated subsequently into a wide variety of combustion experimental conditions. Examples for laminar flame speeds and shock tube ignition delays are shown in Figs. 18 and 19.

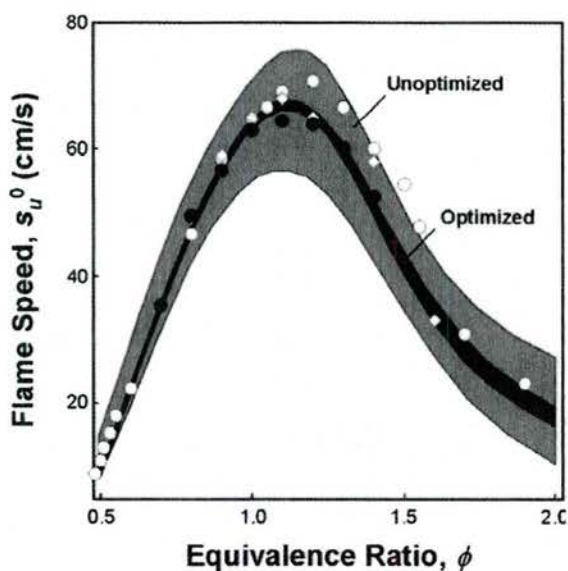


Figure 18. Experimental data (\circ : Egolfopoulos et al. (1990), \bullet : Jomaas et al. (2005), \diamond : Hassan et al. (1998)) and 2σ uncertainty bands computed for the laminar flame speed of ethylene-air mixtures at $p = 1$ atm.

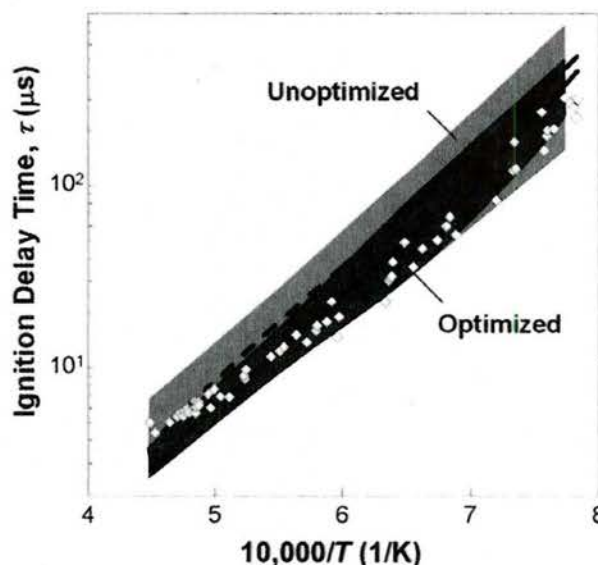


Figure 19. Experimental data (symbols, Brown and Thomas, 1999) and computed (dashed line: as-compiled, unoptimized model; solid line: optimized model, bands: 2σ model uncertainties) ignition delay time of 1% C_2H_4 -3% O_2 -Ar mixtures behind reflected shock waves.

4.9 Gas-kinetic theory analysis of scattering between gas and small particles with application in the transport properties of high molecular weight hydrocarbons in dilute gases

A theoretical study was conducted to examine the uncertainties in the transport theory of molecular clusters and small particles in laminar flow regime (Li and Wang 2003a, 2003b, 2005). The theory features a rigorous gas-kinetic theory analysis, considers the effect of non-rigid body collision, and has been shown to reproduce the Chapman-Enskog theory of molecular transport in the small particle size limit, Epstein's model of particle drag in the rigid-body limit, and the Stokes-Cunningham equation for the drag of micrometer size particles. A key uncertainty in the application of the generalized theory lies in the uncertainty of momentum accommodation of molecules or particles in the size range of a few nanometers. The cause for this uncertainty was attributed to a transition in the dominant mode of gas-particle interactions from specular-like scattering to diffuse scattering. As an example, Fig. 20 depicts this transition by comparing the theoretical reduced collision integrals for polyethylene glycol (PEG)-air molecule interactions and the experimental ones derived by Fernández de la Mora and coworkers (Nasibulin et al., 2002; Ude and Fernández de la Mora, 2003). It was concluded that in order to apply accurately a generalized transport theory for large molecules, a substantially larger set of experimental mobility and diffusivity has to be available.

