LIGNIN DEPOLYMERIZATION AND UPGRADING VIA FAST PYROLYSIS AND ELECTROCATALYSIS FOR THE PRODUCTION OF LIQUID FUELS AND VALUE-ADDED PRODUCTS

By

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ABSTRACT

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The production of liquid hydrocarbon fuels from biomass is needed to replace fossil fuels, which are decreasing in supply at an unsustainable rate. Renewable fuels also address the rising levels of greenhouse gases, an issue for which the Intergovernmental Panel on Climate Change implicated humanity in 2013. In response, the Energy Independence and Security Act (EISA) mandates the production of 21 billion gallons of advanced biofuels by 2022. Biomass fast pyrolysis (BFP) uses heat (400-600 °C) without oxygen to convert biomass to liquids fuel precursors offering an alternative to fossil fuels and a means to meet the EISA mandate. The major product, bio-oil, can be further upgraded to liquid hydrocarbon fuels, while biochar can serve as a solid fuel or soil amendment. The combustible gas co-product is typically burned for process heat. Though the most valuable of the pyrolysis products, the liquid bio-oil is highly oxygenated, corrosive, low in energy content and unstable during storage. As a means of improving bio-oil properties, electrocatalytic hydrogenation (ECH) is employed to reduce and deoxygenate reactive compounds. This work specifically focuses on lignin as a feed material for BFP. As lignin comprises up to 30% of the mass and 40% of the energy stored in biomass, it offers great potential for the production of liquid fuels and value-added products by utilizing fast pyrolysis as a conversion method coupled with electrocatalysis as an upgrading method.
Dedicated to my husband Nicholas James Ballard.
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Chapter 1: Introduction and Background

Introduction

The use of fossil fuels for the production of energy and raw materials has been providing resources for daily human necessities for hundreds of years. However, there are two major reasons why this will not be sustainable in the future. First and foremost fossil fuels are limited and non-renewable since they take millions of years to regenerate, a timeframe irrelevant to current generations of mankind. Second, the use of fossil fuels contributes to rising levels of greenhouse gases, an issue for which the Intergovernmental Panel on Climate Change (IPCC) implicated humanity in 2013.¹ To this end, the use of fossil fuels is not a sustainable form of energy and alternatives should be considered. Furthermore, the use of petroleum creates global energy dependence and all the economic and political issues that come with it. The U.S., for example, is considered to be one of the largest consumers of petroleum in the world, reported to have consumed 18.6 million barrels of petroleum products per day (MMbd) in 2012. According to the Energy Information Administration (EIA) about 40% of that (7.4 MMbd) was imported from abroad so the U.S. could greatly benefit from the displacement of petroleum with renewable sources.² To achieve such a goal, the Energy Independence and Security Act mandates that by the year 2022, 21 billion gallons of advanced biofuels be introduced to displace petroleum.³ To this end, the need for sustainable sources of fuels and chemical raw materials that are environmentally friendly and economically feasible has been a driving force for the conversion of biomass to liquid fuels and value added products. Biomass is considered as a viable alternative due to its potential to be converted to hydrocarbon fuels
and its ability to offset the CO$_2$ emissions due to plant growth. According to the 2011 Billion-ton Study update, biomass has been used as feedstock for producing and supplying about 4% of the total U.S. energy requirements. Furthermore, 66.1% of the renewable energy in the European Union is obtained from biomass, which is more than the amount provided from other renewable sources. Therefore as biomass is becoming more and more important as an alternative energy source, advancements in conversion processes could be very beneficial.

Various processes can be used for the conversion of biomass into biofuels, unlocking the energy stored within the bonds that hold the different components of biomass together. One promising process, and the main focus of this review, is biomass fast pyrolysis (BFP). As its name implies this thermochemical conversion entails rapid heating of biomass to relatively high temperatures in the absence of oxygen. BFP produces a liquid (bio-oil), a solid (char) and gas optimized to maximize the bio-oil fraction. BFP is a promising path from plant matter to liquid biofuels and raw materials for value-added products at low cost. However, undesirable properties of crude bio-oil such as high oxygen, high water content, low heating value and chemical instability prevent it from being commercially viable drop-in petroleum replacement without further upgrading. Furthermore, due to its relatively high acid content bio-oil can corrode steel engines, pipelines and storage tanks, making it incompatible with the current fuel handling and use technologies. Additionally, conversion of biomass to bio-fuels cannot fully displace petroleum fuels as biomass falls short in terms of both carbon content and energy content. As shown in Figure 1.1, even under the best of scenarios, the biomass that is reported to be available for use as feedstock for bio-fuel production (1.3 billion tons/year) can only provide 520 millions tons of
carbon/year and 19 billion GJ (giga joules) of energy/year vs. 860 million tons of carbon and 42 billion GJ of energy per year that can be provided by 1 billion tons of petroleum per year. So more efficient conversion strategies that conserve carbon from biomass need to be explored in addition to increasing the energy content of biomass-derived fuels such as bio-oil using upgrading strategies. Therefore, tackling these problems requires extensive study and understanding of the effect of feed material composition, biomass pretreatment processes, pyrolysis process parameters, and viable upgrading strategies.

![Comparison of available biomass, carbon and energy production in the US based on predictions by the U.S. billion-ton study update vs. U.S. petroleum consumption during 2013](image)

This chapter is structured to cover a brief analysis of the current energy crisis and biomass as a possible solution to this issue. Additionally, the advantages and the potential of utilizing pretreatment methods such as extractive ammonia process (EAP) for lignin extraction is covered. Last but not least, the use of fast pyrolysis coupled with
electrocatalysis as a way of further depolymerizing and upgrading lignin for the production of a viable liquid fuel intermediate is reviewed.

**Research Objectives**

1. *Characterize EAP lignin* to help identify the potential of pretreated biomass lignin as a feedstock for liquid fuel production via fast pyrolysis

2. *Examine the electrocatalysis of lignin-derived monomers* such as 2-methoxyphenol, 3-methoxyphenol and 4-methoxyphenol

3. *Study the use of electrocatalysis for model-lignin dimers with specific linkages to determine its effectiveness for cleaving such linkages.*

4. *Explore direct electrocatalysis of EAP Lignin to gauge the* potential of electrocatalysis as a method for bypassing fast pyrolysis to produce stable lignin fragments.

**Energy Crisis and Environmental Impact**

*Fossil Fuel Use*

The continued consumption of fossil fuels as a source of energy might have some major impacts related to energy consumption as well as environmental issues. Energy consumption is projected to keep increasing through 2030;\(^{10}\) as reported by Mason in 2007, world energy consumption was growing at 2% per year and if it continued to grow at this rate, it would double within the following 35 years.\(^{11}\) Furthermore, according to the 2013 International Energy Outlook report the US Energy Information Administration (EIA) predicts a 56% increase in total world energy consumption from 524 quadrillion Btu in 2010, to 630 quadrillion Btu in 2020, and to 820 quadrillion Btu in 2040.\(^{12}\) In conjunction with increasing energy consumption, energy production from fossil fuels and renewables is
predicted to keep increasing for the next 30 years. The EIA reports that even though the supply of energy from rapidly growing renewable sources and nuclear power are increasing by about 2.5% per year, fossil fuels still continue to dominate the energy supply by providing about 80% of the energy use through 2040. Although there are no clear predictions of when fossil fuels will be completely depleted, some studies point to oil, coal and gas predict depletion in 35, 107 and 37 years respectively. So more efforts need to be made to displace fossils with renewable sources.

Environmental Impact of Climate Change

In addition to the issues related to depleting fossil reserves, the environmental impact of burning fossil fuels for energy production cannot be ignored. Energy production primarily from burning fossil fuels is the main contributor to increased emission of greenhouse gases (GHG) such as CO$_2$ into the atmosphere. These emissions, in turn, are believed to be related to global temperature increase, which induces global climate change linking future energy production to global warming. Hence the warming of the earth within the next century due to the anthropogenic greenhouse emissions from fossil use is inevitable. As Reported by the National Oceanic and Atmospheric Administration’s (NOAA) Global Greenhouse Reference Network, the average CO$_2$ level measured at Mauna Loa Hawaii in April 2014 was 401.30 ppm as compared to April 2013, which was 398.35 ppm. Looking at the trends presented by NOAA since 1960, CO$_2$ in the atmosphere has gradually increased. As a result of the rise in CO$_2$ emissions, global average land and ocean surface temperature has shown an increase of 0.78 °C when comparing the averages between 1850-1900 and 2003-2012 period. If humans continue to emit GHGs at this rate
it is predicted that the global temperatures will rise and could have dangerous anthropogenic interferences (DAI) with the climate system.\textsuperscript{18} The ramifications of climate change could be very drastic resulting in extreme weather, effects on human health, increases ocean acidity and impacts on habitats.

\textit{Social Impacts of Climate Change}

As climate and weather conditions dictate much of our daily existence, these environmental and climate changes in turn have impacts on society with regards to our health, food and water supply, energy, transportation, access to infrastructure, etc.\textsuperscript{19} That stated, due to geographic location and economic status, certain communities or groups will likely feel the impact more than others. Those that have fewer or limited resources will be most impacted by climate change.\textsuperscript{20} Native and indigenous communities restricted by various geographical, economical and cultural boundaries, and populations in developing countries that have weak infrastructures are included in this group. \textsuperscript{21} In most of these cases certain health risks that are climate sensitive such as diarrheal diseases, malnutrition, and malaria will be exacerbated in these poor areas as a result of climate change. This in turn will put a huge dent on the economics of the health sector estimated to reach US $2-4 billion/year by 2030.\textsuperscript{22}

Considering the background information in the previous paragraphs (potential fossil fuel depletion, global climate and environmental impacts and social impacts of deriving energy from fossil fuels), the World Energy Council (WEC) shows that many countries are choosing to reduce their dependence on fossil fuels.\textsuperscript{10} This is leading to tremendous advancements in technologies for energy production from renewable sources.
According to the IEA, one of the key systems that will revolutionize the future is production of biofuels to supply a substantial fraction of the transportation fuels in use by 2030.\textsuperscript{10} Accordingly, lignocellulosic resources will play an increasingly important role in the future of energy production.\textsuperscript{23}

**Biomass Components**

Optimization of the biomass depolymerization process requires an understanding of biomass itself. The term biomass is used to describe all organic material which includes plant-based matter such as crops, trees, algae, land- or water-based plants and even organic waste and animal-based matter.\textsuperscript{23} What has made biomass a unique source of energy is the stored chemical energy that is derived from the sun and stored in the bonds within the organic matter.\textsuperscript{23} Biomass already accounts for 10-14\% of the world’s energy supply\textsuperscript{23} making it the 4\textsuperscript{th} largest energy source.\textsuperscript{24} Further study into the most favorable biomass properties and conversion processes could elevate the potential for bioenergy production. Ideal biomass properties for bioenergy production include high biomass yield per unit land area, low cost and energy input for biomass production and low levels of nutrients and contaminants released in cultivation.\textsuperscript{23} Low levels of water consumption are also desirable. The fulfillment of the above-mentioned criteria can enhance the yields and outcomes of the various conversion methods that can be employed to break down biomass into valuable products such as liquid fuels and chemicals.

In order to understand the break down and conversion of biomass, an understanding of its components is essential. At the macromolecular level biomass is composed of polysaccharides (cellulose and hemicellulose) and lignin. Although it is highly dependant on the type of biomass, hemicellulose accounts for about 20-40 wt\%, cellulose about 35-60
wt% and lignin about 10-25 wt%. Cellulose can be found in cell walls both as amorphous and crystalline polymers made from glucose building units. Similarly hemicellulose is also an amorphous network of pentoses and hexoses. Lignin is a highly complex branched network constructed from monolignols. It acts as the binding element that fills the empty spaces in plant cell walls and serves to hold the cell wall structure together in addition to providing protection against pathogens.

