Final Technical Report

DEVELOPMENT OF DETAILED AND REDUCED KINETICS MECHANISMS FOR SURROGATES OF PETROLEUM-DERIVED AND SYNTHETIC JET FUELS

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Summary/Overview

The oxidation and pyrolysis of *n*-alkanes and *n*-alkenes up to $n\text{-}C_{12}H_{26}$ as well as selected cycloalkanes, *iso*-alkanes, aromatics, and jet fuels were studied experimentally behind reflected shock waves, in flow reactors, and in laminar flames. The measurements included ignition delays and species time evolutions in shock tubes, species profiles in flow reactors, and propagation speeds and ignition/extinction limits of laminar flames. The fundamental kinetic data were used to develop and validate a detailed reaction model for the combustion of *n*-alkanes up to $n\text{-}C_{12}H_{26}$ as well as cyclohexane and mono-alkylated cyclohexane fuels. The resulting JetSurF model is documented online at http://melchior.usc.edu/JetSurF. Validation tests show that the JetSurF (versions 1.0 and 2.0) is capable of predicting the majority of the experimental data satisfactorily.

This was a collaborative three-year research effort between the following universities and investigators:

1. University of Southern California: F.N. Egolfopoulos (PI), H. Wang (co-PI);
2. Drexel University: N.P. Cernansky (co-PI), D.L. Miller (co-PI);
3. Princeton University: C.K. Law (co-PI);
4. Stanford University: C.T. Bowman (co-PI), R.K. Hanson (co-PI), H. Pitsch (co-PI).

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Technical Discussion

1.0 Background

The development of computational capabilities for the design of the next generation of fuel-flexible, air-breathing propulsion systems, represents an area of immense, but underutilized potential. Major hurdles, however, obstruct the pathway to this goal. The immediate problems that need to be solved can be grouped into two categories: (1) understanding and quantifying the combustion properties of practical fuels used in air-breathing propulsion systems and the selection of appropriate surrogate fuels; and (2) developing reliable detailed reaction models and strategies for model reduction for use in large-scale simulations. These project goals are challenging because of the large number of fuel components and classes found in both petroleum-derived and non petroleum-derived jet fuels. It is well accepted that the solution to this problem is to develop surrogates for real fuels that contain kinetically and computationally tractable numbers of components. Until recently the combustion properties of practical jet fuels remained poorly understood and the selection of surrogates was an evolving science.

The problems that need to be solved in order to accomplish the project goals are in the realm of flame and reaction dynamics, combustion kinetics, and reacting flow simulations. Thus, success can be achieved only if the solution approach involves fundamental physics, chemistry, mathematics, as well as engineering and information sciences, including reaction rate theories, transport theories, fluid mechanics, engineering optimization, and nonlinear uncertainty propagation. A multidisciplinary and coordinated approach is essential to achieve the project goals.

Three general tasks were undertaken in the completed research. The first is the detailed and quantitative characterization of kinetic and combustion properties of selected jet fuels as well as a representative number of single-component hydrocarbons and their mixtures. This will aid the development of surrogate fuels that mimic the combustion behavior of real fuels. The second is the development of detailed kinetic models that accurately predict the experimentally observed behavior of the surrogate fuel components and blends. The third is the reduction of the size and stiffness of the detailed kinetic models and the associated error propagation so that they can be used in large-scale simulations of real air-breathing combustors. Two types of jet fuels were the targets in this research effort. The first were conventional petroleum-derived "reference" JP-8 fuels. The second were non petroleum-derived or synthetic jet fuels. By considering these two

types of fuels, both short-term (current fuels and systems) and potential long-term (fuel-flexible energy conversion and design) needs of air-breathing propulsion are addressed.

The primary outcome of this effort was the improved qualitative understanding and quantitative predictability of the combustion properties of practical jet fuels and surrogates, and the development of reliable combustion models that can be used with confidence in large-scale simulations of air-breathing propulsion systems. The potential impact on DoD capabilities is immense. Specifically, DoD can be able to make decisions in shorter times and with fewer resources compared to performing tests in actual gas turbines and other advanced aero-propulsion devices. Additionally, the development of the hydrocarbon-powered scramjet can be accelerated and thus provide an additional tactical advantage to DoD.

2.0 Specifics of Originally Proposed Program

The originally proposed program was multifaceted and the specific approaches were described according to the scientific subtasks. The overall philosophy was and remains that while progress can be made independently in individual tasks, close collaboration and coordination of efforts will produce the most effective progress towards accomplishing the overall objective. Specifically, it was proposed that experimental efforts would be planned so that similar fuels or fuel mixtures and similar conditions are investigated in parallel in flow reactors, shock tubes, and flames. From the initial phase of any surrogate fuel development, this coordination is critical, since agreements observed for the combustion behaviors of real fuels and their surrogates in homogeneous reactors do not necessarily and usually do not extend to flames where more complex kinetic and transport behaviors and couplings are encountered.

2.1 Objectives

The original main objective of the program was: **to combine the multidisciplinary experimental, theoretical, and modeling approaches, developed and pioneered by the individual PIs, in a coordinated effort to provide quantitative information into the mechanisms that control the combustion of jet fuels and their surrogates, and equally importantly, to develop predictive detailed and reduced kinetic models suitable for large-scale computational simulations based on these jet-fuel surrogates.**

The specific objectives were:

1. **Accurate and detailed experimental characterization of kinetic and combustion properties** of selected jet fuels as well as a representative number of single-component hydrocarbons and their mixtures. This would allow for the development of surrogate fuels and the attendant detailed kinetic models. The experiments would be performed in flow reactors, shock tubes, and flame systems. The initial selection of fuels would be based on the recommendations of the Jet Fuel Surrogate Working Group, in which a large number of investigators of the proposing research team participated at the time.

2. **Development of detailed kinetic models** that reproduce closely the experimentally observed behaviors of the surrogate fuel components and their blends. The kinetic models would be compiled and optimized using the experimental data generated as well as available literature data. In addition, effects of molecular transport would be addressed.

3. **Size and stiffness reduction of the detailed kinetic models and associated error** so that the reduced models can be used in large-scale simulations of real combustors. Model reductions would be performed in a systematic way so that the key features of the detailed models are preserved. An additional feature of the proposed effort was the development of systematic methods to address uncertainties in kinetic rate data and their effects on turbulent reacting flow simulations.

2.2 Parameter Space

The proposed fuels were:

- Reference Jet-A and JP-8 samples, including low and high aromatic contents;
- A reference Fischer-Tropsch jet fuel constituted entirely of *n-* and *iso-*paraffins;
- A reference coal-derived jet fuel constituted entirely of *cyclo*-paraffins;
- C_{10-16} *n-* and *iso-*paraffins (e.g., *n*-decane, *n*-dodecane, *iso*-cetane);
- C_{7-12} *cyclo*-paraffins (e.g., *ethyl/propyl/butyl*-cyclohexane, decalin);
- Aromatics (e.g., toluene, *m*-xylene, trimethylbenzene, *1*-methylnaphthalene);
- Multicomponent mixtures of the selected surrogate components.

The proposed thermodynamic conditions were:

- Pressures: 1 to 30 atm;
- Unburned reactant temperatures: 300 to 1250 K;
- Shock tube experimental temperature range: 650 to 2000 K;
- Reactant composition: equivalence ratio bracketed by lean and rich flammability limits, typically ranging from 0.5 to 1.5;
- Inert dilution: zero to high.

The proposed reaction configurations were:

- Homogeneous systems: flow reactors and shock tubes;
- Non-homogeneous systems: non-premixed and premixed flames.

The proposed combustion phenomena were:

- Ignition;
- Propagation;
- Extinction;
- Detailed thermal and species concentration evolutions in space and time.

The proposed global and detailed properties were:

- Ignition delays and temperature and species concentration-time evolutions in shock tubes;
- Species concentration-time evolutions in flow reactors;
- Laminar flame speeds in premixed flames;
- Ignition limits in non-premixed and premixed flames;
- Extinction limits in non-premixed and premixed flames.

3.0 Summary of Completed Tasks

During the reporting period, the following tasks were completed.

3.1 *Flow Reactor Studies, Drexel University*

- Year 1 (Kurman, 2009; Kurman et al., 2009a,b; Natelson et al., 2008; Natelson, 2010a)

    o Experience was developed with the larger hydrocarbons characteristic of JP-8 through PFR experiments by identifying and quantifying the partial oxidation intermediates produced from *n*-dodecane oxidation.

    o Measured the relative reactivity of the xylene isomers as part of the Energy IPT evaluation of components of surrogates for JP-8 (Kurman et al., 2010; Natelson, 2010a; Natelson et al., 2010a,b)

    o Measurements of CO, CO_2, and O_2 identified the Negative Temperature Coefficient regime; however, carbon balances were unacceptably low and the intermediate species measurements could not be used to identify major reaction pathways.

    o Efforts began to identify whether the issue was related to gas sampling or analysis procedures.

- Year 2 (Kurman, 2009, 2010; Kurman et al., 2009b; Natelson, 2010a,b; Natelson et al., 2010b, 2011; Corrubia et al., 2011)

    o Identified cause of the poor atom balances as condensation of heavier intermediates in the existing sample storage system.

    o Facility and operating procedure modifications were implemented to eliminate sample storage and to provide for the direct injection of samples from the PFR to the GC/MS/FID. The new methodology is referred to as the Direct Transfer Controlled Cool Down (DT-CCD) methodology.

    o Achieved carbon balances ranging from 61% to 95% for sample temperatures of 618 K and 800 K, respectively, during initial validation experiments.

- Year 3 (Kurman, 2010; Kurman et al., 2009b, 2011; Natelson, 2010a,b; Natelson et al., 2009, 2011; Corrubia et al., 2011; Farid et al., 2011; Gupta et al., 2011)

- o Repeated experiments for *n*-dodecane oxidation, to ensure reproducibility and estimate errors to use in model development in Year 3.

- o Conducted a series of experiments exploring cycloalkane oxidation. Both *n*-butylcyclohexane (*n*-BCH) and *n*-propylcyclohexane (*n*-PCH) were studied.

- o Performed experiments exploring the oxidation of an *iso*-alkane surrogate component iso-cetane both neat and in a binary mixture with *n*-decane as part of our ongoing efforts to examine low temperature combustion phenomena using diesel fuel components and blends.

- o Began modeling work to identify kinetic pathways important in the production and consumption of non-alkylated lactones.

3.2 Flow Reactor Studies, Stanford University

- Modified an existing variable-pressure flow reactor for operation using liquid fuels.

- Conducted experiments on the oxidation of *n*-dodecane over a range of temperatures, stoichiometries and pressures.

- Compared experimental data with model predictions using the JetSurf reaction mechanism.

3.3 Shock Tube Studies, Stanford University

- Species Time-Histories and Ignition Delay Times for Cyclo-Alkanes (Hong et al., 2011).

- Ethylene Time-History Measurements (Ren et al., 2011).

- Species Time-Histories for *n*-Dodecane (Davidson et al., 2011).

- Species Time-Histories for *n*-Heptane (Davidson et al., 2010a).

- Ignition Delay Times for C_5-C_9 *n*-Alkanes (Davidson et al., 2010b).

3.4 Flame Studies, Princeton University

- Analytical derivation of confined flame propagation (Kelley et al., 2011b).

- o Derived analytical extrapolation procedure for use in experimental determination of laminar flame speeds. This new result improved upon previous procedure and is a significant improvement over historical procedures.

- o Determined influence of pressure perturbations induced by chamber confinement for constant volume combustion vessels.

- o First analytical derivation allowing for general Lewis numbers, temperature dependent transport coefficients, and arbitrary flame geometry.

- Elevated pressure laminar flame speed measurements.

  - o Cyclohexane/Air: 1, 2, 5, 10 atm, 353K.

  - o Methylcyclohexane/Air: 1, 2, 5, 10 atm, 353K.

  - o Ethylcyclohexane/Air: 1 atm (high pressure measurements currently in progress).

3.5 Flame Studies, University of Southern California

- Experimental and modeling studies on the ignition, propagation, and extinction of C_3-C_{12} *n*-alkane flames (You et al., 2009; Holley et al., 2009; Ji et al., 2010; Liu et al., 2011).

- Experimental and modeling studies on the propagation of cyclohexane and mono-alkylated cyclohexane flames (Ji et al., 2011a).

- Experimental and modeling studies on the propagation of mixtures of air with binary liquid fuel mixtures (Ji and Egolfopoulos, 2011a)

- Flame studies of conventional and alternative jet fuels (Ji et al., 2011b)

- Propagation and extinction of benzene and alkylated benzene flames (Ji and Egolfopoulos, 2011b)

3.6 Flame Modeling Studies, Stanford University

- Assessment of counterflow to measure laminar flame speeds using direct numerical simulations (Mittal et al., 2011).

3.7 *Theoretical and Modeling Studies, University of Southern California*

- Improvement of kinetic foundation model for C_{1-4} hydrocarbons (Wang et al., 2007; Sheen et al., 2009; Sheen and Wang, 2011b,c).

- Development of kinetic models and advanced transport models for the single-component *n-*, *iso-*, and *cyclo*-paraffins (Wang et al., 2010; Sirjean et al., 2009a,b; Sirjean et al., 2008; Holley et al., 2009; Ji et al., 2010, 2011; Sheen and Wang, 2011a; Tangko et al., 2011).

- Development of kinetic models and advanced transport models for simple aromatic components (Dames and Wang, 2010, 2011; Taatjes et al., 2010).

- Development of robust methods for detailed kinetic model reduction that consider uncertainty propagation (Sheen et al., 2009a,b; Sheen and Wang, 2011a,b,c; Sirjean et al., 2009c).

3.0 Experimental Approach

A variety of experimental configurations by the investigators were used to complete the proposed tasks. The descriptions of all approaches are presented below.

3.1 Pressurized Flow Reactor, Drexel University

The Pressurized Flow Reactor (PFR) at Drexel University is a turbulent flow reactor designed to study the low (< 650 K) to intermediate temperature (650-1000 K) oxidation of hydrocarbon fuels with relative isolation from physical phenomena such as gradients in temperature and the flow field (Koert and Cernansky, 1992). The PFR contains a 22.5 mm ID, 40 cm long quartz reactor tube to provide a reaction environment with minimal surface effects. The quartz reactor tube is contained within a stainless steel pressure vessel for pressure elevation up to a maximum of 9.5 atm. The volume between the quartz reactor tube and pressure vessel forms an annulus that is at the same pressure as the reaction chamber. Synthetic air and high-pressure pre-vaporized fuel/nitrogen are introduced into an opposed jet annular mixing nozzle at the inlet to the quartz reactor tube. A water-cooled, borosilicate glass-lined stainless steel sample probe extracts and quenches samples from the centerline of the quartz reactor tube and it contains an integrated type-K thermocouple. Figure 1 depicts the schematic of the PFR equipment and setup.
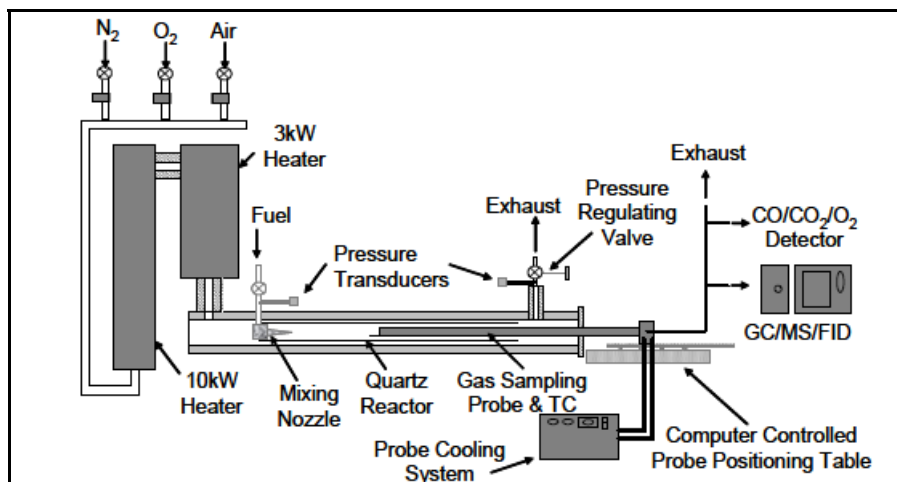

Figure 1. Pressurized Flow Reactor (PFR) schematic.

