Molecule-Based Modeling of Heavy Hydrocarbon Structure and Reactions: Discrete and Statistical Approaches

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Introduction

The considerable interest in molecule-based kinetic models for complex chemistries is motivated by the need to predict product properties as a function of chemical process conditions. This is because the molecular composition is an optimal starting point for the prediction of mixture properties. Reactivity is an especially significant property that can be discerned given a molecule's (and its reaction environment's) structure. Other properties fall into performance and environmental classes. Thus, the potential advantages of molecule-based modeling are clear. Less readily apparent, however, is that the development and operation of molecular models comes with a large requirement for model construction and solution time as well as reactivity information.

The essential challenge of building detailed kinetic models for heavy hydrocarbons is due to the staggering complexity of not only the reaction mixtures but the complexity of each molecule within the mixture. There will often be thousands of "multi-functional" component species. The sheer size of the thus-implied modeling problem engenders a conflict between the need for molecular detail and the formulation and solution of the model.

Methods

We have developed automated strategies to represent heavy hydrocarbon structure and reaction both in terms of discrete molecules and probability density functions (pdf's) for molecular attributes. Monte Carlo simulation of feedstock structure is one method to cast the modeling problem in molecular terms. This technique samples pdf's for the attributes of the heavy hydrocarbon molecular structures to construct a representative molecular sample whose properties are compared against measured properties. Optimization methods are used to minimize the weighted sum of squares difference, and the final set of pdf parameters are the mathematical representation of heavy hydrocarbon structure. Subsequent reaction models can be based on discrete molecules or the molecular attributes of the pdf's. The latter "Attribute Reaction Model" provides a large reduction in the number of reaction equations and thus solution time.

Results and Discussion

Representative results are shown in Figure 1. The combination of a probability density function-based model of initial resid structural attributes and a set of attribute reaction models allowed rapid and accurate simulation of resid structure and reactivity. The use of gamma instead of chi-square distribution functions for the attribute pdf's improved the structural representation, which was excellent for Hondo, Maya and Arabian Light. The structural model provided the initial conditions for the subsequent reaction model which, with no adjustable kinetic parameters, provided an excellent fit for the Arabian Light and Maya resids and a reasonable fit for the Hondo and Arab Heavy resids. The poorer reaction model fit for the Hondo and Arabian Heavy resids is likely due in part to the poorer structural fits for these two resids, i.e., the structural model deviations propagated uncertainty into the reaction model.

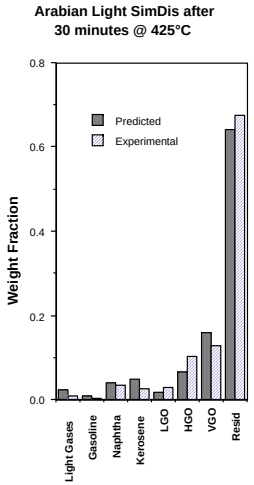

Figure 1. Predicted and experimentally determined boiling point distribution of pyrolysis products for Arabian Light resid.

These approaches should support the development of quantitative reaction models for a wide range of alternative feed stocks for fuels production.

References

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