MECHANISTIC MODELING OF THE (BIO)CONVERSION OF (BIO)MACROMOLECULES

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Fast pyrolysis, a potential strategy for the production of transportation fuels from biomass, involves a complex network of competing reactions, which result in the formation of bio-oil, non-condensable gaseous species, and solid char. Bio-oil is a mixture of anhydro sugars, furan derivatives, and oxygenated aromatic and low molecular weight (LMW) compounds. Previously, the successful modeling of fast pyrolysis reactors for biomass conversion was hampered by lumped kinetic models, which fail to predict the bio-oil composition. Hence, a fundamental understanding of the chemistry and kinetics of biomass pyrolysis is important to evaluate the effects of process parameters like temperature, residence time and pressure on the composition of bio-oil. In this talk, a mechanistic model that was recently developed to characterize the primary products of fast pyrolysis of cellulose is described. The kinetic model of pyrolysis of pure cellulose was then extended to describe cellulose decomposition in the presence of sodium salts. To quantify the effect of sodium, a density functional theory study of glucose dehydration, an important class of decomposition reactions of a cellulose-derived intermediate, was carried out. The kinetic parameters derived were used in the kinetic model to describe Na-mediated pathways, capturing trends in the experimental product distributions as the salt loading was increased based on classic catalytic cycles. In contrast to pyrolysis, conversion of macromolecules such as cellulose in Nature takes place at ambient temperature, aided by enzymes. Mechanistic details of the action of these enzymes will also be discussed and contrasted to high-temperature pyrolysis pathways.

We have also developed a computational discovery platform for identifying and analyzing novel biochemical pathways to target chemicals. Automated network generation that defines and implements the chemistry of what we have coined “generalized enzyme functions” based on knowledge compiled in existing biochemical databases is employed. The output is a set of compounds and the pathways connecting them, both known and novel. To identify the most promising of the thousands of different pathways generated, we link the automated network generation algorithms with pathway evaluation tools. Our method for automated generation of pathways creates *novel compounds and pathways* that have not been reported in biochemical or chemical databases. Thus, our method goes beyond a survey of existing compounds and reactions and provides an alternative to the conventional approaches practiced to develop novel biochemical processes that harness the power of enzymes as catalysts for biorefining applications.