Project 26
Hybrid Approach to Chemical Kinetics Model Development and Evaluation

Motivation and Objectives

➢ **Motivations**

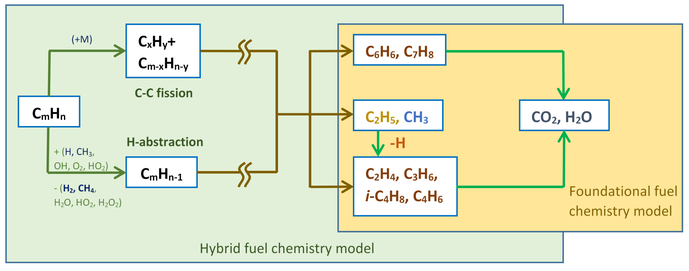
- Next generation of jet engines will operate at pressures far higher than those of current engines for fuel efficiency improvement.
- A basic understanding of the combustion chemistry of jet fuels is critical to the design of high-pressure turbine engines.
- Alternative fuels are expected to enter into the market in the next decade. Their use in commercial aviation is hindered by the lack of quick and inexpensive fuel certification methods.
- Approaches that can quickly and accurately unravel the combustion chemistry of alternative fuels are essential to enable engine design and fuel certification.

Methods and Materials

➢ **Assumptions**

- Early studies [1] suggest that for large hydrocarbon fuels pyrolysis precedes the oxidation of the decomposed fragments in real, liquid fuel combustion. These two reaction processes are decoupled in time scales.
- In flames almost all large hydrocarbon fuels undergo oxidation also in two steps. In the preheat zone of the flame the fuel decomposes into about a half dozen of small molecular fragments in an endothermic process, regardless how complex the composition of the initial fuel is. The fragments then enter into the flame zone and are oxidized to combustion products in the second, exothermic step, which is rate limiting.
- The pyrolysis fragments are dominated by ethylene (C_2H_4), propene (C_3H_6), *iso*-butene (*i*-C_4H_8), 1-butene (1-C_4H_8), methane (CH_4), benzene (C_6H_6), toluene (C_7H_8) and hydrogen (H_2).

➢ **HyChem Approach**



- The kinetic rate of the overall pyrolysis is fast as compared to oxidation, and the distribution of the pyrolysis products has the dominant impact on radical buildup and heat release.
- The overall jet fuel reaction kinetics can be dealt with by combining an experimentally constrained, lumped pyrolysis model with a foundational chemistry model for the oxidation process of decomposition products (e.g., USC Mech II [2]). We term the approach as the hybrid chemistry (**HyChem**) approach.

➢ **Pyrolysis Model – Reactions**

- In HyChem, we write the lumped, pyrolysis model in the form of

$$C_mH_n \rightarrow e_a\left(C_2H_4 + \lambda_3 C_3H_6 + \lambda_{4i}\,i\text{-}C_4H_8 + \lambda_{4n}\,1\text{-}C_4H_8\right) + b_a\left[\chi C_6H_6 + (1-\chi)C_7H_8\right] + \alpha H + (2-\alpha)CH_3 \quad (1)$$

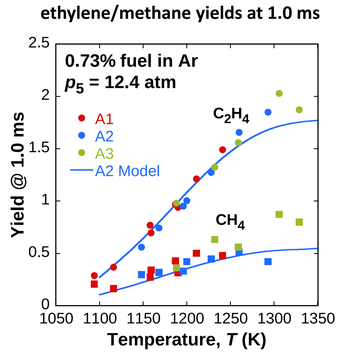
$$C_mH_n + R \rightarrow RH + \gamma CH_4 + e_a\left(C_2H_4 + \lambda_3 C_3H_6 + \lambda_{4i}\,i\text{-}C_4H_8 + \lambda_{4n}\,1\text{-}C_4H_8\right) + b_a\left[\chi C_6H_6 + (1-\chi)C_7H_8\right] + \beta H + (1-\beta)CH_3 \quad (2)$$

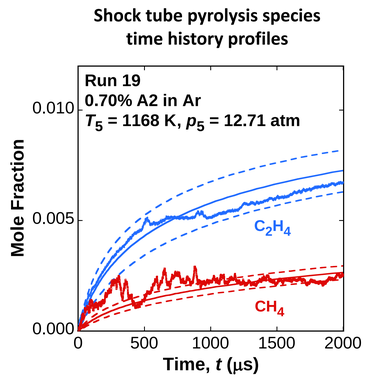
where R = H, CH_3, OH, O, O_2 and HO_2

➢ **Pyrolysis Model – Parameters**

- The model has 11 stoichiometric parameters: e_d, e_o, b_d, b_o, α, β, γ, χ, λ_3, λ_{4i} and λ_{4n}. Under the condition of complete reaction, elemental balances will eliminate four parameters, which are e_d, e_o, b_d *and* b_o.
- The 7 independent parameters, α, β, γ, χ, λ_3, λ_{4i} and λ_{4n}, along with 7 reaction rate constants (k_i, i = 1,2,…,7) can be directly determined from shock tube and flow reactor experiments.

