Project 025 Shock Tube and Flow Reactor Studies of the Kinetics of Jet Fuels

Stanford University

Project Lead Investigator

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- FAA Award Number: 13-C-AJFE-SU-008
- Period of Performance: 11/05/2015 to 11/30/2015
- Task: Area #1 – Chemical Kinetics Combustion Experiments

Project Funding Level

$330,000 from FAA with 1-1 matching funding of $330,000 from Stanford University.

Investigation Team

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Project Overview

Provide shock tube/laser absorption and flow reactor experiments for a fundamental kinetics database for jet fuels. Experiments are expected to continue to reveal the sensitivity of combustion properties to fuel composition for the ultimate use in simplifying the alternative fuel certification process.

Task 1 - Area #1 – Chemical Kinetics Combustion Experiments

Stanford University

Objectives

Experiments provide an extensive fundamental kinetics database for selected jet fuels. These data are used as critical input for Area #2 that seeks to develop a new hybrid and detailed kinetics model for jet fuels (HyChem). These experiments continue to reveal the sensitivity of combustion properties to variations in fuel composition for ultimate use in simplifying the alternative fuel certification process. The team works in close collaboration with Prof. Hai Wang, also of Stanford University, the PI for area #2, who uses the data acquired in our experiments. The data provided will also ensure that the combustion models developed in Area #4 - Combustion Model Development and Validation to model the extinction and ignition processes controlling lean blowout, cold ignition and high altitude relight, are chemically accurate.

Research Approach

The development, refinement and validation of detailed reaction mechanisms describing the pyrolysis and oxidation of fuels require experimental data as targets for kinetics models. Experimentally, the best way to provide these targets at high temperatures and pressures is with shock tube/laser absorption experiments and flow reactor experiments, conducted over a wide range of pressure, temperature, and fuel and oxidizer composition.

Reflected shock wave experiments provide a test environment that does not introduce additional fluid mechanics, turbulence, or heat transfer effects to the target phenomena. This allows isolation of the target phenomena (ignition delay times and species concentration time-histories) in a quiescent high-temperature, high-pressure environment that is very well characterized and hence amenable to modeling. Recent work in our laboratory to develop the Constrained Reaction Volume (CRV) methodology provides an additional tool to provide shock tube data under constant-pressure constraints when needed, to significantly simplify the gasdynamic/thermodymamic models needed to properly simulate reactive reflected shock wave data.

The strength in the Stanford shock tube approach comes with the implementation of laser diagnostics that enable the simultaneous measurement of species time-histories. Using laser absorption we are able to provide quantitative time-histories during fuel pyrolysis and oxidation of the fuel, including transient radicals (e.g., OH, CH3), stable intermediates (e.g., CH4, C2H4, iso-butene and aromatics), combustion products (including CO, CO2, and H2O), and temperature.

In combination with the shock tube experiments, the Stanford Variable Pressure Flow Reactor is used to provide concentration profile data for important stable intermediate and product species (see Flow Reactor Section) during fuel pyrolysis and oxidation for temperatures ranging from 900 - 1200K, for pressures up to 5 bar, and for residence times from 5 - 100 msec. These species provide critical constraints on the development of the HyChem detailed kinetic models of Prof. Hai Wang.

The range of conditions accessible in the flow reactor partially overlap those achievable in the shock tube so that the combination of shock tube and flow reactor experiments provides a comprehensive species data set over a wide range of experimental conditions that is essential for kinetic model development and validation as well as for model reduction to a size needed for implementation in the Area #4 - Combustion Model Development and Evaluation. To our knowledge, our laboratory is the only one worldwide with this combined capability.

Measurements of the pyrolysis and oxidation systems of real fuels, rather than of surrogates or solvent surrogates, provide a direct link to actual fuel behavior. We believe that the combination of high-quality shock tube and flow reactor measurements combined with the HyChem kinetic model based on real fuel decomposition products proposed by Prof. Hai Wang greatly increases the likelihood of the FAA meeting their program objectives.

