Project 025 Shock Tube and Flow Reactor Studies of the Kinetics of Jet Fuels - Rapid IR Fuel Screening

Stanford University

Project Lead Investigator

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University Participants

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- PIs: Professor Ronald K. Hanson
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    1. Area #1: Chemical kinetics combustion experiments

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Investigation Team

- Professor Ronald K. Hanson, PI, research direction
- Alison Ferris, research scientist, research management
- Vivek Boddapati, graduate student, research assistant

Project Overview

The seventh year of this program has focused on developing and refining strategies for the accurate prediction of jet fuel properties (chemical and physical) and composition. To achieve this goal, the research focused on two areas: (a) new spectroscopic measurements of infrared (IR) spectra of jet fuels and pure hydrocarbons and (b) correlation of chemical, physical, and combustion fuel properties with IR spectral features. The results of the IR spectral analysis work will be used to establish the strong sensitivity of the physical and chemical properties of jet fuels to their molecular structure, with the ultimate goal of developing a rapid pre-screening approach, requiring minimal fuel volume, to simplify the certification process for alternative jet fuels. These IR-spectra-based correlation models will also potentially aid in the development of future kinetic models for jet fuel combustion.

Task 1 - Chemical Kinetics Combustion Experiments

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Objective(s)

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 (a) chemical, physical, and combustion properties of jet fuels and (b) functional group and molecular species composition with their IR spectra.

This multi-year research program has culminated in the completion of American Institute of Aeronautics and Astronautics (AIAA) book chapters describing the research progress during the past 7 years, notably the advancements in the understanding of jet fuel chemical kinetics and fuel prescreening techniques.

Research Approach

An important goal of the current research is to characterize jet fuel composition and properties on the basis of the fuel's mid-IR absorption spectrum, measured with a Fourier transform IR (FTIR) spectrometer. Over the past 2 years, a database of spectroscopic measurements and property data 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 and the fuel composition as well as with important physical/combustion properties, such as the initial boiling point (IBP), density, derived cetane number (DCN), and ignition delay times (IDT). Here, an overview of the two research areas (FTIR spectroscopic measurements and IR fuel analysis) is presented along with experimental and modeling results obtained over the past year.

FTIR Spectroscopic Measurements: 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 sharp spectral features, even individual absorption transitions, which can in turn be tied directly to structural characteristics of fuel molecules. This work focuses on the analysis of mid-IR absorption spectra, because of the strong sensitivity of the mid-IR region to hydrocarbon bonding. Initial work in the previous year of the program focused solely on the 3-μm spectral region, which contains the C–H stretch absorption features corresponding to the -CH_2 and -CH_3 functional groups in hydrocarbon molecules. These features are characteristic of *n*-paraffins and isoparaffins, but do not offer any distinctive information about cycloparaffins and aromatic compounds, which are often important constituents of jet fuels. To capture additional features corresponding to these molecular classes, we extended the wavelength range of acquired IR spectra to cover the entire 2- to 15-μm region.

The 2- to 15-μm FTIR spectra of approximately 35 pure hydrocarbons were sourced from the Pacific Northwest National Laboratory (PNNL) spectroscopic database. The spectra of 24 pure hydrocarbon blends were calculated by using the mole-fraction-weighted sums of the spectra of individual components. The measurement of the extended-wavelength spectra of additional pure hydrocarbons and jet fuels required modification of our in-house FTIR spectrometer facility. To this end, the sapphire optical windows on the heated cell were replaced with new ZnSe windows that transmit IR light across 2–15 μm. The system was then subjected to leak testing to ensure that the optical cell was well sealed. A new IR light source was installed in the FTIR spectrophotometer to improve the signal at long wavelengths (12–15 μm). Because a portion of the optical path length of the FTIR setup passed through open atmosphere, interfering absorbance from atmospheric water and carbon dioxide was observed in the spectral measurements. To mitigate the effects of this interfering absorbance on our measurements, we constructed a purge system to enclose the entire optical path, as shown in Figure 1. A line was provided to purge the setup with nitrogen gas, which, unlike water and carbon dioxide, does not absorb IR light.