A Direct Transfer Controlled Cool Down (DT-CCD) methodology is used to minimize the time duration between sample collection and analysis in the GC/MS/FID (Kurman, 2010). The

PFR is heated to the maximum desired reaction temperature of approximately 850 K using pre-heated air from the circulation heaters. Upon reaching the maximum reaction temperature, fuel is injected into a heated nitrogen stream to ensure vaporization prior to entering the mixing nozzle where it is rapidly mixed with synthetic air in the opposed jet annular mixing nozzle. Further dilution with nitrogen is used to limit temperature rise from heat release. To maintain a constant residence time during the controlled cool down, the sample probe is repositioned for each sample. While the GC/MS/FID analysis is performed on the first sample, the PFR temperature is decreased to the next sample temperature. CO and CO_2 concentration is determined with an on-line, continuous NDIR analyzer and O_2 is measured using an electrochemical oxygen sensor.

3.2 Pressurized Flow Reactor, Stanford University

The experiments were conducted in a variable pressure flow reactor, shown in Fig. 2.
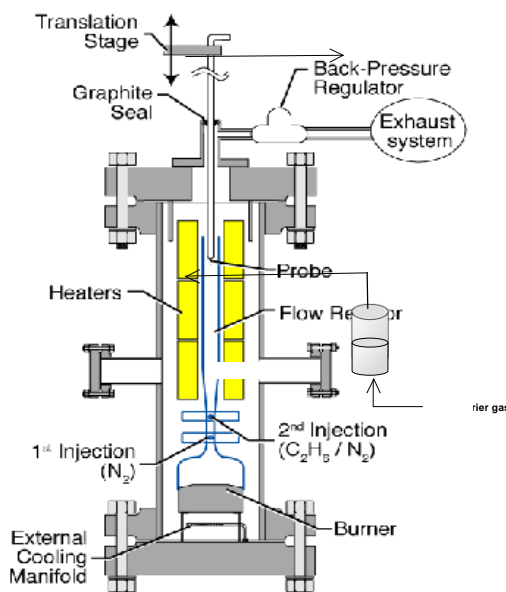

Figure 2. Variable pressure flow reactor.

Liquid *n*-dodecane, vaporized in an evaporator in a thermostated bath, is carried to the flow reactor by a N_2 carrier gas and injected through a series of radial injectors into flowing combustion products from a premixed flame burner operating on $H_2/O_2/N_2$. Upstream of the fuel injectors is another set of radial injectors in which N_2 is injected into the combustion products. Controlling the flow rates of H_2, O_2, N_2 and the fuel/N_2 mixture fixes the temperature and

stoichiometry of the reactant mixture at the entrance to the constant-area flow reactor. Three electrical heating elements located along the length of the reactor maintain the reactor at nearly adiabatic conditions. The concentrations of stable product species and temperature are measured on the centerline along the length of the reactor using traversing an extractive sampling probe and a thermocouple probe, respectively. The extracted gas sample is transferred through a heated sample line to online analyzers for analysis. Oxygen in the sample is measured using a paramagnetic analyzer; stable carbon-containing species are measured using either NDIR analyzers or by gas chromatography. All flow rates and data acquisition are computer controlled via a PC with LabVIEW software. The temperature range of the present experiments ranges between 1000 - 1250K; pressures range from 1 - 10 bar; stoichiometries range from 0.5 (lean) - 1.5 (rich).

3.3 Shock Tube, Stanford University

Shock Tube Facility

Experiments were performed in the 6" (15.24 cm I.D.) shock tube at Stanford. This shock tube has an electro-polished stainless steel driven section with length/diameter (L/D) ratio of 70 and used a helium-filled driver section with an L/D of 30 to burst 0.25 mm thick polycarbonate diaphragms (against a crossed-knife arrangement in a short square section of the shock tube). The shock tube is sealed with Viton O-rings, is operated at room temperature (i.e. without heating) and can be turbo-pumped overnight to an ultimate pressure $\sim 10^{-6}$ torr and to a leak and outgassing rate of $\sim 3 \times 10^{-6}$ torr/min. Typically reflected shock wave experiments were performed hourly and over this time frame the ultimate shock tube pressure before filling was $\sim 5 \times 10^{-6}$ torr and the leak and outgassing rate was $\sim 10^{-5}$ torr/min.

Test gas mixtures were stored in a 40 liter stainless steel tank heated uniformly to 60 ºC, and mixed with a magnetically-driven stirring vane. Mixtures were made using partial pressures and pre-shock filling concentrations in the shock tube were confirmed using *in situ* 3.39 micron laser absorption (Horning et al., 2002). 99.999% Argon and 99.99% oxygen (Praxair) were used with spectroscopic grade (99.9+%) *n*-heptane (Sigma-Aldrich) with no further preparation except for vacuum pumping to removed dissolved volatiles and oxygen.

Incident shock speeds were determined by extrapolating, to the end wall position, shock velocities measured over the last 2 meters of the driven section. Reflected shock conditions were calculated using a standard chemically frozen shock code and standard thermo-chemical data (Kee et al., 1987). Resulting uncertainties in reflected shock temperatures over test times of 1 ms were $<\pm1\%$.

Laser Absorption Measurements

Laser absorption of OH: OH concentration was measured using narrow-linewidth laser absorption near 306.7 nm. The chosen wavelength was the peak of the well-characterized $R_1(5)$ absorption line in the OH A-X (0, 0) band (Herbon et al., 2002). CW laser light at 613.4 nm was generated using a Spectra Physics 380 ring dye laser pumped with a 5 W Coherent Verdi at 532 nm. Light at 306.7 nm was generated by intracavity frequency-doubling, using a temperature-tuned AD*A crystal. The wavelength was set using a high-precision wavemeter and confirmed by experiments at off-center wavelengths. Common mode rejection was used to reduce laser intensity noise to $< 0.1\%$, resulting in a minimum detection sensitivity of < 1 ppm for most conditions in this work. OH concentration was calculated using Beer's law:

$I/I_0 = \exp(-k_v\, P_{total}\, X_{OH}\, L)$ (Eqn. 1),

where I and I_0 are the transmitted and incident beam intensities, k_v is the line-center absorption coefficient at 306.7 nm for OH, P_{total} is the total test gas mixture pressure, X_{OH} is the OH mole fraction, and L is the pathlength, 15.24 cm in the current experiments. The estimated uncertainty in measured X_{OH} is ~ 3%.

Measurements were also performed with the laser tuned off the OH absorption line, and with the laser turned off, to verify that there was no significant interfering absorption or emission.

IR diode laser absorption of CO_2 and H_2O: The recent commercial availability of DFB (distributed feedback) IR diode lasers in the wavelength vicinity of 2.5-2.7 microns has allowed the development of a new CO_2 and H_2O absorption diagnostics (Farooq et al., 2009).

Absorption measurements of CO_2 were made using a fixed-wavelength direct-absorption strategy that provided a detection bandwidth of about 1 MHz. Line-strength, self-broadening and Ar-broadening coefficients were measured previously for the R(28) transition (at 2752.5 nm) used, and the ability to make accurate measurements of CO_2 concentration has previously been

demonstrated in CO_2-Ar mixtures over a temperature range of 300-1500 K. Quantitative CO_2 concentration profiles were generated from the raw traces of fractional absorption using Beer's law and the known absorption coefficient.

Using the same DFB laser technology at wavelengths of 2.5 microns, the detection of water is also possible (Hong et al., 2009). Water concentration time-histories were measured using the IR water transition centered at 2550.96 nm (3920.089 cm^{-1}) within the ν_3 fundamental vibrational band. This line was selected primarily because of its favorable line strength. The line strength and broadening coefficients of this line have been characterized in our laboratory in heated cell experiments before conducting the chemical kinetic studies in a shock tube. In a typical shock tube experiment, with reflected shock temperatures and pressures of 1100 K and 2 atm, 1000 ppm of H_2O in argon over a path-length of 14 cm gives a strong peak absorbance of approximately 7% with a typical signal-to-noise ratio (SNR) of 50-80.

IR He-Ne laser absorption of n-dodecane: *n*-Dodecane mole fraction was monitored with IR He-Ne laser absorption at 3.39 μm. A C-H stretch vibrational absorption feature for many hydrocarbons extends across this wavelength. For certain species, large alkanes in particular, absorption at this wavelength is relatively strong; and absorption by smaller hydrocarbon species, and in particular, decomposition products of *n*-dodecane, is weaker. Thus, at early times the absorption at 3.39 μm is dominated by the absorption by *n*-dodecane and this measurement can be used to monitor the *n*-dodecane time-history. At later times, after the majority of the *n*-dodecane has decomposed, the residual absorption signal is dominated by the decomposition products with the highest absorption cross-section – mole fraction product. Relatively accurate *n*-dodecane profiles over the entire experimental timeframe are possible, if corrections to the 3.39 μm absorption profiles based on subtraction of ethylene (and higher alkene interfering species) are included. High-temperature absorption cross-sections of *n*-dodecane and its decomposition products, and experimental details of this method, are discussed in Klingbeil et al. (2006).

CO_2 laser absorption of C_2H_4: Ethylene mole fraction was monitored by taking advantage of the fortuitous overlap of the P(14) line of the CO_2 gas laser at 10.532 microns with the strong ethylene absorption band near 10.6 microns. Similar to the situation with the C-H stretch absorption band near 3.39 microns, there is a wide CH_2 wag absorption feature near 10.6 microns that is shared in varying (but weaker) strengths (at the P(14) line in particular) by other alkenes

(e.g. ethylene, propene, butene etc.) However, over the experimental timeframe of the current experiments, absorption at 10.532 microns is dominated by ethylene absorption. High-temperature absorption cross-sections of ethylene and related alkenes (as well as CO_2 and H_2O) and experimental details are discussed in Pilla et al. (2009).

3.4 Spherically Expanding Flame Experiments, Princeton University

Conceptually, the design of the apparatus is similar to the previous design for high-pressure flame propagation at room temperature (Tse et al., 2000), modified to allow experimentation with liquid fuels (Kelley et al., 2011a). The apparatus is a double-chambered vessel with one cylindrical chamber radially surrounding the other. The walls of the inner chamber are fitted with a series of holes that can be mechanically opened and closed to allow the union and separation of the gases in the inner and outer chambers. The outer chamber is covered with silicon electrical heaters, hence enabling it to act as an oven to uniformly heat the inner chamber to 80°C, which is the initial gas temperature for all of the present data.

Operationally, after vacuuming both chambers, the connecting holes are closed to seal the inner chamber from the outer chamber. The inner chamber is filled with fuel vapor produced by heating a fuel reservoir maintained at 80°C, followed by a certified mixture of oxidizer and inert gas, which is also preheated to at least 80°C. The outer chamber is filled with a mixture of inert gases to match the density of the gas in the inner chamber. As a secondary check of the equivalence ratio of the mixture, samples of the gas in the tubing connected to the inner chamber are analyzed using a gas chromatograph with a flame ionization detector. All gas samples have been verified to have less than a 2% random error in the equivalence ratio, as is expected based on the gas filling procedure.

After mixing and settling of the gas, the holes between the inner and outer chambers are opened to allow communication between them, while the test gas in the inner chamber is simultaneously spark ignited. This results in a spherical flame that propagates throughout the inner chamber in essentially an isobaric environment before it is quenched upon contacting the inert gases in the outer chamber. The flame surface is visualized using a pinhole Schlieren system coupled to a high-speed camera running typically at 10,000 frames/sec.

The Schlieren images yield the time history of the radius of the spherical flame, from which the stretched flame speed can be determined. The laminar flame speeds are obtained through rigorously derived non-linear extrapolation formula to zero stretch.

3.5 Counterflow Flame Experiments, University of Southern California

Flame ignition, propagation, and extinction experiments were performed under ambient pressure in the counterflow configuration (e.g, Ji et al., 2010), as schematically shown in Fig. 3 along with the details of the burner. Each burner includes several internal and external heating capabilities as well as an aerodynamically designed nozzle and a N_2 co-flow channel surrounding the nozzle. Burners with 7, 14, and 20 mm diameter nozzles, D, were used, and the nozzle separation distances, L, were equal to D.
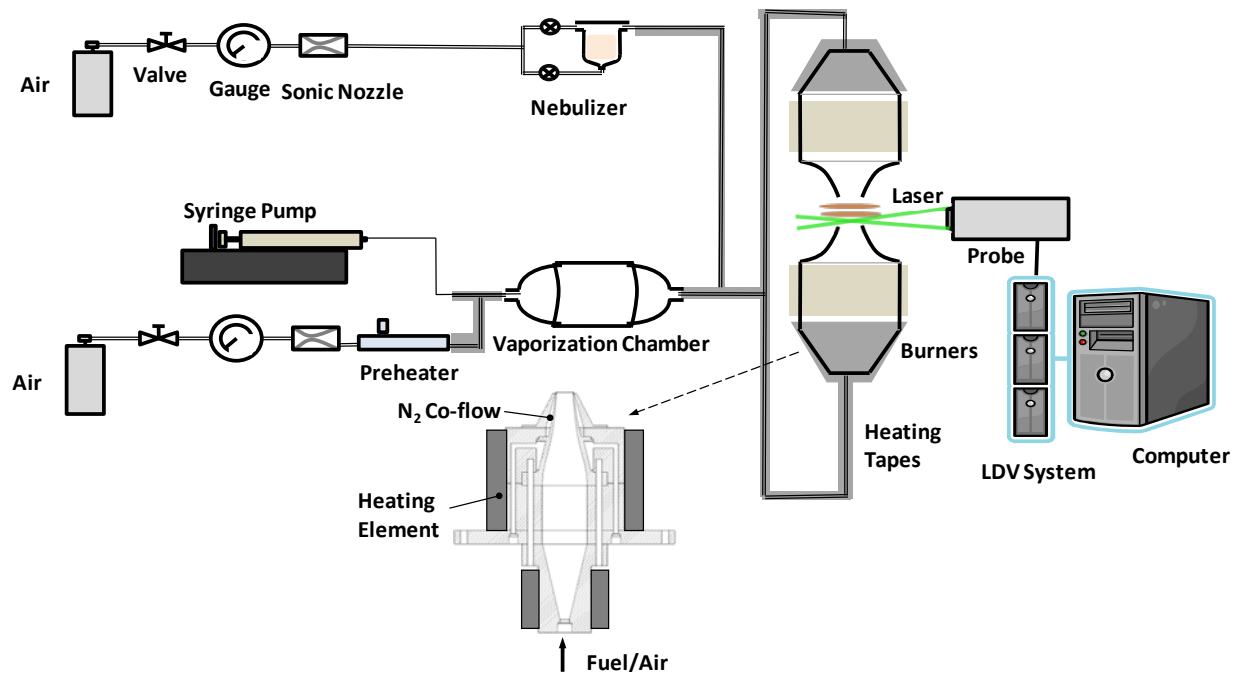

Figure 3. Schematic of the counterflow experimental configuration.

The air and N_2 flow rates are metered using sonic orifices by controlling the pressure upstream of the orifice. The vaporization system consists of a high-precision syringe pump that injects the fuel into a chamber surrounded by a flow of heated air. The wall temperature of the vaporization chamber is monitored by a K-type thermocouple kept approximately 20 K above the boiling point of the fuel to ensure complete vaporization. To prevent fuel condensation, the

gas delivery line is wrapped with heating tape and the post-chamber temperature is monitored by a K-type unsheathed thermocouple. The partial pressure of the fuel is kept below its vapor (saturation) pressure at all times. The burners are heated with ceramic heating jackets. An R-type thermocouple is used to monitor the unburned gas temperature, T_u, at the center of the burner exit.

