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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- PI(s): Prof. Ronald K. Hanson
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- Task(s):
    1. Area #1: Chemical kinetics combustion experiments

Project Funding Level

$110,000 from FAA with 1:1 matching funding of $110,000 from Stanford University.

Investigation Team

- Prof. Ronald K Hanson, principal investigator, research direction
- Dr. David F Davidson, senior research engineer, research management
- Jiankun Shao, graduate student, research assistant
- Yu Wang, graduate student, research assistant
- Nicolas Pinkowski, graduate student, research assistant
- Alison Ferris, graduate student, research assistant

Project Overview

The fifth year of this program aims to continue building a fundamental kinetics database to describe the combustion behavior of modern jet fuels. To this end, the program focused on two project areas: shock tube/laser absorption kinetics measurements to characterize Shell IH2 fuels (now referred to as Shell CPK-0), and the correlation of chemical and physical fuel properties with infrared (IR) spectral features. The results will be used to provide unique input constraints for the development of hybrid-chemistry (HyChem) models and to reveal the sensitivity of combustion properties to fuel composition, with the ultimate goal of simplifying the alternative fuel certification process.

Task 1 - Chemical Kinetics Combustion Experiments

Stanford University

Objective(s)

This work aims to use shock tube/laser absorption experiments to characterize Shell IH2 fuel and extend the fundamental kinetics database built over the past four years; shock tube measurements include ignition delay time (IDT) measurements under conditions comparable to those used to characterize previous FAA fuels and species time-history measurements during fuel pyrolysis. A second area of research is the development of fuel prescreening tools, based on IR absorption ratio measurements of jet fuels. Finally, this multi-year research program aims to culminate in the completion of American Institute of Aeronautics and Astronautics (AIAA) book chapters describing the research progress of the past four years.

IDT and species time-history measurements conducted in shock tubes provide valuable fundamental kinetics data for FAA fuels. These data are a critical input for Area #2, which seeks to develop a new hybrid and detailed kinetics model for jet fuels (HyChem). 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 pressures, temperatures, and fuel and oxidizer compositions.

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 (IDTs 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, CH_3), stable intermediates (e.g., CH_4, C_2H_4, isobutene, CH_2O, and aromatics), combustion products (including CO, CO_2, and H_2O), and temperature. Furthermore, 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.

An important goal of the current research is to investigate the possibility of characterizing jet fuel composition and combustion behavior based on the fuel's IR absorption (Fourier transform IR, FTIR) spectrum. 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 derived cetane number (DCN), lean blowout, and C_2H_4 pyrolysis yields.

Shock tube experiments: methods and results

Stanford has one of the largest and best-equipped shock tube laboratories in the United States, perhaps in the world, with five shock tubes: three large-diameter [12, 14, and 15 cm internal diameter (I.D.)] high-purity shock tubes; one heated, large-diameter, high-purity shock tube (14 cm I.D., see Figure 1a); and one heated high-pressure shock tube (5 cm I.D., capable of achieving >500 atm). Additionally, we have unique capability for species measurements using laser absorption diagnostics (see Figure 1b) developed over the past 30 years. In these experiments, temperatures from <500 to >3000 K, and pressures from sub-atmospheric (0.2 atm) to >500 atm 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.