Shock Tube Experiments

Stanford has the largest and best-equipped shock tube laboratory in the U.S., perhaps in the world, with five shock tubes: three large-diameter (10, 14 and 15 cm I.D.) high-purity shock tubes (see Fig. 1a); one heated high-pressure shock tube (5 cm I.D., capable of achieving 500+ atm); and 10 cm I.D. expansion tube for generating supersonic flows. Additionally, we have unique capability for species measurements using laser absorption (see Fig. 1b) developed over the past 30 years. In these experiments, temperatures from below 500 K to above 3000 K, and pressure from sub-atmospheric (0.2 atm) to 10-500+ atmospheres can be achieved in different carrier gases, such as argon or air, with demonstrated test times up to and exceeding 50 ms at low temperatures.

Three primary types of shock tube experiments are performed.

The first primary shock tube experiments are species concentration time-history measurements obtained during fuel pyrolysis. These data are needed to place strong constraints on the reaction mechanism and the individual reaction rates and pathways. Laser absorption techniques, many pioneered at Stanford, are used to measure these species time-histories. Measurements of fuel concentration time-histories at a wavelength of 3.39 microns and of the stable fuel decomposition product ethylene, C2H4, at a wavelength of 10.53 microns are performed. We also are able to measure the transient radical OH (in the UV at 306 nm), the combustion products CO, CO2 and H2O (in the IR at 2.7, 4.6 and 2.5 microns, respectively) as well as other product species.

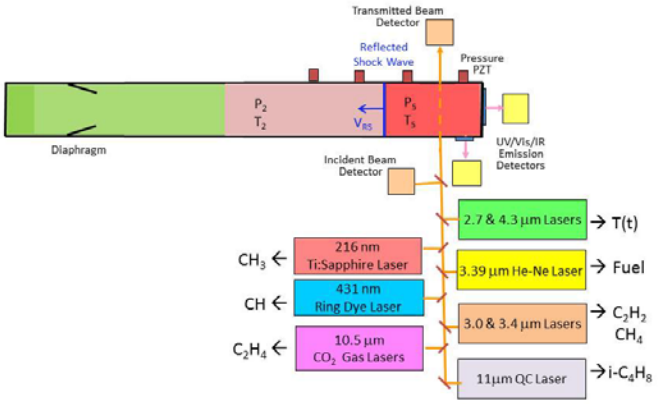
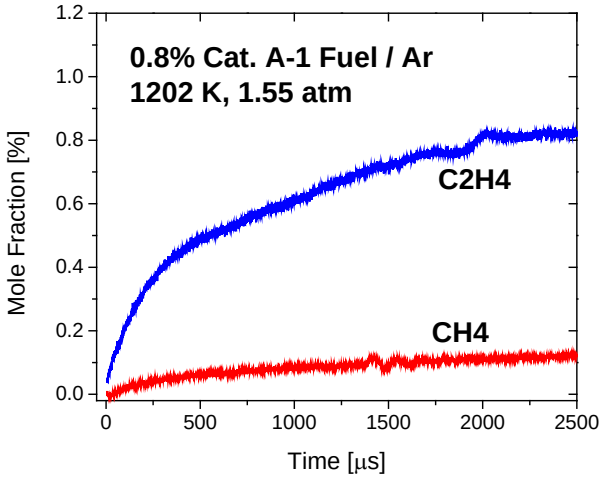


Figure 1a: Stanford 15 cm diameter shock tube. Figure 1b: Schematic of shock tube/laser absorption setup. Simultaneous measurement of multiple species time-histories and temperature with microsecond time resolution are enabled using this arrangement. Only a partial list of accessible species is indicated.

During this first year of this program, using shock tube/laser absorption methods we acquired fuel, ethylene, and methane time-histories for all 9 FAA fuels during pyrolysis. These pyrolysis product yield data are directly applicable to the development of the HyChem model by Prof. Hai Wang. Representative data are shown in Figure 2a. Here the high signal-to-noise ratio of laser absorption data is evident.