Deconstructing these components from the bulk biomass is the key to harnessing biomass-derived energy. Due to the relative simplicity of the structures of cellulose and hemicellulose compared to lignin, these polysaccharides have been extensively utilized as feed for ethanol production. But lignin’s complexity has made it relatively difficult to depolymerize for use as an efficient source of biofuels. In businesses such as the pulp and paper industry, lignin is often a byproduct cellulose extraction and is usually burned for heat or discarded as a waste product. Only 2% (about one million tonnes) of the lignin produced as the byproduct of pulp and paper processing is used to make valuable products, the remainder is burned. Further study into the structure and depolymerization properties of lignin is needed to support fuel and chemical production.

**Lignin: Structure**

The definition of lignin as a specific compound has been a difficult task as lignin has different structures and compositions owing to the randomness of the polymerization process. Lignin is therefore considered not as a specific compound but more as a family of cross-linked phenolic polymers found in secondary cell walls and comprised of different building blocks connected together via different types of linkages. As mentioned above, lignin is composed of three major monolignols: para-coumaryl alcohol, coniferyl alcohol
and sinapyl alcohol. Figure 1.2 shows the structures of these compounds. The type and amount of monolignols present in lignin is different for different types of biomass. Depending on whether the biomass in question is a hardwood, softwood or grass, the lignin content and composition widely vary. Lignin from softwood is primarily made of coniferyl alcohol units; hardwood lignin is mainly made of sinapyl alcohol units while grasses contain all three monolignols.

![Figure 1.2: Three monolignols para-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol](image)

The monolignol precursors are proposed to polymerize via random radical coupling to form dimers and higher oligomers by addition of free radical monomers to the existing dimer or oligomers. These result in linkages such as β-0-4, β-0-5 and β-β (Table 1.1). In other cases, cross coupling of two already forming lignin polymers can also occur whereby two free phenolic guaiacyl and syringyl units join together to form such linkages as 4-0-5 and 5-5. Table 1.1 shows the list of known common linkages in lignin and their relative abundance in hardwoods and softwoods. As can be seen from these numbers, the most abundant and dominant type tends to be β-0-4 linkages. The exact structure of the lignin network is difficult to clearly define, as the structural makeup of lignin and the type of monolignols present in different biomass are different. Furthermore, the processes used
for depolymerization and isolation of lignin components can greatly influence the makeup and bonding arrangements of the resulting products.\textsuperscript{38}
Table 1.1: Major linkage types and their abundance in lignin structure

<table>
<thead>
<tr>
<th>Linkages</th>
<th>Structures$^{26, 28}$</th>
<th>Abundance (%)$^{26, 28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-O-4</td>
<td><img src="image1" alt="β-O-4 structure" /></td>
<td>45-50 (soft wood)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60-62 (hardwood)</td>
</tr>
<tr>
<td>α-O-4</td>
<td><img src="image2" alt="α-O-4 structure" /></td>
<td>6-8 (softwood)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6-8 (hardwood)</td>
</tr>
<tr>
<td>4-O-5</td>
<td><img src="image3" alt="4-O-5 structure" /></td>
<td>4-7 (softwood)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.5-9 (hardwood)</td>
</tr>
<tr>
<td>β-1</td>
<td><img src="image4" alt="β-1 structure" /></td>
<td>1-9 (softwood)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-7 (hardwood)</td>
</tr>
<tr>
<td>5-5</td>
<td><img src="image5" alt="5-5 structure" /></td>
<td>19-27 (softwood)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-9 (hardwood)</td>
</tr>
<tr>
<td>β-5</td>
<td><img src="image6" alt="β-5 structure" /></td>
<td>9-12 (softwood)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-11 (hardwood)</td>
</tr>
<tr>
<td>β-β</td>
<td><img src="image7" alt="β-β structure" /></td>
<td>2-4 (softwood)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-12 (hardwood)</td>
</tr>
</tbody>
</table>
**Lignin: Isolation Processes**

Biomass pretreatment methods are often used prior to conversion to extract and isolate the different components of biomass. In cellulosic ethanol production processes pretreatments is essential to free up cellulose from the hemicellulose and lignin matrix, reduce cellulose crystallinity, hydrolyze hemicellulose, and enhance the porosity of biomass.\(^{39-41}\) Physical, chemical, biological or physicochemical pretreatment methods can be applied as a way of preparing biomass for further conversion.\(^{42}\) Physical methods usually include size reduction, via grinding, to enhance cellulose decrystallization and improve heat or mass transfer during conversion processes.\(^{43}\) Chemical pretreatments such as ozonolysis,\(^{44}\) acid hydrolysis, alkaline hydrolysis, oxidative delignification and organosolv processes all make use of different chemicals and solvents to solubilize lignin and hemicellulose while freeing up cellulose for enzymatic hydrolysis.\(^{40, 45}\) Biological pretreatment implements the use of microorganisms such as white-rot and brown-rot fungi to degrade lignin.\(^{39, 40}\) Physicochemical processes such as steam explosion and CO\(_2\) explosion expose biomass to steam and CO\(_2\) respectively at high pressure followed by a sudden pressure drop.\(^{42, 46}\) These processes result in the explosion of the biomass fibers making cellulose more accessible to enzymatic hydrolysis by degrading hemicellulose and transforming lignin.\(^{39}\)

Ammonia fiber explosion (AFEX) is another physicochemical process that is of interest to this group. AFEX is considered to have good potential as a pretreatment method for biofuel production as it results in the decompression of biomass fibers.\(^{39, 47}\) During the AFEX pretreatment process, liquid ammonia is added to biomass at pressures of 100-400 psi and temperatures of 70-200 °C. The system is then rapidly depressurized resulting in
the explosion of the biomass fibers causing cellulose decrystallization, hemicellulose hydrolysis and lignin depolymerization.\textsuperscript{47-50} AFEX is ideal for cellulosic ethanol production as it enhances feedstock digestibility by increasing the surface area available for digestion (increasing biomass porosity) and by transforming the lignin for better access to cellulose and hemicellulose.\textsuperscript{49} As cellulose and hemicellulose are made accessible for enzymatic hydrolysis, lignin can further be extracted and is often discarded as a waste product or burned for heat.\textsuperscript{40} Ideally this extracted lignin itself has potential to be used as a feedstock for other conversion processes such as fast pyrolysis, which has the ability to further degrade and depolymerize large lignin fractions.

**Fast pyrolysis as a Depolymerization Process**

The selection of what process to use for biomass conversion is dependent upon various factors such as the type of biomass used, environmental standards, economic conditions and the energy value of the fuel produced via certain conversion methods.\textsuperscript{51} There are three main processes utilized for biomass energy production: thermochemical conversion, biochemical conversion and mechanical extraction with esterification.\textsuperscript{51} Biochemical conversion can be further subdivided in to digestion and fermentation and thermochemical conversion can be subdivided into combustion, pyrolysis, gasification and liquefaction.\textsuperscript{51} Direct combustion of the biomass can produce steam for electrical power generation; gaseous fuel can be produced through gasification to be used in combustion or to drive engine turbines; and liquid fuel can be made through fast pyrolysis, which can then be used in a range of different applications.\textsuperscript{8} Compared to various other conversion technologies for liquid fuel production, fast pyrolysis has been developing rapidly due to its potential for providing alternative ways for producing liquid fuels.\textsuperscript{4,52} The liquid fuel from
pyrolysis, with some form of catalytic upgrading, has the potential to be used in engines, turbines and boilers to produce mechanical work, heat and power. Solvent extraction can also be used to produce bio-based chemicals. As the main focus in this study is the depolymerization of lignin, which is traditionally difficult to break down, thermochemical conversion becomes a potential option.

Fast pyrolysis involves rapidly heating biomass to temperatures between 400 °C and 600°C in the absence of oxygen. The decomposition of biomass during fast pyrolysis generates three major products, a liquid referred to as bio-oil (~70%), a solid referred to as biochar (~15%), and a gas (~15%) rich in molecular hydrogen, carbon oxides and light organics. The product yield and quality of the products of fast pyrolysis are highly dependent on temperature, heating rate and pressure. Each component of biomass degrades and decomposes to a different extent under different heating conditions during fast pyrolysis. For example, lignin decomposes over a wide temperature range when compared to cellulose while hemicellulose degrades fast in a narrower temperature range. So temperature and residence time are two very important parameters that need to be controlled and studied in the production of bio-oil from lignin.

Liquid fuel production also requires very low vapor residence time in the range of 1-5 seconds at temperatures of up to 500 °C. Keeping the residence time as low as 1 second helps in avoiding secondary reactions and improves the liquid product yield. At larger vapor residence time and high temperature, secondary cracking of the primary products will result in reduced liquid products. In addition, low temperature (>400 °C) leads to condensation reactions and formation of lower molecular weight liquids, which can further react. It is important to understand that fast pyrolysis requires high heating and heat
transfer rates, a controlled temperature of about 500 °C, low residence time of less than 2 seconds and rapid cooling of the vapors produced to obtain bio-oil.\textsuperscript{7,8}

**Characteristics of Bio-oil**

Bio-based fuels, such as those derived from bio-oil, are considered to be better for the environment than fossil fuels as they are carbon neutral and have low sulfur content.\textsuperscript{53} In addition, bio-oil can easily be stored and transported and has potential to be used for the production of other chemical products. But before bio-oil can be produced and used on a large scale, there are some obstacles that need to be overcome. Bio-oil is comprised of oxygenated organic compounds and is thus not as chemically reduced as petroleum-based fuel. Most of the 400 identified organic compounds\textsuperscript{54} in bio-oil contain 35-40 wt% oxygen.\textsuperscript{53} This is due to high oxygen content of biomass that originates from carbon-oxygen (C=O) bonds.\textsuperscript{55} From a synthetic standpoint, C=O bonds are good junction points for the propagation (polymerization) of carbohydrates to form cellulose and hemicellulose and monolignols to form lignin.\textsuperscript{55} From a conversion standpoint, breaking these junction points provides the key to depolymerizing these large molecules to smaller more useful compounds. After pyrolysis, the class of fragments that are formed such as aldehydes, alcohols, carbohydrates, furans, ketones, and phenolics tend to retain these oxygens creating undesirable properties in bio-oil. The stability of bio-oil is questionable, as the above-mentioned components tend to react during long-term storage to form sludge. For example phenolics and aldehydes react to form resins and water.\textsuperscript{54} In addition to these compounds in bio-oil being reactive, bio-oil is also corrosive due to its high organic acid content (7-12 wt%).\textsuperscript{7} The retention of oxygen from the feedstock also accounts for the low higher heating value (HHV) of bio-oil.\textsuperscript{7} Furthermore, the high water content that is retained
from the feedstock (15-30 wt%) gives bio-oil some negative attributes. For instance, the presence of water contributes to the low heating value, the increase in ignition delay, the reduced combustion rates and phase separation of the bio-oil all undesirable features. Bio-oil can also contain char particle that can clog and erode injector and turbine blades. Table 1.2, adapted from Czernik et al. summarizes some of the properties of bio-oil against the corresponding conventional fuel oil properties. As can be seen from this table, bio-oil falls short in several categories as compared to crude oil. These properties suggest that catalysis is therefore needed to upgrade this product to a reactively stable fuel that is compatible with steel tanks and pipes.

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Bio-oil</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (wt%)</td>
<td>15-30</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.2</td>
<td>0.94</td>
</tr>
<tr>
<td>Elemental composition (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>54-58</td>
<td>85</td>
</tr>
<tr>
<td>H</td>
<td>5.5-7.0</td>
<td>11</td>
</tr>
<tr>
<td>O</td>
<td>35-40</td>
<td>1.0</td>
</tr>
<tr>
<td>N</td>
<td>0-0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>0-0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>HHV MJ/Kg</td>
<td>16-19</td>
<td>40</td>
</tr>
<tr>
<td>Viscosity (@ 50 °C cP)</td>
<td>40-100</td>
<td>180</td>
</tr>
</tbody>
</table>

Research suggests that with chemical upgrading, utilization of better filtration processes and certain modifications of equipment such as diesel engines and boilers, the use of bio-oil on a commercial level could be feasible. In order to improve chemical
upgrading, a better understanding of the chemical mechanisms of pyrolysis and the nature of the products formed during pyrolysis are needed. The next section will describe the use of electrocatlytic hydrogenation and deoxygenation as a possible way of upgrading bio-oil.