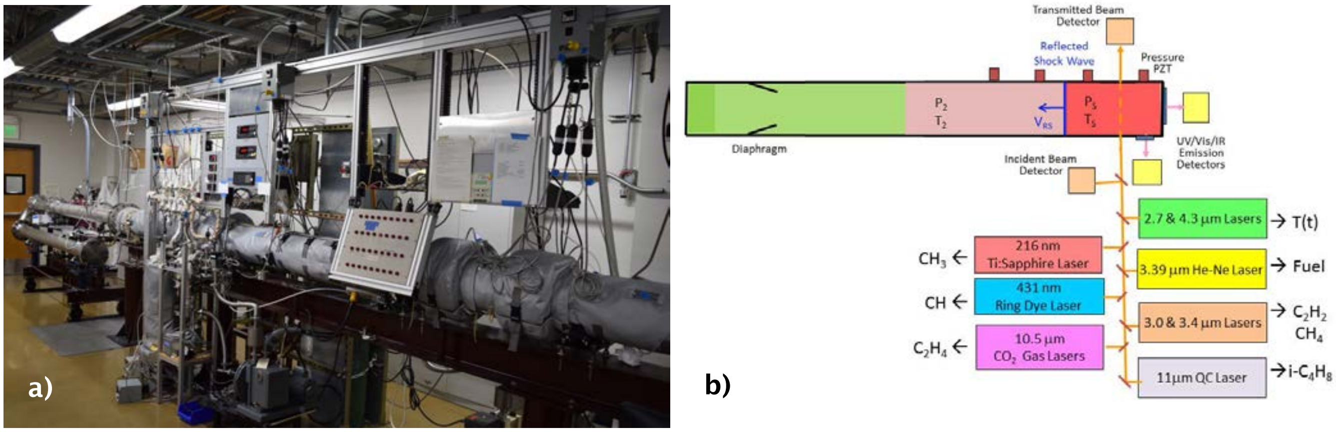

Figure 1. (a) Stanford 14-cm-diameter shock tube; and (b) schematic of shock tube/laser absorption setup. Simultaneous measurement of multiple species time-histories and temperature with microsecond time resolution are enabled using this arrangement (only a partial list of accessible species is indicated).

Two types of shock tube experiments have been performed to characterize the IH2 fuel: IDT experiments and pyrolysis species time-history experiments. Figures 2a and 2b show the IDT results at high and low temperatures, respectively, at 12–13 atm, for the IH2 fuel, a 50/50 blend of IH2 and Jet A, and Jet A; a comparison with Jet A IDT results recorded in the previous year of the project (2018) is also included.

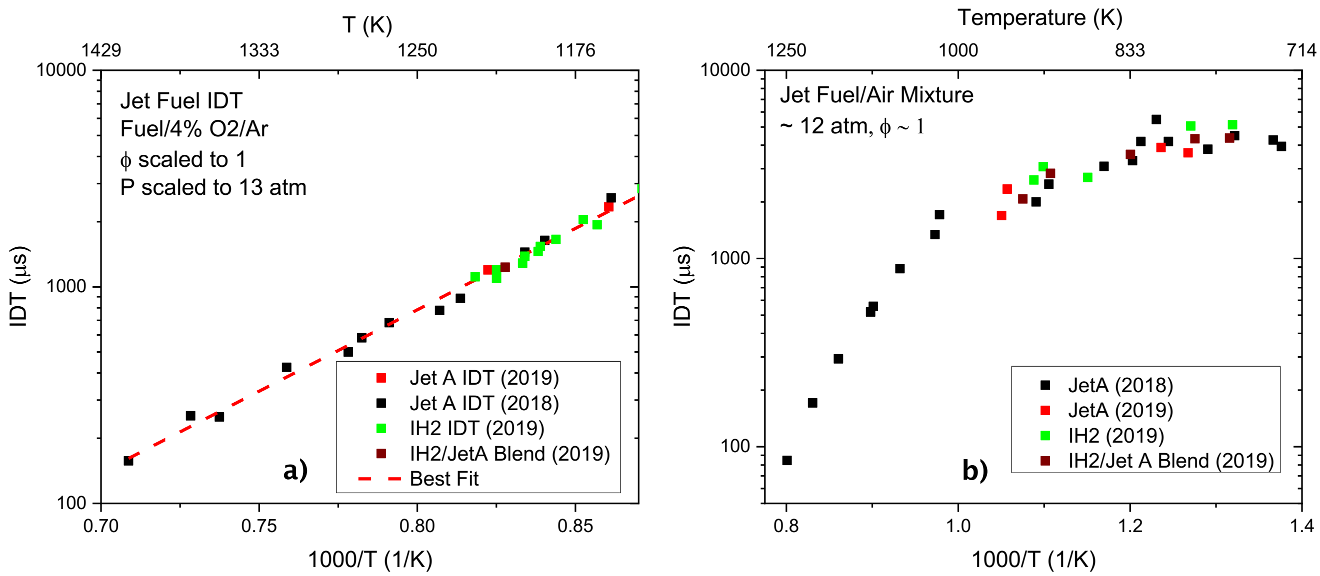

Figure 2. (a) High-temperature jet fuel (IH2 and Jet A) ignition delay time (IDT) results; and (b) low-temperature jet fuel IDT results.