Figure 1. The modified FTIR spectrometer facility, with a purge system constructed to enable purging of the entire optical path length with nitrogen gas during measurements.

Preliminary 2- to 15-μm spectra of toluene, *n*-octane, and iso-octane were measured with the modified system and were found to be in agreement with spectra taken from the PNNL database. Subsequently, the spectra of several jet-fuel-relevant pure hydrocarbons (*n*-dodecane, isocetane, methylcyclohexane, *n*-propylcyclohexane, *trans*-decalin, and 1-methylnaphthalene) were measured at a temperature of 150 °C and added to our database of FTIR spectra. Multiple fuel concentrations were used during the measurement of each fuel to capture the weaker absorption features with a high signal-to-noise ratio. An example measurement of methylcyclohexane (MCH) is shown in Figure 2, with the important spectral features labeled. The dataset was further expanded by measuring the spectra of 17 A and C category jet fuels A1–A8 and C1–C9. These, spectra along with the pure hydrocarbon spectra from PNNL and the calculated blends' spectra were compiled into the training dataset, thus bringing the total to 81 fuels, representing a considerable improvement with respect to the dataset size of 63 fuels in the previous year.

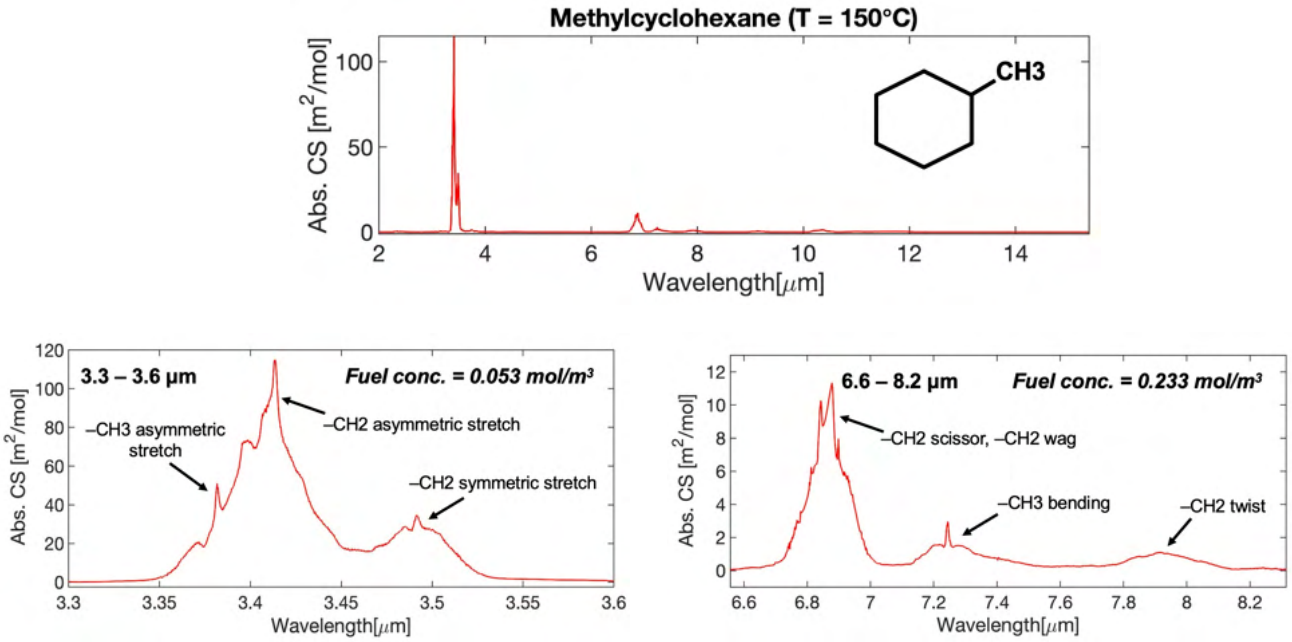

Figure 2. Measured 2- to 15-μm spectrum of methylcyclohexane (top); strong -CH_2 and -CH_3 stretch features in the 3.3- to 3.6-μm region, captured by using a using low fuel concentration (bottom left); relatively weaker -CH_2 and -CH_3 bending features in the 6.6- to 8.2-μm region captured by using a high fuel concentration (bottom right).

