



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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- Pls: Prof. Ronald K. Hanson
- FAA Award Number: 13-C-AJFE-SU-027
- Period of Performance: October 1, 2019, to September 30, 2020
- Task:
 1. Area #1: Chemical kinetics combustion experiments.

Project Funding Level

2019/2020: FAA provided \$110,000 in funding and Stanford University provided 1:1 in matching funds of \$110,000.
2020: FAA provided \$300,000 in funding and Stanford University provided 1:1 in matching funds of \$300,000.

Investigation Team

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

Project Overview

The sixth year of this program has focused on developing strategies for the accurate prediction of jet fuel properties (chemical and physical) and the further development of a fundamental kinetics database to describe the combustion behavior of modern jet fuels. To achieve these two goals, research focused on two project areas: correlation of chemical, physical, and combustion fuel properties with infrared (IR) spectral features, and shock tube/laser absorption kinetics measurements to characterize JP8, JP5, and Jet-A pyrolysis. The results of the infrared (IR) spectral analysis work will be used to reveal the sensitivity of combustion properties to jet fuel composition, with the ultimate goal of developing a rapid pre-screening approach, requiring minimal fuel volume, to simplify the alternative jet fuel certification process. The shock tube/laser absorption results will be used as input constraints for the development and refinement of hybrid-chemistry (HyChem) models for jet fuel combustion.

Task 1 – Chemical Kinetics Combustion Experiments

Stanford University

Objectives

This work aims to develop fuel prescreening tools based on the IR absorption cross-section measurements of jet fuels and their constituent molecules. Specific fuel analysis objectives include developing effective strategies for correlating (1) functional group and molecular species composition and (2) chemical, physical, and combustion properties of jet fuels with their IR spectra.

A second area of research includes shock tube/laser absorption experiments to characterize JP8/JP5/Jet-A fuels and extend the fundamental kinetics database built over the past five years. One particular objective has been to conduct shock tube experiments to obtain species time-history measurements of alkane, alkene, and aromatic formation during pyrolysis under conditions comparable to those used to characterize previous FAA fuels.

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 six years, notably, advancements in our understanding of jet fuel chemical kinetics and fuel prescreening techniques.

Finally, it should be noted that 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

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 mid-IR absorption spectrum, measured using a Fourier transform IR (FTIR) spectrometer. 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 and jet fuel components 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. Presented here is an overview of the two research thrusts (IR fuel analysis and shock tube/laser absorption measurements), along with exemplary experimental results obtained over the past year.

IR fuel analysis: methods and results

An FTIR instrument (Nicolet 6700) and heated cell are used to measure the mid-IR spectra of gas-phase fuel samples. Analysis of gas-phase samples allows for the detection of sharper spectral features, even individual absorption transitions, which can in turn be tied directly to structural characteristics of fuel molecules. This work focuses on analysis of mid-IR absorption spectra, due to the strong sensitivity of the mid-IR region to hydrocarbon bonding. Initial investigations have focused primarily on the 3- μm region, although future work aims to extend this range to 2–15 μm . Advanced statistical methods, including cross-validated models with Lasso regularization, are used to interpret the mid-IR spectra.

In the previous year of this program, a strategy (Strategy 1) was developed for estimating physical and chemical properties of fuels directly from mid-IR spectra. In the current year of this program, three additional strategies (referred to as Strategy 2, 3, and 4) were developed for estimating molecular functional group fractions, global fuel properties, and molecular species constituents, respectively. The workflow of the three newest strategies is shown in Figure 1, and the methods and results for each will be described here.