Overall, similar IDTs are observed for Jet A, IH2, and the IH2/Jet A blend at high temperatures; a weak difference in IDT is observed between the three fuel types below 1000 K. Notably, below 800 K, IH2 IDTs are consistently longer than Jet A IDTs, and IH2/Jet A blend IDTs tend to fall between the two.

In addition to the IDT measurements, the first multi-wavelength laser absorption/shock tube speciation experiments for the Shell IH2 fuel were conducted. Fuel, methane, ethylene, and propene were measured at 1300 K and ~3.5 atm using absorption diagnostics at 3.41, 3.175, 10.532, and 10.958 μm, respectively. Representative data acquired using six simultaneous wavelengths are shown in Figure 3a, and the corresponding mole fraction measurements for the same experiment are shown in Figure 3b. The ultimate goal of this work is to measure fuel, methane, acetylene, ethylene, ethane, propene, isobutene, 1-butene, and aromatics at 1200–1500 K and 3–4 atm using nine absorption diagnostics at 3.41, 3.175, 2.998, 10.532, 3.35, 10.958, 11.345, 10.675, and 3.28 μm, respectively.

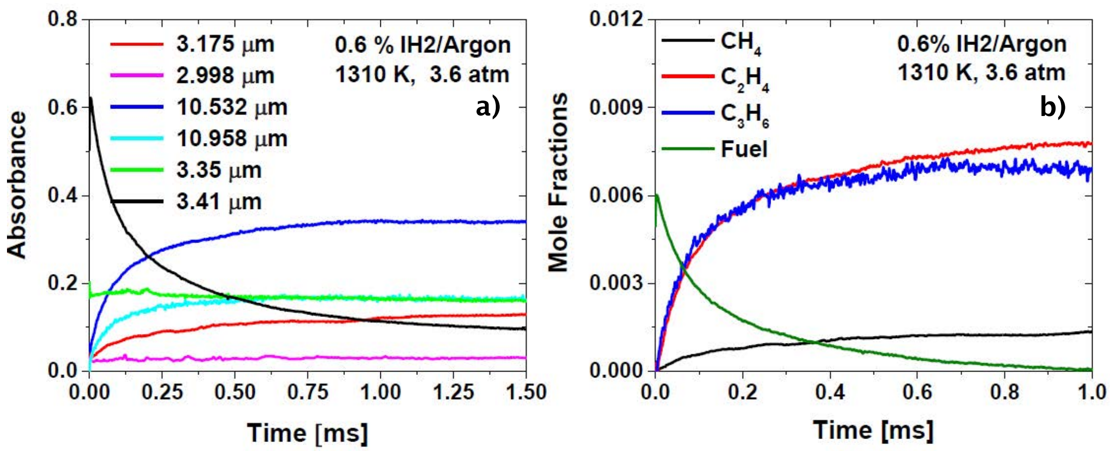

Figure 3. (a) Six-wavelength laser absorption measurements for an IH2/Ar pyrolysis reflected-shock experiment; (b) species mole fraction measurements (methane, ethylene, propene) for the same pyrolysis experiment depicted in Figure 3a.

The IDT and species time-history measurements acquired for the IH2 fuel and its blend with Jet A are directly applicable to the development of the HyChem jet fuel model.

IR spectrum analysis: results

FTIR spectra of Jet A, Shell IH2, and a 50/50 blend of IH2/Jet A were used to characterize their respective fuel compositions by decomposing each spectrum using the major molecular class FTIR spectral database set, developed through prior work done in this program. Figure 4 shows the mid-IR spectra of Jet A, IH2, and the 50/50 blend.

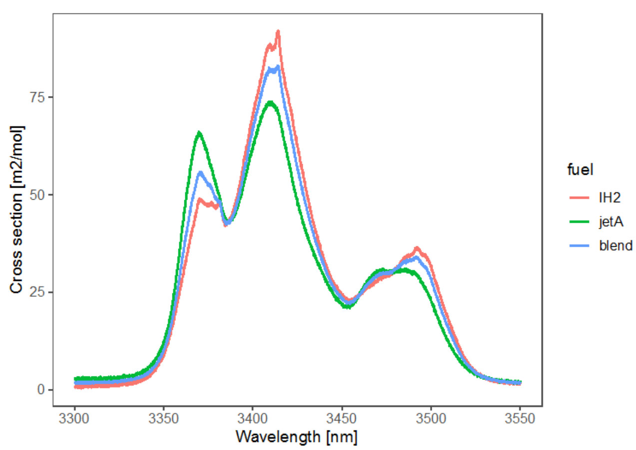

Figure 4. Fourier transform infrared (FTIR) spectra for Jet A, IH2, and a 50/50 blend. A strong absorption feature is seen in all fuels at the *n*-alkane peak near 3.41 μm.

