

# Project 025 Shock Tube Studies of the Kinetics of Jet Fuels

## Stanford University

### Project Lead Investigator

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### University Participants

#### Stanford University

- P.I.: Prof. Ronald K. Hanson
- FAA Award Number: 13-C-AJFE-SU-027
- Period of Performance: October 1, 2021 to September 30, 2022
- Task:
  1. Chemical kinetics combustion experiments.

### Project Funding Level

2021–2022: \$200,000 from the FAA, with 1:1 matching funds of \$200,000 from Stanford University

### Investigation Team

- Prof. Ronald K. Hanson, P.I., research direction
- Alison Ferris, Research Scientist, research management
- Vivek Boddapati, Graduate Student, research assistance

### Project Overview

The eighth 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: new spectroscopic measurements of infrared (IR) spectra of jet fuels and neat hydrocarbons, and correlation of the physical and combustion properties of these fuels with their infrared spectral features. The results of the IR spectral analysis work will be used to establish the strong sensitivity of jet fuels' physical and chemical properties to their molecular structure, with the ultimate goal of developing a rapid pre-screening approach, requiring minimal fuel volume, to streamline the testing and certification process of alternative jet fuels.

## Task 1 - Chemical Kinetics Combustion Experiments

Stanford University

### Objectives

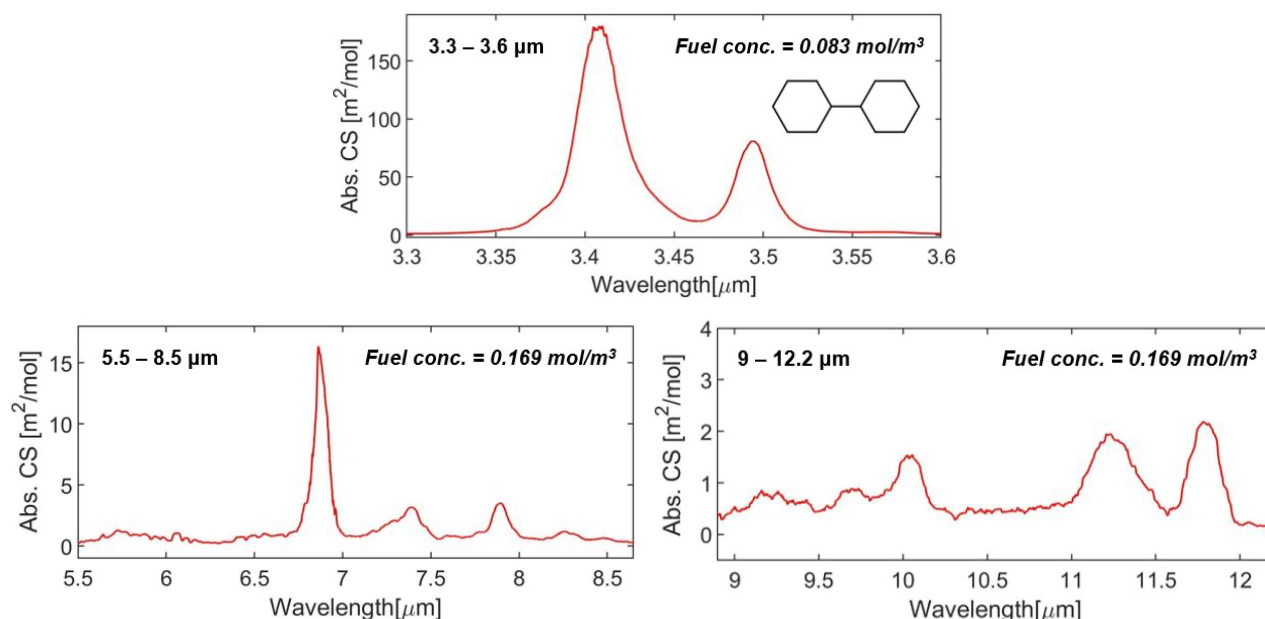
This work is aimed at developing fuel prescreening tools based on the IR absorption cross-section measurements of jet fuels and their constituent molecules. Specific fuel analysis objectives include developing effective strategies for correlating (a) chemical, physical, and combustion properties, and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

