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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	Mechanical Sciences and Engineering 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of Engineering
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Biomass can be converted to bio-oil, a promising energy alternative for limited crude oil. Currently, the cost of bio-oil production is relatively high and the bio-oil is of low yield and poor quality. In this work, [bmim][BF_4] and [bmim][TFSI] were supported on ZrO_2&TiO_2 and silica at varying amounts to deoxygenate pyrolysis vapors and improve the quality of bio-oil. Cellulose, guaiacol, and Japanese cypress were pyrolyzed with these catalysts to determine the upgrading mechanism. In a final study, the previous mentioned ionic liquids and [bmmim][BF_4] were directly mixed with the cellulose as a pretreatment and then the cellulose was pyrolyzed. Cellulose was chosen because it has a low pyrolysis temperature. Doing this type of study with wood would not be possible due to higher necessary pyrolysis temperatures. This is done to see if similar catalytic effects can be achieved within the same pyrolysis reactor. Finally, regeneration studies were conducted on the used catalysts.

From our studies we found that coating the ionic liquid on a catalyst support increases the temperature stability of the ionic liquid compared to using pure ionic liquid. The [bmim][BF_4] on the silica caused an increase of furans and decease in acids and sugars in the final bio-oil from Japanese cypress pyrolysis. The coatings on the ZrO_2&TiO_2 had similar affects as the silica except the ZrO_2&TiO_2 surface did not have a strong affinity to the sugars. Coating the ZrO_2&TiO_2 with [bmim][BF4] also caused a decrease in acids and an increase in furans. The ionic liquid coating had beneficial effects on improving the bio-oil quality by decreasing acids which are known to decrease the stability of the bio-oil and also degrade containers holding and using the bio-oil.

For the cellulose pyrolysis, silica has a strong interaction with sugars containing many hydroxyl groups such as levoglucosan in cellulose due to hydroxyl bonding to the oxygen on the silica surface. It was determined that the sugar decrease observed in the Japanese cypress pyrolysis was due to the strong binding of the hydroxyl group of the sugar onto the sugar of the silica catalyst. However, with the 30% coating of [bmim][TFSI], the sugars were unable to reach the surface of the silica and the sugars ended up in the liquid products. The 30% coating of [bmim][BF_4] did not have such an affect. This shows that different compounds can permeate the ionic liquid layer and others cannot. This technique allows for selective reactions of certain compounds in the pyrolysis gas and also illustrates that both the ionic liquid coating and the catalyst support cause differences in product distribution of the liquid.

Next, cellulose was pretreated with [bmim][TFSI], [bmim][BF_4], and [bmmim][BF_4] to determine the effects of using various ionic liquids to dissolve the cellulose. The cellulose pretreated with ionic liquid was pyrolyzed at various temperatures to investigate the possibility of using ionic liquid as both a solvent and a catalyst. All ionic liquid pretreated cellulose had increased bio-oil yields at 225°C and 250°C. However, at 300°C, the untreated cellulose had the same or higher yield than the ionic liquid pretreated cellulose. The ionic liquid increases bio-oil yields at low temperatures.

The pyranose ring structure breaks apart between 225°C and 250°C for the ionic liquid pretreated cellulose samples, but the pyranose ring structure breaks apart at a temperature higher than 250°C for the untreated cellulose samples. Higher temperatures cause furans to decrease, and ketones, cyclopentanones, and acids to increase in all samples. Also, the

intrinsic basicity of [bmim][TFSI] and the Brønsted acid ionic liquids had different affects on the cellulose pyrolysis. The [bmim][TFSI] increased the furfural in the bio-oil while Brønsted acid ionic liquids increased cyclopentanones. Staged pyrolysis at different temperatures may be effective for separating the pyrolysis liquid yields into different fractions.

Regeneration studies were also conducted on the spent catalysts. These include filtration studies, centrifugation studies, distillation studies, chemical separation, and CO_2 extraction. Overall, the best process was simply to wash the spent catalyst multiple times in water, and then evaporate the water. This resulted in a darkish brown, gooey substance. This substance was analyzed with H-NMR and had the same peaks as pure ionic liquid. This indicates that the ionic liquid can be separated from the catalyst support even after pyrolysis.

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. The ionic liquid could be successfully separated from the catalyst support after pyrolysis using water washing, and may be reused. This indicates that the process may be economically feasible. However, 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.