Towards the Development of an IR Spectra-Based Approach for Characterizing Fuel Combustion Behavior

Pujan Biswas, Vivek Boddapati, Andrew R. Klingberg, Hai Wang, Ronald K. Hanson
Department of Mechanical Engineering, Stanford University
Stanford, CA, USA

1 Introduction

The aviation sector contributes up to 11% of the transportation sector's share towards global greenhouse gas emissions [1,2]. Achieving substantial reductions in these emissions is a formidable challenge, as alternative energy sources for aircraft like hydrogen and batteries face several limitations. Alternatively, sustainable aviation fuels (SAFs), derived from renewable feedstocks, are widely regarded as the most viable solution for mitigating overall aviation-related emissions [3].

Although SAFs promise compatibility with existing engines and infrastructure, their approval process is costly and time-consuming. Rapid and inexpensive assessment of fuel performance over the entire operating regime of aircraft engines can be enabled by robust and compact chemical kinetic models. However, due to the diverse range of molecular structures and carbon numbers present in conventional and alternative jet fuels, the development of accurate, detailed chemical kinetic models is a non-trivial endeavor. These detailed mechanisms often contain thousands of elementary reactions, which makes them computationally intractable. An alternate perspective towards the development of compact chemical kinetic models was conceived at Stanford, called the Hybrid Chemistry (HyChem) approach [4]. Conventional HyChem models rely on experimental constraints to accurately predict fuel combustion behavior under engine-relevant conditions. However, enabling the development of HyChem models for upcoming fuels without requiring experiments that demand large sample volumes could significantly accelerate SAF screening and deployment. This paper lays the foundation for a new concept, namely IR-HyChem, which leverages the sensitivity of a fuel's combustion performance to its molecular structure to directly generate HyChem models based on the fuel's infrared (IR) spectrum.

As highlighted by Wang et al. [4], understanding the distribution of intermediates during fuel pyrolysis is critical to developing HyChem models. Here, the thermal decomposition of seven n- and iso-paraffins was investigated behind reflected shock waves to identify characteristic trends in the high-temperature reactivity of hydrocarbons with varying molecular structures. Laser absorption spectroscopy-based diagnostics were employed to simultaneously measure the evolution of key pyrolysis products (methane, ethylene, and heavier C_3-C_4 alkenes). A preliminary correlation was subsequently developed between measured species' yields and certain IR spectral features of the aforementioned neat hydrocarbons. This correlation was used to develop HyChem models for three real fuels (JP-8, RP-1, and F-24) from their IR spectra. The performance of these models was subsequently assessed against measured ignition delay

Correspondence to: pujanb@stanford.edu

times (IDTs). Moreover, a Monte Carlo analysis of the model uncertainties was performed, and a discussion of possible strategies to further reduce uncertainty is provided in this work.

2 Methodology

A detailed description of the Hybrid Chemistry (HyChem) modeling approach has been provided in [4]. Briefly, HyChem models for any hydrocarbon fuel can be defined using seven lumped reaction steps, with corresponding rate coefficients (k_1-k_7) and seven stoichiometric parameters (α, β, γ, λ_3, $\lambda_{4,1}$, $\lambda_{4,i}$, χ). These parameters are traditionally constrained using speciation data obtained from flow reactor and shock tube pyrolysis experiments. This is feasible owing to the strong sensitivity of the HyChem parameters to the yields of stable intermediates formed during fuel pyrolysis. Since the distribution of these intermediates depends on the fuel's molecular composition, we anticipate that HyChem models can be effectively constrained using information about the fuel's molecular structure.

Analytical techniques, such as infrared spectroscopy can provide valuable insights into the composition and functional groups of complex fuels. As illustrated in Figure 1, distinct functional groups absorb IR light at characteristic frequencies, with variations in absorption cross-sections (CS) offering unique information about a fuel's molecular structure. Therefore, it follows that IR spectra can serve as effective proxies for fuel composition and can be correlated with pyrolysis product yields, providing a pathway to constrain HyChem model parameters.

