Project 025 Shock Tube Studies of the Kinetics of Jet Fuels

Stanford University

Project Lead Investigator

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- P.I.: Prof. Ronald K. Hanson
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    1. Chemical kinetics combustion experiments

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2022–2023: $200,000 from the FAA, with 1:1 matching funds of $200,000 from Stanford University

Investigation Team

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Jesse W. Streicher (research scientist)
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Project Overview

The ninth 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 has focused on two areas: correlation of the physical and combustion properties of hydrocarbon fuels with their infrared (IR) spectral features using nonlinear regression models, and evaluation of these nonlinear models and previously developed linear models on new candidate sustainable aviation fuel (SAF) samples and against standardized property test methods. 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 prescreening 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 four 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/chemical properties such as density, derived cetane number (DCN), net heat of combustion (NHC), and flash point. Here, we present an overview of the two research areas (development of nonlinear models for predicting fuel properties and evaluation of model performance), along with key results obtained over the past year.

Development of nonlinear models for predicting fuel properties

Over the past four 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, Strategy 1 elastic-net-regularized linear models were trained for different properties through the use of an expanded training dataset. While these linear models achieved good prediction accuracy for most properties, certain properties such as the DCN and flash point, which have a nonlinear dependence on fuel composition, showed scope for further improvement. In the current year, nonlinear Strategy 3 models (principal component [PC] analysis + support vector regression [SVR]) were developed for different properties, and their performance was compared with that of the linear Strategy 1 models. The methodology of Strategy 3 is discussed below, along with some results.

Strategy 3 models were developed for nine key physical and chemical properties: molecular weight (MW), hydrogen-to-carbon (H/C) ratio, density, NHC, DCN, threshold sooting index (TSI), initial boiling point (IBP), flash point, and kinematic viscosity (KV). The training dataset included the 2- to 15-μm FTIR spectra of 228 fuels, spanning neat hydrocarbons, blends of neat hydrocarbons, and conventional and alternative jet fuels.

To build Strategy 3 models, the FTIR spectra are first preprocessed by performing PC analysis, which linearly transforms the spectra into a set of orthogonal PCs, in decreasing order of variance captured. This step enables the selection of a subset of PCs as predictors for training regression models, greatly reducing the dimensionality without a significant loss of information. An SVR model is then trained on the transformed features to obtain the best-fit hyperplane for predicting the property of interest. The number of PCs, N_{PC}, and the optimal values of the other model parameters C and σ are chosen via a 10-fold cross-validated grid search. By experimenting with different values of these three parameters, the model selects the combination that results in the minimum cross-validation error (CVE) for each property. This process is demonstrated for the property DCN in Fig. 1. Using the cross-validation approach, only the first 10 PCs are chosen to build the SVR model for DCN. As shown in the left panel of Fig. 1, the first 10 PCs can cumulatively capture close to 99% of the total variance in the FTIR dataset. Thus, discarding the subsequent PCs causes virtually no loss of spectral information. The right panel of Fig. 1 demonstrates the model tuning process over a grid of C and σ values, with N_{PC} fixed at its optimal value of 10. The dashed white lines correspond to the combination of C and σ with the lowest CVE. Therefore, the optimal parameters describing the Strategy 3 model for DCN are $N_{PC} = 10$, $C = 38.05$, and $\sigma = 0.088$.

The performance of the optimized Strategy 3 model was evaluated on the training dataset based on three performance metrics: CVE (an estimate of future prediction error), coefficient of determination (R^2, a measure of goodness of fit), and root-mean-squared error (RMSE) of prediction. The results from the Strategy 3 model were also compared with those of the Strategy 1 model to highlight the improvement in predictive performance due to the use of nonlinear regression. Figure 2 shows the performance of the Strategy 1 and Strategy 3 models on the training dataset for DCN. Figures 2a and 2b show the predicted versus actual DCN and the corresponding residuals obtained using the Strategy 1 model, whereas Figs. 2c and 2d show the predicted versus actual DCN and residuals obtained using the Strategy 3 model. The CVE, R^2, and RMSE for these models are listed in the figure headings. The Strategy 3 model for DCN shows distinctively improved predictive

performance compared with the Strategy 1 model, as evidenced by a reduced CVE and RMSE and increased R^2. Although the CVE of the Strategy 3 model is only 5% lower than that of the linear model, the RMSE is reduced by a factor of 2. Additionally, the higher R^2 value for the Strategy 3 model indicates a stronger correlation between the FTIR spectra and DCN. Similarly improved predictive performance was observed for the Strategy 3 models trained on most of the other properties.