The axial flow velocities are measured along the stagnation streamline, using digital particle image velocimetry (DPIV). The flow is seeded with 0.3-μm diameter silicon oil droplets produced by a heated nebulizer.

To determine the laminar flame speed, the minimum point of the axial velocity profile just upstream of the flame is defined as the reference velocity, $S_{u,ref}$, and the absolute value of the maximum velocity gradient in the hydrodynamic zone is defined as the imposed stretch, K (e.g, Ji et al., 2010). By plotting $S_{u,ref}$ against K, the laminar flame speeds are determined by invoking a computationally-assisted non linear extrapolation to $K = 0$.

Flame ignition experiments are performed by counterflowing fuel/N_2 mixtures against a heated airflow exiting from a quartz tube in which a silicon carbide spiral-heating element is embedded and capable of heating the N_2 up to 1,400 K (Liu et al., 2011). The fuel/N_2 jet is heated using a ceramic heating jacket so that fuel condensation is not taking place. Ignition is achieved by establishing the appropriate flow rates and temperatures at the two burner exits, and by increasing subsequently the fuel flow rate until ignition was observed.

4.0 Modeling Approach

Modeling of Experimental Data

Modeling, analysis, and interpretation of flow reactor, shock tube, and flame were performed using a number of Chemkin-based codes (e.g., Kee et al., 1985, 1986, 1987, 1988, 1989; Egolfopoulos & Campbell, 1996) and several in-house codes (e.g., Sheen & Wang, 2011b).

The full axisymmetric simulation of the counterflow configuration was done with a high-order kinetic energy conserving code (Desjardins, 2008) by using detailed multi- step finite-rate chemistry.   To solve the one-dimensional problem along the stagnation streamline, the FlameMaster code (Pitsch et al., 1996) was used.   A chemical mechanism with 28 species was used to model the methane chemistry in both codes (Peters et al., 1993).

The JetSurF Model

The JetSurF Model (Wang et al., 2010; Sirjean et al., 2009a,b; Sirjean et al., 2008) has been developed and used as a basis for all collaborative activities involved in this effort. The current version (2.0) consists of 348 species and 2163 reactions. The development effort centers on *n*-dodecane and *n*-butyl-cyclohexane, but the model includes also the high-temperature chemistry of all *n*-alkanes up to *n*-dodecane, and mono-alkylated cyclohexanes, including *n*-propylcyclohexane, ethylcyclohexane, methylcyclohexane, and cyclohexane.   JetSurF also includes the foundation chemistry for *iso*-alkanes.   The model is "un-tuned" and work-in-progress. The development effort centers on achieving consistent kinetic parameter assignment and predictions for a wide range of hydrocarbon compounds. The current version also includes limited low-temperature chemistry for cyclohexane and the alkylated cyclohexane compounds, though this part of the model remains weak and requires further work.

The base model is USC-Mech II (111 species, 784 reactions) (Wang et al., 2007) that describes the oxidation of H_2 and CO and the high-temperature chemistry of C_1-C_4 hydrocarbons. The base model considers the pressure dependence for unimolecular and bimolecular chemically activated reactions, and was validated against experimental data ranging from laminar flame speeds, ignition delay times behind shock waves, to species profiles in flow reactors and burner stabilized flames.
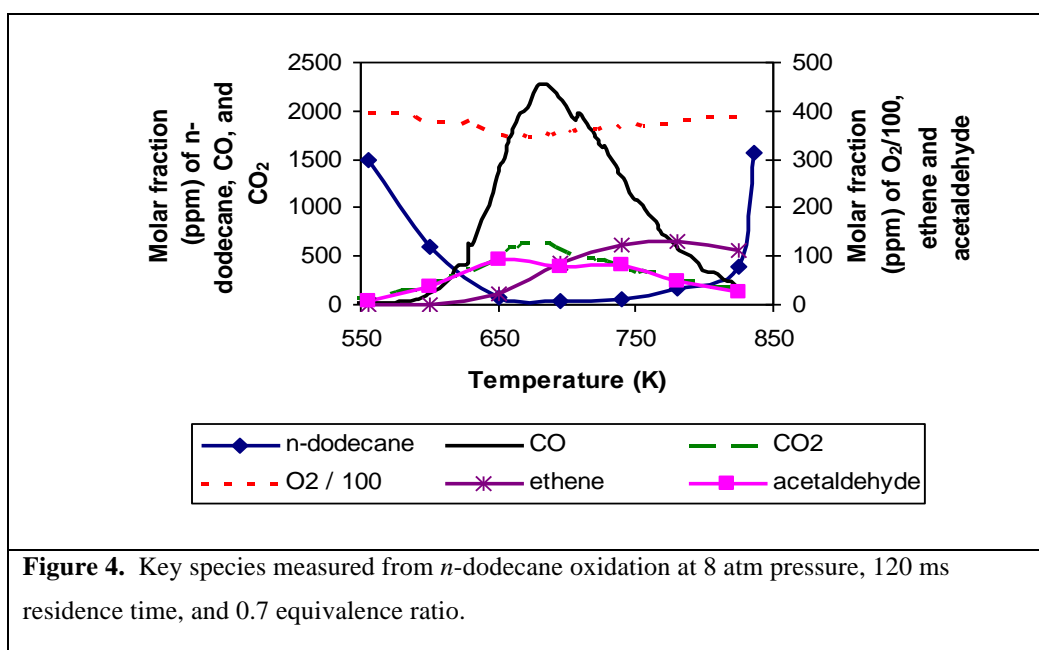
Uncertainty Quantification, Propagation and Minimization

The Method of Uncertainty Minimization using Polynomial Chaos Expansion (MUM-PCE) (Sheen et al., 2009a; Sheen and Wang, 2011) was developed to quantify, propagate and minimize kinetic uncertainties. MUM-PCE combines multi-parameter minimization through solution mapping (Frenklach et al., 1992) with the spectral uncertainty method, as introduced by Najm and coworkers (Reagan et al., 2004). The method was developed as a means of propagating the uncertainties in the rate parameters of a model in its prediction of a combustion property. The method is capable of constraining the model uncertainties with a set of experimental measurements of combustion phenomena with well-characterized uncertainty. In this method, the model is represented by multivariate polynomial response surface at selected experimental points. The polynomials are obtained from sensitivity-analysis based method for laminar flame speed and species profiles (Davis et al., 2004), and central-composite fractional factorial design of resolution VI for ignition delay (Frenklach et al., 1992).
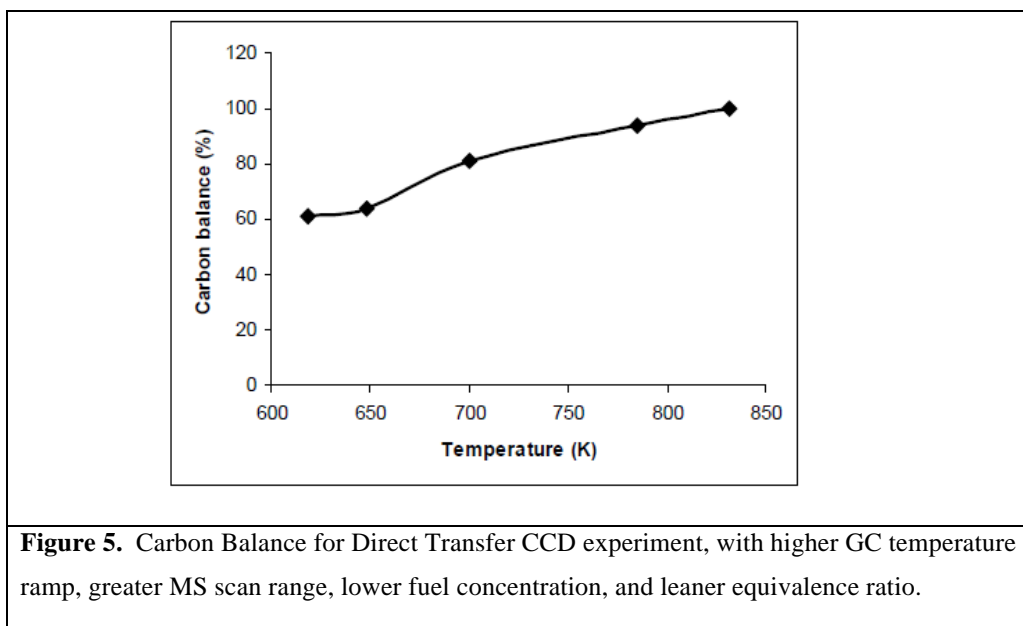
5.0 Results and Discussion

5.1 Flow Reactor Studies, Drexel University

In Year 1, experiments identifying and quantifying the intermediates produced from *n*-dodecane oxidation were conducted, and carbon balances were on average 50% and as low as 20%, depending on the temperature. The low carbon balances did not affect the ability to characterize the range of the negative temperature coefficient reaction regime with *n*-dodecane, Fig. 4 (Kurman et al., 2009a,b; Natelson et al., 2008).

Figure 4. Key species measured from *n*-dodecane oxidation at 8 atm pressure, 120 ms residence time, and 0.7 equivalence ratio.

In Year 2, the first objective was to close the carbon balance. The facility was modified with a new methodology for the direct injection of samples from the PFR to the GC/MS/FID. The new methodology is referred to as the Direct Transfer Controlled Cool Down (DT-CCD) methodology. The stainless steel transfer line was also replaced with a borosilicate glass-lined setup with optimized heating and insulation. The modified facility improved the results greatly. The number of intermediates identified from *n*-dodecane oxidation increased from 30 to 115, and the carbon balance is on average greater than 80%. Figure 5 shows the improved carbon balance with direct transfer of the sample from the PFR to the GC/MS/FID (Kurman et al., 2009a,b, 2011; Kurman, 2010).

Figure 5. Carbon Balance for Direct Transfer CCD experiment, with higher GC temperature ramp, greater MS scan range, lower fuel concentration, and leaner equivalence ratio.

After improving the carbon closure, a series of experiments for *n*-dodecane oxidation, to ensure reproducibility and estimate errors to use in model development, were completed in Year 3. Table 1 summarizes the initial experimental conditions for the three experiments. All experiments were conducted at 8.000 ± 0.025 atm pressure and 120 ± 10 ms residence time.
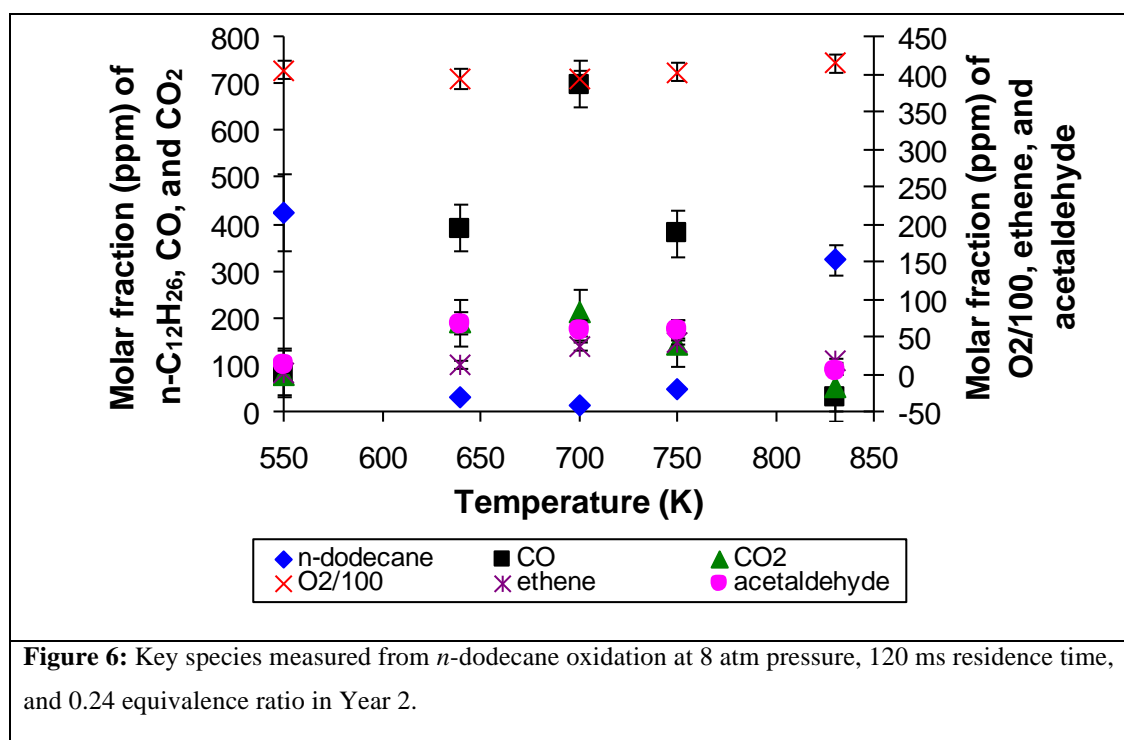
	5/5/2009	6/2/2009	6/4/2009	$\pm$
n-dodecane (ppm)	526	527	540	8
O_2 (ppm)	42,100	42,100	42,100	1250
N_2 (ppm)	Balance	Balance	Balance	-
Equivalence Ratio	0.23	0.23	0.24	0.05

Table 1. Initial conditions for PFR experiments with *n*-dodecane.

Compared to past work studying the oxidation of lighter hydrocarbons at these temperatures, key differences were the production of lactones and carboxylic acids and the high concentration of formaldehyde. Figure 6 shows representative reactivity results, plotting the average measurements of the three experiments. Error bars for carbon oxides and O_2 are based on equipment uncertainty of the non-dispersive infrared analyzer and electrochemical oxygen cell, respectively, and for *n*-dodecane, ethene, and acetaldehyde the error bars are ± 1 standard

deviation of the GC/MS/FID measurements. Figure 7 represents the carbon fraction for formaldehyde production from the PFR experiments along with comparison with formaldehyde production predictions given by the Livermore and Milano model (Kurman, 2010; Kurman et al., 2011). Work is underway to develop chemical mechanisms to account for the formation and consumption of non-alkylated lactones (Gupta et al., 2011).