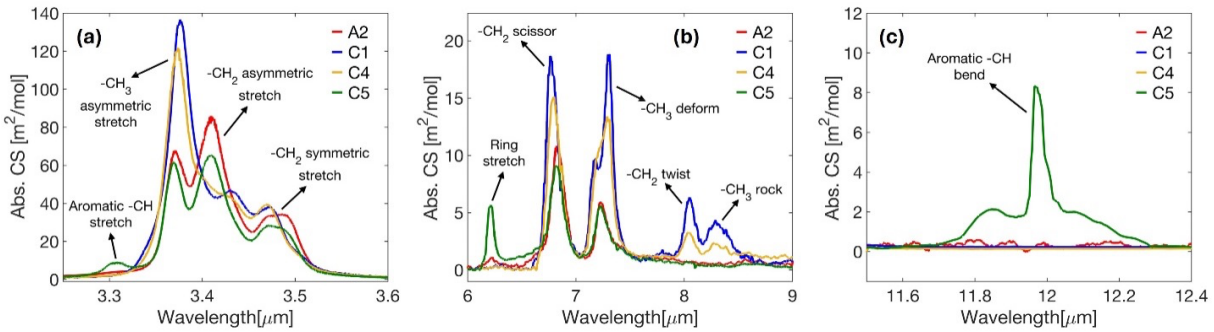

Figure 1: Measured vapor-phase IR spectra of nominal Jet-A fuel (A2) and three synthetic, alternative jet fuels (C1, C4, and C5) revealing the important absorption features in three spectral regions: (a) 3.25-3.6 μm, (b) 6–9 μm, and (c) 11.5–12.4 μm.

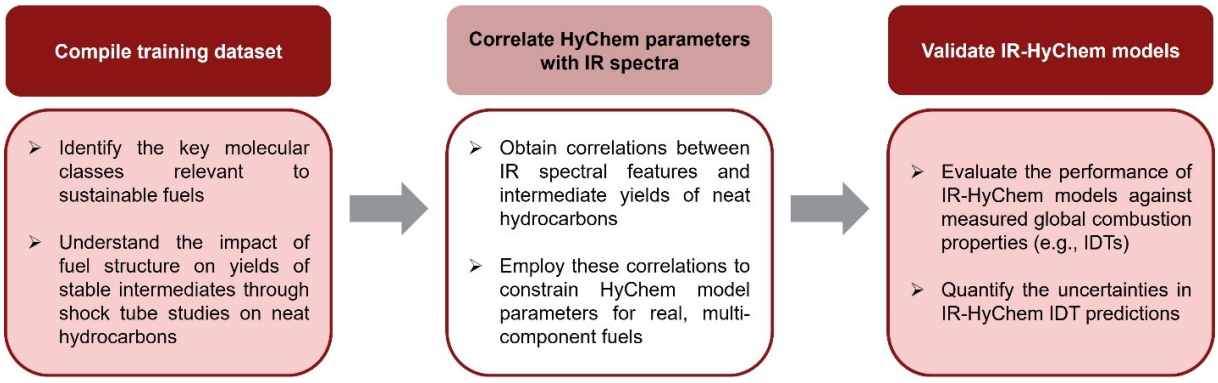

Figure 2: Proposed methodology for developing and evaluating IR-HyChem models for real fuels.

Figure 2 outlines the process for developing HyChem models for real fuels using IR spectra. The first step involves compiling a training dataset of IR spectra and pyrolysis product yields for a set of neat

hydrocarbons with varying molecular structures. In this study, vapor-phase IR spectra of seven aviation-relevant fuels, measured over the 2–15 μm wavelength range using a Fourier Transform Infrared (FTIR) spectrometer, were utilized. The shock tube pyrolysis experiments conducted to determine species yields are delineated in [5]. The second step involves developing correlations of the IR spectra with intermediate yields, which can be used to predict yields for new multi-component fuels and constrain HyChem stoichiometric parameters and rate coefficients. Finally, the constrained IR-HyChem models can be evaluated against experimental measurements of global combustion properties, such as ignition delay times (IDTs) or laminar flame speeds. The current work employs IDTs measured at elevated pressures in a shock tube as validation targets.

3 Results and Discussion

Preliminary IR-spectra based correlations: Clear trends in species yields with varying carbon numbers and degree of branching were observed during pyrolysis. The effects of molecular structure on these trends and stable intermediate formation have been thoroughly discussed in our recent studies [6,7]. In the present work, we correlate the ratio of the measured heavy alkene (>C_2) and ethylene yields with certain infrared spectral features to succinctly demonstrate the IR-HyChem methodology. It should be noted that the resulting IR-HyChem models are only partially constrained since not all species' yields were correlated with IR spectra. Developing correlations to constrain the remaining model parameters will be the focus of future work.