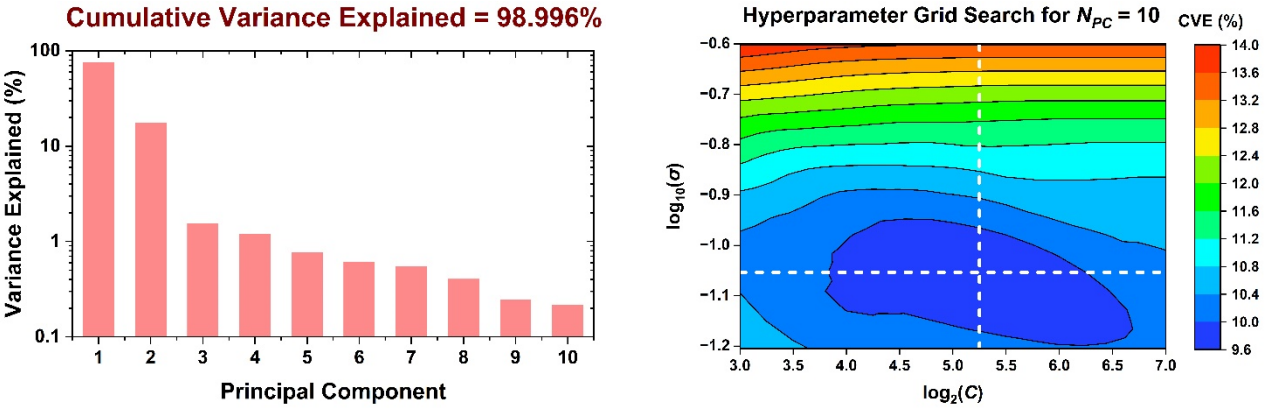

Figure 1. Left: Percentage of variance explained by each of the first 10 principal components. Right: Cross-validated grid search for selecting optimal values of the model parameters C and σ (indicated by dashed white lines). CVE: cross-validation error.

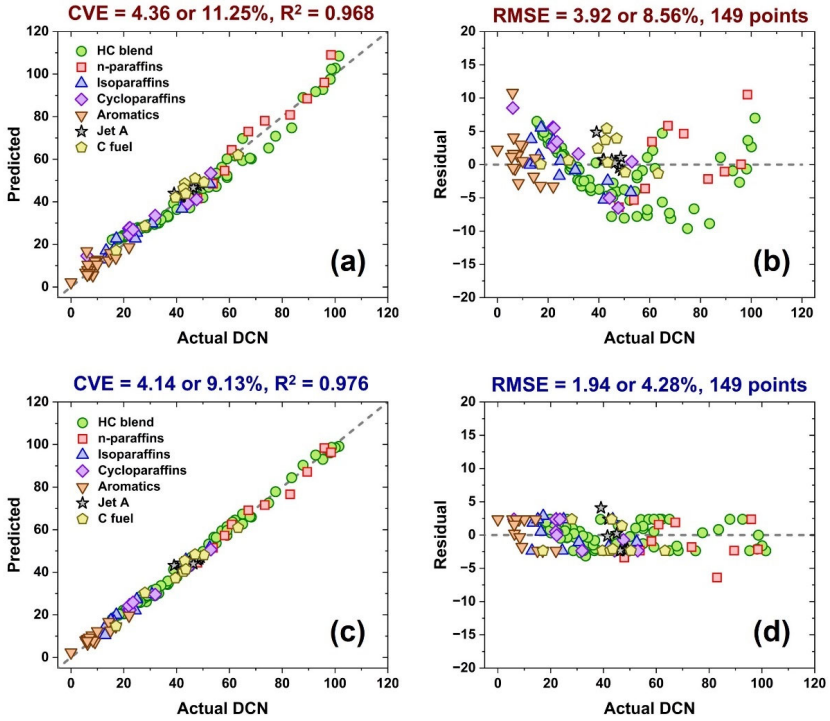

Figure 2. Performance of derived cetane number (DCN) model on training data. (a) Predicted DCN and (b) residuals obtained using the Strategy 1 linear model; (c) predicted DCN and (d) residuals obtained using the Strategy 3 nonlinear model. CVE: cross-validation error; HC: hydrocarbon; RMSE: root-mean-squared error.

