

Title: Predictive Chemical Kinetics for Auto Ignition of Fuel Blends

Nathan Yee,

PhD Advisor: William H. Green

Predictive chemical kinetics plays an important part in the study of chemical systems by reducing the need for expensive experiments. The size and complexity of modern chemical mechanisms increasingly require the use of automated mechanism generators, such as the Reaction Mechanism Generator (RMG) developed by the Green Group. Use of these automated generators for creating quality chemical mechanisms necessitates accurate reaction rates. Unfortunately, the vast majority of kinetic parameters governing rate constants are difficult to experimentally measure. Thus, the goal of this thesis work is the accurate estimation of kinetic parameters and its particular application to the prediction of auto ignition in fuel blends. The work focuses on three different scales: molecular, mechanistic, and macroscopic.

At the molecular scale, modern quantum chemical methods can give kinetic coefficients with accuracy nearing those of experiments. Even when specific kinetic parameters are unavailable, rates can be evaluated by analogy to similar molecules and functional groups. RMG uses an averaging scheme based on arranging functional groups in a hierarchical tree structure. We have been able to continue expansion of the database to novel structures that include nitrogen and sulfur, improve methods for structural representation of chemicals, and showcase high throughput validation for thermochemistry and kinetic parameter estimates.

Studying kinetics at the mechanistic level allows insight into the interaction between chemical reactions. Specifically, we have been interested in finding and analyzing the reaction pathways relevant to auto ignition. To that end, we simplified well-studied fuel mechanisms for propane and methanol. We were able to define clear stages of ignition and report the controlling chemistry during each stage. Understanding of these base fuels provides the basis to analyzing ignition for larger and more novel fuels.

Finally, from a macroscopic perspective we studied ignition for blends of six substituted phenolic additives in gasoline. The chemical mechanisms are modeled in variable volume reaction conditions that emulate end gas conditions in the CFR engine used to evaluate RON numbers. Using mechanisms generated by RMG, we predicted the magnitude and direction each additive has on the timing ignition, which were later proven to be reasonably accurate by experimental determination of RON. The chemical pathways that affect the ignition were analyzed and discussed. This led to a framework for predicting several different aspects of the performance of potential fuel additives, which could help eliminate costly experiments by identifying unsuitable candidates before they are even synthesized.