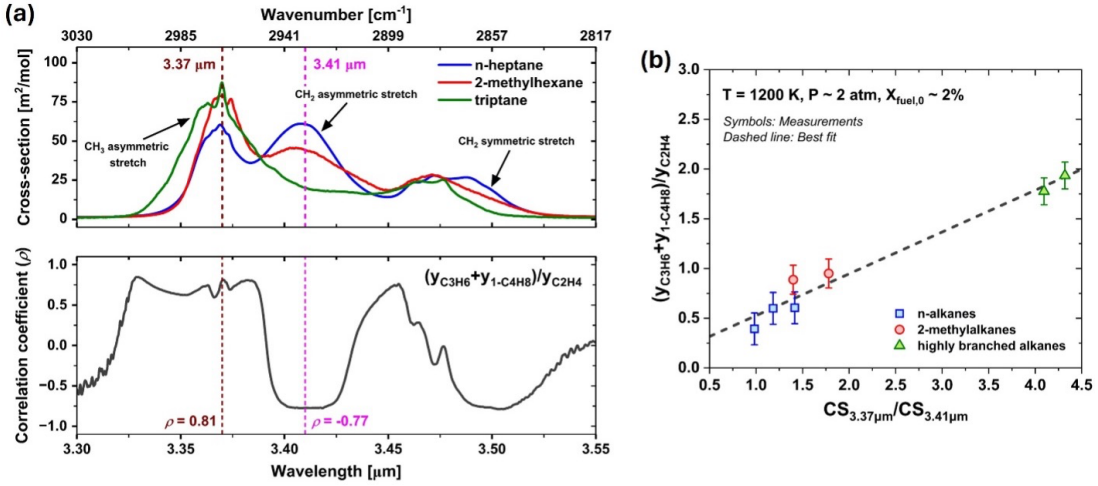

Figure 3: (a) (Top) Representative infrared spectra of n-heptane, 2-methylhexane, and triptane in the 3.3-3.55 μm wavelength range. (Bottom) Pearson correlation coefficient calculated between the ratio of combined propene and 1-butene yields to ethylene yields (at ~1200 K) and IR absorption cross-sections of the seven neat hydrocarbons. (b) Ratio of combined propene and 1-butene yields to ethylene yields plotted against the ratio of absorption cross-sections at 3.37 μm (CH_3 asymmetric stretch) and 3.41 μm (CH_2 asymmetric stretch) for seven fuels studied at temperatures around 1200 K.

Figure 3a (top panel) shows the IR spectra of n-heptane, 2-methylhexane, and triptane in the 3.3-3.55 μm region, which contains spectral features corresponding to the C-H bond stretch in CH_2 and CH_3 groups. Key features include the asymmetric C-H stretch in CH_3 groups at 3.37 μm, the asymmetric C-H stretch in CH_2 groups at 3.41 μm, and the symmetric C-H stretch in CH_2 groups at 3.49 μm. Being a straight chain alkane, n-heptane has the strongest absorption at wavelengths corresponding to CH_2 group features, while its cross-section at 3.37 μm is the lowest among the three fuels shown here. Accordingly, triptane has weaker CH_2 stretch features (3.41 μm and 3.49 μm) and a stronger CH_3 stretch feature. The bottom panel of Fig. 3a presents a preliminary attempt at relating compositional information obtained from IR spectra to pyrolysis product yields. Shown here is the Pearson correlation coefficient (ρ)

evaluated between key intermediates, i.e., combined propene and 1-butene yields to ethylene yields, and the absorption cross-sections of the seven fuels studied in their measured 3.3-3.55 μm IR spectra. The Pearson correlation coefficient is a measure of the degree of linear relationship between two variables, with values close to 1 (or -1) implying a strong positive (or negative) linear correlation. Notably, the wavelengths around the CH_2 and CH_3 group features exhibit strong correlations, with Pearson coefficients of 0.81 and -0.77 at 3.37 μm and 3.41 μm, respectively. This suggests that the ratio of CS at these wavelengths can be utilized to predict heavy alkene to ethylene yield ratios. This is further validated in Fig. 3b, which shows a strong linear correlation between the yield ratio of propene and 1-butene to ethylene and the absorption cross-section ratio at 3.37 μm and 3.41 μm for seven neat hydrocarbons at 1200 K. After measuring the IR spectra of a novel fuel, this relationship can be utilized to help constrain $\lambda_3+\lambda_{4,1}$. This approach has been implemented for the three real fuels, i.e., JP-8, RP-1 and F-24 in this work. The remaining HyChem parameters were constrained using previously developed models for similar jet and rocket fuels whose molecular compositions were similar to the three fuels.