**Bio-oil Upgrading using Electrocatlytic Hydrogenation**

Classical catalytic processes such as those used in the petroleum industry can be employed to upgrade bio-oil to aromatics. These processes include the use of different catalysts at severe conditions such as high temperatures and pressures. Furthermore, hydrogen has to be supplied to enable catalytic hydrogenation and deoxygenation. Such processes incur both capital and operating costs due to the equipment and energy needs for working with pressurized hydrogen at high temperatures, as well as the safety measures needed for these relatively dangerous conditions. Under these severe reactions conditions, catalyst deactivation may occur due to coke formation blocking active sites on the catalyst surface and inhibiting of metal-substrate interactions.\(^{57,58}\) Electrochemical upgrading offers an alternative whereby mild conditions (low temperature and atmospheric pressure) are used to achieve hydrogenation and deoxygenation.\(^{59}\) This method offers certain advantages over catalytic hydrogenation; as the hydrogen needed for reduction is produced in situ in ECH, avoiding the kinetic barrier related to hydrogen dissociation.\(^{60}\) Additionally, mass transport of hydrogen gas is also avoided in ECH.\(^{60}\) Even catalyst poisoning is avoided due to the cathodic potential that can prevent the adsorption of poisons.\(^{60}\)

As shown in Figure 1.3, electrocatalytic hydrogenation occurs via a multistep process whereby the electroreduction of water occurs on the catalyst surface in the cathode compartment producing hydrogen (a). The organic substrate also adsorbed on to
the catalyst surface forming a metal substrate complex ([X=Y]M) (b). The metal/hydrogen ([H]M) complex that is formed on the catalyst then interacts with the neighboring substrate/metal ([X=Y]M) complex on the catalyst causing reduction of the organic substrate (c). The reduced substrate then desorbs from the catalyst (d). Hydrogen evolution also occurs when hydrogen desorbs from the catalyst surface (d,e). 60-63,64 This hydrogen evolution process (e,f) competes with the hydrogenation process (c).

The performance of electrocatalysis is determined by computing the current efficiency, which is defined as the fraction of charge passed that, goes towards producing the desired products. Competition between hydrogen evolution and substrate reduction results in low current efficiency.60 The rates of the two processes are in turn influenced by several other factors such as: bond strength of the substrate that is being reduced, rate and probability of adsorption of the substrate (substrate concentration)64 and strength of bonding of hydrogen to the catalyst surface60 and current density65.
Several materials have been studied for use as electrode materials for ECH based both on their ability to produce molecular hydrogen and their potential to produce the desired products with high selectivity. In conjunction, several studies on different substrates and model compounds have been conducted (Table 1.3). Earlier studies included the use of noble metals such as Pt, Rh and Pd. In an effort to move away from expensive metals, more recent studies have focused on catalysts such as Raney nickel, nickel metal powders or metals supported on carbon.

As outlined in Table 1.3, studies on bio-oil-derived monomers such as guaiacol, phenol, and syringol have shown promising results for the potential of ECH for upgrading these bio-oil components to more stable forms. Studies on lignin-derived bio-oil monomers done by Li et al. have shown successful reduction of phenol, guaiacol and syringol using ruthenium loaded on activated carbon cloth (Ru/ACC). Further studies in this area are
needed to explore the effectiveness of this catalyst to reduce various other lignin-derived monomers. Additionally in these studies, modest current efficiencies of no more than 30% were reported due the hydrogen evolution reaction competition for the total charge passed. Exploration of different conditions to help improve the current efficiency value could be very beneficial.

Studies on lignin-relevant dimers have also shown promising results for the ability of ECH to cleave lignin-derived linkages that could be present in bio-oil. Dabo et al. used several transition metal powders embedded in reticulated vitreous carbon (RVC) to study their effects on 4-O-5 linked lignin dimer 4-phenoxyphenol. In these studies they were able to show the conversion of 4-phenoxyphenol to phenol and traces of cyclohexanone and cyclohexanol. As a fuel intermediate, cyclohexanol is preferred, but phenol is also a desirable product and the ability to selectively choose between cyclohexanol and phenol from lignin dimers would be valuable. In addition, the study of water soluble fractions of bio-oil by Li et al. indicate partial stabilization achieved through ECH. In addition to improving storage properties of bio-oil by preventing some components from polymerization, it was observed that the electrocatalytically treated bio-oil did not exhibit formation of precipitates and value added products such as propylene glycol and ethylene glycol were observed. ECH of bio-oil could have great potential as a bio-oil upgrading scheme and further work in this area should include electrocatalysis of whole bio-oil.
Table 1.3: Electrocatalytic reduction of various substrates using different catalysts

<table>
<thead>
<tr>
<th>Reference</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amouzegar et al. 71, 72, 73</td>
<td>Phenol</td>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>Quiroz et al. 74</td>
<td>m-xylene</td>
<td>Pt/Pt</td>
<td></td>
</tr>
<tr>
<td>Lamy-Pitara et al. 75</td>
<td>Maleic acid</td>
<td>Pt/Pt</td>
<td></td>
</tr>
<tr>
<td>Ilikti et al. 63</td>
<td>Phenol</td>
<td>Raney Ni</td>
<td>30°C, pH 9</td>
</tr>
<tr>
<td>Holt et al. 76</td>
<td>2-cyclohexene-1-one</td>
<td>WS₂ on RVC</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Dalavoy et al. 59</td>
<td>Lactic acid</td>
<td>Ru/C (Ru/RVC)</td>
<td>70°C, 1atm</td>
</tr>
<tr>
<td>Santana et al. 67, 77</td>
<td>Various organic compounds</td>
<td>Ni on Fe</td>
<td></td>
</tr>
<tr>
<td>Li et al. 68</td>
<td>Guaiacol, phenol, syringol</td>
<td>Ru/ACC</td>
<td>25-80°C, 1atm</td>
</tr>
<tr>
<td>Robin et al. 60</td>
<td>Polycyclic aromatics</td>
<td>Raney Ni</td>
<td>80°C</td>
</tr>
<tr>
<td>Mahdavi et al. 64</td>
<td>Conjugated enones</td>
<td>Ni₂B, Ni, Raney Ni</td>
<td></td>
</tr>
<tr>
<td>Mahdavi et al. 62</td>
<td>Lignin model dimers</td>
<td>Raney Ni</td>
<td></td>
</tr>
<tr>
<td>Cyr et al. 61</td>
<td>Lignin model dimers</td>
<td>Raney Ni, Pd/RVC</td>
<td>25-75°C</td>
</tr>
<tr>
<td>Dabo et al. 69</td>
<td>4-phenoxyphenol</td>
<td>Ni, Ni₂B, Raney Ni, Pd/C, Ru/C, Rh/C, Pd/Al₂O₃, Rh/Al₂O₃, Pd/Ni</td>
<td></td>
</tr>
<tr>
<td>Li et al. 70</td>
<td>Water soluble bio-oil</td>
<td>Ru/Acc</td>
<td></td>
</tr>
</tbody>
</table>
Conclusion

Moving away from fossil fuels and displacing them with alternative sources becomes more and more relevant due to the connection of fossil fuel use to global climate change and energy crises. Consequently, energy derived from biomass has become an attractive alternative and could be an essential part of future energy production. However, effective conversion processes are needed to produce liquid fuels and value-added commodities from biomass. Biomass fast pyrolysis, coupled with upgrading processes such as electrocatalytic hydrogenation, offers a promising strategy for the future of bioenergy production. Even though human beings are better at capturing energy in the form of electricity, plants are better at capturing carbon so strategies such as electrocatalytic hydrogenation offer the opportunity to couple carbon free energy to upgrade biomass carbon to insure a more complete utilization of the carbon that is derived from biomass vs. just utilizing the energy available from biomass. Efforts to valorize components of biomass such as lignin offer a significant advantage as lignin is one of the majors source of phenolic compounds in nature that have the potential to provide liquid fuels and value added products thus providing a way to make use of the carbon that is available.

Up to this point this review has outlined the looming environmental and energy related impacts of burning fossil fuels and the potential of biomass components such as lignin to help alleviate some of these issues. Additionally a brief review of pretreatment processes as a way of enhancing biomass depolymerization and extraction of biomass components and the use of fast pyrolysis as a conversion method were covered. Several challenges that prevent fast pyrolysis products such as bio-oil from being used as a drop-in fuel were mentioned along with the potential use of electrocatalytic hydrogenation for
further upgrading. The proceeding chapters will cover electrocatalytic hydrogenation of lignin-derived monomers and dimers and characterization of ammonia extracted lignin for future use as a feed material for bio-oil production.
REFERENCES


74. Li, Z.; Garedew, M.; Lam, C. H.; Jackson, J. E.; Miller, D. J.; Saffron, C. M., Mild electrocatalytic hydrogenation and hydrodeoxygenation of bio-oil derived phenolic compounds using ruthenium supported on activated carbon cloth. *Green Chemistry* 2012, **14** (9), 2540-2549.

75. Dabo, P.; Cyr, A.; Lessard, J.; Brossard, L.; Ménard, H., Electrocatalytic hydrogenation of 4-phenoxyphenol on active powders highly dispersed in a reticulated vitreous

Chapter 2: Electrocatalytic Hydrogenation and Deoxygenation of Lignin Model Compounds using Ruthenium Supported on Activated Carbon Cloth

Abstract

Carbon and energy efficient strategies are needed to produce hydrocarbon fuels from biomass. Fast pyrolysis provides one method for making hydrocarbon fuels from biomass or components of biomass such as lignin in an efficient manner. Bio-oil, the liquid product of fast pyrolysis, has increased bulk density when compared to biomass and is less expensive to transport long distances. However, bio-oil properties include self-reactivity to form viscous sludge and reactivity with metal surfaces causing corrosion. The partial upgrading (stabilization) of bio-oil using electrocatalysis, an approach where electricity serves as the reducing agent, is proposed to improve bio-oil’s properties. This study focuses on the electrocatalytic hydrogenation (ECH) of lignin derived bio-oil products such as alkoxyphenols as well as the potential of this process for cleaving lignin dimer linkages. Ruthenium supported on activated carbon cloth (Ru/ACC) is used as the catalytic cathode under mild conditions (80 °C and 1atm). While studying the ECH of methoxyphenols with the methoxy groups at different positions in the ring, the reduction of the methoxyphenols to methoxycyclohexanol and cyclohexanol was demonstrated. Furthermore, Ru/ACC was found to be capable of cleaving and reducing lignin-derived dimers.

Introduction

Due to the increasing problem of depleting fossil fuels and growing environmental concerns, interest in alternative energy sources has increased substantially. The development of alternative energy production methods that are environmentally friendly,
economically sound and that do not compete with global food supply is essential. To this end, production of fuels from biomass has been gaining attention in recent years. As plants store energy from the sun in the form of chemical bonds, biomass has great potential to make a significant contribution to alternative sources of energy.¹ Biomass is composed of three major components: cellulose, hemicellulose and lignin. Cellulose is a polymer of glucose arranged either in a crystalline or amorphous form.² Hemicellulose is an amorphous, branched polymer of pentoses and hexoses.² Lignin is a highly complex polymer made via the polymerization of three monolignols joined together with carbon-oxygen bonds at the α and/or β positions of a phenyl ring to form a branched network.²⁻⁴ Lignin acts as a binding agent filling up the empty space in plant cell walls.⁵ Depending on the type of biomass, hemicellulose accounts for about 20-40 wt%, cellulose about 35-60 wt% and lignin accounts for about 10-25 wt% and 40% of the energy content of biomass.⁶ Deconstructing different components of biomass in an efficient manner will help in the production of biomass-based liquid fuels and further help displace petroleum.

Cellulose and hemicellulose have been well studied for conversion into fuel ethanol as they are made of simple sugars. Although lignin is an attractive feed for the production of hydrocarbon fuels due to its lower O:C ratio compared to cellulose and hemicellulose, because of its complex structure, lignin has been one of the more difficult components to deconstruct and use as fuel.⁷ Often a byproduct of ethanol and pulp and paper industries, lignin is burned for heat or discarded as a waste product.³ For instance, only 2% (about one million tonnes) of the lignin produced as the byproduct of the pulp and paper industry is in commercial use.⁸ Unraveling this complex polymer and being able to produce valuable monomeric phenols is of great interest.⁹ To this end, lignin extraction, cleaving of α aryl
and β aryl ethers (depolymerization) and conversion offers an alternative method for the production of energy efficient liquid fuel as well as value added products.

