

Shock Tube Measurements of Species Time-Histories during Jet Fuel Pyrolysis and Oxidation

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1 Introduction

The development of compact chemical kinetics model for jet fuel pyrolysis and oxidation requires accurate target data for real jet fuel. Kinetics models based on surrogate fuel mixtures of a few archetypal components and their accompanying detailed reaction mechanisms have been developed but are difficult to implement into CFD codes because of their size [1]. Several reduced mechanism approaches using surrogate models as starting points have been proposed, but these are still not directly linked to real jet fuel [2]. H. Wang [3] has proposed a new approach, a hybrid modeling scheme, that couples a small jet fuel decomposition reaction sub-mechanism with a compact, C₀-C₄ oxidation sub-mechanism. In this approach, the jet fuel decomposition mechanism is constrained to fit experimental data on fuel cracking patterns. The object of the present work is provide initial species time-history data for the development of this model and ignition delay time data to test the model.

Distillate-based kerosenic fuels, including JP-8, have three major types of components: paraffins, cycloparaffins and aromatics. During high-temperature gas-phase pyrolysis, the majority of the carbon in these original jet fuel molecules quickly converts to a reduced set of smaller stable intermediate hydrocarbons [1]. This set of intermediate products includes ethylene C₂H₄, propene C₃H₆, different isomers of butene C₄H₈, methane CH₄, hydrogen H₂, and small aromatics such as benzene C₆H₆ or toluene C₇H₈. In this study we provide quantitative measurements of fuel, C₂H₄, C₃H₆ and CH₄ using using shock tube/laser absorption methods [4]. These data can then be implemented to constrain the decomposition sub-mechanism of the hybrid model. The overall performance of the hybrid model can be tested by comparison of model simulations with ignition delay time measurements. A preliminary version of H. Wang's experimentally-constrained pyrolysis – detailed oxidation (Hybrid ECP-DO) model) based on pyrolysis measurements for POSF10264 JP-8 fuel [5] has been used to compare with these ignition delay time measurements.

2 Experimental Method and Time-History Measurements

Reflected shock wave experiments provide a test environment that minimizes the effects of fluid mechanics, turbulence, and heat transfer. This allows isolation of the target data (ignition delay times and species concentration time-histories in both pyrolysis and oxidation experiments) in a quiescent high-temperature, high-pressure environment that is well-characterized and hence amenable to

modeling. The current measurements were performed in a helium-driven high-pressure shock tube (HPST). In these experiments the shock tube and mixing assembly were both heated to 80 C.

Two JP-8 fuels are studied. POSF 10264 is a high quality JP-8 fuel with a molecular weight of 151.9, an H/C ratio of 2.0, low aromaticity (11.2% by volume), and a LHV of 43.1 MJ/kg. POSF 6169 has a molecular weight of 154, and an H/C ratio of 2.017. Both fuels were supplied by the Air Force Research Laboratory [6].

Laser absorption measurements use the Beer-Lambert law to convert measured fractional transmission of laser light to species concentration: $I/I_0 = \exp(-\sigma N L)$, where I is the transmitted intensity at the laser wavelength λ , I_0 is the incident laser intensity at the same wavelength into the shock tube, σ is the absorption cross-section at the laser wavelength λ , typically in m^2/mole , N is the fuel concentration in moles/m^3 and L is the pathlength or shock tube diameter in m. The combined quantity $\sigma N L$ is known as the absorbance.

Fuel concentration is measured at 3.39 microns using a He-Ne laser. This measurement provides a critical *in situ* measurement of fuel concentration in the shock tube before the experiment, as well as a time history of fuel decomposition and product formation [7]. Absorption cross-sections at 3.39 microns at 80 C, needed for determining JP-8 concentrations, are measured in separate cell experiments.

Ethylene, C_2H_4 , is measured at 10.53 microns using a CO_2 gas laser [8]. Separate cross-section measurements of possible interfering species, such as higher alkenes, were used to determine that negligible interference absorbance is expected for these species. However, at a nearby wavelength, 10.68 microns, ethylene absorbance was significantly reduced, while absorbance from the major secondary alkene, propene, was measurable. Simultaneous measurements at these two wavelengths was used to infer both the propene and ethylene time-histories and their long-time pyrolysis yields.

Figure 1 shows a representative ethylene-time history and Figure 2 shows the measured ethylene product yield at 2 ms for the two JP-8 fuels tested. Nearly identical yields were measured for both fuels, though POSF 6169 appears to have a slightly larger ethylene yield near 1300 K. Of particular note is the large final conversion of fuel carbon to ethylene carbon. At the highest temperatures about 58% of the carbon in the fuel is converted to ethylene. Propene yields based on the P28 determination are also shown in Figure 4. 15% of the fuel carbon is converted to propene at the highest temperatures measured.

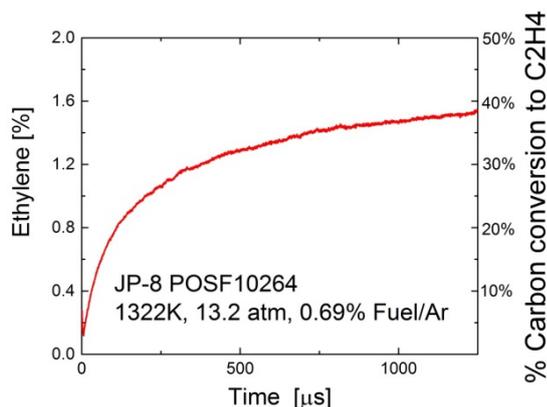


Figure 1. Ethylene time-history during JP-8 fuel decomposition. Initial reflected shock conditions: 1322 K, 13.2 atm, 0.69% fuel in argon.