Model performance and uncertainty analysis: Ignition delay times (IDTs) measured at 12 atm and temperatures between 1150-1400 K were used to validate the partially constrained IR-HyChem models developed in this study. These experiments, conducted in Stanford's High-Pressure Shock Tube (HPST) facility, involved stoichiometric mixtures of the three real fuels in 4% O_2/Ar, with IDTs quantified using an OH* emission diagnostic [8]. Figures 4a, 4b and 4c show the measured IDTs for JP-8, RP-1, and F-24 compared against the predictions of their respective IR-HyChem models. It is evident from these figures that the partially constrained IR-HyChem models can accurately estimate the IDTs of all three fuels over the entire temperature range.

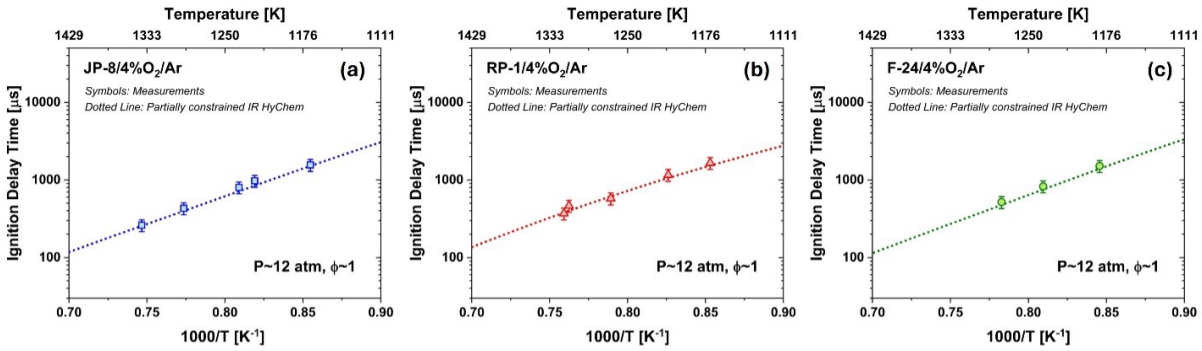

Figure 4: Comparison of the measured ignition delay times (symbols) against partially constrained IR-HyChem model predictions (dotted lines) for (a) JP-8, (b) RP-1, and (c) F-24 in 4% O2/Ar, φ ~ 1.

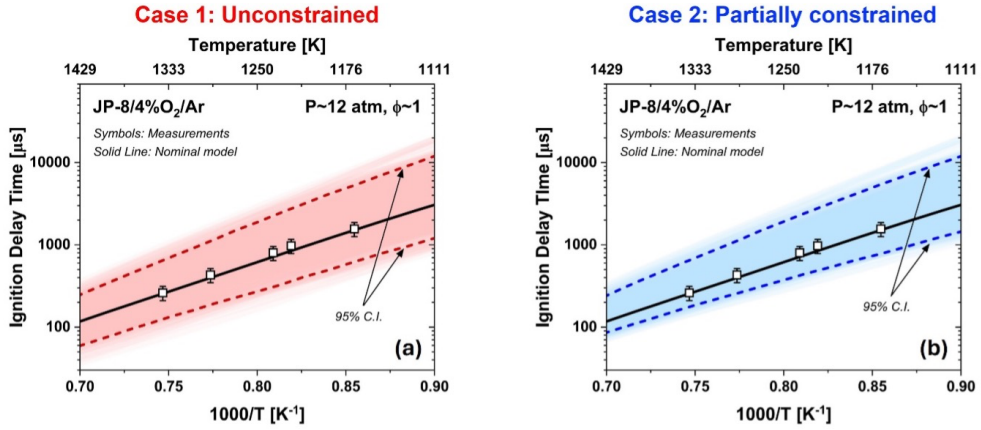

Figure 5: Uncertainty in predicted IDTs of JP-8/ for (a) unconstrained and (b) partially constrained IR-HyChem models. The faded bands around the nominal model predictions represent the variance in IDT

predictions observed across the 500 randomly sampled MC cases. Dashed lines indicate 95% confidence intervals of the model predictions.

