

Biofuels 2018: Hydroprocessing of Lignin for the Production of Liquid Fuels and Chemicals-Charles Xu-Western University, Canada

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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 (Yamazaki et al., 2006). 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 (Sharma and Bakshi, 1991).

However, pyrolysis oils have high oxygen and water contents and only about half the caloric content of petroleum (<20 MJ/kg). High-pressure liquefaction technology, on the other hand, normally operates at moderate temperatures (<400 °C) but higher pressures of 5-20 MPa in the presence of suitable solvents (water or organics) with or without catalysts and has the potential for producing liquid oils (also called bio-oils or bio-crudes) with much higher caloric values (25-35 MJ/kg) (Yamazaki

et al., 2006; Xu and Etcheverry, 2008).

A potentially more profitable exercise is the production of chemicals from only the lignin component of biomass. Biomass is, for the most part, composed of cellulose, hemicelluloses and lignin with very small amounts of other components such as ash and extractives. The typical composition of woody biomass is shown in Figure 1 below.

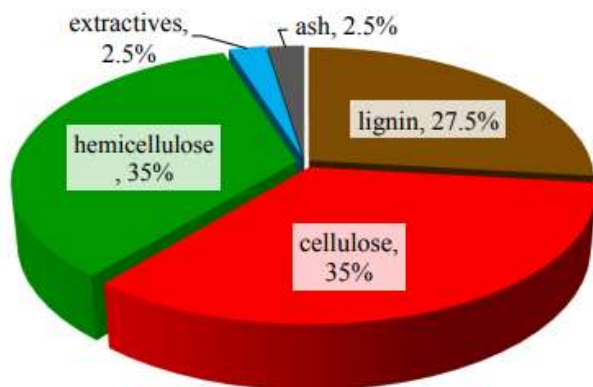


Figure 1. Typical composition of Woody Biomass

Currently the lignin component in biomass is mainly utilized for process heat by direct combustion. The large amounts of lignin produced in pulp mills are problematic in that the recovery boilers present a bottleneck. Lignin is an amorphous polymer (Figure 2) comprised of three types of phenyl propane derivatives: guaiacyl alcohol, syringyl alcohol, and p-coumaryl alcohol (Mohan et al. 2006). It provides support and rigidity to the cell walls and is more resistant to most forms of biological attack in comparison with cellulose and other polysaccharides (Akin and Benner, 1988; Baurhoo et al., 2008; Kirk, 1971) and is the largest natural source of aromatic compounds.

Due to its chemical composition, lignin is a promising source for chemicals and fuels such as phenols and aromatics via thermochemical and/or catalytic decomposition of the lignin molecule into monolignols and other compounds followed by hydroprocessing to remove oxygen. While the removal of oxygen is necessary to minimize re-condensation of the depolymerized lignin and to decrease acidity, the hydrodeoxygenation and hydrogenation of lignin and lignin-derived bio-oils under less severe conditions than those required to upgrade whole biomass-derived bio-oil can produce both high value oxygenated and

deoxygenated compounds from the lignin precursor.

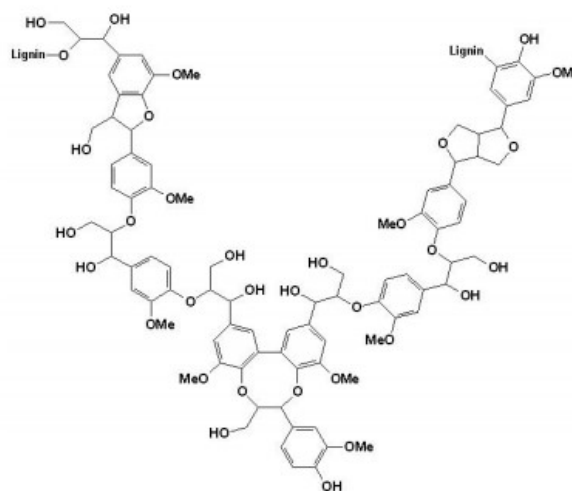


Figure 2: Structure of Lignin

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.

Where possible, the chemical and physical structure of the catalysts, feed and depolymerized products was measured. Typical analyses included: BET, XRD and TGA for the

fresh and spent catalysts; GPC, GC/MS, CHNS, ¹H-NMR, and FTIR for the lignin and depolymerized lignin products and Micro-GC for the gaseous products. The product separation scheme is shown in **Figure 3**.

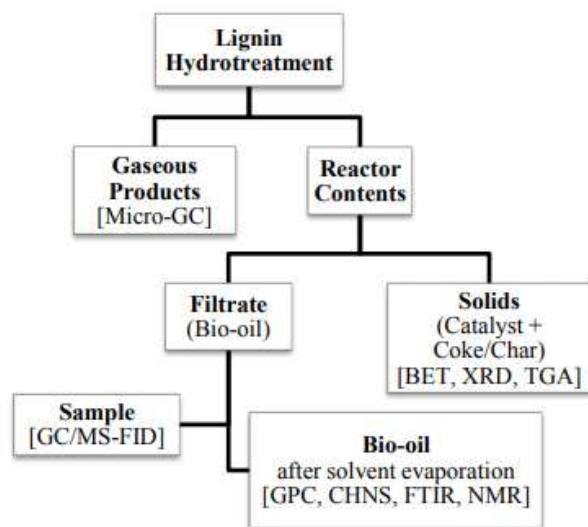


Figure 3: Product Separation Scheme.

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.

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