### Research Approach

An important goal of the current research is to characterize jet fuel composition and properties based on the fuel's mid-IR absorption spectrum, measured using a Fourier transform IR (FTIR) spectrometer. Over the past 3 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 jet fuels with fuel composition and with important physical/combustion properties, such as initial boiling point (IBP), density, derived cetane number (DCN), and ignition delay time (IDT). Here, we present an overview of the two research areas (expansion of the FTIR spectrum/fuel property training dataset and IR fuel analysis), along with experimental and modeling results obtained over the past year.

#### Expansion of the FTIR spectrum and fuel property training dataset:

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 enables the detection of sharp spectral features, and even individual absorption transitions, which can in turn be directly linked to the structural characteristics of fuel molecules. This work focuses on analysis of mid-IR absorption spectra, because of the strong sensitivity of this spectral region to hydrocarbon bonding. Work in the previous year of the program focused on extending the spectral range to cover the full 2- to 15-  $\mu\text{m}$  region, in contrast to the 3.4-  $\mu\text{m}$  region used in the initial work. This process helped us capture additional features corresponding to cycloparaffins and aromatic compounds, which are often important constituents of jet fuels.



**Figure 1.** Measured 2- to 15-  $\mu\text{m}$  spectrum of bicyclohexane: strong features in the 3.3- to 3.6-  $\mu\text{m}$  region, captured with low fuel concentration (top); relatively weaker features in the 5.5- to 8.5-  $\mu\text{m}$  region (bottom left) and the 9- to 12.2-  $\mu\text{m}$  region (bottom right), captured with high fuel concentration.

Using the modified FTIR spectrometer facility at Stanford, we measured the spectra of additional neat hydrocarbons belonging to molecular classes relevant to jet fuels (isoparaffins, cycloparaffins, and aromatic compounds) at a temperature of 150 °C and added them to our database of FTIR spectra. These hydrocarbons are butylcyclohexane, bicyclohexane, tetralin, pentamethylheptane, trans-decalin, 2-methylhexane, 2-methylheptane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane. 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 bicyclohexane is shown in Figure 1, in which the three panels represent regions with important spectral features.

The dataset was further expanded through the addition of FTIR spectra and property data of blends of neat hydrocarbons. The 2- to 15-  $\mu\text{m}$  FTIR spectra of hydrocarbon blends were calculated as the mole-fraction-weighted sum of the spectra of the individual components. Overall, five categories of hydrocarbon blends were added to the training dataset. These categories are as follows:

- BF: 14 two- to three-component blends of *n*-decane, isooctane, and toluene (from the literature)
- Won: 10 binary blends of *n*-dodecane/*n*-decane and toluene (from the literature)
- CB (cycloparaffin blends): 9 binary blends of methylcyclohexane and *n*-butylcyclohexane
- MB (multi-class blends): 70 four-component blends of *n*-dodecane, isooctane, *n*-butylcyclohexane, and *n*-propylbenzene
- AG: 43 three- to five-component blends of *n*-heptane, isooctane, *n*-hexadecane, cyclopentane, and toluene (from the literature)

The addition of these hydrocarbon blends has increased the size of the training dataset to 228 fuels, thus representing a substantial improvement over the dataset size of 81 fuels in the previous year.

The physical/chemical properties of the above-mentioned hydrocarbon blends were either sourced from property measurements reported in the literature, or estimated from the individual components' property values through various property blending correlations as follows:

- Molecular weight (MW): mole fraction-weighted sum
- H/C ratio: ratio of H and C numbers obtained from the mole-fraction-weighted sum
- Net heat of combustion (NHC): mass-fraction-weighted sum
- Density: volume fraction-weighted sum
- Flash point: nonlinear correlation based on volume fractions (from the literature)
- Freezing point: nonlinear correlation based on volume fractions (from the literature)
- Kinematic viscosity (KV): nonlinear correlation based on volume fractions (from the literature)
- Threshold sooting index (TSI): linear correlation based on mole fractions (from the literature)

The use of these blending correlations has enabled us to directly populate the training dataset, thereby circumventing the need for property data measurements.