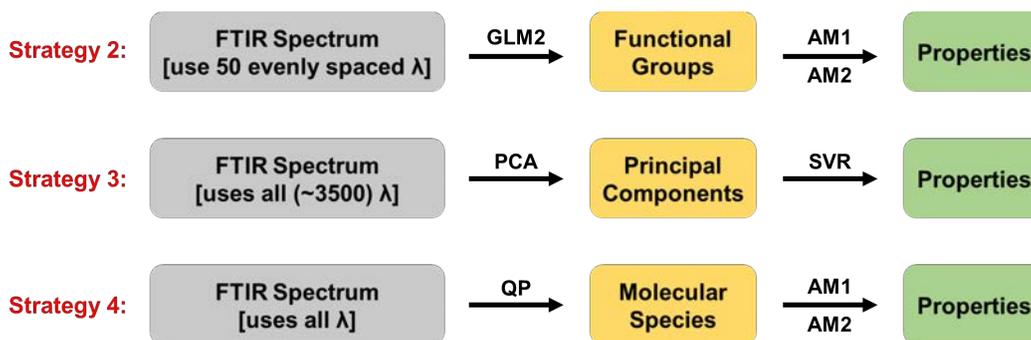


Figure 1. Flow chart of three new strategies developed to estimate physical and chemical properties of conventional jet fuels and sustainable aviation fuels from FTIR spectra. (GLM2 = Generalized Linear Model with Grouped-Lasso Regularization, AM1/AM2 = linear (1)/nonlinear (2) group additivity models, PCA = principal component analysis, SVR = support vector regression, QP = quadratic programming).

Strategy 2 was implemented and used to demonstrate the correlation between FTIR spectra from 3300–3500 nm and $-\text{CH}_2$, $-\text{CH}_3$, and “other” functional groups; subsequent linear and nonlinear group additivity models were then used to estimate 14 physical and chemical properties for 69 hydrocarbon fuels. Optimization of a generalized linear model with grouped-Lasso regularization indicates that 10 wavelengths are necessary to accurately correlate measured absorption cross-sections with the number of $-\text{CH}_2$ and $-\text{CH}_3$ functional groups in each fuel. Figure 2 shows a comparison of known $-\text{CH}_2$ and $-\text{CH}_3$ functional group fractions, defined as the fraction of a fuel’s hydrogen atoms contained in each functional group type, to fitted functional group fractions. The two plots indicate that the linear model with grouped-Lasso regularization is generally a good fit to the data, but that smaller molecules (e.g., hexane, 2,2-dimethylbutane, etc.) may be fit better with alternative spectrum-functional group relations.

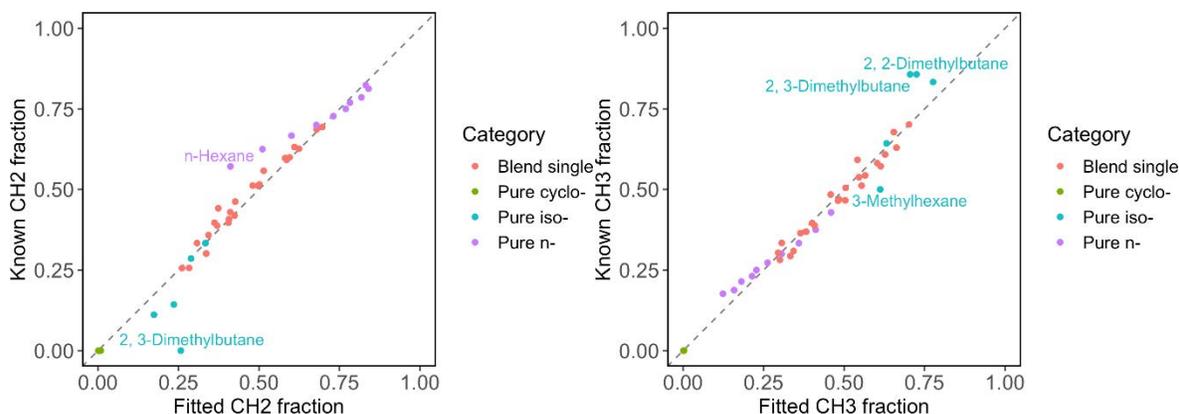


Figure 2. Known fraction of alkyl CH_2 versus fitted fraction of alkyl CH_2 (left) and known fraction of alkyl CH_3 versus fitted fraction of alkyl CH_3 (right). Dashed gray line denotes line of equivalence.

After estimating the functional group fractions of each fuel, the number of each functional group present in each average fuel molecule can be calculated by multiplying the fractions by the total number of hydrogen atoms per average molecule. With the number of each type of functional group in a given fuel known, group additivity models can be used to determine physical and chemical properties.