IR Fuel Analysis: Methods and Results

In the past 2 years of this program, four strategies (strategies 1–4) were developed for estimating physical and chemical properties, functional group fractions, and molecular species constituents of fuels directly from mid-IR spectra in the 3-µm region. In the current year of this program, two of these developed strategies (strategies 1 and 4) were further refined to improve their predictive performance. The methods and results for each strategy are discussed below.

The first iteration of strategy 1 implemented cross-validated linear models with Lasso regularization to correlate the FTIR spectra from 3300 to 3500 nm with a fuel's physical and chemical properties. Although these preliminary models showed good prediction accuracy for *n*-paraffins and isoparaffins, they had higher property prediction error for aromatic compounds. To improve the performance of these models, we modified the training dataset to include the full 2- to 15-µm FTIR spectra of fuels. Furthermore, the models were modified to use Elastic Net regularization instead of Lasso regulation, enabling the selection of optimal model parameters for each property during training. For implementation, a grid search was first performed to choose the combination of model parameters resulting in the minimum cross-validation error (CVE), which were then used to train the final model for each property. Figure 3 demonstrates this improvement in strategy 1 performance on the training data for the property IBP.

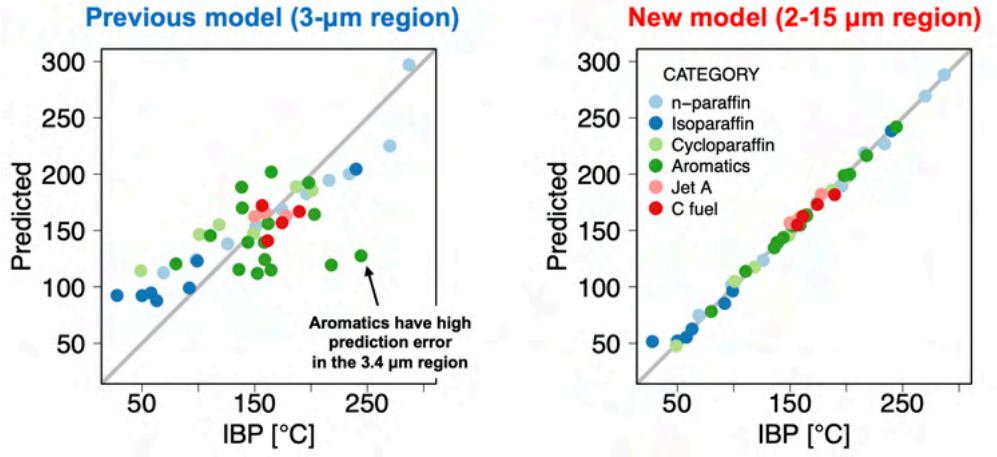

Figure 3. Actual versus predicted values of IBP by using strategy 1 models: previous model based on 3-µm FTIR spectra (left); new model based on 2- to 15-µm FTIR spectra (right).

These two plots indicate that the new model (based on 2- to 15-µm spectra) fits the data much better than the previous model (based only on the 3-µm spectral region). The previous model shows poor prediction for aromatic compounds in particular, which do not have distinctive absorption features in the 3-µm region. The performance improvement is further evidenced by the decrease in CVE (indicative of future predictive performance) and an increased R^2 value (measure of goodness of fit). These results are summarized in Table 1. Similar performance improvements were observed for all properties considered.

Table 1. Strategy 1 performance metrics for IBP: CVE, mean absolute error (MAE) on the training data, and R^2 value.