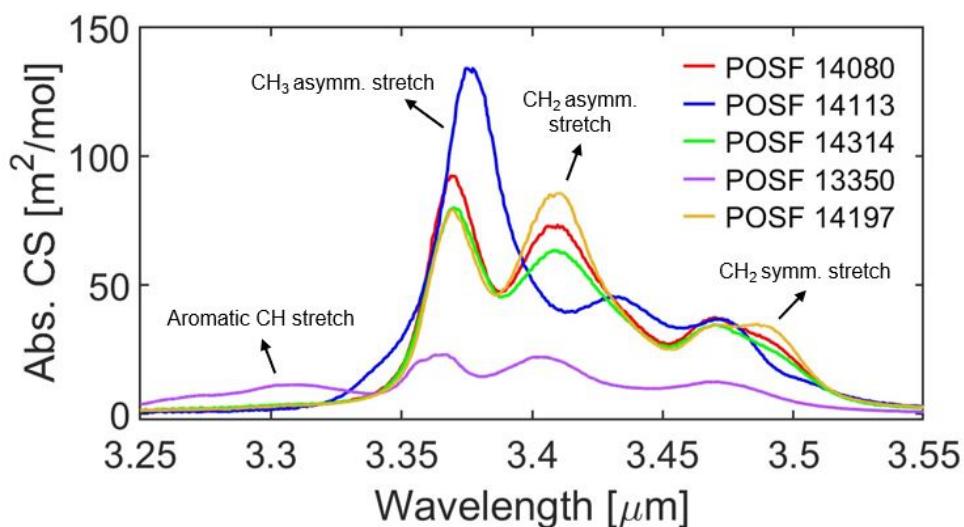
Five new, candidate Sustainable Aviation Fuel (SAF) samples were recently acquired from other ASCENT members (Steve Zabarnick). These fuels show considerable differences in their molecular class distribution, as detailed in Table 1. A brief description of these five SAFs is provided below.

- POSF 14080: synthetic jet fuel processed from biomass; manufactured by Swedish Biofuels
- POSF 14314: synthetic jet fuel processed from biomass; manufactured by Swedish Biofuels
- POSF 14113: bio-sourced isoparaffinic jet fuel; manufactured by Global Bioenergies
- POSF 13350: synthesized aromatic kerosene; manufactured by Virent
- POSF 14197: biojet fuel; manufactured by the Council of Scientific and Industrial Research-Indian Institute of Petroleum (CSIR-IIP)

**Table 1.** Molecular class distributions of the five new SAF samples, according to gas chromatography (GCxGC) analysis.

Molecular class	Weight % (GCxGC)				
	14080 (Swedish Biofuels)	14113 (Global Bioenergies)	14314 (Swedish Biofuels)	13350 (Virent)	14197 (CSIR)
n-paraffins	1.40	0.03	1.16	0.03	18.68
isoparaffins	83.13	99.34	56.95	0.19	63.00
cycloparaffins	8.68	0.22	28.22	2.04	12.05
aromatics	6.78	<0.01	13.66	97.73	6.32

The 2- to 15-  $\mu\text{m}$  FTIR spectra of these five SAF samples were measured. Figure 2 shows a comparison of the spectra of these five fuels in the 3.4-  $\mu\text{m}$  region. The differences in fuel composition result in clear differences in spectral features. As seen in Figure 2, the magnitude of the  $-\text{CH}_3$  asymmetric stretch feature increases, and the  $-\text{CH}_2$  asymmetric stretch feature grows weaker with increasing isoparaffin content. Owing to its high aromatic content, POSF 13350 shows a distinct aromatic  $-\text{CH}$  stretch feature, which is absent in the spectra of the other four fuels. These spectral differences follow the expected trend based on the compositions determined through gas chromatography (GCxGC), and demonstrate the strong sensitivity of the FTIR spectra to fuel composition, a crucial aspect for developing accurate property prediction strategies.