Strategy 3 uses principal component analysis (PCA) and support vector regression (SVR) to directly correlate mid-IR spectral features with physical and chemical fuel properties. PCA is a preprocessing step that transforms input data (FTIR spectra) into its principal components. These principal components are independent linear combinations of the input features, arranged in decreasing order of importance, thereby enabling significant dimensionality reduction without significant information loss. Use of PCA eliminates redundancies in the training data, reduces the chance of overfitting data, and extracts

data-driven latent features that would otherwise not be readily apparent. SVR maps this input data onto a high-dimensional feature space where it can be fit by an appropriate linear hyperplane. Optimal SVR model parameters are chosen by performing a grid search, using the minimum cross-validation error (RMSE) as the performance metric. Table 1 shows the prediction error for three fuel properties—molecular weight (MW), kinematic viscosity (KV) at -20 C, and DCN—as calculated using the Strategy 1 and Strategy 3 approaches. As seen in the tabulated results, Strategy 3 has a lower prediction error than Strategy 1 for all of the properties considered.

Table 1. Prediction errors for three properties (molecular weight, kinematic viscosity, derived cetane number), as calculated using Strategy 1 and Strategy 3.

Method	Prediction Error (RMSE %)		
	MW	KV (-20 C)	DCN
Strategy 1	3.45	9.62	6.51
Strategy 3	2.29	7.09	3.91

Strategy 4 was developed to infer the molecular species content of a fuel from its IR spectrum. This strategy uses a constrained least squares optimization approach to accurately identify the components of a blended fuel and predict their respective mole fractions. This information is then used to determine the C and H number, and consequently, the average molecular weight of the composite fuel. Although still in development, Strategy 4 has been tested on a real fuel (gasoline) and excellent agreement between the estimated and actual fuel composition was observed (see Figure 3).

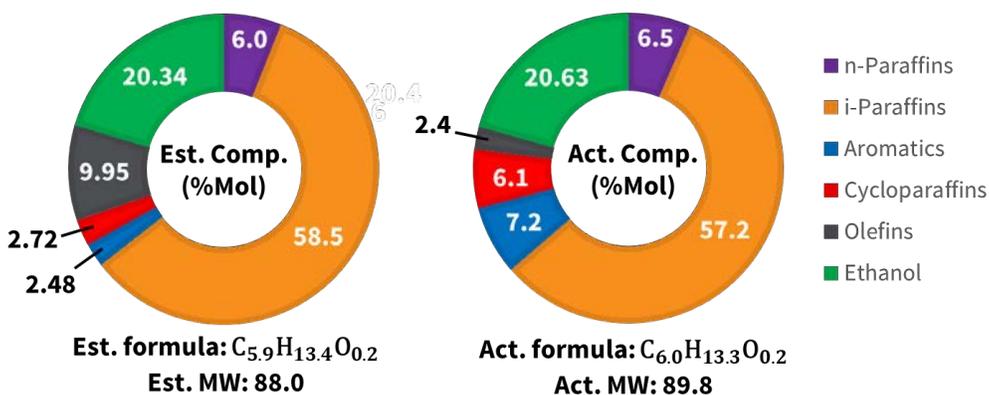


Figure 3. Comparison of estimated and actual compositional breakdown of a real fuel sample (gasoline). Estimates were obtained using Strategy 4.

Overall, the IR analysis results obtained using the three strategies developed over the past year show improved predictive performance relative to the initial spectral analysis strategy developed in the first year of this work (Strategy 1). In addition to being able to predict physical and chemical fuel properties, the newly developed analysis strategies also provide valuable insight into the functional groups and molecular species present in a fuel mixture.

Shock tube experiments: methods and results

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 (ignition time delays (IDTs) and species concentration time-histories) in a quiescent high-temperature, high-pressure environment that is very well characterized and hence amenable to modeling. 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.

The strength in the Stanford shock tube approach comes from the implementation of laser diagnostics that enable the simultaneous measurement of species time-histories. Using laser absorption diagnostics developed over the past 30 years, 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, isobutene, CH₂O, and aromatics), combustion products (including CO, CO₂, and H₂O), and temperature (see Figure 4a). 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. To facilitate shock-tube studies of low-vapor pressure fuels like jet fuels, the shock tube facility must be heated, as is the case in the high-purity, large-diameter (14 cm internal diameter) shock tube facility used in this work (pictured in Figure 4b).