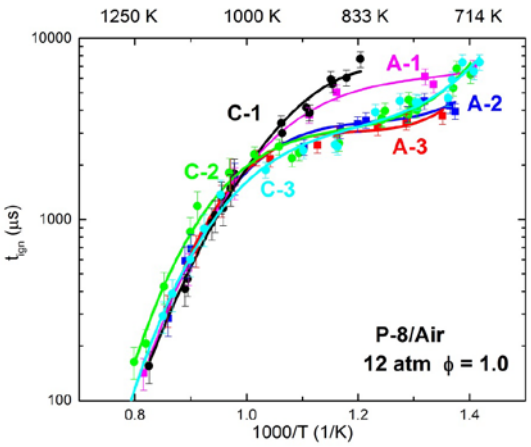


Figure 2a: C2H4 and CH4 mole fraction time-history traces acquired during the pyrolysis of FAA fuel A-1 (JP-8). Figure 2b: Ignition delay times for several FAA fuels in air over the temperature range of 700 to 1250 K.

The second types of shock tube experiments are ignition delay time measurements that define the global behavior of a fuel during oxidation. Comparison with these data provides a direct test and validation of a kinetic model. Ignition delay times can be measured using several different diagnostic methods. Here, we use both emission from OH*, a radical that normally forms during the exponential growth phase of ignition, and pressure, which is monitored using a piezo-electric transducer (PZT).

In the first year using these methods, we extensively examined the ignition delay times of 9 different fuels over a wide range of temperatures (700-1200 K) in an effort to provide the FAA with sufficient information to allow down-selection to a smaller test set. The original 9 fuels were identified as FAA fuels A-1, A-2, A-3, and C-1, C-2, C-3, C-4, C-5, and C-6.

Representative ignition delay time data for these fuels are shown in Figure 2b. As evident in this figure, the low-scatter data provides ignition delay times over a wide temporal range (150-7000 microseconds) using identical facilities and measurement criteria.

The third type of shock tube experiment takes advantage of the wealth of information available in multi-species time-history data during oxidation. Species concentrations in different time regimes during the oxidation process are sensitive to different reactions. An example of the extent of each regime and the type of chemistry seen in these regimes is shown in Figure 3. It should be possible also, for example, to design shock tube/laser absorption experiments where particular species, such as OH or CO, are sensitive to the same reactions that one would find in sensitivity analyses of lean blowout or high altitude relight kinetics. Thus, these shock tube experiments could offer an alternative to WSR (Well-Stirred Reactor) lean-blowout experiments, where the shock tube has the advantages of providing ideal (i.e. perfectly stirred) mixing and a precise uniform temperature environment.

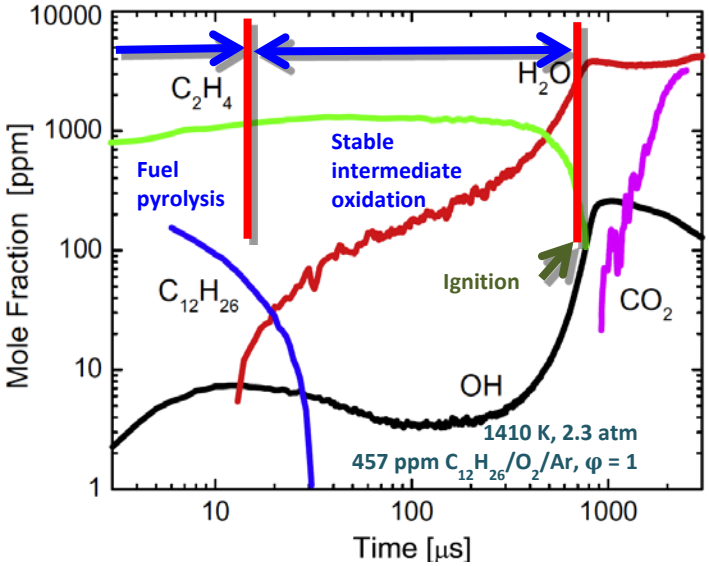


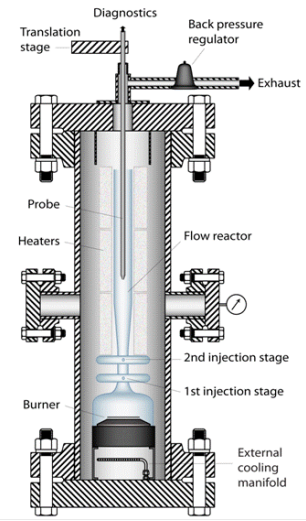
Figure 3: Five species time-history measurements during the oxidation of n-dodecane. Early times are dominated by fuel pyrolysis kinetics; intermediate times are dominated by stable intermediate oxidation; and later times are dominated by ignition and post-ignition product formation.