**Figure 2.** The FTIR spectra of five SAF samples in the 3.4-  $\mu\text{m}$  region.

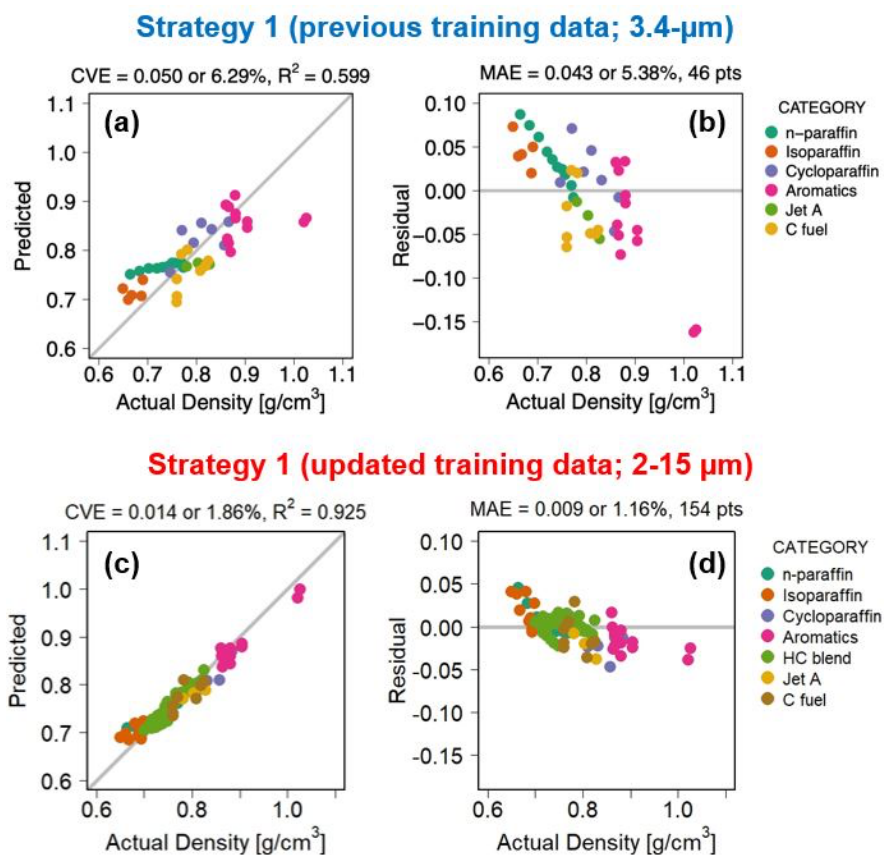
#### IR fuel analysis:

Over the past 3 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 previous year, two of these developed strategies (Strategies 1 and 4) were further refined to improve their predictive performance. In the current year of this program, Strategy 1 models were trained for different properties by using the expanded training dataset, and these updated models were used to make property predictions on an SAF sample provided by Prof. Josh Heyne (ASCENT P65). The methodology of Strategy 1, along with some results are discussed below.

The first iteration of Strategy 1 implemented cross-validated linear models with Lasso regularization to correlate the FTIR spectra from 3,300 to 3,500  $\text{nm}$  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 aromatics. To improve the performance of these models, we modified the training dataset to include the full 2- to 15-  $\mu\text{m}$  FTIR spectra of fuels.

Furthermore, the models were modified to use Elastic-Net regularization instead of Lasso regulation, thereby 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, which was then used to train the final model for each property.

As discussed in the previous section, the training dataset was also augmented by addition of the FTIR spectra and property data of blends of neat hydrocarbons, thereby increasing the total dataset size from 81 fuels to 228 fuels. The modified model parameter optimization Strategy, along with the expanded training data, improved the predictive performance of Strategy 1 models for various physical/chemical properties.



