



Project 025 Shock Tube Studies of the Kinetics of Jet Fuels

Stanford University

Project Lead Investigator

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University Participants

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- P.I.s: Prof. Ronald K Hanson
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Project Funding Level

\$200,000 from FAA with 1-1 matching funding of \$200,000 from Stanford University.

Investigation Team

Prof. Ronald K Hanson, Principal Investigator, Research Direction
Dr. David F Davidson, Senior Research Engineer, Research Management
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Nicolas Pinkowski, Graduate Student, Research Assistant

Project Overview

Provide shock tube/laser absorption 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 1A- Chemical Kinetics Combustion Experiments

Stanford University

Objective(s)

Experiments provide an extensive fundamental kinetics data 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 Professor 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, 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/thermodynamic 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.

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. 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 Professor Hai Wang is meeting the FAA program objectives.

An important goal of the current research is to investigate the possibility of characterizing fuel composition and combustion behavior based on the jet fuel infrared absorption (FTIR) spectra. As the shock tube/spectroscopic research has progressed under FAA support, a large database of kinetic and spectroscopic measurements for a variety of jet fuels has been acquired. Using this database, we have developed correlations between the spectroscopic properties of neat jet fuel with fuel composition and with important combustion parameters such as DCN, LBO and C₂H₄ pyrolysis yields.

Experimental Studies

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.

The primary shock tube experiments are species concentration time-history measurements obtained during fuel pyrolysis. These data are used 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. The following species time-histories measurements have been acquired and used in the development of the HyChem model: fuel at a wavelength of 3.39 or 3.41 microns, and the stable fuel decomposition products: ethylene, methane, propene, and iso-butene, at wavelengths of 10.53, 3.1754, 10.96, and 11.3 microns, respectively. 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.

Representative data acquired using these methods are shown in Figures 2a and 2b along with preliminary HyChem model results. These measurements of the major jet fuel decomposition products during Cat C4 fuel pyrolysis (fuel, ethylene, propene, and isobutene time-histories) were directly applicable to the development of the HyChem Jet Fuel model by Prof. Hai Wang.

FTIR spectra for Jet A (Cat A2 fuel) and average FTIR spectra for the major molecular classes of fuel components are shown in Figures 3a and 3b. FTIR measurements of the jet fuel can be used to characterize the fuel component composition by spectrally decomposing the jet fuel FTIR spectra using the major molecular class FTIR spectral basis set.

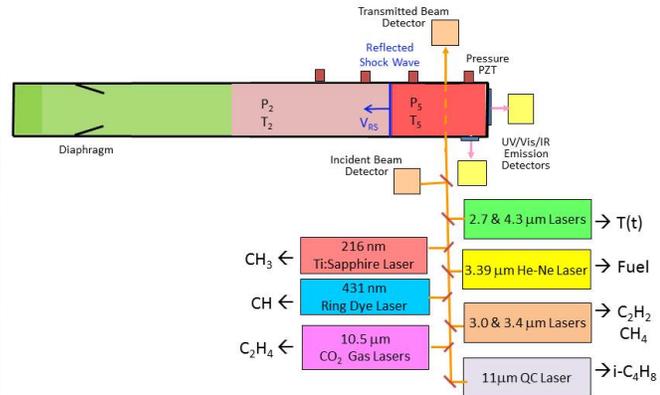


Figure 1a. Stanford 15 cm diameter shock tube. **Figure 1b.** Schematic of shock tube/laser absorption setup. Simultaneous measurement of multiple species time-histories and temperature with microsecond time resolution are enabled using this arrangement. Only a partial list of accessible species is indicated.