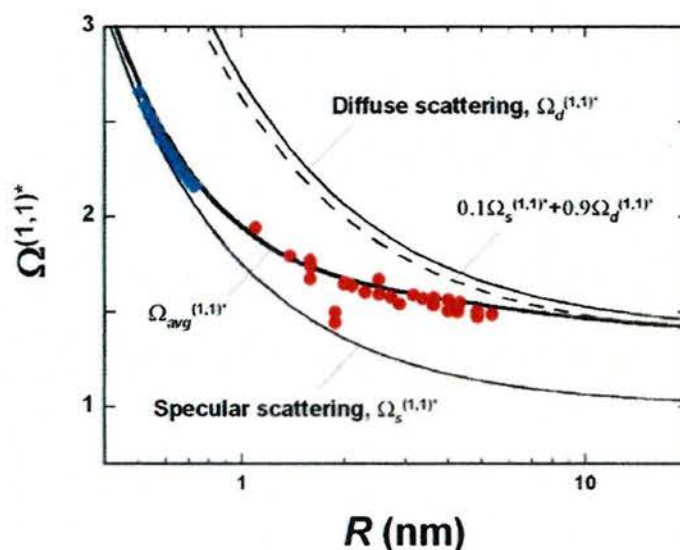


Figure 20. Variations of the reduced collision integrals as a function of the radius of PEG nanoparticles. Symbols are experimental data observed in air at room temperature (diamonds: Nasibulin et al., 2002; circles: Ude and Fernández de la Mora, 2003).

5.0 References

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6.0 Personnel

This research was performed by the PIs, one Research Associate (Baptiste Sirjean), and six graduate students (Adam Holley, Chunsheng Ji, Ning Liu, Xiaoqing You, Enoch Dames, David Sheen).

7.0 Archival Publications

1. Ji, C., Dames, E., Wang, Y.L., Wang, H., Egolfopoulos, F.N., "Propagation and Extinction of Premixed C₅-C₁₂ *n*-Alkane Flames," *Combustion and Flame* **157**, pp. 277-287 (2010).
2. Holley, A.T., You, X.Q., Dames, E., Wang, H., Egolfopoulos, F.N., "Sensitivity of Propagation and Extinction of Large Hydrocarbon Flames to Fuel Diffusion," *Proceedings of the Combustion Institute* **32**, pp. 1157-1163 (2009).
3. Park, O., Veloo, P.S., Liu, N., Egolfopoulos, F.N. "Combustion Characteristics of Alternative Gaseous Fuels," to appear in the *Proceedings of the Combustion Institute* **33**, (2010).
4. Ji, C., Egolfopoulos, F.N. "Flame Propagation of Mixtures of Air with Binary Liquid Fuel Mixtures," to appear in the *Proceedings of the Combustion Institute* **33**, (2010).
5. Ji, C., Dames, E., Sirjean, B., Wang, H., Egolfopoulos, F.N. "An Experimental and Modeling Study of the Propagation of Cyclohexane and Mono-Alkylated Cyclohexane Flames," to appear in the *Proceedings of the Combustion Institute* **33**, (2010).
6. You, X., Wang, H., Goos, E., Sung, C. J., Klippenstein, S. J. "Reaction Kinetics of CO + HO₂ → products: ab initio Transition State Theory Study with Master equation Modeling," *Journal of Physical Chemistry A*, **111**, pp. 4031-4042 (2007).
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9. You, X.Q., Egolfopoulos, F.N., Wang, H., "Detailed and Simplified Kinetic Models for *n*-Dodecane Oxidation: The Role of Fuel Cracking in Aliphatic Hydrocarbon Combustion," *Proceedings of the Combustion Institute* **32**, pp. 403-410 (2009).
10. Smallbone, A., Liu, W., Law, C.K., You, X., Wang, H., "Experiment and Modeling Study of Laminar Flame Speed and Non-Premixed Counterflow Ignition of *n*-Heptane," *Proceedings of the Combustion Institute* **32**, pp. 1245-1252 (2009).
11. Sheen, D.A., You, X., Wang, H., Løvås, T., "Spectral Uncertainty Quantification, Propagation and Optimization of a Detailed Kinetic Model for Ethylene Combustion," *Proceedings of the Combustion Institute* **32**, pp. 535-542 (2009).
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8.0 Interactions/Transitions

