

# SOFTWARE TOOLS TO RESOLVE THE UNIQUE CHALLENGES OF MOLECULAR MEGA-MODELS

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Many processes in the energy and petrochemical industries involve complex systems with multicomponent feedstocks. In order to control the molecular output of these processes, the underlying chemical mechanisms must be understood. Through the use molecular-level models, the chemical kinetics can be deciphered and the process optimized at molecular resolutions. However, molecular-level models of complex real systems can quickly reach mega levels sizes in terms of reactions and/or species. Model development at these scales becomes time consuming and cumbersome affecting all phases: building, solving, kinetic parameter estimation, and editing. Advances in computer science allow for the development of new modeling approaches that decrease the time spent in molecular-level model development. The Dynamic Model Builder (DMB) is a C++ object oriented modeling framework that accounts for varying model sizes while functioning independently of program compilation. In the DMB framework molecular-level kinetic models are created and simulated from system memory. The DMB framework is further enhanced to deal with large systems through parallelization of both the ODE solver and the kinetic parameter estimation routine. DMB's implicit ODE solver routine was parallelized on a CPU-GPU hybrid system using CUDA based MAGMA GPU libraries for the LU decomposition routine. The kinetic parameter estimation objective function simulations were multi-threaded on the CPU using OpenMP. These parallelization approaches decreased kinetic parameter estimation time for large molecular systems. To illustrate the robustness of this modeling framework three reactor models were investigated: lignin pyrolysis, cellulose pyrolysis and diesel hydrocracking.

A molecular-level kinetic model by means of an adapted Freudenberg lignin structure was developed for lignin pyrolysis at the temperature of 600 °C. A detailed reaction network was established taking into account primary and secondary lignin pyrolysis chemistries from literature. An exhaustive method was produced to handle the large structure reactivity by

merging reaction networks. The adapted Freudenberg large lignin structure was modified based on a comparison of the reaction network and experimentally observed products. The evaluation of the kinetic model consisted of validation with molecular species measured in experimental work. The model output showed agreement with experimental results from Zhang et al. (Min Zhang, 2014).

Thermogravimetric analysis (TGA) of cellulose pyrolysis was simulated using a molecular-level kinetic model. A temperature ramp between 373-1073 K was imposed in order to achieve the TGA simulation. A recursive optimization method was utilized to calculate the degree of polymerization of the starting cellulose molecule from literature bulk properties. The model's primary reaction pathways for cellulose decomposition allowed for degradation of the active cellulose molecule by hydrolysis and thermal degradation to create cellobiose, cellobiosan, and glucose. The mechanisms revealed by Agarwal et al. were used to degrade cellobiose (Vishal Agarwal, 2012). An extension of the cellobiose mechanisms were applied to cellobiosan. The reactivity of glucose was captured by the reaction networks proposed in the work of Zhou et al. (Xiaowei Zhou, 2014). Monomer and dimer degradation pathways produced volatiles, furans, aldehydes, ketones, and char through a series of complex reactions. Linear free-energy relationships were applied to minimize the number of model kinetic parameters. Executing the cellulose pyrolysis model in TGA mode provided a prediction of the mass loss. The TGA simulation showed agreement with the experimental trends.

A molecular-level kinetic model has been developed for gas phase diesel hydrocracking on a bifunctional metal acid catalyst. The diesel model feed is a complex mixture of paraffins, multi-branched isoparaffins, naphthenics, and aromatics. The feed composition was estimated based on experimental molecular and bulk information. Linear free energy relationships in the Bell-Evans-Polyani form were applied to minimize the number of model kinetic parameters (Bell, 1936) (Evans & Polanyi, 1935). The model contained 86 independent parameters for control of hydroisomerization and hydrocracking reactions. The kinetic parameters were estimated from experimental data on an isothermal fixed bed reactor with a diesel feed and bifunctional catalyst. Kinetic parameter estimation was aided by the development of new parallel tuning methodologies. The effects of catalyst activity on compound classes are presented.