Method	CVE (%)	MAE (%)	R^2 value
Previous model (3-µm region)	18.93	17.72	0.59
New model (2-15 µm region)	5.61	1.95	0.99

Figure 4 shows the 38 wavelengths selected by the new strategy 1 model, along with their relative contributions to the variation in IBP. This plot clearly shows that the model selects multiple wavelengths outside the 3-µm region, which contribute considerably to IBP prediction, thus explaining the gain in prediction accuracy due to the extended spectral range.

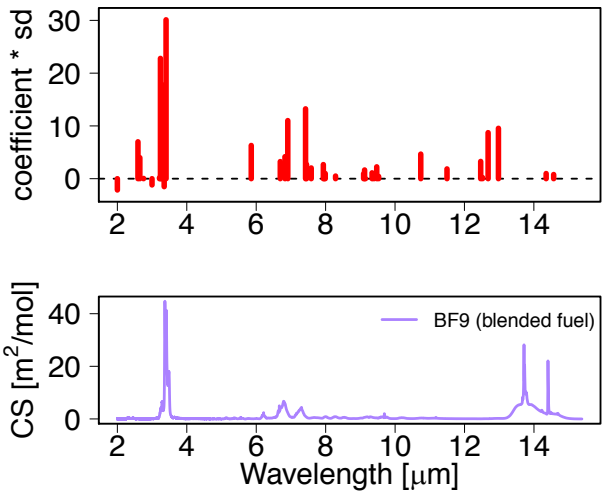

Figure 4. Wavelengths selected by the new strategy 1 model (based on 2- to 15-μm spectra) and their contributions to the variation in IBP (top); representative IR spectrum of BF9, a three-component hydrocarbon blend (bottom).

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 strategy, which was previously restricted to the 3-μm spectral region, was modified to estimate the molecular species composition of fuels based on the extended 2- to 15-μm FTIR spectra. To test this approach, we calculated the spectrum of a six-component mixture of pure hydrocarbons (35% *n*-decane, 7% 3-methylhexane, 22% isooctane, 9% mesitylene, 16% *o*-xylene, and 11% *m*-xylene) with a mole-fraction-weighted sum of the individual components' spectra. Strategy 4 was then used to estimate the composition of this simulated mixture from a set of 35 pure hydrocarbon spectra, all from the PNNL database. Particular emphasis was placed on quantifying the uncertainty in the predicted mole fractions by using a Monte Carlo method and simultaneously varying the spectra of the 35 database components within the FTIR experimental uncertainty range (±1.25%). This method is demonstrated in Figure 5.

