

June 15, 2011

New Strategies for Biomass Deconstruction in the NABC

Production of fuels and chemicals from biomass requires overcoming two major hurdles: conversion of recalcitrant plant biomass to intermediates and reduction of those intermediate molecules to the desired products. In typical biochemical conversion strategies, recalcitrance is overcome with a low temperature thermochemical pretreatment step followed by application of enzymes to fully convert cellulose and hemicellulose to sugars. These sugars are then reduced to fuels like ethanol via fermentative organisms. Biochemical conversion is selective for converting the carbohydrate polymers in plant cell walls, but it typically only uses the lignin fraction of plant cell wall for heat and power. In addition, although biochemical conversion is quite selective, the residence times for typical processes are on the order of days. Thermochemical conversion strategies to overcome recalcitrance, such as pyrolysis and gasification, on the other hand are typically characterized by much faster residence times (order of seconds to minutes) but lower selectivity. Thermochemical conversion is capable of utilizing both the carbohydrate and lignin portions of the plant cell wall. This difference in typical conversion strategies is shown in Figure 1 from a kinetics and thermodynamics perspective.

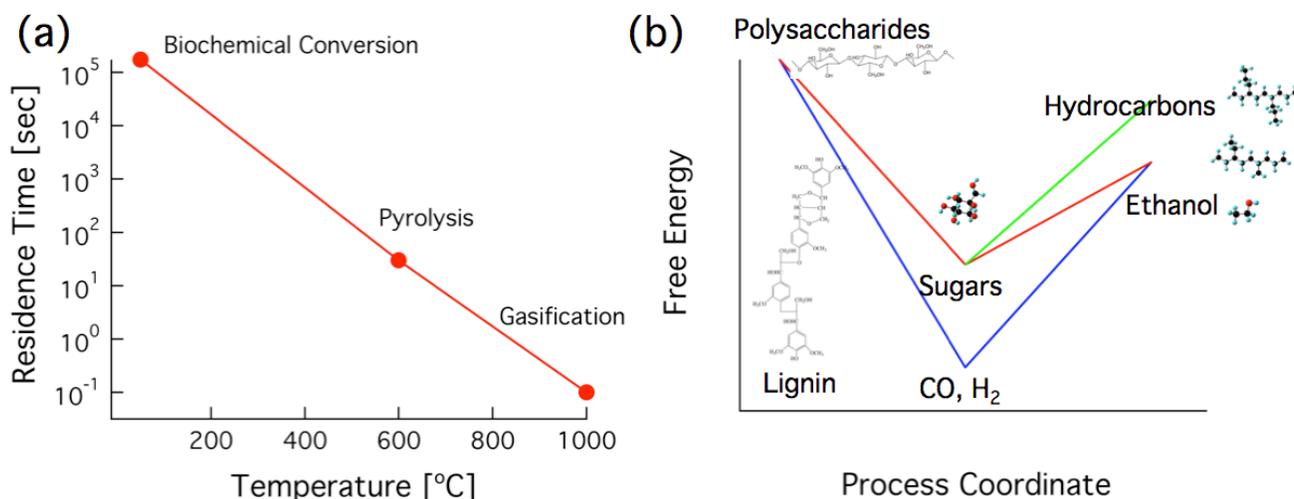


Figure 1. The (a) kinetics and (b) thermodynamics of typical biomass conversion strategies. The Biomass Deconstruction subtask in the NABC is developing strategies to overcome biomass recalcitrance in a temperature and residence time regime between the biochemical and thermochemical conversion regimes as indicated in blue on Figure 1(a). Taken from Chundawat, Beckham, Himmel, and Dale, *Annual Reviews of Chemical and Biomolecular Engineering*, 2 (2011).

The Biomass Deconstruction subtask in the National Advanced Biofuels Consortium (NABC), which is led by NREL, is focused on developing new strategies that operate in temperature and residence times between biochemical conversion and thermochemical conversion. The overall aim is to develop new processes that exhibit selectivity near that of enzymes but that operate at higher temperatures and throughputs. The new deconstruction routes being developed by NREL in the NABC will also be able to selectively utilize not only the carbohydrate fractions of the plant cell wall, but also the lignin

fractions. This cross-cutting technology will be able to link to multiple process strategies being examined in the NABC.

The Biomass Deconstruction subtask is divided into two primary areas: carbohydrate deconstruction to sugars or oxygenated intermediates, and lignin deconstruction to monomeric compounds. Both the carbohydrate and the lignin deconstruction work in this subtask are closely tied to techno-economic analysis for the design of new upstream conversion strategies as well as to the Lignin-to-Fuels subtask for upgrading lignin intermediates. The primary approach for carbohydrates focuses on the development of solid, recyclable catalysts for acid hydrolysis of glycosidic linkages in cellulose and hemicellulose that can operate at higher temperatures than biological catalysts can. This problem is challenging from a heterogeneous catalysis standpoint as solid-solid catalysis is inherently limited by interfacial contact between the catalyst and substrate. Thus, we are focused on a large-scale screen of catalysts over a wide range of conditions to depolymerize solid carbohydrate substrates to soluble sugars or other oxygenated intermediates that can be upgraded to hydrocarbon fuels.

In the case of carbohydrate deconstruction, the chemistry (acid hydrolysis) is well known, and is used in nature by a vast range of glycosyl hydrolase enzymes. In the case of lignin deconstruction, nature typically uses oxidative mechanisms based on radical generation by enzymes such as laccases and peroxidases. As adding additional oxygen to biomass derived compounds is undesirable, and radical chemistry is inherently less selective, the NREL team is focusing first on the development of new, selective catalysts for reductive cleavage of common linkages in lignin, such as aryl-ether linkages shown in Figure 2.

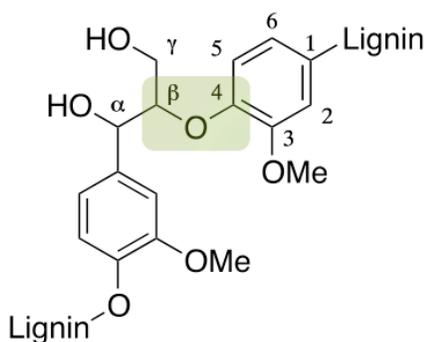


Figure 2. The aryl-ether linkages in lignin are typically on the order of 50% of the chemical bonds, and thus are good candidates for catalytic cleavage. Work in the Biomass Deconstruction subtask in the NABC is focused on reductive catalytic cleavage of this class of linkages. Here we highlight a β -O-4 bond.

To design new catalysts for aryl-ether cleavage, the NREL team is using an integrated computational and experimental approach. Quantum mechanical calculations are being applied to determine the elementary steps and associated kinetics for reductive ether cleavage with newly designed catalysts. Experimentally, we are synthesizing a large library of lignin model compounds to validate our computational results. Toward deconstruction of real lignin, we are also developing strategies to compare the thermodynamics and kinetics of model compound catalysis to real lignins isolated from plant cell walls. This will enable us to connect fundamental insights on small molecule models to realistic lignin depolymerization and subsequent upgrading strategies. Overall, the Biomass Deconstruction subtask will aid in the development and integration of more efficient methods to overcome biomass recalcitrance that will take advantage of the positive attributes of both biochemical and thermochemical conversion and enable efficient utilization of both the carbohydrate and lignin fractions of the plant cell wall.