Next a series of experiments exploring cycloalkane oxidation were conducted. Both *n*-butylcyclohexane (*n*-BCH) and *n*-propylcyclohexane (*n*-PCH) were studied in Year 3. *n*-BCH and *n*-PCH were selected because lighter alkylcyclohexanes (i.e. methylcyclohexane) are not reactive neat at PFR test conditions. In addition, *n*-PCH was studied after *n*-BCH to investigate the effect of alkyl side chain length. Table 2 summarizes the initial experimental conditions for *n*-BCH and Fig. 8 shows representative results. Sixty-five intermediates were identified from *n*-BCH oxidation, and carbon balances were greater than 95%. A semi-global, kinetic model describing the low-temperature reactivity of *n*-BCH has been developed consisting of 30 species and 45 reactions. Modeling results for carbon monoxide are compared in Fig. 8 (Natelson et al., 2009, 2011; Natelson, 2010b; Corrubia et al., 2011).
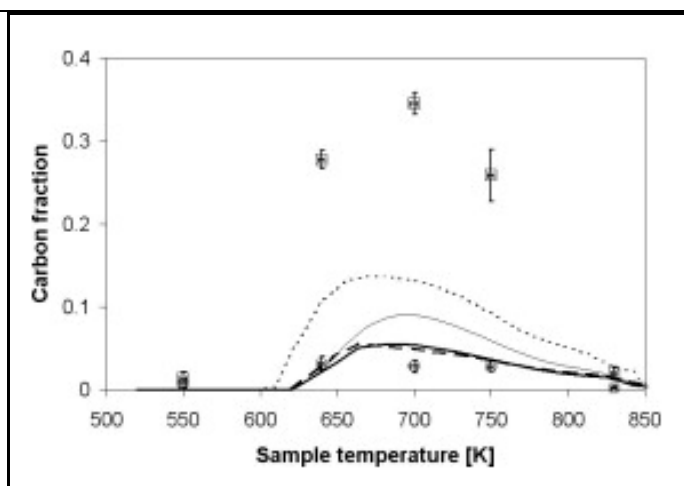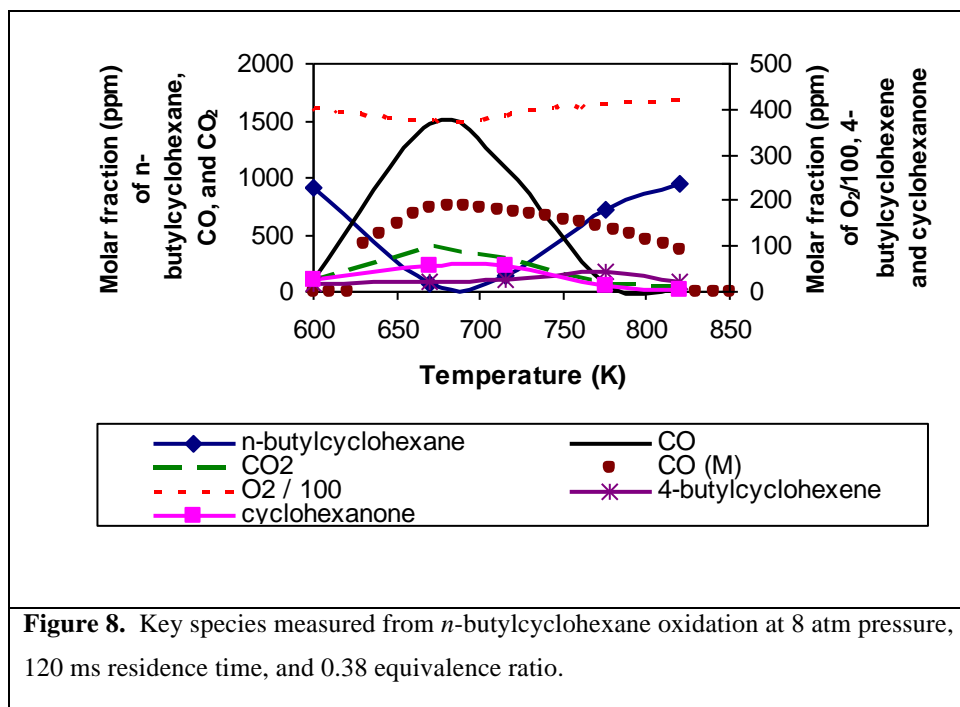

Figure 6: Key species measured from *n*-dodecane oxidation at 8 atm pressure, 120 ms residence time, and 0.24 equivalence ratio in Year 2.

Figure 7. Carbon fractions for formaldehyde from *n*-dodecane oxidation: (□) experimental, (—) Livermore, (—) Milano; and for acetaldehyde plus propanal: (○) experimental, (__ __ __) Livermore, (- - -) Milano.

	6/23/2009	6/30/2009	7/14/2009	±
n-butylcyclohexane (ppm)	1074	1068	1105	19
O_2 (ppm)	42,100	42,100	42,100	1250
N_2 (ppm)	Balance	Balance	Balance	-
Equivalence Ratio	0.23	0.23	0.24	0.05

Table 2. Initial conditions for PFR experiments with *n*-butylcyclohexane.

Figure 8. Key species measured from *n*-butylcyclohexane oxidation at 8 atm pressure, 120 ms residence time, and 0.38 equivalence ratio.

The *n*-propylcyclohexane experiment was performed with temperature range of 550-830 K, pressure of 8 atm and residence time of 120 ms. The initial reactant experimental conditions are given in Table 3. Figure 9 shows the reactivity map for *n*-PCH oxidation along with other representative results of species quantified at elevated levels relative to the remaining intermediates identified. While the detailed intermediate product analysis measured 70 species, only a few major species accounted for most of the initial carbon. Carbon balances ranged from 70% - 100% depending on the sample temperature. The low carbon balance of 70% occurred at 748 K, due to the large yield of heavy intermediates formed at this temperature that have been observed to condense upon contact with cold spots in the sample line. Major intermediates included carbon oxides (CO, CO_2), light aldehydes (1,3,5-trioxane, acetaldehyde, propanal), alkenes (ethene, propene) and cycloalkenes (4-propylcyclohexene, 1-propylcyclohexene). Similar species were identified and quantified with *n*-butylcyclohexane oxidation, thus suggesting similar reaction pathways among both. This study, along with previous work on *n*-butylcyclohexane, will be useful in developing insight into the effect of alkyl side chain length on cylcloalkane oxidation. Future experiments with *n*-propylcyclohexane are planned to establish reproducibility and uncertainties. Additionally, modeling with *n*-propylcyclohexane is planned for comparison with *n*-BCH results (Corrubia et al., 2011).

	9/16/2010	±
n-propylcyclohexane (ppm)	758	-
O_2 (ppm)	42,100	1250
N_2 (ppm)	Balance	-
Equivalence Ratio	0.24	0.05

Table 3. Initial conditions for PFR experiments with *n*-propylcyclohexane.

Figure 9. Key species measured from *n*-propylcyclohexane oxidation at 8 atm pressure, 120 ms residence time, and 0.24 equivalence ratio.
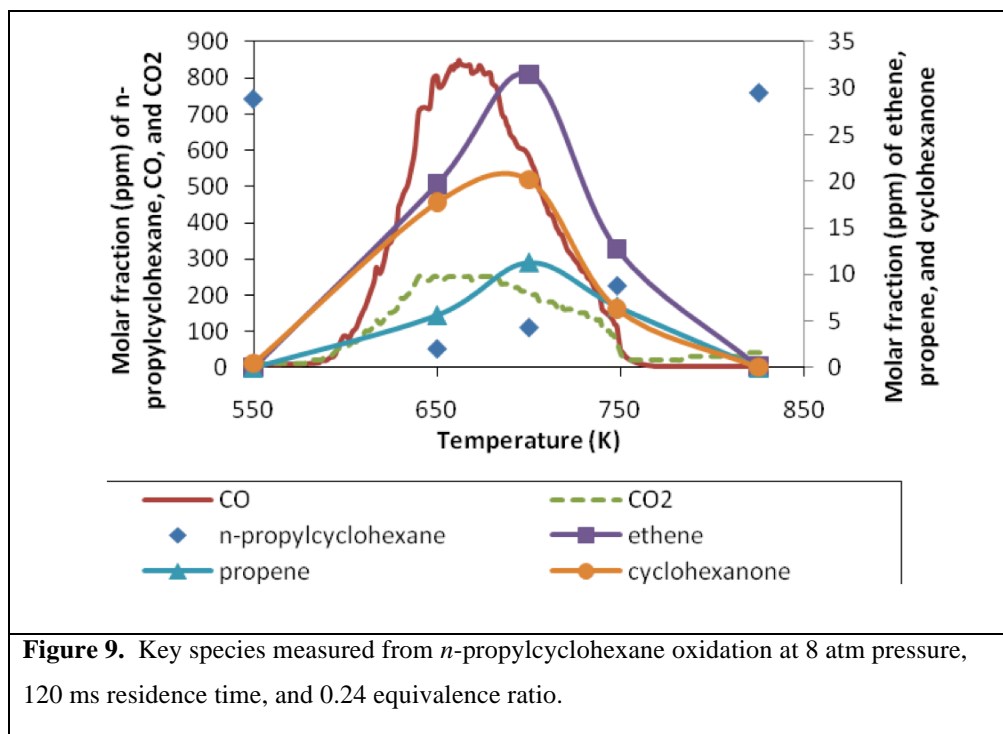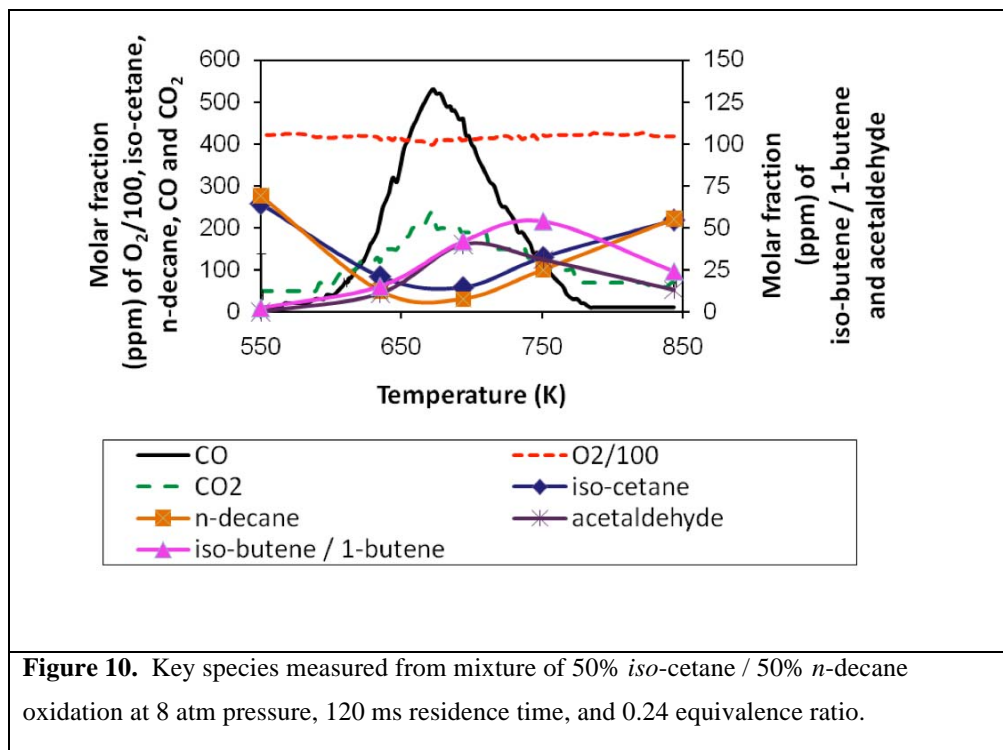
Also, in Year 3, experiments exploring the oxidation of an *iso*-alkane surrogate component, *iso*-cetane, were performed. The initial *iso*-cetane experiment was run with neat *iso*-cetane and insignificant reactivity was observed within experimental uncertainties. To initiate fuel decomposition the radical source surrogate component, *n*-decane, was selected as a blending fuel with *iso*-cetane. Table 4 summarizes the initial reactant experimental conditions for a temperature range of 550 – 850 K, pressure of 8 atm, and residence time of 120 ms. Figure 10

presents representative results for quantified intermediate species, such as, CO, CO_2, *iso*-cetane, *n*-decane, alkenes, and aldehydes (Farid et al., 2011).

	6/30/2010	8/12/2010	±
iso-cetane (% vol.)	100	50	-
n-decane (% vol.)	0	50	-
iso-cetane (ppm)	435	219	-
n-decane (ppm)	0	221	-
O_2 (ppm)	42,100	42,100	1250
N_2 (ppm)	Balance	Balance	-
Equivalence Ratio	0.23	0.23	0.05

Table 4. Initial conditions for PFR experiments with *iso*-cetane.

Figure 10. Key species measured from mixture of 50% *iso*-cetane / 50% *n*-decane oxidation at 8 atm pressure, 120 ms residence time, and 0.24 equivalence ratio.

Key achievements for the Drexel component of the Energy IPT program are:

- Identified temperature region of Negative Temperature Coefficient Behavior during the oxidation of neat *n*-dodecane, *n*-butylcyclohexane, *n*-propylcyclohexane and a binary mixture of *iso*-cetane / *n*-decane at 550-850 K temperatures, 8 atm pressure, and 120 ms residence time via measurements of CO and CO_2 (Kurman, 2009; Kurman et al., 2009a; Natelson et al., 2010a; Corrubia et al., 2011; Farid et al., 2011).

- Proved the applicability of flow reactor results to traditional preignition / autoignition behavior of large hydrocarbon oxidation (Kurman et al., 2011; Natelson et al., 2008, 2010a; Natelson, 2010a).

- Measured the relative reactivity of the xylene isomers as part of the Energy IPT evaluation of components of surrogates for JP-8 (Kurman et al., 2010; Natelson, 2010a; Natelson et al., 2010a,b).

- Improved the measurement of intermediate species formed during the PFR experiments by developing a direct sampling and measurement protocol that produced carbon closures better than 80% in the NTC region (Kurman et al., 2009b, Kurman, 2010; Natelson 2010a,b; Natelson et al., 2010b, 2011; Corrubia et al., 2011).

- Incorporated molecular oxygen measurements in the analytical stream of the PFR to allow examination of oxygen consumption and oxygen closure (Kurman et al., 2009b; Natelson, 2010a; Natelson et al., 2010a).

- Measured stable intermediate species from the oxidation of *n*-dodecane at 550-850 K temperatures, 8 atm pressure, and 120 ms residence time (Kurman, 2010; Kurman et al., 2009a,b, 2011; Natelson, 2010a).

- Measured "new" species from the oxidation of large hydrocarbons in this temperature regime, such as lactones, that modelers have suggested could be formed under these reaction conditions but had never been identified or quantified before. Additional experiments were conducted to exclude the possibility that these species were artifacts of sampling and analysis. Kinetic modeling work has begun to account for the production and consumption of non-alkylated lactones (Kurman, 2010; Kurman et al., 2009a,b, 2011; Natelson, 2010a,b; Natelson et al., 2010b; Gupta et al., 2011).

- Measured stable intermediate species from the oxidation of *n*-butylcyclohexane at 550-850 K temperatures, 8 atm pressure, and 120 ms residence time (Natelson, 2010b; Natelson et al., 2009, 2011).

- Produced a semi-global kinetic model predicting the low temperature oxidation behavior of *n*-butylcyclohexane (Natelson, 2010b; Natelson et al., 2011).

- Measured stable intermediate species from the oxidation of *n*-propylcyclohexane at 550-850 K temperatures, 8 atm pressure, and 120 ms residence time (Corrubia et al., 2011).

- Measured stable intermediate species from the oxidation of *iso*-cetane / *n*-decane mixtures at 550-850 K temperatures, 8 atm pressure, and 120 ms residence time (Farid et al., 2011).