Presentations at Meetings and Conferences

1. "Development of an Experimental Database and Kinetic Models for Surrogate Jet Fuels," M. Colket, T. Edwards, S. Williams, N.P. Cernansky, D.L. Miller, F.N. Egolfopoulos, P. Lindstedt, K. Seshadri, F.L. Dryer, C.K. Law, D. Friend, D.B. Lenhart, H. Pitsch, A. Sarofim, M. Smooke, and W. Tsang, 35th AIAA Aerospace Science Meeting and Exhibit, Reno, Nevada, January 6-9, 2007.
2. "Extinction of Benzene/Air and Toluene/Air Premixed Flames: Experiments and Simulations," Y.L. Wang, A.T. Holley, A. Sifounakis, M.G. Andac, and F.N. Egolfopoulos, paper A11, 5th US Combustion Meeting, San Diego, California, March 26-28, 2007.
3. "Flame Ignition of Mixtures of Dry and Wet Synthesis Gas with Oxygen and Nitrogen," C. Ji, G.F. Schwab, P. Veloo, A.T. Holley, and F.N. Egolfopoulos, paper A32, 5th US Combustion Meeting, San Diego, California, March 26-28, 2007.
4. "Development of an Experimental Database and Chemical Kinetic Models for Surrogate Gasoline Fuels," W. Pitz, N.P. Cernansky, F.L. Dryer, F.N. Egolfopoulos, J.T. Farrell, D.G. Friend, and H. Pitsch paper 2007-01-0175, 2007 SAE World Congress, Detroit, Michigan, April 16-19, 2007.
5. "Experimental and Detailed Numerical Studies of Fundamental Flame Properties of Gaseous and Liquid Fuels," 2007 Contractors Meeting in Chemical Propulsion, *Army Research Office and Air Force Office of Scientific Research*, Boulder, Colorado, June 11-13, 2007.
6. "Identification of Target Validation Data for Development of Surrogate Jet Fuels," M. Colket, T. Edwards, S. Williams, N.P. Cernansky, D.L. Miller, F.N. Egolfopoulos, F.L. Dryer, J. Bellan, P. Lindstedt, K. Seshadri, H. Pitsch, A. Sarofim, M. Smooke, and W. Tsang, 36th AIAA Aerospace Science Meeting and Exhibit, Reno, Nevada, January 7-10, 2008.
7. "Propagation and Extinction of Mixtures of Air with *n*-Dodecane, JP-7, and JP-8 Jet Fuels," C. Ji, X.Q. You, A.T. Holley, Y.L. Wang, F.N. Egolfopoulos, and H. Wang, 36th AIAA Aerospace Science Meeting and Exhibit, Reno, Nevada, January 7-10, 2008.
8. "Detailed and Simplified Kinetic Models for *n*-Dodecane Oxidation: The Role of Fuel Cracking in Aliphatic Hydrocarbon Combustion," by X.Q. You, F.N. Egolfopoulos, and H. Wang, paper No. 08S-023 Spring Technical Meeting, *Western States Section/Combustion Institute*, University of Southern California, Los Angeles, California, March 17-18, 2008.
9. "Propagation and Extinction of Premixed *n*-Dodecane/Air Flames," by C. Ji, X.Q. You, A.T. Holley, Y.L. Wang, F.N. Egolfopoulos, and H. Wang, paper No. 08S-037 Spring Technical Meeting, *Western States Section/Combustion Institute*, University of Southern California, Los Angeles, California, March 17-18, 2008.
10. "Extinction of Dry and Wet Premixed H₂/Air Flames," by P.S. Veloo, G.F. Schwab, Y.L. Wang, C. Ji, A.T. Holley, and F.N. Egolfopoulos, paper No. 08S-046 Spring Technical Meeting, *Western States Section/Combustion Institute*, University of Southern California, Los Angeles, California, March 17-18, 2008.
11. "Sensitivity of Propagation and Extinction of Large Hydrocarbon Flames to Fuel Diffusion," by A.T. Holley, X.Q. You, E. Dames, H. Wang, and F.N. Egolfopoulos, paper No. 08S-047 Spring Technical Meeting, *Western States Section/Combustion Institute*, University of Southern California, Los Angeles, California, March 17-18, 2008.
12. "Experiments and Reaction Models of Fundamental Combustion Properties," 2008 Contractors Meeting in Chemical Propulsion, *Army Research Office and Air Force Office of Scientific Research*, Washington, D.C., June 16-18, 2008.

