ABSTRACT

Degenstein, John C. PhD, Purdue University, May 2016. Fast-Pyrolysis of Biomass Related Model Compounds: A Novel Approach to Experimental Study and Modeling. Major Professors: Rakesh Agrawal, W. Nicholas Delgass, and Fabio H. Ribeiro.

Fast pyrolysis is a potentially attractive method for converting biomass to a low energy-density liquid (bio-oil) that can be further upgraded for use as fuel. Currently there is no agreement concerning the reaction pathways and mechanisms for pyrolysis of any individual component of biomass. This information is important for optimization of the fast-pyrolysis process. The work was divided into four areas, 1–development and validation of analytical methods and reactors, 2–the utilization of these methods to study pyrolysis of biomass and related models, 3–use of available biomass conversion pathways to propose potential integration with the existing fuel and chemicals markets, and 4–a proposed kinetic and multiphase reactor model for the physical and chemical processes that occur during pyrolysis.

In the first area, mass spectrometric methodology was developed for the determination and manipulation of the initial products of fast-pyrolysis of carbohydrates and lignin-related molecules. A fast-pyrolysis probe/linear quadrupole ion trap mass spectrometer combination was used to study the quenched initial fast-pyrolysis products, those that first left the hot pyrolysis surface. The quenched products were ionized in an atmospheric pressure chemical ionization (APCI) source infused with one of two ionization reagents, chloroform or ammonium hydroxide, to aid in ionization. Liquid chromatography-mass spectrometry (LC-MS) methods were also developed and utilized for quantitative characterization of the liquid products from a lab-scale pyrolysis reactor.

In the second area, the aforementioned pyrolysis probe / mass spectrometric methodology was used to study pyrolysis of cellulose (and related models), of lignin model compounds, and of biomass. Based on several observations, the fast pyrolysis of cellulose is suggested to initiate predominantly via two competing processes: the formation of anhydro-oligosaccharides, such as cellobiosan, cellotriosan, and cellopentosan (major route), and the elimination of glycolaldehyde (or isomeric) units from the reducing end of oligosaccharides formed from cellulose during fast pyrolysis. Several products were shown to result entirely from fragmentation of the reducing end of cellobiose, leaving the nonreducing end intact in these products. These findings are in disagreement with mechanisms proposed previously.

Also, in the second area, fast-pyrolysis of several guaiacyl β-O-4 lignin model compounds was studied using both pyroylsis mass spectrometry and pyrolysis gas-chromatography mass spectrometry. The results indicate that the lignin oligomers undergo a number of different types of reaction pathways including Maccoll elimination, homolytic bond dissociation, and elimination of formaldehyde and water.

Also in the second area, a lab-scale, high-pressure, continuous-flow fast-hydropyrolysis and vapor-phase catalytic hydrodeoxygenation (HDO) reactor was tested with cellulose as a model biomass feedstock while varying temperature, pressure and gas composition. The major compounds in the liquid from cellulose fast-pyrolysis (27 bar, 520°C) are levoglucosan and its isomers, formic acid, glycolaldehyde, and water, constituting 51 wt%, 11 wt%, 8 wt% and 24 wt% of liquid respectively. The formation of permanent gases (CO, CO_2, CH_4) and glycolaldehyde and formic acid increased with increasing pyrolysis temperature in the range of 480°C-580°C in high-pressure cellulose fast-pyrolysis, in the absence of hydrogen. Our results showed that high pressures of hydrogen did not have a significant effect on the fast-hydropyrolysis of cellulose at 480°C but suppressed the formation of reactive light oxygenate species like glycolaldehyde and formic acid at 580°C.

In the third area, over 50% yield of oxygenated hydrocarbons was obtained from the lignin fraction of biomass using a novel Zn/Pd/C catalyst. Genetically modi-

fied poplar enhanced in syringyl (S) monomer content yielded only a single product, dihydroeugenol. Lignin-derived methoxyphenols can be deoxygenated further to propylcyclohexane. This effective conversion of lignin enables several newly proposed conversion pathways to useful fuels and chemicals based on conversion of lignin into intact hydrocarbons.

In the fourth area, a new kinetic and multiphase reactor model for the physical and chemical processes that occur during pyrolysis is proposed. This model helps explain the observed difference in average molecular weight between the pyrolysis probe / mass spectrometric reactor and reactors with higher gas-phase temperatures.