Extractive ammonia processing (EAP) is a pretreatment method that is used to separate lignin from cellulose and hemicellulose.\textsuperscript{10} During EAP, ammonia is added to biomass at moderate pressure and temperature. The pressure is then rapidly released to cause the fibers to expand. This process results in cellulose decrystallization, hemicellulose hydrolysis, and partial lignin depolymerization.\textsuperscript{10} The cellulose and hemicellulose can then be subjected to enzymatic hydrolysis for ethanol production while lignin streams are collected, fractionated and extracted. These lignin streams are partially depolymerized and are thus lower in molecular weight than the native lignin complex found in biomass. Lignin monomers and oligomers are more amenable to chemical transformation to higher value fuels and chemicals and are thus better feedstocks than native lignin.

Thermochemical conversion processes such as biomass fast pyrolysis can be applied for further such depolymerization. Biomass fast pyrolysis (BFP) is one of the processes used for the production of liquid bio-fuels from plant matter due to its potential for producing high liquid fuel yields and raw material for value-added products at low costs.\textsuperscript{11,12} Fast pyrolysis involves rapidly heating biomass to temperatures between 400 °C and 600 °C in the absence of oxygen.\textsuperscript{12} The decomposition of biomass during the fast pyrolysis process generates three major products, a liquid referred to as bio-oil, a solid referred to as bio-char, and a non-condensable gas rich in molecular hydrogen, carbon oxides and light organics. However, bio-oil corrosiveness and reactive instability pose significant barriers to the adoption of pyrolysis systems. Catalytic stabilization is needed to produce a stable fuel intermediate that is compatible with common infrastructure materials such as carbon
steel. Classical catalytic upgrading is usually used to hydrogenate and deoxygenate bio-oil, a process that occurs at high temperature and pressure. These severe conditions pose significant barriers for bio-oil upgrading in decentralized facilities, such as catalyst deactivation. To avoid these conditions, electrocatalytic hydrogenation (ECH) is proposed to stabilize bio-oil under mild conditions (25-80 °C and 1 atm).

As lignin is a byproduct of other industries, its utilization as a biofuel feedstock would be beneficial. This effort focuses on the upgrading of model compounds of lignin pyrolysis via electrocatalytic hydrogenation and deoxygenation. To this end, three major studies were conducted. Specifically, our first study builds on previous work done on phenolic monomers such as 2-methoxyphenol by comparing the results of similar experiments using 3-methoxyphenol and 4-methoxyphenol. Concurrently, studies were also performed on lignin dimers with related ether linkages. This second study mainly focuses on cleaving lignin-specific linkages in the dimers. As lignin is converted to phenolic monomers, dimers, and oligomers upon pyrolysis, the transformation of model compounds exhibiting similar bonding arrangements is an indicator of the potential for ECH-mediated depolymerization of biomass lignin. The third study focused on developing better ruthenium loading methods for preparing the catalyst by assessing catalyst performance and deactivation studies as a function of preparation conditions. The overall scope of the project as shown in Figure 2.1 is to gain an understanding of the potential of ECH as an upgrading process for lignin-derived bio-oil by exploring different conditions and catalyst preparation methods. With the success of this process, bio-oil produced at decentralized depots at the site of biomass harvest can be upgraded to a stable, more energy dense form and transported to petroleum processing facilities for hydro-processing to produce liquid fuels.
Figure 2.1: Overall scheme of the project from EAP lignin to liquid fuels

**Experimental Methods**

**Model Compounds**

As a continuation of previous work by this group, a study was done on methoxyphenols with the methoxy group at different positions. The substrates 2-methoxyphenol, 3-methoxyphenol and 4-methoxyphenol were all obtained from Alpha Aesar. Electrocatalytic reduction of each of these compounds was conducted. Lignin dimer studies were also conducted to study the effect of the catalyst on different types of linkages found in lignin. In this study, the lignin dimer 4-phenoxyphenol was obtained from Sigma Aldrich. This compound represents the 4-O-5 type linkage, which is one of the linkages that can be found in lignin. Guaiacyl glycerol-β-guaiacyl ether (Dimer#1) was obtained from John Ralph's lab at University of Wisconsin. Figure 2.2 shows the two dimers used. Guaiacyl glycerol-β-guaiacyl ether is representative of a β-O-4 linkage which is one of the most abundant type of linkages found in lignin.
Figure 2.2: Dimers a) 4-phenoxyphenol (4-O-5) b) Dimer#1 (β-O-4)

Catalyst Preparation

Zorflex ACC (activated carbon cloth) FM 100 was used to support the ruthenium catalyst. As described by Li et. al., the activated carbon cloth was washed overnight in deionized water and oven dried at 105 °C. The ACC support was prepared with catalyst using the incipient wetness method as described by Li et. al. Ru(NH₃)₆Cl₃ solution was used to soak each 1.5 x 3.0 cm piece of ACC. Each cloth was immersed in the solution and soaked for a few minutes. The Ru/ACC catalyst was then dried at room temperature first overnight and stored in a vacuum dicator for another 24 hours then reduced with molecular hydrogen at 310 °C for 12 hrs in a Parr reactor (model 452HC).

Catalyst Characterization

A varian 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES) was used to measure the ruthenium content of the catalyst using the methods as described by Li et. al. Standards were prepared with concentrations of 0.08 ppm, 0.4 ppm, 2 ppm, 10 ppm and 50 ppm using RuCl₃ to construct a calibration curve. The catalyst samples were prepared by digestion in aqua regia for 4 hours in a water bath at 100 °C,
filtration and dilution with DI water. Scanning electron microscopy (SEM) analyses used JEOL JSM-7500F and JEOL 6400V instruments. The Ru/ACC was mounted onto aluminum stubs using carbon paste and dried in a vacuum overnight. Analyses were done using secondary electron imaging and energy-dispersive X-ray (EDX) analysis.

*Electrocatalytic Hydrogenation (ECH) Setup*

A two-chambered electrochemical glass H-cell was used to conduct the experiments. The chambers were separated using a Dupont Nafion-117 membrane. Ruthenium supported on activated carbon cloth (Ru/ACC) was used as the cathode and platinum wire was used as the anode a shown in Figure 2.3 below. An Instek GPR-11H30D power supply was used to provide constant electrical current for the various experiments. To maintain constant temperature for different studies, the whole cell was placed in a water bath and the desired temperature was maintained in the water bath. After the cell setup was completed, a 10 min pre-electrolysis step was performed on the catalyst at 80mA before adding the substrate. After pre-electrolysis, depending on the experiment, the desired amount of substrate was added and the experiment was run at the desired temperature and current density for 4 hours. Samples (0.6 ml) were taken every hour for the methoxyphenol study and every 40 minutes for the dimer studies. Samples were then saturated with NaCl, acidified to pH 1 and extracted into chloroform. The catalyst was placed and sonicated in chloroform for 10 minutes, and filtered prior to analysis by GC/MS and GC/FID.
The electrolytes used for the methoxyphenol study were 30 ml of 0.2 M HCl (catholyte) and 30 ml 0.2 M phosphate buffer (anolyte). The experiments were conducted with 20 mM substrate concentration at 75 °C and 60 mA and product yield and current efficiency were investigated. The effect of different conditions on product yield and current efficiency was also investigated for 4-phenoxyphenol. The varied conditions include: 1) electrolytes, 2) substrate concentration and 3) current density. For the 4-phenoxyphenol studies the cathode/anode electrolytes used were 30 ml 0.2 M HCl/0.2 M phosphate buffer, 0.2 M NaCl/0.2 M phosphate buffer, and 1 M NaOH/1 M NaOH. A temperature of 80 °C was maintained for all three electrolytes used. For the substrate concentration study, three different concentrations (25 mM, 12.5 mM and 6.25 mM) were investigated for all three electrolytes at 100 mA. Current density experiments were conducted for the three different electrolytes at 80 °C and 20 mA, 80 mA and 100 mA.

The same setup was used for the ECH of Dimer#1. Dimer#1 was found to be soluble in 1M NaOH and all experiments involving Dimer#1 were carried out in 30 ml 1M NaOH.
solution on both the cathode and anode compartments. The experiment was conducted for 6 hours and samples were collected every 2 hours. The same extraction method mentioned above was used for GC samples.

Catalyst Deactivation Studies

For the catalyst deactivation studies, the methods used by Li et al.,\textsuperscript{13} were implemented. The same ECH setup described in the above section was utilized but after the first experiment, the catalyst was washed in DI water and stirred overnight in a 20 ml vial containing DI water. The next day the same washed catalyst was used to run the second experiment and so forth. Samples were collected from the cathode solution but no sample was extracted from the cloth so yield calculation did not take into account the organic products that were adsorbed onto the catalyst cloth.

Sample Analysis

Samples were analyzed using a Shimadzu QP-5050A GC/MS (Shimadzu Corp, Columbia, MD). Standards in chloroform were used to identify products by retention time and to construct a four-point calibration curve. This curve was utilized to determine product yields and calculate current efficiency.

Calculations

- Yield\textsubscript{A} = (Moles of A) / (Initial moles of reactant)
- Selectivity\textsubscript{A} = (Moles of A) / (Moles of total products)
Conversion = (Moles of reactant consumed) / (Initial moles of reactants)

Current efficiency = (Charge used generate products) / (Total charge passed)

Current Density = (Current)/ (Unit area of catalyst used)

Results and Discussion

Catalyst Characterization (ICP and SEM)

Activated carbon cloth is an ideal catalyst support because of its high surface area, stable micropore distribution and high electrical conductivity. All catalysts used in these studies were prepared using the incipient wetness method as outlined by Li et al. ICP analysis revealed a ruthenium loading of 3.5-4.0 wt%, which was found to be consistent with the EDX analysis as shown in Table 2.1. The slight differences in the other elements between unloaded vs. loaded carbon cloth can be attributed to the differences in area between the two different pieces of carbon cloth analyzed. Dot map images shown in Figure 2.4 a) and b) show the carbon cloth and the ruthenium dispersed throughout the carbon fabric. As can be seen from the images, there is a relatively uniform distribution of the ruthenium particles. X-ray dot mapping (presence/absence analysis) makes use of a two-dimensional scanning technique where each detected photon appears as dot with the regions of high concentration appearing brighter. As can be seen from Figures 2.5 and 2.6 the SEM image shows a random distribution of the ruthenium particles throughout the cloth.
Table 2.1: Scanning electron microscopy elemental analysis using EDX

<table>
<thead>
<tr>
<th>Element</th>
<th>ACC Control (wt%)</th>
<th>Ru/ACC Unused (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.54</td>
<td>69.46</td>
</tr>
<tr>
<td>Ru</td>
<td>0.00</td>
<td>4.06</td>
</tr>
<tr>
<td>O</td>
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<td>10.78</td>
</tr>
<tr>
<td>Na</td>
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<td>0.19</td>
</tr>
<tr>
<td>Al</td>
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<td>2.40</td>
</tr>
<tr>
<td>Cl</td>
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<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>0.05</td>
<td>0.20</td>
</tr>
<tr>
<td>Zn</td>
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<td>4.25</td>
</tr>
<tr>
<td>Mg</td>
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<td>0.06</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>1.46</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>K</td>
<td>-</td>
<td>6.88</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Figure 2.4: X-ray dot map analysis of Ru/ACC for carbon and ruthenium a) carbon cloth b) ruthenium
Figure 2.5: Scanning electron microscopy images of a) unloaded b) ruthenium loaded

Figure 2.6: Scanning electron microscopy images of loaded cloth a) 100x  b) 300x

Model Compound Studies: Methoxyphenols with Different Methoxy Group Positions

Previous work by this group has demonstrated the successful reduction of guaiacol, syringol and phenol using ECH with ruthenium activated carbon cloth catalyst. The study of these substrates is relevant as these compounds are common products of lignin pyrolysis. In an effort to catalogue the effectiveness of the Ru/ACC catalyst as a means of reduction, several lignin-derived bio-oil model compounds were selected as reactants. To specifically catalogue the effects of varying the ether group position on the aromatic ring, three different substrates were studied: 2-methoxyphenol, 3-methoxyphenol and 4-methoxyphenol. For all reactants, Ru/ACC catalyst was used for 6 hours at conditions of 75
\(^{\circ}C, 60\) mA and catholyte concentration of in 0.2 M HCl. Samples were taken every hour to be extracted and analyzed using GC/MS.