5.2 Flow Reactor Studies, Stanford University

Representative experimental results for *n*-dodecane and comparisons with simulated profiles using the JetSurf 1.0 reaction mechanism are shown in Figs. 11 and 12. The comparisons of measured species profiles with profiles calculated using Jet Surf 1.0 indicate that the calculated reaction time scales are smaller than the measured ones.
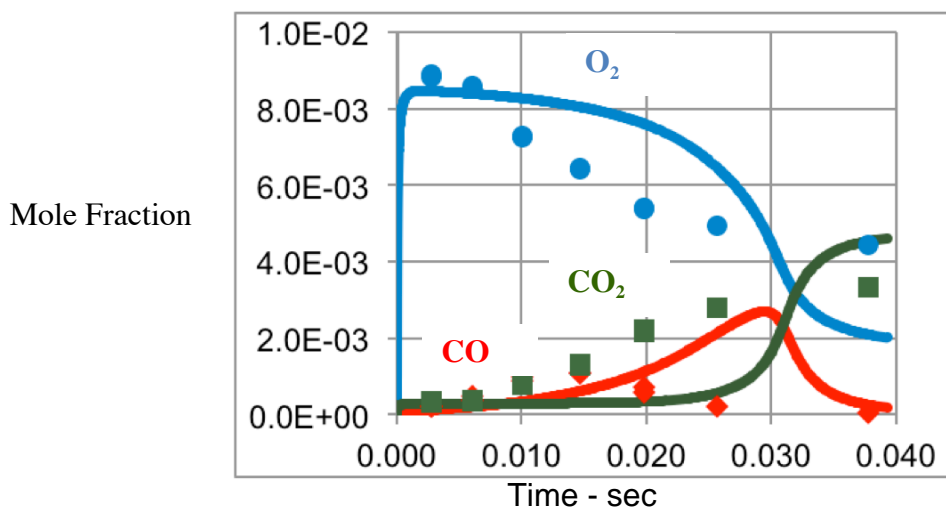

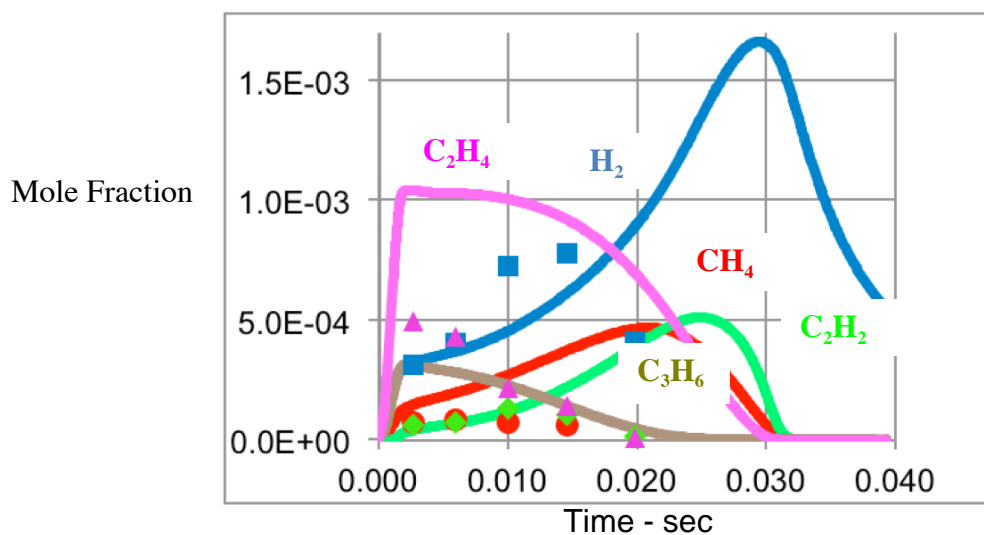**Figure 11**. Comparison of measured and calculated profiles of CO, CO_2 and O_2 for T = 1060K, p = 1 atm, and 290 ppm n-$C_{12}H_{26}$/8600 ppm O_2.

Figure 12. Comparison of measured and calculated profiles of CH_4, C_2H_2, C_2H_4, C_3H_6 and H_2 for the conditions of Fig. 11.

5.3 Shock Tube Studies, Stanford University

5.3.1   Species Time-Histories and Ignition Delay Times for Cyclo-Alkanes

Ignition delay times were measured behind reflected shock waves for cyclohexane, methylcyclohexane, and *n*-butylcyclohexane at 1.5 and 3 atm, equivalence ratios near 1 and 0.5, and temperatures between 1280 and 1480 K.   The observed ignition delay times can be summarized as follows: methylcyclohexane > *n*-butylcyclohexane ≈ cyclohexane. In this study, several reasons are suggested to explain the ordering of the ignition delay times for these three naphthenes. This work provides the first set of ignition delay time data for *n*-butylcyclohexane. In addition, H_2O and OH time-histories were recorded during the oxidation of cyclohexane, methylcyclohexane, *n*-butylcyclohexane, *iso*-octane, and *n*-heptane under similar test conditions. OH time-histories near time-zero are distinctive for each type of fuel studied, and these early-time OH profiles provides critical insight into the influence of molecular structures on ignition behavior, particularly in the case of the cycloalkanes. Comparisons of measured time-histories with simulations from recent cycloalkane oxidation mechanisms are presented also.   Further details on this study may be found in Hong et al. (2011).
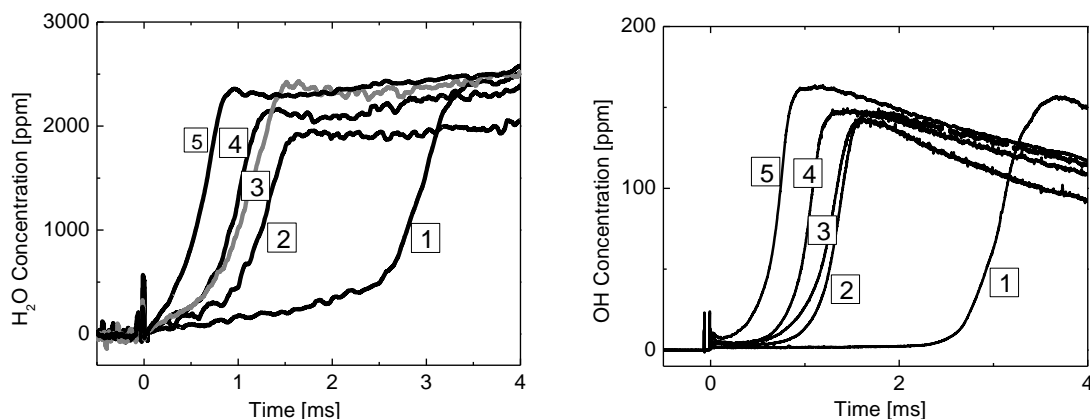

Figure 13. Comparison of H_2O and OH time-histories during oxidation for CH, MCH, BCH, *n*-heptane, and *iso*-octane. Reflected shock conditions for each experiment: 1) 1437 K, 2.2 atm, 350 ppm *iso*-octane/4400 ppm O_2/Ar; 2) 1435 K, 2.2 atm, 340 ppm MCH/4200 ppm O_2/Ar; 3) 1450 K, 2.2 atm, 310 ppm BCH/4200 ppm O_2/Ar; 4) 1441 K, 2.2 atm, 467 ppm CH/4200 ppm O_2/Ar; 5) 1427 K, 2.2 atm, 400 ppm *n*-heptane/4400 ppm O_2/Ar.

5.3.2 Ethylene Time-History Measurements

Ethylene concentration time-histories were measured behind reflected shock waves during the pyrolysis of ethylene, *n*-heptane and methylcyclohexane (MCH) using CO_2 laser absorption spectroscopy. Ethylene was detected implementing the method of Pilla et al. (2010) focusing on the absorption of the P14 line in the $(0\ 0\ 1) \rightarrow (1\ 0\ 0)$ vibrational band of CO_2 at 10.532 μm, but with an improved SNR achieved by utilizing IR photovoltaic detectors and better identification of the P14 line via a MIR wavemeter. Pyrolysis experiments for the three fuels were conducted at temperatures of 1252-1973 K and pressures of 1.92-3.17 atm, with fuel concentrations of 0.1%-1% in argon. Measured ethylene time-histories during *n*-heptane and MCH pyrolysis were compared to the modeled predictions of JetSurF 2.0 mechanisms (Wang et al., 2010), and the kinetic implications of these measurements are discussed. This improved laser absorption diagnostic of ethylene can provide essential information regarding the reaction paths and rates of the formation of alkenes during alkane pyrolysis and oxidation. Further details on this study can be found in Ren et al. (2011)
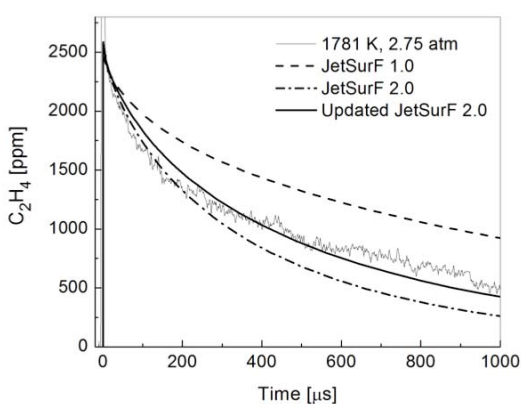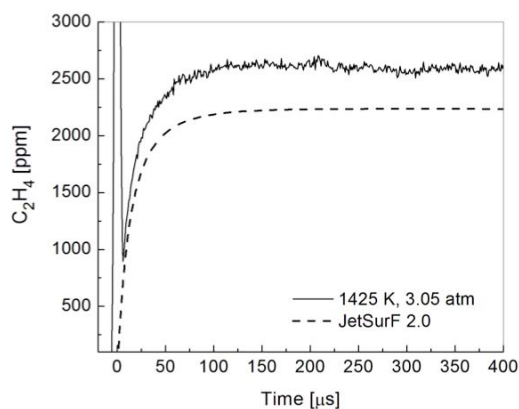
(a) 1781 K, 2.75 atm   (b) 1425 K, 3.05 atm

Figure 14. Ethylene time-histories during the pyrolysis of 1000 ppm *n*-heptane in argon.

5.3.3 Species Time-Histories for n-Dodecane

Concentration time-histories were measured behind reflected shock waves during *n*-dodecane oxidation for five species: *n*-dodecane, C_2H_4, OH, CO_2, and H_2O. Experiments were conducted at temperatures of 1300 to 1600 K and a pressure of 2 atm using mixtures of 400 ppm *n*-dodecane and 7400 ppm oxygen (ϕ=1) in argon. *n*-Dodecane and ethylene were monitored using IR gas laser absorption at 3.39 and 10.53 microns, respectively; OH was monitored using UV laser absorption at 306.5 nm; and CO_2 and H_2O were monitored using tunable IR diode laser absorption at 2.7 and 2.5 microns, respectively. These time-histories provide kinetic targets to test and refine large reaction mechanisms for *n*-dodecane and demonstrate the potential of this type of data for validation of large reaction mechanisms. Comparisons are made with the predictions of two recently developed large-alkane reaction mechanisms, and the need for improved rate measurements of higher alkene reactions is discussed. Further details of this study can be found in Davidson et al. (2011).
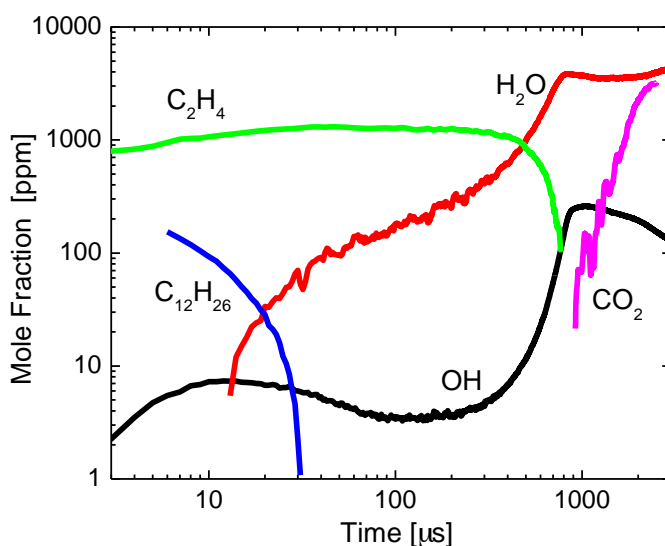

Figure 15. Species time-history measurements for n-dodecane oxidation. Nominal initial conditions: 1410 K, 2.3 atm, 457 ppm *n*-dodecane/O_2/argon, ϕ=1.

5.3.4 Species Time-Histories for n-Heptane

Concentration time-histories were measured behind reflected shock waves during *n*-heptane oxidation for five species: *n*-heptane, C_2H_4, OH, CO_2, and H_2O. Experiments were conducted at temperatures of 1300 to 1600 K and a pressure of 2 atm using a mixture of 300 ppm *n*-heptane and 3300 ppm oxygen ($\phi=1$) in argon. *n*-Heptane and ethylene were monitored using IR gas laser absorption at 3.39 and 10.53 microns, respectively; OH was monitored using UV laser absorption at 306.5 nm; and CO_2 and H_2O were monitored using tunable IR diode laser absorption at 2.7 and 2.5 microns, respectively. These time-histories provide kinetic targets to test and refine large reaction mechanisms for n-heptane and demonstrate the potential of this type of data for validation of large reaction mechanisms. Comparisons are made with the predictions of several recently developed reaction mechanisms. Further details of this study can be found in Davidson et al. (2010a).
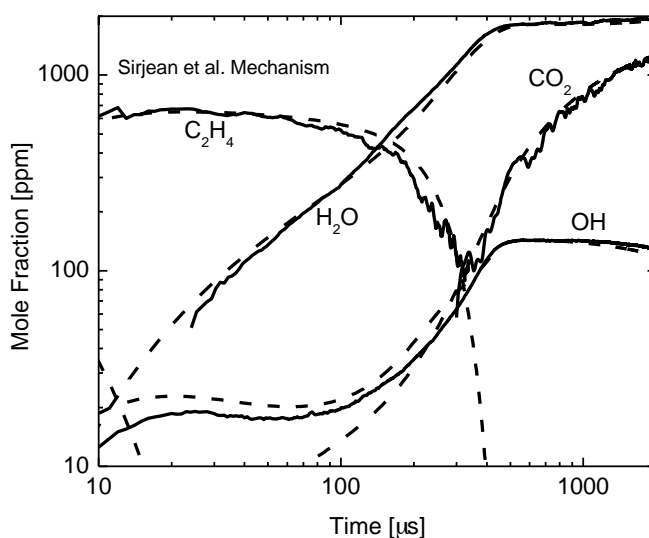

Figure 16. Comparison of laser absorption measurements with the Sirjean et al. (2009) JetSurf model. Reflected shock wave conditions: 1494 K, 2.15 atm, 300 ppm n-heptane/O_2/argon, $\phi=1$.

5.3.5 *Ignition Delay Times for C_5-C_9 n-Alkanes*

Ignition delay time data for higher *n*-alkanes are required for the development and refinement of jet fuel surrogate mechanisms. To fill this need, ignition delay times were measured using pressure and OH* emission diagnostics behind reflected shock waves for a series of higher *n*-alkanes. Reflected shock conditions covered temperatures of 1150-1550 K and pressures of 1-4 atm. Fuel mixtures tested include the four *n*-alkanes: *n*-pentane, *n*-hexane, *n*-octane, and *n*-nonane. All fuels were tested in O_2/argon mixtures with equivalence ratios of 0.5 to 2.0. The *n*-alkane ignition data were compared with the JetSurF reaction mechanism of Sirjean et al. (2009). Further details of this study can be found in Davidson et al. (2010b).
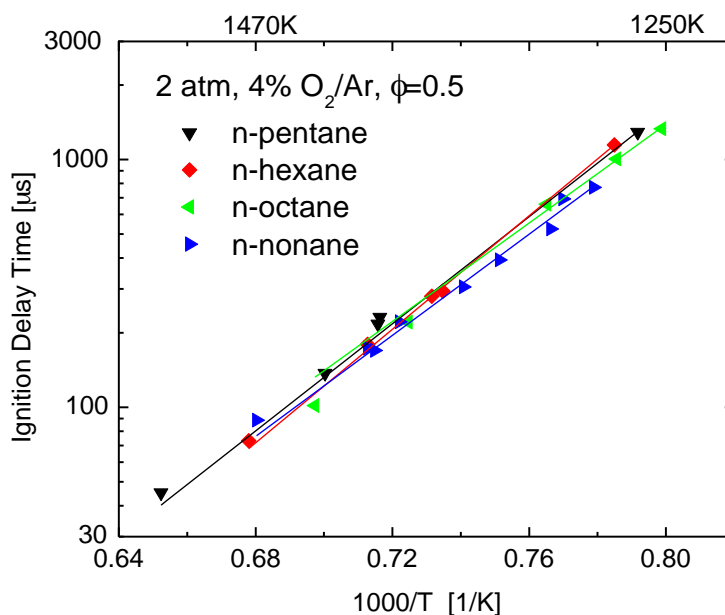

Figure 17. Arrhenius plot of *n*-alkane ignition delay times: ϕ=0.5, 4% O_2/argon, 2 atm.

