ABSTRACT

Easton, Mckay W. Ph.D., Purdue University, August 2016. Density Functional Theory Complements Mass Spectrometry in the Investigation of Biomass Pyrolysis and Ion-Molecule Reaction Mechanisms. Major Professor: Fabio Ribeiro.

Biomass fast-pyrolysis, or the rapid heating in the absence of oxygen, is a promising method for developing a renewable energy economy. Although models of cellulose pyrolysis have existed since the 1970s, current models and hypothesized reaction networks fail to explain the product distribution of pyrolysis of the cellulose dimer, cellobiose. A novel approach to mass spectrometry of pyrolysis vapors allows for identification of initial products to help unlock the reaction pathways that dictate the final product distribution of bio oil. Pyrolysis of glucosaccharide-based compounds, such as cellobiose, cellohexaose, cellotriosan, and cellulose reveal that the reaction pathway of unraveling the reducing end of the sugar by multiple losses of glycolaldehyde (or isomer) is competitive with the well-established mechanism of levoglucosan end production via nucleophilic attack of the hydroxymethylene group at the anomeric carbon concerted with glycosidic bond cleavage. Computational investigation on the reaction barriers of this reducing end unraveling mechanism concurrent with levoglucosan end production and hydrolysis may be able to qualitatively account for the observed products of cellobiose pyrolysis. These reaction mechanisms appear to have further application to hemicellulose model compounds, specifically xylans.