The corresponding fuel properties predicted by the IR analysis of the fuels are shown in Table 1, together with values obtained via traditional measurement methods.

Table 1. Comparison of Jet A and 50/50 IH2/Jet A blend fuel properties estimated using infrared (IR) analysis and corresponding values measured using conventional means. DCN, derived cetane number; IBP, initial boiling point; Vis., viscosity; NHC, net heat of combustion.

Jet A	Measured	IR Estimate	% Variation
DCN	49	46	-6%
Flash pt.	48	45	-6%
IBP	155	156	1%
Kinematic Vis.	4.6	4.7	2%
NHC	43	43	0%
Density	0.80	0.80	0%
Blend	**Measured**	**IR Estimate**	**% Variation**
DCN	44	46	5%
Flash pt.	42	52	24%
IBP	150	166	11%
Kinematic Vis.	4.4	4.6	5%
NHC	43	43	0%
Density	0.82	0.84	2%

The IR analysis results show good agreement with measured property results, suggesting that IR analysis is a promising technique for prescreening potential next-generation jet fuels. The greater variation in flash point and initial boiling point (IBP) results is likely due to insufficient cycloalkane data, which is necessary to fine-tune the IR spectral analysis for fuels such as IH2 that have significant cycloalkane content.

Milestone(s)

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 the fifth year of this program, major advances were made in several areas:

- IDT measurements were acquired for the Shell IH2 fuel and a 50/50 blend of IH2/Jet A from 750 to 1200 K, at 13 to 14 atm.
- Shell IH2 pyrolysis speciation measurements of fuel, methane, ethylene, and propene were begun, with the ultimate goal of measuring methane, acetylene, ethylene, ethane, propene, isobutene, 1-butene, and aromatics at nine laser absorption wavelengths from 1200 to 1500 K at 3–4 atm.
- FTIR spectra of Jet A and IH2 fuels were used to successfully estimate the fuels' properties, including DCN, flash point, IBP, kinematic viscosity, net heat of combustion (NHC), and density.
- The C4 HyChem model was revised and finalized using data collected during Year 4 of this program
- The kinetics and HyChem section of the AIAA volume titled *Fuel Effects on Operability of Aircraft Gas Turbine Combustors* was completed.

Publications

Peer-reviewed journal publications

Ding, Y., Wang, S., & Hanson, R.K. (2019). Sensitive and interference-immune formaldehyde diagnostic for high-temperature reacting gases using two-color laser absorption near 5.6 μm. Combustion and Flame 213, 194-201. https://doi.org/10.1016/j.combustflame.2019.11.042

Pinkowski, N.H., Cassady, S.J., Davidson, D.F., & Hanson, R.K. (2019). Multi-wavelength speciation of high-temperature 1-butene pyrolysis. Fuel 244, 269-281. https://doi.org/10.1016/j.fuel.2019.01.154

Pinkowski, N.H., Ding, Y., Johnson, S.E., Wang, Y., Parise, T.C., Davidson, D.F., & Hanson, R.K. (2019). A multi-wavelength speciation framework for high-temperature hydrocarbon pyrolysis. Journal of Quantitative Spectroscopy and Radiative Transfer 225, 180-205. https://doi.org/10.1016/j.jqsrt.2018.12.038

Pinkowski, N.H., Wang, Y., Cassady, S.J., Davidson, D.F., & Hanson, R.K. (2019). A streamlined approach to hybrid-chemistry modeling for a low cetane-number alternative jet fuel. Combustion and Flame 208, 15-26. https://doi.org/10.1016/j.combustflame.2019.06.024

Shao, J., Ferris, A.M., Choudhary, R., Davidson, D.F., & Hanson, R.K. (2020). A shock tube study of natural gas pyrolysis and ignition at elevated pressures and temperatures. Submitted, Proceedings of the Combustion Institute (38th International Symposium on Combustion).