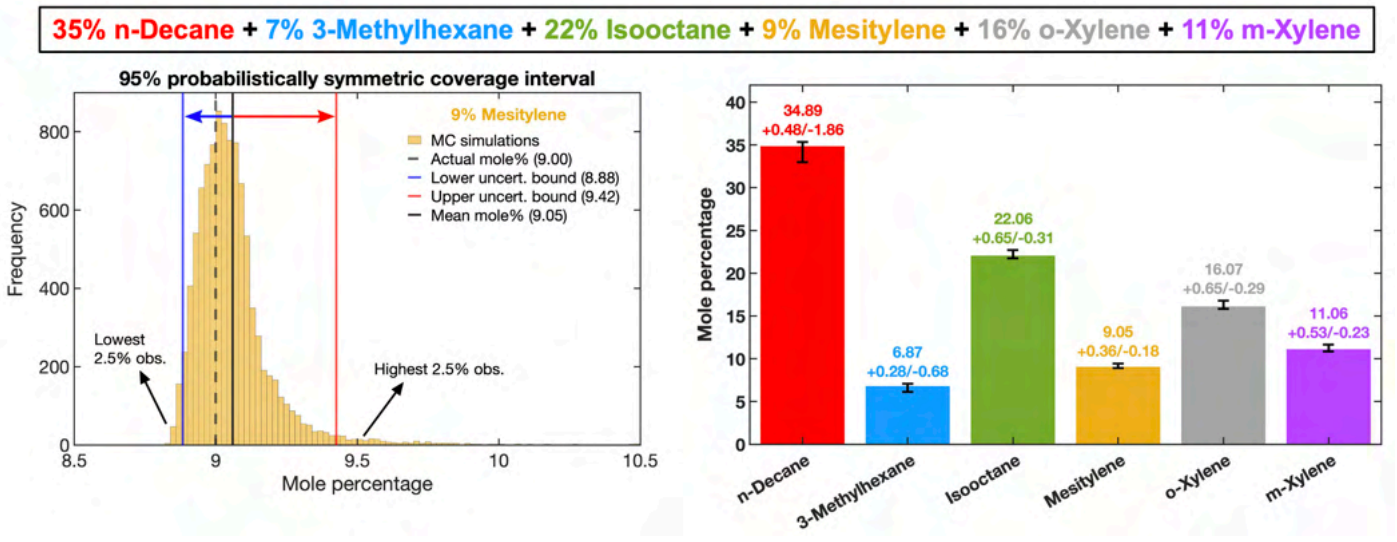

Figure 5. Strategy 4 uncertainty quantification for a simulated six-component mixture. Estimation of 95% confidence interval with Monte Carlo simulations for each component, shown here for mesitylene (left); estimated uncertainties in the mole percentages of the six components predicted with strategy 4 (right).

As seen above, strategy 4 can be used to estimate the molecular composition of blended fuels within tight uncertainty bounds. This information can then be used to accurately determine the basic properties of the composite fuel, such as the C and H number, and the average molecular weight (MW), by using additive models. Figure 6 below draws a comparison between the uncertainties in the predicted MW of the simulated six-component mixture for strategy 1 (both the previous model and the new model) and strategy 4. As seen in this plot, the new strategy 1 model, as expected, is more accurate than the previous model in predicting the mixture MW. However, strategy 4 clearly outperforms strategy 1 in terms of the prediction uncertainty for MW. Hence, strategy 4 provides a more accurate way of predicting certain linearly additive properties of complex fuel mixtures.

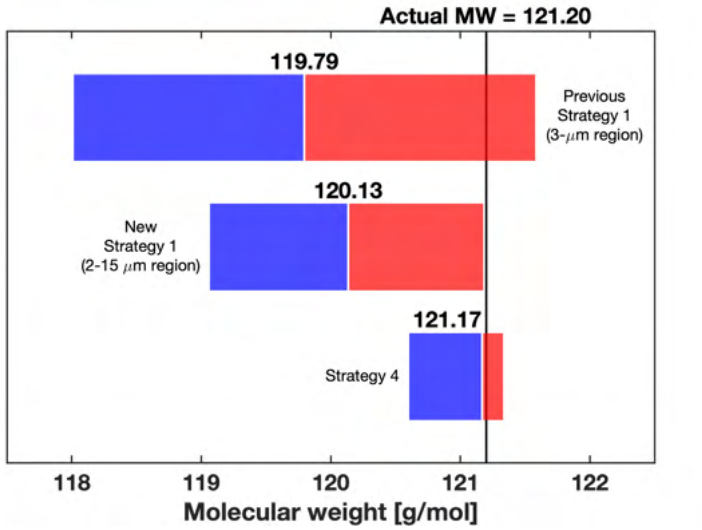

Figure 6. Comparison of uncertainty in the prediction of MW of the simulated six-component mixture by using the previous strategy 1 model (3-μm region), the new strategy 1 model (2- to 15-μm region), and strategy 4.

Overall, the IR analysis results obtained with the two refined strategies (strategies 1 and 4) developed over the past year show improved predictive performance relative to that of the initial spectral analysis strategies developed in the previous 2 years of this work. Together, these strategies provide the capability to accurately predict the physical and chemical properties, and the molecular composition of jet fuels directly based on their IR spectra.