In this work, two pathways are suggested for the reduction of the methoxyphenol to cyclohexanol. As shown in Figure 2.7, the methoxyphenol might be reduced to phenol, followed by reduction to cyclohexanol; or reduction of methoxyphenol to methoxycyclohexanone, methoxycyclohexanol and then to cyclohexanol. As suggested by the schematic in Figure 2.8, electrocatalysis is a multistep process whereby the water on the anode side is oxidized to \(H^+\) and \(O_2\). \(H^+\) ions travel through the selective membrane to the cathode side and chemisorb on the catalyst resulting in a metal/hydrogen complex (a) and metal/methoxyphenol complex forms on the catalyst surface (b). In steps c-f reduction of the substrate and intermediates occurs by addition of the neighboring hydrogens that have been chemisorbed to the catalyst surface. The reduced products then desorb from the catalyst (g-i).\(^{15,16,17}\) As was indicated by Li et al. reduction of methoxyphenol could occur via two routes: 1) the reduction of double bonds forms methoxycyclohexanol then cyclohexanol or 2) demethoxylation to form phenol and then cyclohexanol. Parallel to these steps, hydrogen evolution occurs (j,k) competing with the electrocatalytic reduction of the substrate.
Figure 2.7: Reaction pathways for the reduction of methoxycyclohexanol to cyclohexanol and methoxycyclohexanol

Figure 2.8: Electrocatalytic hydrogenation and hydrogen evolution steps \(^{18}\)

a.  \(2 \text{H}_2\text{O} + 2e^- + \text{Ru} \rightarrow 2[\text{H}]\text{Ru} + 2 \text{OH}^-\)

b.  \(\text{Ru} + \text{Methoxyphenol} \rightarrow [\text{Methoxyphenol]} \text{Ru}\)

c.  \(2[\text{H}]\text{Ru} + [\text{Methoxyphenol]}\text{Ru} \rightarrow [\text{Phenol}]\text{Ru} + [\text{Methanol}]\text{Ru} + \text{Ru}\)

d.  \(6[\text{H}]\text{Ru} + [\text{Phenol}]\text{Ru} \rightarrow [\text{Cyclohexanol}]\text{Ru} + \text{Ru}\)

e.  \(2[\text{H}]\text{Ru} + [\text{Methoxyphenol]}\text{Ru} \rightarrow [\text{Methoxycyclohexanol}]\text{Ru} + \text{Ru}\)
f. \( 2[H]Ru + [\text{Methoxycyclohexanol}]Ru \rightarrow [\text{Cyclohexanol}]Ru + [\text{Methanol}]Ru + Ru \)

g. \( [\text{Phenol}]Ru \rightarrow \text{Phenol} + Ru \)

h. \( [\text{Methoxycyclohexanol}]Ru \rightarrow \text{Methoxycyclohexanol} + Ru \)

i. \( [\text{Cyclohexanol}]Ru \rightarrow \text{Cyclohexanol} + Ru \)

j. \( [H]Ru + H_2O + e^- \rightarrow H_2 + Ru + OH^- \)

k. \( [H]Ru + [H]Ru \rightarrow H_2 + Ru \)

As indicated in Figure 2.9 and Table 2.2, all three substrates proceeded via the parallel route by the formation of phenol followed by cyclohexanol and the formation of methoxycyclohexanol. The absence of phenol in the samples taken at different time steps during each experiment could be indicative of the fact that conversion of phenol to cyclohexanol might be happening rapidly. For the 2-methoxyphenol and 4-methoxyphenol cis/trans isomers were identified. A mass balance of 80% or higher and conversion greater than 80% was observed for all cases with the 2-methoxyphenol showing 100% conversion. A slightly higher current efficiency was also recorded for 2-methoxyphenol. The current efficiency of these reactions was still modest and can be attributed to the competing hydrogen evolution reaction. Further studies in this area should explore the effect of substrate concentration, current density and several other conditions to see the effect of these conditions on improving the current efficiency of the system. Figures 2.10, 2.11, 2.12 show the conversion, product yield and depletion of starting material over the course of each substrate reduction. In each figure it can be observed that for each time point the cyclohexanol and methoxycyclohexanol yields increase simultaneously supporting the claim that the formation of the two products are parallel and not sequential. Figure 2.10 shows sudden increase in the amount of 2-methoxycyclohexanol, this could be due to the
extraction of this product from the cloth and not from the catholyte solution. Product selectivity appears to have favored methoxycyclohexanol slightly but for the most part the catalyst was almost equally selective toward both products.

Table 2.2: Summary table of yield and current efficiency of ECH of methoxyphenols

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Mass Balance (mol%)</th>
<th>Cyclohexanol (mol%)</th>
<th>Methoxy Cyclohexanol (mol%)</th>
<th>Starting material (mol%)</th>
<th>CE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methoxyphenol</td>
<td>80</td>
<td>36</td>
<td>44*</td>
<td>--</td>
<td>20</td>
</tr>
<tr>
<td>3-Methoxyphenol</td>
<td>89</td>
<td>35</td>
<td>38</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>4-Methoxyphenol</td>
<td>84</td>
<td>31</td>
<td>35*</td>
<td>14</td>
<td>16</td>
</tr>
</tbody>
</table>

* cis + trans
Table 2.3: Summary table of selectivity and conversion of ECH of methoxyphenols

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Conversion (mol%)</th>
<th>Selectivity Cyclohexanol (mol%)</th>
<th>Selectivity Methoxycyclohexanol (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methoxyphenol</td>
<td>100</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>3-Methoxyphenol</td>
<td>84</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>4-Methoxyphenol</td>
<td>86</td>
<td>46</td>
<td>54</td>
</tr>
</tbody>
</table>

Figure 2.10: Conversion, product yield and depletion of starting material of ECH of 2-methoxyphenol
Figure 2.11: Conversion, product yield and depletion of starting material of ECH of 3-methoxyphenol

Figure 2.12: Conversion, product yield and depletion of starting material of ECH of 4-methoxyphenol
**Model Compound Studies: 4-0-5 Type Linkage (4-phenoxyphenol)**

Electrocatalysis of the lignin model compound 4-phenoxyphenol (a lignin dimer) was conducted using a divided voltaic cell with ruthenium on activated carbon cloth (Ru/ACC) and HCl, NaCl or NaOH as electrolytes. 4-Phenoxyphenol is a dimer that is representative of the 4-O-5 bonds present in lignin. Previous studies done by Dabo et al. on 4-phenoxyphenol were able to achieve the cleavage of C-O bond using several transition metals embedded on reticulated vitreous carbon (RVC). These results report conversion to phenol and production of trace amounts of cyclohexanol and cyclohexanone.\(^\text{19}\) Our initial results reveal that the electrochemical reduction of 4-phenoxyphenol leads to cyclohexanol and phenol. This study was used to demonstrate the effectiveness of this technique for reducing 4-O-5 type linkages in lignin. As dimers similar to 4-phenoxyphenol exist in the bio-oils of fast pyrolysis, these results are informative for the ECH treatment of bio-oil for further stabilization. In previous work, lignin model compounds and products of lignin pyrolysis were examined to map the reaction pathways for the reduction of each component. In all cases, phenolic monomers from lignin pyrolysis were reduced via ECH. Upon ECH of alkoxyphenols (phenol, syringol and guaiacol), significant amounts of alkoxy-cyclohexanol and cyclohexanol were formed, clearly showing the potential for chemical reduction.\(^\text{13}\) However, the modest current efficiency (electrons used to form the product divided by electrons supplied) implies that further investigation of electrode materials and their optimization is needed.

Electrocatalytic hydrogenation of organic compounds is suggested to occur via a multi-reaction pathway as described by Mahdavi et al.\(^\text{20}\) In this reaction network, hydrogen that is produced by the electroreduction of water is chemisorbed to the electrode surface
(a), causing the organic substrate to be reduced (b-f). At the same time, neighboring hydrogen atoms react to form molecular hydrogen, which desorbs from the electrode (g,h). The hydrogen evolution reaction competes with organic substrate hydrogenation and lowers the current efficiency.\textsuperscript{20, 21} As this competition between the two reactions is highly dependant on the reaction conditions,\textsuperscript{21} this study measured the effects of different electrolytes, substrate concentration and current densities.

\begin{itemize}
  \item a. $2 \text{H}_2\text{O} + 2\text{e}^- + \text{Ru} \rightarrow 2[\text{H}]\text{Ru} + 2\text{OH}^-$
  \item b. $\text{Ru} + 4\text{-phenoxyphenol} \rightarrow [4\text{-phenoxyphenol}]\text{Ru}$
  \item a. $2[\text{H}]\text{Ru} + [4\text{-phenoxyphenol}]\text{Ru} \rightarrow 2[\text{Phenol}]\text{Ru} + \text{Ru}$
  \item b. $4[\text{H}]\text{Ru} + [\text{Phenol}]\text{Ru} \rightarrow [\text{Cyclohexanone}]\text{Ru} + \text{Ru}$
  \item c. $2[\text{H}]\text{Ru} + [\text{Cyclohexanone}]\text{Ru} \rightarrow [\text{Cyclohexanol}]\text{Ru} + \text{Ru}$
  \item d. $2[\text{Phenol}]\text{Ru} \rightarrow 2\text{Phenol} + \text{Ru}$
  \item e. $[\text{Cyclohexanone}]\text{Ru} \rightarrow \text{Cyclohexanone} + \text{Ru}$
  \item f. $[\text{Cyclohexanol}]\text{Ru} \rightarrow \text{Cyclohexanol} + \text{Ru}$
  \item g. $[\text{H}]\text{Ru} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{Ru} + \text{OH}^-$
  \item h. $[\text{H}]\text{Ru} + [\text{H}]\text{Ru} \rightarrow \text{H}_2 + \text{Ru}$
\end{itemize}

\textit{Electrolyte Effect}

As shown in Table 2.4, three different electrolytes were used to conduct the ECH treatments and determine current efficiency on 12.5 mM 4-phenoxyphenol. Results indicated that the Ru/ACC catalyst did reduce 4-phenoxyphenol to phenol and cyclohexanol. ECH can effectively cleave ether bonds in lignin dimers provided that ether bond hydrogenolysis is faster than the hydrogenation of the aromatic rings.\textsuperscript{20} Both phenol
and cyclohexanol were found to be the reduction products for basic and neutral conditions in the catholyte as seen in Table 2.4. However, there is also a possibility of cleaving the ether bond to form hydroquinone, benzene and reduction of hydroquinone. Although none of these two products were observed in solution, there was an unidentified product recovered from the cloth, which could be a reduction product of hydroquinone and account for closing the mass balance. Acidic conditions did produce phenol and cyclohexanol but in such trace amounts that they could not be quantified and so are not reported in this case. Phenol is the suspected intermediate as cyclohexanol was observed at higher amounts for both electrolytes. The reaction pathway in Figure 2.13 depicts the proposed ether bond cleavage producing phenol before hydrogenation saturates the aromatic ring. As was observed from the results below, NaOH was found to be the best electrolyte with higher phenol and cyclohexanol yields and higher current efficiency. This could be because the base dissolves phenol by deprotonating it.