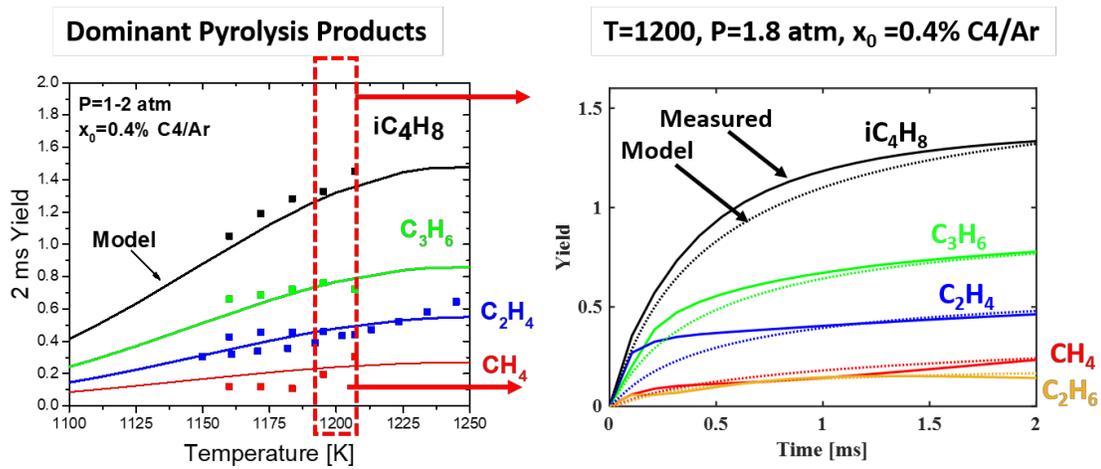


Figure 2a. Variation of the CH₄, C₂H₄, C₂H₆, C₃H₆ and iC₄H₈ pyrolysis yields acquired during the pyrolysis of C₄ fuel as a function of temperature and comparison with a preliminary HyChem model. **Figure 2b.** Representative measurements and preliminary modeling of C₄ pyrolysis at 1200K, 1.8 atm.

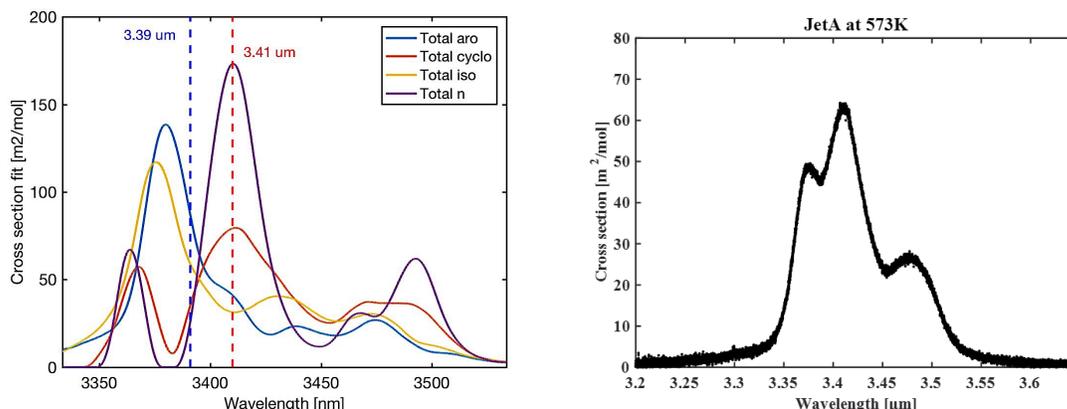


Figure 3a. Average FTIR spectra for alkane (n-, iso-, & cyclo-) and aromatic molecular classes of jet fuel components. Primary wavelengths (3.39 and 3.41 microns) used to measure fuel loading are also indicated. **Figure 3b.** FTIR spectra for Jet A fuel (Cat A2). Strong absorption is seen at the n-alkane peak near 3.41 microns.

Milestones

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

Major Accomplishments

During this fourth year of this program, we made advances in several areas.

We have developed or refined infrared laser diagnostics schemes for ethane at 3.35 microns and for aromatics at 3.28 microns. These diagnostics provide quantitative, sensitive, low-noise detection of key species involved in the combustion of jet fuels.

Using these new diagnostics schemes and our existing systems for ethylene, methane and isobutene, we have acquired refined multi-species data for the decomposition of the important jet fuel pyrolysis product i-butene and for Cat C4 fuel using a nine-IR-wavelength strategy.

In the analysis of this multi-species/multi-wavelength approach we have also assessed the role of minor interfering species (e.g. 1-butene, 2-butene, and allene) on the measured iso-butene and propene pyrolysis yields.

