

Generating Detailed Kinetic Models for Large Pyrolysis Systems

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Detailed kinetic models have been able to accurately predict the behavior of many complex chemical systems. The benefits of such models is numerous, ranging from being able to predict system behavior under conditions not amenable to experiments to the fact that the mere process of generating such models often leads to the discovery of new reaction pathways. Despite this utility, to date these models have mostly been applied to smaller systems of 10 heavy atoms or less. This is because as the size of the molecules grows, the number of possible isomers and thus reactive pairs grows combinatorially. Furthermore, refining these models often involves high-accuracy quantum chemistry calculations that are expensive for larger species. If these challenges can be overcome, though, generating detailed kinetic models for larger systems aims to provide valuable insights into complex systems, such as the pyrolysis of heavy oil or biomass. In this work, we show that advances in automatic mechanism generation software, quantum chemistry methods, and ever increasing amounts of computational power have made the prospect of generating detailed models for larger systems possible. We were able to generate a detailed kinetic model for the pyrolysis a 3-component hydrocarbon mixture with the largest species containing 18 heavy atoms. Despite the size of the molecules, the generated model was able to predict experimental data for this system. We also discuss aspects of refining these models with quantum chemistry calculations, specifically calculating species thermochemistry. We showed that many of the methods for correcting these calculations, including bond-additivity corrections and isodesmic reaction approaches yield similar results, despite some claims to the contrary. Finally, we collected experimental data necessary to validate detailed kinetic models for the pyrolysis of kerogen. As part of this work, we discussed the challenges of collecting such data, and showed the suitability of modern methods and instrumentation towards this task. With this, it is likely that detailed kinetic models will be increasingly used to study larger systems, though this work will likely involve fully-detailed model compound studies in tandem with approaches to reduce the combinatorial complexity of large systems without much loss in accuracy.