![Reaction pathway diagram](image)

**Figure 2.13: Suggested reaction pathway for ECH of 4-phenoxyphenol**

<table>
<thead>
<tr>
<th>Cathode Electrolyte</th>
<th>Current (mA)</th>
<th>Phenol Yield (mol%)</th>
<th>Cyclohexanol Yield (mol%)</th>
<th>Conversion (mol%)</th>
<th>CE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M NaOH</td>
<td>80</td>
<td>21</td>
<td>26</td>
<td>97</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>13</td>
<td>29</td>
<td>97</td>
<td>21</td>
</tr>
<tr>
<td>0.2M NaCl</td>
<td>80</td>
<td>9</td>
<td>16</td>
<td>97</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>8</td>
<td>10</td>
<td>98</td>
<td>10</td>
</tr>
</tbody>
</table>
Current Density and Substrate Concentration

Different current density studies were performed at 20 mA, 80 mA and 100 mA for a substrate concentration of 12.5 mM for 4 hours with NaOH as the electrolyte. The substrate concentration studies were conducted at 100 mA with three different substrate concentrations of 6.25 mM, 12.5 mM and 25 mM. Results summarized in Table 2.5 indicate that at low current density production of phenol is favored but conversion remains low indicating that the complete conversion of 4-phenoxypyphenol was not achieved. In the case of the lower current density experiment small amounts of cyclohexanone were also detected on the cloth. Higher current density favored the production of cyclohexanol. As suggested by Dalavoy et al., this could be due to the increase of surface hydrogen with increased current density resulting in subsequent increase of cyclohexanol yield. But this could also mean an increase in the competing hydrogen evolution reaction resulting in low current efficiency. As was observed from the current density experiments, current efficiency comparisons indicate that the lower current density had the best current efficiency results while current efficiency decreased for higher current density experiments. At lower current density the formation of cyclohexanol was lower but seemed to increase as current density increased suggesting that conversion of phenol to cyclohexanol requires more adsorbed hydrogen to proceed compared to the initial formation of phenol from starting material. Additionally the presence of cyclohexanone at lower current density indicates that conversion of phenol to cyclohexanone, and then to cyclohexanol is happening at a slower rate due to low surface hydrogen concentration. For the substrate concentration studies, lower substrate concentration (6.25 mM) favored better cyclohexanol and phenol yield with current efficiency slightly lower than that for
12.5 mM substrate concentration. 25 mM showed the least conversion, current efficiency as well as product yield. Overall, it can be concluded that higher current density and low substrate concentration favored high cyclohexanol yield while low current density was more selective towards phenol formation.

Table 2.5: Summary of ECH of 4-phenoxyphenol with different current density and substrate concentration

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Current (mA)</th>
<th>Phenol Yield (mol%)</th>
<th>Cyclohexanol Yield (mol%)</th>
<th>Conversion (mol%)</th>
<th>CE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>20</td>
<td>40</td>
<td>19</td>
<td>90</td>
<td>98</td>
</tr>
<tr>
<td>12.5</td>
<td>80</td>
<td>21</td>
<td>26</td>
<td>97</td>
<td>29</td>
</tr>
<tr>
<td>12.5</td>
<td>100</td>
<td>13</td>
<td>29</td>
<td>99</td>
<td>20</td>
</tr>
<tr>
<td>6.25</td>
<td>100</td>
<td>28</td>
<td>54</td>
<td>96</td>
<td>18</td>
</tr>
<tr>
<td>25.0</td>
<td>100</td>
<td>11</td>
<td>7</td>
<td>67</td>
<td>11</td>
</tr>
</tbody>
</table>

Model Compound Studies: β-O-4 type Linkage Dimers

Some studies have shown the successful cleavage of lignin model dimers using Raney nickel. So the effect of Ru/ACC on β-O-4 type linkage dimers was the next step in this study as these types of linkages are the most abundant in lignin. However, the results reported here are only preliminary and further quantification of reactant concentration and product yields is needed. Initial testing of this synthetic dimer shows promising results with its cleavage to guaiacol and vanillin (Figure 2.14) along with other unidentified products. These products are expected given the reaction chemistries that have been previously observed with 4-phenoxyphenol.
Catalyst Deactivation

Catalyst deactivation is an important phenomenon that needs to be understood before the design phase of a catalytic process. Minimizing catalyst deactivation over time is essential to ensure the cost effectiveness of catalyst use as well as process efficiency, product yield and selectivity. A catalyst that can maintain high activity and selectivity towards desired products over time is essential. Ideally, catalysts should remain unaltered by the process they catalyze; but oftentimes catalyst deactivation occurs by a variety of mechanisms. It is important to determine the onset, cause, mechanism and solutions to catalyst deactivation. Catalyst deactivation is known to occur via various mechanisms such as poisoning, sintering, coking or fouling and phase transformation. Poisoning is the loss of activity due to the blocking of the active sites by strongly chemisorbed impurities; sintering is thermally induced structural modification of the catalyst; coking can occur through blocking of the catalyst surface with carbonaceous residue. Phase transformation occurs due to high temperature effects whereby the morphology of the catalyst is changed. In this study, it is important to determine the life
span of the catalyst and if catalyst deactivation does occur, it is beneficial to understand the mechanism by which deactivation occurs.

In this study five experiments were run using the same catalyst. After each use, the catalyst was washed overnight in DI water. Each time the same area of the catalyst was used to assure no variation in activity from using an area that was not used previously. Samples were taken every 40 minutes, extracted and analyzed using GC/MS. In each experiment, a 10 minute pre-electrolysis step was performed to activate the catalyst. In this case, products adsorbed to the activated carbon of the catalyst were not accounted for at the end of the experiment. Usually, the cloth would be sonicated in chloroform to extract adsorbed products such as cyclohexanol. In previous deactivation experiments, the cloth was sonicated in chloroform after each experiment, but this treatment led to complete deactivation of the catalyst. This could be due to the poisoning of the catalyst by chloride, or caused by the complete blockage of active sites by chloroform or its breakdown products. In subsequent studies the cloth was only washed in DI water to avoid any further deactivation effects caused by the use of chloroform. The results of this study are summarized in Table 2.6. Phenol yield decreased with every use. Cyclohexanol yield increased from first use to second use, which can be attributed to residual cyclohexanol on the cloth from the first use. A similar trend can also be observed in the apparent current efficiency data; due to the increase in moles of cyclohexanol observed for the second use, the current efficiency was also highest for the second trial (Figure 2.16). After the second use the cyclohexanol yield follows the same trends as that for phenol; the cyclohexanol yield continues to drop after each experiment, as does the current efficiency. The overall product yield (phenol + cyclohexanol) decreased from one experiment to the next (Figure
Initial selectivity was higher for phenol, but after the first experiment, selectivity increased for cyclohexanol. A change in selectivity is often a sign that some change has occurred in the catalyst and could be a possible indication of catalyst deactivation. But most likely this switch in selectivity could be attributed to the fact that cyclohexanol is captured on the ACC but phenol is not captured on the cloth in any of the 5 experiments resulting in more phenol than cyclohexanol in solution after each run. For the first two trials, conversion was close to 100%, after the second trial, conversion gradually decreased with the fifth reuse falling lower than 40% (Figure 2.17).

**Table 2.6: Summary table of catalyst deactivation study**

<table>
<thead>
<tr>
<th>Use</th>
<th><strong>Phenol Yield</strong> (mol%)</th>
<th><strong>Cyclohexanol Yield</strong> (mol%)</th>
<th><strong>Phenol Selectivity</strong> (mol%)</th>
<th><strong>Cyclohexanol Selectivity</strong> (mol%)</th>
<th><strong>Conversion</strong> (mol%)</th>
<th><strong>CE (%)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.13</td>
<td>14.58</td>
<td>55.43</td>
<td>44.57</td>
<td>99.81</td>
<td>12.51</td>
</tr>
<tr>
<td>2</td>
<td>9.68</td>
<td>18.03</td>
<td>34.95</td>
<td>65.05</td>
<td>98.23</td>
<td>13.96</td>
</tr>
<tr>
<td>3</td>
<td>7.38</td>
<td>16.16</td>
<td>31.37</td>
<td>68.62</td>
<td>88.14</td>
<td>10.28</td>
</tr>
<tr>
<td>4</td>
<td>7.02</td>
<td>14.19</td>
<td>33.10</td>
<td>66.90</td>
<td>73.77</td>
<td>10.61</td>
</tr>
<tr>
<td>5</td>
<td>6.46</td>
<td>13.69</td>
<td>32.07</td>
<td>67.93</td>
<td>38.35</td>
<td>10.12</td>
</tr>
</tbody>
</table>

Figure 2.15: Product yield (phenol + cyclohexanol) for catalyst deactivation test
Figure 2.16: Current efficiency for catalyst deactivation test

Figure 2.17: Conversion for catalyst deactivation test

Conclusion

Methoxyphenol studies clearly indicated that the position of the methoxy group on the aromatic ring did not have a significant effect on the selected path of product formation or the yields of methoxycyclohexanol and cyclohexanol. In the case of 2-methoxyphenol and 4-methoxyphenol the formation of cis and trans isomers of the methoxycyclohexanol were observed. These studies proved the effectiveness of the catalyst in reducing
methoxyphenols to cyclohexanol and methoxycyclohexanol regardless of the position of the methoxy group on the aromatic ring.

From the 4-phenoxyphenol studies a maximum cyclohexanol yield of 54% was measured when NaOH was used as electrolyte at 100 mA for four hours with 6.25 mM substrate concentration. This trial also resulted in a current efficiency of 18%, with the inefficiency due to molecular hydrogen production. Although it was observed that high current efficiency was recorded for low current density experiments, it resulted in higher phenol selectivity, which can be beneficial. It is important to note that current efficiencies are likely far from optimized, and that varying conditions such as current density, electrode materials, electrolytes, electrolyte concentrations, substrate concentration and temperature may further improve these results.

Catalyst deactivation studies uncovered a decrease in activity after two uses. To optimize current efficiency and to increase the service life of the system, areas of ongoing development include improvements in cell design, energy efficiency, and catalytic cathode stability. The organic chemical transformations described here also have synthetic potential. Studies to probe selectivity, the mechanism of the aryl ether cleavage and the range of electrocatalytically convertible substrates are also underway.
REFERENCES


Chapter 3: Characterization of Extractive Ammonia Process Lignin Fractions

Abstract

Lignin is the second most abundant biomass component after holocellulose and accounts for 10-30% of the lignocellulosic biomass by weight (40% by energy). In the nascent alcohol-based biofuels industry, only cellulose and part of the hemicellulose are used for liquids production, while the remaining lignin is burned to provide heat, using it as a low value fuel. Upgrading and sale of higher value products from lignin would improve economics of liquid fuel bioenergy systems. The extractive ammonia process (EAP) is being considered for deployment in centralized biorefineries that produce fuel alcohols such as ethanol and butanol. In lieu of combustion, we propose to convert ammonia-extracted lignin to hydrocarbon fuels and chemicals using a combination of pyrolysis and electrocatalytic reduction. These flexible, simple technologies can be safely deployed at large biorefineries to diversify their product slates and improve their value proposition. The utility of this approach can also be realized at smaller, decentralized processing depots that separate lignin from structural carbohydrates. In this study, lignin characterization and its pyrolysis were performed in an effort to devise a depolymerization protocol. Finally, the depolymerized product was subjected to electrocatalysis to assess the extent of value addition.

Introduction

Due to the energy stored in its components, biomass has a great potential as a feedstock for the production of liquid fuels and value added products. Deconstruction of the biomass for liquid fuel production has recently gained a lot of attention as one of the ways to
displace fossil derived fuels. To this end, advances have been made in pretreatment and conversion methods aiming to efficiently produce fuels from biomass and biomass components. Pretreatments methods offer the opportunity to release and fractionate the components of biomass, making the subsequent conversion processes relatively easier.\textsuperscript{1,2,3} Usually pretreatments are used to reduce the crystallinity of cellulose and remove lignin and hemicellulose while increasing the porosity of the biomass for further ease of fractionation.\textsuperscript{3,4}

The extractive ammonia pretreatment (EAP) improves the rates and extents of subsequent saccharification by separating lignin from cellulose and hemicellulose in the conventional biomass to ethanol conversion strategies.\textsuperscript{5} During EAP, ammonia is added to biomass at moderate pressure (100 to 400 psi) and temperature (70 to 200 $^\circ$C).\textsuperscript{5} The pressure is then rapidly released; this rapid depressurization of the liquid ammonia causes the biomass fibers to expand and explode.\textsuperscript{3, 6} This process results in cellulose decrystallization, hemicellulose hydrolysis, and partial lignin depolymerization.\textsuperscript{5,7,8} The cellulose and hemicellulose can then be subjected to enzymatic hydrolysis for ethanol production while lignin streams are collected, fractionated and extracted. These lignin streams are partially depolymerized and are thus lower in molecular weight than the native lignin complex found in biomass. Lignin monomers and oligomers are more amenable to chemical transformation to higher value fuels and chemicals and are thus better feedstocks than native lignin.

