Development of Catalytic Strategies for Upgrading of Biofuels

Steven Crossley, Surapas Sitthisa, Lance Lobban, Richard Mallinson, and Daniel Resasco*
*School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, Oklahoma 73019 (USA) - *resasco@ou.edu*

Introduction

A combination of experimental model compound studies with kinetic fittings and QSPR prediction to improve desired properties of specific fuels has proven to be effective for creating catalytic strategies for upgrading of light cycle oil (LCO)[1] to diesel fuel as well as removal of aromatics in gasoline while minimizing losses in octane number[2]. The end result is the development of catalytic strategies which maximize both catalytic potential as well as knowledge of the fundamental relationships between molecules and catalysts through extensive catalyst characterization. These same strategies are applied towards upgrading of biofuels from both vegetable oil and cellulosic feedstocks producing both promising catalytic strategies for upgrading of biodiesel, triglycerides, glycerol, as well as various compounds present in bio-oil over heterogeneous catalysts such as supported Pt, Pd, Cu, Pt-Sn as well as various acidic and basic zeolytes.

Materials and Methods

Catalytic strategies have been developed for the upgrading of model compounds representative of both vegetable oil and bio-oil feedstocks. For vegetable oil, model compounds representative of biodiesel, triglycerides, and glycerol have been investigated over acidic, basic, metallic, and bifunctional catalysts under a variety of conditions in order to create fungible diesel or gasoline fuels. Reactions studied include decarbox/onylation, hydrogenation, hydrogenolysis, cracking, and various condensation mechanisms. Through this approach, strategies have been developed to create either diesel or gasoline fuels from these various sources. For pyrolysis oil, compounds investigated include furans, phenols, cresols, aromatic aldehydes, ketones, as well as small water soluble acids and aldehydes. Catalysts investigated include heterogeneous metals such as Pt, Pd, Cu, P-Sn as well as other bimetallic catalysts, acidic catalysts including various zeolytes, basic catalysts such as MgO and Cs doped zeolytes, and bifunctional catalysts as well. In each case, extensive catalyst characterization as well as kinetic studies were conducted in order to understand the fundamental relationships between the catalyst and molecules. Reaction conditions investigated span a wide range from atmospheric pressure to 500psig, under inert and hydrogen environments, from room temperature to 450°C, in batch, semi-batch, and flow reactors. When combined with QSPR in order to predict desired fuel properties, promising catalytic strategies towards the upgrading of each class were accomplished. Careful attention is placed on upgrading multiple properties at once as many tradeoffs are observed when developing strategies. For this reason, not only octane and cetane numbers were investigated, but also water solubility, vapor pressure, stability, and specific volume are investigated for each strategy developed.

Results and Discussion

As an example of this approach applied to biofuels, results from the deoxygenation of furfural can be observed below. Furfural is a model compound chosen to represent one of the many species present in bio-oil. Reactions were conducted in a flow reactor in excess hydrogen over the temperature range from 230-290°C for Pt, Pd, and Cu supported on SiO_2 over the space time range from 8 to 50 g.cat h/mol. Langmuir-Hinshelwood kinetic fittings were found to represent the data quite well, with good agreement found for activation energies and heats of adsorption with previously reported literature values. QSPR models were then introduced to predict the fuel properties which would result from these reactions. Results for Cu and Pd can be observed in figure 1, with Pt behaving very similarly to Pd. One can clearly see the influence of both metal and temperature on fuel properties. For the case of Cu, hydrogenation of the aldehyde group to the alcohol is the dominant step, with increased rates of C-O hydrogenolysis to methylfuran at higher temperatures. In the case of Pd, decarbonylation is a dominant route followed by hydrogenation of the ring at higher conversions. This study shows the importance of each group, while Pd is more effective at quickly eliminating the oxygen group via decarbonylation, copper is better for selectively removing the oxygen via hydrogenation/olysis while preserving the unsaturation in the ring. These types of studies, when compared with other bio-oil model compound studies, provide useful information for developing optimal strategies for bio oil upgrading.

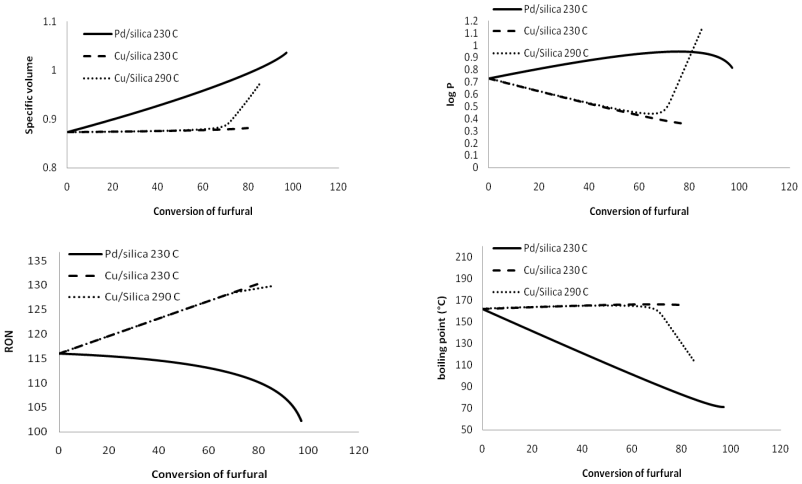

Figure 1: Resulting properties of specific volume, octanol water partition coefficient, research octane number, and boiling point exiting the reactor as determined by a combination of QSPR and kinetic fittings of furfural conversion over Pd and Cu catalysts supported on silica.

References

1. Santana, R.C., Do, P.T., Alvarez, W.E., Taylor, J.D., Sughrue, E.L., and Resasco, D.E. *Fuel, 85*, 643 (2006).
2. Santikunaporn, M., Herrera, J.E., Jongpatiwut, S., Resasco, D.E., Alvarez W.E., and Sughrue, E.L., *J. Catal.*, 228(1), 100, (2004).