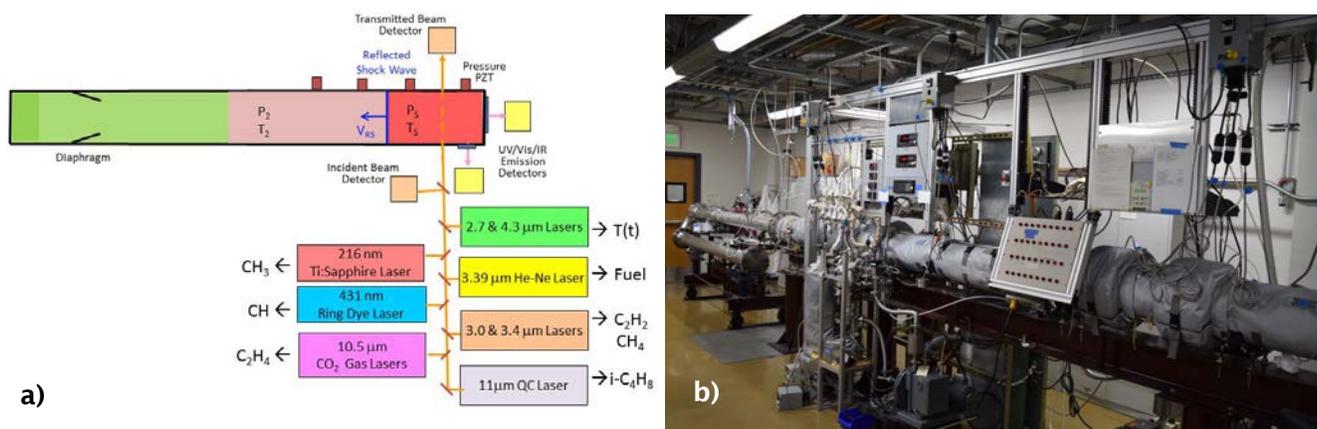


Figure 4. (a) Schematic of shock tube/laser absorption setup. Simultaneous measurement of multiple species time-histories and temperature with microsecond time resolution are enabled using this arrangement (only a partial list of accessible species is indicated); and (b) Stanford 14-cm-diameter, heated shock tube.

In our recent work, an absorbance model, connecting data spanning three years and eight laser wavelengths, was developed to enable the improved spectroscopic study of three jet fuels: JP8, Jet-A, and JP5. Specifically, methane (CH₄), ethylene (C₂H₄), and lumped vinyl-group time-histories, in addition to aromatics (benzene and toluene) yields, were quantified using eight wavelengths over conditions 1040–1480 K, 1–3 atm. Figure 5 shows the C₂H₄ and CH₄ species time-histories at five temperatures for each of the three fuels. Both C₂H₄ and CH₄ time-histories are relatively consistent across each fuel, with JP8 showing stronger C₂H₄ formation at earlier times at high temperatures, and higher CH₄ formation at the highest temperature.