5.4 Flame Studies, Princeton University

In an effort to improve the current understanding of confined flame propagation and to determine laminar flame speeds more accurately through extrapolations from high-pressure spherical flame propagation data, an analytical derivation describing the propagation of confined flames was conducted (Kelley *et al.*, 2011). While many theoretical derivations restrict the Lewis number (the ratio of thermal to mass diffusivity) to be near unity, the present work focused on non-unity Lewis numbers as the components of Jet Fuel and Jet Fuel surrogates often have Lewis numbers that substantially deviate from unity. The analytical work resulted in a new understanding of the influence of adiabatic compression resulting from constant volume combustion, and yielded an improved extrapolation equation for use in extrapolating experimental measurements to determine laminar flame speeds.

Using this improved extrapolation procedure laminar flame speeds for cyclohexane, methylcyclohexane, and ethylcyclohexane were obtained using a high-pressure, high-temperature, dual-chamber combustion vessel. Measurements were obtained at 1, 2, 5, and 10 atm initial pressures, and an initial temperature of 353 K. These measurements were found to be in good agreement with the measurements of Ji *et al.* (2011), taken at atmospheric pressure. Cyclohexane was found to have a higher flame speed than *n*-hexane, which is higher than methyl-cyclohexane. This trend was realized also by Ji *et al.* (2011) and has been extended now to elevated pressures. Further details of this study can be found in Kelley et al. (2011).
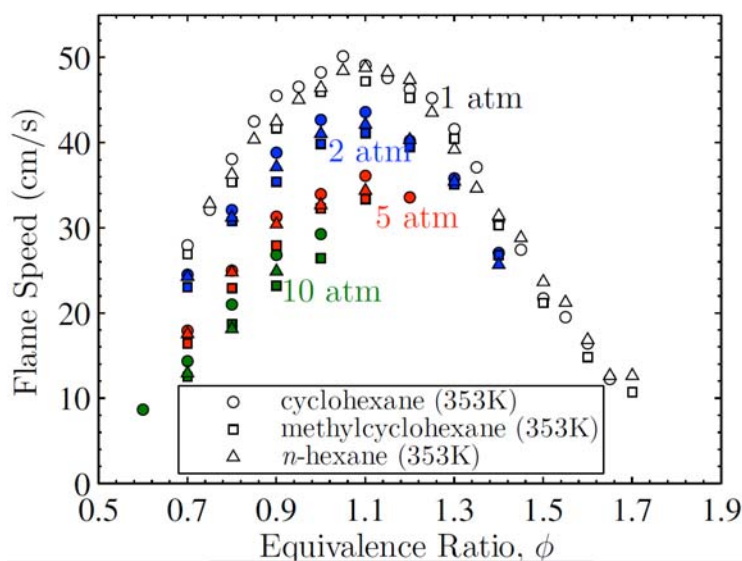

Figure 18. Laminar flame speed measurements for cyclohexane, methylcyclohexane, and *n*-hexane at various pressures, 353K. Data were extrapolated using a new extrapolation procedure (Kelley et al., 2011).

5.5 Flame Studies, University of Southern California

5.5.1 Experimental and Modeling Studies on the Ignition, Propagation, and Extinction of C_3-C_{12} n-Alkane Flames

Ignition temperatures, laminar flame speeds, and extinction strain rates of premixed and non-premixed C_3-C_{12} n-alkane flames were determined at atmospheric pressure and elevated unburned mixture temperatures, over a wide range of reactant compositions. The laminar flame speeds were obtained using a non-linear extrapolation technique utilizing numerical simulations of the counterflow experiments with detailed descriptions of chemical kinetics and molecular transport. 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 the equivalence ratio. It was determined that the laminar flame speeds 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. The laminar flame speeds are predicted with good accuracy for all the n-alkane-air mixtures considered. The experimental extinction strain rates are well predicted by the model for fuel-lean mixtures. The ignition temperatures of non-premixed flames are consistently overpredicted using the JetSurF kinetic model. Further details can be found in You et al. (2009), Holley et al. (2009), Ji et al. (2010), and Liu et al. (2011).
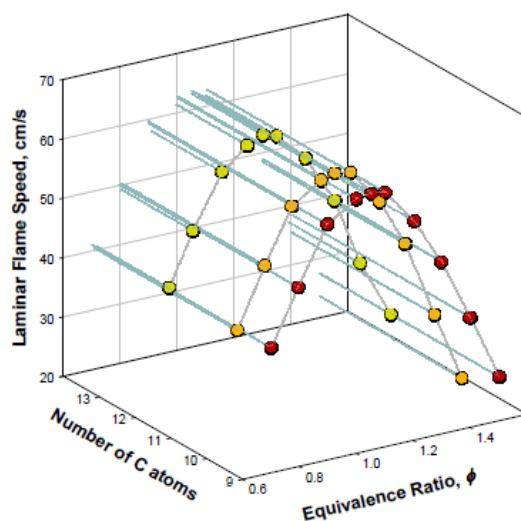

Figure 19. Comparison of experimentally determined laminar flame speeds of mixtures of air with n-C_9H_{20}, n-$C_{10}H_{22}$, and n-$C_{12}H_{26}$ at $T_u = 403$ K.

5.5.2   Propagation of Cyclohexane and Mono-Alkylated Cyclohexane Flames

Laminar flame speeds of cyclohexane/air, methylcyclohexane/air, ethylcyclohexane/air, *n*-propylcyclohexane/air, and *n*-butylcyclohexane/air mixtures were measured in the counterflow configuration at atmospheric pressure, unburned mixture temperature of 353 K, and for a wide range of equivalence ratios.   The results indicate 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 laminar flame speeds, suggesting that the different alkyl groups have a secondary effect on flame propagation. The experimental data were modeled using JetSurF (version 1.1) - a detailed kinetic 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 are 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 do exert influences on flame propagation, leading to the subtle differences in the laminar flame speeds that were observed experimentally. Further details of this study can be found in Ji et al. (2011a).
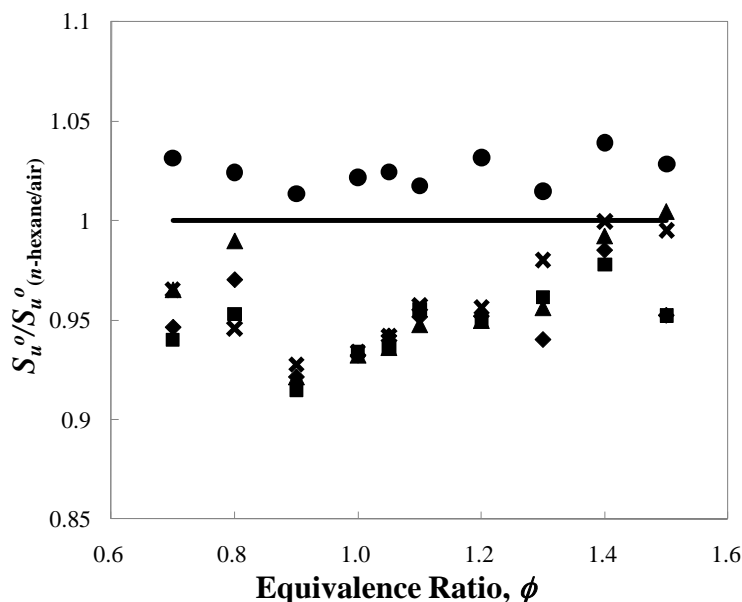

Figure 20. Comparison of experimentally determined laminar flame speeds of (●) cyclohexane/air, (◆) methylcyclohexane/air, (■) ethylcyclohexane/air, (✗) *n*-propylcyclohexane/air, and (▲) *n*-butylcyclohexane/air flames relative to those of (—) *n*-hexane/air flames at $T_u = 353$ K.

5.5.3   Flame Propagation of Mixtures of Air with Binary Liquid Fuel Mixtures

The laminar flame speeds of mixtures of air with 80% *n*-dodecane + 20% methylcyclohexane and 80% *n*-dodecane + 20% toluene, on a per volume basis, were determined in the counterflow configuration over a wide range of equivalence ratio, at atmospheric pressure and 403 K unburned mixture temperature. The choice of the fuel blends was dictated by their anticipated compositions in jet fuels surrogates. Phenomenological analysis shows that the laminar flame speeds of binary fuels mixtures can be estimated using the laminar flame speeds and adiabatic flame temperatures of the neat components. The propagation rates of 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 binary fuel flames is 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. Further details of this study can be found in Ji and Egolfopoulos (2011a).

Figure 21. Computed and estimated laminar flame speeds of *n*-dodecane/toluene/air mixtures and *n*-dodecane/methylcyclohexane/air mixtures at $\phi = 0.7$, 1.0, and 1.4 as a function of fuel blending ratio. Symbols: ($\diamond$) computed adiabatic flame temperatures of *n*-dodecane/toluene/air mixtures and ($\triangle$) *n*-dodecane/methylcyclohexane/air mixt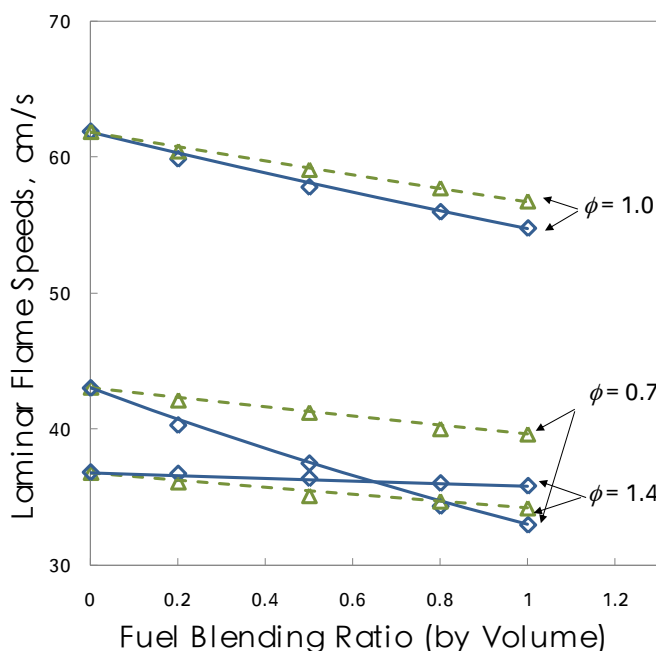ures. Lines: (—) estimated laminar flame speeds of *n*-dodecane/toluene/air mixtures and (---) *n*-dodecane/methylcyclohexane/air mixtures. The x-axis indicates the fuel-blending ratio by volume, 0 indicates pure *n*-dodecane and 1 for pure toluene or pure methylcyclohexane.

5.5.4   Flame Studies of Conventional and Alternative Jet Fuels

Laminar flame speeds and extinction limits of premixed and non-premixed flames of conventional, such as JP-7 and JP-8, and alternative, such as synthetic and bio-derived, jet fuels were determined in the counterflow configuration at atmospheric pressure and elevated unburned reactant temperature. The results were compared against those of flames of n-decane and n-dodecane, both being candidate components of jet fuel surrogates. Results indicate that JP-8/air and JP-7/air flames exhibit lower propagation speeds and resistance to extinction compared to flames of alternative fuels. The reduced reactivities of JP-8/air and JP-7/air flames are caused by the alkyl-cycloparaffins and alkyl-benzenes that are present in notable quantities in conventional jet fuels. The combustion characteristics of bio-derived jet fuels were found to be indistinguishable from those produced synthetically via the Fischer-Tropsch process. The phenomena of flame propagation and extinction were modeled using *n*-decane and *n*-dodecane flames, for which kinetic models are available and whose molecular weight is representative of that of practical jet fuels. Further details of this study can be found in Ji et al. (2011b).
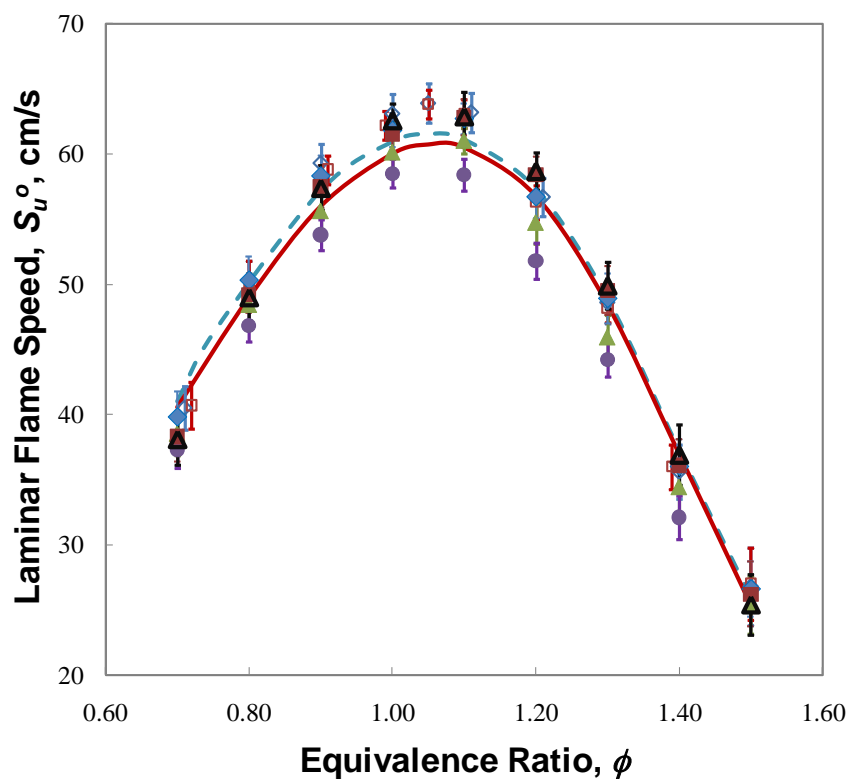
Figure 22. Experimentally determined laminar flame speeds at T_u = 403 K of JP-7/air (▲), JP-8/air (●), S-8/air (♦), Shell-GTL/air (△), R-8/air (■), $n\text{-}C_{10}H_{22}$/air (◇) [24], and $n\text{-}C_{12}H_{26}$/air (□) [24]. Computed laminar flame speeds of $n\text{-}C_{10}H_{22}$/air (···) and $n\text{-}C_{12}H_{26}$/air (—) mixtures using JetSurF 1.0 kinetic model.

5.5.5 *Propagation and Extinction of Benzene and Alkylated Benzenes Flames*

Laminar flame speeds and extinction strain rates of premixed and non-premixed flames of benzene, *n*-propylbenzene, toluene, *o*-, *m*-, and *p*-xylene, and *1,2,4-* and *1,3,5*-trimethylbenzene were determined experimentally and computationally in the counterflow configuration under atmospheric pressure and at elevated unburned mixture temperature. The experimental data revealed that benzene/air mixtures propagate fastest, followed by *n*-propylbenzene/air, toluene/air, xylene-isomers(*o*-, *m*-, *p*-)/air, and trimethylbenzene-isomers(*1,2,4-*, *1,3,5-*)/air flames in descending order. The propagation of aromatics flames was determined to be sensitive on the chemistry of products resulting from the initial fuel consumption. The initial products of fuel consumption in methylated benzene flames (like benzyl and methylbenzyl) were found to be more stable than those in benzene flames (i.e., phenyl), and they are mostly consumed through the reaction with O atom such that the attached methylene group can be transferred to formyl group, which is then assumed to be detached from the ring easily. The reactivity of methylated benzene was shown to decrease monotonously with the increase of the methyl group number. Regarding *n*-propylbenzene, it was found that its consumption produces approximately equal amounts of benzyl and phenyl radicals during its initial consumption, exhibiting thus an intermediate reactivity between benzene and methylated benzenes. The extinction of non-premixed flames was found to reveal more discriminative differences in the reactivity among the three xylene isomers compared to flame propagation. The *o*-xylene/air mixtures were shown to have the highest reactivity, followed by *m*-xylene, and *p*-xylene flames in descending order. Similarly, *1,2,4*-trimethylbenzene flames were found to have a higher reactivity compared to *1,3,5*-trimethylbenzene. The results indicate that the isomer of methylated benzenes with one adjacent methyl pair shows higher reactivity than those with isolated methyl substituents. Further details of this study can be found in Ji and Egolfopoulos (2011b).

