Automatic Generation of Chemical Kinetic Models including Macromolecules in Multiphase Systems

by

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Detailed chemical kinetic models are indispensable tools for unraveling the complexities of industrial and environmental chemistry systems. Many important industrial and environmental chemistries involve thousands of species and hundreds of thousands of complex pathways, which are difficult to resolve manually. To address this challenge, automatic mechanism generation software has been developed. Previous studies have demonstrated the promising quantitative agreements of automatically generated mechanisms with experimental data. However, these studies have primarily focused on small molecules in single-phase systems, overlooking the complexities of multiphase systems and macromolecules commonly found in industrial and environmental processes.

This thesis introduces advancements in three key areas of automatic mechanism generation:

The first part of this thesis extends the current framework of automatic mechanism generation to tackle the longstanding issue of polymer fouling in the industrial system. Two detailed kinetic models are presented for anaerobic fouling and aerobic fouling in distillation columns. Modeling innovations are introduced, which allow one to construct models including thousands of chemical reactions occurring in the liquid and film phases, vapor-liquid equilibria of hundreds of molecules, transport between the phases, and flows between the trays. All of these factors significantly affect the fouling rate. Most of the critical model parameters are derived from quantum chemistry calculations. The modeling method is validated using experimental film growth measurements made with a quartz-crystal microbalance. These models clarify the mechanistic details of the fouling process.

The second part of this thesis develops machine learning models for predicting thermochemical parameters in gas and liquid phases. A decision tree model based on subgraph isomorphism for gas-phase radical thermochemistry is presented. The model demonstrates improved accuracy compared to the existing empirical model and reliable uncertainty estimates for both interpolation and extrapolation tasks. Additionally, the effectiveness of active learning for building models for solvation-free energy is explored under various compositions of initial training sets and uncertainty estimation methods for data acquisition. The possibility of aiding data acquisition with unsupervised learning for active learning is also assessed.

The third part of this thesis adds new features and enhances the performance of multiple packages under the Reaction Mechanism Generator software suite, originally developed by the MIT Green Group. New tools are developed to facilitate thermochemical data augmentation, multiphase simulation for automatic mechanism generation, and the automatic implementation of quasi-steady state assumptions during the simulation of detailed kinetic models. A new species and reaction selection algorithm is developed to enable the automatic generation of mechanisms for molecular growth systems. Various speed improvement techniques are applied to improve both the simulation speed and sensitivity analysis of large-scale

detailed kinetic models.

By addressing these key areas, this thesis contributes to the advancement of automatic mechanism generation, paving the way for more accurate and efficient modeling of complex chemical systems.

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