13. "An Experimental Study of Premixed *m*-Xylene/Air and *n*-Dodecane/*m*-Xylene/Air Flames," by C. Ji, A. Moheet, Y. L. Wang, M. Colket, H. Wang, and F. N. Egolfopoulos, paper 31H2, 6th US Combustion Meeting, Ann Arbor, Michigan, May 17-20, 2009.
14. "Experiments and Reaction Models of Fundamental Combustion Properties," 2009 Contractors Meeting in Chemical Propulsion, *Army Research Office and Air Force Office of Scientific Research*.
15. "Propagation, Extinction, and Ignition of CH₄/H₂/CO/Air Mixtures," by O. Park, P.S. Veloo, and F.N. Egolfopoulos, paper No. 09F-015 Fall Technical Meeting, *Western States Section/Combustion Institute*, University of California at Irvine, Irvine, California, October 26-27, 2009.
16. "Propagation and Extinction of Cyclohexane/air, methyl-Cyclohexane/Air, and *n*-butyl-Cyclohexane/Air Mixtures," by C. Ji and F.N. Egolfopoulos, paper No. 09F-016 Fall Technical Meeting, *Western States Section/Combustion Institute*, University of California at Irvine, Irvine, California, October 26-27, 2009.
17. "Assessment of Counter Flow Arrangement to Measure Laminar Burning Velocities using Direct Numerical Simulations," by V. Mittal, H. Pitsch, and F.N. Egolfopoulos, paper No. 09F-085 Fall Technical Meeting, *Western States Section/Combustion Institute*, University of California at Irvine, Irvine, California, October 26-27, 2009.
18. Sheen, D., Wang, H. "Spectral expansion analysis of kinetic model uncertainty beyond parameter optimization," the Fifth Joint States Section of the Combustion Institute Meeting, San Diego, CA, March 25-28, 2007, paper 07-P24.
19. You, X., Wang, H., Goos, E., Sung, C.-J., Klippenstein, S. J. "Reaction kinetics of CO+HO₂ → products: *ab initio* transition state theory study with master equation modeling," the Fifth Joint States Section of the Combustion Institute Meeting, San Diego, CA, March 25-28, 2007, paper 07-C36.
20. Sheen, D. A., You, X., Wang, H. "Spectral optimization and uncertainty quantification of detailed kinetic model for ethylene combustion," 2007 Fall Meeting of the Western States Section of the Combustion Institute, Livermore, CA, October 16-17, 2007, paper 07F-10.
21. Wang, H. "Transport theory of small spherical particles – how does a molecule become a 'particle'," Proceedings of the Interdisciplinary Transport Phenomena V: Fluid, Thermal, Biological, Materials & Space Sciences, Bansko, Bulgaria, October 14-19, 2007, pp. 15.19-27.
22. Wang, H., Sheen, D., You, X., Lovas, T. "Spectral optimization and uncertainty propagation in detailed kinetic modeling of hydrocarbon combustion," 2008 SIAM International Conference on Numerical Combustion, Monterey, CA, March 31-April 2, 2008.
23. Wang, H. "Reaction mechanisms and H-atom transport issues in modeling lean hydrogen combustion," 2008 SIAM International Conference on Numerical Combustion, Monterey, CA, March 31-April 2, 2008.
24. Wang, H., Sheen, S., You, X., Lovas, T. "Spectral optimization and uncertainty propagation in detailed kinetic modeling of hydrocarbon combustion," 55th JANNAF Propulsion Meeting, Boston, MA, May 12-16, 2008.
25. Taatjes, C. A., Osborn, D. L., Selby, T. M., Meloni, G., Trevitt, A. J., Sirjean, B., Dames, E., Wang, H. "Reaction kinetics of benzene + O(³P) → products: experimental and theoretical study." Poster Paper, 31st International Symposium on Combustion, Montreal, Canada, August 3-8, 2008.