We have acquired FTIR spectra near 3.4 microns for the majority of the FAA Cat A and Cat C fuels as well as verifying the published spectra for single fuel components.

We have developed correlations that relates the measured IR absorption ratio at 3.41 and 3.39 microns to C₂H₄ pyrolysis yield, fuel DCN value, LBO (lean blow out) and IDT (ignition delay times).

We have investigated, and continue to investigate, the link between FTIR spectra measurements and fuel functional groups, combustion properties and HyChem.

Publications

Peer-reviewed journal publications

Archival Publications

S. Wang, T. Parise, S.E. Johnson, D.F. Davidson, R.K. Hanson, "A New Diagnostic for Hydrocarbon Fuels using 3.41-micron Diode Laser Absorption," *Combustion and Flame* 186 129-139 (2017)

T. Parise, D.F. Davidson, R.K. Hanson, "Shock Tube/Laser Absorption Measurements of the Pyrolysis of a Bimodal Test Fuel," *Proceedings of the Combustion Institute* 36 281-288 (2017)



H. Wang, R. Xu, K. Wang, C.T. Bowman, R.K. Hanson, D.F. Davidson, K. Brezinsky, F.N. Egolfopoulos, "A Physics-based approach to modeling real-fuel combustion chemistry - I. Evidence from experiments, and thermodynamic, chemical kinetic and statistical considerations," *Combustion and Flame* 193 502-519 (2018)

R. Xu, K. Wang, S. Banerjee, J. Shao, T. Parise, Y. Zhu, S. Wang, A. Movaghar, D.J. Lee, R. Zhao, X. Han, Y. Gao, T. Lu, K. Brezinsky, F.N. Egolfopoulos, D.F. Davidson, R.K. Hanson, C.T. Bowman, H. Wang, "A physics-based approach to modeling real-fuel combustion chemistry - II. Reaction kinetic models of jet and rocket fuels," *Combustion and Flame* 193 520-537 (2018)

J. Shao, Y. Zhu, S. Wang, D. F. Davidson, R. K. Hanson, "A shock tube study of jet fuel pyrolysis and ignition at elevated pressures and temperatures, *Fuel* 226 338-344 (2018)

N. Pinkowski, T. Parise, Y. Ding, S. Johnson, Y. Wang, D. F. Davidson, R. K. Hanson, "High-temperature infrared absorption cross-sections to facilitate the study of hydrocarbon pyrolysis," submitted to *Journal of Quantitative Spectroscopy and Radiative Transfer*, August 2018

Y. Wang, D. F. Davidson, R. K. Hanson, "A new method of predicting derived cetane number for hydrocarbon fuels," submitted to *Fuel*, September 2018

N. Pinkowski, "Jet fuel chemical kinetics: shock tubes, laser diagnostics, and machine learning methods," ASCENT Program Student Paper Competition 2018

Outreach Efforts

FTIR spectral analysis of a series of jet fuels with varying cetane number from the Army Research Laboratory (ARL) providing fuel characterization data of use to both the FAA and the ARL.

FTIR spectral analysis of a series of jet fuels from geographically varying locations from the Air Force/Wright Patterson Airbase providing fuel characterization data of use to both the FAA and the AFOSR.

Awards

None

Student Involvement

Graduate students are actively involved in the acquisition and analysis of all experimental data. Tom C. Parise successfully defended his Ph.D. thesis that was based on work performed under this contract. Nicolas Pinkowski won an FAA ASCENT Program Student Paper Competition for his paper "Jet fuel chemical kinetics: shock tubes, laser diagnostics, and machine learning methods."

Plans for Next Period

In the next period we plan to:

1. Acquire IDT & speciation data base for SHELL IH2 fuel and develop a HyChem model for this fuel.
2. Complete the kinetics and HyChem section of the AIAA volume entitled *Fuel Effects on Operability of Aircraft Gas Turbine Combustors*.
3. Finalize HyChem model for Cat C4 fuel.
4. Continue development of correlations between IR fuel absorption, pyrolysis yields & combustion properties.
5. Continue exploration of IR absorption as a fuel screening tool and potential fuel specification.
6. Extend correlations of IR absorption to physical properties (e.g., viscosity, surface tension, etc.).