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NABC Includes Fundamentals Team for Pyrolysis Modeling

Pyrolysis modeling is now included as one of the cross-cutting technologies in the National Advanced Biofuels Consortium (NABC) research portfolio. The collaborative team, with members from the National Renewable Energy Laboratory (NREL), Iowa State University (ISU), Colorado School of Mines (CSM), Los Alamos National Laboratory (LANL), and Northwestern University (NU), is focusing on developing improved reaction and reactor models for biomass pyrolysis.

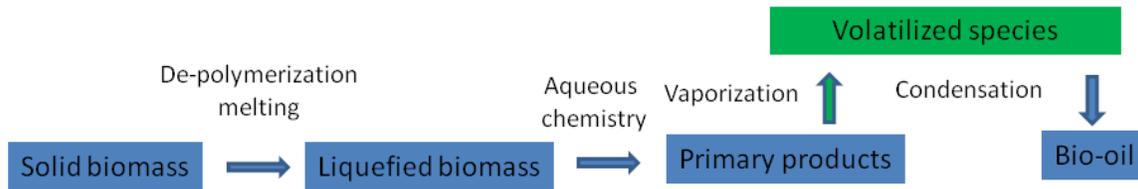
Designing advanced reactors for biomass pyrolysis requires detailed kinetic models that take into account basic reaction parameters including final temperature, heating rate, pressure, feedstock composition, and the presence of reactive gases and indigenous heterogeneous catalysts. Constructing such models for biomass pyrolysis is inherently complex because the product oils consist of hundreds or thousands of distinct and different molecular moieties.

The pyrolysis modeling project team will generate thermal biomass pyrolysis data, synthesize reaction networks, estimate initial rate parameters, and verify the constructed model. Their ultimate goal is to construct detailed quantitative reactor models for biomass thermal pyrolysis that will aid the process strategy teams with process modeling and design and scale-up of chemical reactors.

Results

At the NABC annual meeting held on January 26–27, 2011, in Phoenix, Arizona, the pyrolysis modeling group led by Dr. Robert Baldwin of NREL presented some very interesting results to the consortium members. A particularly informative early stage finding addressed the important question about whether pyrolysis chemistry is predominantly controlled by 1) ionic reactions in the condensed phase or 2) gas phase reactions (Figure 1). Successful predictive modeling of biomass pyrolysis requires knowledge of which chemistry is predominant.

➤ **Primarily ionic reactions in the condensed phase**



➤ **Gas phase reactions of initially formed products (bond fissions, radical reactions)**

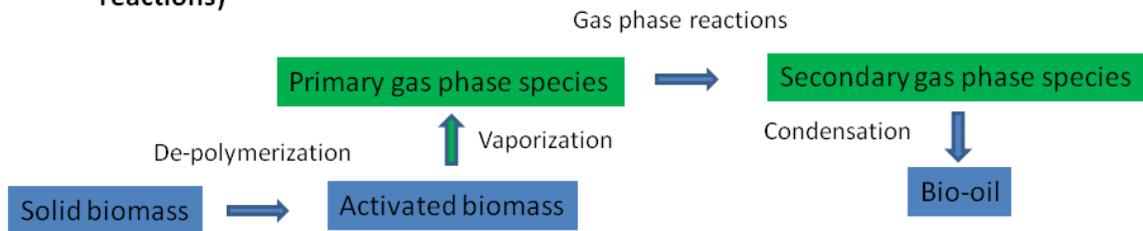


Figure 1. Condensed phase or gas phase reactions for determining pyrolysis chemistry

To determine which reaction domain applies, both an experimental and a mechanistic approach were pursued. Each approach provided very strong evidence that condensed phase ionic reactions predominantly control the chemistry during the initial stages of pyrolysis. A particularly compelling data point is a comparison of calculated rate constants in the gas phase and condensed phase for conversion of levoglucosan to glyceraldehyde. The calculated gas phase rate constants are approximately six orders of magnitude lower than that suggested by the condensed phase rate rule (Figure 2). Similar conclusions are observed for lignin using phenethyl phenyl ether (PPE) as a model compound representing lignin.

This is a significant finding, and future research will focus on predicting thermodynamic properties in the condensed phase.

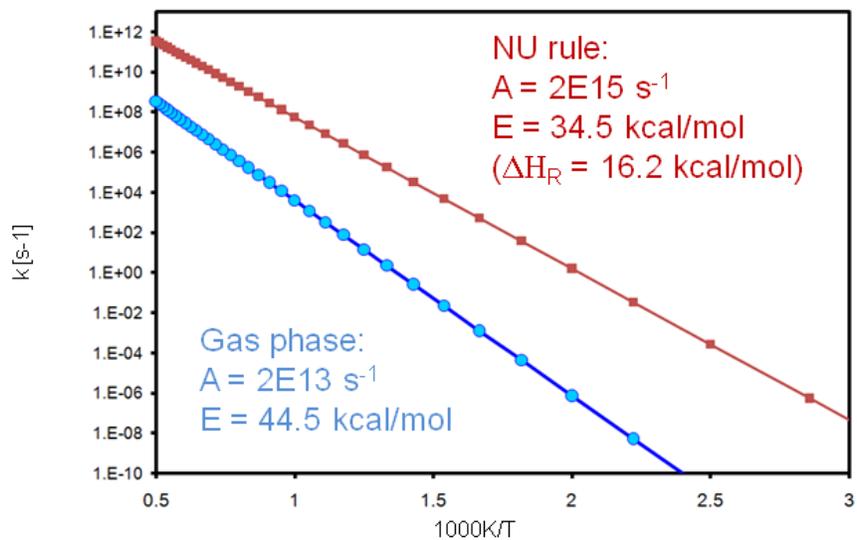


Figure 2. Condensed phase versus gas phase rate constants