EAP enables lignin recovery via variation of ammonia loading, residence time, temperature and pressure. Though direct combustion of lignin is an option, deriving higher value fuels and chemicals is desired as lignin accounts for 10-30 wt% of biomass and 40%
of its energy. The production of lignin, at either centralized or decentralized facilities, provides an opportunity for thermal and electrocatalytic approaches to produce even more liquid fuel. Fast pyrolysis is one such thermochemical approach in which biomass is liquefied by heating in the absence of oxygen to form pyrolysis gas and biochar. Most of the pyrolysis gas can be condensed to liquid “bio-oil” with a bulk density greater than that of the feedstock. Biomass densification near the harvest source reduces the cost of transportation and storage prior to upgrading in a central refinery.

A negative aspect of fast pyrolysis is that bio-oil’s corrosiveness and reactive instability pose significant barriers to the adoption of pyrolysis systems. Catalytic stabilization is needed to produce a stable fuel intermediate that is compatible with common infrastructure materials such as carbon steel. Classical catalytic upgrading is usually used to hydrogenate and deoxygenate bio-oil, a process that occurs at high temperature and pressure. These severe conditions pose significant barriers, such as catalyst deactivation, for bio-oil upgrading in decentralized facilities. To avoid these conditions, electrocatalytic hydrogenation (ECH) is proposed to stabilize bio-oil under mild conditions (25-80 °C and 1 atm). As lignin is converted to phenolic monomers, dimers, and oligomers upon pyrolysis, the transformation of model compounds exhibiting similar bonding arrangements indicates the potential for the ECH of biomass lignin.

In the previous chapter we were able to demonstrate successful ECH of these phenolic monomers and dimers using an activated carbon cloth supported ruthenium cathode. As a continuation of that study this venture attempts to establish a pyrolysis protocol for depolymerizing EAP lignin with heat treatment and electrocatalytic reduction of EAP lignin. Two fractions of lignin were obtained from the EAP pretreatment step. The composition of
these two fractions was determined using elemental analysis and characterized using pyrolysis-GC/MS, thermogravimetric analysis and bomb calorimetry. The results of these analyses suggest that EAP lignin bio-oil can be successfully stabilized using electrocatalytic treatment at small-scale depots or larger biorefineries. Furthermore, as a continuation of model compound ECH, attempts were made to electrocatalytically reduce EAP lignin to smaller fragments. As shown in Figure 3.1, this approach uses extracted lignin that is a byproduct of other conversion schemes, thermochemical conversion to bio-oil and upgrading to a more stable form at a decentralized processing depot before it is transported to a hydroprocessing facility. Hydroprocessing may be unnecessary depending upon the effectiveness of ECH.

Figure 3.1: Overall project scheme from biomass harvesting to pretreatment using extractive ammonia process followed by pyrolysis and electrocatalysis to upgrade to valuable products.
Experimental Methods

EAP Lignin Extraction Method

EAP lignin was obtained from Dr. Bruce Dale’s lab. The extractive ammonia method used for extraction of lignin as provided by the Dale group, is represented in the schematic in Figure 3.2, which shows the extraction process and the resulting molecular weights of EAP product streams. First, corn stover was oven dried at 60 °C for two weeks, milled and stored resulting in a 6 wt% wet basis feed. This feed was then pretreated in 1-liter high-pressure stainless steel tubular reactors. Each reactor contained a mixture of 40 grams of the feed with 240 grams of ammonia for 30 minutes at 120 °C and 83 bar. As the system reached the set point temperature, the liquid ammonia and soluble extractives were released at the bottom of the tank while the ammonia gas was released from the top of the tank. The biomass left in the tubular reactors was then removed and dried overnight in the hood. The solid part was subjected to enzymatic hydrolysis and followed by extraction via solvation in water. For the liquid fraction, ethanol was used to collect ethanol soluble and ethanol insoluble fractions. All of fractions were then resolubilised in water to extract the water-soluble and water-insoluble fractions.

This fractionation process thus yielded four separate fractions: ethanol insoluble/water-insoluble (F1), ethanol insoluble/water-soluble (F2), ethanol soluble/water-insoluble (F3) (Figure 3.3), and ethanol soluble/water-soluble (F4). Characterization of both the F1 and F3 EAP lignin fractions involved py-GC/MS, TGA and
bomb calorimetry. Ultimate analysis was also conducted to directly quantify the amount of elemental carbon, hydrogen, nitrogen and sulfur and indirectly, oxygen by difference.

Figure 3.2: Method used to produce EAP lignins. Lignins are present in oligomeric and polymeric forms as per the molecular weights of each fraction.
Figure 3.3: Ethanol soluble F3 fraction as obtained from liquid ammonia after precipitation in water followed by solubilization in ethanol

*Higher Heating Value (Bomb Calorimetry)*

Bomb calorimetry was used to determine the higher heating value (HHV) of the two fractions using a Parr Plain Jacket Calorimeter (Parr Instruments Co., Molin, IL). Samples of about 110 mg of both fractions were mixed with 10-14 mg of dodecane and combusted to determine the higher heating value.

*Elemental Analysis (CHNS)*

C, H, N, S data was obtained using combustion with automatic analyzer from the Atlantic Microlabs (Norcross, GA). Oxygen was calculated by difference. The samples were not dried prior to analysis.
Thermogravimetric Analysis (TGA)

TGA analysis was performed on both the lignin components. Several grams of each sample were introduced to the TGA. Initially the temperature was held at 30 °C for 10 minutes, then the temperature was increased to 104 °C at a rate of 10 K/min, this temperature was held for 10 minutes, and finally increased to 800 °C at 10 K/min. The mass loss curve and its derivative were plotted to identify those temperatures that correspond to key thermal events, such as water loss, hemicellulose degradation or lignin degradation.

Pyrolysis GC/MS

Py-GC/MS analysis of both F1 and F3 fractions was performed using a micro scale pyrolysis unit (CDS pyroprobe 5250, CDC Analytical inc. Oxford, PA) coupled with a Shimadzu QP_5050A GC/MS (Shimadzu Corp. Columbia, MD). Several micrograms of the lignin fraction were packed in a quartz tube between quartz wool plugs and subjected to py-GC/MS. The pyroprobe was set to 600 °C and held there for 10 seconds with a transfer line temp of 300 °C. The GC used a Restek RTX-1701 column of 60m length, 0.25 mm diameter and 0.25 µm thickness. (Restek, Bellefonte, PA). The GC program was set at 40 °C with a 1 minute hold time, followed by an 8 °C/min ramp to 270 °C with a 10 minute hold. The injection and interface temperature were set at 280 °C. A split injection with a 1:100 split ratio was used. Helium flow through the column was maintained at 1 ml/min. The mass spectra were collected in electron ionization mode with the mass-to-charge ratio set to range from 33 to 300. Compounds were identified by comparison of the mass spectra of
the major peaks with the National Institute of Standards and Technology (NIST) library to obtain the best possible matches.

Catalyst Preparation

Zorflex ACC (activated carbon cloth) FM 100 was used to support the ruthenium catalyst. As described by Li et. al.,\textsuperscript{13} the activated carbon cloth was washed overnight in deionized water and oven dried at 105 °C. The ACC support was prepared with catalyst using the incipient wetness method as described by Li et. al.\textsuperscript{13} Ru(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{3} solution was used to soak each 1.5 x 3.0 cm piece of ACC. Each cloth was immersed in the solution and soaked for a few minutes. The Ru/ACC catalyst was then dried at room temperature first overnight and stored in a vacuum dessicator for another 24 hours then reduced with molecular hydrogen at 500 psi and 310 °C for 12 hours in a Parr reactor (model 452HC).

Electrocatalytic Hydrogenation of EAP Lignin

Electrocatalysis of the F3 fraction was performed in a two-chambered electrochemical glass H-cell separated by a Dupont Nafion-117 membrane. Ruthenium supported on activated carbon cloth (Ru/ACC) was used as the cathode and platinum wire was used as the anode as shown in Figure 3.4. A constant temperature of 80 °C was maintained by placing the whole cell in a heated silicon oil bath. An Instek GPR-11H30D power supply was used to provide constant current. 1M NaOH was used as the electrolyte. After cell setup was completed, a 10 min pre-electrolysis step was performed on the catalyst at 80mA before adding the substrate. After pre-electrolysis, 0.045 gm of substrate
was added and the experiment was run at 80°C and 80mA for 27 hours. Samples (1 ml) were taken at 12, 24, 26 and 27 hours.

*Figure 3.4: Two chambered H-cell setup*

**Size Exclusion Chromatography**

Samples (0.25 ml) were taken and diluted using the SEC’s mobile phase (0.1 M NaNO₃ 0.01 M NaOH) and analyzed using an Agilent 1100 HPLC fitted with a Waters Ultrahydrogel™ 250 7.8 x 300mm column. Both diode array (DAD) and refractive index detectors were utilized. A flow rate of 1 ml/min was used with 20 µl injection volume and a column temperature of 35 °C. As lignin standards were not available the molecular weight distribution was not determined. The intensity of the detector signal vs. the elution time was plotted with larger molecules assumed to elute first followed by smaller molecules eluting out later. The remainder of each sample was then saturated with NaCl acidified to pH 1 and extracted using chloroform for analysis using GC/MS to identify any depolymerization products. The catalyst was placed in 5 ml of chloroform, sonicated for 10 minutes, and filtered prior to analysis by GC/MS.
Results and Discussion

HHV, Elemental Analysis and TGA

The reported values for the higher heating value of biomass is 12-19 MJ/Kg and bio-oil is 16-19 MJ/Kg\textsuperscript{14}. Calorimetry yielded a higher heating value of 30.12 MJ/Kg for the low molecular weight lignin (F3) and 21.20 MJ/Kg for the high molecular weight lignin (F1) as shown in Table 3.3. As expected, the HHV values for the F1 and F3 fractions are higher than those of the parent corn stover.

The F3 fraction elemental analysis revealed the levels of oxygen present in this lignin fraction. Bio-oil tends to retain most of the oxygen that is present in the parent biomass, which could be up to 35-60 wt\textsuperscript{%}\textsuperscript{15}. The presence of such a large amount of oxygen in bio-oil is the main reason for the vast differences in properties between bio-oil and conventional fuel oil\textsuperscript{16}. Such undesirable properties as low energy content\textsuperscript{10}; instability in storage due to high reactivity\textsuperscript{17}; immiscibility with non-polar petroleum fuels\textsuperscript{10} etc. are all properties that can be attributed to high oxygen content. Furthermore, high reactivity results in the formation of additional water as a side product, which affects the combustion properties of the fuel. As can be seen from the elemental analysis results in Table 3.1, the F3 fraction has less oxygen than reported oxygen values for biomass-derived bio-oil. Pyrolysis coupled with electrocatalysis can further help reduce the amount of oxygen resulting in a higher energy content fuel.
Table 3.1: HHV and elemental analysis of F3 and F1 fraction

<table>
<thead>
<tr>
<th></th>
<th>HHV (MJ/Kg)*</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O  (By difference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F3</td>
<td>30.12</td>
<td>65.68</td>
<td>8.13</td>
<td>2.62</td>
<td>0.0</td>
<td>23.57</td>
</tr>
<tr>
<td>F1</td>
<td>21.20</td>
<td>44.36</td>
<td>5.43</td>
<td>3.78</td>
<td>0.19</td>
<td>46.24</td>
</tr>
</tbody>
</table>

The DTG curves for the F3 and F1 fractions were obtained by differentiating the TGA curve for both fractions. The results reveal that there is a major thermal event at 354 °C (refer to Figure 3.5 and 3.6). The DTG curve of the F3 fraction (Figure 3.5) stretches over a large range, which is typical of lignin thermal degradation. The F3 DTG curve shows typical characteristics of lignin DTG curves found in the literature. If it were to be compared to cellulose or hemicellulose DTG curves, it would be noted that this lignin DTG curve is a lot less sharp. This can be attributed to the inhomogeneous nature of the lignin polymer. Unlike hemicellulose and cellulose, which are relatively homogeneous polymers composed of simple sugars that decompose at a high rate within a narrow temperature range,\textsuperscript{18} lignin is composed of monolignols that form complex and diverse cross linkages that make it more resistant to thermal degradation.\textsuperscript{9, 19} This gives lignin a wide range of temperatures over which it undergoes thermal decomposition. The F1 fraction in comparison shows a sharper DTG peak as compared to the F3 curve. As compared to DTG curves in the literature\textsuperscript{20} this curve suggests that the F1 lignin might contain some cellulose residues. The sharpness of the DTG peak for this particular fraction could be indicative of residual cellulose and hemicellulose from the extraction process.
Although TGA and DTG curve provide a representation of the thermal degradation temperature of lignin, the heating rates employed in thermogravimetric analysis are far from the heating rates the lignin will experience in a typical pyrolysis reactor which can approach rates of 300-1000 °C/s. In addition to not being able to provide realistic heating values for fast pyrolysis, TGA studies fall short due to their inability to provide information...
about what compounds are being formed during the thermal degradation process.\textsuperscript{21} However, the TGA data obtained in this study provides relevant guidelines for setting up a protocol for pyrolysis of EAP lignin using large-scale pyrolysis screw conveyor reactor.

