Investigation of pH and Char Particles on Bio-oil Aging Reactions

Caitlin D. Naske, Sarah E. Crosby, Andrew McMaster, Keisha B. Walters

Dave C. Swalm School of Chemical Engineering

Mississippi State University

Bio-oil produced by biomass pyrolysis has been shown to degrade over time and at elevated temperatures resulting in increased viscosity that makes processing and handling difficult. Char particles remaining in the bio-oil after pyrolysis and condensation are thought to catalyze polymerization reactions leading to the viscosity increases during bio-oil aging. Pyrolysis bio-oil has a low pH as produced (pH ~2-3) and the effect of the low pH on the polymerization reactions is unknown. Samples of pyrolysis bio-oil were produced from ground clear wood cottonwood and pine biomass using an auger reactor under vacuum. Neat bio-oil was aged up to 21 days at 80 °C and 28 days at 50 °C. The pH of pine clear wood fractionated bio-oil was adjusted by the addition of dry KOH to obtain nominal pH values of 5, 7 and 9 and these pH-adjusted samples were aged at 80 °C up to 14 days. Pine whole tree fractionated bio-oil was filtered prior to aging by vacuum filtration followed by centrifugal filtration with a 0.2 µm pore size filter and then aged at 80 °C up to 21 days. All bio-oil samples were characterized with Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), and combined gas chromatography-mass spectroscopy (GC/MS); select samples were analyzed by electrospray ionization mass spectroscopy (ESI-MS). GPC analysis showed an increase in molecular weight and PDI during aging. The ESI-MS results revealed a polymeric pattern in several of the bio-oil samples, including the aged samples. Light microscopy was used to compare the filtered and neat bio-oil and verified that a large amount of the char particles were removed by centrifugal filtration. Upon aging, the pH adjusted bio-oil samples displayed a decrease in pH with the pH change largest for the pH 9 samples followed by pH 7 and then pH 5. FTIR spectra of the un-aged pH adjusted samples show a shift and broadening in the hydroxyl peak and significant differences in the 1800-1500 cm^{-1} range compared to neat bio-oil spectra. Comparison of FTIR spectra between the neat and filtered samples show little or no differences.