Evaluation of model performance

Comparing the prediction accuracy of the IR analysis strategies with standard property test methods is a crucial step in evaluating model performance. To enable such a comparison, the reproducibility RMSE values associated with standard test methods for all properties were calculated via correlations obtained from the literature, as shown in Table 1. The exception is MW, which is typically estimated using two-dimensional gas chromatography (GCxGC), as no standard reproducibility errors have been reported in the literature for MW estimation using this method. Also included in Table 1 are the prediction RMSE values of both the Strategy 1 and Strategy 3 models for these properties. As shown in this table, the Strategy 3 models for density, NHC, DCN, and flash point have lower RMSE values than the corresponding Strategy 1 models. In particular, the use of nonlinear regression greatly improves the prediction accuracy for the DCN and flash point. Whereas Strategy 1 has a lower prediction error than the reproducibility error of the ASTM method for three of the properties (H/C ratio, NHC, and TSI), Strategy 3 achieves a lower RMSE than the ASTM reproducibility error for five properties (H/C ratio, NHC, DCN, TSI, and flash point). This result suggests that the uncertainty associated with these experimental property values in the training dataset is expected to impact the uncertainty in the predicted property values to a greater extent than the modeling approach itself. In contrast, the ASTM reproducibility errors associated with density, IBP, and KV are smaller than their respective Strategy 3 prediction errors. Hence, the contribution of the modeling approach to the uncertainty in these property estimations is comparable to, if not slightly greater than, that of the measurement uncertainty in the training data.

Table 1. Comparison of the predictive performance of Strategy 1 and Strategy 3 models for eight physical and chemical properties with the reproducibility errors of the corresponding standard test methods from ASTM.

Property	Standard ASTM method	ASTM reproducibility error (%)	RMSE (%) of Strategy 1	RMSE (%) of Strategy 3
H/C ratio	D5291	5.80	1.69	1.86
Density	D4052	0.28	1.41	1.02
NHC	D4809	0.747	0.213	0.154
DCN	D6890	4.70	8.56	4.28
TSI	D1322	22.63	2.93	3.81
IBP	D86	3.11	3.54	5.09
Flash pt.	D93	10.94	15.22	6.29
KV	D445	0.50	3.43	4.18

DCN: derived cetane number; H/C: hydrogen to carbon; IBP: initial boiling point; KV: kinematic viscosity; NHC: net heat of combustion; RMSE: root-mean-squared error; TSI: threshold sooting index.

Table 2. Molecular class distributions of the five new sustainable aviation fuel 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

CSIR: Council of Scientific and Industrial Research.

Another key step in assessing model performance involves making predictions on unseen test data that were not included in the training dataset. To that end, five candidate SAF samples were acquired in the previous year from other ASCENT members (Steve Zabarnick). These fuels showed considerable differences in their molecular class distribution, as detailed in Table 2. 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)

The Strategy 1 and Strategy 3 models were employed to predict the properties of these five SAF candidates based on their measured 2- to 15-μm FTIR spectra. The predictions of both the Strategy 1 and Strategy 3 models are shown in Table 3, along with the reference property values for one of these samples, POSF 14197. The Strategy 1 and Strategy 3 model predictions match closely with the reference values of all properties for this fuel. However, the nonlinear Strategy 3 models outperform the linear Strategy 1 models for five properties: MW, H/C ratio, density, KV, and flash point. Similar performance improvements were observed in the case of the remaining four SAF samples, with Strategy 3 performing better than Strategy 1 for most properties considered. The reduced prediction error of the Strategy 3 models compared with the Strategy 1 models further highlights the impact of the nonlinear regression technique on predictive performance.

Table 3. Strategy 1 and Strategy 3 property predictions for the POSF 14197 sustainable aviation fuel sample (from the Council of Scientific and Industrial Research-Indian Institute of Petroleum).