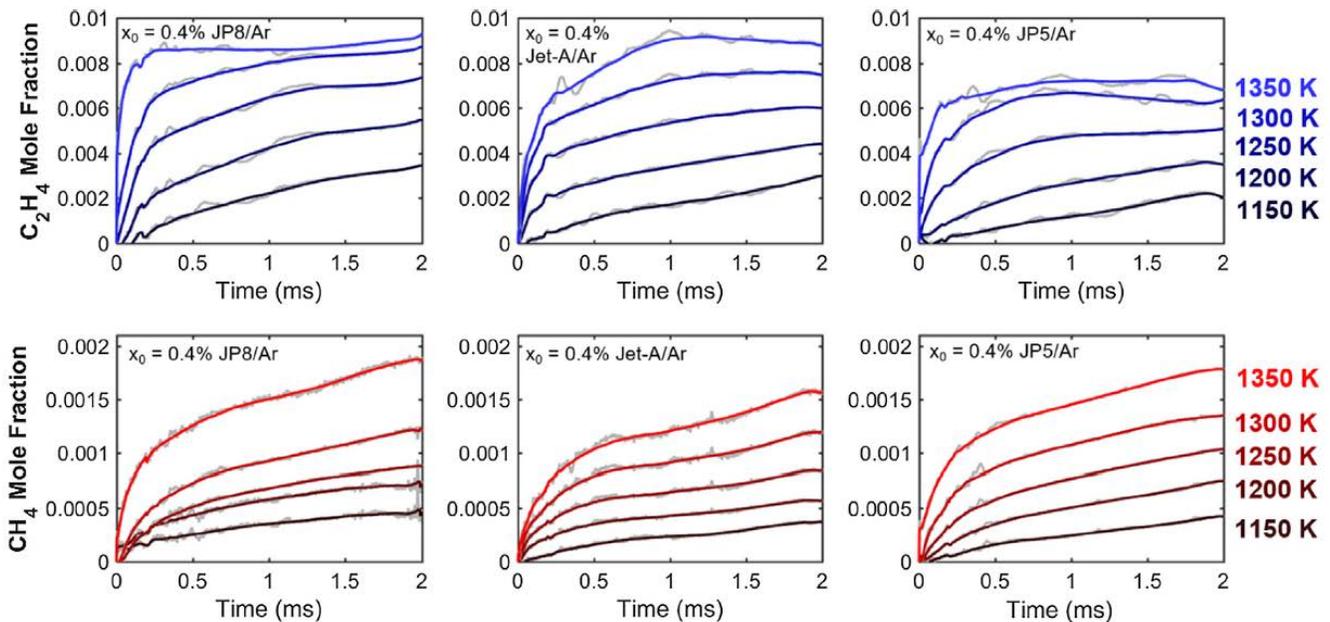


Figure 5. Mole fraction time-histories of ethylene (top row) and methane (bottom row) during pyrolysis of 0.4% JP8 (left), Jet-A (center), and JP5 (right) at 1.8 atm.

Figure 6 shows the mole fraction time-histories of vinyl groups during the pyrolysis of JP8, Jet-A, and JP5. The mole fractions shown correspond to the combined formation of propene (one vinyl group), 1-butene (one vinyl group), and twice 1,3-butadiene (two vinyl groups). Notably, the vinyl-group time-history for Jet-A begins to decay at high temperatures, while JP8's vinyl-group time-histories continue to grow. This is likely caused by a different blend of vinyl-group-containing species between the two fuels: the larger molecules 1-butene and 1,3-butadiene break down faster than propene, indicating their presence is more prevalent in the Jet-A pyrolysis system than the JP8 pyrolysis system.

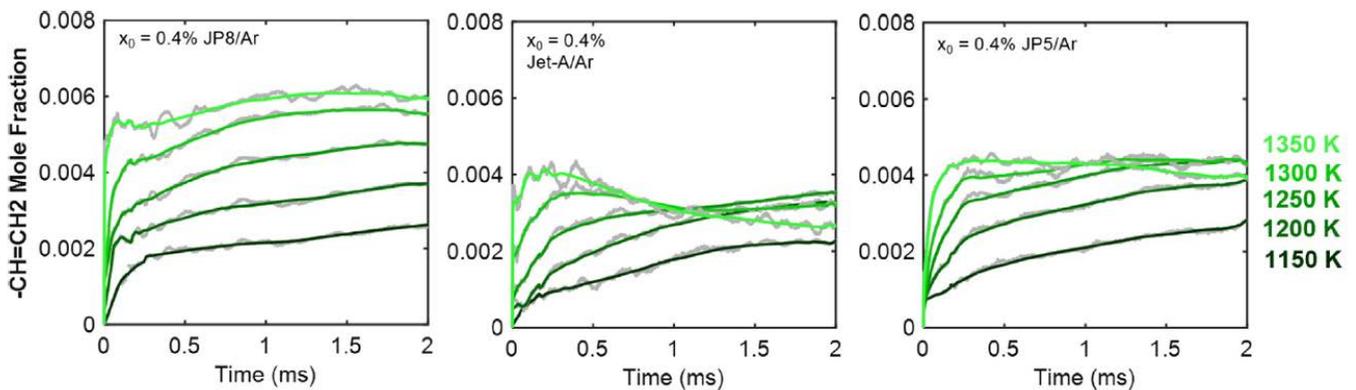


Figure 6. Mole fraction time-histories of vinyl groups during the pyrolysis of JP8 (left), Jet-A (center), and JP5 (right) between 1150–1350 K.

Figure 7 shows aromatics (benzene and toluene) yields at 2 ms, 1350 K, and 1.8 atm for the three jet fuels. The JP8 and Jet-A results show close agreement with HyChem model predictions, while the JP5 measurements show lower aromatics yields than predicted by HyChem.