To quantify uncertainty in predicted IDTs due to model parameter uncertainties, we performed a Monte Carlo (MC) analysis by generating 500 randomly sampled IR-HyChem models, with JP-8 as the test fuel. The analysis was conducted for two cases: (1) unconstrained and (2) partially constrained models. In both cases, parameters were randomly selected within their feasible sets, with the unconstrained model only subject to element balance. In contrast, the partially constrained model had parameters constrained based on correlations from the previous subsection, tightening their bounds subject to measurement uncertainty in intermediate yields and IR spectra. Although the uncertainty in model predictions is found to be larger than experimental uncertainty (± 15%) for both MC cases, the partially constrained model still shows improved performance compared to the unconstrained model. In particular, the 95% confidence interval of the partially constrained model predictions is smaller by ~5% at 1120 K, and almost 30% at 1420 K compared to the unconstrained case. This underscores the impact that constraining even a subset of IR-HyChem model parameters can have on the overall uncertainty in combustion property predictions.

Finally, to provide insights into reducing model uncertainties, we performed sensitivity analyses of IDTs with respect to the IR-HyChem parameters at 1100 K and 1400 K, as shown in Figs. 6a and 6b. At 1400 K, IDTs exhibit the highest sensitivity to λ_3, whereas at 1100 K, sensitivity to λ_3 decreases, with parameters such as β showing increased influence. Since the IR-spectra-based correlation imposed tighter bounds on λ_3, the partially constrained model has a lower prediction uncertainty at higher temperatures than the unconstrained model. Conversely, since parameters like β remain unconstrained, the difference in prediction uncertainty is less pronounced at lower temperatures. This analysis suggests that further minimizing uncertainty in IR-HyChem model predictions could be achieved by developing additional IR-spectra-based correlations to constrain remaining stoichiometric and kinetic parameters.

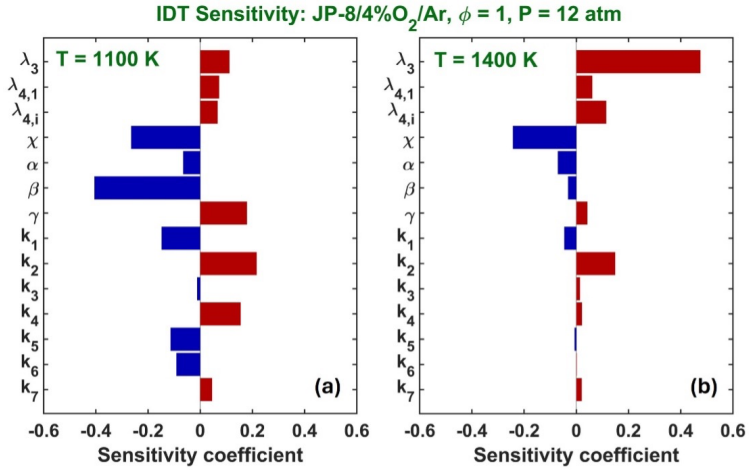

Figure 6: Sensitivity of IDTs (JP-8/4% O2/Ar, Φ ~ 1, P ~ 12 atm) to the HyChem stoichiometric parameters and rate coefficients at (a) 1100 K and (b) 1400 K.

4 Summary

A novel methodology, termed IR-HyChem, was proposed for modeling the combustion behavior of real fuels based on their infrared (IR) spectra to enable low-volume characterization of next-generation sustainable fuels. A training dataset of normal and branched alkanes was compiled using their vapor-phase, 2-15 μm FTIR spectra and pyrolysis product yields measured in a shock tube. A preliminary linear correlation was obtained between the ratio of heavy alkene (>C_2) to ethylene yields and the ratio of IR absorption cross-sections at two wavelengths corresponding to CH_3 and CH_2 functional groups.

This correlation was employed to partially constrain HyChem models for three real fuels: JP-8, RP-1, and F-24. The predicted ignition delay times (IDTs) using these models were found to agree well with experimental measurements for all three fuels. A Monte Carlo (MC) uncertainty analysis was performed by randomly sampling HyChem parameters within their respective feasible sets for two test cases: (1) unconstrained and (2) partially constrained IR-HyChem models of JP-8. Since the unconstrained model was only subject to element balance, it showed higher variance in predicted IDTs compared to the partially constrained case, which imposed constraints derived from IR spectra. A brute-force sensitivity analysis for IDTs suggested that the model uncertainties could be further minimized by developing additional IR spectra-based correlations to constrain the remaining stoichiometric parameters and rate coefficients, which will be the focus of future work. The authors believe that the IR-HyChem approach has the potential to significantly scale down the fuel volumes and costs associated with the regulatory testing and approval process of sustainable fuel candidates.

5 Acknowledgments

This research was partially supported by the U.S. Air Force Research Laboratory Award Number FA9550-20-1-0398 under the supervision of Matthew Billingsley. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the AFRL.

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