Stanford Variable Pressure Flow Reactor

A schematic diagram of the Stanford Variable Pressure Flow Reactor is shown in Fig. 4a. The facility comprises a quartz reactor tube housed in a stainless steel pressure vessel. A premixed laminar burner provides high-temperature vitiated air and this air is mixed with fuel vapor prior to entering the reactor tube. Electrical resistance heaters surrounding the reactor tube provide for nearly adiabatic reactor conditions. Gas samples are extracted by a cooled translating probe which also is used to measure gas temperature.

A variety of on-line analyzers, including a four-column gas chromatograph and a new GC/mass spectrometer, obtained using AFOSR funds, are available to measure multiple stable species profiles simultaneously over reaction time scales up to 100 ms. Species that can be measured with these analyzers includes C1 - C12 alkanes, C2 - C8 alkenes, cycloalkanes, allenes, aromatics, including benzene, toluene, and naphthalene, C1 - C3 aldehydes, H2, CO, CO2, and O2. Many of these species are not currently accessible in proposed shock tube experiments.

This facility has been used to study the oxidation and pyrolysis of pure liquid hydrocarbon fuels as well as distillate fuels, including n-dodecane and JP-8 (A-1), under funding by the AFOSR.



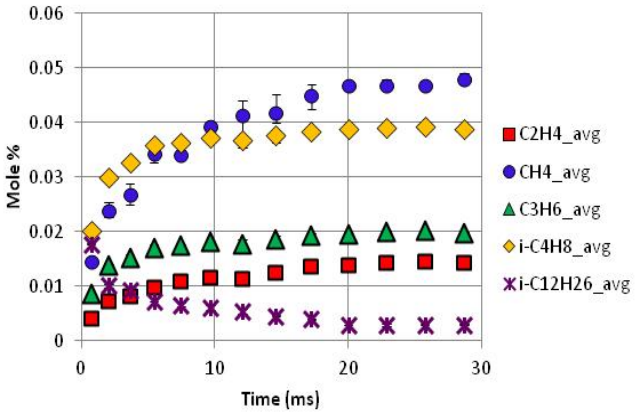


Fig. 4a: Stanford Variable Pressure Flow Reactor. Figure 4b: Species profiles during pyrolysis of C-1 at 1 atm and initial temperature of 1010K.

Milestone(s)

Major Milestones included regular reporting of experimental results and analysis at monthly meetings for both the Testing Working Group and the Steering Working Group, as well as reporting at FAA Quarterly meetings.

Major Accomplishments

During the first year of this program, using shock tube/laser absorption methods we acquired fuel, ethylene, and methane time-histories for all 9 FAA fuels during pyrolysis. In flow reactor experiments this set of species was extend (as described above) using gas chromatography measurements. These pyrolysis product yield data are directly applicable to the development of the HyChem model by Prof. Hai Wang.

In addition, we extensively examined the ignition delay times of 9 different fuels over a wide range of temperatures (700-1200 K) in an effort to provide the FAA with sufficient information to allow down-selection to a smaller test set. The original 9 fuels were identified as FAA fuels A-1, A-2, A-3, and C-1, C-2, C-3, C-4, C-5, and C-6.

Publications

Published Conference Proceedings

Davidson, D. F., Tugestke, A., Zhu, Y., Wang, S., Hanson, R. K., "Species time-history measurements during jet fuel pyrolysis," 30th International Symposium on Shock Waves, Paper 179, Tel Aviv, Israel, July 2015.

Zhu, Y., Wang, S., Davidson, D. F., Hanson, R. K., "Shock tube measurements of species time-histories during jet fuel pyrolysis and oxidation," 25th International Colloquium on the Dynamics of Explosions and Reactive Systems, Paper 262, Leeds, UK, August 2015.

F. Davidson, Y. Zhu, S. Wang, T. Parise, R. Sur, R. K. Hanson, "Shock Tube Measurements of Jet and Rocket Fuels," 54th American Institute of Aeronautics and Astronautics Aerospace Sciences Meeting, January 4-8, 2016, San Diego, CA.

