BIFUNCTIONAL ZEOLITES FOR BIOMASS HYDROPYROLYSIS

D.P. Gamliel and J.A. Valla*
University of Connecticut - Storrs
Storrs, CT 06238

Abstract

The goal of this work is to investigate the role of operating conditions and catalyst building blocks (support/metals) on the biomass hydropyrolysis process. Ni, Ru and Pd were tested as metals impregnated on ZSM-5 and γ-Al_2O_3 supports. All the materials were characterized using N_2 adsorption/desorption, X-ray diffraction (XRD), Temperature Program Reduction (TPR) and *in-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The hydropyrolysis experiments were performed in a pyrolysis-gas chromatography (PyGC) microsystem under high H_2 pressure. Here we will present how the different catalyst properties (metal and support) and the operating conditions (pressure, temperature) affect CO_x removal (decarboxylation or decarbonylation) and hydrogenation reactions.

Introduction

With the demand for liquid hydrocarbon fuels ever-increasing, and the effects of climate change already being felt, there is significant interest in replacing existing fossil-based-energy resources and technologies with renewable and sustainable ones. While automobiles may some-day be powered by electricity generated from carbon neutral sources, the aviation industry will continue to demand carbon-based and energy-dense jet fuel. Biomass is the only renewable carbon source, which must be efficiently converted to supply the world with sustainable liquid fuels.

Biomass catalytic fast pyrolysis (CFP), has been widely studied as one method for generation of liquid hydrocarbons. The primary goal of CFP research has been the formation of mono-aromatic hydrocarbons (MAHs), as a potential drop-in carbon source for existing refineries. Unfortunately, these bio-fuels suffer from high oxygen content, high viscosity, high acidity and instability, and also from low H/C ratio required for aviation fuels. All of the aforementioned issues are a result of the presence of oxygenated compounds and unsaturated C=C double bonds. Thus, upgrading of the pyrolysis vapors is necessary. Hydrodeoxygenation (HDO) has been widely investigated as a second step in the upgrading process. Inspired by hydroconversion processes in refinery applications, NiMo and CoMo catalysts have been studied used as HDO catalysts. However, none of the current hydroconversion catalysts applied to the petroleum feedstocks are necessarily optimal for upgrading of biomass pyrolysis vapors, because petroleum feedstocks do not contain significant amounts of oxygen atoms. A different option which is gaining a lot of interest lately is an integrated hydropyrolysis and hydrodeoxygenation process where biomass is pyrolyzed in the presence of high H_2 pressure and the vapors are simultaneously upgraded using an HDO catalyst. The optimum design of such a catalyst is the key to the success of this process.

Several variables must be taken into consideration, which will affect catalyst performance during this catalytic hydropyrolysis process, including: support material, metal choice and loading. Venkatakrishnan et al. (2014) designed a unique hydropyrolysis reactor, and studied HDO with γAl_2O_3 supported Pt and Ru catalysts and concluded that

the ideal HDO catalysts would promote acid catalyzed dehydration of –OH groups present in pyrolysis vapors, while enhancing preferential C-O hydrogenolysis over metal active sites. Zhao et al. (2012) studied hydroprocessing of phenolic species using Ni/ZSM-5 catalysts. They concluded that strong zeolite Brønsted acid sites, aided by the proper pore size material could effectively promote C-C coupling, while removing oxygen bonds. Metallic Ni species and hydrogen at high pressure were required to saturate aromatic C=C bonds. The goal of our work is to understand how the reaction operating conditions and the catalyst building blocks (support/ metals) affect reaction and quality of the products during the integrated hydropyrloysis/HDO process.

Methods and Materials

Three catalyst supports were considered in the present study: γAl_2O_3, ZSM-5 and USY zeolite, with USY having the highest surface area. Pd, Ru and Ni were impregnated in the supports by wet impregnation. Here we present the results of 3% Ni on ZSM-5 support. The surface area and the macropore and mesopore volume of the catalysts were measured by N_2 adsorption/desorption. Metal phases were identified using X-ray diffraction. Acid sites (including Brønsted and Lewis acidity) were measured using *in-situ* DRIFTS with pyridine as a probe molecule. *In-situ* IR CO adsorption was also used to identify the topology and the state of each metal species on the support. All hydropyrolysis experiments were performed using a PyGC system. Catalyst and biomass were physically mixed and placed in a quartz tube microreactor. The mixture was pyrolyzed at a set point of 600 °C, in either a H_2 or Ar atmosphere at 15, 200 or 450 psig.