5.6   *Flame Modeling Studies, Stanford University*

The validity of the one-dimensional assumption and the procedure used to extrapolate strained burning velocities to determine the unstretched laminar flame speed (Ji et al., 2010) was assessed. Direct numerical simulations of the experimental setup were performed and results were compared with a one-dimensional similarity formulation. The simulation domain is shown in Fig. 23. Very good agreement demonstrating the validity of the one-dimensional assumption was found if a top-hat nozzle exit velocity profile is used. However, it was determined that the non-linear extrapolation function, which is based on results from a one-dimensional formulation, is not as good, if strong non-uniformities in the nozzle exit velocity are present. This difference stems from significant radial temperature curvature effects on the centerline due to the non-uniform velocity. Including the radial curvature in the one-dimensional formulation leads to the correct extrapolation as shown in Fig. 24. Thus, experimental studies measuring laminar flame speeds need to ensure that the nozzle velocity profile is very close to a top-hat. If that is not feasible, the radial temperature curvature profile needs to be estimated and considered in the one-dimensional simulations in order to obtain the correct laminar burning velocity. Further details of this study can be found in Mittal et al. (2011).
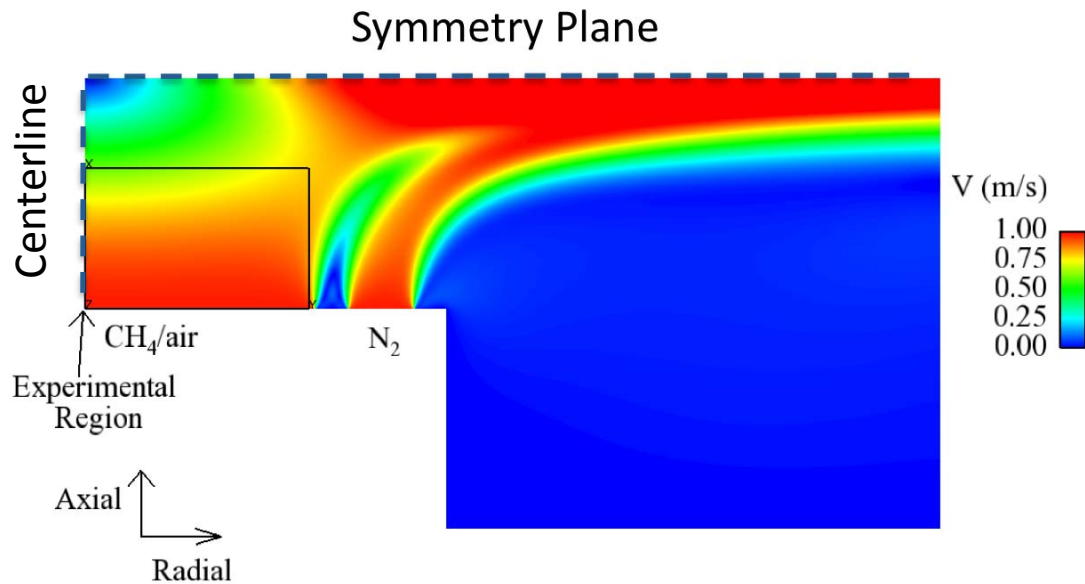
Figure 23. Simulation domain.
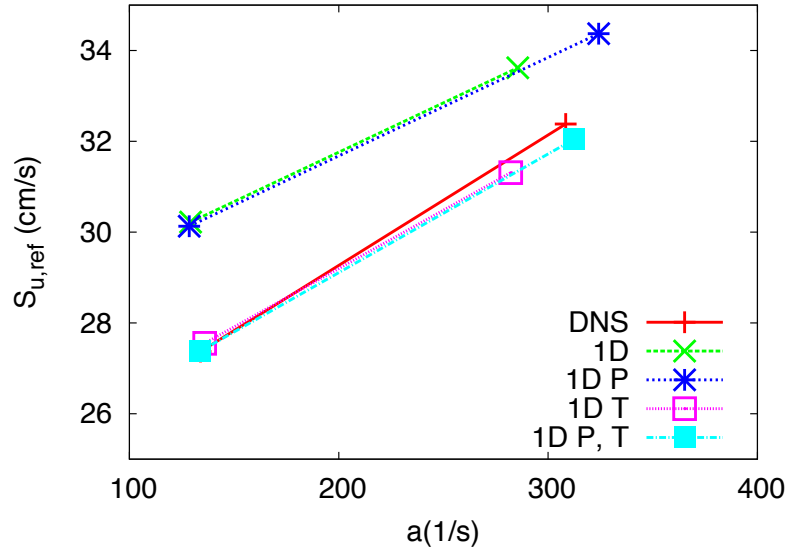
Figure 24. Variation of reference flame speed, $S_{u,ref}$, with stretch, a,, for various experimental nozzle velocity profiles in which different curvature effects are present. 1D represents runs with the original one-dimensional formulation. 1D P represents simulations when the non-uniform pressure curvature is included from the DNS. 1D T provides data for the runs when the radial temperature curvature is included from the DNS. Similarly, 1D P,T represents runs when the non-uniform radial curvature of temperature and pressure is included.

5.7 Theoretical and Modeling Studies, University of Southern California

5.7.1 Kinetic Foundation Model for C_{1-4} Hydrocarbons

USC Mech II (Wang et al., 2007) has been used as the kinetic foundation model for JetSurF. The model was constructed based on a wide variety of modeling studies and ab initio calculations (Davis et al., 1999a,b,c; Qin et al., 2000; Laskin and Wang, 1999; Laskin et al., 2000; Davis et al., 2005; Joshi and Wang, 2006; You et al., 2007). Since its online publication, USC Mech II has been re-examined through the course of the current project. In particular, the underlying uncertainty of the model was studied in detail using MUM-PCE (Sheen et al., 2009; Sheen and Wang, 2011b,c). For example, Fig. 25 shows the computed 2σ standard deviation of USC Mech II when it was used to predict the laminar flame speed of ethylene-air mixtures at 5 atm. The shaded band represents the probability density function of the prediction uncertainty. Methods have also been developed to narrow the predictive uncertainty on the basis of experimental data (Davis et al., 2009; Davis and Wang, 2011b).
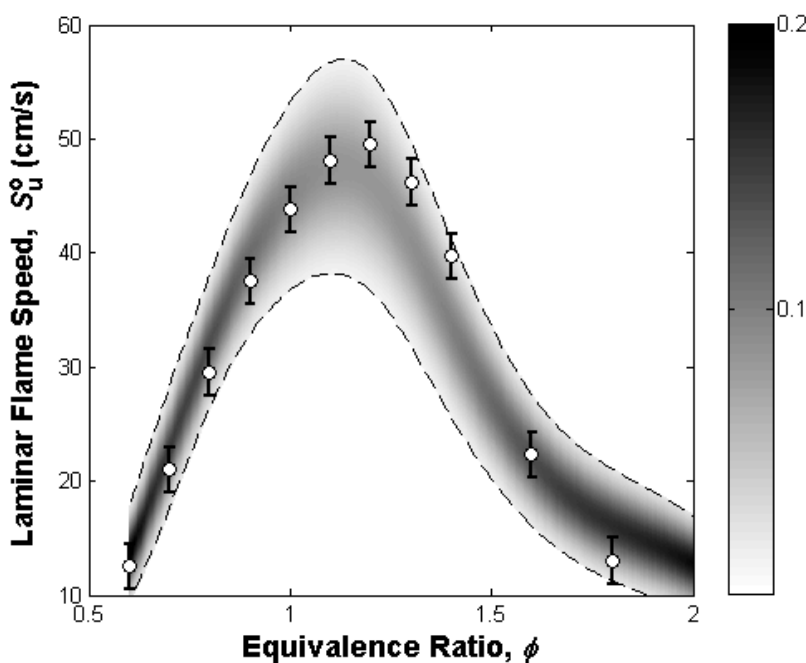

Figure 25. Variation of laminar flame speed of ethylene-air mixture with equivalence ratio at 5 atm. Symbols are the data from Jomaas et al. (2005). The shaded bands indicate the 2σ standard deviation on the model prediction uncertainty; color indicates the probability density as indicated by the color bar, and the actual $\pm 2\sigma$ curves are indicated by the dashed lines.

5.7.2   Kinetic Modules and Advanced Transport Models for the Single-Component n-, iso-, and Cyclo-Paraffins

JetSurF 2.0 (Wang et al., 2010) was developed in two steps. In the first step, USC Mech II was appended by a set of reactions describing the high-temperature pyrolysis and oxidation of n-alkanes from *n*-pentane to *n*-dodecane, leading to the release of JetSurF1.0 (Sirjean et al., 2009a). In the second step, the high-temperature chemistry of cyclohexane and mono-alkylated cyclohexane was added, leading to the release of JetSurF1.1 (Sirjean et al., 2009b). A unique feature of JetSurF is that it includes a rigorous description of its predictive uncertainty, as will be discussed later.

JetSurF and its various versions have been tested extensively over a wide range of conditions, as documented on the JetSurF web page (http://melchior.usc.edu/JetSurF/JetSurF2.0/Index.html). Additional tests were made in numerous publications of the all PIs involved in this effort (e.g., Holley et al., 2009; Ji et al., 2010, 2011; Sheen and Wang, 2011a; Tangko et al., 2011) and can be found elsewhere in this report.

5.7.3   Kinetic Models and Advanced Transport Models for Simple Aromatic Components

The abundance of recent literature concerning elementary rate parameters for aromatic compounds highlights the need for an updated chemical model accurately reflecting the current state of knowledge. In particular, the work on the products of benzene + $O(^3P)$ (Taatjes et al., 2010) is expected to have a great impact on all aromatics combustion reaction models, since this reaction is of critical importance to ring breakdown and secondary chain branching.

A model for the high-temperature oxidation of benzene and toluene is proposed using the most recently available kinetic parameters. As a hierarchical extension to USC Mech II, validations against experimental data obtained from shock tubes, flow reactors, and laminar premixed flames illustrate the need for further improvements. The results show that updating the benzene + O reactions in USC Mech II led to a considerable difference in overall model results. The inclusion of new and updated single-ringed aromatics rates made minor difference in improving model performance against laminar flame speeds. In general, the overall oxidation rates are slower than those predicted with USC Mech II, suggesting there may be inadequately described oxidation pathways in our current understanding of the chemistry of aromatics

oxidation. Among the possibilities, phenol and cyclopentadiene chemistry should be further investigated. This work has been reported in Dames and Wang (2010).

5.7.4 Development of Robust Methods for Detailed Kinetic Model Reduction that Consider Uncertainty Propagation

Reliable simulations of reacting flow systems require a well-characterized, detailed chemical model as a foundation. Accuracy of such a model can be assured, in principle, by systematic studies of individual rate coefficients. However, the inherent uncertainties in the rate data leave a model still characterized by a kinetic rate parameter space, which will be persistently finite in its size. Without a careful analysis of how this uncertainty space propagates into the model predictions, those predictions can at best be trusted only semi-quantitatively. In this work, the Method of Uncertainty Minimization using Polynomial Chaos Expansions (MUM-PCE) is proposed to quantify these uncertainties. An as-compiled, detailed $H_2/CO/C_1$-C_4 kinetic model and a set of ethylene combustion data are used as an example. In this method, the uncertainty in the rate parameters of the as-compiled model is quantified. Then, the model is subjected to a rigorous mathematical analysis by constraining the rate coefficients against the combustion data, as well as a consistency-screening process. Lastly, the uncertainty of the constrained model is calculated using an inverse spectral technique, and then propagated into a range of simulation conditions to demonstrate the utilities and limitations of the method.

MUM-PCE has been applied to quantify the uncertainty of JetSurF 2.0. For example, Fig. 26 illustrates a comparison of the experimental data (Vasu et al., 2009) and the JetSurF predictions. The small dots shown Fig. 26 were computed by a Monte Carlo sampling of the reaction rate parameter uncertainties. As seen, the predictive uncertainty is substantially larger than low temperatures than at high temperatures. The ability of MUM-PCE in quantifying the kinetic uncertainty allows for the design of more effective experiments that can constrain the model uncertainty in a systematic fashion. In this way, true progress in the accuracy and fundamental validity of the model may now be measured.
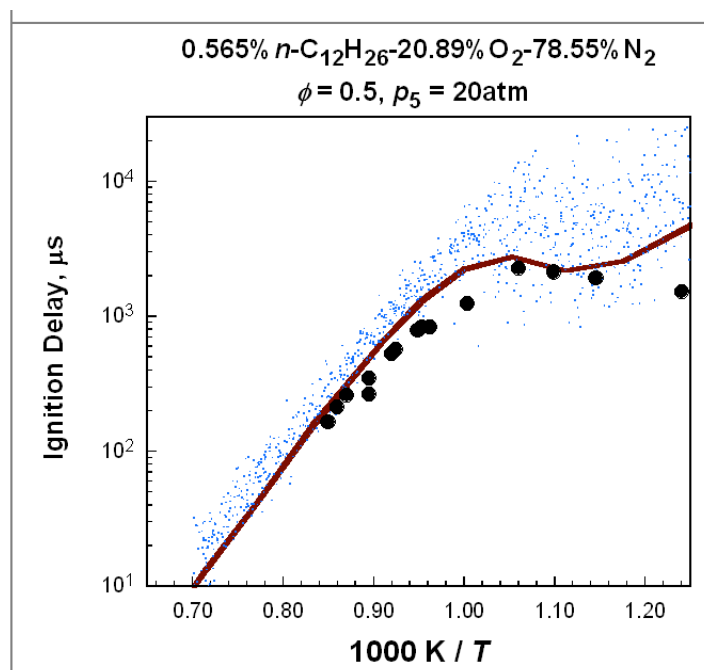
Figure 26. Comparison of the experimental (solid circles, Vasu et al., 2009) and computed (line and small dots) ignition delay time of *n*-dodecane oxidation in oxygen diluted with argon.

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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**: 403-410 (2009).

7.0 Personnel

This research was performed by the PIs, a number of research associates, and a number of graduate research assistants.

8.0 Archival Publications

Cernasky/Miller (Drexel University)

Corrubia, J.A., Farid, F., Cernansky, N.P., Miller, D.L., "The Low to Intermediate Temperature Oxidation of *n*-Propylcyclohexane in a Pressurized Flow Reactor," in preparation (2011).

Farid, F., Corrubia, J.A., Cernansky, N.P., Miller, D.L., "The Low to Intermediate Temperature Oxidation of *iso*-Cetane/*n*-Decane Mixtures in a Pressurized Flow Reactor," in preparation (2011).

Gupta, A., Miller, D.L., Cernansky, N.P., "Development of a Low-Temperature Hydrocarbon Kinetic Mechanism which Forms Non-Alkylated Lactones," in preparation for submission to Combustion Science and Technology (2011).

Kurman, M.S. "The Preignition and Autoignition Oxidation of Alternatives to Petroleum Derived JP-8 and their Surrogate Components in a Pressurized Flow Reactor and Single Cylinder Research Engine," M.S. Thesis, Drexel University, Philadelphia, PA, (2009).

Kurman, M.S., "The Preignition Oxidation Chemistry of *n*-Decane and *n*-Dodecane in a Pressurized Flow Reactor and Their Use as Jet Fuel Surrogate Components," Ph.D. Dissertation, Drexel University, Philadelphia, PA, (2010).

Kurman, M.S., Natelson, R.H., Cernansky, N.P., Miller, D.L., "Speciation of the Reaction Intermediates from *n*-Dodecane Oxidation in the Low Temperature Regime," *Proceedings of the Combustion Institute*, **33**, Issue 1, pp. 159-166, (2011).

Natelson, R.H., Kurman, M.S., Cernansky, N.P., Miller, D.L., "Experimental Investigation of Surrogates for Jet and Diesel Fuels," *Fuel*, **87**, pp. 2339-2342, (2008).

