REACTION PATHWAY ANALYSIS OF THE (BIO)CONVERSION OF (BIO)MACROMOLECULES

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Abstract

Reaction pathway analysis is a powerful tool to design novel routes to chemicals, identify optimal processing conditions, and suggest strategies for catalyst design. We have developed methods for the assembly of kinetic models of substantive detail to be built that enable the atomic scale to be linked with the process scale. We have applied our methodology to a wide range of different problems, including production of silicon nanoparticles, biochemical transformations, polymerization and depolymerization, and tropospheric ozone formation. While the chemistries we have studied are seemingly very disparate, applying a common methodology to study them reveals that there are many features of complex reaction networks that are ubiquitous, and a kinetic modeling framework can be a tool that unifies understanding of chemical and biological catalytic systems. This talk will focus on mechanistic modeling of a range of conditions for converting hydrocarbons derived from renewable sources, starting with quantitative analysis of chemical catalysis by native inorganic constituents and transitioning to mechanistic understanding of how enzymes achieve exquisite selectivity for similar conversion processes, leading to the potential for the design of novel biochemical pathways.

Keywords

Reaction pathway analysis, biomass conversion, kinetic modeling, biochemical pathways, pyrolysis.

Fast Pyrolysis of Biomass

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 (Vinu and Broadbelt, 2012; Zhao et al., 2014 a, b). 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 (Mayes et al., 2014, 2015). The theoretical results reveal alterations in the reaction rate coefficients when sodium is present and a change in the relative rates of different reactions. These kinetic parameters 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. Analysis of contributions of different pathways to the formation of major and minor products allows potential intervention strategies to maximize the yields of desirable products to be suggested. As shown in Figure 1 as an example, the relative contributions of the formation routes for levoglucosan during pyrolysis of cellulose at 500 °C as a function of NaCl loading was analyzed. The model predicts that levoglucosan directly formed from decomposition of cellulosic chains through end-chain initiation and depropagation decreased from 28.3 to 2.44 wt%, and from 22.2 to 0.68 wt%, respectively, as the NaCl concentration was increased from 0 to 0.31 mmol/g. However, these two pathways still account for the majority of the final yield of levoglucosan, although the pathway of glucose dehydration contributes increasingly from 6.46 to 39.6 %.

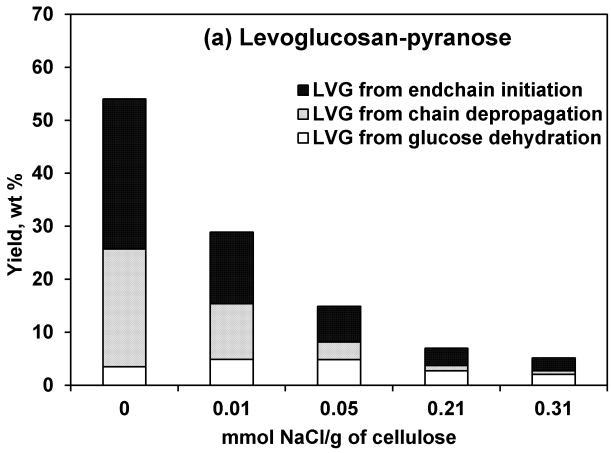

Figure 1. Contributions of different pathways to the formation of levoglucosan in fast pyrolysis of cellulose dosed with varying amounts of NaCl at 500 °C.

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.

Design of Novel Biochemical Pathways

We have also developed a computational discovery platform for identifying and analyzing novel biochemical pathways to target chemicals (Hatzimanikatis et al, 2004). 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. The simplest screening metrics to rank pathways are pathway length and number of known reactions. More sophisticated screening tools include thermodynamic feasibility and potential of known enzymes for carrying out novel reactions. 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. An example of the creation of novel pathways for the production of a commodity chemical currently synthesized by non-biological routes will be shown. In addition, methods for identifying enzymes that can putatively catalyze novel reactions that are predicted by the pathway design approaches will be revealed.

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