Shao, J., Wei, W., Choudhary, R., Davidson, D.F., & Hanson, R.K. (2019). Shock tube measurement of the CH3+C2H6→ CH4+C2H5 rate constant. The Journal of Physical Chemistry A. 123, 42, 9096-9101 https://doi.org/10.1021/acs.jpca.9b07691

Shao, J., Zhu, Y., Wang, S., Davidson, D.F., & Hanson, R.K. (2018). A shock tube study of jet fuel pyrolysis and ignition at elevated pressures and temperatures. Fuel 226 338-344. https://doi.org/10.1016/j.fuel.2018.04.028

Wang, K., Xu, R., Parise, T., Shao, J., Movaghar, A., Lee, D.J., Part, J., Gao, Y., Lu, T., Egolfopoulos, F., Davidson, D.F., Hanson, R.K., Bowman, C.T., & Wang, H. (2018). A physics-based approach to modeling real-fuel combustion chemistry – IV. HyChem modeling of combustion kinetics of a bio-derived jet fuel and its blends with a conventional jet a. Combustion and Flame 198**,** 477-489. https://doi.org/10.1016/j.combustflame.2018.07.012

Wang, Y., Davidson, D.F., & Hanson, R.K. (2019). A new method of predicting derived cetane number for hydrocarbon fuels. Fuel 241 319-326. https://doi.org/10.1016/j.fuel.2018.12.027

Wang, Y., Ding, Y., Wei, W., Cao, Y., Davidson, D.F., & Hanson, R.K. (2019). On estimating physical and chemical properties of hydrocarbon fuels using mid-infrared FTIR spectra and regularized linear models. Fuel 255, 115715. https://doi.org/10.1016/j.fuel.2019.115715

Published conference proceedings

Pinkowski, N., Davidson, D.F., & Hanson, R.K. (2019). Multi-wavelength speciation of high-temperature alternative and conventional jet fuel pyrolysis. Paper 2019-1769, AIAA SciTech Forum, San Diego, CA. https://arc.aiaa.org/doi/pdf/10.2514/6.2019-1769

Wang, Y., Cao, Y., Davidson, D.F., & Hanson, R.K. (2019). Ignition delay time measurements for distillate and synthetic jet fuels. Paper 2019-2248, AIAA SciTech Forum, San Diego, CA. https://arc.aiaa.org/doi/pdf/10.2514/6.2019-2248

Outreach Efforts

Multi-wavelength speciation measurements of various jet fuels were presented by Nico Pinkowski at the AIAA SciTech Forum in San Diego, CA, in January 2019 ("Multi-wavelength speciation of high-temperature alternative and conventional jet fuel pyrolysis"). At the same AIAA SciTech Forum, Yu Wang presented jet-fuel IDT measurements ("Ignition Delay Time Measurements for Distillate and Synthetic Jet Fuels").

Awards

None.

Student Involvement

Graduate students are actively involved in the acquisition and analysis of all experimental data. Nicolas Pinkowski (current graduate student) performed the multi-wavelength speciation experiments and presented the results at the AIAA SciTech Forum in San Diego in January 2019. Yu Wang (current graduate student) performed the IR spectral analysis/fuel prescreening work and presented the results at the AIAA SciTech Forum in San Diego in January 2019. Jiankun Shao successfully defended his PhD thesis, which was based in part on work performed under this contract. Rui Xu also successfully defended his PhD thesis on the HyChem modeling approach, which was refined using work performed under this contract. Both Dr. Jiankun Shao and Dr. Rui Xu are currently employed as postdoctoral fellows at Stanford University. Alison Ferris (current graduate student) has additionally contributed to the project through compilation of experimental results and report writing.

Plans for Next Period

In the next period, we plan to:

- Complete time-resolved, Shell IH2 pyrolysis speciation measurements of methane, acetylene, ethylene, ethane, propene, isobutene, 1-butene, and aromatics using nine laser absorption wavelengths from 1200 to 1500 K at 3–4 atm
- Acquire aldehyde (CH_2O) species time-histories in low-temperature oxidation experiments to further refine HyChem performance at low temperatures
- Develop and validate a HyChem model for the pyrolysis and oxidation of the Shell IH2 fuel
- Apply FTIR analysis to the characterization of neat IH2 fuel (obtain additional cycloparaffin property data; e.g., flash point, DCN)