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Research Thesis Outline

Research Title: Mechanistic investigation of upgrading pyrolyzed biomass vapors with supported ionic liquid catalysts to improve bio-oil quality

Chapter 1: [Introduction to biofuels] introduces the biofuels topic, the motivation for the research, and also introduces the catalyst design. The objective of this research is to use supported ionic liquid catalysts to upgrade pyrolysis vapors. The ionic liquid layer is expected to be more easily regenerated than solid catalysts. Also, cellulose and guaiacol will be pyrolyzed with the catalysts to get a better idea about the interactions between the pyrolysis vapors and the catalyst surface. Past research on biofuels and conversion process to convert biomass to biofuels is explained. Explains how process parameters such as temperature, gas residence time, and particle size can all affect the bio-oil yield and quality. Discusses various pyrolysis equipment set-ups and explains advantages and disadvantages of the fixed bed reactor.

Chapter 2: [Design of experiment (DOE) and system calibration] introduces and explains all the materials used in these experiments including the ionic liquids and pyrolysis feed materials and catalysts supports. In this chapter, initial experimentation results are shown for the newly constructed fixed bed reactor and the results are verified with extensive design of experiments and error analysis. The affects of the process parameters are also discussed.

Chapter 3: [Study of cellulose, guaiacol, and wood pyrolyzed with silica, ZSM-5, and ZrO_2-TiO_2], initial testing with the catalyst supports are conducted and discussed in this chapter. Silica, ZSM-5 and ZrO_2-TiO_2 are used as catalysts to pyrolyzed cellulose, guaiacol, and wood. The results are analyzed with gas chromatography–mass spectrometry (GC-MS) and the chemical compositions are investigated. This chapter gives the basis for future chapters to investigate the affects of the various ionic liquids used in this study.

Chapter 4: [Japanese cypress pyrolysis vapors catalyzed with supported ionic liquid [bmim][BF_4] on silica and ZrO_2&TiO_2], begins the study of using ionic liquid as a catalyst to upgrade pyrolysis vapors. The synthesized ionic liquid supported catalysts were extensively investigated with Raman, surface area and pore volume calculations based on nitrogen adsorption data, acid site distribution using NH_3 pulse and thermogravimetric differential thermal analysis (TG-DTA) analysis to observe the weight loss profiles of the ionic liquid coated catalysts. Next the catalyst was used to improve pyrolysis vapors. From the results, a simple mechanism was proposed for furan production from sugar from the catalyst.

Chapter 5: [Cellulose pyrolysis catalyzed using [bmim][BF_4] and [bmim][TFSI] ionic liquids supported on silica and ZrO_2&TiO_2], covers the affects of the supported ionic liquid catalysts on cellulose pyrolysis. Also, rather than just [bmim][BF_4], [bmim][TFSI] is also

used for the study. This ionic liquid is basic while the [bmim][BF_4] is considered an acidic ionic liquid. The two different ionic liquids had different affects on the pyrolysis vapors. Based on the results, both the catalyst support, interactions between the catalyst support and the ionic liquid and the ionic liquid itself cause differences in the cellulose bio-oil. Levoglucosan and levoglucosenone production from cellulose mechanisms are proposed. Finally, the used catalyst was regenerated and analyzed using proton nuclear magnetic resonance (H-NMR).

Chapter 6: [Pyrolysis of cellulose mixed with ionic liquids [bmim][TFSI], [bmim][BF_4], and [bmmim][BF_4] to improve liquid yield at low temperatures], is a study where the ionic liquid is directly mixed with the cellulose before pyrolysis. Also, another ionic liquid is studied to investigate the affects of the cation while keeping the anion the same. The ionic liquids have high temperature stability so should be able to be separated from the cellulose after pyrolysis. The cellulose mixed with ionic liquid had different bio-oil yields and chemical compositions than cellulose powder. These results are discussed.

Chapter 7: [General Conclusion], this chapter summarizes the previous chapters and gives recommendations for future studies. In this research, ionic liquid was successfully coated on catalyst supports and used to upgrade pyrolysis vapors. The resultant Japanese cypress bio-oil had fewer acidic and sugar compounds, and increased furans. The results of cellulose pyrolysis also show that both the catalyst support and the type of ionic liquid coating make a difference on the liquid products. Regeneration studies were also conducted, and the catalyst was successfully regenerated. Further research is needed to purify the ionic liquid after pyrolysis and determine the best ionic liquid and catalyst support combination for upgrading pyrolysis vapors.