**Figure 3.** Strategy 1 model performance on training data: (a) predicted density and (b) residuals, on the basis of the previous dataset (3.4- $\mu\text{m}$  region, without hydrocarbon blends); (c) predicted density and (d) residuals, on the basis of the updated dataset (2- to 15-  $\mu\text{m}$  region, with added hydrocarbon blends).

Figure 3 shows the predictive performance of the Strategy 1 model for density on the training dataset fuels, comparing the model trained on the previous dataset (3.4- $\mu\text{m}$  region spectra, without hydrocarbon blends) with that trained on the updated dataset (2- to 15-  $\mu\text{m}$  spectra, with added hydrocarbon blends). These plots indicate that the updated Strategy 1 model fits the data much better than the previous model. The previous model shows poor prediction for aromatics in particular, which do not have distinctive absorption features in the 3.4- $\mu\text{m}$  region. The predictive performance of each model is evaluated according to three metrics: the cross-validation error (CVE, indicative of future predictive performance), the mean absolute error of prediction (MAE), and the  $R^2$  value (measure of goodness of fit). The updated model shows a reduction in CVE by a factor of 3.6, and a reduction by nearly a factor of 5 in the MAE as compared with the previous model. The updated model also has a substantially higher  $R^2$  value, thus indicating a better fit to the training data. Similar performance improvement was observed for all properties considered.



The previous and updated Strategy 1 models were also used to make property predictions on unseen test data. This step is often a crucial component in assessing the performance of machine learning models. The test data considered here are three volumetric blends of A2 (distillate jet fuel) and C1 (synthetic, alcohol-to-jet fuel). Table 2 shows the density predictions of the previous and updated Strategy 1 models for the three test fuel blends. This table clearly shows that the updated model performs better on the test data, achieving an error reduction on the order of 60%-90%, as compared with the previous model for density.

**Table 2.** Predictive performance of the previous and updated Strategy 1 models on test data (A2/C1 jet fuel blends).

Property	Fuel blend (% vol.)	Actual	Previous dataset (3.4- $\mu\text{m}$ )		Updated dataset (2-15 $\mu\text{m}$ )	
			Predicted	Error (%)	Predicted	Error (%)
Density [ $\text{g}/\text{cm}^3$ ]	80% A2 / 20% C1	0.795	0.763	-4.05	0.783	-1.52
	50% A2 / 50% C1	0.781	0.744	-4.80	0.774	-0.92
	20% A2 / 80% C1	0.768	0.722	-5.97	0.764	-0.55

The Strategy 1 models were finally used to predict the properties of an SAF sample provided by Prof. Josh Heyne (ASCENT P65). The measured 2- to 15-  $\mu\text{m}$  FTIR spectrum of this fuel indicated that cycloparaffins were major constituents of the fuel. The predictions of both the previous and updated Strategy 1 models, along with the reference property values are shown in Table 3. The reduction in prediction error of the updated model on the SAF sample, with respect to the previous model, further highlights the impact of the extended spectral range as well as the larger training dataset size on the predictive performance. The updated Strategy 1 predictions closely match the reference values for most properties. However, the relatively higher prediction error in the case of MW, DCN, and IBP indicate that scope exists for improving the IR analysis strategies through use of nonlinear regression techniques.

**Table 3.** Strategy 1 property predictions of the SAF sample obtained from Prof. Josh Heyne (ASCENT P65).

Property	3.4- $\mu\text{m}$ region model		2-15 $\mu\text{m}$ region model		Reference values
	Predicted	CVE (%)	Predicted	CVE (%)	
MW (g/mol)	108.4	8.99	150	2.83	140
H/C ratio	1.48	6.88	1.98	1.71	2.00
NHC (MJ/kg)	43.0	0.88	43.5	0.25	43.7
DCN	7.81	15.59	24.8	11.20	18
Density @ 20°C ( $\text{g}/\text{cm}^3$ )	0.861	6.29	0.817	1.46	0.821
IBP (°C)	118	18.93	154	14.31	179.8
TSI	41.2	33.01	12.4	7.59	10.8

Overall, the IR analysis results obtained over the past year by using the extended wavelength range and the expanded training dataset show improved predictive performance over that of the spectral analysis strategies developed in the previous years of this work. These strategies enable accurate prediction of the physical and chemical properties of alternative jet fuels directly based on their infrared spectra.