Property	Strategy 1 model		Strategy 3 model		Reference values
	Predicted	Error (%)	Predicted	Error (%)	
MW (g/mol)	159	0.62	160	0	**160**
H/C ratio	2.08	-1.23	2.12	0.66	**2.106**
NHC (MJ/kg)	43.8	0.23	43.5	-0.46	**43.7**
Density @ 20℃ (g/cm^3)	0.762	0.21	0.760	-0.05	**0.7604**
IBP (℃)	161	1.90	162	2.53	**158**
KV (mm^2/s)	3.81	-2.05	3.86	-1.02	**3.9**
Flash Pt. (℃)	47.5	3.26	44.8	-2.61	**46**

H/C: hydrogen to carbon; IBP: initial boiling point; KV: kinematic viscosity; MW: molecular weight; NHC: net heat of combustion.

Overall, the IR analysis results obtained over the past year for the nonlinear regression models showed improved predictive performance relative to the spectral analysis strategies developed in the previous years of this work and were found to achieve high prediction accuracy on candidate SAF samples. These strategies provide the capability to accurately predict the physical and chemical properties of alternative jet fuels directly based on their IR spectra.

Milestones

Major milestones included regularly reporting experimental results and analyses at the Fall and Spring ASCENT meetings (October 2022 and April 2023) and presenting results at the 13th U.S. National Combustion Meeting (March 2023, College Station, TX) and the 29th International Colloquium on the Dynamics of Explosions and Reactive Systems (July 2023, Seoul National University Siheung, Korea).

Major Accomplishments

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

- With the use of an expanded, extended-wavelength-range training dataset, Strategy 3 models were trained for nine physical and chemical properties: MW, H/C ratio, density, NHC, DCN, TSI, IBP, flash point, and KV. The model parameters were chosen based on a 10-fold cross-validated grid search to achieve optimal predictive performance for each property;
- The nonlinear Strategy 3 models showed an improvement in prediction accuracy compared with the previously developed linear Strategy 1 models for most of the properties in terms of three performance metrics: CVE, R^2, and RMSE;
- The prediction RMSE values of both the Strategy 1 and Strategy 3 models were compared with the reproducibility errors of standard ASTM property test methods. The Strategy 3 models achieved lower prediction errors than the ASTM methods for five properties: H/C ratio, NHC, DCN, TSI, and flash point; and
- The Strategy 1 and Strategy 3 models were used to predict properties of five candidate SAF samples. While both strategies were able to predict the SAF properties to a high degree of accuracy, the Strategy 3 models generally performed better than the Strategy 1 models on these fuel samples.

Publications

Peer-reviewed journal publications

Boddapati, V., Ferris, A. M., & Hanson, R. K. (2024). Predicting the physical and chemical properties of sustainable aviation fuels using elastic-net-regularized linear models based on extended-wavelength FTIR spectra. *Fuel, 356,* pp. 129557. https://doi.org/10.1016/j.fuel.2023.129557

Outreach Efforts

Our IR fuel analysis work was presented at the Fall ASCENT Advisory Committee Meeting (October 25–27, 2022) and the Spring ASCENT SAF Meeting (April 25–27, 2023). Research was also presented at the 13th U.S. National Combustion Meeting (March 19–22, 2023) in College Station, TX, and the 29th International Colloquium on the Dynamics of Explosions and Reactive Systems (July 23–28, 2023) at Seoul National University Siheung, Korea. An abstract titled "Towards the development of an IR spectra-based approach for characterizing fuel properties and combustion behavior" was accepted for presentation at the Joint Army Navy NASA Air Force Interagency Propulsion Committee meeting (December 2023).

Awards

None.

Student Involvement

Graduate students are actively involved in the acquisition and analysis of all experimental data and model development. Vivek Boddapati (current graduate student) performed the IR spectral analysis/fuel prescreening. Jesse Streicher (current research scientist) has also contributed to the project through research management.

Plans for Next Period

In the next period, we plan to

- review other fuel property prediction methods (e.g., GCxGC, near-IR methods, Raman spectroscopy, etc.) reported in the literature and compare their prediction accuracies with those attainable via our FTIR method;
- continue expanding the training dataset by measuring the 2- to 15-μm spectra of relevant neat hydrocarbons, conventional jet fuels, and SAFs and investigate the value of further extending the wavelength range beyond the 2- to 15-μm region, particularly to access strong, isolated spectral features corresponding to molecular classes such as cycloparaffins and olefins;
- explore batch distillation of multicomponent 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; and
- explore the potential for predicting additional thermochemical properties of fuels based on FTIR spectra (e.g., gas-phase specific heat capacity, enthalpy, and entropy).