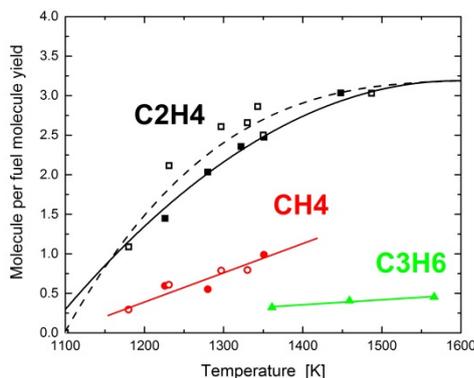


Figure 2. Product yields at 2 ms for JP-8 pyrolysis. Initial reflected shock conditions: 13 atm, 0.7% fuel in argon. Open symbols POSF6169; solid symbols POSF10264.

Methane, CH_4 , was measured at 3.17 microns using a tunable diode laser [9]. At this wavelength, modeling simulations show that only ethylene has a significant interference absorbance. This interference can be subtracted by knowing the ethylene cross-section at 3.17 microns as a function of temperature and by using the measured ethylene concentration from the 10.53 micron measurement.

Figure 5 shows a representative methane time-history, and the measured methane product yields are shown in Figure 4. Little difference is seen between the two fuel samples in CH_4 yield. Of note is that only a relatively small fraction of the JP-8 fuel carbon ends up in the form of CH_4 , 9%, at the highest temperature measured. More carbon was carried into the larger alkene, i.e. propene, than into methane.

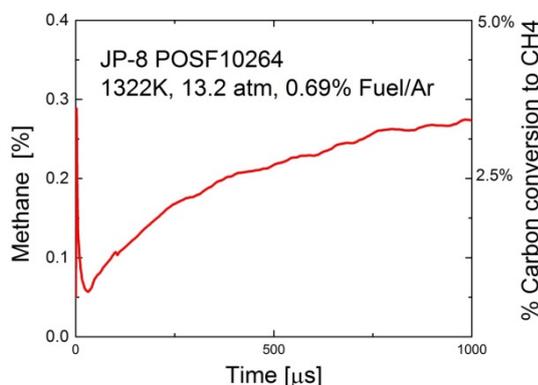


Figure 3. Methane time-history during JP-8 fuel decomposition. Initial reflected shock conditions: 1322 K, 13.2 atm, 0.69% fuel in argon. The spike near time zero is a result of momentary steering of the diagnostic probe beam away from the detector surface by the reflected shock wave.

The species time-history measurements for ethylene, propene and methane, provide strong constraints on the jet fuel decomposition products as needed for the fuel decomposition portion of the hybrid kinetics model. The aromatic content of the products can also be separately confirmed or estimated from additional measurements.

3 Ignition Delay Time Measurements

A preliminary version of the experimentally-constrained pyrolysis – detailed oxidation (Hybrid ECP-DO) model based on the above pyrolysis measurements for POSF10264 JP-8 fuel was developed by H. Wang. Figure 4 shows representative ignition delay times for the two JP-8 fuels: POSF6169 and POSF10264 and simulations based on this model [5]. Ignition delay times were measured using side wall emission and pressure using the methods of reference 16. Note that the preliminary hybrid model captures the $\phi=0.5$ and 1.0 data accurately, but fails for the $\phi=2.1$ data. The simulations for the 54.4 atm data are also in reasonable agreement with the model. The model was not tuned to any ignition delay time measurements and is based only on data derived from 13-16 atm pyrolysis experiments.

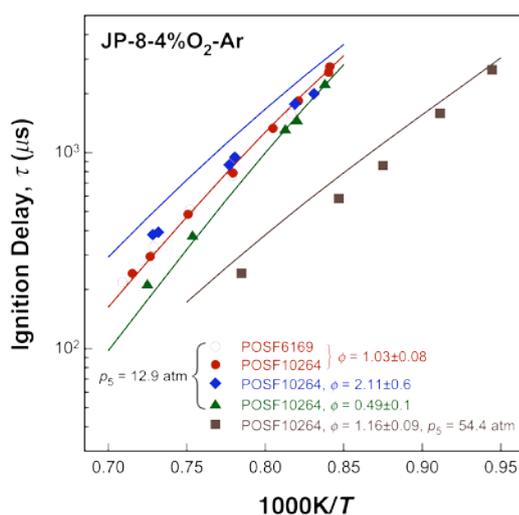


Figure 6. Ignition delay times for JP-8.

4 Future Work

We are continuing to refine the hybrid model approach in two ways. First, we are developing new or improved species diagnostics for important decomposition products. In particular, we are developing a sensor near 11.35 microns for the measurement of isobutene, which is expected to be a major decomposition product of branched and cycloalkanes [10]. Second, we are studying a larger operating space for this model. Measurements are needed over a wider range of temperature, pressure, and fuel loading. As well, measurements are needed for a wider range of fuel samples, particularly fuels that fit the DoD jet fuel specifications but would be classed as outliers because of extreme variations in composition (e.g. aromatic content) or because of radically different composition (e.g. some alternative fuels). Since the hybrid methodology should be applicable for the high-temperature oxidation of all hydrocarbon fuels, testing of other types of fuels, such as diesels, gasolines, or RP fuels, is also planned.

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