Outreach Efforts

Presentations at the 30th International Symposium on shock Waves, Tel Aviv, Israel July 2015; and at the 25th International Colloquium on the Dynamics of Explosions and Reactive Systems, Leeds, UK, August 2015.

Awards

None

Student Involvement

Graduate students are actively involved in the acquisition and analysis of all experimental data.

Plans for Next Period

Advances in the HyChem model development based on the experimental and theoretical work so far in Year I indicate that there are several important issues that should be addressed as the model is further developed and validated. Three issues in particular, are important.

The first is the development of a protocol for specification of sub-model kinetic parameters. The HyChem model currently requires 6 constraining relationships based on pyrolysis experiment. These include ethylene and methane yields, currently derived from shock tube/laser absorption experiments, and propene/ethylene and butane/ethylene ratios, and benzene and toluene yields, currently derived from flow reactor/gas chromatography experiments. A critical question in the advancement of this modeling scheme is if these specifications can be derived from an independent fuel analysis or are shock tube and flow reactor experiments required? Further understanding of the relationship of these parameters with fuel composition is needed. This effort has been characterized recently as developing a "Fuel X" model.

The second is the need to establish temperature and pressure boundaries for the validity of the HyChem modeling approach. Current in-house validation of the model is based on a small set of ignition delay time and flow reactor experiments over limited ranges of pressure, temperature, equivalence ratio, and fuel concentration. Direct testing over a wider range of test conditions, using both shock tubes and flow reactors, should provide a first-order limits of the applicability of the HyChem model.

Finally, the third issue that may become important is the possible need to extend the HyChem model to the NTC (negative temperature coefficient) regime. The unique oxygen-addition chemistry in this low temperature regime can become important at higher pressures, but also at longer residence times. Recommendations to extend the HyChem model into the NTC regime would be based on needs derived from engine simulations using these operating conditions.

These issues can begin to be addressed within the proposed Experimental and Modeling Prioritization Matrix for Year 2 provided by the FAA and given in the accompanying Table. This matrix and these issues, in conjunction with discussions and collaboration with Prof. Hai Wang and the FAA, should provide the necessary prioritization for fuel and test conditions for both the shock tube and flow reactor experiments consistent with the proposed funding.

Experimental and Modeling Prioritization Matrix for Year 2

Shock Tube

	Fuel	Success Criteria	Ign Delay	Diagnostic Speciation	P, atm	T, K	Pyrolysis	Oxidation
1	A-2	1, 2	Y	aromatics, CH4, C2H4, isobutene, C3H6	0.4, 1.2	900-1300	Y	Y
2	C-1	1, 2	Y	aromatics, CH4, C2H4, isobutene, C3H6	0.4, 1.2	900-1300	Y	Y
3	C-5	1, 2	Y	aromatics, CH4, C2H4, isobutene, C3H6	0.4, 1.2	900-1300	Y	Y
4	A-3	1, 2	Y	aromatics, CH4, C2H4, isobutene, C3H6	0.4, 1.2	900-1300	Y	Y
5	C-6	1, 2	Y	aromatics, CH4, C2H4, isobutene, C3H6	0.4, 1.2	900-1300	Y	Y
6	Blended A2-C1	1, 2	Y	aromatics, CH4, C2H4, isobutene, C3H6	0.4, 1.2, 12	900-1300	Y	Y
7	New fuel	1, 2	Y	aromatics, CH4, C2H4, isobutene, C3H6	0.4, 1.2, 12	900-1300	Y	Y

Flow Reactor

	Fuel	Success Criteria	Ign Delay	Diagnostic Speciation	P, atm	T, K	Pyrolysis	Partial Oxidation
1	A-2	2	NA	Species up to 100 amu	1	920-980	Y(980)	Y(920)
2	C-1	2	NA	Species up to 100 amu	1	920-980	Y(980)	Y(920)
3	C-5	2	NA	Species up to 100 amu	1	920-980	Y(980)	Y(920)
4	A-3	2	NA	Species up to 100 amu	1	920-980	Y(980)	Y(920)
5	C-6	2	NA	Species up to 100 amu	1	920-980	Y(980)	Y(920)
6	Blended A2-C1	2	NA	Species up to 100 amu	1	920-980	Y(980)	Y(920)
7	New fuel	2	NA	Species up to 100 amu	1	920-980	Y(980)	Y(920)