NABC Fundamentals and Modeling Team Tackles Understanding Biomass Intermediate Chemistry

Biomass is a complex mixture of components, broadly classified into cellulose, hemicellulose, and lignin, the amount of which varies depending on the feedstock source. Lignin itself varies considerably depending on the source, comprised of different amounts of monomeric building blocks, connected by different linkages. When different conversion chemistries are used to produce fuels and chemicals from biomass, this complexity creates significant challenges in being able to predict the composition of the product slate. The Fundamentals and Modeling Team of the National Advanced Biofuels Consortium (NABC) is taking on this challenge, using a combined experimental and modeling approach to unravel the chemistry underlying biomass conversion at the mechanistic level, allowing for the greatest opportunity for prediction.

The team first tackled cellulose, one of the components of biomass whose structure is well defined and thus lends itself to fundamental study. Experiments at Iowa State University studied neat cellulose decomposition under fast pyrolysis conditions over a range of temperatures and for different cellulose initial chain lengths and crystallinity indexes. They quantified the yields of a wide range of products in detail, including the main product, levoglucosan, and other low molecular weight products, including glycoaldehyde, hydroxymethylfurfural, and formic acid. Under fast pyrolysis conditions, the degree of polymerization for long chains and the crystallinity index did not affect the product yields. The Broadbelt group at Northwestern University developed the first mechanistic model of cellulose pyrolysis that was able to capture the changes in the product distribution as a function of temperature. In addition, this universal model was able to capture the experimental product yields from glucose and cellobiose and maltohexaose, 1,4-alpha- and 1,4-beta-linked oligosaccharides, by simply changing the initial molecular weight of the reactant. The model is able to predict the time dependence of all products, while the micropyrolyzer experiments are currently able to quantify the endpoint of the decomposition. To obtain additional information about the dynamics of cellulose decomposition from experiments, David Thorn and his team at Los Alamos National Laboratory are carrying out time-resolved experiments that are able to detect the early degradation events of cellulose on the time scale of milliseconds.

Cellulose is rarely encountered as a pure feedstock, however, as inorganic contaminants such as sodium- and calcium-based salts are present in naturally-occurring biomass. Therefore, the team turned its attention to understanding the role of alkali metals on cellulose decomposition. The Iowa State University team observed strong effects of low amounts of salts, including a significant decrease in the levoglucosan yields. Initial modeling efforts are able to capture this effect by enhancing the rate constant for dehydration reactions. To rationalize this change, quantum chemical calculations are being carried out in the Broadbelt group and molecular simulations are being conducted in the Gnanakaran group at Los Alamos National Laboratory. Results to date reveal that sodium ions bind to the backbone of cellulose and its derivatives and

perturb the kinetics under pyrolysis conditions. Development of a detailed kinetic model that quantifies these effects is underway.

While cellulose is an important component of biomass that leads to usable fuels and chemicals, the role of lignin in determining the product slate and the economic viability of biomass conversion technologies cannot be overstated. Lignin is a voluminous component, comprising a significant portion of the carbon in biomass, is recalcitrant, and can affect downstream conversion processes due to the presence of aromatic moieties and non-labile bonds. Moreover, the inability to utilize the lignin for other than fuel value severely impacts the economic viability of thermochemical conversion. The Fundamentals and Modeling Team has thus turned its attention to unraveling the degradation of lignin.

Experiments in the Shanks lab and in Robert Brown's group at Iowa State University have provided significant insight into how lignin behaves under pyrolysis conditions. Monomers, dimers, and other small molecules have been quantified in detail. However, the product distribution is comprised of such a large number of species that it is difficult to uncover reaction pathways and kinetics that would inform mechanistic understanding. Indeed, the initial structure of lignin is not known precisely, but rather has only been quantified in terms of monomer composition, bond composition, molecular weight, and degree of branching. To capture these measures, a stochastic approach employing probability distribution functions is being used in the Broadbelt lab to create libraries of lignin structures for different biomass sources. These structures will subsequently be used in the development of detailed kinetic models of lignin conversion.

Given the complexity of lignin, the team conceived of experiments and modeling analysis of lignin model compounds, small molecules that mimic the essential bond types, monomers, and substituents that would be encountered in real lignin. The Beckham group at the National Renewable Energy Laboratory has created a library of model compounds, shown in Figure 1, that are being scrutinized by the team. For example, the Shanks laboratory has analyzed the products being formed from the s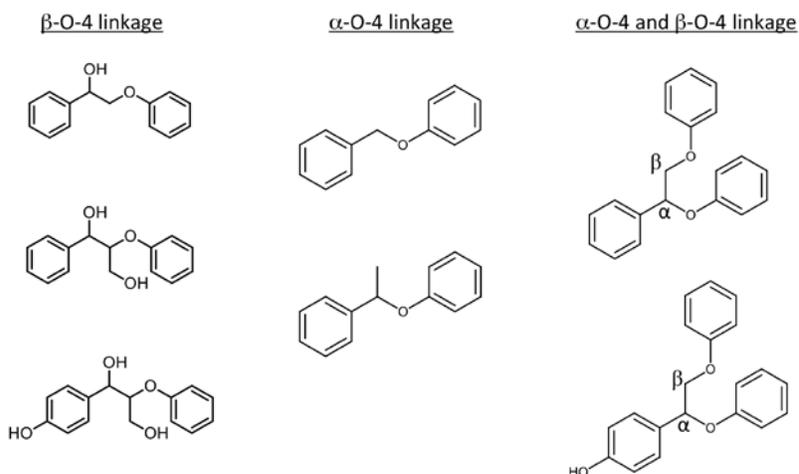implest model compound containing a β-O-4 linkage under fast pyrolysis conditions and has identified species with molecular weights higher than the starting material, suggesting the prevalence of condensation reactions. Labeling studies in the Thorn group allow the origin of the atoms comprising the condensation products to be identified, leading to a set of likely reaction pathways. Tony Dean and his group at Colorado School of Mines are using quantum chemical calculations and kinetic

Figure 1. Library of model compounds being used to unravel decomposition chemistry of lignin.

models based on rate rules to understand the mechanisms of these decomposition reactions.

While pyrolysis is an attractive technology for biomass conversion, a number of strategies being studied in the NABC involve the addition of a catalyst as an agent to accelerate the rate of decomposition of biomass and tailor the product distribution. The Fundamentals and Modeling Team is also addressing how different catalysts can perturb the reaction chemistry of biomass conversion, with a focus on lignin. As a compelling example of how theory and experiment can be used to understand decomposition chemistry in the presence of catalysts, the Broadbelt group and Beckham group have examined lignin model compounds in the presence of strong acids and demonstrated concordance between the experimental product distribution and reaction mechanisms and pathways predicted by quantum chemical calculations. Fundamental understanding of various biomass deconstruction and deoxygenation catalysts is also currently being developed.