Abstract

**Molecules to Engines: Combustion Chemistry of Alcohols and their Application to Advanced Engines**

by

Shamel Sarfaraz Merchant

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A major challenge in energy is the identification of viable liquid fuels as alternatives to petroleum-based fuels. There are a wide variety of candidate fuels to select from and assessing each new fuel is far from trivial. Small variations in chemical structure can cause large changes in a fuel’s performance. Simultaneously, engine designs are also changing rapidly. Accurately predicting how new fuels will perform in future engines are in many ways more valuable than knowing which fuels perform well in today’s engines. Predictive theoretical modeling is required to efficiently screen candidates.

The selection of a good candidate fuel requires the development of detailed kinetic models capable of accurately predicting fuel behavior over the entire range of engine operating conditions. Despite the fact that most literature models succeed to accurately predict primary combustion products and high temperature ignition delay, two areas require further scientific understanding: peroxy chemistry and polycyclic aromatic hydrocarbon (PAH) formation. The first section of this thesis describes significant contributions to both these areas. Peroxy chemistry is important for accurately predicting ignition in future engine designs based on the concept of low temperature combustion (LTC). This thesis provides a clear explanation of how peroxy chemistry affects low temperature ignition behavior. Simple analytical expressions are provided for the time constant for radical growth and first-stage ignition delay. To improve the understanding of PAH formation, ab-intio calculations to indene and naphthalene from cyclopentadiene and cyclopentadienyl radical were performed. The calculated gas phase rate constants and thermochemistry were used to develop the first elementary micro-kinetic model for the formation of indene and naphthalene from cyclopentadiene. The model is validated against cyclopentadiene pyrolysis data in flow reactors.

The second section of this thesis presents a combined computational-experimental approach to rapidly construct accurate combustion chemistry simulations for alcohol fuels. In this approach experiments and quantum chemical calculations are carried out in parallel, informing an evolving chemical kinetic model.
This approach was used to understand and predictively model the combustion chemistry of iso-butanol and pentanol isomers. Detailed kinetic models for iso-butanol and pentanol isomers are presented which are validated against a large number of datasets spanning the entire range of operating conditions seen during real engine operation. We see that for many performance parameters, the model predictions are as accurate as experiment and help provide mechanistic insight into differing reactivity of a fuel’s isomers. Lastly, we show how detailed kinetic model can be applied in multi-dimensional CFD simulations of a new type of engine, the reactivity controlled compression ignition engine (RCCI), in order to make predictions of how iso-butanol will affect the engine efficiency and emissions. This thesis covers the entire process of predictively accessing a fuel by taking a new fuel molecule, developing a detailed model, and evaluating it in a new engine design in order to make informed decisions.

Thesis Supervisor: William H. Green

Title: Hoyt C. Hotzel Professor of Chemical Engineering