26. Sheen, D. A., Løvås, T., Wang, H. "Reduction of detailed chemical models with controlled uncertainty," Second International Workshop on Model Reduction in Reacting Flows, Center for Applied Mathematics, University of Notre Dame, March 30 - April 1, 2009.
27. Sheen, D. A., Løvås, T., Wang, H. "Reduction of detailed chemical models with controlled uncertainty," 6th U.S. National Combustion Meeting, May 17-20, 2009, Ann Arbor, Michigan. Paper 23.F2.
28. Sheen, D. A., Wang, H. "Necessity of nonlinear terms in polynomial chaos expansions for uncertainty propagation." 6th U.S. National Combustion Meeting, May 17-20, 2009, Ann Arbor, Michigan. Paper 21G4.
29. Sirjean, B., Wang, H., Tsang, W. "New Experimental and theoretical insights of the role of tunneling in n-alkyl radicals isomerization," 6th U.S. National Combustion Meeting, May 17-20, 2009, Ann Arbor, Michigan. Paper 22.G2.
30. Sirjean, B., Dames, E., Sheen, D. A., Wang, H. "Simplified chemical kinetic models for high-temperature oxidation of C_1 to C_{12} n-alkanes," 6th U.S. National Combustion Meeting, May 17-20, 2009, Ann Arbor, Michigan. Paper 23.F1.
31. Taatjes, C. A., Osborn, D. L., Selby, T.M., Meloni, G., Trevitt, A.J., Sirjean, B., Dames, E., Wang, H. "Products of the benzene + O(3p) reaction: Experimental and theoretical study," 6th U.S. National Combustion Meeting, May 17-20, 2009, Ann Arbor, Michigan. Paper 22G1.
32. Sheen, D. A., Wang, H. "Quantitative analysis of hierarchical strategies of building combustion reaction models," 2009 Fall Western States Section Meeting of the Combustion Institute, Irvine, CA, October 26-27, 2009, paper 09F-50.
33. Dames, E., Wang, H. "Kinetic modeling of one-ring aromatic compounds," 2010 Spring Technical Meeting of the Western States Sections of the Combustion Institute, University of Colorado at Boulder, CO, March 22-23, 2010.

Technical Interactions with AFRL Researchers

Several meetings with Dr. Tim Edwards of AFRL took place during the reporting period. The purpose of these meetings was to discuss the measurements on the propagation, ignition, and extinction limits of flames of neat hydrocarbon fuels as well as a variety of petroleum-derived and synthetic jet fuels that were supplied to the USC Combustion and Fuels Laboratory by Dr. Edwards. The discussions has focused on both the experimental and modeling work pertaining to jet fuels and their surrogates, as well as ongoing work on smaller hydrocarbons in the C_1 - C_4 range.

Other Technical Interactions

A close interaction was established with Professors Ron Hanson, Tom Bowman and Heinz Pitsch of Stanford University, Professor C.K. Law of Princeton University, Professors Nick Cernansky and David Miller of Drexel University, Professor Angela Violi of University of Michigan, Dr. Wing Tsang of National Institute of Standards and Technology, and Dr. Meredith Colket of United Technologies Research Center on the experimental and modeling aspects of this research. Additionally, collaborative research efforts were initiated with Dr. Stephen Klippenstein of the Argonne National Laboratory and Dr. Craig Taatjes of the Sandia National Laboratories

Inventions, Technology Transitions and Transfers

Part of the work described in this report resulted in the following technology transition and transfer:

Performer: Dr. Hai Wang, University of Southern California, (213) 740-0499
Customer: Dr. Meredith Colket, United Technology Research Center, 411 Silver Lane
East Hartford, CT 06108
Phone: (860) 610-7000
Result: Reaction model for predicting aromatics and soot formation in fuel rich flames
Application: Low-emission gas turbine engines