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Bowman/Hanson/Pitsch (Stanford University)

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Davidson, D.F., Ranganath, S.C., Lam, K.-Y., Liaw, M., Hong, Z., Hanson, R.K., "Ignition Delay Time Measurements of Normal Alkanes and Simple Oxygenates," *Journal of Propulsion and Power* **26** pp. 280-287 (2010).

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Hanson, R.K., "Application of Quantitative Laser Sensors to Kinetics, Propulsion and Practical Energy Systems," *Proceedings of the Combustion Institute* **33**, pp. 1-40 (2011).

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Law (Princeton University)

Kelley, A. P., Law, C. K., "Nonlinear Effects in the Extraction of Laminar Flame Speeds from Expanding Spherical Flames," *Combustion and Flame* **156**, pp. 1844-1851 (2009).

Kelley, A. P., Bechtold, J. K, Law, C. K., "Propagation of Confined Premixed Flames", *Journal of Fluid Mechanics*, *submitted* (2011).

Kelley, A. P., Smallbone, A. J., Zhu, D. L., Law, C. K., "Laminar Flame Speeds of C_5 to C_8 *n*-Alkanes at Elevated Pressures: Experimental Determination, Fuel Similarity, and Stretch Sensitivity," *Proceedings of the Combustion Institute* **33**, pp. 963-970 (2011).

Kelley, A. P. Liu, W., Xin, Y.X., Smallbone, A. J., Law, C. K., "Laminar Flame Speeds, Non-Premixed Stagnation Ignition, and Reduced Mechanisms in the Oxidation of *iso*-Octane," *Proceedings of the Combustion Institute* **33**, pp. 501-508 (2011).

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Egolfopoulos/Wang (University of Southern California)

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**: 1157-1163 (2009).

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Ji, C., Egolfopoulos, F.N., "Flame Propagation of Mixtures of Air with Binary Liquid Fuel Mixtures," *Proceedings of the Combustion Institute* **33:** 955-961 (2011).

Ji, C., Egolfopoulos, F.N., "Propagation and Extinction of Benzene and Alkylated Benzene Flames," in preparation (2011).

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Taatjes, C.A., Osborn, D.L., Selby, T.M., Meloni, G., Trevitt, A.J., Epifanivskii, E., Krylov, A.I., Sirjean, B., Dames, E., Wang, H., "Products of the Benzene + O(^{3}P) Reaction," *Journal of Physical Chemistry A*, **114**, 3355-3370 (2010).

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**: 403-410 (2009).

9.0 Interactions/Transitions

9.1 Presentations at Meetings and Conferences

Cernansky/Miller (Drexel University)

"Development of Detailed and Reduced Kinetic Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels: Drexel Flow Reactor Studies at Low and Intermediate Temperatures," Miller, D.L., Cernansky, N.P., presented at the *Multi-Agency Coordination Committee Combustion Research Fuels Research Review*, Gaithersburg, MD, September 8-10 2008.

"Preignition Oxidation Chemistry of the Major JP-8 Surrogate Component: *n*-Dodecane," Kurman, M.S., Natelson, R.H., Cernansky, N.P., Miller, D.L., Paper No. 2009-1526, *47th AIAA Aerospace Sciences Meeting*, American Institute of Aeronautics and Astronautics, Orlando, FL, January 5-8, 2009.

"New Methodology for Jet Fuel Surrogate Oxidation and Intermediate Speciation in the Low Temperature Regime," Kurman, M.S., Natelson, R.H., Cernansky, N.P., Miller, D.L., Paper No. 23G2 presented at the *6th U.S. National Combustion Meeting*, Ann Arbor, MI, May 17-20, 2009.

"Development of Detailed and Reduced Kinetic Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels: Drexel Flow Reactor Studies at Low and Intermediate Temperatures," Miller, D.L., Cernansky, N.P., Kurman, M., Natelson, R., presented at the *Multi-Agency Coordination Committee Combustion Research Fuels Research Review*, Los Angeles, CA, September 15-17, 2009.

"Low Temperature Oxidation of n-Butylcyclohexane," Natelson, R.H., Kurman, M.S., Cernansky, N.P., Miller, D.L., Paper No. A26, Fall Technical Meeting, *Eastern States Section of the Combustion Institute*, University of Maryland, College Park, MD, October 18-21, 2009.

"Speciation of the Reaction Intermediates from *n*-Dodecane Oxidation in the Low Temperature Regime," Kurman, M.S., Natelson, R.H., Cernansky, N.P., Miller, D.L., PROCI-D-10-00373, *Proceedings of the Combustion Institute*, Tsinghua University, Beijing, China, August 1-6, 2010.

"Development of Detailed and Reduced Kinetic Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels: Drexel Flow Reactor Studies at Low and Intermediate Temperatures," Miller, D.L., Cernansky, N.P., Kurman, M.S., Natelson, R.H., Corrubia, J, Farid, F., presented at the *Multi-Agency Coordination Committee Combustion Research Fuels Research Review*, Princeton, NJ, September 20-23, 2010.

"The Low to Intermediate Temperature Oxidation of *n*-Propylcyclohexane in a Pressurized Flow Reactor," Corrubia, J.A., Farid, F., Cernansky, N.P., Miller, D.L., Paper No. 2A12 presented at the *7th U.S. National Combustion Meeting*, Atlanta, GA, March 20-23, 2011.

"Development of a Low-Temperature Hydrocarbon Kinetic Mechanism which Forms Non-Alkylated Lactones," Gupta, A., Miller, D.L., Cernansky, N.P., Paper No. 1A08 presented at the *7th U.S. National Combustion Meeting*, Atlanta, GA, March 20-23, 2011.

Bowman/Hanson/Pitsch (Stanford University)

"Shock Tube Measurements of Ethylene Concentration Time-Histories during Ethylene, *n*-Heptane and Methylcyclohexane pyrolysis,*" W. Ren, D. F. Davidson, R. K. Hanson, *7th US Combustion Meeting,* Atlanta GA, March 20-23, 2011; oral presentation.

"Multi-Species Time-History Measurements during *n*-Dodecane Oxidation behind Reflected Shock Waves," D. F. Davidson, Z. Hong, G. L. Pilla, A. Farooq, R. D. Cook, R. K. Hanson, *Proceedings of the Combustion Institute* **33**, pp. 151-157 (2011); oral presentation.

"Application of Quantitative Laser Sensors to Kinetics, Propulsion and Practical Energy Systems," R. K. Hanson, *Proceedings of the Combustion Institute* **33**, pp. 1-40 (2011); Hottel Lecture presentation.

"Multi-Species Measurements behind Reflected Shock Waves in Hydrocarbons using Laser Absorption," D. F. Davidson, Z. Hong, G. L. Pilla, A. Farooq, R. D. Cook, R. K. Hanson, Paper AIAA-2010-0198, *48th AIAA Aerospace Sciences Meeting*, Orlando FL, January 2010; oral presentation.

"Species Time-History Measurements during *n*-Heptane Oxidation behind Reflected Shock Waves," D. F. Davidson, Z. Hong, G. L. Pilla, A. Farooq, R. D. Cook, R. K. Hanson, Paper 31F1, *6th U. S. National Combustion Meeting*, Ann Arbor MI, May 2009; oral presentation.

"Recent Advances in Laser Diagnostic Methods for Shock Tube Chemical Kinetics Studies," R. D. Cook, D. F. Davidson, R. K. Hanson, *Gordon Research Conference on Laser Diagnostics in Combustion*, August 2009; oral presentation.

"Assessment of counter flow arrangement to measure laminar burning velocities using direct numerical simulations," V. Mittal, H. Pitsch, F.N. Egolfopoulos, paper No. 09F-80, Fall Technical Meeting, Western States Section/Combustion Institute, University of California at Irvine, Irvine, California, October 26-27, 2009.

Law (Princeton University)

"Propagation of Confined Premixed Flames", Kelley, A. P., Bechtold, J. K, and Law, C. K., paper No. L11, *7th U.S. National Combustion Meeting*, Georgia Institute of Technology, Atlanta, Georgia, March 20-23, 2011.

"Laminar Flame Speeds of C_5 to C_8 *n*-Alkanes at Elevated Pressures: Experimental Determination, Fuel Similarity, and Stretch Sensitivity," Kelley, A. P., Smallbone, A. J., Zhu, D. L., and Law, C. K., *33rd International Symposium on Combustion*, Tsinghua University, Beijing, China, August 1-6, 2010.

"Laminar Flame Speeds, Non-Premixed Stagnation Ignition, and Reduced Mechanisms in the Oxidation of *iso*-Octane," Kelley, A. P. Liu, W., Xin, Y.X., Smallbone, A. J., and Law, C. K., *33rd International Symposium on Combustion*, Tsinghua University, Beijing, China, August 1-6, 2010.

Egolfopoulos/Wang (University of Southern California)

"Detailed and Simplified Kinetic Models for *n*-Dodecane Oxidation: The Role of Fuel Cracking in Aliphatic Hydrocarbon Combustion," You, X.Q., Egolfopoulos, F.N., Wang H., 32nd International Combustion on Symposium, 2008.

"Sensitivity of Propagation and Extinction of Large Hydrocarbon Flames to Fuel Diffusion," Holley, A.T., You, X.Q., Dames, E., Wang, H., Egolfopoulos, F.N., 32nd International Combustion on Symposium, 2008.

"Combustion Characteristics of Practical Fuels," Egolfopoulos, F.N., Department of Thermal Engineering, *Tsinghua University, Beijing*, China, October 6, 2008.

"Combustion Characteristics of Practical Fuels," Egolfopoulos, F.N., *Solar Turbines Inc.,* San Diego, California, November 3, 2008.

"Detailed and Simplified Kinetic Models for *n*-Dodecane Oxidation: The Role of Fuel Cracking in Aliphatic Hydrocarbon Combustion," 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.

"Propagation and Extinction of Premixed *n*-Dodecane/Air Flames," 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.

"Sensitivity of Propagation and Extinction of Large Hydrocarbon Flames to Fuel Diffusion," 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

"Reduction of Detailed Chemical Models with Controlled Uncertainty," Sheen, D. A., Løvås, T., Wang, H., 6th U.S. National Combustion Meeting, Ann Arbor, Michigan. Paper 23F2, May 17-20, 2009.

"An Experimental Study of Premixed *m*-Xylene/Air and *n*-Dodecane/*m*-Xylene/Air Flames," 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.

"Simplified Chemical Kinetic Models for High-Temperature Oxidation of C_1 to C_{12} *n*-Alkanes," Sirjean, B., E. Dames, D. A. Sheen, H. Wang, 6th U.S. National Combustion Meeting, Ann Arbor, Michigan. Paper 23F1, May 17-20, 2009.

"Necessity of Nonlinear Terms in Polynomial Chaos Expansions for Uncertainty Propagation." Sheen, D. A., H. Wang, 6th U.S. National Combustion Meeting, Ann Arbor, Michigan. Paper 21G4, May 17-20, 2009.

"New Experimental and Theoretical Insights of the Role of Tunneling in *n*-Alkyl Radicals Isomerization," Sirjean, B., H. Wang, W. Tsang, 6th U.S. National Combustion Meeting, Ann Arbor, Michigan. Paper 22G2, May 17-20, 2009.

"Propagation and Extinction of Cyclohexane/air, *methyl*-Cyclohexane/Air, and *n-butyl*-Cyclohexane/Air Mixtures," 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.

"Combustion Characteristics of Conventional and Synthetic Jet Fuels," C. Ji, Y.L. Wang, H. Wang, and F.N. Egolfopoulos, paper No. 09F-075 Fall Technical Meeting, *Western States Section/Combustion Institute*, University of California at Irvine, Irvine, California, October 26-27, 2009.

"Assessment of Counter Flow Arrangement to Measure Laminar Burning Velocities using Direct Numerical Simulations," 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.

"Quantitative Analysis of Hierarchical Strategies of Building Combustion Reaction Models," Sheen, D. A., H. Wang, 2009 Fall Western States Section Meeting of the Combustion Institute, Irvine, CA, paper 09F-50, October 26-27, 2009.

"Kinetic Modeling of One-Ring Aromatic Compounds," Dames, E., Wang, H., 2010 Spring Technical Meeting of the Western States Sections of the Combustion Institute, University of Colorado at Boulder, CO, March 22-23, 2010.

"Flame Propagation of Mixtures of Air with Binary Liquid Fuel Mixtures," Ji, C., Egolfopoulos, F.N., 33rd International Combustion on Symposium, 2010.

"An Experimental and Modeling Study of the Propagation of Cyclohexane and Mono-Alkylated Cyclohexane Flames," Ji, C., Dames, E., Sirjean, B., Wang, H., Egolfopoulos, F.N., 33rd International Combustion on Symposium, 2010.

"Theory and Kinetic Modeling of Isomerization Reactions Between Benzylic and Methylphenyl Type Radicals," Dames, E., H. Wang, 7th US National Meeting of Combustion, Atlanta, Georgia, paper 1B17, March 20-23, 2011.

"Theory and Kinetic Modeling of Initiation Reactions for Cyclohexane and Several of its Mono-Alkylated Derivatives," Dames, E., A. Krylov, H. Wang, H., 7th US National Meeting of Combustion, Atlanta, Georgia, paper 1B16, March 20-23, 2011.

"Modeling the Pressure Dependence of H_2/O_2/Diluent Mass Burning Rates," Sheen, D. A., H. Wang, 7th US National Meeting of Combustion, Atlanta, Georgia, paper 1B07, March 20-23, 2011.

"Combustion Kinetic Modeling Using Multispecies Time-Histories in Shock-Tube Oxidation of *n*-Heptane," Sheen, D. A., H. Wang, 7th US National Meeting of Combustion, Atlanta, Georgia, paper 1A14, March 20-23, 2011.

"Combustion Kinetic Modeling Using Multispecies Time-Histories in Shock-Tube Oxidation of *n*-Dodecane," Tangko, R., Sheen, D. A., Wang, H., 7th US National Meeting of Combustion, Atlanta, Georgia, paper 2A18, March 20-23, 2011.

9.2 Web Releases

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9.3 Technical Interactions with AFRL Researchers

The PIs had several meetings with Dr. Tim Edwards and Dr. Mel Roquemore of AFRL/WP during the reporting period. In these meetings numerous aspects of the ongoing work regarding practical jet fuels as well as the relevant neat hydrocarbons were discussed. Additionally, the possibility to extend the reach of JetSurF model and apply it for models of soot formation in gas turbine engines was addressed.

9.4 Other Technical Interactions

The PIs established very close interactions among themselves and all studies, experimental and theoretical, were planned upon close consultation with each other and upon reaching consensus. Close interactions were established also with Professor Angela Violi of the University of Michigan, Professor Peter Lindstedt of Imperial College of Science, Technology and Medicine, London, and Dr. Wing Tsang of National Institute of Standards and Technology.

Additionally, several meetings with Dr. John Farrell of EXXON Corp. took place. Discussions with Dr. Farrell covered the influence of fuel compositional variability and aging on jet fuels, as well as the availability of narrow distillate cuts of jet fuel surrogate components.

There was also continued interaction over the reporting period of this contract with Profs. Matthew Oehlslaeger of RPI and Eric Peterson of Texas A&M. These discussions covered a comparison of related experiments and refinements in shock tube operation critical to ensuring high quality ignition delay time data.

Dr. Nicholas Cernansky and Dr. David Miller of Drexel University have been collaborating with Dr. Frederick Dryer of Princeton University regarding the experimental conditions of future PFR experiments that each group will investigate in their individual facilities. The Drexel and

Princeton groups desire to operate each of their PFR's as close to the same experimental conditions, as deemed possible by each facilities experimental constraints. PFR reactivity maps and concentration-temperature histories will be compared to determine reliability of PFR studies.

Finally, the JetSurF model has been integrated into the SERDP Soot Model, in collaboration with Meredith Colket of UTRC.