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論文審査の要旨及び審査員

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論文審査の要旨 (2000 字程度)

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

Chapter 1: [Introduction to biofuels] introduces biofuels, the motivation for this 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 understand interactions between the pyrolysis vapors and the catalyst surface. Past research on biofuels and conversion processes to convert biomass to biofuels is explained. 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. 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 ZrO₂-TiO₂], initial testing with the catalyst supports are conducted and discussed in this chapter. Silica, ZSM-5 and ZrO₂-TiO₂ 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][BF₄] on silica and ZrO₂&TiO₂], begins the study of using ionic liquid as a catalyst coating 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 NH₃ 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][BF₄] and [bmim][TFSI] ionic liquids supported on silica and ZrO₂&TiO₂], covers the affects of the supported ionic liquid catalysts on cellulose pyrolysis. Also, rather than just [bmim][BF₄], [bmim][TFSI] is also used for the study. This ionic liquid is basic while the [bmim][BF₄] 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 (¹H-NMR).

Chapter 6: [Pyrolysis of cellulose mixed with ionic liquids [bmim][TFSI], [bmim][BF₄], and [bmmim][BF₄] 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 cellulose mixed with ionic liquid had different bio-oil yields and chemical compositions than cellulose powder.

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.

Based upon the chapter summary above, this dissertation fulfills the conditions for conferment of the degree of Doctor of Engineering as agreed by the committee.

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