

# FOLLOWING THE EVOLUTION OF MOLECULAR STRUCTURES IN BIOMASS PYROLYSIS USING KINETIC MONTE CARLO SIMULATIONS

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## *Abstract*

A kinetic Monte Carlo (kMC) algorithm was developed and used to model thermal reaction networks of complex feedstocks, such as pyrolysis reactions of cellulose. The simulation integrates ab initio quantum calculated rate constants for the elementary kinetic transformations, graph theory-based algorithms to analyze molecular structures, stochastic algorithms to simulate complex reaction networks, and classical molecular dynamics simulations to rapidly and efficiently relax molecular structures. The simulation defines chemical species via their atomic structures, where detailed 3D coordinates and bonding patterns of individual atoms are followed directly. Molecular structures are identified and tracked based on bonding patterns of atoms. Coordinates of atoms are tracked and updated using classical molecular dynamics. This simulation is able to follow the intrinsic kinetics and molecular composition of the reacting systems of interest, such as thermal conversion of cellulose. The simulations follow the kinetics and product distributions with some success.

## *Keywords*

Biomass pyrolysis, Kinetic Monte Carlo, Complex reaction networks

## **Introduction**

Biomass has been examined extensively as an alternative energy source to fossil fuels, as its conversion to fuel is carbon neutral (Bridgewater, 2012). The oxygenate functional groups in biomass also offer promising paths to form valuable reaction intermediates such as levoglucosans, furans and other light oxygenates, which can be converted to value-added chemicals (Bridgewater, 2012). One of the most accessible ways to convert biomass to fuels and chemicals is fast pyrolysis (Zhu et al., 2017). An economically viable biomass conversion process demands high selectivity and stringent control of the product distributions. Current approaches to biomass fast pyrolysis are limited due to the lack of the ability to actively control the selectivity of the products.

Recent studies have shown that variables such as reaction temperature, concentration of metal ion catalysts, and even macroscopic dimensions of the biomass feedstock particles significantly alter reaction mechanisms, kinetics and product distribution of biomass fast pyrolysis (Zhu et

al., 2017). These experimentally observed complexities indicate that the kinetics and selectivity of thermal reactions are ultimately dictated by the molecular transformations that are directly influenced by molecular structures and local chemical environments. Understanding the molecular processes that proceed in biomass pyrolysis is crucial for the design and operation of large scale and economical biomass conversion facilities. Accurate reaction models and kinetics for the complex network of thermal reactions involved in biomass pyrolysis are required.

Herein we present detailed and molecular-based kMC simulations that can model the kinetics for the fast pyrolysis and the thermal reaction networks for biomass and other complex feedstocks. This approach avoids the loss of detailed atomic structural information with lumping methods. It also allows for unique kinetic manifestations that can result from the local structure of these feedstocks that would otherwise be lost in composition-based deterministic models.

## Computational Methods

In the simulation, detailed information of individual atoms including 3D coordinates and chemical bonding patterns are tracked as a function of time and reaction conditions. Chemical reactions are defined as functions that update identity, coordinates and connectivity of atoms using logical operations. Gillespie's Stochastic Simulation Algorithm (SSA) (Gillespie, 1976) is used to advance time steps of the simulation. Graph theory based search algorithms including depth first search (DFS) and breadth first search (BFS) are used to analyze molecular structures and subsequently enumerate chemical reaction events. Rate constants of the chemical reactions are obtained through first principle calculations of model compounds. Molecular structures are relaxed with classical molecular dynamics (MD) simulations between chemical reaction steps. MD simulations are executed using Large-scale Atomic/Molecular Massively Parallel Simulation (LAMMPS) with OPLS-AA (Damm et al., 1997) classical force field. Relaxed molecular structures are analyzed by a spatial analysis algorithm to capture effects of local environment on reaction kinetics.

## Simulation of Cellulose Pyrolysis

The KMC simulation method is used herein to examine the transglycosylation of cellulose at pyrolysis conditions. As shown in Figure 1, cellulose molecules undergo a series of elementary C-O bond activation reactions stochastically. Their molecular structures are relaxed with classical MD between reaction steps.

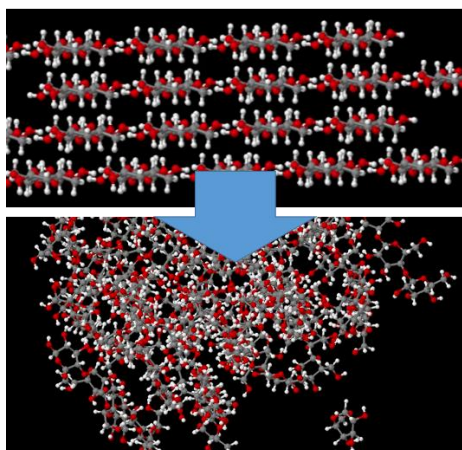


Figure 1. Simulation tracks explicit molecular structures as reactions occur

Reaction kinetics and product distribution can be derived by analyzing the temporally-resolved molecular structures produced by the simulation. As shown in Figure 2, the simulations nicely capture the two kinetic regimes at

high and low temperatures observed experimentally (Zhu et al., 2017).

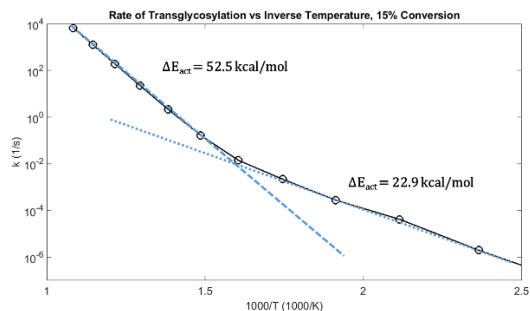


Figure 2. Simulation captures two kinetic regimes observed in experiments

## Conclusion

An elementary-step molecular-level kinetic Monte Carlo simulation scheme has been developed to study reaction networks of complex feedstocks. The detailed atomic scale information that is retained in this simulation allow the simulations to follow molecular transformation, the local molecular environment and the changes that result as a function of reaction conditions. The simulation is able to track the intrinsic kinetics for model pyrolysis reactions of cellulose with success in capturing reaction kinetics.

## Acknowledgments

The authors sincerely appreciate financial support from University of Minnesota Department of Chemical Engineering and Material Science as well as computational resources from Minnesota Supercomputing Institute.

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