\textit{Pyrolysis GC/MS}

The major peaks obtained in the case of the F3 fraction were consistent with the compounds that are expected from lignin pyrolysis, as shown in Figure 3.7. The lack of any peaks typical of carbohydrate pyrolysis such as C2-C4 aldehydes and ketones, levoglucosan or furans and the presence of large amounts of phenols such as phenol, guaiacol, creosol, 4-ethylguaiacol, syringol, 4-vinylphenol, etc, support the purity of this lignin fraction. Since plant-derived phenols are considered to have relevance as they have a potential to replace petroleum-based phenols which are often high in cost,\textsuperscript{22} conversion of these lignin fraction to phenolic monomers via fast pyrolysis will be beneficial. However, further studies should be conducted to determine the yields of products from EAP lignin pyrolysis to assess the potential of this method to produce liquid fuels.

![Py/GC chromatogram of F3 fraction with peak labels outlined in Table 3.2](image)

\textbf{Figure 3.7:} Py/GC chromatogram of F3 fraction with peak labels outlined in Table 3.2
Table 3.2: Retention times of products from Py/GC-MS of F3 fraction

<table>
<thead>
<tr>
<th>#</th>
<th>Compound Name</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unidentified</td>
<td>3.633</td>
</tr>
<tr>
<td>2</td>
<td>Carbon Dioxide</td>
<td>3.89</td>
</tr>
<tr>
<td>3</td>
<td>Phenol</td>
<td>16.294</td>
</tr>
<tr>
<td>4</td>
<td>Guaiacol</td>
<td>16.802</td>
</tr>
<tr>
<td>5</td>
<td>3-Methylphenol</td>
<td>17.994</td>
</tr>
<tr>
<td>6</td>
<td>Creosol</td>
<td>18.833</td>
</tr>
<tr>
<td>7</td>
<td>3-Ethylphenol</td>
<td>19.673</td>
</tr>
<tr>
<td>8</td>
<td>4-Ethylguaiacol</td>
<td>20.418</td>
</tr>
<tr>
<td>9</td>
<td>4-Vinylphenol</td>
<td>21.266</td>
</tr>
<tr>
<td>10</td>
<td>4-Vinylguaiacol</td>
<td>21.497</td>
</tr>
<tr>
<td>11</td>
<td>Syringol</td>
<td>22.394</td>
</tr>
<tr>
<td>12</td>
<td>Isoeugenol</td>
<td>23.81</td>
</tr>
<tr>
<td>13</td>
<td>1,2,4-Trimethoxybenzene</td>
<td>23.945</td>
</tr>
<tr>
<td>14</td>
<td>2-Butyl-1,1,3-trimethylcyclohexane</td>
<td>25.144</td>
</tr>
<tr>
<td>15</td>
<td>3-Tert-butyl-4-hydroxyanisole</td>
<td>26.099</td>
</tr>
<tr>
<td>16</td>
<td>Phenol, 2,6-Dimethoxy-4-(2-propenyl)-</td>
<td>28.071</td>
</tr>
</tbody>
</table>

Electrocatalytic Hydrogenation of EAP Lignin

In an effort to stabilize lignin-derived bio-oil, electrocatalytic hydrogenation was employed. Several lignin model compounds were chosen for electrocatalytic reduction. Previous work as detailed in Chapter 2 showed that both monomeric and dimeric lignins are reduced to such products as alkoxy cyclohexanols, phenol and cyclohexanol. This demonstrates that Ru/ACC catalyst can be effective in reducing lignin-derived model compounds. Instead of model compounds, EAP lignin is used to extend the results of model compounds studies to an authentic biomass stream. As EAP lignin has high molecular weight, some form of depolymerization is necessary. Though fast pyrolysis may be used to
reduce molecular weight, the direct ECH of EAP lignin was studied to gauge the extent of depolymerization achieved through electroreduction. To achieve these goals, electrocatalysis of EAP lignin was also performed Ru/ACC catalyst at 80°C and 80mA for 27 hours. As the F3 EAP fraction is insoluble in water but soluble in basic conditions, 1M NaOH was used as an electrolyte in the ECH study. During the experiment it was observed that there was an increase in voltage around the 12-hours and a further rapid increase in voltage after the 26 hours. This could suggest that due to the basic conditions of the electrolyte solution and the presence of oxygen, polymerization of the lignin oligomers might have occurred. The sudden jump in voltage indicates polymer formation around 26 hours, which results in decreased conductivity because of blockage on the catalyst surface. Under galvanostatic control, the voltage increases to maintain the desired current. As the voltage exceeded 100 volts, the experiment was stopped after 27 hours. Samples were taken periodically for further GPC analysis but the results were inconclusive. Further analysis of the samples using GC/MS did not show any chromatographic peaks, which could indicate a lack of analytes between mass to charge ratios from 30 to 300. As such, the products have molecular too large to be detected by the GC/MS method employed. In lieu of basic conditions, acidic and neutral conditions could be explored in the cathode compartment of ECH to enhance depolymerization. Further, the use of pyrolysis or perhaps oxidative approaches may be needed to create low molecular weight reactants for reduction by ECH.

**Conclusion**

As one of the components of biomass and a component responsible for a large fraction of the energy stored in biomass, lignin has great potential for hydrocarbon fuel
production. However in today’s biofuel production efforts lignin is often a by-product that is not being utilized efficiently due to the lack of efficient depolymerization schemes for lignin conversion to fuels or value-added commodities. Processes such as fast pyrolysis could prove very beneficial in solving this problem. In this study, the main reason for characterizing the EAP lignin was to determine its potential as a possible feed material for fast pyrolysis and subsequent ECH. These characterization results give a certain amount of insight towards setting up a lignin depolymerization scheme using fast pyrolysis coupled with electrocatalysis. The results are summarized below.

- **Higher heating value and elemental analysis**: these results indicated that the F3 fraction had a larger heating value and less oxygen then F1, potentially making it a better feed material. As pyrolysis oils tend to retain most of the oxygen from the feed material, having a lignin fraction with less oxygen to begin with makes it a more desirable feed.

- **Thermogravimetric analysis**: TGA/DTG curves for both fractions indicate that the decomposition of lignin occurred over a wide range of temperatures with a major thermal event occurring at around 345 °C. This gives us an idea of what temperatures to explore when implementing pyrolysis of these fractions at a large scale. But it is important to note that heating rates applied during TGA analysis are much lower than those of an actual fast pyrolysis reactor. TGA results, though useful for setting pilot-scale reactor operating temperatures, should not be relied upon as a scale-up criterion, i.e. the results of slow pyrolysis will differ from fast pyrolysis. Additionally it was noted that the F3 fraction showed a DTG curve typical of pure lignin samples while F1 showed a DTG curve typical of samples with residual
cellulose and hemicellulose. Thus, F3 will probably be a better feed material if the target is to pyrolyze lignin rich feedstock.

- **Pyrolysis GC/MS:** these results gave a very good indication of what the pyrolysis products of the F3 fraction might look like at temperatures close to 600 °C. However, further py-GC/MS experiments should be conducted to quantify the overall yields of molecular products from pyrolysis.

- **ECH of F3 fraction:** Currently, the ECH of the F3 fraction did not provide an interpretable outcome because the lignin fraction likely polymerized during ECH. Exploration of different electrolytes and electrocatalytic conditions might depolymerize the EAP lignin into components than can be further reduced by ECH.
REFERENCES


Chapter 4: Conclusions and Future Work

Conclusions

Two extracted ammonia process (EAP) lignin fractions (F1 and F3) were characterized to assess the potential of these fractions to serve as pyrolysis feed material. Elemental analysis indicated that the F3 fraction had lower oxygen and higher carbon contents than the F1 fraction, making F3 a more desirable feed material for liquid fuel production via fast pyrolysis. Thermogravimetric analysis (TGA) of this F3 fraction indicated a major thermal event around 354 °C with the DTG profile extending over a large range of temperatures as is typical for the thermal degradation of lignin rich feed. Pyrolysis GC/MS analysis indicated the formation of phenolic monomers typical of lignin derived compounds in bio-oil. ECH of the F3 fraction was performed under basic conditions to assess the potential of ECH for lignin depolymerization. In this case the polymerization of the lignin might have occurred so further studies need to be conducted to explore various conditions that might support the depolymerization of this fraction instead of polymerizing it.

Studies on 2-methoxyphenol, 3-methoxyphenol and 4-methoxyphenol were performed to study the effect of different positions of the methoxy group on the aromatic ring. Results indicated no major effect of the position of the groups. Cyclohexanol and methoxycyclohexanol were observed as products for all cases with almost equal selectivities. Highest conversion was observed for 2-methoxypehnhol. Current efficiency for all cases was modest with 2-methoxyphenol showing a slightly better value of 20%. In studying the lignin dimer 4-phenoxyphenol, conversion of the substrate to phenol and cyclohexanol was observed confirming the ability of the Ru/ACC to cleave 4-O-5 linkages.
ECH was performed using different electrolytes, substrate concentrations and current densities to study the effect of these conditions on product yield, selectivity, conversion and current efficiency. Lower current density strongly favored phenol selectivity while high current density favored cyclohexanol selectivity. 1 M NaOH gave the highest product yield. A β-0-4 linked dimer was also subjected to ECH resulting in the production of guaiacol and vanillin. Further studies need to be conducted to probe the mechanism of the cleavage of this linkage type.

Reusing the catalyst five times for the ECH of 4-phenoxyphenol was performed for catalyst deactivation studies. The results indicated the gradual deactivation of the catalyst after each experiment. Due to residual cyclohexanol adsorbed to the catalyst, cyclohexanol yield for the second experiment was higher than that of the other experiment also resulting in higher apparent current efficiency for that run. Efforts should be made to wash the catalyst effectively to extract cyclohexanol before reusing it. The effects of different solvents should be studied to achieve this goal.

**Future Work**

As a way of exploring the potential of this pyrolysis/electrocatalysis system for the depolymerization and valorization of extractive lignin, here are a few future plans:

1. Further characterization of the EAP lignin should be performed to define the detailed structure of the lignin.
2. Overall yield determination of lignin pyrolysis using py-GC/MS.
3. Small-scale pyrolysis of the EAP lignin should be performed to produce usable quantities of bio-oil for ECH studies.
4. Different conditions should be explored for the direct ECH of EAP lignin to determine whether ECH may function independently as a viable depolymerization scheme.

5. ECH of a number of lignin-derived bio-oil monomers and mixtures of monomers should be performed to determine the effectiveness of this process for lignin-derived bio-oil upgrading.

6. ECH of other types of lignin linkages should be explored to build upon the existing work.

7. Efforts should be made to improve the modest current efficiency of the system.

8. Studies should be done to determine the exact cause of catalyst deactivation and how the catalyst can be reactivated.

9. Explore other less expensive metals as catalysts.