## Milestones

Major milestones included regular reporting of experimental results and analysis at the Fall and Spring ASCENT meetings (October 2021 and April 2022), and presentation of results at the 39<sup>th</sup> International Symposium on Combustion (July 2022, Vancouver, British Columbia).

## Major Accomplishments

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

- The 2- to 15-  $\mu\text{m}$  FTIR spectra of butylcyclohexane, bicyclohexane, tetralin, pentamethylheptane, trans-decalin, 2-methylhexane, 2-methylheptane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane were measured and added to the training dataset.
- The 2- to 15-  $\mu\text{m}$  FTIR spectra of blends of neat hydrocarbons were calculated using linear addition of the individual components' spectra and were added to the training dataset, thus increasing the sample size from 81 fuels to 228 fuels.
- Property blending correlations were used to estimate the molecular weight, H/C ratio, net heat of combustion, density, flash point, freezing point, kinematic viscosity, and threshold sooting index of these hydrocarbon blends.
- Strategy 1 models were trained for these properties by using the expanded dataset (228 fuels). The models trained on the expanded dataset showed an improvement in prediction accuracy over that of the earlier models trained on the limited dataset (81 fuels).
- Strategy 1 models were used to predict properties of an SAF sample provided by Prof. Josh Heyne (ASCENT P65): molecular weight, H/C ratio, net heat of combustion, derived cetane number, density, initial boiling point, and threshold sooting index. The models trained on the 2- to 15-  $\mu\text{m}$  FTIR spectra showed improvement in prediction accuracy over that of the models trained on just the 3.4- $\mu\text{m}$  region.
- The 2- to 15-  $\mu\text{m}$  FTIR spectra of five new SAF samples (procured from Swedish Biofuels, Global Bioenergies, Virent, and the Council of Scientific and Industrial Research) were measured. Property predictions are forthcoming.

## Publications

### Peer-reviewed journal publications

Boddapati, V., Ferris, A. M., Hanson, R. K. (2022), "On the use of extended-wavelength FTIR spectra for the prediction of combustion properties of jet fuels and their constituent species," *Proceedings of the Combustion Institute* 39.

<https://doi.org/10.1016/j.proci.2022.08.041>

## Outreach Efforts

Our IR fuel analysis work was presented at the Virtual Fall ASCENT Advisory Board Meeting (October 26–28, 2021), and at the Spring ASCENT Advisory Board Meeting (April 5–7, 2022). Research was also presented at the 39<sup>th</sup> International Symposium on Combustion (July 24–29, 2022) in Vancouver, British Columbia.

## 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. Alison Ferris (current research scientist) has additionally contributed to the project through research management and report writing.

## Plans for Next Period

In the next period, we plan to:

- Revisit Strategy 3 models (principal component analysis plus support vector regression) to better capture nonlinear spectrum-property relationships and compare their performance with the linear Strategy 1 models.
- Use the updated Strategy 1 models to make property predictions for the five new SAF samples and compare the predictions against the actual property values.
- Review other fuel property prediction methods (e.g., GCxGC, near IR, etc.) reported in the literature; compare prediction accuracies with those attainable with our FTIR method.
- Continue measuring the 2- to 15-  $\mu\text{m}$  spectra of relevant neat hydrocarbons, conventional jet fuels, and SAFs.
- Explore batch distillation of multi-component fuels as a potential way to isolate molecular classes with weaker spectral features (e.g., cycloparaffins, aromatics, etc.) and possibly identify strategies to make more accurate property predictions based on the FTIR spectra of individual distillate fractions.