

Biofuels 2018: Hydroprocessing of lignin for the production of liquid fuels and chemicals- Charles Xu- Western University, Canada

Charles Xu

Department of Chemical and Biochemical Engineering, Western University, Canada

ABSTRACT

Forestry biomass and residues (such as harvesting residues, sawdust, and bark) and lignin a by-product from pulping processes can be promising bio-renewable sources for the production of liquid fuels and chemicals. The lignin component of woody biomass is of particular interest as it comprises the world's largest natural source of aromatic compounds and is produced in large quantities as a by-product of pulp and paper processing. The main challenge in lignin utilization for fuels and chemicals is that it is composed of very large molecules with low heating values (due to high oxygen content) and low reactivity. Accordingly, the overall objective of this work is the production of chemicals and fuels by the catalytic hydro processing of lignin and lignin-derived bio-oils aiming to reduce their molecular weights and oxygen contents. This work investigated the catalytic hydro processing of a number of different lignin's for the production of fuels and chemicals. Several supported metal hydrogenation catalysts were investigated for the depolymerisation, deoxygenation, and desulfurization of Kraft lignin (KL) organosolv lignin (OL) and hydrolysis lignin (HL) under hydrogen atmospheres to produce depolymerized lignins or lignin-derived bio-oils. Screening of catalysts was performed using guaiacol as a model compound. The most effective catalyst under the conditions tested was found to be 1wt.% Mo-doped 5wt.% Ru supported on activated charcoal (MoRu/AC). The selected catalyst proved to be very effective for hydro processing of organosolv lignin, hydrolysis lignin (HL) and depolymerized hydrolysis lignin (DHL).

INTRODUCTION

The main objective of this project was to investigate and develop effective carbon-supported hydroprocessing catalysts for the depolymerization of lignin as well as the upgrading of lignin-derived bio-oil. The chemical and physical properties of the resulting products were analyzed to demonstrate the effectiveness of these catalysts. Concerns about declining non-renewable fossil resources, energy security, climate change and sustainability are increasing worldwide. On a global level this has resulted in an increased interest in the development of alternatives to fossil resources not only for energy, but also for chemical production. There are a number of promising alternatives to fossil resources, however, lignocellulosic biomass such as forestry residues and wood waste (bark, sawdust, etc.) seem to be the most promising. They are widely available, renewable and a non-food resource. Therefore woody biomass holds the promise of being a sustainable resource for both energy and chemical production.

Bio-energy is a blanket term that refers to all forms of renewable energy that are derived from biomass feedstocks. Biomass feedstocks typically have a heating value comparable to that of low rank coal (lignite and sub-bituminous coals). In order to make use of these resources it is, therefore, necessary to develop cost-effective technologies to convert them into liquid bio-fuels. Thermo-chemical processes for the production of liquid bio-fuels include indirect liquefaction processes e.g. gasification combined with various catalytic processes for production of synthetic fuels (e.g., methanol, ethanol and high quality diesel), and direct liquefaction technologies mainly pyrolysis and high pressure liquefaction processes. Direct liquefaction of biomass followed by upgrading and refining is regarded as a promising approach in addition to them there are indirect liquefaction processes such as the MTG (Mobil methanol to gasoline) and the SMDS (Shell middle distillate synthesis) processes currently under development.

APPROACHES AND METHODOLOGY

Lignin is a complex polymer with a high average molecular weight and some types of lignin such as Kraft lignin and hydrolysis lignin are not soluble in common organic solvents, which prevents their direct use as a substitute for petroleum-based chemicals in the synthesis of bio-based polymer materials. Therefore, samples of these lignins including organosolv lignin, Kraft lignin and hydrolysis lignin were depolymerized into the lower molecular weight products.

The depolymerization was conducted concurrently with hydrogenation/hydrodeoxygenation of the lignins and the overall process has been termed hydroprocessing instead of hydrotreatment to avoid confusion, as hydrotreatment has a specific meaning in the petroleum industry. The depolymerization of larger quantities of lignin was carried out in a 500 mL Parr stirred autoclave reactor. Under hydrogen at different temperatures, pressures and reaction times the lignins and depolymerized lignins were reacted in the presence of various catalysts.

RESULTS

The aim of this work was to investigate the depolymerization and hydroprocessing of several different types of lignin (Kraft lignin, organosolv lignin, and hydrolysis lignin) in the presence of catalysts and supercritical acetone to obtain lower molecular weight and deoxygenated compounds suitable for use as substitutes for fuels and chemicals from fossil resources. In the

first study, a number of different metal catalysts and support materials were successfully employed in the depolymerization and hydroprocessing of Kraft and organosolv lignin. Carbon-supported catalysts were found to outperform catalysts supported on alumina.

The effectiveness of novel mixed noble metal/transition metal MoRu catalysts was investigated using guaiacol as a model compound for lignin. Guaiacol conversion was most effective in the presence of activated carbon-supported MoRu catalyst. Based on this work, the depolymerization and hydroprocessing of organosolv lignin using these MoRu catalysts was investigated. OL was successfully hydroprocessed and depolymerized into DOLs composed of aromatic compounds with increased hydrogen contents, decreased oxygen contents and greatly decreased molecular weights.

Further work investigated the effectiveness of the mixed noble metal/transition metal MoRu catalyst on the hydroprocessing and depolymerization of hydrolysis lignin and resulted in bio-oils composed of aromatic compounds with increased hydrogen contents, decreased oxygen contents and greatly reduced molecular weights. Continuing this work, the hydroprocessing of depolymerized hydrolysis lignin (hydrolysis lignin that had been hydrolyzed in the presence of a strong acid) was moderately successful in producing bio-oils of reduced molecular weight.

CONCLUSION

Ru metal is a much more effective catalyst in the hydroprocessing of Kraft lignin (KL) and organosolv lignin (OL) in supercritical acetone than Ni metal. Additionally, 198 the carbon-supported Ru (and NiMoW-based FHUDES-2) catalyst performed better than alumina-supported Ru catalyst. A systematic study of the effectiveness of carbon-supported Ru and novel noble metal/transition metal MoRu catalysts on the hydroprocessing of guaiacol revealed that activated carbon-supported MoRu and Mo catalyst were more effective than the reference Ru/C catalyst, exhibiting greater than 90% guaiacol conversion. All of the catalysts tested in the depolymerization and hydroprocessing of organosolv lignin in supercritical acetone were effective.

Hydrolysis lignin (HL) was successfully depolymerized (liquefied) in the presence of hydrogen, carbon-supported mixed noble metal/transition metal catalysts and supercritical acetone solvent, producing low molecular weight bio-oils (as low as 380 g/mol) with high yields around 85 wt.%, that remained liquid at temperatures below freezing. Depolymerized hydrolysis lignin (DHL), produced by processing HL in the presence of ethylene glycol and H₂SO₄, was successfully hydroprocessed and further depolymerized into lower molecular weight products after reaction with MoRu/AC and Ru/C catalysts in supercritical acetone under hydrogen.

However, despite the decrease in molecular weight, these bio-oils were very viscous and unsuitable for use without further processing.