Results – Fuel Pyrolysis

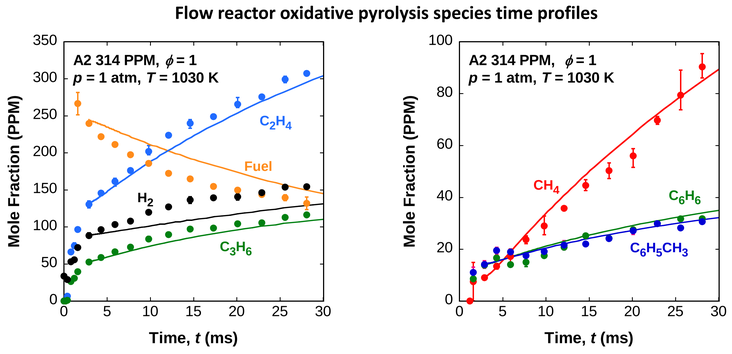




Data: Hanson group

- The 14 unknown parameters, α, β, γ, χ, λ_3, λ_{4i}, λ_{4n} and k_i, (i = 1,2,…,7) may be determined from shock and flow reactor experiments under a wide range of conditions. The left figure shows the ethylene/methane yields at 1.0 ms during shock tube pyrolysis of selected jet fuels over the temperature range of 1050 to 1350 K, along with model predictions. The right figure shows one selected case of shock tube pyrolysis species time histories. The temperature sensitivity (±15 K) is shown with the **dashed lines**. The fuel oxidative pyrolysis section presents the species time profiles during flow reactor oxidative pyrolysis for a Jet A fuel, along with model predictions.

Results – Fuel Oxidative Pyrolysis



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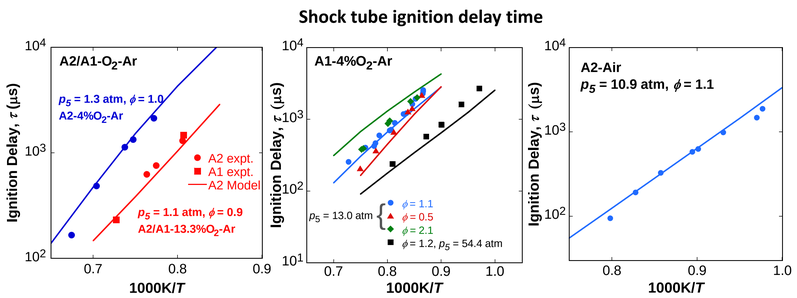
Results – Fuel Oxidation



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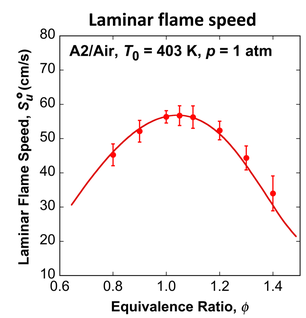
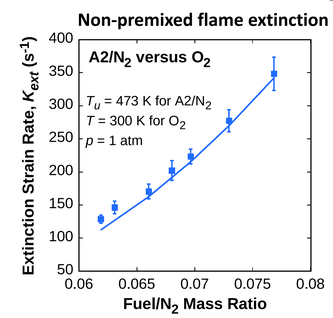
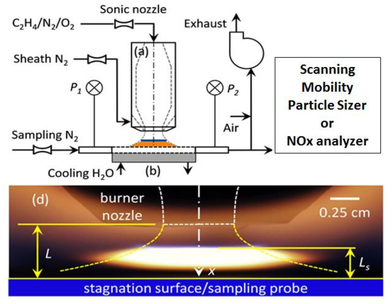


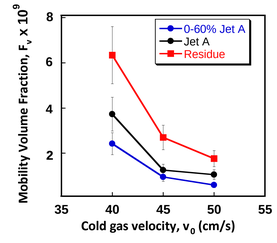


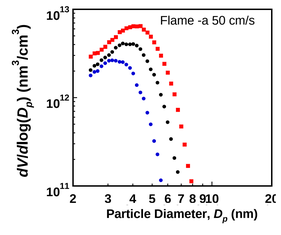
Data: Egolfopoulos group

Extension to NOx and Soot



- Soot measurements were made in premixed stagnation flames to examine the sooting properties of Jet A as function of its distillate fraction.
- Tail end of the distillation curve produces significantly more soot than the light fraction and the fuel as received.
- NOx measurements in premixed stagnation flames are underway with the goal of extending HyChem to predict NOx formation from jet fuels.





Conclusions and Next Steps

- The HyChem approach provides a direct path towards real, liquid fuel combustion chemistry modeling. The resulting model is capable of predicting a wide range of combustion behaviors of typical jet fuels.
- An automatic code for model derivation and refinement is currently under development.
- NOx chemistry and soot model are under development.

References

[1] Davidson, D. F., Z. Hong, G. L. Pilla, A. Farooq, R. D. Cook, and R. K. Hanson. "Multi-species time-history measurements during n-dodecane oxidation behind reflected shock waves." *Proceedings of the Combustion Institute* 33, no. 1 (2011): 151-157.

[2] Hai Wang, Xiaoqing You, Ameya V. Joshi, Scott G. Davis, Alexander Laskin, Fokion Egolfopoulos, and Chung K. Law, USC Mech Version II.High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds. http://ignis.usc.edu/USC_Mech_II.htm, May 2007.