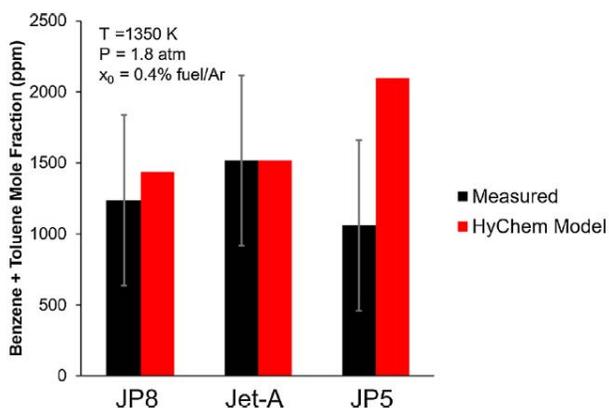


Figure 7. Inferred aromatics (benzene and toluene) mole fractions at 1350 K and 2 ms during the pyrolysis of JP8, Jet-A, and JP5 (black) compared with HyChem models (red).

Overall, this shock tube/laser absorption work has provided valuable new insights into the formation of jet fuel pyrolysis products methane, ethylene, propene, 1-butene, 1,3-butadiene, benzene, and toluene. Data were generally found to agree with existing HyChem model results and serve as independent validation of our understanding of jet fuel pyrolysis and oxidation chemistry.

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

- Measurements of methane (CH_4), ethylene (C_2H_4), and lumped vinyl-group time-histories, in addition to aromatics (benzene and toluene) yields, were acquired in pyrolysis experiments for three jet fuels (JP8, Jet-A, JP5) spanning 1040–1480 K, 1–3 atm.
- A strategy (Strategy 2) was developed for using IR spectra (3.3–3.6 μm) to estimate the number/fractional presence of CH_2 , CH_3 , and “other” functional groups in a fuel, which in turn can be used to infer physical/combustion properties of the fuel.
- A strategy (Strategy 3) was developed to infer physical and combustion properties of fuels from their IR spectra (3.3–3.6 μm) via principal component analysis using complex, non-linear models.
- A strategy (Strategy 4) was developed to more accurately identify individual molecular species components and their mole fractions in blended fuels.
- A paper entitled “Spectroscopic inference of alkane, alkene, and aromatic formation during high-temperature JP8, JP5, and Jet-A pyrolysis” was published in the journal *Fuel* (Pinkowski et al., 2020). A paper entitled “A new strategy of characterizing hydrocarbon fuels using FTIR spectra and generalized linear model with grouped-Lasso regularization” was accepted for publication in the journal *Fuel* (Wang et al., 2020).
- Our contribution to the jet fuel prescreening section of the AIAA volume titled *Fuel Effects on Operability of Aircraft Gas Turbine Combustors* was completed.

Publications

Peer-reviewed journal publications

N. Pinkowski, S. Cassady, D.F. Davidson, R.K. Hanson, “Spectroscopic inference of alkane, alkene, and aromatic formation during high-temperature JP8, JP5, and Jet-A pyrolysis,” *Fuel* 269 117420 (2020).

<https://doi.org/10.1016/j.fuel.2020.117420>

Y. Wang, W. Wei, R.K. Hanson, “A new strategy of characterizing hydrocarbon fuels using FTIR spectra and generalized linear model with grouped-Lasso regularization,” *Fuel*, accepted September 30, 2020.



Outreach Efforts

Our IR fuel analysis work was presented via poster at the Fall ASCENT Virtual Meeting, September 29-30, 2020.

Awards

Professor Hanson delivered the 100th Beacon lecture at Tsinghua University, China.

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. Yu Wang and Vivek Boddapati (current graduate students) performed the IR spectral analysis/fuel prescreening. 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:

- Expand the capability of the Stanford FTIR spectrometer to collect measurements over an expanded mid-IR spectral range (2–15 μm)
- Compile a training dataset containing the full (2–15 μm) vapor-phase FTIR spectra of real fuels and neat hydrocarbons (specifically those larger than C₈ and relevant to jet fuels) using spectral databases and measurements at Stanford.
- Assess the improvement in predictive performance of Strategies 1–4 using the full spectral range compared to just the 3.4 μm region.
- Apply these wide-spectrum IR analysis methods to prescreening and characterization of real, sustainable aviation fuel (SAF) candidates.
 - Acquire candidate SAF fuel samples and property data from National Jet Fuels Combustion Program (NJFCP) partners.
- Investigate further refinement in IR spectral analysis methods to enhance prediction accuracy and applicability to a wider range of jet fuels, particularly those derived from bio-derived feedstocks.