Milestone(s)

Major milestones included regular reporting of experimental results and analysis at the National Jet Fuels Combustion Program (NJFCP) teleconferences (October, 2020 and February, 2021), as well as the Fall and Spring ASCENT meetings (September 2020 and April 2021).

Major Accomplishments

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

- The FTIR spectrometer facility was modified to enable spectroscopic measurements in the extended wavelength region spanning 2- to 15-μm.
- New 2- to 15-μm FTIR spectra of jet-fuel-relevant pure hydrocarbons, and A and C category real fuels were measured.
- An expanded training dataset of FTIR spectra and property data was compiled by using a combination of in-house measurements and the PNNL spectral database.
- The previously developed strategy 1 model was modified with the extended spectral range and hyperparameter tuning methods to select the optimal model parameters for each property.
- The strategy 4 model was refined by implementing a Monte Carlo method to quantify uncertainties in the predicted mole fractions of a simulated six-component mixture and was further used to accurately estimate the mixture's MW with high confidence.

- 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

Wang, Y., Wei, W., Hanson, R. K. (2021). A new strategy of characterizing hydrocarbon fuels using FTIR spectra and generalized linear model with grouped-Lasso regularization. Fuel, *287*, 119419. https://doi.org/10.1016/j.fuel.2020.119419

Published book chapters

Park, J. W., Xu, C., Gao, Y., Lu, T. F., Shao, J. K., Pinkowski, N. H., Wang, S., Wang, Y., Cao, Y., Hanson, R. K., Davidson, D. F., & Colket, M. B. (2021). Chemical kinetics. In: J. Heyne, & M. Colket (Eds.), *Fuel effects on operability of aircraft gas turbine combustors* (pp. 255-293). American Institute of Aeronautics and Astronautics, Inc.

Heyne, J., Yang, Z., Boehm, R., Rauch, B., Le Clercq, P., Hanson, R., Ferris, A., Dooley, S., Ure, A., Blakey, S., Lewis, C., Colket, M. (2021). Prescreening of sustainable aviation jet fuels. In: J. Heyne, & M. Colket (Eds.), *Fuel effects on operability of aircraft gas turbine combustors* (pp. 487-523). American Institute of Aeronautics and Astronautics, Inc.

Outreach Efforts

Our IR fuel analysis work was presented at the Joint NJFCP Meetings on October 20, 2020 and February 2, 2021; the Virtual Fall ASCENT Advisory Board Meeting, September 29–30, 2020; and the Virtual Spring ASCENT Advisory Board Meeting, April 27–29, 2021. We have also begun collaborating with Professor Joshua Heyne's group at the University of Dayton in examining the effects of isomeric structure on jet fuel combustion properties.

Awards

None

Student Involvement

Graduate students are actively involved in the acquisition and analysis of all experimental data. Vivek Boddapati (current graduate student) performed the IR spectral analysis/fuel prescreening. Yu Wang successfully defended his PhD thesis, which was partly based on work performed under this contract. Alison Ferris (current research scientist) has additionally contributed to the project through research management, compilation of experimental results, and report writing.

Plans for Next Period

In the next period, we plan to perform the following:

- Acquire additional FTIR measurements and property data of neat hydrocarbons and real fuels to further expand the current dataset
- Train strategy 3 models (principal component analysis + support vector regression) by using the expanded 2- to 15-μm spectra and assess the improvement in predictive performance compared with just the 3-μm region, particularly for highly non-linear properties (e.g., kinematic viscosity)
- Apply these wide-spectrum IR analysis methods to the prescreening and characterization of real, sustainable aviation fuel (SAF) candidates.
    - Acquire candidate SAF samples and property data from ASCENT/NJFCP partners
- Investigate further refinement of IR analysis strategies to enhance their predictive accuracy and applicability to a wider range of jet fuels, particularly those from bio-derived feedstocks
- Explore the potential of IR spectral analysis methods for predicting important combustion parameters and subsequently guiding the development of kinetic models for jet fuel combustion