Catalytic Hydropyrolysis with ZSM-5 and Ni-ZSM-5

Figure 1 shows the Brønsted acid (B.A.S.) and Lewis acid (L.A.S.) sites of γAl_2O_3, ZSM-5 and USY zeolite. Both ZSM-5 and USY zeolite both Brønsted and Lewis acid sites, whereas alumina only has Lewis acidity. Once Ni was impregnated on the ZSM-5, the Lewis acidity increased significantly at the expense of Brønsted acid sites.
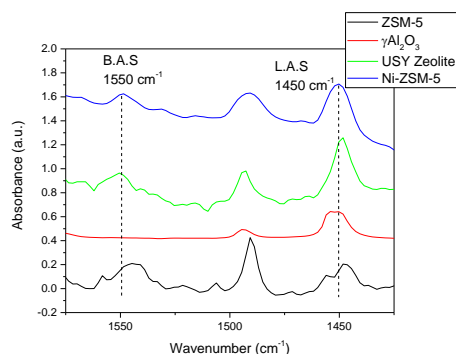

Figure 1. Pyridine sorption of each support and Ni-ZSM-5 monitored via DRIFTS

Figure 2 shows the liquid (a), solid (b) and permanent gas (c) carbon yields as a function of pressure for each catalyst and atmosphere. Solid yield increases at higher pressure for most conditions, at the expense of gas and liquids, but conspicuously decreases when the Ni/ZSM-5 catalyst is present at high hydrogen pressure. A corollary increase in gas yield is also observed at this condition, as nearly 20% of the carbon in the original biomass was converted to methane, which is depicted in Figure 2(f). Also from Figure 2(e), liquid alkanes formation increases as a function of pressure, but alkanes are only present in a hydrogen atmosphere. The Ni/ZSM-5 catalyst also promotes alkanes production. Finally, mono-aromatic hydrocarbons (MAH) formation is enhanced at higher hydrogen pressures, while poly-aromatic hydrocarbon (PAH) yields decrease at higher pressure (not shown).
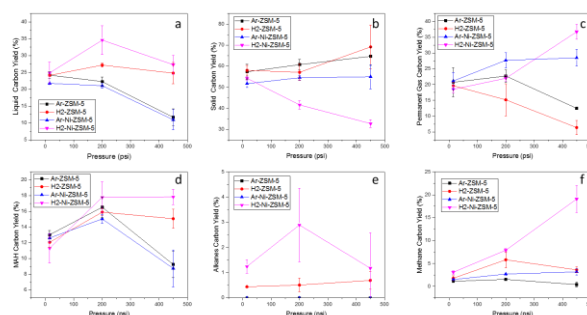

Figure 2. liquid (a), solid (b), permanent gas (c), MAH (d), alkanes (e) and methane (f) yields for fast (hydro)pyrolysis of miscanthus

Conclusions

Catalytic hydropyrolysis for the transformation of biomass into jet fuels is a promising process. Hydrogen pressure does not significantly affect the quality of the pyrolysis products, unless a metallic catalyst (Ni/ZSM-5 in this case) is present. This presentation will focus on catalyst building block choice, and how hydropyrolysis operating conditions affect hydropyrolysis product yields.

References

Venkatakrishnan, V.K., Degenstein, J.C., Smeltz, A.D., Delgass, W.N., Agrawal, R., Ribeiro, F.H., 2014. High-pressure fast-pyrolysis, fast-hydropyrolysis and catalytic hydrodeoxygenation of cellulose: production of liquid fuel from biomass. *Green Chem.* 16, 792.

Zhao, C., Kasakov, S., He, J., Lercher, J. a., 2012. Comparison of kinetics, activity and stability of Ni/HZSM-5 and Ni/Al 2O3-HZSM-5 for phenol hydrodeoxygenation. *J. Catal.* 296, 12–23.